Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Asymmetric Synthesis of δ-substituted-β-keto esters and β-substituted ketones via Carboxyl-assisted Site- and Enantio-selective Addition Reactions

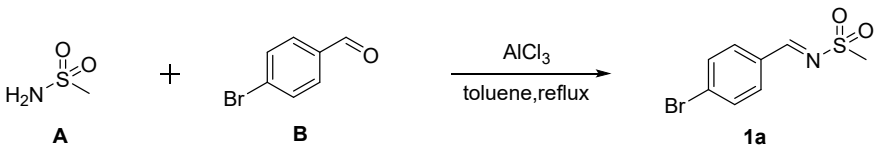
Huiling Zhu,† Peng Liu,† Hongxin Liu,† Ebrahim-Alkhalil M. A. Ahmed,† Xingen Hu,†‡* Juan Li,† Hong-Ping Xiao,† Xinhua Li,† and Jun Jiang†*

† College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, China.
‡ Wenzhou University of Technology, Wenzhou, China.
Email: junjiang@wzu.edu.cn; hxgwzu@126.com.

1. General Information

Chemicals were received from commercial sources without further purification or prepared by literature methods. ^{1}H-NMR and ^{13}C-NMR spectra were measured on a 500 MHz Bruker spectrometer, using $CDCl_3$, DMSO or Acetone as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Data for ^{1}H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C-NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). HRMS (Micromass GCTMS) spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. HPLC analysis was performed on Shimdzu LC-20A. Chiralpak AS, AD, OD, were purchased from Daicel Chemical Industries, LTD. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (300-400 mesh).

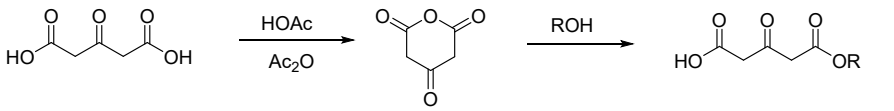
2. General procedure for synthesis of imines 1a.[1]



A **B** **1a**

In a typical procedure, methanesulfonamide (**A**, 856 mg, 5 mmol), 4-bromobenzaldehyde (**B**, 925 mg, 5 mmol) and aluminum chloride (133 mg, 1 mmol) were heated at reflux in toluene for 12 h using a Dean-Stark apparatus. Toluene was removed by evaporation then ethyl acetate (100 mL) was added to the remaining solid. The mixture was filtered and the solvent was removed by evaporation. The solid was washed with a diethyl ether/pentane: 15/25 (2 × 40 mL) to afford the imine as white. (1.2 g, 91% yield).

3. Preparation of monoester 3-oxoglutarate.[2]



3-oxoglutaric anhydride **monoester 3-oxoglutarate**

R=Me, Et, ^{i}Pr, n-butyl

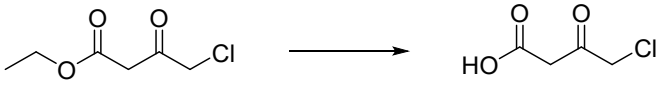
(1) Preparation of 3-oxoglutaric anhydride.

3-Oxoglutaric acid (100 g, 0.68 mol) was added by portions to a solution of acetic acid (150 mL) and acetic anhydride (100 mL) at 5 °C and stirred below 10 °C. The acid dissolved slowly and a pale yellow solid precipitated over 3 h. The product was filtered, washed with acetic acid (100 mL), and followed by toluene (100 mL × 3). The resultant white powder was dried at high vacuum to afford 76 g (86.7%) of the desired 3-oxoglutairc anhydride, which was used directly in the following step.

(2) Preparation of monoester 3-oxoglutarate.

To 3-oxoglutairc anhydride (2 g, 16 mmol) was add cold dry alcohol (12 mL). The mixture was stirred at room temperature for 2 h and the solvent was evaporated to give a brown liquid product with quantitative yield, which was used directly for the next step without further purification.

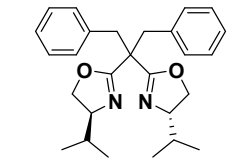
4. Preparation of 4-chloro-3-oxobutanoic acid.[3]



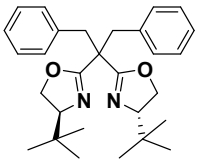
In a 50 mL beaker, a mixture of ethyl 4-chloroacetoacetate (3.3 g, 20 mmol) and 5 mL of conc. hydrochloric acid (37 %) was stirred for 24 h at room temperature. The reaction mixture was poured on ice and extracted twice with ethyl acetate. The combined organic layer was dried over magnesium sulfate and the solvent was removed by evaporation. in vacuo at 25 °C.

5. Optimizing reaction condition of 1a and 2a.

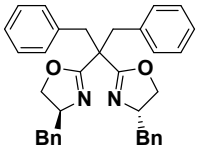
General procedure for the catalytic asymmetric synthesis of product **3a**: A clean and dried Schlenk tube was charged with $CuSO_4$ (20 mol %), ligand $\mathbf{L_8}$ (22 mol %) and 1.0 mL EtOH. The mixture was stirred vigorously at room temperature for two hours. Subsequently, **1a** (0.1 mmol, 1 equiv.) and **2a** (0.2 mmol, 2 equiv.) were added, and the resulting mixture was stirred at 25 °C temperature for 16 hours until the reaction completed. The reaction mixture was then purified through flash column chromatography on a silica gel to yield the target products.



L_1



L_2



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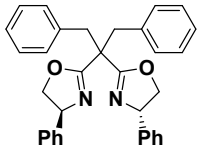

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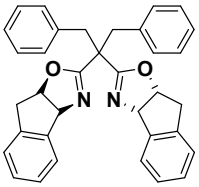
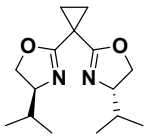


L_5



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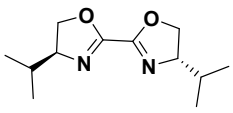
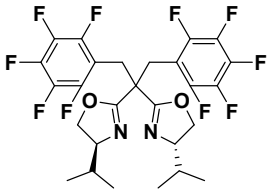


L_7



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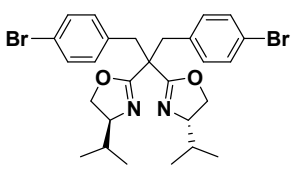

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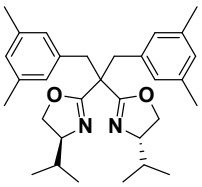
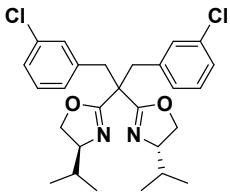


L_{10}



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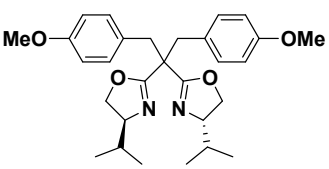
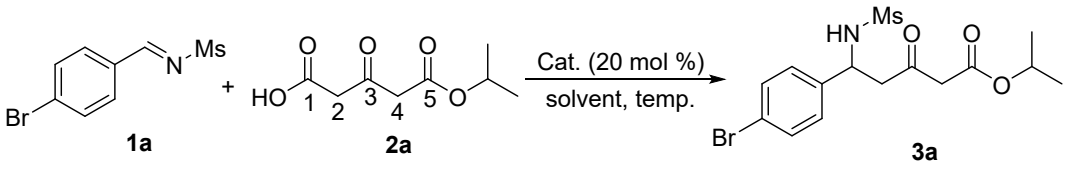


L_{12}



Entry	Catalyst	Solvent	T (^{o}C/ h)	Yield (%)[b]	ee (%)[c]
1	$Ni(OAc)_2.4H_2O$	THF	25/16	58%	--
2	$Cu(OAc)_2$	THF	25/16	24%	--
3	$CuSO_4$	THF	25/16	26%	--
4	$Zn(OTf)_2$	THF	25/16	--	--
5	$Co(OAc)_2.4H_2O$	THF	25/16	49%	--
6	$Pd(OAc)_2$	THF	25/16	--	--
7	$Fe(acac)_3$	THF	25/16	--	--
8	$Ni(OAc)_2.4H_2O$ +L_1	THF	25/16	11%	4%
9	$Co(OAc)_2.4H_2O$+L_1	THF	25/16	14%	3%
10	$Cu(OAc)_2$+L_1	THF	25/16	54%	64%
11	$CuSO_4$+L_1	THF	25/16	48%	66%
12	$Cu(acac)_2$+L_1	THF	25/16	61%	53%
13	$CuCl_2.2H_2O$+L_1	THF	25/16	--	--
14	$CuSO_4$+L_1	DMF	25/16	83%	3%
15	$CuSO_4$+L_1	EtOAc	25/16	56%	69%
16	$CuSO_4$+L_1	Dioxane	25/16	64%	66%
17	$CuSO_4$+L_1	MeOH	25/16	59%	72%
18	$CuSO_4$+L_1	EtOH	25/16	66%	75%
19	$CuSO_4$+L_2	EtOH	25/16	43%	9%
20	$CuSO_4$+L_3	EtOH	25/16	45%	23%
21	$CuSO_4$+L_4	EtOH	25/16	65%	11%
22	$CuSO_4$+L_5	EtOH	25/16	38%	44%
23	$CuSO_4$+L_6	EtOH	25/16	16%	39%
24	$CuSO_4$+L_7	EtOH	25/16	31%	5%
25	$CuSO_4$+L_8	EtOH	25/16	70%	86%
26	$CuSO_4$+L_9	EtOH	25/16	66%	79%
27	$CuSO_4$+L_{10}	EtOH	25/16	64%	67%
28	$CuSO_4$+L_{11}	EtOH	25/16	65%	77%
29	$CuSO_4$+L_{12}	EtOH	25/16	60%	72%

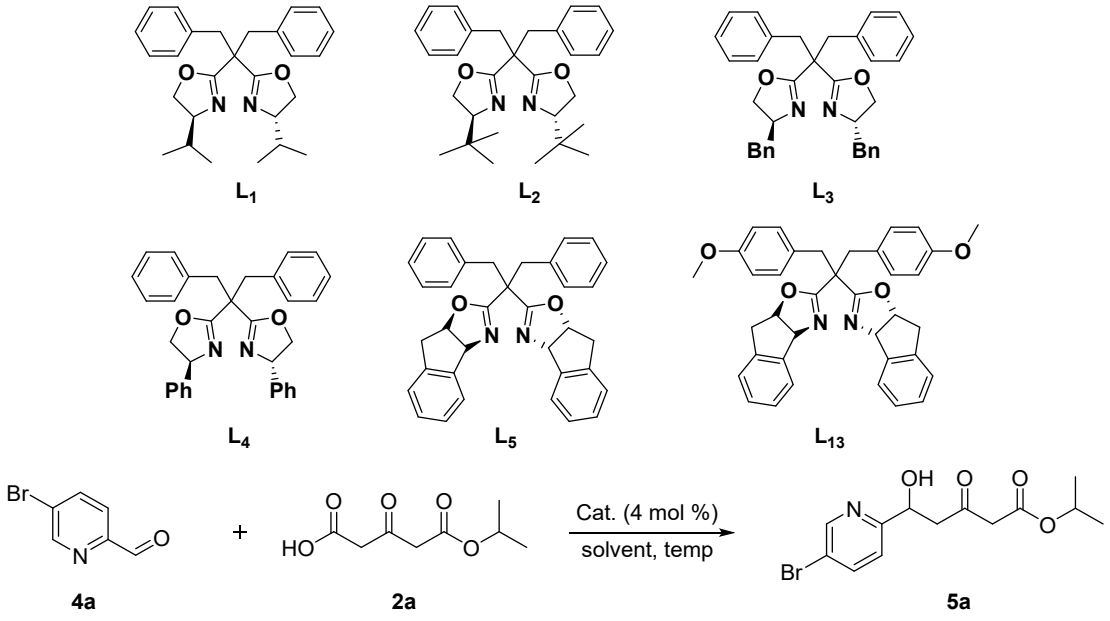
[a]General reaction conditions: **1a** (0.1 mmol), **2** (0.2 mmol), ligand (22 mol%), and catalyst (20 mol%) in 1 mL of solvent at a specific temperature. [b]Isolated yield. [c]Determined by chiral HPLC analysis.

6. Optimizing reaction condition of 2a and aldehydes.

6.1 Optimizing reaction condition of 2a with 4a.

A clean and dried Schlenk tube was charged with $NiCl_2(PPh_3)_2$ (4 mol %), ligand $\mathbf{L_{13}}$ (4.4 mol %). The mixture was stirred vigorously at room temperature for two hours. Subsequently, **2a** (0.2 mmol, 2 equiv.) and **4a** (0.1 mmol, 1 equiv.) were added, and the resulting mixture was stirred at

the corresponding temperature for a specific time until the reaction completed. The reaction mixture was then purified through flash column chromatography on a silica gel to yield the target products.

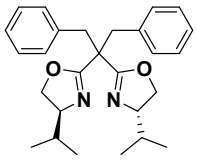


Entry	Catalyst	Solvent	T (°C/ h)	Yield (%)[b]	ee (%)[c]
1	$NiCl_2(PPh_3)_2$+L_4	CH_3CN	25/6	90%	31%
2	$NiCl_2(PPh_3)_2$+L_4	Toluene	25/6	74%	27%
3	$NiCl_2(PPh_3)_2$+L_4	DCM	25/6	91%	26%
4	$NiCl_2(PPh_3)_2$+L_4	ether	25/6	89%	27%
5	$NiCl_2(PPh_3)_2$+L_4	EtOAc	25/6	88%	30%
6	$NiCl_2(PPh_3)_2$+L_1	CH_3CN	25/6	87%	36%
7	$NiCl_2(PPh_3)_2$+L_2	CH_3CN	25/6	91%	34%
8	$NiCl_2(PPh_3)_2$+L_3	CH_3CN	25/6	95%	44%
8	$NiCl_2(PPh_3)_2$+L_5	CH_3CN	25/6	90%	48%
9	$NiCl_2(PPh_3)_2$+L_{13}	CH_3CN	25/6	90%	79%

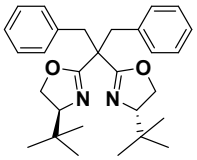
[a] General reaction conditions: **4a** (0.1 mmol), **2** (0.2 mmol), ligand (4.4 mol %), and catalyst (4 mol %) in 0.4 mL of solvent at a specific temperature. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

6.2 Optimizing reaction condition of 2a with 4e.

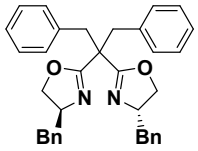
A clean and dried Schlenk tube was charged with $Cu(OAc)_2$•H_2O (5 mol %), ligand $\mathbf{L_{16}}$(5.5 mol %). The mixture was stirred vigorously at room temperature for two hours. Subsequently, **2a** (0.2 mmol, 2 equiv.) and **4e** (0.1 mmol, 1 equiv.) were added, and the resulting mixture was stirred at the corresponding temperature for a specific time until the reaction completed. The reaction mixture was then purified through flash column chromatography on a silica gel to yield the target products.



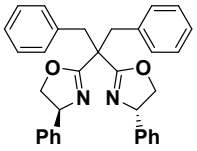
L_1



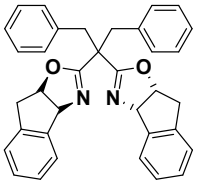
L_2



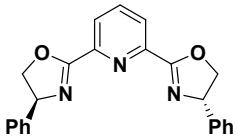
L_3



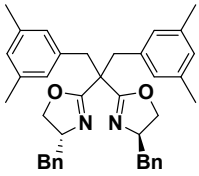
L_4



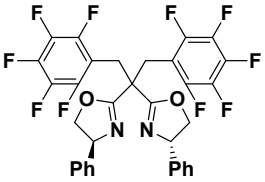
L_5



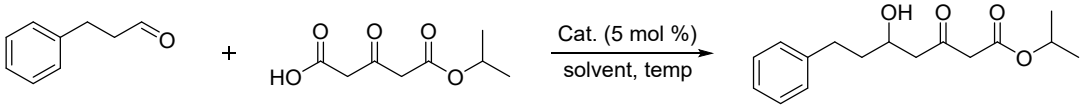
L_{14}



L_{15}



L_{16}

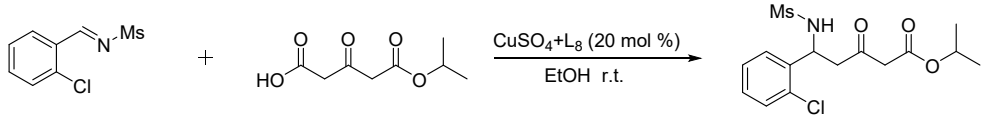


4e **2a** **5e**

Entry	Catalyst	Solvent	T (°C/ h)	Yield (%)[b]	ee (%)[c]
1	$Ni(OAc)_2$+L_4	CH_3CN	25/6	35%	8%
2	$CuSO_4$+L_4	CH_3CN	25/6	27%	17%
3	$Cu(OAc)_2$•H_2O +L_4	CH_3CN	25/6	32%	18%
4	$Cu(OAc)_2$•H_2O +L_4	THF	25/6	83%	24%
5	$Cu(OAc)_2$•H_2O +L_4	DCM	25/6	25%	31%
6	$Cu(OAc)_2$•H_2O +L_4	MeOH	25/6	--	--
7	$Cu(OAc)_2$•H_2O +L_4	EtOAc	25/6	74%	22%
8	$Cu(OAc)_2$•H_2O +L_1	THF	25/6	60%	9%
9	$Cu(OAc)_2$•H_2O +L_2	THF	25/6	57%	10%
10	$Cu(OAc)_2$•H_2O +L_3	THF	25/6	64%	4%
11	$Cu(OAc)_2$•H_2O +L_5	THF	25/6	53%	-7%
12	$Cu(OAc)_2$•H_2O +L_4	THF	0/36	78%	26%
13	$Cu(OAc)_2$•H_2O +L_4	THF	-10/72	77%	36%
14	$Cu(OAc)_2$•H_2O +L_4	THF	-15/84	73%	33%
15	$Cu(OAc)_2$•H_2O +L_{14}	THF	-10/72	64%	8%
16	$Cu(OAc)_2$•H_2O +L_{15}	THF	-10/72	71%	-24%
17	$Cu(OAc)_2$•H_2O +L_{16}	THF	-10/72	78%	65%
18	$Cu(OAc)_2$•H_2O +L_{16}	DME	-10/72	78%	69%

[a] General reaction conditions: **4e** (0.1 mmol), **2** (0.2 mmol), ligand (5.5 mol %), and catalyst (5 mol %) in 1 mL of solvent at a specific temperature. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

7. Millimole-scale catalytic synthesis of 3f.[a]

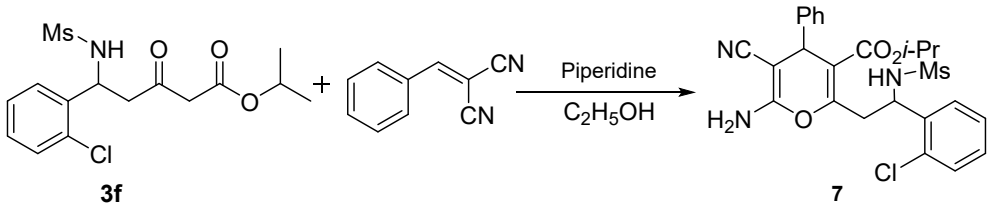


1f **2a** **3f**

A clean and dried 100 mL round bottom flask was charged with $CuSO_4$ (20 mol %), ligand (22 mol %) and 50 mL of EtOH. The mixture was stirred vigorously at room temperature for 2

hours, then **1f** (1.1 g, 5 mmol) and **2** (1.88 g, 10 mmol) were added, and the resulting mixture was stirred at the 25 °C for 48 hours. After completion of reaction (monitored by TLC), the remaining solvent was removed in vacuum. The crude product was purified by flash chromatography on silica gel using hexanes/ EtOAc (6:1-2:1) as eluent to give the desired product **3f** as a yellow liquid (1.29 g, 72% yield, 96% e.e.).

8. Experimental procedure for the synthesis of isopropyl 6-amino-2-(2-(2-chlorophenyl)-2-(methylsulfonamido)ethyl)-5-cyano-4-phenyl-4H-pyran-3-carboxylate 7. [4]

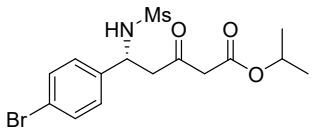


3f **7**

3f (36.2 mg, 0.1 mmol, 95% ee) and 2-benzylidenemalononitrile (0.1 mmol) in absolute ethanol (2 mL) were stirred at room temperature for 10 minutes, followed by the addition of piperidine (20 mol %). The reaction mixture was stirred at room temperature for 4hs. Dissolve the precipitate solid in hot ethanol. Concentrate the precipitate solid with silica. The crude product was purified via flash chromatography on silica gel using petroleum ether/ EtOAc (1:1) as eluent, to give the final product **7** as a white solid (42.3 mg, 82%, major:98% ee, minor:95% ee, 1.4:1 d.r.).

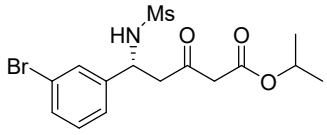
9. The data of the products 3, 5-9

isopropyl 5-(4-bromophenyl)-5-(methylsulfonamido)-3-oxopentanoate (3a): This compound was



prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (28.6 mg, 70% yield) as a colorless liquid. $[\alpha]_D^{25}$ = + 16.2 (c = 0.2 in EtOAc); enantiomeric excess: 86%. Daicel Chiralpak OD-H, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 11.835 min, t_R (minor) = 16.565 min; ^{1}H NMR (500 MHz, CDCl3) δ 7.49 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.6 Hz, 2H), 5.67 (d, J = 7.3 Hz, 1H), 5.03 (dt, J = 12.5, 6.3 Hz, 1H), 4.97 – 4.86 (m, 1H), 3.40 (q, J = 15.7 Hz, 2H), 3.18 (dd, J = 17.7, 7.7 Hz, 1H), 3.00 (dd, J = 17.7, 4.9 Hz, 1H), 2.77 (s, 3H), 1.23 (d, J = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.5, 166.5, 139.5, 132.1, 128.4, 122.1, 69.7, 53.2, 49.7, 49.2, 41.5, 21.7; HRMS (ESI): Calcd for $C_{15}H_{20}BrNO_5S$[M + Na]+: 428.0138; found: 428.0140.

isopropyl 5-(3-bromophenyl)-5-(methylsulfonamido)-3-oxopentanoate (3b): This compound was



prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (22.0 mg, 54% yield) as a colorless liquid. $[\alpha]_D^{25}$ = + 16.3 (c = 0.1 in EtOAc); enantiomeric excess: 88%. Daicel Chiralpak OD-H, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 16.334 min, t_R (minor) = 21.520 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.43 (dd, *J* = 5.4, 2.4 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 5.70 (d, *J* = 7.3 Hz, 1H), 5.04 (dt, *J* = 12.6, 6.3 Hz, 1H), 4.93 (td, *J* = 7.7, 5.0 Hz, 1H),

3.41 (q, *J* = 15.7 Hz, 2H), 3.19 (dd, *J* = 17.8, 7.8 Hz, 1H), 3.01 (dd, *J* = 17.8, 4.8 Hz, 1H), 2.80 (s, 3H), 1.24 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.3, 166.5, 142.9, 131.3, 130.5, 129.7, 125.3, 123.0, 69.7, 53.2, 49.7, 49.2, 41.5, 21.7; HRMS (ESI): Calcd for $C_{15}H_{20}BrNO_5S$[M + Na]+: 428.0138; found: 428.0140.

isopropyl 5-(2-bromophenyl)-5-(methylsulfonamido)-3-oxopentanoate (3c): This compound was prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (27.7 mg, 68% yield) as a colorless liquid. $[\alpha]_D^{25}$ = + 29.7 (c = 0.2 in EtOAc); enantiomeric excess: 95%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 11.924 min, t_R (minor) = 18.940 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.1 Hz, 1H), 5.87 (d, *J* = 7.3 Hz, 1H), 5.34 – 5.26 (m, 1H), 5.04 (dt, *J* = 12.4, 6.0 Hz, 1H), 3.43 (q, *J* = 15.8 Hz, 2H), 3.18 (dd, *J* = 17.9, 7.9 Hz, 1H), 3.09 (dd, *J* = 18.8, 5.0 Hz, 1H), 2.85 (s, 3H), 1.26 – 1.21 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.6, 166.6, 139.2, 133.4, 129.6, 128.8, 128.0, 122.1, 69.6, 53.2, 49.6, 47.8, 41.0, 21.7; HRMS (ESI): Calcd for $C_{15}H_{20}BrNO_5S$[M + Na]+: 428.0138; found: 428.0140.

isopropyl 5-(2-fluorophenyl)-5-(methylsulfonamido)-3-oxopentanoate (3d): This compound was prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (18.4 mg, 53% yield) as a colorless liquid. $[\alpha]_D^{25}$ = + 18.2 (c = 0.2 in EtOAc); enantiomeric excess: 94%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 10.433 min, t_R (minor) = 15.493 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.6 Hz, 1H), 7.29 (dd, *J* = 14.8, 8.2 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.09 – 7.03 (m, 1H), 5.51 (d, *J* = 7.8 Hz, 1H), 5.20 – 5.12 (m, 1H), 5.04 (dd, *J* = 12.2, 6.0 Hz, 1H), 3.46 – 3.34 (m, 2H), 3.27 (dd, *J* = 17.9, 7.3 Hz, 1H), 3.10 (dd, *J* = 17.8, 5.0 Hz, 1H), 2.82 (s, 3H), 1.23 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.3, 166.4, 160.1 (d, *J* = 245.9 Hz), 129.9 (d, *J* = 8.6 Hz), 129.0 (d, *J* = 4.0 Hz), 127.3 (d, *J* = 12.6 Hz), 124.7 (d, *J* = 3.4 Hz), 115.9 (d, *J* = 21.4 Hz), 69.5, 49.7, 49.3, 48.1, 41.2, 21.6; HRMS (ESI): Calcd for $C_{15}H_{20}FNO_5S$[M + Na]+: 368.0938; found: 368.0944.

isopropyl 5-(4-chlorophenyl)-5-(methylsulfonamido)-3-oxopentanoate (3e): This compound was prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (23.2 mg, 64% yield) as a colorless liquid. $[\alpha]_D^{25}$ = + 22.6 (c = 0.2 in EtOAc); enantiomeric excess: 85%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 10.694 min, t_R (minor) = 15.271 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 5.54 (d, *J* = 7.2 Hz, 1H), 5.03 (dt, *J* = 12.6, 6.3 Hz, 1H), 4.96 – 4.91 (m, 1H), 3.39 (q, *J* = 15.7 Hz, 2H), 3.20 (dd, *J* = 17.7, 7.5 Hz, 1H), 3.01 (dd, *J* = 17.7, 4.9 Hz, 1H), 2.78 (s, 3H), 1.24 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.6, 166.5, 138.9, 134.0, 129.1, 128.0, 69.7, 53.2, 49.8, 49.1, 41.5, 21.7; HRMS (ESI): Calcd for $C_{15}H_{20}ClNO_5S$[M + Na]+: 384.0643; found: 384.0650.

isopropyl 5-(2-chlorophenyl)-5-(methylsulfonamido)-3-oxopentanoate (3f): This compound was prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (25.3 mg, 70% yield) as a colorless liquid. $[\alpha]_D^{25}$ = + 21.9 (c = 0.3 in EtOAc); enantiomeric excess: 95%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 11.304 min, t_R (minor) = 17.528 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.37 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.30 (td, *J* = 7.6, 1.2 Hz, 1H), 7.24 (td, *J* = 7.6, 1.6 Hz, 1H), 5.83 (d, *J* = 7.9 Hz, 1H), 5.32 (td, *J* = 7.8, 4.6 Hz, 1H), 5.03 (dt, *J* = 12.5, 6.3 Hz, 1H), 3.48 – 3.36 (m, 2H), 3.21 (dd, *J* = 17.9, 7.8 Hz, 1H), 3.10 (dd, *J* = 17.9, 4.6 Hz, 1H), 2.84 (s, 3H), 1.23 (dd, *J* = 6.2, 3.5 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.5, 166.5, 137.7, 132.0, 130.1, 129.3, 128.7, 127.4, 69.5, 51.2, 49.6, 47.6, 41.1, 21.6; HRMS (ESI): Calcd for $C_{15}H_{20}ClNO_5S$[M + Na]+: 384.0643; found: 384.0650.

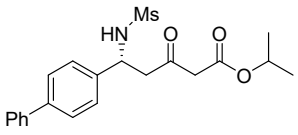
isopropyl 5-(methylsulfonamido)-3-oxo-5-(2-(trifluoromethyl)phenyl)pentanoate (3g): This compound was prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (23.7 mg, 60% yield) as a colorless liquid. $[\alpha]_D^{25}$ = + 10.6 (c = 0.2 in EtOAc); enantiomeric excess: 95%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 7.760 min, t_R (minor) = 17.604 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 5.85 (d, *J* = 5.4 Hz, 1H), 5.35 (d, *J* = 4.1 Hz, 1H), 5.05 (dt, *J* = 12.5, 6.3 Hz, 1H), 3.44 (q, *J* = 15.8 Hz, 2H), 3.07 (dd, *J* = 17.8, 9.2 Hz, 1H), 2.94 (dd, *J* = 17.9, 3.1 Hz, 1H), 2.88 (s, 3H), 1.24 (dd, *J* = 6.2, 2.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.3, 166.7, 140.0, 132.6, 128.5, 128.0, 126.2 (d, *J* = 5.8 Hz), 69.7, 49.6, 49.5, 49.3, 40.4, 21.6; HRMS (ESI): Calcd for $C_{16}H_{20}F_3NO_5S$[M + H]+: 418.0906; found: 418.0894.

methyl 4-(5-isopropoxy-1-(methylsulfonamido)-3,5-dioxopentyl)benzoate (3h): This compound was prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (29.3 mg, 76% yield) as a colorless liquid. $[\alpha]_D^{25}$ = + 8.5 (c = 0.3 in EtOAc); enantiomeric excess: 86%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 17.048 min, t_R (minor) = 21.725 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 5.71 (d, *J* = 7.2 Hz, 1H), 5.06 – 4.99 (m, 2H), 3.92 (s, 3H), 3.41 (q, *J* = 15.8 Hz, 2H), 3.23 (dd, *J* = 17.8, 7.8 Hz, 1H), 3.03 (dd, *J* = 17.8, 4.7 Hz, 1H), 2.78 (s, 3H), 1.23 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.4, 166.5, 145.4, 130.3, 130.0, 126.7, 126.6, 69.7, 53.5, 52.2, 49.7, 49.1, 41.5, 21.7; HRMS (ESI): Calcd for $C_{17}H_{23}NO_7S$[M + Na]+: 408.1087; found: 408.1101.

isopropyl (*R*)-5-(methylsulfonamido)-5-(3-nitrophenyl)-3-oxopentanoate (3i): This compound was prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (28.0 mg, 75% yield) as a yellow liquid. $[\alpha]_D^{25}$ = + 21.5 (c = 0.2 in EtOAc); enantiomeric excess: 91%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 17.084 min, t_R (minor) = 24.147 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27

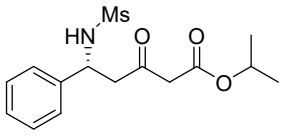
(s, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.60 – 7.51 (m, 1H), 5.92 (d, *J* = 6.8 Hz, 1H), 5.14 – 4.99 (m, 2H), 3.45 (q, *J* = 15.9 Hz, 2H), 3.27 (dd, *J* = 18.0, 8.3 Hz, 1H), 3.04 (dd, *J* = 18.0, 4.3 Hz, 1H), 2.91 (s, 3H), 1.24 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.1, 166.7, 148.6, 143.2, 133.0, 129.9, 122.9, 121.5, 69.8, 52.9, 49.5, 49.1, 41.3, 21.6; HRMS (ESI): Calcd for $C_{15}H_{20}N_2O_7S$[M + H]+: 373.1064; found: 373.1049.

isopropyl 5-([1,1'-biphenyl]-4-yl)-5-(methylsulfonamido)-3-oxopentanoate (3j): This compound



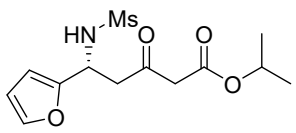
was prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (25.8 mg, 64% yield) as a white solid. MP = 125.0 – 125.1 °C, $[\alpha]_D^{25}$ = + 19.9 (c = 0.2 in EtOAc); enantiomeric excess: 80%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 21.185 min, t_R (minor) = 27.760 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 4H), 7.43 (dd, *J* = 7.9, 5.4 Hz, 4H), 7.35 (t, *J* = 7.3 Hz, 1H), 5.65 (d, *J* = 7.5 Hz, 1H), 5.07 – 4.98 (m, 2H), 3.49 – 3.35 (m, 2H), 3.25 (dd, *J* = 17.6, 7.5 Hz, 1H), 3.08 (dd, *J* = 17.6, 5.1 Hz, 1H), 2.77 (s, 3H), 1.23 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.7, 166.5, 141.1, 140.3, 139.3, 128.8, 127.7, 127.6, 127.1, 127.0, 69.5, 53.6, 49.9, 49.4, 41.5, 21.7; HRMS (ESI): Calcd for $C_{21}H_{25}NO_5S$[M + Na]+: 426.1346; found: 426.1338.

isopropyl 5-(methylsulfonamido)-3-oxo-5-phenylpentanoate (3k): This compound was prepared



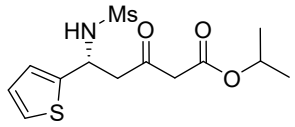
according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (17.1 mg, 52% yield) as a colorless liquid. $[\alpha]_D^{25}$ = + 17.5 (c = 0.1 in EtOAc); enantiomeric excess: 83%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 30.789 min, t_R (minor) = 37.288 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (s, 4H), 7.30 (d, *J* = 3.8 Hz, 1H), 5.66 (d, *J* = 7.1 Hz, 1H), 5.03 (dt, *J* = 12.0, 6.1 Hz, 1H), 4.96 (dd, *J* = 12.6, 6.7 Hz, 1H), 3.40 (q, *J* = 15.7 Hz, 2H), 3.21 (dd, *J* = 17.5, 7.4 Hz, 1H), 3.05 (dd, *J* = 17.5, 4.4 Hz, 1H), 2.71 (s, 3H), 1.23 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.7, 166.5, 140.2, 129.0, 128.2, 126.7, 69.5, 53.8, 49.9, 49.4, 41.5, 21.7; HRMS (ESI): Calcd for $C_{15}H_{21}NO_5S$[M + Na]+: 350.1032; found: 350.1020.

isopropyl 5-(furan-2-yl)-5-(methylsulfonamido)-3-oxopentanoate (3l): This compound was



prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (27.4 mg, 86% yield) as a colorless liquid. $[\alpha]_D^{25}$ = + 10.0 (c = 0.2 in EtOAc); enantiomeric excess: 83%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 9.370 min, t_R (minor) = 13.266 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (s, 1H), 6.33 (d, *J* = 2.8 Hz, 2H), 5.46 (d, *J* = 8.6 Hz, 1H), 5.03 (ddd, *J* = 15.2, 10.7, 6.6 Hz, 2H), 3.49 – 3.39 (m, 2H), 3.28 (dd, *J* = 17.7, 6.5 Hz, 1H), 3.14 (dd, *J* = 17.8, 5.6 Hz, 1H), 2.83 (s, 3H), 1.25 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.3, 166.4, 152.2, 142.4, 110.7, 107.7, 69.5, 49.8, 47.6, 46.5, 41.3, 21.7; HRMS (ESI): Calcd for $C_{13}H_{19}NO_6S$[M + Na]+: 340.0825; found: 340.0831.

isopropyl 5-(methylsulfonamido)-3-oxo-5-(thiophen-2-yl)pentanoate (3m): This compound was prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as



eluent, obtained (27.7 mg, 83% yield) as a colorless liquid. $[\alpha]_D^{25}$ = + 27.0 (c = 0.2 in EtOAc); enantiomeric excess: 82%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 12.675 min, t_R (minor) = 17.419 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 5.1, 0.9 Hz, 1H), 7.06 (d, *J* = 3.4 Hz, 1H), 6.96 (dd, *J* = 5.0, 3.6 Hz, 1H), 5.63 (d, *J* = 7.9 Hz, 1H), 5.22 (dd, *J* = 13.8, 6.1 Hz, 1H), 5.04 (dt, *J* = 12.5, 6.3 Hz, 1H), 3.48 – 3.39 (m, 2H), 3.31 (dd, *J* = 17.8, 6.6 Hz, 1H), 3.18 (dd, *J* = 17.8, 5.2 Hz, 1H), 2.78 (s, 3H), 1.24 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.5, 166.3, 143.8, 127.1, 125.7, 125.4, 69.5, 49.9, 49.7, 49.5, 41.6, 21.7; HRMS (ESI): Calcd for $C_{13}H_{19}NO_5S_2$[M + Na]+: 356.0597; found: 356.0592.

isopropyl (*E*)-5-(methylsulfonamido)-3-oxo-7-phenylhept-6-enoate (3n): This compound was prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (31.6 mg, 89% yield) as a yellow liquid. $[\alpha]_D^{25}$ = + 10.9 (c = 0.1 in EtOAc); enantiomeric excess: 72%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 21.790 min, t_R (minor) = 23.458 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dt, *J* = 27.8, 10.2 Hz, 5H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.26 (dd, *J* = 15.9, 7.7 Hz, 1H), 5.36 (d, *J* = 8.6 Hz, 1H), 5.05 (dt, *J* = 12.5, 6.4 Hz, 1H), 4.49 (d, *J* = 5.4 Hz, 1H), 3.49 – 3.39 (m, 2H), 3.04 (d, *J* = 5.0 Hz, 2H), 2.96 (s, 3H), 1.24 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.4, 166.3, 135.7, 132.7, 128.7, 128.3, 127.5, 126.6, 69.5, 52.5, 49.9, 48.2, 41.9, 21.7; HRMS (ESI): Calcd for $C_{17}H_{23}NO_5S$[M + Na]+: 376.1189; found: 376.1177.

isopropyl 5-(methylsulfonamido)-3-oxo-5-(p-tolyl)pentanoate (3o): This compound was prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (18.1 mg, 53% yield) as a colorless liquid. $[\alpha]_D^{25}$ = + 15.3 (c = 0.1 in EtOAc); enantiomeric excess: 78%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 11.214 min, t_R (minor) = 14.296 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.52 (d, *J* = 7.4 Hz, 1H), 5.02 (dt, *J* = 12.5, 6.3 Hz, 1H), 4.94 – 4.89 (m, 1H), 3.45 – 3.32 (m, 2H), 3.19 (dd, *J* = 17.5, 7.4 Hz, 1H), 3.03 (dd, *J* = 17.5, 5.2 Hz, 1H), 2.70 (s, 3H), 2.33 (s, 3H), 1.23 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.7, 166.4, 138.0, 137.2, 129.7, 126.6, 69.4, 53.7, 49.9, 49.4, 41.5, 21.6, 21.0; HRMS (ESI): Calcd for $C_{16}H_{23}NO_5S$[M + Na]+: 364.1189; found: 364.1176.

isopropyl 5-(2-fluorophenyl)-5-((4-methylphenyl)sulfonamido)-3-oxopentanoate (3p): This compound was prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (3:1, v/ v) as eluent, obtained (23.2 mg, 55% yield) as a colorless liquid. $[\alpha]_D^{25}$ = + 14.3 (c = 0.2 in EtOAc); enantiomeric excess: 87%. Daicel Chiralpak OD-H, hexane/iso-propanol= 85/15, flow rate 1.0 mL/min, 25℃: t_R (major) = 11.9 min, t_R (minor) = 17.6 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.19 – 7.10 (m, 4H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.85 (dd, *J* = 10.3, 8.7 Hz, 1H), 5.73 (d, *J* = 8.7 Hz, 1H), 5.03 – 4.95 (m, 2H), 3.36 – 3.23 (m, 2H), 3.17 (dd, *J* = 17.6, 6.1 Hz, 1H), 3.04 (dd, *J* = 17.6, 6.3 Hz, 1H), 2.34 (s, 3H), 1.19 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.2, 166.2, 159.8 (d, *J* = 245.4 Hz), 143.3, 137.0,

129.4, 129.3 (d, *J* = 3.8 Hz), 129.3 (d, *J* = 4.1 Hz), 127.1, 126.4 (d, *J* = 12.4 Hz), 124.1 (d, *J* = 3.3 Hz), 115.5, 115.4, 69.4, 49.8, 49.3, 48.1, 21.6, 21.4; HRMS (ESI): Calcd for $C_{21}H_{24}FNO_5S$[M + Na]+: 444.1251; found: 444.1266.

N-(4-chloro-1-(3-nitrophenyl)-3-oxobutyl)methanesulfonamide (3q): This compound was prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (25.6 mg, 80% yield) as a yellow liquid. $[\alpha]_D^{25}$ = + 27.7 (c = 0.2 in EtOAc); enantiomeric excess: 89%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 22.505 min, t_R (minor) = 30.043 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 5.86 (d, *J* = 7.6 Hz, 1H), 5.11 (dd, *J* = 12.4, 7.1 Hz, 1H), 4.08 (s, 2H), 3.34 (dd, *J* = 18.1, 7.6 Hz, 1H), 3.15 (dd, *J* = 18.1, 4.6 Hz, 1H), 2.90 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.1, 148.7, 142.7, 132.9, 130.1, 123.2, 121.5, 52.9, 48.0, 46.1, 41.7; HRMS (ESI): Calcd for $C_{11}H_{13}ClN_2O_5S$[M + H]+: 321.0306; found: 321.0303.

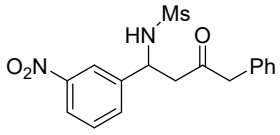
N-(4-bromo-1-(3-nitrophenyl)-3-oxobutyl)methanesulfonamide (3r): This compound was prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (22.9 mg, 63% yield) as a colorless liquid. $[\alpha]_D^{25}$ = + 29.3 (c = 0.2 in EtOAc); enantiomeric excess: 88%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 22.519 min, t_R (minor) = 29.975 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 6.06 (t, *J* = 10.1 Hz, 1H), 5.12 (dd, *J* = 12.5, 7.6 Hz, 1H), 4.18 – 4.06 (m, 2H), 3.34 (dd, *J* = 18.1, 8.1 Hz, 1H), 3.11 (dd, *J* = 18.0, 4.7 Hz, 1H), 2.90 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.9, 148.6, 143.0, 133.0, 130.1, 123.1, 121.5, 52.9, 48.2, 46.3, 41.5; HRMS (ESI): Calcd for $C_{11}H_{13}BrN_2O_5S$[M + H]+: 364.9801; found: 364.9787.

N-(1-(3-nitrophenyl)-3-oxohexyl)methanesulfonamide (3s): This compound was prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (24.0 mg, 76% yield) as a colorless liquid. $[\alpha]_D^{25}$ = + 27.7 (c = 0.2 in EtOAc); enantiomeric excess: 82%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 12.037 min, t_R (minor) = 15.733 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.14 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 5.92 (d, *J* = 7.5 Hz, 1H), 5.04 (dd, *J* = 12.2, 7.2 Hz, 1H), 3.09 (dd, *J* = 17.8, 7.2 Hz, 1H), 2.95 (dd, *J* = 17.8, 4.9 Hz, 1H), 2.89 (s, 3H), 2.37 (td, *J* = 7.2, 4.4 Hz, 2H), 1.56 (dd, *J* = 14.7, 7.4 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.1, 148.6, 143.4, 133.0, 129.9, 122.9, 121.5, 53.1, 48.7, 45.3, 41.6, 16.9, 13.5; HRMS (ESI): Calcd for $C_{13}H_{18}N_2O_5S$[M + Na]+: 337.0829; found: 337.0842.

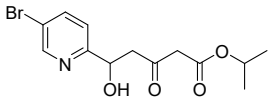
N-(4-methyl-1-(3-nitrophenyl)-3-oxopentyl)methanesulfonamide (3t): This compound was prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (16.4

mg, 52% yield) as a colorless liquid. $[\alpha]_D^{25}$ = + 25.0 (c = 0.2 in EtOAc); enantiomeric excess: 85%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 14.644 min, t_R (minor) = 18.547 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 1H), 5.95 (d, *J* = 7.3 Hz, 1H), 5.04 (dd, *J* = 12.2, 7.1 Hz, 1H), 3.15 (dd, *J* = 17.8, 7.1 Hz, 1H), 2.99 (dd, *J* = 17.8, 4.8 Hz, 1H), 2.90 (s, 3H), 2.55 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.04 (dd, *J* = 9.2, 7.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.8, 148.5, 143.5, 133.0, 129.9, 122.9, 121.4, 53.2, 46.5, 41.6, 41.3, 17.7, 17.7; HRMS (ESI): Calcd for $C_{13}H_{18}N_2O_5S$[M + Na]+: 337.0829; found: 337.0842.

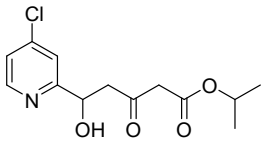
N-(1-(3-nitrophenyl)-3-oxo-4-phenylbutyl)methanesulfonamide (3u): This compound was prepared according to the typical procedure, which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (29.6 mg, 81% yield) as a colorless liquid. $[\alpha]_D^{25}$ = + 32.9 (c = 0.3 in EtOAc); enantiomeric excess: 93%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 80/ 20, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 25.584 min, t_R (minor) = 32.251 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 – 8.05 (m, 2H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 7.4 Hz, 3H), 7.07 (d, *J* = 6.7 Hz, 2H), 5.95 (dd, *J* = 6.7, 3.7 Hz, 1H), 5.00 (dd, *J* = 12.7, 7.1 Hz, 1H), 3.66 (s, 2H), 3.12 (dd, *J* = 17.8, 7.2 Hz, 1H), 2.96 (dd, *J* = 17.8, 4.8 Hz, 1H), 2.83 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.3, 148.5, 143.1, 132.9, 132.7, 129.8, 129.4, 128.9, 127.4, 122.8, 121.4, 53.1, 50.6, 47.8, 41.5; HRMS (ESI): Calcd for $C_{17}H_{18}N_2O_5S$[M + H]+: 363.1009; found: 363.1005.



isopropyl 5-(5-bromopyridin-2-yl)-5-hydroxy-3-oxopentanoate (5a): which purified using petroleum ether/ EtOAc (3:1, v/ v) as eluent, obtained (29.8 mg, 90% yield) as a colorless liquid. $[\alpha]_D^{25}$ = +30.3 (c = 0.3 in EtOAc); enantiomeric excess: 79%. Daicel Chiralpak AD-H, hexane/ iso-propanol = 85/ 15, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 10.084 min, t_R (minor) = 10.649 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.8 Hz, 1H), 7.83 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 5.18 (dd, *J* = 7.9, 3.3 Hz, 1H), 5.05 (dt, *J* = 18.3, 6.0 Hz, 1H), 3.89 (br, 1H), 3.49 (s, 2H), 3.18 (dd, *J* = 17.4, 3.7 Hz, 1H), 3.02 (dd, *J* = 17.3, 8.2 Hz, 1H), 1.25 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.8, 166.3, 159.6, 149.6, 139.5, 121.9, 119.4, 69.6, 69.3, 50.3, 49.7, 21.7; HRMS (ESI): Calcd for $C_{13}H_{16}BrNO_4$[M + Na]+: 352.0155; found: 352.0143.



isopropyl 5-(4-chloropyridin-2-yl)-5-hydroxy-3-oxopentanoate (5b): which purified using petroleum ether/ EtOAc (3:1, v/ v) as eluent, obtained (24.4 mg, 85% yield) as a colorless liquid. $[\alpha]_D^{25}$ = +33.7 (c = 0.2 in EtOAc); enantiomeric excess: 70%. Daicel Chiralpak AD-H, hexane/ iso-propanol = 85/ 15, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 10.681 min, t_R (minor) = 9.328 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 5.3 Hz, 1H), 7.54 (s, 1H), 7.21 (dd, *J* = 5.1, 1.6 Hz, 1H), 5.20 (dd, *J* = 8.1, 2.9 Hz, 1H), 5.05 (dt, *J* = 12.7, 6.3 Hz, 1H), 4.01 (br, 1H), 3.50 (s, 2H), 3.20 (dd, *J* = 17.4, 3.4 Hz, 1H), 3.01 (dd, *J* = 17.4, 8.4 Hz, 1H), 1.26 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.7, 166.4, 162.9, 149.4, 145.1, 122.9, 121.0, 69.6, 69.3, 50.2, 49.7, 21.7; HRMS (ESI): Calcd for $C_{13}H_{16}ClNO_4$[M + Na]+: 308.0660; found: 308.0647.



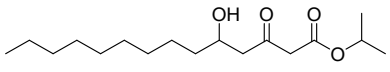
isopropyl 5-(3-chloropyridin-2-yl)-5-hydroxy-3-oxopentanoate (5c): which purified using petroleum ether/ EtOAc (3:1, v/ v) as eluent, obtained (23.5 mg, 82% yield) as a colorless liquid. $[\alpha]_D^{25}$ = +36.9 (c = 0.2 in EtOAc); enantiomeric excess: 73%. Daicel Chiralpak AD-H, hexane/ iso-propanol = 85/ 15, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 10.486 min, t_R (minor) = 11.985 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.3 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.25 (dd, *J* = 8.0, 5.0 Hz, 1H), 5.51 (s, 1H), 5.06 (dt, *J* = 12.5, 6.4 Hz, 1H), 4.49 (d, *J* = 6.6 Hz, 1H), 3.61 – 3.51 (m, 2H), 3.08 (d, *J* = 15.9 Hz, 1H), 2.86 (dd, *J* = 15.9, 8.9 Hz, 1H), 1.26 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.0, 166.6, 156.8, 146.5, 137.7, 129.4, 124.0, 69.0, 66.8, 50.5, 48.8, 21.7; HRMS (ESI): Calcd for $C_{13}H_{16}ClNO_4$[M + Na]+: 308.0660; found: 308.0647.

isopropyl 5-(5-chloropyridin-2-yl)-5-hydroxy-3-oxopentanoate (5d): which purified using petroleum ether/ EtOAc (3:1, v/ v) as eluent, obtained (27.8 mg, 97% yield) as a colorless liquid. $[\alpha]_D^{25}$ = +38.3 (c = 0.2 in EtOAc); enantiomeric excess: 72%. Daicel Chiralpak AD, hexane/iso-propanol= 85/15, flow rate 1.0 mL/min, 25°C: t_R (major) = 8.8 min, t_R (minor) = 9.2 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 5.25 – 5.16 (m, 1H), 5.09 – 5.01 (m, 1H), 3.96 (s, 1H), 3.49 (s, 2H), 3.18 (dd, *J* = 17.4, 3.5 Hz, 1H), 3.02 (dd, *J* = 17.4, 8.2 Hz, 1H), 1.25 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.9, 166.4, 159.2, 147.4, 136.6, 130.8, 121.4, 69.5, 69.2, 50.3, 49.8, 21.7, 21.7; HRMS (ESI): Calcd for $C_{13}H_{16}ClNO_4$[M + Na]+: 308.0660; found: 308.0647.

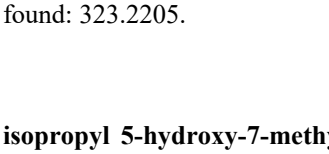
isopropyl 5-hydroxy-3-oxo-7-phenylheptanoate (5e): which purified using petroleum ether/ EtOAc (3:1, v/ v) as eluent, obtained (21.8 mg, 78% yield) as a colorless liquid. $[\alpha]_D^{25}$ = -5.7(c = 0.2 in EtOAc); enantiomeric excess: 69%. Daicel Chiralpak OD-H, hexane/ iso-propanol = 85/ 15, flow rate 1.0 mL/ min, 25 °C: t_R (major) = 24.364 min, t_R (minor) = 16.665 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.6 Hz, 2H), 7.21 – 7.16 (m, 3H), 5.05 (dt, *J* = 12.5, 6.2 Hz, 1H), 4.12 – 4.05 (m, 1H), 3.42 (s, 2H), 2.84 – 2.77 (m, 1H), 2.68 (ddd, *J* = 13.3, 8.7, 3.5 Hz, 3H), 1.82 (ddd, *J* = 14.3, 8.8, 4.5 Hz, 1H), 1.75 – 1.67 (m, 1H), 1.25 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.8, 166.5, 141.7, 128.5, 128.4, 125.9, 69.3, 66.8, 50.2, 49.6, 38.1, 31.7, 21.7; HRMS (ESI): Calcd for $C_{16}H_{22}O_4$[M + Na]+: 301.1410; found: 301.1418.

isopropyl 5-hydroxy-7-(5-methylfuran-2-yl)-3-oxoheptanoate (5f): which purified using petroleum ether/ EtOAc (3:1, v/ v) as eluent, obtained (21.6 mg, 76% yield) as a colorless liquid. $[\alpha]_D^{25}$ = -6.0(c = 0.2 in EtOAc); enantiomeric excess: 65%. Daicel Chiralpak OD, hexane/iso-propanol= 95/5, flow rate 1.0 mL/min, 25°C: t_R (major) = 11.5 min, t_R (minor) = 12.5 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85 (d, *J* = 17.0 Hz, 2H), 5.06 (dt, *J* = 12.5, 6.2 Hz, 1H), 4.11 (s, 1H), 3.43 (s, 2H), 2.90 (s, 1H), 2.79 – 2.62 (m, 4H), 2.24 (s, 3H), 1.78 (dt, *J* = 16.1, 7.0 Hz, 2H), 1.26 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.8, 166.5, 153.4, 150.5, 105.9, 105.8, 69.3, 66.7, 50.2, 49.5, 34.8, 24.1, 21.7, 21.7, 13.5; HRMS (ESI): Calcd for $C_{15}H_{22}O_5$[M + Na]$^+$: 305.1359; found: 305.1366.

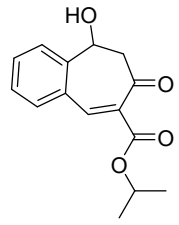
isopropyl 5-hydroxy-3-oxotetradecanoate (5g): which purified using petroleum ether/ EtOAc (3:1, v/ v) as eluent, obtained (13.9 mg, 46% yield) as a colorless liquid. $[\alpha]_D^{25}$ = +2.6(c = 0.1 in EtOAc); enantiomeric excess: 67%. Daicel Chiralpak OD, hexane/iso-propanol= 95/5, flow rate 1.0 mL/min, 25℃: t_R (major) = 6.9 min, t_R (minor) = 7.4 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 – 4.99 (m, 1H), 4.07 (s, 1H), 3.44 (s, 2H), 2.74 (dd, *J* = 17.5, 2.5 Hz, 1H), 2.63 (dd, *J* = 17.5, 8.9 Hz, 1H), 1.41 (s, 2H), 1.27 (d, *J* = 5.8 Hz, 20H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.9, 166.5, 69.2, 67.6, 50.3, 49.6, 36.5, 31.9, 29.6, 29.5, 29.5, 29.3, 25.4, 22.7, 21.7, 14.1; HRMS (ESI): Calcd for $C_{17}H_{32}O_4$[M + Na]+: 323.2193; found: 323.2205.



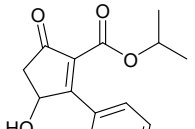
isopropyl 5-hydroxy-7-methyl-3-oxooctanoate (5h): which purified using petroleum ether/ EtOAc (3:1, v/ v) as eluent, obtained (13.9 mg, 60% yield) as a colorless liquid. $[\alpha]_D^{25}$ = +5.0(c = 0.1 in EtOAc); enantiomeric excess: 75%. Daicel Chiralpak OD, hexane/iso-propanol= 97/3, flow rate 0.7 mL/min, 25℃: t_R (major) = 11.6 min, t_R (minor) = 12.3 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 – 5.00 (m, 1H), 4.22 – 4.10 (m, 1H), 3.44 (d, *J* = 1.1 Hz, 2H), 2.72 (dd, *J* = 17.6, 3.0 Hz, 1H), 2.62 (dd, *J* = 17.6, 8.8 Hz, 1H), 1.83 – 1.75 (m, 1H), 1.52 – 1.44 (m, 1H), 1.27 (d, *J* = 6.3 Hz, 6H), 1.20 – 1.12 (m, 1H), 0.92 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.0, 166.5, 69.2, 65.7, 50.3, 50.1, 45.5, 24.4, 23.3, 22.0, 21.7; HRMS (ESI): Calcd for $C_{12}H_{22}O_4$[M + Na]+: 253.1410; found: 253.1422.



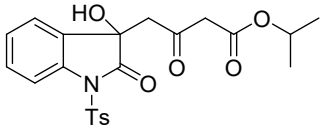
isopropyl 5-hydroxy-7-oxo-6,7-dihydro-5H-benzo[7]annulene-8-carboxylate (5i): which purified using petroleum ether/ EtOAc (3:1, v/ v) as eluent, obtained (9.6 mg, 37% yield) as a colorless liquid. $[\alpha]_D^{25}$ = -63.4(c = 0.1 in EtOAc); enantiomeric excess: 40%. Daicel Chiralpak OD-H, hexane/iso-propanol= 85/15, flow rate 1.0 mL/min, 25℃: t_R (major) = 8.2 min, t_R (minor) = 9.3 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 17.0, 7.8 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 5.22 – 5.16 (m, 2H), 3.23 – 3.10 (m, 2H), 1.34 (t, *J* = 5.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.3, 165.7, 143.6, 143.4, 134.0, 133.9, 131.5, 130.4, 128.3, 126.1, 69.4, 67.8, 52.8, 21.8, 21.8; HRMS (ESI): Calcd for $C_{15}H_{16}O_4$[M + H]+: 261.1122; found: 261.1137.



isopropyl 3-hydroxy-2-(4-nitrophenyl)-5-oxocyclopent-1-ene-1-carboxylate (5j): which purified using petroleum ether/ EtOAc (3:1, v/ v) as eluent, obtained (23.0 mg, 75% yield) as a colorless liquid. $[\alpha]_D^{25}$ = -58.6(c = 0.1 in EtOAc); enantiomeric excess: 61%. Daicel Chiralpak OD-H, hexane/iso-propanol= 85/15, flow rate 1.0 mL/min, 25℃: t_R (major) = 11.7 min, t_R (minor) = 16.3 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.7 Hz, 2H), 7.76 (d, *J* = 8.6 Hz, 2H), 5.43 (d, *J* = 5.0 Hz, 1H), 5.15 (dt, *J* = 12.4, 6.3 Hz, 1H), 3.08 (dd, *J* = 18.7, 6.4 Hz, 1H), 2.62 (d, *J* = 18.7 Hz, 1H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.18 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 168.1, 162.9, 148.9, 138.4, 136.6, 129.4, 123.8, 70.2, 70.1, 44.8, 21.6, 21.4; HRMS (ESI): Calcd for $C_{15}H_{15}NO_6$[M + H]+: 306.0972; found: 306.0964.

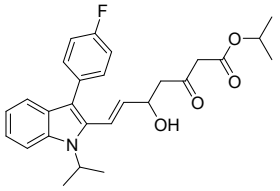


isopropyl 4-(3-hydroxy-2-oxo-1-tosylindolin-3-yl)-3-oxobutanoate (5k): which purified using petroleum ether/ EtOAc (1:1, v/ v) as eluent, obtained (39.2 mg, 88%



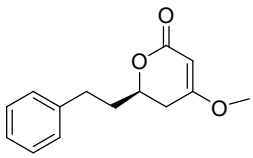
yield) as a colorless liquid. $[\alpha]_D^{25}$ = -58.6(c = 0.1 in EtOAc); enantiomeric excess: 75%. Daicel Chiralpak AD, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25℃: t_R (major) = 34.0 min, t_R (minor) = 25.8 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.32 (dd, *J* = 16.3, 7.7 Hz, 3H), 7.17 (t, *J* = 7.5 Hz, 1H), 4.97 (dt, *J* = 12.3, 6.1 Hz, 1H), 3.29 (ddd, *J* = 58.7, 35.8, 17.6 Hz, 4H), 2.41 (s, 3H), 1.20 (d, *J* = 6.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.3, 174.6, 166.0, 145.8, 139.3, 134.7, 130.8, 129.8, 128.2, 128.0, 125.3, 124.2, 113.9, 73.7, 69.5, 49.9, 49.1, 21.7, 21.7, 21.6; HRMS (ESI): Calcd for $C_{22}H_{23}NO_7S$[M + Na]+: 468.1087; found: 468.1081.

isopropyl (E)-7-(3-(4-fluorophenyl)-1-isopropyl-1H-indol-2-yl)-5-hydroxy-3-oxohept-6-enoate (5l):

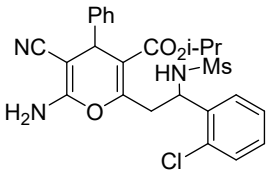


which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (15.1 mg, 33% yield) as a yellow liquid. $[\alpha]_D^{25}$ = +36.0(c = 0.2 in EtOAc); enantiomeric excess: 69%. Daicel Chiralpak IA, hexane/iso-propanol= 95/5, flow rate 1.0 mL/min, 25℃: t_R (major) = 12.0 min, t_R (minor) = 15.3 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.38 (dd, *J* = 8.5, 5.6 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.13 – 7.05 (m, 3H), 6.73 (d, *J* = 16.0 Hz, 1H), 5.67 (dd, *J* = 16.0, 5.3 Hz, 1H), 5.06 (dt, *J* = 12.5, 6.3 Hz, 1H), 4.83 (dt, *J* = 14.0, 7.0 Hz, 1H), 4.72 – 4.65 (m, 1H), 3.41 (s, 2H), 2.67 (d, *J* = 5.7 Hz, 2H), 1.65 (d, *J* = 7.0 Hz, 6H), 1.25 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.8, 166.4, 161.5 (d, *J* = 244.9 Hz), 136.9, 135.1, 133.3, 132.0, 132.0, 131.7 (d, *J* = 3.3 Hz), 128.4, 121.8, 119.7, 119.5, 119.3, 115.4, 115.2, 114.8, 111.6, 69.4, 68.1, 50.2, 48.9, 47.8, 21.8, 21.7; HRMS (ESI): Calcd for $C_{27}H_{30}FNO_4$[M+ H]+: 452.2232; found: 452.2243.

(R)-4-methoxy-6-phenethyl-5,6-dihydro-2H-pyran-2-one: which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (15.3 mg, 66% yield) as a colorless crystals. $[\alpha]_D^{25}$ = +91.1(c = 0.2 in EtOAc); enantiomeric excess: 69%. Daicel Chiralpak OB, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25℃: t_R (major) = 28.1 min, t_R (minor) = 35.5 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 5.13 (s, 1H), 4.35 (ddt, *J* = 12.1, 8.1, 4.0 Hz, 1H), 3.72 (s, 3H), 2.91 – 2.83 (m, 1H), 2.81 – 2.73 (m, 1H), 2.50 (dd, *J* = 16.9, 12.1 Hz, 1H), 2.30 (dd, *J* = 17.0, 3.7 Hz, 1H), 2.12 (dtd, *J* = 14.1, 8.8, 5.6 Hz, 1H), 1.96 – 1.88 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 167.3, 140.9, 128.5, 128.5, 126.2, 90.3, 74.8, 56.0, 36.3, 33.0, 31.0.



isopropyl 6-amino-2-(2-(2-chlorophenyl)-2-(methylsulfonamido)ethyl)-5-cyano-4-phenyl-4H-pyran-3-carboxylate (7): which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained (42.5 mg, 82% yield) as a yellow solid. MP = 192.6 – 192.7 ℃, major:$[\alpha]_D^{25}$ = -25.0(c = 0.1 in EtOAc); enantiomeric excess: 98%. Daicel Chiralpak AS-H, hexane/iso-propanol= 85/15, flow rate 1.0 mL/min, 25℃: t_R (major) = 26.405 min, t_R (minor) = 22.270 min; minor:$[\alpha]_D^{25}$ = +21.1(c = 0.2 in EtOAc); enantiomeric excess: 95%. Daicel Chiralpak IA, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25℃: t_R (major) = 11.210 min, t_R (minor) = 9.822 min; ^{1}H NMR (400 MHz, DMSO) δ 8.07 (d, *J* = 9.0 Hz, 1H), 7.68 (dd, *J* = 5.9, 3.6 Hz, 1H), 7.47 (dd, *J* = 5.9, 3.4 Hz, 1H), 7.34 (dd, *J* = 5.9, 3.5 Hz, 2H), 7.16 (q, *J* = 6.0 Hz, 3H), 6.79 (s, 2H), 6.76 – 6.72 (m, 2H), 5.36 (dd, *J* = 16.1, 8.8 Hz, 1H), 4.77 – 4.70 (m, 1H), 4.18 (s, 1H), 3.54 (dd, *J* = 14.1, 8.9 Hz, 1H), 3.19 (dd, *J* = 13.9, 6.9 Hz, 1H), 2.68 (s, 3H), 1.09 (d, *J* = 6.2 Hz, 3H), 0.83 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR



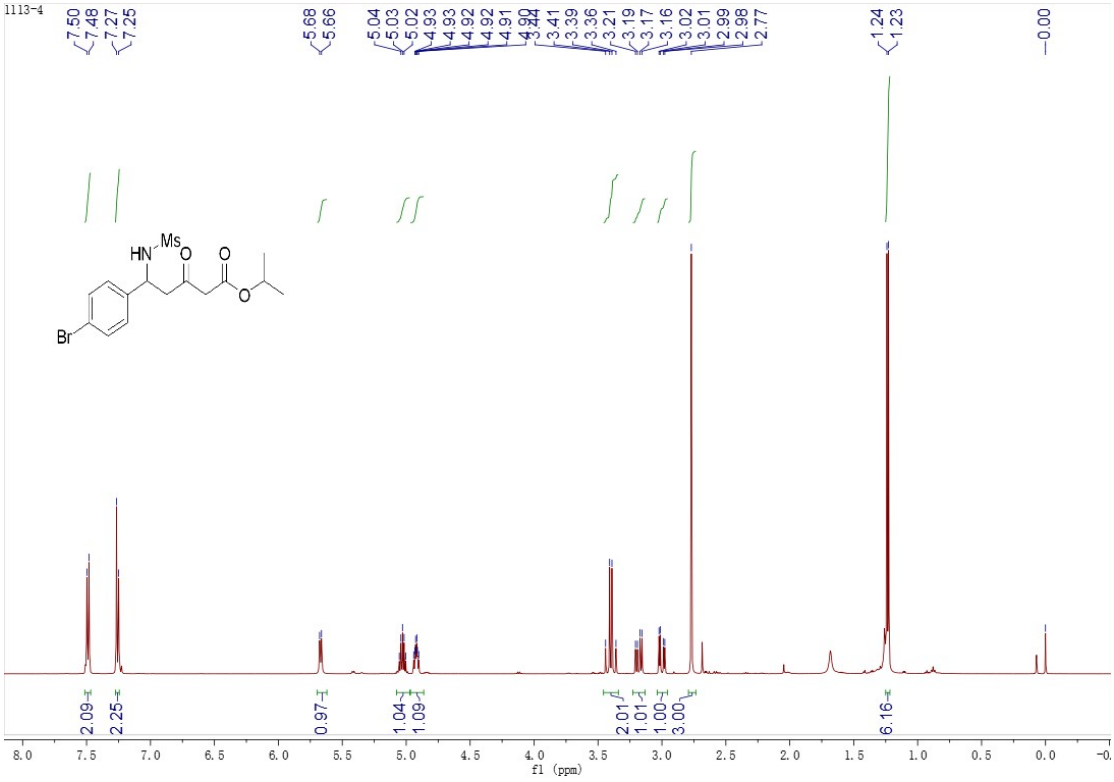
(126 MHz, DMSO) δ 164.8, 158.4, 154.9, 144.9, 138.9, 132.4, 129.8, 129.7, 128.7, 128.0, 127.5, 127.0, 120.1, 109.9, 68.3, 57.4, 51.3, 41.4, 39.4, 37.3, 21.8, 21.3; HRMS (ESI): Calcd for $C_{25}H_{26}ClN_3O_5S$[M + H]+: 516.1354; found: 516.1339.

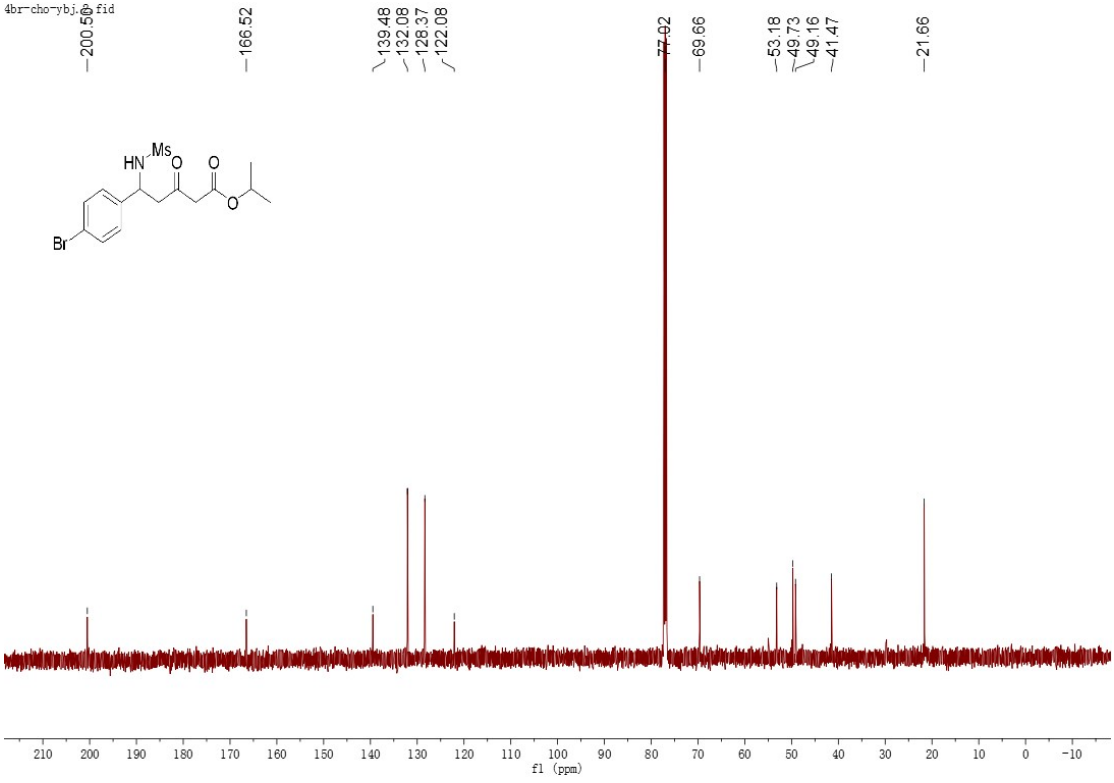
2-amino-7-(3-chloropyridin-2-yl)-5-oxo-4-phenyl-7,8-dihydro-4H,5H-pyrano[4,3-b]pyran-3-carbonitrile (8): which purified using petroleum ether/ EtOAc (1:1, v/ v) as eluent, obtained (32.9 mg, 87% yield) as a white solid. MP = 216.7 – 216.8 °C, $[\alpha]_D^{25}$ = -27.0(c = 0.1 in EtOAc), major: enantiomeric excess: 66%; minor: enantiomeric excess: 62%. Daicel Chiralpak AD, hexane/isopropanol= 70/30, flow rate 1.0 mL/min, 25℃: t_R (major) = 7.0 min, t_R (minor) = 13.7 min; $t_{R'}$ (major) = 12.8 min, $t_{R'}$ (minor) = 8.8 min; ^{1}H NMR (500 MHz, DMSO) δ 8.64 (s, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.62 – 7.52 (m, 1H), 7.37 (t, *J* = 7.1 Hz, 2H), 7.31 (d, *J* = 7.3 Hz, 2H), 7.27 (t, *J* = 7.0 Hz, 1H), 7.17 (s, 2H), 6.00 (d, *J* = 10.1 Hz, 1H), 4.29 (s, 1H), 3.62 (dd, *J* = 17.2, 12.0 Hz, 1H), 2.89 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR (126 MHz, DMSO) δ 164.0, 159.7, 158.5, 151.2, 148.1, 144.5, 138.8, 131.8, 129.0, 128.1, 127.5, 126.6, 119.9, 104.5, 73.8, 58.5, 36.9, 28.3; HRMS (ESI): Calcd for $C_{20}H_{14}ClN_3O_3$[M + H]+: 380.0796; found: 380.0795.

Isopropyl 6-amino-2-(2-(2-chlorophenyl)-2-hydroxyethyl)-5-cyano-4-phenyl-4H-pyran-3-carboxylate (9): which purified using petroleum ether/ EtOAc (2:1, v/ v) as eluent, obtained as mixtures of diastereomers, white solid (40.0 mg, 91% yield). MP = 144.2 – 144.3 °C, $[\alpha]_D^{25}$ = +28.3(c = 0.2 in EtOAc), major: enantiomeric excess: 78%; minor: enantiomeric excess: 75%. Daicel Chiralpak AD, hexane/isopropanol= 85/15, flow rate 1.0 mL/min, 25℃: t_R (major) = 11.0 min, t_R (minor) = 13.3 min; $t_{R'}$ (major) = 14.0 min, $t_{R'}$ (minor) = 18.7 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.6 Hz, 2H), 7.70 (dd, *J* = 7.1, 4.4 Hz, 2H), 7.29 (d, *J* = 6.6 Hz, 3H), 7.22 (ddd, *J* = 18.9, 9.4, 5.5 Hz, 9H), 5.44 (td, *J* = 8.3, 4.3 Hz, 2H), 4.84 (dtd, *J* = 18.7, 12.5, 6.2 Hz, 2H), 4.68 (s, 2H), 4.61 (s, 2H), 4.45 (s, 2H), 3.49 (dd, *J* = 14.2, 8.7 Hz, 1H), 3.39 (dd, *J* = 13.9, 8.1 Hz, 1H), 3.19 (dd, *J* = 13.9, 4.4 Hz, 1H), 3.08 (dd, *J* = 14.2, 3.8 Hz, 1H), 1.13 (dd, *J* = 13.4, 6.2 Hz, 6H), 0.88 (d, *J* = 6.2 Hz, 3H), 0.84 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 165.3, 157.6, 157.5, 157.4, 155.5, 155.2, 146.9, 146.7, 143.7, 143.5, 137.6, 137.5, 129.5, 129.3, 128.6, 128.5, 127.7, 127.7, 127.1, 127.1, 124.0, 123.9, 119.1, 110.7, 110.6, 68.6, 68.4, 68.0, 67.8, 61.9, 61.8, 39.2, 39.1, 38.1, 37.7, 21.8, 21.7, 21.1, 21.1; HRMS (ESI): Calcd for $C_{24}H_{23}ClN_2O_4$[M + H]+: 440.1372; found: 440.1385.

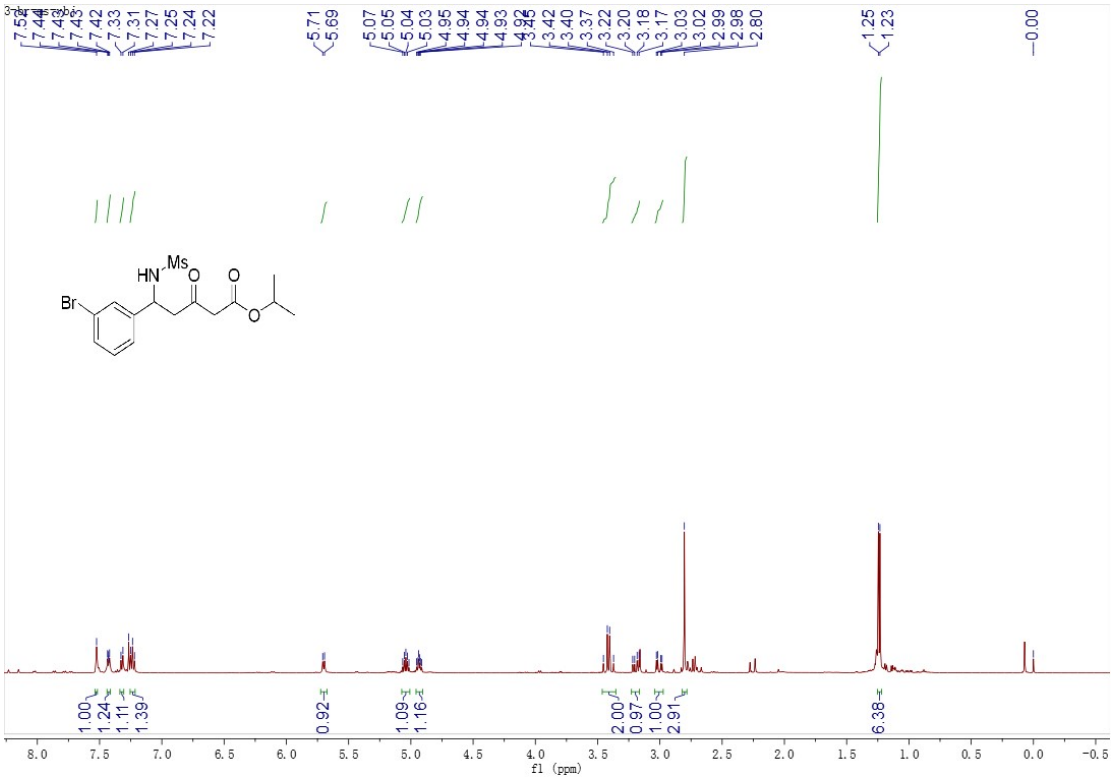
10. The NMR of 3, 5-9

3a





3b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3.22
3.20
3.18
3.17
3.03
3.02
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2.98
2.80
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1.23
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Ms
O
O
O
Br
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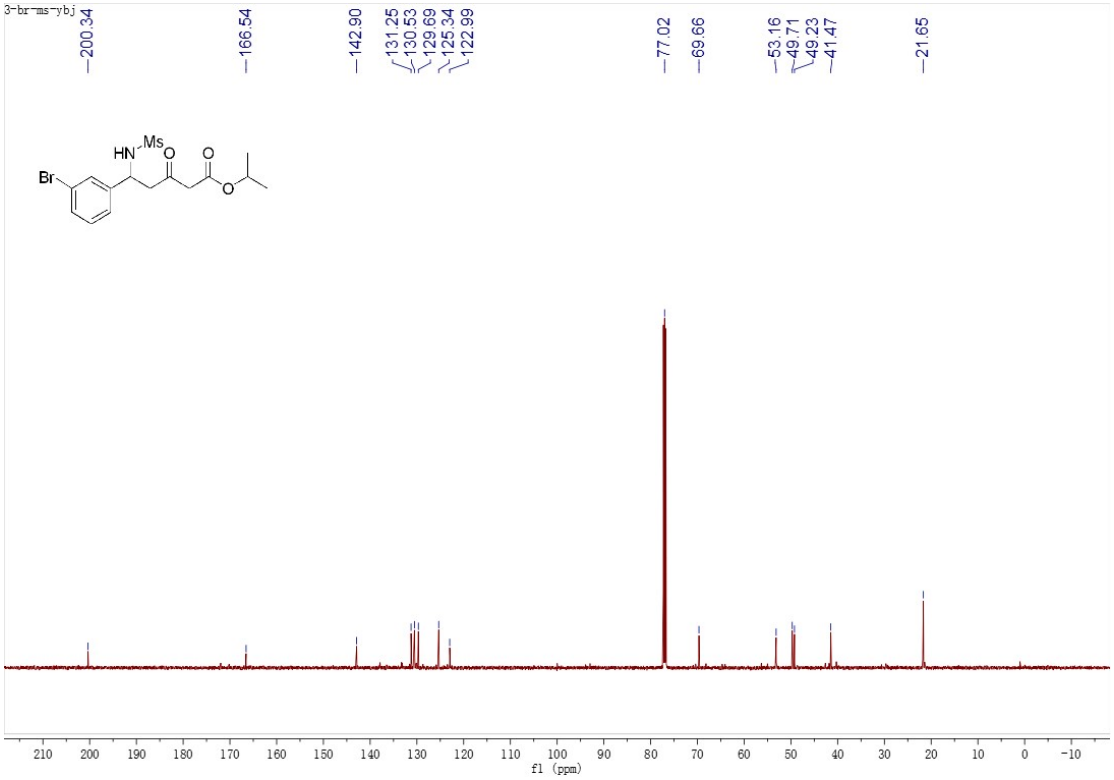
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Ms
O
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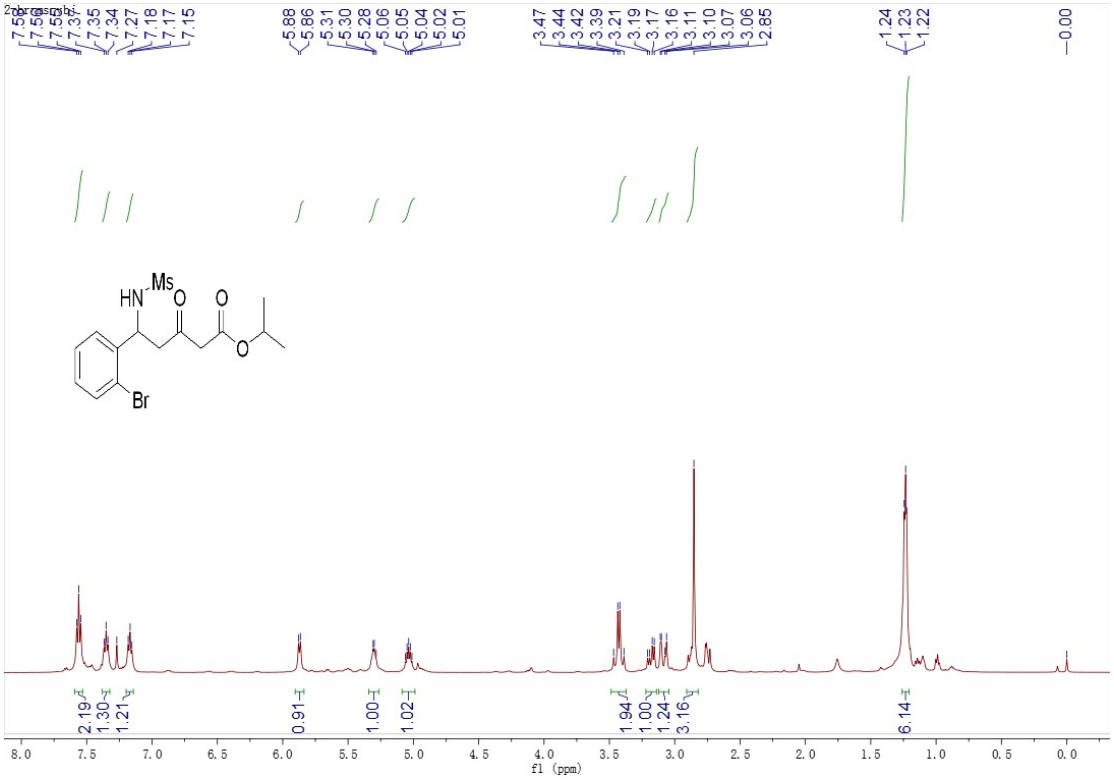
O
Br
f1 (ppm)

3c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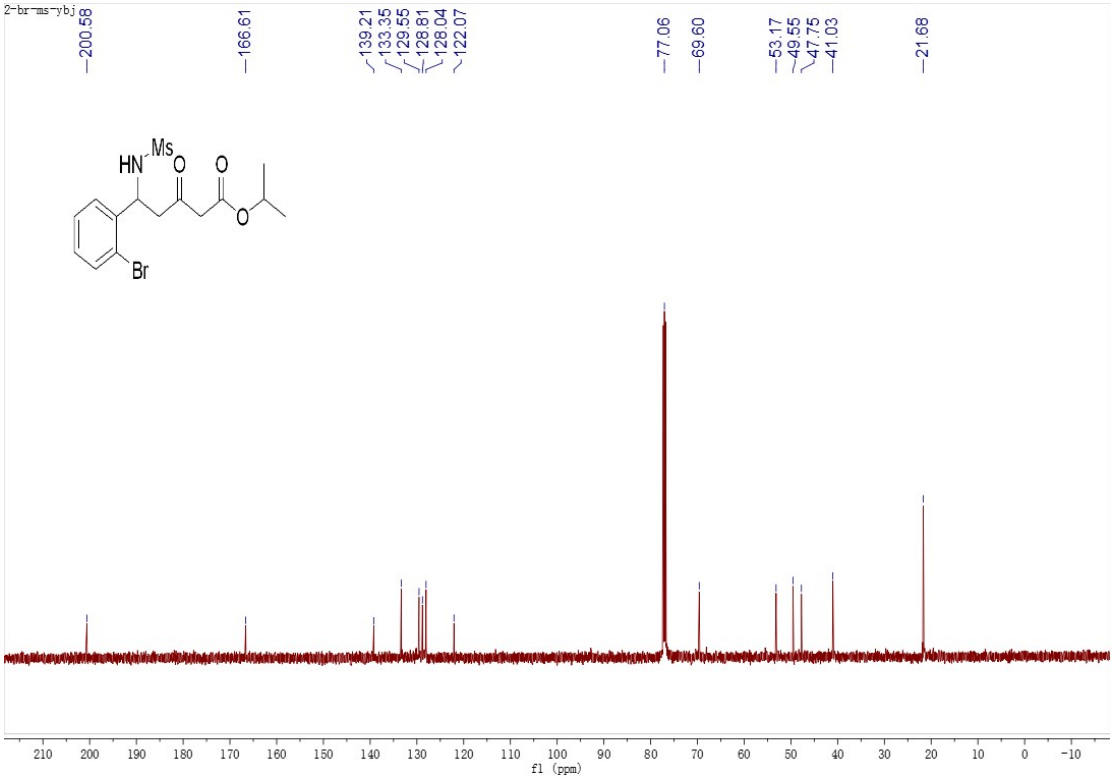
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Ms
O
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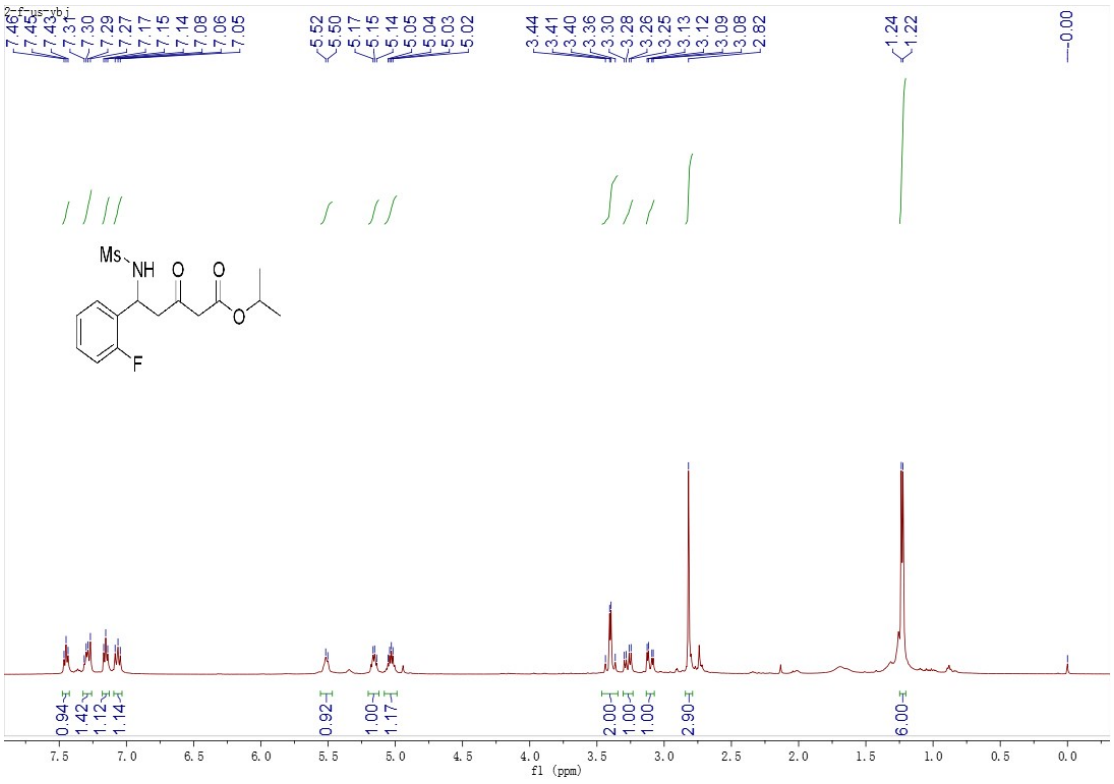
Br
f1 (ppm)

3d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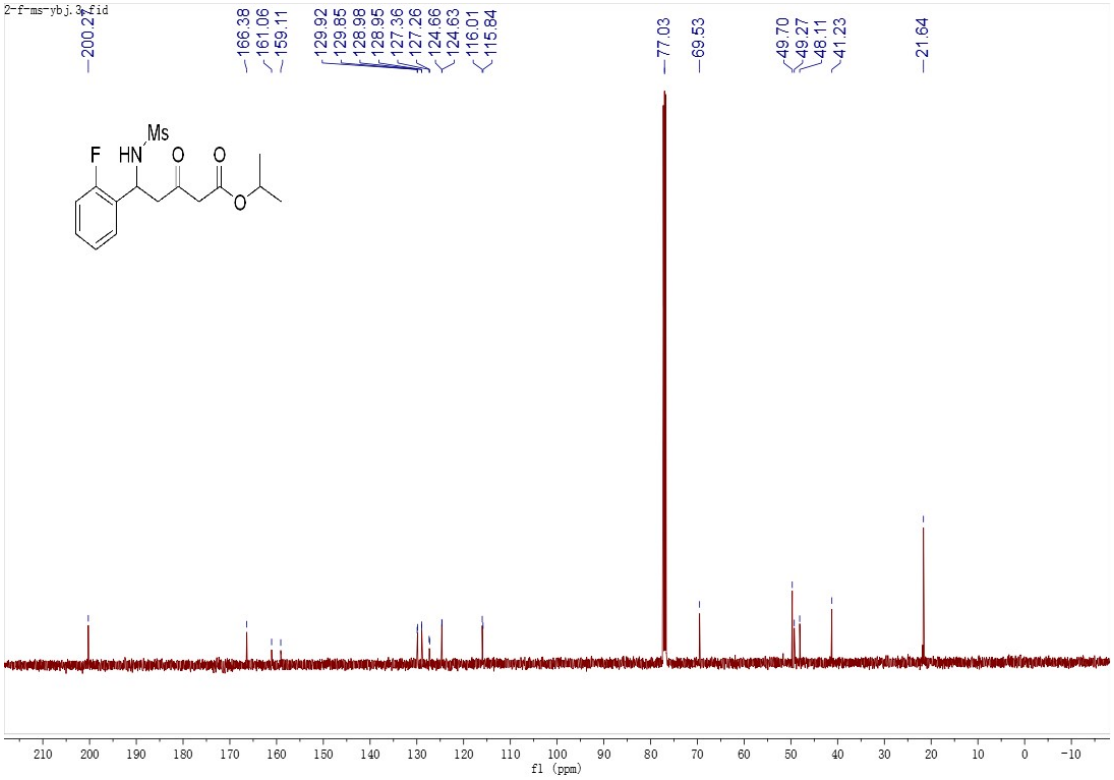
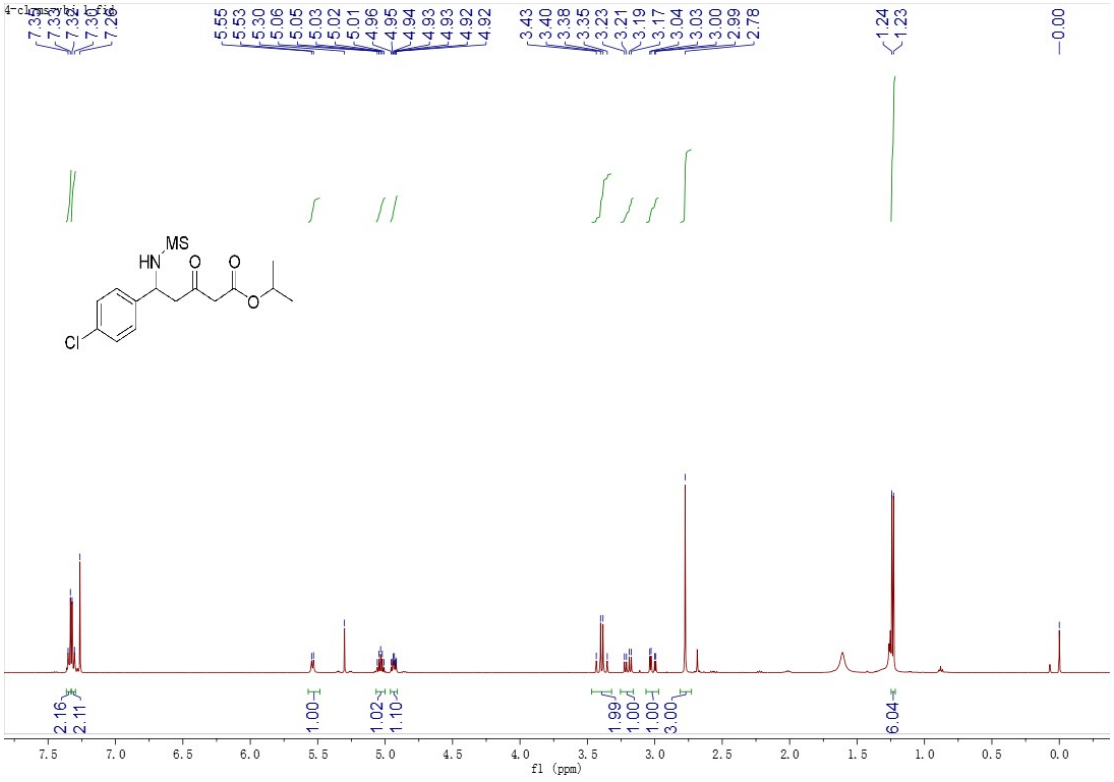
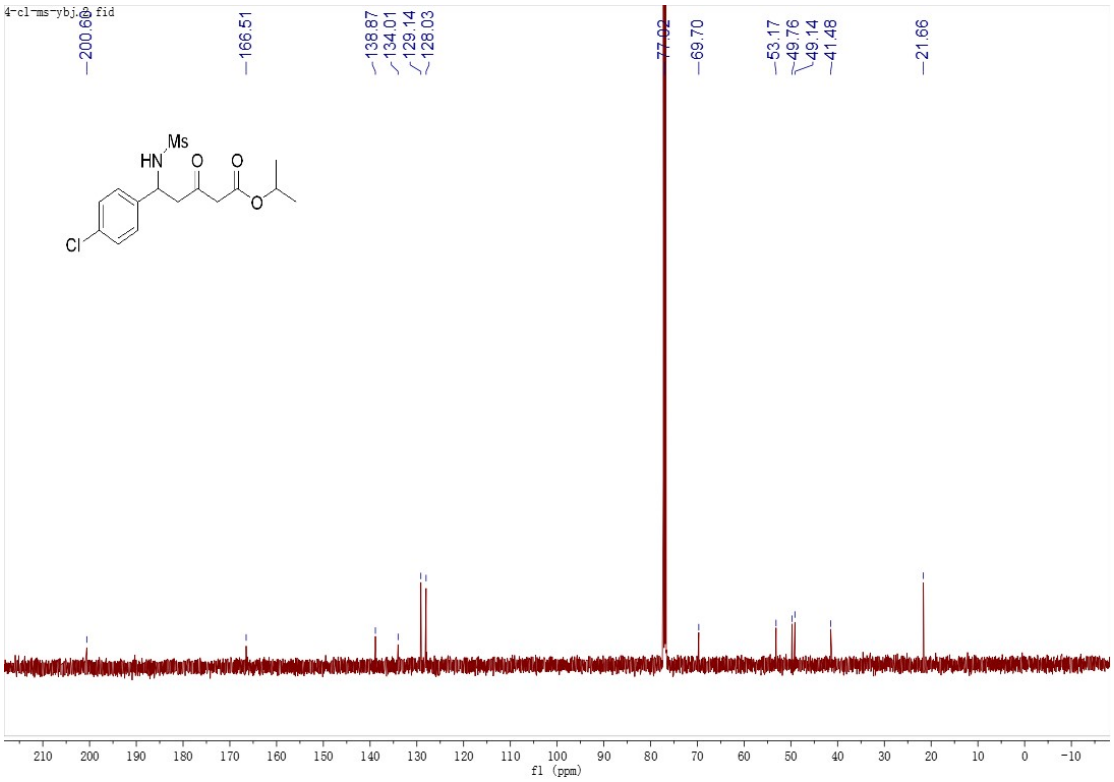
O
O
O
F
0.94
1.42
1.12
1.14
0.92
1.00
1.17
2.00
1.00
1.00
2.90
6.00
f1 (ppm)

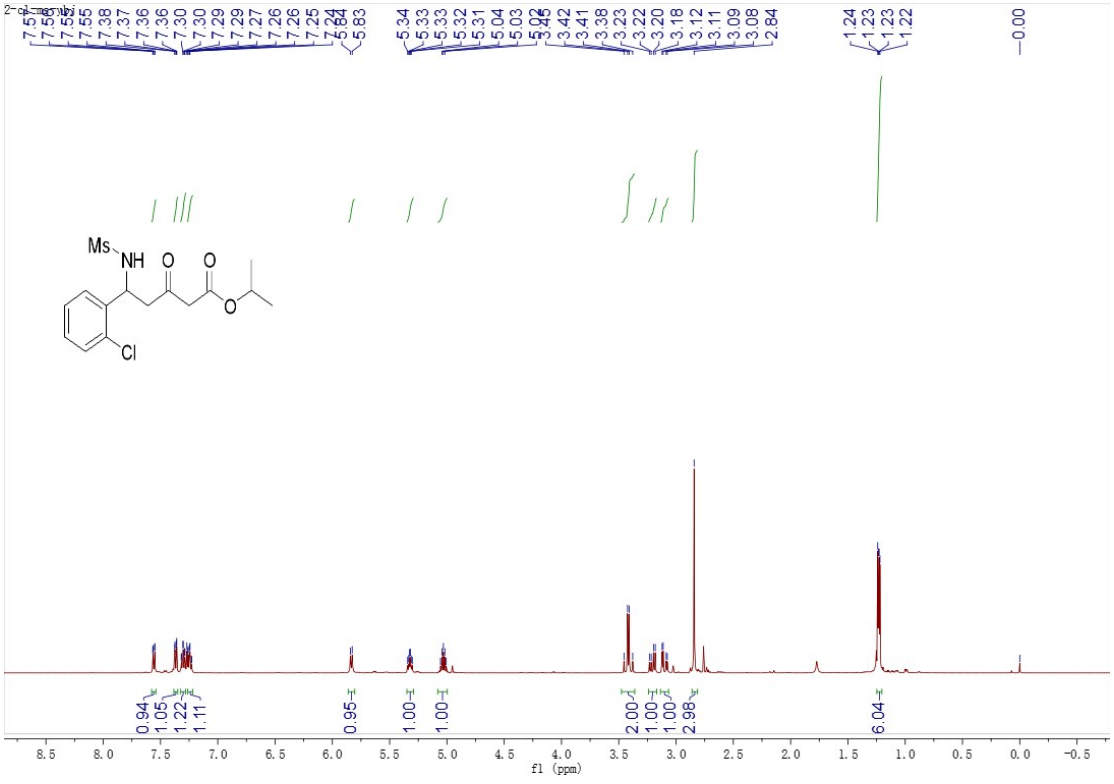

2-f-ms-ybj.3.fid
200.27
166.38
161.06
159.11
129.92
129.85
128.98
128.95
127.36
127.26
124.66
124.63
116.01
115.84
77.03
69.53
49.70
49.27
48.11
41.23
21.64
Ms
F
HN
O
O
O
f1 (ppm)

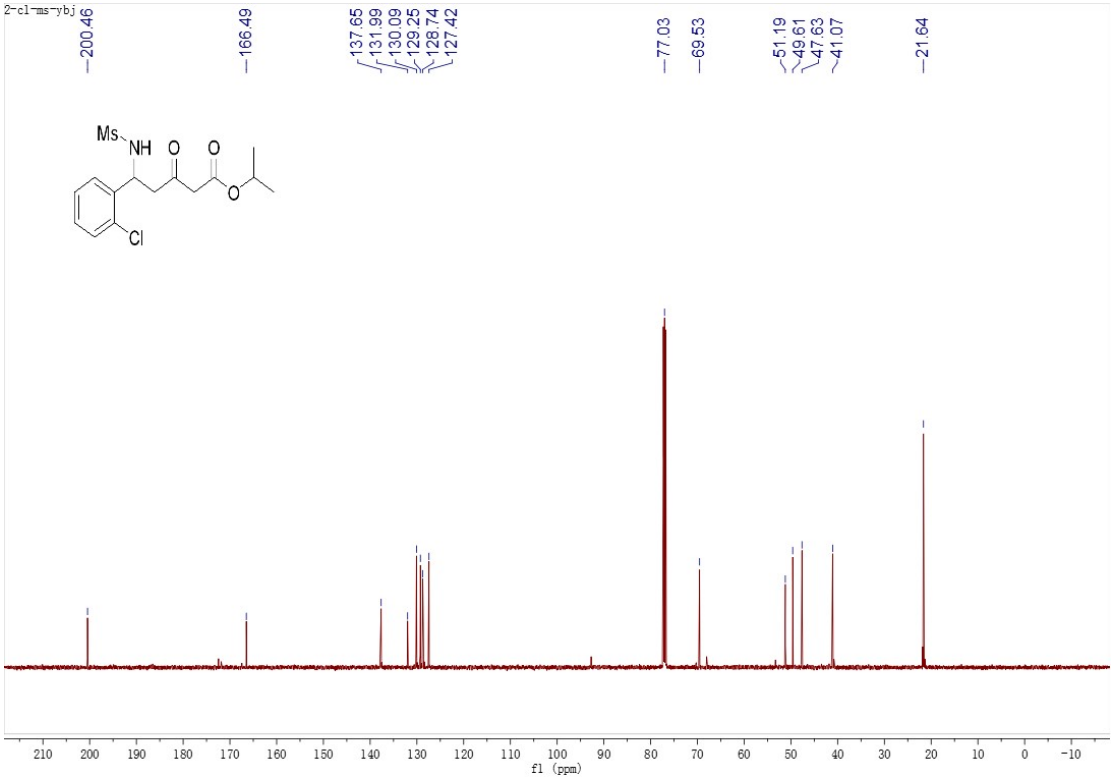
3e


7.35
7.33
7.32
7.30
7.26
5.55
5.53
5.30
5.06
5.05
5.03
5.02
5.01
4.96
4.95
4.94
4.93
4.92
4.92
3.43
3.40
3.38
3.35
3.23
3.21
3.19
3.17
3.04
3.03
3.00
2.99
2.78
1.24
1.23
0.00
MS
HN
O
O
O
Cl
2.16
2.11
1.00
1.02
1.10
1.99
1.00
1.00
3.00
6.04
f1 (ppm)

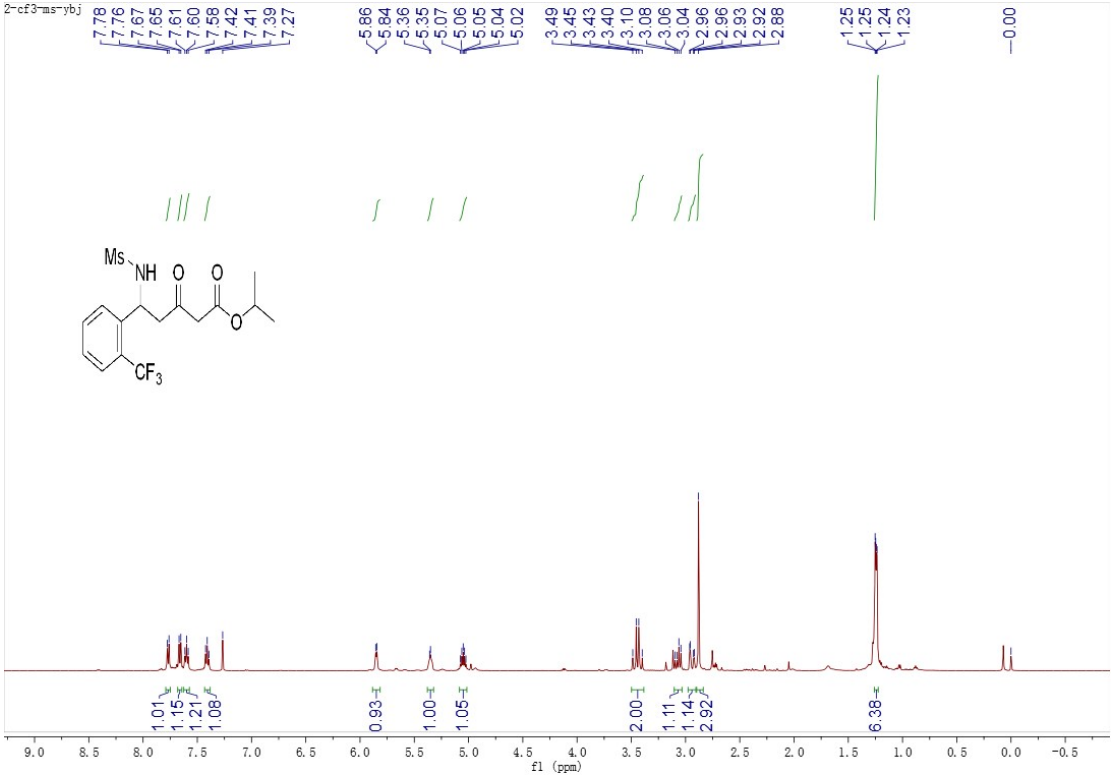

4-cl-ms-ybj-c.fid
200.66
166.51
138.87
134.01
129.14
128.03
77.02
69.70
53.17
49.76
49.14
41.48
21.66
Ms
HN
O
O
O
Cl
f1 (ppm)

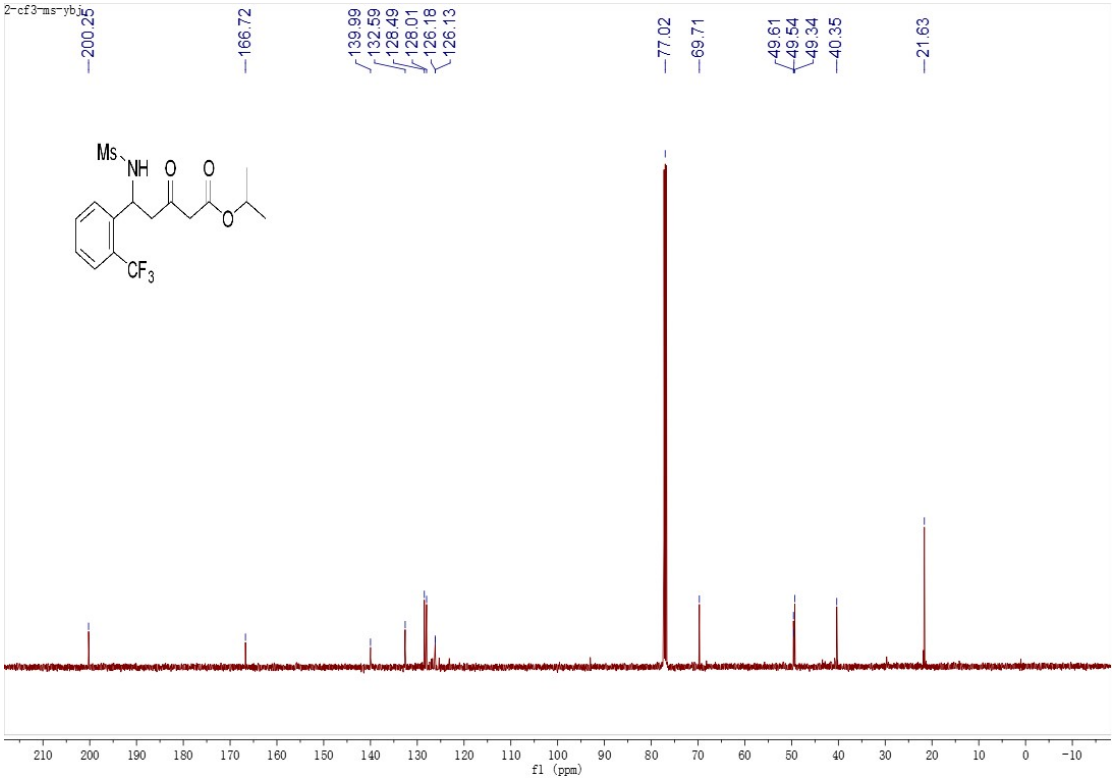
3f


2-cl-ms-ybj
7.58
7.55
7.38
7.37
7.36
7.30
7.29
7.27
7.26
7.25
5.84
5.83
5.34
5.33
5.32
5.31
5.04
5.03
3.42
3.41
3.38
3.23
3.22
3.20
3.18
3.12
3.11
3.09
3.08
2.84
1.24
1.23
1.22
0.00
Ms
NH
O
O
O
Cl
0.94
1.05
1.22
1.11
0.95
1.00
1.00
2.00
1.00
2.98
6.04
f1 (ppm)

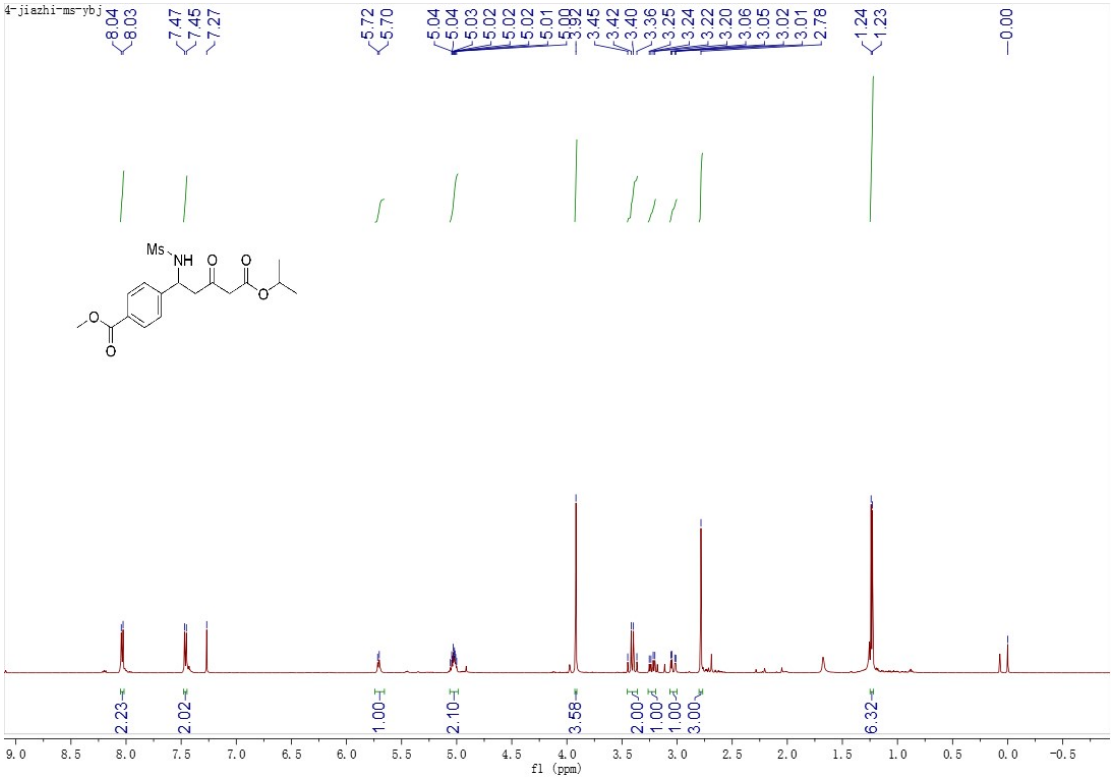

2-cl-ms-ybj
200.46
166.49
137.65
131.99
130.09
129.25
128.74
127.42
77.03
69.53
51.19
49.61
47.63
41.07
21.64
Ms
NH
O
O
O
Cl
f1 (ppm)

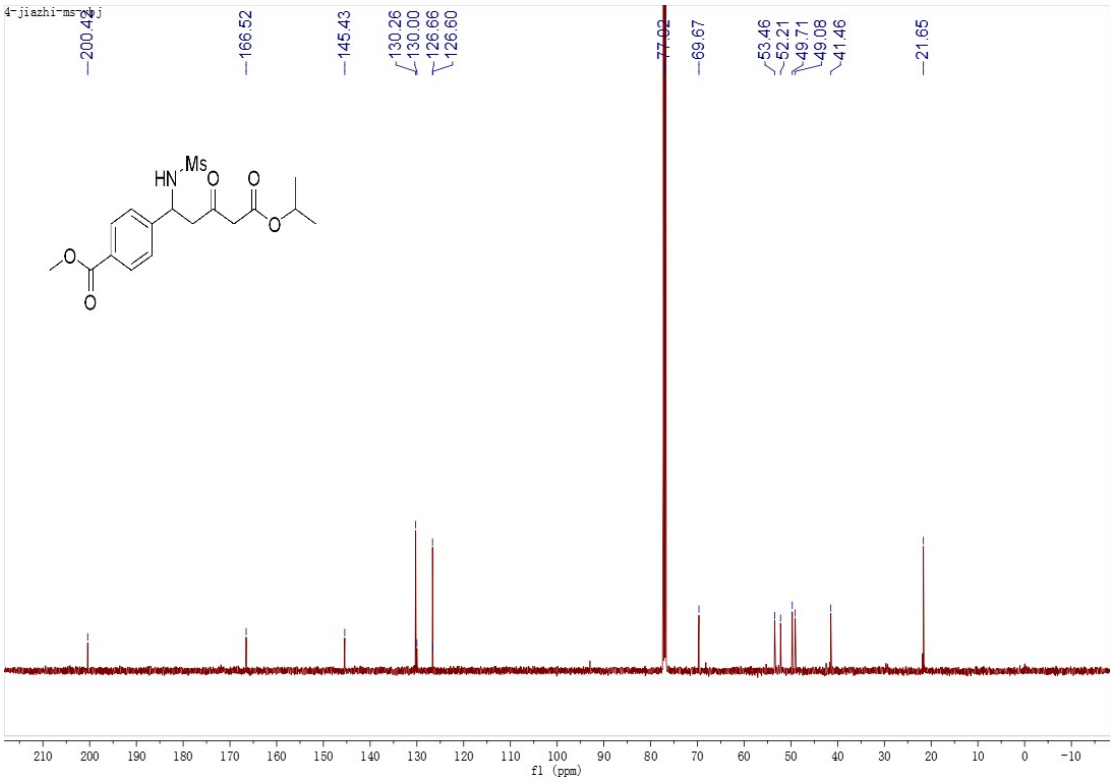
3g


2-cf3-ms-ybj
7.78
7.76
7.67
7.65
7.61
7.60
7.58
7.42
7.41
7.39
7.27
5.86
5.84
5.36
5.35
5.07
5.06
5.05
5.04
5.02
3.49
3.45
3.43
3.40
3.10
3.08
3.06
3.04
2.96
2.96
2.93
2.92
2.88
1.25
1.25
1.24
1.23
0.00
Ms
NH
O
O
O
CF3
1.01
1.15
1.21
1.08
0.93
1.00
1.05
2.00
1.11
1.14
2.92
6.38
f1 (ppm)

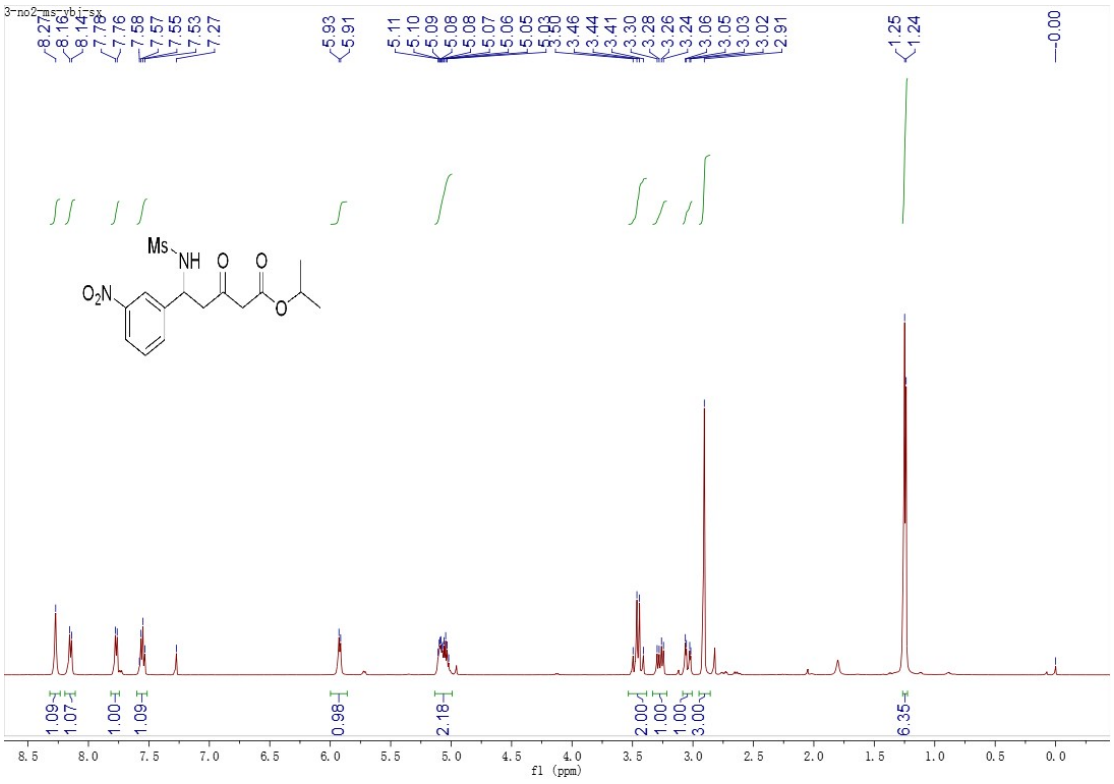

2-cf3-ms-ybj
200.25
166.72
139.99
132.59
128.49
128.01
126.18
126.13
77.02
69.71
49.61
49.54
49.34
40.35
21.63
Ms
NH
O
O
O
CF3
f1 (ppm)

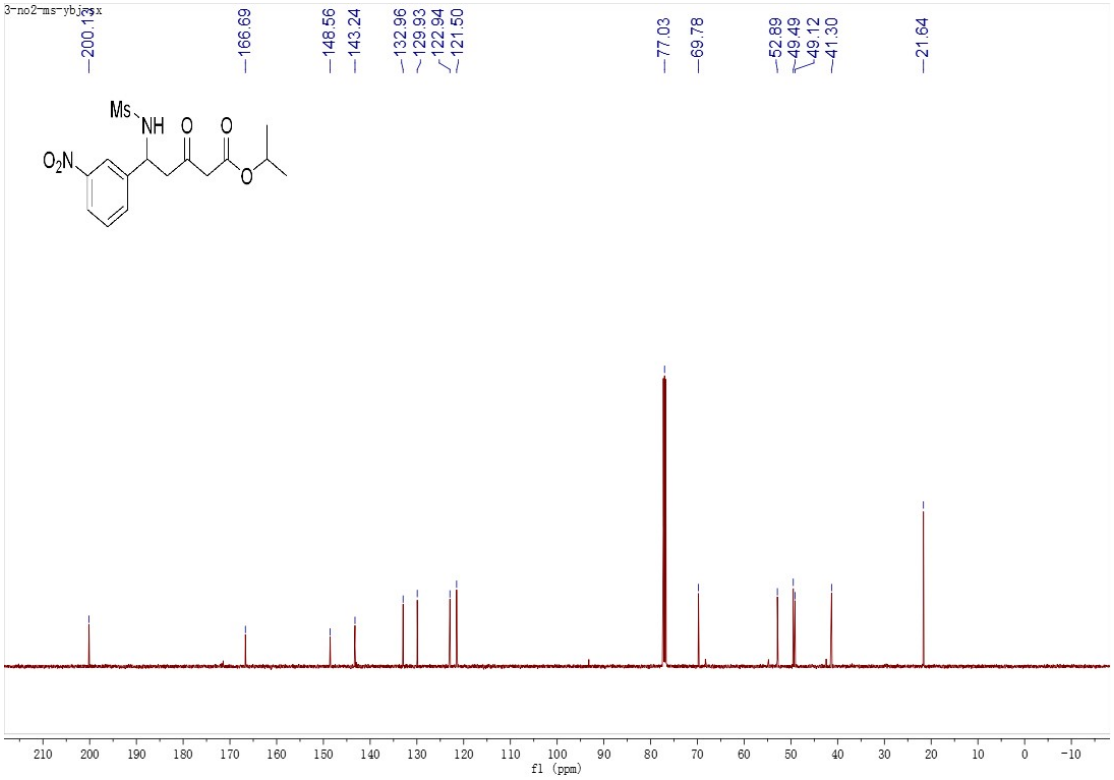
3h


4-jiazhi-ms-ybj
8.04
8.03
7.47
7.45
7.27
5.72
5.70
5.04
5.04
5.03
5.02
5.02
5.02
5.01
3.45
3.42
3.40
3.36
3.25
3.24
3.22
3.20
3.06
3.05
3.02
3.01
2.78
1.24
1.23
0.00
Ms
NH
O
O
O
O
O
2.23
2.02
1.00
2.10
3.58
2.00
1.00
1.00
3.00
6.32
f1 (ppm)

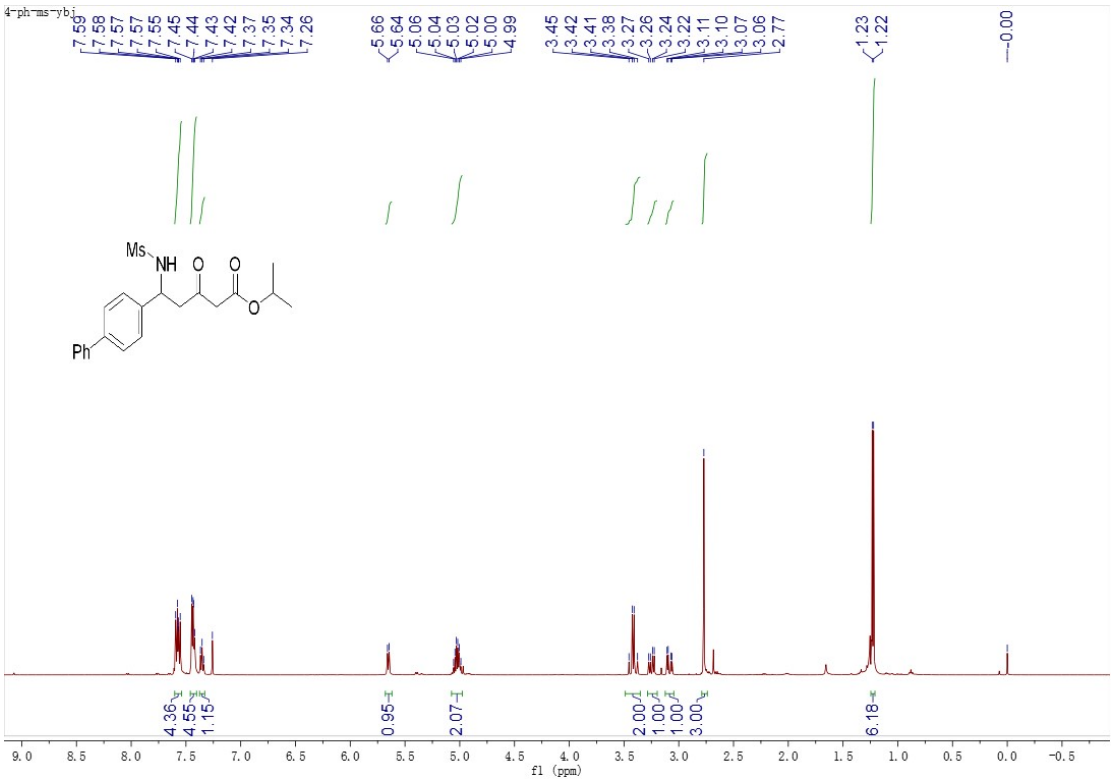

200.42
166.52
145.43
130.26
130.00
126.66
126.60
77.02
69.67
53.46
52.21
49.71
49.08
41.46
21.65
HN
Ms
O
O
O
O
O
f1 (ppm)

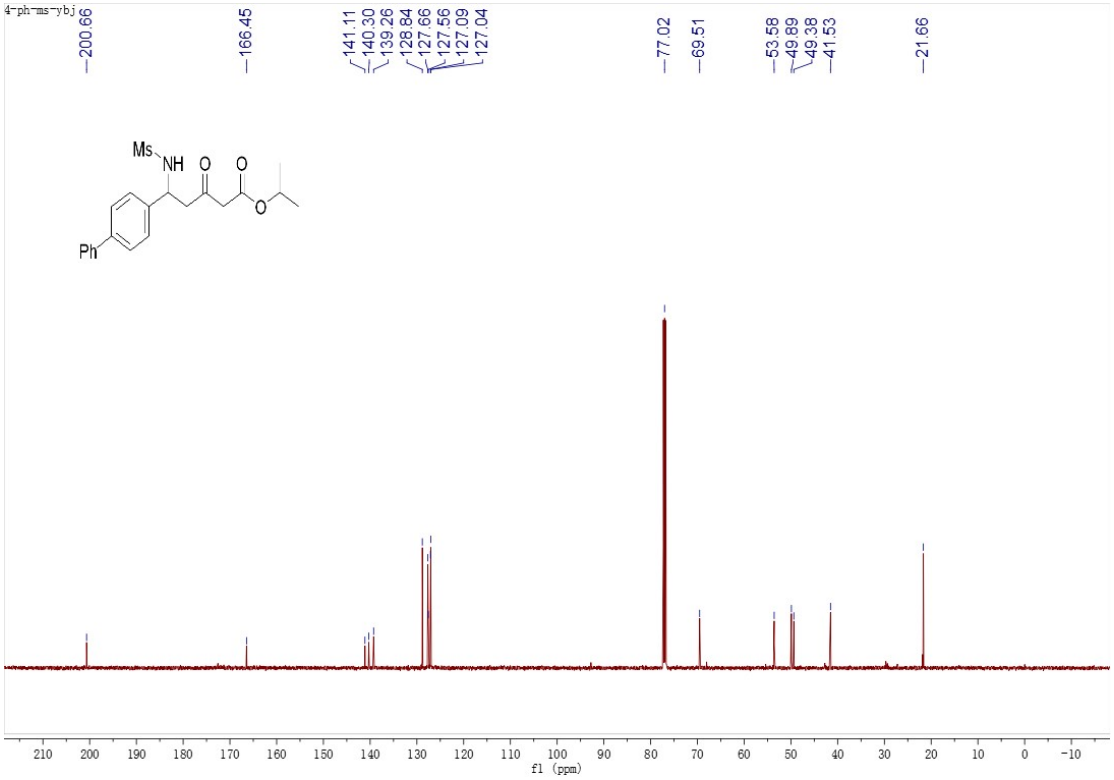
3i


8.27
8.16
8.14
7.78
7.76
7.58
7.57
7.55
7.53
7.27
5.93
5.91
5.11
5.10
5.09
5.08
5.08
5.07
5.06
5.05
3.46
3.44
3.41
3.30
3.28
3.26
3.24
3.06
3.05
3.03
3.02
2.91
1.25
1.24
0.00
Ms
NH
O
O
O
O2N
1.09
1.07
1.00
1.09
0.98
2.18
2.00
1.00
1.00
3.00
6.35
f1 (ppm)

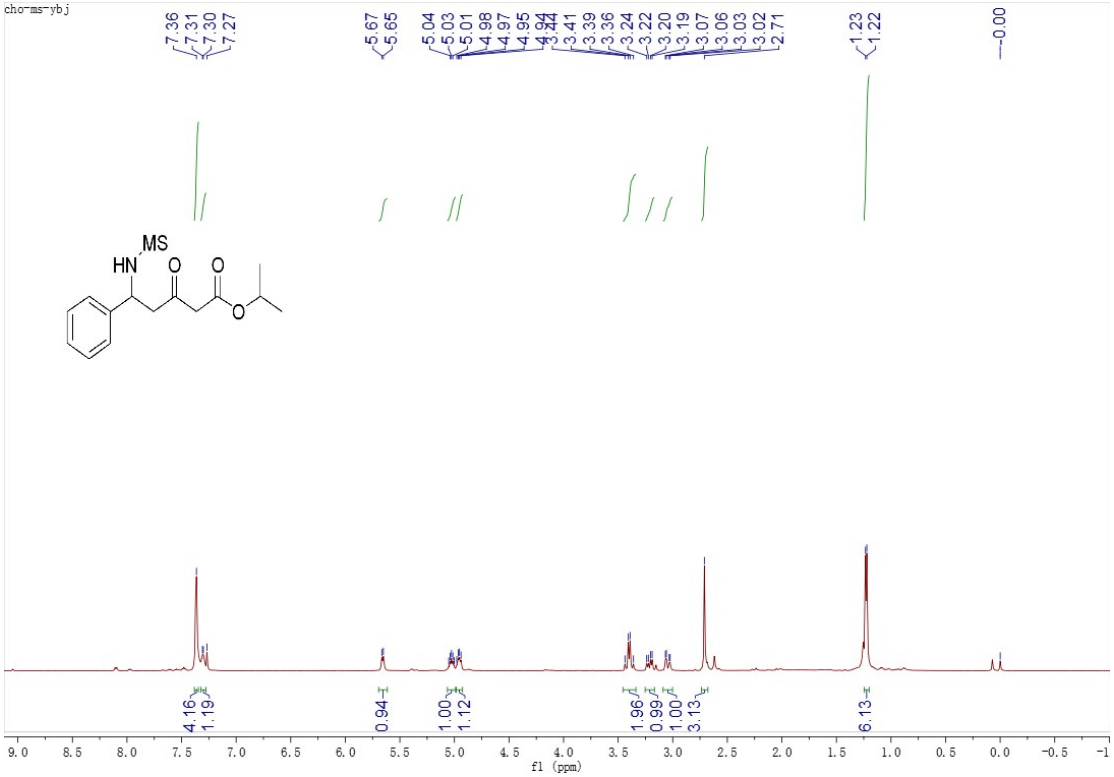

3-no2-ms-ybj-13c
200.13
166.69
148.56
143.24
132.96
129.93
122.94
121.50
77.03
69.78
52.89
49.49
49.12
41.30
21.64
Ms
NH
O
O
O
O2N
f1 (ppm)

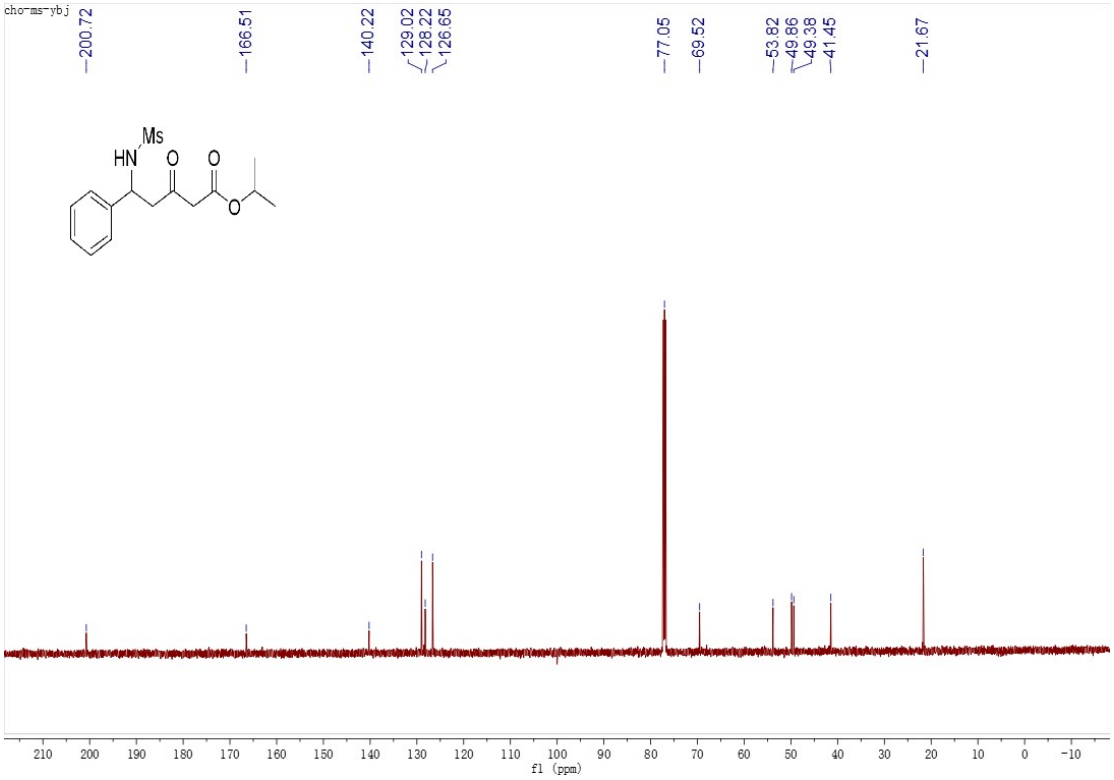
3j


4-ph-ms-ybj
7.59
7.58
7.57
7.55
7.45
7.44
7.43
7.42
7.37
7.35
7.34
7.26
5.66
5.64
5.06
5.04
5.03
5.02
5.00
4.99
3.45
3.42
3.41
3.38
3.27
3.26
3.24
3.22
3.11
3.10
3.07
3.06
2.77
1.23
1.22
0.00
Ms
NH
O
O
O
Ph
4.36
4.55
1.15
0.95
2.07
2.00
1.00
1.00
3.00
6.18
f1 (ppm)

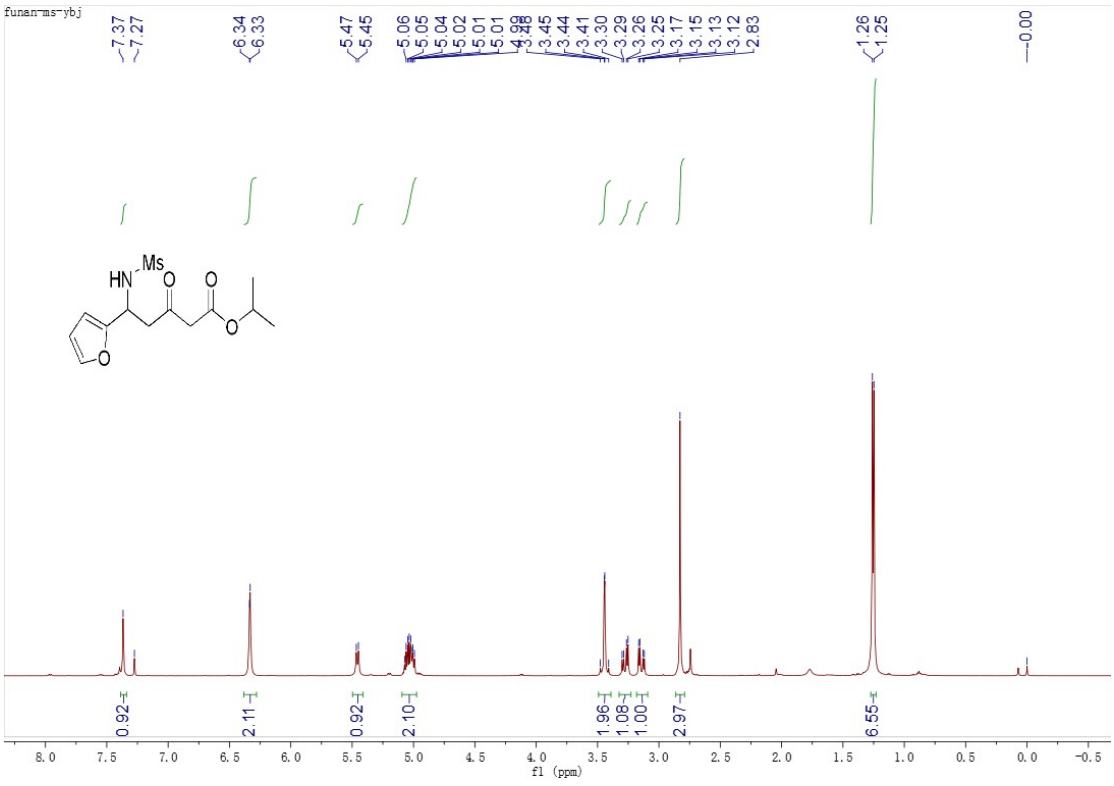

4-ph-ms-ybj
200.66
166.45
141.11
140.30
139.26
128.84
127.66
127.56
127.09
127.04
77.02
69.51
53.58
49.89
49.38
41.53
21.66
Ms
NH
O
O
O
Ph
f1 (ppm)

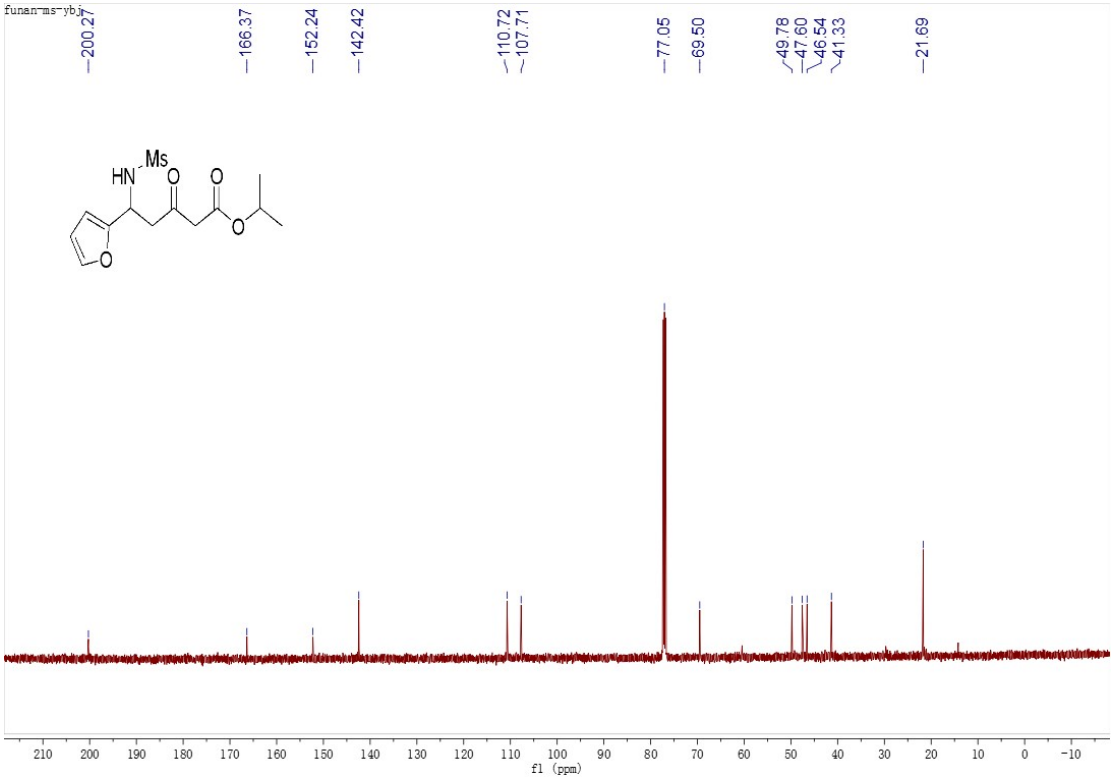
3k


cho-ms-ybj
7.36
7.31
7.30
7.27
5.67
5.65
5.04
5.03
5.01
4.98
4.97
4.95
4.94
3.41
3.39
3.36
3.24
3.22
3.20
3.19
3.07
3.06
3.03
3.02
2.71
1.23
1.22
0.00
MS
HN
O
O
O
4.16
1.19
0.94
1.00
1.12
1.96
0.99
1.00
3.13
6.13
f1 (ppm)

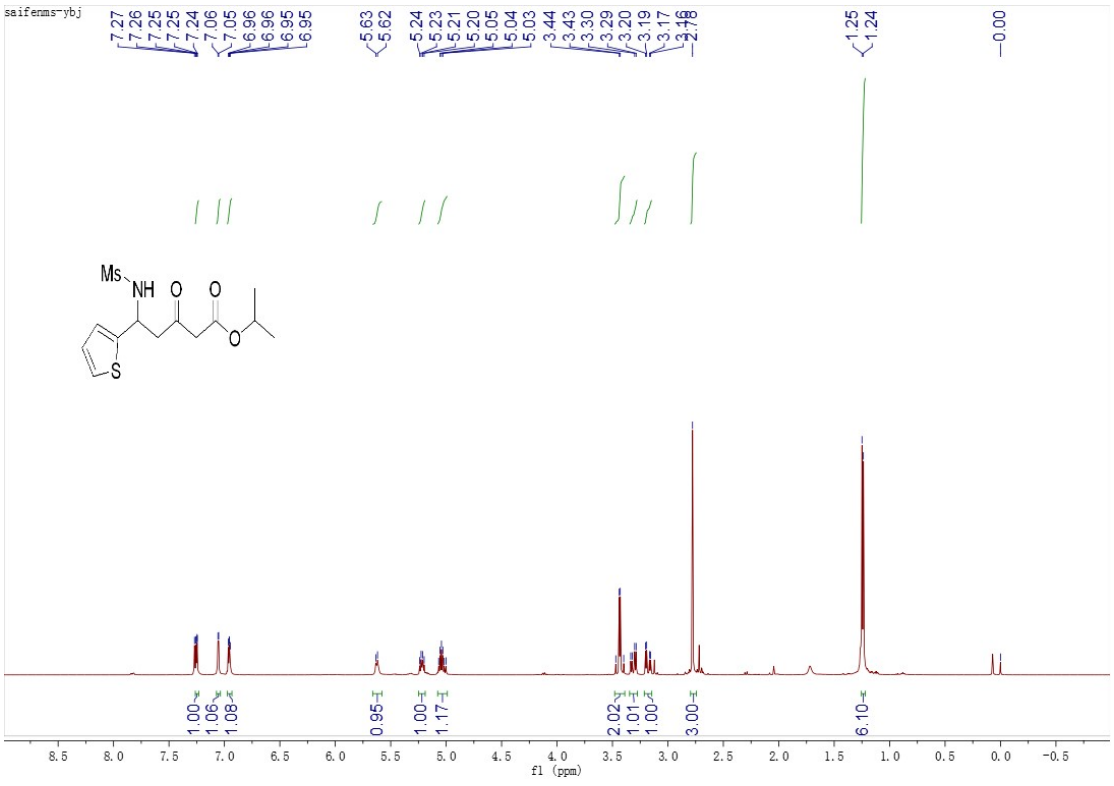

cho-ms-ybj
200.72
166.51
140.22
129.02
128.22
126.65
77.05
69.52
53.82
49.86
49.38
41.45
21.67
Ms
HN
O
O
O
f1 (ppm)

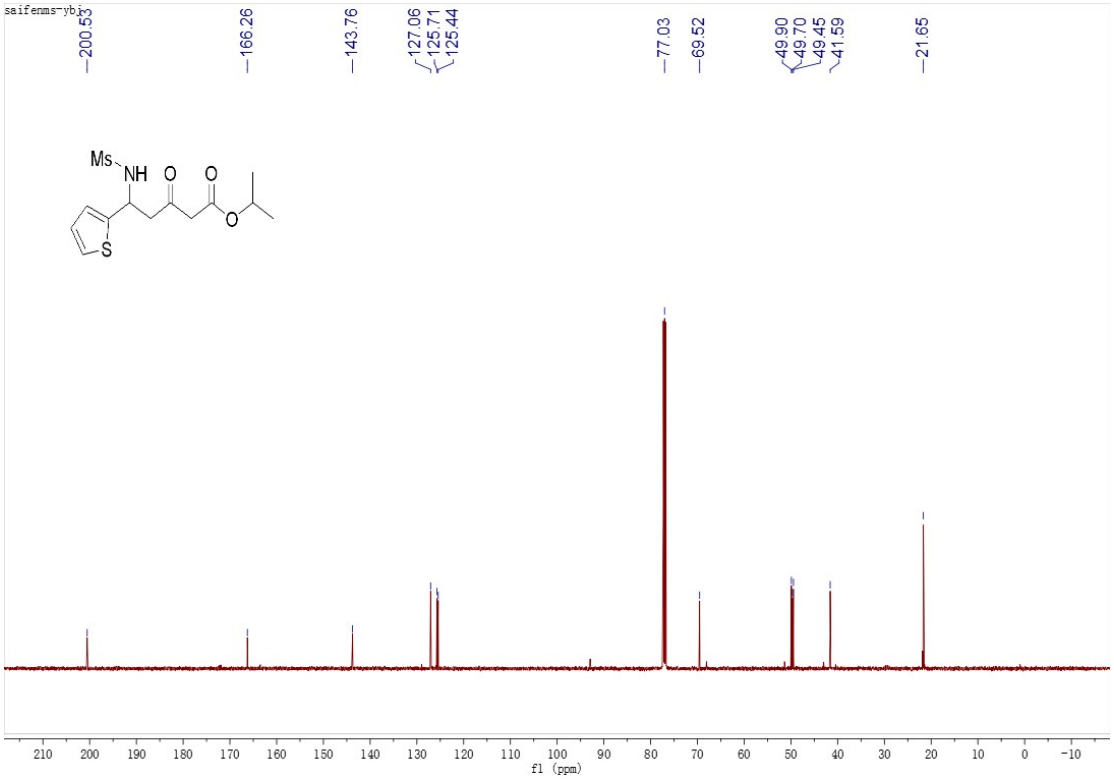
3l


funan-ms-ybj
7.37
7.27
6.34
6.33
5.47
5.45
5.06
5.05
5.04
5.02
5.01
5.01
3.45
3.44
3.41
3.30
3.29
3.26
3.25
3.17
3.15
3.13
3.12
2.83
1.26
1.25
0.00
Ms
HN
O
O
O
O
0.92
2.11
0.92
2.10
1.96
1.08
1.00
2.97
6.55
f1 (ppm)

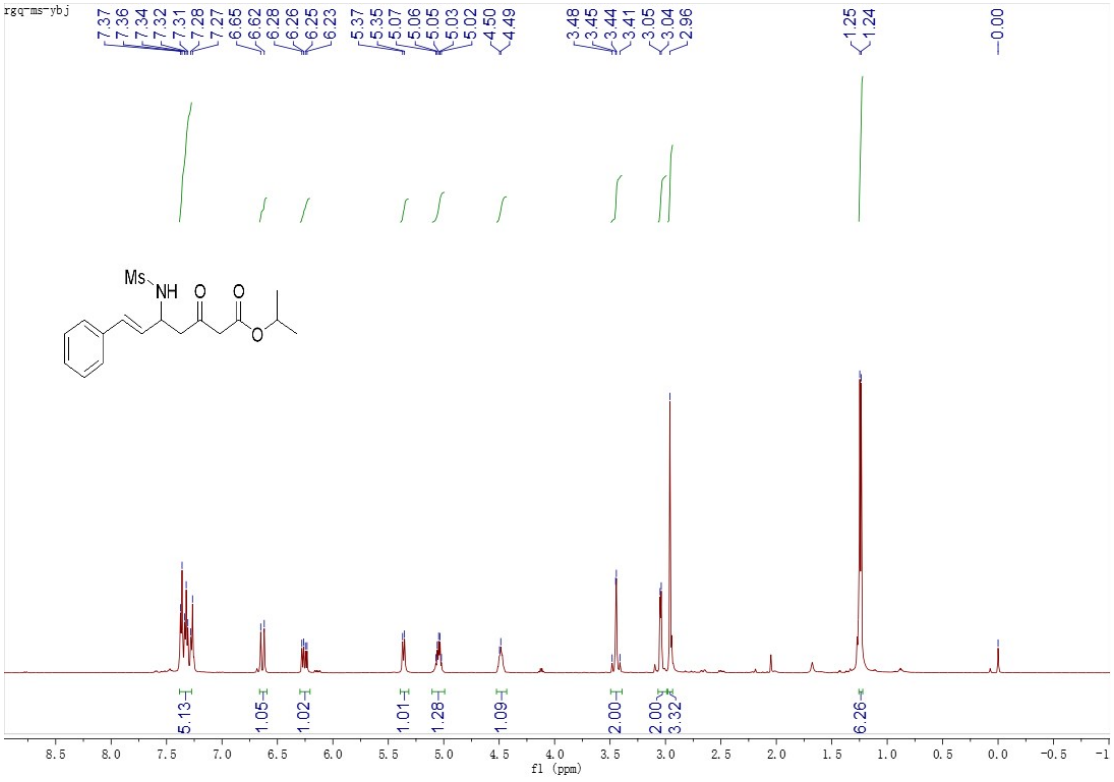

funan-ms-ybj
200.27
166.37
152.24
142.42
110.72
107.71
77.05
69.50
49.78
47.60
46.54
41.33
21.69
HN
Ms
O
O
O
O
f1 (ppm)

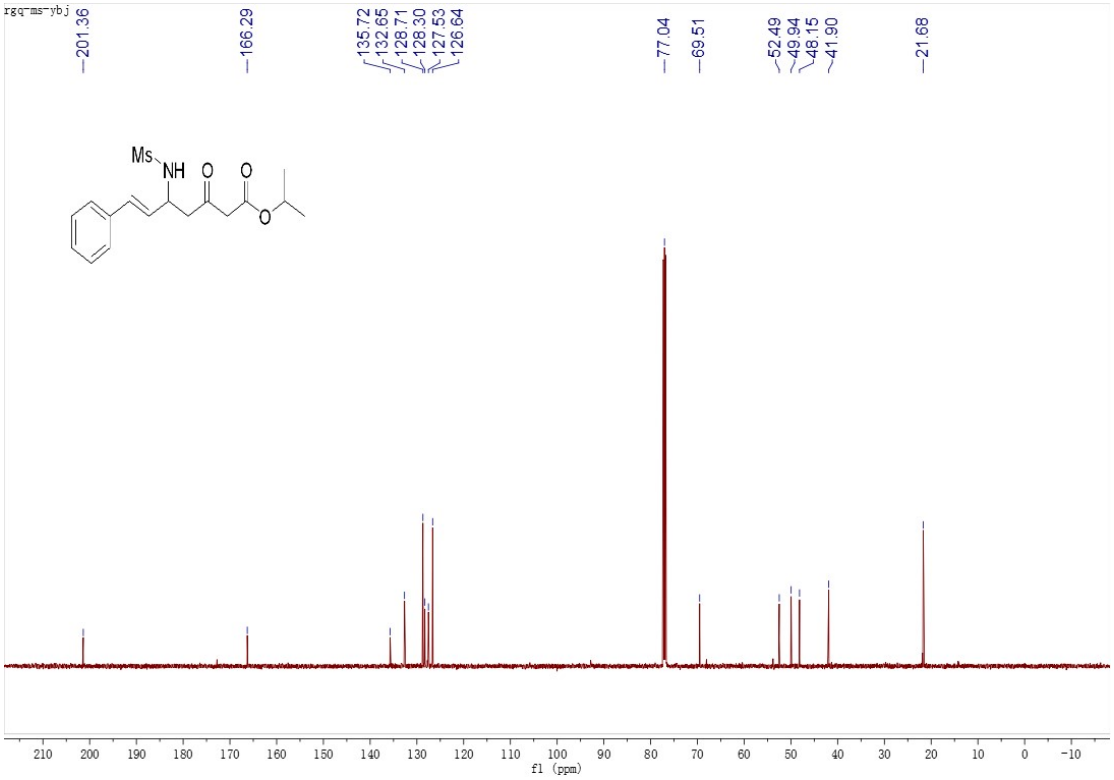
3m


saifenms-ybj
7.27
7.26
7.25
7.25
7.24
7.06
7.05
6.96
6.96
6.95
6.95
5.63
5.62
5.24
5.23
5.21
5.20
5.05
5.04
5.03
3.44
3.43
3.30
3.29
3.20
3.19
3.17
3.16
2.78
1.25
1.24
0.00
Ms
NH
O
O
O
S
1.00
1.06
1.08
0.95
1.00
1.17
2.02
1.01
1.00
3.00
6.10
f1 (ppm)

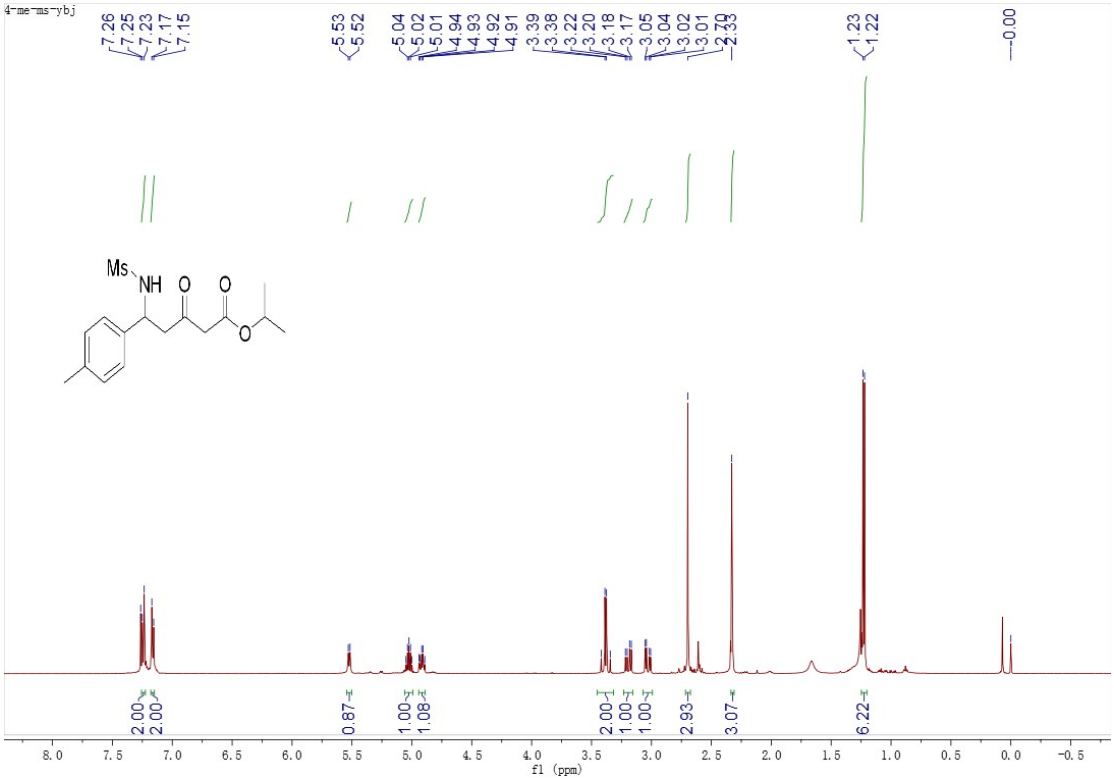

saifenms-ybj
200.53
166.26
143.76
127.06
125.71
125.44
77.03
69.52
49.90
49.70
49.45
41.59
21.65
Ms
NH
O
O
O
S
f1 (ppm)

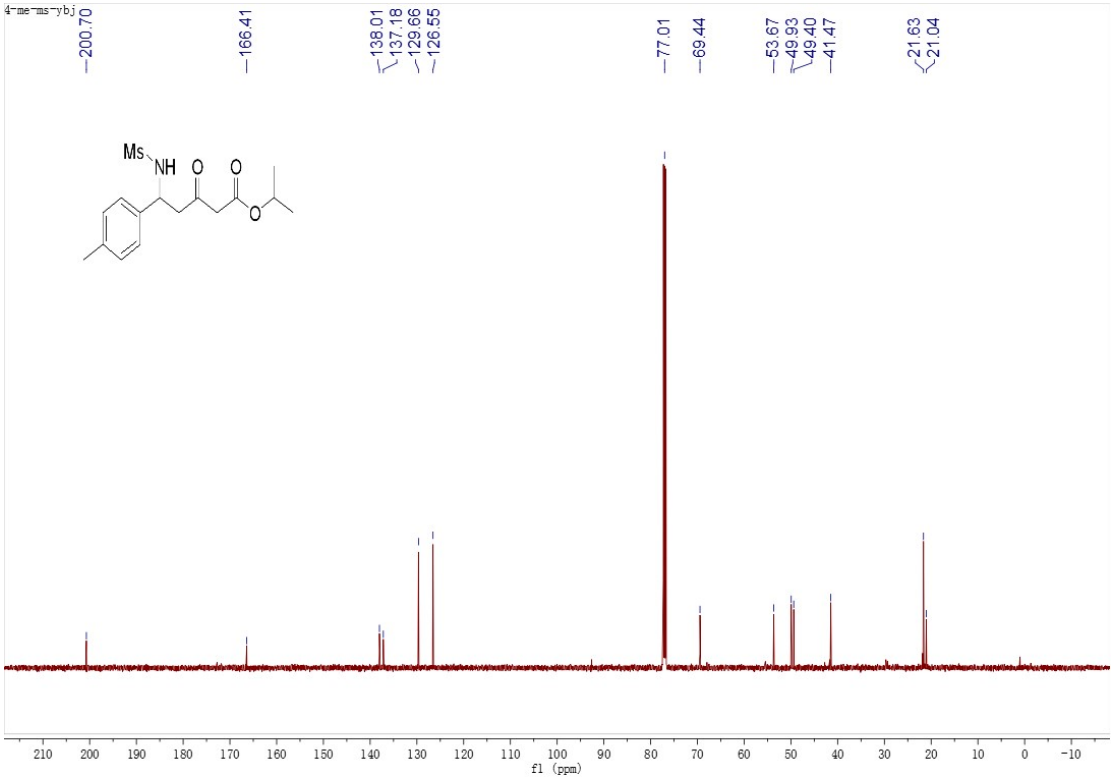
3n


rgq-ms-ybj
7.37
7.36
7.34
7.32
7.31
7.28
7.27
6.65
6.62
6.28
6.26
6.25
6.23
5.37
5.35
5.07
5.06
5.05
5.03
5.02
4.50
4.49
3.48
3.45
3.44
3.41
3.05
3.04
2.96
1.25
1.24
0.00
Ms
NH
O
O
O
5.13
1.05
1.02
1.01
1.28
1.09
2.00
2.00
3.32
6.26
f1 (ppm)

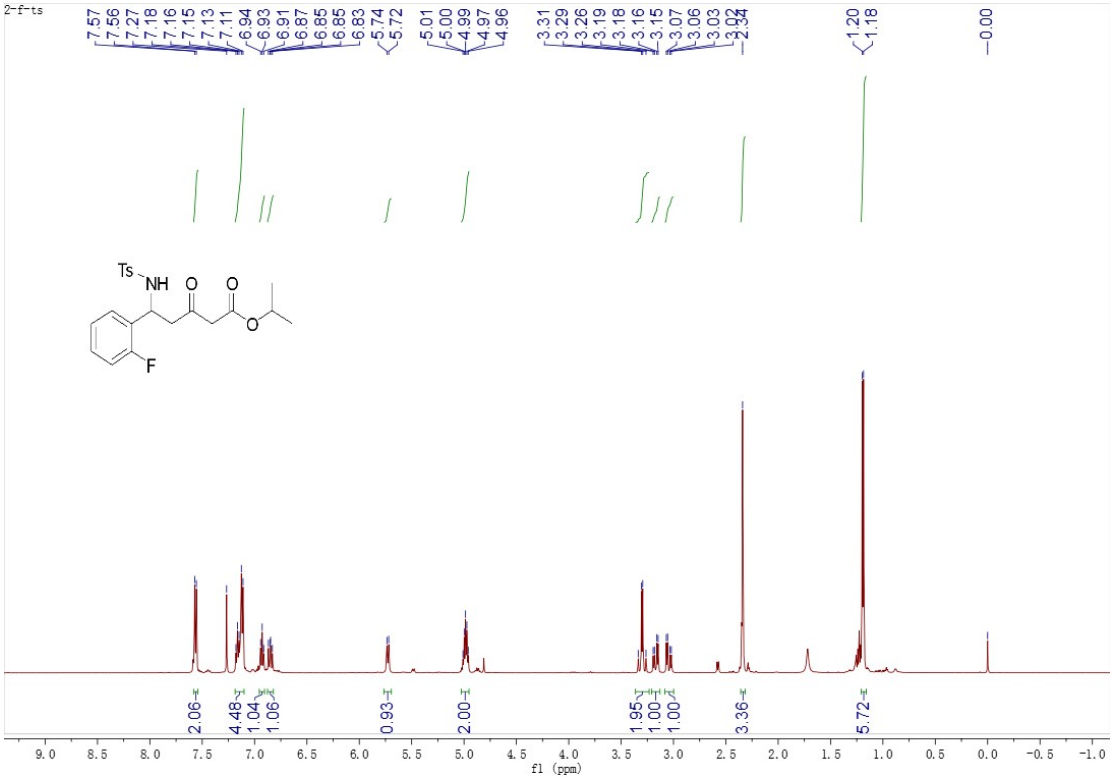

rgq-ms-ybj
201.36
166.29
135.72
132.65
128.71
128.30
127.53
126.64
77.04
69.51
52.49
49.94
48.15
41.90
21.68
Ms
NH
O
O
O
f1 (ppm)

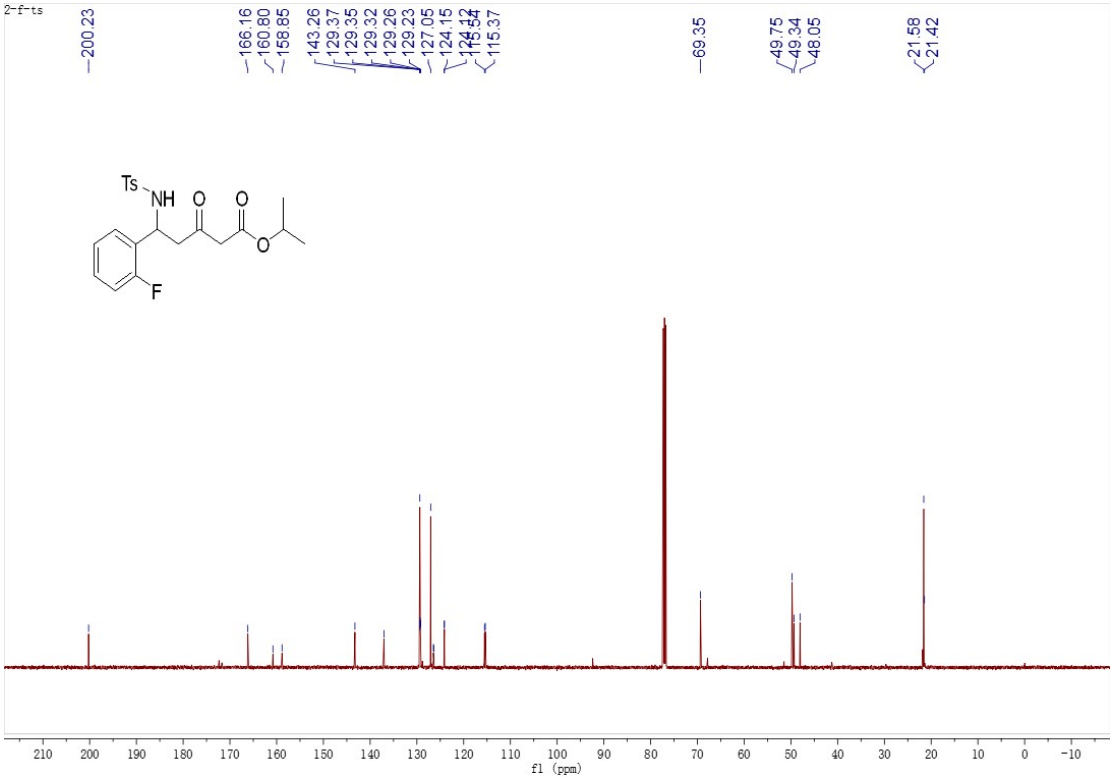
3o


4-me-ms-ybj
7.26
7.25
7.23
7.17
7.15
5.53
5.52
5.04
5.02
5.01
4.94
4.93
4.92
4.91
3.39
3.38
3.22
3.20
3.18
3.17
3.05
3.04
3.02
3.01
2.33
1.23
1.22
0.00
Ms
NH
O
O
O
2.00
2.00
0.87
1.00
1.08
2.00
1.00
1.00
2.93
3.07
6.22
f1 (ppm)

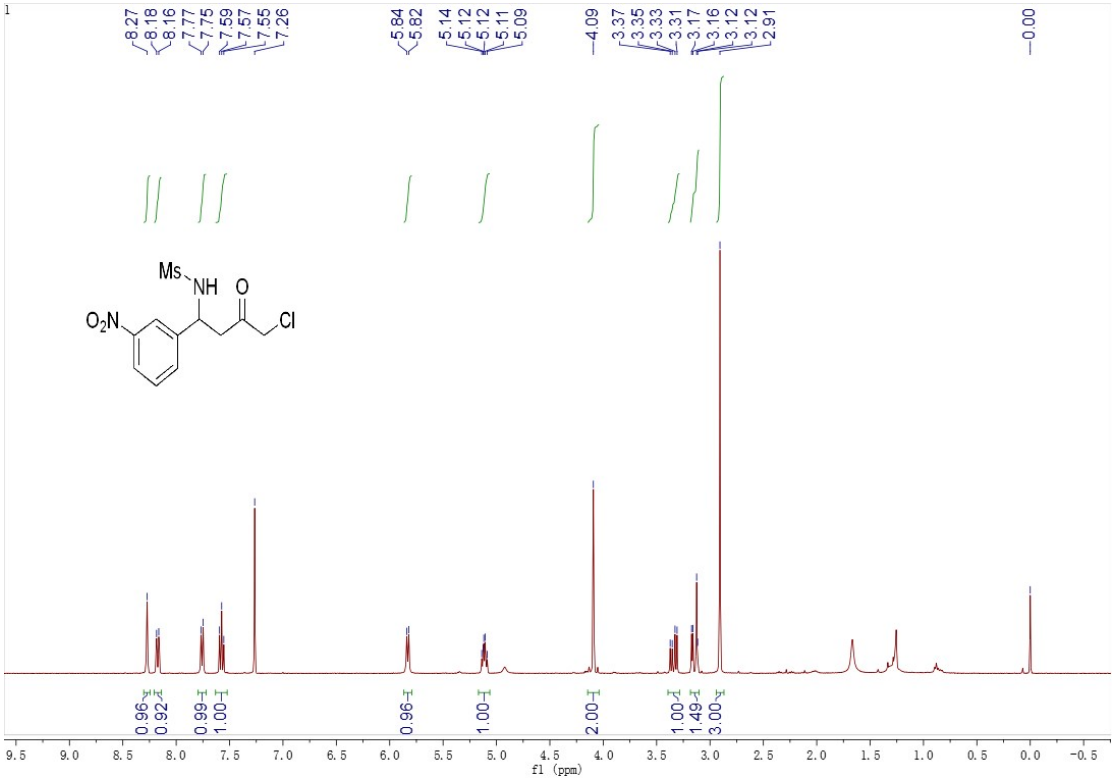

4-me-ms-ybj
200.70
166.41
138.01
137.18
129.66
126.55
77.01
69.44
53.67
49.93
49.40
41.47
21.63
21.04
Ms
NH
O
O
O
f1 (ppm)

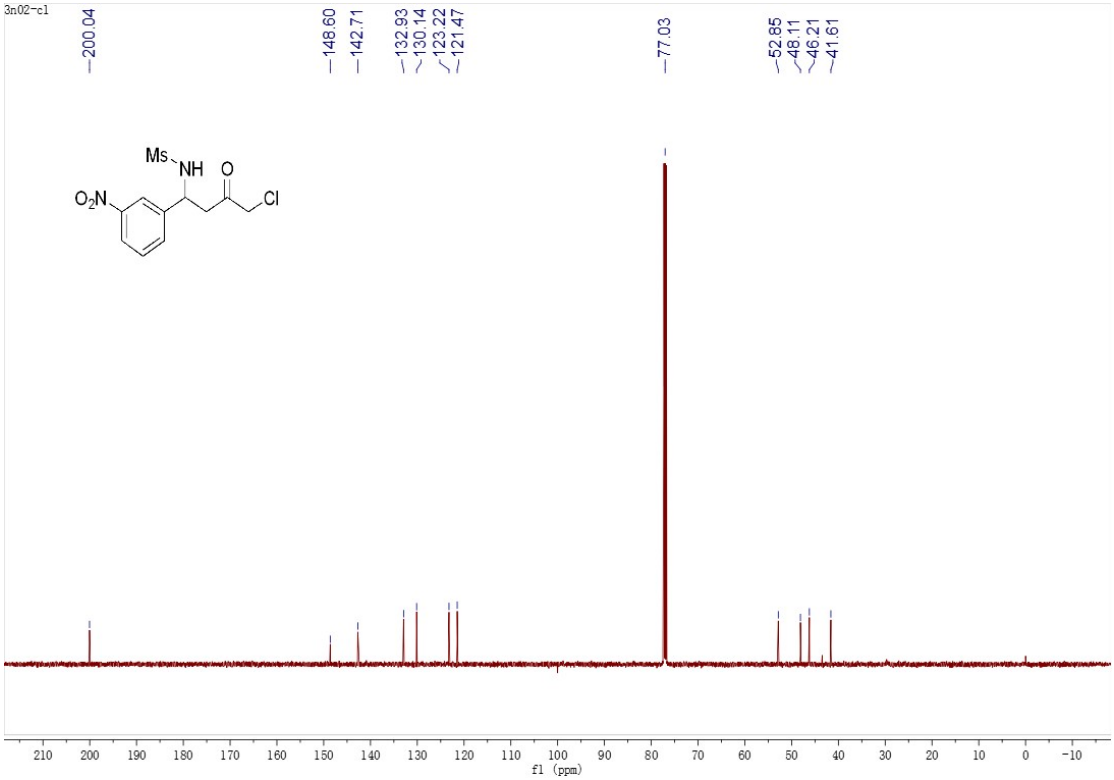
3p


2-f-ts
7.57
7.56
7.27
7.18
7.16
7.15
7.13
7.11
6.94
6.93
6.91
6.87
6.85
6.85
6.83
5.74
5.72
5.01
5.00
4.99
4.97
4.96
3.31
3.29
3.26
3.19
3.18
3.16
3.15
3.07
3.06
3.03
3.02
2.94
1.20
1.18
0.00
Ts
NH
O
O
O
F
2.06
4.48
1.04
1.06
0.93
2.00
1.95
1.00
1.00
3.36
5.72
f1 (ppm)

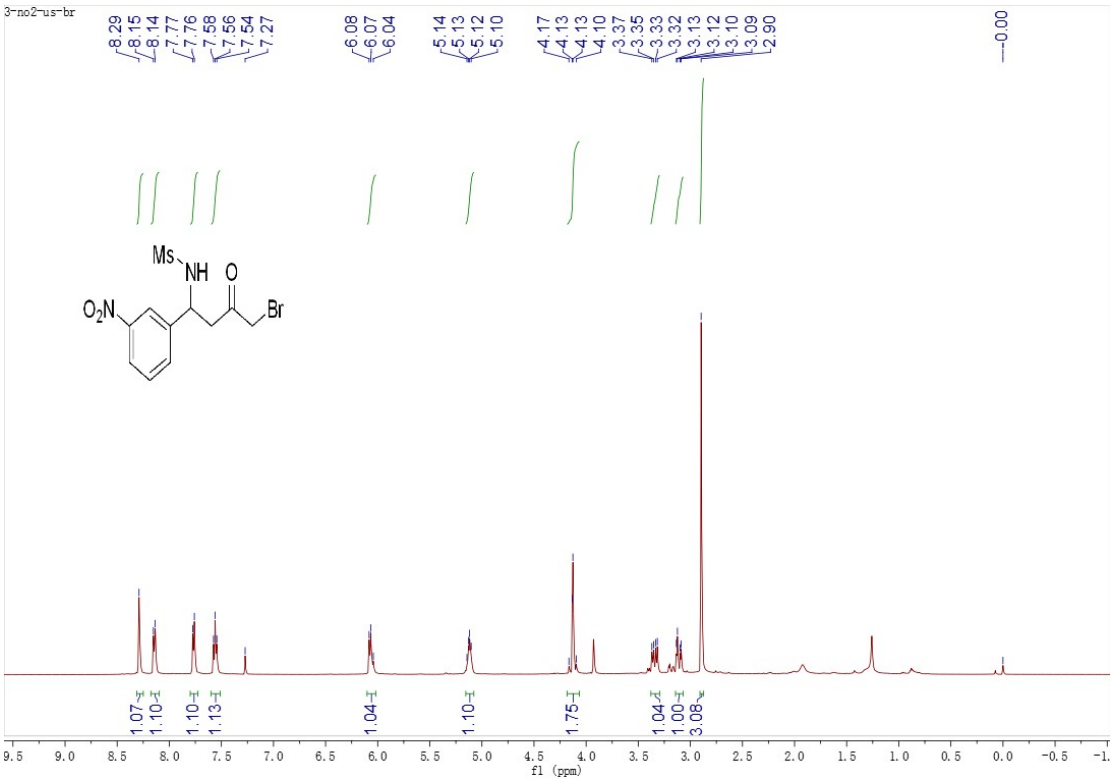

2-f-ts
200.23
166.16
160.80
158.85
143.26
129.37
129.35
129.32
129.26
129.23
127.05
124.15
115.37
69.35
49.75
49.34
48.05
21.58
21.42
Ts
NH
O
O
O
F
f1 (ppm)

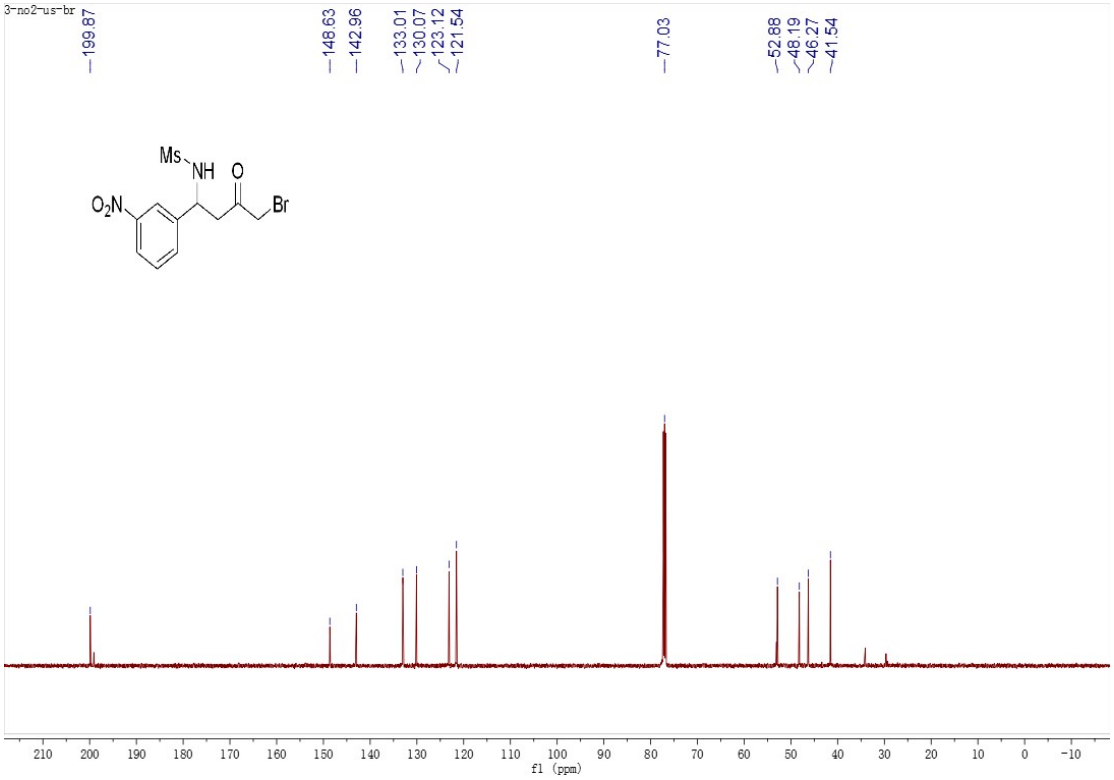
3q


1
8.27
8.18
8.16
7.77
7.75
7.59
7.57
7.55
7.26
5.84
5.82
5.14
5.12
5.12
5.11
5.09
4.09
3.37
3.35
3.33
3.31
3.17
3.16
3.12
3.12
2.91
0.00
Ms
NH
O
O2N
Cl
0.96
0.92
0.99
1.00
0.96
1.00
2.00
1.00
1.49
3.00
f1 (ppm)

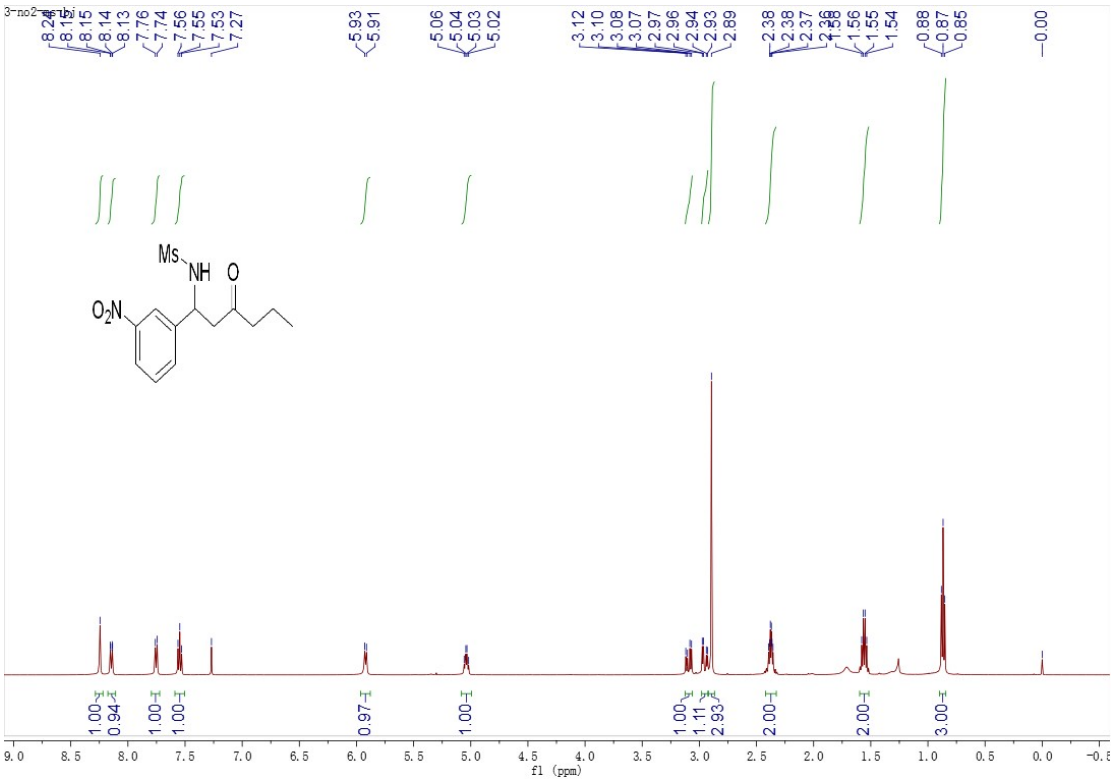

3n02-cl
200.04
148.60
142.71
132.93
130.14
123.22
121.47
77.03
52.85
48.11
46.21
41.61
Ms
NH
O
O2N
Cl
f1 (ppm)

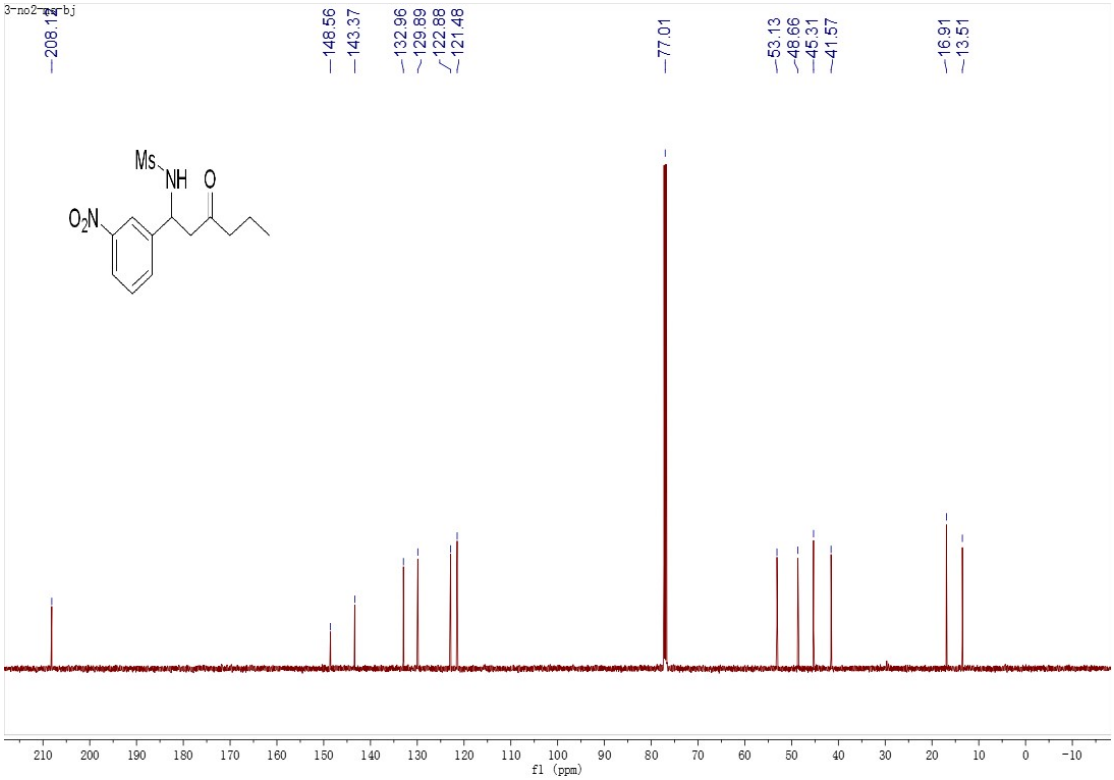
3r


3-no2-us-br
8.29
8.15
8.14
7.77
7.76
7.58
7.56
7.54
7.27
6.08
6.07
6.04
5.14
5.13
5.12
5.10
4.17
4.13
4.13
4.10
3.37
3.35
3.33
3.32
3.13
3.12
3.10
3.09
2.90
0.00
Ms
NH
O
O2N
Br
1.07
1.10
1.10
1.13
1.04
1.10
1.75
1.04
1.00
3.08
f1 (ppm)

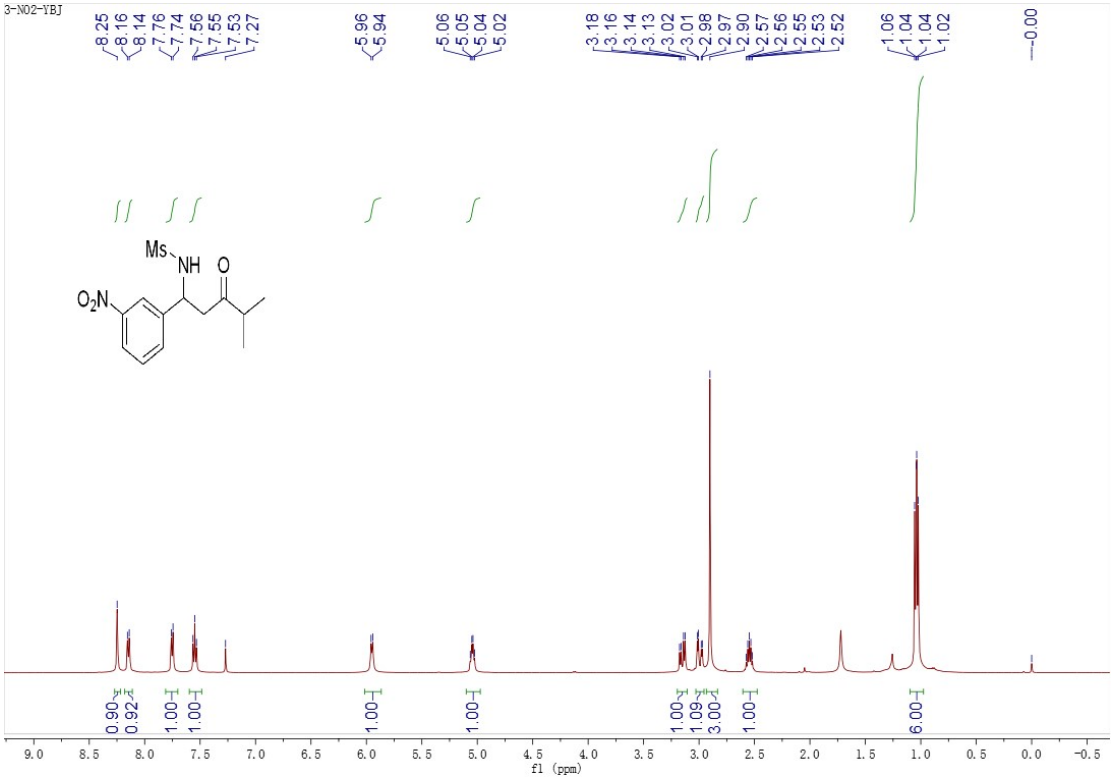

3-no2-us-br
199.87
148.63
142.96
133.01
130.07
123.12
121.54
77.03
52.88
48.19
46.27
41.54
Ms
NH
O
O2N
Br
f1 (ppm)

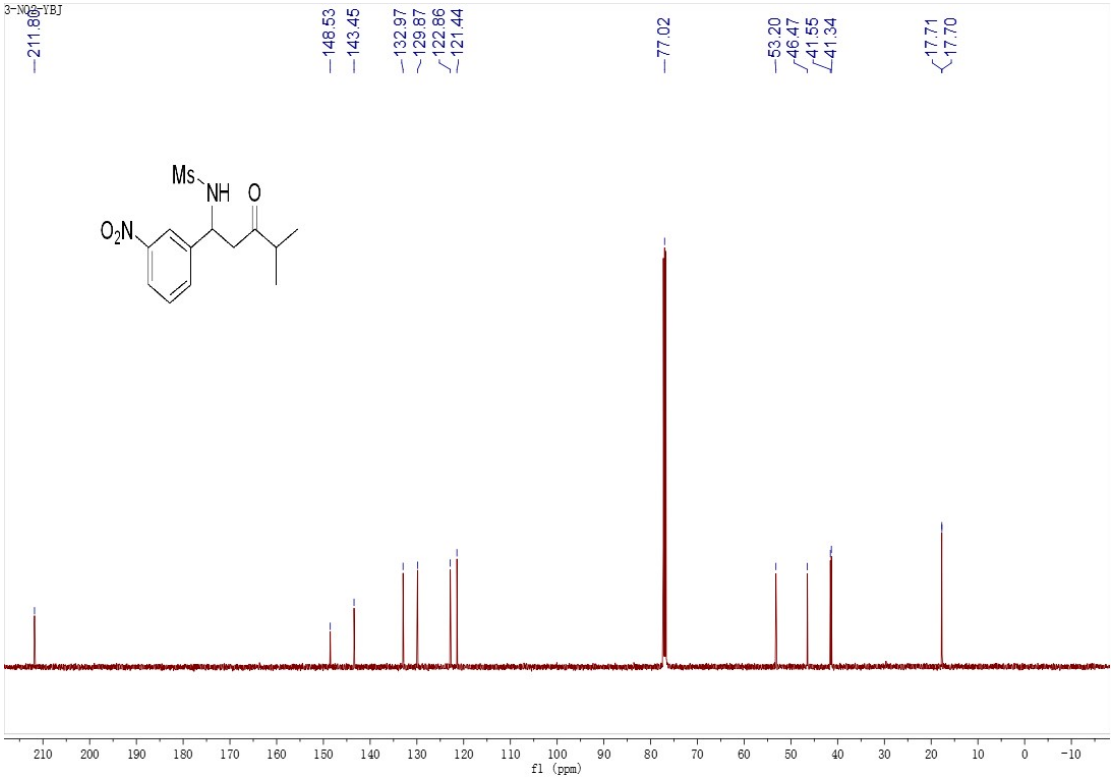
3s


3-no2-us-bi
8.26
8.15
8.14
8.13
7.76
7.74
7.56
7.55
7.53
7.27
5.93
5.91
5.06
5.04
5.03
5.02
3.12
3.10
3.08
3.07
2.97
2.96
2.94
2.93
2.89
2.38
2.38
2.37
2.36
1.56
1.55
1.54
0.88
0.87
0.85
0.00
Ms
NH
O
O2N
1.00
0.94
1.00
1.00
0.97
1.00
1.00
1.11
2.93
2.00
2.00
3.00
f1 (ppm)

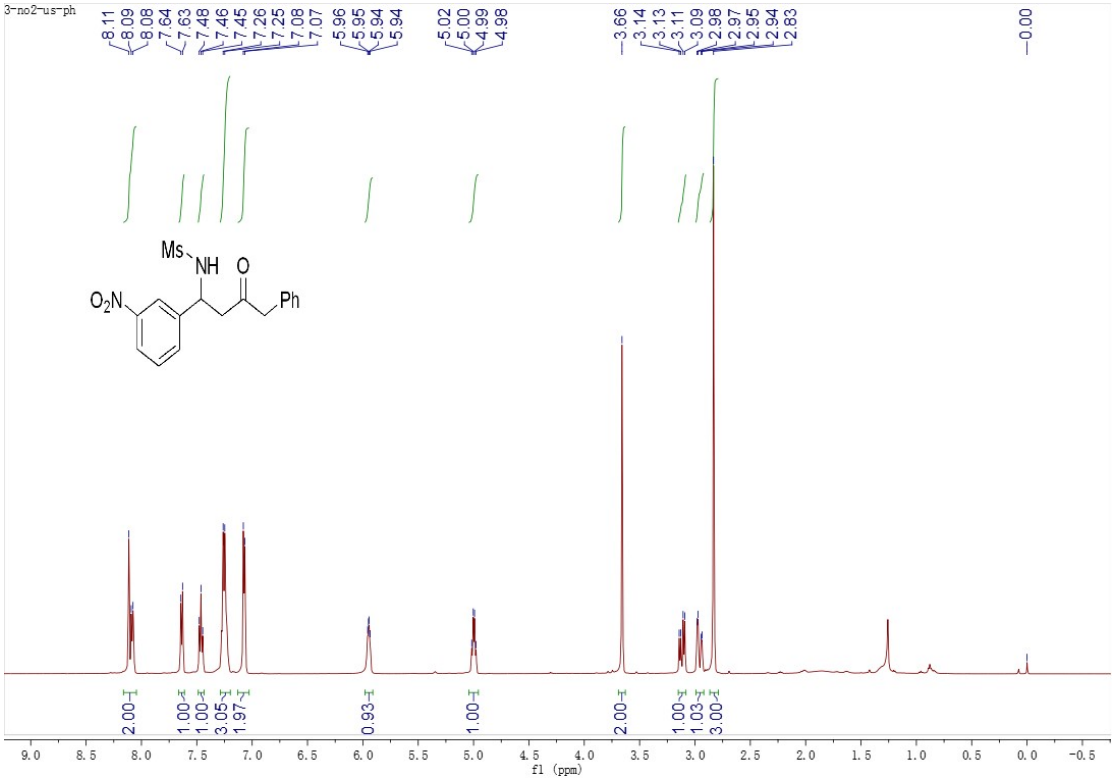

3-no2-ybj
208.12
148.56
143.37
132.96
129.89
122.88
121.48
77.01
53.13
48.66
45.31
41.57
16.91
13.51
Ms
NH
O
O2N
f1 (ppm)

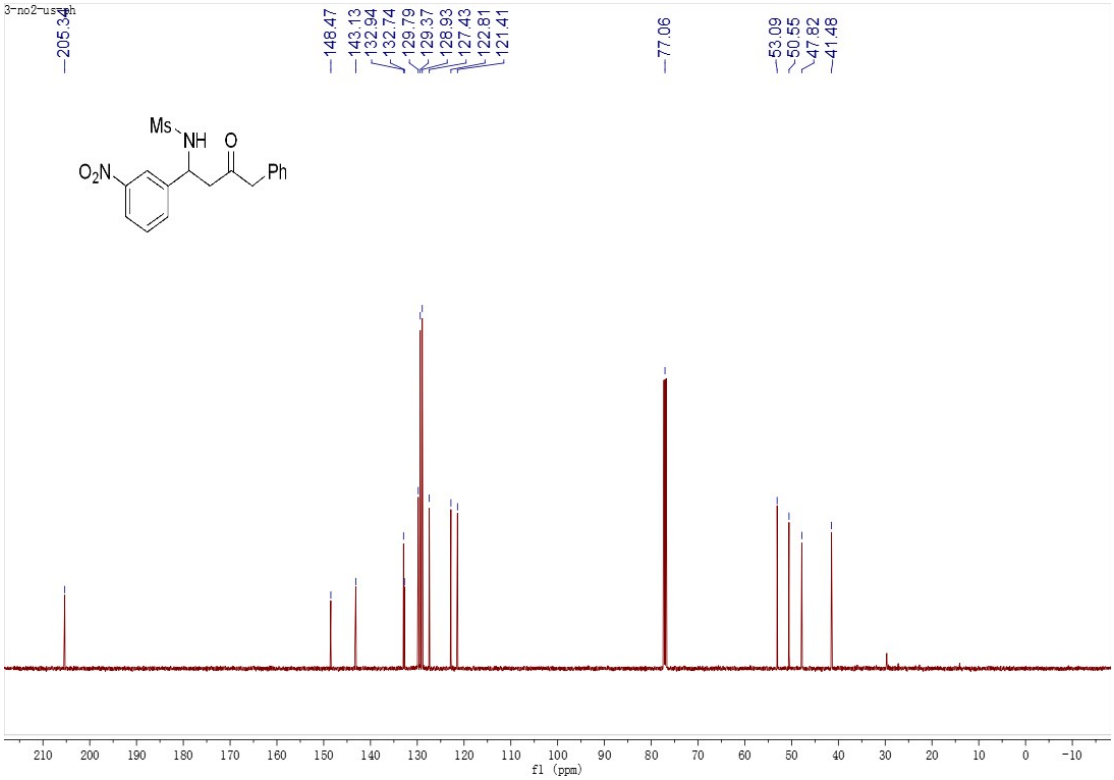
3t


3-NO2-YBJ
8.25
8.16
8.14
7.76
7.74
7.56
7.55
7.53
7.27
5.96
5.94
5.06
5.05
5.04
5.02
3.18
3.16
3.14
3.13
3.02
3.01
2.98
2.97
2.90
2.57
2.56
2.55
2.53
2.52
1.06
1.04
1.04
1.02
0.00
Ms
NH
O
O2N
0.90
0.92
1.00
1.00
1.00
1.00
1.00
1.09
3.00
1.00
6.00
f1 (ppm)

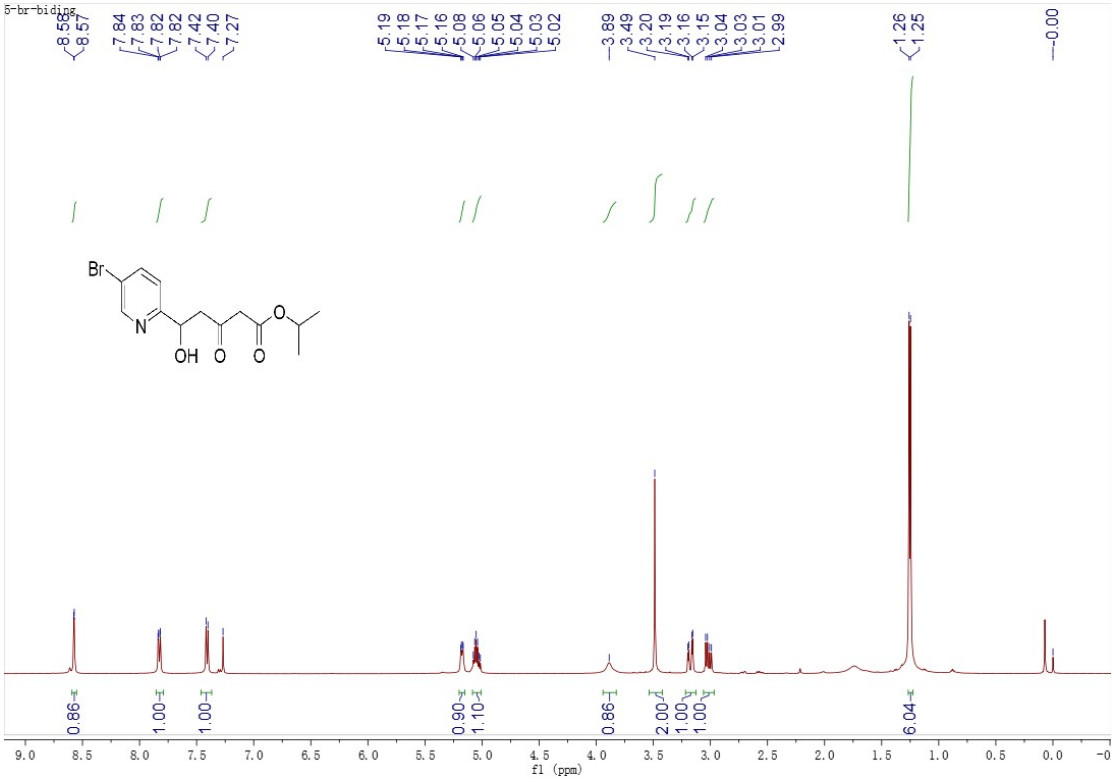

3-NO2-YBJ
211.86
148.53
143.45
132.97
129.87
122.86
121.44
77.02
53.20
46.47
41.55
41.34
17.71
17.70
Ms
NH
O
O2N
f1 (ppm)

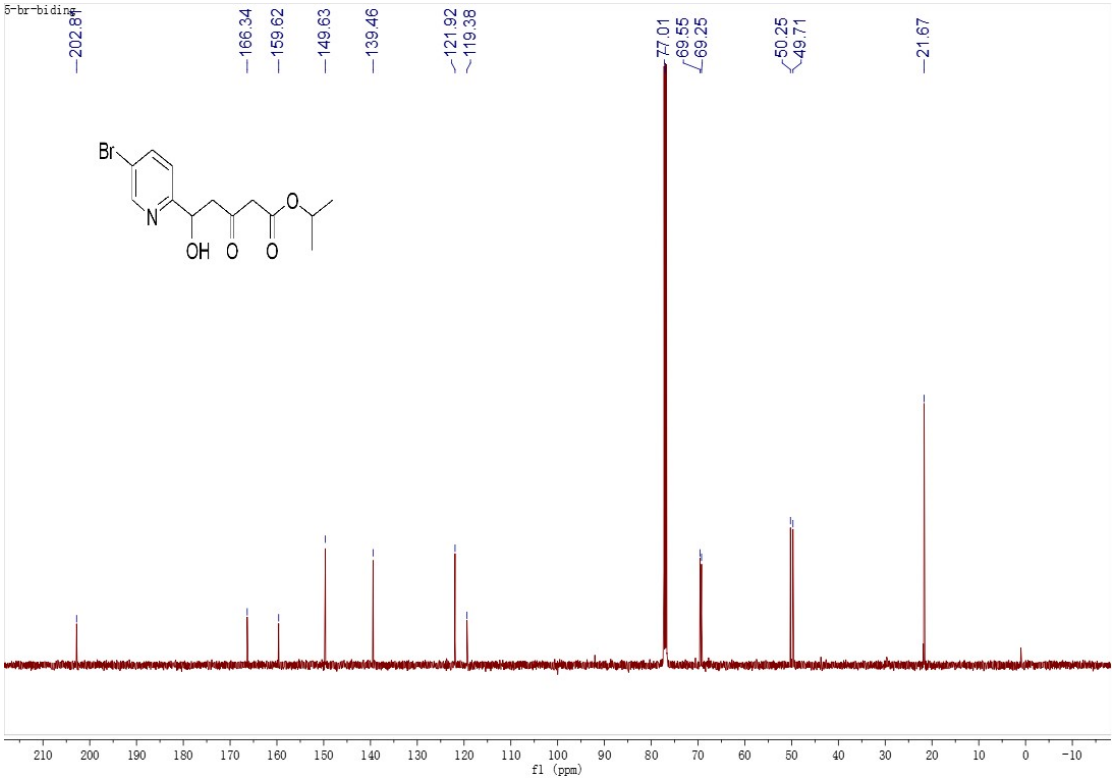
3u


3-no2-us-ph
8.11
8.09
8.08
7.64
7.63
7.48
7.46
7.45
7.26
7.25
7.08
7.07
5.96
5.95
5.94
5.94
5.02
5.00
4.99
4.98
3.66
3.14
3.13
3.11
3.09
2.98
2.97
2.95
2.94
2.83
0.00
Ms
NH
O
O2N
Ph
2.00
1.00
1.00
3.05
1.97
0.93
1.00
2.00
1.00
1.03
3.00
f1 (ppm)

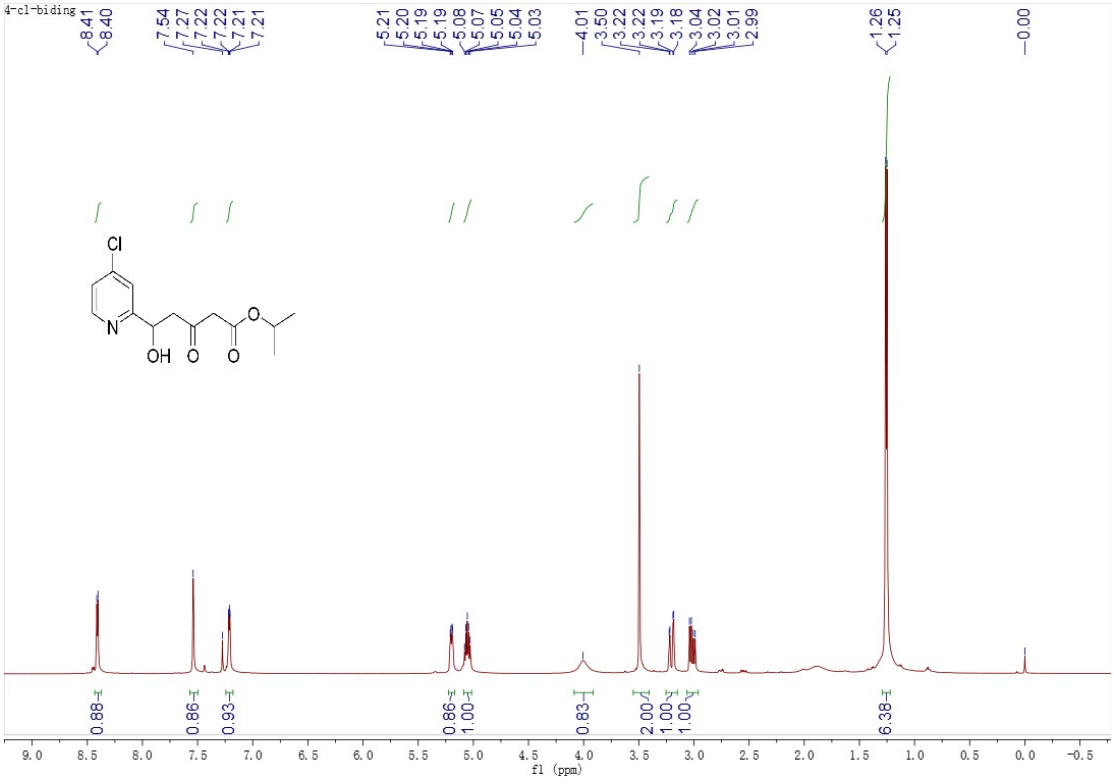

3-no2-usual
205.34
148.47
143.13
132.94
132.74
129.79
129.37
128.93
127.43
122.81
121.41
77.06
53.09
50.55
47.82
41.48
Ms
NH
O
O2N
Ph
f1 (ppm)

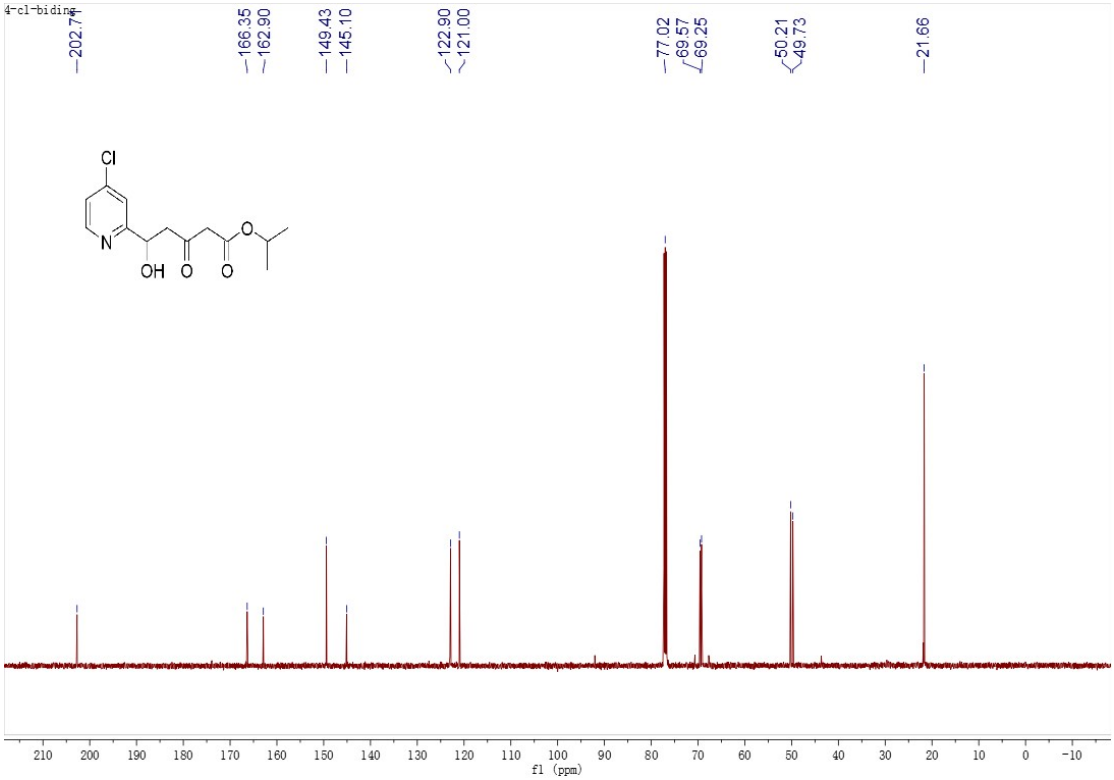
5a


5-br-biding
8.58
8.57
7.84
7.83
7.82
7.82
7.42
7.40
7.27
5.19
5.18
5.17
5.16
5.08
5.06
5.05
5.04
5.03
5.02
3.89
3.49
3.20
3.19
3.16
3.15
3.04
3.03
3.01
2.99
1.26
1.25
0.00
Br
N
OH
O
O
O
0.86
1.00
1.00
0.90
1.10
0.86
2.00
1.00
1.00
6.04
f1 (ppm)

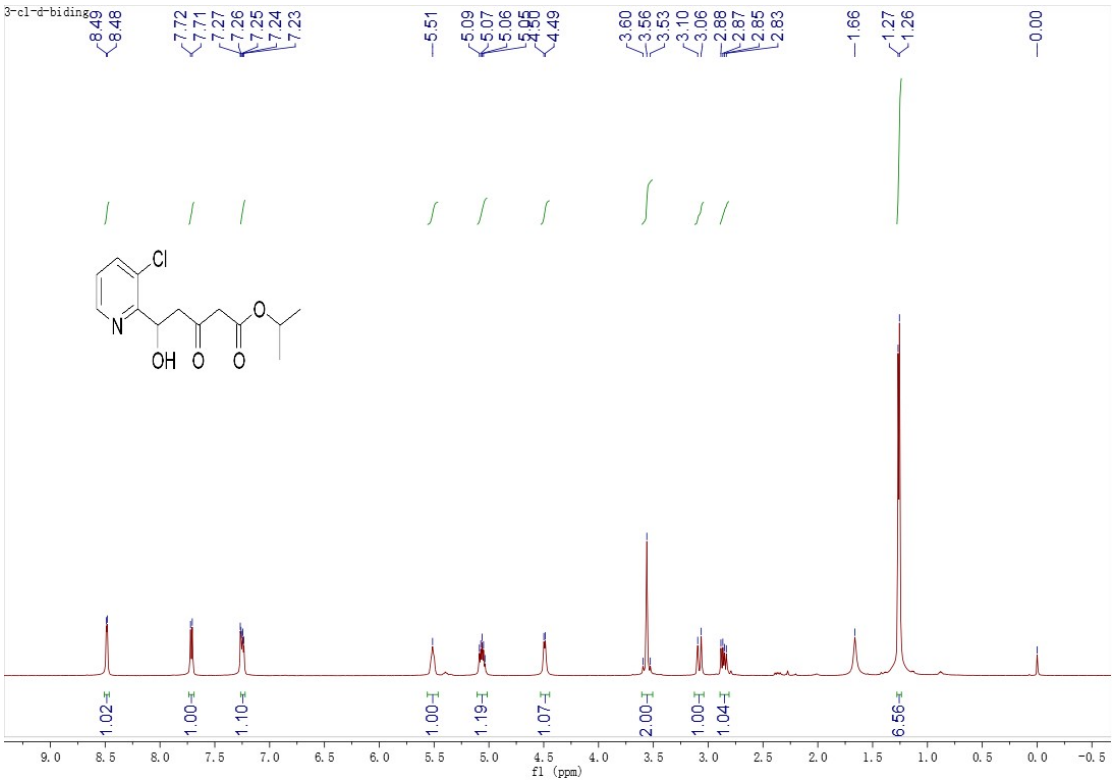

5-br-biding
202.84
166.34
159.62
149.63
139.46
121.92
119.38
77.01
69.55
69.25
50.25
49.71
21.67
Br
N
OH
O
O
O
f1 (ppm)

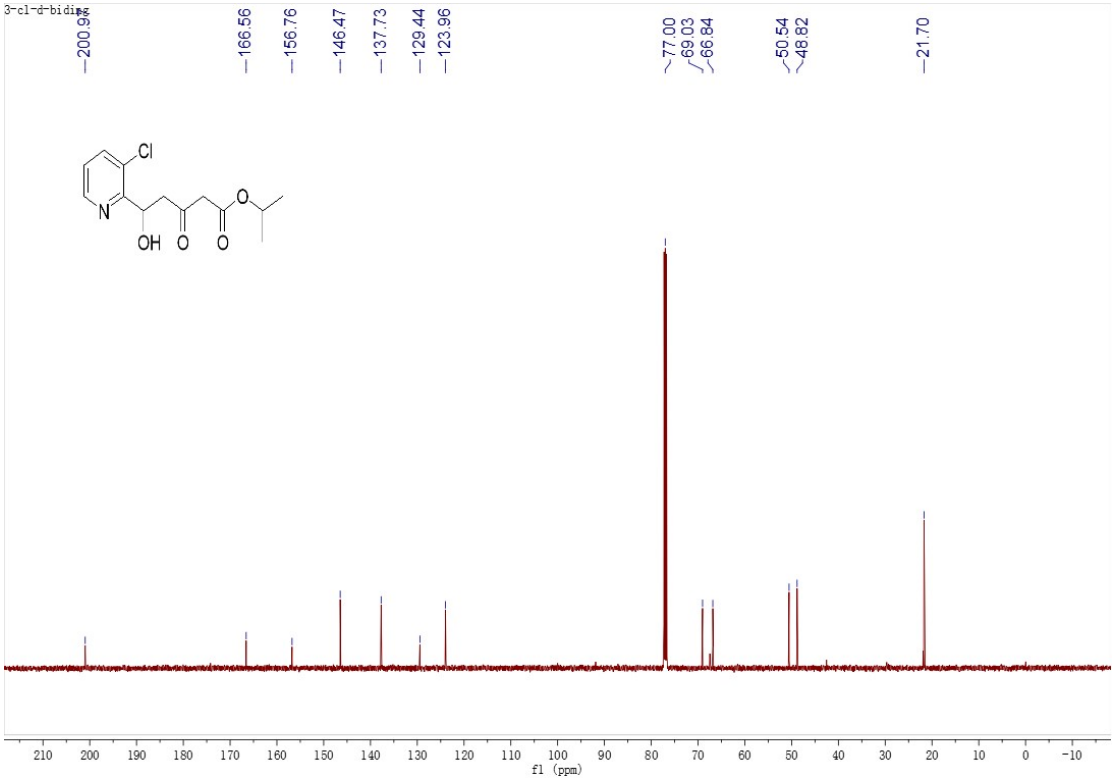
5b


4-cl-biding
8.41
8.40
7.54
7.27
7.22
7.22
7.21
7.21
5.21
5.20
5.19
5.19
5.08
5.07
5.05
5.04
5.03
4.01
3.50
3.22
3.22
3.19
3.18
3.04
3.02
3.01
2.99
1.26
1.25
0.00
Cl
N
OH
O
O
O
0.88
0.86
0.93
0.86
1.00
0.83
2.00
1.00
1.00
6.38
f1 (ppm)

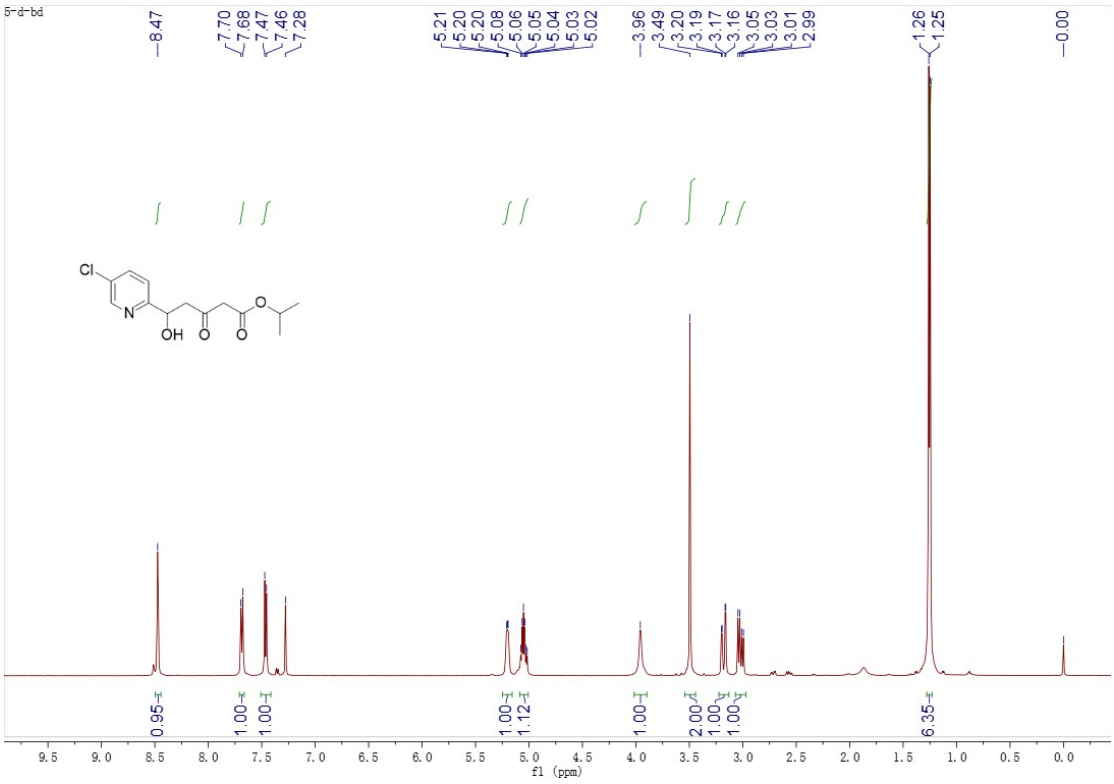

4-cl-biding
202.74
166.35
162.90
149.43
145.10
122.90
121.00
77.02
69.57
69.25
50.21
49.73
21.66
Cl
N
OH
O
O
O
f1 (ppm)

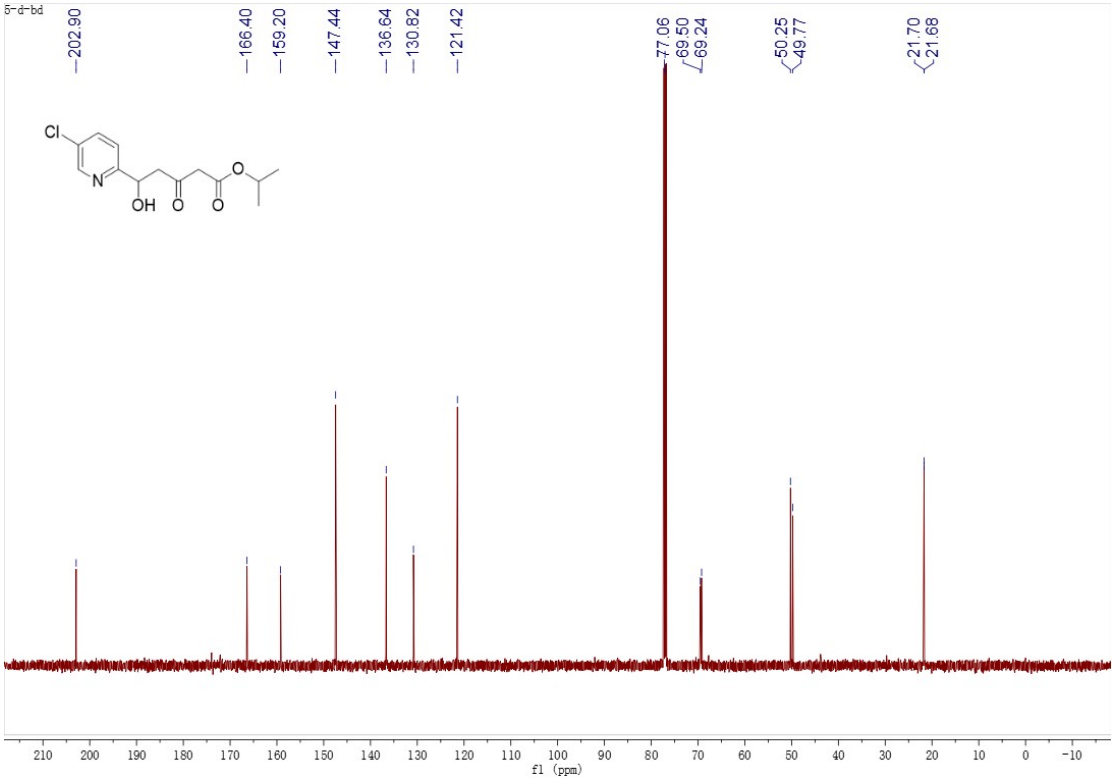
5c


3-cl-d-biding
8.49
8.48
7.72
7.71
7.27
7.26
7.25
7.24
7.23
5.51
5.09
5.07
5.06
4.50
4.49
3.60
3.56
3.53
3.10
3.06
2.88
2.87
2.85
2.83
1.66
1.27
1.26
0.00
Cl
N
OH
O
O
O
1.02
1.00
1.10
1.00
1.19
1.07
2.00
1.00
1.04
6.56
f1 (ppm)

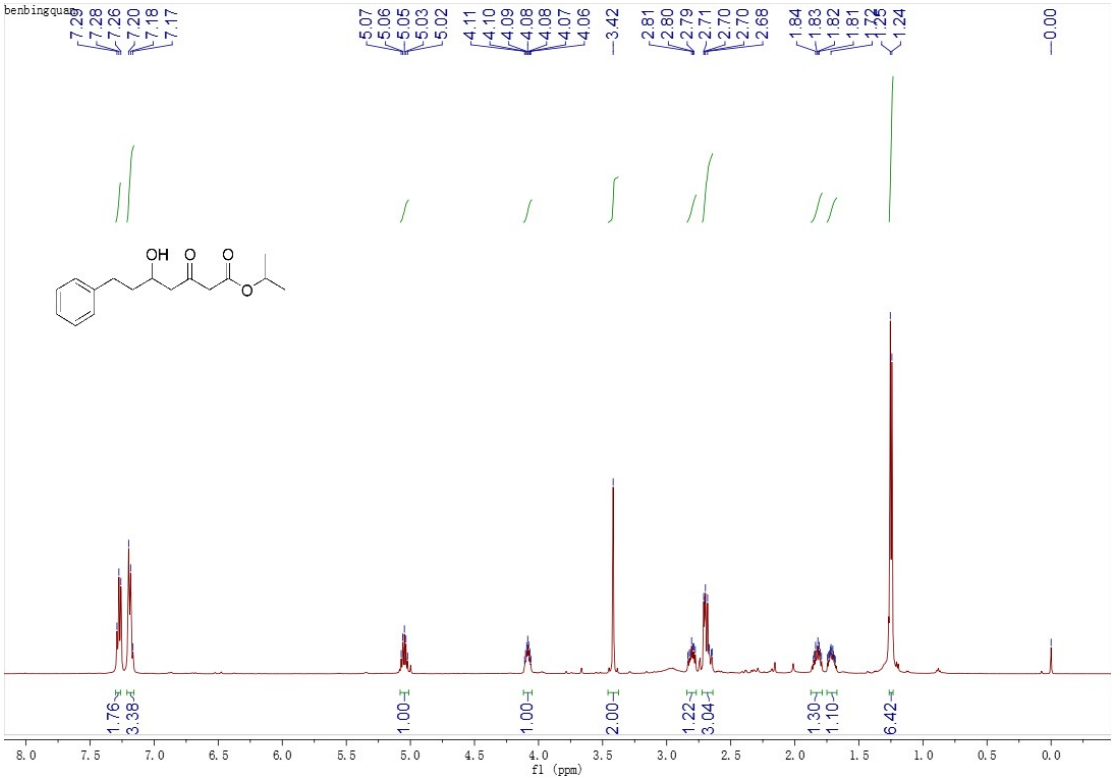

3-cl-d-bidi
200.98
166.56
156.76
146.47
137.73
129.44
123.96
77.00
69.03
66.84
50.54
48.82
21.70
Cl
N
OH
O
O
O
f1 (ppm)

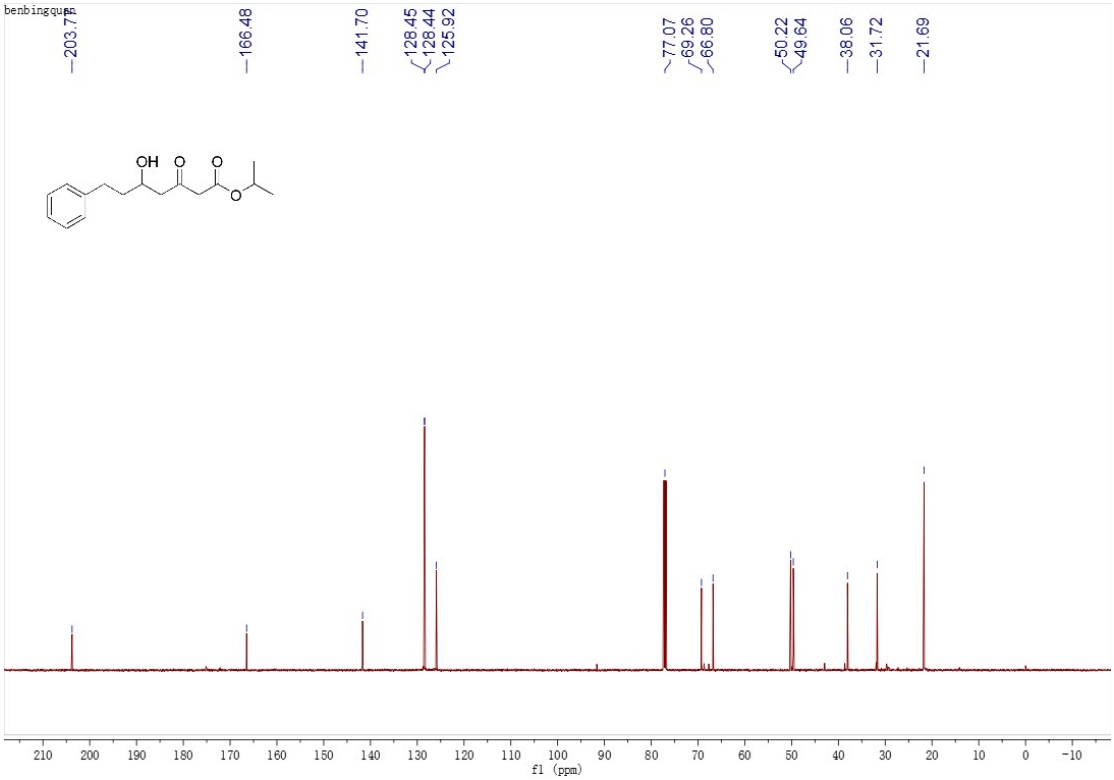
5d


5-d-bd
8.47
7.70
7.68
7.47
7.46
7.28
5.21
5.20
5.20
5.08
5.06
5.05
5.04
5.03
5.02
3.96
3.49
3.20
3.19
3.17
3.16
3.05
3.03
3.01
2.99
1.26
1.25
0.00
Cl
N
OH
O
O
O
0.95
1.00
1.00
1.00
1.12
1.00
2.00
1.00
1.00
6.35
f1 (ppm)

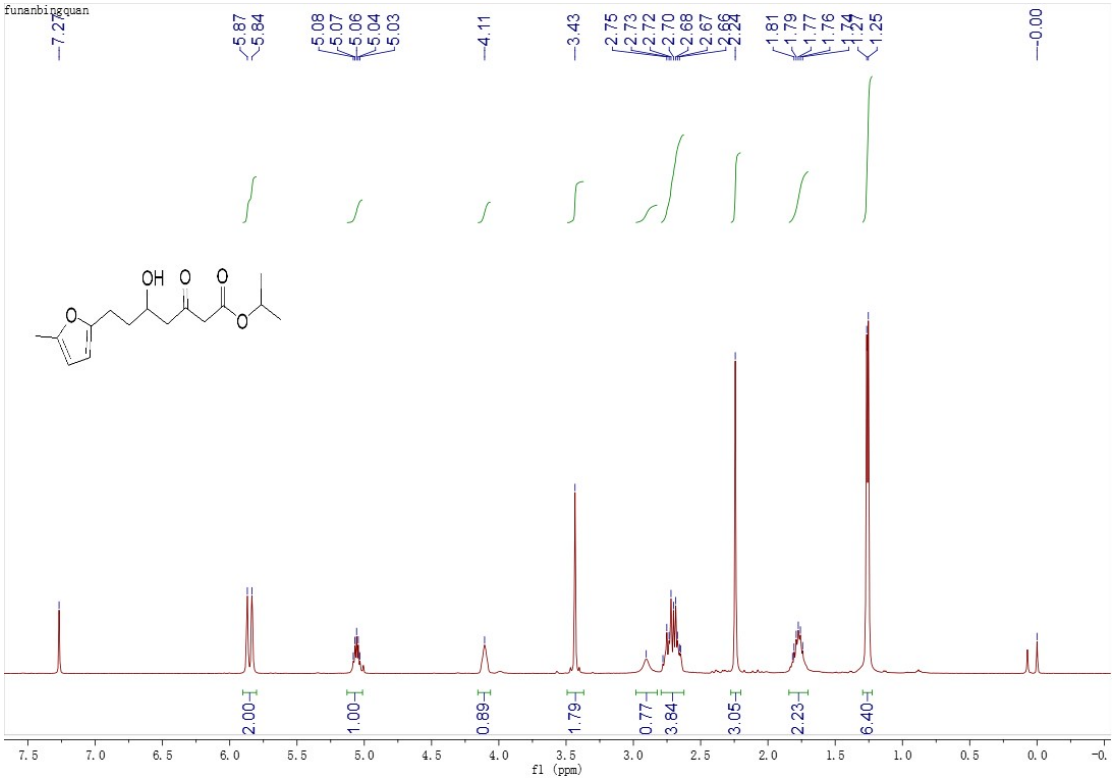

5-d-bd
202.90
166.40
159.20
147.44
136.64
130.82
121.42
77.06
69.50
69.24
50.25
49.77
21.70
21.68
Cl
N
OH
O
O
O
f1 (ppm)

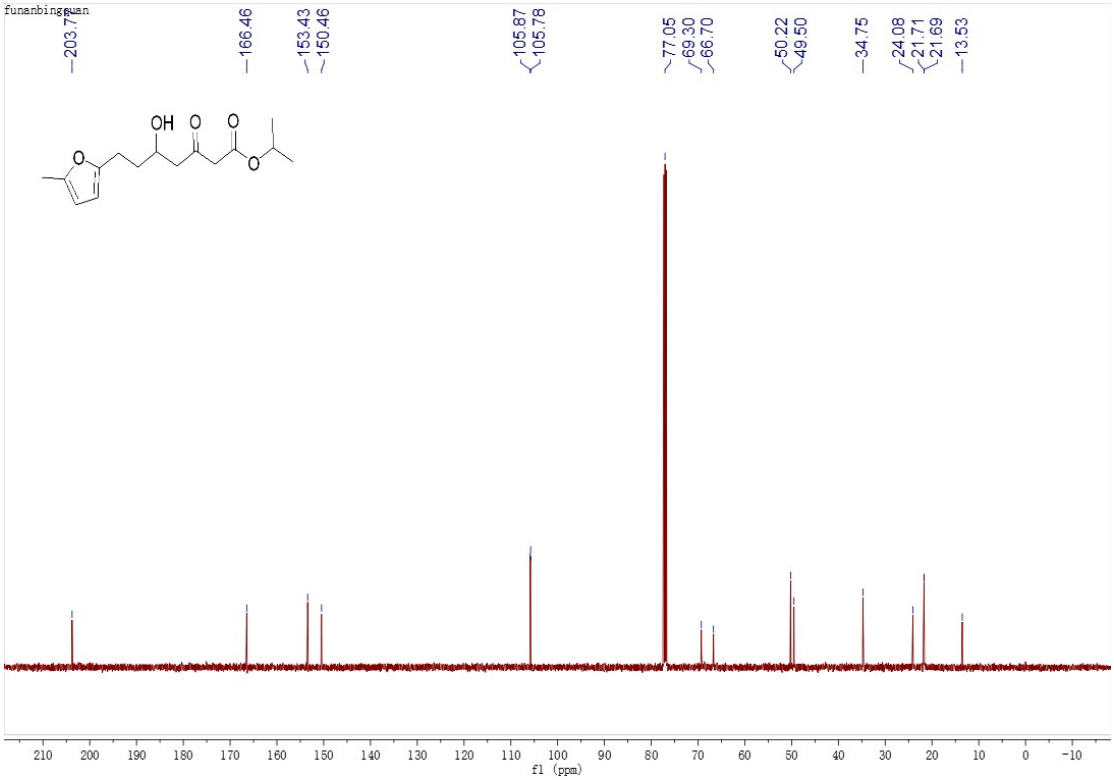
5e


benbingquan
7.29
7.28
7.26
7.20
7.18
7.17
5.07
5.06
5.05
5.03
5.02
4.11
4.10
4.09
4.08
4.08
4.07
4.06
3.42
2.81
2.80
2.79
2.71
2.70
2.70
2.68
1.84
1.83
1.82
1.81
1.24
0.00
OH
O
O
O
1.76
3.38
1.00
1.00
2.00
1.22
3.04
1.30
1.10
6.42
f1 (ppm)

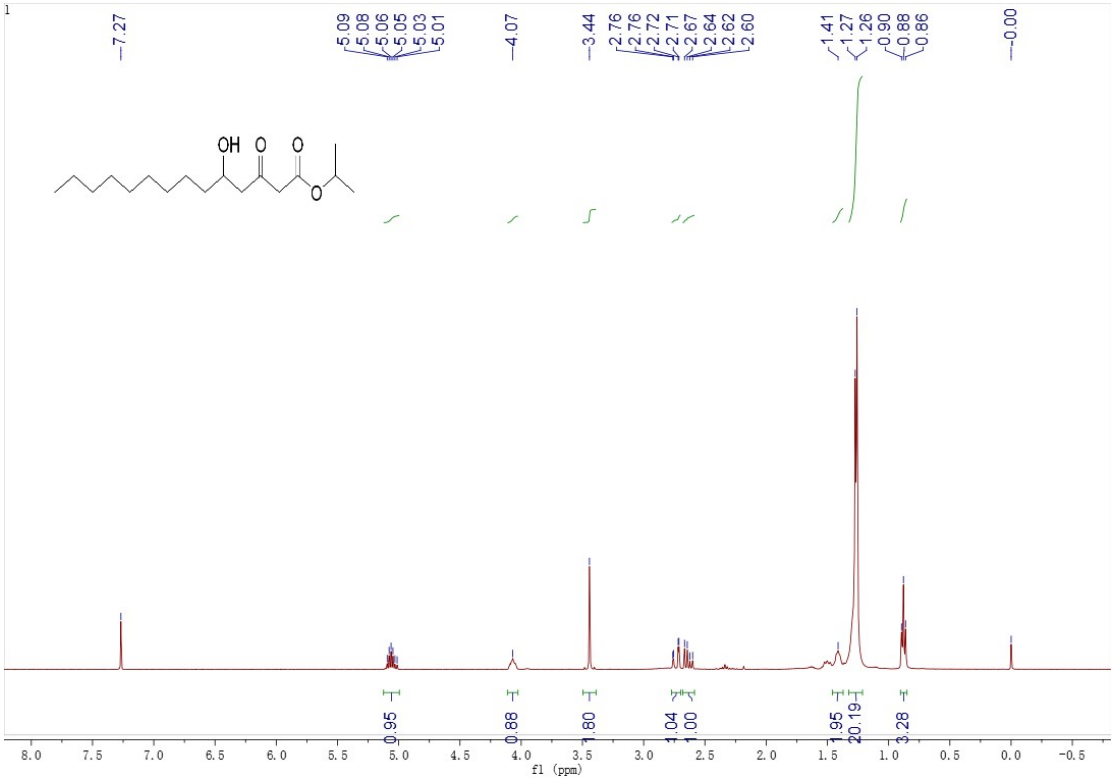

benbingquan
203.75
166.48
141.70
128.45
128.44
125.92
77.07
69.26
66.80
50.22
49.64
38.06
31.72
21.69
OH
O
O
O
f1 (ppm)

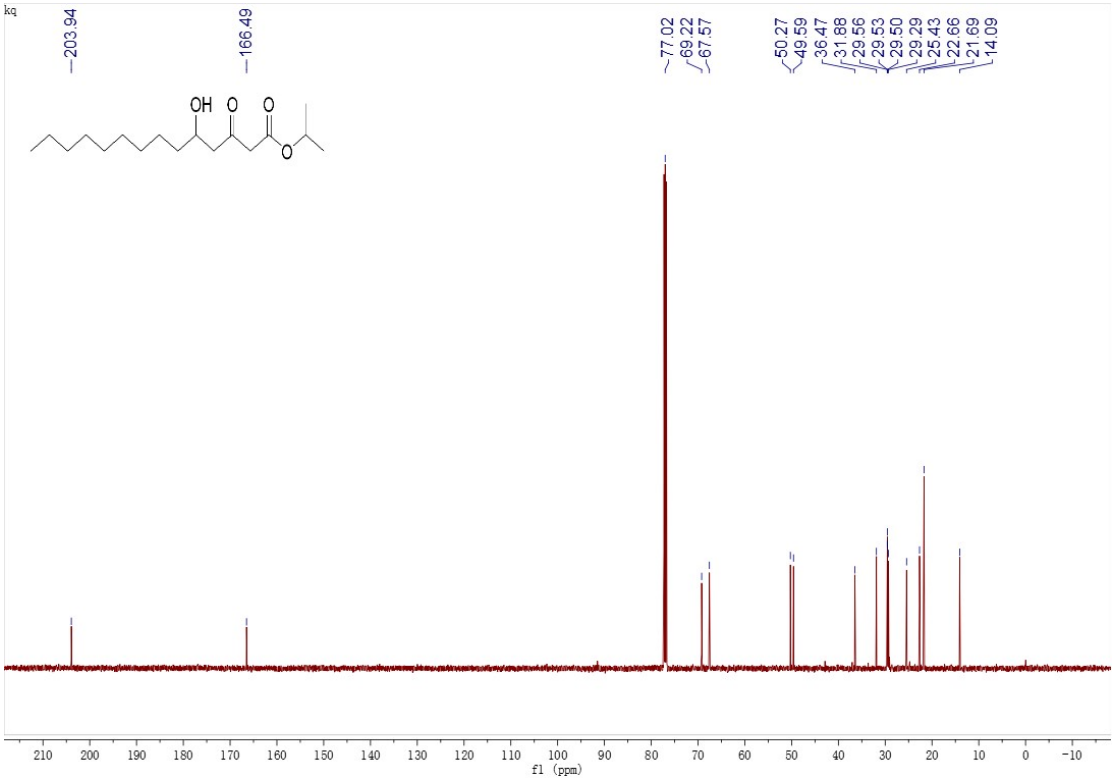
5f


funanbingquan
7.27
5.87
5.84
5.08
5.07
5.06
5.04
5.03
4.11
3.43
2.75
2.73
2.72
2.70
2.68
2.67
2.66
2.24
1.81
1.79
1.77
1.76
1.25
0.00
OH
O
O
O
2.00
1.00
0.89
1.79
0.77
3.84
3.05
2.23
6.40
f1 (ppm)

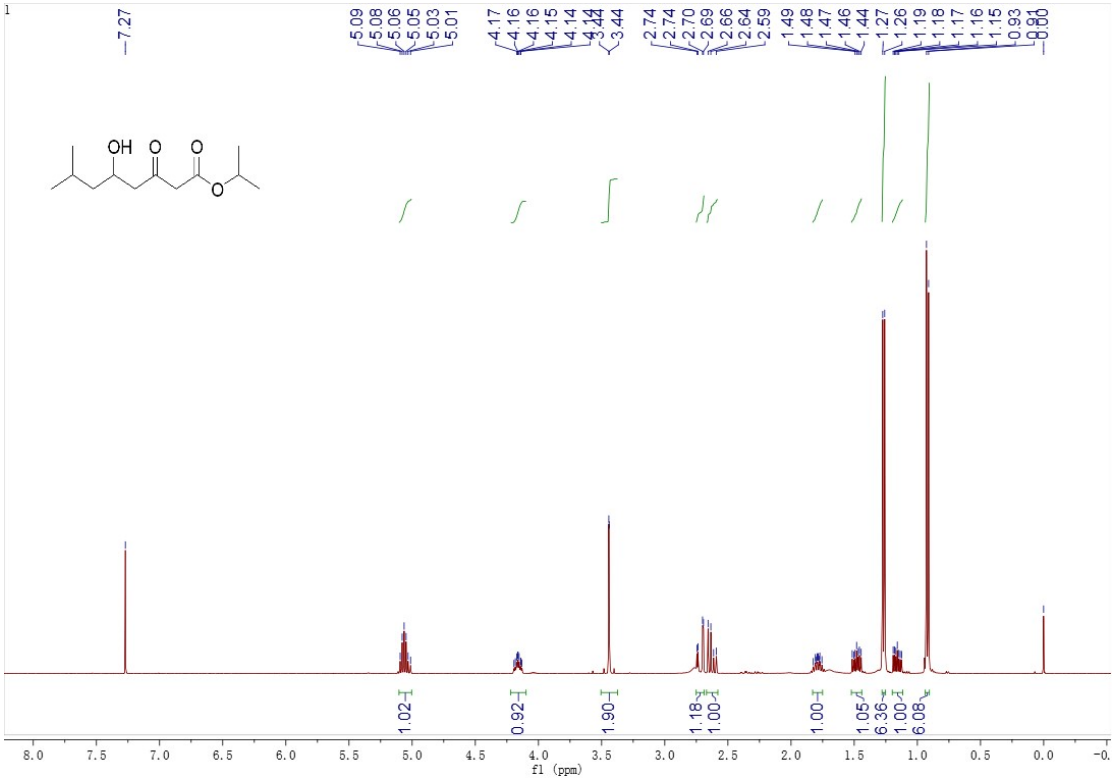

funanbingguan
203.72
166.46
153.43
150.46
105.87
105.78
77.05
69.30
66.70
50.22
49.50
34.75
24.08
21.71
21.69
13.53
OH
O
O
O
f1 (ppm)

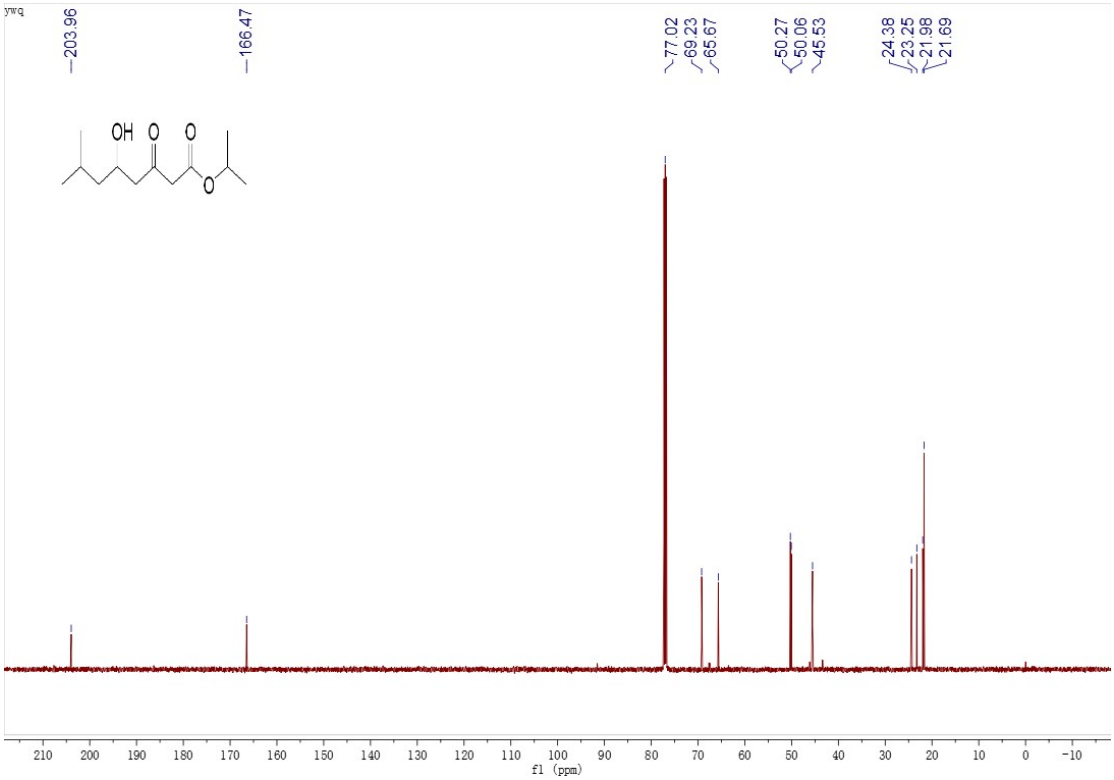
5g


1
7.27
5.09
5.08
5.06
5.05
5.03
5.01
4.07
3.44
2.76
2.72
2.71
2.67
2.64
2.62
2.60
1.41
1.27
1.26
0.90
0.88
0.86
0.00
OH
O
O
O
0.95
0.88
1.80
1.04
1.00
1.95
20.19
3.28
f1 (ppm)

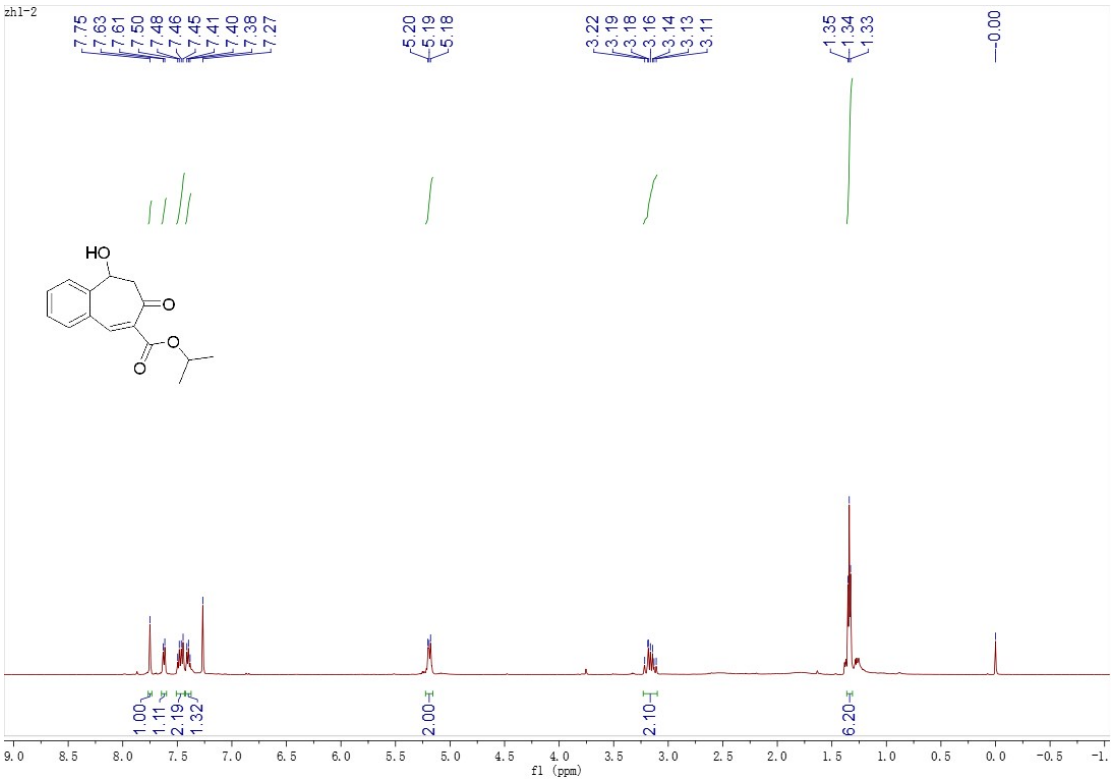

kq
203.94
166.49
77.02
69.22
67.57
50.27
49.59
36.47
31.88
29.56
29.53
29.50
29.29
25.43
22.66
21.69
14.09
OH O O
O
f1 (ppm)

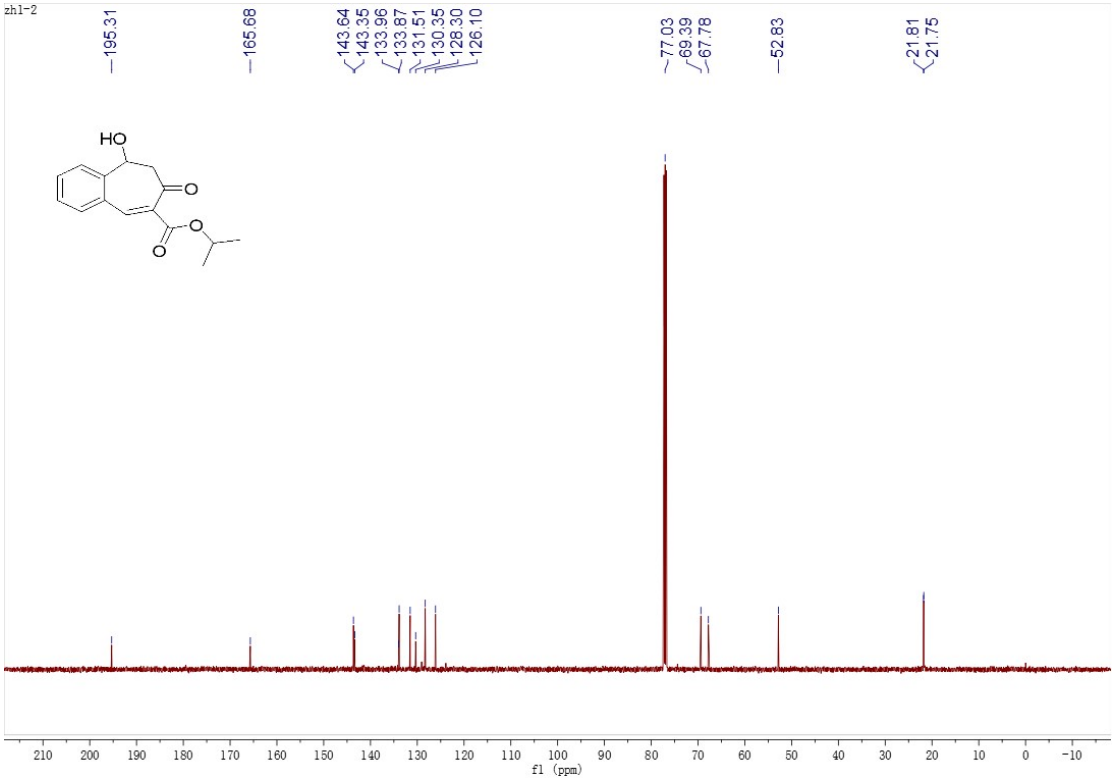
5h


7.27
5.09
5.08
5.06
5.05
5.03
5.01
4.17
4.16
4.16
4.15
4.14
3.44
2.74
2.74
2.70
2.69
2.66
2.64
2.59
1.49
1.48
1.47
1.46
1.44
1.27
1.26
1.19
1.18
1.17
1.16
1.15
0.93
0.91
0.00
OH O O
O
1.02
0.92
1.90
1.18
1.00
1.00
1.05
6.36
1.00
6.08
f1 (ppm)

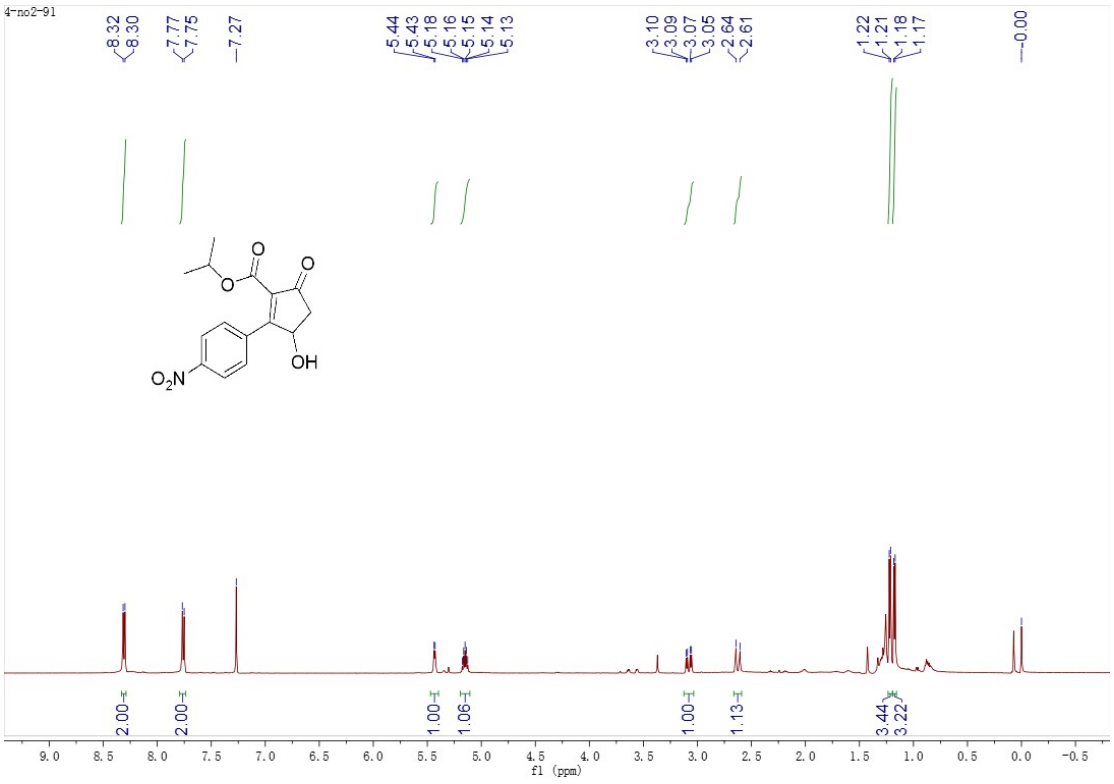

ywq
203.96
166.47
77.02
69.23
65.67
50.27
50.06
45.53
24.38
23.25
21.98
21.69
OH
O
O
O
f1 (ppm)

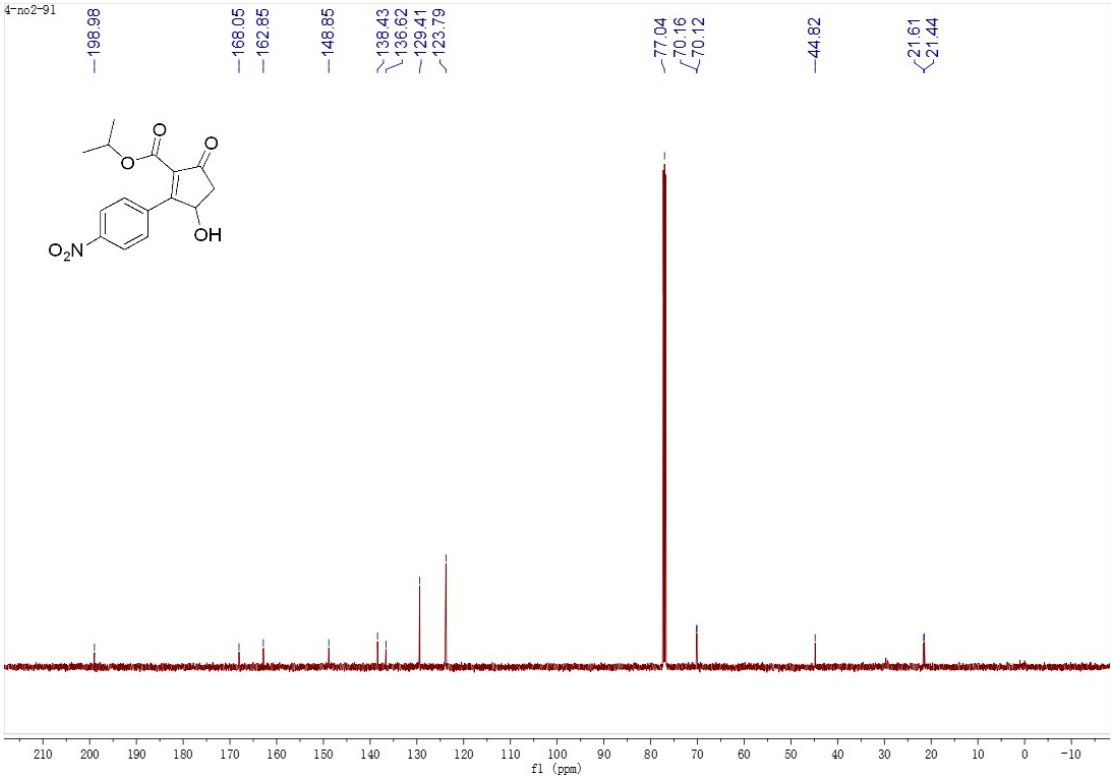
5i


zhl-2
7.75
7.63
7.61
7.50
7.48
7.46
7.45
7.41
7.40
7.38
7.27
5.20
5.19
5.18
3.22
3.19
3.18
3.16
3.14
3.13
3.11
1.35
1.34
1.33
0.00
HO
O
O
O
1.00
1.11
2.19
1.32
2.00
2.10
6.20
f1 (ppm)

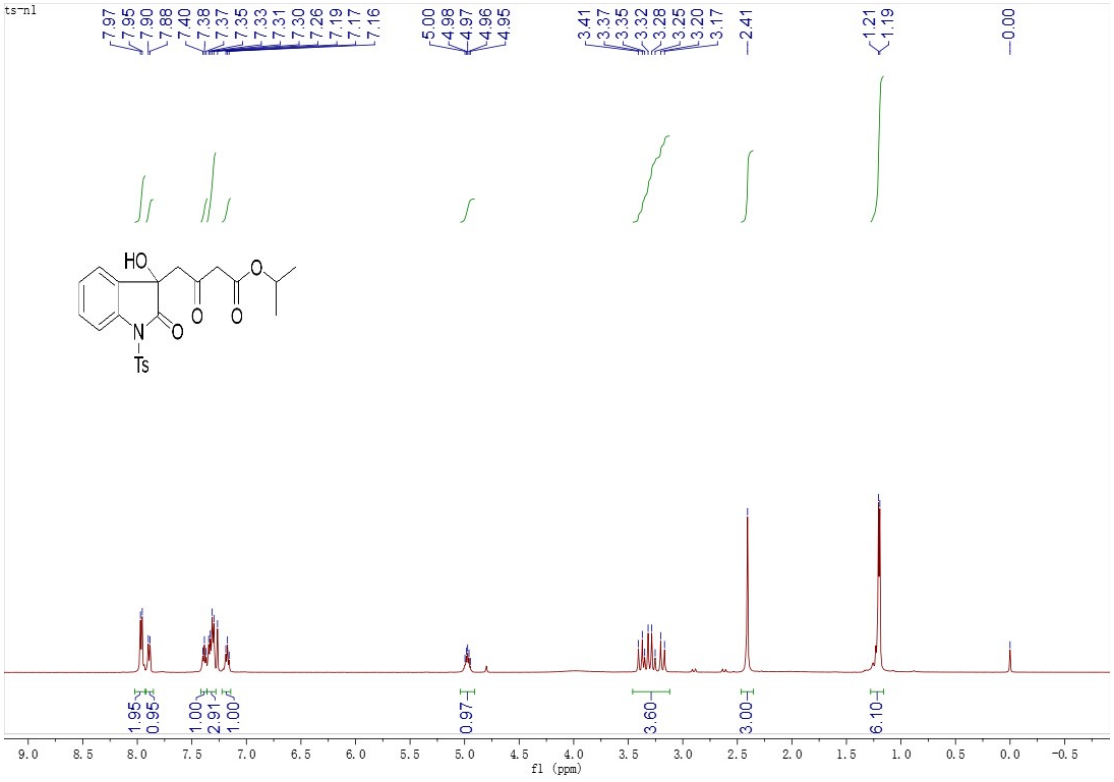

zh1-2
195.31
165.68
143.64
143.35
133.96
133.87
131.51
130.35
128.30
126.10
77.03
69.39
67.78
52.83
21.81
21.75
HO
O
O
O
f1 (ppm)

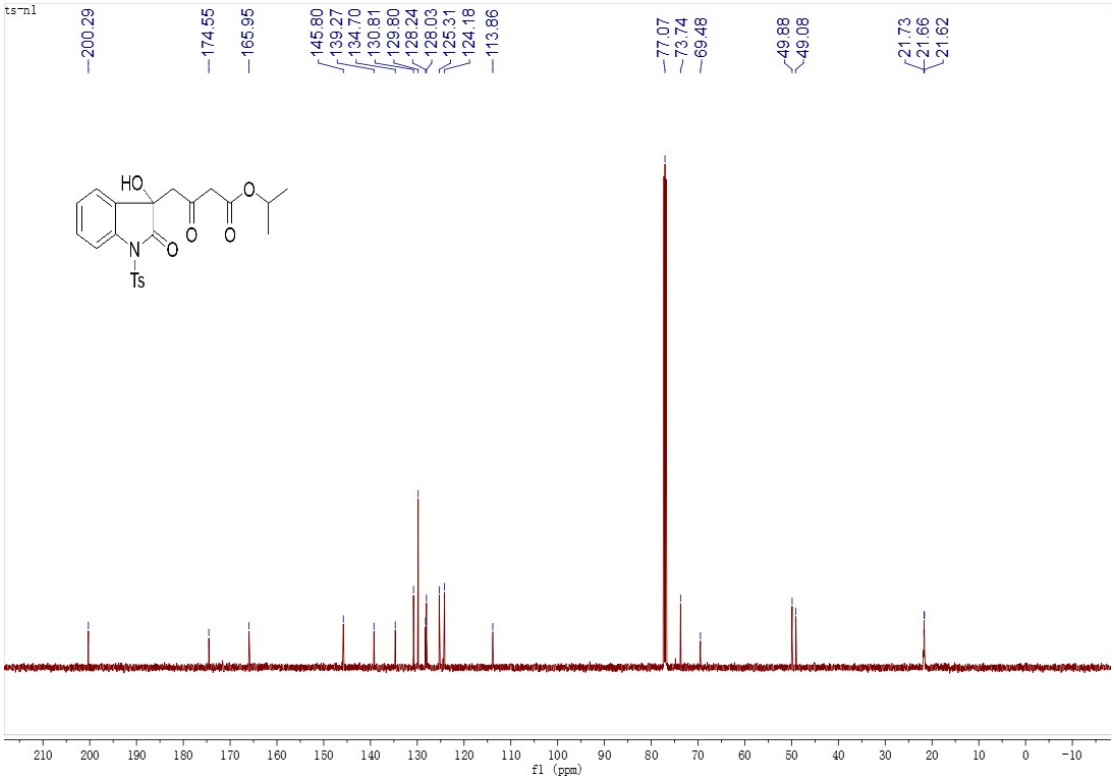
5j


4-no2-91
8.32
8.30
7.77
7.75
7.27
5.44
5.43
5.18
5.16
5.15
5.14
5.13
3.10
3.09
3.07
3.05
2.64
2.61
1.22
1.21
1.18
1.17
0.00
O
O
O
OH
O2N
2.00
2.00
1.00
1.06
1.00
1.13
3.44
3.22
f1 (ppm)

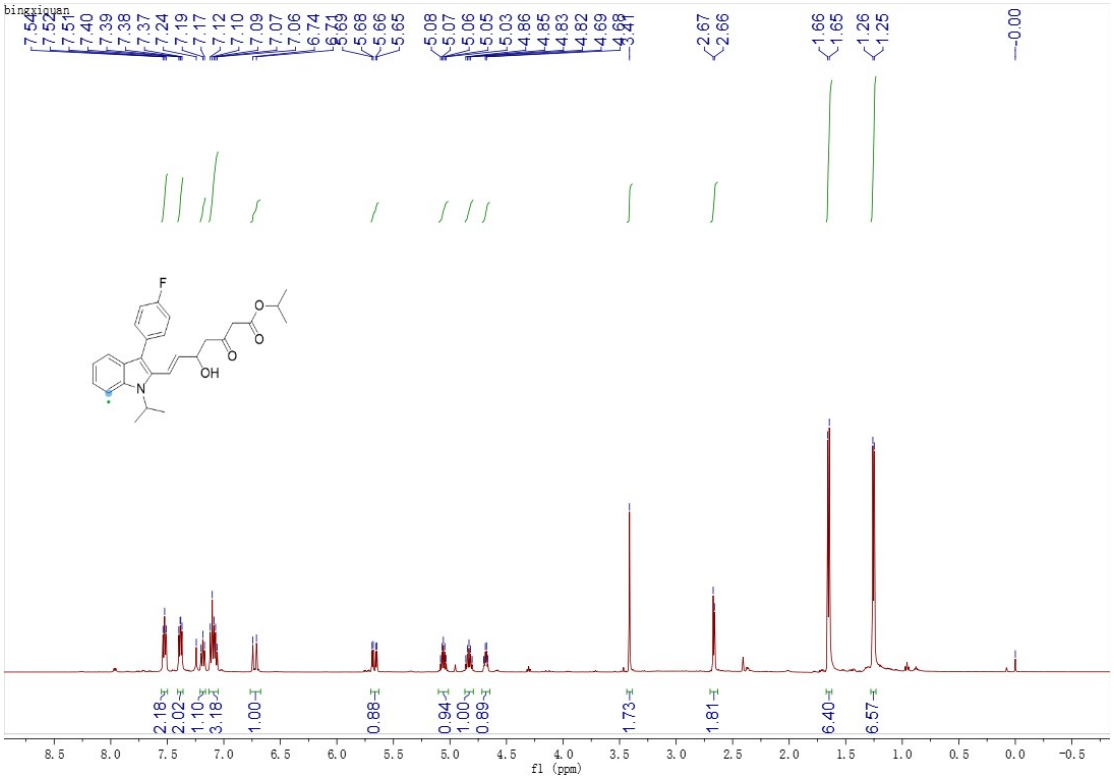

4-no2-91
198.98
168.05
162.85
148.85
138.43
136.62
129.41
123.79
77.04
70.16
70.12
44.82
21.61
21.44
O
O
O
OH
O2N
f1 (ppm)

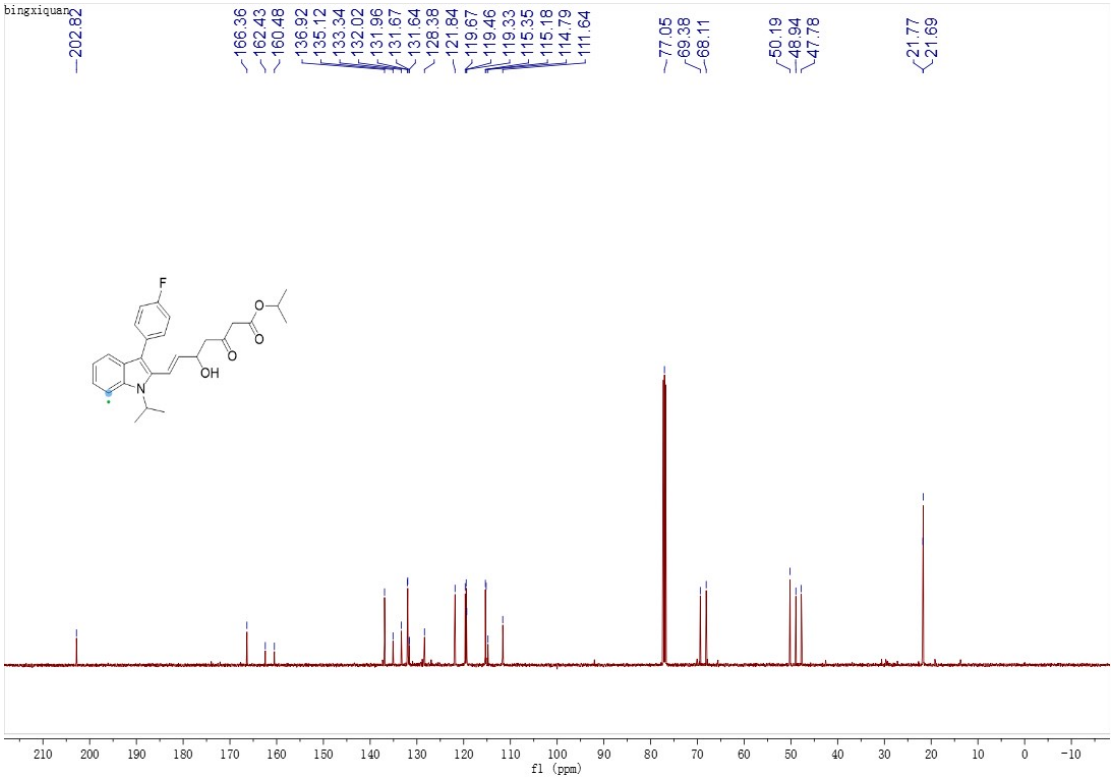
5k


ts-n1
7.97
7.95
7.90
7.88
7.40
7.38
7.37
7.35
7.33
7.31
7.30
7.26
7.19
7.17
7.16
5.00
4.98
4.97
4.96
4.95
3.41
3.37
3.35
3.32
3.28
3.25
3.20
3.17
2.41
1.21
1.19
0.00
HO
O
O
O
N
O
Ts
1.95
0.95
1.00
2.91
1.00
0.97
3.60
3.00
6.10
f1 (ppm)

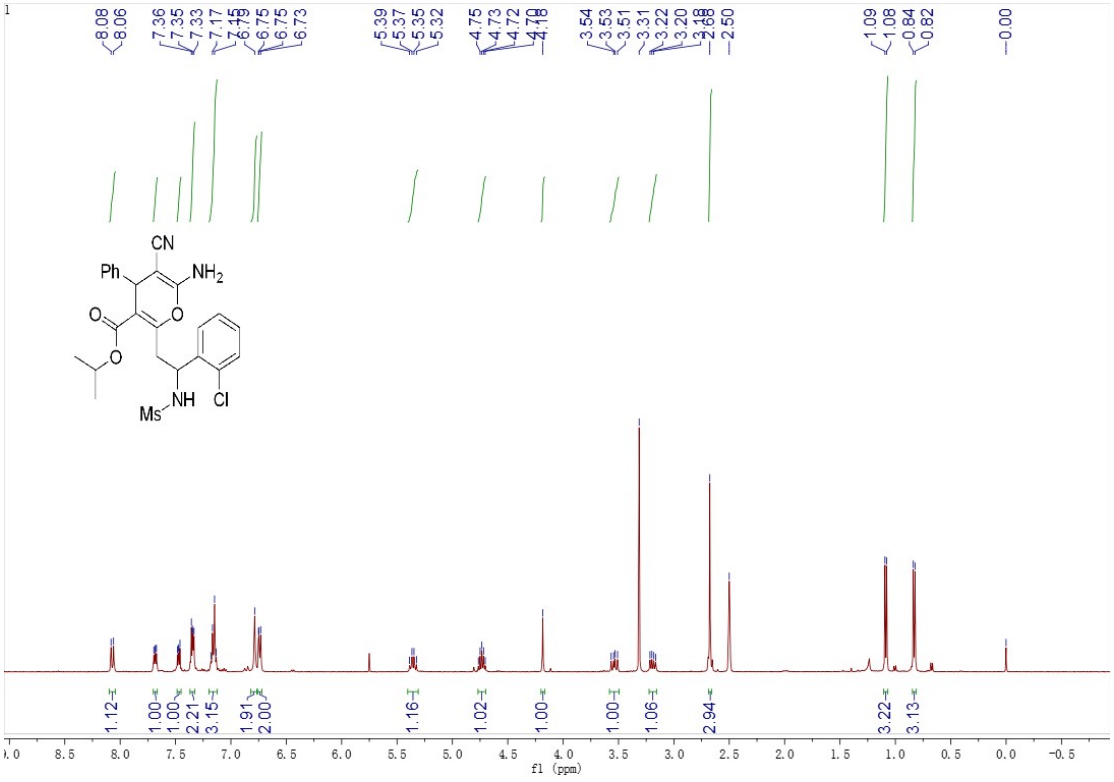

ts-n1
200.29
174.55
165.95
145.80
139.27
134.70
130.81
129.80
128.24
128.03
125.31
124.18
113.86
77.07
73.74
69.48
49.88
49.08
21.73
21.66
21.62
HO
O
O
O
N
O
Ts
f1 (ppm)

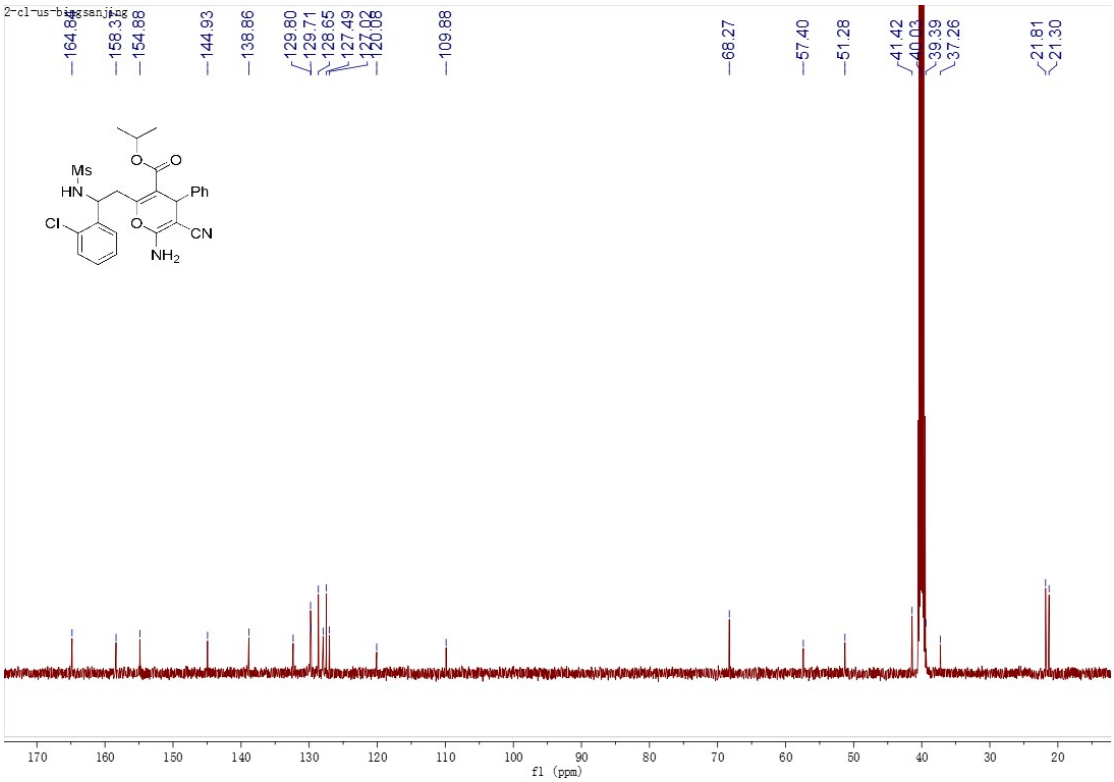
5l


binxiquan
7.54
7.52
7.51
7.40
7.39
7.38
7.37
7.24
7.19
7.17
7.12
7.10
7.09
7.07
7.06
6.74
6.71
5.69
5.68
5.66
5.65
5.08
5.07
5.06
5.05
5.03
4.86
4.85
4.83
4.82
4.69
4.68
4.41
2.67
2.66
1.66
1.65
1.26
1.25
0.00
F
O
O
OH
N
2.18
2.02
1.10
3.18
1.00
0.88
0.94
1.00
0.89
1.73
1.81
6.40
6.57
f1 (ppm)

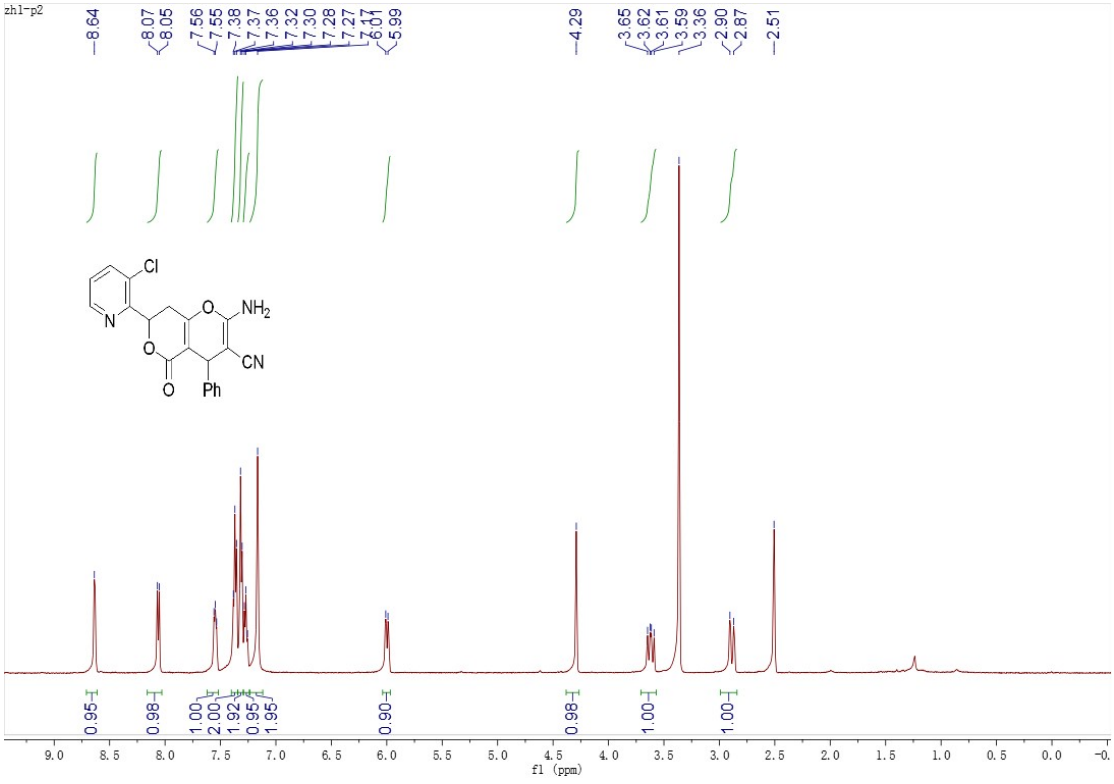

bingxiquan
202.82
166.36
162.43
160.48
136.92
135.12
133.34
132.02
131.96
131.67
131.64
128.38
121.84
119.67
119.46
119.33
115.35
115.18
114.79
111.64
77.05
69.38
68.11
50.19
48.94
47.78
21.77
21.69
F
O
O
O
OH
N
f1 (ppm)

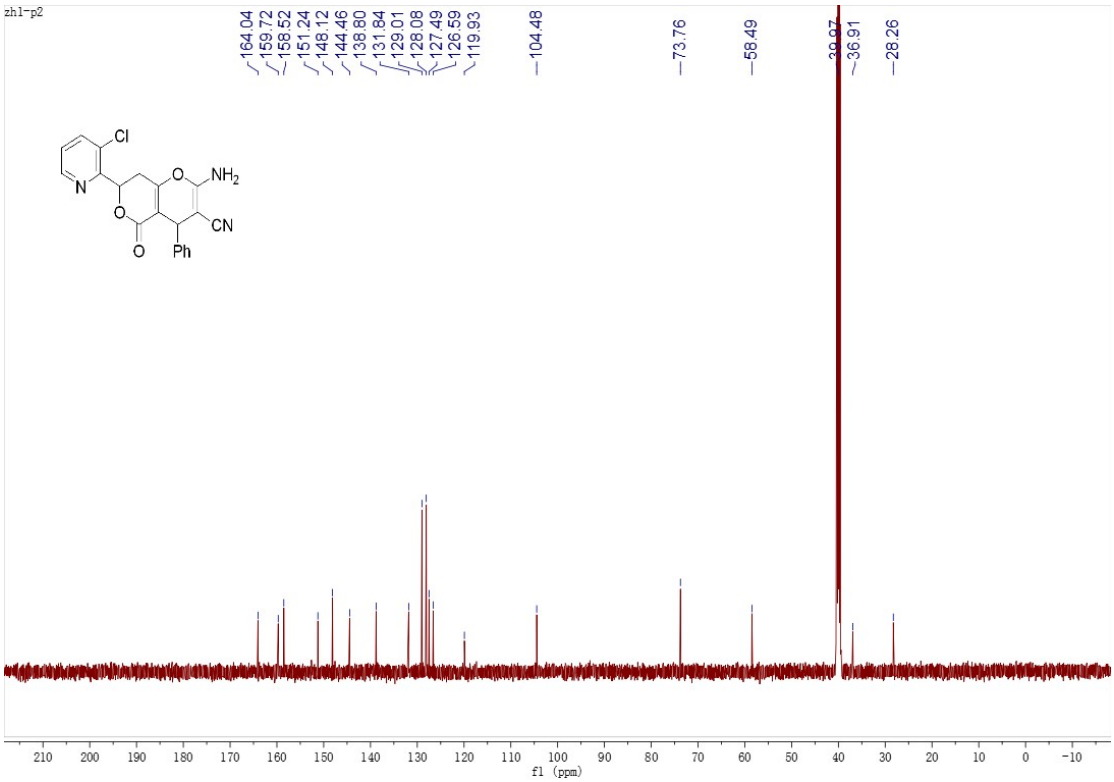
7


1
8.08
8.06
7.36
7.35
7.33
7.17
6.79
6.75
6.75
6.73
5.39
5.37
5.35
5.32
4.75
4.73
4.72
4.70
4.18
3.54
3.53
3.51
3.31
3.22
3.20
2.68
2.50
1.09
1.08
0.84
0.82
0.00
CN
Ph
NH2
O
O
O
NH
Ms
Cl
1.12
1.00
1.00
2.21
3.15
1.91
2.00
1.16
1.02
1.00
1.00
1.06
2.94
3.22
3.13
f1 (ppm)

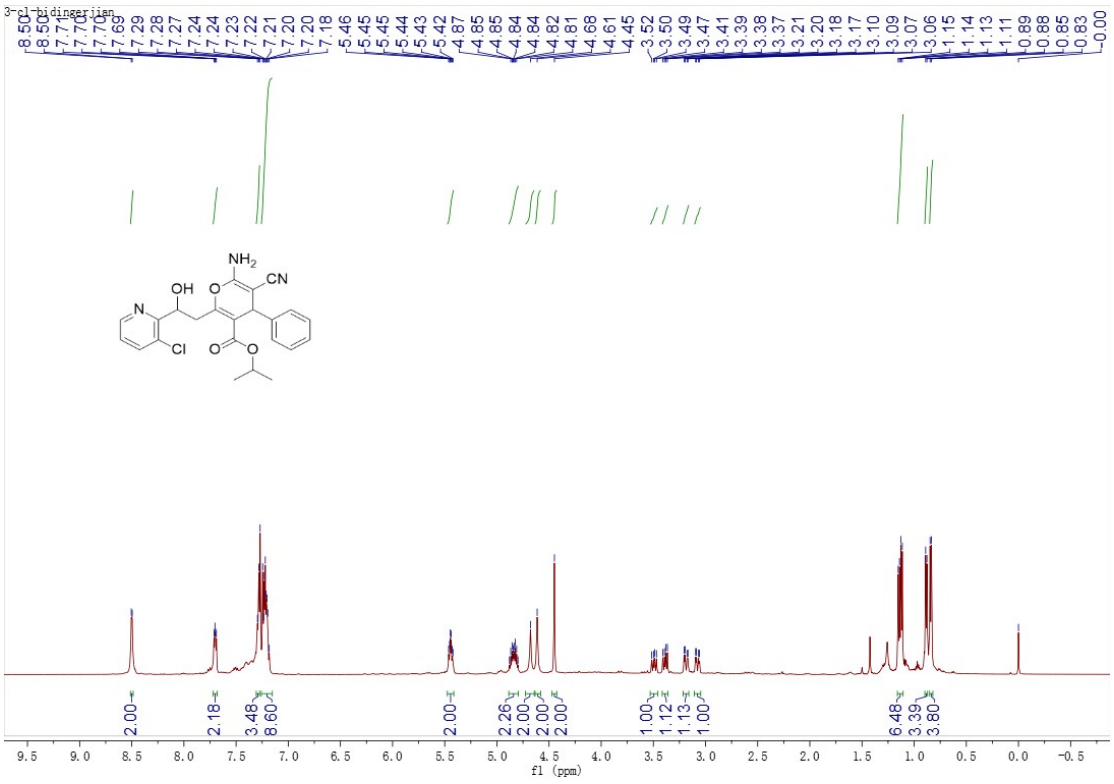

2-cl-us-bigsanjipg
164.84
158.31
154.88
144.93
138.86
129.80
129.71
128.65
127.49
127.02
120.08
109.88
68.27
57.40
51.28
41.42
40.03
39.39
37.26
21.81
21.30
Ms
HN
Cl
O
O
Ph
CN
O
NH2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

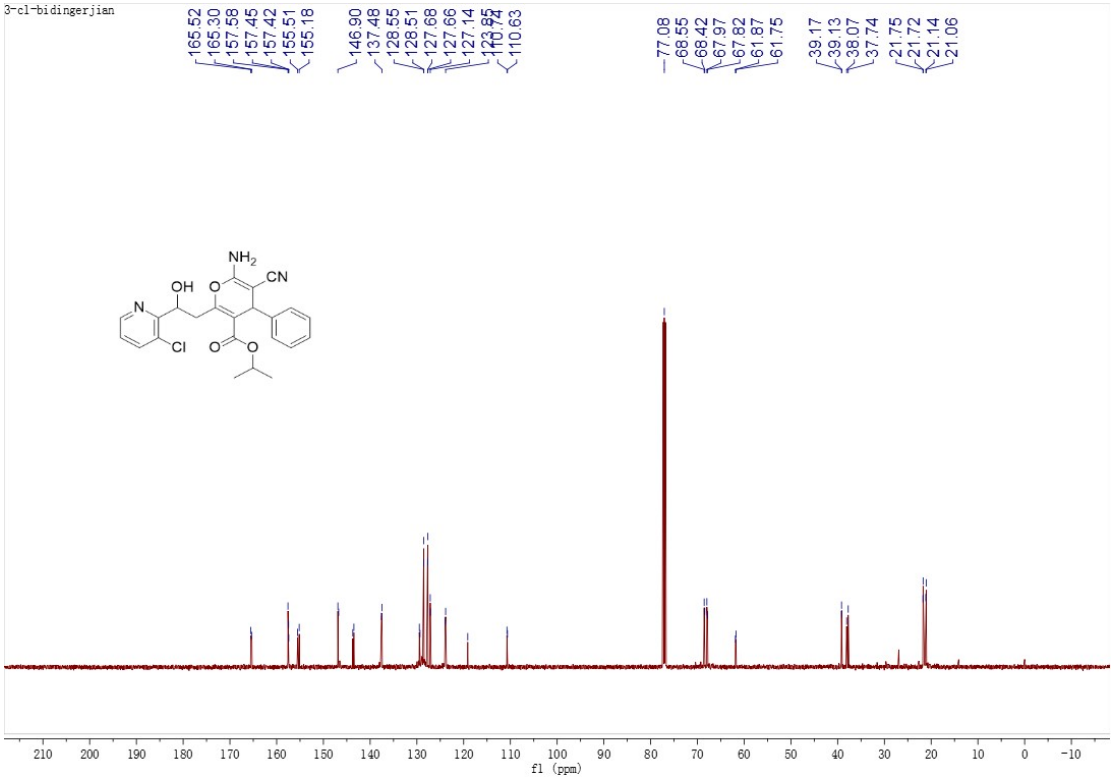
8


zhl-p2
8.64
8.07
8.05
7.56
7.55
7.38
7.37
7.36
7.32
7.30
7.28
7.27
7.17
6.01
5.99
4.29
3.65
3.62
3.61
3.59
3.36
2.90
2.87
2.51
Cl
N
O
O
O
NH2
CN
Ph
0.95
0.98
1.00
2.00
1.92
0.95
1.95
0.90
0.98
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

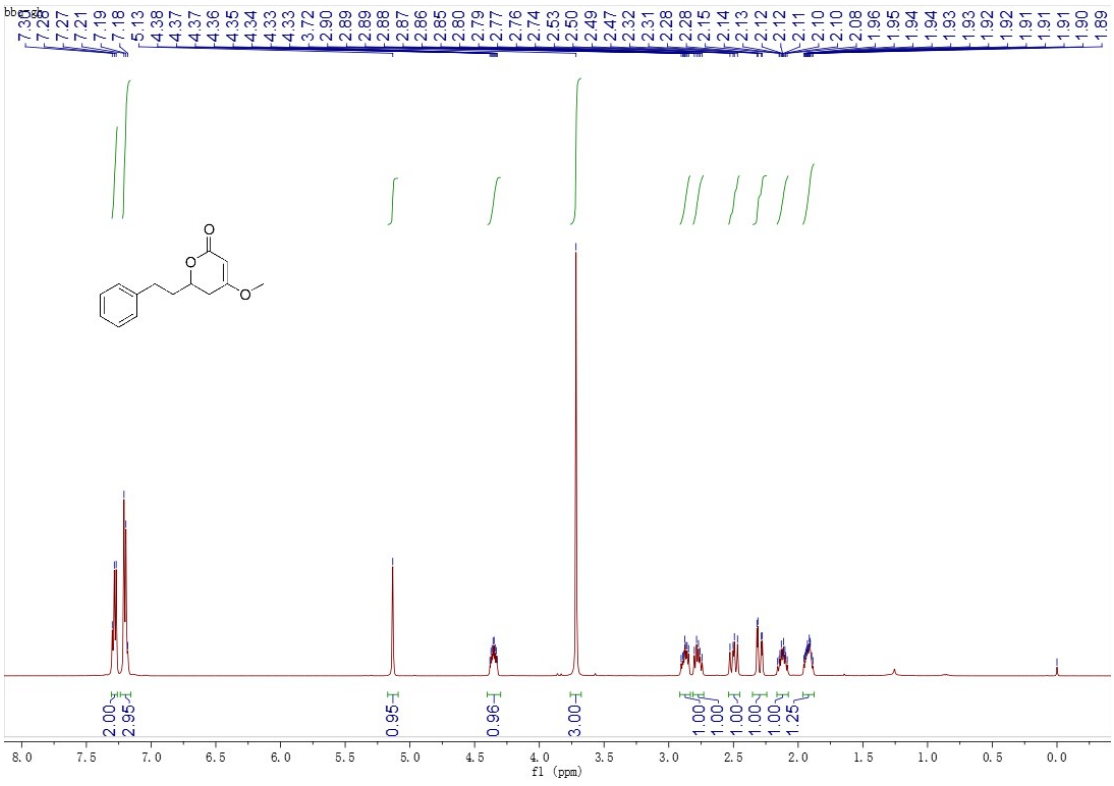


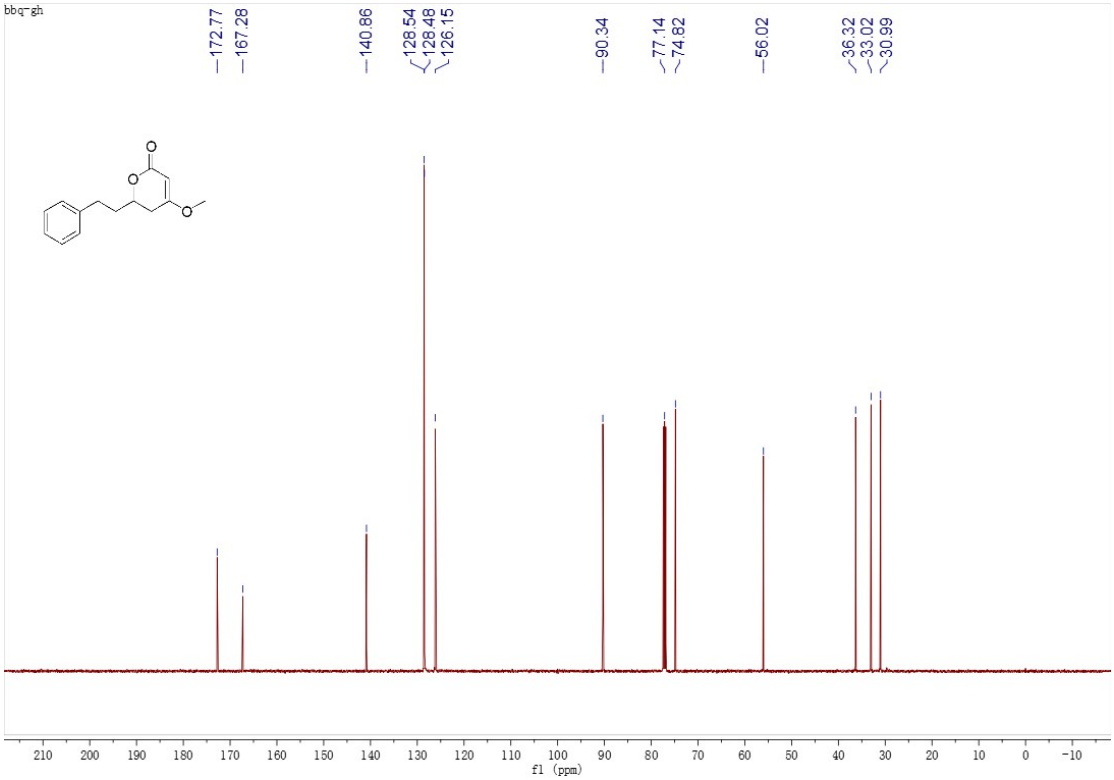
9 (mixture of diastereoisomers)



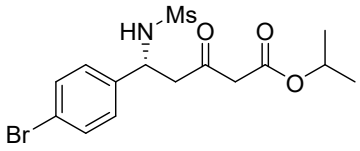


(+)-dihydroxykavain

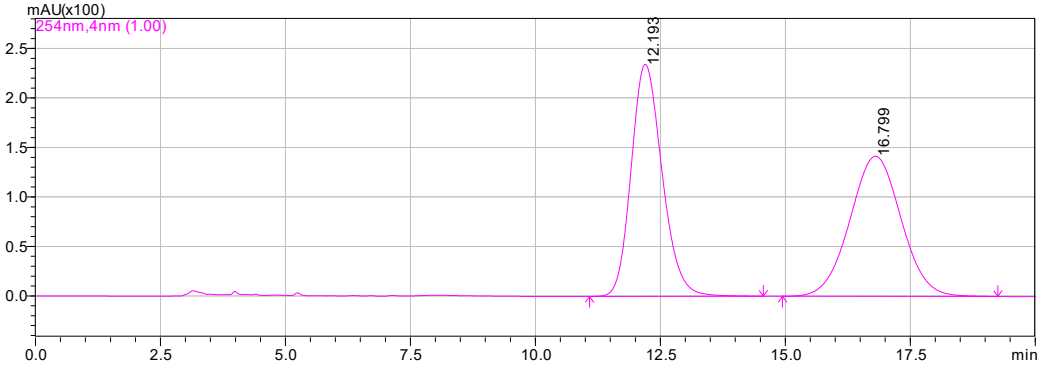




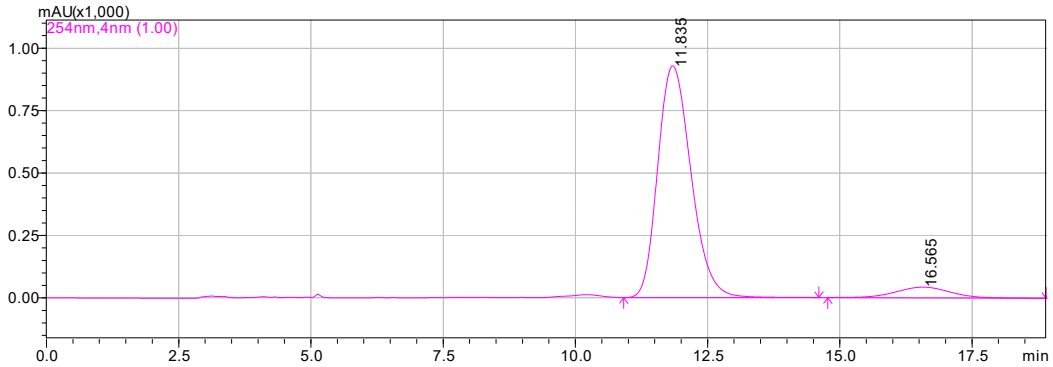
11. The HPLC of 3, 5-9



3a

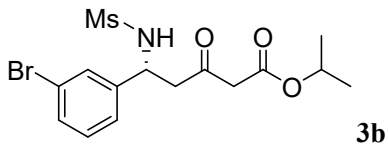


Peak	Ret. Time	Area	Area%
A	12.193	10111346	50.0380
B	16.799	10095975	49.9620

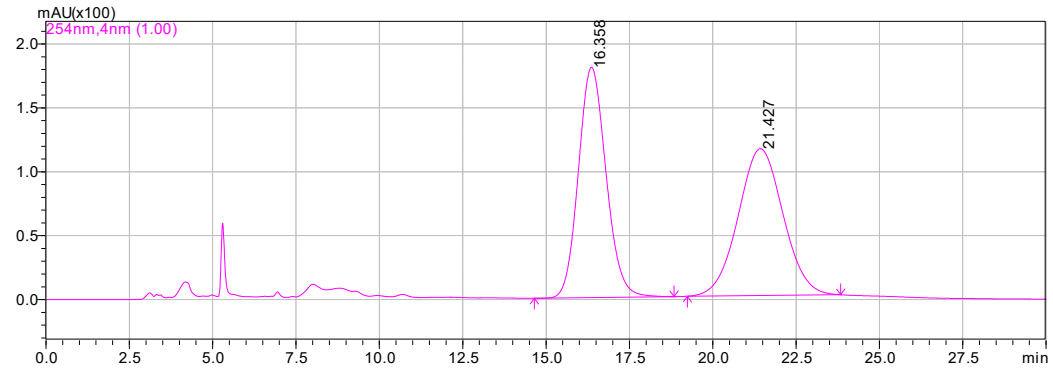


Peak	Ret. Time	Area	Area%
A	11.835	40581911	92.9609
B	16.565	3072892	7.0391

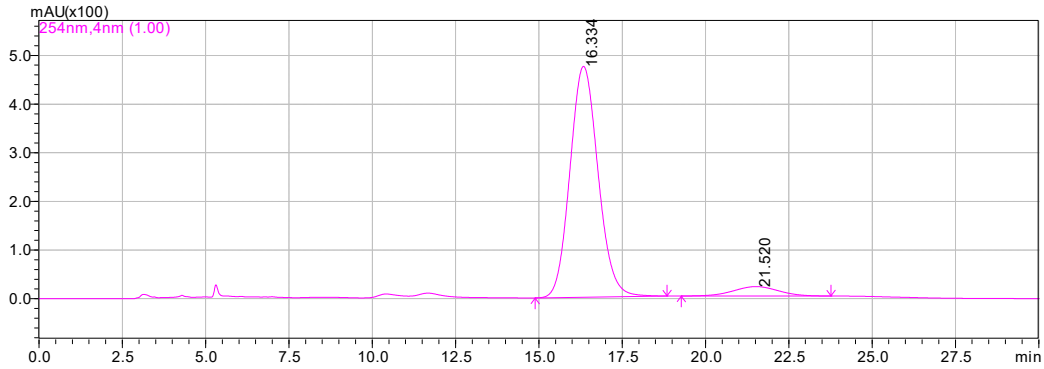
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 11.8 min, t_R (minor) = 16.6 min.



3b

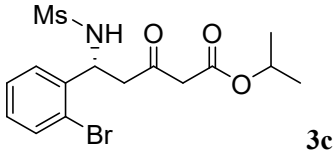


Peak	Ret. Time	Area	Area%
A	16.358	10399046	49.1071
B	21.427	10777216	50.8929

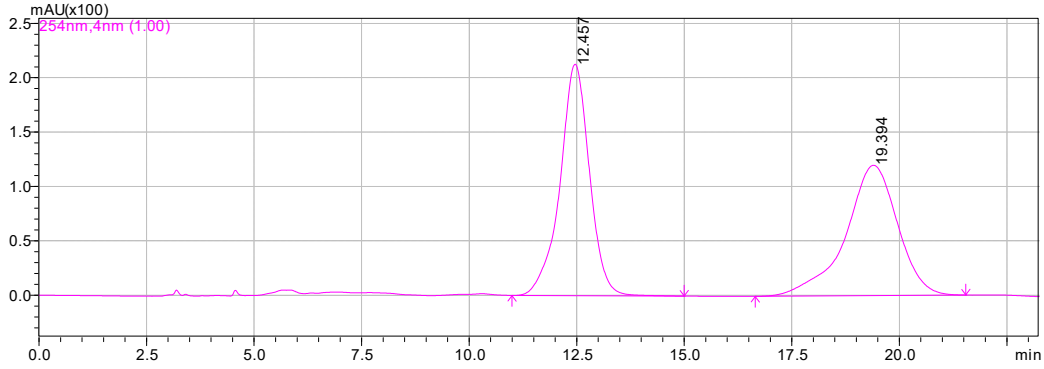


Peak	Ret. Time	Area	Area%
A	16.334	27839440	93.8083
B	21.520	1837493	6.1917

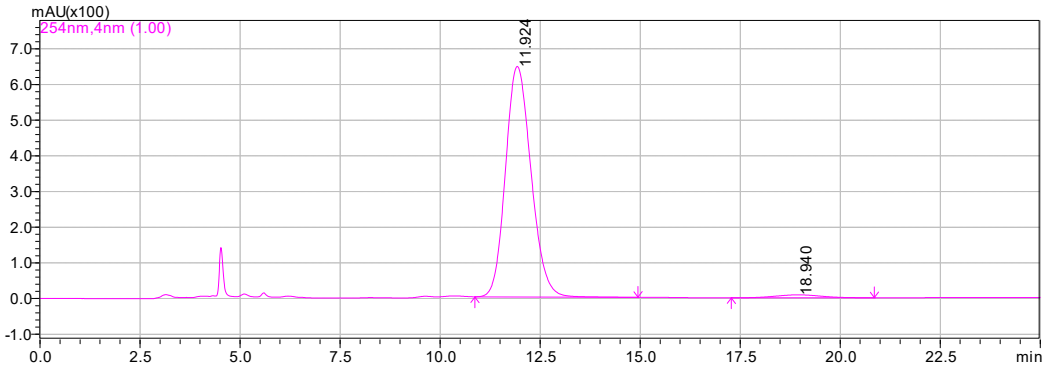
Daicel Chiralpak OD-H, hexane/iso-propanol= 85/15, flow rate 1.0 mL/min, 25°C: t_R (major) = 16.3 min, t_R (minor) = 21.5 min.



3c

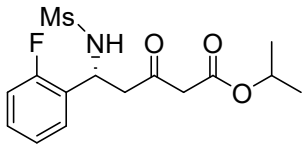


Peak	Ret. Time	Area	Area%
A	12.457	10174915	50.1701
B	19.394	10105912	49.8299

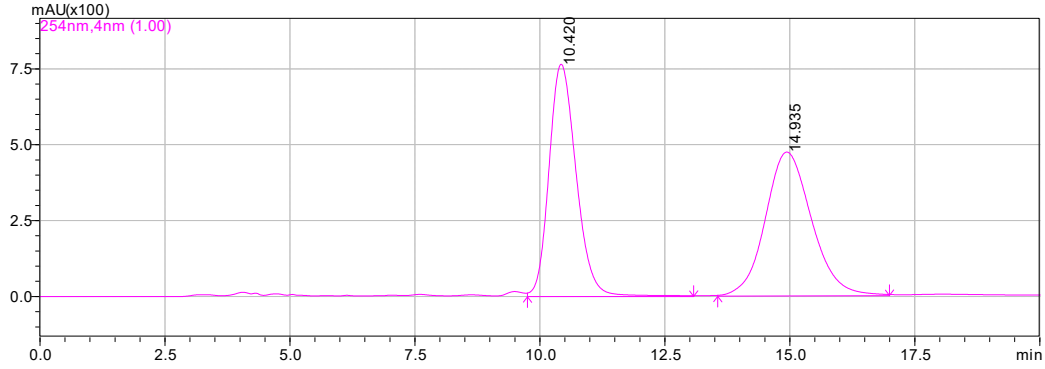


Peak	Ret. Time	Area	Area%
A	11.924	28759980	97.6962
B	18.940	678204	2.3038

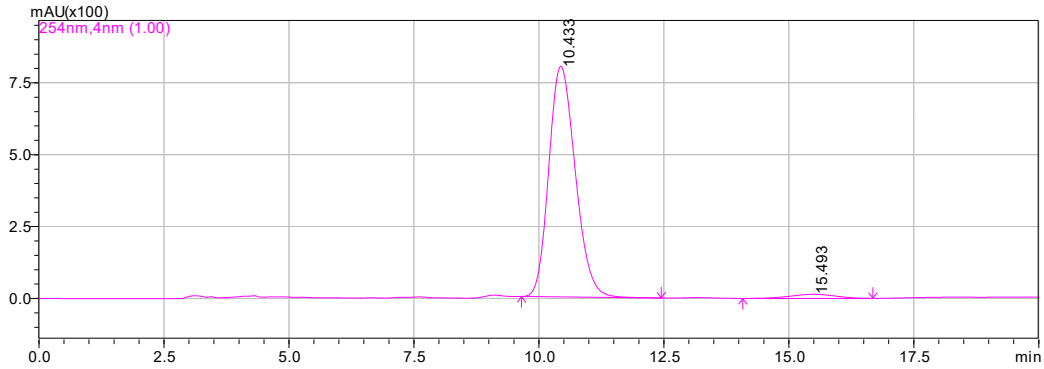
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 11.9 min, t_R (minor) = 18.9 min.



3d

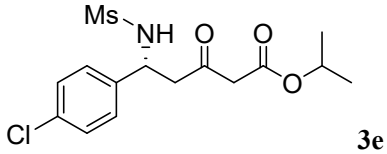


Peak	Ret. Time	Area	Area%
A	10.420	28998793	48.7163
B	14.935	30527052	51.2837

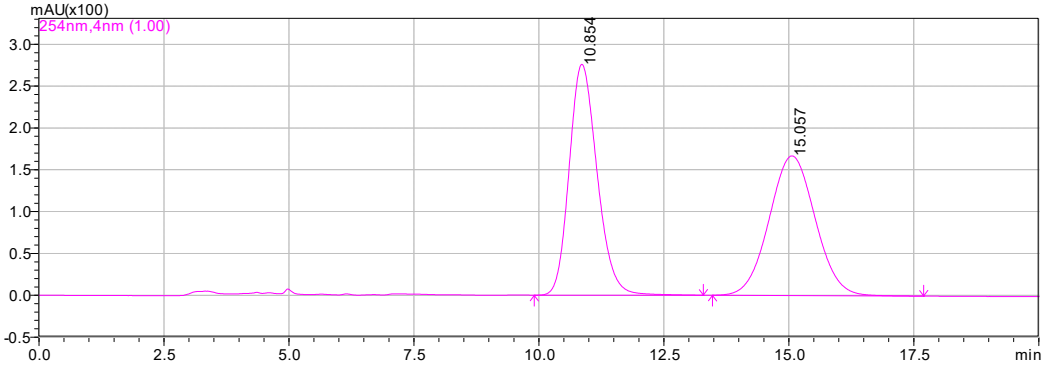


Peak	Ret. Time	Area	Area%
A	10.433	29631393	97.1320
B	15.493	874935	2.8680

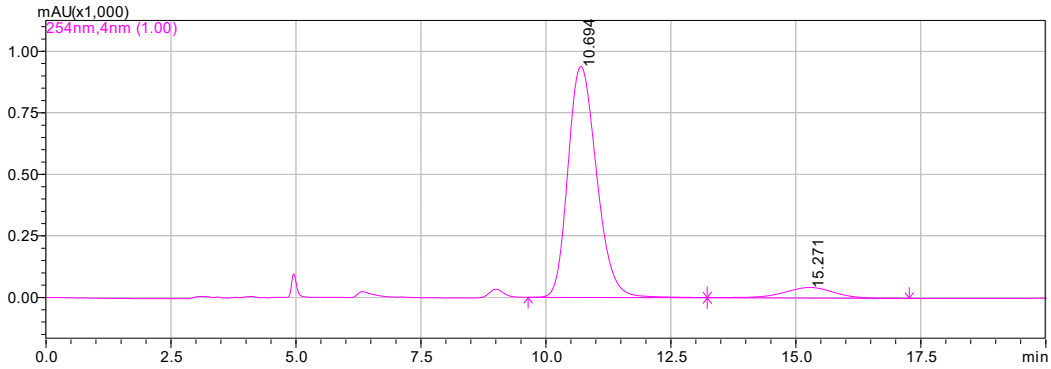
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 10.4 min, t_R (minor) = 15.5 min.



3e

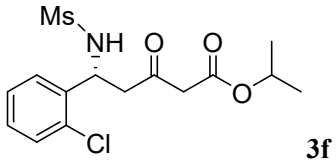


Peak	Ret. Time	Area	Area%
A	10.854	10731352	50.1027
B	15.057	10687355	49.8973

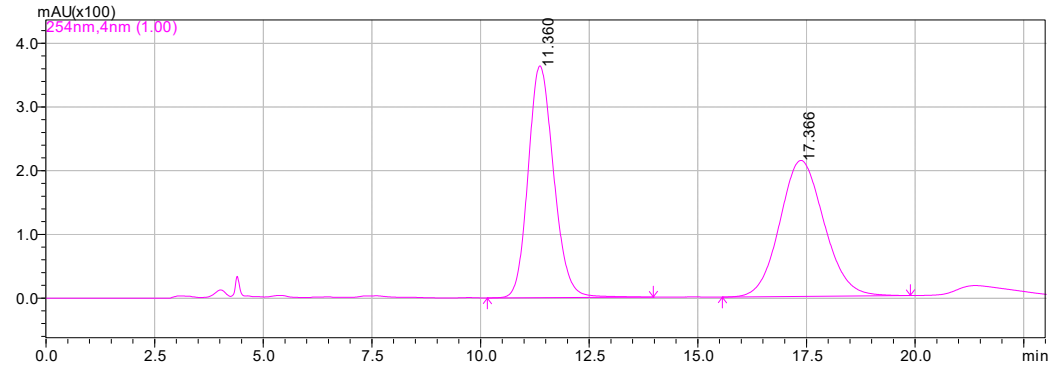


Peak	Ret. Time	Area	Area%
A	10.694	37404862	92.5196
B	15.271	3024249	7.4804

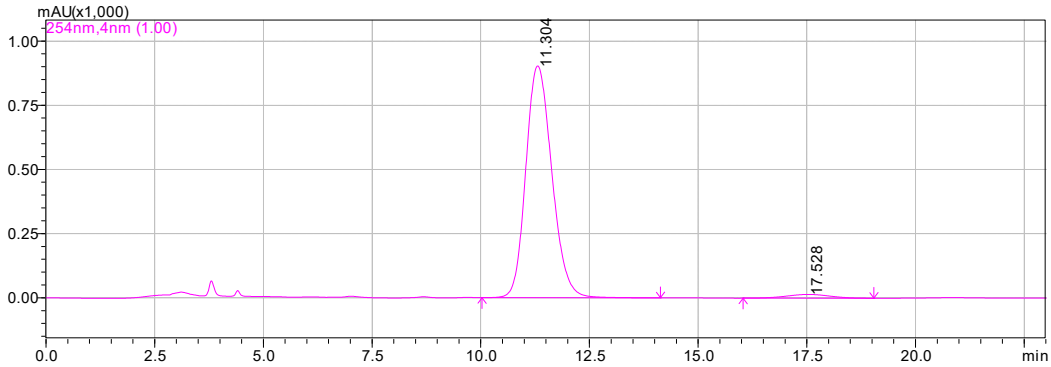
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 10.7 min, t_R (minor) = 15.3 min.



3f

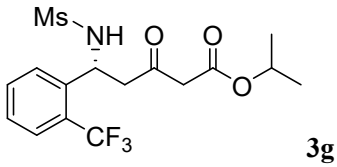


Peak	Ret. Time	Area	Area%
A	11.360	14885692	49.5490
B	17.366	15156685	50.4510

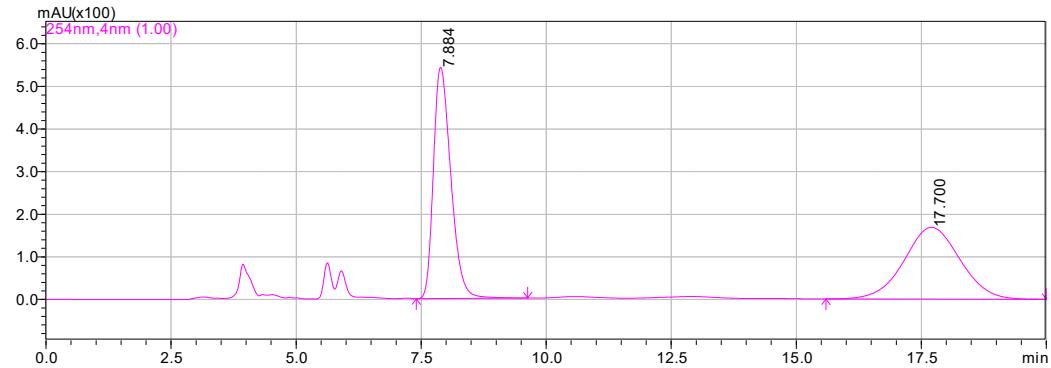


Peak	Ret. Time	Area	Area%
A	11.304	37683307	97.3802
B	17.528	1013786	2.6198

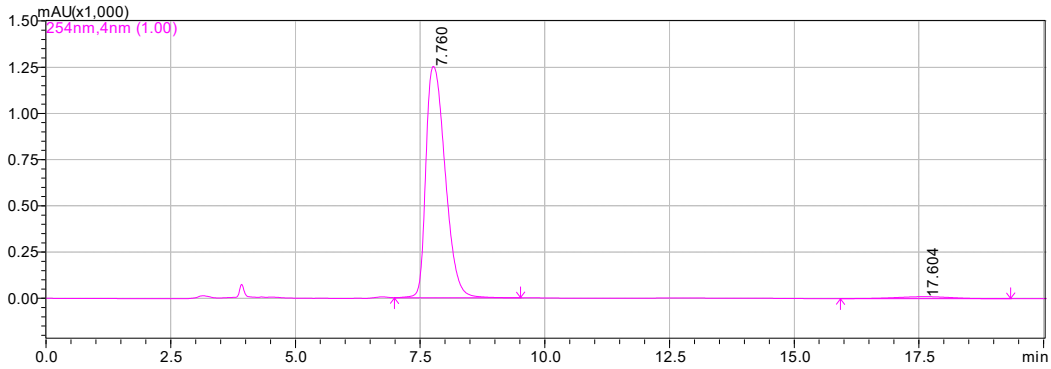
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 11.3 min, t_R (minor) = 17.5 min.



3g

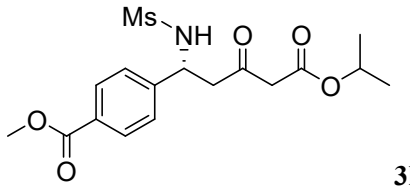


Peak	Ret. Time	Area	Area%
A	7.884	13184698	50.0437
B	17.700	13161660	49.9563

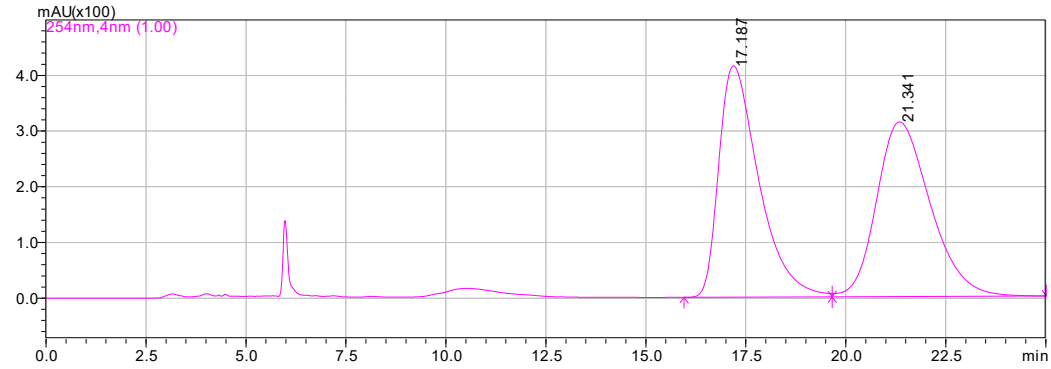


Peak	Ret. Time	Area	Area%
A	7.760	33599175	97.6028
B	17.604	825210	2.3972

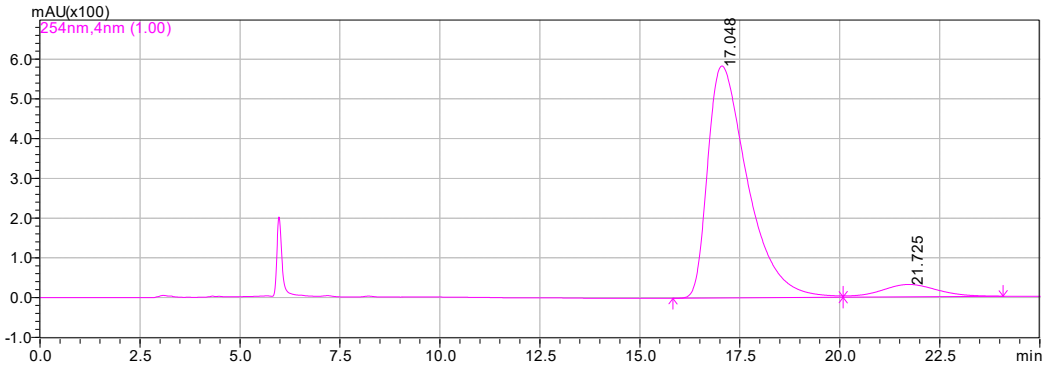
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 7.8 min, t_R (minor) = 17.6 min.



3h

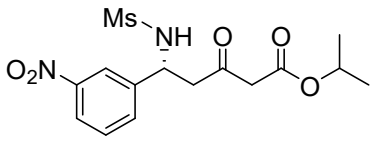


Peak	Ret. Time	Area	Area%
A	17.187	28908530	49.6565
B	21.341	29308457	50.3435

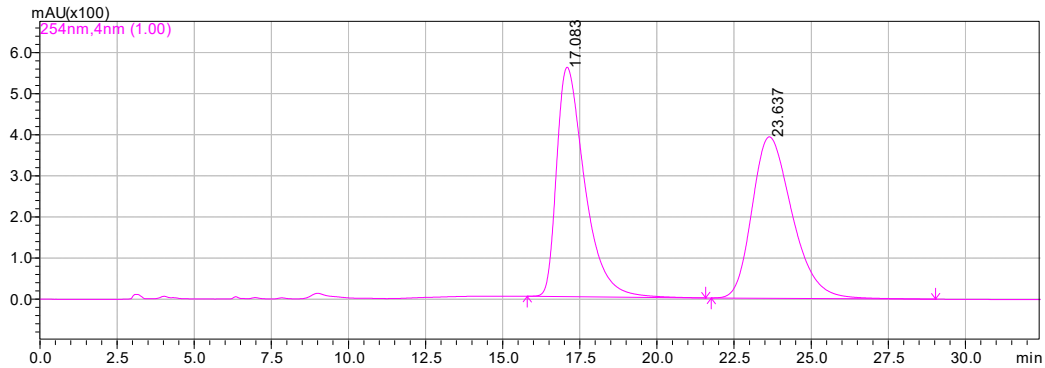


Peak	Ret. Time	Area	Area%
A	17.048	40506688	93.0546
B	21.725	3023346	6.9454

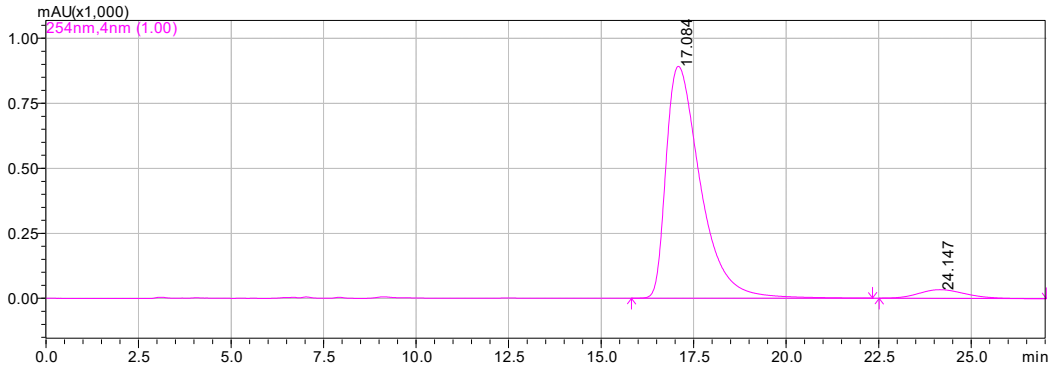
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 17.0 min, t_R (minor) = 21.7 min.



3i

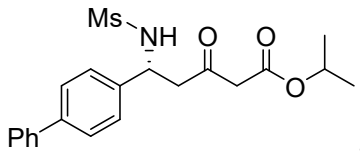


Peak	Ret. Time	Area	Area%
A	17.083	35358923	49.8951
B	23.637	35507656	50.1049

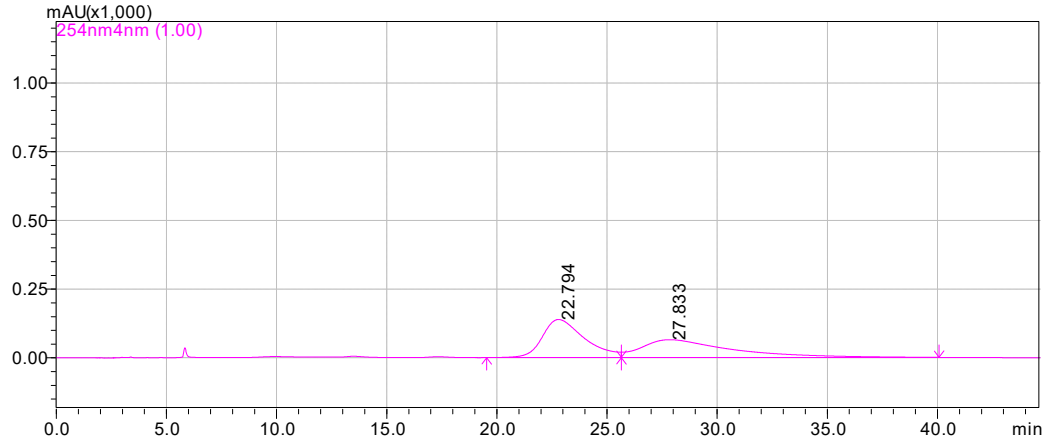


Peak	Ret. Time	Area	Area%
A	17.084	57500727	95.1805
B	24.147	2911599	4.8195

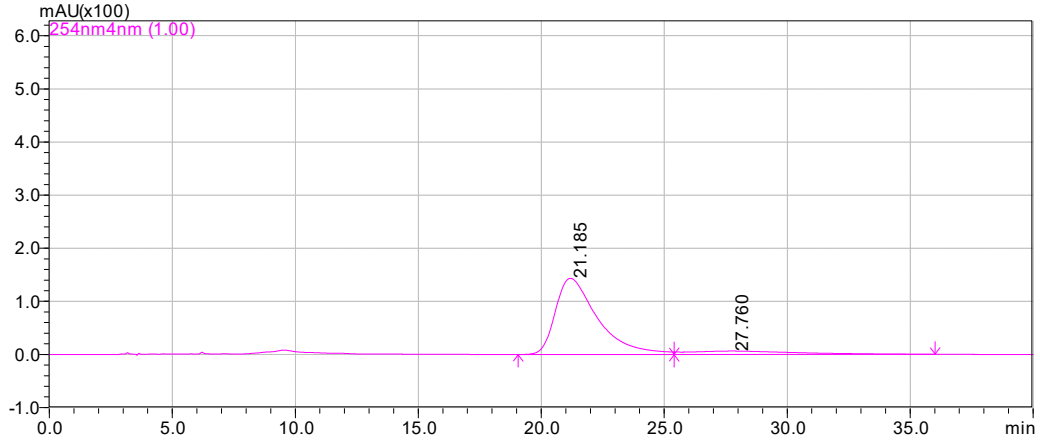
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 17.1 min, t_R (minor) = 24.1 min.



3j

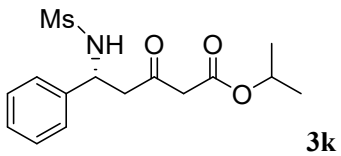


Peak	Ret. Time	Area	Area%
A	22.794	18416269	50.3096
B	27.833	18189625	49.6904

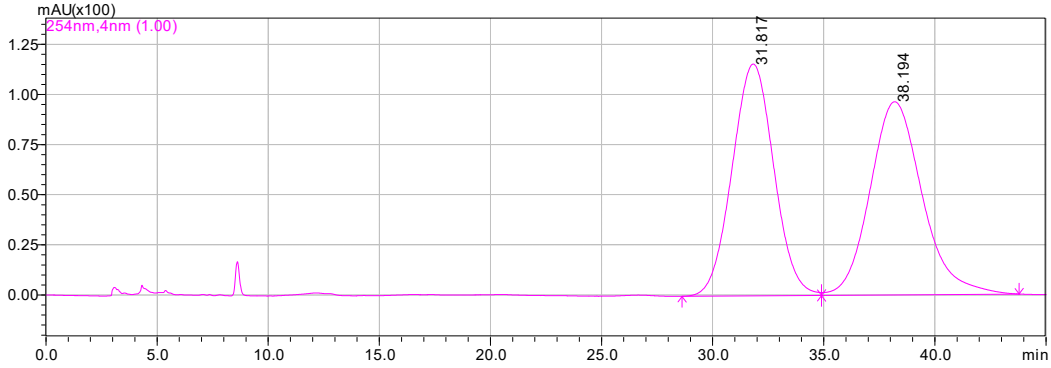


Peak	Ret. Time	Area	Area%
A	21.185	17095700	89.9158
B	27.760	1917305	10.0842

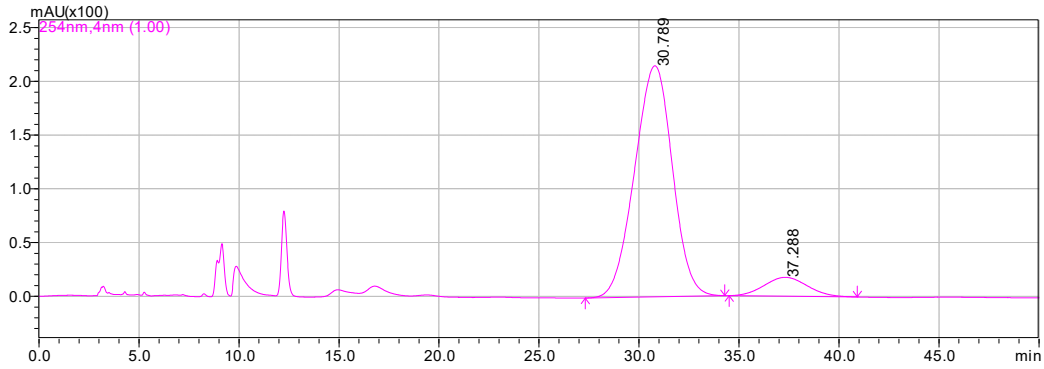
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 21.2 min, t_R (minor) = 27.8 min.



3k

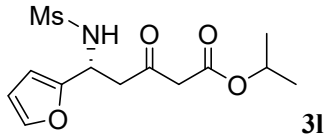


Peak	Ret. Time	Area	Area%
A	31.817	15096456	48.9726
B	38.194	15729870	51.0274

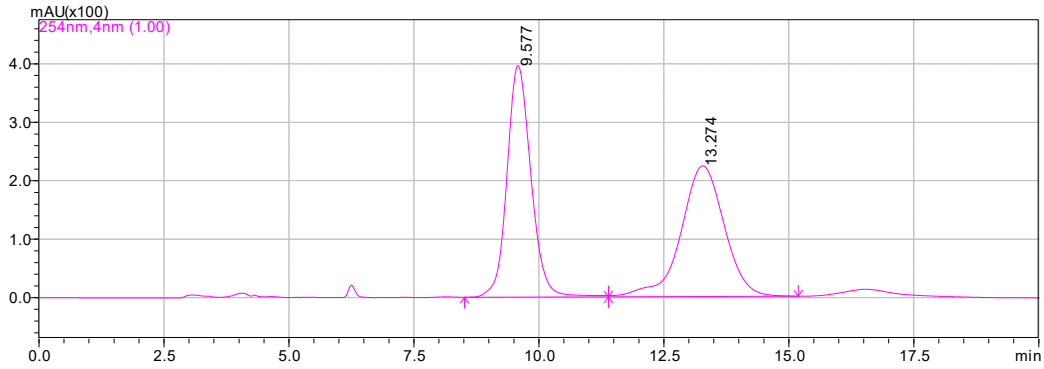


Peak	Ret. Time	Area	Area%
A	30.789	28259692	91.4336
B	37.288	2647661	8.5664

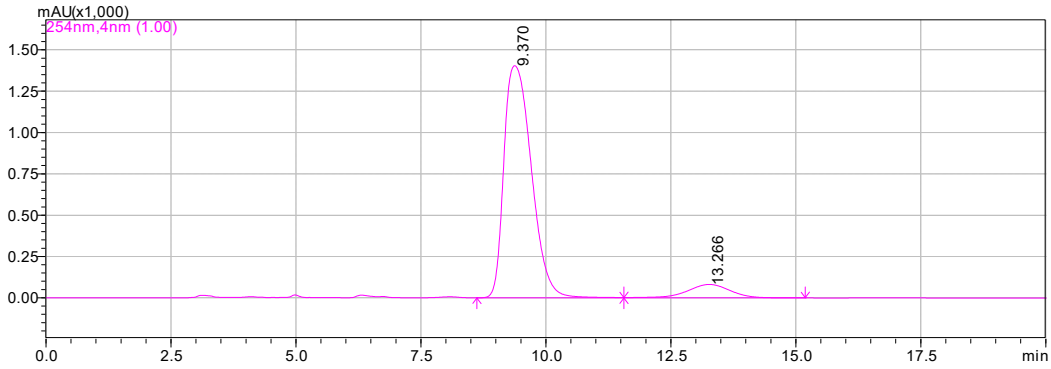
Daicel Chiralpak OD-H, hexane/iso-propanol= 90/10, flow rate 1.0 mL/min, 25°C: t_R (major) = 30.8 min, t_R (minor) = 37.3 min.



3l

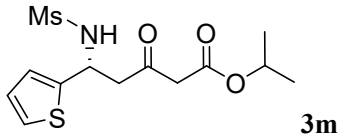


Peak	Ret. Time	Area	Area%
A	9.577	13220042	49.5379
B	13.274	13466680	50.4621

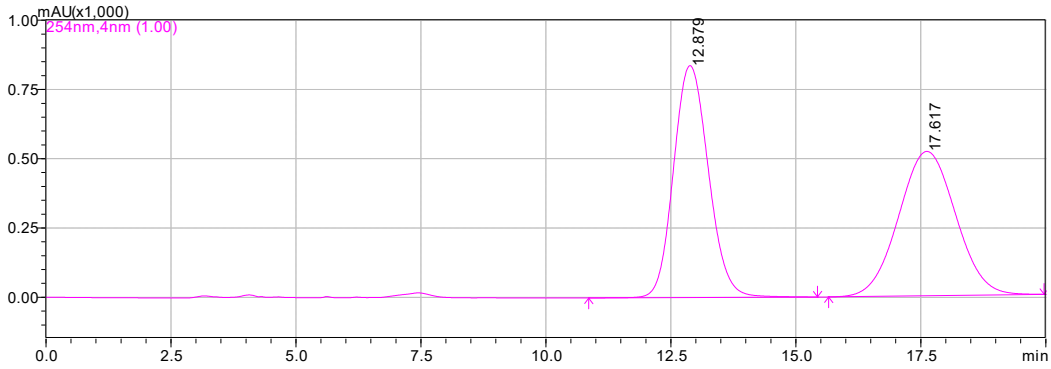


Peak	Ret. Time	Area	Area%
A	9.370	53813694	91.6532
B	13.266	4900767	8.3468

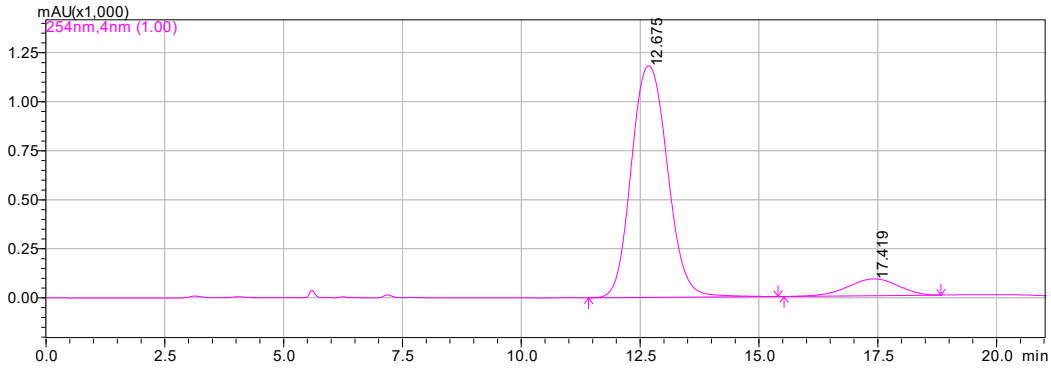
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 9.4 min, t_R (minor) = 13.3 min.



3m

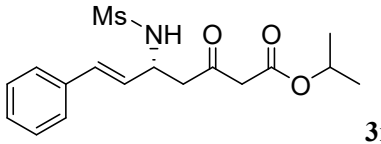


Peak	Ret. Time	Area	Area%
A	12.879	40690955	49.6021
B	17.617	41343737	50.3979

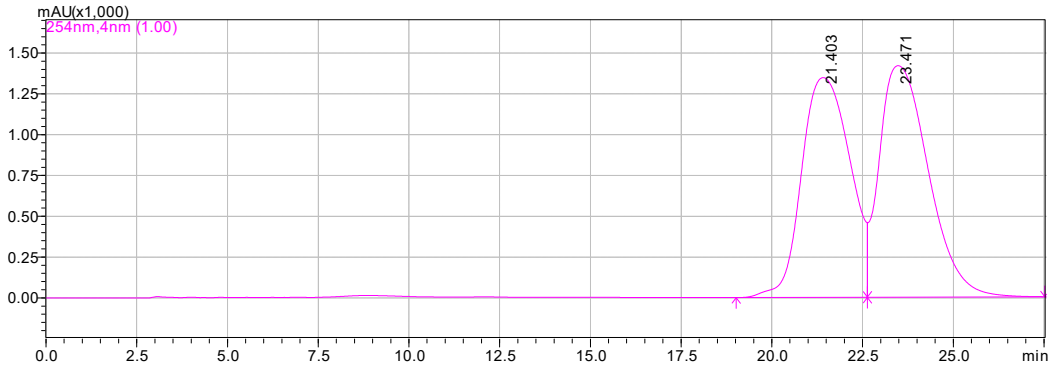


Peak	Ret. Time	Area	Area%
A	12.675	62430363	90.8215
B	17.419	6309264	9.1785

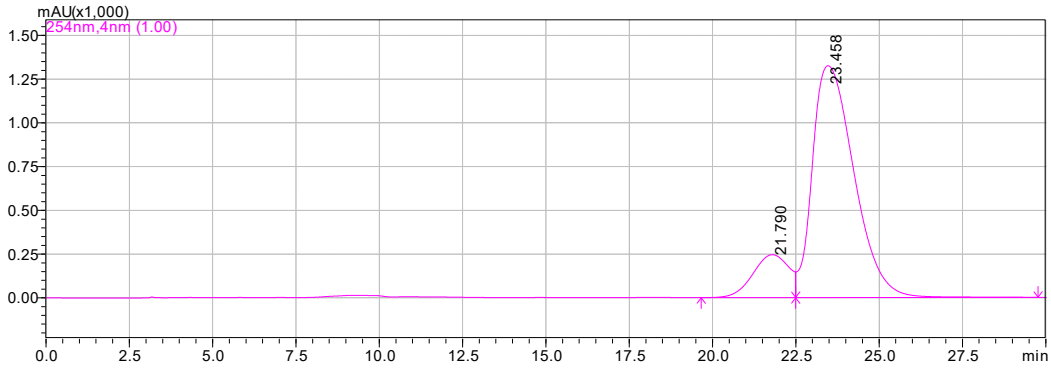
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 12.7 min, t_R (minor) = 17.4 min.



3n

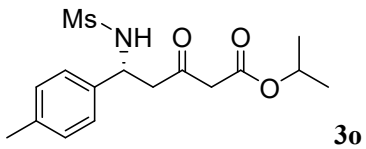


Peak	Ret. Time	Area	Area%
A	21.403	124993191	48.3499
B	23.471	133524577	51.6501

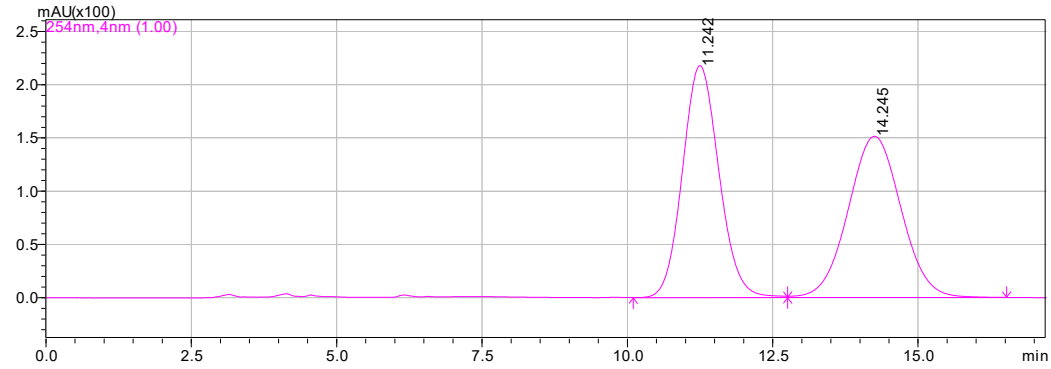


Peak	Ret. Time	Area	Area%
A	21.790	18331560	13.7571
B	23.458	114920430	86.2429

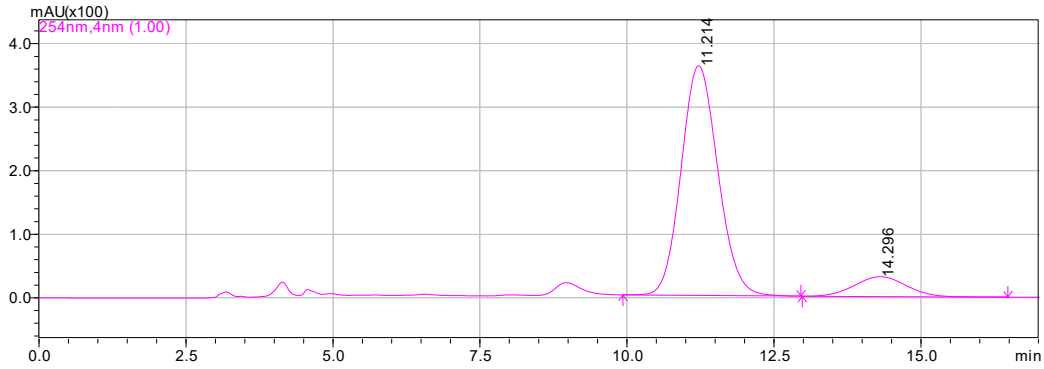
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 21.8 min, t_R (minor) = 23.5 min.



3o

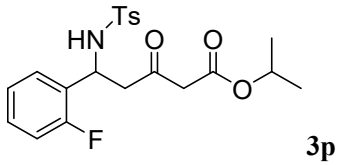


Peak	Ret. Time	Area	Area%
A	11.242	9519456	49.8437
B	14.245	9579172	50.1563

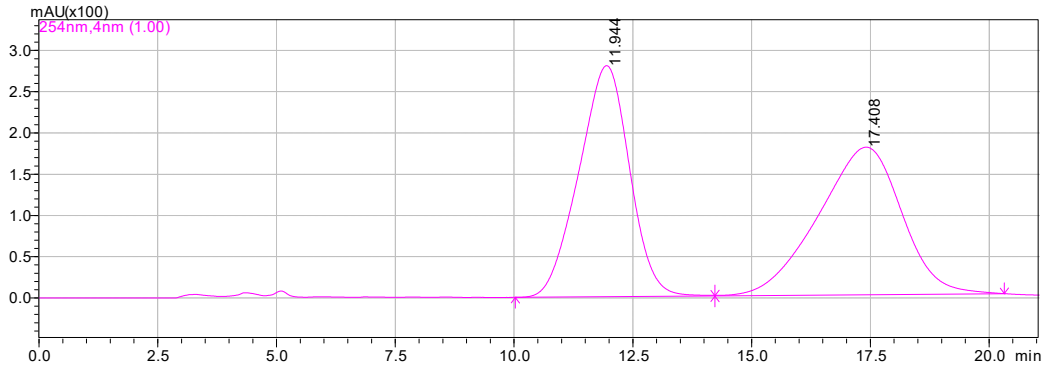


Peak	Ret. Time	Area	Area%
A	11.214	15732842	89.1786
B	14.296	1909110	10.8214

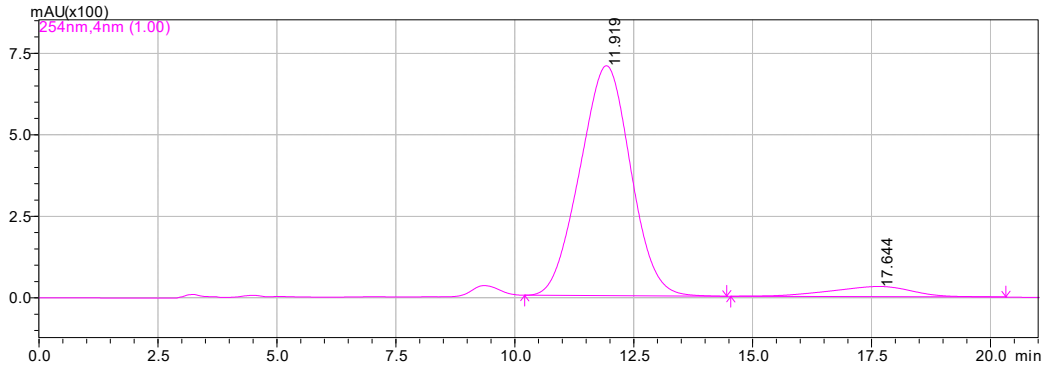
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 11.2 min, t_R (minor) = 14.3 min.



3p

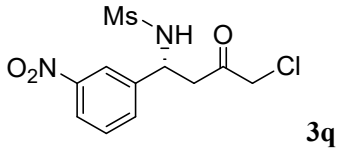


Peak	Ret. Time	Area	Area%
A	11.944	20798107	48.7456
B	17.408	21868519	51.2544

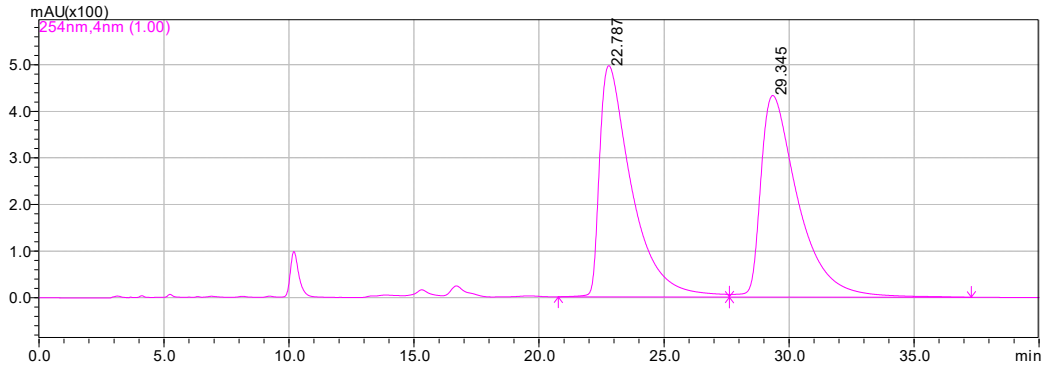


Peak	Ret. Time	Area	Area%
A	11.919	52316344	93.2903
B	17.644	3762731	6.7097

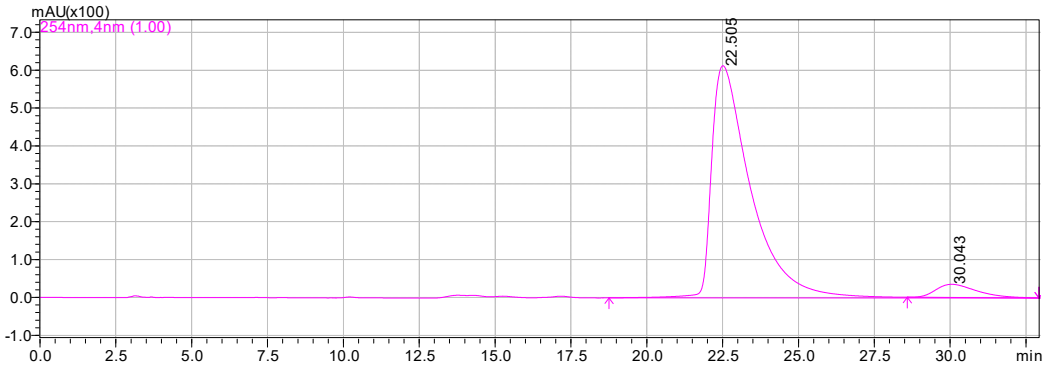
Daicel Chiralpak OD-H, hexane/iso-propanol= 85/15, flow rate 1.0 mL/min, 25°C: t_R (major) = 11.9 min, t_R (minor) = 17.6 min.



3q

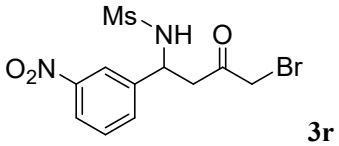


Peak	Ret. Time	Area	Area%
A	22.787	44263658	49.6626
B	29.345	44865108	50.3374

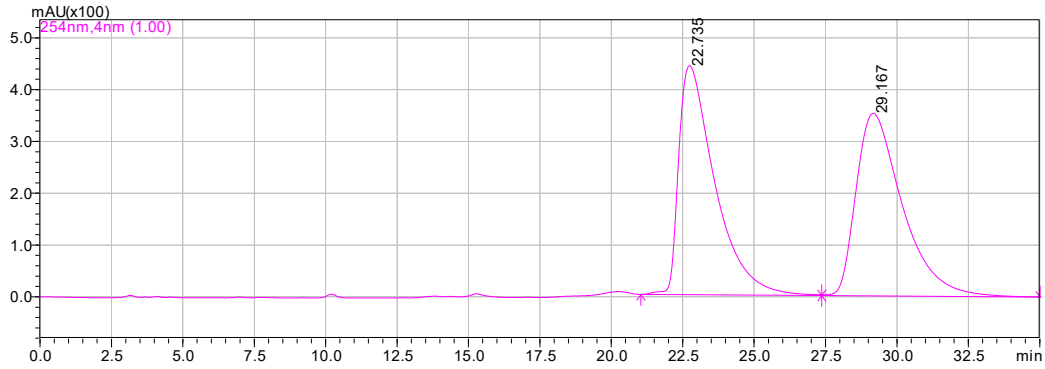


Peak	Ret. Time	Area	Area%
A	22.505	55327949	94.4658
B	30.043	3241348	5.5342

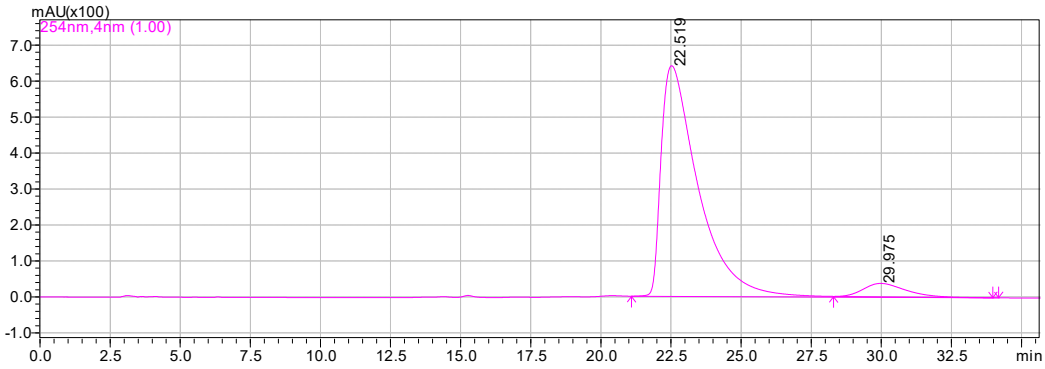
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 22.5 min, t_R (minor) = 30.0 min.



3r

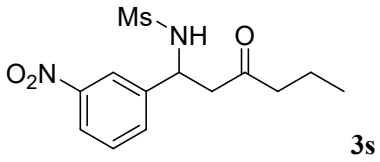


Peak	Ret. Time	Area	Area%
A	22.735	39051427	49.5694
B	29.167	39729916	50.4306

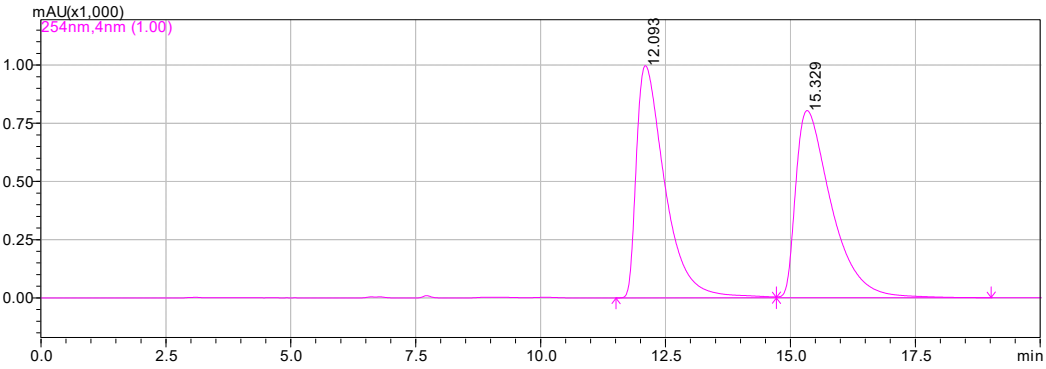


Peak	Ret. Time	Area	Area%
A	22.519	59356588	93.8238
B	29.975	3907331	6.1762

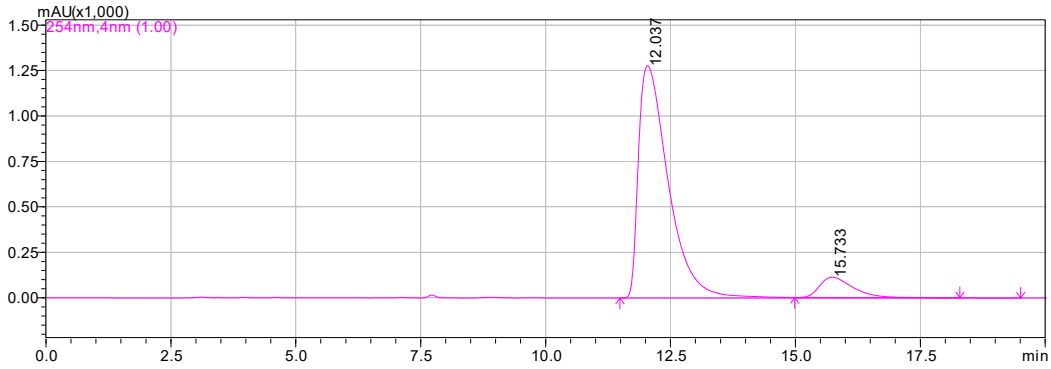
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 22.5 min, t_R (minor) = 30.0 min.



3s

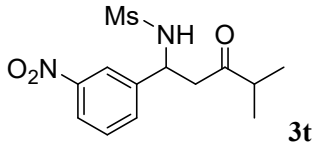


Peak	Ret. Time	Area	Area%
A	12.093	39731965	49.8784
B	15.329	39925622	50.1216

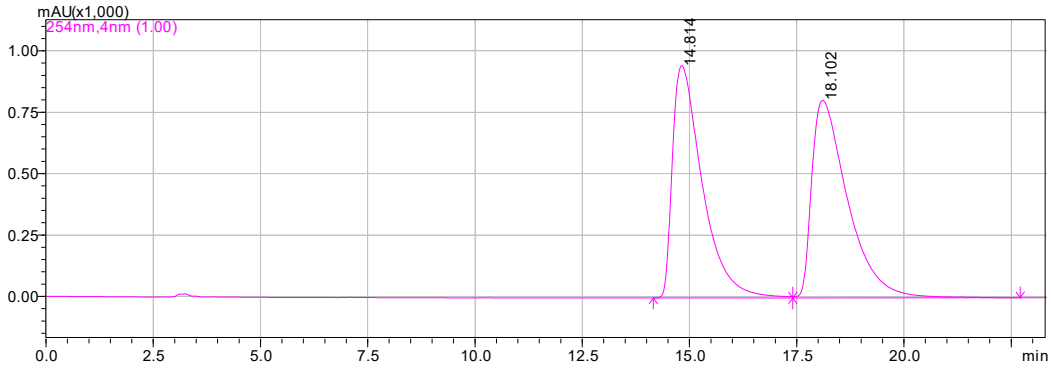


Peak	Ret. Time	Area	Area%
A	12.037	53444968	91.1498
B	15.733	5189223	8.8502

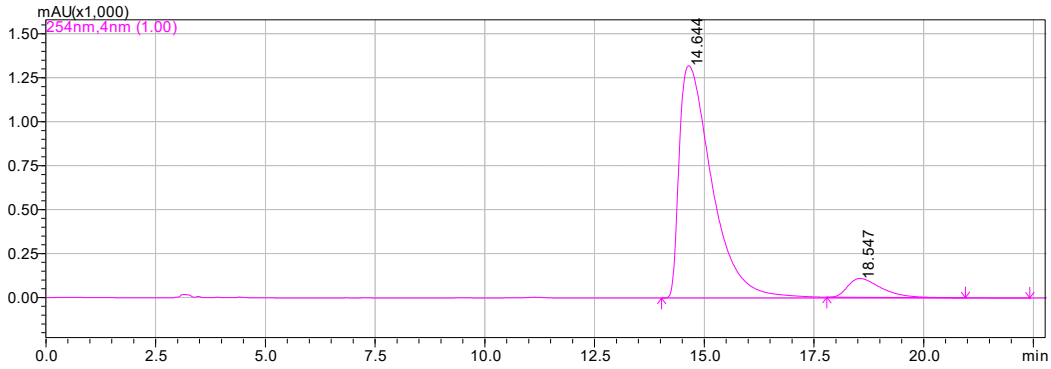
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 12.0 min, t_R (minor) = 15.7 min.



3t

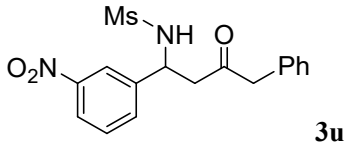


Peak	Ret. Time	Area	Area%
A	14.814	45848157	49.4594
B	18.102	46850346	50.5406

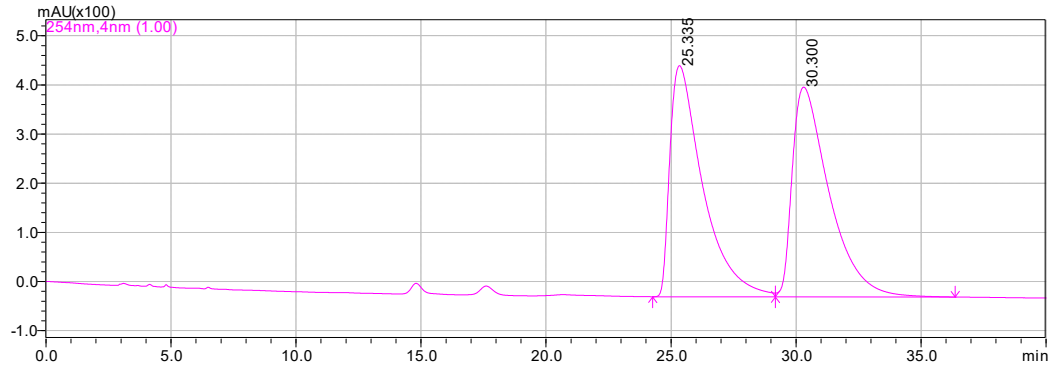


Peak	Ret. Time	Area	Area%
A	14.644	69162944	92.4325
B	18.547	5662402	7.5675

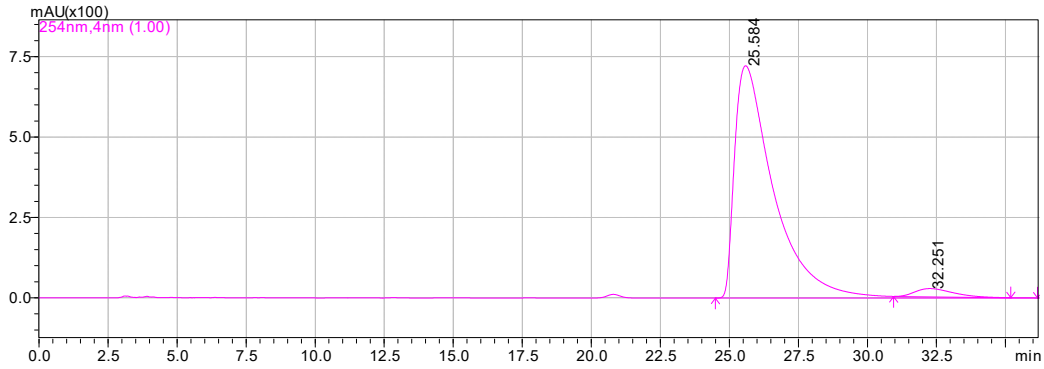
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 14.6 min, t_R (minor) = 18.5 min.



3u

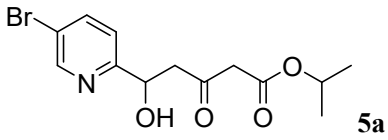


Peak	Ret. Time	Area	Area%
A	25.335	43211693	49.5880
B	30.300	43929813	50.4120

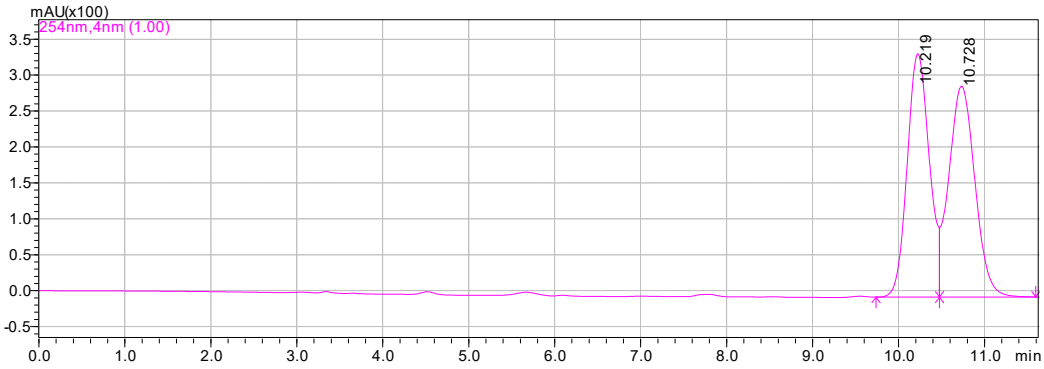


Peak	Ret. Time	Area	Area%
A	25.584	71531076	96.7067
B	32.251	2435921	3.2933

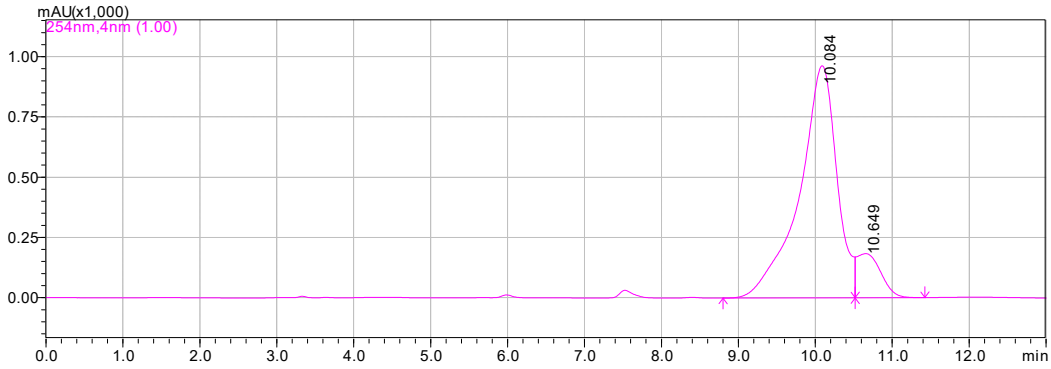
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 25.6 min, t_R (minor) = 32.3 min.



5a

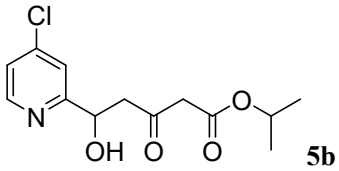


Peak	Ret. Time	Area	Area%
A	10.219	6077882	49.4801
B	10.728	6205599	50.5199

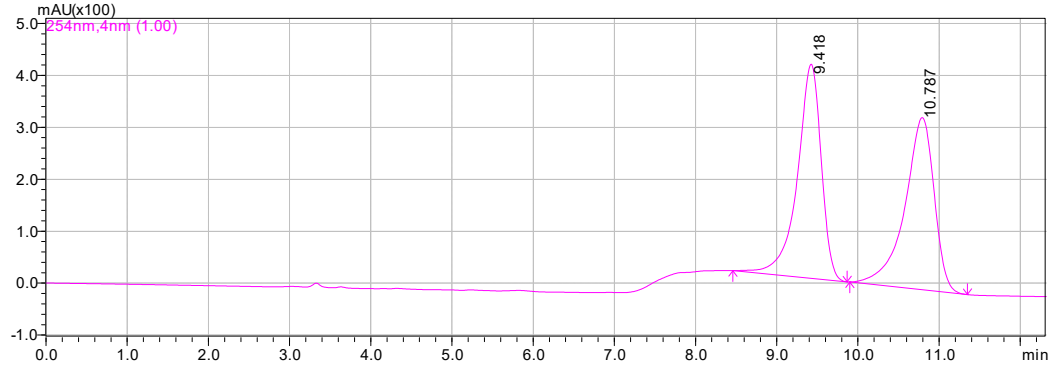


Peak	Ret. Time	Area	Area%
A	10.084	32634276	89.2666
B	10.649	3923924	10.7334

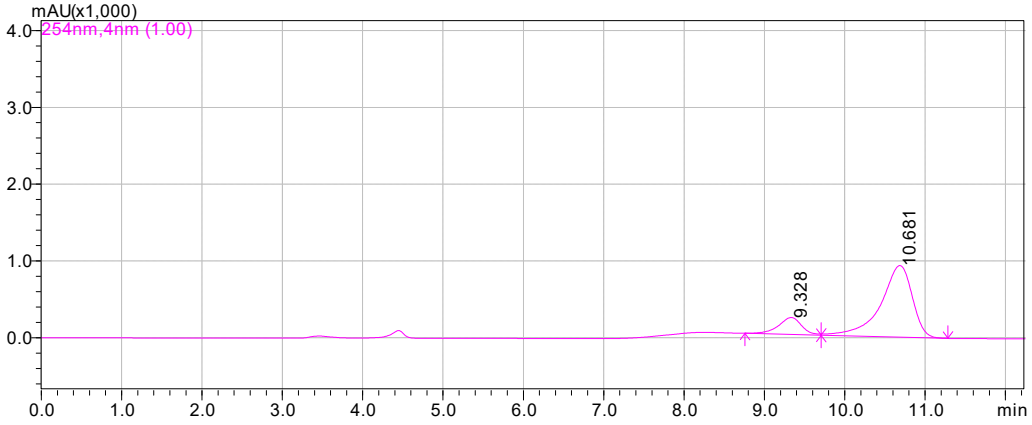
Daicel Chiralpak AD, hexane/iso-propanol= 85/15, flow rate 1.0 mL/min, 25°C: t_R (major) = 10.1 min, t_R (minor) = 10.6 min.



5b

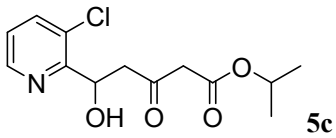


Peak	Ret. Time	Area	Area%
A	9.418	8442426	50.3141
B	10.787	8337006	49.6859

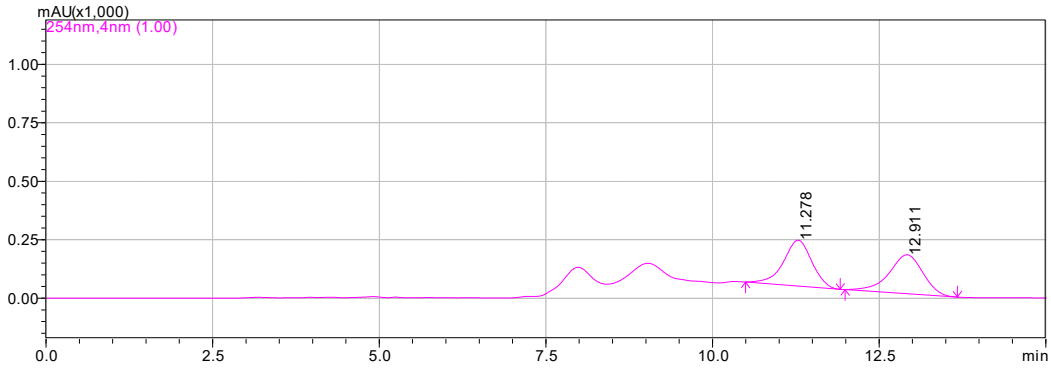


Peak	Ret. Time	Area	Area%
A	9.328	4440397	14.8368
B	10.681	25487854	85.1632

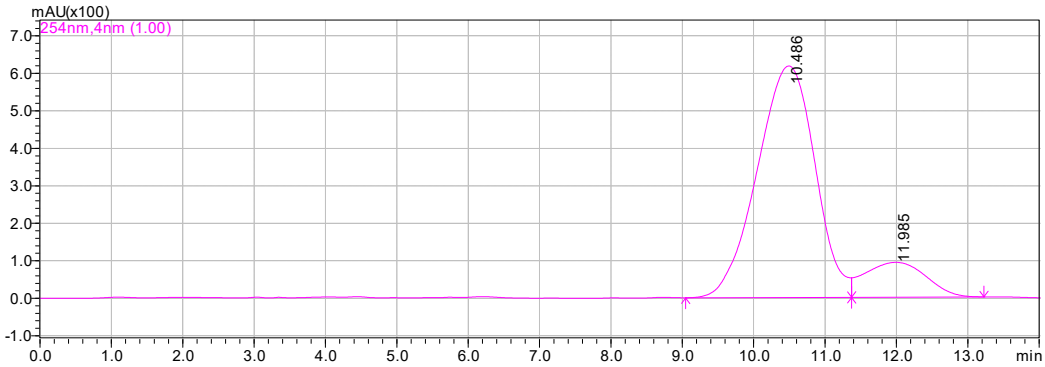
Daicel Chiralpak AD, hexane/iso-propanol= 85/15, flow rate 1.0 mL/min, 25°C: t_R (major) = 9.2 min, t_R (minor) = 10.4 min.



5c

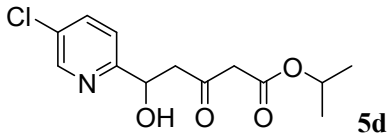


Peak	Ret. Time	Area	Area%
A	11.278	5813604	49.7711
B	12.911	5867085	50.2289

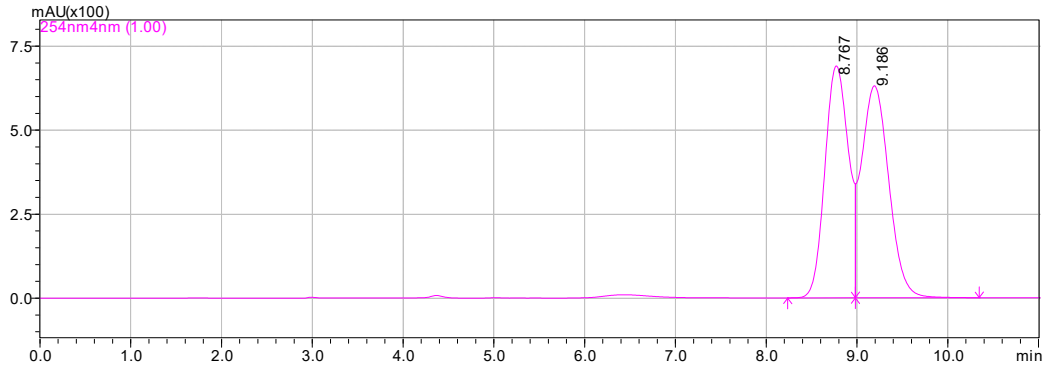


Peak	Ret. Time	Area	Area%
A	10.486	34801469	86.3166
B	11.985	5516919	13.6834

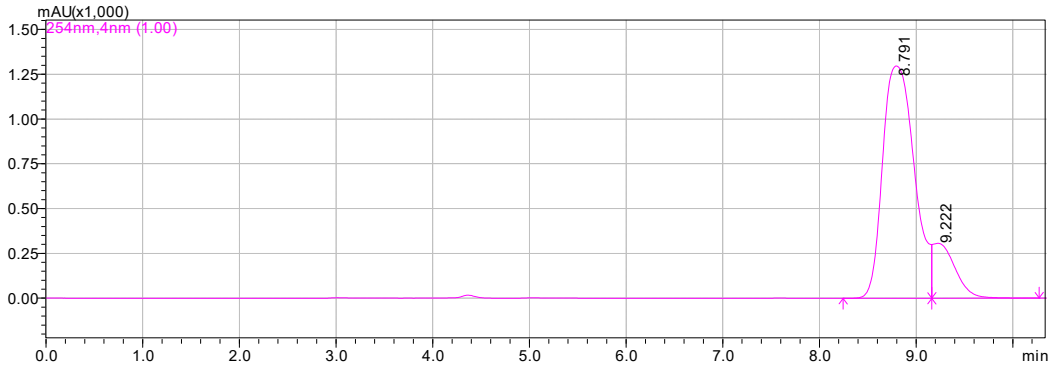
Daicel Chiralpak AD, hexane/iso-propanol= 85/15, flow rate 1.0 mL/min, 25°C: t_R (major) = 10.5 min, t_R (minor) = 12.0 min.



5d

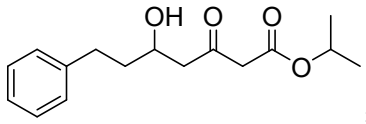


Peak	Ret. Time	Area	Area%
A	8.767	12540848	48.8141
B	9.186	13150164	51.1859

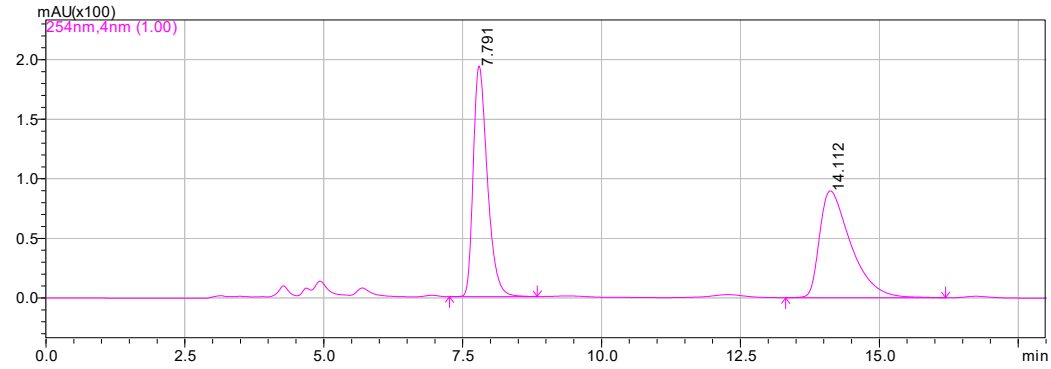


Peak	Ret. Time	Area	Area%
A	8.791	29674175	85.9470
B	9.222	4851961	14.0530

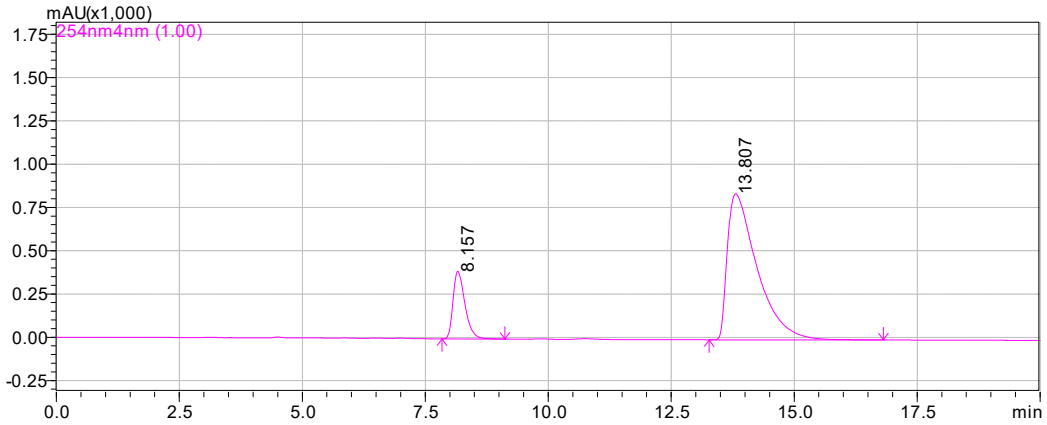
Daicel Chiralpak AD, hexane/iso-propanol= 85/15, flow rate 1.0 mL/min, 25°C: t_R (major) = 8.8 min, t_R (minor) = 9.2 min.



5e

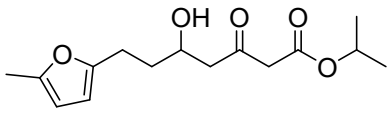


Peak	Ret. Time	Area	Area%
A	7.791	3425101	49.3834
B	14.112	3510636	50.6166

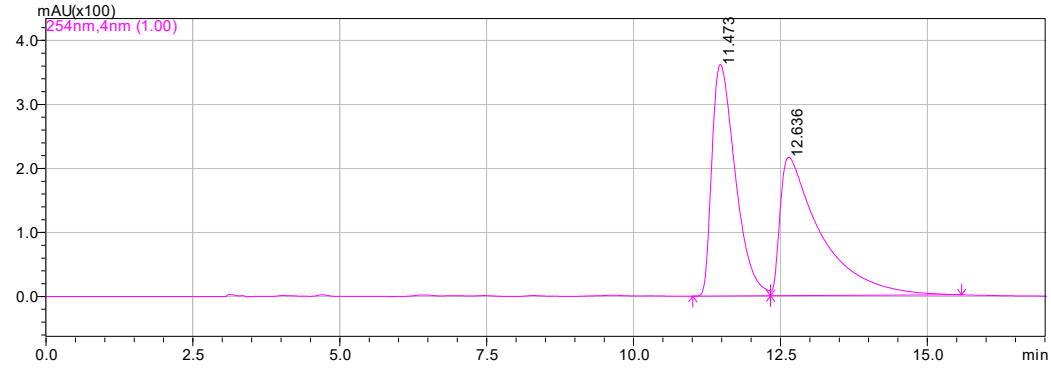


Peak	Ret. Time	Area	Area%
A	8.157	6608501	15.7342
B	13.807	35392253	84.2658

Daicel Chiralpak OD, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 8.2 min, t_R (minor) = 13.8 min.

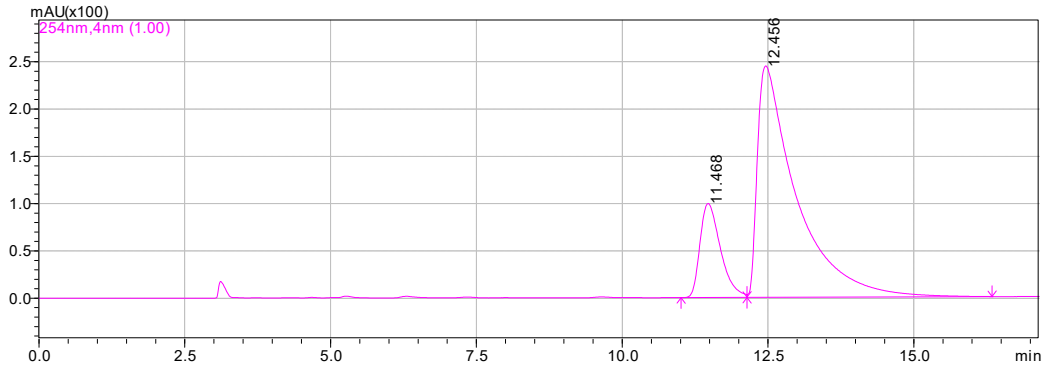


5f



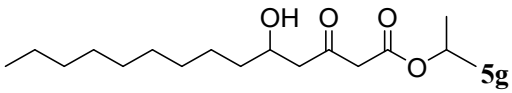
Peak	Ret. Time	Area	Area%
A	11.473	10052166	49.0996

B	12.636	10420835	50.9004

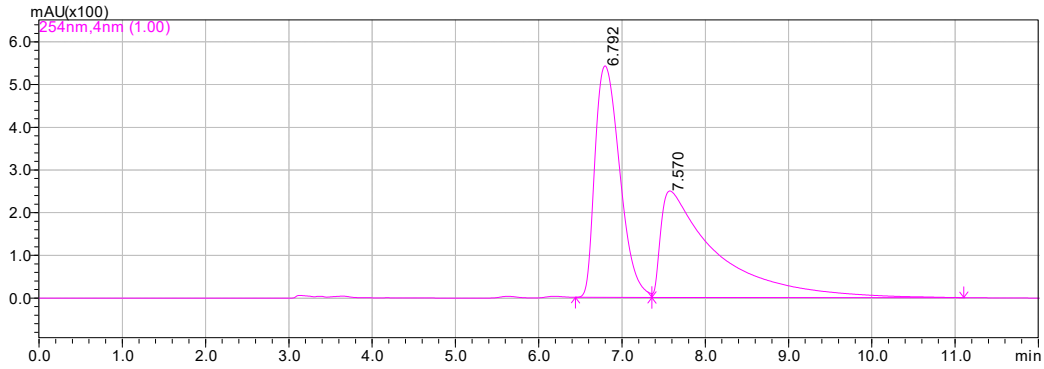


Peak	Ret. Time	Area	Area%
A	11.468	2431210	17.6143
B	12.456	11371249	82.3857

Daicel Chiralpak OD, hexane/iso-propanol= 95/5, flow rate 1.0 mL/min, 25°C: t_R (major) = 11.5 min, t_R (minor) = 12.5 min.

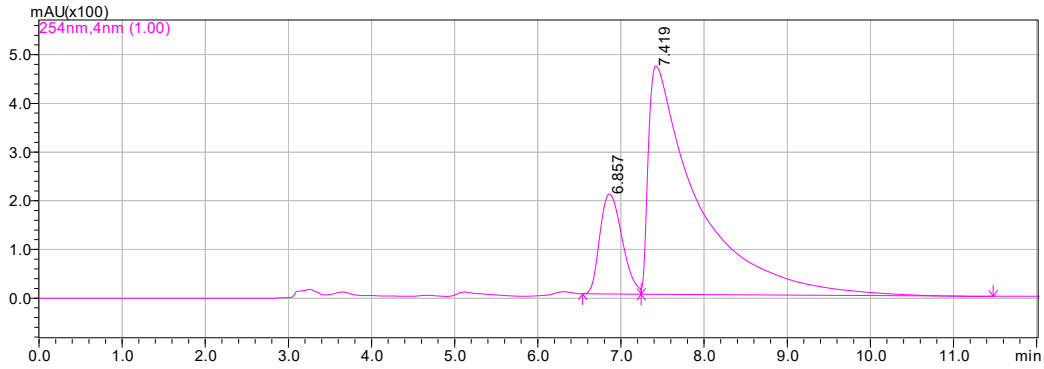


5g



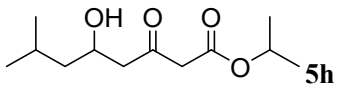
Peak	Ret. Time	Area	Area%
A	6.792	11200122	49.1094

B	7.570	11606346	50.8906

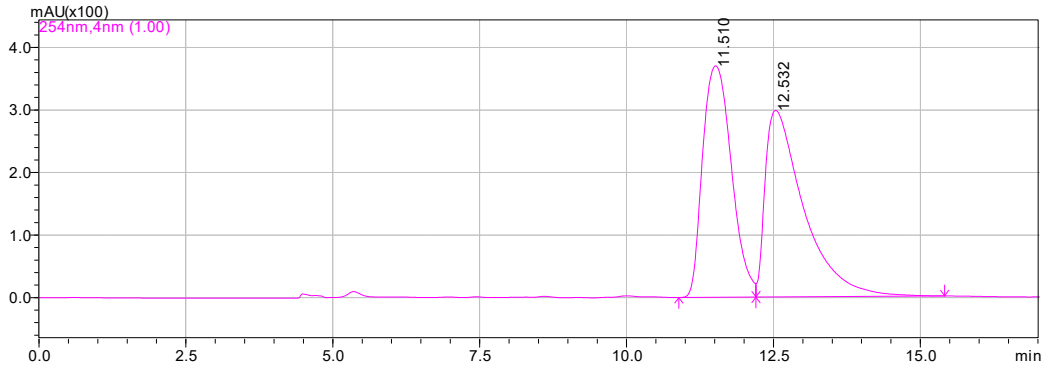


Peak	Ret. Time	Area	Area%
A	6.857	3831512	16.4859
B	7.419	19409576	83.5141

Daicel Chiralpak OD, hexane/iso-propanol= 95/5, flow rate 1.0 mL/min, 25°C: t_R (major) = 6.9 min, t_R (minor) = 7.4 min.

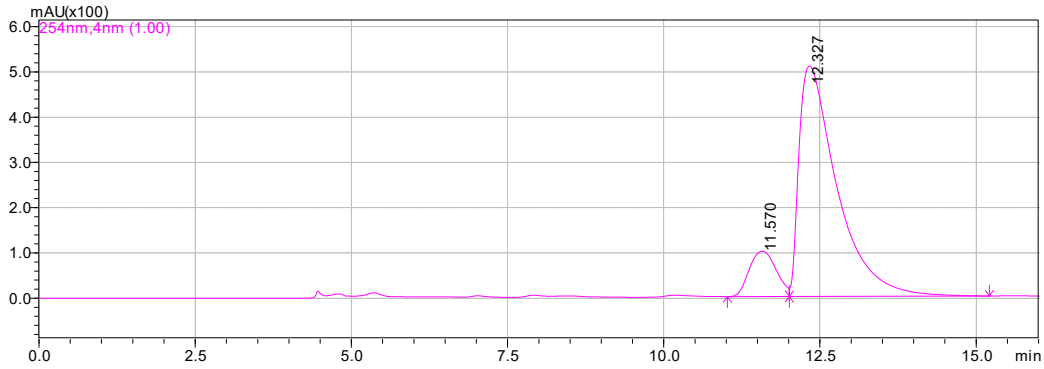


5h



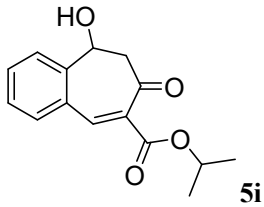
Peak	Ret. Time	Area	Area%
A	11.510	12670021	48.1437

B	12.532	13647044	51.8563

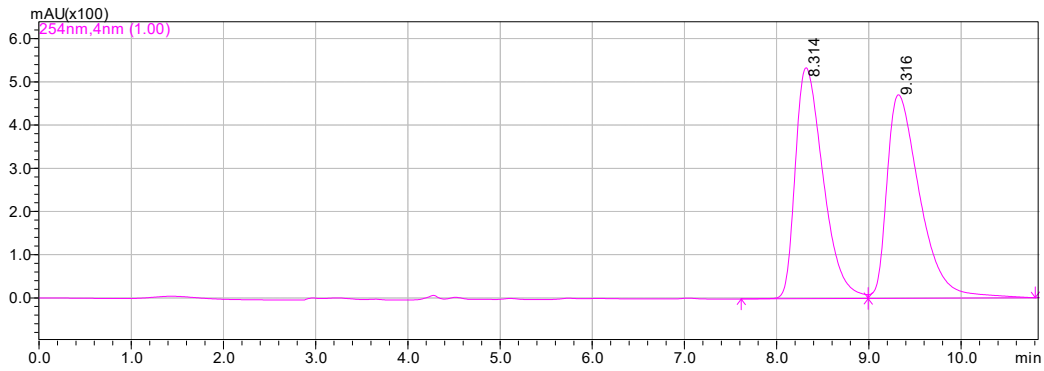


Peak	Ret. Time	Area	Area%
A	11.570	3016153	12.3275
B	12.327	21450644	87.6725

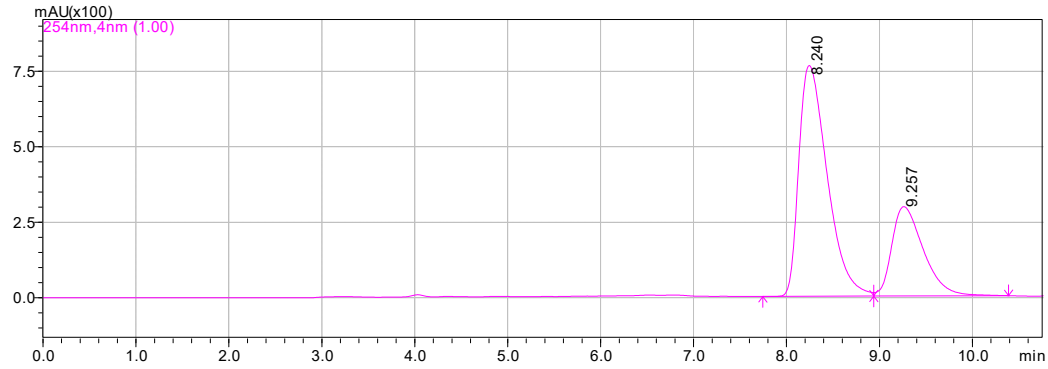
Daicel Chiralpak OD, hexane/iso-propanol= 97/3, flow rate 0.7 mL/min, 25°C: t_R (major) = 11.6 min, t_R (minor) = 12.3 min.



5i

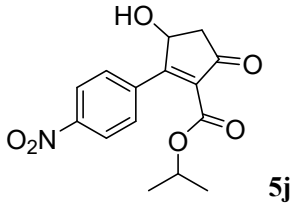


Peak	Ret. Time	Area	Area%
A	8.314	11225878	49.0596
B	9.316	11656229	50.9404

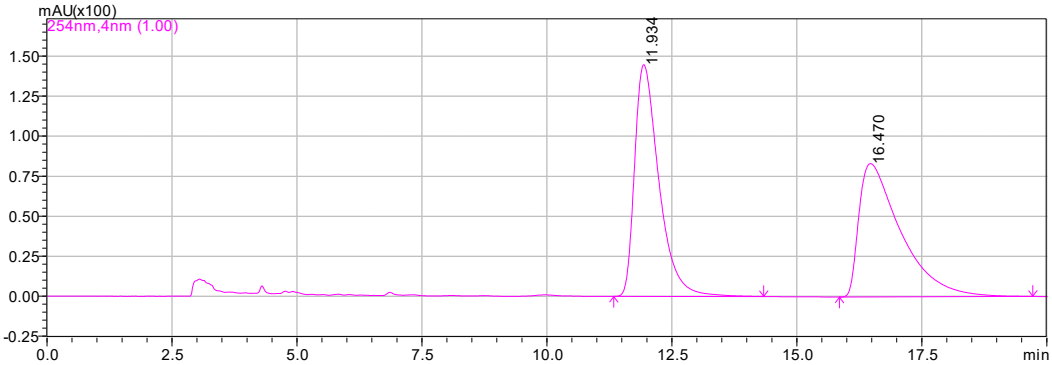


Peak	Ret. Time	Area	Area%
A	8.240	16228651	69.8702
B	9.257	6998219	30.1298

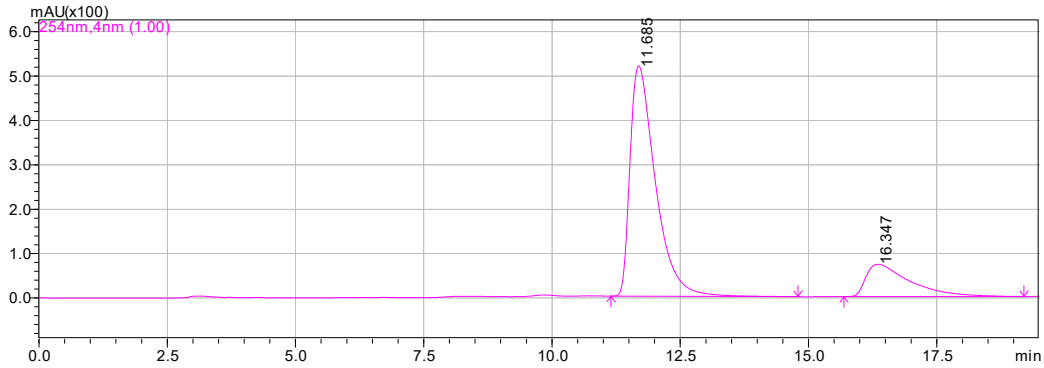
Daicel Chiralpak OD-H, hexane/iso-propanol= 85/15, flow rate 1.0 mL/min, 25°C: t_R (major) = 8.2 min, t_R (minor) = 9.3 min.



5j

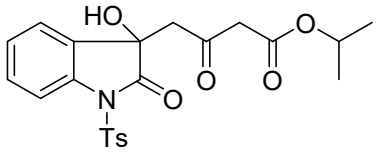


Peak	Ret. Time	Area	Area%
A	11.934	4911629	50.2486
B	16.470	4863029	49.7514

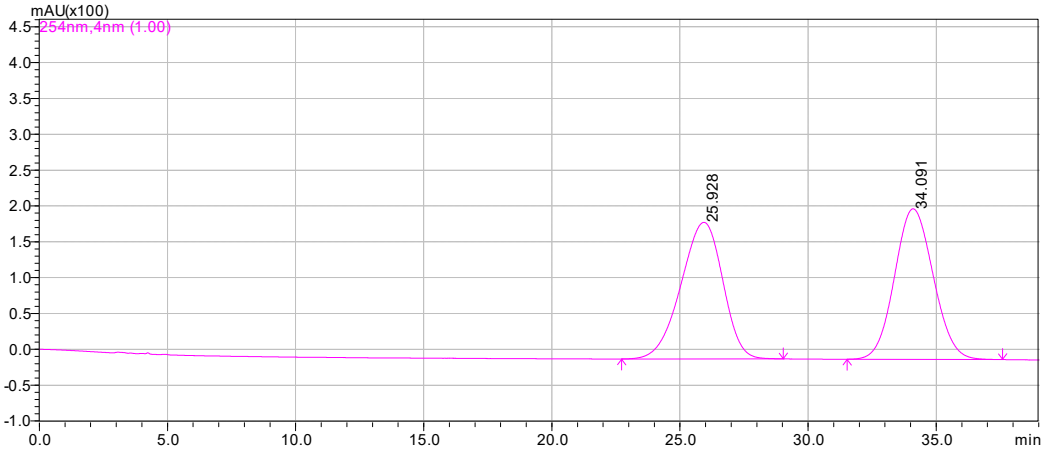


Peak	Ret. Time	Area	Area%
A	11.685	17865401	80.5883
B	16.347	4303339	19.4117

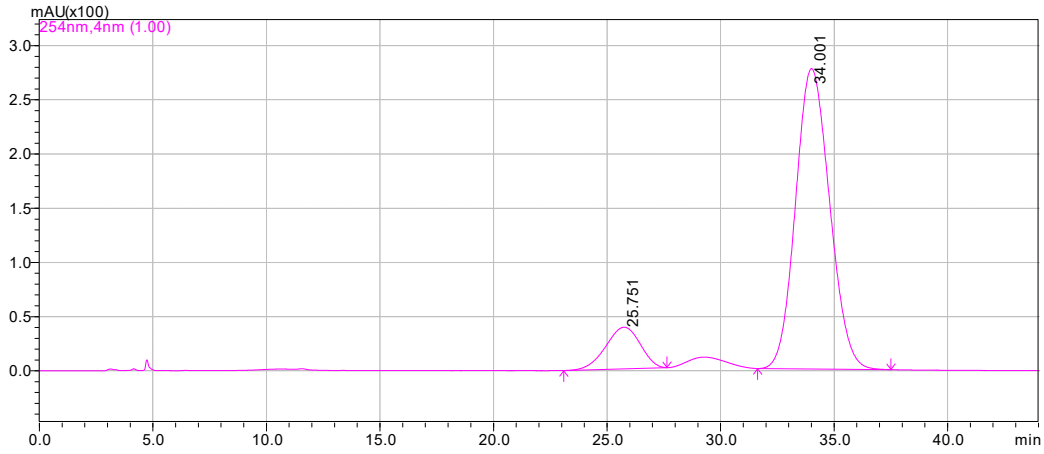
Daicel Chiralpak OD-H, hexane/iso-propanol= 85/15, flow rate 1.0 mL/min, 25°C: t_R (major) = 11.7 min, t_R (minor) = 16.3 min.



5k



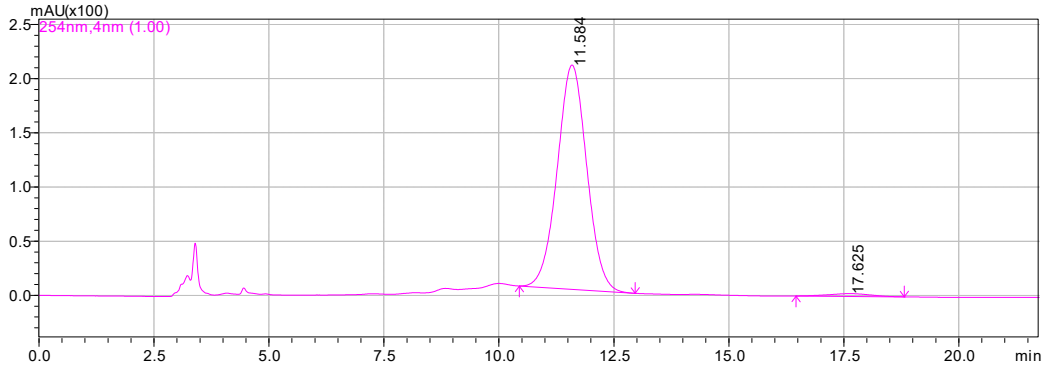
Peak	Ret. Time	Area	Area%
A	25.928	21688054	49.5608
B	34.091	22072486	50.4392



Peak	Ret. Time	Area	Area%
A	25.751	4061332	12.3160
B	34.001	28914688	87.6840

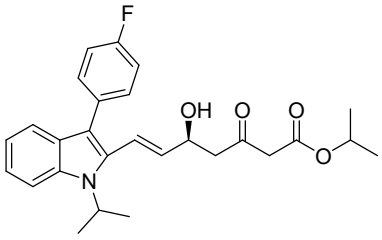
Daicel Chiralpak IA, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 34.0 min, t_R (minor) = 25.8 min.

5mmol scale synthesis of **3f**

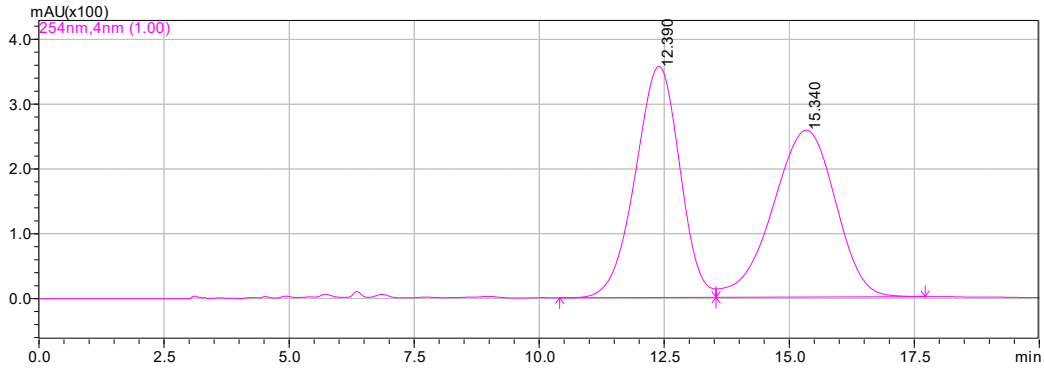


Peak	Ret. Time	Area	Area%
A	11.584	9261304	98.2122
B	17.625	168586	1.7878

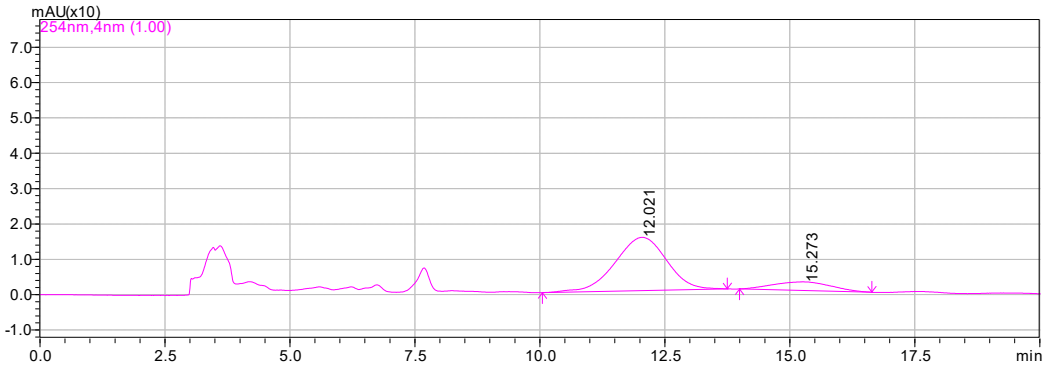
Daicel Chiralpak OD-H, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 11.6 min, t_R (minor) = 17.6 min.



5l

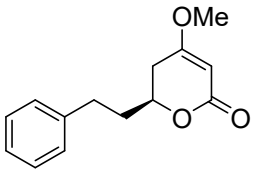


Peak	Ret. Time	Area	Area%
A	12.390	22003935	49.5342
B	15.340	22417779	50.4658

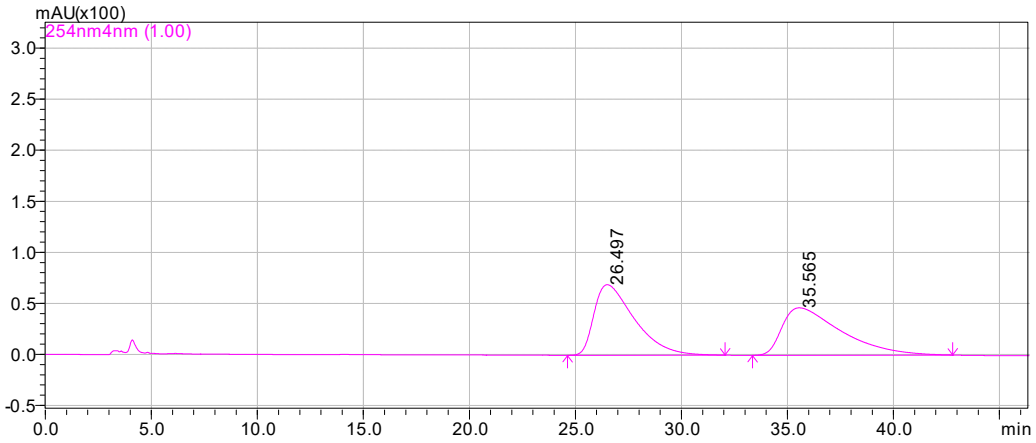


Peak	Ret. Time	Area	Area%
A	12.021	1085168	84.6032
B	15.273	197488	15.3968

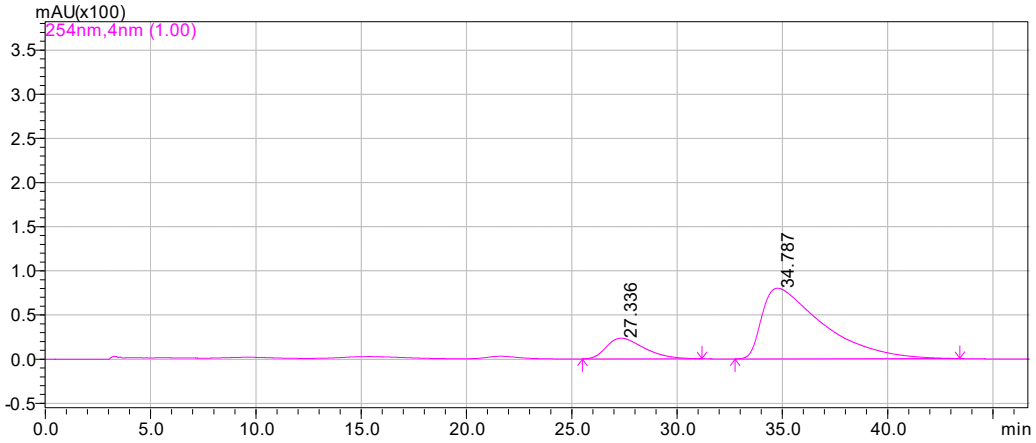
Daicel Chiralpak IA, hexane/iso-propanol= 95/5, flow rate 1.0 mL/min, 25°C: t_R (major) = 12.0 min, t_R (minor) = 15.3 min.



(+)-dihydroxykavain

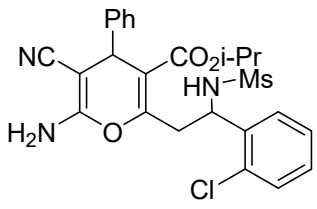


Peak	Ret. Time	Area	Area%
A	26.497	9185622	50.4669
B	35.565	9015668	49.5331

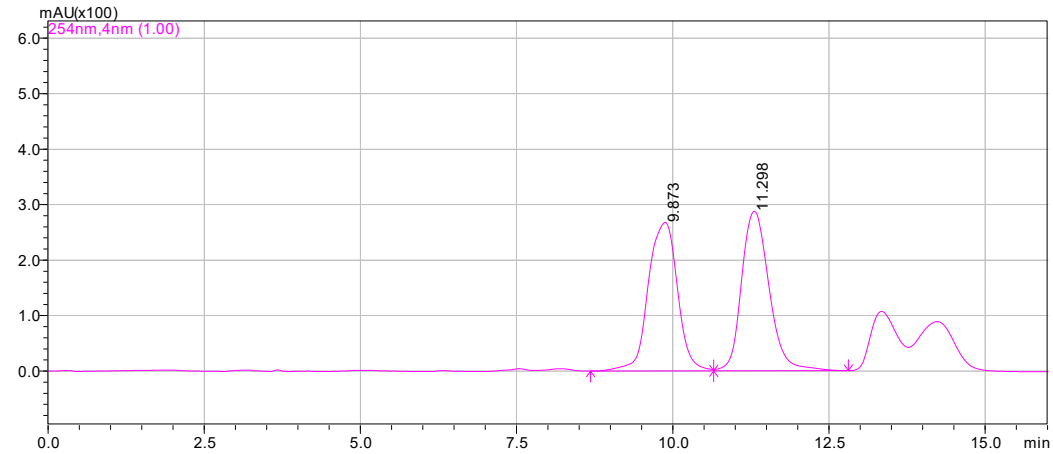


Peak	Ret. Time	Area	Area%
A	27.336	2917094	15.3860
B	34.787	16042292	84.6140

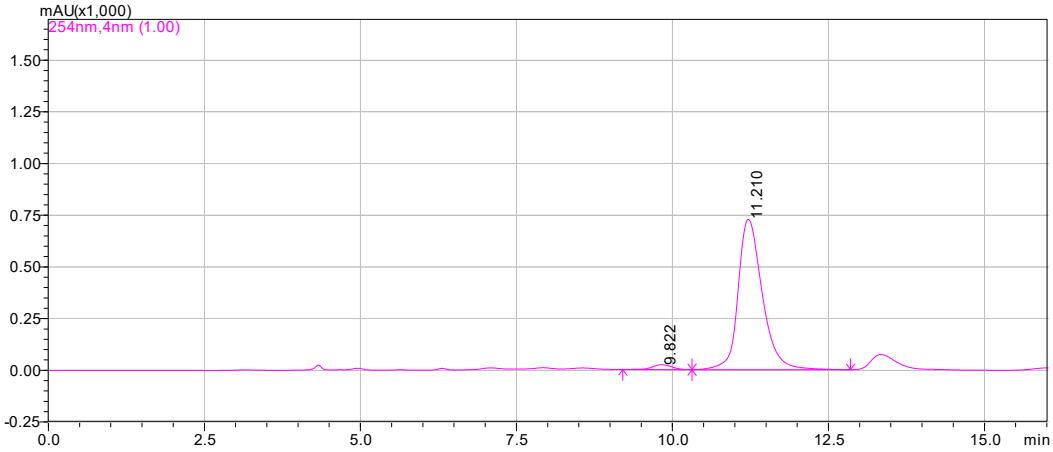
Daicel Chiralpak OB, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 34.8 min, t_R (minor) = 27.3 min.



7(minor)

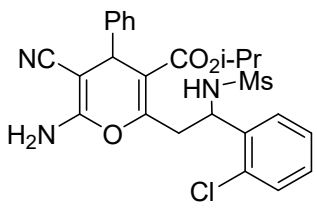


Peak	Ret. Time	Area	Area%
A	9.873	8737009	49.6521
B	11.298	8859452	50.3479

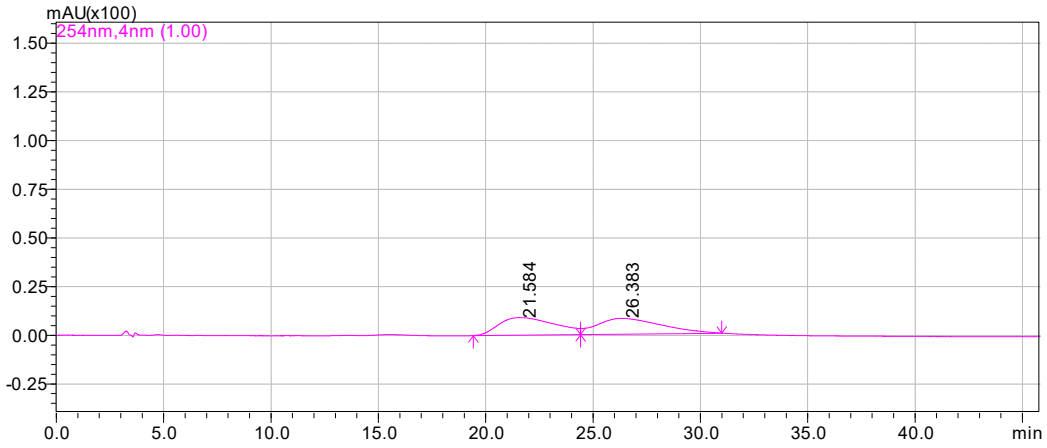


Peak	Ret. Time	Area	Area%
A	9.822	506838	2.5215
B	11.210	19593622	97.4785

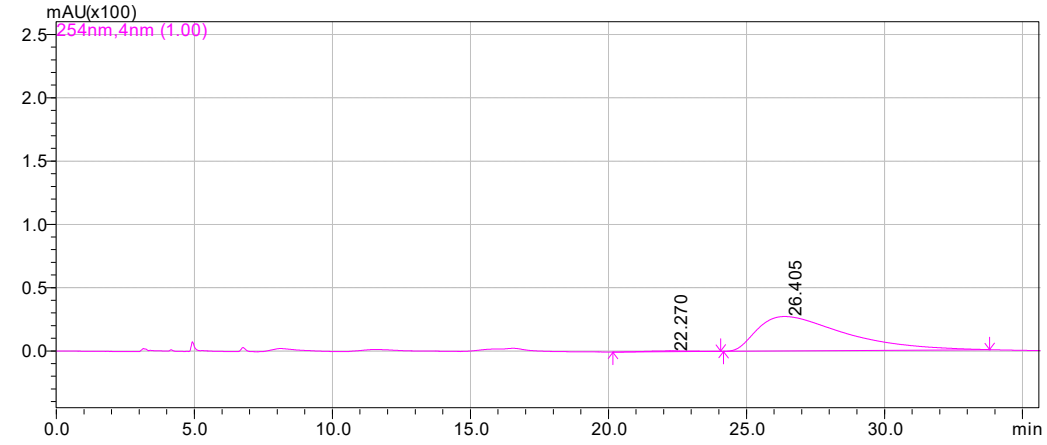
Daicel Chiralpak IA, hexane/iso-propanol= 80/20, flow rate 1.0 mL/min, 25°C: t_R (major) = 11.2 min, t_R (minor) = 9.8 min.



7(major)

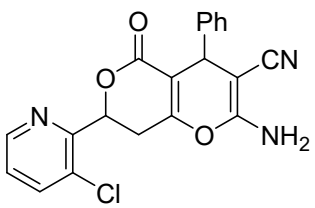


Peak	Ret. Time	Area	Area%
A	21.584	1645745	49.2040
B	26.383	1698992	50.7960

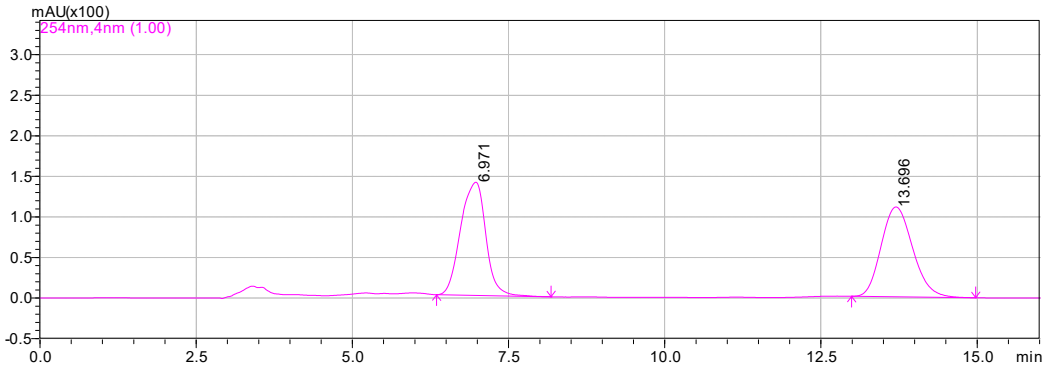


Peak	Ret. Time	Area	Area%
A	22.270	72998	1.1949
B	26.405	6036308	98.8051

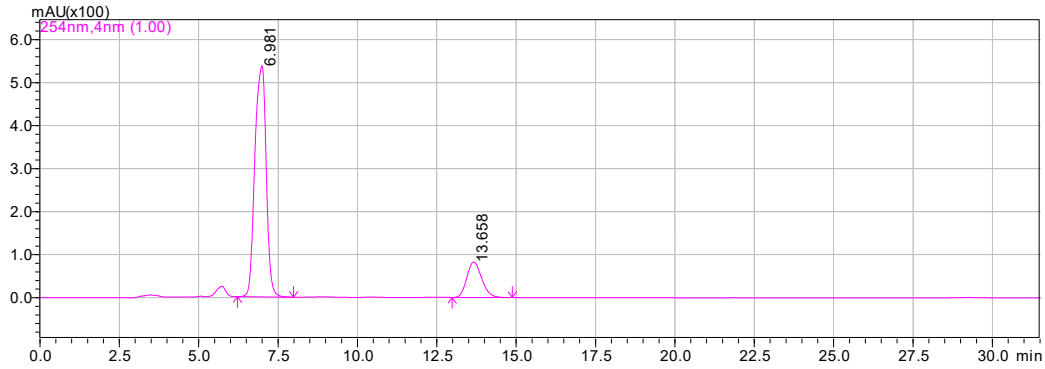
Daicel Chiralpak AS-H, hexane/iso-propanol= 85/15, flow rate 1.0 mL/min, 25°C: t_R (major) = 26.4 min, t_R (minor) = 22.3 min.



8(major)

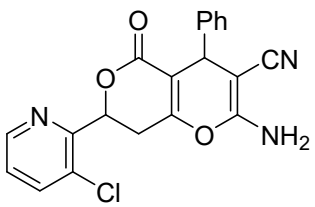


Peak	Ret. Time	Area	Area%
A	6.971	3921511	50.2516
B	13.696	3882244	49.7484

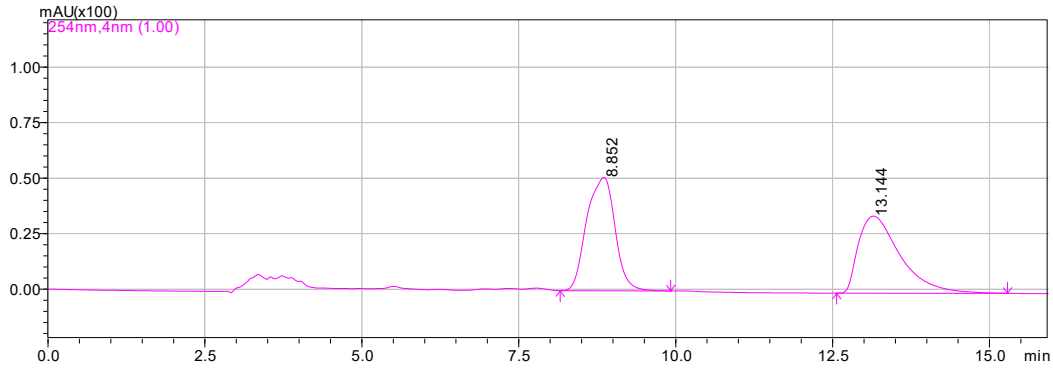


Peak	Ret. Time	Area	Area%
A	6.981	13316717	83.2122
B	13.658	2686603	16.7878

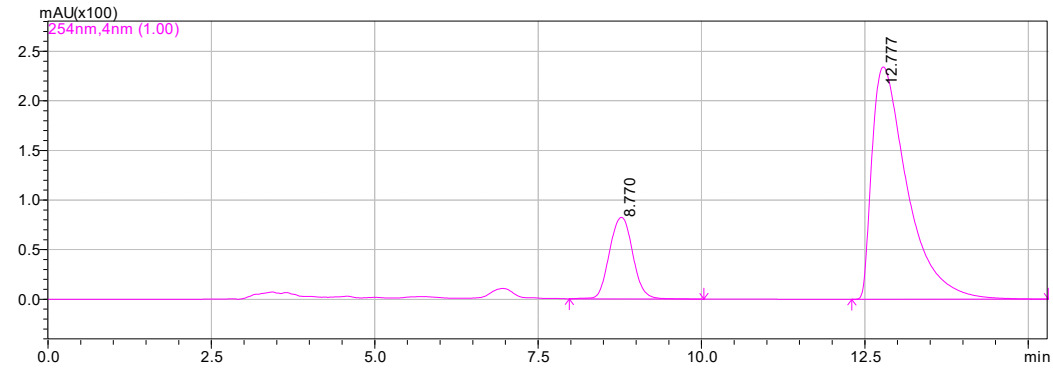
Daicel Chiralpak AD, hexane/iso-propanol= 70/30, flow rate 1.0 mL/min, 25°C: t_R (major) = 7.0 min, t_R (minor) = 13.7 min.



8(minor)

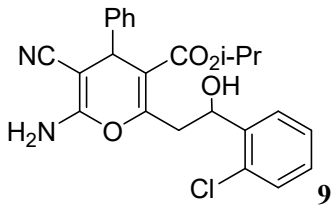


Peak	Ret. Time	Area	Area%
A	8.852	1599810	49.9602
B	13.144	1602360	50.0398

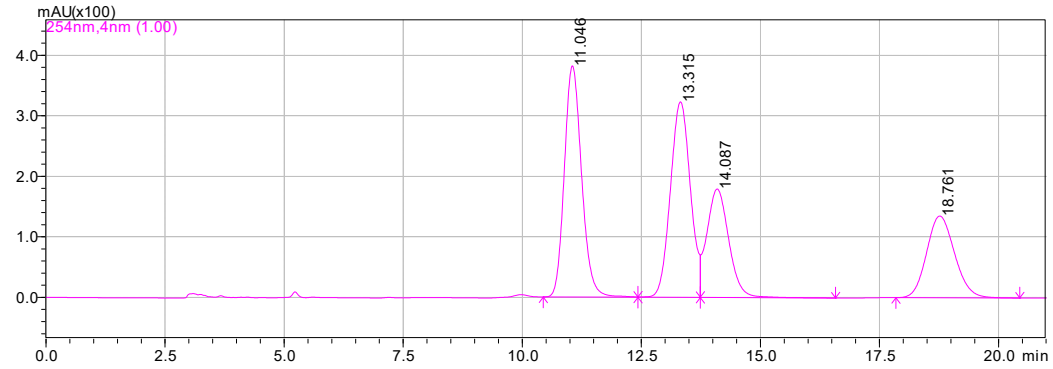


Peak	Ret. Time	Area	Area%
A	8.770	2049029	18.8726
B	12.777	8808141	81.1274

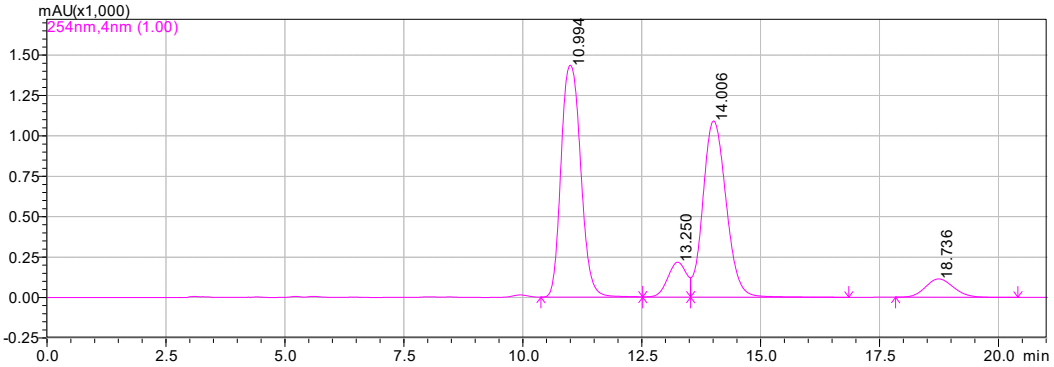
Daicel Chiralpak AD, hexane/iso-propanol= 70/30, flow rate 1.0 mL/min, 25°C: t_R (major) = 12.8 min, t_R (minor) = 8.8 min.



9



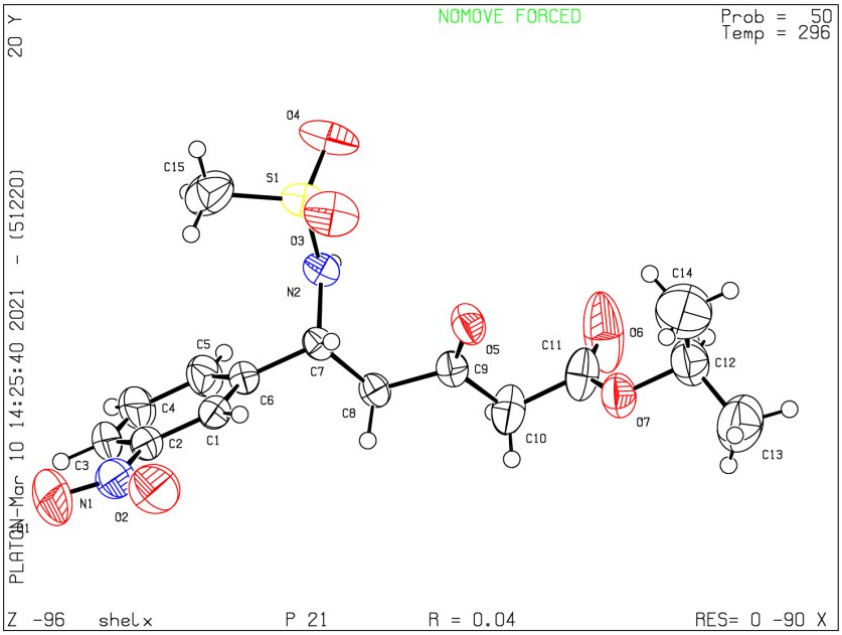
Peak	Ret. Time	Area	Area%
A	11.046	9634528	31.7647
B	13.315	9433882	31.1032
C	14.087	5739934	18.9244
D	18.761	5522565	18.2077



Peak	Ret. Time	Area	Area%
A	10.994	41385477	46.4993
B	13.250	5952075	6.6875
C	14.006	37010414	41.5836
D	18.736	4654493	5.2296

Daicel Chiralpak AD, hexane/iso-propanol= 85/15, flow rate 1.0 mL/min, 25°C: t_R (major) = 11.0 min, t_R (minor) = 13.3 min; $t_{R'}$ (major) = 14.0 min, $t_{R'}$ (minor) = 18.7 min.

12. The crystal structure of 3i (CCDC 2132429 contains the supplementary crystallographic data of 3i)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Prob = 50
Temp = 296
20 Y
PLATON-Mar 10 14:25:40 2021 - (51220)
O4
C15
S1
O3
N2
C14
O5
C11
O6
C5
C7
C9
C12
C6
C4
C8
O7
C2
C1
C10
C13
C3
N1
O2
Z -96 shelx P 21 R = 0.04 RES= 0 -90 X