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Nickel-Catalyzed Direct Thiolation of Unactivated C(sp^3)–H Bonds with Disulfides

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Supporting Information

Table of Contents:

1. General Information

All the materials and solvents were purchased from commercial suppliers, such as Adamas-beta®, Energy Chemical, TCI etc and used without additional purification. NMR spectra were recorded on a Bruke Avance operating for ^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz, using TMS as internal standard. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal (77.16 ppm for ^{13}C NMR). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument or a low-resolution MS instrument using EI ionization.

2. Experimental Section

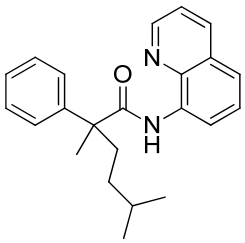
2.1 Preparation of Substrates

Compounds **1a-1b, 1d, 1i-1k, 1m-1o** were known compounds.[1] Compounds **1c, 1e, 1f, 1h, 1l** were prepared according to the following procedures.

General Procedure for the Preparation of Starting Materials 1

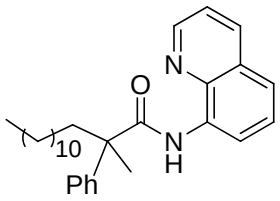
To a solution of LDA (10 mL, 2 M in THF) in THF (10 mL) was added the acid (10 mmol) dropwise at 0 ºC, then the reaction mixture was refluxed for 2 h. After cooling to room temperature, the according alkyl iodide (30 mmol) was added dropwise, then it was refluxed overnight. Then the reaction solution was diluted with water and washed with ethyl acetate, the aqueous phase was then acidified with 2 M HCl to pH ≈ 2 and extracted with ethyl acetate three times, the combined organic phase was then dried with anhydrous magnesium sulfate. After concentrating, it was dissolved in CH_2Cl_2 (ca. 30 mL), then DMF (0.2 mL) was added following by $(COCl)_2$ (20 mmol) dropwise at 0 ºC，the reaction mixture was then stirred at room temperature for another 5 h . After that the solution was evaporated in vacuum, then anhydrous CH_2Cl_2 (40 mL) was added following by adding the CH_2Cl_2 solution of

8-aminoquinoline (1.73 g, 12 mmol), Et_3N (1.38 mL, 10 mmol) and DMAP (6.1 mg, 0.05 mmol) dropwise in ice bath. Then it was stirred at room temperature overnight, washed with water and dried with anhydrous magnesium sulfate. After concentrating, the residue was purified by flash column chromatography to afford corresponding 8-aminoquinoline amide **1**.



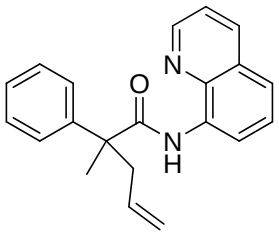
2,5-dimethyl-2-phenyl-*N*-(quinolin-8-yl)hexanamide 1c

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (br, 1H), 8.76 (d, *J* = 7.6 Hz, 1H), 8.60 (d, *J* = 2.8 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.53 - 7.49 (m, 3H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.41 - 7.34 (m, 3H), 7.29 (d, *J* = 7.2 Hz, 1H), 2.25 (td, *J* = 13.2, 4.4 Hz, 1H), 2.15 (td, *J* = 12.4, 4.4 Hz,, 1H), 1.74 (s, 3H), 1.62 - 1.60 (m, 1H), 1.55 – 1.52 (m, 1H), 1.15 – 1.06 (m, 1H), 0.88 (dd, *J* = 6.4, 4.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.57, 148.16, 144.26, 138.77, 136.13, 134.83, 128.80, 127.92, 127.41, 126.96, 126.84, 121.50, 121.27, 116.06, 51.94, 37.03, 33.55, 28.73, 23.68, 22.70, 22.68.



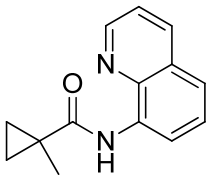
2-methyl-2-phenyl-*N*-(quinolin-8-yl)tetradecanamide 1e

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (br, 1H), 8.76 (d, *J* = 7.6 Hz, 1H), 8.60 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.08 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.53 – 7.49 (m, 3H), 7.44 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.40 – 7.34 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 1H), 2.27 – 2.20 (m, 1H), 2.16 – 2.09 (m, 1H), 1.74 (s, 3H), 1.32 – 1.25 (m, 20H), 0.87 (t, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.51, 148.14, 144.33, 138.76, 136.11, 134.83, 128.78, 127.91, 127.41, 126.94, 126.80, 121.47, 121.24, 116.06, 52.04, 39.23, 32.01, 30.34, 29.73, 29.54, 29.44, 24.65, 23.75, 22.79, 14.23.



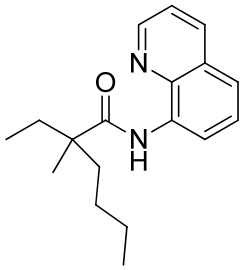
2-methyl-2-phenyl-*N*-(quinolin-8-yl)pent-4-enamide 1f

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (br, 1H), 8.76 (d, *J* = 7.2 Hz, 1H), 8.60 (d, *J* = 3.6 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.53 - 7.49 (m, 3H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.41 - 7.34 (m, 3H), 7.30 (t, *J* = 7.2 Hz, 1H), 5.72 - 5.62 (m, 1H), 5.13 (d, *J* = 16.8 Hz, 1H), 5.05 (d, *J* = 10.0 Hz, 1H), 3.01 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.91 (dd, *J* = 14.0, 6.4 Hz, 1H), 1.76 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.94, 148.20, 143.43, 138.73, 136.15, 134.73, 134.26, 128.86, 127.91, 127.39, 127.18, 126.89, 121.52, 121.38, 118.60, 116.10, 51.61, 43.85, 23.51.



1-methyl-*N*-(quinolin-8-yl)cyclopropanecarboxamide 1h

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (br, 1H), 8.83 (d, *J* = 4.0 Hz, 1H), 8.75 (d, *J* = 7.2 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.55 - 7.44 (m, 3H), 1.65 (s, 3H), 1.39 (dd, *J* = 5.6, 4.0 Hz, 2H), 0.75 (q, *J* = 3.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.77, 148.28, 138.71, 136.34, 134.78, 128.00, 127.49, 121.60, 121.26, 116.20, 20.70, 19.89, 16.86.

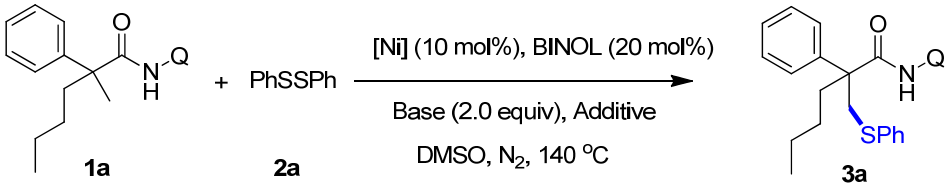


2-ethyl-2-methyl-*N*-(quinolin-8-yl)hexanamide 1l

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (br, 1H), 8.82 (d, *J* = 6.0 Hz, 2H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.55 – 7.43 (m, 3H), 1.94 – 1.80 (m, 2H), 1.68 - 1.63 (m, 1H), 1.58 - 1.52 (m, 1H), 1.37 – 1.31 (m, 7H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.89,

148.07, 138.64, 136.08, 134.54, 127.79, 127.25, 121.38, 121.03, 115.99, 47.46, 39.66, 32.84, 26.70, 23.22, 20.61, 13.90, 8.90.

2.3 Optimization of Reaction Conditions[a]

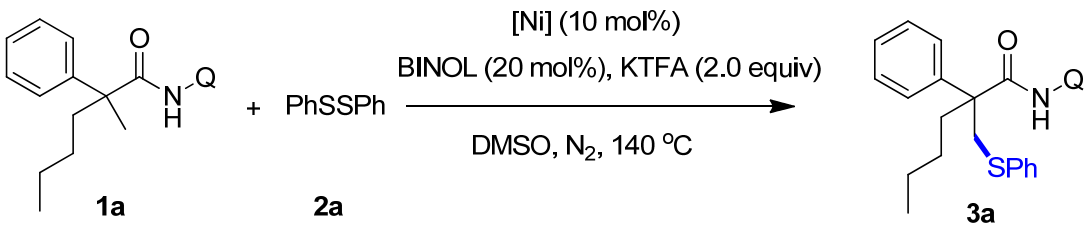


Entry	[Ni]	Base	Additive (equiv)	Yield[b]
1	$NiCl_2·6H_2O$	KTFA	---	24%
2	$Ni(acac)_2$	KTFA	---	19%
3	$Ni(OTf)_2$	KTFA	---	20%
4	NiI_2	KTFA	---	24%
5	$NiCl_2$	KTFA	---	23%
6	(dppp) $NiCl_2$	KTFA	---	27%
7	(dppp) $NiCl_2$	KTFA	$Cu(OAc)_2$ (2.0)	trace
8	(dppp) $NiCl_2$	KTFA	CuF_2 (2.0)	N.R
9	(dppp) $NiCl_2$	KTFA	CuO (2.0)	42%
10	(dppp) $NiCl_2$	KTFA	$Cu(OH)_2$ (2.0)	40%
11	(dppp) $NiCl_2$	KTFA	$Cu(OH)_2CO_3$ (2.0)	45%
12	(dppp) $NiCl_2$	KTFA	Ag_2O (2.0)	37%
13	(dppp) $NiCl_2$	KTFA	Ag_2CO_3 (2.0)	20%
14	(dppp) $NiCl_2$	KTFA	Ag_2O (1.0)	56% (53%[c])
15	(dppp) $NiCl_2$	Na_2CO_3	Ag_2O (1.0)	39%
16	(dppp) $NiCl_2$	$NaHCO_3$	Ag_2O (1.0)	23%
17	(dppp) $NiCl_2$	K_2CO_3	Ag_2O (1.0)	20%
18	(dppp) $NiCl_2$	NaOAc	Ag_2O (1.0)	17%
19	(dppp) $NiCl_2$	NaTFA	Ag_2O (1.0)	44%
20	(dppp) $NiCl_2$	LiTFA	Ag_2O (1.0)	35%
21	---	KTFA	Ag_2O (1.0)	N.R

[a] Reactions were carried out by using **1a** (0.1 mmol), **2a** (0.2 mmol), DMSO (1 mL), 140 °C, N_2, 12 h. [b] ^1H NMR yield using CH_2Br_2 as the internal standard. [c] Isolated yield in parenthesis.

Additional condition screening

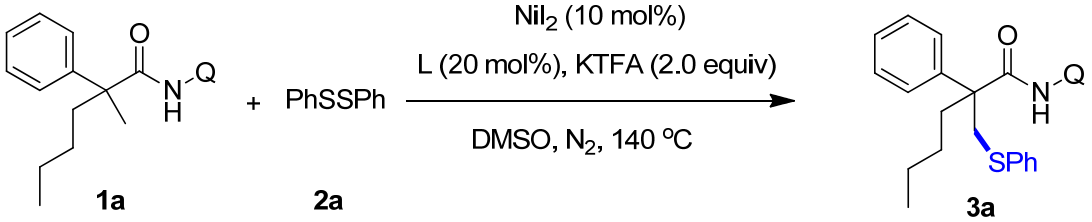
Table S1. Screening of Catalyst[a]



Entry	[Ni] (10 mol%)	Yield[b]
1	$NiCl_2 \cdot 6H_2O$	24%
2	$Ni(acac)_2$	19%
3	$Ni(OTf)_2$	20%
4	NiI_2	24%
5	$NiCl_2$	23%
6	(dppp) $NiCl_2$	27%
7	$(PPh_3)_2NiCl_2$	23%
8	$Ni(ClO_4)_2 \cdot 6H_2O$	22%
9	$NiBr_2$	20%

[a] Reactions were carried out by using **1a** (0.1 mmol), **2a** (0.2 mmol), BINOL (0.02 mmol), KTFA (0.2 mmol), DMSO (1 mL), 140 °C, N_2, 12 h. [b] ^1H NMR yield using CH_2Br_2 as the internal standard.

Table S2. Screening of Ligand[a]



Entry	L (20 mol%)	Yield[b]
1	dppe	15%
2	dppp	13%
3	dppb	13%
4	dppbz	19%
5	1,10-Phen	8%
6	BINAP	10%
7	DME	17%
8	BDMAE	15%
9	TMEDA	12%
10	MesCOOH	18%
11	PhCOOH	10%
12	AdCOOH	17%
13	Boc-Ile-OH	10%
14	Boc-Pro-OH	20%
15	Boc-Gly-OH	14%
16	BINOL	24%

[a] Reactions were carried out by using **1a** (0.1 mmol), **2a** (0.2 mmol), NiI_2 (0.01 mmol), KTFA (0.2 mmol), DMSO (1 mL), 140 °C, N_2, 12 h. [b]^{1}H NMR yield using CH_2Br_2 as the internal standard.

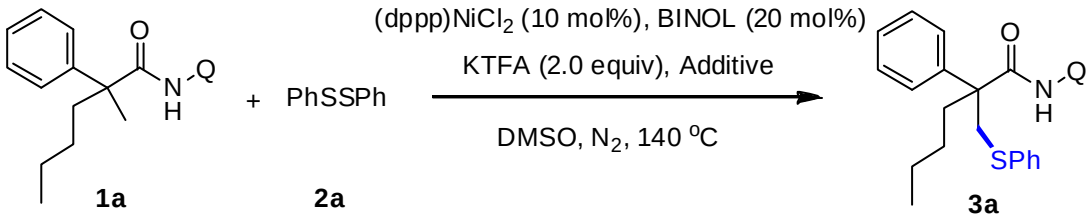
Table S3. Screening of Additive[a]

1a **2a** **3a**

Entry	Additive (2.0 equiv)	Yield[b]
1	$Mn(OAc)_2$	trace
2	MnO_2	26%
3	$Ce(NH_4)_2(NO_3)_2$	N.R
4	Fe_2O_3	34%
5	$PhI(OAc)_2$	N.R
6	CrO_3	N.R
7	$ZnCl_2$	30%
8	$Zn(OAc)_2$	35%
9	$Cu(OAc)_2$	trace
10	Cu_2O	31%
11	CuO	36%
12	$Cu(OH)_2$	37%
13	$Cu(OH)_2CO_3$ (2.0)	42%

[a] Reactions were carried out by using **1a** (0.1 mmol), **2a** (0.2 mmol), NiI_2 (0.01 mmol), BINOL (0.02 mmol), KTFA (0.2 mmol), DMSO (1 mL), 140 °C, N_2, 12 h. [b]^{1}H NMR yield using CH_2Br_2 as the internal standard.

Table S4. Screening of Additive with $(dppp)NiCl_2$[a]



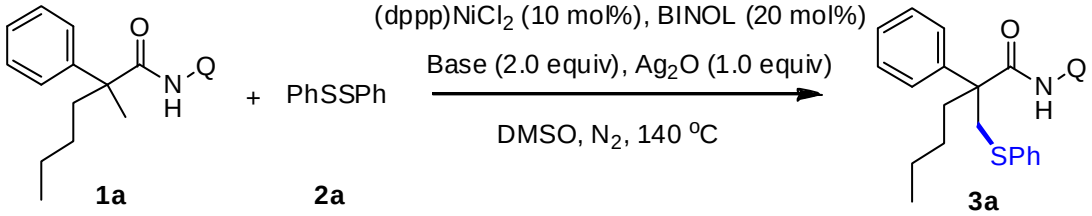
1a **2a** **3a**

Entry	Additive (equiv)	Yield[b]
1	$Cu(OAc)_2$ (2.0)	trace
2	CuF_2 (2.0)	N.R
3	CuO (2.0)	42%
4	$Cu(OH)_2$ (2.0)	40%
5	$Cu(OH)_2CO_3$ (2.0)	45%

6	Ag_2CO_3 (2.0)	20%
7	Ag_2O (2.0)	37%
8	Ag_2O (1.5)	45%
9	Ag_2O (1.0)	56%
10	Ag_2O (0.5)	47%

[a] Reactions were carried out by using **1a** (0.1 mmol), **2a** (0.2 mmol), (dppp)$NiCl_2$ (0.01 mmol), BINOL (0.02 mmol), KTFA (0.2 mmol), DMSO (1 mL), 140 °C, N_2, 12 h. [b]^{1}H NMR yield using CH_2Br_2 as the internal standard.

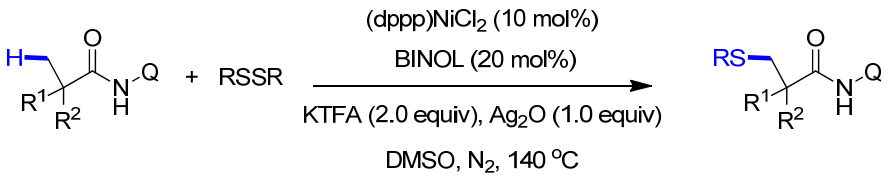
Table S5. Screening of Base[a]



Entry	Base (2.0 equiv)	Yield[b]
1	KTFA	56%
2	Na_2CO_3	39%
3	$NaHCO_3$	23%
4	K_2CO_3	20%
5	NaOAc	17%
6	NaTFA	44%
7	LiTFA	35%
8	Li_2CO_3	20%
9	K_3PO_4 (1.0 equiv)	trace

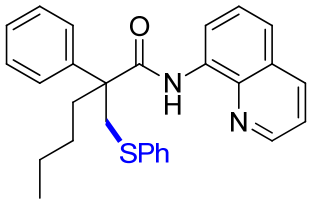
[a] Reactions were carried out by using **1a** (0.1 mmol), **2a** (0.2 mmol), (dppp)$NiCl_2$ (0.01 mmol), BINOL (0.02 mmol), DMSO (1 mL), 140 °C, N_2, 12 h. [b]^{1}H NMR yield using CH_2Br_2 as the internal standard.

2.3 General Procedure for the Thiolation



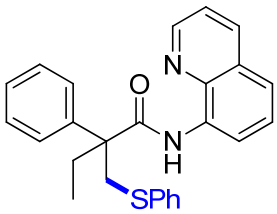
To a 50 mL Schlenk tube was added substrate (0.1 mmol), RSSR (0.2 mmol), BINOL (5.7 mg, 0.02 mmol), Ag_2O (23.2 mg, 0.1 mmol), KTFA (30.4 mg, 0.2 mmol), (dppp)$NiCl_2$ (5.4 mg, 0.01 mmol) and DMSO (1 mL). The vial was evacuated and filled with N_2 (1 atm), and stirred at 140 °C for 12 h. The mixture was then cooled to

room temperature, diluted with ethyl acetate (3×20 mL), filtrated through ceilt and washed with water and brine. The combined phase was then dried with anhydrous magnesium sulfate. After concentration, the resulting residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the product.



2-phenyl-2-((phenylthio)methyl)-*N*-(quinolin-8-yl)hexanamide 3a

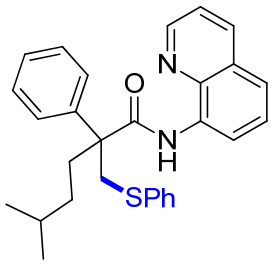
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (br, 1H), 8.72 (d, *J* = 7.6 Hz, 1H), 8.58 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.07 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.53 – 7.43 (m, 4H), 7.37 – 7.33 (m, 3H), 7.29 – 7.26 (m, 3H), 7.15 (t, *J* = 7.2 Hz, 2H), 7.09 - 7.06 (m, 1H), 3.85 (d, *J* = 12.4 Hz, 1H), 3.77 (d, *J* = 12.8 Hz, 1H), 2.52 – 2.45 (m, 1H), 2.36 – 2.28 (m, 1H), 1.33 - 1.28 (m, 4H), 0.83 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.60, 148.30, 141.76, 138.77, 137.24, 136.19, 134.58, 130.13, 128.83, 128.79, 127.98, 127.61, 127.42, 127.34, 126.10, 121.60, 121.49, 116.27, 56.03, 41.81, 34.84, 26.60, 23.28, 14.01; **HRMS** (EI-TOF) calcd for $C_{28}H_{28}N_2OS$ (M^+): 440.1922, found: 440.1920.



2-phenyl-2-((phenylthio)methyl)-*N*-(quinolin-8-yl)butanamide 3b

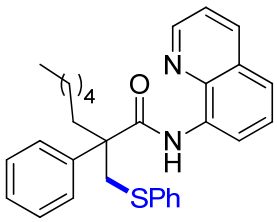
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (br, 1H), 8.73 (d, *J* = 7.6 Hz, 1H), 8.59 – 8.58 (m, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.49 (m, 3H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.33 (m, 3H), 7.29 - 7.27 (m, 3H), 7.14 (t, *J* = 7.6 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 1H), 3.85 (d, *J* = 12.8 Hz, 1H), 3.77 (d, *J* = 12.8 Hz, 1H), 2.59 - 2.50 (m, 1H), 2.46 - 2.38

(m, 1H), 0.96 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.45, 148.31, 141.53, 138.75, 137.19, 136.20, 134.57, 130.08, 128.84, 128.80, 127.98, 127.64, 127.40, 126.09, 121.59, 121.49, 116.25, 56.38, 41.13, 27.90, 8.97; **HRMS** (EI-TOF) calcd for $C_{26}H_{24}N_2OS$ (M^+): 412.1609, found: 412.1605.



5-methyl-2-phenyl-2-((phenylthio)methyl)-*N*-(quinolin-8-yl)hexanamide 3c

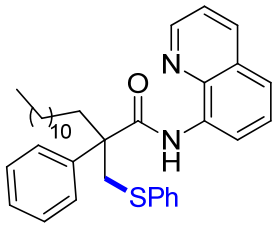
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (br, 1H), 8.71 (d, J = 7.6 Hz, 1H), 8.58 – 8.57 (m, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.52 -7.49 (m, 3H), 7.44 (d, J = 8.0 Hz, 1H), 7.37 – 7.33 (m, 3H), 7.28 -7.25 (m, 3H), 7.15 (t, J = 8.0 Hz, 2H), 7.09 - 7.06 (m, 1H), 3.83 (d, J = 12.8 Hz, 1H), 3.77 (d, J = 12.8 Hz, 1H), 2.53 – 2.46 (m, 1H), 2.37 – 2.30 (m, 1H), 1.55 – 1.48 (m, 1H), 1.23 – 1.16 (m, 2H), 0.84 (d, J = 6.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.58, 148.27, 141.80, 138.76, 137.25, 136.17, 134.57, 130.16, 128.82, 128.79, 127.97, 127.59, 127.41, 127.31, 126.10, 121.59, 121.48, 116.28, 55.97, 41.76, 33.20, 32.83, 28.63, 22.63, 22.58; **HRMS** (EI-TOF) calcd for $C_{29}H_{30}N_2OS$ (M^+): 454.2079, found: 454.2079.



2-phenyl-2-((phenylthio)methyl)-*N*-(quinolin-8-yl)octanamide 3d

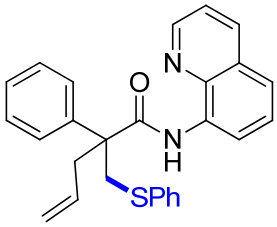
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (br, 1H), 8.72 (d, J = 7.6 Hz, 1H), 8.58 – 8.57 (m, 1H), 8.07 (dd, J = 8.0, 1.2 Hz, 1H), 7.52 – 7.49 (m, 3H), 7.45 – 7.43 (m, 1H), 7.37 – 7.32 (m, 3H), 7.28 – 7.25 (m, 3H), 7.15 (t, J = 7.6 Hz, 2H), 7.07 (t, J = 7.6 Hz, 1H), 3.85 (d, J = 12.6 Hz, 1H), 3.77 (d, J = 12.8 Hz, 1H), 2.50 – 2.46 (m, 1H), 2.34 – 2.30

(m, 1H), 1.29 -1.26 (m, 4H), 1.19 (d, J = 3.5 Hz, 4H), 0.78 - 0.77 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.60, 148.28, 141.77, 138.76, 137.25, 136.18, 134.57, 130.15, 128.82, 128.79, 127.97, 127.59, 127.41, 127.32, 126.10, 121.58, 121.47, 116.26, 56.07, 41.83, 35.02, 31.62, 29.83, 24.36, 22.69, 14.12; **HRMS** (EI-TOF) calcd for $C_{30}H_{32}N_2OS$ (M^+): 468.2235, found: 468.2235.



2-phenyl-2-((phenylthio)methyl)-*N*-(quinolin-8-yl)tetradecanamide 3e

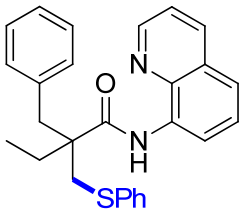
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (br, 1H), 8.72 (d, J = 6.8 Hz, 1H), 8.58 (d, J = 2.4 Hz, 1H), 8.07 (dd, J = 8.0, 1.2 Hz, 1H), 7.53 – 7.44 (m, 4H), 7.37 -7.33 (m, 3H), 7.29 -7.25 (m, 3H), 7.15 (t, J = 7.2 Hz, 2H), 7.08 (t, J = 7.2 Hz, 1H), 3.84 (d, J = 12.8 Hz, 1H), 3.77 (d, J = 12.8 Hz, 1H), 2.55 – 2.46 (m, 1H), 2.33 – 2.30 (m, 1H), 1.28 (s, 5H), 1.21 -1.15 (m, 15H), 0.87 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.61, 148.28, 141.77, 138.76, 137.26, 136.18, 134.58, 130.14, 128.82, 128.79, 127.97, 127.60, 127.42, 127.33, 126.10, 121.58, 121.47, 116.26, 56.07, 41.81, 34.97, 32.04, 30.13, 29.74, 29.71, 29.66, 29.46, 29.40, 24.35, 22.82, 14.26; **HRMS** (EI-TOF) calcd for $C_{36}H_{44}N_2OS$ (M^+): 552.3174, found: 552.3170.



2-phenyl-2-((phenylthio)methyl)-*N*-(quinolin-8-yl)pent-4-enamide 3f

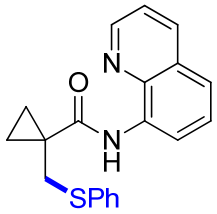
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (br, 1H), 8.71 (d, J = 7.2 Hz, 1H), 8.58 (d, J = 2.8 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.52 – 7.44 (m, 4H), 7.40 – 7.33 (m, 3H), 7.31 – 7.27 (m, 3H), 7.11 (t, J = 7.2 Hz, 2H), 7.05 (t, J = 7.2 Hz, 1H), 5.73 - 5.63 (m, 1H), 5.15 (d, J = 16.8 Hz, 1H), 5.08 (d, J = 10.0 Hz, 1H), 3.79 (s, 2H), 3.24 (dd, J = 14.0, 7.2 Hz, 1H), 3.15 (dd, J = 13.6, 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.81,

148.29, 140.99, 138.75, 136.98, 136.19, 134.48, 132.90, 130.36, 128.91, 128.76, 127.97, 127.77, 127.41, 127.35, 126.17, 121.59, 121.55, 119.84, 116.33, 55.97, 41.72, 39.69; **HRMS** (EI-TOF) calcd for $C_{27}H_{24}N_2OS$ (M^+): 424.1609, found: 424.1608.



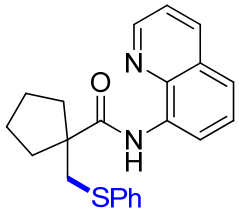
2-benzyl-2-((phenylthio)methyl)-*N*-(quinolin-8-yl)butanamide 3g

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (br, 1H), 8.74 (d, *J* = 4.4 Hz, 2H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.52 (q, *J* = 8.2 Hz, 2H), 7.44 – 7.39 (m, 3H), 7.23 - 7.09 (m, 8H), 3.39 (d, *J* = 12.0 Hz, 1H), 3.30 – 3.21 (m, 3H), 1.97 (q, *J* = 7.2 Hz, 2H), 1.02 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.08, 148.37, 138.90, 136.91, 136.36, 134.28, 130.24, 130.10, 128.93, 128.34, 128.04, 127.57, 126.81, 126.21, 121.68, 121.57, 116.59, 53.24, 41.20, 38.74, 28.31, 8.93; **HRMS** (EI-TOF) calcd for $C_{27}H_{26}N_2OS$ (M^+): 426.1766, found: 426.1760.



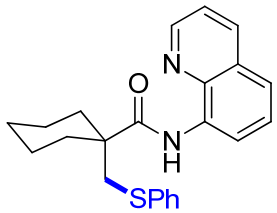
1-((phenylthio)methyl)-*N*-(quinolin-8-yl)cyclopropanecarboxamide 3h

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.80 (br, 1H), 8.76 (dd, *J* = 6.8, 1.2 Hz, 1H), 8.72 (dd, *J* = 4.0, 0.8 Hz 1H), 8.15 (d, *J* = 7.2 Hz, 1H), 7.59 - 7.48 (m, 4H), 7.43 (dd, *J* = 8.4, 4.0 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 3.49 (s, 2H), 1.49 (dd, *J* = 6.8, 4.4 Hz, 2H), 0.94 (dd, *J* = 6.8, 4.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.46, 148.29, 138.89, 136.37, 136.09, 134.95, 131.32, 129.12, 128.10, 127.56, 127.05, 121.68, 121.51, 116.60, 40.87, 25.19, 16.39; **HRMS** (EI-TOF) calcd for $C_{20}H_{18}N_2OS$ (M^+): 334.1140, found: 334.1138.



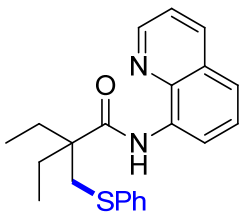
1-((phenylthio)methyl)-*N*-(quinolin-8-yl)cyclopentanecarboxamide 3i

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.30 (br, 1H), 8.80 (d, *J* = 2.8 Hz, 1H), 8.71 (dd, *J* = 7.8, 2.0 Hz, 1H), 8.15 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.52 – 7.43 (m, 3H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 3.43 (s, 2H), 2.37 – 2.34 (m, 2H), 1.97 – 1.93 (m, 2H), 1.86 - 1.82 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.55, 148.33, 138.92, 136.93, 136.37, 134.62, 130.13, 128.81, 128.02, 127.53, 126.15, 121.63, 121.43, 116.52, 57.11, 43.73, 36.12, 24.86; **HRMS** (EI-TOF) calcd for $C_{22}H_{22}N_2OS$ (M^+): 362.1453, found: 362.1452.



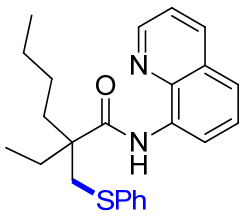
1-((phenylthio)methyl)-*N*-(quinolin-8-yl)cyclohexanecarboxamide 3j

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.40 (br, 1H), 8.82 (dd, *J* = 4.0, 1.2 Hz, 1H), 8.71 (dd, *J* = 5.6, 2.8 Hz, 1H), 8.15 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.30 (d, *J* = 7.2 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 3.32 (s, 2H), 2.33 (d, *J* = 10.4 Hz, 2H), 1.73 – 1.58 (m, 7H), 1.43 – 1.34 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.54, 148.36, 139.03, 136.87, 136.34, 134.51, 130.12, 128.74, 128.02, 127.52, 126.06, 121.62, 121.44, 116.60, 49.25, 44.74, 33.95, 25.89, 22.99; **HRMS** (EI-TOF) calcd for $C_{23}H_{24}N_2OS$ (M^+): 376.1609, found: 376.1608.



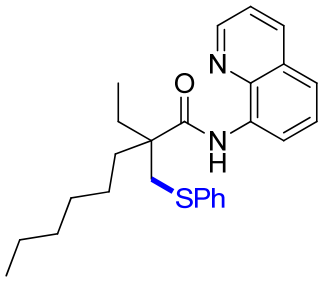
2-ethyl-2-((phenylthio)methyl)-*N*-(quinolin-8-yl)butanamide 3k

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.33 (br, 1H), 8.81 (d, *J* = 2.8 Hz, 1H), 8.76 (dd, *J* = 6.8, 1.6 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.40 (m, 5H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 3.41 (s, 2H), 2.06 – 1.87 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.96, 148.41, 138.95, 137.09, 136.42, 134.49, 130.15, 128.90, 128.07, 127.57, 126.17, 121.69, 121.49, 116.52, 52.18, 38.73, 28.13, 8.73; **HRMS** (EI-TOF) calcd for $C_{22}H_{24}N_2OS$ (M^+): 364.1609, found: 364.1608.



2-ethyl-2-((phenylthio)methyl)-*N*-(quinolin-8-yl)hexanamide 3l

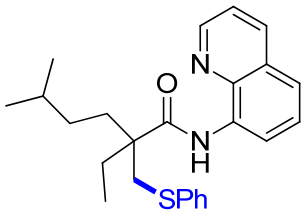
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.33 (br, 1H), 8.82 – 8.81 (m, 1H), 8.75 (d, *J* = 6.8 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.41 (m, 5H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 3.45 – 3.38 (m, 2H), 2.05 - 1.88 (m, 3H), 1.84 – 1.78 (m, 1H), 1.41 - 1.28 (m, 4H), 0.92 (t, *J* = 7.6 Hz, 3H), 0.84 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.11, 148.40, 138.96, 137.15, 136.41, 134.51, 130.17, 128.90, 128.07, 127.57, 126.17, 121.70, 121.47, 116.52, 51.87, 39.02, 35.47, 28.58, 26.45, 23.26, 14.03, 8.72; **HRMS** (EI-TOF) calcd for $C_{24}H_{28}N_2OS$ (M^+): 392.1922, found: 392.1919.



2-ethyl-2-((phenylthio)methyl)-*N*-(quinolin-8-yl)octanamide 3m

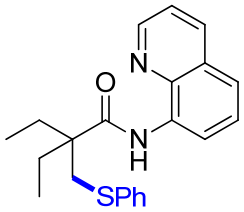
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (br, 1H), 8.81 (d, *J* = 2.4 Hz, 1H), 8.75 (dd, *J* = 6.8, 1.6 Hz, 1H), 8.16 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.54 – 7.41 (m, 5H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 3.45 – 3.37 (m, 2H), 2.06 – 1.78 (m, 4H), 1.27 – 1.21 (m, 8H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.82 - 0.79 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.12, 148.39, 138.96, 137.17, 136.41, 134.51, 130.19, 128.90, 128.07,

127.57, 126.18, 121.69, 121.46, 116.52, 51.91, 39.03, 35.71, 31.70, 29.83, 28.63, 24.24, 22.72, 14.16, 8.74; **HRMS** (EI-TOF) calcd for $C_{26}H_{32}N_2OS$ (M^+): 420.2235, found: 420.2240.



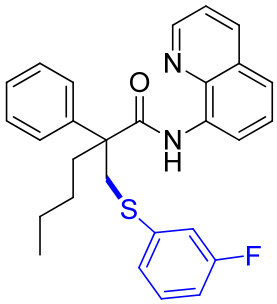
2-ethyl-5-methyl-2-((phenylthio)methyl)-*N*-(quinolin-8-yl)hexanamide 3n

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.33 (br, 1H), 8.81 (d, *J* = 2.8 Hz, 1H), 8.74 (dd, *J* = 6.8, 1.2 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.41 (m, 5H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 3.43 (d, *J* = 12.8 Hz, 1H), 3.38 (d, *J* = 12.4 Hz, 1H), 2.07 – 1.78 (m, 4H), 1.53 - 1.45 (m, 1H), 1.23 – 1.10 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.85 (d, *J* = 6.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.10, 148.38, 138.96, 137.176, 136.40, 134.51, 130.18, 128.90, 128.07, 127.57, 126.16, 121.69, 121.45, 116.51, 51.81, 38.96, 33.47, 33.09, 28.60, 22.64, 22.59, 8.71; **HRMS** (EI-TOF) calcd for $C_{25}H_{30}N_2OS$ (M^+): 406.2079, found: 406.2083.



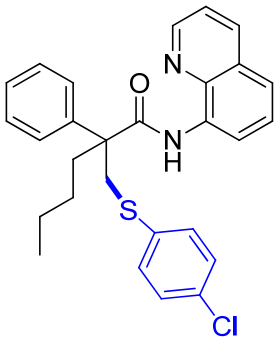
2-ethyl-2-((phenylthio)methyl)-*N*-(quinolin-8-yl)butanamide 3o

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.33 (br, 1H), 8.81 (d, *J* = 2.8 Hz, 1H), 8.76 (dd, *J* = 6.8, 1.6 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.40 (m, 5H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 3.41 (s, 2H), 2.06 – 1.87 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.96, 148.41, 138.95, 137.09, 136.42, 134.49, 130.15, 128.90, 128.07, 127.57, 126.17, 121.69, 121.49, 116.52, 52.18, 38.73, 28.13, 8.73; **HRMS** (EI-TOF) calcd for $C_{24}H_{28}N_2OS$ (M^+): 392.1922, found: 392.1920.



2-(((3-fluorophenyl)thio)methyl)-2-phenyl-*N*-(quinolin-8-yl)hexanamide 5a

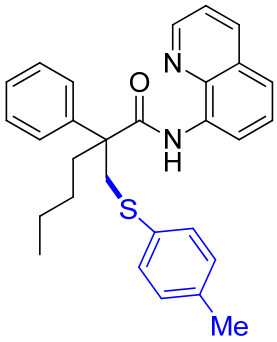
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (br, 1H), 8.72 (d, *J* = 7.2 Hz, 1H), 8.58 (d, *J* = 3.2 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.54 – 7.44 (m, 4H), 7.38 - 7.34 (m, 3H), 7.28 (d, *J* = 6.8 Hz, 1H), 7.12 - 7.06 (m, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 9.6 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 3.83 (d, *J* = 12.8 Hz, 1H), 3.77 (d, *J* = 12.4 Hz, 1H), 2.52 - 2.44 (m, 1H), 2.35 – 2.28 (m, 1H), 1.36 - 1.32 (m, 4H), 0.85 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.42, 162.70 (d, *J* = 246.1 Hz), 148.33, 141.48, 139.69, 138.73, 136.20, 134.49, 129.94 (d, *J* = 8.6 Hz), 128.87, 127.97, 127.74, 127.40, 127.33, 125.14 (d, *J* = 3.0 Hz), 121.60 (d, *J* = 5.7 Hz), 116.33 (d, *J* = 23.0 Hz), 116.26, 112.87 (d, *J* = 21.0 Hz), 55.92, 41.50, 34.85, 26.60, 23.27, 14.00; **HRMS** (EI-TOF) calcd for $C_{28}H_{27}FN_2OS$ (M^+): 458.1828, found: 458.1826.



2-(((4-chlorophenyl)thio)methyl)-2-phenyl-N-(quinolin-8-yl)hexanamide 5b

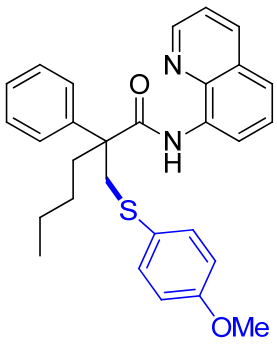
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (br, 1H), 8.70 (d, *J* = 6.8 Hz, 1H), 8.58 (d, *J* = 2.8 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.53 -7.44 (m, 4H), 7.35 (t, *J* = 7.0 Hz, 3H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 3.80 (d, *J* = 12.8 Hz, 1H), 3.74 (d, *J* = 12.8 Hz, 1H), 2.51 - 2.43 (m, 1H), 2.35 – 2.28 (m, 1H), 1.36 – 1.27 (m, 4H), 0.85 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.42, 148.30, 141.55, 138.72, 136.22, 135.69, 134.47, 132.12, 131.53, 128.86, 128.82, 127.97,

127.68, 127.40, 127.34, 121.62, 121.58, 116.26, 56.04, 42.26, 34.86, 26.58, 23.28, 14.01; **HRMS** (EI-TOF) calcd for $C_{28}H_{27}ClN_2OS$ (M^+): 474.1533, found: 474.1531.



2-phenyl-*N*-(quinolin-8-yl)-2-((p-tolylthio)methyl)hexanamide 5c

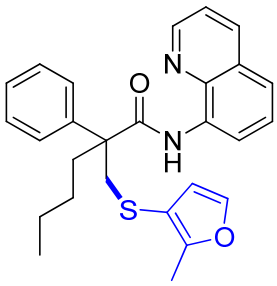
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (br, 1H), 8.71 (d, *J* = 7.6 Hz, 1H), 8.58 (d, *J* = 2.8 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.52 – 7.48 (m, 3H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.38 -7.32 (m, 3H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 3.82 (d, *J* = 12.8 Hz, 1H), 3.74 (d, *J* = 12.8 Hz, 1H), 2.51 - 2.43 (m, 1H), 2.36 – 2.28 (m, 1H), 2.23 (s, 3H), 1.32 – 1.23 (m, 4H), 0.83 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.59, 148.26, 141.88, 138.75, 136.25, 136.15, 134.59, 133.45, 130.87, 129.55, 128.80, 127.95, 127.52, 127.40, 127.32, 121.56, 121.43, 116.25, 56.10, 42.49, 34.84, 26.56, 23.28, 21.07, 14.01; **HRMS** (EI-TOF) calcd for $C_{29}H_{30}N_2OS$ (M^+): 454.2079, found: 454.2078.



2-(((4-methoxyphenyl)thio)methyl)-2-phenyl-*N*-(quinolin-8-yl)hexanamide 5d

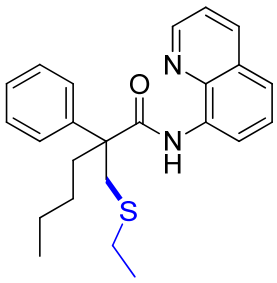
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (br, 1H), 8.71 (d, *J* = 7.2 Hz, 1H), 8.59 (d, *J* = 2.8 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.52 – 7.43 (m, 4H), 7.37 - 7.33 (m, 3H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 3.80 – 3.68 (m, 5H), 2.50 – 2.43 (m, 1H), 2.36 – 2.28 (m, 1H), 1.33 -1.29 (m, 2H), 1.26 – 1.22 (m, 2H),

0.84 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.61, 158.89, 148.26, 141.93, 138.75, 136.16, 134.61, 133.69, 128.77, 127.95, 127.48, 127.40, 127.35, 121.57, 121.40, 116.25, 114.42, 56.25, 55.40, 43.84, 34.84, 26.54, 23.30, 14.04; **HRMS** (EI-TOF) calcd for $C_{29}H_{30}N_2O_2S$ (M^+): 470.2028, found: 470.2026.



2-(((2-methylfuran-3-yl)thio)methyl)-2-phenyl-*N*-(quinolin-8-yl)hexanamide 5e

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (br, 1H), 8.71 (d, *J* = 7.2 Hz, 1H), 8.59 (d, *J* = 2.8 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.44 (m, 4H), 7.40 – 7.33 (m, 3H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 1.2 Hz, 1H), 6.11 (d, *J* = 1.2 Hz, 1H), 3.61 (d, *J* = 12.8 Hz, 1H), 3.51 (d, *J* = 12.8 Hz, 1H), 2.50 – 2.43 (m, 1H), 2.36 – 2.28 (m, 1H), 2.17 (s, 3H), 1.38 - 1.25 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.60, 154.25, 148.27, 141.90, 140.41, 138.76, 136.20, 134.62, 128.77, 127.97, 127.48, 127.43, 127.36, 121.59, 121.43, 116.22, 114.81, 111.51, 56.16, 43.42, 34.61, 26.54, 23.33, 14.05, 11.85; **HRMS** (EI-TOF) calcd for $C_{27}H_{28}N_2O_2S$ (M^+): 444.1871, found: 444.1870.



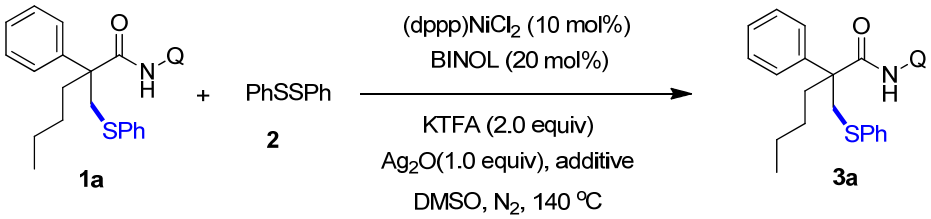
2-((ethylthio)methyl)-2-phenyl-*N*-(quinolin-8-yl)hexanamide 5f

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (br, 1H), 8.75 (d, *J* = 7.6 Hz, 1H), 8.61 – 8.60 (m, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.54 - 7.44 (m, 4H), 7.39 – 7.34 (m, 3H), 7.29 (d, *J* = 6.8 Hz, 1H), 3.44 (d, *J* = 13.2 Hz, 1H), 3.33 (d, *J* = 12.8 Hz, 1H), 2.50 - 2.42 (m, 1H), 2.26 (dd, *J* = 14.0, 6.8 Hz, 3H), 1.42 - 1.30 (m, 4H), 1.12 (td, *J* = 7.2, 1.2 Hz, 3H), 0.89 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.04, 148.31, 142.25,

138.81, 136.20, 134.70, 128.74, 128.01, 127.46, 127.40, 121.60, 121.44, 116.26, 56.09, 39.09, 34.91, 27.60, 26.62, 23.37, 14.92, 14.08; **HRMS** (EI-TOF) calcd for $C_{24}H_{28}N_2OS$ (M^+): 392.1922, found: 392.1920.

2.4 Mechanistic Investigation

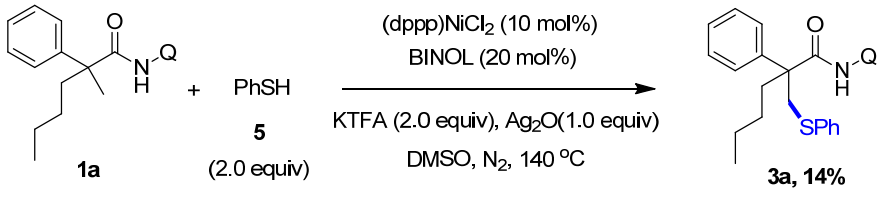
Radical Scavenger Reactions



additive (1.0 equiv)	Yield
1,4-dinitrobenzene	44%
TEMPO	48%
1,4-diphenylethylene	54%

To a 50 mL Schlenk tube was added substrate **1a** (0.1 mmol), PhSSPh (0.2 mmol), BINOL (5.7 mg, 0.02 mmol), Ag_2O (23.2 mg, 0.1 mmol), additive (0.1 mmol), KTFA (30.4 mg, 0.2 mmol), (dppp)$NiCl_2$ (5.4 mg, 0.01 mmol) and DMSO (1 mL). The vial was evacuated and filled with N_2 (1 atm) then stirred at 140 °C for 12 h. The mixture was then cooled to room temperature, diluted with ethyl acetate (3×20 mL), filtrated through ceilt and washed with water and brine. The combined phase was then dried with anhydrous magnesium sulfate. After concentration, the resulting residue was analyzed with NMR using CH_2Br_2 as the internal standard.

Thiolation with benzenethiol 5



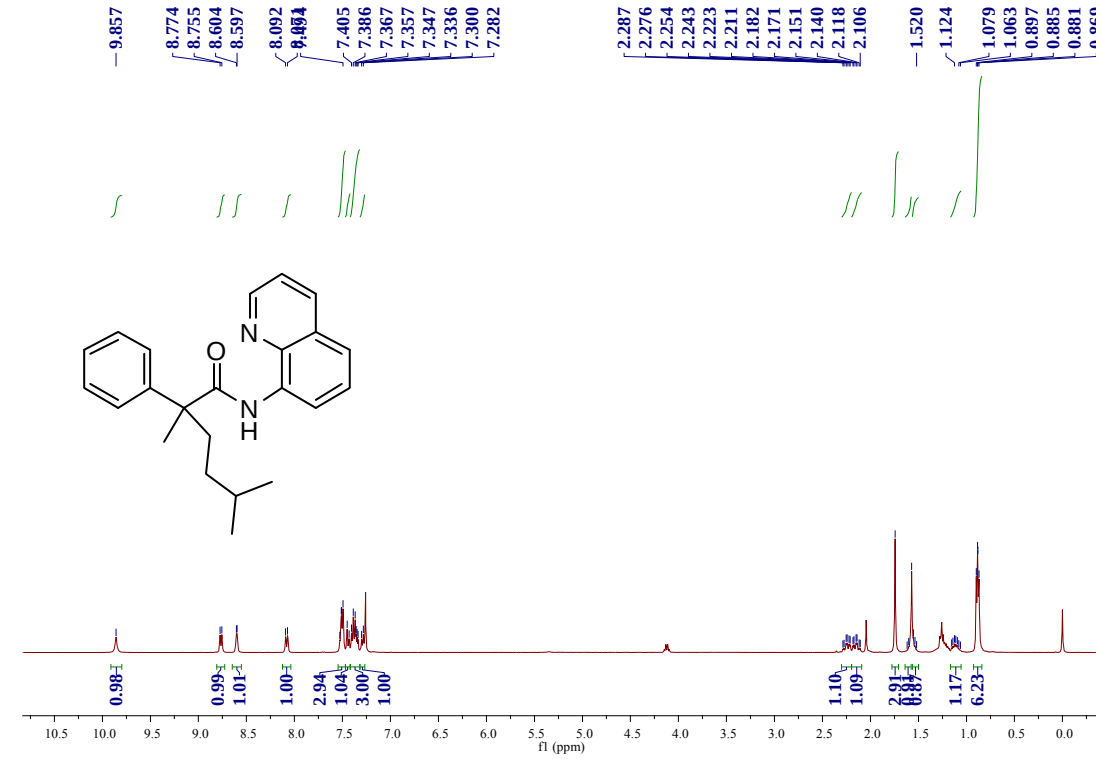
To a 50 mL Schlenk tube was added substrate **1a** (0.1 mmol), PhSH (0.2 mmol), BINOL (5.7 mg, 0.02 mmol), Ag_2O (23.2 mg, 0.1 mmol), KTFA (30.4 mg, 0.2 mmol), (dppp)$NiCl_2$ (5.4 mg, 0.01 mmol) and DMSO (1 mL). The vial was evacuated and filled with N_2 (1 atm) then stirred at 140 °C for 12 h. The mixture was then cooled to room temperature, diluted with ethyl acetate (3×20 mL), filtrated through ceilt and washed with water and brine. The combined phase was then dried with anhydrous magnesium sulfate. After concentration, the resulting residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the product.

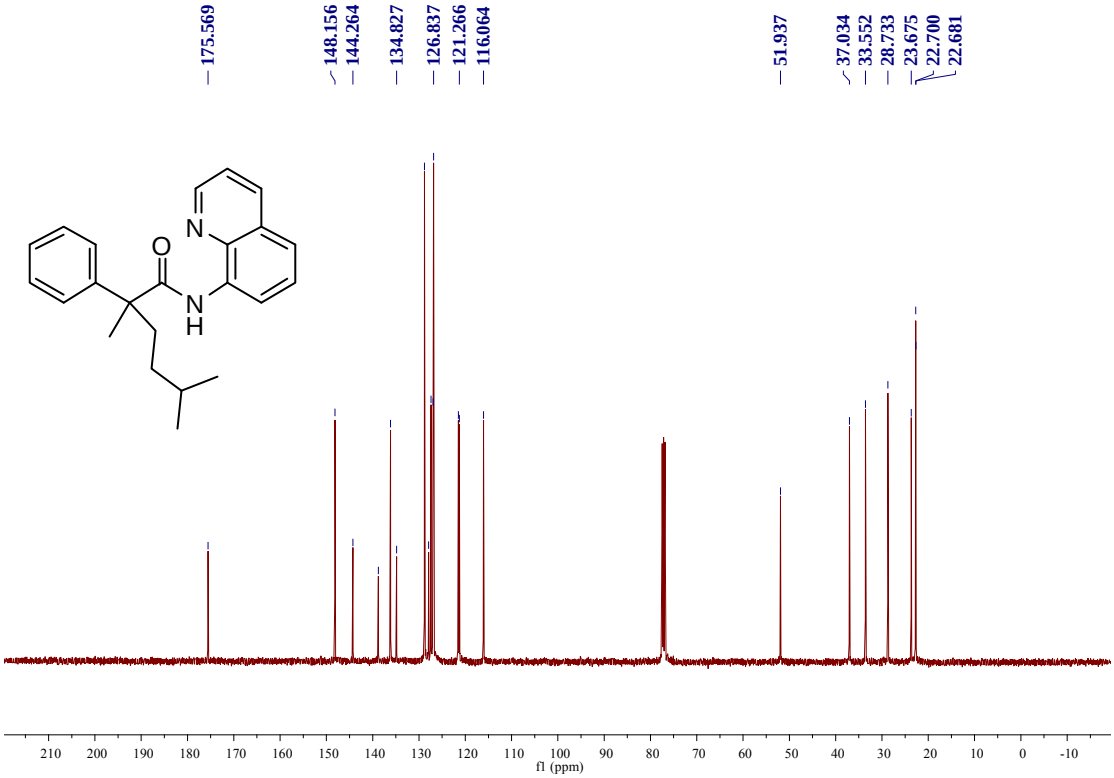
3. References:

1. Wu, X.-S.; Zhao, Y.; Ge, H.-B. *J. Am. Chem. Soc.*, 2014, ***136***, 1789-1792.

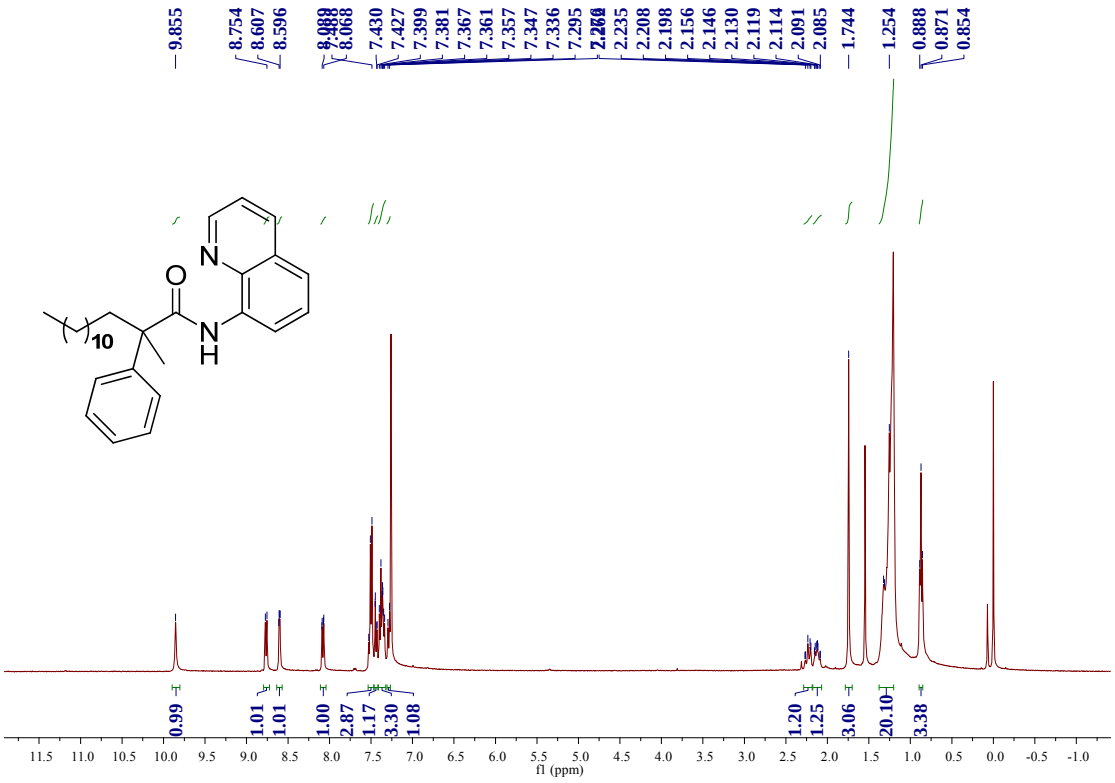
4. NMR Spectra

1c





1e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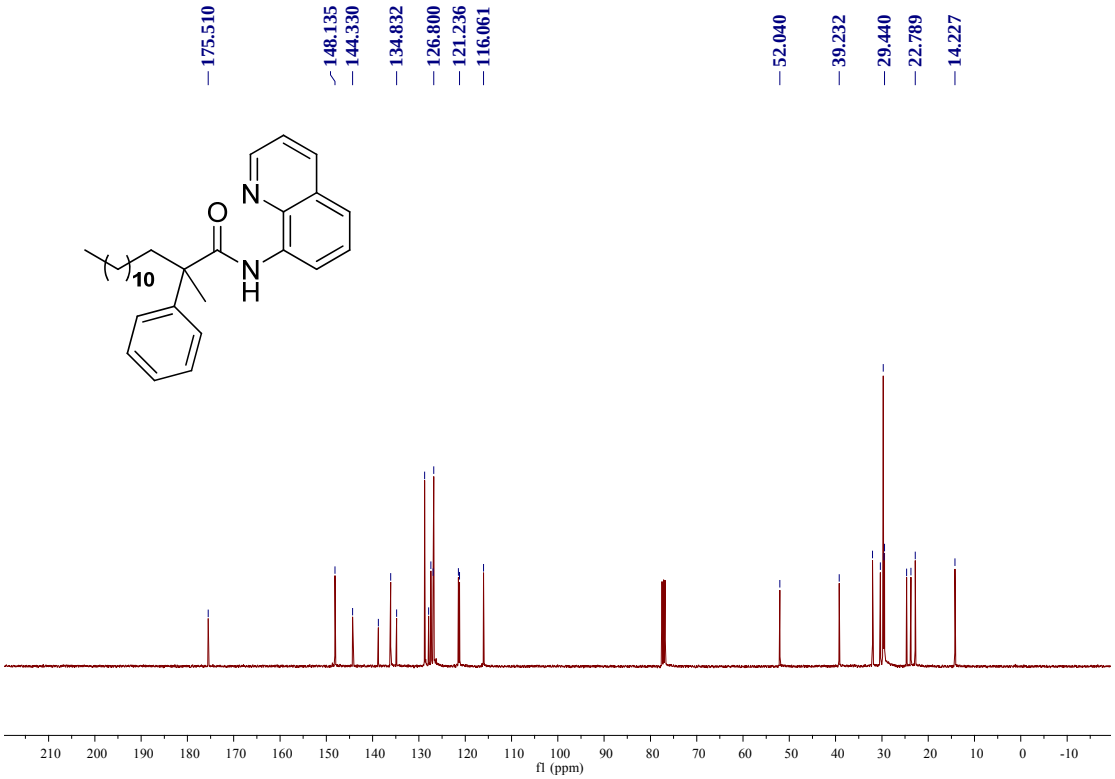
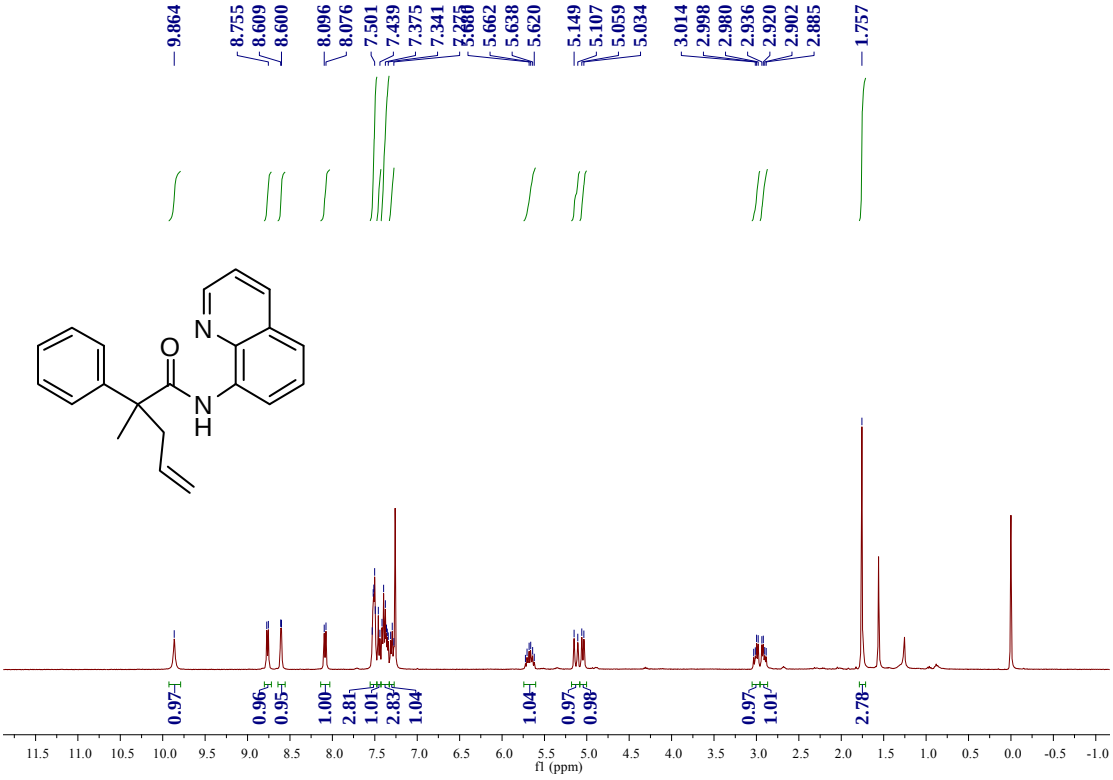
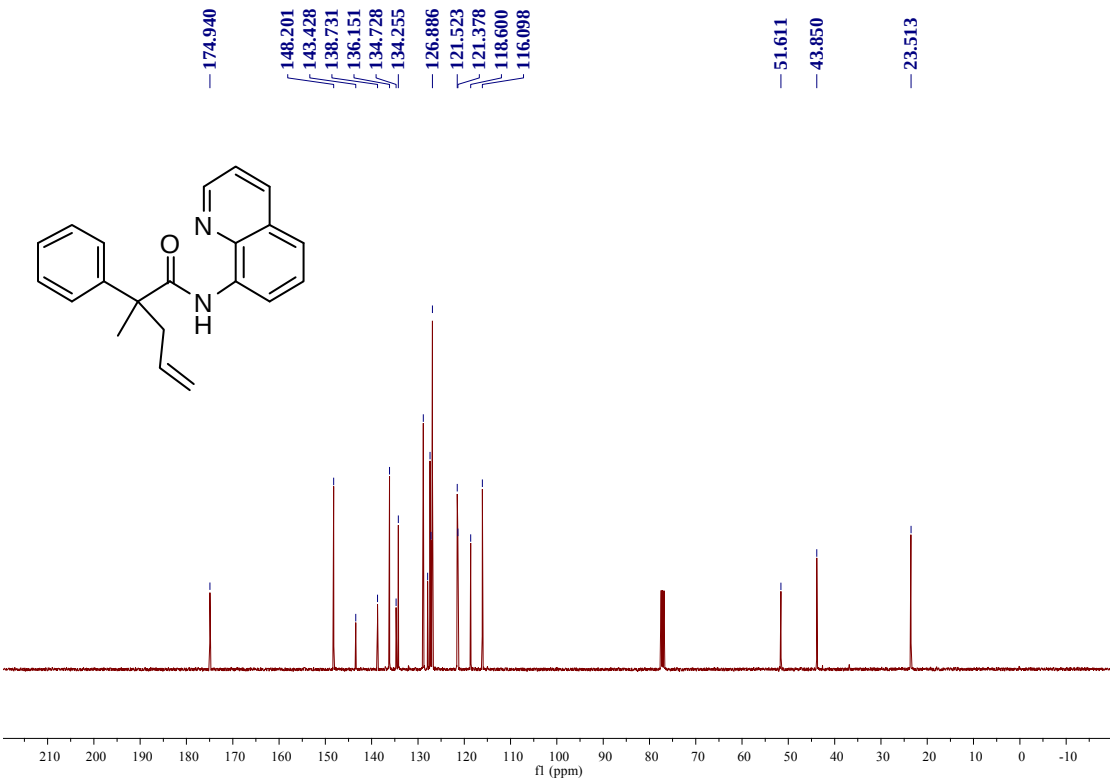
8.607
8.596
8.068
7.430
7.427
7.399
7.381
7.367
7.361
7.357
7.347
7.336
7.295
2.235
2.208
2.198
2.156
2.146
2.130
2.119
2.114
2.091
2.085
1.744
1.254
0.888
0.871
0.854
0.99
1.01
1.01
1.00
2.87
1.17
3.30
1.08
1.20
1.25
3.06
20.10
3.38
f1 (ppm)


175.510
148.135
144.330
134.832
126.800
121.236
116.061
52.040
39.232
29.440
22.789
14.227
f1 (ppm)

1f


9.864
8.755
8.609
8.600
8.096
8.076
7.501
7.439
7.375
7.341
5.662
5.638
5.620
5.149
5.107
5.059
5.034
3.014
2.998
2.980
2.936
2.920
2.902
2.885
1.757
0.97
0.96
0.95
1.00
2.81
1.01
2.83
1.04
1.04
0.97
0.98
0.97
1.01
2.78
f1 (ppm)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143.428
138.731
136.151
134.728
134.255
126.886
121.523
121.378
118.600
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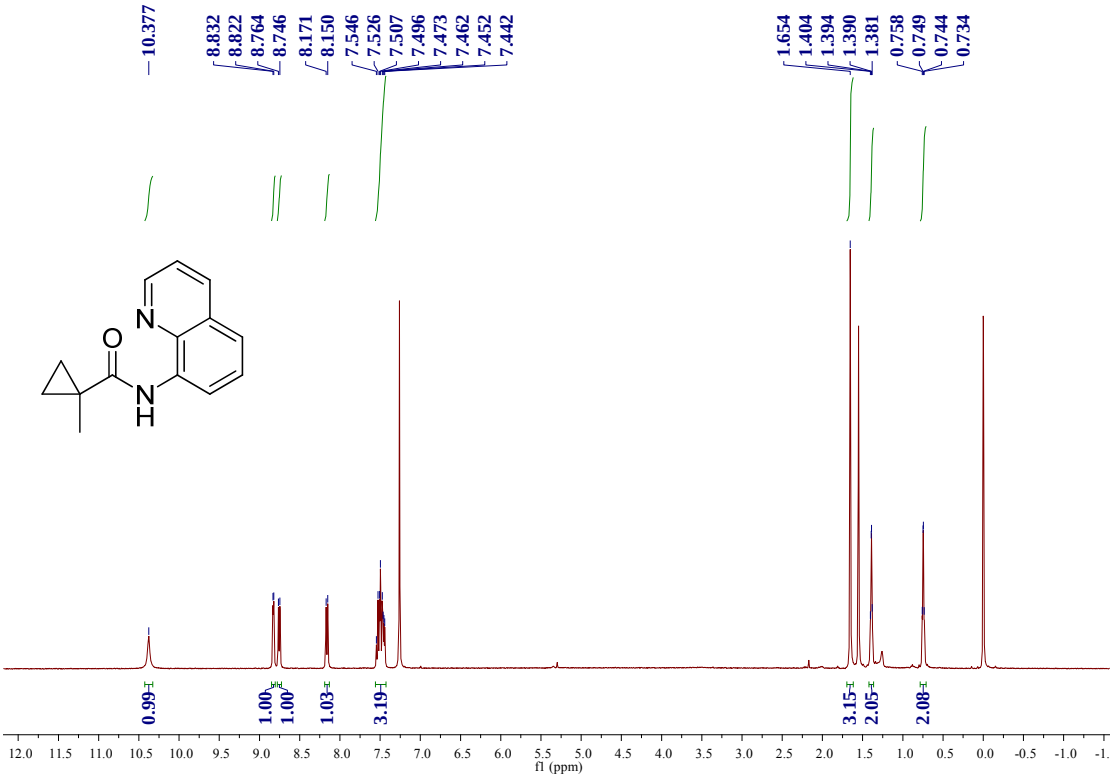
51.611
43.850
23.513
f1 (ppm)

1h


10.377
8.832
8.822
8.764
8.746
8.171
8.150
7.546
7.526
7.507
7.496
7.473
7.462
7.452
7.442
1.654
1.404
1.394
1.390
1.381
0.758
0.749
0.744
0.734
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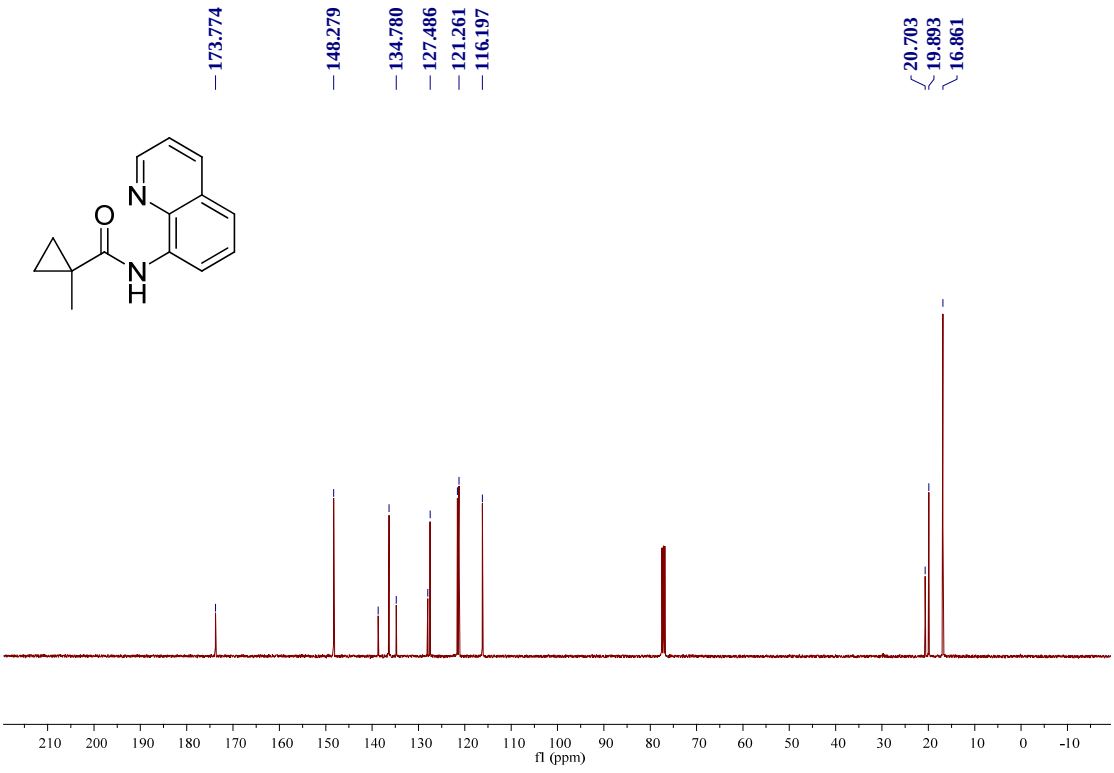
1.00
1.03
3.19
3.15
2.05
2.08
f1 (ppm)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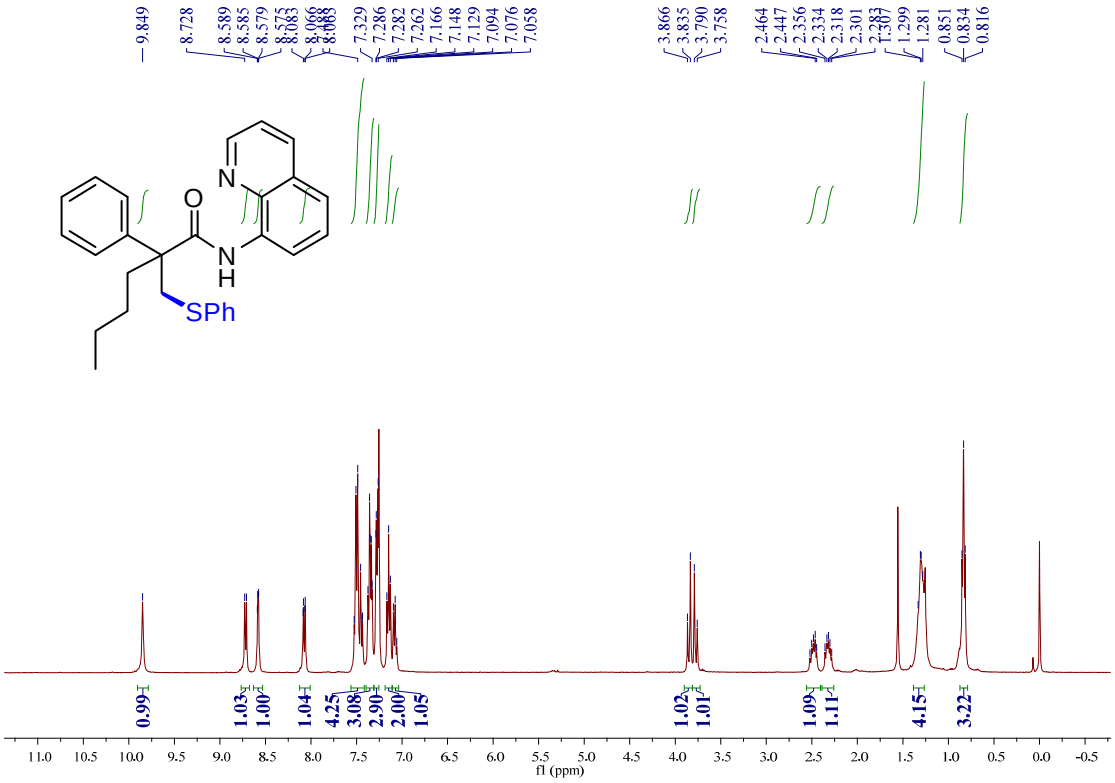
116.197
20.703
19.893
16.861
f1 (ppm)

3a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8.575
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7.282
7.262
7.166
7.148
7.129
7.094
7.076
7.058
3.866
3.835
3.790
3.758
2.464
2.447
2.356
2.334
2.318
2.301
1.307
1.299
1.281
0.851
0.834
0.816
O
N
N
H
SPh
0.99
1.03
1.00
1.04
4.25
3.08
2.90
2.00
1.05
1.02
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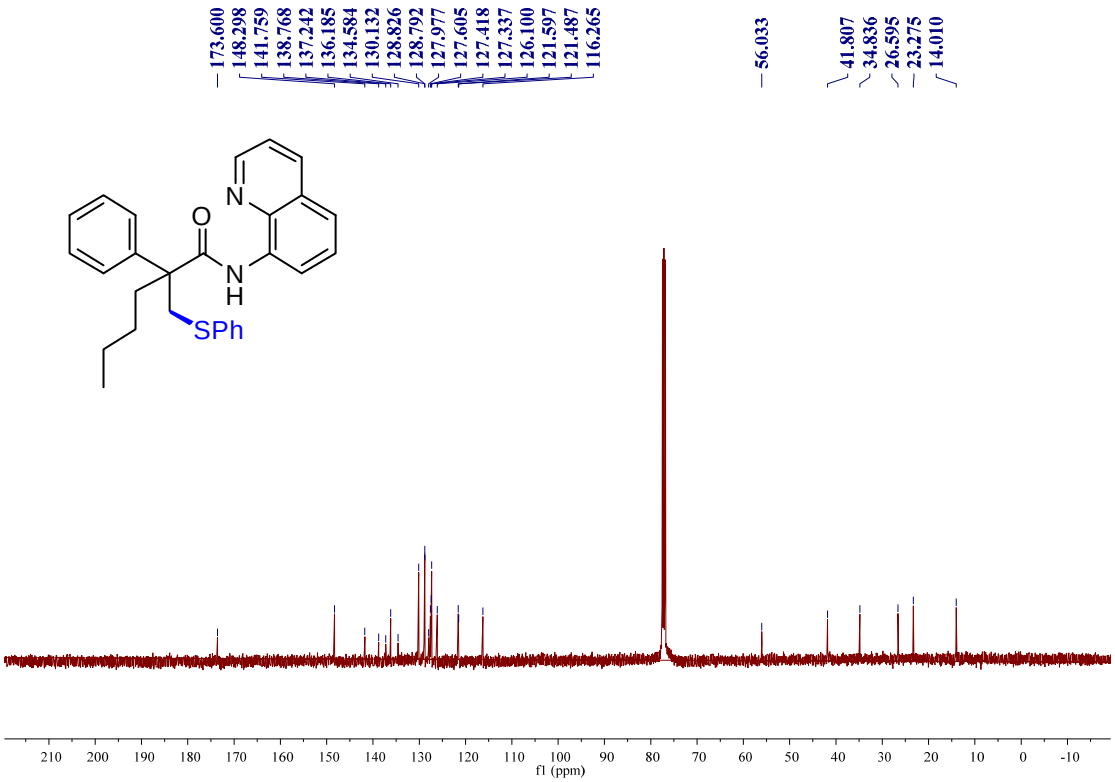
1.09
1.11
4.15
3.22
fl (ppm)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137.242
136.185
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130.132
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127.977
127.605
127.418
127.337
126.100
121.597
121.487
116.265
56.033
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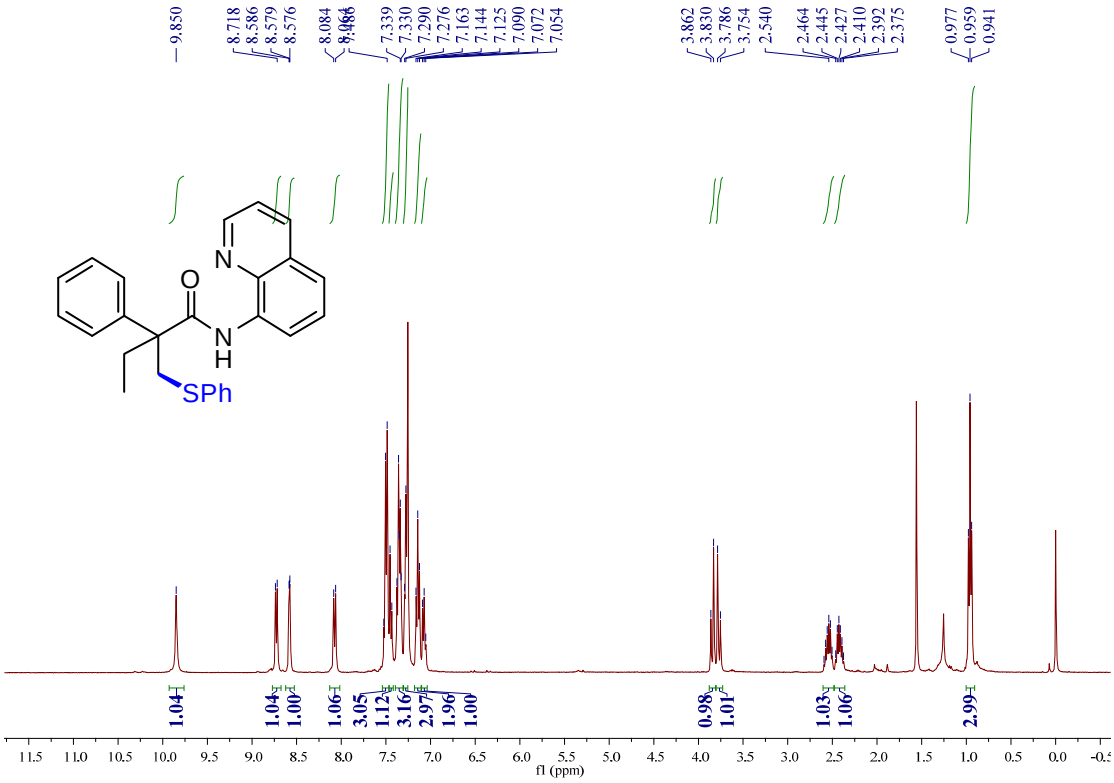
34.836
26.595
23.275
14.010
O
N
N
H
SPh
fl (ppm)

3b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8.066
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7.290
7.276
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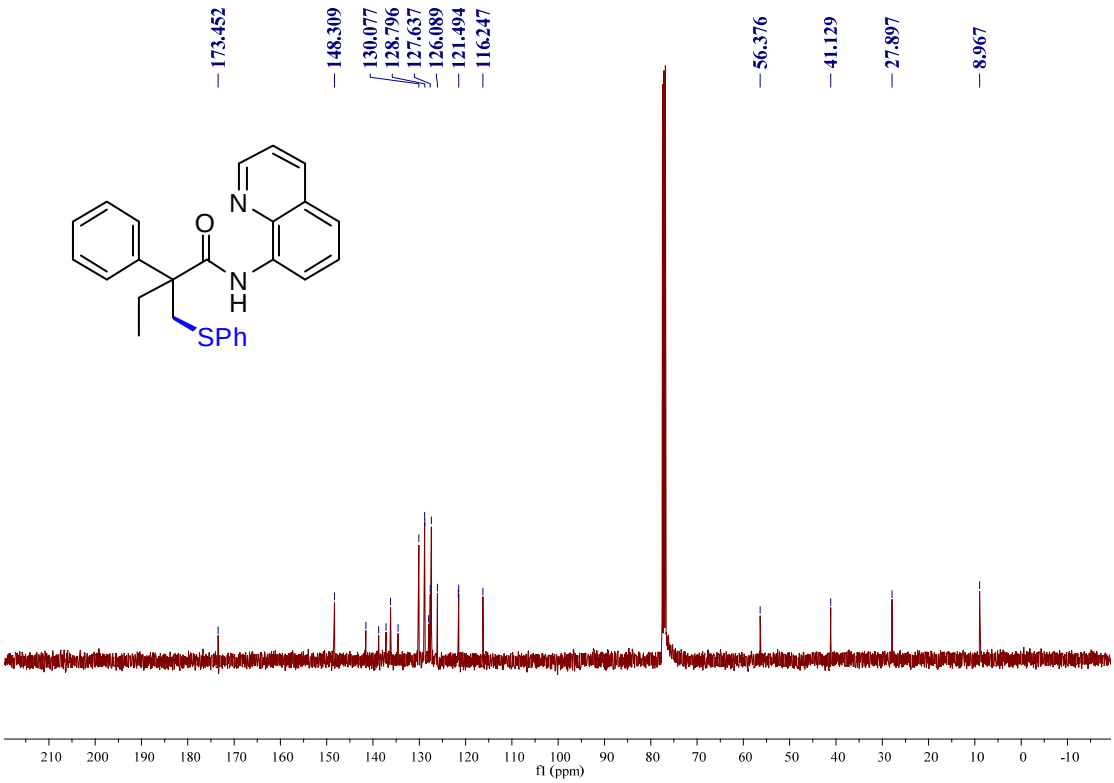
7.144
7.125
7.090
7.072
7.054
3.862
3.830
3.786
3.754
2.540
2.464
2.445
2.427
2.410
2.392
2.375
0.977
0.959
0.941
1.04
1.04
1.00
1.06
3.05
1.12
3.16
2.97
1.96
1.00
0.98
1.01
1.03
1.06
2.99
N
O
N
H
SPh
f1 (ppm)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56.376
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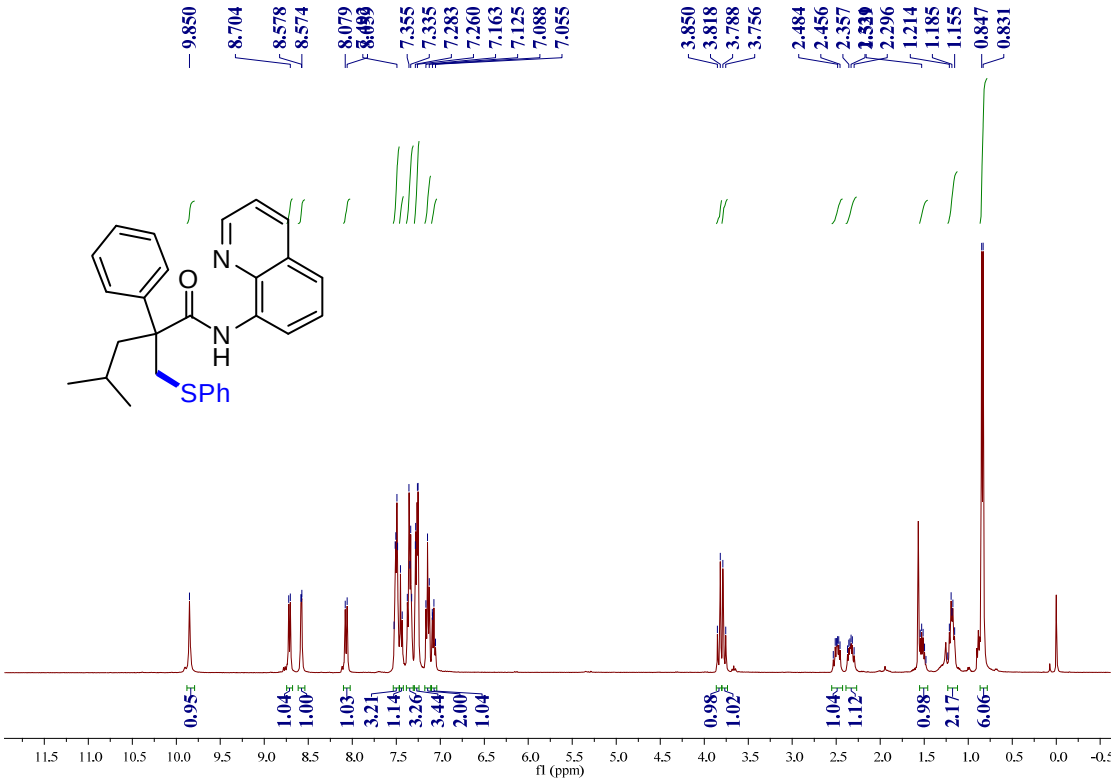
27.897
8.967
N
O
N
H
SPh
f1 (ppm)

3c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8.578
8.574
8.079
7.355
7.335
7.283
7.260
7.163
7.125
7.088
7.055
3.850
3.818
3.788
3.756
2.484
2.456
2.357
2.296
1.214
1.185
1.155
0.847
0.831
0.95
1.04
1.00
1.03
3.21
1.14
3.26
3.44
2.00
1.04
0.98
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1.04
1.12
0.98
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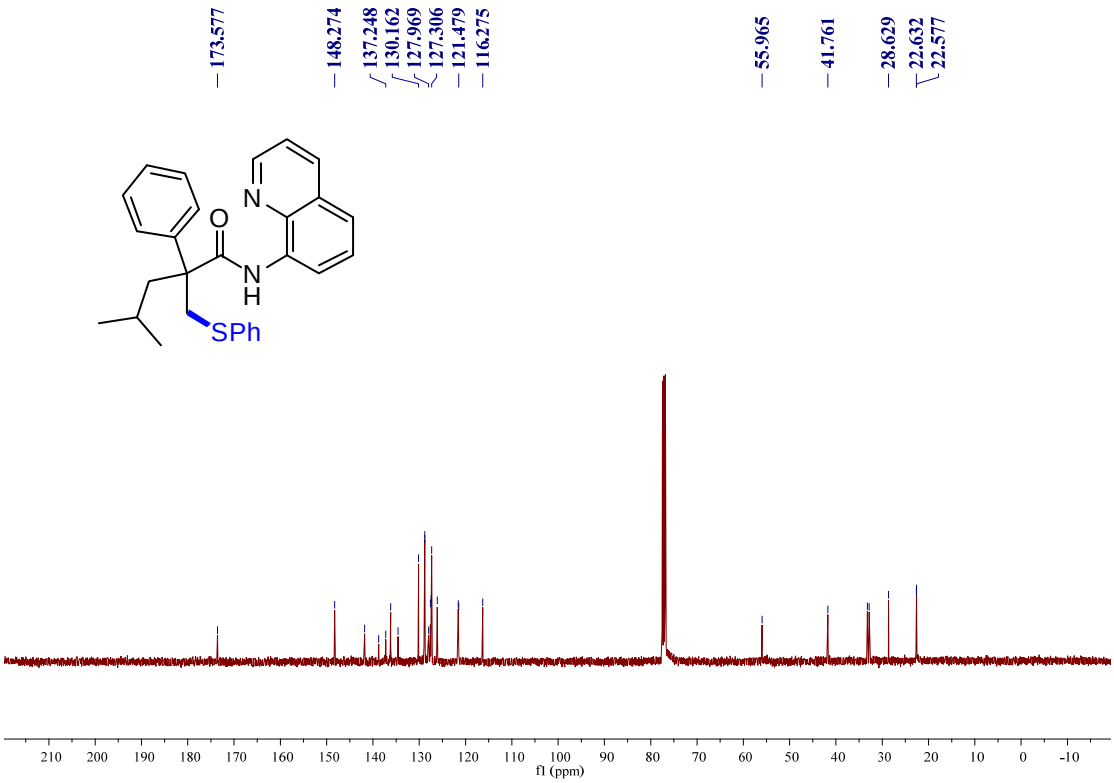
O
N
H
SPh
f1 (ppm)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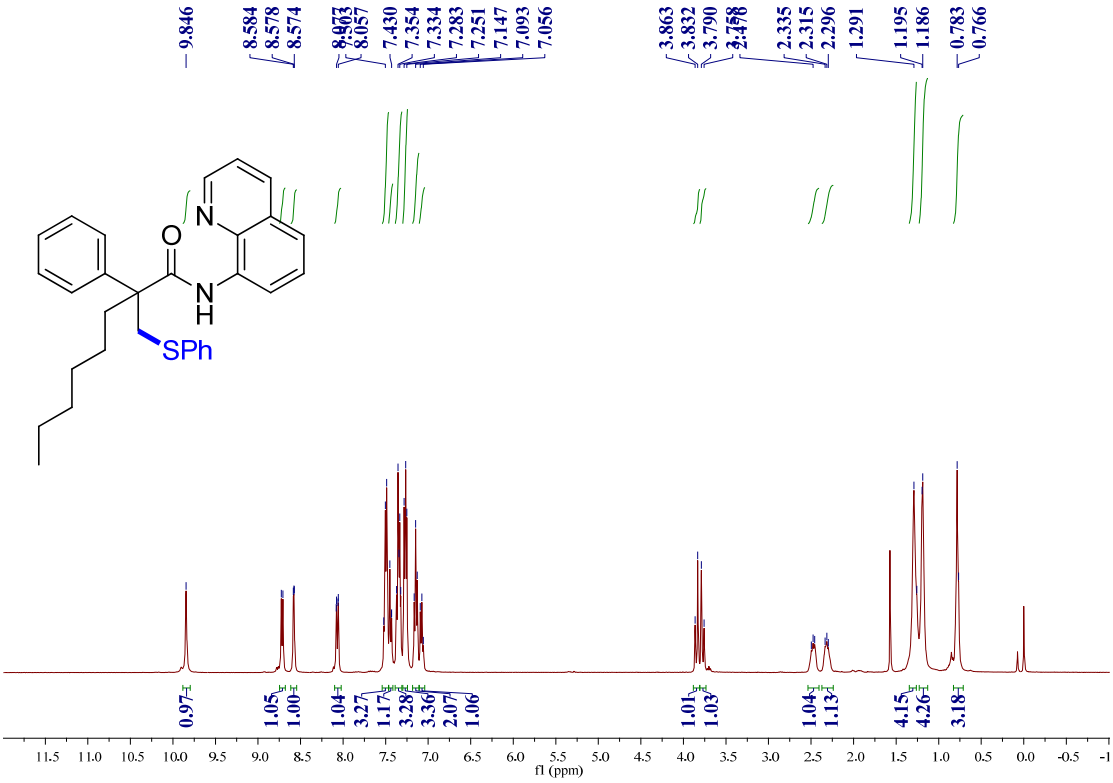
O
N
H
SPh
f1 (ppm)

3d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7.334
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7.251
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7.093
7.056
3.863
3.832
3.790
2.335
2.315
2.296
1.291
1.195
1.186
0.783
0.766
N
O
N
H
SPh
0.97
1.05
1.00
1.04
3.27
1.17
3.28
3.36
2.07
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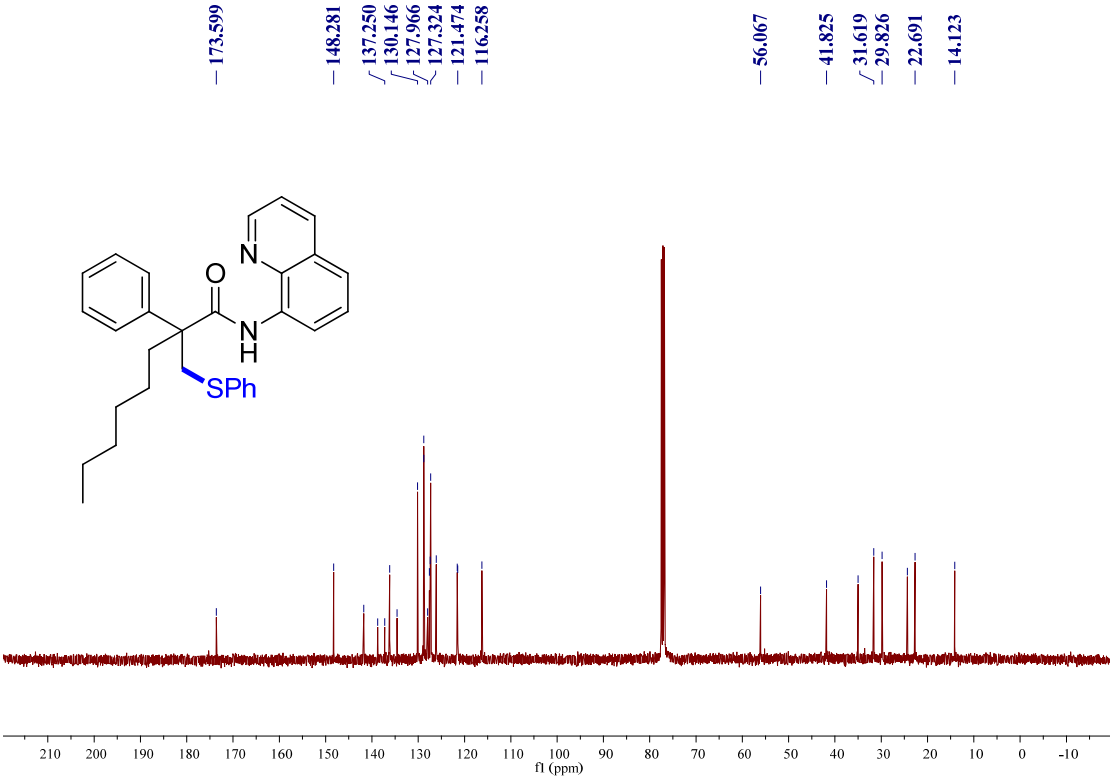
1.03
1.04
1.13
4.15
4.26
3.18
fl (ppm)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116.258
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31.619
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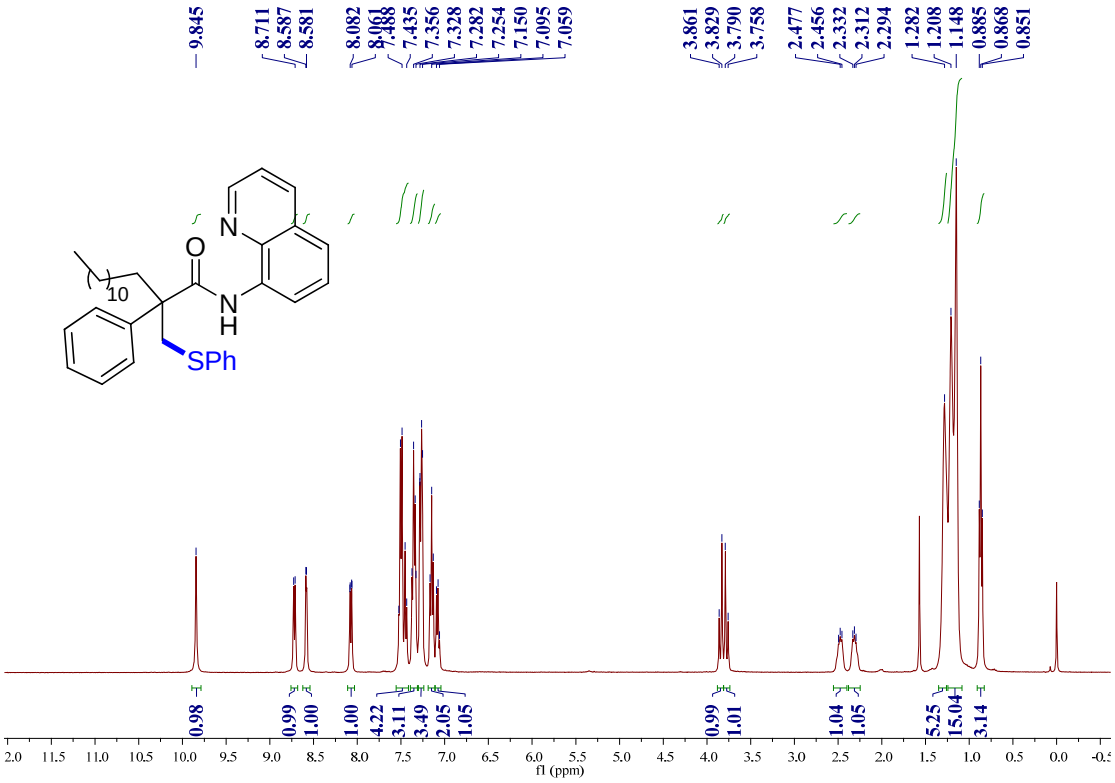
22.691
14.123
N
O
N
H
SPh
fl (ppm)

3e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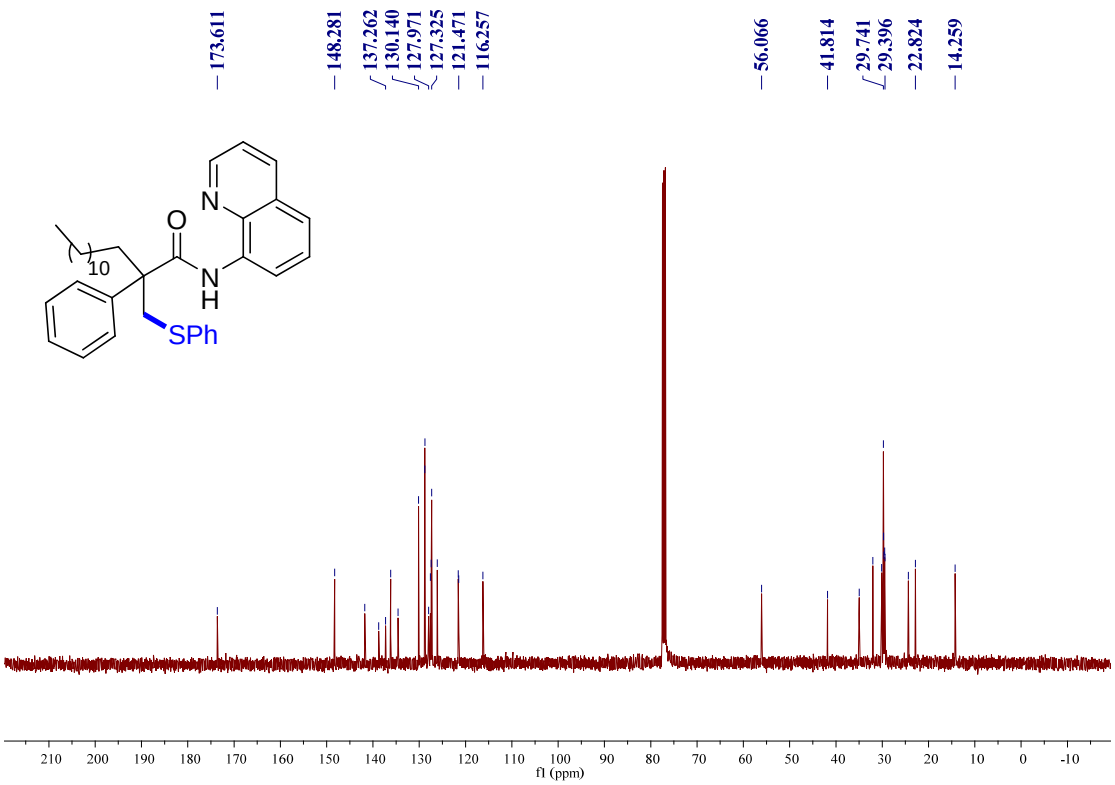
3.758
2.477
2.456
2.332
2.312
2.294
1.282
1.208
1.148
0.885
0.868
0.851
0.98
0.99
1.00
1.00
4.22
3.11
3.49
2.05
1.05
0.99
1.01
1.04
1.05
5.25
15.04
3.14
N
O
N
H
10
SPh
f1 (ppm)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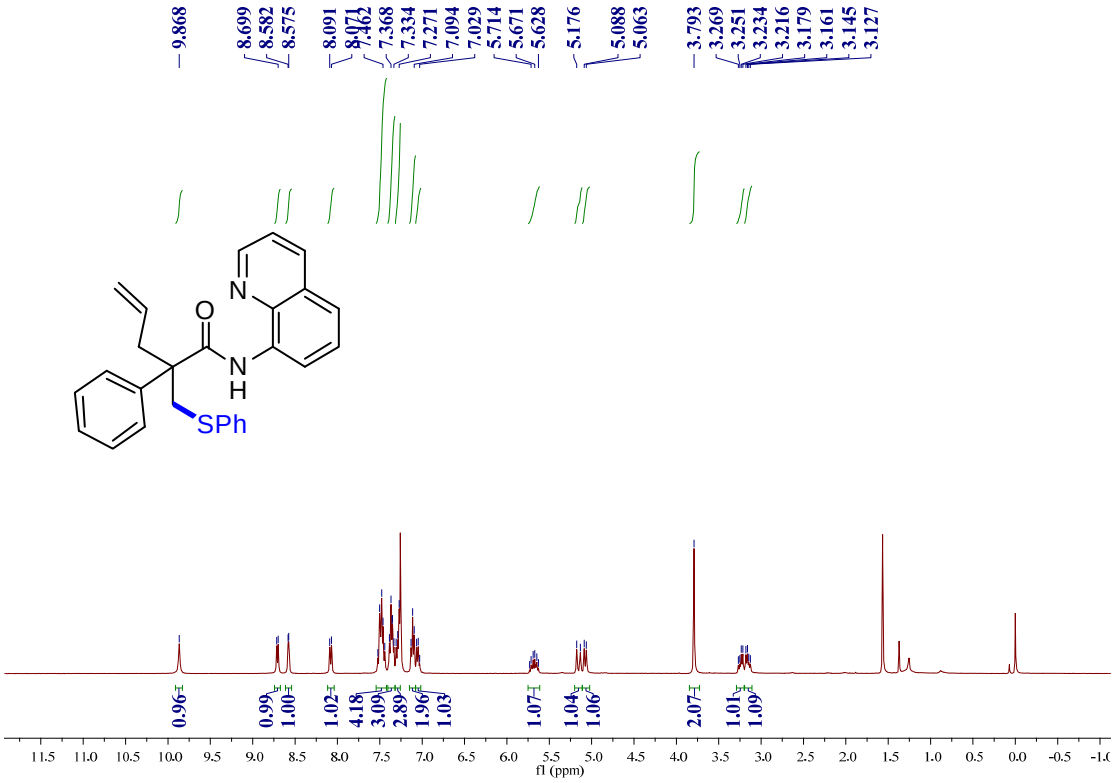
N
O
N
H
10
SPh
f1 (ppm)

3f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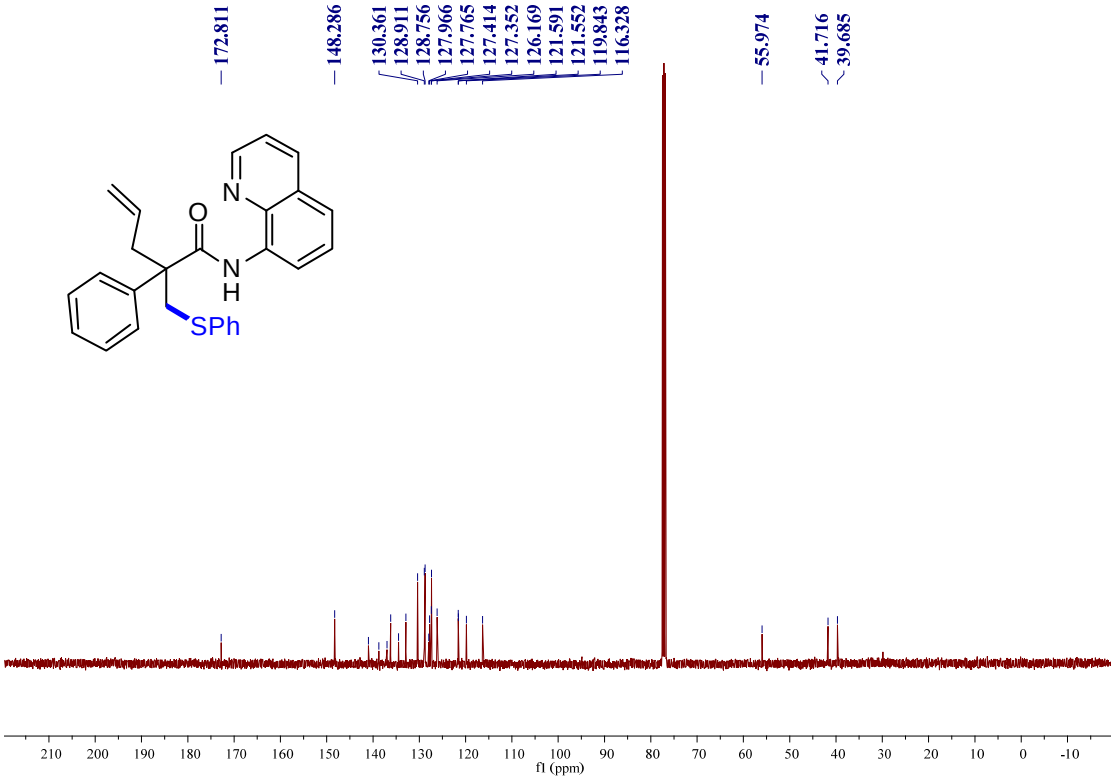
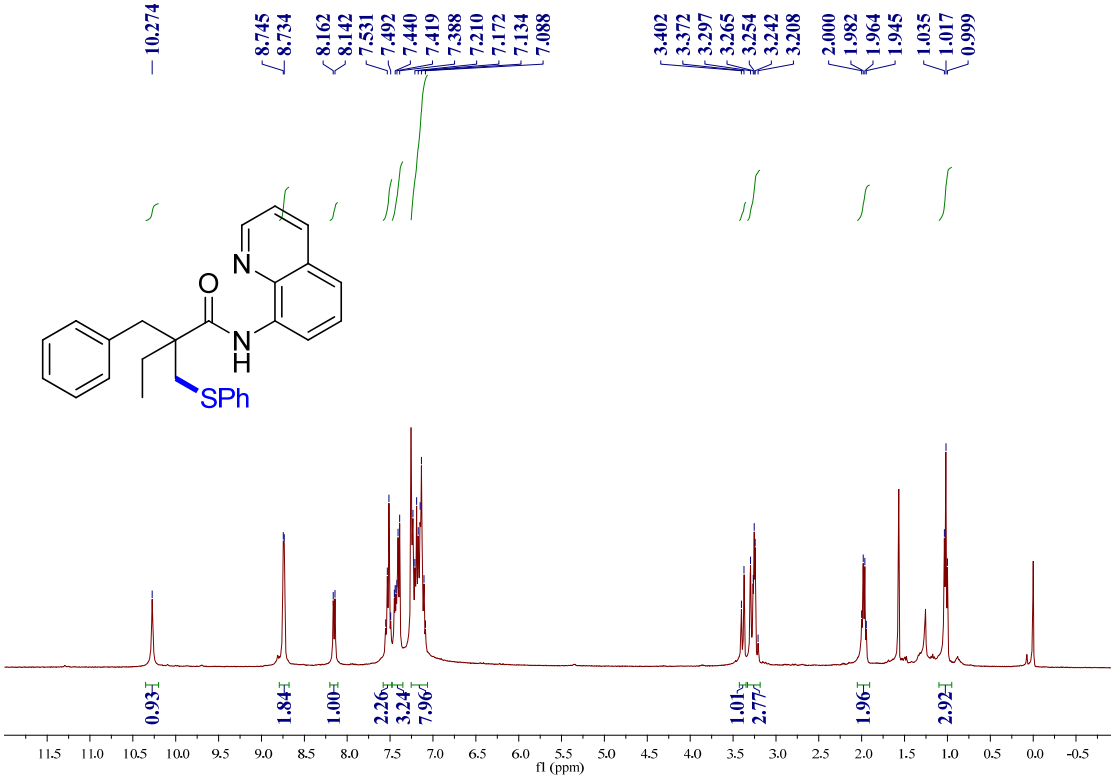
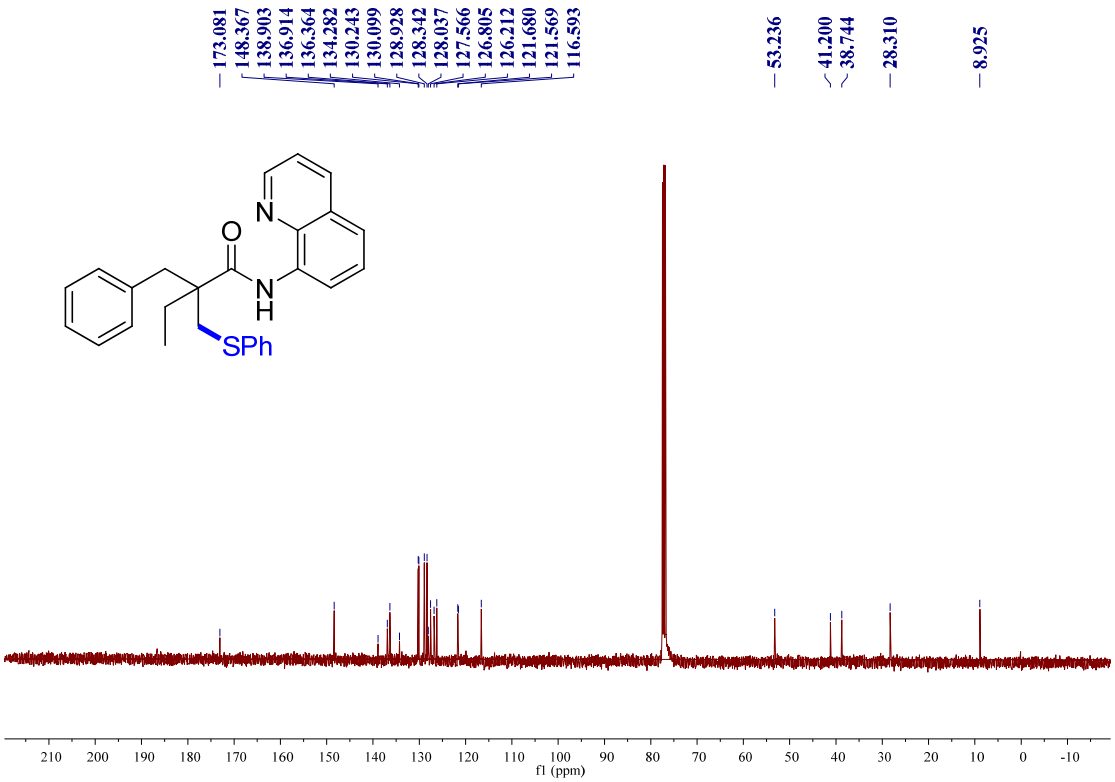
5.671
5.628
5.176
5.088
5.063
3.793
3.269
3.251
3.234
3.216
3.179
3.161
3.145
3.127
N
O
N
H
SPh
0.96
0.99
1.00
1.02
4.18
3.09
2.89
1.96
1.03
1.07
1.04
1.06
2.07
1.01
1.09
f1 (ppm)

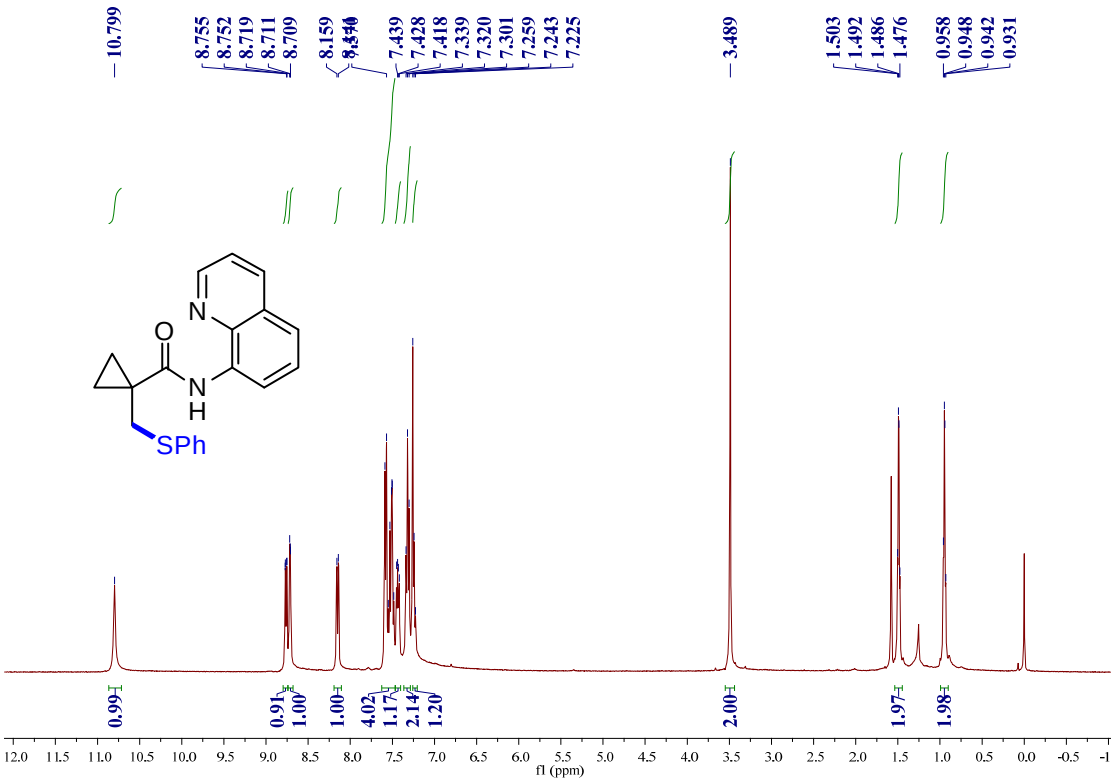

172.811
148.286
130.361
128.911
128.756
127.966
127.765
127.414
127.352
126.169
121.591
121.552
119.843
116.328
55.974
41.716
39.685
N
O
N
H
SPh
f1 (ppm)

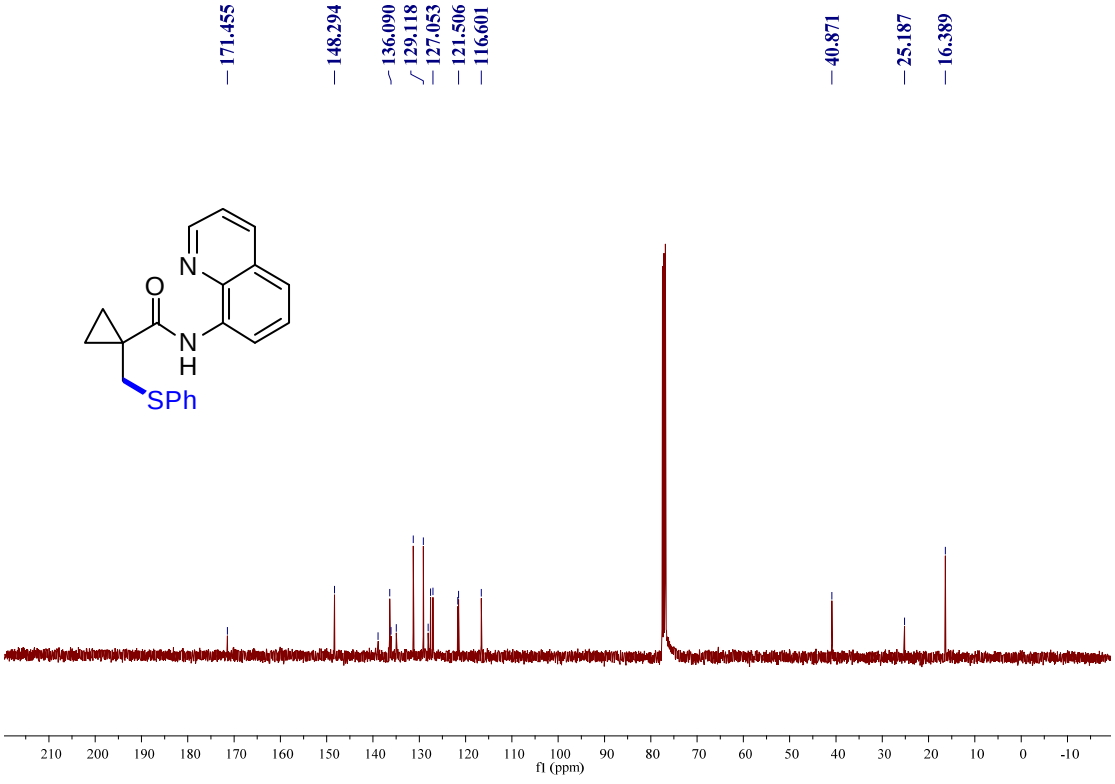
3g


10.274
8.745
8.734
8.162
8.142
7.531
7.492
7.440
7.419
7.388
7.210
7.172
7.134
7.088
3.402
3.372
3.297
3.265
3.254
3.242
3.208
2.000
1.982
1.964
1.945
1.035
1.017
0.999
N
O
N
H
SPh
0.93
1.84
1.00
2.26
3.24
7.96
1.01
2.77
1.96
2.92
fl (ppm)

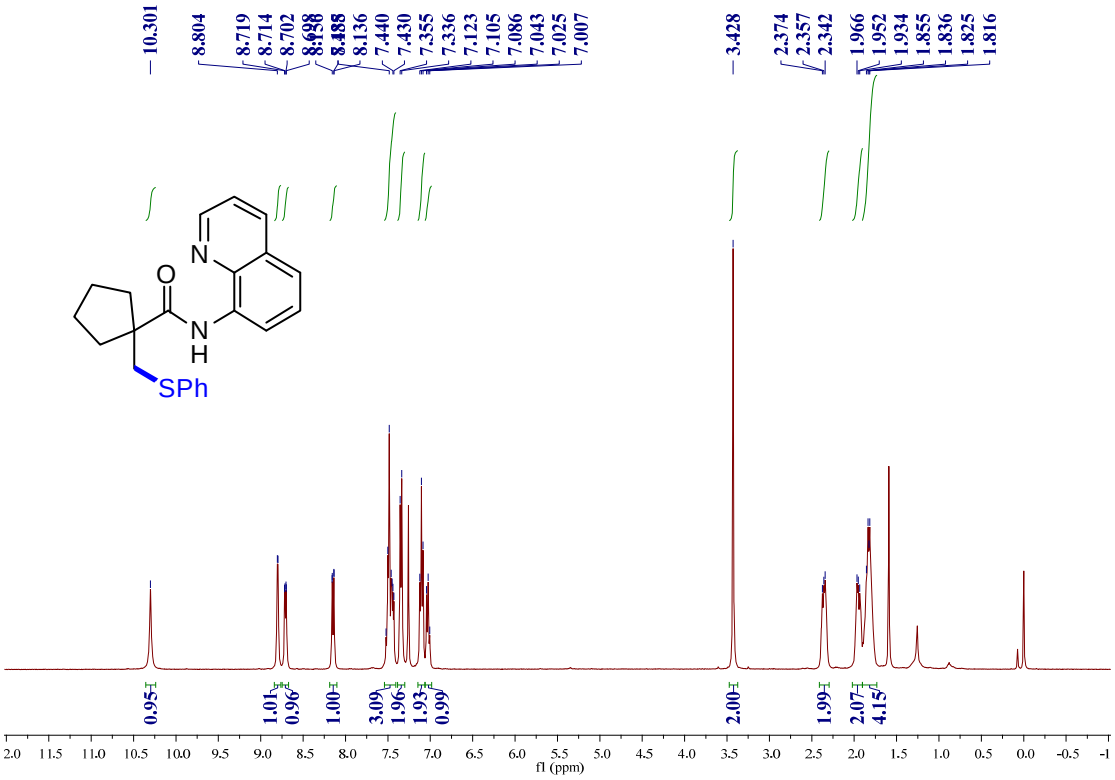

173.081
148.367
138.903
136.914
136.364
134.282
130.243
130.099
128.928
128.342
128.037
127.566
126.805
126.212
121.680
121.569
116.593
53.236
41.200
38.744
28.310
8.925
N
O
N
H
SPh
fl (ppm)

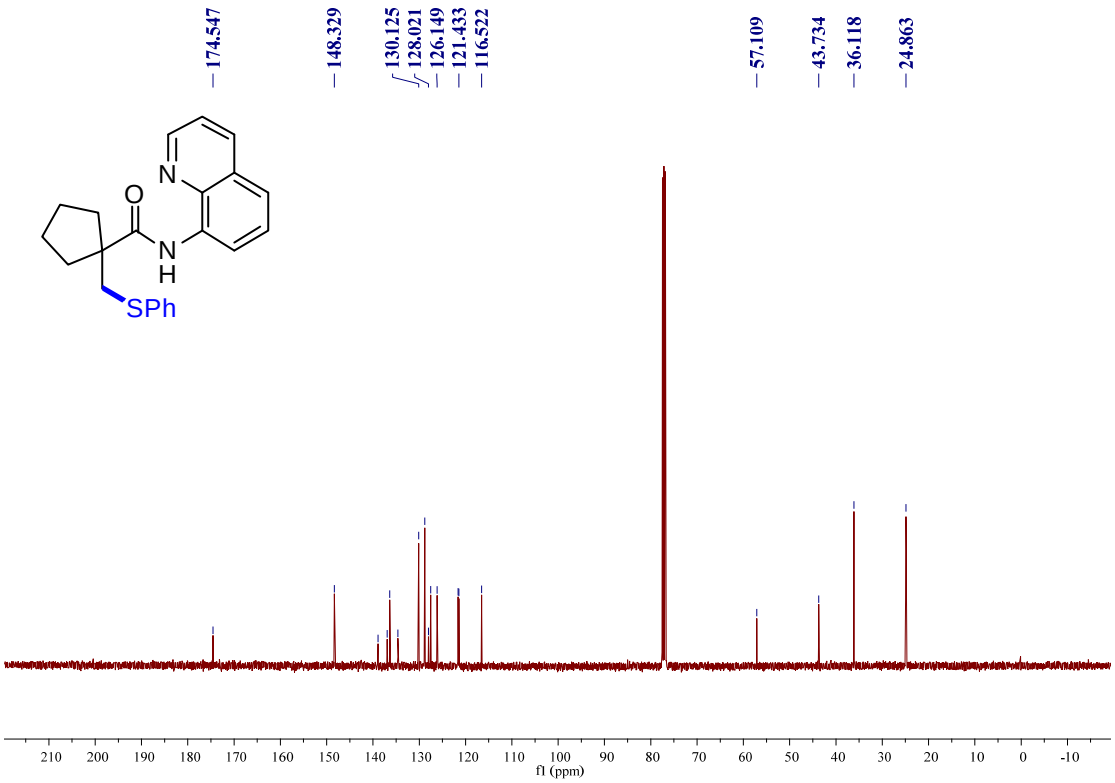
3h


10.799
8.755
8.752
8.719
8.711
8.709
8.159
7.439
7.428
7.418
7.339
7.320
7.301
7.259
7.243
7.225
3.489
1.503
1.492
1.486
1.476
0.958
0.948
0.942
0.931
0.99
0.91
1.00
1.00
4.02
1.17
2.14
1.20
2.00
1.97
1.98
N
O
N
H
SPh
f1 (ppm)

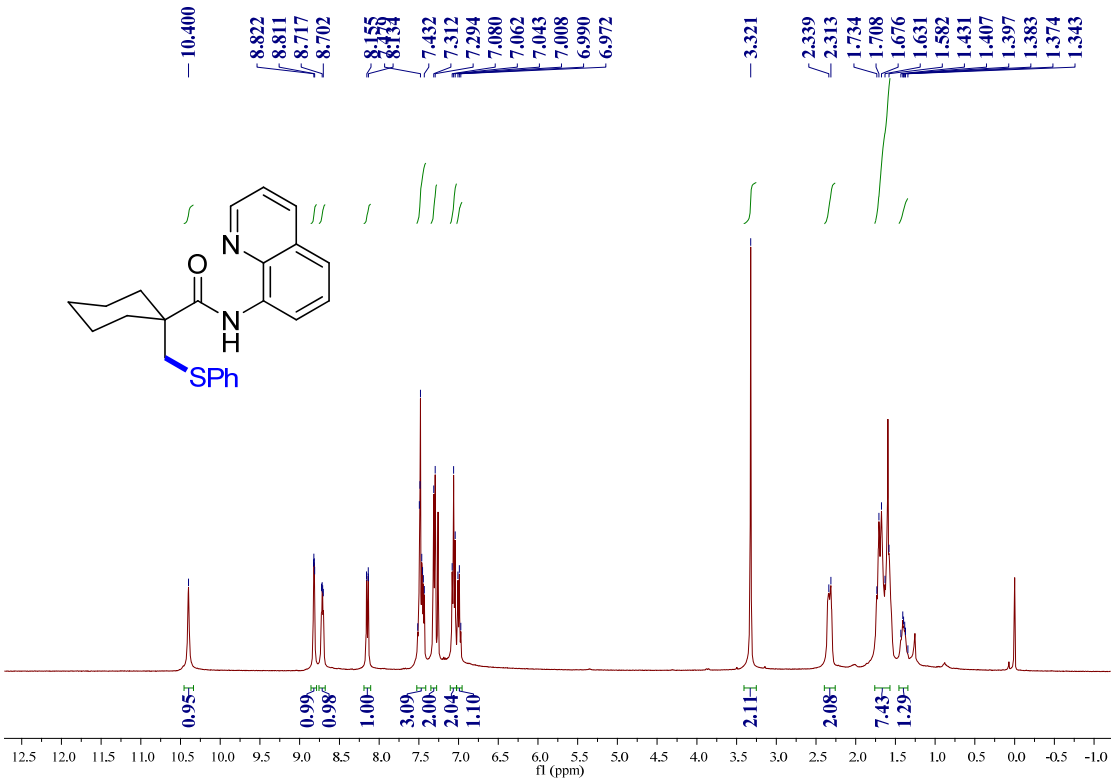

171.455
148.294
136.090
129.118
127.053
121.506
116.601
40.871
25.187
16.389
N
O
N
H
SPh
f1 (ppm)

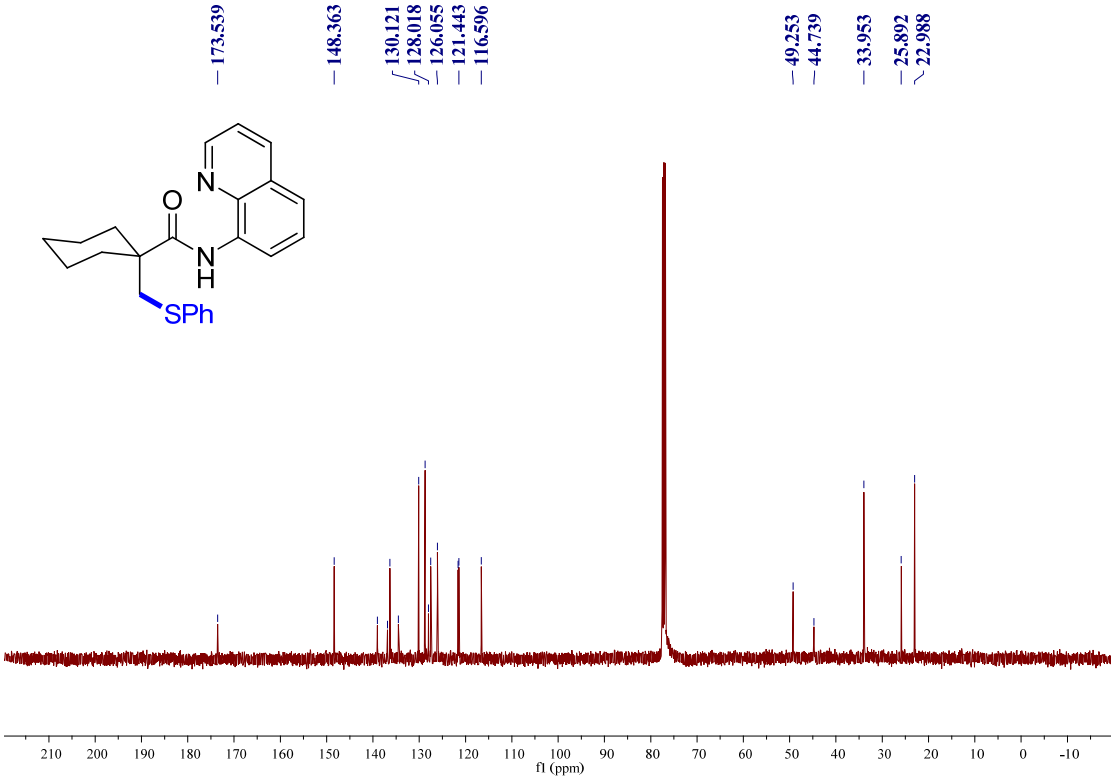
3i


10.301
8.804
8.719
8.714
8.702
8.136
7.440
7.430
7.355
7.336
7.123
7.105
7.086
7.043
7.025
7.007
3.428
2.374
2.357
2.342
1.966
1.952
1.934
1.855
1.836
1.825
1.816
0.95
1.01
0.96
1.00
3.09
1.96
1.93
0.99
2.00
1.99
2.07
4.15
N
O
N
H
SPh
f1 (ppm)

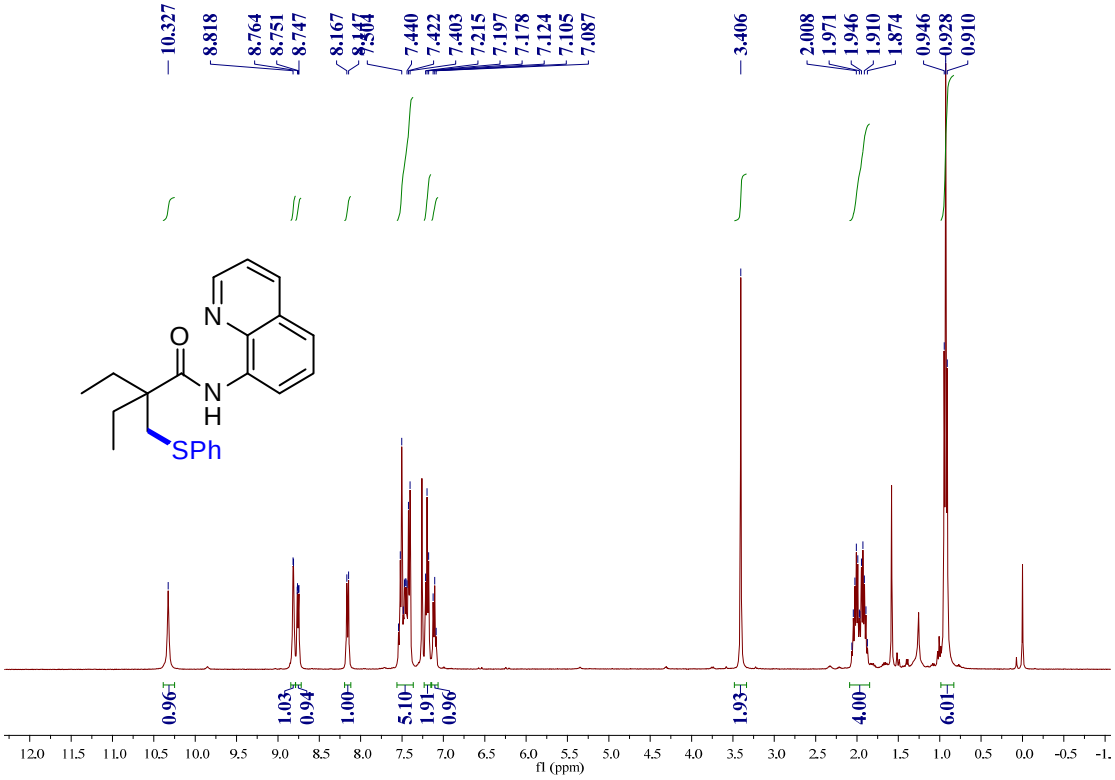

174.547
148.329
130.125
128.021
126.149
121.433
116.522
57.109
43.734
36.118
24.863
N
O
N
H
SPh
f1 (ppm)

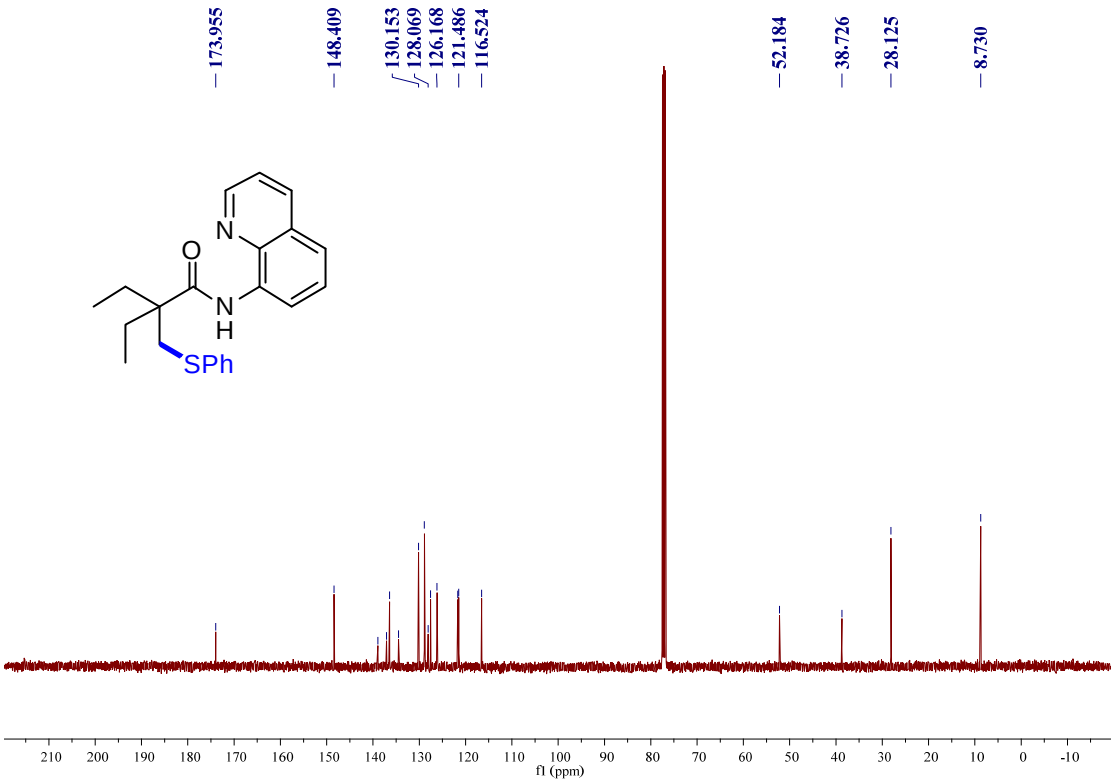
3j


10.400
8.822
8.811
8.717
8.702
8.155
8.134
7.432
7.312
7.294
7.080
7.062
7.043
7.008
6.990
6.972
3.321
2.339
2.313
1.734
1.708
1.676
1.631
1.582
1.431
1.407
1.397
1.383
1.374
1.343
0.95
0.99
0.98
1.00
3.09
2.00
2.04
1.10
2.11
2.08
7.43
1.29
O
N
H
SPh
f1 (ppm)

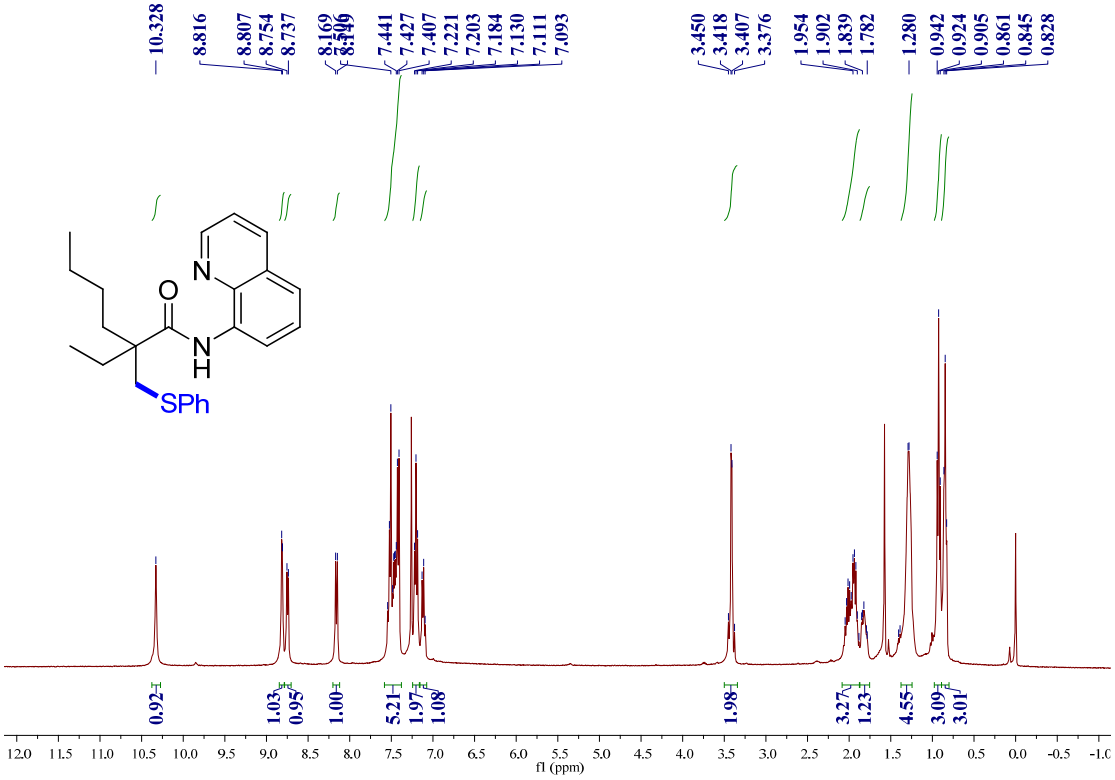

173.539
148.363
130.121
128.018
126.055
121.443
116.596
49.253
44.739
33.953
25.892
22.988
O
N
H
SPh
f1 (ppm)

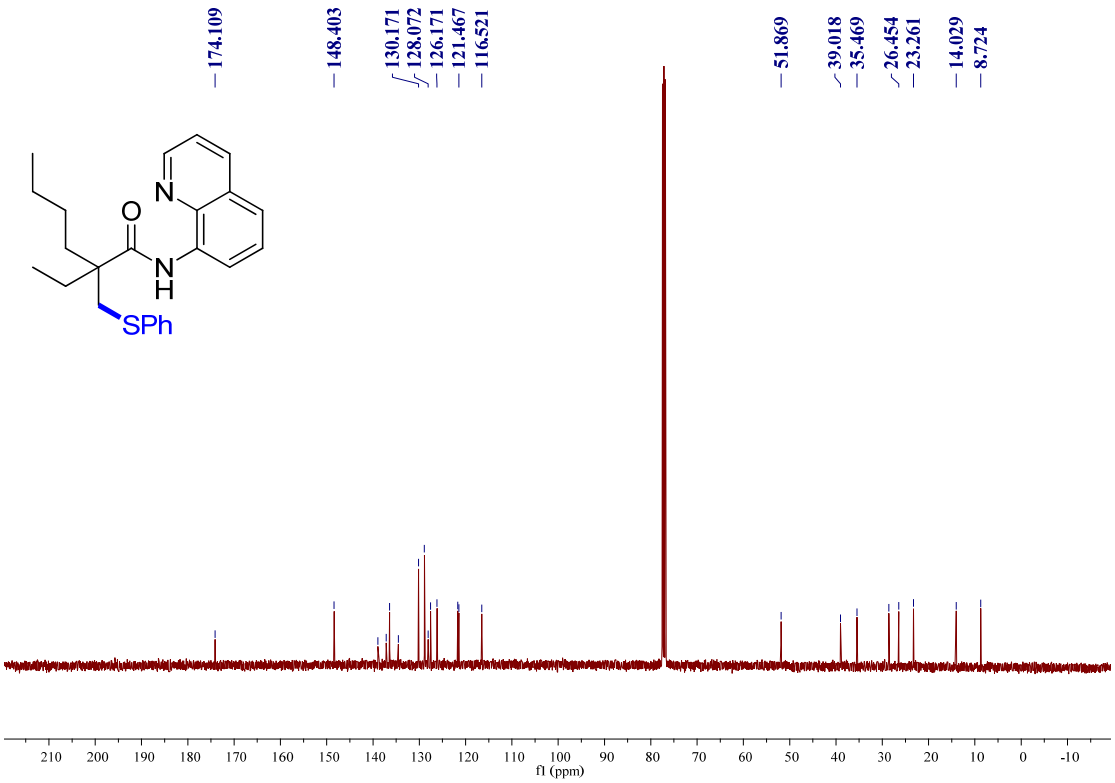
3k


10.327
8.818
8.764
8.751
8.747
8.167
7.440
7.422
7.403
7.215
7.197
7.178
7.124
7.105
7.087
3.406
2.008
1.971
1.946
1.910
1.874
0.946
0.928
0.910
0.96
1.03
0.94
1.00
5.10
1.91
0.96
1.93
4.00
6.01
N
O
N
H
SPh
f1 (ppm)

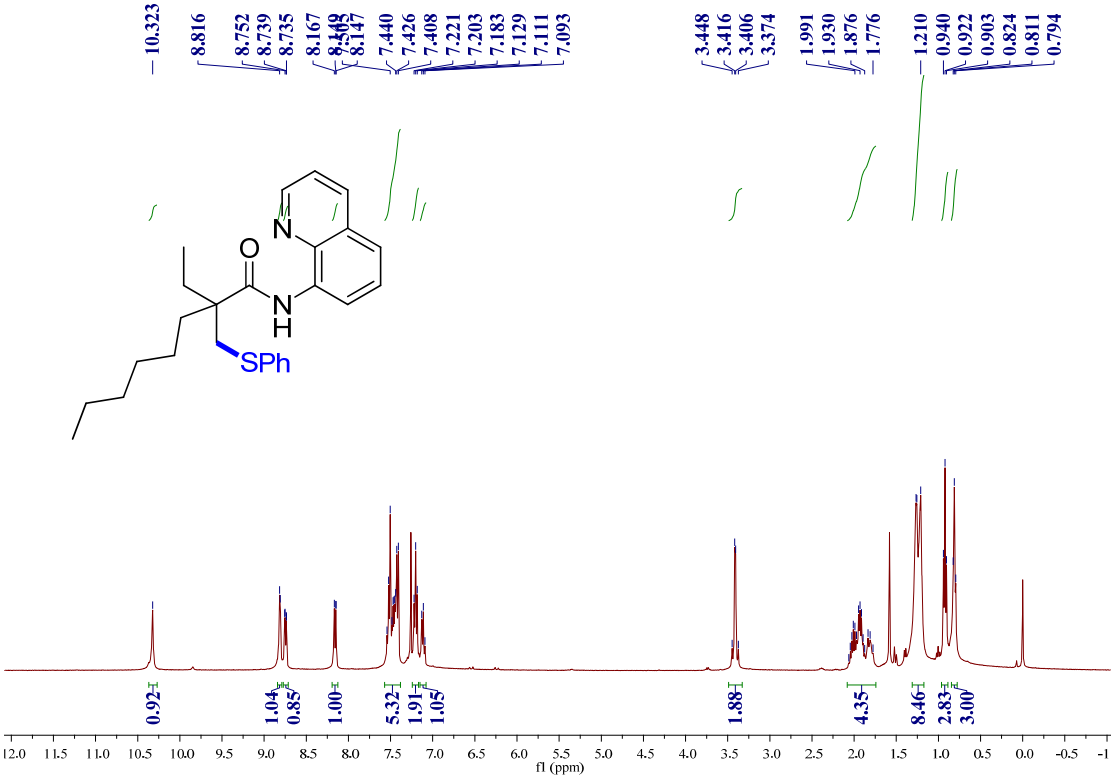

173.955
148.409
130.153
128.069
126.168
121.486
116.524
52.184
38.726
28.125
8.730
N
O
N
H
SPh
f1 (ppm)

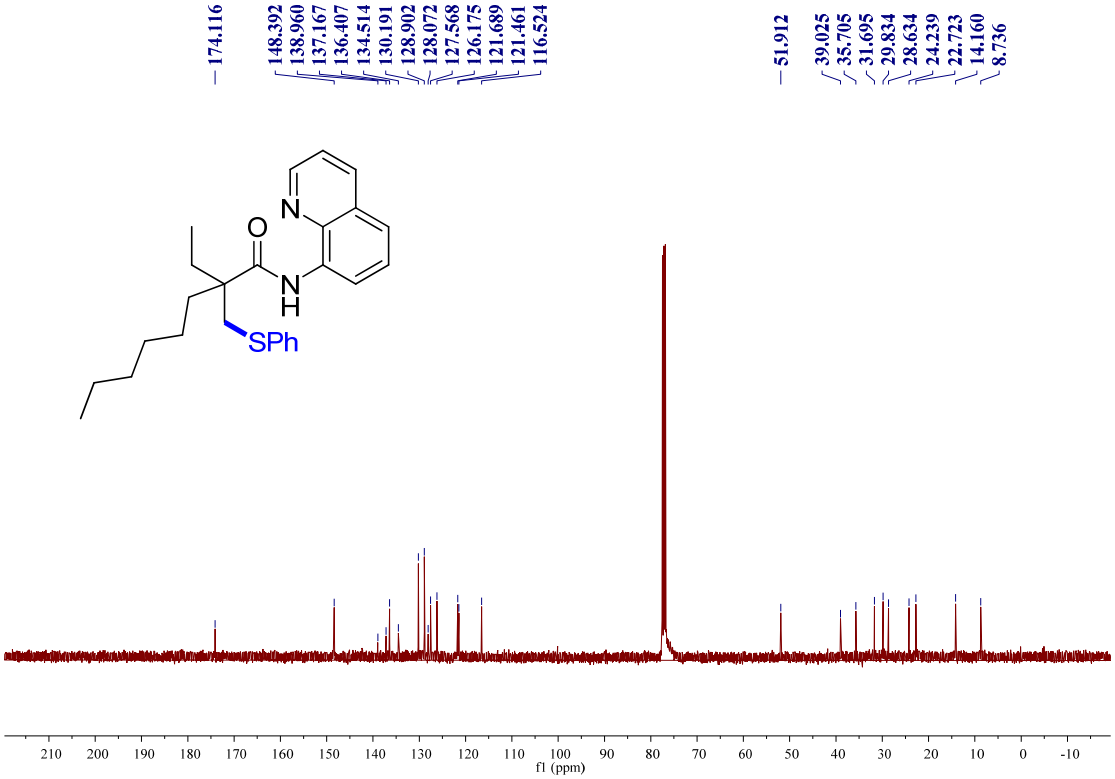
3l


10.328
8.816
8.807
8.754
8.737
8.169
8.146
7.441
7.427
7.407
7.221
7.203
7.184
7.130
7.111
7.093
3.450
3.418
3.407
3.376
1.954
1.902
1.839
1.782
1.280
0.942
0.924
0.905
0.861
0.845
0.828
0.92
1.03
0.95
1.00
5.21
1.97
1.08
1.98
3.27
1.23
4.55
3.09
3.01
N
O
N
H
SPh
f1 (ppm)

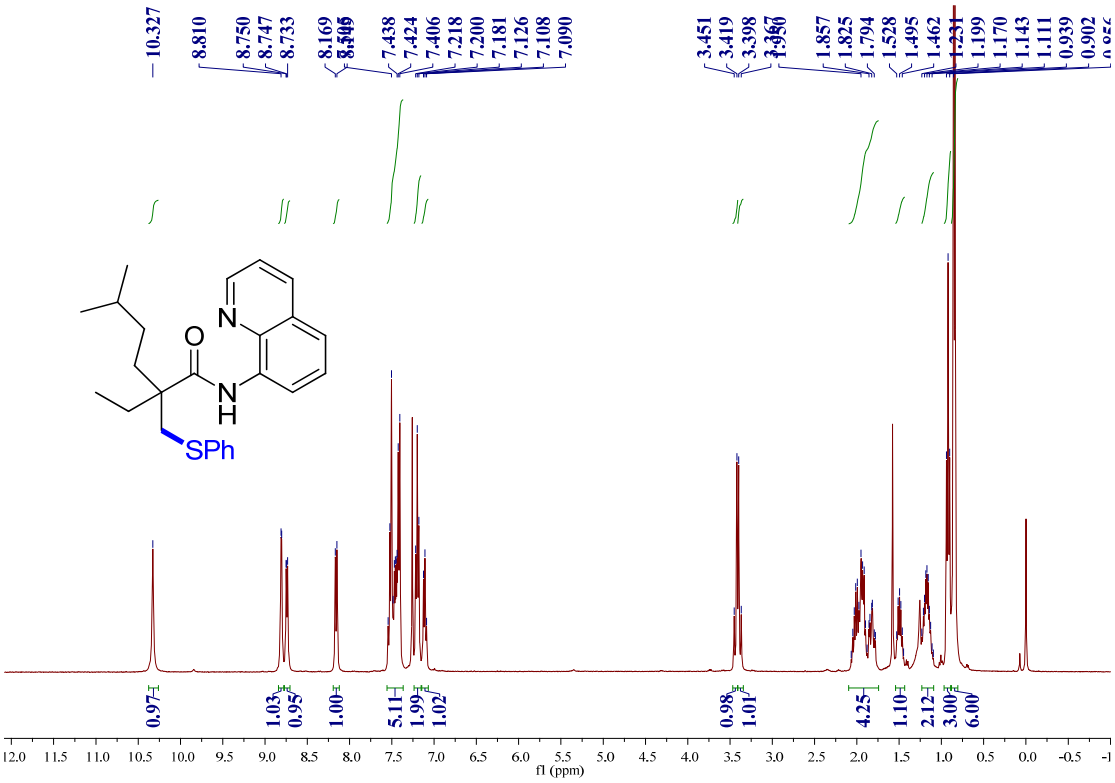

174.109
148.403
130.171
128.072
126.171
121.467
116.521
51.869
39.018
35.469
26.454
23.261
14.029
8.724
N
O
N
H
SPh
f1 (ppm)

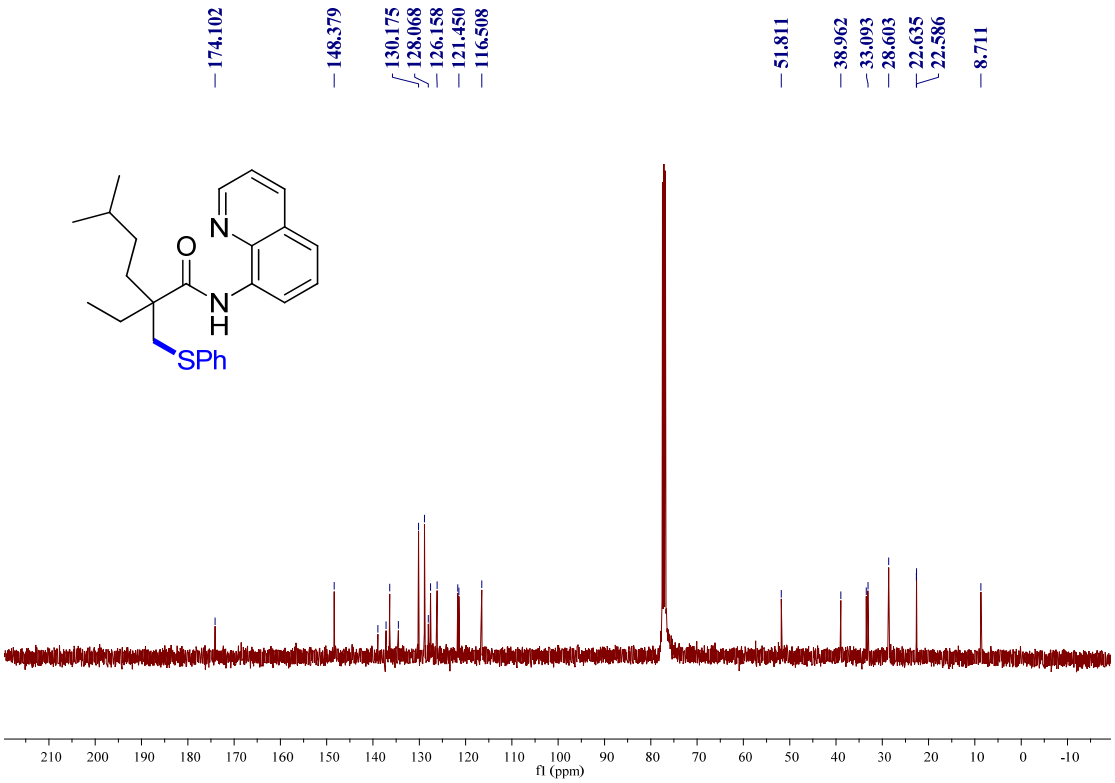
3m


10.323
8.816
8.752
8.739
8.735
8.167
8.149
8.147
7.440
7.426
7.408
7.221
7.203
7.183
7.129
7.111
7.093
3.448
3.416
3.406
3.374
1.991
1.930
1.876
1.776
1.210
0.940
0.922
0.903
0.824
0.811
0.794
N
O
N
H
SPh
0.92
1.04
0.85
1.00
5.32
1.91
1.05
1.88
4.35
8.46
2.83
3.00
f1 (ppm)

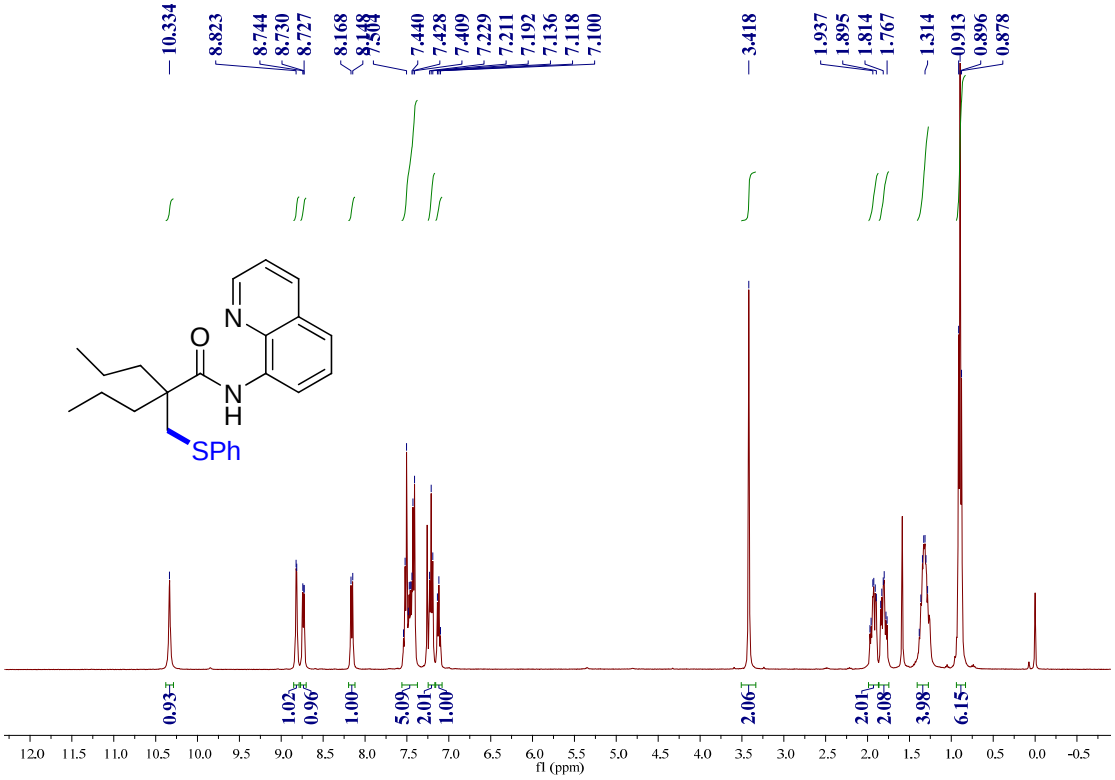

174.116
148.392
138.960
137.167
136.407
134.514
130.191
128.902
128.072
127.568
126.175
121.689
121.461
116.524
51.912
39.025
35.705
31.695
29.834
28.634
24.239
22.723
14.160
8.736
N
O
N
H
SPh
f1 (ppm)

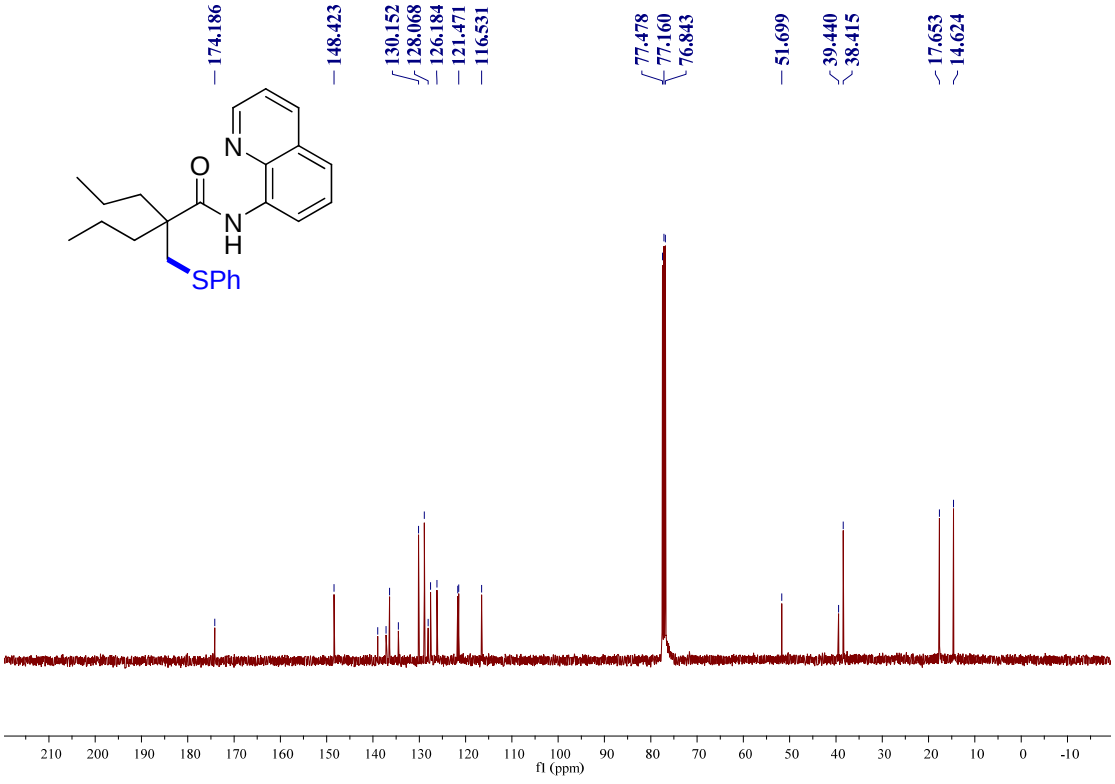
3n


10.327
8.810
8.750
8.747
8.733
8.169
7.438
7.424
7.406
7.218
7.200
7.181
7.126
7.108
7.090
3.451
3.419
3.398
1.857
1.825
1.794
1.528
1.495
1.462
1.231
1.199
1.170
1.143
1.111
0.939
0.902
0.97
1.03
0.95
1.00
5.11
1.99
1.02
0.98
1.01
4.25
1.10
2.12
3.00
6.00
O
N
N
H
SPh
f1 (ppm)

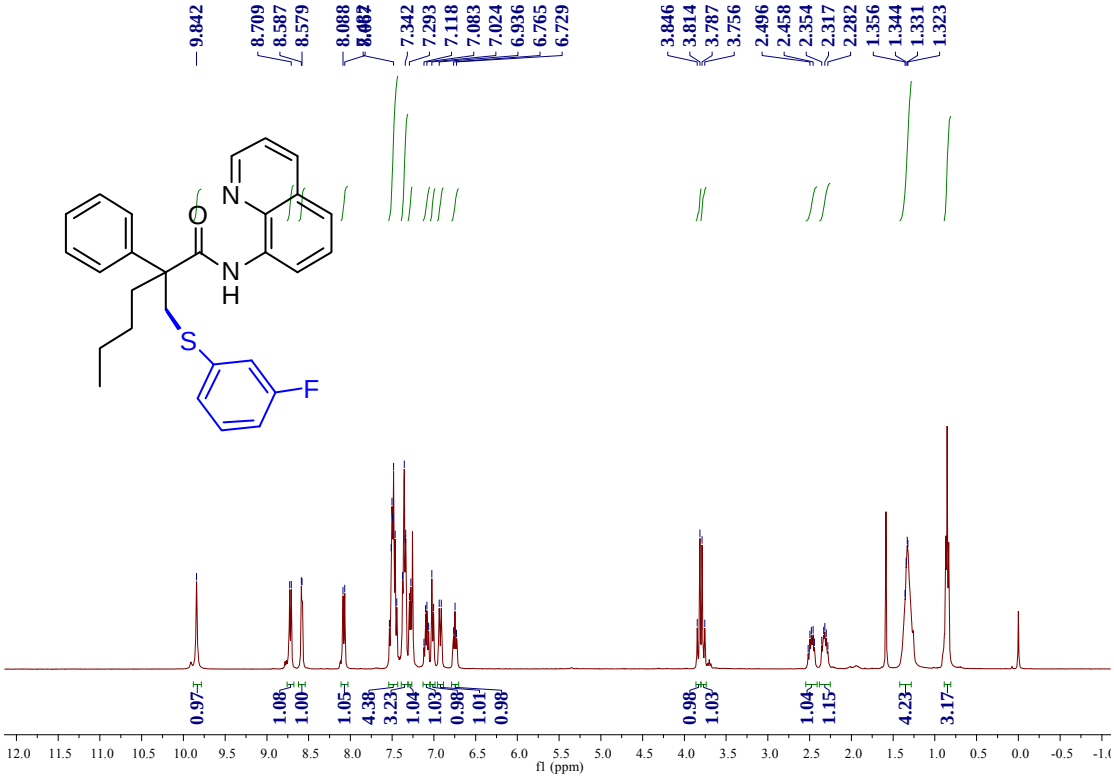

174.102
148.379
130.175
128.068
126.158
121.450
116.508
51.811
38.962
33.093
28.603
22.635
22.586
8.711
O
N
N
H
SPh
f1 (ppm)

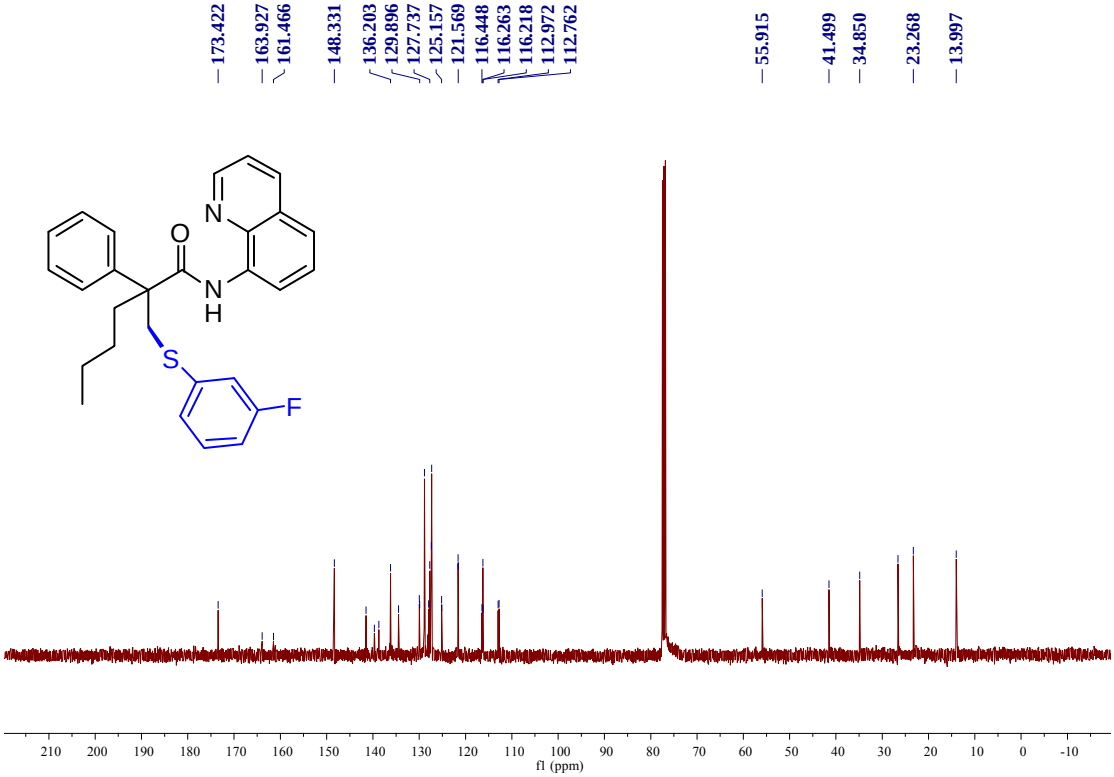
3o


10.334
8.823
8.744
8.730
8.727
8.168
8.148
7.504
7.440
7.428
7.409
7.229
7.211
7.192
7.136
7.118
7.100
3.418
1.937
1.895
1.814
1.767
1.314
0.913
0.896
0.878
0.93
1.02
0.96
1.00
5.09
2.01
1.00
2.06
2.01
2.08
3.98
6.15
N
O
N
H
SPh
f1 (ppm)

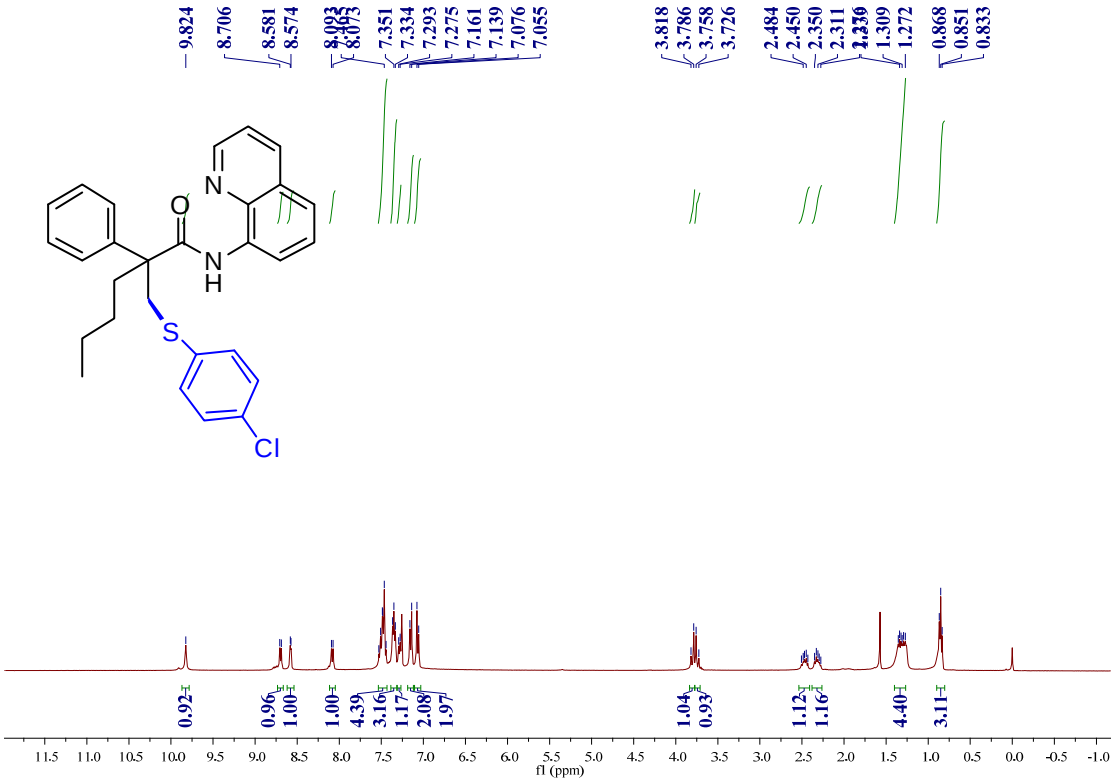

174.186
148.423
130.152
128.068
126.184
121.471
116.531
77.478
77.160
76.843
51.699
39.440
38.415
17.653
14.624
N
O
N
H
SPh
f1 (ppm)

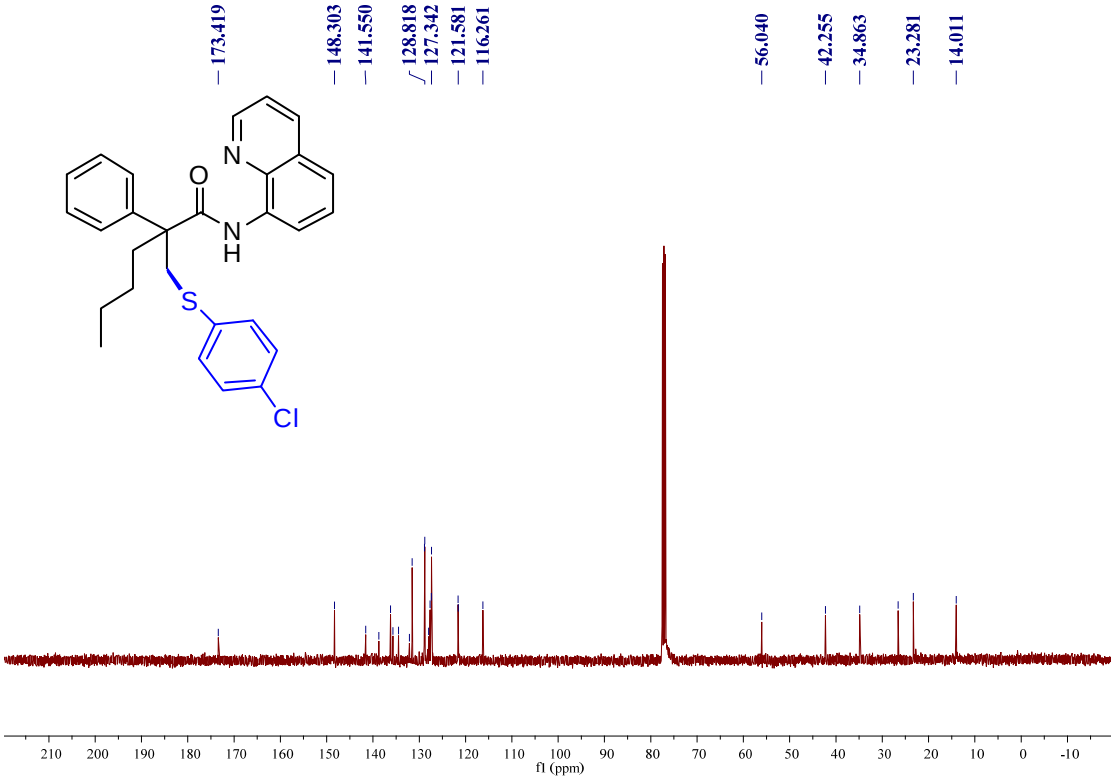
5a


9.842
8.709
8.587
8.579
8.088
7.342
7.293
7.118
7.083
7.024
6.936
6.765
6.729
3.846
3.814
3.787
3.756
2.496
2.458
2.354
2.317
2.282
1.356
1.344
1.331
1.323
0.97
1.08
1.00
1.05
4.38
3.23
1.04
1.03
0.98
1.01
0.98
0.98
1.03
1.04
1.15
4.23
3.17
f1 (ppm)

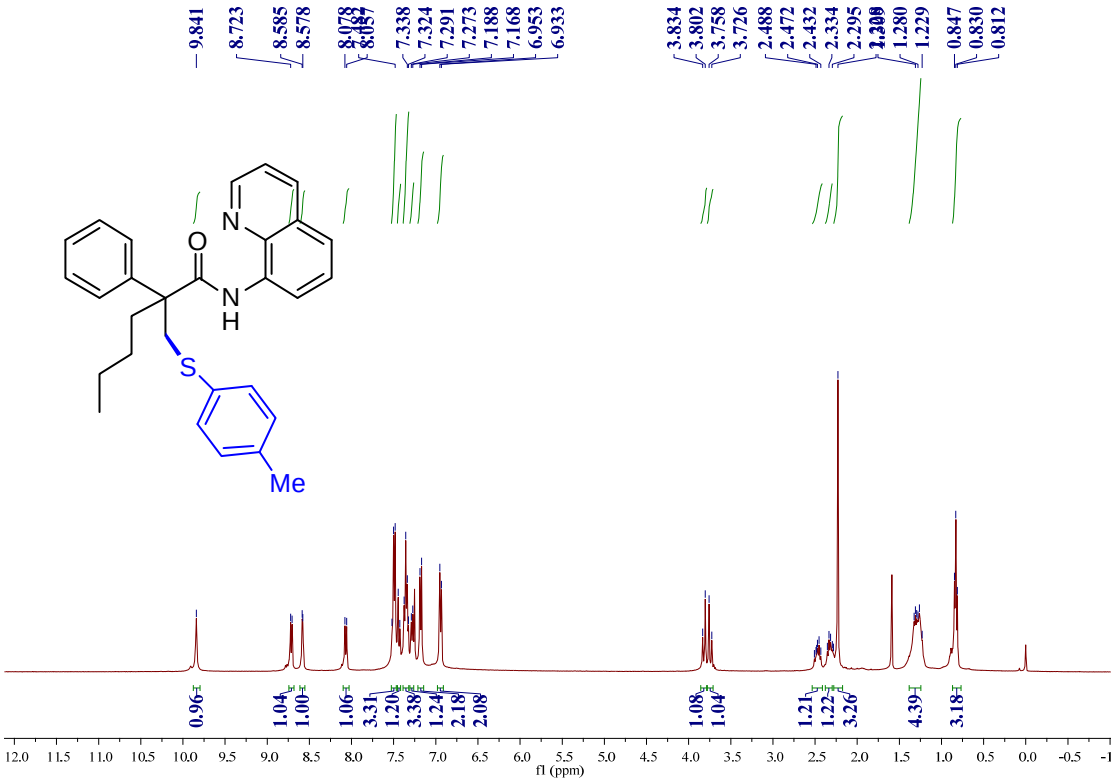

173.422
163.927
161.466
148.331
136.203
129.896
127.737
125.157
121.569
116.448
116.263
116.218
112.972
112.762
55.915
41.499
34.850
23.268
13.997
f1 (ppm)

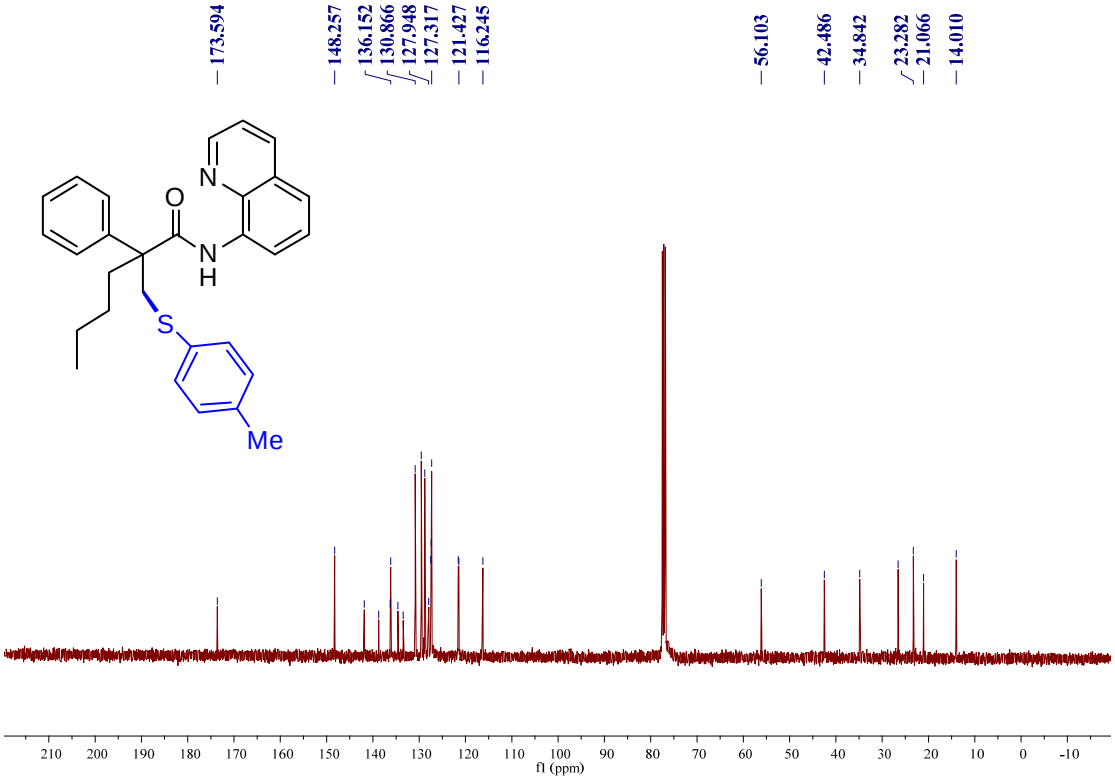
5b


9.824
8.706
8.581
8.574
8.093
8.073
7.351
7.334
7.293
7.275
7.161
7.139
7.076
7.055
3.818
3.786
3.758
3.726
2.484
2.450
2.350
2.311
1.309
1.272
0.868
0.851
0.833
0.92
0.96
1.00
1.00
4.39
3.16
1.17
2.08
1.97
1.04
0.93
1.12
1.16
4.40
3.11
f1 (ppm)

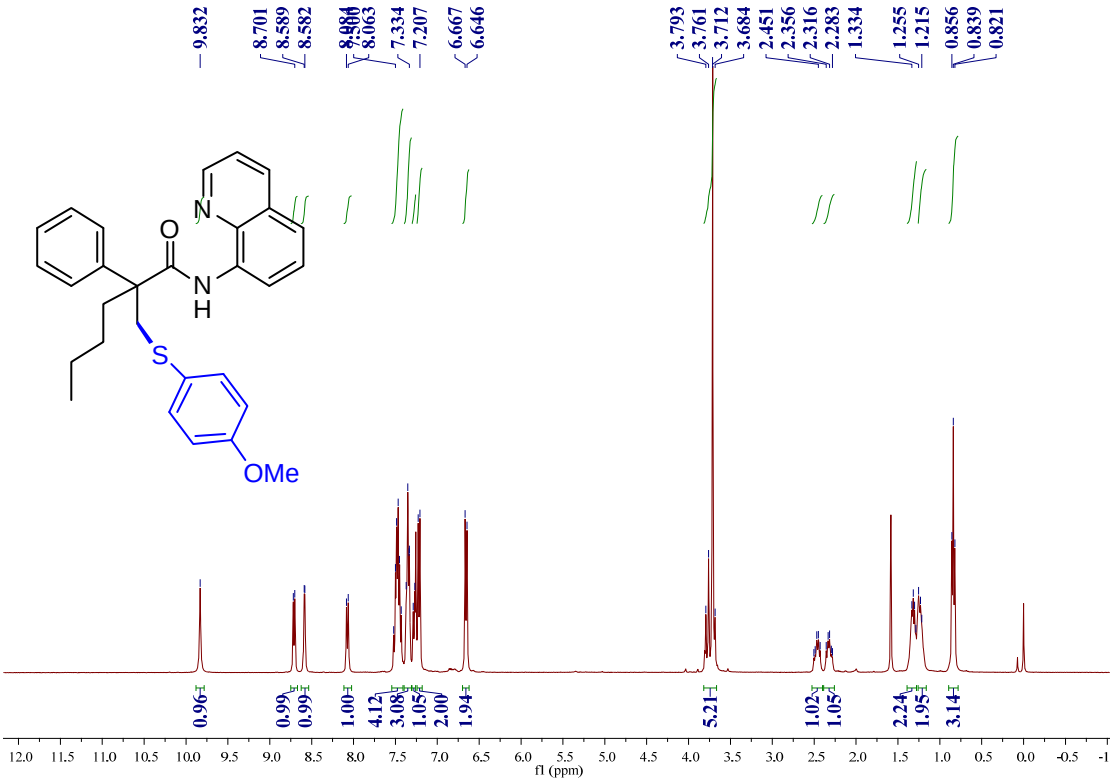

173.419
148.303
141.550
128.818
127.342
121.581
116.261
56.040
42.255
34.863
23.281
14.011
f1 (ppm)

5c


9.841
8.723
8.585
8.578
8.078
8.057
7.338
7.324
7.291
7.273
7.188
7.168
6.953
6.933
3.834
3.802
3.758
3.726
2.488
2.472
2.432
2.334
2.295
1.280
1.229
0.847
0.830
0.812
N
O
N
H
S
Me
0.96
1.04
1.00
1.06
3.31
1.20
3.38
1.24
2.18
2.08
1.08
1.04
1.21
1.22
3.26
4.39
3.18
fl (ppm)


173.594
148.257
136.152
130.866
127.948
127.317
121.427
116.245
56.103
42.486
34.842
23.282
21.066
14.010
N
O
N
H
S
Me
fl (ppm)

5d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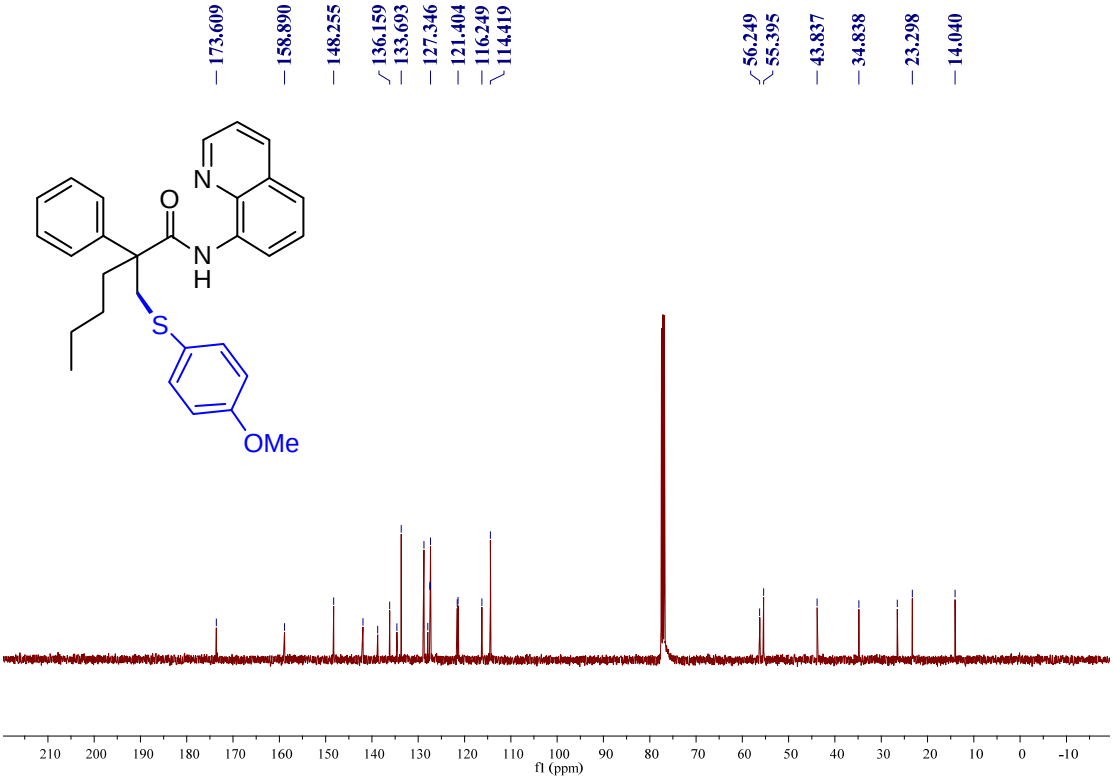
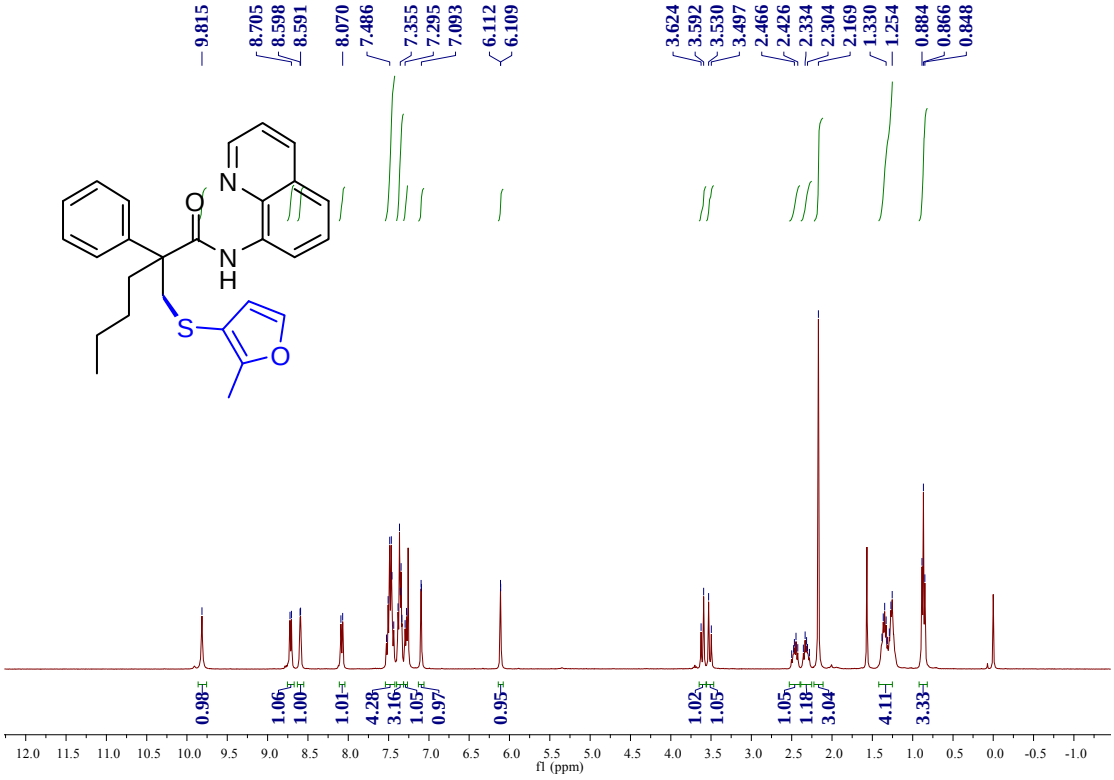
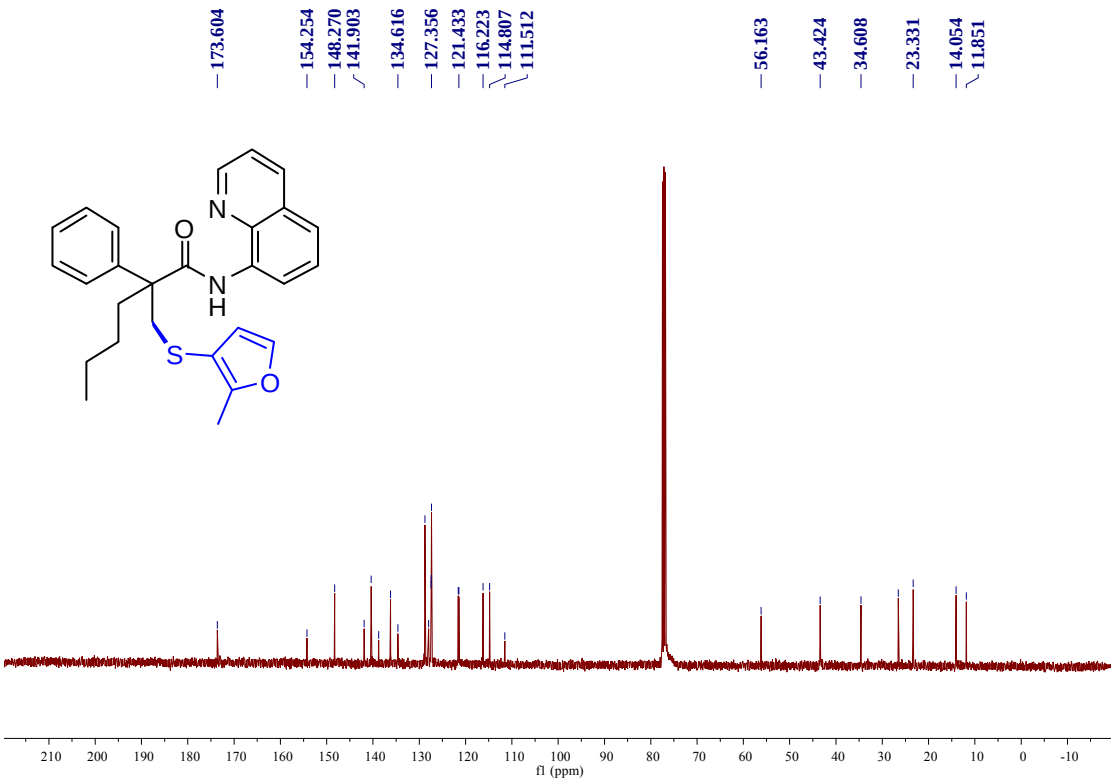
8.582
8.063
7.334
7.207
6.667
6.646
3.793
3.761
3.712
3.684
2.451
2.356
2.316
2.283
1.334
1.255
1.215
0.856
0.839
0.821
0.96
0.99
0.99
1.00
4.12
3.08
1.05
2.00
1.94
5.21
1.02
1.05
2.24
1.95
3.14
O
N
H
S
OMe
f1 (ppm)

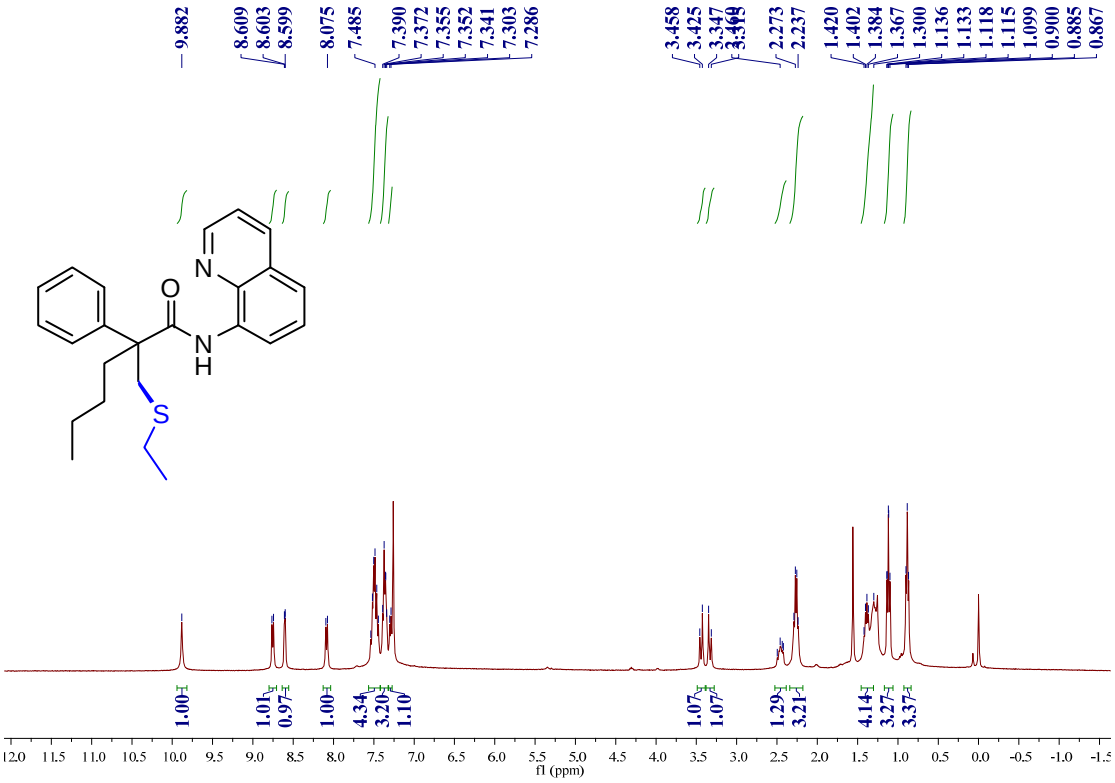

173.609
158.890
148.255
136.159
133.693
127.346
121.404
116.249
114.419
56.249
55.395
43.837
34.838
23.298
14.040
O
N
H
S
OMe
f1 (ppm)

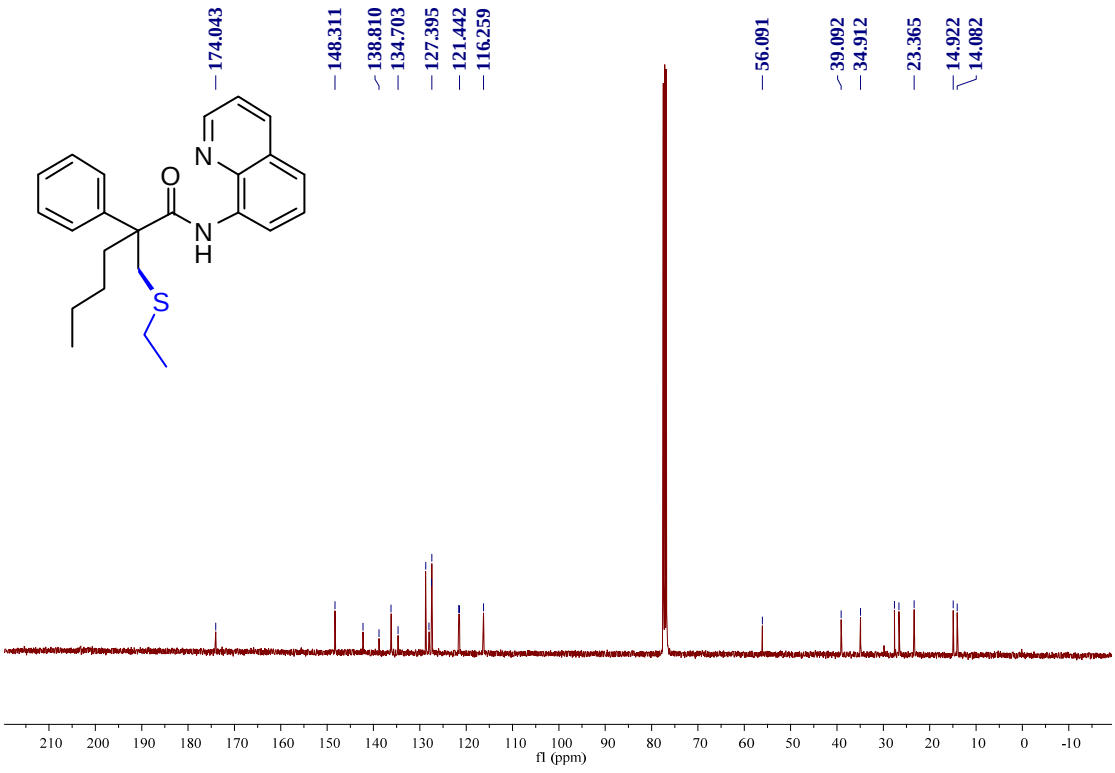
5e


9.815
8.705
8.598
8.591
8.070
7.486
7.355
7.295
7.093
6.112
6.109
3.624
3.592
3.530
3.497
2.466
2.426
2.334
2.304
2.169
1.330
1.254
0.884
0.866
0.848
0.98
1.06
1.00
1.01
4.28
3.16
1.05
0.97
0.95
1.02
1.05
1.05
1.18
3.04
4.11
3.33
f1 (ppm)


173.604
154.254
148.270
141.903
134.616
127.356
121.433
116.223
114.807
111.512
56.163
43.424
34.608
23.331
14.054
11.851
f1 (ppm)

5f


9.882
8.609
8.603
8.599
8.075
7.485
7.390
7.372
7.355
7.352
7.341
7.303
7.286
3.458
3.425
3.347
2.273
2.237
1.420
1.402
1.384
1.367
1.300
1.136
1.133
1.118
1.115
1.099
0.900
0.885
0.867
O
N
H
S
1.00
1.01
0.97
1.00
4.34
3.20
1.10
1.07
1.07
1.29
3.21
4.14
3.27
3.37
fl (ppm)


174.043
148.311
138.810
134.703
127.395
121.442
116.259
56.091
39.092
34.912
23.365
14.922
14.082
O
N
H
S
fl (ppm)