Supporting Information

Sulfur…Oxygen Interaction Controlled (*Z*)-Selective a*nti*-Markovnikov Vinyl Sulfides

Content

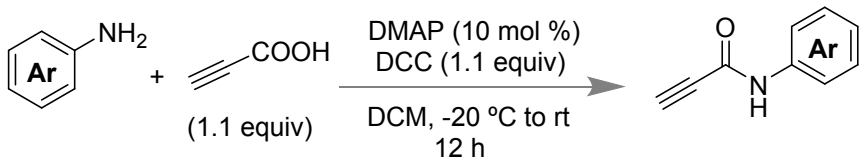
EXPERIMENTAL SECTION

General Aspects. All the chemicals were purchased from commercial sources and used as received. All the reactions were generally carried out under an open atmosphere unless otherwise noted. The reactions were monitored by TLC on aluminum sheets pre-coated with silica gel. Chromatographic purifications of the compounds were performed using silica gel (Mess 230-400) and ethyl acetate/hexane as eluent. ^{1}H and ^{13}C spectra of the compounds were recorded on Bruker 400 and 700 MHz instruments at 25 ºC. The chemical shift value (δ, ppm) was reported to the residual chloroform (7.26 for ^{1}H and 77.16 ppm for ^{13}C) and DMSO-d_6 (2.50 for ^{1}H and 39.52 ppm for ^{13}C). Mass spectra were recorded as ESI-TOF (HRMS). Infrared spectra were recorded on neat solids using KBr pellets and described in wavenumber (cm^{-1}). Digital melting point apparatus was used to record the Melting Point of the compound in degree centigrade (°C) and are uncorrected.

SYNTHESIS

General procedures for the synthesis of N-phenylpropiolamide derivatives. In a round-bottomed flask, a solution of propiolic acid (3.54 mmol, 1.1 equiv) in 10 mL CH_2Cl_2 (DCM) was allowed to stir at -20 °C and 4-dimethylaminopyridine (0.32 mmol, 0.1 equiv), dicyclohexylcarbodiimide (3.54 mmol, 1.1 equiv) in 5 mL CH_2Cl_2 were added dropwise. Then a solution of aniline (3.22 mmol, 1.0 equiv) in 5 mL CH_2Cl_2 was then injected dropwise. Afterward, the reaction mixture was stirred at room temperature (rt) for another 12 h. After completion of the reaction, the crude mixture was diluted in DCM and the following organic content was washed by 0.5 M aq. HCl, dried over Na_2SO_4, and concentrated under reduced

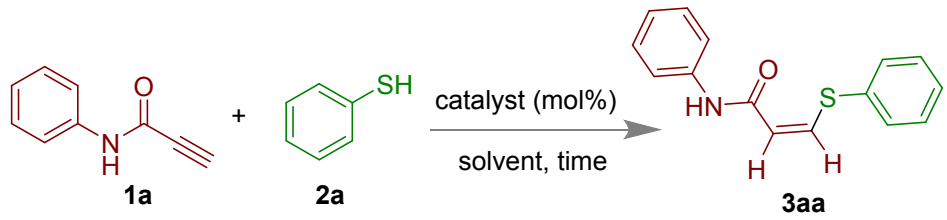
pressure. The crude residue was purified by column chromatography to give the desired starting materials N-phenylpropiolamide derivatives as yellow solid.



Scheme S1

General procedure for the synthesis of 3aa. In a round bottom flask, the thiophenol (**2a**) (54 mg, 0.0.495 mmol) was dissolved in 1 mL EtOH and Lithium *tert*-butoxide (0.33 mg, 0.00413 mmol) was added to the solution. After that, compound (**1a**) (60 mg, 0.413 mmol) was immediately added and the reaction mixture was allowed to stir in the open air for 10 min, and reaction progress was monitored by TLC. After completion of the reaction, excess EtOH was removed under reduced pressure and column chromatography was done in EtOAC/Hexane to isolate the desired product **3aa**.

Table S1. Optimization of the reaction condition.[a]



Entry	Solvent	Catalyst (mol %)	Time	Yield of 3aa (%)[a]	Ratios of Z/E[b]
1	CH_3CN	^tBuOLi (5.0)	30 min	90	92:8

2	CCl_4	^{t}BuOLi (5.0)	30 min	78	80:20
3	H_2O	^{t}BuOLi (5.0)	2 h	73	80:20
4	$CHCl_3$	^{t}BuOLi (5.0)	30 min	85	86:14
5	MeOH	^{t}BuOLi (5.0)	30 min	81	90:10
6	EtOH	^{t}BuOLi (5.0)	30 min	95	97:3
7	EtOH	^{t}BuOK (5.0)	30 min	94	97:3
8	EtOH	^{t}BuOLi (1.0)	30 min	95	97:3
9	EtOH	^{t}BuOLi (1.0)	10 min	95	97:3
10	EtOH	-	16 h	76	82:18
11	EtOH	-	24 h	0[c]	-
12	-	^{t}BuOLi (1.0)	30 min	90	97:3
13	^{t}BuOH:H_2O	-	12 h	77[d]	84:16
14	^{t}BuOH:H_2O	^{t}BuOLi (1.0)	4 h	76[e]	84:16
15	EtOH	^{t}BuOLi (1.0)	10 min	92[f]	97:3
16	EtOH	^{t}BuOLi (1.0)	10 min	93[g]	97:3
17	EtOH	-	30 min	0[h]	-

[a]Isolated yields after column chromatography, [b]mixture of Z/E isomers determined by crude ^{1}H NMR analysis; Reaction conditions: **1a** (60 mg, 0.413 mmol), **2a** (54 mg, 0.495 mmol) and ^{t}BuOLi (0.33mg, 0.00413 mmol) in 1 mL EtOH under open air at room temperature. [c]Reaction was performed under an inert atmosphere in absence of ^{t}BuOLi. [d]*tert*-BuOH:H_2O (1:1) at pH 4.8. [e]*tert*-BuOH:H_2O (1:1) at pH 7.4. [f]at inert. [g]under dark at inert. [h]Visible light (14W white LEDs) at inert atmosphere.

EPR Experiment. EPR spectra were recorded at 298 K using an EPR spectrometer derived at 9.4335 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; center fieldset: 3480.00 G; time constant: 0.16 ms; scan time: 122.88 s; modulation amplitude: 20.0 G; modulation frequency: 100 kHz; receiver gain: 2.00×10^{2} ; microwave power: $7.14e^{-001}$ mW.

Spin-trapping experiment in the presence of DMPO.[1] A mixture of thiophenol **2a** (0.495 mmol)**,** *N*-phenylpropiolamide **1a** (0.413 mmol), ^{t}BuOLi (0.00413 mmol, 1 mol %), and DMPO (20 µL) were stirred in 1.0 mL CH_3CN for 2 min. Following, 20 µL solutions were quickly transferred into an EPR tube and toluene (200 µL) was added to analyze EPR. A similar experiment was performed without thiophenol **2a**. A sharp signal was observed for the first case but no signal was found when the experiment was carried out in absence of thiophenol.

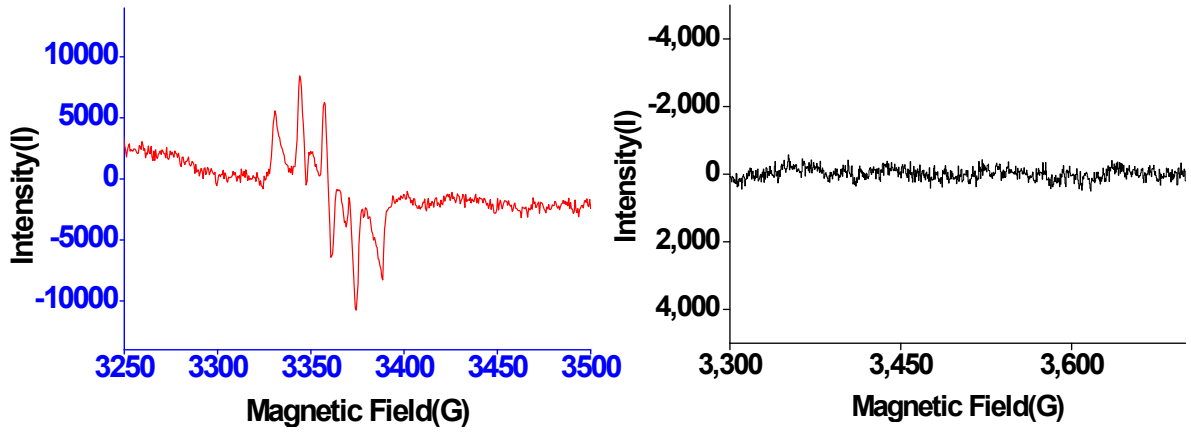


Fig. S1. a) EPR experiment with DMPO; g = 2.00752 b) under standard condition; c) in absence of thiophenol

Crystallographic Investigation

Good quality crystals of compounds **3ga** and **6** were obtained after slow evaporation of ethanol and water mixture (ca. 50%). The crystals data were collected with Bruker SMART D8 goniometer equipped with an APEX CCD detector and with an INCOATEC micro source (Cu-Kα radiation, λ = 0.71073 Å). SAINT+[2] and SADABS[3] were used to integrate the intensities and to correct the absorption respectively The structure was resolved by direct methods and refined on F^2 with SHELXL-97.[2] ORTEP Drawing of the compounds show ellipsoid contour at the 50% probability level

Compound (3ga) (CCDC 2044667)

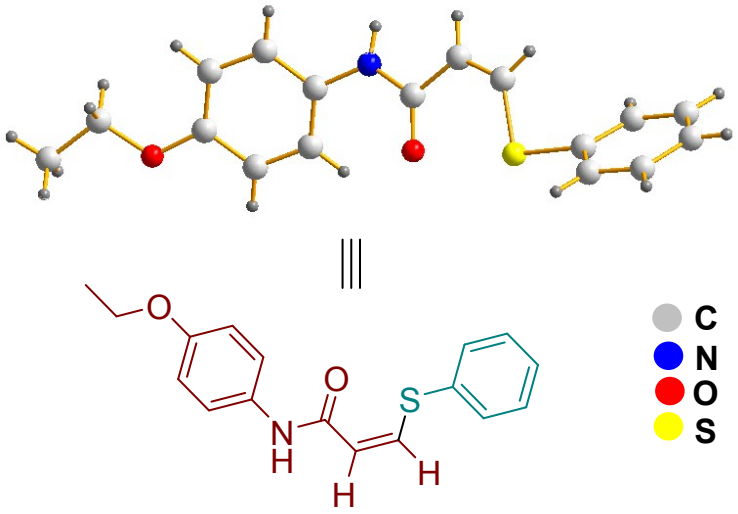


Fig. S2. Crystal structure of (**3ga**) (CCDC 2044667).

Crystallographic Data for (3ga)

Empirical formula	$C_{17}H_{17}NO_2S$
Formula weight	299.37
Temperature/K	100.00(10)

Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	9.77820(12)
b/Å	17.7960(2)
c/Å	18.3352(2)
α/°	90
β/°	101.9230(12)
γ/°	90
Volume/Å^3	3121.73(7)
Z	8
ρcalcg/cm^3	1.274
μ/mm^{-1}	1.868
F(000)	1264.0
Crystal size/mm^3	0.2 × 0.18 × 0.18
Radiation	CuKα (λ = 1.54184)
Reflections collected	47713
Independent reflections	6378 [Rint = 0.0731, Rsigma = 0.0307]
Goodness-of-fit on F2	1.029
Final R indexes [I>=2σ (I)]	R1 = 0.0416, wR2 = 0.1117
Final R indexes [all data]	R1 = 0.0430, wR2 = 0.1128
Largest diff. peak/hole / e Å^{-3}	0.36/-0.38

Compound 6 (CCDC 2044669)

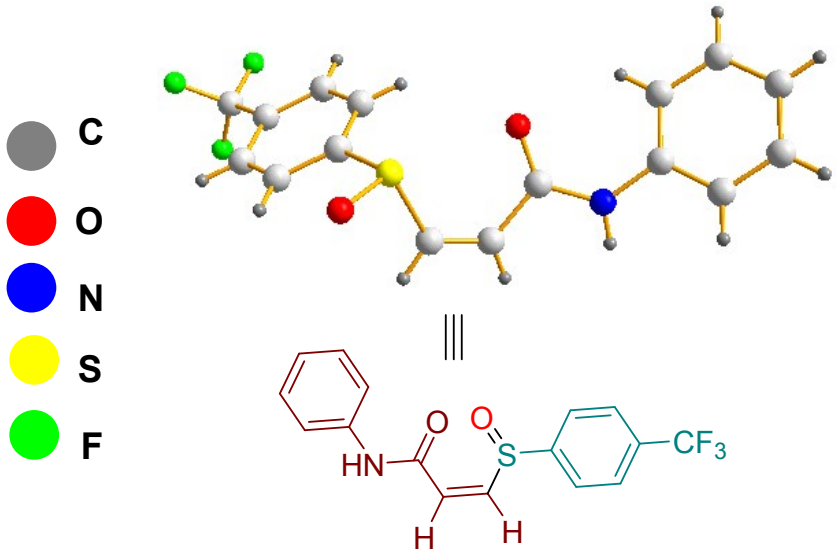


Fig. S3. Crystal structure of **6** (CCDC 2044669).

Crystallographic Data for 6

Empirical formula	$C_{16}H_{12}F_3NO_2S$
Formula weight	339.33
Temperature/K	298.9(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	14.97283(16)
b/Å	5.15517(5)
c/Å	20.2206(3)
α/°	90

β/°	90.3507(11)
γ/°	90
Volume/Å^3	1560.74(3)
Z	4
ρcalcg/cm^3	1.444
μ/mm^{-1}	2.227
F(000)	696.0
Crystal size/mm^3	0.2 × 0.18 × 0.17
Radiation	CuKα (λ = 1.54184)
Reflections collected	24037
Independent reflections	3304 [Rint = 0.0375, Rsigma = 0.0194
Goodness-of-fit on F2	1.129
Final R indexes [I>=2σ (I)]	R1 = 0.0566, wR2 = 0.1674
Final R indexes [all data]	R1 = 0.0596, wR2 = 0.1708
Largest diff. peak/hole / e Å^{-3}	0.56/-0.40

Theoretical Investigations

All calculations were performed using software package Gaussian 09 ver. D01.[4] The geometry of Z- and E-vinyl sulfides (**3ga**) was optimized by density functional theory (DFT) at RB3LYP/6-31+G (d, p) level.

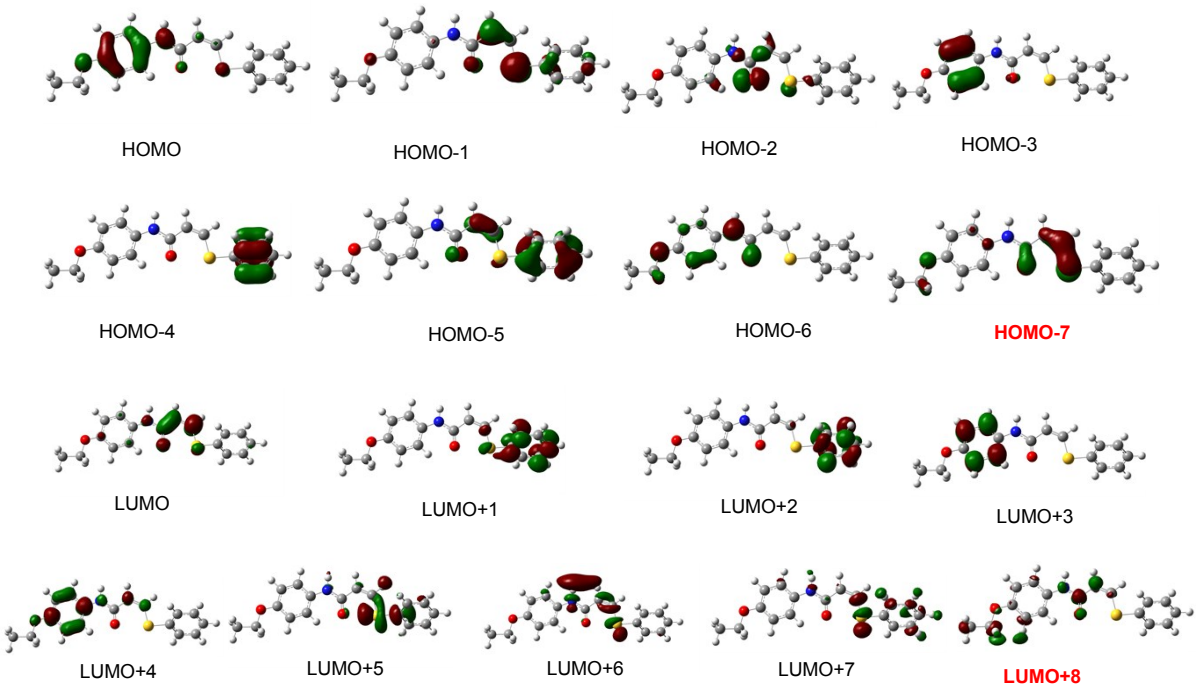


Fig. S4. Pictorial representation of different HOMOs and LUMOs from NBO analysis.

XYZ Coordinates and Thermochemical Data of Z-isomer (3ga) (Energies in Hartree)

Total energy = -1261.488992 hartree
Total electronic and zero-point Energies = -1261.152523 hartree
Total electronic and thermal Energies = -1261.132736 hartree
Total electronic and thermal Enthalpies = -1261.131792 hartree
Total electronic and thermal Free Energies = -1261.204451 hartree

C	8.29787100	-1.52696000	-0.27131100
H	8.67833200	-0.92546900	-1.10148900
H	8.71409300	-1.13140300	0.65929400
H	8.64758300	-2.55595700	-0.39876100
C	6.78038300	-1.49124600	-0.23631600
H	6.39392000	-2.09890800	0.59440700
H	6.35813600	-1.89292900	-1.16855000
O	6.38564000	-0.13099900	-0.06938100
C	5.05091300	0.15876900	-0.00785700
C	4.01926900	-0.78086300	-0.09637100
C	4.72628300	1.51267800	0.15709900
C	2.68188800	-0.38286800	-0.02227300
H	4.23660800	-1.83444400	-0.22426700
C	3.39999100	1.90865600	0.23118500
H	5.53039900	2.23764600	0.22513700

C	2.35782400	0.96900600	0.14304100
H	1.88797600	-1.11252600	-0.09152400
H	3.16658600	2.96352900	0.35980400
N	1.03523600	1.45250300	0.22727200
H	0.95464600	2.45255600	0.33906100
C	-0.15038600	0.75049900	0.17945300
O	-0.21699700	-0.47388100	0.04396500
C	-1.35678900	1.58585600	0.30318200
H	-1.25390100	2.65811100	0.45125200
C	-2.60209000	1.07272600	0.24782400
H	-3.45677400	1.73407500	0.35242200
S	-3.02312300	-0.61823900	0.03051300
C	-4.81658700	-0.47921800	-0.05302100
C	-5.45500200	0.36555400	-0.97113800
C	-5.58463900	-1.30683800	0.77496600
C	-6.84794600	0.40138600	-1.03546000
H	-4.86361800	0.98386100	-1.63956000
C	-6.97738300	-1.28196400	0.69073400
H	-5.09043200	-1.95990100	1.48757200
C	-7.61225800	-0.42376900	-0.20807100
H	-7.33551200	1.06301600	-1.74565100
H	-7.56567700	-1.92570900	1.33810600
H	-8.69624800	-0.40063100	-0.26703700

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis

Threshold for printing: 0.50 kcal/mol

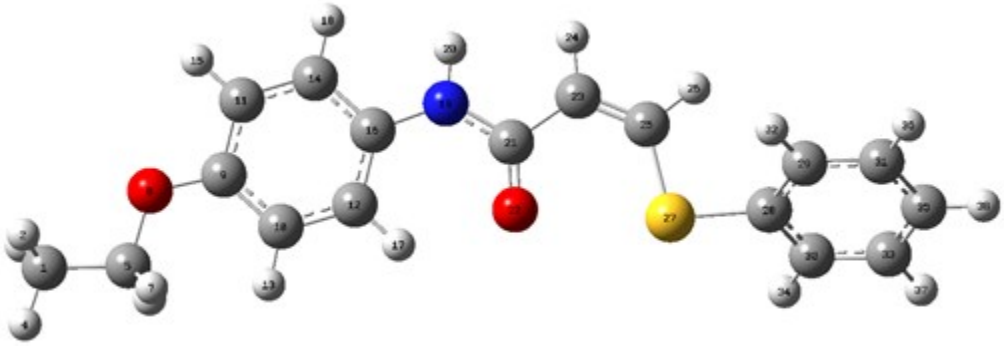


Fig. S5. Optimized stucture of Z-isomer **(3ga)**

Donor NBO (i)	Acceptor NBO (j)	E(2)kcal/mol

LP (1) O 22	RY*(1) C 21	14.19
LP (1) O 22	BD*(1) C 12 - H 17	1.38
LP (1) O 22	BD*(1) N 19 - C 21	1.34
LP (1) O 22	BD*(1) C 21 - C 23	2.75
LP (1) O 22	BD*(1) S 27 - C 28	0.88
LP (1) O 22	RY*(2) C 21	0.66
LP (2) O 22	RY*(4) C 21	1.96
LP (2) O 22	BD*(1) C 12 - H 17	1.71
LP (2) O 22	BD*(1) N 19 - C 21	25.94
LP (2) O 22	BD*(1) C 21 - C 23	16.83
LP (2) O 22	BD*(1) S 27 - C 28	2.65

XYZ Coordinates and Thermochemical Data of E-isomer (3ga) (Energies in Hartree)

Total energy = -1261.490697 hartree
Total electronic and zero-point Energies = -1261.187517 hartree
Total electronic and thermal Energies = -1261.167480 hartree
Total electronic and thermal Enthalpies = -1261.166536 hartree
Total electronic and thermal Free Energies = -1261.240174 hartree

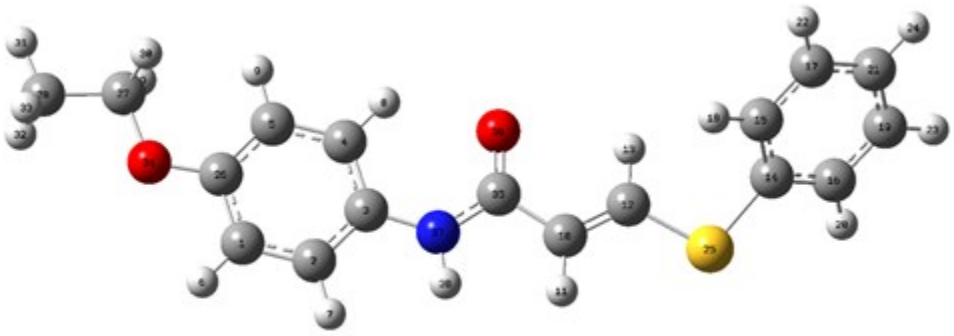


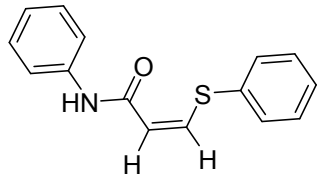
Fig. S6. Optimized stucture of E-isomer **(3ga)**

C	-4.76475	-1.39792	0.44539
C	-3.41677	-1.72667	0.45836

C	-2.43538	-0.77813	0.11426
C	-2.84263	0.51243	-0.24504
C	-4.20287	0.8436	-0.25827
H	-5.51928	-2.13085	0.71136
H	-3.12024	-2.73492	0.73986
H	-2.09916	1.25027	-0.51172
H	-4.48292	1.85114	-0.54136
C	1.3065	-1.25898	0.04305
H	1.24495	-2.29847	0.3589
C	2.49401	-0.6722	-0.19004
H	2.51763	0.37333	-0.48905
C	5.19764	-0.15085	0.00444
C	4.99578	0.92316	0.88251
C	6.3663	-0.2144	-0.76627
C	5.9509	1.93848	0.96666
H	4.10376	0.96377	1.49939
C	7.32735	0.79345	-0.65725
H	6.51599	-1.04123	-1.45389
C	7.11982	1.875	0.20273
H	5.78472	2.77322	1.64137
H	8.23073	0.73867	-1.25766
H	7.86352	2.66254	0.27803
S	4.03339	-1.50996	-0.11155
C	-5.17241	-0.10421	0.08574
C	-7.00481	1.42307	-0.24788
C	-8.5195	1.39773	-0.14231
H	-6.68788	1.6708	-1.27071
H	-6.57727	2.17237	0.43307
H	-8.92757	2.37907	-0.40596
H	-8.94285	0.65224	-0.82201
H	-8.83319	1.15434	0.87717
O	-6.5218	0.12414	0.10334
C	0.05646	-0.47402	-0.12474
O	0.04794	0.70867	-0.47029
N	-1.0859	-1.19434	0.15363
H	-0.94699	-2.15619	0.43016

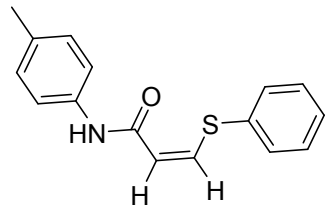
CHARATERIZATION DATA

(Z)-N-Phenyl-3-(phenylthio)acrylamide (3aa): R_f = 0.45 (20% ethyl acetate in hexane); yellow



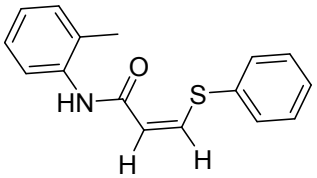
solid; yield 95% (100 mg); mp 154-156 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.13 (s, 1H), 7. 65 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.40-7.35 (m, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.25 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.0, 144.0, 139.2, 136.9, 129.7, 129.4, 128.8, 127.6, 123.1, 118.8, 117.0; IR (KBr) ῡ 3303, 3054, 2935, 1644, 690; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{13}NOSNa$ 278.0610; found 278.0636.

(Z)-3-(Phenylthio)-N-(p-tolyl)acrylamide (3ba): R_f = 0.5 (20% ethyl acetate in hexane); pale



yellow solid; yield 85% (86 mg); mp 163-167 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.48 (m, 4H), 7.41 (s, 1H) , 7.38-7.29 (m, 3H), 7.17 (d, *J* = 9.8 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.00 (d, *J* = 9.8 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 147.0, 137.2, 135.5, 133.9, 131.0, 129.6, 129.4, 128.1, 119.8, 115.8, 21.0; IR (KBr) ῡ 3310, 2915, 2339, 1657, 688; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{16}NOS$ 270.0947; found 270.0966.

(Z)-3-(Phenylthio)-N-(o-tolyl)acrylamide (3ca): R_f = 0.55 (20% ethyl acetate in hexane); white



solid; yield 87% (88 mg); mp 160-164 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.39-7.31 (m, 3H), 7.23-7.18 (m, 3H), 7.08-7.00 (m, 2H), 6.02 (d, *J* = 9.8 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 147.5, 137.3, 135.9, 131.1, 130.5, 129.7, 129.4, 128.2, 127.0, 125.0,

122.7, 115.6, 18.0; IR (KBr) ῡ 3206, 3034, 2922, 1634, 689; HRMS (ESI/Q-TOF) m/z: [M + Na]$^+$ calcd for $C_{16}H_{15}NOSNa$ 292.0767; found 292.0761.

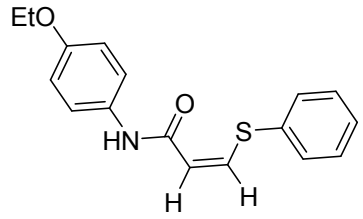
(Z)-N-(2,4-Dimethylphenyl)-3-(phenylthio)acrylamide (3da): R_f = 0.6 (20% ethyl acetate in hexane); white solid; yield 79% (78 mg); mp 182-184 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.85-7.84 (m, 1H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 9.0 Hz, 1H), 7.03-6.99 (m, 3H), 6.03 (d, *J* = 9.0 Hz, 1H), 2.29 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 164.4, 147.0, 137.3, 134.7, 133.2, 131.14, 131.08, 129.4, 128.6, 128.1, 127.4, 123.0, 115.7, 21.0, 17.9; IR (KBr) ῡ 3387, 3003, 1733, 1274, 657; HRMS (ESI/Q-TOF) m/z: [M + Na]$^+$ calcd for $C_{17}H_{17}NOSNa$ 306.0923; found 306.0925.

(Z)-N-(4-Isopropylphenyl)-3-(phenylthio)acrylamide (3ea): R_f = 0.5 (20% ethyl acetate in hexane); white solid; yield 76% (72 mg); mp 173-174 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.50 (d, *J* = 6.8 Hz, 3H), 7.38-7.34 (m, 2H), 7.34-7.30 (m, 2H), 7.20-7.16 (m, 3H), 5.99 (d, *J* = 9.8 Hz, 1H), 2.87 (sept, *J* = 6.8 Hz, 1H), 1.23 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 147.1, 145.0, 137.3, 135.8, 131.1, 129.4, 128.1, 127.0, 119.9, 115.7, 33.7, 24.1; IR (KBr) ῡ 3294, 2955, 1600, 822, 691; HRMS (ESI/Q-TOF) m/z: [M + Na]$^+$ calcd for $C_{18}H_{19}NOSNa$ 320.1080; found 320.1065.

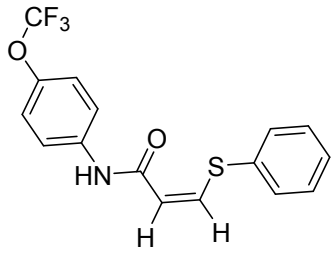
(Z)-N-(4-(tert-Butyl)phenyl)-3-(phenylthio)acrylamide (3fa): R_f = 0.65 (20% ethyl acetate in hexane); white solid; yield 82% (76 mg); mp 183-185 ºC; ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.52-7.50 (m, 3H), 7.39-7.30 (m, 6H), 7.20 (d, *J* = 9.8 Hz, 1H), 5.99 (d, *J* = 9.8 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 147.30, 147.27, 137.3, 135.4, 131.1, 129.4, 128.1, 125.9, 119.5, 115.6, 34.5, 31.5; IR (KBr) ῡ 3299, 2962, 1597, 694; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{21}NOSNa$ 334.1236; found 334.1236.

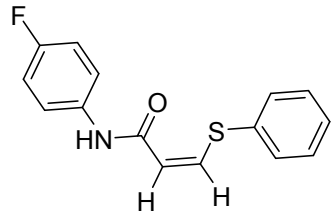
(Z)-N-(4-Ethoxyphenyl)-3-(phenylthio)acrylamide (3ga): R_f = 0.55 (30% ethyl acetate in hexane); white solid; yield 90% (85 mg); mp 163-165 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50-7.48 (m, 4H), 7.40-7.30 (m, 4H), 7. 17 (d, *J* = 9.8 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.97 (d, *J* = 9.8 Hz, 1H), 4.00 (q, *J* = 6.8 Hz, 2H), 1.39 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 155.8, 146.8, 137.3, 131.11, 131.06, 129.4, 128.1, 121.5, 115.7, 114.9, 63.8, 15.0; IR (KBr) ῡ 3321, 2977, 2339, 1632, 685; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}NO_2SNa$ 322.0872; found 322.0869.



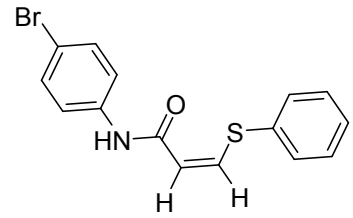
(Z)-3-(Phenylthio)-N-(4-(trifluoromethoxy)phenyl)acrylamide (3ha): R_f = 0.45 (30% ethyl acetate in hexane); white solid; yield 95% (85 mg); mp 170-174 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.6 H z, 2H), 7.51-7.47 (m, 2H), 7.44 (s, 1H), 7.39-7.31 (m, 3H), 7.26-7.24 (m, 1H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.00 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 148.4, 145.4, 136.9, 136.7, 131.1, 129.5, 128.3, 121.8, 120.9, 119.3, 115.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.11; IR (KBr) ῡ 3330, 3057, 2359, 1636, 668; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{12}F_3NO_2SNa$ 362.0433; found 362.0415.



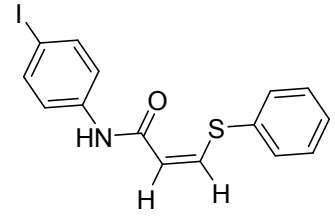
(Z)-N-(4-Fluorophenyl)-3-(phenylthio)acrylamide (3ia): R_f = 0.5 (30% ethyl acetate in hexane); white solid; yield 76% (76 mg); mp 153-157 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.50 (m, 2H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.44-7.38 (m, 1H), 7.37-7.31 (m, 3H), 7.21 (d, *J* = 9.8 Hz, 1H), 7.00 (t, *J* = 8.4 Hz, 2H), 5.99 (dd, *J* = 9.8, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 159.5 (d, $^1J_{CF}$ = 243.4 Hz), 147.8, 137.0, 134.1, 131.0, 129.4, 128.2, 121.6 (d, $^3J_{CF}$ = 6.2 Hz), 115.7 (d, $^2J_{CF}$ = 22.4 Hz), 115.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.12; IR (KBr) ῡ 3305, 2921, 2341, 1634, 688; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{13}FNOS$ 274.0696; found 274.0694.



(Z)-N-(4-Bromophenyl)-3-(phenylthio)acrylamide (3ja): R_f = 0.55 (30% ethyl acetate in hexane); white solid; yield 83% (74 mg); mp 166-168 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.50-7.48 (m, 3H), 7.42-7.31 (m, 6H), 7.23 (d, *J* = 9.8 Hz, 1H), 5.98 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 148.3, 137.2, 136.9, 132.1, 131.1, 129.5, 128.3, 121.3, 116.9, 115.2; IR (KBr) ῡ 3327, 3052, 2964, 1624, 690, 681; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{13}BrNOS$ 333.9896; found 333.9885.

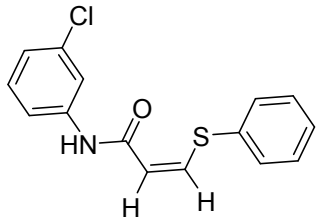


(Z)-N-(4-Iodophenyl)-3-(phenylthio)acrylamide (3ka): R_f = 0.6 (30% ethyl acetate in hexane); white solid; yield 89% (75 mg); mp 165-167 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.60 (m, 2H), 7.51-7.48 (m, 2H), 7.41-7.37 (m, 3H), 7.36-7.32 (m, 2H), 7.25 (d, *J* = 9.8 Hz, 1H), 7.23 (s, 1H), 5.96

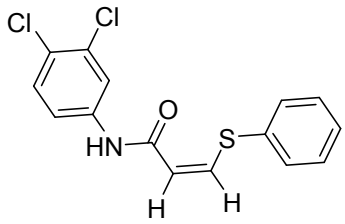


(d, J = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 148.4, 138.0, 137.9, 136.9, 131.1, 129.5, 128.3, 121.6, 115.2, 87.5; IR (KBr) ῡ 3327, 3077, 2324, 1651, 681, 506; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{13}INOS$ 381.9757; found 381.9743.

(Z)-N-(3-Chlorophenyl)-3-(phenylthio)acrylamide (3la): R_f = 0.65 (30% ethyl acetate in hexane); pale yellow solid; yield 78% (63 mg); mp 156-160 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.52-7.50 (m, 2H), 7.42-7.32 (m, 4H), 7.32-7.26 (m, 2H), 7.23 (t, J = 8.0 Hz, 1H), 7.08 (d, J = 7.8 Hz, 1H), 5.98 (d, J = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 148.7, 139.2, 136.9, 134.9, 131.1, 130.1, 129.5, 128.3, 124.4, 119.9, 117.6, 115.0; IR (KBr) ῡ 3302, 2922, 2851, 1674, 745, 691; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{13}ClNOS$ 290.0401; found 290.0379.



(Z)-N-(3,4-Dichlorophenyl)-3-(phenylthio)acrylamide (3ma): R_f = 0.6 (30% ethyl acetate in hexane); white solid; yield 77% (70 mg); mp 154-156 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.87 (m, 1H), 7.64 (s, 1H), 7.49-7.46 (m, 2H), 7.40-7.37 (m, 2H), 7.35-7.31 (m, 2H), 7.27-7.24 (m, 2H), 6.01 (d, J = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 148.9, 137.5, 136.6, 132.9, 131.1, 130.5, 129.5, 128.4, 127.4, 121.5, 119.1, 114.9; IR (KBr) ῡ 3319, 3060, 2916, 1537, 745, 690; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{11}Cl_2NOSNa$ 345.9831; found 345.9836.



(Z)-N-(3-Chloro-4-fluorophenyl)-3-(phenylthio)acrylamide (3na): R_f = 0.55 (30% ethyl acetate in hexane); yellow solid; yield 68% (63 mg); mp 162-164 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.83 (m, 1H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.39-7.32 (m, 5H), 7.27-7.25 (m, 1H), 7.09-7.05 (t, *J* = 8.6 Hz, 1H), 5.97 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 154.9 (d, $^1J_{CF}$ = 246.2 Hz), 148.7, 136.8, 134.7 (d, $^4J_{CF}$ = 3.2 Hz), 131.1, 129.5, 128.4, 122.0, 121.3 (d, $^2J_{CF}$ = 18.4 Hz), 119.4 (d, $^{4'}J_{CF}$ = 3.4 Hz), 116.7 (d, $^{2'}J_{CF}$ = 22.0 Hz), 114.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.68; IR (KBr) ῡ 3294, 2957, 2852, 1652, 1241, 745, 692; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{11}ClFNOSNa$ 330.0126; found 330.0120.

(Z)-N-(4-Bromo-2-methylphenyl)-3-(phenylthio)acrylamide (3oa): R_f = 0.6 (30% ethyl acetate in hexane); white solid; yield 93% (81 mg); mp 166-170 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.50-7.47 (m, 2H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.39-7.31 (m, 4H), 7.26-7.21 (m, 2H), 5.98 (d, *J* = 9.8 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 148.1, 138.7, 137.3, 137.0, 132.7, 131.1, 129.5, 128.3, 121.9, 119.5, 118.6, 115.3, 23.1; IR (KBr) ῡ 3327, 3055, 2341, 1634, 680, 555; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{14}BrNOSNa$ 369.9872; found 369.9865.

(Z)-N-methyl-N-phenyl-3-(phenylthio)acrylamide (3pa): R_f = 0.75 (20% ethyl acetate in hexane); colorless liquid; yield 68% (69 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.48 -7.47 (m, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.34-7.31 (m, 3H), 7.30-7.28 (m, 1H), 7.22 (d, *J* = 7.4 Hz, 2H), 6.99 (d, *J* = 9.8 Hz,

1H), 5.79 (d, *J* = 9.8 Hz, 1H), 3.37 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 166.5, 146.7, 143.9, 137.8, 131.1, 129.8, 129.3, 127.9, 127.6, 127.4, 113.7, 37.1; IR (KBr) ῡ 3052, 2930, 2322, 1680, 680; HRMS (ESI/Q-TOF) m/z: [M + Na]+ calcd for $C_{16}H_{15}NOSNa$ 292.0767; found 292.0778.

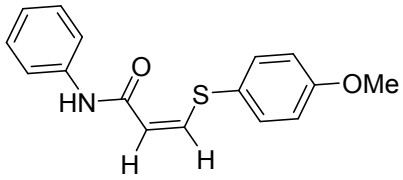
(Z)-N-Phenyl-3-(p-tolylthio)acrylamide (3ab): R_f = 0.5 (20% ethyl acetate in hexane); yellow solid; yield 78% (86 mg); mp 183-187 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 6.2 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.33-7.29 (m, 3H), 7.19-7.16 (m, 3H), 7.10 (t, *J* = 7.4 Hz, 1H), 5.96 (d, *J* = 9.8 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 148.5, 138.4, 138.1, 133.7, 131.3, 130.2, 129.1, 124.3, 119.7, 115.2, 21.3; IR (KBr) ῡ 3300, 3033, 2849, 2335, 1633, 692; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{15}NOSNa$ 292.0767; found 292.0758.

(Z)-N-Phenyl-3-(o-tolylthio)acrylamide (3ac): R_f = 0.55 (20% ethyl acetate in hexane); pale yellow solid; yield 69% (77 mg); mp 155-157 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.4 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.36 (s, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.27-7.19 (m, 3H), 7.11 (d, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 9.8 Hz, 1H), 6.00 (d, *J* = 9.8 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 148.1, 139.9, 138.1, 136.2, 132.6, 130.7, 129.1, 128.7, 127.0, 124.3, 119.7, 115.6, 21.0; IR (KBr) ῡ 3357, 3054, 1596, 691; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{16}NOS$ 270.0947; found 270.0923.

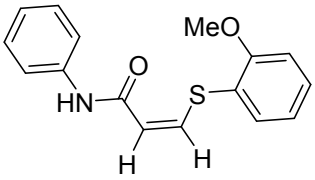
(Z)-3-((2,4-Dimethylphenyl)thio)-N-phenylacrylamide (3ad): R_f = 0.7 (20% ethyl acetate in hexane); yellow solid; yield 80% (94 mg); mp 186-188 ºC; ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 6.6 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.26 (s, 1H), 7.12-7.07 (m, 2H), 7.04-7.02 (m, 2H), 5.96 (d, *J* = 9.8 Hz, 1H), 2.43 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 148.9, 139.9, 138.9, 138.2, 133.0, 132.7, 131.6, 129.1, 127.8, 124.3, 119.7, 115.3, 21.2, 21.0; IR (KBr) ῡ 3454, 2919, 2312, 1634, 686; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}NOSNa$ 306.0923; found 306.0915.

(Z)-3-((4-Methoxyphenyl)thio)-N-phenylacrylamide (3ae): R_f = 0.45 (30% ethyl acetate in hexane); white solid; yield 82% (96 mg); mp 171-173 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 6.6 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.33-7.26 (m, 3H), 7.12-7.07 (m, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.93 (d, *J* = 9.8 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 160.1, 149.5, 138.1, 133.5, 129.1, 127.9, 124.3, 119.7, 115.0, 114.9, 55.5; IR (KBr) ῡ 3266, 3129, 2357, 1618, 1210, 694; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{16}NO_2S$ 286.0896; found 286.0871.



(Z)-3-((2-Methoxyphenyl)thio)-N-phenylacrylamide (3af): R_f = 0.4 (30% ethyl acetate in hexane); white solid; yield 80% (94 mg); mp 169-171 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 6.6 Hz, 2H), 7.53 (s, 1H), 7.46 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.34-7.30 (m, 1H), 7.28-7.26 (m, 2H), 7.11 (d, *J* = 9.8 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.96-6.90 (m, 2H), 6.01 (d, *J* = 9.8 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 158.4, 147.6, 138.2, 133.3, 130.1, 129.0, 124.5, 124.1, 121.2, 119.8, 115.5, 111.5, 56.0; IR (KBr) ῡ 3305, 3052, 2934, 1645, 692; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{16}NO_2S$ 286.0896; found 286.0869.



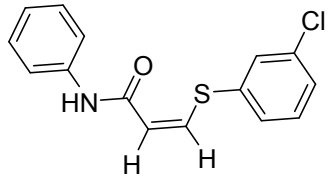
(Z)-3-((4-Fluorophenyl)thio)-*N*-phenylacrylamide (3am): R_f = 0.45 (20% ethyl acetate in hexane); white solid; yield 96% (108 mg); mp 182-184 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.14 (s, 1H), 7.65 (d, J = 7.4 Hz, 2H), 7.59-7.56 (m, 2H), 7.33-7.25 (m, 5H), 7.05 (t, J = 7.3 Hz, 1H), 6.23 (d, J = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.0, 161.8 (d, $^1J_{CF}$ = 245.3 Hz), 144.6, 139.2, 132.6 (d, $^4J_{CF}$ = 3.0 Hz), 132.5 (d, $^3J_{CF}$ = 8.4 Hz), 128.8, 123.2, 118.9, 116.8, 116.4 (d, $^2J_{CF}$ = 22.0 Hz); ^{19}F NMR (377 MHz, DMSO-d_6) δ -114.17; IR (KBr) ῡ 3309, 3055, 2337, 1625, 1303, 688; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{13}FNOS$ 274.0696; found 274.0696.

(Z)-3-((2-Fluorophenyl)thio)-N-phenylacrylamide (3an): R_f = 0.35 (20% ethyl acetate in hexane); pale yellow solid; yield 84% (94 mg); mp 145-148 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 6.8 Hz, 2H), 7.51 (td, J = 7.8, 1.6 Hz, 1H), 7.43 (s, 1H), 7.37-7.29 (m, 3H), 7.16-7.06 (m, 4H), 6.04 (d, J = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 161.6 (d, $^1J_{CF}$ = 247.6 Hz), 146.6, 138.0, 134.1, 130.7 (d, $^3J_{CF}$ = 7.8 Hz), 129.1, 124.9 (d, $^4J_{CF}$ = 3.8 Hz), 124.4, 123.8 (d, $^2J_{CF}$ = 17.8 Hz), 119.9, 116.4 (d, $^2J_{CF}$ = 22.4 Hz), 116.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.61; IR (KBr) ῡ 3322, 2923, 2851, 1652, 1309, 692; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{12}FNOSNa$ 296.0516; found 296.0513.

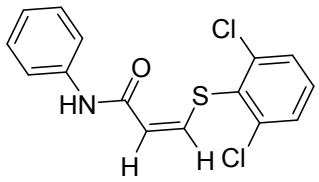
(Z)-3-((4-Chlorophenyl)thio)-N-phenylacrylamide (3aj): R_f = 0.5 (20% ethyl acetate in hexane); yellow solid; yield 92% (110 mg); mp 205-210 ºC; ^{1}H

NMR (400 MHz, DMSO-d_6) δ 10.16 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 9.8 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.27 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.0, 143.3, 139.1, 135.9, 132.4, 131.4, 129.3, 128.8, 123.2, 118.9, 117.3; IR (KBr) ῡ 3345, 3035, 2923, 2359, 1633, 692; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{12}ClNOSNa$ 312.0220; found 312.0207.

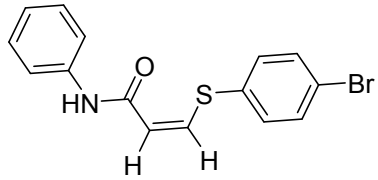
(Z)-3-((3-Chlorophenyl)thio)-N-phenylacrylamide (3ak): R_f = 0.65 (30% ethyl acetate in hexane); white solid; yield 80% (95 mg); mp 156-158 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 6.8 Hz, 2H), 7.48-7.47 (m, 1H), 7.38-7.29 (m, 6H), 7.16 (dd, *J* = 9.8, 1.2 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.04 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 146.1, 139.1, 137.9, 135.1, 130.6, 130.5, 129.2, 129.0, 128.3, 124.5, 119.8, 116.3; IR (KBr) ῡ 3305, 2955, 1733, 779, 694; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{12}ClNOSNa$ 312.0220; found 312.0212.



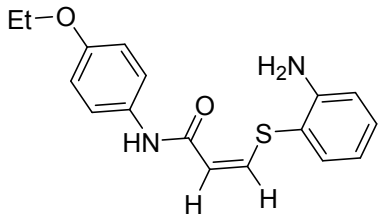
(Z)-3-((2,6-Dichlorophenyl)thio)-*N*-phenylacrylamide (3al): R_f = 0.6 (30% ethyl acetate in hexane); pale yellow solid; yield 88% (118 mg); mp 186-188 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.34-7.30 (m, 3H), 7.27-7.23 (m, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 9.8 Hz, 1H), 6.06 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 146.8, 140.1, 137.9, 134.6, 130.7, 129.1, 129.0, 124.4, 119.7, 115.8; IR (KBr) ῡ 3446, 2924, 1700, 778, 690; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{11}Cl_2NOSNa$ 345.9831; found 345.9814.



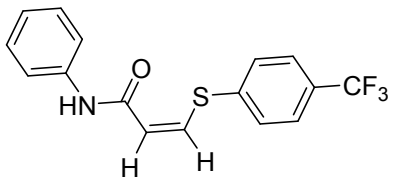
(Z)-3-((4-Bromophenyl)thio)-N-phenylacrylamide (3ai): R_f = 0.55 (20% ethyl acetate in hexane); yellow solid; yield 89% (124 mg); mp 211-215 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.16 (s, 1H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.49-7.47 (m, 2H), 7.38 (d, *J* = 9.8 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.27 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.0, 143.1, 139.1, 136.4, 132.2, 131.6, 128.8, 123.2, 120.8, 118.9, 117.4; IR (KBr) ῡ 3340, 2918, 2359, 1637, 692, 602; HRMS (ESI/Q-TOF) m/z: [M + Na]$^+$ calcd for $C_{15}H_{12}BrNOSNa$ 355.9715; found 355.9721.



(Z)-3-((2-Aminophenyl)thio)-N-(4-ethoxyphenyl)acrylamide (3gg): R_f = 0.35 (30% ethyl acetate in hexane); white solid; yield 73% (72 mg); mp 169-173 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.85-6.82 (m, 3H), 6.75-6.70 (m, 2H), 5.98 (d, *J* = 9.8 Hz, 1H), 4.24 (s, 2H), 3.99 (q, *J* = 6.8 Hz, 2H), 1.39 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 155.9, 148.2, 147.8, 135.4, 131.1, 130.9, 121.6, 119.2, 118.8, 116.5, 115.5, 114.9, 63.8, 15.0; IR (KBr) ῡ 3305, 2978, 1557, 1181, 694; HRMS (ESI/Q-TOF) m/z: [M + Na]$^+$ calcd for $C_{17}H_{18}N_2O_2SNa$ 337.0981; found 337.0966.

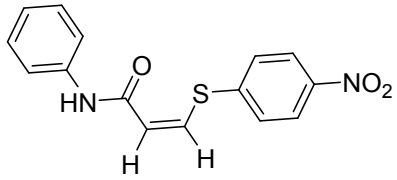


(Z)-*N*-Phenyl-3-((4-(trifluoromethyl)phenyl)thio)acrylamide (3ah): R_f = 0.5 (30% ethyl acetate in hexane); yellow solid; yield 87% (116 mg); mp 202-206 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.21 (s, 1H), 7.78-7.73 (m, 4H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 9.8 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.34 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz,

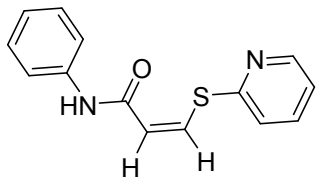


DMSO-d_6) δ 163.9, 142.4, 141.3, 139.1, 129.4, 128.8, 127.6 (q, $^2J_{CF3}$ = 32.0 Hz), 126.1 (q, $^4J_{CF3}$ = 3.4 Hz), 124.10 (q, $^1J_{CF3}$ = 272.0 Hz), 123.3, 118.9, 118.2; ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.02; IR (KBr) ῡ 3344, 3045, 2922, 1643, 1225, 693; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{12}F_3NOSNa$ 346.0484; found 346.0471.

(Z)-3-((4-Nitrophenyl)thio)-N-phenylacrylamide (3ao): R_f = 0.4 (30% ethyl acetate in hexane); yellow solid; yield 88% (108 mg); mp 210-215 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.26 (s, 1H), 8.23 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.66 (s, 1H), 7.66-7.62 (m, 2H) 7.33 (t, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.40 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.8, 146.1, 145.9, 139.6, 139.0, 130.3, 128.8, 124.2, 123.4, 119.0, 118.9; IR (KBr) ῡ 3208, 2920, 1568, 694; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{13}N_2O_3S$ 301.0641; found 301.0641.



(Z)-*N*-Phenyl-3-(pyridin-2-ylthio)acrylamide (3ap): R_f = 0.45 (30% ethyl acetate in hexane); yellow solid; yield 90% (95 mg); mp 103-108 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49-8.48 (m, 1H), 8.46-8.43 (m, 1H), 7.87 (s, 1H), 7.62-7.60 (m, 2H), 7.56-7.52 (m, 1H), 7.29-7.26 (m, 3H), 7.09-7.05 (m, 2H), 6.22 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 156.0, 149.6, 139.2, 138.1, 136.9, 129.0, 124.3, 123.4, 121.3, 119.9, 116.4; IR (KBr) ῡ 3303, 2955, 1645, 1136, 691; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{12}N_2OSNa$ 279.0563; found 279.0562.



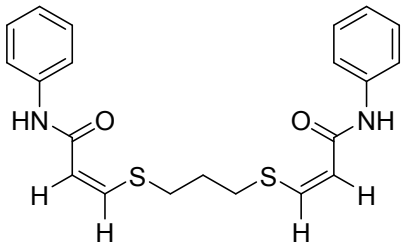
(Z)-3-((2,4-Diphenyloxazol-5-yl)thio)-N-phenylacrylamide (3aq): R_f = 0.5 (20% ethyl acetate in hexane); yellow solid; yield 93% (153 mg); mp 168-173 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.8 Hz, 1H), 7.67 (d, *J* = 6.8 Hz, 2H), 7.59 (s, 1H), 7.59-7.57 (m, 3H), 7.41-7.33 (m, 9H), 7.14 (t, *J* = 7.0 Hz, 1H), 6.24 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 158.8, 147.9, 139.0, 137.6, 136.51, 132.1, 129.3, 128.90(×2), 128.86, 128.8, 128.6, 128.1, 126.6, 124.8, 120.0, 117.7; IR (KBr) ῡ 3274, 3045, 2922, 1596, 689; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{24}H_{18}N_2O_2SNa$ 421.0981; found 421.0959.

(2Z, 2'Z)-3,3'-(1,4-Phenylenebis(sulfanediyl))bis(N-phenylacrylamide) (3ar): R_f = 0.5 (30% ethyl acetate in hexane); pale yellow solid; yield 96% (175 mg); mp >230 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.16 (s, 2H), 7.65 (d, *J* = 7.4 Hz, 4H), 7.64-7.56 (m, 4H), 7.41 (d, *J* = 9.8 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 4H), 7.05 (t, *J* = 7.4 Hz, 2H), 6.28 (d, *J* = 9.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.0, 143.2, 139.2, 136.3, 130.4, 128.8, 123.2, 118.9, 117.3; IR (KBr) ῡ 3222, 3049, 1637, 1258, 692; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{24}H_{20}N_2O_2S_2Na$ 455.0858; found 455.0848.

(Z)-3-((4-(((E)-3-Oxo-3-(phenylamino)prop-1-en-1-yl)thio)phenyl)thio)-N-phenylacrylamide (3ar): R_f = 0.55 (30% ethyl acetate in hexane); solid; yield ~1% (~2 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.19 (s, 1H), 9.93 (s, 1H), 7.68-7.64 (m, 5H), 7.61-7.57 (m, 4H), 7.48 (d, *J* = 9.8 Hz, 1H), 7.34-7.31 (m, 2H), 7.30-7.27 (m, 2H), 7.08-7.01 (m, 2H), 6.31 (d, *J* = 9.8 Hz, 1H), 6.06 (d, *J* = 14.8 Hz, 1H); ^{13}C NMR (175 MHz, DMSO-d_6) δ 164.0, 161.9, 142.5,

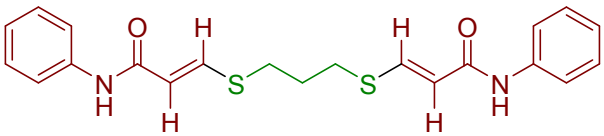
140.5, 139.2, 139.1(×2), 138.2, 133.2, 130.5, 129.6, 128.8, 128.8, 123.3, 120.0, 119.2(×2), 118.9(×2), 117.7; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{24}H_{20}N_2O_2S_2Na$ 455.0858; found 455.0821.

(2Z,2'Z)-3,3'-(Propane-1,3-diylbis(sulfanediyl))bis(N-phenylacrylamide) (3as): R_f = 0.7



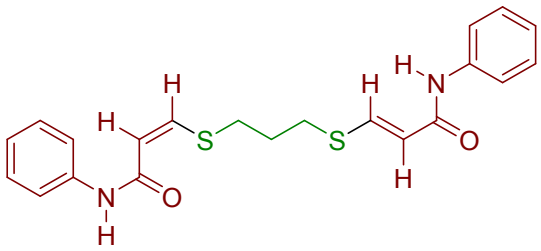
(30% ethyl acetate in hexane); quasi-solid; yield 72% (160 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 6.8 Hz, 4H), 7.33 (t, *J* = 7.8 Hz, 4H), 7.22 (s, 2H), 7.11 (t, *J* = 7.4 Hz, 2H), 7.00 (d, *J* = 9.8 Hz, 2H), 5.96 (d, *J* = 9.8 Hz, 2H), 2.94 (t, *J* = 6.8 Hz, 4H), 2.09 (p, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 146.9, 138.2, 129.0, 124.2, 119.9, 116.3, 34.6, 30.5; IR (KBr) ῡ 3301, 2918, 2849, 1652, 743, 686; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{22}N_2O_2S_2Na$ 421.1015; found 421.1015.

(2E,2'E)-3,3'-(Propane-1,3-diylbis(sulfanediyl))bis(N-phenylacrylamide) (3as): R_f = 0.75



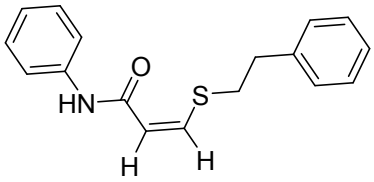
(30% ethyl acetate in hexane); solid; yield 7% (16 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.89 (s, 2H), 7.63 (d, *J* = 7.8 Hz, 4H), 7.59 (d, *J* = 15.0 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 4H), 7.04 (t, *J* = 7.4 Hz, 2H), 6.16 (d, *J* = 15.0 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 4H), 2.07-2.01 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.1, 141.2, 139.3, 128.7, 123.1, 119.1, 118.2, 30.1, 27.9; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{22}N_2O_2S_2Na$ 421.1015; found 421.1018.

(Z)-3-((3-(((E)-3-Oxo-3-(phenylamino)prop-1-en-1-yl)thio)propyl)thio)-Nphenylacrylamide

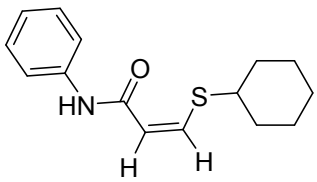


(3as): R_f = 0.75 (30% ethyl acetate in hexane); semi-solid; yield 12% (27 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.15 (s, 1H), 7.69 (d, *J* = 7.1 Hz, 2H), 7.62-7.59 (m, 3H), 7.27-7.25 (m, 4H), 7.09-7.06 (m, 2H), 6.89 (d, *J* = 9.9 Hz, 1H), 6.07 (d, *J* = 9.9 Hz, 1H), 6.04 (d, *J* = 14.7 Hz, 1H), 2.81-2.78 (m, 4H), 1.97-1.93 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.0, 163.4, 146.7, 142.2, 138.7, 138.1, 129.1, 129.0, 124.4, 124.1, 120.2, 119.9, 117.4, 116.6, 35.4, 29.5, 28.7; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{22}N_2O_2S_2Na$ 399.1195; found 399.1197.

(Z)-3-(Phenethylthio)-*N*-phenylacrylamide (3at): R_f = 0.45 (20% ethyl acetate in hexane); white solid; yield 67% (78 mg); mp 160-164 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.0 Hz, 2H), 7.38 (s, 1H), 7.32-7.27 (m, 4H), 7.24-7.21 (m, 3H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 9.8 Hz, 1H), 5.91 (d, *J* = 9.8 Hz, 1H), 3.03-2.94 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 147.4, 139.7, 138.2, 129.0, 128.7, 128.7, 126.7, 124.1, 119.6, 115.7, 37.9, 36.9; IR (KBr) ῡ 3222, 3023, 2944, 1634, 692; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}NOSNa$ 306.0923; found 306.0922.



(Z)-3-(cyclohexylthio)-*N*-phenylacrylamide (3au): R_f = 0.55 (10% ethyl acetate in hexane); white solid; yield 62% (67 mg); mp 137-140 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.42 (s, 1H), 7.29-7.25 (m, 2H), 7.07-7.04 (m, 2H), 5.92 (d, *J* = 10.1 Hz, 1H), 2.83-2.76 (m, 1H),



2.03-1.99 (m , 2H), 1.82-1.78 (m, 2H), 1.63-1.59 (m, 1H), 1.50-1.40 (m, 2H), 1.38-1.21 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 145.7, 138.3, 129.0, 124.0, 119.7, 115.3, 47.9, 33.6, 25.9, 25.5; IR (KBr) ῡ 3308, 2927, 2851, 1668, 691; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{19}NOSNa$ 284.1080; found 284.1091.

(Z)-3-(*iso*-Butylthio)-*N*-phenylacrylamide (3av): R_f = 0.75 (20% ethyl acetate in hexane); white solid; yield 65% (63 mg); mp 120-123 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 6.8 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.23 (s, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 10.0 Hz, 1H), 5.89 (d, *J* = 10.0 Hz, 1H), 2.66 (d, *J* = 6.8 Hz, 2H), 1.90 (nonet, *J* = 6.6 Hz, 1H), 1.03 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 148.8, 138.3, 129.1, 124.1, 119.6, 115.2, 46.0, 29.5, 21.8; IR (KBr) ῡ 3341, 3054, 2359, 1627, 750, 689; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{13}H_{17}NOSNa$ 258.0923; found 258.0928.

(Z)-3-((Furan-2-ylmethyl)thio)-*N*-phenylacrylamide (3aw): R_f = 0.35 (20% ethyl acetate in hexane); white solid; yield 92% (98 mg); mp 111-115 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 6.6 Hz, 2H), 7.37-7.36 (m, 1H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.23 (s, 1H), 7.09-7.06 (m, 2H), 6.33-6.31 (m, 1H), 6.25 (d, *J* = 3.2 Hz, 1H), 5.94 (d, *J* = 9.8 Hz, 1H), 3.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 151.1, 146.1, 142.7, 138.1, 129.0, 124.2, 119.7, 116.0, 110.7, 108.2, 32.1; IR (KBr) ῡ 3312, 2923, 1642, 691; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{13}NO_2SNa$ 282.0559; found 282.0562.

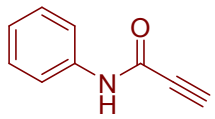
(Z)-*N*-Phenyl-3-((4-(trifluoromethyl)phenyl)sulfinyl)acrylamide 6: R_f = 0.45 (50% ethyl acetate in hexane); white solid; yield 95% (60 mg); mp >230 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.68 (s, 1H), 8.06 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 9.8 Hz, 1H), 6.69 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.7, 152.7, 150.3, 138.2, 130.9 (q, $^2J_{CF3}$ = 32.0 Hz), 129.0, 128.7, 126.3 (q, $^3J_{CF3}$ = 3.4 Hz), 125.8, 124.4, 123.8 (q, $^1J_{CF3}$ = 272.6 Hz), 119.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.54; IR (KBr) ῡ 3305, 3033, 2974, 1668, 1000, 696; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{13}F_3NO_2S$ 340.0614; found 340.0587.

(Z)-3-([1,1'-Biphenyl]-4-ylthio)-N-phenylacrylamide 7: R_f = 0.45 (20% ethyl acetate in hexane); white solid; yield 76% (60 mg); mp 177-180 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.15 (s, 1H), 7.74-7.60 (m, 8H), 7.55-7.44 (m, 3H), 7.39 (t, *J* = 6.8 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.28 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.1, 143.7, 139.3, 139.20, 139.18, 136.0, 130.2, 129.0, 128.8, 127.8, 127.6, 126.6, 123.2, 118.9, 117.1; IR (KBr) ῡ 3397, 3040, 2916, 1657, 697; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{17}NOSNa$ 354.0923; found 354.0919.

(Z)-3-Phenyl-3-(phenylthio)-N-(p-tolyl)acrylamide (3ra):[5] R_f = 0.6 (20% ethyl acetate in hexane); white solid; yield 83% (75 mg); mp 167-172 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.26-7.25 (m, 2H), 7.19-7.18 (m, 2H), 7.14-7.13 (m, 5H),

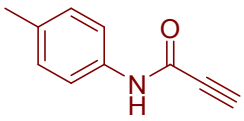
7.07-7.06 (m, 3H), 6.24 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.6, 153.3, 138.7, 135.6, 134.0, 133.3, 132.7, 129.6, 128.8, 128.7, 128.6, 128.0, 127.7, 121.9, 119.9, 21.0; IR (KBr) ῡ 3362, 2927, 2396, 1676, 691; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{19}NOSNa$ 368.1080; found 368.1070.

***N*-Phenylpropiolamide 1a:**[6] R_f = 0.75 (20% ethyl acetate in hexane); yellow solid; yield 64%



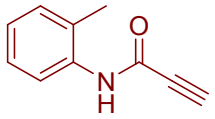
(301 mg); mp 81-84 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 2.92 (s, 1H).

***N*-(*p*-Tolyl)propiolamide 1b:**[7] R_f = 0.35 (20% ethyl acetate in hexane); yellow solid; yield 61%



(270 mg); mp 126-129 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 2.90 (s, 1H), 2.32 (s, 3H).

***N*-(*o*-Tolyl)propiolamide 1c:** R_f = 0.35 (20% ethyl acetate in hexane); yellow solid; yield 89%



(400 mg); mp 133-135 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.24 (s, 1H), 7.29-7.23 (m, 2H), 7.20-7.13 (m, 2H), 4.34 (s, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.2, 134.8, 132.7, 130.4, 126.3, 126.1, 125.8, 78.4, 76.9, 17.8; IR (KBr) ῡ 3256, 3023, 2926, 2359, 2107, 1677; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{10}NO$ 160.0757; found 160.0764.

***N*-(2,4-Dimethylphenyl)propiolamide 1d:** R_f = 0.35 (20% ethyl acetate in hexane); yellow solid; yield 70% (300 mg); mp 151-153 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.6 Hz, 1H), 7.24 (s, 1H), 7.03-7.01 (m, 2H), 2.91 (s, 1H), 2.30 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 136.1, 132.0, 131.4, 129.5, 127.6, 123.6, 77.8, 74.0, 21.0, 17.8; IR (KBr) ῡ 3279, 3088, 2969, 2107, 1672, 745; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{12}NO$ 174.0913; found 174.0937.

***N*-(4-*iso*-Propylphenyl)propiolamide 1e:** R_f = 0.35 (20% ethyl acetate in hexane); semi solid; yield 67% (280 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 2.90 (s, 1H), 2.93-2.83 (m, 1H), 1.23 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 145.9, 134.9, 126.9, 120.5, 77.7, 74.4, 33.6, 24.0; IR (KBr) ῡ 3273, 2959, 2108, 1699, 833; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{14}NO$ 188.1070; found 188.1088.

***N*-(4-(*tert*-Butyl)phenyl)propiolamide 1f:** R_f = 0.4 (20% ethyl acetate in hexane); semi solid; yield 58% (234 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 2.90 (s, 1H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 148.3, 134.5, 126.0, 120.1, 77.8, 74.2, 34.5, 31.4; IR (KBr) ῡ 3299, 2981, 2109, 1599, 741; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{16}NO$ 202.1226; found 202.1245.

***N*-(4-Ethoxyphenyl)propiolamide 1g:** R_f = 0.30 (20% ethyl acetate in hexane); grey solid; yield 85% (350 mg); mp 95-103 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.42-7.39 (m, 3H), 6.87-6.85 (d, J = 9.0 Hz, 2H), 4.01 (q, J = 7.0 Hz, 2H), 2.90 (s, 1H), 1.40 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 149.9, 130.1, 122.0, 114.9, 77.8, 74.2, 63.9, 14.9; IR (KBr) ῡ 3292, 3064, 2970, 2340, 2109, 1635; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{12}NO_2$ 190.0863; found 190.0865.

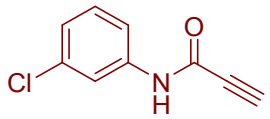
***N*-(4-(Trifluoromethoxy)phenyl)propiolamide 1h:** R_f = 0.4 (30% ethyl acetate in hexane); yellow solid; yield 91% (210 mg); mp 123-127 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.58-7.56 (m, 2H), 7.19 (d, J = 8.6 Hz, 2H), 2.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 146.0, 135.7, 122.0, 121.4, 120.6 (q, J = 257.8 Hz), 77.4, 74.8; IR (KBr) ῡ 3303, 3073, 2111, 1670, 1240; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_7F_3NO_2$ 230.0423; found 230.0437.

***N*-(4-Fluorophenyl)propiolamide 1i:** R_f = 0.35 (20% ethyl acetate in hexane); yellow solid; yield 79% (350 mg); mp 175-177 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.50-7.47 (m, 2H), 7.03 (t, J = 8.6 Hz, 2H), 2.93 (s, 1H).

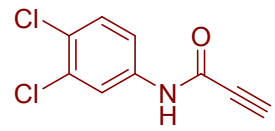
***N*-(4-Bromophenyl)propiolamide 1j**:[7] R_f = 0.35 (20% ethyl acetate in hexane); yellow solid; yield 62% (241 mg); mp 184-188 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.46 (d, J = 9.0 Hz, 2H), 7.41 (d, J = 9.0 Hz, 2H), 2.95 (s, 1H).

***N*-(4-Iodophenyl)propiolamide 1k:** R_f = 0.25 (20% ethyl acetate in hexane); white solid; yield 64% (237 mg); mp 206-211 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.90 (s, 1H), 7.66 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 4.44 (s, 1H); ^{13}C

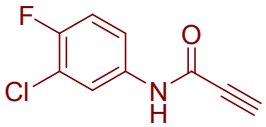
NMR (100 MHz, DMSO-d_6) δ 149.7, 138.0, 137.5, 121.8, 88.1, 78.2, 77.5; IR (KBr) ῡ 3294, 2922, 2108, 1655, 508; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for C_9H_7INO 271.9567; found 271.9558.

***N*-(3-Chlorophenyl)propiolamide 1l:**[7] R_f = 0.6 (20% ethyl acetate in hexane); yellow solid; 

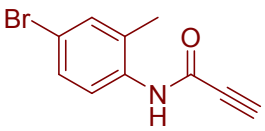
yield 54% (230 mg); mp 164-166 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.99 (s, 1H), 7.75 (t, *J* = 2.0 Hz, 1H), 7.50-7.48 (m, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 4.48 (s, 1H).

***N*-(3,4-Dichlorophenyl)propiolamide 1m:** R_f = 0.3 (20% ethyl acetate in hexane); yellow solid; 

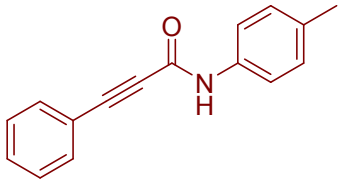
yield 88% (350 mg); mp 179-184 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 2.0 Hz, 1H), 7.55 (s, 1H), 7.40 (d, *J* = 8.6 Hz, 1H), 7.36-7.33 (m, 1H), 2.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 137.6, 132.1, 130.1, 127.0, 121.5, 119.3, 77.8, 74.3; IR (KBr) ῡ 3284, 3096, 2110, 1643, 675; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_9H_6Cl_2NO$ 213.9821; found 213.9812.

***N*-(3-Chloro-4-fluorophenyl)propiolamide 1n:** R_f = 0.3 (30% ethyl acetate in hexane); yellow 

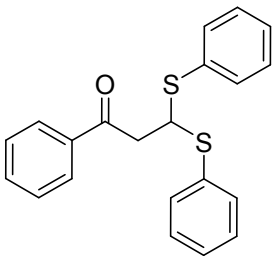
solid; yield 68% (280 mg); mp 153-155 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.00 (s, 1H), 7.86 (d, *J* = 5.2 Hz, 1H), 7.52-7.50 (m, 1H), 7.40-7.38 (m, 1H), 4.48 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8 (d, $^1J_{CF}$ = 246.4 Hz), 145.0, 134.6, 122.3, 120.8 (d, $^2J_{CF}$ = 18.4 Hz), 119.9 (d, $^3J_{CF}$ = 6.8 Hz), 116.46 (d, $^2J_{CF}$ = 22.0 Hz), 77.9, 74.2; IR (KBr) ῡ 3268, 2925, 2850, 2108, 1645, 1238, 686; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for C_9H_6ClFNO 198.0116; found 198.0106.

***N*-(4-Bromo-2-methylphenyl)propiolamide 1o:** R_f = 0.36 (20% ethyl acetate in hexane); 

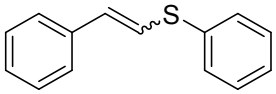
yellow solid; yield 57% (220 mg); mp 123-126 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.46-7.44 (m, 2H), 7.23 (dd, *J* = 8.6, 2.6 Hz, 1H), 2.93 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 139.0, 136.2, 132.9, 122.3, 120.6, 119.1, 77.6, 74.5, 23.2; IR (KBr) ῡ 3280, 2925, 2853, 2109, 1607, 671; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_9BrNO$ 237.9862; found 237.9879.

3-Phenyl-N-(p-tolyl)propiolamide 1r:[8] R_f = 0.75 (20% ethyl acetate in hexane); yellow solid; 

yield 76% (499 mg); mp 146-148 ºC (lit.[8]143-145); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.58-7.56 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 3H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H).

1-phenyl-3,3-bis(phenylthio)propan-1-one 5:[9] R_f = 0.45 (5% ethyl acetate in hexane); colorless 

liquid; yield 88% (142 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92-7.90 (m, 2H), 7.67-7.64 (m, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.46-7.43 (m, 4H), 7.39-7.30 (m, 6H), 5.16 (t, *J* = 6.6 Hz, 1H), 3.59 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.1, 136.1, 133.6, 133.4, 131.9, 129.2, 128.8, 128.1, 127.9, 54.1, 43.9.

phenyl(styryl)sulfane 4:[10] R_f = 0.85 (in hexane); colorless liquid; yield 79% (98 mg); 1H NMR 

(400 MHz, CDCl3) δ 7.58-7.28 (m, 10H), 6.92 (d, J = 15.5 Hz, 1H), 6.76 (d, J = 15.5 Hz, 1H), 6.63 (d, J = 10.8 Hz, 1H), 6.53 (d, J = 10.7 Hz, 1H).

REFERENCES

1. H. Wang, Y. Li, Z. Tang, S. Wang, H. Zhang, H. Cong and A. Lei, *ACS Catal.*, 2018, **8**, 10599-10605.
2. G. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112-122.
3. SADABS, Bruker AXS, Madison, Wisconsin, USA, 2004
4. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Journal*, 2009.
5. M. Pramanik, K. Choudhuri, S. Chakraborty, A. Ghosh and P. Mal, *Chem. Commun.*, 2020, **56**, 2991-2994.
6. N. T. Coles, M. F. Mahon and R. L. Webster, *Chem. Commun.*, 2018, **54**, 10443-10446.
7. Y. Zhou, J. Feng, L. Feng, D. Xie, H. Peng, M. Cai and H. He, *J. Agric. Food. Chem.*, 2019, **67**, 12538-12546.
8. M. Kissane, M. Murphy, E. O'Brien, J. Chopra, L. Murphy, S. G. Collins, S. E. Lawrence and A. R. Maguire, *Org. Biomol. Chem.*, 2011, **9**, 2452-2472.
9. B. C. Ranu, S. Banerjee and R. Jana, *Tetrahedron*, 2007, **63**, 776-782.
10. K. Choudhuri, M. Pramanik, A. Mandal and P. Mal, *Asian J. Org. Chem.*, 2018, **7**, 1849–1855.

NMR SPECTRA

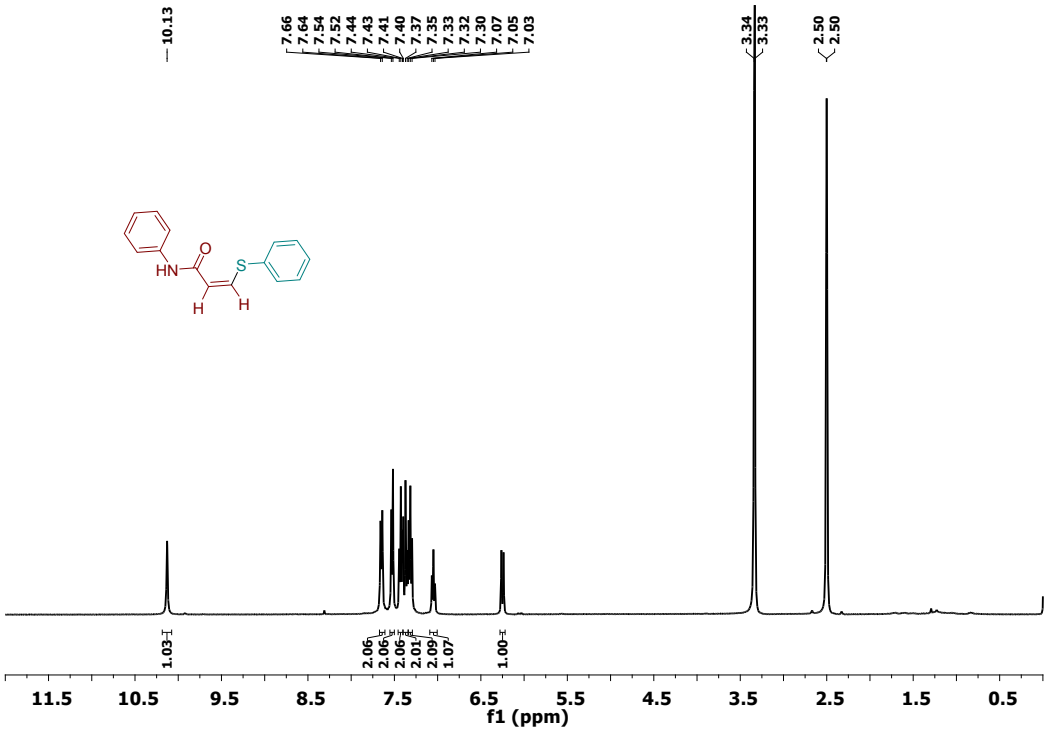


Fig. S7. ^{1}H NMR spectrum of (Z)-N-phenyl-3-(phenylthio) acrylamide (**3aa**)

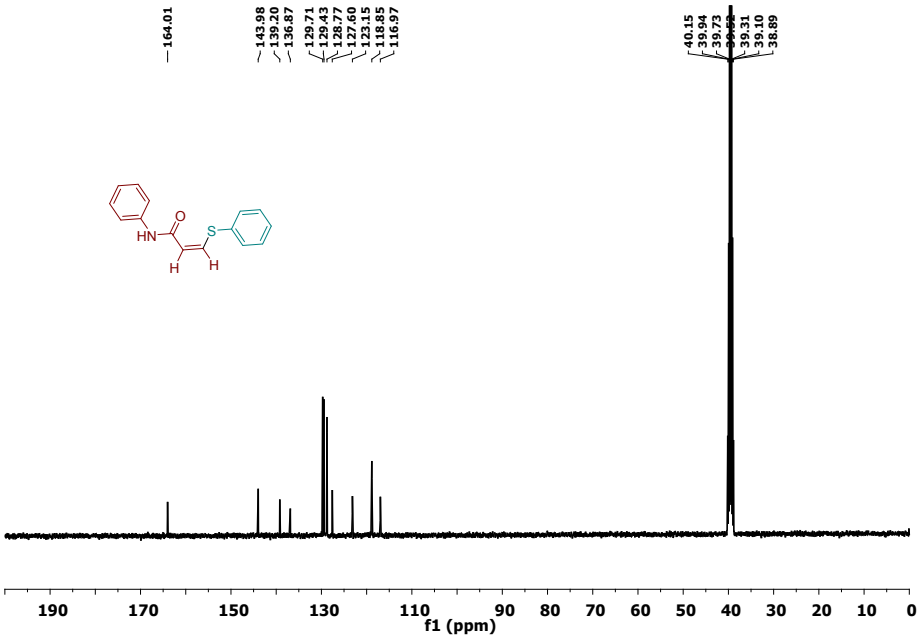


Fig. S8. ^{13}C NMR spectrum of (Z)-N-phenyl-3-(phenylthio)acrylamide (**3aa**)

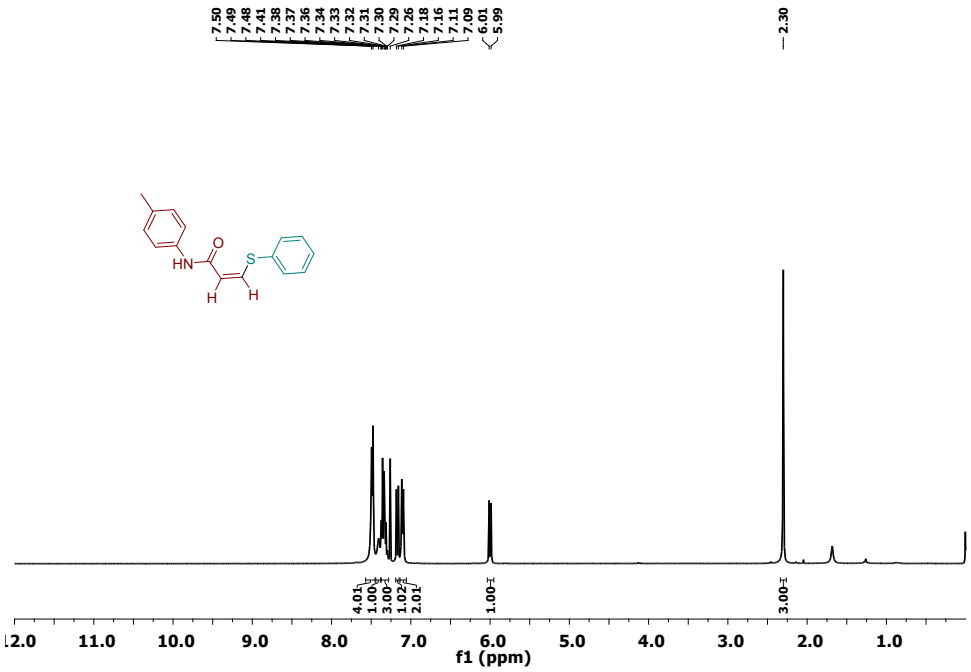


Fig. S9. ^{1}H NMR spectrum of (Z)-3-(phenylthio)-N-(p-tolyl)acrylamide (**3ba**)

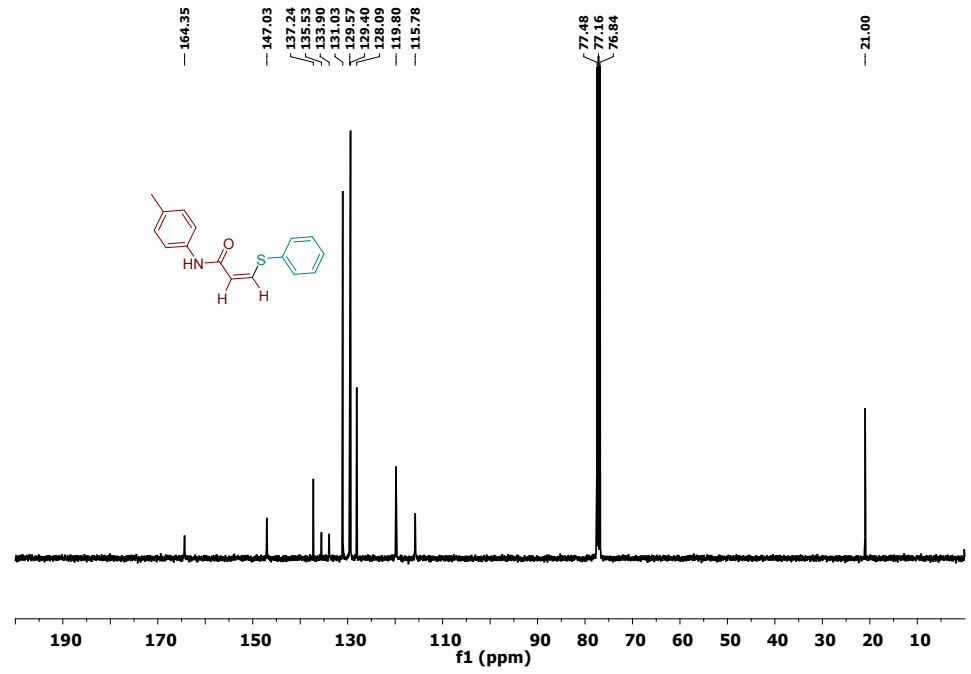


Fig. S10. ^{13}C NMR spectrum of (Z)-3-(phenylthio)-N-(p-tolyl)acrylamide (**3ba**)

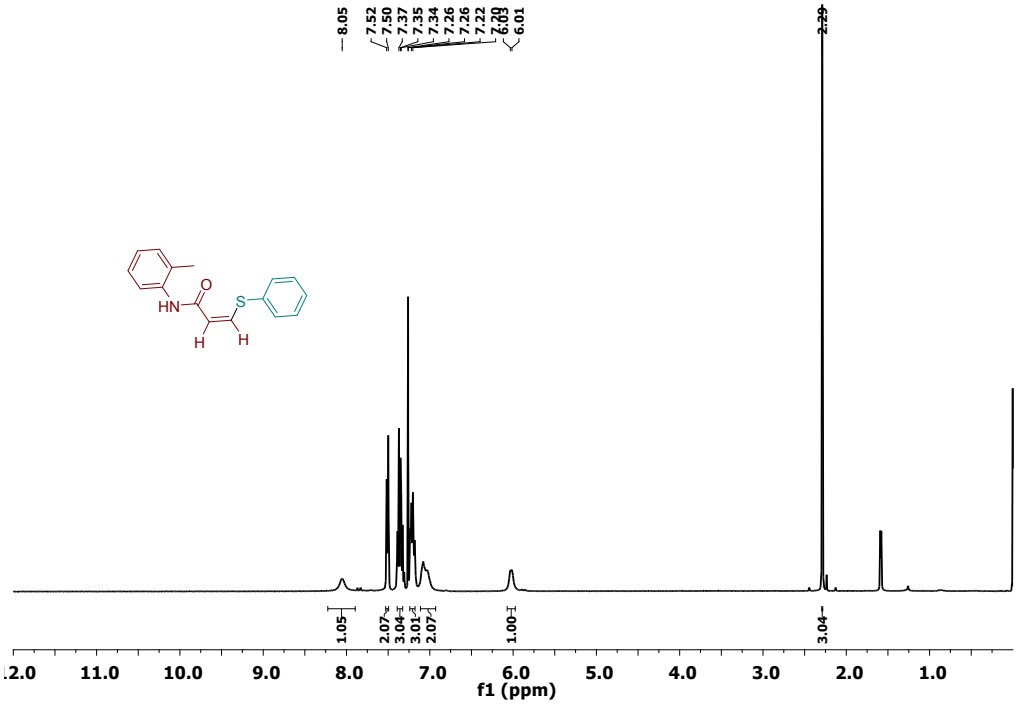


Fig. S11. ^{1}H NMR spectrum of (Z)-3-(phenylthio)-N-(o-tolyl)acrylamide (**3ca**)

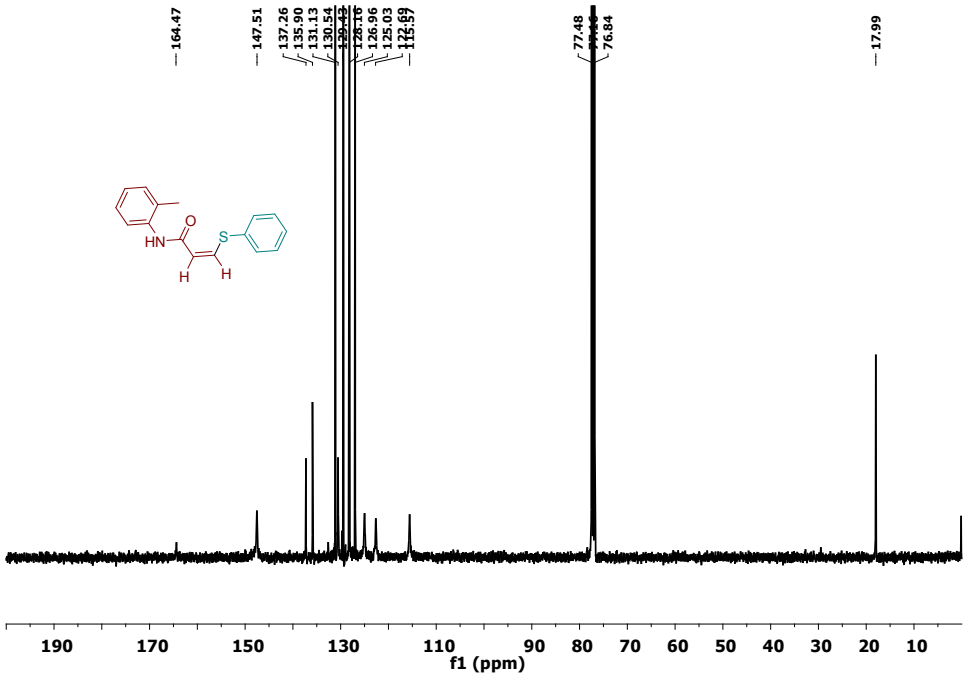


Fig. S12. ^{13}C NMR spectrum of (Z)-3-(phenylthio)-N-(o-tolyl)acrylamide (**3ca**)

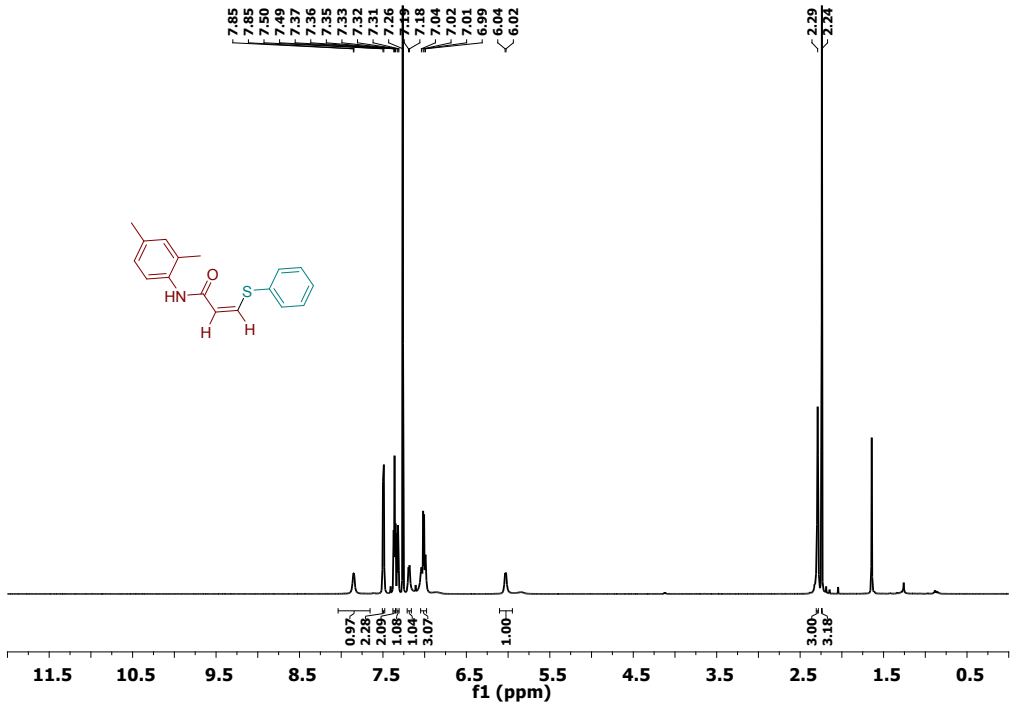


Fig. S13. ^{1}H NMR spectrum of (Z)-N-(2,4-dimethylphenyl)-3-(phenylthio)acrylamide (**3da**)

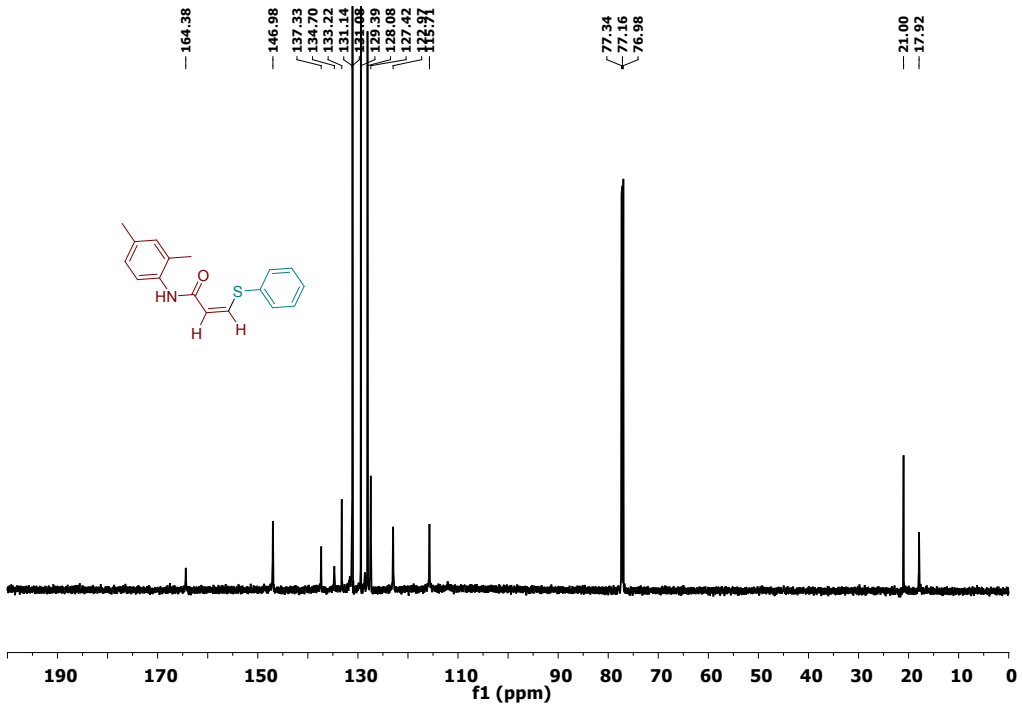


Fig. S14. ^{13}C NMR spectrum of (Z)-N-(2,4-dimethylphenyl)-3-(phenylthio)acrylamide (**3da**)

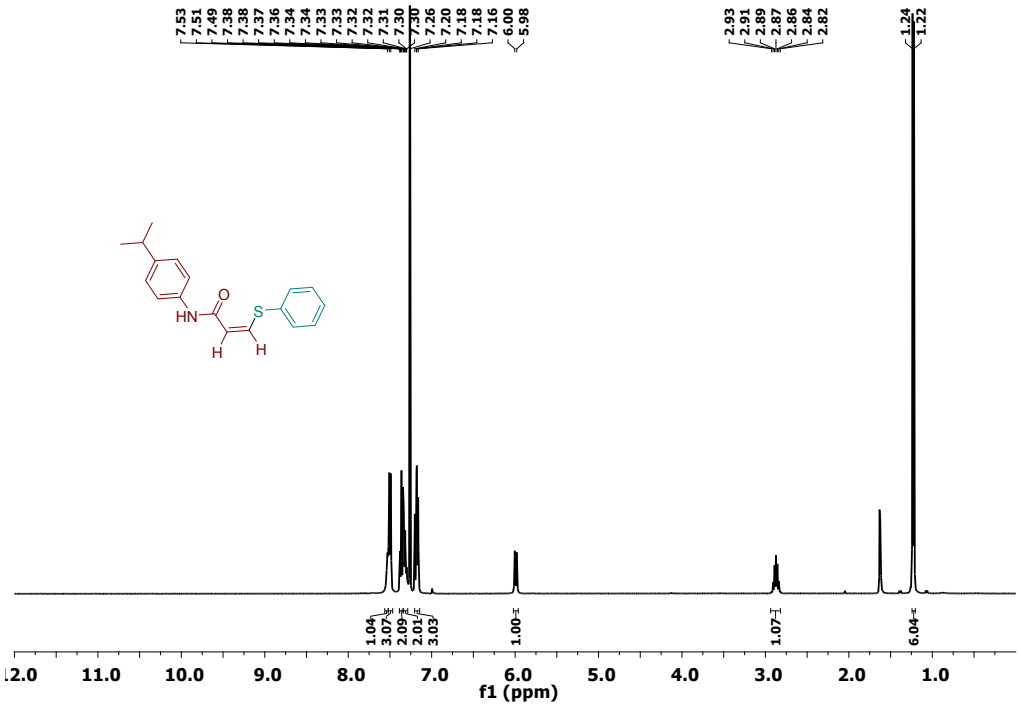


Fig. S15. ^{1}H NMR spectrum of (Z)-N-(4-isopropylphenyl)-3-(phenylthio)acrylamide (**3ea**)

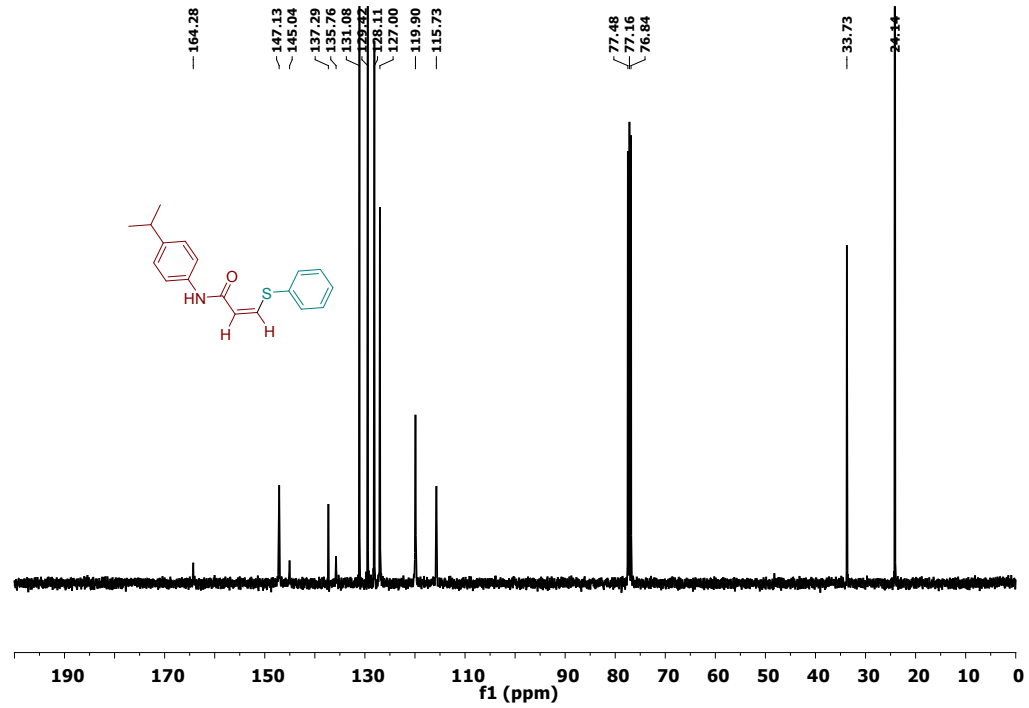


Fig. S16. ^{13}C NMR spectrum of (Z)-N-(4-isopropylphenyl)-3-(phenylthio)acrylamide (**3ea**)

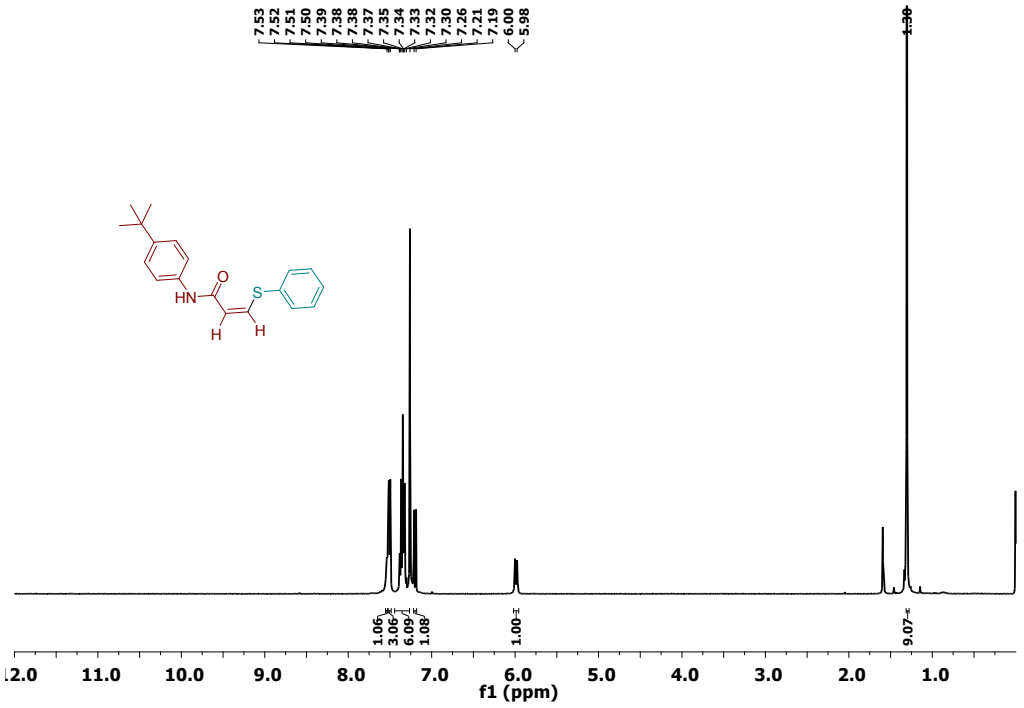


Fig. S17. [1]H NMR spectrum of (Z)-N-(4-(tert-butyl)phenyl)-3-(phenylthio)acrylamide (**3fa**)

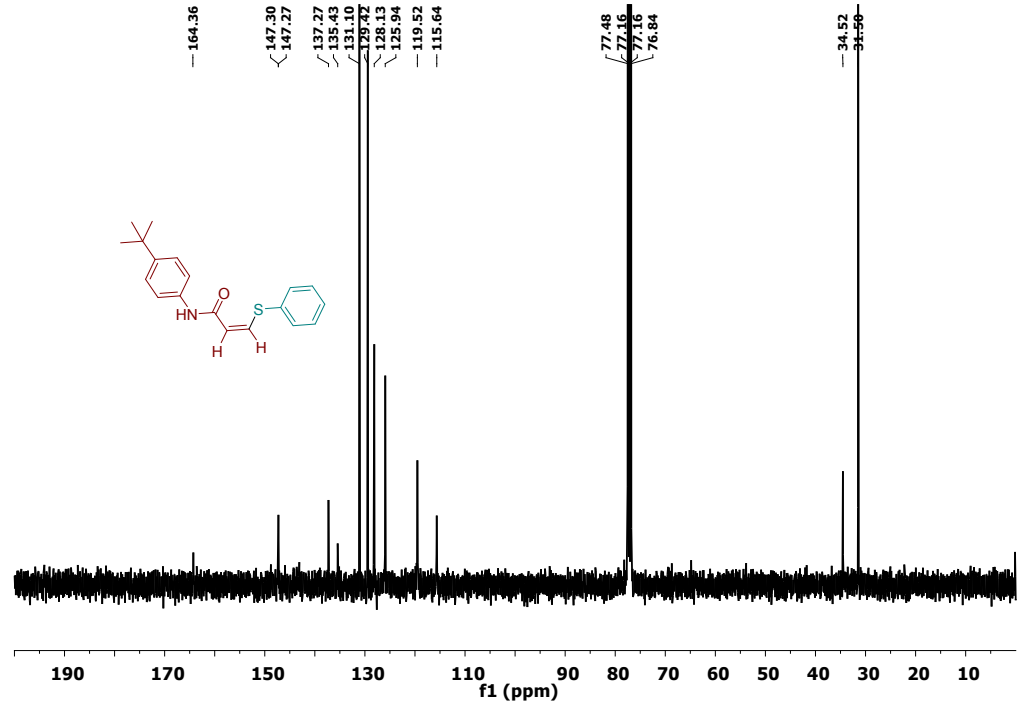


Fig. S18. [13]C NMR spectrum of (Z)-N-(4-(tert-butyl)phenyl)-3-(phenylthio)acrylamide (**3fa**)

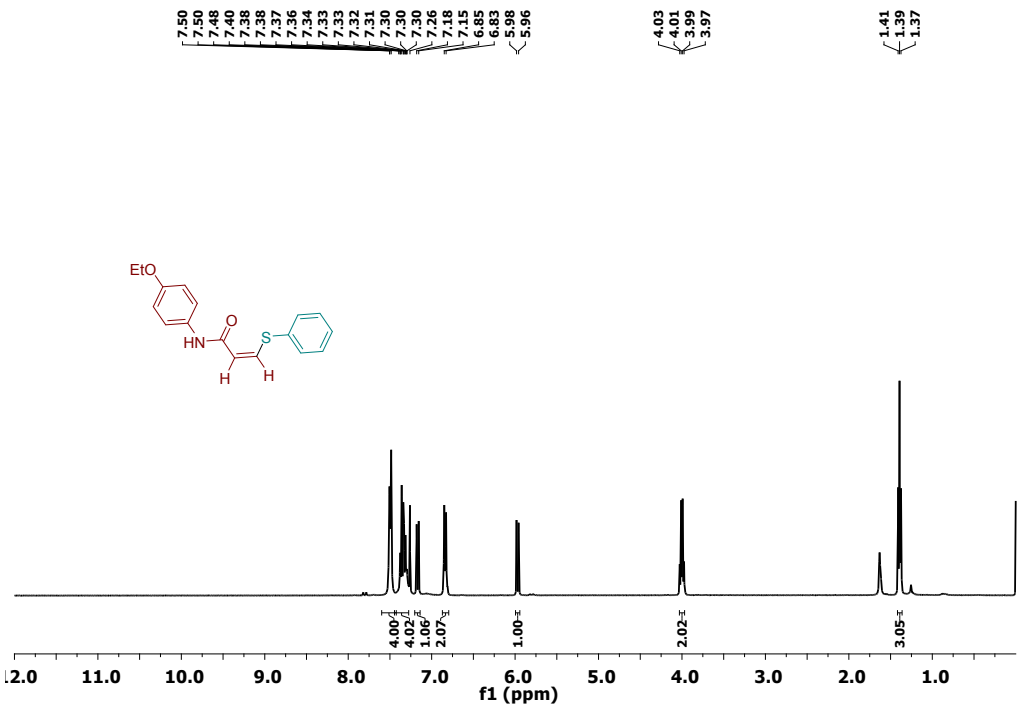


Fig. S19. ^{1}H NMR spectrum of (Z)-N-(4-ethoxyphenyl)-3-(phenylthio)acrylamide (**3ga**)

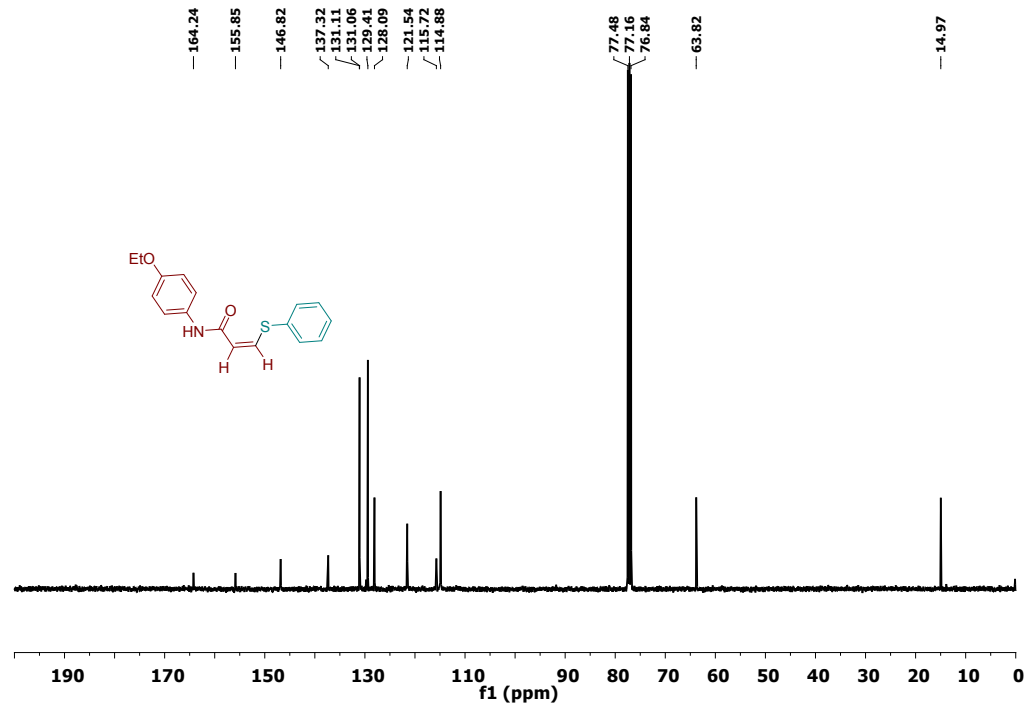


Fig. S20. ^{13}C NMR spectrum of (Z)-N-(4-ethoxyphenyl)-3-(phenylthio)acrylamide (**3ga**)

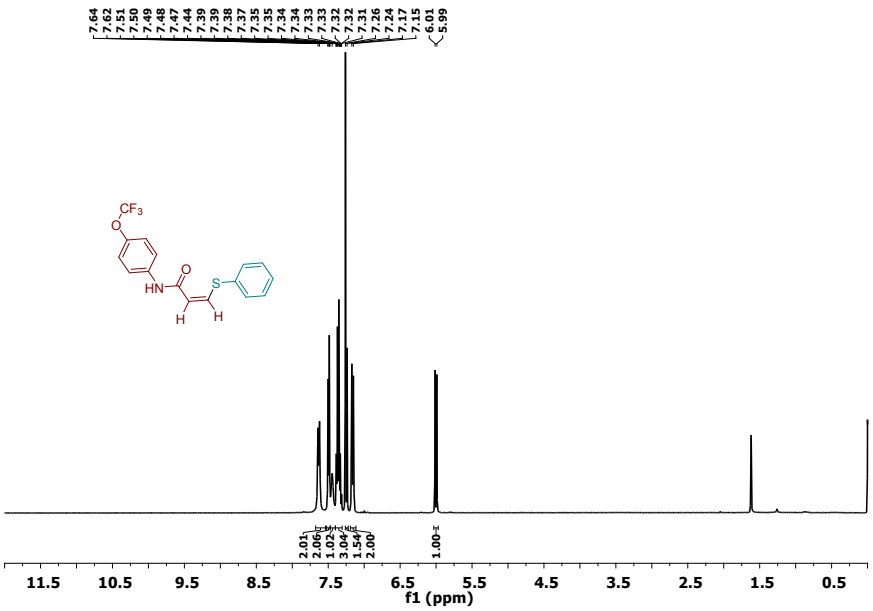


Fig. S21. [1]H NMR spectrum of (Z)-3-(phenylthio)-N-(4-(trifluoromethoxy)phenyl)acrylamide (**3ha**)

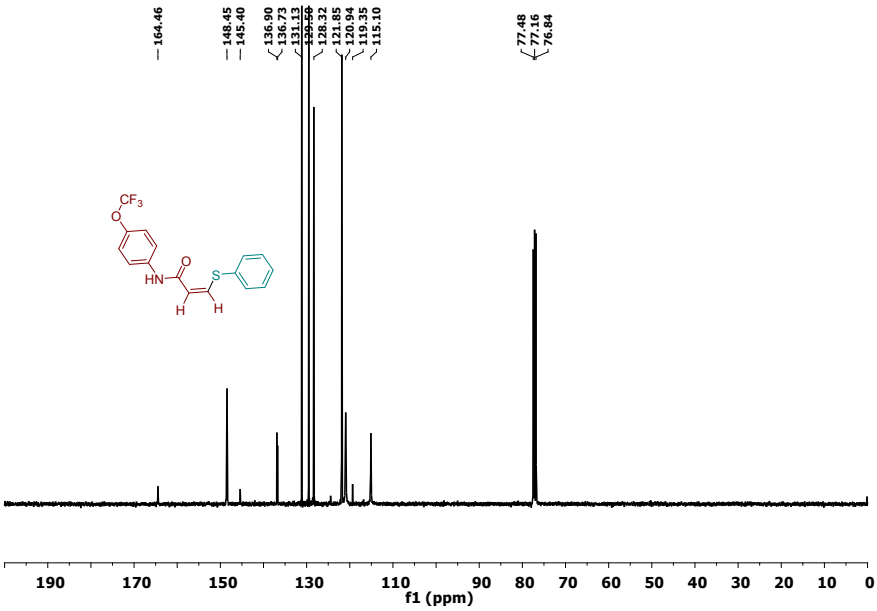


Fig. S22. [13]C NMR spectrum of (Z)-3-(phenylthio)-N-(4-(trifluoromethoxy)phenyl)acrylamide (**3ha**)

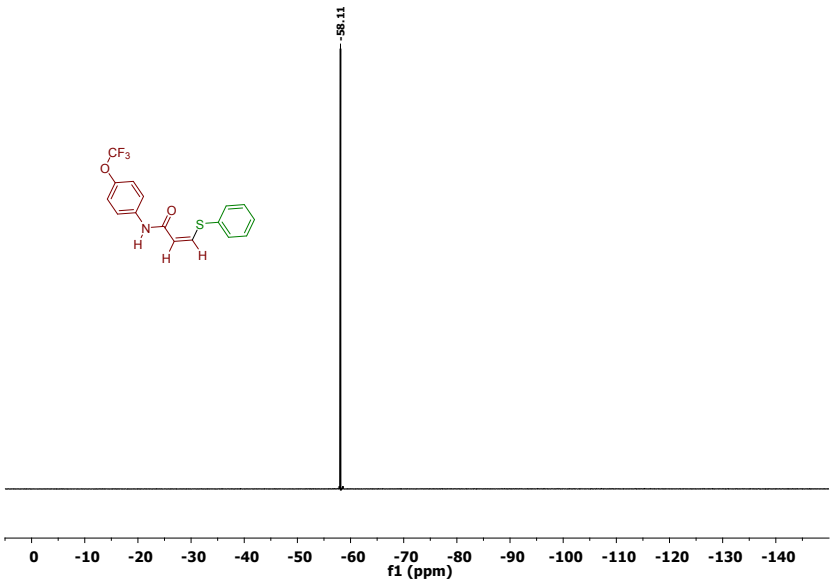


Fig. S23. ^{19}F NMR spectrum of (Z)-3-(phenylthio)-N-(4-(trifluoromethoxy)phenyl)acrylamide (**3ha**)

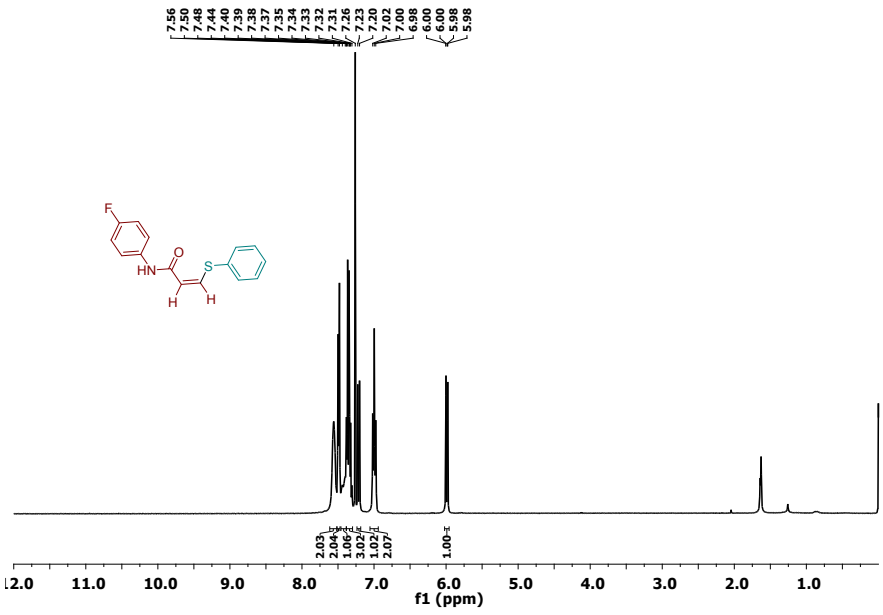


Fig. S24. ^{1}H NMR spectrum of (Z)-N-(4-fluorophenyl)-3-(phenylthio)acrylamide (**3ia**)

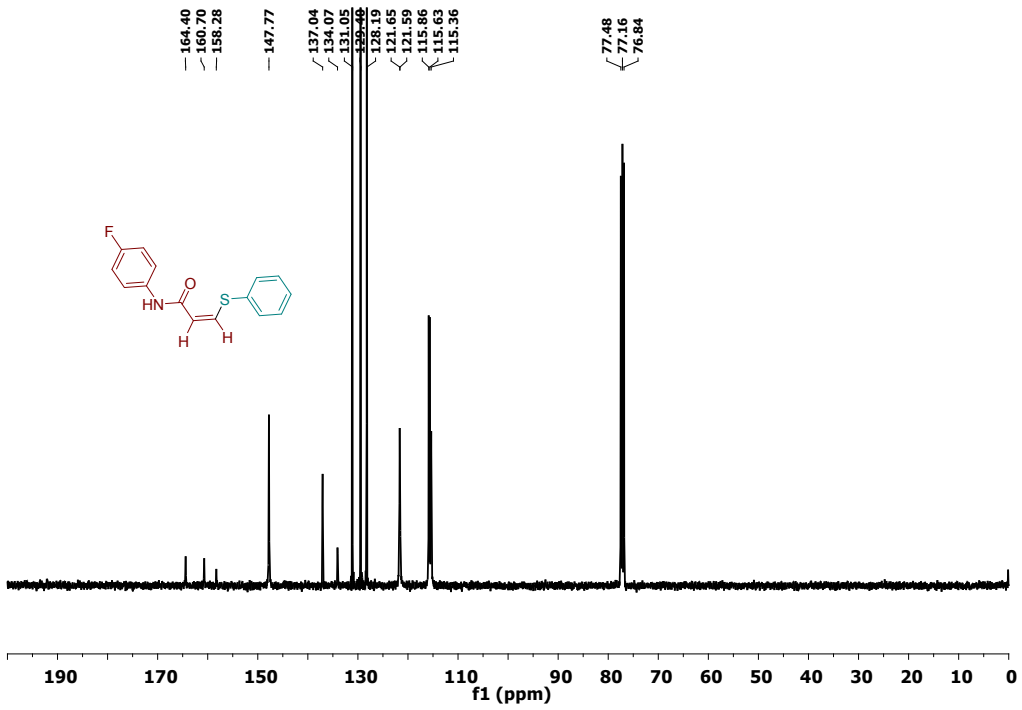


Fig. S25. ^{13}C NMR spectrum of (Z)-N-(4-fluorophenyl)-3-(phenylthio)acrylamide (**3ia**)

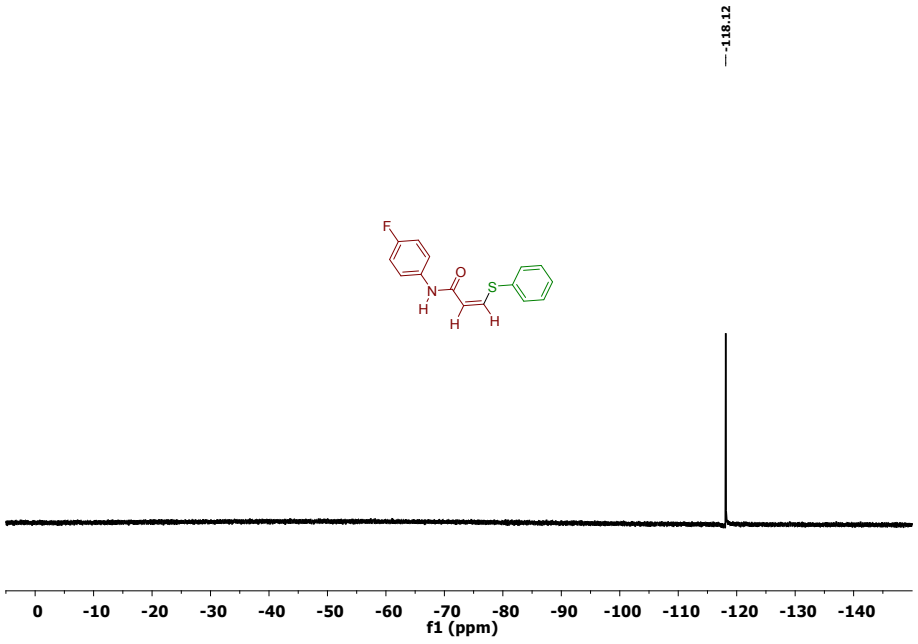


Fig. S26. ^{19}F NMR spectrum of (Z)-N-(4-fluorophenyl)-3-(phenylthio)acrylamide (**3ia**)

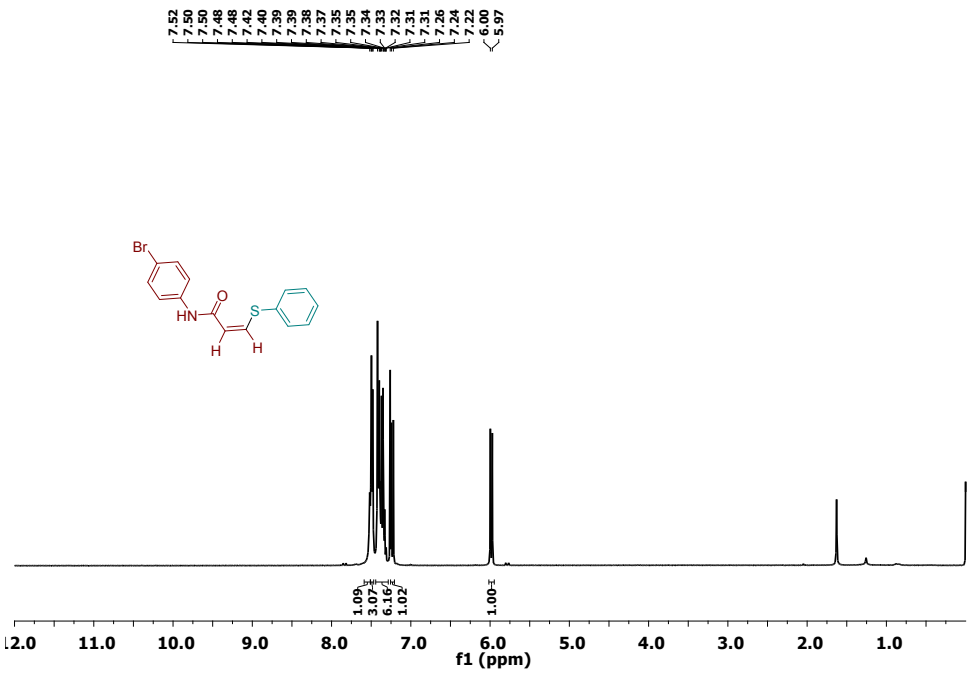


Fig. S27. ^{1}H NMR spectrum of (Z)-N-(4-bromophenyl)-3-(phenylthio)acrylamide (**3ja**)

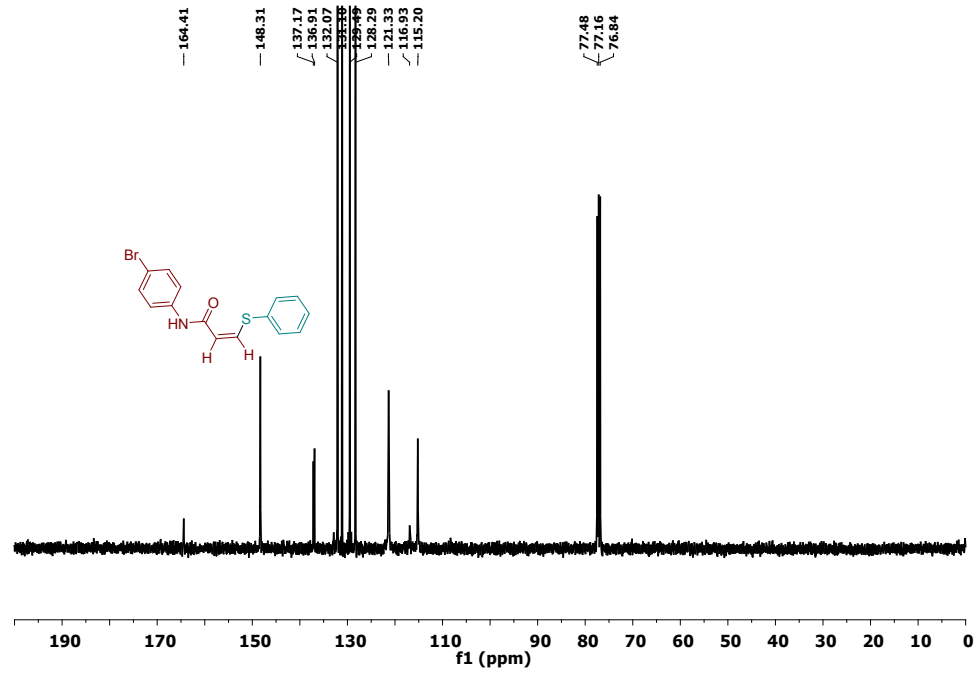


Fig. S28. ^{13}C NMR spectrum of (Z)-N-(4-bromophenyl)-3-(phenylthio)acrylamide (**3ja**)

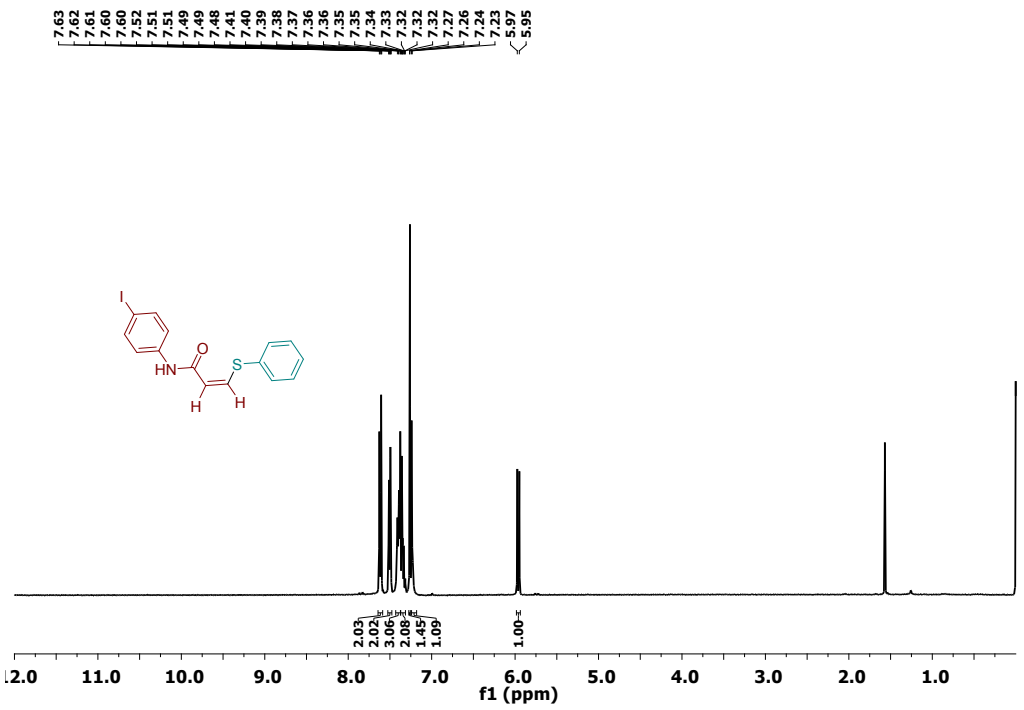


Fig. S29. ^{1}H NMR spectrum of (Z)-N-(4-iodophenyl)-3-(phenylthio)acrylamide (**3ka**)

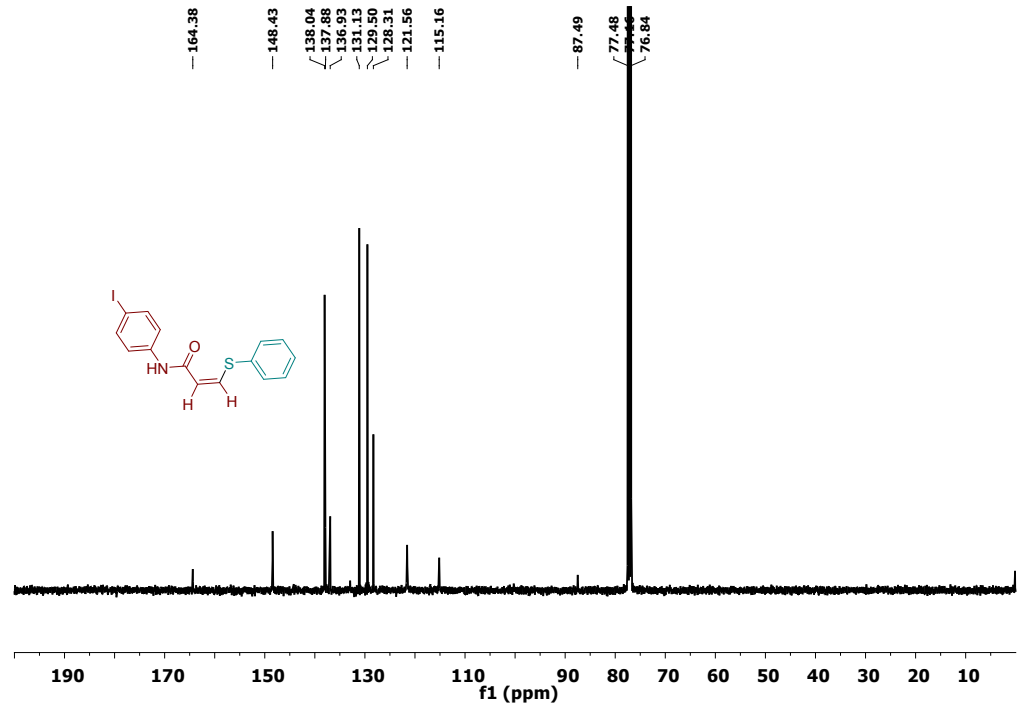


Fig. S30. ^{13}C NMR spectrum of (Z)-N-(4-iodophenyl)-3-(phenylthio)acrylamide (**3ka**)

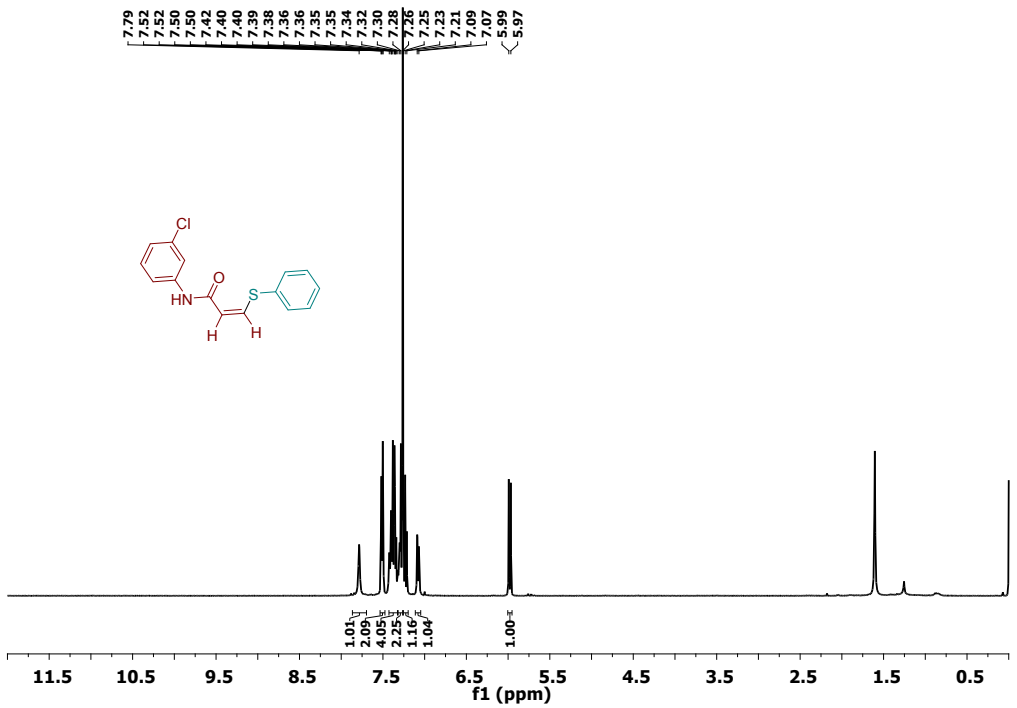


Fig. S31. ^{1}H NMR spectrum of (Z)-N-(3-chlorophenyl)-3-(phenylthio)acrylamide (**3la**)

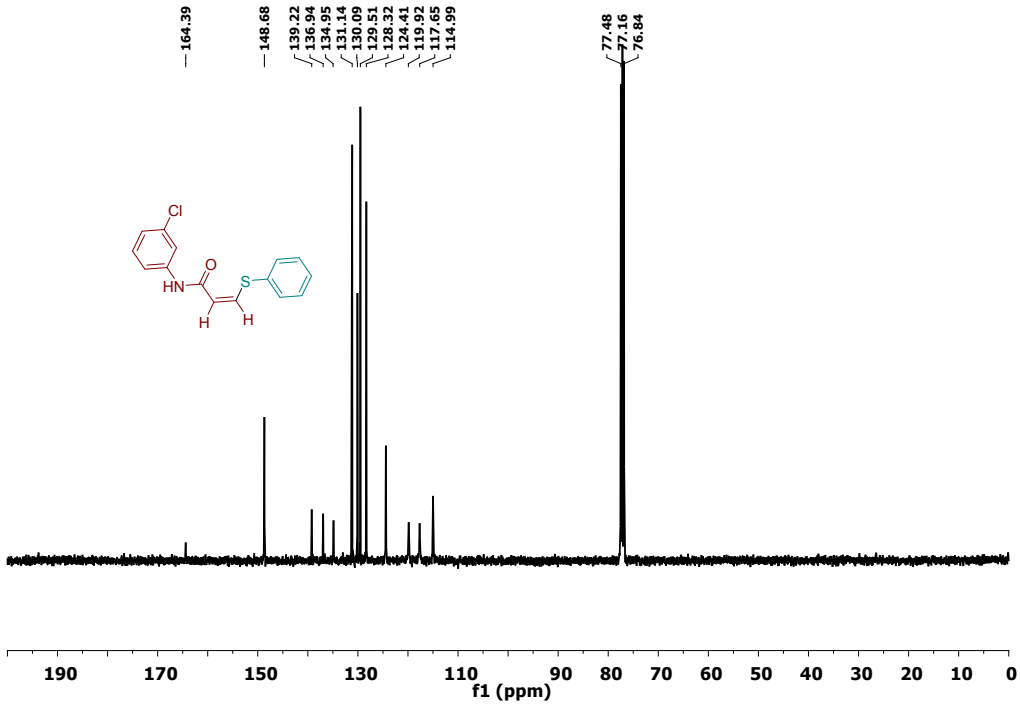


Fig. S32. ^{13}C NMR spectrum of (Z)-N-(3-chlorophenyl)-3-(phenylthio)acrylamide (**3la**)

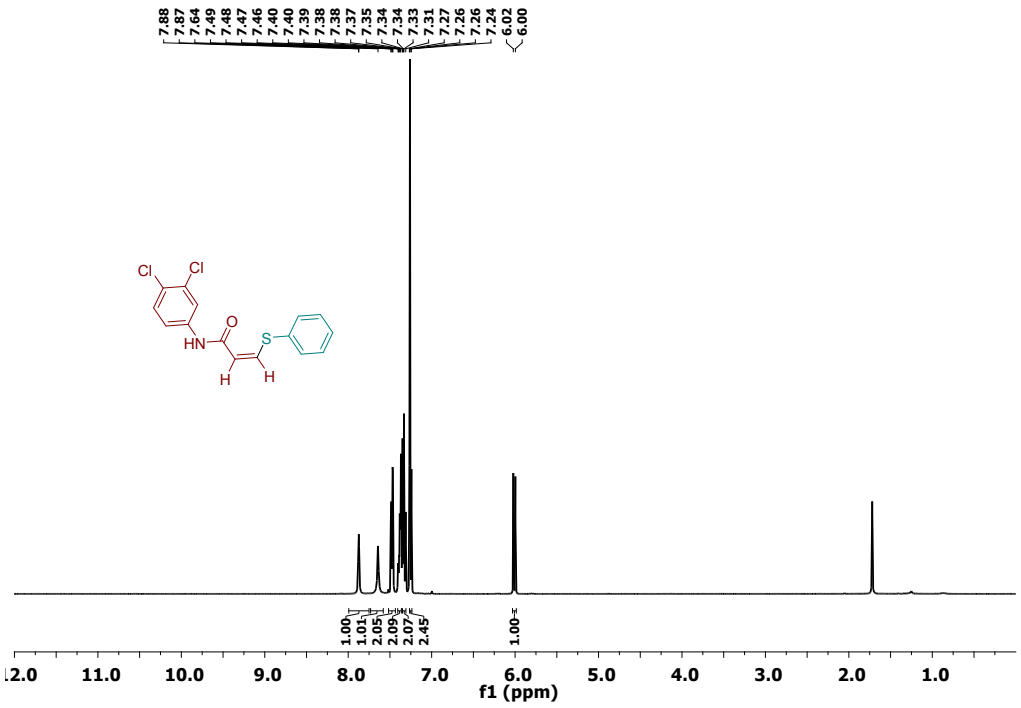


Fig. S33. ^{1}H NMR spectrum of (Z)-N-(3,4-dichlorophenyl)-3-(phenylthio)acrylamide (**3ma**)

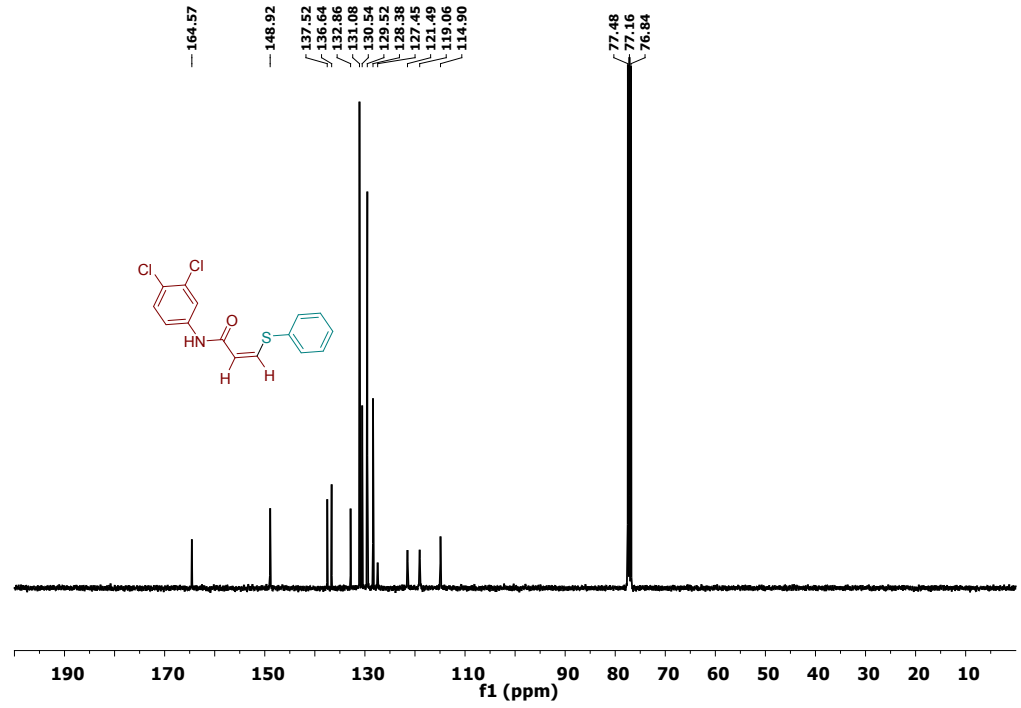


Fig. S34. ^{13}C NMR spectrum of (Z)-N-(3,4-dichlorophenyl)-3-(phenylthio)acrylamide (**3ma**)

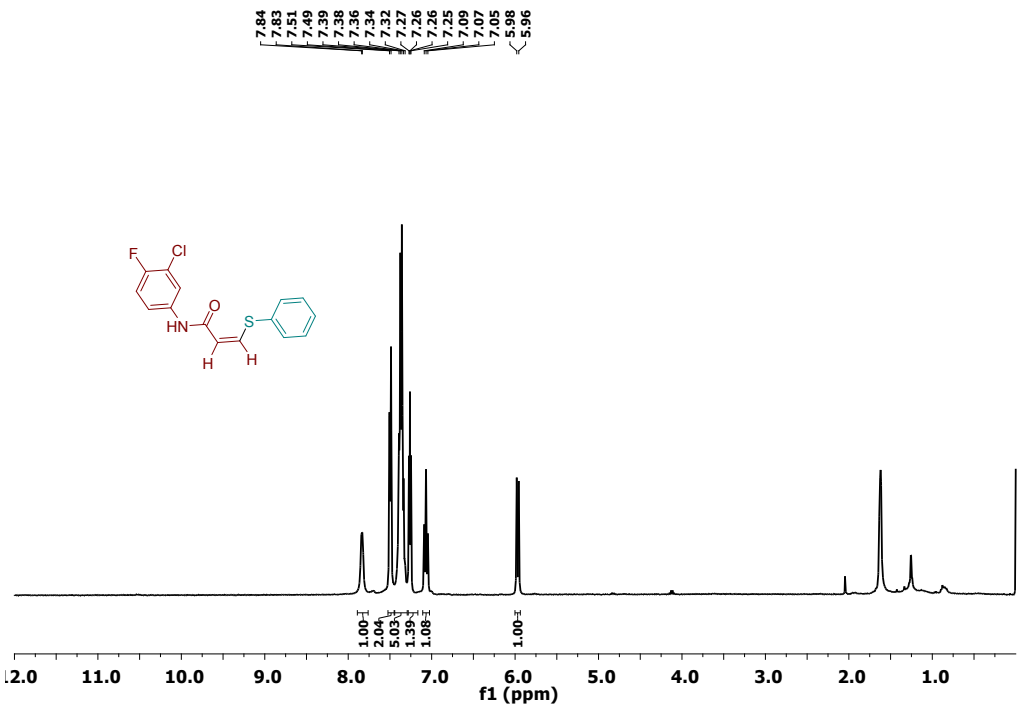


Fig. S35. ^{1}H NMR spectrum of (Z)-N-(3-chloro-4-fluorophenyl)-3-(phenylthio)acrylamide(**3na**)

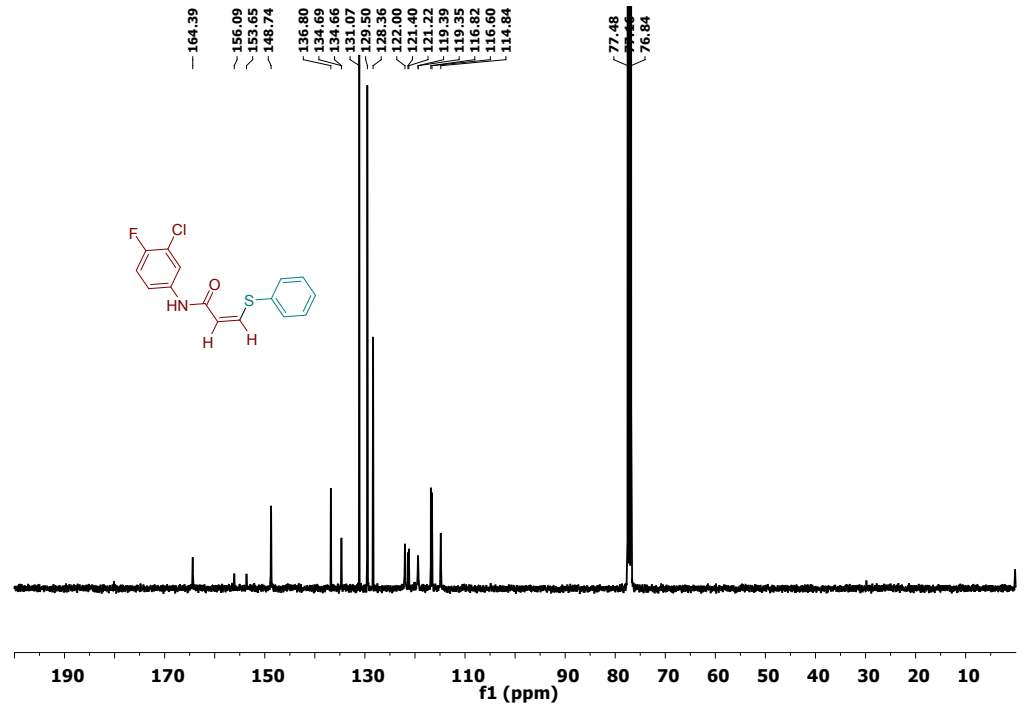


Fig. S36. ^{13}C NMR spectrum of (Z)-N-(3-chloro-4-fluorophenyl)-3-(phenylthio)acrylamide(**3na**)

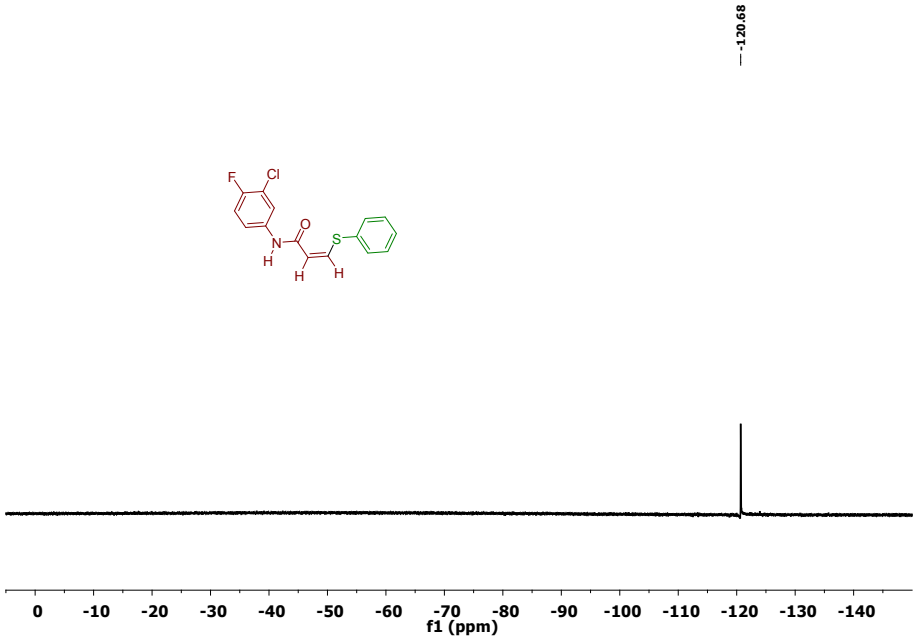


Fig. S37. ^{19}F NMR spectrum of (Z)-N-(3-chloro-4-fluorophenyl)-3-(phenylthio)acrylamide(**3na**)

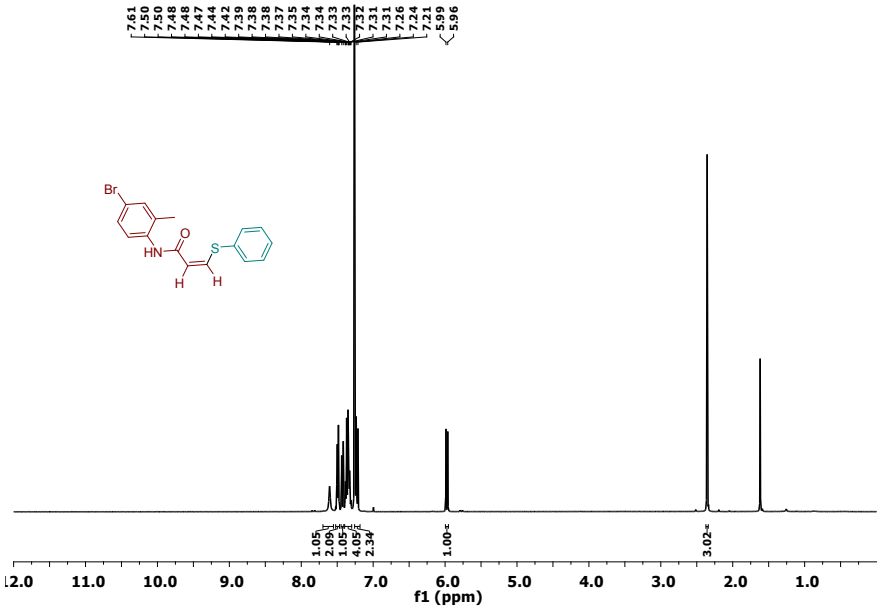


Fig. S38. ^{1}H NMR spectrum of (Z)-N-(4-bromo-2-methylphenyl)-3-(phenylthio)acrylamide (**3oa**)

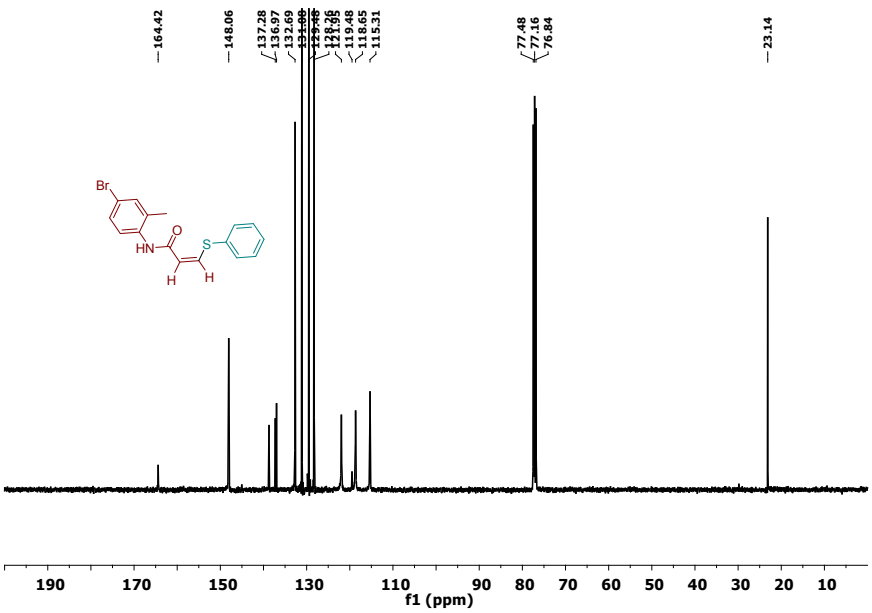


Fig. S39. ^{13}C NMR spectrum of (Z)-N-(4-bromo-2-methylphenyl)-3-(phenylthio)acrylamide (**3oa**)

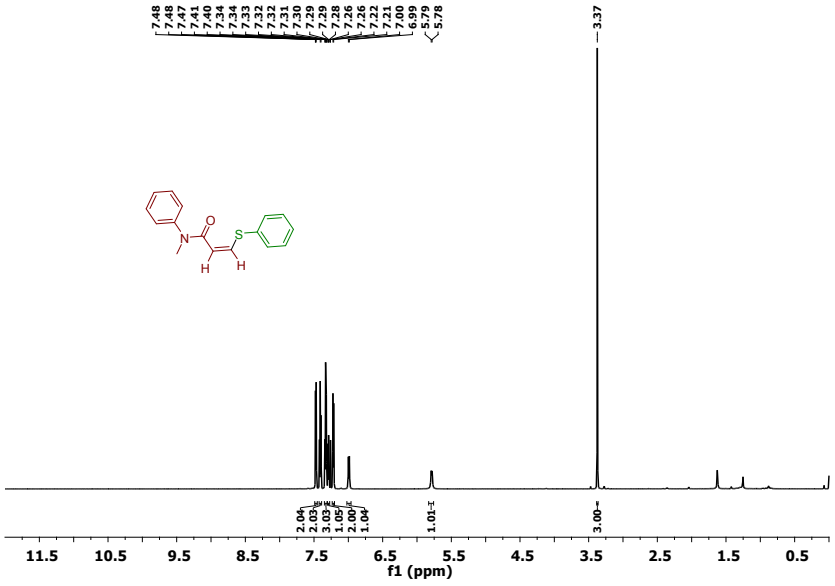


Fig. S40. ^{1}H NMR spectrum of (Z)-N-methyl-N-phenyl-3-(phenylthio)acrylamide (**3pa**)

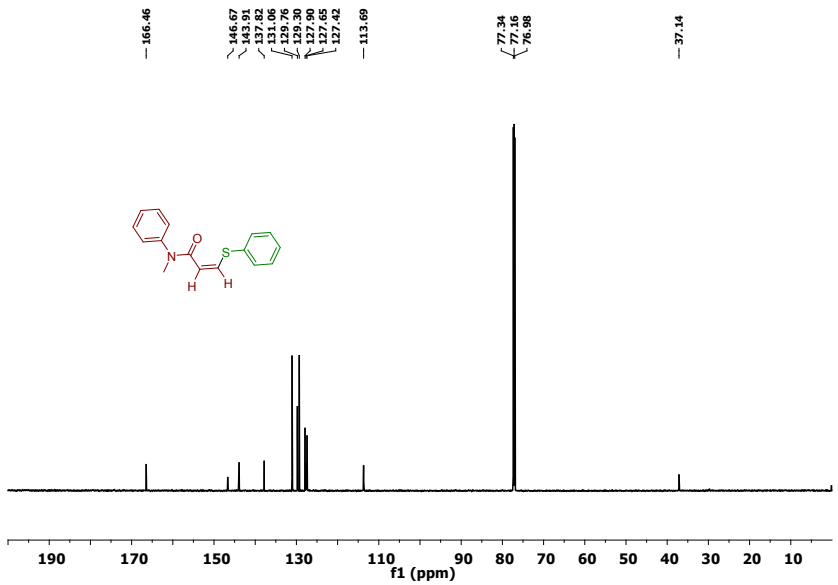


Fig. S41. ^{13}C NMR spectrum of (Z)-N-methyl-N-phenyl-3-(phenylthio)acrylamide (**3pa**)

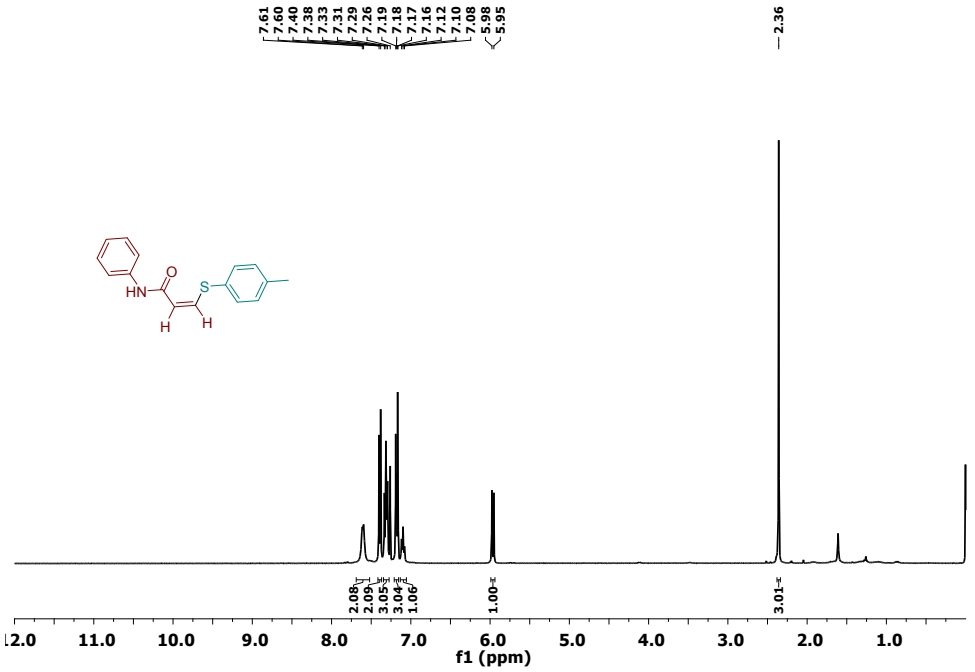


Fig. S42. ^{1}H NMR spectrum of (Z)-N-phenyl-3-(p-tolylthio)acrylamide (**3ab**)

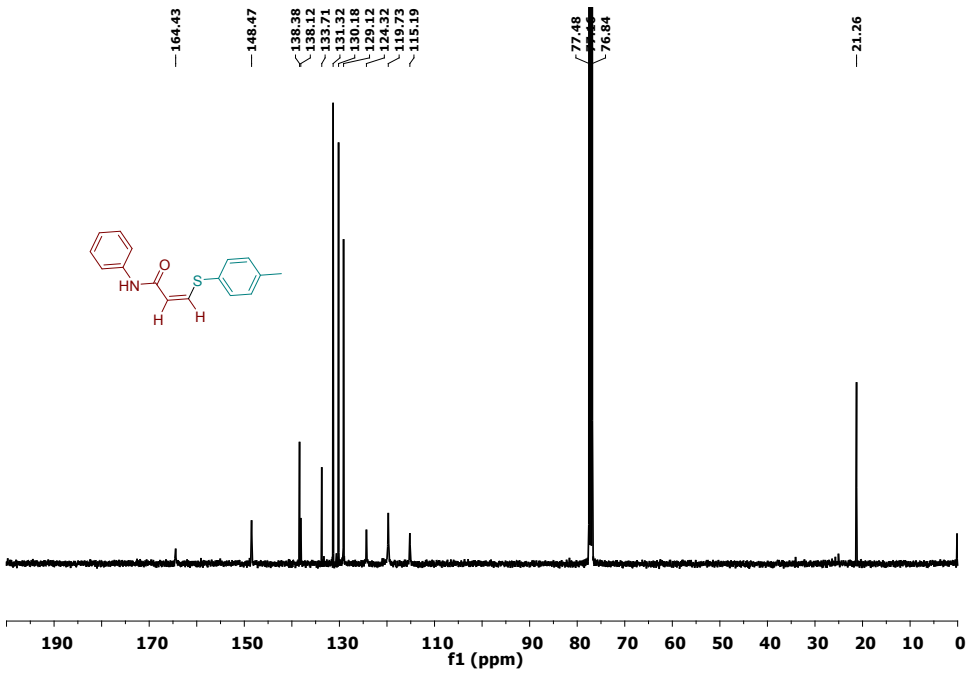


Fig. S43. ^{13}C NMR spectrum of (Z)-N-phenyl-3-(p-tolylthio)acrylamide (**3ab**)

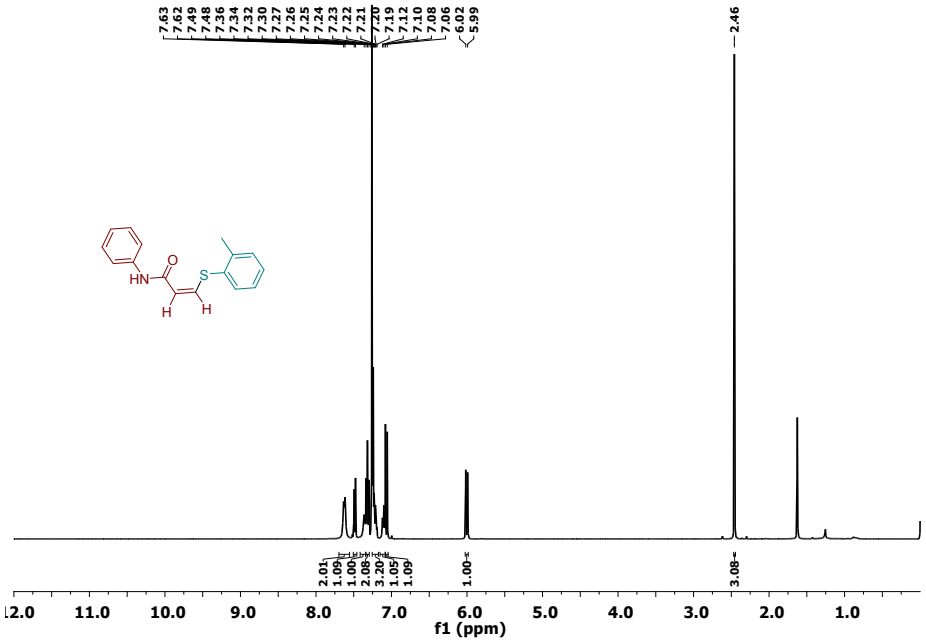


Fig. S44. ^{1}H NMR spectrum of (Z)-N-phenyl-3-(o-tolylthio)acrylamide (**3ac**)

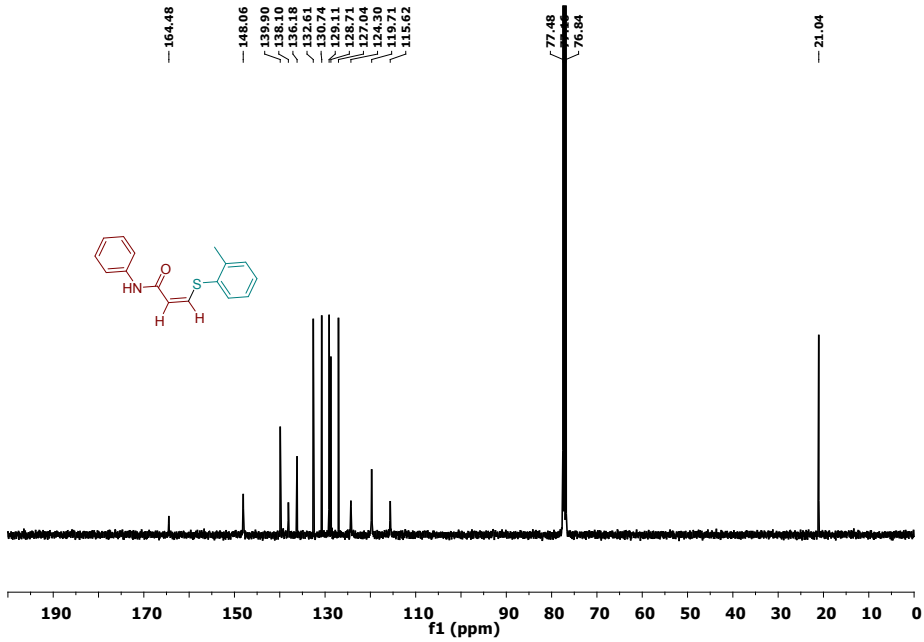


Fig. S45. ^{13}C NMR spectrum of (Z)-N-phenyl-3-(o-tolylthio)acrylamide (**3ac**)

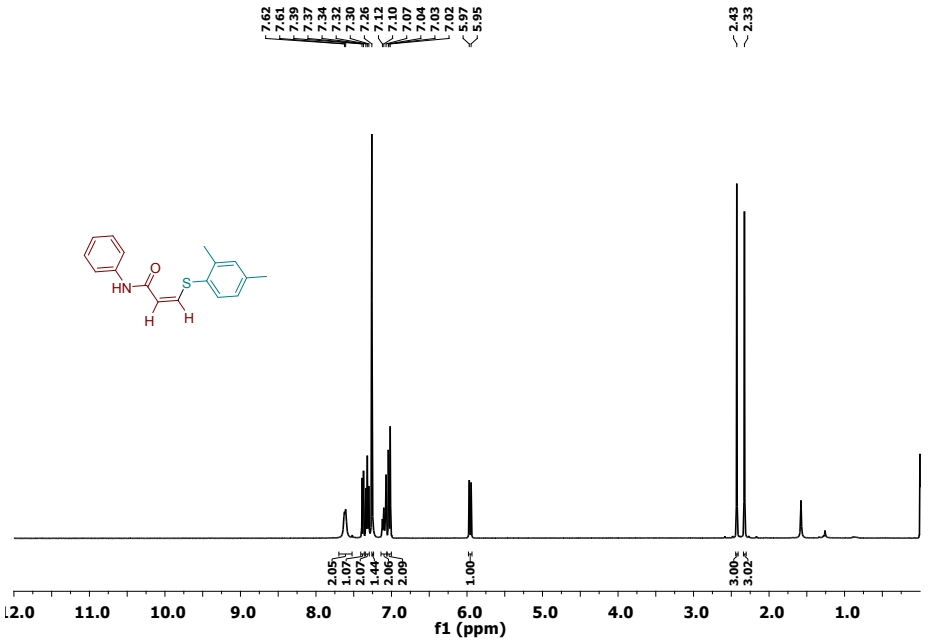


Fig. S46. ^{1}H NMR spectrum of (Z)-3-((2,4-dimethylphenyl)thio)-N-phenylacrylamide (**3ad**)

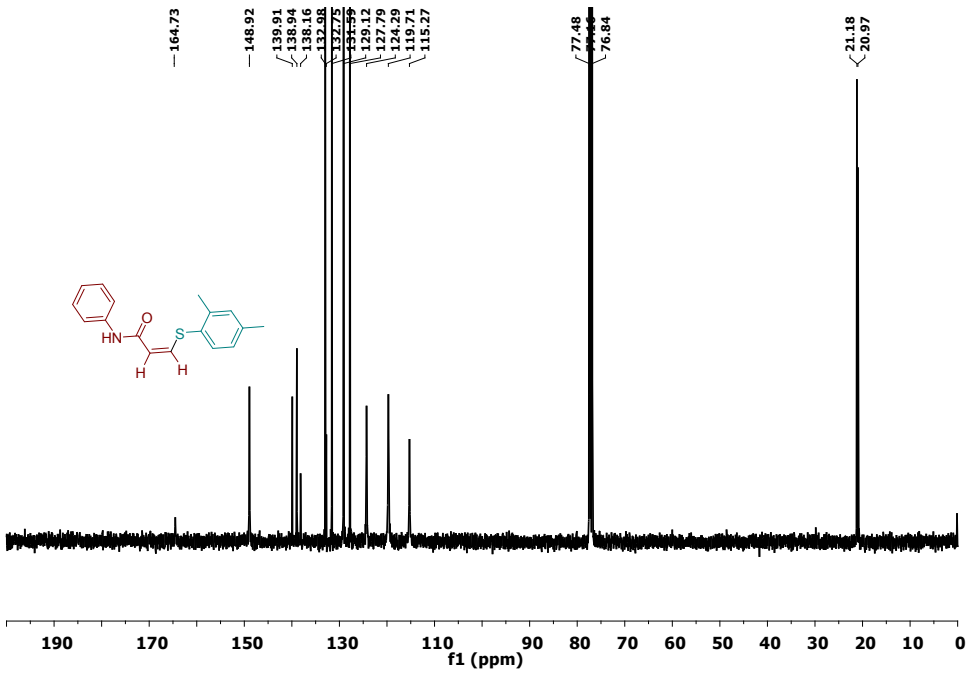


Fig. S47. ^{13}C NMR spectrum of (Z)-3-((2,4-dimethylphenyl)thio)-N-phenylacrylamide (**3ad**)

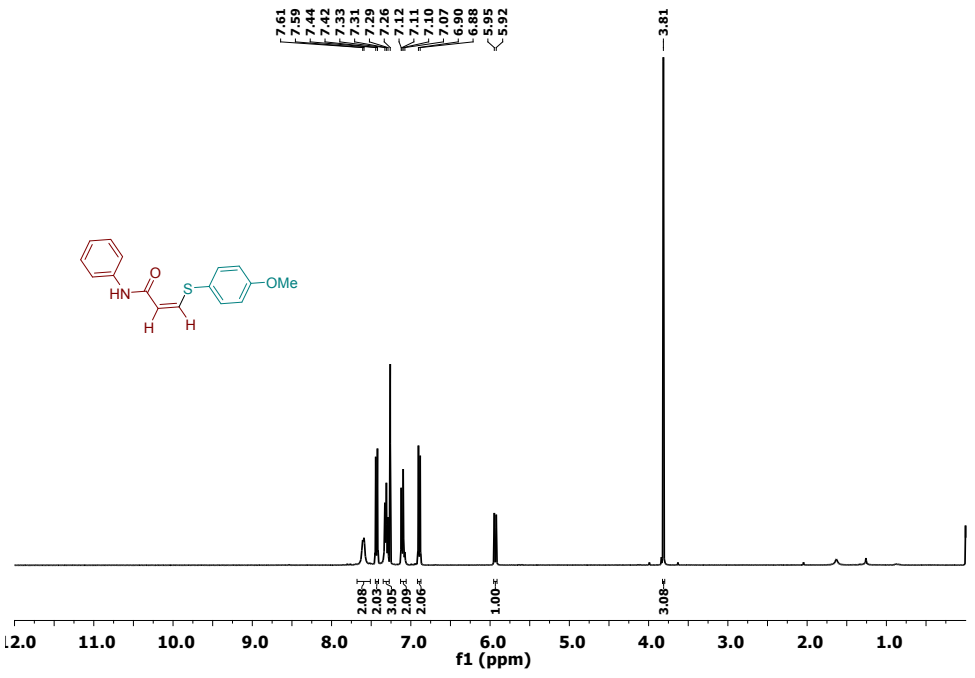


Fig. S48. ^{1}H NMR spectrum of (Z)-3-((4-methoxyphenyl)thio)-N-phenylacrylamide (**3ae**)

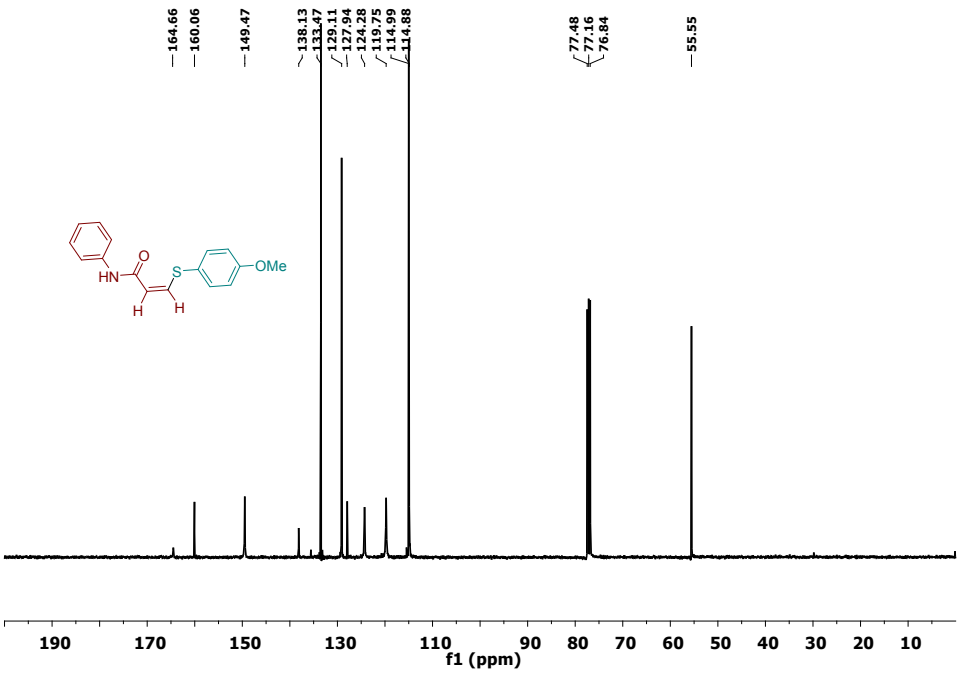


Fig. S49. ^{13}C NMR spectrum of (Z)-3-((4-methoxyphenyl)thio)-N-phenylacrylamide (**3ae**)

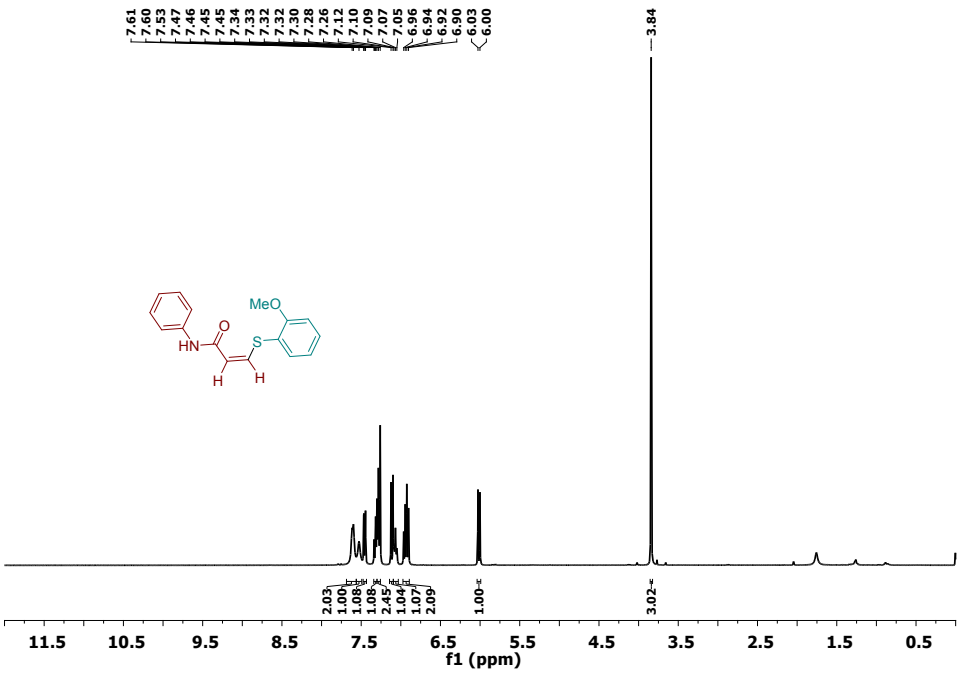


Fig. S50. ^{1}H NMR spectrum of (Z)-3-((2-methoxyphenyl)thio)-N-phenylacrylamide (**3af**)

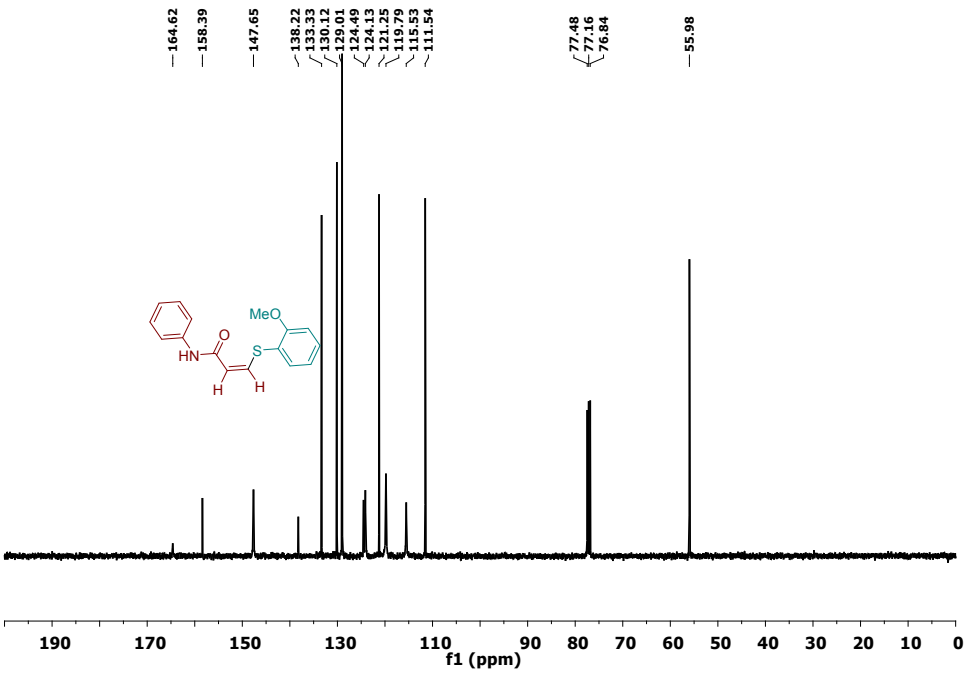


Fig. S51. ^{13}C NMR spectrum of (Z)-3-((2-methoxyphenyl)thio)-N-phenylacrylamide (**3af**)

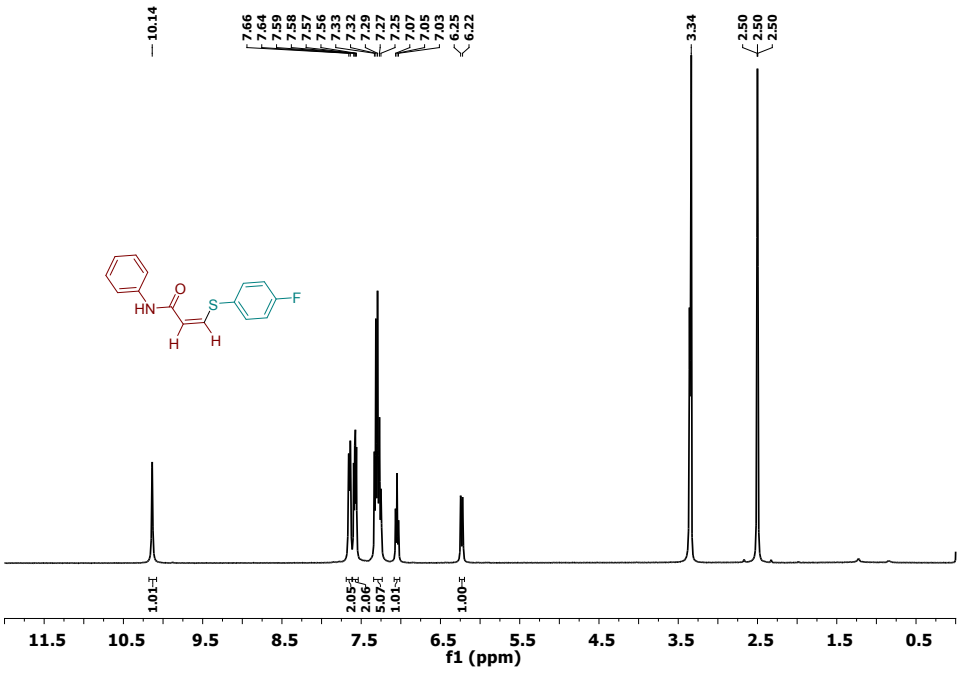


Fig. S52. ^{1}H NMR spectrum of (Z)-3-((4-fluorophenyl)thio)-N-phenylacrylamide (**3am**)

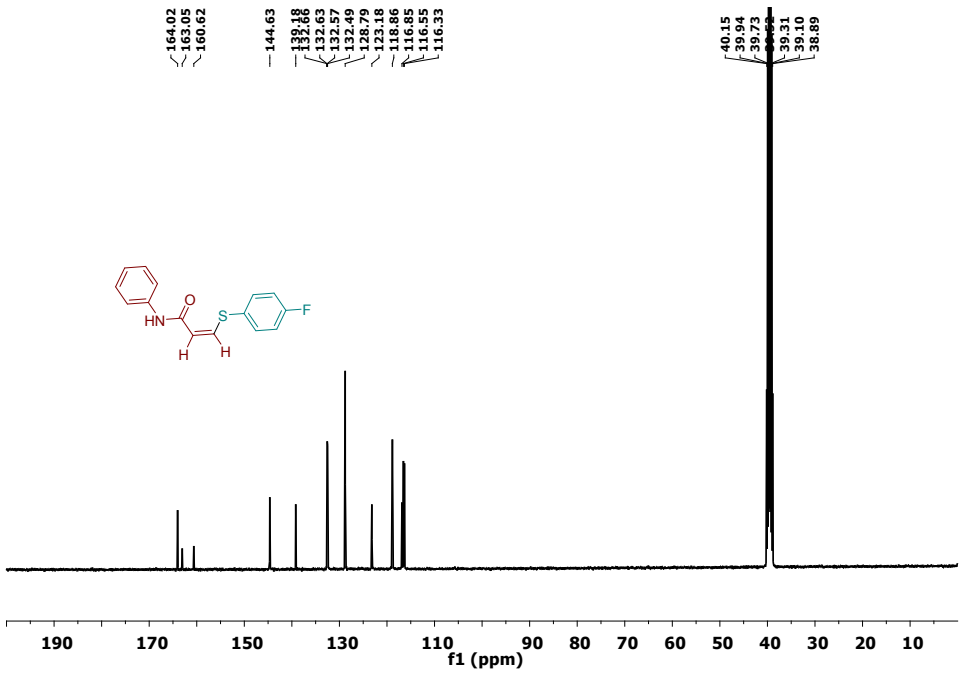


Fig. S53. ^{13}C NMR spectrum of (Z)-3-((4-fluorophenyl)thio)-N-phenylacrylamide (**3am**)

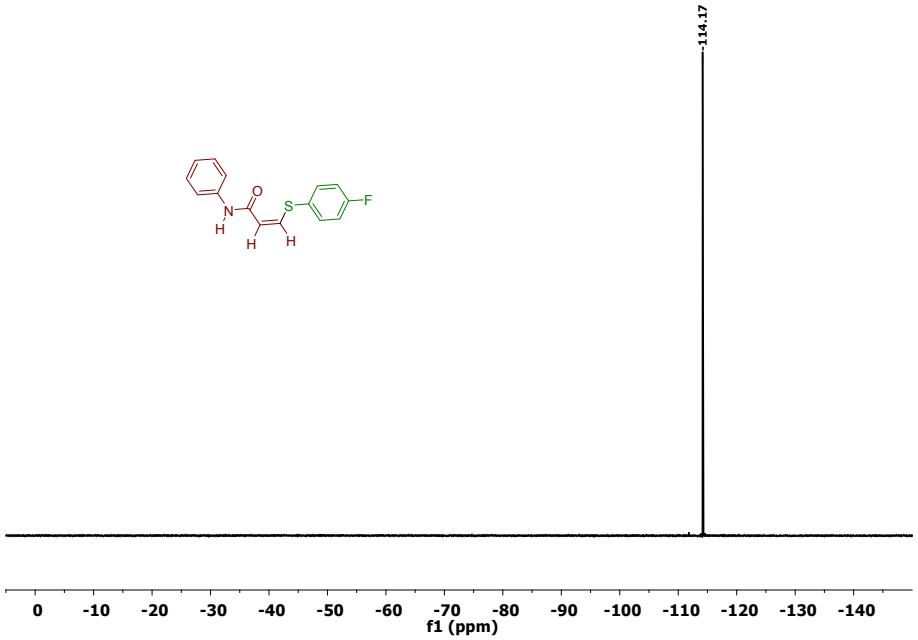


Fig. S54. ^{19}F NMR spectrum of (Z)-3-((4-fluorophenyl)thio)-N-phenylacrylamide (**3am**)

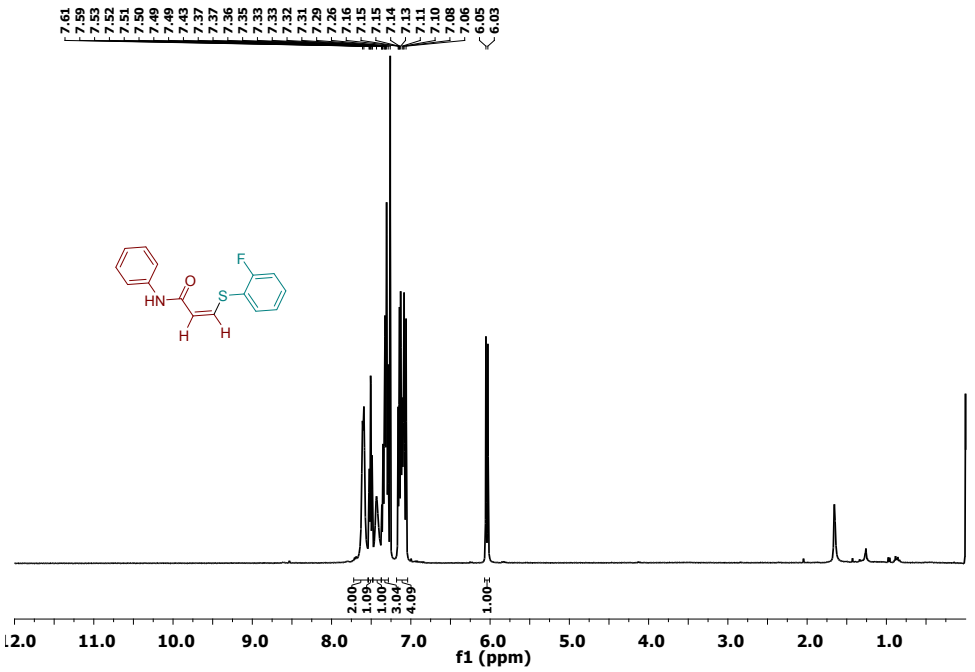


Fig. S55. ^{1}H NMR spectrum of (Z)-3-((2-fluorophenyl)thio)-N-phenylacrylamide (**3an**)

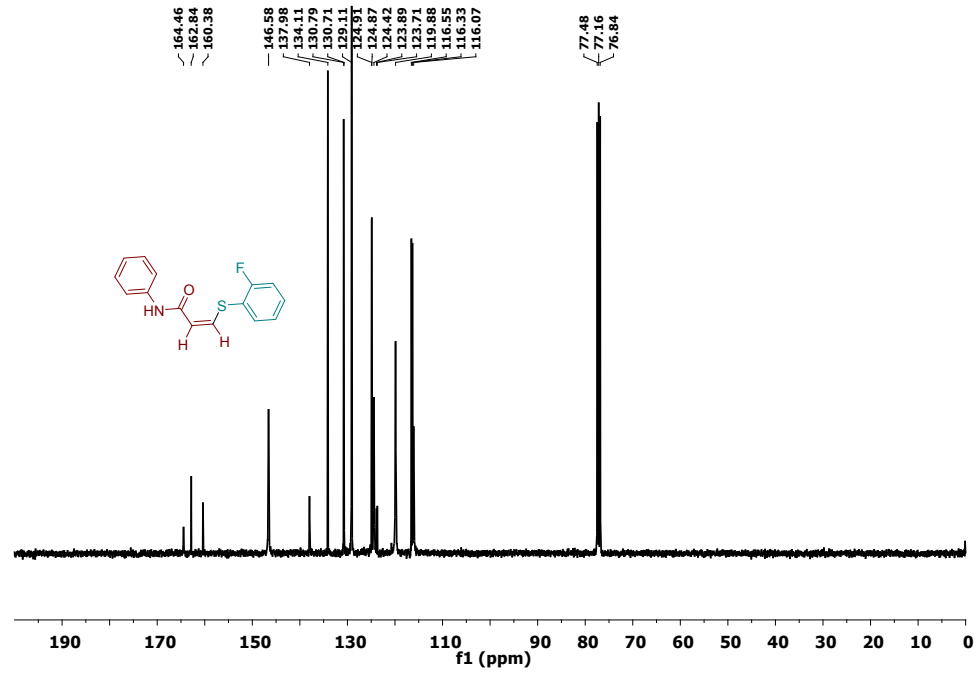


Fig. S56. ^{13}C NMR spectrum of (Z)-3-((2-fluorophenyl)thio)-N-phenylacrylamide (**3an**)

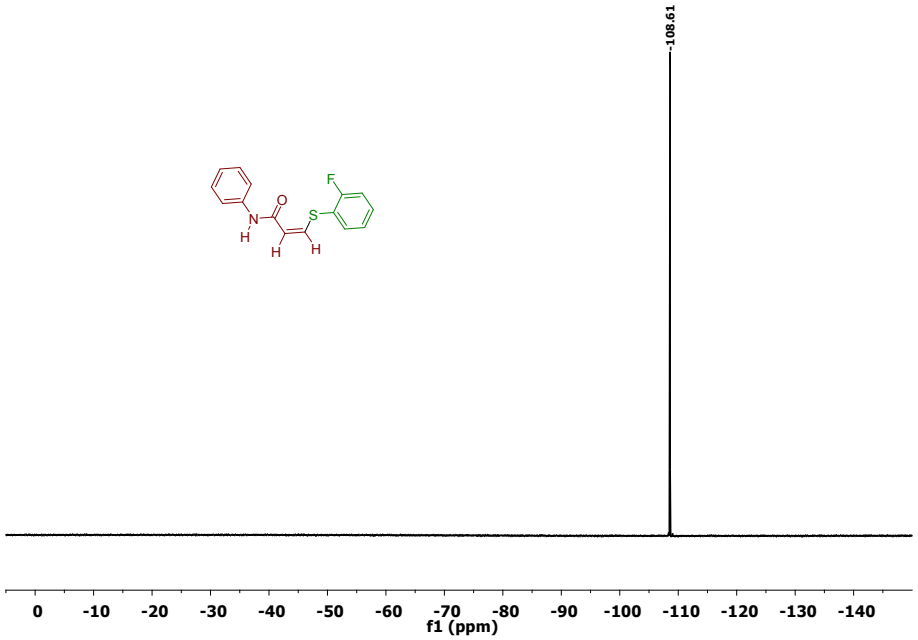


Fig. S57. ^{19}F NMR spectrum of (Z)-3-((2-fluorophenyl)thio)-N-phenylacrylamide (**3an**)

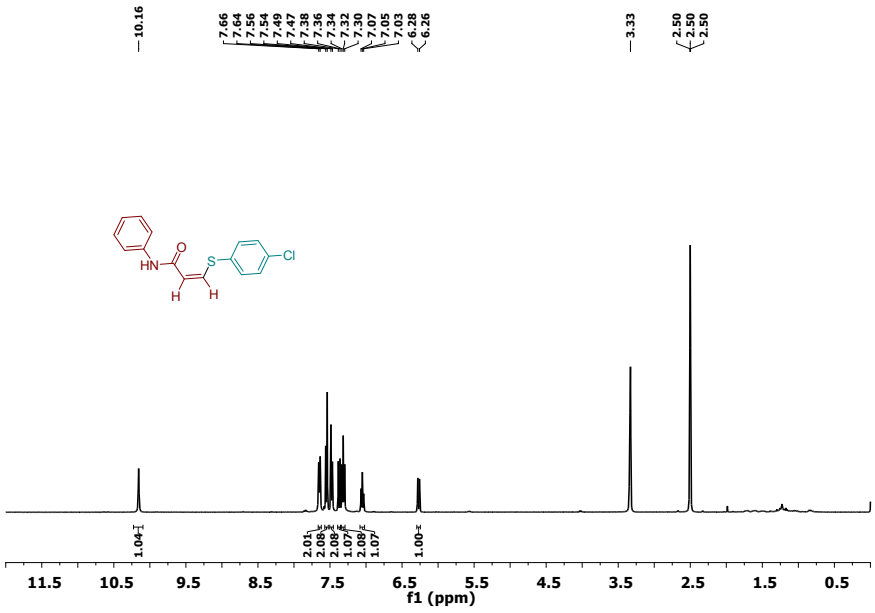


Fig. S58. ^{1}H NMR spectrum of (Z)-3-((4-chlorophenyl)thio)-N-phenylacrylamide (**3aj**)

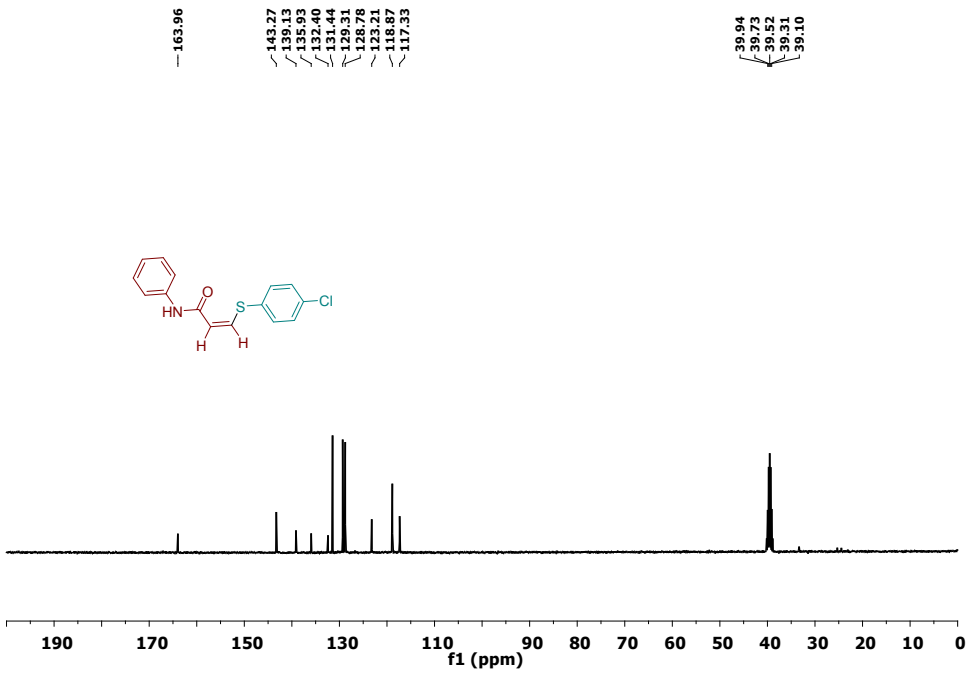


Fig. S59. ^{13}C NMR spectrum of (Z)-3-((4-chlorophenyl)thio)-N-phenylacrylamide (**3aj**)

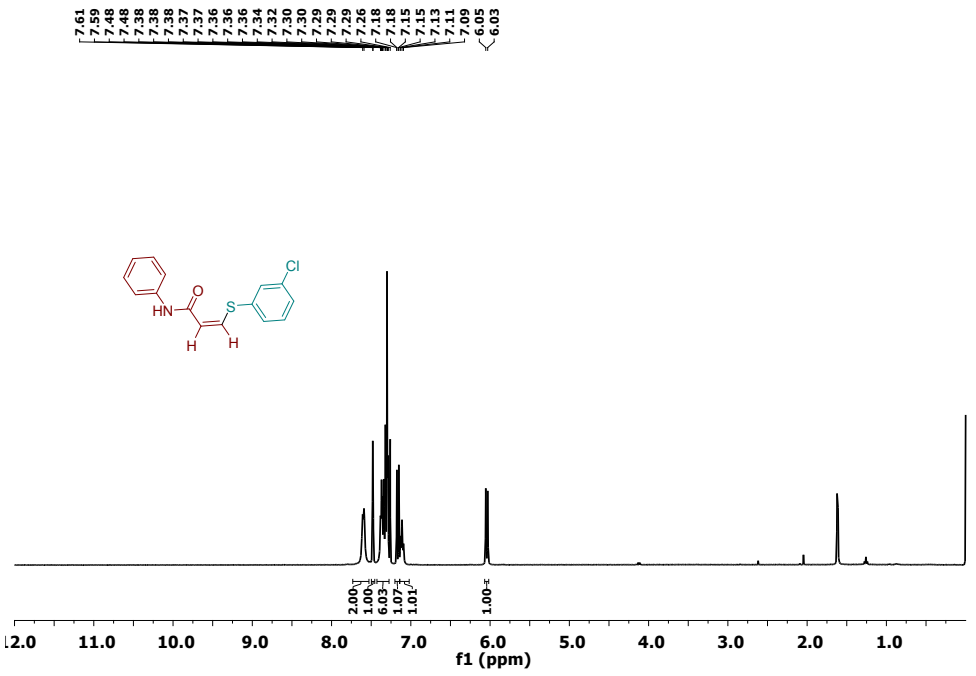


Fig. S60. ^{1}H NMR spectrum of (Z)-3-((3-chlorophenyl)thio)-N-phenylacrylamide (**3ak**)

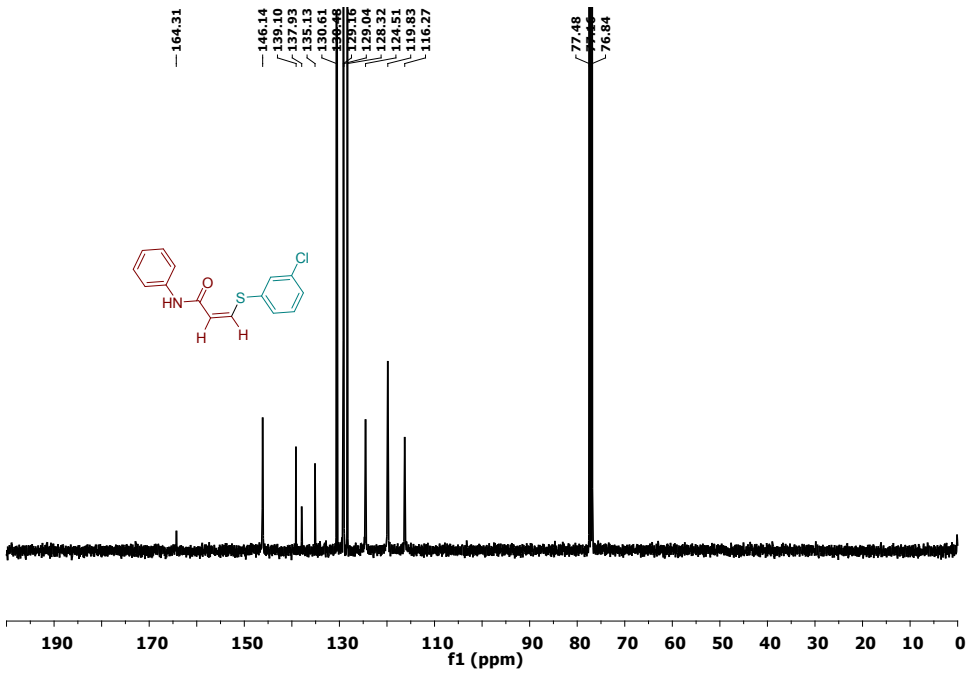


Fig. S61. ^{13}C NMR spectrum of (Z)-3-((3-chlorophenyl)thio)-N-phenylacrylamide (**3ak**)

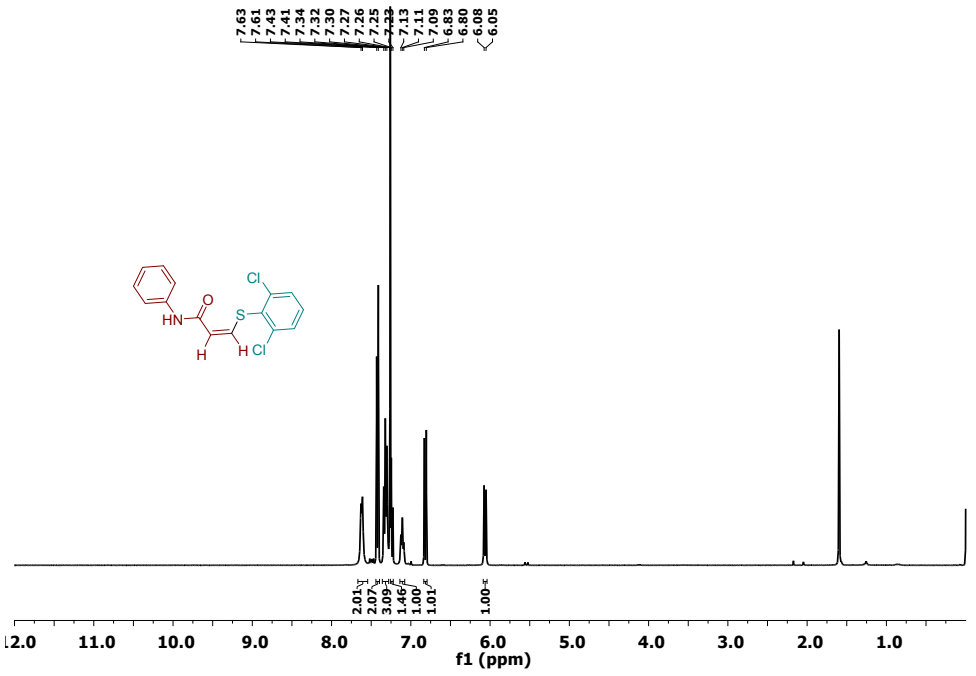


Fig. S62. ^{1}H NMR spectrum of (Z)-3-((2,6-dichlorophenyl)thio)-N-phenylacrylamide (**3al**)

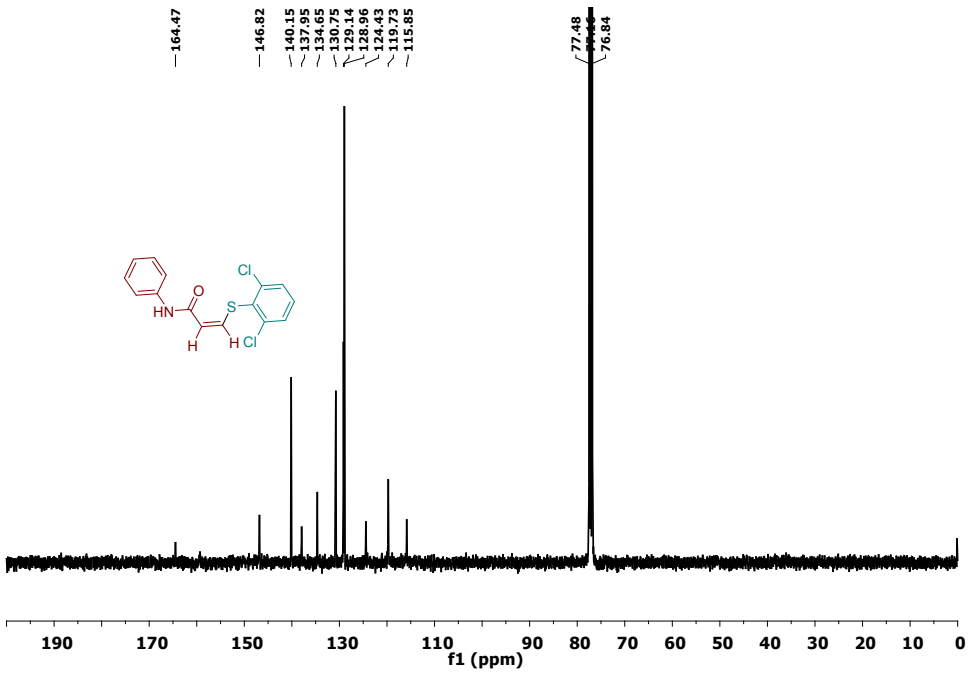


Fig. S63. ^{13}C NMR spectrum of (Z)-3-((2,6-dichlorophenyl)thio)-N-phenylacrylamide (**3al**)

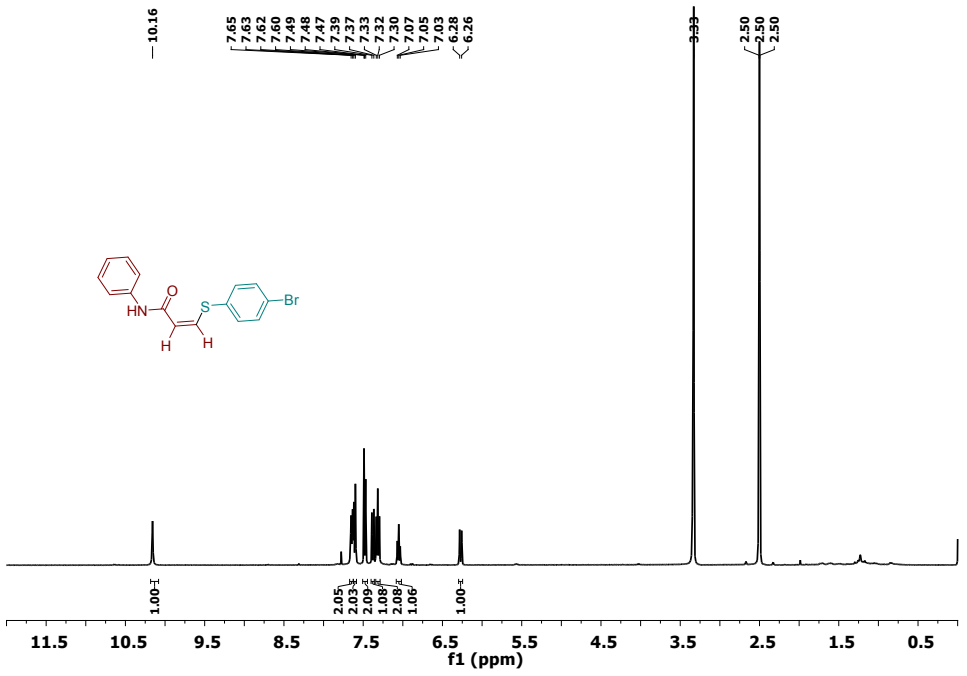


Fig. S64. ^{1}H NMR spectrum of (Z)-3-((4-bromophenyl)thio)-N-phenylacrylamide (**3ai**)

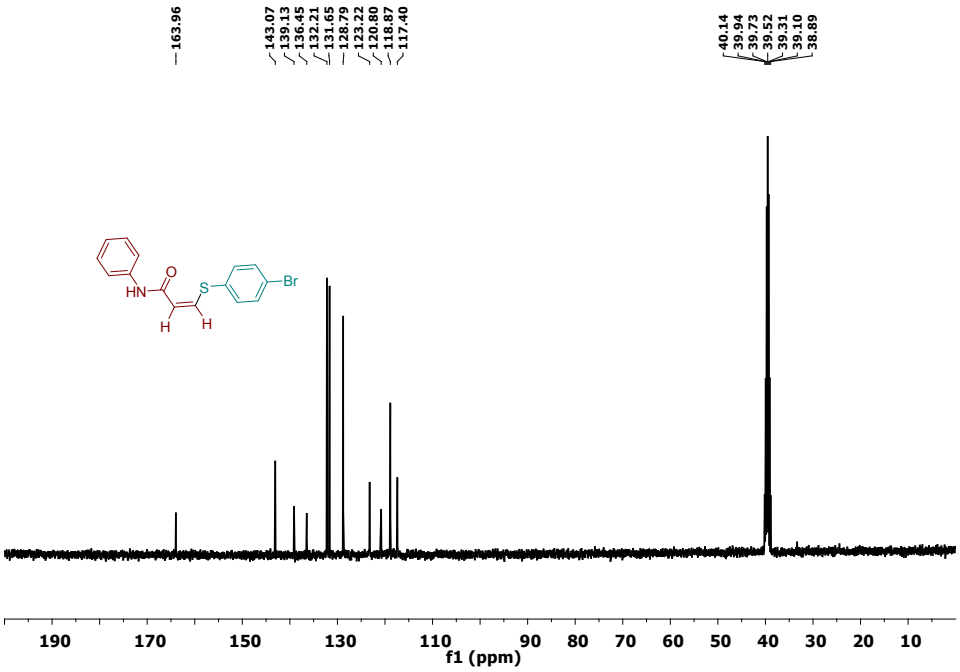


Fig. S65. ^{13}C NMR spectrum of (Z)-3-((4-bromophenyl)thio)-N-phenylacrylamide (**3ai**)

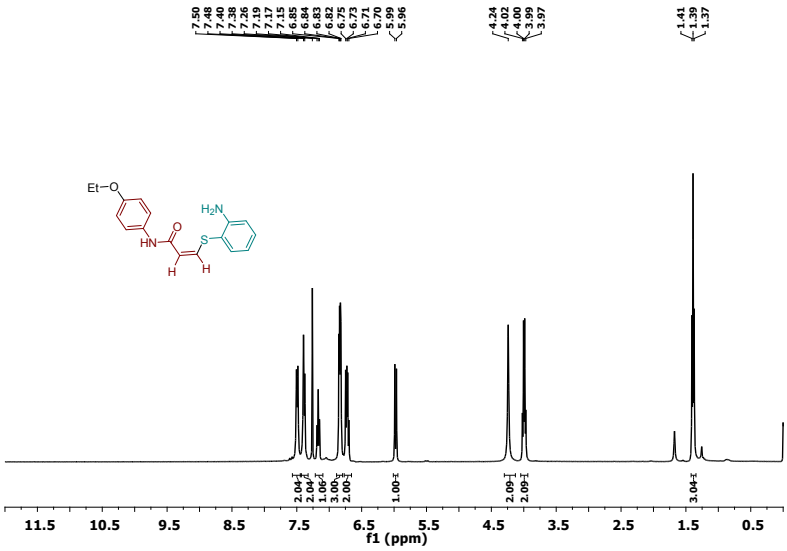


Fig. S66. ^{1}H NMR spectrum of (Z)-3-((2-aminophenyl)thio)-N-(4-ethoxyphenyl)acrylamide (**3gg**)

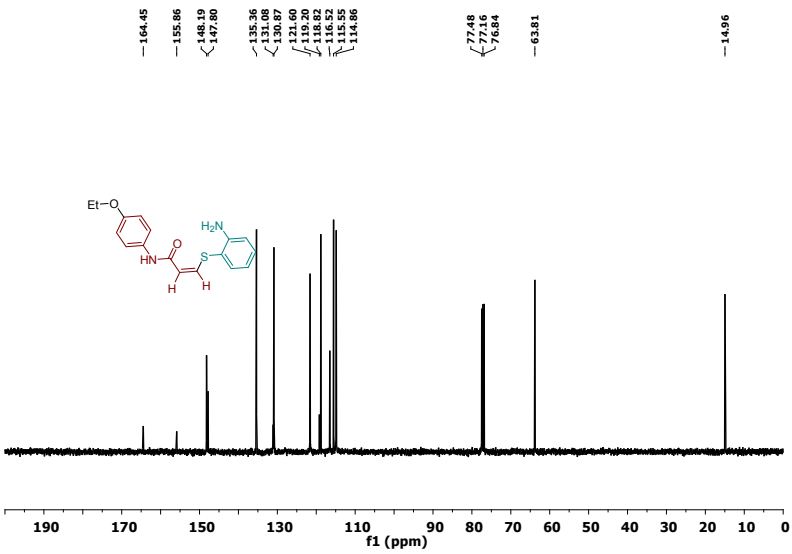


Fig. S67. ^{13}C NMR spectrum of (Z)-3-((2-aminophenyl)thio)-N-(4-ethoxyphenyl)acrylamide (**3gg**)

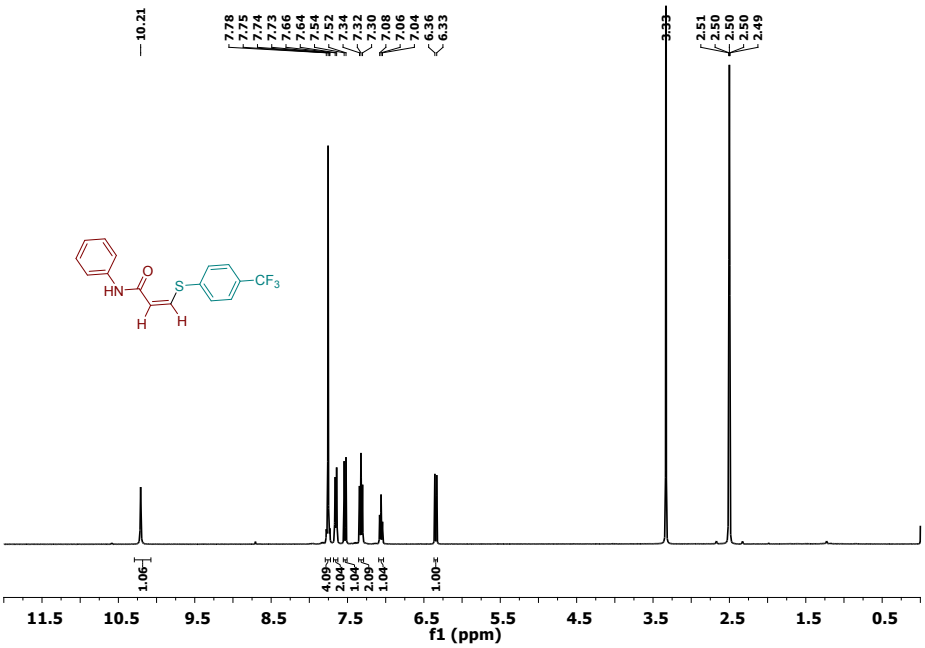


Fig. S68. ^{1}H NMR spectrum of (Z)-N-phenyl-3-((4-(trifluoromethyl)phenyl)thio)acrylamide (**3ah**)

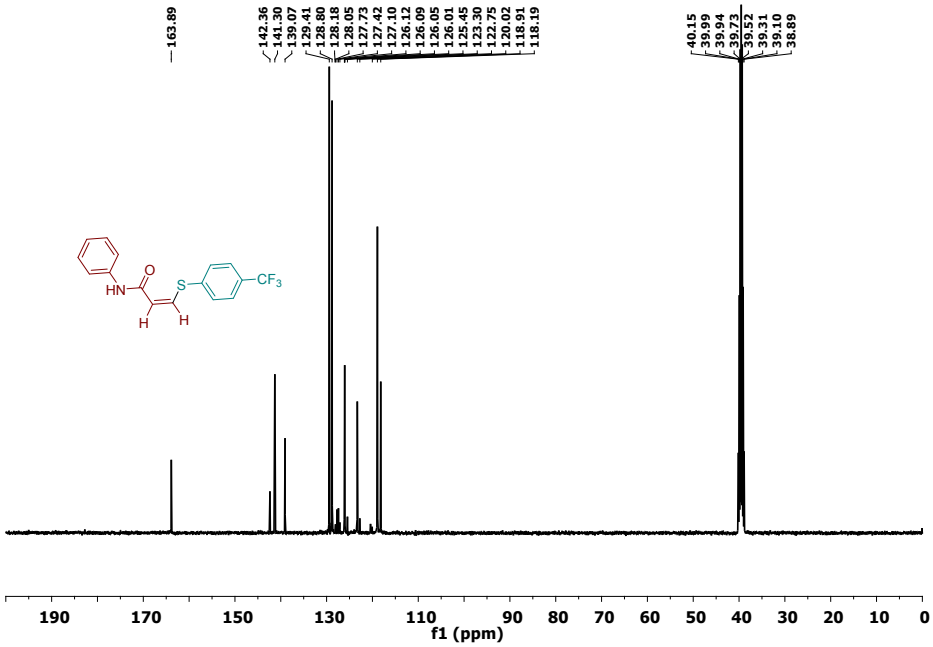


Fig. S69. ^{13}C NMR spectrum of (Z)-N-phenyl-3-((4-(trifluoromethyl)phenyl)thio)acrylamide (**3ah**)

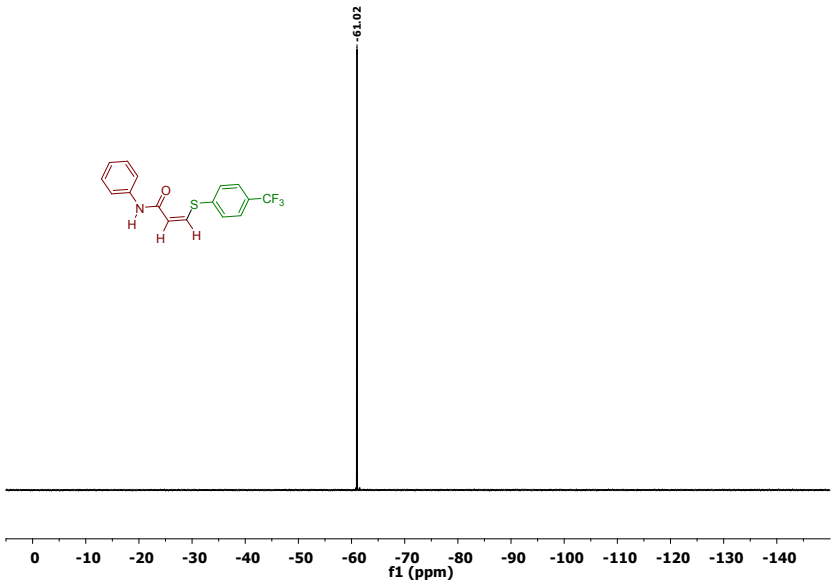


Fig. S70. ^{19}F NMR spectrum of (Z)-N-phenyl-3-((4-(trifluoromethyl)phenyl)thio)acrylamide (**3ah**)

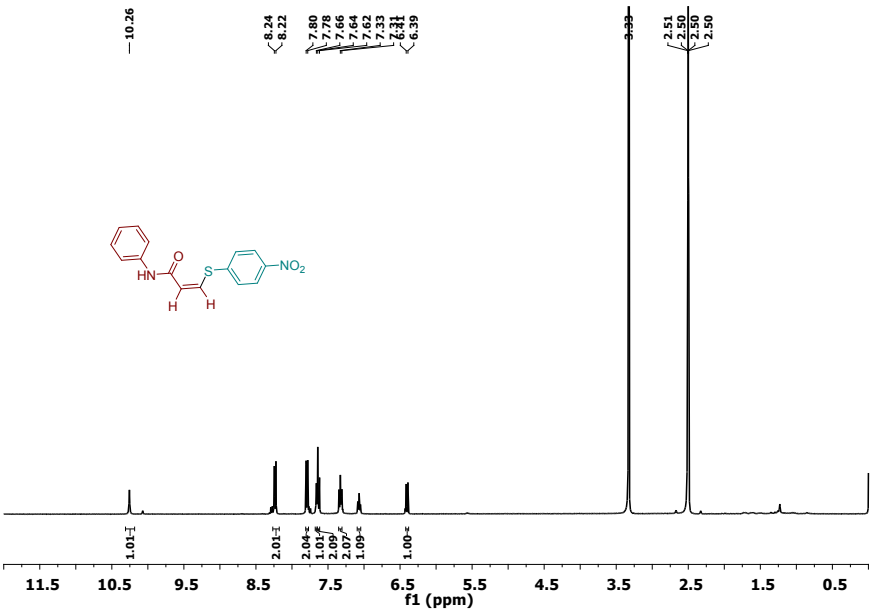


Fig. S71. ^{1}H NMR spectrum of (Z)-3-((4-nitrophenyl)thio)-N-phenylacrylamide (**3ao**)

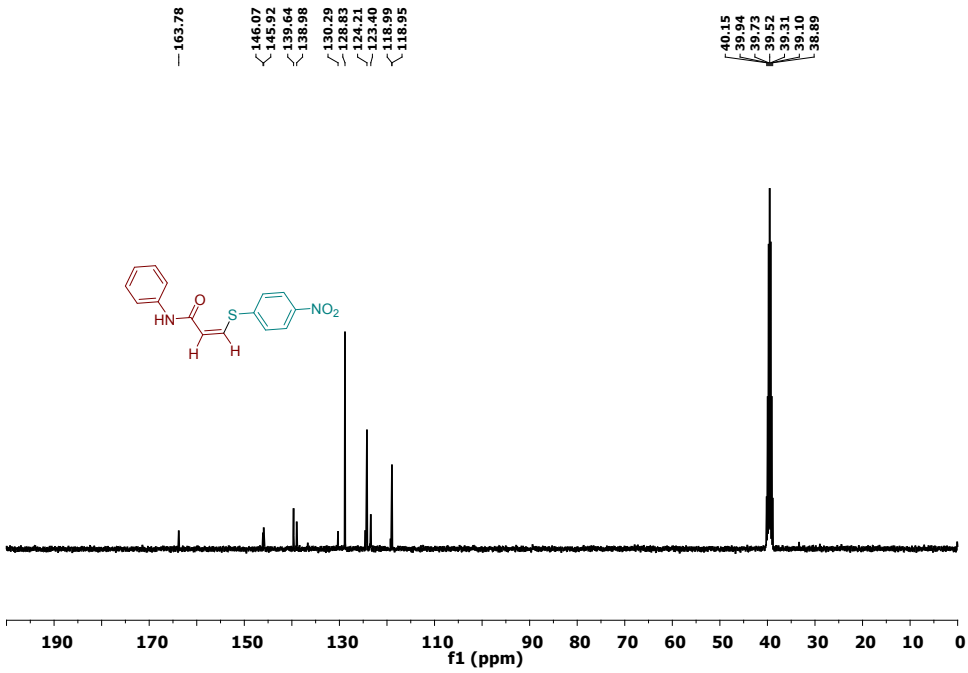


Fig. S72. ^{13}C NMR spectrum of (Z)-3-((4-nitrophenyl)thio)-N-phenylacrylamide (**3ao**)

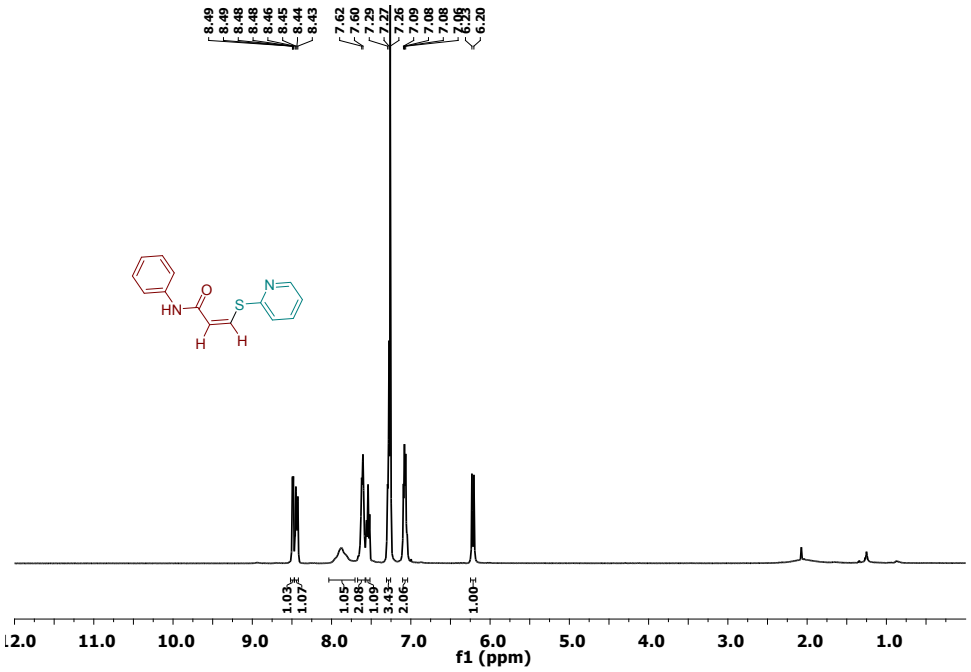


Fig. S73. ^{1}H NMR spectrum of (Z)-N-phenyl-3-(pyridin-2-ylthio)acrylamide (**3ap**)

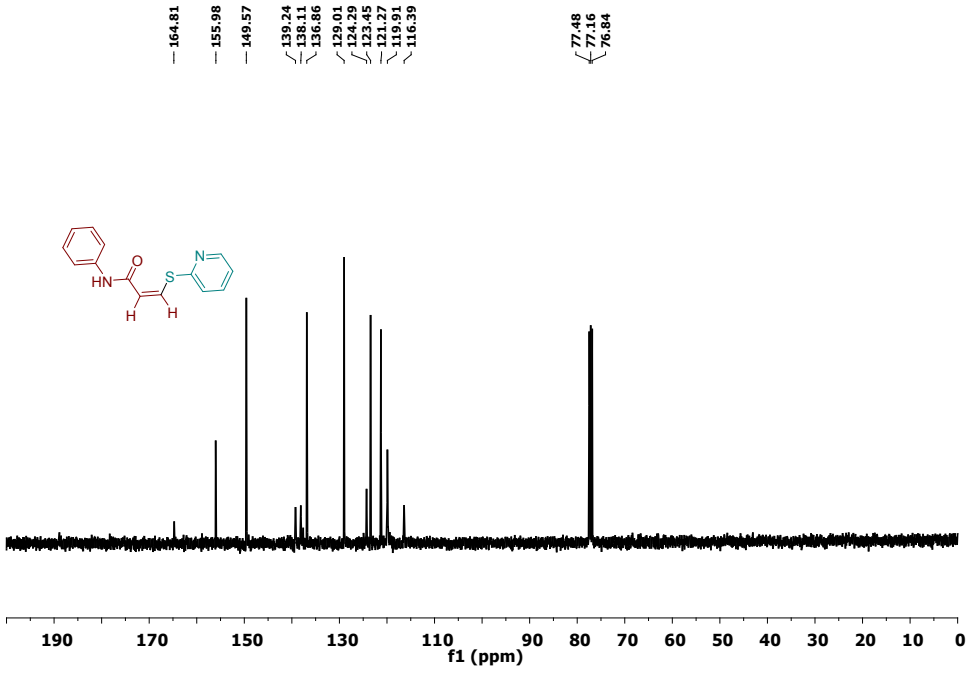


Fig. S74. ^{13}C NMR spectrum of (Z)-N-phenyl-3-(pyridin-2-ylthio)acrylamide (**3ap**)

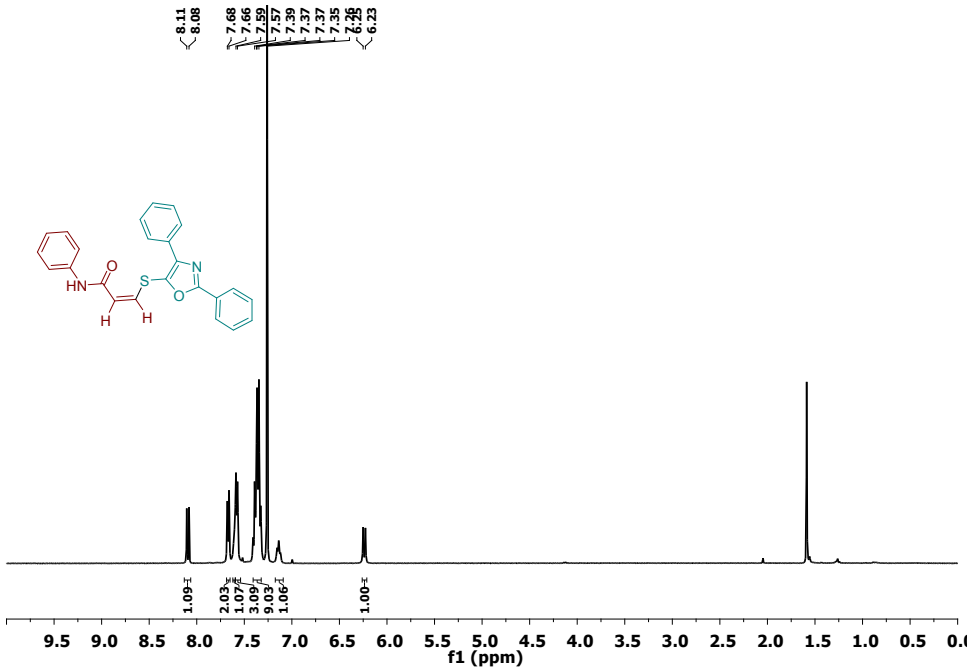


Fig. S75. [1]H NMR spectrum of (Z)-3-((2,4-diphenyloxazol-5-yl)thio)-N-phenylacrylamide (**3aq**)

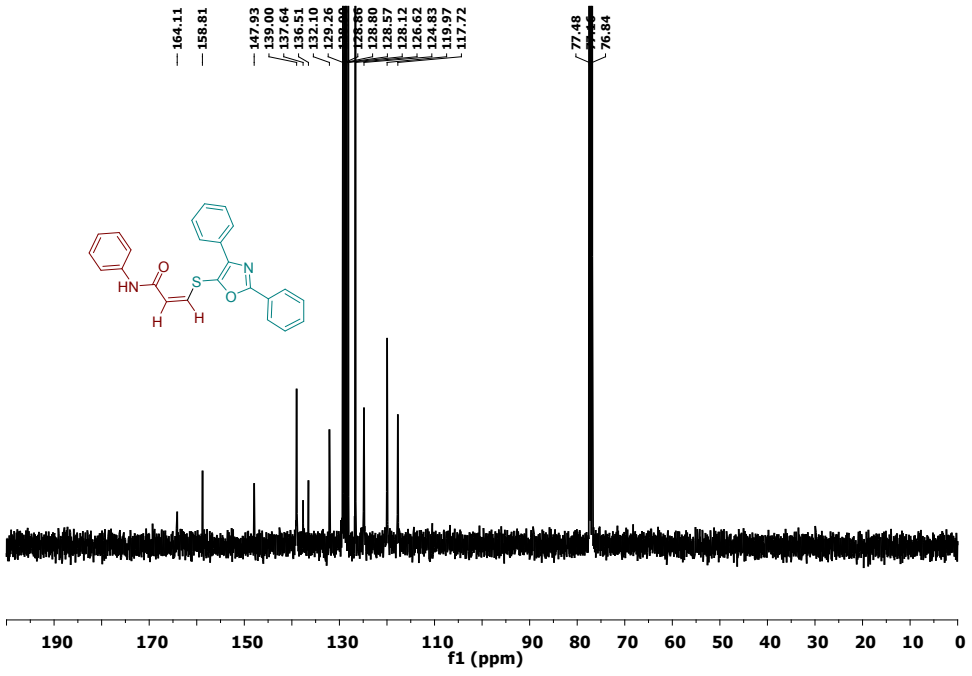


Fig. S76. [13]C NMR spectrum of (Z)-3-((2,4-diphenyloxazol-5-yl)thio)-N-phenylacrylamide (**3aq**)

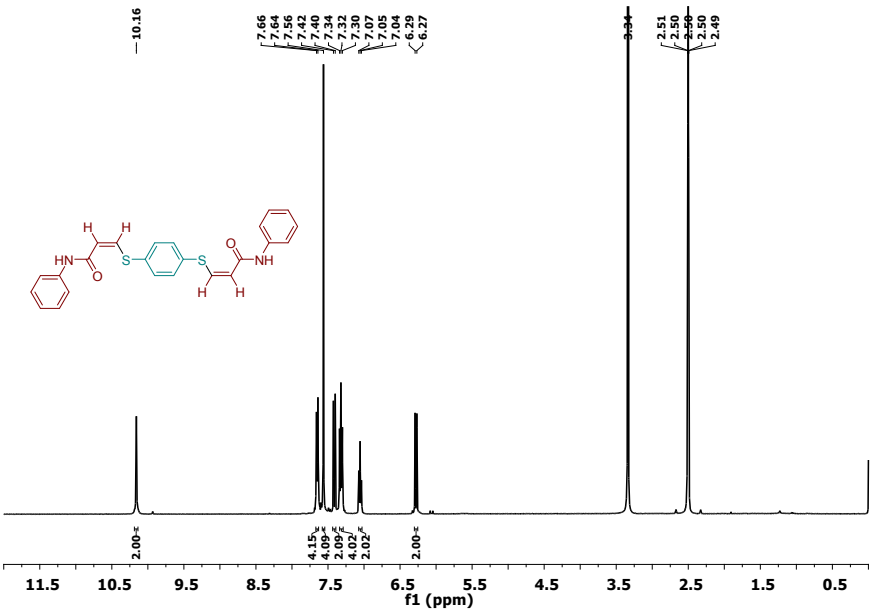


Fig. S77. ^{1}H NMR spectrum of (2Z,2'Z)-3,3'-(1,4-phenylenebis(sulfanediyl))bis(N-phenylacrylamide) (**3ar**)

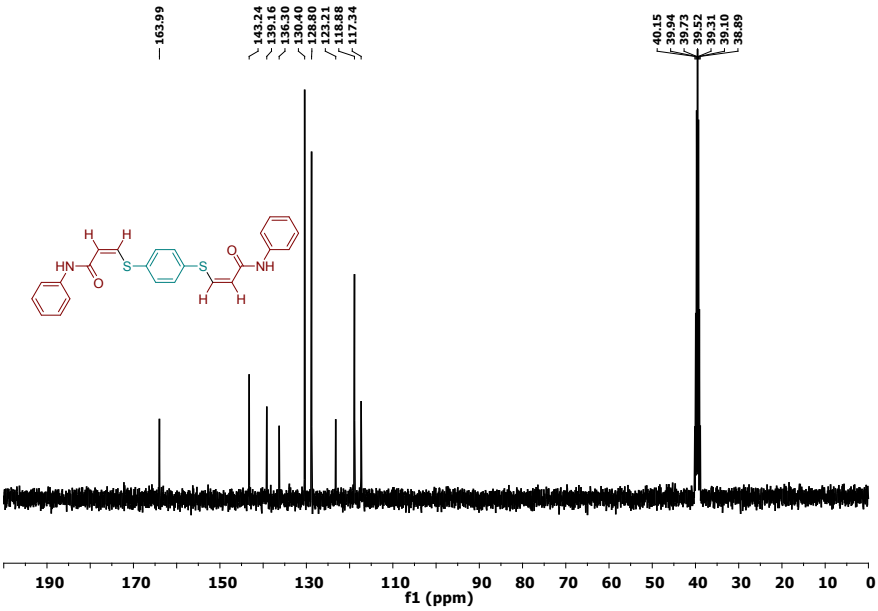


Fig. S78. ^{13}C NMR spectrum of (2Z,2'Z)-3,3'-(1,4-phenylenebis(sulfanediyl))bis(N-phenylacrylamide) (**3ar**)

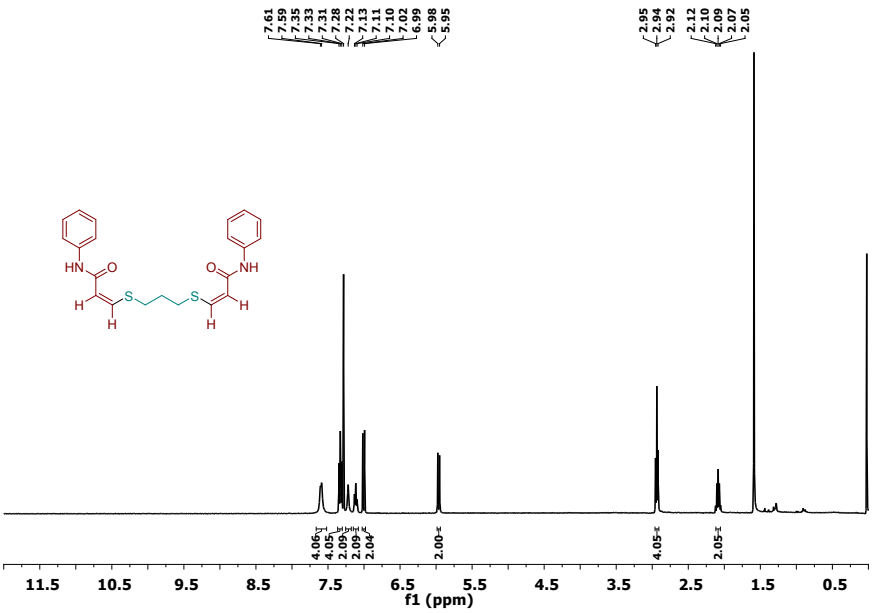


Fig. S79. ^{1}H NMR spectrum of (2Z,2'Z)-3,3'-(propane-1,3-diylbis(sulfanediyl))bis(N-phenylacrylamide) (**3as**)

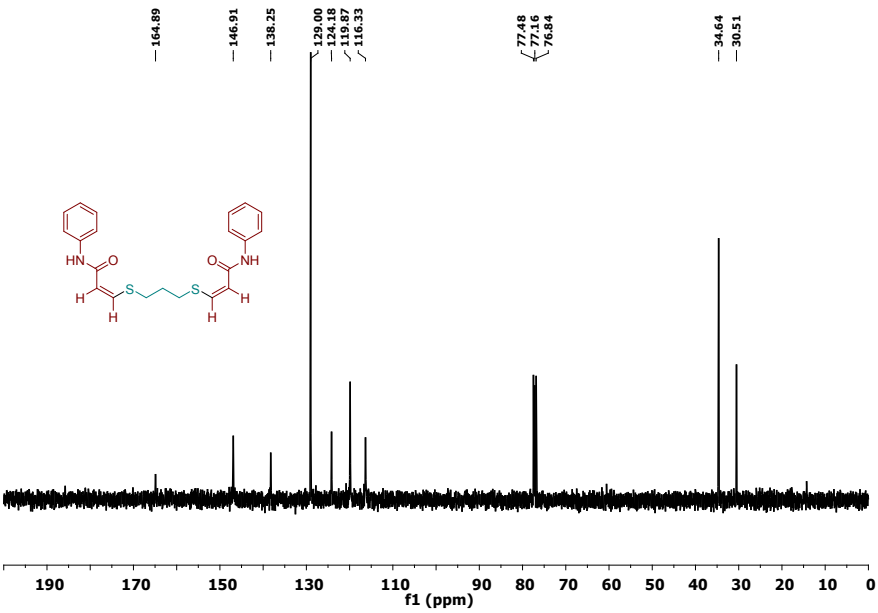


Fig. S80. ^{13}C NMR spectrum of (2Z,2'Z)-3,3'-(propane-1,3-diylbis(sulfanediyl))bis(N-phenylacrylamide) (**3as**)

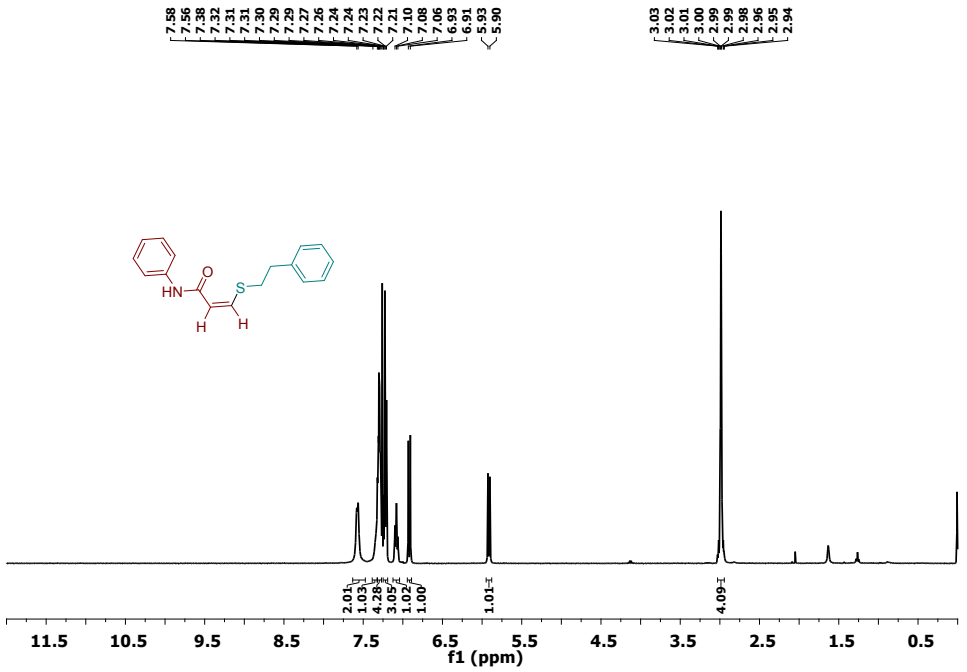


Fig. S81. ^{1}H NMR spectrum of (Z)-3-(phenethylthio)-N-phenylacrylamide (**3at**)

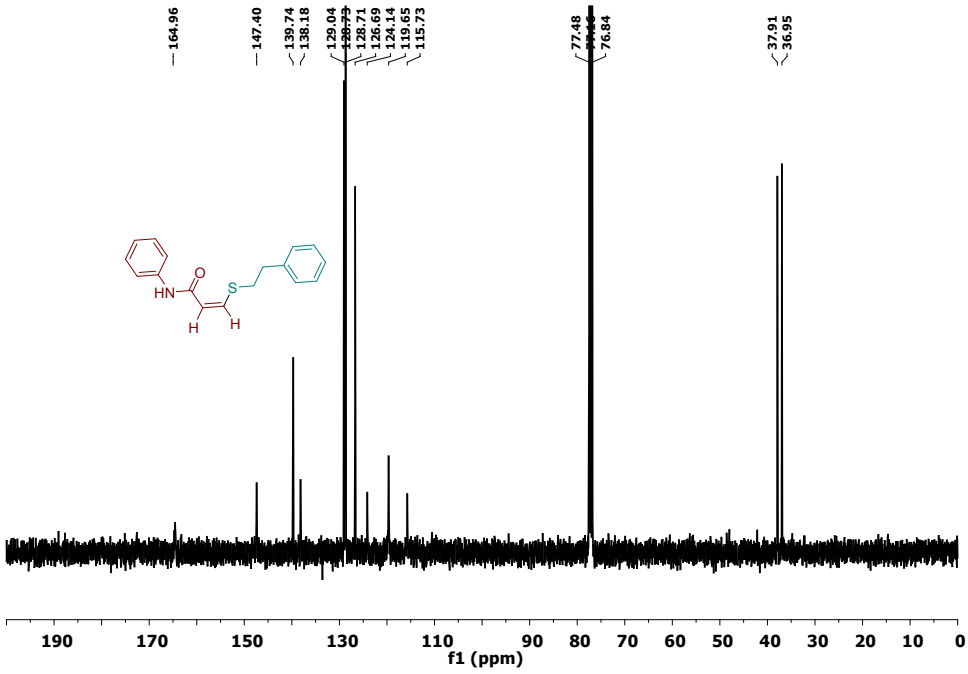


Fig. S82. ^{13}C NMR spectrum of (Z)-3-(phenethylthio)-N-phenylacrylamide (**3at**)

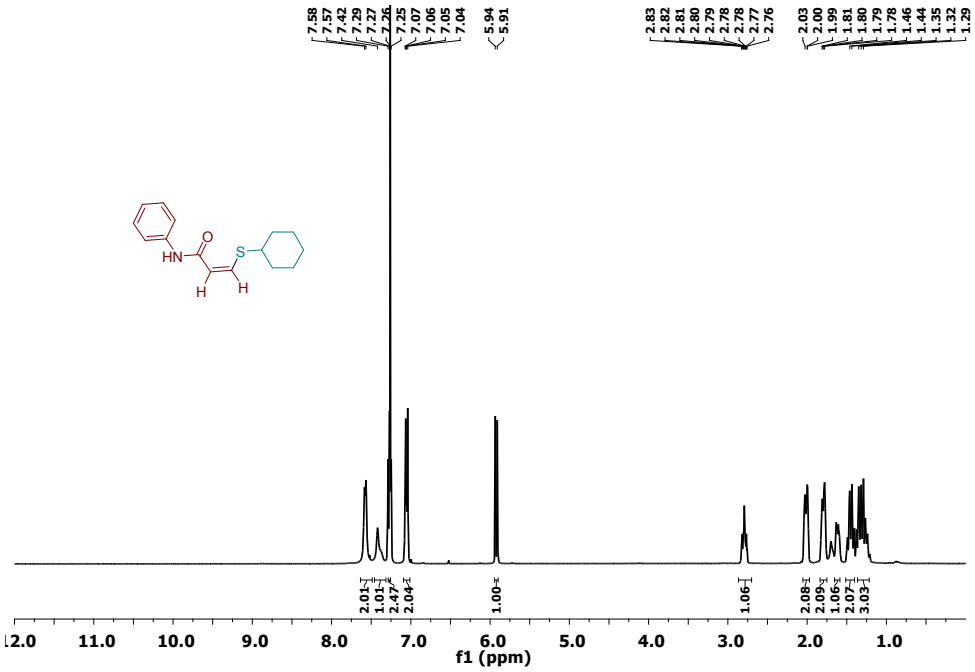


Fig. S83. ^{1}H NMR spectrum of (Z)-3-(cyclohexylthio)-N-phenylacrylamide (**3au**)

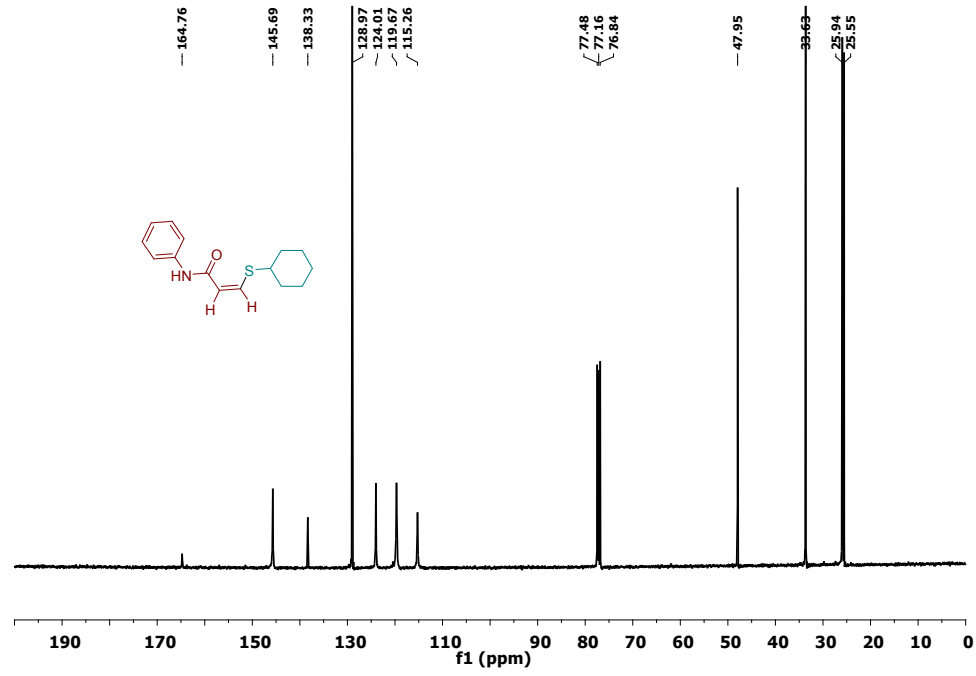


Fig. S84. ^{13}C NMR spectrum of (Z)-3-(cyclohexylthio)-N-phenylacrylamide (**3au**)

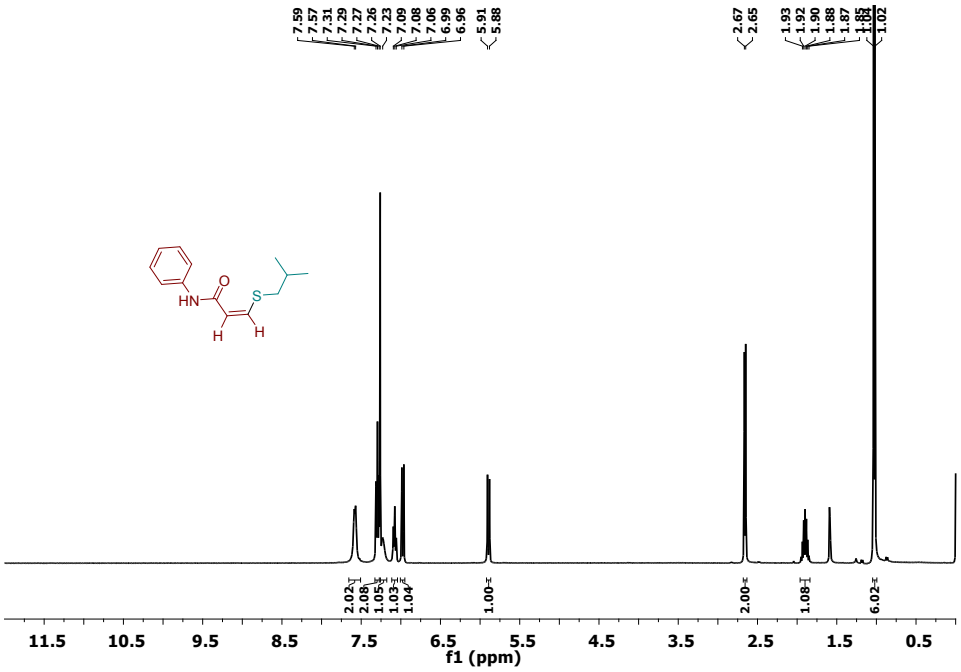


Fig. S85. ^{1}H NMR spectrum of (Z)-3-(isobutylthio)-N-phenylacrylamide (**3av**)

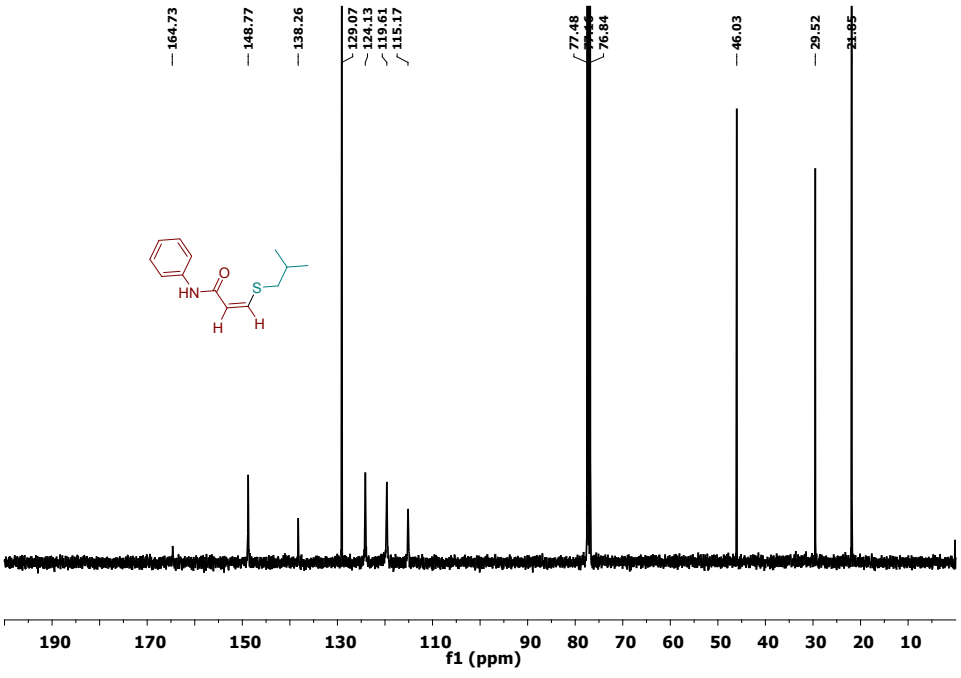


Fig. S86. ^{13}C NMR spectrum of (Z)-3-(isobutylthio)-N-phenylacrylamide (**3av**)

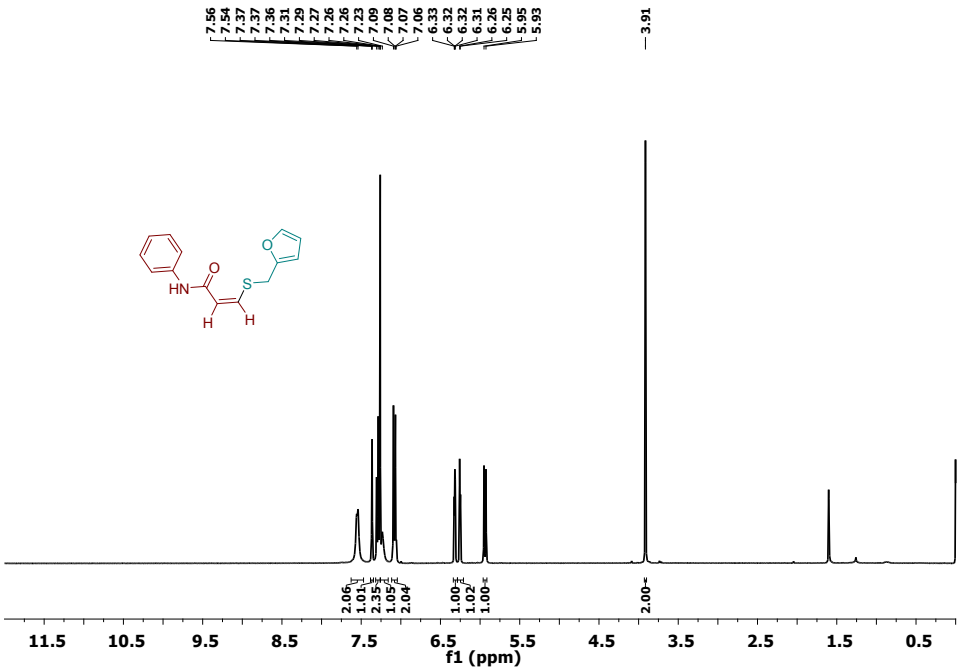


Fig. S87. ^{1}H NMR spectrum of (Z)-3-((furan-2-ylmethyl)thio)-N-phenylacrylamide (**3aw**)

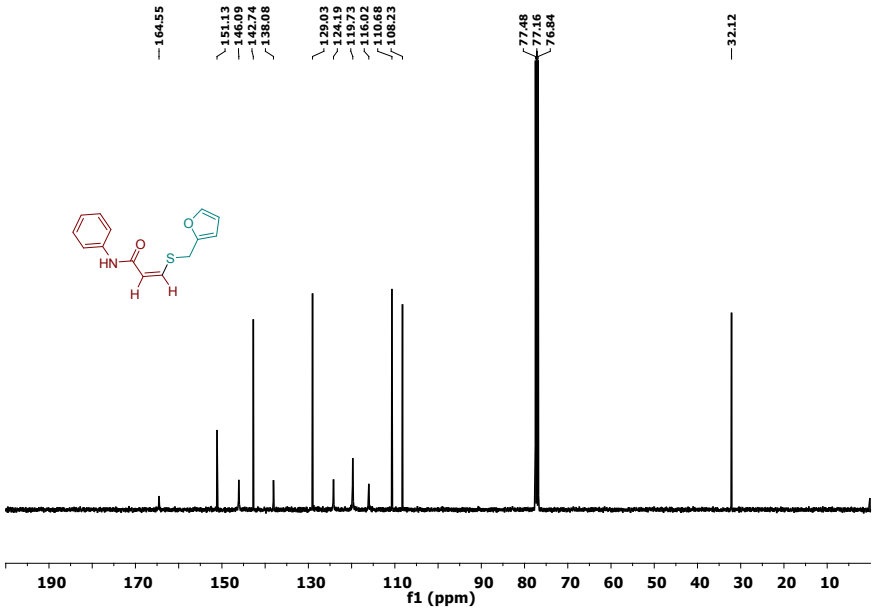


Fig. S88. ^{13}C NMR spectrum of (Z)-3-((furan-2-ylmethyl)thio)-N-phenylacrylamide (**3aw**)

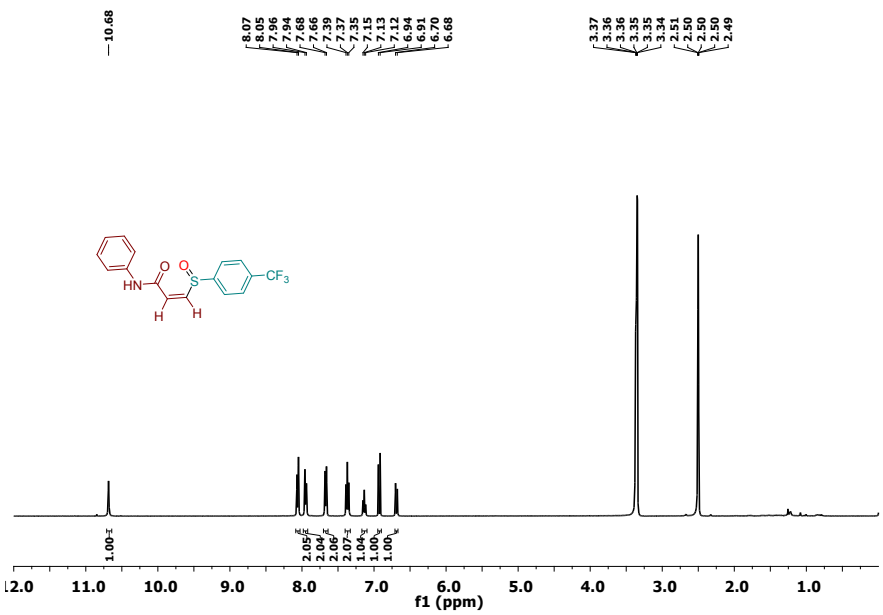


Fig. S89. [1]H NMR spectrum of (Z)-N-phenyl-3-((4-(trifluoromethyl)phenyl)sulfinyl)acrylamide **6**

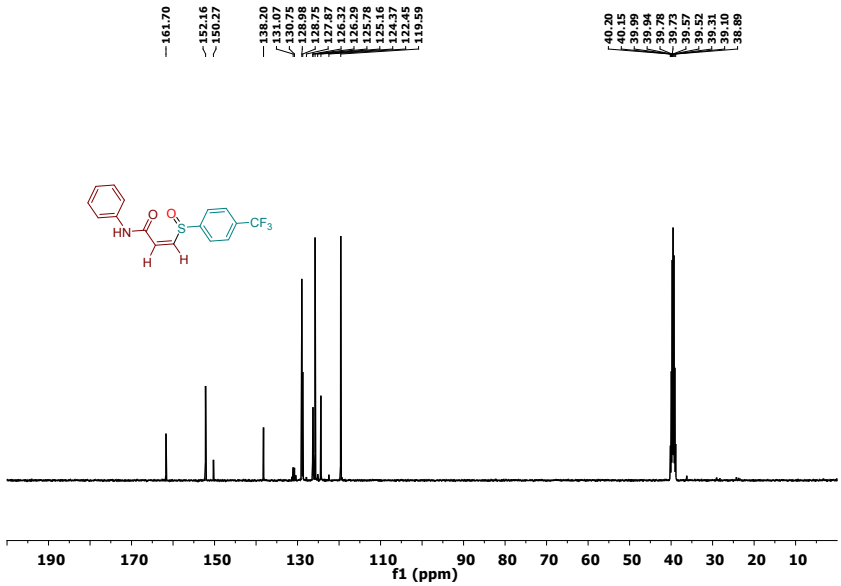


Fig. S90. [13]C NMR spectrum of (Z)-N-phenyl-3-((4-(trifluoromethyl)phenyl)sulfinyl)acrylamide **6**

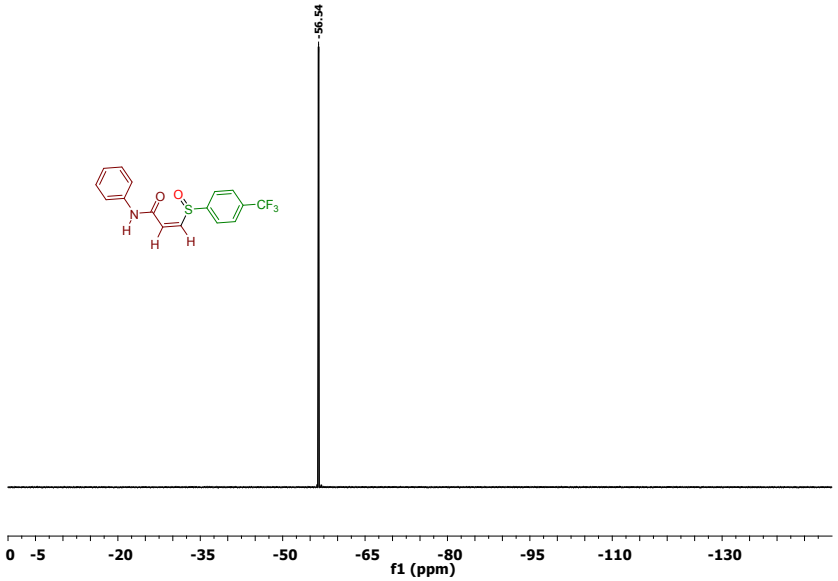


Fig. S91. ^{19}F NMR spectrum of (Z)-N-phenyl-3-((4-(trifluoromethyl)phenyl)sulfinyl)acrylamide **6**

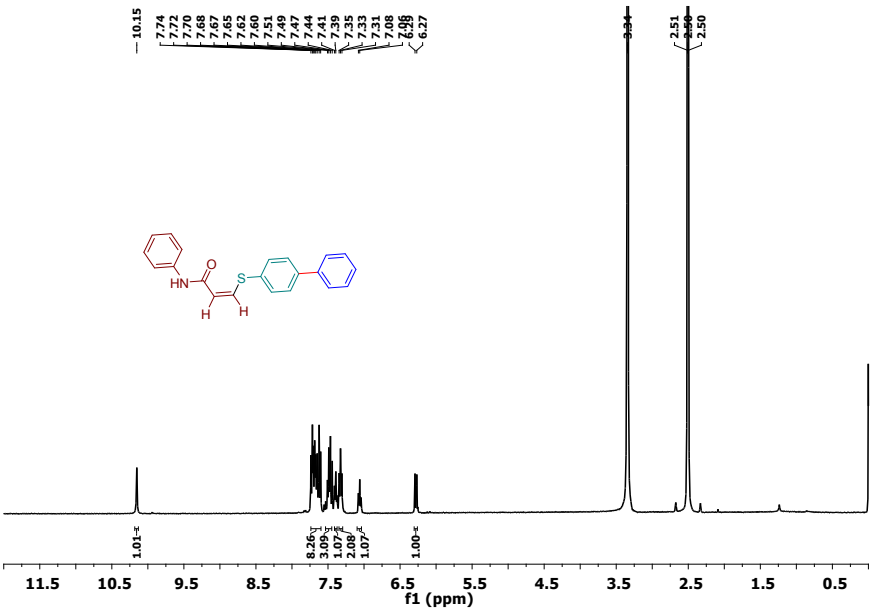


Fig. S92. ^{1}H NMR spectrum of (Z)-3-([1,1'-biphenyl]-4-ylthio)-N-phenylacrylamide **7**

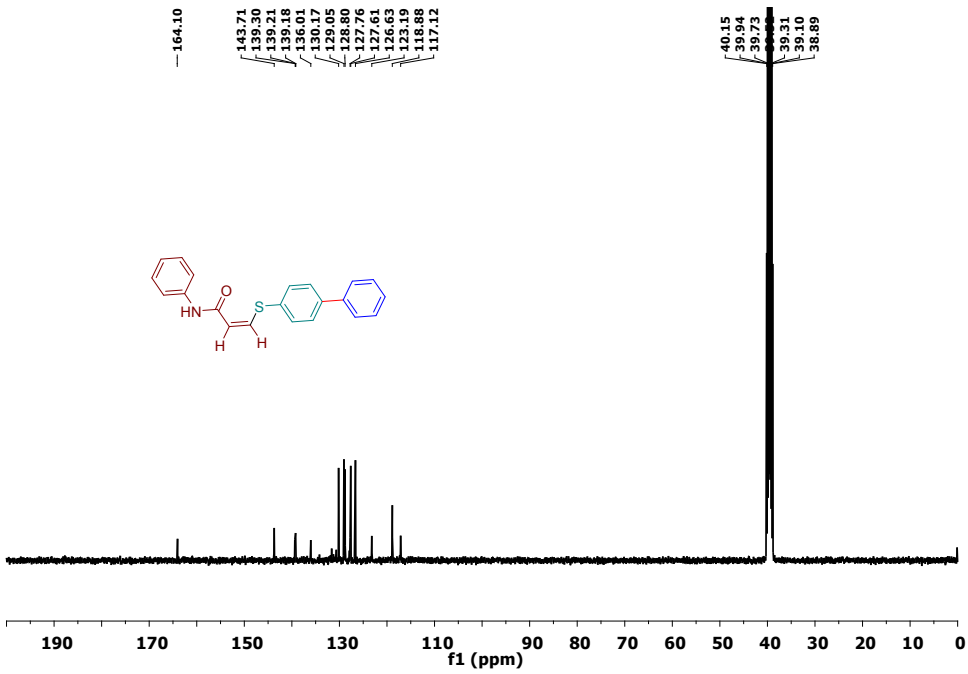


Fig. S93. ^{13}C NMR spectrum of (Z)-3-([1,1'-biphenyl]-4-ylthio)-N-phenylacrylamide **7**

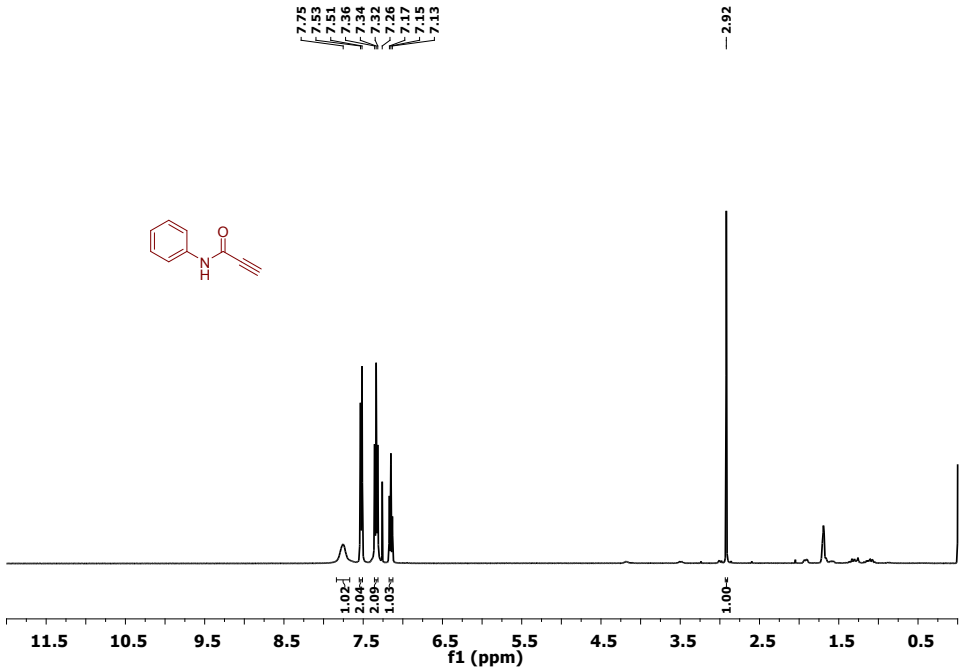


Fig. S94. ^{1}H NMR spectrum of N-phenylpropiolamide (**1a**)

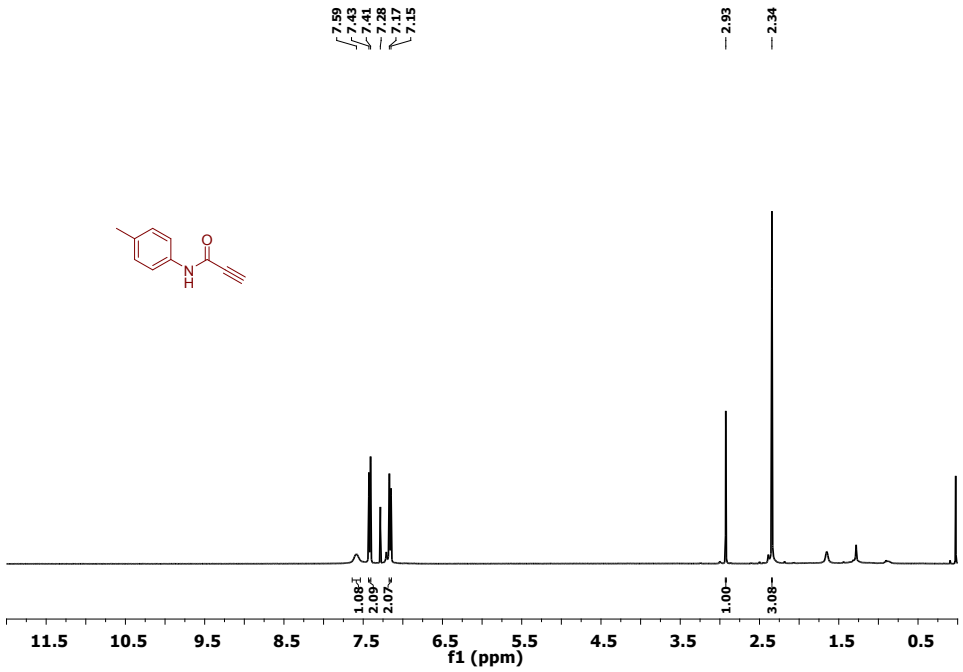


Fig. S95. ^{1}H NMR spectrum of N-(p-tolyl)propiolamide (**1b**)

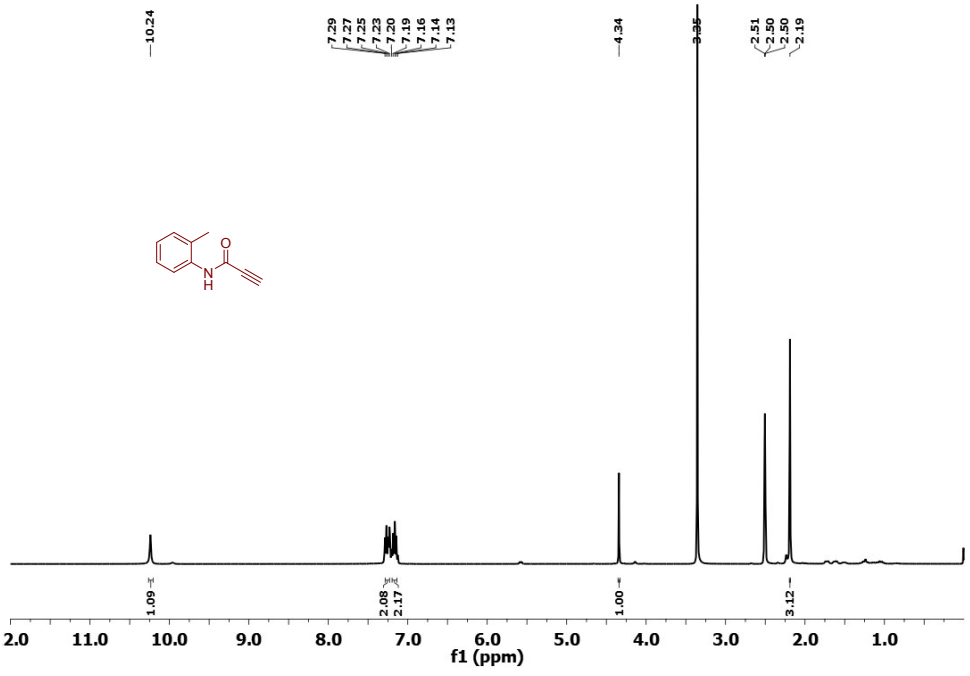


Fig. S96. ^{1}H NMR spectrum of N-(o-tolyl)propiolamide (**1c**)

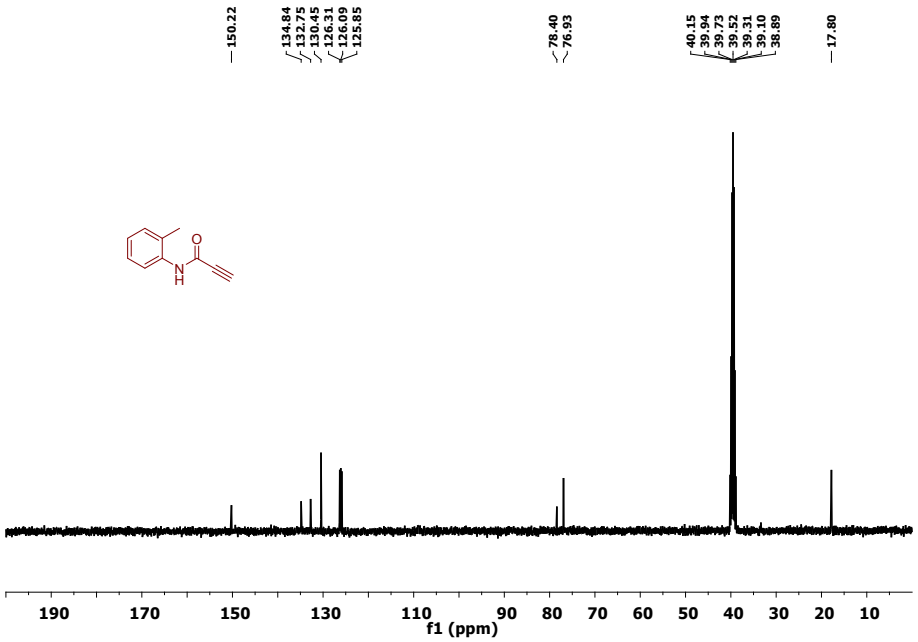


Fig. S97. ^{13}C NMR spectrum of N-(o-tolyl)propiolamide (**1c**)

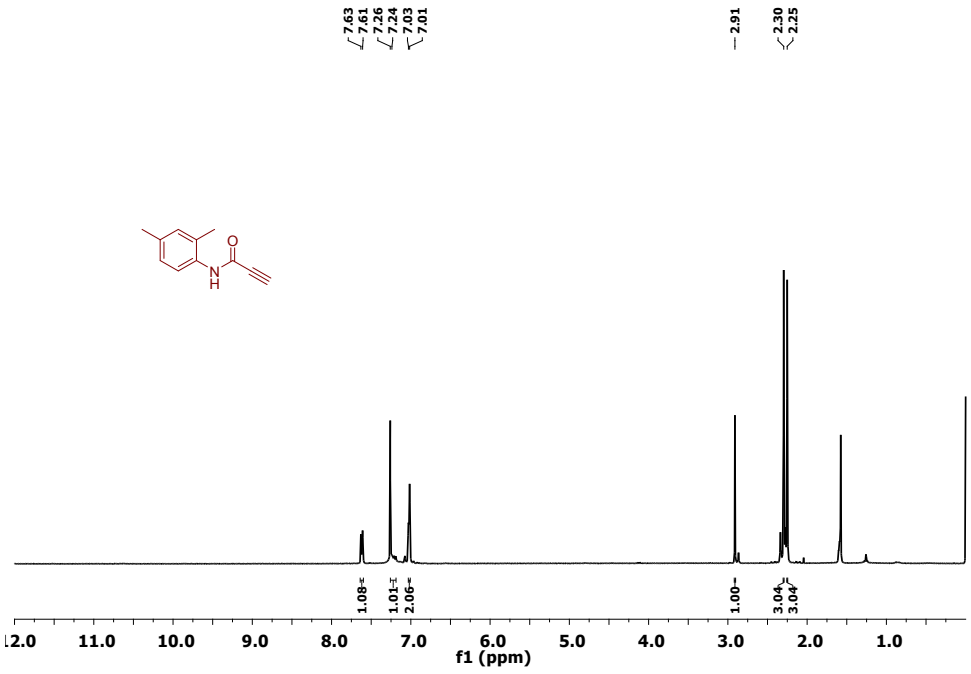


Fig. S98. ^{1}H NMR spectrum of N-(2,4-dimethylphenyl)propiolamide (**1d**)

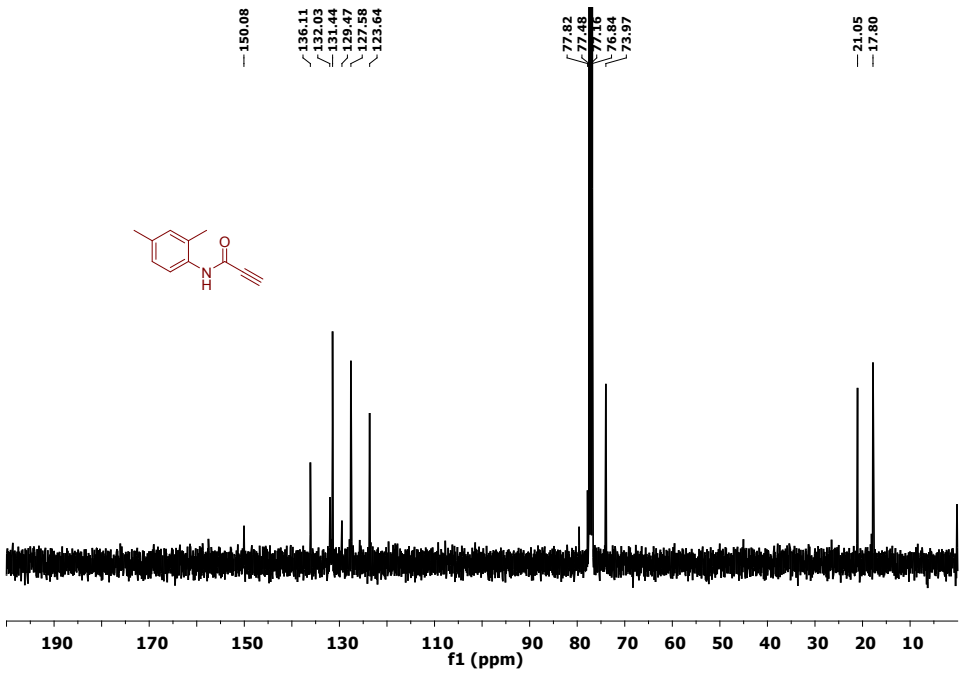


Fig. S99. ^{13}C NMR spectrum of N-(2,4-dimethylphenyl)propiolamide (**1d**)

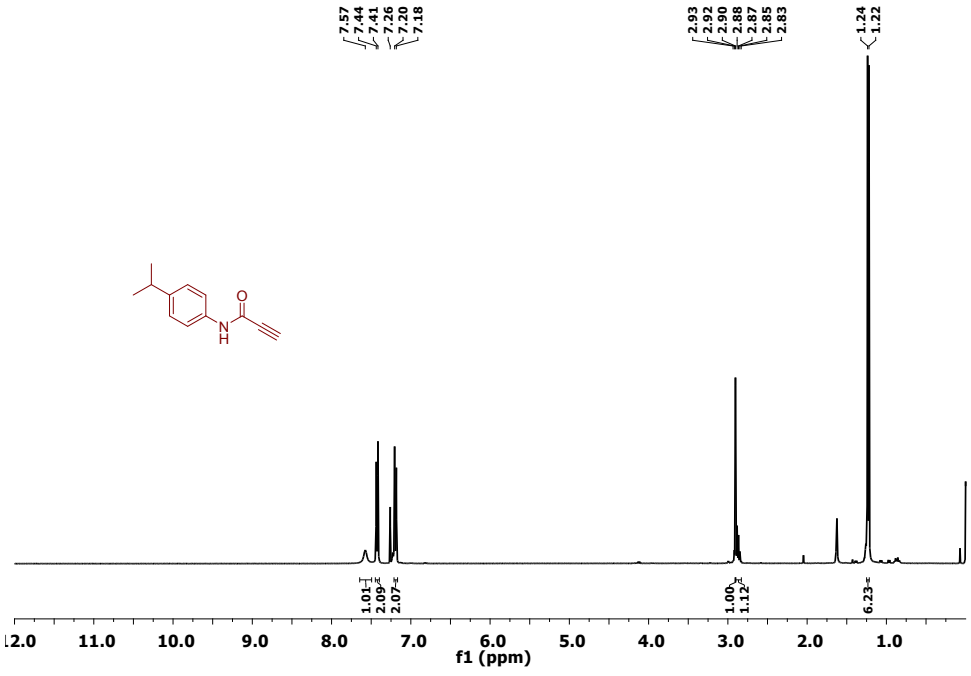


Fig. S100. ^{1}H NMR spectrum of N-(4-isopropylphenyl)propiolamide (**1e**)

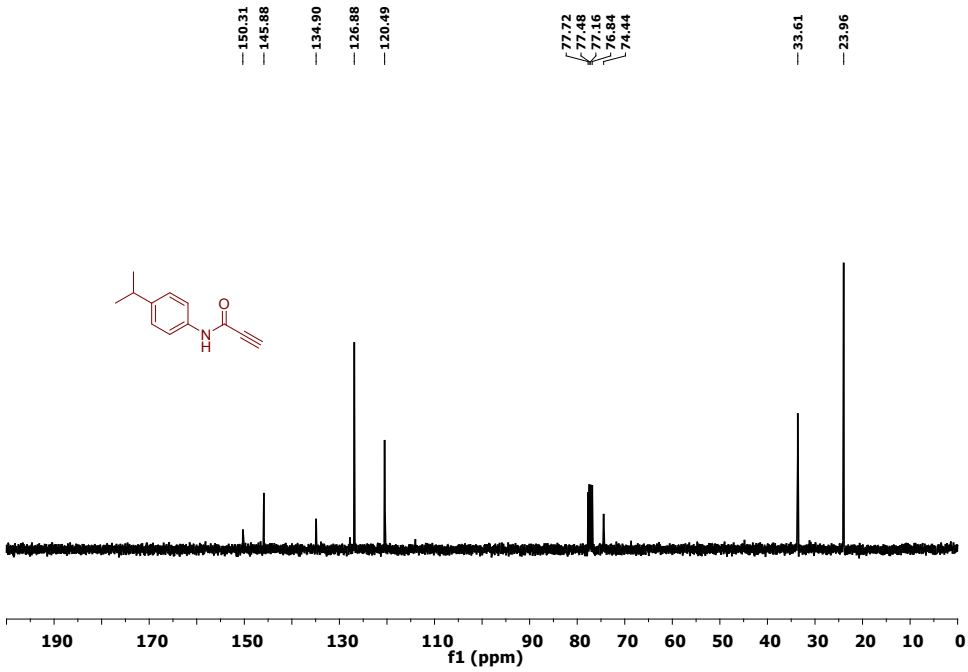


Fig. S101. ^{13}C NMR spectrum of N-(4-isopropylphenyl)propiolamide (**1e**)

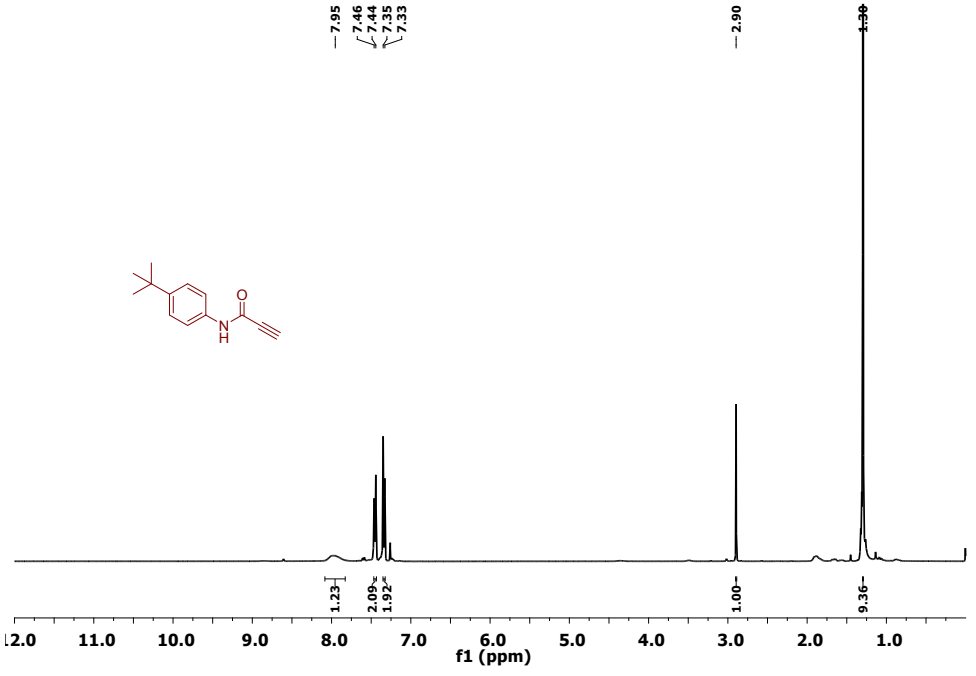


Fig. S102. ^{1}H NMR spectrum of N-(4-(tert-butyl)phenyl)propiolamide (**1f**)

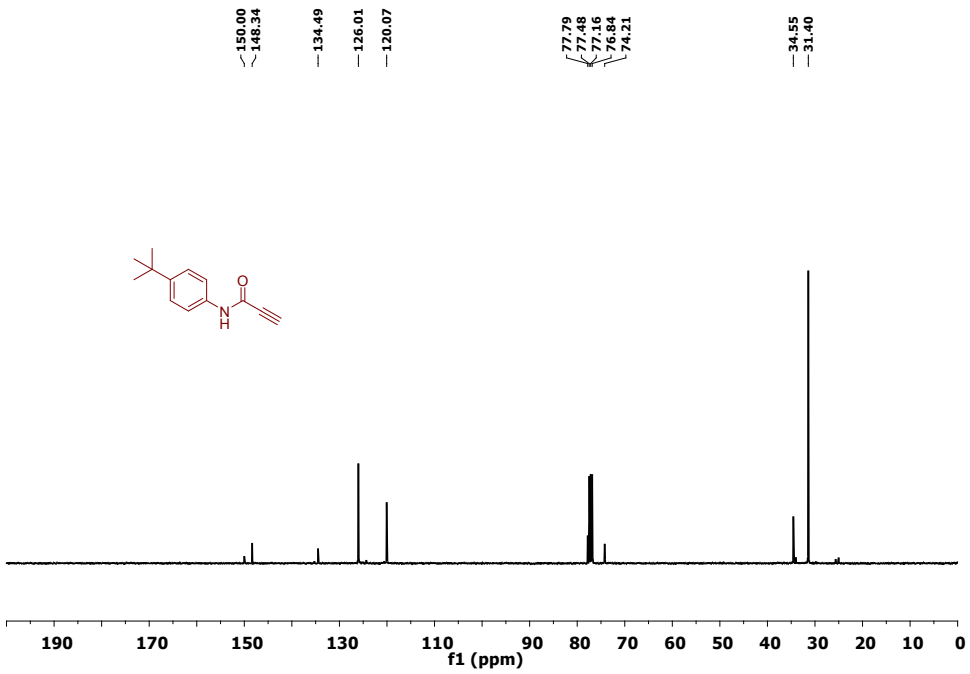


Fig. S103. ^{13}C NMR spectrum of N-(4-(tert-butyl)phenyl)propiolamide (**1f**)

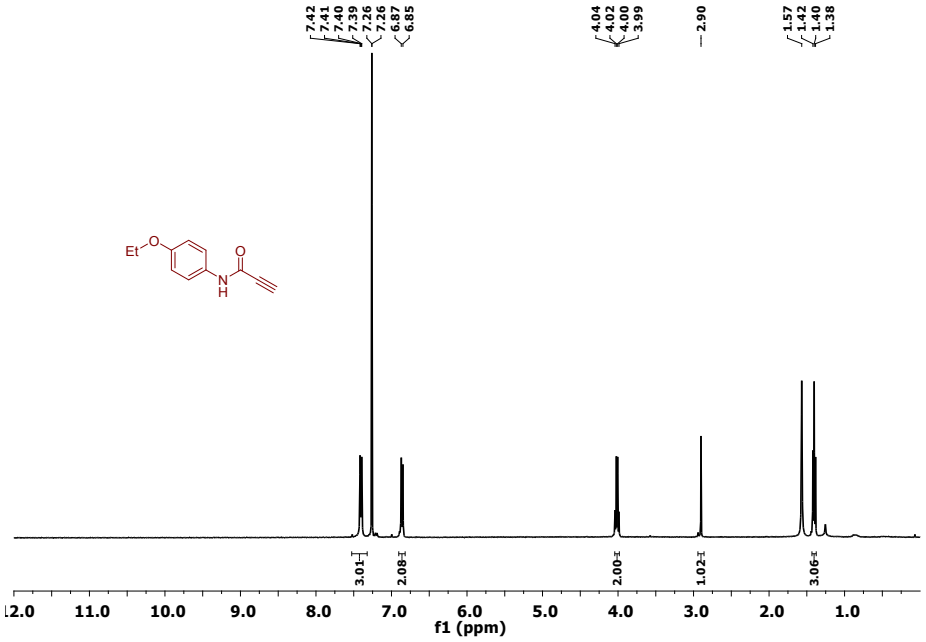


Fig. S104. ^{1}H NMR spectrum of N-(4-ethoxyphenyl)propiolamide (**1g**)

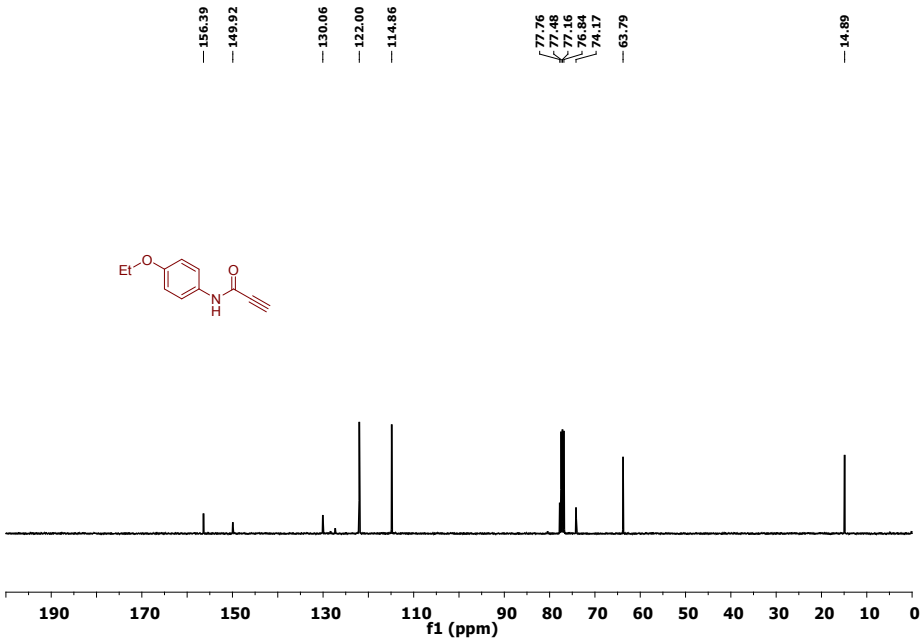


Fig. S105. ^{13}C NMR spectrum of N-(4-ethoxyphenyl)propiolamide (**1g**)

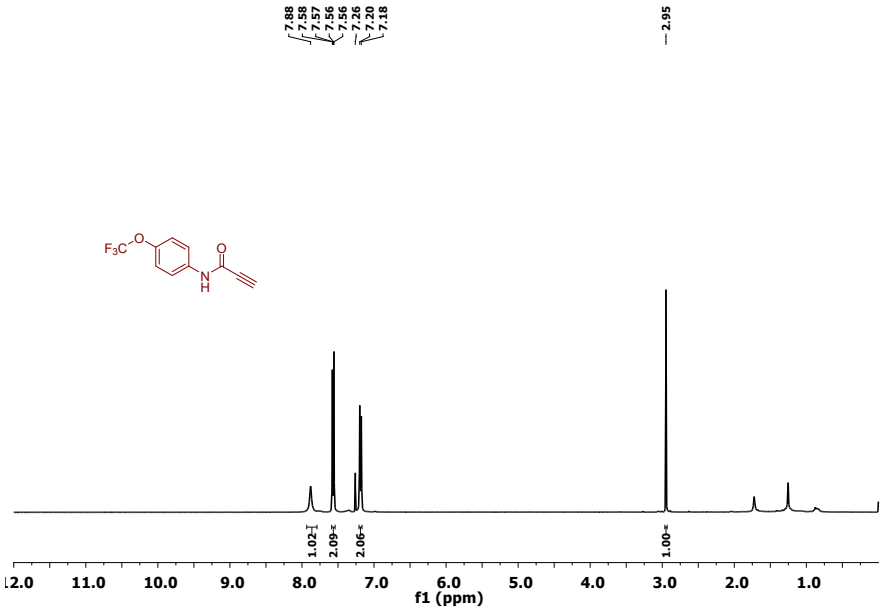


Fig. S106. ^{1}H NMR spectrum of N-(4-(trifluoromethoxy)phenyl)propiolamide (**1h**)

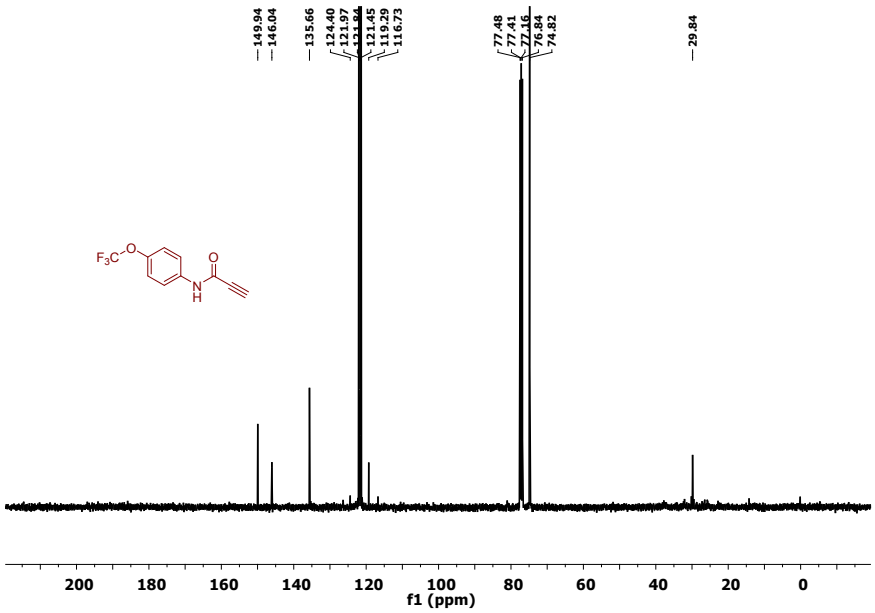


Fig. S107. ^{13}C NMR spectrum of N-(4-(trifluoromethoxy)phenyl)propiolamide (**1h**)

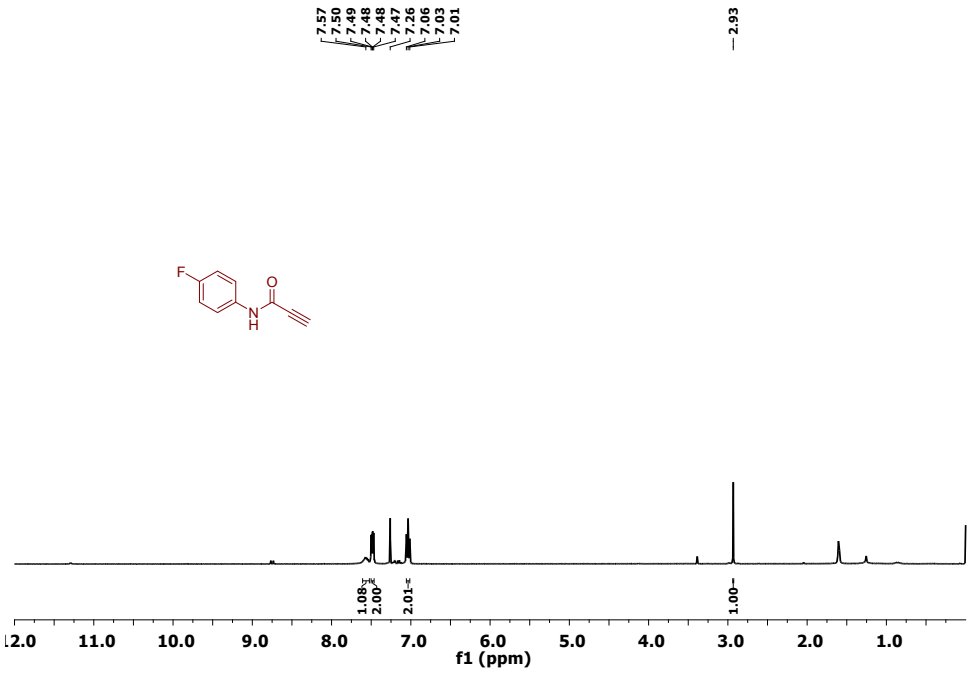


Fig. S108. ^{1}H NMR spectrum of N-(4-fluorophenyl)propiolamide (**1i**)

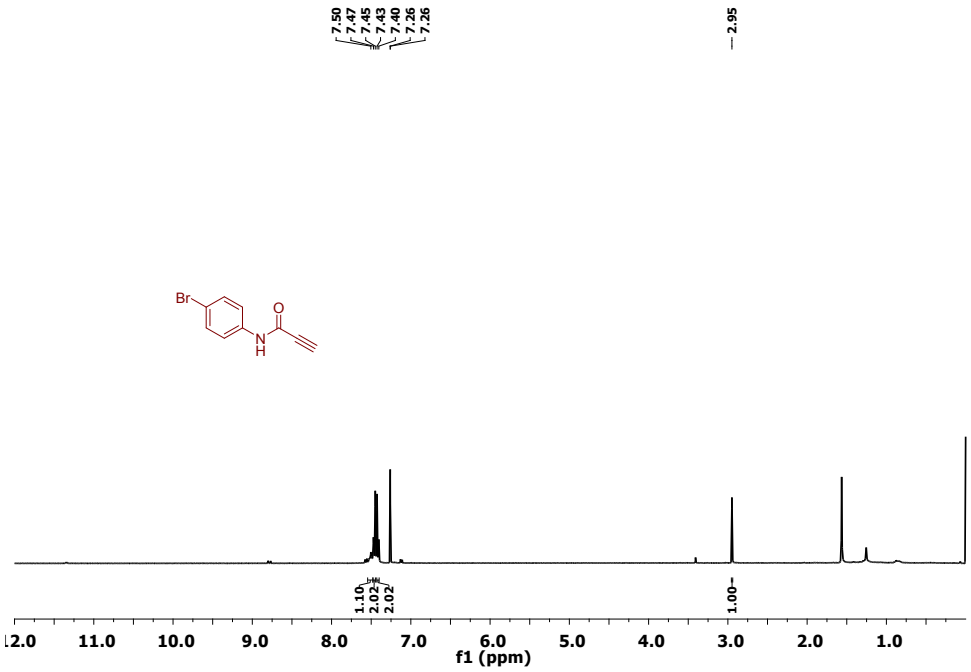


Fig. S109. [1]H NMR spectrum of N-(4-bromophenyl)propiolamide (**1j**)

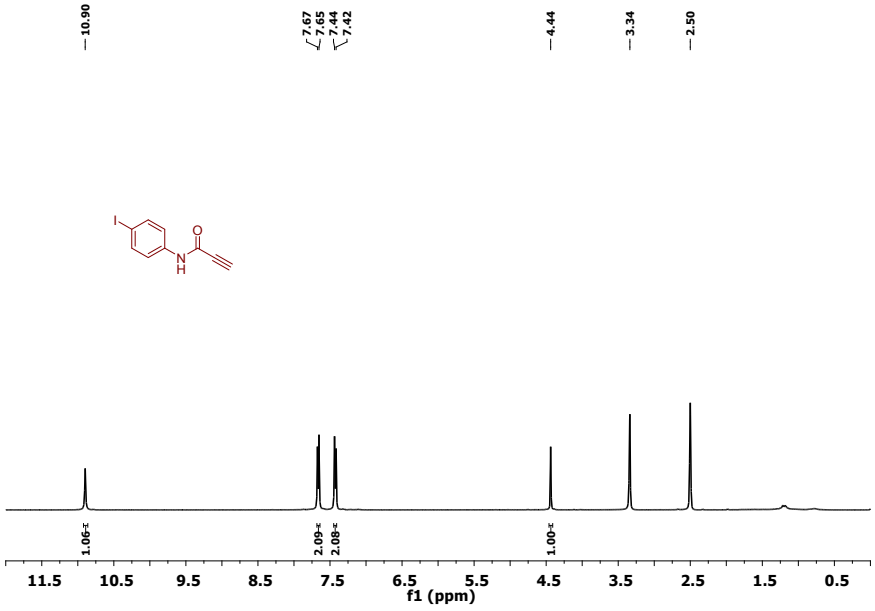


Fig. S110. [1]H NMR spectrum of N-(4-iodophenyl)propiolamide (**1k**)

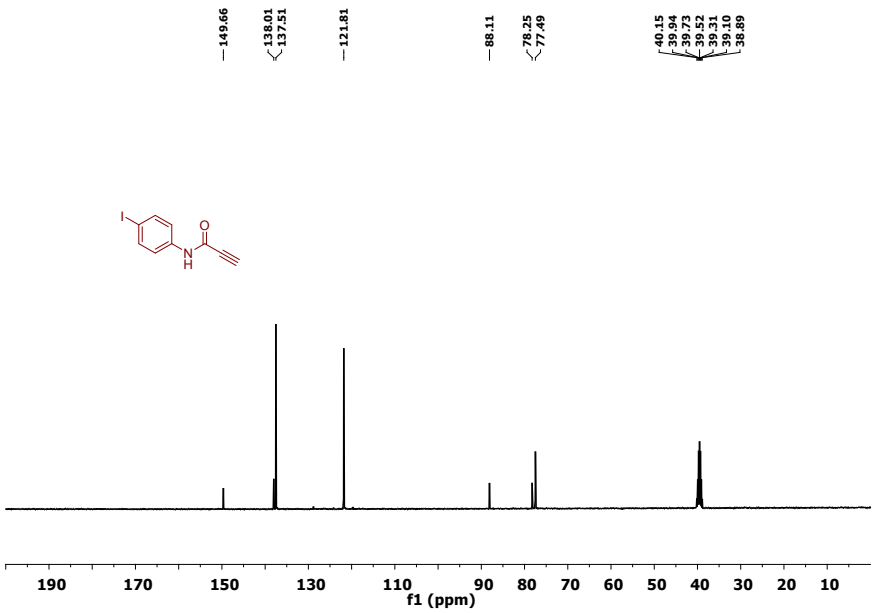


Fig. S111. ^{13}C NMR spectrum of N-(4-iodophenyl)propiolamide (**1k**)

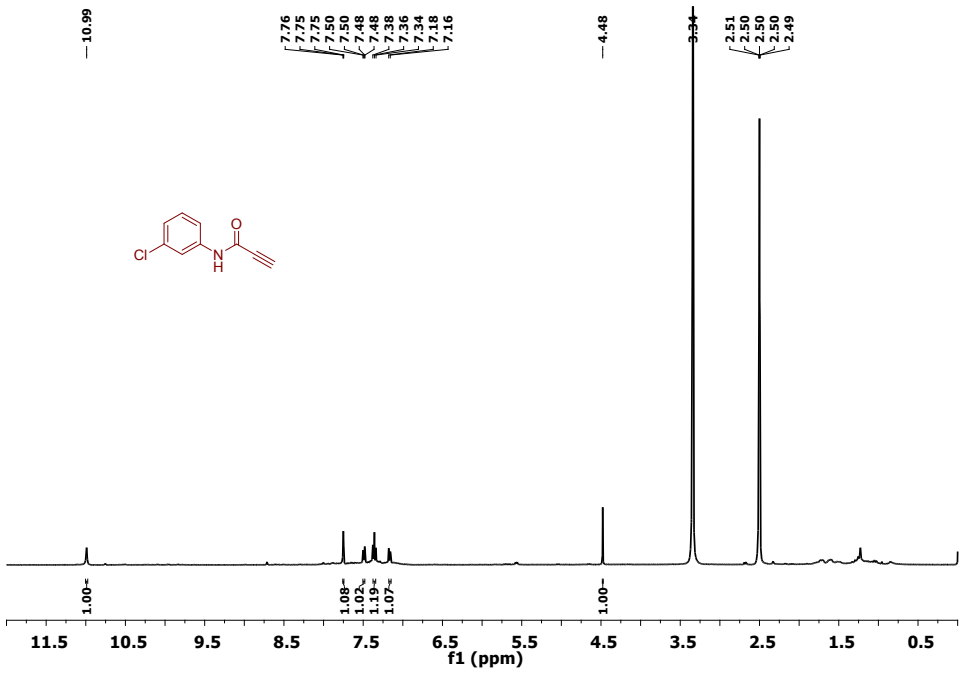


Fig. S112. ^{1}H NMR spectrum of N-(3-chlorophenyl)propiolamide (**1l**)

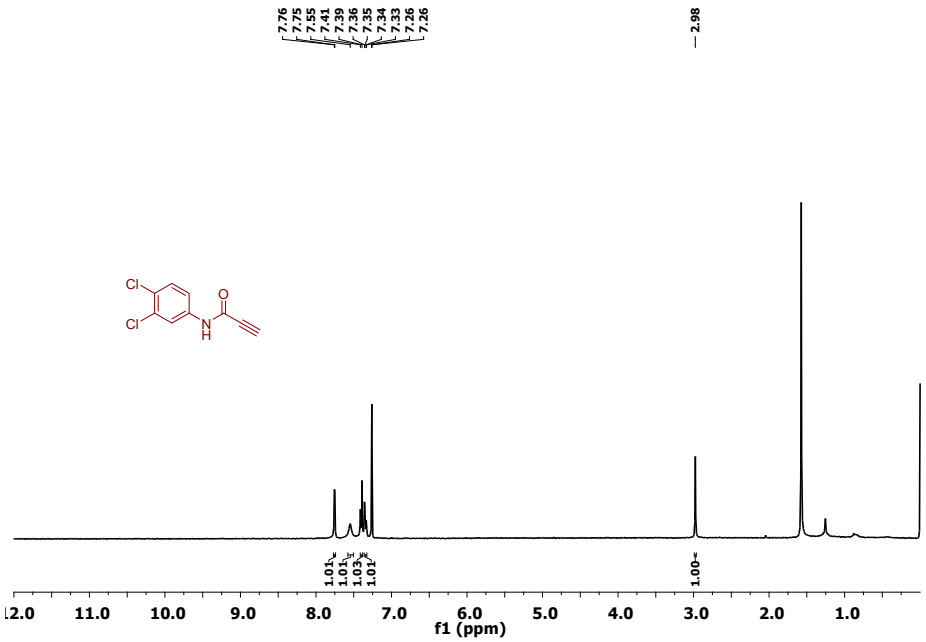


Fig. S113. ^{1}H NMR spectrum of N-(3,4-dichlorophenyl)propiolamide (**1m**)

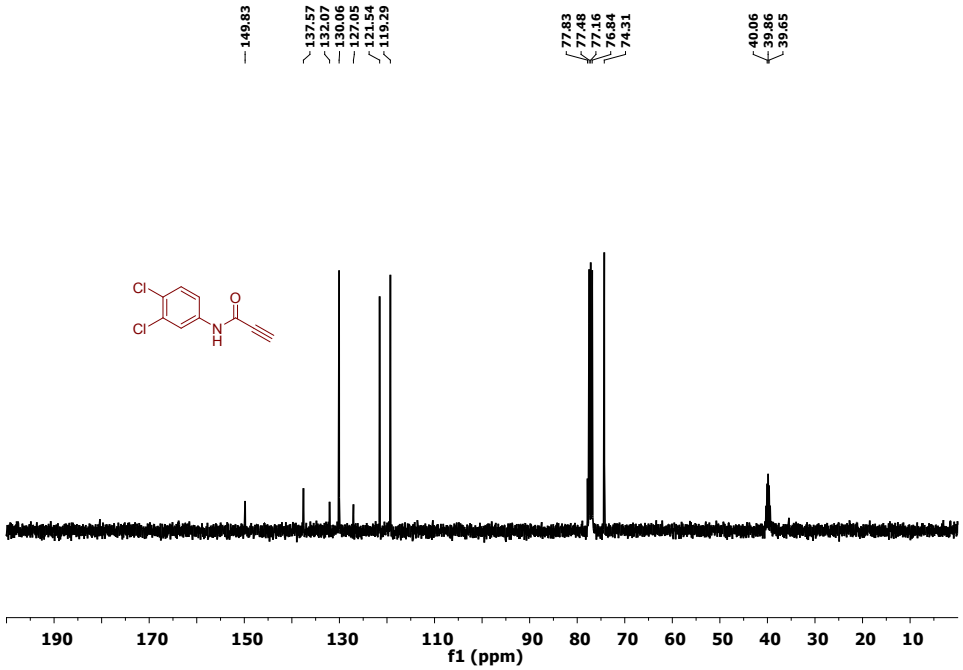


Fig. S114. ^{13}C NMR spectrum of N-(3,4-dichlorophenyl)propiolamide (**1m**) [$CDCl_3$+DMSO-d_6 mixture]

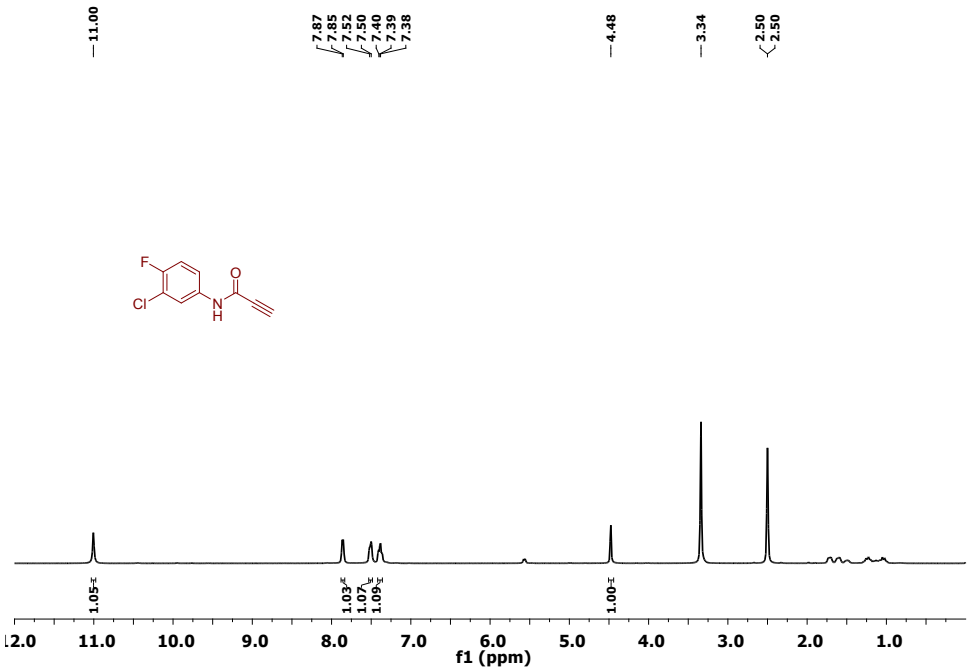


Fig. S115. ^{1}H NMR spectrum of N-(3-chloro-4-fluorophenyl)propiolamide (**1n**)

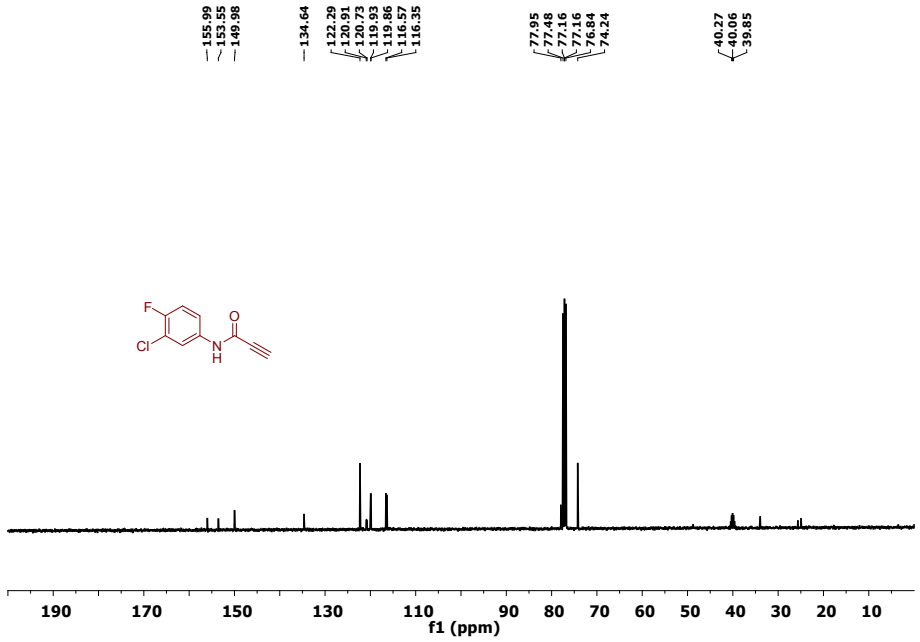


Fig. S116. ^{13}C NMR spectrum of N-(3-chloro-4-fluorophenyl)propiolamide (**1n**)

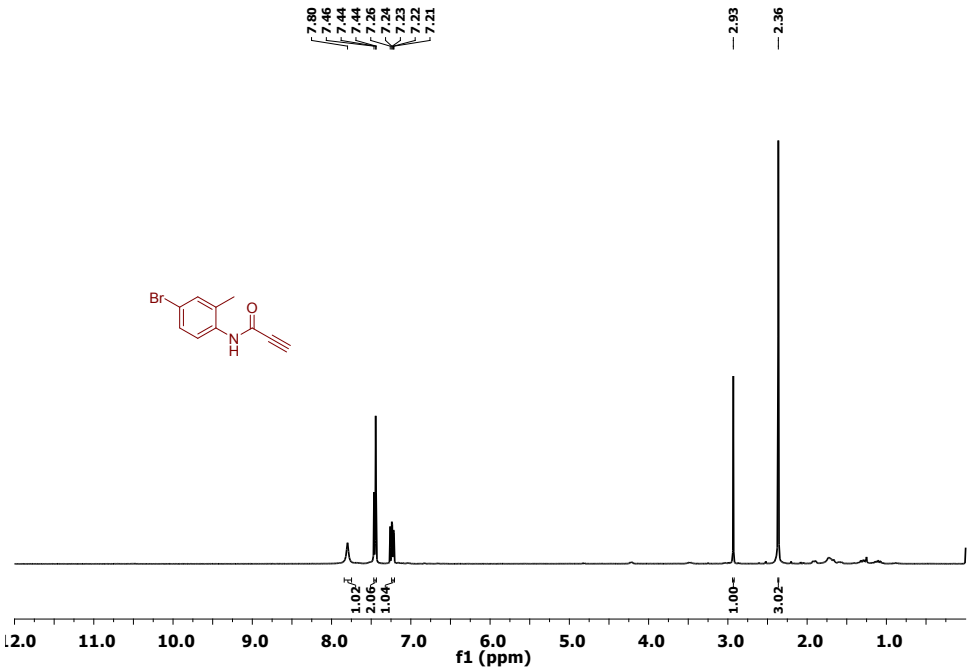


Fig. S117. ^{1}H NMR spectrum of N-(4-bromo-2-methylphenyl)propiolamide (**1o**)

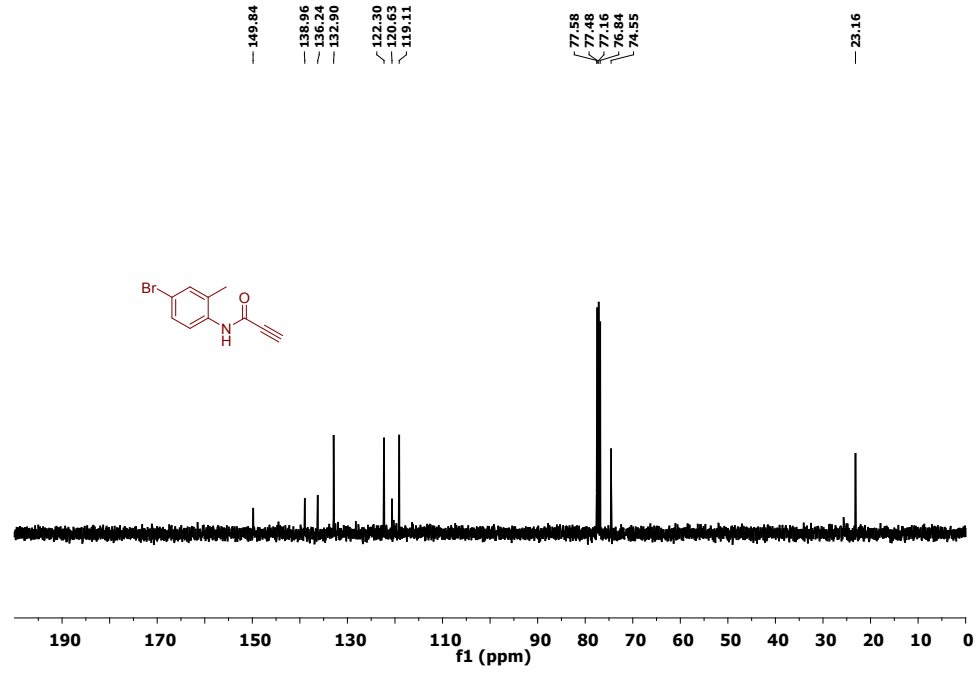


Fig. S118. ^{13}C NMR spectrum of N-(4-bromo-2-methylphenyl)propiolamide (**1o**)

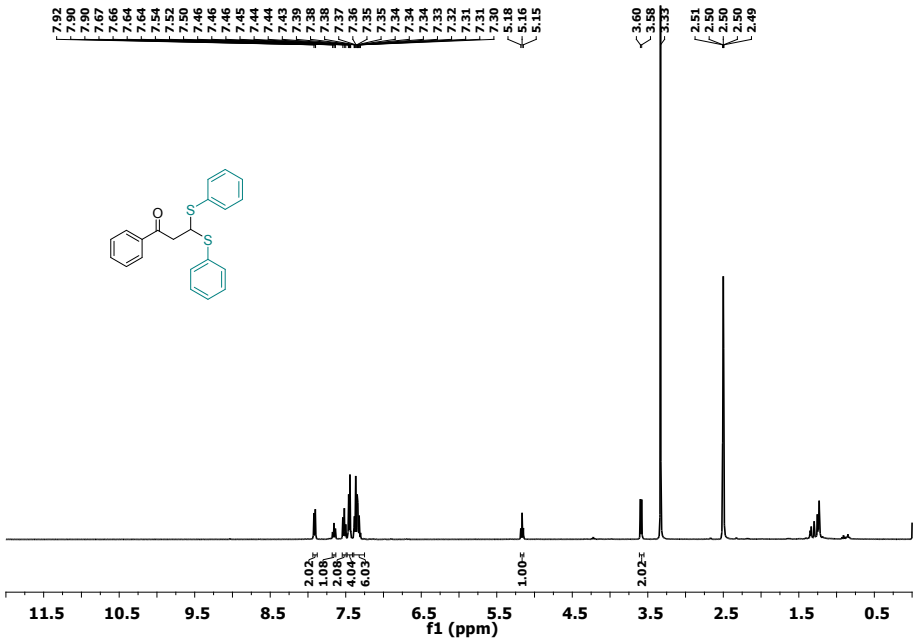


Fig. S119. ^{1}H NMR spectrum of 1-phenyl-3,3-bis(phenylthio)propan-1-one **5**

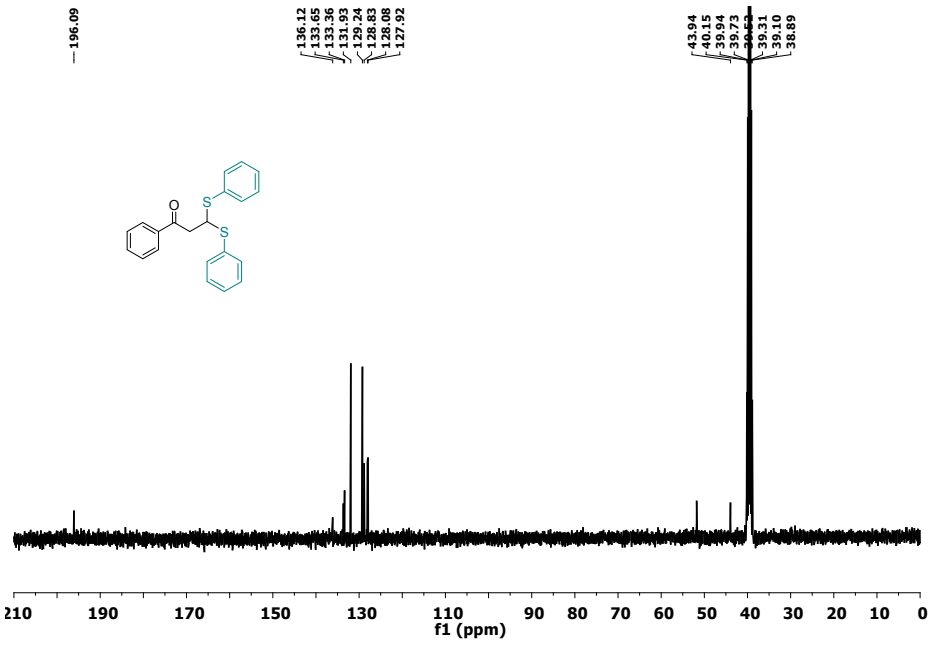


Fig. S120. ^{13}C NMR spectrum of 1-phenyl-3,3-bis(phenylthio)propan-1-one **5**

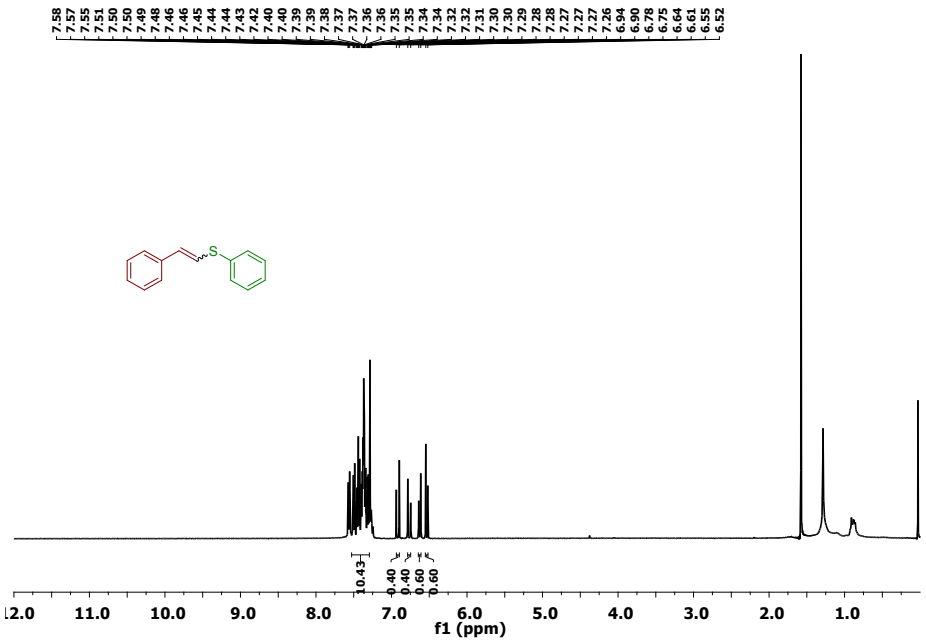


Fig. S121. [1]H NMR spectrum of phenyl(styryl)sulfane **4**.

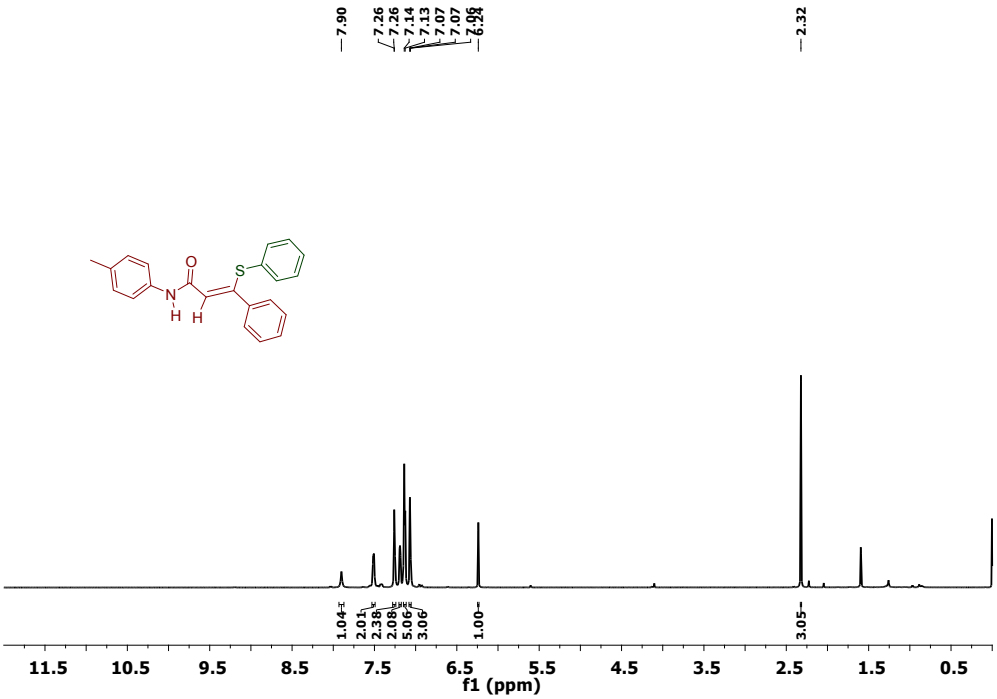


Fig. S122. [1]H NMR spectrum of (Z)-3-phenyl-3-(phenylthio)-N-(p-tolyl)acrylamide (**3ra**)

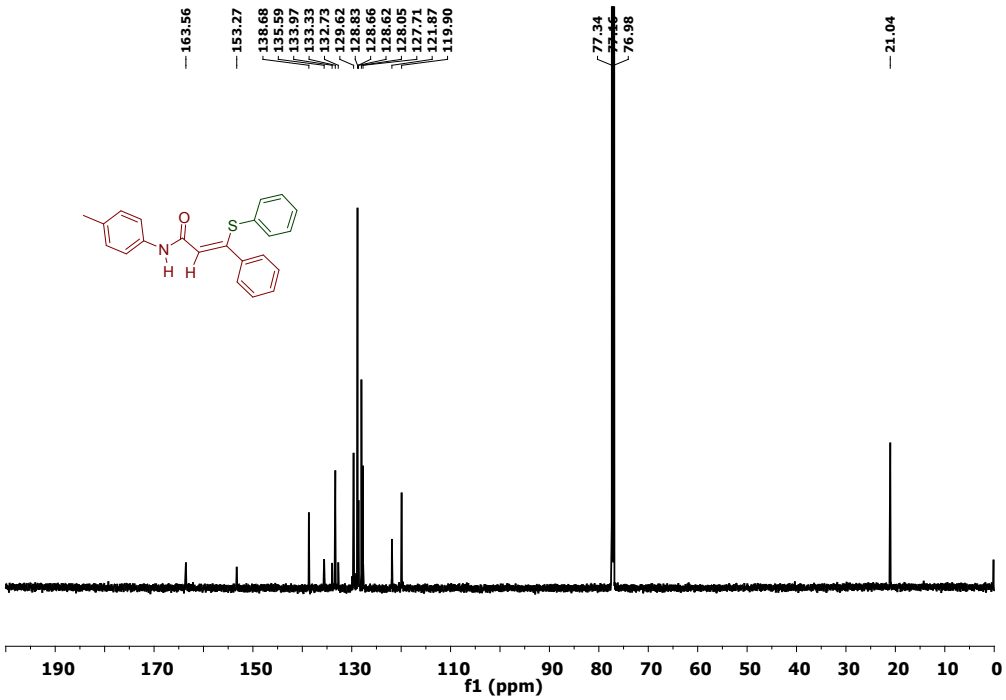


Fig. S123. ^{13}C NMR spectrum of (Z)-3-phenyl-3-(phenylthio)-N-(p-tolyl)acrylamide (**3ra**)

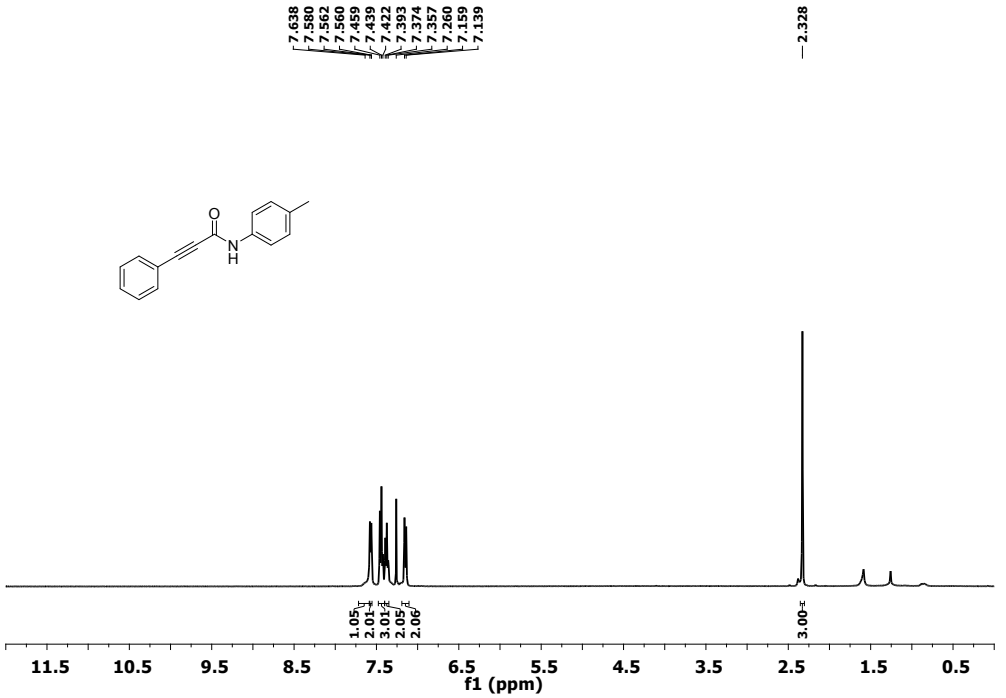
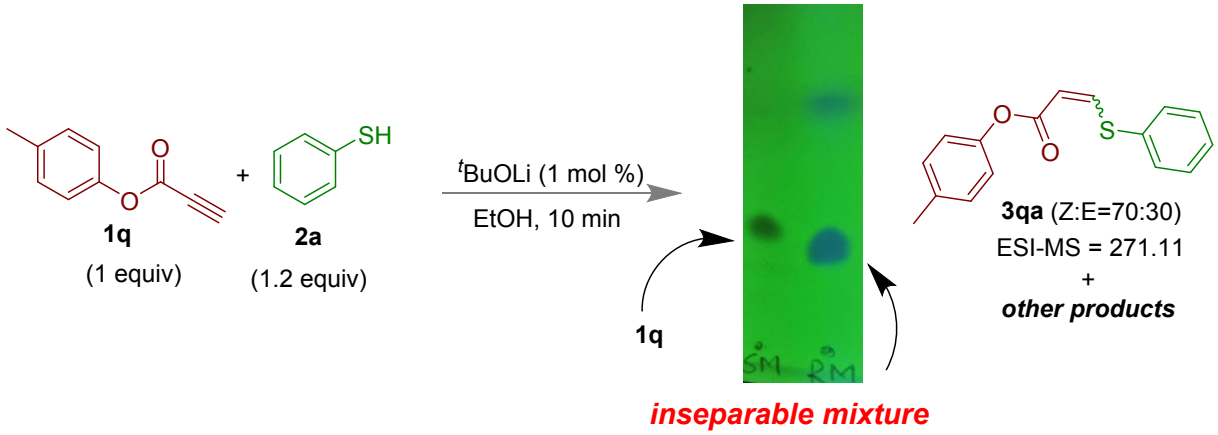


Fig. S124. ^{1}H NMR spectrum of 3-phenyl-N-(p-tolyl)propiolamide **1r**

Control experiment



Scheme S2. Reaction of p-tolyl propiolate **1q** and thiophenol **2a**

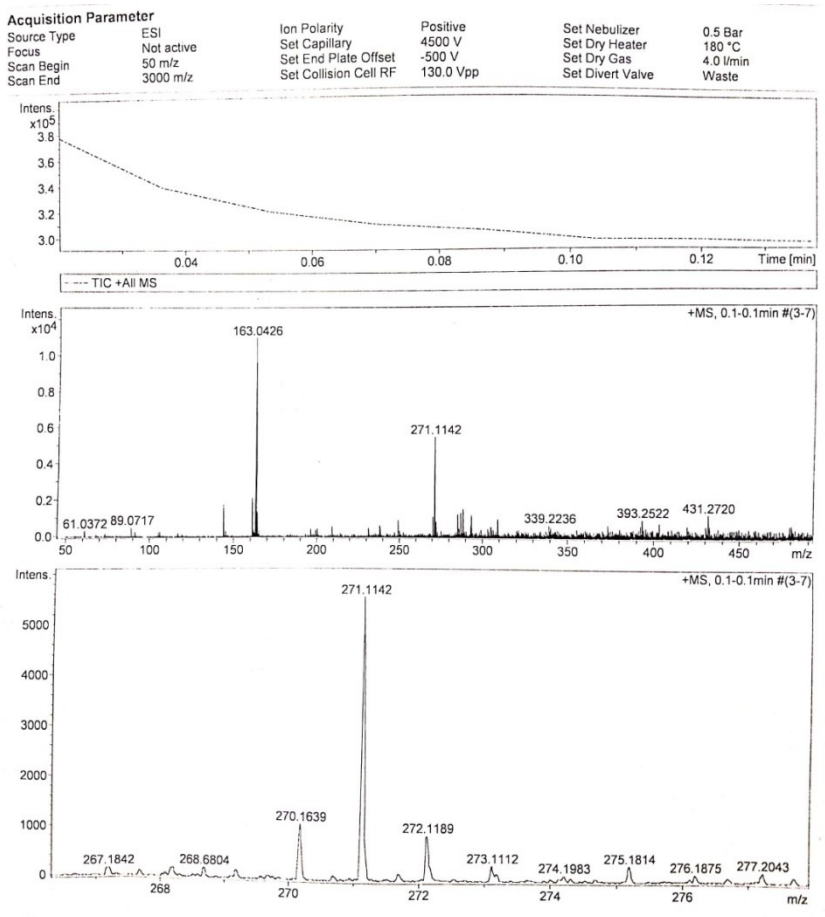


Fig. S125. ESI-MS spectrum of inseparable reaction mixture of reaction of **1q** and **2a**.

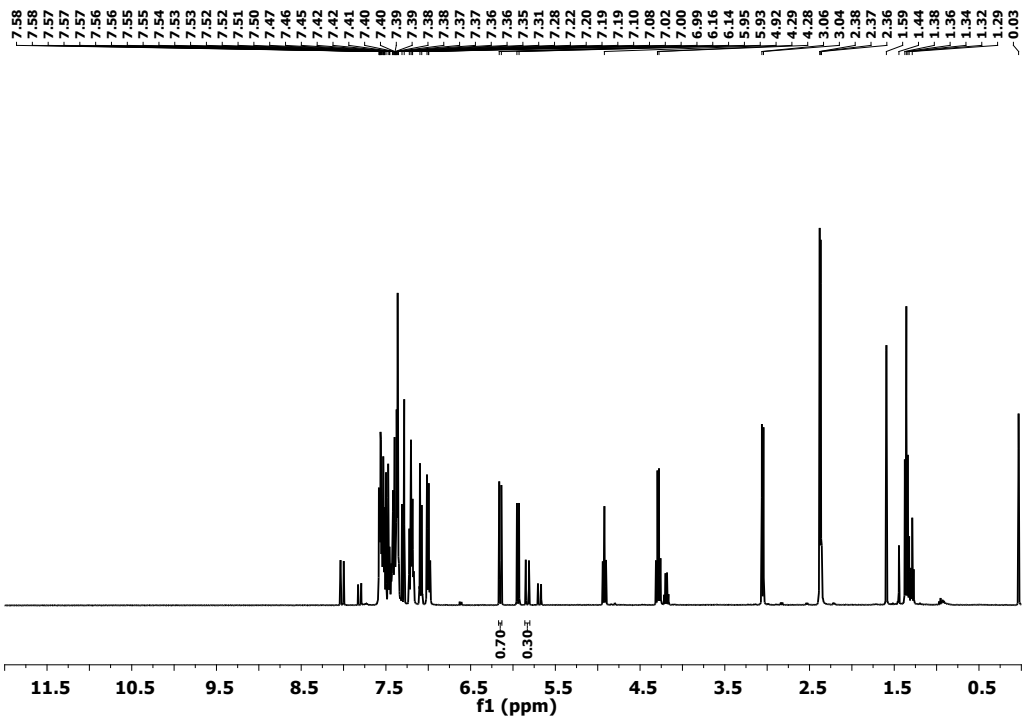
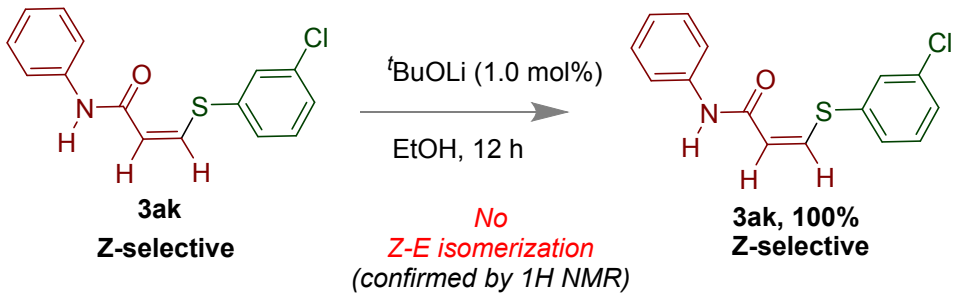


Fig.126. ^{1}H NMR spectrum of inseparable mixture from reaction of **1q** and **2a**.



Scheme S3. Reaction of **3ak** using ^{t}BuOLi and EtOH.

Crude ^{1}H NMR of Reaction Mixture:

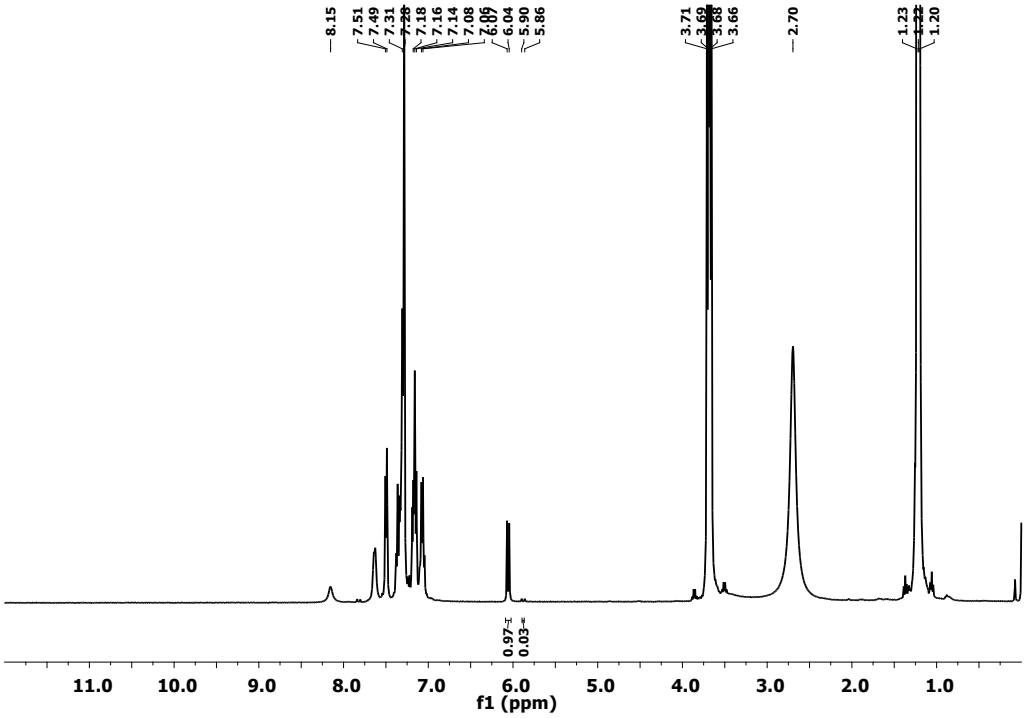


Fig. S127. ^{1}H NMR spectrum of crude N-phenyl-3-(phenylthio) acrylamide (**3aa**)

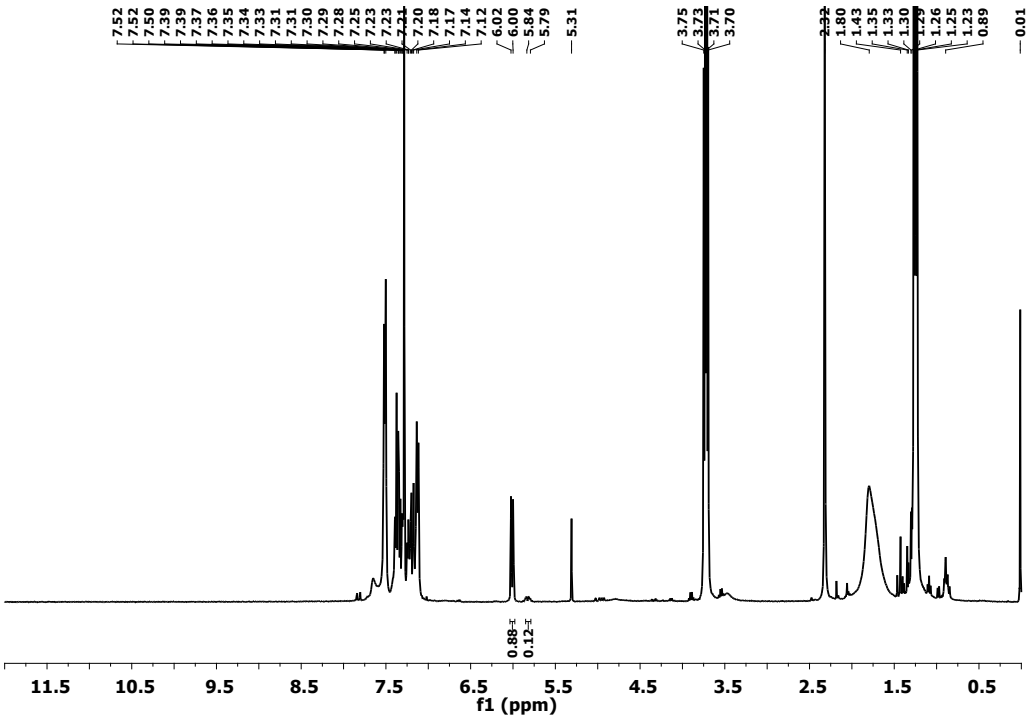


Fig. S128. ^{1}H NMR spectrum of crude 3-(phenylthio)-N-(p-tolyl)acrylamide (**3ba**)

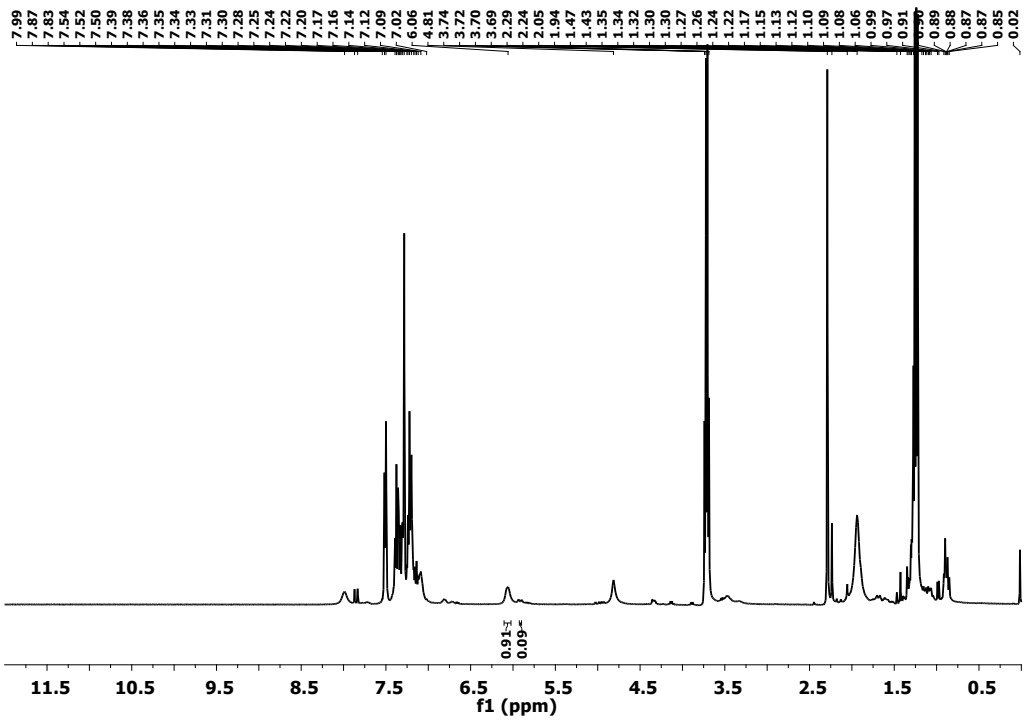


Fig. S129. [1]H NMR spectrum of crude 3-(phenylthio)-N-(o-tolyl)acrylamide (**3ca**)

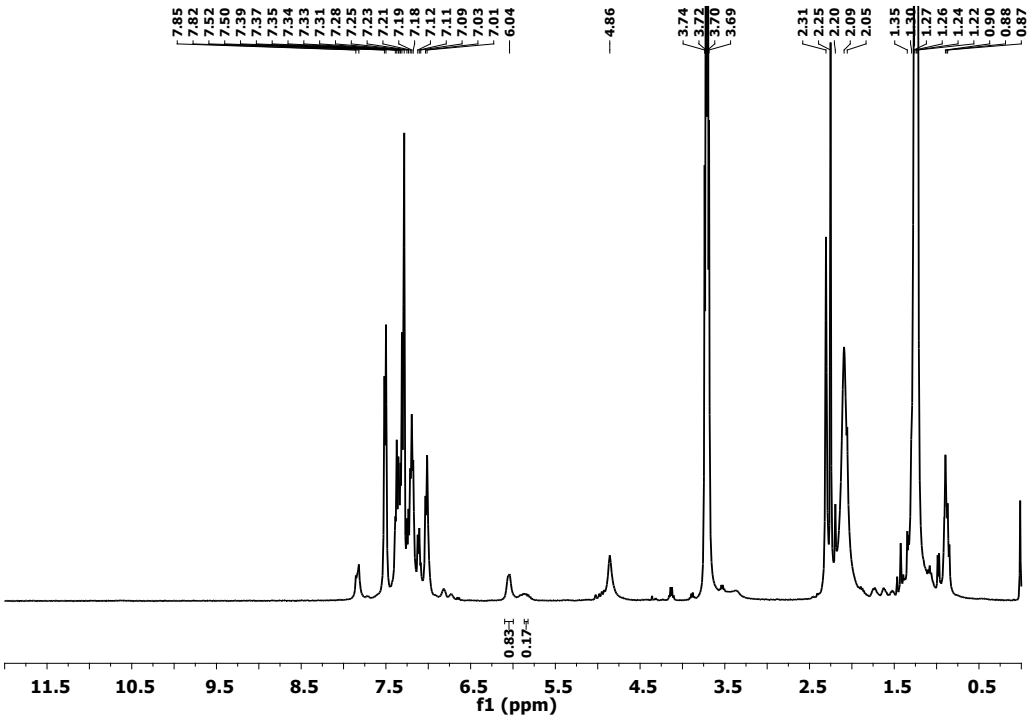


Fig. S130. [1]H NMR spectrum of crude N-(2,4-dimethylphenyl)-3-(phenylthio)acrylamide (**3da**)

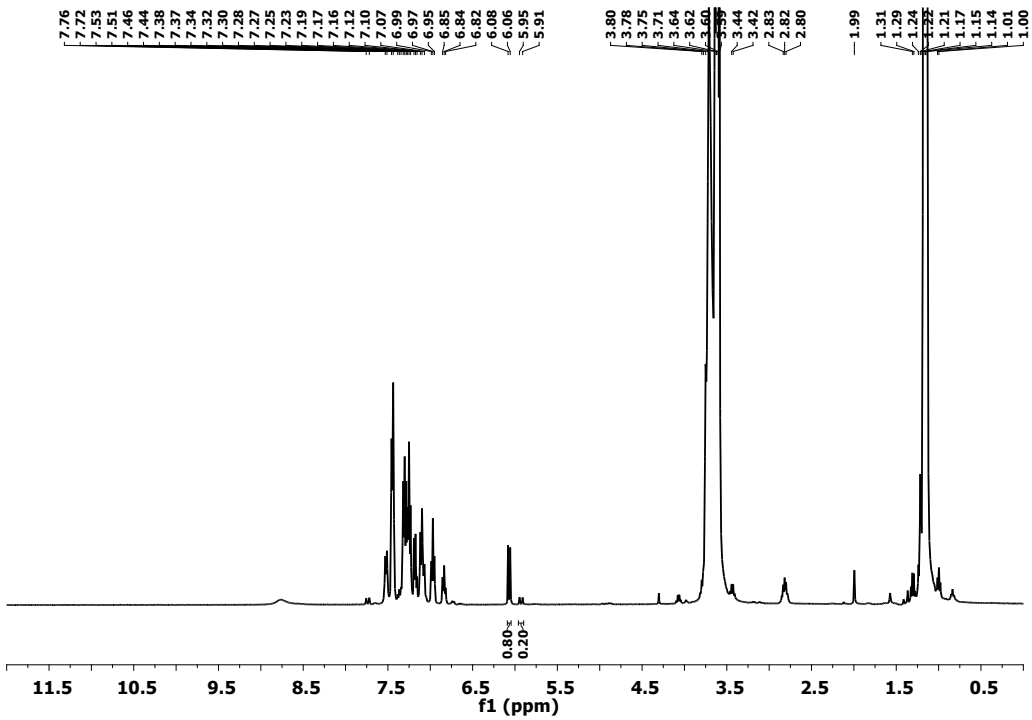


Fig. S131. ^{1}H NMR spectrum of crude N-(4-isopropylphenyl)-3-(phenylthio)acrylamide (**3ea**)

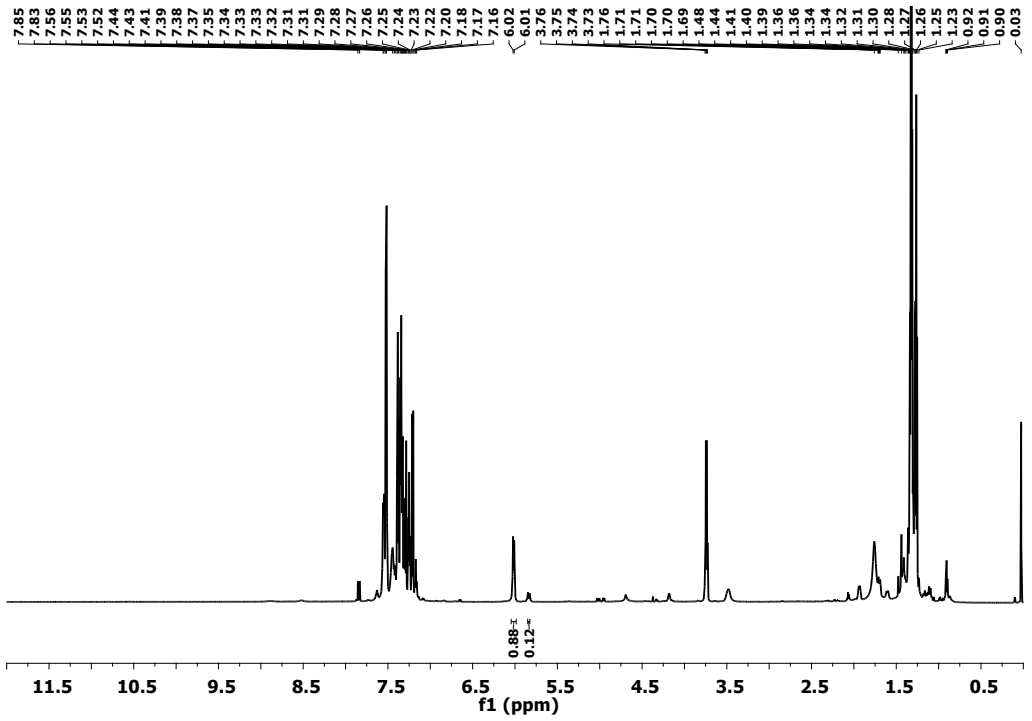


Fig. S132. ^{1}H NMR spectrum of crude N-(4-(tert-butyl)phenyl)-3-(phenylthio)acrylamide (**3fa**)

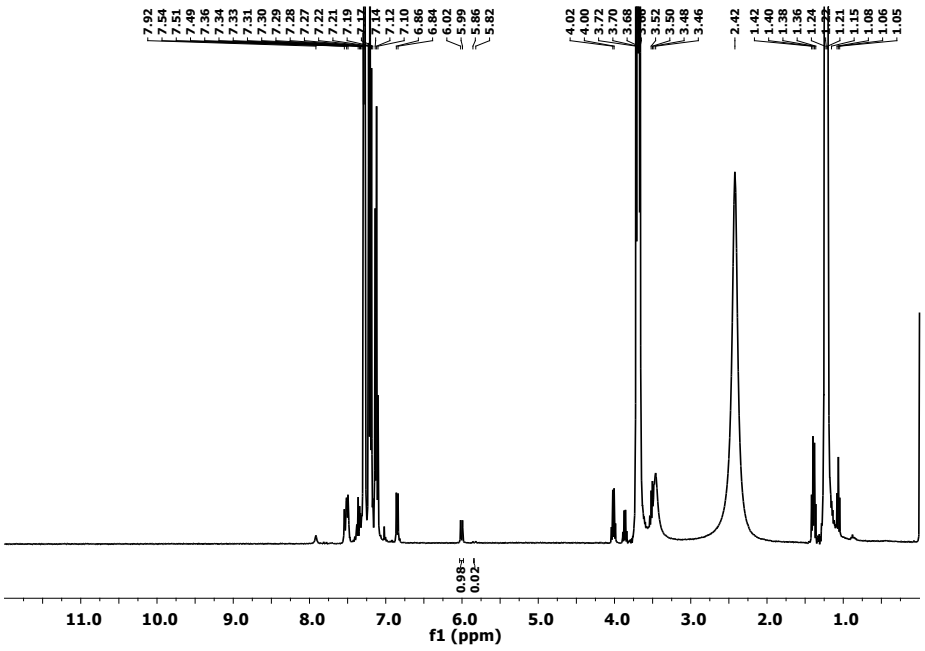


Fig. S133. ^{1}H NMR spectrum of crude N-(4-ethoxyphenyl)-3-(phenylthio)acrylamide (**3ga**)

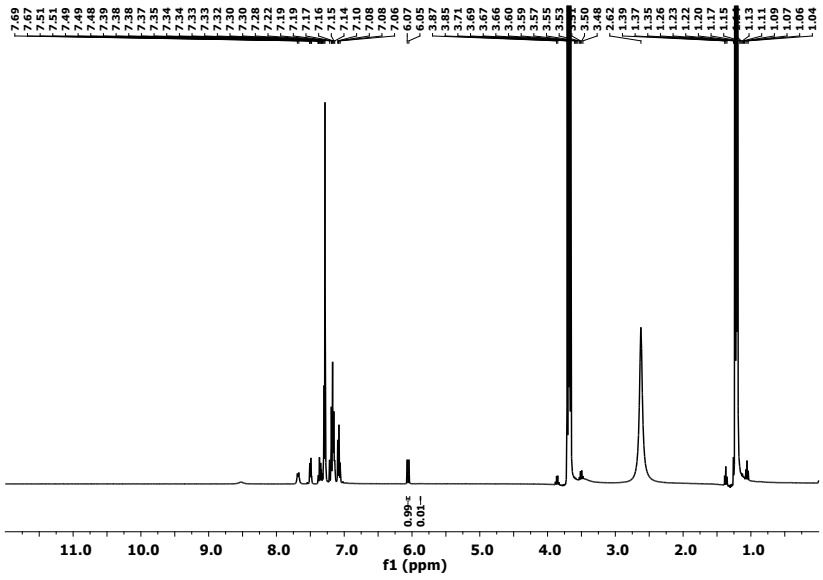


Fig. S134. ^{1}H NMR spectrum of crude 3-(phenylthio)-N-(4-(trifluoromethoxy)phenyl)acrylamide (**3ha**)

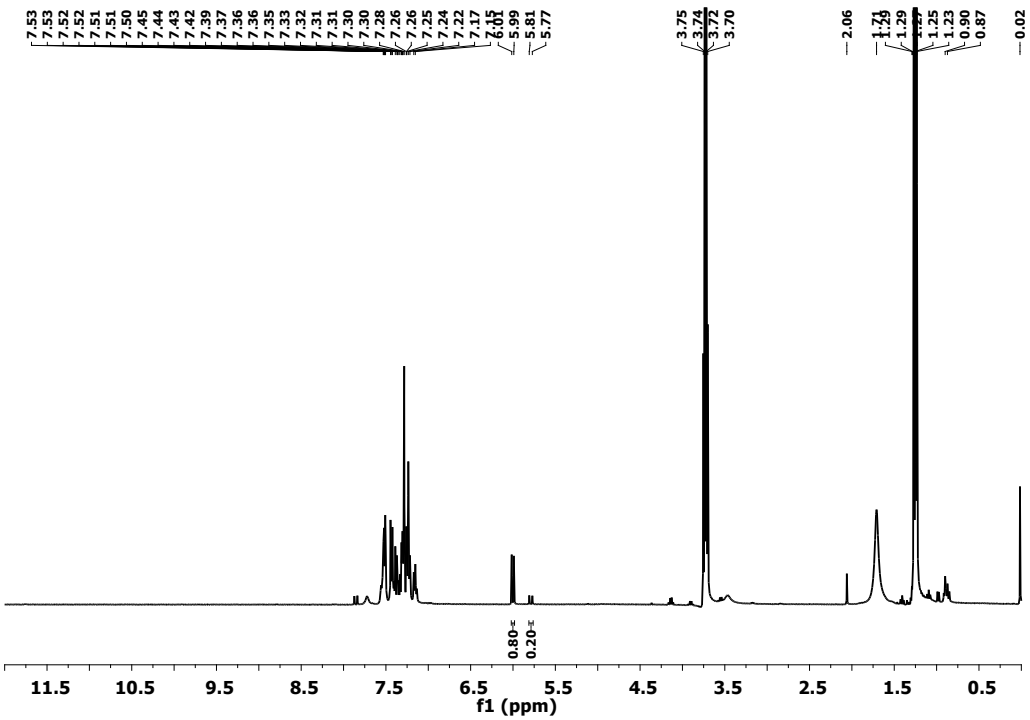


Fig. S135. [1]H NMR spectrum of crude N-(4-fluorophenyl)-3-(phenylthio)acrylamide (**3ia**)

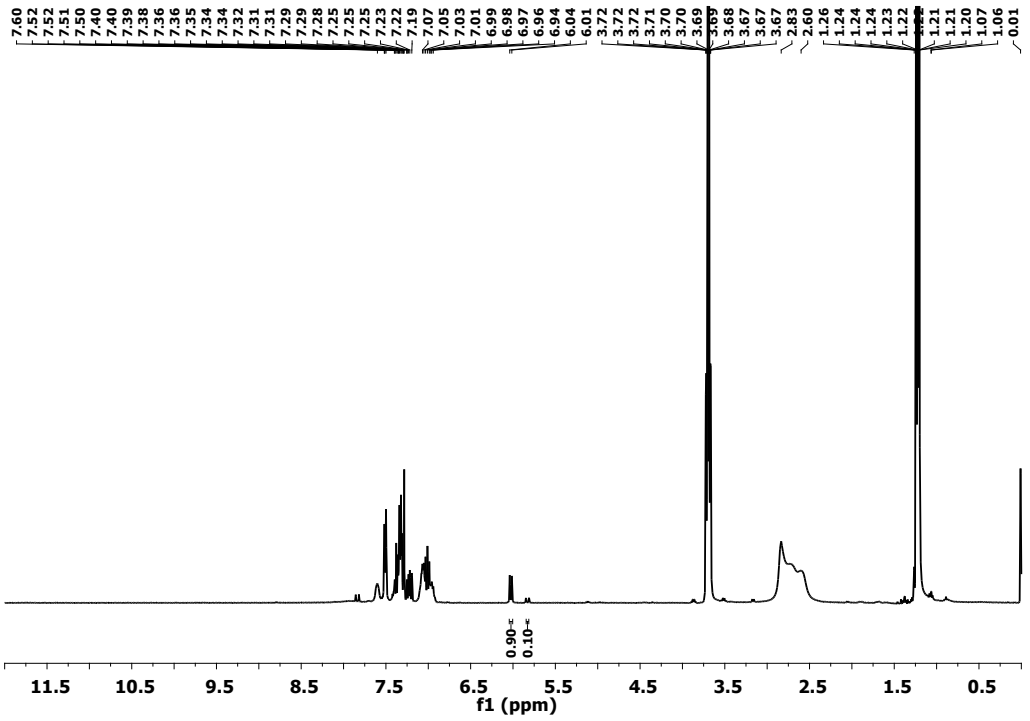


Fig. S136. [1]H NMR spectrum of crude N-(4-bromophenyl)-3-(phenylthio)acrylamide (**3ja**)

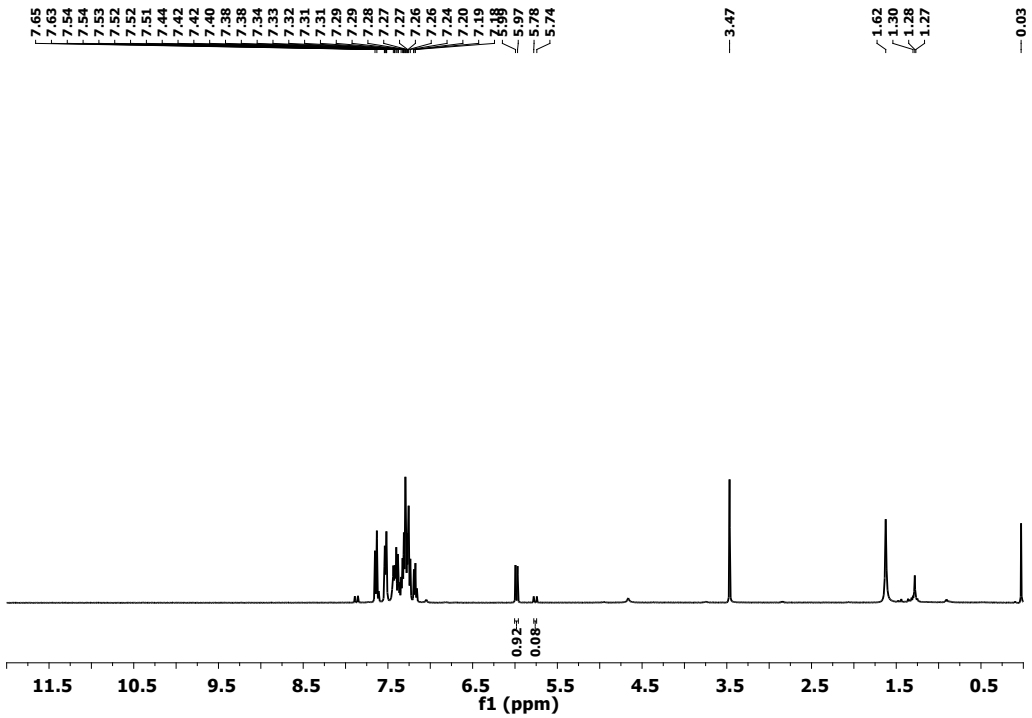


Fig. S137. ^{1}H NMR spectrum of crude N-(4-iodophenyl)-3-(phenylthio)acrylamide (**3ka**)

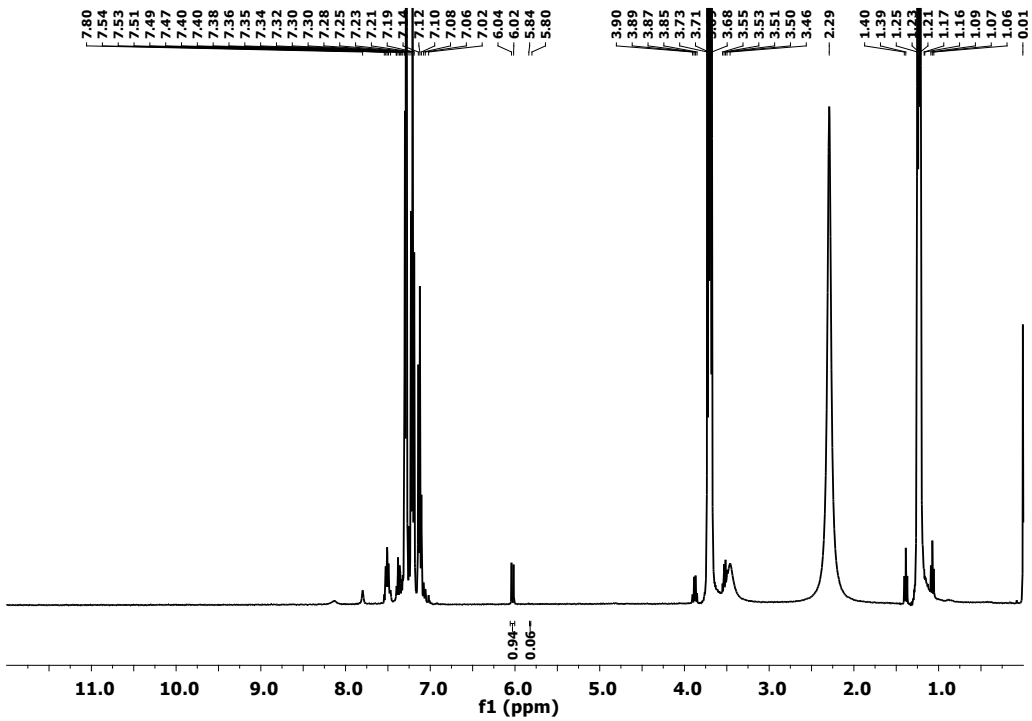


Fig. S138. ^{1}H NMR spectrum of crude N-(3-chlorophenyl)-3-(phenylthio)acrylamide (**3la**)

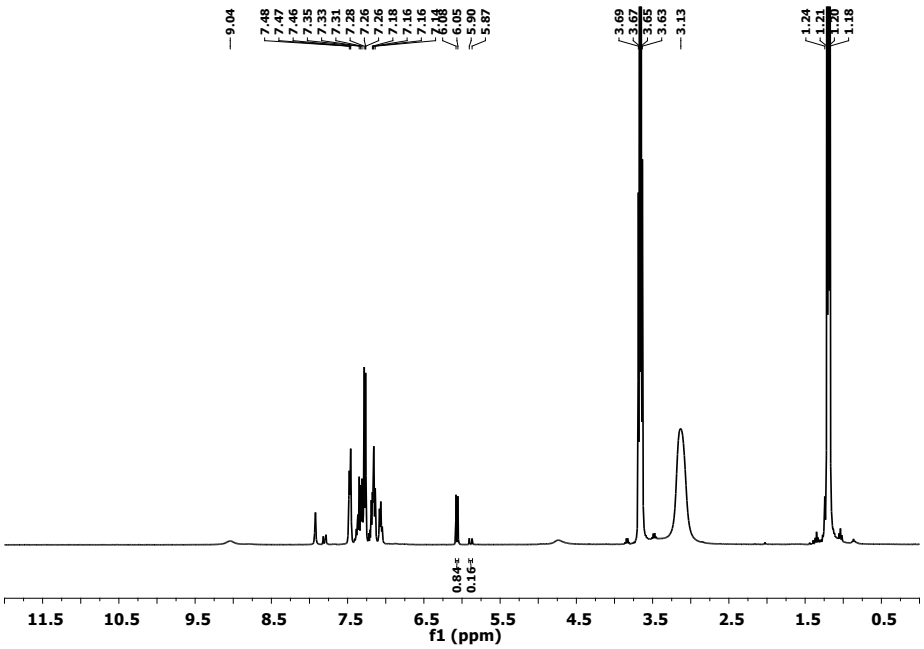


Fig. S139. [1]H NMR spectrum of crude N-(3,4-dichlorophenyl)-3-(phenylthio)acrylamide (**3ma**)

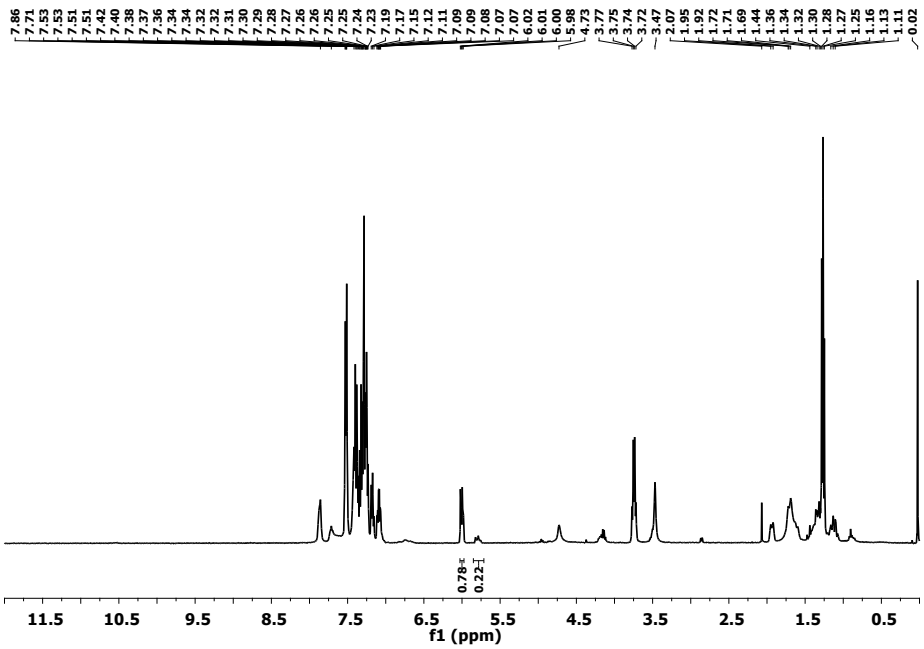


Fig. S140. [1]H NMR spectrum of crude N-(3-chloro-4-fluorophenyl)-3-(phenylthio)acrylamide(**3na**)

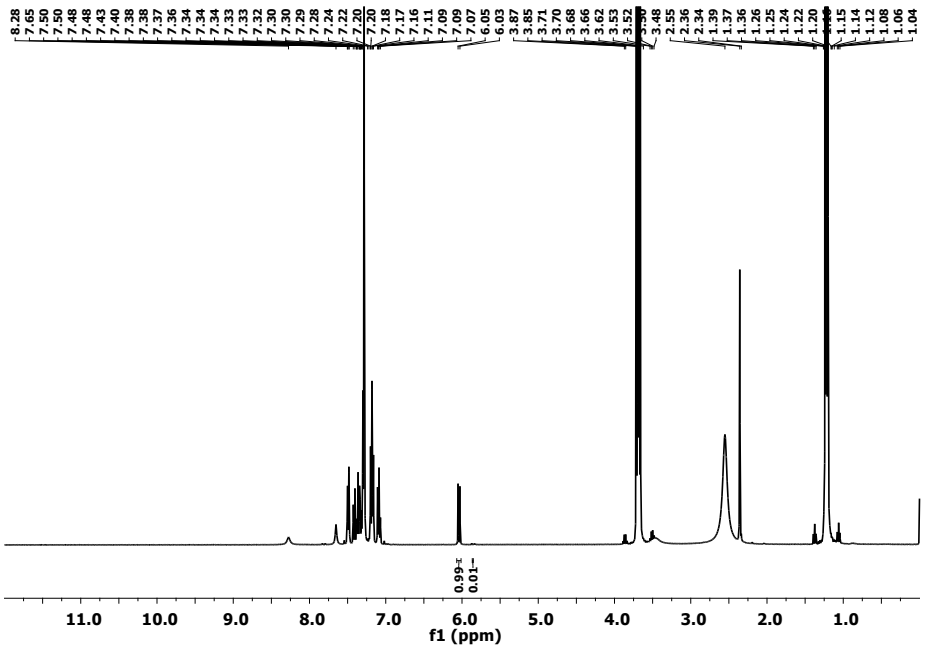


Fig. S141. [1]H NMR spectrum of crude N-(4-bromo-2-methylphenyl)-3-(phenylthio)acrylamide (**3oa**)

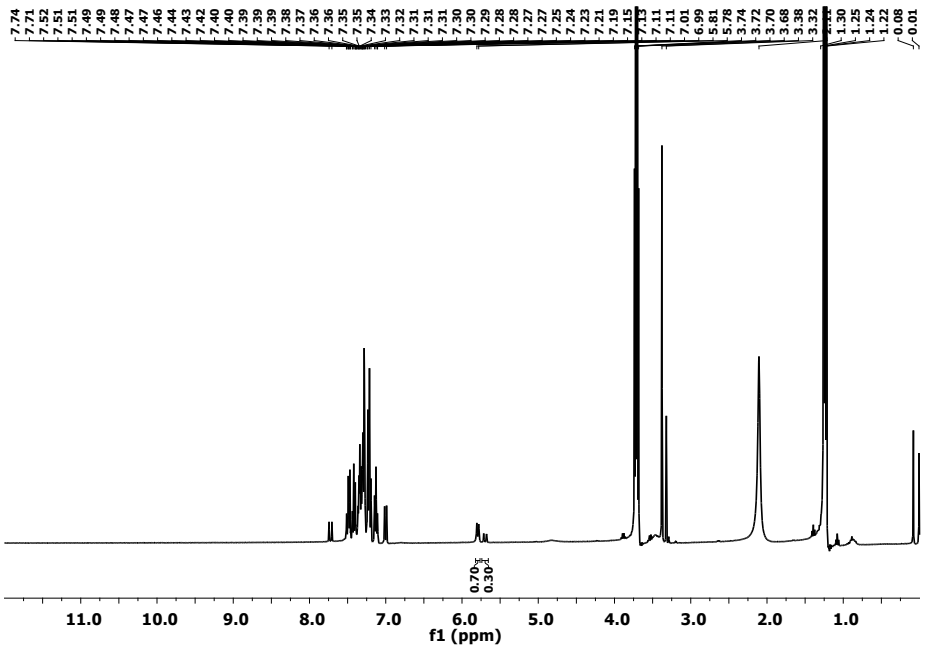


Fig. S142. [1]H NMR spectrum of crude N-methyl-N-phenyl-3-(phenylthio)acrylamide (**3pa**)

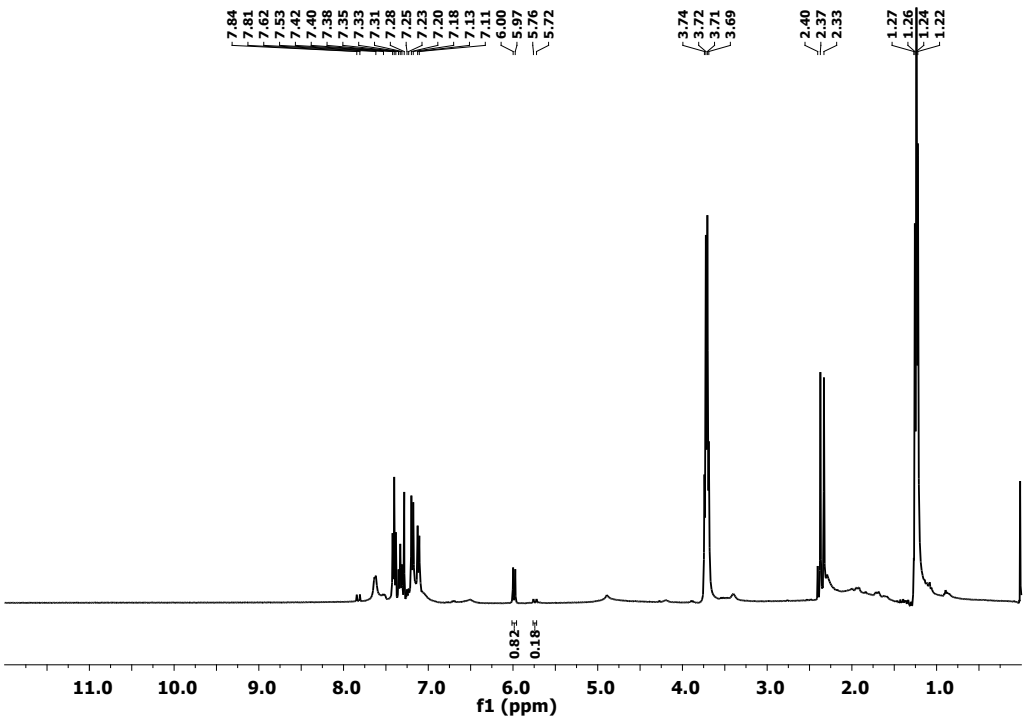


Fig. S143. [1]H NMR spectrum of crude N-phenyl-3-(p-tolylthio)acrylamide (**3ab**)

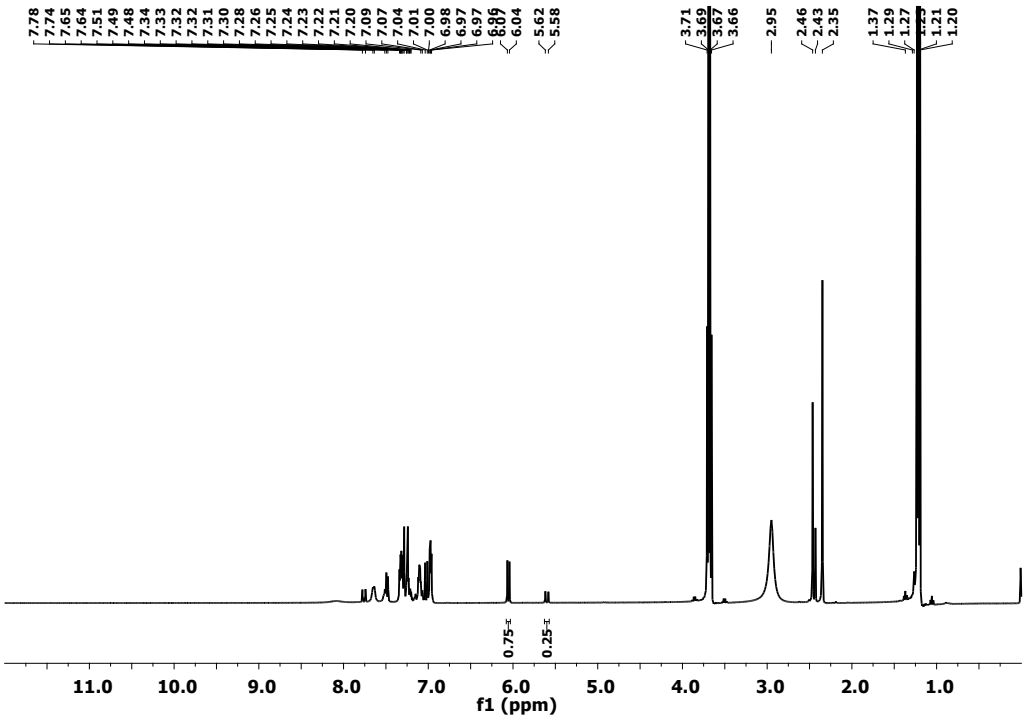


Fig. S144. [1]H NMR spectrum of crude N-phenyl-3-(o-tolylthio)acrylamide (**3ac**)

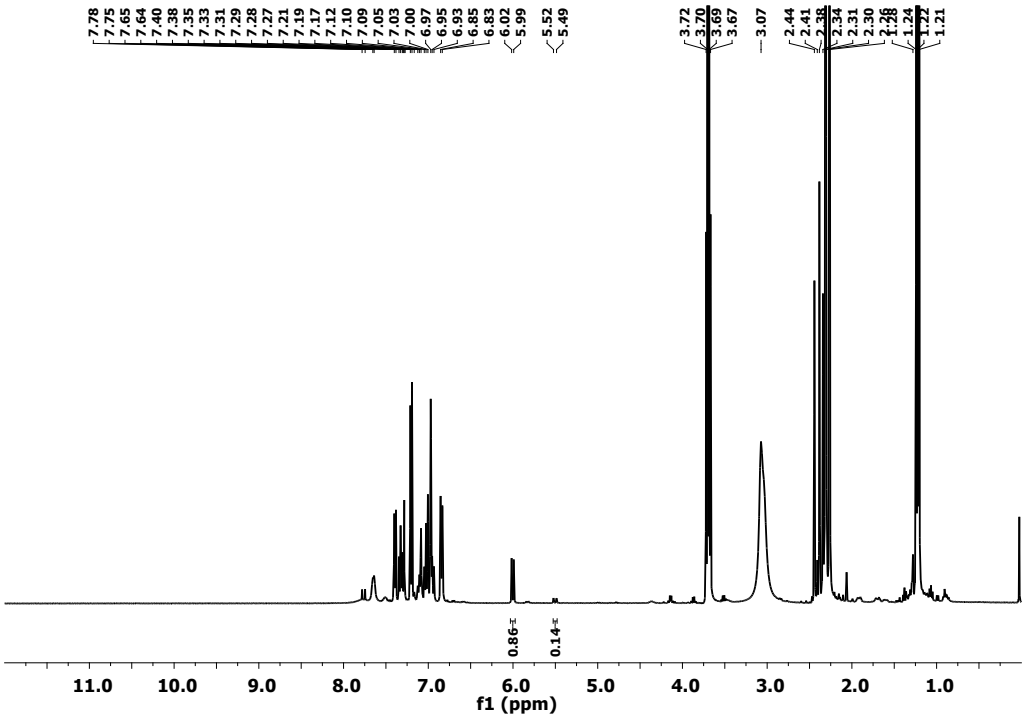


Fig. S145. [1]H NMR spectrum of crude 3-((2,4-dimethylphenyl)thio)-N-phenylacrylamide (**3ad**)

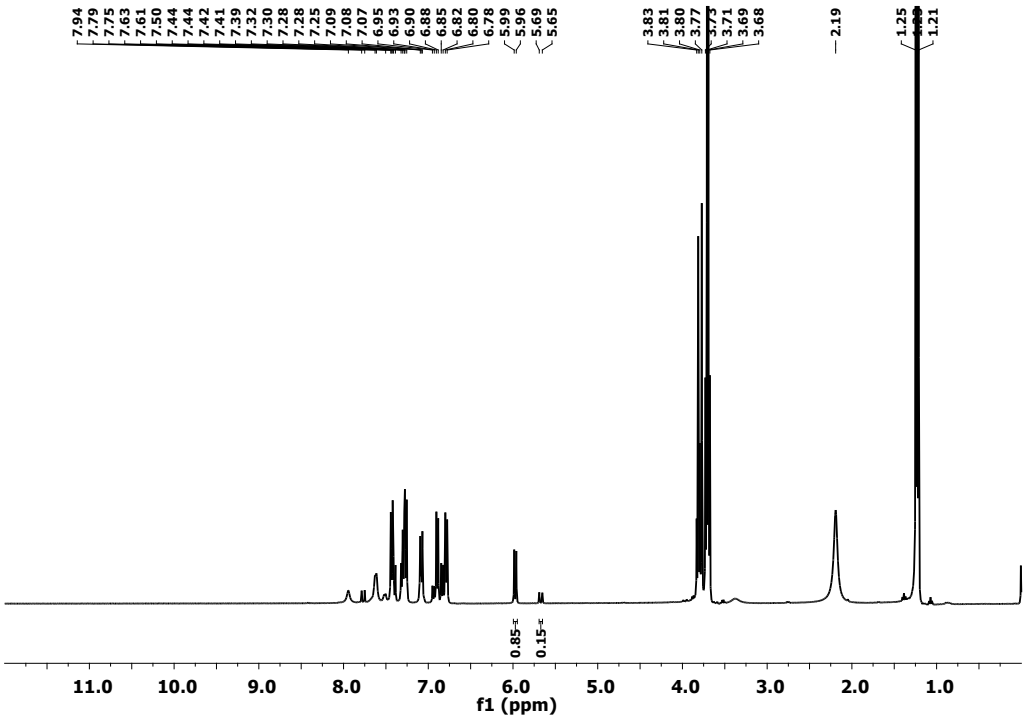


Fig. S146. [1]H NMR spectrum of crude 3-((4-methoxyphenyl)thio)-N-phenylacrylamide (**3ae**)

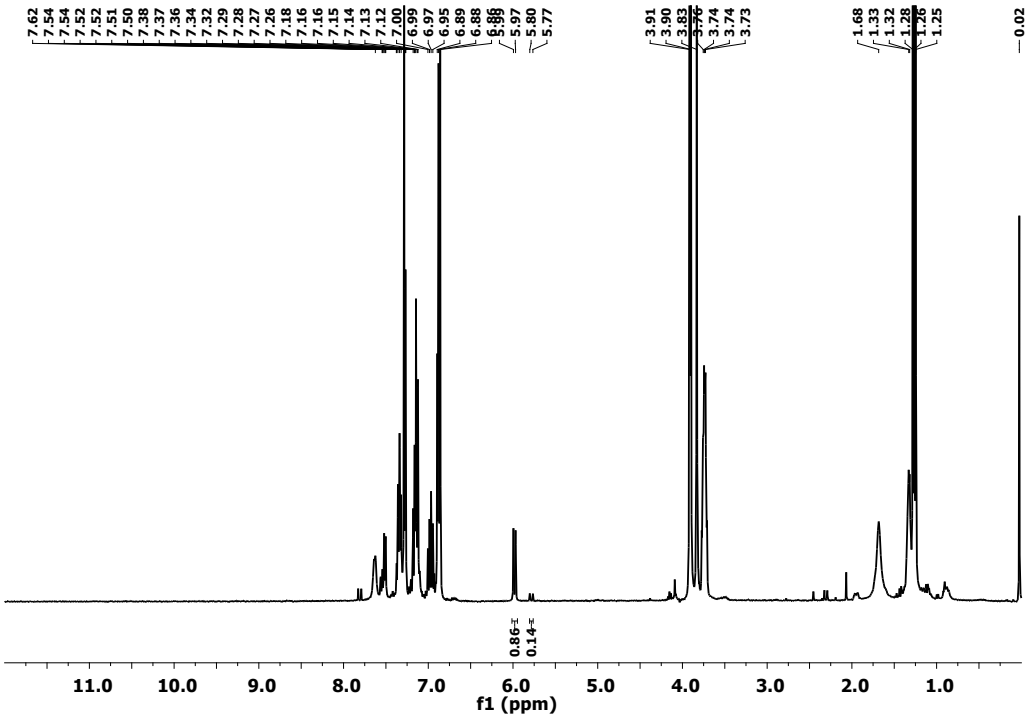


Fig. S147. [1]H NMR spectrum of crude 3-((2-methoxyphenyl)thio)-N-phenylacrylamide (**3af**)

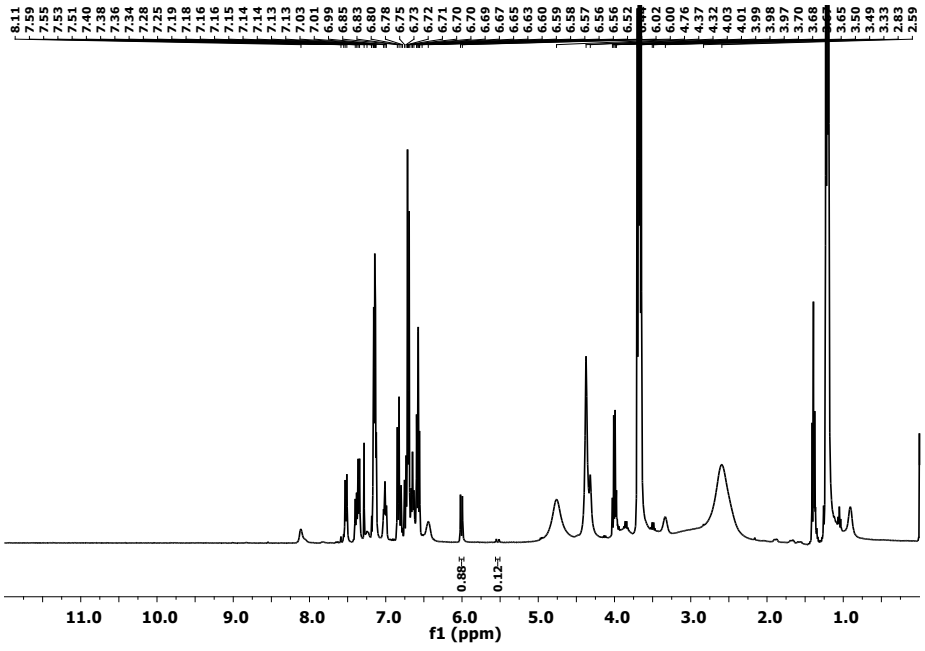


Fig. S148. [1]H NMR spectrum of crude 3-((2-aminophenyl)thio)-N-(4-ethoxyphenyl)acrylamide (**3gg**)

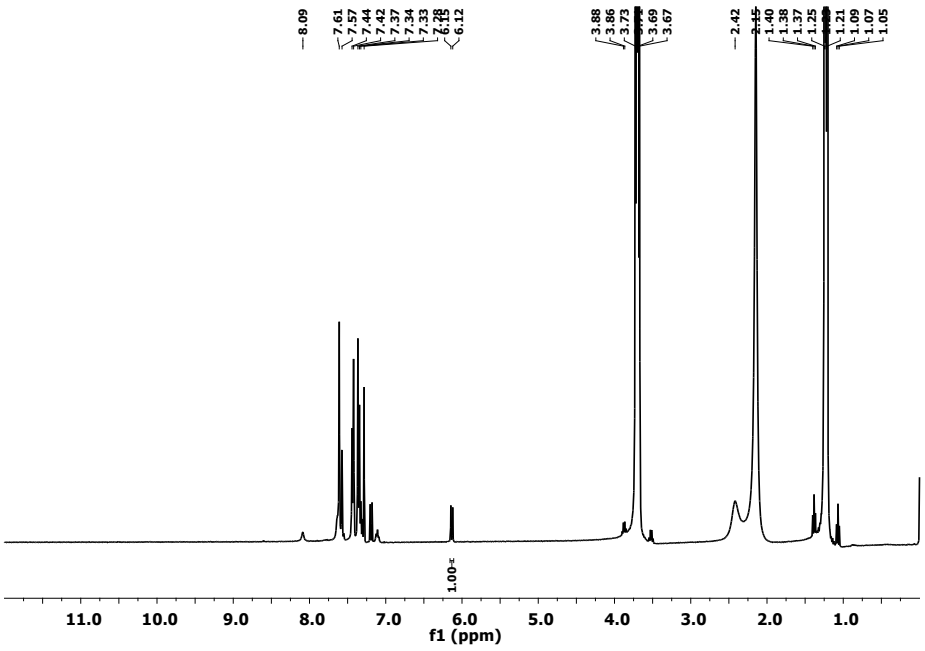


Fig. S149. ^{1}H NMR spectrum of crude N-phenyl-3-((4-(trifluoromethyl)phenyl)thio)acrylamide (**3ah**)

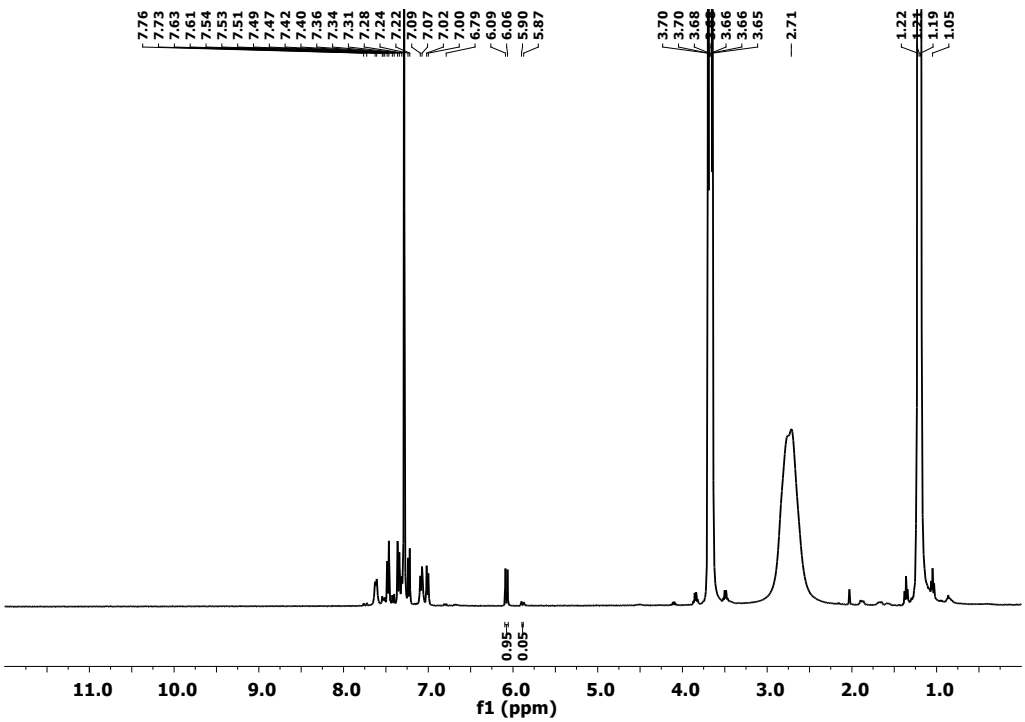


Fig. S150. ^{1}H NMR spectrum of crude 3-((4-bromophenyl)thio)-N-phenylacrylamide (**3ai**)

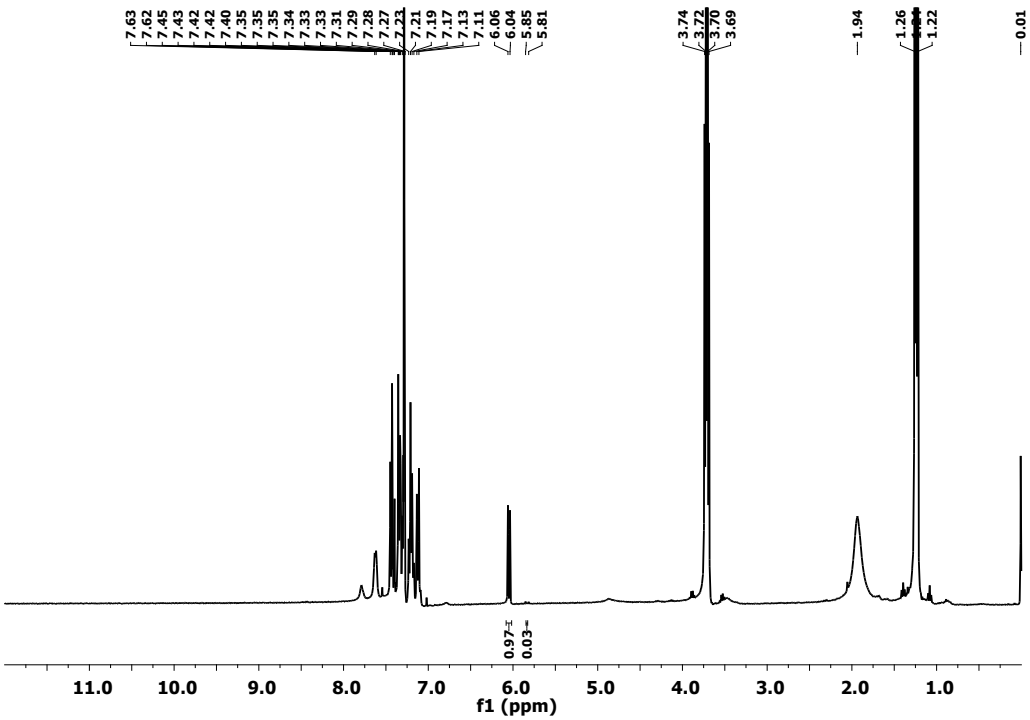


Fig. S151. [1]H NMR spectrum of crude 3-((4-chlorophenyl)thio)-N-phenylacrylamide (**3aj**)

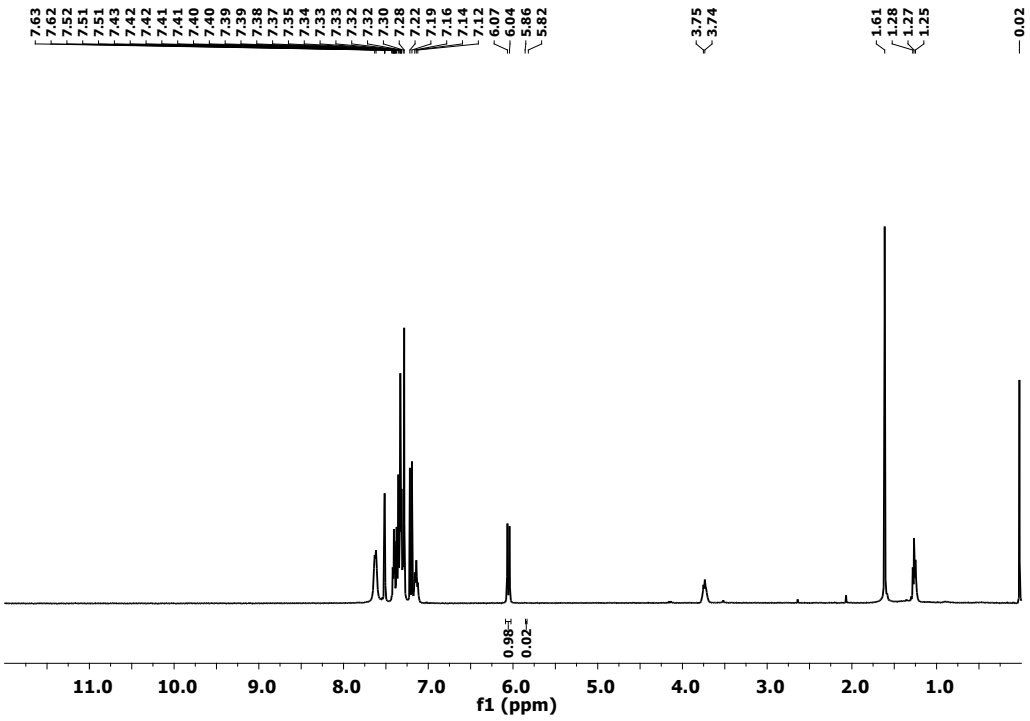


Fig. S152. [1]H NMR spectrum of crude 3-((3-chlorophenyl)thio)-N-phenylacrylamide (**3ak**)

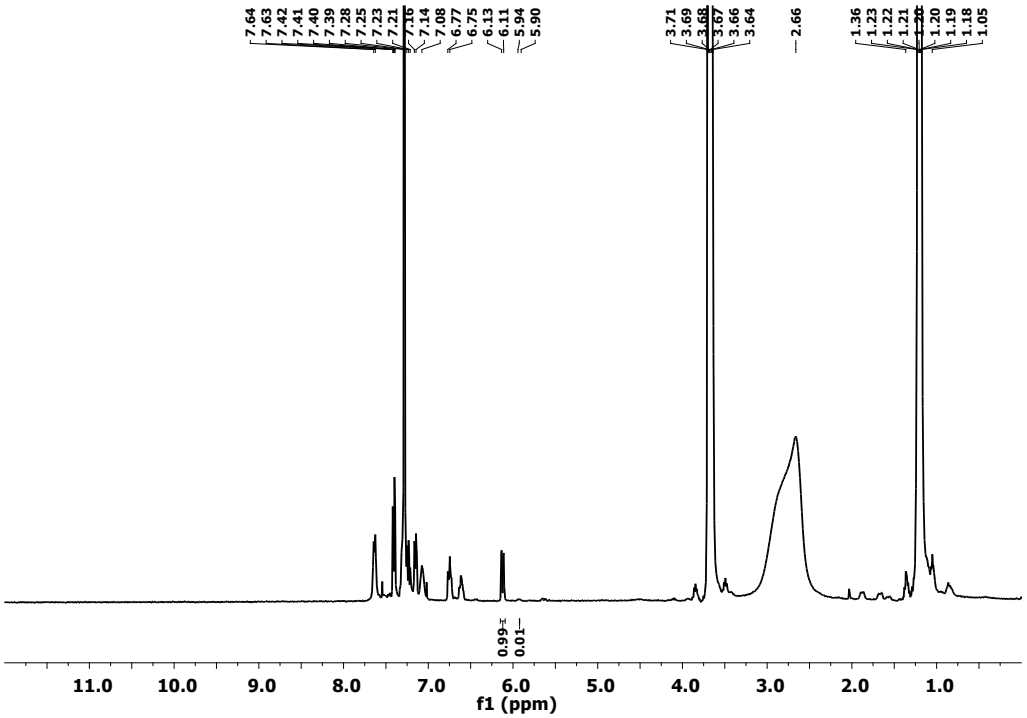


Fig. S153. [1]H NMR spectrum of crude 3-((2,6-dichlorophenyl)thio)-N-phenylacrylamide (**3al**)

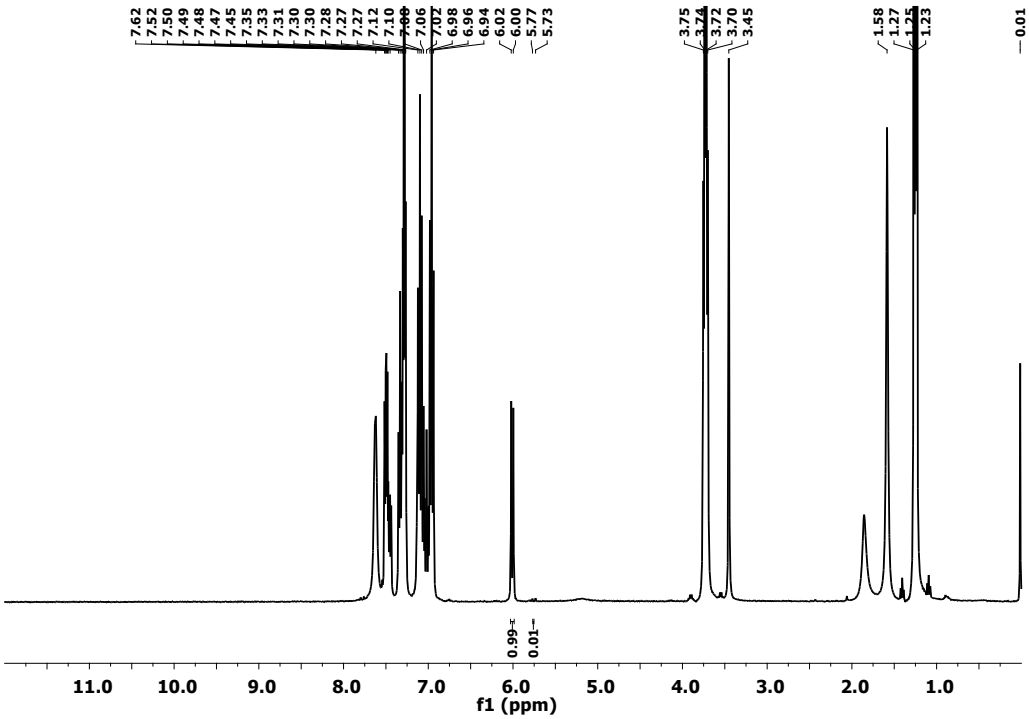


Fig. S154. [1]H NMR spectrum of crude 3-((4-fluorophenyl)thio)-N-phenylacrylamide (**3am**)

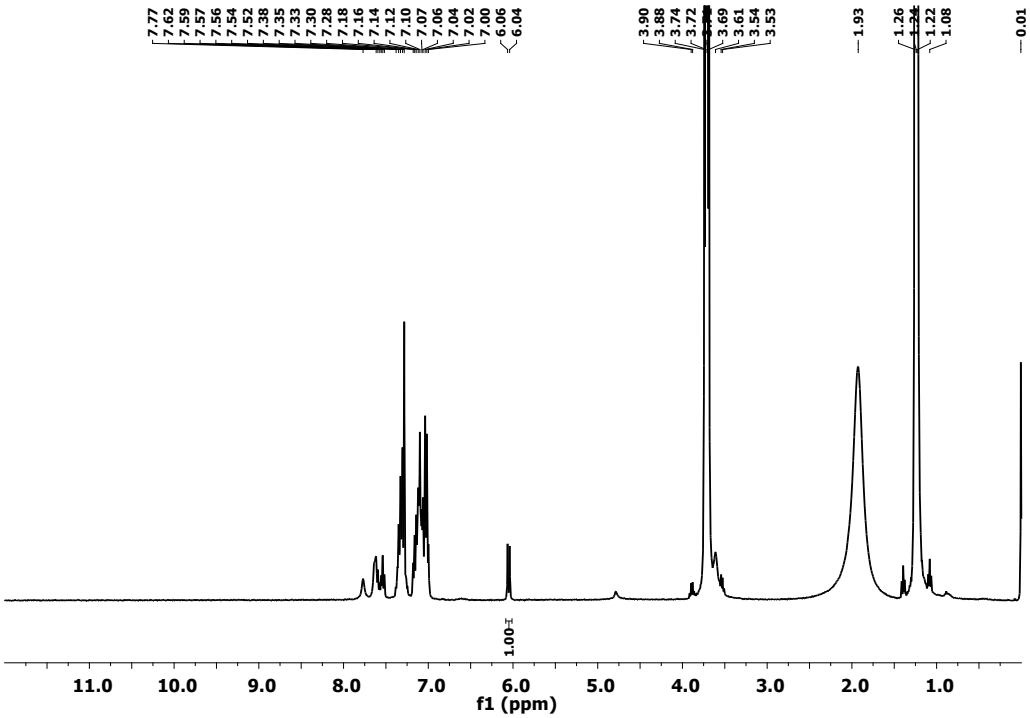


Fig. S155. [1]H NMR spectrum of crude 3-((2-fluorophenyl)thio)-N-phenylacrylamide (**3an**)

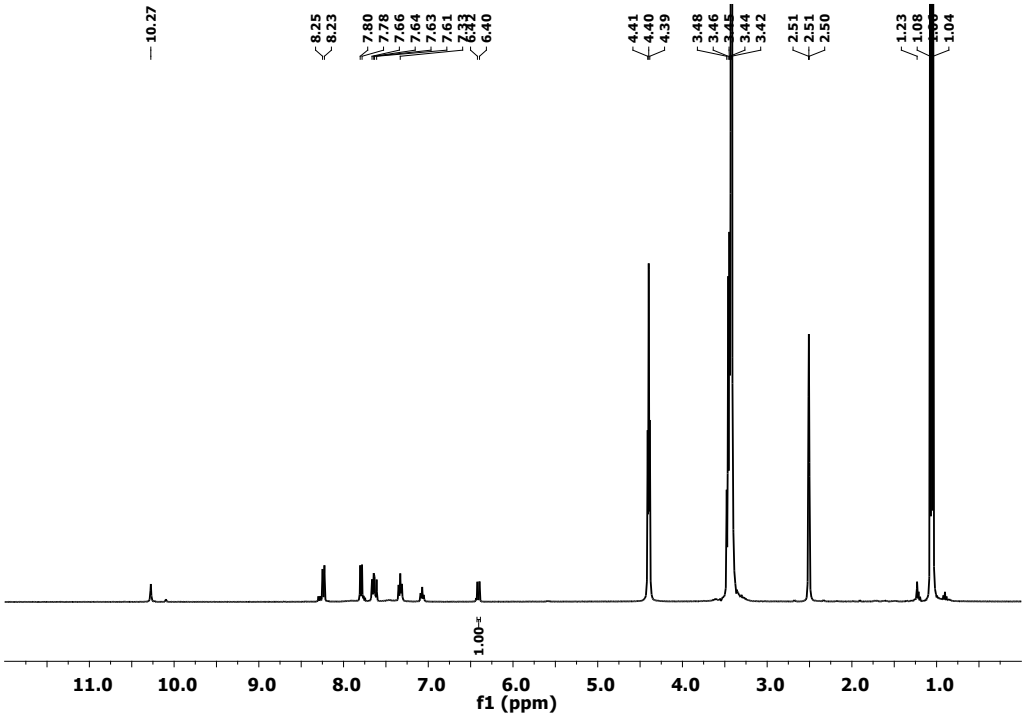


Fig. S156. [1]H NMR spectrum of crude 3-((4-nitrophenyl)thio)-N-phenylacrylamide (**3ao**)

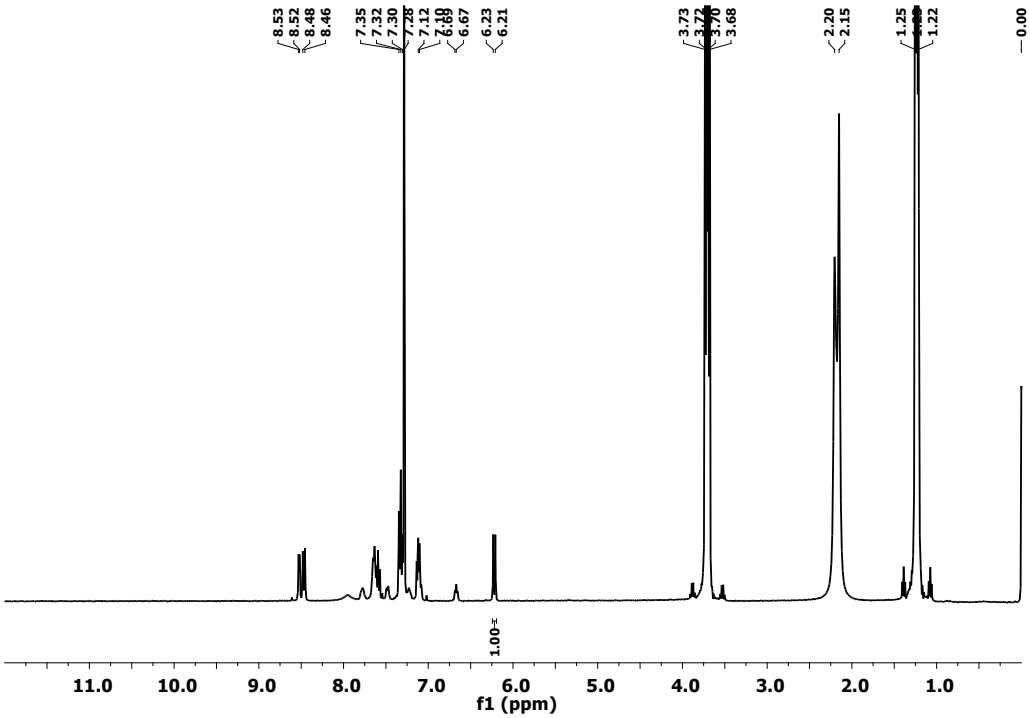


Fig. S157. [1]H NMR spectrum of crude N-phenyl-3-(pyridin-2-ylthio)acrylamide (**3ap**)

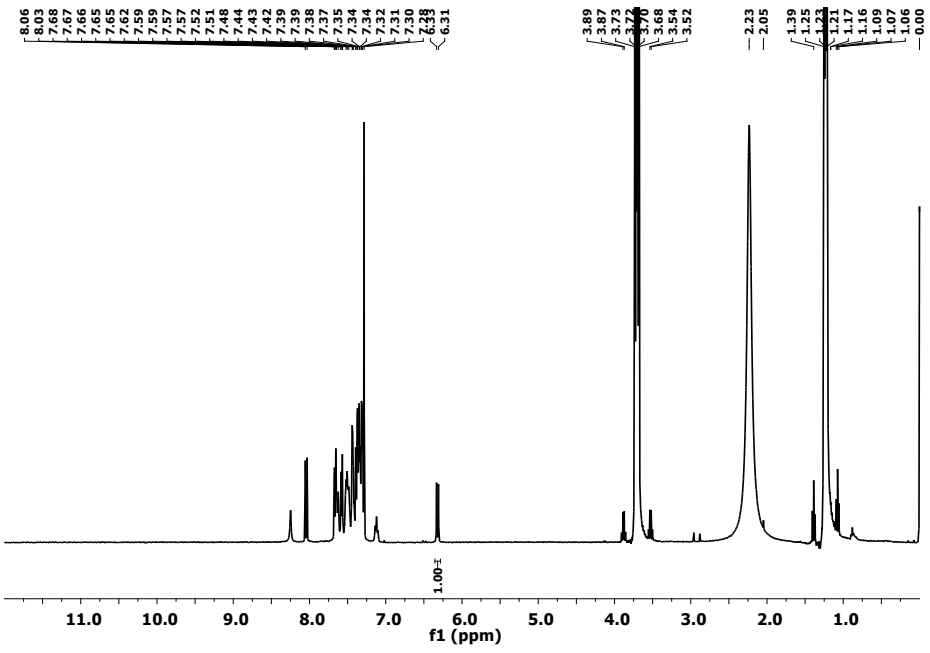


Fig. S158. [1]H NMR spectrum of crude 3-((2,4-diphenyloxazol-5-yl)thio)-N-phenylacrylamide (**3aq**)

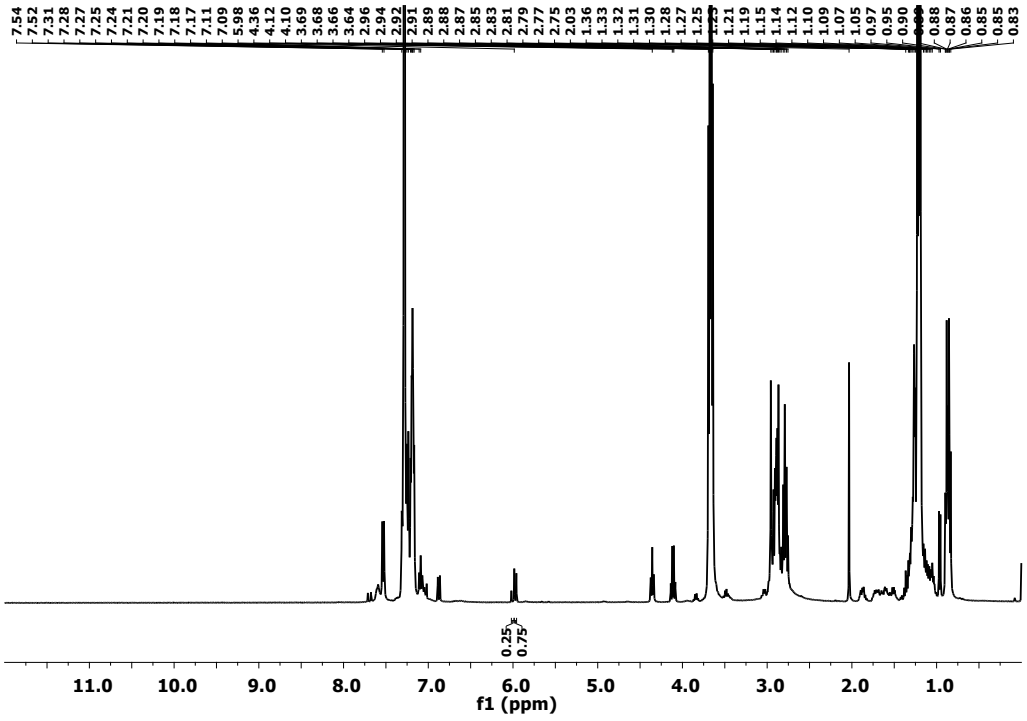


Fig. S159. ^{1}H NMR spectrum of crude 3-(phenethylthio)-N-phenylacrylamide (**3at**)

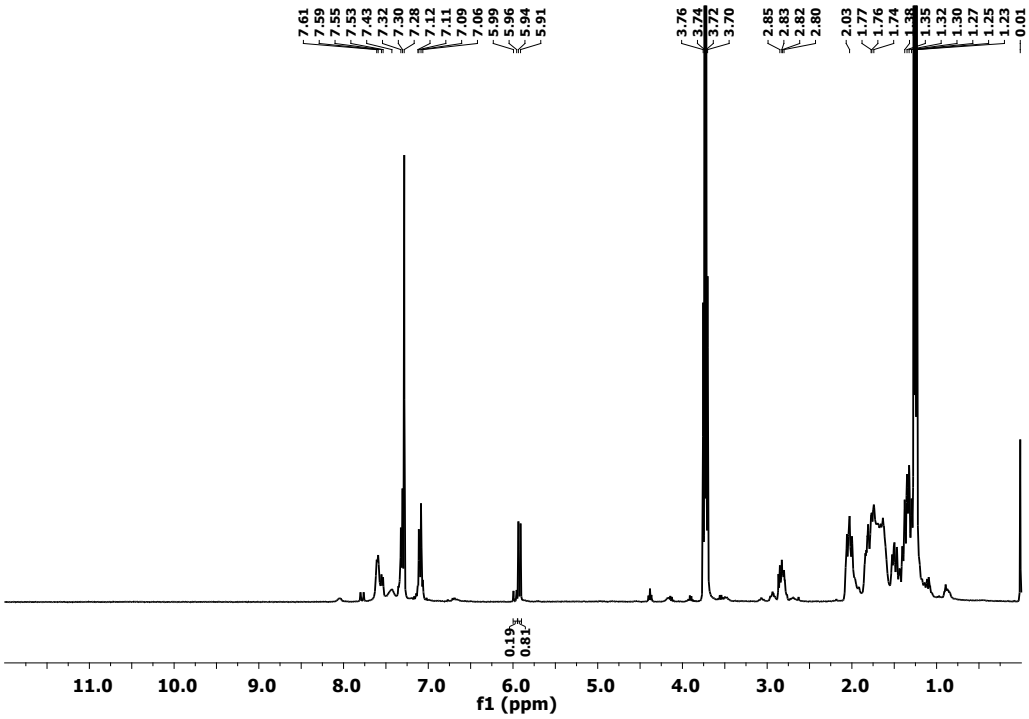


Fig. S160. ^{1}H NMR spectrum of crude 3-(cyclohexylthio)-N-phenylacrylamide (**3au**)

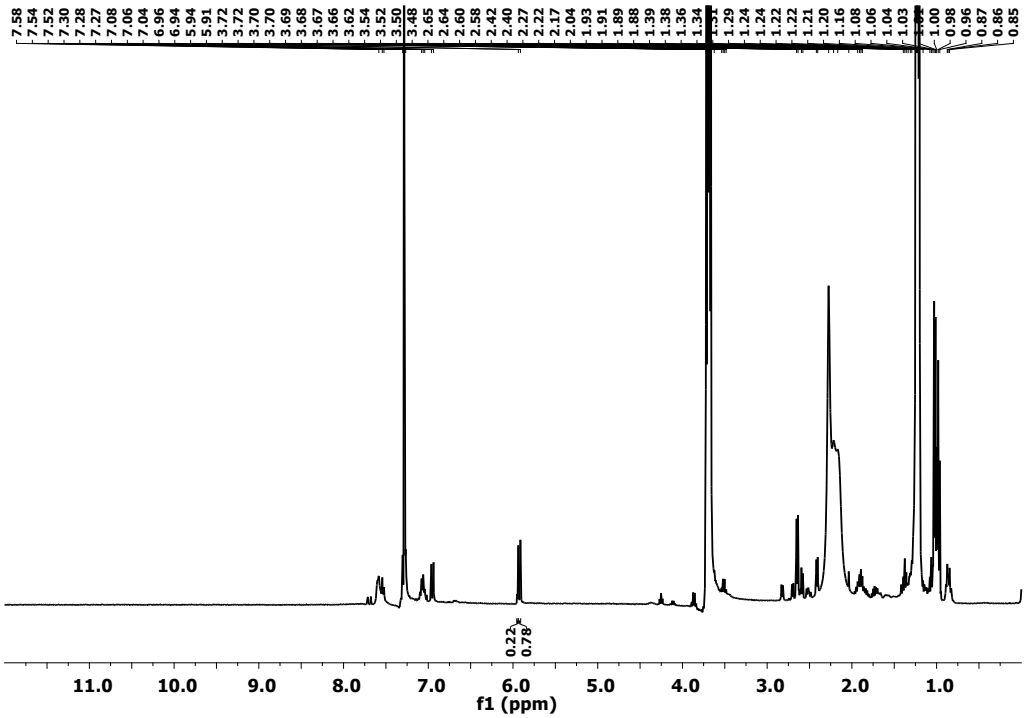


Fig. S161. [1]H NMR spectrum of crude 3-(isobutylthio)-N-phenylacrylamide (**3av**)

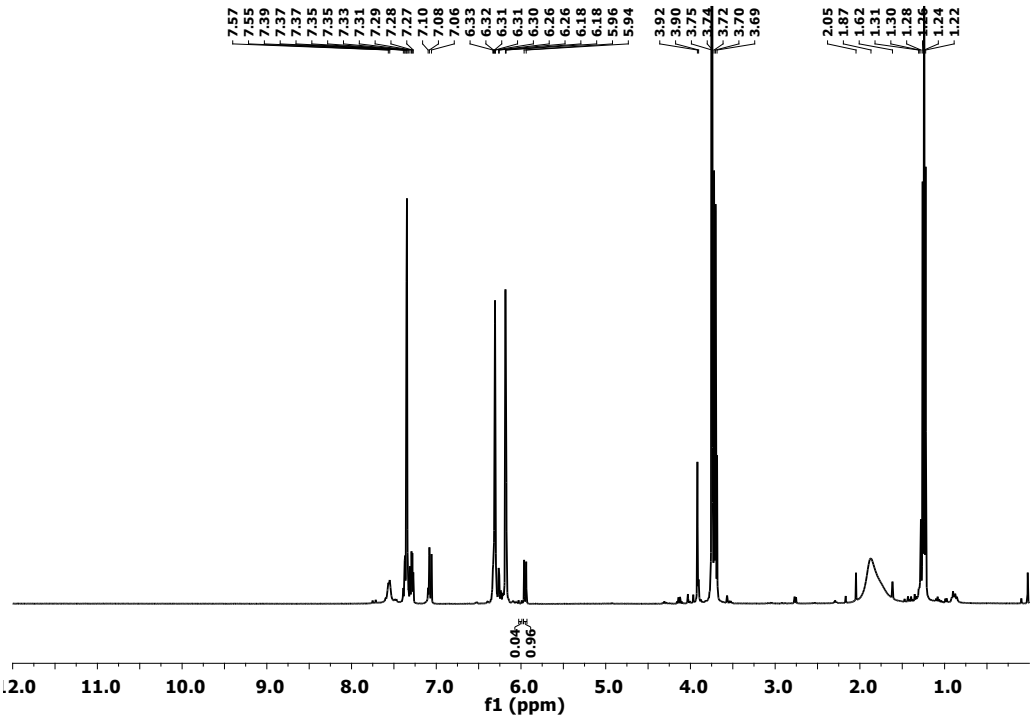


Fig. S162. [1]H NMR spectrum of crude 3-((furan-2-ylmethyl)thio)-N-phenylacrylamide (**3aw**).

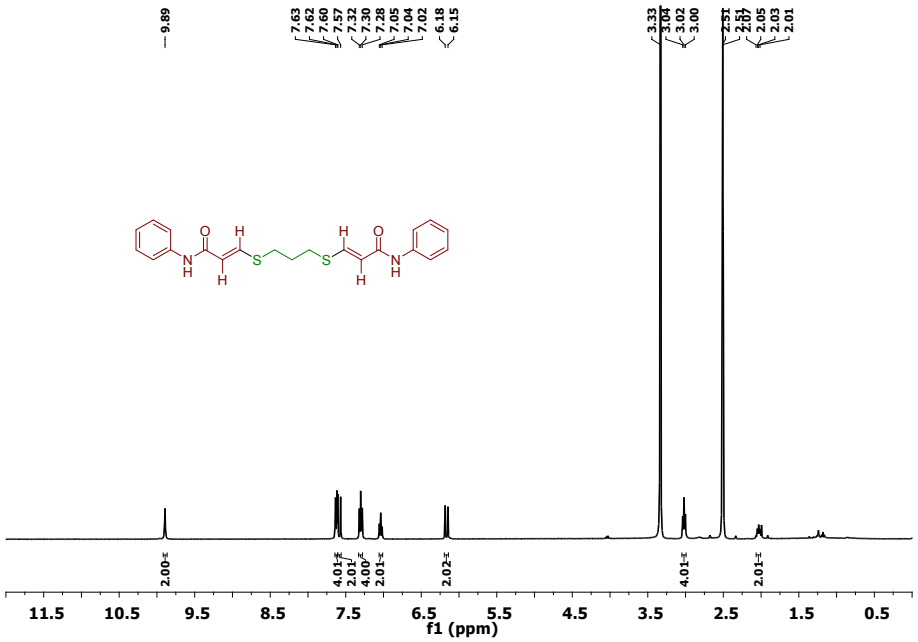


Fig. S163. ^{1}H NMR spectrum of (2E,2'E)-3,3'-(Propane-1,3-diylbis(sulfanediyl))bis(N-phenylacrylamide) (**3as**).

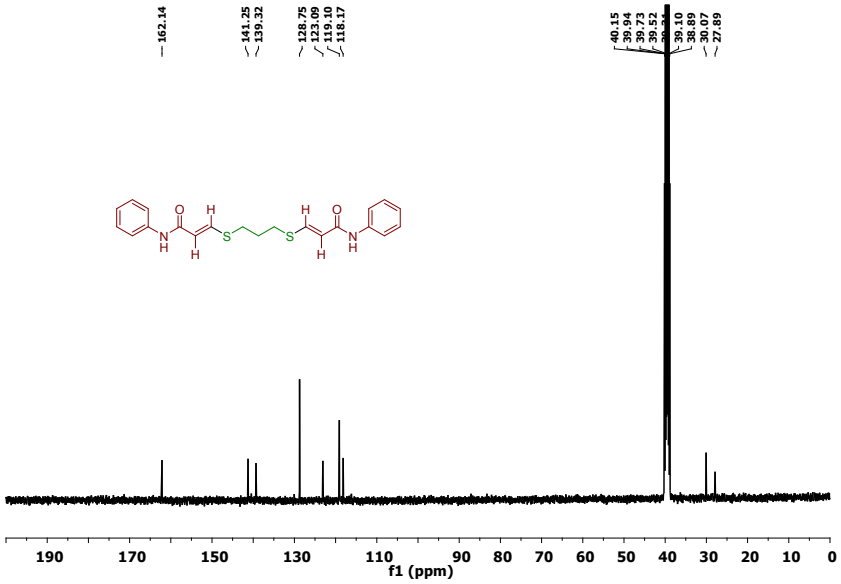


Fig. S164. ^{13}C NMR spectrum of (2E,2'E)-3,3'-(Propane-1,3-diylbis(sulfanediyl))bis(N-phenylacrylamide) (**3as**).

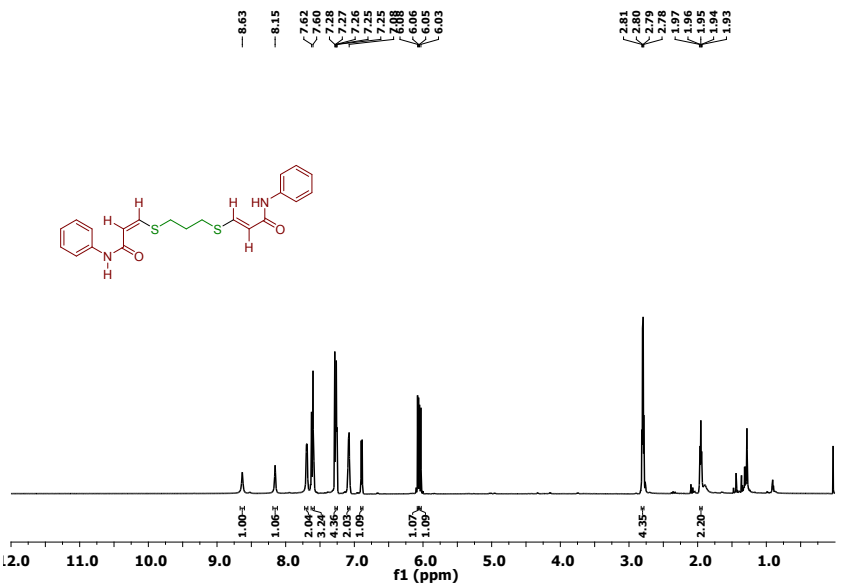


Fig. S165. ^{1}H NMR spectrum of (Z)-3-((3-(((E)-3-Oxo-3-(phenylamino)prop-1-en-1-yl)thio)propyl)thio)-Nphenylacrylamide (**3as**).

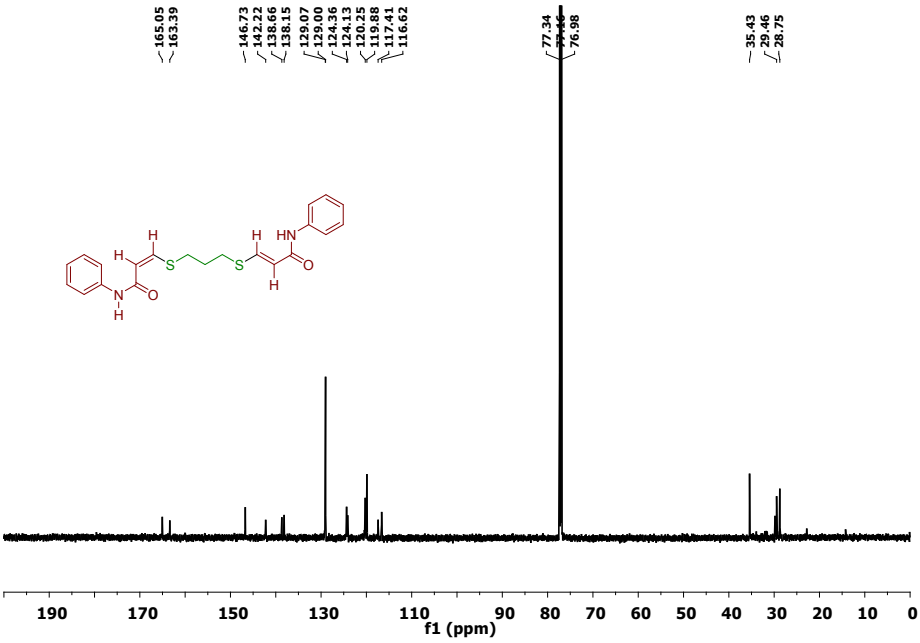


Fig. S166. ^{13}C NMR spectrum of (Z)-3-((3-(((E)-3-Oxo-3-(phenylamino)prop-1-en-1-yl)thio)propyl)thio)-Nphenylacrylamide (**3as**).

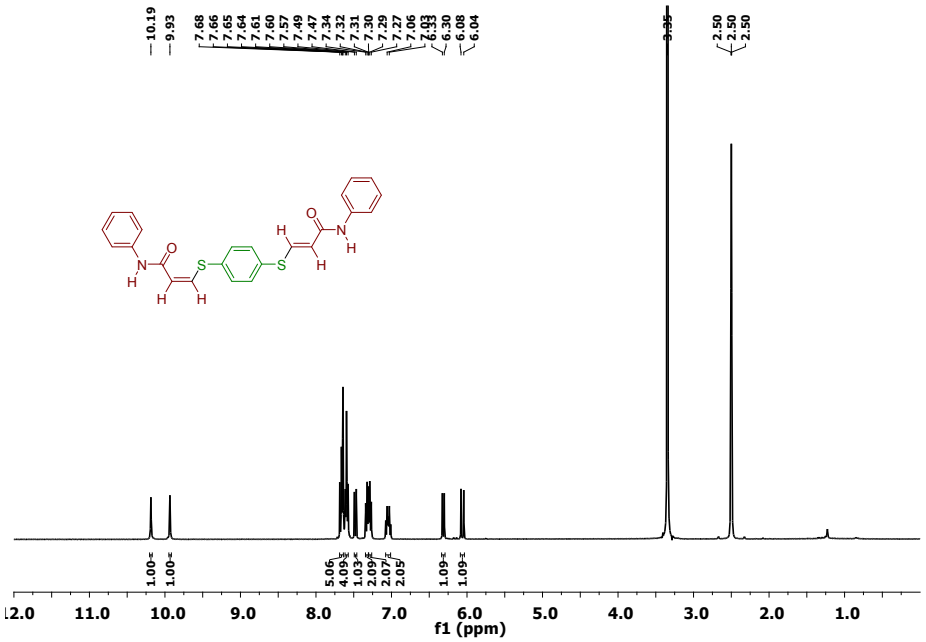


Fig. S167. ^{1}H NMR spectrum of (Z)-3-((4-(((E)-3-oxo-3-(phenylamino)prop-1-en-1-yl)thio)phenyl)thio)-N-phenylacrylamide (**3ar**).

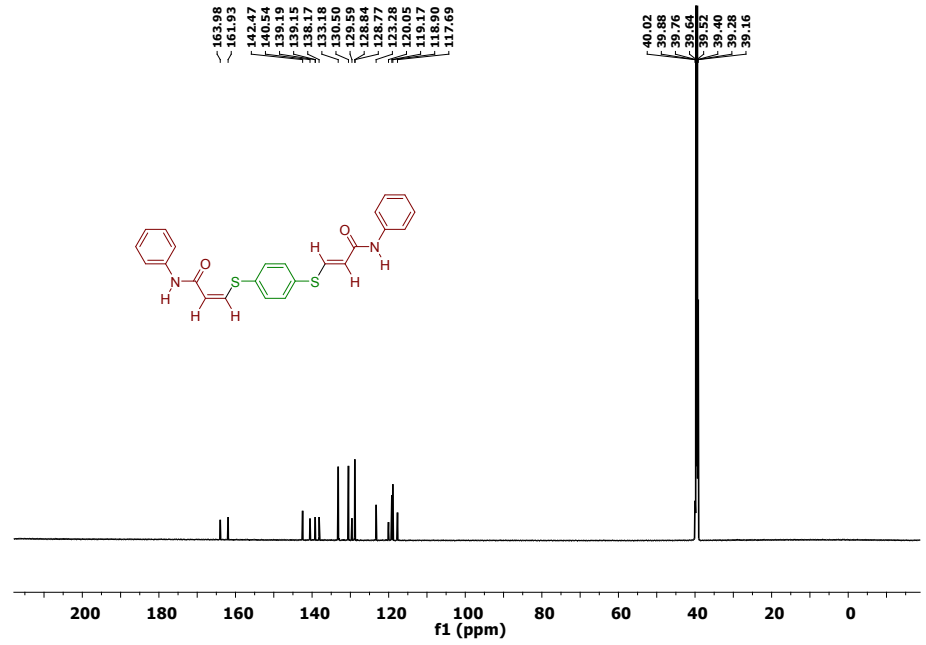


Fig. S168. ^{13}C NMR spectrum of (Z)-3-((4-(((E)-3-oxo-3-(phenylamino)prop-1-en-1-yl)thio)phenyl)thio)-N-phenylacrylamide (**3ar**).