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Supporting Information

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Supporting Information for

Chiral Brönsted Acid Catalyzed Asymmetric Baeyer-Villiger Reaction of 3-Substituted Cyclobutanones Using Aqueous H_2O_2

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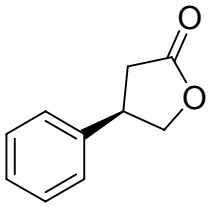
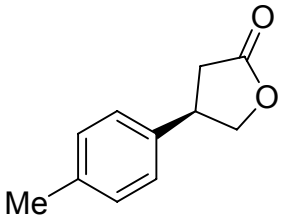
General Methods. Melting point was measured with XT-4 micro melting point apparatus and uncorrected. NMR spectra were recorded on a Varian Mercury 300 (^{1}H 300 MHz; ^{19}F 282 MHZ) spectrometer in $CDCl_3$. Chemical shifts are expressed in ppm with TMS as an internal standard (δ = 0 ppm) for ^{1}H NMR. Coupling constants, *J*, are listed in hertz. Data for ^{19}F NMR were reported in terms of chemical shift (δ, ppm). HPLC analysis was carried out on a JASCO PU 2089 liquid chromatograph with a UV 2075 detector. Specific optical rotations and CD spectra were obtained on PE-341 and JASCO 810 spectrometers, respectively. Unless stated otherwise, all solvents were purified and dried according to standard methods prior to use.

General Procedure for Asymmetric Baeyer-Villiger Oxidation

To a 5-mL Schlenk tube was charged 7.6 mg of **(*R*)-1r (**10 mol %, 0.01 mmol), 0.1 mmol of 3-substituted cyclobutanone **2** and 1 mL of $CHCl_3$. The mixture was stirred and cooled to -40°C, and then 1.5 equiv. of aqueous H_2O_2 (30%) was added at this temperature. The reaction mixture was stirred for 18-36 h at -40°C. After completion of the reaction, H_2O_2 was decomposed with aqueous Na_2SO_3 and the product **3** was isolated by column chromatography on silica gel with petroleum ether / ethyl acetate = 6/1 as the eluent. The enantiomeric excess was determined by chiral HPLC analysis.

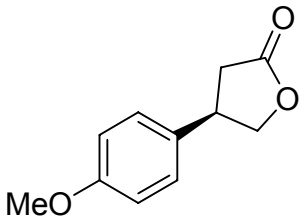


(-)-(*R*)-4-phenyldihydrofuran-2(3H)-one (3a)[1]**:** white solid, 99% yield, m.p. 60-62°C (lit[1] 59-60°C); $[\alpha]_D^{20}$ = -46.7 (*c* 0.48, $CHCl_3$), 88.0% *ee*; [Lit.[1]: $[\alpha]_D^{20}$ = -67.2 (*c* 2.0, $CHCl_3$) for *R*–isomer with 99% *ee*]. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.22-7.41 (m, 5 H), 4.68 (dd, *J* = 9.0, 8.6 Hz, 1 H), 4.28 (dd, *J* = 8.4, 8.4 Hz, 1 H), 3.74-3.86 (m, 1 H), 2.94 (dd, *J* = 17.4, 9.0 Hz, 1 H), 2.68 (dd, *J* = 17.4, 9.0 Hz, 1 H) ppm. The enantiomeric excess was determined by chiral HPLC analysis on a Chiralpak AS-H column (hexane/2-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 220 nm), t_R = 40.4 min (major); 46.9 min (minor).

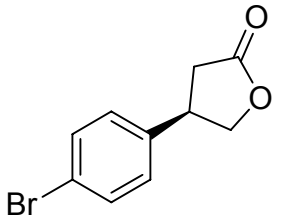


(-)-(*R*)-4-(4-tolyl)dihydrofuran-2(3H)-one (3b)[2]**:** yellow solid; 99% yield, m.p. 66-68°C (lit[2] 63.5-65°C); $[\alpha]_D^{20}$ = -31.5 (*c* 0.67, $CHCl_3$), 93% *ee*; [Lit.[2]: $[\alpha]_D^{21}$ =

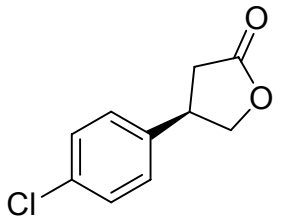
+50 (*c* = 1.25, $CHCl_3$) for *S*-isomer]. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.10-7.20 (m, 4 H), 4.65 (dd, *J* = 8.4, 8.4 Hz, 1 H), 4.24 (dd, *J* = 8.5, 8.4 Hz, 1 H), 3.72-3.79 (m, 1 H), 2.90 (dd, *J* = 17.1, 8.7 Hz, 1 H), 2.65 (dd, *J* = 17.1, 8.7 Hz, 1 H), 2.35 (s, 3 H) ppm; The enantiomeric excess was determined by chiral HPLC analysis on a Chiralpak AD-H column (hexane/2-PrOH = 95/5, flow rate = 0.7 mL/min, λ = 214 nm), t_R = 17.9 min (minor), 18.9 min (major).



(-)-(*R*)-4-(4-methoxyphenyl)dihydrofuran-2(3H)-one (3c)[3]**:** yellow solid; 99% yield, m.p. 92-94°C; $[\alpha]_D^{20}$ = -28.3 (*c* 0.90, $CHCl_3$) for *R*-isomer with 85% *ee*. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.15 (d, *J* = 7.3, 2.1 Hz, 2 H), 6.90 (dd, *J* = 7.2, 2.4 Hz, 2 H), 4.64 (dd, *J* = 8.7, 8.1 Hz, 1 H), 4.22 (dd, *J* = 8.7, 8.4 Hz, 1 H), 3.81 (s, 3 H), 3.71-3.83 (m, 1 H), 2.90 (dd, *J* = 17.4, 8.7 Hz, 1 H), 2.63 (dd, *J* = 17.4, 9.3 Hz, 1 H) ppm; The enantiomeric excess was determined by chiral HPLC analysis on a Chiralpak AD-H column (hexane/2-PrOH = 95/5, flow rate = 0.7 mL/min, λ = 214 nm), t_R = 31.8 min (minor), 33.5 min (major).

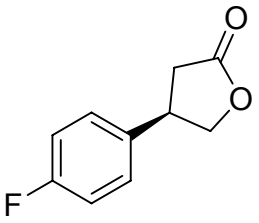


(-)-(*R*)-4-(4-bromophenyl)dihydrofuran-2(3*H*)-one (3d)[3]**:** yellow soild; 99% yield, m.p. 84-86°C; $[\alpha]_D^{20}$ = -30.7 (*c* 1.18, $CHCl_3$) for *R*-isomer with 83% *ee*. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.7 Hz, 1 H), 7.12 (d, *J* = 8.4 Hz, 1 H), 4.66 (dd, *J* = 8.7, 7.8 Hz, 1 H), 4.23 (dd, *J* = 8.4, 7.5 Hz, 1 H), 3.73-3.79 (m, 1 H), 2.94 (dd, *J* = 17.7, 8.7 Hz, 1 H), 2.63 (dd, *J* = 17.4, 8.4 Hz, 1 H); The enantiomeric excess was determined by chiral HPLC analysis on a Chiralpak AD-H column (hexane/2-PrOH = 95/5, flow rate = 0.7 mL/min, λ = 230 nm), t_R = 31.9 min (minor), 33.8 min (major).

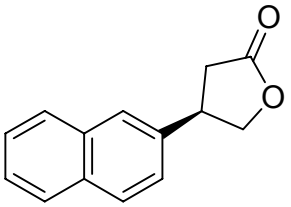


(-)-(*R*)-4-(4-chlorophenyl)dihydrofuran-2(3H)-one (3e) [4]**:** yellow solid; 99%

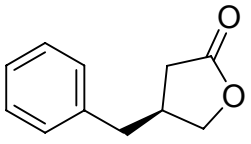
yield, m.p. 72-74°C (lit[4] 73-75°C); $[\alpha]_D^{20}$ = -47.2 (*c* 0.90, $CHCl_3$) for *R*-isomer with 81.7% *ee* [Lit.[4]: $[\alpha]_D^{20}$ = -48.5 (*c* 1.38, $CHCl_3$) for *R*-isomer]. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 8.4 Hz, 2 H), 7.17 (d, *J* = 7.8 Hz, 2 H), 4.66 (dd, *J* = 8.4, 8.4 Hz, 1 H), 4.24 (dd, *J* = 9.0, 8.2 Hz, 1 H), 3.74-3.81 (m, 1 H), 2.94 (dd, *J* = 17.7, 8.7 Hz, 1 H), 2.63 (dd, *J* = 17.7, 8.7 Hz, 1 H) ppm. The enantiomeric excess was determined by chiral HPLC analysis on a Chiralpak AD-H column (hexane/2-PrOH = 95/5, flow rate = 0.7 mL/min, λ = 230 nm), t_R = 28.9 min (minor), 30.5 min (major).



(-)-(*R*)-4-(4-fluorophenyl)dihydrofuran-2(3H)-one (3f) [3]**:** yellow solid; 99% yield, m.p. 58-60°C; $[\alpha]_D^{20}$ = -40.2 (*c* 0.85, $CHCl_3$) for *R*-isomer with 84% *ee*. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.19-7.24 (m, 2 H), 7.03-7.10 (m, 2 H), 4.66 (dd, *J* = 9.3, 8.1 Hz, 1 H), 4.24 (dd, *J* = 9.0, 7.8 Hz, 1 H), 3.75-3.82 (m, 1 H), 2.94 (dd, *J* = 17.1, 8.4 Hz, 1 H), 2.64 (dd, *J* = 17.1, 8.7 Hz, 1 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ = -114.88 ppm. The enantiomeric excess was determined by chiral HPLC analysis on a Chiralpak AD-H column (hexane/2-PrOH = 95/5, flow rate = 0.7 mL/min, λ = 214 nm), t_R = 27.2 min (minor), 28.4 min (major).

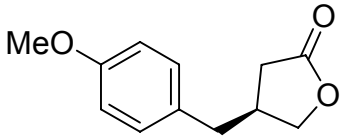


(-)-(*R*)-4-(naphthalen-2-yl)dihydrofuran-2(3H)-one (3g)[5]**:** white powder, 91% yield, m.p. 116-117°C; $[\alpha]_D^{20}$ = -57.9 (*c* 0.90, $CHCl_3$) for *R*-isomer with 86% *ee*. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.80-7.89 (m, 3 H), 7.68 (s, 1 H), 7.48-7.53 (m, 2 H), 7.33-7.37 (m, 1 H), 4.75 (dd, *J* = 9.0, 8.1 Hz, 1 H), 4.39 (dd, *J* = 9.0, 8.1 Hz, 1 H), 3.94-4.00 (m,1 H), 3.02 (dd, *J* = 17.4, 8.7 Hz, 1 H), 2.79 (dd, *J* = 17.4, 9.0 Hz, 1 H) ppm. The enantiomeric excess was determined by chiral HPLC analysis on a Chiralpak AD-H column (hexane/2-PrOH = 95/5, flow rate = 0.7 mL/min, λ = 254 nm), t_R = 29.1 min (minor), 31.9 min (major).

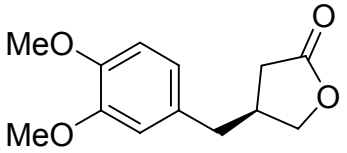


(-)-(*S*)-4-benzyldihydrofuran-2(3H)-one (3h) [6]**:** yellow oil; 99% yield, $[\alpha]_D^{20}$ =

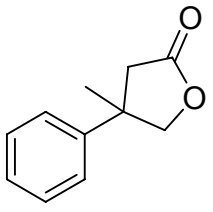
-3.8 (*c* 0.80, $CHCl_3$) for *S*-isomer with 58% *ee* [Lit.[6]: $[\alpha]_D^{30}$ = -8.64 (*c* 0.71, $CHCl_3$) for *S*-isomer). ^1H NMR (300 MHz, $CDCl_3$) δ = 7.14-7.35 (m, 5 H), 4.34 (dd, *J* = 8.7, 6.6 Hz, 1 H), 4.04 (dd, *J* = 8.7, 6.6 Hz, 1 H), 2.76-2.89 (m, 3 H), 2.61 (dd, *J* = 17.5, 7.5 Hz, 1 H), 2.29 (dd, *J* = 17.5, 6.9 Hz, 1 H) ppm. The enantiomeric excess was determined by chiral HPLC analysis on a Chiralpak AD-H column (hexane/2-PrOH = 95/5, flow rate = 0.7 mL/min, λ = 214 nm), t_R = 23.2 min (minor), 25.0 min (major).



(-)-(*S*)-4-(4-methoxybenzyl)dihydrofuran-2(3H)-one (3i) [7]**:** white solid; 99% yield, m.p. 58-60°C (lit[7] 56.5-59°C); $[\alpha]_D^{25}$ = -4.2 (*c* 1.0, $CHCl_3$) for *S*-isomer with 57% *ee*; [Lit.[5]: $[\alpha]_D^{20}$ = -5.8 (*c* 2.18, $CHCl_3$) for *S*-isomer]. ^1H NMR (300 MHz, $CDCl_3$) δ = 7.07 (d, *J* =8.7 Hz, 2 H), 6.84 (d, *J* = 8.1 Hz, 2 H), 4.33 (dd, *J* = 9.3, 6.9 Hz, 1 H), 4.03 (dd, *J* = 9.3, 6.0 Hz, 1 H), 3.80 (s, 3 H), 2.70-2.85 (m, 3 H), 2.59 (dd, *J* = 17.4, 8.1 Hz, 1 H), 2.27 (dd, *J* = 17.1, 7.2 Hz, 1 H) ppm. The enantiomeric excess was determined by chiral HPLC analysis on a Chiralpak AD-H column (hexane/2-PrOH = 95/5, flow rate = 0.7 mL/min, λ = 214 nm), t_R = 32.7 min (minor), 34.7 min (major).



(-)-(*S*)-4-(3,4-dimethoxybenzyl)dihydrofuran-2(3H)-one(3j)[8]**:** colorless oil, 99% yield, $[\alpha]_D^{20}$ = -3.9 (*c* 1.1, $CHCl_3$) for *S*-isomer with 55% *ee*; [Lit.[8]: $[\alpha]_D^{23}$ = -7.54 (*c* 1.9, $CHCl_3$) for *S*-isomer]. ^1H NMR (300 MHz, $CDCl_3$) δ = 6.82 (d, *J* = 8.1 Hz, 1 H), 6.66-6.72 (m, 2 H), 4.33 (dd, *J* = 9.3, 6.6 Hz, 1 H), 4.05 (dd, *J* = 9.3, 6.3 Hz, 1 H), 3.88 (s, 3 H), 3.87 (s, 3 H), 2.70-2.87 (m, 3 H), 2.61 (dd, *J* = 17.4, 8.1 Hz, 1 H), 2.33 (dd, *J* = 18.0, 9.3 Hz, 1 H) ppm. The enantiomeric excess was determined by chiral HPLC analysis on a Chiralpak AD-H column (hexane/2-PrOH = 95/5, flow rate = 0.7 mL/min, λ = 214 nm), t_R = 57.5 min (minor), 59.0 min (major).



(+)-4-methyl-4-phenyldihydrofuran-2(3H)-one (3k) [9]**:** yellow oil, 99% yield, $[\alpha]_D^{20}$ = +7.3 (*c* 0.73, $CHCl_3$) for the isomer with 61% *ee*. ^1H NMR (300 MHz,

$CDCl_3$) δ 7.17-7.41 (m, 5 H), 4.42 (s, 2 H), 2.92 (d, *J* = 16.8 Hz, 1 H), 2.67 (d, *J* = 16.8 Hz, 1 H), 1.52 (s, 3 H). The enantiomeric excess was determined by chiral HPLC analysis on a Chiralpak AD-H column (hexane/2-PrOH = 90/10, flow rate = 0.7 mL/min, λ = 214 nm), t_R = 13.4 min (minor), 16.8 min (major).

References:

[1] B. H. Lipshutz, J. M. Servesko, B. R. Taft, *J. Am. Chem. Soc*. **2004**, *126*, 8352-8353.

[2] L. W. Lawston, T. D. Inch, *J. Chem. Chem*., *Perkin Tran. 1* **1983**, 2629-2635.

[3] S. Murahashi, S. Ono, Y. Imada, *Angew. Chem*. **2002**, *114*, 2472-2474; *Angew. Chem. Int. Ed. Engl*. **2002**, *41*, 2366-2368.

[4] M. Hayahsi, K. Ogasawara, *Heterocycles*, **2003**, *59*, 785-792.

[5] K. Ito, A. Ishii, T. Kuroda, T. Katsuki, *Synlett* **2003**, 643-646.

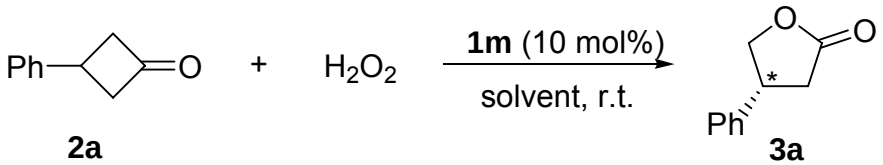
[6] S. Takano, K. Ohashi, T. Sujihara, K. Ogasawara, *Chem. Lett.* **1991**, 203-206.

[7] S. Shiotani, H. Okada, T. Yamamoto, K. Nakamata, *Heterocycles* **1996**, *43*, 113-126.

[8] E. Brown, A. Daugan, *Tetrahedron* **1989**, *45*, 141-145.

[9] H. Toshio, K. Nobuaki, T. Masayoshi, *Tetrahedron: Asymmetry* **1993**, *4*, 1475-1478.

Table S1. Solvent effect on the BV oxidation of **2a** using 1.5 equiv. of aqueous H_2O_2 (30%) in the presence of **1m** as the catalyst.[a]

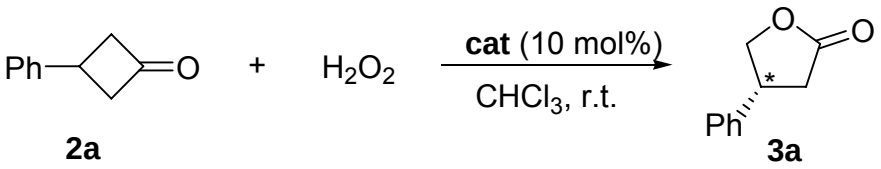


2a **3a**

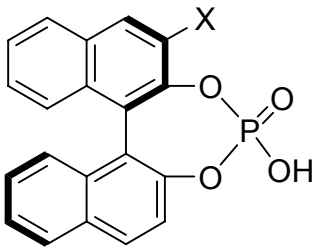
Entry	Sovent	Yield [%][b]	*Ee* [%][c]
1	CH_2Cl_2	68	45
2	$CHCl_3$	72	54
3	CCl_4	69	28
4	$ClCH_2CH_2Cl$	80	44
5	Toluene	93	33
6	Hexane	48	2
7	Et_2O	21	-6
8	MeOH	no reaction	n.d.
9	EtOH	no reaction	n.d.
10	EtOAc	no reaction	n.d.
11	THF	no reaction	n.d.
12	CH_3CN	no reaction	n.d.

[a] The reaction was carried out at room temperature with [**2a**] = 0.1 M to give **3a**. [b] The yield of isolated product. [c] The enantiomeric excess of **3a** was determined by HPLC analysis on a chiral column (Chiralpak AS-H).

Table S2. Relationship between the *ee* of the product and the *ee* of the catalyst.[a]



2a **3a**



X = Pyren-1-yl

ee of cat. [%]	*ee* of **3a** [%][b]
0	0
20	8
40	18
80	41
100	51

[a] The reaction was carried out at room temperature with [**2a**] = 0.1 M in $CHCl_3$. [b] The enantiomeric excess of **3a** was determined by HPLC analysis on a chiral column (Chiralpak AS-H).

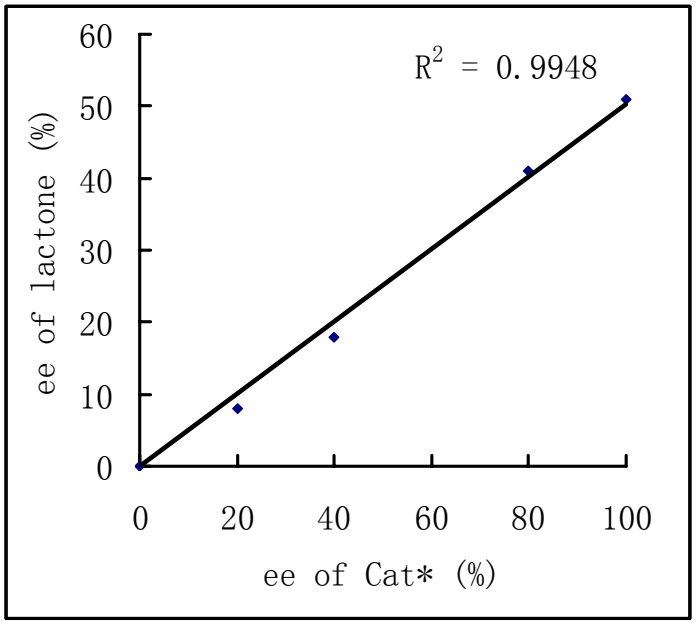
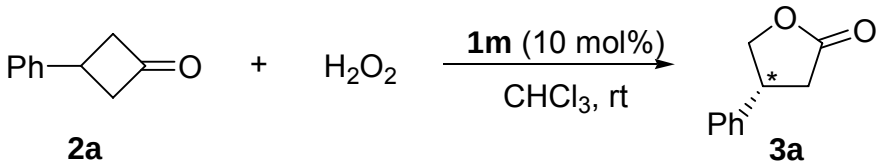


Figure S1. NLE effect in the catalysis of BV oxidation of **3a** using a chiral phosphoric acid as the catalyst in $CHCl_3$ at room temperature.

Table S3. Concentration effect on the enantioselectivity of BV oxidation of **2a** in the presence of **1m**



2a **3a**

Entry	Time(h)	[1m] (M)	Yield(%)[a]	E.e.(%)[b]
1	24	0.02	84	51
2	24	0.01	90	53
3	24	0.0067	83	55
4	24	0.005	79	55
5	24	0.004	83	55
6	24	0.0033	83	55
7	24	0.0028	83	55

[a] The yield of isolated product. [b] The enantiomeric excess of **3a** was determined by HPLC analysis on a chiral column (Chiralpak AS-H).

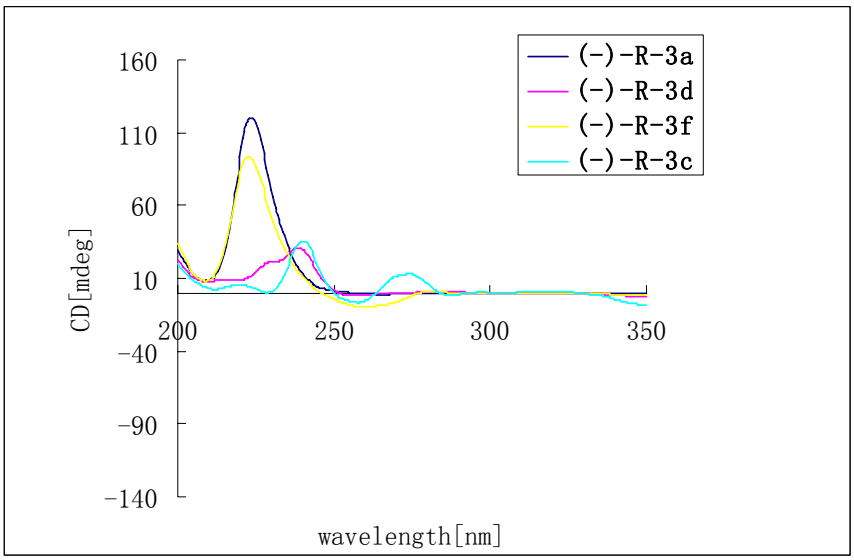


Figure S2. CD spectra for **3a, 3c, 3d** and **3f** in methanol, (*R*)-**3a** is an authentic sample.

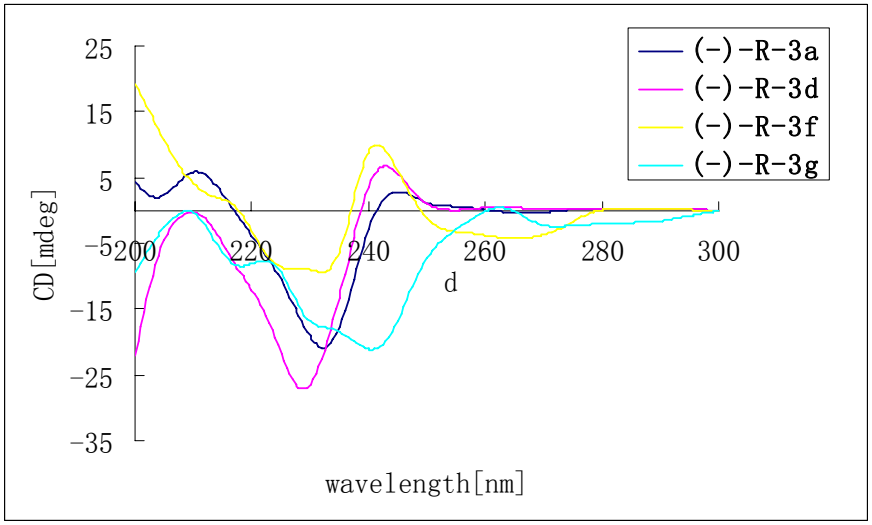
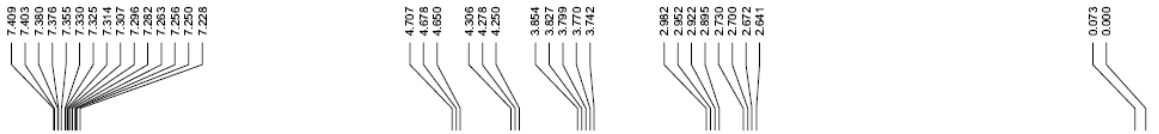


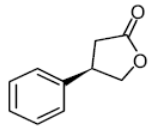
Figure S3. CD spectra of **3a, 3d, 3f** and **3g** in chloroform, (*R*)-**3a** is an authentic sample.

From Figure S2 and S3, it can be concluded that **3c, 3d, 3f** and **3g** should have the same absolute configuration as that of **3a**.

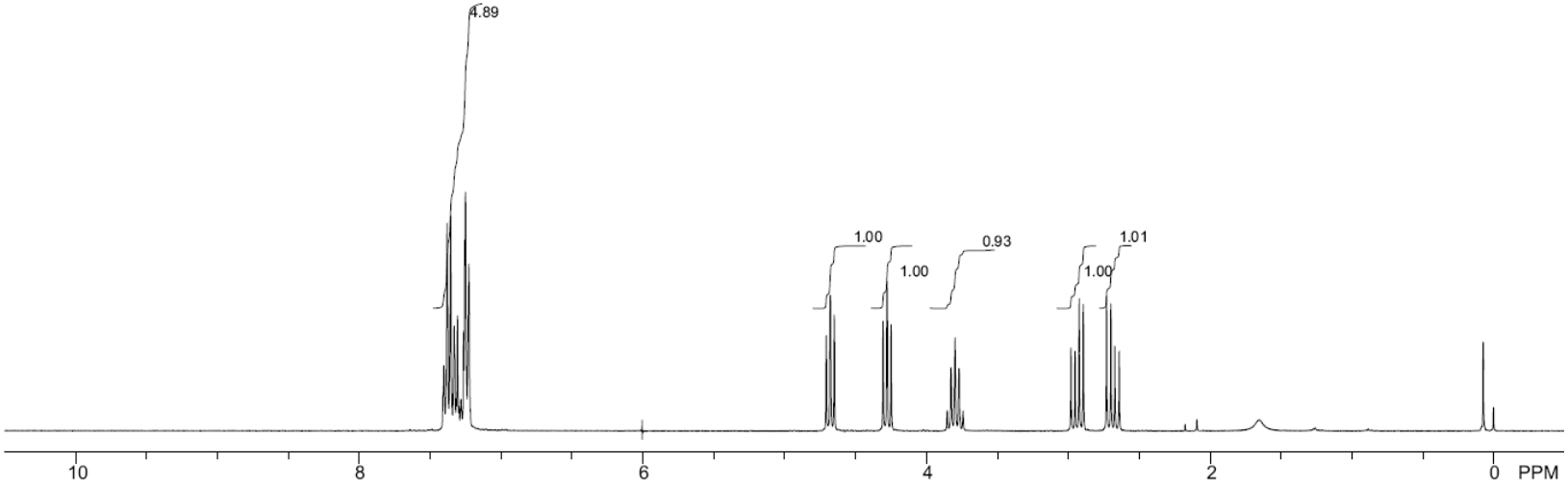

7.409
7.403
7.380
7.376
7.355
7.330
7.325
7.314
7.307
7.296
7.282
7.263
7.256
7.250
7.228
4.707
4.678
4.650
4.306
4.278
4.250
3.854
3.827
3.799
3.770
3.742
2.982
2.952
2.922
2.895
2.730
2.700
2.672
2.641
0.073
0.000

3a:

(-)



xsm-11-43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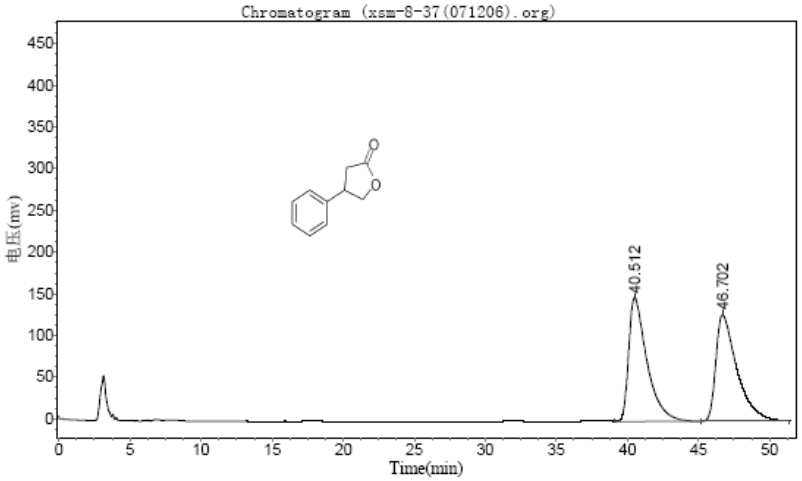
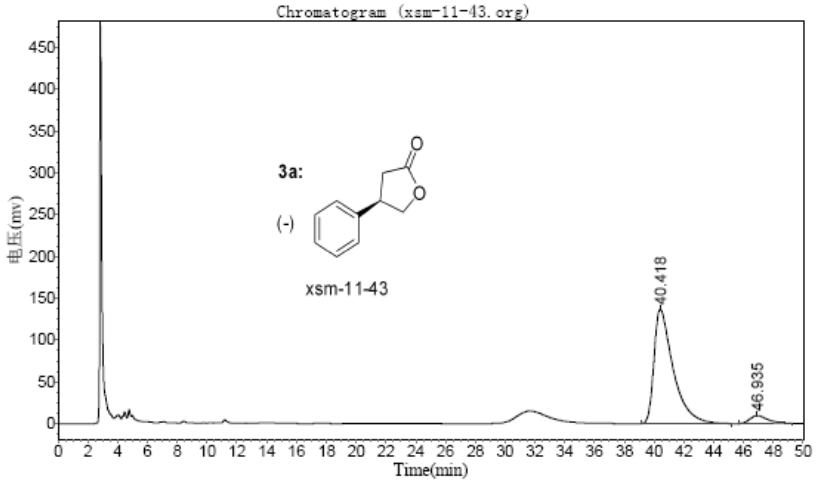
1.00
0.93
1.00
1.01
10
8
6
4
2
0
PPM



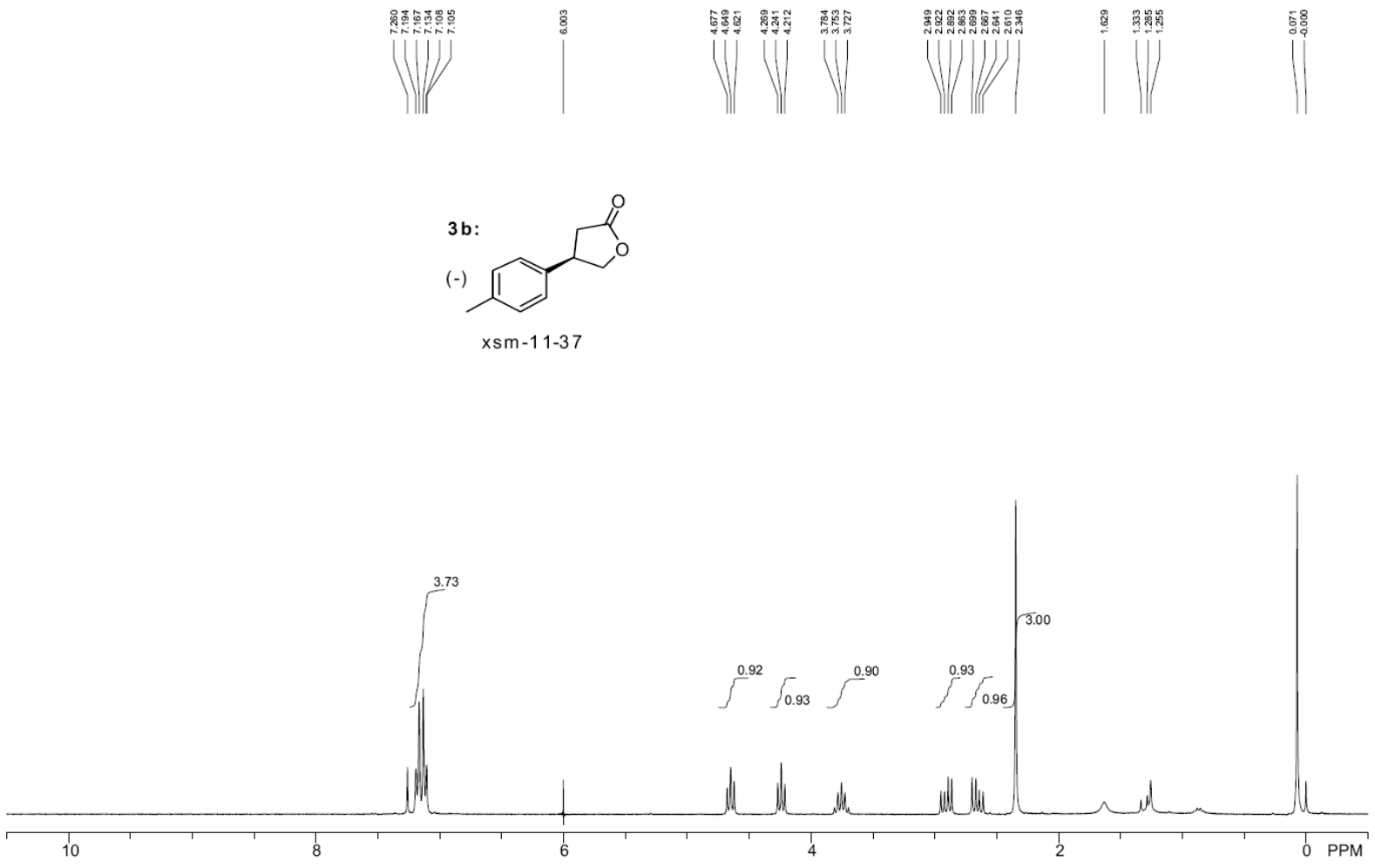
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		40.512	148461.172	13324734.000	50.0986
2		46.702	127987.039	13272300.000	49.9014
Total			276448.211	26597034.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		40.418	136511.922	12186496.000	94.0317
2		46.935	9336.074	773484.875	5.9683
Total			145847.996	12959980.875	100.0000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7.157
7.134
7.108
7.105
6.003
4.677
4.649
4.621
4.269
4.241
4.212
3.784
3.753
3.727
2.949
2.922
2.892
2.863
2.699
2.667
2.641
2.610
2.346
1.629
1.333
1.285
1.255
0.071
-0.000
3b:
(-)
O
O
xsm-11-37
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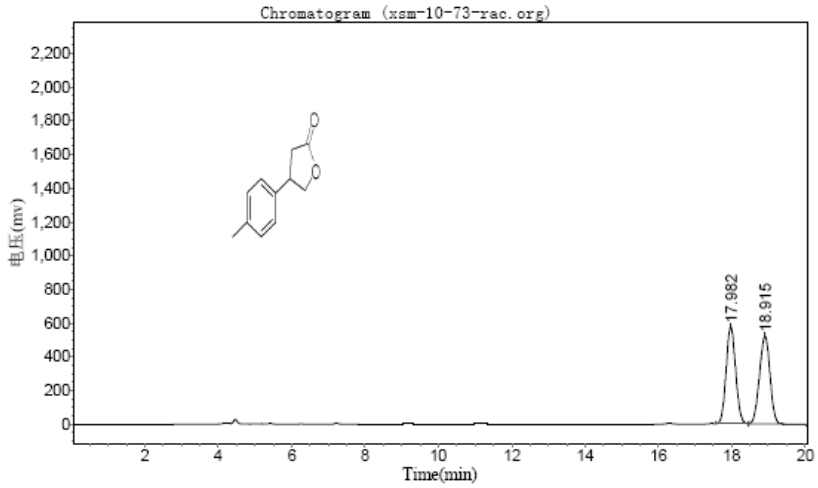
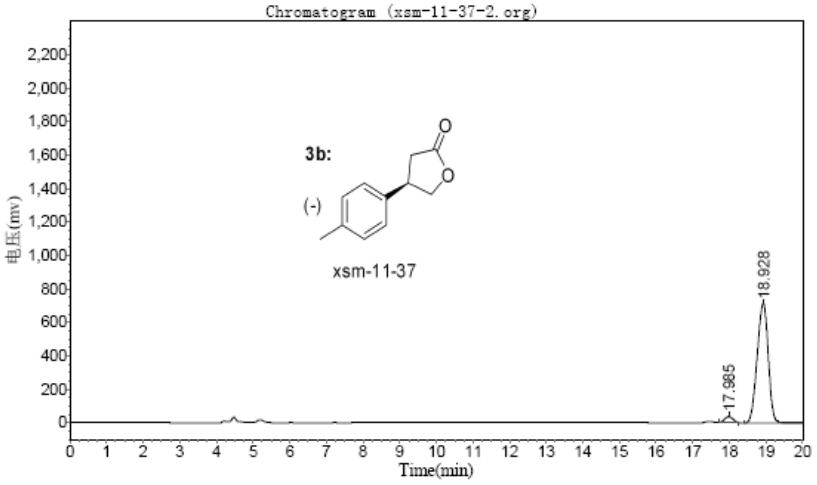
0.93
0.90
0.93
0.96
3.00
10
8
6
4
2
0
PPM



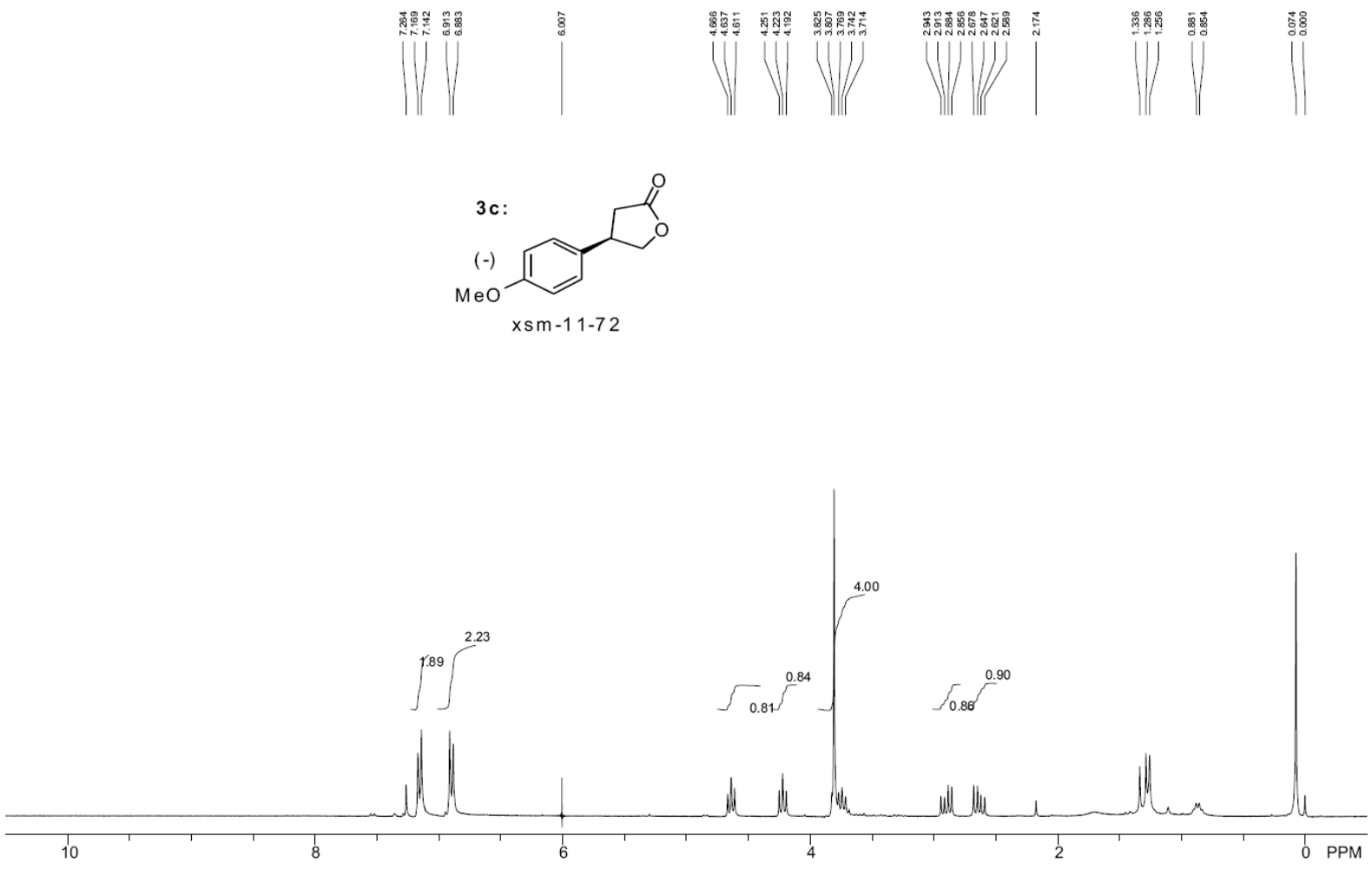
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.982	577510.188	10543849.000	49.9838
2		18.915	522548.313	10550693.000	50.0162
Total			1100058.500	21094542.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.985	34570.641	543436.813	3.4990
2		18.928	713920.688	14987666.000	96.5010
Total			748491.328	15531102.813	100.0000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7.142
6.913
6.883
6.007
4.666
4.637
4.611
4.251
4.223
4.192
3.825
3.807
3.769
3.742
3.714
2.943
2.913
2.884
2.856
2.678
2.647
2.621
2.589
2.174
1.336
1.286
1.256
0.881
0.854
0.074
0.000
3c:
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MeO
O
O
xsm-11-72
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0.84
4.00
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0.90
10
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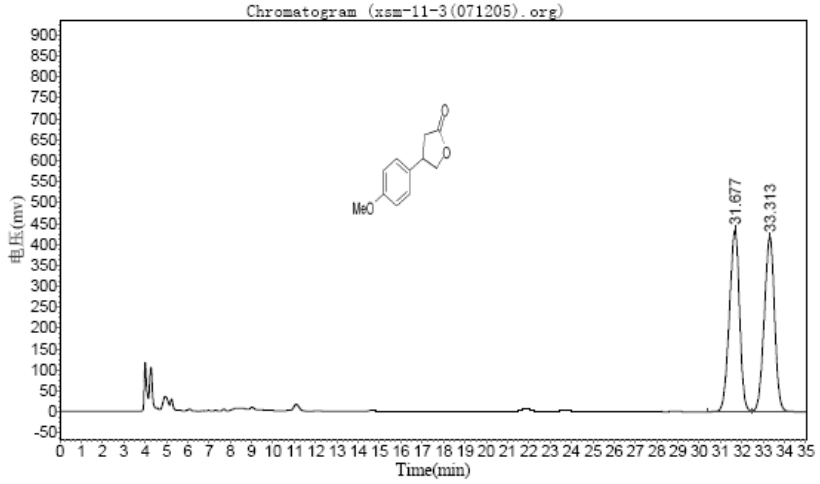
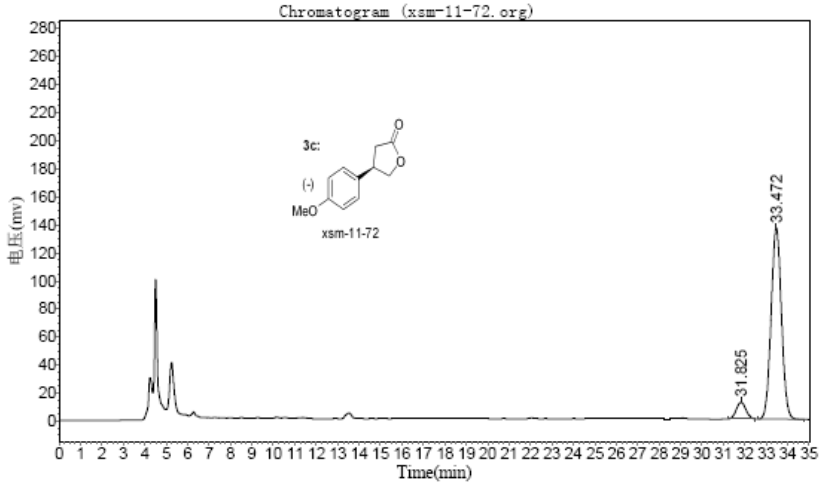
PPM



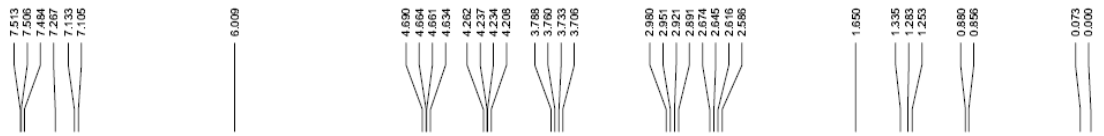
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		31.677	433089.281	14371134.000	50.4848
2		33.313	416969.563	14095121.000	49.5152
Total			850058.844	28466255.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		31.825	11903.113	368892.094	7.4513
2		33.472	136356.969	4581846.000	92.5487
Total			148260.082	4950738.094	100.0000


7.513
7.506
7.484
7.297
7.133
7.105
6.009
4.690
4.664
4.651
4.634
4.262
4.237
4.234
4.208
3.788
3.760
3.733
3.706
2.980
2.951
2.921
2.891
2.674
2.645
2.616
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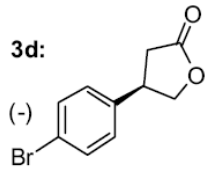
1.253
0.880
0.856
0.073
0.000

3d: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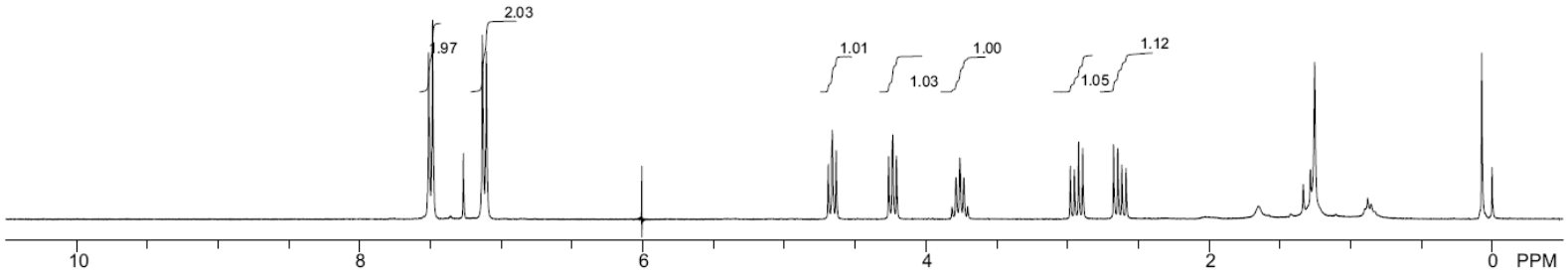
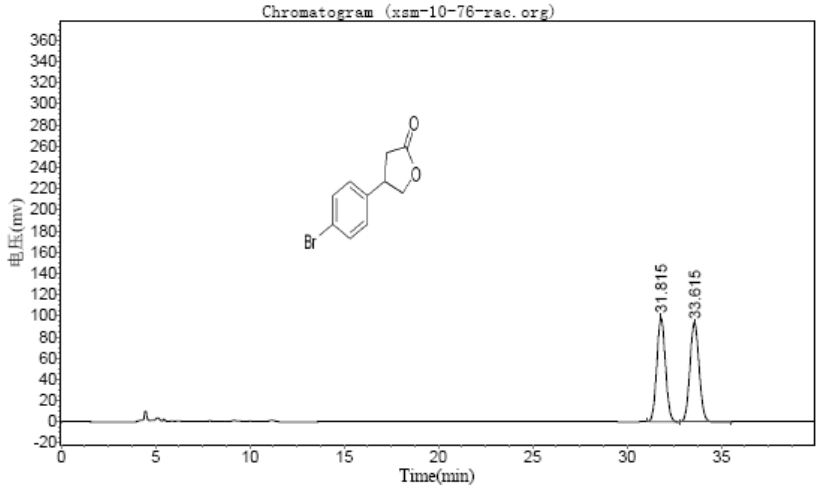
Br

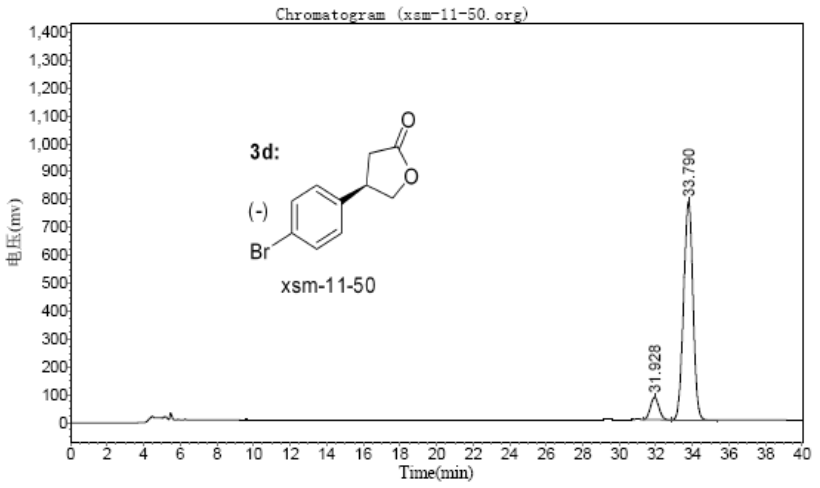
xsm-11-50


2.03
1.97
1.01
1.03
1.00
1.05
1.12
10
8
6
4
2
0
PPM



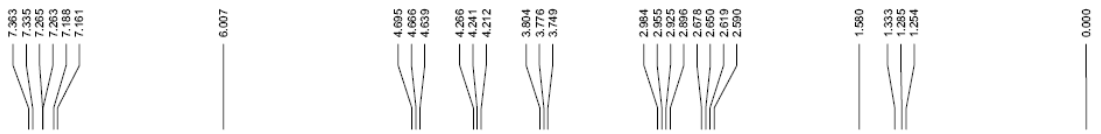
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		31.815	97797.234	3170604.000	49.7894
2		33.615	93569.594	3197429.250	50.2106
Total			191366.828	6368033.250	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		31.928	80181.266	2594646.000	8.5116
2		33.790	782434.813	27888898.000	91.4884
Total			862616.078	30483544.000	100.0000


7.363
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7.265
7.263
7.188
7.161
6.007
4.695
4.666
4.639
4.266
4.241
4.212
3.804
3.776
3.749
2.984
2.955
2.925
2.896
2.678
2.650
2.619
2.590
1.580
1.333
1.285
1.254
0.000

3e:

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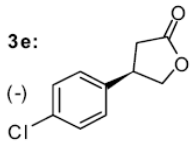
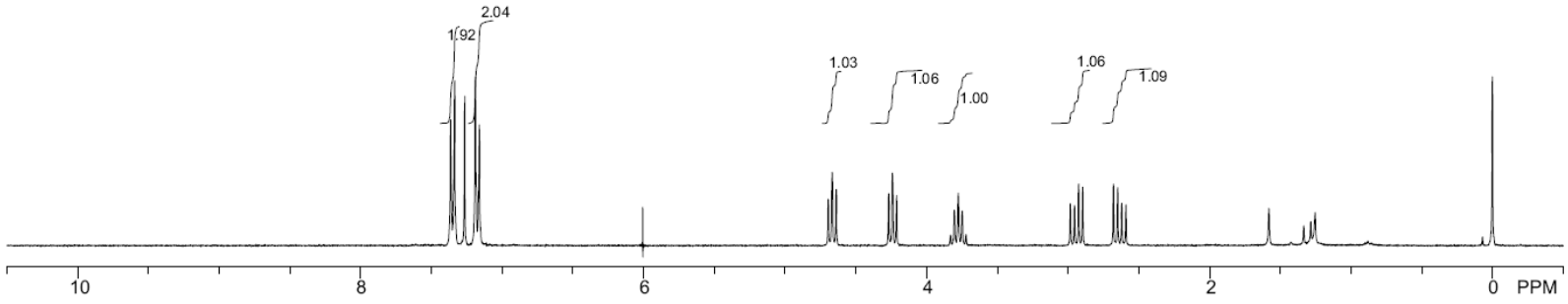
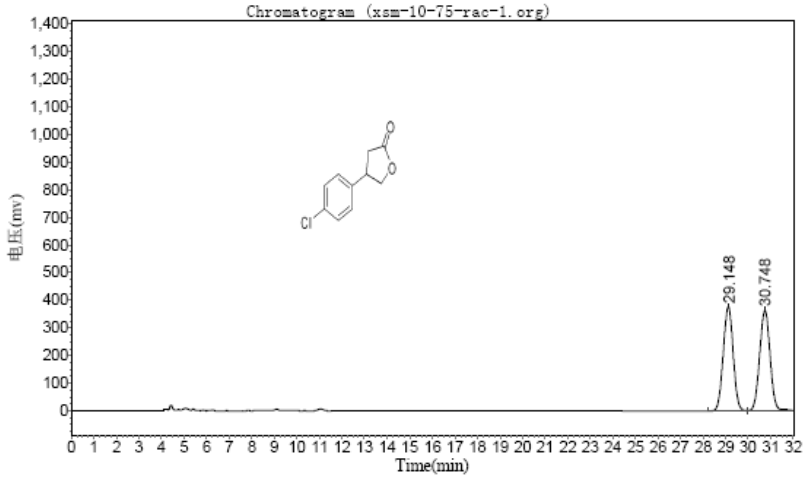

O
O
Cl

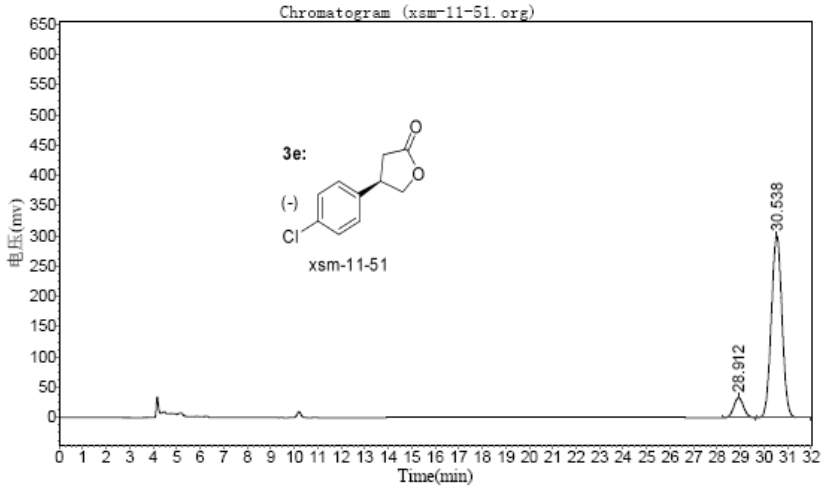
xsm-11-51


2.04
1.92
1.03
1.06
1.00
1.06
1.09
10
8
6
4
2
0
PPM



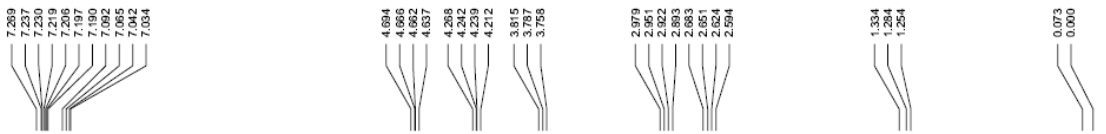
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		29.148	375561.094	11562442.000	49.5773
2		30.748	361990.281	11759593.000	50.4227
Total			737551.375	23322035.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.912	32965.449	956492.313	9.1461
2		30.538	300592.750	9501417.000	90.8539
Total			333558.199	10457909.313	100.0000


7.269
7.237
7.230
7.219
7.206
7.197
7.190
7.092
7.065
7.042
7.034
4.694
4.666
4.662
4.637
4.268
4.242
4.239
4.212
3.815
3.787
3.758
2.979
2.951
2.922
2.893
2.683
2.651
2.624
2.594
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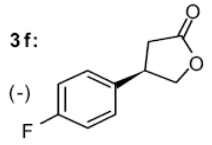
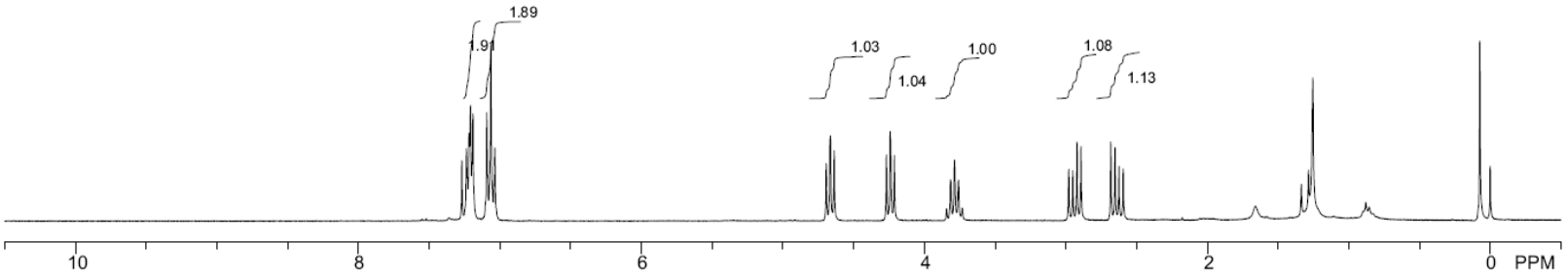
1.284
1.254
0.073
0.000

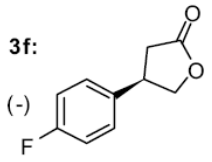
3f:

(-)

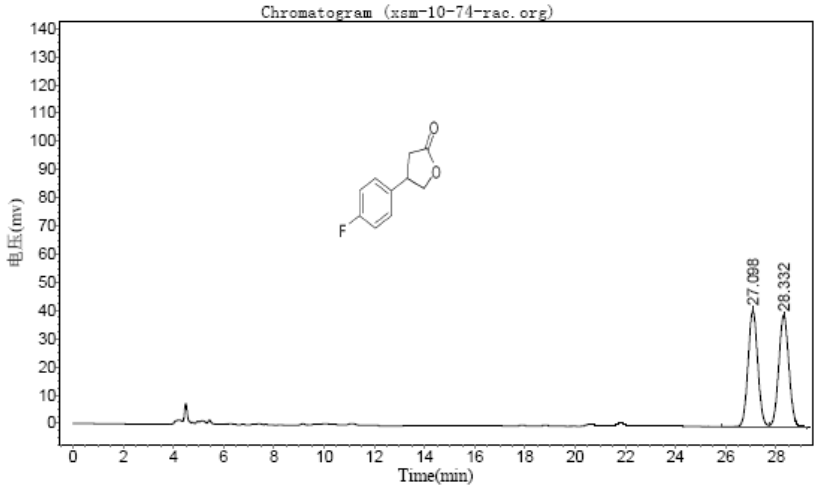

O
O
F

xsm-11-52


1.89
1.91
1.03
1.04
1.00
1.08
1.13
10
8
6
4
2
0
PPM

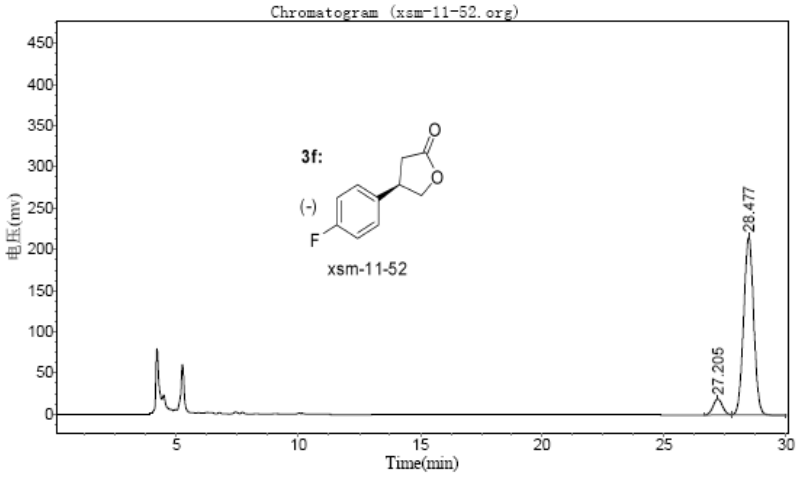


xsm-11-52-F



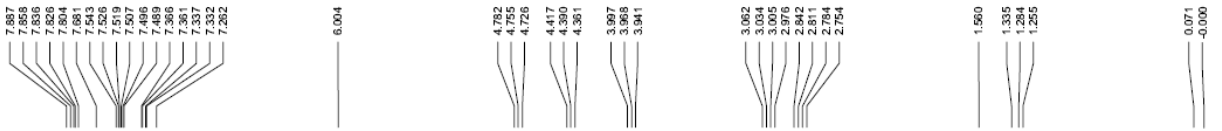
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.098	41054.000	1107401.250	50.0175
2		28.332	39423.000	1106625.750	49.9825
Total			80477.000	2214027.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.205	19225.258	510590.094	7.6431
2		28.477	215268.156	6169790.500	92.3569
Total			234493.414	6680380.594	100.0000


7.887
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7.804
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7.526
7.519
7.507
7.496
7.489
7.366
7.361
7.337
7.332
7.262
6.004
4.782
4.755
4.726
4.417
4.390
4.361
3.997
3.968
3.941
3.062
3.034
3.005
2.976
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1.335
1.284
1.255
0.071
-0.000

3g:

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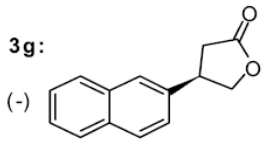

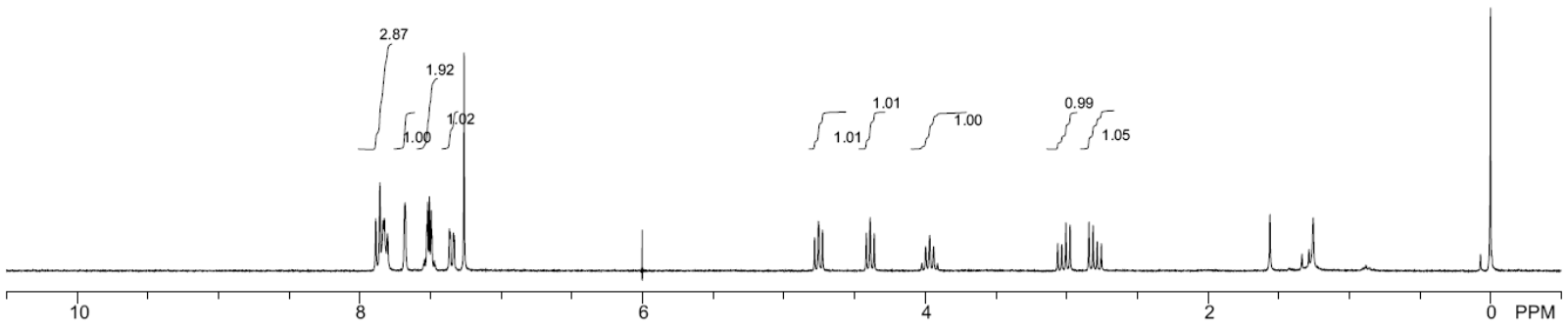
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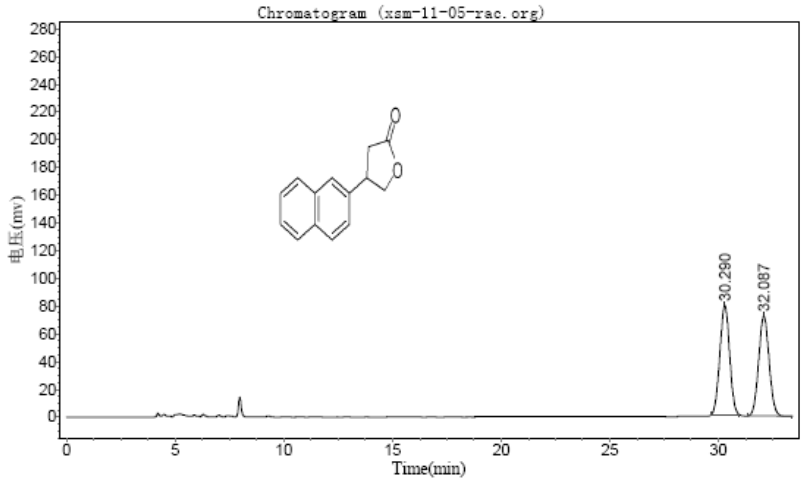
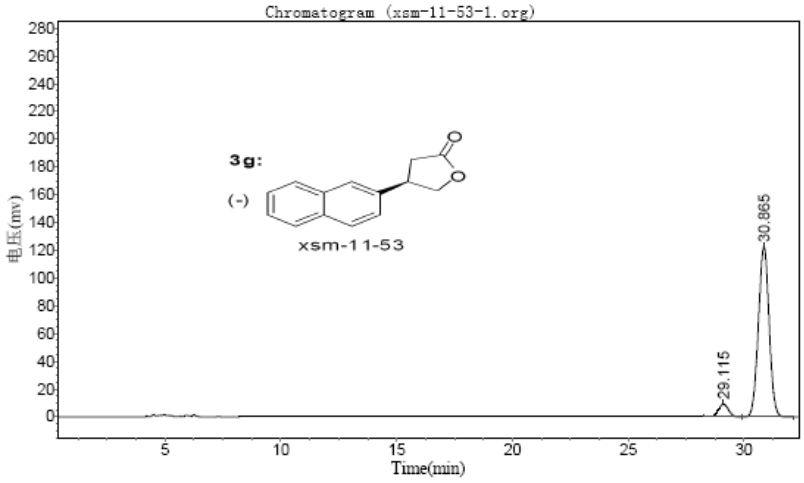
1.00
0.99
1.05
10
8
6
4
2
0
PPM



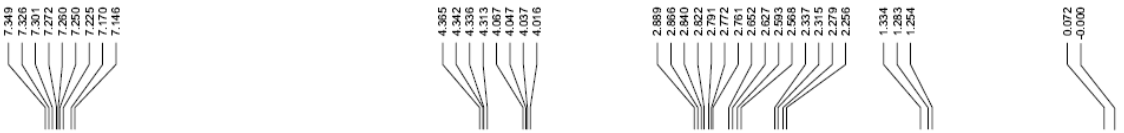
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		30.290	78845.227	2470052.000	50.5412
2		32.087	71845.039	2417152.750	49.4588
Total			150690.266	4887204.750	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		29.115	9389.758	283649.000	6.6930
2		30.865	122228.852	3954341.500	93.3070
Total			131618.609	4237990.500	100.0000


7.349
7.326
7.301
7.272
7.260
7.250
7.225
7.170
7.146
4.365
4.342
4.336
4.313
4.067
4.047
4.037
4.016
2.889
2.866
2.840
2.822
2.791
2.772
2.761
2.652
2.627
2.593
2.568
2.337
2.315
2.279
2.256
1.334
1.283
1.254
0.072
-0.000

3h:

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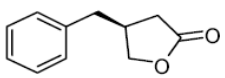
O
O

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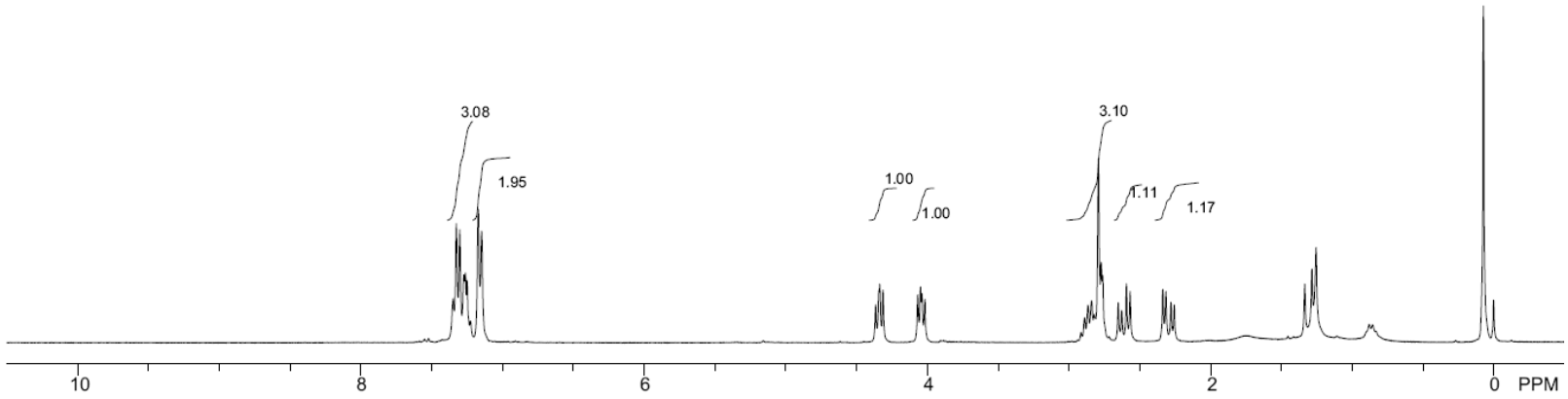
3.08
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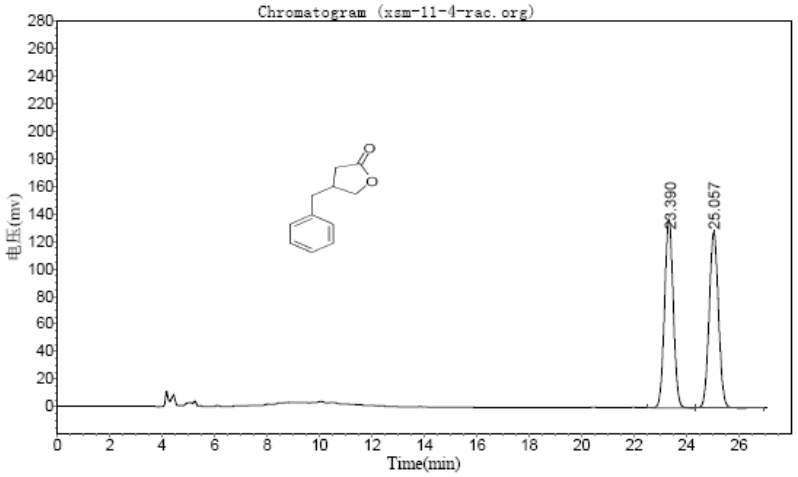
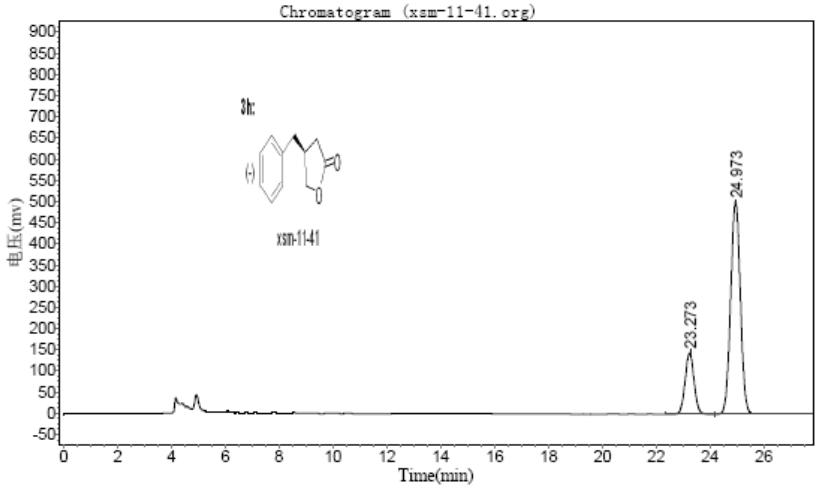
1.00
1.00
3.10
1.11
1.17
10
8
6
4
2
0
PPM



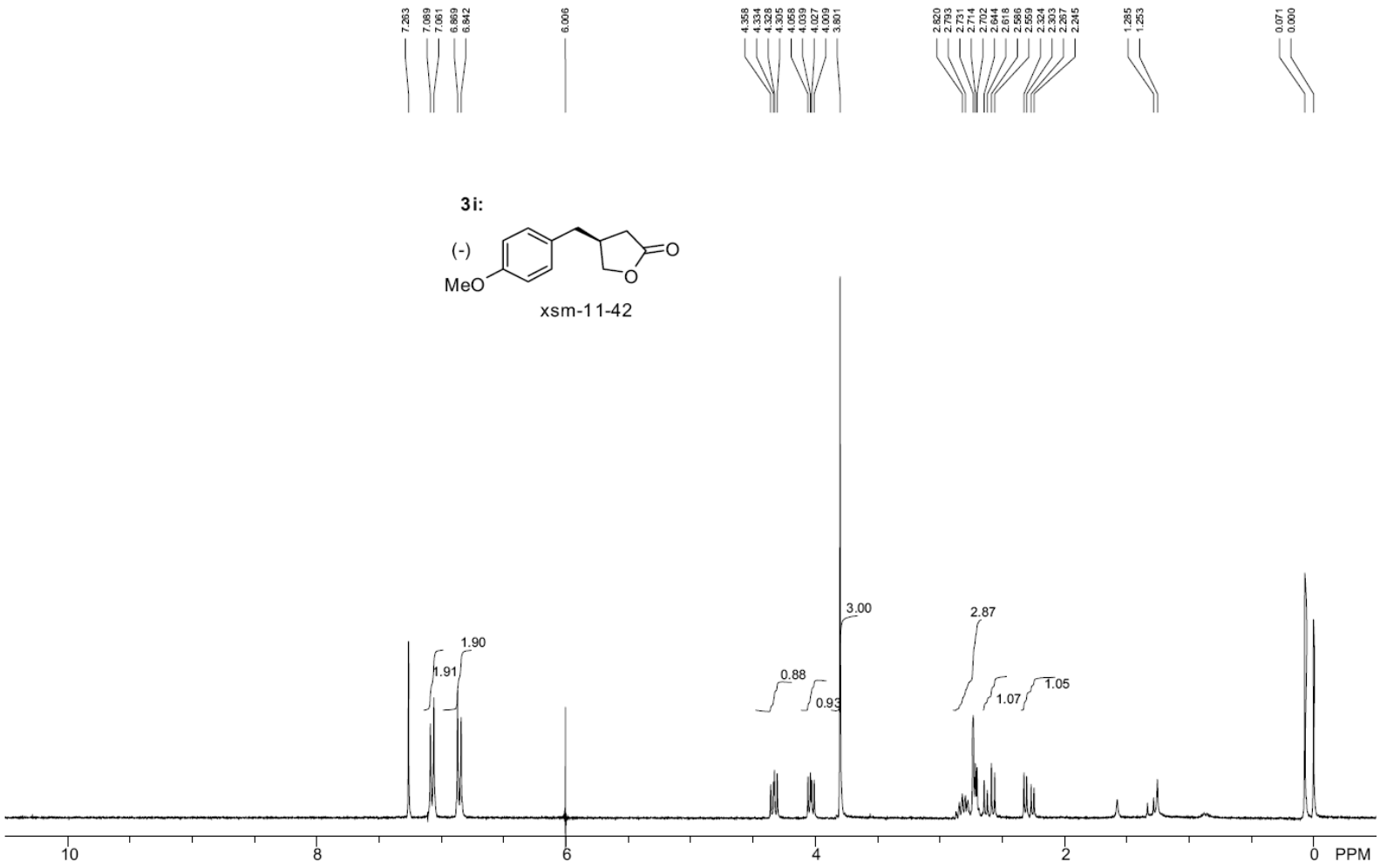
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.390	133838.203	3170580.250	50.0038
2		25.057	126396.320	3170098.000	49.9962
Total			260234.523	6340678.250	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.273	143389.531	3325873.000	20.9169
2		24.973	501076.125	12574528.000	79.0831
Total			644465.656	15900401.000	100.0000


7.263
7.089
7.061
6.869
6.842
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2.731
2.714
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2.618
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2.324
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2.267
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1.285
1.253
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xsm-11-42
1.90
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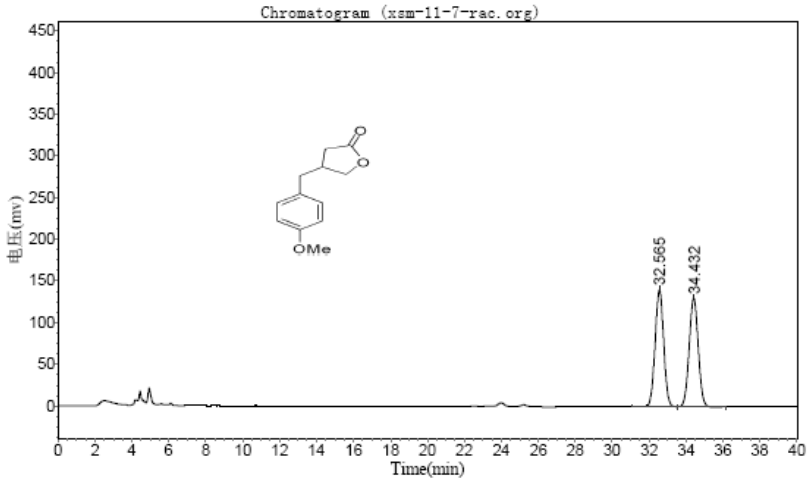
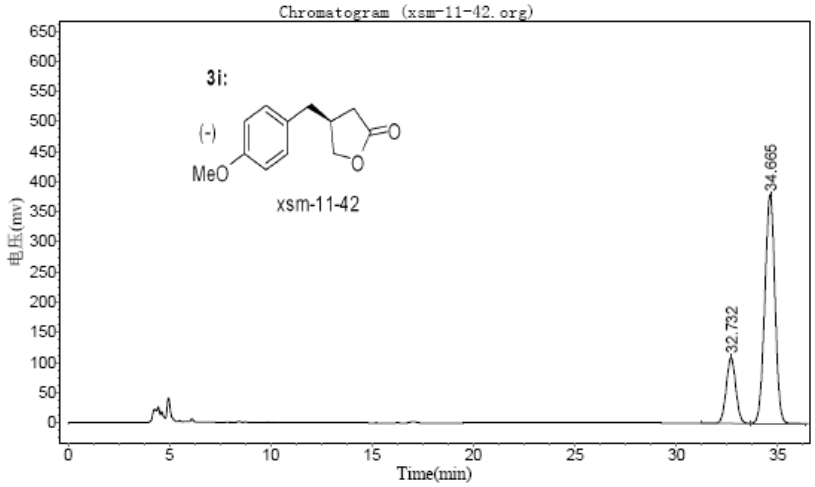


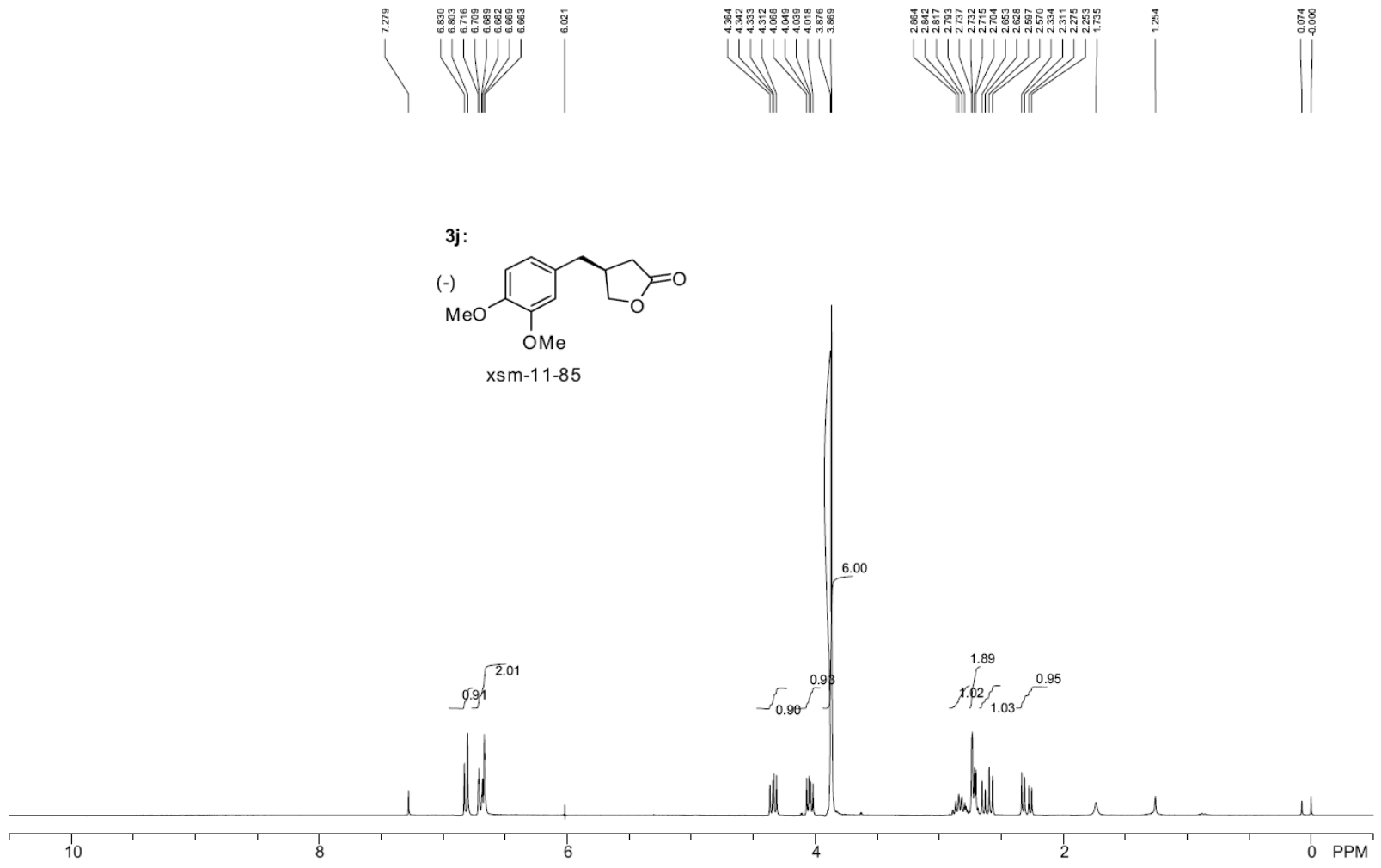
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		32.565	139715.344	4566143.000	50.3963
2		34.432	130618.414	4494321.000	49.6037
Total			270333.758	9060464.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		32.732	108294.406	3581633.500	21.2789
2		34.665	378413.344	13250196.000	78.7211
Total			486707.750	16831829.500	100.0000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6.803
6.716
6.709
6.689
6.682
6.669
6.663
6.021
4.364
4.342
4.333
4.312
4.068
4.049
4.039
4.018
3.876
3.869
2.864
2.842
2.817
2.793
2.737
2.732
2.715
2.704
2.653
2.628
2.597
2.570
2.334
2.311
2.275
2.253
1.735
1.254
0.074
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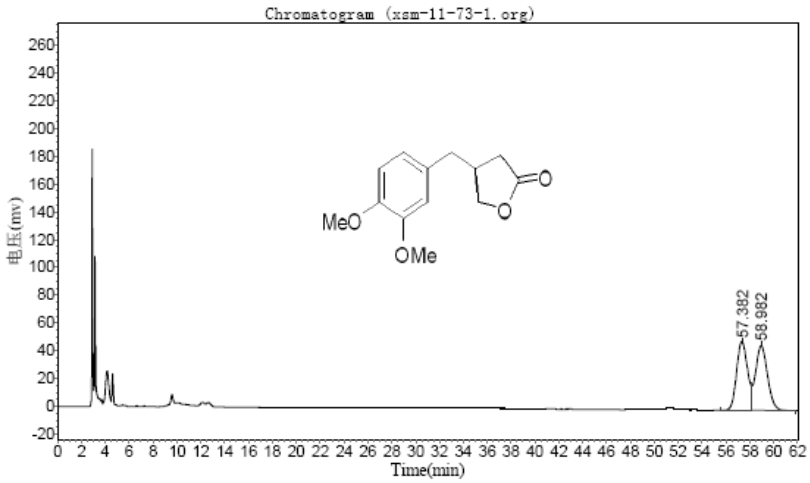
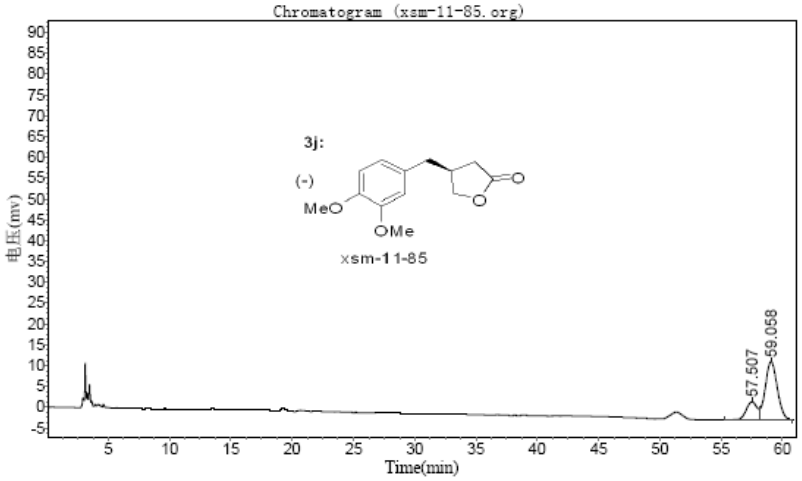


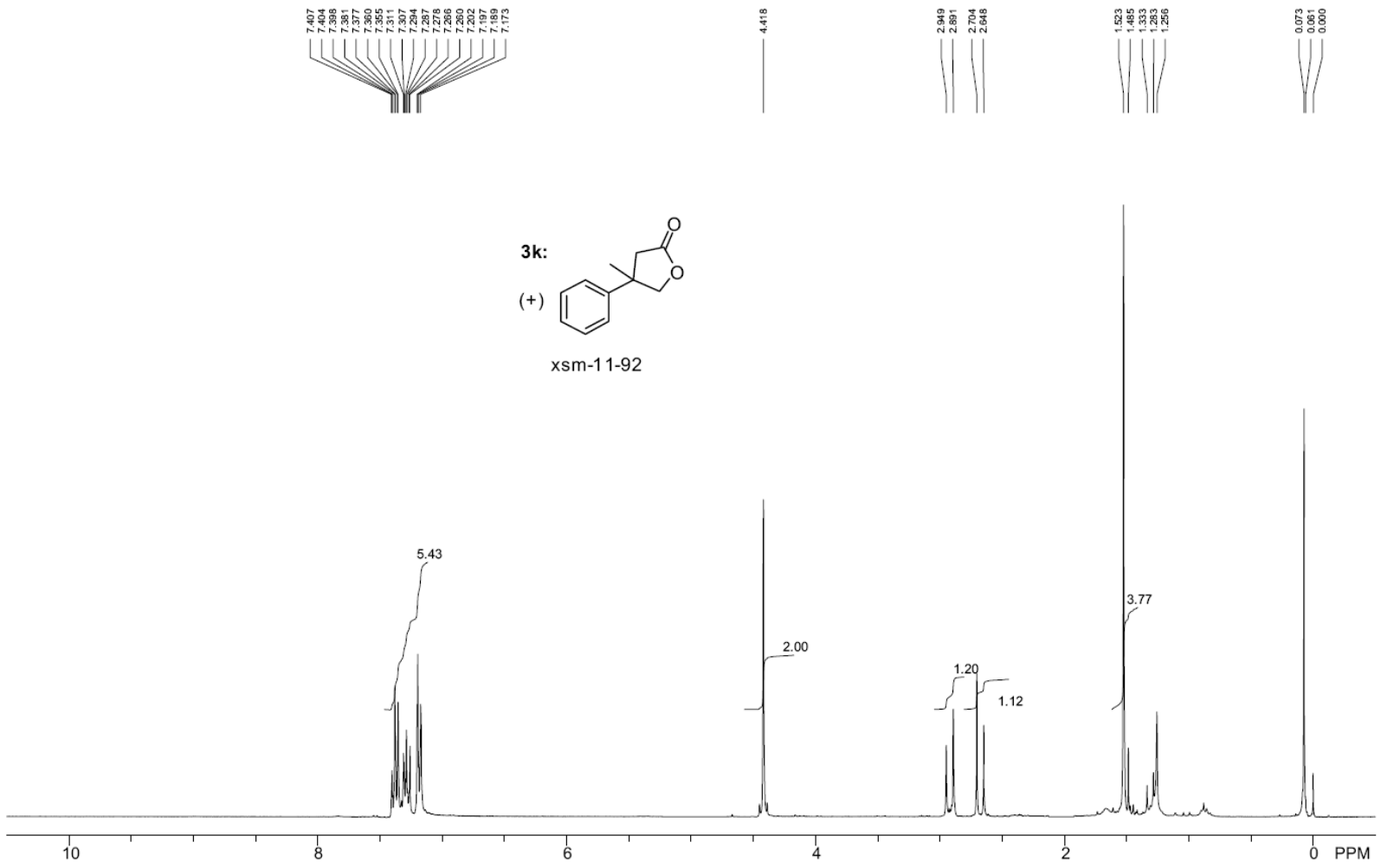
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		57.382	49456.828	3184712.500	49.5002
2		58.982	46582.254	3249021.750	50.4998
Total			96039.082	6433734.250	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		57.507	4370.330	272590.719	22.1782
2		59.058	14005.797	956500.875	77.8218
Total			18376.126	1229091.594	100.0000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7.355
7.311
7.307
7.294
7.287
7.278
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7.260
7.202
7.197
7.189
7.173
4.418
2.949
2.891
2.704
2.648
1.523
1.485
1.333
1.283
1.256
0.073
0.061
0.000
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5.43
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1.20
1.12
3.77
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8
6
4
2
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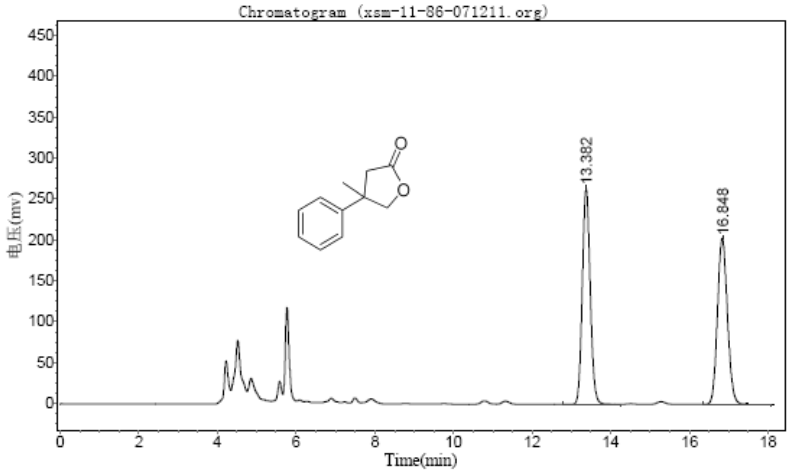
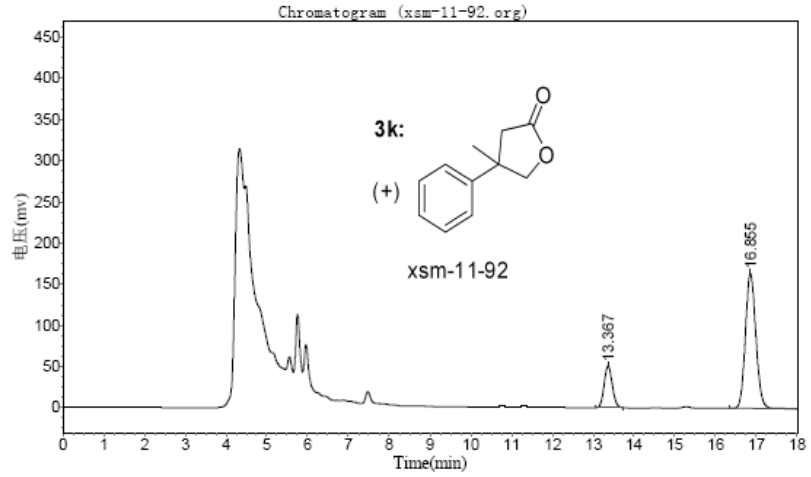
PPM



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.382	262657.563	3689598.750	50.6919
2		16.848	202464.406	3588880.000	49.3081
Total			465121.969	7278478.750	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.367	50854.379	704733.688	19.4390
2		16.855	163899.297	2920622.500	80.5610
Total			214753.676	3625356.188	100.0000