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Asymmetric Catalytic aza-Morita-Baylis-Hillman Reaction (aza-MBH): A Remarkable Functional Group-Caused Reversal Asymmetric Induction

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RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required)

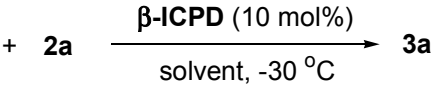
Content

Experimental Section.

General Remarks. Unless otherwise stated, all reactions were carried out under argon atmosphere. All solvents were purified by distillation. Activated olefins were obtained from Tokyo Chemical Industry (Tokyo Kasei Co. Ltd.) and used without purification. All salicyl *N*-tosylated imines[1] and organocatalyst β-ICPD[2] were synthesized according to the literature. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_D$-values are given in unit of 10 deg^{-1} cm^2 g^{-1}. ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; coupling constants *J* are given in Hz. ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrophotometers (75 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Chiral HPLC was performed on a SHIMADZU SPD-10A *vp* series with chiral columns (Chiralpak AD-H, and OD-H columns 4.6 x 250 mm, (Daicel Chemical Ind., Ltd.)). Elementary analysis was taken on a Carlo-Erba 1106 analyzer. Mass spectra were recorded by EI, and HRMS was measured on a HP-5989 instrument. The corresponding racemates of **3** were prepared according to previous paper.[3]

In optimization studies, aza-MBH reaction of imine **1a** with **2a** catalysed by **β-ICPD** (10 mol%) was carried out in a series of solvents such as DCM, acetonitrile (MeCN), ethyl acetate (EA) and dioxane as well as at various temperatures. We found that the best reaction conditions are to carry out the reaction in THF at –30 ^{o}C. Solvent effects are outlined in Table SI-1, indicating that solvents DCM, MeCN, EA and dioxane are not as effective as THF.

Table SI-1. Solvent effects in aza-MBH reaction of salicyl *N*-tosylimines with MVK **2a** catalyzed by **β-ICPD**.

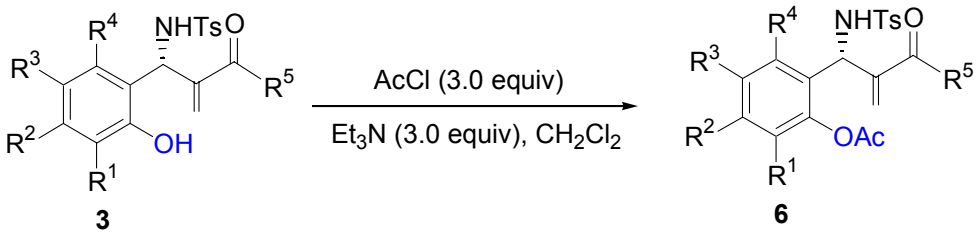


entry	solvent	time/h	yield/%[a]	ee[b]
1	DCM	48	86	78
2	MeCN	60	91	73
3	EA	24	87	85
4	Dioxane	24	98	86

[a] Isolated yields. [b] Determined by chiral HPLC.

Determination of the enantiomeric excesses of **3**.

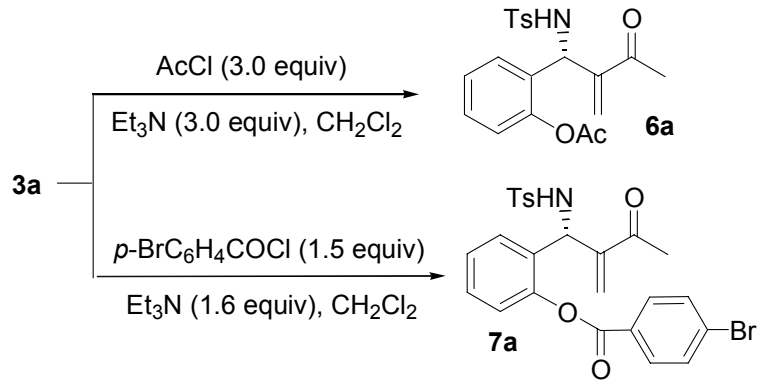
The racemates of **3** in the aza-MBH reaction of salicyl *N*-tosylimines with MVK and EVK were easily obtained in moderate to excellent yields in the presence of 1,4-diazabicyclo[2,2,2]octane (DABCO) (10 mol%) in toluene or THF according to our previous paper.[3] The achieved ee of the corresponding aza-MBH adduct **3** was determined by chiral HPLC or after converting to its acetate **6** (92% ee) by treatment with acetyl chloride in the presence of triethylamine (Et_3N) in dichloromethane (DCM) (Scheme SI-1) (also see the following chiral HPLC).



Scheme SI-1. Acylation of adduct **3** with acetyl chloride in the presence of triethylamine.

Determination of the absolute configuration of **3**.

Moreover, the absolute structure of the product **3a** was also determined by converting **3a** to **6a** and its derivative **7a**, which was obtained by treatment of **3a** with 4-bromobenzoyl chloride in DCM in the presence of Et_3N (Scheme SI-2). The single crystals of **6a** and **7a** suitable for X-ray crystal structural analyses could be obtained by recrystallization from DCM and hexane (1/4). Their ORTEP drawings have been shown in Figures 1 and 2.[4] We utilized compound **7a** containing a bromine atom on the benzene ring for X-ray diffraction because more reliable result could be obtained when a heavy atom such as "Br" is included in the substrate.[5]



Scheme SI-2. Acylation of **3a** in DCM.

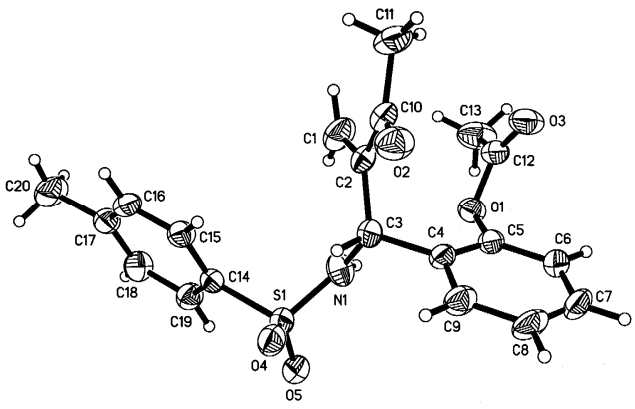


Figure 1. ORTEP drawing of **6a**

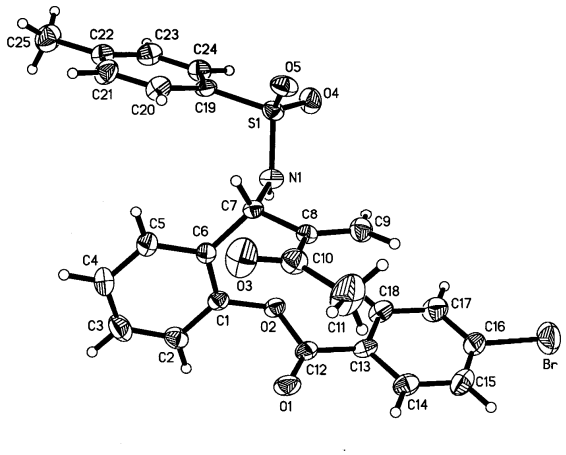
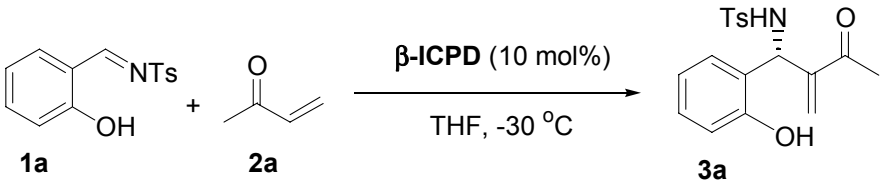


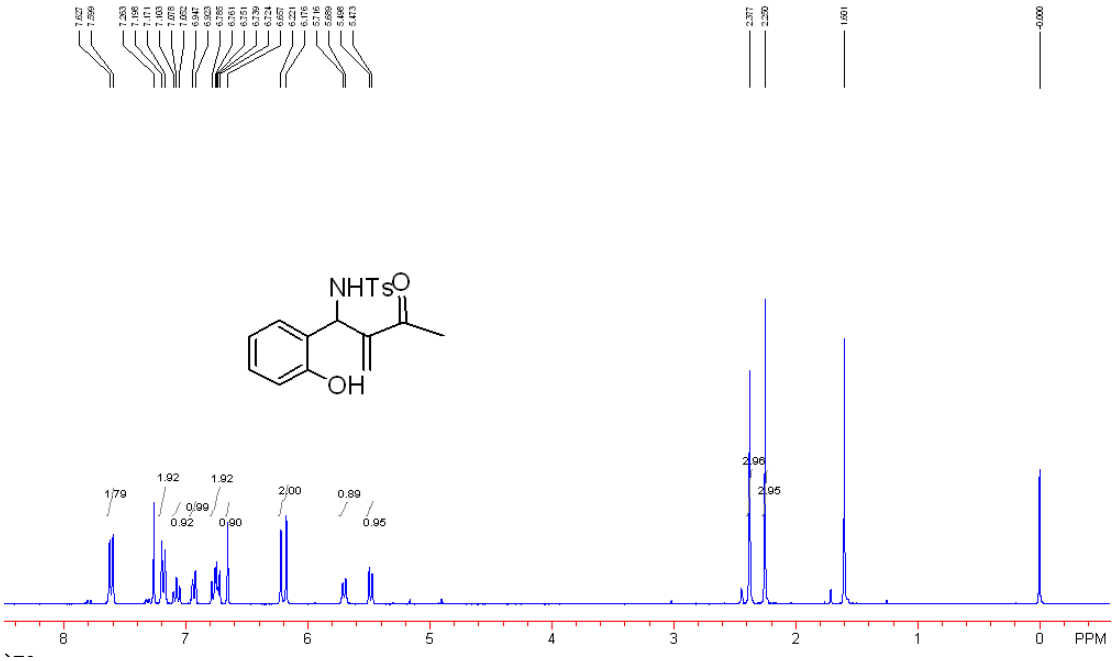
Figure 2. ORTEP drawing of **7a**.

General Procedure for the Preparation of 3 and 6 Using 3a or 6a as an Example.



To a solution of **1a** (0.25 mmol, 61 mg) and catalyst [e.g.: **β-ICPD** (0.025 mmol, 13 mg)] in 1.0 mL of THF was added MVK (41 μL, 0.50 mmol) at -30 °C under argon atmosphere. The reaction solution was monitored by TLC plates. After completion, the solution was directly transferred for purification by a silica gel column chromatography (eluent: EtOAc/PE = 2/3) to give the corresponding compound **3a** in >99% yield and 91% ee (see the Chiral HPLC shown below).

***N*-(3-Acetyl-3,4-dihydro-2H-chromen-4-yl)-4-methylbenzenesulfonamide 3a**: White solid (plates obtained by recrystallization from CH_2Cl_2/PE = 3/1), $[\alpha]_D^{20}$ 77 (c 1.6, $CHCl_3$), mp: 80-82 °C. IR (KBr) ν 3411, 3161, 1688, 1599, 1454, 1322, 1152 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.25 (3H, s, Me), 2.38 (3H, s, Me), 5.49 (1H, d, *J* = 7.3 Hz, CH), 5.70 (1H, d, *J* = 7.3 Hz, NH), 6.17 (1H, s, =CH), 6.22 (1H, s, =CH), 6.66 (1H, s, OH), 6.72-6.79 (2H, m, Ar), 6.94 (1H, d, *J* = 7.2 Hz, Ar), 7.08 (1H, t, *J* = 7.0 Hz, Ar), 7.18 (2H, d, *J* = 8.3 Hz, Ar), 7.61 (2H, d, *J* = 8.3 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 21.5, 26.2, 53.4, 117.0, 120.7, 124.8, 127.1, 128.0, 128.1, 129.1, 129.4, 136.4, 143.5, 146.4, 153.1, 200.0; MS (EI) m/e 190 (M^+-155, 64.2), 148 (M^+-167, 62.7), 131 (M^+-214, 76.7), 91 (M^+-254, 100.0), 65 (M^+-280, 45.4), 43 (M^+-302, 93.2); HRMS (MALDI) calcd. for $C_{18}H_{19}NO_4SNa^+$: 368.0927, Found: 368.0934.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7.263
7.198
7.171
7.103
7.075
7.052
6.947
6.923
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6.739
6.734
6.685
6.221
6.176
5.716
5.689
5.498
5.473
2.377
2.259
1.601
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NHTs
O
OH
1.79
1.92
0.92
0.99
1.92
0.90
2.00
0.89
0.95
2.96
2.95
8
7
6
5
4
3
2
1
0
PPM

Chiral HPLC trace

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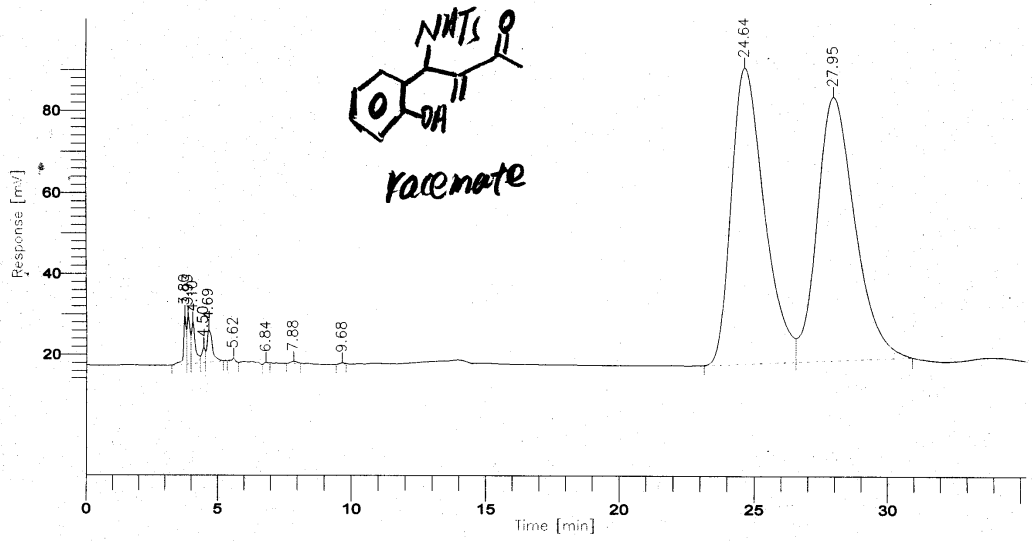

DEFAULT REPORT

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3	4.097	103119.56	10213.76	0.79	VV
4	4.500	33949.72	3693.74	0.26	VV
5	4.690	109000.31	8067.12	0.84	VB
6	5.617	7581.00	787.63	0.06	BB
7	6.842	3380.50	303.00	0.03	BB
8	7.875	7121.50	451.53	0.05	BB
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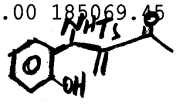
racemate 

Chiral HPLC report: racemate **3a** with a Chiralpak OD-H column: hexane/*i*PrOH = 90/10, 0.8 mL/min, 214 nm, t_{major} = 24.35 min, t_{minor} = 28.08 min.

Chiral HPLC trace

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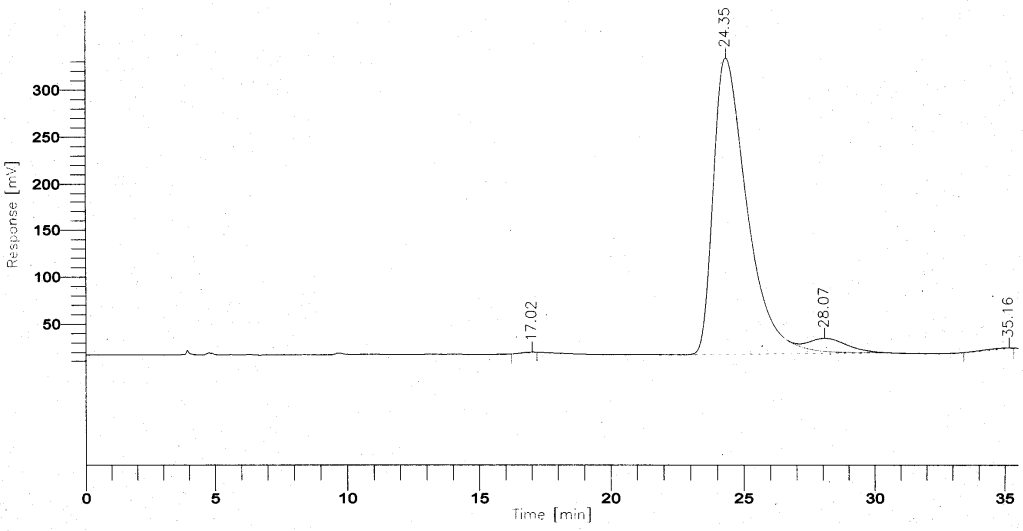

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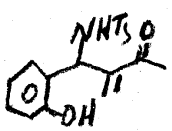
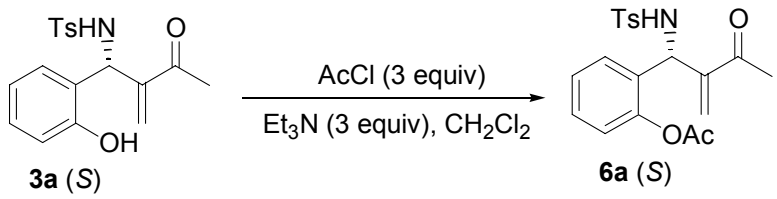


ee% = 91%

OD-H 90/10 0.8 214

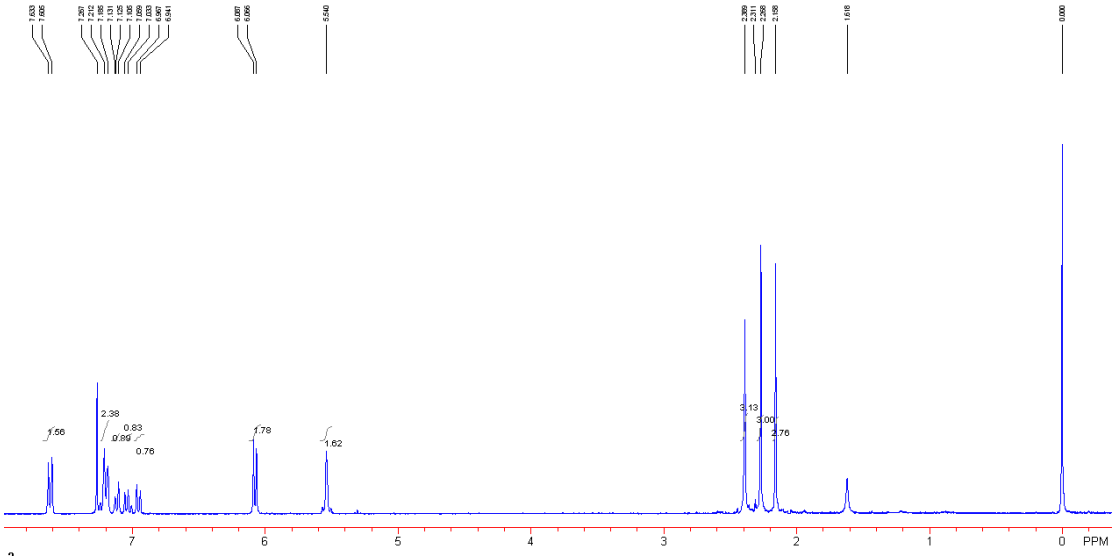
Chiral HPLC report: Enantiomeric excess of **3a** was determined by HPLC with a Chiralpak OD-H column: hexane/*i*PrOH = 90/10, 0.8 mL/min, 214 nm, t_{major} = 24.35 min, t_{minor} = 28.08 min; 91% *ee*.

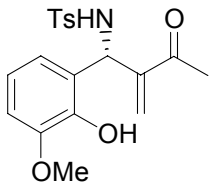


3a (*S*) **6a** (*S*)

To a solution of **3a** (0.10 mmol, 35 mg) in 1.0 mL of DCM was added Et_3N (42 μL, 0.30 mmol) and AcCl (21 μL, 0.3 mmol) at 0 ^oC under argon atmosphere, then the solution was stirred at room temperature. The reaction solution was monitored by TLC plates. After completion, the solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatography (eluent: EtOAc/PE = 1/2) to give the corresponding compound **6a** in excellent yield.

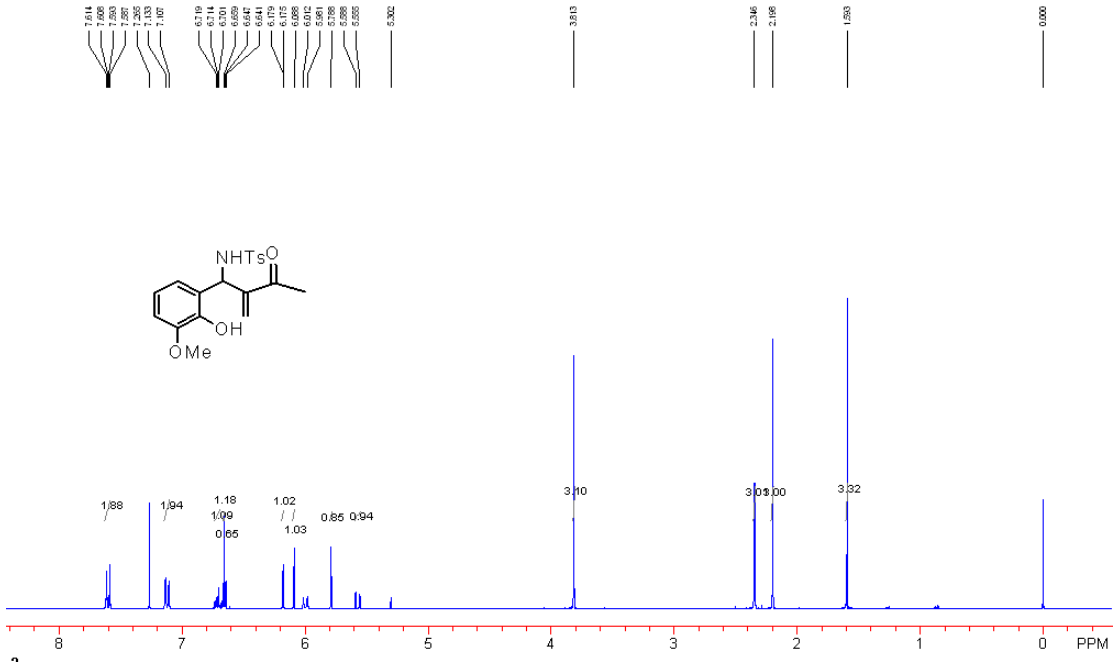
2-(2-Methylene-1-(4-methylphenylsulfonamido)-3-oxobutyl)phenyl acetate 6a: White solid (needles obtained by recrystallization from CH_2Cl_2/PE = 5/1); $[\alpha]_D^{20}$ 10 (c 1.5, $CHCl_3$); mp. 98-100 ^oC; IR (KBr) ν 3282, 2920, 1766, 1678, 1330, 1200, 1161 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.16 (3H, s, Me), 2.27 (3H, s, Me), 2.36 (3H, s, Me), 5.54 (1H, s, CH), 5.54 (1H, s, NH), 6.07 (1H, s, =CH), 6.09 (1H, s, =CH), 6.95 (1H, d, *J* = 7.8 Hz, Ar), 7.01-7.06 (1H, m, Ar), 7.11-7.13 (1H, m, Ar), 7.22-7.27 (1H, m, Ar), 7.25 (2H, d, *J* = 8.4 Hz, Ar), 7.62 (2H, d, *J* = 8.4 Hz, Ar). MS (ESI) m/e 388 (M^++H); HPLC: AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t_{major} = 14.79 min, t_{minor} = 10.96 min; *ee*% = 92% (please see the Chiral HPLC trace shown in S49).

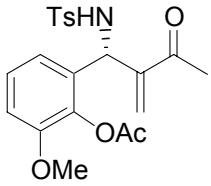




3b

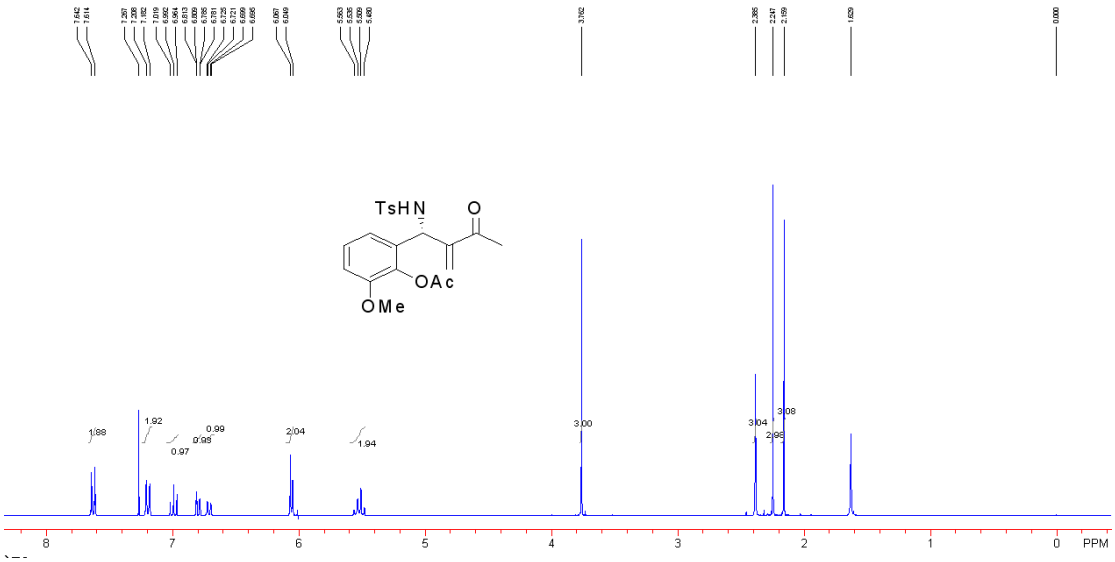
N-(1-(2-Hydroxy-3-methoxyphenyl)-2-methylene-3-oxobutyl)-4-methylbenzenesulfonamide 3b: White solid (plates obtained by recrystallization from EtOAc/PE = 4/1); yield: 99.5%; *ee* 93%; $[\alpha]_D^{20}$ 63 (c 0.66, $CHCl_3$); mp: 107-111 ^oC. IR (KBr) ν 3306, 2925, 1673, 1596, 1481, 1442,1333, 1273, 1223, 1159, 1055 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.20 (3H, s, Me), 2.35 (3H, s, Me), 3.81(3H, s, Me), 5.58 (1H, d, *J* = 9.6 Hz, CH), 5.79 (1H, s, OH), 5.99 (1H, d, *J* = 9.6 Hz, NH), 6.09 (1H, s, =CH), 6.18 (1H, s, =CH), 6.66-6.64 (2H, m, Ar), 6.72-6.70 (1H, m, Ar), 7.12 (2H, d, *J* = 8.0 Hz, Ar), 7.60 (2H, d, *J* = 8.0 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 21.4, 26.3, 54.0, 56.0, 109.7, 119.6, 121.1, 124.0, 127.1, 127.2, 127.2, 129.1, 137.3, 142.5, 142.9, 146.2, 198.6. MS (EI) m/e 375 (M^+, 0.6), 204 (M^+-171, 66.5), 161 (M^+-214, 100.0). HRMS (MALDI) calcd. for $C_{19}H_{21}NO_5SNa^+$: 398.1032, Found: 398.1024.

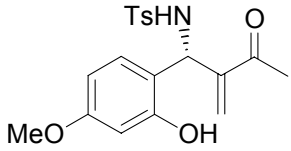




6b

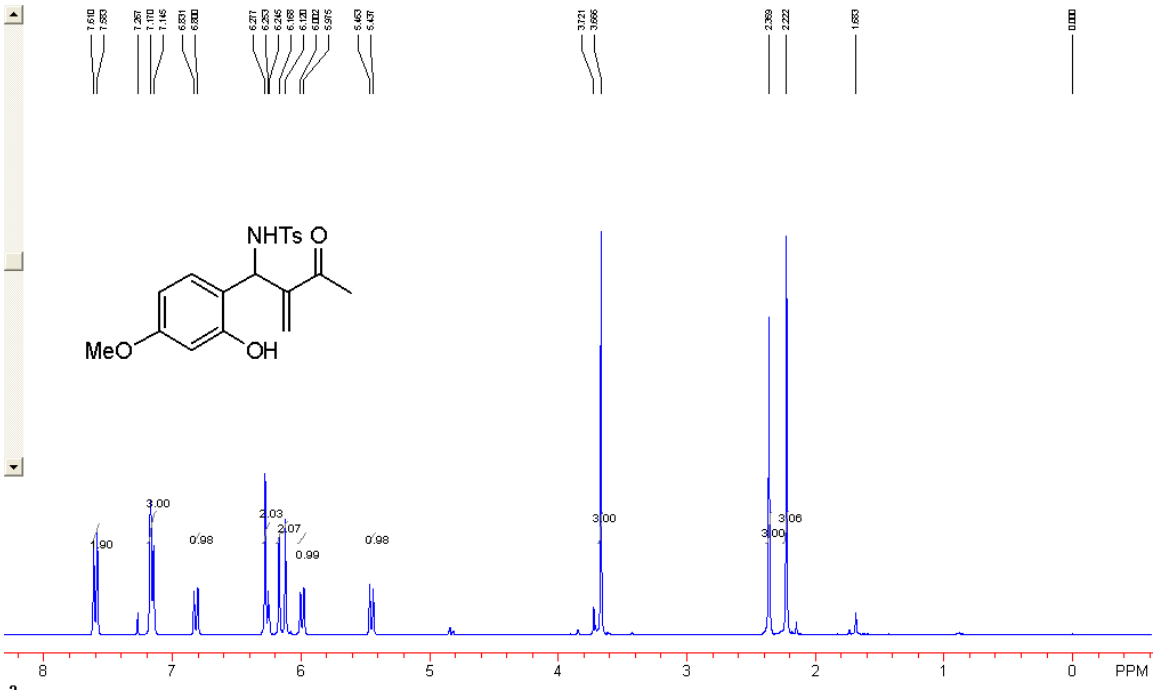
2-Methoxy-6-(2-methylene-1-(4-methylphenylsulfonamido)-3-oxobutyl)phenyl acetate 6b: Yellow solid (plates obtained by recrystallization from CH_2Cl_2/PE = 8/1); *ee* 93%; $[\alpha]_D^{20}$ 58 (c 0.33, $CHCl_3$); mp. 110-112 ^oC; IR (KBr) ν 3282, 2925, 1767, 1679, 1481, 1440, 1277, 1162, 1054 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.15 (3H, s, Me), 2.25 (3H, s, Me), 2.38 (3H, s, Me), 3.76(3H, s, Me), 5.48-5.56 (1H, m, CH), 5.48-5.56 (1H, m, NH), 6.01 (1H, s, =CH), 6.05 (1H, s, =CH), 6.71 (1H, dd, *J* = 1.2, 8.1 Hz, Ar), 6.80 (1H, dd, *J* = 1.2, 8.1 Hz, Ar), 6.99 (1H, t, *J* = 8.1 Hz, Ar), 7.19 (2H, d, *J* = 8.4 Hz, Ar), 7.63 (2H, d, *J* = 8.4 Hz, Ar). MS (ESI) m/e 418 (M^++H); HPLC: OD column; λ = 230 nm; eluent: Hexane/Isopropanol = 75/25; Flow rate: 0.6 mL/min; t_{major} = 13.63 min, t_{minor} = 27.46 min; *ee*% = 93%.

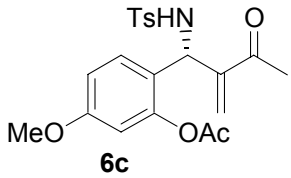




3c

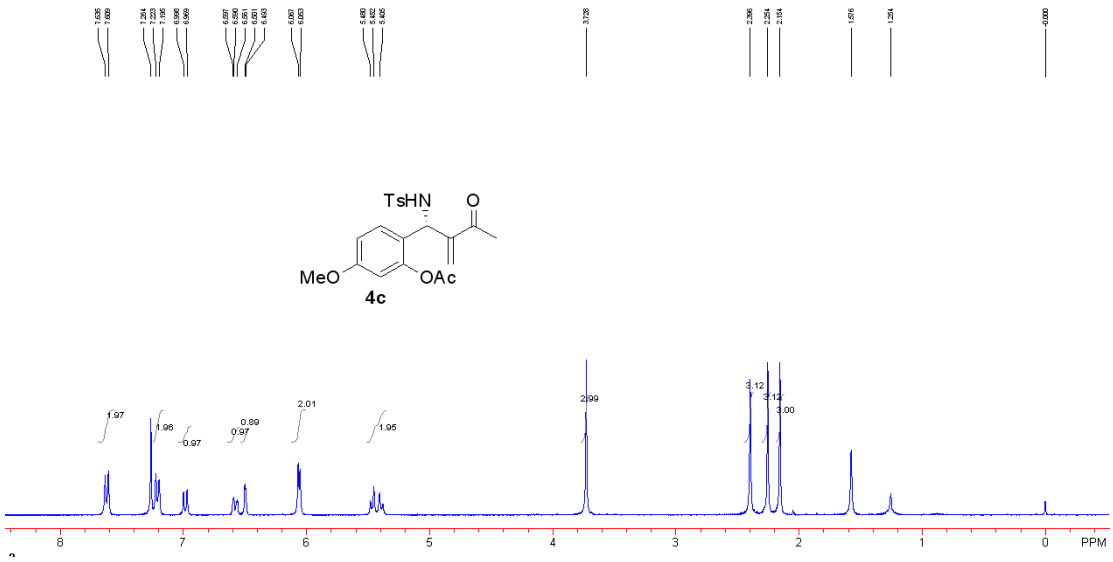
***N*-(1-(2-Hydroxy-4-methoxyphenyl)-2-methylene-3-oxobutyl)-4-methylbenzenesulfonamide 3c**: White solid (needles obtained by recrystallization from EtOAc/PE = 5/1); yield: 98%; *ee* 92%; $[\alpha]_D^{20}$ 147 (c 0.51, $CHCl_3$); mp: 110-112 ^oC. IR (KBr) ν 2923, 2839, 1920, 1703, 1674, 1618, 1519, 1444, 1320, 1160, cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.22 (3H, s, Me), 2.37 (3H, s, Me), 3.67(3H, s, Me), 5.45 (1H, d, *J* = 7.8 Hz, CH), 5.99 (1H, d, *J* = 7.8 Hz, NH), 6.12 (1H, s, =CH), 6.17 (1H, s, =CH), 6.22-6.25 (2H, m, Ar), 6.82 (1H, d, *J* = 9.3 Hz, Ar), 7.16 (2H, d, *J* = 8.1 Hz, Ar), 7.59 (2H, d, *J* = 8.1 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 21.4, 26.2, 53.1, 55.2, 102.5, 106.5, 117.2, 127.1, 127.7, 128.8, 129.4, 136.4, 143.4, 146.6, 154.3, 160.2, 200.0; MS (MALDI) m/e 398 (M^++23, 100.0). HRMS (MALDI) calcd. for $C_{19}H_{21}NO_5SNa^+$: 398.1032, Found: 398.1030.

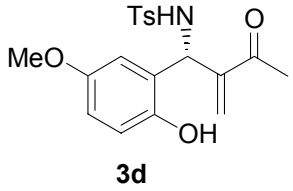




6c

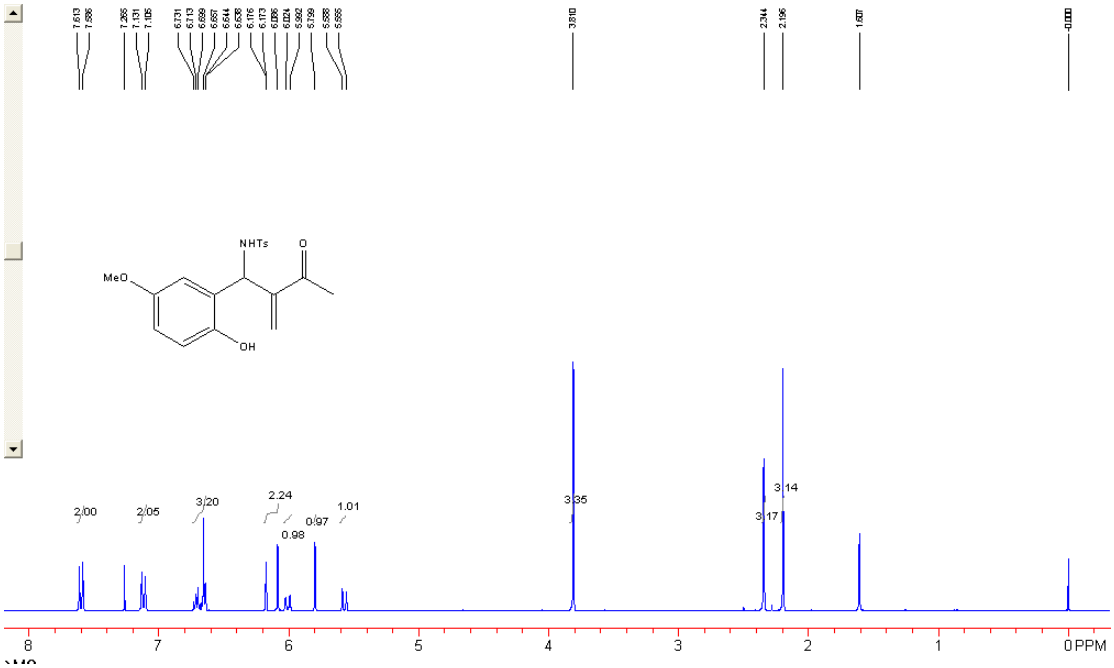
5-Methoxy-2-(2-methylene-1-(4-methylphenylsulfonamido)-3-oxobutyl)phenyl acetate 6c: White solid (cubes obtained by recrystallization from CH_2Cl_2/PE = 5/1); *ee* 92%; $[\alpha]_D^{20}$ 47 (c 0.27, $CHCl_3$); mp:121-123 ^oC; IR (KBr) ν 3281, 2924, 1769, 1679, 1617, 1506, 1431, 1369, 1034, 815 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.15 (3H, s, Me), 2.25 (3H, s, Me), 2.40 (3H, s, Me), 3.73 (3H, s, Me), 5.39 (1H, d, *J* = 8.0 Hz, CH), 5.47 (1H, d, *J* = 8.0 Hz, NH), 6.05 (1H, s, =CH), 6.07 (1H, s, =CH), 6.50 (1H, s, Ar), 6.58 (1H, d, *J* = 9.1 Hz, Ar), 6.98 (1H, d, *J* = 9.1 Hz, Ar), 7.21 (2H, d, *J* = 8.1 Hz, Ar), 7.62 (2H, d, *J* = 8.1 Hz, Ar). MS (ESI) m/e 435 (M^++18); HPLC: AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{major} = 18.80 min; t_{minor} = 32.38 min; *ee*% = 92%.

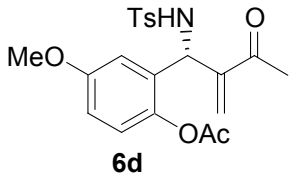




3d

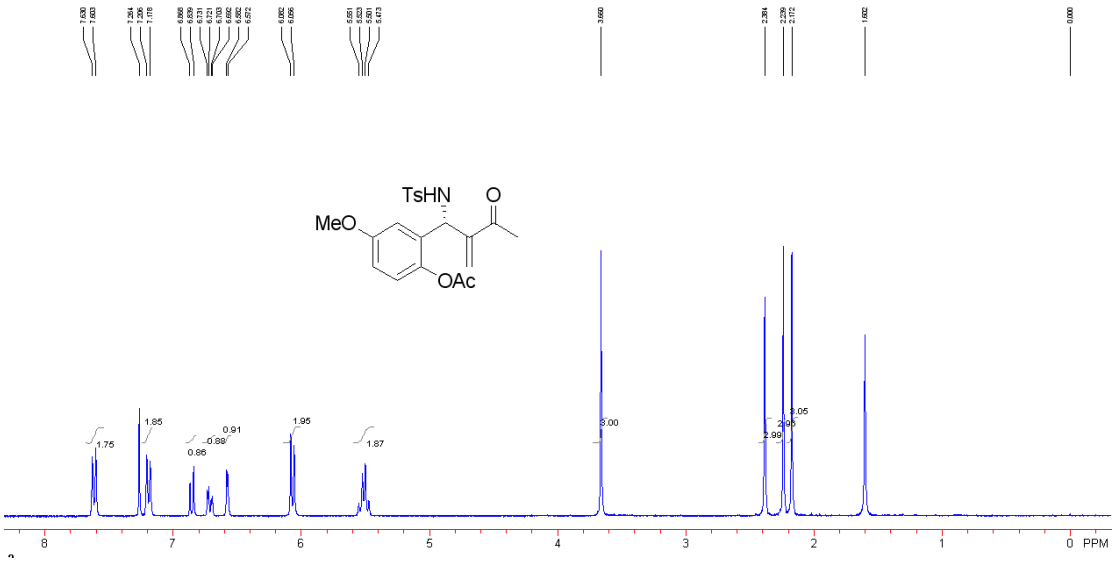
***N*-(1-(2-Hydroxy-5-methoxyphenyl)-2-methylene-3-oxobutyl)-4-methylbenzenesulfonamide 3d**: White solid (cubes obtained by recrystallization from CH_2Cl_2/PE = 3/1): 95%; *ee* 99.9%; $[\alpha]_D^{20}$ 98 (c 0.95, $CHCl_3$), mp: 107-110 ^oC. IR (KBr) ν 3306, 1676, 1596, 1481, 1442, 1335, 1274, 1222, 1160, 1055 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.20 (3H, s, Me), 2.34 (3H, s, Me), 3.81(3H, s, Me), 5.57 (1H, d, *J* = 9.7 Hz, CH), 5.82 (1H, s, OH), 6.01 (1H, d, *J* = 9.7 Hz, NH), 6.09 (1H, s, =CH), 6.17 (1H, s, =CH), 6.64-6.73 (3H, m, Ar), 7.12 (2H, d, *J* = 8.1 Hz, Ar), 7.60 (2H, d, *J* = 8.1 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 21.4, 26.3, 54.0, 55.9, 109.7, 119.5, 121.1, 124.0, 127.1, 127.2, 129.1, 137.3, 142.5, 142.8, 146.2, 146.2, 198.6. MS (EI) m/e 204 (M^+-171, 54.4), 161 (M^+-214, 100.0), 91 (M^+-284, 26.9), 43 (M^+-332, 44.5). HRMS (EI) calcd. for $C_{19}H_{21}NO_5S$: 375.1140, Found: 375.1131.

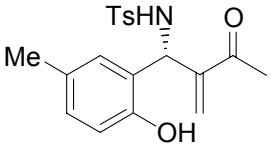




6d

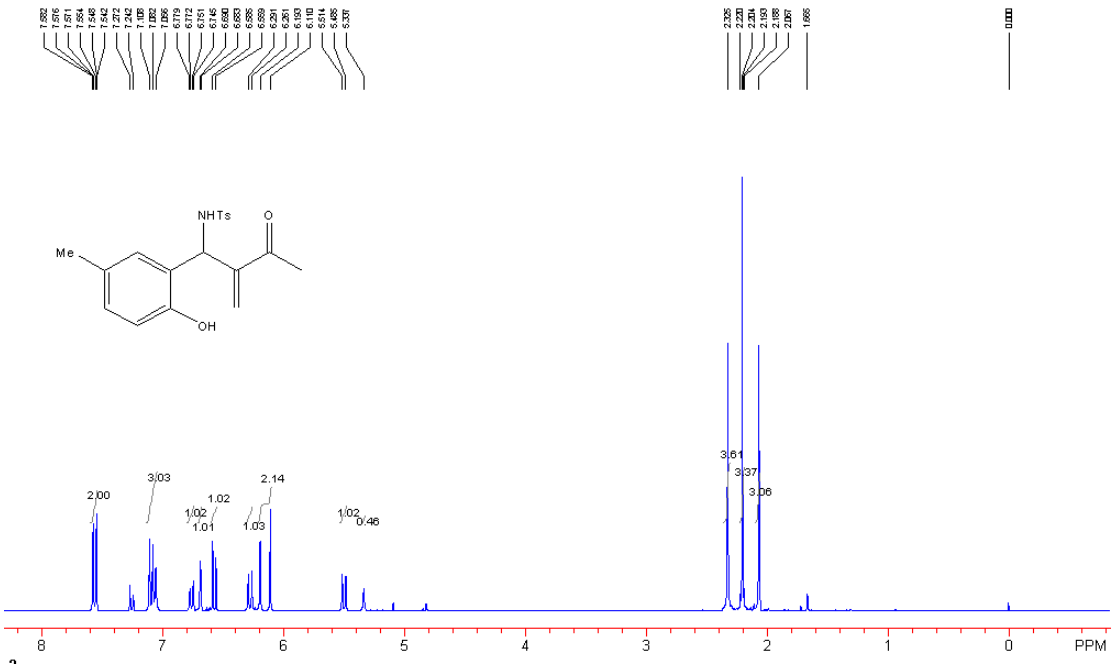
Methoxy-2-(2-methylene-1-(4-methylphenylsulfonamido)-3-oxobutyl)phenyl acetate 6d: Yellow solid (needles obtained by recrystallization from CH_2Cl_2/PE = 6/1): *ee* 99.9%; $[\alpha]_D^{20}$ 45 (c 1.0, $CHCl_3$); mp.98-100 ^oC; IR (KBr) ν 3282, 2922, 1762, 1679, 1598, 1497, 1194, 1161, 1038 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.17 (3H, s, Me), 2.24 (3H, s, Me), 2.38 (3H, s, Me), 3.66 (3H, s, Me), 5.49 (1H, d, *J* = 8.6 Hz, CH), 5.54 (1H, d, *J* = 8.6 Hz, NH), 6.06 (1H, s, =CH), 6.08 (1H, s, =CH), 6.50 (1H, d, *J* = 2.7 Hz, Ar), 6.71 (1H, dd, *J* = 2.7, 8.4 Hz, Ar), 6.85 (1H, d, *J* = 8.4 Hz, Ar), 7.19 (2H, d, *J* = 8.1 Hz, Ar), 7.62 (2H, d, *J* = 8.1 Hz, Ar); MS (ESI) m/e 418 (M^++H); HPLC: AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{major} = 17.23 min; t_{minor} = 13.00 min; *ee*% = 99.9%.

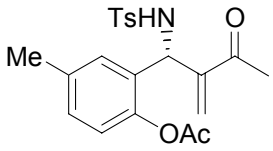




3e

***N*-[2-Acetyl-1-(2-hydroxy-5-methylphenyl)-allyl]-4-methylbenzenesulfonamide 3e**: White solid (cubes obtained by recrystallization from CH_2Cl_2/PE = 2/1): 96%; *ee* 92%; $[\alpha]_D^{20}$ 94 (c 0.90, $CHCl_3$); mp: 148-150 ^oC. IR (KBr) ν 3400, 3300, 2924, 2860, 1919, 1678, 1598, 1511, 1431, 1334, 1165, 1057 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.07 (3H, s, Me), 2.20 (3H, s, Me), 2.33 (3H, s, Me), 5.50 (1H, d, *J* = 9.0 Hz, CH), 6.11 (1H, s, =CH), 6.19 (1H, s, =CH), 6.28 (1H, d, *J* = 9.0 Hz, NH), 6.57 (1H, d, *J* = 8.1 Hz, Ar), 6.69 (1H, d, *J* = 2.0 Hz, Ar), 6.76 (1H, dd, *J* = 2.0, 8.1 Hz, Ar), 7.06 (1H, s, OH), 7.10 (2H, d, *J* = 8.7 Hz, Ar), 7.62 (2H, d, *J* = 8.7 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 20.2, 21.3, 26.1, 53.4, 116.4, 124.1, 126.1, 127.0, 127.7, 128.9, 129.2, 129.5, 136.5, 143.2, 146.5, 150.9, 199.8. MS (MALDI) m/e 382 (M^++23, 100.0). HRMS (MALDI) calcd. for $C_{19}H_{21}NO_4SNa^+$: 382.1083, found: 382.1098.

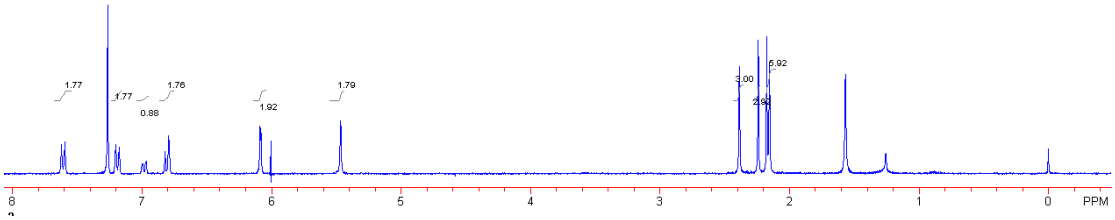


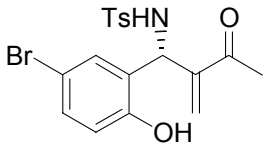


6e

4-Methyl-2-(2-methylene-1-(4-methylphenylsulfonamido)-3-oxobutyl)phenyl acetate 6e: White solid (cubes obtained by recrystallization from EtOAc/PE = 4/1): *ee* 92%; $[\alpha]_D^{20}$ 40 (c 0.73, $CHCl_3$); mp. 147-149 ^oC; IR (KBr) ν 3282, 2924, 1854, 1917, 1763, 1679, 1598, 1497, 1194, 1161, 1061 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.14 (3H, s, Me), 2.17 (3H, s, Me), 2.24 (3H, s, Me), 2.39 (3H, s, Me), 5.47 (1H, s, CH), 5.47 (1H, s, NH), 6.08 (1H, s, =CH), 6.10 (1H, s, =CH), 6.79-6.82 (2H, m, Ar), 6.97-7.02 (1H, m, Ar), 7.19 (2H, d, J = 8.6 Hz, Ar), 7.61 (2H, d, J = 8.6 Hz, Ar); MS (ESI) m/e 402 (M^++H); HPLC: OD column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{major} = 14.63 min; t_{minor} = 10.13 min; *ee*% = 92%.

4e

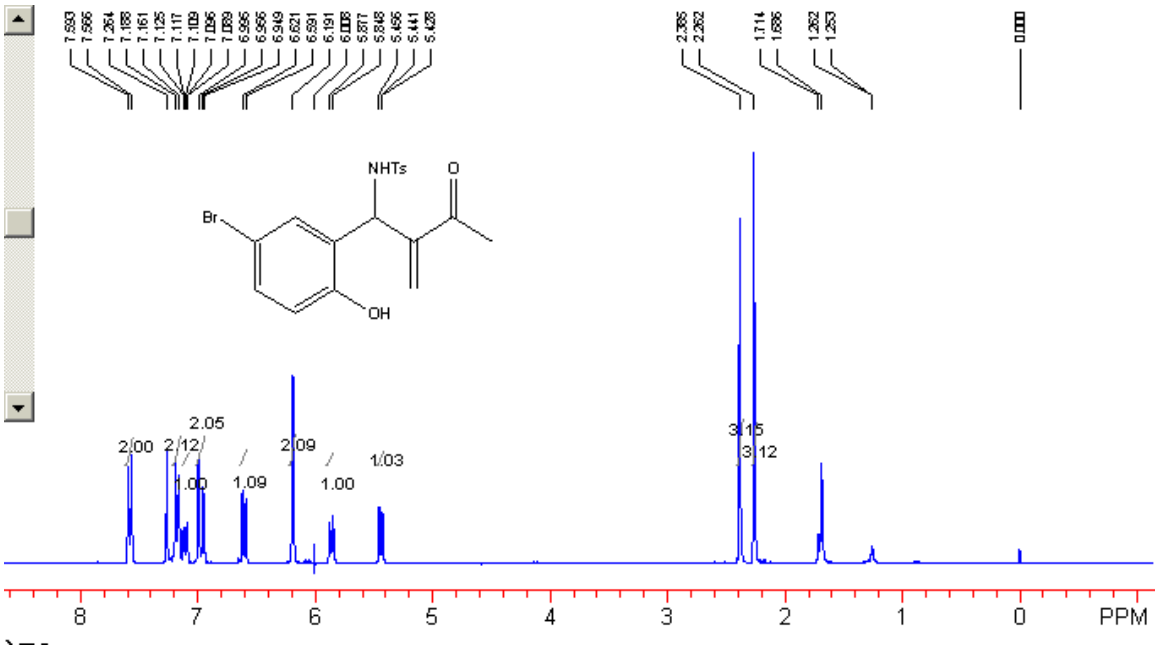


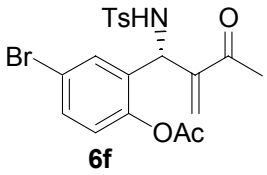


3f

***N*-(1-(5-Bromo-2-hydroxyphenyl)-2-methylene-3-oxobutyl)-4-methylbenzenesulfonamide**

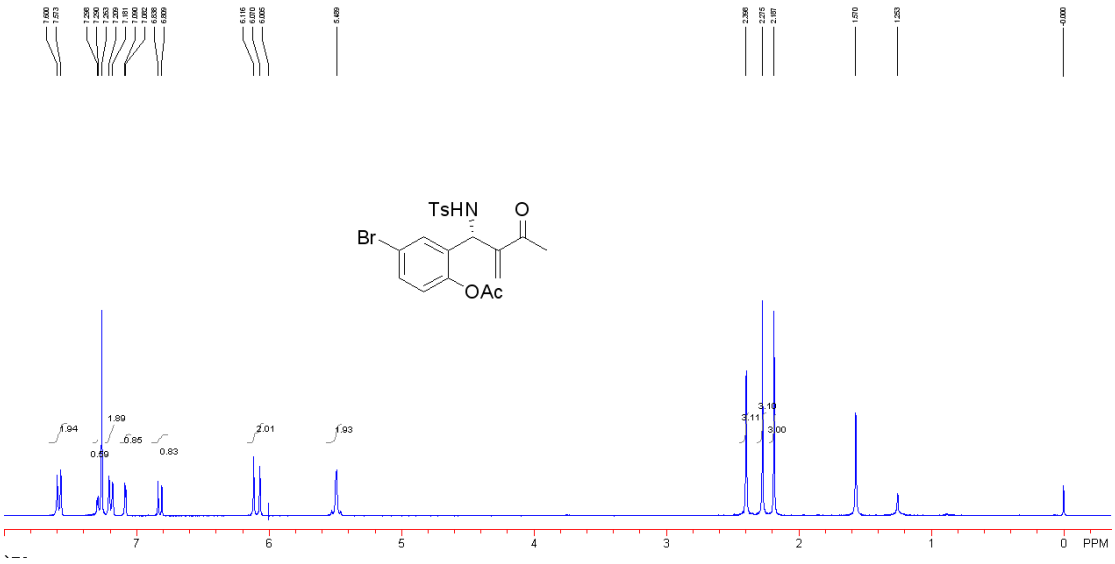
3f: White solid (cubes obtained by recrystallization from CH_2Cl_2/PE = 3/1): 95%; *ee* 90%; $[\alpha]_D^{20}$ 70 (c 0.96, $CHCl_3$); mp: 124-126 ^oC. IR (KBr) ν 3309, 2922, 1916, 1673, 1598, 1494, 1328, 1159 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.17 (3H, s, Me), 2.30 (3H, s, Me), 5.40 (1H, d, *J* = 9.0 Hz, CH), 6.01 (1H, d, *J* = 9.0 Hz, NH), 6.10 (1H, s, =CH), 6.13 (1H, s, =CH), 6.52 (1H, d, *J* = 8.4 Hz, Ar), 6.89 (1H, d, *J* = 1.8 Hz, Ar), 7.02 (1H, dd, *J* = 1.8, 8.4 Hz, Ar), 7.07 (1H, s, OH), 7.13 (2H, d, *J* = 7.2 Hz, Ar), 7.71 (2H, d, *J* = 7.2 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 21.5, 26.2, 53.2, 112.6, 118.6, 126.6, 127.0, 128.5, 129.5, 131.0, 131.6, 136.1, 143.8, 145.8, 152.4, 199.8. MS (MALDI) m/e 446 (M^++23), 448 (M^++25, 100.0). HRMS (MALDI) calcd. for $C_{18}H_{18}NO_4SBrNa^+$: 446.0031, Found: 446.0032.

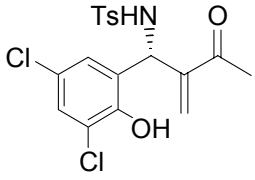




6f

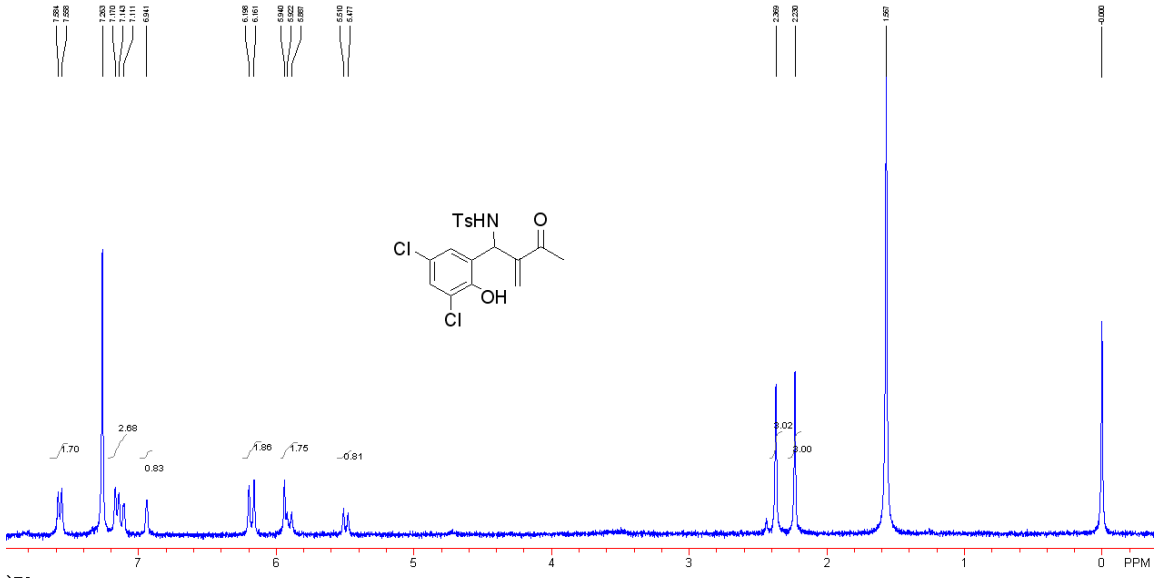
4-Bromo-2-(2-methylene-1-(4-methylphenylsulfonamido)-3-oxobutyl)phenyl acetate 6f: White solid (cubes obtained by recrystallization from CH_2Cl_2/PE = 5/1): *ee* 90%, $[\alpha]_D^{20}$ 70 (c 0.96, $CHCl_3$), mp. 118-120 ^oC; IR (KBr) ν 3283, 2924, 1765, 1679, 1598, 1479, 1265, 1198, 1163, 1013 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.19 (3H, s, Me), 2.28 (3H, s, Me), 2.39 (3H, s, Me), 5.47 (1H, d, *J* = 8.0 Hz, CH), 5.49 (1H, d, *J* = 8.0 Hz, NH), 6.07 (1H, s, =CH), 6.12 (1H, s, =CH), 6.82 (1H, d, *J* = 8.7 Hz, Ar), 7.09 (1H, d, *J* = 2.4 Hz, Ar), 7.19 (2H, d, *J* = 8.1 Hz, Ar), 7.28 (1H, dd, *J* = 2.4, 8.7 Hz, Ar), 7.59 (2H, d, *J* = 8.1 Hz, Ar). MS (ESI) m/e 467 (M^++H); HPLC: OD column; λ = 230 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.5 mL/min; t_{major} = 17.38 min; t_{minor} = 14.46 min; *ee*% = 90%.

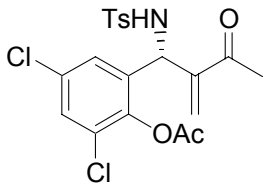




3g

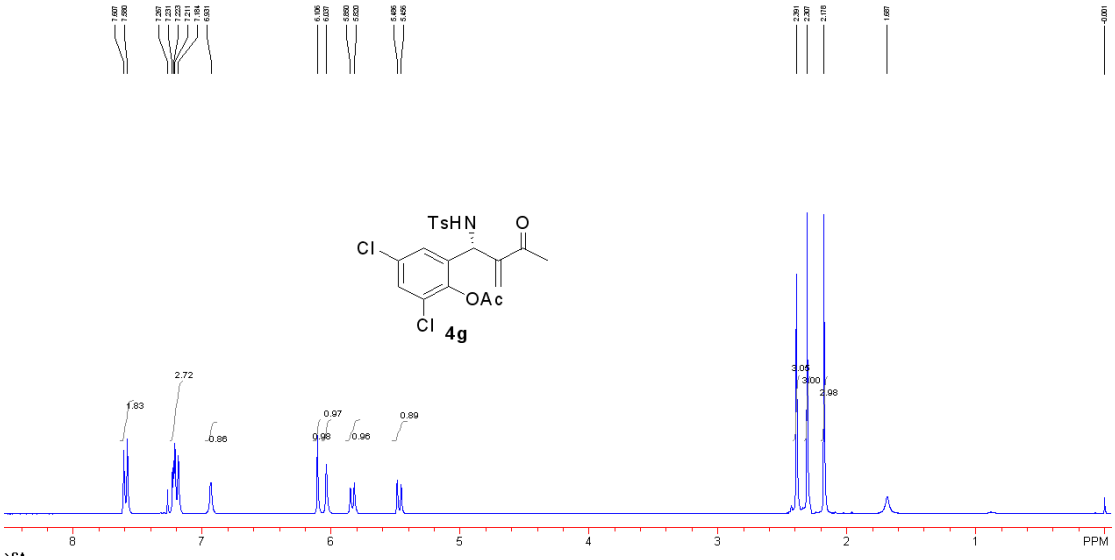
***N*-(1-(3,5-Dichloro-2-hydroxyphenyl)-2-methylene-3-oxobutyl)-4-methylbenzenesulfona mide 3g**: White solid (plates obtained by recrystallization from CH_2Cl_2/PE = 5/1): 95%; *ee* 90%; $[\alpha]_D^{20}$ 35 (c 0.47, $CHCl_3$); mp: 169-170 ^oC. IR (KBr) ν 3273, 2924, 2853, 2101, 1712, 1674, 1598, 1557, 1495, 1332, 1161, 1093, 1068 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.23 (3H, s, Me), 2.36 (3H, s, Me), 5.52 (1H, d, *J* = 9.6 Hz, CH), 6.11 (1H, d, *J* = 9.6 Hz, NH), 6.15 (1H, s, =CH), 6.16 (1H, s, =CH), 6.20 (1H, s, OH), 6.94 (1H, d, *J* = 2.4 Hz, Ar), 7.09 (1H, d, *J* = 2.4 Hz, Ar), 7.15 (2H, d, *J* = 8.4 Hz, Ar), 7.58 (2H, d, *J* = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 21.3, 26.0, 63.8, 120.8, 125.2, 126.8, 127.1, 127.5, 127.7, 128.4, 129.1, 136.6, 143.4, 145.0, 146.9, 197.0. MS (EI) m/e 201 (M^+-212, 21.2), 199 (M^+-214, 35.5), 171 (M^+-242, 25.0), 155 (M^+-258, 28.9), 91 (M^+-322, 100.0), 43 (M^+-370, 86.7). HRMS (EI) calcd. for $C_{18}H_{17}Cl_2NO_4S$: 413.0255, Found: 413.0258.

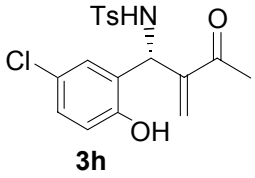




6g

2,4-Dichloro-6-(2-methylene-1-(4-methylphenylsulfonamido)-3-oxobutyl)phenyl acetate 6g: White solid (cubes obtained by recrystallization from EtOAc/PE = 2/1): *ee* 90%; $[\alpha]_D^{20}$ 74 (c 0.70, $CHCl_3$); mp. 165-166 ^oC; IR (KBr) ν 3281, 2924, 2853, 1772, 1681, 1573, 1453 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.18 (3H, s, Me), 2.31 (3H, s, Me), 2.40 (3H, s, Me), 5.47 (1H, d, *J* = 9.0 Hz, CH), 5.84 (1H, d, *J* = 9.0 Hz, NH), 6.04 (1H, s, =CH), 6.11 (1H, s, =CH), 6.93 (1H, s, Ar), 7.20 (2H, d, *J* = 8.1 Hz, Ar), 7.23 (1H, d, *J* = 2.4 Hz, Ar), 7.59 (2H, d, *J* = 8.1 Hz, Ar); MS (EI) m/e 266 (M^+-155, 6.00), 91 (M^+-330, 46.38), 43 (M^+-378, 100); HPLC: AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.6 mL/min; t_{major} = 12.46 min; t_{minor} = 15.54 min; *ee*% = 95%.

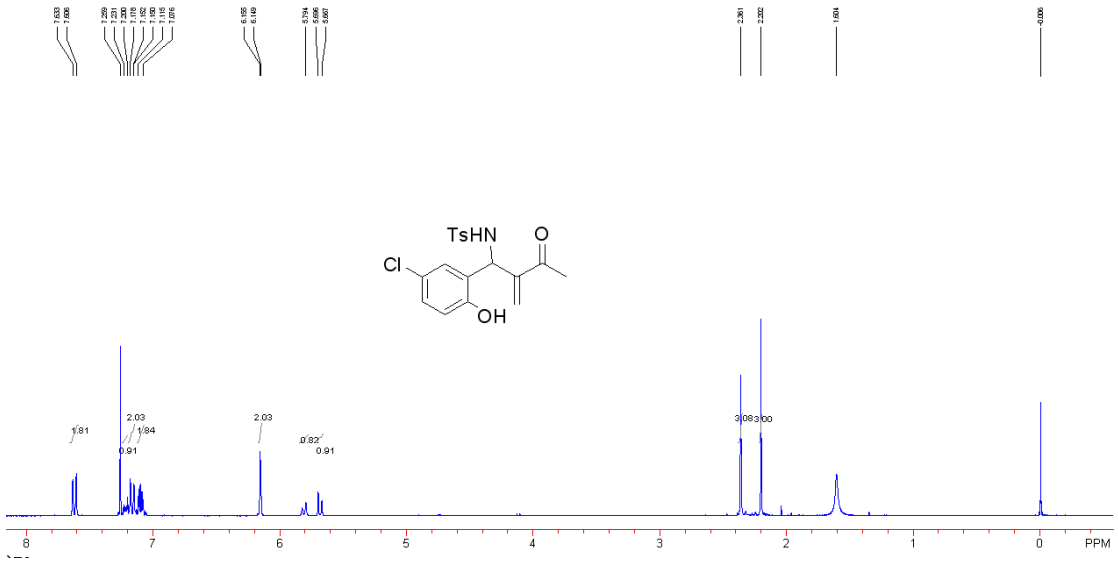


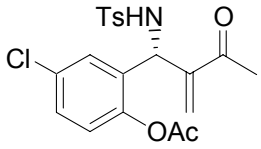


3h

***N*-(1-(5-Chloro-2-hydroxyphenyl)-2-methylene-3-oxobutyl)-4-methylbenzenesulfonamide**

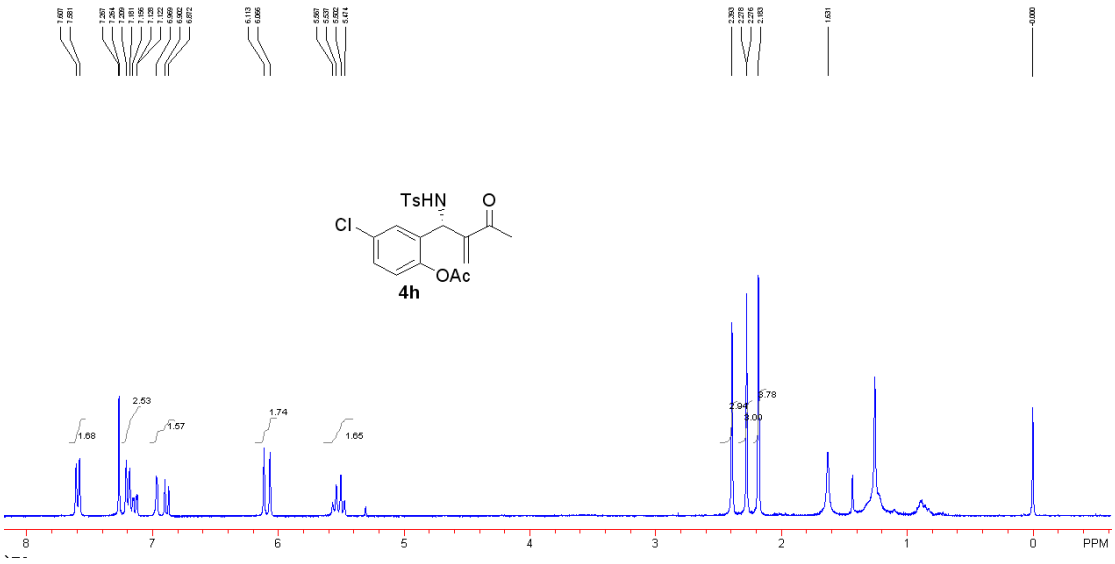
3h: White solid (needles obtained by recrystallization from CH_2Cl_2/PE = 4/1): 96% yield; *ee* 90%; $[\alpha]_D^{20}$ 74 (c 0.70, $CHCl_3$); mp: 124-126 ^oC. IR (KBr) ν 3281, 2923, 1709, 1486, 1332, 1161, 1093 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.26 (3H, s, Me), 2.38 (3H, s, Me), 5.44 (1H, d, *J* = 8.4 Hz, CH), 5.85 (1H, d, *J* = 8.4 Hz, NH), 6.19 (1H, s, =CH), 6.20 (1H, s, =CH), 6.66 (1H, d, *J* = 8.1 Hz, Ar), 6.83 (1H, d, *J* = 2.4 Hz, Ar), 6.97 (1H, dd, *J* = 2.4, 8.1 Hz, Ar), 6.99 (1H, s, OH), 7.18 (2H, d, *J* = 8.1 Hz, Ar), 7.59 (2H, d, *J* = 8.1 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 21.5, 26.2, 53.2, 118.5, 125.5, 126.4, 127.1, 127.8, 128.6, 128.9, 129.5, 136.2, 143.8, 145.9, 151.9, 199.9. MS (MALDI) m/e 402 (M^++23, 100.0). HRMS (MALDI) calcd. for $C_{18}H_{18}NO_4SClNa^+$: 402.0533, Found: 402.0537.

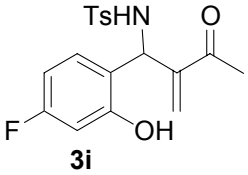




6h

4-Chloro-2-(2-methylene-1-(4-methylphenylsulfonamido)-3-oxobutyl)phenyl acetate 6h: White solid (plates obtained by recrystallization from EtOAc/PE = 3/1): *ee* 90%; $[\alpha]_D^{20}$ 74 (c 0.70, $CHCl_3$); mp. 118-120 ^oC; IR (KBr) ν 3287, 2924, 1917, 1767, 1680, 1482, 1165 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.15 (3H, s, Me), 2.22 (3H, s, Me), 2.53 (3H, s, Me), 5.50 (1H, d, *J* = 9.0 Hz, CH), 5.52 (1H, d, *J* = 9.0 Hz, NH), 6.04 (1H, s, =CH), 6.09 (1H, s, =CH), 6.88 (1H, d, *J* = 9.0 Hz, Ar), 6.96 (1H, d, *J* = 1.5 Hz, Ar), 7.14 (1H, dd, *J* = 9.0, 1.5 Hz, Ar), 7.19 (2H, d, *J* = 8.2 Hz, Ar), 7.59 (2H, d, *J* = 8.2 Hz, Ar). MS (EI) m/e 266 (M^+-155, 6.00), 91 (M^+-330, 46.38), 43 (M^+-378, 100); HPLC: AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{major} = 14.38 min; t_{minor} = 17.54 min; *ee*% = 90%.

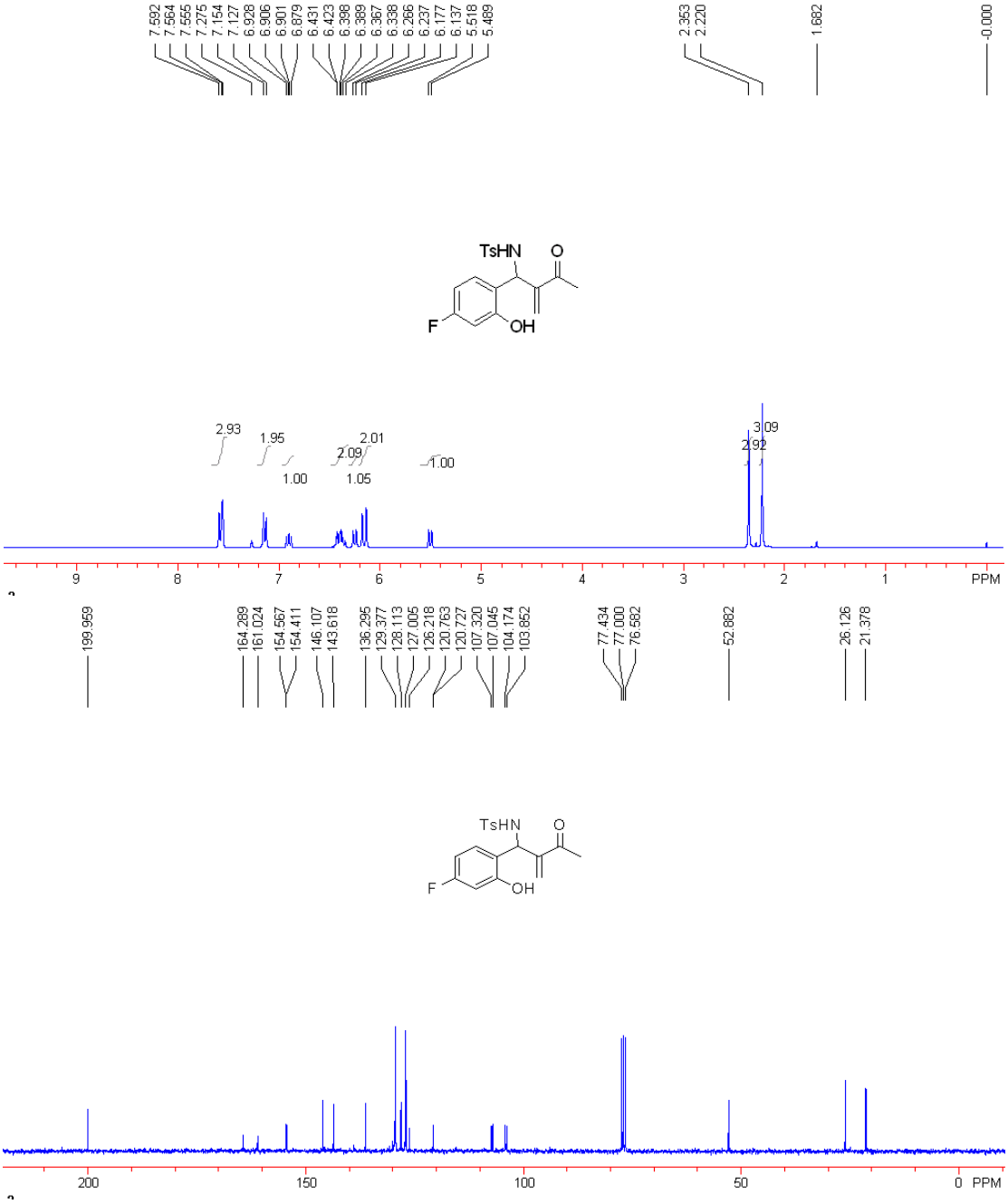


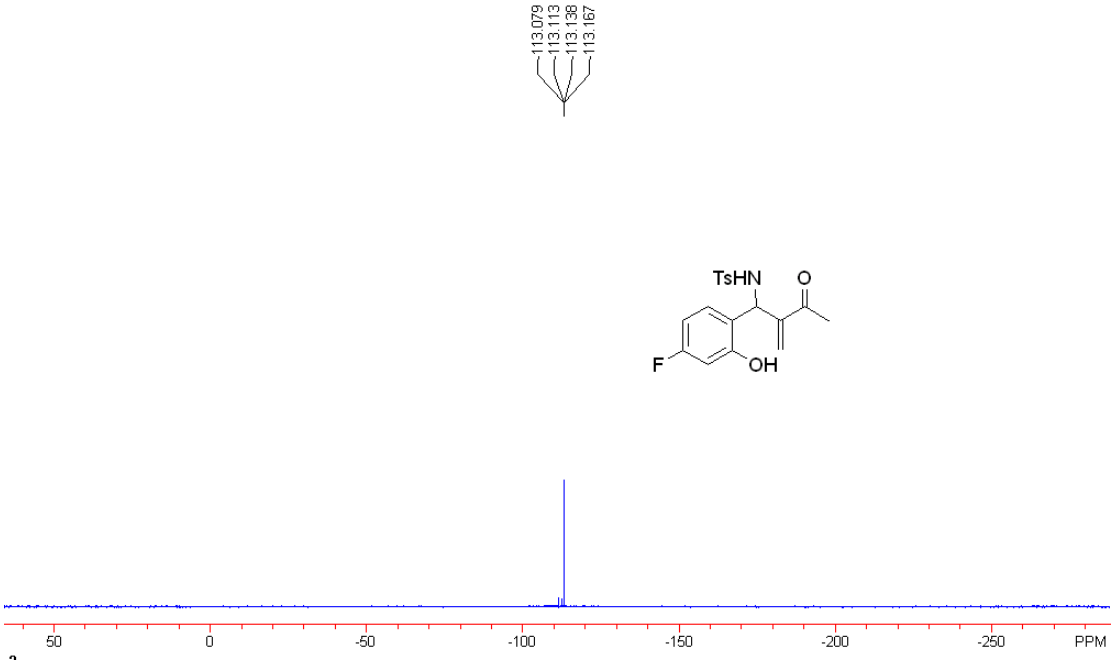


N-(1-(4-fluoro-2-hydroxyphenyl)-2-methylene-3-oxobutyl)-4-methylbenzenesulfonamide

3i. This is a new compound. White solid (needles obtained by recrystallization from EtOAc/PE = 2/1): Mp. 70-72 ^{o}C; *ee* 94%; $[\alpha]^{20}_{D}$ = +59.2 ($CHCl_3$, 0.90); IR (CH_2Cl_2) ν 3286, 2925, 1673, 1613, 1517, 1434, 1328, 1158, 1093, 670 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.22 (3H, s, CH_3), 2.35 (3H, s, CH_3), 5.51 (1H, d, J = 9.3 Hz, CH), 6.13 (1H, s, =CH), 6.17 (1H, s, =CH), 6.29 (1H, d, J = 9.3 Hz, NH), 6.33-6.42 (2H, m, Ar), 6.90 (1H, dd, J_1 = 6.6 Hz, J_2 = 8.4 Hz, Ar), 7.14 (2H, d, J = 7.8 Hz, Ar), 7.53 (1H, s, OH), 7.57 (2H, d, J = 8.1 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.4, 26.1, 52.9, 104.0 (d, J = 24.2 Hz), 107.2 (d, J = 20.6 Hz), 120.7 (d, J = 2.7 Hz), 126.2, 127.0, 128.1, 129.5 (d, J = 11.0 Hz), 136.3, 143.6, 146.1, 154.5 (d, J = 11.7 Hz), 162.7 (d, J = 244.9 Hz), 199.9. ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ -113.12 (q, J = 9.6 Hz). MS (ESI) *m/z* 385.0, 346.0, 193.0. HRMS (MALDI) Calcd. for

$C_{18}H_{18}FNO_4S$ requires (M^++Na^+) 386.0833, Found 386.0832.

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113.113
113.138
113.167
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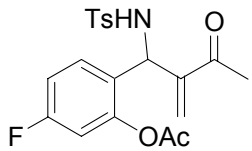
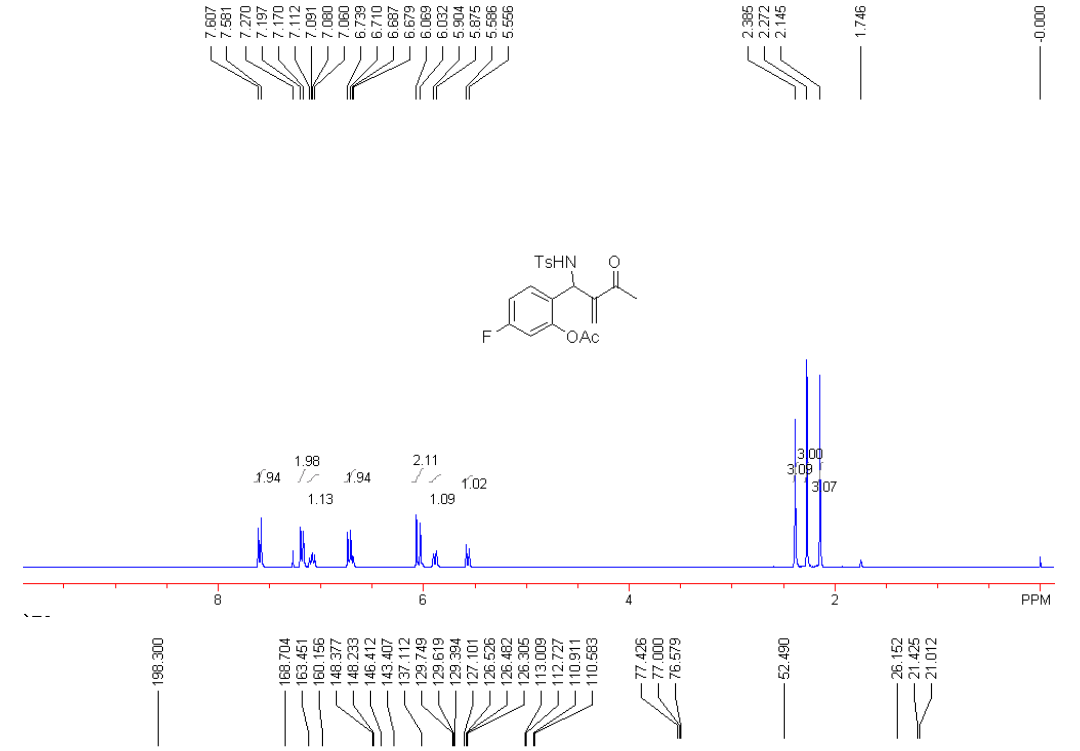
O
F
OH
50
0
-50
-100
-150
-200
-250
PPM



6i

5-fluoro-2-(2-methylene-1-(4-methylphenylsulfonamido)-3-oxobutyl)phenyl acetate 6i. This is a new compound. White solid (needles obtained by recrystallization from CH_2Cl_2/PE = 2/3): Mp. 110-112 ^oC; $[\alpha]^{20}_D$ = +27.8 ($CHCl_3$, 1.15); IR (CH_2Cl_2) ν 3284, 3080, 1771, 1680, 1500, 1197, 672 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.14 (3H, s, CH_3), 2.27 (3H, s, CH_3), 2.39 (3H, s, CH_3), 5.57 (1H, d, *J* = 8.7 Hz, CH), 5.89 (1H, d, *J* = 8.7 Hz, NH), 6.03 (1H, s, =CH), 6.07 (1H, s, =CH), 6.68-6.74 (2H, m, Ar), 7.09 (1H, dd, J_1 = 6.3 Hz, J_2 = 9.6 Hz, Ar), 7.18 (2H, d, *J* = 8.7 Hz, Ar), 7.59 (2H, d, *J* = 7.8 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.0, 21.4, 26.2, 52.5, 110.7 (d, *J* = 24.6 Hz), 112.9 (d, *J* = 21.2 Hz), 126.3, 126.5 (d, *J* = 3.3 Hz), 127.1, 129.4, 129.7 (d, *J* = 9.8 Hz), 137.1, 143.4, 146.4, 148.3 (d, *J* = 10.8 Hz), 161.8 (d, *J* = 247.1 Hz), 168.7, 198.3. ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ -112.15 (q, *J* = 6.8 Hz). MS (ESI) *m/z* 406.0, 235.0. HRMS (MALDI) Calcd. for $C_{20}H_{20}FNO_5S$ requires (M^++Na^+) 428.0941, Found 428.0938. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column: hexane/*i*PrOH = 75/25, 0.7 mL/min, 254 nm, t_{major} = 9.48 min, t_{minor} = 14.83 min; 94% *ee*.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7.581
7.270
7.197
7.170
7.112
7.091
7.080
7.060
6.739
6.710
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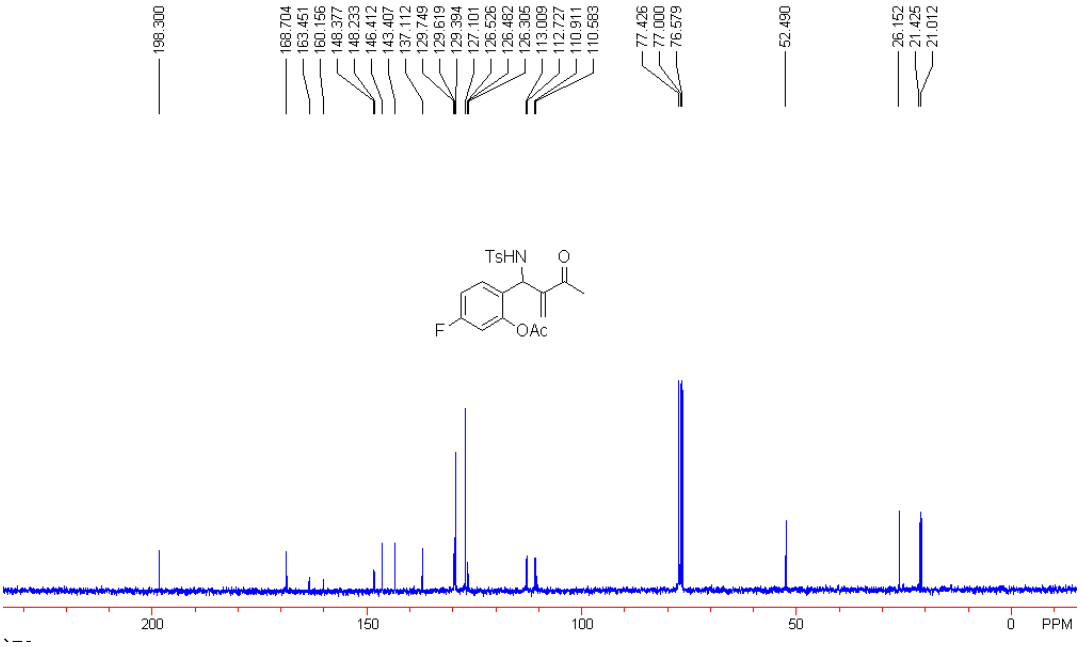
6.679
6.069
6.032
5.904
5.875
5.586
5.556
2.385
2.272
2.145
1.746
-0.000
TsHN
O
F
OAc
1.94
1.98
1.13
1.94
2.11
1.09
1.02
3.00
3.09
3.07
8
6
4
2
PPM


198.300
168.704
163.451
160.156
148.377
148.233
146.412
143.407
137.112
129.749
129.619
129.394
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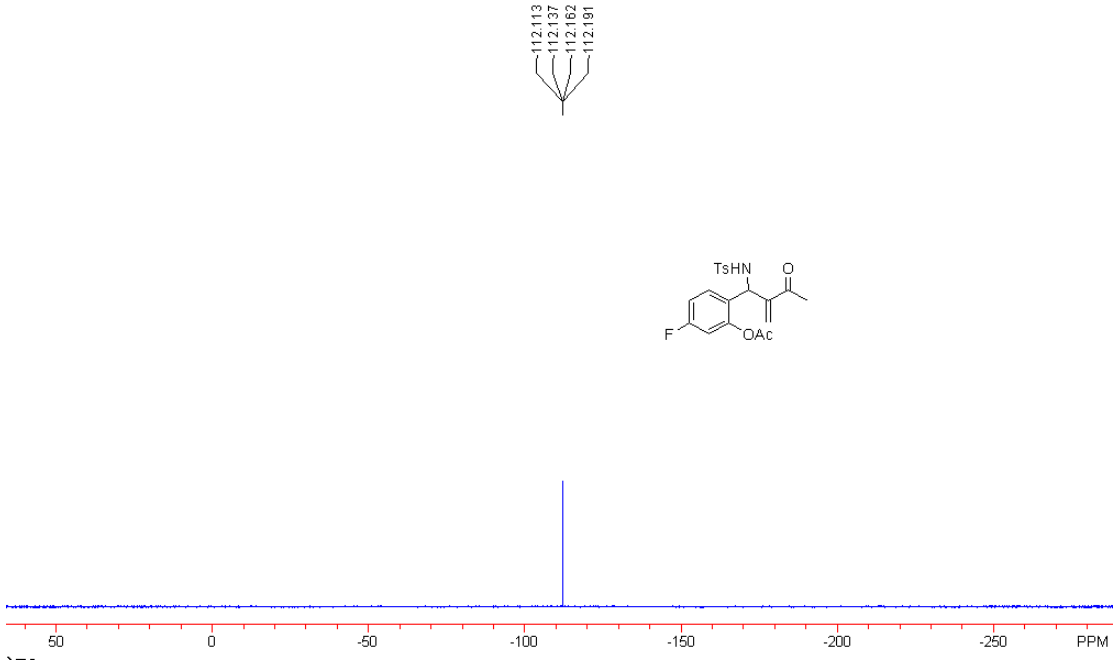
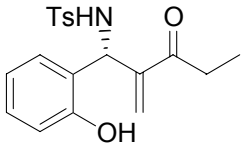
126.526
126.482
126.305
113.009
112.727
110.911
110.583
77.426
77.000
76.579
52.490
26.152
21.425
21.012
TsHN
O
F
OAc
200
150
100
50
0
PPM



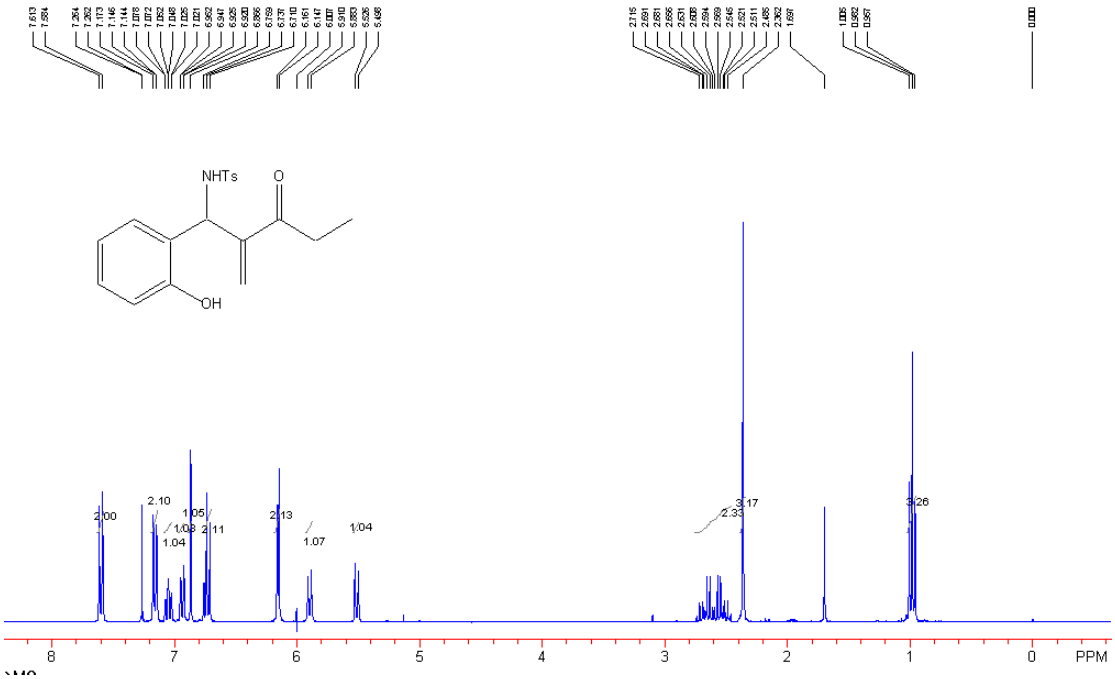


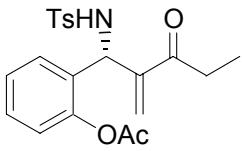
3k

***N*-(1-(2-Hydroxyphenyl)-2-methylene-3-oxopentyl)-4-methylbenzenesulfonamid 3k**:

White solid (cubes obtained by recrystallization from CH_2Cl_2/PE = 3/1), yield: 99%; *ee* 92%; $[\alpha]_D^{20}$ 80 (c 0.50, $CHCl_3$); mp: 48-50 °C. IR (KBr) ν 3301, 2979, 2939, 2879, 1919, 1676, 1598, 1458, 1414, 1332, 1158, 1093, 950 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.98 (3H, t, *J* = 7.2 Hz, Me), 2.36 (3H, s, Me), 2.49-2.72 (2H, m, CH_2), 5.51 (1H, d, *J* = 8.3 Hz, CH), 5.90 (1H, d, *J* = 8.3 Hz, NH), 6.15 (2H, d, *J* = 4.2 Hz, =CH_2), 6.71-6.76 (1H, m, Ar), 6.87 (1H, s, OH), 6.94 (1H, dd, *J* = 8.1, 1.5 Hz, Ar), 7.02-7.09 (1H, m, Ar), 7.16 (2H, d, *J* = 8.7 Hz, Ar), 7.60 (2H, d, *J* = 8.7 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 7.9, 21.4, 31.1, 55.5, 112.9, 114.4, 117.9, 125.8, 126.3, 127.0, 129.3, 129.6, 136.5, 143.4, 146.9, 153.4, 202.5; MS (EI) m/e 204 (M^+-155, 42.8), 148 (M^+-211, 66.0), 146 (M^+-213, 20.0), 131 (M^+-228, 43.4), 91

(M^+-268, 100.0), 65 (M^+-294, 30.2), 57 (M^+-302, 81.2), 55 (M^+-304, 16.3). Anal. Calcd. for $C_{19}H_{21}NO_4S$ requires C, 63.49; H, 5.89; N, 3.90%. Found: C, 63.53; H, 5.89; N, 3.74%.

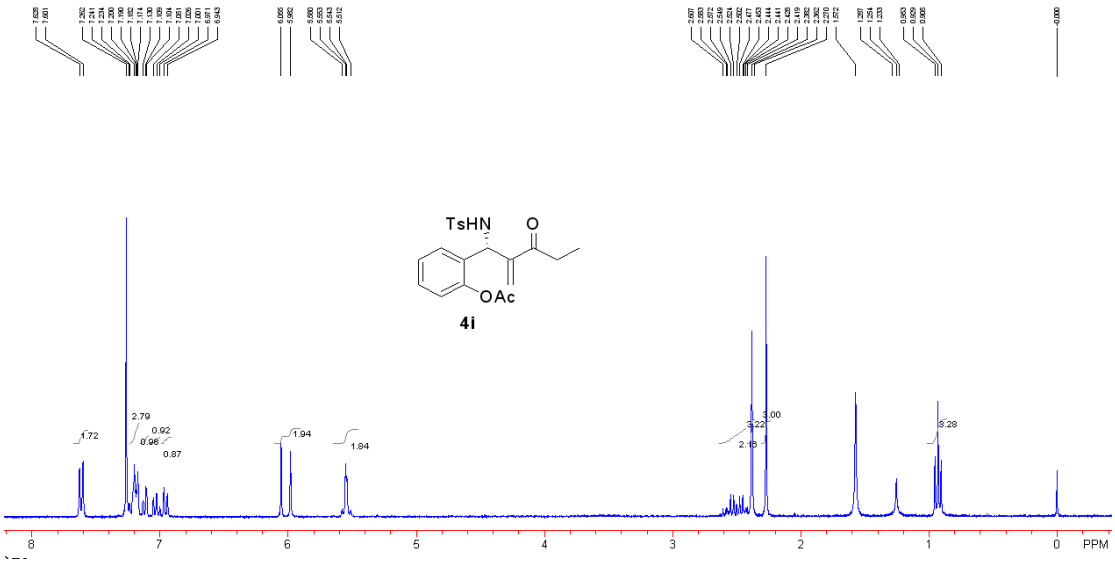


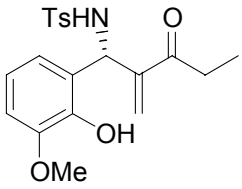


6k

2-(2-Methylene-1-(4-methylphenylsulfonamido)-3-oxopentyl)phenyl acetate 6k: Colorless solid (plates obtained by recrystallization from CH_2Cl_2/PE = 4/1): *ee* 92%; $[\alpha]_D^{20}$ 27 (c 0.53, $CHCl_3$); mp. 70-72 ^oC; IR (KBr) ν 3283, 2977, 2926, 2854, 1766, 1681, 1598, 1489, 1370, 1336, 1201, 1094 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.93 (3H, t, *J* = 7.2 Hz, Me), 2.27 (3H, s, Me), 2.38 (3H, s, Me), 2.42-2.61 (2H, m, CH_2), 5.50 (1H, d, *J* = 8.0 Hz, CH), 5.60 (1H, d, *J* = 8.0 Hz, NH), 5.98 (1H, s, =CH), 6.06 (1H, s, =CH), 6.95 (1H, d, *J* = 8.4 Hz, Ar), 7.03 (1H, t, *J* = 7.5 Hz, Ar), 7.12 (1H, dd, *J* = 1.5, 7.8 Hz, Ar), 7.17-7.20 (1H, m, Ar), 7.18 (2H, d, *J* = 8.1 Hz, Ar), 7.61 (2H, d, *J* = 8.1 Hz, Ar). MS (EI) m/e 246 (M^+-155, 24.80), 91

(M^+-310, 100), 43 (M^+-358, 95.29); HPLC: AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.5 mL/min; t_{major} = 39.54 min; t_{minor} = 60.96 min; *ee*% = 92%.

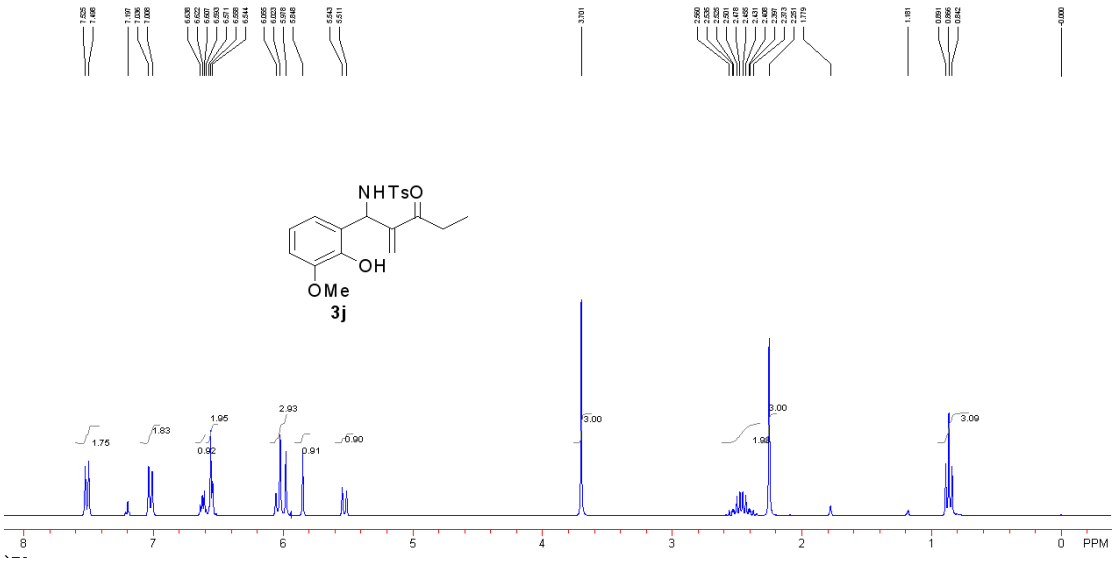


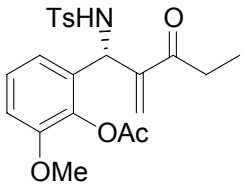


3l

***N*-(1-(2-Hydroxy-3-methoxyphenyl)-2-methylene-3-oxopentyl)-4-methylbenzenesulfonamide 3l**: White solid (needles obtained by recrystallization from CH_2Cl_2/PE = 5/1), yield: 96%; *ee* 94%; $[\alpha]_D^{20}$ 55 (c 1.21, $CHCl_3$); mp: 95-97 °C. IR (KBr) ν 3355, 3268, 2977, 2939, 2843, 1918, 1679, 1597, 1482, 1443, 1158, 1093, 955, 904, 815, 670 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.87 (3H, t, *J* = 7.4 Hz, Me), 2.51 (3H, s, Me), 2.33-2.56 (2H, m, CH_2), 3.70 (1H, s, CH_3), 5.53 (1H, d, *J* = 9.6 Hz, CH), 5.85 (1H, s, OH), 5.98-6.06 (3H, m, NH and $=CH_2$), 6.54-6.64 (3H, m, Ar), 7.02 (2H, d, *J* = 8.3 Hz, Ar), 7.51 (2H, d, *J* = 8.3 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 7.8, 21.3, 31.2, 54.1, 55.9, 109.6, 119.4, 120.9, 124.0, 125.6, 127.0,

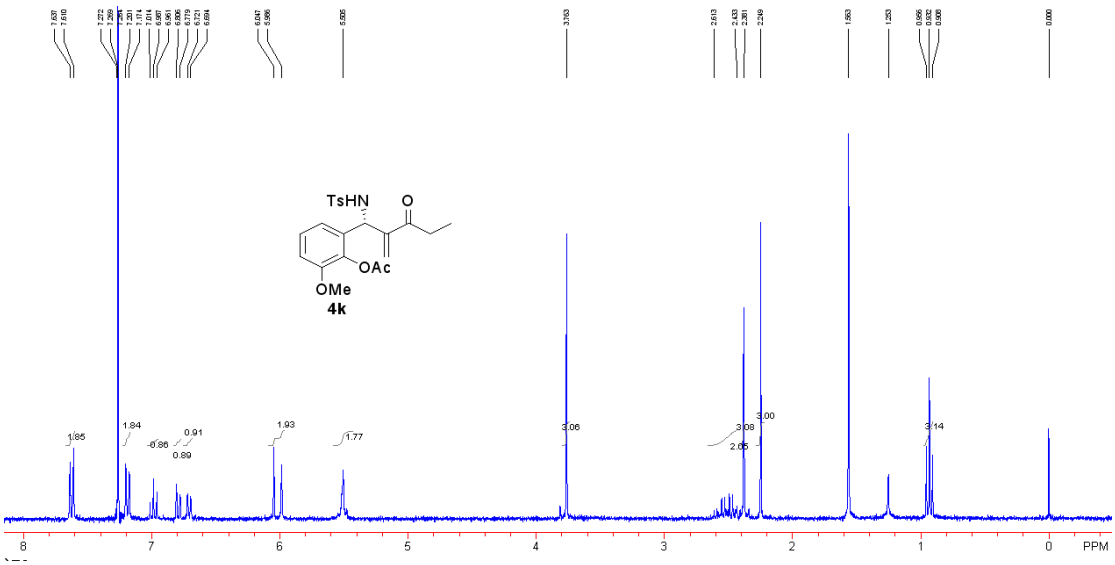
129.0, 137.2, 142.4, 142.8, 145.7, 146.2, 201.3; MS (EI) m/e 171 (M^+-218, 17.3), 155 (M^+-234, 20.9), 108 (M^+-281, 13.1), 107 (M^+-282, 25.7), 91 (M^+-298, 100.0), 89 (M^+-300, 11.2), 65 (M^+-324, 34.4), 63 (M^+-326, 12.4). Anal. Calcd. for $C_{20}H_{23}NO_5S$ requires C, 61.68; H, 5.95; N, 3.60%. Found: C, 61.46; H, 5.65; N, 3.22%.

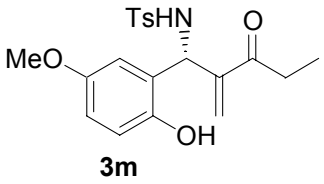




2-Methoxy-6-(2-methylene-1-(4-methylphenylsulfonamido)-3-oxopentyl)phenyl acetate 6l: White solid (cubes obtained by recrystallization from CH_2Cl_2/PE = 3/1): *ee* 94%, $[\alpha]_D^{20}$ 32 (c 0.80, $CHCl_3$), mp. 115-117 ^oC; IR (KBr) ν 3282, 2920, 1768, 1682, 1481, 1334, 1278, 1161, 1091, 1053 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.93 (3H, t, *J* = 7.2 Hz, Me), 2.25 (3H, s, Me), 2.34 (3H, s, Me), 2.38-2.59 (2H, m, CH_2), 3.76 (3H, s, Me), 5.49 (1H, s, CH), 5.49 (1H, s, NH), 5.99 (1H, s, =CH), 6.05 (1H, s, =CH), 6.71 (1H, d, *J* = 8.1 Hz, Ar), 6.80 (1H, d, *J* = 8.1 Hz, Ar), 6.99 (1H, t, *J* = 7.8 Hz, Ar), 7.23 (2H, d, *J* = 8.1 Hz, Ar), 7.62 (2H, d, *J* = 8.1

Hz, Ar). MS (ESI) m/e 432 (M^++1); HPLC: AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.6 mL/min; t_{major} = 12.75 min; t_{minor} = 20.49 min; *ee*% = 94%.

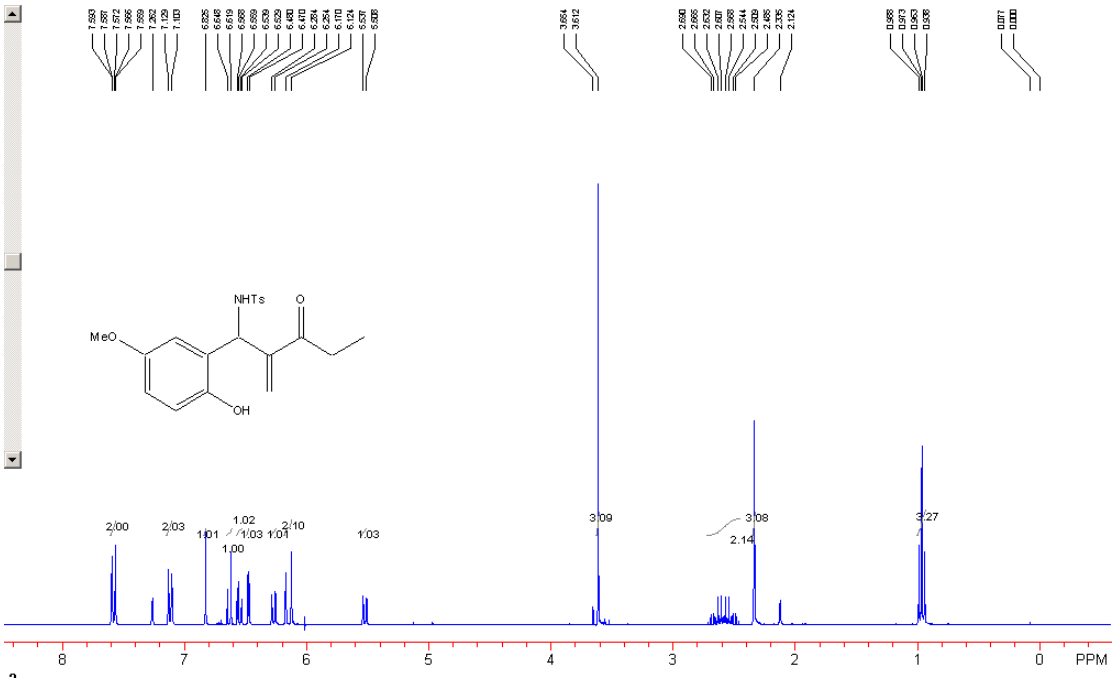


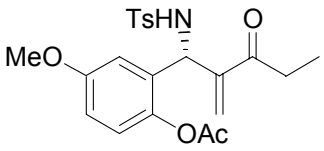


3m

***N*-(1-(2-Hydroxy-5-methoxyphenyl)-2-methylene-3-oxopentyl)-4-methylbenzenesulfonamide 3m**: White solid (plates obtained by recrystallization from CH_2Cl_2/PE = 5/1); yield: 97%, *ee* 94%, $[\alpha]_D^{20}$ 73 (c 1.23, $CHCl_3$), mp: 90-92 °C. IR (KBr) ν 3357, 3272, 2977, 2986, 2785, 1901, 1711, 1597, 1482, 1443, 1158, 1093 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.00 (3H, t, *J* = 7.5 Hz, Me), 2.37 (3H, s, Me), 2.50-2.74 (2H, m, CH_2), 3.65 (1H, s, CH_3), 5.47 (1H, d, *J* = 8.4 Hz, CH), 5.79 (1H, d, *J* = 8.4 Hz, NH), 6.19 (2H, d, *J* = 9.0 Hz, =CH_2), 6.45 (1H, d, *J* = 2.7 Hz, Ar), 6.49 (1H, s, OH), 6.01 (1H, dd, *J* = 8.7, 2.6 Hz, Ar), 6.68 (1H, d, *J* = 8.7 Hz, Ar), 7.15-7.18 (2H, m, Ar), 7.59-7.63 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 7.9,

21.4, 31.1, 53.2, 55.5, 112.9, 114.0, 117.9, 125.8, 126.3, 127.0, 129.3, 129.6, 136.5, 143.4, 146.9, 153.3, 202.5; MS (EI) m/e 218 (M^+-171, 57.74), 203 (M^+-186, 25.7), 189 (M^+-200, 31.1), 178 (M^+-211, 19.1), 161 (M^+-228, 69.8), 91 (M^+-298, 100.0), 65 (M^+-324, 44.3), 57 (M^+-332, 60.8). Anal. Calcd. for $C_{20}H_{23}NO_5S$ requires C, 61.68; H, 5.95; N, 3.60%. Found: C, 61.60; H, 5.79; N, 3.18%.

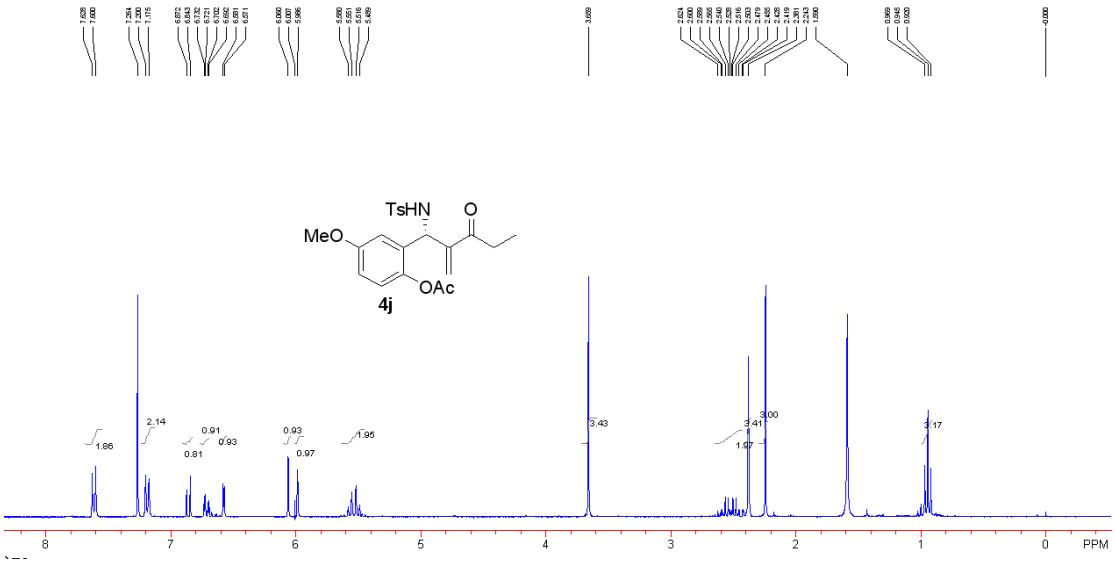


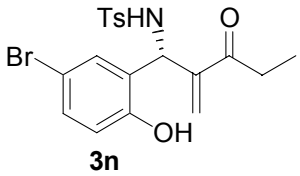


6m

4-Methoxy-2-(2-methylene-1-(4-methylphenylsulfonamido)-3-oxopentyl)phenyl acetate 6m: White solid (needles obtained by recrystallization from CH_2Cl_2/PE = 3/1): *ee* 95%; $[\alpha]_D^{20}$ 21 (c 0.53, $CHCl_3$); mp. 98-100 ^oC; IR (KBr) ν 3273, 2925, 1762, 1681, 1497 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.95 (3H, t, *J* = 7.5 Hz, Me), 2.24 (3H, s, Me), 2.38 (3H, s, Me), 2.42-2.62 (2H, m, CH_2), 3.67 (1H, s, Me), 5.50 (1H, d, *J* = 8.4 Hz, CH), 5.57 (1H, d, *J* = 8.4

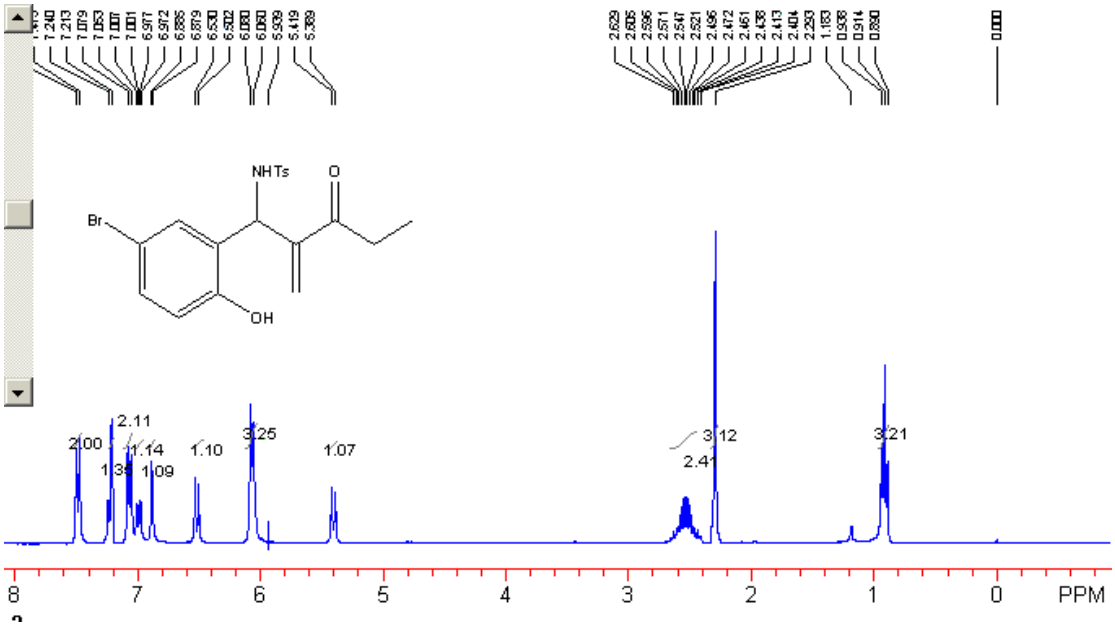
Hz, NH), 5.99 (1H, s, =CH), 6.06 (1H, s, =CH), 6.58 (1H, d, *J* = 3.0 Hz, Ar), 6.71 (1H, dd, *J* = 7.5, 3.0 Hz, Ar), 6.86 (1H, d, *J* = 8.7 Hz, Ar), 7.19 (2H, d, *J* = 8.1 Hz, Ar), 7.61 (2H, d, *J* = 8.1 Hz, Ar). MS (ESI) m/e 449 (M^+ + 18), 432 (M^+ + 1). HPLC: OD column; λ = 230 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.6 mL/min; t_{major} = 22.29 min; t_{minor} = 20.71 min; *ee*% = 95%.

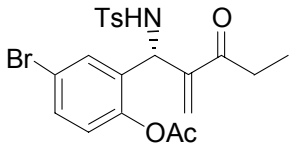




***N*-(1-(5-Bromo-2-hydroxyphenyl)-2-methylene-3-oxopentyl)-4-methylbenzenesulfonamide 3n**: Yellow solid (plates obtained by recrystallization from CH_2Cl_2/PE = 4/1); yield: 95%; *ee* 92%; $[\alpha]_D^{20}$ 54 (c 1.00, $CHCl_3$); mp: 66-68 °C. IR (KBr) ν 3277, 2983, 1938, 1676,1598, 1493, 1416, 1331, 1159, 1093, 813, 670 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.91 (3H, t, *J* = 7.2 Hz, Me), 2.92 (3H, s, Me), 2.44-2.61 (2H, m, CH_2), 5.40 (1H, d, *J* = 9.3 Hz, CH), 6.06-6.08 (3H, m, =CH_2 and NH), 6.52 (1H, d, *J* = 8.4 Hz, Ar), 6.88 (1H, d, *J* = 2.1 Hz, OH),

6.99 (1H, dd, J = 8.4, 1.8 Hz, Ar), 7.38 (1H, d, J = 7.8 Hz, Ar), 7.15-7.24 (1H, m, Ar), 7.49 (2H, d, J = 7.8 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 7.8, 21.44, 31.1, 53.2, 112.5, 118.6, 126.3, 126.7, 127.0, 129.4, 129.6, 131.5, 136.1, 143.7, 145.4, 152.3, 202.4; MS (EI) m/e 209 (M^+-228, 15.9), 171 (M^+-266, 16.6), 155 (M^+-282, 18.3), 91 (M^+-346, 100.0), 65 (M^+-372, 28.0), 63 (M^+-374, 15.3), 57 (M^+-380, 52.3), 51 (M^+-386, 15.5). Anal. Calcd. for $C_{19}H_{20}BrNO_4S$ requires C, 52.06; H, 4.60; N, 3.20%. Found: C, 51.73; H, 4.61; N, 3.07%.

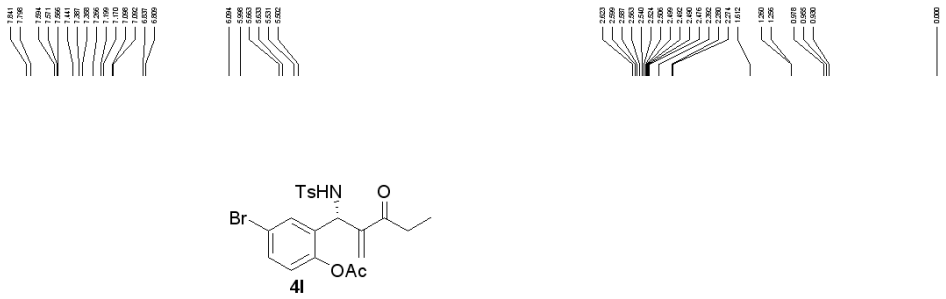


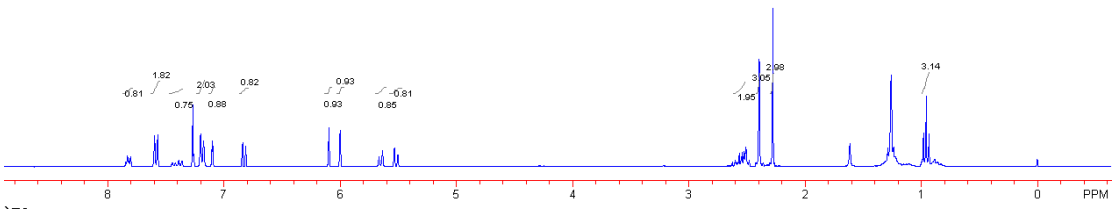


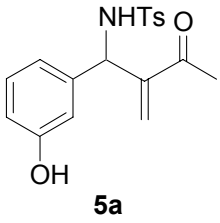
6n

4-Bromo-2-(2-methylene-1-(4-methylphenylsulfonamido)-3-oxopentyl)phenyl acetate 6n: Yellow solid (cubes obtained by recrystallization from CH_2Cl_2/PE = 3/1): *ee* 92%, $[\alpha]_D^{20}$ 22 (c 0.70, $CHCl_3$), mp. 69-71 ^oC; IR (KBr) ν 3283, 2924, 1765, 1679, 1598, 1479, 1265, 1198, 1163, 1013 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.96 (3H, t, J = 7.2 Hz, Me), 2.28 (3H, s, Me), 2.39 (3H, s, Me), 2.44-2.62 (2H, m, CH_2), 5.52 (1H, d, J = 8.8 Hz, CH), 5.64 (1H, d, J

= 8.8 Hz, NH), 6.00 (1H, s, =CH), 6.09 (1H, s, =CH), 6.82 (1H, d, *J* = 8.4 Hz, Ar), 7.10 (1H, d, *J* = 1.8 Hz), 7.18 (2H, d, *J* = 8.0 Hz, Ar), 7.34-7.44 (1H, m, Ar), 7.58 (2H, d, *J* = 8.0 Hz, Ar). MS (ESI) m/e 479 (M^++18), 499 (M^++20); HPLC: OD column; λ = 230 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.6 mL/min; t_{major} = 11.29 min; t_{minor} = 9.54 min; *ee*% = 92%.







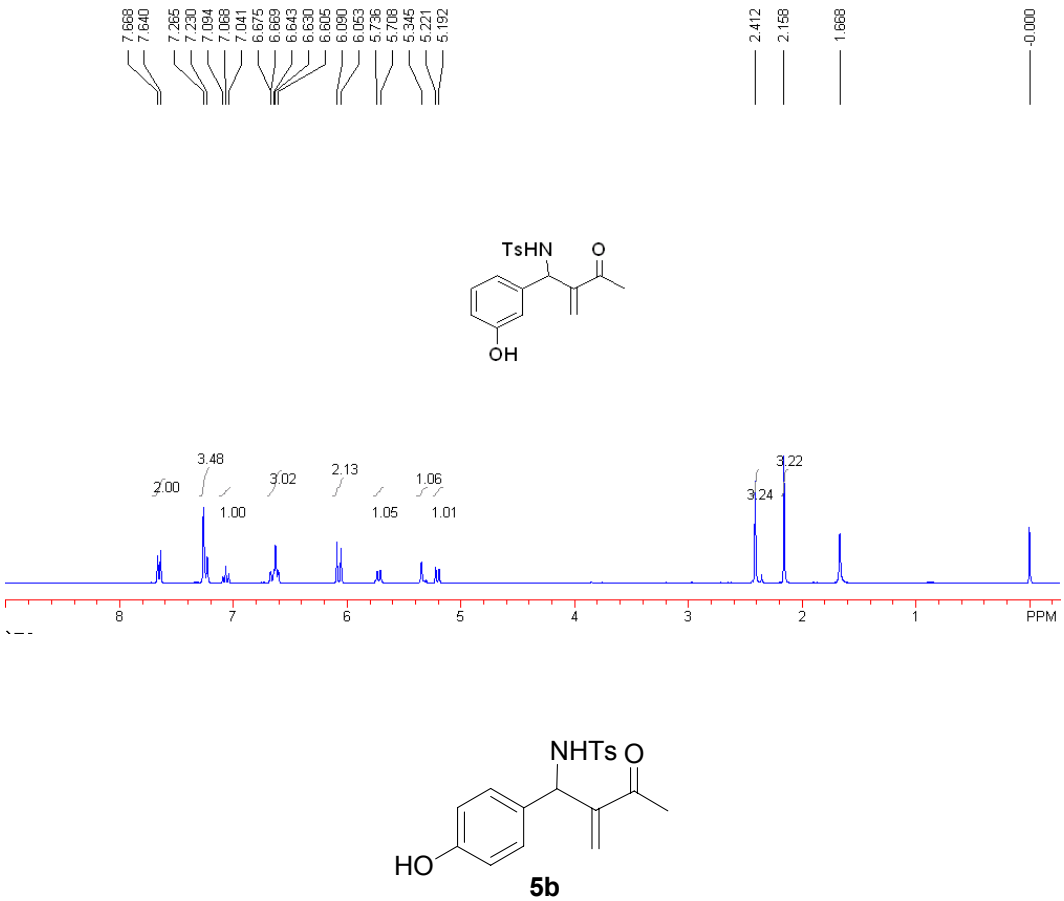
5a

N-(1-(3-hydroxyphenyl)-2-methylene-3-oxobutyl)-4-methylbenzenesulfonamide 5a.

This is a new compound. IR (CH_2Cl_2) ν 3410, 3291, 2925, 1707, 1674, 1600, 1159, 965, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.15 (3H, s, CH_3), 2.40 (3H, s, CH_3), 5.21 (1H, d, *J* = 8.7 Hz, CH), 5.34 (1H, s, OH), 5.72 (1H, d, *J* = 8.7 Hz, NH), 6.04 (1H, s, =CH), 6.08 (1H, s, =CH), 6.58-6.73 (3H, m, Ar), 7.05 (1H, t, *J* = 7.8 Hz, Ar), 7.23 (2H, d, *J* = 8.1 Hz, Ar), 7.64 (2H, d, *J* = 8.1 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.5, 26.3, 58.5, 113.5, 114.8, 118.4,

127.2, 128.6, 129.5, 129.7, 137.2, 140.5, 143.5, 146.2, 155.9, 199.1. MS (ESI) *m/z* 346 (M^++1), 175. HRMS(MALDI) Calcd. for $C_{18}H_{19}NO_4S$ requires (M^++Na^+) 368.0925, Found 368.0927.

$[\alpha]^{20}_D$ = -1.6 ($CHCl_3$, 0.55); Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column: hexane/*i*PrOH = 90/10, 0.5 mL/min, 230 nm, t_{minor} = 39.46 min; t_{major} = 48.71 min, -2.0% *ee* (**β-ICPD** used as the catalyst).



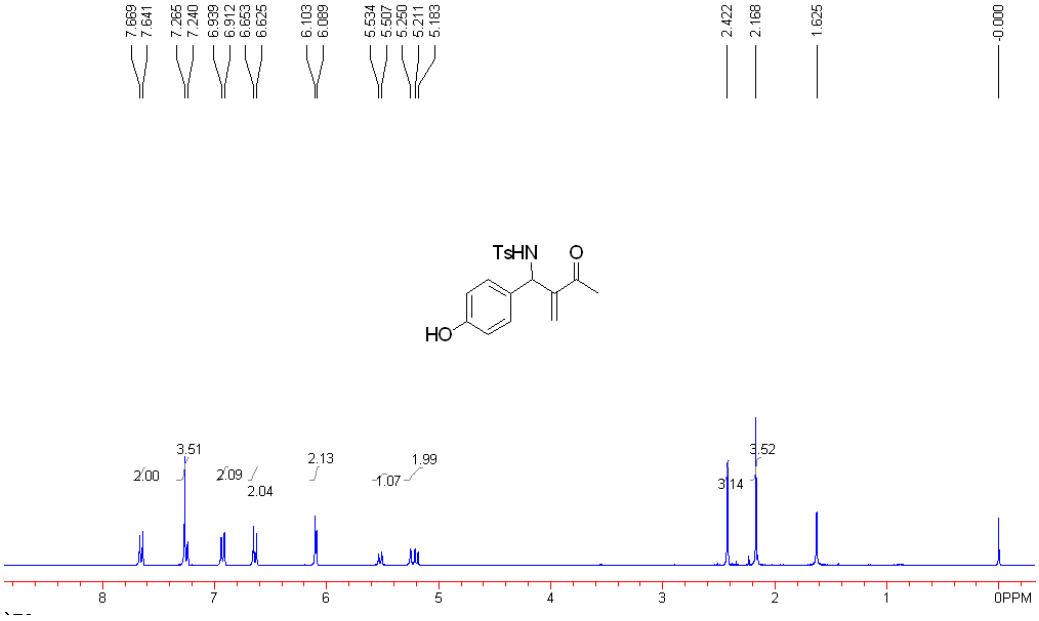
5b

N-(1-(4-hydroxyphenyl)-2-methylene-3-oxobutyl)-4-methylbenzenesulfonamide 5b.

This is a new compound. IR (CH_2Cl_2) ν 3370, 3065, 2923, 2853, 1591, 1568, 1441, 1289, 1152, 1068 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.17 (3H, s, CH_3), 2.42 (3H, s, CH_3), 5.20 (1H, d, *J* = 8.4 Hz, CH), 5.25 (1H, s, OH), 5.52 (1H, d, *J* = 8.4 Hz, NH), 6.09 (1H, s, =CH), 6.10 (1H, s, =CH), 6.64 (2H, d, *J* = 8.7 Hz, Ar), 6.93 (2H, d, *J* = 8.7 Hz, Ar), 7.25 (2H,

d, J = 8.1 Hz, Ar), 7.66 (2H, d, J = 8.1 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.5, 26.2, 48.0, 116.5, 124.3, 126.2, 127.6, 129.8, 134.1, 135.0, 144.5, 163.1, 169.7, 196.7. MS (EI) *m/z* 190 (M^+-155, 93.7), 155 (21.7), 131 (20.1), 96 (16.5), 91 (100.0). Anal. Calcd. For C18H19NO4S requires C, 62.59; H, 5.54; N, 4.06%. Found: C, 62.67; H, 5.63; N, 3.86%.

$[\alpha]^{20}_D$ = +7.0 ($CHCl_3$, 0.30); Enantiomeric excess was determined by HPLC with a Chiralcel OJ-H column: hexane/*i*PrOH = 60/40, 0.5 mL/min, 230 nm, t_{major} = 28.54 min, t_{minor} = 37.96 min; 10.1% *ee* (**β-ICPD** used as the catalyst).



References:

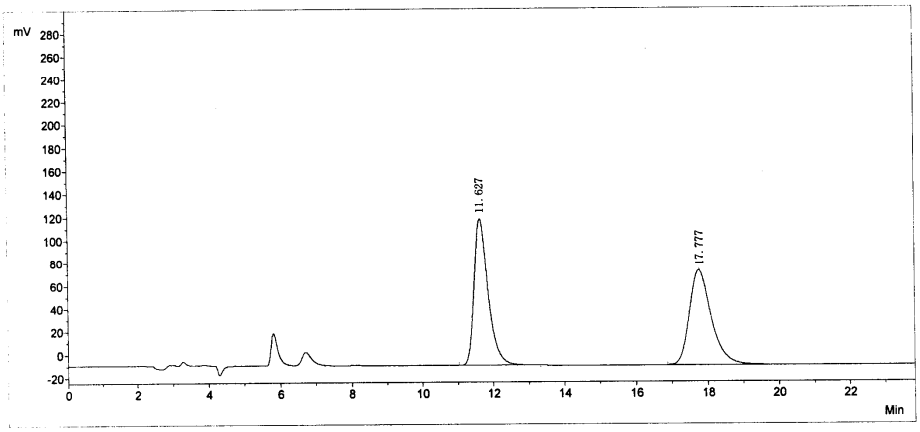
1. Shi, Y. L.; Shi, M. *Org. Lett.* **2005**, *7*, 3057-3060.
2. Iwabuchi, Y.; Nakatani, M.; Yokoyama, N.; Hatakeyama, S. *J. Am. Chem. Soc.* **1999**, *121*, 10219-10220.
3. Qi, M.-J.; Shi, M. *Tetrahedron* **2007**, *63*, 10415-10424.
4. The X-ray crystal data of **6a** (CCDC 601323) and **7a** (CCDC 633231) have been summarized in the Supporting Information.
5. Kuroda, R.; Mason, S. F. *J. Chem. Soc., Dalton* **1979**, 727.

Chiral HPLC charts:

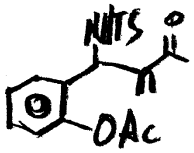
Chiral HPLC trace

HPLC REPORT

Sample Name:lxg-9-47.che
Date:2008-02-28
Time:10:01
Method:
column:
the mobile phase:
Velocity:
the detection wavelength:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	11.627	127616.0	3508537.2	50.4465
2	2	17.777	81843.0	3446428.9	49.5535
Total			209459.0	6954966.1	100.0000



racemate

HPLC: Chiralcel AD-H column: hexane/*i*PrOH = 70/30, 0.7 mL/min, 230 nm, t_{major} = 10.88 min, t_{minor} = 16.38 min; *racemate*.

Chiral HPLC trace

HPLC REPORT

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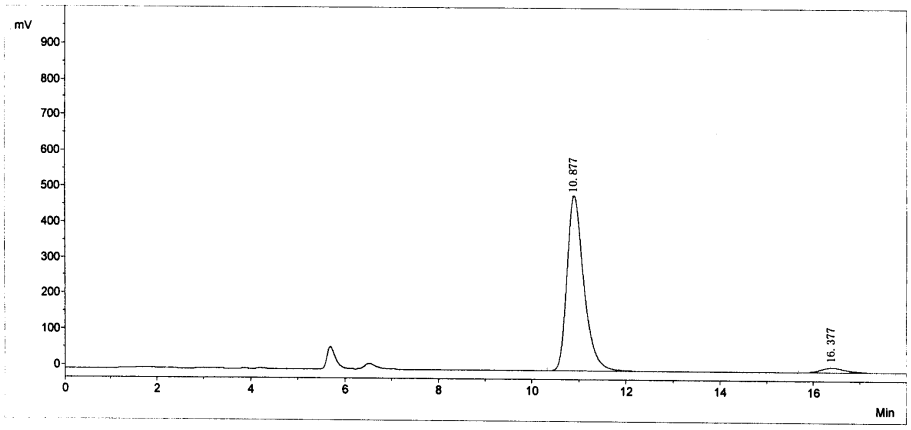
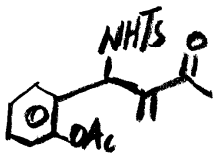
Time:10:44
Method:
column:
the mobile phase:
Velocity:
the detection wavelength:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	10.877	482642.0	12101970.4	95.9880
2	2	16.377	13551.0	505824.9	4.0120
Total			496193.0	12607795.3	100.0000



ee% = 92%

AD-H 70/30 0.7 230

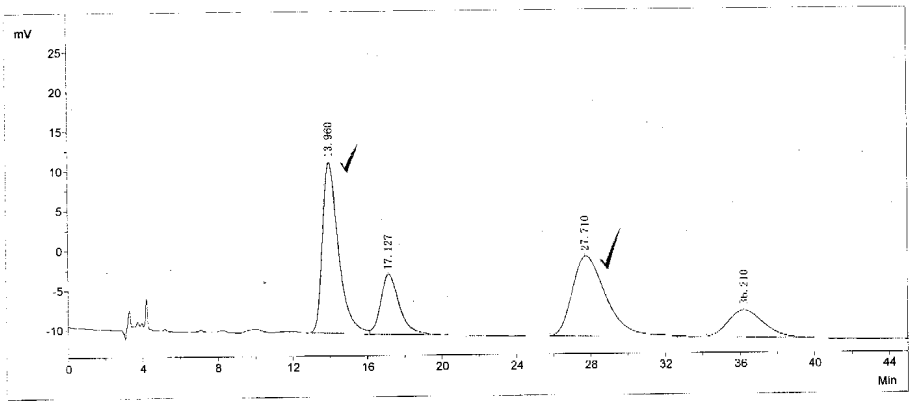
HPLC: Compound **3a** (acetate **6a**), Chiralcel AD-H column: hexane/*i*PrOH = 70/30, 0.7 mL/min, 230 nm, t_{major} = 10.88 min, t_{minor} = 16.38 min; 92% *ee*.

Chiral HPLC trace

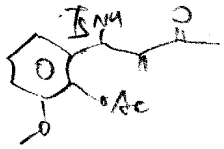
金属有机HPLC分析报告

样品文件名:92-93-rac.che
分析日期:2005-11-15
流动相:
检测波长:

分析者:
色谱柱:
流速:
柱压:

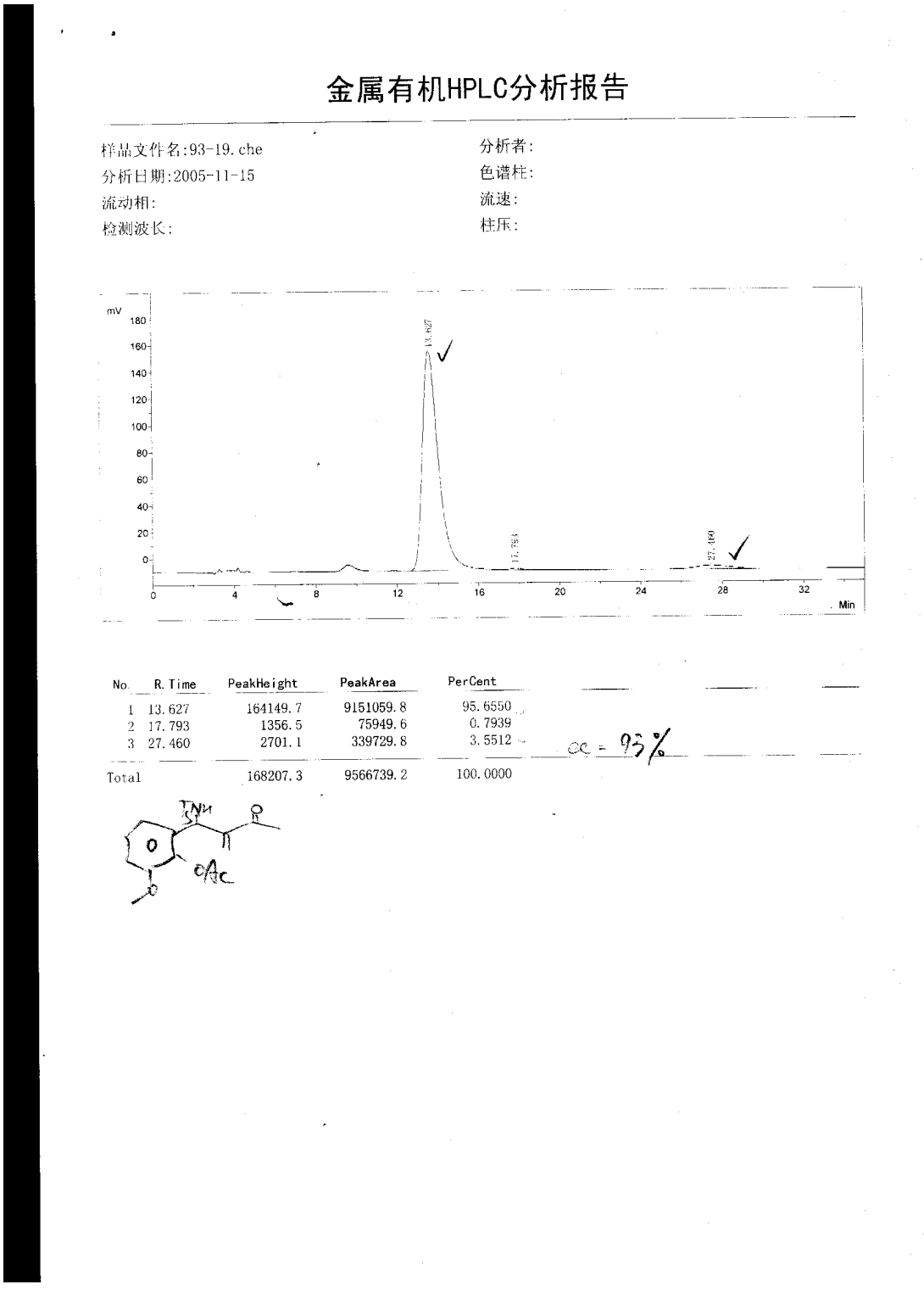


No.	R.Time	PeakHeight	PeakArea	PerCent
1	13.960	21448.9	1285668.1	36.3723
2	17.127	7508.0	523543.1	14.8114
3	27.710	10065.5	1278452.5	36.1682
4	36.210	3388.4	447077.3	12.6481
Total		42410.8	3534740.9	100.0000



HPLC: OD column; λ = 230 nm; eluent: Hexane/Isopropanol = 75/25; Flow rate: 0.6 mL/min; t_{major} = 13.63 min, t_{minor} = 27.46 min; *racemate*.

Chiral HPLC trace



金属有机HPLC分析报告

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分析日期:2005-11-15
流动相:
检测波长:

分析者:
色谱柱:
流速:
柱压:

No.	R. Time	PeakHeight	PeakArea	PerCent
1	13.627	164149.7	9151059.8	95.6550
2	17.793	1356.5	75949.6	0.7939
3	27.460	2701.1	339729.8	3.5512
Total		168207.3	9566739.2	100.0000

ee = 93%

HPLC: Compound **3b** (acetate **6b**), OD column; λ = 230 nm; eluent: Hexane/Isopropanol = 75/25; Flow rate: 0.6 mL/min; t_{major} = 13.63 min, t_{minor} = 27.46 min; *ee*% = 93%.

Chiral HPLC trace

金属有机HPLC分析报告

样品文件名:q3-55-ad-70-30.che　　分析者:
分析日期:2005-11-22　　色谱柱:
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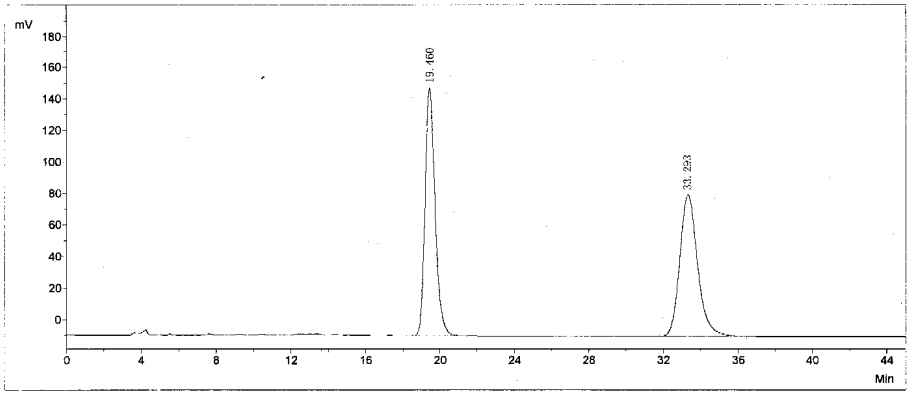
检测波长:　　柱压:



No.	R.Time	PeakHeight	PeakArea	PerCent
1	19.460	156792.8	5879002.2	49.7401
2	33.293	89134.4	5940449.0	50.2599
Total		245927.2	11819451.2	100.0000

HPLC: AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{major} = 18.80 min; t_{minor} = 32.38 min; *racemate*.

Chiral HPLC trace

金属有机HPLC分析报告

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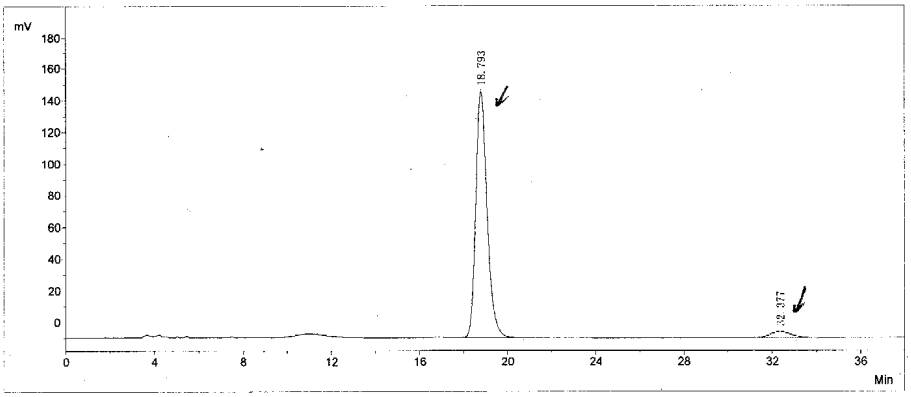
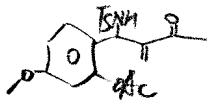
分析日期:2005-11-23　　色谱柱:
流动相:　　流速:
检测波长:　　柱压:



No.	R.Time	PeakHeight	PeakArea	PerCent
1	18.793	155438.2	5526313.8	95.6966
2	32.377	4037.9	248516.5	4.3034
Total		159476.1	5774830.3	100.0000

ee = 92 %



HPLC: Compound **3c** (acetate **6c**), AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{major} = 18.80 min; t_{minor} = 32.38 min; *ee*% = 92%.

Chial HPLC trace

色谱分析报告

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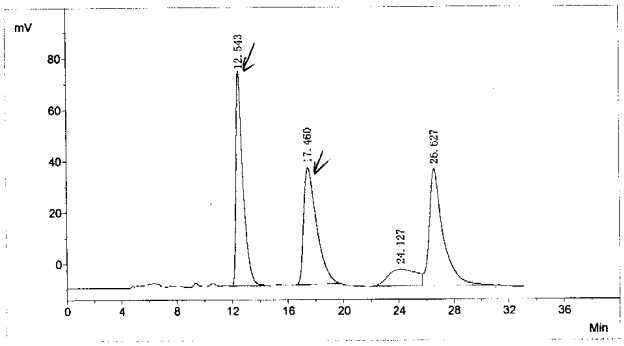

No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	12.543	82366.1	2889641.7	29.2243 ✓
2	2	Unknown	17.460	45034.8	2905212.1	29.3818 ✓
3	3	Unknown	24.127	6392.7	926929.8	9.3745
4	4	Unknown	26.627	45279.6	3166022.4	32.0195
Total				179073.2	9887806.0	100.0000

HPLC: AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{major} = 17.23 min; t_{minor} = 13.00 min; *racemate*.

Chiral HPLC trace

色谱分析报告

样品名称:分析谱图　　样品文件名:q3-17.che
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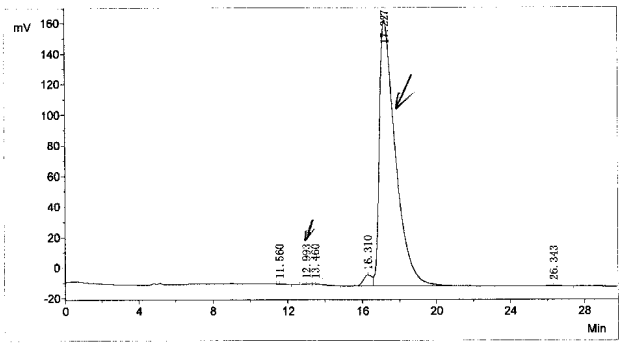
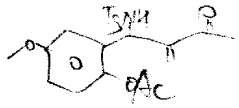


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	11.560	107.8	1757.4	0.0165
2	2	Unknown	12.993	320.5	6158.8	0.0577
3	4	Unknown	16.310	7261.1	228257.7	2.1373
4	5	Unknown	17.227	173720.5	10426197.7	97.6281
5	6	Unknown	26.343	370.7	17135.2	0.1604
Total				181780.6	10679506.8	100.0000

ee = 99.9



HPLC: Compound **3d** (acetate **6d**), AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{major} = 17.23 min; t_{minor} = 13.00 min; *ee*% = 99.9%.

Chiral HPLC trace

金属有机HPLC分析报告

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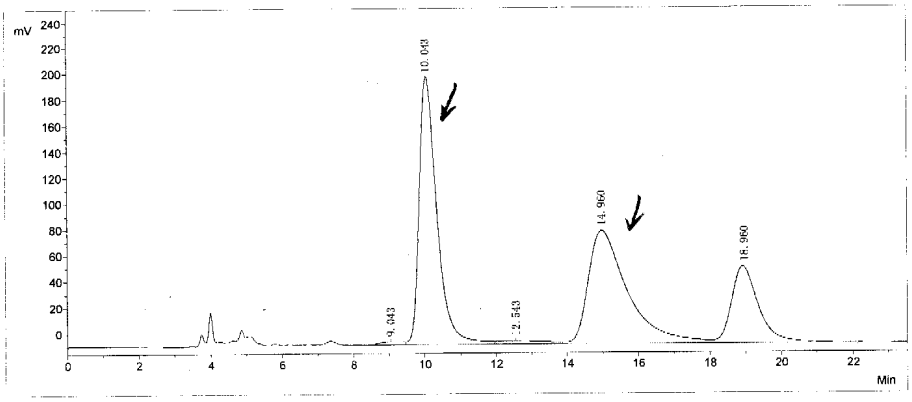

No.	R.Time	PeakHeight	PeakArea	PerCent	
1	9.043	2612.7	112506.6	0.6532	
2	10.043	205109.5	7119835.5	41.3378	✓
3	12.543	2645.7	240618.3	1.3970	
4	14.960	86647.6	6644958.4	38.5807	✓
5	18.960	58527.6	3105617.7	18.0312	
Total		355543.0	17223536.5	100.0000	

HPLC: OD column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{major} = 14.63 min; t_{minor} = 10.13 min; *racemate*.

Chiral HPLC trace

金属有机HPLC分析报告

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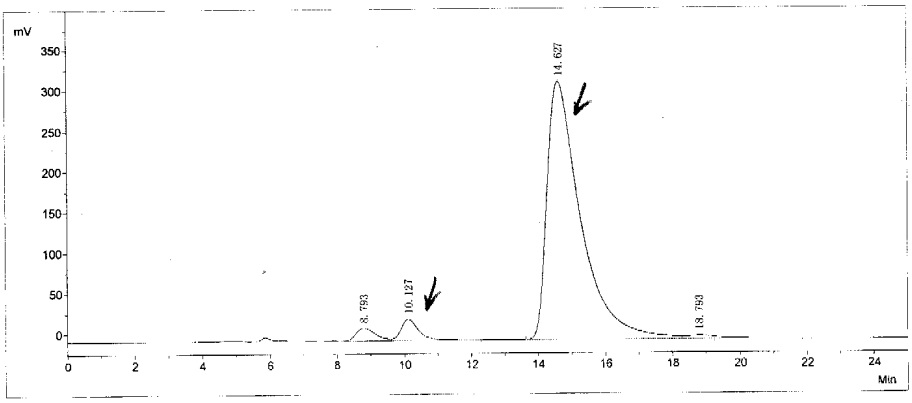
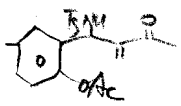
检测波长:

分析者:
色谱柱:
流速:
柱压:



No.	R.Time	PeakHeight	PeakArea	PerCent
1	8.793	15383.6	627622.5	2.6100
2	10.127	26222.6	949830.8	3.9499
3	14.627	317001.7	22154886.0	92.1328
4	18.793	4447.4	314348.6	1.3072
Total		363055.3	24046687.9	100.0000

EE = 91.8 ≈ 92%

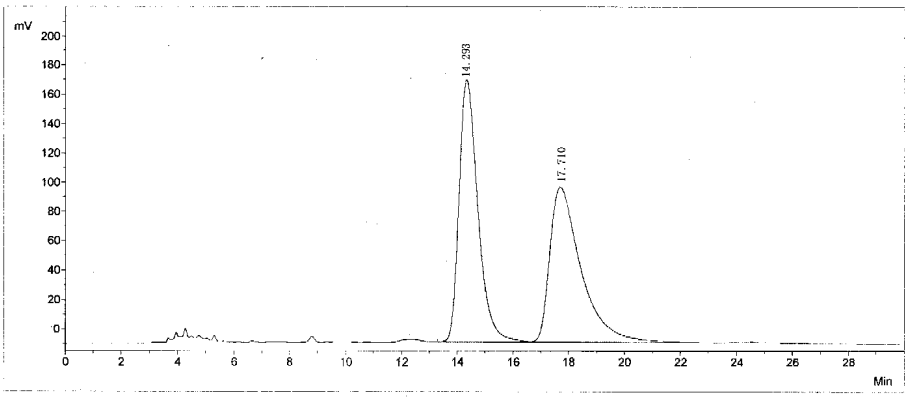


HPLC: Compound **3e** (acetate **6e**), OD column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{major} = 14.63 min; t_{minor} = 10.13 min; *ee*% = 92%.

Chiral HPLC trace

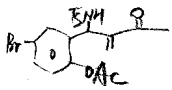
金属有机HPLC分析报告

样品文件名:q3-37S.che　　分析者:
分析日期:2005-11-24　　色谱柱:
流动相:　　流速:
检测波长:　　柱压:



No.	R.Time	PeakHeight	PeakArea	PerCent
1	14.293	176562.6	8372302.9	50.4277
2	17.710	105495.8	8230278.5	49.5723
Total		282058.4	16602581.4	100.0000

ee=

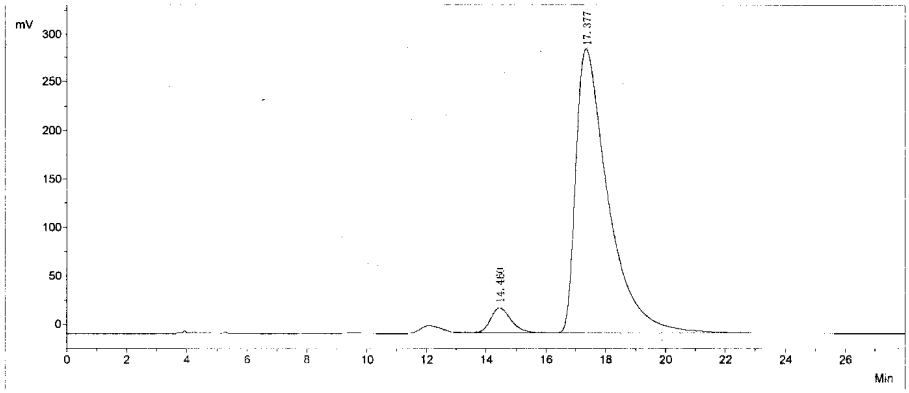


HPLC: OD column; λ = 230 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.5 mL/min; t_{major} = 17.38 min; t_{minor} = 14.46 min; *racemate*.

Chiral HPLC trace

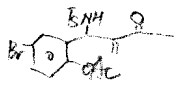
金属有机HPLC分析报告

样品文件名:q3-28s.chc　　分析者:
分析日期:2005-11-24　　色谱柱:
流动相:　　流速:
检测波长:　　柱压:



No.	R.Time	PeakHeight	PeakArea	PerCent
1	14.460	25788.3	1238472.1	5.3176
2	17.377	292085.5	22051601.7	94.6824
Total		317873.8	23290073.8	100.0000

EE = 89.4 ≈ 90%

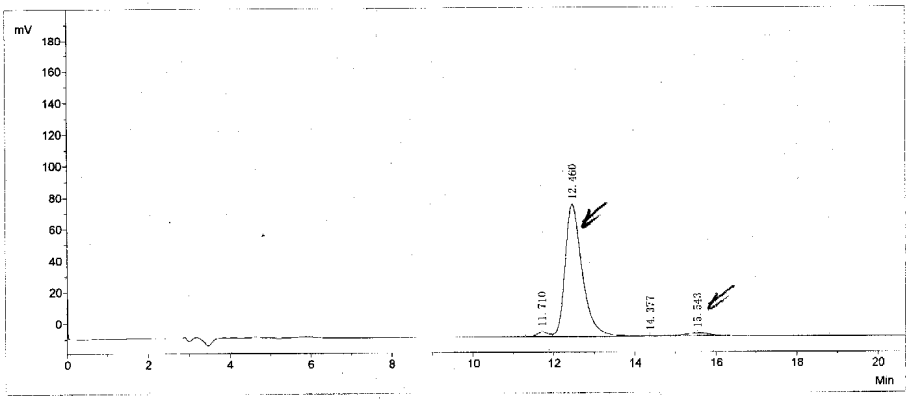


HPLC: Compound **3f** (acetate **6f**), OD column; λ = 230 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.5 mL/min; t_{major} = 17.38 min; t_{minor} = 14.46 min; *ee*% = 90%.

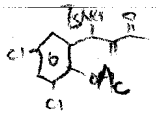
Chiral HPLC trace

金属有机HPLC分析报告

样品文件名:q-1-ad-h.che　　分析者:
分析日期:2006-05-23　　色谱柱:
流动相:　　流速:
检测波长:　　柱压:



No.	R.Time	PeakHeight	PeakArea	PerCent
1	11.710	2905.4	56906.2	2.1917
2	12.460	83649.1	2454688.4	94.5421
3	14.377	314.6	9049.4	0.3485
4	15.543	1766.4	75751.8	2.9176
Total		88635.5	2596395.8	100.0000



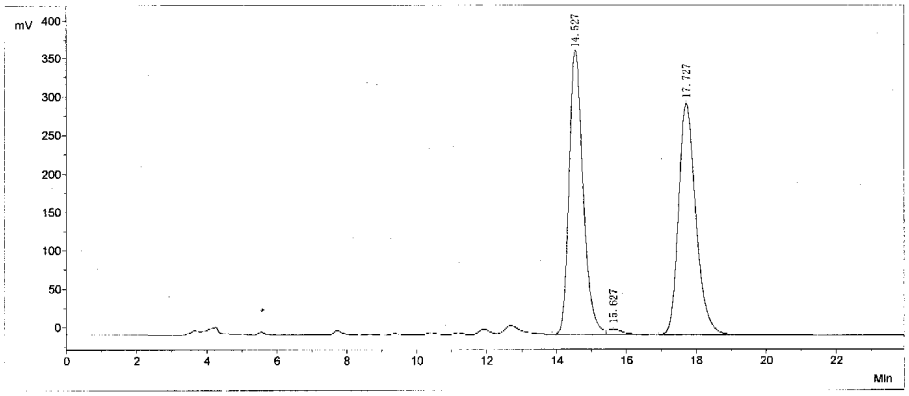
ee = 95%

HPLC: Compound **3g** (acetate **6g**), AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.6 mL/min; t_{major} = 12.46 min; t_{minor} = 15.54 min; *ee*% = 95%.

Chiral HPLC trace

金属有机HPLC分析报告

样品文件名:q3-52.che　　分析者:
分析日期:2005-11-22　　色谱柱:
流动相:　　流速:
检测波长:　　柱压:



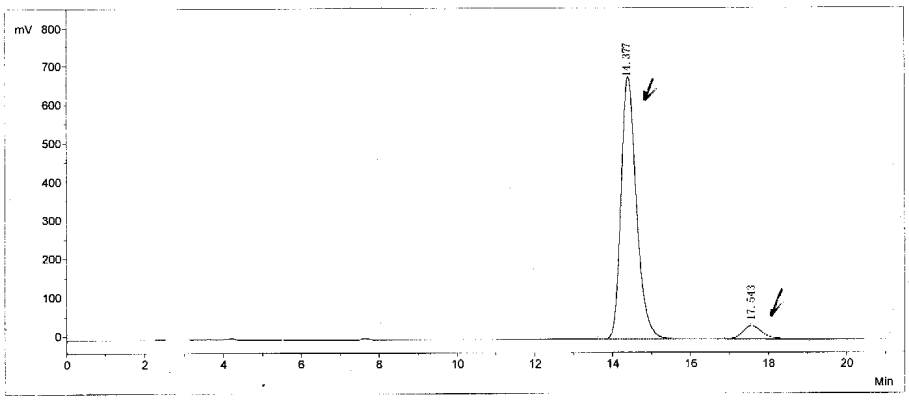
No.	R.Time	PeakHeight	PeakArea	PerCent
1	14.527	366806.5	10284430.0	49.5118
2	15.627	6745.8	189330.9	0.9115
3	17.727	300088.7	10297915.6	49.5767
Total		673641.0	20771676.5	100.0000

HPLC: AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{major} = 14.38 min; t_{minor} = 17.54 min; *racemate*.

Chiral HPLC trace

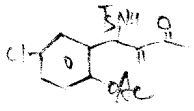
金属有机HPLC分析报告

样品文件名:q3-32.che
分析者:
分析日期:2005-11-22
色谱柱:
流动相:
流速:
检测波长:
柱压:



No.	R.Time	PeakHeight	PeakArea	PerCent	
1	14.377	665013.2	18705678.9	94.2694	✓
2	17.543	33600.5	1137104.1	5.7306	✓
Total		698613.8	19842783.0	100.0000	

ee = 90%



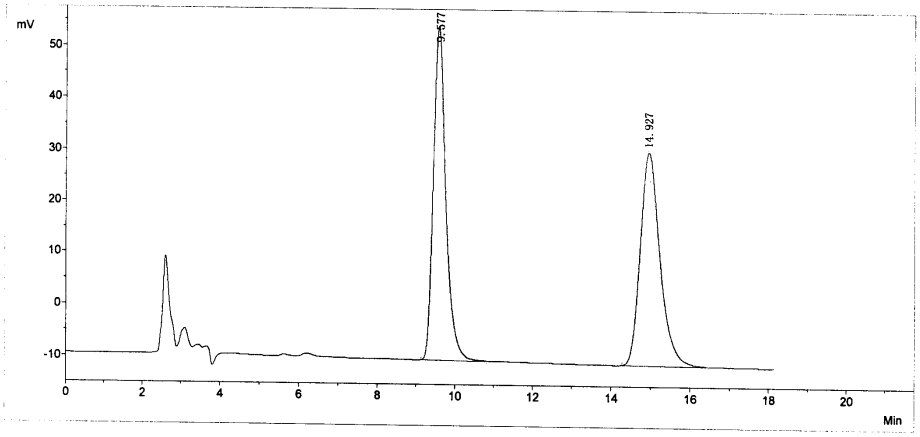
HPLC: Compound **3h** (acetate **6h**), AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.5 mL/min; t_{major} = 14.38 min; t_{minor} = 17.54 min; *ee*% = 90%.

Chiral HPLC trace

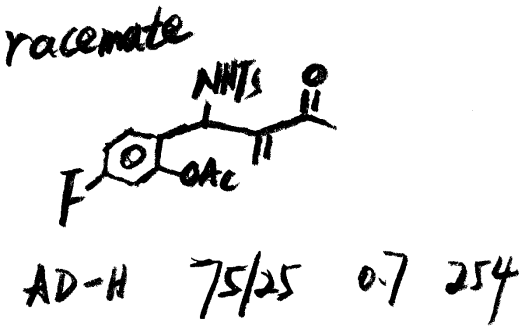
HPLC REPORT

Sample Name:lxg-10-38 ad 75.che
Time:14:19
column: AD-H
Velocity: 75/25 0.7 254

Date:2008-05-06
Method:
the mobile phase:
the detection wavelength:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	9.577	63418.4	1429772.0	50.2061
2	2	14.927	41010.2	1418034.7	49.7939
Total			104428.6	2847806.7	100.0000



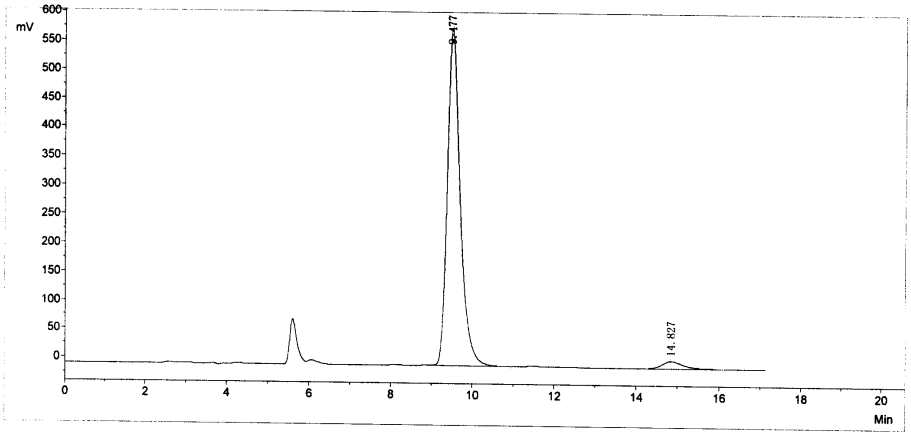
AD-H 75/25 0.7 254

Chiral HPLC report: racemate **3i**, a Chiralcel AD-H column: hexane/*i*PrOH = 75/25, 0.7 mL/min, 254 nm, t_{major} = 9.48 min, t_{minor} = 14.83 min.

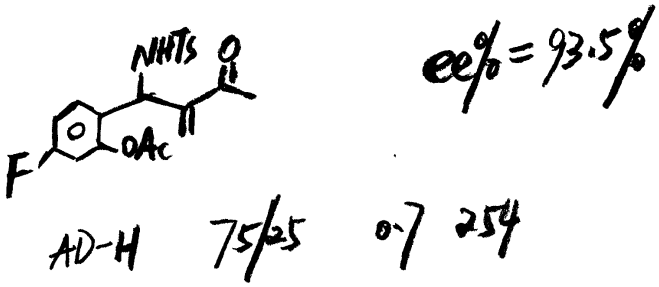
HPLC REPORT

Sample Name:lxg-10-35.che
Time:15:13
column:
Velocity:

Date:2008-05-06
Method:
the mobile phase:
the detection wavelength:



No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	9.477	574991.6	12820877.7	96.7223
2	2	14.827	12276.1	434465.2	3.2777
Total			587267.7	13255342.9	100.0000



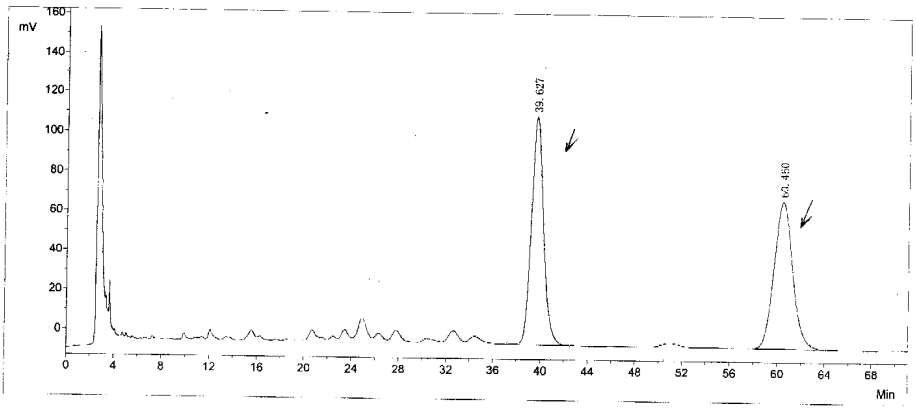
Chiral HPLC report: Enantiomeric excess of compound **3i** (acetate **6i**) was determined by HPLC with a Chiralcel AD-H column: hexane/*i*PrOH = 75/25, 0.7 mL/min, 254 nm, t_{major} = 9.48 min, t_{minor} = 14.83 min; 94% *ee*.

Chiral HPLC trace

金属有机HPLC分析报告

样品文件名:q3-74-s.che
分析日期:2005-12-14
流动相:
检测波长:

分析者:
色谱柱:
流速:
柱压:



No.	R.Time	PeakHeight	PeakArea	PerCent
1	39.627	114710.8	8212532.0	50.3988
2	60.460	74308.4	8082547.3	49.6012
Total		189019.2	16295079.3	100.0000

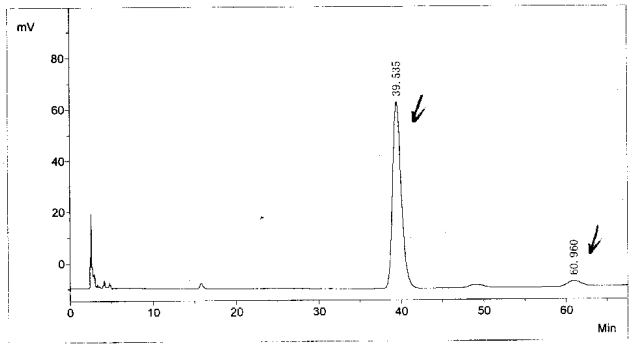
HPLC: AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.5 mL/min; t_{major} = 39.54 min; t_{minor} = 60.96 min; *racemate*.

Chiral HPLC trace

色谱分析报告

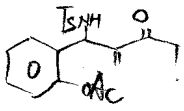
样品名称:送样分析
样品批号:
分析日期:2005-12-15
色谱柱:
流速:
柱压:

样品文件名:q3-75-s.che
分析者:
分析时间:10:33
流动相:
检测波长:



序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1	Unknown	39.535	72677.8	5323109.8	96.0310
2	2	Unknown	60.960	2077.2	220004.7	3.9690
合计:				74755.0	5543114.5	100.0000

ee = 92.1% ≈ 92%

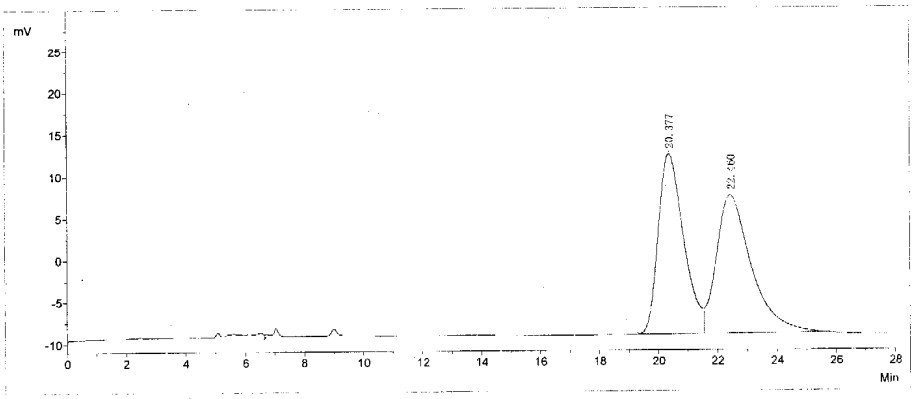


HPLC: Compound **3k** (acetate **6k**), AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.5 mL/min; t_{major} = 39.54 min; t_{minor} = 60.96 min; *ee*% = 92%.

Chiral HPLC trace

金属有机HPLC分析报告

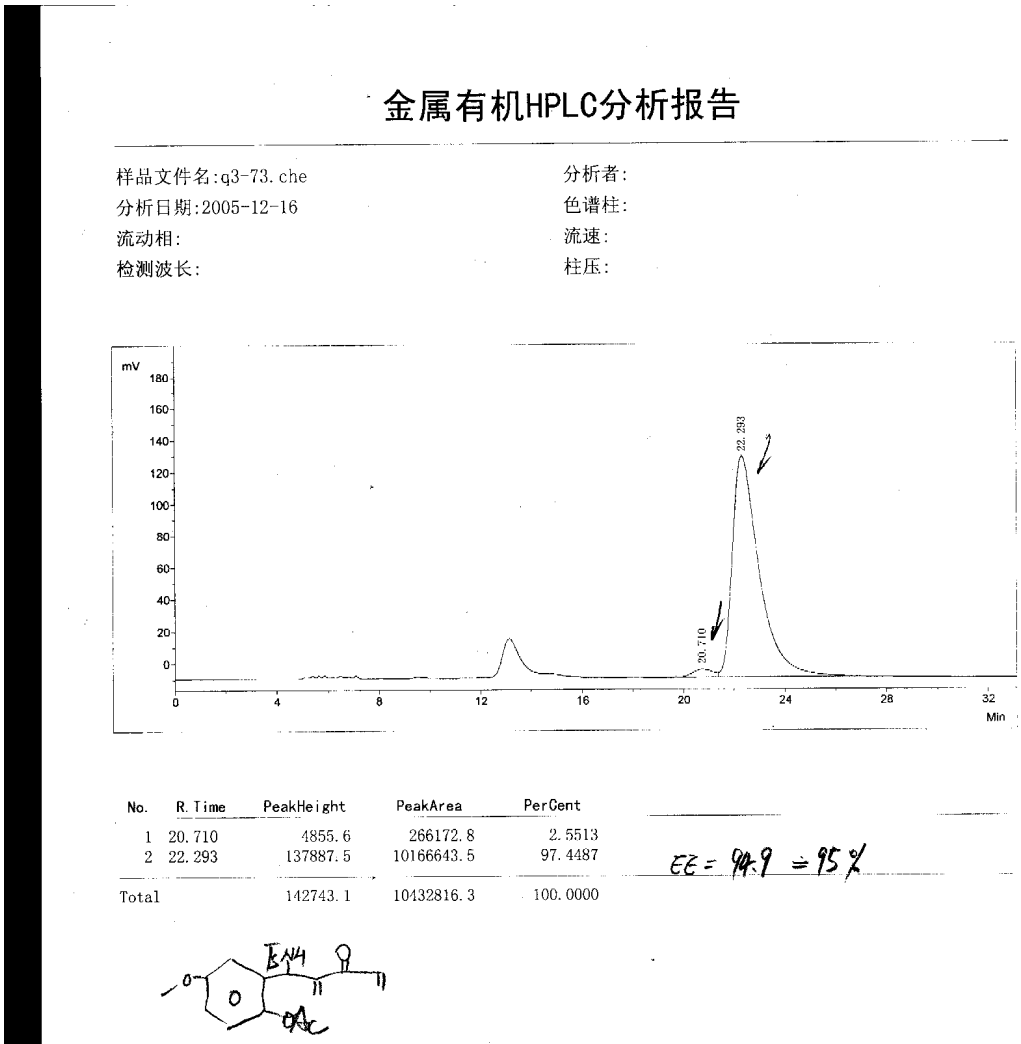
样品文件名:q3-72-od-h-c-80-20.che　　分析者:
分析日期:2005-12-16　　色谱柱:
流动相:　　流速:
检测波长:　　柱压:



No.	R.Time	PeakHeight	PeakArea	PerCent
1	20.377	21507.0	1280327.5	48.6875
2	22.460	16546.9	1349355.5	51.3125
Total		38053.9	2629683.0	100.0000

HPLC: OD column; λ = 230 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.6 mL/min; t_{major} = 22.29 min; t_{minor} = 20.71 min; *racemate*.

Chiral HPLC trace

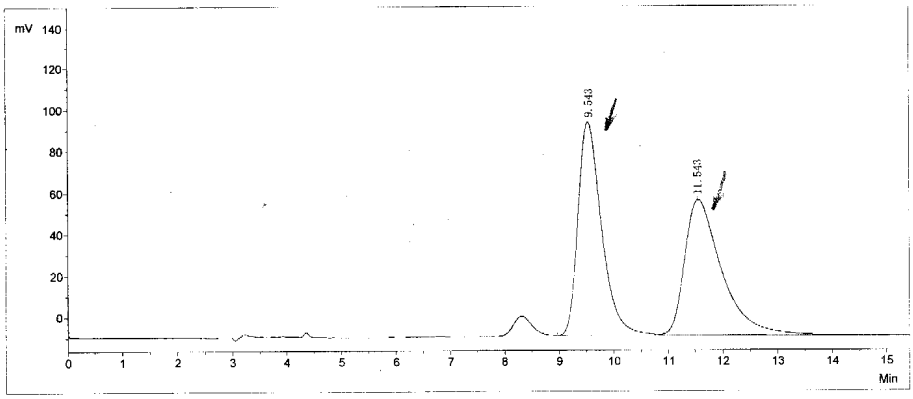


HPLC: Compound **3l** (acetate **6l**), OD column; λ = 230 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.6 mL/min; t_{major} = 22.29 min; t_{minor} = 20.71 min; *ee*% = 95%.

Chiral HPLC trace

金属有机HPLC分析报告

样品文件名:q3-47s.che　　分析者:
分析日期:2005-12-19　　色谱柱:
流动相:　　流速:
检测波长:　　柱压:



No.	R.Time	PeakHeight	PeakArea	PerCent
1	9.543	102733.1	3103539.0	50.1068
2	11.543	65420.4	3090307.2	49.8932
Total		168153.6	6193846.2	100.0000

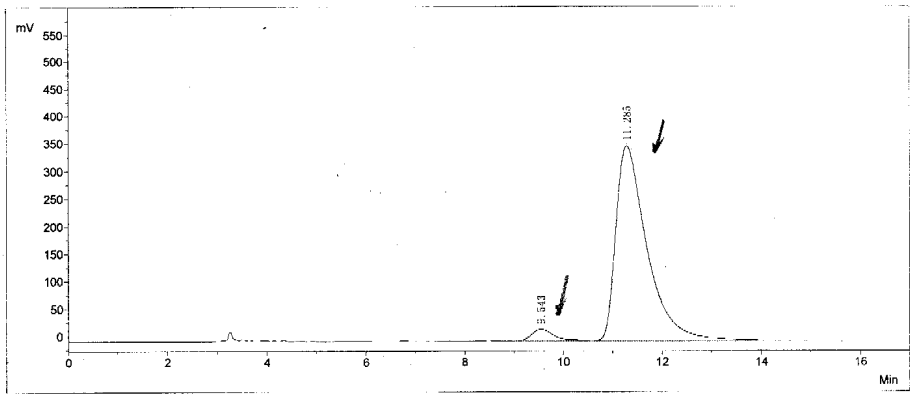
HPLC: OD column; λ = 230 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.6 mL/min; t_{major} = 11.29 min; t_{minor} = 9.54 min; *racemate*.

Chiral HPLC trace

金属有机HPLC分析报告

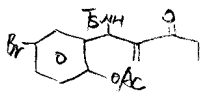
样品文件名:q3-36.che
分析日期:2005-12-19
流动相:
检测波长:

分析者:
色谱柱:
流速:
柱压:



No.	R.Time	PeakHeight	PeakArea	PerCent
1	9.543	21536.5	673239.1	4.1363
2	11.285	353852.4	15603239.8	95.8637
Total		375388.9	16276478.9	100.0000

EE = 91.7 ≈ 92 %

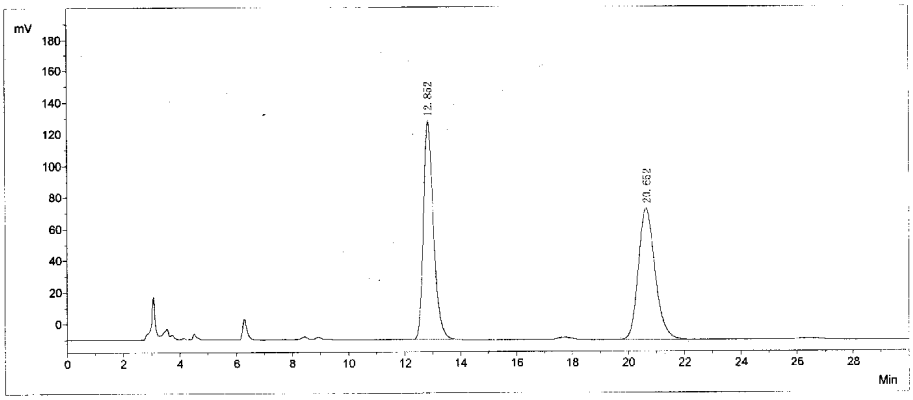


HPLC: Compound **3m** (acetate **6m**), OD column; λ = 230 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.6 mL/min; t_{major} = 11.29 min; t_{minor} = 9.54 min; *ee*% = 92%.

Chiral HPLC trace

金属有机HPLC分析报告

样品文件名:q3-50s.che　　分析者:
分析日期:2005-12-20　　色谱柱:
流动相:　　流速:
检测波长:　　柱压:



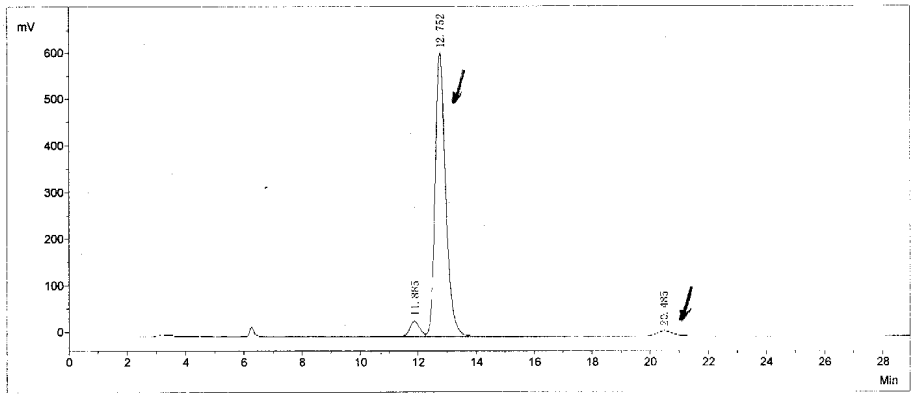
No.	R.Time	PeakHeight	PeakArea	PerCent
1	12.852	137492.9	3435099.0	50.1883
2	20.652	82647.4	3409326.1	49.8117
Total		220140.3	6844425.1	100.0000

HPLC: AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.6 mL/min; t_{major} = 12.75 min; t_{minor} = 20.49 min; *racemate*.

Chiral HPLC trace

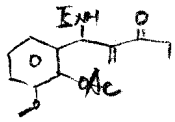
金属有机HPLC分析报告

样品文件名:q3-30.che　　分析者:
分析日期:2005-12-20　　色谱柱:
流动相:　　流速:
检测波长:　　柱压:



No.	R.Time	PeakHeight	PeakArea	PerCent
1	11.885	32343.1	754701.7	4.5671
2	12.752	607815.8	15317715.2	92.6961
3	20.485	11178.3	452251.0	2.7368
Total		651337.2	16524667.9	100.0000

ee = 92.3% ≈ 94%

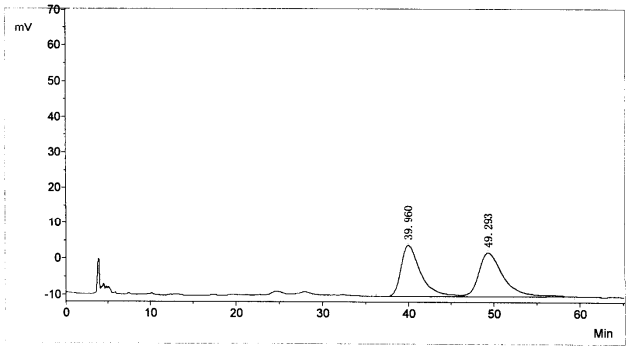


HPLC: Compound **3n** (acetate **6n**), AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.6 mL/min; t_{major} = 12.75 min; t_{minor} = 20.49 min; *ee*% = 94%.

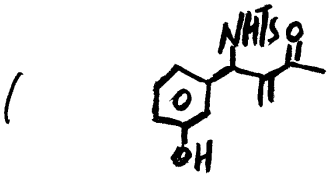
HPLC REPORT

Sample Name: jyq-3-35-3-9-1-od-150.che
Time: 12:12
Column: OD-H (15cmm) 90/0
Wave Length: 0.5 230
色谱柱:
流速:

Date: 2008-05-26
Method:
Flow Rate:
Mobile Phase:
流动相:
检测波长:



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	39.960	14140.6	2250997.4	48.2991
2	2	Unknown	49.293	12089.1	2409541.6	51.7009
Total				26229.7	4660539.0	100.0000



racemate

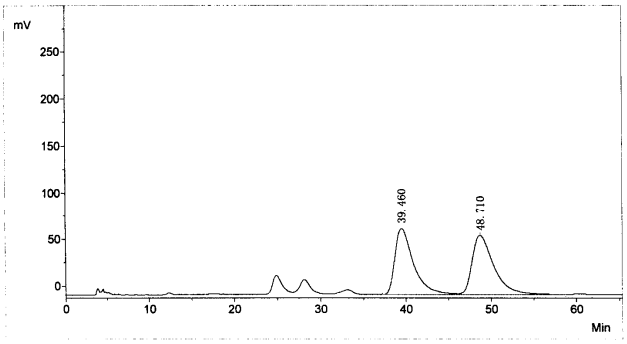
OD-H 90/10 0.5 230

Chiral HPLC report: racemate. a Chiralcel OD-H column: hexane/*i*PrOH = 90/10, 0.5 mL/min, 230 nm, t_{major} = 40.29 min, t_{minor} = 49.79 min

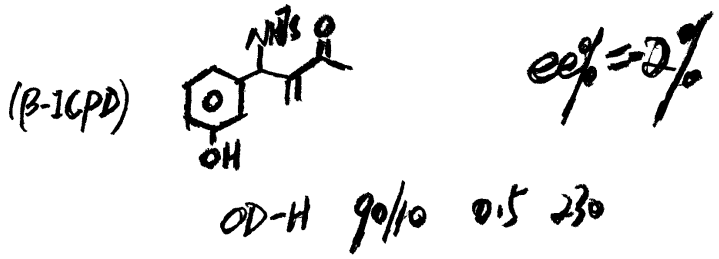
Chiral HPLC trace

HPLC REPORT

Sample Name:jyq-3-25.che
Date:2008-05-26
Time:14:19
Method:
Column:
Flow Rate:
Wave Length:
Mobile Phase:



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	39.460	70492.0	10735366.6	49.0749
2	2	Unknown	48.710	62984.4	11140108.2	50.9251
Total				133476.4	21875474.8	100.0000

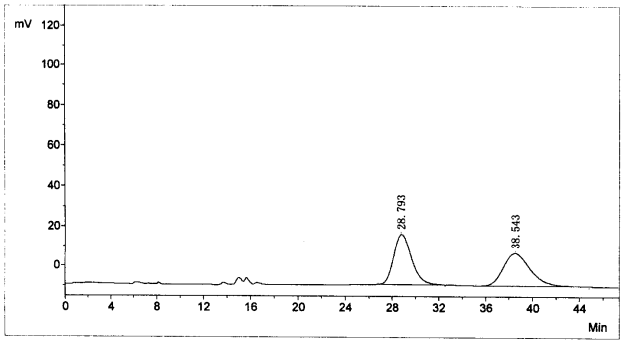


Chiral HPLC report: Enantiomeric excess of **5a** was determined by HPLC with a Chiralcel OD-H column: hexane/*i*PrOH = 90/10, 0.5 mL/min, 230 nm, t_{minor} = 39.46 min; t_{major} = 48.71 min, -2.0% *ee*.

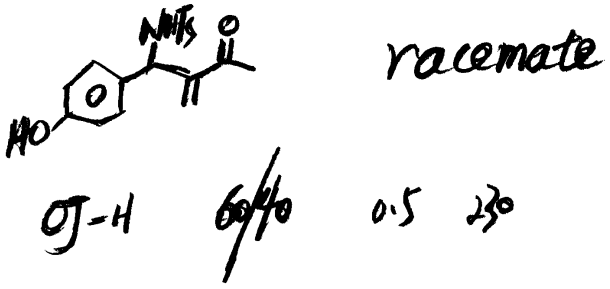
Chiral HPLC trace

HPLC REPORT

Sample Name: lxg-10-48-2-oj-6-4.che
Time: 12:50
Column: OJ-H (250mm) 0.5 60/40
Wave Length: 230
Date: 2008-05-23
Method:
Flow Rate:
Mobile Phase:



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	28.793	25410.3	2713595.0	50.4845
2	2	Unknown	38.543	16502.3	2661505.4	49.5155
Total				41912.5	5375100.4	100.0000



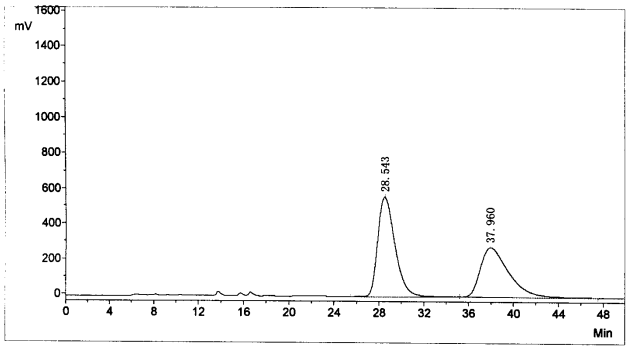
Chiral HPLC report: racemate with a Chiralcel OJ-H column: hexane/*i*PrOH = 60/40, 0.5 mL/min, 230 nm, t_{major} = 28.54 min, t_{minor} = 37.96 min.

Chiral HPLC trace

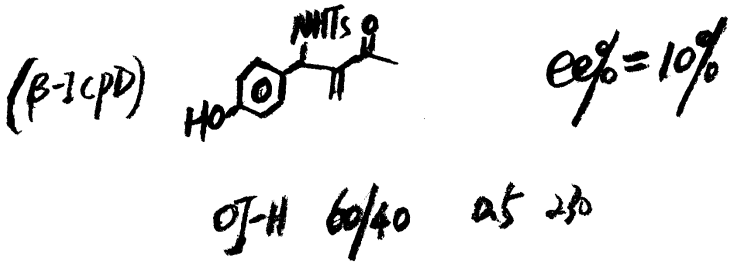
HPLC REPORT

Sample Name:p-OH-3.che
Time:15:16
Column:
Wave Length:

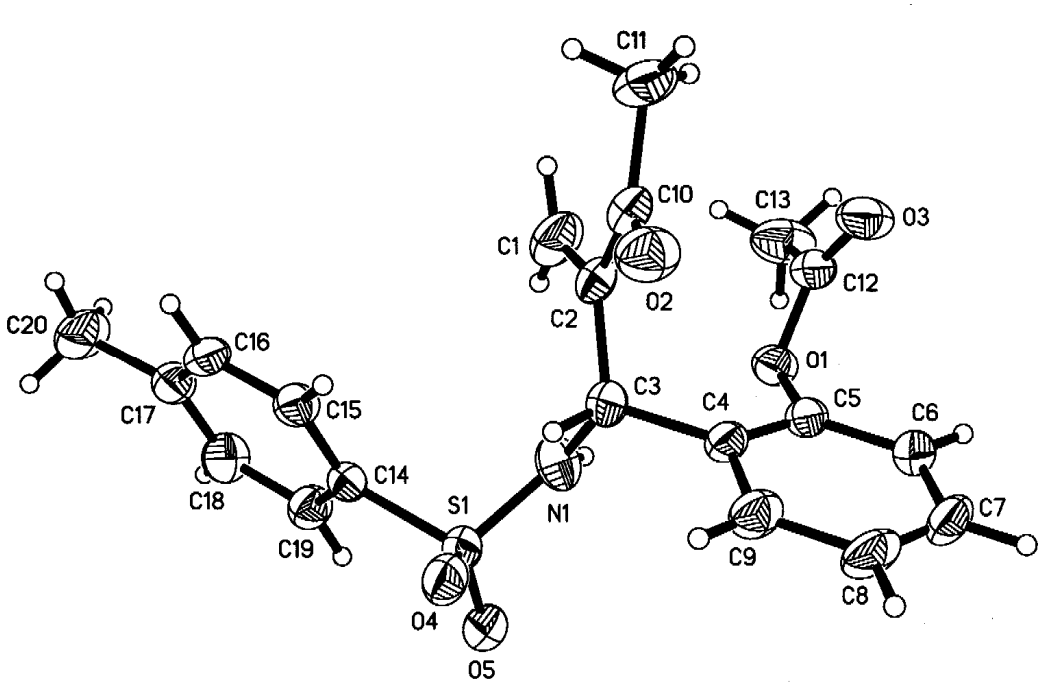
Date:2008-05-23
Method:
Flow Rate:
Mobile Phase:



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	28.543	565429.4	60013922.6	55.0961
2	2	Unknown	37.960	278293.2	48912065.3	44.9039
Total				843722.5	108925987.9	100.0000



Chiral HPLC report: Enantiomeric excess of **5b** was determined by HPLC with a Chiralcel OJ-H column: hexane/*i*PrOH = 60/40, 0.5 mL/min, 230 nm, t_{major} = 28.54 min, t_{minor} = 37.96 min; 10% *ee*.



The crystal data of **6a** have been deposited in CCDC with number 601323. Empirical Formula: $C_{20}H_{21}NO_2S$; Formula Weight: 387.44; Crystal Color, Habit: colorless, prismatic; Crystal System: Monoclinic; Lattice Type: Primitive; Lattice Parameters: a = 8.8105(13)Å, b = 9.4689(13)Å, c = 12.1148(17)Å, $\alpha = 90^o$, $\beta = 103.853(2)^o$, $\gamma = 90^o$, V = 981.3(2)Å^3; Space group: P2(1); Z = 2; D_{calc} = 1.311 g/cm^3; F_{000} = 408; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0636, 0.1529.

Table 1. Crystal data and structure refinement for cd2677.

Identification code	cd2677
Empirical formula	C20 H21 N O5 S
Formula weight	387.44
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 8.8105(13) A alpha = 90 deg. b = 9.4689(13) A beta = 103.853(2) deg. c = 12.1148(17) A gamma = 90 deg.
Volume	981.3(2) A^3
Z, Calculated density	2, 1.311 Mg/m^3
Absorption coefficient	0.195 mm^-1
F(000)	408
Crystal size	0.510 x 0.485 x 0.228 mm
Theta range for data collection	1.73 to 27.00 deg.
Limiting indices	-8<=h<=11, -12<=k<=11, -15<=l<=14
Reflections collected / unique	5737 / 4019 [R(int) = 0.1286]
Completeness to theta = 27.00	99.6 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.53634
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4019 / 2 / 255
Goodness-of-fit on F^2	0.977
Final R indices [I>2sigma(I)]	R1 = 0.0636, wR2 = 0.1529
R indices (all data)	R1 = 0.0727, wR2 = 0.1580
Absolute structure parameter	-0.10(10)
Largest diff. peak and hole	0.471 and -0.339 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd2677.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	-529(1)	9579(1)	10187(1)	52(1)
O(1)	1466(3)	12099(3)	7557(2)	56(1)
O(2)	2616(4)	7528(4)	7491(3)	83(1)
O(3)	3283(3)	11888(4)	6561(2)	80(1)
O(4)	-1038(3)	8208(3)	9779(2)	63(1)
O(5)	-1659(3)	10623(3)	10292(2)	67(1)
N(1)	469(4)	10214(4)	9365(3)	62(1)
C(1)	3734(6)	10203(6)	9529(4)	86(1)
C(2)	2833(4)	9431(5)	8743(3)	59(1)
C(3)	1052(4)	9413(4)	8535(2)	54(1)
C(4)	224(4)	9861(4)	7338(3)	50(1)
C(5)	480(4)	11113(4)	6864(3)	51(1)
C(6)	-285(5)	11504(5)	5782(3)	65(1)
C(7)	-1376(5)	10597(6)	5143(3)	73(1)
C(8)	-1699(4)	9353(6)	5602(3)	77(1)
C(9)	-921(4)	8968(5)	6694(3)	65(1)
C(10)	3455(5)	8414(5)	8029(3)	67(1)
C(11)	5146(5)	8516(8)	7973(4)	105(2)
C(12)	2829(4)	12464(4)	7284(3)	59(1)
C(13)	3588(6)	13632(6)	8016(5)	92(2)
C(14)	741(4)	9365(4)	11537(3)	48(1)
C(15)	1847(4)	8304(4)	11705(3)	55(1)
C(16)	2826(4)	8141(4)	12773(3)	61(1)
C(17)	2736(4)	9019(5)	13666(3)	63(1)
C(18)	1606(5)	10063(4)	13469(3)	68(1)
C(19)	596(4)	10239(4)	12408(3)	60(1)
C(20)	3789(5)	8811(7)	14827(4)	91(1)

Table 3. Bond lengths [A] and angles [deg] for cd2677.

S(1)-O(4)	1.424(3)
S(1)-O(5)	1.430(3)
S(1)-N(1)	1.596(3)
S(1)-C(14)	1.758(3)
O(1)-C(12)	1.364(4)
O(1)-C(5)	1.408(4)
O(2)-C(10)	1.202(5)
O(3)-C(12)	1.180(4)
N(1)-C(3)	1.448(4)
N(1)-H(1)	0.834(19)
C(1)-C(2)	1.307(6)
C(1)-H(1A)	0.9300
C(1)-H(1B)	0.9300
C(2)-C(10)	1.485(6)
C(2)-C(3)	1.529(5)
C(3)-C(4)	1.519(4)
C(3)-H(3)	0.98(4)
C(4)-C(5)	1.359(5)
C(4)-C(9)	1.401(5)
C(5)-C(6)	1.373(5)
C(6)-C(7)	1.381(6)
C(6)-H(6)	0.9300
C(7)-C(8)	1.362(7)
C(7)-H(7)	0.9300
C(8)-C(9)	1.384(6)
C(8)-H(8)	0.9300
C(9)-H(9)	0.9300
C(10)-C(11)	1.510(6)
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-C(13)	1.474(6)
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-C(19)	1.370(5)
C(14)-C(15)	1.380(5)
C(15)-C(16)	1.381(5)
C(15)-H(15)	0.9300
C(16)-C(17)	1.382(5)
C(16)-H(16)	0.9300
C(17)-C(18)	1.383(6)
C(17)-C(20)	1.501(5)
C(18)-C(19)	1.387(5)
C(18)-H(18)	0.9300
C(19)-H(19)	0.9300
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600

O(4)-S(1)-O(5)	119.53(17)
O(4)-S(1)-N(1)	107.54(16)
O(5)-S(1)-N(1)	107.14(17)
O(4)-S(1)-C(14)	107.18(15)
O(5)-S(1)-C(14)	107.37(16)
N(1)-S(1)-C(14)	107.56(17)
C(12)-O(1)-C(5)	118.5(3)
C(3)-N(1)-S(1)	125.2(3)
C(3)-N(1)-H(1)	119(3)
S(1)-N(1)-H(1)	116(3)
C(2)-C(1)-H(1A)	120.0
C(2)-C(1)-H(1B)	120.0
H(1A)-C(1)-H(1B)	120.0
C(1)-C(2)-C(10)	122.9(4)
C(1)-C(2)-C(3)	123.2(4)
C(10)-C(2)-C(3)	113.8(3)
N(1)-C(3)-C(4)	110.3(3)
N(1)-C(3)-C(2)	113.6(3)

C(4)-C(3)-C(2)	113.2(3)
N(1)-C(3)-H(3)	94(2)
C(4)-C(3)-H(3)	114(2)
C(2)-C(3)-H(3)	110(2)
C(5)-C(4)-C(9)	117.4(3)
C(5)-C(4)-C(3)	123.8(3)
C(9)-C(4)-C(3)	118.7(3)
C(4)-C(5)-C(6)	123.0(3)
C(4)-C(5)-O(1)	117.9(3)
C(6)-C(5)-O(1)	118.8(3)
C(5)-C(6)-C(7)	118.9(4)
C(5)-C(6)-H(6)	120.5
C(7)-C(6)-H(6)	120.5
C(8)-C(7)-C(6)	119.7(4)
C(8)-C(7)-H(7)	120.2
C(6)-C(7)-H(7)	120.2
C(7)-C(8)-C(9)	120.9(4)
C(7)-C(8)-H(8)	119.5
C(9)-C(8)-H(8)	119.5
C(8)-C(9)-C(4)	119.9(4)
C(8)-C(9)-H(9)	120.0
C(4)-C(9)-H(9)	120.0
O(2)-C(10)-C(2)	120.3(4)
O(2)-C(10)-C(11)	120.4(4)
C(2)-C(10)-C(11)	119.4(4)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
O(3)-C(12)-O(1)	122.6(4)
O(3)-C(12)-C(13)	127.4(4)
O(1)-C(12)-C(13)	110.1(3)
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(19)-C(14)-C(15)	121.2(3)
C(19)-C(14)-S(1)	119.4(3)
C(15)-C(14)-S(1)	119.4(2)
C(14)-C(15)-C(16)	118.7(3)
C(14)-C(15)-H(15)	120.6
C(16)-C(15)-H(15)	120.6
C(15)-C(16)-C(17)	121.7(3)
C(15)-C(16)-H(16)	119.1
C(17)-C(16)-H(16)	119.1
C(16)-C(17)-C(18)	118.0(3)
C(16)-C(17)-C(20)	121.1(4)
C(18)-C(17)-C(20)	120.9(4)
C(17)-C(18)-C(19)	121.4(3)
C(17)-C(18)-H(18)	119.3
C(19)-C(18)-H(18)	119.3
C(14)-C(19)-C(18)	119.0(4)
C(14)-C(19)-H(19)	120.5
C(18)-C(19)-H(19)	120.5
C(17)-C(20)-H(20A)	109.5
C(17)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(17)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd2677.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	50(1)	61(1)	44(1)	6(1)	7(1)	-4(1)
O(1)	50(1)	68(2)	53(1)	-7(1)	15(1)	-4(1)
O(2)	70(2)	98(2)	80(2)	-16(2)	17(2)	5(2)
O(3)	48(2)	122(3)	71(2)	-26(2)	17(1)	-9(2)
O(4)	62(2)	70(2)	52(1)	7(1)	3(1)	-4(1)
O(5)	61(2)	74(2)	64(2)	13(1)	13(1)	11(1)
N(1)	85(2)	53(2)	53(2)	-5(1)	25(2)	-5(2)
C(1)	69(3)	110(3)	62(2)	-2(2)	-13(2)	0(3)
C(2)	48(2)	80(2)	42(2)	9(2)	-4(1)	0(2)
C(3)	53(2)	66(2)	40(1)	1(2)	7(1)	-2(2)
C(4)	40(2)	67(2)	41(1)	-3(1)	5(1)	4(1)
C(5)	41(2)	68(2)	42(2)	-6(2)	9(1)	2(2)
C(6)	54(2)	93(3)	48(2)	8(2)	13(2)	11(2)
C(7)	54(2)	115(4)	43(2)	-3(2)	-6(2)	17(2)
C(8)	46(2)	114(4)	59(2)	-25(2)	-11(2)	-1(2)
C(9)	51(2)	75(2)	62(2)	-8(2)	1(2)	-6(2)
C(10)	52(2)	93(3)	50(2)	13(2)	0(2)	11(2)
C(11)	47(2)	174(6)	86(3)	4(3)	0(2)	19(3)
C(12)	45(2)	75(2)	59(2)	-1(2)	12(2)	1(2)
C(13)	62(3)	106(3)	109(4)	-35(3)	23(3)	-17(3)
C(14)	44(2)	56(2)	44(1)	4(1)	11(1)	-5(1)
C(15)	50(2)	70(2)	46(2)	-5(2)	13(1)	3(2)
C(16)	42(2)	82(3)	56(2)	5(2)	7(2)	9(2)
C(17)	48(2)	90(3)	48(2)	3(2)	6(2)	-7(2)
C(18)	76(3)	80(2)	47(2)	-15(2)	12(2)	-2(2)
C(19)	57(2)	69(2)	54(2)	-1(2)	9(2)	3(2)
C(20)	66(3)	137(4)	58(2)	-5(3)	-11(2)	0(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd2677.

	x	y	z	U(eq)
H(1A)	4815	10128	9661	103
H(1B)	3294	10827	9957	103
H(6)	-72	12367	5485	78
H(7)	-1888	10834	4402	88
H(8)	-2452	8753	5177	92
H(9)	-1158	8119	6999	78
H(11A)	5315	7932	7366	157
H(11B)	5806	8202	8680	157
H(11C)	5391	9479	7837	157
H(13A)	4251	13254	8698	138
H(13B)	2804	14222	8208	138
H(13C)	4204	14180	7618	138
H(15)	1931	7711	11111	66
H(16)	3566	7422	12894	73
H(18)	1520	10660	14061	82
H(19)	-166	10939	12289	73
H(20A)	4519	8067	14800	137
H(20B)	3173	8563	15353	137
H(20C)	4348	9670	15070	137
H(1)	600(50)	11090(20)	9400(40)	70(13)
H(3)	700(40)	8500(40)	8770(30)	60(11)

Table 6. Torsion angles [deg] for cd2677.

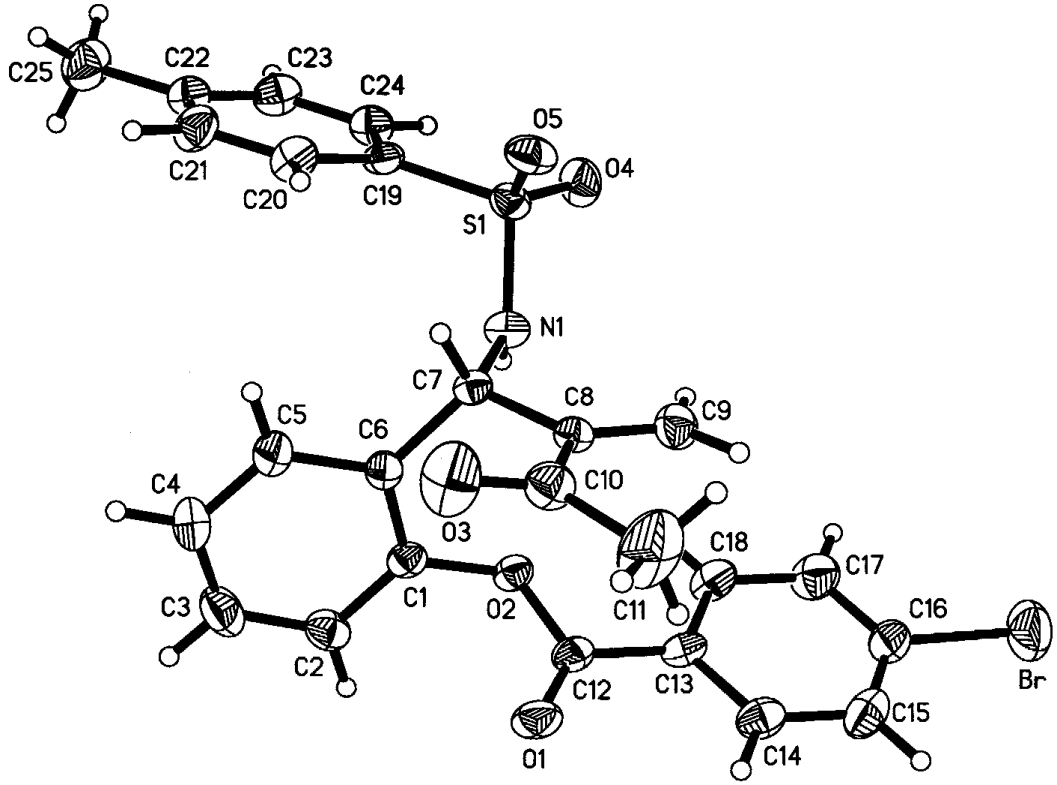
O(4)-S(1)-N(1)-C(3)	-13.4(4)
O(5)-S(1)-N(1)-C(3)	-143.0(3)
C(14)-S(1)-N(1)-C(3)	101.8(3)
S(1)-N(1)-C(3)-C(4)	112.3(4)
S(1)-N(1)-C(3)-C(2)	-119.4(4)
C(1)-C(2)-C(3)-N(1)	-6.1(6)
C(10)-C(2)-C(3)-N(1)	169.6(3)
C(1)-C(2)-C(3)-C(4)	120.7(4)
C(10)-C(2)-C(3)-C(4)	-63.6(4)
N(1)-C(3)-C(4)-C(5)	72.5(4)
C(2)-C(3)-C(4)-C(5)	-56.0(5)
N(1)-C(3)-C(4)-C(9)	-104.6(4)
C(2)-C(3)-C(4)-C(9)	126.8(4)
C(9)-C(4)-C(5)-C(6)	-2.4(5)
C(3)-C(4)-C(5)-C(6)	-179.6(3)
C(9)-C(4)-C(5)-O(1)	171.4(3)
C(3)-C(4)-C(5)-O(1)	-5.8(5)
C(12)-O(1)-C(5)-C(4)	116.4(4)
C(12)-O(1)-C(5)-C(6)	-69.5(4)
C(4)-C(5)-C(6)-C(7)	0.5(5)
O(1)-C(5)-C(6)-C(7)	-173.3(3)
C(5)-C(6)-C(7)-C(8)	1.6(6)
C(6)-C(7)-C(8)-C(9)	-1.5(6)
C(7)-C(8)-C(9)-C(4)	-0.5(6)
C(5)-C(4)-C(9)-C(8)	2.4(5)
C(3)-C(4)-C(9)-C(8)	179.8(3)
C(1)-C(2)-C(10)-O(2)	164.6(5)
C(3)-C(2)-C(10)-O(2)	-11.2(5)
C(1)-C(2)-C(10)-C(11)	-16.3(6)
C(3)-C(2)-C(10)-C(11)	167.9(4)
C(5)-O(1)-C(12)-O(3)	-7.5(6)
C(5)-O(1)-C(12)-C(13)	172.8(4)
O(4)-S(1)-C(14)-C(19)	-135.5(3)
O(5)-S(1)-C(14)-C(19)	-5.9(3)
N(1)-S(1)-C(14)-C(19)	109.1(3)
O(4)-S(1)-C(14)-C(15)	43.4(3)
O(5)-S(1)-C(14)-C(15)	173.0(3)
N(1)-S(1)-C(14)-C(15)	-72.0(3)
C(19)-C(14)-C(15)-C(16)	-0.5(5)
S(1)-C(14)-C(15)-C(16)	-179.4(3)
C(14)-C(15)-C(16)-C(17)	-0.7(5)
C(15)-C(16)-C(17)-C(18)	1.2(6)
C(15)-C(16)-C(17)-C(20)	178.9(4)
C(16)-C(17)-C(18)-C(19)	-0.5(6)
C(20)-C(17)-C(18)-C(19)	-178.1(4)
C(15)-C(14)-C(19)-C(18)	1.2(5)
S(1)-C(14)-C(19)-C(18)	-179.9(3)
C(17)-C(18)-C(19)-C(14)	-0.7(6)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd2677 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(4)#1	0.834(19)	2.23(3)	3.019(4)	157(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y+1/2,-z+2



The crystal data of **7a** have been deposited in CCDC with number 632081. Empirical Formula: $C_{25}H_{22}BrNO_5S$; Formula Weight: 528.41; Crystal Color, Habit: colorless, prismatic; Crystal System: Orthorhombic; Lattice Type: Primitive; Lattice Parameters: a = 8.9781(11)Å, b = 10.3536(12)Å, c = 25.647(3)Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 2384.0(5)Å^3; Space group: P2(1)2(1)2(1); Z = 4; D_{calc} = 1.472 g/cm^3; F_{000} = 1080; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0407, 0.0785.

Table 1. Crystal data and structure refinement for cd26535.

Identification code	cd26535
Empirical formula	C25 H22 Br N O5 S
Formula weight	528.41
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 8.9781(11) A alpha = 90 deg. b = 10.3536(12) A beta = 90 deg. c = 25.647(3) A gamma = 90 deg.
Volume	2384.0(5) A^3
Z, Calculated density	4, 1.472 Mg/m^3
Absorption coefficient	1.848 mm^-1
F(000)	1080
Crystal size	0.506 x 0.422 x 0.347 mm
Theta range for data collection	2.12 to 26.99 deg.
Limiting indices	-11<=h<=11, -12<=k<=13, -32<=l<=23
Reflections collected / unique	14054 / 5149 [R(int) = 0.0543]
Completeness to theta = 26.99	99.7 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.64925
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5149 / 1 / 309
Goodness-of-fit on F^2	0.847
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.0785
R indices (all data)	R1 = 0.0653, wR2 = 0.0830
Absolute structure parameter	0.002(7)
Extinction coefficient	0.0101(6)
Largest diff. peak and hole	0.475 and -0.443 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd26535.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br	4370(1)	4310(1)	9643(1)	93(1)
S(1)	3306(1)	1977(1)	6398(1)	42(1)
O(1)	-59(3)	6504(2)	7665(1)	56(1)
O(2)	145(2)	4405(2)	7464(1)	39(1)
O(3)	2333(3)	6856(2)	6315(1)	87(1)
O(4)	3721(2)	983(2)	6757(1)	60(1)
O(5)	4413(2)	2753(2)	6148(1)	54(1)
N(1)	2260(3)	2954(2)	6720(1)	40(1)
C(1)	-529(3)	4637(3)	6980(1)	37(1)
C(2)	-2058(3)	4837(3)	6956(1)	49(1)
C(3)	-2706(4)	4955(4)	6480(2)	65(1)
C(4)	-1863(4)	4908(3)	6034(1)	64(1)
C(5)	-348(4)	4729(3)	6069(1)	52(1)
C(6)	355(3)	4576(3)	6543(1)	36(1)
C(7)	2016(3)	4300(3)	6566(1)	34(1)
C(8)	2911(3)	5224(3)	6900(1)	36(1)
C(9)	3713(3)	4846(3)	7301(1)	51(1)
C(10)	2920(4)	6572(3)	6721(1)	53(1)
C(11)	3690(6)	7589(4)	7044(2)	104(2)
C(12)	370(3)	5449(3)	7777(1)	41(1)
C(13)	1245(3)	5096(3)	8244(1)	43(1)
C(14)	1749(4)	6108(3)	8551(1)	51(1)
C(15)	2651(4)	5866(4)	8975(1)	61(1)
C(16)	3044(4)	4634(4)	9084(1)	56(1)
C(17)	2547(4)	3612(4)	8790(1)	65(1)
C(18)	1635(4)	3851(3)	8365(1)	55(1)
C(19)	2225(3)	1247(3)	5907(1)	40(1)
C(20)	1755(3)	1960(3)	5485(1)	52(1)
C(21)	879(4)	1401(3)	5111(1)	57(1)
C(22)	487(4)	132(3)	5137(1)	52(1)
C(23)	981(3)	-590(3)	5554(1)	54(1)
C(24)	1833(4)	-38(3)	5940(1)	47(1)
C(25)	-475(4)	-478(4)	4720(1)	75(1)

Table 3. Bond lengths [A] and angles [deg] for cd26535.

Br-C(16)	1.894(3)
S(1)-O(4)	1.430(2)
S(1)-O(5)	1.430(2)
S(1)-N(1)	1.609(3)
S(1)-C(19)	1.760(3)
O(1)-C(12)	1.194(3)
O(2)-C(12)	1.360(3)
O(2)-C(1)	1.402(3)
O(3)-C(10)	1.204(4)
N(1)-C(7)	1.466(4)
N(1)-H(1)	0.813(17)
C(1)-C(6)	1.375(4)
C(1)-C(2)	1.390(4)
C(2)-C(3)	1.358(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.374(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.376(5)
C(4)-H(4)	0.9300
C(5)-C(6)	1.380(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.519(4)
C(7)-C(8)	1.516(4)
C(7)-H(7)	0.93(2)
C(8)-C(9)	1.314(4)
C(8)-C(10)	1.469(4)
C(9)-H(9A)	0.9300
C(9)-H(9B)	0.9300
C(10)-C(11)	1.508(5)
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-C(13)	1.478(4)
C(13)-C(18)	1.371(4)
C(13)-C(14)	1.387(4)
C(14)-C(15)	1.378(4)
C(14)-H(14)	0.9300
C(15)-C(16)	1.353(5)
C(15)-H(15)	0.9300
C(16)-C(17)	1.374(5)
C(17)-C(18)	1.384(4)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
C(19)-C(20)	1.376(4)
C(19)-C(24)	1.379(4)
C(20)-C(21)	1.369(4)
C(20)-H(20)	0.9300
C(21)-C(22)	1.362(4)
C(21)-H(21)	0.9300
C(22)-C(23)	1.378(4)
C(22)-C(25)	1.512(4)
C(23)-C(24)	1.375(4)
C(23)-H(23)	0.9300
C(24)-H(24)	0.9300
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
O(4)-S(1)-O(5)	120.79(13)
O(4)-S(1)-N(1)	105.88(14)
O(5)-S(1)-N(1)	106.41(14)
O(4)-S(1)-C(19)	107.16(14)
O(5)-S(1)-C(19)	107.69(13)
N(1)-S(1)-C(19)	108.43(13)
C(12)-O(2)-C(1)	116.8(2)
C(7)-N(1)-S(1)	123.1(2)
C(7)-N(1)-H(1)	119(2)
S(1)-N(1)-H(1)	114(2)

C(6)-C(1)-C(2)	122.7(3)
C(6)-C(1)-O(2)	117.7(2)
C(2)-C(1)-O(2)	119.4(3)
C(3)-C(2)-C(1)	118.5(3)
C(3)-C(2)-H(2)	120.8
C(1)-C(2)-H(2)	120.8
C(2)-C(3)-C(4)	120.7(3)
C(2)-C(3)-H(3)	119.7
C(4)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	119.6(3)
C(3)-C(4)-H(4)	120.2
C(5)-C(4)-H(4)	120.2
C(4)-C(5)-C(6)	121.7(3)
C(4)-C(5)-H(5)	119.1
C(6)-C(5)-H(5)	119.1
C(1)-C(6)-C(5)	116.7(3)
C(1)-C(6)-C(7)	123.0(2)
C(5)-C(6)-C(7)	120.3(2)
N(1)-C(7)-C(8)	111.6(2)
N(1)-C(7)-C(6)	109.6(2)
C(8)-C(7)-C(6)	115.1(2)
N(1)-C(7)-H(7)	105.1(14)
C(8)-C(7)-H(7)	106.4(13)
C(6)-C(7)-H(7)	108.5(12)
C(9)-C(8)-C(10)	121.7(3)
C(9)-C(8)-C(7)	123.0(3)
C(10)-C(8)-C(7)	115.1(3)
C(8)-C(9)-H(9A)	120.0
C(8)-C(9)-H(9B)	120.0
H(9A)-C(9)-H(9B)	120.0
O(3)-C(10)-C(8)	120.1(3)
O(3)-C(10)-C(11)	120.4(3)
C(8)-C(10)-C(11)	119.6(3)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
O(1)-C(12)-O(2)	122.4(3)
O(1)-C(12)-C(13)	126.4(3)
O(2)-C(12)-C(13)	111.1(3)
C(18)-C(13)-C(14)	119.9(3)
C(18)-C(13)-C(12)	123.5(3)
C(14)-C(13)-C(12)	116.5(3)
C(15)-C(14)-C(13)	120.1(3)
C(15)-C(14)-H(14)	119.9
C(13)-C(14)-H(14)	119.9
C(16)-C(15)-C(14)	119.2(3)
C(16)-C(15)-H(15)	120.4
C(14)-C(15)-H(15)	120.4
C(15)-C(16)-C(17)	121.9(3)
C(15)-C(16)-Br	119.2(3)
C(17)-C(16)-Br	118.9(3)
C(16)-C(17)-C(18)	119.1(3)
C(16)-C(17)-H(17)	120.5
C(18)-C(17)-H(17)	120.5
C(13)-C(18)-C(17)	119.8(3)
C(13)-C(18)-H(18)	120.1
C(17)-C(18)-H(18)	120.1
C(20)-C(19)-C(24)	119.2(3)
C(20)-C(19)-S(1)	120.1(3)
C(24)-C(19)-S(1)	120.7(2)
C(21)-C(20)-C(19)	120.0(3)
C(21)-C(20)-H(20)	120.0
C(19)-C(20)-H(20)	120.0
C(22)-C(21)-C(20)	121.5(3)
C(22)-C(21)-H(21)	119.3
C(20)-C(21)-H(21)	119.3
C(21)-C(22)-C(23)	118.5(3)
C(21)-C(22)-C(25)	121.1(3)
C(23)-C(22)-C(25)	120.4(3)

C(24)-C(23)-C(22)	120.8(3)
C(24)-C(23)-H(23)	119.6
C(22)-C(23)-H(23)	119.6
C(23)-C(24)-C(19)	119.9(3)
C(23)-C(24)-H(24)	120.1
C(19)-C(24)-H(24)	120.1
C(22)-C(25)-H(25A)	109.5
C(22)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(22)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd26535.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br	80(1)	133(1)	65(1)	2(1)	-19(1)	6(1)
S(1)	41(1)	36(1)	49(1)	-2(1)	1(1)	6(1)
O(1)	79(2)	35(1)	53(1)	-6(1)	1(1)	15(1)
O(2)	49(1)	33(1)	36(1)	-2(1)	1(1)	2(1)
O(3)	128(2)	45(2)	89(2)	19(1)	-29(2)	-10(2)
O(4)	72(2)	44(1)	63(1)	4(1)	-19(1)	12(1)
O(5)	40(1)	54(1)	68(1)	-7(1)	15(1)	0(1)
N(1)	45(1)	29(1)	44(2)	5(1)	11(1)	-1(1)
C(1)	45(2)	27(2)	40(2)	-3(1)	0(2)	0(1)
C(2)	37(2)	50(2)	59(2)	-1(2)	6(2)	-2(2)
C(3)	40(2)	72(3)	84(3)	-1(2)	-12(2)	6(2)
C(4)	59(2)	78(3)	55(2)	2(2)	-20(2)	8(2)
C(5)	51(2)	66(2)	39(2)	-1(2)	-5(2)	5(2)
C(6)	39(2)	31(2)	38(2)	0(1)	-3(1)	-1(1)
C(7)	40(2)	32(2)	30(2)	3(1)	4(1)	0(1)
C(8)	33(2)	37(2)	38(2)	-1(1)	4(1)	2(1)
C(9)	44(2)	50(2)	57(2)	-4(2)	-4(2)	-2(2)
C(10)	55(2)	44(2)	59(2)	-1(2)	1(2)	-1(2)
C(11)	144(4)	50(3)	119(4)	-12(2)	-36(3)	-24(3)
C(12)	41(2)	44(2)	37(2)	-7(2)	9(1)	-3(2)
C(13)	54(2)	41(2)	36(2)	-6(2)	12(2)	0(2)
C(14)	59(2)	42(2)	52(2)	-5(2)	9(2)	-6(2)
C(15)	62(2)	72(3)	49(2)	-13(2)	4(2)	-22(2)
C(16)	56(2)	71(3)	40(2)	-5(2)	0(2)	3(2)
C(17)	87(3)	63(3)	46(2)	6(2)	1(2)	11(2)
C(18)	78(2)	44(2)	43(2)	-3(2)	1(2)	2(2)
C(19)	45(2)	41(2)	33(2)	-3(1)	8(1)	8(1)
C(20)	70(2)	39(2)	45(2)	4(2)	3(2)	-1(2)
C(21)	76(3)	55(2)	40(2)	4(2)	-2(2)	5(2)
C(22)	50(2)	56(2)	49(2)	-4(2)	3(2)	2(2)
C(23)	61(2)	42(2)	60(2)	-8(2)	8(2)	-10(2)
C(24)	55(2)	35(2)	52(2)	5(2)	2(2)	4(2)
C(25)	72(2)	81(3)	70(2)	-15(2)	-6(2)	-16(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd26535.

	x	y	z	U(eq)
H(2)	-2624	4889	7259	58
H(3)	-3731	5068	6456	78
H(4)	-2313	4997	5709	77
H(5)	217	4710	5765	62
H(9A)	4306	5436	7479	61
H(9B)	3687	3987	7407	61
H(11A)	4722	7365	7084	127
H(11B)	3227	7639	7380	127
H(11C)	3613	8410	6872	127
H(14)	1478	6952	8471	61
H(15)	2985	6541	9183	73
H(17)	2819	2771	8875	78
H(18)	1288	3169	8163	66
H(20)	2031	2823	5455	62
H(21)	546	1898	4833	68
H(23)	735	-1461	5575	65
H(24)	2144	-531	6223	57
H(25A)	-203	-1369	4679	112
H(25B)	-331	-31	4396	112
H(25C)	-1503	-421	4821	112
H(7)	2400(20)	4360(20)	6229(8)	58(5)
H(1)	1640(30)	2600(30)	6900(9)	42(9)

Table 6. Torsion angles [deg] for cd26535.

O(4)-S(1)-N(1)-C(7)	158.2(2)
O(5)-S(1)-N(1)-C(7)	28.5(3)
C(19)-S(1)-N(1)-C(7)	-87.1(2)
C(12)-O(2)-C(1)-C(6)	106.3(3)
C(12)-O(2)-C(1)-C(2)	-77.6(3)
C(6)-C(1)-C(2)-C(3)	1.1(5)
O(2)-C(1)-C(2)-C(3)	-174.7(3)
C(1)-C(2)-C(3)-C(4)	-1.5(5)
C(2)-C(3)-C(4)-C(5)	0.6(6)
C(3)-C(4)-C(5)-C(6)	0.9(5)
C(2)-C(1)-C(6)-C(5)	0.3(4)
O(2)-C(1)-C(6)-C(5)	176.1(2)
C(2)-C(1)-C(6)-C(7)	-177.3(3)
O(2)-C(1)-C(6)-C(7)	-1.4(4)
C(4)-C(5)-C(6)-C(1)	-1.3(5)
C(4)-C(5)-C(6)-C(7)	176.3(3)
S(1)-N(1)-C(7)-C(8)	-103.1(2)
S(1)-N(1)-C(7)-C(6)	128.2(2)
C(1)-C(6)-C(7)-N(1)	69.8(3)
C(5)-C(6)-C(7)-N(1)	-107.6(3)
C(1)-C(6)-C(7)-C(8)	-56.9(4)
C(5)-C(6)-C(7)-C(8)	125.6(3)
N(1)-C(7)-C(8)-C(9)	-4.6(4)
C(6)-C(7)-C(8)-C(9)	121.1(3)
N(1)-C(7)-C(8)-C(10)	170.7(2)
C(6)-C(7)-C(8)-C(10)	-63.6(3)
C(9)-C(8)-C(10)-O(3)	170.3(3)
C(7)-C(8)-C(10)-O(3)	-5.1(4)
C(9)-C(8)-C(10)-C(11)	-8.7(5)
C(7)-C(8)-C(10)-C(11)	175.9(3)
C(1)-O(2)-C(12)-O(1)	4.4(4)
C(1)-O(2)-C(12)-C(13)	-173.2(2)
O(1)-C(12)-C(13)-C(18)	176.3(3)
O(2)-C(12)-C(13)-C(18)	-6.2(4)
O(1)-C(12)-C(13)-C(14)	-7.3(5)
O(2)-C(12)-C(13)-C(14)	170.1(3)
C(18)-C(13)-C(14)-C(15)	0.6(5)
C(12)-C(13)-C(14)-C(15)	-175.9(3)
C(13)-C(14)-C(15)-C(16)	0.5(5)
C(14)-C(15)-C(16)-C(17)	-1.3(5)
C(14)-C(15)-C(16)-Br	176.6(2)
C(15)-C(16)-C(17)-C(18)	1.0(5)
Br-C(16)-C(17)-C(18)	-176.9(3)
C(14)-C(13)-C(18)-C(17)	-0.9(5)
C(12)-C(13)-C(18)-C(17)	175.4(3)
C(16)-C(17)-C(18)-C(13)	0.1(5)
O(4)-S(1)-C(19)-C(20)	-175.4(2)
O(5)-S(1)-C(19)-C(20)	-44.1(3)
N(1)-S(1)-C(19)-C(20)	70.7(3)
O(4)-S(1)-C(19)-C(24)	5.0(3)
O(5)-S(1)-C(19)-C(24)	136.3(2)
N(1)-S(1)-C(19)-C(24)	-108.9(3)
C(24)-C(19)-C(20)-C(21)	1.4(5)
S(1)-C(19)-C(20)-C(21)	-178.2(2)
C(19)-C(20)-C(21)-C(22)	-1.7(5)
C(20)-C(21)-C(22)-C(23)	0.5(5)
C(20)-C(21)-C(22)-C(25)	-179.8(3)
C(21)-C(22)-C(23)-C(24)	1.0(5)
C(25)-C(22)-C(23)-C(24)	-178.8(3)
C(22)-C(23)-C(24)-C(19)	-1.2(5)
C(20)-C(19)-C(24)-C(23)	0.0(5)
S(1)-C(19)-C(24)-C(23)	179.6(2)

Symmetry transformations used to generate equivalent atoms:

Table 6. Torsion angles [deg] for cd26535.

O(4)-S(1)-N(1)-C(7)	158.2(2)
O(5)-S(1)-N(1)-C(7)	28.5(3)
C(19)-S(1)-N(1)-C(7)	-87.1(2)
C(12)-O(2)-C(1)-C(6)	106.3(3)
C(12)-O(2)-C(1)-C(2)	-77.6(3)
C(6)-C(1)-C(2)-C(3)	1.1(5)
O(2)-C(1)-C(2)-C(3)	-174.7(3)
C(1)-C(2)-C(3)-C(4)	-1.5(5)
C(2)-C(3)-C(4)-C(5)	0.6(6)
C(3)-C(4)-C(5)-C(6)	0.9(5)
C(2)-C(1)-C(6)-C(5)	0.3(4)
O(2)-C(1)-C(6)-C(5)	176.1(2)
C(2)-C(1)-C(6)-C(7)	-177.3(3)
O(2)-C(1)-C(6)-C(7)	-1.4(4)
C(4)-C(5)-C(6)-C(1)	-1.3(5)
C(4)-C(5)-C(6)-C(7)	176.3(3)
S(1)-N(1)-C(7)-C(8)	-103.1(2)
S(1)-N(1)-C(7)-C(6)	128.2(2)
C(1)-C(6)-C(7)-N(1)	69.8(3)
C(5)-C(6)-C(7)-N(1)	-107.6(3)
C(1)-C(6)-C(7)-C(8)	-56.9(4)
C(5)-C(6)-C(7)-C(8)	125.6(3)
N(1)-C(7)-C(8)-C(9)	-4.6(4)
C(6)-C(7)-C(8)-C(9)	121.1(3)
N(1)-C(7)-C(8)-C(10)	170.7(2)
C(6)-C(7)-C(8)-C(10)	-63.6(3)
C(9)-C(8)-C(10)-O(3)	170.3(3)
C(7)-C(8)-C(10)-O(3)	-5.1(4)
C(9)-C(8)-C(10)-C(11)	-8.7(5)
C(7)-C(8)-C(10)-C(11)	175.9(3)
C(1)-O(2)-C(12)-O(1)	4.4(4)
C(1)-O(2)-C(12)-C(13)	-173.2(2)
O(1)-C(12)-C(13)-C(18)	176.3(3)
O(2)-C(12)-C(13)-C(18)	-6.2(4)
O(1)-C(12)-C(13)-C(14)	-7.3(5)
O(2)-C(12)-C(13)-C(14)	170.1(3)
C(18)-C(13)-C(14)-C(15)	0.6(5)
C(12)-C(13)-C(14)-C(15)	-175.9(3)
C(13)-C(14)-C(15)-C(16)	0.5(5)
C(14)-C(15)-C(16)-C(17)	-1.3(5)
C(14)-C(15)-C(16)-Br	176.6(2)
C(15)-C(16)-C(17)-C(18)	1.0(5)
Br-C(16)-C(17)-C(18)	-176.9(3)
C(14)-C(13)-C(18)-C(17)	-0.9(5)
C(12)-C(13)-C(18)-C(17)	175.4(3)
C(16)-C(17)-C(18)-C(13)	0.1(5)
O(4)-S(1)-C(19)-C(20)	-175.4(2)
O(5)-S(1)-C(19)-C(20)	-44.1(3)
N(1)-S(1)-C(19)-C(20)	70.7(3)
O(4)-S(1)-C(19)-C(24)	5.0(3)
O(5)-S(1)-C(19)-C(24)	136.3(2)
N(1)-S(1)-C(19)-C(24)	-108.9(3)
C(24)-C(19)-C(20)-C(21)	1.4(5)
S(1)-C(19)-C(20)-C(21)	-178.2(2)
C(19)-C(20)-C(21)-C(22)	-1.7(5)
C(20)-C(21)-C(22)-C(23)	0.5(5)
C(20)-C(21)-C(22)-C(25)	-179.8(3)
C(21)-C(22)-C(23)-C(24)	1.0(5)
C(25)-C(22)-C(23)-C(24)	-178.8(3)
C(22)-C(23)-C(24)-C(19)	-1.2(5)
C(20)-C(19)-C(24)-C(23)	0.0(5)
S(1)-C(19)-C(24)-C(23)	179.6(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd26535 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(1)#1	0.813(17)	2.130(18)	2.941(3)	174(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y-1/2,-z+3/2