Supporting Information

(*Z*)-Selective *anti*-Markovnikov or Markovnikov Thiol-Yne-Click Reactions of an Internal Alkyne by Amide Hydrogen Bond Control

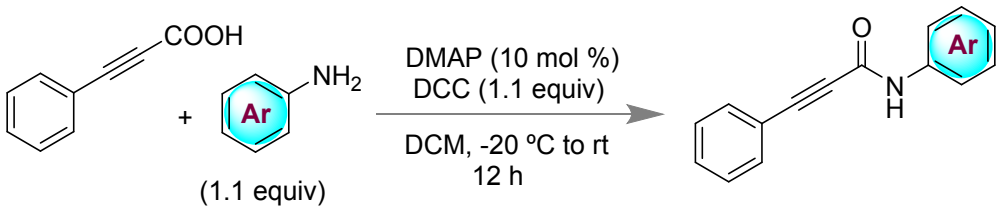
Content

EXPERIMENTAL SECTION

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

Synthesis

General procedures for the synthesis of N,3-diphenylpropiolamide derivatives.



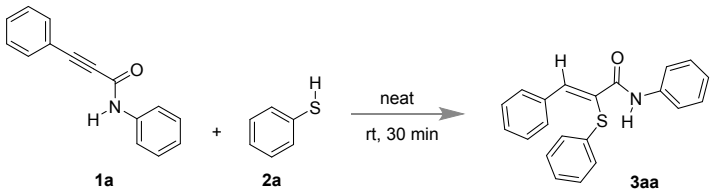
Scheme S1

In an oven dried round bottomed flask, a solution of propionic acid (3.54 mmol, 1.1 equiv) in 10 mL CH_2Cl_2 was stirred 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 injected drop wise. Then a solution of aniline derivatives (3.22 mmol, 1.0 equiv) in 5 mL CH_2Cl_2 was then added drop wise. Afterwards, the reaction mixture was allowed to stir at room temperature for 12 h.

After completion, the reaction mixture was diluted in CH_2Cl_2 and following organic content was washed 3 times by 0.5 M aq. HCl, dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by a silica gel column chromatography to give the corresponding desired starting materials N,3-diphenylpropiolamide derivatives as solid.

Procedure for the Thiol Yne Click reaction and representative synthesis of 3aa. The compound (**1a**) (60 mg, 0.271 mmol) was taken in a round bottom flask and followed by thiophenol (**2a**) (89 mg, 0.813 mmol) was added dropwise at open atmosphere. Following, the reaction mixture stirred for 30 min while monitored by TLC (*for solid-solid component, few drops of EtOH was added to make the reaction mixture homogeneous*). After completion of the reaction, column chromatography was done in EtOAC/Hexane to isolate the desired product **3aa** and to recover excess thiol (~1.5 equiv).

Optimization Reaction Condition (Table S1):



Entry	Thiol (equiv)	Solvent	Yield (%)[a]
1	1	-	50
2	1.5	-	68
3	2	-	81
4	3	-	97
5	3	EtOH	82
6	3	H_2O	86
7	3	$CHCl_3$	40
8	3	DMSO	59
9	3	Toluene	27
10	3	-	93[b]

[a]Isolated yields after column chromatography; Reaction conditions: **1a** (0.271 mmol), **2a** (0.813 mmol), room temperature, 30 min. [b]Reaction was performed under inert atmosphere.

Crystallographic Investigation

The compound (**3aa**) was recrystallized by the 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 = 1.54184 Å). SAINT+[1] and SADABS[2] 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.[3]

Compound (3aa) (CCDC 1910745)

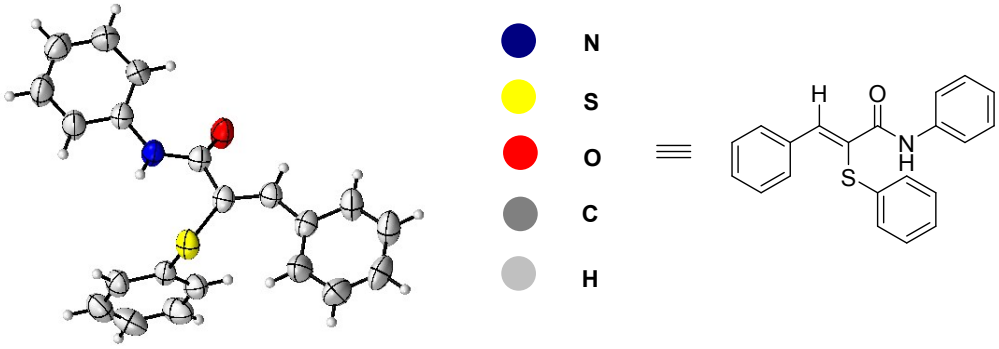


Fig. S1. Crystal structure of (**3aa**) (CCDC 1910745).

Crystallographic Data for (3aa)

Empirical formula	$C_{21}H_{17}NOS$
Formula weight	331.43
Temperature/K	299
Crystal system	Orthorhombic
Space group	$Pca2_1$
a/Å	16.2527(7)
b/Å	5.8894(2)
c/Å	18.0008(7)

α/°	90
β/°	90
γ/°	90
Volume/Å	1723.01(12)
Z	4
ρ_{calc}g/cm^3	1.213
μ/mm^{-1}	1.703
F(000)	629.0
Crystal size/mm^3	0.2×0.2×0.18
Radiation	CuKα (λ = 1.54184)
Reflections collected	13559
Independent reflections	3374 [R_{int} = 0.1472, R_{sigma} = 0.0660]
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0648, wR_2 = 0.1754
Final R indexes [all data]	R_1 = 0.0703, wR_2 = 0.1855
Largest diff. peak/hole / e Å^{-3}	0.58/-0.47

Compound 7 (CCDC 1965122)

The compound **7** was crystallized directly from the reaction mixture of compound **6** and **(2f)** in EtOH. The crystals data were collected with Bruker SMART D8 goniometer equipped with an APEX CCD detector and with an INCOATEC micro source (Mo-Kα radiation, λ = 0.71073 Å). SAINT+[4] and SADABS[5] 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.

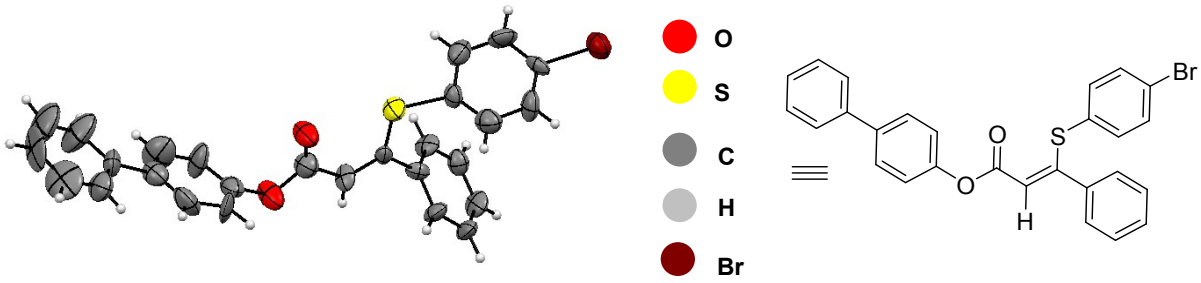


Fig. S2. Crystal structure of compound **7** (CCDC 1965122).

Crystallographic Data for compound 7

Empirical formula	$C_{27}H_{19}BrO_2S$
Formula weight	487.41
Temperature/K	296
Crystal system	Triclinic
Space group	P-1
a/Å	6.5137(5)
b/Å	22.7108(19)
c/Å	32.675(3)
α/°	108.215(5)
β/°	93.851(5)
γ/°	96.920(5)
Volume/Å	4529.7(7)
Z	2
ρ_{calc}g/cm^3	1.427
μ/mm^{-1}	1.928
F(000)	1982.0
Crystal size/mm^3	0.26×0.18×0.12
Radiation	MoKα (λ = 0.71073)

Reflections collected	51290
Independent reflections	16535 [R_{int} = 0.1142, R_{sigma} = 0.1507]
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.1058, wR_2 = 0.2309
Final R indexes [all data]	R_1 = 0.2549, wR_2 = 0.2858
Largest diff. peak/hole / e $Å^{-3}$	1.11/-0.71

NMR Experiment:

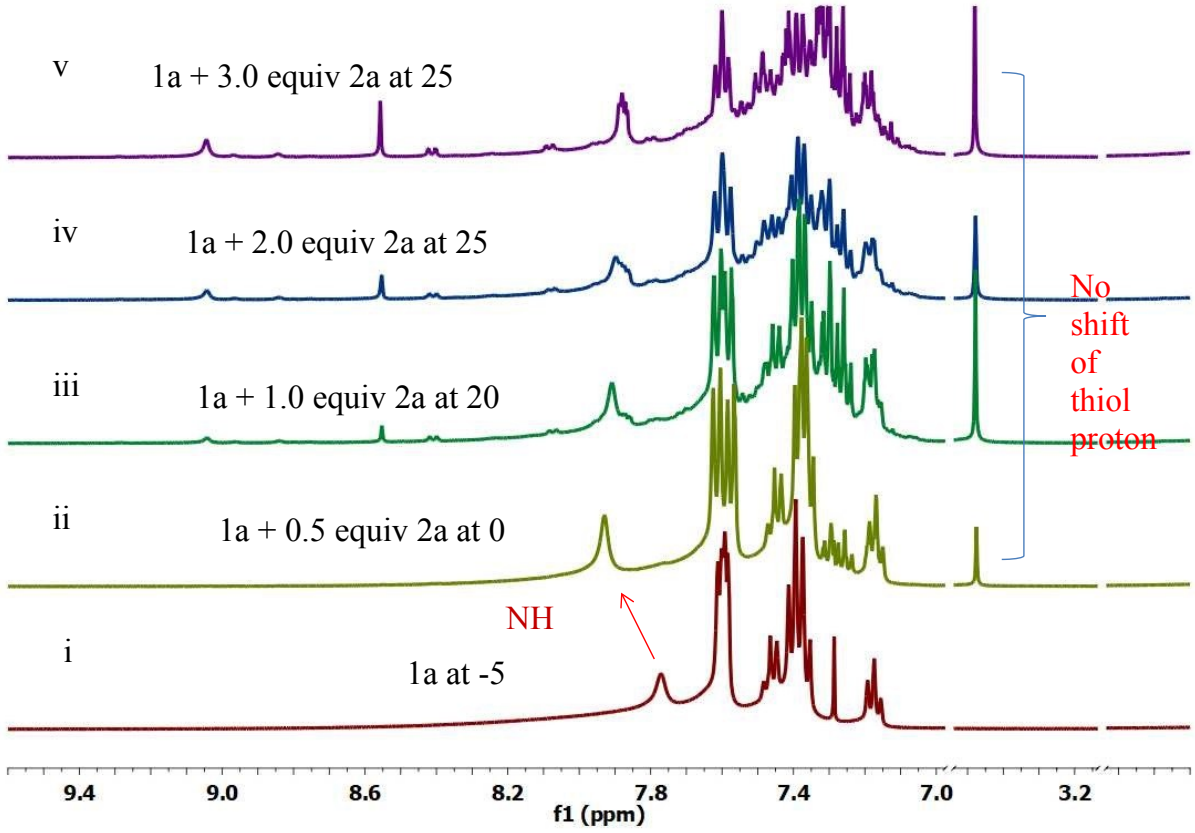


Fig. S3. ^{1}H NMR spectra of reaction mixture **1a** and **2a** (**i-v**) in $CDCl_3$ solvent at different temperature.

EPR experiment:

EPR spectra was recorded at 298 K using EPR spectrometer derived at 9.4335 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; centre field set: 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.

Reaction of Propiolamide 1a with Thiophenol 2a in presence of DMPO under standard condition: A mixture of propiolamide **1a** (60 mg, 0.271 mmol)**,** thiophenol (89 mg, 0.813 mmol) and DMPO (20 µL) were stirred for 20 minutes at room temperature. Afterwards, 20 µL solution was quickly transferred into EPR tube and 200 µL toluene was added to analyze EPR. No signal was observed, indicating reaction did not go through radical intermediate.

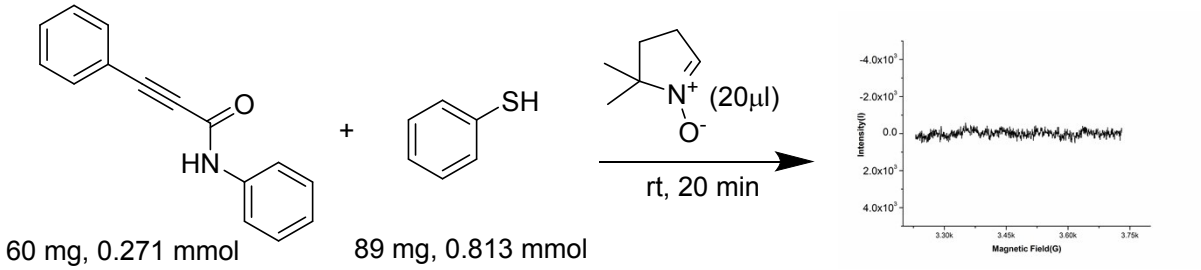
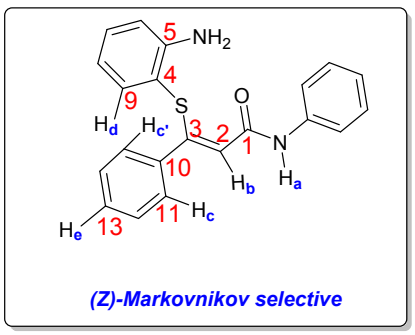


Fig. S4. EPR spectra of reaction mixture **1a** and **2a** in presence of spin trapping reagent DEMPO in Toluene solvent.

Structure elucidation for Compound (3ak)

Proposed structure is as follows:



Justification for proposed structure (3ak):

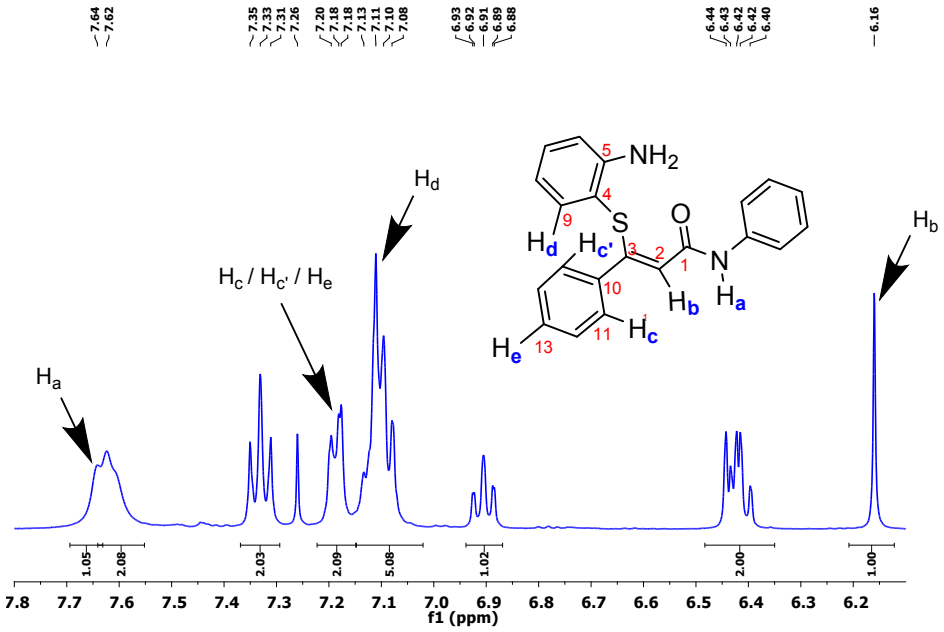


Fig. S5. ^{1}H NMR spectrum of Compound **(3ak)** with expanded aromatic region. The signature peaks are assigned through ^{1}H-^{13}C HMBC and HSQC NMR study below.

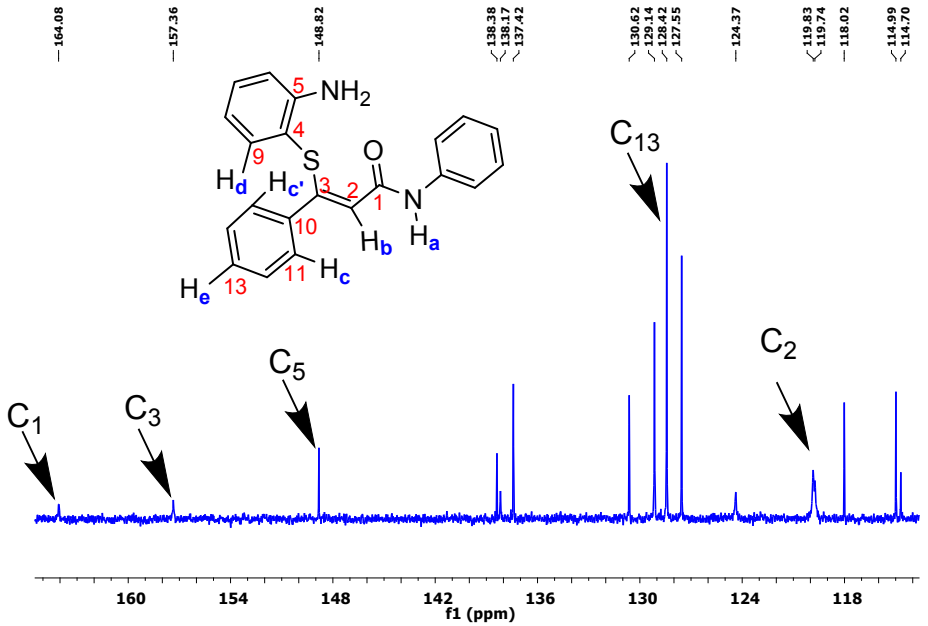


Fig. S6. ^{13}C NMR spectrum of Compound (3ak) with expanded aromatic region. The signature peaks are assigned through ^{1}H-^{13}C HMBC and HSQC NMR study below.

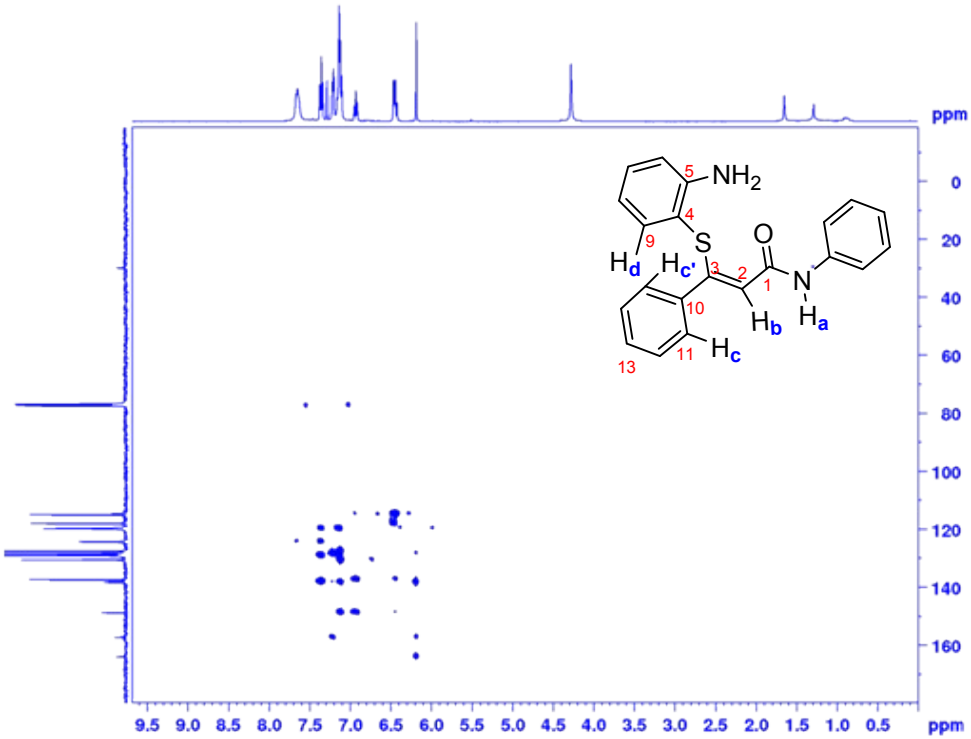


Fig. S7. HMBC full spectra. Number of points used along indirect and direct dimension was 256 and 2048 with a spectral width of 23900 Hz and 5200 Hz. 16 transients were recorded with a prescan delay of 3s. All the 2D NMR were recorded in $CDCl_3$ Solvent. $CDCl_3$ is not calibrated(taken as 7.284 ppm instead of 7.26 ppm).

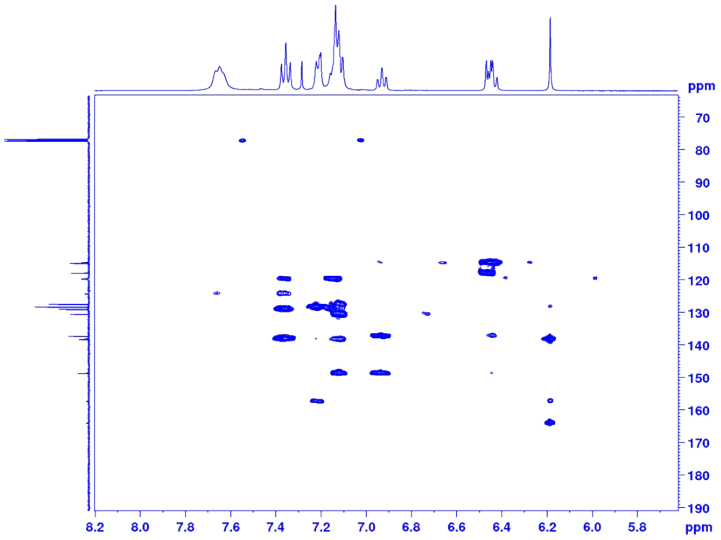


Fig. S8. HMBC spectra of aromatic region showing strong 3 bond correlation and very week 2 bond correlation.

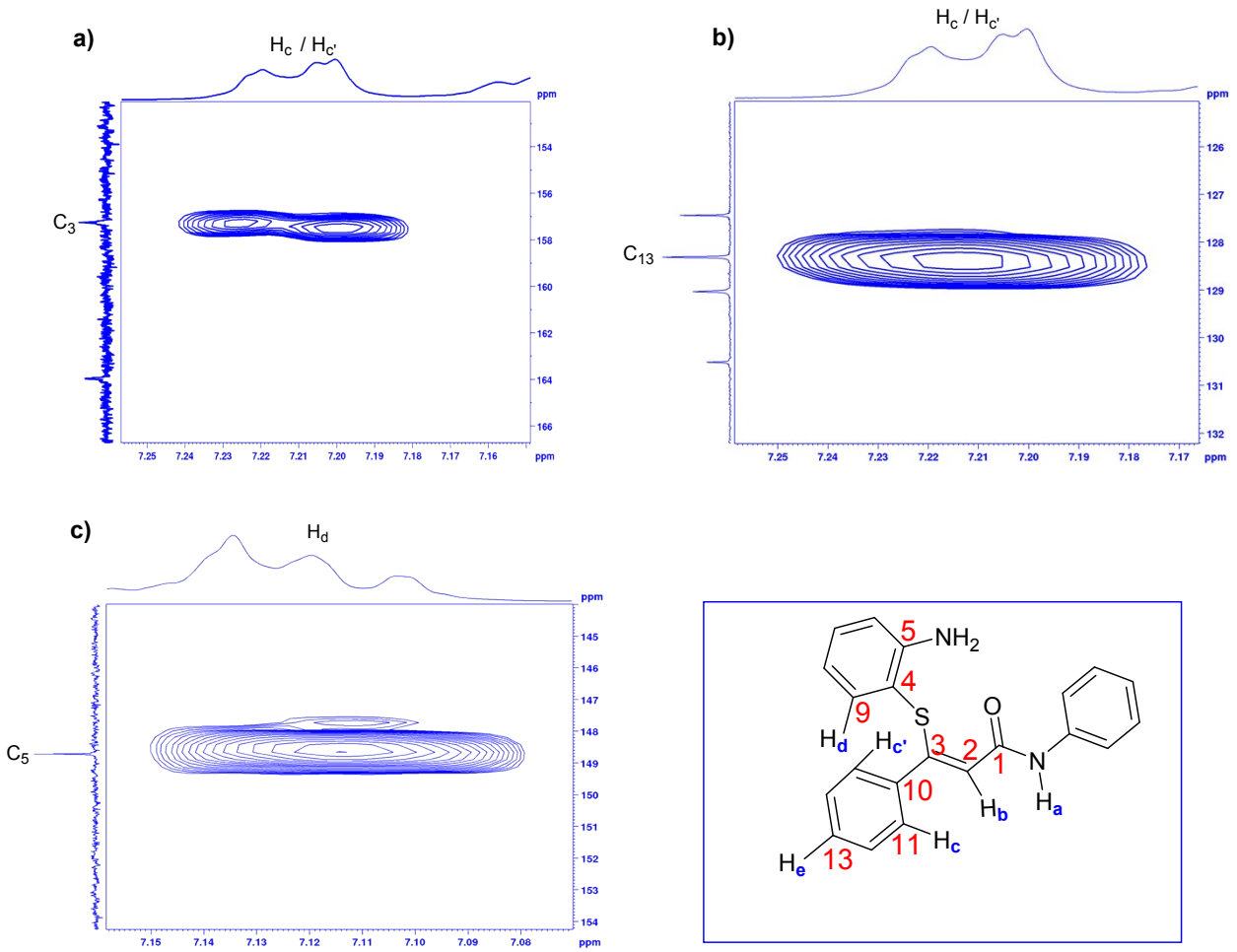


Fig. S9. ^{1}H-^{13}C HMBC NMR spectra having three bond correlation. **a)** Three bond correlation between $H_c/H_{c'}$ and C_3. **b)** Three bond correlation between $H_c/H_{c'}$ and C_{13}. **c)** Three bond correlation between $H_c/H_{c'}$ and C_5.

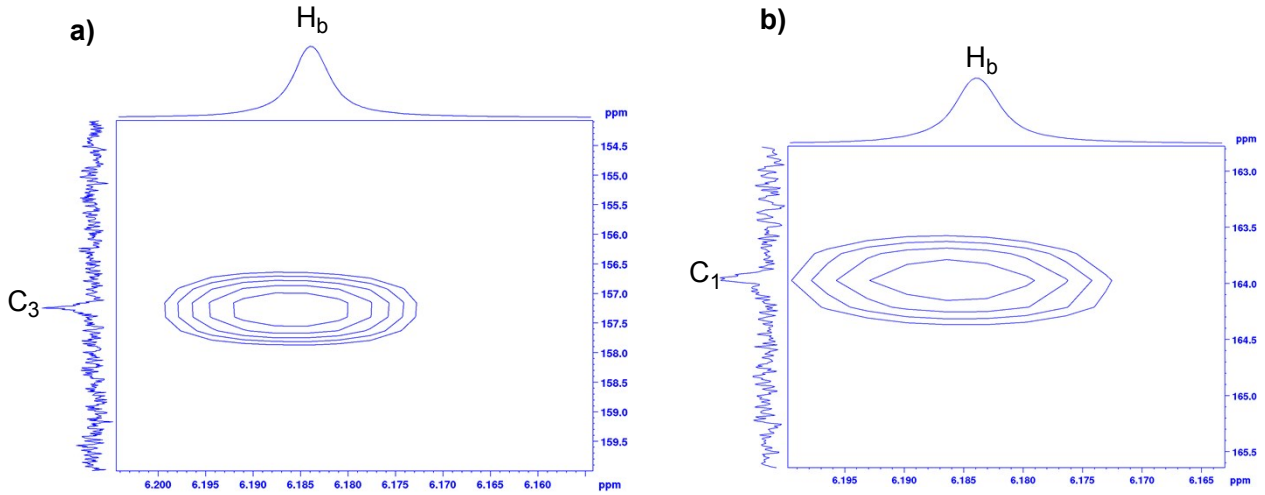


Fig. S10. ^{1}H-^{13}C HMBC NMR spectra with two bond correlation. **a)** Two bond correlation between Hb and C_3. **b)** Two Bond correlation between H_b and C_1.

From the above 2D HMBC assignments it can be concluded that the Hc/Hc'(7.2 ppm) is connected to C_3 (157.2 ppm) via 3 bond coupling whereas it is also connected to C_{13}(128.2 ppm) via 3 bond coupling. Thus it can be concluded the the resonance at 7.2 ppm should come form $H_C/_C$'. C_5(148.7) shows a strong 3 bond correlation with the proton resonating at 7.1 ppm thus indicating that this corresponds to H_d.

H_b(6.18 ppm) shows a two bond correlation with C_3(157.2 ppm) and C_1(163.8 ppm).Thus it is now confirmed that the carbon resonated at C_3 must be 157.2.

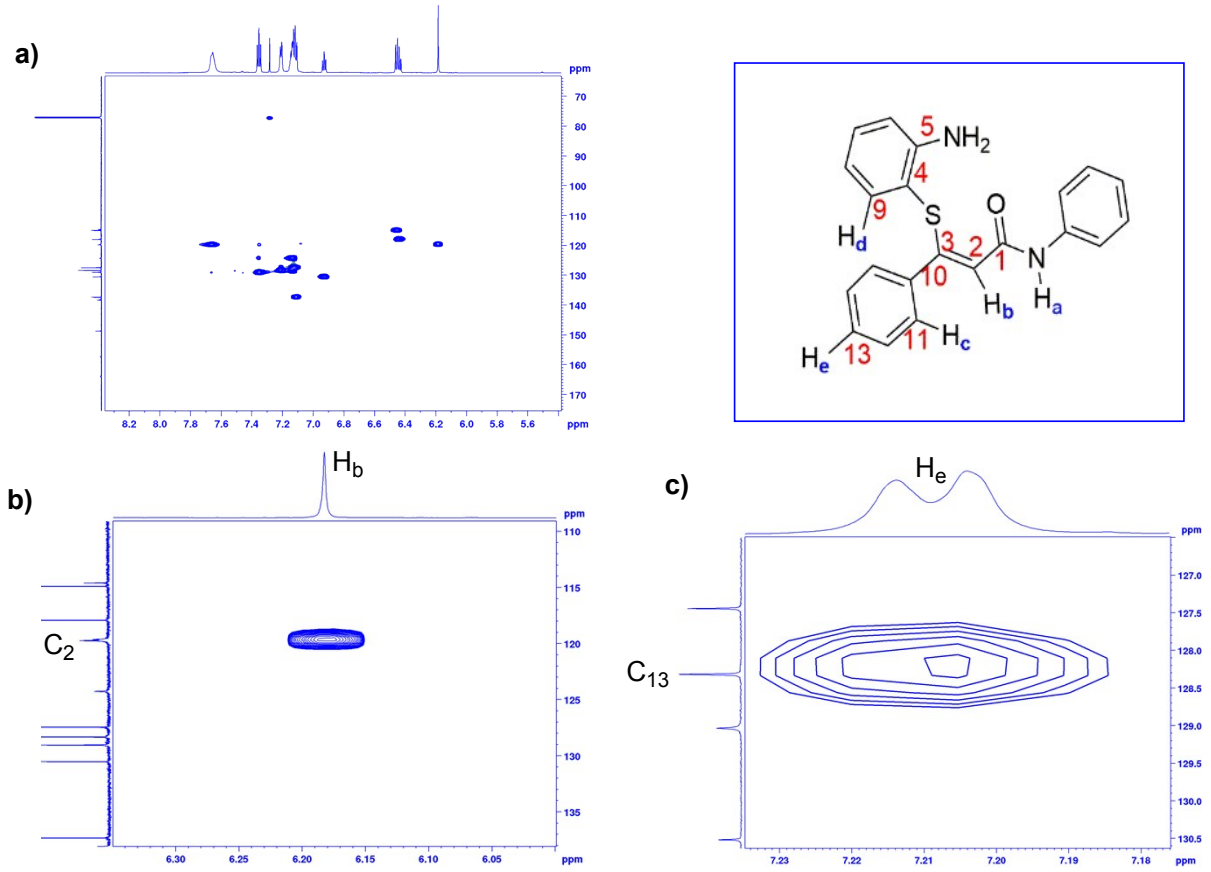


Fig. S11. HSQC Spectra: **a)** Expanded aromatic region. **b)** One bond correlation of H_b with C_2. **c)** One bond correlation of H_e with C_{13}.

From HSQC study it is observed that single bond connectivity of H_b is with C_2(119.2 ppm). C_{13} also shows a single bond correlation with H_e(7.2 ppm) which further confirms that C_{13} resonates at 128.2 ppm.

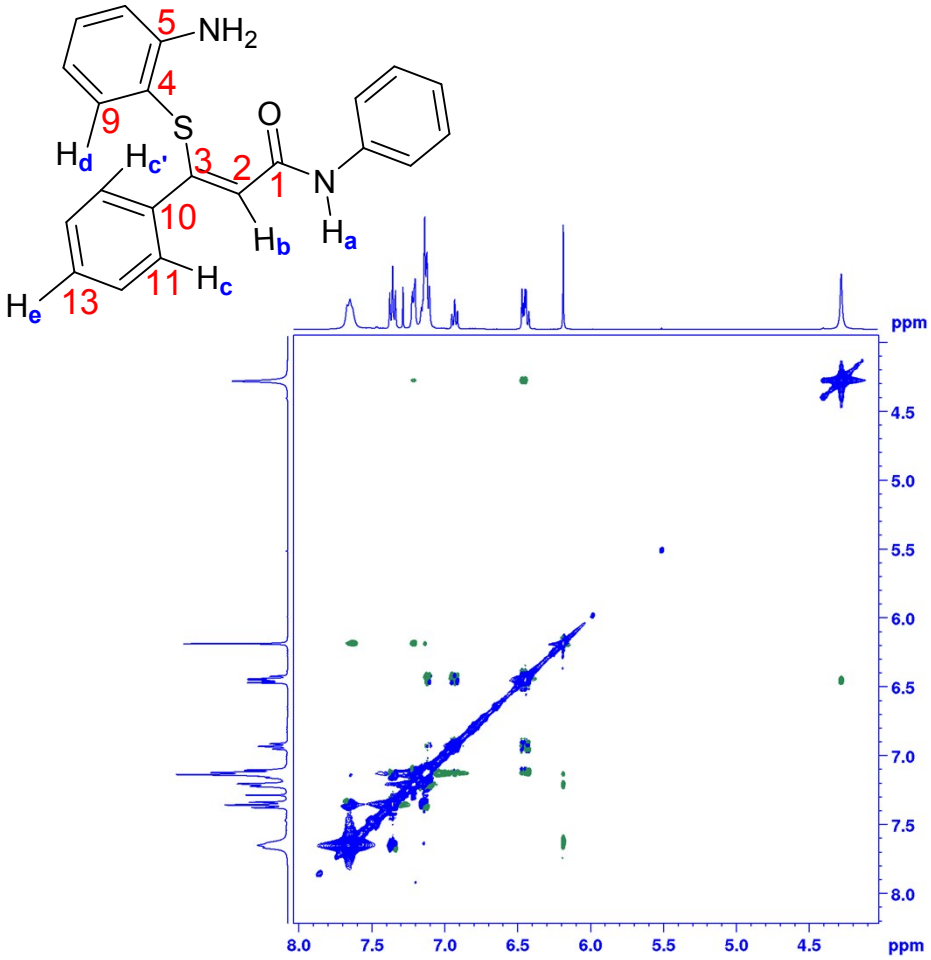


Fig. S12. ROESY spectra of compound **3ak**. Number of points in acquisition and indirect dimension was 2048 and 256 with spinlock pulse of duration 270ms. 8 transients with a prescan delay of 3 second was used to ensure complete relaxation.Spectral with along both indirect and direct dimension was adjusted to 4125 Hz.

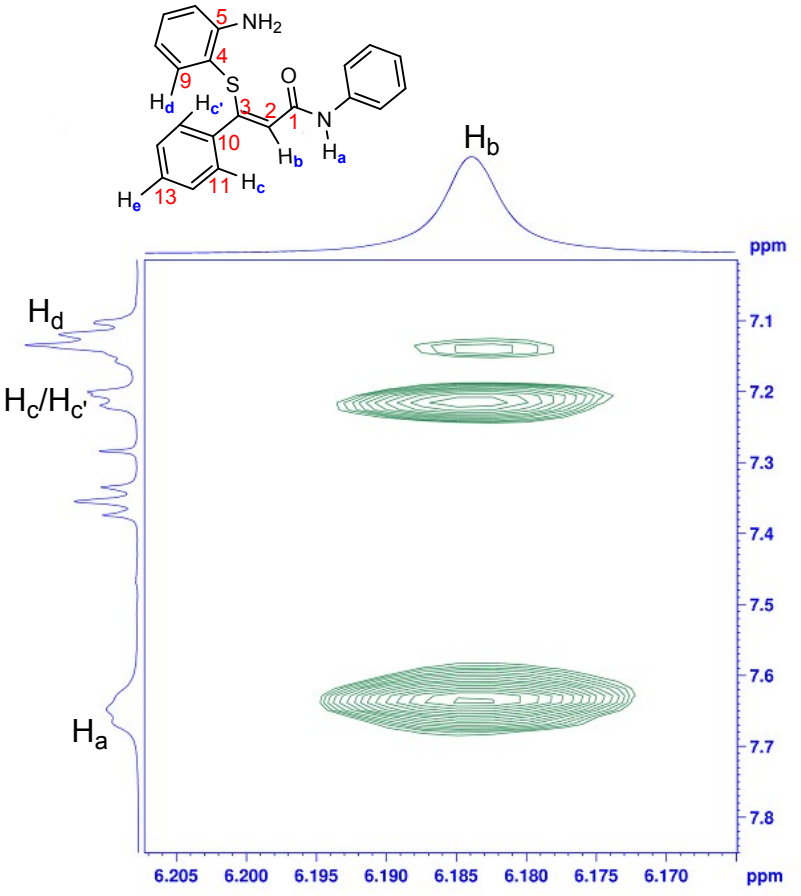


Fig. S13. Expanded region of the ROESY spectra.

^{1}H-^{1}H ROESY NMR study shows a strong correlation between H_b(6.18 ppm) and H_a (7.64 ppm).This confirmes the Markovnikov selectivity of compound (**3ak**). On the other hand, another strong correlation of H_b(6.18 ppm) with Hc/Hc'(7.20 ppm) is obserbed. It confirms the (Z)-selectivity of the compound **(3ak)**. However there is a very weak interaction of H_b with H_d. The ratio of integrals between the two cross peaks are approximately 1:0.10.

In order to understand this interaction we have done structure optimization through DFT(B3LYP/6311G).The optimized structure is shown below.

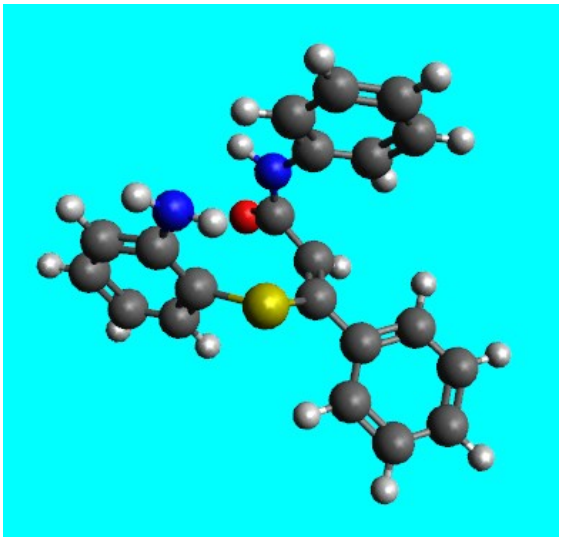
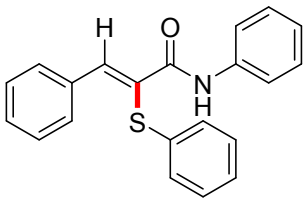


Fig. S14. Optimized geometry via B3LYP DFT method using 6311G basis set with quadratic convergence.

In the optimized structure it is clearly seen that the distance between H_b and H_d is very high(3.90Å) compared to H_b and H_c (2.36 Å). As the intensity of roesy cross peaks are inversely propotional to sixth power of distance ($1/r^6$), the intensity ratio in the present case between H_b-H_c and Hb-Hd is expected to be 1:0.06 which is close to the experimentally observed ratio of 1:0.10. This confirmes exclusive formation of (Z)-selective Markovnikov product.

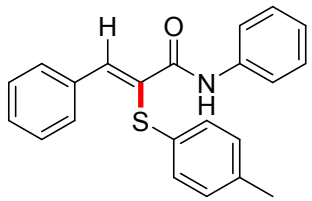
NMR CHARATERIZATION DATA

(Z)-N,3-diphenyl-2-(phenylthio)acrylamide (3aa): R_f = 0.6 (20% ethyl acetate in hexane);



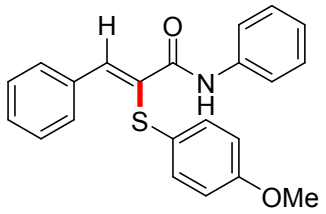
white solid; yield 97% (87 mg); mp 96-98 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.53 (s, 1H), 7.86-7.85 (m, 2H), 7.47 (d, *J* = 7.7 Hz, 2H), 7.40-7.39 (m, 3H), 7.31-7.30 (m, 3H), 7.29-7.27 (m, 3H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.7, 147.6, 137.8, 134.6, 134.3, 130.9, 130.3, 129.8, 129.1, 128.6, 127.9, 126.9, 124.8, 124.3, 120.2; IR (KBr) ῡ 3347, 3057, 2924, 1674, 691; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{17}NOSNa$ 354.0923; found 354.0927.

(Z)-N,3-diphenyl-2-(*p*-tolylthio)acrylamide (3ab): R_f = 0.7 (20% ethyl acetate in hexane);



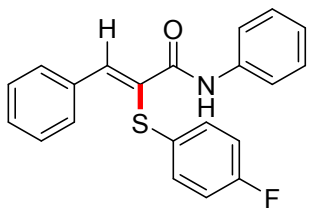
white solid; yield 98% (91 mg); mp 122-124 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.48 (s, 1H), 7.89-7.85 (m, 2H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.41-7.37 (m, 3H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 7.09 (t, *J* = 8.0 Hz, 3H), 2.27 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.3, 147.1, 137.9, 137.0, 134.7, 130.9, 130.6, 130.6, 130.2, 129.1, 128.6, 127.4, 124.9, 124.7, 120.2, 21.1; IR (KBr) ῡ 3344, 2923, 1667, 690; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{20}NOS$ 346.1260; found 346.1258.

(Z)-2-((4-methoxyphenyl)thio)-N,3-diphenylacrylamide (3ac): R_f = 0.5 (20% ethyl acetate



in hexane); white solid; yield 66% (65 mg); in 1 mL EtOH 82% (80 mg); mp 140-141 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.40 (s, 1H), 7.87 (d, *J* = 7.7 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.42-7.38 (m, 3H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.26-7.24 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.74 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.3, 159.2, 146.1, 137.8, 134.7, 130.9, 130.1, 129.7, 129.1, 128.6, 126.0, 124.7, 124.6, 120.1, 115.5, 55.5; IR (KBr) ῡ 3334, 2924, 2348, 1666, 691; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{19}NO_2SNa$ 384.1029; found 384.1041.

(Z)-2-((4-fluorophenyl)thio)-N,3-diphenylacrylamide (3ad): R_f = 0.6 (20% ethyl acetate in



hexane); white solid; yield 81% (77 mg); mp 113-114 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.47 (s, 1H), 7.85-7.84 (m, 2H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.41-7.40 (m, 3H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.28-7.26 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 8.6 Hz, 2H); ^{13}C NMR

(175 MHz, $CDCl_3$) δ 163.0, 162.0 (d, $^1J_{CF}$ = 247.2 Hz), 147.3, 137.7, 134.4, 130.9, 130.4, 129.3 (d, $^3J_{CF}$ = 8.1 Hz), 129.3 (d, $^4J_{CF}$ = 3.2 Hz), 129.2, 128.6, 124.9(×2), 120.2, 117.0 (d, $^2J_{CF}$ = 22.3 Hz); IR (KBr) ῡ 3353, 2923, 1661, 1314, 690; HRMS (ESI/Q-TOF) m/z: [M + Na]$^+$ calcd for $C_{21}H_{16}NFOSNa$ 372.0829; found 372.0846.

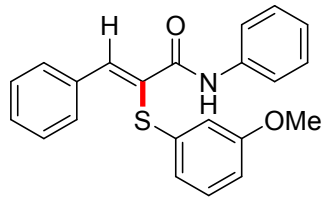
(Z)-2-((4-chlorophenyl)thio)-N,3-diphenylacrylamide (3ae): R_f = 0.7 (20% ethyl acetate in hexane); white solid; yield 86% (86 mg); mp 135-138 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.53 (s, 1H), 7.83-7.82 (m, 2H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.41-7.40 (m, 3H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.12 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 162.9, 148.1, 137.6, 134.3, 132.9, 132.8, 130.9, 130.5, 130.0, 129.2, 128.7, 128.3, 124.9, 123.8, 120.2; IR (KBr) ῡ 3348, 2924, 2853, 1663, 754, 690; HRMS (ESI/Q-TOF) m/z: [M + H]$^+$ calcd for $C_{21}H_{17}ClNOS$ 366.0714 ; found 366.0684.

(Z)-2-((4-bromophenyl)thio)-N,3-diphenylacrylamide (3af): R_f = 0.5 (20% ethyl acetate in hexane); white solid; yield 91% (101mg); mp 142-144 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.53 (s, 1H), 7.82-7.81 (m, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.41-7.39 (m, 5H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 162.9, 148.3, 137.6, 134.3, 133.6, 132.8, 130.9, 130.5, 129.9, 128.7, 128.5, 124.9, 123.6, 120.7, 120.2; IR (KBr) ῡ 3353, 2924, 2359, 1661, 690, 667; HRMS (ESI/Q-TOF) m/z: [M + H]$^+$ calcd for $C_{21}H_{17}BrNOS$ 410.0179; found 410.0209.

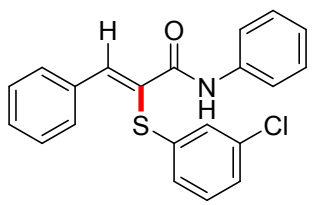
(Z)-N,3-diphenyl-2-((4-(trifluoromethyl)phenyl)thio)acrylamide (3ag): R_f = 0.6 (20% ethyl acetate in hexane); white solid; yield 91% (99 mg); mp

138-141 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.63 (s, 1H), 7.82- 7.80 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.41-7.40 (m, 3H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 162.8, 149.3, 139.5, 137.5, 134.2, 130.9, 130.7, 129.2, 128.8 (q, $^2J_{CF}$ = 32 Hz), 128.7, 126.6 (q, $^4J_{CF}$ = 3.6 Hz), 126.6, 125.0, 124.0 (q, $^1J_{CF}$ = 272 Hz), 122.5, 120.3; IR (KBr) ῡ 3363, 2923, 1659, 1326, 688; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}F_3NOS$ 400.0977; found 400.0970.

(Z)-2-((3-methoxyphenyl)thio)-N,3-diphenylacrylamide (3ah): R_f = 0.7 (20% ethyl acetate in hexane); white solid; yield 78% (76 mg); mp 101-103 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.53 (s, 1H), 7.86-7.85 (m, 2H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.40-7.39 (m, 3H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 8.2 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.90 (dd, *J* = 7.7, 0.7 Hz, 1H), 6.84 (s, 1H), 6.72 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.1, 160.5, 147.8, 137.8, 135.5, 134.5, 130.9, 130.7, 130.3, 129.1, 128.6, 124.7, 124.14, 120.2, 119.3, 112.6, 112.6, 55.4; IR (KBr) ῡ 3345, 2924, 2359, 1668, 689; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{19}NO_2SNa$ 384.1029; found 384.1015.



(Z)-2-((3-chlorophenyl)thio)-N,3-diphenylacrylamide (3ai): R_f = 0.6 (20% ethyl acetate in hexane); white solid; yield 90% (89 mg); mp 150-152 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.58 (s, 1H), 7.84-7.81 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.42-7.40 (m, 3H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.30 (s, 1H), 7.23-7.10 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 148.7, 137.6, 136.4, 135.6, 134.3, 130.9, 130.8, 130.6, 129.2, 128.7, 127.1, 126.7, 124.9, 124.9, 123.2,



120.3; IR (KBr) ῡ 3348, 2348, 1665, 774, 690; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}ClNOS$ 366.0714; found 366.0713.

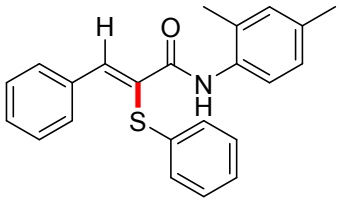
(Z)-2-((2-fluorophenyl)thio)-N,3-diphenylacrylamide (3aj): R_f = 0.6 (20% ethyl acetate in hexane); white solid; yield 79% (75 mg); mp 105-108 ºC; ^1H NMR (700 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.51 (s, 1H), 7.87-7.86 (m, 2H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.45-7.39 (m, 3H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.21-7.16 (m, 2H), 7.11 (t, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 8.7 Hz, 1H), 7.03 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.0, 160.2 (d, $^1J_{CF}$ = 245.2 Hz), 147.9, 137.7, 134.4, 130.9, 130.4, 129.9, 129.1, 129.0 (d, $^3J_{CF}$ = 7.6 Hz), 128.6, 125.5 (d, $^4J_{CF}$ = 3.4 Hz), 124.8, 123.7, 121.3 (d, $^2J_{CF}$ = 17.0 Hz), 120.2, 116.1 (d, $^2J_{CF}$ = 21.3 Hz); IR (KBr) ῡ 3355, 3056, 2924, 1652, 1178, 689; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}FNOS$ 350.1009; found 350.1003.

(Z)-3-((2-aminophenyl)thio)-N,3-diphenylacrylamide (3ak): R_f = 0.4 (20% ethyl acetate in hexane); brownish white solid; yield 86% (81 mg); mp 175-176 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.20-7.18 (m, 2H), 7.13-7.08 (m, 5H), 7.93-6.88 (m, 1H), 6.44-6.40 (m, 2H), 6.16 (s, 1H), 4.25 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 157.4, 148.8, 138.4, 138.2, 137.4, 130.6, 129.1, 128.4, 127.5, 124.4, 119.8, 119.7, 118.0, 115.0, 114.7; IR (KBr) ῡ 3432, 3359, 2923, 2359, 1607, 668; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{18}N_2OSNa$ 369.1032 ; found 369.1020.

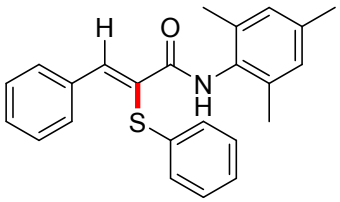
(Z)-3-phenyl-2-(phenylthio)-N-(p-tolyl)acrylamide (3ba): R_f = 0.4 (20% ethyl acetate in hexane); white solid; yield 96% (85 mg); mp 108-111 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.51 (s, 1H), 7.86-

7.84 (m, 2H), 7.42-7.38 (m, 3H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.31-7.26 (m, 4H), 7.19-7.16 (m, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 147.4, 135.2, 134.6, 134.4, 134.4, 130.9, 130.2, 129.8, 129.6, 128.6, 127.2, 126.8, 124.4, 120.3, 21.0; IR (KBr) ῡ 3360, 2921, 2369, 1676, 689; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{20}NOS$ 346.1260; found 346.1277.

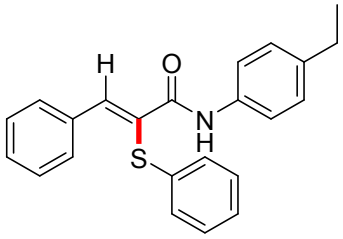
(Z)-N-(2,4-dimethylphenyl)-3-phenyl-2-(phenylthio)acrylamide (3ca): R_f = 0.6 (20% ethyl acetate in hexane); white solid; yield 91% (79 mg); mp 143-146 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.56 (s, 1H), 7.86-7.85 (m, 2H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.41-7.38 (m, 3H), 7.31-7.27 (m, 4H), 7.18 (t, *J* = 7.0 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.92 (s, 1H), 2.26 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 162.9, 147.9, 134.9, 134.7, 134.6, 133.3, 131.2, 130.8, 130.2, 129.8, 129.1, 128.6, 127.4, 126.9, 126.7, 124.3, 122.4, 21.0, 17.3; IR (KBr) ῡ 3365, 2923,2853, 1673, 690; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{23}H_{21}NOSNa$ 382.1236; found 382.1250.



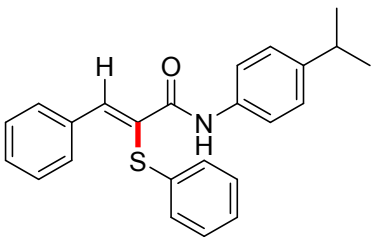
(Z)-N-mesityl-3-phenyl-2-(phenylthio)acrylamide (3da): R_f = 0.8 (20% ethyl acetate in hexane); white solid; yield 88% (75 mg); mp 158-160 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.39 (s, 1H), 7.88-7.87 (m, 2H), 7.42-7.38 (m, 3H), 7.35 (d, *J* = 7.0 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.83 (s, 2H), 2.24 (s, 3H), 1.89 (s, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.6, 147.4, 137.2, 135.3, 134.8, 134.7, 131.3, 130.8, 130.1, 129.8, 129.0, 128.5, 127.4, 126.8, 124.3, 21.0, 18.1; IR (KBr) ῡ 3259, 2923, 2853, 1646, 689; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{24}NOS$ 374.1573; found 374.1576.



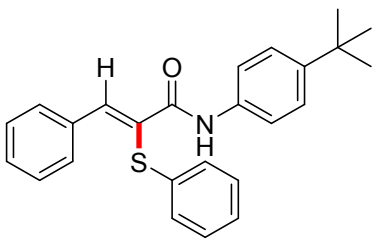
(Z)-N-(4-ethylphenyl)-3-phenyl-2-(phenylthio)acrylamide (3ea): R_f = 0.6 (20% ethyl acetate in hexane); white solid; yield 97% (84 mg); mp 115-117 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.52 (s, 1H), 7.86-7.84 (m, 2H), 7.42-7.38 (m, 5H), 7.32-7.26 (m, 4H), 7.19-7.18 (m, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 147.4, 140.9, 135.4, 134.6, 134.4, 130.9, 130.2, 129.8, 128.6, 128.4, 127.2, 126.8, 124.4, 120.4, 28.5, 15.8; IR (KBr) ῡ 3341, 2959, 1716, 667; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{22}NOS$ 360.1417; found 360.1426.



(Z)-N-(4-isopropylphenyl)-3-phenyl-2-(phenylthio)acrylamide (3fa): R_f = 0.7 (20% ethyl acetate in hexane); white solid; yield 89% (76 mg); mp 129-133 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.53 (s, 1H), 7.86-7.85 (m, 2H), 7.41-7.38 (m, 5H), 7.31 (d, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 2H), 2.86 (sept, *J* = 7.0 Hz, 1H), 1.22 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.0, 147.5, 145.5, 135.5, 134.6, 134.4, 130.9, 130.2, 129.8, 128.6, 127.2, 127.0, 126.8, 124.4, 120.4, 33.7, 24.1; IR (KBr) ῡ 3359, 2957, 2868, 2358, 1652, 690; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{24}H_{23}NOSNa$ 396.1393; found 396.1409.

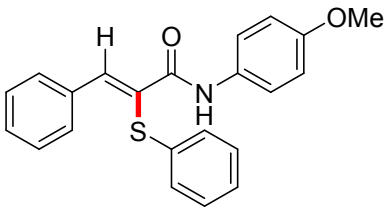


(Z) N-(4-(tert-butyl)phenyl)-3-phenyl-2-(phenylthio)acrylamide (3ga): R_f = 0.8 (20% ethyl acetate in hexane); white solid; yield 95% (79 mg); mp 137-139 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.53 (s, 1H), 7.86-7.84 (m, 2H), 7.40-7.38 (m, 5H), 7.33-7.28 (m, 6H), 7.18 (t, *J* = 6.8 Hz, 1H), 1.29 (s, 9H); ^{13}C

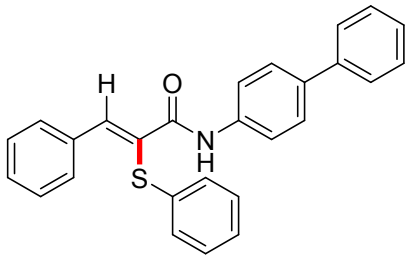


NMR (100 MHz, $CDCl_3$) δ 163.1, 147.8, 147.5, 135.2, 134.6, 134.4, 130.9, 130.2, 129.8, 128.6, 127.2, 126.8, 125.9, 124.4, 120.0, 34.5, 31.5; IR (KBr) ῡ 3338, 3069, 2962, 1661, 689; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{25}H_{25}NOSNa$ 410.1549; found 410.1562.

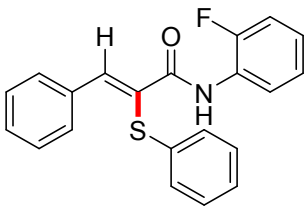
(Z)-N-(4-methoxyphenyl)-3-phenyl-2-(phenylthio)acrylamide (3ha): R_f = 0.6 (20% ethyl acetate in hexane); white solid; yield 79% (68 mg); mp 129-131 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.51 (s, 1H), 7.85-7.83 (m, 2H), 7.42-7.39 (m, 3H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.31-7.26 (m, 4H), 7.20-7.17 (m, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 156.8, 147.2, 134.6, 134.5, 130.9, 130.8, 130.2, 129.8, 128.6, 127.2, 126.8, 124.4, 122.0, 114.3, 55.6; IR (KBr) ῡ 3348, 2923, 2359, 1672, 689; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{19}NO_2SNa$ 384.1029; found 384.1024.



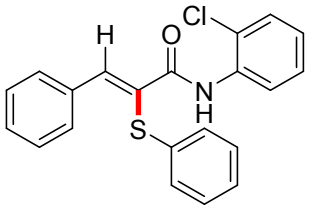
(Z)-N-([1,1'-biphenyl]-4-yl)-3-phenyl-2-(phenylthio)acrylamide (3ia): R_f = 0.5 (20% ethyl acetate in hexane); brownish white solid; yield 43% (36 mg); mp 163-167 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.54 (s, 1H), 7.88-7.86 (m, 2H), 7.56-7.52 (m, 6H), 7.43-7.40 (m, 5H), 7.34-7.28 (m, 5H), 7.19 (t, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 147.7, 140.6, 137.7, 137.1, 134.6, 134.3, 130.9, 130.3, 129.9, 128.9, 128.6, 127.7, 127.3, 127.2, 127.0, 126.9, 124.3, 120.5; IR (KBr) ῡ 3316, 2922, 1652, 687; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{22}NOS$ 408.1417; found 408.1433.



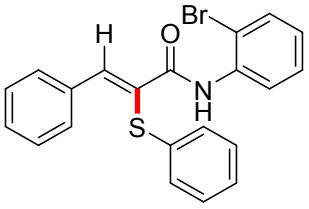
(Z)-N-(2-fluorophenyl)-3-phenyl-2-(phenylthio)acrylamide (3ja): R_f = 0.7 (20% ethyl acetate in hexane); white solid; yield 98% (86 mg); mp 125-127 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.52 (s, 1H), 8.38 (t, *J* = 8.0 Hz, 1H), 7.90-7.89 (m, 2H), 7.43-7.39 (m, 3H), 7.33 (d, *J* = 7.0 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.0 Hz, 1H), 7.13-7.12 (m, 1H), 7.05-7.01 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.2, 152.9 (d, $^1J_{CF}$ = 244.4 Hz), 147.8, 134.4, 134.0, 131.0, 130.4, 129.7, 128.6, 127.6, 127.0, 126.5 (d, $^3J_{CF}$ = 10.0 Hz), 124.6 (d, $^4J_{CF}$ = 1.6 Hz), 124.63, 124.59, 121.5, 114.9 (d, $^2J_{CF}$ = 19.0 Hz); IR (KBr) ῡ 3358, 2924, 1699, 1320, 690; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{16}FNOSNa$ 372.0829; found 372.0834.



(Z)-N-(2-chlorophenyl)-3-phenyl-2-(phenylthio)acrylamide (3ka): R_f = 0.75 (20% ethyl acetate in hexane); white solid; yield 98% (84 mg); mp 117-119 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 8.54 (s, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 7.90-7.89 (m, 2H), 7.41-7.40 (m, 3H), 7.32-7.25 (m, 6H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.3, 148.3, 134.9, 134.5, 134.1, 131.0, 130.5, 129.7, 129.2, 128.6, 127.8, 127.4, 126.8, 124.8, 124.6, 123.6, 121.3; IR (KBr) ῡ 3330, 3059, 2926, 1699, 738, 689; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}ClNOS$ 366.0714; found 366.0718.

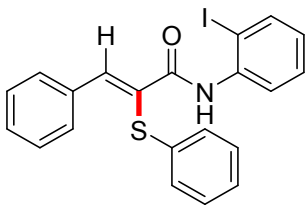


(Z)-N-(2-bromophenyl)-3-phenyl-2-(phenylthio)acrylamide (3la): R_f = 0.85 (20% ethyl acetate in hexane); white solid; yield 88% (72 mg); mp 124-126 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 8.55 (s, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 7.90-7.88 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 1H),

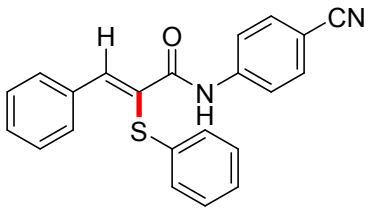


7.41-7.40 (m, 3H), 7.32-7.25 (m, 5H), 7.17 (t, J = 7.2 Hz, 1H), 6.95 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 148.4, 136.1, 134.5, 134.2, 132.5, 131.0, 130.5, 129.7, 128.6, 128.4, 127.3, 126.8, 125.3, 124.4, 121.6, 114.0; IR (KBr) ῡ 3314, 1672, 737, 688; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{16}BrNOSNa$ 432.0028; found 432.0041.

(Z)-N-(2-iodophenyl)-3-phenyl-2-(phenylthio)acrylamide (3ma): R_f = 0.8 (20% ethyl acetate in hexane); white solid; yield 76% (60 mg); mp 128-130 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.57 (s, 1H), 8.36 (dd, J = 8.2, 1.1 Hz, 1H), 7.89-7.88 (m, 2H), 7.74 (dd, J = 7.7, 1.4 Hz, 1H), 7.41-7.4 (m, 3H), 7.35-7.31 (m, 3H), 7.28-7.26 (m, 2H), 7.17 (t, J = 7.4 Hz, 1H), 6.82-6.80 (m, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.6, 148.6, 139.1, 138.7, 134.5, 134.4, 131.0, 130.5, 129.7, 129.2, 128.6, 127.2, 126.7, 126.1, 124.2, 121.6, 89.8; IR (KBr) ῡ 3293, 3058, 1672, 688, 524; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{16}INOSNa$ 479.9889; found 479.9904.



(Z)-N-(4-cyanophenyl)-3-phenyl-2-(phenylthio)acrylamide (3na): R_f = 0.5 (20% ethyl acetate in hexane); brownish white solid; yield 74% (64 mg); mp > 180 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.52 (s, 1H), 7.88-7.86 (m, 2H), 7.63-7.57 (m, 4H), 7.42-7.41 (m, 3H), 7.32-7.29 (m, 4H), 7.22-7.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 148.7(×2), 141.7, 134.2, 133.8, 133.3, 131.0, 130.8, 130.0, 128.7, 127.2, 123.5, 119.9, 118.9, 107.6; IR (KBr) ῡ 3325, 2359, 1661, 687; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}N_2OS$ 357.1056; found 357.1067.



(Z)-N-(4-nitrophenyl)-3-phenyl-2-(phenylthio)acrylamide (3oa): R_f = 0.3 (20% ethyl acetate in hexane); brownish white solid; yield 70% (59 mg); mp 156-157 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.53 (s, 1H), 8.18 (d, *J* = 8.8 Hz, 2H), 7.88-7.86 (m, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.43-7.41 (m, 3H), 7.31-7.30 (m, 4H), 7.23-7.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 149.0, 143.9, 143.5, 134.1, 133.7, 131.1, 130.8, 130.0, 128.7, 127.23, 127.18, 125.1, 123.5, 119.5; IR (KBr) ῡ 3356, 2924, 2359, 1700, 1558, 689; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}N_2O_3S$ 377.0954; found 377.0952.

(Z)-N-(3-chlorophenyl)-3-phenyl-2-(phenylthio)acrylamide (3pa): R_f = 0.8 (20% ethyl acetate in hexane); white solid; yield 98% (84 mg); mp 102-103 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.52 (s, 1H), 7.86-7.85 (m, 2H), 7.60 (s, 1H), 7.41-7.40 (m, 3H), 7.31-7.28 (m, 5H), 7.22-7.18 (m, 2H), 7.07 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.3, 148.1, 138.9, 134.8, 134.4, 134.1, 131.0, 130.5, 130.0, 129.9, 128.6, 127.1, 127.0, 124.8, 123.9, 120.2, 118.1; IR (KBr) ῡ 3341, 3059, 1667, 738, 689; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{16}ClNOSNa$ 388.0533; found 388.0545.

(Z)-N-(4-chloro-2-methylphenyl)-3-phenyl-2-(phenylthio)acrylamide (3qa): R_f = 0.85 (20% ethyl acetate in hexane); white solid; yield 98% (82 mg); mp 137-139 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.57 (s, 1H), 7.92 (d, *J* = 9.1 Hz, 1H), 7.87-7.85 (m, 2H), 7.42-7.40 (m, 3H), 7.30-7.29 (m, 4H), 7.21-7.18 (m, 1H), 7.17 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.09 (s, 1H), 1.94 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.0, 148.5, 134.6, 134.5, 134.4, 130.9, 130.6, 130.4, 130.2, 130.0, 129.8, 128.6, 126.84,

126.83, 126.81, 123.8, 123.3, 17.3; IR (KBr) ῡ 3351, 3056, 1670, 765, 690; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{18}ClNOSNa$ 402.0690; found 402.0674.

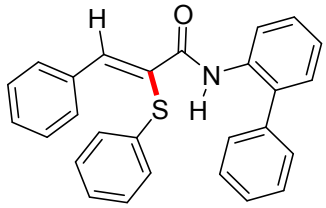
((Z)-N-benzyl-3-phenyl-2-(phenylthio)acrylamide (3ra): R_f = 0.45 (20% ethyl acetate in hexane); white solid; yield 88% (68 mg); mp 102-103 ºC; ^1H NMR (700 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.82 (d, *J* = 6.3 Hz, 2H), 7.39-7.36 (m, 4H), 7.28-7.26 (m, 2H), 7.23-7.21 (m, 3H), 7.20-7.17 (m, 3H), 6.91 (d, *J* = 6.3 Hz, 2H), 4.46 (d, *J* = 6.3 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.1, 146.7, 137.9, 134.8, 134.7, 130.8, 130.0, 129.7, 128.7, 128.5, 127.4, 127.4, 127.3, 126.6, 124.4, 44.4; IR (KBr) ῡ 3314, 2924, 2853, 1651, 690; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{19}NOSNa$ 368.1080; found 368.1080.

(Z)-N-(naphthalen-1-yl)-3-phenyl-2-(phenylthio)acrylamide (3sa): R_f = 0.4 (10% ethyl acetate in hexane); white solid; yield 78% (64 mg); mp 160-164 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.63 (s, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.91-7.89(m, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.49-7.45 (m, 2H), 7.45-7.41 (m, 6H), 7.34 (t, *J* = 7.8 Hz, 3H), 7.30-7.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 148.3, 134.6, 134.57, 134.1, 132.5, 130.9, 130.4, 129.9, 128.8, 128.6, 127.3 127.2, 126.9, 126.4, 126.0, 125.9, 125.9, 124.3, 120.6, 120.5; IR (KBr) ῡ 3366, 3052, 2360, 1671, 689; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{25}H_{19}NOSNa$ 404.1080; found 404.1093.

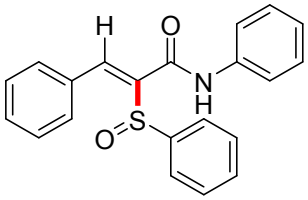
(Z)-3-phenyl-2-(phenylthio)-N-(quinolin-3-yl)acrylamide (3ta): R_f = 0.4 (30% ethyl acetate in hexane); white solid; yield 62% (52 mg); mp 169-173 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.73 (d,

J = 2.4 Hz, 1H), 8.60 (d, *J* = 2.5 Hz, 1H), 8.56 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.90-7.88 (m, 2H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.64-7.60 (m, 1H), 7.54-7.50 (m, 1H), 7.43-7.41 (m, 3H), 7.36-7.28 (m, 4H), 7.21-7.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 148.2, 145.9, 144.3, 134.3, 134.0, 131.3, 131.0, 130.6, 130.0, 129.2, 128.7, 128.6, 128.3, 127.9, 127.4, 127.3, 127.2, 124.2, 123.9; IR (KBr) ῡ 3346, 2954, 2339, 1663, 688; HRMS (ESI/Q-TOF) m/z: [M + H]$^+$ calcd for $C_{24}H_{19}N_2OS$ 383.1213; found 383.1235.

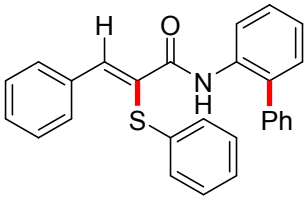
(Z)-N-([1,1'-biphenyl]-2-yl)-3-phenyl-2-(phenylthio)acrylamide (3ua): R_f = 0.75 (10% ethyl acetate in hexane); colorless liquid; yield 48% (39 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 8.66 (d, *J* = 8.2 Hz, 1H), 8.55 (s, 1H), 7.83-7.81 (m, 2H), 7.43-7.40 (m, 4H), 7.37-7.35 (m, 3H), 7.26-7.24 (m, 2H), 7.22-7.10 (m, 5H), 6.92-6.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 147.8, 138.0, 135.3, 134.5, 134.2, 132.3, 130.8, 130.2, 129.5, 129.4, 129.4, 129.1, 128.5, 128.5, 127.9, 126.7, 126.3, 124.4, 124.1, 120.0; IR (KBr) ῡ 3331, 2359, 1668, 689; HRMS (ESI/Q-TOF) m/z: [M + Na]$^+$ calcd for $C_{27}H_{21}NOSNa$ 4430.1236; found 430.1239.



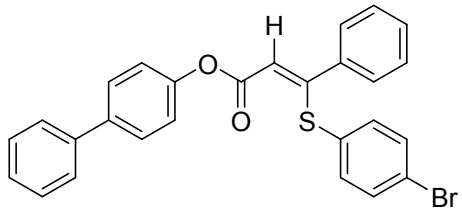
(R,Z)-N,3-diphenyl-2-(phenylsulfinyl)acrylamide 4: R_f = 0.55 (20% ethyl acetate in hexane); white solid; yield 90% (66 mg); mp 141-142 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.33 (s, 1H), 8.40 (s, 1H), 7.68-7.66 (m, 2H), 7.60-7.59 (m, 2H), 7.50-7.44 (m, 8H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.09 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 161.4, 147.8, 141.4, 137.8, 134.9, 132.5, 131.3, 130.94, 130.90, 129.8, 129.1(×2), 124.7, 124.4, 120.8; IR (KBr) ῡ 3352, 3058, 2348, 1677, 1316, 690; HRMS (ESI/Q-TOF) m/z: [M + Na]$^+$ calcd for $C_{21}H_{17}NO_2SNa$ 370.0872; found 370.0862.



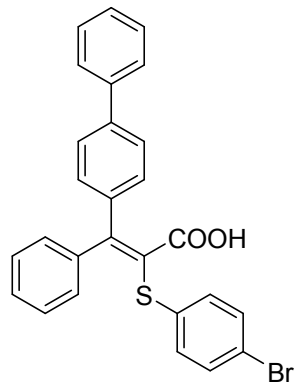
(Z)-N-([1,1'-biphenyl]-2-yl)-3-phenyl-2-(phenylthio)acrylamide 5: R_f = 0.85 (20% ethyl acetate in hexane); liquid; yield 98% (58 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.41 (s, 1H), 8.62 (d, *J* = 7.7 Hz, 1H), 8.52 (s, 1H), 7.81-7.80 (m, 2H), 7.43-7.35 (m, 7H), 7.24 (dd, *J* = 7.7, 1.4 Hz, 2H), 7.20-7.20-7.18 (m, 1H), 7.18-7.15 (m, 2H), 7.14 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.1, 147.9, 138.0, 135.3, 134.5, 134.2, 132.3, 130.9, 130.2, 129.5, 129.4, 129.2(×2), 128.6, 128.5, 128.0, 126.7, 126.4, 124.4, 124.2, 120.1; IR (KBr) ῡ 3334, 3057, 1642, 1495, 691; HRMS (ESI/Q-TOF) m/z: [M + H]$^+$ calcd for $C_{27}H_{22}NOS$ 408.1417; found 408.1423.



[1,1'-biphenyl]-4-yl (Z)-3-((4-bromophenyl)thio)-3-phenylacrylate 7: R_f = 0.4 (10% ethyl acetate in hexane); white solid; yield 42% (41 mg); mp 108-112 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.51 (m, 4H), 7.43-7.27 (m, 5H), 7.22-7.12 (m, 6H), 6.98-6.88 (m, 3H), 6.26 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 161.9, 150.3, 140.6, 139.0, 137.9, 137.0, 135.5, 133.4, 131.8, 129.2, 128.9, 128.9, 128.3, 127.4, 127.3, 122.6, 122.1, 115.5; IR (KBr) ῡ 3055, 2923, 2360, 1712, 690.

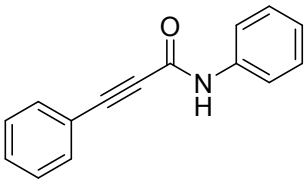


(E)-3-([1,1'-biphenyl]-4-yl)-2-((4-bromophenyl)thio)-3-phenylacrylic acid 8[6]: R_f = 0.5 (40% ethyl acetate in hexane); yellow solid; yield 56% (54 mg); ^{1}H NMR (400 MHz, DMSO) δ 12.99 (s, 1H), 7.68-7.65 (m, 4H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.42-7.37 (m, 3H), 7.36-7.33 (m, 3H), 7.31-7.28 (m, 4H); ^{13}C NMR (100 MHz, DMSO) δ 167.4, 149.6, 140.4, 140.1, 139.8, 139.3, 133.7, 132.0,

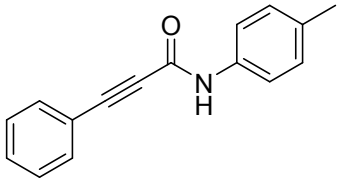


131.3, 129.1, 129.0, 128.8, 128.5, 128.3, 127.8, 126.6, 126.5, 125.9, 120.1; IR (KBr) ῡ 3475, 2924, 1680, 698.

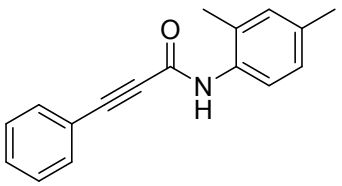
N,3-diphenylpropiolamide 1a:[7] R_f = 0.7 (20% ethyl acetate in hexane); brownish white solid; yield 90% (650 mg); mp 126-128 ºC (lit.[7]124-125 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.59-7.55 (m, 4H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.38-7.32 (m, 4H), 7.14 (t, *J* = 7.4 Hz, 1H).



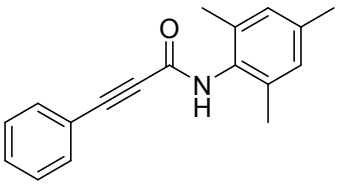
3-phenyl-N-(p-tolyl)propiolamide 1b:[8] R_f = 0.8 (20% ethyl acetate in hexane); yellow solid; yield 91% (598 mg); mp 144-145 ºC (lit.[8]143-145); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.58-7.56 (m, 2H), 7.46-7.42 (m, 3H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H).



N-(2,4-dimethylphenyl)-3-phenylpropiolamide 1c:[9] R_f = 0.85 (20% ethyl acetate in hexane); brown solid; yield 74% (450 mg); mp 136-138 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.46-7.43 (m, 1H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.31-7.26 (m, 1H), 7.09-7.02 (m, 2H), 2.31 (s, 3H), 2.29 (s, 3H).

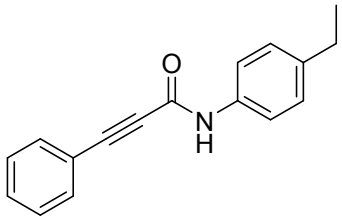


N-mesityl-3-phenylpropiolamide 1d: R_f = 0.85 (20% ethyl acetate in hexane); yellow solid; yield 63% (355 mg); mp 140-142 ºC; ^{1}H NMR (400 MHz, DMSO) δ 10.02 (s, 1H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.48-7.40 (m, 3H), 6.83 (s, 2H), 2.16 (s, 3H), 2.06 (s, 6H); ^{13}C NMR (100 MHz, DMSO) δ 150.8, 136.2, 134.9, 132.3, 131.2, 130.4, 129.1, 128.4, 119.8, 84.1, 83.7,



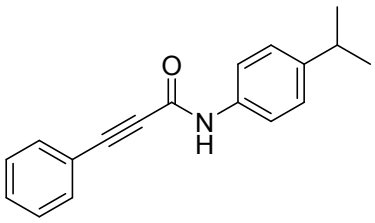
20.5, 18.1; IR (KBr) ῡ 3212, 2981, 2920, 2217, 1634; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{17}NONa$ 286.1202; found 286.1216.

N-(4-ethylphenyl)-3-phenylpropiolamide 1e: R_f = 0.5 (20% ethyl acetate in hexane);



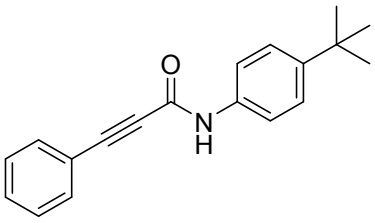
yellow solid; yield 93% (575 mg); mp 126-128 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.57 (d, *J* = 6.8 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.39-7.35 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 135.2, 132.7, 130.3, 128.6, 128.4, 120.35, 120.30, 120.1, 85.7, 83.7, 28.4, 15.7; IR (KBr) ῡ 3262, 2964, 2209, 1636; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{16}NO$ 250.1226; found 250.1235.

N-(4-isopropylphenyl)-3-phenylpropiolamide 1f: R_f = 0.6 (20% ethyl acetate in hexane);



brown solid; yield 82% (480 mg); mp 133-136 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.52 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 2.90 (sept, *J* = 6.8 Hz, 1H), 1.24 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 145.9, 135.1, 132.7, 130.4, 128.7, 127.2, 120.25, 120.17, 85.7, 83.6, 33.8, 24.1; IR (KBr) ῡ 3259, 2956, 2209, 1639; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{18}NO$ 264.1383; found 264.1394.

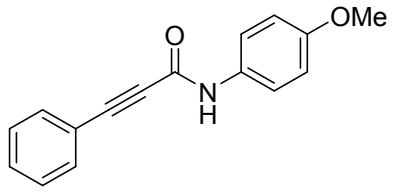
N-(4-(tert-butyl)phenyl)-3-phenylpropiolamide 1g: R_f = 0.8 (20% ethyl acetate in hexane);



yellow solid; yield 87% (489 mg); mp 148-150 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.52 (s, 1H); 7.51-7.47 (m, 2H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.40-7.36 (m,

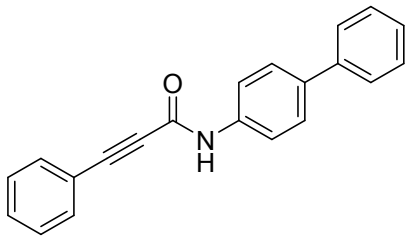
4H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 148.1, 134.8, 132.7, 130.4, 128.7, 126.1, 120.2, 119.9, 85.7, 83.7, 34.6, 31.4; IR (KBr) ῡ 3258, 3055, 2962, 2211, 1632; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{19}NONa$ 300.1359; found 300.1344.

N-(4-methoxyphenyl)-3-phenylpropiolamide 1h:[10] R_f = 0.4 (20% ethyl acetate in hexane);



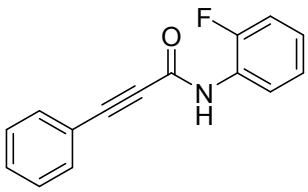
brownish solid; yield 93% (570 mg); mp 128-130 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.56 (m, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.39-7.36 (m, 2H), 7.32-7.30 (m, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H).

N-([1,1'-biphenyl]-4-yl)-3-phenylpropiolamide 1i: R_f = 0.7 (20% ethyl acetate in hexane);



yellow solid; yield 75% (399 mg); mp 184-186 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.64 (m, 3H), 7.60-7.57 (m, 6H), 7.47-7.32 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 140.5, 138.0, 136.7, 132.8, 130.5, 129.0, 128.8, 127.9, 127.4, 127.0, 120.4, 120.1, 86.0, 83.6; IR (KBr) ῡ 3258, 2923, 2359, 1639; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{16}NO$ 298.1226; found 298.1227.

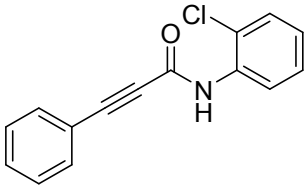
N-(2-fluorophenyl)-3-phenylpropiolamide 1j: R_f = 0.8 (20% ethyl acetate in hexane);



yellow solid; yield 85% (550 mg); mp 110-113 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (t, *J* = 8.0 Hz, 1H), 7.77 (s, 1H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.49-7.44 (m, 1H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.17-7.08 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 151.00, 150.9, 132.8, 130.6, 128.7, 125.1 (d, $^3J_{CF}$ = 7.6 Hz), 124.8 (d, $^4J_{CF}$ = 3.5 Hz), 122.1, 119.9, 115.0 (d, $^2J_{CF}$ = 19.1 Hz), 86.3, 83.3;

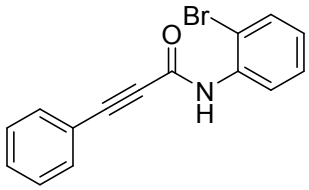
IR (KBr) $\bar{\upsilon}$ 3232, 2212, 1649, 1322; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{10}FNONa$ 262.0639; found 262.0629.

N-(2-chlorophenyl)-3-phenylpropiolamide 1k:[11] R_f = 0.8 (20% ethyl acetate in hexane);



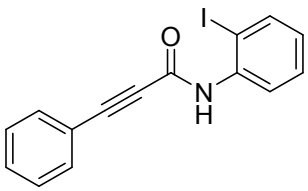
off white solid; yield 84% (620 mg); mp 104-105 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.4 Hz, 1H), 8.00 (s, 1H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.48-7.45 (m, 1H), 7.42-7.38 (m, 3H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H).

N-(2-bromophenyl)-3-phenylpropiolamide 1l:[11] R_f = 0.6 (20% ethyl acetate in hexane);



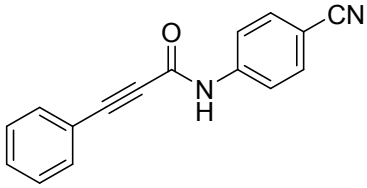
yellowish white solid; yield 76% (401 mg); mp 101-103 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.0 Hz, 1H), 7.99 (s, 1H), 7.63-7.56 (m, 3H), 7.48-7.45 (m, 1H), 7.42-7.38 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H).

N-(2-iodophenyl)-3-phenylpropiolamide 1m:[11] R_f = 0.8 (20% ethyl acetate in hexane);



brown solid; yield 66% (315 mg); mp 100-103 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.42-7.36 (m, 4H), 6.89 (t, *J* = 7.2 Hz, 1H).

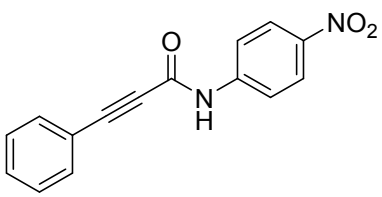
N-(4-cyanophenyl)-3-phenylpropiolamide 1n: R_f = 0.3 (20% ethyl acetate in hexane);



brown solid; yield 64% (401 mg); mp 156-158 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 151.1, 141.4, 133.5,

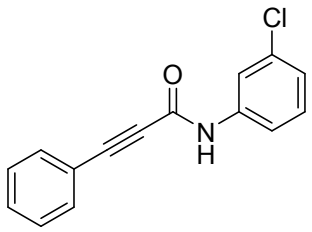
132.9, 130.9, 128.9, 119.8, 119.5, 118.7, 108.0, 87.3, 83.0; IR (KBr) ῡ 3288, 2923, 2210, 1650, 1592; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{11}N_2O$ 247.0866; found 247.0859.

N-(4-nitrophenyl)-3-phenylpropiolamide 1o: R_f = 0.45 (20% ethyl acetate in hexane);



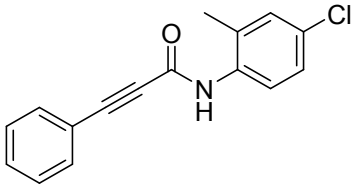
yellowish white solid; yield 67% (389 mg); mp 166-168 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.91 (s, 1H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.50-7.45 (m, 1H), 7.42-7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 144.0, 143.2, 133.2, 132.8, 131.0, 128.8, 125.3, 119.5, 87.7, 82.9; IR (KBr) ῡ 3266, 2207, 1642, 1552, 1331; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{10}N2O_3$ 267.0764; found 267.0767.

N-(3-chlorophenyl)-3-phenylpropiolamide 1p:[12] R_f = 0.6 (20% ethyl acetate in hexane);



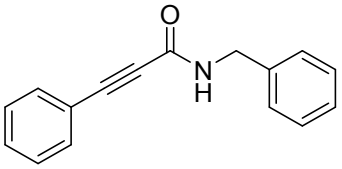
brown solid; yield 95% (686 mg); mp 110-112 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.59-7.56 (m, 2H), 7.47-7.36 (m, 4H), 7.29-7.26 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 1H).

N-(4-chloro-2-methylphenyl)-3-phenylpropiolamide 1q: R_f = 0.55 (20% ethyl acetate in

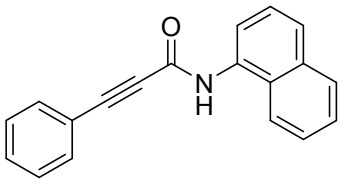


hexane); off white solid; yield 86% (585 mg); mp 146-148 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.8 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.48-7.44 (m, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.30 (s, 1H), 7.21 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 133.7, 132.8, 130.95, 130.92, 130.6, 130.5, 128.8, 127.1, 124.5, 119.9, 86.2, 83.3, 17.9; IR (KBr) ῡ 3195, 2359, 1628, 1518, 756; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{13}ClNO$ 270.0680; found 270.0686.

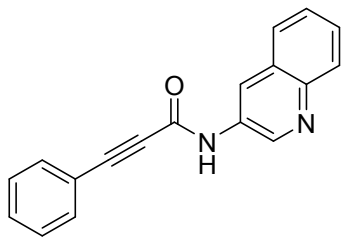
N-benzyl-3-phenylpropiolamide 1r:[13] R_f = 0.6 (20% ethyl acetate in hexane); yellowish white solid; yield 90% (586 mg); mp 116-118 ºC (lit[13].108-110 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.51 (m, 2H), 7.43-7.40 (m, 2H), 7.37-7.31 (m, 7H), 4.55 (d, *J* = 6.0 Hz, 2H).



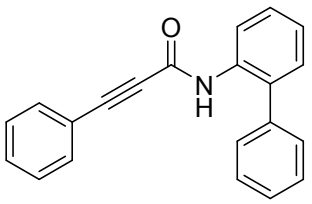
N-(naphthalen-1-yl)-3-phenylpropiolamide (1s):[14] R_f = 0.45 (10% ethyl acetate in hexane); yellow solid; yield 61% (350 mg); mp 177-181 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.59-7.51 (m, 3H), 7.50-7.47 (m, 1H), 7.43-7.39 (m, 2H).



3-phenyl-N-(quinolin-3-yl)propiolamide (1t): R_f = 0.35 (30% ethyl acetate in hexane); white solid; yield 35% (200 mg); mp 154-156 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.85 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 2H), 7.51-7.48 (m, 2H), 7.42-7.39 (m, 1H), 7.33-7.30 (m, 2H); IR (KBr) ῡ 3345, 2929, 2360, 1663; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{13}N_2O$ 273.1022; found 273.1037.



N-([1,1'-biphenyl]-2-yl)-3-phenylpropiolamide (1u):[11] R_f = 0.6 (20% ethyl acetate in hexane); brownish white solid; yield 62% (330 mg); mp 171-174 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.2 Hz, 1H), 7.54-7.46 (m, 5H), 7.44-7.38 (m, 5H), 7.36-7.32 (m, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.24-7.20 (m, 1H).



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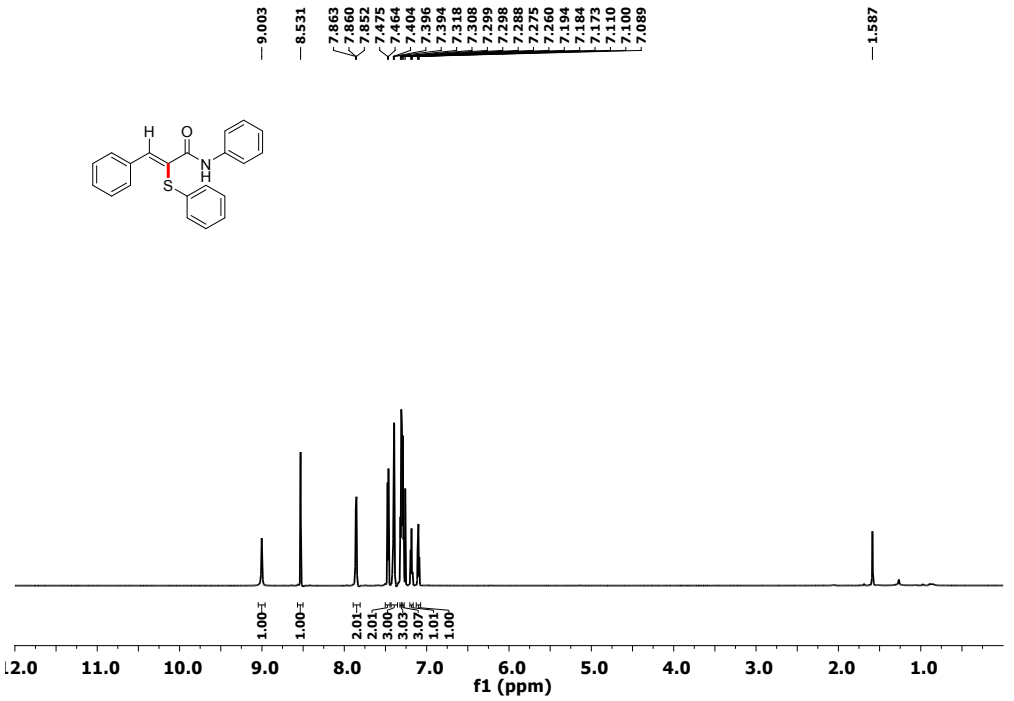


Fig. S15. ^{1}H NMR spectrum of (Z)-N,3-diphenyl-2-(phenylthio)acrylamide (**3aa**)

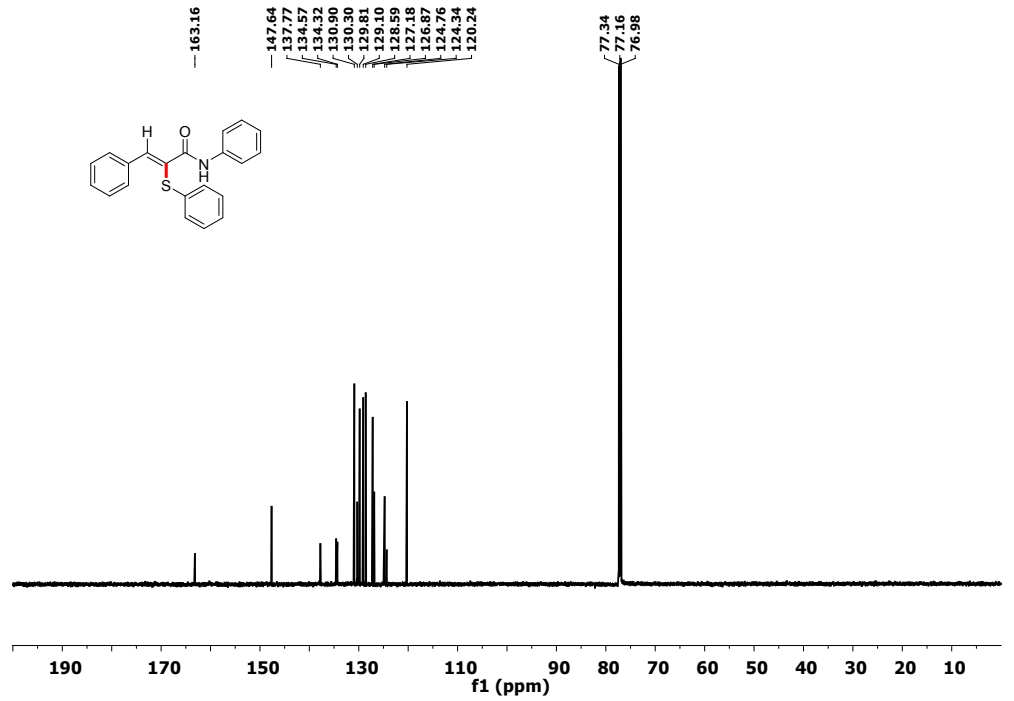


Fig. S16. ^{13}C NMR spectrum of (Z)-N,3-diphenyl-2-(phenylthio)acrylamide (**3aa**)

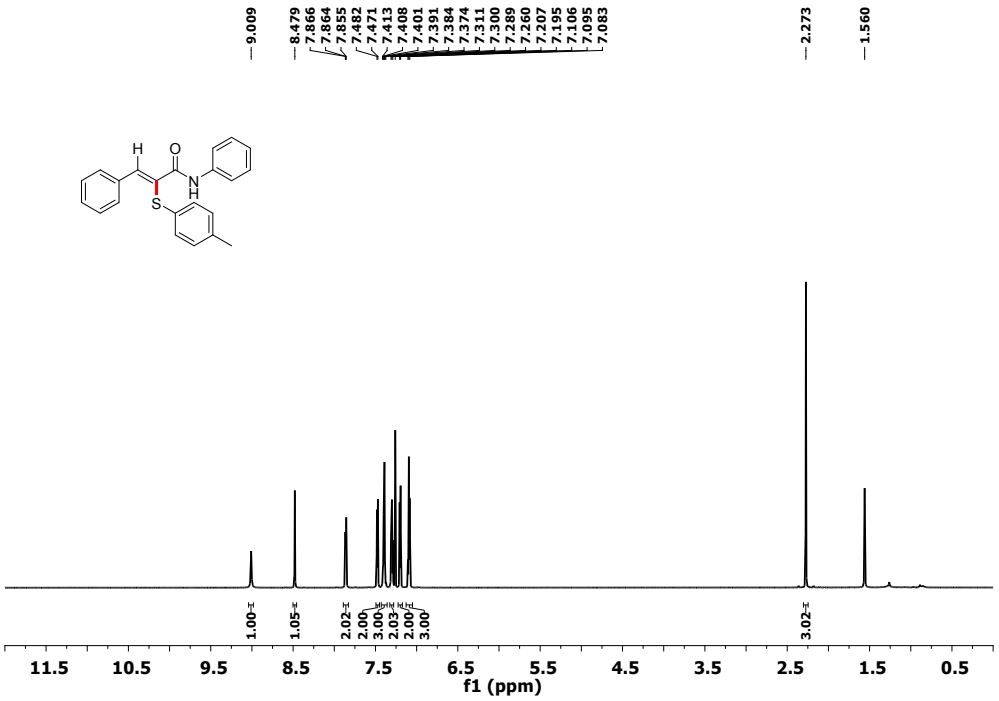


Fig. S17. [1]H NMR spectrum of (Z)-N,3-diphenyl-2-(p-tolylthio)acrylamide (**3ab**)

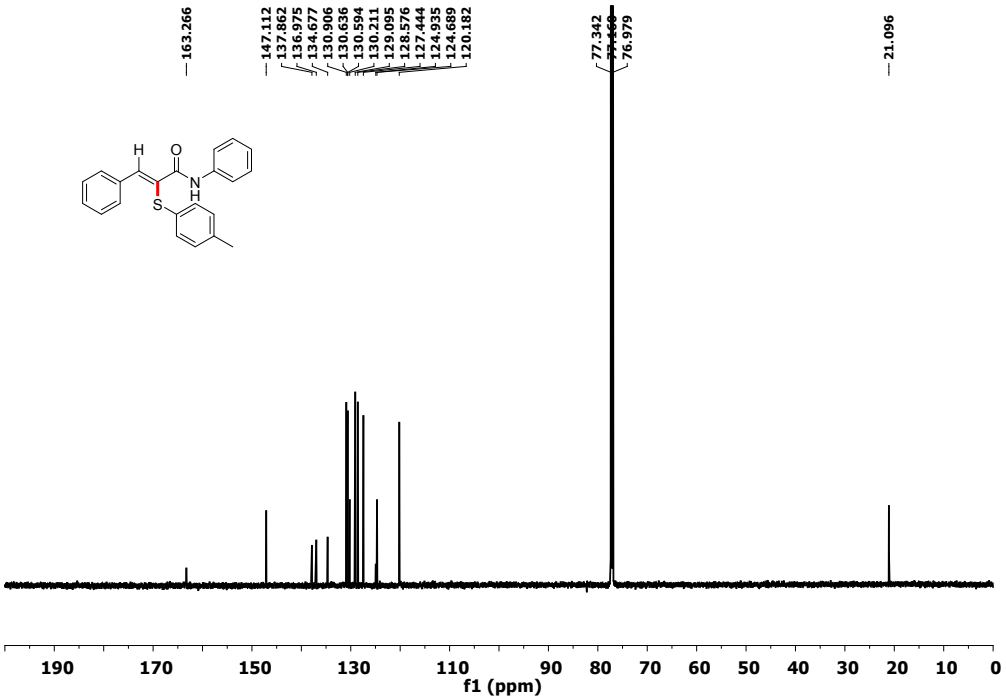


Fig. S18. [13]C NMR spectrum of (Z)-N,3-diphenyl-2-(p-tolylthio)acrylamide (**3ab**)

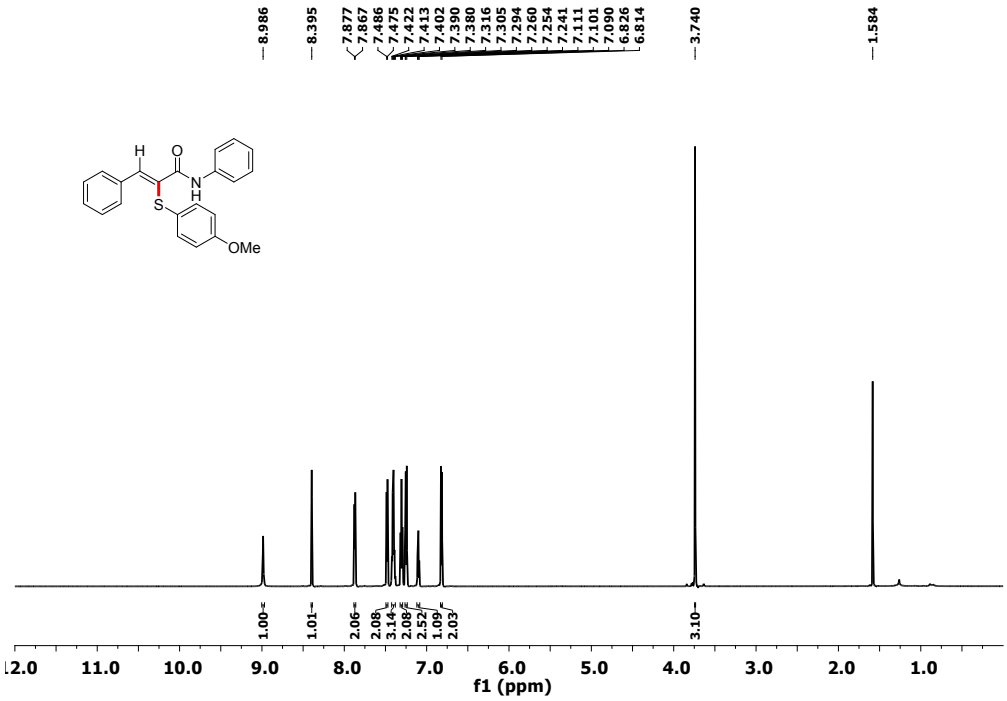


Fig. S19. ^{1}H NMR spectrum of (Z)-2-((4-methoxyphenyl)thio)-N,3-diphenylacrylamide **(3ac)**

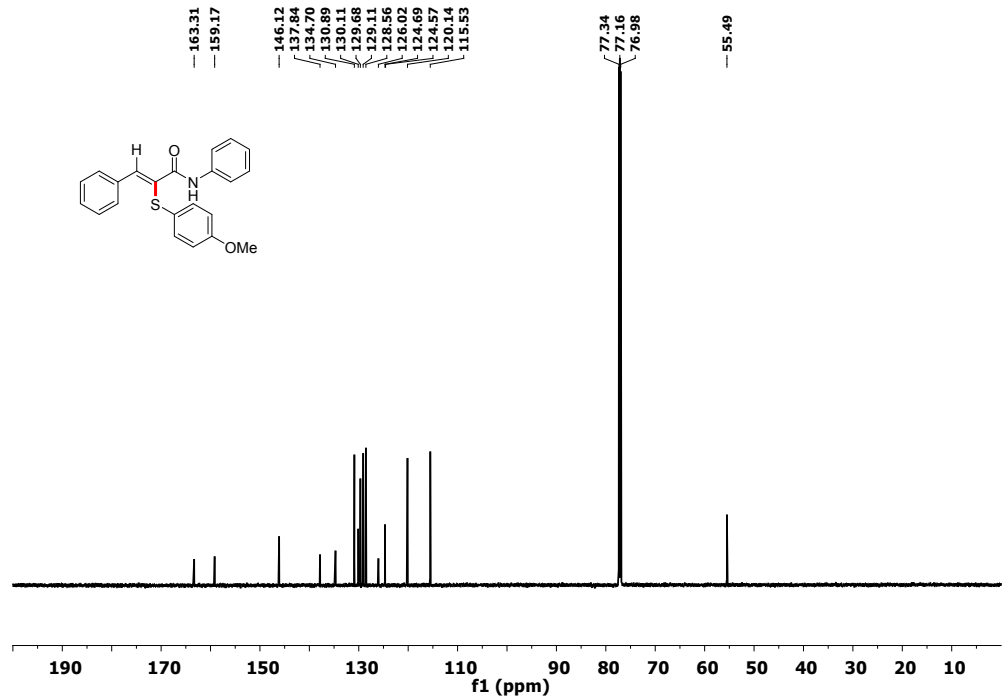


Fig. S20. ^{13}C NMR spectrum of (Z)-2-((4-methoxyphenyl)thio)-N,3-diphenylacrylamide **(3ac)**

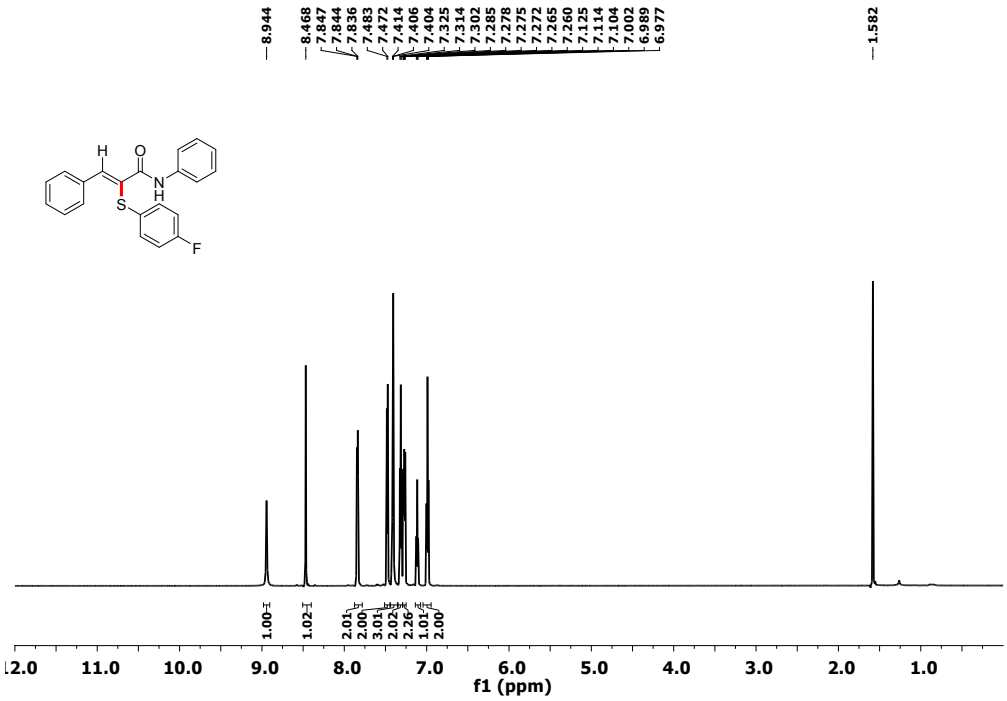


Fig. S21. [1]H NMR spectrum of (Z)-2-((4-fluorophenyl)thio)-N,3-diphenylacrylamide **(3ad)**

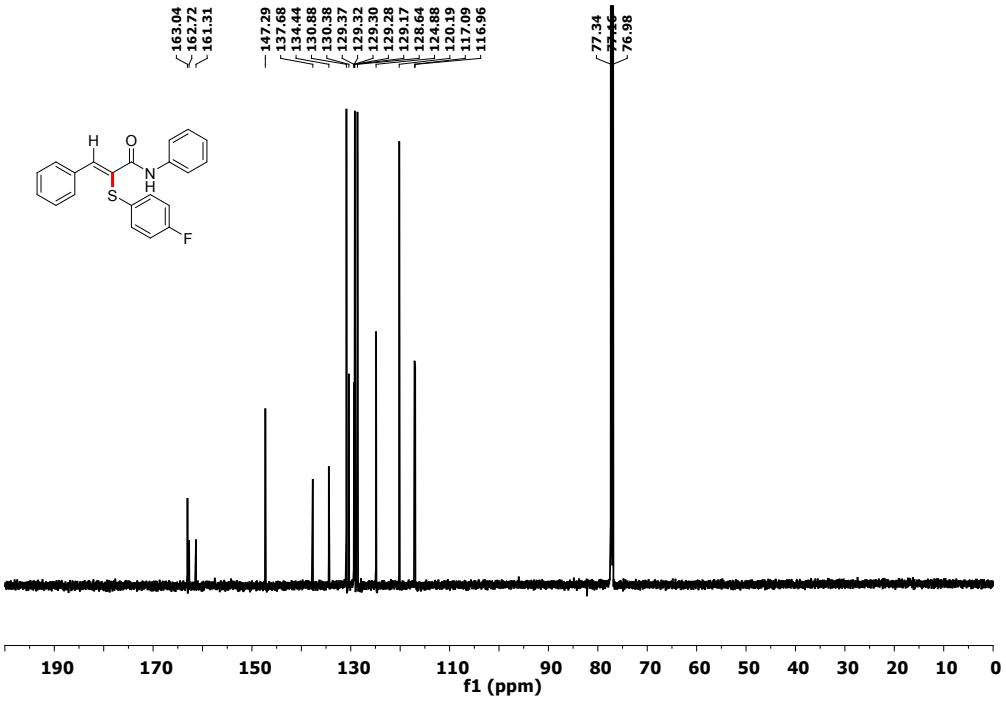


Fig. S22. [13]C NMR spectrum of (Z)-2-((4-fluorophenyl)thio)-N,3-diphenylacrylamide **(3ad)**

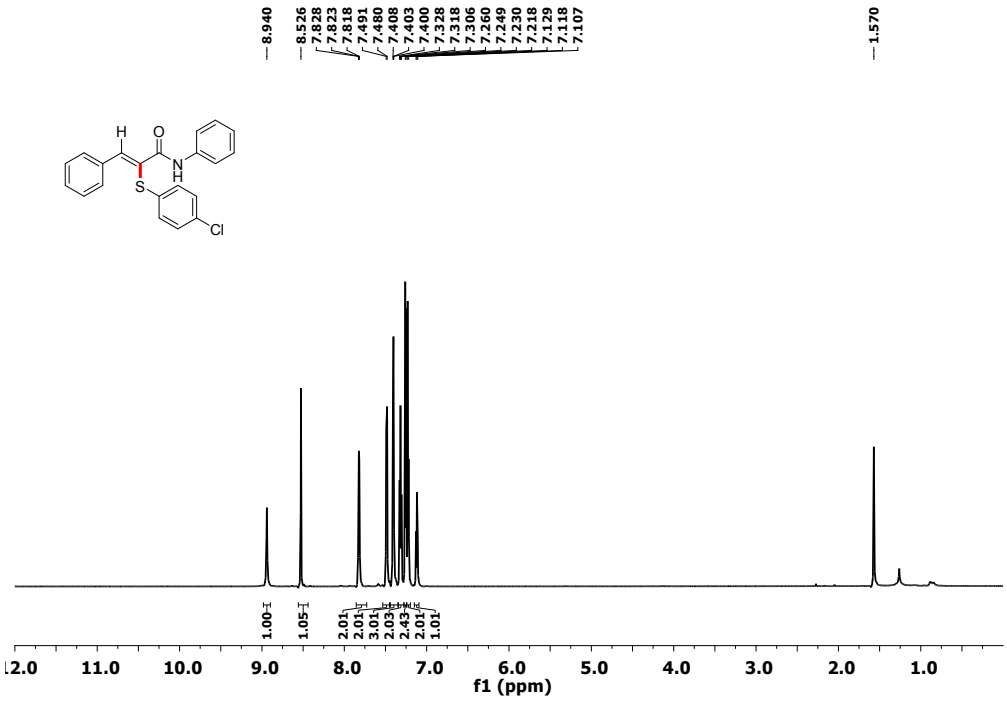


Fig. S23. [1]H NMR spectrum of (Z)-2-((4-chlorophenyl)thio)-N,3-diphenylacrylamide **(3ae)**

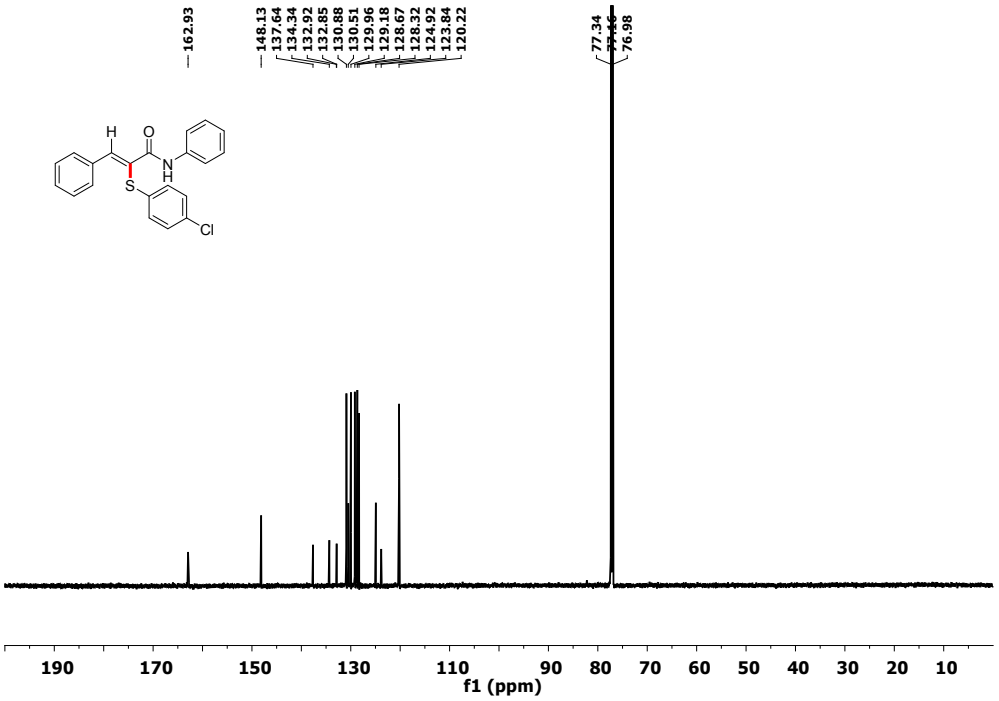


Fig. S24. [13]C NMR spectrum of (Z)-2-((4-chlorophenyl)thio)-N,3-diphenylacrylamide **(3ae)**

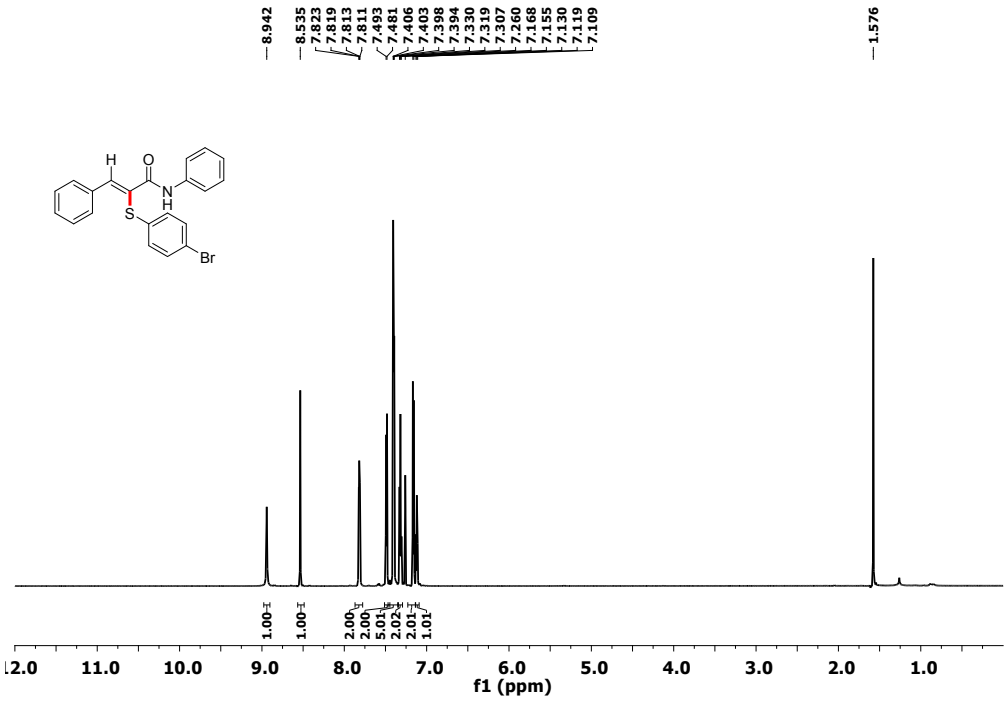


Fig. S25. [1]H NMR spectrum of (Z)-2-((4-bromophenyl)thio)-N,3-diphenylacrylamide **(3af)**

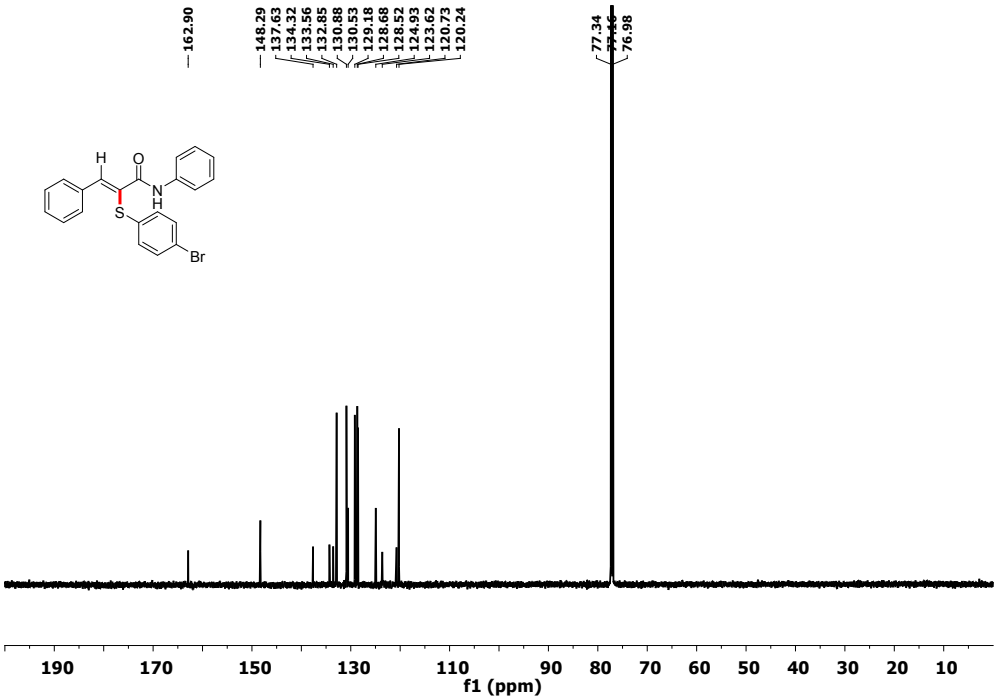


Fig. S26. [13]C NMR spectrum of (Z)-2-((4-bromophenyl)thio)-N,3-diphenylacrylamide **(3af)**

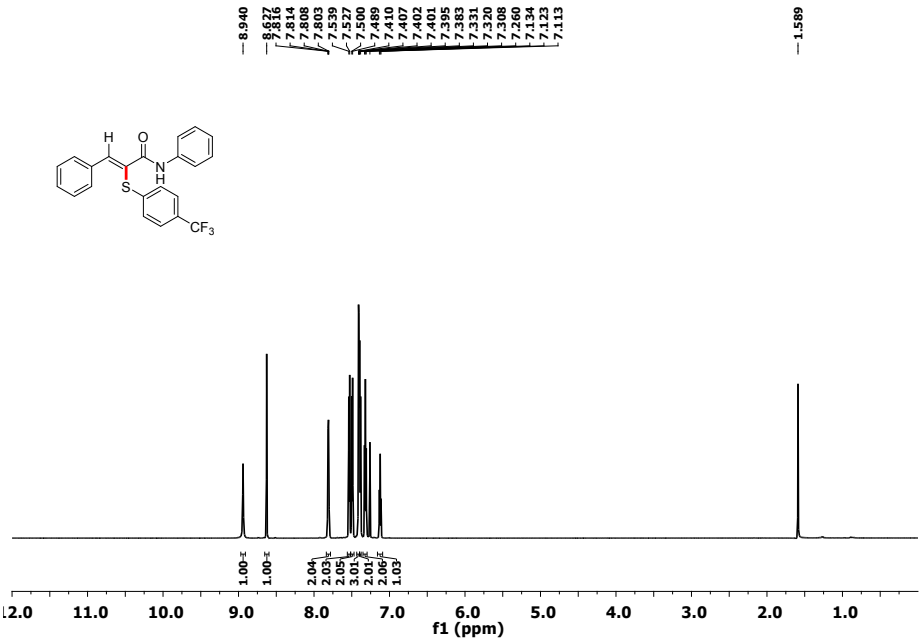


Fig.S27.[1]H NMR spectrum of (Z)-N,3-diphenyl-2((4(trifluoromethyl)phenyl)thio)acrylamide **(3ag)**

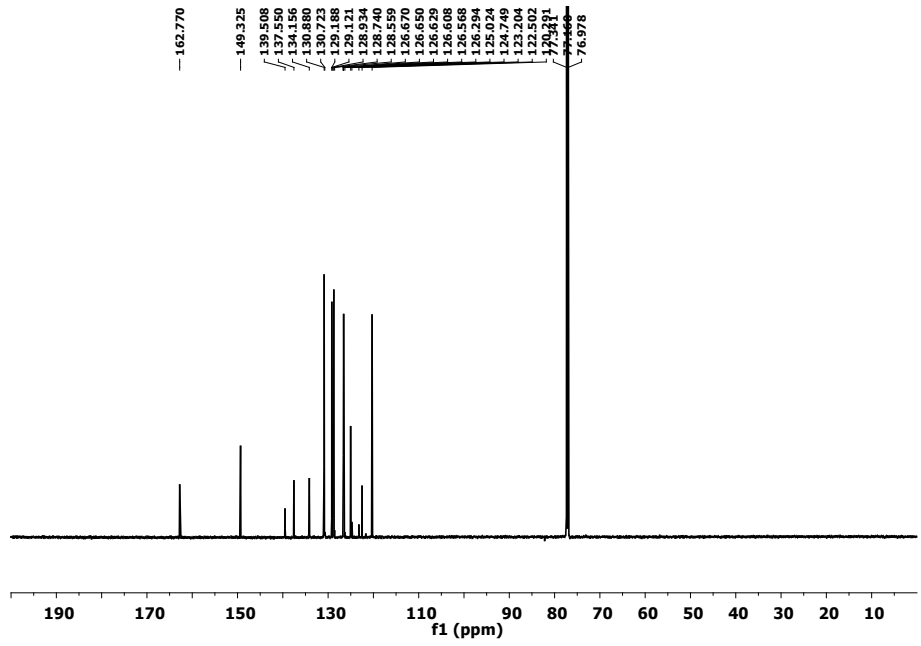


Fig. S28. [13]C NMR spectrum of (Z)-N,3-diphenyl-2-((4-(trifluoromethyl)phenyl)thio)acrylamide **(3ag)**

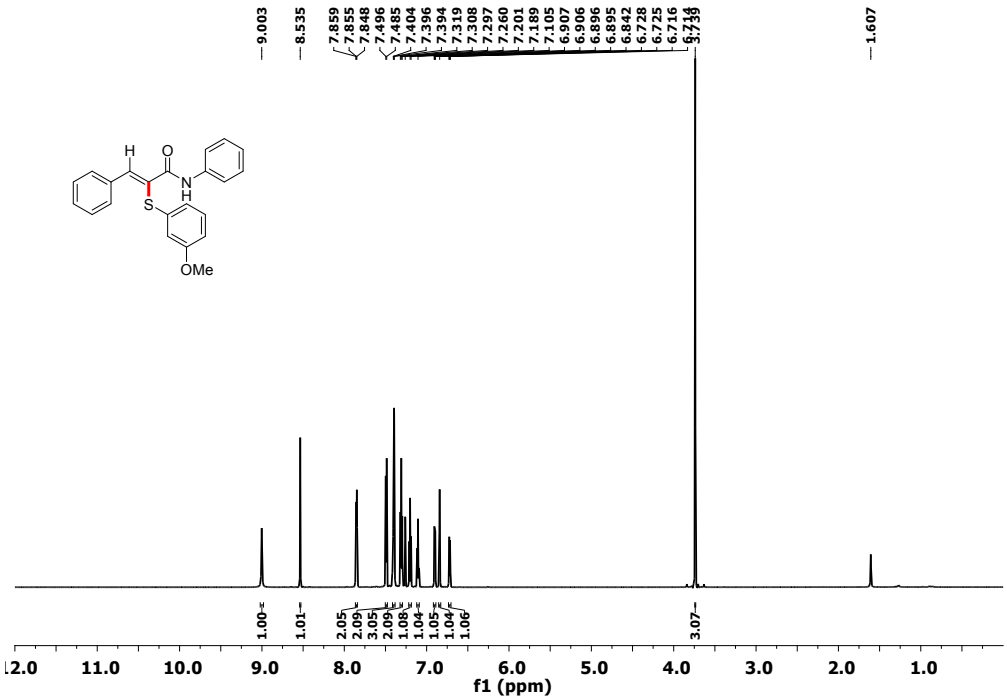


Fig. S29. [1]H NMR spectrum of (Z)-2-((3-methoxyphenyl)thio)-N,3-diphenylacrylamide

(3ah)

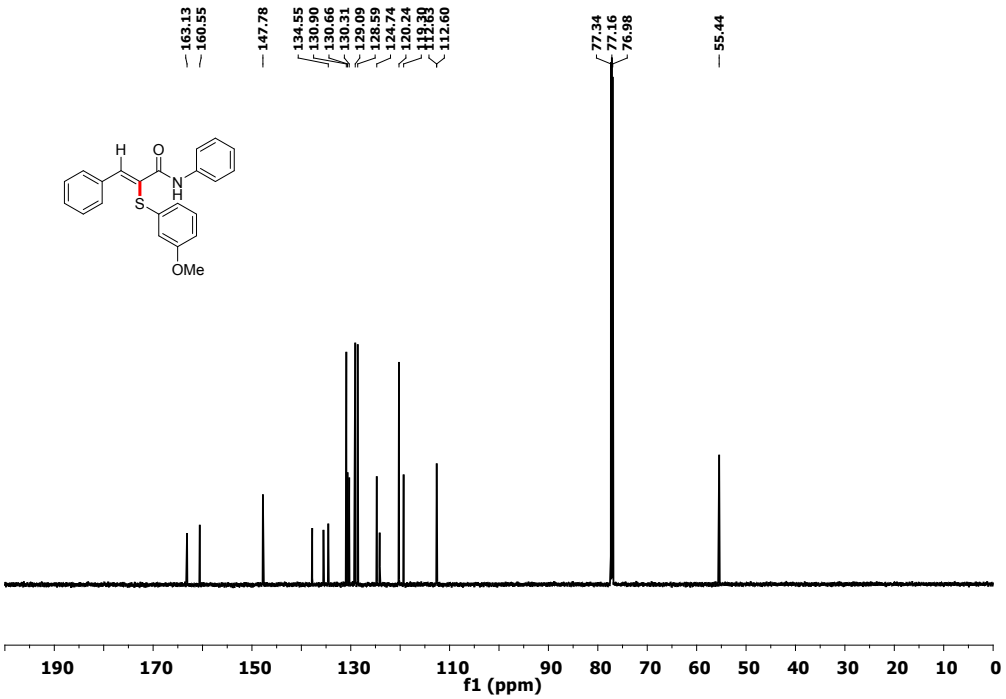


Fig. S30. [13]C NMR spectrum of (Z)-2-((3-methoxyphenyl)thio)-N,3-diphenylacrylamide

(3ah)

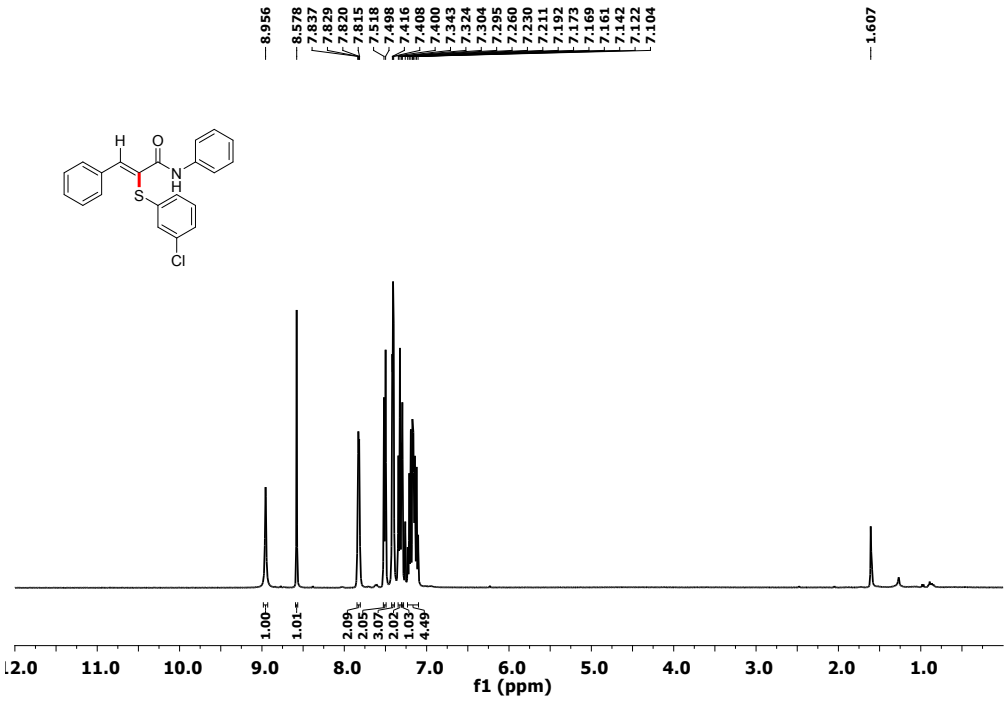


Fig. S31. [1]H NMR spectrum of (Z)-2-((3-chlorophenyl)thio)-N,3-diphenylacrylamide **(3ai)**

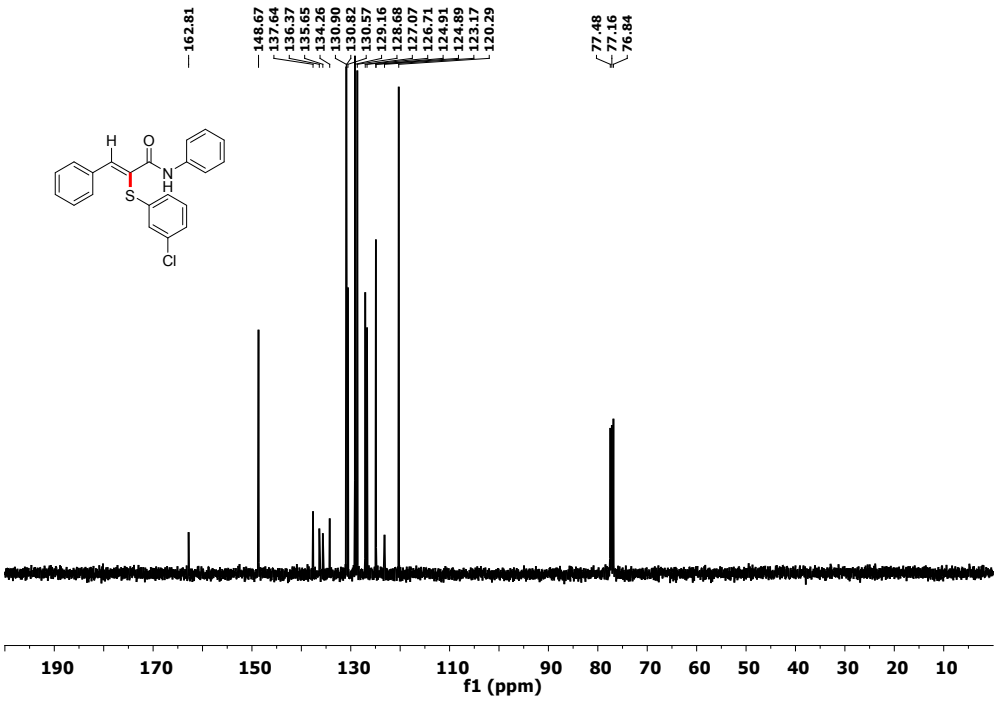


Fig. S32. [13]C NMR spectrum of (Z)-2-((3-chlorophenyl)thio)-N,3-diphenylacrylamide **(3ai)**

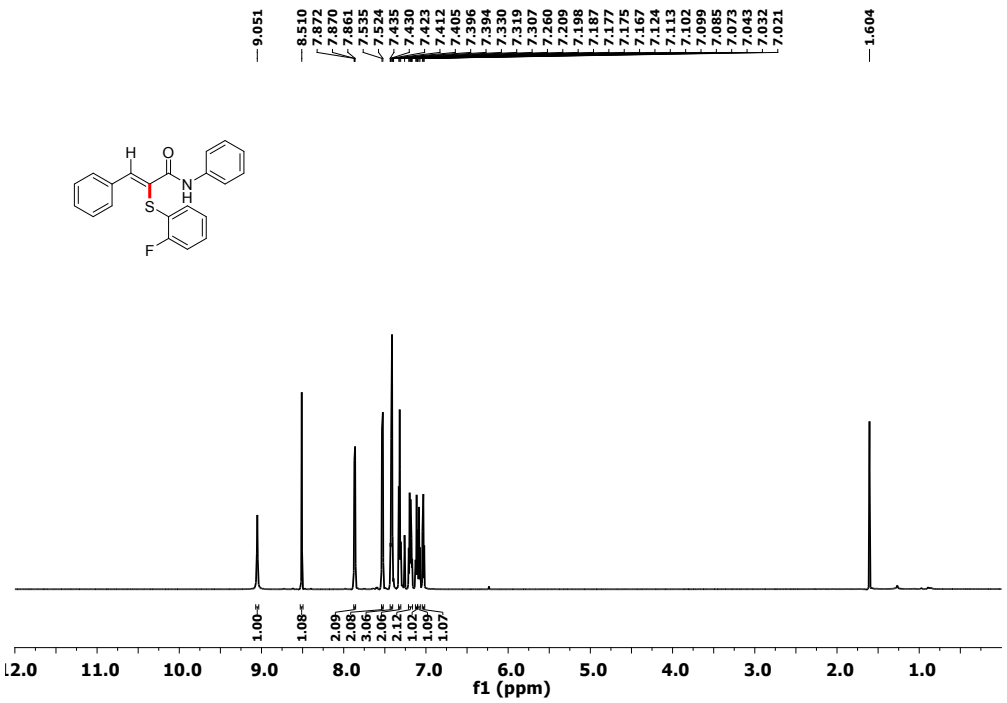


Fig. S33. ^{1}H NMR spectrum of (Z)-2-((2-fluorophenyl)thio)-N,3-diphenylacrylamide **(3aj)**

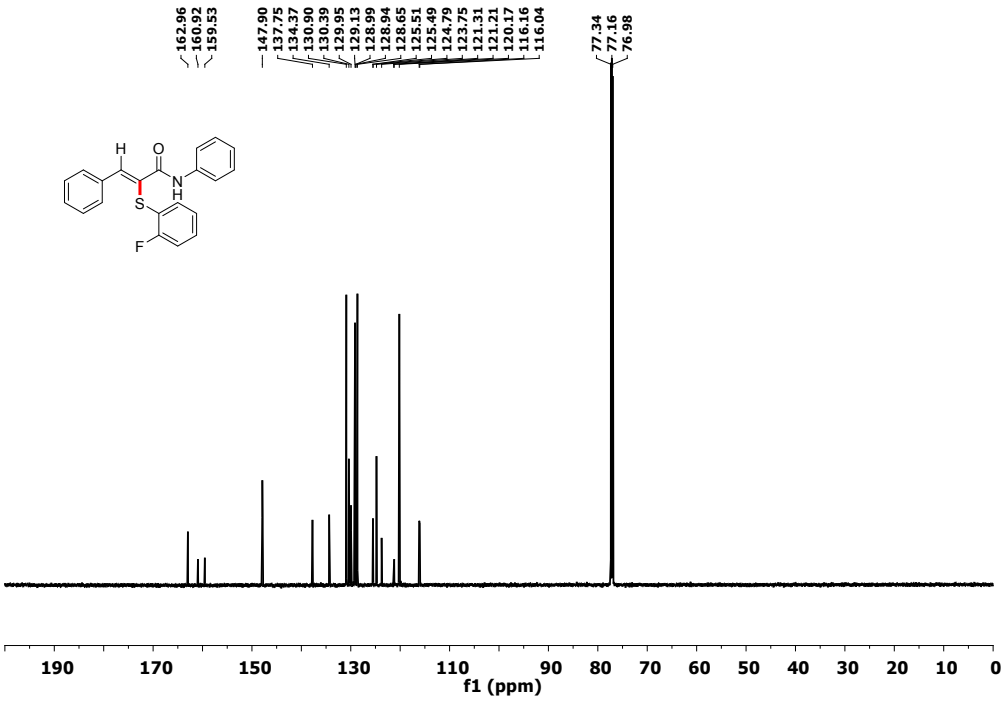


Fig. S34. ^{13}C NMR spectrum of (Z)-2-((2-fluorophenyl)thio)-N,3-diphenylacrylamide **(3aj)**

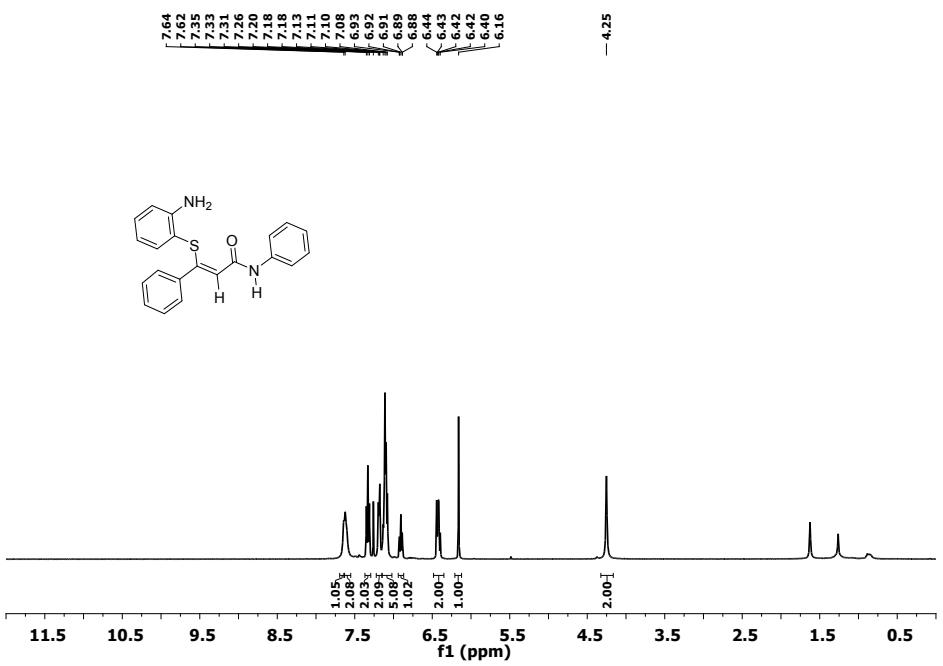


Fig. S35. [1]H NMR spectrum of (Z)-3-((2-aminophenyl)thio)-N,3-diphenylacrylamide **(3ak)**

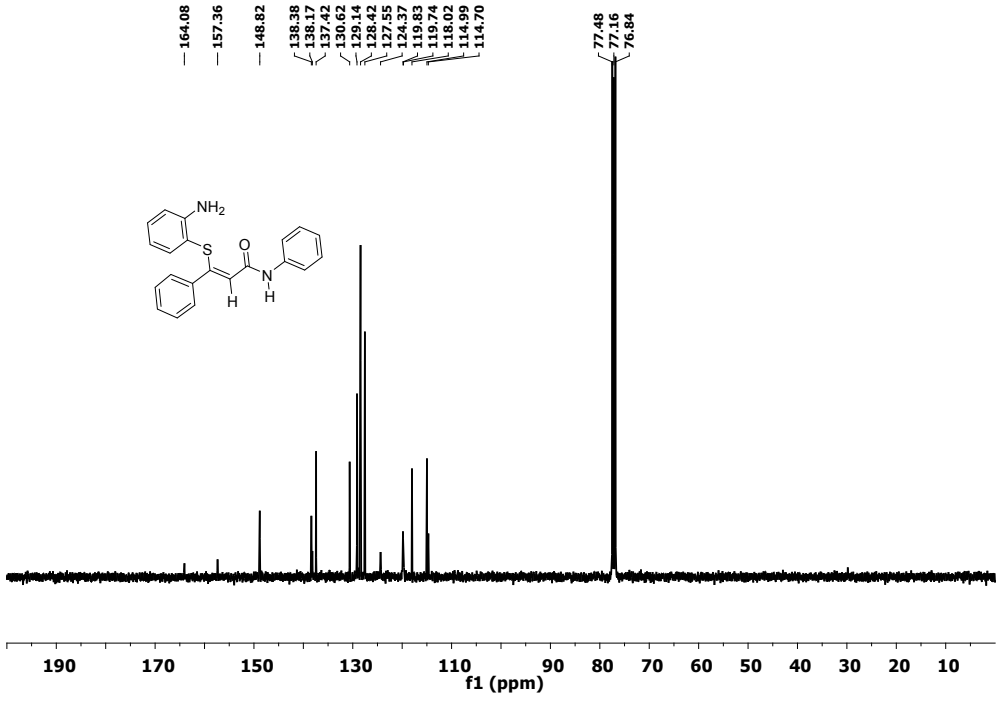


Fig. S36. [13]C NMR spectrum of (Z)-2-((2-aminophenyl)thio)-N,3-diphenylacrylamide **(3ak)**

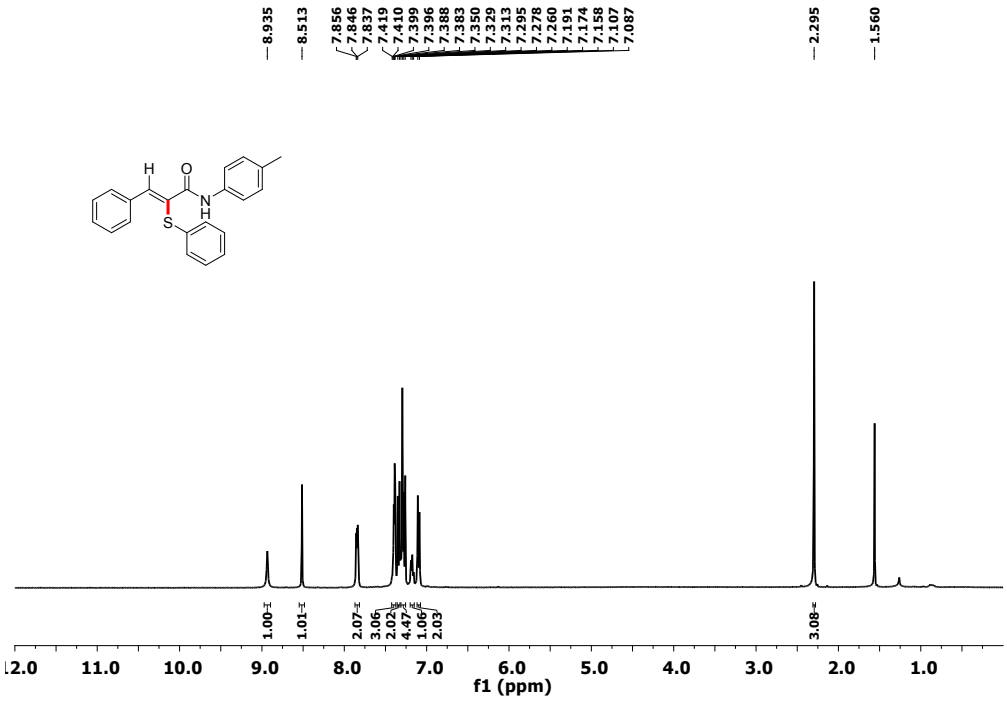


Fig. S37. ^{1}H NMR spectrum of (Z)-3-phenyl-2-(phenylthio)-N-(p-tolyl)acrylamide **(3ba)**

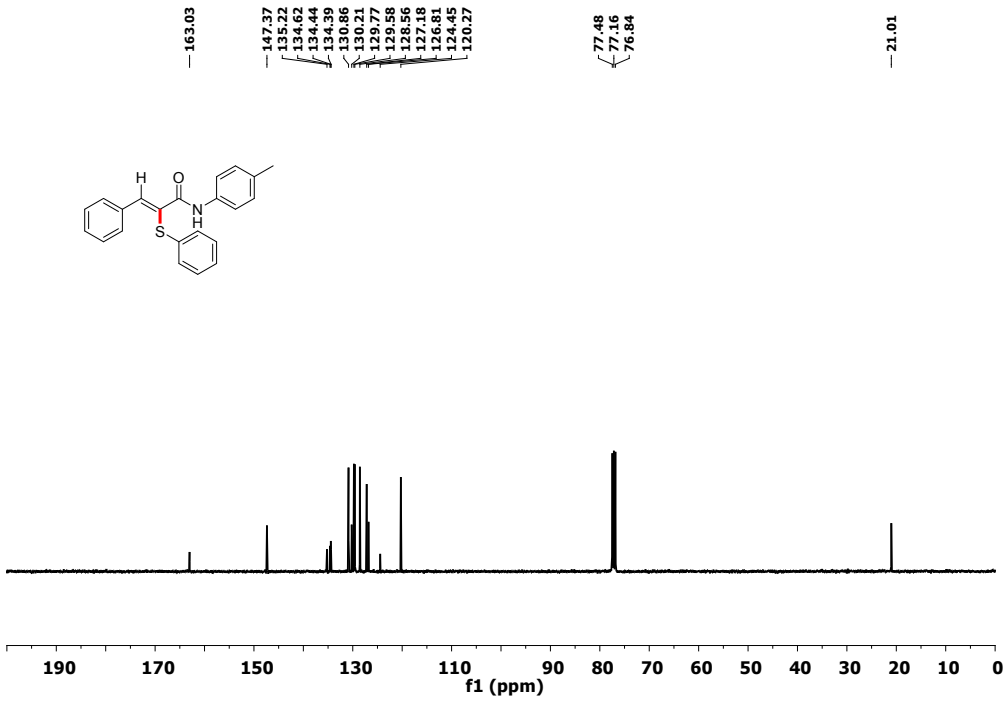


Fig. S38. ^{13}C NMR spectrum of (Z)-3-phenyl-2-(phenylthio)-N-(p-tolyl)acrylamide **(3ba)**

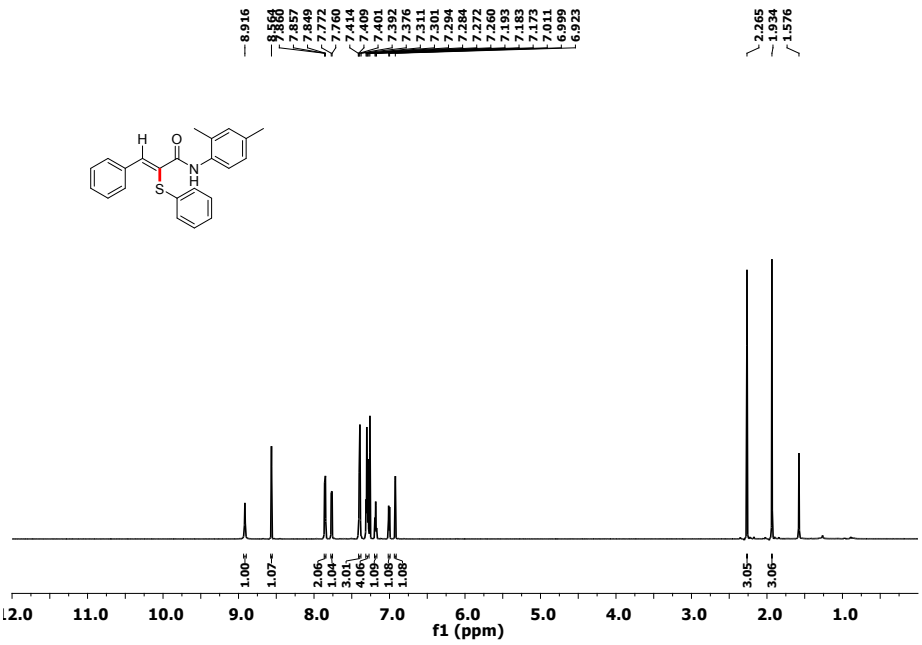


Fig. S39. ^{1}H NMR spectrum of (Z)-N-(2,4-dimethylphenyl)-3-phenyl-2-(phenylthio)acrylamide **(3ca)**

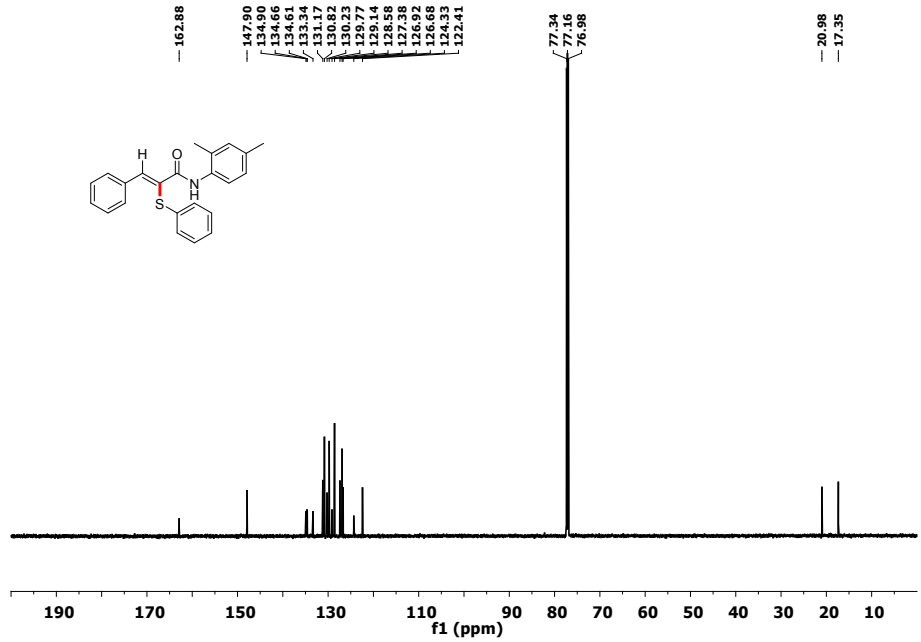


Fig. S40. ^{13}C NMR spectrum of (Z)-N-(2,4-dimethylphenyl)-3-phenyl-2-(phenylthio)acrylamide **(3ca)**

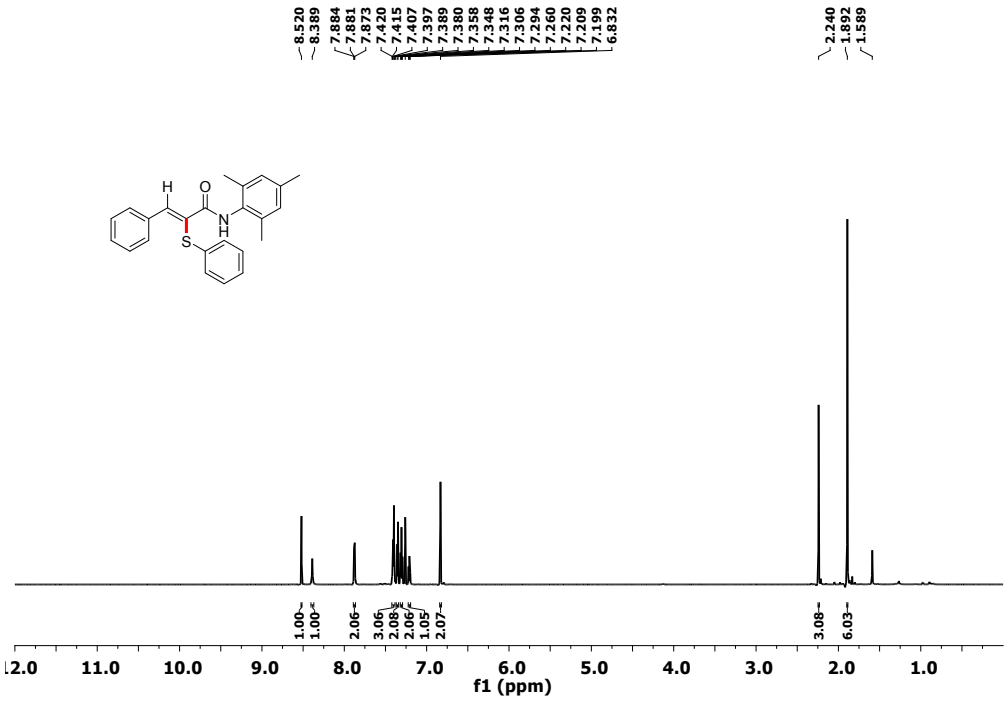


Fig. S41. [1]H NMR spectrum of (Z)-N-mesityl-3-phenyl-2-(phenylthio)acrylamide **(3da)**

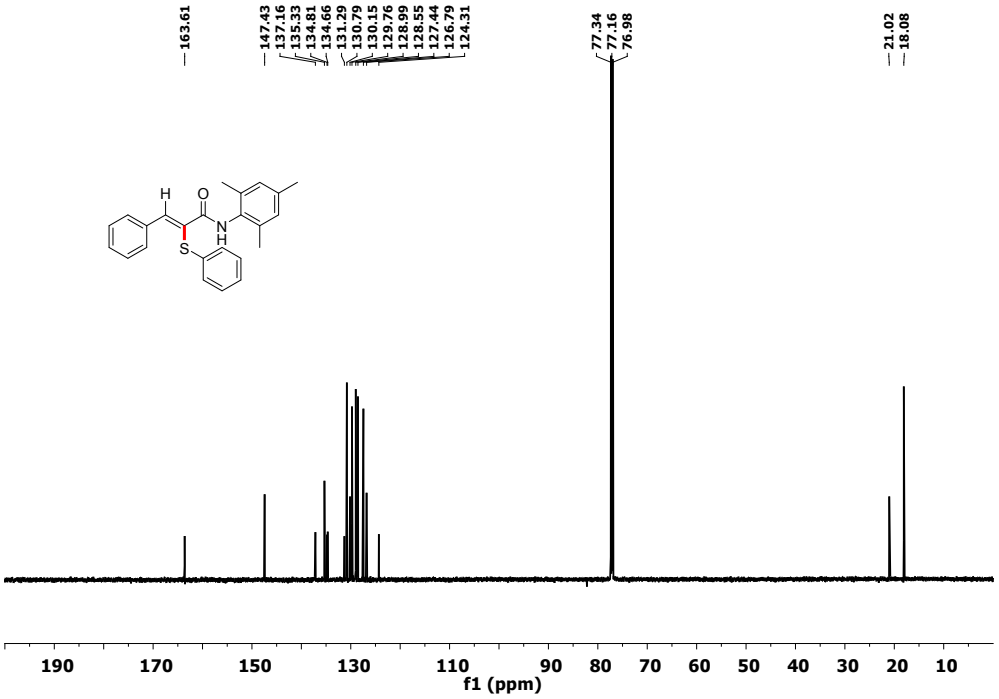


Fig. S42. [13]C NMR spectrum of (Z)-N-mesityl-3-phenyl-2-(phenylthio)acrylamide **(3da)**

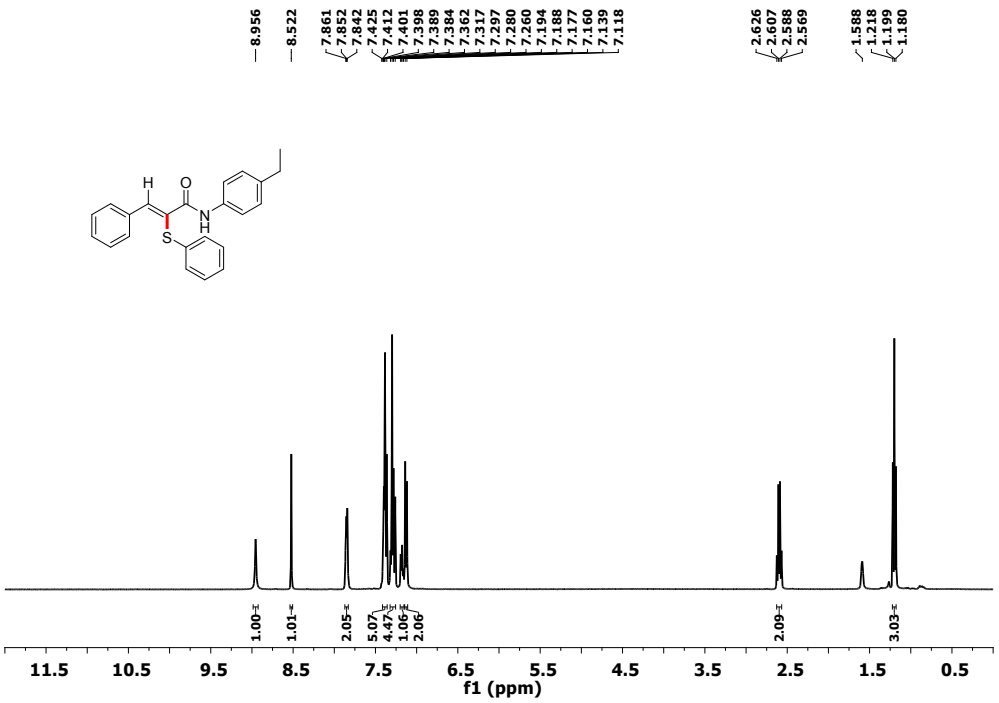


Fig. S43. ^{1}H NMR spectrum of (Z)-N-(4-ethylphenyl)-3-phenyl-2-(phenylthio)acrylamide

(3ea)

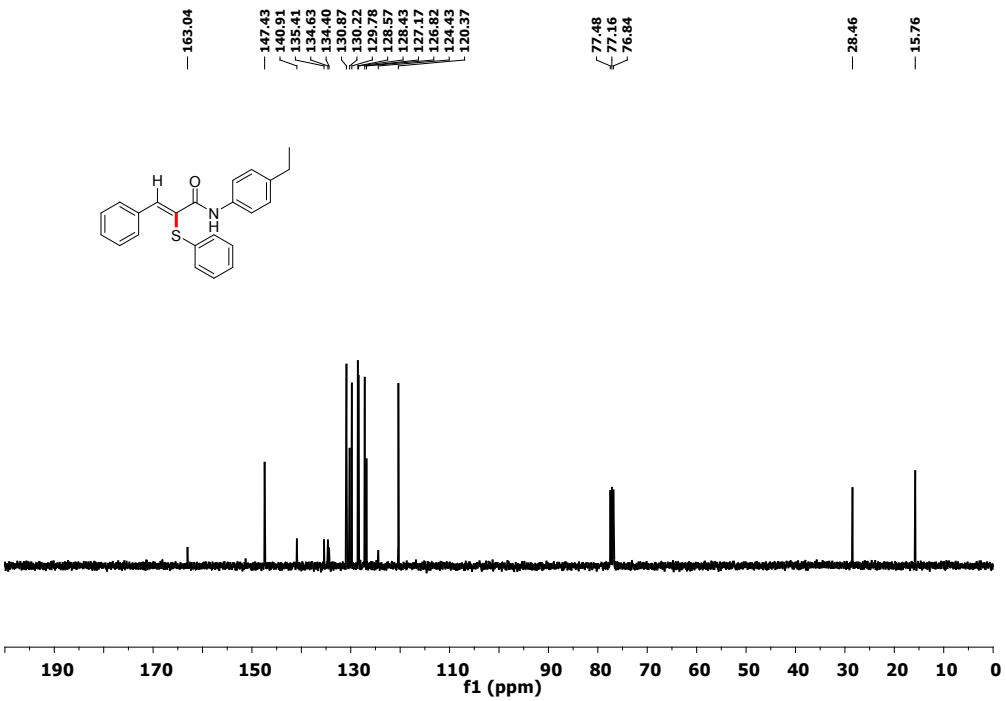


Fig. S44. ^{13}C NMR spectrum of (Z)-N-(4-ethylphenyl)-3-phenyl-2-(phenylthio)acrylamide

(3ea)

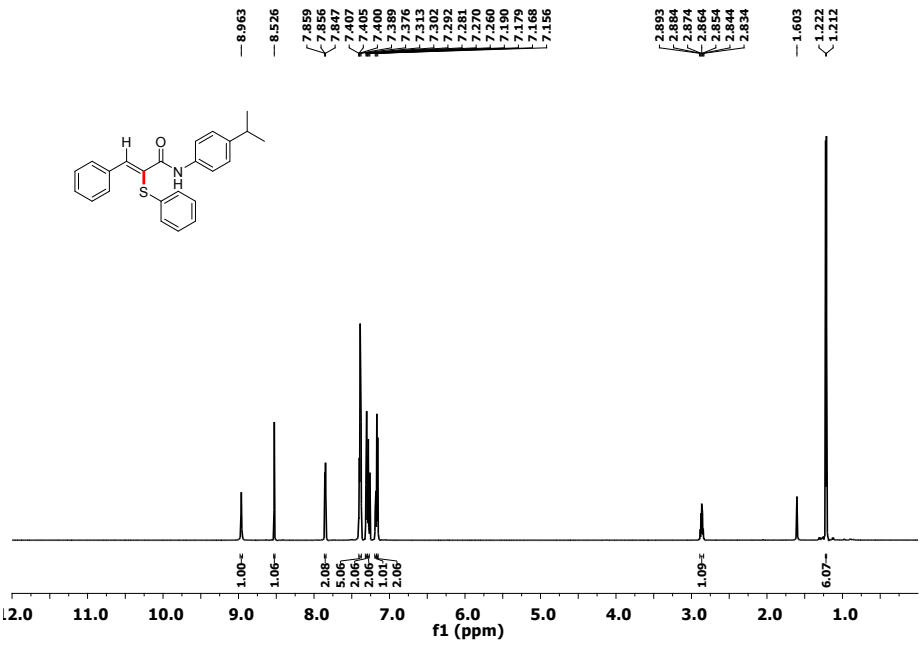


Fig. S45. ^{1}H NMR spectrum of (Z)-N-(4-isopropylphenyl)-3-phenyl-2-(phenylthio)acrylamide **(3fa)**

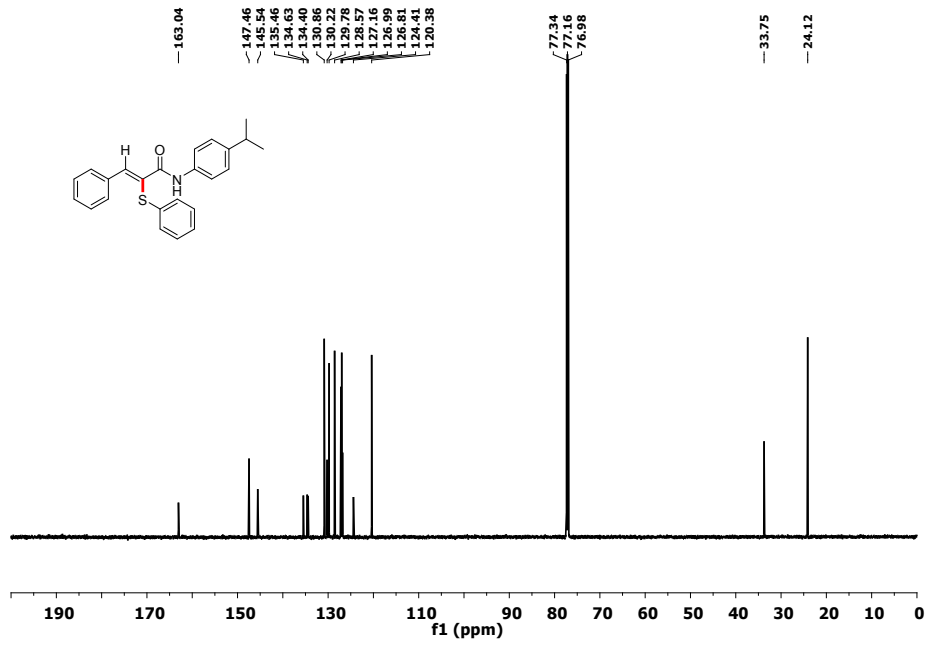


Fig. S46. ^{13}C NMR spectrum of (Z)-N-(4-isopropylphenyl)-3-phenyl-2-(phenylthio)acrylamide **(3fa)**

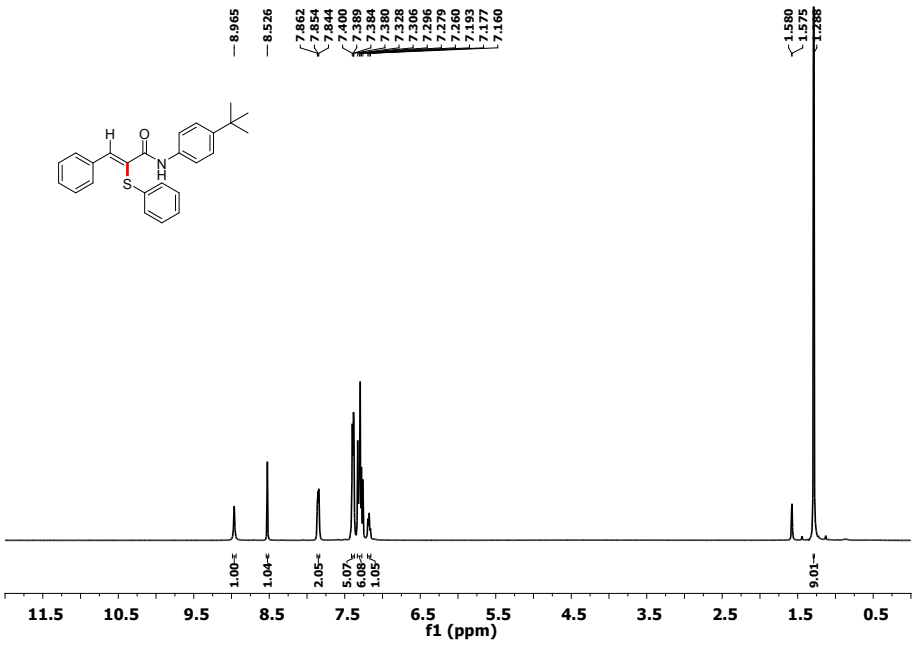


Fig. S47. ^{1}H NMR spectrum of (Z)-N-(4-(tert-butyl)phenyl)-3-phenyl-2-(phenylthio)acrylamide **(3ga)**

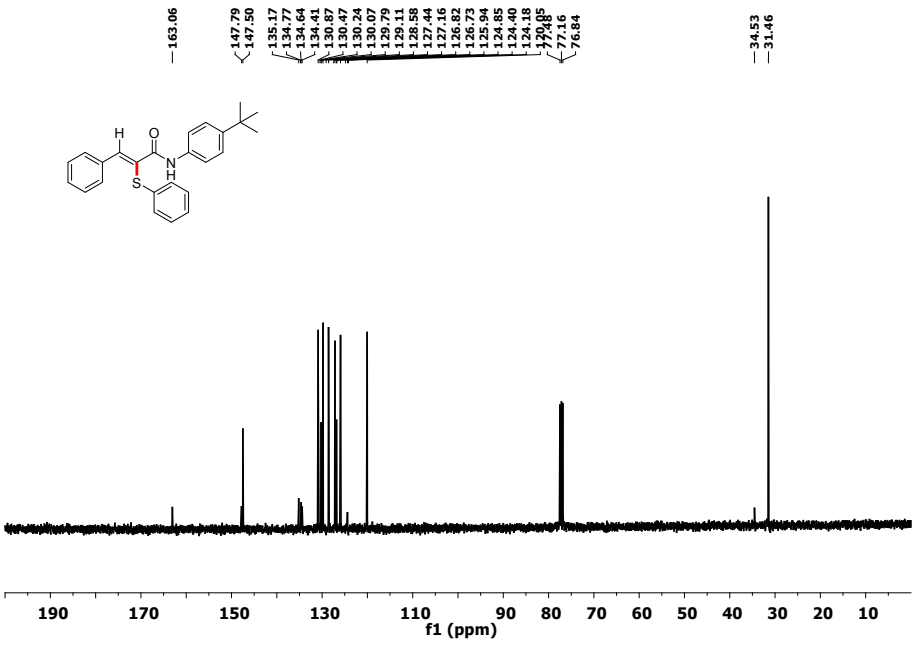


Fig. S48. ^{13}C NMR spectrum of (Z)-N-(4-(tert-butyl)phenyl)-3-phenyl-2-(phenylthio)acrylamide **(3ga)**

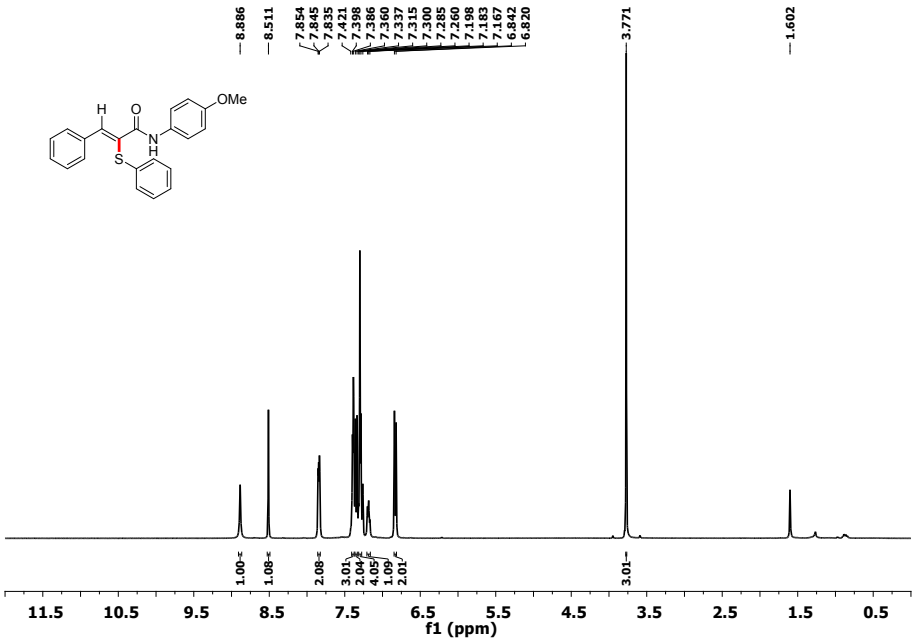


Fig. S49. ^{1}H NMR spectrum of (Z)-N-(4-methoxyphenyl)-3-phenyl-2-(phenylthio)acrylamide **(3ha)**

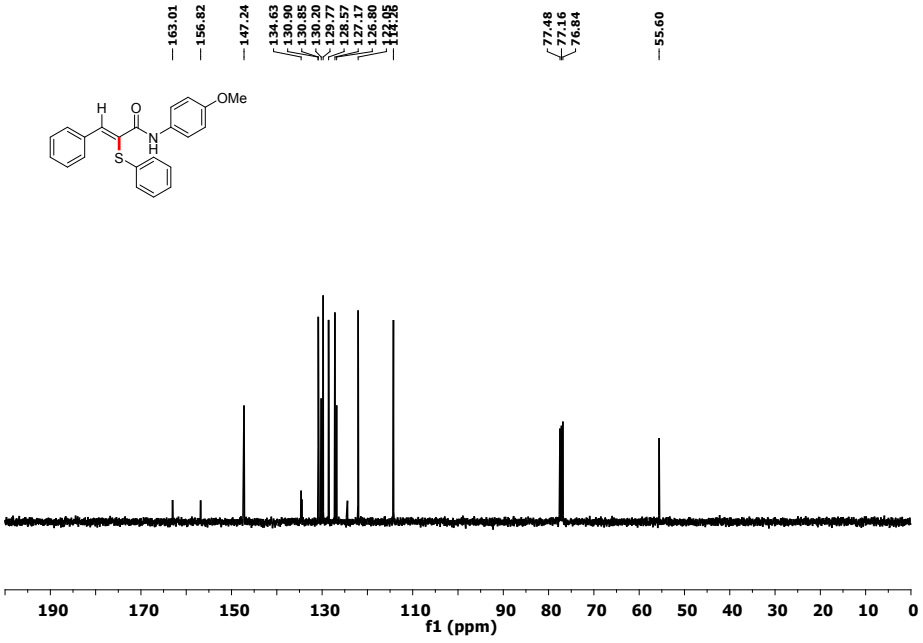


Fig. S50. ^{13}C NMR spectrum of (Z)-N-(4-methoxyphenyl)-3-phenyl-2-(phenylthio)acrylamide **(3ha)**

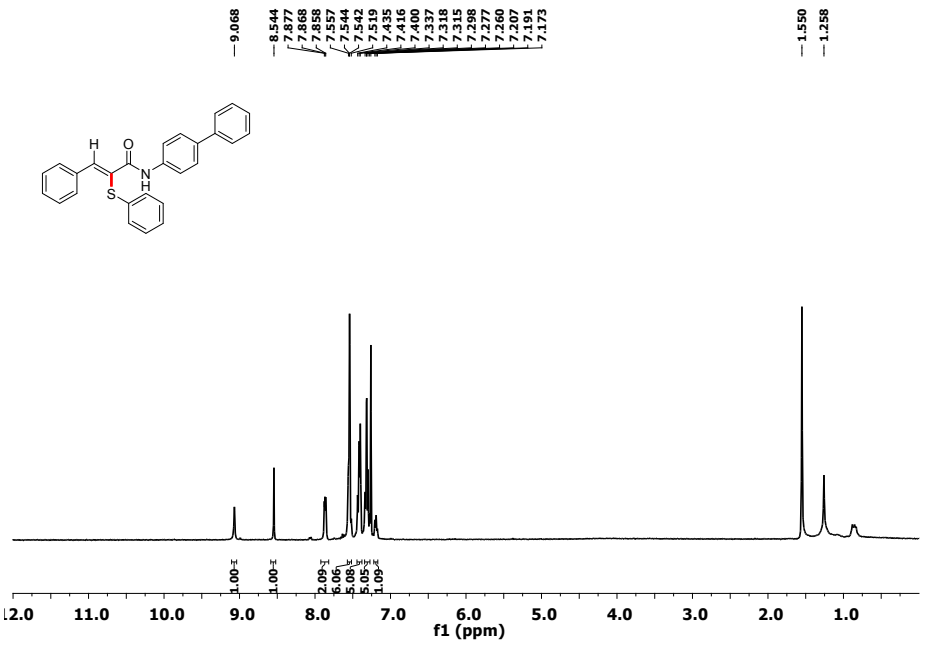


Fig. S51. ^{1}H NMR spectrum of (Z)-N-([1,1'-biphenyl]-4-yl)-3-phenyl-2-(phenylthio)acrylamide **(3ia)**

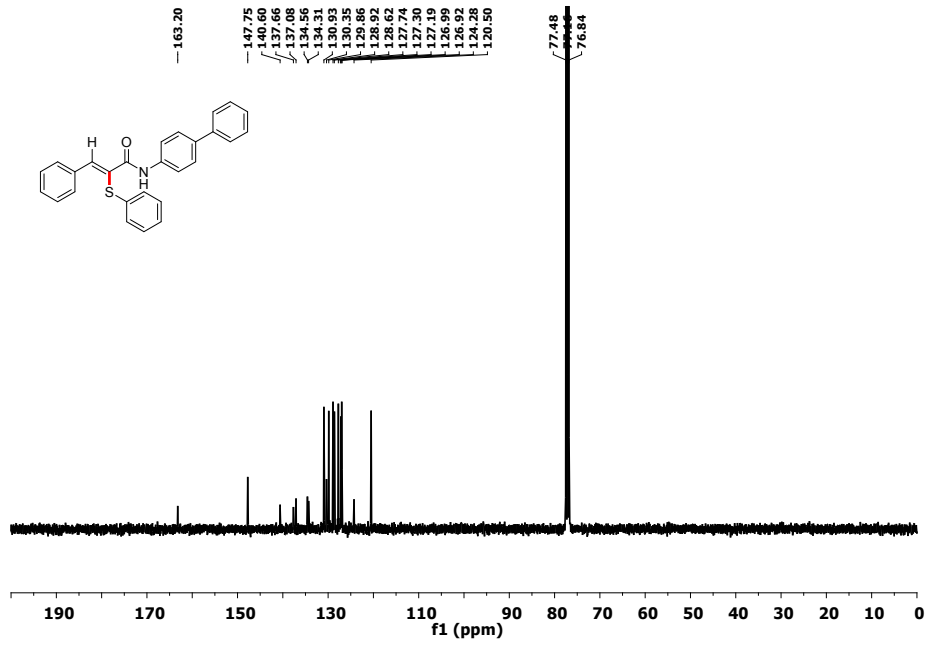


Fig. S52. ^{13}C NMR spectrum of (Z)-N-([1,1'-biphenyl]-4-yl)-3-phenyl-2-(phenylthio)acrylamide **(3ia)**

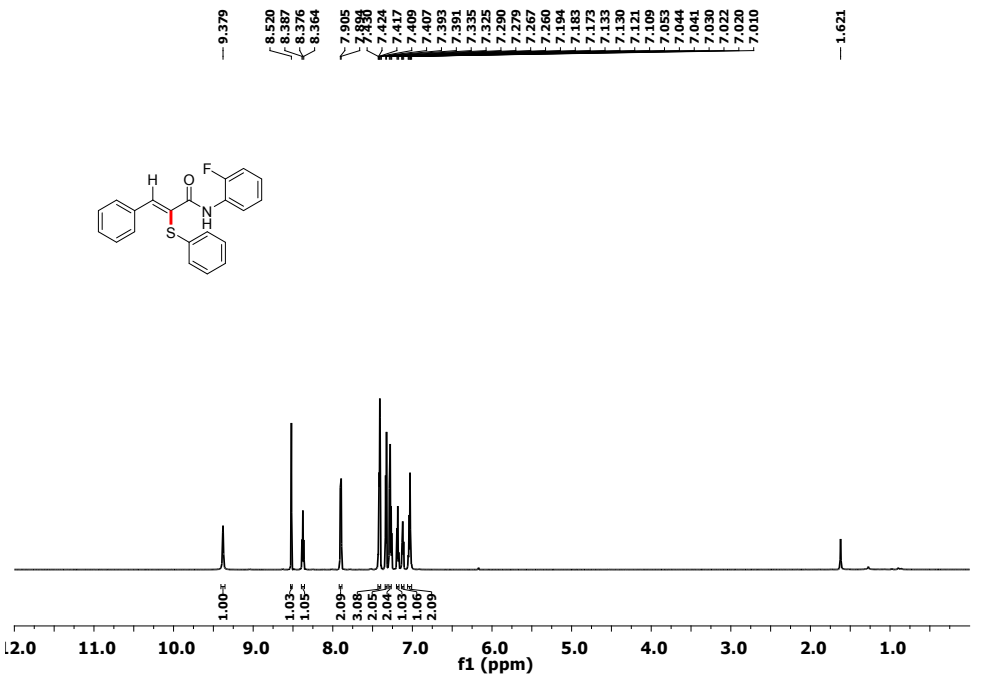


Fig. S53. [1]H NMR spectrum of (Z)-N-(2-fluorophenyl)-3-phenyl-2-(phenylthio)acrylamide

(3ja)

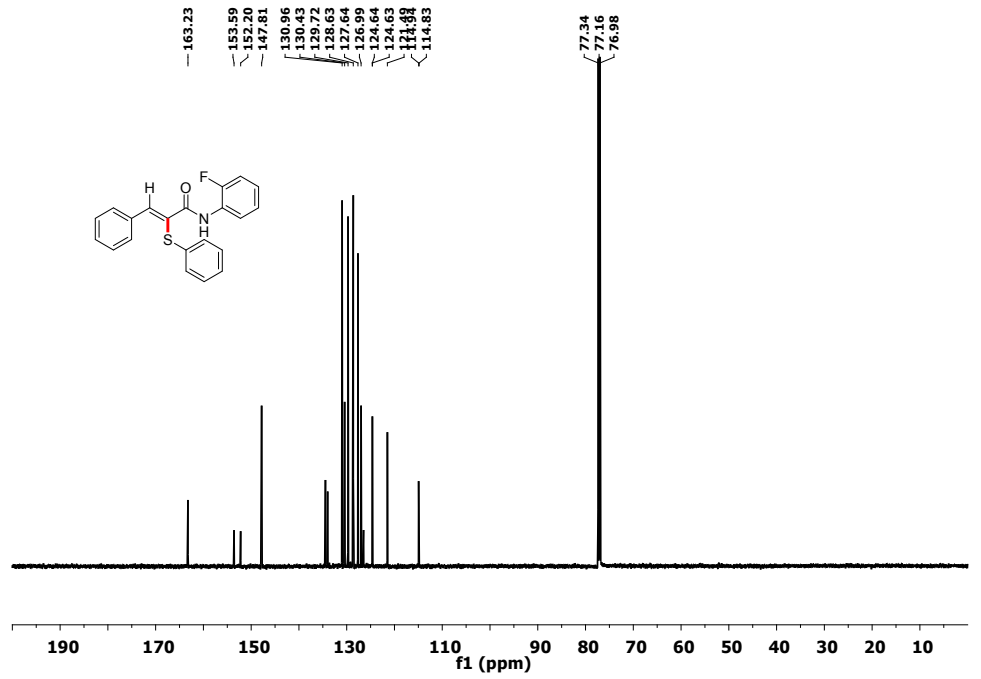


Fig. S54. [13]C NMR spectrum of (Z)-N-(2-fluorophenyl)-3-phenyl-2-(phenylthio)acrylamide

(3ja)

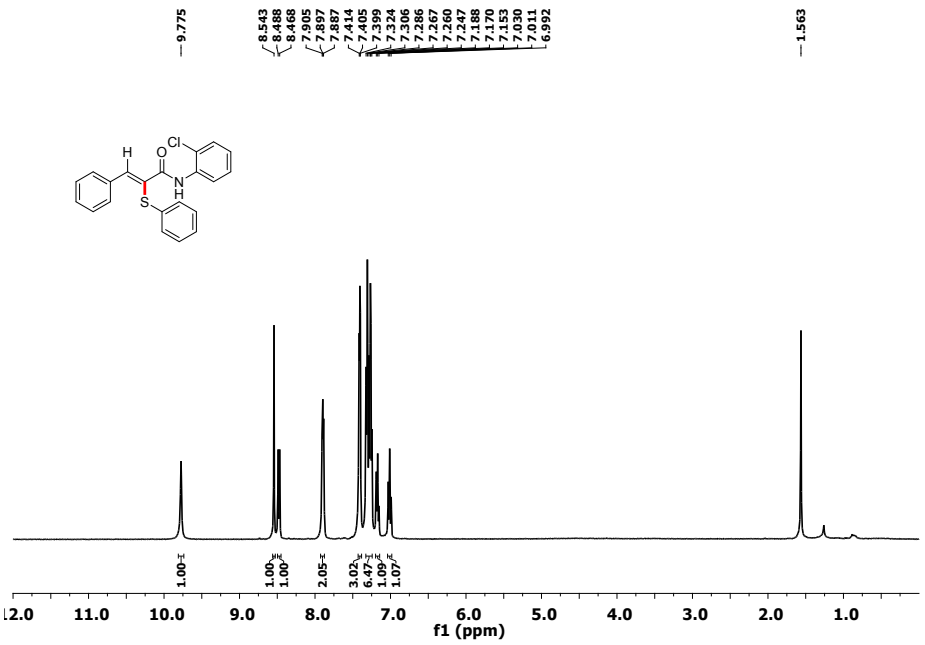


Fig. S55. ^{1}H NMR spectrum of (Z)-N-(2-chlorophenyl)-3-phenyl-2-(phenylthio)acrylamide **(3ka)**

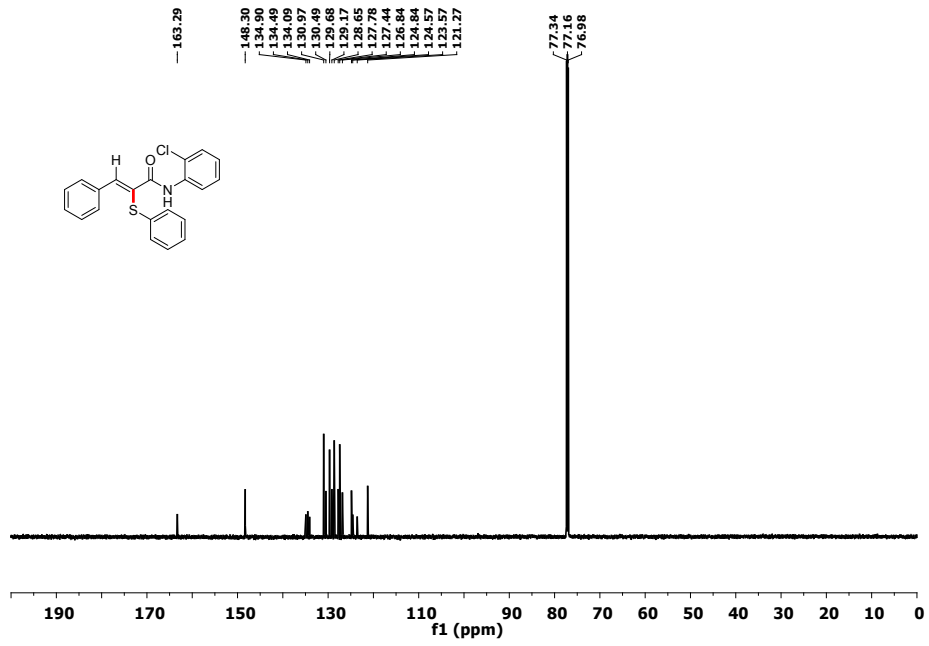


Fig. S56. ^{13}C NMR spectrum of (Z)-N-(2-chlorophenyl)-3-phenyl-2-(phenylthio)acrylamide **(3ka)**

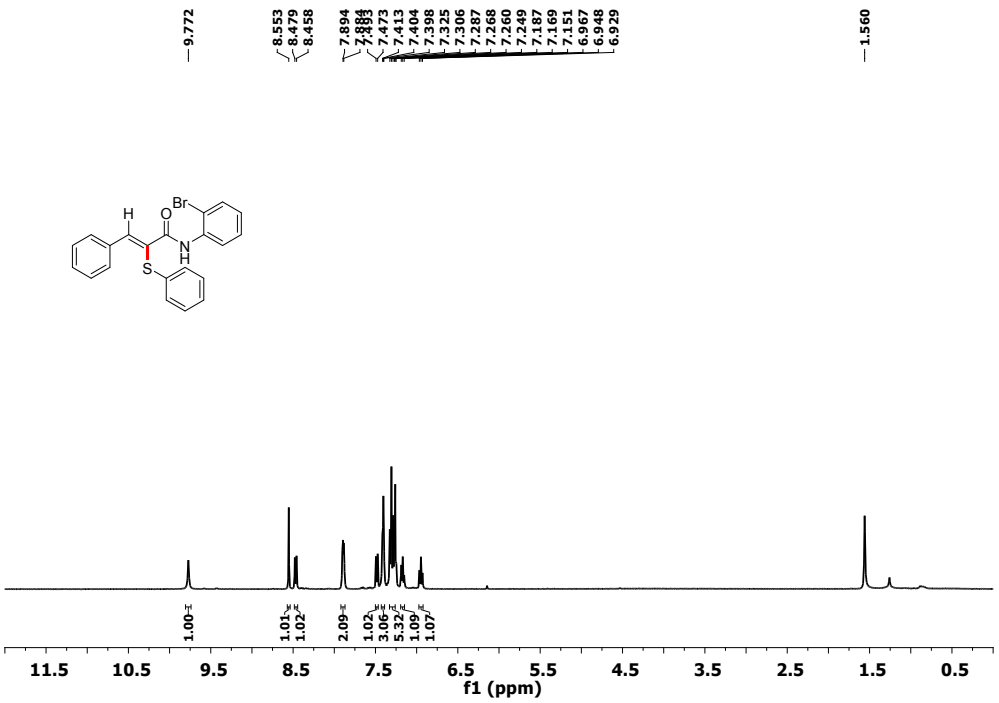


Fig. S57. ^{1}H NMR spectrum of (Z)-N-(2-bromophenyl)-3-phenyl-2-(phenylthio)acrylamide

(3la)

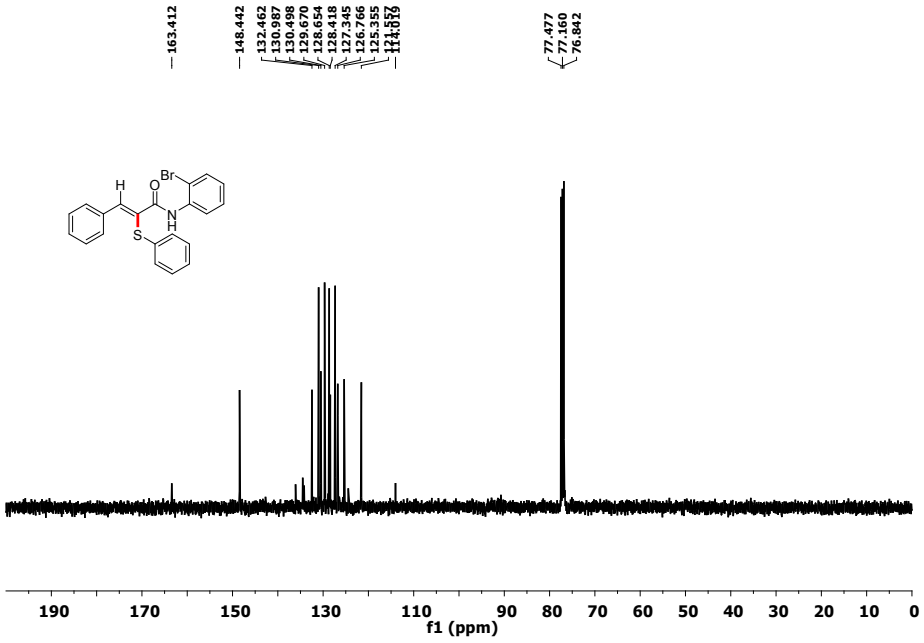


Fig. S58. ^{13}C NMR spectrum of (Z)-N-(2-bromophenyl)-3-phenyl-2-(phenylthio)acrylamide

(3la)

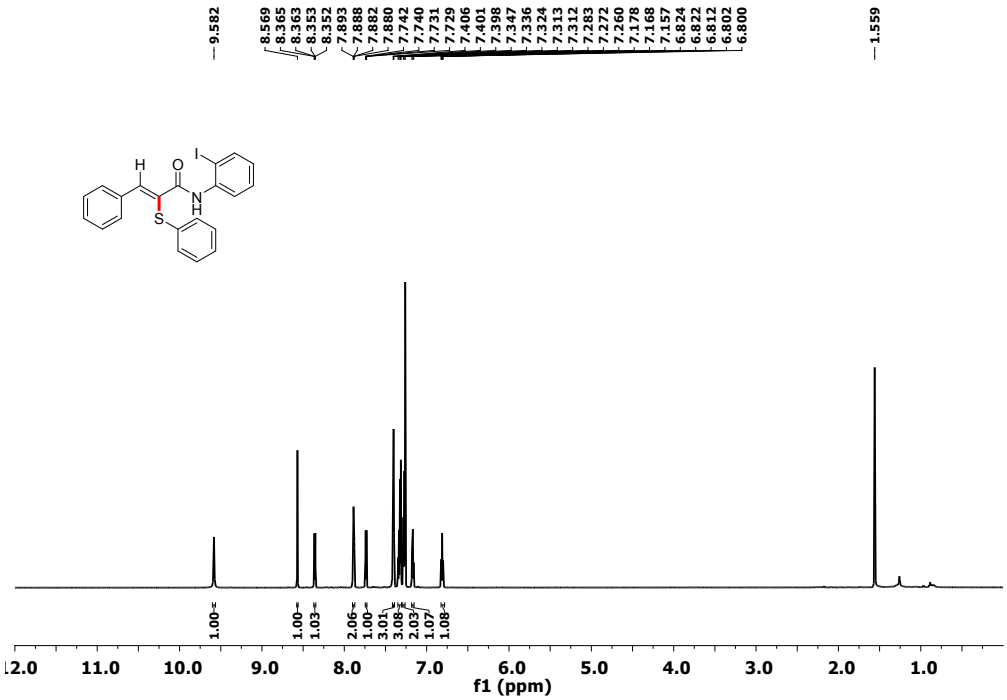


Fig. S59. ^{1}H NMR spectrum of (Z)-N-(2-iodophenyl)-3-phenyl-2-(phenylthio)acrylamide **(3ma)**

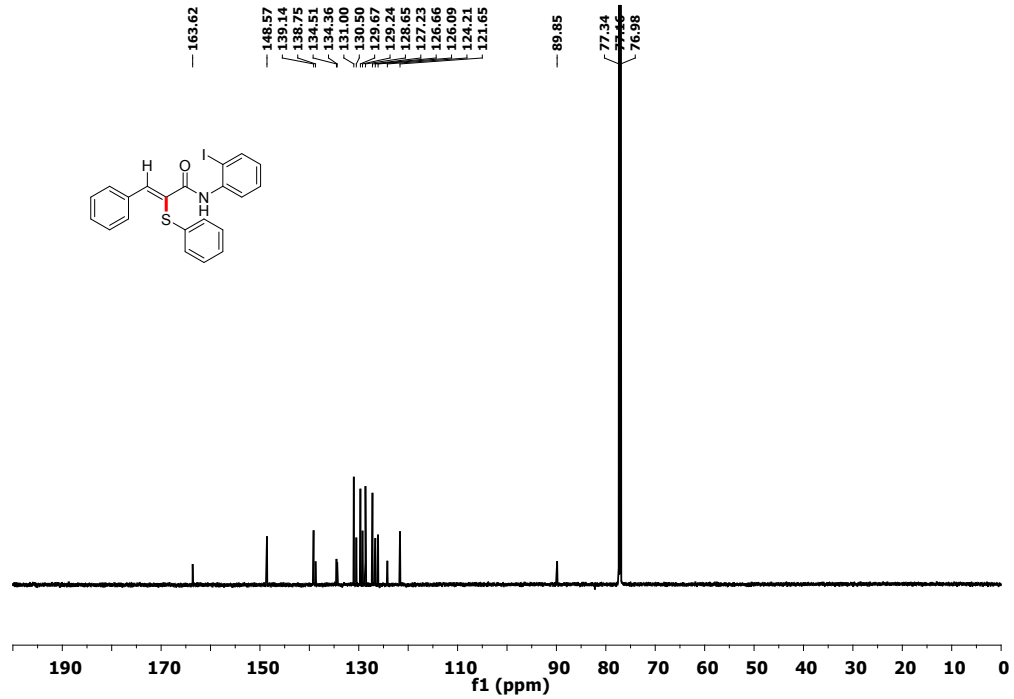


Fig. S60. ^{13}C NMR spectrum of (Z)-N-(2-iodophenyl)-3-phenyl-2-(phenylthio)acrylamide **(3ma)**

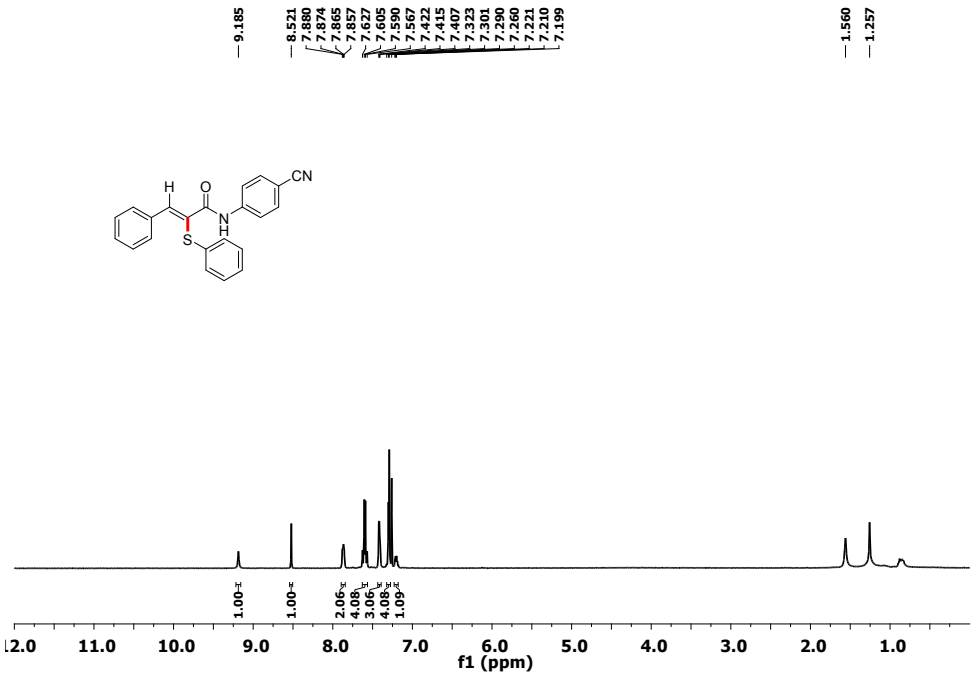


Fig. S61. [1]H NMR spectrum of (Z)-N-(4-cyanophenyl)-3-phenyl-2-(phenylthio)acrylamide

(3na)

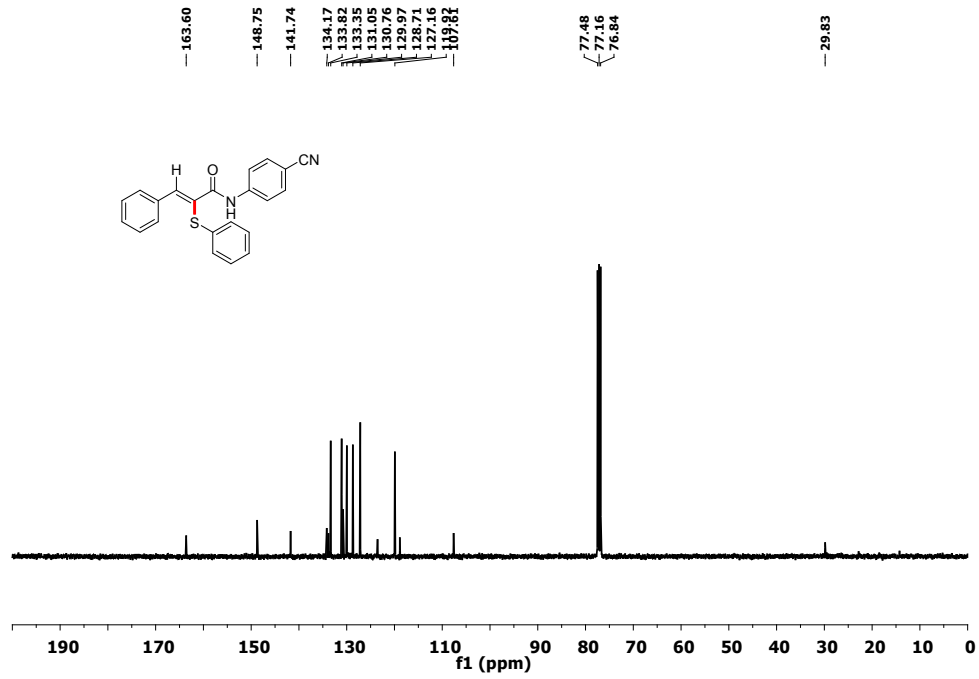


Fig. S62. [13]C NMR spectrum of (Z)-N-(4-cyanophenyl)-3-phenyl-2-(phenylthio)acrylamide

(3na)

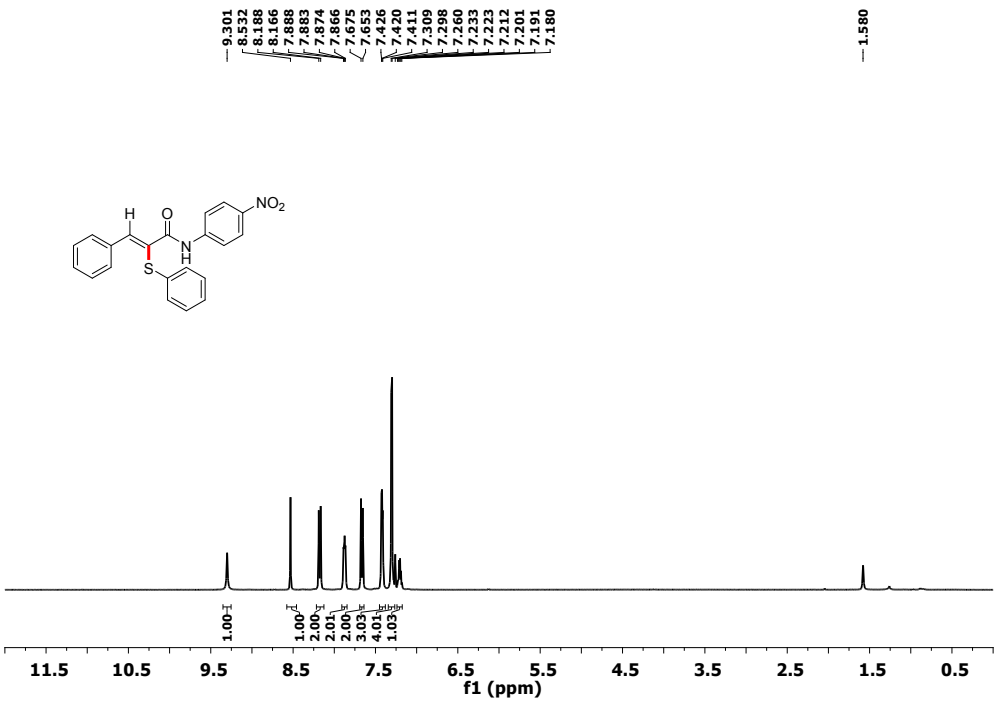


Fig. S63. [1]H NMR spectrum of (Z)-N-(4-nitrophenyl)-3-phenyl-2-(phenylthio)acrylamide

(3oa)

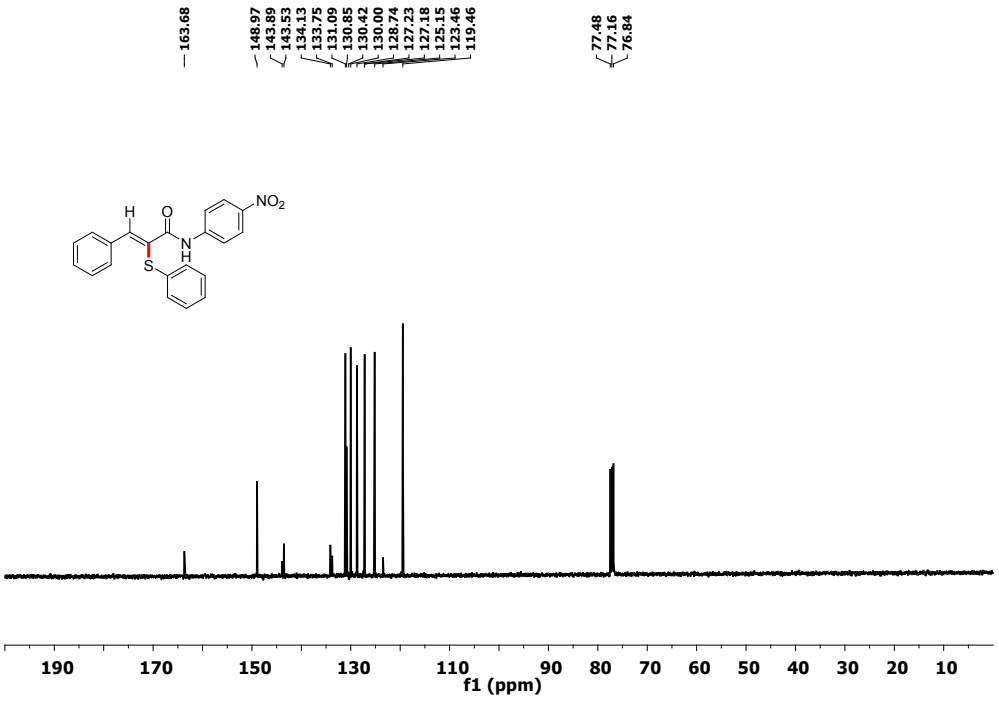


Fig. S64. [13]C NMR spectrum of (Z)-N-(4-nitrophenyl)-3-phenyl-2-(phenylthio)acrylamide

(3oa)

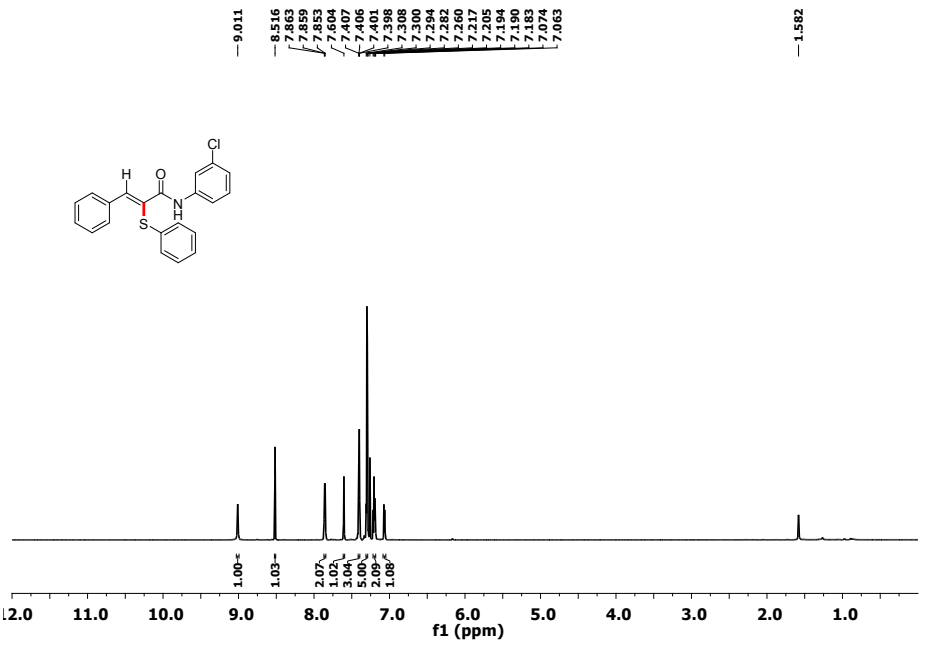


Fig. S65. ^{1}H NMR spectrum of (Z)-N-(3-chlorophenyl)-3-phenyl-2-(phenylthio)acrylamide **(3pa)**

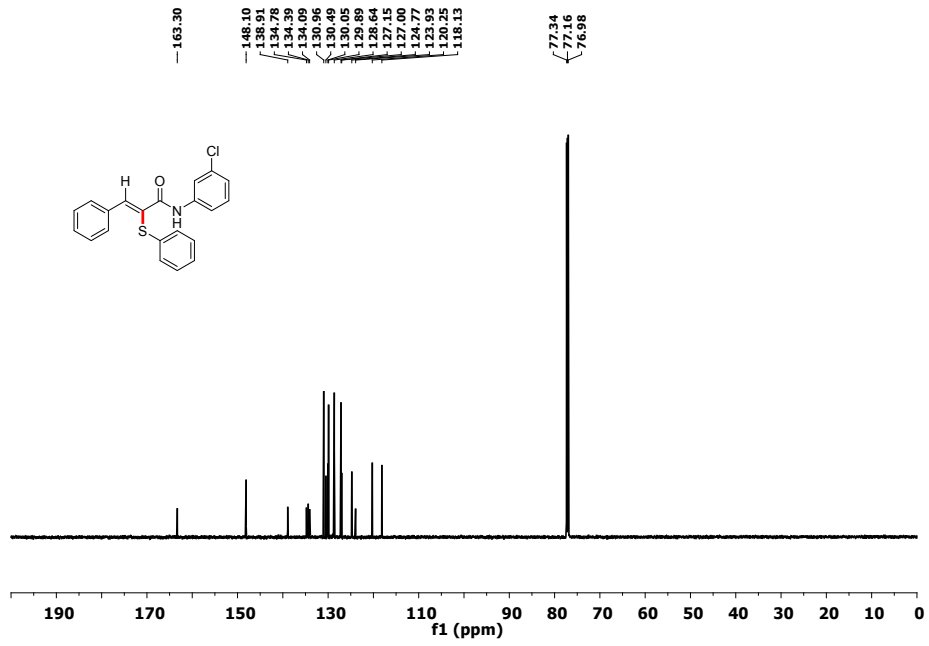


Fig. S66. ^{13}C NMR spectrum of ^{1}H NMR spectrum of (Z)-N-(3-chlorophenyl)-3-phenyl-2-(phenylthio)acrylamide **(3pa)**

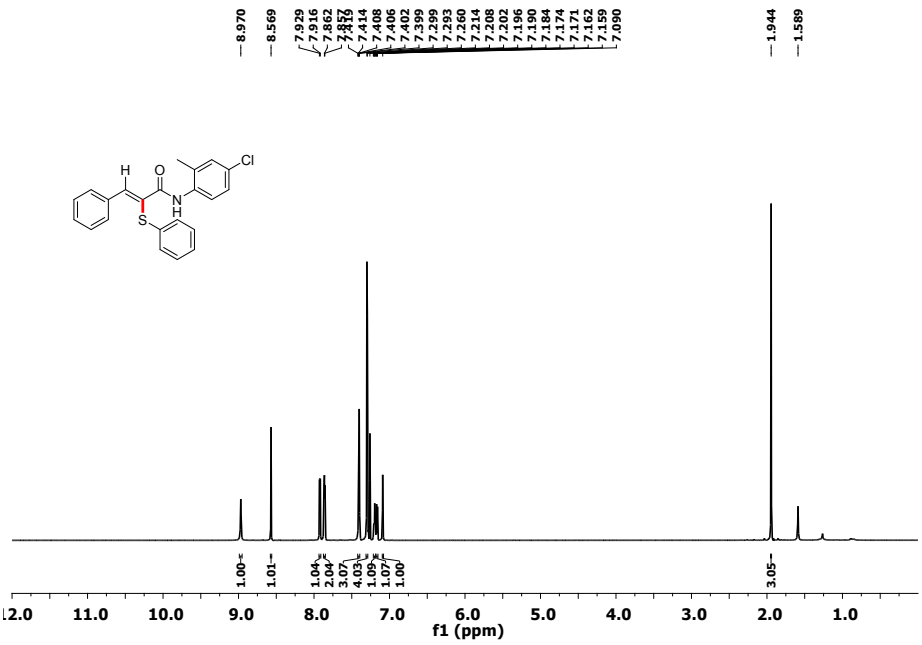


Fig. S67. ^{1}H NMR spectrum of (Z)-N-(4-chloro-2-methylphenyl)-3-phenyl-2-(phenylthio)acrylamide **(3qa)**

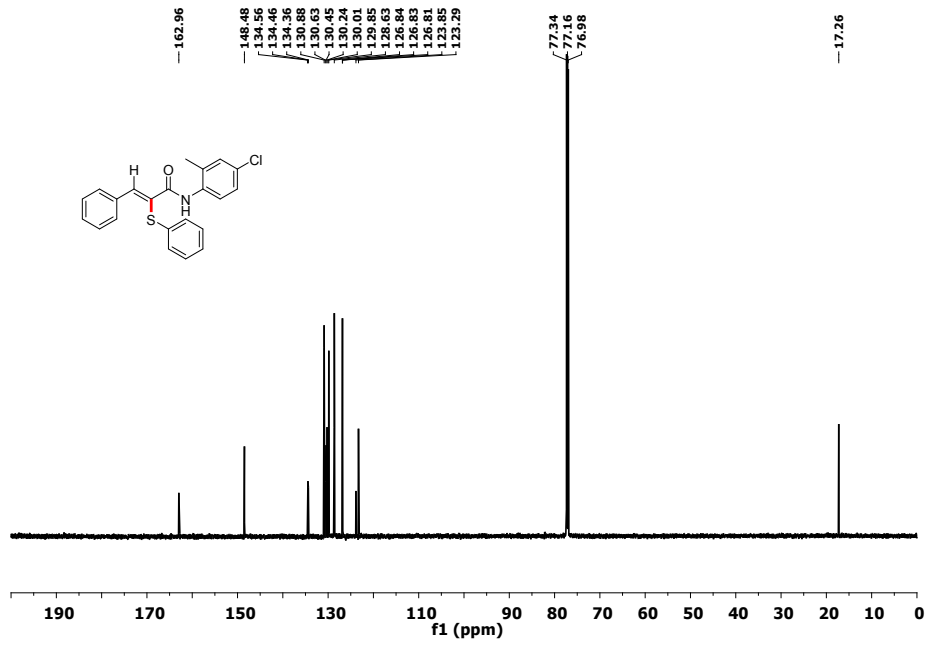


Fig. S68. ^{13}C NMR spectrum of (Z)-N-(4-chloro-2-methylphenyl)-3-phenyl-2-(phenylthio)acrylamide **(3qa)**

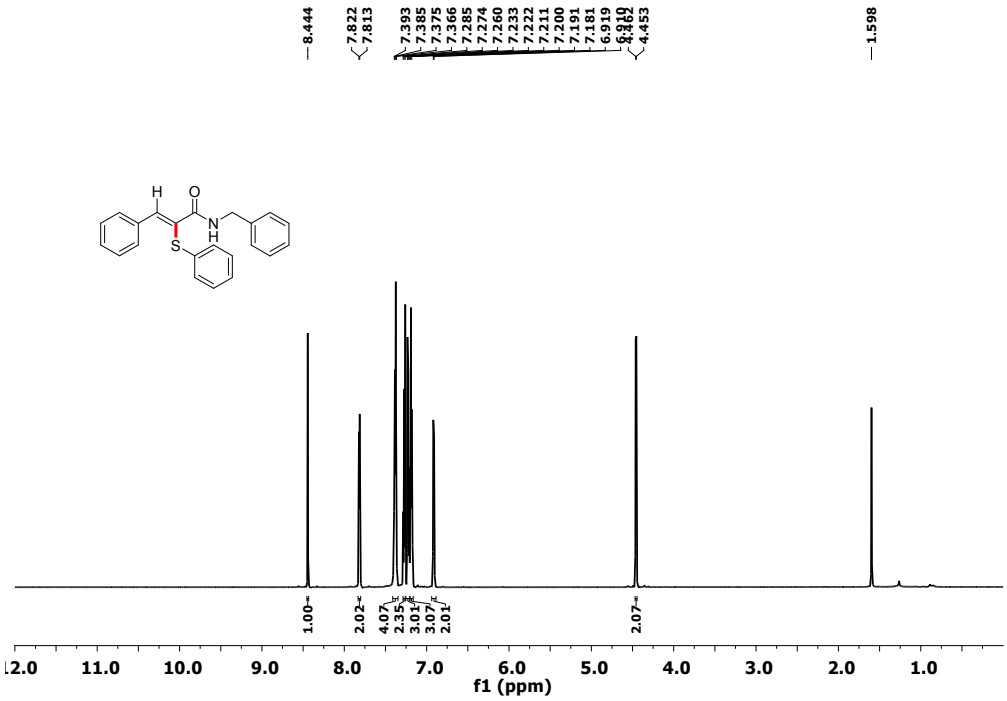


Fig. S69. [1]H NMR spectrum of ((Z)-N-benzyl-3-phenyl-2-(phenylthio)acrylamide **(3ra)**

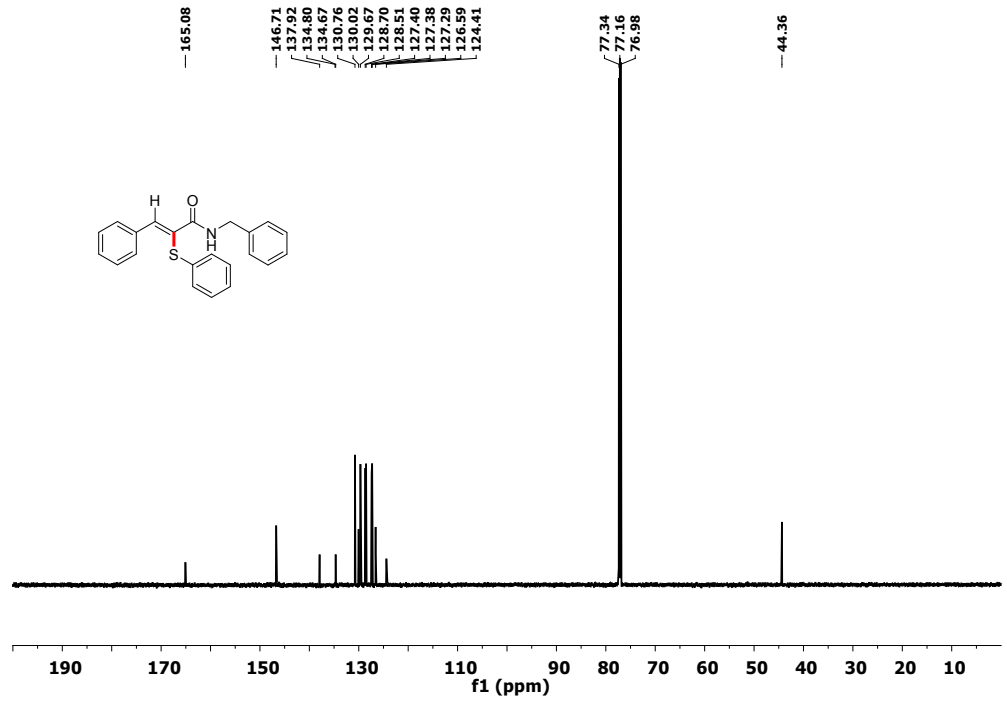


Fig. S70. [13]C NMR spectrum of ((Z)-N-benzyl-3-phenyl-2-(phenylthio)acrylamide **(3ra)**

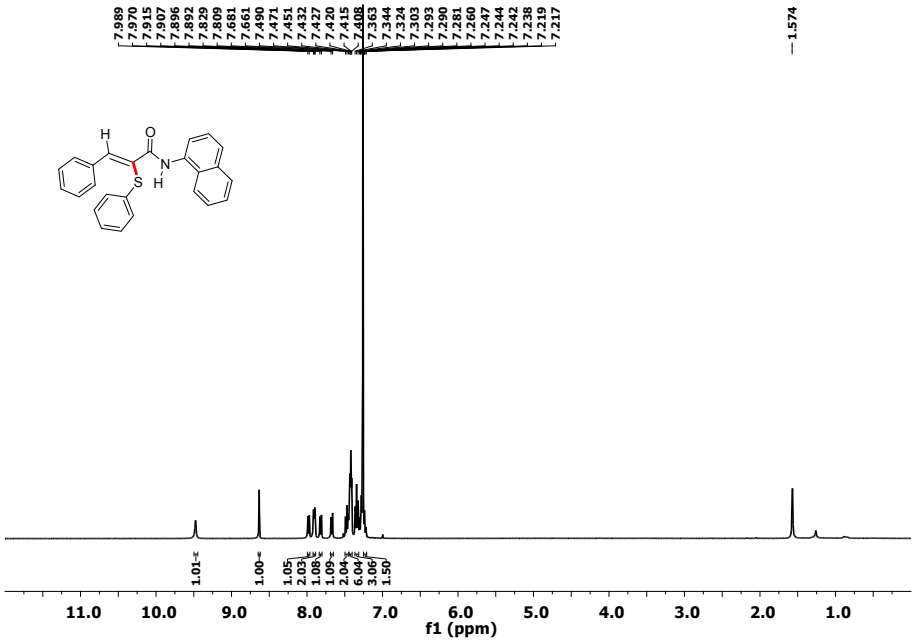


Fig. S71. ^{1}H NMR spectrum of (Z)-N-(naphthalen-1-yl)-3-phenyl-2-(phenylthio)acrylamide **(3sa)**

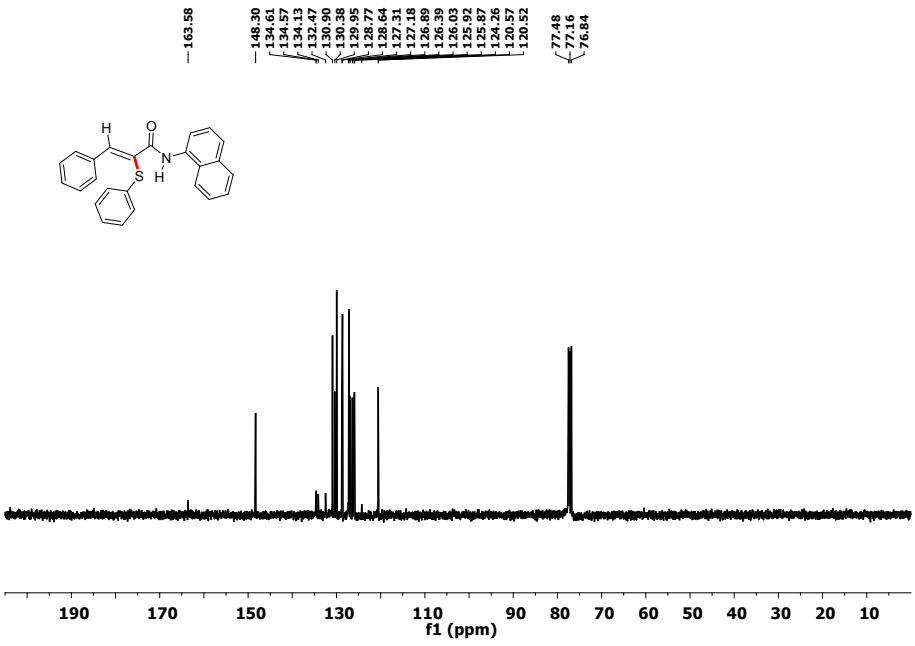


Fig. S72. ^{13}C NMR spectrum of (Z)-N-(naphthalen-1-yl)-3-phenyl-2-(phenylthio)acrylamide **(3sa)**

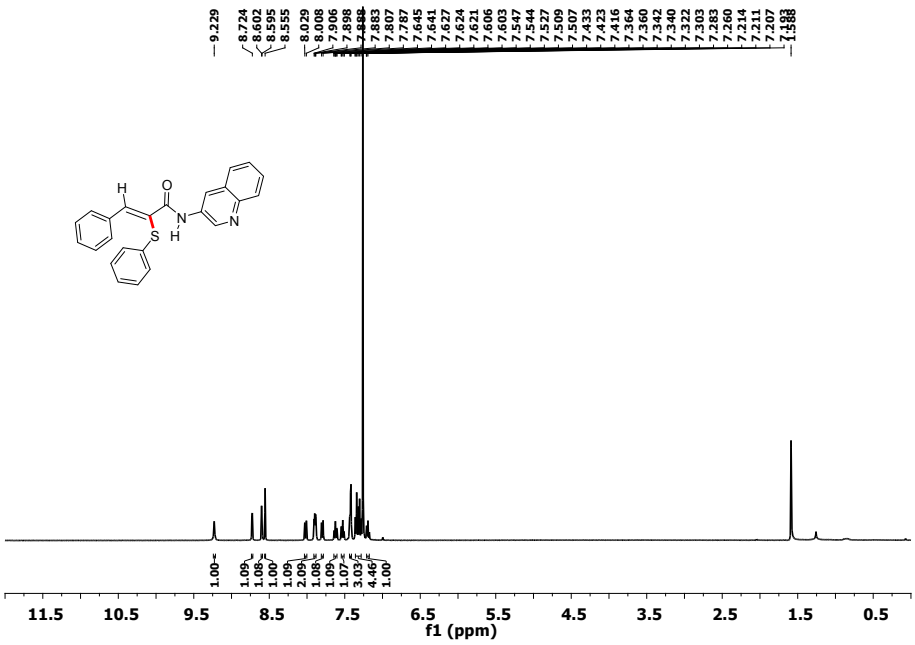


Fig. S73. ^{1}H NMR spectrum of (Z)-3-phenyl-2-(phenylthio)-N-(quinolin-3-yl)acrylamide

(3ta)

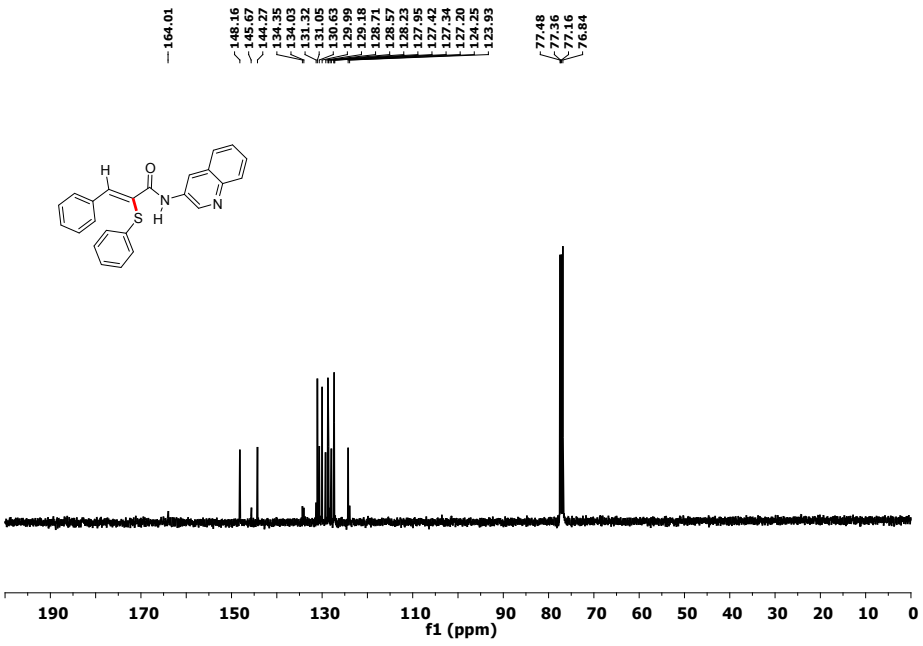


Fig. S74. ^{13}C NMR spectrum of (Z)-3-phenyl-2-(phenylthio)-N-(quinolin-3-yl)acrylamide

(3ta)

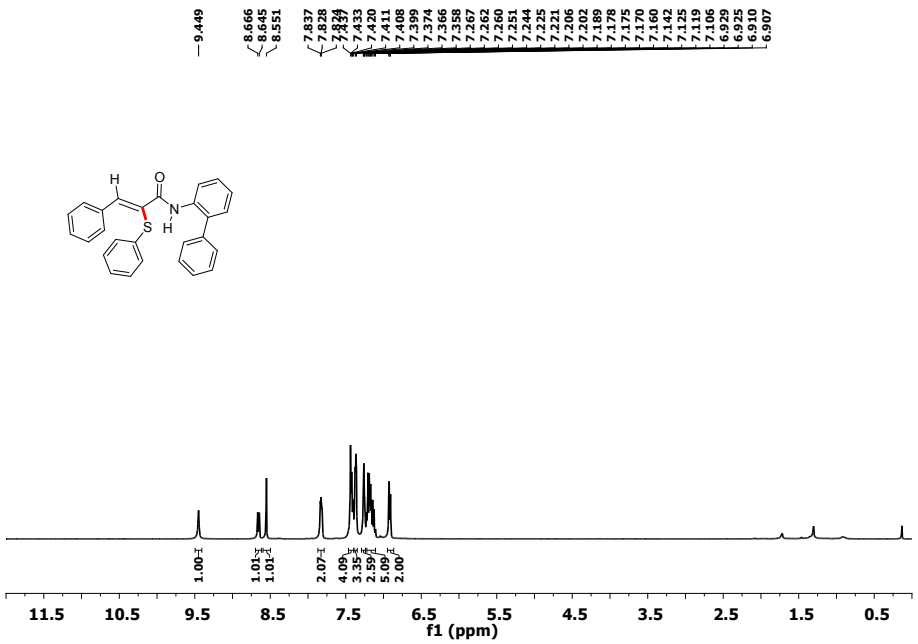


Fig. S75. ^{1}H NMR spectrum of (Z)-N-([1,1'-biphenyl]-2-yl)-3-pheny2(phenylthio)acrylamide

(3ua)

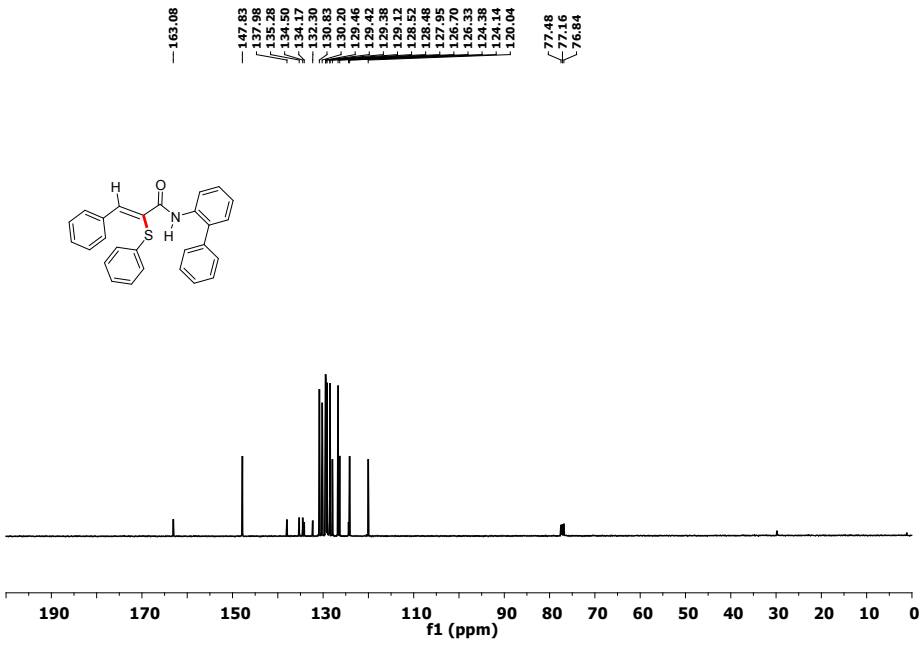


Fig. S76. ^{13}C NMR spectrum of (Z)-N-([1,1'-biphenyl]-2-yl)-3pheny2(phenylthio)acrylamide

(3ua)

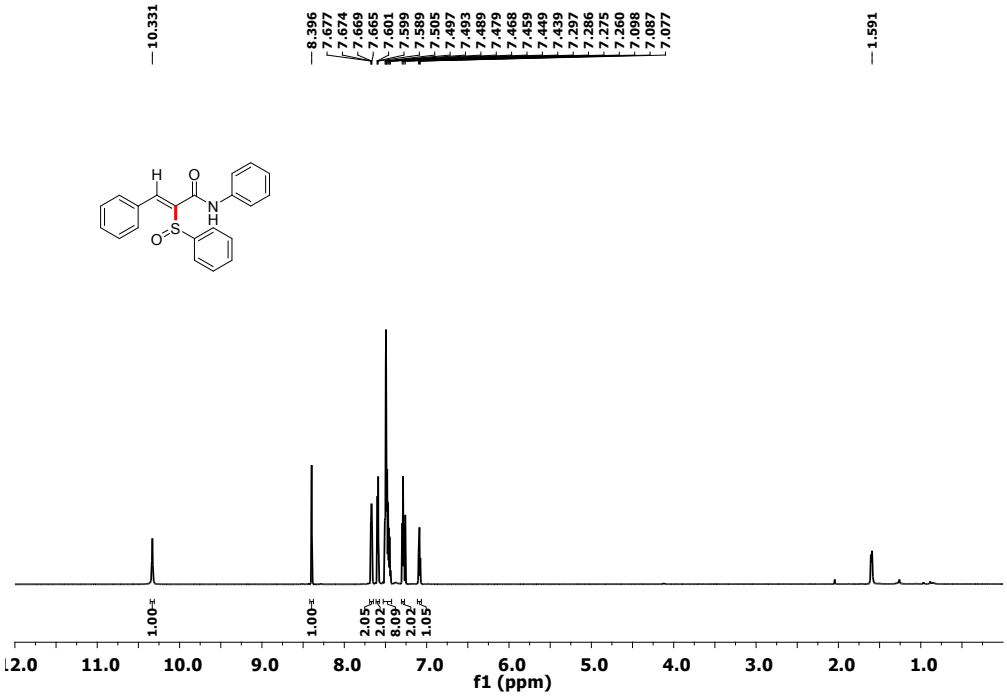


Fig.S77. [1]H NMR spectrum of (R,Z)-N,3-diphenyl-2-(phenylsulfinyl)acrylamide **4**

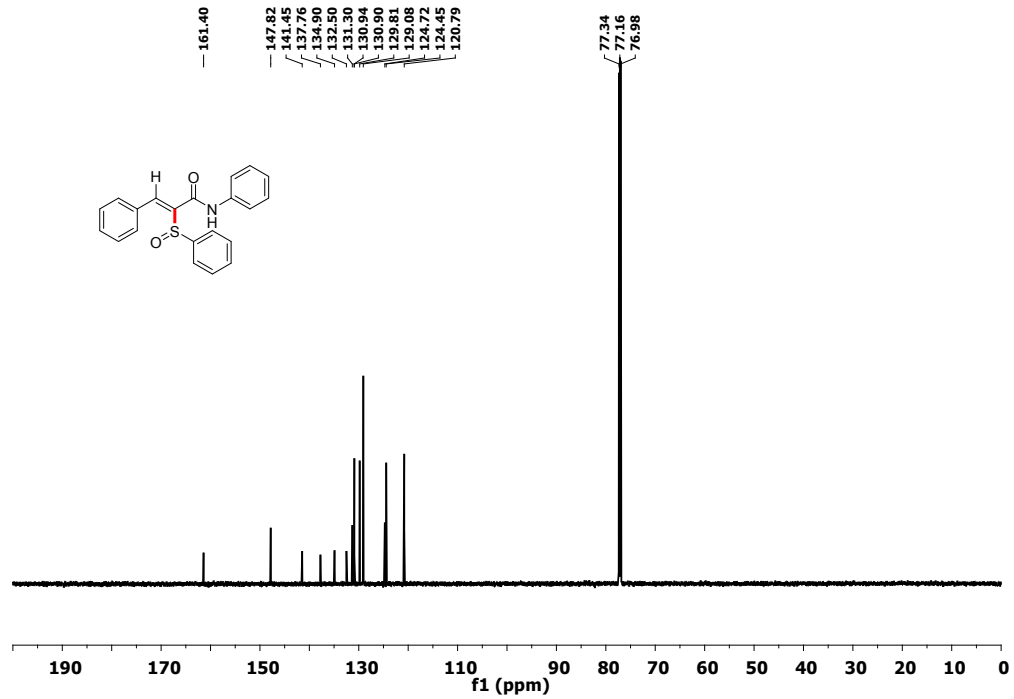


Fig. S78. [13]C NMR spectrum of (R,Z)-N,3-diphenyl-2-(phenylsulfinyl)acrylamide **4**

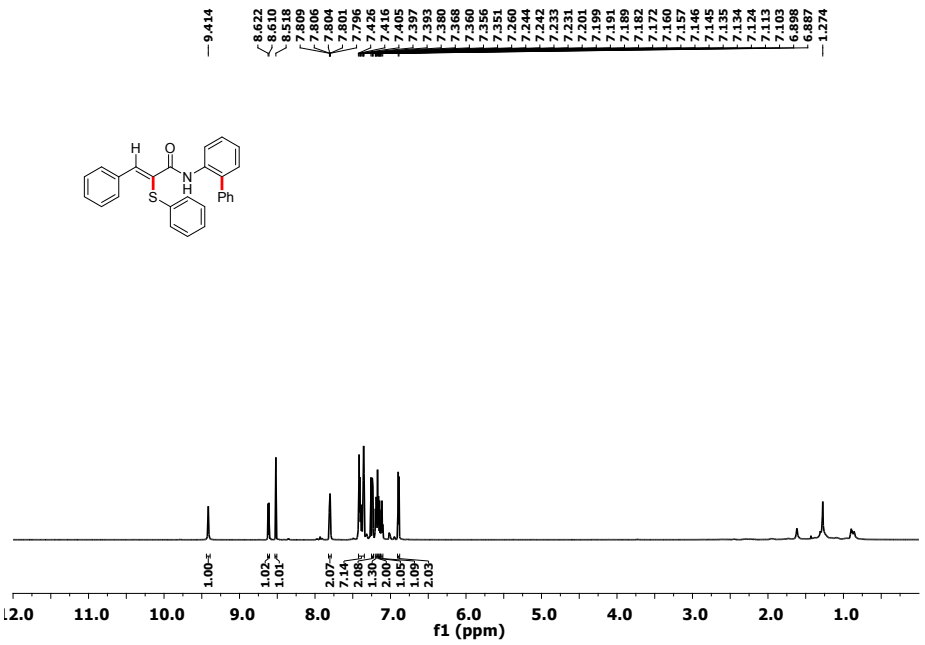


Fig. S79. ^{1}H NMR spectrum of (Z)-N-([1,1'-biphenyl]-2-yl)-3-phenyl-2-(phenylthio)acrylamide **5**

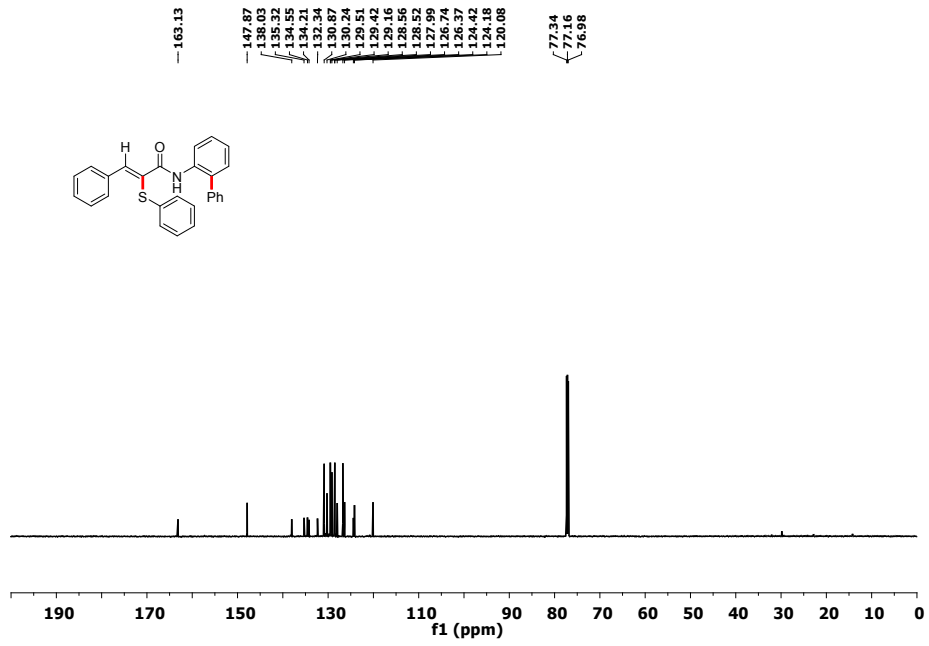


Fig. S80. ^{13}C NMR spectrum of (Z)-N-([1,1'-biphenyl]-2-yl)-3-phenyl-2-(phenylthio)acrylamide **5**

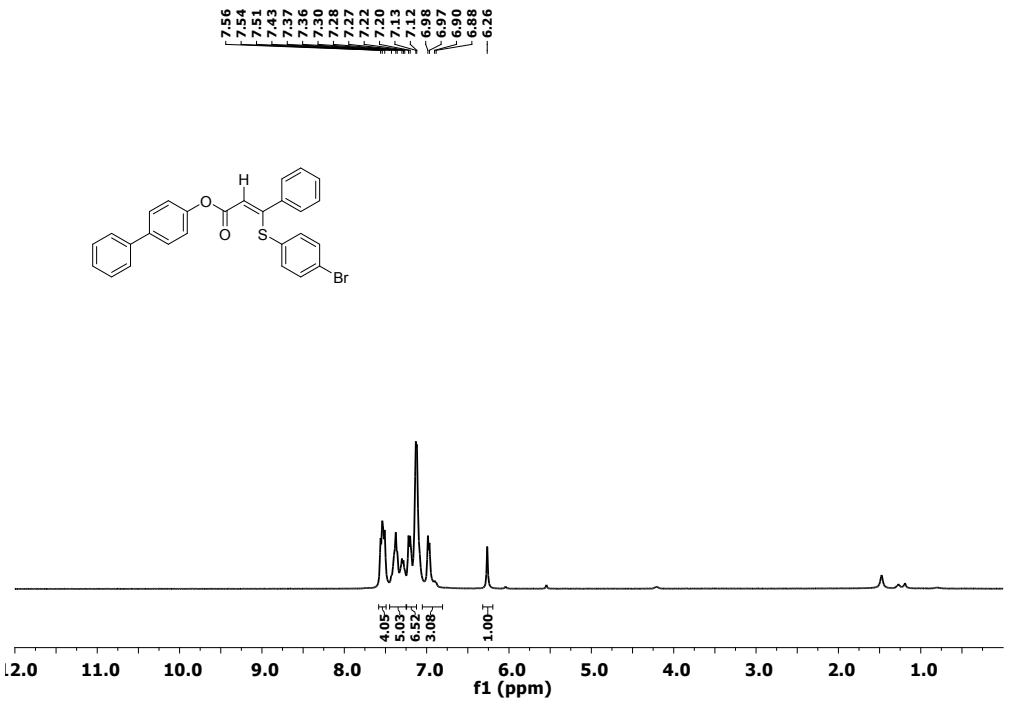


Fig. S81. ^{1}H NMR spectrum of [1,1'-biphenyl]-4-yl (Z)-3-((4-bromophenyl)thio)-3-phenylacrylate**7**

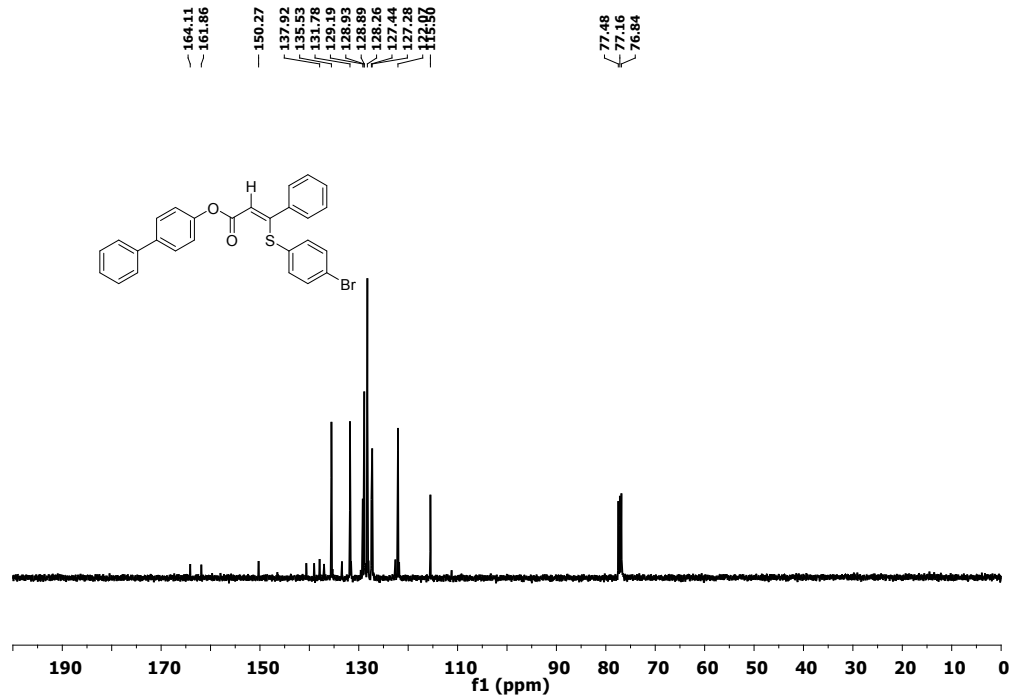


Fig. S82. ^{13}C NMR spectrum of [1,1'-biphenyl]-4-yl (Z)-3-((4-bromophenyl)thio)-3-phenylacrylate**7**

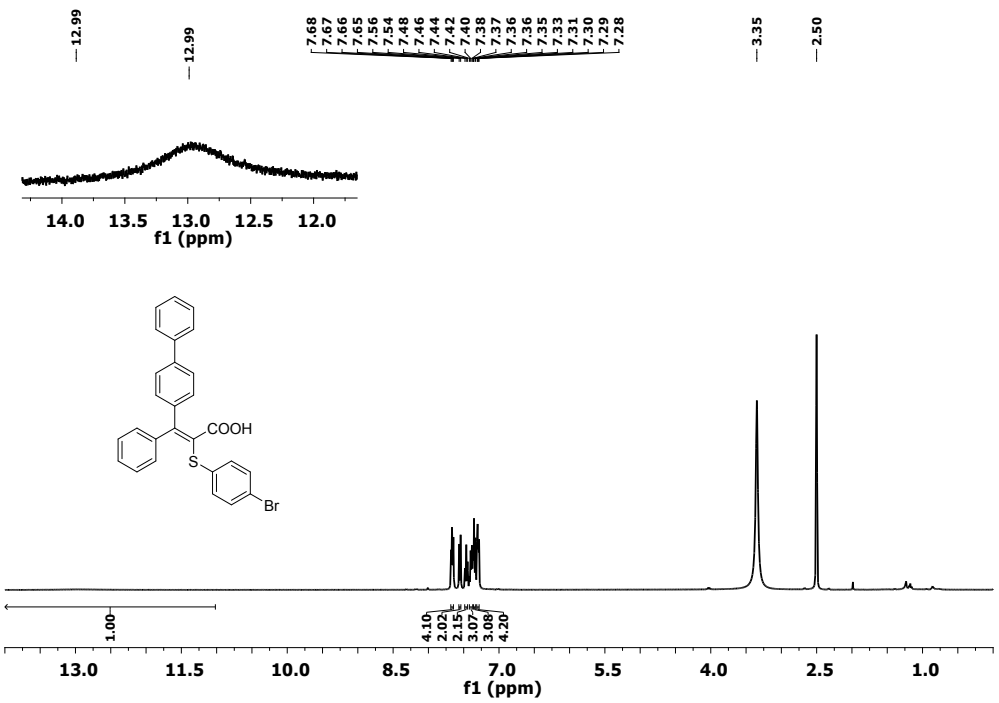


Fig. S83. [1]H NMR spectrum of (E)-3-([1,1'-biphenyl]-4-yl)-2-((4-bromophenyl)thio)-3-phenylacrylic acid **8**

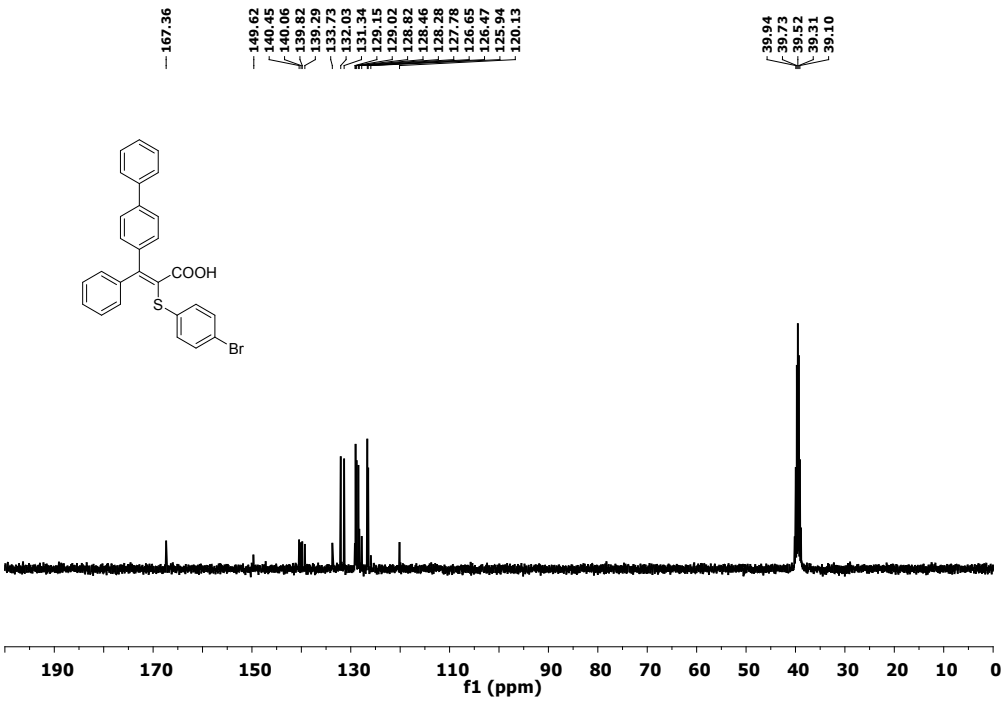


Fig. S84. [13]C NMR spectrum of (E)-3-([1,1'-biphenyl]-4-yl)-2-((4-bromophenyl)thio)-3-phenylacrylic acid **8**

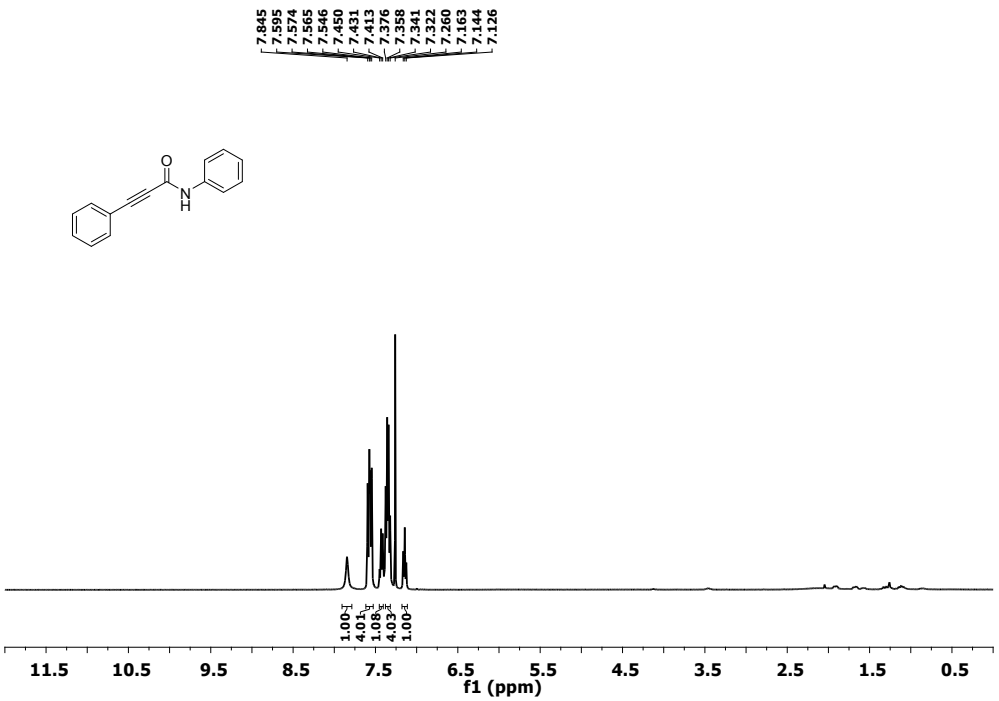


Fig. S85. [1]H NMR spectrum of N,3-diphenylpropiolamide **1a**

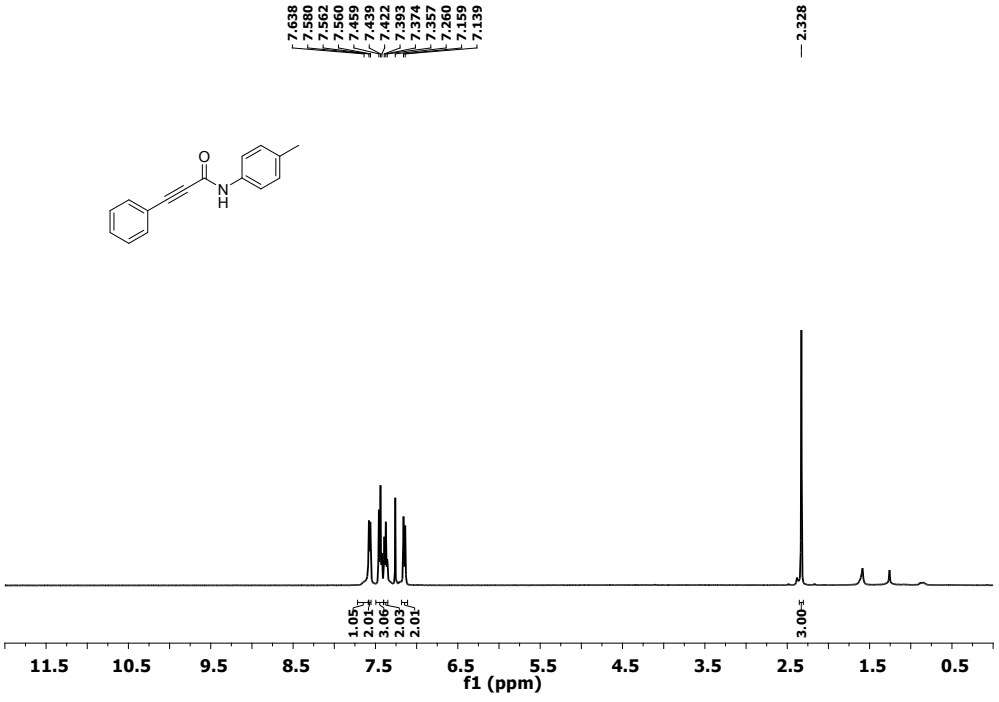


Fig. S86. [1]H NMR spectrum of 3-phenyl-N-(p-tolyl)propiolamide **1b**

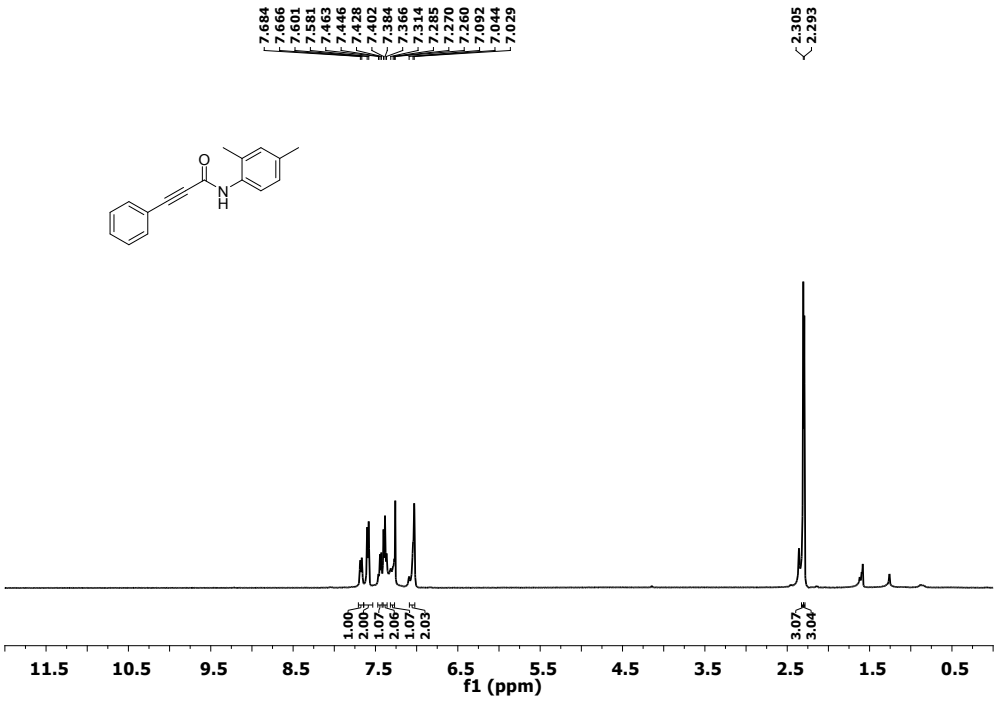


Fig. S87. [1]H NMR spectrum of N-(2,4-dimethylphenyl)-3-phenylpropiolamide **1c**

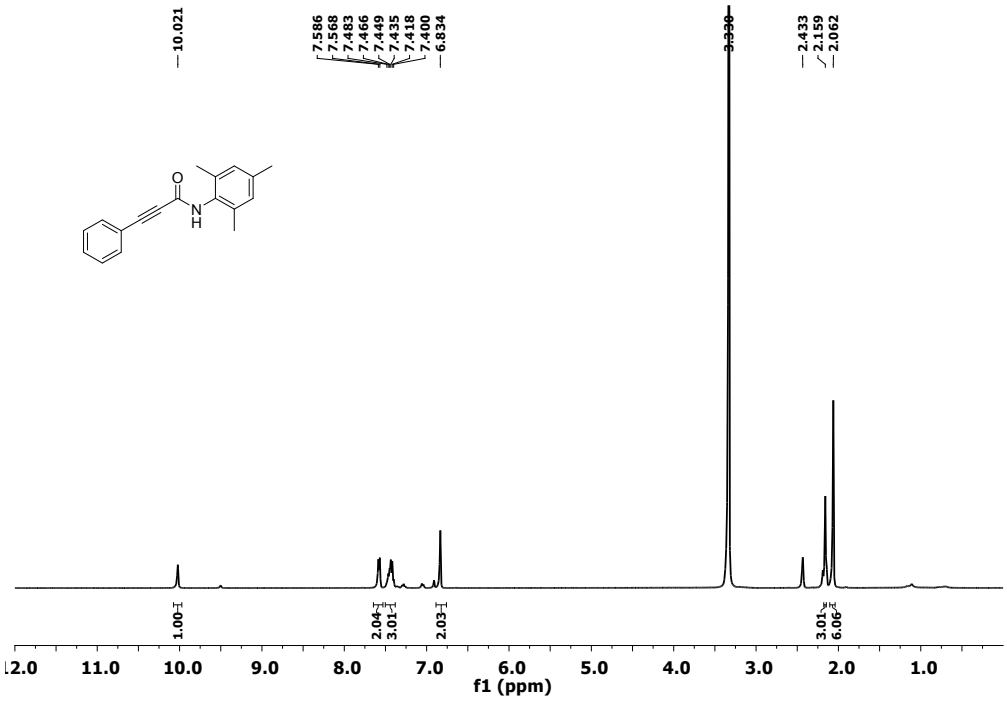


Fig. S88. [1]H NMR spectrum of N-mesityl-3-phenylpropiolamide **1d**

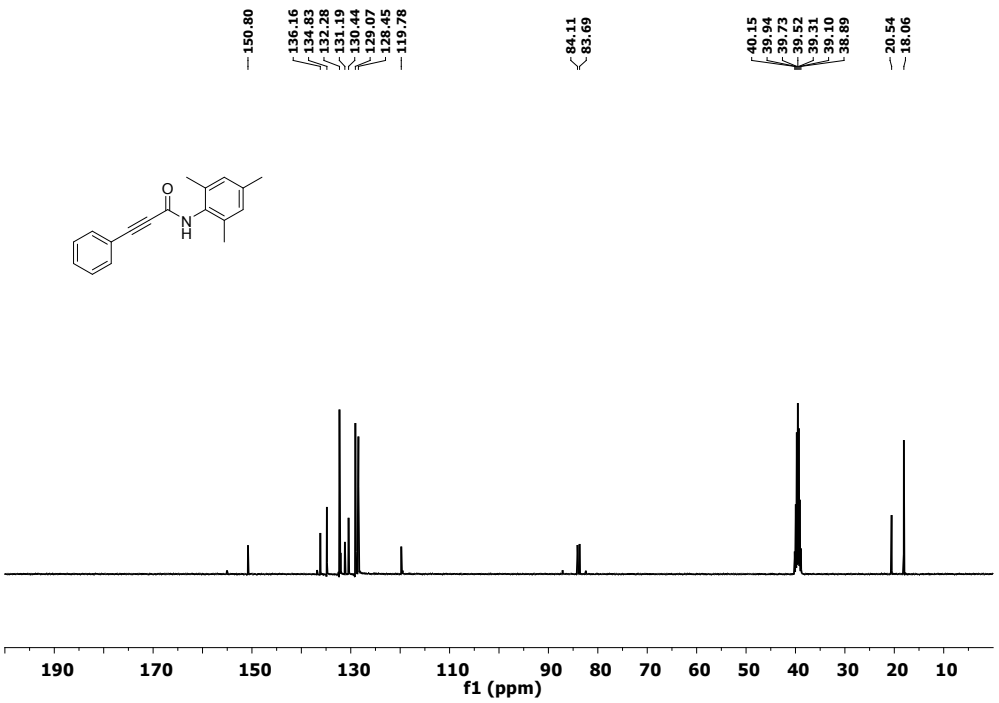


Fig. S89. ^{13}C NMR spectrum of N-mesityl-3-phenylpropiolamide **1d**

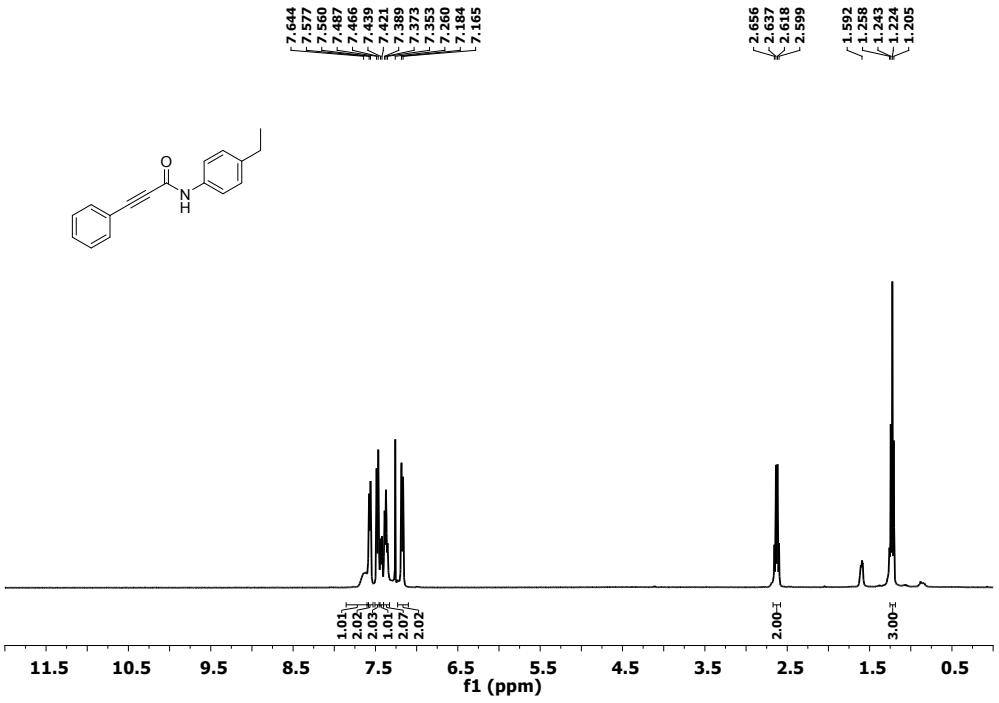


Fig. S90. ^{1}H NMR spectrum of N-(4-ethylphenyl)-3-phenylpropiolamide **1e**

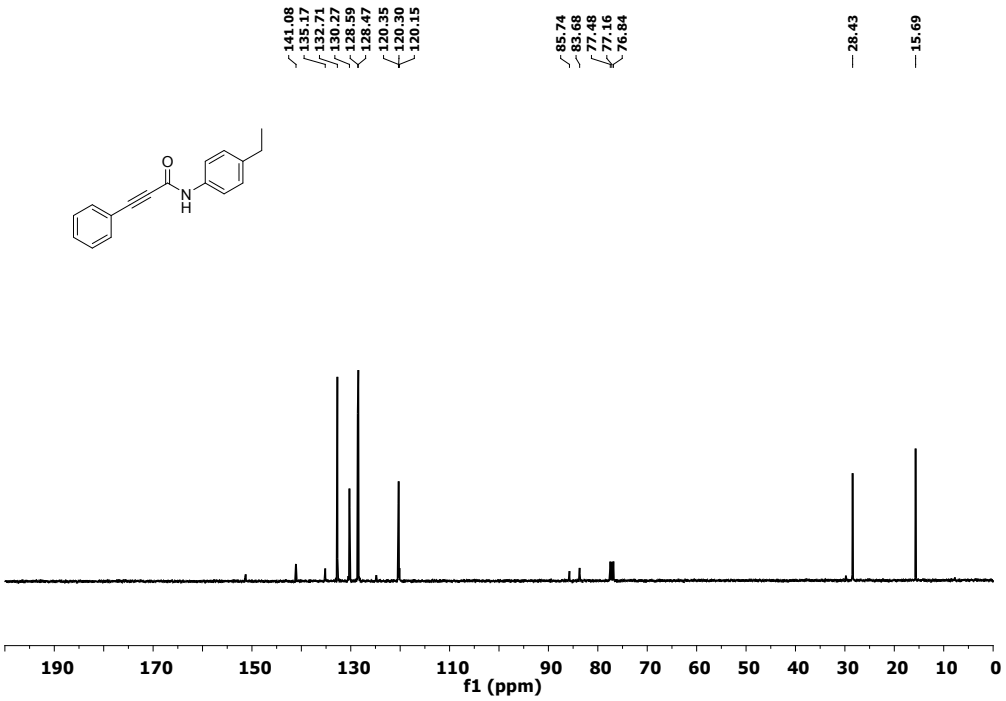


Fig. S91. ^{13}C NMR spectrum of N-(4-ethylphenyl)-3-phenylpropiolamide **1e**

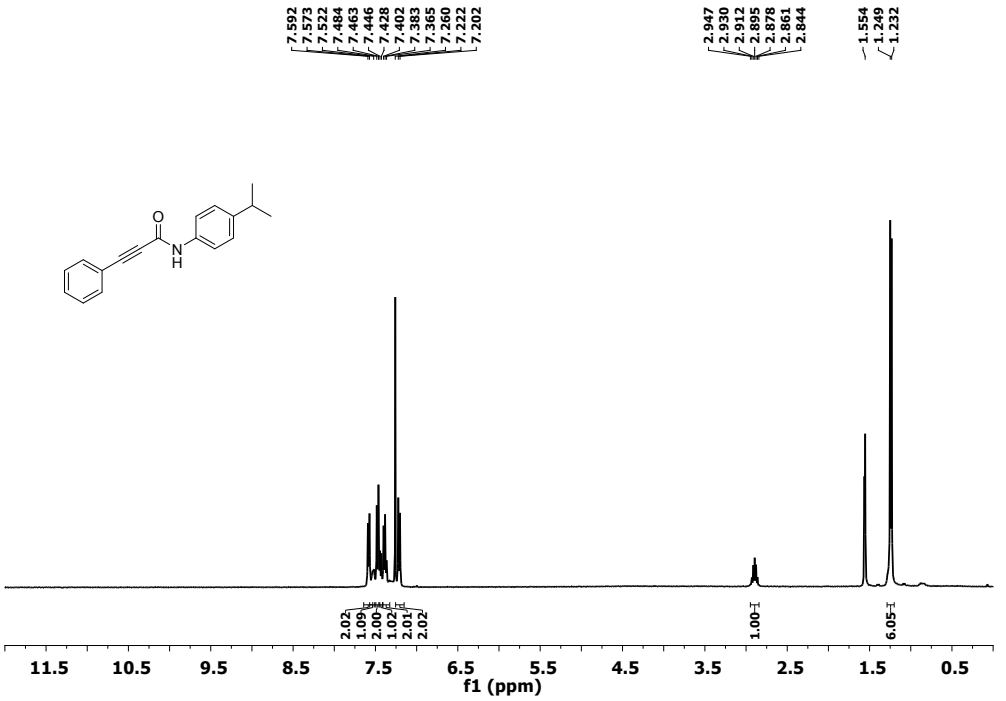


Fig. S92. ^{1}H NMR spectrum of N-(4-isopropylphenyl)-3-phenylpropiolamide **1f**

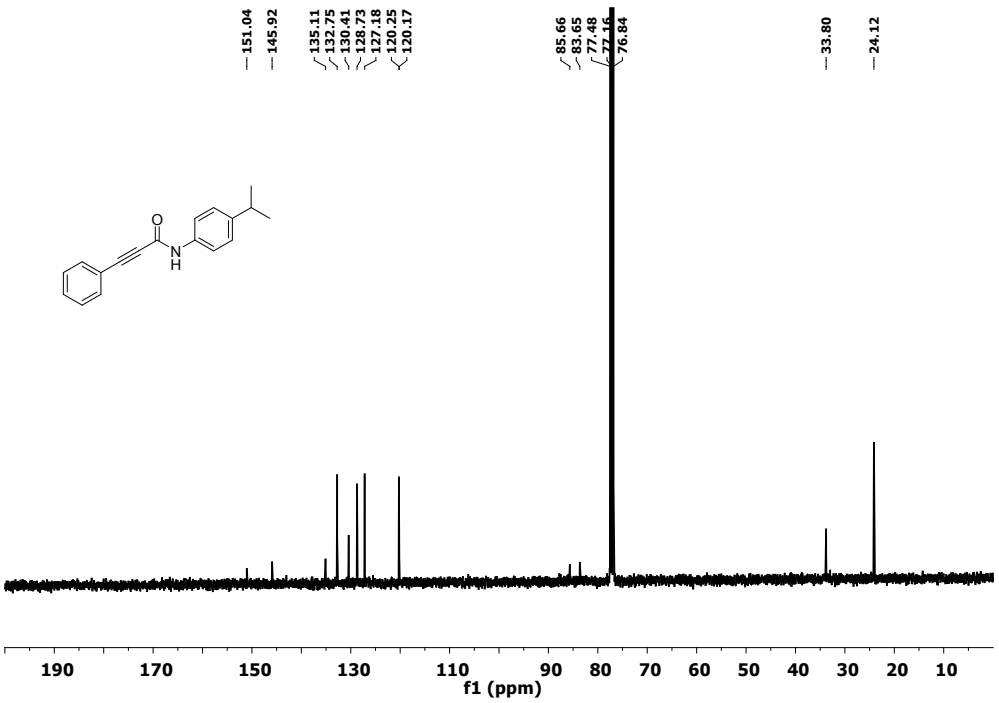


Fig. S93. ^{13}C NMR spectrum of N-(4-isopropylphenyl)-3-phenylpropiolamide **1f**

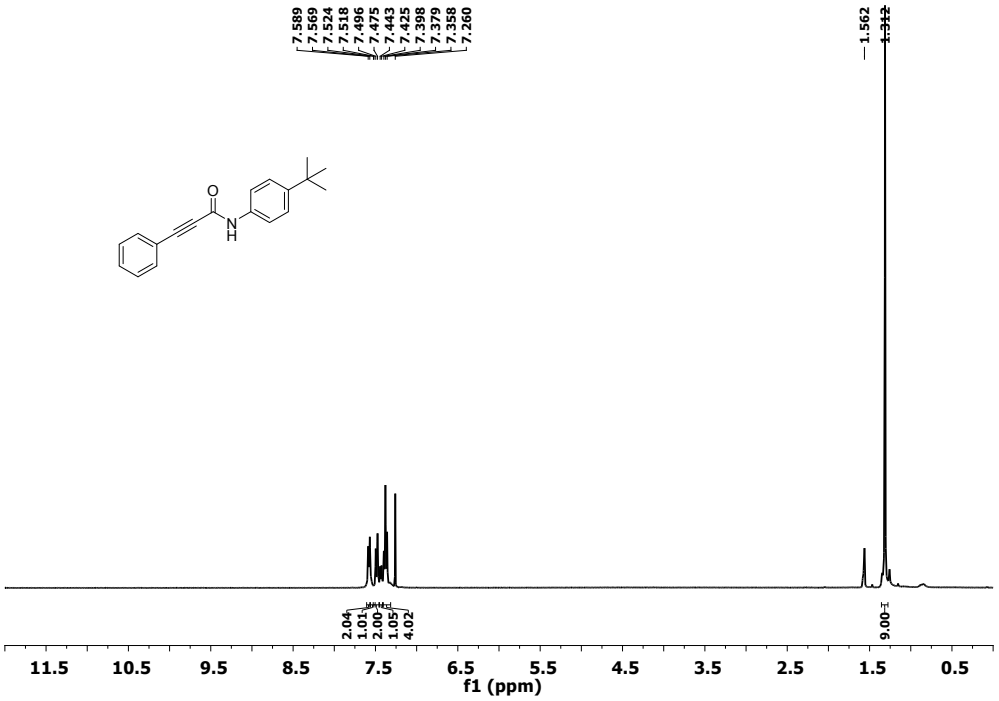


Fig. S94. ^{1}H NMR spectrum of N-(4-(tert-butyl)phenyl)-3-phenylpropiolamide **1g**

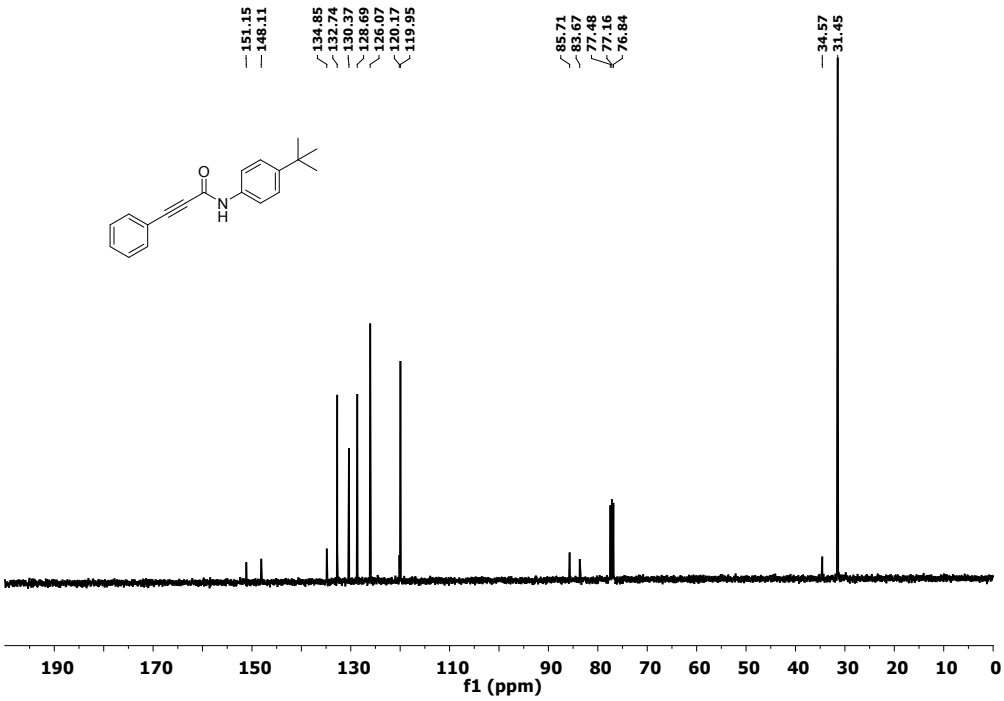


Fig. S95. ^{13}C NMR spectrum of N-(4-(tert-butyl)phenyl)-3-phenylpropiolamide **1g**

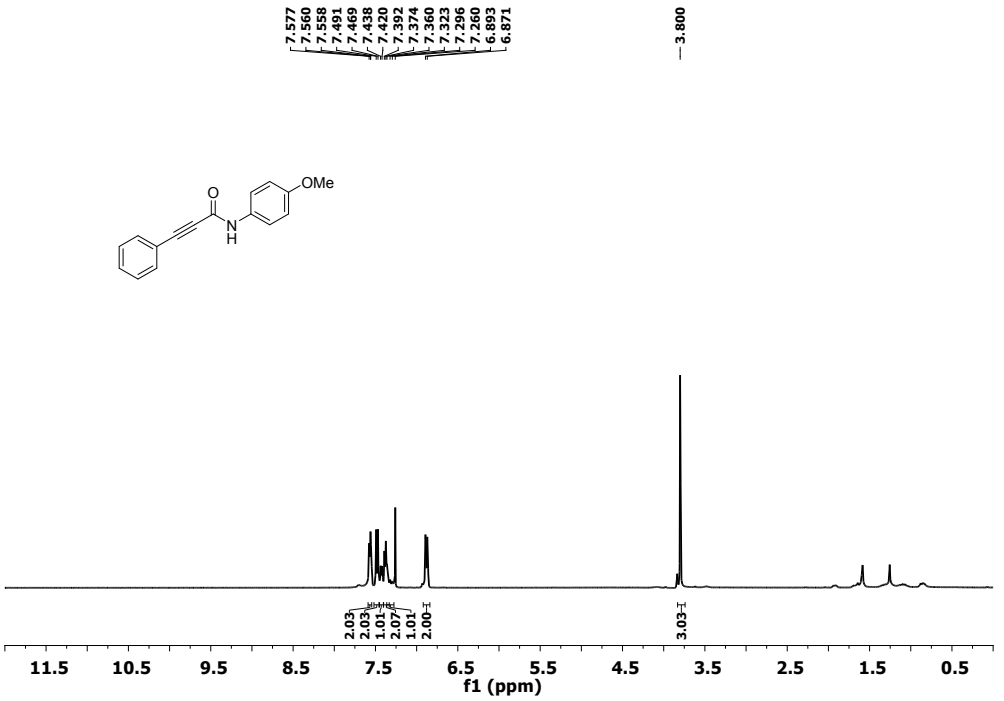


Fig. S96. ^{1}H NMR spectrum of N-(4-methoxyphenyl)-3-phenylpropiolamide **1h**

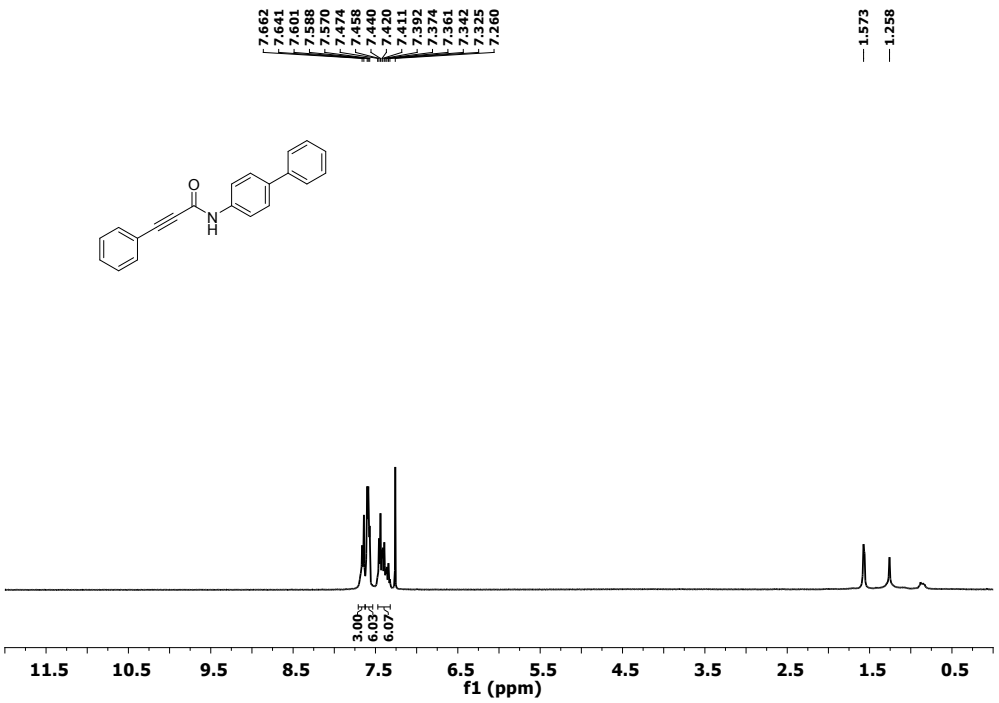


Fig. S97. ^{1}H NMR spectrum of N-([1,1'-biphenyl]-4-yl)-3-phenylpropiolamide **1i**

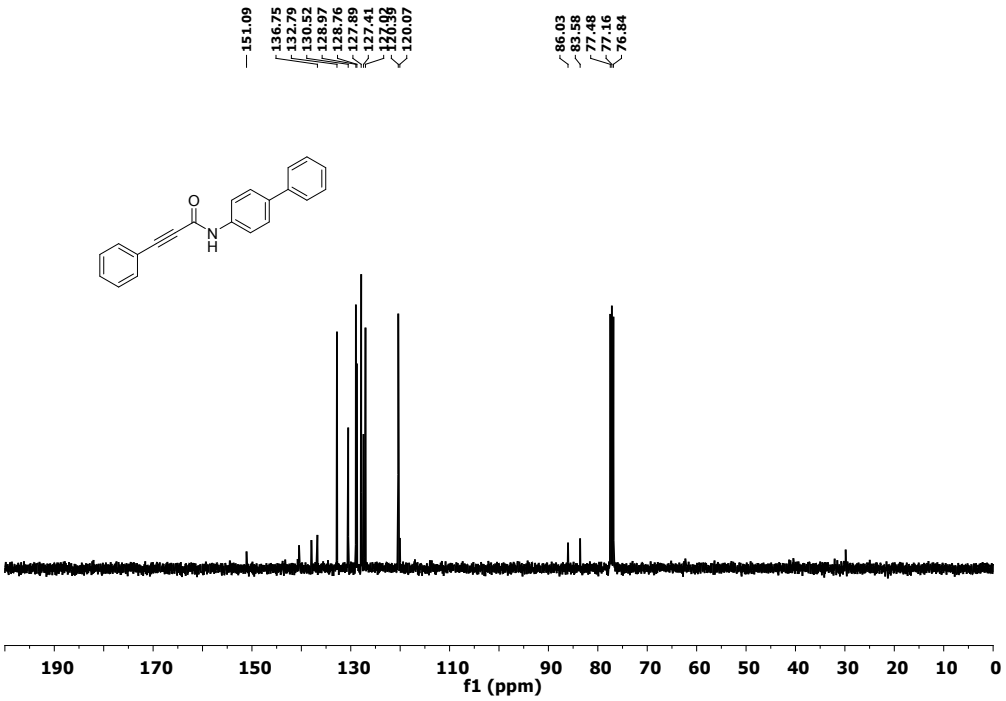


Fig. S98. ^{13}C NMR spectrum of N-([1,1'-biphenyl]-4-yl)-3-phenylpropiolamide **1i**

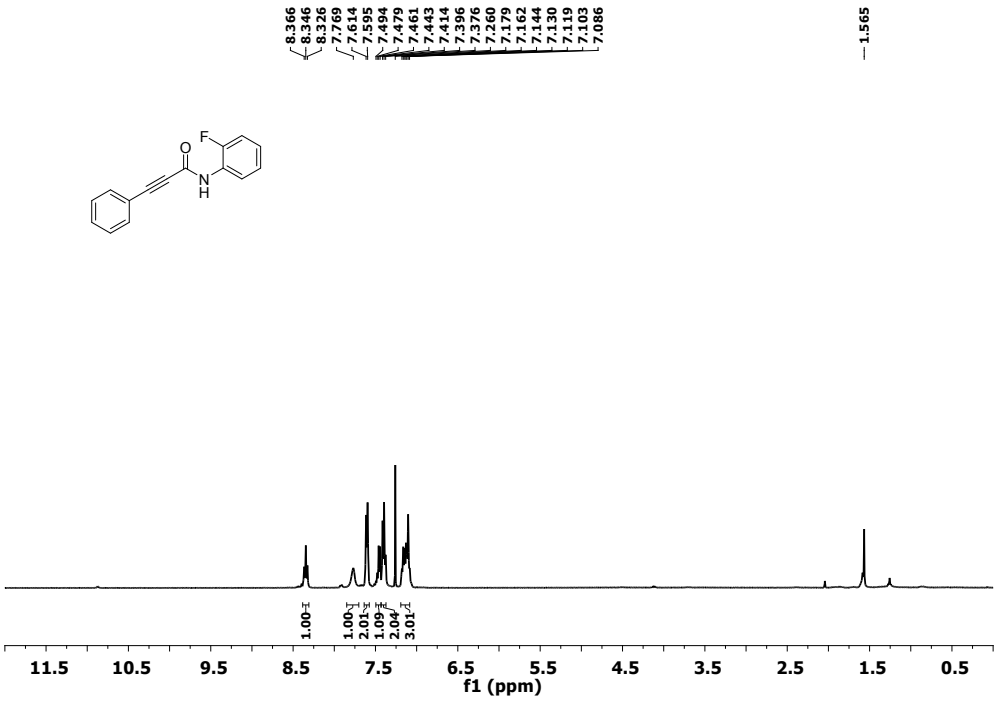


Fig. S99. ^{1}H NMR spectrum of N-(2-fluorophenyl)-3-phenylpropiolamide **1j**

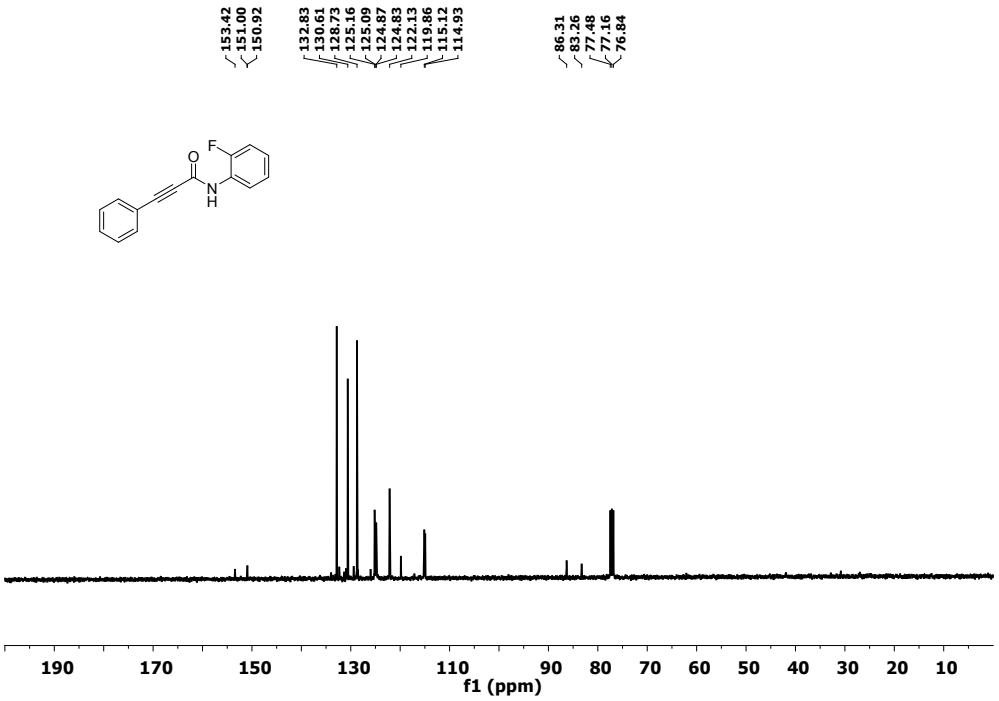


Fig. S100. ^{13}C NMR spectrum of N-(2-fluorophenyl)-3-phenylpropiolamide **1j**

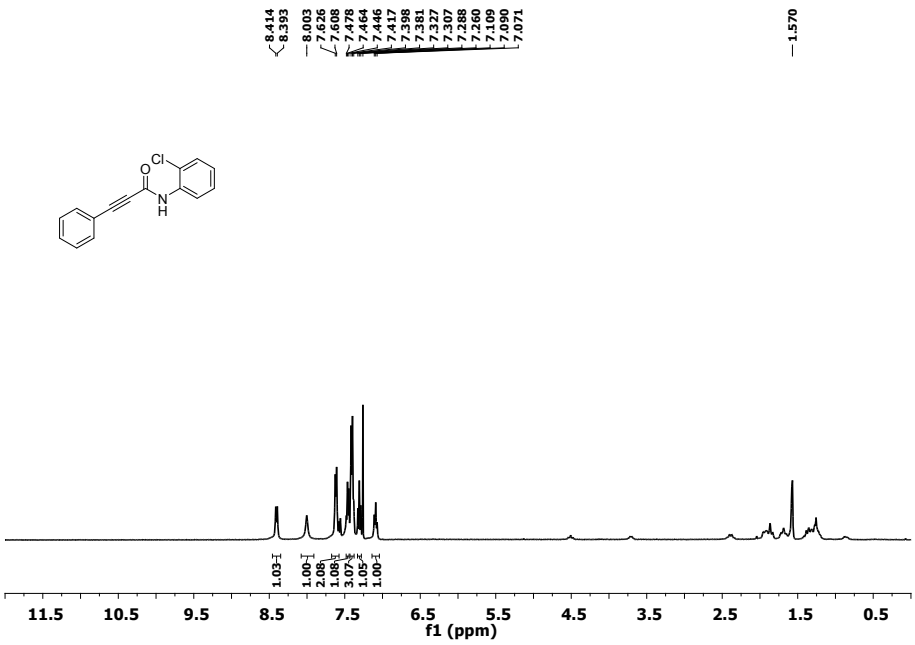


Fig. S101. [1]H NMR spectrum of N-(2-chlorophenyl)-3-phenylpropiolamide **1k**

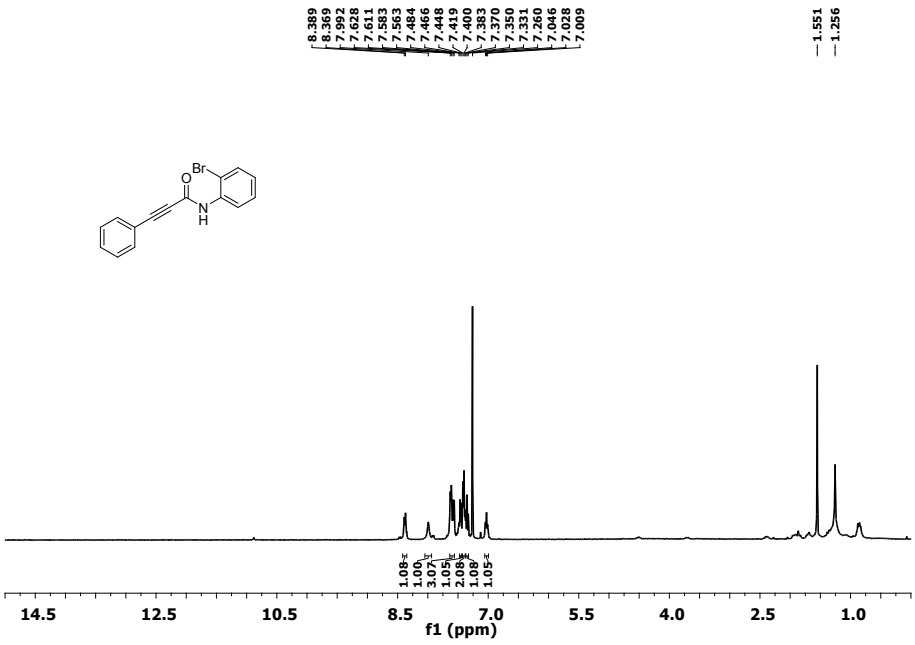


Fig. S102. [1]H NMR spectrum of N-(2-bromophenyl)-3-phenylpropiolamide **1l**

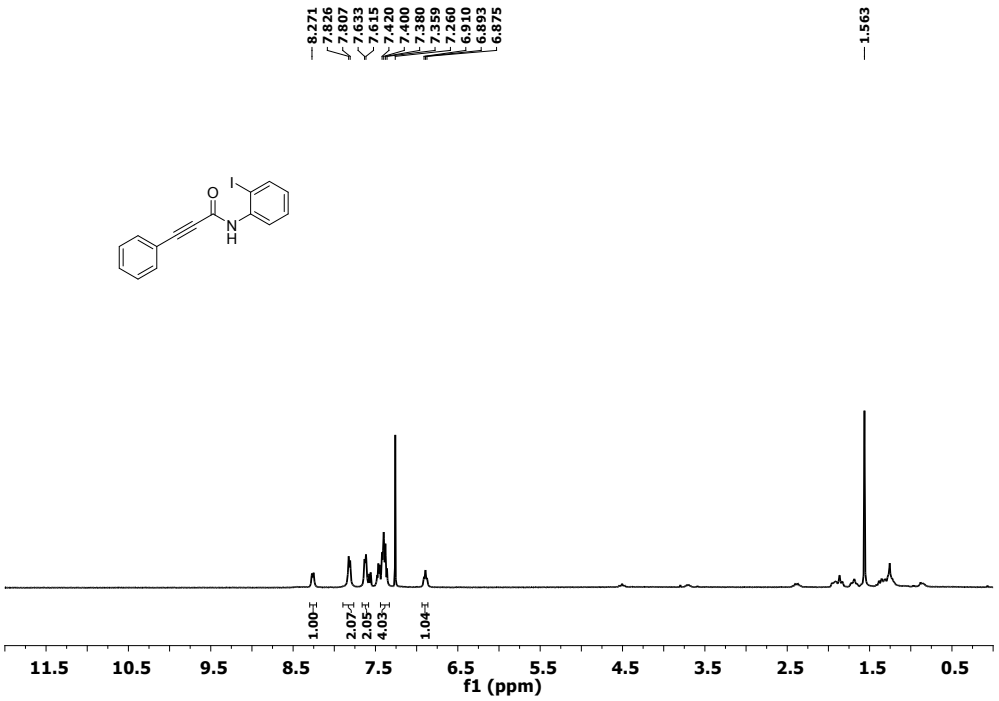


Fig. S103. [1]H NMR spectrum of N-(2-iodophenyl)-3-phenylpropiolamide **1m**

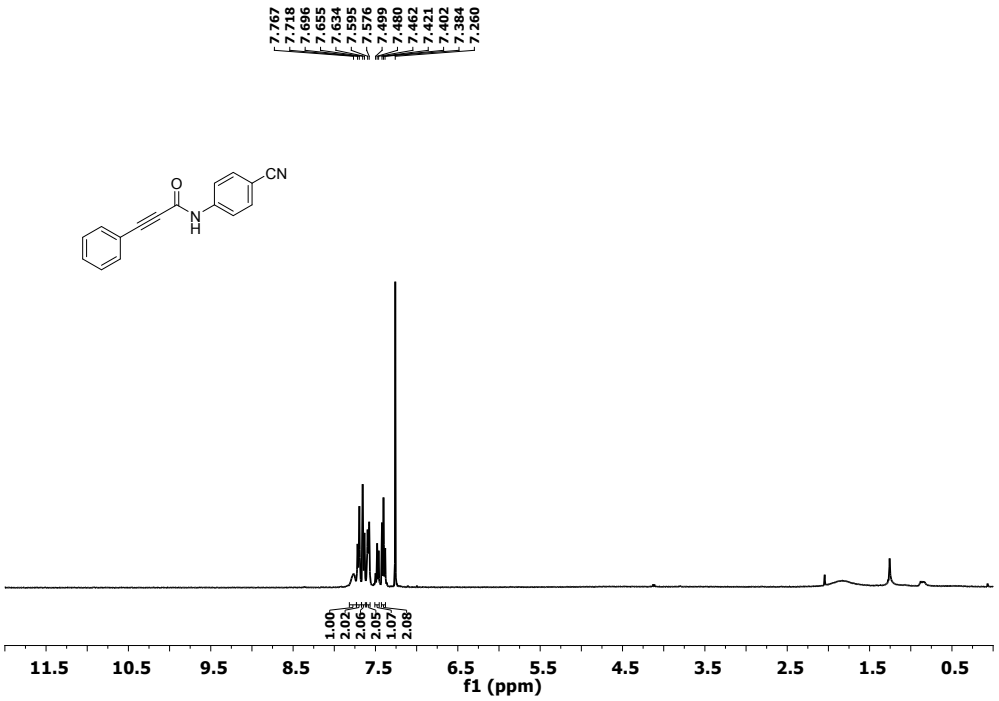


Fig. S104. [1]H NMR spectrum of N-(4-cyanophenyl)-3-phenylpropiolamide **1n**

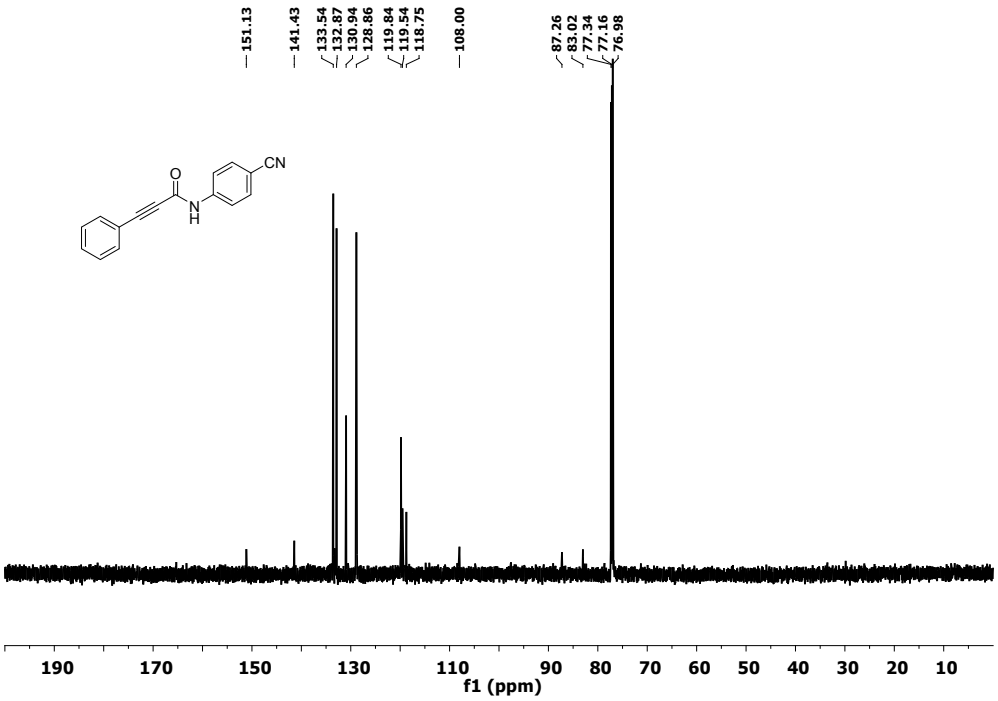


Fig. S105. ^{13}C NMR spectrum of N-(4-cyanophenyl)-3-phenylpropiolamide **1n**

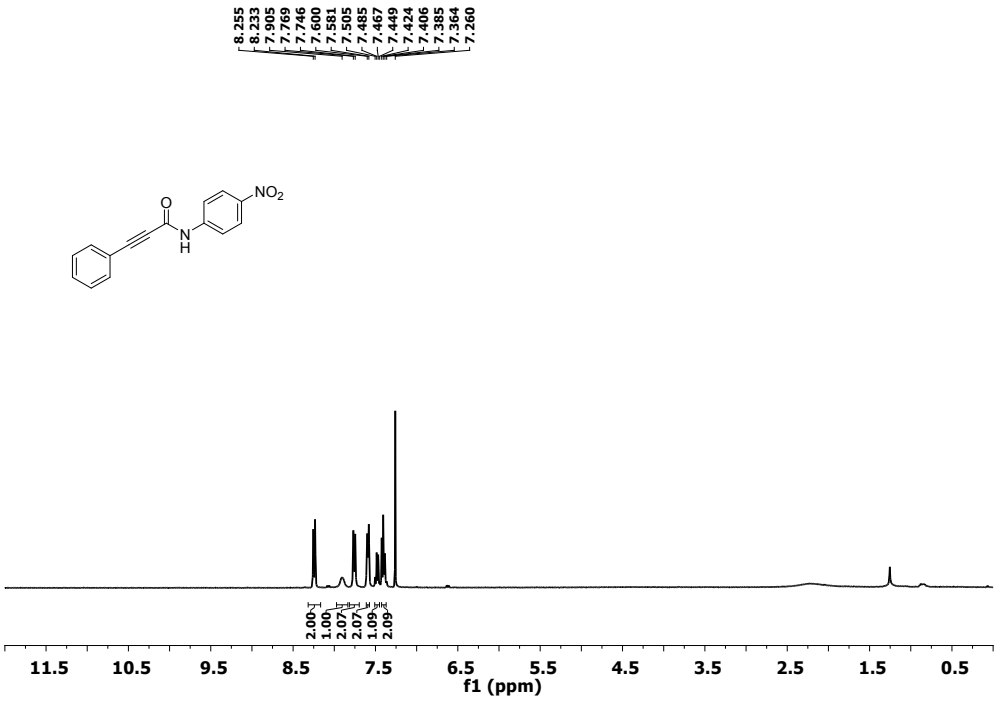


Fig. S106. ^{1}H NMR spectrum of N-(4-nitrophenyl)-3-phenylpropiolamide **1o**

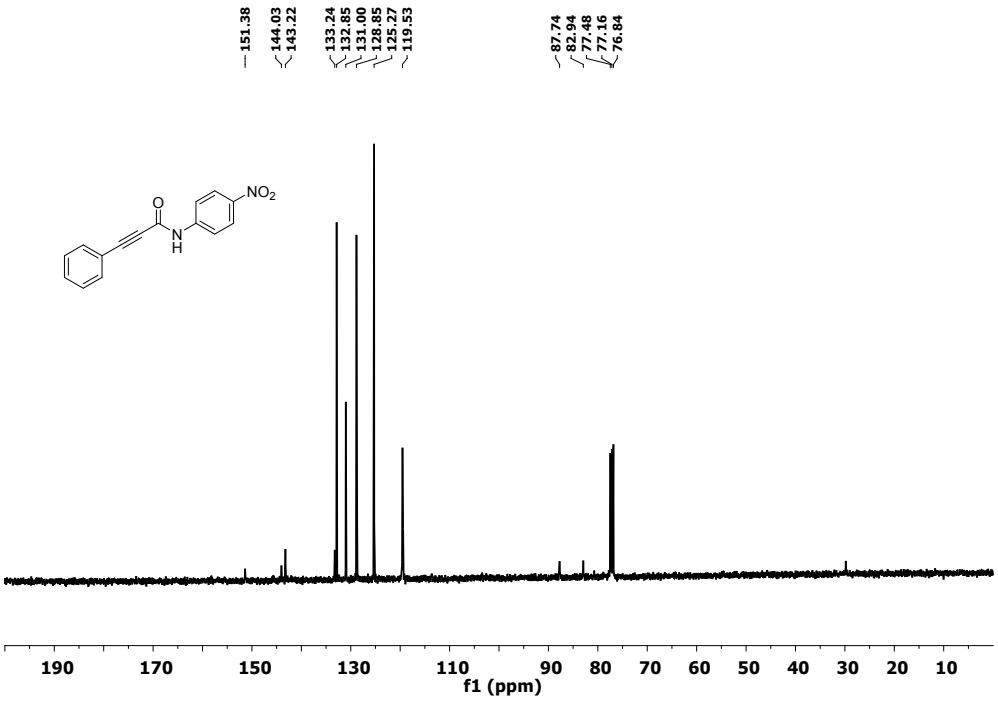


Fig. S107. ^{13}C NMR spectrum of N-(4-nitrophenyl)-3-phenylpropiolamide **1o**

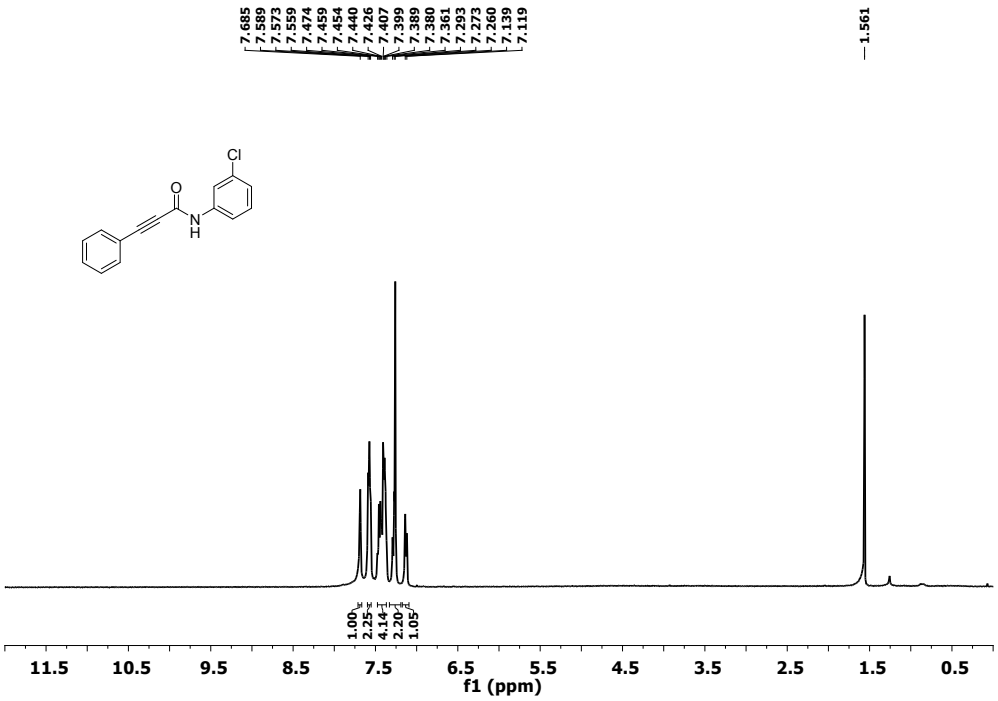


Fig. S108. ^{1}H NMR spectrum of N-(3-chlorophenyl)-3-phenylpropiolamide **1p**

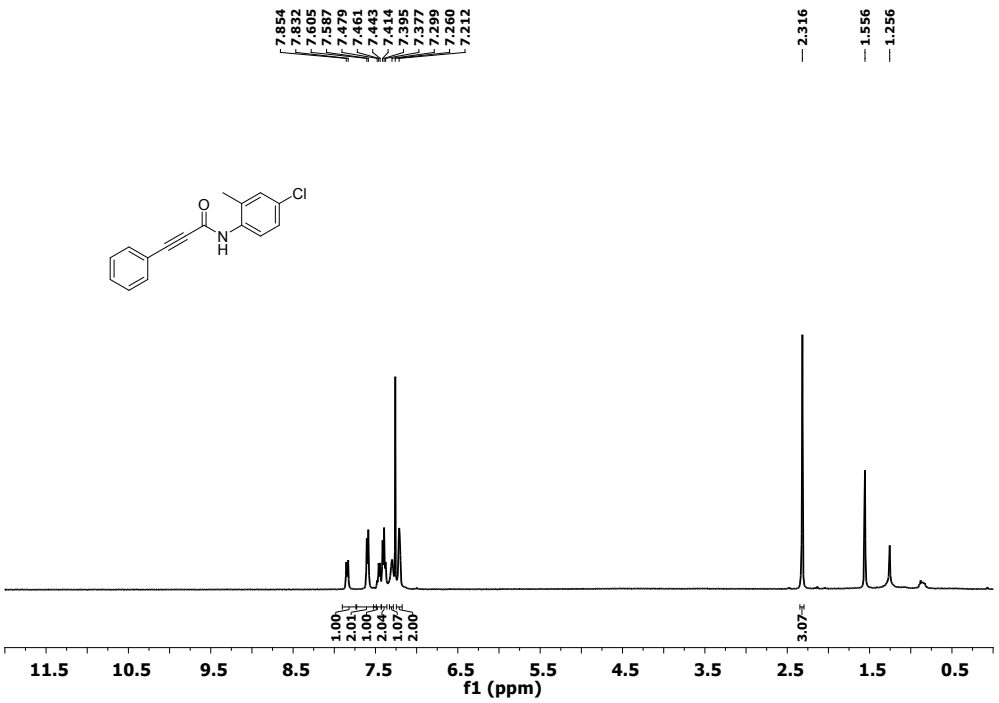


Fig. S109. ^{1}H NMR spectrum of N-(4-chloro-2-methylphenyl)-3-phenylpropiolamide **1q**

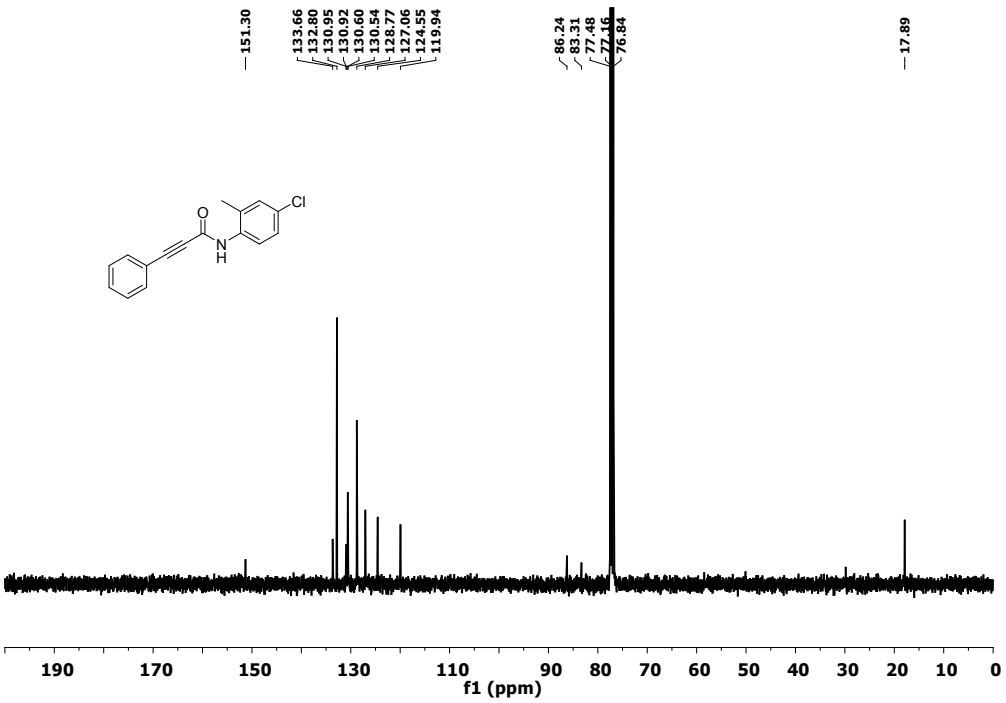


Fig. S110. ^{13}C NMR spectrum of N-(4-chloro-2-methylphenyl)-3-phenylpropiolamide **1q**

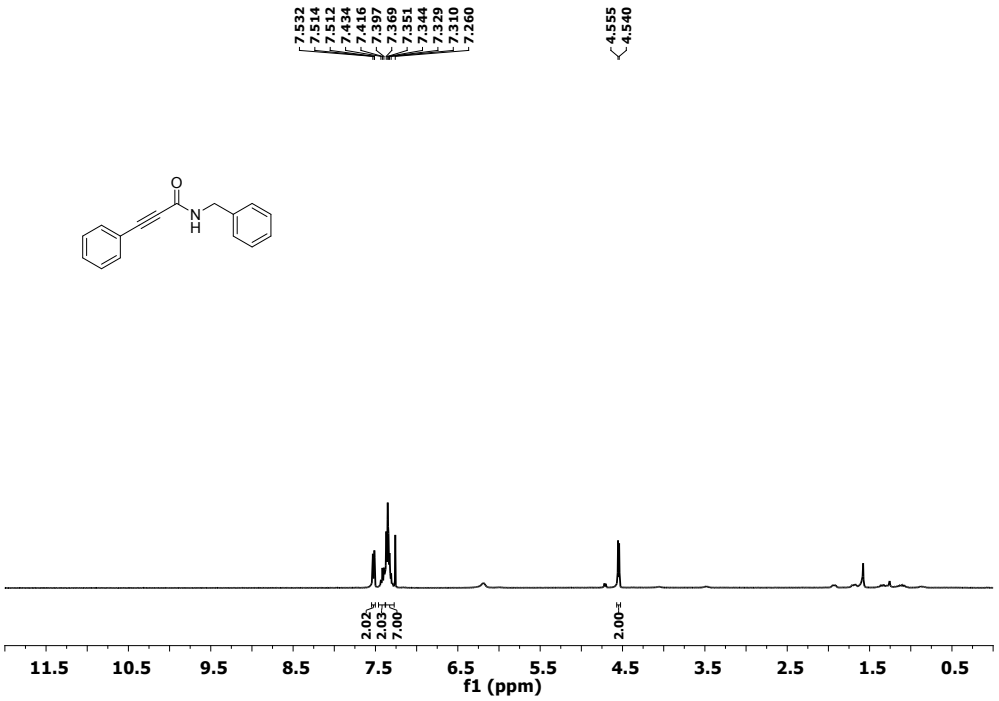


Fig. S111. [1]H NMR spectrum of N-benzyl-3-phenylpropiolamide **1r**

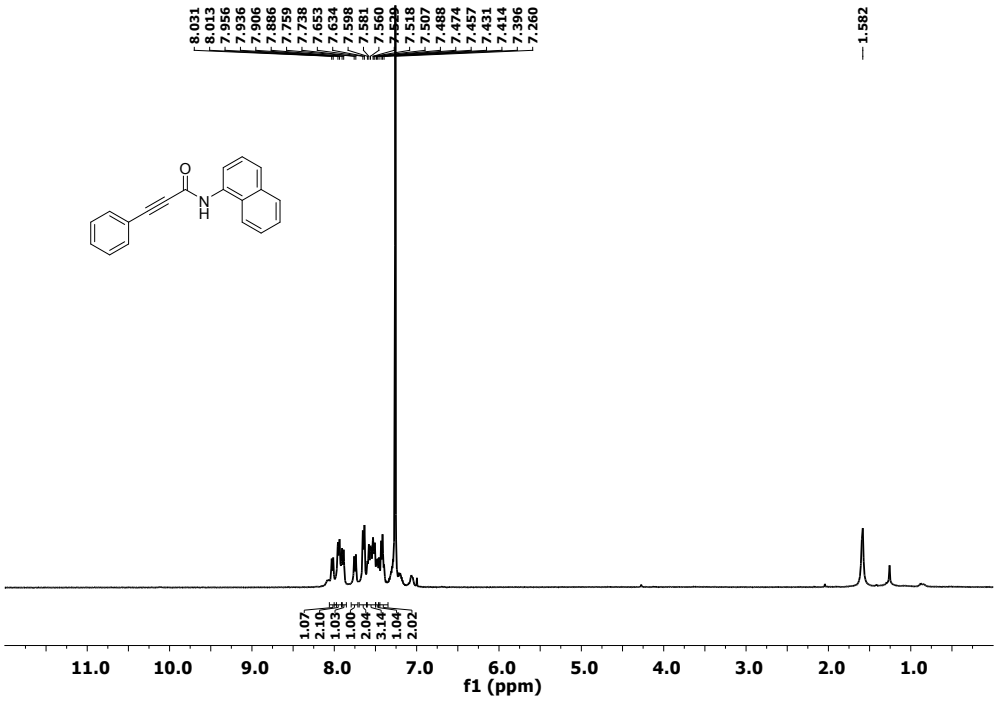


Fig. S112. [1]H NMR spectrum of N-(naphthalen-1-yl)-3-phenylpropiolamide**1s**

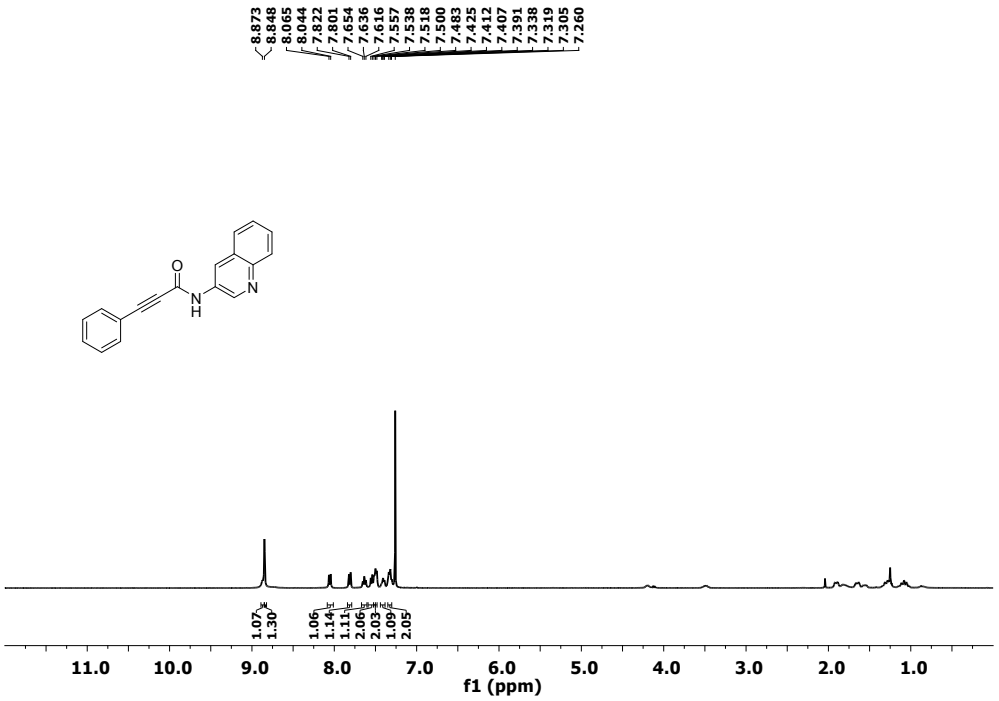


Fig. S113. [1]H NMR spectrum of 3-phenyl-N-(quinolin-3-yl)propiolamide**1t**

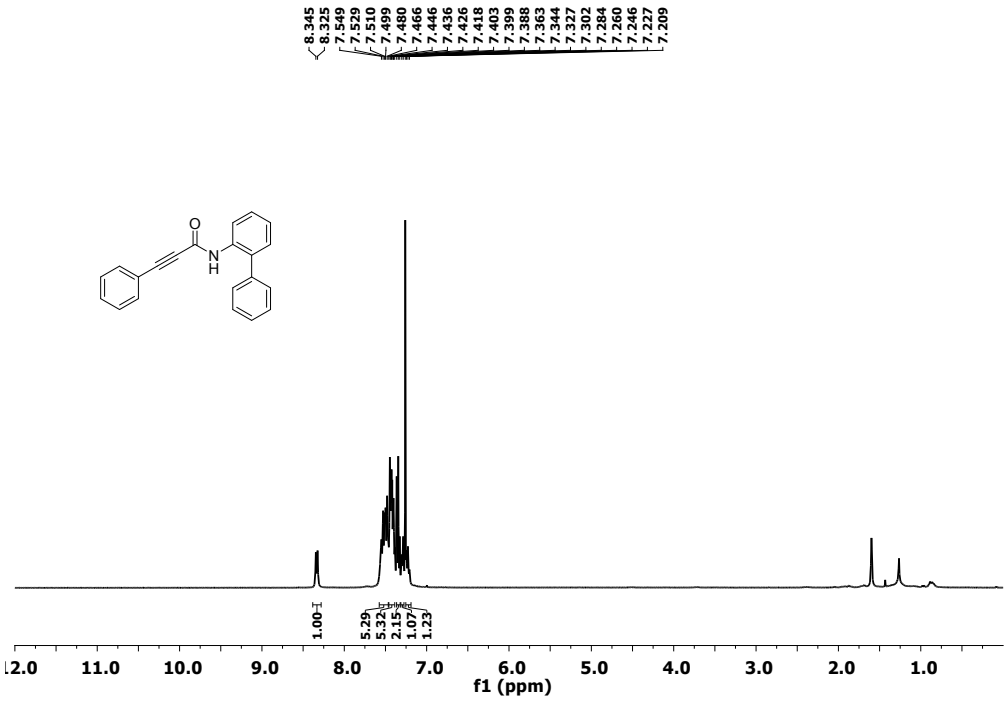
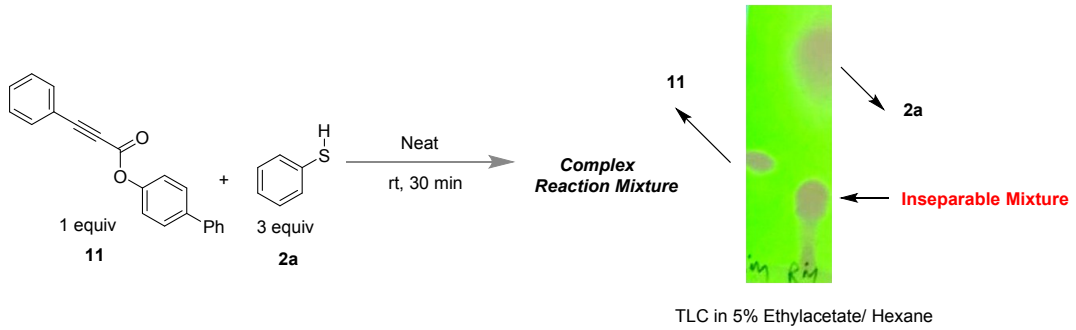


Fig. S114. [1]H NMR spectrum of N-([1,1'-biphenyl]-2-yl)-3-phenylpropiolamide**1u**

Reaction of Compound 11 and 2a.



Scheme S2.

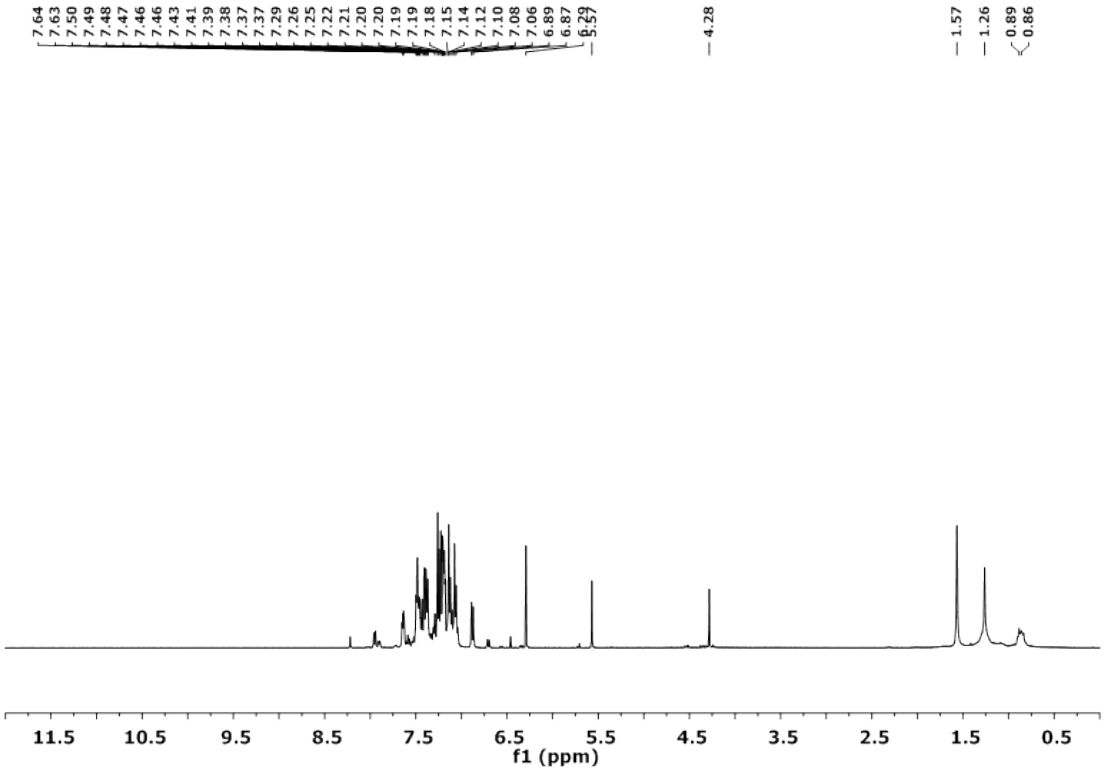
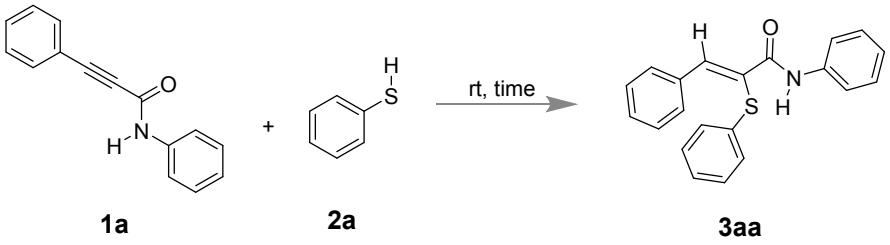


Fig. S115. ^{1}H NMR spectrum of inseparable reaction mixture of phenyl 3-phenylpropiolate **6** and thiophenol **2a**

Reaction of compound 1a and 2a



Scheme S3.

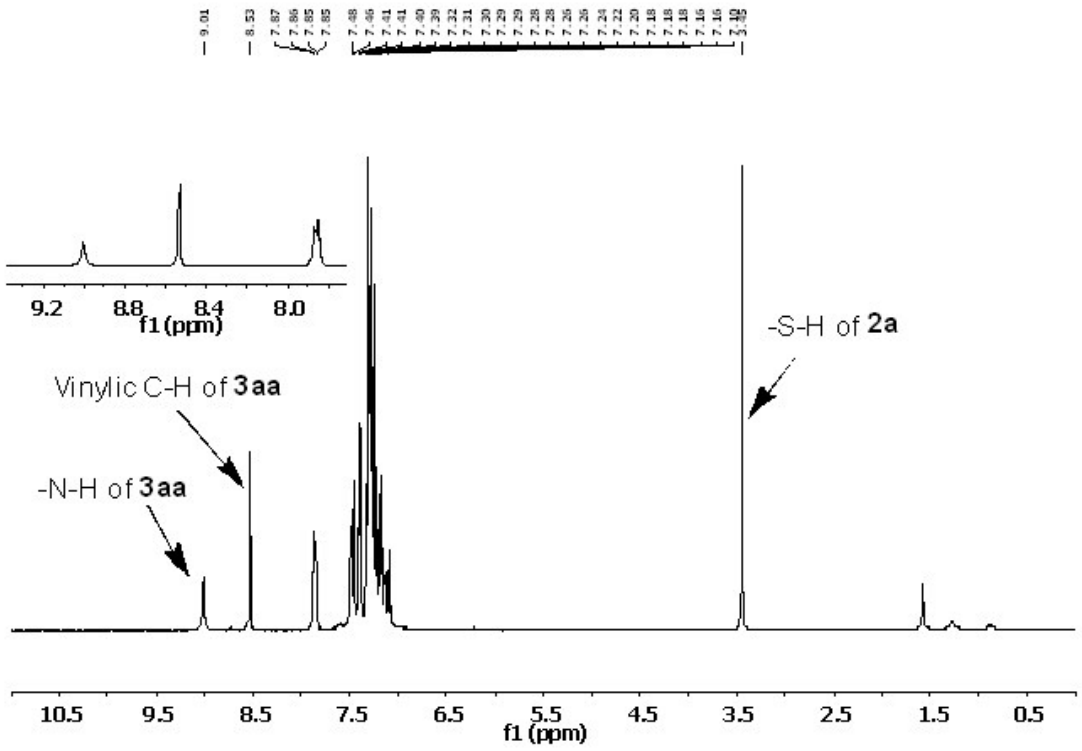
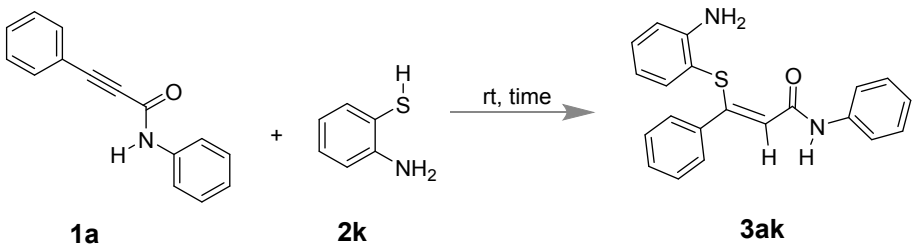


Fig. S117. ^{1}H NMR spectrum of crude reaction mixture of phenyl 3-phenylpropiolamide **1a** and thiophenol **2a**

Reaction of Compound 1a and 2k.



1a **2k** **3ak**

Scheme S4.

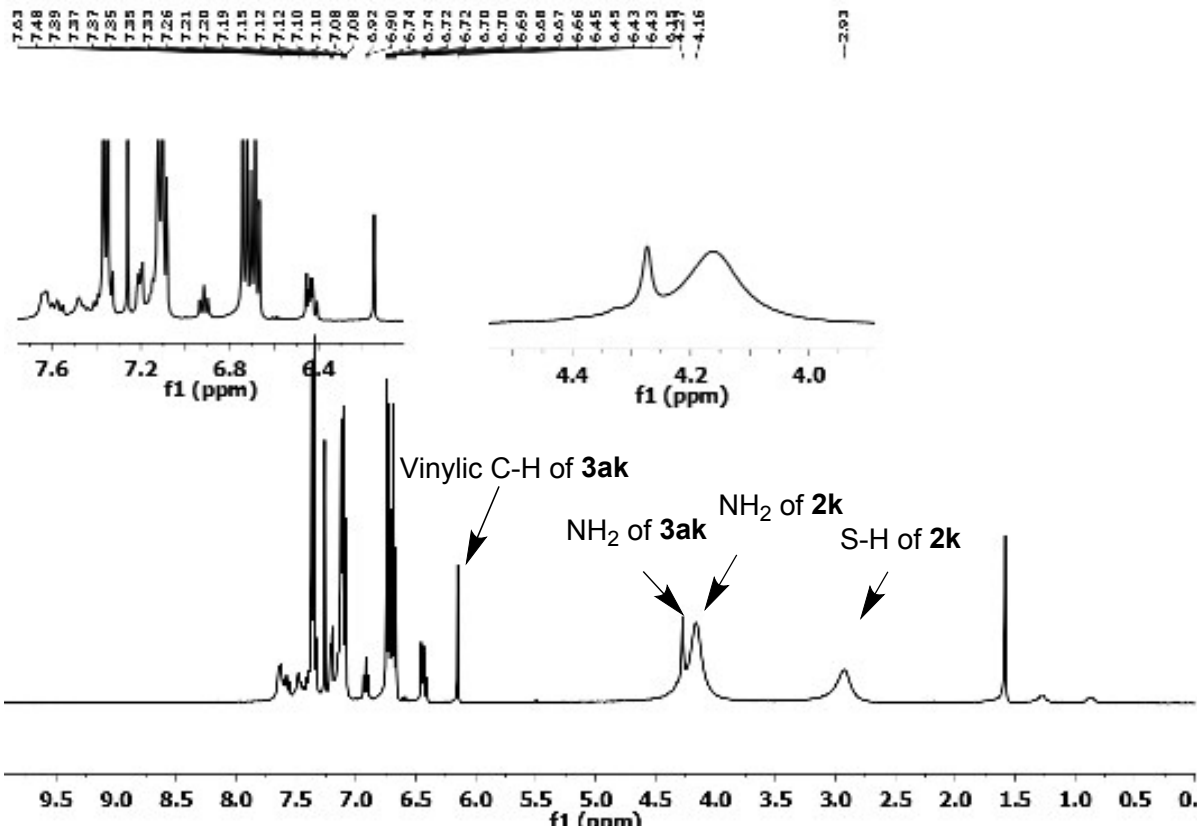


Fig. S118. ^{1}H NMR spectrum of crude reaction mixture of phenyl 3-phenylpropiolamide **1a** and 2-amino thiophenol **2k**