Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

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A: General Remarks and Starting Materials

General Remarks

Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker AV-400 spectrometer (400 MHz and 100 MHz) or AV-500 spectrometer (500 MHz and 125 MHz). Chemical shifts (δ) for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual solvent peak ($CDCl_3$: δ 7.26). Chemical shifts (δ) for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.16). Data are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, q = quartet, quint = quintet, m = multiplet), coupling constants (*J*) in Hertz (Hz), integration; "app" is used to denote the apparent splitting of a signal.

High resolution mass spectrometry (HRMS) was carried out using a Waters Micromass GCT spectrometer equipped with an ESI source.

Optical rotations were measured on an Autopol III automatic polarimeter (Rudolph Research analytical). $[\alpha]_D^T$ values are reported in 10^{-1} deg cm^2 g^{-1}; concentrations (*c*) are quoted in g/100 mL; D refers to the D-line of sodium (589 nm); temperatures (T) are given in degrees Celsius (℃).

Melting points were measured on a XT3A apparatus.

Enantiomeric excesses were determined by HPLC analysis on an Agilent HPLC 1200 Series instrument, using the chiral stationary phase column (25 cm x 4.6 mm internal diameter) specified in the individual experiment.

Starting Materials

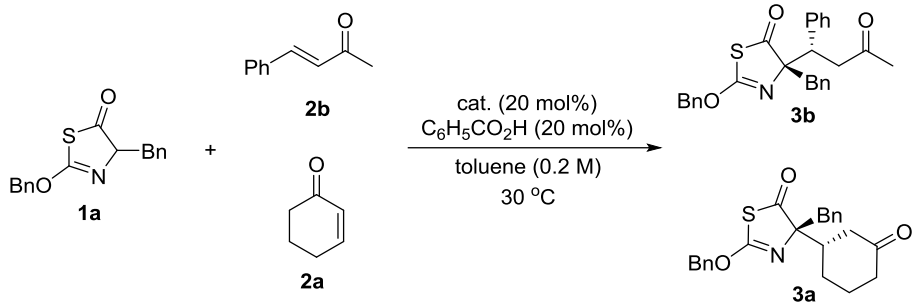
All solvents and inorganic reagents were purchased from commercial suppliers and used without purification. All of thiazolones[1] and α,β-unsaturated ketones[2] were prepared according to the literature.

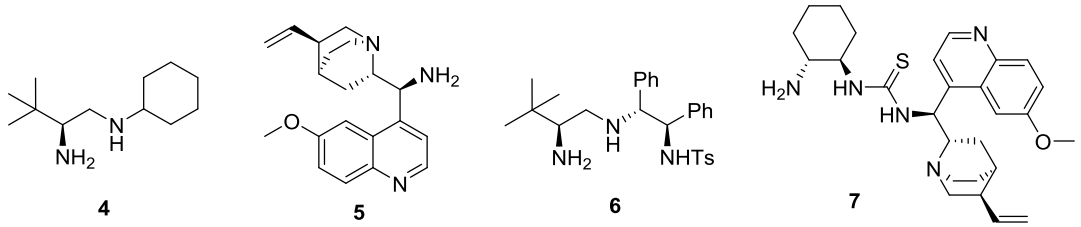
[1] Y. H. Lin, K. K. Andersen, *Eur. J. Org. Chem.* **2002**, 557.

[2] W. Zhang, R. Benmohamed, A. C. Arvanites, R. I. Morimoto, R. J. Ferrante, D. R. Kirsch, R. B. Silverman, *Bioorganic & Medicinal Chemistry*, **2012**, 20, 1029.

B: Optimization Tables

Table S1 Screening of chiral amine catalysts[a]

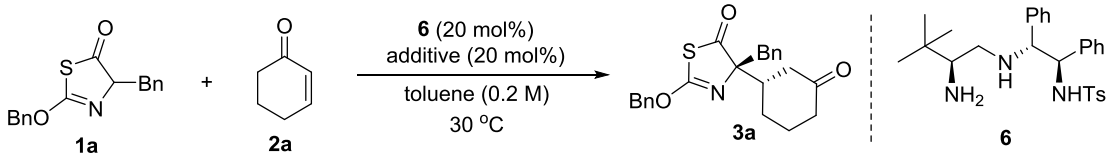




entry	cat.	yield (%)[b]	dr[c]	ee (%)[d]
1	**4**	28.2	n.d.	51
2[e]	**4**	31.8	n.d.	51
3[f]	**4**	5.3	n.d.	34
4	**5**	9	4/1	60
5	**6**	34	>19/1	88
6	**7**	34	5/1	-52
7[g]	**4**	2	n.d.	71

[a] Unless otherwise stated, reactions were performed with **1a** (0.15 mmol), **2a/2b** (0.1 mmol), and catalyst (0.02 mmol) in trichloromethane (0.5 mL) for 24 h. [b] Isolated yield after column chromatography. [c] Dr. values were determined by crude ^{1}H NMR. [d] Ee values were determined by HPLC analysis on a chiral stationary phase. [e] The reaction was performed with **1a** (0.1 mmol), **2a** (0.15 mmol). [f] The reaction was performed at 4 °C. [g] The reaction was performed with **1a** (0.15 mmol), **2b** (0.1 mmol).

Table S2 The effect of additive on the Michael reaction [a]

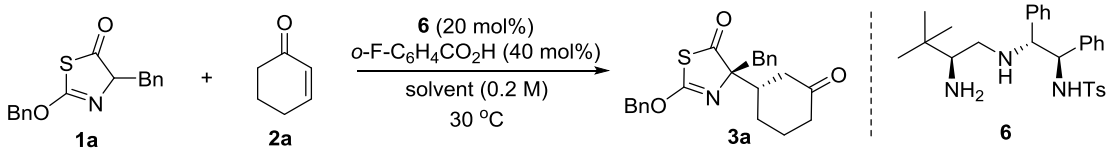


entry	additive	yield (%)[b]	dr[c]	ee (%)[d]
1	*o*-F-$C_6H_4CO_2H$	60	>19/1	93
2	*p*-OMe-$C_6H_4CO_2H$	28	>19/1	76

3	N-Boc-*L*-Leu	46	>19/1	89
4	$C_6H_5CO_2H$	41	>19/1	83
5[e]	$C_6H_5CO_2H$	51	>19/1	93

[a] Unless otherwise stated, reactions were performed with **1a** (0.15 mmol), **2a** (0.1 mmol), catalyst (0.02 mmol) and additive (0.02 mmol) in toluene (0.5 mL) for 24 h. [b] Isolated yield after column chromatography. [c] Dr. values were determined by crude ^{1}H NMR. [d] Ee values were determined by HPLC analysis on a chiral stationary phase. [e] The additive loading being 40 mol%.

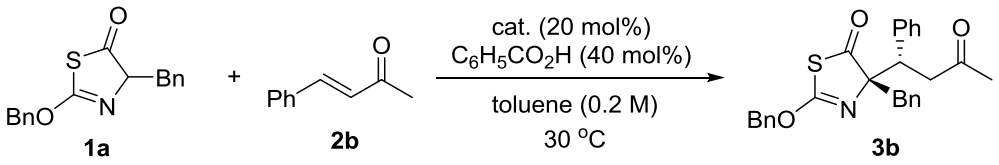
Table S3 The effect of solvent on the Michael reaction [a]

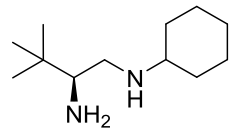


entry	solvent	yield (%)[b]	dr[c]	ee (%)[d]
1	toluene	56	>19/1	93
2	$CHCl_3$	64	>19/1	95
3	1,4-dioxane	47	>19/1	75
4[e]	toluene	70	7/1	82

[a] Unless otherwise stated, reactions were performed with **1a** (0.15 mmol), **2a** (0.1 mmol), catalyst (0.02 mmol) and additive (0.04 mmol) in solvent (0.5 mL) for 36 h. [b] Isolated yield after column chromatography. [c] Dr. values were determined by crude ^{1}H NMR. [d] Ee values were determined by HPLC analysis on a chiral stationary phase. [e] The reaction was performed at 80 °C.

Table S4 Screening of chiral amine catalysts[a]

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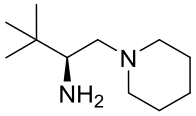
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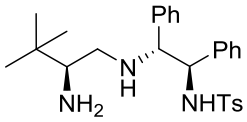
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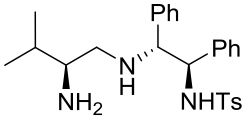
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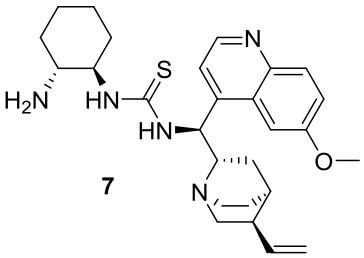
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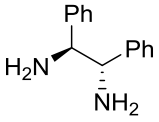
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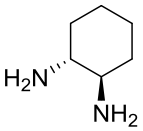
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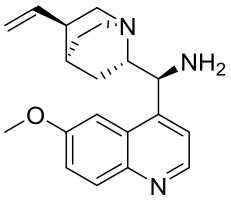
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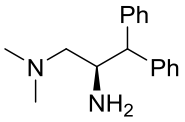
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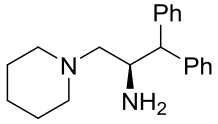
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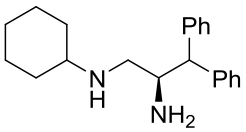
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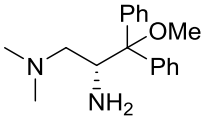
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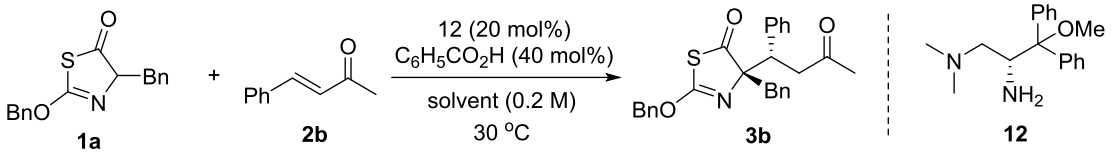
entry	cat.	conv. (%)[b]	dr[c]	ee (%)[d]
1	**4**	33	>19/1	80
2	**8**	48	>19/1	56
3	**7**	Full	>19/1	-46
4[e]	**6**	89	>19/1	73
5	**6**	69	>19/1	73
6[f]	**6**	52	>19/1	74
7	**9**	69	>19/1	37
8	**12**	27	>19/1	84
9	**15**	full	>19/1	20
10	**16**	79	>19/1	-20
11	**14**	29	>19/1	-33
12	**11**	58	>19/1	-70
13	**10**	21	>19/1	-30

[a] Unless otherwise stated, reactions were performed with **1a** (0.1 mmol), **2b** (0.15 mmol), catalyst (0.02 mmol) and additive (0.04 mmol) in toluene (0.5 mL) for 36 h. [b] The conversion values were determined by crude ^{1}H NMR. [c] Dr. values were determined by crude ^{1}H NMR. [d] Ee values were determined by HPLC analysis on a chiral stationary phase. [e] Additive loading being 0.02 mmol. [f] The reaction was performed with catalyst (0.01 mmol), additive (0.02 mmol).

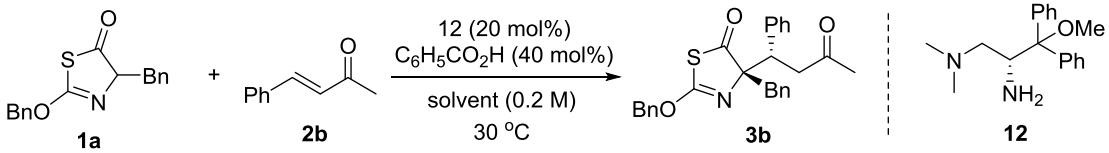
Table S5 Screening of solvent [a]



entry	solvent	conv. (%)[b]	dr[c]	ee (%)[d]
1	$CHCl_3$	18	>19/1	90
2	THF	<5	>19/1	75
3	EtOAc	30	>19/1	82
4	EtOH	Full	>19/1	71
5	*n*-Hexane	40	>19/1	81
6	DMF	<5	>19/1	53
7	CF_3CH_2OH	70	>19/1	77
8	HFIP	n.r.	n.d.	n.d.
9	CH_3OH	Full	>19/1	60
10	1,4-dioxane	33	>19/1	88
11	MTBE	18	>19/1	91
12	Et_2O	29	>19/1	83
13	Toluene	27	>19/1	84

[a] Unless otherwise stated, reactions were performed with **1a** (0.1 mmol), **2b** (0.15 mmol), catalyst (0.02 mmol) and additive (0.04 mmol) in solvent (0.5 mL) for 36 h. [b] The conversion values were determined by crude ^{1}H NMR. [c] Dr. values were determined by crude ^{1}H NMR. [d] Ee values were determined by HPLC analysis on a chiral stationary phase. [e] Additive loading being 0.02 mmol. [f] The reaction was performed with catalyst (0.01 mmol), additive (0.02 mmol).

Table S6 Screening of mixed solvent [a]

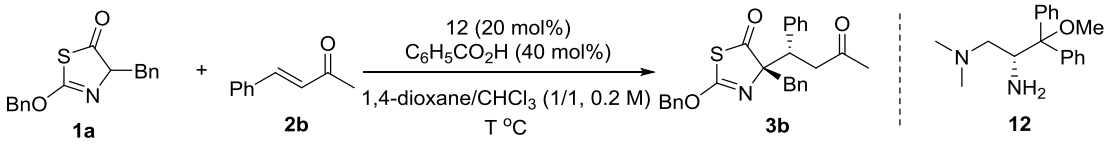


entry	solvent	solvent ratio	conv. (%)[b]	dr[c]	ee (%)[d]
1	EtOH/$CHCl_3$	1/1	79	>19/1	81
2	EtOH/$CHCl_3$	1/3	55	>19/1	80
3	EtOH/$CHCl_3$	1/9	42	>19/1	87
4	$CHCl_3$/CF_3CH_2OH	1/1	35	>19/1	77
5	$CHCl_3$/CH_3OH	1/1	Full	>19/1	74
6	$CHCl_3$/1,4-dioxane	1/1	34	>19/1	94
7	MTBE/$CHCl_3$	1/1	19	>19/1	93
8	Et_2O/$CHCl_3$	1/1	23	>19/1	92
10	1,4-dioxane/MeOH	1/1	56	>19/1	72
11[e]	1,4-dioxane/$CHCl_3$	1/1	56	>19/1	95

[a] Unless otherwise stated, reactions were performed with **1a** (0.1 mmol), **2b** (0.15 mmol), **12** (0.02 mmol) and additive (0.04 mmol) in solvent (0.5 mL) for 24 h. [b] The conversion values were

determined by crude ^{1}H NMR. [c] Dr. values were determined by crude ^{1}H NMR. [d] Ee values were determined by HPLC analysis on a chiral stationary phase. [e] The reaction was performed for 4 d.

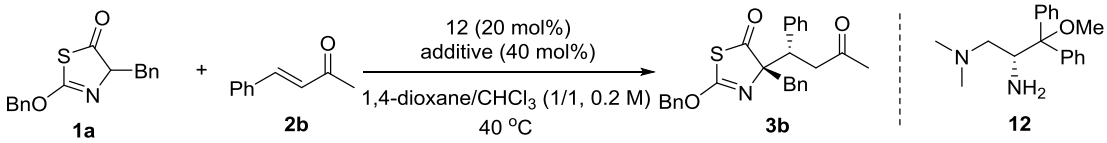
Table S7 Screening of reaction temperature [a]



entry	T(°C)	conv. (%)[b]	dr[c]	ee (%)[d]
1	30	37	>19/1	94
2	40	45	>19/1	94
3	100	26	>19/1	44
4[e]	80	Full	>19/1	53

[a] Unless otherwise stated, reactions were performed with **1a** (0.1 mmol), **2b** (0.15 mmol), catalyst (0.02 mmol) and additive (0.04 mmol) in solvent (0.5 mL) for 24 h. [b] The conversion values were determined by crude ^{1}H NMR. [c] Dr. values were determined by crude ^{1}H NMR. [d] Ee values were determined by HPLC analysis on a chiral stationary phase. [e] The reaction was performed under argon.

Table S8 Screening of additive [a]

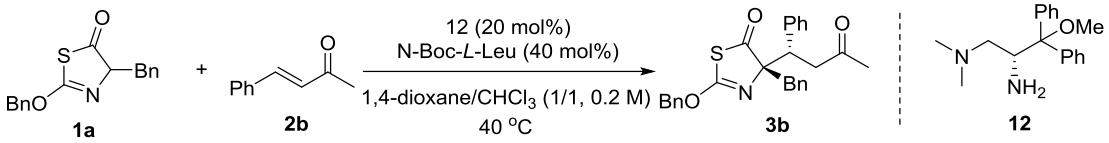


entry	acid additive	conv./%	dr/%	ee/%
1	TsOH	48	>19/1	73
2	AcOH	33	>19/1	93
3[e]	$C_6H_5CO_2H$	34	>19/1	94
4	$C_6H_5CO_2H$	45	>19/1	94
5	*p*-Me-$C_6H_4CO_2H$	26	>19/1	88
6	*o*-F-$C_6H_4CO_2H$	40	>19/1	94
7	3,5-$(NO_2)_2$-$C_6H_3CO_2H$	58	>19/1	92
8	N-Boc-*L*-Trp	37	>19/1	93
9	N-Boc-*D*-Phg	61	>19/1	94
10	N-Boc-*L*-Val	36	>19/1	94
11	N-Boc-*L*-Phg	51	>19/1	94
12	N-Boc-*L*-Pro	59	>19/1	95
13	N-Boc-*L*-Leu	72	>19/1	95
14	N-Boc-*D*-Phe	49	>19/1	94

[a] Unless otherwise stated, reactions were performed with **1a** (0.1 mmol), **2b** (0.15 mmol), catalyst (0.02 mmol) and additive (0.04 mmol) in solvent (0.5 mL) for 24 h. [b] The conversion values were

determined by crude ^{1}H NMR. [c] Dr. values were determined by crude ^{1}H NMR. [d] Ee values were determined by HPLC analysis on a chiral stationary phase. [e] 20 mol% acid additive loading.

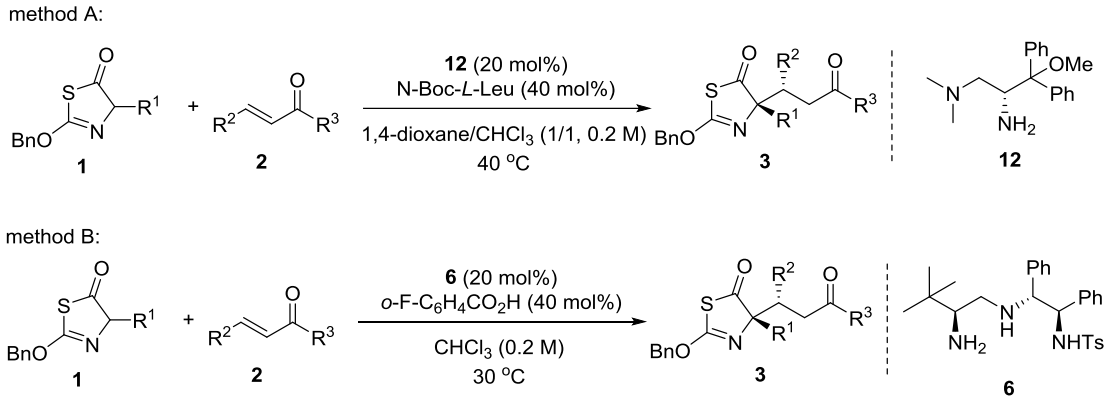
Table S9 Screening of substrate ratio [a]



entry	1a/2b	yield/%	dr/%	ee/%
1	3/1	23.1	>19/1	91
2	2/1	25.8	>19/1	91
3	1.5/1	35.4	>19/1	92
4	1/1.5	44.1	>19/1	92
5	1/2	53.2	>19/1	92
6	1/3	70.7	>19/1	95
7	1/4	70.7	>19/1	95
8	1/5	87.8	>19/1	95
9	1/6	90	>19/1	95

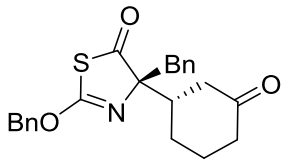
[a] Unless otherwise stated, reactions were performed with **1a** (0.1 mmol), **2b** (0.15 mmol), catalyst (0.02 mmol) and additive (0.04 mmol) in solvent (0.5 mL) for 24 h. [b] The conversion values were determined by crude ^{1}H NMR. [c] Dr. values were determined by crude ^{1}H NMR. [d] Ee values were determined by HPLC analysis on a chiral stationary phase. [e] 20 mol% acid additive loading.

C: General Procedure for the Michael Addition Reaction:

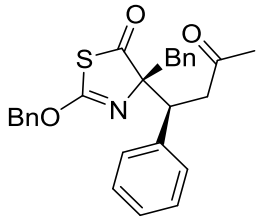


Method A: To a mixture of catalyst **12** (0.04 mmol) and N-Boc-*L*-Leucine (0.08 mmol) in 1,4-dioxane/$CHCl_3$ (1/1, 1.0 mL) was added thiazolone **1** (0.20 mmol) and linear α,β-unsaturated ketone **2** (0.60 mmol) subsequently. The reaction was stirred at 40 °C for about 96 h. After the reaction was complete, the reaction mixture was concentrated and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 10:1-5:1) to afford the product **3**.

Method B: To a mixture of catalyst **6** (0.04 mmol) and *o*-F-$C_6H_4CO_2H$ (0.08 mmol) in $CHCl_3$ (1.0 mL) was added thiazolone **1** (0.20 mmol) and cyclic α,β-unsaturated ketone **2** (0.60 mmol) subsequently. The reaction was stirred at 30 ºC for about 96 h. After the reaction was complete, the reaction mixture was concentrated and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 10:1-5:1) to afford the product **3**.

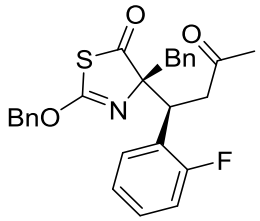


3a, **(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-3-oxocyclohexyl)thiazol-5(4*H*)-one**. The product was obtained in 70% yield, pale yellow solid. Mp 98-99 °C; $[\alpha]^{20}_D$ = -213.3 ° (c = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.43 – 7.32 (m, 5H), 7.21 – 7.12 (m, 3H), 7.04 – 6.94 (m, 2H), 5.48 – 5.32 (m, 2H), 3.08 (dd, *J* = 74.3, 12.9 Hz, 2H), 2.41 – 2.24 (m, 3H), 2.15 (ddd, *J* = 22.8, 16.5, 9.7 Hz, 3H), 2.02 – 1.93 (m, 1H), 1.70 – 1.54 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 210.08, 209.51, 160.60, 135.43, 134.30, 130.57, 128.61, 128.55, 127.97, 126.95, 90.97, 71.07, 45.76, 42.50, 42.12, 40.97, 25.81, 24.45. HRMS(EI) calcd for $C_{23}H_{23}NO_3S$ $[M]^+$ 393.1399, found: 393.1394; HPLC (DAICEL Chiralpak IB *n*-Hexane/Isopropanol = 19/1, flow 1.0 mL/min, detection at 220 nm) retention time = 8.70 min (major) and 9.65 min (minor), ee 96%.

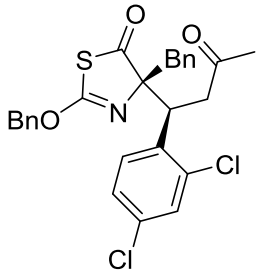


3b, **(*S*)-4-12benzyl-2-(benzyloxy)-4-((*S*)-3-oxo-1-phenylbutyl)thiazol-5(4*H*)-one**. The product was obtained in 64% yield, pale yellow oil. $[\alpha]^{20}_D$ =85.0 ° (c = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.48 – 7.37 (m, 5H), 7.18 – 7.14 (m, 3H), 7.10 (dt, *J* = 5.3, 4.1 Hz, 3H), 7.03 (dd, *J* = 6.4, 2.8 Hz, 2H), 6.97 – 6.89 (m, 2H), 5.45 (dd, *J* = 40.2, 11.9 Hz, 2H), 3.84 (dd, *J* = 9.1, 4.8 Hz, 1H), 3.21 – 3.06 (m, 4H), 2.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 207.62, 205.47, 160.10, 137.15, 134.54, 133.42, 129.58, 128.37, 127.67, 127.63, 127.58, 127.02, 126.88, 126.12, 125.82, 90.61, 69.79, 46.52, 44.20, 41.79, 29.53. HRMS(EI) calcd for $C_{27}H_{25}NO_3S$ $[M]^+$ 443.1555, found: 443.1552; HPLC (DAICEL Chiralpak IB *n*-Hexane/Isopropanol = 7/3, flow 0.8 mL/min, detection at 220 nm) retention time = 7.00 min (major) and

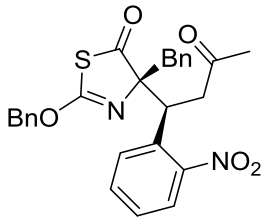
6.82 min (minor), ee 95%.



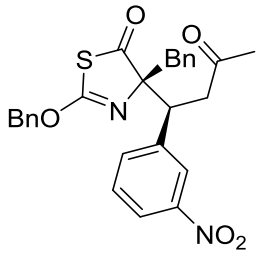
3c, **(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-1-(2-fluorophenyl)-3-oxobutyl)thiazol-5(4*H*)-one**. The product was obtained in 74% yield, yellow oil. $[\alpha]^{20}_{D}$ = -14.6 ° (c = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.49 – 7.37 (m, 5H), 7.18 – 7.11 (m, 4H), 7.04 – 7.00 (m, 2H), 6.99 – 6.93 (m, 1H), 6.86 (ddd, *J* = 20.7, 10.6, 4.0 Hz, 2H), 5.46 (dd, *J* = 31.7, 11.9 Hz, 2H), 4.25 (dd, *J* = 9.4, 5.0 Hz, 1H), 3.22 – 3.05 (m, 4H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 207.85, 205.95, 160.96, 135.53, 134.28, 130.67, 129.00, 128.92, 128.73, 128.67, 128.64, 127.92, 126.90, 125.59, 125.45, 123.81, 123.77, 115.78, 115.54, 91.13, 70.90, 44.68, 42.60, 30.17, 29.71. HRMS(EI) calcd for $C_{27}H_{24}FNO_3S$ $[M]^+$ 461.1461, found: 461.1455; HPLC (DAICEL Chiralpak IB *n*-Hexane/Isopropanol = 9/1, flow 1.0 mL/min, detection at 220 nm) retention time = 7.55 min (major) and 8.79 min (minor), ee 92%.



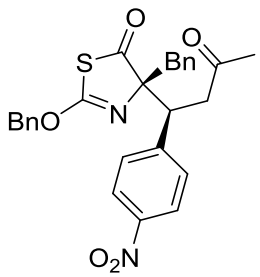
3d, **(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-1-(2,4-dichlorophenyl)-3-oxobutyl)thiazol-5(4*H*)-one**. The product was obtained in 77% yield, yellow oil. $[\alpha]^{20}_{D}$ = 44.0 ° (c = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.50 – 7.40 (m, 5H), 7.32 (d, *J* = 2.2 Hz, 1H), 7.21 – 7.15 (m, 3H), 7.04 (dd, *J* = 6.4, 3.0 Hz, 2H), 6.88 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.60 (d, *J* = 8.5 Hz, 1H), 5.45 (dd, *J* = 67.4, 11.9 Hz, 2H), 4.45 (dd, *J* = 10.4, 4.0 Hz, 1H), 3.27 – 3.08 (m, 3H), 2.92 (dd, *J* = 17.0, 10.4 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 207.00, 205.51, 161.34, 135.99, 135.58, 135.13, 134.00, 133.43, 130.70, 129.70, 129.38, 128.89, 128.82, 128.68, 127.97, 127.03, 126.81, 90.86, 71.02, 45.72, 42.82, 41.37, 30.23. HRMS(EI) calcd for $C_{27}H_{23}Cl_2NO_3S$ $[M]^+$ 511.0776, found: 511.0782; HPLC (DAICEL Chiralpak IB *n*-Hexane/Isopropanol = 7/3, flow 0.8 mL/min, detection at 220 nm) retention time = 7.41 min (major) and 8.10 min (minor), ee 90%.



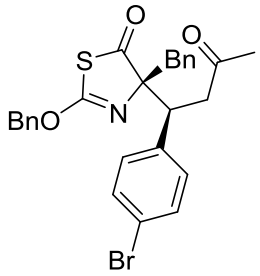
3e, **(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-1-(2-nitrophenyl)-3-oxobutyl)thiazol-5(4*H*)-one**. The product was obtained in 95% yield, yellow oil. $[\alpha]^{20}_{D}$ = 114.3 ° (c = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 4.2 Hz, 4H), 7.45 – 7.39 (m, 1H), 7.28 (td, *J* = 7.8, 1.4 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.20 – 7.12 (m, 3H), 7.00 (dd, *J* = 7.4, 1.9 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 5.44 (dd, *J* = 60.7, 11.9 Hz, 2H), 4.79 (dd, *J* = 9.4, 4.5 Hz, 1H), 3.29 (dd, *J* = 16.6, 4.7 Hz, 1H), 3.15 (dd, *J* = 30.6, 12.8 Hz, 2H), 3.02 (dd, *J* = 16.4, 9.6 Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 208.07, 205.57, 161.45, 150.78, 135.49, 133.81, 132.76, 132.02, 130.67, 129.36, 128.88, 128.82, 128.70, 128.01, 127.96, 127.07, 124.87, 91.09, 71.11, 45.61, 43.12, 39.86, 29.93. HRMS(EI) calcd for $C_{27}H_{24}N_2O_5S$ $[M]^+$ 488.1406, found: 488.1409; HPLC (DAICEL Chiralpak IB *n*-Hexane/Isopropanol = 7/3, flow 0.8 mL/min, detection at 220 nm) retention time = 9.53 min (major) and 11.78 min (minor), ee 90%.



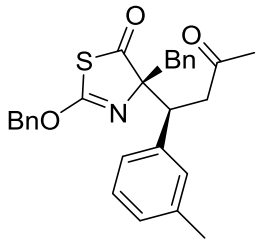
3f, **(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-1-(3-nitrophenyl)-3-oxobutyl)thiazol-5(4*H*)-one**. The product was obtained in 95% yield, pale yellow solid. Mp 77-78 °C; $[\alpha]^{20}_{D}$ = 52.0 ° (c = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.08 (d, *J* = 1.6 Hz, 1H), 8.04 (dt, *J* = 7.2, 2.1 Hz, 1H), 7.51 – 7.37 (m, 5H), 7.38 – 7.30 (m, 2H), 7.22 – 7.13 (m, 3H), 7.01 (dd, *J* = 7.4, 2.0 Hz, 2H), 5.51 (dd, *J* = 36.3, 11.7 Hz, 2H), 4.01 (dd, *J* = 9.4, 4.3 Hz, 1H), 3.33 (dd, *J* = 18.0, 4.3 Hz, 1H), 3.24 – 3.10 (m, 3H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 208.40, 205.37, 161.88, 147.83, 140.83, 136.57, 134.99, 133.85, 130.57, 129.14, 128.88, 128.84, 128.72, 128.04, 127.11, 123.42, 122.31, 91.11, 71.48, 46.58, 44.92, 42.74, 30.59. HRMS(EI) calcd for $C_{27}H_{24}N_2O_5S$ $[M]^+$ 488.1406, found: 488.1411; HPLC (DAICEL Chiralpak IB *n*-Hexane/Isopropanol = 7/3, flow 0.8 mL/min, detection at 220 nm) retention time = 9.64 min (minor) and 10.64 min (major), ee 90%.



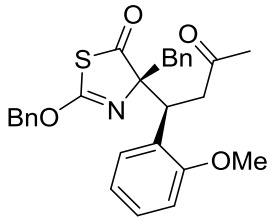
3g, **(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-1-(4-nitrophenyl)-3-oxobutyl)thiazol-5(4*H*)-one**. The product was obtained in 95% yield, pale yellow solid. Mp 100-101 °C; $[\alpha]^{20}_{D}$ = 14.9 ° (c = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.89 (d, *J* = 8.8 Hz, 2H), 7.52 – 7.43 (m, 5H), 7.19 (dd, *J* = 4.9, 1.5 Hz, 3H), 7.04 (dd, *J* = 6.6, 2.9 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 5.47 (dd, *J* = 67.7, 11.9 Hz, 2H), 3.93 (dd, *J* = 9.7, 4.1 Hz, 1H), 3.26 (dd, *J* = 17.9, 4.1 Hz, 1H), 3.16 (dd, *J* = 24.3, 9.2 Hz, 2H), 3.09 (dd, *J* = 14.2, 6.0 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 208.26, 205.52, 161.48, 140.14, 135.59, 133.87, 130.60, 130.20, 128.98, 128.89, 128.72, 128.07, 127.15, 124.19, 123.10, 91.22, 71.18, 46.91, 44.75, 42.95, 30.55. HRMS(EI) calcd for $C_{27}H_{24}N_2O_5S$ $[M]^+$ 488.1406, found: 488.1400; HPLC (DAICEL Chiralpak IB *n*-Hexane/Isopropanol = 7/3, flow 0.8 mL/min, detection at 220 nm) retention time = 8.17 min (major) and 8.75 min (minor), ee 96%.



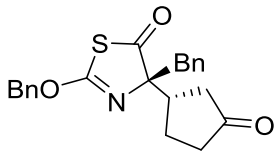
3h, **(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-1-(4-bromophenyl)-3-oxobutyl)thiazol-5(4*H*)-one**. The product was obtained in 81% yield, yellow oil. $[\alpha]^{20}_{D}$ = 19.1 ° (c = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.52 – 7.39 (m, 5H), 7.23 – 7.14 (m, 5H), 7.03 (dt, *J* = 7.5, 3.8 Hz, 2H), 6.72 (d, *J* = 8.4 Hz, 2H), 5.44 (dd, *J* = 53.1, 11.9 Hz, 2H), 3.78 (dd, *J* = 9.6, 4.4 Hz, 1H), 3.19 – 3.09 (m, 3H), 3.02 (dd, *J* = 17.3, 9.7 Hz, 1H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 208.52, 206.04, 161.36, 137.36, 135.59, 134.22, 131.19, 130.99, 130.60, 128.84, 128.79, 128.66, 127.99, 126.99, 121.26, 91.41, 70.95, 46.83, 45.02, 42.89, 30.63. HRMS(EI) calcd for $C_{27}H_{24}BrNO_3S$ $[M]^+$ 521.0660, found: 521.0657; HPLC (DAICEL Chiralpak IB *n*-Hexane/Isopropanol = 7/3, flow 0.8 mL/min, detection at 220 nm) retention time = 6.89 min (major) and 7.75 min (minor), ee 92%.



3i, **(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-3-oxo-1-(m-tolyl)butyl)thiazol-5(4*H*)-one**. The product was obtained in 34% yield, orange oil. $[\alpha]^{20}_{D}$ = 72.7 ° (c = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.51 – 7.37 (m, 5H), 7.19 – 7.13 (m, 3H), 7.05 – 6.98 (m, 3H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.88 (s, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 5.46 (q, *J* = 11.9 Hz, 2H), 3.81 (dd, *J* = 9.0, 4.9 Hz, 1H), 3.23 – 3.05 (m, 4H), 2.23 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 208.62, 206.61, 161.17, 138.16, 137.46, 135.47, 134.52, 130.63, 130.47, 128.71, 128.67, 128.65, 127.96, 127.90, 126.83, 126.16, 91.62, 70.82, 47.56, 45.38, 42.85, 30.57, 21.45. HRMS(EI) calcd for $C_{28}H_{27}NO_3S$ $[M]^+$ 457.1712, found: 457.1709; HPLC (DAICEL Chiralpak IB *n*-Hexane/Isopropanol = 7/3, flow 0.8 mL/min, detection at 220 nm) retention time = 7.14 min (minor) and 9.35 min (major), ee 93%.

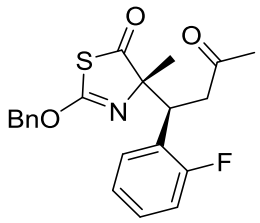


3j, **(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-1-(2-methoxyphenyl)-3-oxobutyl)thiazol-5(4*H*)-one**. The product was obtained in 58% yield, yellow oil. $[\alpha]^{20}_{D}$ = 34.0 ° (c = 1.00 in CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): 7.45 (d, *J* = 4.4 Hz, 4H), 7.42 – 7.36 (m, 1H), 7.18 – 7.11 (m, 4H), 7.03 (dd, *J* = 6.5, 2.9 Hz, 2H), 6.81 (t, *J* = 6.0 Hz, 2H), 6.71 (t, *J* = 7.5 Hz, 1H), 5.45 (dd, *J* = 33.6, 11.9 Hz, 2H), 4.54 (s, 1H), 3.84 (s, 3H), 3.20 (dd, *J* = 33.1, 12.9 Hz, 2H), 3.12 – 2.92 (m, 2H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 207.39, 206.99, 160.80, 157.11, 135.60, 134.74, 130.73, 128.67, 128.63, 128.38, 127.83, 126.75, 126.72, 120.19, 111.13, 91.38, 70.73, 55.84, 45.61, 42.69, 30.04, 29.71. HRMS(EI) calcd for $C_{28}H_{27}NO_4S$ $[M]^+$ 473.1661, found: 473.1666; HPLC (DAICEL Chiralpak IB *n*-Hexane/Isopropanol = 9/1, flow 1.0 mL/min, detection at 220 nm) retention time = 5.32 min (major) and 10.03 min (minor), ee 96%.

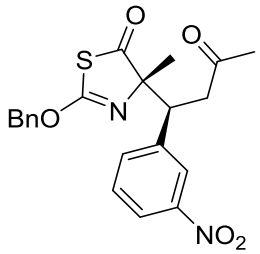


3k, **(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-3-oxocyclopentyl)thiazol-5(4*H*)-one**. The

product was obtained in 68% yield, yellow oil. $[\alpha]^{20}_D$ = -35.0 ° (c = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 – 7.33 (m, 5H), 7.22 – 7.15 (m, 3H), 7.02 (dd, *J* = 7.4, 1.8 Hz, 2H), 5.45 – 5.34 (m, 2H), 3.14 (dd, *J* = 57.6, 13.0 Hz, 2H), 2.75 (tt, *J* = 10.7, 7.2 Hz, 1H), 2.36 (dd, *J* = 18.1, 8.4 Hz, 1H), 2.32 – 2.23 (m, 1H), 2.23 – 2.10 (m, 2H), 2.10 – 1.97 (m, 1H), 1.72 (ddd, *J* = 18.0, 11.0, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 217.06, 209.20, 160.77, 135.17, 134.27, 130.45, 128.72, 128.61, 128.48, 128.00, 126.99, 89.99, 71.19, 44.03, 42.51, 39.29, 37.86, 24.57. HRMS(EI) calcd for $C_{22}H_{21}NO_3S$ $[M]^+$ 379.1242, found: 379.1245; HPLC (DAICEL Chiralpak IA, *n*-Hexane/EtOH = 9/1, flow 1.0 mL/min, detection at 220nm) retention time = 6.40 min (major) and 7.80 min (minor), ee 96%.

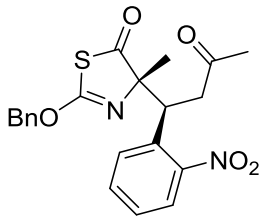


3l, **(*S*)-2-(benzyloxy)-4-((*S*)-1-(2-fluorophenyl)-3-oxobutyl)-4-methylthiazol-5(4*H*)-one**. The product was obtained in 78% yield, pale yellow oil. $[\alpha]^{20}_D$ = 17.3 ° (c = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.54 – 7.33 (m, 5H), 7.14 (ddd, *J* = 15.2, 5.2, 1.7 Hz, 1H), 6.99 – 6.91 (m, 1H), 6.89 – 6.81 (m, 1H), 6.80 – 6.71 (m, 1H), 5.45 (dd, *J* = 66.7, 11.9 Hz, 2H), 4.09 (dd, *J* = 9.0, 5.5 Hz, 1H), 3.11 – 2.96 (m, 2H), 2.04 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 207.96, 206.06, 159.62, 135.42, 128.93, 128.85, 128.75, 128.68, 128.64, 123.75, 123.72, 115.71, 115.48, 87.23, 70.92, 44.34, 30.12, 29.71, 22.99. HRMS(EI) calcd for $C_{21}H_{20}FNO_3S$ $[M]^+$ 385.1148, found: 385.1151; HPLC (DAICEL Chiralpak IB *n*-Hexane/Isopropanol = 9/1, flow 1.0 mL/min, detection at 220 nm) retention time = 6.81 min (major) and 7.27 min (minor), ee 92%.

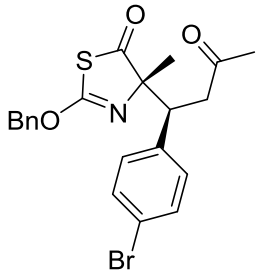


3m, **(*S*)-2-(benzyloxy)-4-methyl-4-((*S*)-1-(3-nitrophenyl)-3-oxobutyl)thiazol-5(4*H*)-one**. The product was obtained in 67% yield, pale yellow solid. Mp 86-87 °C; $[\alpha]^{20}_D$ = 30.2 ° (c = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.10 – 8.00 (m, 2H), 7.49 – 7.36 (m, 5H), 7.34 – 7.28 (m, 2H), 5.53 – 5.44 (m, 2H), 3.85 (dd,

J = 9.3, 4.5 Hz, 1H), 3.21 (dd, *J* = 18.0, 4.5 Hz, 1H), 3.12 (dd, *J* = 18.0, 9.4 Hz, 1H), 2.11 (s, 3H), 1.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 208.39, 205.46, 160.43, 147.83, 140.82, 136.39, 134.80, 129.11, 128.91, 128.89, 128.72, 123.25, 122.31, 87.15, 71.59, 46.37, 44.55, 30.52, 23.08. HRMS(EI) calcd for $C_{21}H_{20}N_2O_5S$ $[M]^+$ 412.1093, found: 412.1088; HPLC (DAICEL Chiralpak IC, *n*-Hexane/EtOH = 9/1, flow 0.8 mL/min, detection at 220nm) retention time = 11.70 min (minor) and 12.94 min (major), ee 92%.

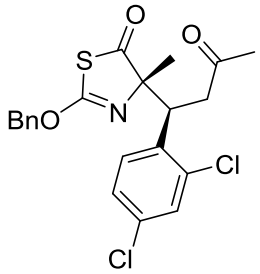


3n, **(*S*)-2-(benzyloxy)-4-methyl-4-((*S*)-1-(2-nitrophenyl)-3-oxobutyl)thiazol-5(4*H*)-one**. The product was obtained in 80% yield, pale yellow oil. $[\alpha]^{20}_D$ = 108.4 ° (c = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.71 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.52 – 7.39 (m, 5H), 7.31 – 7.26 (m, 1H), 7.20 (dd, *J* = 11.1, 4.2 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 5.43 (dd, *J* = 83.8, 11.9 Hz, 2H), 4.61 (dd, *J* = 9.2, 4.7 Hz, 1H), 3.19 (dd, *J* = 16.5, 4.9 Hz, 1H), 2.93 (dd, *J* = 16.3, 9.5 Hz, 1H), 2.13 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 207.86, 205.64, 160.01, 150.77, 135.42, 132.75, 131.97, 128.87, 128.82, 128.69, 127.96, 124.79, 87.21, 71.09, 45.23, 29.86, 29.70, 23.47. HRMS(EI) calcd for $C_{21}H_{20}N_2O_5S$ $[M]^+$ 412.1093, found: 412.1098; HPLC (DAICEL Chiralpak IB *n*-Hexane/Isopropanol = 9/1, flow 1.0 mL/min, detection at 220 nm) retention time = 14.02 min (major) and 16.52 min (minor), ee 90%.

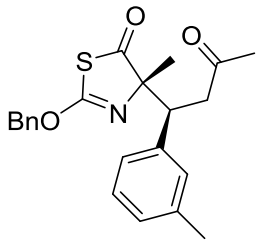


3o, **(*S*)-2-(benzyloxy)-4-((*S*)-1-(4-bromophenyl)-3-oxobutyl)-4-methylthiazol-5(4*H*)-one**. The product was obtained in 74% yield, pale yellow solid. Mp 104-105 °C; $[\alpha]^{20}_D$ = 26.6 ° (c = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.52 – 7.39 (m, 5H), 7.22 – 7.14 (m, 2H), 6.70 – 6.61 (m, 2H), 5.44 (dd, *J* = 80.2, 11.9 Hz, 2H), 3.61 (dd, *J* = 9.6, 4.6 Hz, 1H), 3.03 (dd, *J* = 17.3, 4.6 Hz, 1H), 2.94 (dd, *J* = 17.3, 9.6 Hz, 1H), 2.02 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 208.60, 206.13, 159.93, 137.33, 135.50, 131.15, 130.79, 128.83, 128.76, 128.65, 121.20, 87.46,

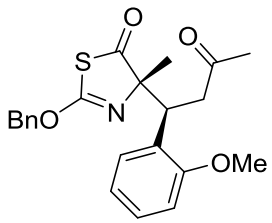
70.92, 46.65, 44.63, 30.55, 23.25. HRMS(EI) calcd for $C_{21}H_{20}BrNO_3S$ $[M]^+$ 445.0347, found: 445.0341; HPLC (DAICEL Chiralpak IC, *n*-Hexane/EtOH = 9/1, flow 0.8 mL/min, detection at 220nm) retention time = 7.28 min (minor) and 7.87 min (major), ee 92%.



3p, **(*S*)-2-(benzyloxy)-4-((*S*)-1-(2,4-dichlorophenyl)-3-oxobutyl)-4-methylthiazol-5(4*H*)-one**. The product was obtained in 76% yield, pale yellow solid. Mp 102-103 °C; $[\alpha]^{20}_D$ = 22.6 ° (c = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.55 – 7.41 (m, 5H), 7.31 (d, *J* = 2.2 Hz, 1H), 6.85 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.54 (d, *J* = 8.5 Hz, 1H), 5.44 (dd, *J* = 89.5, 11.9 Hz, 2H), 4.29 (dd, *J* = 10.3, 4.0 Hz, 1H), 3.03 (dd, *J* = 17.0, 4.1 Hz, 1H), 2.84 (dd, *J* = 17.0, 10.4 Hz, 1H), 2.01 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 207.02, 205.60, 159.98, 135.89, 135.52, 135.15, 133.35, 129.63, 129.17, 128.90, 128.83, 128.68, 126.76, 86.96, 71.00, 45.34, 41.16, 30.15, 23.27. HRMS(EI) calcd for $C_{21}H_{19}Cl_2NO_3S$ $[M]^+$ 435.0463, found: 435.0468; HPLC (DAICEL Chiralpak IC, *n*-Hexane/EtOH = 9/1, flow 0.8 mL/min, detection at 220nm) retention time = 7.13 min (minor) and 8.30 min (major), ee 91%.

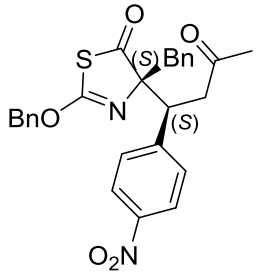


3q, **(*S*)-2-(benzyloxy)-4-methyl-4-((*S*)-3-oxo-1-(m-tolyl)butyl)thiazol-5(4*H*)-one**. The product was obtained in 30% yield, pale yellow oil. $[\alpha]^{20}_D$ = 16.4 ° (c = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.49 – 7.34 (m, 5H), 7.02 – 6.93 (m, 2H), 6.85 (s, 1H), 6.67 (d, *J* = 7.1 Hz, 1H), 5.45 (dd, *J* = 58.1, 11.9 Hz, 2H), 3.65 (dd, *J* = 8.2, 5.9 Hz, 1H), 3.11 – 2.98 (m, 2H), 2.22 (s, 3H), 2.03 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 208.84, 206.70, 159.79, 138.14, 137.43, 135.33, 130.30, 128.73, 128.66, 127.93, 127.88, 125.91, 87.67, 70.87, 47.38, 44.96, 30.51, 29.71, 23.19. HRMS(EI) calcd for $C_{22}H_{23}NO_3S$ $[M]^+$ 381.1399, found: 381.1404; HPLC (DAICEL Chiralpak IC, *n*-Hexane/EtOH = 9/1, flow 0.8 mL/min, detection at 220nm) retention time = 7.38 min (minor) and 9.32 min (major), ee 88%.



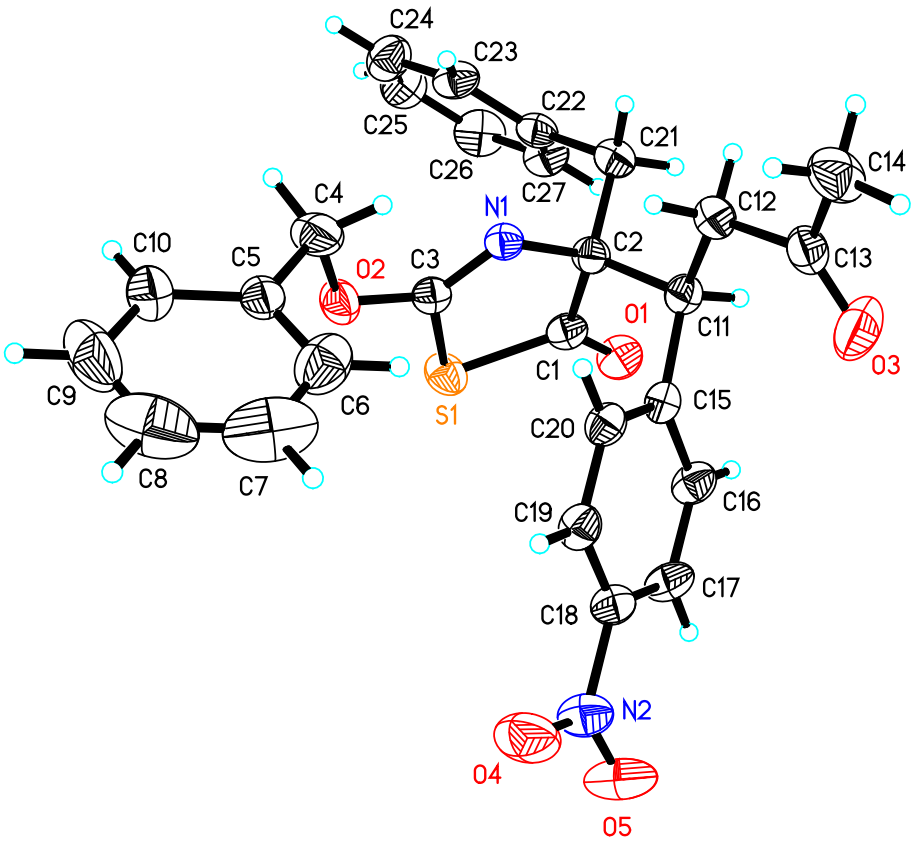
3r, **(*S*)-2-(benzyloxy)-4-((*S*)-1-(2-methoxyphenyl)-3-oxobutyl)-4-methylthiazol-5(4*H*)-one**. The product was obtained in 39% yield, pale yellow oil. $[\alpha]^{20}_{D}$ = 26.0 ° (c = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.50 – 7.36 (m, 6H), 7.16 – 7.10 (m, 1H), 6.84 – 6.72 (m, 2H), 5.50 (dd, *J* = 42.2, 30.3 Hz, 2H), 4.37 (dd, *J* = 9.6, 5.3 Hz, 1H), 3.80 (s, 3H), 3.02 – 2.86 (m, 2H), 1.98 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 207.56, 207.10, 159.51, 157.07, 135.49, 128.77, 128.69, 128.63, 128.54, 128.29, 126.74, 120.10, 111.05, 87.38, 70.72, 55.78, 45.27, 29.95, 29.71, 23.15. HRMS(EI) calcd for $C_{22}H_{23}NO_4S$ $[M]^+$ 397.1348, found: 397.1353; HPLC (DAICEL Chiralpak AD *n*-Hexane/Isopropanol = 19/1, flow 0.8 mL/min, detection at 220 nm) retention time = 9.71 min (major) and 10.69 min (minor), ee 89%.

D. Determination of Absolute Configuration



The absolute configuration of compound **3g** was unambiguously assigned by single crystal X-ray analysis. Crystals of **3g** were obtained by slow evaporation of a mixture of *n*-pentane/ethyl acetate at room temperature.

Crystal data for **3g**: CCDC1946331


C24
C23
C22
C25
C26
C27
C21
C14
C12
C4
N1
C10
C5
O2
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C2
C13
O1
C11
O3
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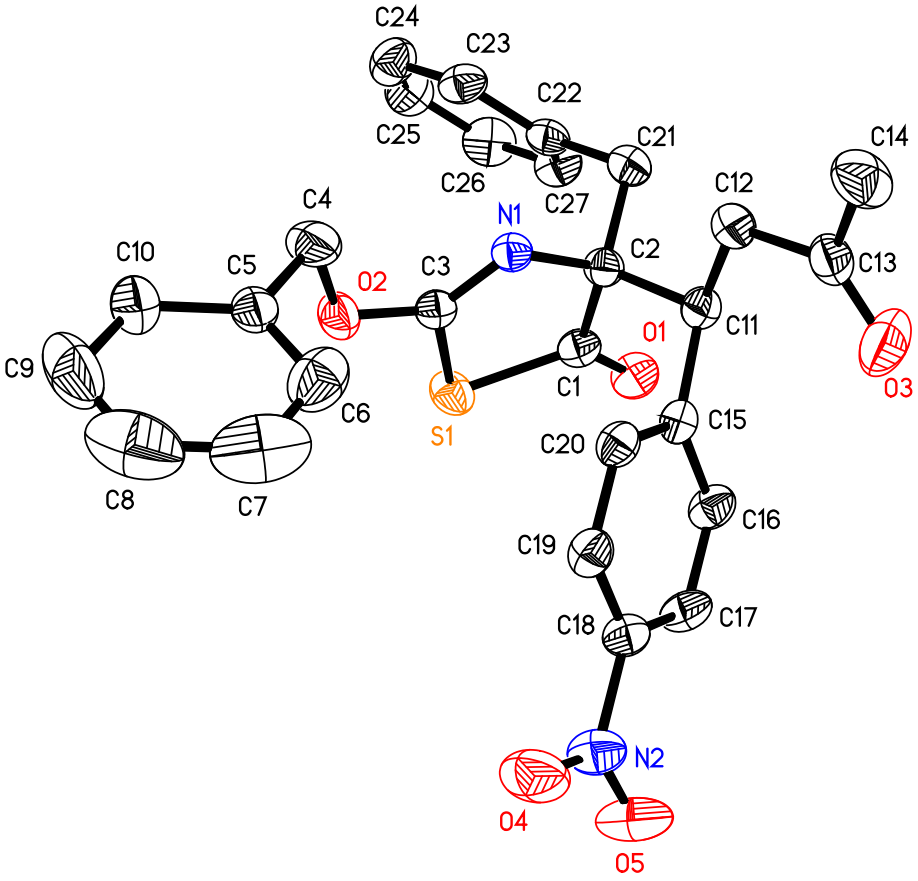
C16
C19
C17
C18
N2
O4
O5


C24
C23
C22
C25
C26
C27
C21
C14
C12
C4
N1
C10
C5
C3
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O2
C11
O1
C9
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C16
C19
C17
C18
N2
O4
O5

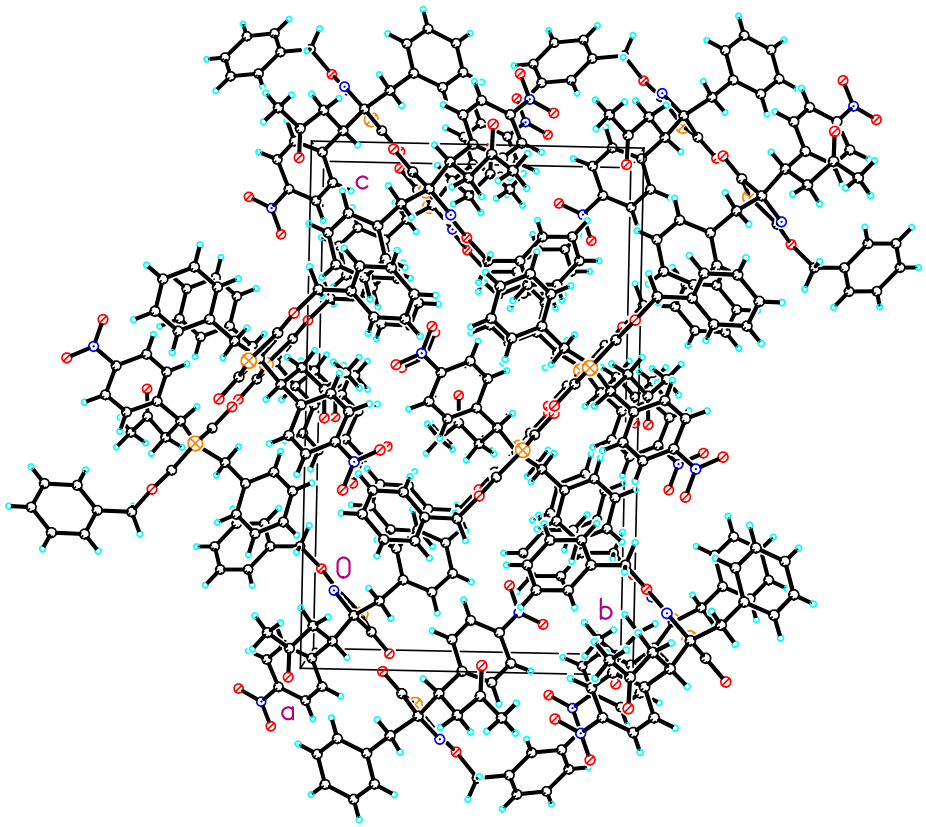

c
0
b
a

Table 1. Crystal data and structure refinement for cd16615.

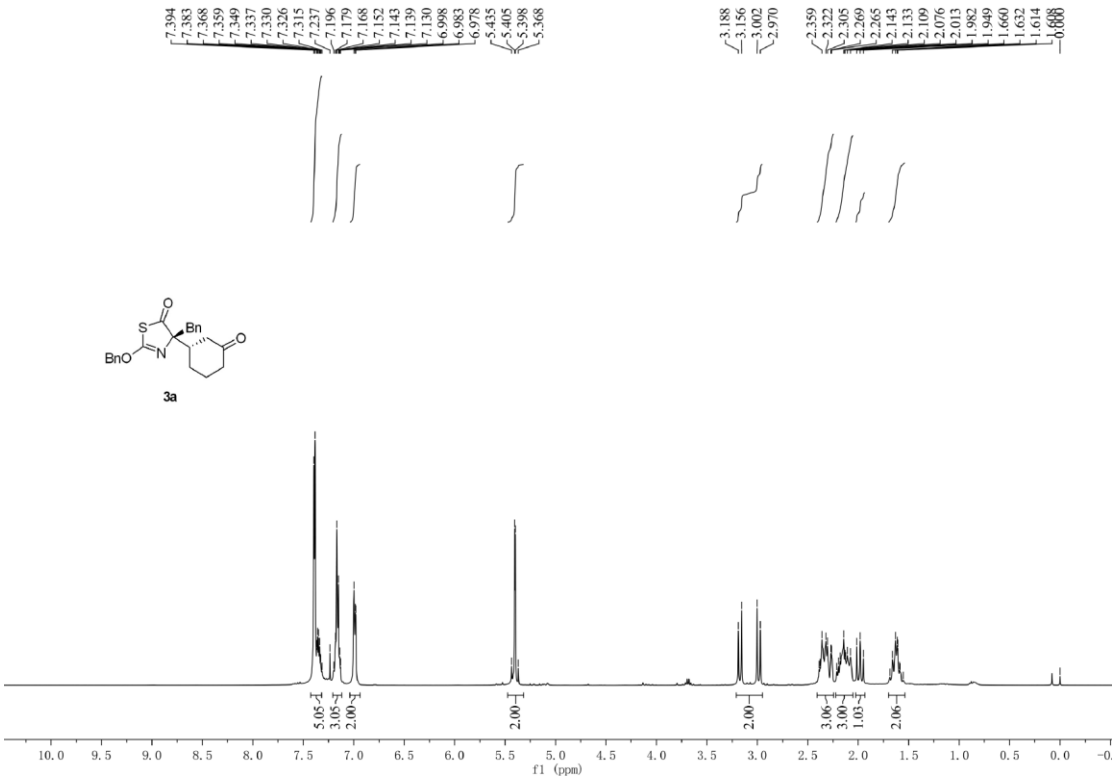
Identification code	cd16615	
Empirical formula	C27 H24 N2 O5 S	
Formula weight	488.54	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.5917(13) Å	= 90 °.
	b = 13.421(2) Å	= 90 °.
	c = 21.279(3) Å	= 90 °.
Volume	2453.7(6) $Å^3$	
Z	4	
Density (calculated)	1.322 Mg/m^3	
Absorption coefficient	0.173 mm^{-1}	
F(000)	1024	
Crystal size	0.200 x 0.180 x 0.130 mm^3	
Theta range for data collection	1.794 to 25.496 °.	
Index ranges	-8<=h<=10, -15<=k<=16, -25<=l<=25	
Reflections collected	14194	
Independent reflections	4575 [R(int) = 0.0365]	
Completeness to theta = 25.242 °	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6173	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4575 / 0 / 305	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0433, wR2 = 0.1057	
R indices (all data)	R1 = 0.0522, wR2 = 0.1114	
Absolute structure parameter	-0.01(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.174 and -0.160 e.$Å^{-3}$	

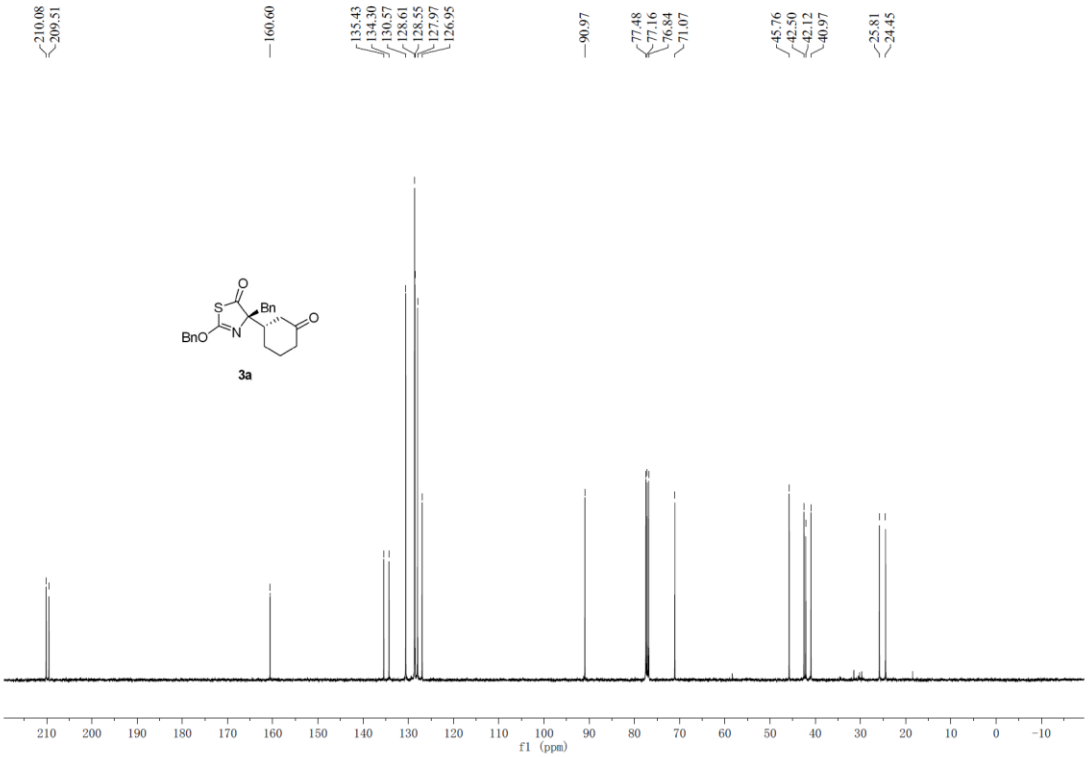
Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for cd16615. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

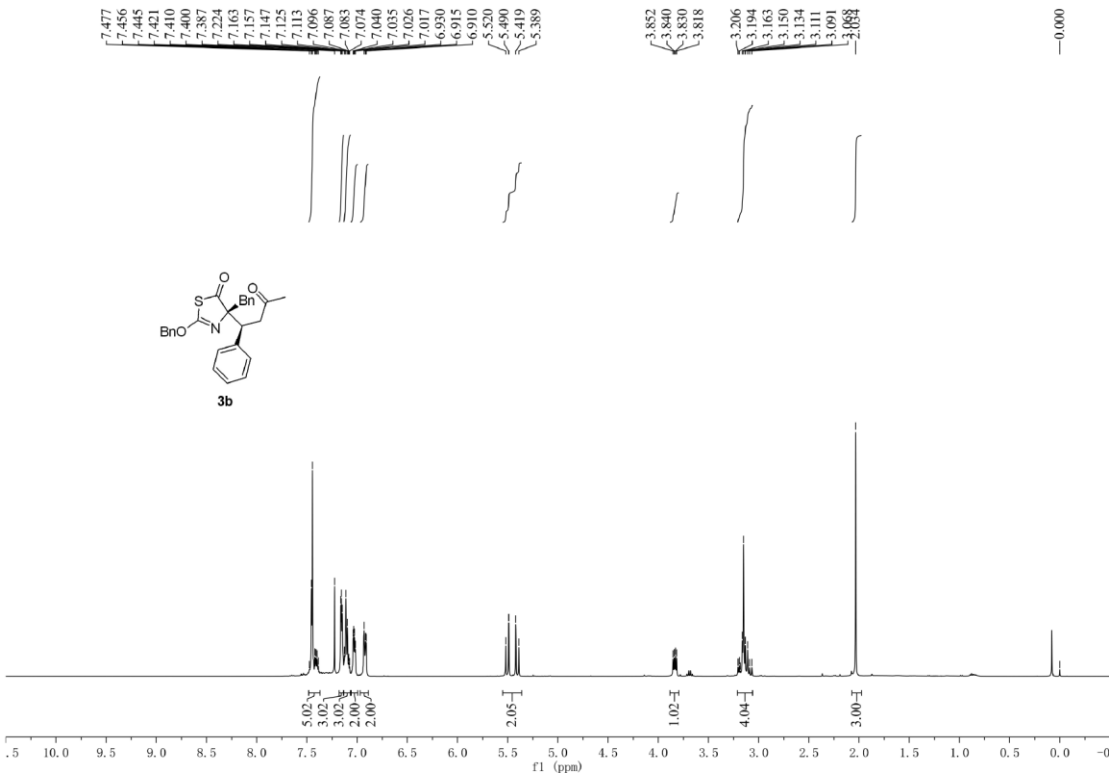
	x	y	z	U(eq)
S(1)	6877(1)	3428(1)	9210(1)	58(1)
N(1)	9353(3)	4229(2)	8676(1)	43(1)
N(2)	6713(4)	6578(3)	11035(2)	71(1)
O(1)	8893(3)	2452(2)	9926(1)	63(1)
O(2)	6939(3)	4725(2)	8310(1)	60(1)
O(3)	13176(4)	5443(3)	10251(1)	97(1)
O(4)	6233(4)	7339(2)	10802(2)	100(1)
O(5)	6321(5)	6273(2)	11551(2)	102(1)
C(1)	8726(4)	3043(2)	9505(1)	48(1)
C(2)	10030(3)	3570(2)	9141(1)	45(1)
C(3)	7894(4)	4208(2)	8672(1)	44(1)
C(4)	7681(5)	5394(3)	7851(2)	79(1)
C(5)	6925(3)	6383(2)	7881(1)	55(1)
C(6)	7350(4)	7052(3)	8349(1)	90(1)
C(7)	6649(5)	7984(2)	8379(2)	126(2)
C(8)	5524(5)	8248(2)	7940(2)	134(3)
C(9)	5099(4)	7579(3)	7472(2)	114(2)
C(10)	5799(3)	6647(2)	7442(1)	79(1)
C(11)	11016(4)	4188(2)	9621(1)	47(1)
C(12)	12319(4)	4753(3)	9285(2)	56(1)
C(13)	13300(4)	5419(3)	9692(2)	59(1)
C(14)	14461(5)	6041(3)	9356(2)	83(1)
C(15)	9946(4)	4858(2)	10004(1)	44(1)
C(16)	9392(4)	4537(3)	10586(2)	56(1)
C(17)	8330(4)	5090(3)	10918(1)	60(1)
C(18)	7841(4)	5980(3)	10679(2)	54(1)
C(19)	8392(4)	6339(2)	10111(1)	53(1)
C(20)	9431(4)	5765(2)	9780(2)	48(1)
C(21)	11025(4)	2757(2)	8814(2)	53(1)
C(22)	10062(4)	2049(2)	8418(2)	50(1)
C(23)	9630(4)	2290(3)	7811(2)	58(1)
C(24)	8732(5)	1647(3)	7458(2)	72(1)

C(25)	8273(5)	754(3)	7706(2)	79(1)
C(26)	8691(5)	511(3)	8306(2)	78(1)
C(27)	9587(5)	1143(3)	8660(2)	66(1)

E: NMR Spectra of Michael Adducts



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5.389
3.852
3.840
3.830
3.818
3.206
3.194
3.163
3.150
3.134
3.111
3.091
0.000
BnO
Bn
3b
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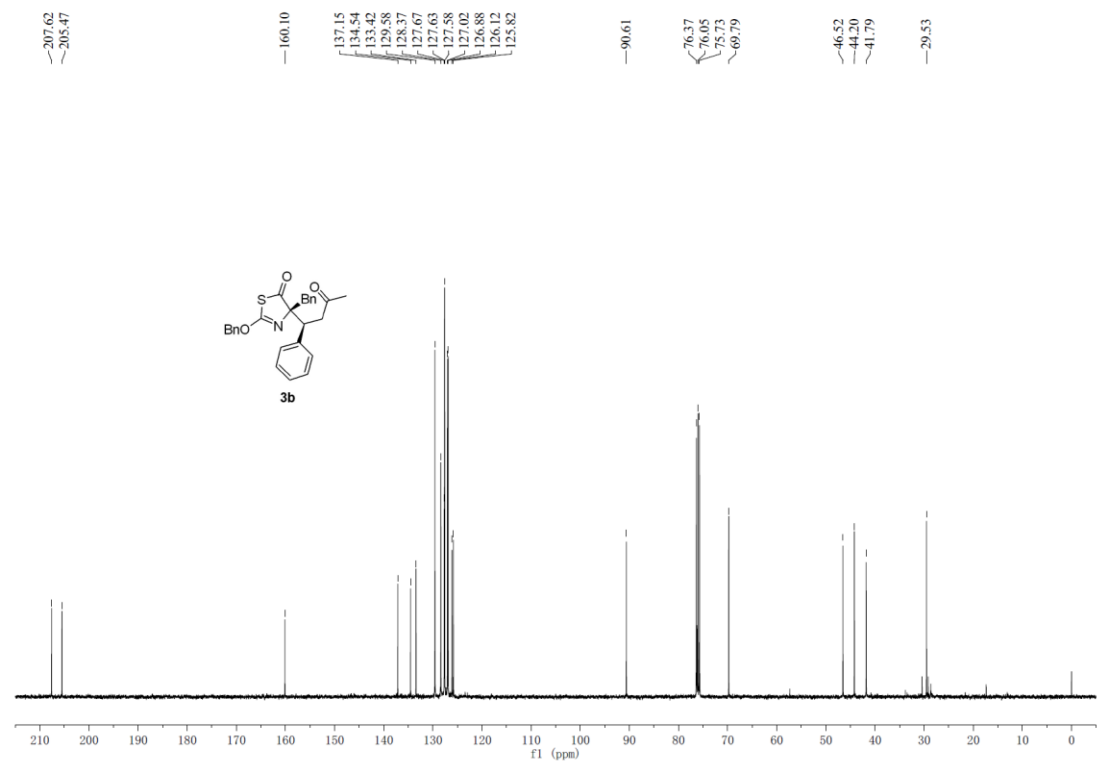
3.02
3.02
2.00
2.00
2.05
1.02
4.04
3.00
f1 (ppm)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127.63
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126.12
125.82
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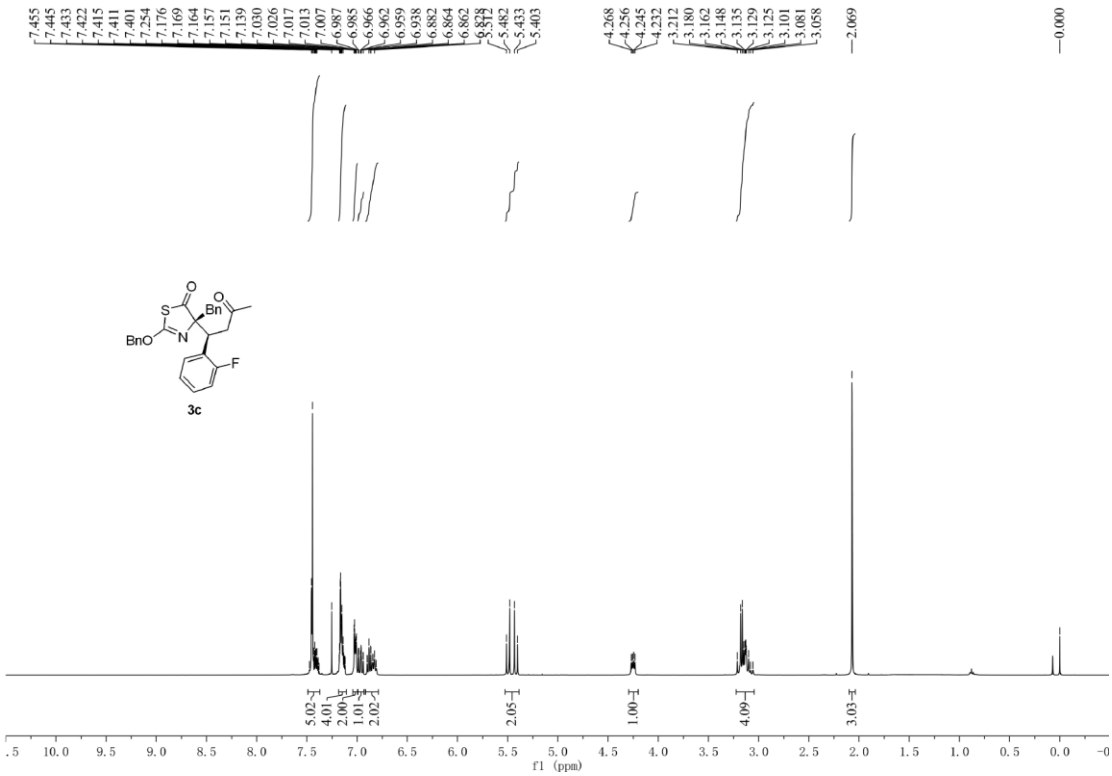
41.79
29.53
BnO
Bn
3b
f1 (ppm)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7.139
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7.013
7.007
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6.985
6.966
6.962
6.959
6.938
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6.864
6.862
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4.232
3.212
3.180
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3.148
3.135
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3.058
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O
S
N
BnO
Bn
O
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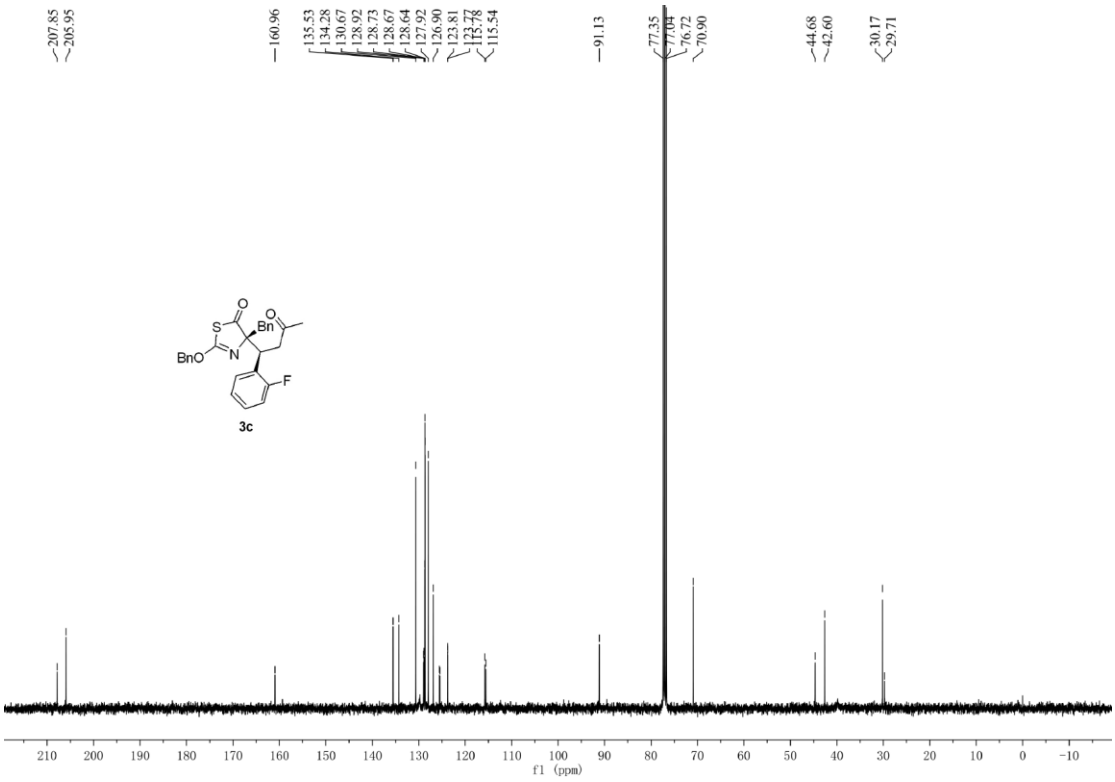
1.00
4.09
3.03
f1 (ppm)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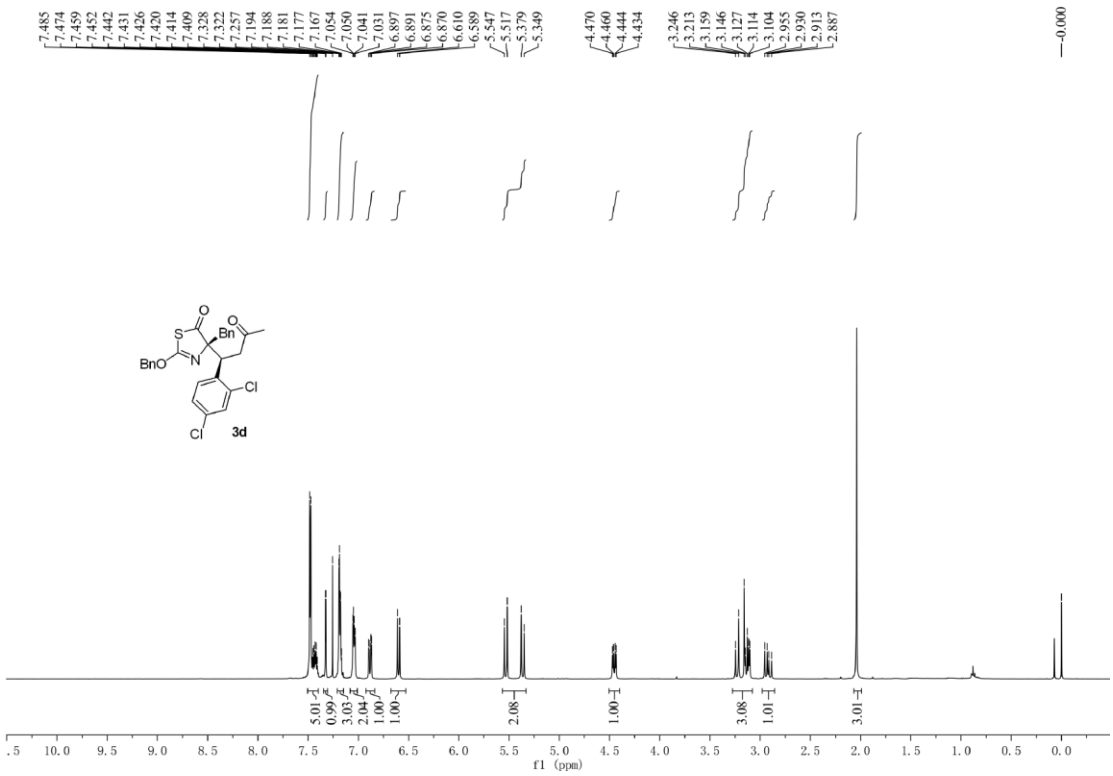
BnO
Bn
O
F
3c
f1 (ppm)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7.031
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6.610
6.589
5.547
5.517
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3.246
3.213
3.159
3.146
3.127
3.114
3.104
2.955
2.930
2.913
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BnO
Bn
O
S
N
O
Cl
Cl
3d
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0.99
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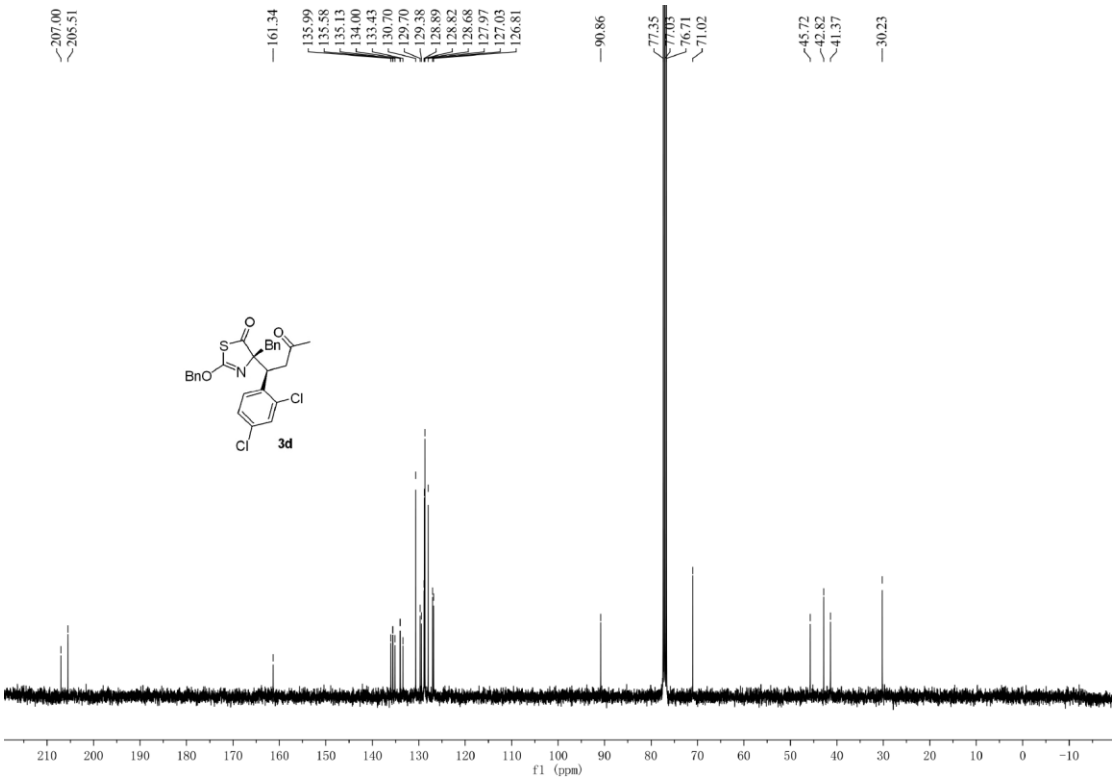
1.00
2.08
1.00
3.08
1.01
3.01
f1 (ppm)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90.86
77.35
77.03
76.71
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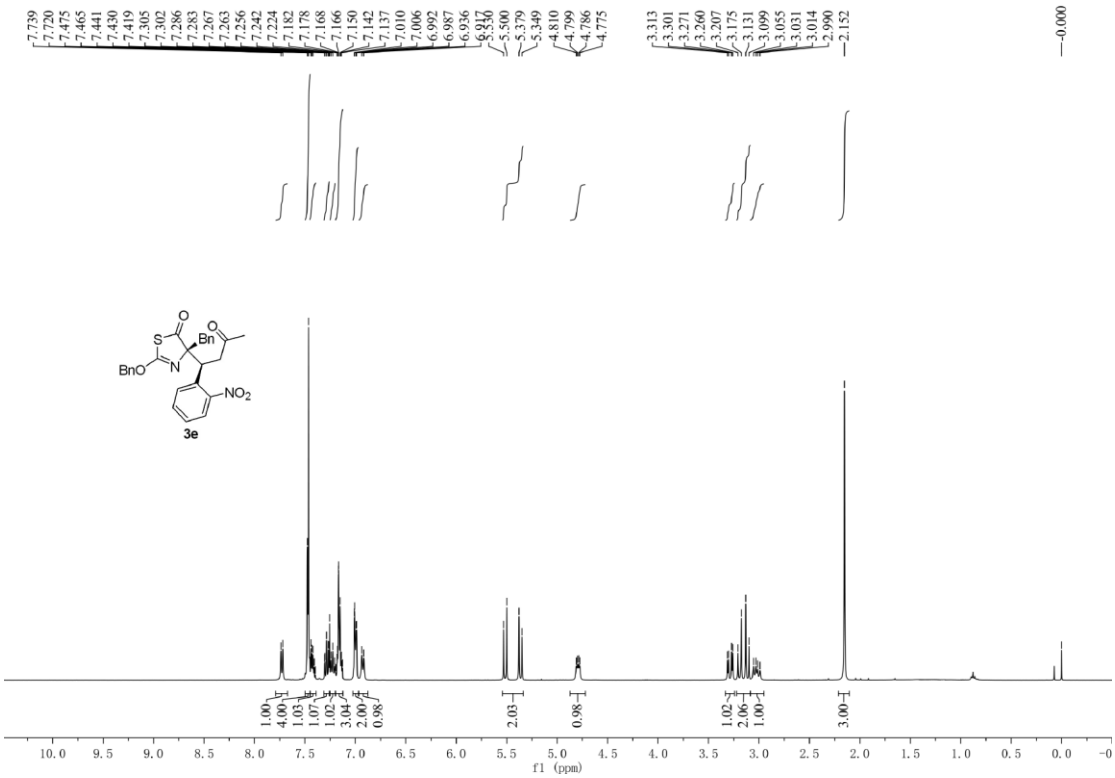
45.72
42.82
41.37
30.23
BnO
Bn
O
S
N
O
Cl
Cl
3d
f1 (ppm)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7.256
7.242
7.224
7.182
7.178
7.168
7.166
7.150
7.142
7.137
7.010
7.006
6.992
6.987
6.936
6.933
5.500
5.379
5.349
4.810
4.799
4.786
4.775
3.313
3.301
3.271
3.260
3.207
3.175
3.131
3.099
3.055
3.031
3.014
2.990
2.152
-0.000
BnO
Bn
NO2
3e
1.00
4.00
1.03
1.07
1.02
3.04
2.00
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2.03
0.98
1.02
2.06
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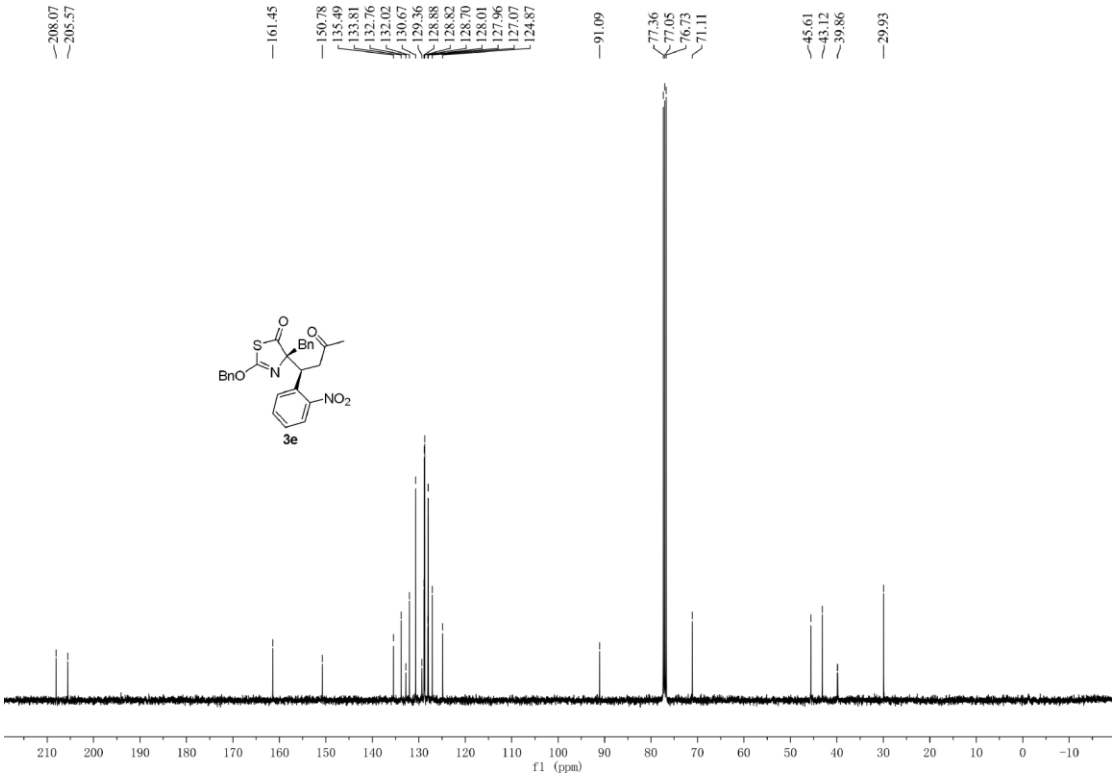
3.00
f1 (ppm)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128.01
127.96
127.07
124.87
91.09
77.36
77.05
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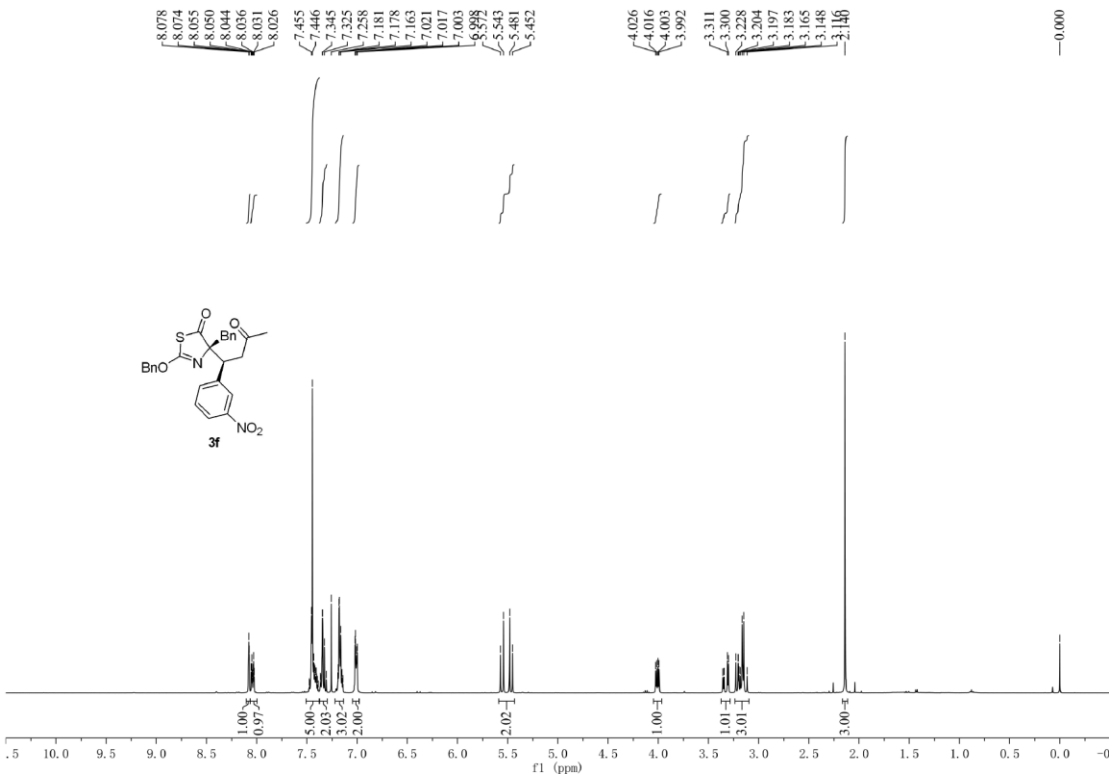
45.61
43.12
39.86
29.93
BnO
Bn
NO2
3e
f1 (ppm)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7.181
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7.163
7.021
7.017
7.003
6.998
5.543
5.481
5.452
4.026
4.016
4.003
3.992
3.311
3.300
3.228
3.204
3.197
3.183
3.165
3.148
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BnO
Bn
NO2
3f
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2.00
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1.01
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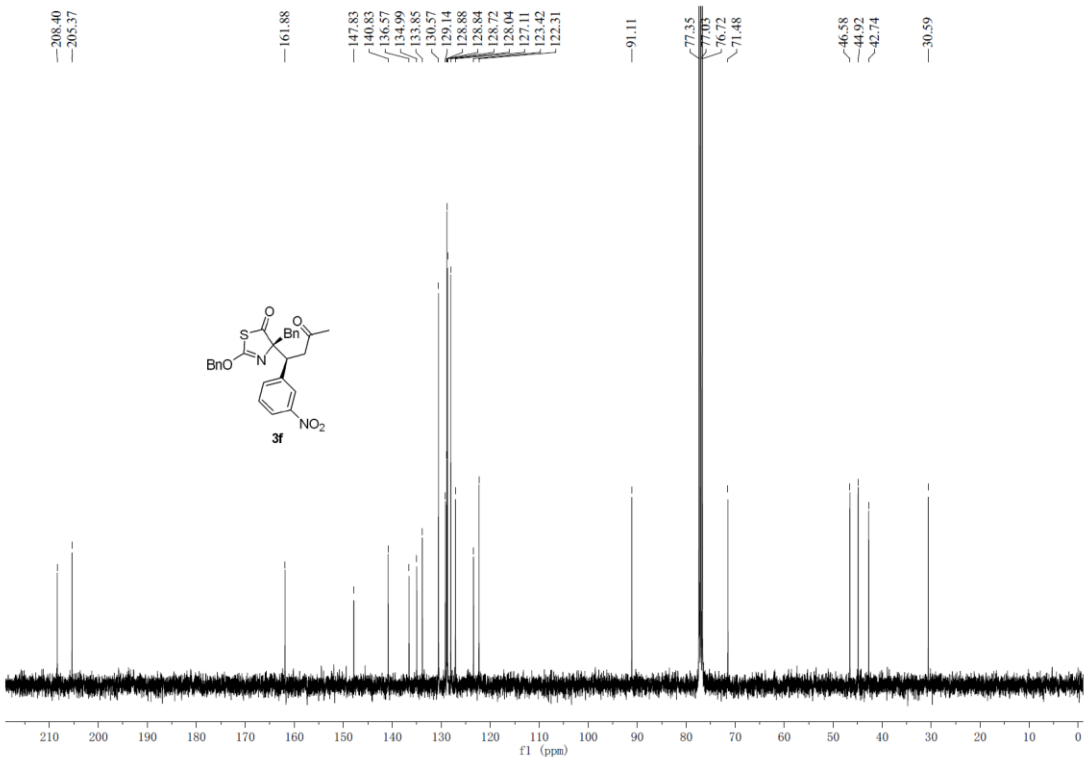
3.00
f1 (ppm)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122.31
91.11
77.35
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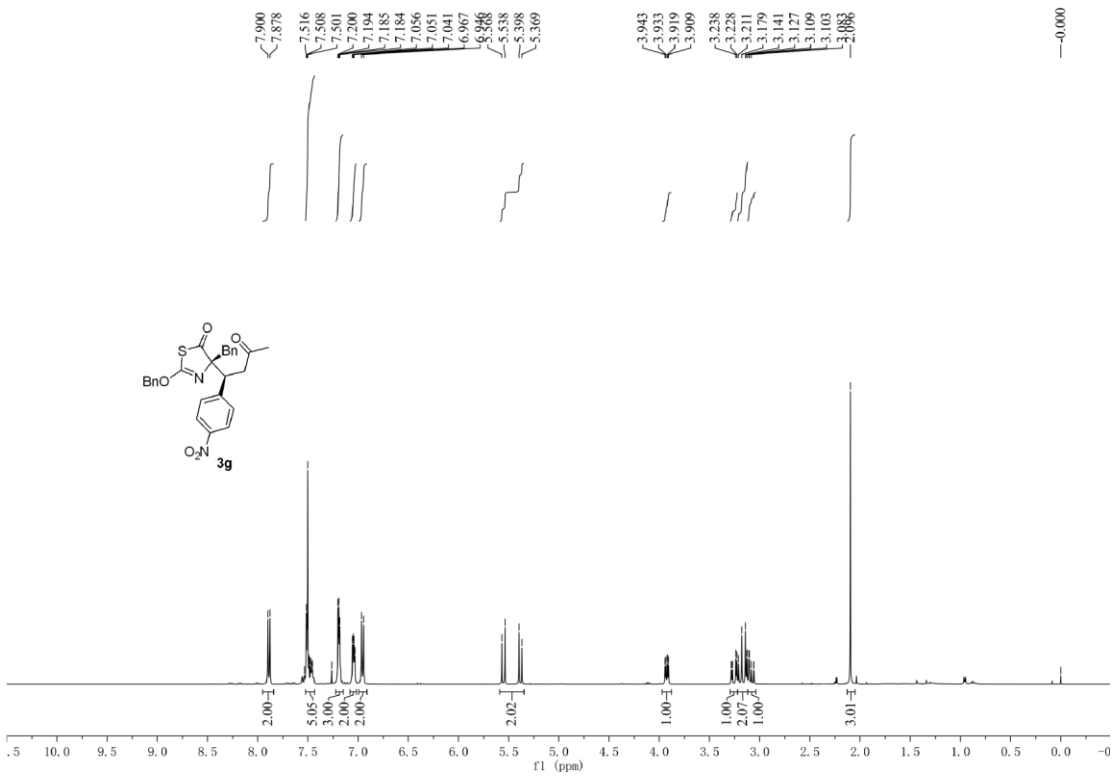
42.74
30.59
BnO
Bn
NO2
3f
f1 (ppm)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7.185
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7.051
7.041
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5.398
5.369
3.943
3.933
3.919
3.909
3.238
3.228
3.211
3.179
3.141
3.127
3.109
3.103
2.098
-0.000
BnO
Bn
3g
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2.00
2.00
2.02
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1.00
2.07
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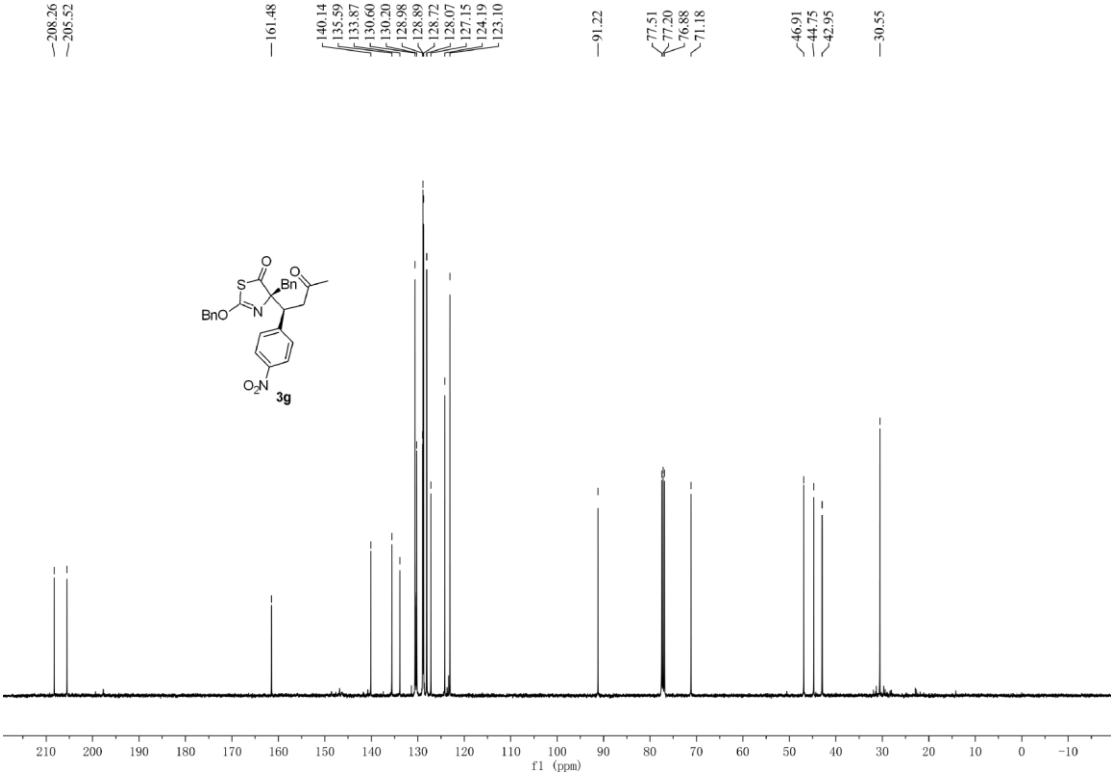
3.01
f1 (ppm)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124.19
123.10
91.22
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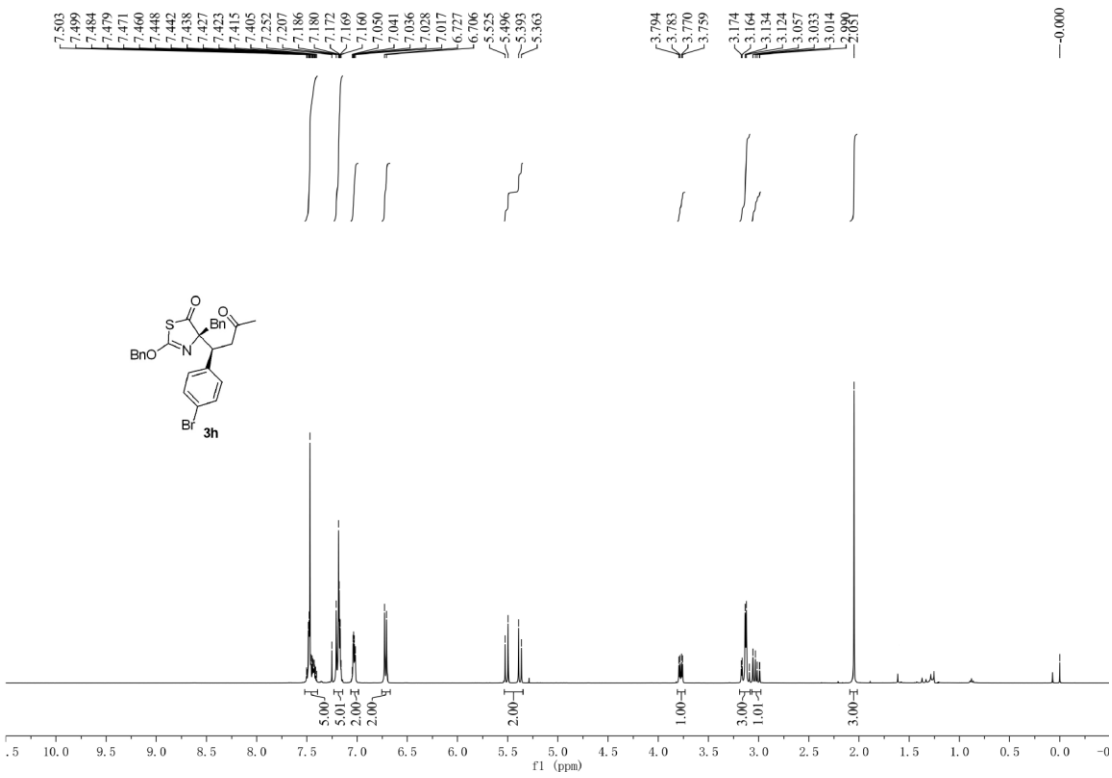
71.18
46.91
44.75
42.95
30.55
BnO
Bn
3g
f1 (ppm)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7.415
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7.252
7.207
7.186
7.180
7.172
7.169
7.160
7.050
7.041
7.036
7.028
7.017
6.727
6.706
5.525
5.496
5.393
5.363
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3.783
3.770
3.759
3.174
3.164
3.134
3.124
3.057
3.033
3.014
2.880
2.051
0.000
BnO
Bn
Br
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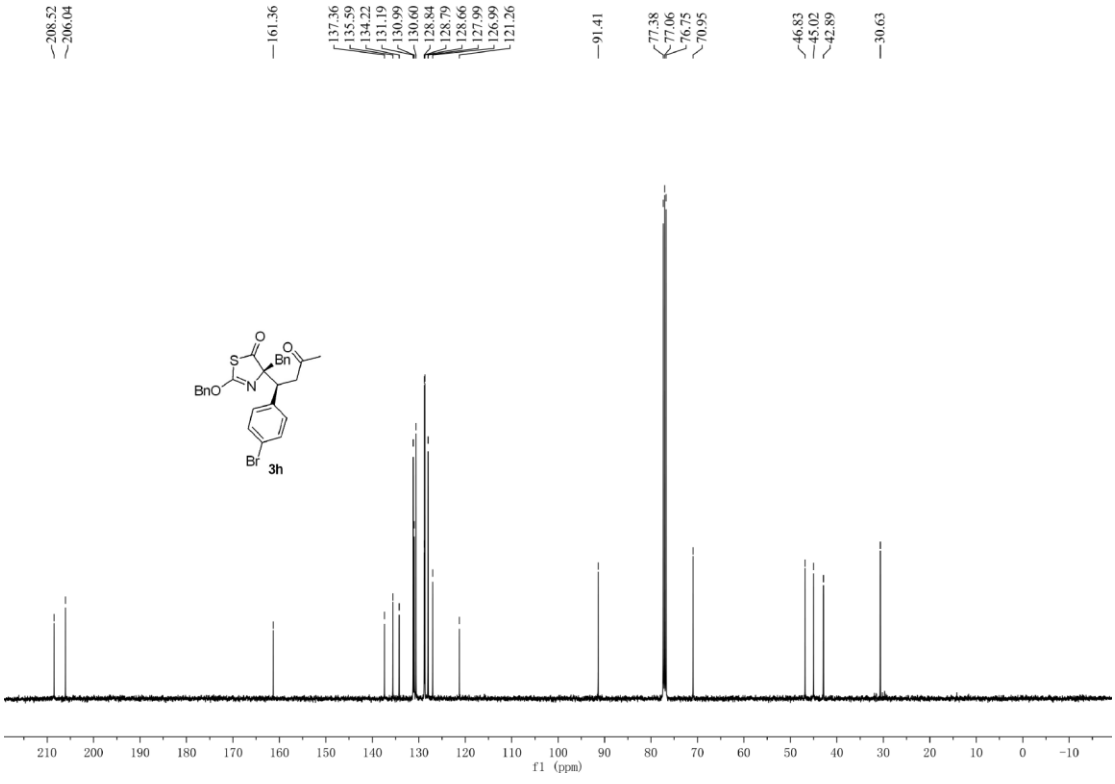
5.01
2.00
2.00
2.00
1.00
3.00
1.01
3.00
f1 (ppm)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130.60
128.84
128.79
128.66
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121.26
91.41
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70.95
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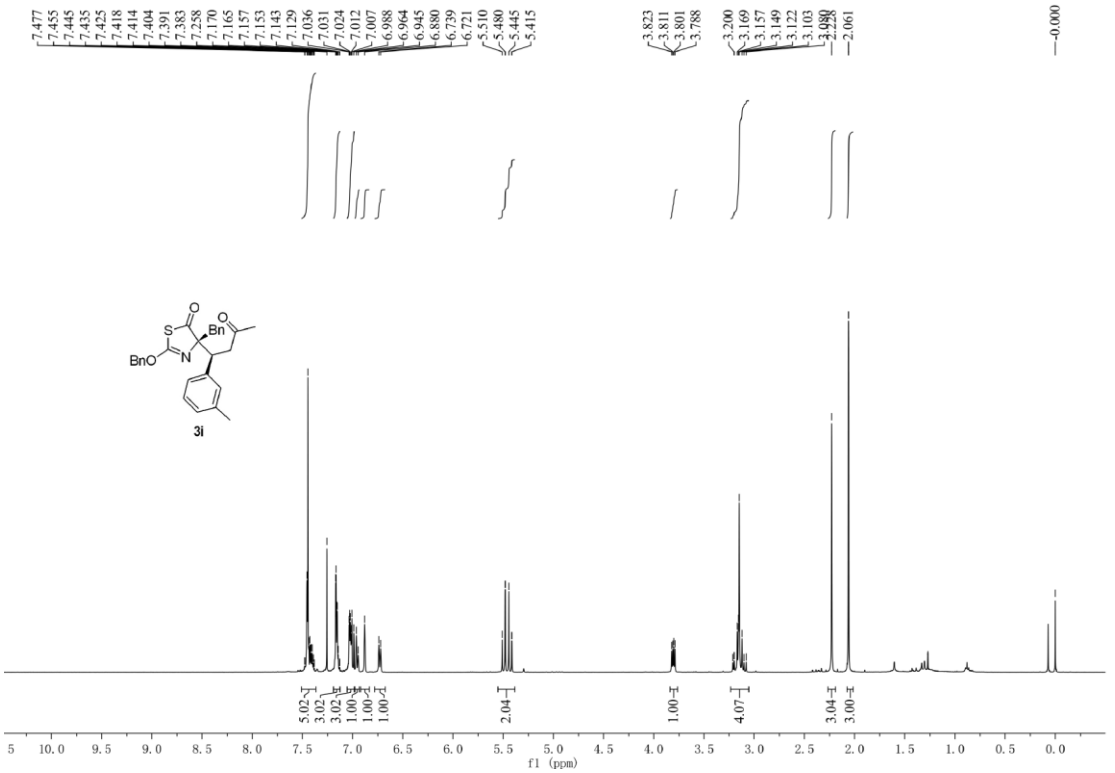
45.02
42.89
30.63
BnO
Bn
Br
3h
f1 (ppm)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7.165
7.157
7.153
7.143
7.129
7.036
7.031
7.024
7.012
7.007
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6.964
6.945
6.880
6.739
6.721
5.510
5.480
5.445
5.415
3.823
3.811
3.801
3.788
3.200
3.169
3.157
3.149
3.122
3.103
3.080
2.228
2.061
-0.000
BnO
Bn
3i
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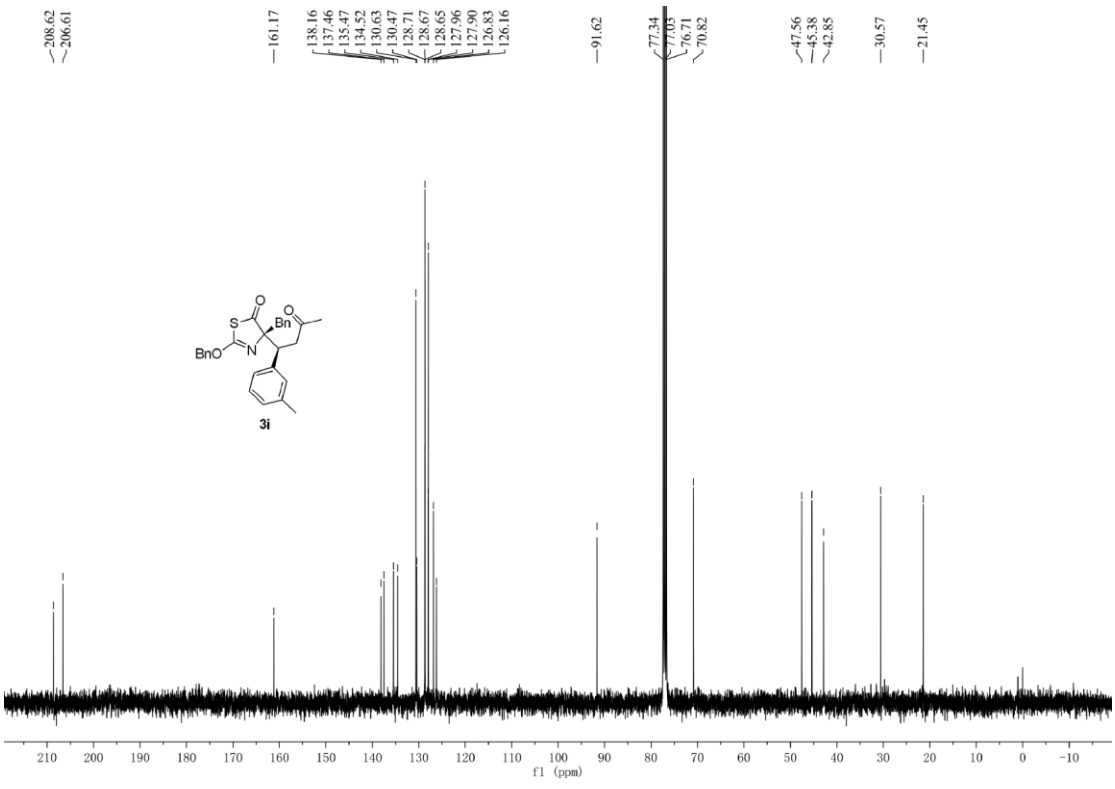
3.02
3.02
1.00
1.00
1.00
2.04
1.00
4.07
3.04
3.00
f1 (ppm)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127.90
126.83
126.16
91.62
77.34
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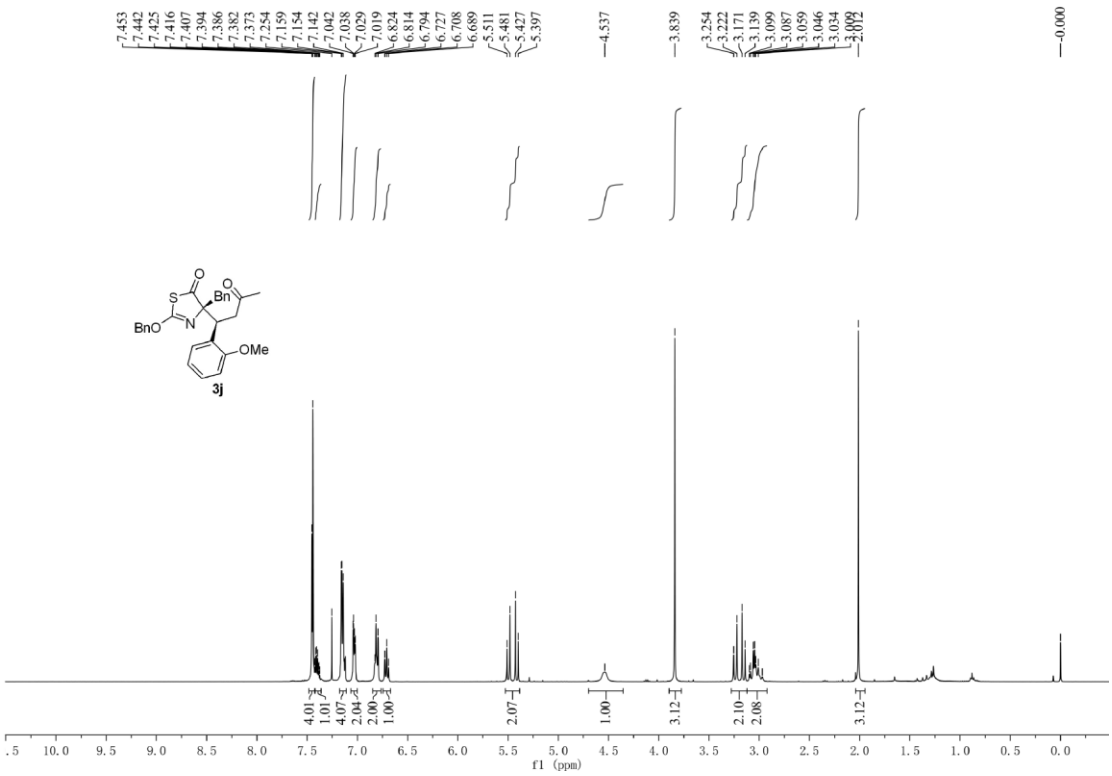
47.56
45.38
42.85
30.57
21.45
BnO
Bn
3i
f1 (ppm)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7.042
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7.019
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5.397
4.537
3.839
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3.139
3.099
3.087
3.059
3.046
3.034
3.009
2.012
-0.000
BnO
Bn
OMe
3j
4.01
1.01
4.07
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2.00
1.00
2.07
1.00
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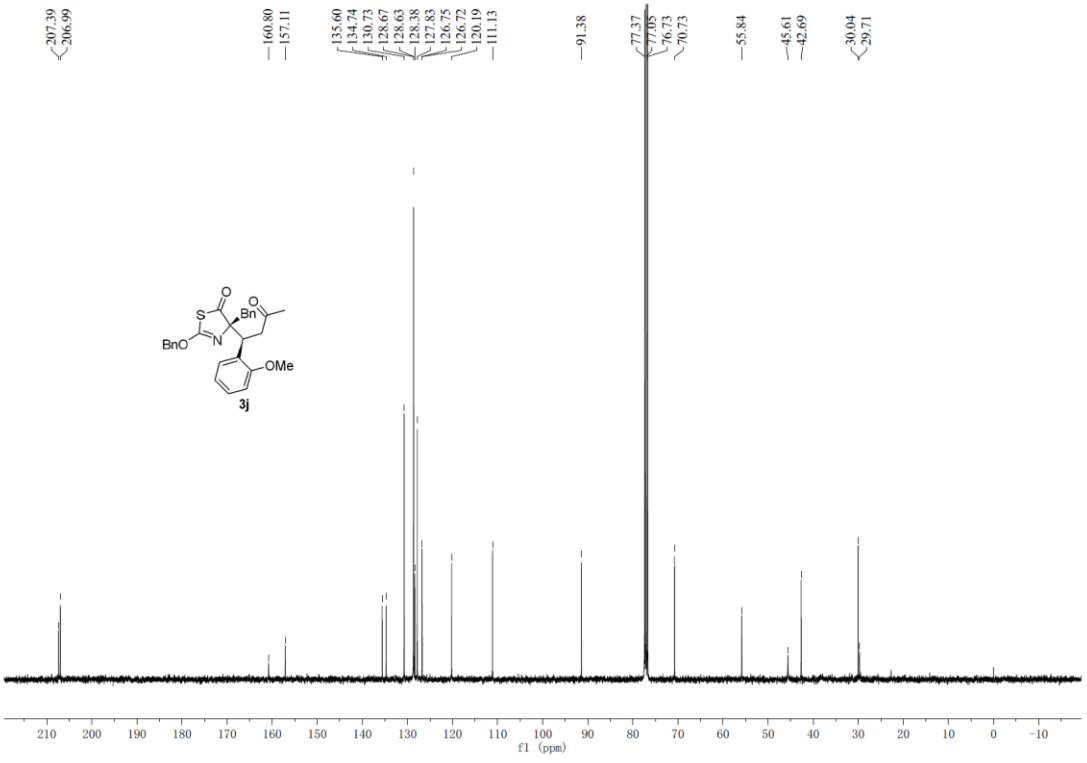
2.10
2.08
3.12
f1 (ppm)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91.38
77.37
77.05
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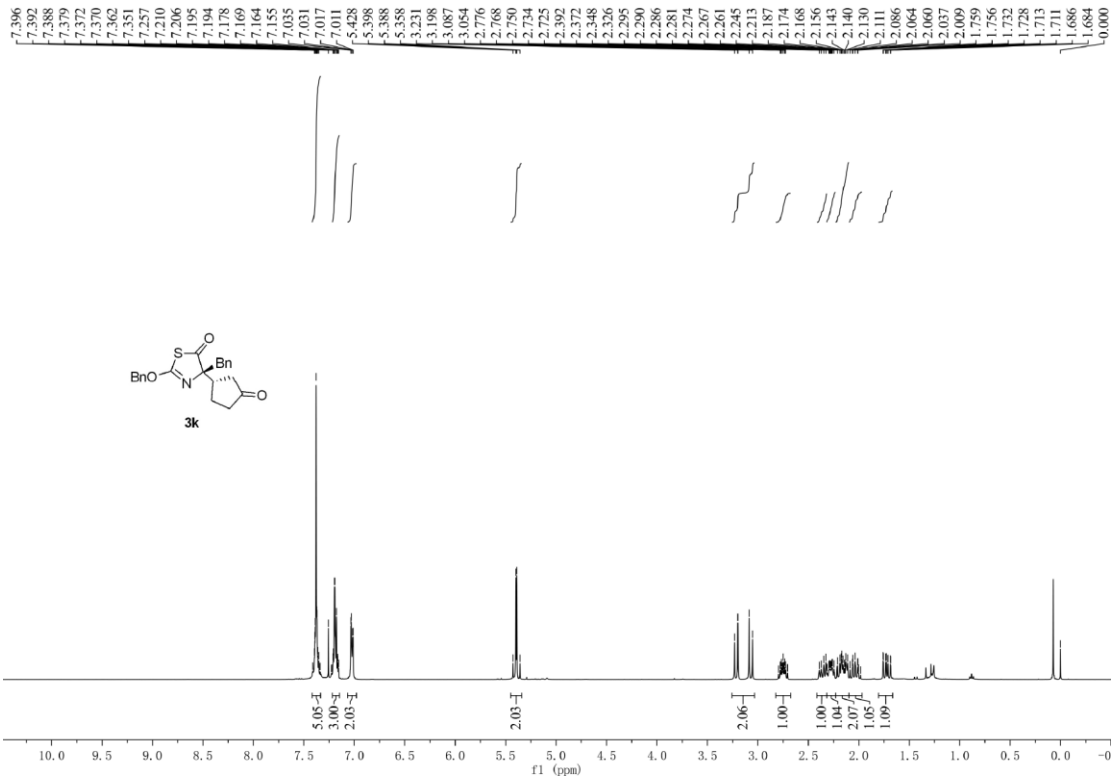
55.84
45.61
42.69
30.04
29.71
BnO
Bn
OMe
3j
f1 (ppm)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7.169
7.164
7.155
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2.156
2.143
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1.756
1.732
1.728
1.713
1.711
1.686
1.684
0.000
BnO
S
O
N
Bn
O
3k
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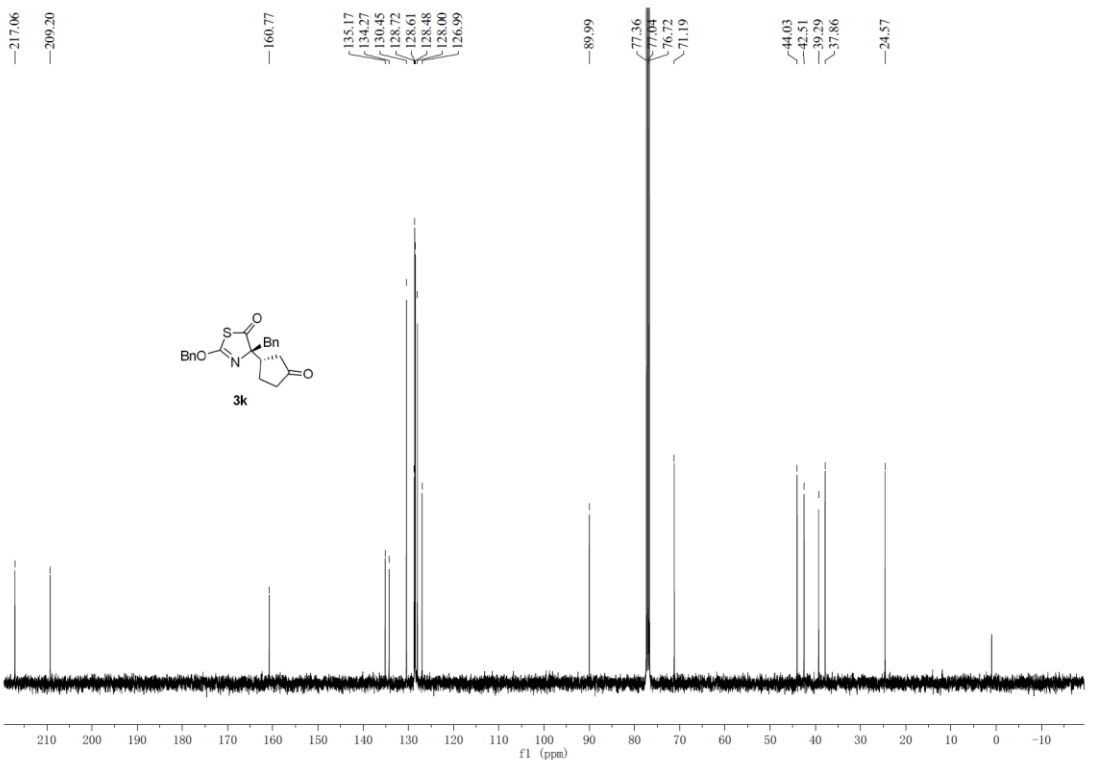
3.00
2.03
2.03
2.06
1.00
1.00
1.04
2.07
1.05
1.09
f1 (ppm)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76.72
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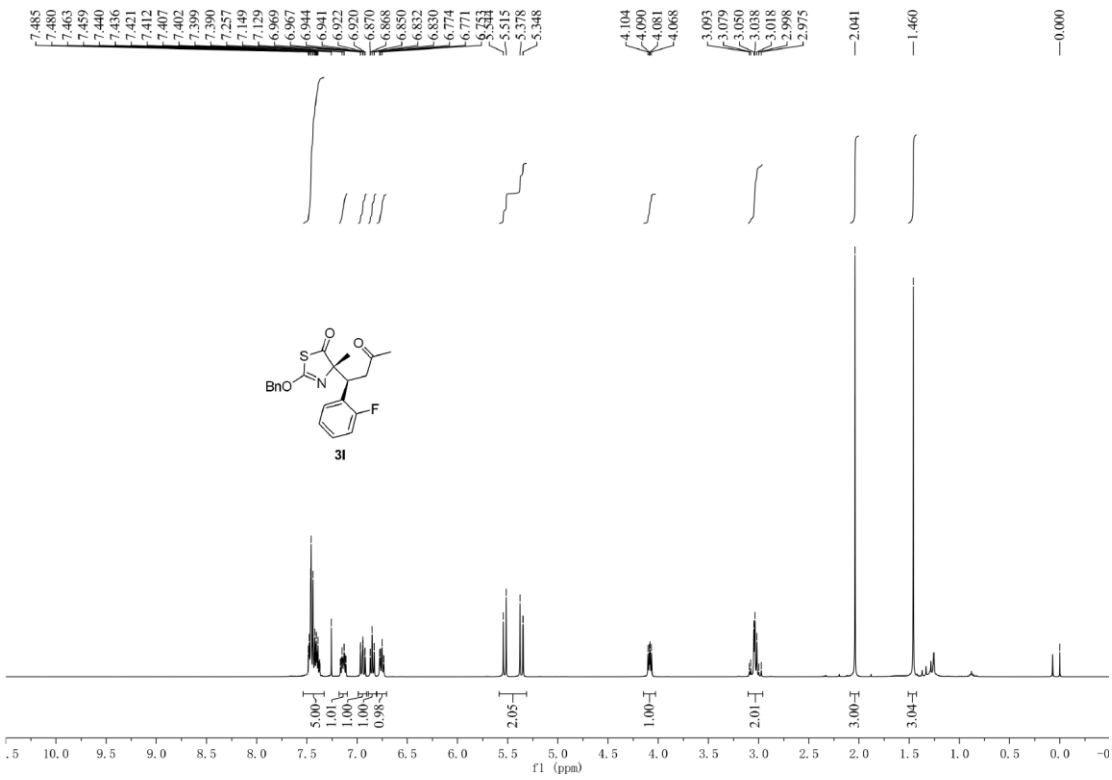
24.57
BnO
S
O
N
Bn
O
3k
f1 (ppm)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7.149
7.129
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6.967
6.944
6.941
6.922
6.920
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6.868
6.850
6.832
6.830
6.774
6.771
5.515
5.378
5.348
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4.090
4.081
4.068
3.093
3.079
3.050
3.038
3.018
2.998
2.975
2.041
1.460
0.000
BnO
F
3l
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1.00
1.00
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2.01
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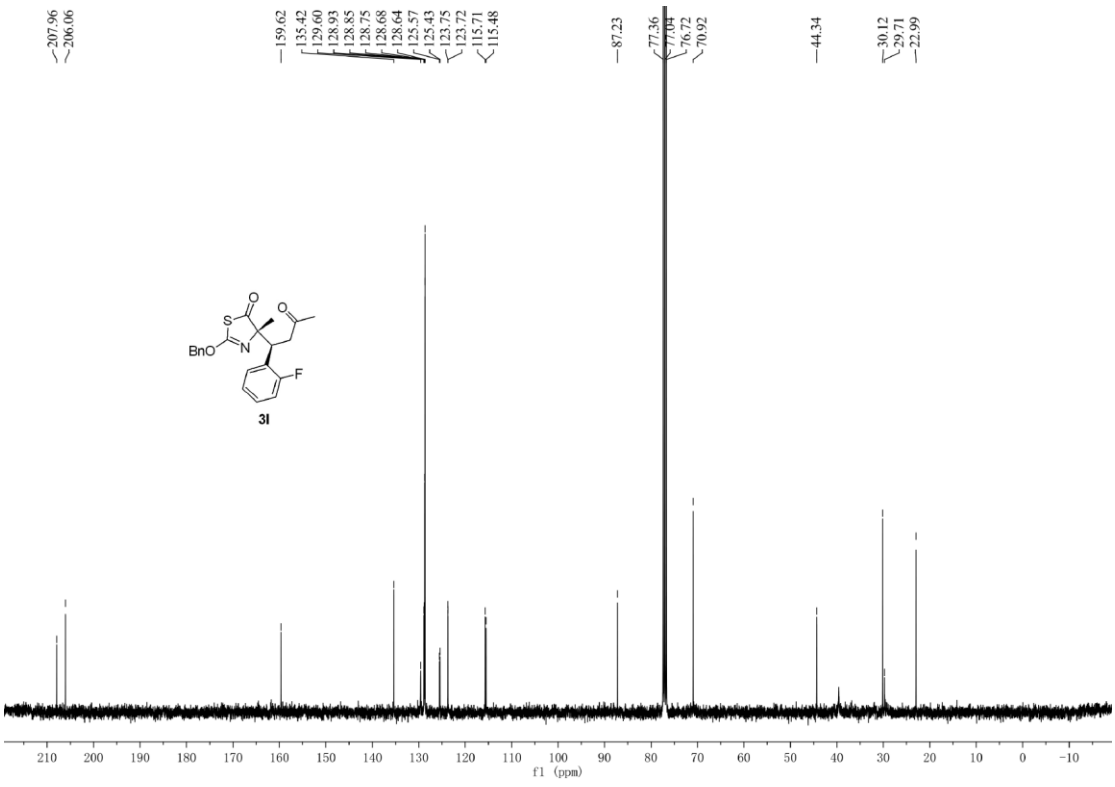
3.04
f1 (ppm)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123.75
123.72
115.71
115.48
87.23
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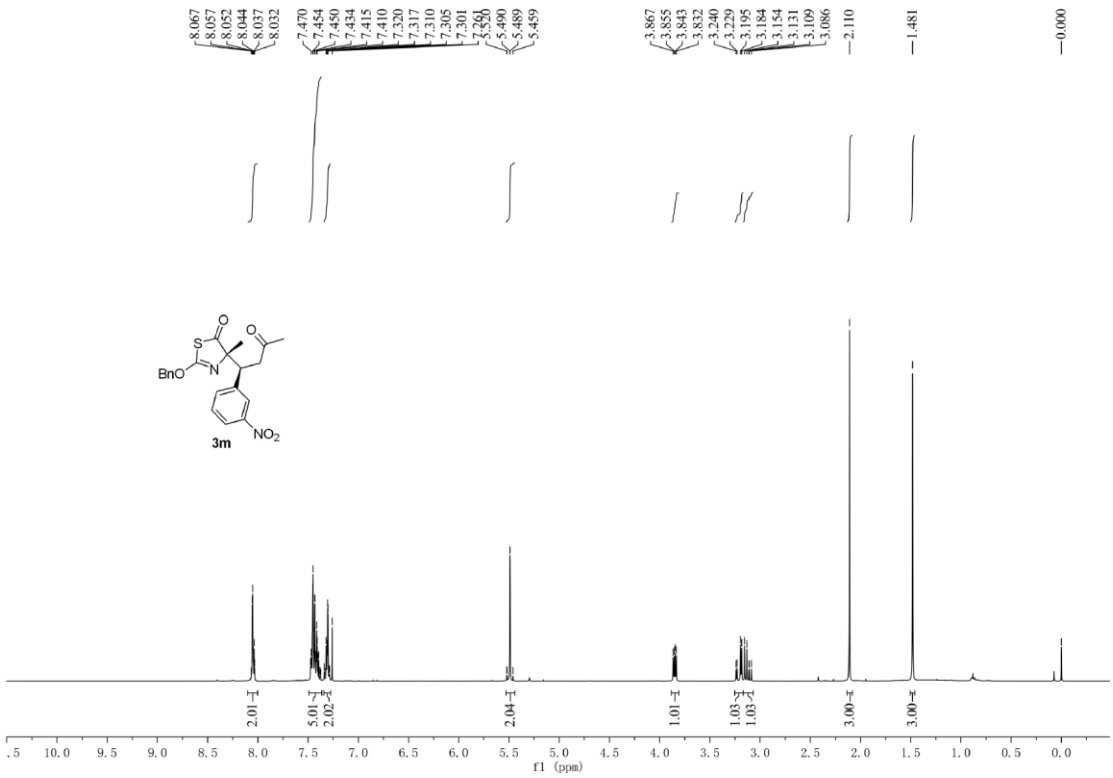
76.72
70.92
44.34
30.12
29.71
22.99
BnO
F
3l
f1 (ppm)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7.317
7.310
7.305
7.301
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5.489
5.459
3.867
3.855
3.843
3.832
3.240
3.229
3.195
3.184
3.154
3.131
3.109
3.086
2.110
1.481
0.000
BnO
O
S
N
O
NO2
3m
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5.01
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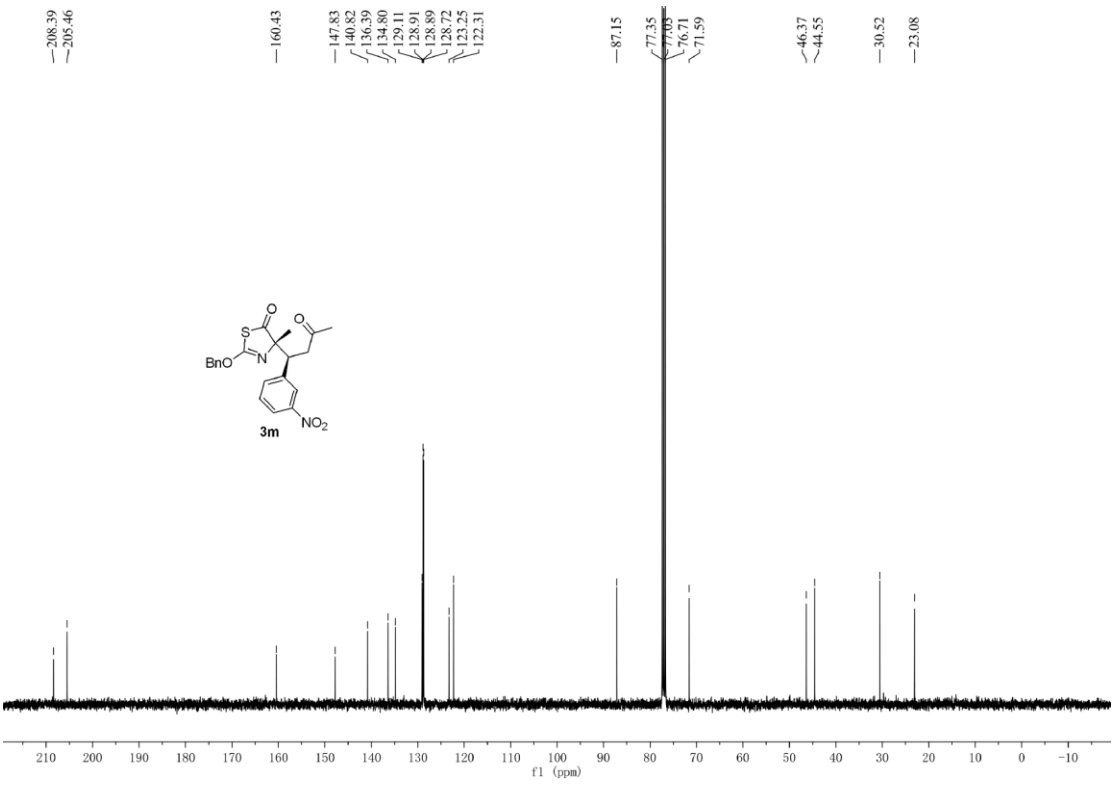
2.04
1.01
1.03
1.03
3.00
3.00
f1 (ppm)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128.89
128.72
123.25
122.31
87.15
77.35
77.03
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44.55
30.52
23.08
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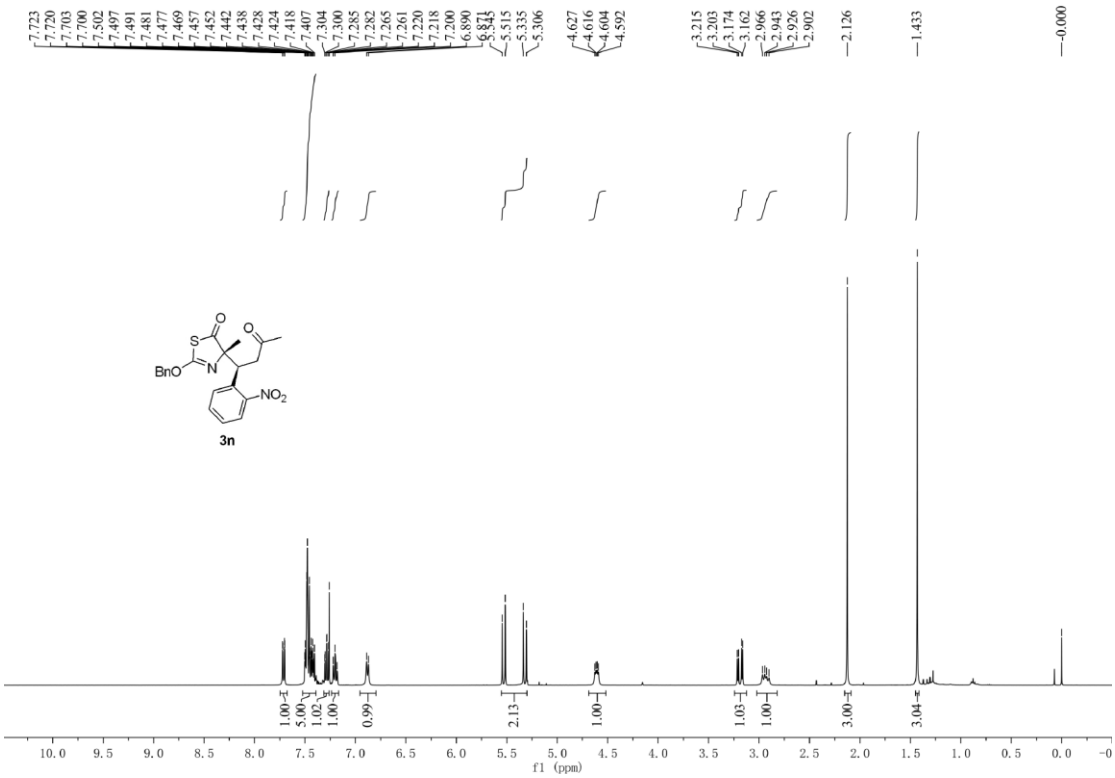
O
S
N
O
NO2
3m
f1 (ppm)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7.261
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7.218
7.200
6.890
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5.306
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4.616
4.604
4.592
3.215
3.203
3.174
3.162
2.966
2.943
2.926
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BnO
NO2
3n
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1.00
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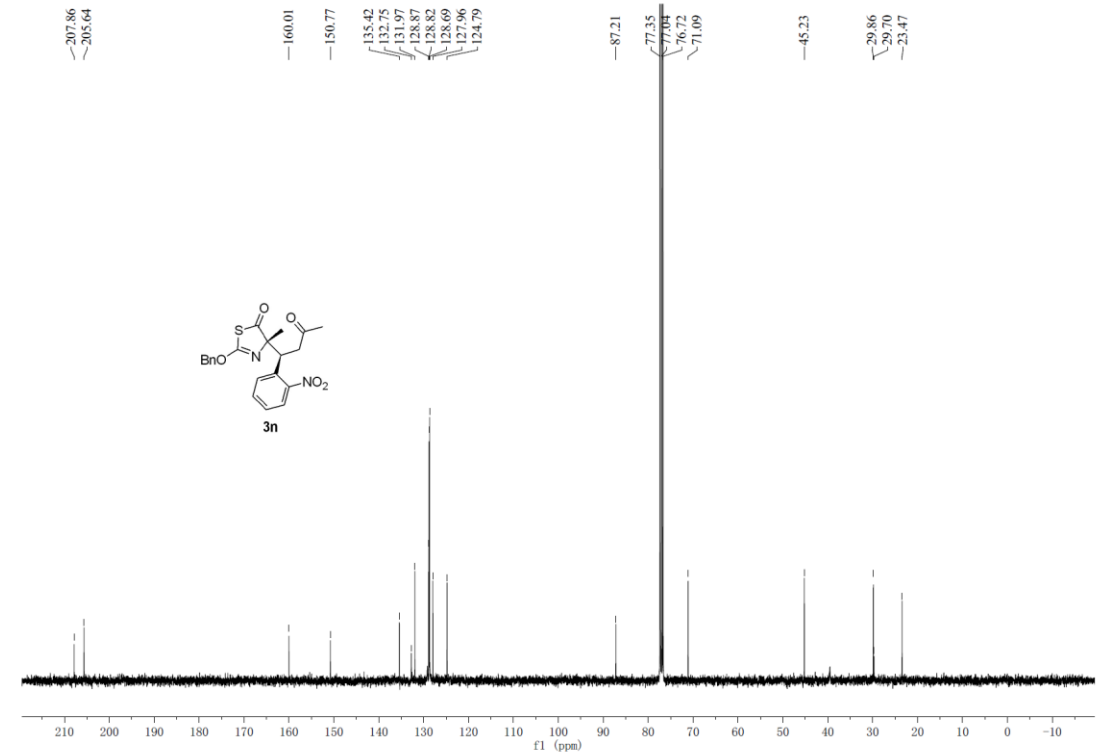
f1 (ppm)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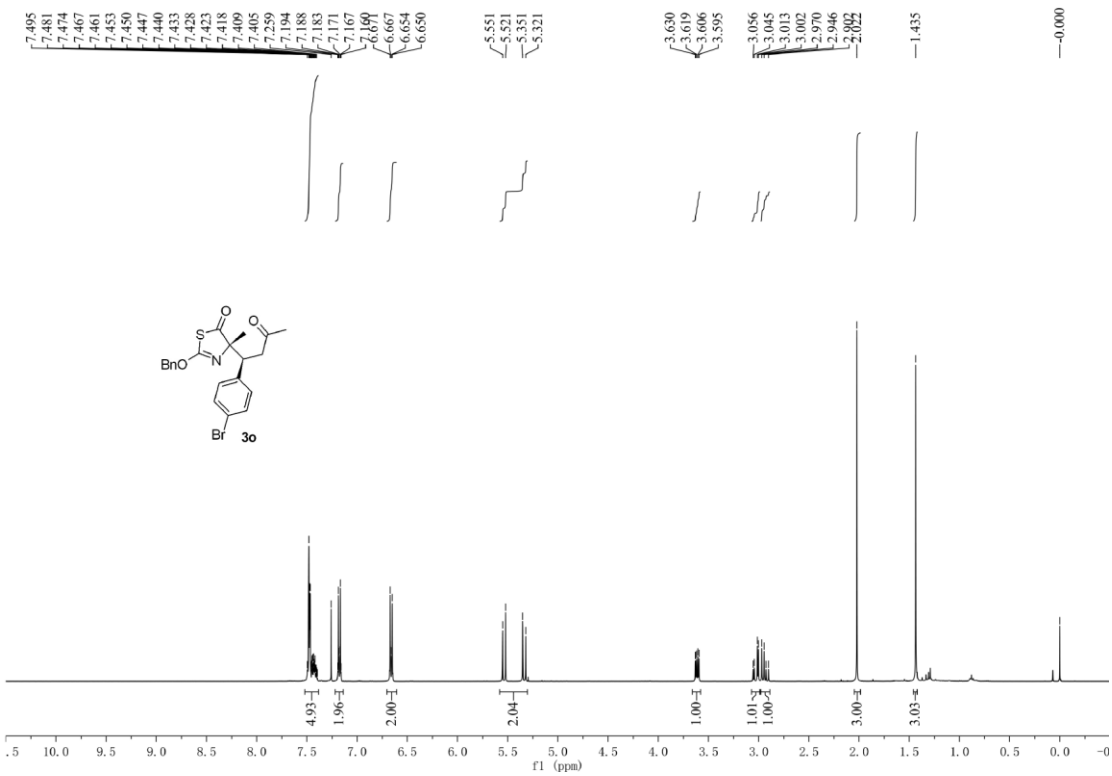
29.70
23.47
BnO
NO2
3n
f1 (ppm)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7.188
7.183
7.171
7.167
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5.351
5.321
3.630
3.619
3.606
3.595
3.056
3.045
3.013
3.002
2.970
2.946
2.022
1.435
-0.000
BnO
Br
3o
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2.00
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1.00
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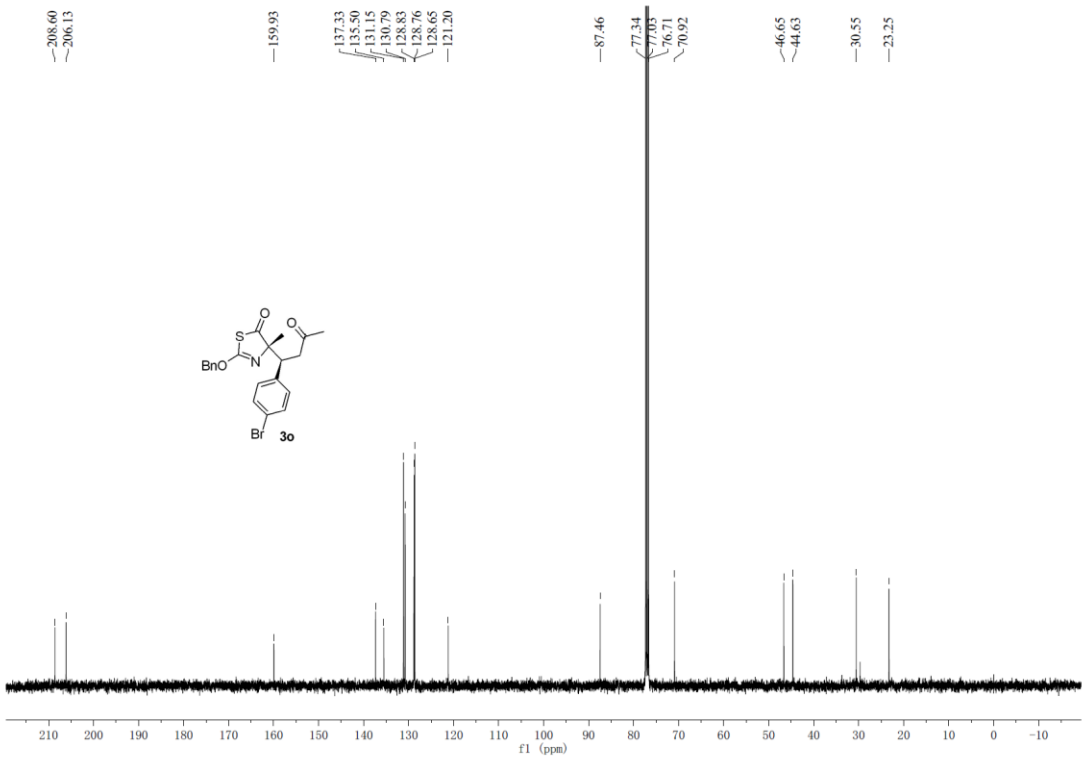
1.00
3.00
3.03
f1 (ppm)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121.20
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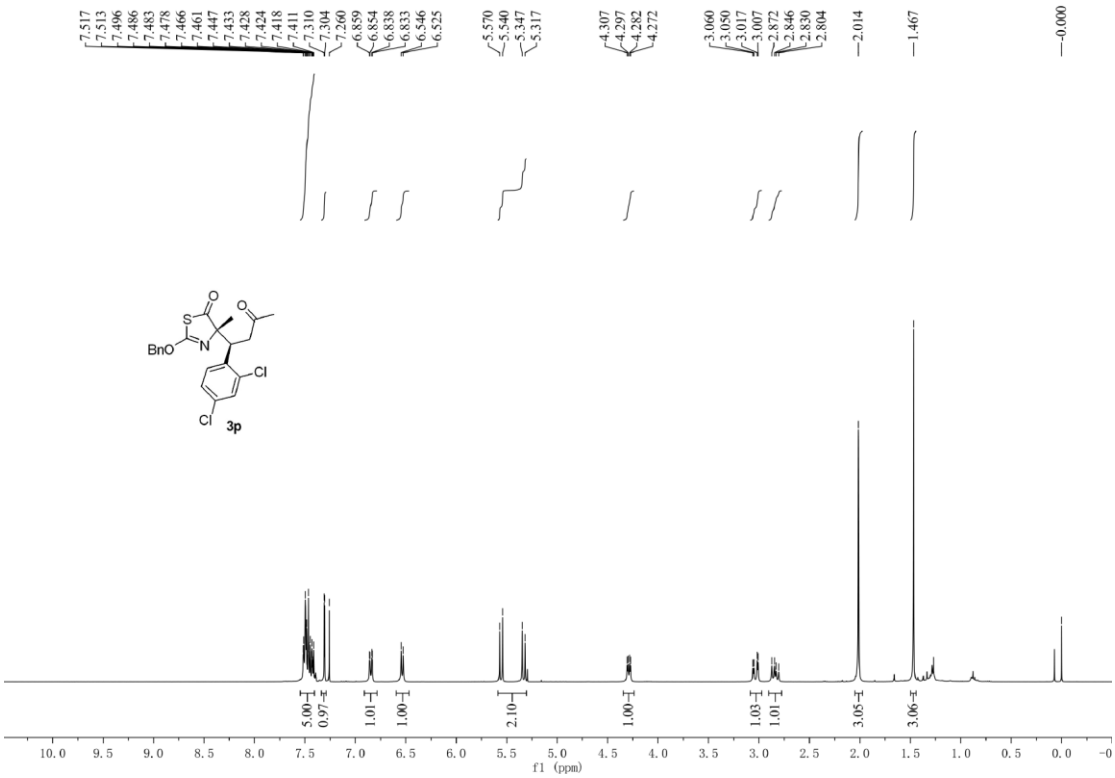
70.92
46.65
44.63
30.55
23.25
BnO
Br
3o
f1 (ppm)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4.282
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BnO
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O
O
Cl
Cl
3p
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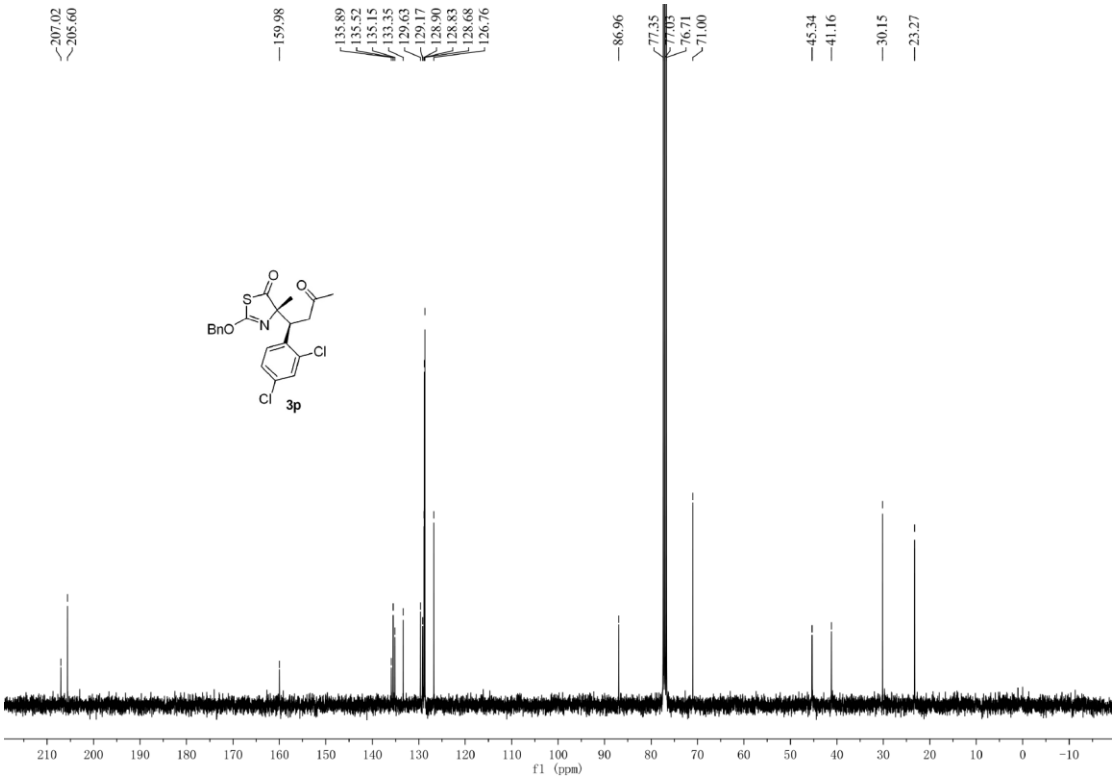
2.10
1.00
1.03
1.01
3.05
3.06
f1 (ppm)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133.35
129.63
129.17
128.90
128.83
128.68
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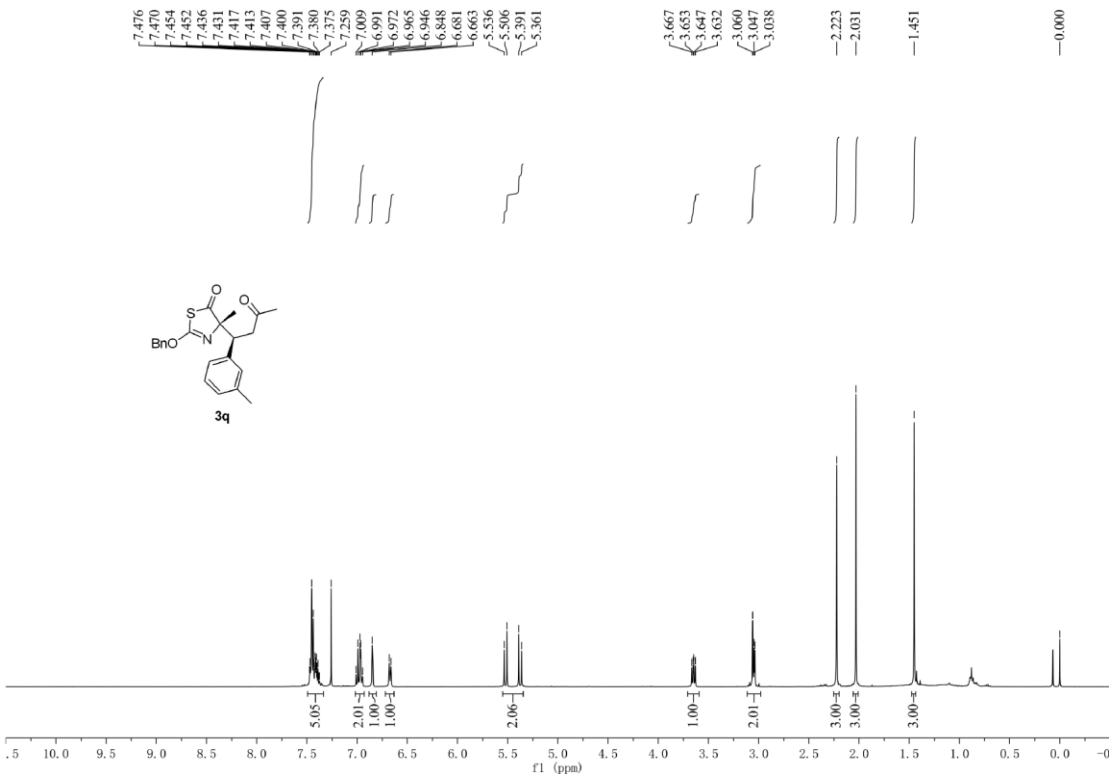
86.96
77.35
77.03
76.71
71.00
45.34
41.16
30.15
23.27
BnO
S
N
O
O
Cl
Cl
3p
f1 (ppm)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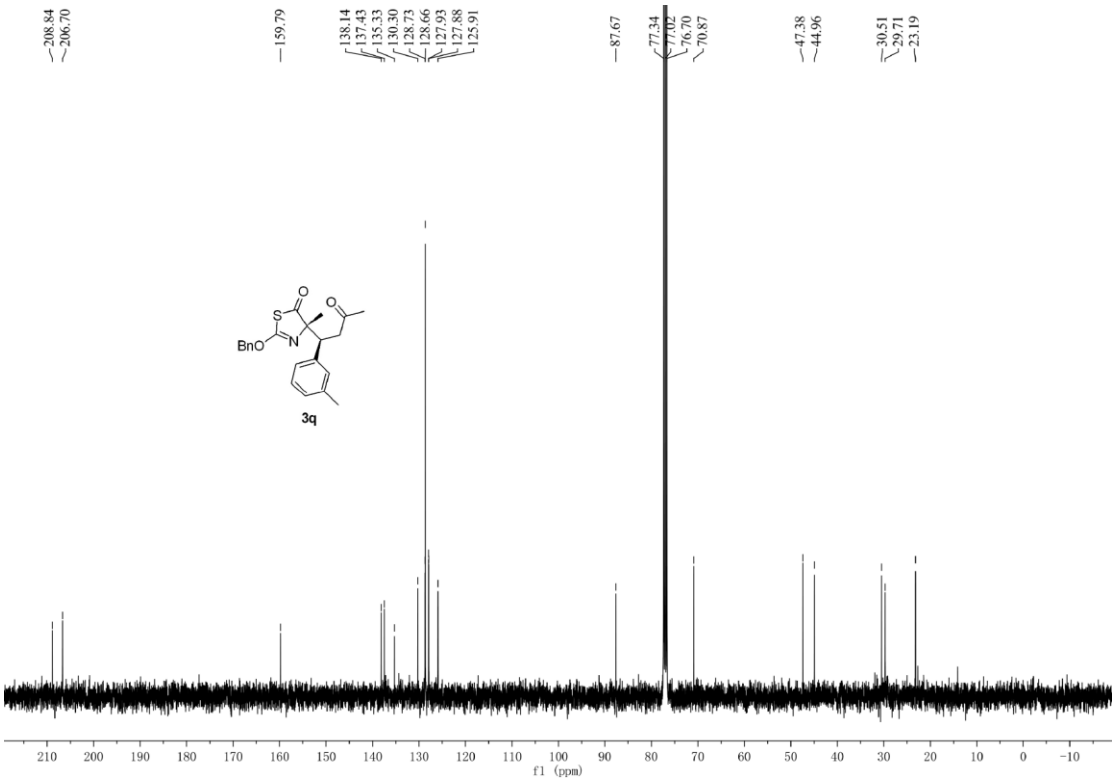
7.380
7.375
7.259
7.009
6.991
6.972
6.965
6.946
6.848
6.681
6.663
5.536
5.506
5.391
5.361
3.667
3.653
3.647
3.632
3.060
3.047
3.038
2.223
2.031
1.451
0.000
BnO
3q
5.05
2.01
1.00
1.00
2.06
1.00
2.01
3.00
3.00
3.00
f1 (ppm)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127.88
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87.67
77.34
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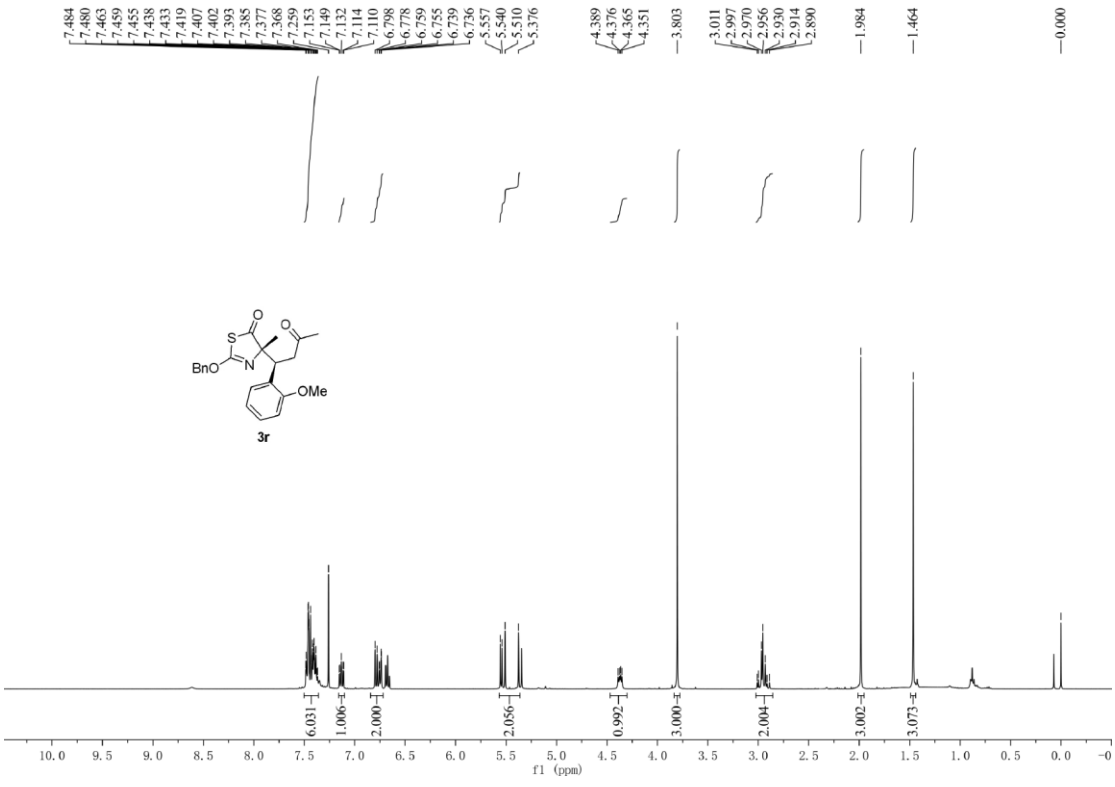
30.51
29.71
23.19
BnO
3q
f1 (ppm)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7.368
7.299
7.153
7.149
7.132
7.114
7.110
6.798
6.778
6.759
6.755
6.739
6.736
5.557
5.540
5.510
5.376
4.389
4.376
4.365
4.351
3.803
3.011
2.997
2.970
2.956
2.930
2.914
2.890
1.984
1.464
0.000
BnO
OMe
3r
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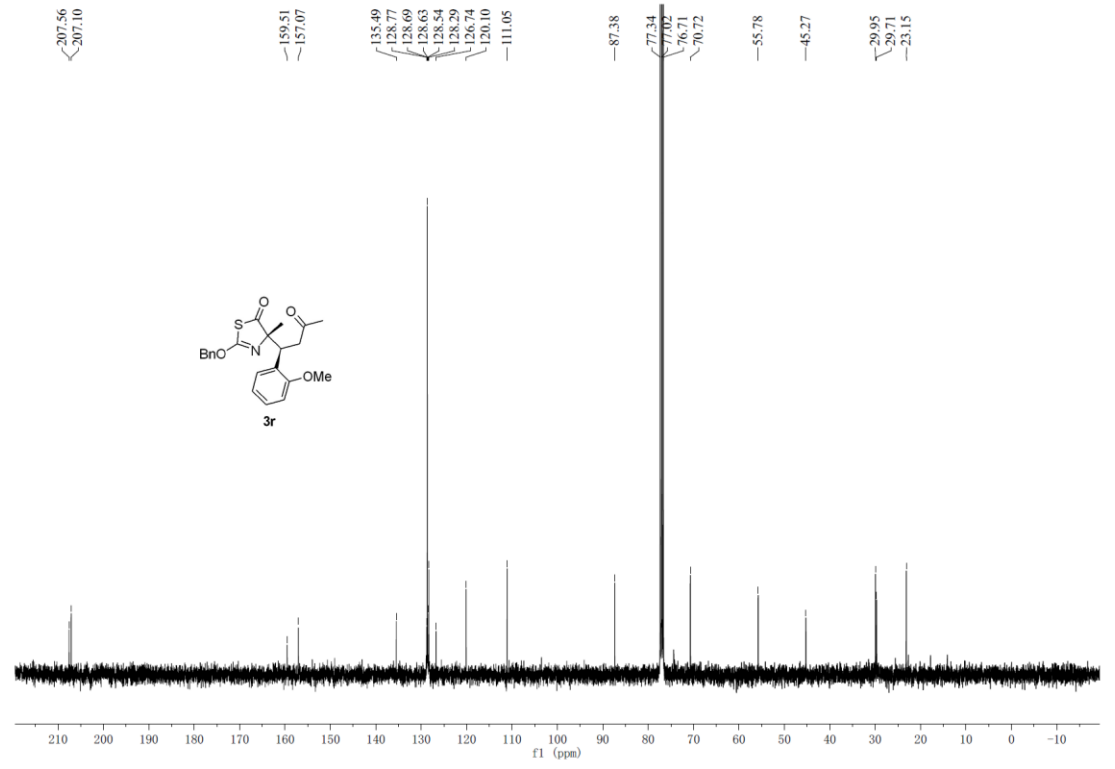
1.006
2.000
2.056
0.992
3.000
2.004
3.002
3.073
f1 (ppm)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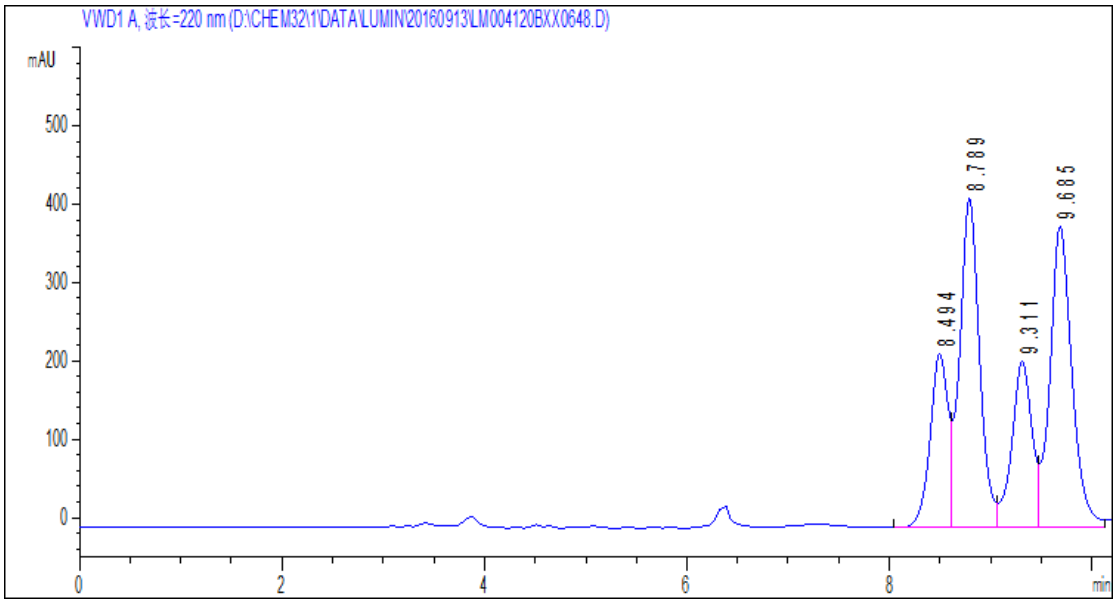
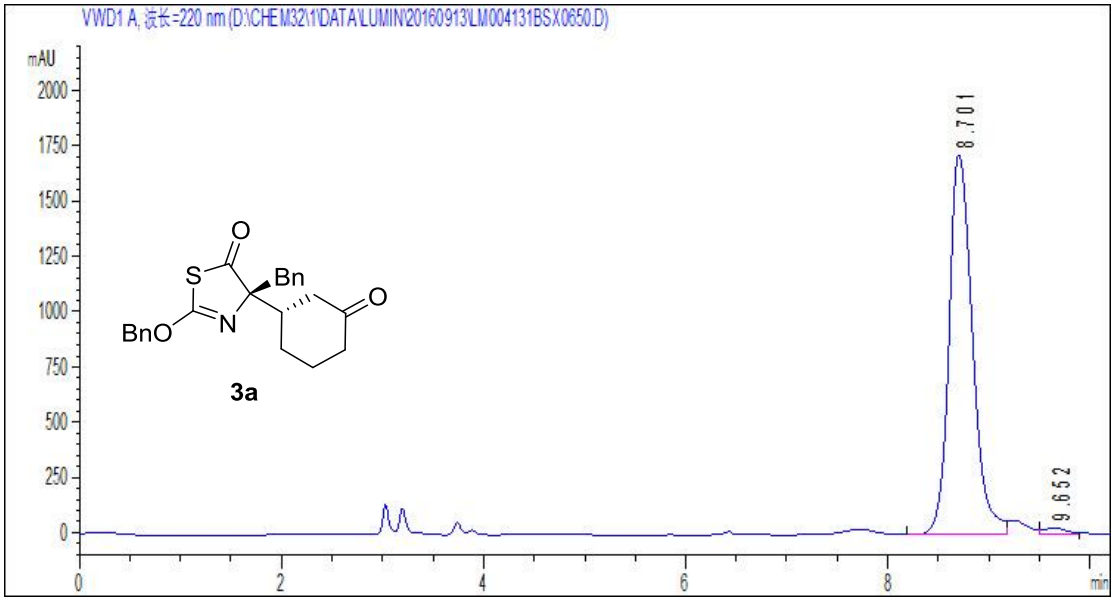
111.05
87.38
77.34
77.02
76.71
70.72
55.78
45.27
29.95
29.71
23.15
BnO
OMe
3r
f1 (ppm)

F: HPLC Traces of Michael Adducts

(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-3-oxocyclohexyl)thiazol-5(4*H*)-one (3a)

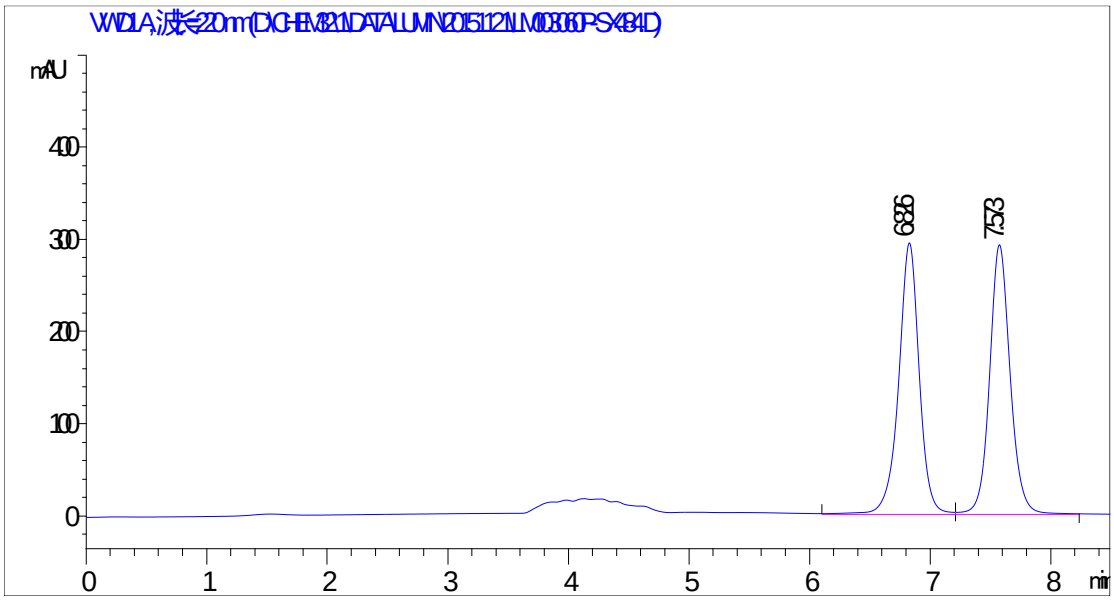


#	Time	Area	Height	Width	Symmetry	Area %
1	8.494	2798.2	222.5	0.1875	1.151	16.172
2	8.789	5706.9	420.5	0.2035	0.899	32.982
3	9.311	2968.8	213	0.2078	1.056	17.158
4	9.685	5829.2	384.8	0.2248	0.795	33.689

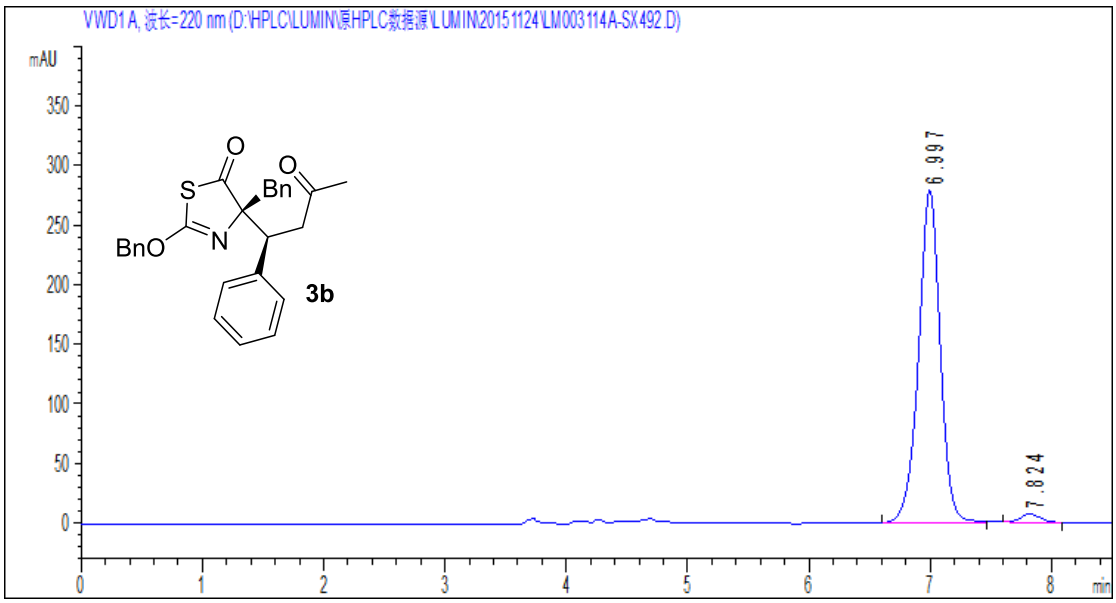


#	Time	Area	Height	Width	Symmetry	Area %
1	8.701	27915.5	1719.8	0.2505	0.689	98.109
2	9.652	538	32.1	0.2794	0.8	1.891

(*S*)-4-12benzyl-2-(benzyloxy)-4-((*S*)-3-oxo-1-phenylbutyl)thiazol-5(4*H*)-one (3b)

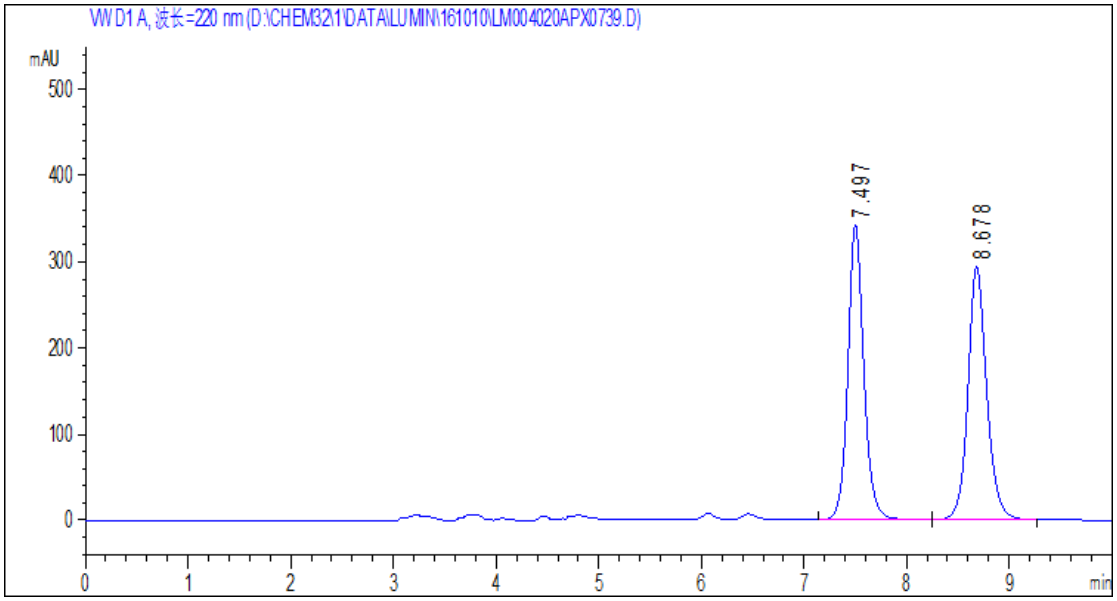


#	Time	Area	Height	Width	Symmetry	Area %
1	6.826	3550.9	295.1	0.1797	1.088	50.393
2	7.573	3495.5	292.8	0.1989	0.882	49.607

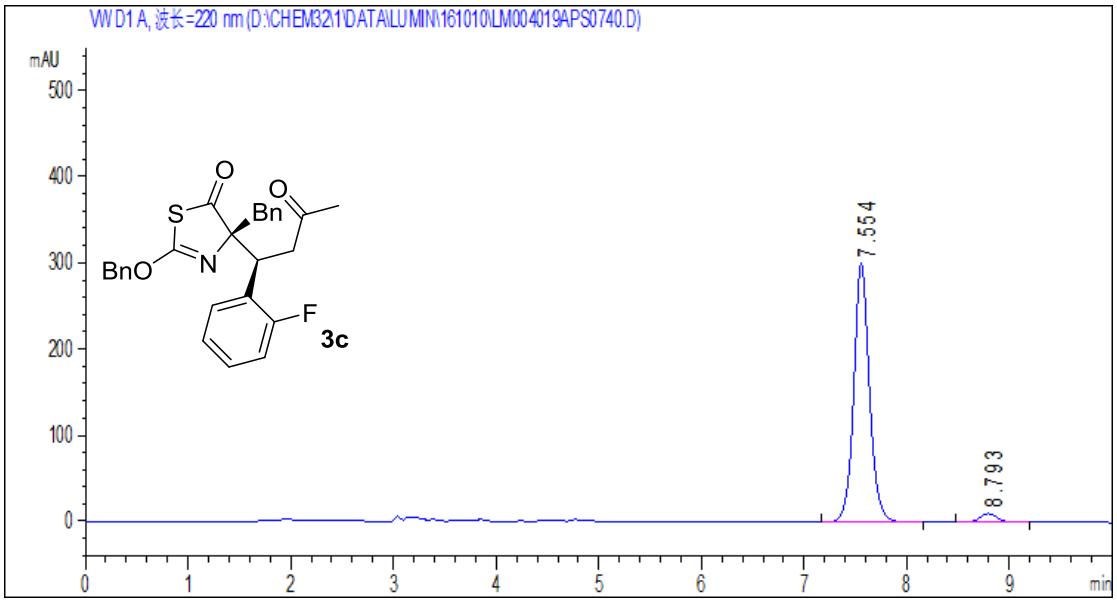


#	Time	Area	Height	Width	Symmetry	Area %
1	6.997	3446.7	278.7	0.2061	1.044	97.743
2	7.824	79.6	7.1	0.1876	0.893	2.257

(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-1-(2-fluorophenyl)-3-oxobutyl)thiazol-5(4*H*)-one (3c)

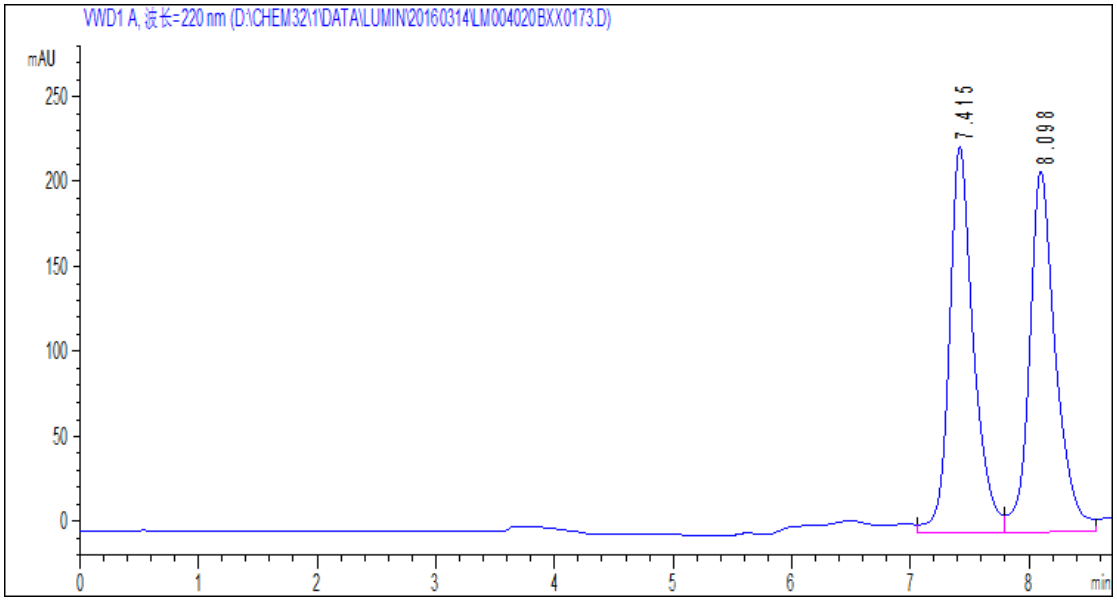


#	Time	Area	Height	Width	Symmetry	Area %
1	7.497	3743.2	343	0.1637	0.83	49.911
2	8.678	3756.6	294.3	0.1926	0.815	50.089

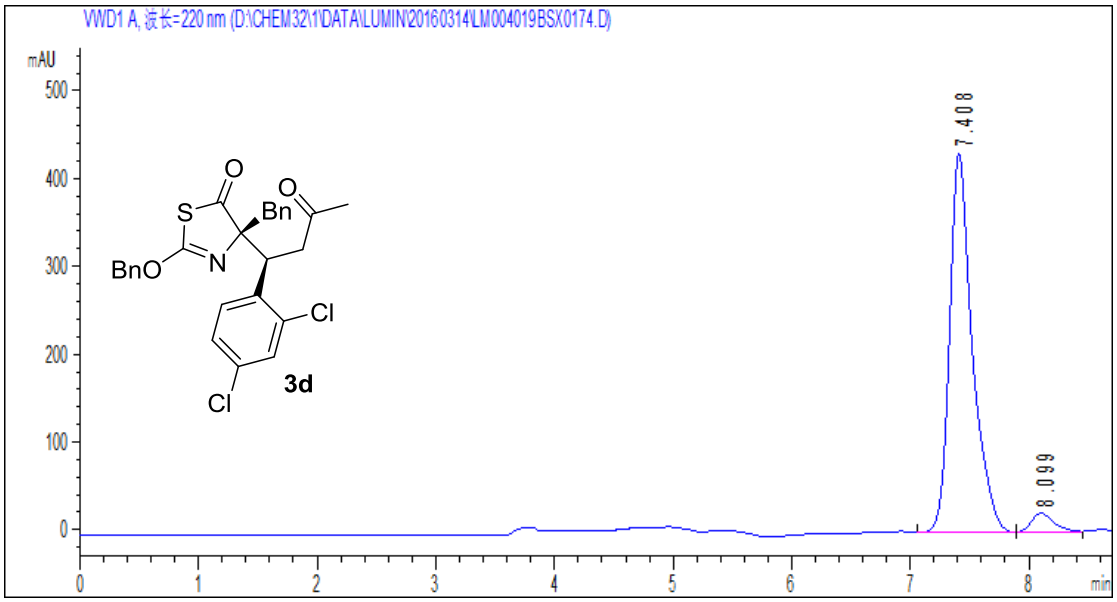


#	Time	Area	Height	Width	Symmetry	Area %
1	7.554	3194.2	300.3	0.1605	0.867	96.221
2	8.793	125.5	10.2	0.1861	0.923	3.779

(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-1-(2,4-dichlorophenyl)-3-oxobutyl)thiazol-5(4*H*)-one (3d)

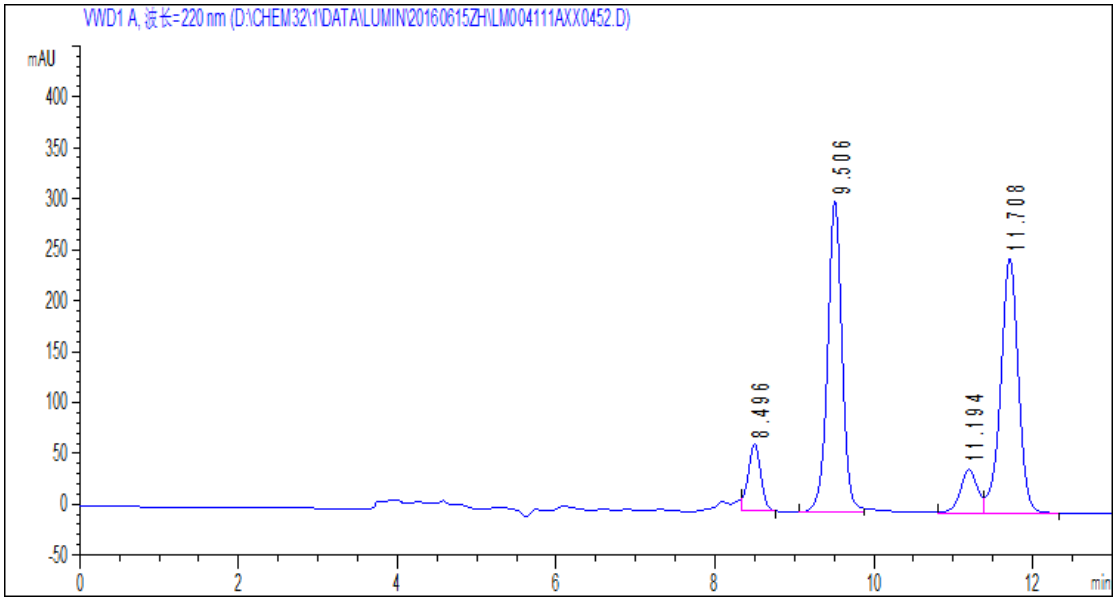


#	Time	Area	Height	Width	Symmetry	Area %
1	7.415	3229	227.7	0.2076	0.73	49.749
2	8.098	3261.6	213	0.2238	0.718	50.251

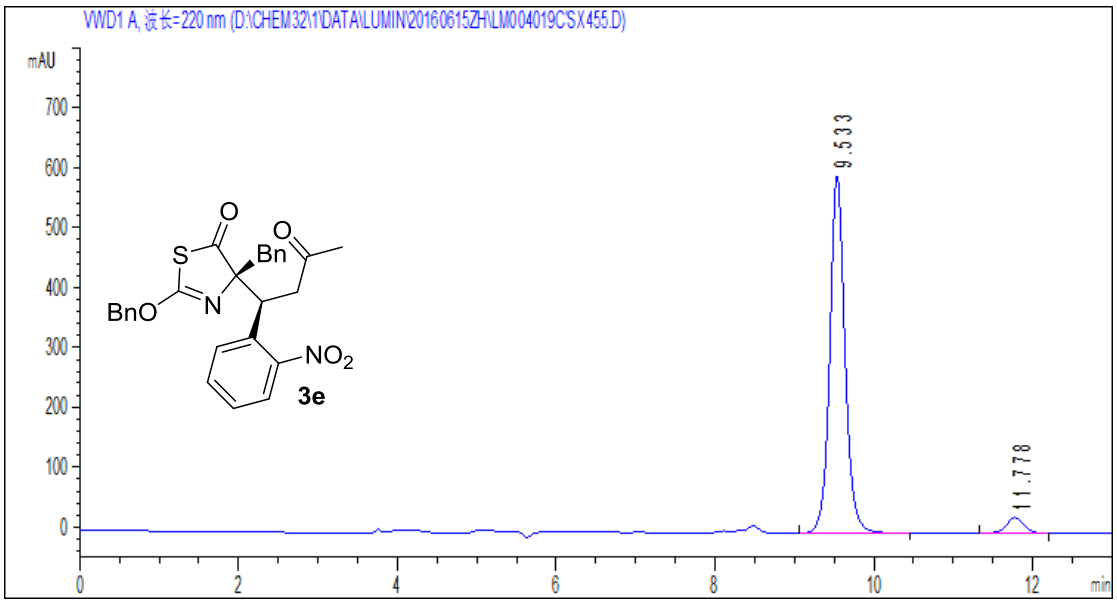


#	Time	Area	Height	Width	Symmetry	Area %
1	7.408	5753.9	432	0.222	0	95.234
2	8.099	288	21.9	0.2189	0.714	4.766

(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-1-(2-nitrophenyl)-3-oxobutyl)thiazol-5(4*H*)-one (3e)

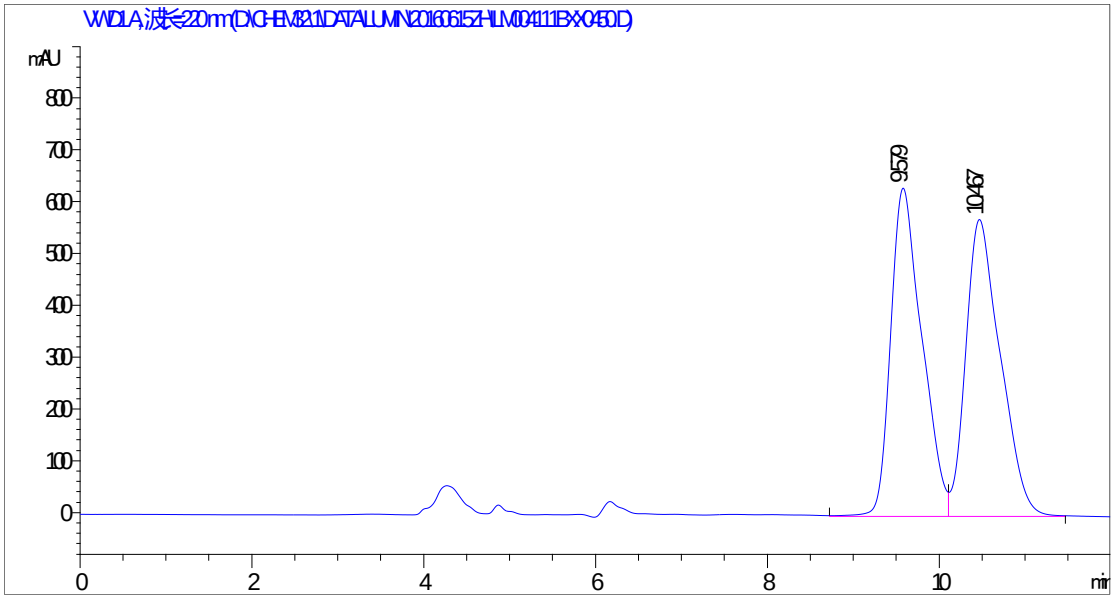


#	Time	Area	Height	Width	Symmetry	Area %
1	8.496	719.6	65.5	0.183	0.996	7.893
2	9.506	3873	305.8	0.2111	0.983	42.478
3	11.194	658.8	43.1	0.2547	0.995	7.226
4	11.708	3866.3	250.5	0.2573	1.02	42.404

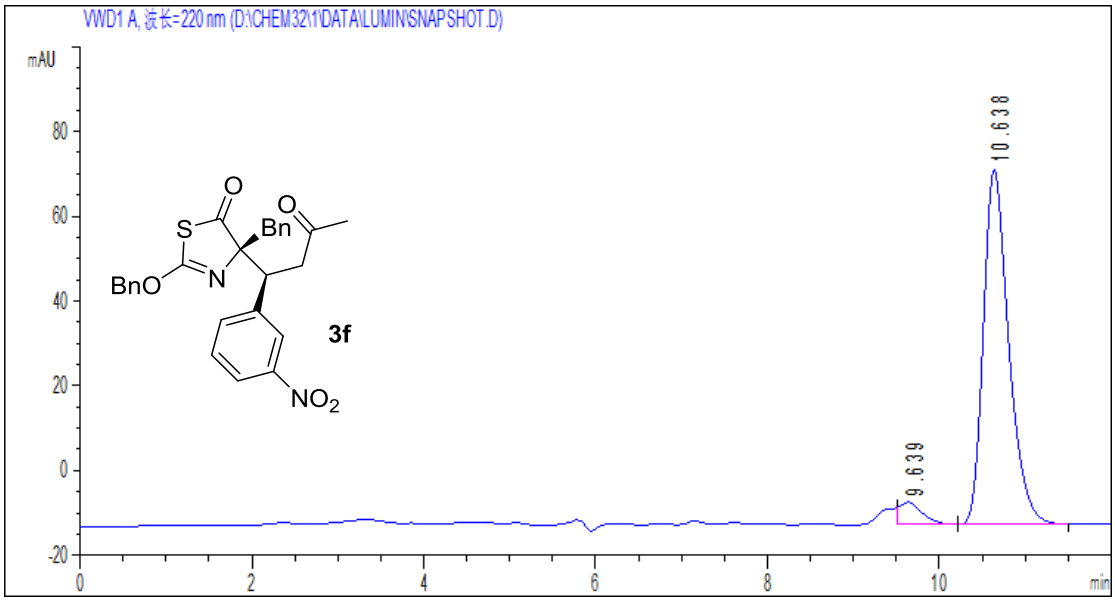


#	Time	Area	Height	Width	Symmetry	Area %
1	9.533	7957.2	597.4	0.202	0.862	95.048
2	11.778	414.6	26.4	0.2619	1.003	4.952

(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-1-(3-nitrophenyl)-3-oxobutyl)thiazol-5(4*H*)-one (3f)

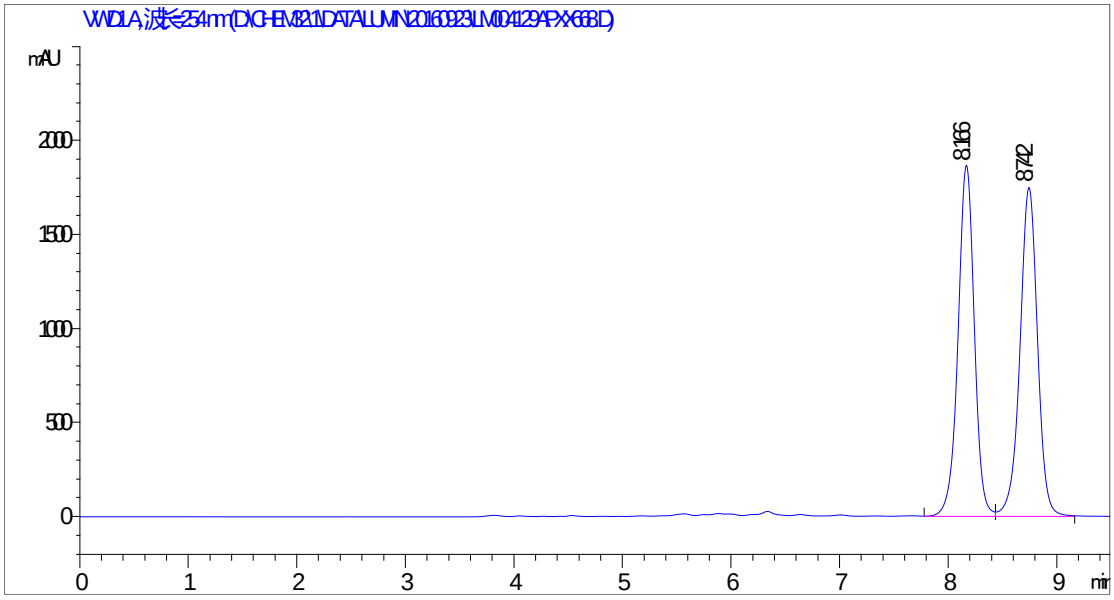


#	Time	Area	Height	Width	Symmetry	Area %
1	9.579	16122.6	634.9	0.3691	0.643	50.010
2	10.467	16116.3	574.3	0.4677	0.633	49.990

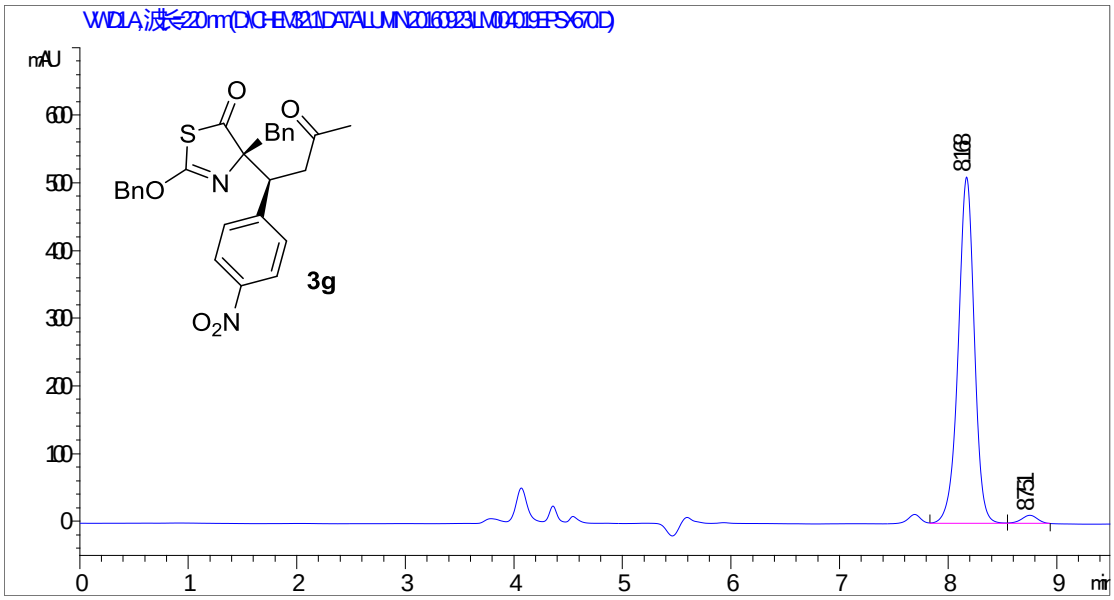


#	Time	Area	Height	Width	Symmetry	Area %
1	9.639	98.6	5.3	0.308	0.581	5.432
2	10.638	1716.8	83.8	0.3104	0.697	94.568

(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-1-(4-nitrophenyl)-3-oxobutyl)thiazol-5(4*H*)-one (3g)

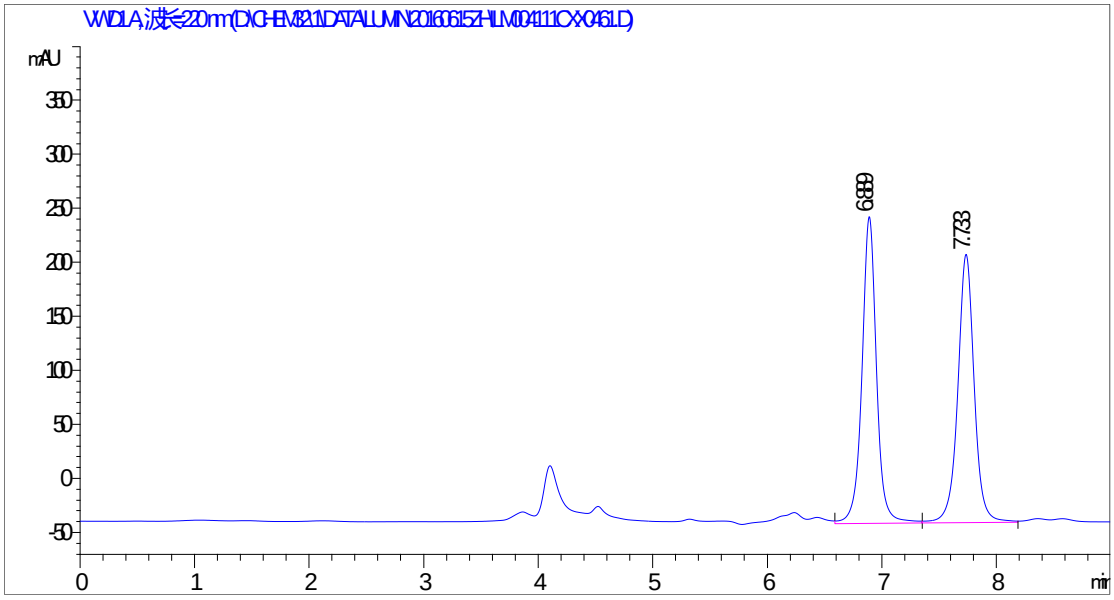


#	Time	Area	Height	Width	Symmetry	Area %
1	8.166	19570.3	1869.4	0.16	1.032	49.738
2	8.742	19776.4	1752	0.1881	1.02	50.262

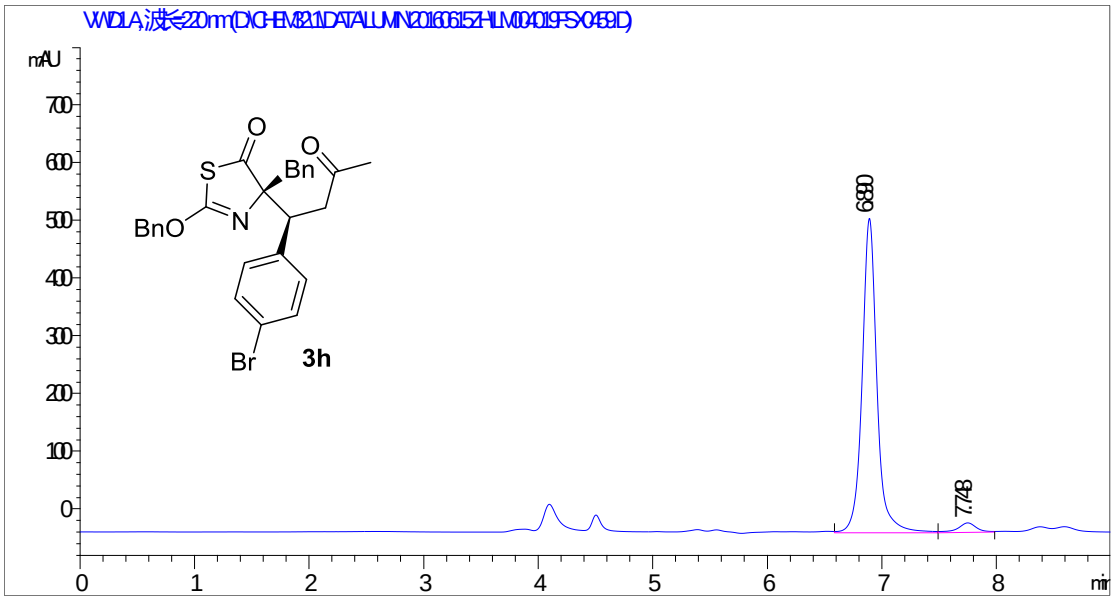


#	Time	Area	Height	Width	Symmetry	Area %
1	8.168	5287.3	512.1	0.1721	0	97.655
2	8.751	127	12.2	0.1735	1.098	2.345

(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-1-(4-bromophenyl)-3-oxobutyl)thiazol-5(4*H*)-one (3h)

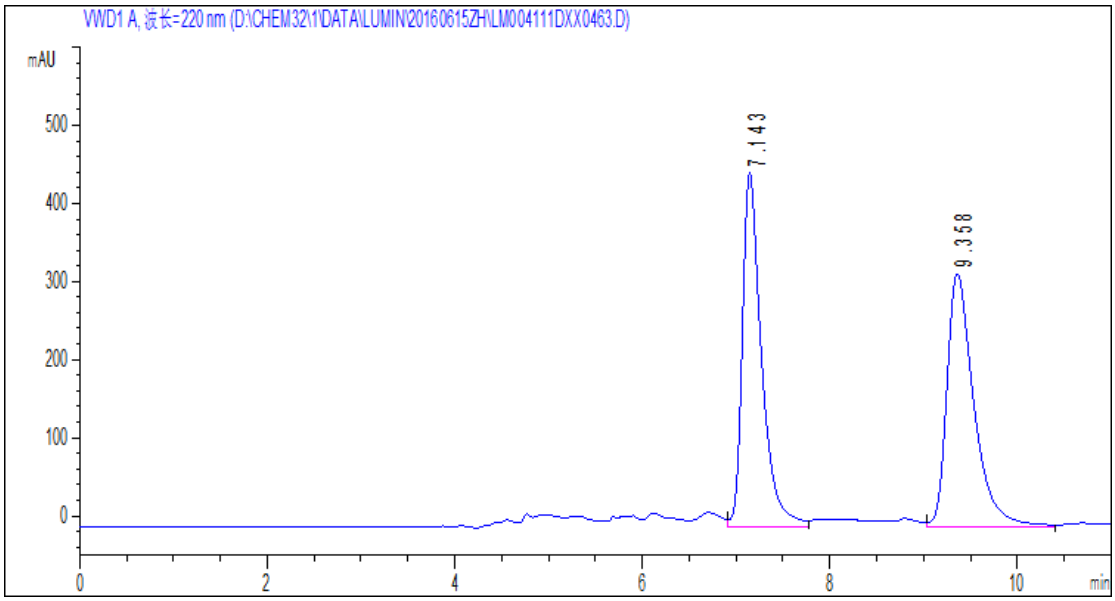


#	Time	Area	Height	Width	Symmetry	Area %
1	6.889	2522.3	284.2	0.1327	0.963	50.312
2	7.733	2491	248.7	0.1518	0.979	49.688

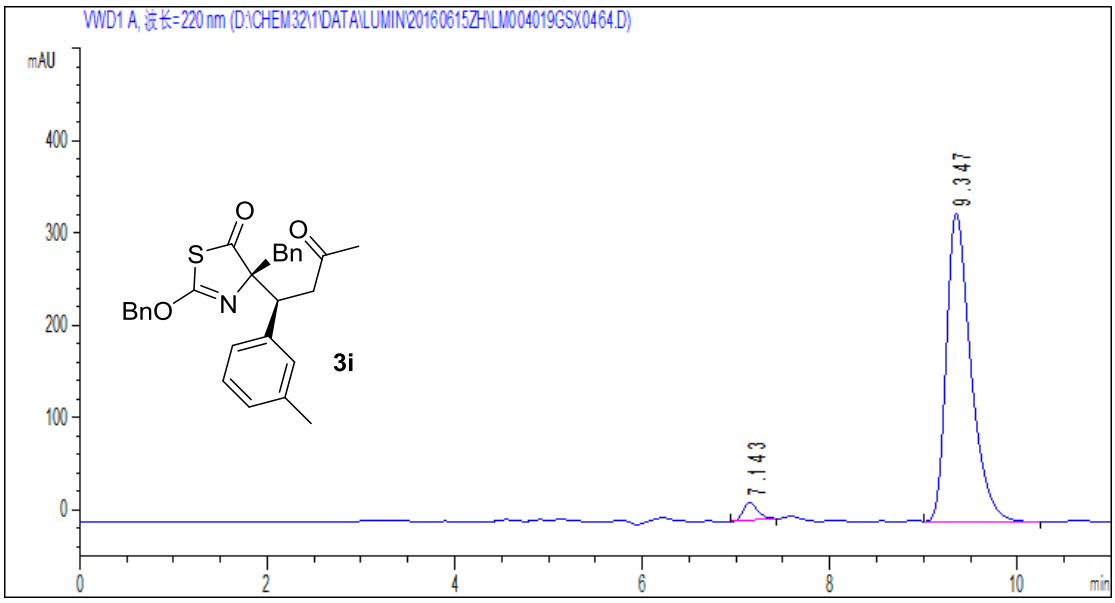


#	Time	Area	Height	Width	Symmetry	Area %
1	6.89	4919.1	545.6	0.1343	0.898	95.968
2	7.748	206.7	17.1	0.1758	1.062	4.032

(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-3-oxo-1-(m-tolyl)butyl)thiazol-5(4*H*)-one (3i)

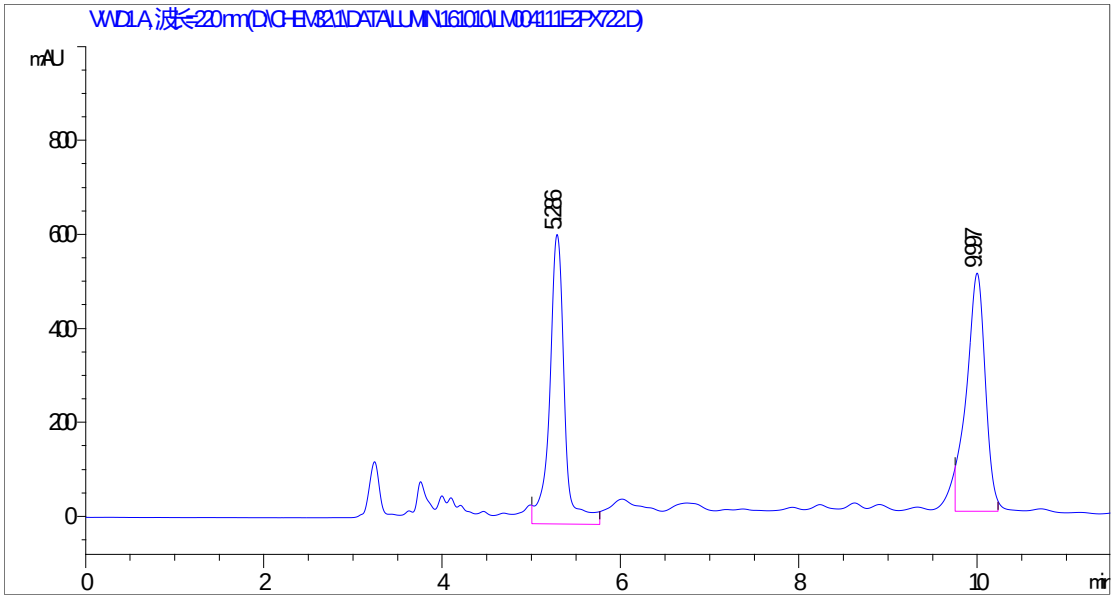


#	Time	Area	Height	Width	Symmetry	Area %
1	7.143	6477.1	453.2	0.209	0.57	49.718
2	9.358	6550.7	324.9	0.3022	0.58	50.282

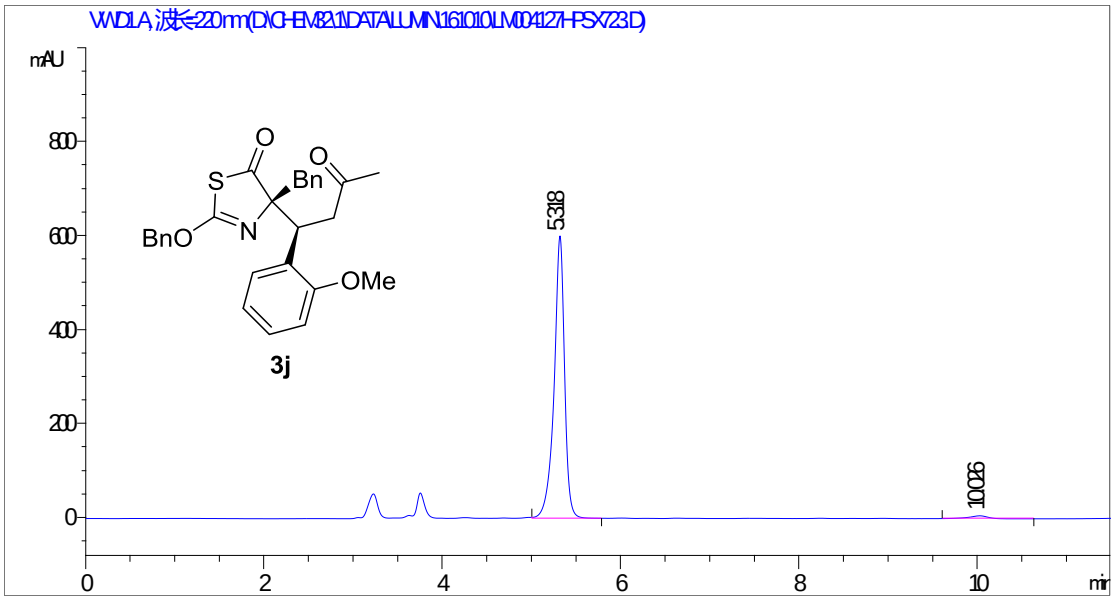


#	Time	Area	Height	Width	Symmetry	Area %
1	7.143	219.5	19.3	0.1893	0.773	3.495
2	9.347	6059.2	334.6	0.3018	0.652	96.505

(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-1-(2-methoxyphenyl)-3-oxobutyl)thiazol-5(4*H*)-one (3j)

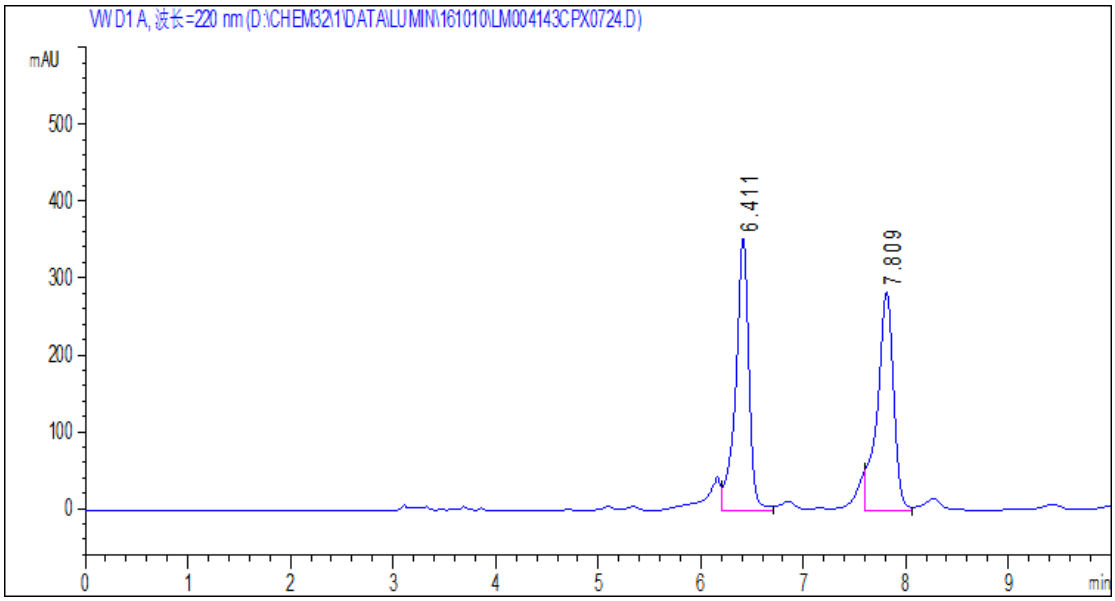


#	Time	Area	Height	Width	Symmetry	Area %
1	5.286	7138.4	617	0.1928	0.96	49.224
2	9.997	7363.4	508	0.2416	1.238	50.776

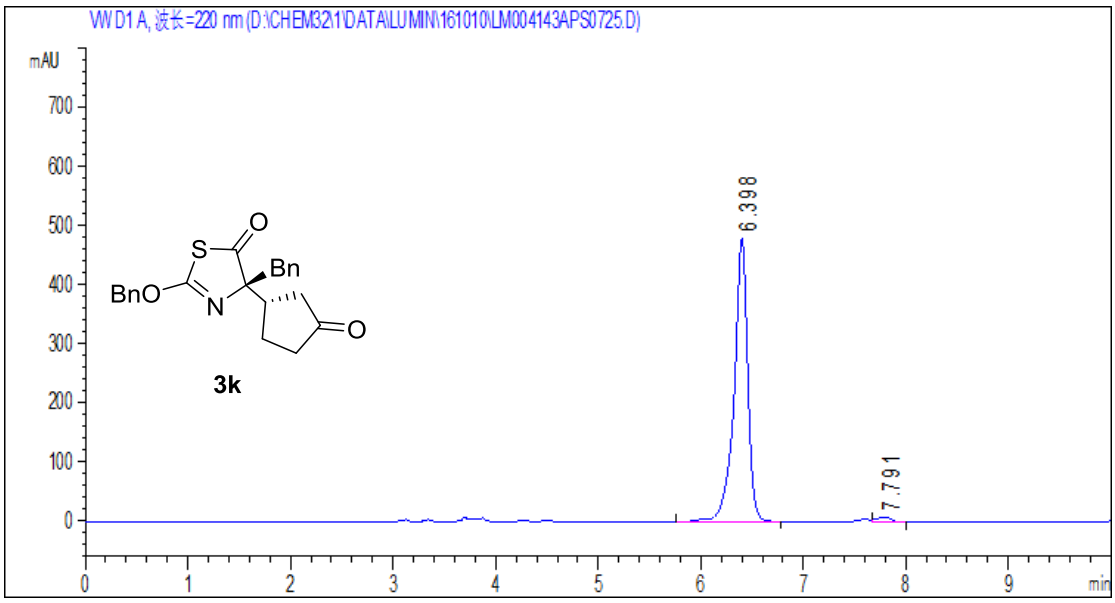


#	Time	Area	Height	Width	Symmetry	Area %
1	5.318	4936.7	601.9	0.1367	1.23	98.021
2	10.026	99.7	6.3	0.2638	1.499	1.979

(*S*)-4-benzyl-2-(benzyloxy)-4-((*S*)-3-oxocyclopentyl)thiazol-5(4*H*)-one (3k)

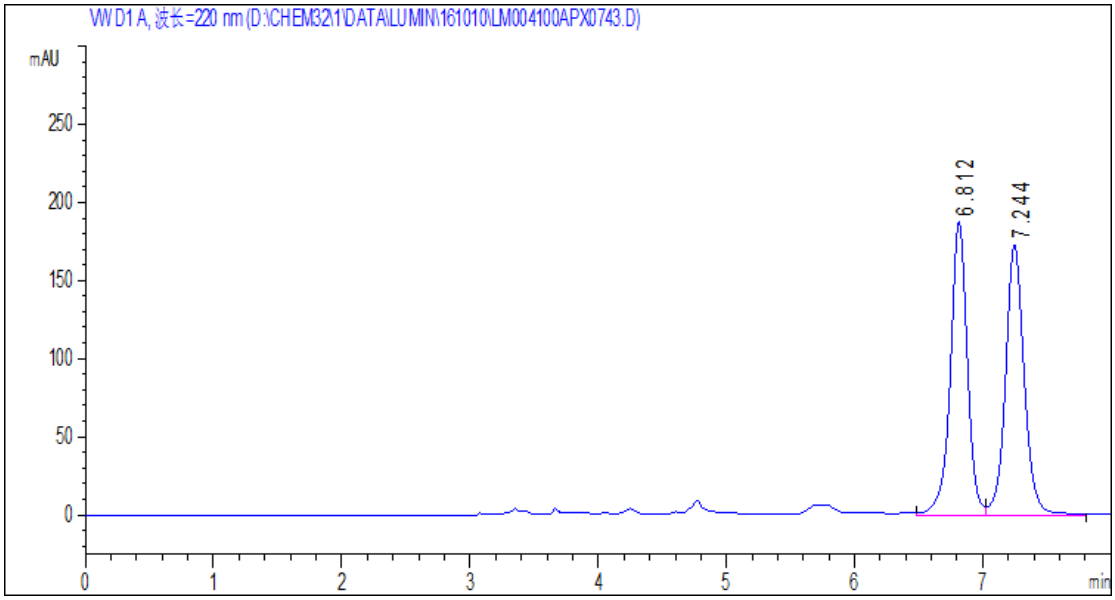


#	Time	Area	Height	Width	Symmetry	Area %
1	6.411	3184.1	355	0.1323	1.248	50.484
2	7.809	3123	284.3	0.1831	1.242	49.516

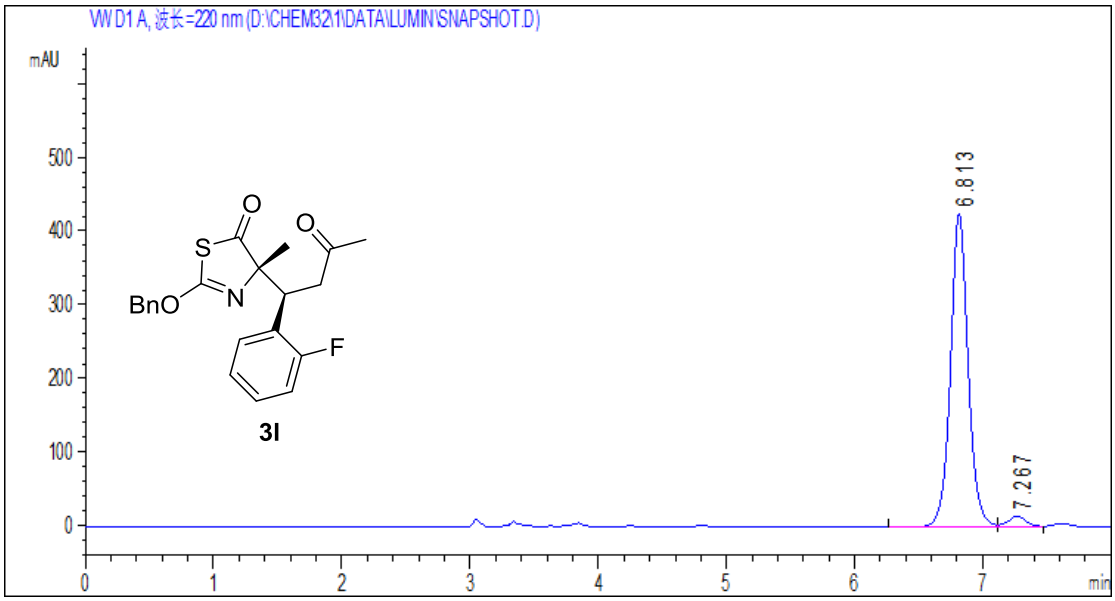


#	Time	Area	Height	Width	Symmetry	Area %
1	6.398	4513.1	481.4	0.137	1.321	97.907
2	7.791	96.5	9.4	0.1712	1.06	2.093

(*S*)-2-(benzyloxy)-4-((*S*)-1-(2-fluorophenyl)-3-oxobutyl)-4-methylthiazol-5(4*H*)-one (3l)

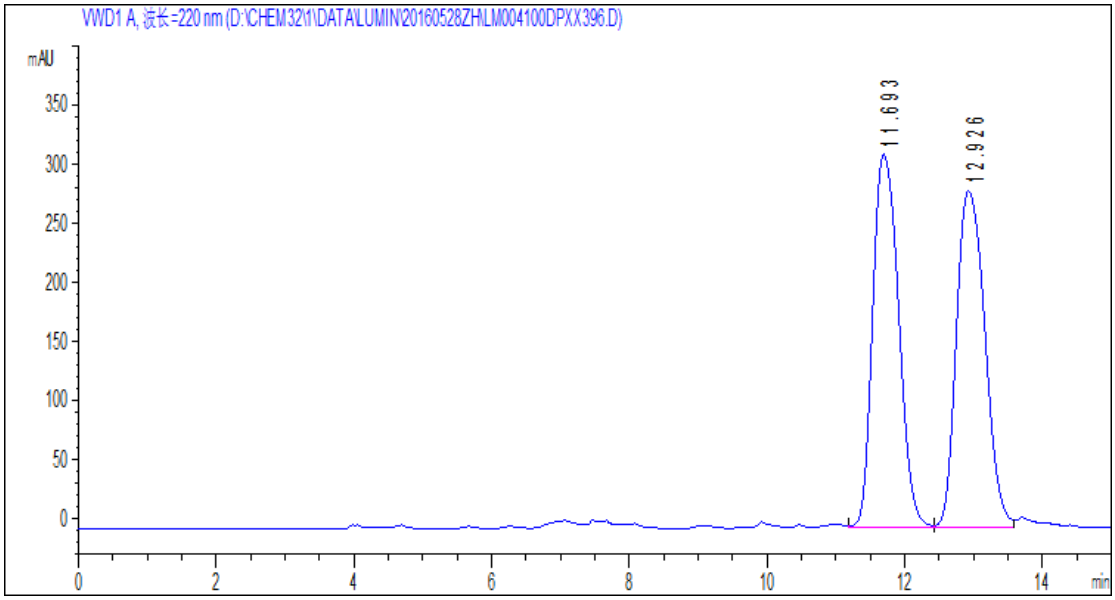


#	Time	Area	Height	Width	Symmetry	Area %
1	6.812	1739.3	187.9	0.14	1.036	49.585
2	7.244	1768.5	173.5	0.1524	0.85	50.415

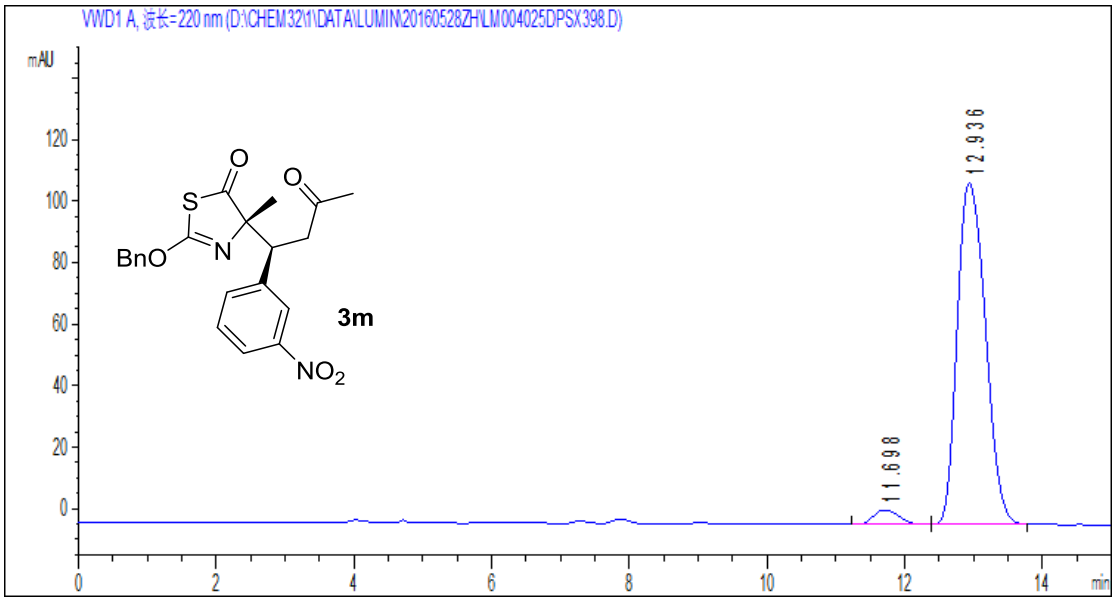


#	Time	Area	Height	Width	Symmetry	Area %
1	6.813	4078.8	425.8	0.1452	0.909	96.360
2	7.267	154.1	14.9	0.1555	0.957	3.640

(*S*)-2-(benzyloxy)-4-methyl-4-((*S*)-1-(3-nitrophenyl)-3-oxobutyl)thiazol-5(4*H*)-one (3m)

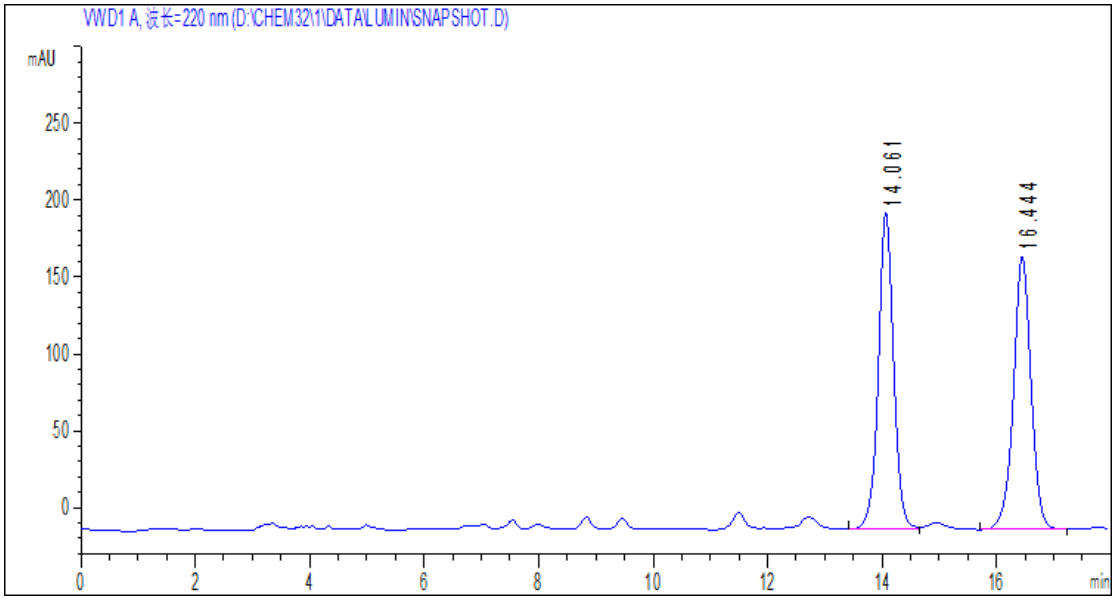


#	Time	Area	Height	Width	Symmetry	Area %
1	11.693	8311.3	316.5	0.4228	0.71	50.190
2	12.926	8248.5	285.3	0.4669	0.717	49.810

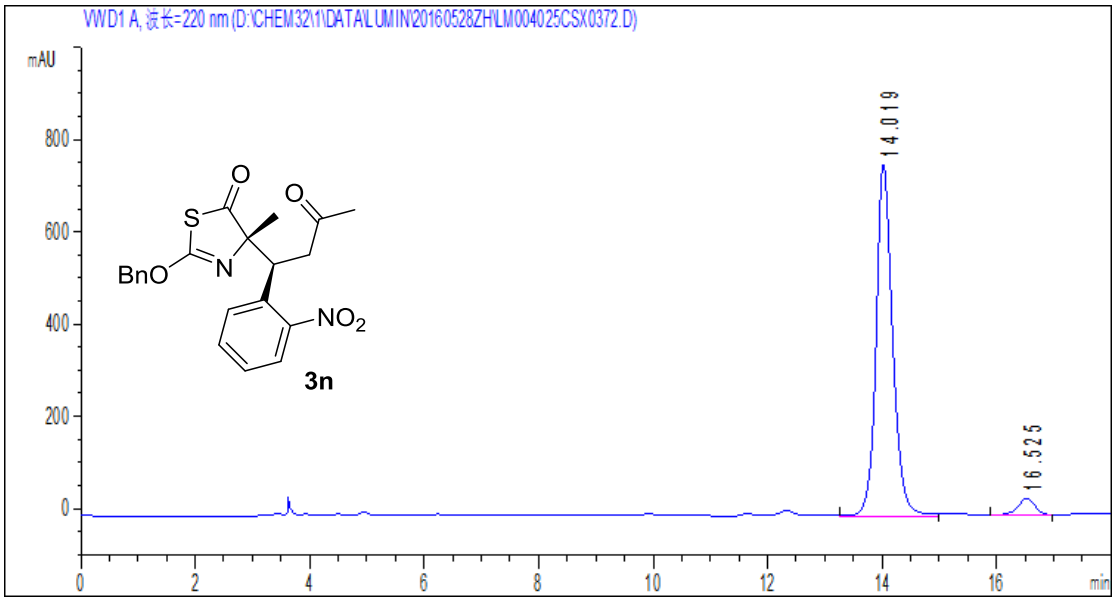


#	Time	Area	Height	Width	Symmetry	Area %
1	11.698	119.3	4.6	0.4079	0.705	3.645
2	12.936	3153.8	110.9	0.4585	0.712	96.355

(*S*)-2-(benzyloxy)-4-methyl-4-((*S*)-1-(2-nitrophenyl)-3-oxobutyl)thiazol-5(4*H*)-one (3n)

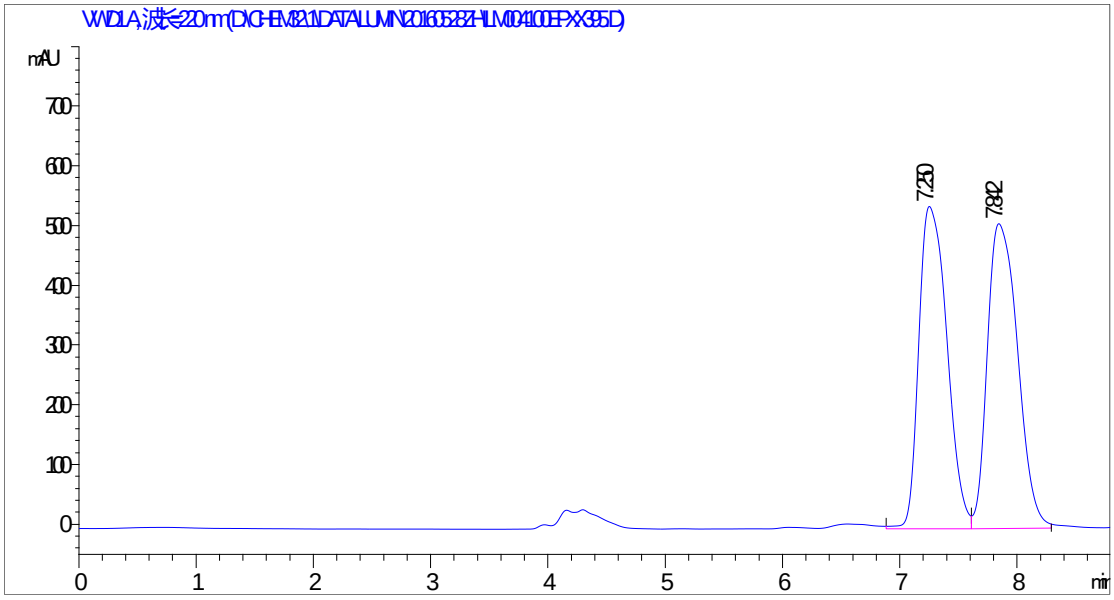


#	Time	Area	Height	Width	Symmetry	Area %
1	14.061	3842.3	205.9	0.2817	0.922	50.187
2	16.444	3813.6	177.8	0.3244	0.967	49.813

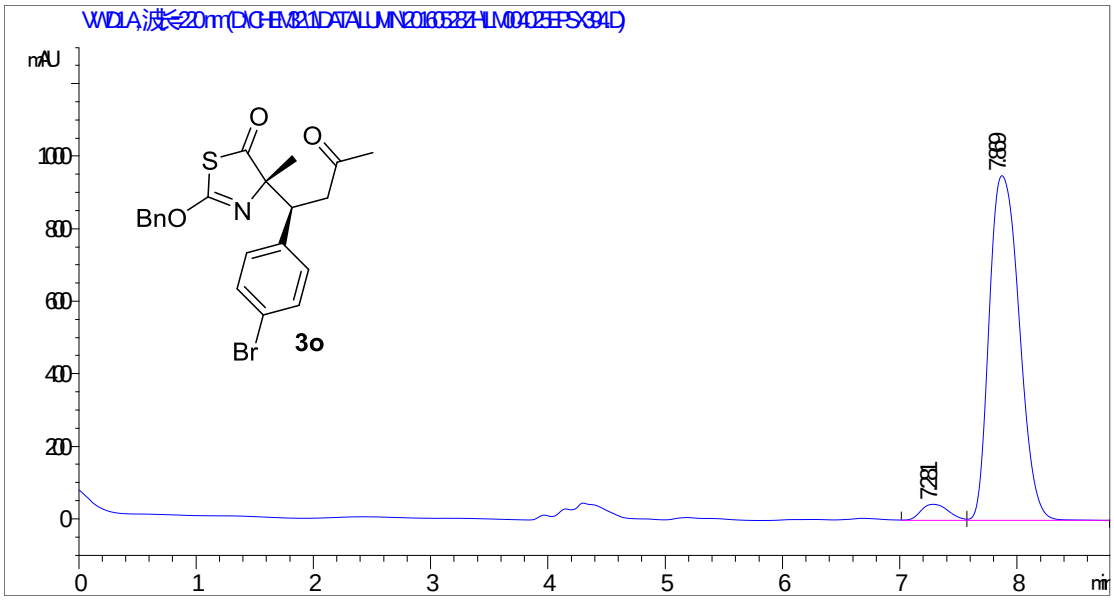


#	Time	Area	Height	Width	Symmetry	Area %
1	14.019	15245.6	761.1	0.3007	0.754	95.126
2	16.525	781.1	36.7	0.3543	1.09	4.874

(*S*)-2-(benzyloxy)-4-((*S*)-1-(4-bromophenyl)-3-oxobutyl)-4-methylthiazol-5(4*H*)-one (3o)

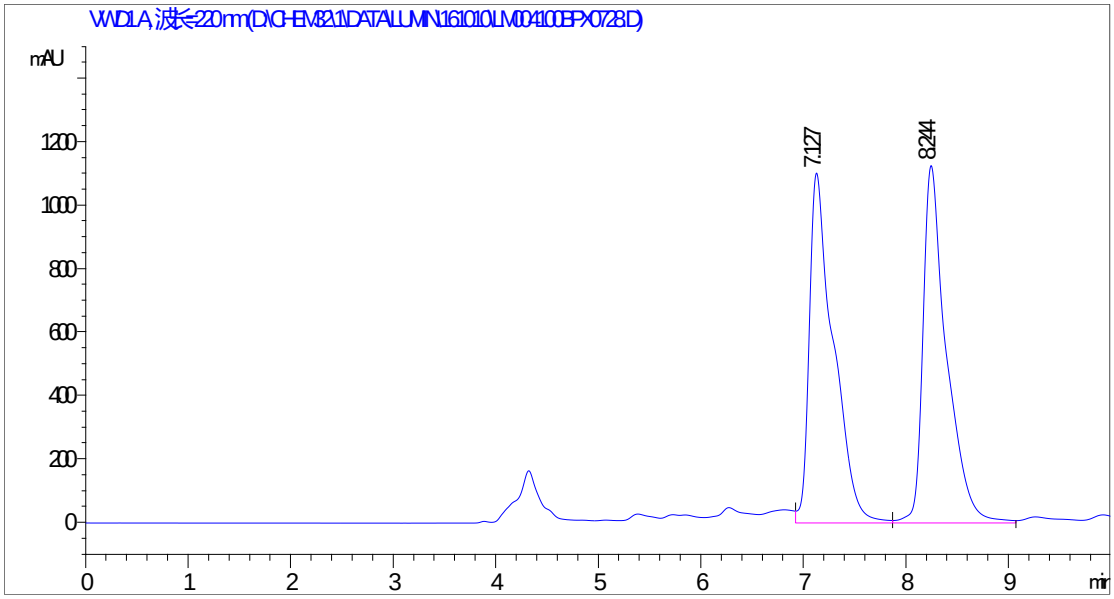


#	Time	Area	Height	Width	Symmetry	Area %
1	7.25	9016	539.8	0.2691	0.595	49.540
2	7.842	9183.5	510.8	0.2996	0.607	50.460

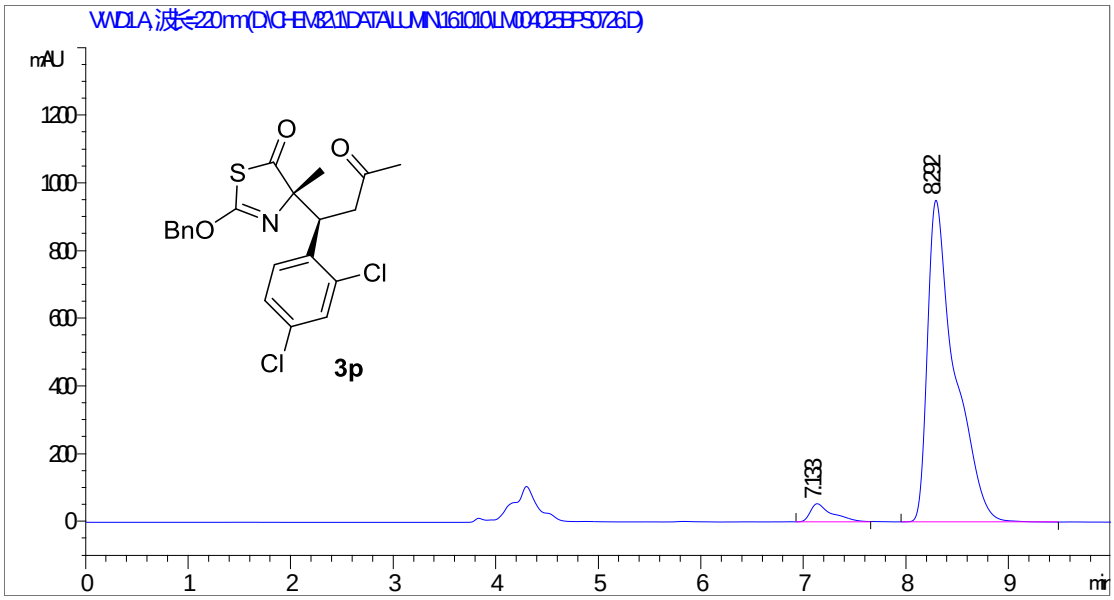


#	Time	Area	Height	Width	Symmetry	Area %
1	7.281	761.4	45.4	0.2672	0.77	4.282
2	7.869	17020.5	951.8	0.2872	0.699	95.718

(*S*)-2-(benzyloxy)-4-((*S*)-1-(2,4-dichlorophenyl)-3-oxobutyl)-4-methylthiazol-5(4*H*)-one (3p)

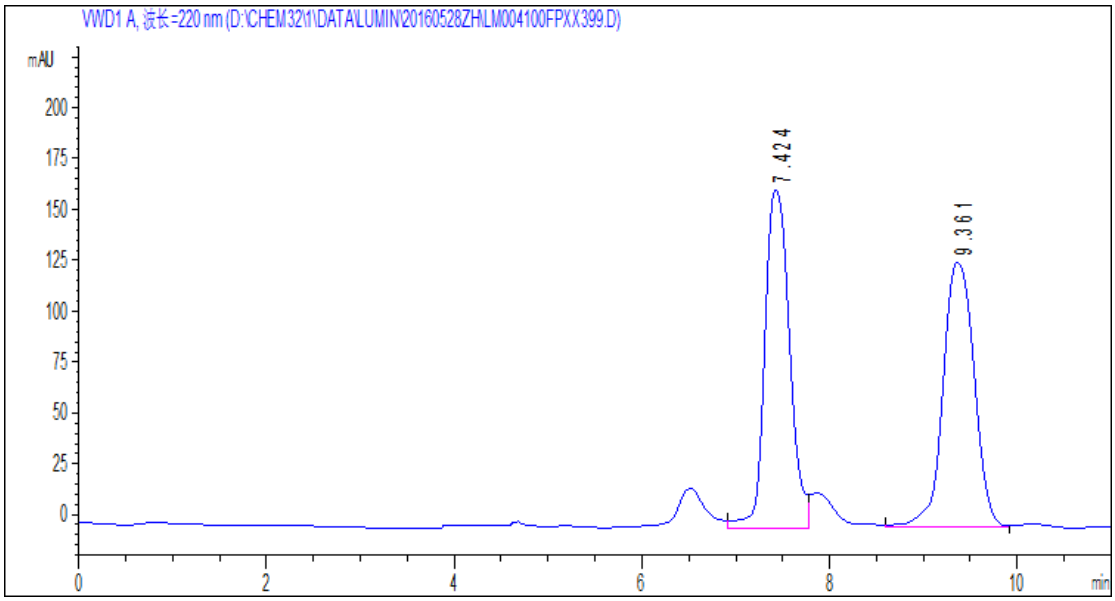


#	Time	Area	Height	Width	Symmetry	Area %
1	7.127	18031.9	1103.4	0.2271	0.402	49.991
2	8.244	18038.5	1126.7	0.2305	0.492	50.009

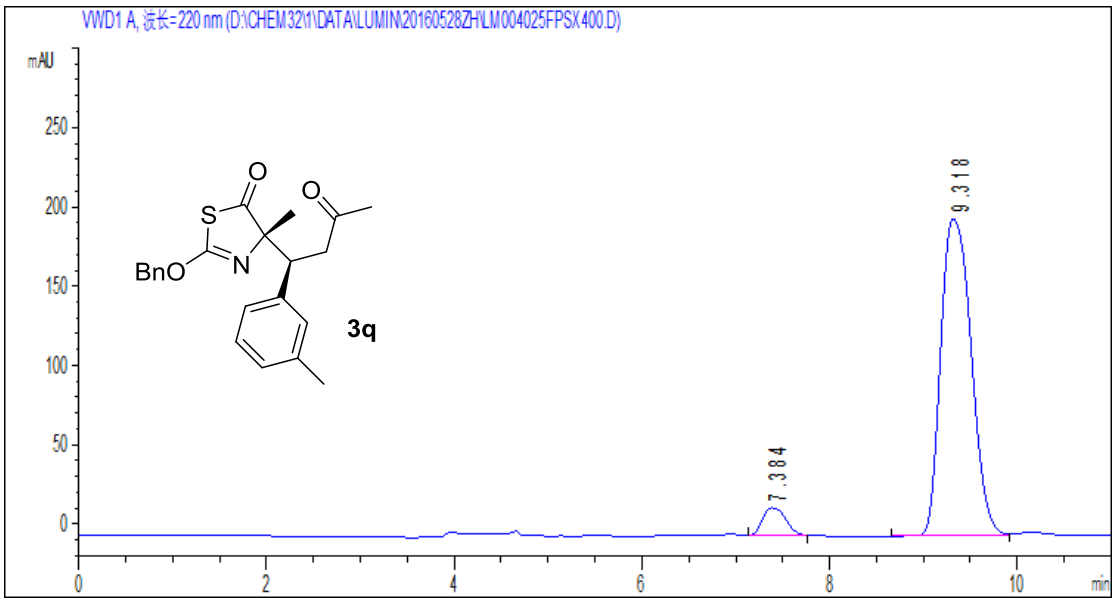


#	Time	Area	Height	Width	Symmetry	Area %
1	7.133	842.6	54.6	0.2572	0.437	4.574
2	8.292	17577.9	951.3	0.2622	0.412	95.426

(*S*)-2-(benzyloxy)-4-methyl-4-((*S*)-3-oxo-1-(m-tolyl)butyl)thiazol-5(4*H*)-one (3q)

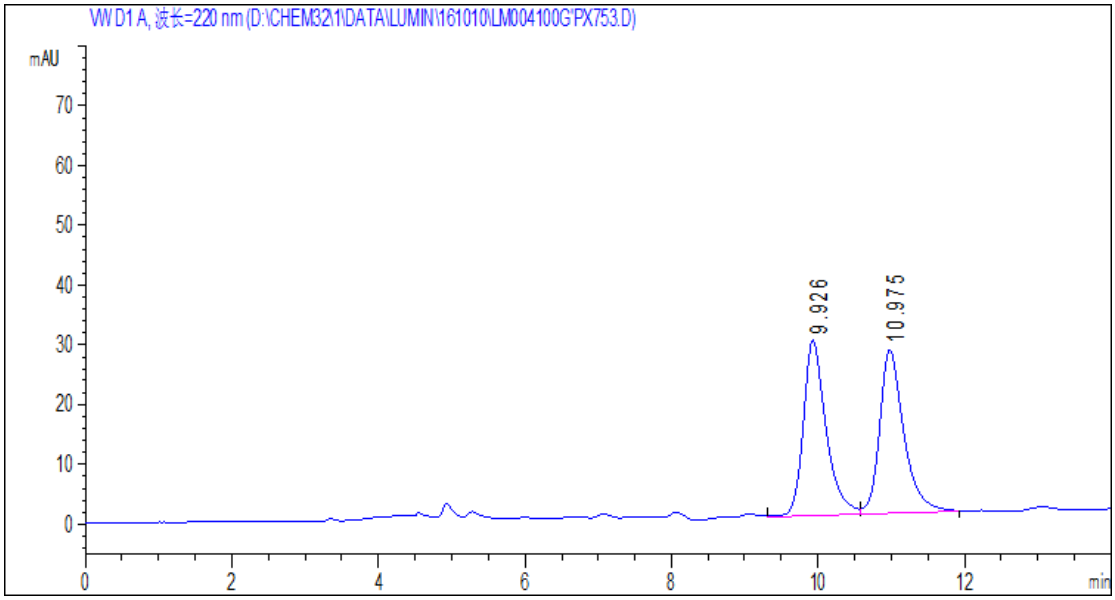


#	Time	Area	Height	Width	Symmetry	Area %
1	7.424	3064.6	166.8	0.2901	0.784	50.059
2	9.361	3057.3	130.8	0.3702	0.885	49.941

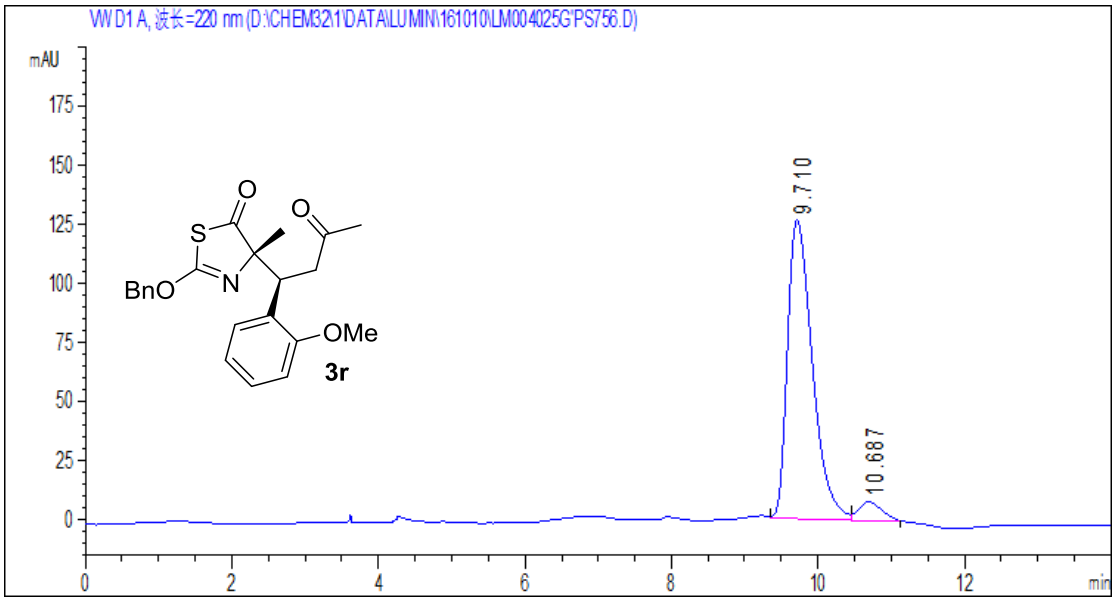


#	Time	Area	Height	Width	Symmetry	Area %
1	7.384	291.6	17.3	0.2814	0.671	6.055
2	9.318	4523.3	200	0.3657	0.695	93.945

(*S*)-2-(benzyloxy)-4-((*S*)-1-(2-methoxyphenyl)-3-oxobutyl)-4-methylthiazol-5(4*H*)-one (3r)



#	Time	Area	Height	Width	Symmetry	Area %
1	9.926	638.3	29.4	0.3202	0.685	50.297
2	10.975	630.7	27.4	0.3426	0.672	49.703



#	Time	Area	Height	Width	Symmetry	Area %
1	9.71	2983.1	126.4	0.3932	0	94.466
2	10.687	174.8	7.9	0.3708	0.725	5.534