Supporting Information for

Catalytic Asymmetric Synthesis of Chiral Thiohydantoins *via* Domino Cyclization Reaction of *β,γ*-Unsaturated *α*-Ketoester and *N,N'*-Dialkylthiourea

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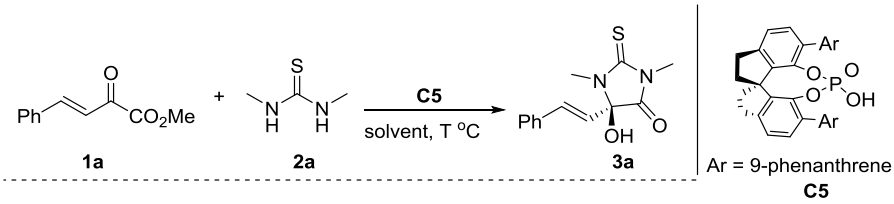
Contents

1. General information

All reactions were carried out in oven-dried Schlenk, and monitored by thin layer chromatography (TLC). All reagents were reagent grade quality and purchased from commercial sources unless otherwise indicated. NMR spectra were recorded with a 600 MHz or 400 MHz spectrometer for ^{1}H NMR, 150 MHz or 100 MHz for ^{13}C NMR. Chemical shifts δ are given in ppm relative to the residual proton signals of the deuterated solvent $CDCl_3$ for ^{1}H and ^{13}C NMR. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), multiplet (m), sextex (sext). High resolution mass spectra were recorded on a 3000 mass spectrometer. For column chromatography, silica gel (200-300 mesh) was used as the stationary phase. Chiral HPLC analysis recorded on Thermo scientific Dionex Ultimate 3000. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in solvent). Optical rotations recorded on Autopol Automatic Polarimeter. HRMS was recorded on an ABI/Sciex QStar Mass Spectrometer (ESI).

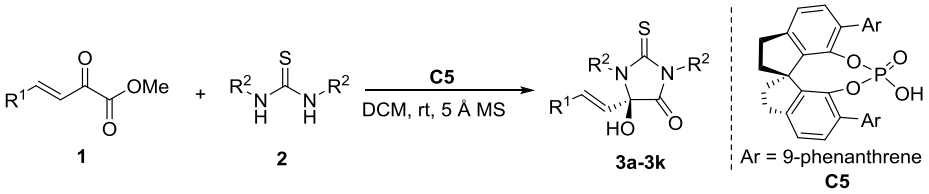
2. Screening of the reaction conditions



Entry	Solvent	T °C	Additive	Yield[b] (%)	ee[c] (%)
1	$CHCl_3$	RT		52	88
2	CH_3OH	RT		Trace	
3	H_2O	RT		NR	
4	Dioxane	RT		NR	
5	CH_3CN	RT		15	88
6	EtOAc	RT		23	85
7	DCM	RT	K_2CO_3	98	0
8	DCM	RT	Na_2CO_3	97	0
9	DCM	RT	CF_3COOH	95	0
10	DCM	RT	CH_3COOH	93	0
11	DCM	RT	HCOOH	93	0
12	DCM	RT	Citric acid	95	0
13[d]	DCM	RT	5 Å MS	83	97
14[e]	DCM	0 °C	5 Å MS	63	92
15[f]	DCM	-20 °C	5 Å MS	58	92

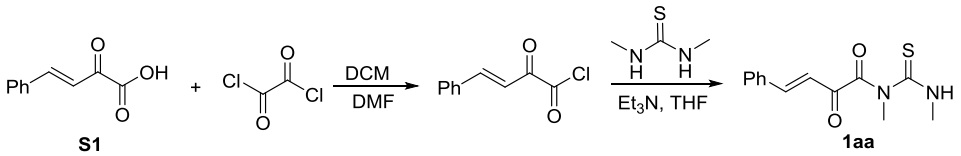
[a]Unless otherwise noted, the reaction conditions were as follows: Cat. (20 mol%), **1a** (0.1 mmol), **2a** (0.4 mmol), and additive (1 equiv) in solvent (2 mL) at room temperature for 24 h. [b]Isolated yields. [c]Determined by chiral HPLC analysis. [d]Under N_2. [e]At 0 °C. [f]At -20 °C.

3. General procedure for consturct chiral thiohydantoins



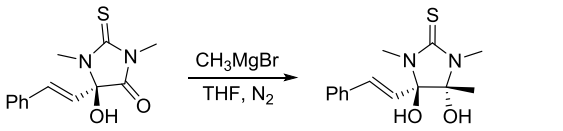
In a test tube, *N,N'*-dialkylthiourea **2** (0.4 mmol), **C5** (0.02 mmol, 20 mol %), 5 Å MS (40 mg) and *β,γ*-unsaturated *α*-ketoester **1** (0.1 mmol) were added. Then, DCM (1.0 mL) was added and the mixture was stirred at room temperature until **1** was consumed (determined by TLC). Then the solvent was removed and the mixture was purified by preparation of thin layer chromatography silica gel plate (PE/EA = 3:1) or flash column chromatography (PE/EA = 5:1) to afford the products.

4. Synthesis of reaction intermediates 1aa

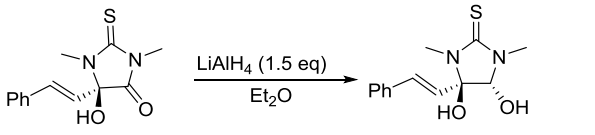


1aa were synthesized from **S1** according to the literature procedure. [1-2]

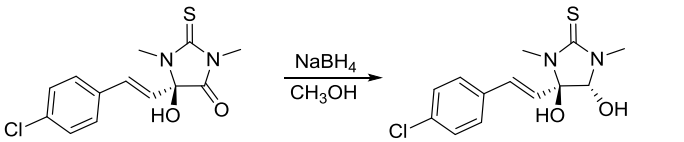
5. Transformation of products



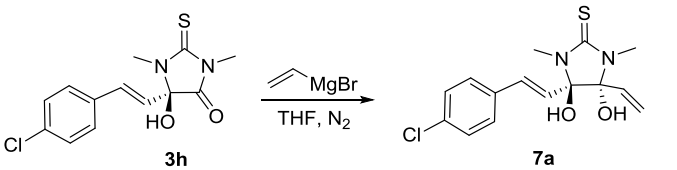
Compound **4a** was prepared according to the reported procedures.[3] To a Schlenk tube equipped with a magnetic stir bar, compound **3a** (26.2 mg, 0.1 mmol, 97% ee) were added. The tube was evacuated and backfilled with N_2 for 3 times and then charged with dry THF (2.0 mL) via syringe. To above stirred solution was added methyl magnesium bromide (0.3 mL of 1.0 M solution in THF, 3.0 equiv) slowly and the reaction was stirred at room temperature for 3.0 h. After the reaction was complete (monitored by TLC). The crude product was quenched with saturated aqueous $NaHCO_3$, and extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried and concentrated. Then the residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate = 3/1) to afford product **4a** as a white solid.



Compound **5a** was prepared according to the reported procedures.[4] $LiAlH_4$ (5.7 mg, 0.15 mmol) was added to a solution of **3a** (26.2 mg, 0.1 mmol, 97% ee) in anhydrous Et_2O (1.5 mL). The reaction mixture was stirred at room temperature for 1.0 h and the reaction was monitored by TLC. Upon completion, the solvents were removed in vacuo. The crude product was then purified by preparative thin layer chromatography (petroleum ether /ethyl acetate = 3/1) to afford product **5a** as a white solid.



Compound **7a** was prepared according to the reported procedures.[3]To a solution of **3h** (29.6 mg, 0.1 mmol, 97% ee) in MeOH, $NaBH_4$ (11.3 mg, 0.3 mmol, 3.0 equiv) was added at the room tempreture for 2.0 h. After **3 h** was consumed (determined by TLC), saturated NH_4Cl aqueous solution (2 mL) was added. The aqueous phase was extracted with ethyl acetate (3 × 10 mL) and the combined organic phases were dried and concentrated. The residue was purified by column chromatography (petroleum ether /ethyl acetate = 3/1) to afford product **6a** as a white solid.

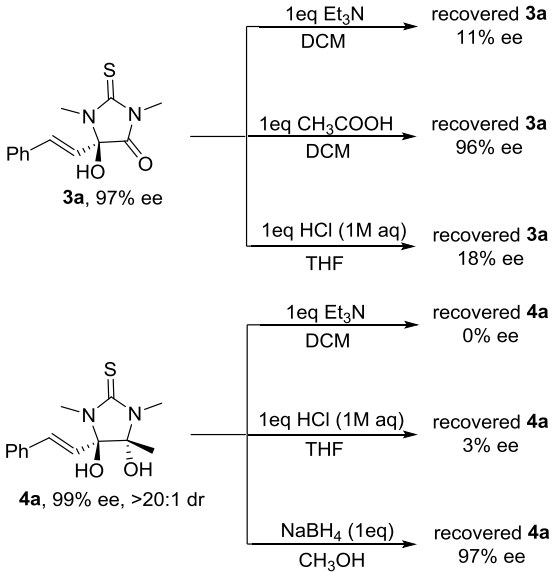


3h
97% ee

7a
93% yield, dr > 20:1, 96% ee

Compound **7a** was prepared according to the reported procedures.[4] To a Schlenk tube equipped with a magnetic stir bar, compound **3h** (29.6 mg, 0.1 mmol, 97% ee) were added. The tube was evacuated and backfilled with N_2 for 3 times and then charged with dry THF (2.0 mL) via syringe. To above stirred solution was added vinyl magnesium bromide (0.3 mL of 1.0 M solution in THF, 0.3 mmol, 3.0 equiv) slowly and the reaction was stirred at room temperature for 3.0 h. After the reaction was complete (monitored by TLC). The crude product was quenched with saturated aqueous $NaHCO_3$, and extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried and concentrated. Then the residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate = 3/1) to afford product **7a** as a white solid.

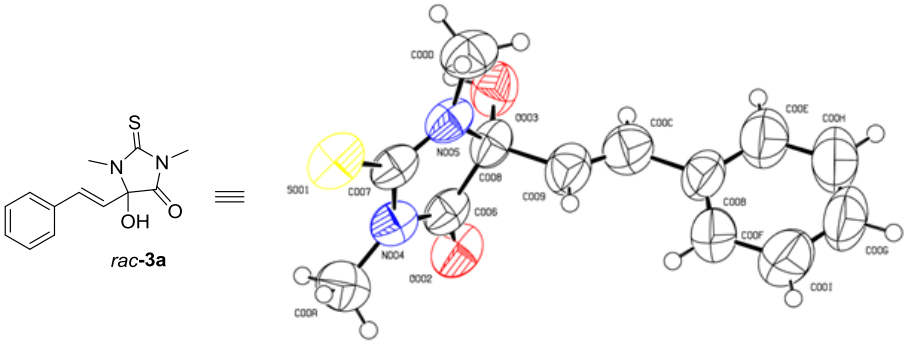
Configurationally stability assessment of 3a and 4a in basic and acidic conditions



The configurationally stability of **3a** and **4a** were tested in basic and acidic conditions. Treated with Et_3N and 1.0 M hydrochloric acid, **3a** was almost racemic. Treated with CH_3COOH, the ee value of recovered compound **3a** was maintained. Hydrochloric acid and Et_3N all could racemize **4a**. However, the ee value of **4a** is maintained by treatment with $NaBH_4$.

6. The X-ray data for thiohydantoin *rac*-3a and 5a and 7a

Recrystallization in petroleum ether/dichloromethane/ diethyl ether afforded crystals suitable for X-ray analysis.



A single-crystal X-ray diffraction data for *rac*-**3a** was collected on a Supernova Atlas S2 CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. The unit cell parameters and the data reduction were obtained with the CrysAlisPro software. During data processing a data scaling and empirical or multi-scan absorption corrections were also performed with CrysAlisPro software.

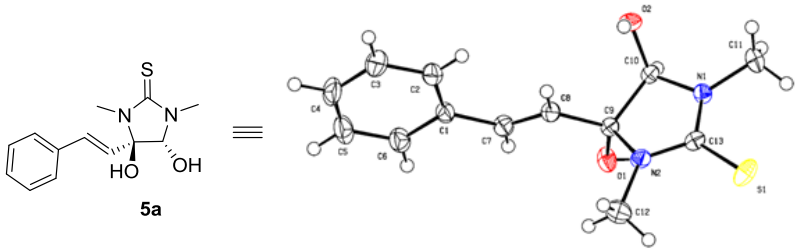
CCDC 2102585 (*rac*-**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table 1 Crystal data and structure refinement for *rac*-3a

Identification code	*rac*-**3a**
Empirical formula	$C_{13}H_{14}N_2O_2S$
Formula weight	262.32
Temperature/K	294.78(10)
Crystal system	monoclinic
Space group	P21/c
a/Å	13.7357(9)
b/Å	15.0653(8)
c/Å	6.8017(4)
α/°	90
β/°	92.185(6)
γ/°	90
Volume/Å^3	1406.47(14)
Z	4
ρcalcg/cm^3	1.239
μ/mm^{-1}	0.226
F(000)	552.0

Crystal size/mm^3	0.38 × 0.18 × 0.09
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/	6.576 to 59.332
Index ranges	-13 ≤ h ≤ 18, -20 ≤ k ≤ 15, -9 ≤ l ≤ 8
Reflections collected	11515
Independent reflections	3451 [R_{int} = 0.0446, R_{sigma} = 0.0522]
Data/restraints/parameters	3451/0/166
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0805, wR_2 = 0.1854
Final R indexes [all data]	R_1= 0.1505, wR_2= 0.2240
Largest diff. peak/hole / e Å-3	0.60/-0.24

Recrystallization in petroleum ether/dichloromethane/ diethyl ether afforded crystals suitable for X-ray analysis.



Single-crystal X-ray diffraction data for **5a** ($C_{13}H_{16}N_2O_2S$) was collected on a Supernova Atlas S2 CCD detector with graphite-monochromated Cu Kα radiation (λ = 1.54184 Å) at rt. The unit cell parameters and the data reduction were obtained with the CrysAlisPro software. During data processing a data scaling and empirical or multi-scan absorption corrections were also performed with CrysAlisPro software. The structure was solved with the ShelXT structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization.

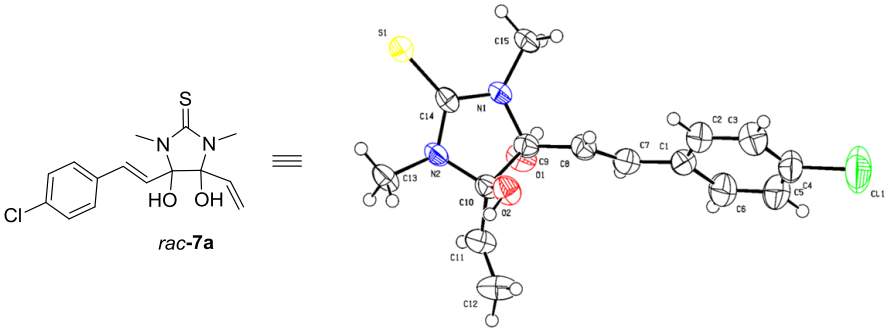
CCDC 2131212 (**5a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table 1 Crystal data and structure refinement for 5a

Identification code	**5a**
Empirical formula	$C_{13}H_{16}N_2O_2S$
Formula weight	264.34
Temperature/K	169.99(10)
Crystal system	monoclinic
Space group	P21
a/Å	7.66580(10)
b/Å	7.56550(10)

c/Å	12.02920(10)
α/°	90
β/°	94.0280(10)
γ/°	90
Volume/Å3	695.918(14)
Z	2
ρcalcg/cm3	1.261
μ/mm-1	2.041
F(000)	280.0
Crystal size/mm3	0.13 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.368 to 143.106
Index ranges	-9 ≤ h ≤ 8, -9 ≤ k ≤ 9, -14 ≤ l ≤ 14
Reflections collected	15527
Independent reflections	2687 [Rint = 0.0527, Rsigma = 0.0309]
Data/restraints/parameters	2687/1/167
Goodness-of-fit on F2	1.104
Final R indexes [I>=2σ (I)]	R_1 = 0.0520, wR_2 = 0.1415
Final R indexes [all data]	R_1 = 0.0537, wR_2 = 0.1432
Largest diff. peak/hole / e Å-3	0.29/-0.25
Flack/Hooft parameter	0.00(4)/-0.003(8)

Recrystallization in petroleum ether/dichloromethane/ diethyl ether afforded crystals suitable for X-ray analysis.



A single-crystal X-ray diffraction data for *rac*-**7a** was collected on a Supernova Atlas S2 CCD detector with graphite-monochromated Cu Kα radiation (λ = 1.54184 Å) at room temperature. The unit cell parameters and the data reduction were obtained with the CrysAlisPro software. During data processing a data scaling and empirical or multi-scan absorption corrections were also performed with CrysAlisPro software.

CCDC 2164313 (*rac*-**7a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via

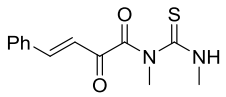
www.ccdc.cam.ac.uk/data_request/cif

Table 1 Crystal data and structure refinement for *rac*-7a.

Identification code	*rac*-**7a**
Empirical formula	$C_{15}H_{17}ClN_2O_2S$
Formula weight	324.81
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.5771(3)
b/Å	8.1384(2)
c/Å	14.3128(3)
α/°	90
β/°	109.039(2)
γ/°	90
Volume/Å^3	1605.10(6)
Z	4
ρ_{calc}g/cm^3	1.344
μ/mm^{-1}	3.370
F(000)	680.0
Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	12.632 to 142.748
Index ranges	$-17 \le h \le 15$, $-9 \le k \le 8$, $-17 \le l \le 17$
Reflections collected	7394
Independent reflections	3060 [R_{int} = 0.0436, R_{sigma} = 0.0438]
Data/restraints/parameters	3060/0/194
Goodness-of-fit on F^2	0.997
Final R indexes [I>=2σ (I)]	R_1 = 0.0659, wR_2 = 0.1923
Final R indexes [all data]	R_1 = 0.0754, wR_2 = 0.1985
Largest diff. peak/hole / e Å^{-3}	0.53/-0.70

7. The analytical and spectral characterization data for products

(*E*)-*N*-methyl-*N*-(methylcarbamothioyl)-2-oxo-4-phenylbut-3-enamide (1aa)



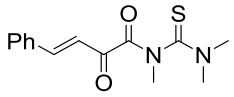
Light yellow solid.

TLC: R_f = 0.45 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.37 – 7.30 (m, 3H), 6.92 (d, *J* = 15.6 Hz, 1H), 6.04 (d, *J* = 16.2 Hz, 1H), 3.30 (s, 3H), 3.24 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.1, 172.6, 135.8, 134.6, 129.2, 128.8, 127.2, 121.0, 86.8, 29.3, 28.3.

(*E*)-*N*-(dimethylcarbamothioyl)-*N*-methyl-2-oxo-4-phenylbut-3-enamide (1ab)



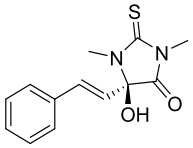
Yellow oil.

TLC: R_f = 0.60 (petroleum ether/ethyl acetate = 10:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.36 – 7.32 (m, 2H), 7.31 – 7.27 (m, 1H), 6.97 (d, *J* = 16.2 Hz, 1H), 6.11 (d, *J* = 16.2 Hz, 1H), 3.81 (s, 3H), 3.35 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.1, 135.6, 135.5, 128.8, 128.7, 127.1, 124.6, 100.8, 53.0, 50.5.

(*R, E*)-5-hydroxy-1,3-dimethyl-5-styryl-2-thioxoimidazolidin-4-one (3a)



White solid, m.p. = 112.8-113.2 °C. 19.6 mg, 83% yield, 97% ee. HPLC CHIRALCEL OD-H, n-hexane/2-propanol = 95/5, flow rate = 0.6 mL/min, λ = 250 nm, retention time: 22.501 min (major), 26.942 min (minor). $[\alpha]_D^{23}$ = 90.3 (c = 0.48, CH_2Cl_2).

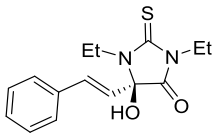
TLC: R_f = 0.50 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H), 7.35 – 7.29 (m, 3H), 6.91 (d, *J* = 15.6 Hz, 1H), 6.03 (d, *J* = 16.2 Hz, 1H), 4.32 (s, 1H), 3.29 (s, 3H), 3.23 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.1, 172.8, 135.9, 134.6, 129.2, 128.8, 127.2, 120.9, 86.9, 29.3, 28.3.

HRMS (ESI): exact mass calcd for $C_{13}H_{14}N_2O_2SNa$ $[M+Na]^+$ requires m/z 258.0668, found m/z 258.0673

***(R, E)*-1,3-diethyl-5-hydroxy-5-styryl-2-thioxoimidazolidin-4-one (3b)**



White solid, m.p. = 122.8-124.2 °C. 18.1 mg, 63% yield, 91% ee. HPLC CHIRALCEL OD-H, n-hexane/2-propanol = 95/5, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 16.712min (minor), 20.975 min (major). $[\alpha]_D^{23}$ = 78.5 (c = 0.25, CH_2Cl_2).

TLC: R_f = 0.55 (petroleum ether/ethyl acetate = 5:1) [UV].

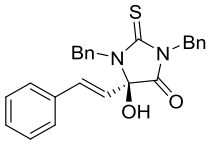
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.36 – 7.29 (m, 3H), 6.96 (d, *J* = 15.6 Hz, 1H), 6.00 (d, *J* = 15.6 Hz, 1H), 4.34 (s, 1H), 3.97 – 3.84 (m, 3H), 3.63 (sext, *J* = 7.2 Hz, 1H), 1.32 (t, *J* = 6.6 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 180.9, 172.7, 135.6, 134.8, 129.1, 128.9, 127.2, 121.6, 87.3, 38.7, 36.9,

13.9, 13.1.

HRMS (ESI): exact mass calcd for $C_{15}H_{18}N_2O_2SNa$ $(M+Na)^+$ requires m/z 313.0981, found m/z 313.0980.

(*R, E*)-1,3-dibenzyl-5-hydroxy-5-styryl-2-thioxoimidazolidin-4-one (3c)



White solid, m.p. = 138.3-139.6 °C. 21.5 mg, 47% yield, 92% ee. HPLC CHIRALCEL IE, n-hexane/2-propanol = 95/15, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 31.601 min (minor), 36.871 min (major). $[\alpha]_D^{23}$ = 54.2 (c = 0.21, CH_2Cl_2).

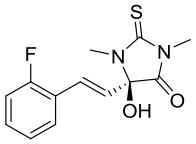
TLC: R_f = 0.56 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.32 – 7.29 (m, 3H), 7.28 – 7.24 (m, 5H), 7.23 – 7.21 (m, 1H), 7.16 – 7.15 (m, 2H), 6.89 (d, *J* = 15.6 Hz, 1H), 5.82 (d, *J* = 16.2 Hz, 1H), 5.08 (dd, *J* = 14.4 Hz, 22.8 Hz, 2H), 5.00 (dd, *J* = 15.0 Hz, 33.6 Hz, 2H), 3.64 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 136.7, 135.7, 134.7, 129.0, 128.7, 128.6, 128.5, 127.9, 127.7, 127.2, 121.8, 87.2, 46.9, 45.4.

HRMS (ESI): exact mass calcd for $C_{25}H_{22}N_2O_2SNa$ $(M+Na)^+$ requires m/z 437.1294, found m/z 437.1298.

(*R, E*)-5-(2-fluorostyryl)-5-hydroxy-1,3-dimethyl-2-thioxoimidazolidin-4-one (3d)



Colorless oil, 21.1 mg, 75% yield, 91% ee. HPLC CHIRALCEL OJ, n-hexane/2-propanol = 90/10, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 26.924min (major), 31.687 min (minor). $[\alpha]_D^{23}$ = 6.5 (c = 0.40, CH_2Cl_2).

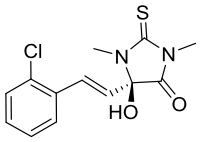
TLC: R_f = 0.45 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.8 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.07 – 7.04 (m, 2H), 6.14 (d, *J* = 16.2, 1H), 4.71 (s, 1H), 3.28 (s, 3H), 3.22 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.1, 172.9, 161.5, 159.8, 130.6 (d, $J_{C\text{-}F}$ = 7.9 Hz), 128.8 (d, $J_{C\text{-}F}$ = 3.1 Hz), 128.5 (d, $J_{C\text{-}F}$ = 3.3 Hz), 124.3 (d, $J_{C\text{-}F}$ = 3.3 Hz), 123.7 (d, $J_{C\text{-}F}$ = 6.4 Hz), 122.6 (d, $J_{C\text{-}F}$ = 11.8 Hz), 116.1 (d, $J_{C\text{-}F}$ = 22.5 Hz) 86.9, 29.3, 28.3.

HRMS (ESI): exact mass calcd for $C_{13}H_{14}FN_2O_2S$ $(M+H)^+$ requires m/z 281.0755, found m/z 281.0760

(*R, E*)-5-(2-chlorostyryl)-5-hydroxy-1,3-dimethyl-2-thioxoimidazolidin-4-one (3e)



Colorless oil, 19.4 mg, 66 yield, 92% ee. HPLC CHIRALCEL ID, n-hexane/2-propanol = 95/5, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 16.425 min (minor), 20.865 min (major). $[\alpha]_D^{23}$ = 22.4 (c = 0.26, CH_2Cl_2).

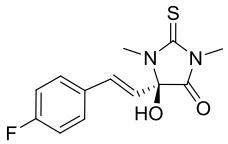
TLC: R_f = 0.50 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.48 (m, 1H), 7.37 – 7.36 (d, *J* = 15.6 Hz, 2H), 7.26 – 7.23 (m, 1H), 6.03 (d, *J* = 15.6, 1H), 4.61 (s, 1H), 3.29 (s, 3H), 3.25 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.1, 172.8, 133.9, 132.9, 132.2, 130.1, 129.9, 127.4, 127.1, 123.9, 86.8, 29.4, 28.4.

HRMS (ESI): exact mass calcd for $C_{13}H_{14}ClN_2O_2S$ $(M+H)^+$ requires m/z 297.0459, found m/z 297.0468.

(*R, E*)-5-(4-fluorostyryl)-5-hydroxy-1,3-dimethyl-2-thioxoimidazolidin-4-one (3f)



White solid, m.p. = 112.8-113.2 °C. 21.1 mg, 75% yield, 96% ee. HPLC CHIRALCEL AD-H, n-hexane/2-propanol = 90/10, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 14.050min (major), 18.322 min (minor). $[\alpha]_D^{23}$ = 18.7 (c = 0.18, CH_2Cl_2).

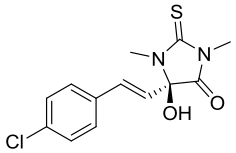
TLC: R_f = 0.50 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.03 (t, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 15.6 Hz, 1H), 5.95 (d, *J* = 15.6 Hz, 1H), 4.62 (s, 1H), 3.28 (s, 3H), 3.22 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 182.1, 173.0, 134.8, 130.9 (d, J_{C-F} = 3.0 Hz), 129.0 (d, J_{C-F} = 9.2 Hz), 120.8 (d, J_{C-F} = 3.0 Hz), 116.0 (d, J_{C-F} = 31.5 Hz), 87.0, 29.4, 28.4.

HRMS (ESI): exact mass calcd for $C_{13}H_{13}FN_2O_2SNa$ $(M+Na)^+$ requires m/z 303.0574, found m/z 303.0580.

(*R, E*)-5-(4-chlorostyryl)-5-hydroxy-1,3-dimethyl-2-thioxoimidazolidin-4-one (3g)



White solid, m.p. = 110.2-112.1 °C. 20.8 mg, 71% yield, 97% ee. HPLC CHIRALCEL AD-H, n-hexane/2-propanol = 95/5, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 43.483min (minor), 57.492 min (major). $[\alpha]_D^{23}$ = 42.5 (c = 0.60, CH_2Cl_2).

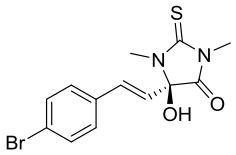
TLC: R_f = 0.58 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 4H), 6.89 (d, *J* = 15.6, 1H), 6.01 (d, *J* = 15.6, 1H), 3.75 (s, 1H), 3.30 (s, 3H), 3.23 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.2, 172.2, 135.1, 134.7, 133.1, 129.1, 128.4, 121.6, 86.6, 29.3, 28.3.

HRMS (ESI): exact mass calcd for $C_{13}H_{14}ClN_2O_2S$ $(M+H)^+$ requires m/z 297.0459, found m/z 297.0460.

(*R, E*)-5-(4-bromostyryl)-5-hydroxy-1,3-dimethyl-2-thioxoimidazolidin-4-one (3h)



White solid, m.p. = 83.7-85.6 °C. 25.4 mg, 75% yield, 93% ee. HPLC CHIRALCEL AD-H, n-hexane/2-propanol = 90/10, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 24.392min (minor), 32.170 min (major). $[\alpha]_D^{23}$ = 77.7 (c = 0.31, CH_2Cl_2).

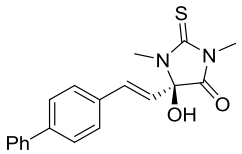
TLC: R_f = 0.50 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.28 – 7.23 (m, 3H), 6.87 (d, *J* = 16.0 Hz, 1H), 6.02 (d, *J* = 16.0 Hz, 1H), 3.88 (s, 1H), 3.30 (s, 3H), 3.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 182.3, 172.4, 134.9, 133.6, 132.2, 128.8, 123.5, 121.9, 86.8, 29.4, 28.5.

HRMS (ESI): exact mass calcd for $C_{13}H_{13}BrN_2O_2SNa$ $(M+Na)^+$ requires m/z 362.9773, found m/z 362.9779

(*R, E*)-5-(2-([1,1'-biphenyl]-4-yl)vinyl)-5-hydroxy-1,3-dimethyl-2-thioxoimidazolidin-4-one (3i)



White solid, m.p. = 132.8-134.2 °C. 18.5 mg, 55% yield, 93% ee. HPLC CHIRALCEL OD-H, n-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 13.857min (major), 18.140 min (minor). $[\alpha]_D^{23}$ = 17.8 (c = 0.24, CH_2Cl_2).

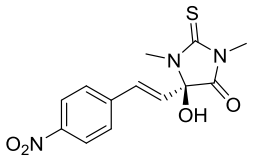
TLC: R_f = 0.48 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 4H), 7.47 – 7.42 (m, 4H), 7.37 – 7.34 (m, 1H), 6.96 (d, *J* = 16.2 Hz, 1H), 6.08 (d, *J* = 16.2 Hz, 1H), 4.24 (s, 1H), 3.32 (s, 3H), 3.25 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 142.1, 140.3, 135.5, 129.0, 127.8, 127.8, 127.6, 127.1, 121.1, 86.9, 29.4, 28.4.

HRMS (ESI): exact mass calcd for $C_{19}H_{19}N_2O_2S$ $(M+H)^+$ requires m/z 339.1162, found m/z 339.1165

(*R, E*)-5-hydroxy-1,3-dimethyl-5-(4-nitrostyryl)-2-thioxoimidazolidin-4-one (3j)



White solid, m.p. = 201.1-203.5 °C. 16.2 mg, 53% yield, 90% ee. HPLC CHIRALCEL IE, n-hexane/2-propanol = 90/10, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 30.735 min (minor), 33.487 min (major). $[\alpha]_D^{23}$ = 11.3 (c = 0.15, CH_2Cl_2).

TLC: R_f = 0.45 (petroleum ether/ethyl acetate = 5:1) [UV].

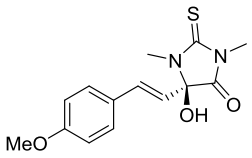
^{1}H NMR (600 MHz, CD_3OD) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.11 (d, *J* = 16.0 Hz,

1H), 6.41 (d, *J* = 16.0 Hz, 1H), 3.29 (s, 3H), 3.21 (s, 3H).

^{13}C NMR (150 MHz, CD_3OD) δ 183.6, 173.9, 149.2, 143.3, 134.4, 129.2, 128.5, 125.1, 88.1, 29.4, 28.5.

HRMS (ESI): exact mass calcd for $C_{13}H_{13}N_3O_4SNa$ $(M+Na)^+$ requires m/z 330.0519, found m/z 330.0529.

(*R, E*)-5-hydroxy-5-(4-methoxystyryl)-1,3-dimethyl-2-thioxoimidazolidin-4-one (3k)



Colorless oil, 14.3 mg, 49% yield, 96% ee. HPLC CHIRALCEL IE, n-hexane/2-propanol = 90/10, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 18.665 min (major), 20.170 min (minor). $[\alpha]_D^{23}$ = 6.4 (c = 0.17, CH_2Cl_2).

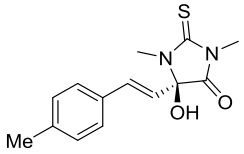
TLC: R_f = 0.55 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (150 MHz, $CDCl_3$) δ 7.33 – 7.32 (m, 2H), 6.86 – 6.85 (m, 2H), 6.83 (d, *J* = 16.2 Hz, 1H), 5.90 (d, *J* = 15.6 Hz, 1H), 4.21 (s, 1H), 3.82 (s, 3H), 3.28 (s, 3H), 3.23 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.1, 172.8, 160.4, 135.2, 128.6, 127.3, 118.5, 114.2, 87.0, 55.3, 29.3, 28.3.

HRMS (ESI): exact mass calcd for $C_{14}H_{16}N_2O_3SNa$ $(M+Na)^+$ requires m/z 315.0774, found m/z 315.0775.

(*R, E*)-5-hydroxy-1,3-dimethyl-5-(4-methylstyryl)-2-thioxoimidazolidin-4-one (3l)



White solid, m.p. = 102.8-104.2 °C. 19.0 mg, 69% yield, 94% ee. HPLC CHIRALCEL OD-H, n-hexane/2-propanol = 95/5, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 19.045 min (major), 21.570 min (minor). $[\alpha]_D^{23}$ = 54.6 (c = 0.41, CH_2Cl_2).

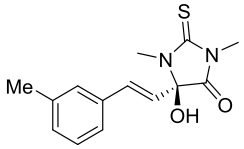
TLC: R_f = 0.55 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.85 (d, *J* = 16.2 Hz, 1H), 5.98 (d, *J* = 15.6 Hz, 1H), 4.54 (s, 1H), 3.27 (s, 3H), 3.21 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.0, 173.0, 139.3, 135.7, 131.9, 129.5, 127.2, 119.9, 87.1, 29.3, 28.3, 21.3.

HRMS (ESI): exact mass calcd for $C_{14}H_{16}N_2O_2SNa$ $(M+Na)^+$ requires m/z 299.0825, found m/z 299.0830.

(*R, E*)-5-hydroxy-1,3-dimethyl-5-(3-methylstyryl)-2-thioxoimidazolidin-4-one (3m)



White solid, m.p. = 109.8-112.7 °C. 22.3 mg, 81% yield, 96% ee. HPLC CHIRALCEL OD-H, n-hexane/2-propanol = 95/5, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 24.598 min (minor), 27.423 min (major). $[\alpha]_D^{23}$ = 46.5 (c = 0.54, CH_2Cl_2).

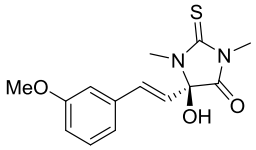
TLC: R_f = 0.60 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 3H), 7.13 (d, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 16.2 Hz, 1H), 6.02 (d, *J* = 15.6 Hz, 1H), 4.71 (s, 1H), 3.27 (s, 3H), 3.22 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.1, 173.2, 138.5, 136.0, 134.7, 130.1, 128.8, 127.9, 124.5, 120.9, 87.2, 29.4, 28.4, 21.4.

HRMS (ESI): exact mass calcd for $C_{14}H_{16}N_2O_2SNa$ $(M+Na)^+$ requires m/z 299.0825, found m/z 299.0834.

(*R, E*)-5-hydroxy-5-(3-methoxystyryl)-1,3-dimethyl-2-thioxoimidazolidin-4-one (3n)



White solid, m.p. = 103.5-104.7 °C.19.5 mg, 67% yield, 92% ee. HPLC CHIRALCEL OD-H, n-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 11.355 min (major), 15.088 min (minor). $[\alpha]_D^{23}$ = 32.6 (c = 0.25, CH_2Cl_2).

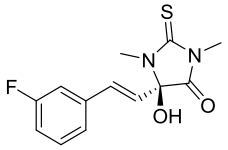
TLC: R_f = 0.55 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (t, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.92 (t, *J* = 1.8 Hz, 1H), 6.87 – 6.85 (m, 2H), 6.02 (d, *J* = 15.6 Hz, 1H), 4.58 (s, 1H), 3.80 (s, 3H), 3.27 (s, 3H), 3.22 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.0, 172.9, 159.8, 135.9, 135.7, 129.8, 121.3, 119.8, 115.0, 112.2, 86.9, 55.3, 29.3, 28.3.

HRMS (ESI): exact mass calcd for $C_{14}H_{16}N_2O_3SNa$ $(M+Na)^+$ requires m/z 315.0774, found m/z 315.0778.

(*R, E*)-5-(3-fluorostyryl)-5-hydroxy-1,3-dimethyl-2-thioxoimidazolidin-4-one (3o)



White solid, m.p. = 116.7-117.3 °C. 20.1 mg, 72% yield, 93% ee. HPLC CHIRALCEL OD-H, n-hexane/2-propanol = 95/5, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 26.955 min (major), 28.860 min (minor). $[\alpha]_D^{23}$ = 15.7 (c = 0.15, CH_2Cl_2).

TLC: R_f = 0.55 (petroleum ether/ethyl acetate = 5:1) [UV].

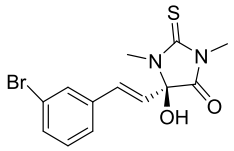
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 9.6 Hz, 1H), 7.01 (td, *J* = 8.4, 2.4 Hz, 1H), 6.90 (d, *J* = 16.2 Hz, 1H), 6.04 (d, *J* = 15.9 Hz, 1H), 4.35 (s, 1H), 3.29 (s, 3H), 3.22 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.2, 172.7, 163.9, 162.3, 137.0 (d, J_{C-F} = 7.5 Hz), 134.9 (d, J_{C-F} = 3.0 Hz), 130.5 (d, J_{C-F} = 7.5 Hz), 123.2 (d, J_{C-F} = 3.0 Hz), 122.5, 116.1 (d, J_{C-F} = 21.1 Hz), 113.8 (d, J_{C-F} = 22.0 Hz), 86.8, 29.4, 28.4.

182.23 , 172.70 , 137.01 , 136.96 , 134.96 , 134.94 , 130.50 , 130.45 , 123.29 , 123.27 , 122.59 , 116.28 , 116.13 , 113.85 , 113.70 , 86.82 , 29.42 , 28.47 .

HRMS (ESI): exact mass calcd for $C_{13}H_{13}FN_2O_2SNa$ $(M+Na)^+$ requires m/z 303.0574, found m/z 303.0579.

(*R, E*)-5-(3-bromostyryl)-5-hydroxy-1,3-dimethyl-2-thioxoimidazolidin-4-one (3p)



White solid, m.p. = 122.1-123.9 °C. 25.1 mg, 74% yield, 72% ee. HPLC CHIRALCEL AD-H, n-hexane/2-propanol = 95/5, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 21.545 min (minor), 25.020 min (major). $[\alpha]_D^{23}$ = -7.6 (c = 0.20, CH_2Cl_2).

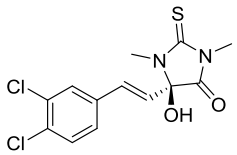
TLC: R_f = 0.50 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 16.2 Hz, 1H), 6.04 (d, *J* = 15.6 Hz, 1H), 4.03 (s, 1H), 3.30 (s, 3H), 3.23 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.1, 172.4, 136.7, 134.5, 132.0, 130.3, 129.9, 125.9, 122.9, 122.6, 86.6, 29.3, 28.3.

HRMS (ESI): exact mass calcd for $C_{13}H_{13}BrN_2O_2SNa$ $(M+Na)^+$ requires m/z 362.9773, found m/z 362.9780.

(*R, E*)-5-(3,4-dichlorostyryl)-5-hydroxy-1,3-dimethyl-2-thioxoimidazolidin-4-one (3q)



White solid, m.p. = 137.8-138.8 °C. 26.9 mg, 82% yield, 97% ee. HPLC CHIRALCEL OD-H, n-hexane/2-propanol = 95/5, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 24.438 min (minor), 28.122 min (major). $[\alpha]_D^{23}$ = 9.6 (c = 0.10, CH_2Cl_2).

TLC: R_f = 0.55 (petroleum ether/ethyl acetate = 5:1) [UV].

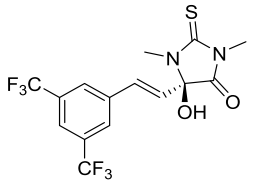
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 2.0 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.21 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.85 (d, *J* = 15.6 Hz, 1H), 6.02 (d, *J* = 15.6 Hz, 1H), 4.30 (s, 1H), 3.29 (s, 3H), 3.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 182.2, 172.6, 134.8, 133.8, 133.2, 130.9, 128.9, 126.4, 123.2, 86.7,

29.4, 28.5.

HRMS (ESI): exact mass calcd for $C_{13}H_{12}Cl_2N_2O_2SNa$ $(M+Na)^+$ requires m/z 352.9889, found m/z 352.9897

(*R, E*)-5-(3,5-bis(trifluoromethyl)styryl)-5-hydroxy-1,3-dimethyl-2-thioxoimidazolidin-4-one (3r)



White solid, m.p. = 139.5-141.3 °C. 22.8 mg, 57% yield, 92% ee. HPLC CHIRALCEL OJ, n-hexane/2-propanol = 90/10, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 12.368 min (minor), 16.435 min (major). $[\alpha]_D^{23}$ = 18.0 (c = 0.40, CH_2Cl_2).

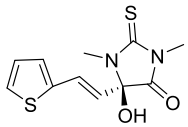
TLC: R_f = 0.50 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.75 (m, 3H), 7.05 (d, *J* = 16.2 Hz, 1H), 6.20 (d, *J* = 16.2 Hz, 1H), 4.26 (s, 1H), 3.31 (s, 3H), 3.24 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.0, 172.2, 136.7, 133.3, 132.3 (q, $J_{C\text{-}F}$ = 33.0 Hz), 132.2, 127.0 (d, $J_{C\text{-}F}$ = 3.0 Hz), 127.0, 123.9 (q, $J_{C\text{-}F}$ = 271.5 Hz), 122.5(d, $J_{C\text{-}F}$ = 3.0 Hz), 122.1, 86.5, 29.3, 28.4.

HRMS (ESI): exact mass calcd for $C_{15}H_{12}F_6N_2O_2SNa$ $(M+Na)^+$ requires m/z 421.0416, found m/z 421.0420.

(*R, E*)-5-hydroxy-1,3-dimethyl-5-(2-(thiophen-2-yl)vinyl)-2-thioxoimidazolidin-4-one (3s)



Colorless oil, 14.7 mg, 55% yield, 96% ee. HPLC CHIRALCEL OD-H, n-hexane/2-propanol = 98/2, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 72.015 min (major), 81.788 min (minor). $[\alpha]_D^{23}$ = 6.4 (c = 0.20, CH_2Cl_2).

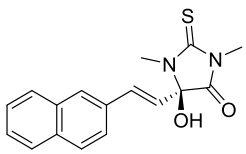
TLC: R_f = 0.60 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 1H), 7.11 – 7.08 (m, 1H), 7.06 (d, *J* = 15.6 Hz, 1H), 7.02 – 6.96 (m, 1H), 5.84 (d, *J* = 15.6 Hz, 1H), 4.04 (s, 1H), 3.29 (s, 3H), 3.23 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.0, 172.5, 139.5, 129.0, 128.6, 127.7, 126.5, 119.8, 86.6, 29.3, 28.3.

HRMS (ESI): exact mass calcd for $C_{11}H_{12}N_2O_2S_2Na$ $(M+Na)^+$ requires m/z 291.0232, found m/z 291.0235.

(*R, E*)-5-hydroxy-1,3-dimethyl-5-(2-(naphthalen-2-yl)vinyl)-2-thioxoimidazolidin-4-one (3t)



White solid, m.p. = 112.8-113.2 °C. 18.1 mg, 58% yield, 83% ee. HPLC CHIRALCEL OD-H,

n-hexane/2-propanol = 95/5, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 29.727 min (major), 38.342 min (minor). $[\alpha]_D^{23}$ = 36.2 (c = 0.22, CH_2Cl_2).

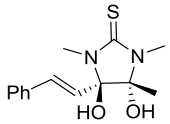
TLC: R_f = 0.50 (petroleum ether/ethyl acetate = 5:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 4H), 7.55 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.08 (d, *J* = 16.2 Hz, 1H), 6.16 (d, *J* = 16.2 Hz, 1H), 4.32 (s, 1H), 3.32 (s, 3H), 3.27 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 182.2, 172.8, 136.0, 132.1, 128.7, 128.4, 128.3, 127.8, 126.8, 126.7, 123.4, 121.3, 87.0, 29.4, 28.4.

HRMS (ESI): exact mass calcd for $C_{17}H_{16}N_2O_2SNa$ $(M+Na)^+$ requires m/z 335.0825, found m/z 335.0830.

(*4R, 5R*)-4,5-dihydroxy-1,3,4-trimethyl-5-((*E*)-styryl)imidazolidine-2-thione (4a)



White solid, m.p. = 101.8-103.2 °C. 26.5 mg, 95% yield, 99% ee. HPLC CHIRALCEL IA, n-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 8.773 min (major), 10.695 min (minor). $[\alpha]_D^{23}$ = 20.1 (c = 0.16, CH_2Cl_2).

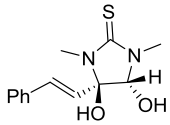
TLC: R_f = 0.40 (petroleum ether/ethyl acetate = 3:1) [UV].

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 – 7.46 (m, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.32 – 7.25 (m, 1H), 6.89 (d, *J* = 16.0 Hz, 1H), 6.43 – 6.35 (m, 2H), 6.14 (s, 1H), 3.03 (s, 3H), 2.92 (s, 3H), 1.37 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 191.4, 145.7, 142.0, 138.3, 137.5, 136.3, 136.1, 101.6, 101.5, 38.7, 38.0, 28.7.

HRMS (ESI): exact mass calcd for $C_{14}H_{19}N_2O_2S$ $(M+H)^+$ requires m/z 279.1162, found m/z 279.1169.

(*4R, 5R*)-4,5-dihydroxy-1,3-dimethyl-4-((*E*)-styryl)imidazolidine-2-thione (5a)



White solid, m.p. = 98.8-101.2 °C. 25.8 mg, 98% yield, 91% ee. HPLC CHIRALCEL IA, n-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 8.865 min (minor), 9.093 min (major). $[\alpha]_D^{23}$ = 50.0 (c = 0.1, CH_2Cl_2).

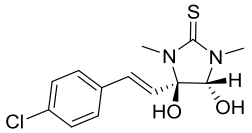
TLC: R_f = 0.20 (petroleum ether/ethyl acetate = 3:1) [UV].

^{1}H NMR (400 MHz, DMSO-d_6) δ7.52 – 7.46 (m, 2H), 7.40 – 7.34 (m, 2H), 7.32 – 7.28 (m, 1H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.69 (s, 1H), 6.59 (d, *J* = 7.2 Hz, 1H), 6.27 (d, *J* = 16.0 Hz, 1H), 4.80 (d, *J* = 7.2 Hz, 1H), 3.06 (s, 3H), 2.88 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 181.8, 136.4, 132.8, 129.2, 128.5, 127.2, 126.5, 90.9, 90.8, 31.6, 29.2.

HRMS (ESI): exact mass calcd for $C_{13}H_{16}N_2O_2SNa$ $(M+Na)^+$ requires m/z 287.0825, found m/z 287.0816.

(*4R, 5R*)-4-((*E*)-4-chlorostyryl)-4,5-dihydroxy-1,3-dimethylimidazolidine-2-thione (6a)



White solid, m.p. = 91.8-93.2 °C. 28.4 mg, 97% yield, 97% ee. HPLC CHIRALCEL IA, n-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 10.488 min (minor), 17.005 min (major). $[\alpha]_D^{23}$ = 42.2 (c = 0.26, CH_2Cl_2).

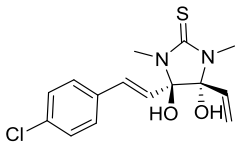
TLC: R_f = 0.40 (petroleum ether/ethyl acetate = 3:1) [UV].

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 16.2 Hz, 1H), 6.72 (s, 1H), 6.61 (d, *J* = 7.2 Hz, 1H), 6.29 (d, *J* = 16.2 Hz, 1H), 4.80 (d, *J* = 7.8 Hz, 1H), 3.06 (s, 3H), 2.87 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 138.3, 138.1, 136.7, 100.0, 99.9, 49.7, 49.5, 49.3, 49.1, 48.9, 48.7, 48.5, 38.4.

HRMS (ESI): exact mass calcd for $C_{13}H_{16}N_2O_2S$ $(M+H)^+$ requires m/z 299.0616, found m/z 299.0609.

(*4R, 5R*)-4-((*E*)-4-chlorostyryl)-4,5-dihydroxy-1,3-dimethyl-5-vinylimidazolidine-2-thione (7a)



White solid, m.p. = 85.3-88.9 °C. 30.2 mg, 93% yield, 96% ee. HPLC CHIRALCEL IA, n-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, λ = 254 nm, retention time: 8.368 min (minor), 38.342 min (major). $[\alpha]_D^{23}$ = 17.5 (c = 0.20, CH_2Cl_2).

TLC: R_f = 0.40 (petroleum ether/ethyl acetate = 3:1) [UV].

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.49 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 16.0 Hz, 1H), 6.56 (s, 1H), 6.45 – 6.32 (m, 2H), 5.99 (dd, *J* = 17.2 Hz, 10.8 Hz, 1H), 5.45 (ddd, *J* = 30.0 Hz, 17.2 Hz, 2.0 Hz, 1H), 2.93 (s, 3H), 2.90 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 182.6, 135.4, 134.9, 132.8, 132.1, 129.2, 128.9, 127.4, 119.8, 93.1, 93.0, 29.8, 29.7.

HRMS (ESI): exact mass calcd for $C_{15}H_{18}N_2O_2S$ $(M+H)^+$ requires m/z 325.0772, found m/z 325.0780.

8. Reference

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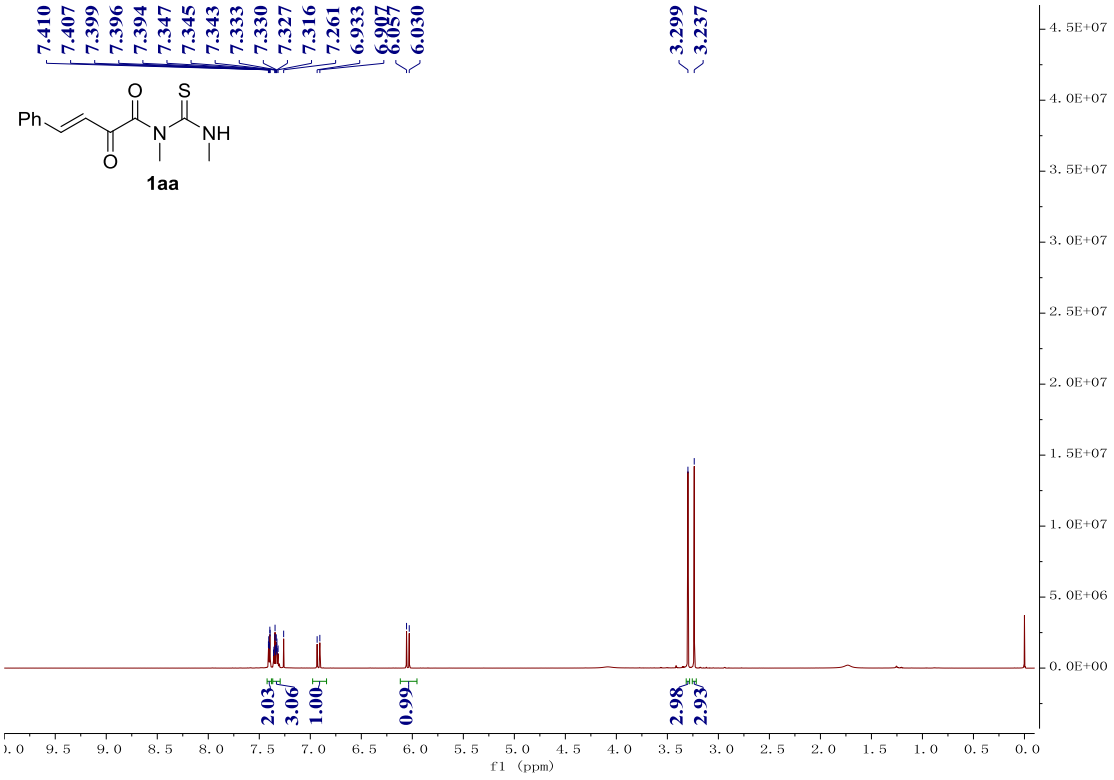
(2) R. Saito, N. Uemura, H. Ishikawa, A. Magara, Y. Yoshida, T. Mino, Y. Kasashima and M. Sakamoto, Umpolung cyclization reaction of *N*-cinnamoylthioureas in the presence of DBU. *Org. Biomol. Chem.*, 2018, **16**, 7910−7919.

(3) H.-F. Tu, C. Zheng, R.-Q. Xu, X.-J. Liu and S.-L. You, Iridium-Catalyzed Intermolecular Asymmetric Dearomatization of *β*-Naphthols with Allyl Alcohols or Allyl Ethers. *Angew. Chem., Int. Ed.*, 2017, **56**, 3237-3241.

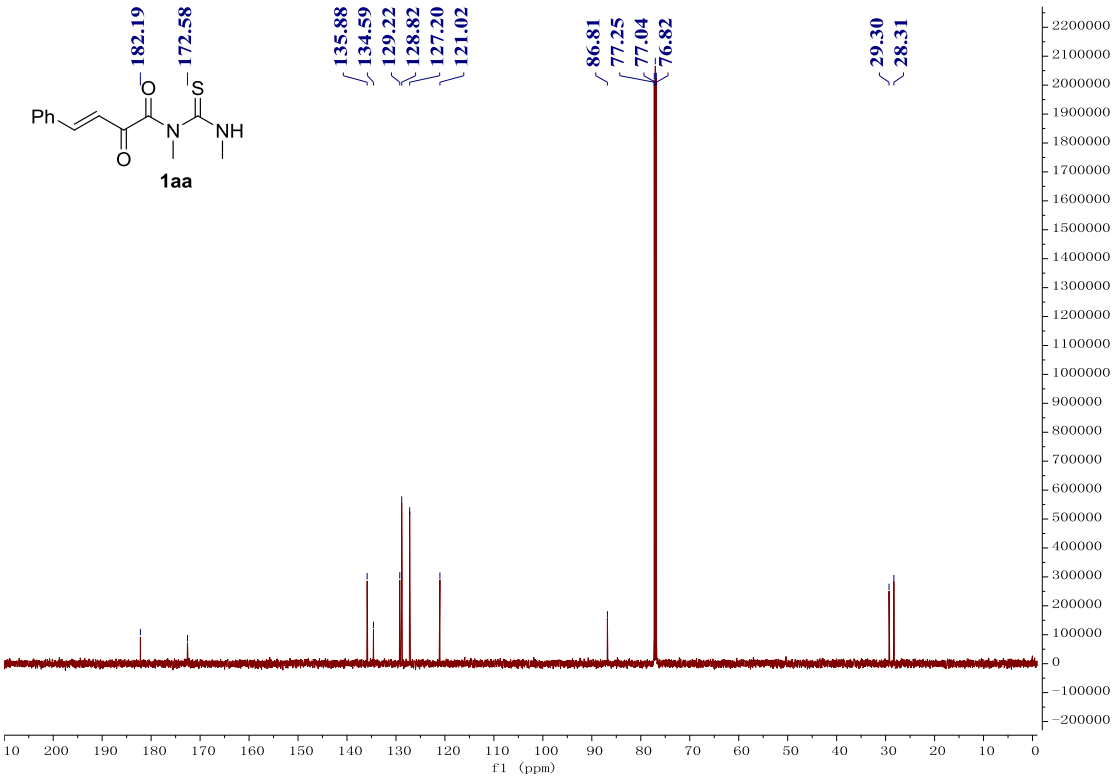
(4) L. Dai, X. Li, Z. Zeng, S. Dong, Y. Zhou, X. Liu and X. Feng, Catalytic Asymmetric Acyloin Rearrangements of α-Ketols, *α*-Hydroxy Aldehydes, and *α*-Iminols by *N*,*N*′-Dioxide−Metal Complexes. *Org. Lett.*, 2020, **22**, 5041−5045.

9. Copies of NMR spectra for the adducts

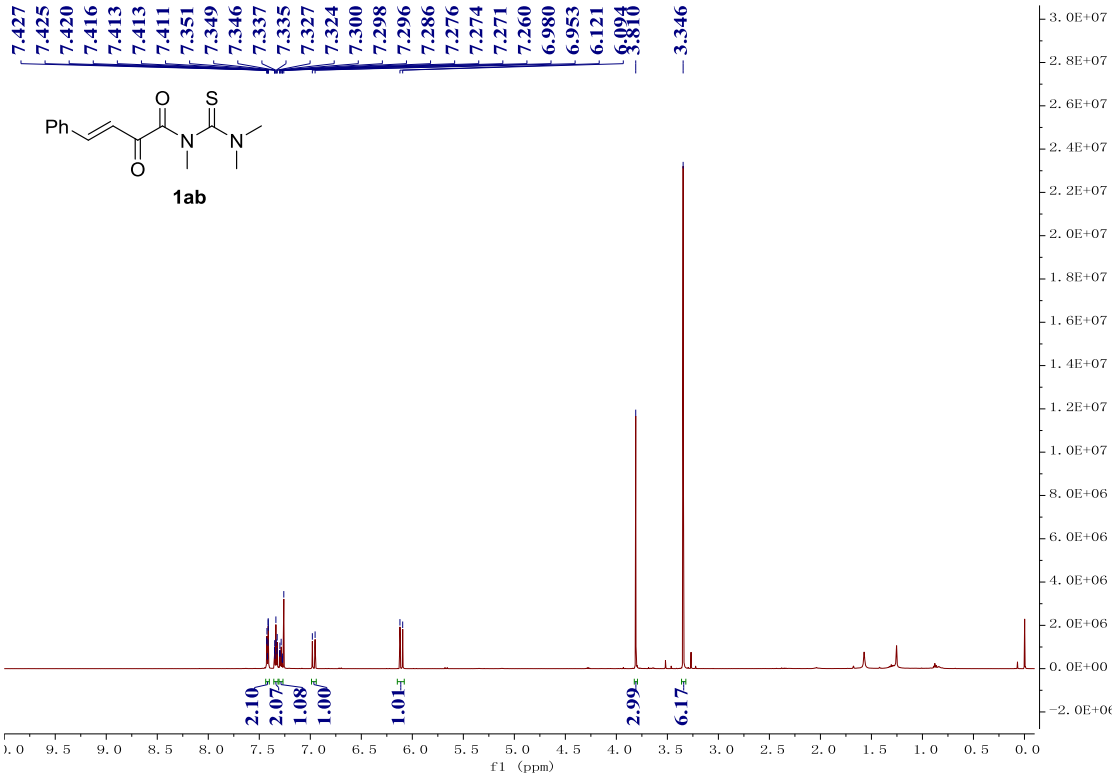
^{1}H NMR for 1aa



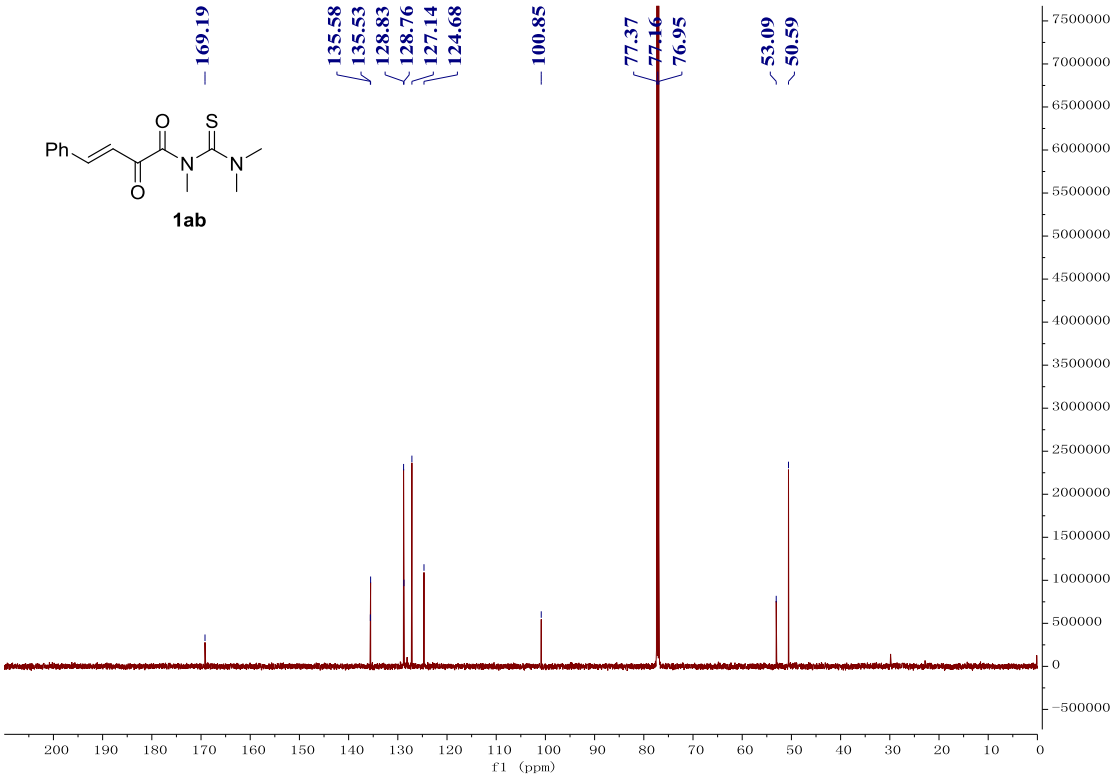
^{13}C NMR for 1aa



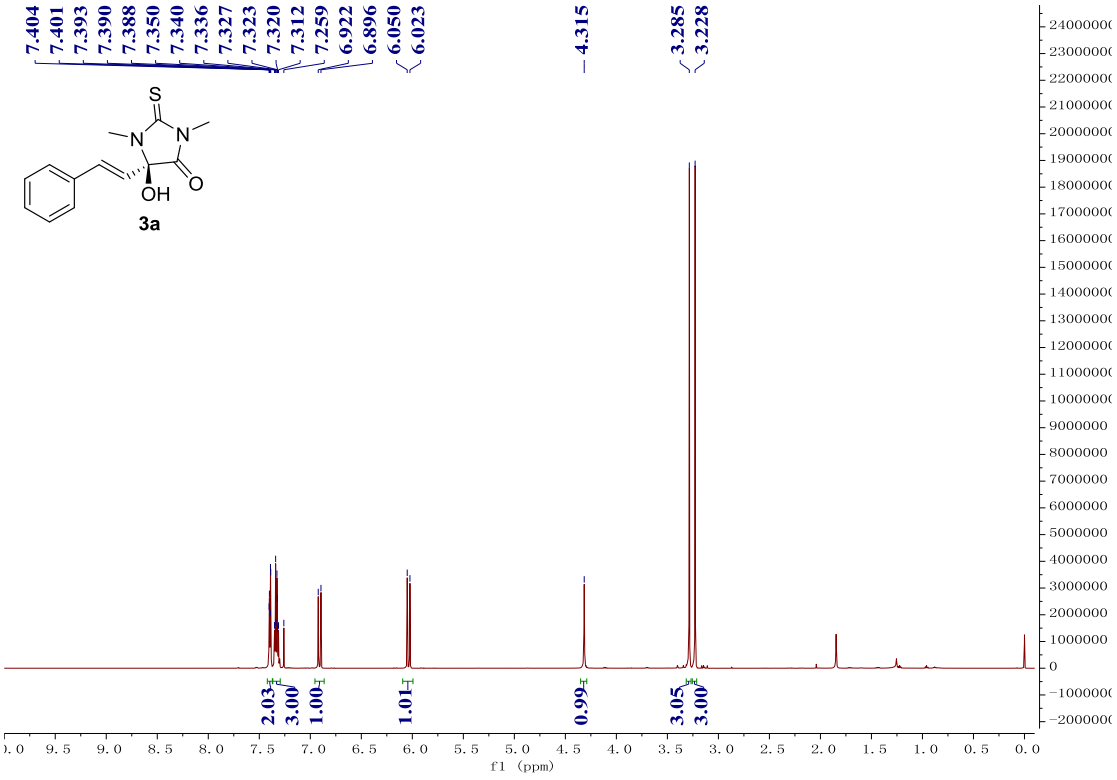
^{1}H NMR for 1ab



^{13}C NMR for 1ab



^{1}H NMR for 3a



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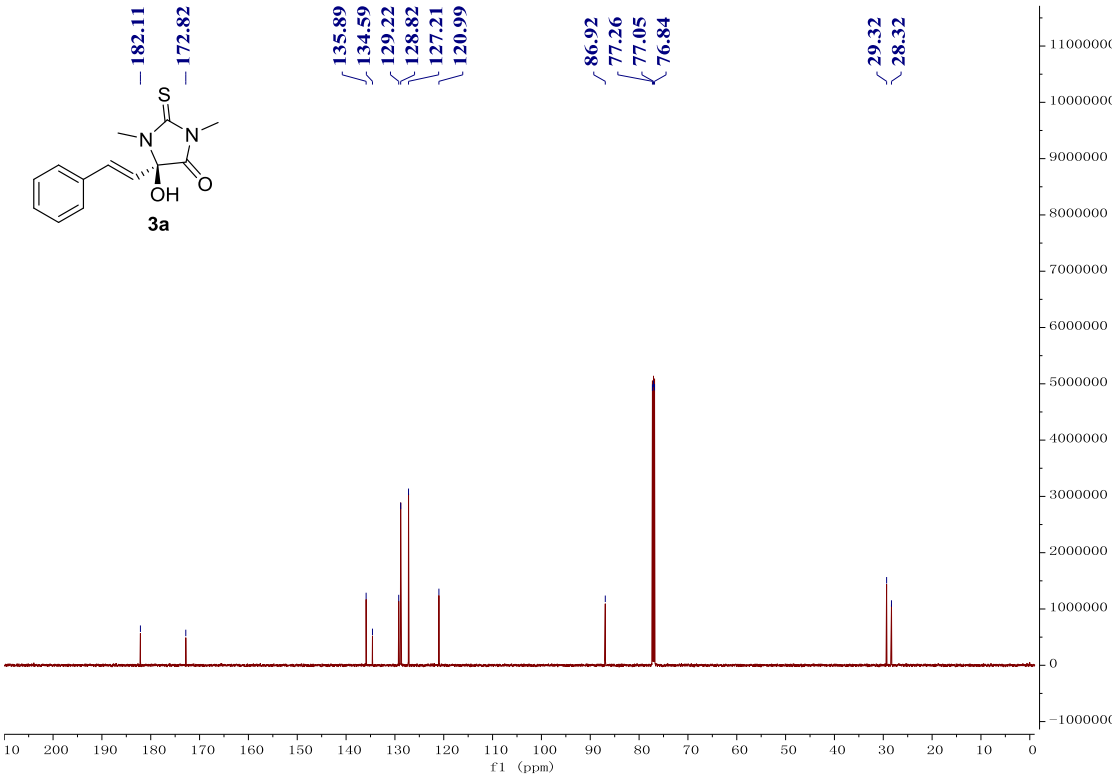
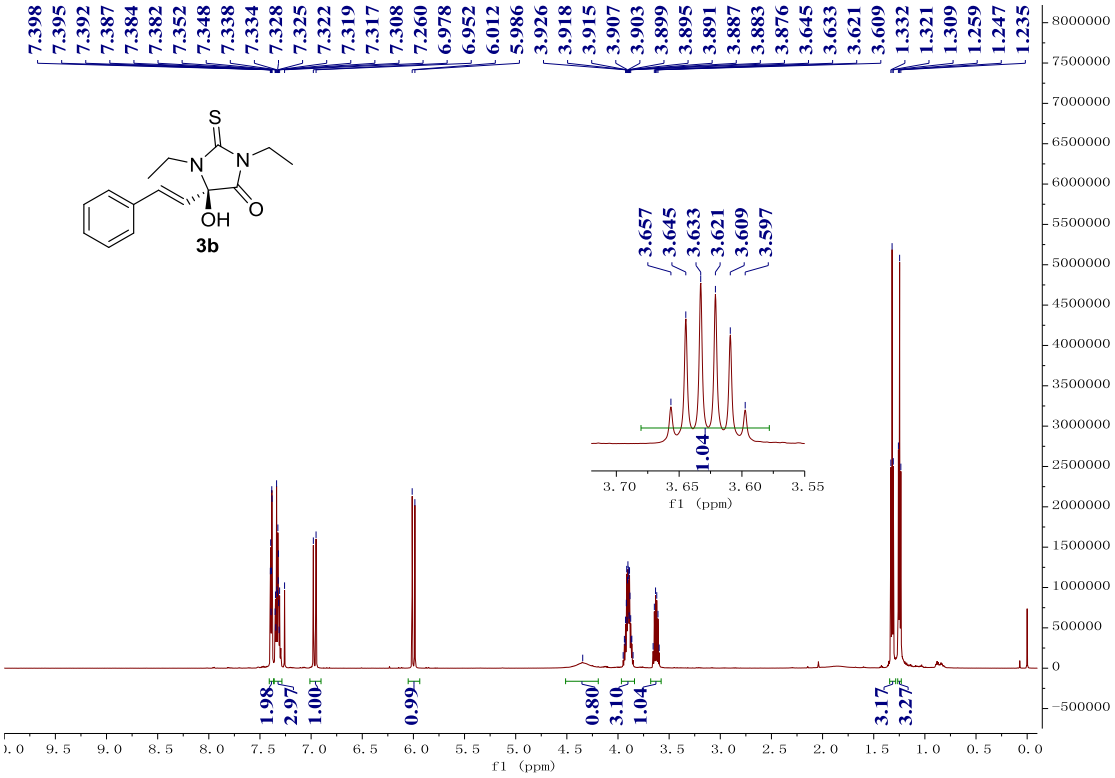
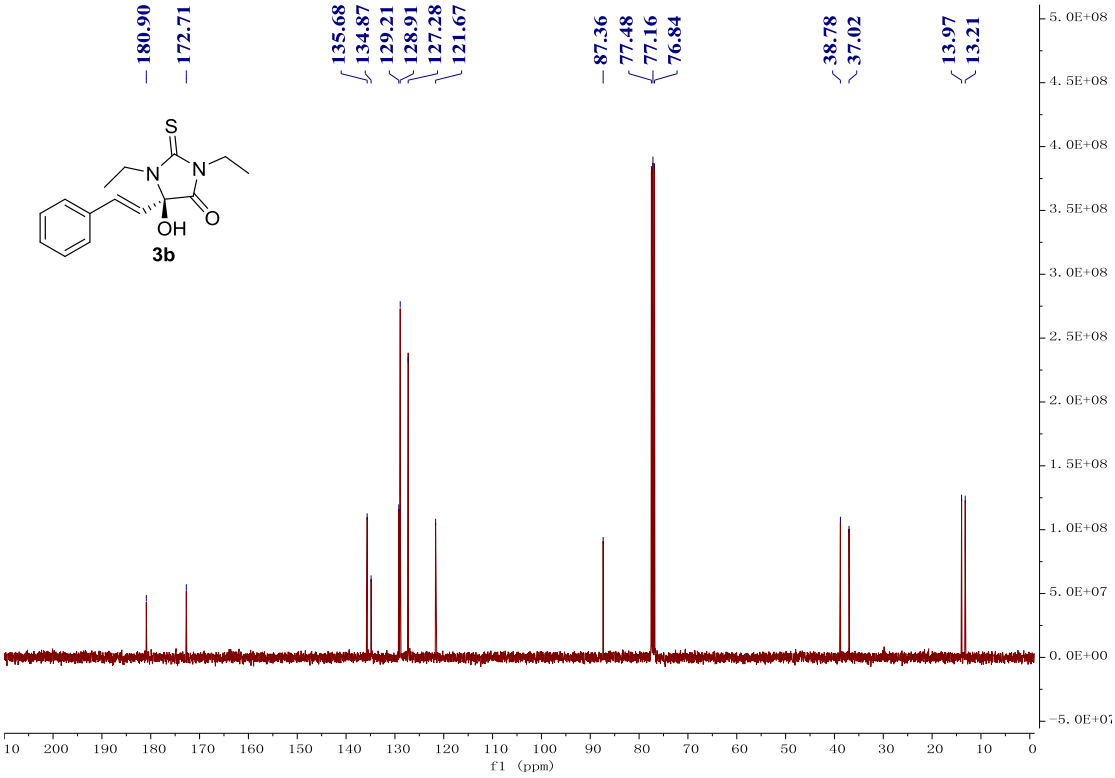


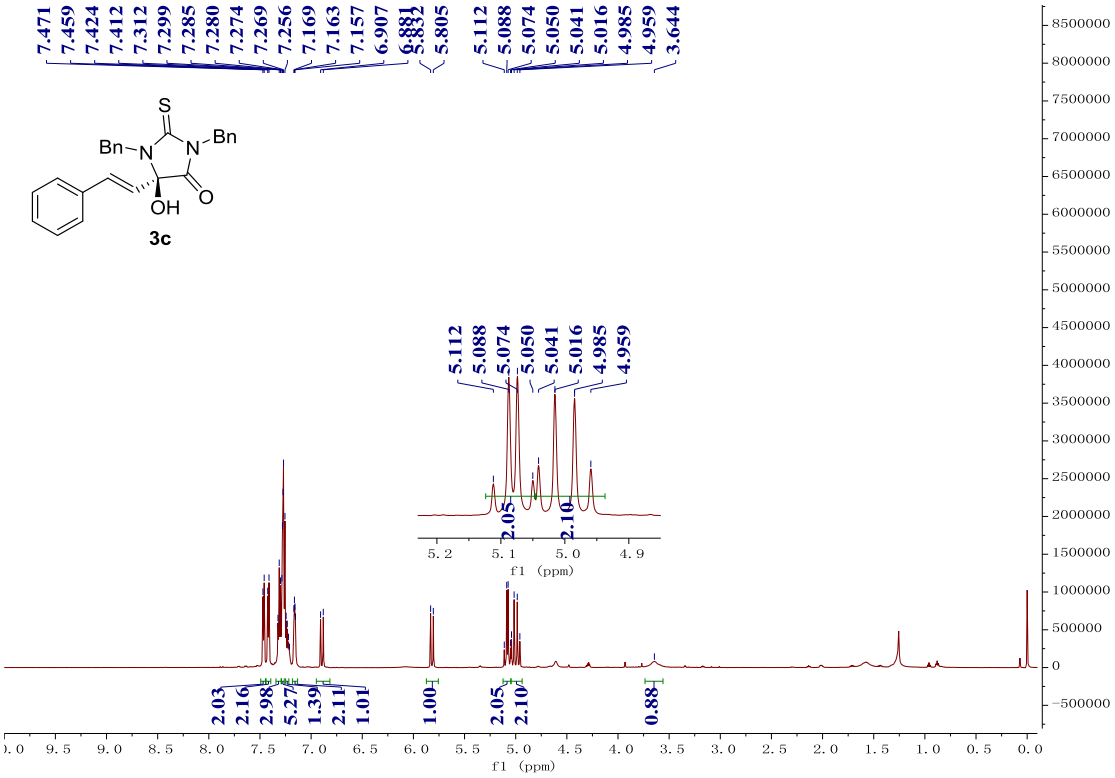
^{1}H NMR for 3b



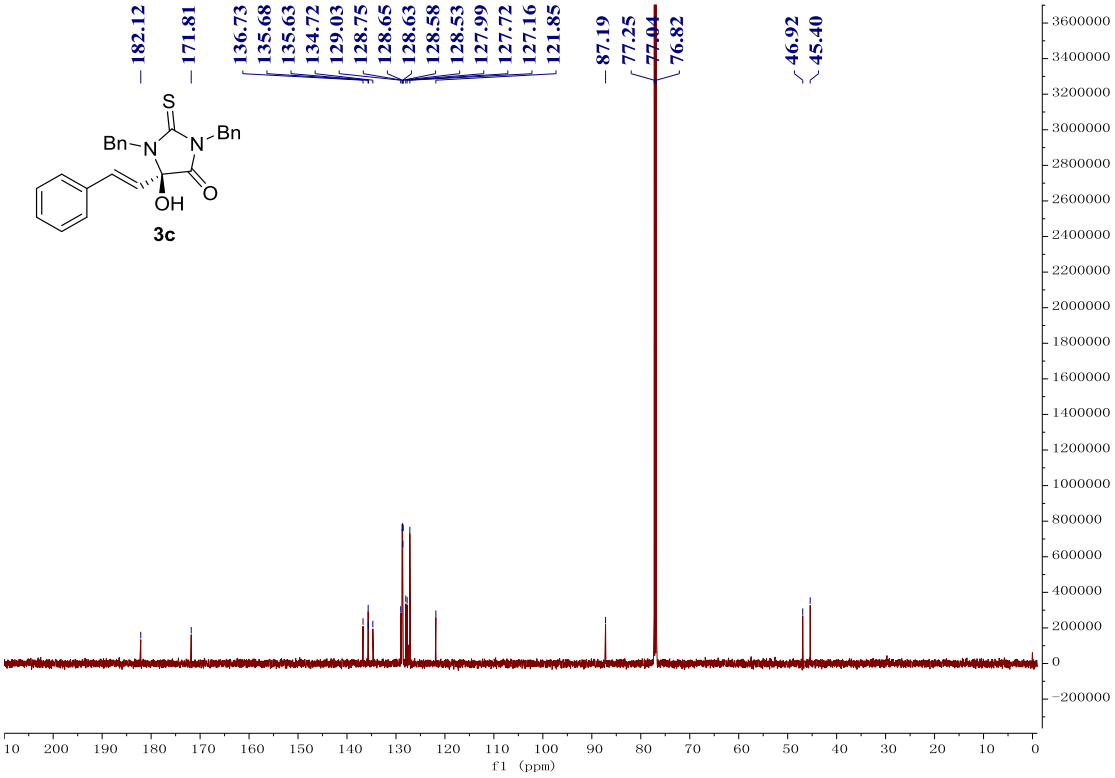
^{13}C NMR for 3b



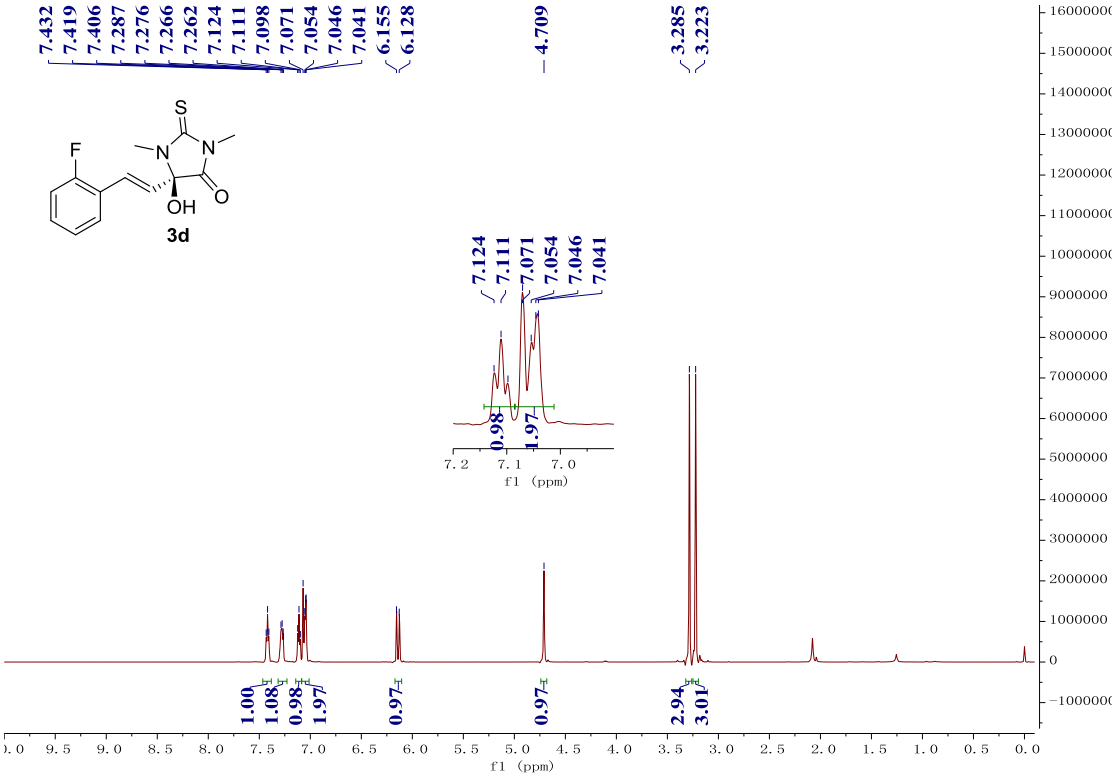
^{1}H NMR for 3c



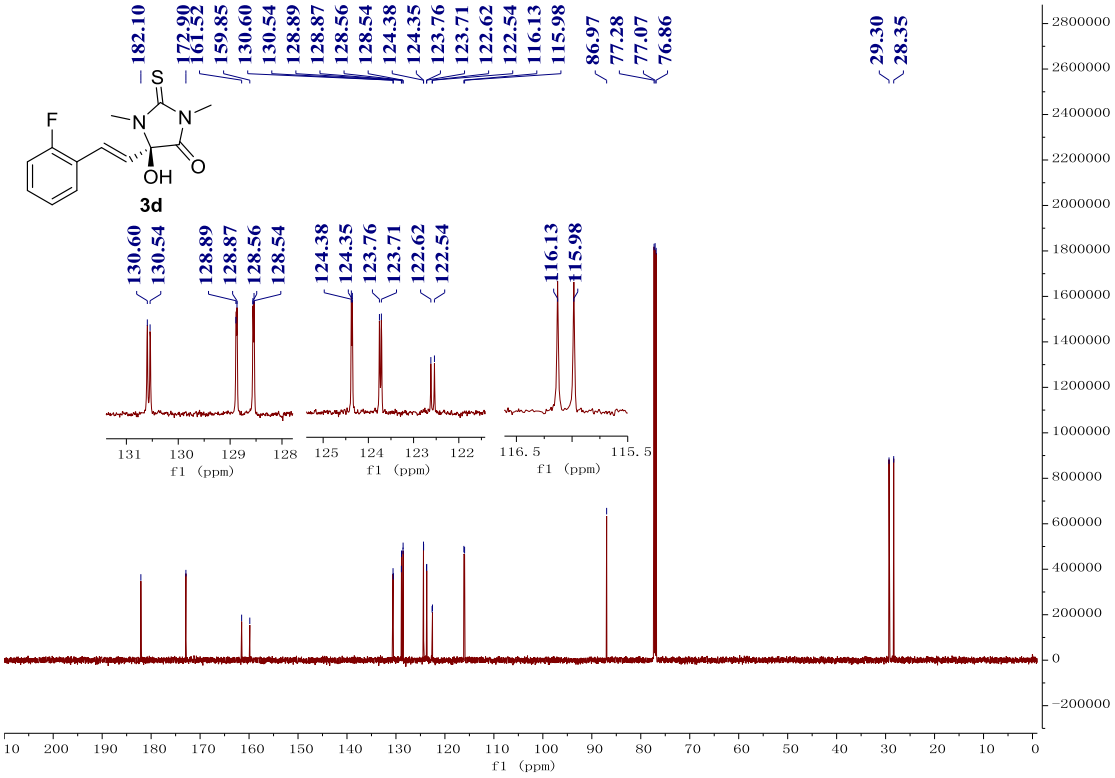
^{13}C NMR for 3c



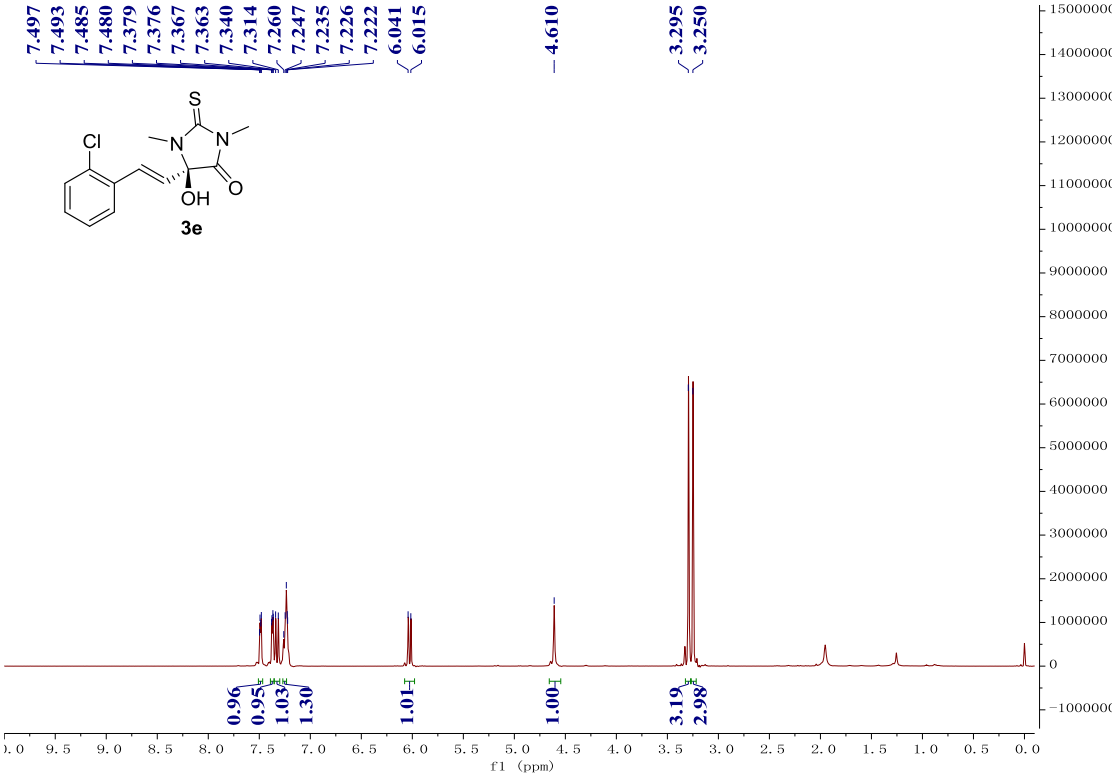
^{1}H NMR for 3d



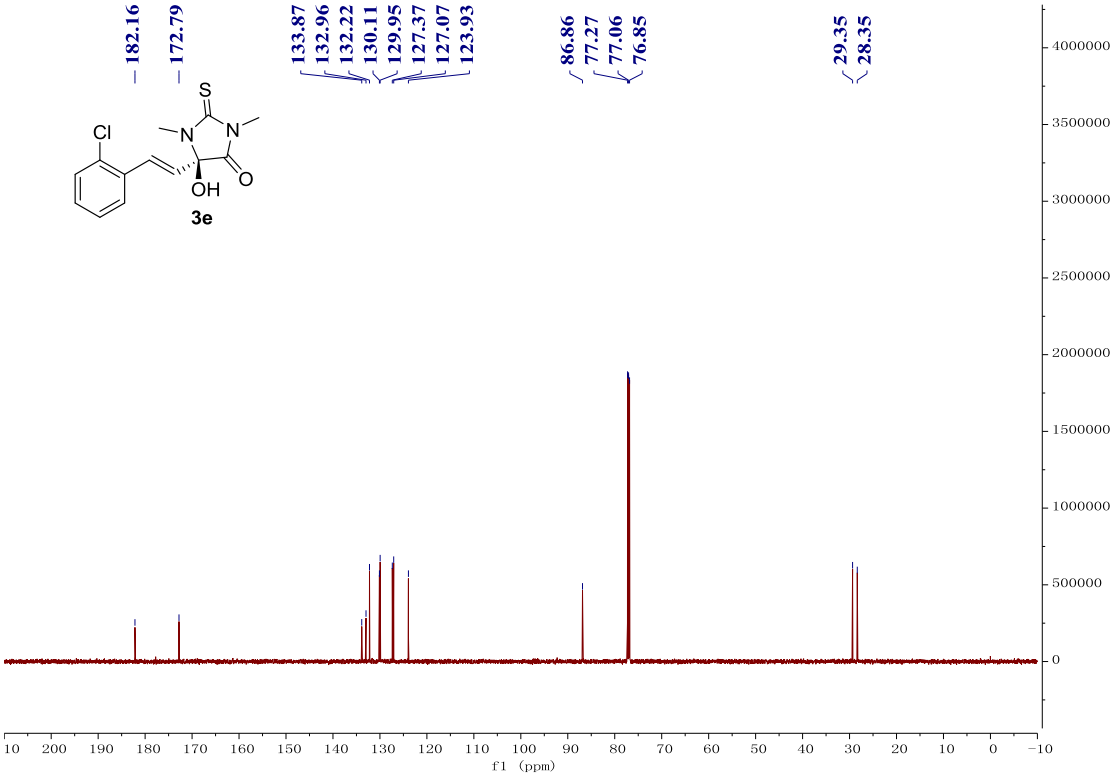
^{13}C NMR for 3d



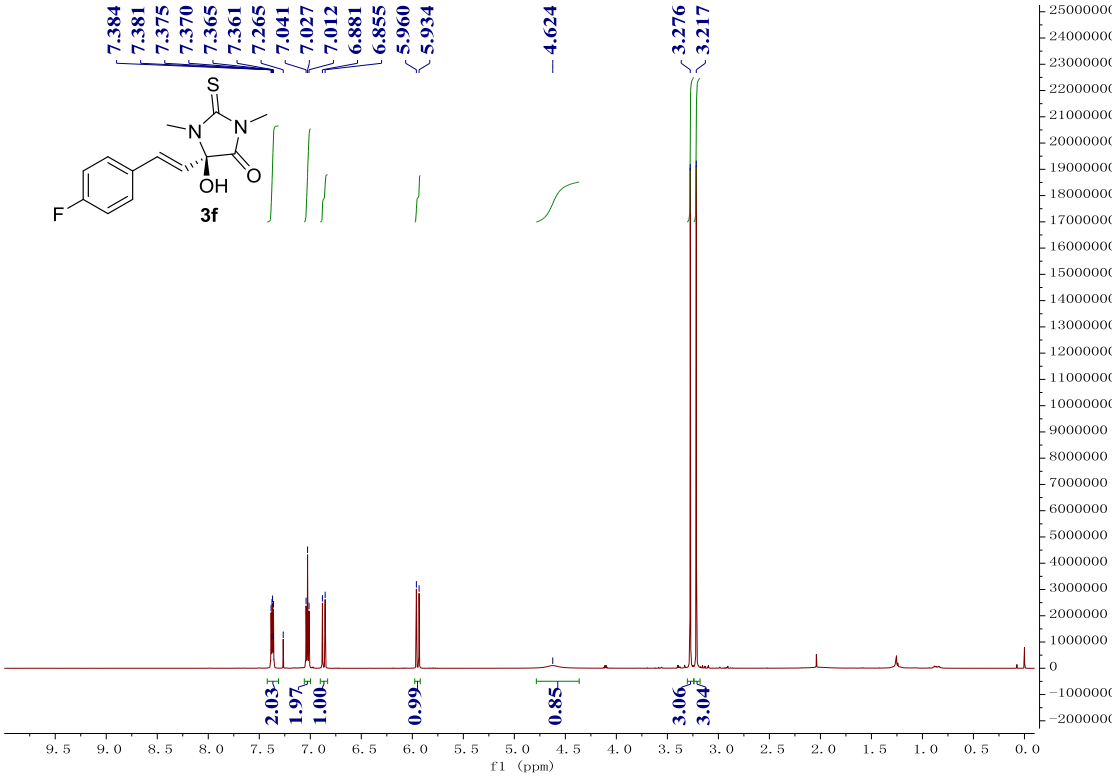
^{1}H NMR for 3e



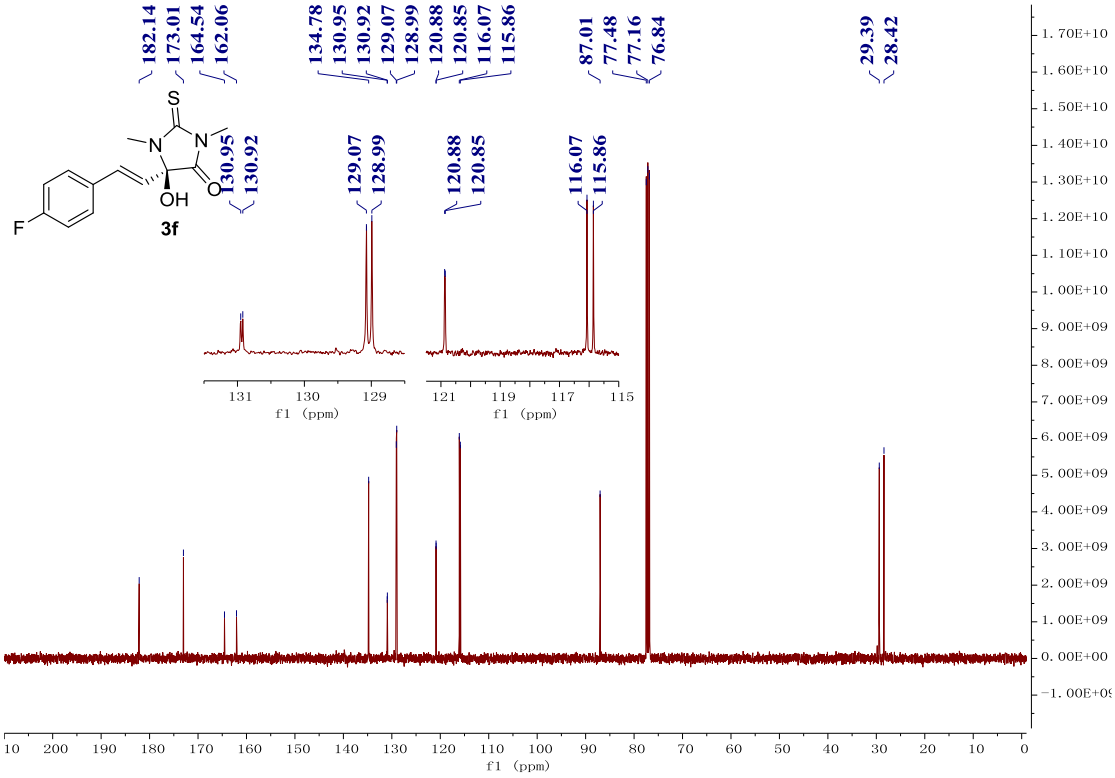
^{13}C NMR for 3e



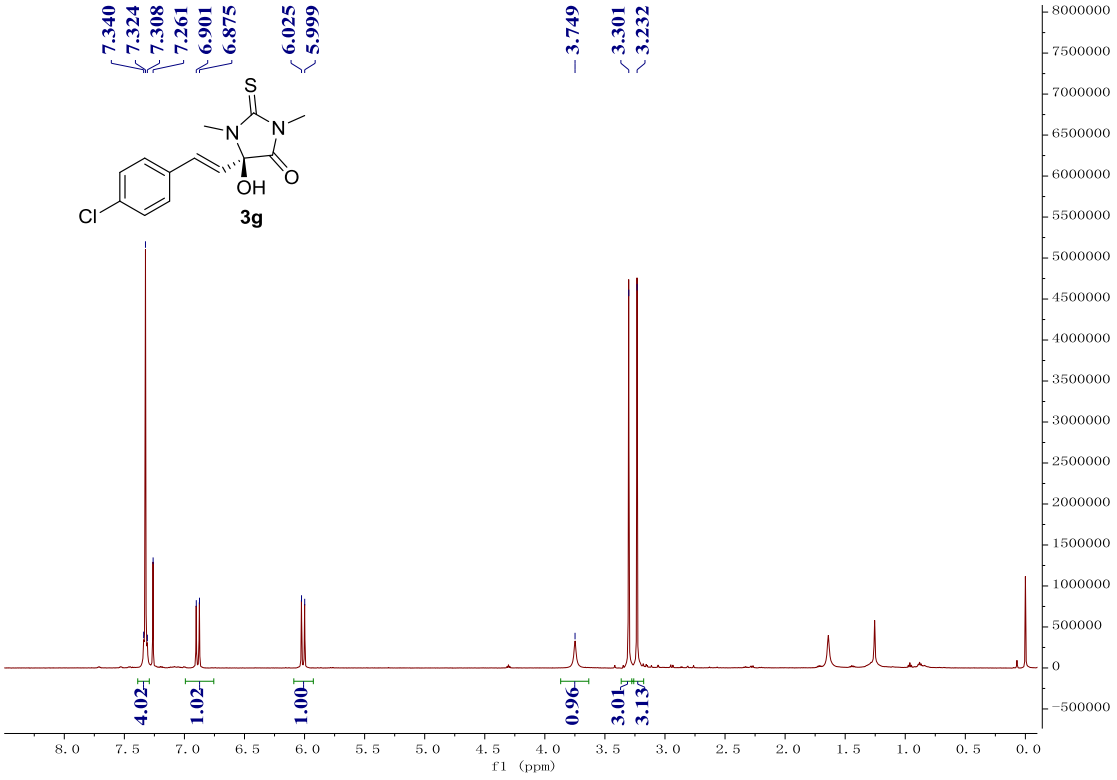
^{1}H NMR for 3f



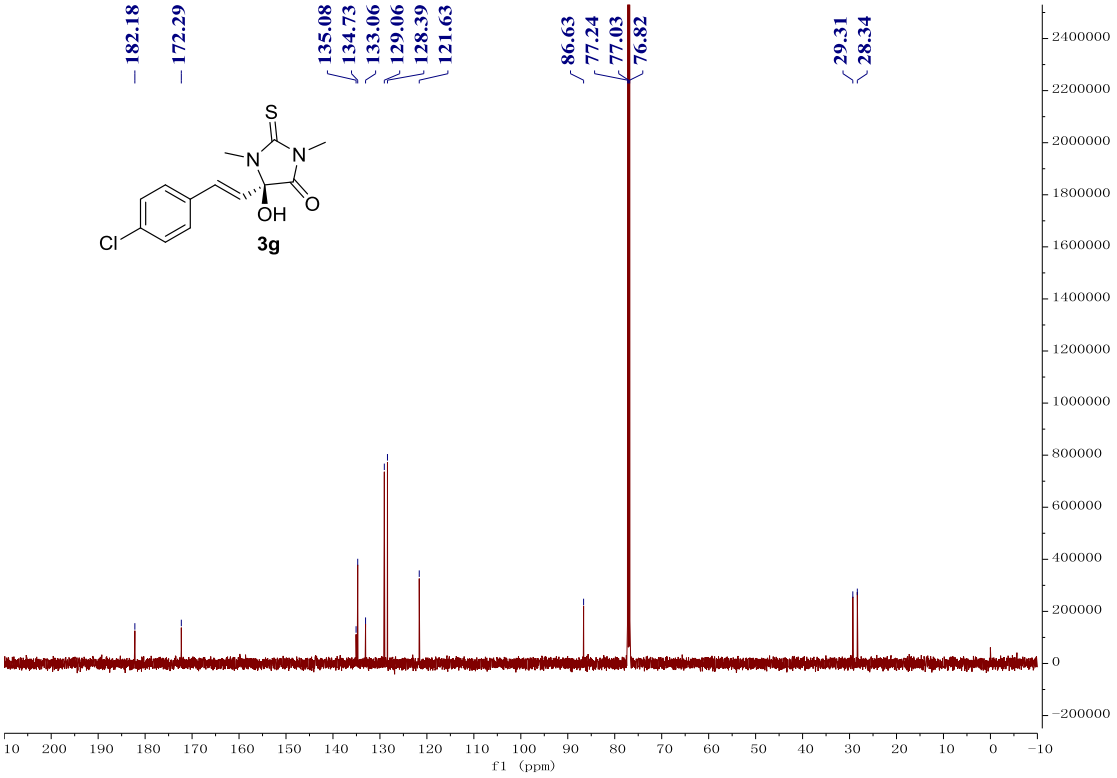
^{13}C NMR for 3f



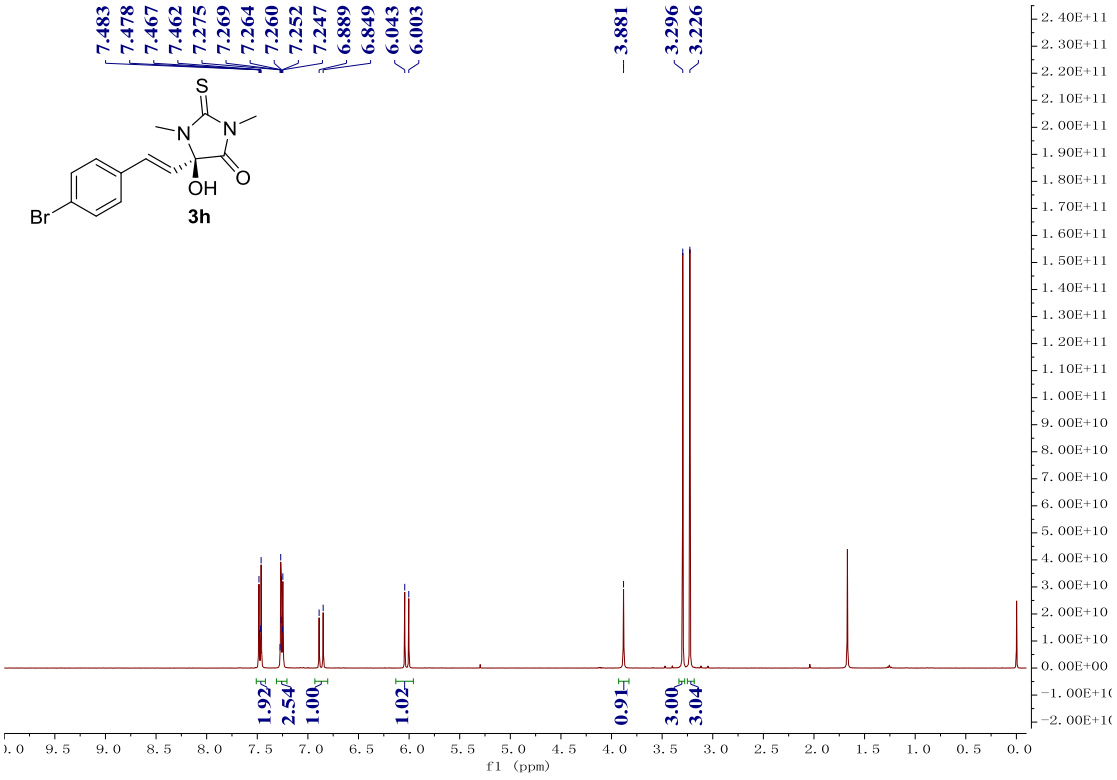
^{1}H NMR for 3g



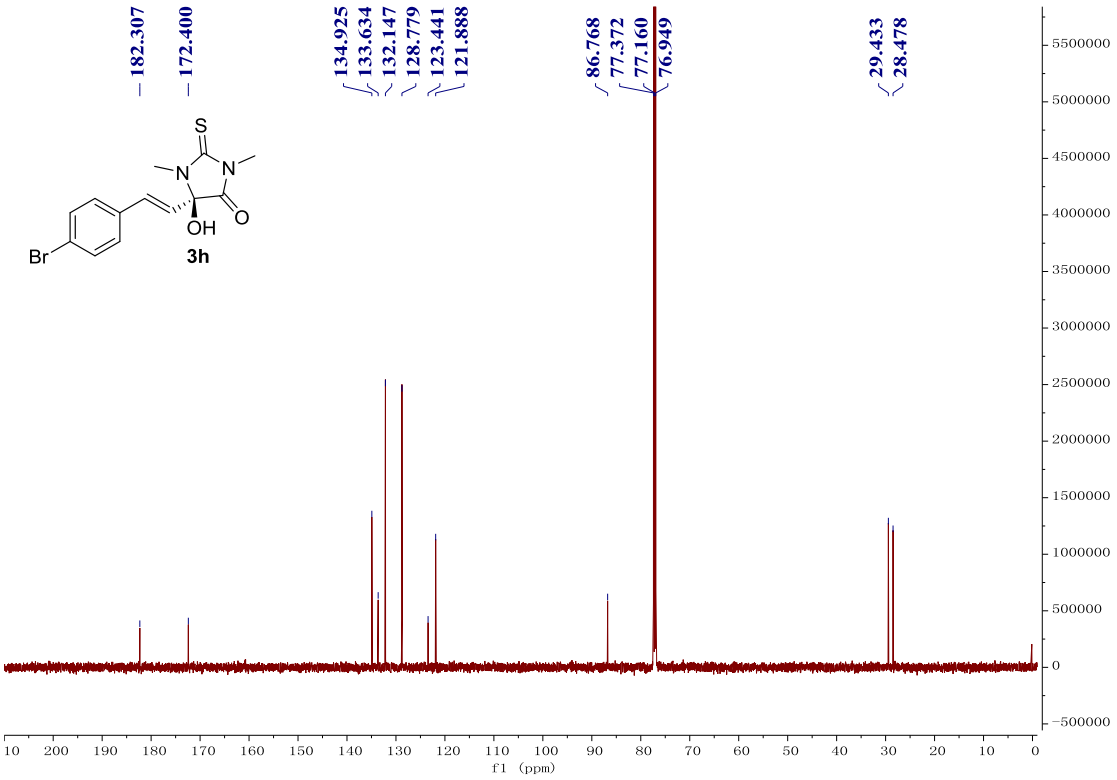
^{13}C NMR for 3g



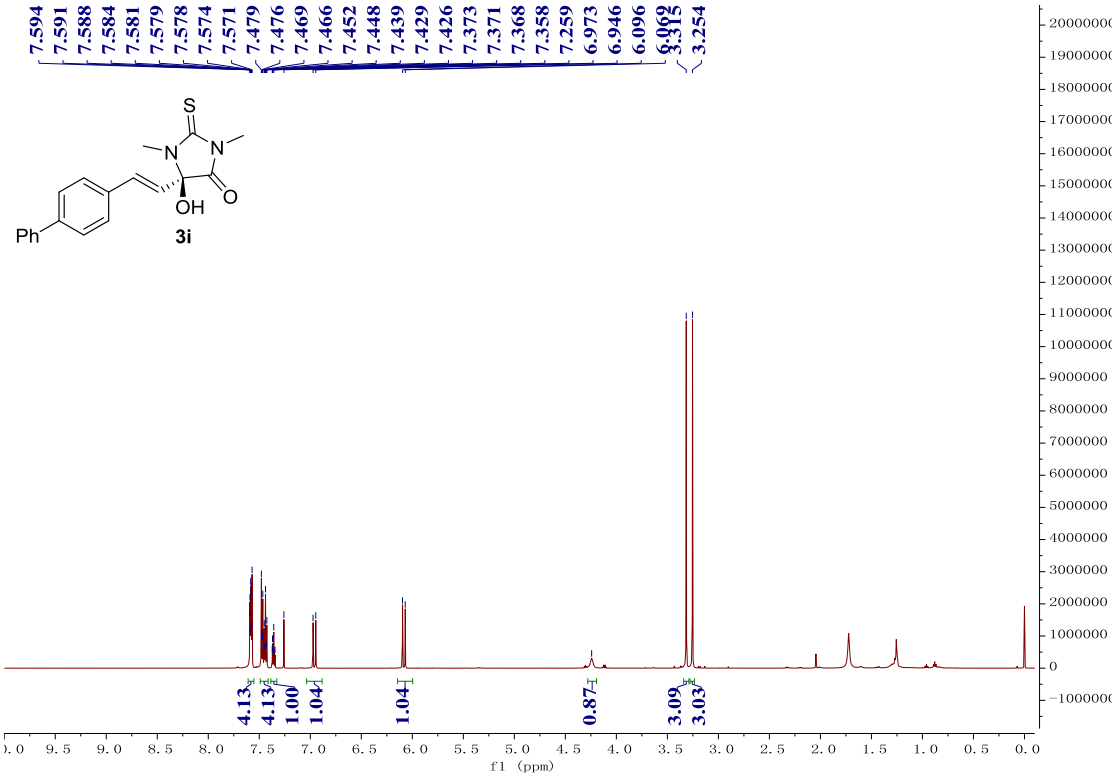
^{1}H NMR for 3h



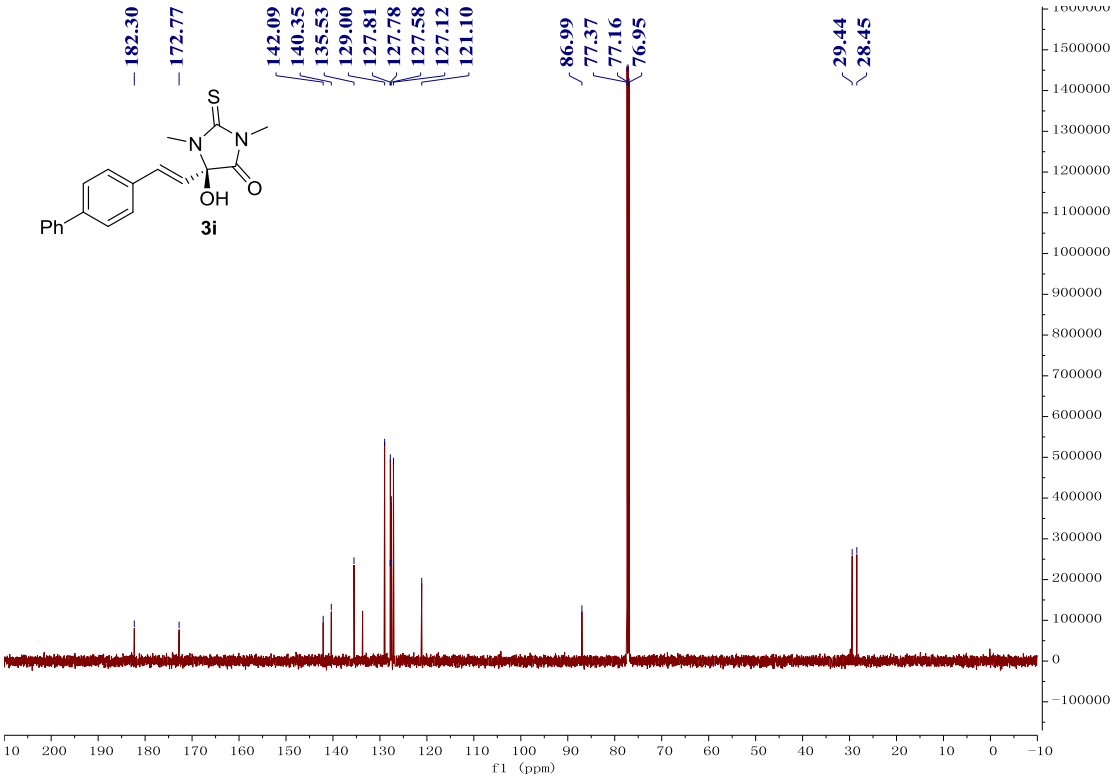
^{13}C NMR for 3h



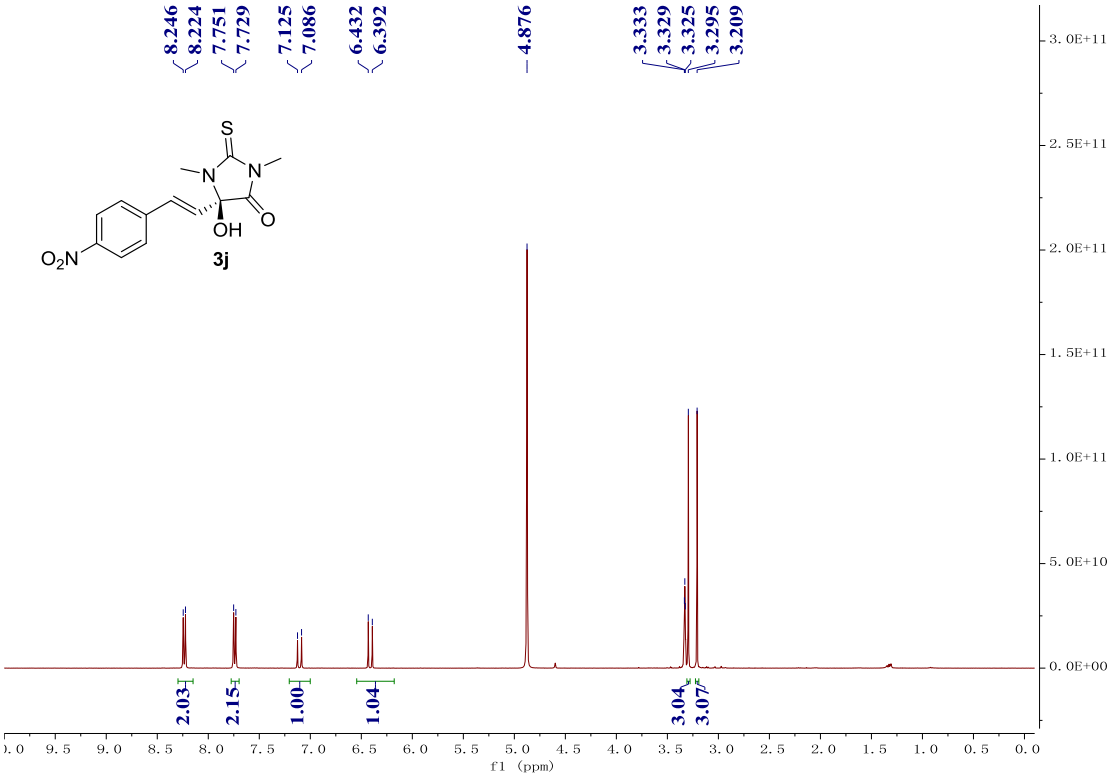
^{1}H NMR for 3i



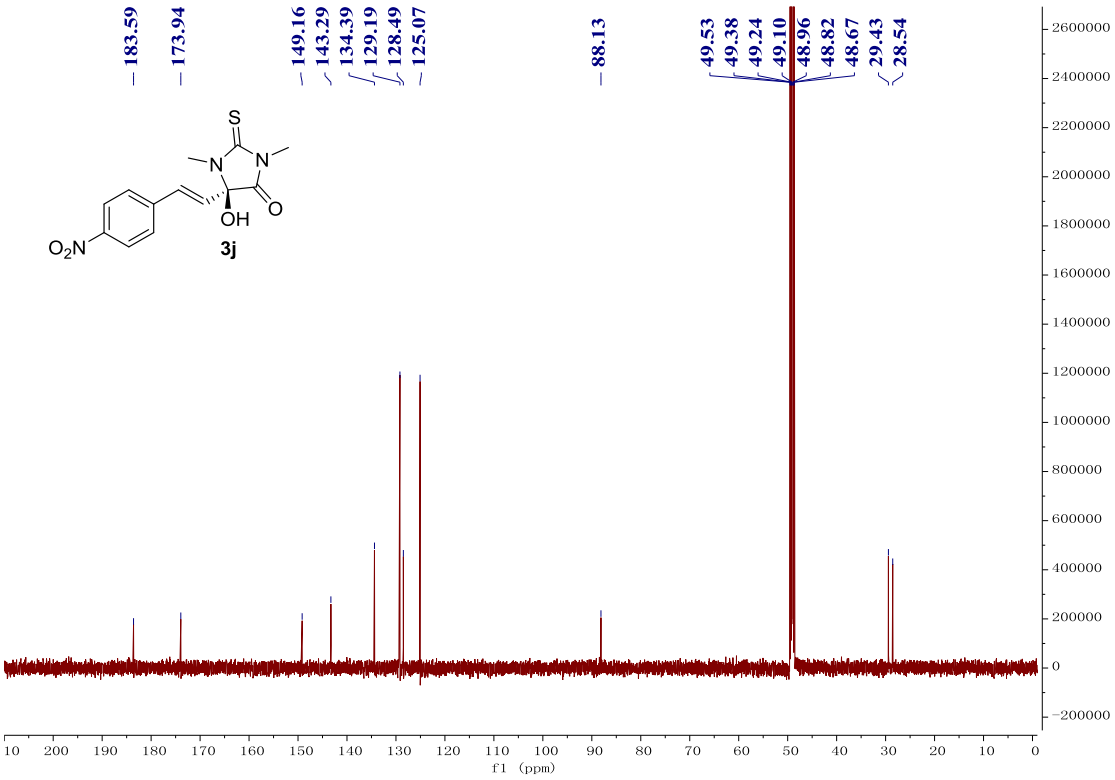
^{13}C NMR for 3i



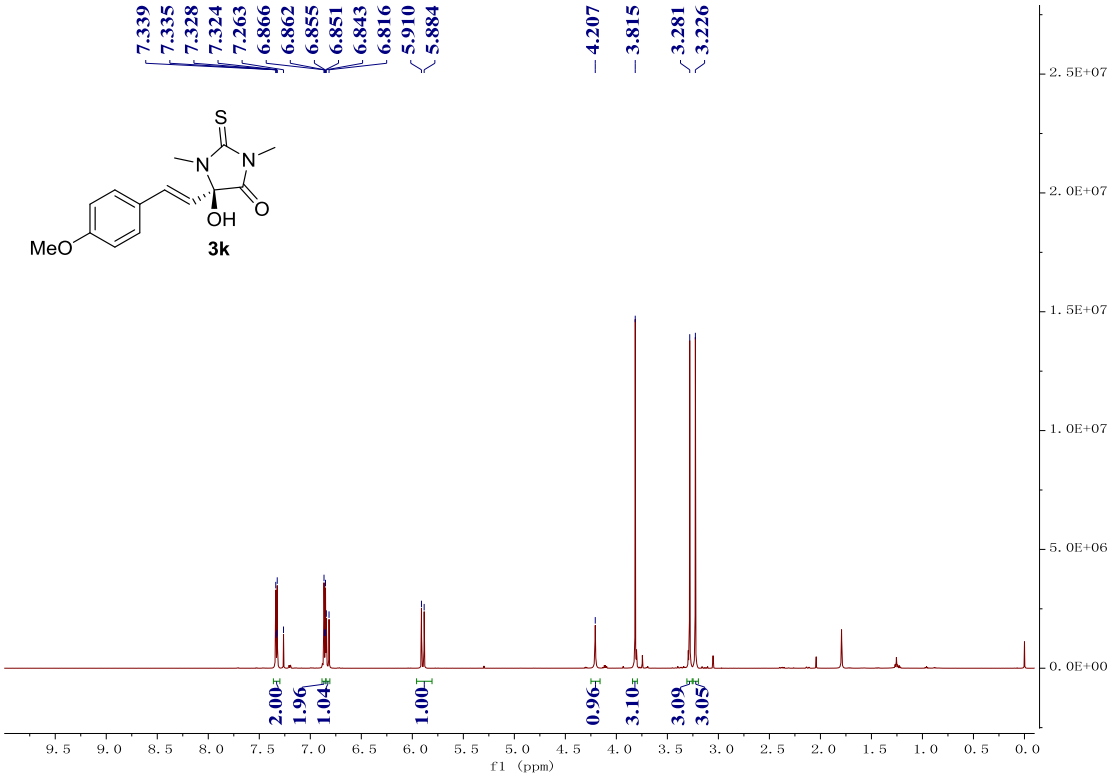
^{1}H NMR for 3j



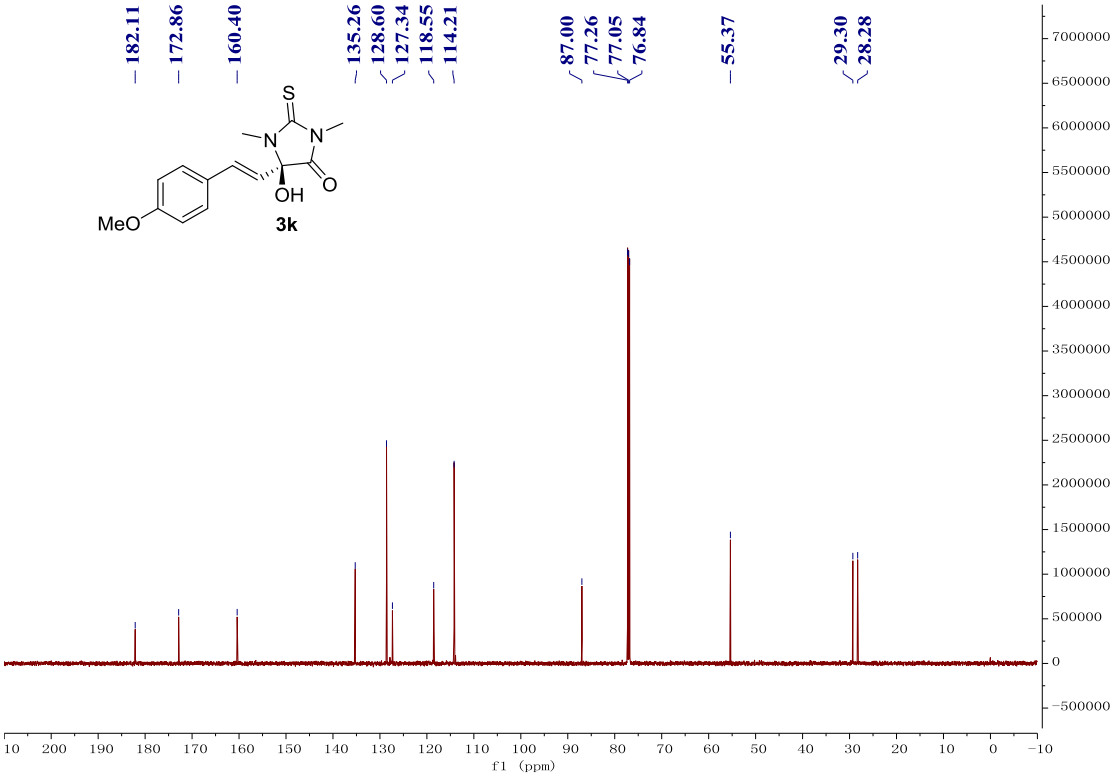
^{13}C NMR for 3j



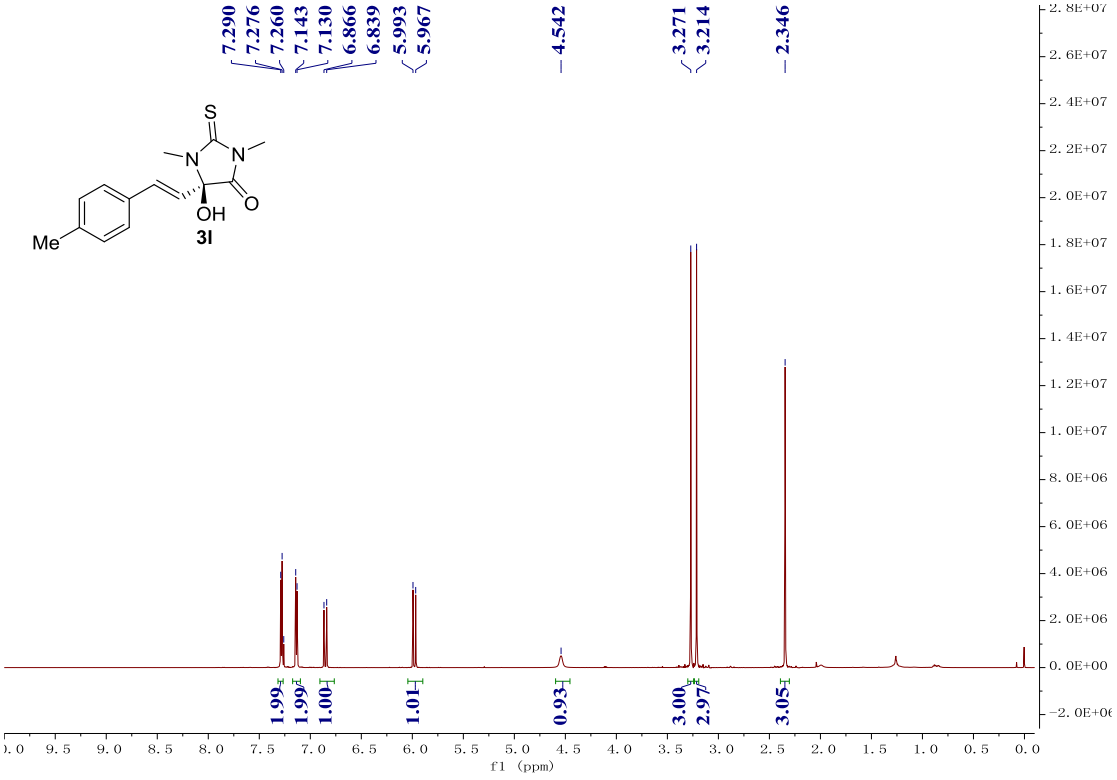
^{1}H NMR for 3k



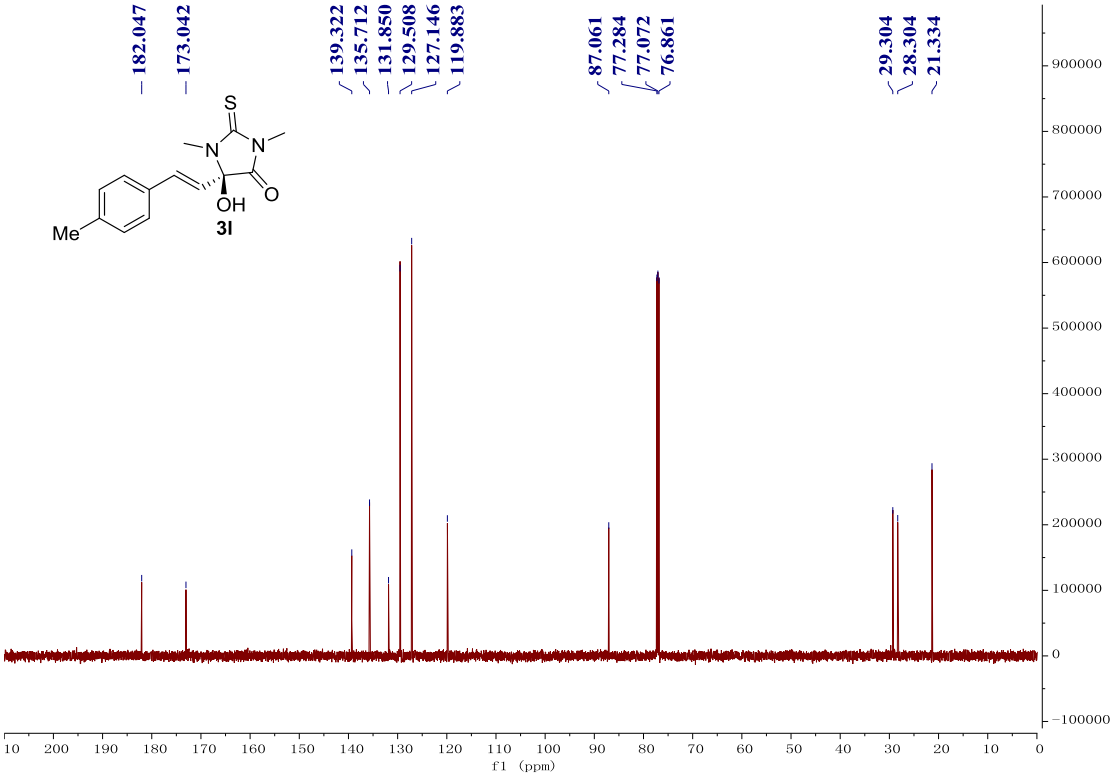
^{13}C NMR for 3k



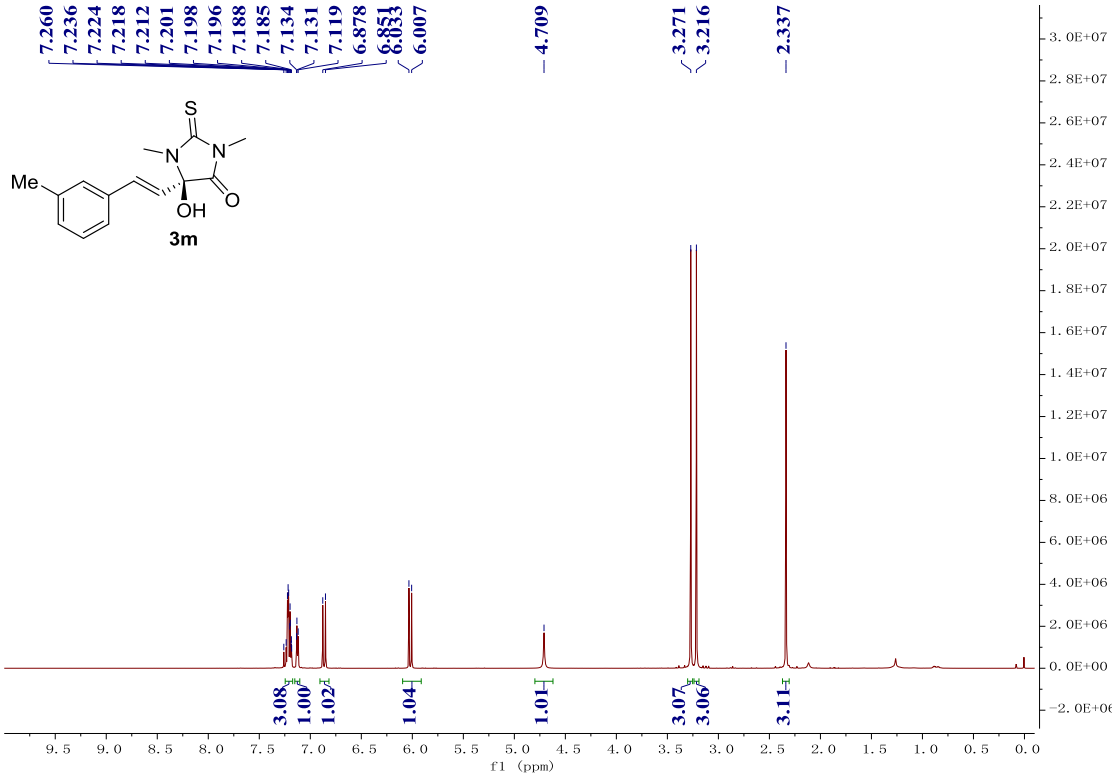
^{1}H NMR for 3l



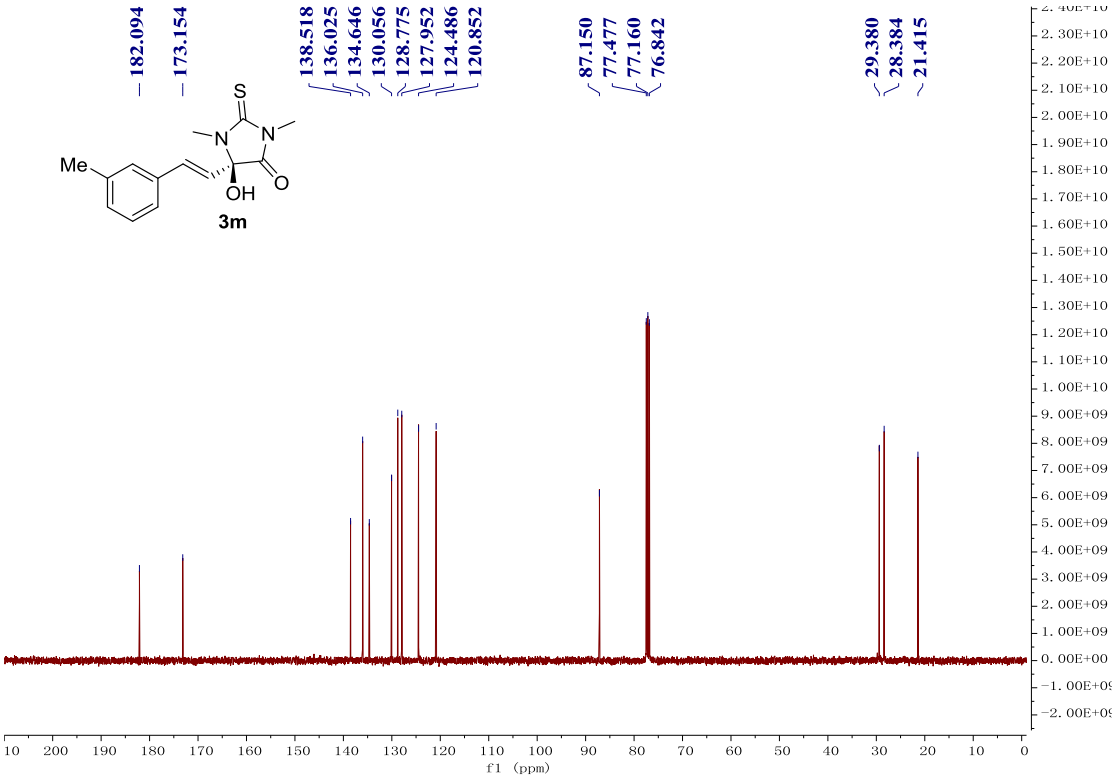
^{13}C NMR for 3l



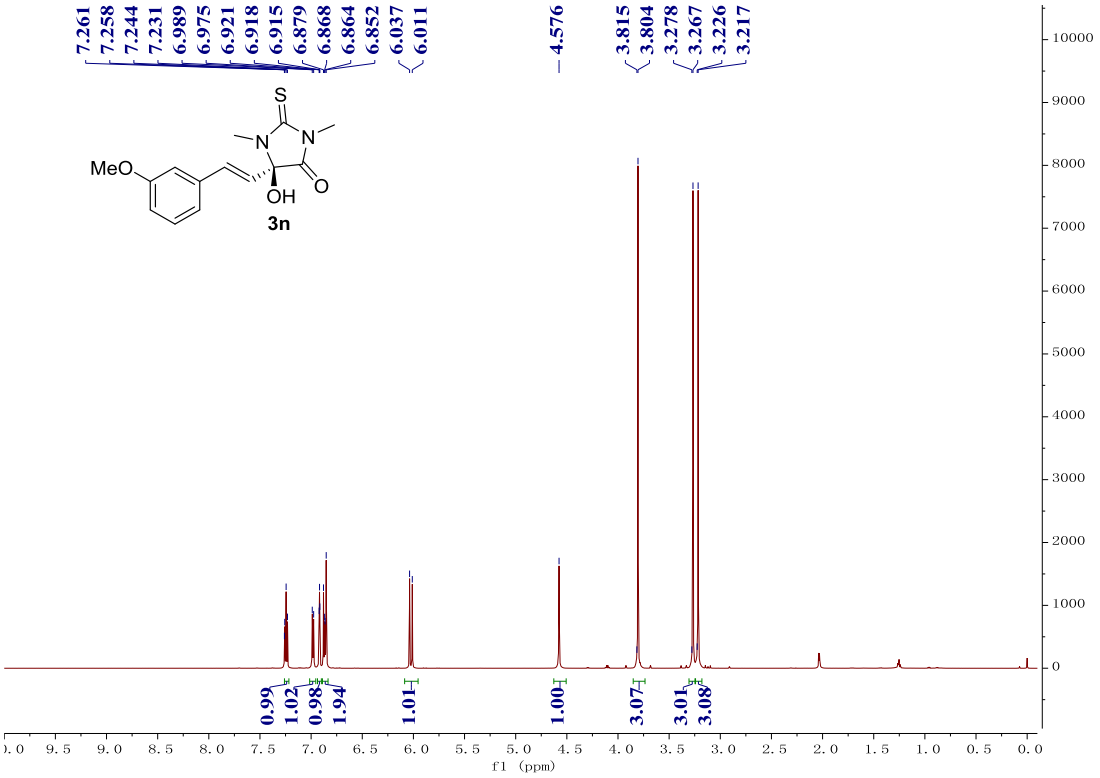
^{1}H NMR for 3m



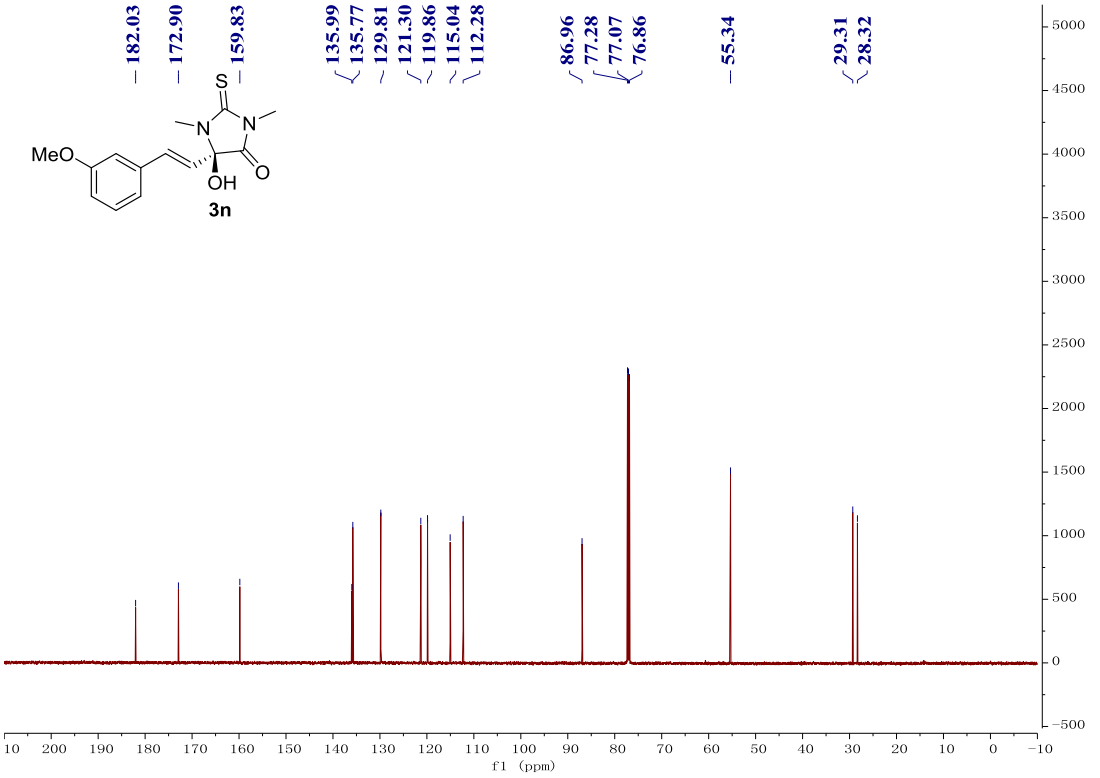
^{13}C NMR for 3m



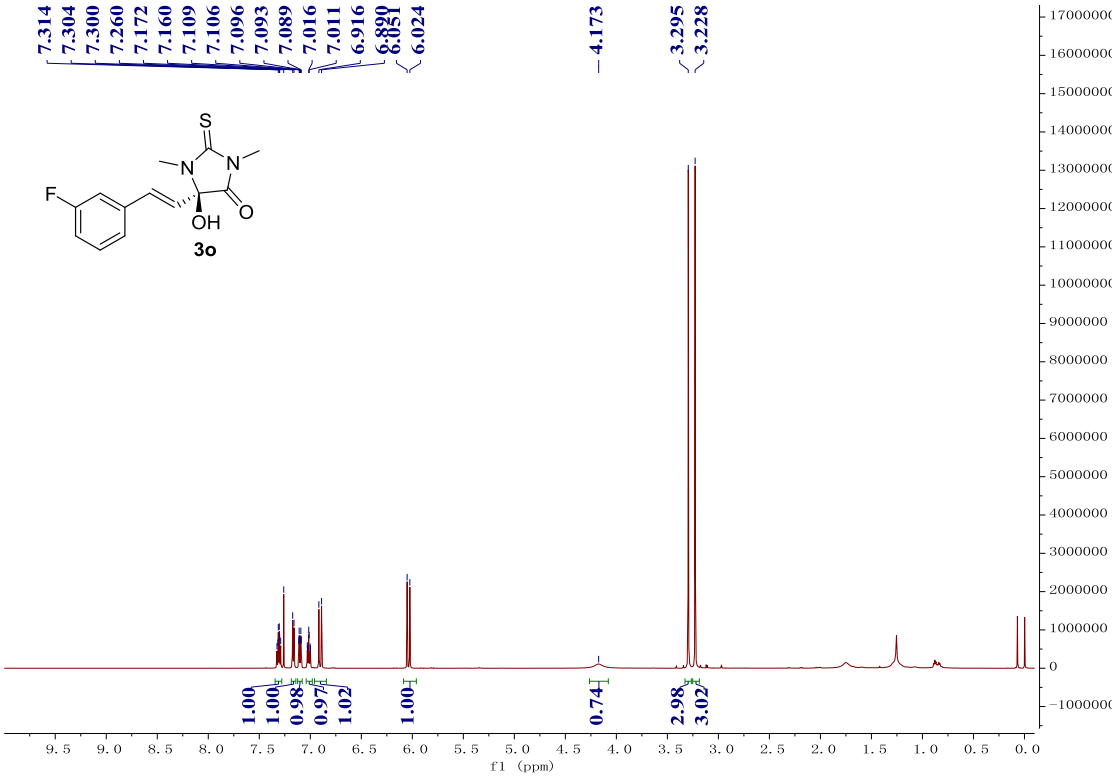
^{1}H NMR for 3n



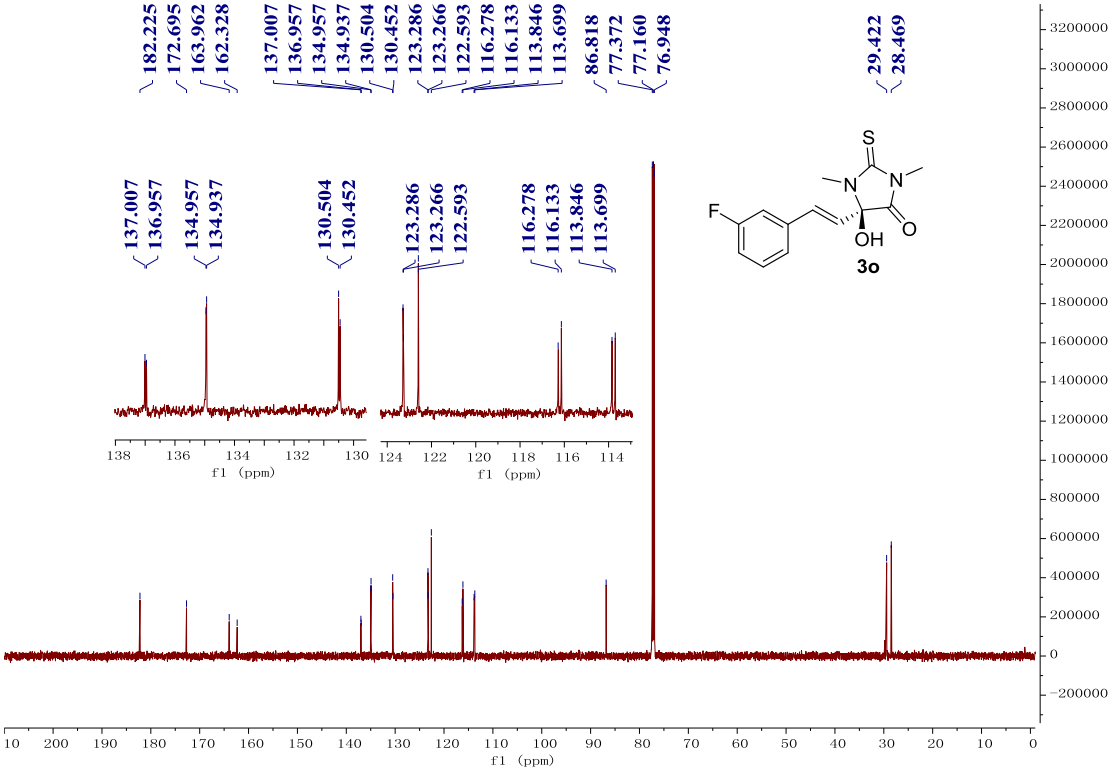
^{13}C NMR for 3n



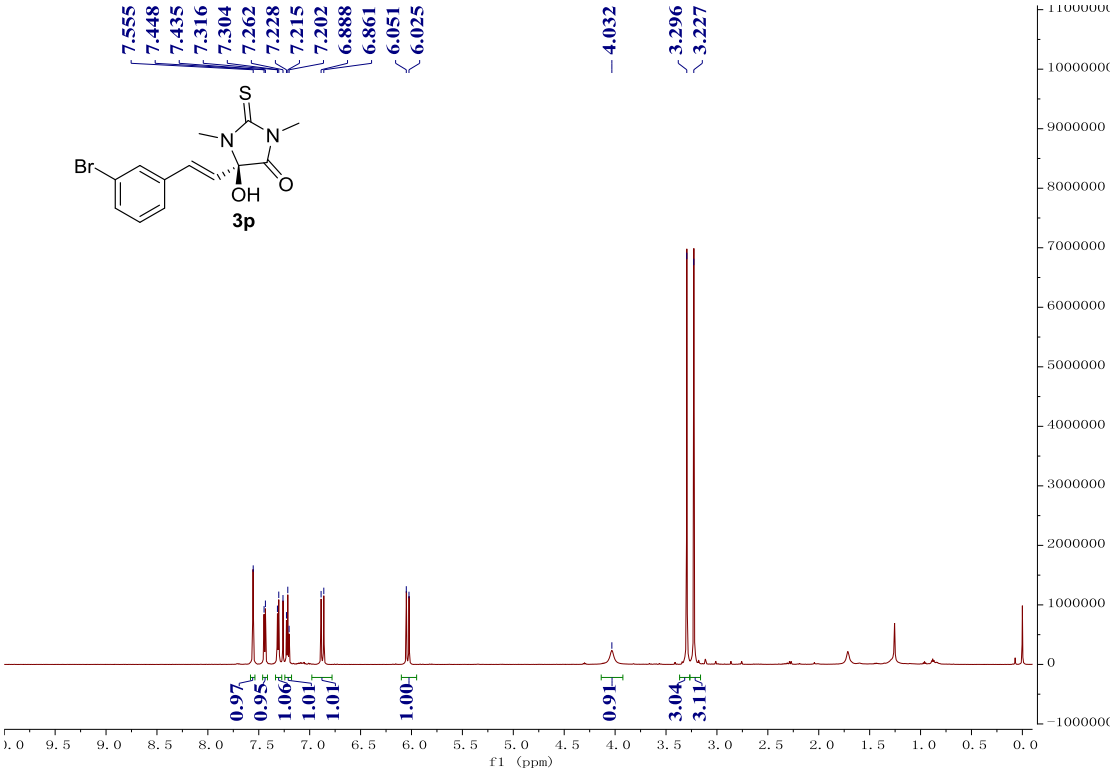
^{1}H NMR for 3o



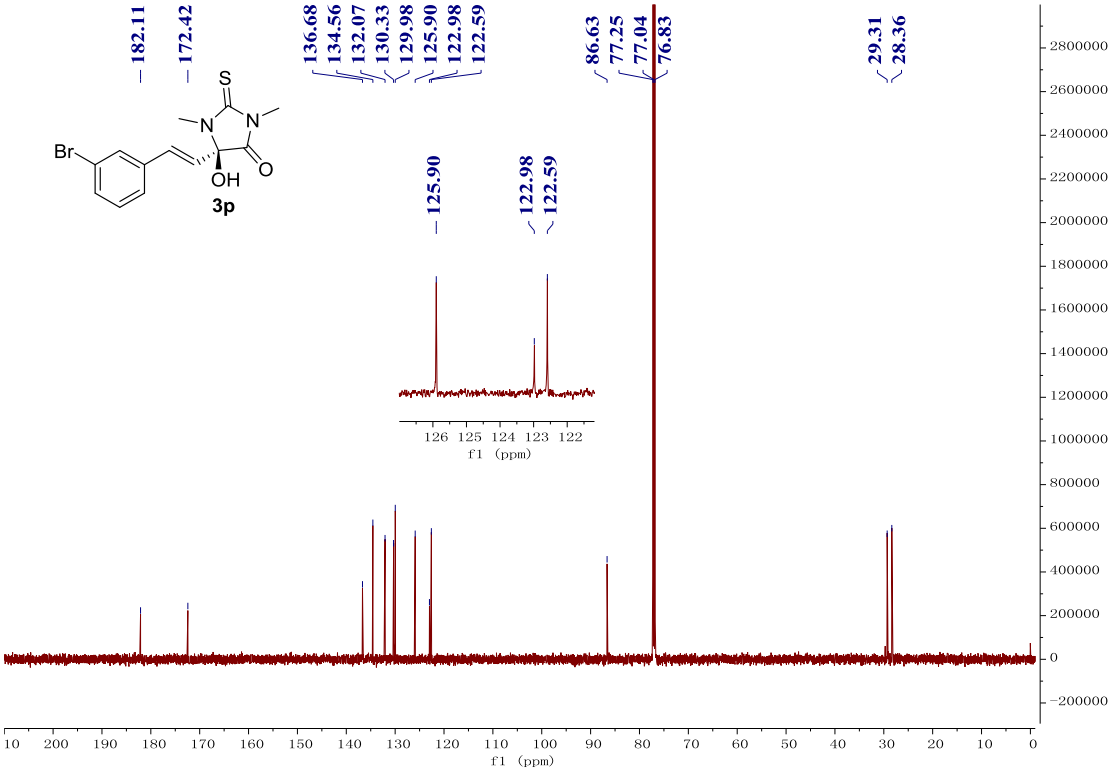
^{13}C NMR for 3o



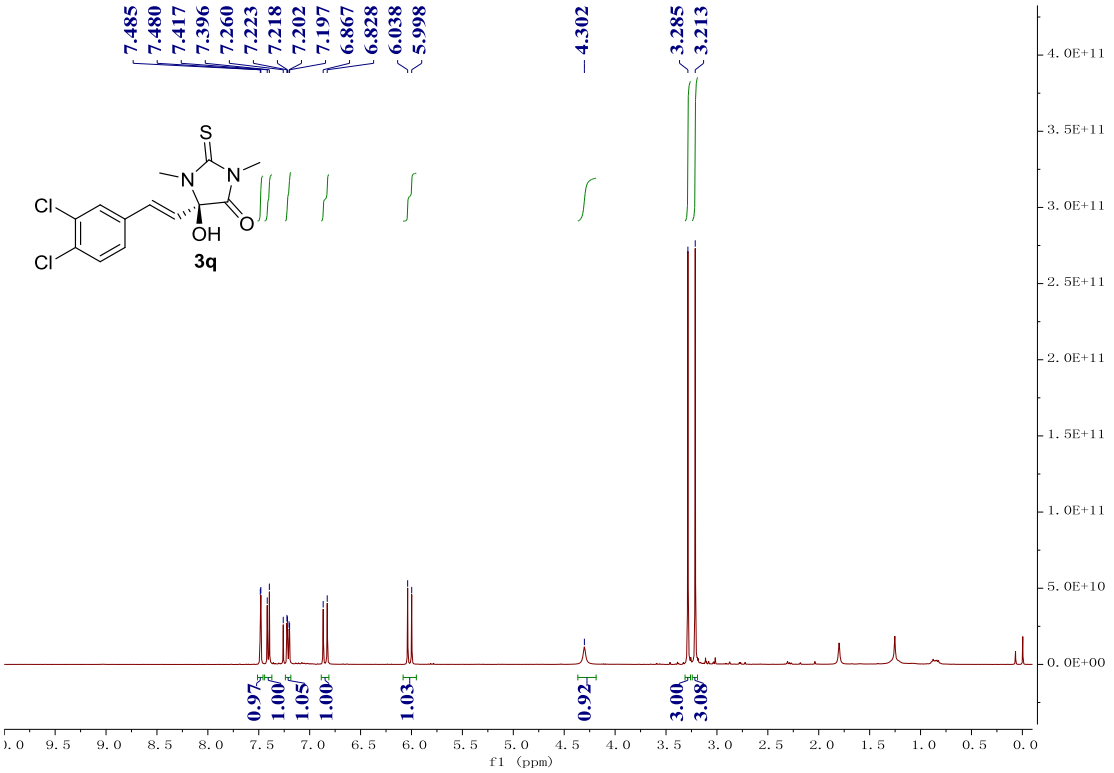
^{1}H NMR for 3p



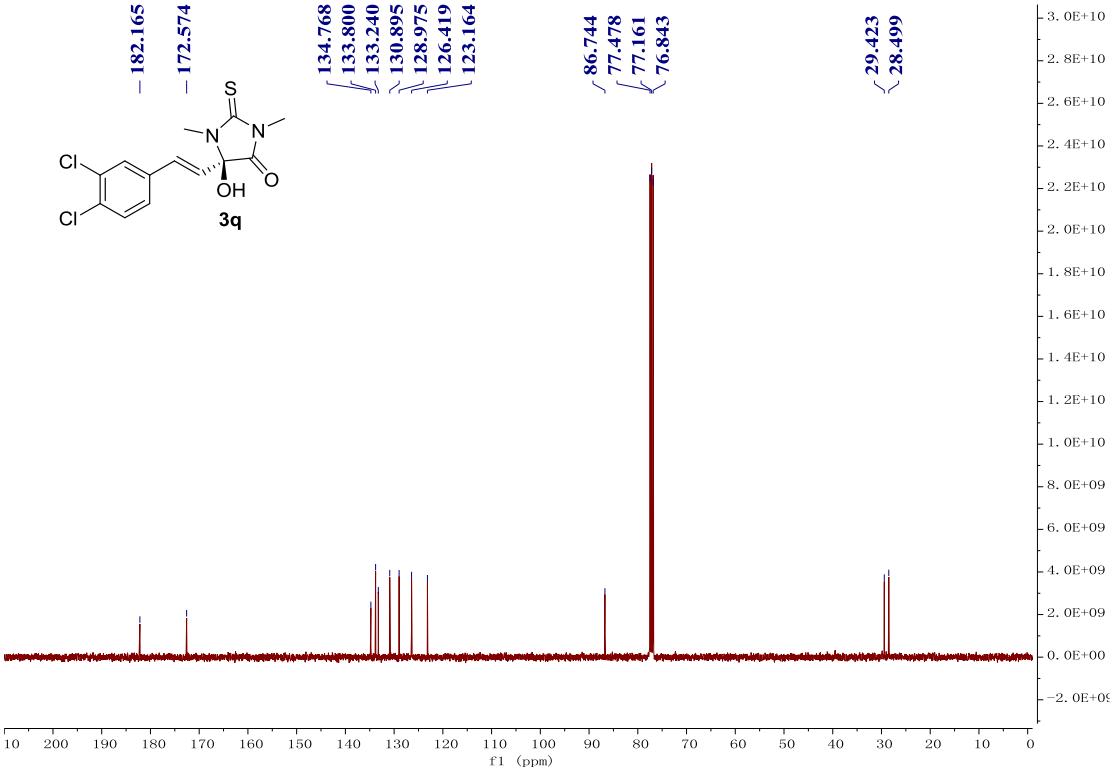
^{13}C NMR for 3p



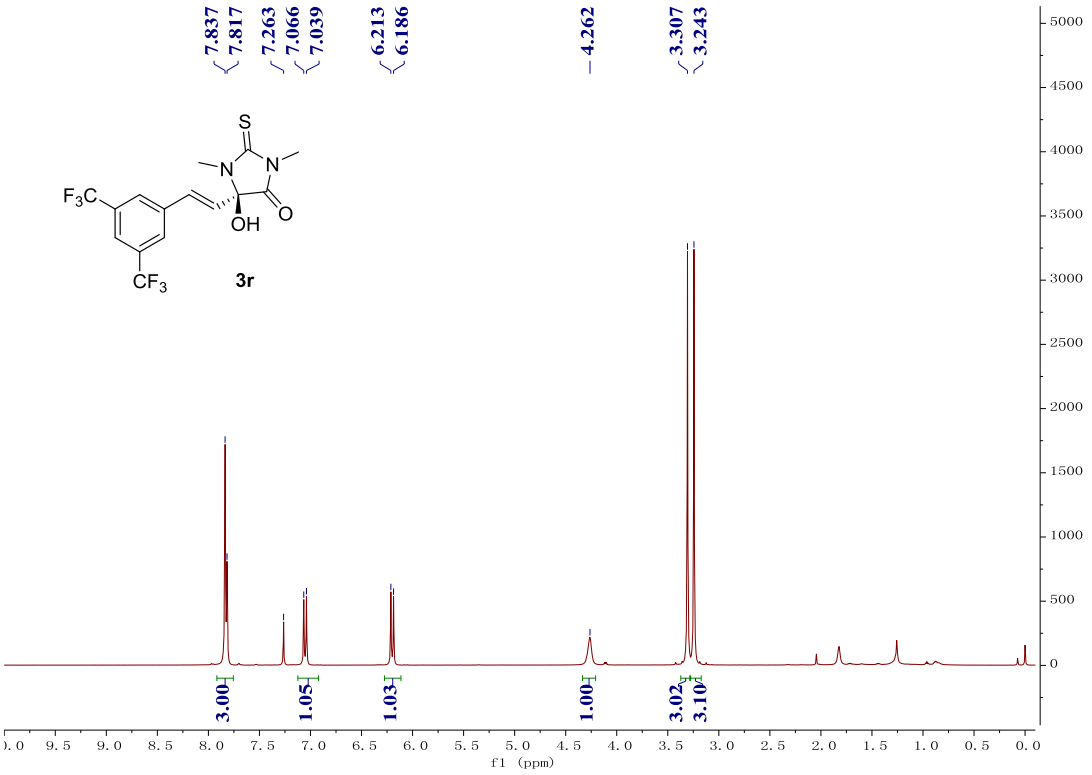
^{1}H NMR for 3q



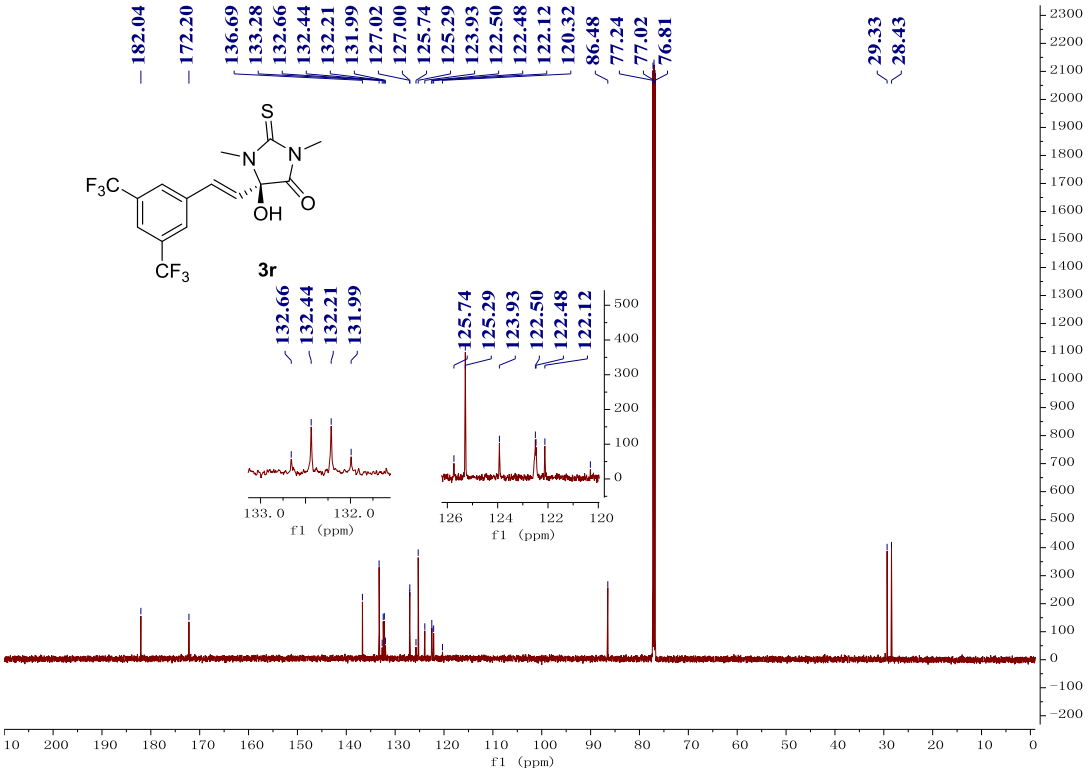
^{13}C NMR for 3q



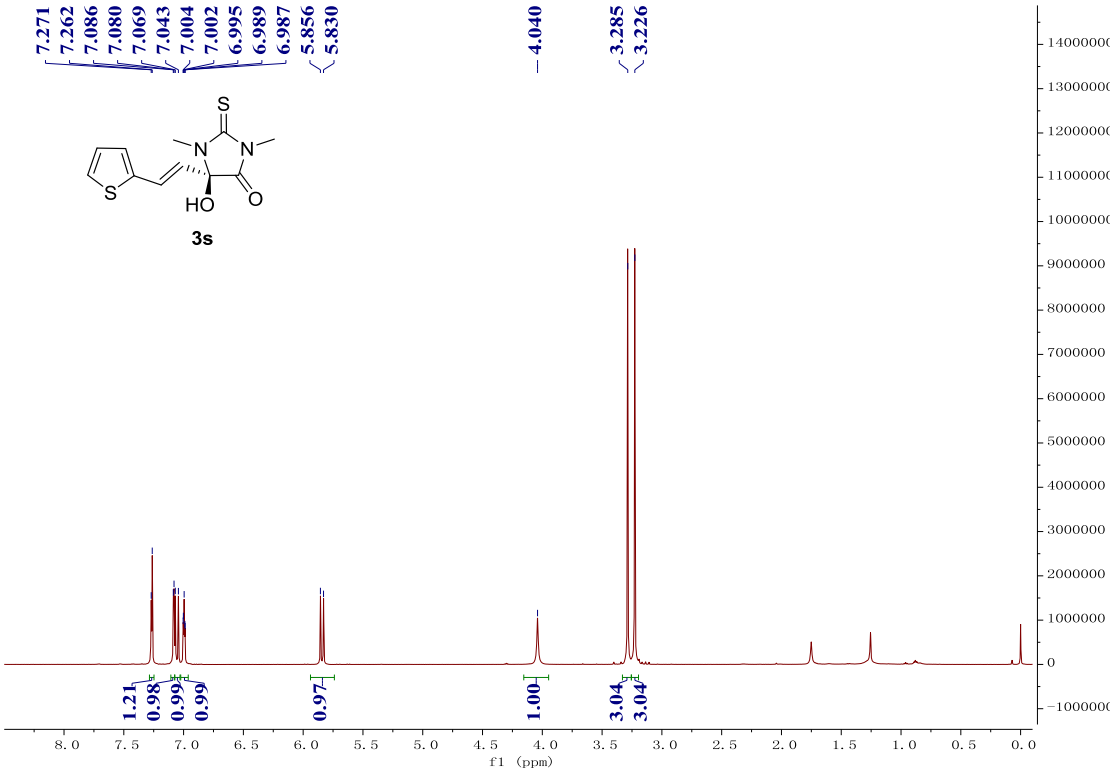
^{1}H NMR for 3r



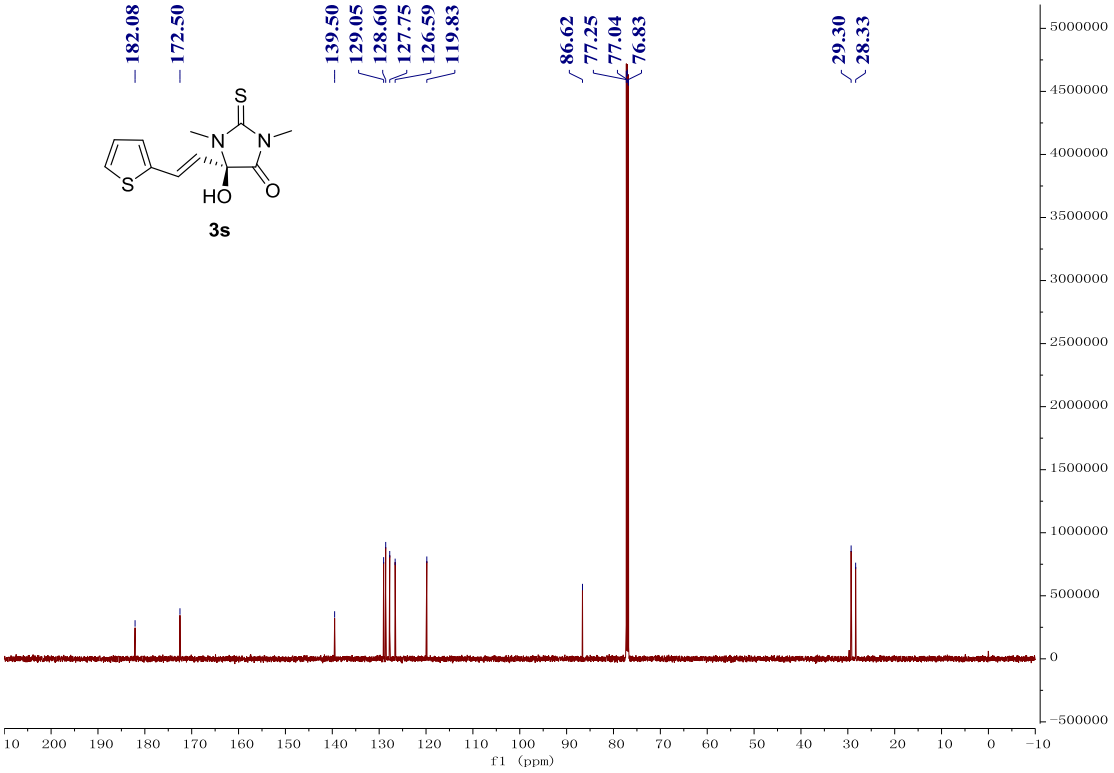
^{13}C NMR for 3r



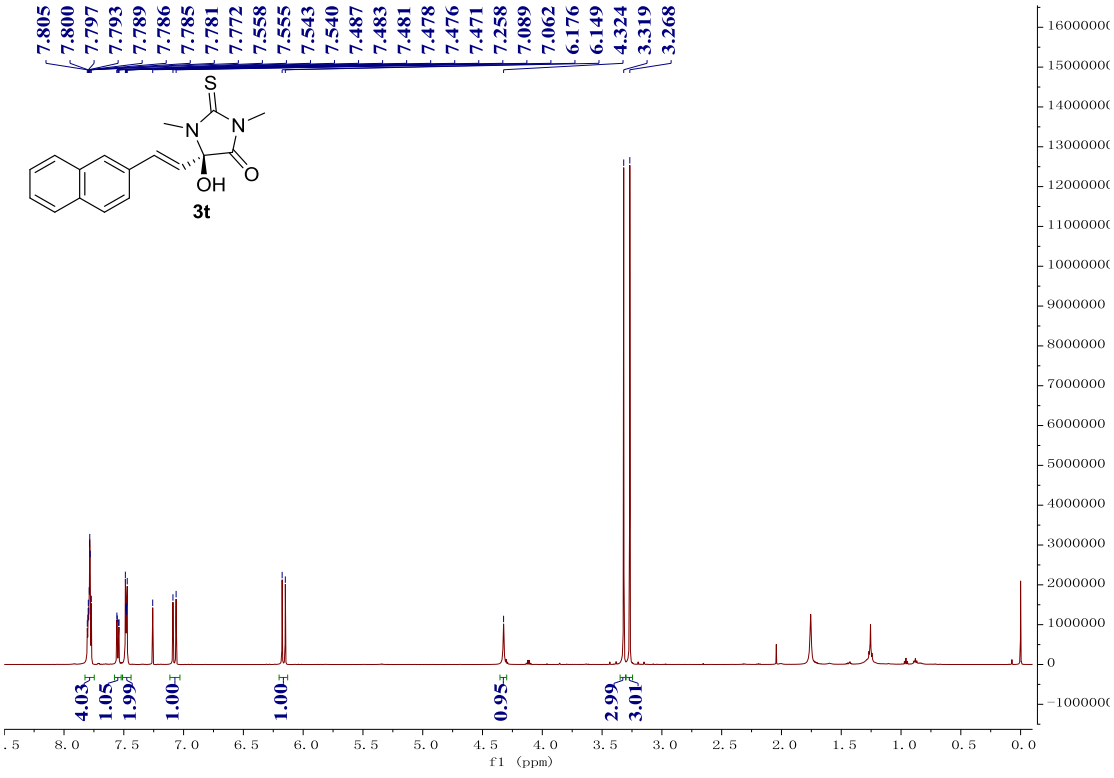
^{1}H NMR for 3s



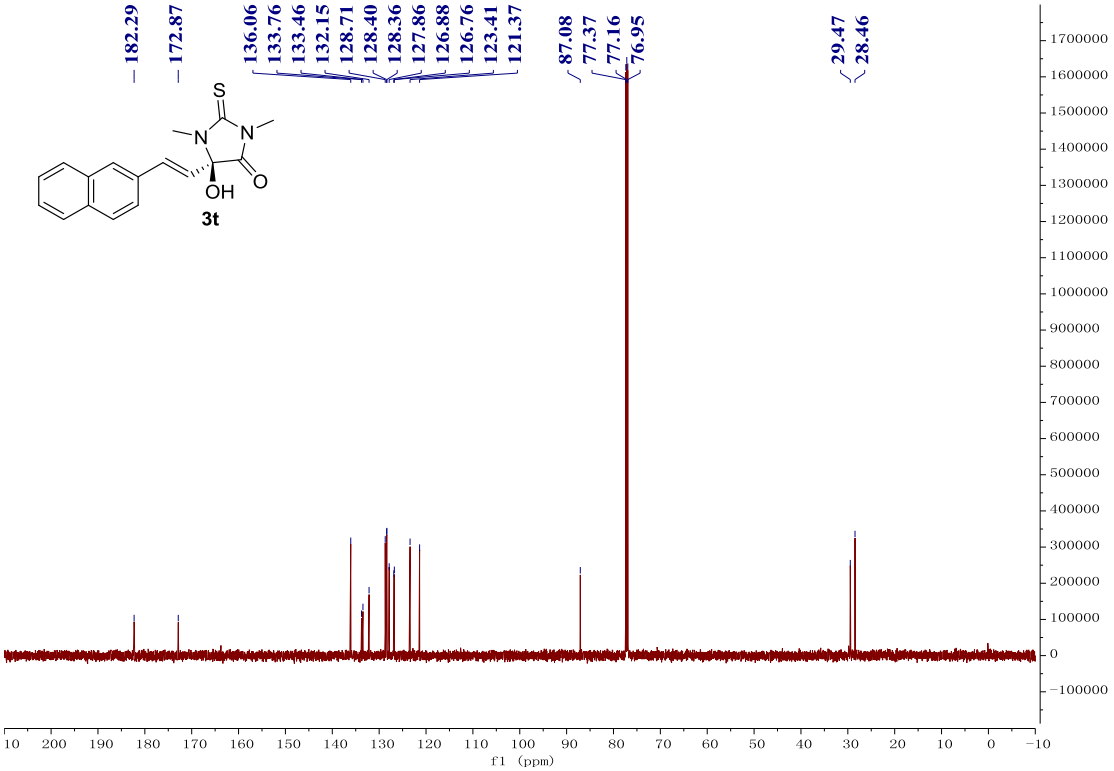
^{13}C NMR for 3s



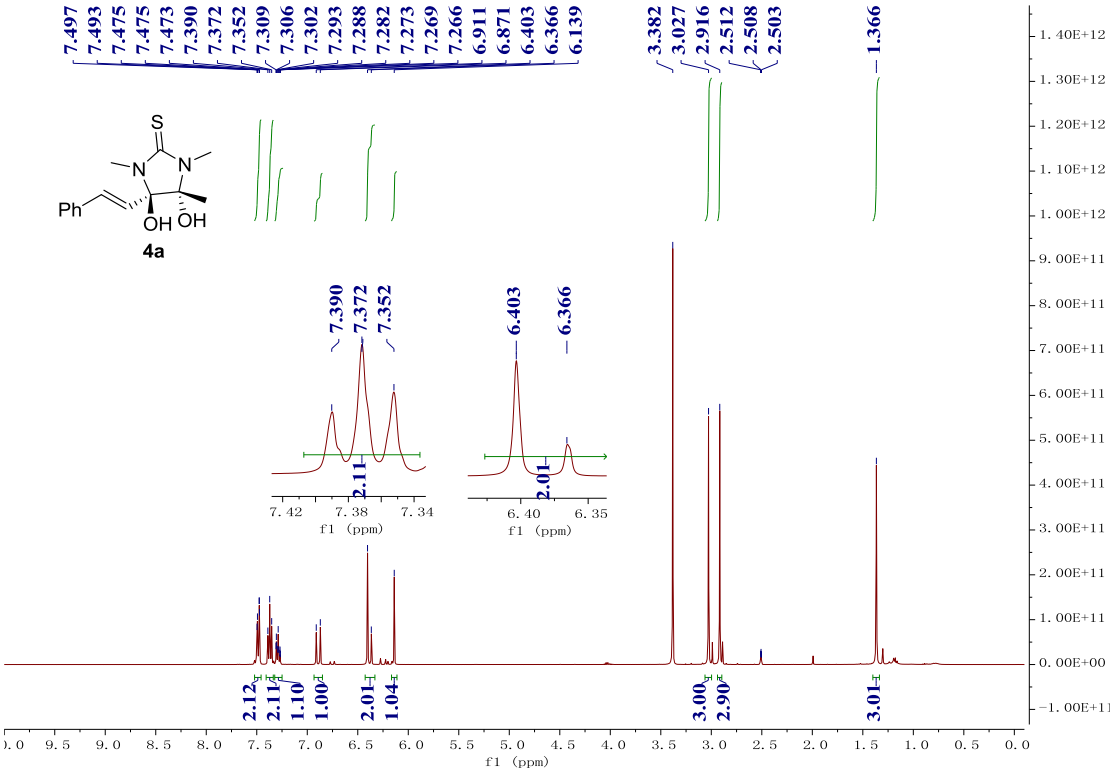
^{1}H NMR for 3t



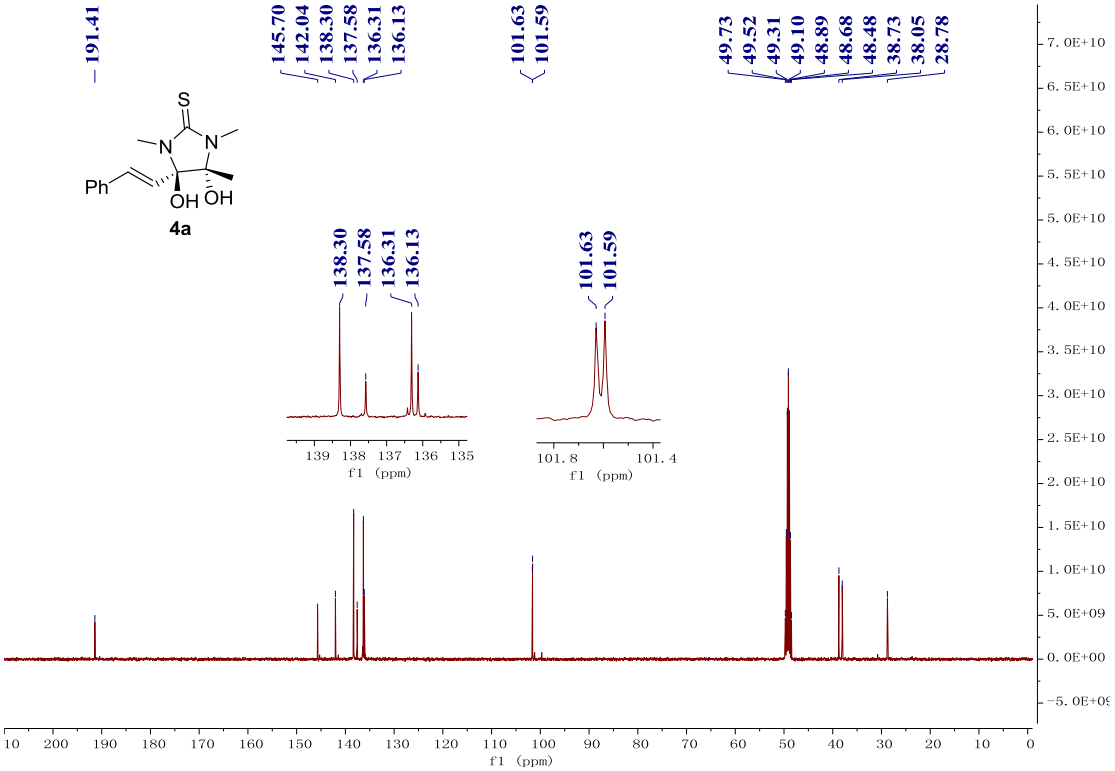
^{13}C NMR for 3t



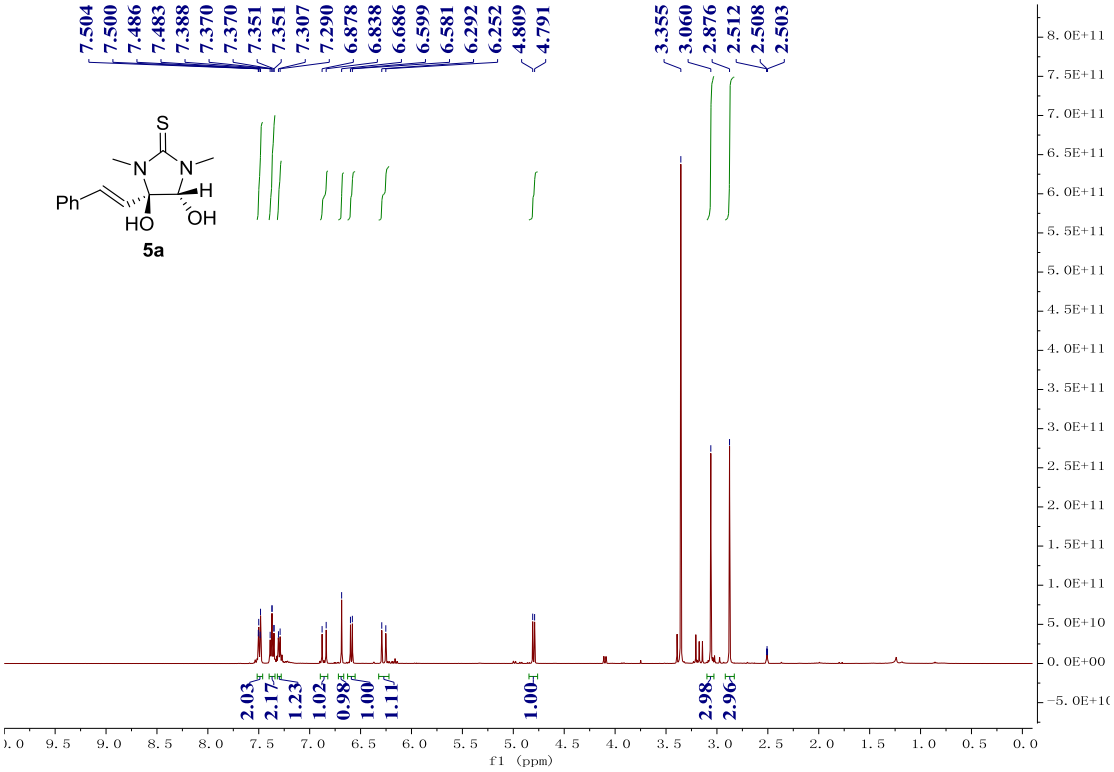
^{1}H NMR for 4a



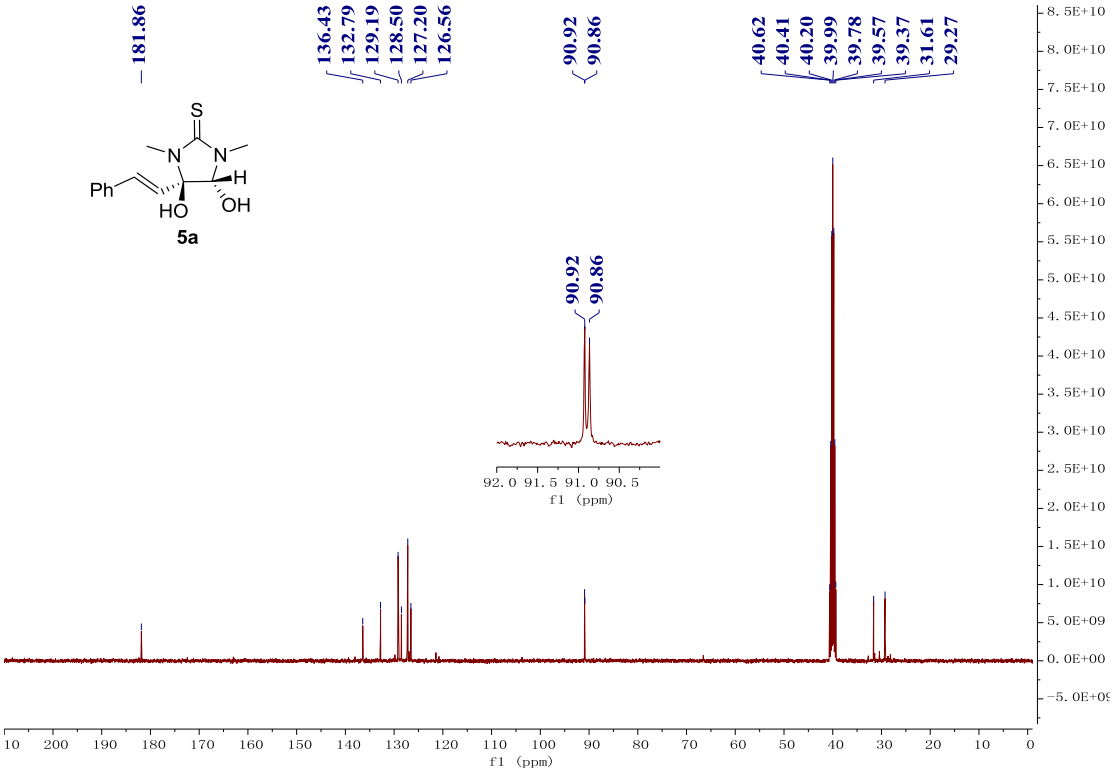
^{13}C NMR for 4a



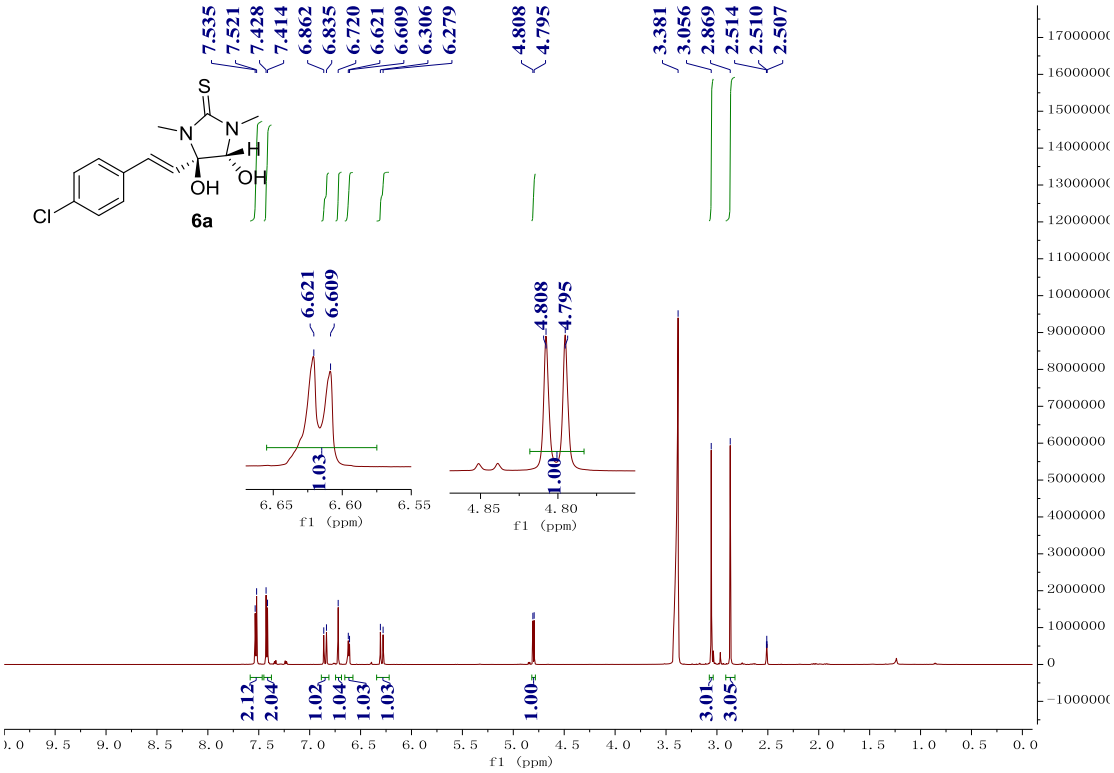
^{1}H NMR for 5a



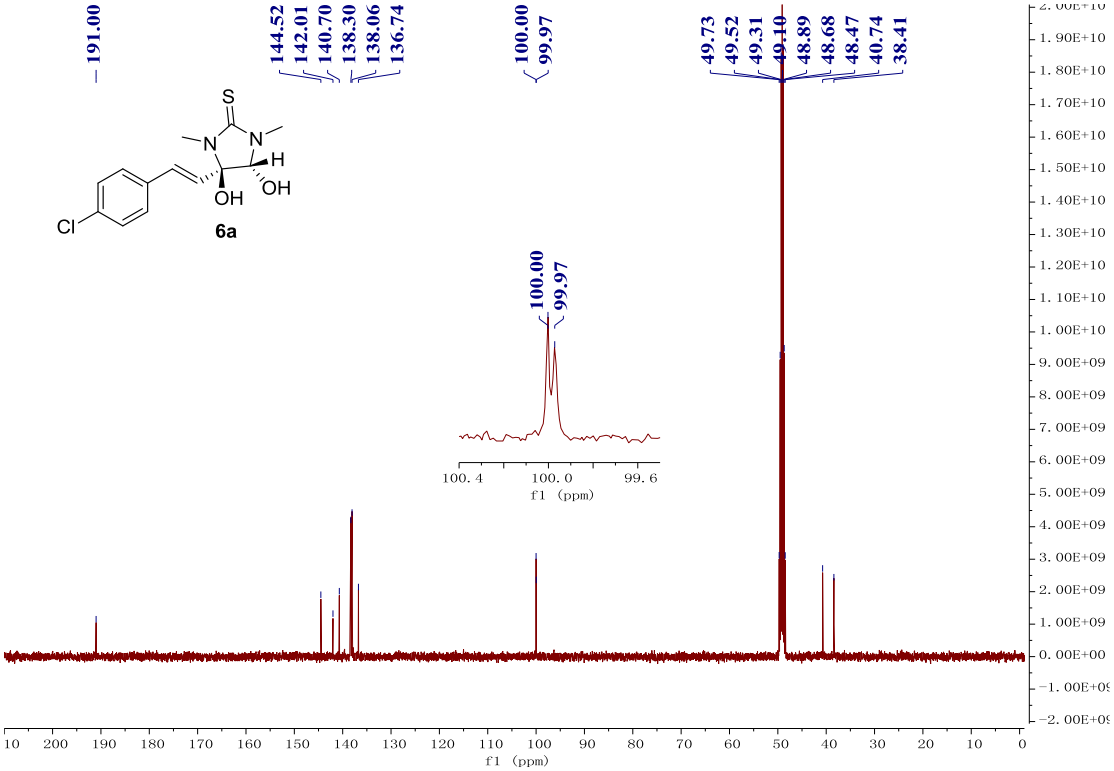
^{13}C NMR for 5a



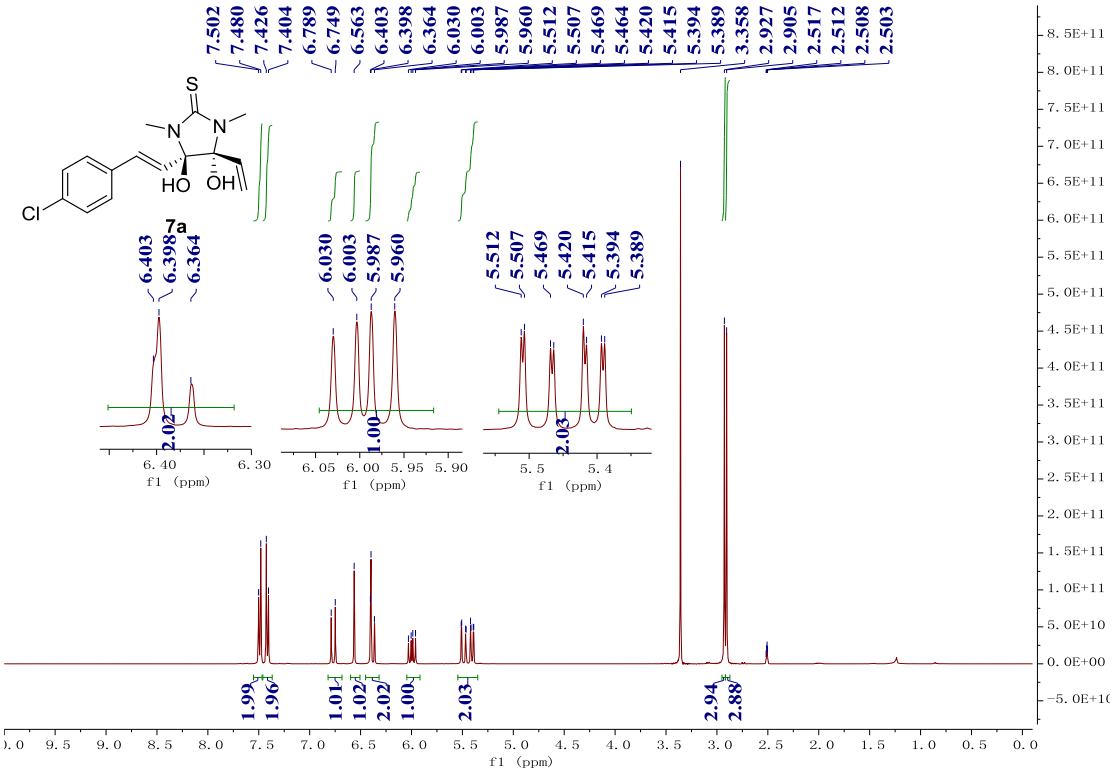
^{1}H NMR for 6a



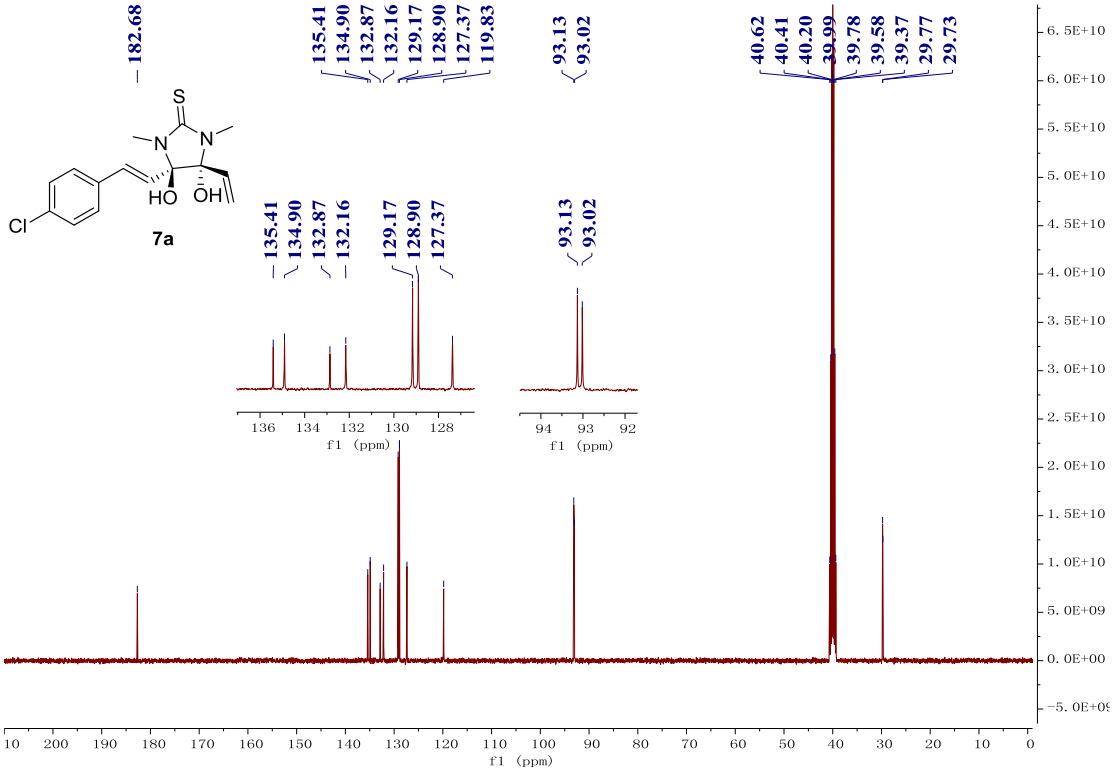
^{13}C NMR for 6a



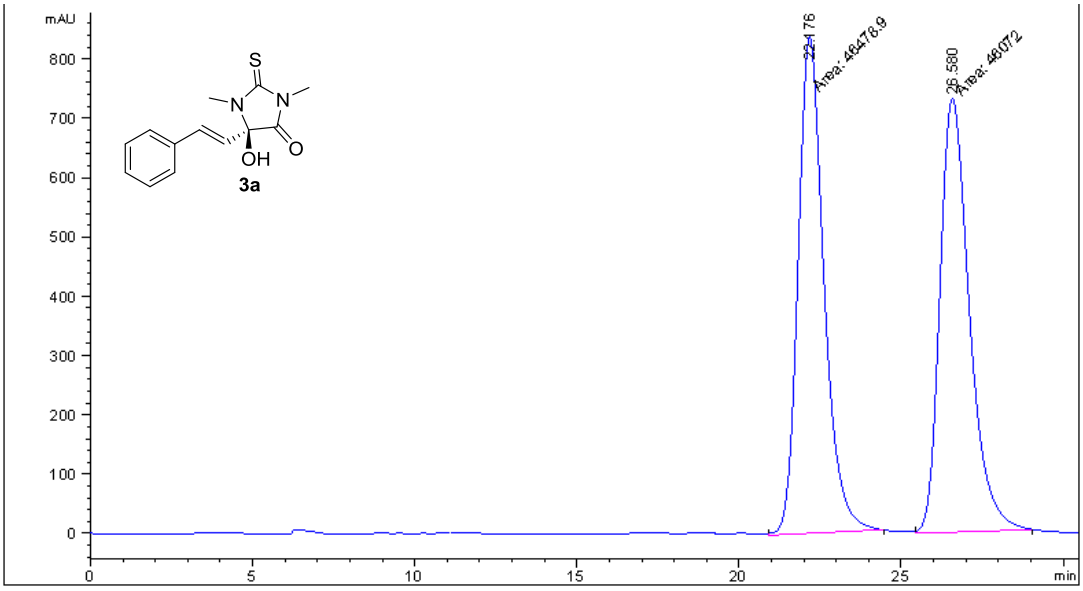
^{1}H NMR for 7a



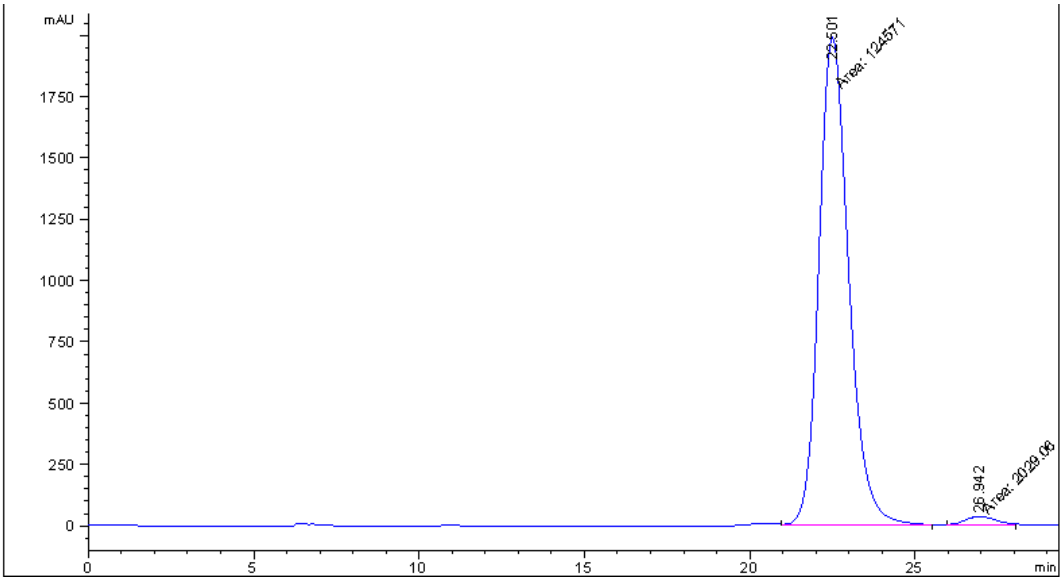
^{13}C NMR for 7a



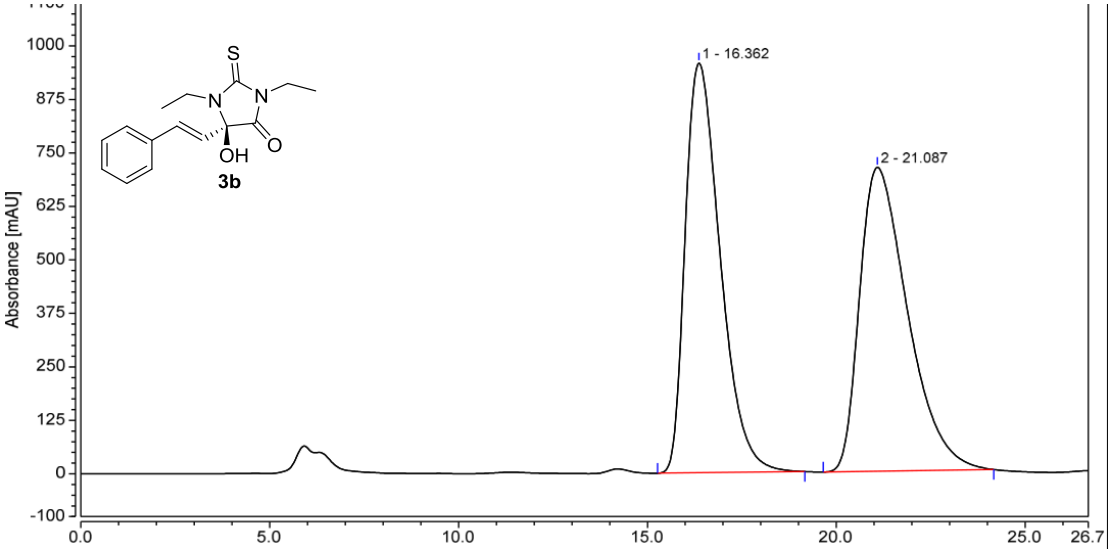
10. Copies of HPLC spectra for racemic and chiral compounds



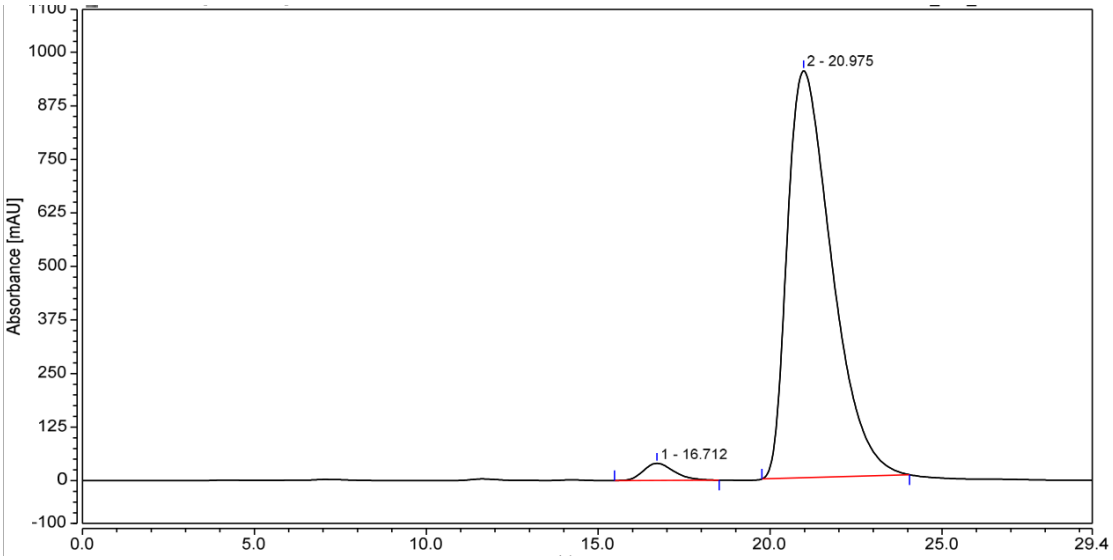
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.176	MM	0.9261	4.64789e4	836.41827	50.2198
2	26.580	MM	1.0504	4.60720e4	730.99817	49.7802
Totals :				9.25509e4	1567.41644	



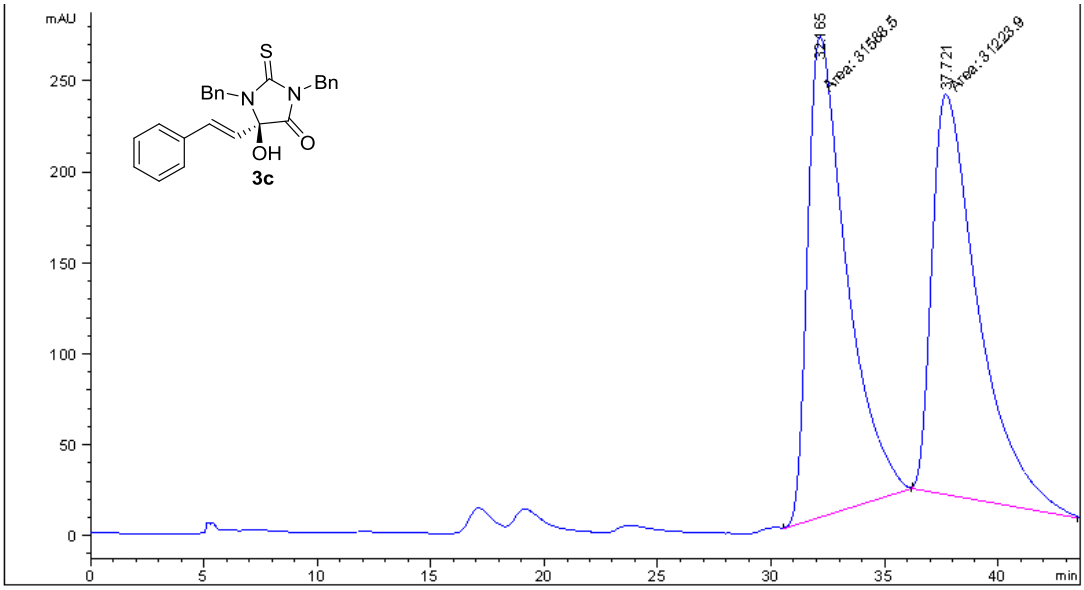
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.501	MM	1.0450	1.24571e5	1986.71655	98.3973
2	26.942	MM	1.0497	2029.05884	32.21723	1.6027
Totals :				1.26600e5	2018.93378	



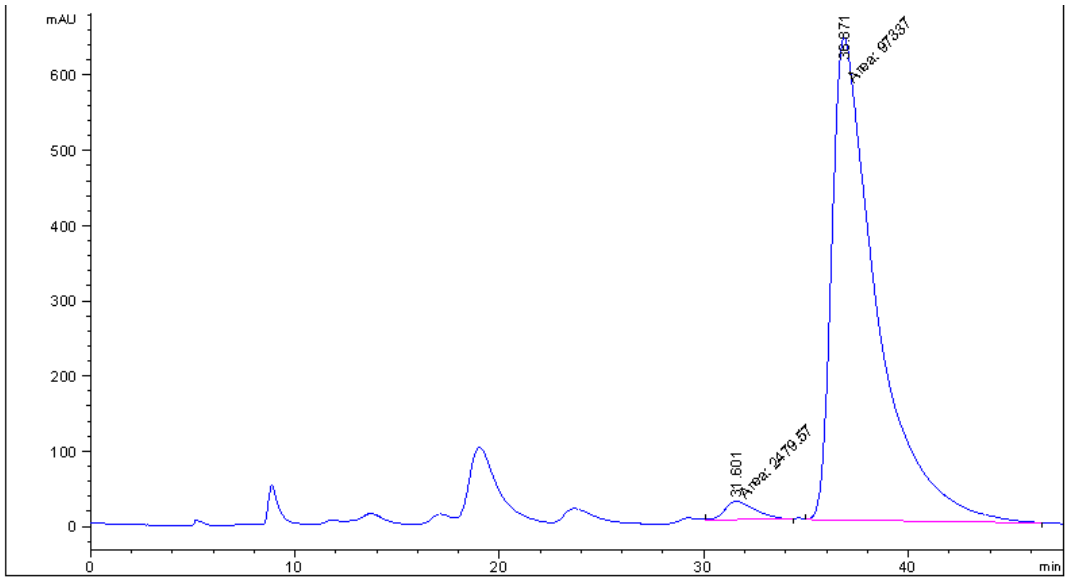
Entry	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	16.362	1028.525	957.887	49.57	57.41
2	21.087	1046.509	710.637	50.43	42.59
Total:		**2075.035**	**1668.524**	**100.00**	**100.00**



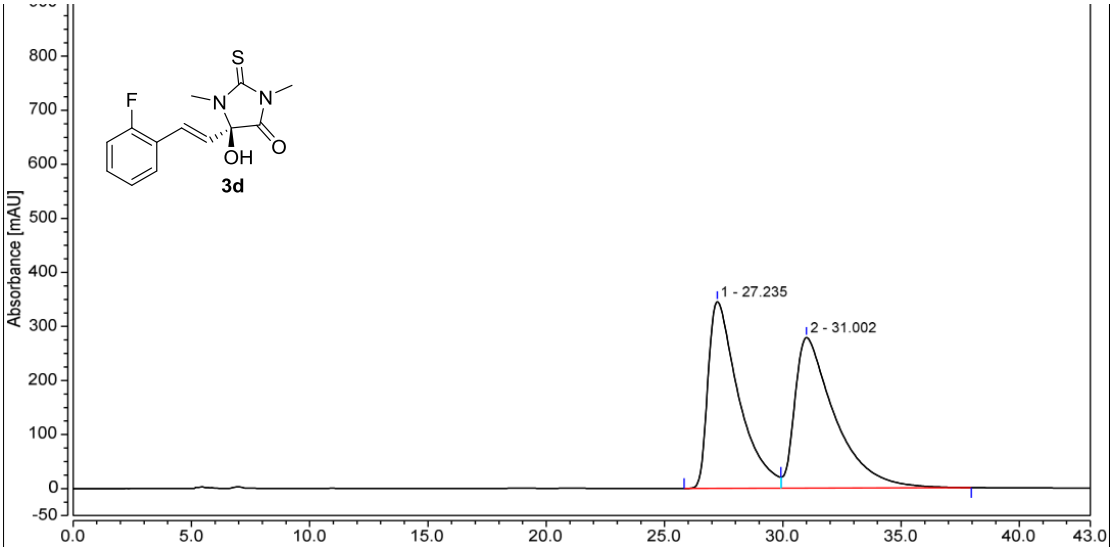
Entry	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	16.712	41.030	39.903	2.80	4.03
2	20.975	1423.922	950.177	97.20	95.97
Total:		**1464.952**	**990.080**	**100.00**	**100.00**



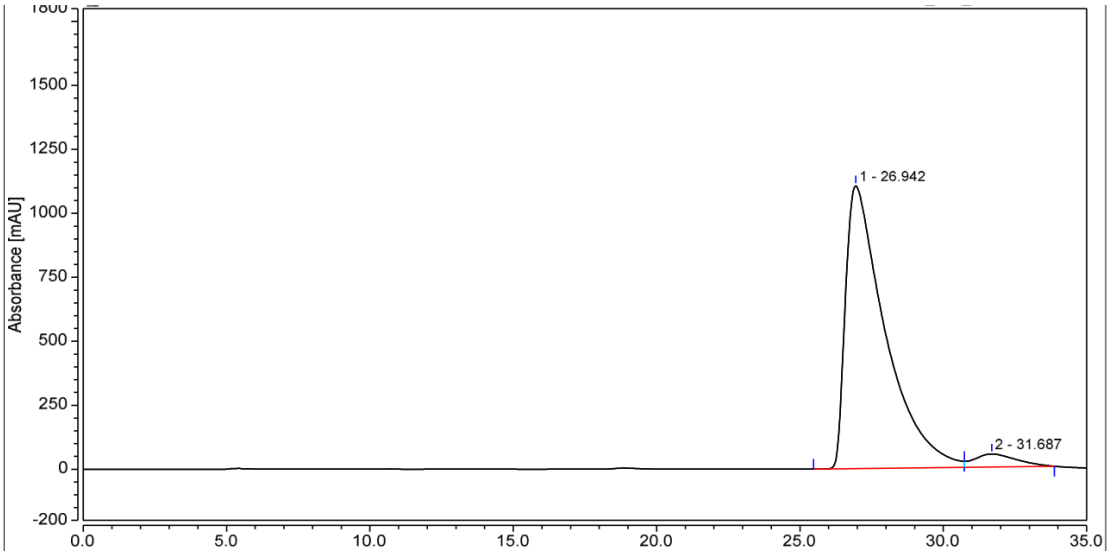
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.165	MM	1.9939	3.15885e4	264.04755	50.2902
2	37.721	MM	2.3666	3.12239e4	219.89545	49.7098
Totals :				6.28124e4	483.94299	



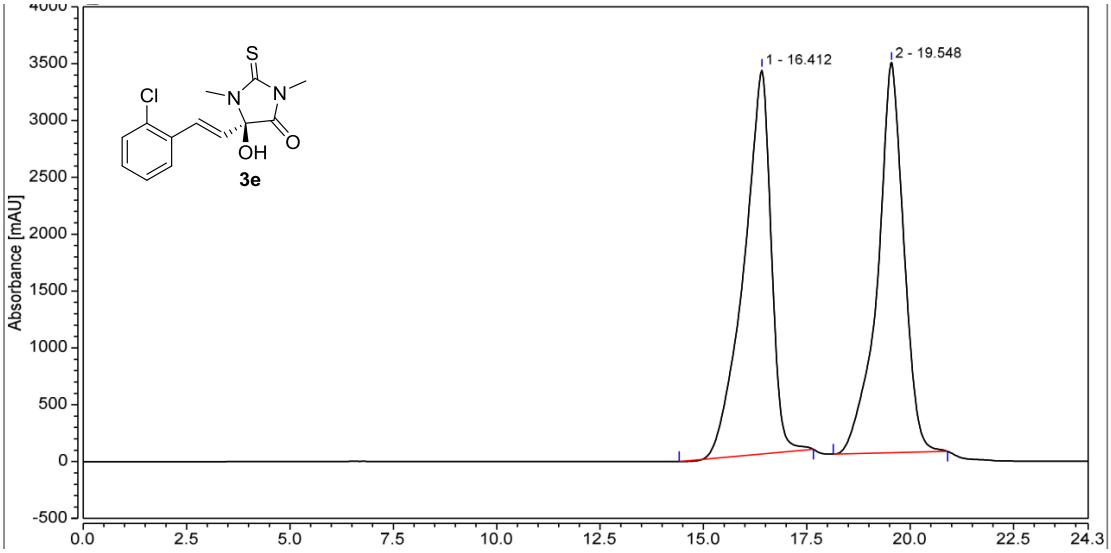
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.601	MM	1.6996	2479.57471	24.31470	2.4841
2	36.871	MM	2.5263	9.73370e4	642.15143	97.5159
Totals :				9.98166e4	666.46613	



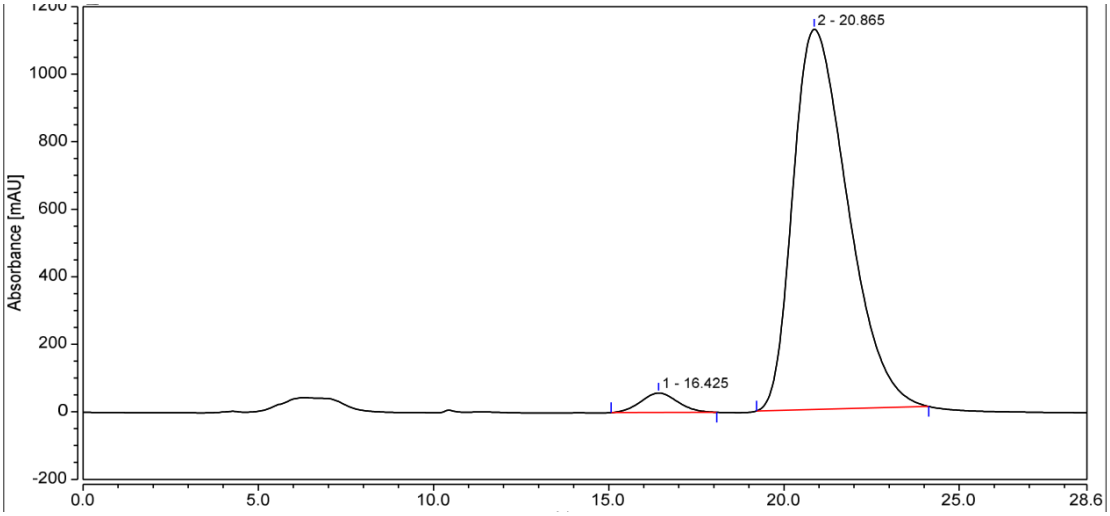
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	27.235	517.976	345.636	48.61	55.36
2	31.002	547.649	278.755	51.39	44.64
Total:		**1065.624**	**624.391**	**100.00**	**100.00**



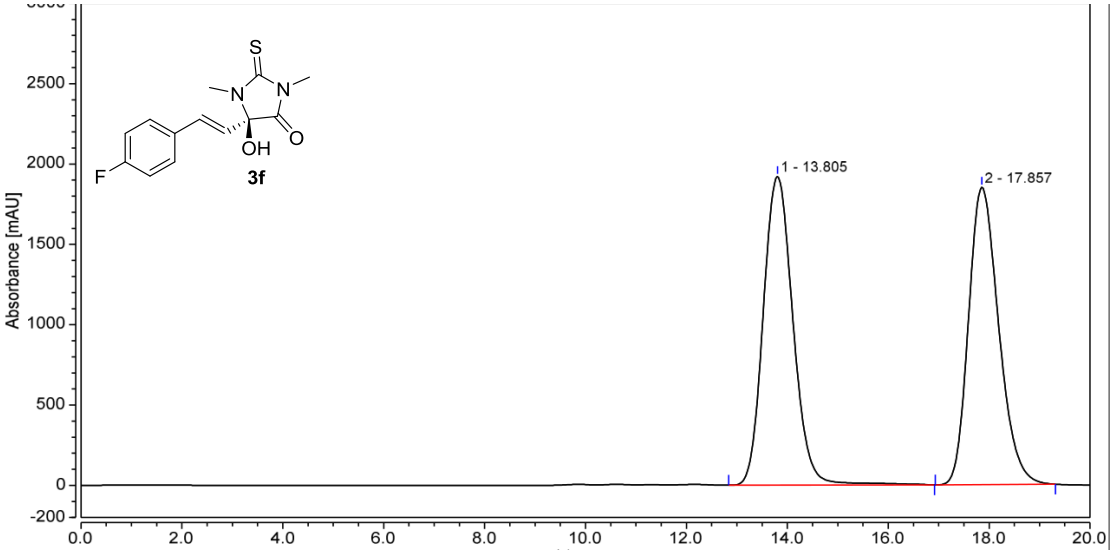
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	26.942	1775.029	1105.184	95.34	95.60
2	31.687	86.850	50.889	4.66	4.40
Total:		**1861.878**	**1156.073**	**100.00**	**100.00**



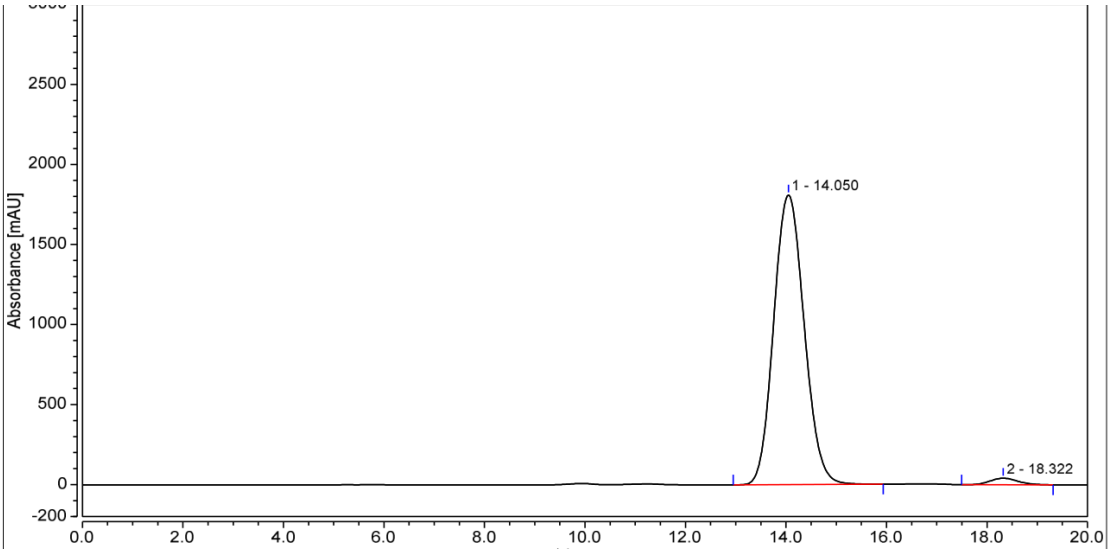
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	16.412	2579.205	3384.141	50.50	49.64
2	19.548	2528.068	3433.611	49.50	50.36
Total:		**5107.273**	**6817.752**	**100.00**	**100.00**



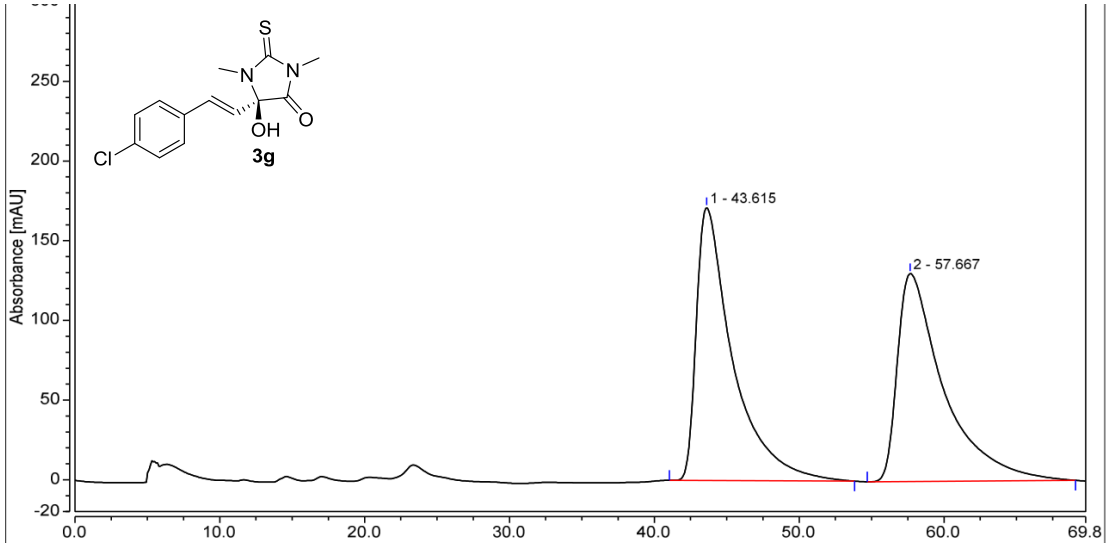
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	16.425	70.604	57.738	3.34	4.88
2	20.865	2044.596	1126.038	96.66	95.12
Total:		**2115.200**	**1183.776**	**100.00**	**100.00**



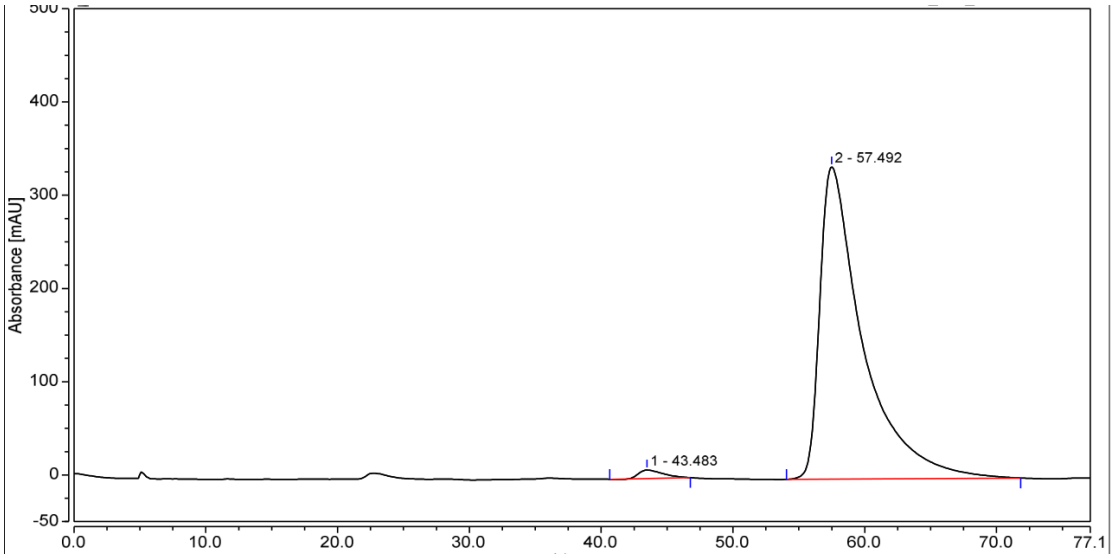
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	13.805	1313.670	1921.410	50.62	50.93
2	17.857	1281.575	1851.389	49.38	49.07
Total:		**2595.245**	**3772.799**	**100.00**	**100.00**



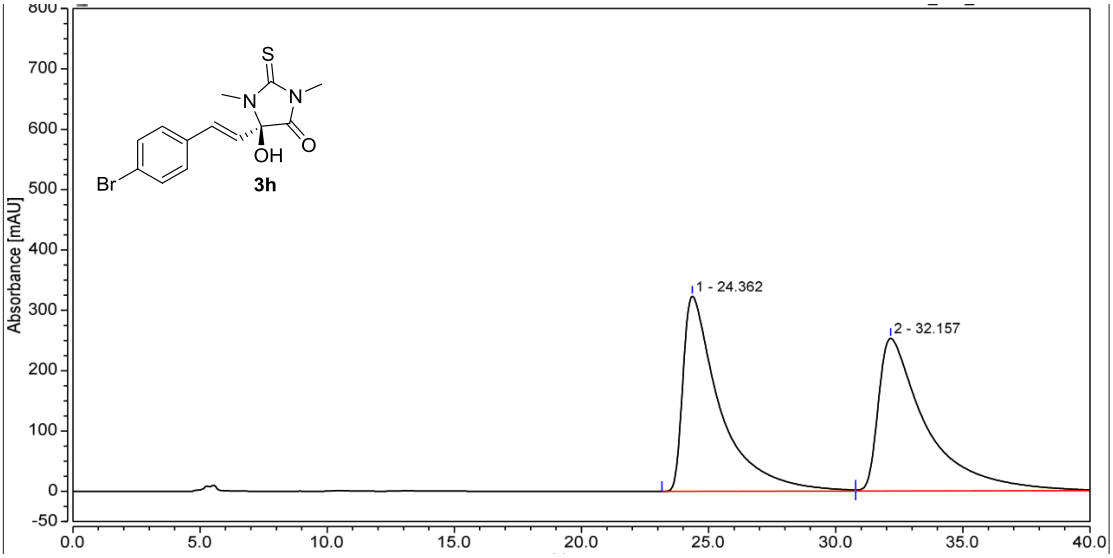
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	14.050	1270.542	1809.550	97.93	97.77
2	18.322	26.896	41.320	2.07	2.23
Total:		**1297.438**	**1850.869**	**100.00**	**100.00**



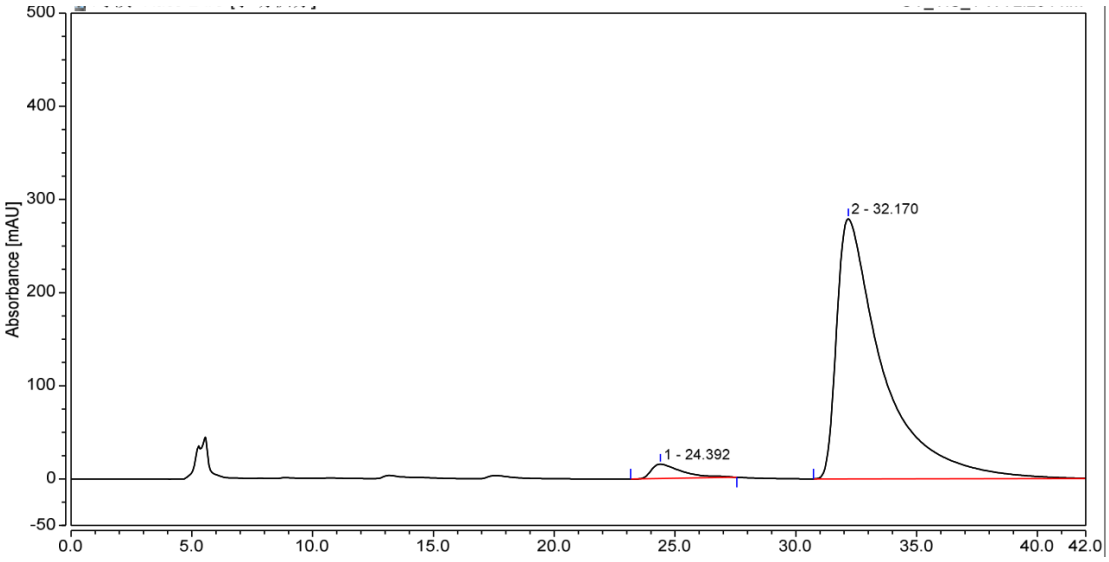
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	43.615	497.907	171.189	50.84	56.75
2	57.667	481.476	130.474	49.16	43.25
Total:		**979.384**	**301.663**	**100.00**	**100.00**



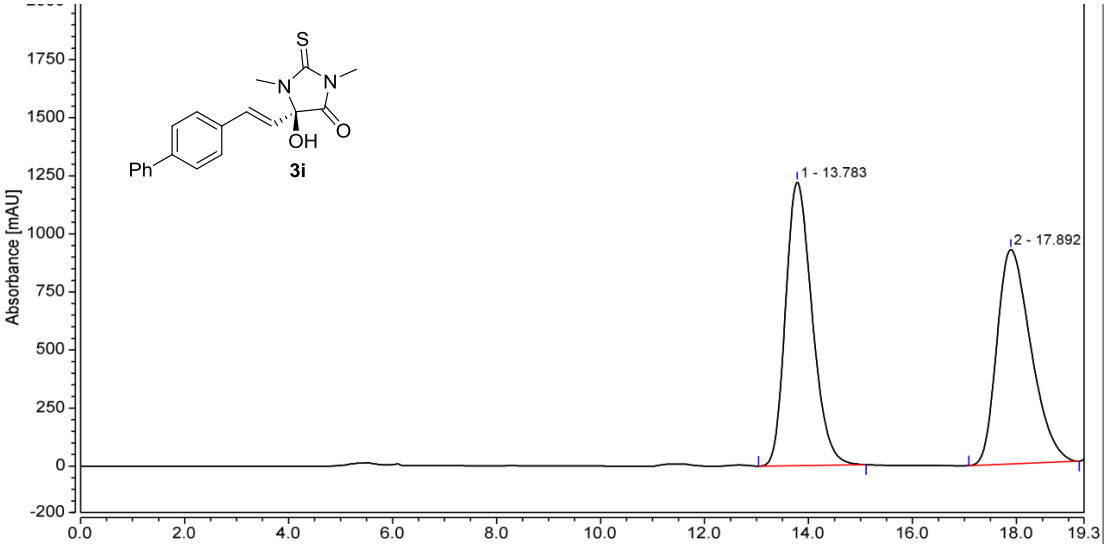
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	43.483	19.293	9.108	1.51	2.65
2	57.492	1261.999	334.838	98.49	97.35
Total:		**1281.292**	**343.946**	**100.00**	**100.00**



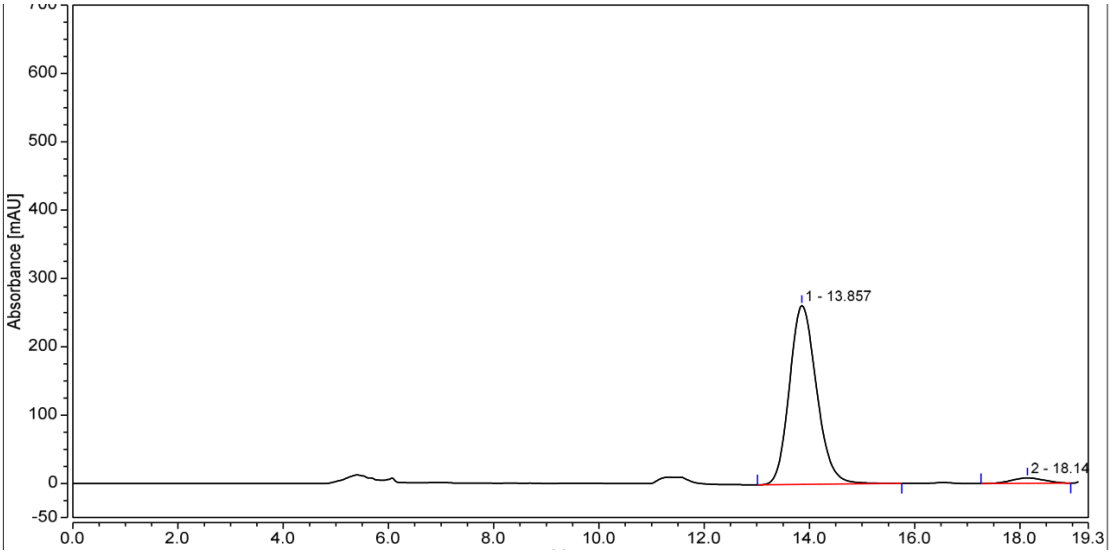
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	24.362	547.272	323.326	49.71	56.10
2	32.157	553.573	253.029	50.29	43.90
Total:		**1100.846**	**576.355**	**100.00**	**100.00**



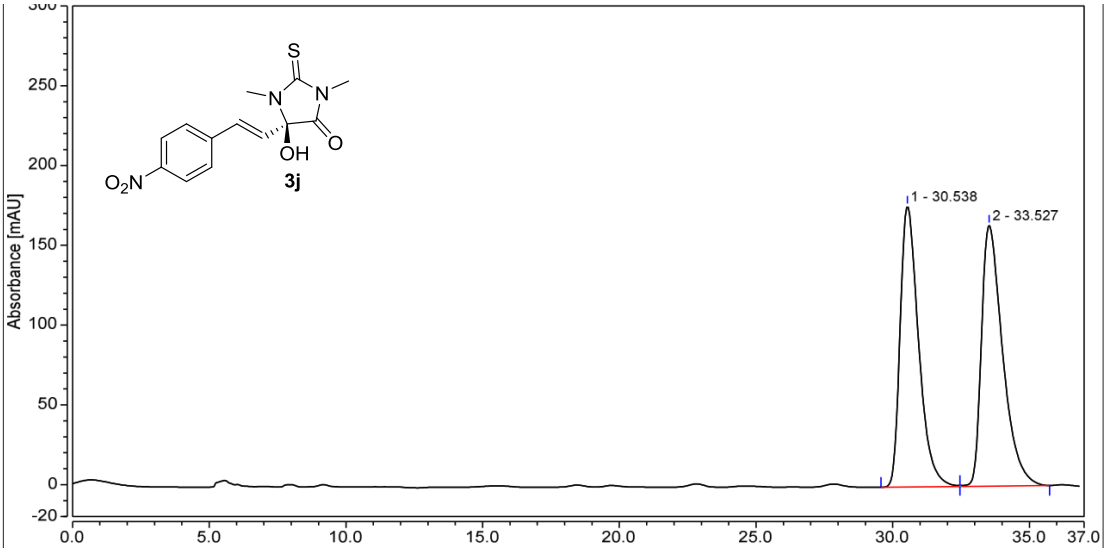
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	24.392	22.573	15.420	3.53	5.23
2	32.170	616.088	279.276	96.47	94.77
Total:		**638.660**	**294.696**	**100.00**	**100.00**



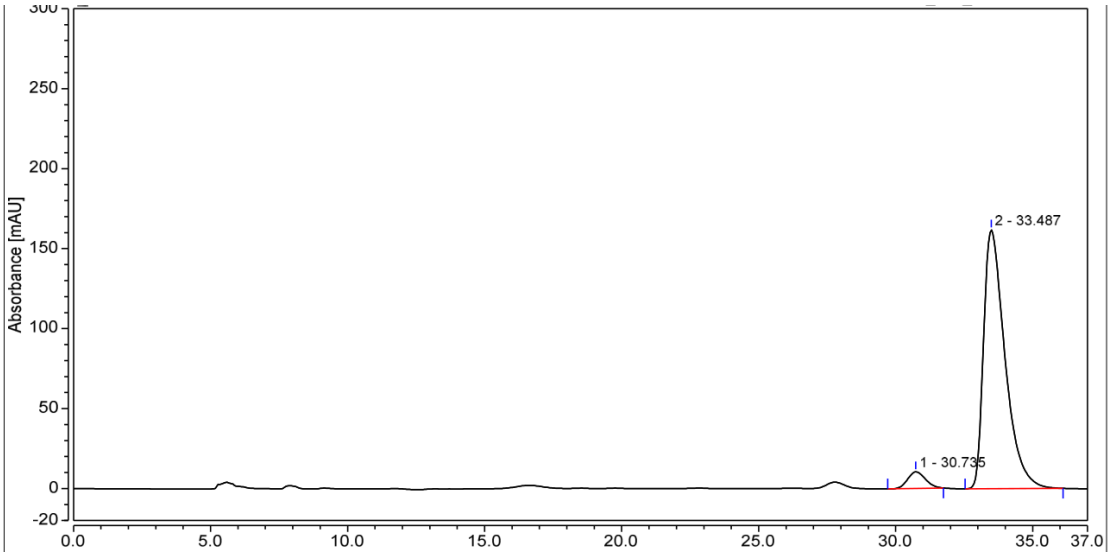
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	13.783	721.572	1221.429	50.77	56.94
2	17.892	699.727	923.687	49.23	43.06
Total:		**1421.299**	**2145.116**	**100.00**	**100.00**



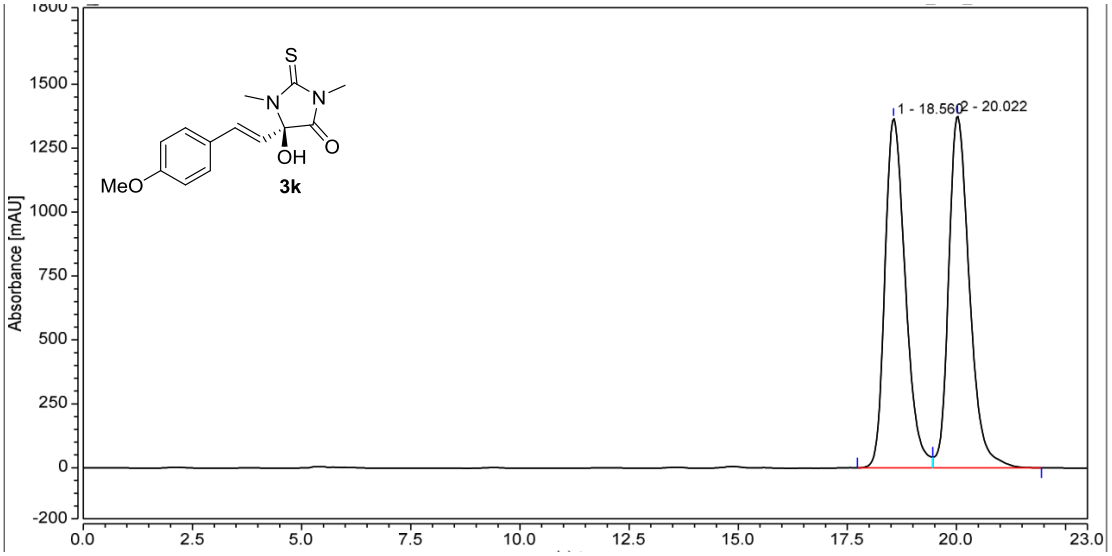
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	13.857	156.621	261.743	96.44	97.05
2	18.140	5.787	7.969	3.56	2.95
Total:		**162.408**	**269.712**	**100.00**	**100.00**



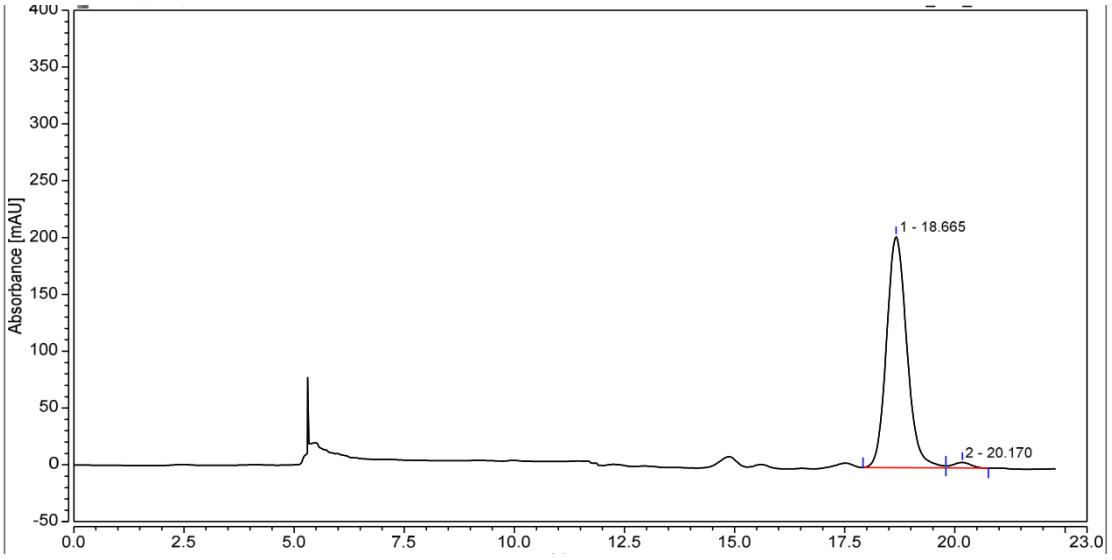
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	30.538	137.914	176.122	48.46	51.84
2	33.527	146.699	163.598	51.54	48.16
Total:		**284.612**	**339.720**	**100.00**	**100.00**



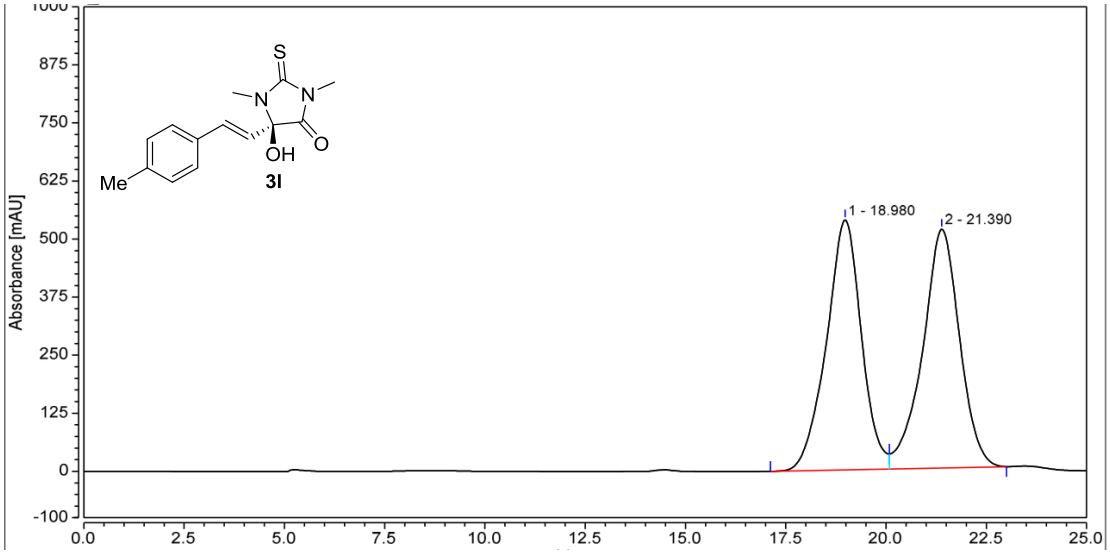
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	30.735	7.810	10.373	5.07	6.02
2	33.487	146.323	161.801	94.93	93.98
Total:		**154.133**	**172.175**	**100.00**	**100.00**



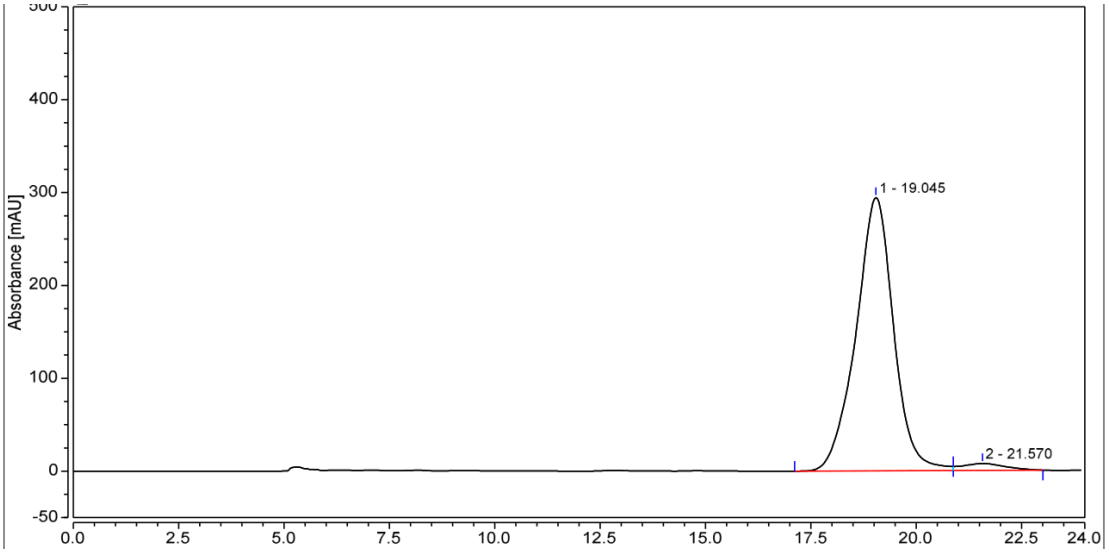
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	18.560	741.826	1367.002	49.38	49.81
2	20.022	760.366	1377.468	50.62	50.19
Total:		**1502.192**	**2744.470**	**100.00**	**100.00**



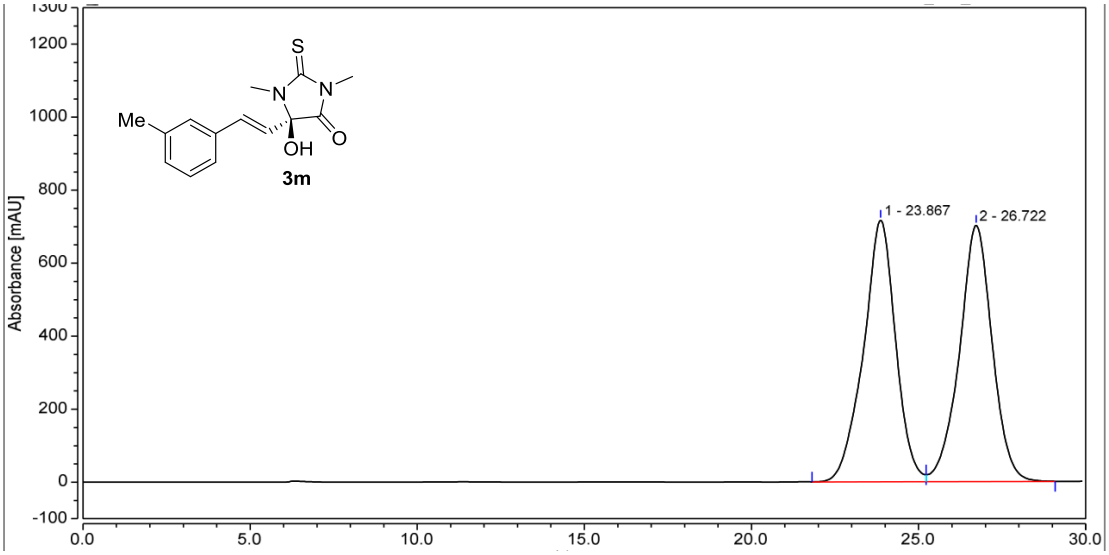
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	18.665	109.032	203.452	97.89	97.66
2	20.170	2.345	4.867	2.11	2.34
Total:		**111.377**	**208.320**	**100.00**	**100.00**



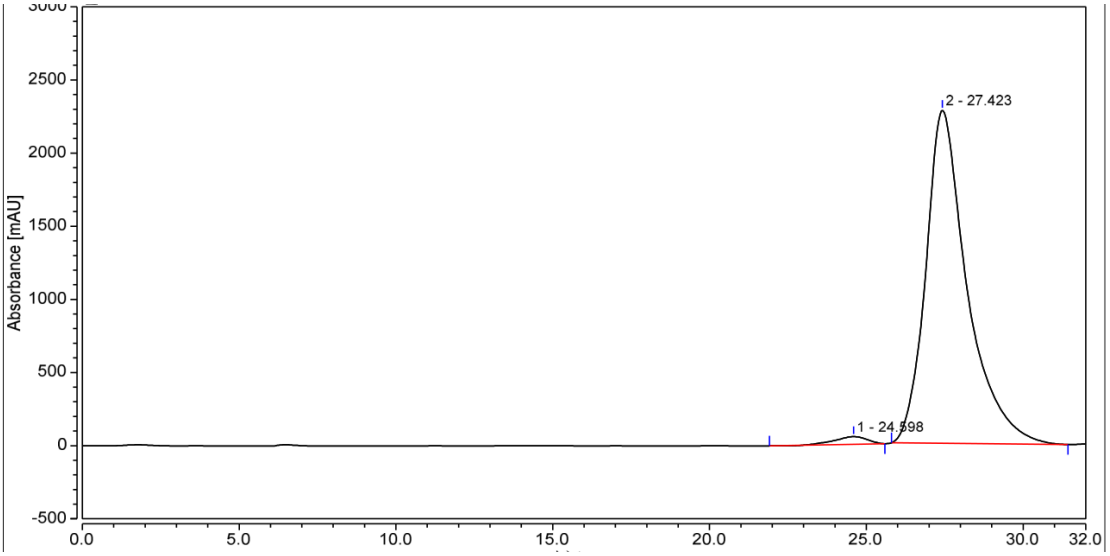
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	18.980	543.955	538.390	49.79	51.14
2	21.390	548.451	514.309	50.21	48.86
Total:		**1092.406**	**1052.699**	**100.00**	**100.00**



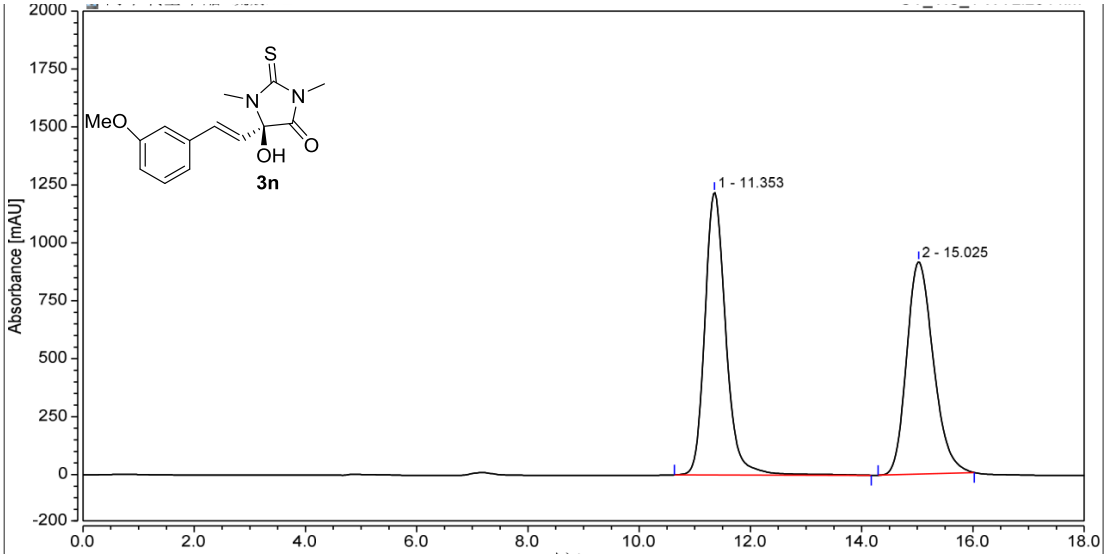
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	19.045	304.305	294.306	97.23	97.56
2	21.570	8.668	7.361	2.77	2.44
Total:		**312.973**	**301.667**	**100.00**	**100.00**



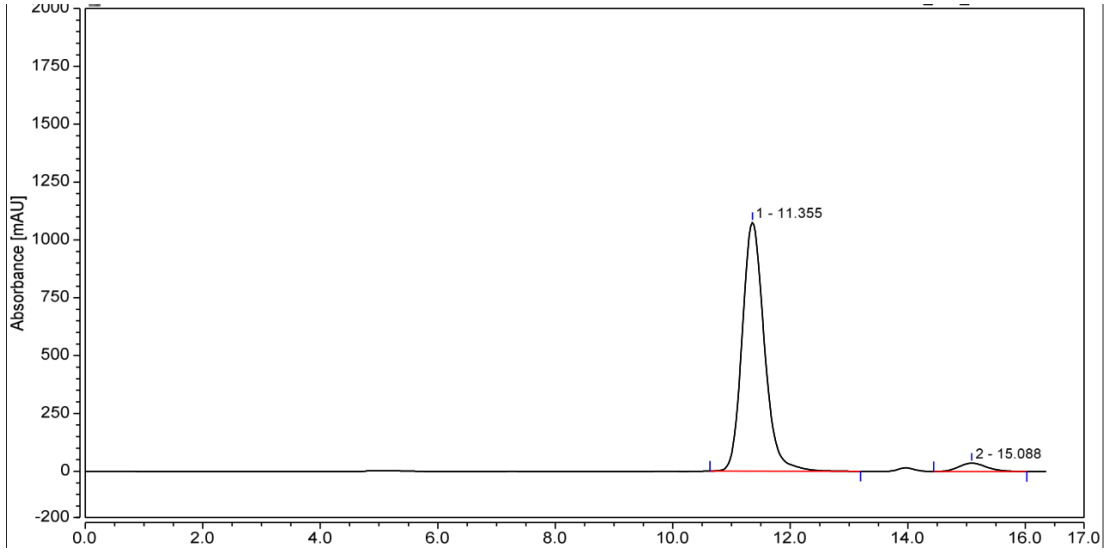
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	23.867	799.553	716.493	50.07	50.52
2	26.722	797.356	701.787	49.93	49.48
Total:		**1596.909**	**1418.281**	**100.00**	**100.00**



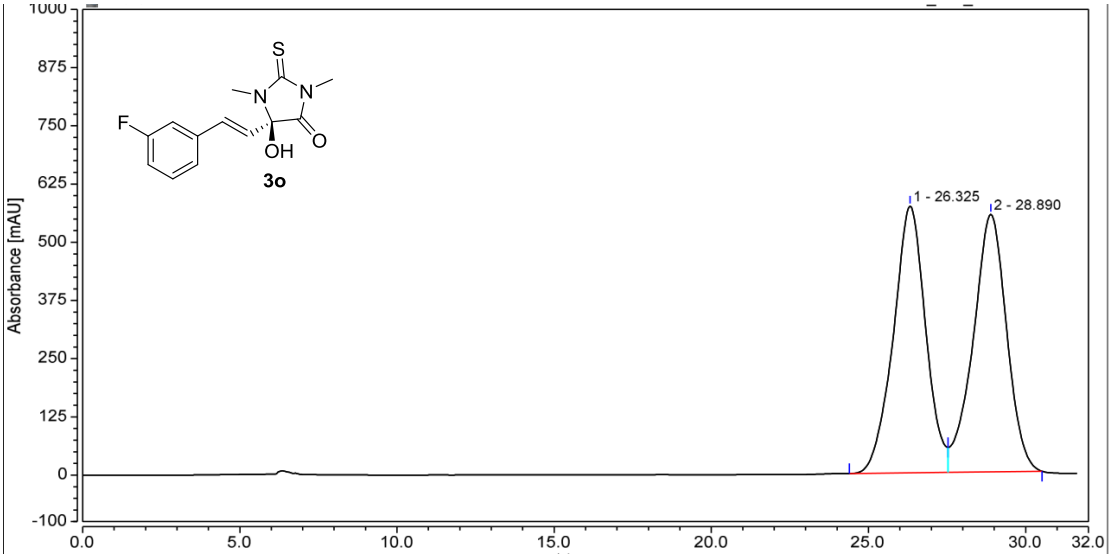
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	24.598	62.932	52.377	1.78	2.25
2	27.423	3469.123	2276.011	98.22	97.75
Total:		**3532.056**	**2328.387**	**100.00**	**100.00**



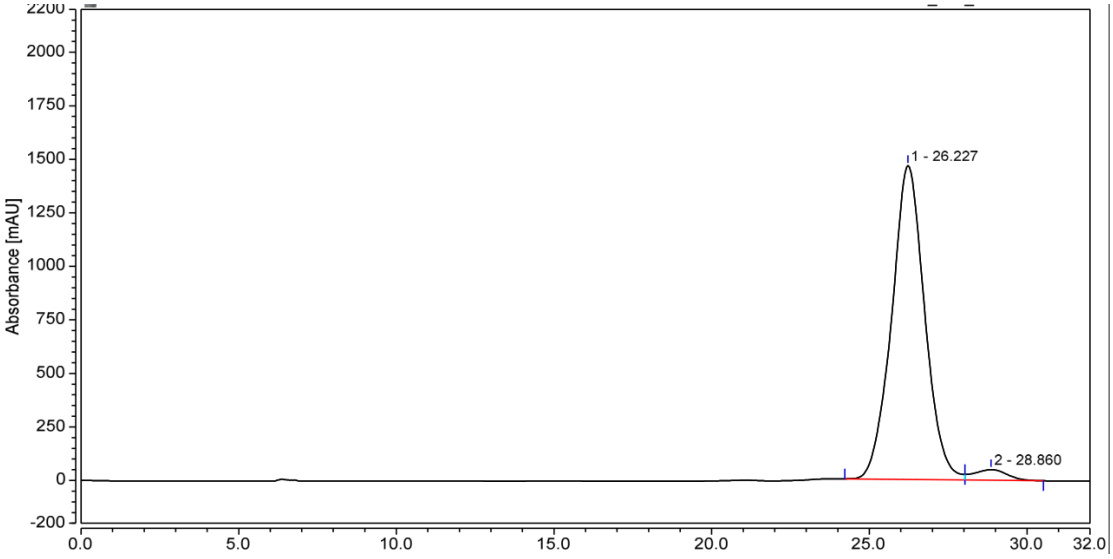
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	11.353	533.818	1220.256	51.11	57.11
2	15.025	510.565	916.236	48.89	42.89
Total:		**1044.383**	**2136.492**	**100.00**	**100.00**



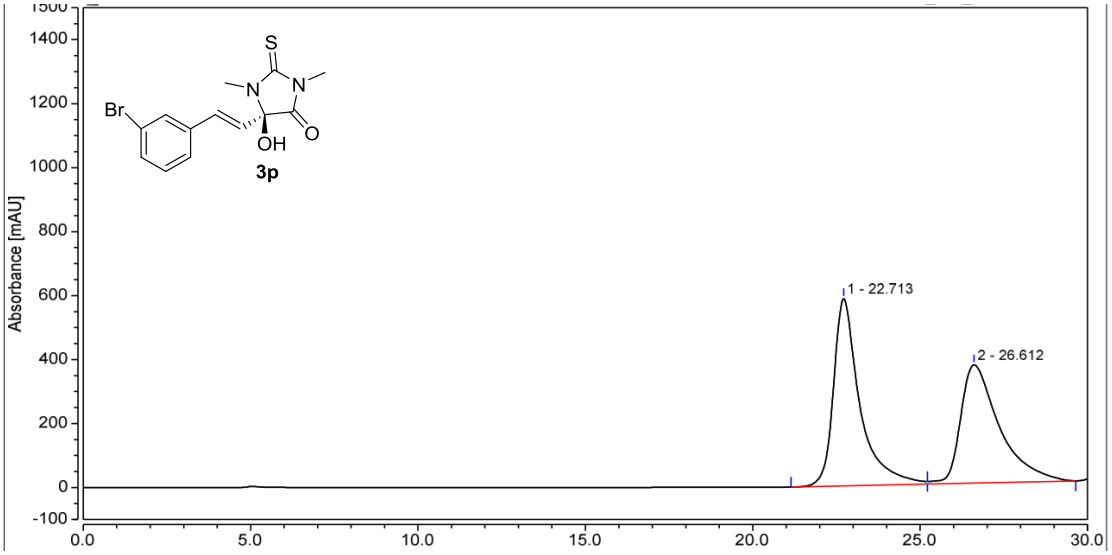
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	11.355	467.643	1074.785	95.91	96.77
2	15.088	19.928	35.907	4.09	3.23
Total:		**487.571**	**1110.692**	**100.00**	**100.00**



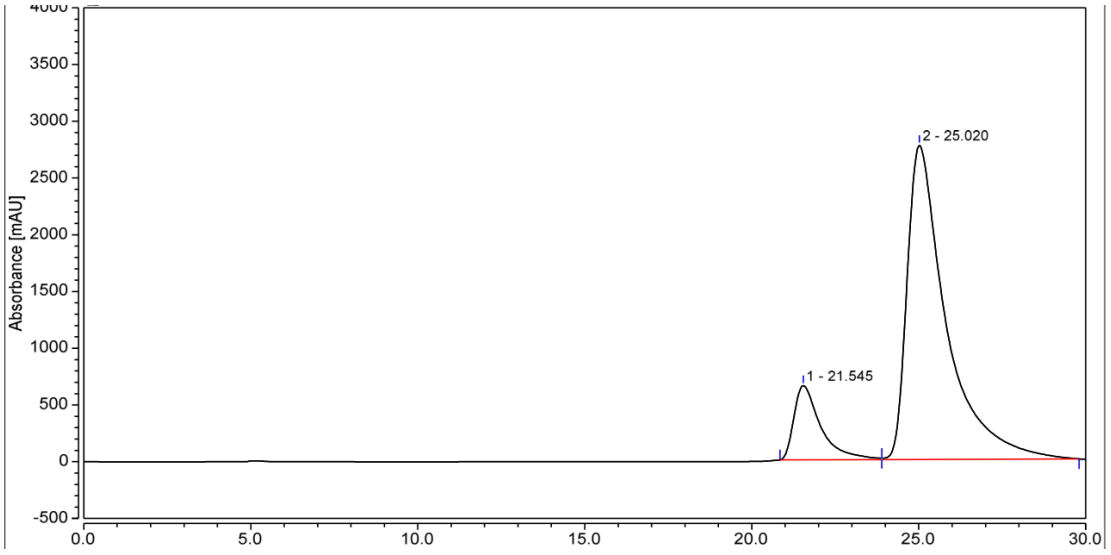
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	26.325	682.549	573.021	49.98	50.88
2	28.890	683.156	553.248	50.02	49.12
Total:		**1365.704**	**1126.269**	**100.00**	**100.00**



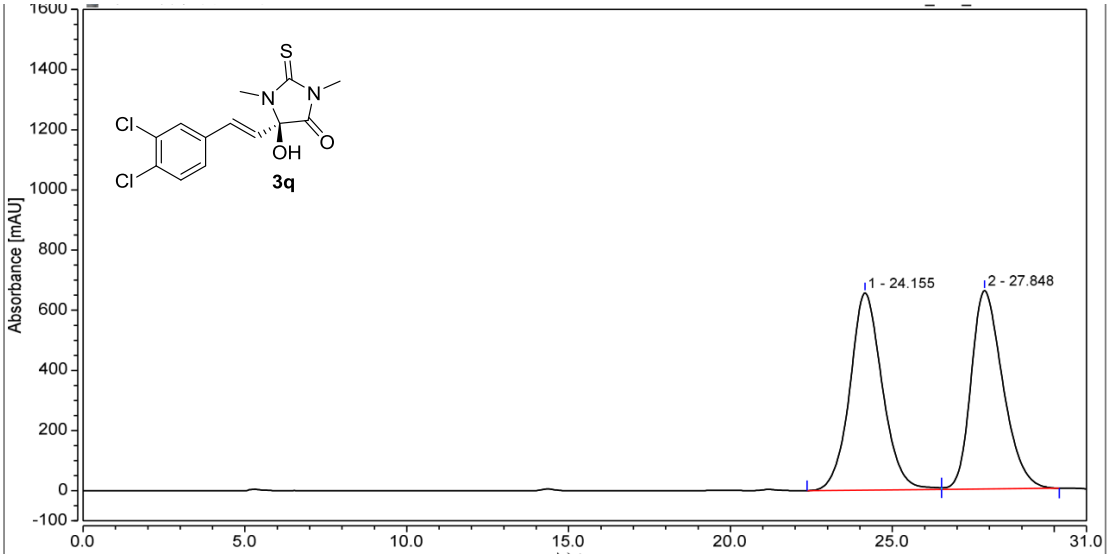
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	26.227	1777.975	1466.861	96.69	96.70
2	28.860	60.960	50.022	3.31	3.30
Total:		**1838.935**	**1516.884**	**100.00**	**100.00**



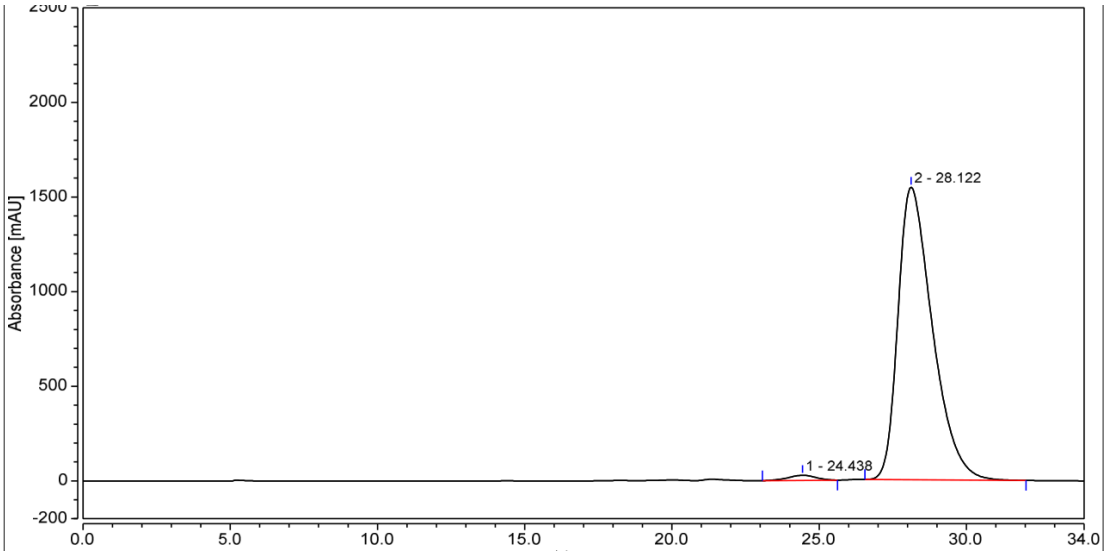
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	22.713	535.701	585.715	51.94	61.29
2	26.612	495.707	369.934	48.06	38.71
Total:		**1031.409**	**955.649**	**100.00**	**100.00**



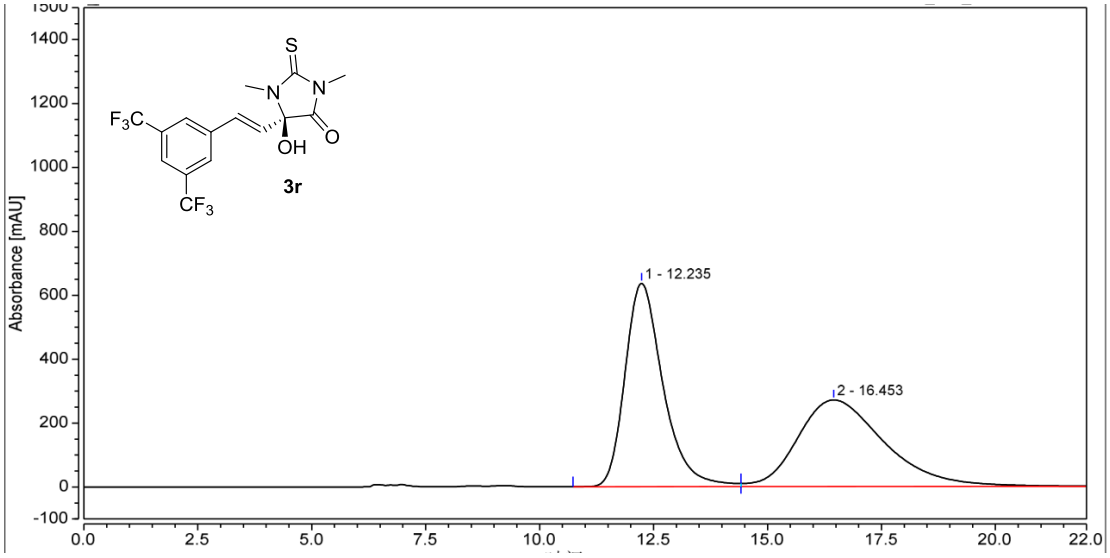
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	21.545	610.002	654.845	14.01	19.13
2	25.020	3743.827	2768.548	85.99	80.87
Total:		**4353.829**	**3423.393**	**100.00**	**100.00**



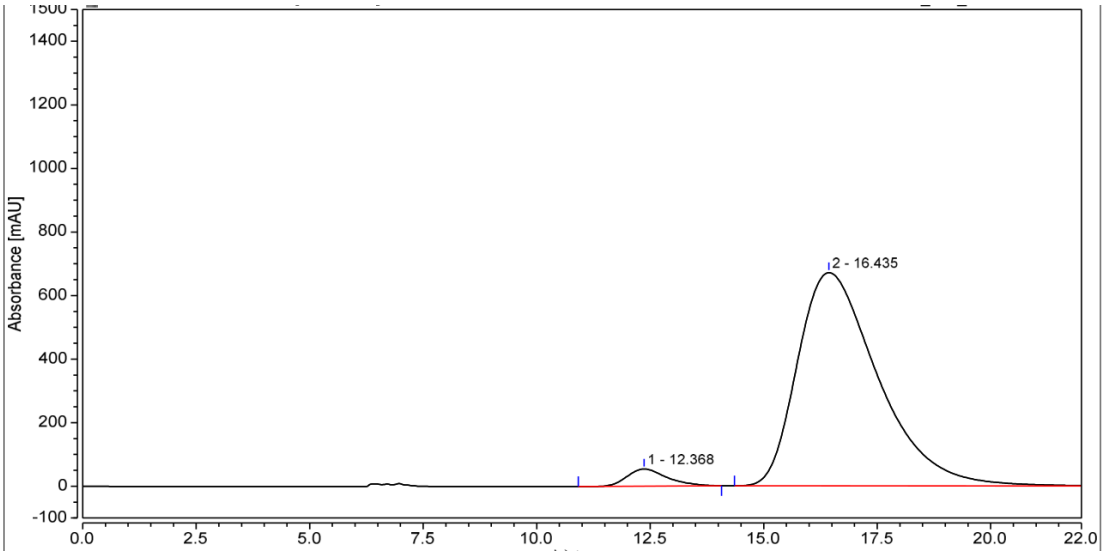
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	24.155	760.698	655.631	50.39	49.86
2	27.848	749.026	659.219	49.61	50.14
Total:		**1509.724**	**1314.849**	**100.00**	**100.00**



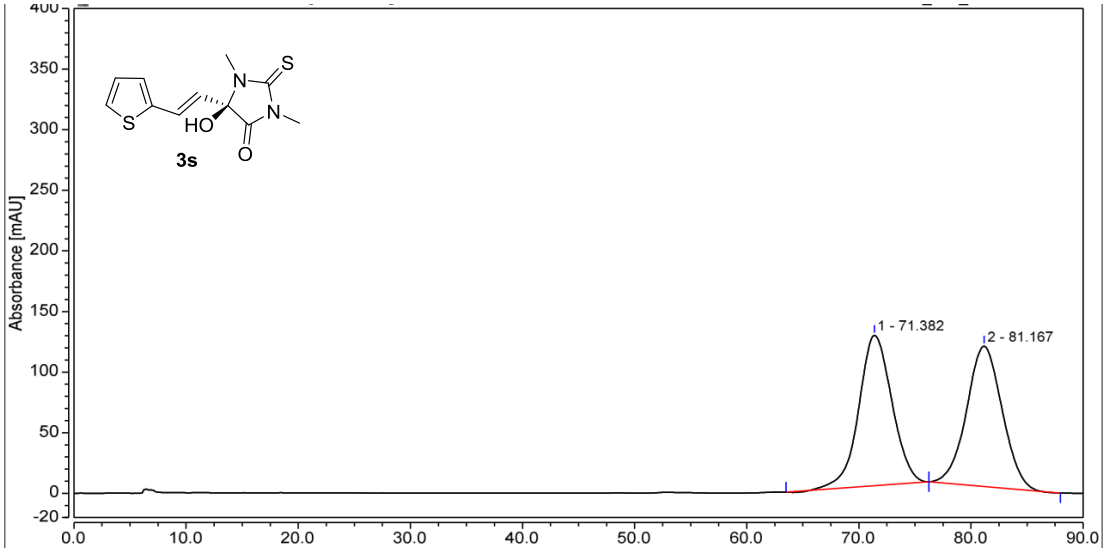
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	24.438	29.207	26.828	1.38	1.71
2	28.122	2093.024	1545.813	98.62	98.29
Total:		**2122.231**	**1572.641**	**100.00**	**100.00**



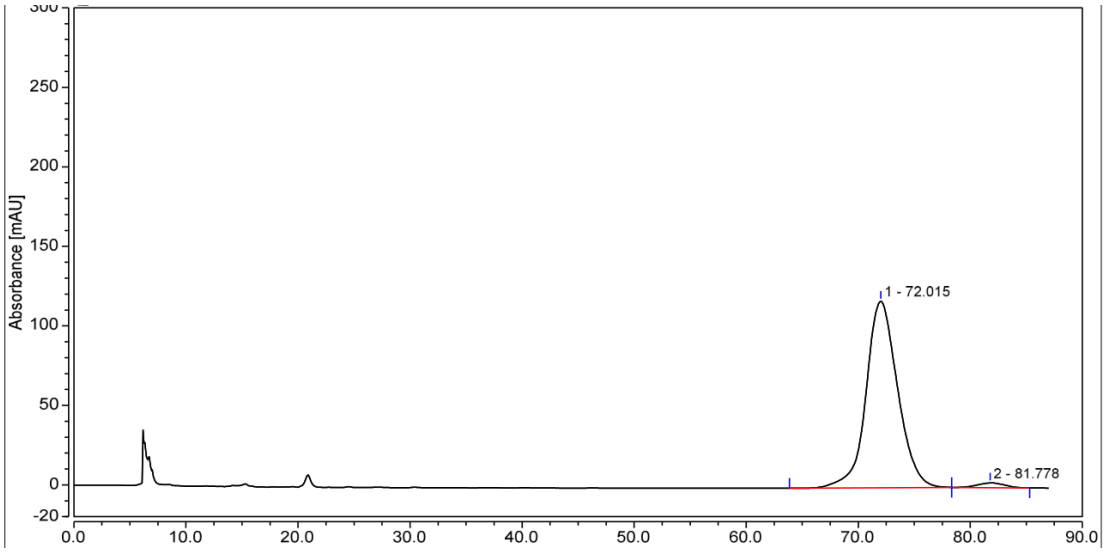
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.235	616.941	636.617	50.81	70.14
2	16.453	597.157	270.983	49.19	29.86
Total:		**1214.098**	**907.600**	**100.00**	**100.00**



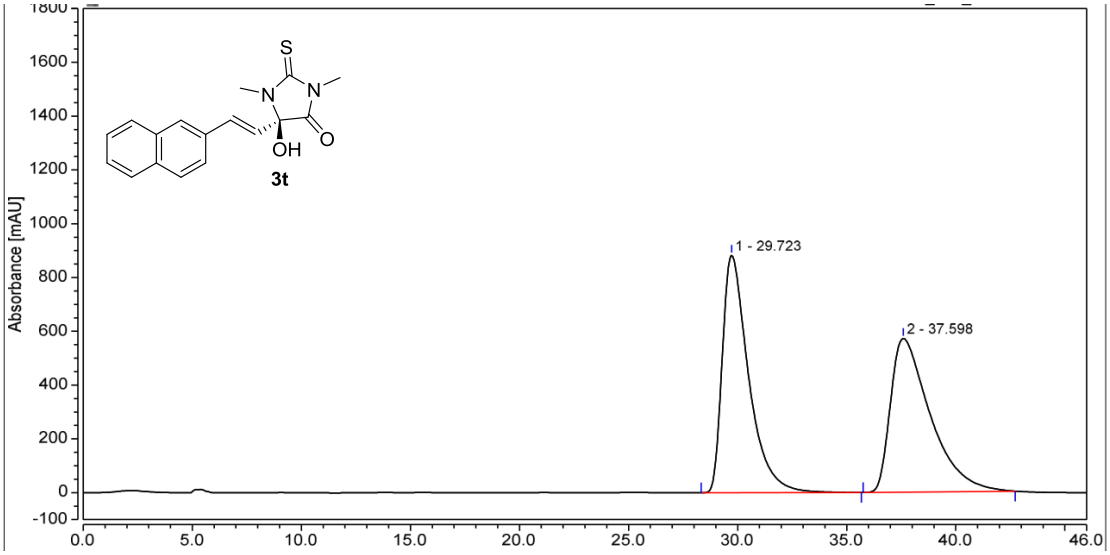
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.368	54.949	54.134	3.82	7.46
2	16.435	1382.811	671.281	96.18	92.54
Total:		**1437.760**	**725.416**	**100.00**	**100.00**



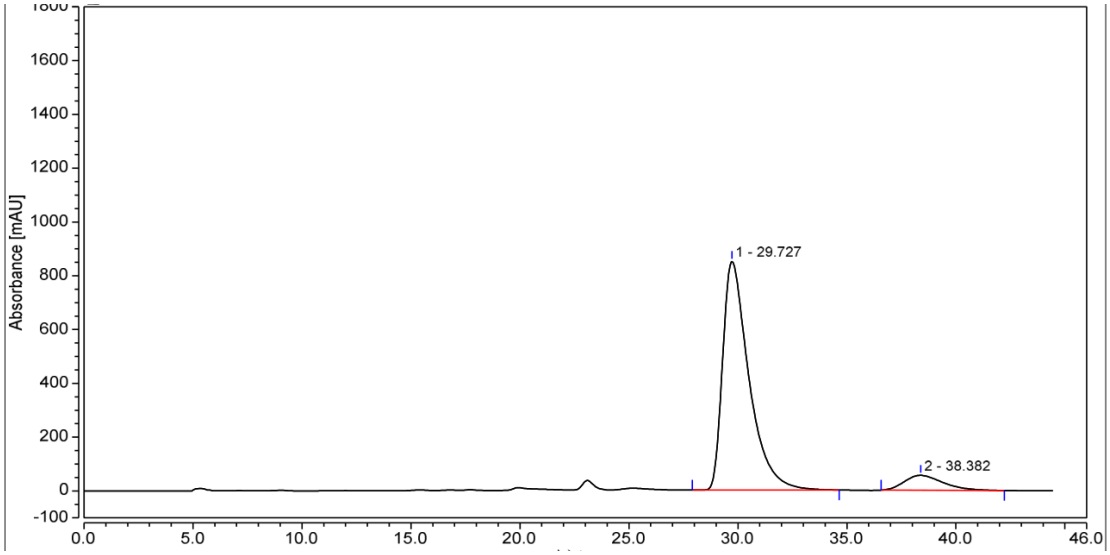
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	71.382	425.024	124.132	50.00	51.71
2	81.167	424.992	115.923	50.00	48.29
Total:		**850.016**	**240.054**	**100.00**	**100.00**



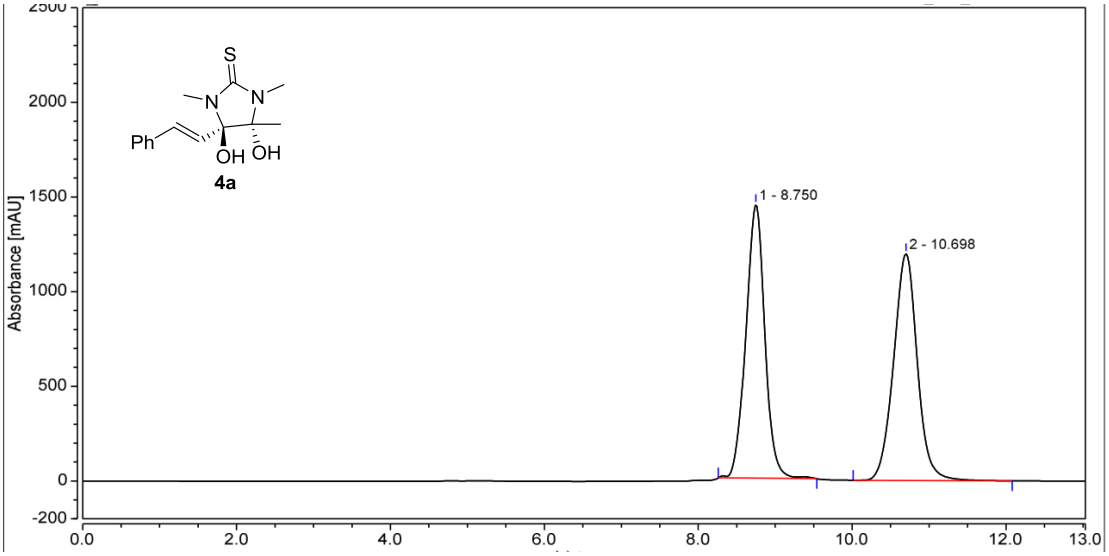
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	72.015	383.609	117.377	97.86	97.49
2	81.778	8.375	3.018	2.14	2.51
Total:		**391.984**	**120.396**	**100.00**	**100.00**



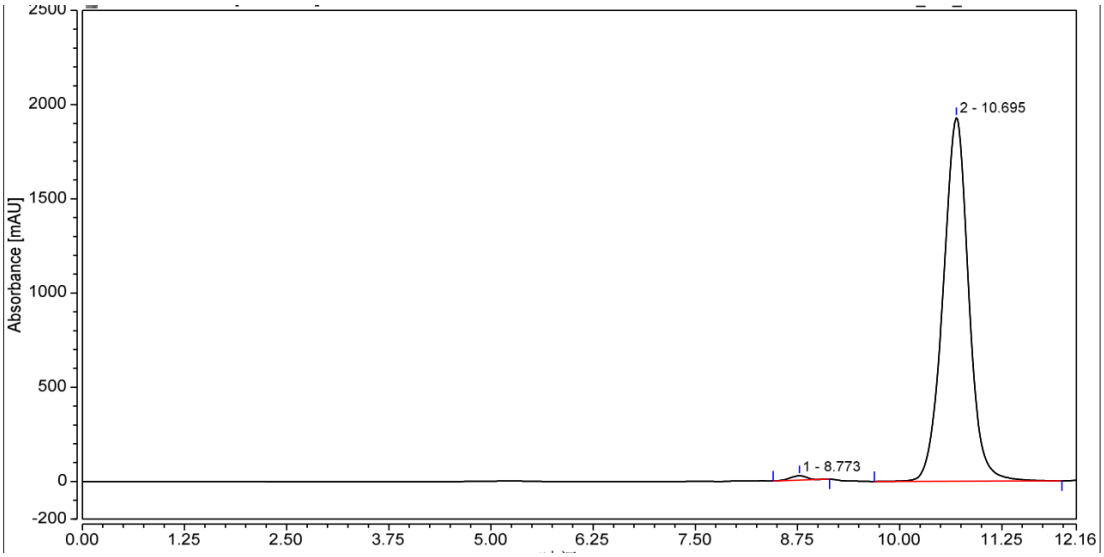
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	29.723	1235.849	882.955	50.54	60.69
2	37.598	1209.572	571.836	49.46	39.31
Total:		**2445.420**	**1454.792**	**100.00**	**100.00**



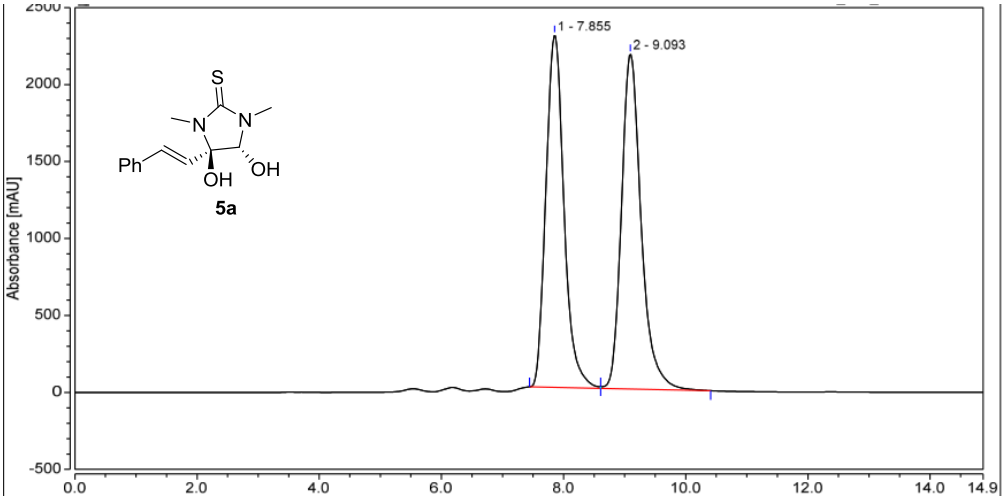
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	29.727	1188.871	849.937	91.21	93.87
2	38.382	114.502	55.531	8.79	6.13
Total:		**1303.372**	**905.468**	**100.00**	**100.00**



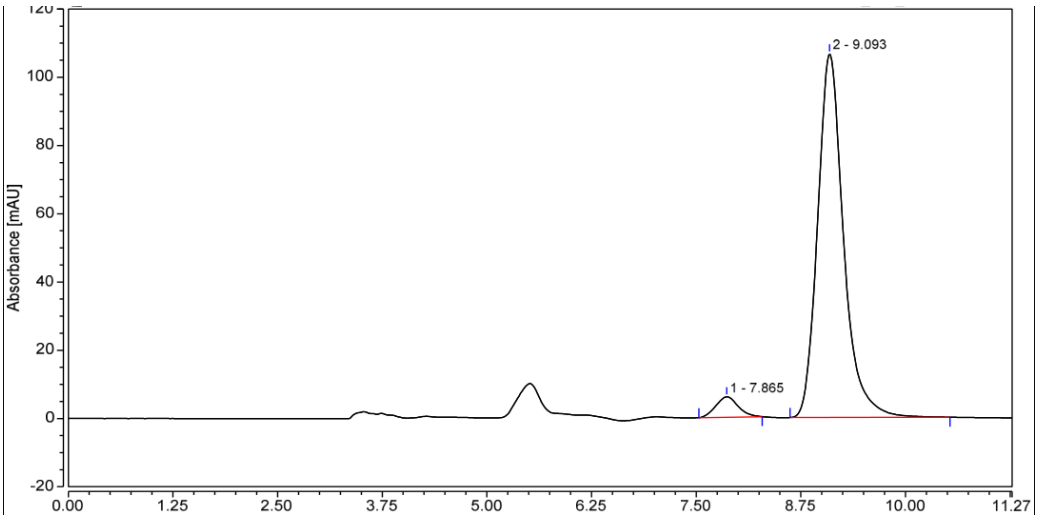
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.750	415.071	1445.796	49.35	54.69
2	10.698	425.957	1197.802	50.65	45.31
Total:		**841.028**	**2643.597**	**100.00**	**100.00**



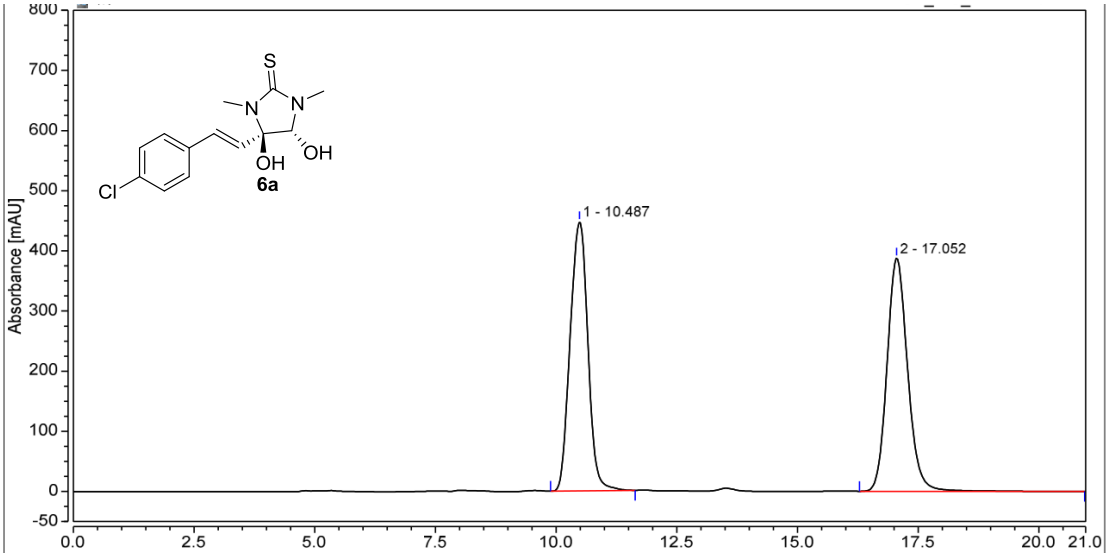
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.773	5.501	23.136	0.78	1.18
2	10.695	699.438	1930.104	99.22	98.82
Total:		**704.940**	**1953.240**	**100.00**	**100.00**



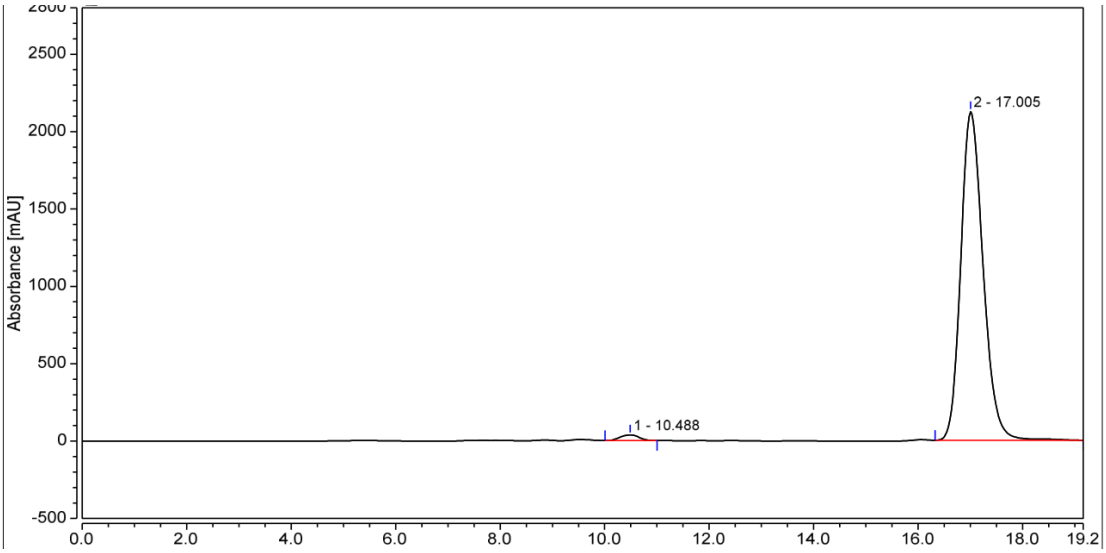
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.855	784.885	2291.352	49.11	51.27
2	9.093	813.467	2178.250	50.89	48.73
Total:		**1598.352**	**4469.602**	**100.00**	**100.00**



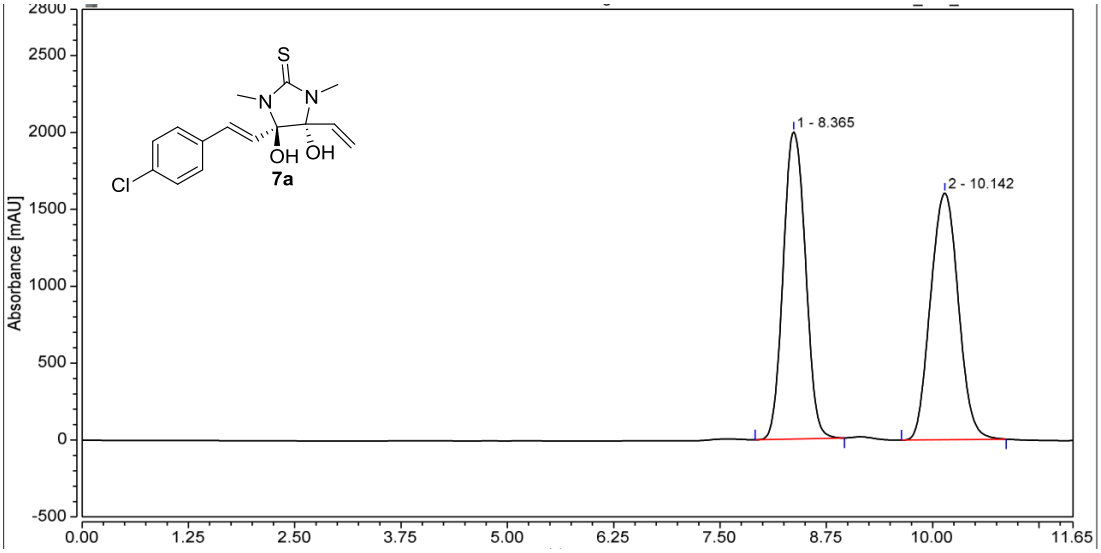
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.865	1.837	5.978	4.59	5.31
2	9.093	38.209	106.595	95.41	94.69
Total:		**40.046**	**112.573**	**100.00**	**100.00**



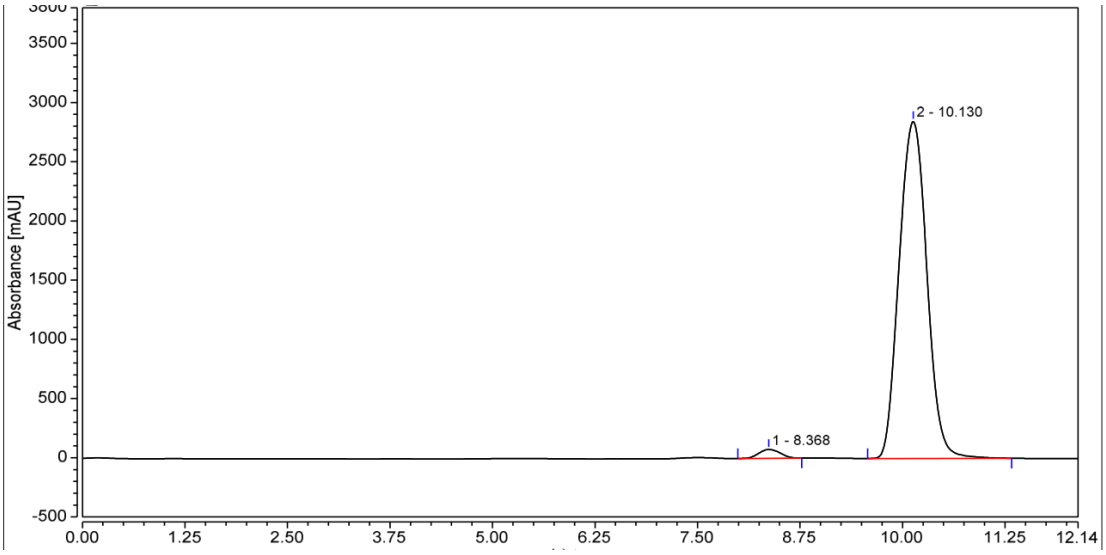
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.487	190.737	447.712	49.82	53.57
2	17.052	192.128	387.971	50.18	46.43
Total:		**382.865**	**835.683**	**100.00**	**100.00**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.488	15.604	37.377	1.46	1.73
2	17.005	1053.159	2124.721	98.54	98.27
Total:		**1068.763**	**2162.098**	**100.00**	**100.00**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.365	605.198	1996.798	49.89	55.46
2	10.142	607.804	1603.744	50.11	44.54
Total:		**1213.002**	**3600.542**	**100.00**	**100.00**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.368	22.436	73.732	1.97	2.52
2	10.130	1115.423	2847.026	98.03	97.48
Total:		**1137.858**	**2920.757**	**100.00**	**100.00**