

Supporting Information

Direct *ortho*-Thiolation of Arenes and Alkenes by Nickel Catalysis

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General Information

All reactions were performed under N₂ atmosphere in a 25 mL sealed tube. DMSO was dried and distilled before use following standard procedures. The other materials and solvents were purchased from common commercial sources and used without additional purification, if there is no special version. Starting materials, including 2-methyl-*N*-(quinolin-8-yl)benzamide (**1a**),¹ 2-fluoro-*N*-(quinolin-8-yl)benzamide (**2b**),⁵ 3-methoxy-*N*-(quinolin-8-yl)benzamide (**1c**),¹ 3-(dimethylamino)-*N*-(quinolin-8-yl)benzamide (**1d**),⁴ 3-methyl-*N*-(quinolin-8-yl)benzamide (**1e**),⁴ 3-chloro-*N*-(quinolin-8-yl)benzamide (**1f**),⁵ *N*-(quinolin-8-yl)biphenyl-4-carbox amide(**1g**),⁵ 4-methyl-*N*-(quinolin-8-yl)benzamide (**1h**),² 4-bromo-*N*-(quinolin-8-yl)benzamide (**1i**),¹ 4-chloro-*N*-(quinolin-8-yl)benzamide (**1j**),⁶ 2,4-dimethyl-*N*-(quinolin-8-yl)benzamide (**1k**),⁵ 3,4-dimethoxy-*N*-(quinolin-8-yl)benzamide (**1l**),⁵ *N*-(quinolin-8-yl)benzamide (**1m**),² *N*-(quinolin-8-yl)-1-naphthamide (**1n**),⁴ *N*-(quinolin-8-yl)-2-naphthamide (**1o**),⁴ *N*-(quinolin-8-yl)furan-3-carboxamide (**1p**),¹ and *N*-(quinolin-8-yl)thiophene-2-carboxamide (**1q**),¹ were synthesized according to literature procedures. ¹H NMR spectra were recorded at 400 MHz using TMS as internal standard, ¹³C NMR spectra were recorded at 100 MHz using TMS as internal standard. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), and triplet (t). Mass spectroscopy data of the products were collected on an HRMS-TOF instrument.

General Procedure for the Preparation of acrylamide

To a cooled suspension of sodium hydride (60% in oil dispersion, 486 mg, 0.18 mol) in xylene (11 mL) was slowly added EtOH (2.1 mL) at 0 °C. Diethyl oxalate (3.3 mL, 30 mol) was slowly added thereto and then carboxylate ester (30 mol) was added. After stirring at room temperature for 14 h, the precipitated white powder was collected by filtration with IPE. The obtained powder was dissolved in H₂O (9.4 mL), and then 37% aqueous aldehyde (30 mol) was added. After the mixture was stirred for 1 h, K₂CO₃ (3.7 g, 26 mmol) was added thereto, and the stirring was continued for 14 h. The reaction mixture was poured into a mixture of H₂O (50 mL) and Et₂O (25 mL). The organic layer was washed with H₂O and brine, dried and concentrated to provide the ethyl acrylate as an oil.

An aqueous solution of 2 N sodium hydroxide (24 mL) was added to different ethyl acrylate, then the reaction mixture was refluxed for 1 h. After cooling down to room temperature, the resulting mixture was extracted with diethyl ether several times (2 x 20 mL). The aqueous layer was then acidified with 3 N aqueous HCl solutions (pH = 2), and extracted with ethyl ether (3 x 20 mL). The combined organic extracts were dried over sodium sulfate, filtered and concentrated. The crude acrylic acids (80 - 95%) were used directly for the subsequent reactions without further purification.

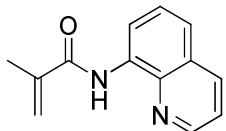
Oxalyl chloride (5.40 mL, 60 mmol) was added slowly to a stirred solution of the carboxylic acid (30 mmol) in CH₂Cl₂ (30 mL) and DMF (0.15 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C and another 16 h at room temperature, and evaporated in vacuo to give the crude acid chloride, which was used directly for the next step without further purification.

The acid chloride was added dropwise to a solution of 8-aminoquinoline (1.01 g, 7.0 mmol) and Et₃N (1.7 mL, 12 mmol) in CH₂Cl₂ (12 mL). The mixture was stirred

overnight at room temperature. Then the mixture was diluted with CH₂Cl₂ (10 mL), washed successively with water, saturated aqueous NaHCO₃, and brine. The organic layer was dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/hexane, to afford corresponding 8-aminoquinolinyl amides.

Analytical Data for Starting Materials

N-(quinolin-8-yl)methacrylamide (**5a**)



Rf 0.46 (hexane/EtOAc = 5/1). M. p. 59.6-60.5 °C. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.36 (s, 1H), 8.79-8.84 (m, 2H), 8.13-8.15 (m, 1H), 7.54 (m, *J* = 8.4 Hz, 1H), 7.49 (dd, *J*₁ = 1.2 Hz; *J*₂ = 8.0 Hz, 1H), 7.44 (dd, *J*₁ = 4.4 Hz; *J*₂ = 8.4 Hz, 1H), 6.05 (s, 1H), 5.55 (s, 1H), 2.19 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 166.5, 148.2, 140.7, 138.6, 136.4, 134.4, 128.0, 127.4, 121.6, 120.7, 116.5, 18.7. HRMS (EI-TOF) calcd for C₁₃H₁₂N₂O (M⁺): 212.0950, found: 212.0955.

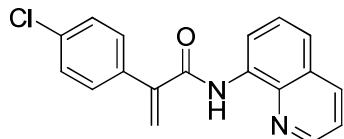
(E)-2-phenyl-*N*-(quinolin-8-yl)but-2-enamide (**5b**)



Rf 0.33 (hexane/EtOAc = 5/1). M. p. 76.4-76.7 °C. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.47 (s, 1H), 8.89 (dd, *J*₁ = 1.2 Hz; *J*₂ = 7.6 Hz, 1H), 8.81 (dd, *J*₁ = 1.6 Hz; *J*₂ = 4.4 Hz, 1H), 8.15 (dd, *J*₁ = 1.6 Hz; *J*₂ = 8.4 Hz, 1H), 7.65 (d, *J* = 0.4 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.51 (dd, *J*₁ = 1.2 Hz; *J*₂ = 8.0 Hz, 1H), 7.40-7.46 (m, 5H), 7.31-7.35 (m, 1H), 2.35 (d, *J* = 1.6 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 167.7, 148.3, 138.7, 136.5, 136.2, 135.0, 134.7, 132.9, 129.6, 128.5, 128.0, 128.0, 127.5,

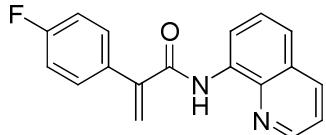
121.7, 121.6, 116.7, 14.4. HRMS (EI-TOF) calcd for C₁₉H₁₆N₂O (M⁺): 288.1263, found: 288.1263.

2-(4-chlorophenyl)-N-(quinolin-8-yl)acrylamide (5c)



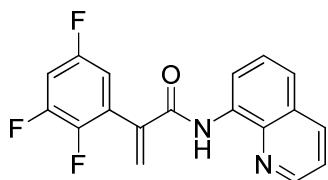
Rf 0.30 (hexane/EtOAc = 5/1). M. p. 104.2-105.8 °C. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.27 (s, 1H), 8.87 (dd, J₁ = 1.6 Hz; J₂ = 7.2 Hz, 1H), 8.70 (dd, J₁ = 1.2 Hz; J₂ = 4.0 Hz, 1H), 8.17 (dd, J₁ = 1.6 Hz; J₂ = 8.4 Hz, 1H), 7.58 (t, J = 8.0 Hz, 1H), 7.54 (dd, J₁ = 1.6 Hz; J₂ = 8.4 Hz, 1H), 7.48-7.51 (m, 2H), 7.40-7.45 (m, 3H), 6.29 (s, 1H), 5.85 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz) δ 165.6, 148.3, 144.9, 138.5, 136.6, 135.2, 134.7, 134.3, 129.7, 128.9, 128.0, 127.5, 122.3, 122.1, 121.7, 117.0. HRMS (EI-TOF) calcd for C₁₈H₁₃ClN₂O (M⁺): 308.0716, found: 308.0716.

2-(4-fluorophenyl)-N-(quinolin-8-yl)acrylamide (5d)



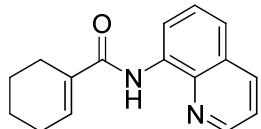
Rf 0.30 (hexane/EtOAc = 5/1). M. p. 96.8-97.2 °C. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.28 (s, 1H), 8.88 (dd, J₁ = 1.6 Hz; J₂ = 7.2 Hz, 1H), 8.70 (dd, J₁ = 1.6 Hz; J₂ = 4.4 Hz, 1H), 8.18 (dd, J₁ = 1.6 Hz; J₂ = 8.4 Hz, 1H), 7.52-7.61 (m, 4H), 7.45 (dd, J₁ = 4.0 Hz; J₂ = 8.0 Hz, 1H), 7.13 (t, J = 8.8 Hz, 2H), 6.29 (s, 1H), 5.83 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz) δ 165.7, 163.0 (d, J_{C-F} = 246.3 Hz), 148.3, 144.9, 138.6, 136.3, 134.4, 132.8 (d, J_{C-F} = 4.1 Hz), 130.2 (d, J_{C-F} = 8.2 Hz), 127.9, 127.4, 122.1 (d, J_{C-F} = 6.4 Hz), 121.7, 116.5, 115.7 (d, J_{C-F} = 11.4 Hz). HRMS (EI-TOF) calcd for C₁₈H₁₃FN₂O (M⁺): 292.1012, found: 292.1012.

N-(quinolin-8-yl)-2-(2,3,5-trifluorophenyl)acrylamide (5e)



Rf 0.30 (hexane/EtOAc = 5/1). M. p. 100.4-101.8 °C. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.29 (s, 1H), 8.83 (dd, J_1 = 2.0 Hz; J_2 = 6.8 Hz, 1H), 8.73 (dd, J_1 = 1.2 Hz; J_2 = 4.4 Hz, 1H), 8.19 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.54-7.60 (m, 2H), 7.46 (dd, J_1 = 4.0 Hz; J_2 = 8.0 Hz, 1H), 7.30-7.36 (m, 1H), 7.00-7.06 (m, 1H), 6.50 (s, 1H), 5.81 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 164.1, 156.3 (m, J_{C-F} = 247.1 Hz), 150.4 (m, J_{C-F} = 251.3 Hz), 148.4, 146.8 (m, J_{C-F} = 242.8 Hz), 139.0, 138.6, 136.4, 134.1, 127.9, 127.4, 125.6, 122.1, 121.7, 121.2 (ddd, J_{C-F} = 7.8 Hz, 17.0 Hz, 27.3 Hz), 119.0 (dd, J_{C-F} = 2.6 Hz, 110.2 Hz), 116.7, 119.0 (dd, J_{C-F} = 2.6 Hz, 110.2 Hz), 106.2 (dd, J_{C-F} = 20.7 Hz, 28.1 Hz). HRMS (EI-TOF) calcd for $\text{C}_{18}\text{H}_{11}\text{F}_3\text{N}_2\text{O} (\text{M}^+)$: 328.0823, found: 328.0825.

N-(quinolin-8-yl)cyclohex-1-enecarboxamide (5f)



Rf 0.33 (hexane/EtOAc = 5/1). M. p. 62.1-62.7 °C. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.25 (s, 1H), 8.81-8.85 (m, 2H), 8.16 (dd, J_1 = 2.0 Hz; J_2 = 8.4 Hz, 1H), 7.55 (t, J = 8.4 Hz, 1H), 7.49 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.46 (dd, J_1 = 4.0 Hz; J_2 = 8.0 Hz, 1H), 6.95-6.97 (m, 1H), 2.50-2.52 (m, 2H), 2.27-2.32 (m, 2H), 1.77-1.83 (m, 2H), 1.66-1.71 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.8, 148.1, 138.7, 136.5, 134.9, 134.7, 134.2, 128.0, 127.6, 121.6, 121.3, 116.6, 25.7, 24.4, 22.3, 21.6. HRMS (EI-TOF) calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O} (\text{M}^+)$: 252.1263, found: 252.1267.

Optimization of the Thioetherification of Alkenes Conditions^a

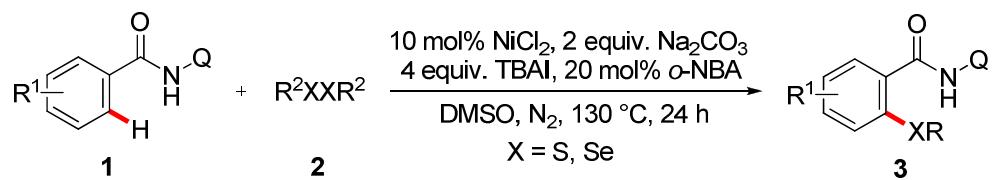
1a + **2a** → **3a**

Entry	Cat.Ni	Base	Additive	Ligand	Solvent	Yield (%) ^b
1	Ni(OTf) ₂	Na ₂ CO ₃	TBAI	<i>o</i> -NBA ^c	DMF	79
2	(Cy ₃ P) ₂ NiCl ₂	Na ₂ CO ₃	TBAI	<i>o</i> -NBA	DMF	61
3	NiCl ₂	Na ₂ CO ₃	TBAI	<i>o</i> -NBA	DMF	81
4	NiI ₂	Na ₂ CO ₃	TBAI	<i>o</i> -NBA	DMF	77
5	Ni(COD) ₂	Na ₂ CO ₃	TBAI	<i>o</i> -NBA	DMF	<5
6	-	Na ₂ CO ₃	TBAI	<i>o</i> -NBA	DMF	NR
7	NiCl₂	Na₂CO₃	TBAI	<i>o</i>-NBA	DMSO	92
8	NiCl ₂	Na ₂ CO ₃	TBAI	<i>o</i> -NBA	Toluene	89
9	NiCl ₂	Na ₂ CO ₃	TBAI	<i>o</i> -NBA	NMP	Trace
10	NiCl ₂	Na ₂ CO ₃	TBAI	<i>o</i> -NBA	DMA	66
11	NiCl ₂	-	TBAI	<i>o</i> -NBA	DMSO	NR
12	NiCl ₂	K ₂ CO ₃	TBAI	<i>o</i> -NBA	DMSO	80
13	NiCl ₂	NaHCO ₃	TBAI	<i>o</i> -NBA	DMSO	32
14	NiCl ₂	Cs ₂ CO ₃	TBAI	<i>o</i> -NBA	DMSO	NR
15	NiCl ₂	KOt-Bu	TBAI	<i>o</i> -NBA	DMSO	NR
16	NiCl ₂	Li ₂ CO ₃	TBAI	<i>o</i> -NBA	DMSO	20
17	NiCl ₂	Na ₂ CO ₃	-	<i>o</i> -NBA	DMSO	40
18	NiCl ₂	Na ₂ CO ₃	TBAI	<i>o</i> -NBA	DMSO	61 ^d
19	NiCl ₂	Na ₂ CO ₃	NaI	<i>o</i> -NBA	DMSO	72
20	NiCl ₂	Na ₂ CO ₃	CuI	<i>o</i> -NBA	DMSO	Trace
21	NiCl ₂	Na ₂ CO ₃	ZnI ₂	<i>o</i> -NBA	DMSO	78
22	NiCl ₂	Na ₂ CO ₃	PhI(OAc) ₂	<i>o</i> -NBA	DMSO	Trace
23	NiCl ₂	Na ₂ CO ₃	I ₂	<i>o</i> -NBA	DMSO	Trace
24	NiCl ₂	Na ₂ CO ₃	TBAI	-	DMSO	76
25	NiCl ₂	Na ₂ CO ₃	TBAI	PhCOOH	DMSO	79
26	NiCl ₂	Na ₂ CO ₃	TBAI	MesCOOH	DMSO	81
27	NiCl ₂	Na ₂ CO ₃	TBAI	Ac-Gly-OH	DMSO	76
28	NiCl ₂	Na ₂ CO ₃	TBAI	PPh ₃	DMSO	41
29	NiCl ₂	Na ₂ CO ₃	TBAI	Xantphos	DMSO	Trace
30	NiCl ₂	Na ₂ CO ₃	TBAI	1,10-Phen	DMSO	42
31	NiCl ₂	Na ₂ CO ₃	TBAI	<i>o</i> -NBA	DMSO	87 ^e
32	NiCl ₂	Na ₂ CO ₃	TBAI	<i>o</i> -NBA	DMSO	75 ^f
33	NiCl ₂	Na ₂ CO ₃	TBAI	<i>o</i> -NBA	DMSO	83 ^g
34	NiCl ₂	Na ₂ CO ₃	TBAI	<i>o</i> -NBA	DMSO	86 ^h

^a Reactions were carried out by using **1a** (0.1 mmol), **2a** (0.2 mmol), Cat. Ni (0.01 mmol), base

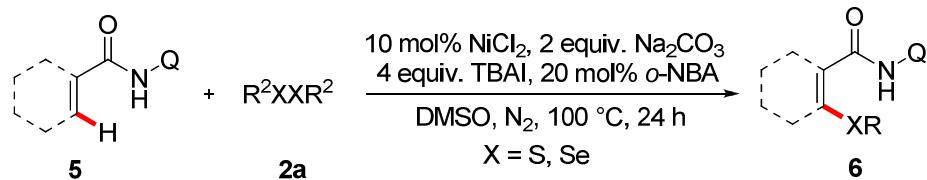
(0.2 mmol), additive (0.4 mmol), ligand (0.02 mmol), solvent (1.0 ml), 130 °C, N₂, 24 h. ^b Isolated yield. ^c *o*-NBA is *o*-nitrobenzoic acid. ^d 2 equiv. TBAI was used. ^e Air. ^f O₂. ^g 120 °C. ^h 140 °C.

Typical Procedure for the Thioetherification of Arenes



A 25 mL sealed tube was charged with *N*-(quinolin-8-yl)benzamide **1** (0.2 mmol), disulfide or diselenide **2** (0.4 mmol), NiCl₂ (2.6 mg, 0.02 mmol), Na₂CO₃ (42.4 mg, 0.4 mmol) and DMSO (2.0 mL). The vial was evacuated and filled with N₂ atmosphere, and stirred at 130 °C for 24 h. The mixture was then cooled to room temperature, diluted with EtOAc, filtered through a celite pad, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/hexane (1:20 ~ 1:5, v/v), to afford the desired alkylated product **3**.

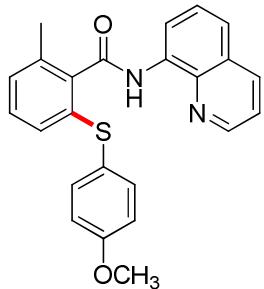
Typical Procedure for the Thioetherification of Alkenes



A 25 mL sealed tube was charged with *N*-(quinolin-8-yl)acrylamide **1** (0.2 mmol), disulfide or diselenide **2** (0.4 mmol), NiCl₂ (2.6 mg, 0.02 mmol), Na₂CO₃ (42.4 mg, 0.4 mmol) and DMSO (2.0 mL). The vial was evacuated and filled with N₂ atmosphere, and stirred at 130 °C for 24 h. The mixture was then cooled to room temperature, diluted with EtOAc, filtered through a celite pad, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/hexane (1:20 ~ 1:5, v/v), to afford the desired alkylated product **6**.

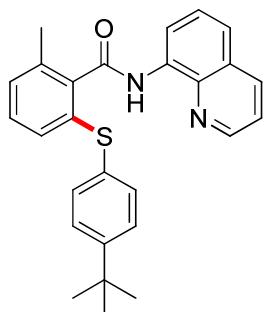
Analytical Data for Products

2-(4-methoxyphenylthio)-6-methyl-N-(quinolin-8-yl)benzamide (3a)



Rf 0.20 (hexane/EtOAc = 10/1). M. p. 132.6-134.2 °C. 73.6 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 9.97 (s, 1H), 9.01 (d, J = 7.6 Hz, 1H), 8.72 (dd, J_1 = 1.6 Hz; J_2 = 4.0 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.54-7.62 (m, 2H), 7.43 (dd, J_1 = 4.0 Hz; J_2 = 8.0 Hz, 1H), 7.38 (d, J = 8.8 Hz, 2H), 7.18 (t, J = 8.0 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.77 (dd, J_1 = 2.0 Hz; J_2 = 6.8 Hz, 2H), 3.72 (s, 3H), 3.45 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.1, 159.7, 148.2, 138.5, 138.2, 136.3, 135.8, 135.7, 135.3, 134.4, 129.5, 128.5, 128.0, 128.0, 127.5, 124.6, 122.0, 121.6, 116.9, 114.9, 55.3, 19.6. HRMS (EI-TOF) calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$ (M^+): 400.1245, found: 400.1239.

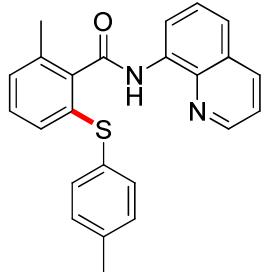
2-(4-*tert*-butylphenylthio)-6-methyl-N-(quinolin-8-yl)benzamide (3b)



Rf 0.40 (hexane/EtOAc = 10/1). M. p. 116.1-117.6 °C. 76.7 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 9.89 (s, 1H), 8.90 (d, J = 7.2 Hz, 1H), 8.62 (d, J = 3.2 Hz, 1H), 8.07 (dd, J_1 = 0.8 Hz; J_2 = 8.4 Hz, 1H), 7.45-7.53 (m, 2H), 7.34 (dd, J_1 = 4.0 Hz; J_2 = 8.0 Hz, 1H), 7.22-7.25 (m, 2H), 7.13-7.17 (m, 3H), 7.08 (d, J = 7.6 Hz, 2H), 2.38 (s, 3H), 1.16 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.0, 149.5, 147.1, 138.4, 137.4,

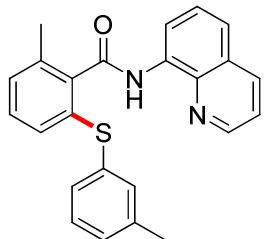
135.3, 134.9, 133.3, 133.0, 130.8, 130.5, 128.5, 128.1, 126.9, 126.7, 126.4, 125.2, 120.9, 120.5, 115.9, 33.5, 30.2, 18.6. HRMS (EI-TOF) calcd for C₂₇H₂₆N₂OS (M⁺): 426.1766, found: 426.1767.

2-methyl-N-(quinolin-8-yl)-6-(*p*-tolylthio)benzamide (3c)



Rf 0.30 (hexane/EtOAc = 10/1). M. p. 131.7-132.7 °C. 66.8 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 9.95 (s, 1H), 8.99 (dd, J₁ = 1.2 Hz; J₂ = 8.4 Hz, 1H), 8.69 (dd, J₁ = 1.6 Hz; J₂ = 4.0 Hz, 1H), 8.15 (dd, J₁ = 1.6 Hz; J₂ = 8.4 Hz, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.54 (dd, J₁ = 1.2 Hz; J₂ = 8.0 Hz, 1H), 7.42 (dd, J₁ = 4.4 Hz; J₂ = 8.0 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 7.6 Hz, 1H), 7.13 (t, J = 8.4 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H), 2.23 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 167.1, 148.2, 139.3, 138.5, 137.6, 136.3, 136.0, 134.4, 132.5, 131.4, 130.0, 129.6, 129.3, 129.0, 128.6, 128.0, 127.5, 122.0, 121.6, 116.9, 21.1, 19.6. HRMS (EI-TOF) calcd for C₂₄H₂₀N₂OS (M⁺): 384.1296, found: 384.1299.

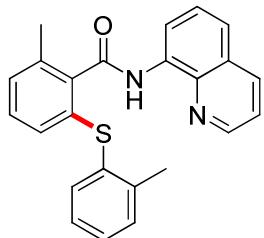
2-methyl-N-(quinolin-8-yl)-6-(*m*-tolylthio)benzamide (3d)



Rf 0.30 (hexane/EtOAc = 10/1). M. p. 132.8-133.7 °C. 66.1 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 9.93 (s, 1H), 8.98 (dd, J₁ = 1.6 Hz; J₂ = 7.6 Hz, 1H), 8.65 (dd, J₁ = 1.6 Hz; J₂ = 4.0 Hz, 1H), 8.11 (dd, J₁ = 1.2 Hz; J₂ = 8.4 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.50-7.52 (m, 1H), 7.38 (dd, J₁ = 4.0 Hz; J₂ = 8.4 Hz, 1H), 7.28 (t, J = 3.2

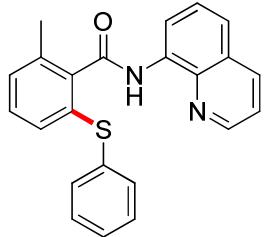
Hz, 1H), 7.21-7.24 (m, 2H), 7.15 (d, J = 7.2 Hz, 2H), 7.08 (t, J = 8.0 Hz, 1H), 6.92 (d, J = 7.2 Hz, 1H), 2.46 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.0, 148.1, 140.0, 138.9, 136.3, 136.0, 135.2, 134.3, 133.4, 132.9, 132.2, 131.4, 129.7, 129.5, 129.0, 128.7, 128.1, 128.0, 127.4, 122.0, 121.6, 116.8, 21.2, 19.7. HRMS (EI-TOF) calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{OS} (\text{M}^+)$: 384.1296, found: 384.1300.

2-methyl-N-(quinolin-8-yl)-6-(*o*-tolylthio)benzamide (3e)



Rf 0.30 (hexane/EtOAc = 10/1). M. p. 133.8-134.6 °C. 48.4 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.00 (s, 1H), 8.98 (dd, J_1 = 1.6 Hz; J_2 = 7.2 Hz, 1H), 8.68 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 8.12 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.52 (dd, J_1 = 1.6 Hz; J_2 = 8.0 Hz, 1H), 7.39 (dd, J_1 = 4.0 Hz; J_2 = 8.4 Hz, 1H), 7.32-7.35 (m, 1H), 7.19 (t, J = 8.0 Hz, 1H), 7.08-7.14 (m, 4H), 6.94 (d, J = 7.6 Hz, 1H), 2.46 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.0, 148.2, 140.1, 138.9, 138.5, 136.3, 136.1, 134.4, 133.7, 133.7, 133.4, 130.6, 129.7, 128.8, 128.3, 128.0, 128.0, 127.4, 126.8, 121.6, 116.9, 20.7, 19.7. HRMS (EI-TOF) calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{OS} (\text{M}^+)$: 384.1296, found: 384.1297.

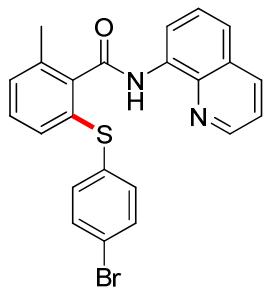
2-methyl-6-(phenylthio)-N-(quinolin-8-yl)benzamide (3f)



Rf 0.30 (hexane/EtOAc = 10/1). M. p. 146.7-148.4 °C. 54.0 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 9.96 (s, 1H), 8.97 (dd, J_1 = 1.2 Hz; J_2 = 7.2 Hz, 1H), 8.67 (dd, J_1 = 1.6 Hz; J_2 = 4.4 Hz, 1H), 8.15 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.58 (t, J =

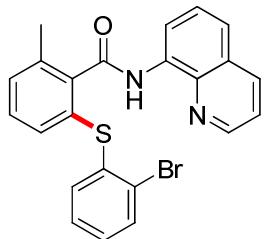
8.0 Hz, 1H), 7.55 (dd, J_1 = 3.2 Hz; J_2 = 8.0 Hz, 1H), 7.41 (dd, J_1 = 4.0 Hz; J_2 = 8.0 Hz, 1H), 7.32-7.34 (m, 2H), 7.24 (d, J = 6.4 Hz, 1H), 7.21 (d, J = 6.4 Hz, 3H), 7.14-7.18 (m, 2H), 2.47 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.0, 148.1, 140.1, 138.4, 136.4, 136.1, 135.7, 134.2, 133.0, 131.3, 130.4, 129.7, 129.6, 129.1, 127.9, 127.4, 127.1, 122.0, 121.6, 116.9, 19.6. HRMS (EI-TOF) calcd for $\text{C}_{23}\text{H}_{18}\text{N}_2\text{OS}$ (M^+): 370.1140, found: 370.1137.

2-(4-bromophenylthio)-6-methyl-N-(quinolin-8-yl)benzamide (3g)



Rf 0.26 (hexane/EtOAc = 10/1). M. p. 121.1-122.3 °C. 79.7 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 9.85 (s, 1H), 8.94 (dd, J_1 = 1.6 Hz; J_2 = 7.2 Hz, 1H), 8.64 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 8.12 (dd, J_1 = 2.0 Hz; J_2 = 8.0 Hz, 1H), 7.57 (t, J = 8.4 Hz, 1H), 7.52 (dd, J_1 = 1.6 Hz; J_2 = 8.0 Hz, 1H), 7.40 (dd, J_1 = 4.0 Hz; J_2 = 8.0 Hz, 1H), 7.28-7.29 (m, 2H), 7.22-7.24 (m, 3H), 7.10 (dd, J_1 = 1.6 Hz; J_2 = 6.4 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.8, 148.3, 141.1, 138.3, 136.5, 136.3, 135.7, 134.2, 132.1, 132.0, 131.6, 131.5, 130.5, 129.9, 127.9, 127.4, 122.1, 121.7, 120.8, 116.8, 19.7. HRMS (EI-TOF) calcd for $\text{C}_{23}\text{H}_{17}\text{BrN}_2\text{OS}$ (M^+): 448.0245, found: 448.0247.

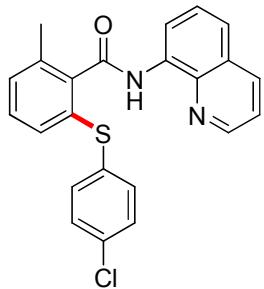
2-(2-bromophenylthio)-6-methyl-N-(quinolin-8-yl)benzamide (3h)



Rf 0.25 (hexane/EtOAc = 10/1). M. p. 132.7-133.7 °C. 80.6 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 9.84 (s, 1H), 8.82 (dd, J_1 = 1.6 Hz; J_2 = 7.2 Hz, 1H), 8.50

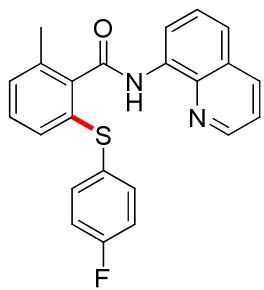
(dd, $J_1 = 1.6$ Hz; $J_2 = 4.0$ Hz, 1H), 7.99 (dd, $J_1 = 1.6$ Hz; $J_2 = 8.4$ Hz, 1H), 7.43 (t, $J = 8.4$ Hz, 1H), 7.39 (dd, $J_1 = 1.6$ Hz; $J_2 = 8.0$ Hz, 1H), 7.27-7.29 (m, 1H), 7.26 (dd, $J_1 = 4.0$ Hz; $J_2 = 8.0$ Hz, 1H), 7.13-7.19 (m, 3H), 7.06-7.09 (m, 1H), 7.03 (dd, $J_1 = 2.0$ Hz; $J_2 = 8.0$ Hz, 1H), 6.83-6.88 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.7, 148.2, 141.5, 138.4, 138.1, 136.6, 136.3, 134.3, 133.0, 131.8, 131.3, 130.7, 130.0, 128.0, 127.9, 127.7, 127.4, 124.0, 122.1, 121.6, 116.9, 19.7. HRMS (EI-TOF) calcd for $\text{C}_{23}\text{H}_{17}\text{BrN}_2\text{OS} (\text{M}^+)$: 448.0245, found: 448.0250.

2-(4-chlorophenylthio)-6-methyl-N-(quinolin-8-yl)benzamide (3i)



Rf 0.37 (hexane/EtOAc = 10/1). M. p. 131.5-132.2 °C. 66.3 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 9.77 (s, 1H), 8.87 (dd, $J_1 = 1.2$ Hz; $J_2 = 7.2$ Hz, 1H), 8.57 (dd, $J_1 = 1.6$ Hz; $J_2 = 4.0$ Hz, 1H), 8.07 (dd, $J_1 = 1.2$ Hz; $J_2 = 8.0$ Hz, 1H), 7.47-7.50 (m, 2H), 7.34 (dd, $J_1 = 4.0$ Hz; $J_2 = 8.0$ Hz, 1H), 7.15-7.22 (m, 3H), 7.11 (d, $J = 8.4$ Hz, 2H), 7.02 (d, $J = 8.4$ Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 165.7, 147.1, 139.8, 137.2, 135.4, 135.3, 133.8, 133.1, 131.8, 130.9, 130.7, 130.3, 129.3, 128.8, 128.1, 126.9, 126.3, 121.0, 120.6, 115.8, 18.6. HRMS (EI-TOF) calcd for $\text{C}_{23}\text{H}_{17}\text{ClN}_2\text{OS} (\text{M}^+)$: 404.0750, found: 404.0750.

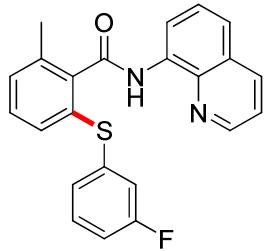
2-(4-fluorophenylthio)-6-methyl-N-(quinolin-8-yl)benzamide (3j)



Rf 0.31 (hexane/EtOAc = 10/1). M. p. 134.4-135.6 °C. 72.2 mg. White solid; ^1H

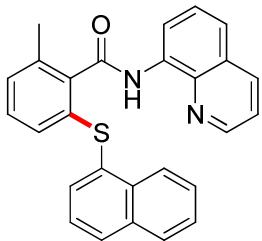
NMR (CDCl_3 , 400 MHz) δ 9.83 (s, 1H), 8.88 (dd, $J_1 = 1.6$ Hz; $J_2 = 7.2$ Hz, 1H), 8.58 (dd, $J_1 = 1.6$ Hz; $J_2 = 4.4$ Hz, 1H), 8.04 (dd, $J_1 = 1.6$ Hz; $J_2 = 8.0$ Hz, 1H), 7.48 (t, $J = 8.4$ Hz, 1H), 7.43 (dd, $J_1 = 1.6$ Hz; $J_2 = 8.4$ Hz, 1H), 7.31 (dd, $J_1 = 4.0$ Hz; $J_2 = 8.0$ Hz, 1H), 7.21-7.25 (m, 2H), 7.14 (t, $J = 7.6$ Hz, 1H), 7.07 (t, $J = 6.8$ Hz, 2H), 5.78 (t, $J = 8.8$ Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.9, 162.3 (d, $J_{\text{C}-\text{F}} = 245.8$ Hz), 148.2, 139.8, 138.4, 136.3, 136.2, 134.3, 134.0 (d, $J_{\text{C}-\text{F}} = 8.1$ Hz), 133.4, 130.5 (d, $J_{\text{C}-\text{F}} = 4.0$ Hz), 130.0, 129.7 (d, $J_{\text{C}-\text{F}} = 5.9$ Hz), 128.0, 127.4, 121.9 (d, $J_{\text{C}-\text{F}} = 42.4$ Hz), 116.9, 116.4, 116.2, 19.6. HRMS (EI-TOF) calcd for $\text{C}_{23}\text{H}_{17}\text{FN}_2\text{OS} (\text{M}^+)$: 388.1046, found: 388.1051.

2-(3-fluorophenylthio)-6-methyl-N-(quinolin-8-yl)benzamide (3k)



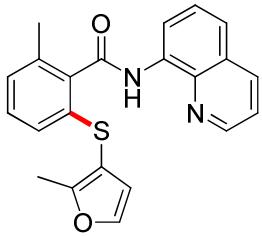
Rf 0.36 (hexane/EtOAc = 10/1). M. p. 124.6-124.8 °C. 62.1 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 9.89 (s, 1H), 8.94 (dd, $J_1 = 1.6$ Hz; $J_2 = 7.6$ Hz, 1H), 8.65 (dd, $J_1 = 1.6$ Hz; $J_2 = 4.0$ Hz, 1H), 8.14 (dd, $J_1 = 1.6$ Hz; $J_2 = 8.0$ Hz, 1H), 7.57 (t, $J = 8.4$ Hz, 1H), 7.53 (dd, $J_1 = 1.6$ Hz; $J_2 = 8.0$ Hz, 1H), 7.40 (dd, $J_1 = 4.0$ Hz; $J_2 = 8.4$ Hz, 1H), 7.32-7.34 (m, 2H), 7.26-7.29 (m, 1H), 7.06-7.12 (m, 1H), 7.01 (d, $J = 8.0$ Hz, 1H), 6.93-6.96 (m, 1H), 6.74-6.78 (m, 1H), 2.48 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.8, 162.9 (d, $J_{\text{C}-\text{F}} = 246.9$ Hz), 148.1, 141.4, 139.1, 139.0, 138.4, 136.6, 136.3, 134.2, 132.1, 130.7, 130.2 (d, $J_{\text{C}-\text{F}} = 9.5$ Hz), 129.9, 127.9, 127.4, 125.5 (d, $J_{\text{C}-\text{F}} = 2.5$ Hz), 122.1, 121.6, 116.9 (d, $J_{\text{C}-\text{F}} = 5.9$ Hz), 116.6, 113.6 (d, $J_{\text{C}-\text{F}} = 20.0$ Hz), 19.7. HRMS (EI-TOF) calcd for $\text{C}_{23}\text{H}_{17}\text{FN}_2\text{OS} (\text{M}^+)$: 388.1046, found: 388.1044.

2-methyl-6-(naphthalen-1-ylthio)-N-(quinolin-8-yl)benzamide (3l)



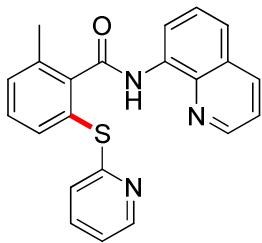
Rf 0.27 (hexane/EtOAc = 10/1). M. p. 148.7-149.3 °C. 68.1 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 9.95 (s, 1H), 8.88 (d, J = 7.6 Hz, 1H), 8.56 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 8.24-8.26 (m, 1H), 7.96 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.58-7.63 (m, 4H), 7.43 (t, J = 8.0 Hz, 1H), 7.37 (dd, J_1 = 1.2 Hz; J_2 = 8.0 Hz, 1H), 7.23-7.28 (m, 3H), 6.96 (t, J = 3.2 Hz, 2H), 6.74 (dd, J_1 = 3.2 Hz; J_2 = 6.0 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 165.9, 147.1, 137.3, 137.3, 135.2, 134.9, 133.3, 133.2, 133.0, 132.4, 131.8, 130.1, 128.5, 128.1, 127.6, 127.2, 127.0, 126.8, 126.3, 125.7, 125.2, 124.7, 124.5, 120.9, 120.5, 115.8, 18.5. HRMS (EI-TOF) calcd for $\text{C}_{27}\text{H}_{20}\text{N}_2\text{OS} (\text{M}^+)$: 420.1296, found: 420.1299.

2-methyl-6-(2-methylfuran-3-ylthio)-N-(quinolin-8-yl)benzamide (3m)



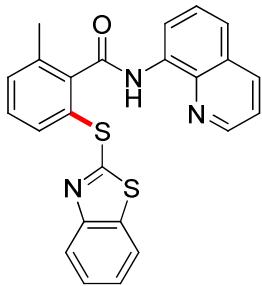
Rf 0.35 (hexane/EtOAc = 10/1). M. p. 116.7-117.3 °C. 73.3 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.09 (s, 1H), 9.04 (dd, J_1 = 1.2 Hz; J_2 = 7.6 Hz, 1H), 8.74 (dd, J_1 = 1.6 Hz; J_2 = 4.4 Hz, 1H), 8.15 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.55 (dd, J_1 = 1.2 Hz; J_2 = 8.4 Hz, 1H), 7.42 (dd, J_1 = 4.4 Hz; J_2 = 8.4 Hz, 1H), 7.31 (d, J = 1.6 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H), 7.06 (d, J = 7.6 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 6.37 (d, J = 1.6 Hz, 1H), 2.45 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.0, 156.9, 148.3, 141.2, 138.6, 136.7, 136.4, 135.8, 135.6, 134.4, 129.5, 128.1, 127.8, 127.5, 125.4, 122.1, 121.7, 117.0, 115.4, 108.1, 19.6, 11.9. HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2\text{S} (\text{M}^+)$: 374.1089, found: 374.1085.

2-methyl-6-(pyridin-2-ylthio)-N-(quinolin-8-yl)benzamide (3n)



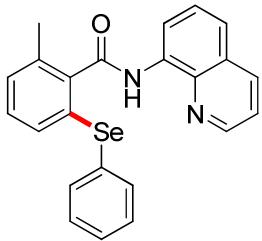
Rf 0.60 (hexane/EtOAc = 1/1). M. p. 182.3-183.7 °C. 45.2 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.15 (s, 1H), 8.92 (dd, J_1 = 1.6 Hz; J_2 = 7.2 Hz, 1H), 8.60 (dd, J_1 = 1.6 Hz; J_2 = 4.0 Hz, 1H), 8.37-8.37 (m, 1H), 8.09 (dd, J_1 = 1.6 Hz; J_2 = 8.0 Hz, 1H), 7.48-7.55 (m, 3H), 7.34-7.41 (d, 4H), 7.02 (d, J = 8.0 Hz, 1H), 6.86-6.89 (m, 1H), 2.50 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.1, 160.5, 149.9, 148.0, 143.6, 138.6, 136.7, 136.5, 136.2, 134.4, 134.3, 131.8, 129.9, 127.9, 127.4, 127.3, 122.0, 122.0, 121.5, 119.8, 117.1, 19.7. HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{17}\text{N}_3\text{OS}$ (M^+): 371.1092, found: 371.1093.

2-(benzo[d]thiazo-2-ylthio)-6-methyl-N-(quinolin-8-yl)benzamide (3o)



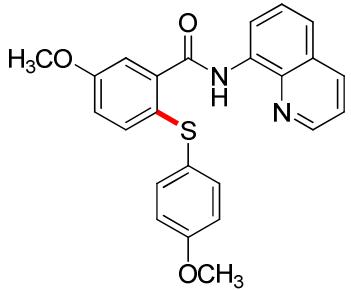
Rf 0.70 (hexane/EtOAc = 1/1). M. p. 140.9-141.5 °C. 53.0 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 9.93 (s, 1H), 8.85 (dd, J_1 = 1.6 Hz; J_2 = 7.6 Hz, 1H), 7.95 (dd, J_1 = 1.2 Hz; J_2 = 8.4 Hz, 1H), 7.78 (dd, J_1 = 1.2 Hz; J_2 = 4.0 Hz, 1H), 7.62-7.66 (m, 2H), 7.59 (d, J = 7.6 Hz, 1H), 7.42-7.47 (m, 1H), 7.40-7.42 (m, 3H), 7.47 (t, J = 8.0 Hz, 1H), 7.19-7.20 (m, 1H), 7.09 (dd, J_1 = 4.0 Hz; J_2 = 8.0 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 168.9, 166.3, 154.0, 147.8, 143.2, 138.3, 137.4, 136.0, 135.9, 134.8, 134.0, 133.1, 130.3, 127.7, 127.2, 126.3, 125.9, 124.1, 122.2, 122.0, 121.3, 120.8, 117.1, 19.7. HRMS (EI-TOF) calcd for $\text{C}_{24}\text{H}_{17}\text{N}_3\text{OS}_2$ (M^+): 427.0813, found: 427.0815.

2-methyl-6-(phenylselanyl)-N-(quinolin-8-yl)benzamide (3p)



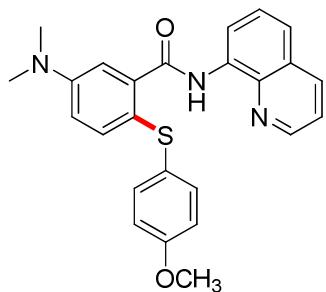
Rf 0.40 (hexane/EtOAc = 10/1). M. p. 160.1-160.9 °C. 40.1 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 9.96 (s, 1H), 8.98 (dd, J₁ = 1.2 Hz; J₂ = 7.6 Hz, 1H), 8.69 (dd, J₁ = 1.6 Hz; J₂ = 4.4 Hz, 1H), 8.17 (dd, J₁ = 1.6 Hz; J₂ = 8.4 Hz, 1H), 7.61 (t, J = 8.4 Hz, 1H), 7.56 (dd, J₁ = 1.2 Hz; J₂ = 8.4 Hz, 1H), 7.48-7.50 (m, 2H), 7.43 (dd, J₁ = 4.0 Hz; J₂ = 8.4 Hz, 1H), 7.27-7.29 (m, 1H), 7.17-7.20 (m, 5H), 2.49 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 167.6, 148.1, 140.6, 138.4, 136.5, 135.9, 134.2, 133.9, 131.7, 130.9, 129.9, 129.6, 129.5, 129.3, 128.0, 127.6, 127.5, 122.1, 121.6, 117.1, 19.9. HRMS (EI-TOF) calcd for C₂₃H₁₈N₂OSe (M⁺): 418.0584, found: 418.0589.

5-methoxy-2-(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4a)



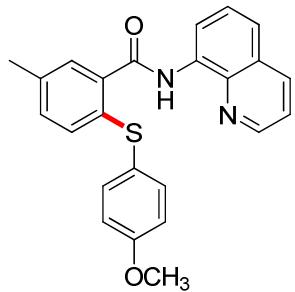
Rf 0.70 (hexane/EtOAc = 1/1). M. p. 109.1-110.0 °C. 76.6 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.55 (s, 1H), 8.82 (dd, J₁ = 1.6 Hz; J₂ = 7.6 Hz, 1H), 8.75 (dd, J₁ = 1.6 Hz; J₂ = 4.0 Hz, 1H), 8.16 (dd, J₁ = 1.6 Hz; J₂ = 8.4 Hz, 1H), 7.58 (t, J = 8.0 Hz, 1H), 7.54 (dd, J₁ = 1.6 Hz; J₂ = 8.4 Hz, 1H), 7.44 (dd, J₁ = 4.0 Hz; J₂ = 8.0 Hz, 1H), 7.32-7.35 (m, 3H), 7.21 (d, J = 8.8 Hz, 1H), 6.91 (dd, J₁ = 2.8 Hz; J₂ = 8.8 Hz, 1H), 6.77 (dd, J₁ = 2.0 Hz; J₂ = 6.8 Hz, 2H), 384 (s, 3H), 3.73 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 166.2, 159.4, 158.6, 148.3, 138.7, 138.4, 136.3, 134.6, 134.3, 133.6, 128.0, 127.4, 127.3, 126.0, 121.9, 121.6, 117.2, 116.9, 114.9, 113.9, 55.6, 55.3. HRMS (EI-TOF) calcd for C₂₄H₂₀N₂O₃S (M⁺): 416.1195, found: 416.1192.

5-(dimethylamino)-2-(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4b)



Rf 0.60 (hexane/EtOAc = 1/1). M. p. 149.4-150.0 °C. 71.2 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.46 (s, 1H), 8.83 (d, *J* = 7.2 Hz, 1H), 8.60 (dd, *J*₁ = 1.6 Hz; *J*₂ = 4.0 Hz, 1H), 8.05 (dd, *J*₁ = 1.6 Hz; *J*₂ = 8.4 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.42 (dd, *J*₁ = 1.6 Hz; *J*₂ = 8.4 Hz, 1H), 7.32 (dd, *J*₁ = 4.0 Hz; *J*₂ = 8.0 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 7.14 (dd, *J*₁ = 1.6 Hz; *J*₂ = 7.2 Hz, 1H), 7.02 (d, *J* = 3.2 Hz, 1H), 6.65 (dd, *J*₁ = 1.2 Hz; *J*₂ = 8.8 Hz, 1H), 6.61 (dd, *J*₁ = 2.0 Hz; *J*₂ = 6.8 Hz, 1H), 3.60 (s, 3H), 2.91 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz) δ 167.3, 158.6, 150.0, 148.1, 140.1, 138.7, 136.2, 135.7, 134.8, 132.2, 128.3, 127.9, 127.4, 121.7, 121.5, 118.8, 116.8, 114.6, 112.4, 55.3, 40.4. HRMS (EI-TOF) calcd for C₂₅H₂₃N₃O₂S (M⁺): 429.1511, found: 429.1512.

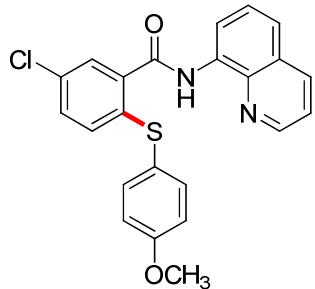
2-(4-methoxyphenylthio)-5-methyl-N-(quinolin-8-yl)benzamide (4c)



Rf 0.31 (hexane/EtOAc = 5/1). M. p. 135.3-135.5 °C. 60.8 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.48 (s, 1H), 8.95 (dd, *J*₁ = 1.2 Hz; *J*₂ = 7.6 Hz, 1H), 8.77 (dd, *J*₁ = 1.2 Hz; *J*₂ = 4.0 Hz, 1H), 8.14 (dd, *J*₁ = 1.6 Hz; *J*₂ = 8.0 Hz, 1H), 7.57 (t, *J* = 8.4 Hz, 2H), 7.51 (dd, *J*₁ = 1.6 Hz; *J*₂ = 8.4 Hz, 1H), 7.40-7.44 (m, 3H), 7.10 (dd, *J*₁ = 1.6 Hz; *J*₂ = 8.4 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.82-6.84 (m, 2H), 3.75 (s, 3H), 2.36 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 166.6, 159.9, 148.2, 138.7, 136.3, 135.9, 135.8, 135.3, 134.7, 131.8, 129.9, 128.8, 128.0, 127.4, 124.6, 121.8, 121.6, 116.8, 115.0,

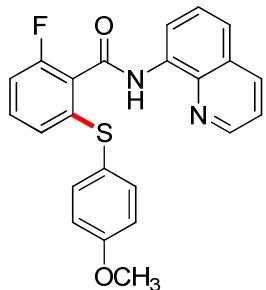
55.3, 20.9. HRMS (EI-TOF) calcd for C₂₄H₂₀N₂O₂S (M⁺): 400.1245, found: 400.1246.

5-chloro-2-(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4d)



Rf 0.37 (hexane/EtOAc = 5/1). M. p. 126.0-126.5 °C. 63.9 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.47 (s, 1H), 8.92 (dd, J₁ = 1.6 Hz; J₂ = 6.8 Hz, 1H), 8.81 (dd, J₁ = 1.6 Hz; J₂ = 4.0 Hz, 1H), 8.18 (dd, J₁ = 1.6 Hz; J₂ = 8.4 Hz, 1H), 7.73 (d, J = 3.2 Hz, 1H), 7.55-7.62 (m, 2H), 7.43-7.49 (m, 3H), 7.24 (dd, J₁ = 2.4 Hz; J₂ = 8.8 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 6.88 (dd, J₁ = 2.0 Hz; J₂ = 7.6 Hz, 2H), 3.79 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 165.0, 160.4, 148.4, 138.6, 138.3, 136.6, 136.4, 135.8, 134.3, 131.2, 130.8, 130.3, 128.0, 127.9, 127.4, 123.1, 122.2, 121.8, 117.0, 115.3, 55.4. HRMS (EI-TOF) calcd for C₂₃H₁₇ClN₂O₂S (M⁺): 420.0699, found: 420.0700.

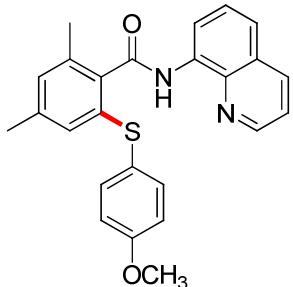
2-fluoro-6-(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4e)



Rf 0.31 (hexane/EtOAc = 5/1). M. p. 123.5-124.1 °C. 50.9 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.35 (s, 1H), 9.01 (dd, J₁ = 1.6 Hz; J₂ = 7.2 Hz, 1H), 8.80 (dd, J₁ = 1.6 Hz; J₂ = 4.0 Hz, 1H), 8.19 (dd, J₁ = 1.6 Hz; J₂ = 8.4 Hz, 1H), 7.56-7.61 (m, 2H), 7.45-7.48 (m, 3H), 7.20 (dd, J₁ = 1.6 Hz; J₂ = 8.0 Hz, 1H), 6.93-6.98 (m, 1H), 6.87 (dd, J₁ = 2.0 Hz; J₂ = 6.8 Hz, 2H), 6.77 (d, J = 8.0 Hz, 1H), 3.78 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 162.0, 160.4, 159.8 (d, J_{C-F} = 274.9 Hz), 148.3, 142.2 (d, J_{C-F} = 2.6 Hz), 138.5, 136.8, 136.3, 134.3, 131.0 (d, J_{C-F} = 8.7 Hz), 128.0, 127.5,

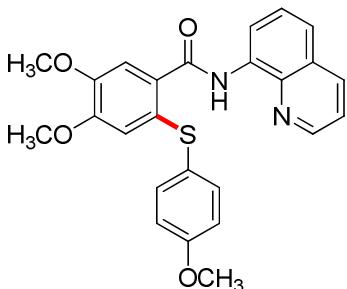
124.2 (d, $J_{C-F} = 2.5$ Hz), 123.3, 122.9, 122.2, 121.7, 117.1, 115.2, 112.7 (d, $J_{C-F} = 22.6$ Hz), 55.3. HRMS (EI-TOF) calcd for $C_{23}H_{17}FN_2O_2S$ (M^+): 404.0995, found: 404.0992.

2-(4-methoxyphenylthio)-4,6-dimethyl-N-(quinolin-8-yl)benzamide (4f)



R_f 0.24 (hexane/EtOAc = 10/1). M. p. 129.1-130.4 °C. 79.5 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 9.94 (s, 1H), 8.99 (dd, $J_1 = 1.2$ Hz; $J_2 = 7.6$ Hz, 1H), 8.70 (dd, $J_1 = 1.6$ Hz; $J_2 = 4.4$ Hz, 1H), 8.14 (dd, $J_1 = 1.6$ Hz; $J_2 = 8.4$ Hz, 1H), 7.59 (t, $J = 8.0$ Hz, 1H), 7.53 (dd, $J_1 = 1.6$ Hz; $J_2 = 8.4$ Hz, 1H), 7.41 (dd, $J_1 = 4.0$ Hz; $J_2 = 8.0$ Hz, 1H), 7.37 (dd, $J_1 = 2.0$ Hz; $J_2 = 6.8$ Hz, 2H), 6.93 (s, 1H), 6.86 (s, 1H), 6.75 (dd, $J_1 = 2.0$ Hz; $J_2 = 6.4$ Hz, 2H), 3.71 (s, 3H), 2.41 (s, 3H), 2.24 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 167.3, 159.6, 148.2, 139.5, 138.5, 136.3, 136.0, 135.7, 135.1, 135.0, 134.5, 129.6, 128.9, 128.0, 127.5, 125.0, 121.9, 121.6, 116.8, 114.8, 55.3, 21.3, 19.5. HRMS (EI-TOF) calcd for C₂₅H₂₂N₂O₂S (M^+): 414.1402, found: 414.1406.

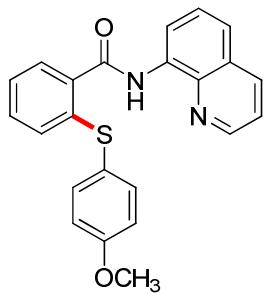
4,5-dimethoxy-2-(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4g)



R_f 0.60 (hexane/EtOAc = 1/1). M. p. 140.5-141.7 °C. 60.7 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.82 (s, 1H), 8.90 (dd, $J_1 = 1.6$ Hz; $J_2 = 7.2$ Hz, 1H), 8.75 (dd, $J_1 = 1.6$ Hz; $J_2 = 4.4$ Hz, 1H), 8.16 (dd, $J_1 = 1.6$ Hz; $J_2 = 8.4$ Hz, 1H), 7.58 (t, $J = 8.4$

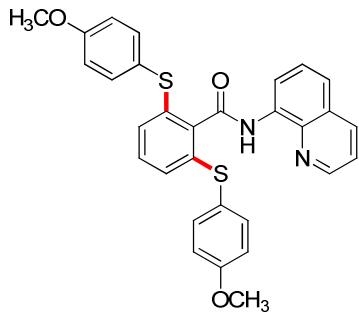
Hz, 1H), 7.53 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.44 (dd, J_1 = 4.0 Hz; J_2 = 8.4 Hz, 1H), 7.41 (s, 1H), 7.36 (dd, J_1 = 2.0 Hz; J_2 = 6.8 Hz, 2H), 6.81 (dd, J_1 = 2.0 Hz; J_2 = 6.8 Hz, 2H), 6.77 (s, 1H), 3.95 (s, 3H), 3.76 (d, J = 1.2 Hz, 6H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 165.9, 159.5, 150.9, 148.2, 148.0, 138.8, 136.3, 134.8, 134.2, 129.2, 128.6, 128.0, 127.5, 125.9, 121.7, 121.6, 116.8, 114.9, 114.7, 112.2, 56.3, 56.0, 55.3. HRMS (EI-TOF) calcd for $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_4\text{S}$ (M^+): 446.1300, found: 446.1300.

2-(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4h)



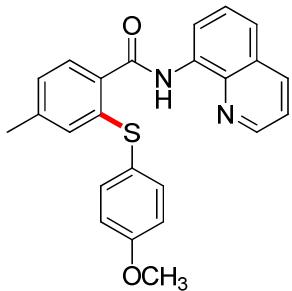
Rf 0.30 (hexane/EtOAc = 5/1). M. p. 103.9-141.7 °C. 46.8 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.51 (s, 1H), 8.97 (dd, J_1 = 1.2 Hz; J_2 = 7.2 Hz, 1H), 8.80 (dd, J_1 = 1.6 Hz; J_2 = 4.0 Hz, 1H), 8.18 (dd, J_1 = 1.6 Hz; J_2 = 8.0 Hz, 1H), 7.78 (dd, J_1 = 1.6 Hz; J_2 = 7.6 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.55 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.45-7.49 (m, 3H), 7.22-7.31 (m, 2H), 7.00 (dd, J_1 = 1.2 Hz; J_2 = 7.6 Hz, 1H), 6.89 (dd, J_1 = 2.0 Hz; J_2 = 6.4 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.4, 160.2, 148.3, 140.0, 138.7, 136.7, 136.4, 134.6, 134.4, 130.9, 128.8, 128.0, 127.5, 125.3, 123.6, 121.8, 121.7, 116.8, 115.2, 55.4. HRMS (EI-TOF) calcd for $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$ (M^+): 386.1089, found: 386.1085.

2,6-bis(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4h')



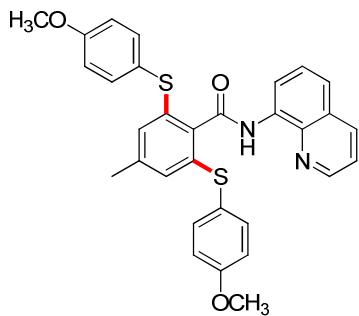
Rf 0.70 (hexane/EtOAc = 1/1). M. p. 132.0-133.0 °C. 31.7 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.09 (s, 1H), 9.04 (dd, J_1 = 1.2 Hz; J_2 = 7.6 Hz, 1H), 8.75 (dd, J_1 = 1.6 Hz; J_2 = 8.0 Hz, 1H), 8.17 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.61 (t, J = 8.4 Hz, 1H), 7.55 (dd, J_1 = 1.2 Hz; J_2 = 8.4 Hz, 1H), 7.41-7.46 (m, 5H), 7.07 (t, J = 8.0 Hz, 1H), 6.88 (d, J = 8.0 Hz, 2H), 6.78-6.82 (m, 4H), 3.74 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 165.4, 160.1, 148.2, 138.5, 137.7, 136.7, 136.3, 136.0, 134.4, 129.8, 128.0, 127.5, 127.2, 123.6, 122.0, 121.6, 117.1, 115.0, 55.3. HRMS (EI-TOF) calcd for $\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}_3\text{S}_2$ (M^+): 524.1228, found: 524.1222.

2-(4-methoxyphenylthio)-4-methyl-N-(quinolin-8-yl)benzamide (4i)



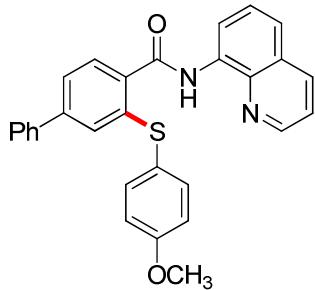
Rf 0.30 (hexane/EtOAc = 5/1). M. p. 118.1-119.0 °C. 30.6 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.52 (s, 1H), 8.96 (dd, J_1 = 1.2 Hz; J_2 = 7.6 Hz, 1H), 8.79 (dd, J_1 = 1.6 Hz; J_2 = 4.0 Hz, 1H), 8.17 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.59 (t, J = 8.4 Hz, 1H), 7.53 (dd, J_1 = 1.2 Hz; J_2 = 8.0 Hz, 1H), 7.44-7.48 (m, 3H), 7.05 (d, J = 7.6 Hz, 1H), 6.88 (d, J = 8.8 Hz, 2H), 6.83 (s, 1H), 3.80 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.4, 160.1, 148.2, 141.3, 139.7, 138.7, 136.5, 136.4, 134.7, 131.8, 129.4, 128.1, 128.0, 127.5, 126.3, 123.9, 121.7, 121.6, 116.7, 115.1, 55.3, 21.5. HRMS (EI-TOF) calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$ (M^+): 400.1245, found: 400.1244.

2,6-bis(4-methoxyphenylthio)-4-methyl-N-(quinolin-8-yl)benzamide (4i')



Rf 0.60 (hexane/EtOAc = 1/1). M. p. 120.1-120.7 °C. 37.4 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 9.96 (s, 1H), 8.93 (dd, J_1 = 1.2 Hz; J_2 = 7.6 Hz, 1H), 8.65 (dd, J_1 = 1.6 Hz; J_2 = 4.0 Hz, 1H), 8.07 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H), 7.45 (dd, J_1 = 1.2 Hz; J_2 = 8.0 Hz, 1H), 7.31-7.36 (m, 5H), 6.71 (dd, J_1 = 2.0 Hz; J_2 = 6.8 Hz, 4H), 6.67 (s, 2H), 3.65 (s, 6H), 2.05 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 165.6, 159.9, 148.1, 140.1, 138.5, 137.1, 136.2, 135.7, 135.0, 134.5, 128.5, 128.0, 127.5, 124.0, 121.9, 121.6, 117.0, 114.9, 55.3, 21.4. HRMS (EI-TOF) calcd for $\text{C}_{31}\text{H}_{26}\text{N}_2\text{O}_3\text{S}_2$ (M^+): 538.1385, found: 538.1392.

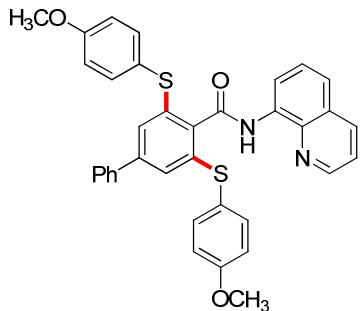
3-(4-methoxyphenylthio)-N-(quinolin-8-yl)biphenyl-4-carboxamide (4j)



Rf 0.30 (hexane/EtOAc = 5/1). M. p. 124.7-125.3 °C. 28.5 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.59 (s, 1H), 8.98 (dd, J_1 = 1.6 Hz; J_2 = 7.6 Hz, 1H), 8.81 (dd, J_1 = 1.6 Hz; J_2 = 4.0 Hz, 1H), 8.19 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 8.4 Hz, 1H), 7.56 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.51 (dd, J_1 = 2.0 Hz; J_2 = 6.8 Hz, 2H), 7.45-7.48 (m, 2H), 7.38-7.42 (m, 4H), 7.33-7.37 (m, 1H), 7.27 (d, J = 1.6 Hz, 1H), 6.89 (dd, J_1 = 2.0 Hz; J_2 = 6.8 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.2, 160.2, 148.3, 143.7, 140.5, 139.9, 138.7, 136.5, 136.4, 135.8, 134.7, 133.1, 128.9, 128.6, 128.0, 127.5, 127.1, 124.2, 123.6, 121.9, 121.7, 116.8, 115.2, 115.0, 55.4. HRMS (EI-TOF) calcd for $\text{C}_{29}\text{H}_{22}\text{N}_2\text{O}_2\text{S}$ (M^+):

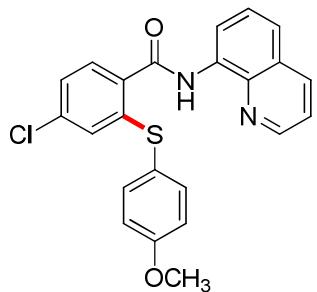
462.1402, found: 462.1404.

3,5-bis(4-methoxyphenylthio)-N-(quinolin-8-yl)biphenyl-4-carboxamide (4j')



Rf 0.65 (hexane/EtOAc = 1/1). M. p. 177.0-178.0 °C. 49.4 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.04 (s, 1H), 8.96 (dd, J₁ = 1.6 Hz; J₂ = 7.6 Hz, 1H), 8.67 (dd, J₁ = 1.6 Hz; J₂ = 4.0 Hz, 1H), 8.09 (dd, J₁ = 1.2 Hz; J₂ = 8.4 Hz, 1H), 7.53 (t, J = 8.0 Hz, 1H), 7.48 (dd, J₁ = 1.2 Hz; J₂ = 8.0 Hz, 1H), 7.35-7.39 (m, 5H), 7.19-7.27 (m, 5H), 7.06 (s, 2H), 6.71 (dd, J₁ = 2.0 Hz; J₂ = 6.8 Hz, 4H), 3.64 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz) δ 164.3, 158.9, 147.1, 141.8, 138.6, 137.5, 136.9, 135.2, 134.8, 134.7, 133.3, 127.8, 126.9, 126.9, 126.5, 126.0, 125.3, 122.6, 120.9, 120.6, 116.0, 114.0, 54.2. HRMS (EI-TOF) calcd for C₃₆H₂₈N₂O₃S₂ (M⁺): 600.1541, found: 600.1541.

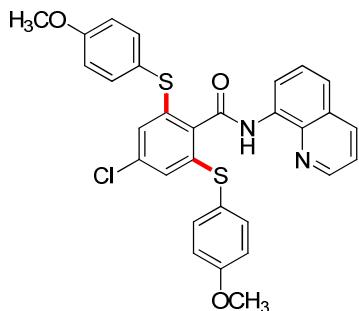
4-chloro-2-(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4k)



Rf 0.24 (hexane/EtOAc = 10/1). M. p. 126.3-127.4 °C. 26.2 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.50 (s, 1H), 8.94 (dd, J₁ = 1.6 Hz; J₂ = 7.2 Hz, 1H), 8.81 (dd, J₁ = 1.6 Hz; J₂ = 4.4 Hz, 1H), 8.19 (dd, J₁ = 1.6 Hz; J₂ = 8.4 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 7.55-7.60 (m, 2H), 7.46-7.50 (m, 3H), 7.20 (dd, J₁ = 1.6 Hz; J₂ = 8.0 Hz, 1H), 6.94 (dd, J₁ = 2.0 Hz; J₂ = 6.8 Hz, 2H), 6.89 (d, J = 1.6 Hz, 1H), 3.83 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 165.4, 160.7, 148.3, 142.9, 138.6, 137.3, 137.1, 136.4,

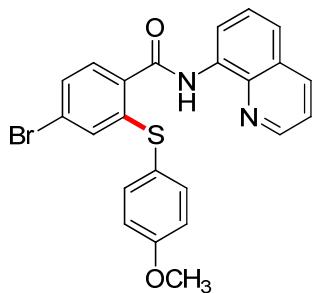
134.4, 132.1, 129.1, 128.0, 127.7, 127.5, 125.2, 122.2, 122.0, 121.7, 116.9, 116.5, 55.4. HRMS (EI-TOF) calcd for $C_{23}H_{17}ClN_2O_2S$ (M^+): 420.0699, found: 420.0692.

4-chloro-2,6-bis(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4k')



Rf 0.70 (hexane/EtOAc = 1/1). M. p. 143.0-145.0 °C. 52.2 mg. White solid; 1H NMR ($CDCl_3$, 400 MHz) δ 10.15 (s, 1H), 9.02 (dd, J_1 = 1.6 Hz; J_2 = 7.6 Hz, 1H), 8.79 (dd, J_1 = 1.6 Hz; J_2 = 4.4 Hz, 1H), 8.18 (dd, J_1 = 1.6 Hz; J_2 = 8.0 Hz, 1H), 7.61 (t, J = 8.4 Hz, 1H), 7.57 (dd, J_1 = 1.6 Hz; J_2 = 8.0 Hz, 1H), 7.43-7.47 (m, 5H), 6.85 (dd, J_1 = 2.0 Hz; J_2 = 6.8 Hz, 4H), 6.72 (s, 2H), 3.77 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.6, 160.5, 148.3, 140.2, 138.5, 136.6, 136.3, 135.9, 134.2, 128.0, 127.5, 125.5, 122.2, 122.1, 121.7, 117.1, 115.3, 114.5, 55.4. HRMS (EI-TOF) calcd for $C_{30}H_{23}ClN_2O_3S_2$ (M^+): 558.0839, found: 558.0835.

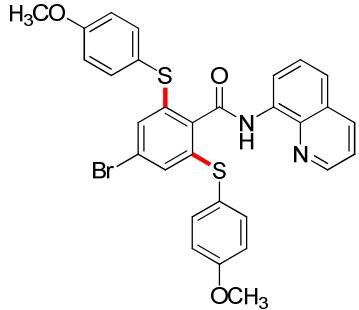
4-bromo-2-(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4l)



Rf 0.24 (hexane/EtOAc = 10/1). M. p. 141.7-142.5 °C. 35.8 mg. White solid; 1H NMR ($CDCl_3$, 400 MHz) δ 10.50 (s, 1H), 8.93 (dd, J_1 = 1.6 Hz; J_2 = 8.8 Hz, 1H), 8.81 (dd, J_1 = 1.6 Hz; J_2 = 4.0 Hz, 1H), 8.19 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.56-7.64 (m, 3H), 7.46-7.50 (m, 3H), 7.36 (dd, J_1 = 2.0 Hz; J_2 = 8.0 Hz, 1H), 7.06 (d, J = 2.0 Hz, 1H), 6.93 (dd, J_1 = 2.0 Hz; J_2 = 6.8 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR ($CDCl_3$, 100

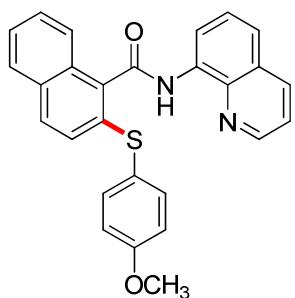
MHz) δ 165.5, 160.6, 148.3, 142.9, 138.6, 137.0, 136.8, 136.4, 134.4, 132.6, 130.7, 129.3, 128.2, 128.0, 127.5, 125.7, 122.1, 121.7, 116.8, 115.5, 55.4. HRMS (EI-TOF) calcd for C₂₃H₁₇BrN₂O₂S (M⁺): 464.0194, found: 464.0198.

4-bromo-2,6-bis(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4l')



Rf 0.65 (hexane/EtOAc = 1/1). M. p. 146.0-147.0 °C. 55.8 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.06 (s, 1H), 8.93 (dd, J₁ = 1.6 Hz; J₂ = 7.6 Hz, 1H), 8.70 (dd, J₁ = 1.6 Hz; J₂ = 4.0 Hz, 1H), 8.10 (dd, J₁ = 1.6 Hz; J₂ = 8.4 Hz, 1H), 7.53 (t, J = 8.0 Hz, 1H), 7.49 (dd, J₁ = 1.6 Hz; J₂ = 8.0 Hz, 1H), 7.34-7.40 (m, 5H), 6.82 (s, 2H), 6.77 (dd, J₁ = 2.0 Hz; J₂ = 6.8 Hz, 4H), 3.69 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz) δ 164.6, 160.5, 148.3, 140.2, 138.5, 136.5, 134.2, 134.2, 128.5, 128.0, 127.5, 124.1, 122.2, 122.1, 121.7, 117.2, 115.3, 114.6, 55.4. HRMS (EI-TOF) calcd for C₃₀H₂₃BrN₂O₃S₂ (M⁺): 602.0333, found: 602.0330.

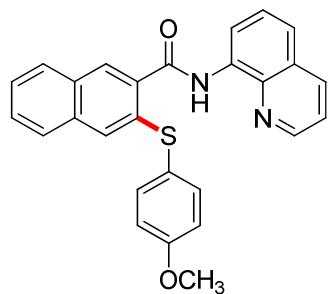
2-(4-methoxyphenylthio)-N-(quinolin-8-yl)-1-naphthamide (4m)



Rf 0.30 (hexane/EtOAc = 5/1). M. p. 167.3-167.9 °C. 76.8 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.22 (s, 1H), 9.14 (dd, J₁ = 1.2 Hz; J₂ = 7.6 Hz, 1H), 8.66 (dd, J₁ = 1.6 Hz; J₂ = 4.0 Hz, 1H), 8.15 (dd, J₁ = 1.6 Hz; J₂ = 8.4 Hz, 1H), 8.01-8.03 (m, 1H), 7.81 (dd, J₁ = 2.0 Hz; J₂ = 6.4 Hz, 1H), 7.75 (dd, J = 8.8 Hz, 1H), 7.65 (t, J = 8.0

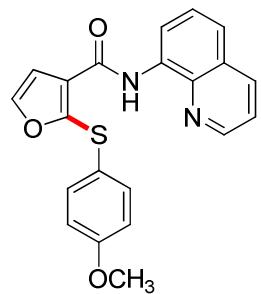
Hz, 1H), 7.58 (d, J_1 = 1.2 Hz; J_2 = 8.4 Hz, 1H), 7.43-7.51 (m, 4H), 7.40 (dd, J_1 = 4.0 Hz; J_2 = 8.4 Hz, 1H), 7.25-7.28 (m, 1H), 6.79-6.83 (m, 2H), 3.75 (s, 3H). ^{13}C NMR (CDCl₃, 100 MHz) δ 166.7, 159.9, 148.3, 138.5, 136.3, 135.3, 135.2, 134.5, 133.3, 131.9, 130.6, 129.9, 128.1, 128.0, 127.7, 127.5, 126.4, 125.0, 124.6, 122.2, 121.7, 117.0, 115.0, 55.3. HRMS (EI-TOF) calcd for C₂₇H₂₀N₂O₂S (M⁺): 436.1245, found: 436.1241.

3-(4-methoxyphenylthio)-N-(quinolin-8-yl)-2-naphthamide (4n)



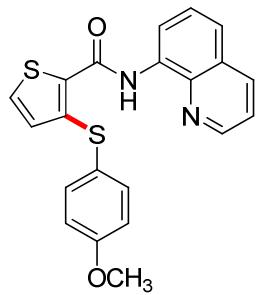
Rf 0.30 (hexane/EtOAc = 5/1). M. p. 115.1-115.8 °C. 80.2 mg. White solid; ^1H NMR (CDCl₃, 400 MHz) δ 10.57 (s, 1H), 8.99 (dd, J_1 = 1.2 Hz; J_2 = 7.2 Hz, 1H), 8.79 (dd, J_1 = 1.6 Hz; J_2 = 4.0 Hz, 1H), 8.25 (s, 1H), 8.18 (dd, J_1 = 1.6 Hz; J_2 = 8.0 Hz, 1H), 7.86-7.89 (m, 1H), 7.61 (t, J = 8.0 Hz, 2H), 7.56 (dd, J_1 = 1.2 Hz; J_2 = 8.4 Hz, 1H), 7.44-7.50 (m, 6H), 6.87 (dd, J_1 = 2.0 Hz; J_2 = 6.8 Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (CDCl₃, 100 MHz) δ 166.5, 160.1, 148.3, 138.7, 136.3, 135.7, 134.7, 134.3, 133.8, 130.8, 128.4, 128.3, 128.0, 128.0, 127.8, 127.0, 126.3, 123.9, 121.9, 121.7, 116.9, 115.2, 55.3. HRMS (EI-TOF) calcd for C₂₇H₂₀N₂O₂S (M⁺): 436.1245, found: 436.1245.

2-(4-methoxyphenylthio)-N-(quinolin-8-yl)furan-3-carboxamide (4o)



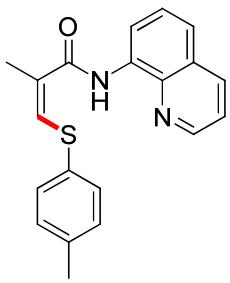
Rf 0.30 (hexane/EtOAc = 5/1). M. p. 105.0-106.0 °C. 33.8 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 11.51 (s, 1H), 8.94 (dd, J_1 = 1.6 Hz; J_2 = 7.2 Hz, 1H), 8.84 (dd, J_1 = 1.6 Hz; J_2 = 4.0 Hz, 1H), 8.19 (dd, J_1 = 1.2 Hz; J_2 = 8.0 Hz, 1H), 7.61 (dd, J_1 = 1.6 Hz; J_2 = 7.2 Hz, 2H), 7.58 (d, J = 7.6 Hz, 1H), 7.55 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.51 (d, J = 1.6 Hz, 1H), 7.48 (dd, J_1 = 4.4 Hz; J_2 = 8.0 Hz, 1H), 7.05 (d, J = 2.0 Hz, 1H), 6.85 (dd, J_1 = 1.6 Hz; J_2 = 6.8 Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 160.4, 160.1, 148.1, 146.6, 145.0, 138.9, 136.4, 134.9, 133.8, 128.1, 127.5, 125.1, 122.7, 121.8, 121.6, 117.3, 114.9, 112.5, 55.4. HRMS (EI-TOF) calcd for $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_3\text{S} (\text{M}^+)$: 376.0882, found: 376.0884.

3-(4-methoxyphenylthio)-N-(quinolin-8-yl)thiophene-2-carboxamide (4p)



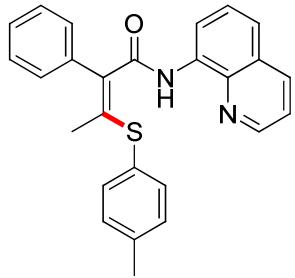
Rf 0.30 (hexane/EtOAc = 5/1). M. p. 140.2-141.1 °C. 35.3 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 11.48 (s, 1H), 8.91 (dd, J_1 = 1.6 Hz; J_2 = 7.2 Hz, 1H), 8.82 (dd, J_1 = 1.6 Hz; J_2 = 4.4 Hz, 1H), 8.17 (dd, J_1 = 1.6 Hz; J_2 = 8.0 Hz, 1H), 7.52-7.59 (m, 4H), 7.45 (dd, J_1 = 4.0 Hz; J_2 = 8.0 Hz, 1H), 7.40 (d, J = 5.2 Hz, 1H), 6.88 (dd, J_1 = 2.0 Hz; J_2 = 6.8 Hz, 2H), 6.78 (d, J = 5.2 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 160.2, 160.0, 148.3, 138.9, 136.6, 136.3, 134.9, 134.5, 134.0, 131.9, 128.9, 128.0, 127.4, 124.7, 121.9, 121.6, 117.3, 115.0, 55.4. HRMS (EI-TOF) calcd for $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2\text{S}_2 (\text{M}^+)$: 392.0653, found: 392.0649.

(Z)-2-methyl-N-(quinolin-8-yl)-3-(*p*-tolylthio)acrylamide (6a)



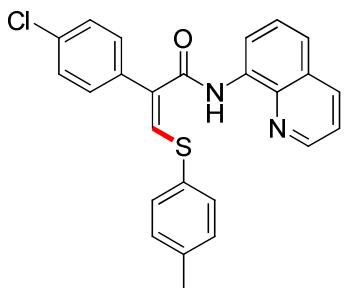
Rf 0.37 (hexane/EtOAc = 5/1). M. p. 141.7-142.5 °C. 48.1 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.21 (s, 1H), 8.71-8.74 (m, 2H), 8.07 (dd, J₁ = 1.6 Hz; J₂ = 8.0 Hz, 1H), 7.57 (d, J = 1.2 Hz, 1H), 7.46 (t, J = 8.0 Hz, 1H), 7.41 (dd, J₁ = 1.6 Hz; J₂ = 8.0 Hz, 1H), 7.37 (dd, J₁ = 4.0 Hz; J₂ = 8.0 Hz, 1H), 7.32 (dd, J₁ = 1.6 Hz; J₂ = 6.4 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 2.28 (s, 3H), 2.18 (d, J = 0.4 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 164.6, 148.2, 138.8, 138.1, 138.0, 136.4, 134.6, 130.8, 130.6, 130.1, 127.9, 127.5, 127.3, 121.6, 121.5, 116.5, 21.2, 14.5. HRMS (EI-TOF) calcd for C₂₀H₁₈N₂OS (M⁺): 334.1140, found: 334.1142.

(Z)-2-phenyl-N-(quinolin-8-yl)-3-(p-tolylthio)but-2-enamide (6b)



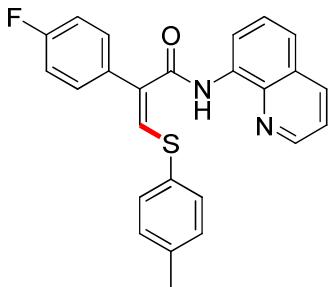
Rf 0.30 (hexane/EtOAc = 5/1). M. p. 130.3-131.3 °C. 55.8 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.39 (s, 1H), 8.92-8.94 (d, J = 6.8 Hz, 1H), 8.78 (dd, J₁ = 1.6 Hz; J₂ = 4.4 Hz, 1H), 8.17-8.19 (m, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.53 (dd, J₁ = 1.2 Hz; J₂ = 8.0 Hz, 1H), 7.46 (dd, J₁ = 4.4 Hz; J₂ = 8.0 Hz, 1H), 7.15-7.28 (m, 7H), 6.87 (d, J = 7.6 Hz, 2H), 2.018 (s, 3H), 2.11 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 168.4, 148.0, 139.4, 137.9, 137.2, 136.6, 134.6, 133.7, 133.0, 132.7, 129.9, 129.7, 129.6, 129.2, 128.0, 127.8, 127.6, 121.7, 121.6, 116.9, 21.1, 19.2. HRMS (EI-TOF) calcd for C₂₆H₂₂N₂OS (M⁺): 410.1453, found: 410.1451.

(Z)-2-(4-chlorophenyl)-N-(quinolin-8-yl)-3-(*p*-tolylthio)acrylamide (6c)



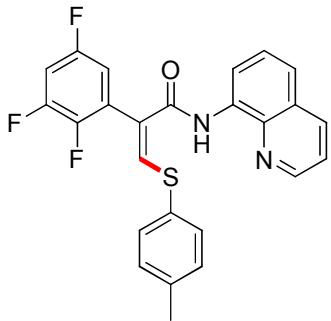
Rf 0.28 (hexane/EtOAc = 5/1). M. p. 160.4-161.2 °C. 46.4 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 9.88 (s, 1H), 8.72 (d, *J* = 7.2 Hz, 1H), 8.47 (d, *J* = 2.8 Hz, 1H), 8.00-8.03 (m, 2H), 7.35-7.49 (m, 6H), 7.26-7.31 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 2.28(s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 161.7, 147.2, 142.2, 137.7, 137.3, 135.1, 133.8, 133.5, 132.2, 130.4, 129.9, 129.6, 129.3, 129.1, 128.5, 126.8, 126.3, 120.6, 120.5, 115.3, 20.1. HRMS (EI-TOF) calcd for C₂₅H₁₉ClN₂OS (M⁺): 430.0907, found: 430.0910.

(Z)-2-(4-fluorophenyl)-N-(quinolin-8-yl)-3-(*p*-tolylthio)acrylamide (6d)



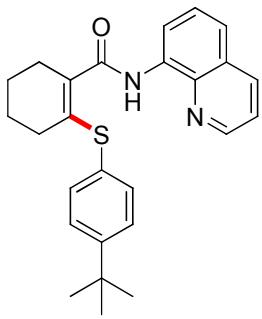
Rf 0.28 (hexane/EtOAc = 5/1). M. p. 161.7-162.2 °C. 52.2 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.15 (s, 1H), 8.96 (dd, *J*₁ = 1.2 Hz; *J*₂ = 7.6 Hz, 1H), 8.56 (dd, *J*₁ = 1.6 Hz; *J*₂ = 4.0 Hz, 1H), 8.11 (dd, *J*₁ = 1.6 Hz; *J*₂ = 8.0 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.45-7.50 (m, 5H), 7.37 (dd, *J*₁ = 4.0 Hz; *J*₂ = 8.0 Hz, 1H), 7.14-7.19 (m, 5H), 2.36 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 164.7, 162.7 (d, *J*_{C-F} = 245.2 Hz), 148.2, 146.3, 138.7, 38.3, 136.2, 134.4, 134.1, 133.6 (d, *J*_{C-F} = 2.9 Hz), 131.3 (d, *J*_{C-F} = 4.3 Hz), 131.2, 130.1, 128.9, 127.8, 127.4, 121.6 (d, *J*_{C-F} = 20.9 Hz), 116.4, 116.0 (d, *J*_{C-F} = 21.2 Hz), 21.2. HRMS (EI-TOF) calcd for C₂₅H₁₉FN₂OS (M⁺): 414.1202, found: 414.1202.

(Z)-N-(quinolin-8-yl)-3-(*p*-tolylthio)-2-(2,3,5-trifluorophenyl)acrylamide (6e)



Rf 0.28 (hexane/EtOAc = 5/1). M. p. 160.8-161.9 °C. 52.2 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.05 (s, 1H), 8.91 (dd, J₁ = 1.2 Hz; J₂ = 7.2 Hz, 1H), 8.59 (dd, J₁ = 1.6 Hz; J₂ = 4.0 Hz, 1H), 8.14 (dd, J₁ = 1.6 Hz; J₂ = 8.4 Hz, 1H), 7.56 (t, J = 8.0 Hz, 1H), 7.51 (dd, J₁ = 1.6 Hz; J₂ = 8.4 Hz, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.39 (dd, J₁ = 4.0 Hz; J₂ = 8.4 Hz, 1H), 7.29-7.34 (m, 1H), 7.27 (s, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.05-7.12 (m, 1H), 2.37 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 167.3, 162.8 (d, J_{C-F} = 159.9 Hz), 149.7, 148.2, 144.3, 138.5 (d, J_{C-F} = 7.2 Hz), 136.4, 135.7 (d, J_{C-F} = 10.6 Hz), 135.2, 134.1, 133.6, 131.4, 130.2, 129.2, 127.7 (d, J_{C-F} = 43.4 Hz), 125.0, 121.8, 121.6, 121.2, 119.7 (d, J_{C-F} = 18.1 Hz), 116.6, 114.7 (d, J_{C-F} = 10.9 Hz), 21.2. HRMS (EI-TOF) calcd for C₂₅H₁₇F₃N₂OS (M⁺): 450.1014, found: 450.1017.

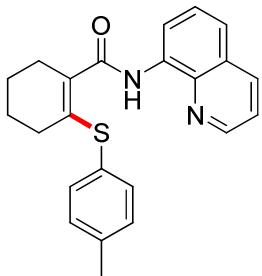
2-(4-*tert*-butylphenylthio)-N-(quinolin-8-yl)cyclohex-1-enecarboxamide (6fa)



Rf 0.26 (hexane/EtOAc = 5/1). M. p. 103.2-103.8 °C. 54.1 mg. White solid; ¹H NMR (CDCl₃, 400 MHz) δ 10.26 (s, 1H), 8.88 (dd, J₁ = 1.2 Hz; J₂ = 7.2 Hz, 1H), 8.74 (dd, J₁ = 1.6 Hz; J₂ = 4.4 Hz, 1H), 8.14 (dd, J₁ = 1.2 Hz; J₂ = 8.4 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.48 (dd, J₁ = 1.2 Hz; J₂ = 8.4 Hz, 1H), 7.40-7.43 (m, 3H), 7.32 (dd, J₁ = 1.6 Hz; J₂ = 6.4 Hz, 2H), 2.63-2.66 (m, 2H), 2.18-2.21 (m, 2H), 1.73-1.78 (m, 2H),

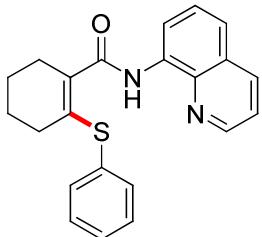
1.66-1.70 (m, 2H), 1.31 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.8, 150.9, 148.0, 138.6, 136.4, 134.6, 133.1, 132.9, 129.8, 128.0, 127.5, 125.9, 121.5, 121.4, 116.7, 34.6, 31.3, 31.2, 28.3, 23.3, 21.0. HRMS (EI-TOF) calcd for $\text{C}_{26}\text{H}_{28}\text{N}_2\text{OS}$ (M^+): 416.1922, found: 416.1918.

***N*-(quinolin-8-yl)-2-(*p*-tolylthio)cyclohex-1-enecarboxamide (6fb)**



Rf 0.27 (hexane/EtOAc = 5/1). M. p. 112.2-113.4 °C. 56.9 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.27 (s, 1H), 8.90 (dd, J_1 = 1.2 Hz; J_2 = 7.6 Hz, 1H), 8.76 (dd, J_1 = 1.6 Hz; J_2 = 4.0 Hz, 1H), 8.15 (dd, J_1 = 1.2 Hz; J_2 = 8.4 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.49 (dd, J_1 = 1.2 Hz; J_2 = 8.0 Hz, 1H), 7.40-7.44 (m, 3H), 7.13 (d, J = 8.0 Hz, 2H), 2.63-2.66 (m, 2H), 2.34 (s, 3H), 2.15-2.18 (m, 2H), 1.74-1.76 (m, 2H), 1.64-1.67 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.8, 148.0, 138.9, 138.6, 137.9, 136.4, 134.6, 133.7, 133.4, 132.4, 129.7, 128.0, 127.6, 121.5, 121.4, 116.7, 31.2, 28.3, 23.2, 22.0, 21.2. HRMS (EI-TOF) calcd for $\text{C}_{23}\text{H}_{22}\text{N}_2\text{OS}$ (M^+): 374.1453, found: 374.1450.

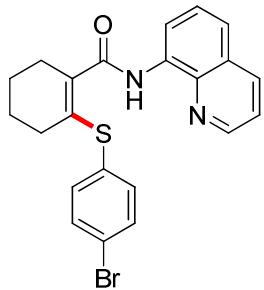
2-(phenylthio)-*N*-(quinolin-8-yl)cyclohex-1-enecarboxamide (6fc)



Rf 0.26 (hexane/EtOAc = 5/1). M. p. 120.2-121.3 °C. 46.8 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.26 (s, 1H), 8.88 (dd, J_1 = 1.2 Hz; J_2 = 7.6 Hz, 1H), 8.71 (dd, J_1 = 1.6 Hz; J_2 = 4.4 Hz, 1H), 8.13 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.54 (t, J = 8.4 Hz, 1H), 7.49 (d, J = 6.8 Hz, 3H), 7.41 (dd, J_1 = 4.0 Hz; J_2 = 8.4 Hz, 1H), 7.37-7.34

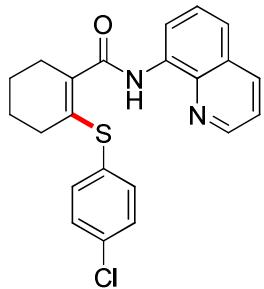
(m, 3H), 2.64-2.67 (m, 2H), 2.19-2.22 (m, 2H), 1.74-1.78 (m, 2H), 1.67-1.71 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.9, 148.0, 138.5, 137.1, 136.4, 134.5, 133.7, 132.8, 132.5, 129.4, 128.9, 128.0, 127.5, 121.5, 121.5, 116.7, 31.3, 28.4, 23.2, 22.0. HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{OS}$ (M^+): 360.1296, found: 360.1297.

2-(4-bromophenylthio)-N-(quinolin-8-yl)cyclohex-1-enecarboxamide (6fd)



Rf 0.25 (hexane/EtOAc = 5/1). M. p. 140.1-141.8 °C. 67.5 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.19 (s, 1H), 8.86 (dd, J_1 = 1.2 Hz; J_2 = 7.2 Hz, 1H), 8.72 (dd, J_1 = 1.6 Hz; J_2 = 8.0 Hz, 1H), 8.14 (dd, J_1 = 1.6 Hz; J_2 = 8.0 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.49 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.41-7.44 (m, 3H), 7.33 (dd, J_1 = 1.6 Hz; J_2 = 6.4 Hz, 2H), 2.64-2.67 (m, 2H), 2.17-2.21 (m, 2H), 1.74-1.78 (m, 2H), 1.68-1.72 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.7, 148.1, 138.5, 136.4, 136.1, 135.7, 134.4, 134.1, 133.1, 132.4, 131.2, 128.0, 127.5, 121.7, 121.6, 116.7, 31.4, 28.4, 23.3, 21.9. HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{19}\text{BrN}_2\text{OS}$ (M^+): 438.0401, found: 438.0403.

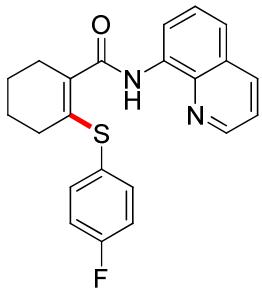
2-(4-chlorophenylthio)-N-(quinolin-8-yl)cyclohex-1-enecarboxamide (6fe)



Rf 0.26 (hexane/EtOAc = 5/1). M. p. 141.4-142.3 °C. 59.1 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.20 (s, 1H), 8.85 (dd, J_1 = 1.2 Hz; J_2 = 7.2 Hz, 1H), 8.72 (dd, J_1 = 1.6 Hz; J_2 = 4.0 Hz, 1H), 8.14 (dd, J_1 = 1.6 Hz; J_2 = 8.4 Hz, 1H), 7.54 (t, J = 8.0

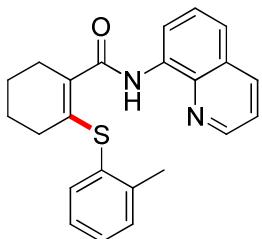
Hz, 1H), 7.49 (dd, J_1 = 1.2 Hz; J_2 = 8.0 Hz, 1H), 7.39-7.44 (m, 3H), 7.27-7.30 (m, 2H), 2.63-2.67 (m, 2H), 2.18-2.20 (m, 2H), 1.74-1.79 (m, 2H), 1.68-1.72 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.7, 148.1, 138.6, 136.5, 136.4, 135.2, 134.5, 134.0, 133.7, 132.3, 129.1, 128.0, 127.5, 121.6, 121.6, 116.6, 31.3, 28.4, 23.3, 21.9. HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{19}\text{ClN}_2\text{OS}$ (M^+): 394.0907, found: 394.0905.

2-(4-fluorophenylthio)-*N*-(quinolin-8-yl)cyclohex-1-enecarboxamide (6ff)



Rf 0.26 (hexane/EtOAc = 5/1). M. p. 168.5-168.7 °C. 56.0 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.23 (s, 1H), 8.89 (dd, J_1 = 1.2 Hz; J_2 = 7.6 Hz, 1H), 8.77 (dd, J_1 = 1.6 Hz; J_2 = 4.0 Hz, 1H), 8.16 (dd, J_1 = 1.6 Hz; J_2 = 8.0 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.47-7.52 (m, 3H), 7.44 (dd, J_1 = 4.0 Hz; J_2 = 8.0 Hz, 1H), 6.99-7.04 (m, 2H), 2.63-2.66 (m, 2H), 2.13-2.16 (m, 2H), 1.74-1.78 (m, 2H), 1.65-1.70 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.7, 162.6 (d, J_{C-F} = 246.2 Hz), 148.0, 138.6, 138.3, 136.5, 135.5 (d, J_{C-F} = 8.1 Hz), 134.5, 133.1, 128.6 (d, J_{C-F} = 2.2 Hz), 128.0, 127.6, 121.6 (d, J_{C-F} = 5.4 Hz), 116.8, 116.0 (d, J_{C-F} = 21.7 Hz), 31.2, 28.3, 23.2, 21.9. HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{19}\text{FN}_2\text{OS}$ (M^+): 378.1202, found: 378.1206.

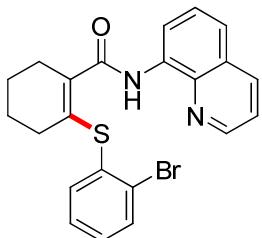
***N*-(quinolin-8-yl)-2-(*o*-tolylthio)cyclohex-1-enecarboxamide (6ga)**



Rf 0.26 (hexane/EtOAc = 5/1). M. p. 105.9-106.7 °C. 45.6 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.29 (s, 1H), 8.90 (dd, J_1 = 1.2 Hz; J_2 = 7.6 Hz, 1H), 8.74 (dd,

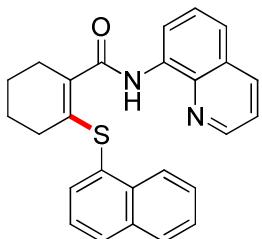
J_1 = 1.6 Hz; J_2 = 4.0 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.54 (t, J = 7.2 Hz, 1H), 7.20-7.52 (m, 2H), 7.45 (dd, J_1 = 4.0 Hz; J_2 = 8.0 Hz, 1H), 7.19 (t, J = 5.6 Hz, 3H), 2.65-2.68 (m, 2H), 2.40 (s, 3H), 2.08-2.11 (m, 2H), 1.76-1.79 (m, 2H), 1.66-1.69(m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.8, 152.4, 140.8, 138.2, 136.7, 136.3, 134.5, 133.8, 132.9, 132.6, 130.3, 129.3, 128.0, 128.0, 127.6, 122.5, 121.4, 117.1, 31.0, 28.3, 23.2, 22.0, 20.9. HRMS (EI-TOF) calcd for $\text{C}_{23}\text{H}_{22}\text{N}_2\text{OS}$ (M^+): 374.1453, found: 374.1450.

2-(2-bromophenylthio)-N-(quinolin-8-yl)cyclohex-1-enecarboxamide (6gb)



Rf 0.25 (hexane/EtOAc = 5/1). M. p. 165.8-166.6 °C. 59.6 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.22 (s, 1H), 8.86 (d, J = 7.2 Hz, 1H), 8.66 (d, J = 2.8 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.46-7.56 (m, 4H), 7.39 (dd, J_1 = 4.0 Hz; J_2 = 8.4 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.10-7.13 (m, 1H), 2.66-2.68 (m, 2H), 2.20-2.21 (m, 2H), 1.78-1.81 (m, 2H), 1.70-1.73 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.5, 148.0, 138.6, 136.3, 136.2, 135.7, 135.4, 134.5, 133.4, 133.2, 128.7, 127.9, 127.8, 127.4, 127.3, 121.6, 121.5, 116.7, 31.2, 28.5, 23.3, 21.9. HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{19}\text{BrN}_2\text{OS}$ (M^+): 438.0401, found: 438.0405.

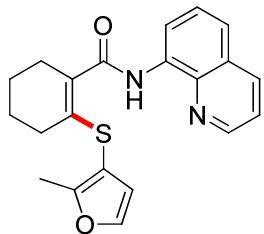
2-(naphthalen-1-ylthio)-N-(quinolin-8-yl)cyclohex-1-enecarboxamide (6h)



Rf 0.26 (hexane/EtOAc = 5/1). M. p. 121.4-123.1 °C. 58.2 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.35 (s, 1H), 8.95 (dd, J_1 = 1.2 Hz; J_2 = 7.6 Hz, 1H), 8.74 (dd,

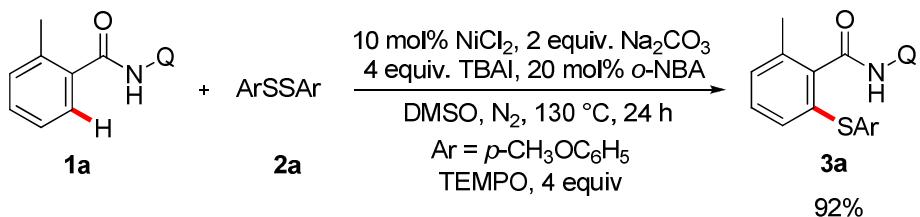
$J_1 = 1.6$ Hz; $J_2 = 4.0$ Hz, 1H), 8.46 (d, $J = 8.0$ Hz, 1H), 8.12 (dd, $J_1 = 1.2$ Hz; $J_2 = 8.4$ Hz, 1H), 7.82-7.84 (m, 3H), 7.43-7.57 (m, 5H), 7.41 (dd, $J_1 = 4.0$ Hz; $J_2 = 8.0$ Hz, 1H), 2.67-2.70 (m, 2H), 2.01-2.04 (m, 2H), 1.69-1.74 (m, 2H), 1.53-1.57 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.6, 148.1, 140.9, 138.7, 136.4, 134.9, 134.7, 133.9, 133.5, 130.5, 130.5, 129.3, 128.5, 128.0, 127.6, 126.9, 126.3, 125.8, 125.6, 121.6, 121.4, 116.7, 30.8, 28.2, 23.1, 22.0. HRMS (EI-TOF) calcd for $\text{C}_{26}\text{H}_{22}\text{N}_2\text{OS}$ (M^+): 410.1453, found: 410.1455.

2-(2-methylfuran-3-ylthio)-*N*-(quinolin-8-yl)cyclohex-1-enecarboxamide (6i)



Rf 0.26 (hexane/EtOAc = 5/1). M. p. 100.3-101.7 °C. 34.2 mg. White solid; ^1H NMR (CDCl_3 , 400 MHz) δ 10.28 (s, 1H), 8.94 (dd, $J_1 = 1.2$ Hz; $J_2 = 7.6$ Hz, 1H), 8.82 (dd, $J_1 = 1.6$ Hz; $J_2 = 4.4$ Hz, 1H), 8.18 (dd, $J_1 = 1.6$ Hz; $J_2 = 8.0$ Hz, 1H), 7.56 (t, $J = 8.0$ Hz, 1H), 7.51 (dd, $J_1 = 1.6$ Hz; $J_2 = 8.4$ Hz, 1H), 7.46 (dd, $J_1 = 4.4$ Hz; $J_2 = 8.0$ Hz, 1H), 7.31 (d, $J = 1.6$ Hz, 1H), 6.40 (d, $J = 1.6$ Hz, 1H), 2.63-2.65 (m, 2H), 2.35 (s, 3H), 2.14-2.18 (m, 2H), 1.75-1.78 (m, 2H), 1.66-1.69 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.3, 156.8, 148.0, 140.9, 140.6, 136.5, 134.7, 128.0, 127.6, 126.9, 121.5, 121.3, 116.8, 116.3, 115.5, 108.3, 30.7, 27.8, 23.1, 22.1, 11.9. HRMS (EI-TOF) calcd for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$ (M^+): 364.1245, found: 364.1248.

Radical Trapping Experiment



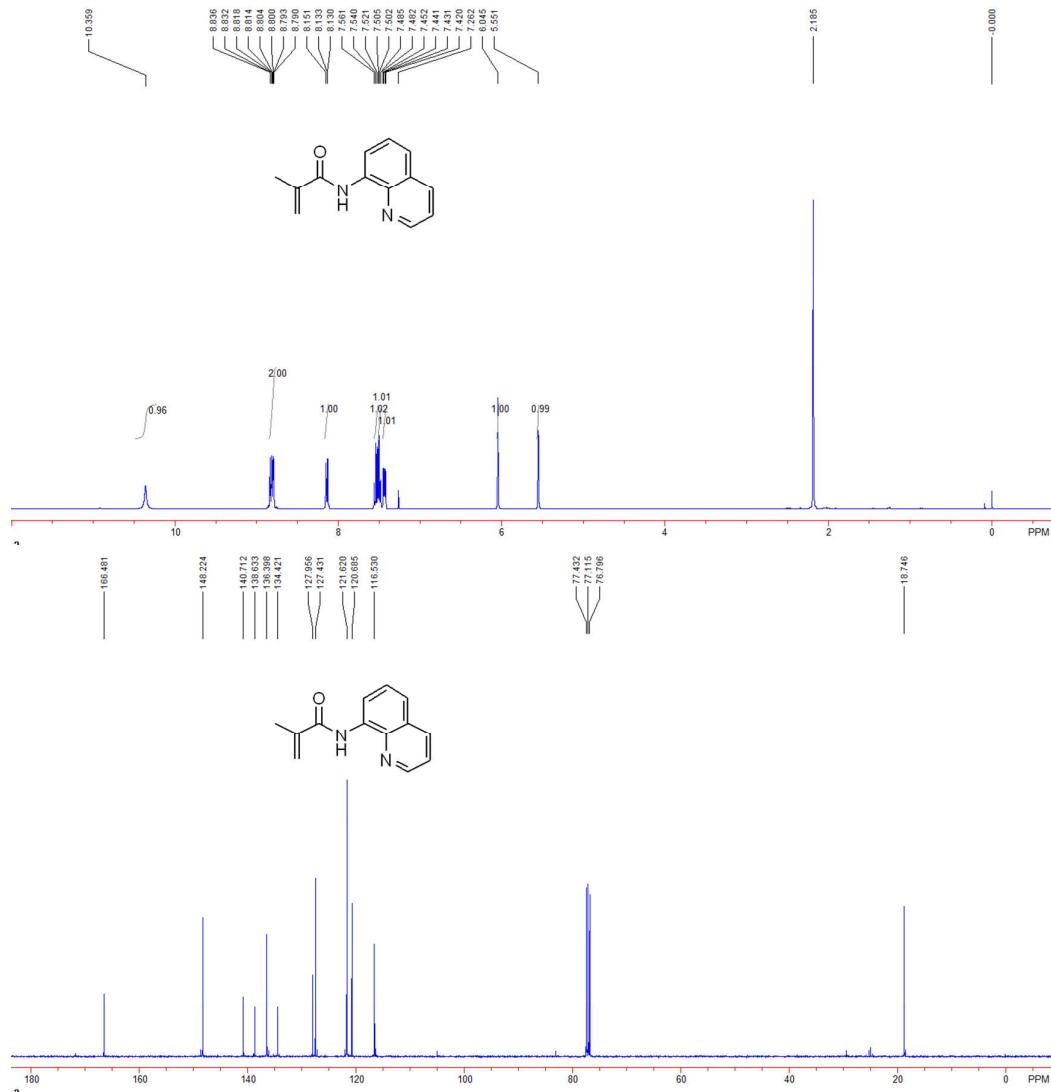
A 25 mL sealed tube was charged with *N*-(quinolin-8-yl) acrylamide **1a** (0.1 mmol), disulfide or diselenide **2a** (0.2 mmol), NiCl_2 (1.3 mg, 0.01 mmol), Na_2CO_3 (21.2 mg, 0.2 mmol) DMSO (1.0 mL) and tempo (62.5 mg, 0.4 mmol). The vial was evacuated and filled with N_2 atmosphere, and stirred at 130 °C for 24 h. The mixture was then cooled to room temperature, diluted with EtOAc, filtered through a celite pad, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/hexane (1:20 ~ 1:5, v/v), to afford the desired alkylated product **3a** (yield = 92%).

References

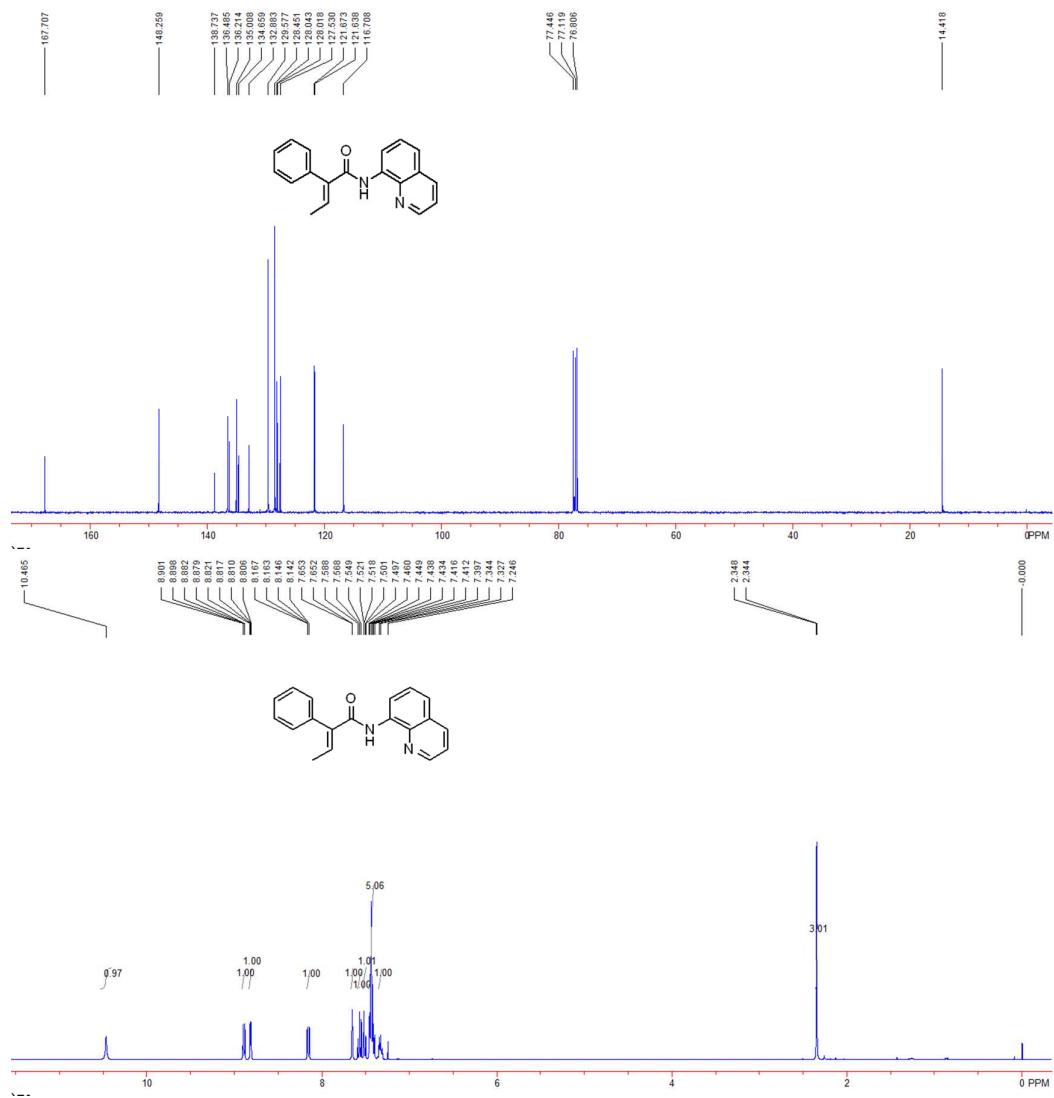
1. Tran, L. D.; Popov, I.; Daugulis, O. *J. Am. Chem. Soc.* **2012**, *134*, 18237.
2. Grigorjeva, L.; Daugulis, O. *Angew. Chem., Int. Ed.* **2014**, *53*, 10209
3. Monks, B. M.; Fruchey, E. R.; Cook, S. P. *Angew. Chem., Int. Ed.* **2014**, *53*, 11065
4. Gou, F.-R.; Wang, X.-C.; Huo, P.-F.; Bi, H.-P.; Guan, Z.-H.; Liang, Y.-M. *Org. Lett.* **2009**, *11*, 5726.
5. Ano, Y.; Tobisu, M.; Chatani, N. *Org. Lett.* **2012**, *14*, 354.
6. Cong, X.; Li, Y.; Wei, Y.; Zeng, X. *Org. Lett.* **2014**, *16*, 3926.
7. Allu, S.; Swamy, K. C. K. *J. Org. Chem.* **2014**, *79*, 3963

Copies of ^1H and ^{13}C NMR Spectra

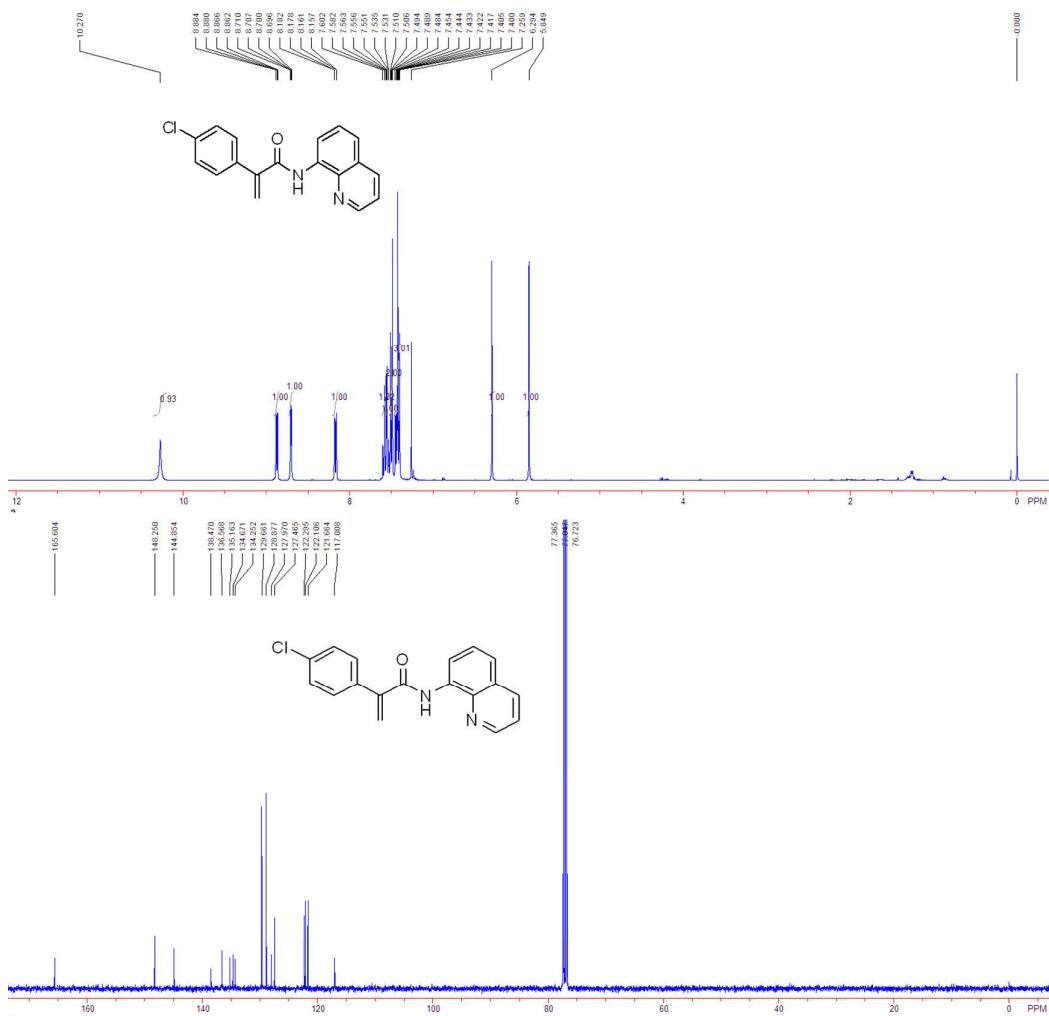
N-(quinolin-8-yl)methacrylamide (**5a**)



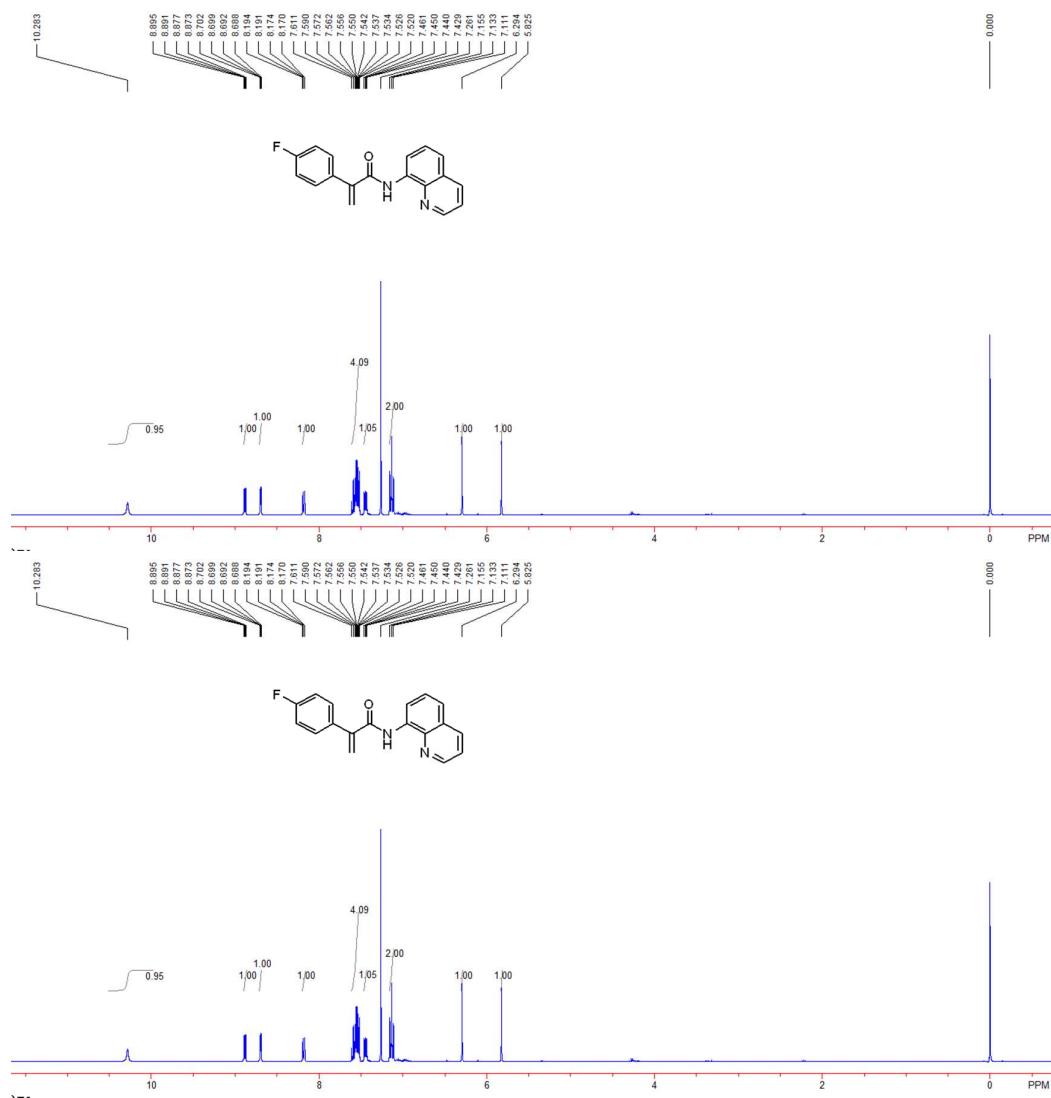
(E)-2-phenyl-N-(quinolin-8-yl)but-2-enamide (5b)



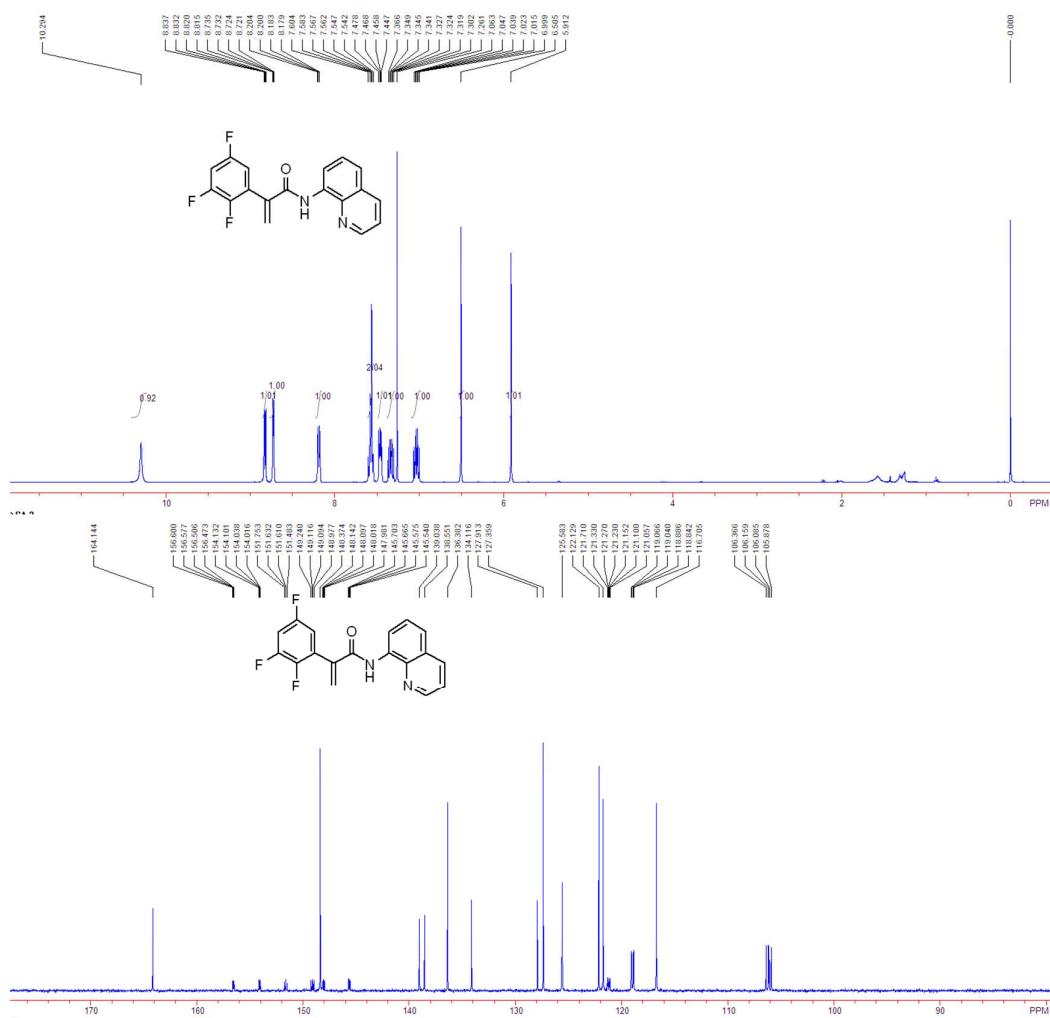
2-(4-chlorophenyl)-N-(quinolin-8-yl)acrylamide (5c)



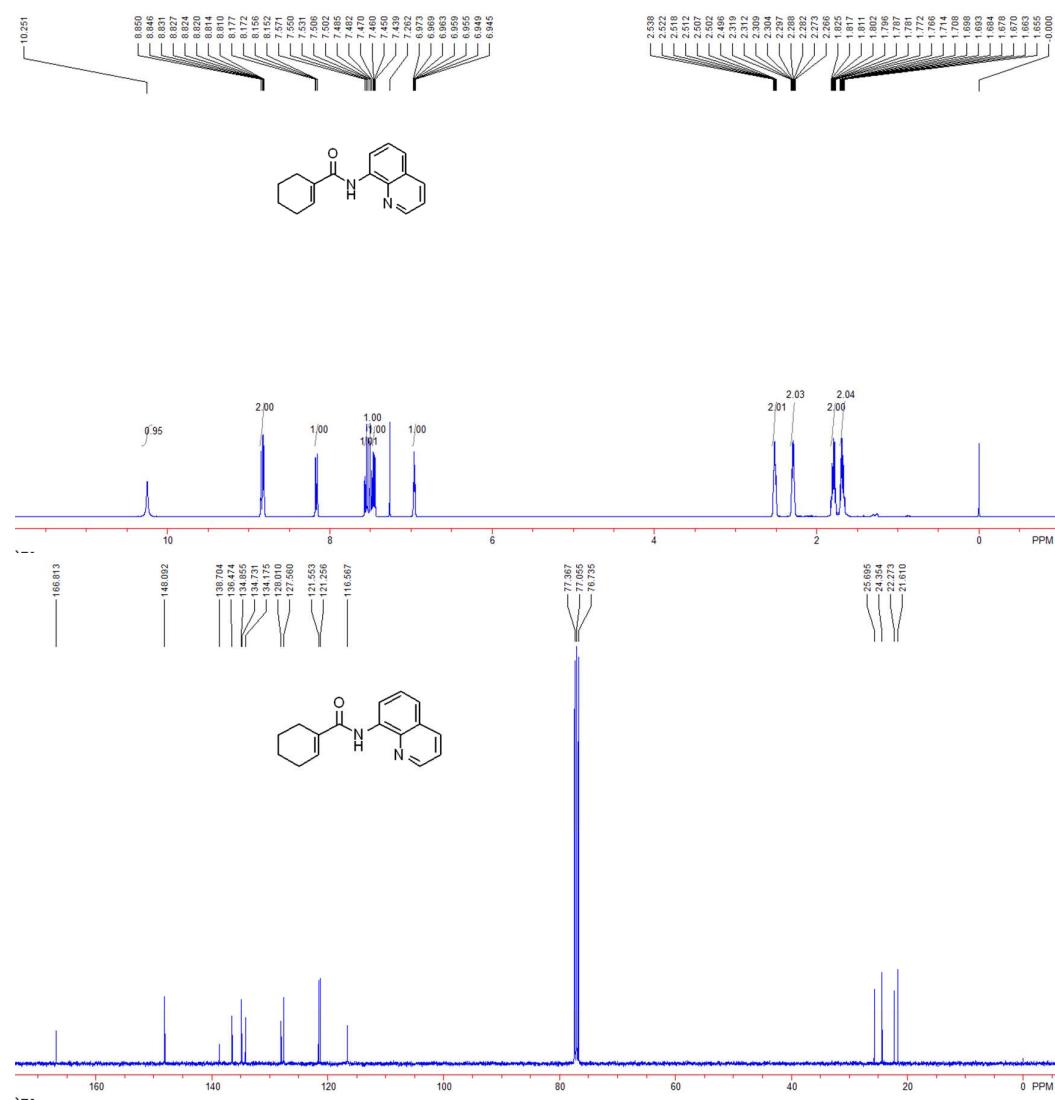
2-(4-fluorophenyl)-*N*-(quinolin-8-yl)acrylamide (5d)



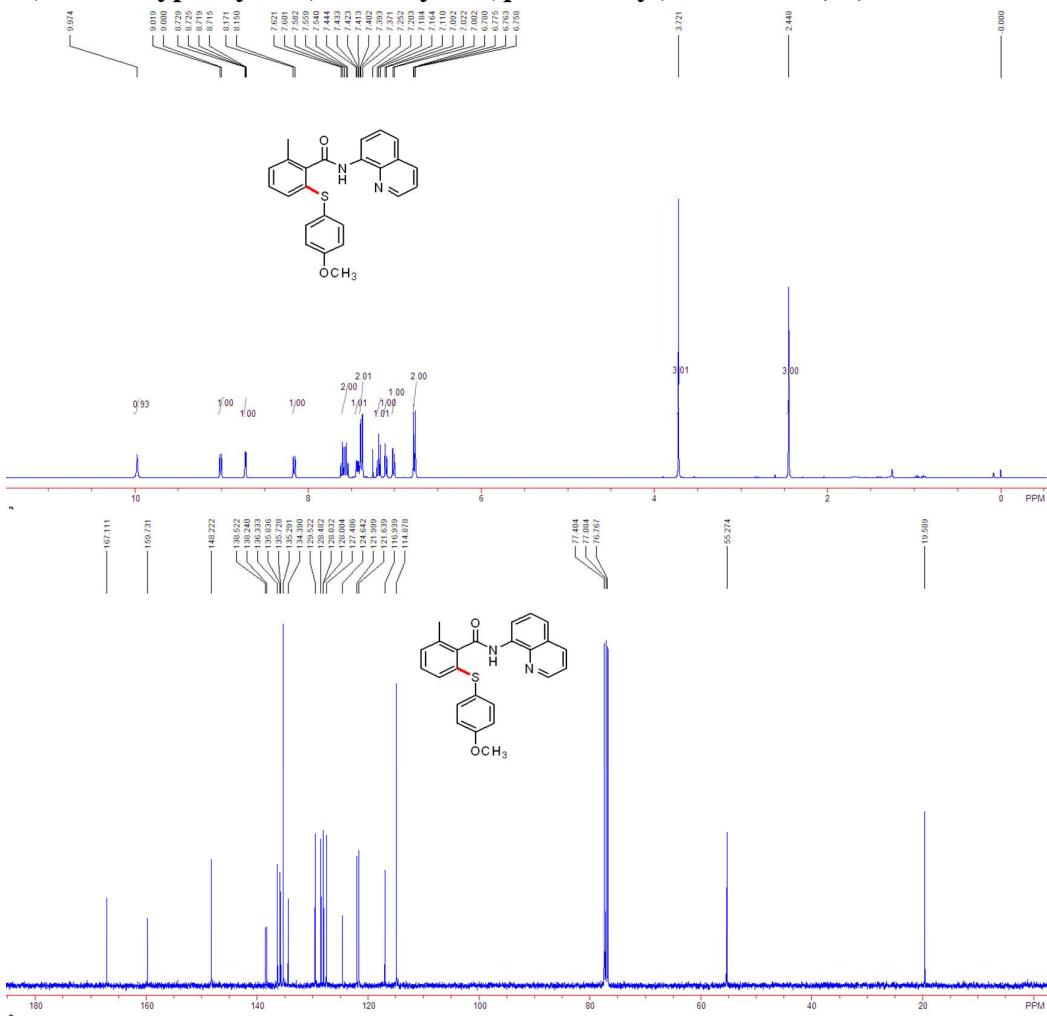
N-(quinolin-8-yl)-2-(2,3,5-trifluorophenyl)acrylamide (5e)



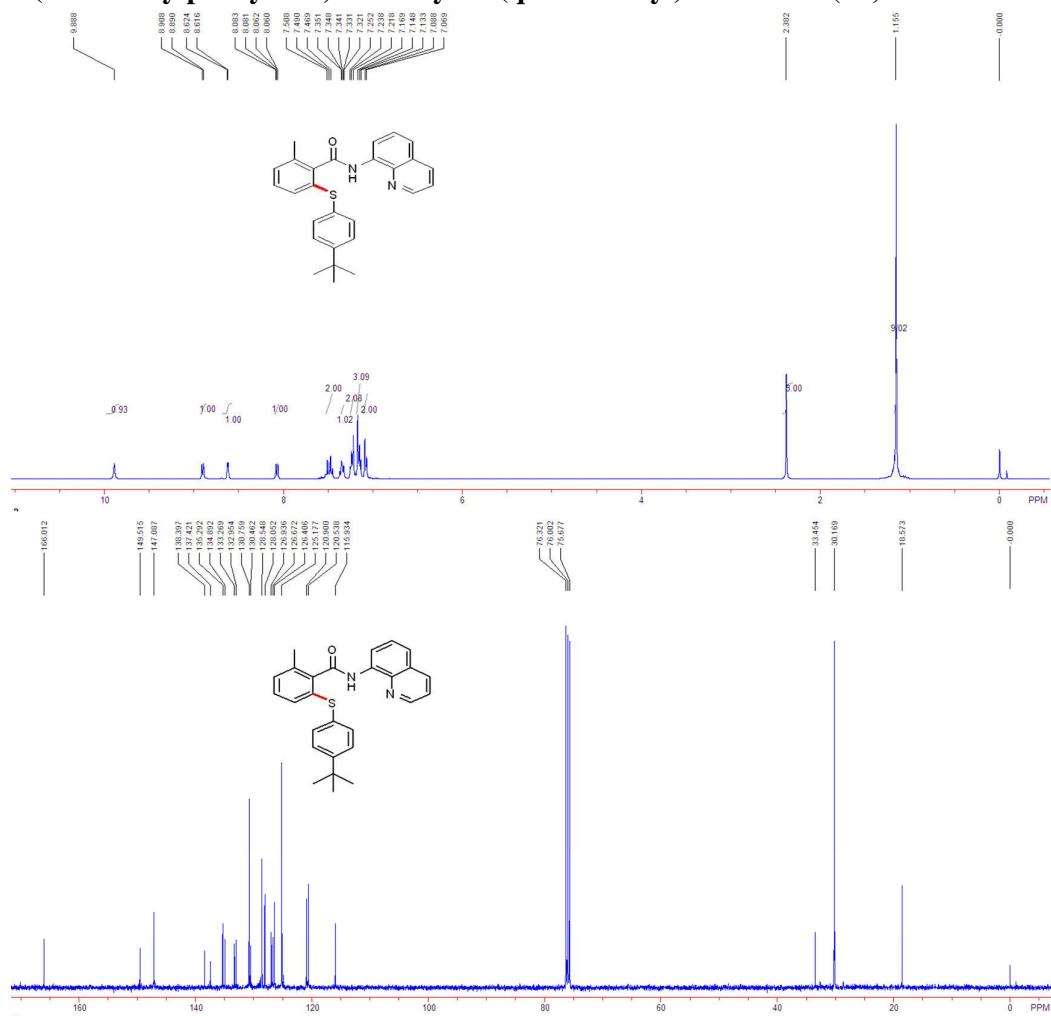
***N*-(quinolin-8-yl)cyclohex-1-enecarboxamide (**5f**)**



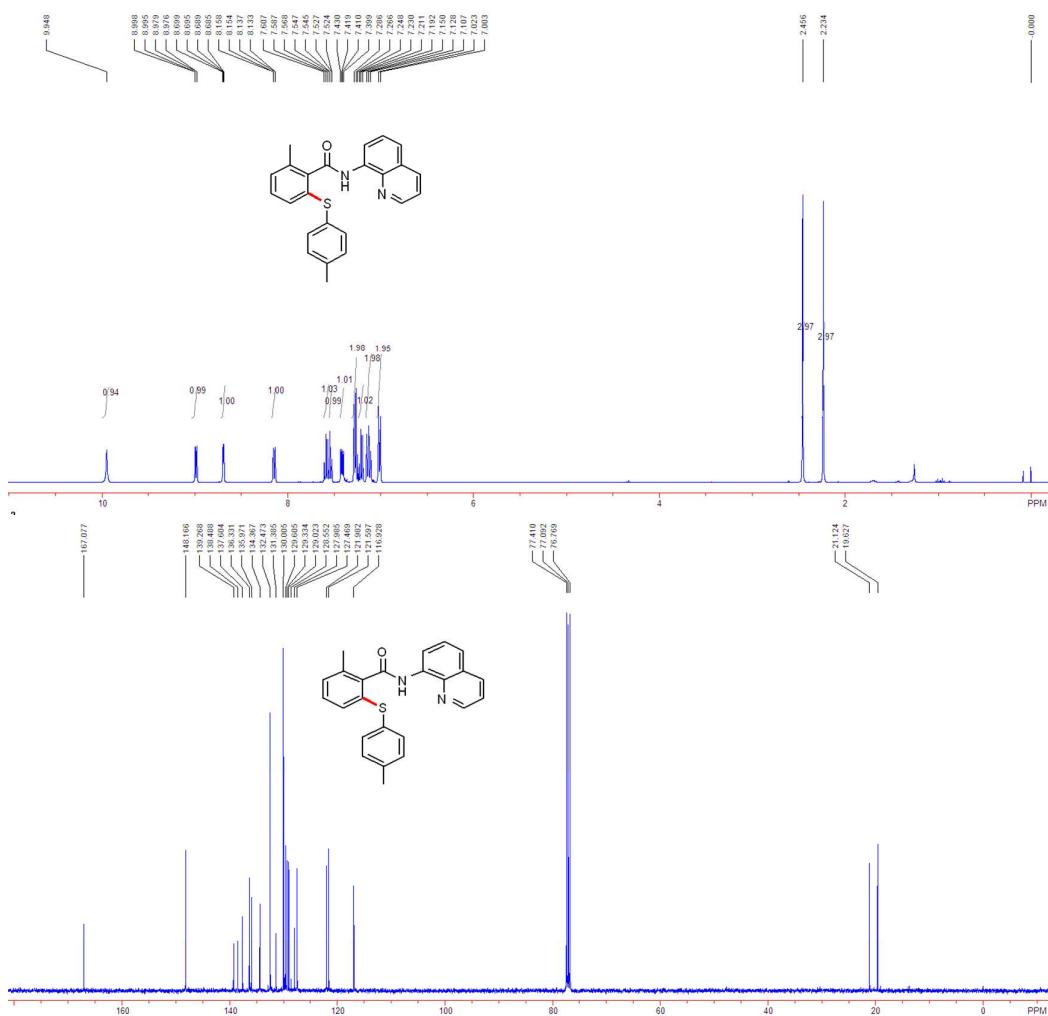
2-(4-methoxyphenylthio)-6-methyl-N-(quinolin-8-yl)benzamide (3a)



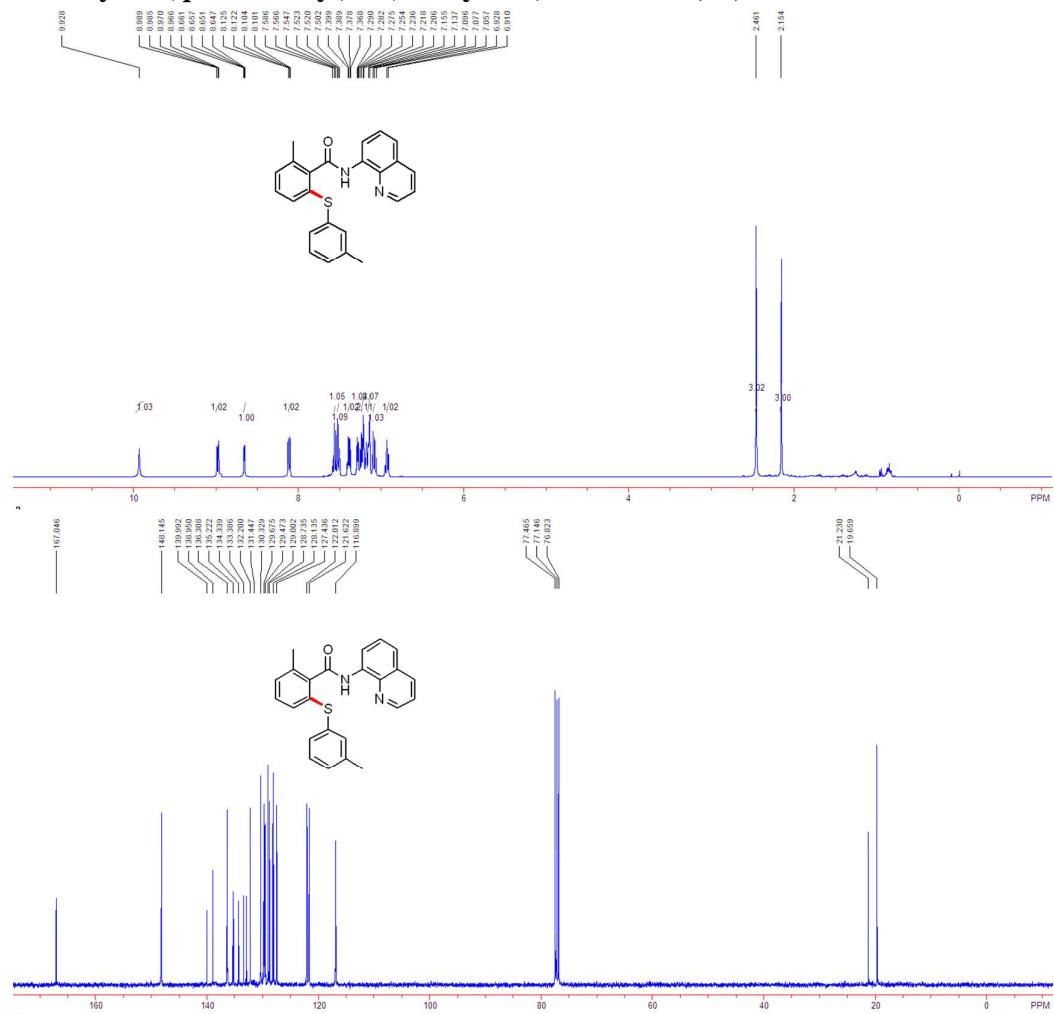
2-(4-*tert*-butylphenylthio)-6-methyl-N-(quinolin-8-yl)benzamide (3b)



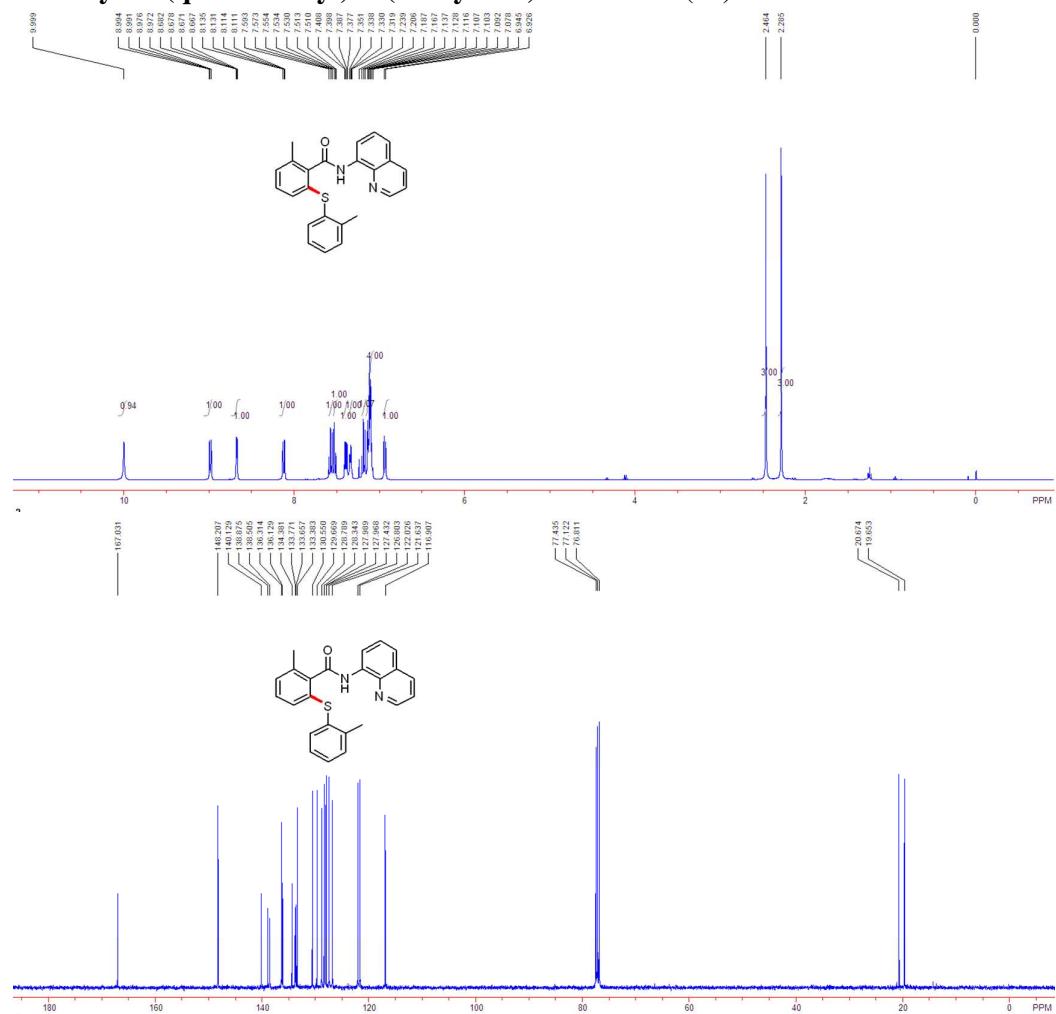
2-methyl-N-(quinolin-8-yl)-6-(*p*-tolylthio)benzamide (3c)



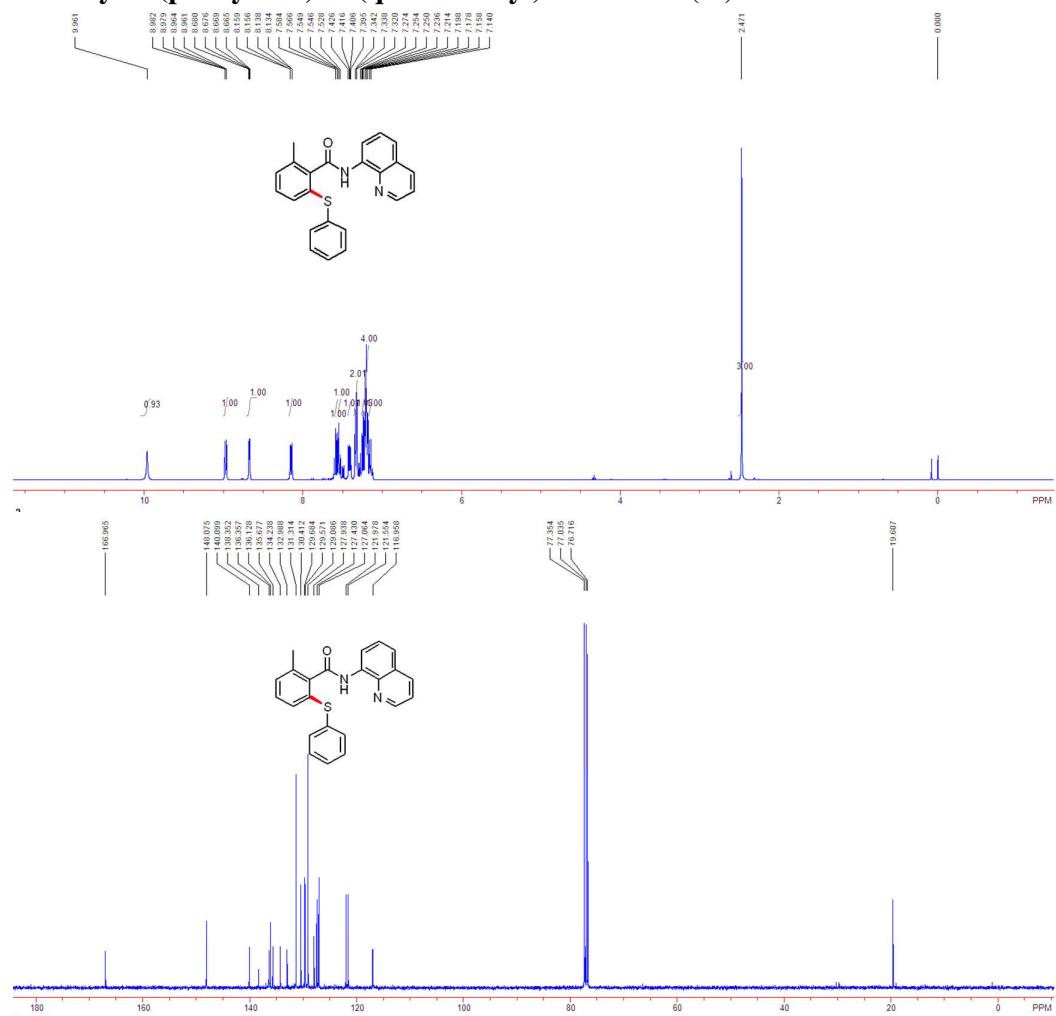
2-methyl-N-(quinolin-8-yl)-6-(*m*-tolylthio)benzamide (3d)



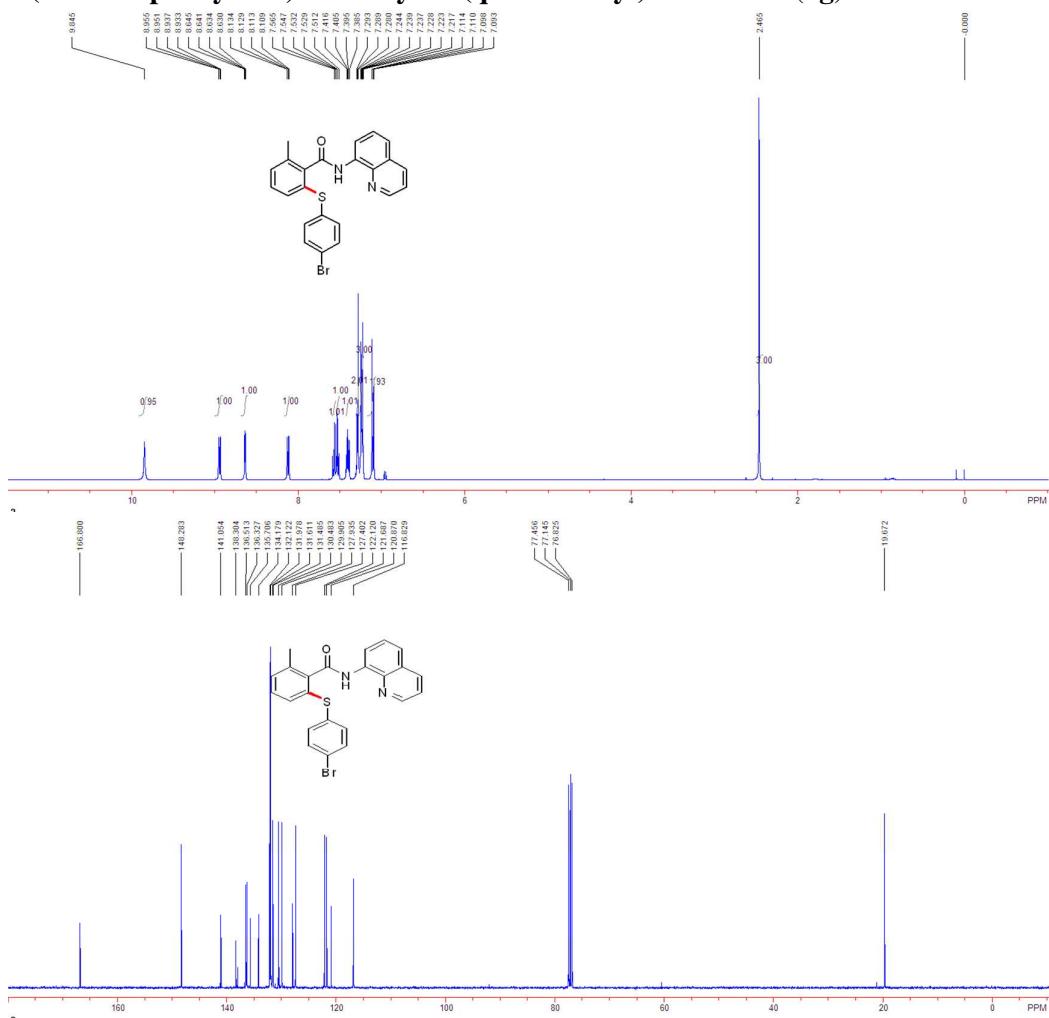
2-methyl-N-(quinolin-8-yl)-6-(*o*-tolylthio)benzamide (3e)



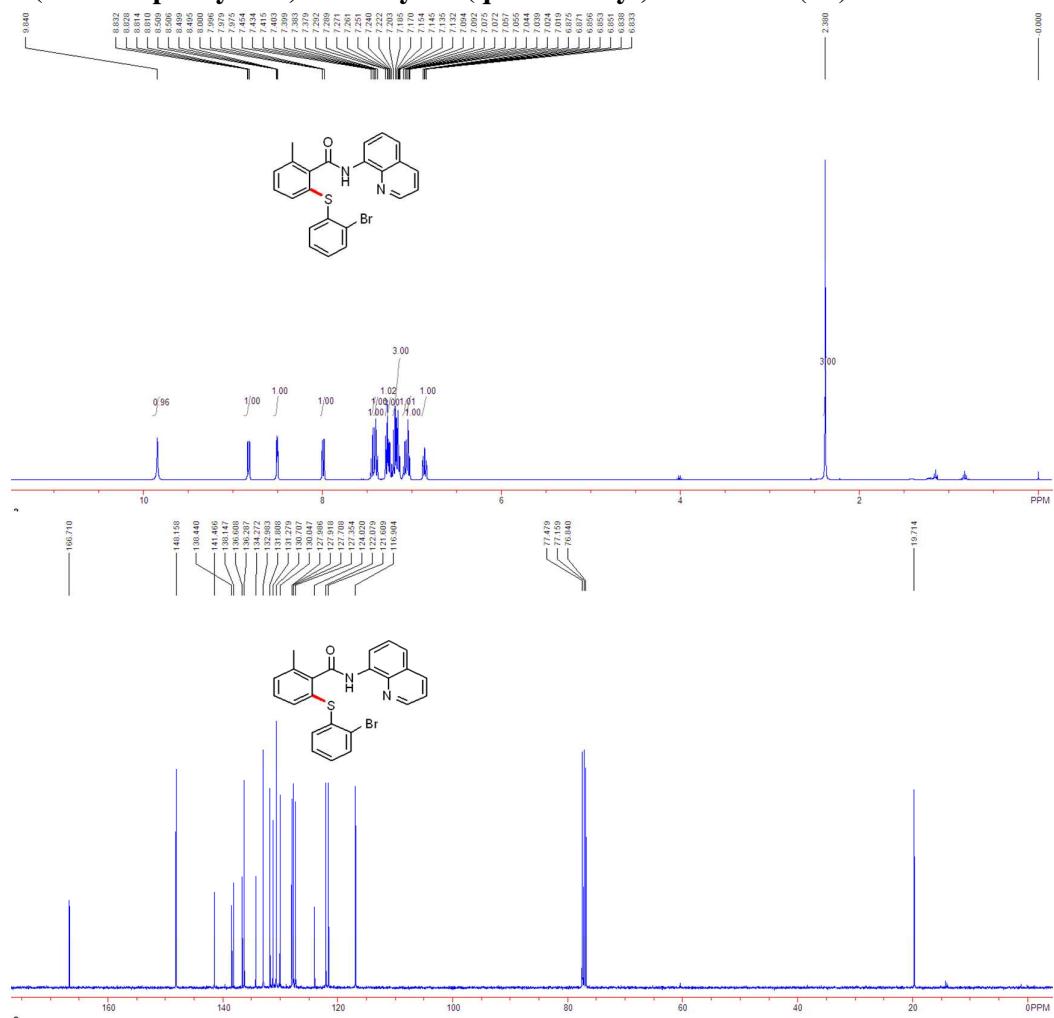
2-methyl-6-(phenylthio)-N-(quinolin-8-yl)benzamide (3f)



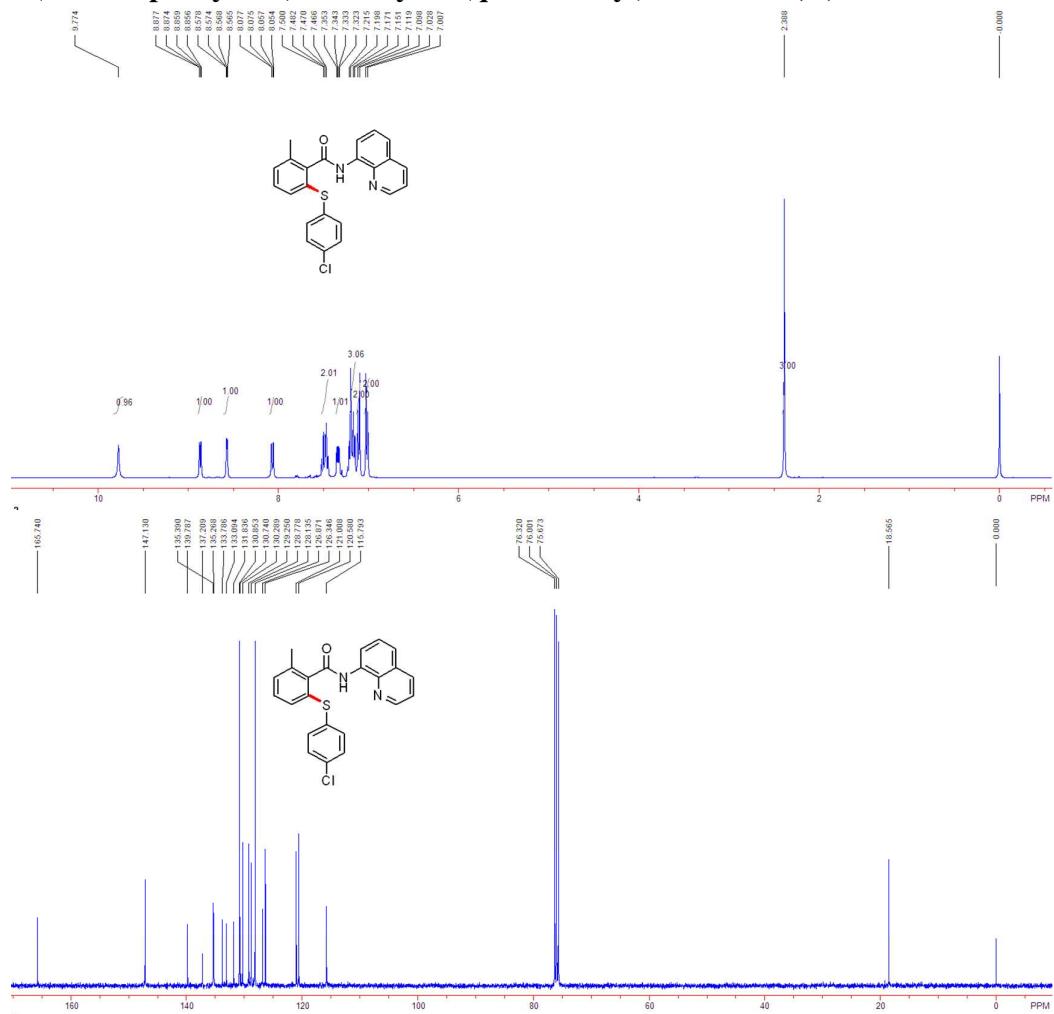
2-(4-bromophenylthio)-6-methyl-N-(quinolin-8-yl)benzamide (3g)



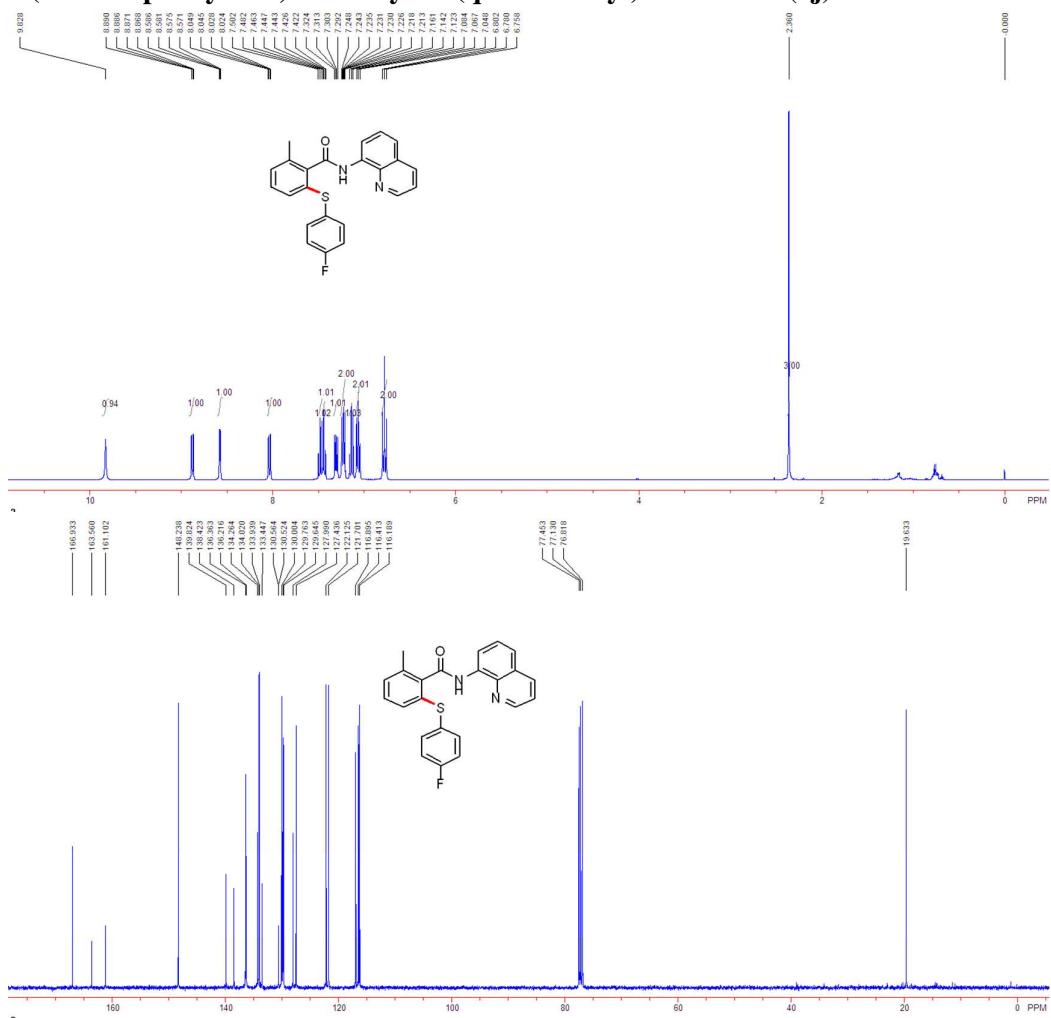
2-(2-bromophenylthio)-6-methyl-N-(quinolin-8-yl)benzamide (3h)



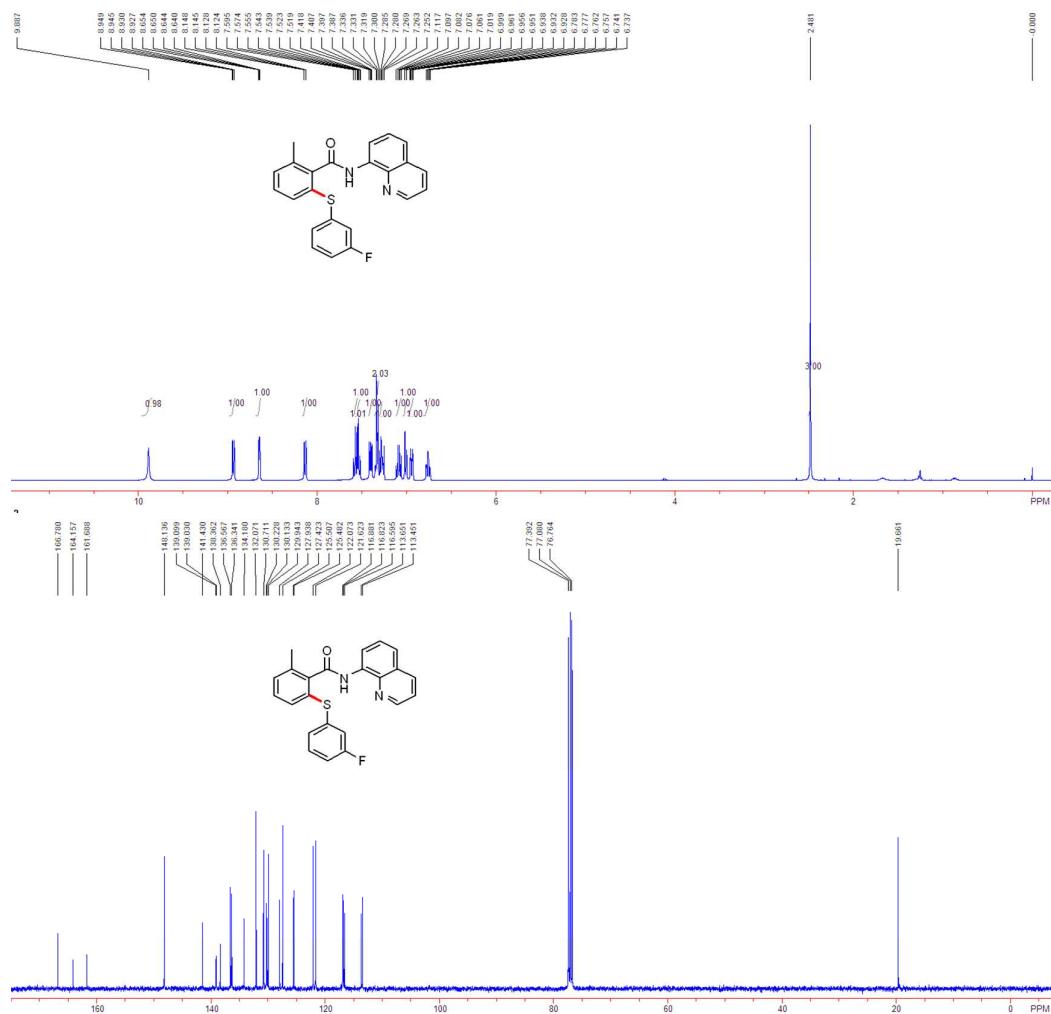
2-(4-chlorophenylthio)-6-methyl-N-(quinolin-8-yl)benzamide (3i)



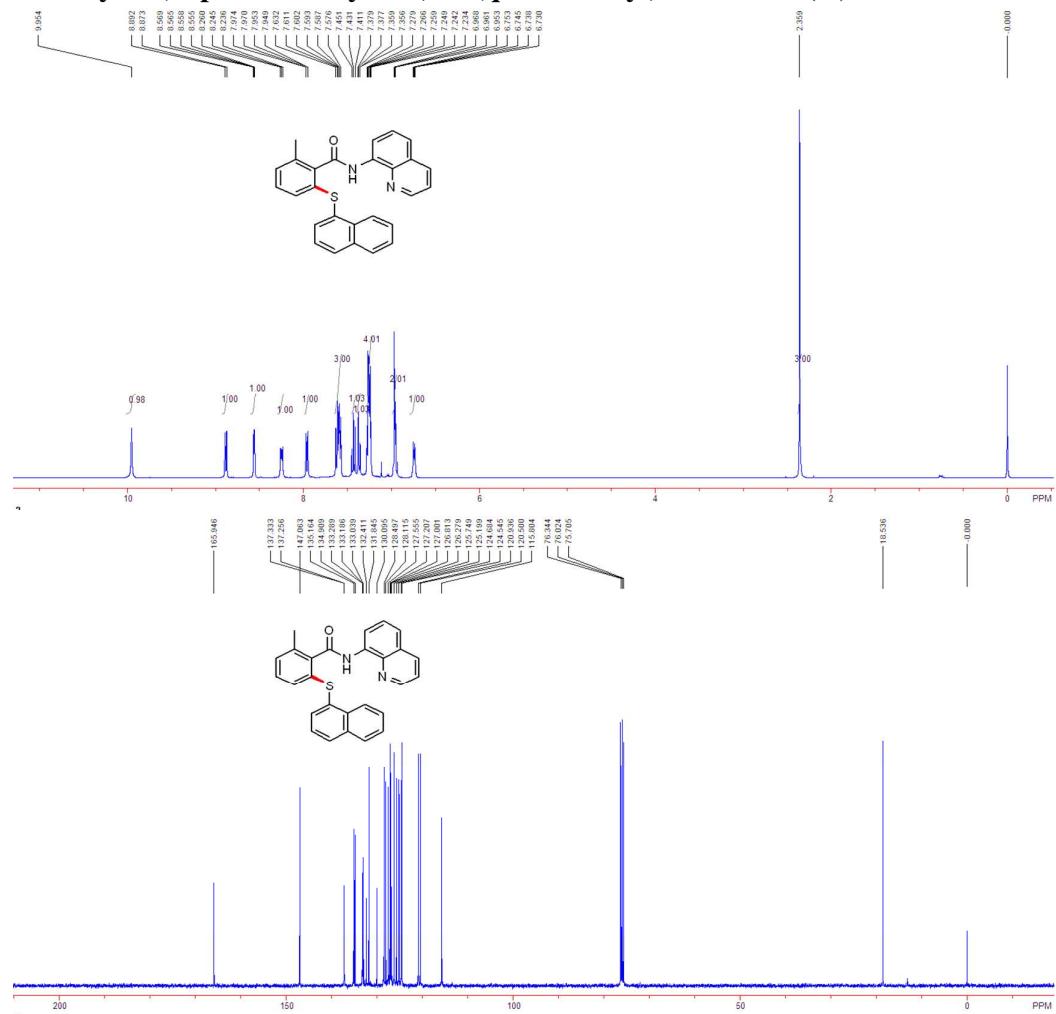
2-(4-fluorophenylthio)-6-methyl-*N*-(quinolin-8-yl)benzamide (3j)



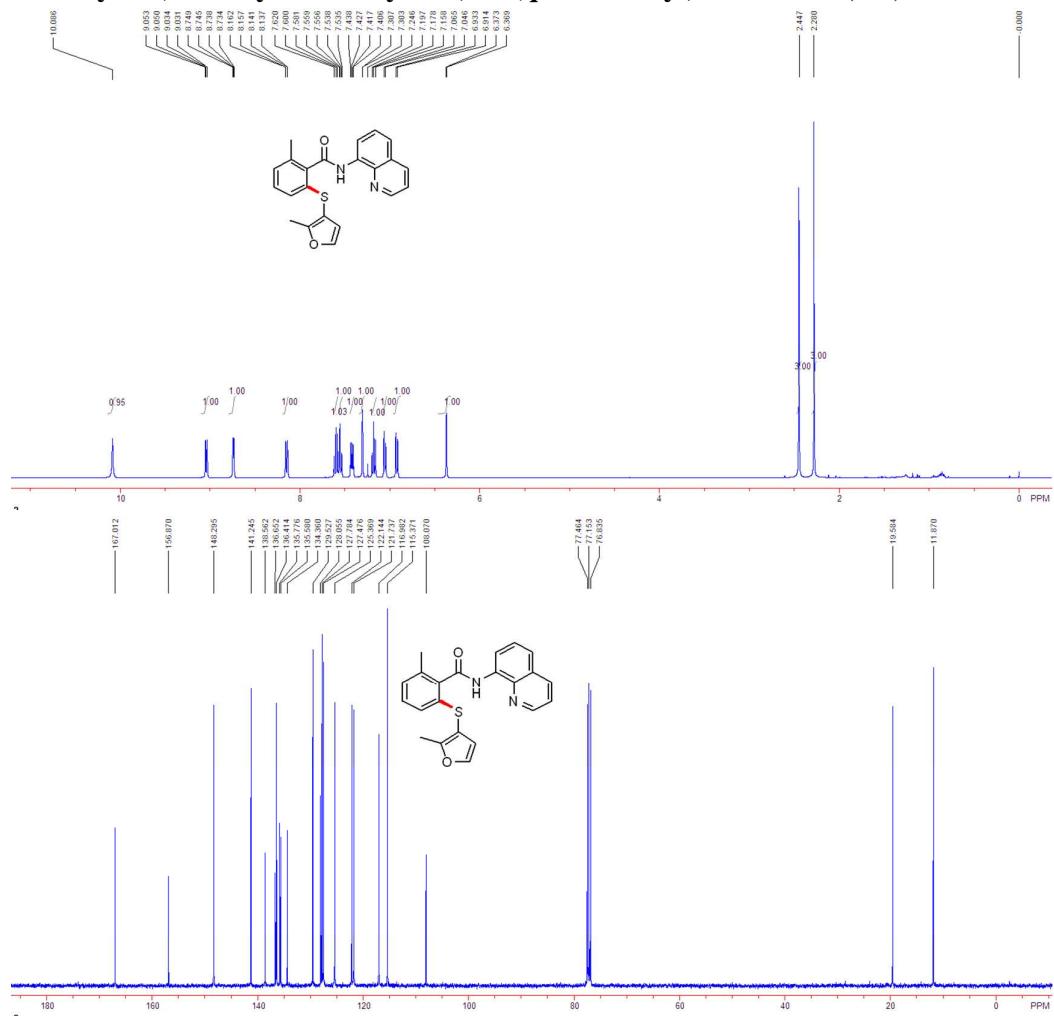
2-(3-fluorophenylthio)-6-methyl-N-(quinolin-8-yl)benzamide (3k)



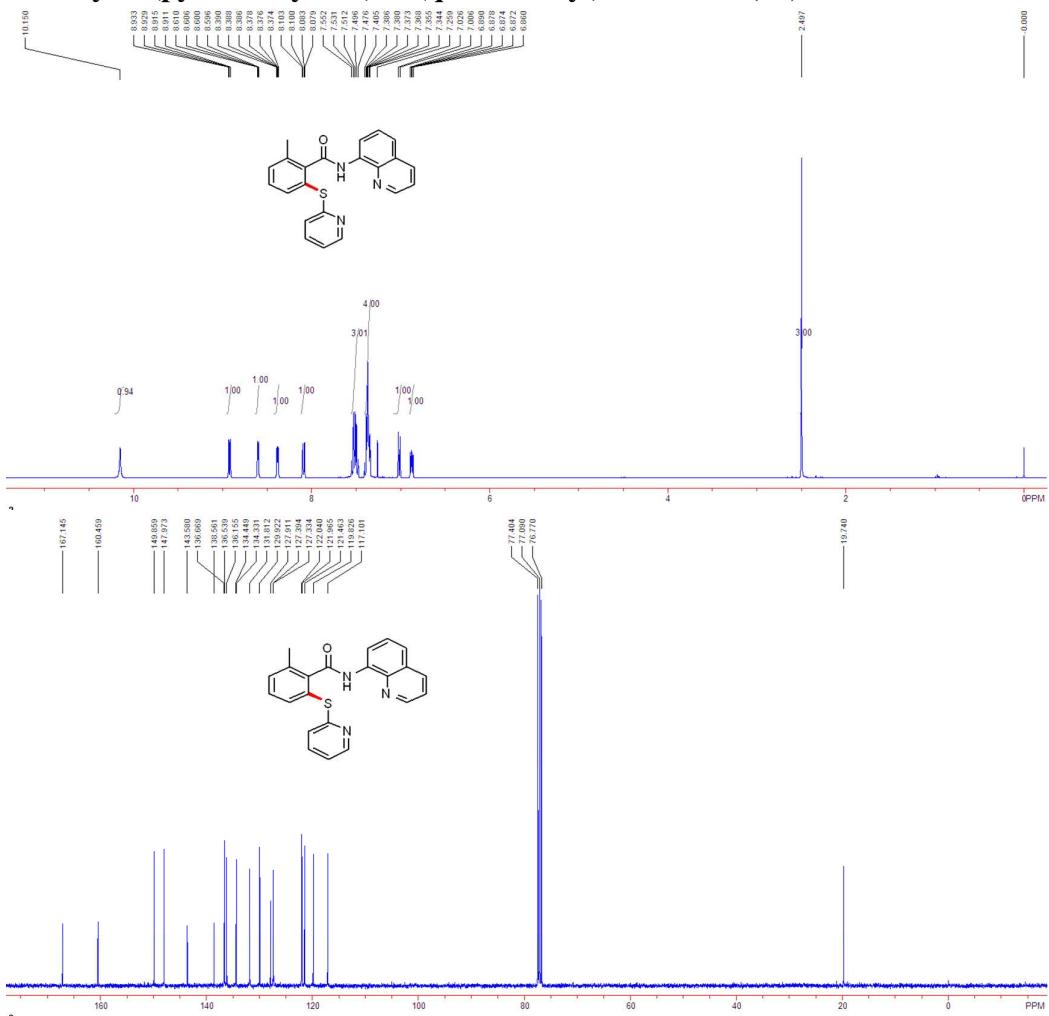
2-methyl-6-(naphthalen-1-ylthio)-N-(quinolin-8-yl)benzamide (3l)



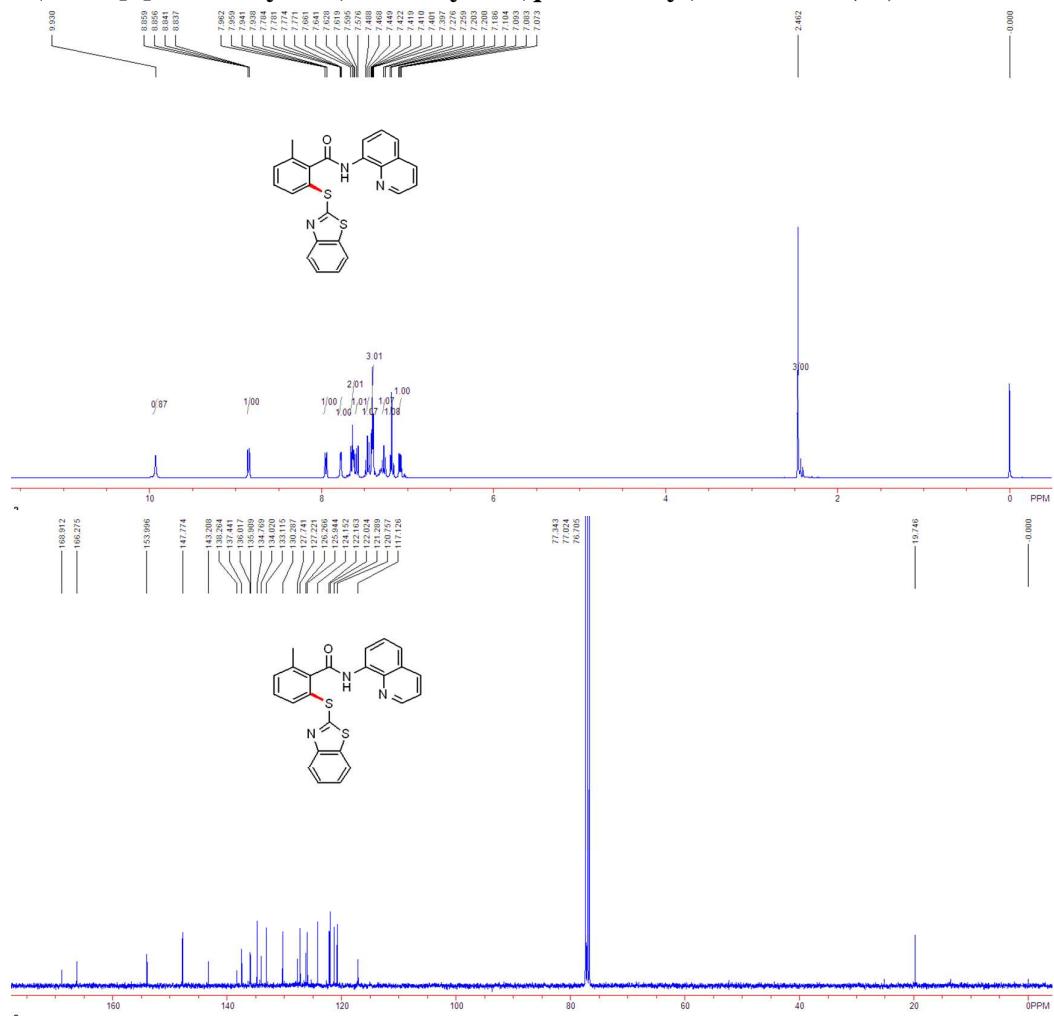
2-methyl-6-(2-methylfuran-3-ylthio)-N-(quinolin-8-yl)benzamide (3m)



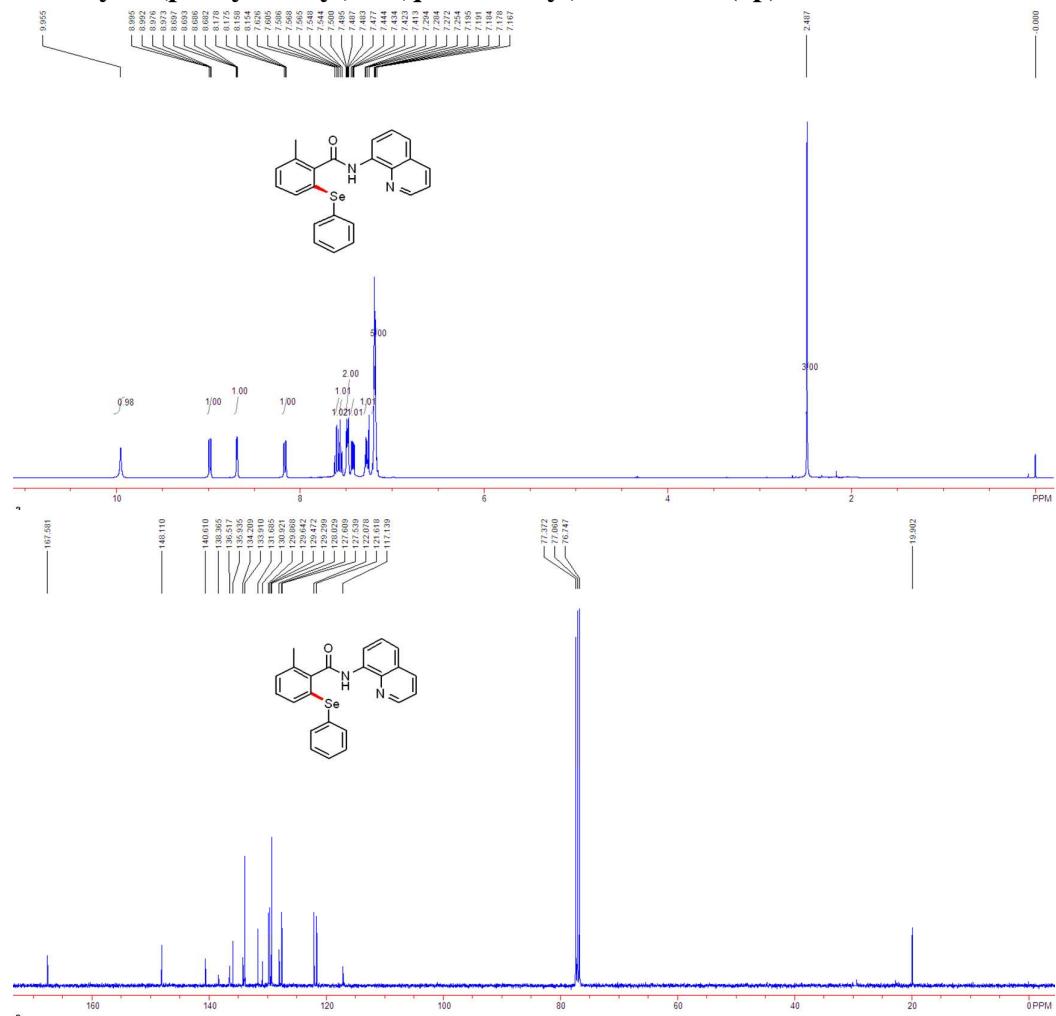
2-methyl-6-(pyridin-2-ylthio)-N-(quinolin-8-yl)benzamide (3n)



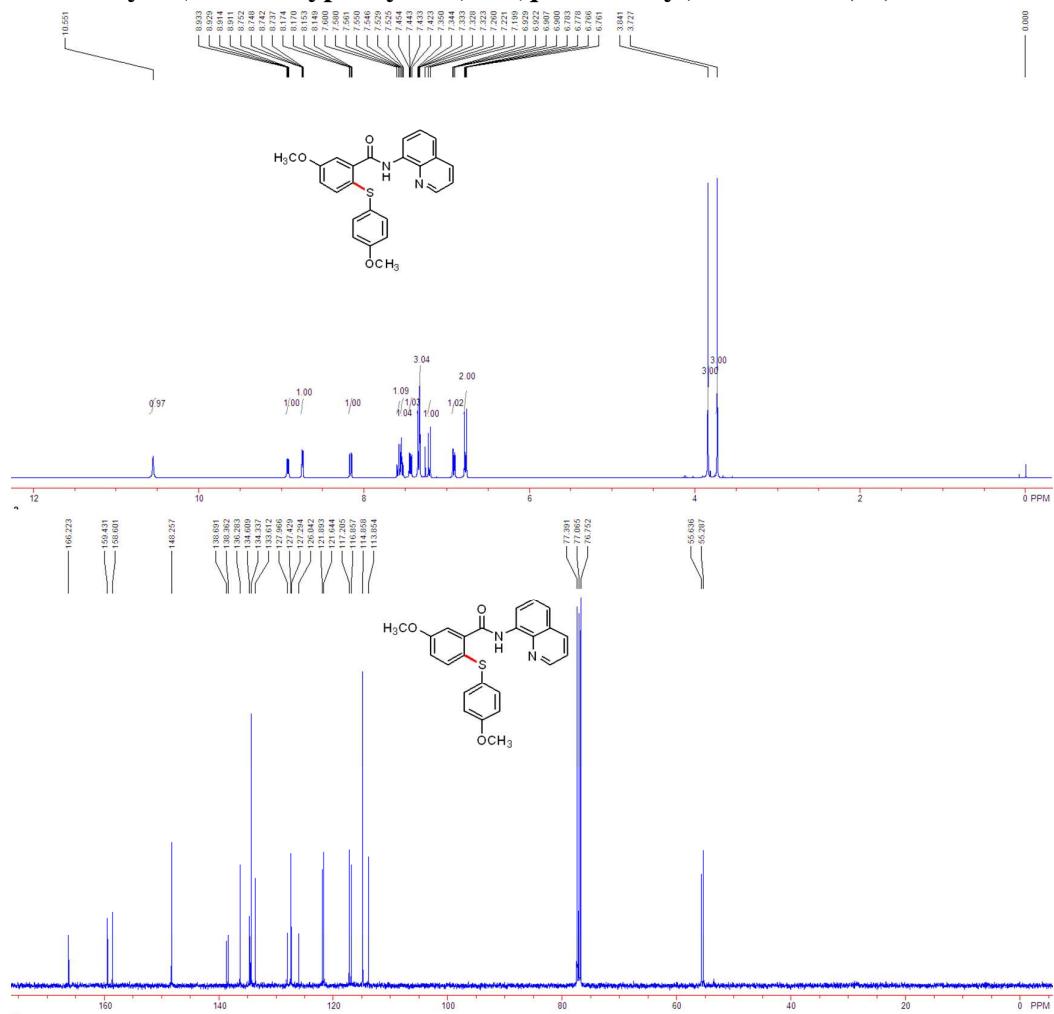
2-(benzo[d]thiazo-2-ylthio)-6-methyl-N-(quinolin-8-yl)benzamide (3o)



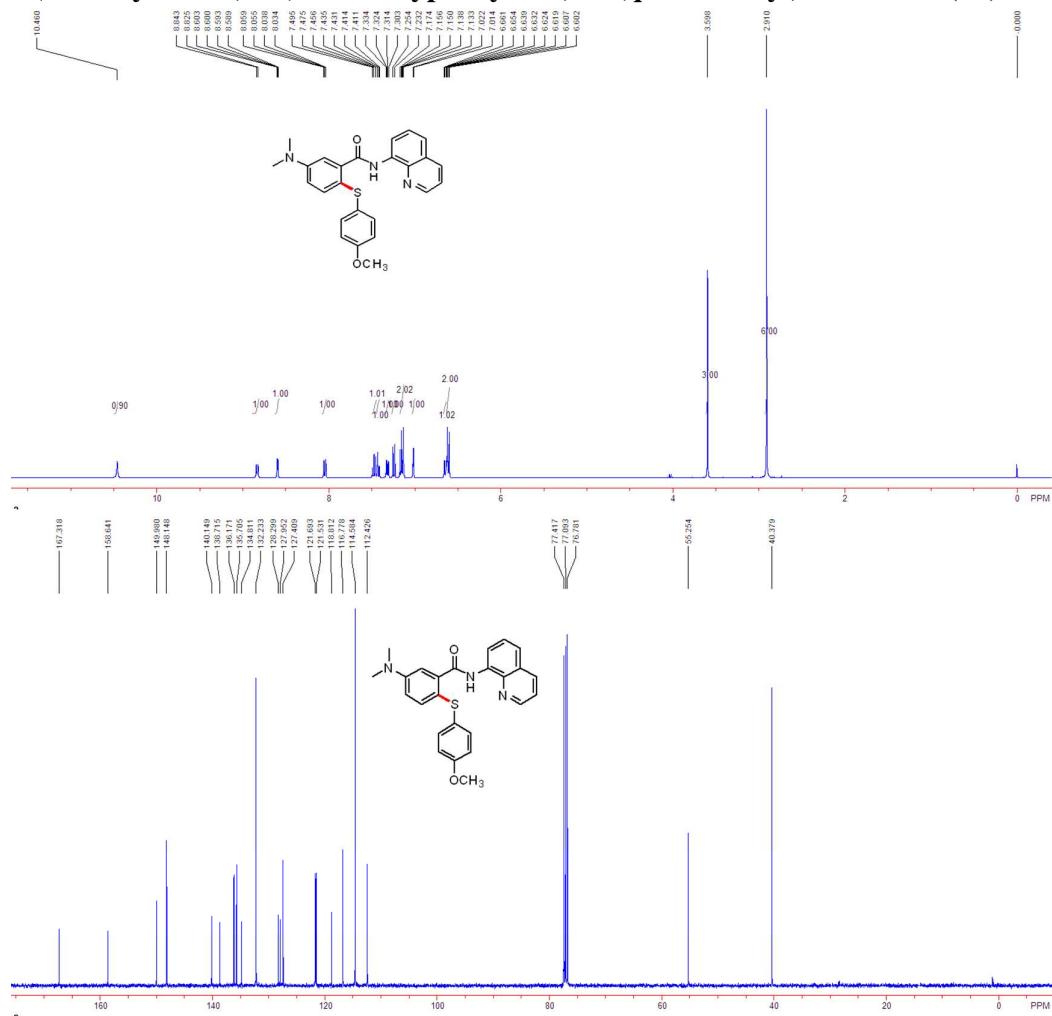
2-methyl-6-(phenylselanyl)-N-(quinolin-8-yl)benzamide (3p)



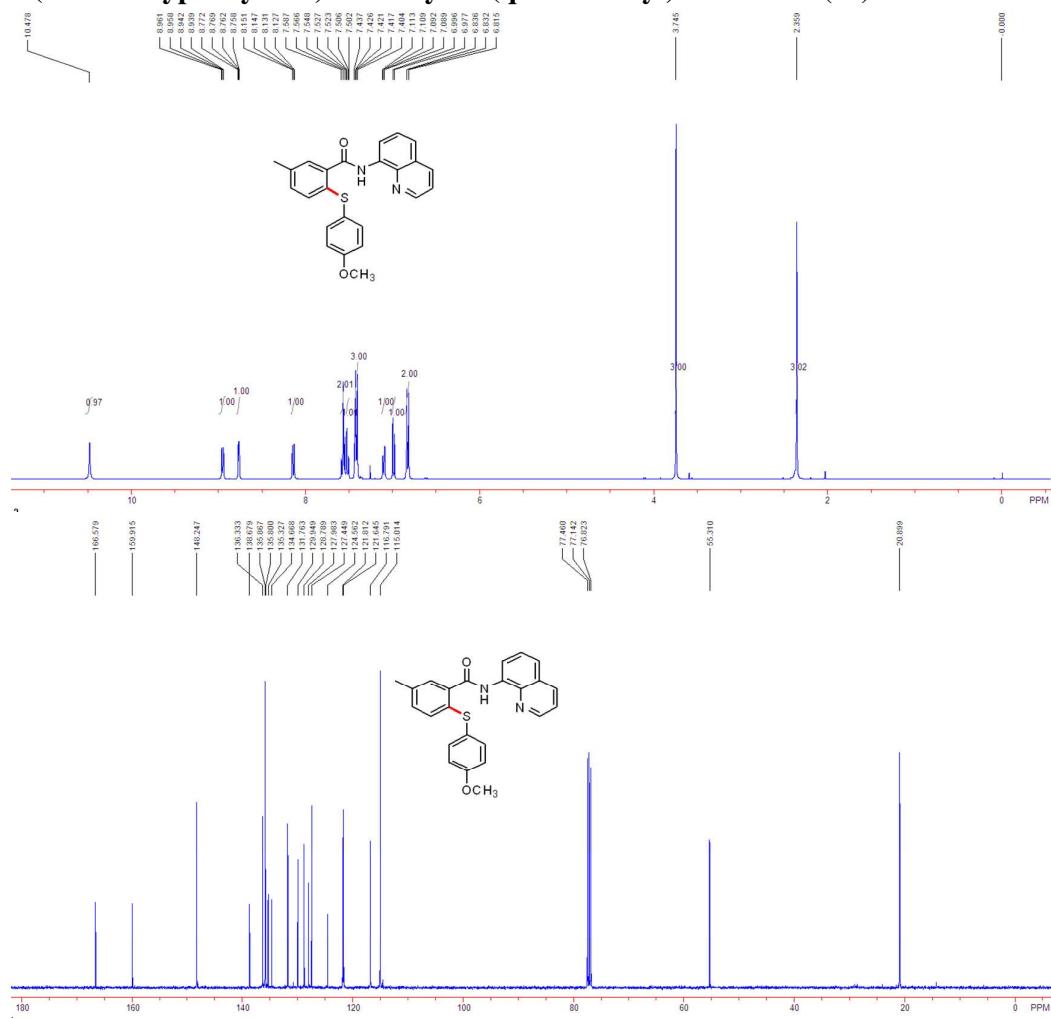
5-methoxy-2-(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4a)



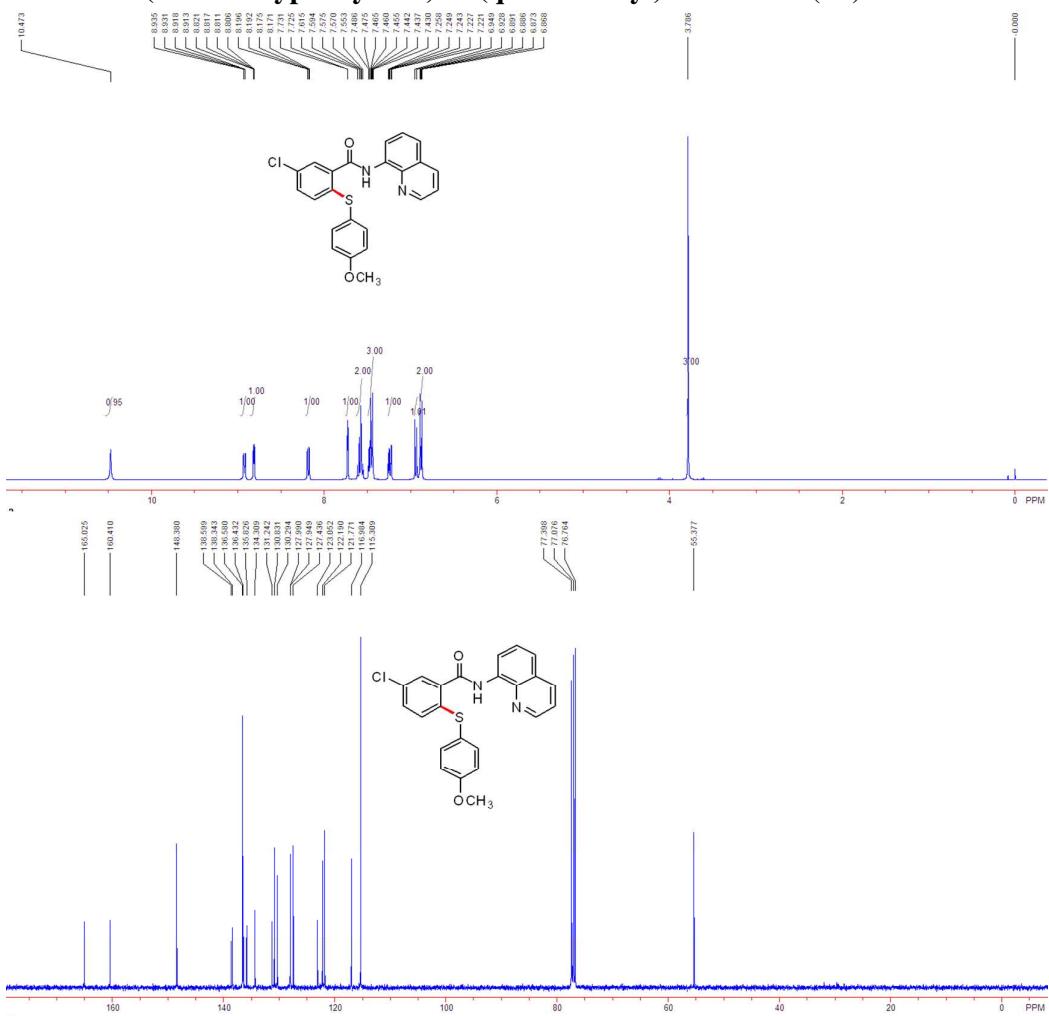
5-(dimethylamino)-2-(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4b)



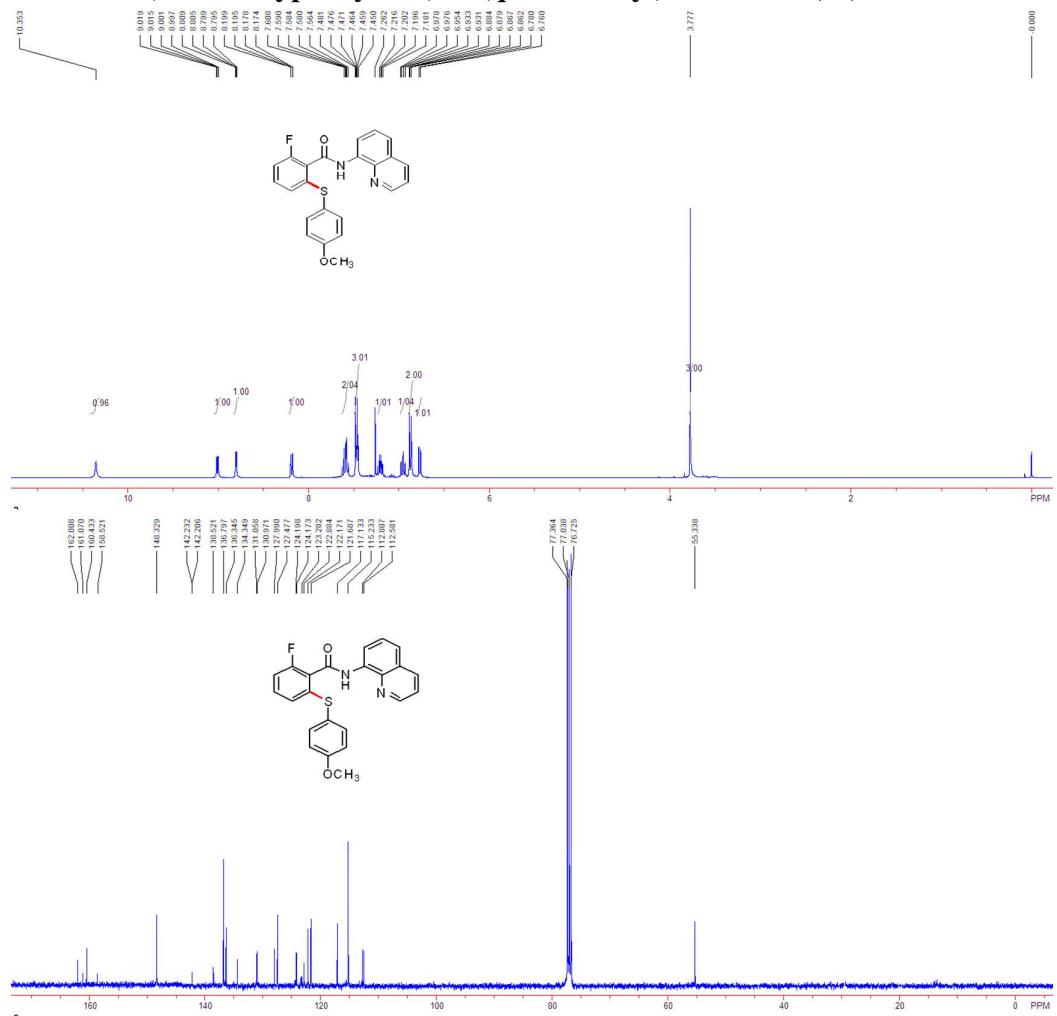
2-(4-methoxyphenylthio)-5-methyl-N-(quinolin-8-yl)benzamide (4c)



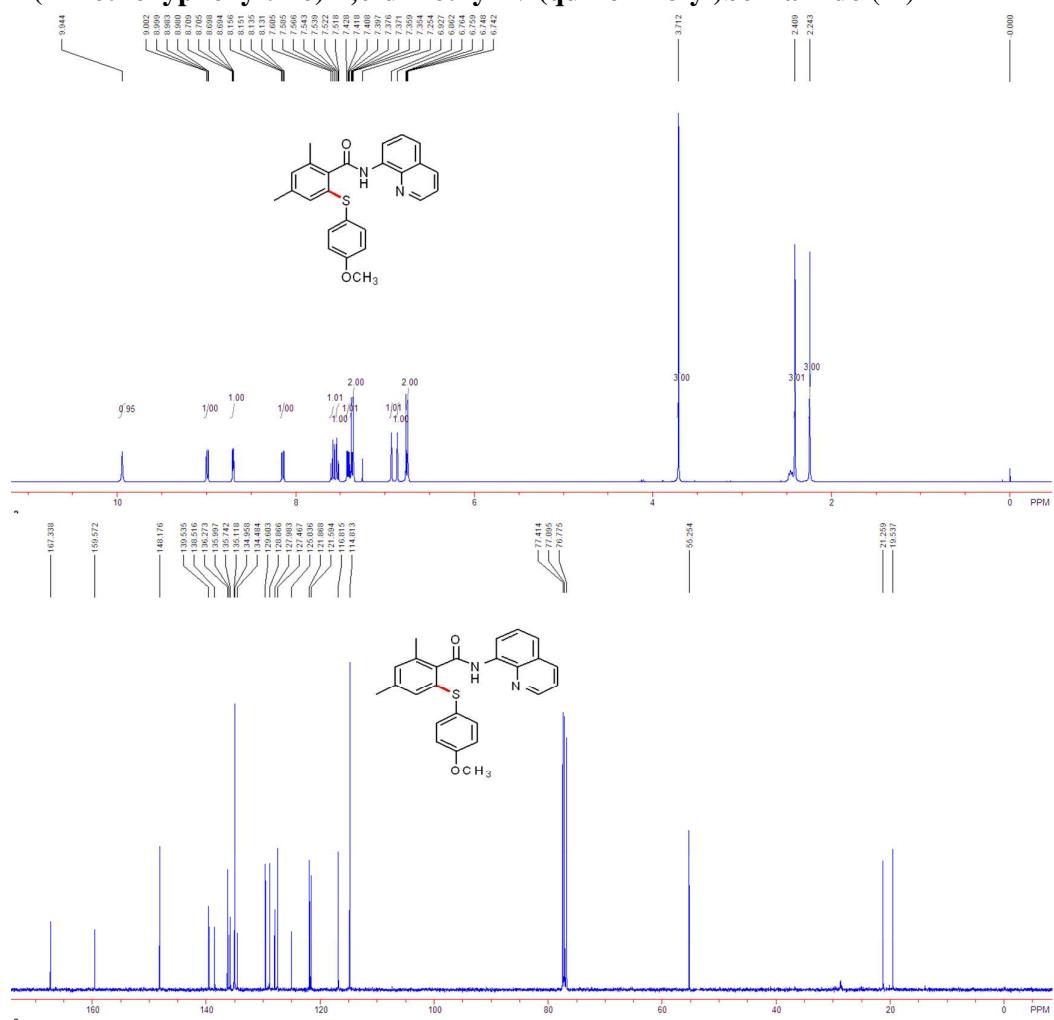
5-chloro-2-(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4d)



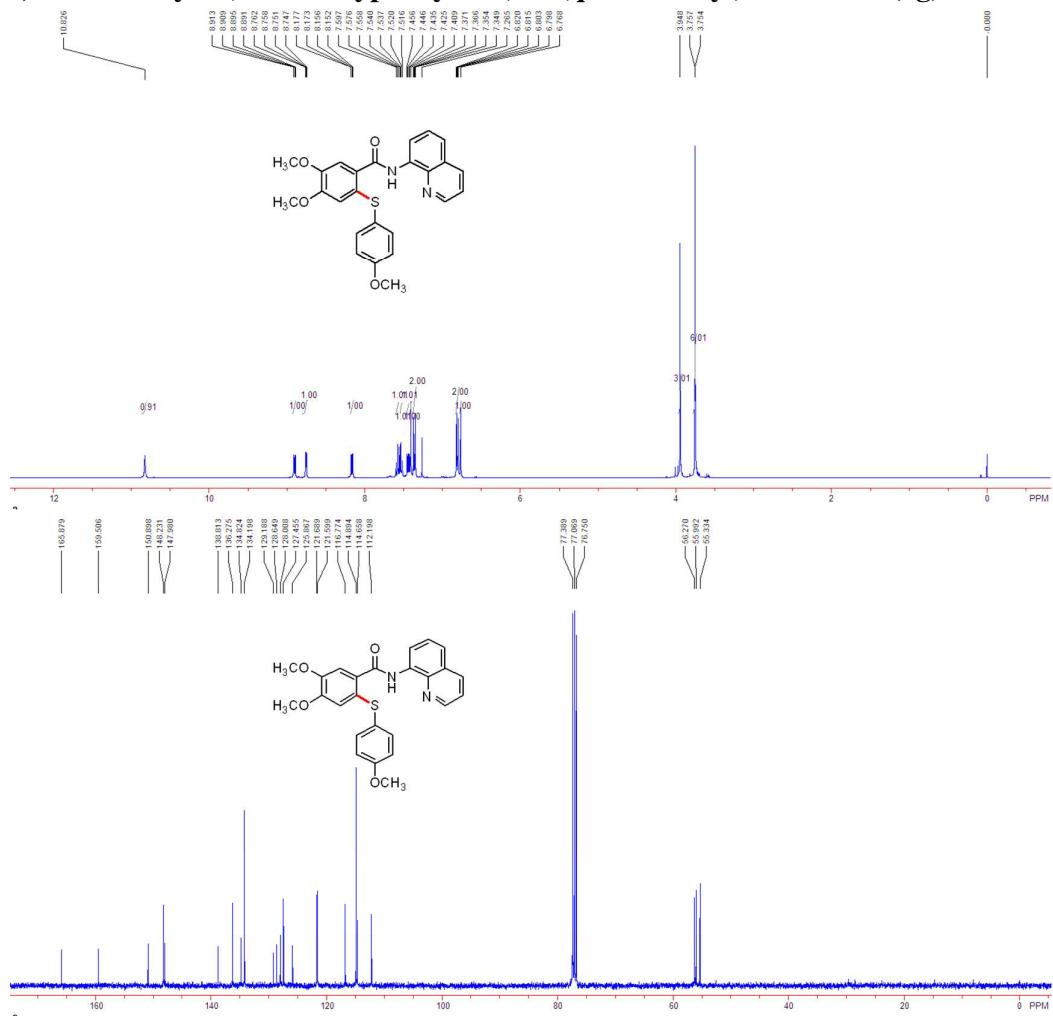
2-fluoro-6-(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4e)



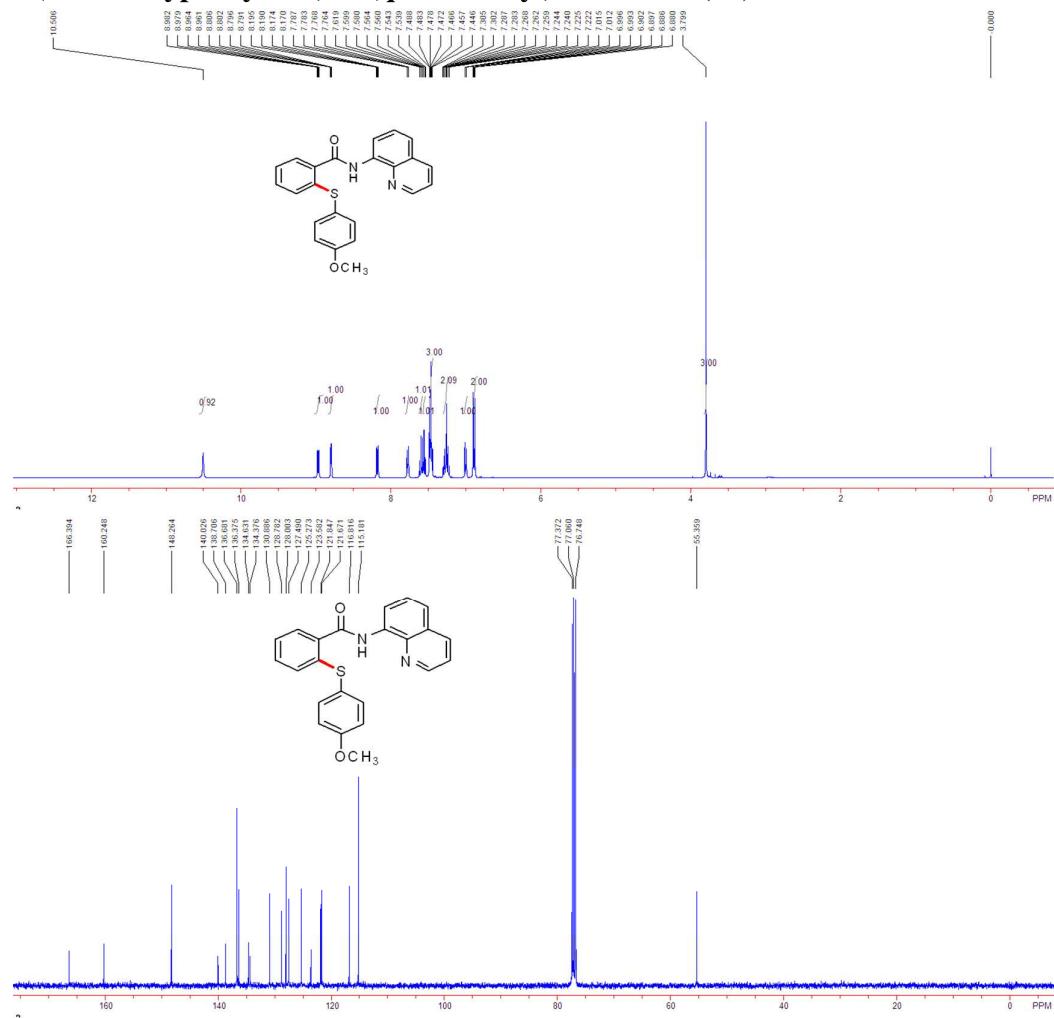
2-(4-methoxyphenylthio)-4,6-dimethyl-N-(quinolin-8-yl)benzamide (**4f**)



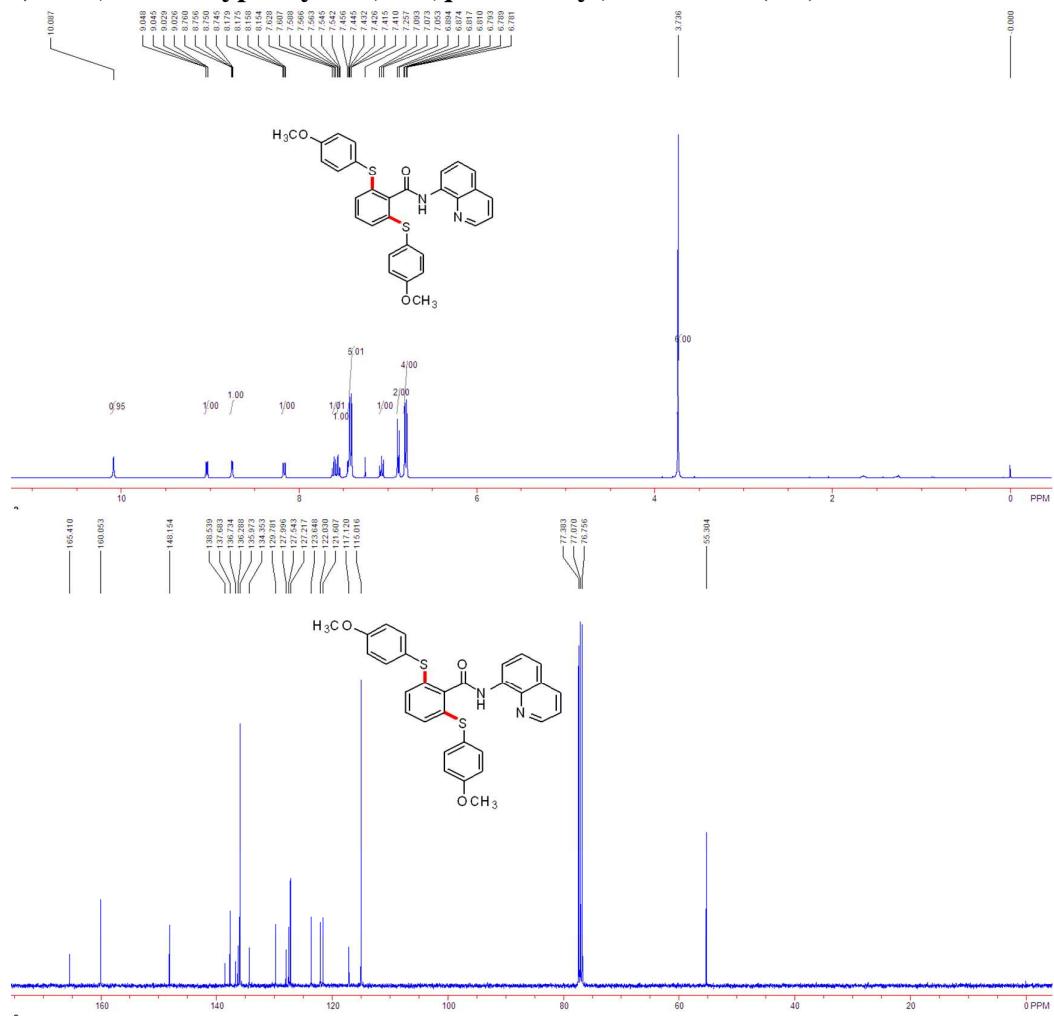
4,5-dimethoxy-2-(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4g)



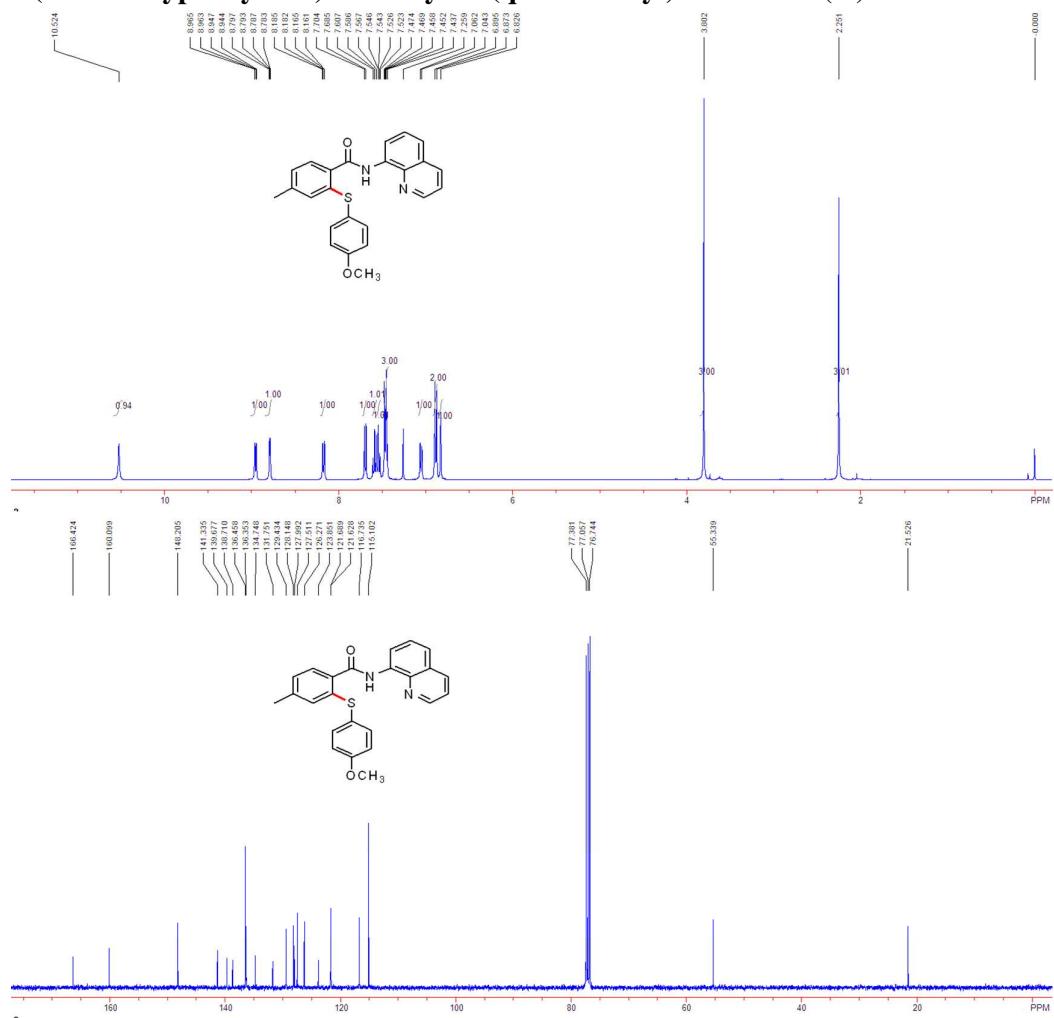
2-(4-methoxyphenylthio)-*N*-(quinolin-8-yl)benzamide (4h)



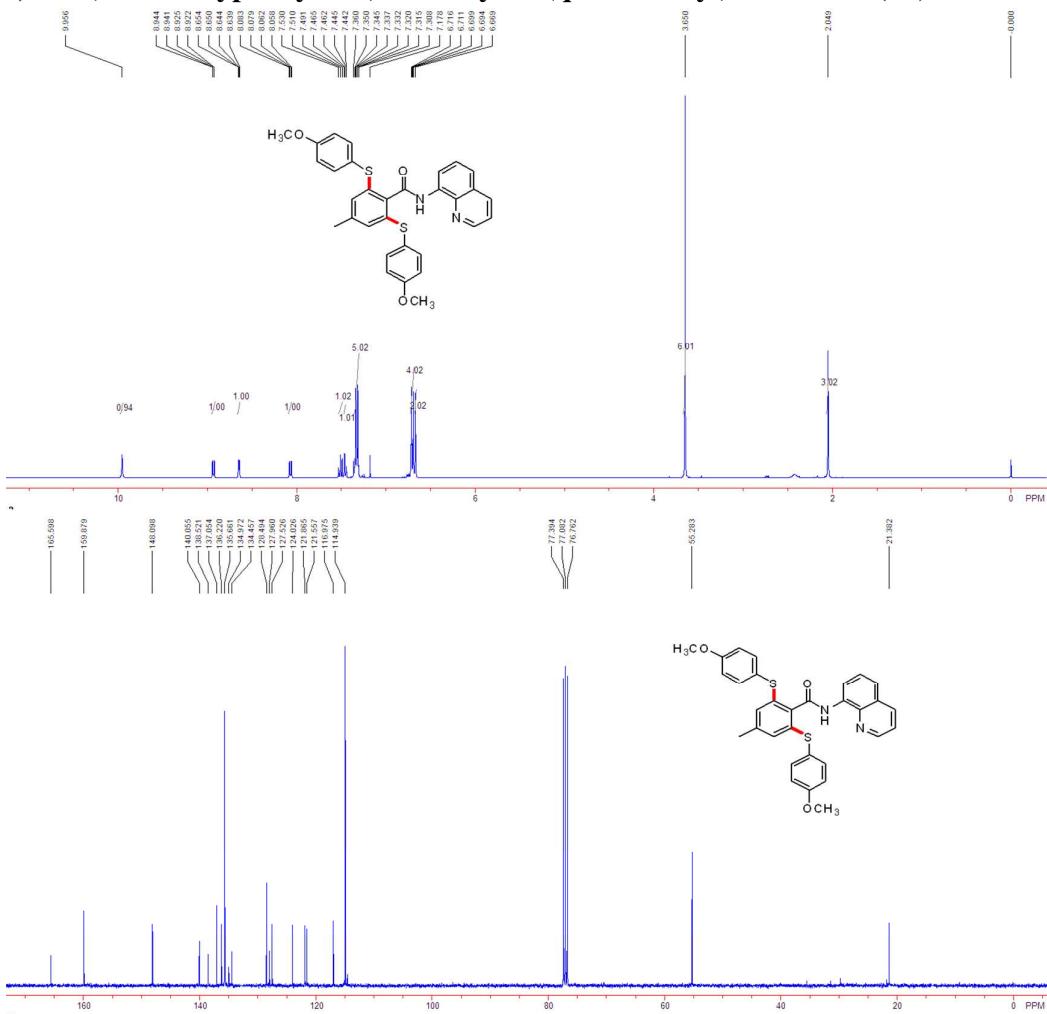
2,6-bis(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4h')



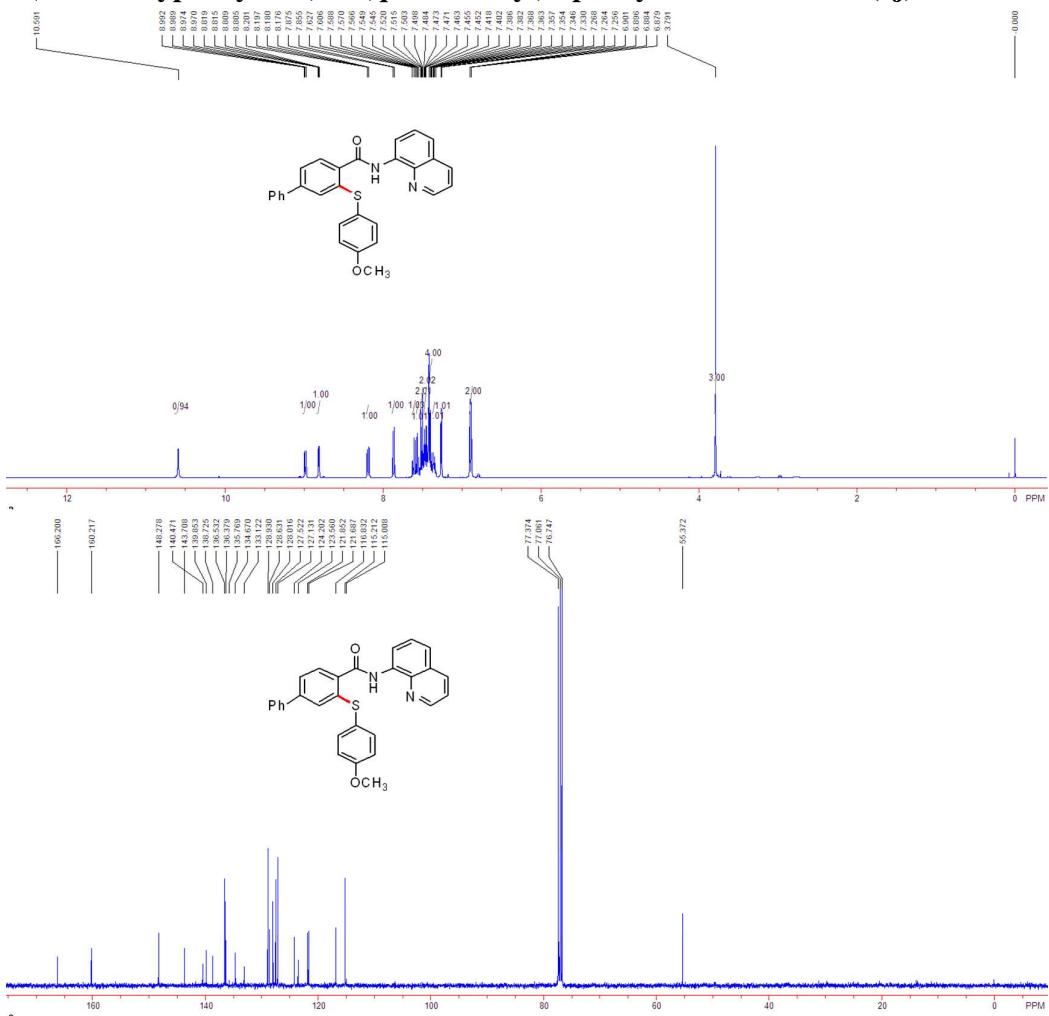
2-(4-methoxyphenylthio)-4-methyl-N-(quinolin-8-yl)benzamide (4i)



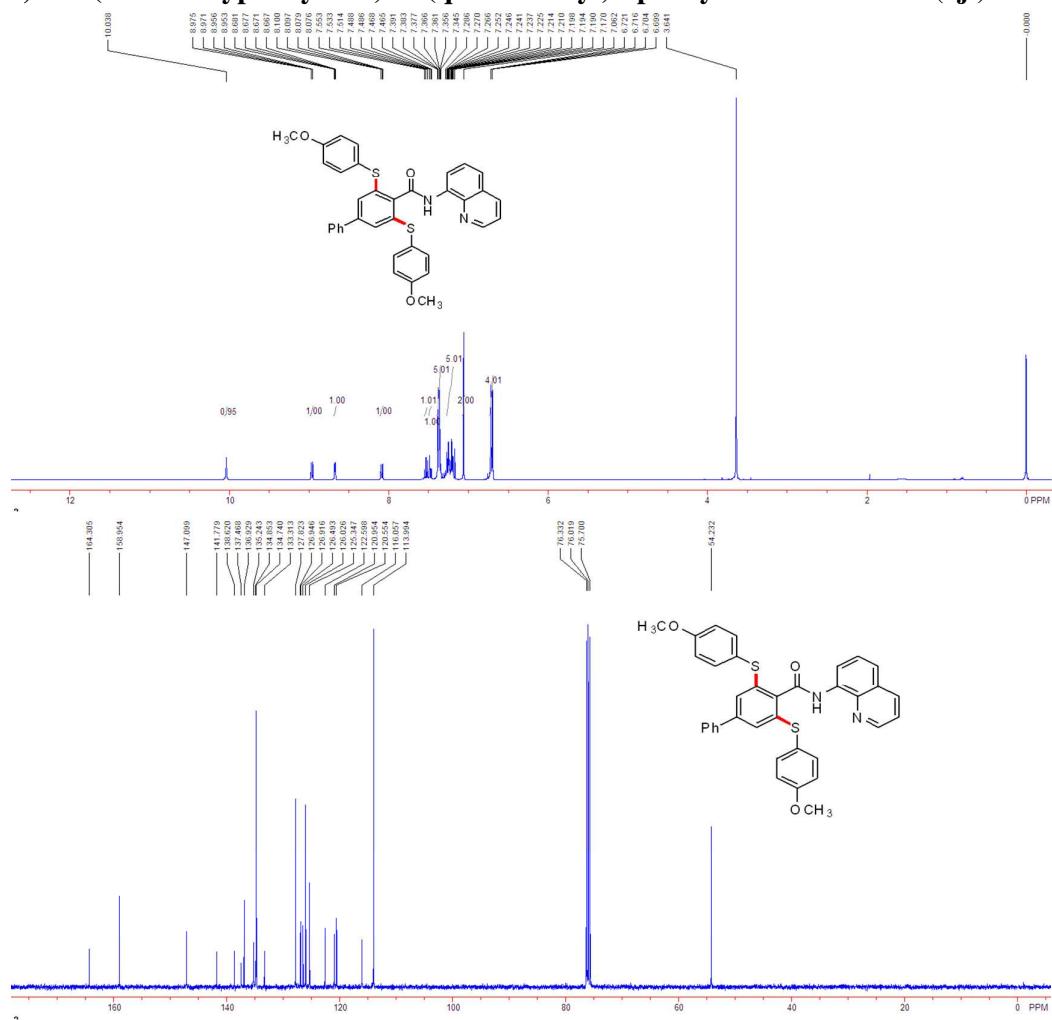
2,6-bis(4-methoxyphenylthio)-4-methyl-N-(quinolin-8-yl)benzamide (4i')



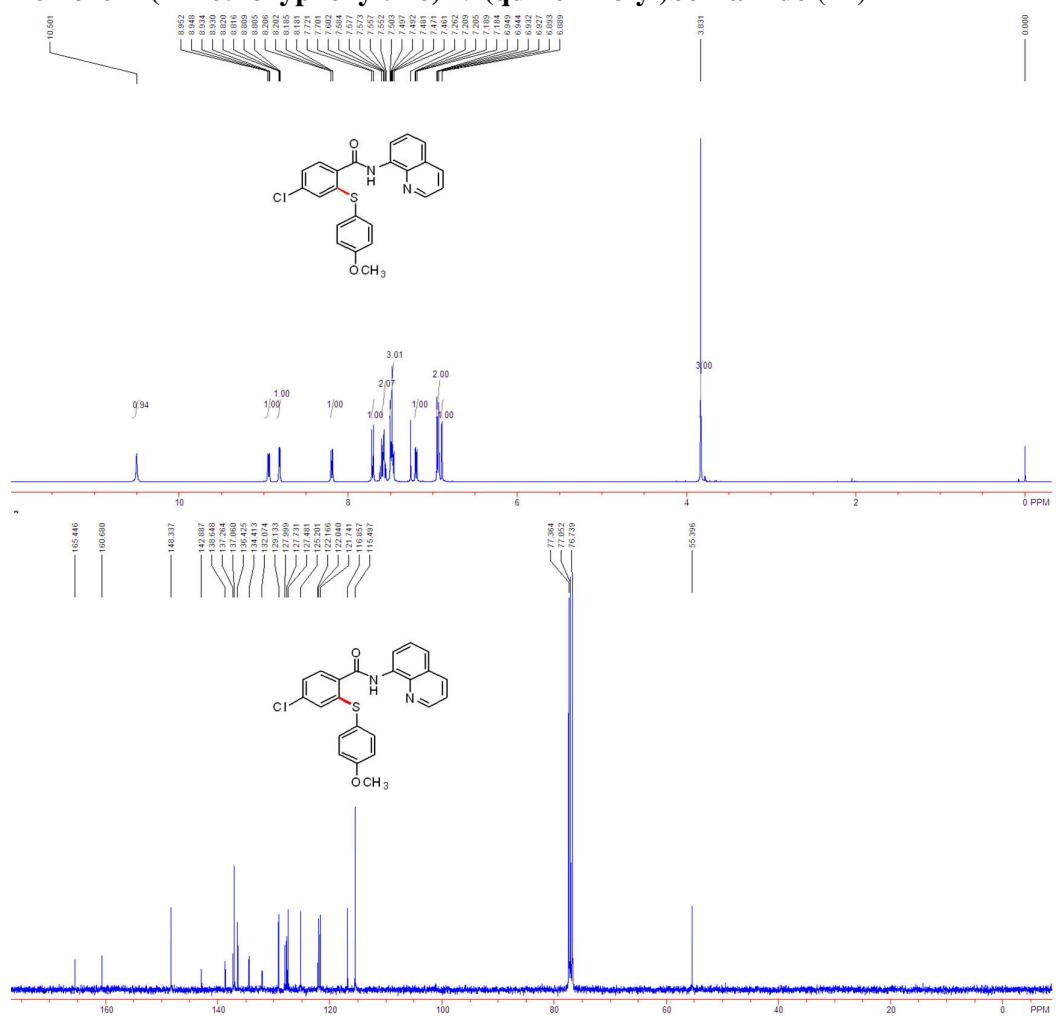
3-(4-methoxyphenylthio)-N-(quinolin-8-yl)biphenyl-4-carboxamide (4j)



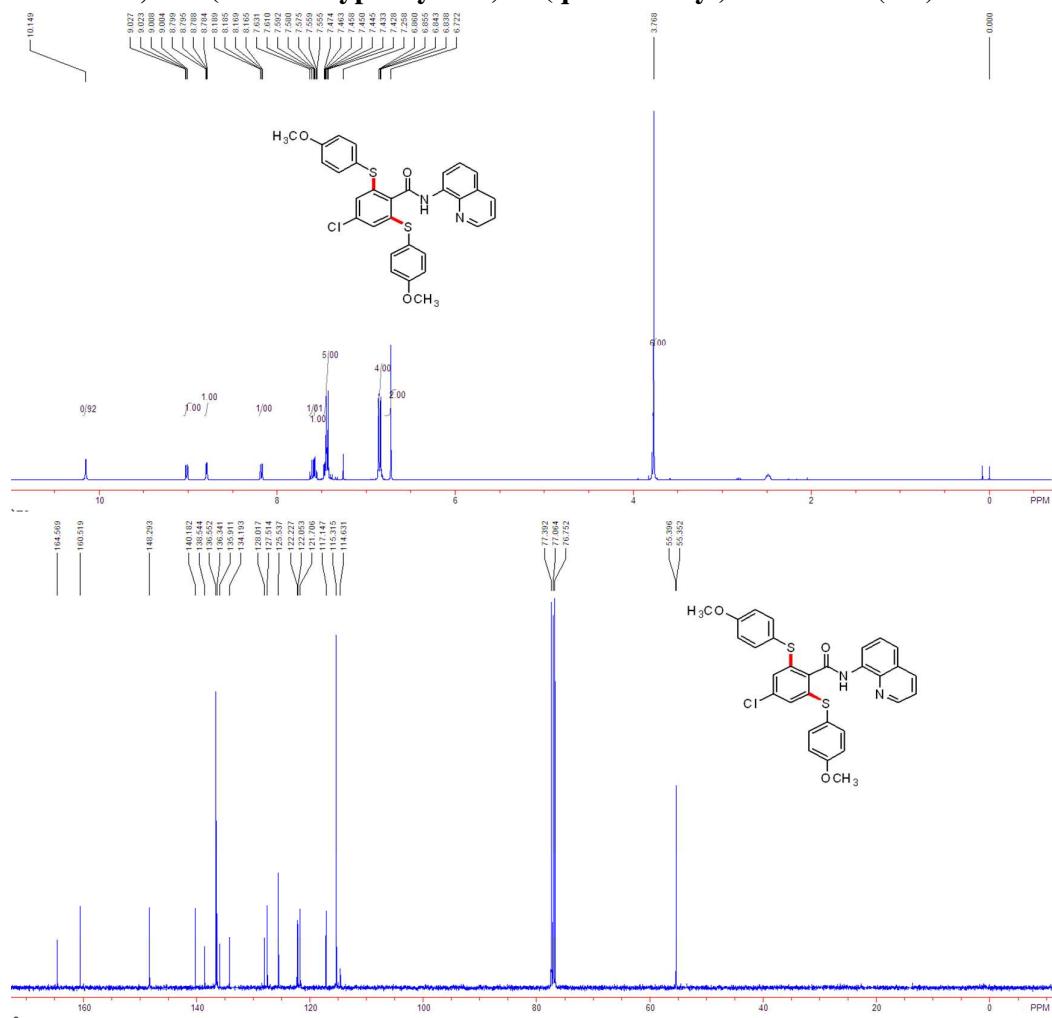
3,5-bis(4-methoxyphenylthio)-N-(quinolin-8-yl)biphenyl-4-carboxamide (4j')



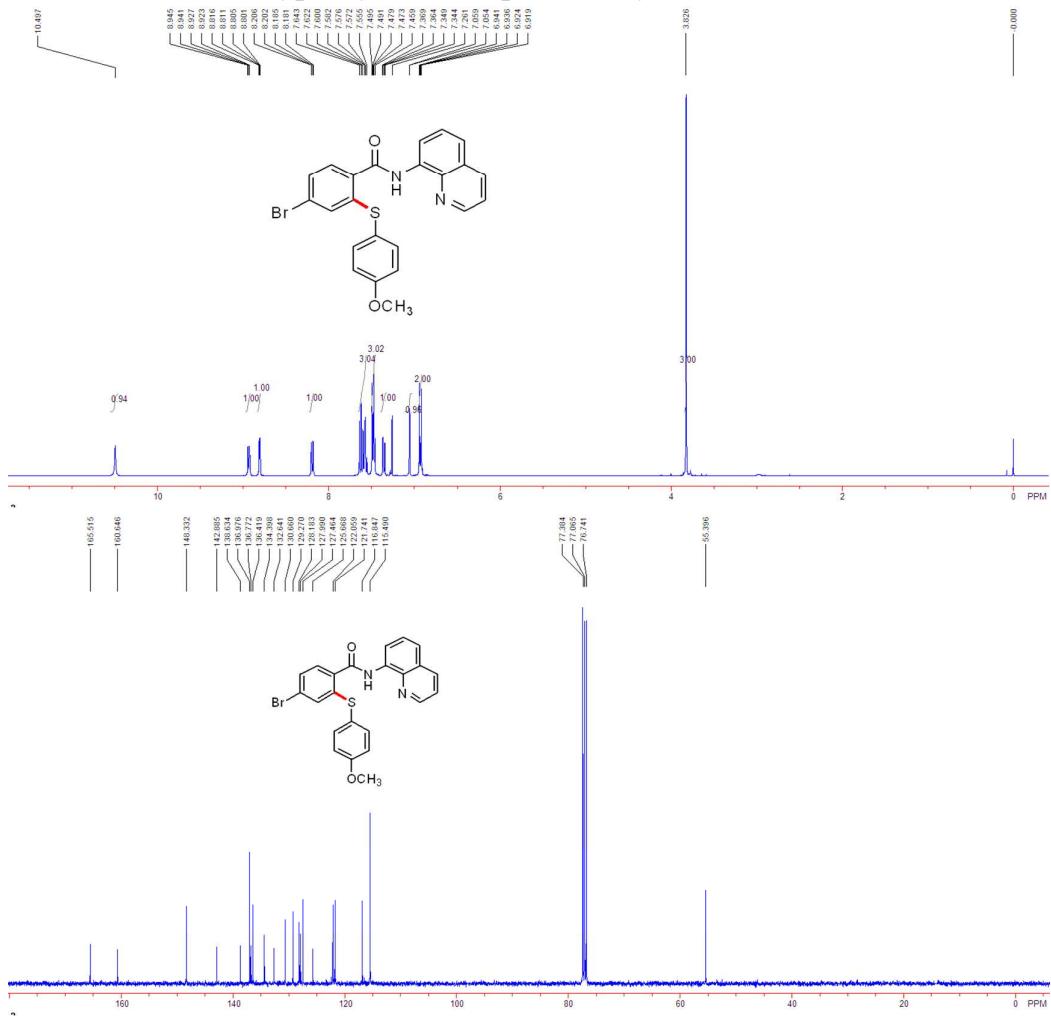
4-chloro-2-(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4k)



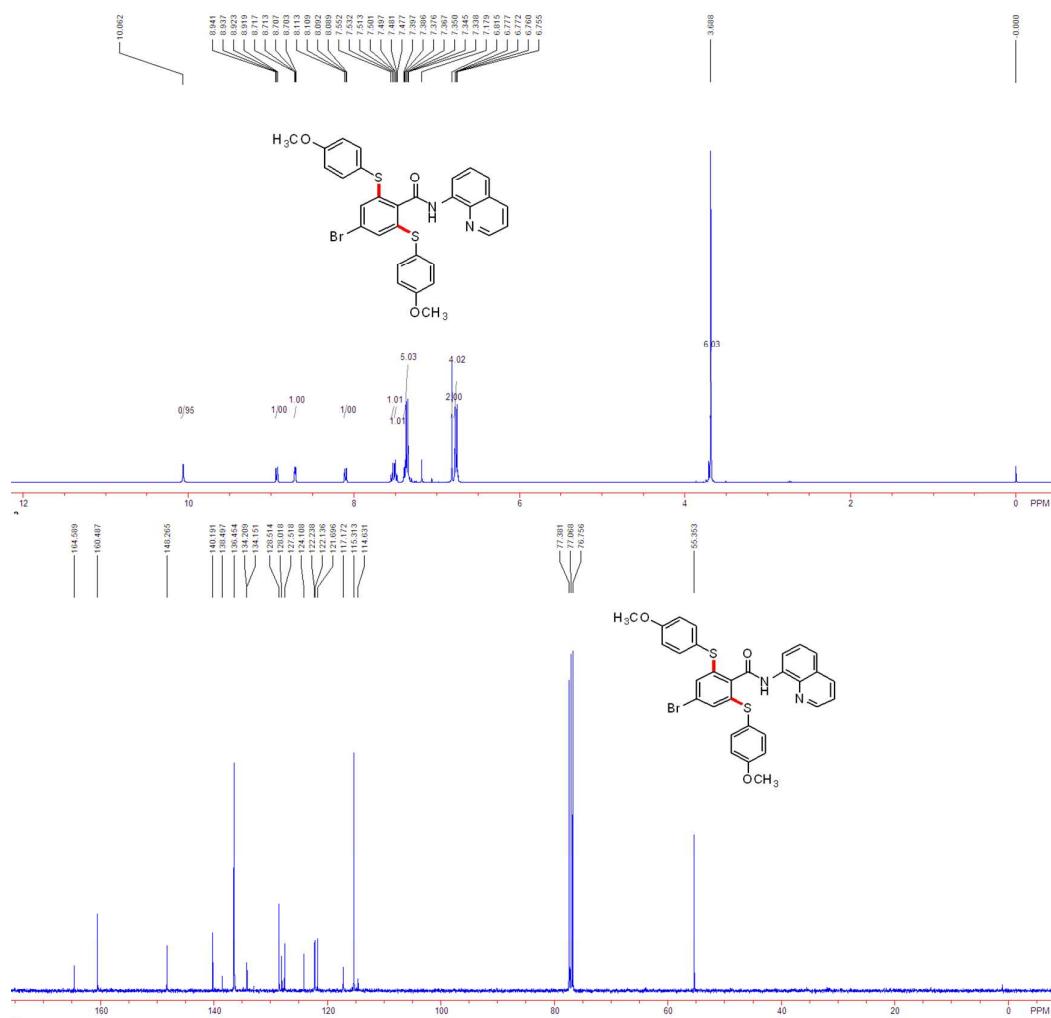
4-chloro-2,6-bis(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4k')



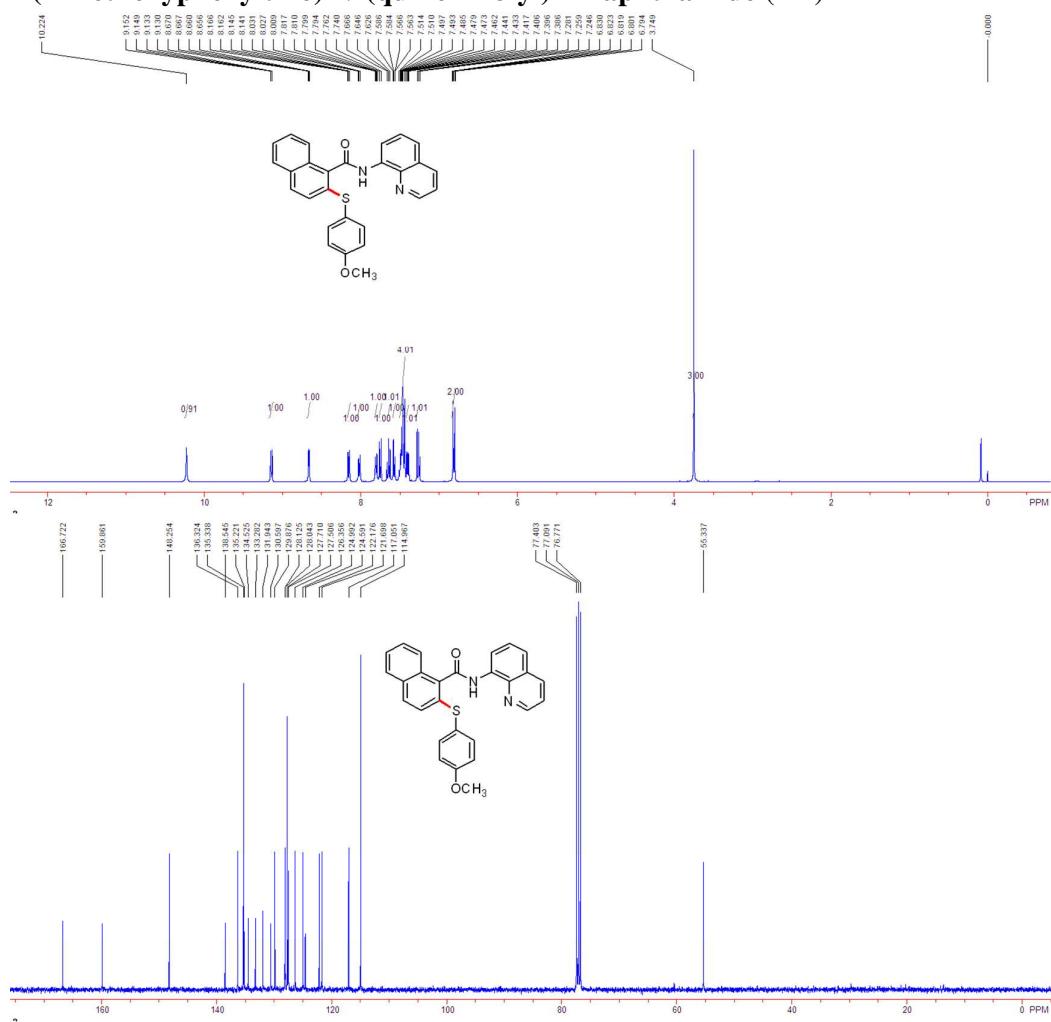
4-bromo-2-(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4l)



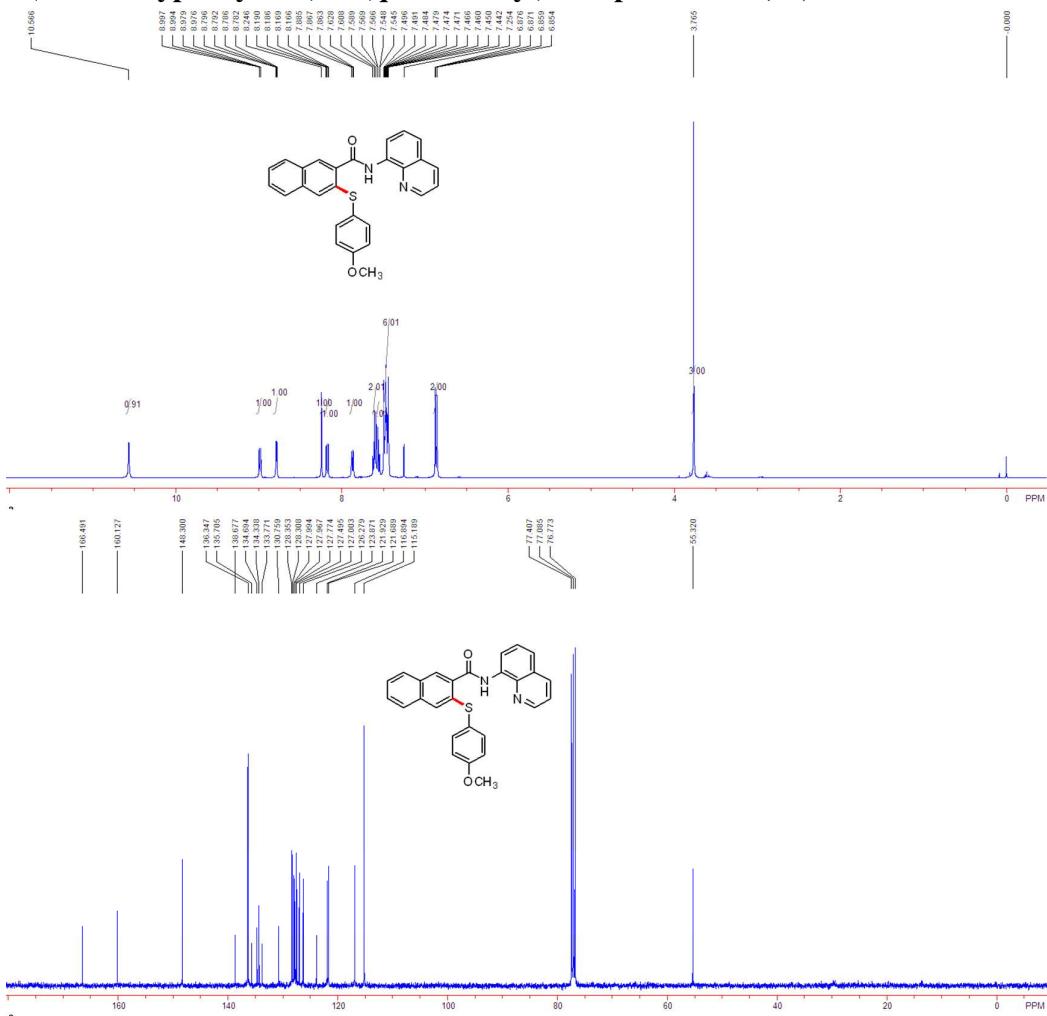
4-bromo-2,6-bis(4-methoxyphenylthio)-N-(quinolin-8-yl)benzamide (4l')



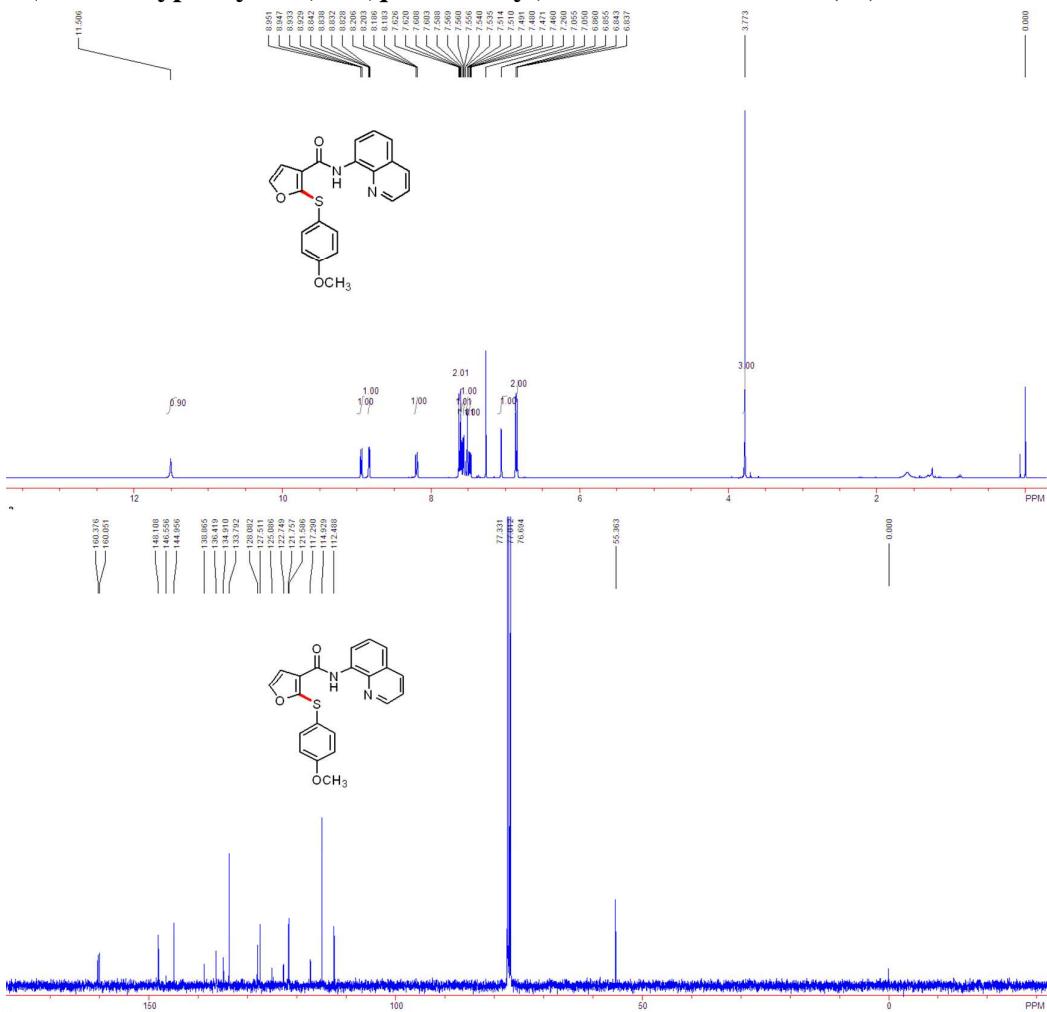
2-(4-methoxyphenylthio)-N-(quinolin-8-yl)-1-naphthamide (4m)



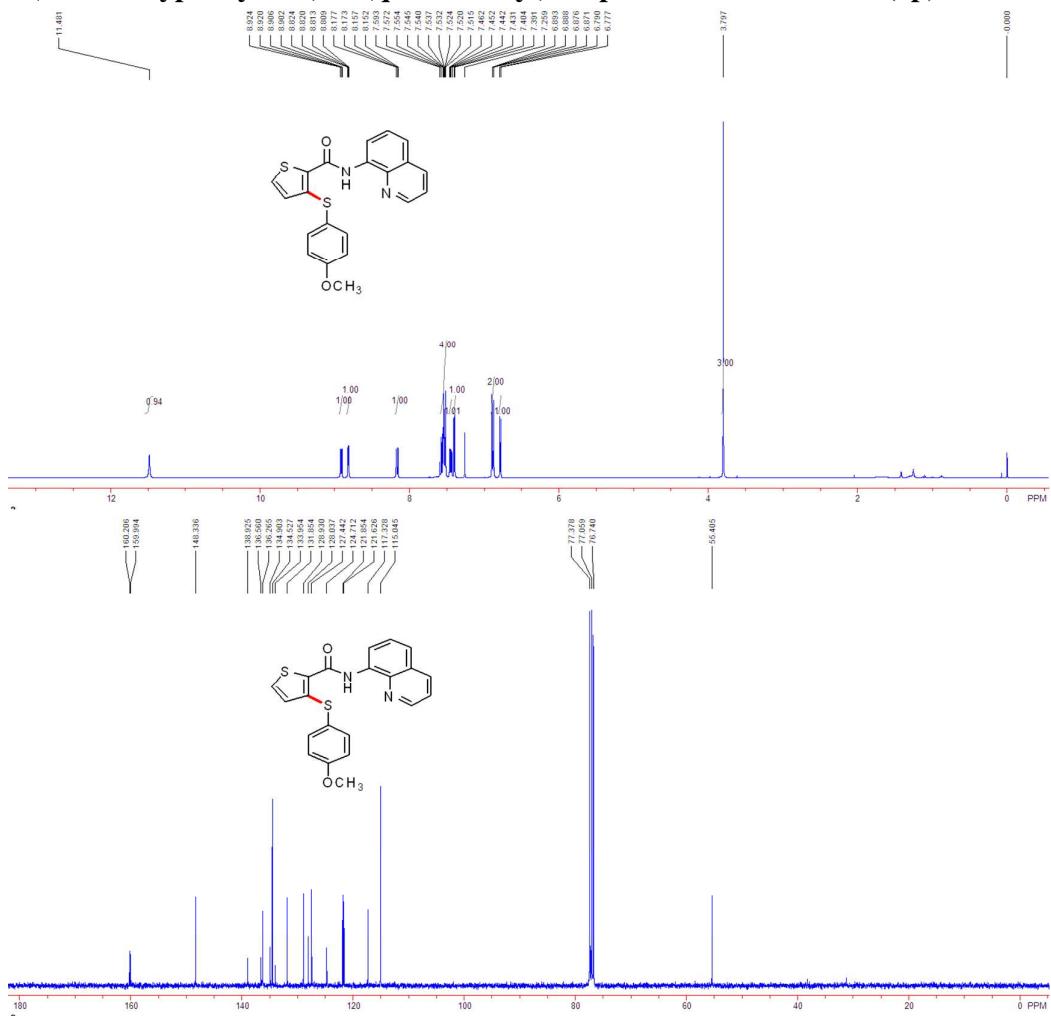
3-(4-methoxyphenylthio)-N-(quinolin-8-yl)-2-naphthamide (4n)



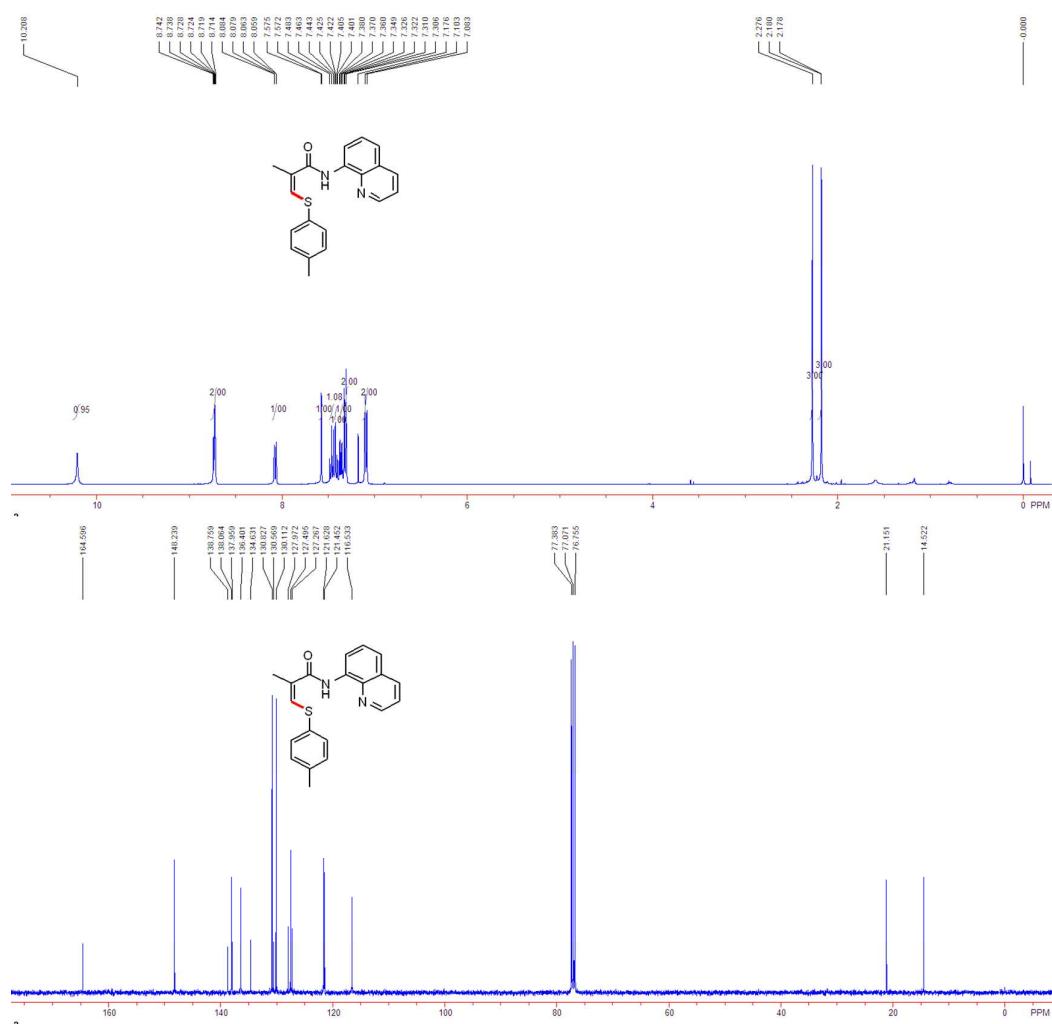
2-(4-methoxyphenylthio)-N-(quinolin-8-yl)furan-3-carboxamide (4o)

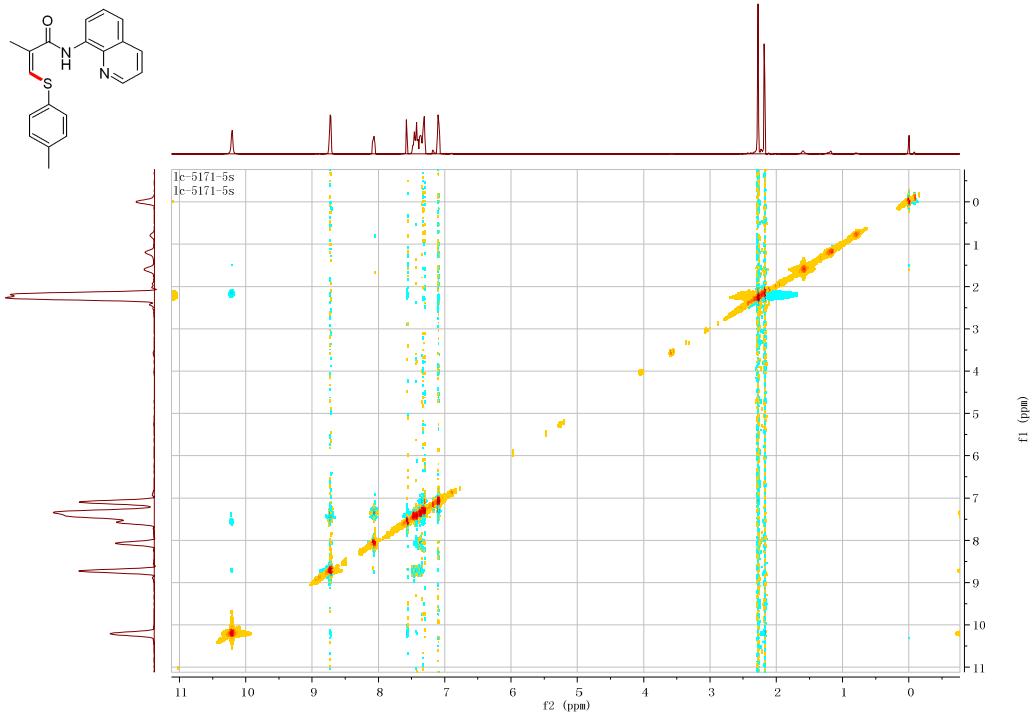


3-(4-methoxyphenylthio)-N-(quinolin-8-yl)thiophene-2-carboxamide (4p)

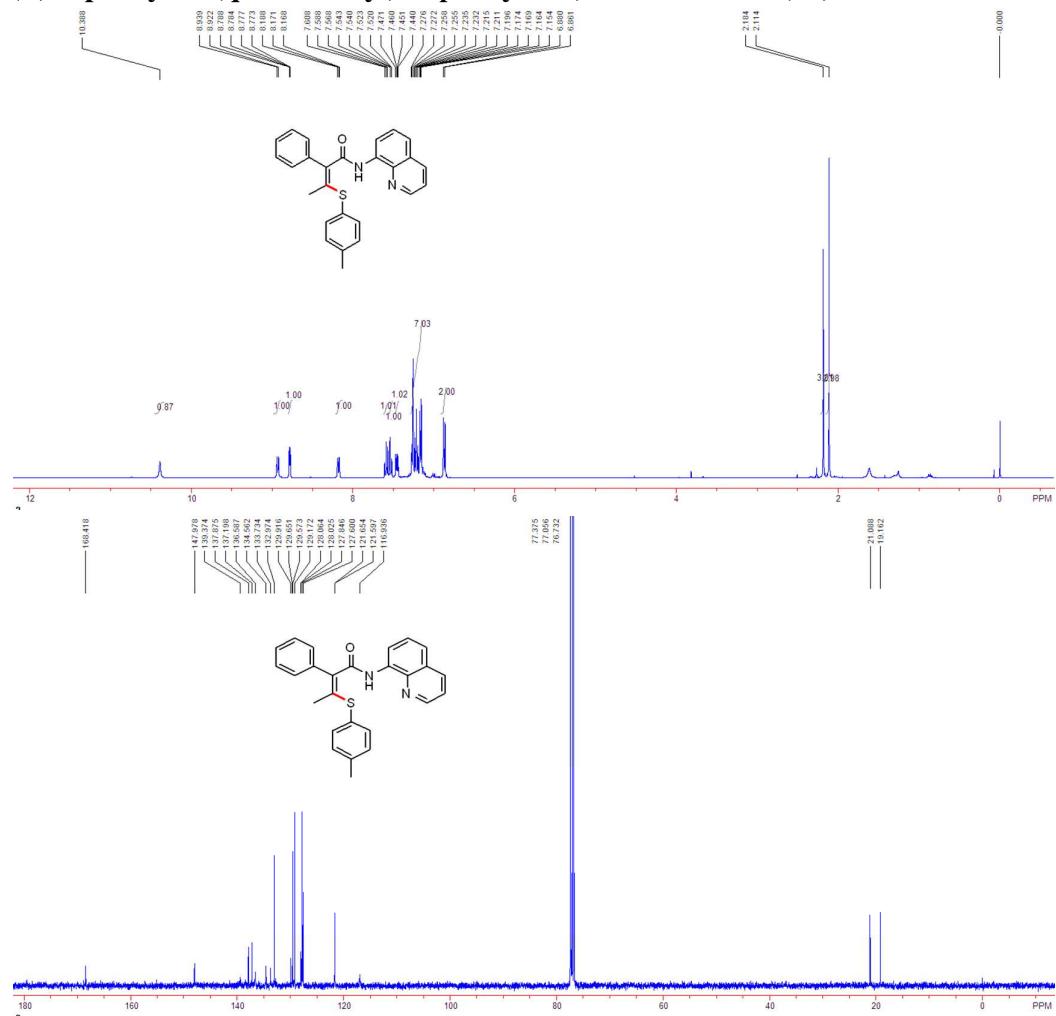


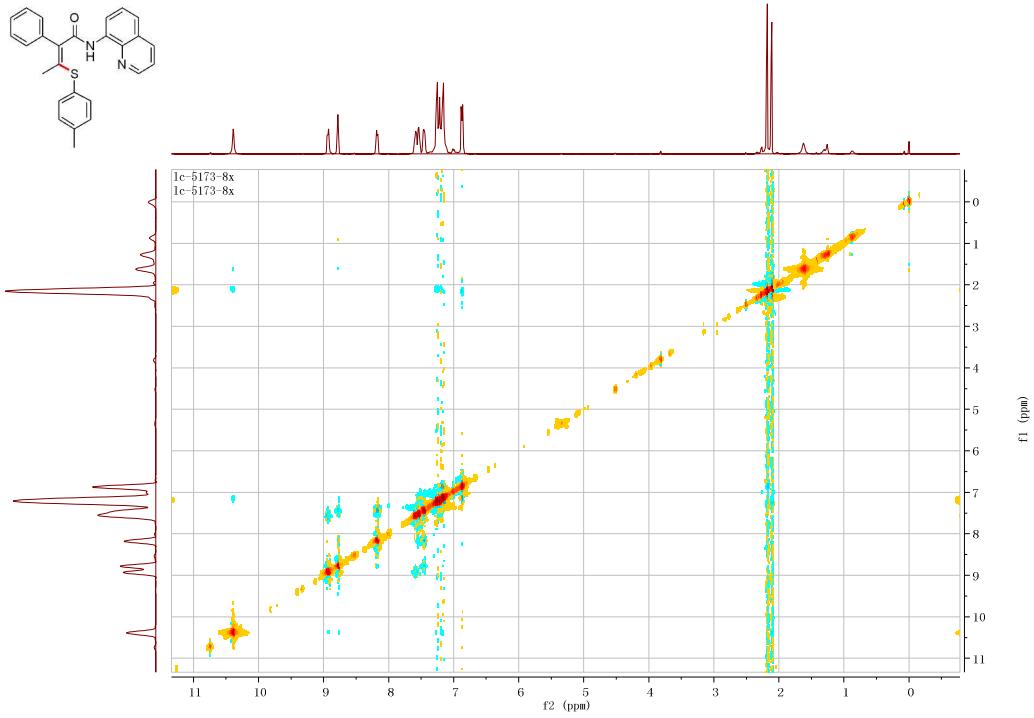
(Z)-2-methyl-N-(quinolin-8-yl)-3-(*p*-tolylthio)acrylamide (6a**)**



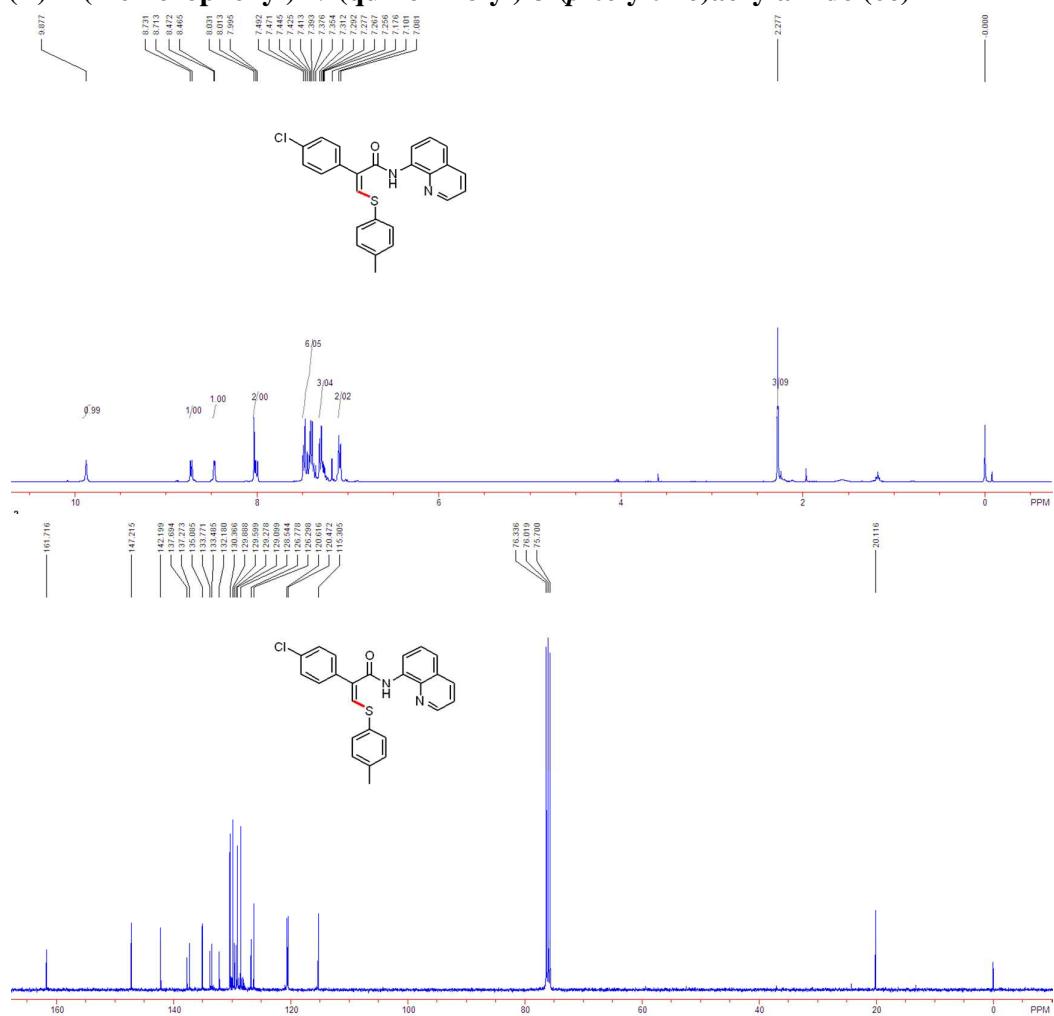


(Z)-2-phenyl-N-(quinolin-8-yl)-3-(*p*-tolylthio)but-2-enamide (6b)

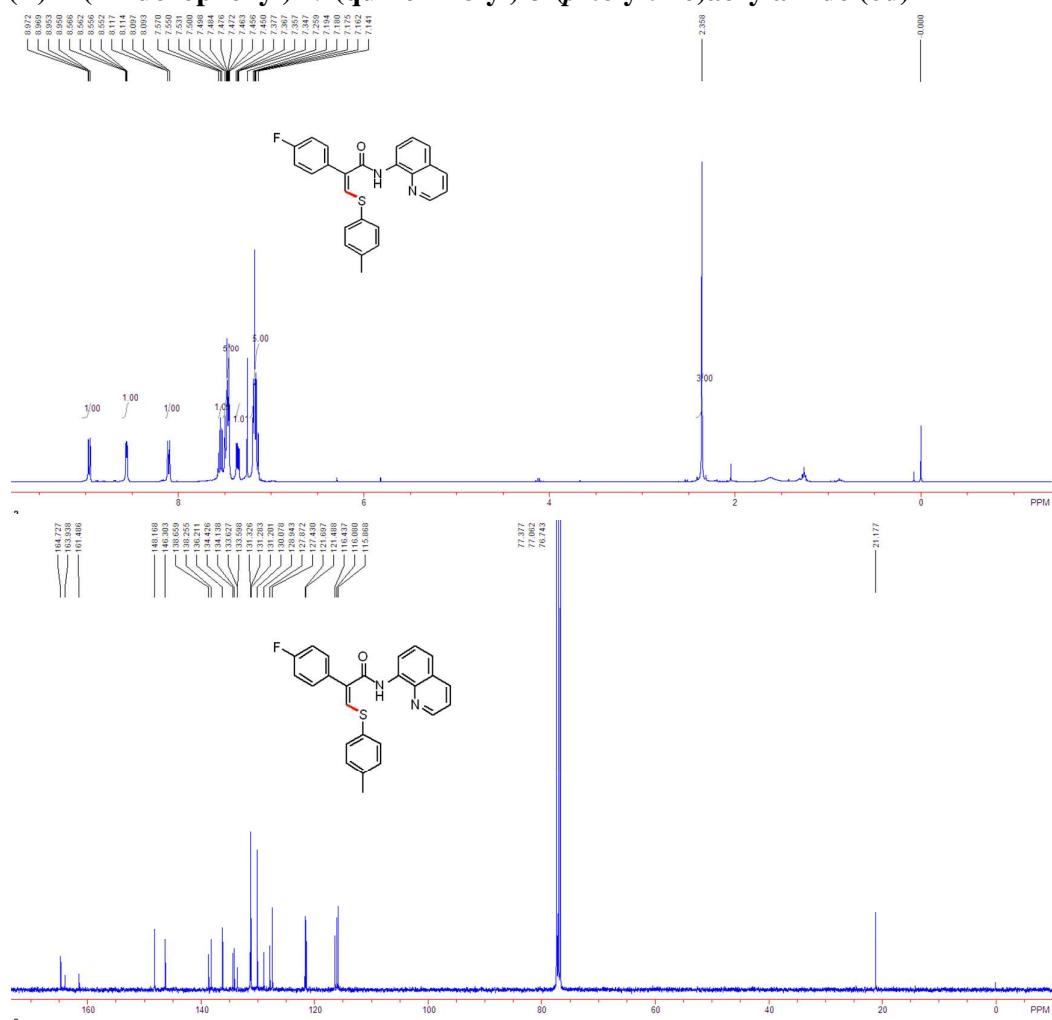




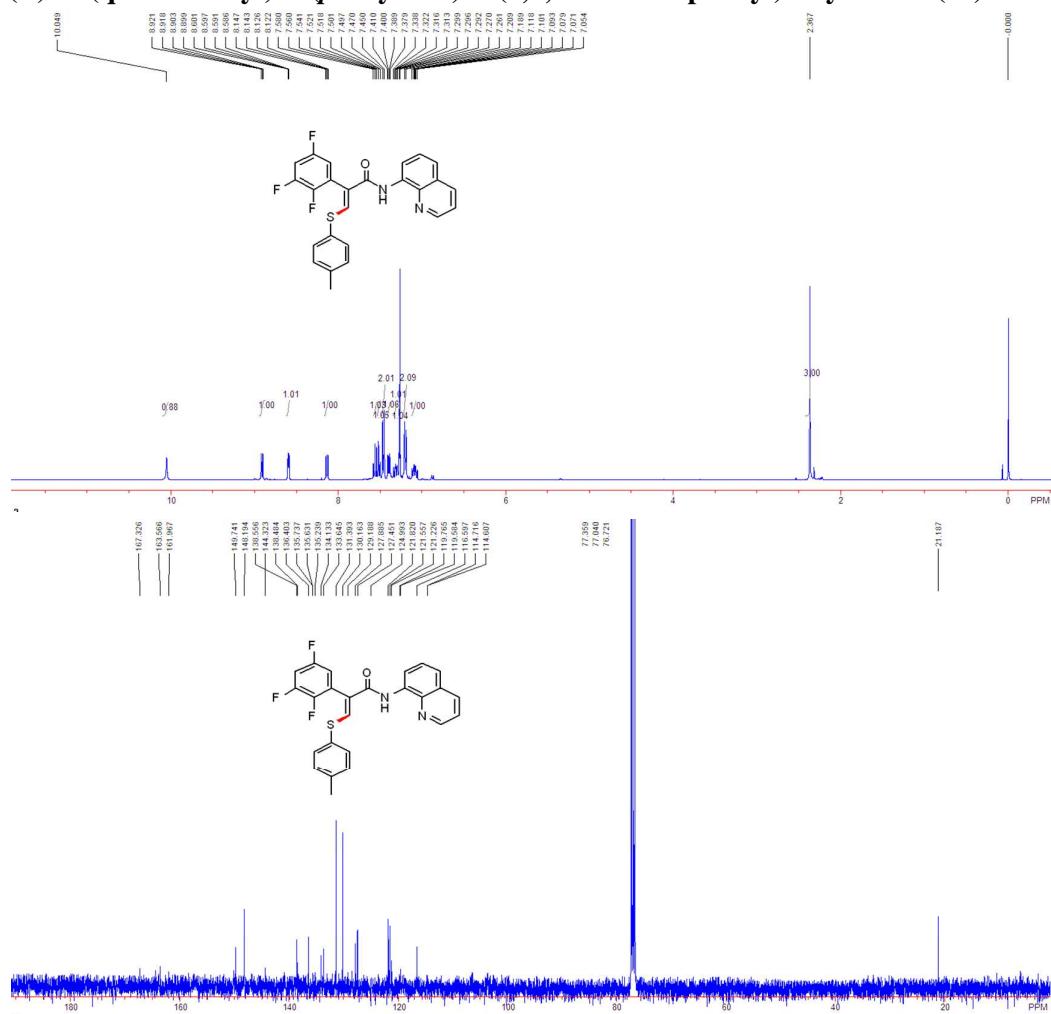
(Z)-2-(4-chlorophenyl)-N-(quinolin-8-yl)-3-(*p*-tolylthio)acrylamide (6c)



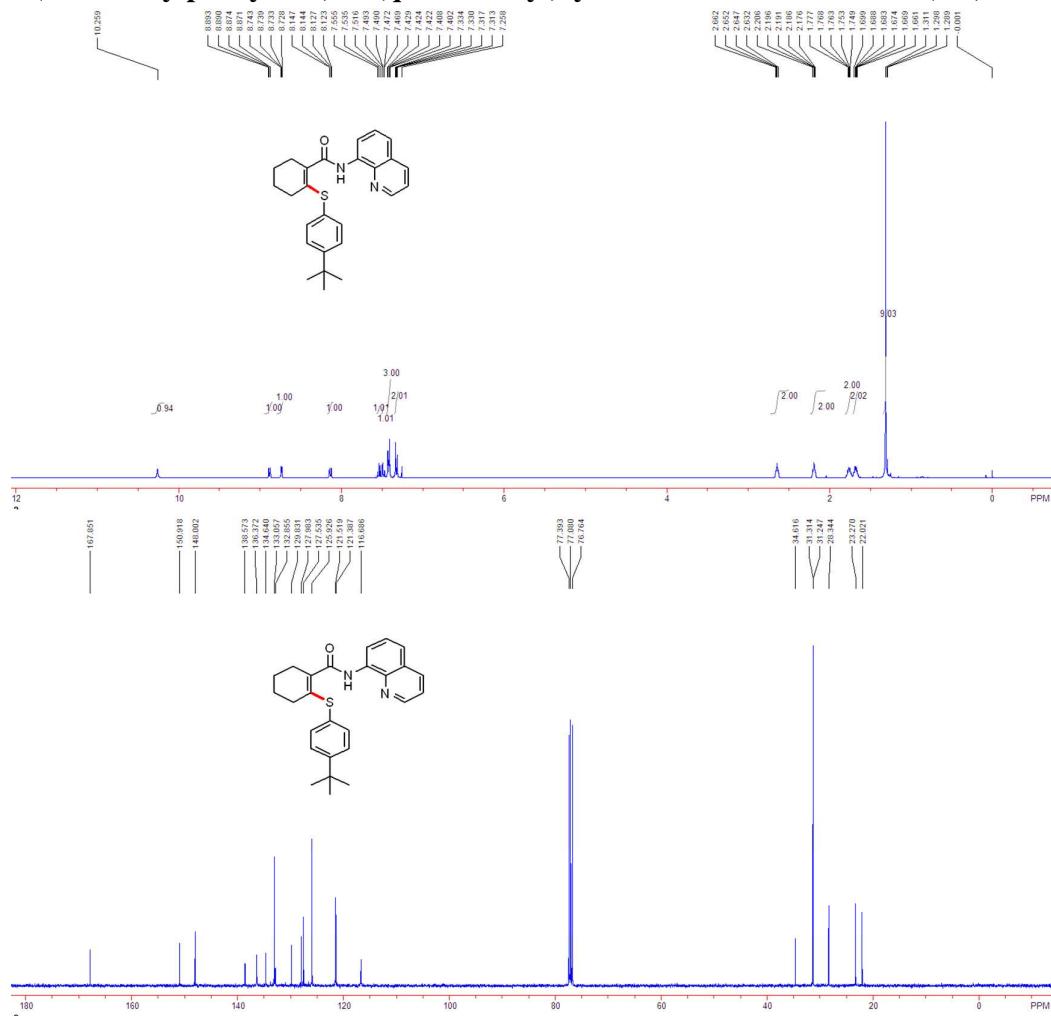
(Z)-2-(4-fluorophenyl)-N-(quinolin-8-yl)-3-(*p*-tolylthio)acrylamide (6d)



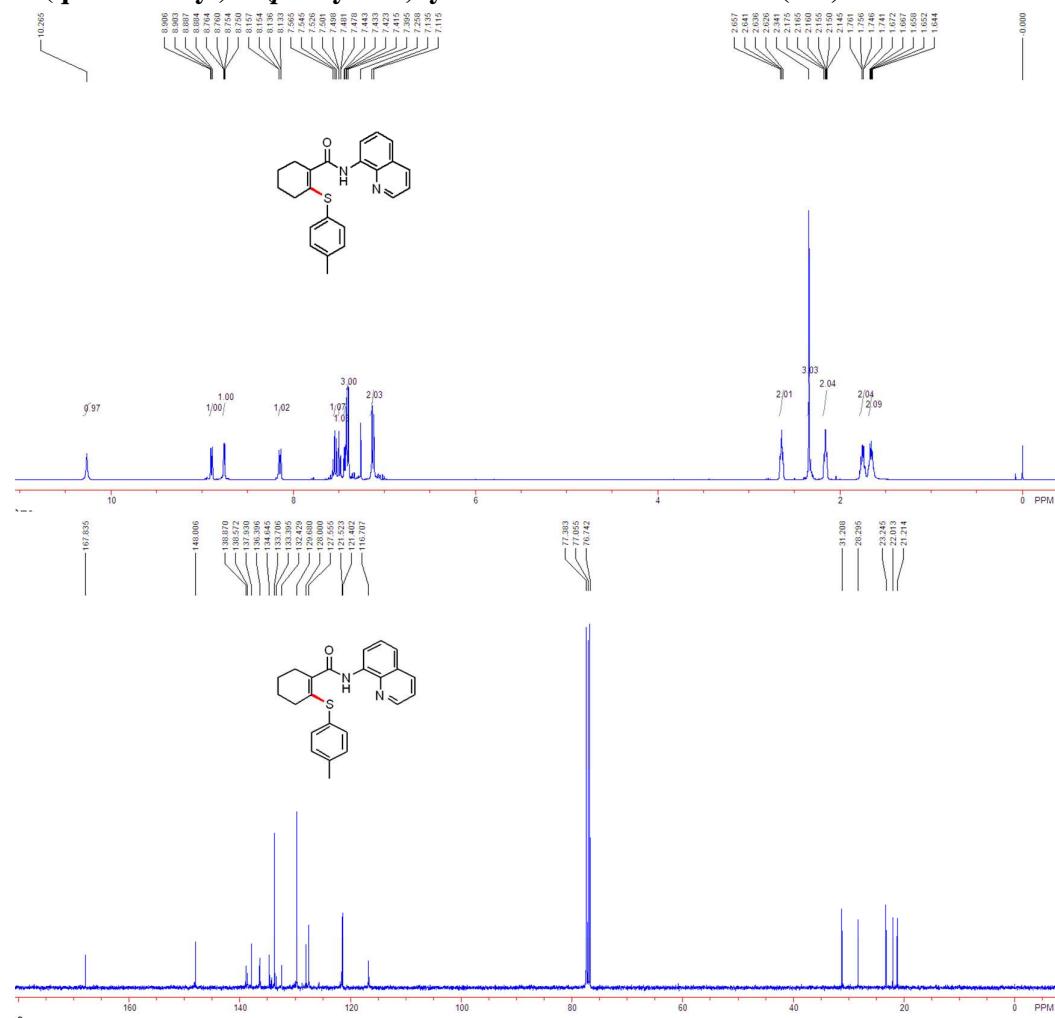
(Z)-N-(quinolin-8-yl)-3-(*p*-tolylthio)-2-(2,3,5-trifluorophenyl)acrylamide (6e)



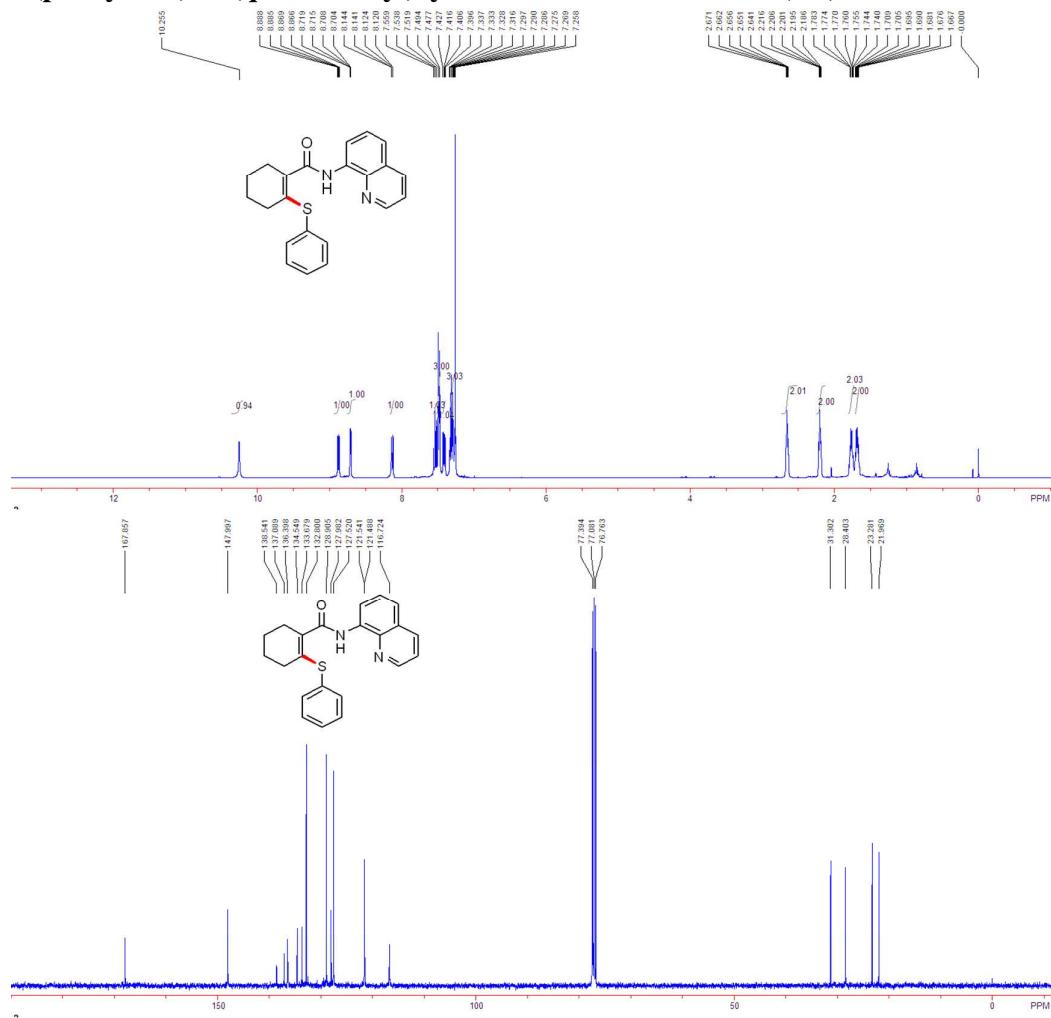
2-(4-*tert*-butylphenylthio)-N-(quinolin-8-yl)cyclohex-1-enecarboxamide (6fa)



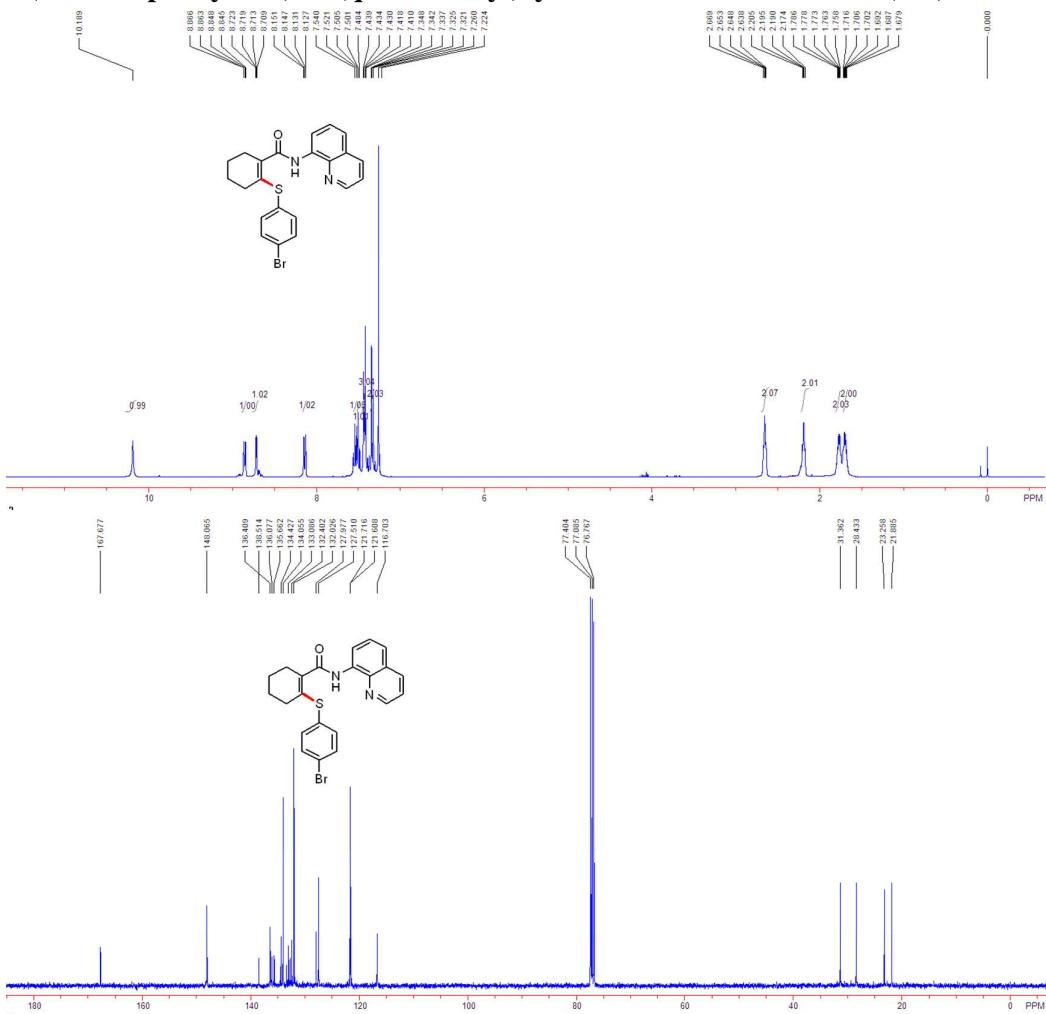
N-(quinolin-8-yl)-2-(*p*-tolylthio)cyclohex-1-enecarboxamide (6fb)



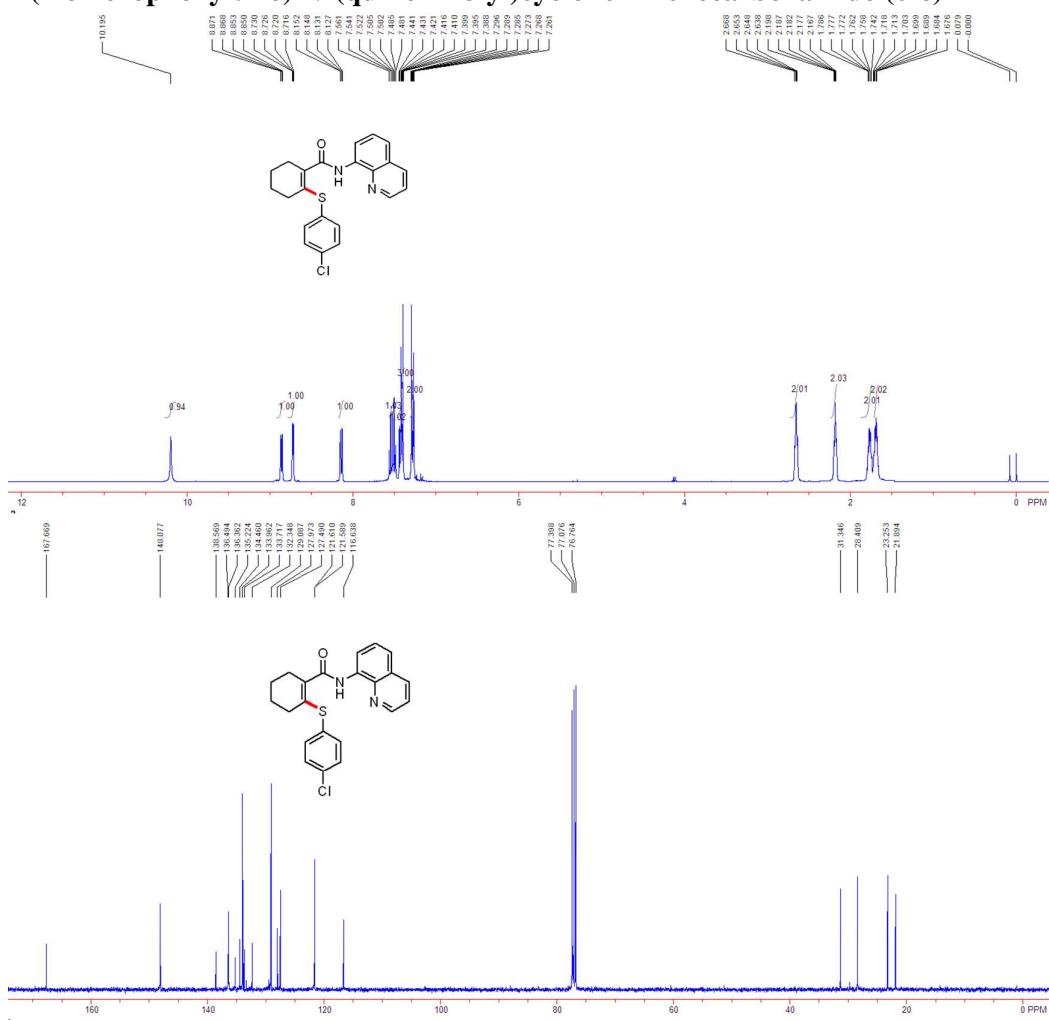
2-(phenylthio)-N-(quinolin-8-yl)cyclohex-1-enecarboxamide (6fc)



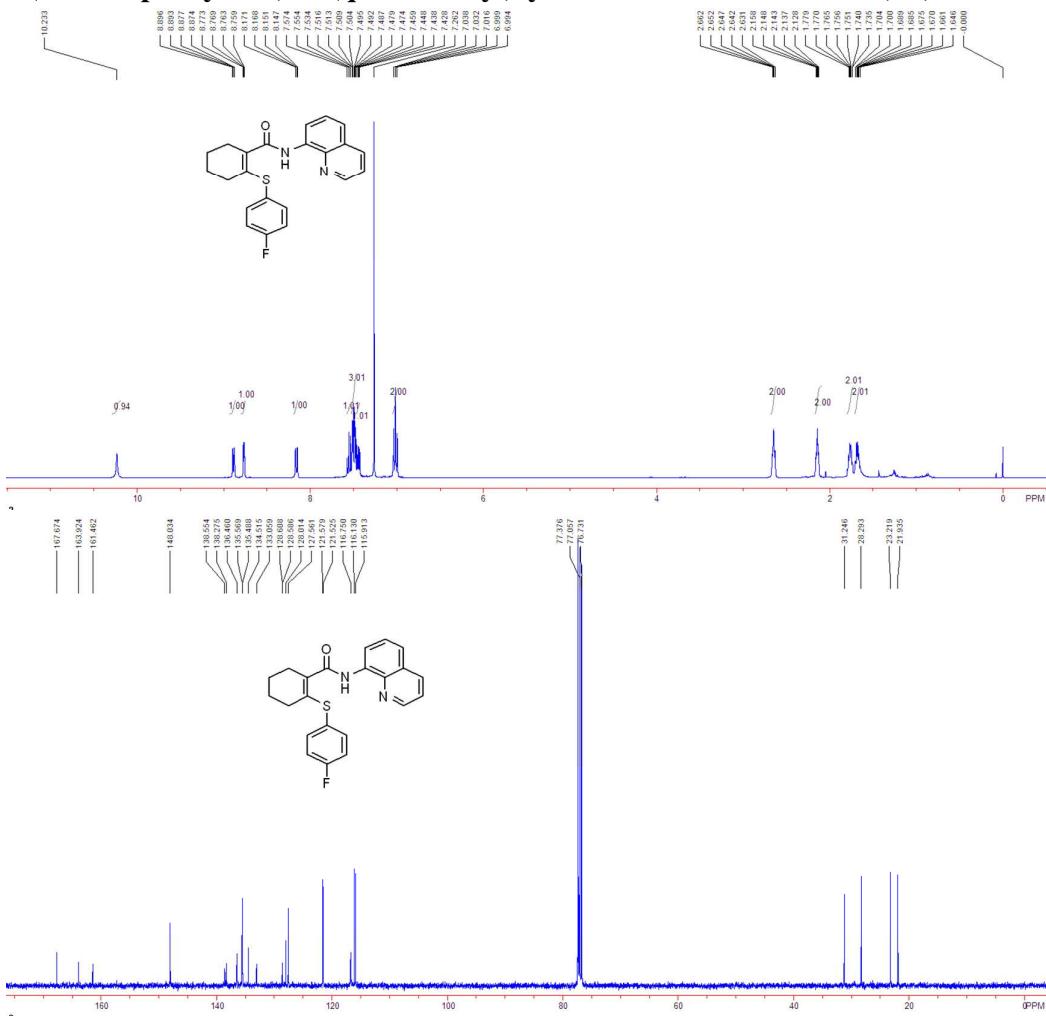
2-(4-bromophenylthio)-N-(quinolin-8-yl)cyclohex-1-enecarboxamide (6fd)



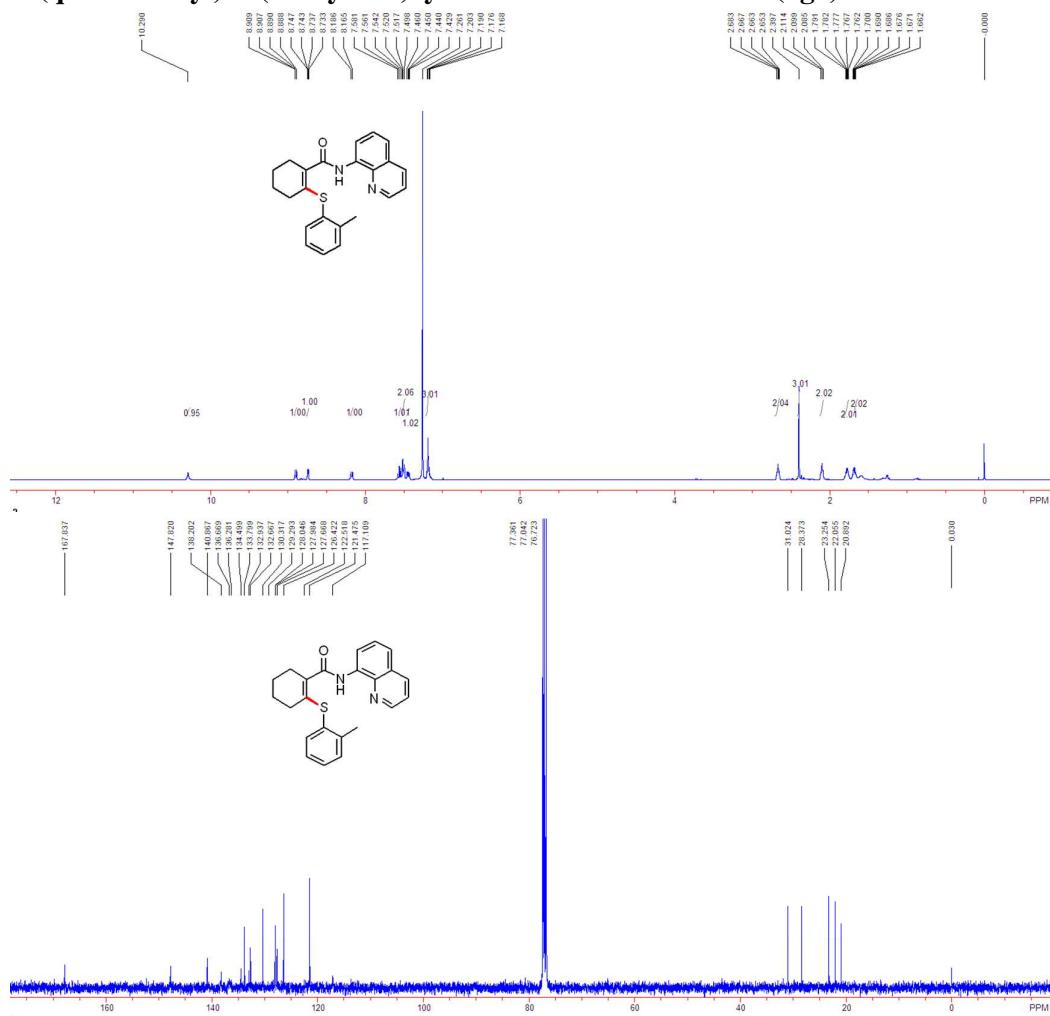
2-(4-chlorophenylthio)-N-(quinolin-8-yl)cyclohex-1-enecarboxamide (6fe)



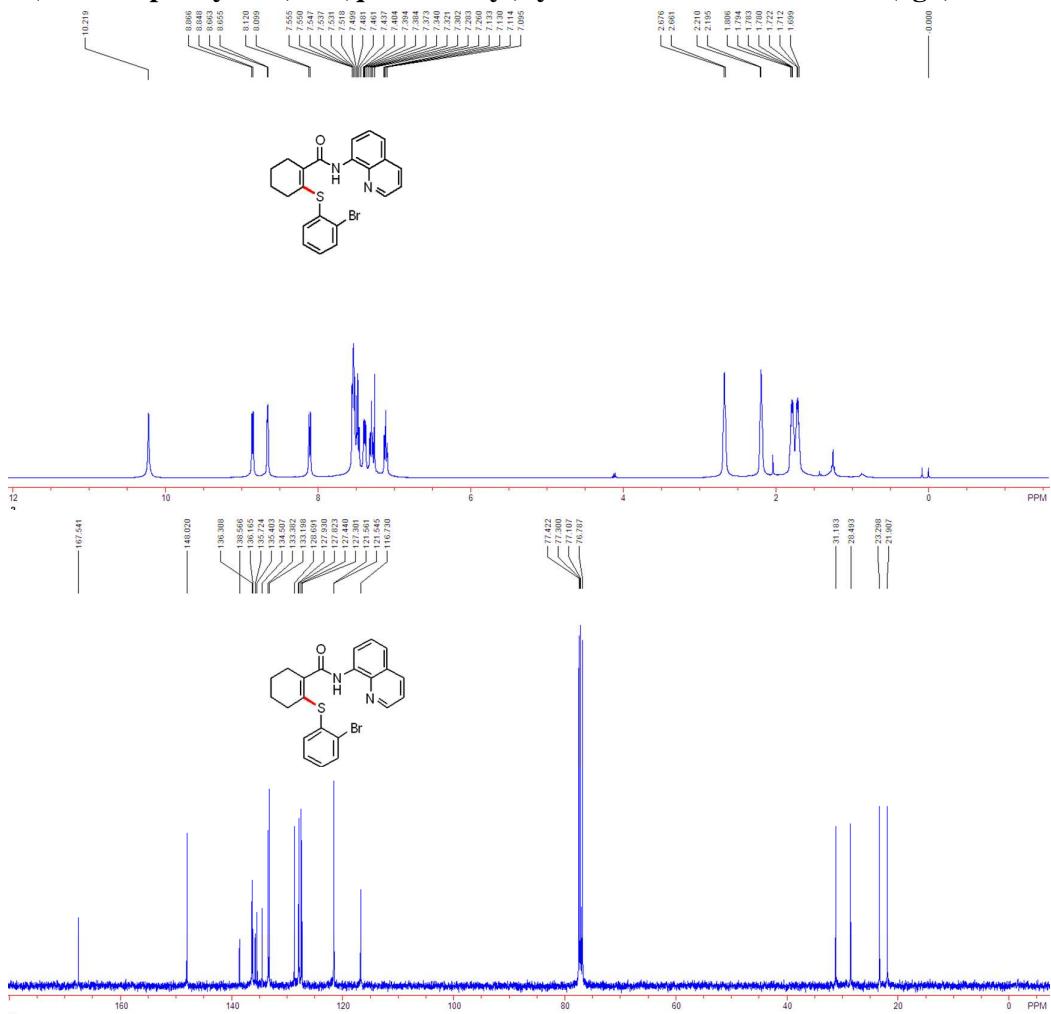
2-(4-fluorophenylthio)-N-(quinolin-8-yl)cyclohex-1-enecarboxamide (6ff)



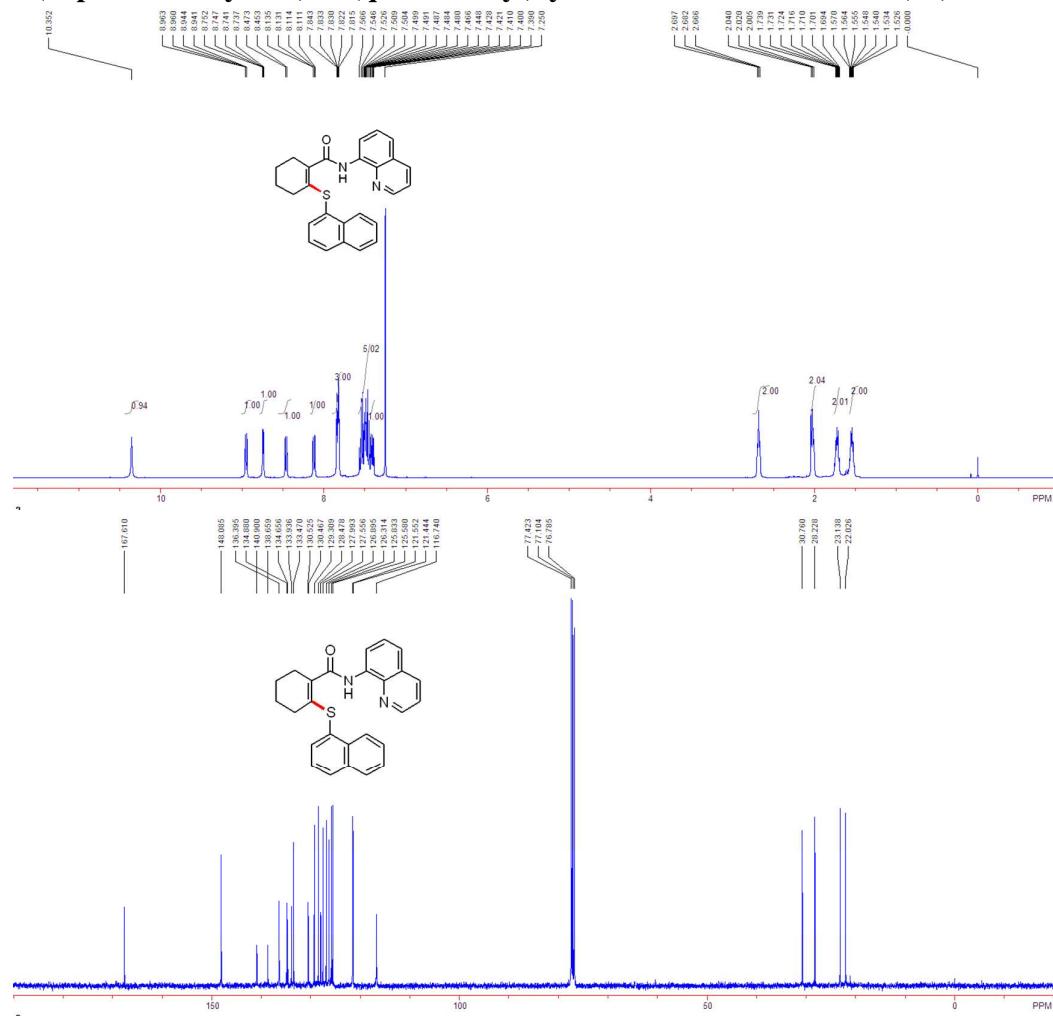
***N*-(quinolin-8-yl)-2-(*o*-tolylthio)cyclohex-1-enecarboxamide (6ga)**



2-(2-bromophenylthio)-N-(quinolin-8-yl)cyclohex-1-enecarboxamide (6gb)



2-(naphthalen-1-ylthio)-N-(quinolin-8-yl)cyclohex-1-enecarboxamide (6h)



2-(2-methylfuran-3-ylthio)-N-(quinolin-8-yl)cyclohex-1-enecarboxamide (6i)

