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Enantioselective desymmetrization of *meso*-aziridines with benzenethiols catalyzed by chiral bifunctional quaternary phosphonium salts derived from α-amino acids

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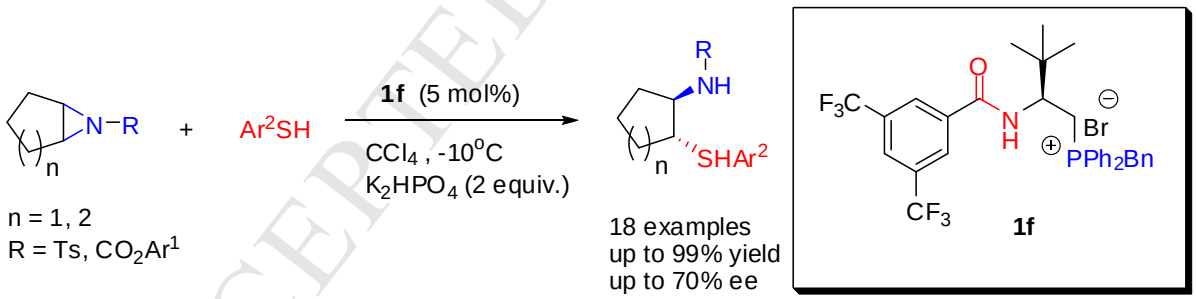

n = 1, 2
R = Ts, CO_2Ar^1

18 examples
up to 99% yield
up to 70% ee

Enantioselective desymmetrization of *meso*-aziridines with aromatic thiols catalyzed by chiral bifunctional quaternary phosphonium salts derived from α-amino acids

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Abstract: Desymmetrization of *meso*-aziridines with aromatic thiols was realized by using α-amino acids-derived chiral quaternary phosphonium salts catalysts to provide chiral β-amino sulfides with high yields (up to 99%) and in moderate enantioselectivities (up to 70%).

Keywords: Desymmetrization, *meso*-aziridine, aromatic thiols, chiral quaternary phosphonium salt, chiral β-amino sulfide.

1. Introduction

The enantioselective desymmetrization of *meso*-aziridines via ring opening with various nucleophiles is a powerful synthetic method for the preparation of a variety of substituted chiral amines.[1] In this field, different kinds of nucleophiles have been used through chiral metal catalysis[2] or organocatalysis.[3] In particular, the catalytic asymmetric ring openings of *meso*-aziridines with sulfur-based nucleophiles provide facile access to various chiral *β*-aminosulfur compounds, which are both useful synthons in stereoselective synthesis and also have great values in pharmaceutical industry.[4] Della Sala[5] and Antilla et al.[6] have achieved excellent enantioselectivities in the ring-opening of *meso*-aziridines with thiols (TMS-SPh and HSPh) by using chiral phosphoric acid catalysts. Other strategies using chiral cinchona alkaloid derivatives,[7] prolinols[8] and guanidines[9] as catalysts or using α-isothiocyanato imides[10] as sulfur-based nucleophiles have also been reported, however these methods only obtain moderate enantioselectivities or have limitations of substrates.

On the other hand, the asymmetric phase-transfer catalysis has been proven to be an efficient tool in synthesizing chiral compounds.[11] Although a few of chiral phosphonium salts catalysts have been developed and used in asymmetric reactions,[12] chiral phosphonium salts have been rarely studied compared to chiral ammonium salts. Especially, the asymmetric ring-opening reaction of aziridines under phase-transfer conditions has only been achieved by using chiral quaternary ammonium catalysts.[13] Our group have focused on the development of amino acid-derived catalysts and their applications to various enantioselective reactions.[14] Recently, we have developed chiral bifunctional phosphonium salts from amino acids as efficient asymmetric phase-transfer catalysts, with which excellent enantioselectivity could be obtained in aza-Henry reaction[15] and Michael addition reaction[16]. Herein, we wish to describe the application of chiral phosphonium salts to catalyze the desymmetrization of *meso*-aziridines with thiols.

2. Results and discussion

Using the reaction between *N*-tosylaziridine **2a** and 4-Cl benzenethiol **3a** as the model reaction, we first investigated the catalytic efficiency of different phosphonium salt catalysts (Figure 1) bearing different chiral skeletons and differently protected amino groups (Table 1). We found that both structural elements have significant influence on the reaction, and the catalyst **1f** derived from *L*-tert-Leucine with the amide structure gave the highest enantioselectivity (entries 1-6). Then the effect of solvent and base were examined by using **1f** as a catalyst (entries 7-14). Apparently, halohydrocarbon solvents and mild bases are favoured for the enantioselectivity, and when CCl_4 and K_2HPO_4 were used, an improved enantioselectivity of 60%ee was obtained (entry 14). To further increase the enantioselectivity, we made more efforts in modifying the structure of the catalyst **1f** by varying both the substitutions of the amide moiety and the phosphonium center (entries 15-20), but no better enantioselectivity was obtained. When we lowered the reaction temperature to -10^{o}C, the product **4a** was obtained in 64% ee with 94% yield, but lowering the temperature further to -20^{o}C led to significantly decreased ee and yield (entries 21-22). The absolute configuration of **4a** was assigned to be (1*S*, 2*S*) by comparison of the optical rotation values with the literature data.[7b]

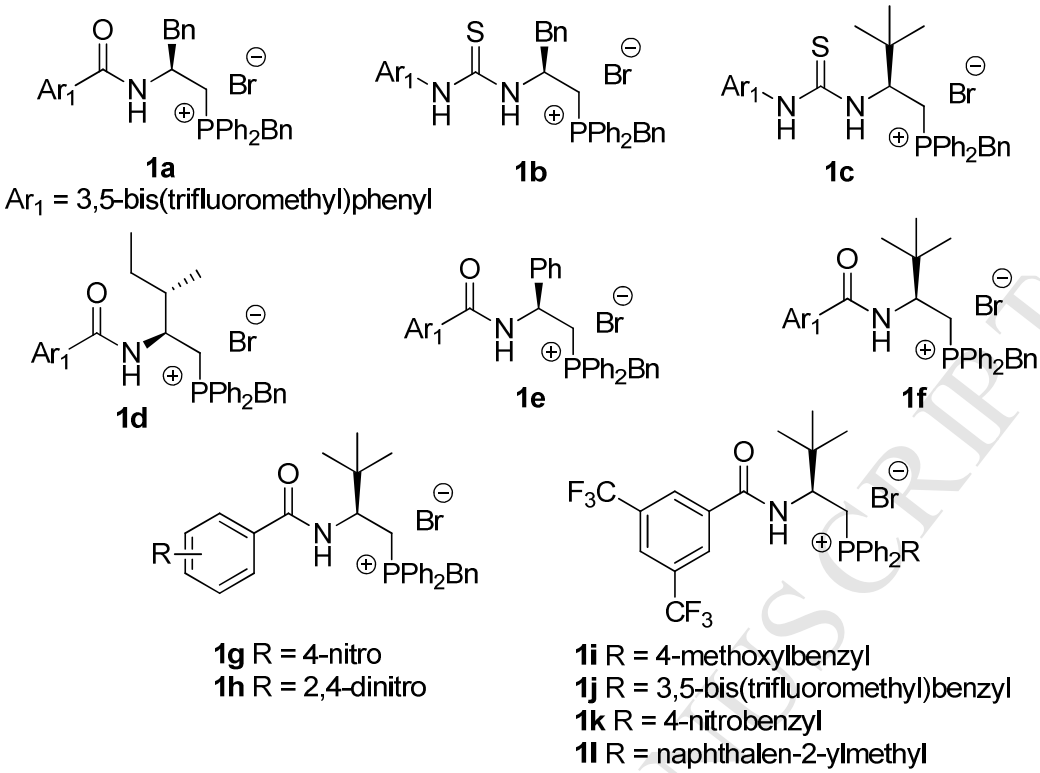
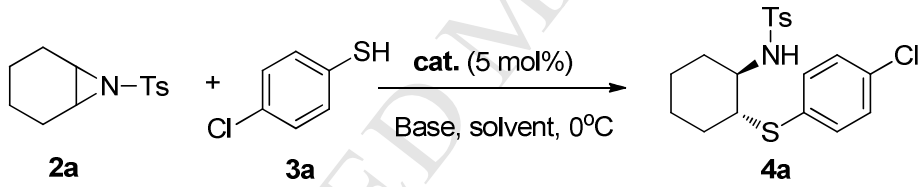


Fig. 1 Chiral phosphonium salts

Table 1 Screening of catalysts, solvents and bases[a]



2a 3a 4a

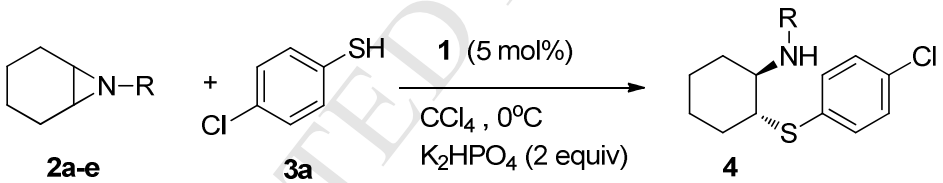
Entry	Catalyst	Solvent	Base	Yield[b](%)	Ee[c](%)
1	**1a**	toluene	33% aq K_2CO_3	90	25
2	**1b**	toluene	33% aq K_2CO_3	88	-5
3	**1c**	toluene	33% aq. K_2CO_3	88	-23
4	**1d**	toluene	33% aq. K_2CO_3	91	36
5	**1e**	toluene	33% aq. K_2CO_3	90	17
6	**1f**	toluene	33% aq. K_2CO_3	90	45
7	**1f**	CH_2Cl_2	33% aq. K_2CO_3	92	16
8	**1f**	TBME	33% aq. K_2CO_3	94	5
9	**1f**	$CHCl_3$	33% aq. K_2CO_3	90	36
10	**1f**	CCl_4	33% aq. K_2CO_3	95	51
11	**1f**	CCl_4	50% aq. K_2HPO_4	92	60
12	**1f**	CCl_4	50% aq. Cs_2CO_3	97	53
13	**1f**	CCl_4	$KHCO_3$	99	56
14	**1f**	CCl_4	K_2HPO_4	99	60
15	**1g**	CCl_4	K_2HPO_4	99	30
16	**1h**	CCl_4	K_2HPO_4	99	33
17	**1i**	CCl_4	K_2HPO_4	99	58

18	**1j**	CCl_4	K_2HPO_4	99	50
19	**1k**	CCl_4	K_2HPO_4	99	55
20	**1l**	CCl_4	K_2HPO_4	99	59
21[d]	**1f**	CCl_4	K_2HPO_4	94	64
22[e]	**1f**	CCl_4	K_2HPO_4	40	53

[a] Reactions were carried out using 0.1 mmol of **2a** , 0.15 mmol of **3a**, 5 mol% of catalyst **1**, 0.2 mmol or 0.16 mL of base, 12 h. [b] Isolated yields. [c] Determined by chiral stationary phase HPLC. [d] Reaction at -10 ^oC, 24 h. [e] Reaction at -20 ^oC, 48 h.

The influence of the N-protecting group of the aziridine was also investigated with catalyst **1f** or **1c** (Table 2). Under the similar reaction conditions, *N*-tosylaziridine **2a** gave the product with 60% ee (entry 1), while *N*-Boc-aziridine **2b** and 4-nitrobenzoyl aziridine **2c** gave very low enantioselectivity (entries 2-3). 3,5-Dinitrobenzoyl aziridine **2d** and 3,5-bistrifluoromethylbenzoyl aziridine **2e** gave 17% ee and 30% ee , respectively. To our surprise, the same reactions of the aziridines **2d** and **2e** with catalyst **1c** gave the desired products in 62% ee and 33% ee, respectively, with the opposite absolute configurations to those obtained with catalyst **1f** (entries 4-5).

Table 2 Screening of *N*-substituted aziridines **2**[a]



Entry	**2** (R)	Catalyst	Time (h)	Yield[b](%)	Ee[c] (%)
1	**2a** (Ts)	**1f**	9	99	60
2	**2b** (Boc)	**1f**	9	99	0
3	**2c** (4-nitrobenzoyl)	**1f**	12	95	20
4	**2d** (3,5-dinitrobenzoyl)	**1f**	11	99	17
		1c	20	98	-62
5	**2e** (3,5-bisCF_3benzoyl)	**1f**	18	99	30
		1c	18	99	-33

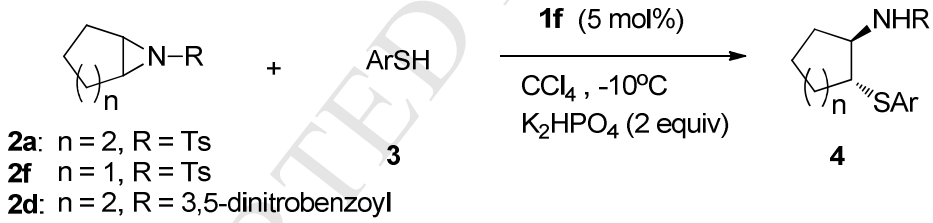
[a] Reactions were carried out using 0.1 mmol of **2**, 0.15 mmol **3a**, 5 mol% of **1**. [b] Isolated yields. [c] Determined by chiral stationary phase HPLC.

Next, a series of aromatic thiols **3** were subjected to the reaction with

N-tosylaziridine **2a** under the optimized conditions [catalyst **1f** (5 mol%), CCl_4, K_2HPO_4 (2 equiv), -10 ^oC] (Table 3). In general, excellent yields and moderate enantioselectivities were obtained. For thiols **3** bearing differently substituted benzene groups, those with electron-donating substituents provided relatively lower ee values and yields (entries 5, 6 and 12) than those with electron-withdrawing ones. Notably, a *meta* effect was observed: *m*-substituted aryl thiols gave slightly higher ee values (70%) (entries 3 and 10). Moreover, naphthyl-1-thiol **3n** and naphthyl-2-thiol **3o** gave the desired products in similarly excellent yields and moderate enantioselectivities (entries 14 and 15). However, the use of heteroaryl thiol **3m** led to significantly reduced yield and enantioselectivity, in which only 60% yield and 30% ee were obtained (entry 13). To our delight, the useful aziridine **2f** derived from cyclopentene was also worked to provide comparable results (entry 16).

In addition, the *o*-bromo-substituted product **4k** was subjected to a Pd-catalyzed cyclization to provide the phenothiazine product **5** in 70% yield without appreciable decrease in the ee (Scheme 3).

Table 3 Scope study with different thiols **3**[a]



2a: n = 2, R = Ts
2f n = 1, R = Ts
2d: n = 2, R = 3,5-dinitrobenzoyl

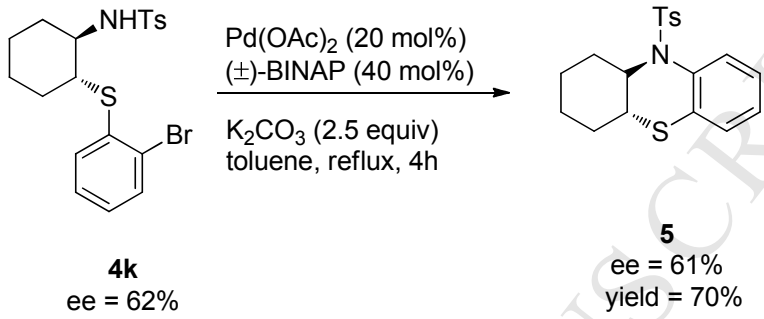
3

4

Entry	**2**	**3**	**Ar**	**4**	Yield[b] (%)	Ee[c] (%)
1	**2a**	**3a**	4-ClC_6H_4	**4a**	98	64
2	**2a**	**3b**	Ph	**4b**	83	59
3	**2a**	**3c**	2-ClC_6H_4	**4c**	97	62
4	**2a**	**3d**	3-ClC_6H_4	**4d**	98	70
5	**2a**	**3e**	4-$CH_3C_6H_4$	**4e**	70	56
6	**2a**	**3f**	4-$OCH_3C_6H_4$	**4f**	80	57
7	**2a**	**3g**	4-FC_6H_4	**4g**	96	62
8	**2a**	**3h**	4-$NO_2C_6H_4$	**4h**	98	60
9	**2a**	**3i**	4-BrC_6H_4	**4i**	94	67
10	**2a**	**3j**	3-BrC_6H_4	**4j**	94	70
11	**2a**	**3k**	2-BrC_6H_4	**4k**	90	62
12	**2a**	**3l**	2-$NH_2C_6H_4$	**4l**	93	44
13	**2a**	**3m**	4-pyridyl	**4m**	60	30

14	**2a**	**3n**	1-naphthyl	**4n**	90	54
15	**2a**	**3o**	2-naphthyl	**4o**	92	57
16	**2f**	**3b**	Ph	**4p**	95	51
17[d]	**2d**	**3a**	Ph	**4q**	98	-62

[a] Reactions were carried out using 0.1 mmol of **2**, 0.15 mmol of **3**, 5 mol% of **1f**, 24 h. [b] Isolated yields. [c] Determined by chiral stationary phase HPLC. [d] 5 mol% of catalyst **1c** was used.



4k
ee = 62%

5
ee = 61%
yield = 70%

Scheme 3 Transformation of the compound **4k**

3. Conclusion

In conclusion, we have developed a new approach for the desymmetrization of *meso*-aziridines with aromatic thiols by using chiral bifunctional quaternary phosphonium salts as catalysts. A series of β-amino sulfides were obtained in high yields and in moderate enantioselectivities. This work expands the application scope of asymmetric phase-transfer catalysis with α-amino acid-derived chiral phosphonium salts.

4. Experimental

4.1 General information

The ^{1}H NMR spectra were recorded on a Bruker (400 MHz) spectrometer. All chemical shifts (δ) were given in ppm. Data were reported as follows: chemical shift, integration, multiplicity (s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a DPX-400 (400 MHz). Flash column chromatography was performed using H silica gel. For thin-layer chromatography (TLC), silica gel plates (HSGF 254) were used and compounds were visualized by irradiation with UV light. Analytical high performance liquid chromatography (HPLC) was carried out on SHIMADZU equipment using chiral columns. Melting points were determined on a SGW X-4 melting point apparatus and were uncorrected. Optical rotations were measured on a JASCO P-1010 Polarimeter at λ = 589 nm. IR spectra were recorded on a Perkin-Elmer 983G instrument. Mass spectra analysis was performed on API 200 LC/MS system (Applied Biosystems Co. Ltd.).

All reagents purchased from commercial sources were purified by standard techniques prior to use. Aziridines were prepared according to literature procedures.[2b, 3] Preparation and characterization of the catalysts **1a**-**1e** were reported in the published literatures. [15]

4.2 Preparation of catalysts 1f to 1l

To a solution of the corresponding α-amino acid-derived bifunctional phosphine (1.0 equiv) in anhydrous toluene was added the corresponding benzylic halide (1.2 equiv), and the resulting mixture was stirred at 110 ^{o}C for 8 h. Then the mixture was allowed to cool to ambient temperature and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography to afford the desired phase transfer catalyst (CH_2Cl_2/MeOH = 20 : 1).

4.2.1 . (*S*)-Benzyl(2-(3,5-bis(trifluoromethyl)benzamido)-3,3-dimethylbutyl)diphenyl phosphonium bromide(**1f**).

Yield: 90%; White solid. m.p. = 137-138^{o}C; $[\alpha]_D^{24}$ = 48.6 (*c* = 1.0, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.22 (bs, 1H), 8.53 (s, 2H), 7.90-7.93 (m, 3H), 7.65-7.69 (m, 3H), 7.46-7.54 (m, 5H), 7.11-7.21 (m, 4H), 6.91-6.93 (m, 2H), 5.32-5.34 (m, 1H), 4.89 (d, *J* = 14.4 Hz, 1H), 4.44-4.53 (m, 1H), 4.10-4.11 (m, 1H), 2.57-2.64 (m, 1H), 1.00 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 164.2, 134.7, 134.3 (d, J_{C-P} = 3.1 Hz), 134.0 (d, J_{C-P} = 9.5 Hz), 133.8 (d, J_{C-P} = 5.0 Hz), 131.2 (q, J_{C-F} = 36 Hz), 130.3 (d, J_{C-P} = 5.5 Hz), 129.8 (d, J_{C-P} = 12.3 Hz), 129.6 (d, J_{C-P} = 12.3 Hz), 128.8 (d, J_{C-P} = 2.9 Hz), 128.6 (d, J_{C-P} = 2.5 Hz), 128.4 (d, J_{C-P} = 3.5 Hz), 127.1, 127.0, 124.7, 123.0 (q, J_{C-F} = 271.7 Hz), 117.6, 117.0, 116.7, 116.1, 52.3 (d, J_{C-P} = 5.6 Hz), 37.3 (d, J_{C-P} = 11.7 Hz), 30.5, 30.1, 26.4, 22.5, 22.0; ^{31}P-NMR (163 MHz, $CDCl_3$): δ 25.2; ^{19}F-NMR (282 MHz, $CDCl_3$): δ -62.5; IR (Neat) 3227, 2963, 1662, 1539, 1438, 1337, 1279, 1181, 1136, 1134, 803, 743, 700; HRMS(MALDI): calcd. for $[M\text{-}Br]^+$ ($C_{34}H_{33}NOF_6P$) requires 616.2204, found 616.2197.

4.2.2. (*S*)-Benzyl(3,3-dimethyl-2-(4-nitrobenzamido)butyl)diphenylphosphonium bromide(**1g**)

Yield: 90%; yellow solid. m.p. = 153-154^{o}C; $[\alpha]_D^{24}$ = 222.6 (*c* = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.96 (d, *J* = 9.2 Hz, 1H), 8.29 (d, *J* = 8.8 Hz, 2H), 8.20 (d, *J* = 8.8 Hz, 2H), 7.89-7.94 (m, 2H), 7.62-7.69 (m, 3H), 7.53-7.55 (m, 8H), 7.16-7.20 (m, 1H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.88-6.90 (m, 2H), 5.26-5.33 (m, 1H), 4.98 (t, *J* = 14.2 Hz, 1H), 4.37-4.46 (m, 1H), 4.03-4.10 (m, 1H), 2.55-2.62 (m, 1H), 0.96 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 164.9, 149.3, 137.9, 134.7 (d, J_{C-P} = 2.6 Hz), 134.5 (d, J_{C-P} = 2.9 Hz), 133.9 (d, J_{C-P} = 8.5 Hz), 133.7 (q, J_{C-P} = 11.1 Hz), 130.3 (d, J_{C-P} = 5.5 Hz), 129.8 (d, J_{C-P} = 2.4 Hz), 129.7 (d, J_{C-P} = 2.6 Hz), 129.4, 128.8 (d, J_{C-P} = 3.0 Hz), 128.3 (d, J_{C-P} = 3.6 Hz), 127.1, 127.0, 123.0, 117.2, 117.0, 116.4, 116.2, 52.1 (d, J_{C-P} = 5.5 Hz), 37.2 (d, J_{C-P} = 11.8 Hz), 29.9, 29.5, 26.3, 22.9, 22.4; ^{31}P-NMR (163 MHz, $CDCl_3$): δ 26.1; IR (Neat) 3240, 3057, 2964, 1659, 1601, 1524, 1489, 1341, 1110, 1015, 841, 744; HRMS(MALDI): calcd. for $[M\text{-}Br]^+$ ($C_{32}H_{34}N_2O_3P$) requires 525.2307, found 525.2286.

4.2.3 .(*S*)-Benzyl(2-(3,5-dinitrobenzamido)-3,3-dimethylbutyl)diphenylphosphonium bromide(**1h**)

Yield: 88%; yellow solid. m.p. = 166-167^{o}C; $[\alpha]_D^{24}$ = 99.5 (*c* = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.48 (d, *J* = 8.8 Hz, 1H), 9.08 (s, 2H), 9.03 (s, 1H),

7.92-7.97 (m, 2H), 7.51-7.79 (m, 8H), 7.07-7.18 (m, 3H), 6.89-6.90 (m, 2H), 4.85-5.01 (m, 2H), 4.23-4.49 (m, 2H), 3.00 (t, J = 14.4 Hz, 1H), 2.51 (s, 1H), 1.02 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 163.2, 148.0, 136.5, 134.8 (d, J_{C-P} = 3.1 Hz), 134.5 (d, J_{C-P} = 2.7 Hz), 134.1 (d, J_{C-P} = 9.5 Hz), 133.8 (q, J_{C-P} = 9.0 Hz), 130.4 (d, J_{C-P} = 5.6 Hz), 130.0, 129.9 (d, J_{C-P} = 0.8 Hz), 129.8, 128.9 (d, J_{C-P} = 3.1 Hz), 128.5, 128.4, 127.0, 126.9, 120.9, 117.4, 117.0, 116.6, 116.1, 110.0, 52.6 (d, J_{C-P} = 5.5 Hz), 37.5 (d, J_{C-P} = 11.5 Hz), 30.4, 30.0, 26.4, 22.6, 22.1; ^{31}P-NMR (163 MHz, $CDCl_3$): δ 25.9; IR (Neat) 3220, 2962, 1664, 1541, 1343, 1110, 1076, 803, 729, 689; HRMS(MALDI): calcd. for $[M-Br]^+$ ($C_{32}H_{33}N_3O_5P$) requires 570.2154, found 570.2167.

4.2.4.(*S*)-(2-(3,5-Bis(trifluoromethyl)benzamido)-3,3-dimethylbutyl)(4-methoxybenzyl)diphenylphosphonium bromide(**1i**)

Yield: 94%; White solid. m.p. = 131-133°C; $[\alpha]_D^{24}$ = 38.7 (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.16 (d, J = 4.4 Hz, 1H), 8.51 (s, 2H), 7.88-7.92 (m, 3H), 7.64-7.69 (m, 3H), 7.54-7.55 (m, 2H), 7.42-7.43 (m, 3H), 6.82-6.85 (m, 2H), 6.65 (d, J = 8.4 Hz, 2H), 5.25-5.32 (m, 1H), 4.78-4.86 (m, 1H), 4.43-4.52 (m, 1H), 4.00-4.05 (m, 1H), 3.72 (s, 3H), 2.59 (t, J = 14.2 Hz, 1H), 1.01 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 164.2, 159.5 (d, J_{C-P} = 3.6 Hz), 134.6, 134.2 (d, J_{C-P} = 2.9 Hz), 134.1, 134.0, 133.8, 133.7, 131.5 (d, J_{C-P} = 5.4 Hz), 131.2 (q, J_{C-F} = 33.5 Hz), 129.9, 129.8, 129.7, 129.5, 128.6 (d, J_{C-P} = 2.2 Hz), 124.7, 123.0 (q, J_{C-F} = 271.8 Hz), 118.4, 118.3, 117.7, 117.2, 116.9, 116.3, 114.3 (d, J_{C-P} = 2.9 Hz), 55.1, 52.3 (d, J_{C-P} = 5.6 Hz), 37.4 (d, J_{C-P} = 11.6 Hz), 29.9, 29.4, 26.4, 22.2, 21.7; ^{31}P-NMR (163 MHz, $CDCl_3$): δ 24.4; ^{19}F-NMR (282 MHz, $CDCl_3$): δ -62.5; IR (Neat) 3225, 3050, 2963, 1662, 1539, 1514, 1439, 1280, 1181, 1136, 1019, 801, 743, 681; HRMS(MALDI): calcd. for $[M-Br]^+$ ($C_{35}H_{35}NO_2F_6P$) requires 646.2310, found 646.2288.

4.2.5.(*S*)-(2-(3,5-Bis(trifluoromethyl)benzamido)-3,3-dimethylbutyl)(3,5-bis(trifluoromethyl)benzyl)diphenylphosphonium bromide(**1j**)

Yield: 94%; White solid. m.p. = 147-149°C; $[\alpha]_D^{24}$ = 47.7 (c = 0.3, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.09-9.12 (m, 1H), 8.53 (s, 2H), 7.95-8.01 (m, 3H), 7.54-7.76 (m, 9H), 7.29 (s, 2H), 5.43-5.50 (m, 2H), 4.39-4.48 (m, 2H), 2.78-2.88 (m, 1H), 0.99 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 164.3, 135.4 (d, J_{C-P} = 2.6 Hz), 134.8 (d, J_{C-P} = 3.0 Hz), 134.7, 134.2, 134.1, 134.0, 133.9, 132.1 (d, J_{C-P} = 3.2 Hz), 131.8 (d, J_{C-P} = 3.3 Hz), 131.4 (q, J_{C-F} = 33.6 Hz), 130.9, 130.8, 130.6, 130.5 (d, J_{C-P} = 4.8 Hz), 130.3, 130.2, 130.0, 129.8, 128.5 (d, J_{C-P} = 2.3 Hz), 124.9 (d, J_{C-P} = 3.3 Hz), 123.0 (q, J_{C-F} = 271.6 Hz), 122.4 (q, J_{C-F} = 271.5 Hz), 121.9 (d, J_{C-P} = 3.6 Hz), 115.7, 115.5, 114.9, 114.6, 52.4 (d, J_{C-P} = 5.8 Hz), 37.4 (d, J_{C-P} = 11.9 Hz), 30.8, 30.3, 23.5, 23.0; ^{31}P-NMR (163 MHz, $CDCl_3$): δ 27.7; ^{19}F-NMR (282 MHz, $CDCl_3$): δ -62.6, -63.2; IR (Neat) 3237, 2969, 2925, 1666, 1374, 1279, 1179, 1135, 903, 801，682; HRMS(MALDI): calcd. for $[M-Br]^+$ ($C_{36}H_{31}NOF_{12}P$) requires 752.1952, found 752.1939.

4.2.6.(*S*)-(2-(3,5-Bis(trifluoromethyl)benzamido)-3,3-dimethylbutyl)(4-nitrobenzyl)diphenylphosphonium bromide(**1k**)

Yield: 92%; White solid. m.p. = 145-146°C; $[\alpha]_D^{24}$ = 51.9 (c = 1.0, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.09 (d, J = 8.4 Hz, 1H), 8.50 (s, 2H), 7.93-8.02 (m, 4H), 7.61-7.79 (m, 5H), 7.48-7.49 (m, 3H), 7.18 (d, J = 2.0 Hz, 1H), 7.16 (d, J = 2.0 Hz, 1H), 5.37-5.53 (m, 2H), 4.22-4.47 (m, 2H), 2.75 (t, J = 14.4 Hz, 1H), 0.99 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 164.1, 147.4 (d, J_{C-P} = 4.2 Hz), 135.7, 135.6, 135.2 (d,

$J_{C\text{-}P}$ = 2.8 Hz), 134.8, 134.5 (d, $J_{C\text{-}P}$ = 2.7 Hz), 134.2, 134.1, 134.0, 133.99, 131.7, 131.5, 131.42, 131.40, 131.1, 130.7, 130.1 (d, $J_{C\text{-}P}$ = 12.2 Hz), 129.7 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.8, 128.7, 128.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 124.8, 123.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 123.0 (q, $J_{C\text{-}F}$ = 271.7 Hz), 116.2, 115.7, 115.4, 114.9, 52.4 (d, $J_{C\text{-}P}$ = 5.7 Hz), 37.3 (d, $J_{C\text{-}P}$ = 11.8 Hz), 31.0, 30.5, 26.3, 26.1, 23.5, 23.1; ^{31}P-NMR (163 MHz, $CDCl_3$): δ 26.6; ^{19}F-NMR (282 MHz, $CDCl_3$): δ -62.5; IR (Neat) 3232, 3056, 2963, 1666, 1526, 1439, 1347, 1280, 1182, 1136, 1017, 859, 801， 743, 698；HRMS(MALDI): calcd. for $[M\text{-}Br]^+$ ($C_{34}H_{32}N_2F_6O_3P$) requires 661.2055, found 661.2045.

4.2.7.(*S*)-(2-(3,5-Bis(trifluoromethyl)benzamido)-3,3-dimethylbutyl)(naphthalen-1-yl methyl)diphenylphosphonium bromide(**1l**)

Yield: 90%; White solid. m.p. = 133-134^{o}C; $[\alpha]_D^{24}$ = 41.9 (*c* = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.36 (br, 1H), 8.55 (s, 2H), 7.91-7.95 (m, 3H), 7.36-7.66 (m, 14H), 6.97 (d, *J* = 8.8 Hz, 1H), 5.40-5.43 (m, 1H), 4.98-5.06 (m, 1H), 4.26-4.27 (m, 1H), 2.62 (t, *J* = 14.0 Hz, 1H), 0.99 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 164.3, 134.7, 134.3 (d, $J_{C\text{-}P}$ = 3.0 Hz), 134.1 (d, $J_{C\text{-}P}$ = 9.6 Hz), 133.8 (d, $J_{C\text{-}P}$ = 8.9 Hz), 132.8 (d, $J_{C\text{-}P}$ = 3.3 Hz), 132.5 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.3 (q, $J_{C\text{-}F}$ = 33.6 Hz), 130.0 (d, $J_{C\text{-}P}$ = 7.2 Hz), 129.9, 129.7 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.7, 128.6 (d, $J_{C\text{-}P}$ = 2.5 Hz), 127.5 (d, $J_{C\text{-}P}$ = 1.6 Hz), 127.4 (d, $J_{C\text{-}P}$ = 1.4 Hz), 127.35, 127.31, 126.69, 126.67, 124.8, 124.3, 124.2, 123.2 (q, $J_{C\text{-}F}$ = 271.8 Hz), 117.6, 117.1, 116.8, 116.3, 52.4 (d, $J_{C\text{-}P}$ = 5.7 Hz), 37.4 (d, $J_{C\text{-}P}$ = 11.7 Hz), 30.8, 30.4, 26.4, 26.2, 22.5, 22.0; ^{31}P-NMR (163 MHz, $CDCl_3$): δ 25.2; ^{19}F-NMR (282 MHz, $CDCl_3$): δ -62.5; IR (Neat) 3229, 2963, 2926, 2907, 1663, 1541, 14383, 1363, 1279, 1181, 1136, 821, 742, 681; HRMS(MALDI): calcd. for $[M\text{-}Br]^+$ ($C_{38}H_{35}NOF_6P$) requires 666.2360, found 666.2347.

4.3 General procedure for the enantioselective desymmetrization of *meso*-aziridines with benzenethiols

To a suspension of the corresponding benzenethiol **3** (0.15 mmol) in CCl_4 (1.0 ml) was added catalyst **1f** (5 mol%) and K_2HPO_4 (0.2 mmol) sequentially, and the resulting mixture was stirred at -10 ^{o}C for 5 min. Then aziridine **2** (0.1 mmol) was added. The resulting suspension was vigorously stirred at -10 ^{o}C for 24 h, and then directly purified by column chromatography (silica gel: petroleum ether/AcOEt = 10:1 – 5:1) on silica gel to afford the product **4**.

4.3.1. *N*-((1*R*,2*R*)-2-((4-Chlorophenyl)thio)cyclohexyl)-4-methylbenzenesulfonamide (**4a**)[17]

Yield: 94%; white solid. Enantiomeric excess: 64%, $[\alpha]_D^{25}$ = -20.2 (*c* = 2.7, $CHCl_3$), determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 9:1, flow rate 0.7 ml/min, t_{minor} = 23.1 min, t_{major} = 21.1 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.20-7.26 (m, 4H), 5.32-5.37 (m, 1H), 2.92-3.01 (m, 2H), 2.43 (s, 3H), 2.17-2.20 (m, 1H), 1.98-2.01 (m, 1H), 1.26-1.69 (m, 6H).

4.3.2. *N*-((1*R*,2*R*)-2-(Phenylthio)cyclohexyl)-3,5-bis(trifluoromethyl)benzamide (**4b**)[17]

Yield: 85%; white solid. Enantiomeric excess: 59%, $[\alpha]_D^{28}$ = -11.3 (*c* = 1.4, $CHCl_3$), determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 85:15, flow rate 1.0 ml/min, t_{minor} = 12.2 min, t_{major} = 11.1 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.22-7.26 (m, 5H), 5.25 (d, *J* =

3.6 Hz, 1H), 2.88-3.00 (m, 2H), 2.43 (s, 3H), 2.25-2.27 (m, 1H), 2.00-2.03 (m, 1H), 1.57-1.62 (m, 3H), 1.25-1.42 (m, 3H); MS (ESI): m/z 384.1 (M^++Na).

4.3.3. *N*-((1*R*,2*R*)-2-((2-Chlorophenyl)thio)cyclohexyl)-4-methylbenzenesulfonamide (**4c**) [17]

Yield: 95%; white solid. Enantiomeric excess: 62%, $[\alpha]_D^{26}$ = -4.1 (*c* = 1.85, $CHCl_3$), determined by HPLC (Phenomenex Cellulose-2 column, hexane/*i*-PrOH 9:1, flow rate 1.0 ml/min, t_{minor} = 28.8 min, t_{major} = 23.0 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.28-7.33 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.10-7.12 (m, 2H), 5.08-5.10 (m, 1H), 3.01-3.02 (m, 2H), 2.35 (s, 3H), 2.19-2.21 (m, 1H), 1.95-1.98 (m, 1H), 1.41-1.57 (m, 3H), 1.19-1.29 (m, 3H); MS (ESI): m/z 418.0 (M^++Na).

4.3.4. *N*-((1*R*,2*R*)-2-((3-Chlorophenyl)thio)cyclohexyl)-4-methylbenzenesulfonamide (**4d**)

Yield: 95%; white solid. m.p. = 71-73°C. Enantiomeric excess: 70%, $[\alpha]_D^{27}$ = 1.99 (*c* = 1.85, $CHCl_3$), determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 85:15, flow rate 1.0 ml/min, t_{minor} = 11.1 min, t_{major} = 9.9 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.08-7.12 (m, 4H), 4.98-5.01 (m, 1H), 2.91-2.98 (m, 2H), 2.36 (s, 3H), 2.15-2.17 (m, 1H), 1.96-1.98 (m, 1H), 1.53-1.55 (m, 1H), 1.19-1.37 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.4, 137.5, 135.7, 134.6, 131.8, 130.2, 130.0, 129.7, 127.4, 127.2, 55.1, 51.0, 32.0, 31.2, 24.2, 23.1, 21.6; IR (Neat) 3278, 2932, 2870, 1580, 1543, 1459, 1330, 1158, 1093, 820, 778, 670, 569, 551; HRMS(MALDI): calcd. for $[M+Na]^+$ ($C_{19}H_{22}NClS_2O_2$) requires 418.0678, found 418.0682.

4.3.5. 4-Methyl-*N*-((1*R*,2*R*)-2-(*p*-tolylthio)cyclohexyl)benzenesulfonamide (**4e**)[17]

Yield: 80%; white solid. Enantiomeric excess: 57%, $[\alpha]_D^{28}$ = -14.6 (*c* = 1.3, $CHCl_3$), determined by HPLC (Chiralpak AS-H column, hexane/*i*-PrOH 1:4, flow rate 0.3 ml/min, t_{minor} = 86.5 min, t_{major} = 41.7 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 5.16-5.17 (m, 1H), 2.83-2.85 (m, 1H), 2.68-2.71 (m, 1H), 2.37 (s, 3H), 2.26 (s, 3H), 1.50-1.54 (m, 1H), 1.15-1.28 (m, 6H); MS (ESI): m/z 398.2 (M^++Na).

4.3.6. *N*-((1*R*,2*R*)-2-((4-Methoxyphenyl)thio)cyclohexyl)-4-methylbenzenesulfonamide (**4f**)[17]

Yield: 70%; white solid. Enantiomeric excess: 56%, $[\alpha]_D^{28}$ = -21.3 (*c* = 1.05, $CHCl_3$), determined by HPLC (Chiralpak AS-H column, hexane/*i*-PrOH 1:4, flow rate 0.3 ml/min, t_{minor} = 80.1 min, t_{major} = 61.7 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 5.21-5.24 (m, 1H), 3.73 (s, 3H), 2.79-2.84 (m, 1H), 2.56-2.60 (m, 1H), 2.37 (s, 3H), 2.23-2.26 (m, 1H), 1.88-1.93 (m, 1H), 1.50-1.54 (m, 1H), 1.14-1.24(m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.9, 143.3, 137.6, 136.4, 129.7, 127.3, 122.3, 114.5, 55.3, 52.3, 32.5, 31.8, 24.9, 23.5, 21.6; HRMS(MALDI): calcd. for $[M+Na]^+$ ($C_{20}H_{25}NS_2O_3$) requires 414.1174, found 414.1173.

4.3.7. *N*-((1*R*,2*R*)-2-((4-Fluorophenyl)thio)cyclohexyl)-4-methylbenzenesulfonamide (**4g**)[17]

Yield: 99%; white solid. Enantiomeric excess: 61%, $[\alpha]_D^{27}$ = -17.6 (*c* = 2.1, $CHCl_3$), determined by HPLC (Phenomenex Cellulose-2 column, hexane/*i*-PrOH 95:5, flow rate 0.7 ml/min, t_{minor} = 74.6 min, t_{major} = 61.7 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 6.97 (t, *J* = 8.8 Hz, 2H), 5.29-5.31 (m, 1H), 2.98-3.00 (m, 1H), 2.81-2.86 (m, 1H), 2.47 (s, 3H), 2.26-2.27 (m, 1H), 1.98-2.00 (m, 1H), 1.60-1.64 (m, 2H), 1.26-1.40(m, 4H); MS (ESI): m/z 402.0 (M^++Na).

4.3.8. 4-Methyl-*N*-((1*R*,2*R*)-2-((4-nitrophenyl)thio)cyclohexyl)benzenesulfonamide (**4h**)

Yield: 99%; yellow solid. m.p. = 64-65°C. Enantiomeric excess: 60%, $[\alpha]_D^{26}$ = 58.2 (*c* = 2.35, $CHCl_3$), determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 4:1, flow rate 1.0 ml/min, t_{minor} = 20.4 min, t_{major} = 16.6 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.03 (d, *J* = 6.4 Hz, 1H), 3.24-3.38 (m, 2H), 2.47 (s, 3H), 2.16-2.17 (m, 2H), 1.60-1.65 (m, 4H), 1.29-1.45(m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 145.5, 143.7，137.,5, 129.7, 128.4, 127.1, 123.9, 54.7, 49.1, 31.3, 30.4, 23.6, 22.7, 21.5; IR (Neat) 3276, 2932, 1577, 1510, 1337, 1157, 1093, 853, 814, 742, 666, 572; HRMS(MALDI): calcd. for $[M+Na]^+$ ($C_{19}H_{22}N_2S_2O_4$) requires 429.0919, found 429.0900.

4.3.9. *N*-((1*R*,2*R*)-2-((4-Bromophenyl)thio)cyclohexyl)-4-methylbenzenesulfonamide (**4i**)[17]

Yield: 93%; white solid. Enantiomeric excess: 67%, $[\alpha]_D^{28}$ = 4.28 (*c* = 2.0, $CHCl_3$), determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 85:15, flow rate 1.0 ml/min, t_{minor} = 14.1 min, t_{major} = 12.0 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 5.29 (d, *J* = 4.8 Hz, 1H), 2.87-2.94 (m, 2H), 2.36 (s, 3H), 2.10-2.12 (m, 1H), 1.91-1.97 (m, 1H), 1.49-1.51 (m, 2H), 1.29-1.35(m, 1H), 1.18-2.00 (m, 3H); MS (ESI): m/z 462.0 (M^++Na).

4.3.10.
N-((1*R*,2*R*)-2-((3-Bromophenyl)thio)cyclohexyl)-4-methylbenzenesulfonamide (**4j**)

Yield: 94%; white solid. m.p. = 80-82°C. Enantiomeric excess: 71%, $[\alpha]_D^{26}$ = 3.5 (*c* = 2.0, $CHCl_3$), determined by HPLC (Phenomenex Cellulose-2 column, hexane/*i*-PrOH 9:1, flow rate 1.0 ml/min, t_{minor} = 26.7 min, t_{major} = 20.9 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.39 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.13-7.19 (m, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 4.94 (d, *J* = 4.4 Hz, 1H), 2.91-2.99 (m, 2H), 2.36 (s, 3H), 2.15-2.17 (m, 1H), 1.93-1.97 (m, 1H), 1.53-1.55 (m, 1H), 1.33-1.35 (m, 1H), 1.19-1.23 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.4, 137.4, 136.1, 134.6, 130.7, 130.3, 129.7, 127.2, 122.7, 55.1, 51.1, 32.0, 31.2, 24.2, 23.1, 21.6; IR (Neat) 3276, 2934, 2857, 1574, 1556, 1459, 1327, 1156, 1093, 813, 778, 754, 666, 572, 551; HRMS(MALDI): calcd. for $[M+Na]^+$ ($C_{19}H_{22}NBrS_2O_2$) requires 462.0173, found 462.0170.

4.3.11.
N-((1*R*,2*R*)-2-((2-Bromophenyl)thio)cyclohexyl)-4-methylbenzenesulfonamide (**4k**)

Yield: 90%; white solid. m.p. = 93-95°C. Enantiomeric excess: 63%, $[\alpha]_D^{22}$ = -6.48 (*c* = 1.13, CH_2Cl_2), determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 9:1,

flow rate 1.0 ml/min, t_{minor} = 20.6 min, t_{major} = 15.3 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.28-7.30 (m, 1H), 7.14-7.22 (m, 3H), 7.02 (t, *J* = 8.0 Hz, 1H), 5.12-5.19 (m, 1H), 3.00-3.03 (m, 2H), 2.35 (s, 3H), 2.20-2.22 (m, 1H), 1.95-1.98 (m, 1H), 1.43-1.55 (m, 3H), 1.18-1.31 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.4, 137.1, 135.3, 133.4, 132.8, 129.7, 128.4, 127.9, 127.3, 127.0, 55.1, 50.4, 32.3, 31.1, 24.2, 23.1, 21.6; IR (Neat) 3277, 2934, 2857, 1448, 1327, 1157, 1093, 1019, 895, 814, 749, 667, 571, 551; HRMS(MALDI): calcd. for $[M+H]^+$ ($C_{19}H_{23}NBrS_2O_2$) requires 440.0343, found 440.0348.

4.3.12. *N*-((1*R*,2*R*)-2-((2-Aminophenyl)thio)cyclohexyl)-4-methylbenzenesulfonamide (**4l**)[17]

Yield: 93%; white solid. Enantiomeric excess: 44%, $[\alpha]_D^{26}$ = -26.5 (*c* = 1.7, $CHCl_3$), determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 4:1, flow rate 1.0 ml/min, t_{minor} = 27.4 min, t_{major} = 19.1 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.03-7.10 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 6.55 (t, *J* = 7.6 Hz, 1H), 5.12-5.16 (m, 1H), 4.26 (s, 2H), 2.97-3.00 (m, 1H), 2.63-2.69 (m, 1H), 2.35 (s, 3H), 2.10-2.11 (m, 1H), 1.88-1.89 (m, 1H), 1.48-1.54 (m, 2H), 1.28-1.37 (m, 1H), 1.08-1.18 (m, 3H); MS (ESI): m/z 377.0 (M^++H).

4.3.13. 4-Methyl-*N*-((1*R*,2*R*)-2-(pyridin-4-ylthio)cyclohexyl)benzenesulfonamide (**4m**)

Yield: 60%; yellow solid. m.p. = 116-118°C. Enantiomeric excess: 30%, $[\alpha]_D^{26}$ = 58.2 (*c* = 2.35, $CHCl_3$), determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 4:1, flow rate 1.0 ml/min, t_{minor} = 15.5 min, t_{major} = 11.6 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 6.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 6.0 Hz, 2H), 4.98 (d, *J* = 6.0 Hz, 1H), 3.39-3.40 (m, 1H), 3.23-3.26 (m, 1H), 2.46 (s, 3H), 2.18-2.20 (m, 2H), 1.29-1.44 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.2, 147.8, 143.5, 137.6, 129.7, 127.1, 122.1, 54.5, 47.6, 31.3, 30.4, 23.6, 22.7, 21.5; IR (Neat) 3058, 2934, 2858, 1580, 1449, 1326, 1157, 1093, 813, 571, 594; HRMS(MALDI): calcd. for $[M+Na]^+$ ($C_{18}H_{22}N_2S_2O_2$) requires 385.1020, found 385.1020.

4.3.14. 4-Methyl-*N*-((1*R*,2*R*)-2-(naphthalen-1-ylthio)cyclohexyl)benzenesulfonamide (**4n**)

Yield: 90%; white solid. m.p. = 88-91°C. Enantiomeric excess: 54%, $[\alpha]_D^{27}$ = -23.0 (*c* = 1.8, $CHCl_3$), determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 85:15, flow rate 1.0 ml/min, t_{minor} = 14.1 min, t_{major} = 10.8 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8.0 Hz, 1H), 7.88-7.90 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.53-7.60 (m, 3H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.29 (d, *J* = 4.4 Hz, 1H), 3.04-3.21 (m, 2H), 2.43 (s, 3H), 2.30-2.32 (m, 1H), 1.95-1.98 (m, 1H), 1.29-1.44 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.3, 137.4, 134.4, 134.1, 132.4, 130.8, 129.6, 128.8, 128.6, 127.3, 126.7, 126.3, 125.6, 125.5, 55.5, 51.5, 32.2, 31.4, 24.2, 23.2, 21.6; IR (Neat) 3276, 2934, 2857, 1628, 1254, 1157; HRMS(MALDI): calcd. for $[M+H]^+$ ($C_{23}H_{26}NS_2O_2$) requires 412.1394, found 412.1399.

4.3.15. 4-Methyl-*N*-((1*R*,2*R*)-2-(naphthalen-2-ylthio)cyclohexyl)benzenesulfonamide (**4o**)[17]

Yield: 91%; white solid. Enantiomeric excess: 57%, $[\alpha]_D^{28}$ = 19.4 (*c* = 1.85, $CHCl_3$), determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 4:1, flow rate 1.0

ml/min, t_{minor} = 13.1 min, t_{major} = 10.1 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74-7.86 (m, 6H), 7.51-7.53 (m, 2H), 7.37-7.39 (m, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 5.42-5.43 (m, 1H), 3.10-3.14 (m, 2H), 2.41 (s, 3H), 2.29-2.31 (m, 1H), 2.09-2.12 (m, 1H), 1.60-1.62 (m, 2H), 1.31-1.33 (m, 4H); MS (ESI): m/z 434.1 (M^++Na).

4.3.16. 4-Methyl-*N*-((1*R*,2*R*)-2-(phenylthio)cyclopentyl)benzenesulfonamide (**4p**)[17]

Yield: 95%; white solid. Enantiomeric excess: 51%, $[\alpha]_D^{26}$ = 11.2 (*c* = 1.6, $CHCl_3$), determined by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH 95:5, flow rate 1.0 ml/min, t_{minor} = 29.7 min, t_{major} = 32.5 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.17-7.20 (m, 7H), 4.71 (d, *J* = 4.0 Hz, 1H), 3.21-3.27 (m, 2H), 2.36 (s, 3H), 2.00-2.01 (m, 2H), 1.58-1.65 (m, 2H), 1.39-1.54 (m, 2H); MS (ESI): m/z 370.1 (M^++Na).

4.3.17. *N*-((1*S*,2*S*)-2-((4-Chlorophenyl)thio)cyclohexyl)-3,5-dinitrobenzamide (**4q**)

Yield: 99%; yellow solid. m.p. = 191-192^{o}C. Enantiomeric excess: 62%, $[\alpha]_D^{22}$ = 33.2 (*c* = 0.83, $CHCl_3$), determined by HPLC (Chiralpak AD-H column hexane/*i*-PrOH 9:1, flow rate 1.0 ml/min, t_{minor} = 18.2 min, t_{major} = 14.2 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.05-9.07 (m, 1H), 8.68 (d, *J* = 1.6 Hz, 2H), 7.33-7.35 (m, 2H), 7.07-7.18 (m, 3H), 6.19 (d, *J* = 6.8 Hz, 1H), 3.94-3.96 (m, 1H), 3.07 (td, *J* = 3.6 Hz, *J* = 7.6 Hz, 1H), 2.14-2.24 (m, 2H), 1.72-1.75 (m, 2H), 1.28-1.46 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 162.0, 148.5, 137.9, 134.2, 132.1, 129.2, 127.1, 121.0, 68.0, 54.8, 53.5, 51.7, 33.6, 32.9, 29.7, 25.9, 25.6, 24.6; IR (Neat) 3306, 3096, 2937, 1644, 1541, 1476, 1343, 1095, 1013, 918, 821, 730; HRMS(MALDI): calcd. for $[M+H]^+$ ($C_{23}H_{26}NS_2O_2$) requires 412.1394, found 412.1399; HRMS(MALDI): calcd. for $[M+H]^+$ ($C_{19}H_{19}N_3ClSO_5$) requires 436.0722, found 436.0728.

4.3.18. (4a*R*,10a*R*)-10-Tosyl-2,3,4,4a,10,10a-hexahydro-1*H*-phenothiazine(**5**)[18]

Yield: 70%; yellow oil. Enantiomeric excess: 61%, $[\alpha]_D^{25}$ = -22.8 (*c* = 1.7, CH_2Cl_2), determined by HPLC (Phenomenex Cellulose-2 column, hexane/*i*-PrOH 85:15, flow rate 1.0 ml/min, t_{minor} = 6.98 min, t_{major} = 6.22 min, λ = 254 nm); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.17-7.20 (m, 7H), 4.71 (d, *J* = 4.0 Hz, 1H), 3.21-3.27 (m, 2H), 2.36 (s, 3H), 2.00-2.01 (m, 2H), 1.58-1.65 (m, 2H), 1.39-1.54 (m, 2H); MS (ESI): m/z 382.2 (M^++Na).

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:

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Electronic Supplementary Information

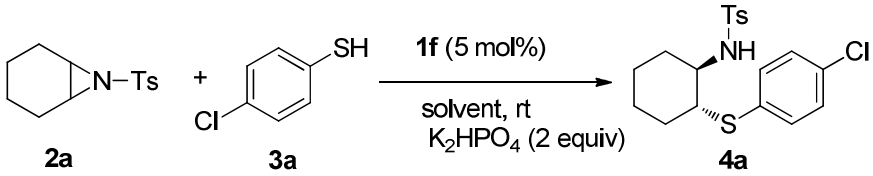
Enantioselective desymmetrization of *meso*-aziridines with benzenethiols catalyzed by chiral bifunctional quaternary phosphonium salts

Jiaxing Zhang,[a] Dongdong Cao,[b] Hongyu Wang,[b] Gang Zhao,[b]* and Yongjia Shang[a]*

Contents

1. Optimization of reaction conditions with catalyst 1f (TableS1, Table S2)

Table S1 Screening of solvents[a]

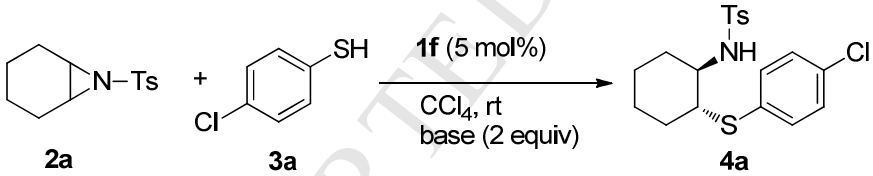


2a **3a** **4a**

Entry	Solvent	Time (h)	Ee[b](%)
1	CCl_4	4	41
2	$CHCl_2CH_2Cl$	4	3
3	1,2-dichlorobenzene	4	16
4	*p*-xylene	4	25
5	$PhCF_3$	4	21
6	mesitylene	4	11
7	CH_3CN	12	4
8	MTBE	12	14
9	THF	12	-10
10	EtOH	12	-

[a] Reactions were carried out using (0.1 mmol) of **2a**, (0.15 mmol) **3a**, 5 mol% of **1f**, 0.2 mmol of K_2HPO_4. [b] Determined by chiral stationary phase HPLC.

Table S2 Screening of bases[a]

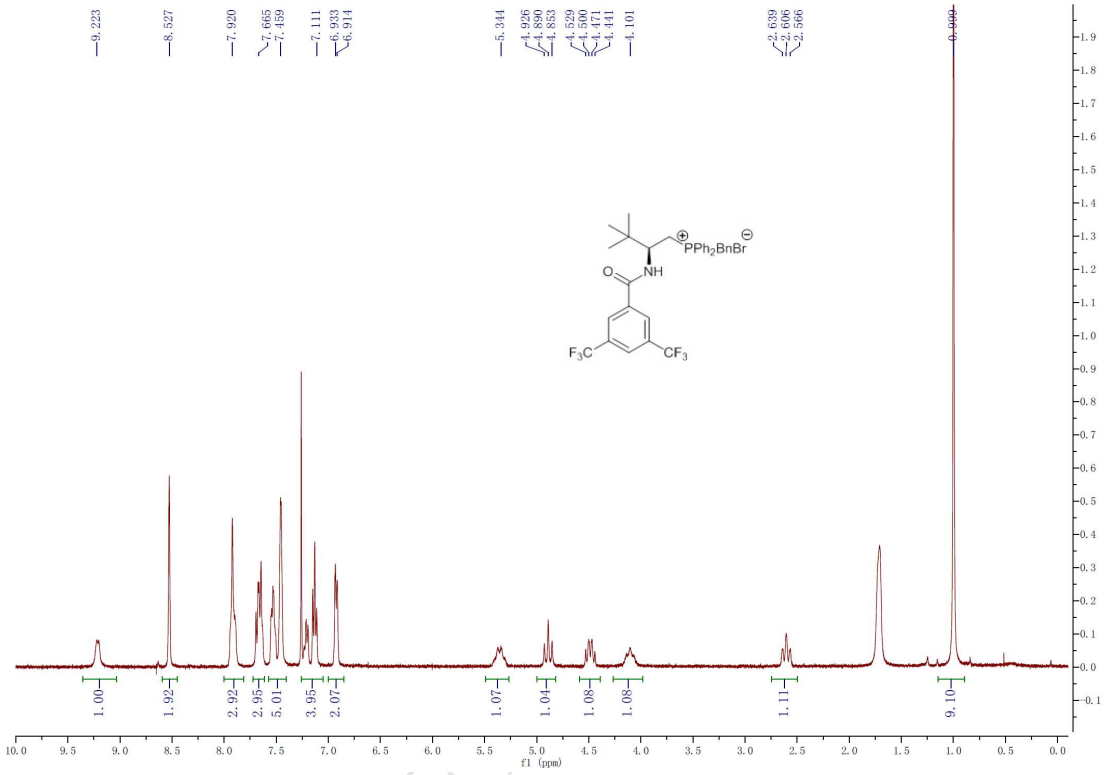


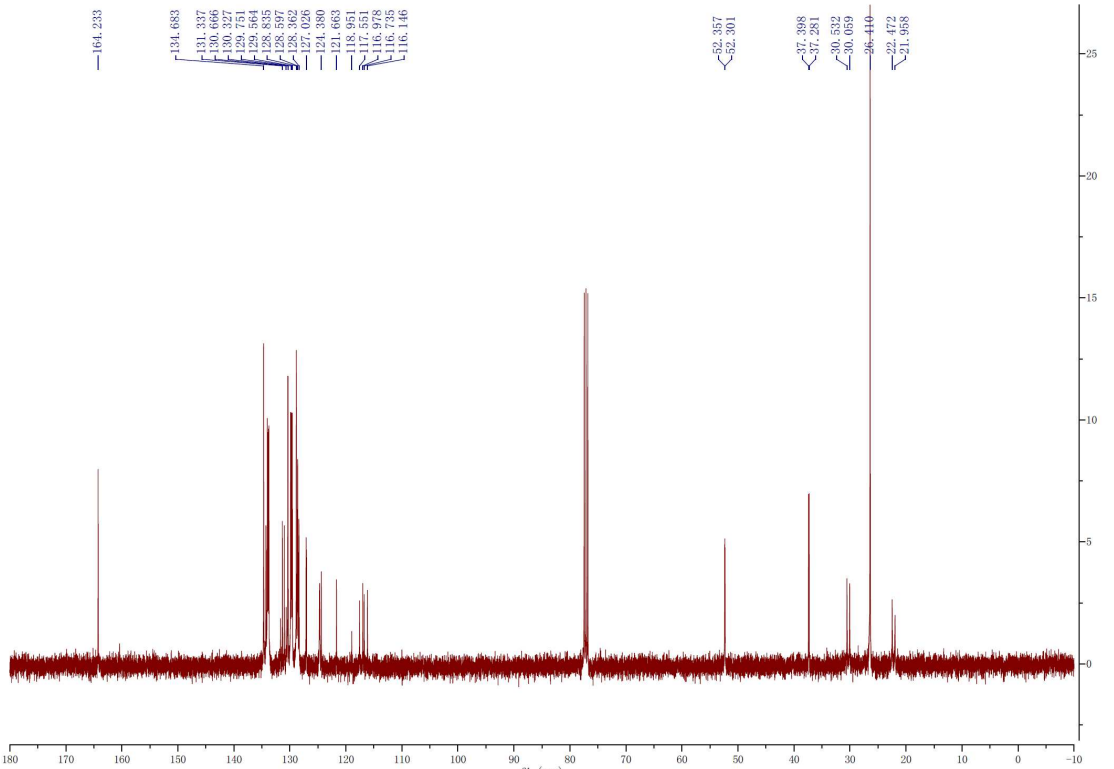
2a **3a** **4a**

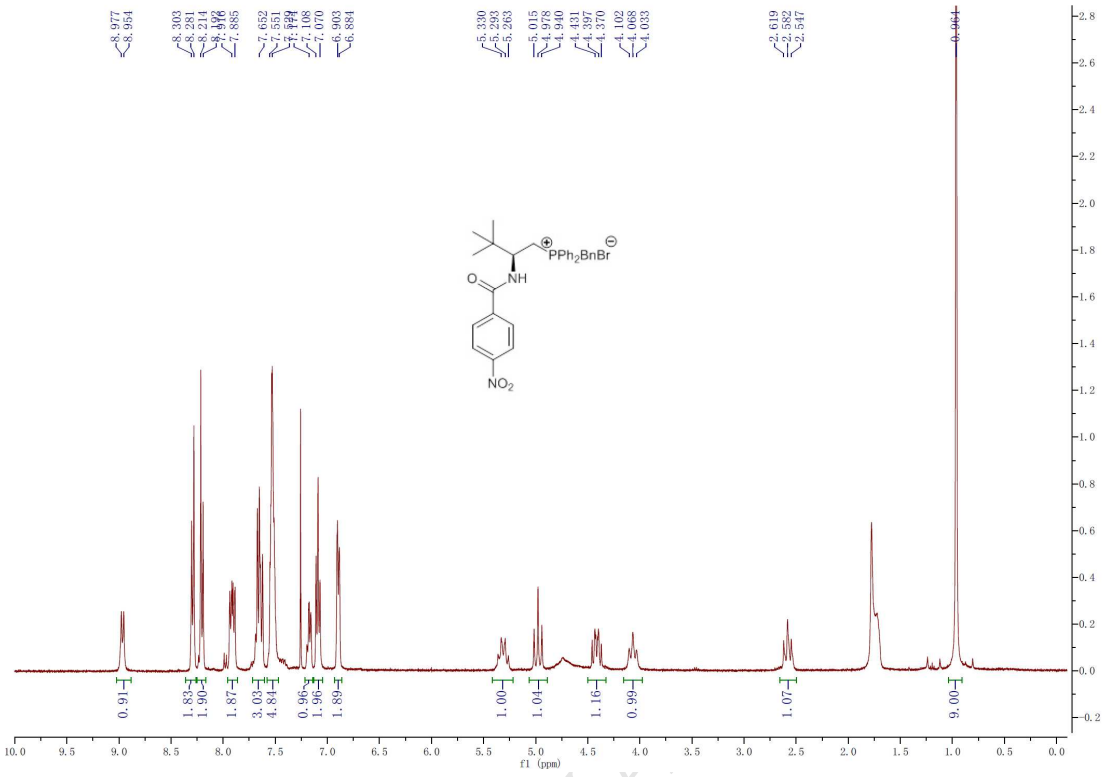
Entry	Base	Time (h)	Yield[b] (%)	Ee[c](%)
1	PhCOONa	4	99	47
2	DABCO	4	99	37
3	DBU	4	99	0
4	DIPEA	4	99	19
5	DMAP	4	99	27
6	KF	4	99	43(59[d])
7	CsF	4	99	27
8	CH_3COOK	4	99	34
9	PhCOOK	4	90	48(57[d])
10	Et_3N	4	99	48(32[d])
11	$KHCO_3$	12	99	56[d]

[a] Reactions were carried out using (0.1 mmol) of **2a**, (0.15 mmol) **3a**, 5 mol% of **1f**. [b] Isolated yields. [c] Determined by chiral stationary phase HPLC. [d] Reaction at 0°C.

2. NMR spectra copies for catalysts (1f-1l) and some products



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NO2
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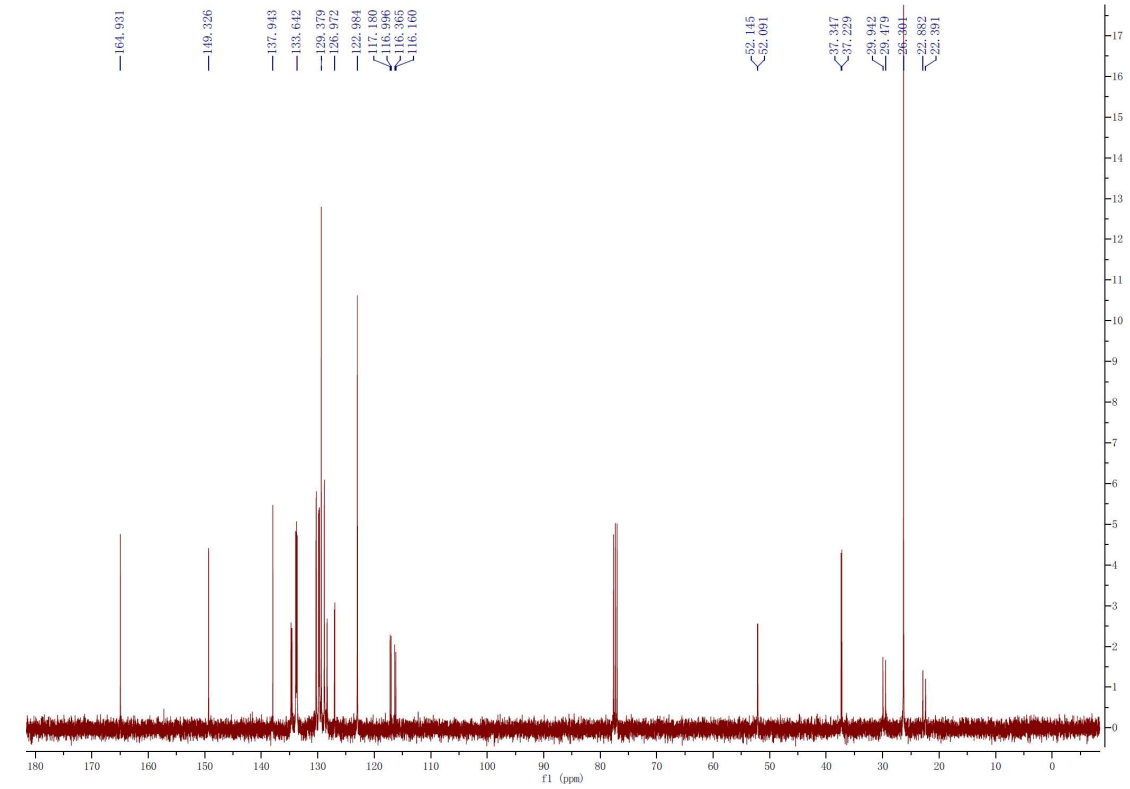
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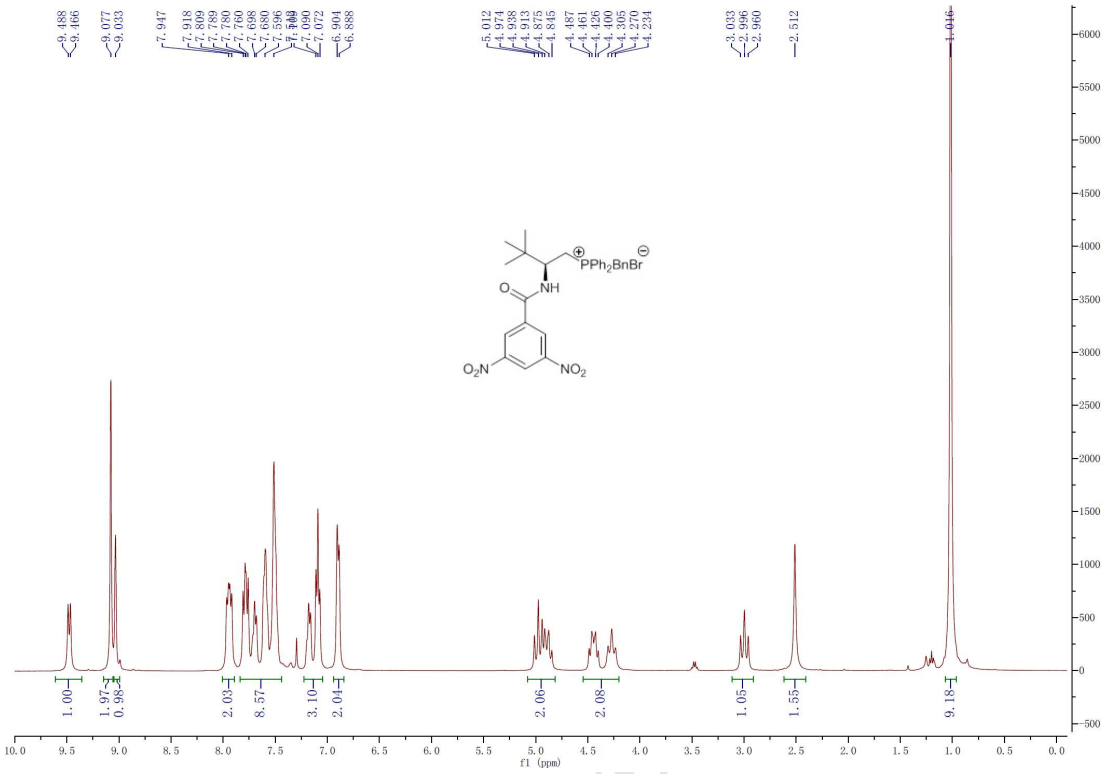
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2.04
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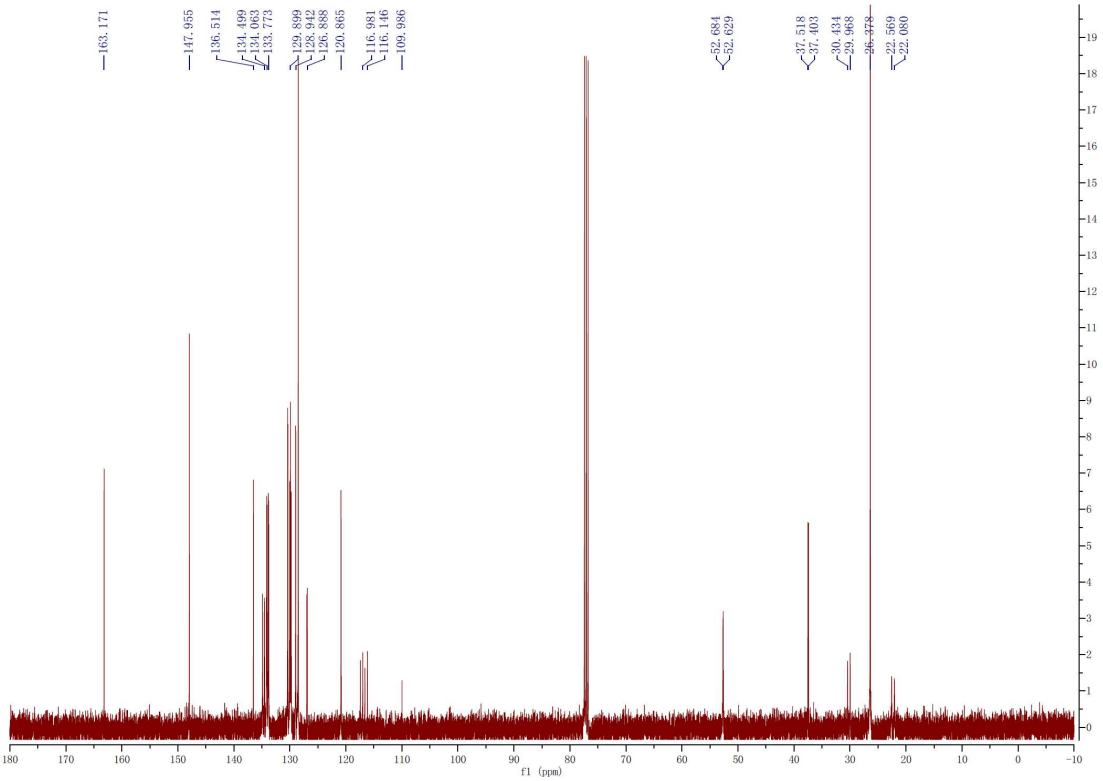
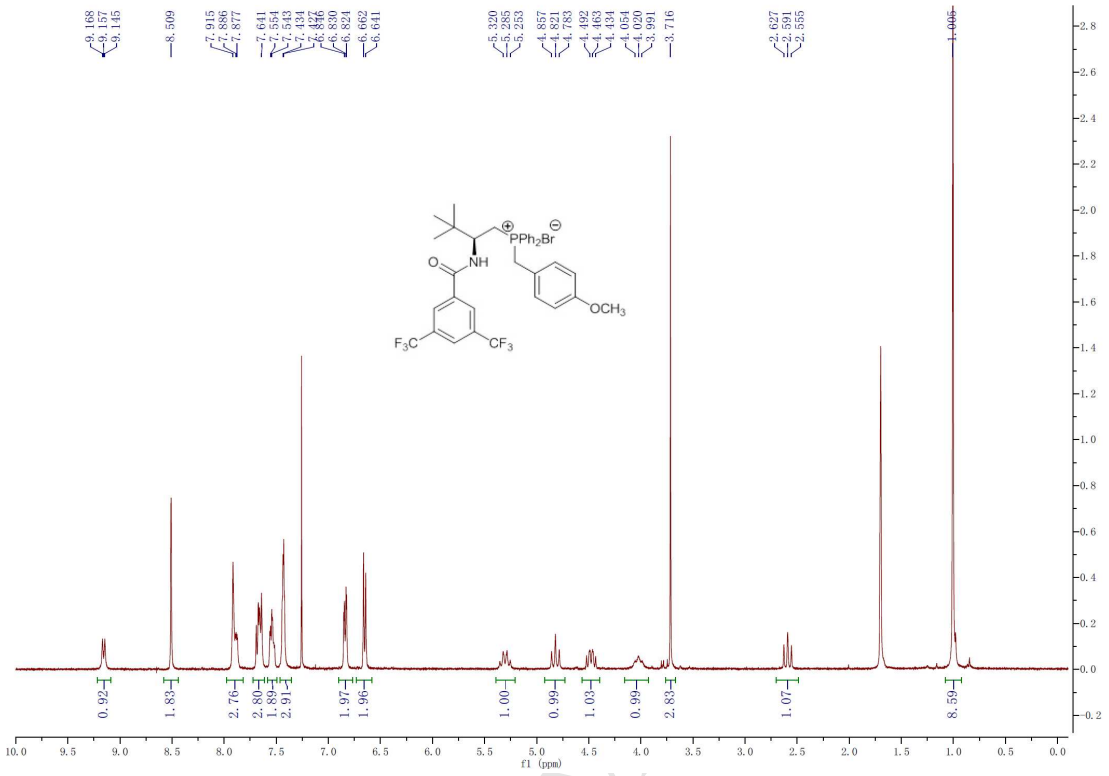
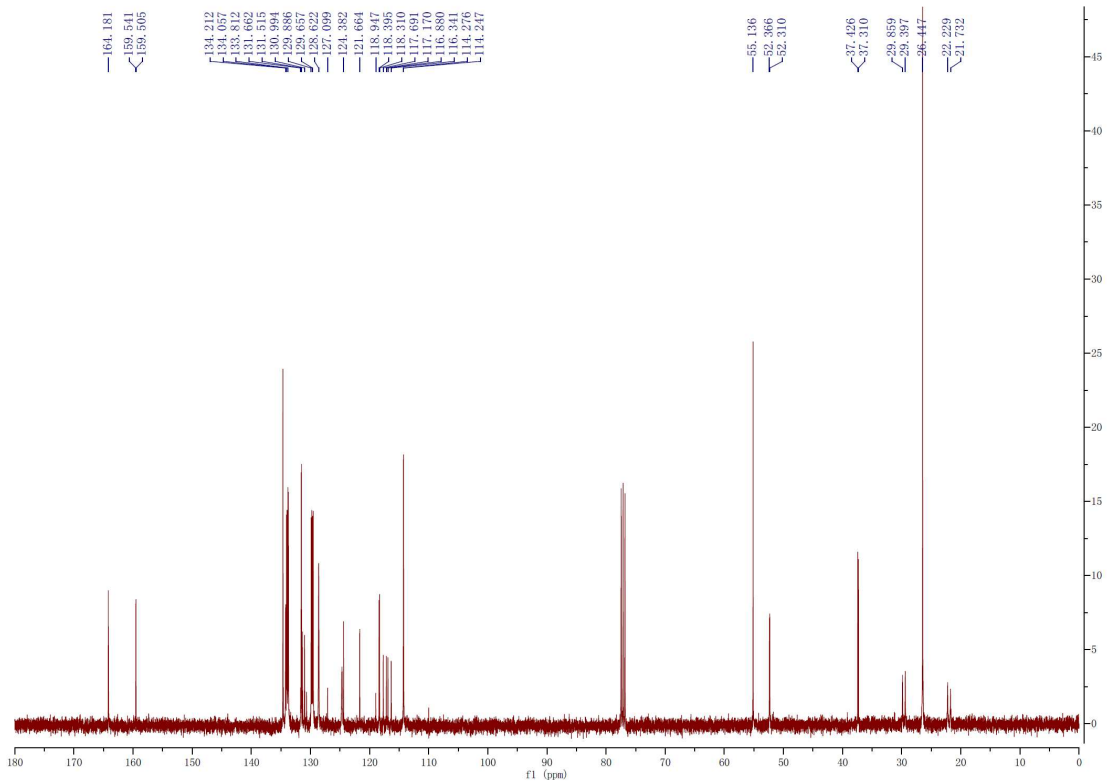
1.55
9.18
f1 (ppm)


163.171
147.955
136.514
134.499
134.063
133.773
129.899
128.942
126.888
120.865
116.981
116.146
109.986
52.684
52.629
37.518
37.403
30.434
29.968
26.378
22.569
22.080
f1 (ppm)


9.168
9.157
9.145
8.509
7.915
7.886
7.877
7.641
7.554
7.543
7.434
7.427
6.846
6.830
6.824
6.662
6.641
5.320
5.285
5.253
4.857
4.821
4.783
4.492
4.463
4.434
4.054
4.020
3.991
3.716
2.627
2.591
2.555
1.006
PPh2Br
NH
O
OCH3
F3C
CF3
0.92
1.83
2.76
2.80
1.89
2.91
1.97
1.96
1.00
0.99
1.03
0.99
2.83
1.07
8.59
f1 (ppm)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134.212
134.057
133.812
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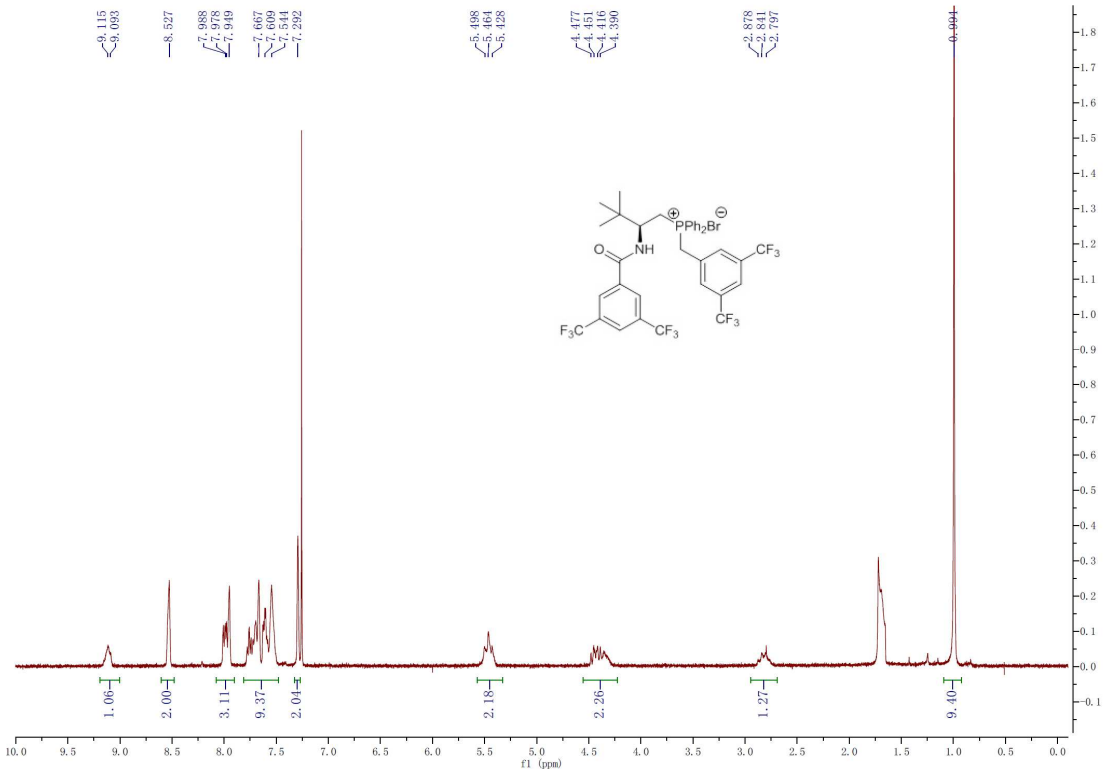
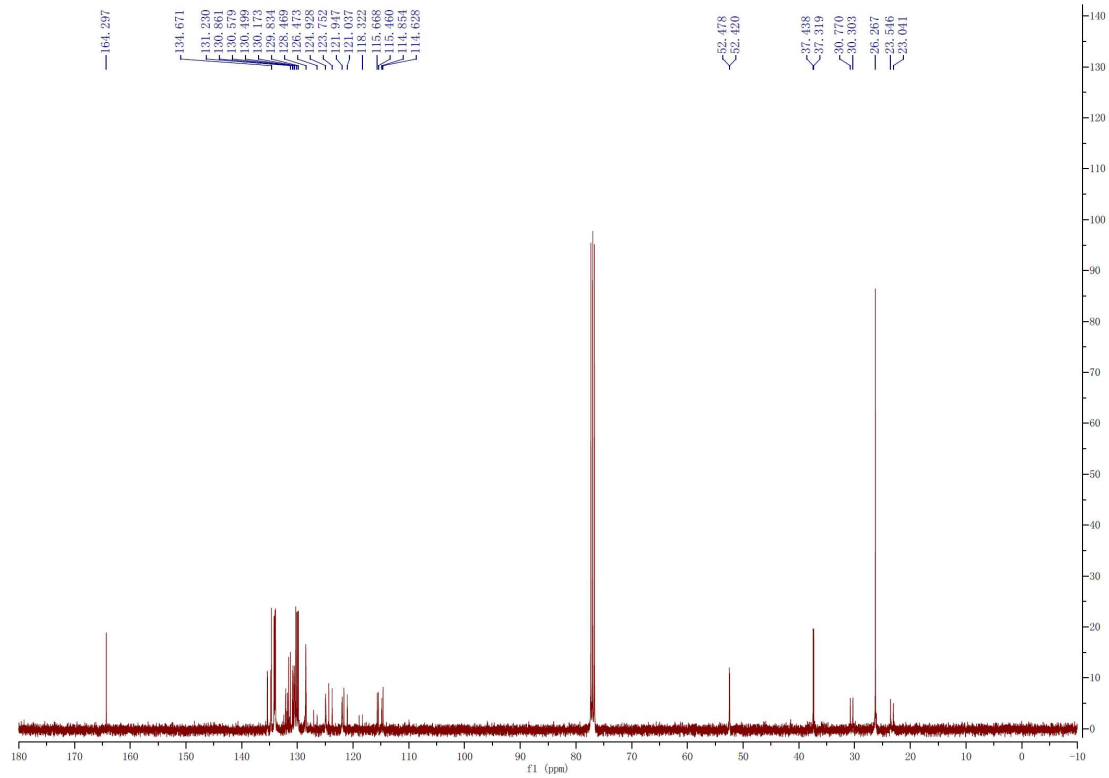
131.515
130.994
129.886
129.657
128.622
127.099
124.382
121.664
118.947
118.395
118.310
117.691
117.170
116.880
116.541
114.276
114.247
55.136
52.366
52.310
37.426
37.310
29.859
29.397
26.447
22.229
21.732
f1 (ppm)


9.115
9.093
8.527
7.988
7.978
7.949
7.667
7.609
7.544
7.292
5.498
5.464
5.428
4.477
4.451
4.416
4.390
2.878
2.841
2.797
0.994
PPh2Br
NH
O
CF3
F3C
CF3
CF3
1.06
2.00
3.11
9.37
2.04
2.18
2.26
1.27
9.40
f1 (ppm)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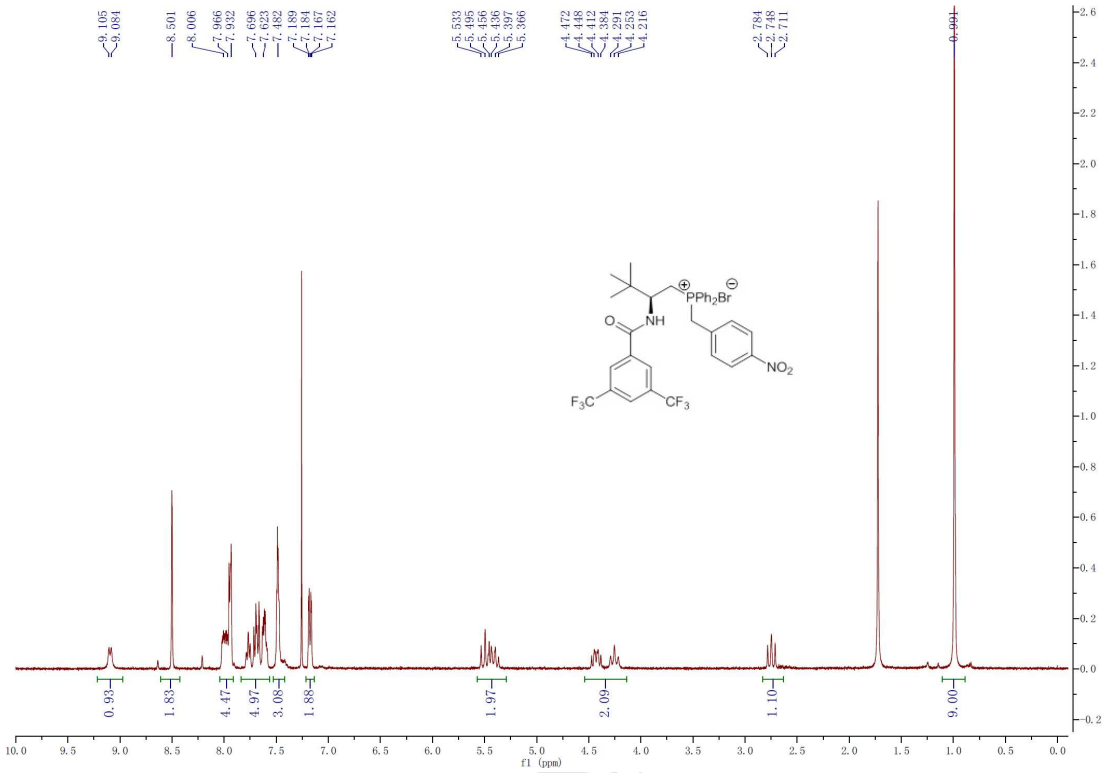
134.671
131.230
130.861
130.579
130.499
130.173
129.834
128.469
126.473
124.928
123.752
121.947
121.037
118.322
115.668
115.460
114.854
114.628
52.478
52.420
37.438
37.319
30.770
30.303
26.267
23.546
23.041
f1 (ppm)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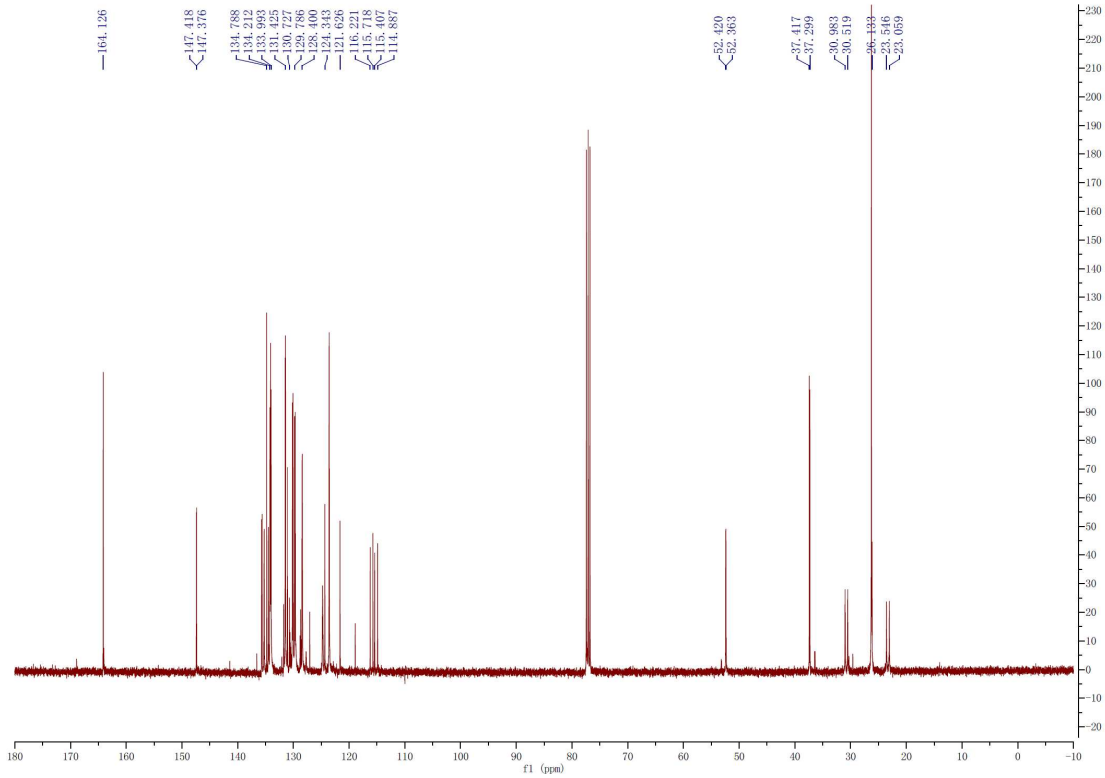
9.084
8.501
8.006
7.966
7.932
7.696
7.623
7.482
7.189
7.184
7.167
7.162
5.533
5.495
5.496
5.496
5.397
5.366
4.472
4.448
4.412
4.384
4.291
4.253
4.216
2.784
2.748
2.711
0.991
PPh2Br
NH
O
NO2
F3C
CF3
0.93
1.83
4.47
4.97
3.08
1.88
1.97
2.09
1.10
9.00
f1 (ppm)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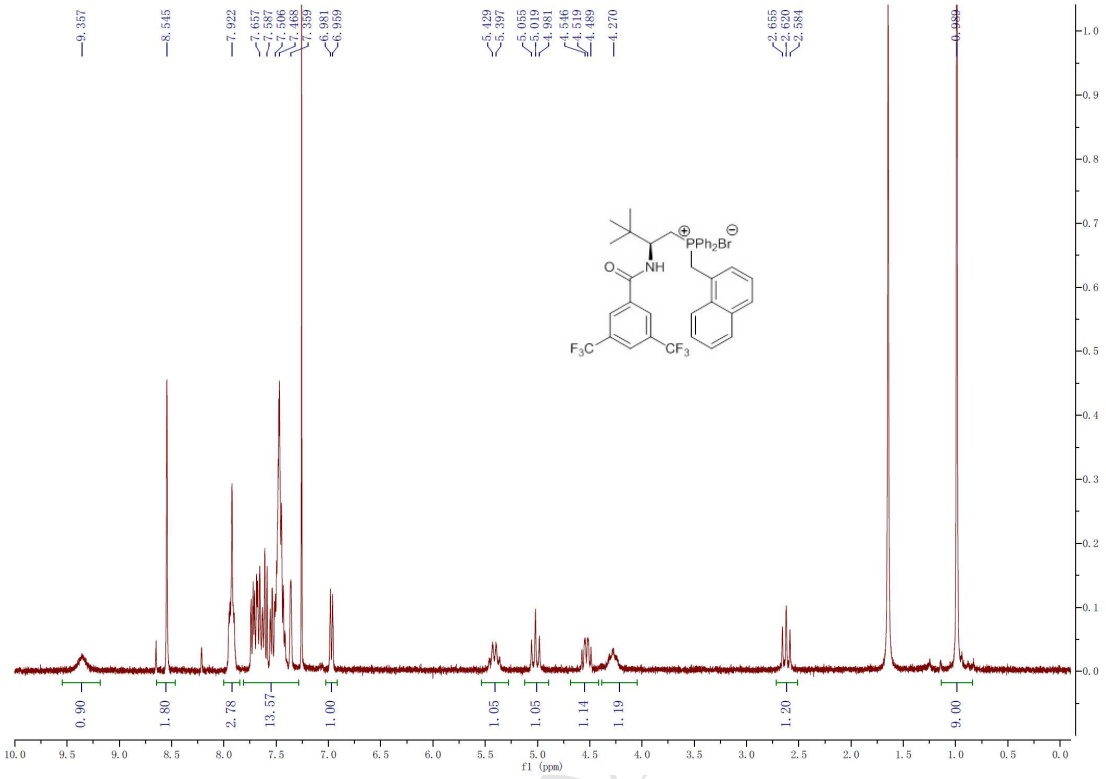
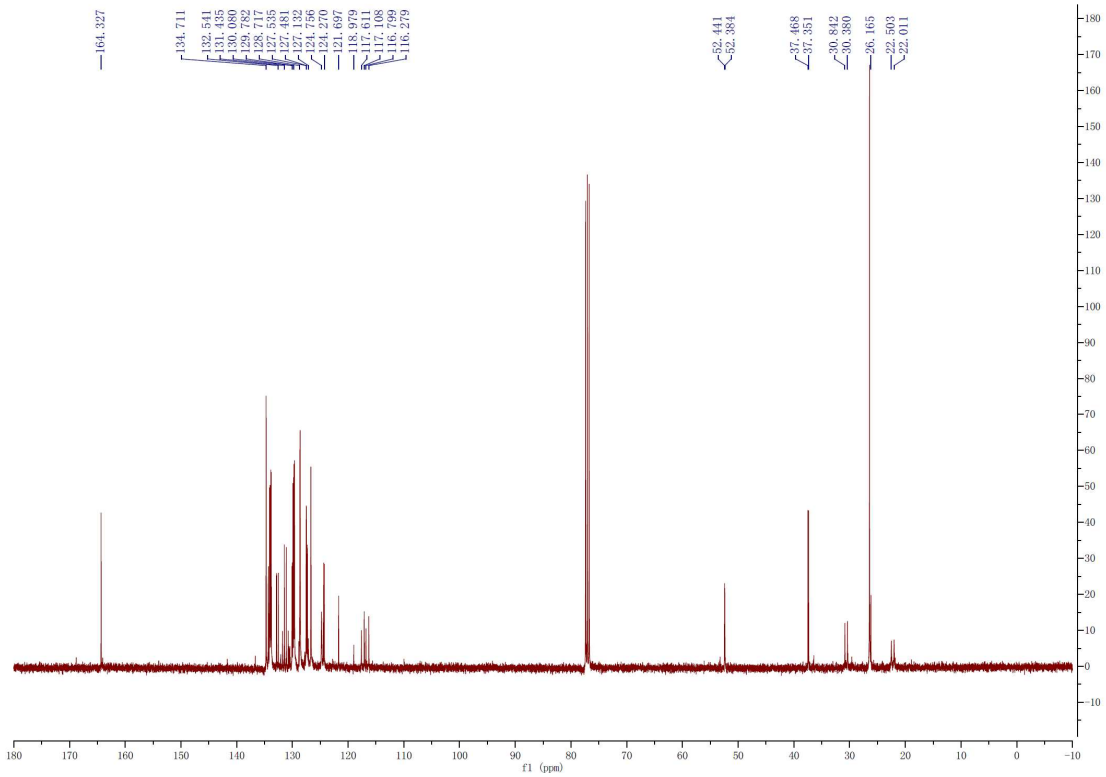
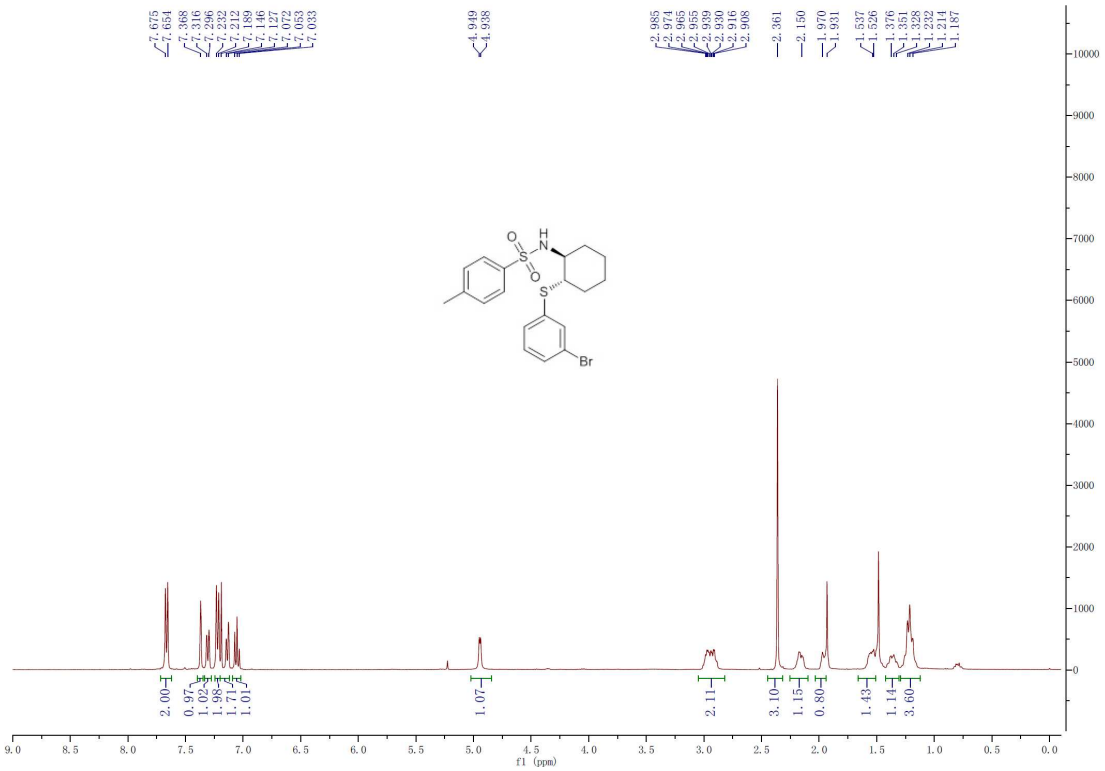
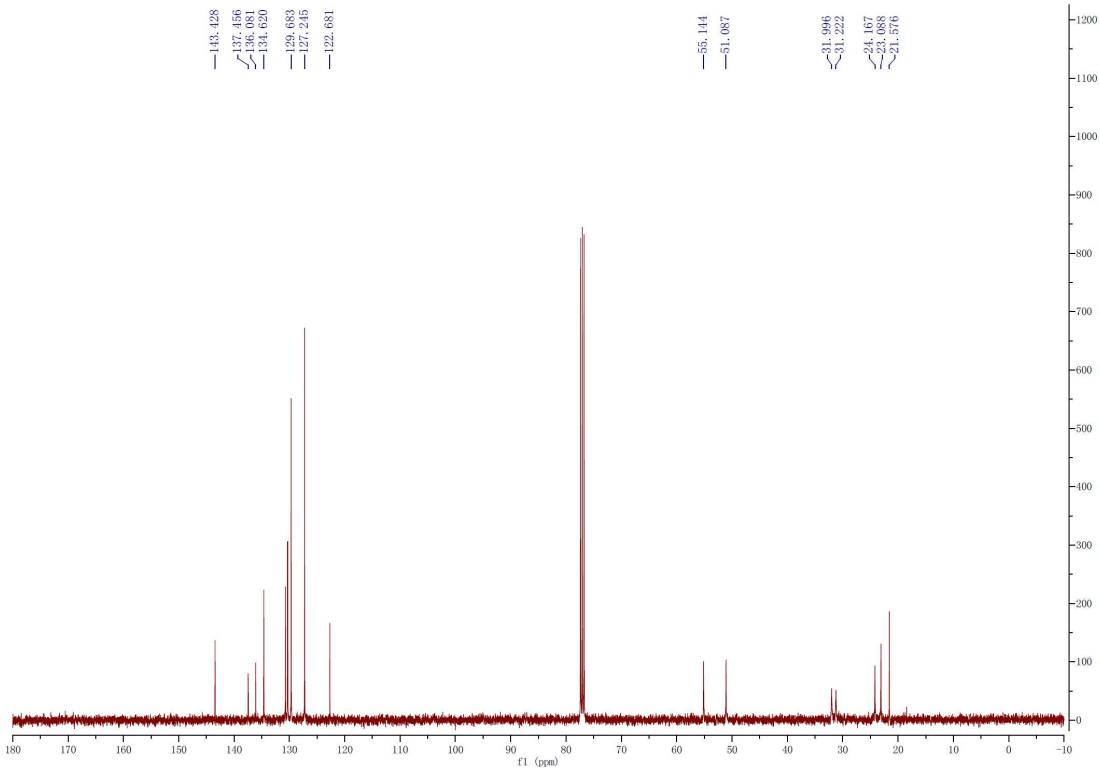
147.376
134.788
134.212
133.993
131.425
130.727
129.786
128.400
124.343
121.696
116.221
115.718
115.407
114.887
52.420
52.363
37.417
37.299
30.983
30.519
26.133
25.546
25.059
f1 (ppm)


9.357
8.545
7.922
7.657
7.587
7.506
7.468
7.359
6.981
6.959
5.429
5.397
5.055
5.019
4.981
4.546
4.519
4.489
4.270
2.655
2.620
2.584
0.880
PPh2Br
NH
O
F3C
CF3
0.90
1.80
2.78
13.57
1.00
1.05
1.05
1.14
1.19
1.20
9.00
f1 (ppm)


164.327
134.711
132.541
131.435
130.080
129.782
128.717
127.585
127.341
127.132
124.756
124.270
121.697
118.979
117.611
117.108
116.799
116.279
52.441
52.384
37.468
37.351
30.842
30.380
26.165
22.503
22.011
f1 (ppm)


7.675
7.654
7.368
7.316
7.296
7.232
7.212
7.189
7.146
7.127
7.072
7.053
7.033
4.949
4.938
2.985
2.974
2.965
2.955
2.939
2.930
2.916
2.908
2.361
2.150
1.970
1.931
1.537
1.526
1.376
1.351
1.328
1.232
1.211
1.187
O
H
N
S
O
S
Br
2.00
0.97
1.02
1.98
1.71
1.01
1.07
2.11
3.10
1.15
0.80
1.43
1.14
3.60
f1 (ppm)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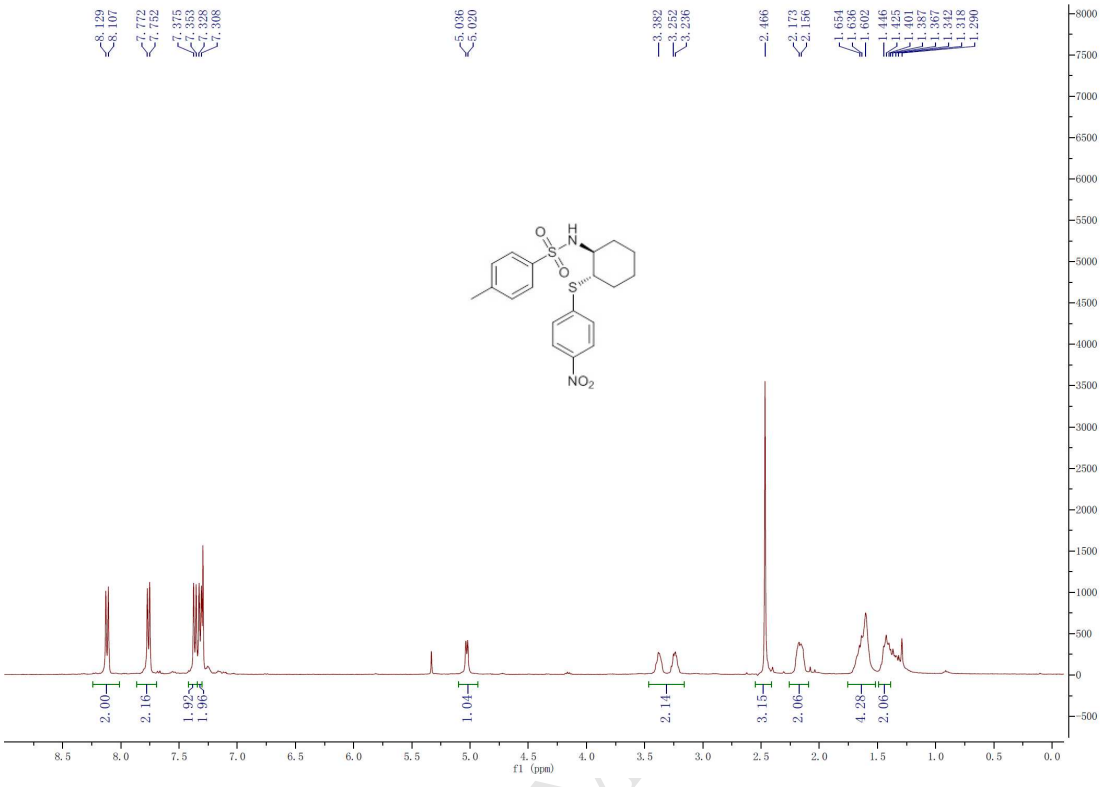
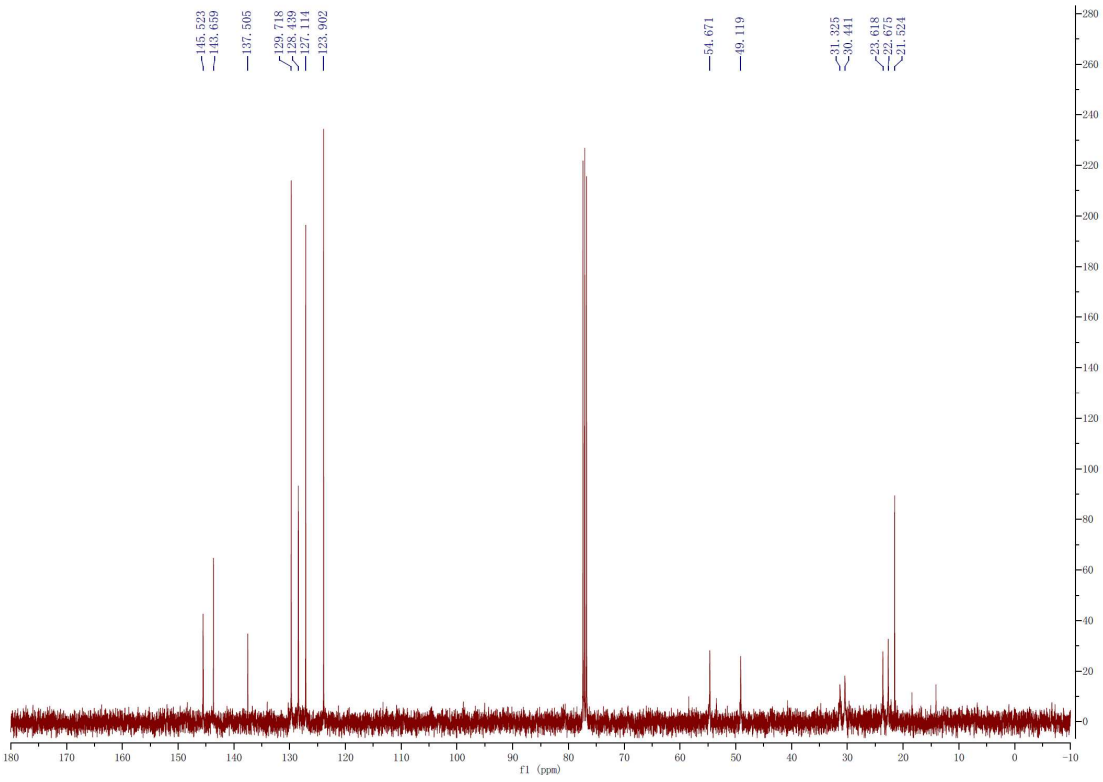
137.456
136.081
134.620
129.683
127.245
122.681
55.144
51.087
31.996
31.222
24.167
23.088
21.576
f1 (ppm)


8.129
8.107
7.772
7.752
7.375
7.353
7.338
7.308
5.036
5.020
3.382
3.252
3.236
2.466
2.173
2.156
1.654
1.636
1.602
1.446
1.425
1.401
1.387
1.367
1.342
1.318
1.290
2.00
2.16
1.92
1.96
1.04
2.14
3.15
2.06
4.28
2.06
f1 (ppm)


145.523
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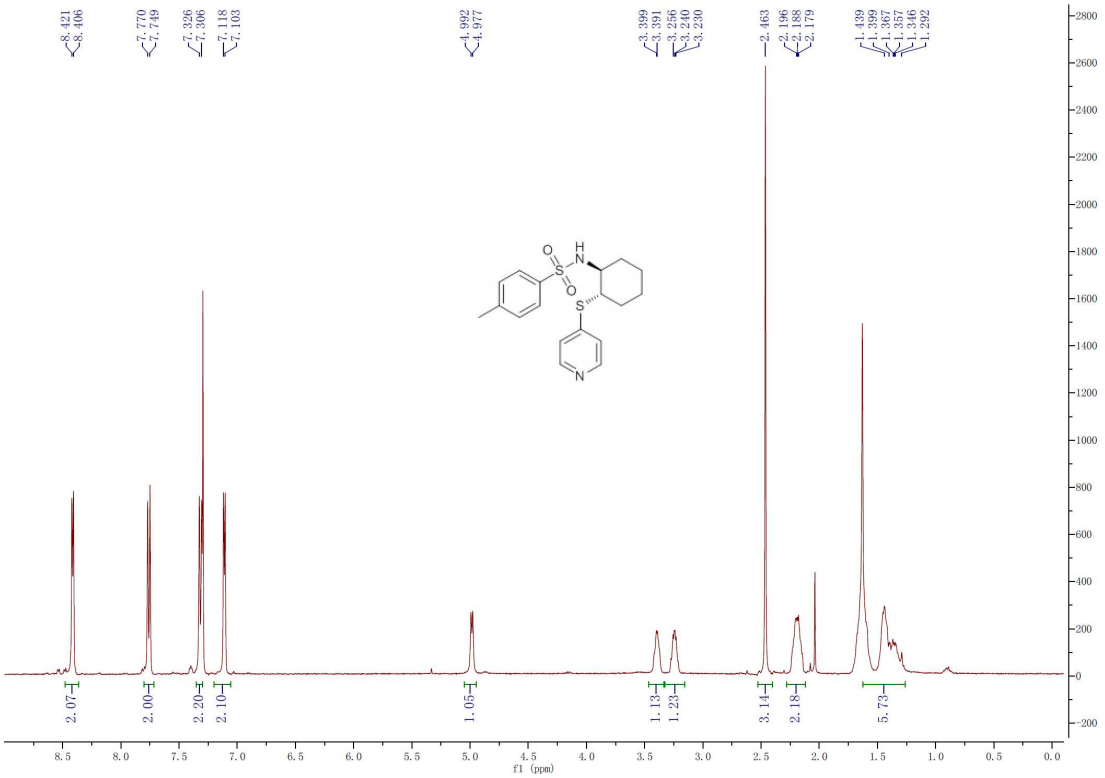
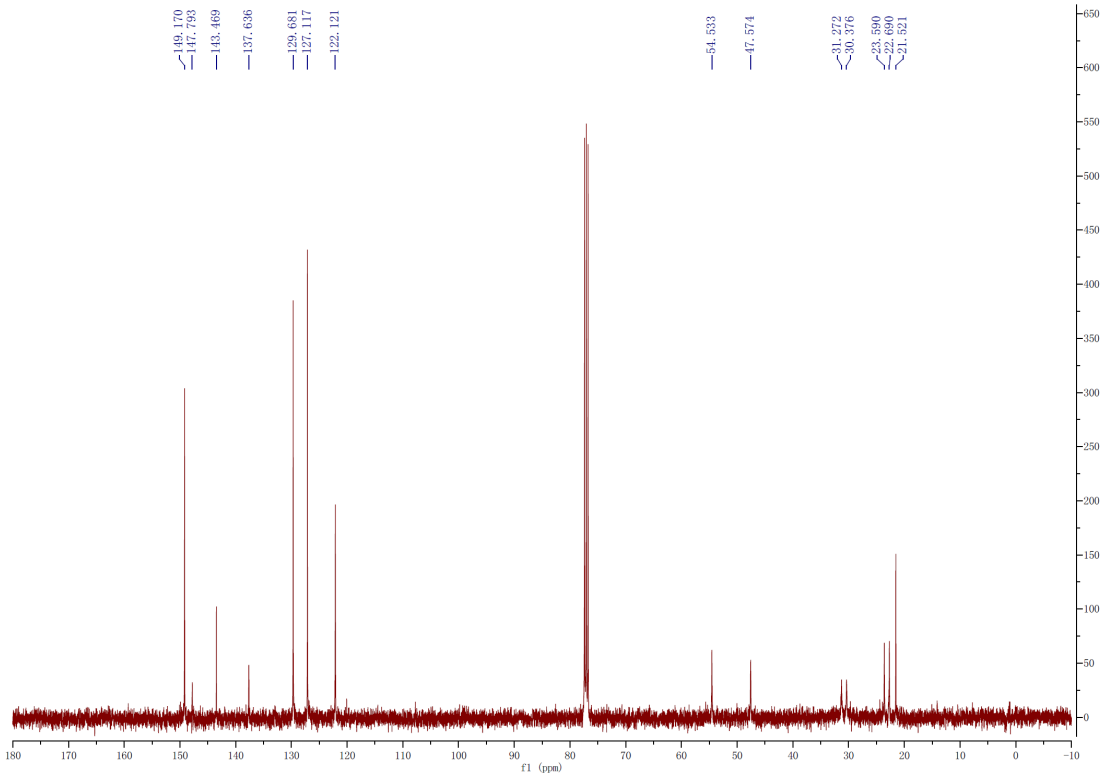
137.505
129.718
128.439
127.114
123.902
54.671
49.119
31.325
30.441
23.618
22.675
21.524
f1 (ppm)


8.421
8.406
7.770
7.749
7.326
7.306
7.118
7.103
4.992
4.977
3.399
3.391
3.256
3.240
3.230
2.463
2.196
2.188
2.179
1.439
1.399
1.367
1.357
1.346
1.292
2.07
2.00
2.20
2.10
1.05
1.13
1.23
3.14
2.18
5.73
f1 (ppm)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143.469
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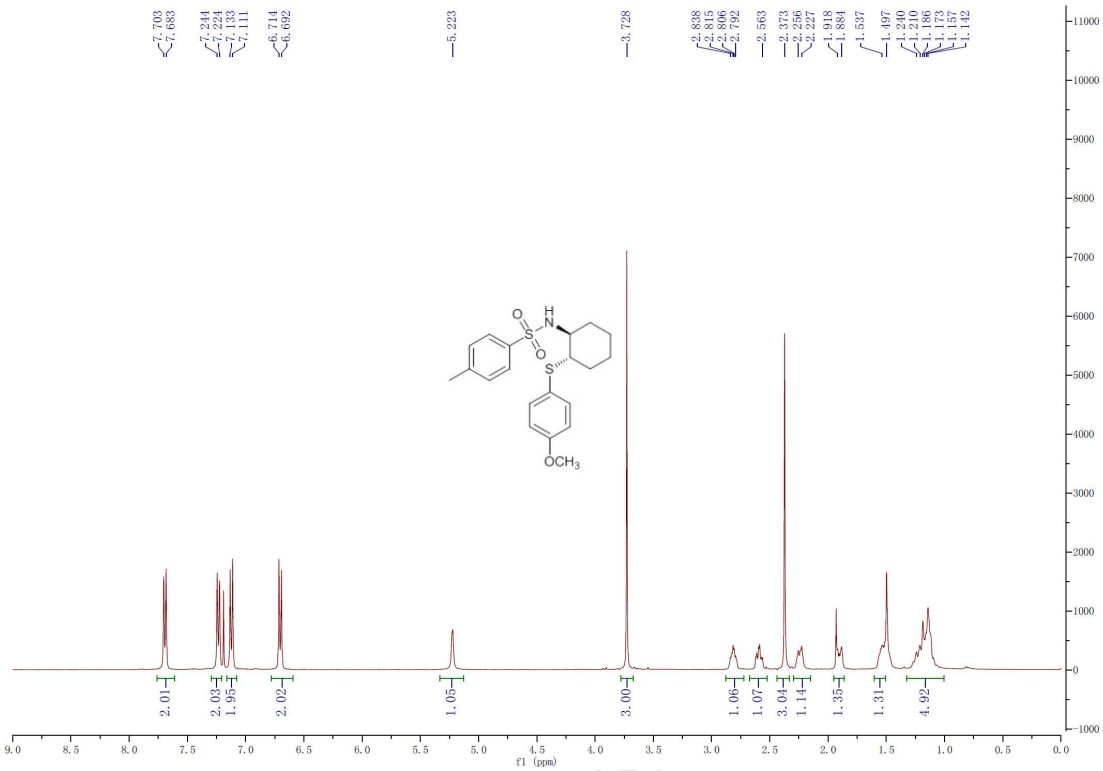
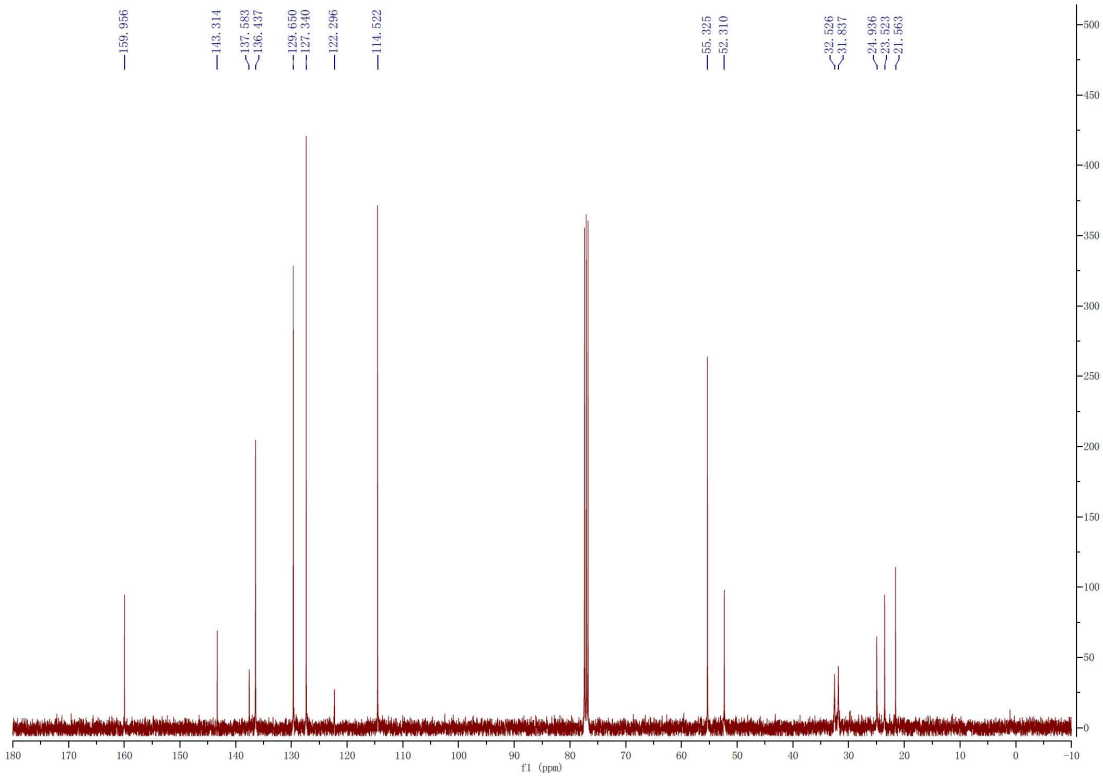
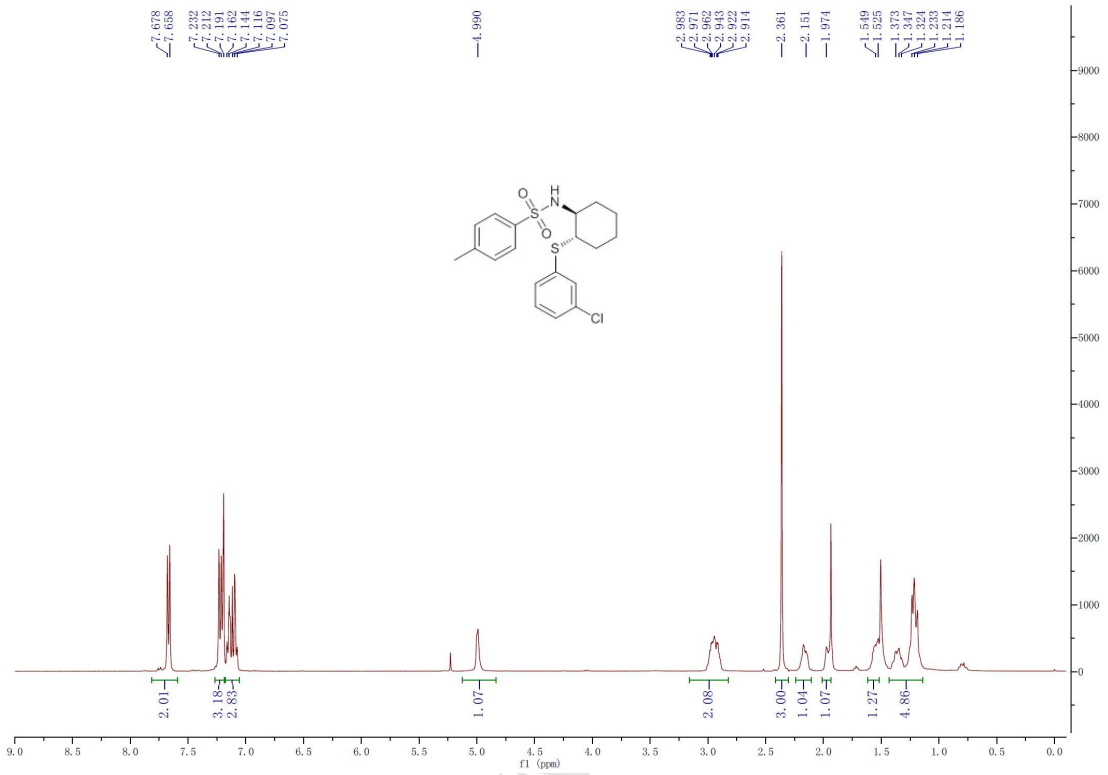
127.117
122.121
54.533
47.574
31.272
30.376
23.590
22.690
21.521
f1 (ppm)


7.703
7.683
7.244
7.224
7.133
7.111
6.714
6.692
5.223
3.728
2.838
2.815
2.806
2.792
2.563
2.373
2.256
2.227
1.918
1.884
1.537
1.497
1.240
1.210
1.186
1.173
1.157
1.142
OCH3
2.01
2.03
1.95
2.02
1.05
3.00
1.06
1.07
3.04
1.14
1.35
1.31
4.92
f1 (ppm)


159.956
143.314
137.583
136.437
129.650
127.340
122.296
114.522
55.325
52.310
32.526
31.837
24.936
23.523
21.563
f1 (ppm)


7.678
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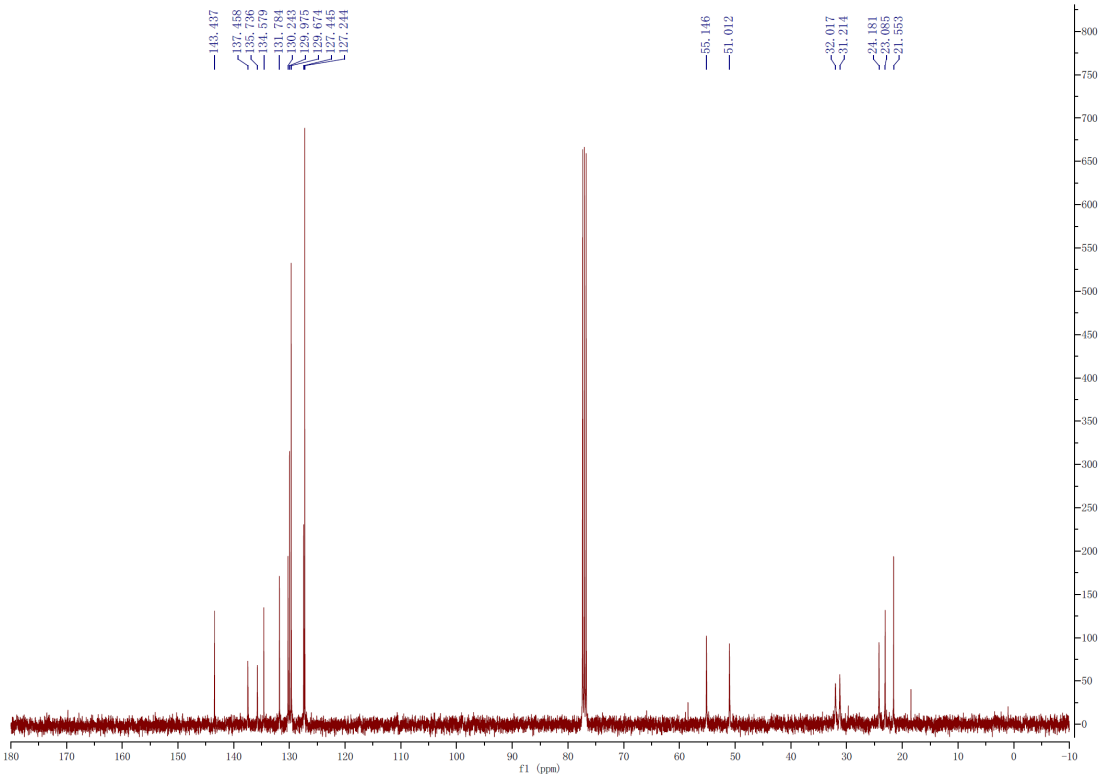
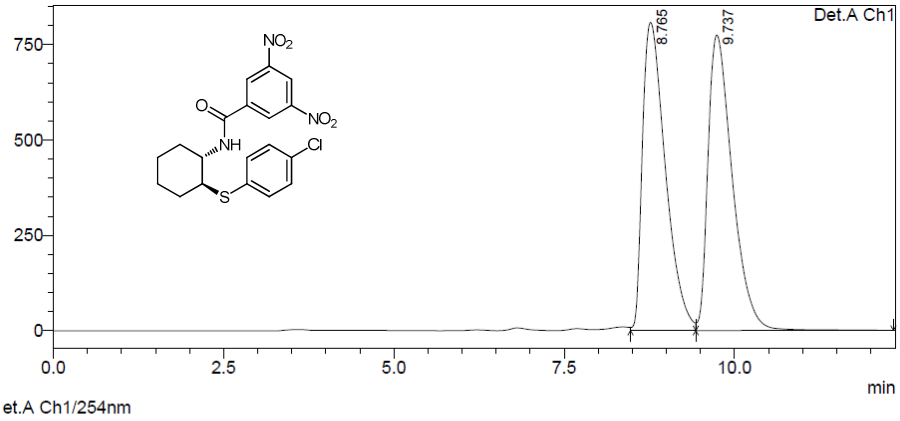
7.232
7.212
7.191
7.162
7.144
7.116
7.097
7.075
4.990
2.983
2.971
2.962
2.943
2.922
2.914
2.361
2.151
1.974
1.549
1.525
1.373
1.347
1.324
1.233
1.214
1.186
2.01
3.18
2.83
1.07
2.08
3.00
1.04
1.07
1.27
4.86
f1 (ppm)


143.437
137.458
135.736
134.579
131.784
130.243
129.975
129.674
127.445
127.244
55.146
51.012
32.017
31.214
24.181
23.085
21.553
f1 (ppm)

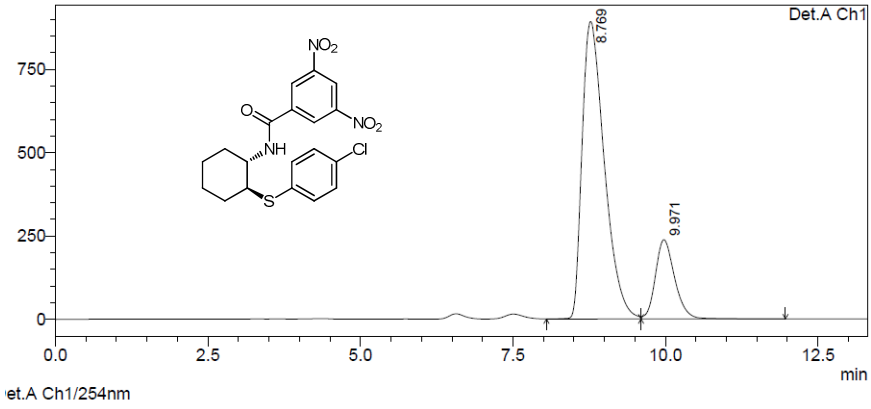
3. HPLC spectra for compounds



PeakTable

Detector A Ch1 254nm

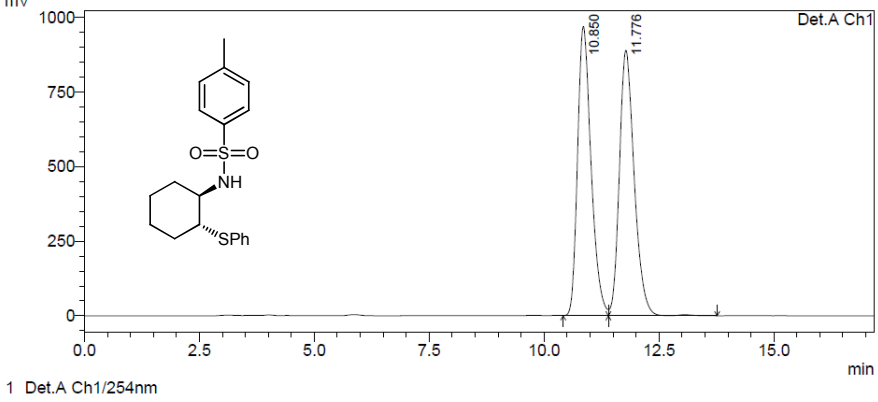
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.765	18915230	807804	49.523	51.051
2	9.737	19279797	774540	50.477	48.949
Total		38195027	1582345	100.000	100.000



PeakTable

Detector A Ch1 254nm

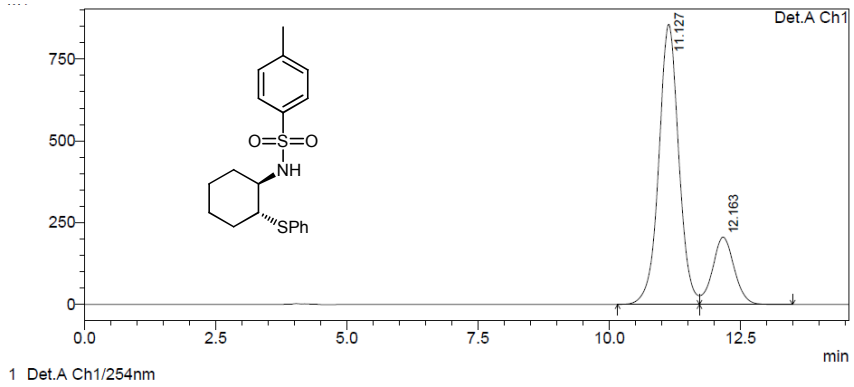
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.769	22667500	892870	81.263	78.945
2	9.971	5226452	238128	18.737	21.055
Total		27893952	1130999	100.000	100.000



PeakTable

Detector A Ch1 254nm

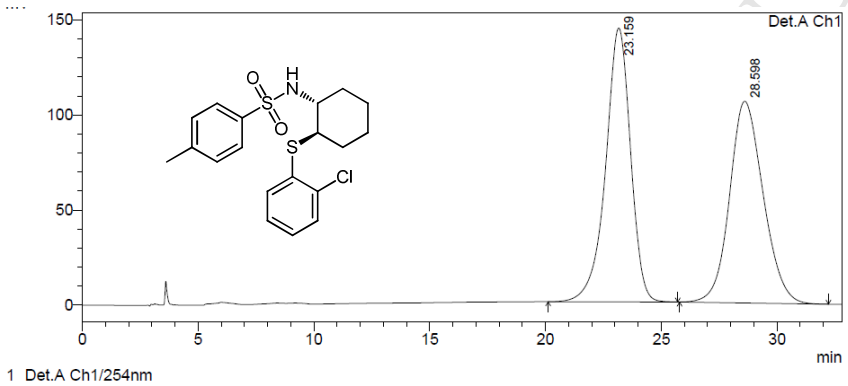
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.850	19847654	969797	49.861	52.146
2	11.776	19958323	889977	50.139	47.854
Total		39805977	1859774	100.000	100.000



PeakTable

Detector A Ch1 254nm

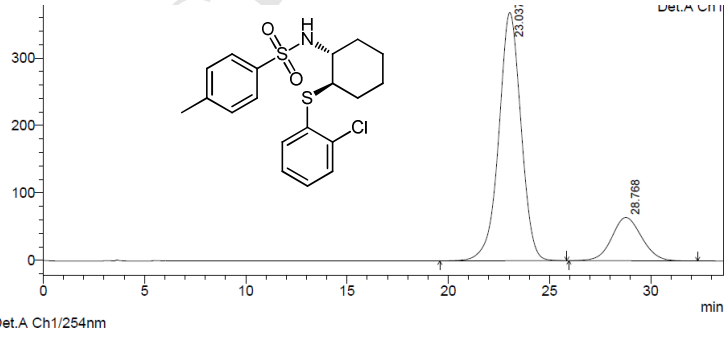
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.127	22672175	856942	79.339	80.614
2	12.163	5904178	206083	20.661	19.386
Total		28576353	1063025	100.000	100.000



PeakTable

Detector A Ch1 254nm

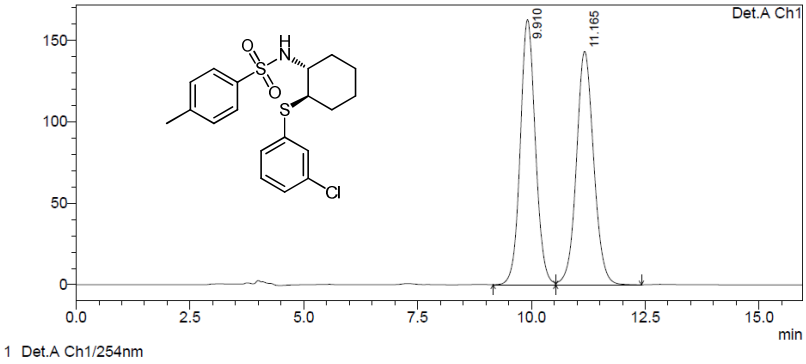
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.159	10786913	144007	50.182	57.587
2	28.598	10708468	106064	49.818	42.413
Total		21495381	250071	100.000	100.000



PeakTable

Detector A Ch1 254nm

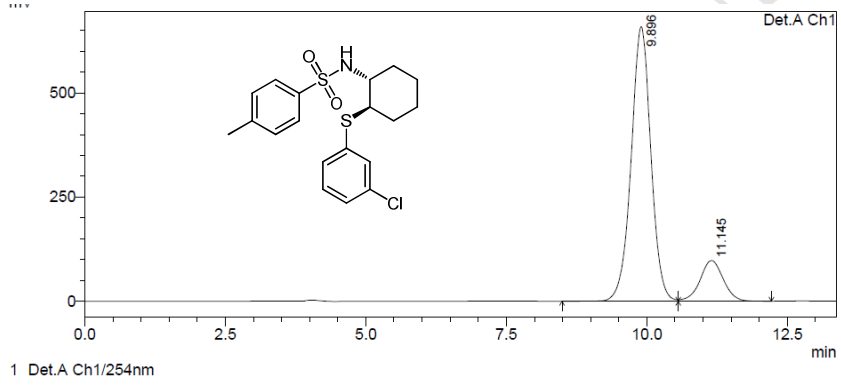
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.037	28041665	367969	80.973	85.157
2	28.768	6589084	64139	19.027	14.843
Total		34630748	432108	100.000	100.000



PeakTable

Detector A Ch1 254nm

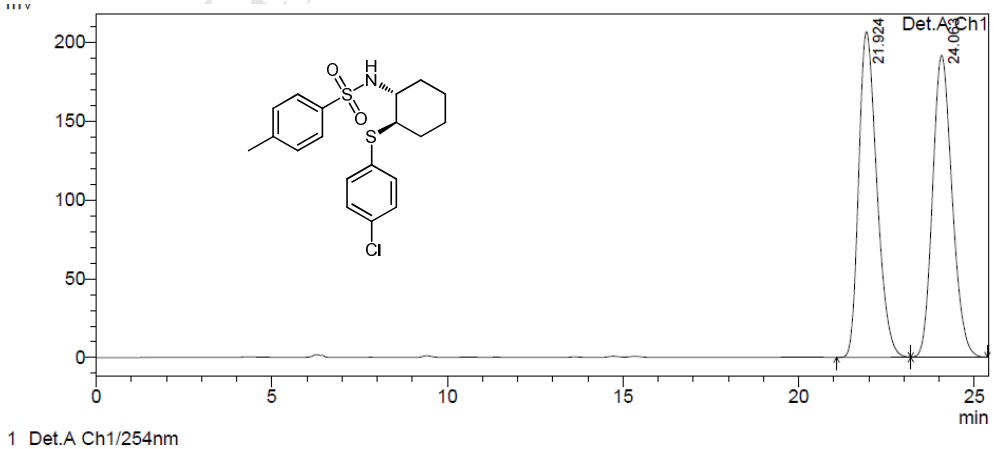
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.910	3770128	162869	49.809	53.178
2	11.165	3799074	143401	50.191	46.822
Total		7569202	306270	100.000	100.000



PeakTable

Detector A Ch1 254nm

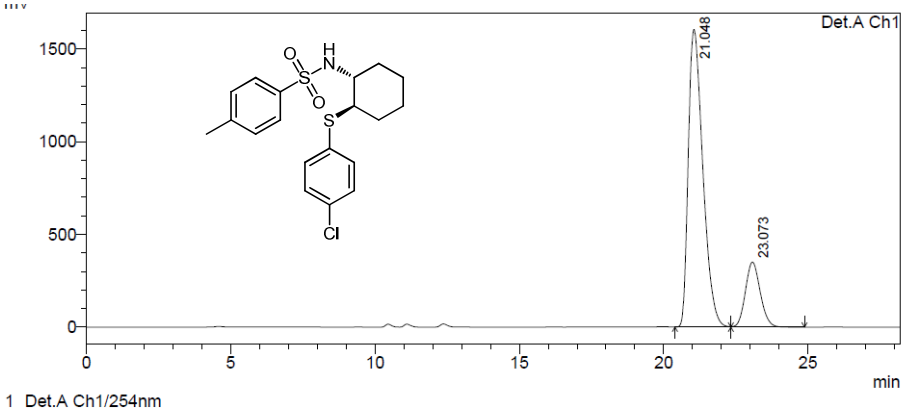
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.896	16133894	658866	85.156	87.065
2	11.145	2812354	97882	14.844	12.935
Total		18946248	756748	100.000	100.000



PeakTable

Detector A Ch1 254nm

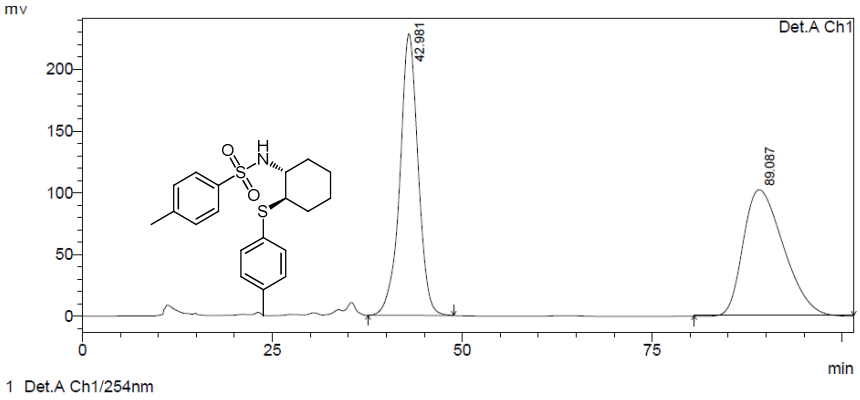
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.924	7407908	206541	50.022	51.880
2	24.063	7401278	191569	49.978	48.120
Total		14809186	398110	100.000	100.000



PeakTable

Detector A Ch1 254nm

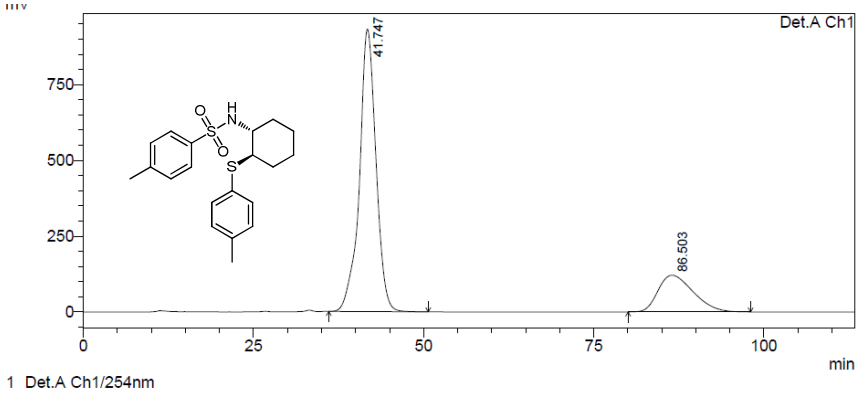
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.048	56284240	1605221	81.803	82.079
2	23.073	12520398	350485	18.197	17.921
Total		68804638	1955706	100.000	100.000



PeakTable

Detector A Ch1 254nm

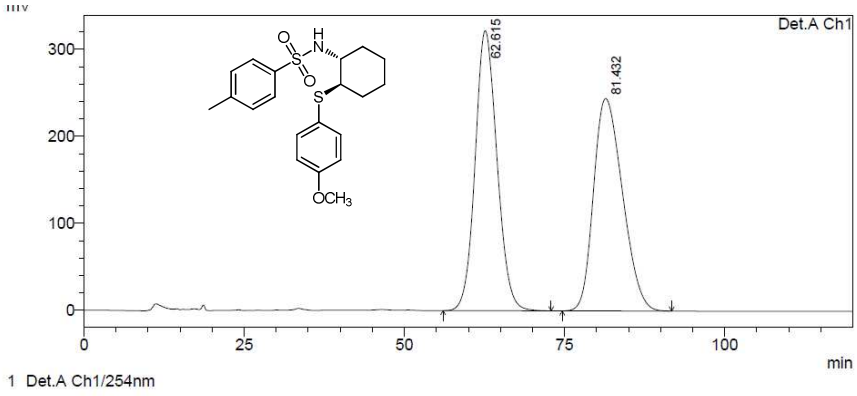
Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.981	38074106	228100	50.509	69.137
2	89.087	37306450	101824	49.491	30.863
Total		75380555	329924	100.000	100.000



PeakTable

Detector A Ch1 254nm

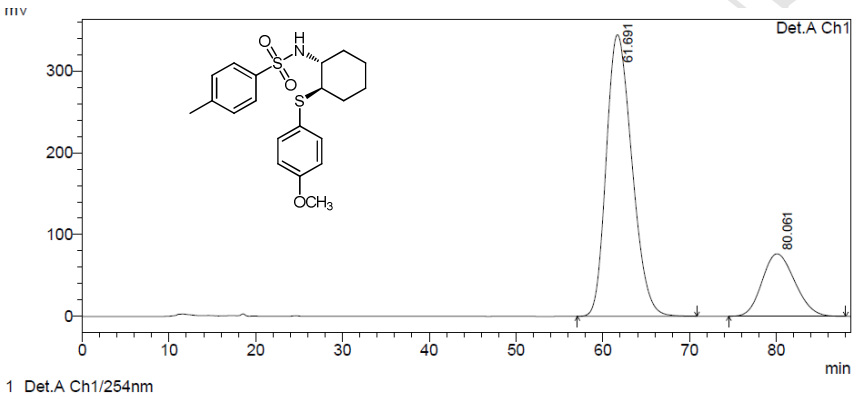
Peak#	Ret. Time	Area	Height	Area %	Height %
1	41.747	157723190	931885	78.388	88.509
2	86.503	43486070	120987	21.612	11.491
Total		201209260	1052872	100.000	100.000



PeakTable

Detector A Ch1 254nm

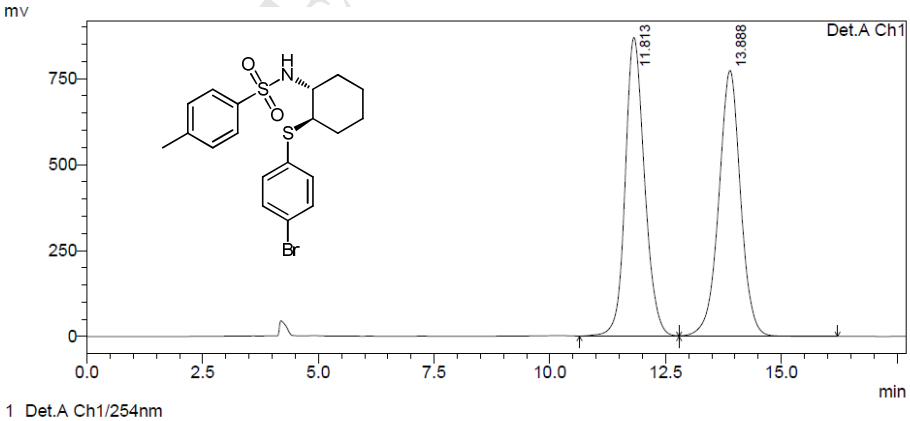
Peak#	Ret. Time	Area	Height	Area %	Height %
1	62.615	76647306	321852	49.948	56.857
2	81.432	76806769	244217	50.052	43.143
Total		153454075	566069	100.000	100.000



PeakTable

Detector A Ch1 254nm

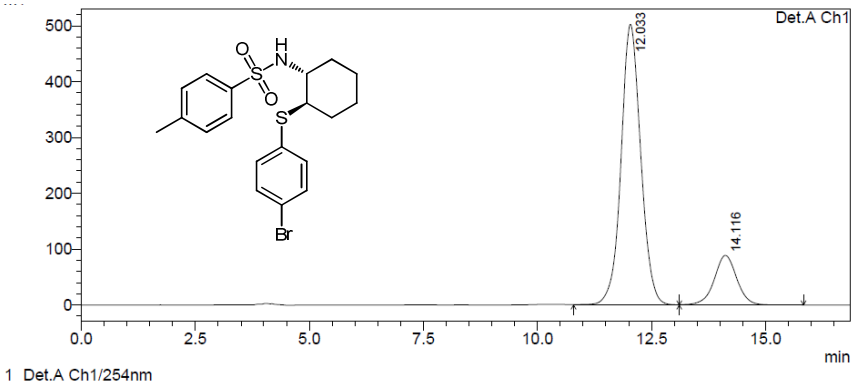
Peak#	Ret. Time	Area	Height	Area %	Height %
1	61.691	70914584	343878	77.982	81.832
2	80.061	20022714	76348	22.018	18.168
Total		90937298	420226	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.813	25352265	870097	49.923	52.928
2	13.888	25430760	773839	50.077	47.072
Total		50783026	1643937	100.000	100.000

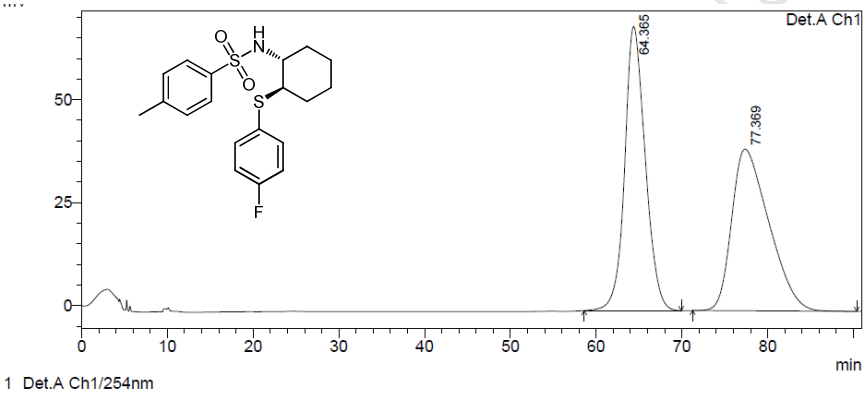


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.033	15126532	502549	83.205	84.986
2	14.116	3053351	88779	16.795	15.014
Total		18179883	591328	100.000	100.000

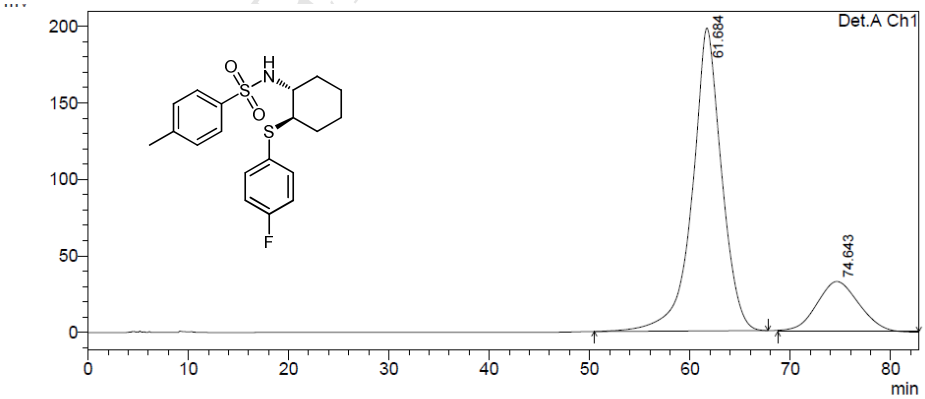


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	64.365	11528682	68982	49.373	63.740
2	77.369	11821496	39242	50.627	36.260
Total		23350178	108225	100.000	100.000

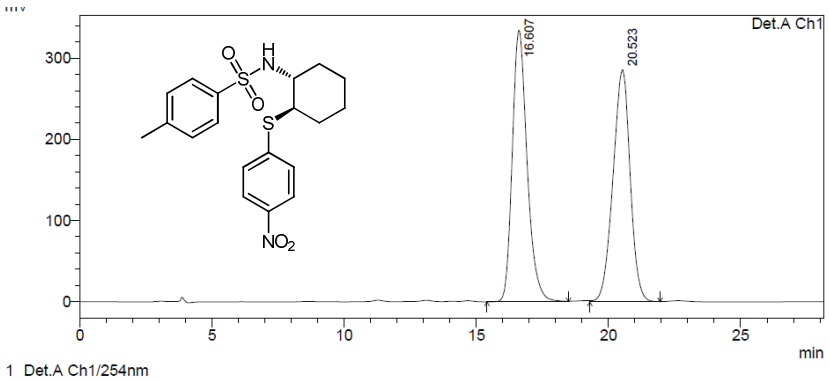


1 Det.A Ch1/254nm

PeakTable

)etector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	61.684	40018097	197841	80.648	85.797
2	74.643	9602902	32750	19.352	14.203
Total		49620999	230590	100.000	100.000

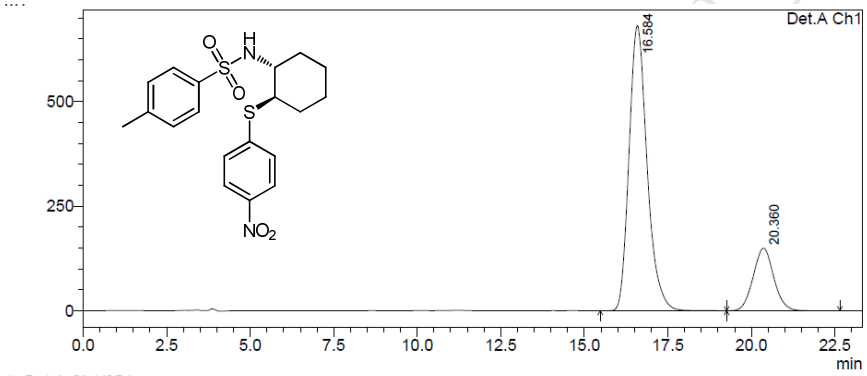


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.607	13119878	334757	50.296	53.926
2	20.523	12965270	286017	49.704	46.074
Total		26085148	620774	100.000	100.000

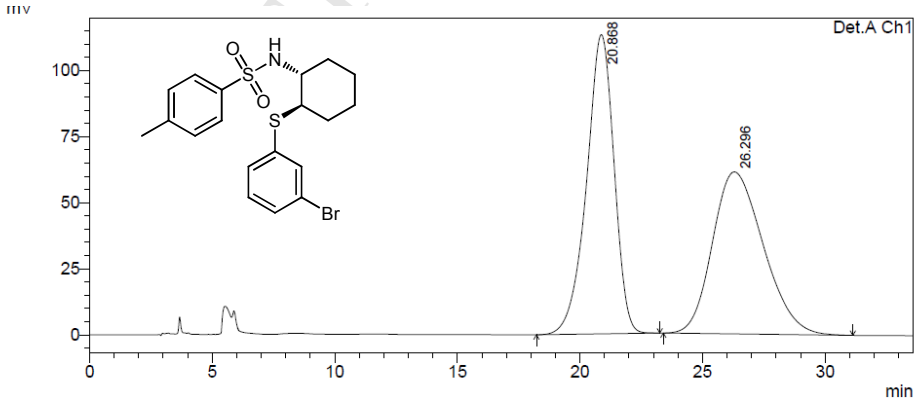


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.584	25625309	681299	79.993	82.012
2	20.360	6409161	149433	20.007	17.988
Total		32034470	830732	100.000	100.000

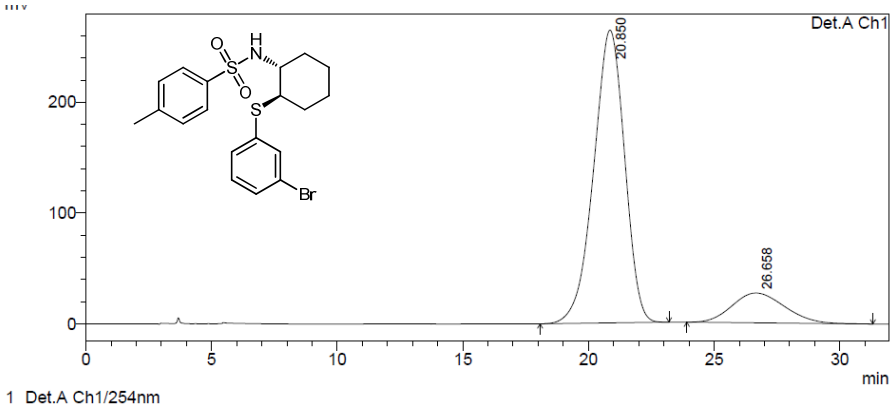


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.868	8843332	113201	49.969	64.879
2	26.296	8854249	61280	50.031	35.121
Total		17697581	174481	100.000	100.000

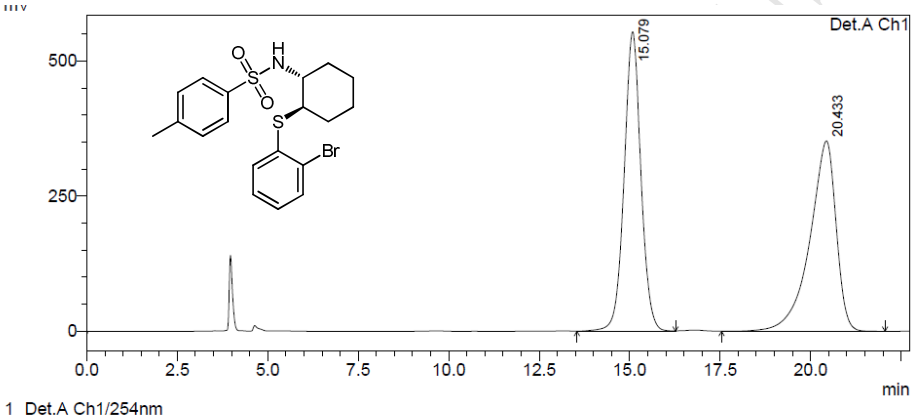


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.850	22651781	264167	85.284	90.765
2	26.658	3908757	26879	14.716	9.235
Total		26560538	291046	100.000	100.000

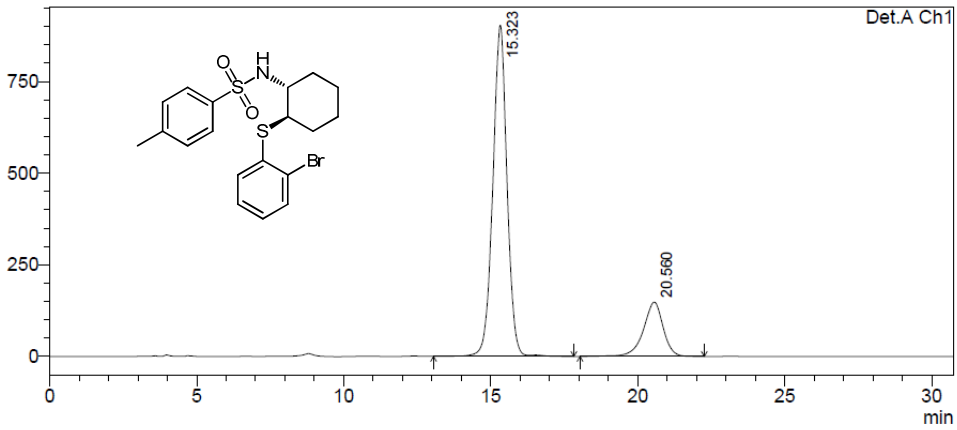


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.079	17944872	554426	50.153	61.139
2	20.433	17835069	352410	49.847	38.861
Total		35779941	906836	100.000	100.000

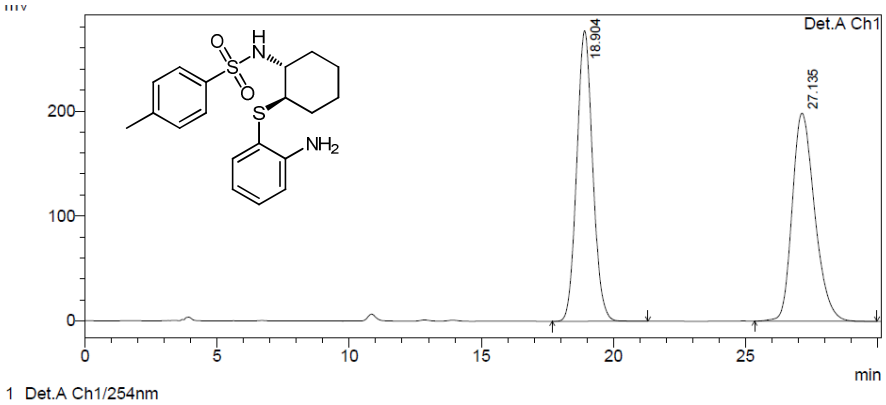


Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

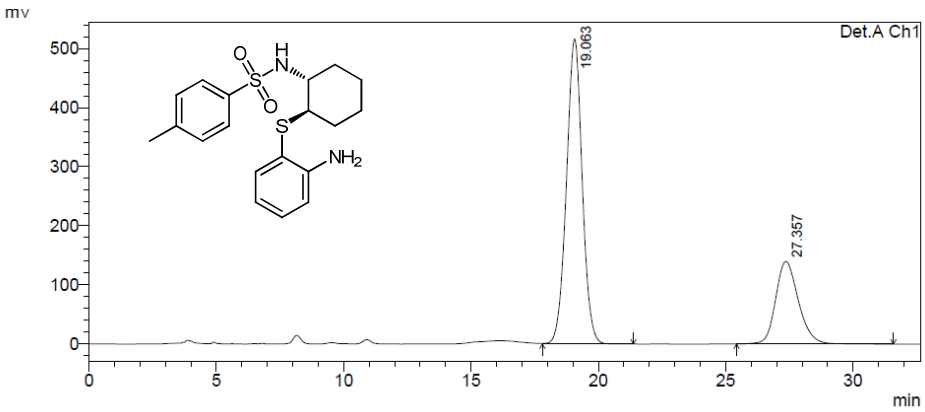
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.323	30325295	903634	81.354	85.920
2	20.560	6950411	148084	18.646	14.080
Total		37275706	1051718	100.000	100.000



PeakTable

Detector A Ch1 254nm

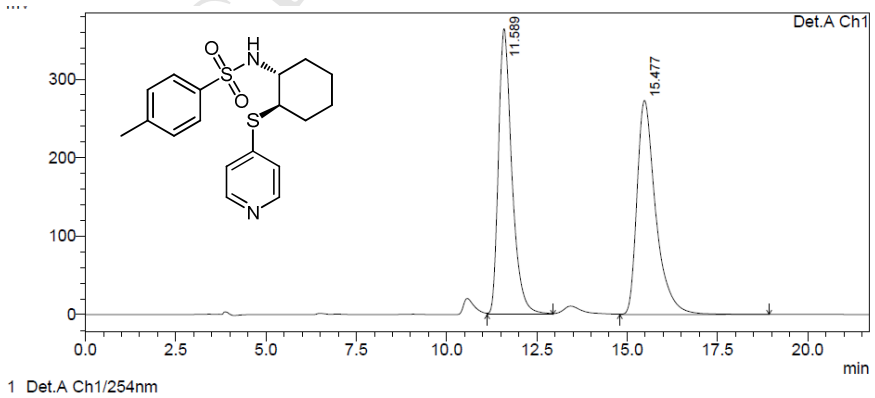
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.904	11637367	277044	49.793	58.266
2	27.135	11734151	198436	50.207	41.734
Total		23371518	475480	100.000	100.000



PeakTable

Detector A Ch1 254nm

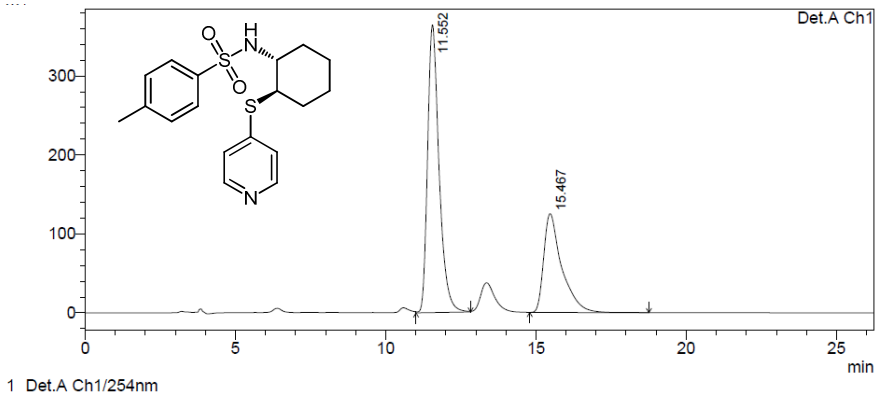
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.063	22205831	516060	71.811	78.687
2	27.357	8716921	139778	28.189	21.313
Total		30922752	655838	100.000	100.000



PeakTable

Detector A Ch1 254nm

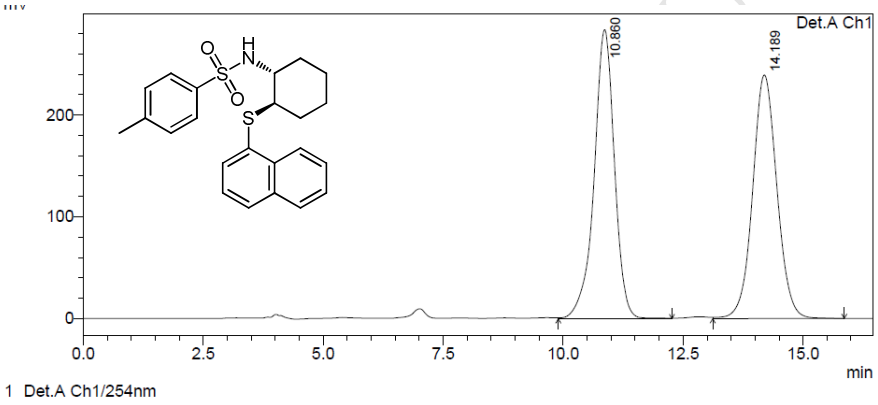
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.589	9501245	364398	49.151	57.189
2	15.477	9829469	272783	50.849	42.811
Total		19330714	637181	100.000	100.000



PeakTable

Detector A Ch1 254nm

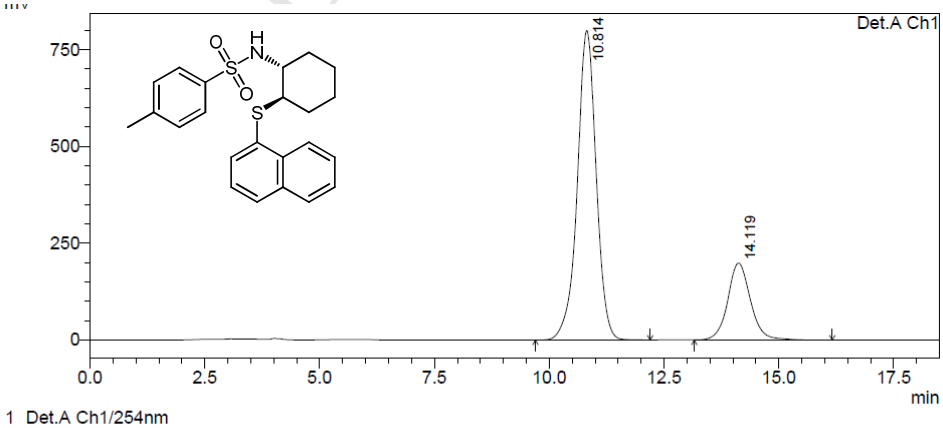
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.552	9702577	364545	65.035	74.433
2	15.467	5216444	125217	34.965	25.567
Total		14919021	489762	100.000	100.000



PeakTable

Detector A Ch1 254nm

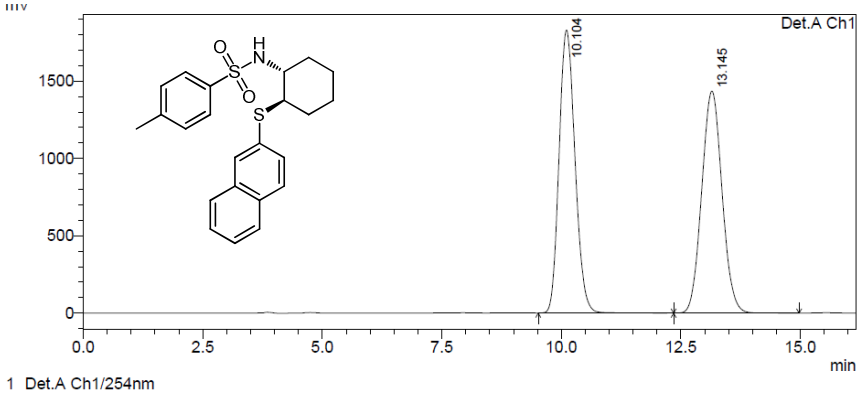
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.860	8399800	283927	49.953	54.264
2	14.189	8415500	239302	50.047	45.736
Total		16815299	523228	100.000	100.000



PeakTable

Detector A Ch1 254nm

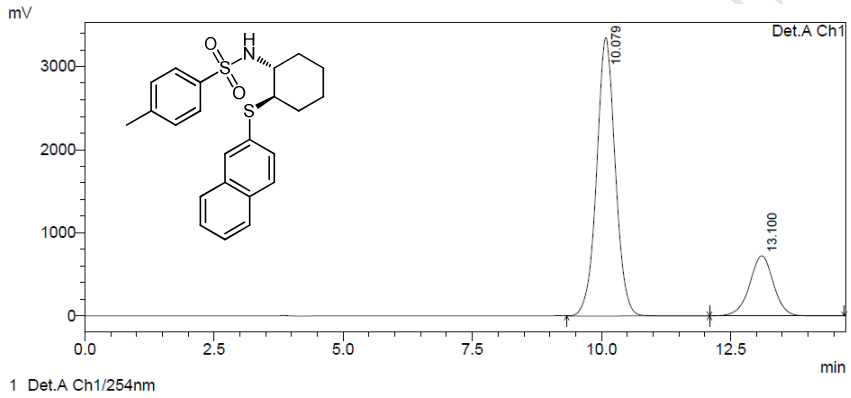
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.814	22981273	799609	76.966	80.078
2	14.119	6877773	198930	23.034	19.922
Total		29859045	998539	100.000	100.000



PeakTable

Detector A Ch1 254nm

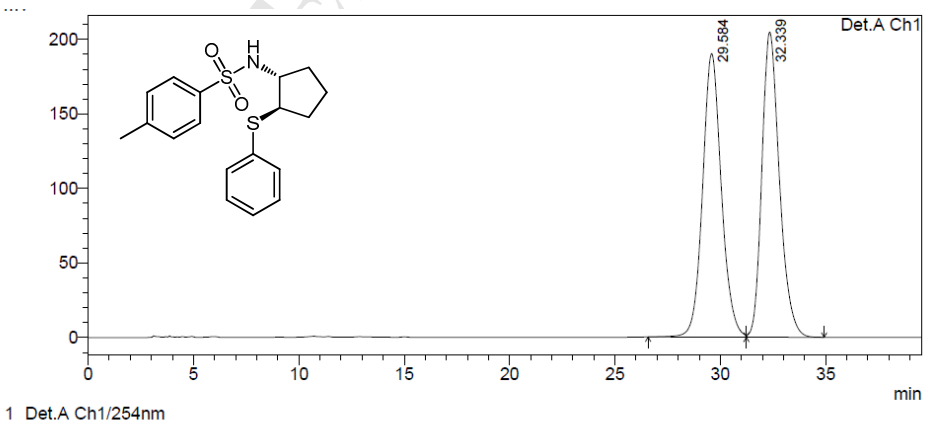
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.104	42627782	1830857	50.063	56.047
2	13.145	42520837	1435781	49.937	43.953
Total		85148619	3266639	100.000	100.000



PeakTable

Detector A Ch1 254nm

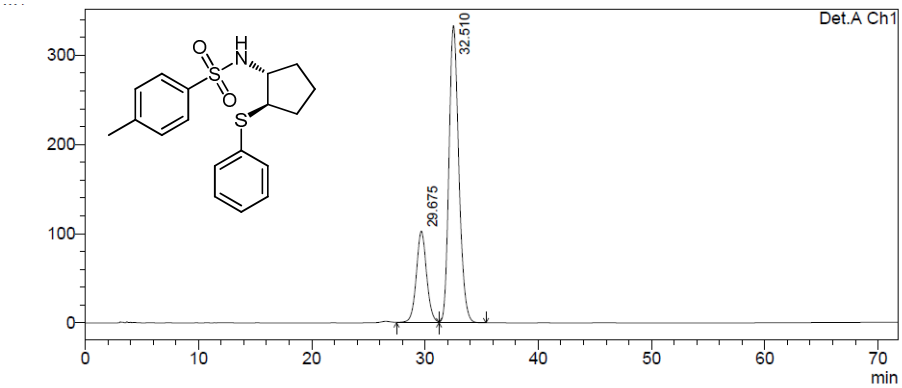
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.079	84114649	3347770	78.313	82.238
2	13.100	23293140	723081	21.687	17.762
Total		107407789	4070851	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.584	11778506	190123	49.838	48.163
2	32.339	11855189	204623	50.162	51.837
Total		23633695	394745	100.000	100.000

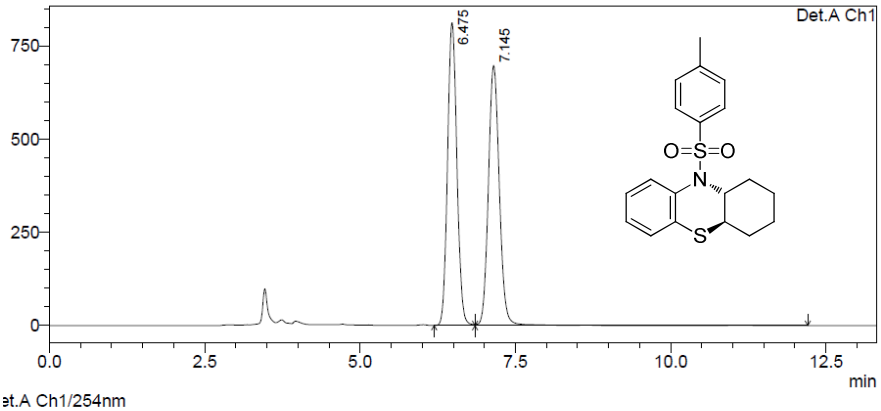


1 Det.A Ch1/254nm

PeakTable

etector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.675	6526084	102751	24.407	23.567
2	32.510	20211985	333249	75.593	76.433
Total		26738070	435999	100.000	100.000

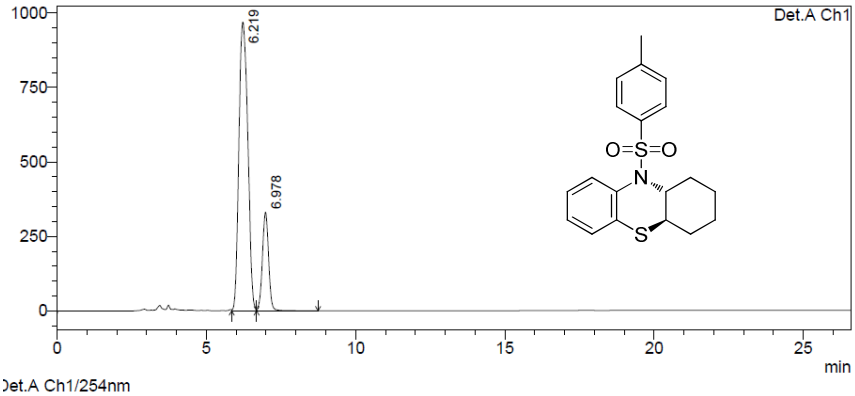


et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.475	8515079	813087	49.874	53.802
2	7.145	8558096	698175	50.126	46.198
Total		17073175	1511262	100.000	100.000



Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.219	20073517	969510	80.693	74.554
2	6.978	4802909	330901	19.307	25.446
Total		24876427	1300411	100.000	100.000