Supporting Information

Gold(I)-Catalyzed Enantioselective Synthesis of Polycyclic Indoline Skeletons and Enantiomerically Enriched *β*-Substituted Tryptamine-Allenes by Kinetic Resolution

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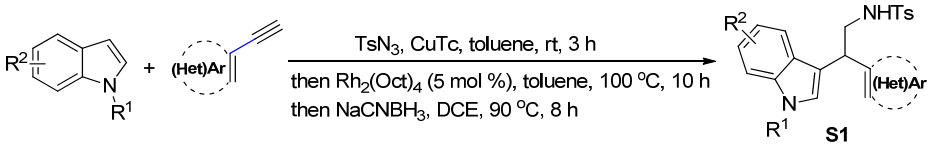
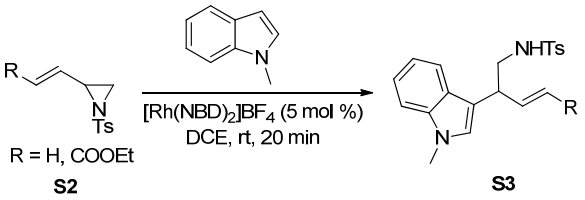
CONTENTS

1. General remarks. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. Unless otherwise noted, all reaction mixtures were stirred with a magnetic stir bar in flame-dried glassware under argon atmosphere. All the temperatures were referred to the used oil baths. Extracts were dried over $MgSO_4$ or Na_2SO_4 and solvents were removed in a rotary evaporator. TLC analysis of reaction mixtures was performed on Huanghai GF_{254} silica gel coated plates. Flash column chromatography was performed using 300-400 mesh silica gel (Huanghai GF254) and 250-400 mesh silica gel (Silicycle UltraPure silica gels). MP was obtained with a Yanagimoto micro melting point apparatus and is uncorrected. Infra-red spectra were measured on a spectrometer. ^1H NMR spectra were recorded for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. ^{19}F NMR spectra were recorded for a solution in $CDCl_3$ with $CFCl_3$ as the external reference. *J*-values are in Hz. Mass and HRMS spectra were recorded by ESI method.

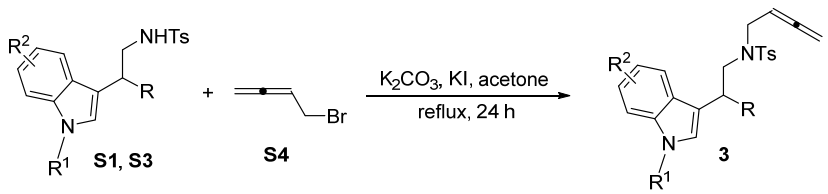
2. General procedure for synthesis of 1.



The compounds **S1** are prepared according to known procedures.[1]



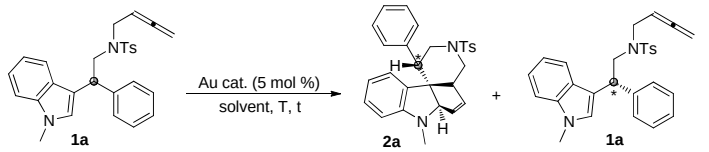
The compounds **S2** and **S3** are prepared according to known procedures.[2]



To an oven-dried reaction bottle was sequentially added **S1** or **S3** (4.00 mmol), K_2CO_3 (8.00 mmol), KI (0.40 mmol) and **S4** (4.80 mmol) in acetone (20.00 mL). The resulting mixture was stirred under reflux. When the reaction was complete as monitored by TLC, it was cooled to room temperature. The solution was filtered through a short column of silica gel eluting with ethyl acetate, and then the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 15/1) to give the corresponding product **1**.

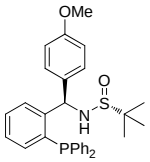
3. Conditions screening for kinetic resolution of racemic indole-allenes 1.

Table S1 Conditions screening for kinetic resolution of racemic indole-allenes **1**.[a,b,c,d]

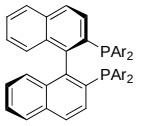


entry[a]	Au cat.	solvent	T (°C)	t/h	yield (%)[b]		ee (%)[c]		s-factor[d]
					2a	**1a**	**2a**	**1a**	
1	**L1**Au(MeCN)SbF_6	toluene	0	48	0	>99	-	-	-
2	**L2**$(AuSbF_6)_2$	toluene	0	48	0	>99	-	-	-
3	**L3**$AuSbF_6$	toluene	0	48	<5	95	-	-	-
4	**L4(**$AuSbF_6)_2$	toluene	0	48	<5	94	-	-	-
5	**L5(**$AuSbF_6)_2$	toluene	0	48	31	<5	92	-	-
6	**L5**$(AuNTf_2)_2$	toluene	0	48	33	40	91	87	10.1
7	**L5**$(AuNTf_2)_2$	toluene	10	48	30	37	89	82	8.9
8	**L5**$(AuNTf_2)_2$	toluene	-10	48	30	45	91	65	6.2
9[e]	**L5**$(AuNTf_2)_2$	toluene	0	30	45	45	93	96	32.0
10[f]	**L5***$(AuNTf_2)_2$*	*toluene*	*0*	*30*	*49*	*45*	*91*	*97*	*35.7*
11	**L5**$(AuNTf_2)_2$	CH_2Cl_2	0	30	16	65	93	73	14.8
12	**L6**$(AuNTf_2)_2$	toluene	-10	30	31	46	92	74	9.5

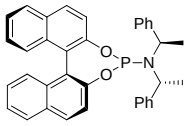
[a] The reaction conditions: 0.1 M in solvent. [b] The yield was determined by ^{1}H NMR spectroscopic data using 1,3,5-trimethoxybenzene as an internal standard. [c] Determined by HPLC on a chiral stationary phase. [d] Selectivity (*s*-factor) calculated as s = ln[(1-C)(1-eeSM)]/ln [(1-C)(1+eeSM)]. [e] 4Å MS (50 mg) was added. [f] 0.05 M.



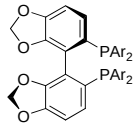
Ming-phos (**L1**)



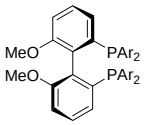
Ar = 3,5-$(Me)_2C_6H_3$; (*R*)-xylyl-BINAP (**L2**)



(S_a, *R*, *R*)-Feringa ligand (**L3**)



Ar = 3,5-$(Me)_2C_6H_3$; (*R*)-DM-Segphos (**L4**)
Ar = 3,5-(^{t}Bu)$_2$-4-MeOC_6H_2; (*R*)-DTBM-Segphos (**L5**)

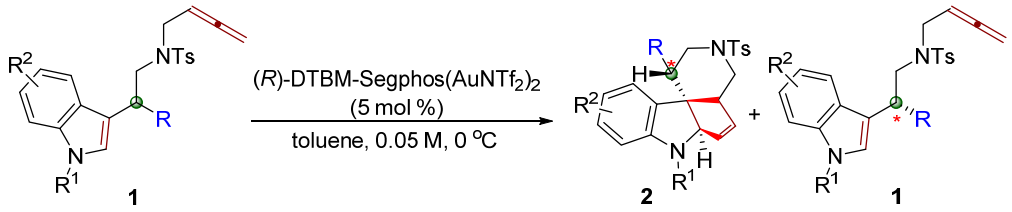


Ar = 3,5-(^{t}Bu)$_2$-4-MeOC_6H_2;
(*R*)-DTBM-MeO-BIPHEP (**L6**)

Our studies were initiated by examining the reactivity of racemic indole-allene **1a** in the presence of a series of gold complexes derived from chiral ligands **L1-L6** (Table S1). It was found that, chiral phosphine ligands **L1** and **L2** coordinated gold catalysts had no catalytic activities for the reaction (entries 1-2). When Feringa phosphoramidite-based ligand (**L3**) and biaryl bisphosphine ligand (*R*)-DM-Segphos (**L4**) incorporated gold catalyst were employed, only trace of cyclization product **2a** was detected by ^{1}H NMR analysis (entries 3-4). Further examination of chiral phosphine ligands revealed that sterically more demanding (*R*)-DTBM-Segphos (**L5**) furnished **2a** in 31% yield along with 92% ee value at 0 °C (entry 5). Next, we investigated the counterion effect by pre-preparing cationic gold catalysts and found

that NTf_2 was the better counterion, giving the cycloadduct **2a** in 33% yield along with 91% ee and enantiomerically enriched **1a** in 40% yield along with 87% ee (*s*-factor = 10.1) at 0 ^oC (entry 6). The reaction conditions with regard to temperature and concentration were then examined. We found that when 4Å molecular sieves (50 mg) was added into the reaction mixture or concentration of the reaction solution was deceased to 0.05 M in toluene, the *s*-factor could be dramatically improved to 32.0 or 35.7 at 0 ^oC (entries 7-10). Carrying out the reaction in DCM or using (*R*)-DTBM-MeO-BIPHEP($AuNTf_2$)$_2$ (**L6**) as the catalyst did not further enhance the kinetic resolution efficiency (entries 11-12). The optimal conditions shown in entry 10 of Table S1 could afford **2a** in 49% yield and 91% ee as well as **1a** in 45% yield and 97% ee along with a *s*-factor of 35.7. This synthetic strategy could provide a convenient and highly efficient method to prepare diversified enantiomerically enriched polycyclic indolines and β-substituted tryptamine-allene motifs.

4. General procedure for the gold(I)-catalyzed kinetic resolution of racemic indole-allenes 1.



To a flame dried Schlenk tube was added unsymmetrical indole-allene **1** (0.1 mmol), (*R*)-DTBMSegphos($AuNTf_2$)$_2$ (5.0 mol %) and the tube was evacuated and backfilled with argon for three times. Then, anhydrous toluene (2.0 mL) was added into tube under argon atmosphere. The reaction mixture was allowed to stir at 0 ^{o}C. The solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography on silica gel to give the enantiomerically enriched compound **1** and desired product **2**.

5. Proposed reaction mechanism.

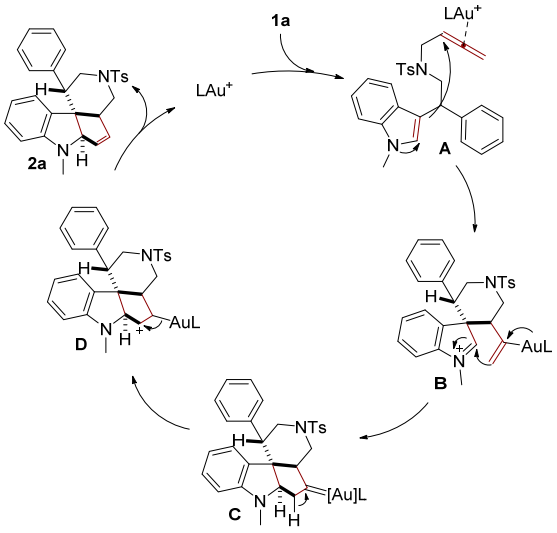


Figure S1 Proposed reaction mechanism.

A plausible reaction mechanism for this gold(I)-catalyzed tandem intramolecular cyclization is outlined in Figure S1 on the basis of the the previous literature. Coordination of gold(I) complex with allene moiety in **1a** generates intermediate **A**, which then initiates a nucleophilic attack from C3 position of indole to allene moiety, resulting in the cyclized intermediate **B**. Intermediate **B** undergoes a further intramolecular cyclization to give a Au-carbenoid intermediate **C**, which follows a 1,2-hydrogen migration to afford intermediate **D**. The release of gold(I) catalyst produces the cycloaddition product **2a** and restarts the next catalytic cycle.

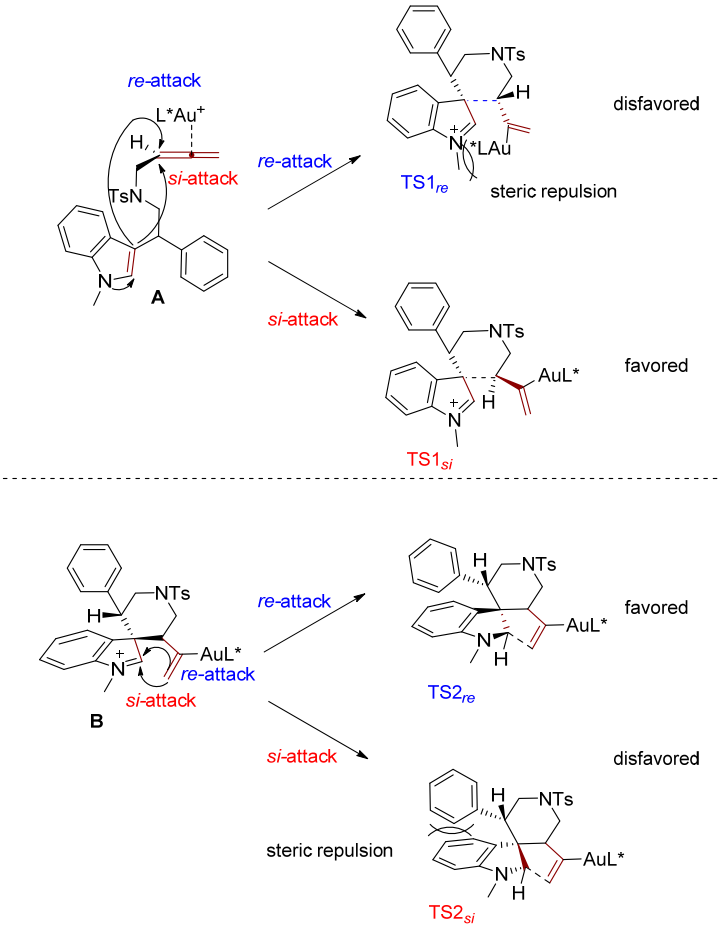
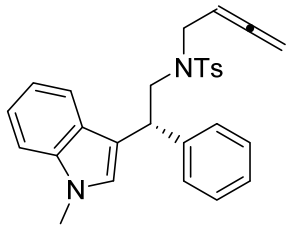


Figure S2 Proposed key transition states for stereochemical control.

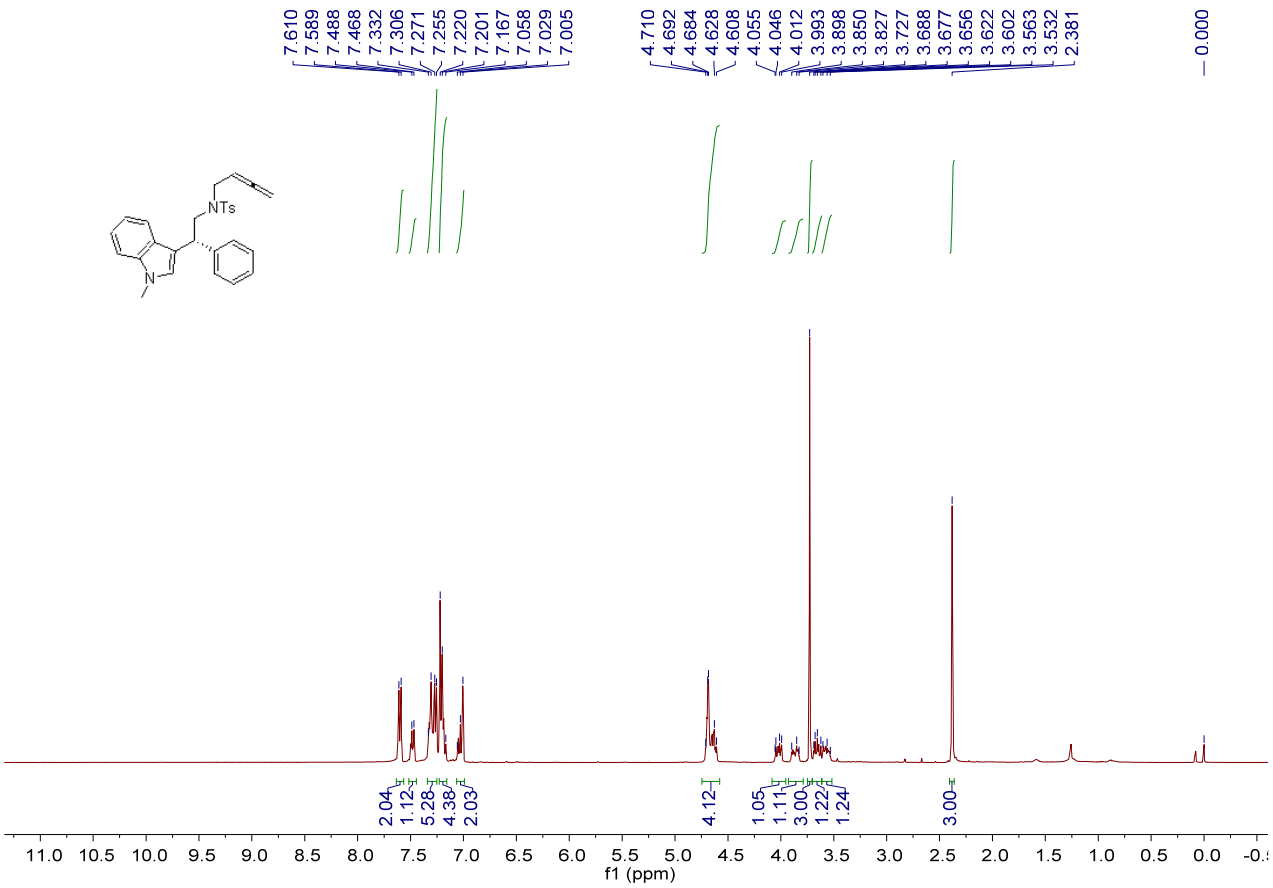
Proposed key transition states for the stereochemical control are illustrated in Figure S2. The intermediate **A** can undergo a nucleophilic attack from C3 position of indole to allene moiety via *re*-face or *si*-face to generate intermediate **B**. Probably due to the steric repulsion between the benzene ring moiety and chiral phosphine ligand ($TS1_{re}$), the *si*-face attack is preferred in this step. Subsequently, the olefinic moiety of intermediate **B** attacks the C2 position of indole via *re*-face or *si*-face to form intermediate **C**. In this step, *re*-face attack is probably the dominated pathway since the *si*-face attack is disfavored due to the steric repulsion between the benzene ring and indole moiety ($TS2_{si}$).

6. Characterization and spectra charts for compounds 1.



(*R*)-*N*-(buta-2,3-dien-1-yl)-4-methyl-*N*-(2-(1-methyl-1*H*-indol-3-yl)-2-phenylethyl)benzenesulfon amide 1a

A white solid, 45% yield (20.5 mg). M.p.: 53-56 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.38 (s, 3H), 3.53-3.61 (m, 1H), 3.62-3.69 (m, 1H), 3.73 (s, 3H), 3.82-3.90 (m, 1H), 3.99-4.06 (m, 1H), 4.60-4.71 (m, 4H), 7.00-7.06 (m, 2H), 7.16-7.22 (m, 4H), 7.25-7.34 (m, 5H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 32.7, 41.4, 46.2, 50.8, 76.1, 85.2, 109.1, 114.6, 118.8, 119.1, 121.5, 126.6, 126.9, 127.1, 127.2, 128.2, 128.4, 129.5, 136.9, 137.1, 142.0, 143.1, 209.2. IR (CH_2Cl_2) ν 2920, 1949, 1599, 1474, 1334, 1160, 1093, 1010, 903, 858, 750, 659 cm^{-1}. MS (ESI) *m/z* (%): 457.19 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{28}H_{29}N_2O_2S^{+1}$ $[M+H]^+$ requires 457.1944, found: 457.1941. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70 mL/min; t_{minor} = 23.35 min, t_{major} = 26.05 min; ee% = 97%; $[\alpha]_D^{25}$ = -23.0 (c 0.70, CH_2Cl_2)].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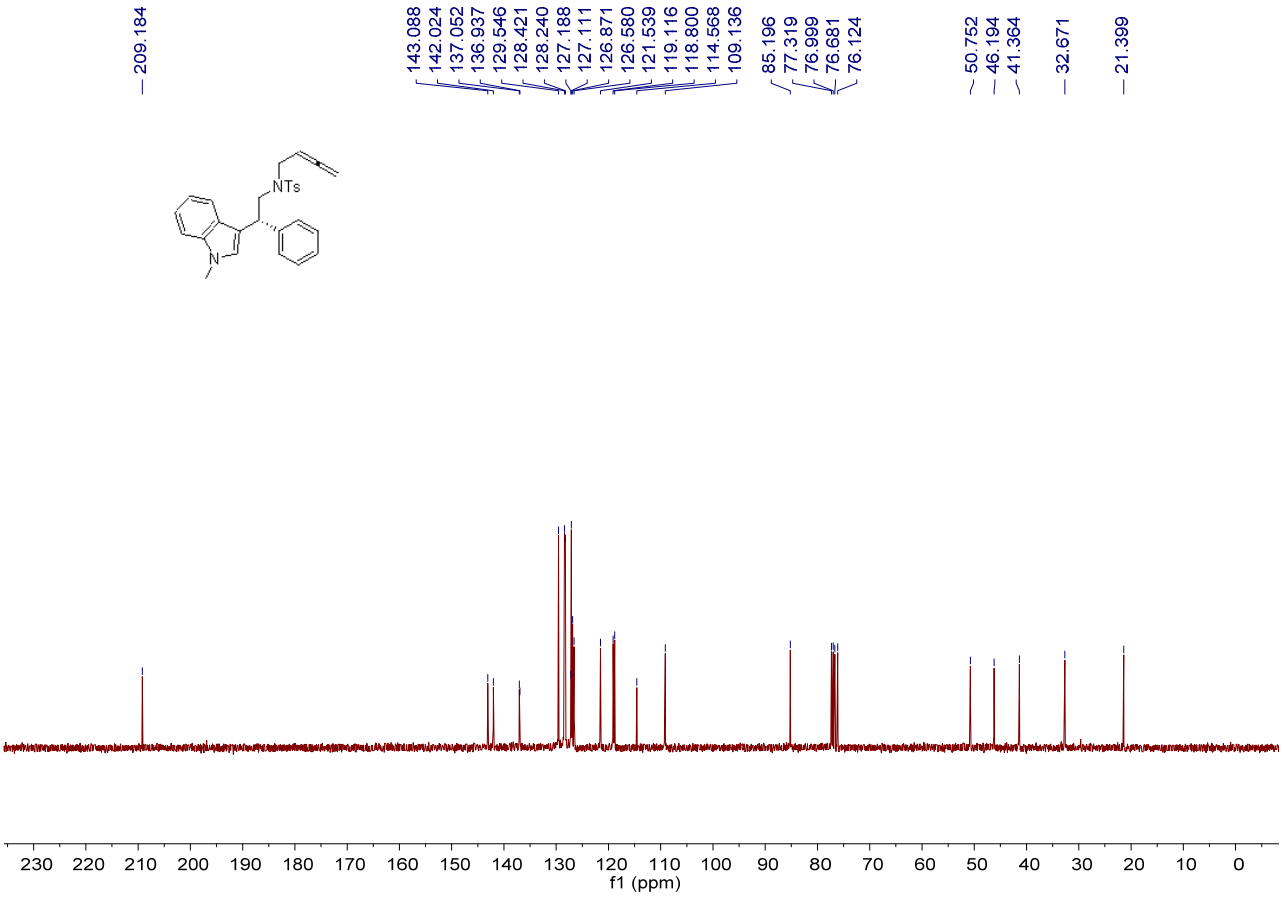
f1 (ppm)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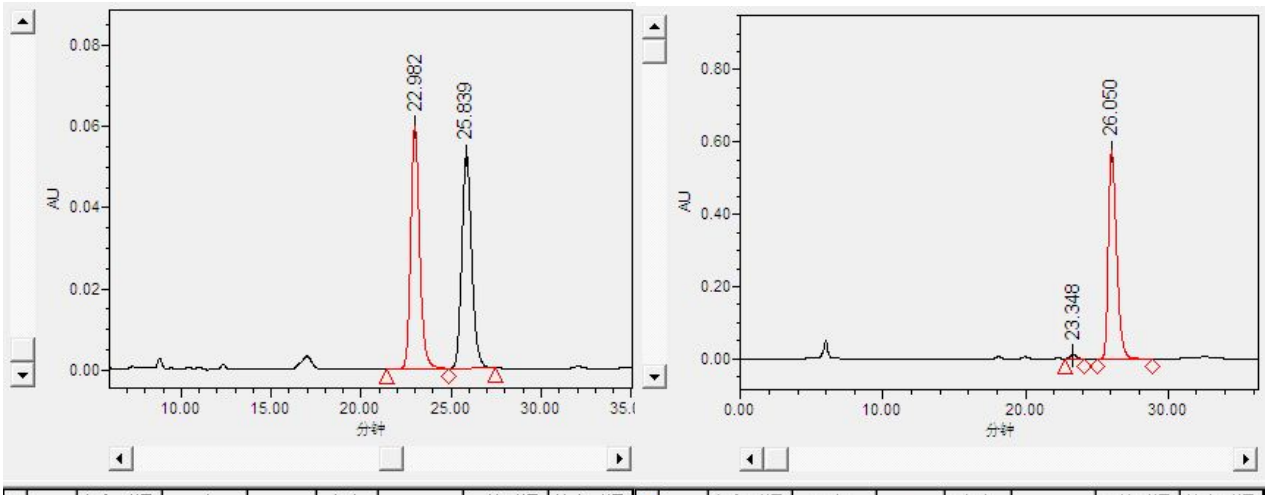

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1		22.982	2087482	50.52	59875	BV	21.433	24.833
2		25.839	2044255	49.48	52728	VB	24.833	27.483

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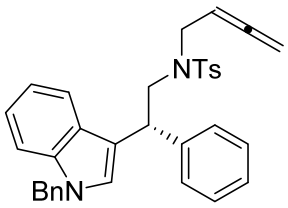
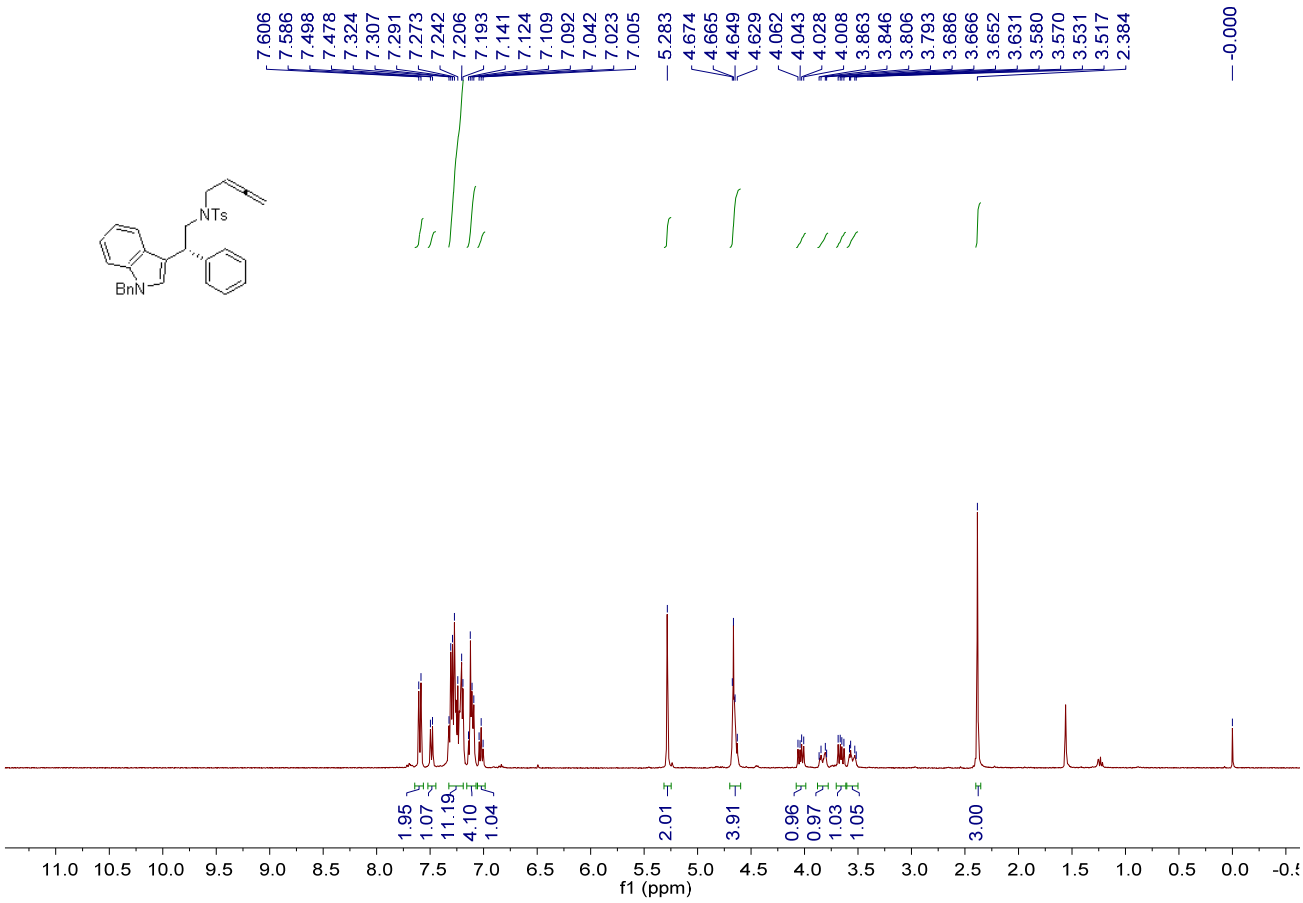
1		23.348	340608	1.45	10929	bv	22.833	24.083
2		26.050	23110603	98.55	574854	VV	25.000	28.883

Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70 mL/min; t_{minor} = 23.35 min, t_{major} = 26.05 min; ee% = 97%].



(*R*)-*N*-(2-(1-benzyl-1*H*-indol-3-yl)-2-phenylethyl)-*N*-(buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide 1b

A white solid, 48% yield (25.5 mg). M.p.: 65-68 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.38 (s, 3H), 3.51-3.58 (m, 1H), 3.66 (dd, *J* = 14.0, 8.0 Hz, 1H), 3.79-3.87 (m, 1H), 4.03 (dd, *J* = 14.0, 8.0 Hz, 1H), 4.62-4.68 (m, 4H), 5.28 (s, 2H), 7.00-7.05 (m, 1H), 7.09-7.15 (m, 4H), 7.19-7.33 (m, 11H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 41.6, 46.3, 50.0, 50.9, 76.1, 85.3, 109.7, 115.2, 119.1, 119.3, 121.8, 126.4, 126.5, 126.6, 127.1, 127.4, 127.6, 128.3, 128.4, 128.6, 129.5, 136.6, 137.1, 137.5, 142.0, 143.1, 209.2. IR (CH_2Cl_2) ν 3028, 2918, 2850, 1952, 1598, 1466, 1331, 1155, 1092, 936, 897, 846, 738, 657 cm^{-1}. MS (ESI) *m/z* (%): 533.22 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{34}H_{33}N_2O_2S^{+1}$ $[M+H]^+$ requires 533.2257, found: 533.2253. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70 mL/min; t_{minor} = 21.38 min, t_{major} = 22.70 min; ee% = 84%; $[\alpha]_D^{25}$ = -68.5 (c 0.16, CH_2Cl_2)].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3.863
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3.631
3.580
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NTs
BnN
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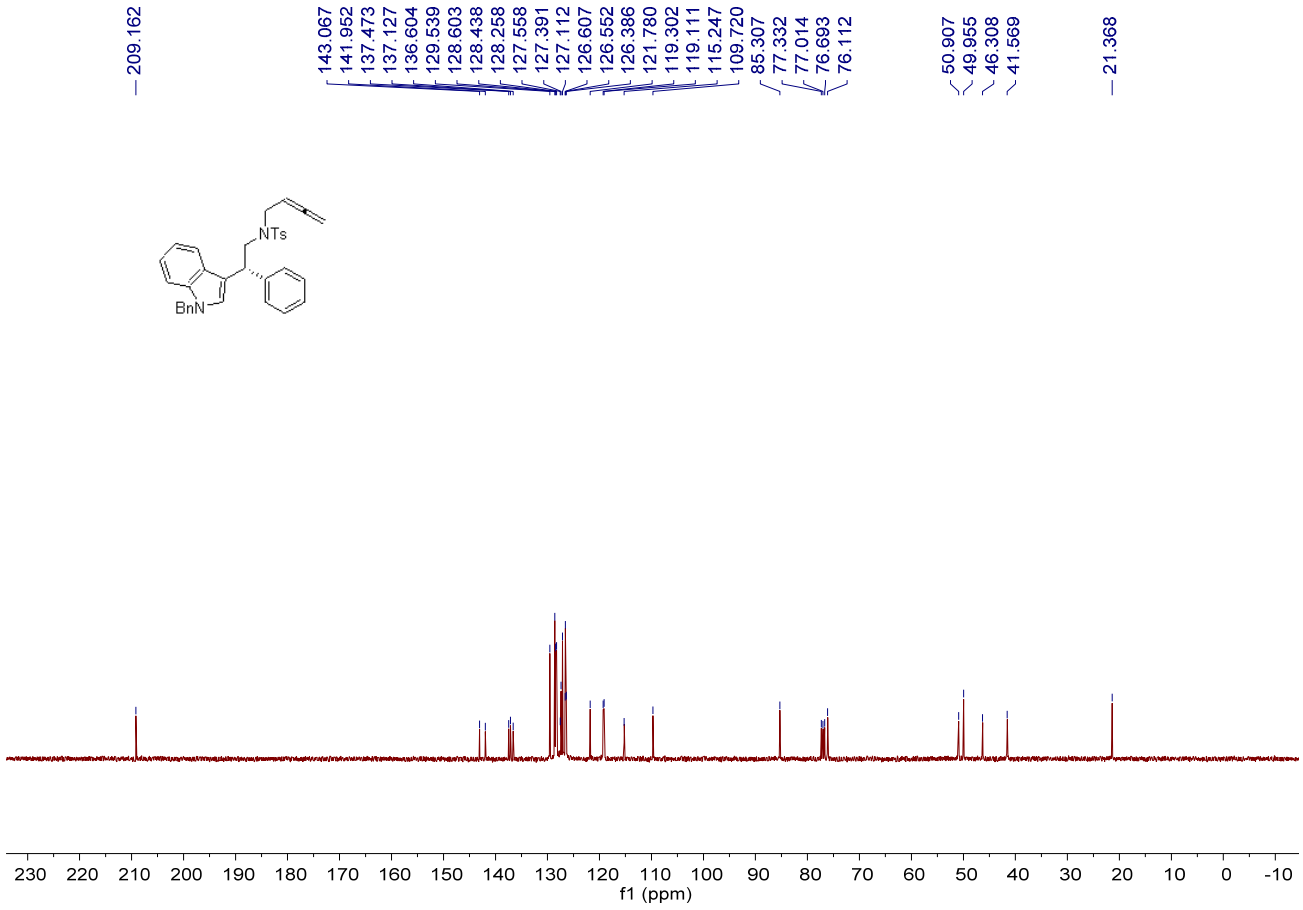
f1 (ppm)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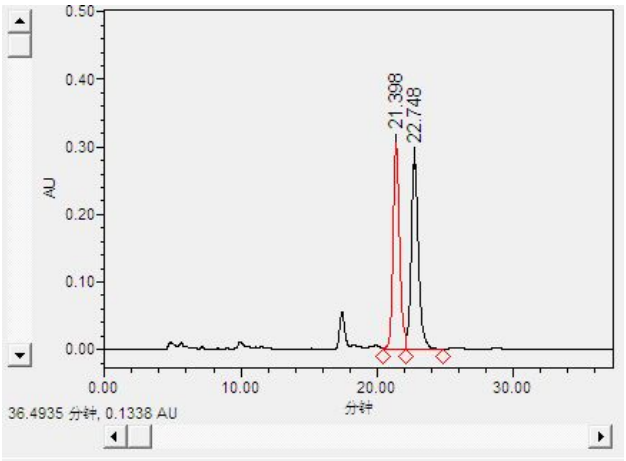
BnN
f1 (ppm)



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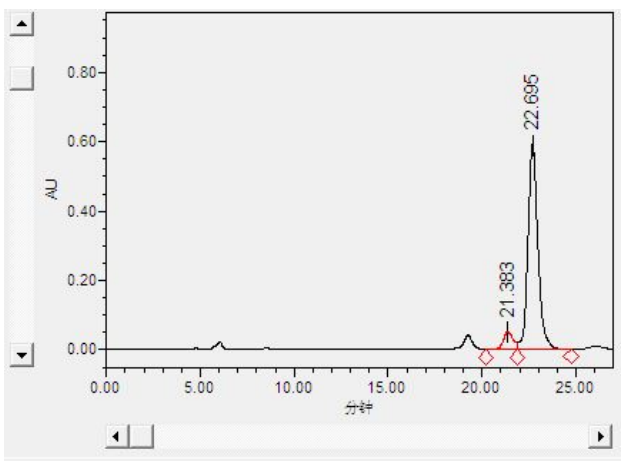
2		22.748	10610250	50.73	284558	VV	22.150	24.850



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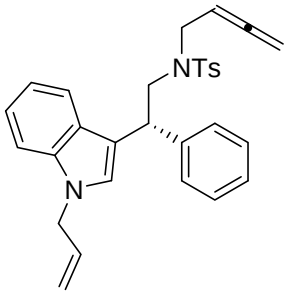
1		21.383	1958847	8.12	52358	VV	20.217	21.867
2		22.695	22169691	91.88	591854	VV	21.867	24.750

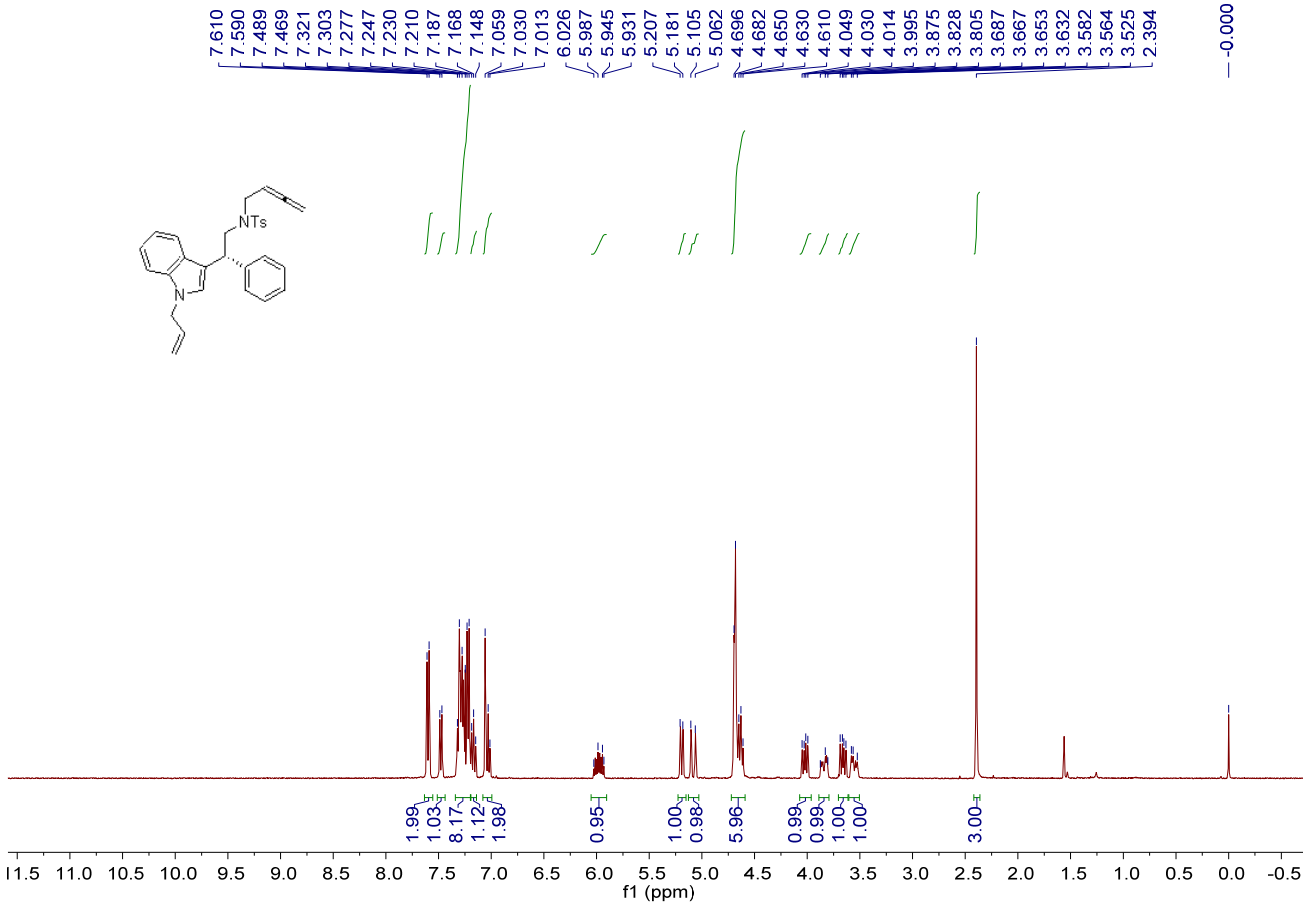
Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70 mL/min; t_{minor} = 21.38 min, t_{major} = 22.70 min; ee% = 84%].

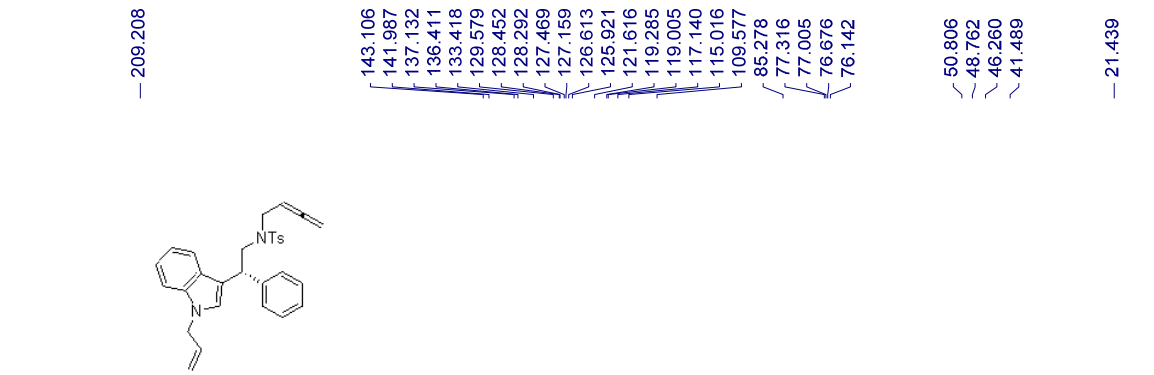


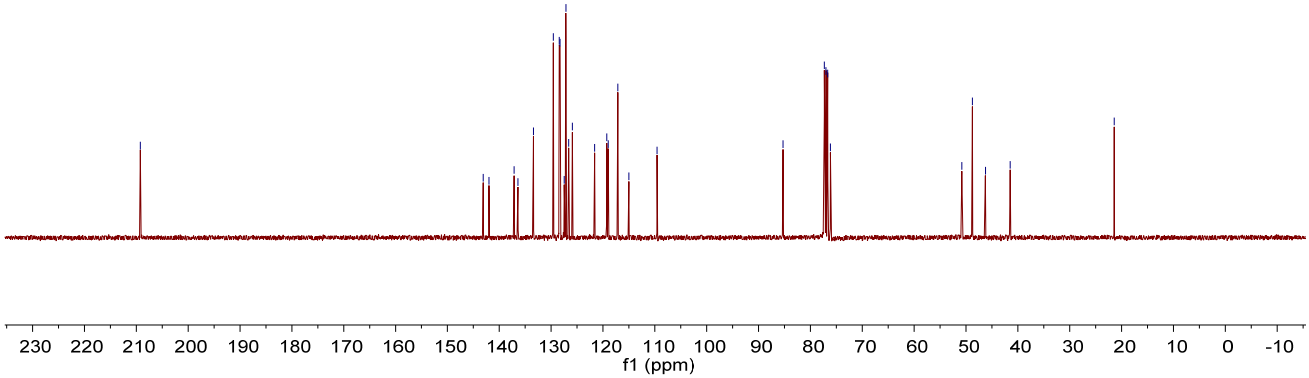
(*R*)-*N*-(2-(1-allyl-1*H*-indol-3-yl)-2-phenylethyl)-*N*-(buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide 1c

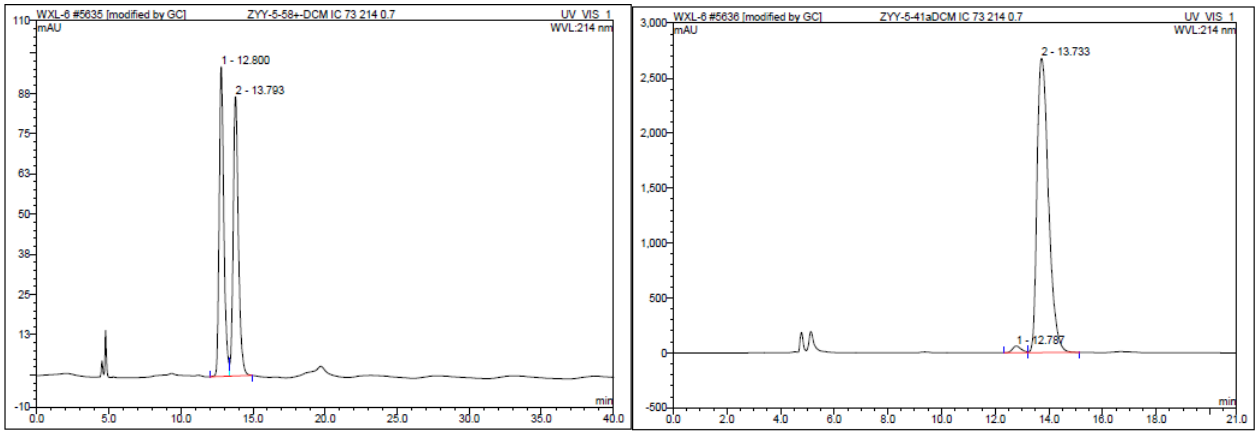
A white solid, 46% yield (22.2 mg). M.p.: 60-63 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.39 (s, 3H), 3.52-3.59 (m, 1H), 3.63-3.69 (m, 1H), 3.80-3.88 (m, 1H), 3.99-4.05 (m, 1H), 4.61-4.70 (m, 6H), 5.08 (d, *J* = 17.2 Hz, 1H), 5.19 (d, *J* = 10.4 Hz, 1H), 5.93-6.03 (m, 1H), 7.01-7.06 (m, 2H), 7.14-7.19 (m, 1H), 7.21-7.33 (m, 8H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 41.5, 46.3, 48.8, 50.8, 76.1, 85.3, 109.6, 115.0, 117.1, 119.0, 119.3, 121.6, 125.9, 126.6, 127.2, 127.5, 128.3, 128.5, 129.6, 133.4, 136.4, 137.1, 142.0, 143.1, 209.2. IR (CH_2Cl_2) ν 3064, 2902, 1960, 1595, 1462, 1330, 1154, 1089, 858, 741, 673 cm^{-1}. MS (ESI) *m/z* (%): 483.21 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{30}H_{31}N_2O_2S^{+1}$ $[M+H]^+$ requires 483.2101, found: 483.2102. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 12.78 min, t_{major} = 13.73 min; ee% =

97%; $[\alpha]_D^{25}$ = -78.0 (c 0.10, CH_2Cl_2)].





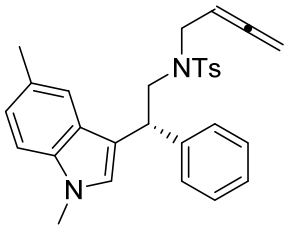




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.80	n.a.	96.210	35.874	49.76	n.a.	BM
2	13.79	n.a.	86.748	36.225	50.24	n.a.	MB
Total:			182.958	72.099	100.00	0.000	

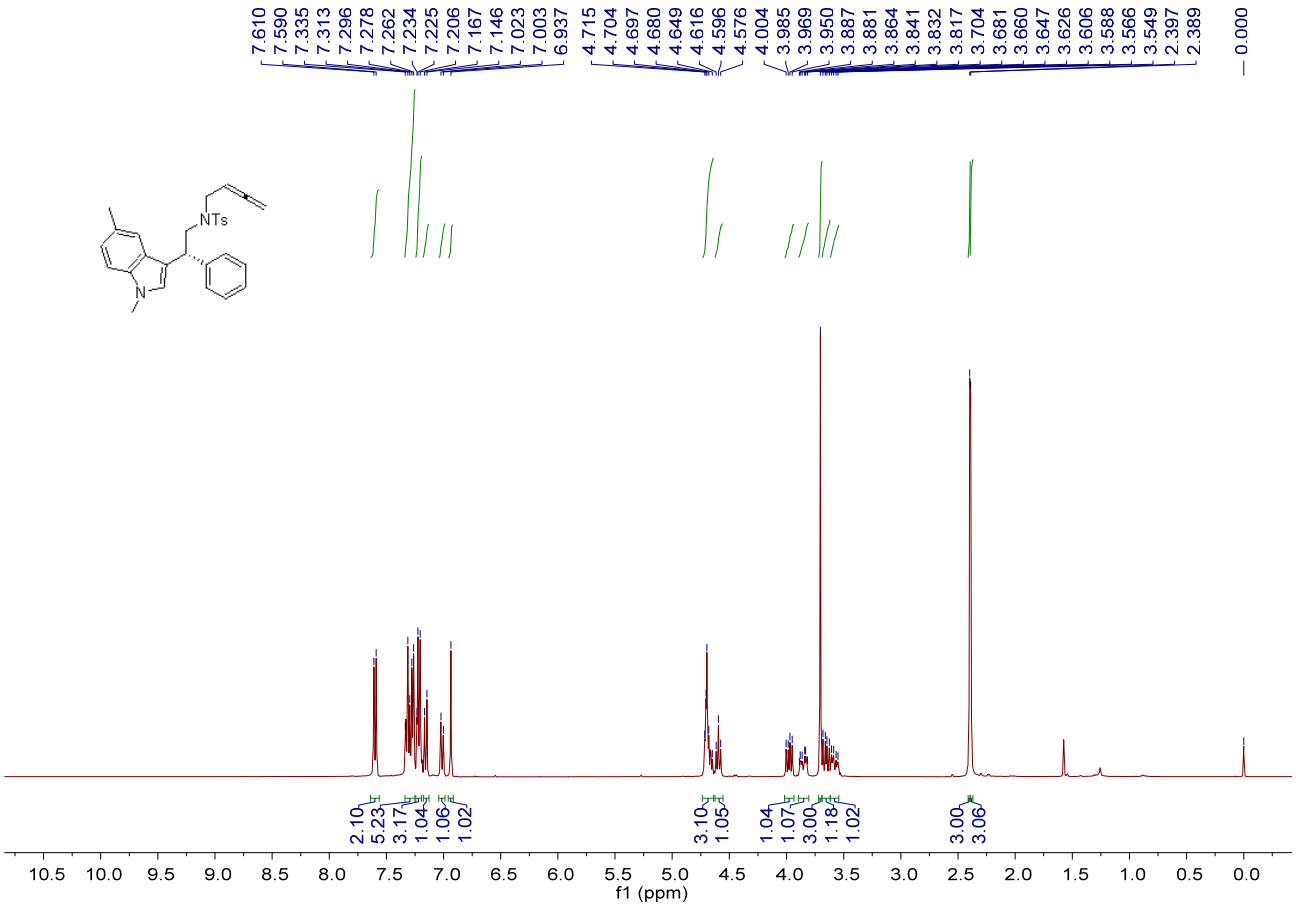
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.79	n.a.	60.580	22.632	1.68	n.a.	BM
2	13.73	n.a.	2678.287	1324.251	98.32	n.a.	MB
Total:			2738.866	1346.883	100.00	0.000	

Translation: Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 12.78 min, t_{major} = 13.73 min; ee% = 97%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(*R*)-*N*-(buta-2,3-dien-1-yl)-*N*-(2-(1,5-dimethyl-1*H*-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide 1d

A white solid, 48% yield (22.5 mg). M.p.: 83-86 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.39 (s, 3H), 2.40 (s, 3H), 3.54-3.61 (m, 1H), 3.65 (dd, *J* = 13.6, 8.4 Hz, 1H), 3.70 (s, 3H), 3.81-3.89 (m, 1H), 3.97 (dd, *J* = 14.0, 7.6 Hz, 1H), 4.60 (t, *J* = 8.0 Hz, 1H), 4.64-4.72 (m, 3H), 6.94 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.20-7.24 (m, 3H), 7.26-7.34 (m, 5H), 7.60 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.47, 21.49, 32.8, 41.3, 46.2, 50.8, 76.1, 85.3, 108.9, 114.0, 118.8, 123.2, 126.6, 127.0, 127.2, 127.4, 128.0, 128.3, 128.5, 129.6, 135.4, 137.2, 142.1, 143.1, 209.3. IR (CH_2Cl_2) ν 2921, 2850, 1698, 1608, 1510, 1450, 1335, 1273, 1159, 1015, 941, 769, 656 cm^{-1}. MS (ESI) *m/z* (%): 471.20 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{29}H_{31}N_2O_2S^{+1}$ $[M+H]^+$ requires 471.2101, found: 471.2097. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.50 mL/min; t_{minor} = 24.61 min, t_{major} = 27.33 min; ee% = 96%; $[\alpha]_D^{25}$ = -25.0 (c 0.20, CH_2Cl_2)].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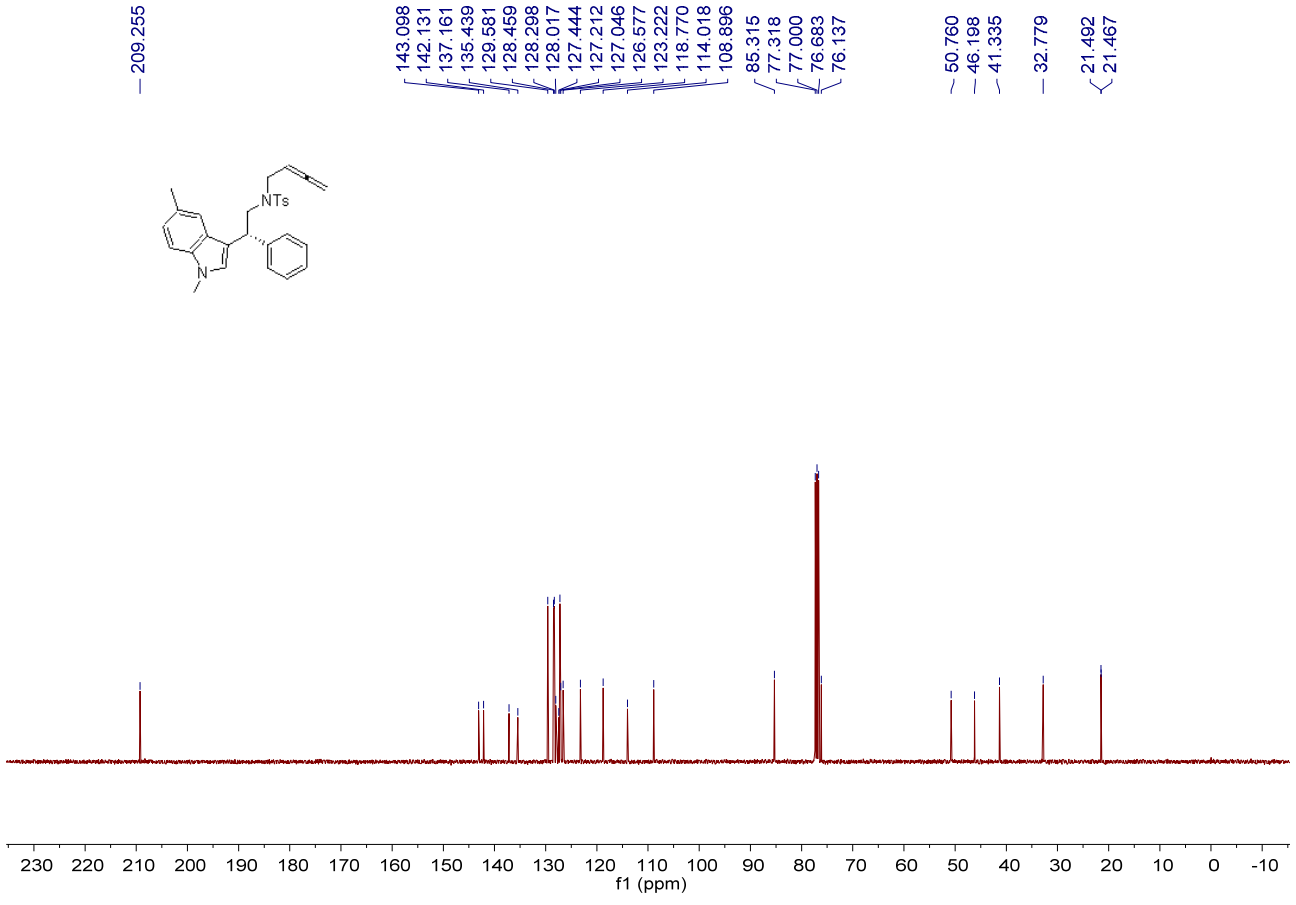
6.937
4.715
4.704
4.697
4.680
4.649
4.616
4.596
4.576
4.004
3.985
3.969
3.950
3.887
3.881
3.864
3.841
3.832
3.817
3.704
3.681
3.660
3.647
3.626
3.606
3.588
3.566
3.549
2.397
2.389
0.000
NTs
2.10
5.23
3.17
1.04
1.06
1.02
3.10
1.05
1.04
1.07
3.00
1.18
1.02
3.00
3.06
f1 (ppm)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128.298
128.017
127.444
127.212
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123.222
118.770
114.018
108.896
85.315
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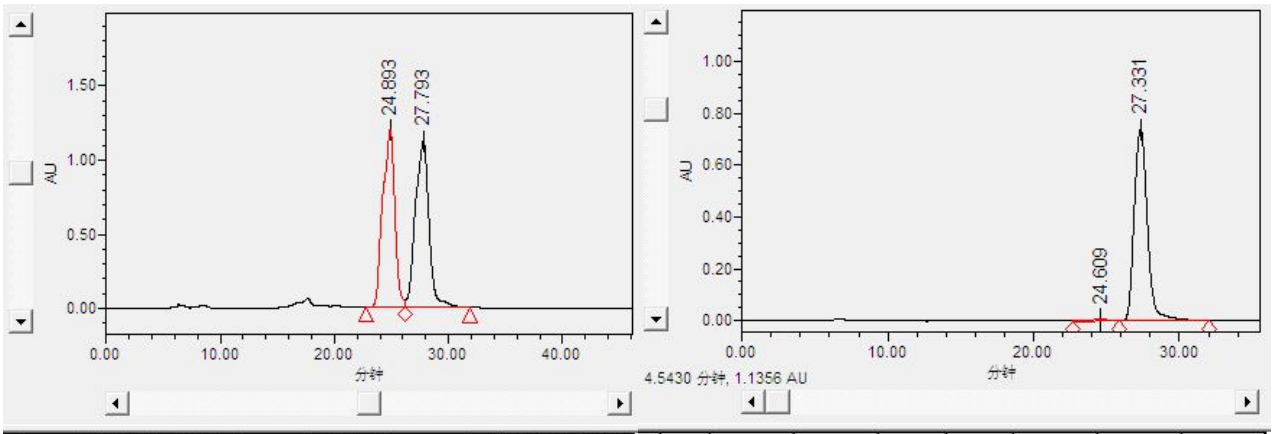
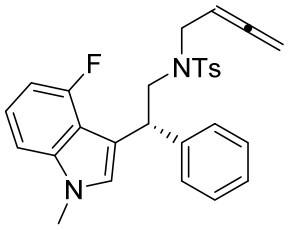
32.779
21.492
21.467
NTs
f1 (ppm)



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		24.893	87602551	48.49	1194995	BV	22.833	26.183
2		27.793	93042592	51.51	1120962	VB	26.183	31.883

	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		24.609	791966	1.65	8287	VV	22.667	25.850
2		27.331	47319194	98.35	742384	VV	25.850	32.000

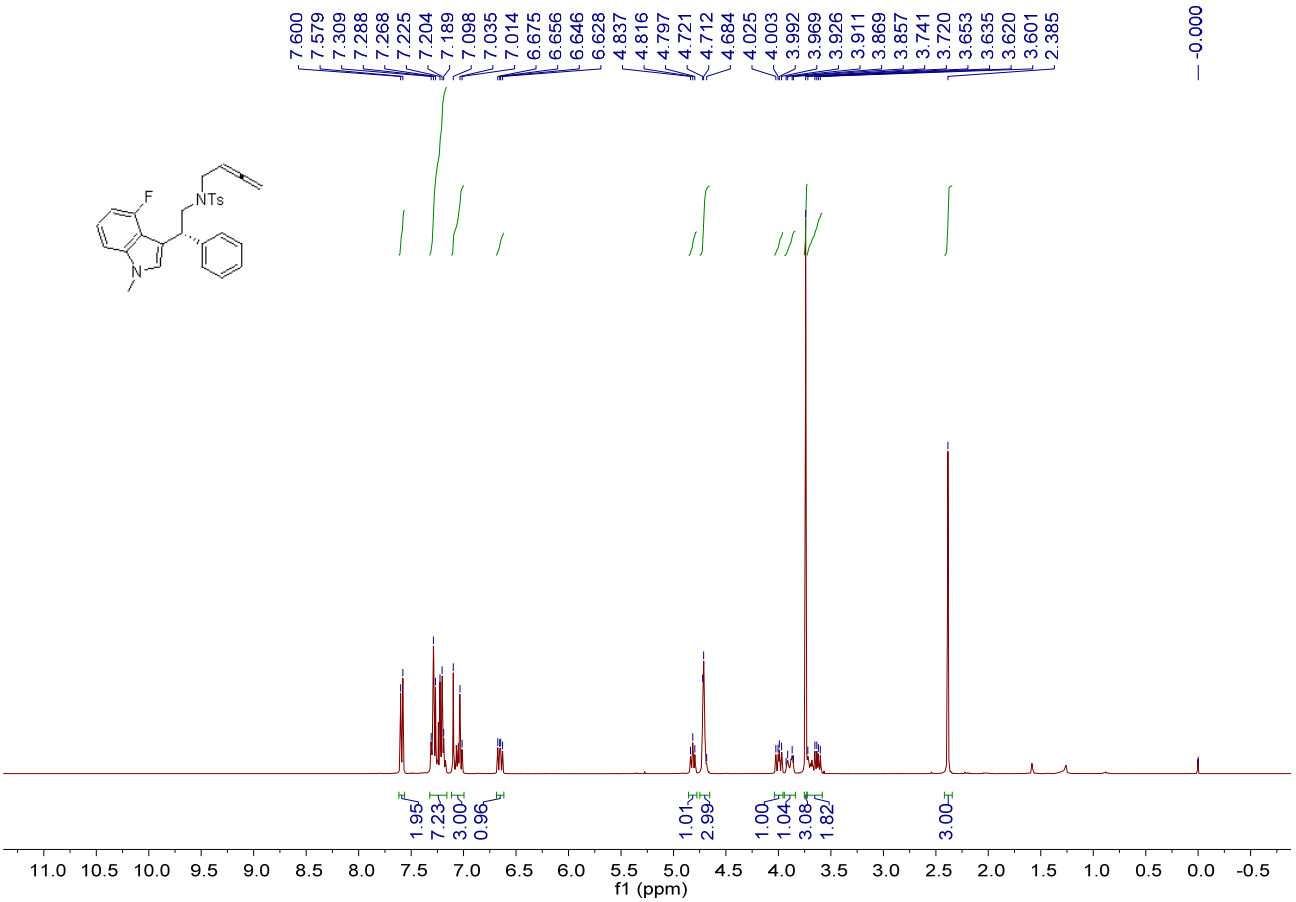
Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.50 mL/min; t_{minor} = 24.61 min, t_{major} = 27.33 min; ee% = 96%].

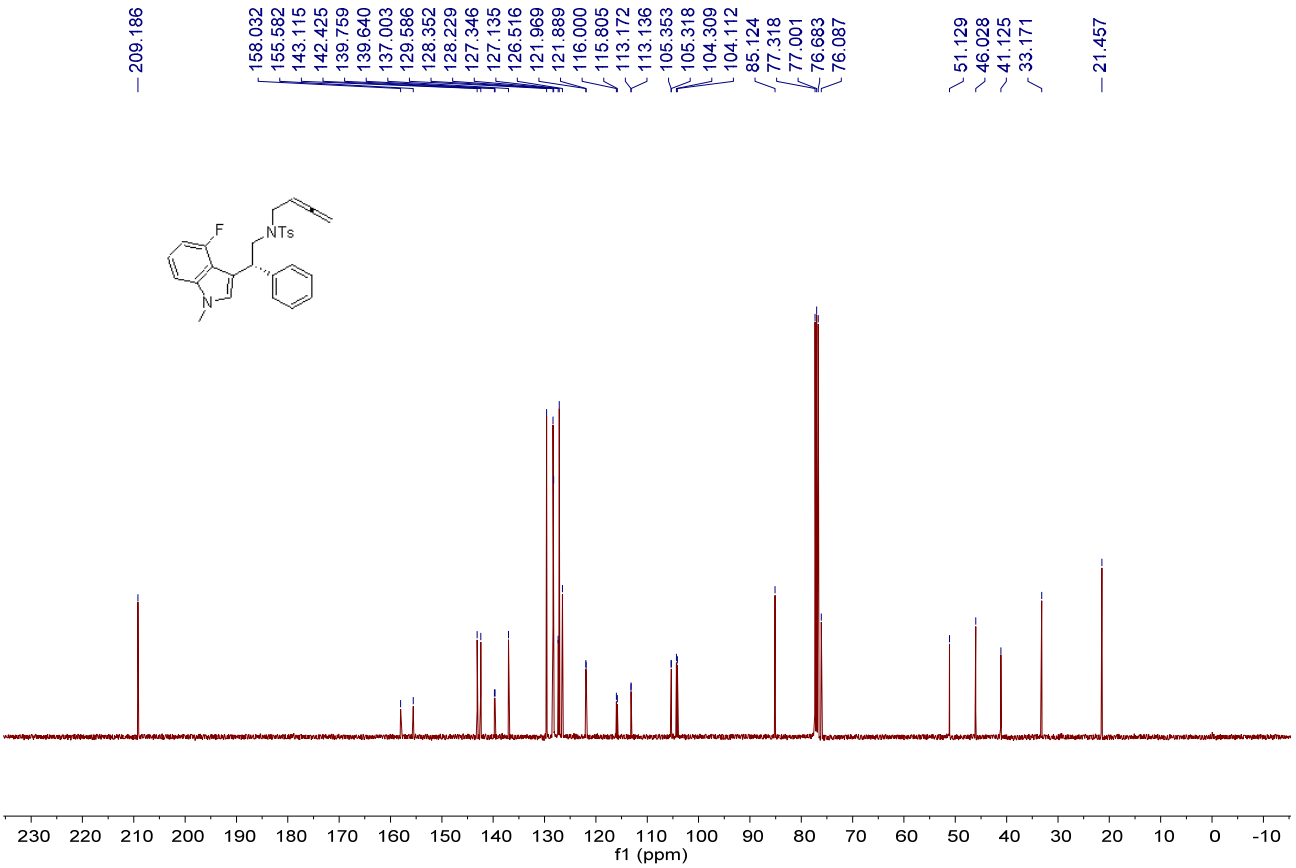


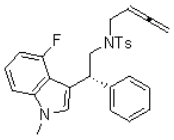
(*R*)-*N*-(buta-2,3-dien-1-yl)-*N*-(2-(4-fluoro-1-methyl-1*H*-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide 1e

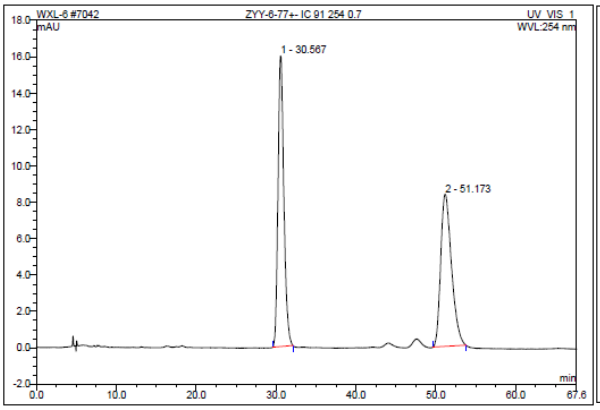
A white solid, 50% yield (23.8 mg). M.p.: 117-120 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.39 (s, 3H), 3.60-3.72 (m, 2H), 3.74 (s, 3H), 3.85-3.93 (m, 1H), 4.00 (dd, *J* = 13.6, 8.8 Hz, 1H), 4.68-4.73 (m, 3H), 4.82 (t, *J* = 8.0 Hz, 1H), 6.62-6.68 (m, 1H), 7.01-7.10 (m, 3H), 7.18-7.31 (m, 7H), 7.59 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 33.2, 41.1, 46.0, 51.1, 76.1, 85.1, 104.2 (d, *J* = 19.7 Hz), 105.3 (d, *J* = 3.5 Hz), 113.1 (d, *J* = 3.6 Hz), 115.9 (d, *J* = 19.5 Hz), 121.9 (d, *J* = 8.0 Hz), 126.5, 127.1, 127.3, 128.2, 128.4, 129.6, 137.0, 139.7 (d, *J* = 11.9 Hz), 142.4, 143.1, 156.8 (d, *J* = 245.0 Hz), 209.2. ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -121.7. IR (CH_2Cl_2) ν 2914, 2861, 1956, 1627, 1498, 1331, 1236, 1152, 1091, 984, 844, 771, 658 cm^{-1}. MS (ESI) *m/z* (%): 475.18 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{28}H_{28}N_2O_2FS^{+1}$ $[M+H]^+$ requires 475.1850, found: 475.1844. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 30.62 min, t_{major} = 50.90 min; ee% =

68%; $[\alpha]_D^{25}$ = -47.1 (c 0.08, CH_2Cl_2)].

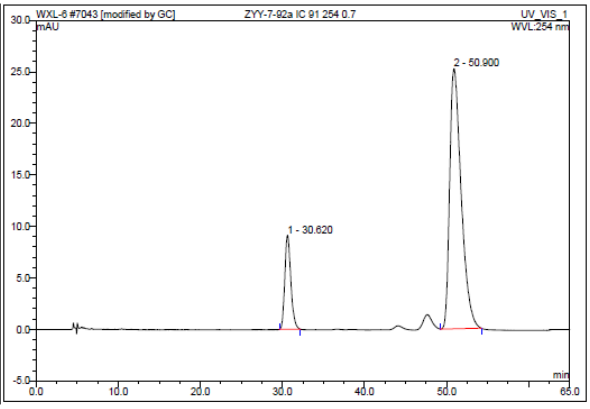






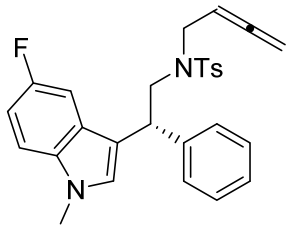


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	30.57	n.a.	15.986	13.537	50.80	n.a.	BMB
2	51.17	n.a.	8.367	13.109	49.20	n.a.	BMB
Total:			24.353	26.646	100.00	0.000	



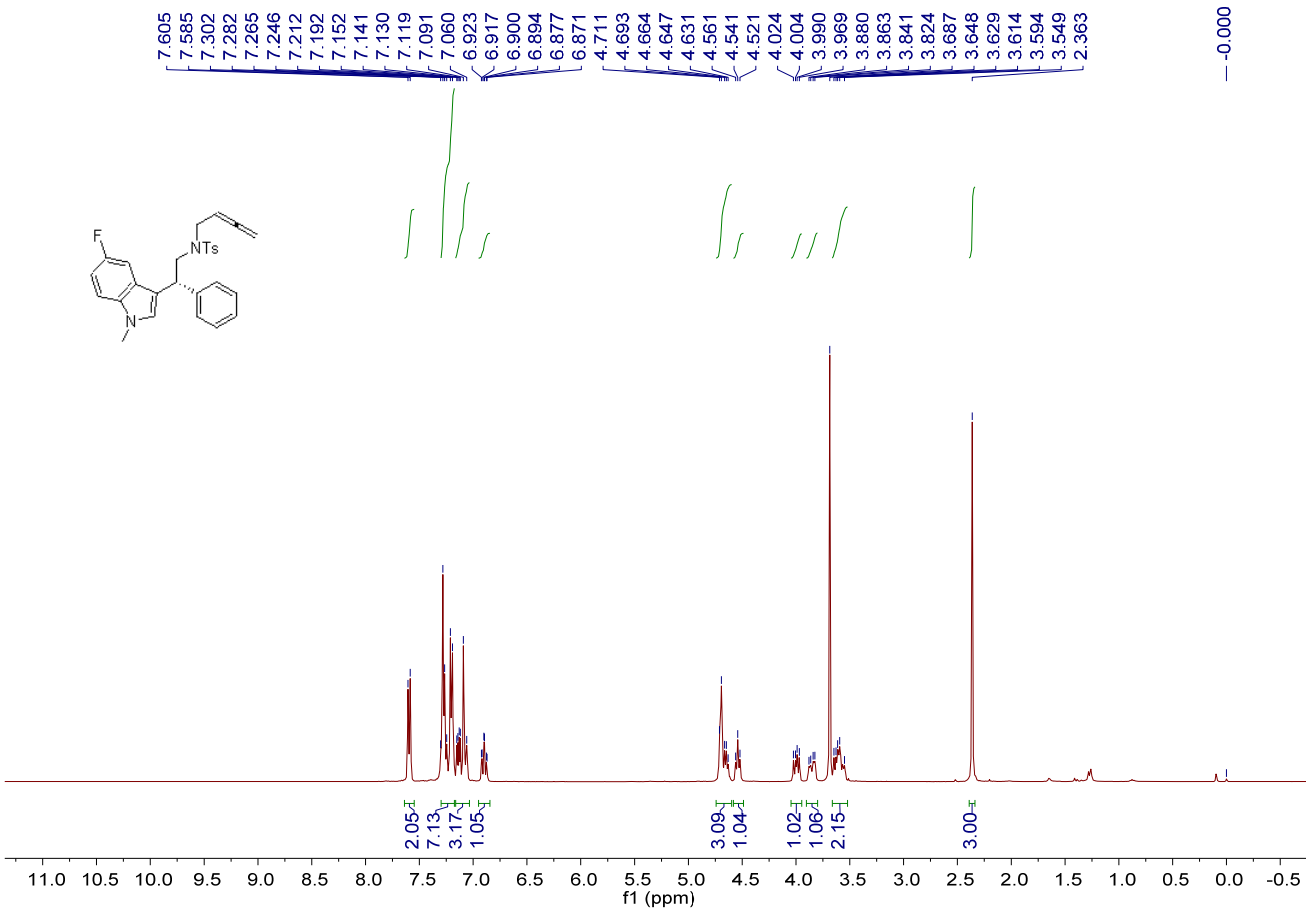
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	30.62	n.a.	9.126	7.747	15.90	n.a.	BMB
2	50.90	n.a.	25.254	40.984	84.10	n.a.	BMB*
Total:			34.380	48.731	100.00	0.000	

Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 30.62 min, t_{major} = 50.90 min; ee% = 68%].



(*R*)-*N*-(buta-2,3-dien-1-yl)-*N*-(2-(5-fluoro-1-methyl-1*H*-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide 1f

A white solid, 46% yield (21.8 mg). M.p.: 104-107 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.36 (s, 3H), 3.54-3.65 (m, 2H), 3.69 (s, 3H), 3.82-3.88 (m, 1H), 4.00 (dd, *J* = 13.6, 8.0 Hz, 1H), 4.54 (t, *J* = 8.0 Hz, 1H), 4.63-4.72 (m, 3H), 6.87-6.93 (m, 1H), 7.06-7.16 (m, 3H), 7.19-7.31 (m, 7H), 7.59 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 32.9, 41.3, 46.2, 50.7, 76.2, 85.2, 103.9 (d, *J* = 23.9 Hz), 109.7, 109.8, 109.9, 110.0, 114.4 (d, *J* = 4.8 Hz), 126.7, 127.1, 127.4 (d, *J* = 9.7 Hz), 128.1, 128.5, 129.6, 133.6, 137.0, 141.8, 143.2, 157.4 (d, *J* = 232.6 Hz), 209.2. ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -125.2. IR (CH_2Cl_2) ν 3034, 1954, 1597, 1489, 1339, 1157, 1098, 953, 848, 770, 661 cm^{-1}. MS (ESI) *m/z* (%): 475.18 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{28}H_{28}N_2O_2FS^{+1}$ $[M+H]^+$ requires 475.1850, found: 475.1846. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_{minor} = 20.34 min, t_{major} = 22.40 min; ee% = 92%; $[\alpha]_D^{25}$ = -162.5 (c 0.08, CH_2Cl_2)].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3.648
3.629
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3.594
3.549
2.363
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F
NTs
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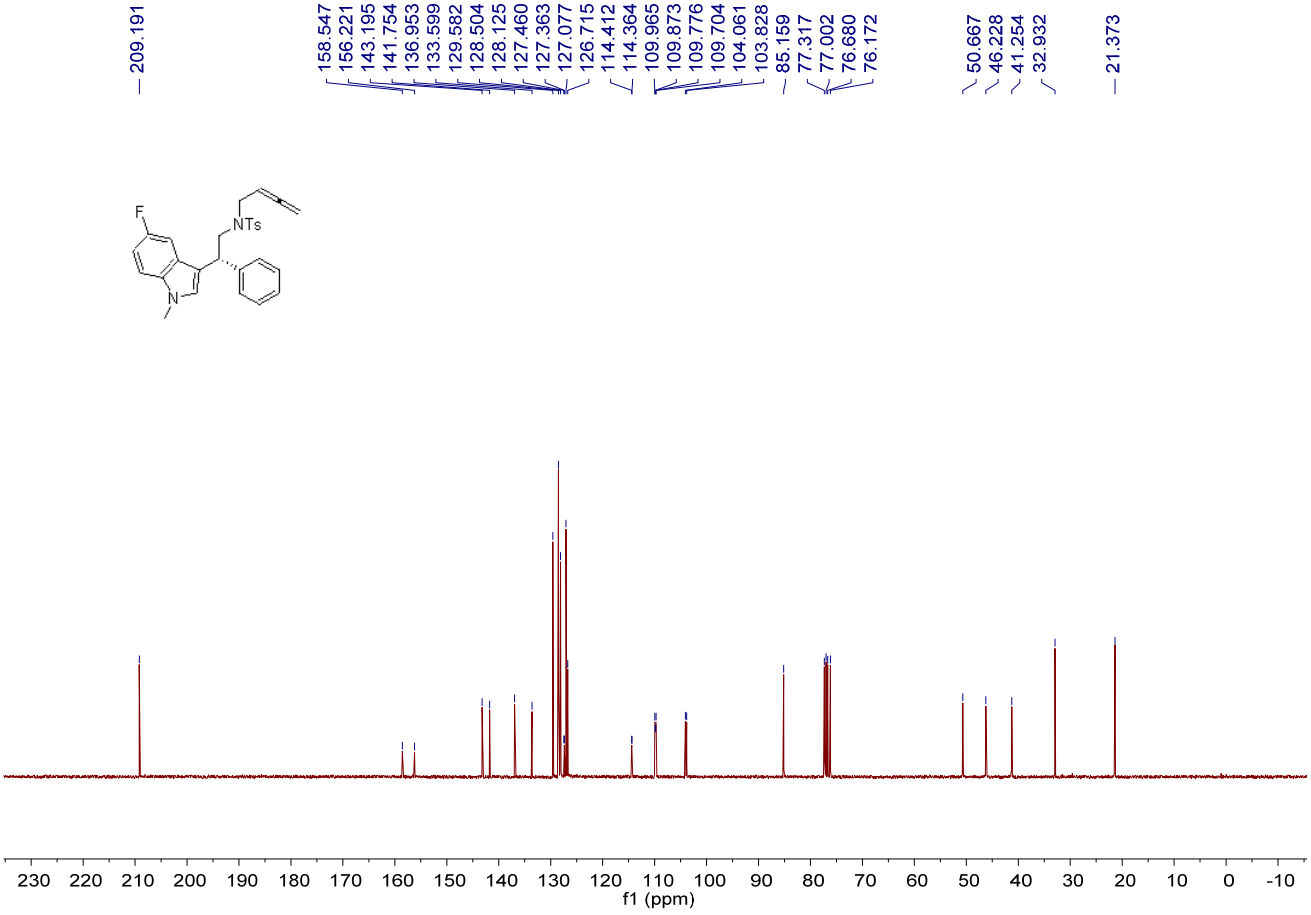
1.05
3.09
1.04
1.02
1.06
2.15
3.00
f1 (ppm)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127.077
126.715
114.412
114.364
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109.776
109.704
104.061
103.828
85.159
77.317
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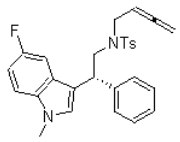
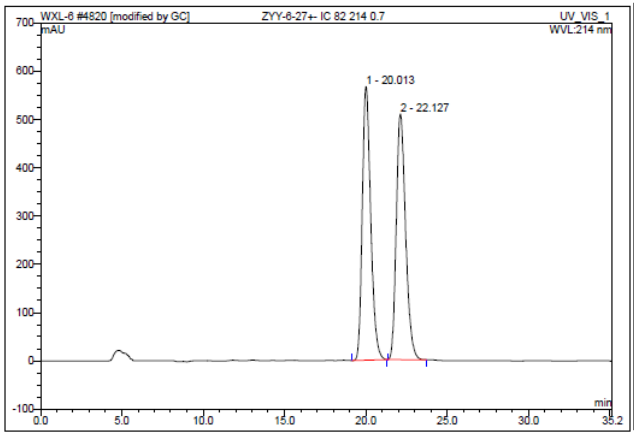
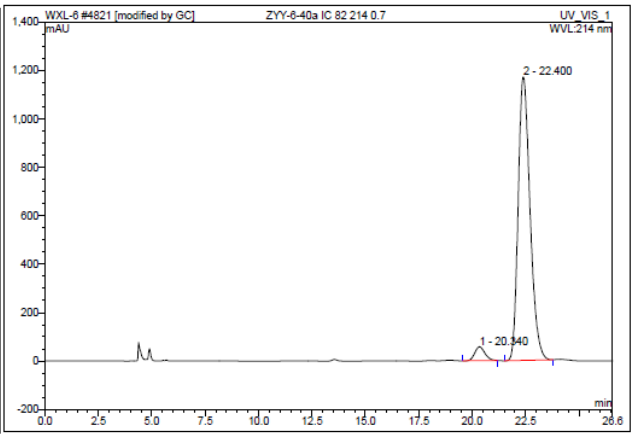
F
NTs
N
f1 (ppm)



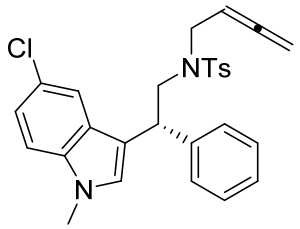




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.01	n.a.	566.470	339.928	50.17	n.a.	BMB*
2	22.13	n.a.	508.922	337.643	49.83	n.a.	BMB*
Total:			1075.392	677.570	100.00	0.000	

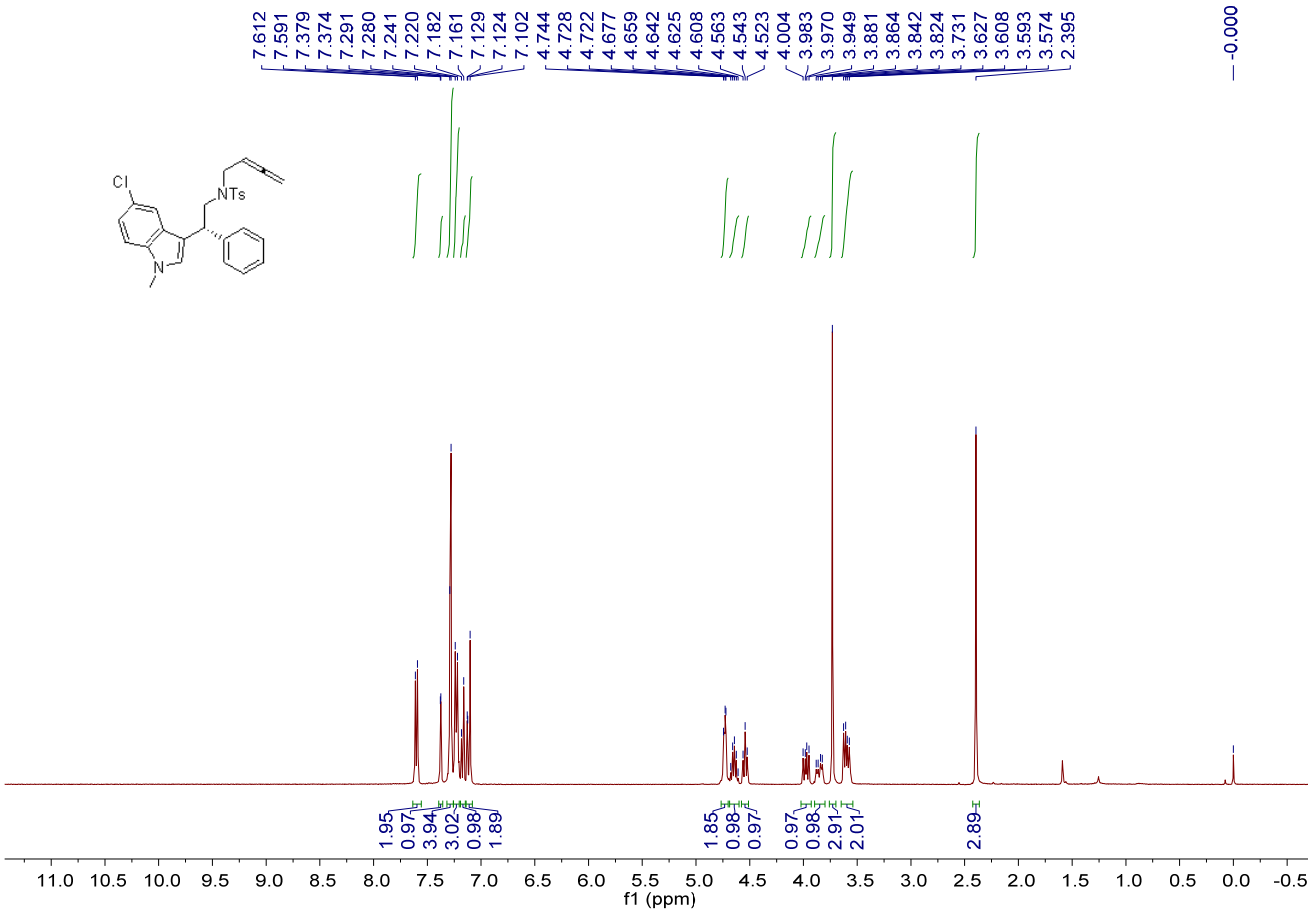
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.34	n.a.	56.926	31.119	3.97	n.a.	BMB*
2	22.40	n.a.	1170.189	753.285	96.03	n.a.	BMB*
Total:			1227.115	784.404	100.00	0.000	

Translation: Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_{minor} = 20.34 min, t_{major} = 22.40 min; ee% = 92%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(*R*)-*N*-(buta-2,3-dien-1-yl)-*N*-(2-(5-chloro-1-methyl-1*H*-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide 1g

A white solid, 46% yield (22.5 mg). M.p.: 112-115 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 3.57-3.63 (m, 2H), 3.73 (s, 3H), 3.82-3.89 (m, 1H), 3.98 (dd, *J* = 13.6, 8.4 Hz, 1H), 4.54 (t, *J* = 8.0 Hz, 1H), 4.60-4.68 (m, 1H), 4.72-4.75 (m, 2H), 7.10-7.13 (m, 2H), 7.16-7.19 (m, 1H), 7.22-7.25 (m, 3H), 7.28-7.30 (m, 4H), 7.37 (d, *J* = 2.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 33.0, 41.0, 46.2, 50.7, 76.3, 85.1, 110.3, 114.1, 118.5, 121.9, 124.7, 126.8, 127.2, 128.2, 128.3, 128.4, 128.6, 129.7, 135.4, 137.0, 141.7, 143.3, 209.2. IR (CH_2Cl_2) ν 3028, 2922, 1953, 1598, 1478, 1336, 1155, 1091, 941, 852, 795, 701, 656 cm^{-1}. MS (ESI) *m/z* (%): 491.15 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{28}H_{28}N_2O_2ClS^{+1}$ $[M+H]^+$ requires 491.1555, found: 491.1552. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 50/50; Flow rate: 0.70 mL/min; t_{minor} = 10.30 min, t_{major} = 11.34 min; ee% = 92%; $[\alpha]_D^{25}$ = 37.33 (c 0.10, CH_2Cl_2)].


7.612
7.591
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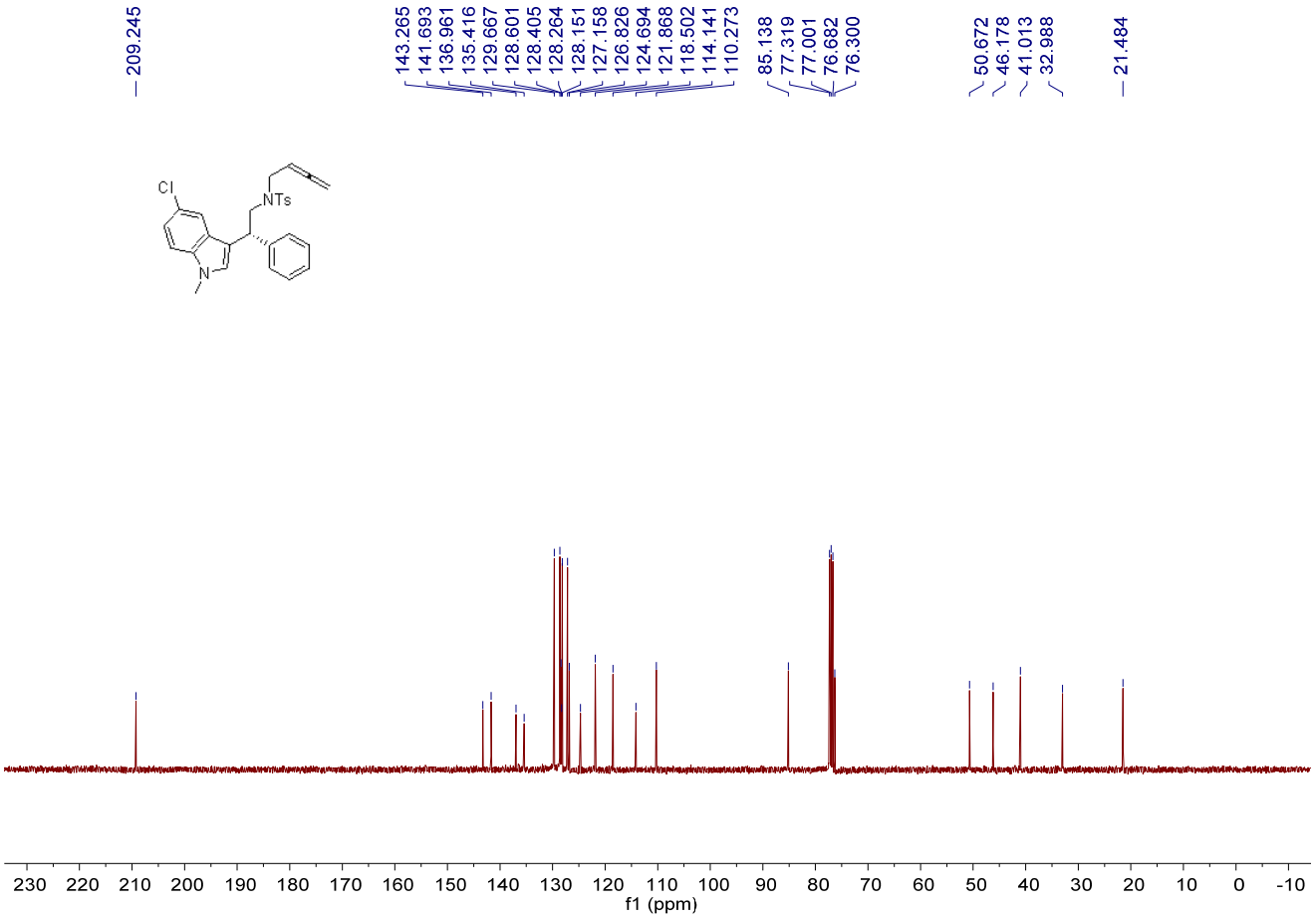
7.280
7.241
7.220
7.182
7.161
7.129
7.124
7.102
4.744
4.728
4.722
4.677
4.659
4.642
4.625
4.608
4.563
4.543
4.523
4.004
3.983
3.970
3.949
3.881
3.864
3.842
3.824
3.731
3.627
3.608
3.593
3.574
2.395
-0.000
Cl
NTs
N
1.95
0.97
3.94
3.02
0.98
1.89
1.85
0.98
0.97
0.97
0.98
2.91
2.01
2.89
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


209.245
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141.693
136.961
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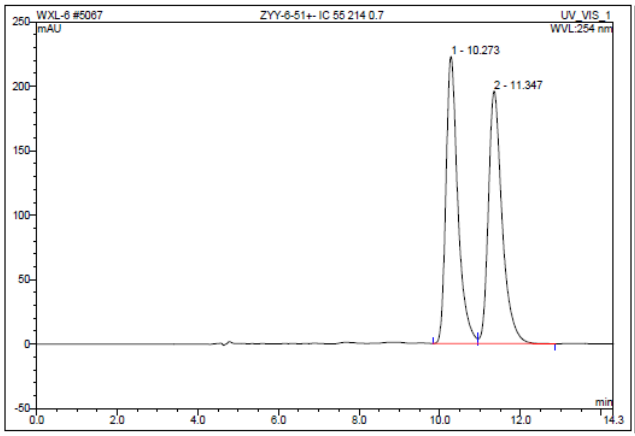
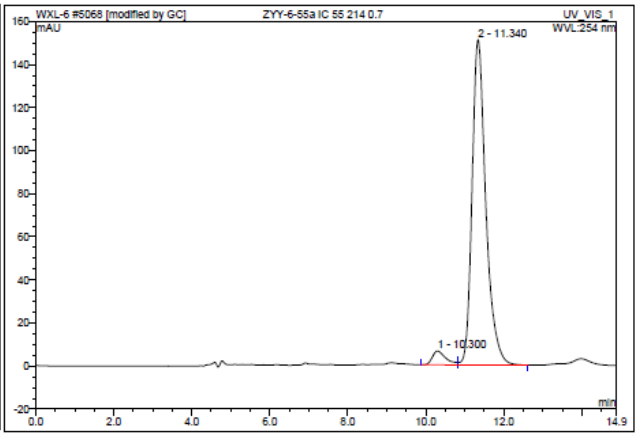
128.601
128.405
128.264
128.151
127.158
126.826
124.694
121.868
118.502
114.141
110.273
85.138
77.319
77.001
76.682
76.300
50.672
46.178
41.013
32.988
21.484
Cl
NTs
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

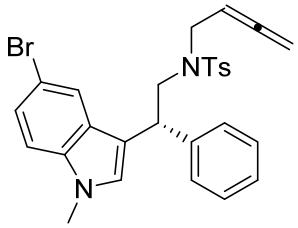




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.27	n.a.	222.536	76.225	49.62	n.a.	BM
2	11.35	n.a.	195.806	77.402	50.38	n.a.	MB
Total:			418.341	153.627	100.00	0.000	

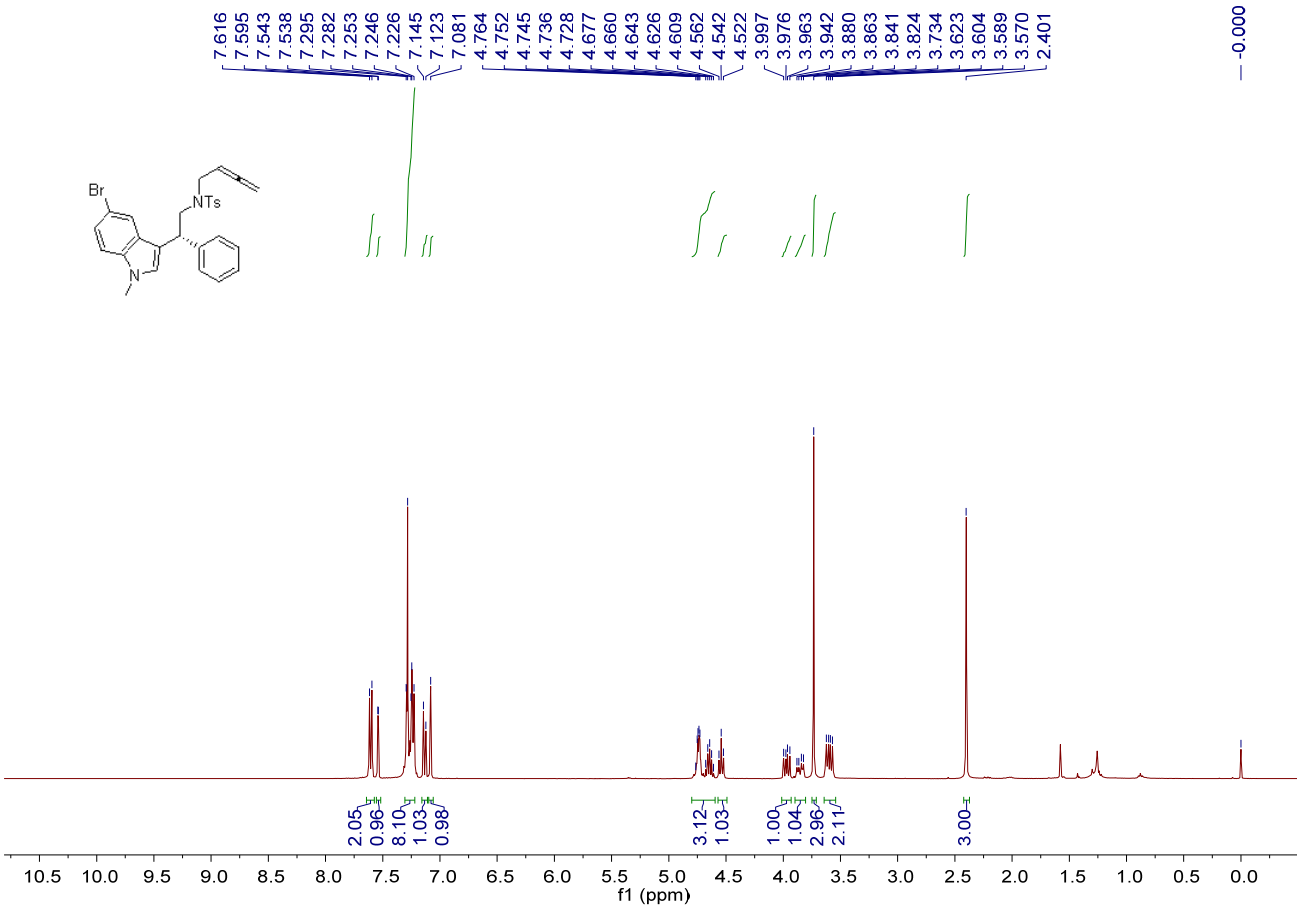
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.30	n.a.	6.456	2.593	4.03	n.a.	BM
2	11.34	n.a.	151.112	61.717	95.97	n.a.	MB
Total:			157.568	64.310	100.00	0.000	

Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 50/50; Flow rate: 0.70 mL/min; t_{minor} = 10.30 min, t_{major} = 11.34 min; ee% = 92%].



(*R*)-*N*-(2-(5-bromo-1-methyl-1*H*-indol-3-yl)-2-phenylethyl)-*N*-(buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide 1h

A white solid, 48% yield (25.6 mg). M.p.: 101-104 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 3.57-3.63 (m, 2H), 3.73 (s, 3H), 3.82-3.88 (m, 1H), 3.97 (dd, *J* = 13.6, 8.4 Hz, 1H), 4.54 (t, *J* = 8.0 Hz, 1H), 4.60-4.77 (m, 3H), 7.08 (s, 1H), 7.12-7.15 (m, 1H), 7.22-7.30 (m, 8H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 33.0, 41.0, 46.2, 50.7, 76.3, 85.2, 110.7, 112.3, 114.1, 121.6, 124.4, 126.8, 127.2, 128.2, 128.3, 128.6, 129.0, 129.7, 135.7, 137.0, 141.7, 143.3, 209.2. IR (CH_2Cl_2) ν 2913, 1952, 1597, 1475, 1335, 1157, 1061, 946, 842, 794, 708, 663 cm^{-1}. MS (ESI) *m/z* (%): 535.10 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{28}H_{28}N_2O_2BrS^{+1}$ $[M+H]^+$ requires 535.1049, found: 535.1046. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 14.19 min, t_{major} = 16.03 min; ee% = 80%; $[\alpha]_D^{25}$ = -30.0 (c 0.10, CH_2Cl_2)].


7.616
7.595
7.543
7.538
7.295
7.282
7.253
7.246
7.226
7.145
7.123
7.081
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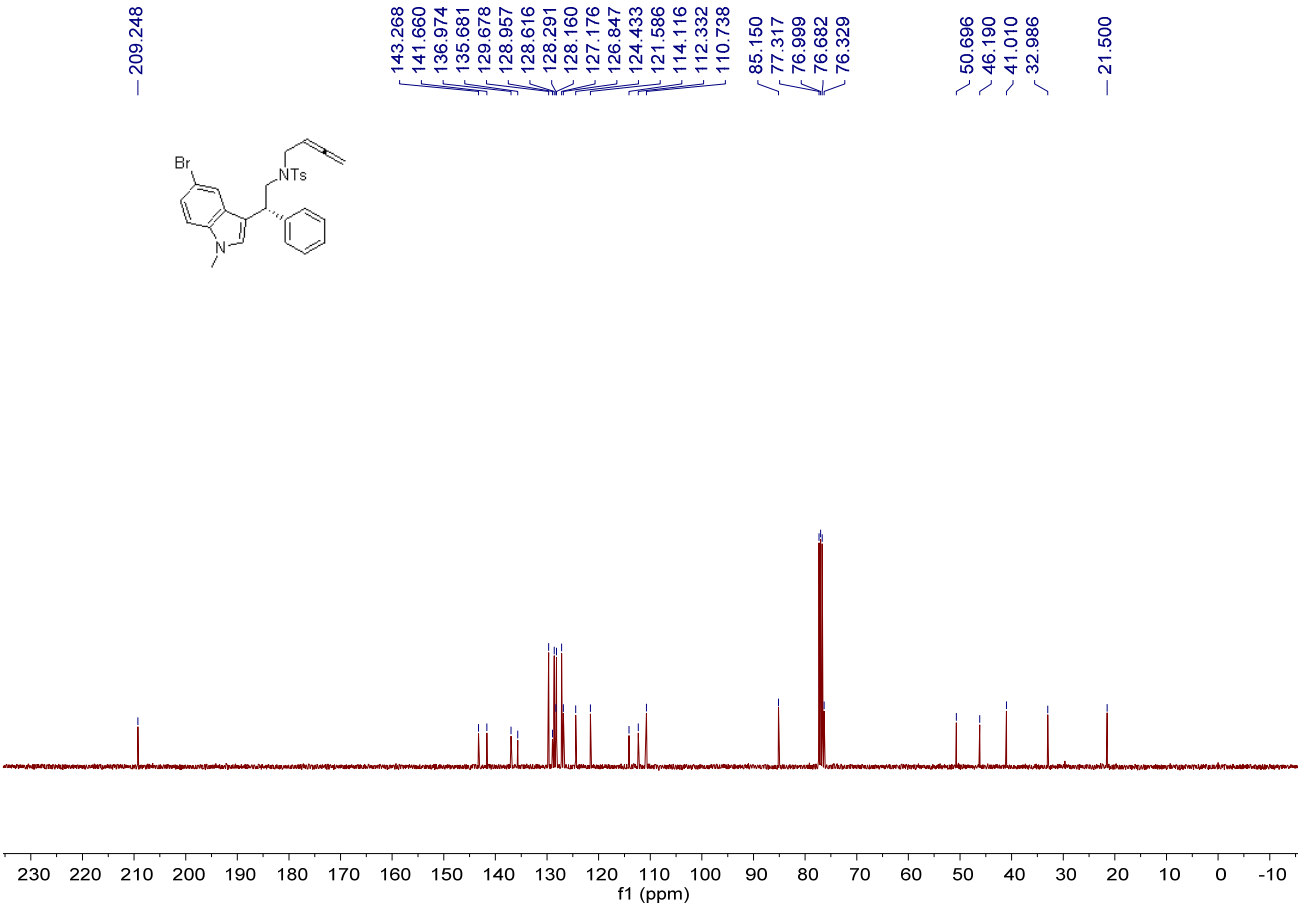
4.752
4.745
4.736
4.728
4.677
4.660
4.643
4.626
4.609
4.562
4.542
4.522
3.997
3.976
3.963
3.942
3.880
3.863
3.841
3.824
3.734
3.623
3.604
3.589
3.570
2.401
-0.000
Br
NTs
N
2.05
0.96
8.10
1.03
0.98
3.12
1.03
1.00
1.04
2.96
2.11
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


209.248
143.268
141.660
136.974
135.681
129.678
128.957
128.616
128.291
128.160
127.176
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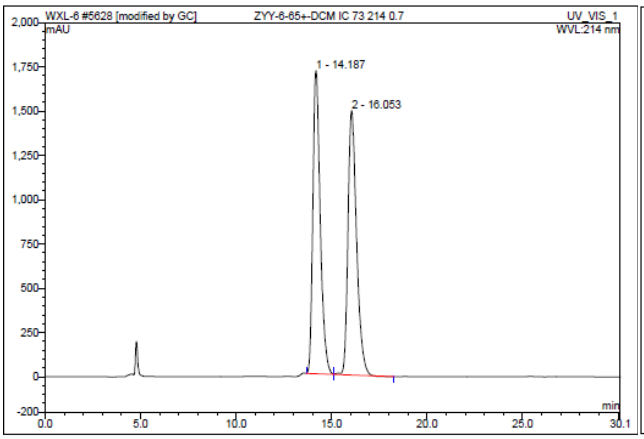
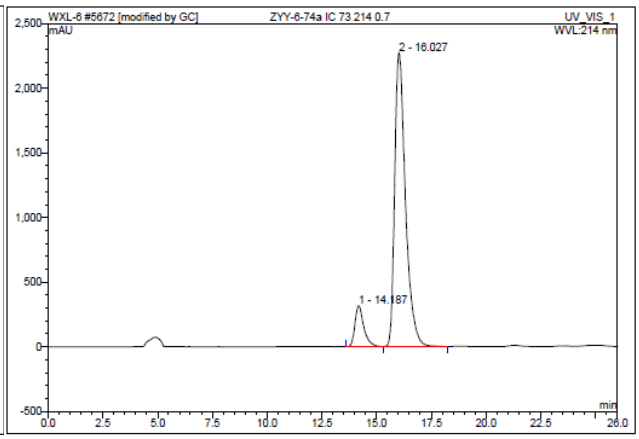
124.433
121.586
114.116
112.332
110.738
85.150
77.317
76.999
76.682
76.329
50.696
46.190
41.010
32.986
21.500
Br
NTs
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

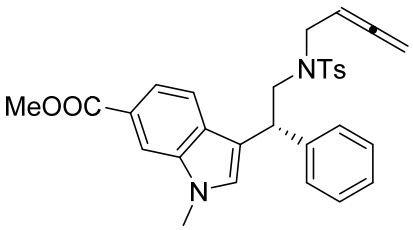




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.19	n.a.	1711.406	765.567	49.53	n.a.	BM *
2	16.05	n.a.	1493.208	779.987	50.47	n.a.	MB*
Total:			3204.614	1545.555	100.00	0.000	

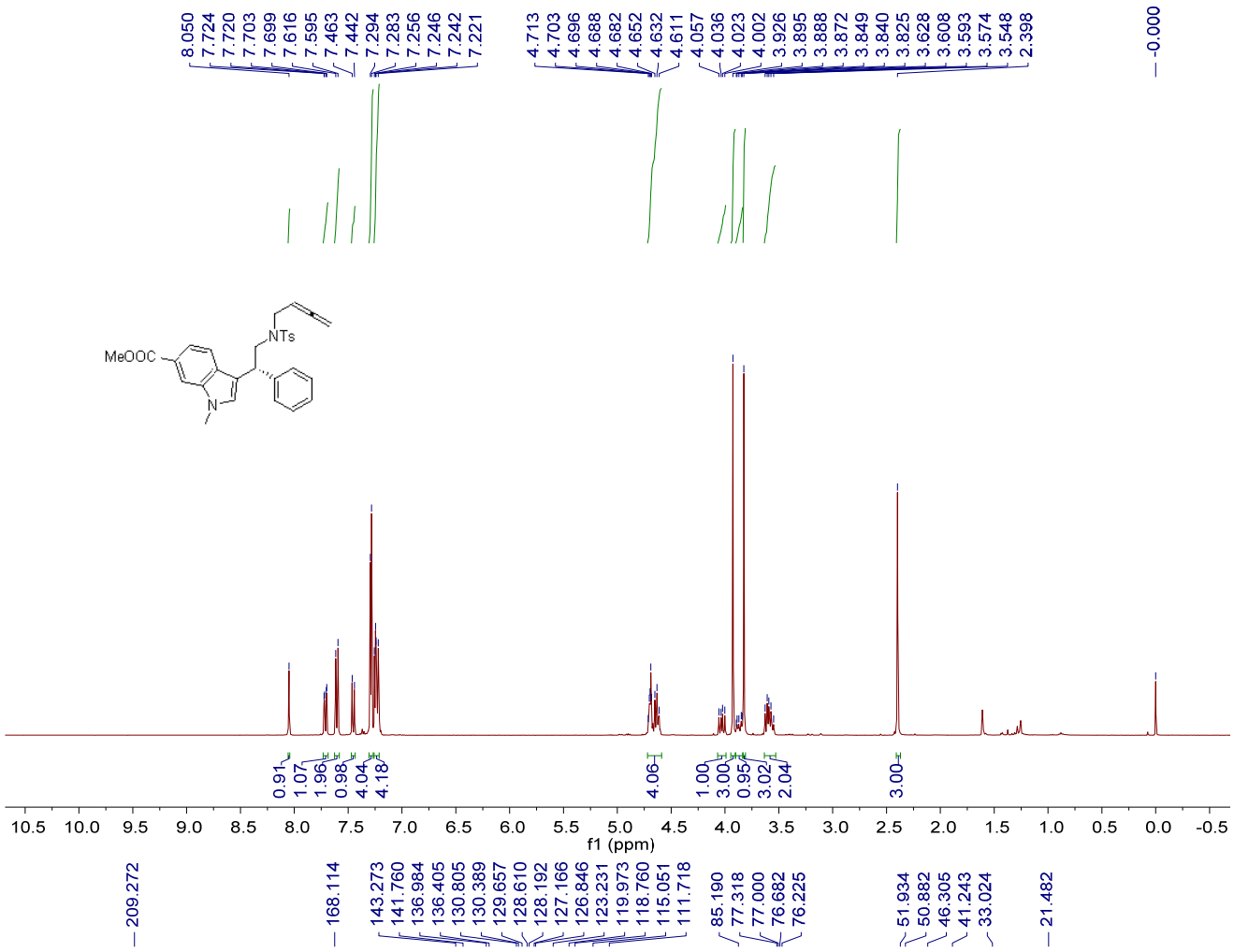
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.19	n.a.	317.014	148.580	10.26	n.a.	Ru
2	16.03	n.a.	2271.580	1299.892	89.74	n.a.	BMB*
Total:			2588.594	1448.472	100.00	0.000	

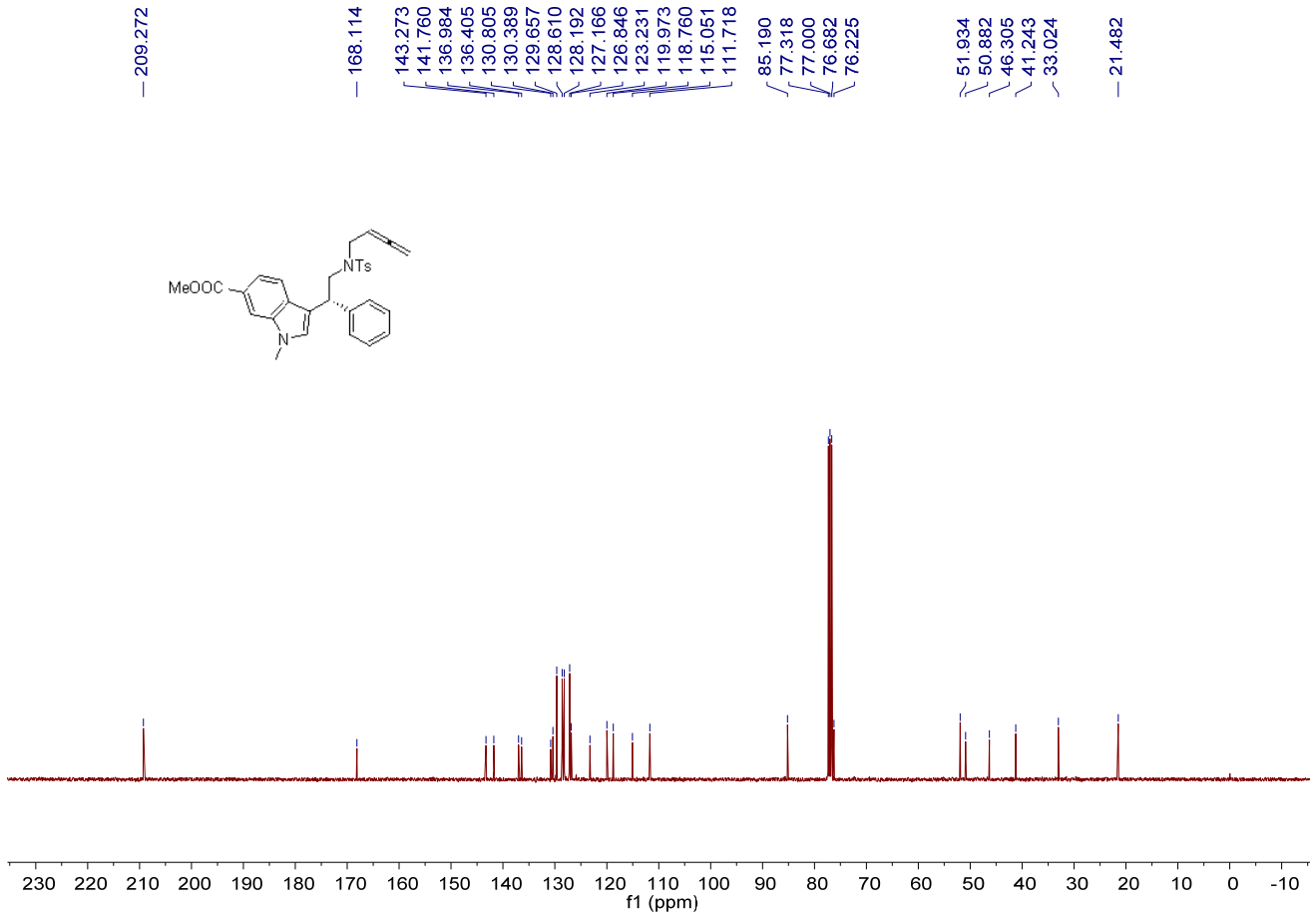
Translation: Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 14.19 min, t_{major} = 16.03 min; ee% = 80%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).

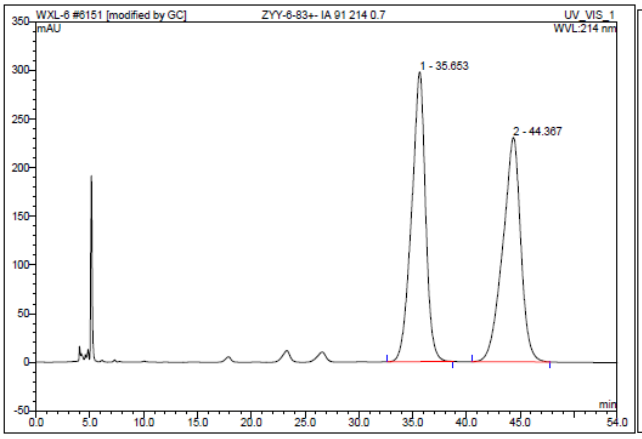


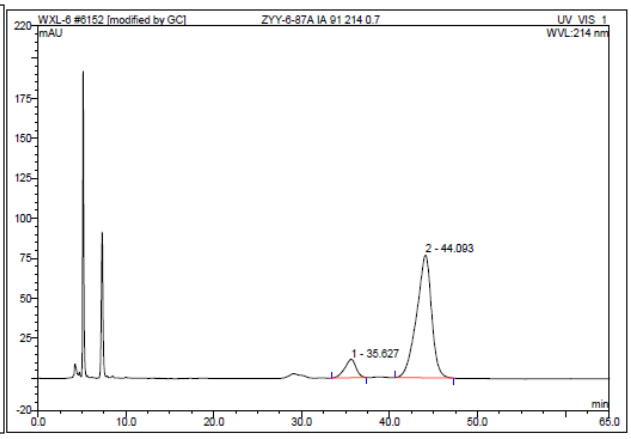
(*R*)-Methyl 3-(2-(*N*-(buta-2,3-dien-1-yl)-4-methylphenylsulfonamido)-1-phenylethyl)-1-methyl-1*H*-indole-6-carboxylate 1i

A white solid, 50% yield (25.7 mg). M.p.: 170-173 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 3.54-3.63 (m, 2H), 3.83 (s, 3H), 3.84-3.90 (m, 1H), 3.93 (s, 3H), 4.03 (dd, *J* = 13.6, 8.4 Hz, 1H), 4.61-4.72 (m, 4H), 7.22-7.26 (m, 4H), 7.29 (d, *J* = 8.4 Hz, 4H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.69-7.73 (m, 1H), 8.05 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 33.0, 41.2, 46.3, 50.9, 51.9, 76.2, 85.2, 111.7, 115.1, 118.8, 120.0, 123.2, 126.8, 127.2, 128.2, 128.6, 129.7, 130.4, 130.8, 136.4, 137.0, 141.8, 143.3, 168.1, 209.3. IR (CH_2Cl_2) ν 2923, 2860, 1948, 1703, 1478, 1341, 1160, 1106, 979, 882, 748, 659 cm^{-1}. MS (ESI) *m/z* (%): 515.19 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{30}H_{31}N_2O_4S^{+1}$ $[M+H]^+$ requires 515.1999, found: 515.1993. Enantiomeric excess was determined by HPLC with a Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 35.63 min, t_{major} = 44.09 min; ee% = 80%; $[\alpha]_D^{25}$ = -17.8 (c 0.12, CH_2Cl_2)].


8.050
7.724
7.720
7.703
7.699
7.616
7.595
7.463
7.442
7.294
7.283
7.256
7.246
7.242
7.221
4.713
4.703
4.696
4.688
4.682
4.652
4.632
4.611
4.057
4.036
4.023
4.002
3.926
3.895
3.888
3.872
3.849
3.840
3.825
3.628
3.608
3.593
3.574
3.548
2.398
-0.000
MeOOC
NTs
N
0.91
1.07
1.96
0.98
4.04
4.18
4.06
1.00
3.00
0.95
3.02
2.04
3.00
f1 (ppm)


209.272
168.114
143.273
141.760
136.984
136.405
130.805
130.389
129.657
128.610
128.192
127.166
126.846
123.231
119.973
118.760
115.051
111.718
85.190
77.318
77.000
76.682
76.225
51.934
50.882
46.305
41.243
33.024
21.482
MeOOC
NTs
N
f1 (ppm)

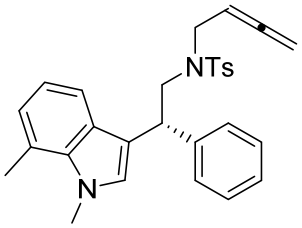




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	35.65	n.a.	297.597	447.143	49.97	n.a.	BMB
2	44.37	n.a.	230.502	447.639	50.03	n.a.	BMB
Total:			528.098	894.783	100.00	0.000	

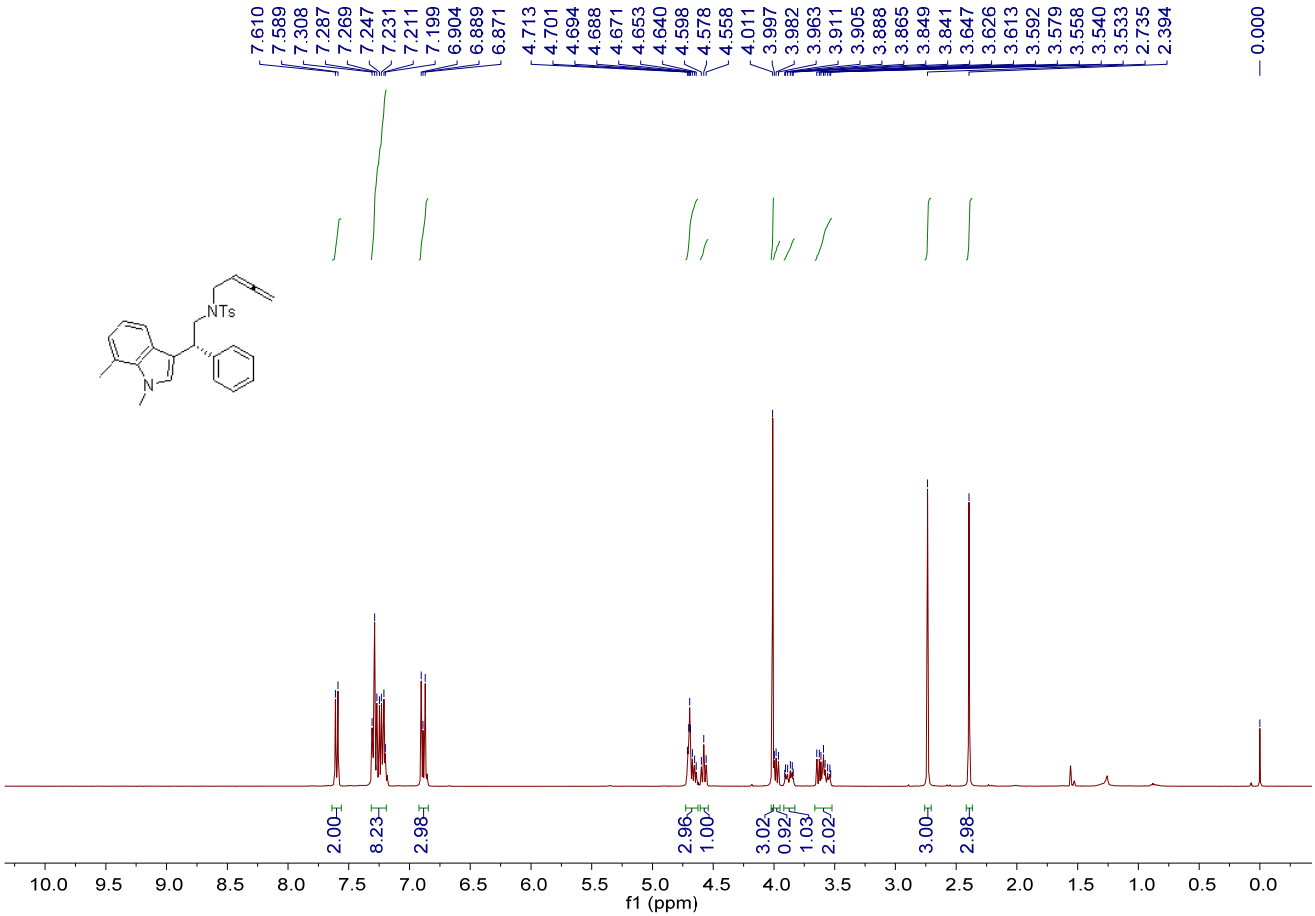
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	35.63	n.a.	11.547	17.283	10.24	n.a.	BMB
2	44.09	n.a.	76.659	151.424	89.76	n.a.	BMB
Total:			88.207	168.707	100.00	0.000	

Translation: Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 35.63 min, t_{major} = 44.09 min; ee% = 80%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(*R*)-*N*-(buta-2,3-dien-1-yl)-*N*-(2-(1,7-dimethyl-1*H*-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide 1j

A white solid, 46% yield (21.7 mg). M.p.: 102-105 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.39 (s, 3H), 2.74 (s, 3H), 3.53-3.65 (m, 2H), 3.84-3.92 (m, 1H), 3.98 (dd, *J* = 13.6, 7.6 Hz, 1H), 4.01 (s, 3H), 4.58 (t, *J* = 8.0 Hz, 1H), 4.64-4.72 (m, 3H), 6.87-6.91 (m, 3H), 7.19-7.31 (m, 8H), 7.60 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.7, 21.5, 36.8, 41.1, 46.2, 50.7, 76.2, 85.3, 114.2, 117.2, 119.2, 121.2, 124.3, 126.6, 127.2, 128.30, 128.34, 128.5, 128.7, 129.6, 135.7, 137.2, 142.1, 143.1, 209.3. IR (CH_2Cl_2) ν 2923, 2867, 1956, 1451, 1156, 959, 808, 769, 660 cm^{-1}. MS (ESI) *m/z* (%): 471.20 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{29}H_{31}N_2O_2S^{+1}$ $[M+H]^+$ requires 471.2101, found: 471.2097. Enantiomeric excess was determined by HPLC with a Chiralcel ID3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_{minor} = 13.29 min, t_{major} = 14.58 min; ee% = 97%; $[\alpha]_D^{25}$ = -119.6 (c 0.6, CH_2Cl_2)].


7.610
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7.287
7.269
7.247
7.231
7.211
7.199
6.904
6.889
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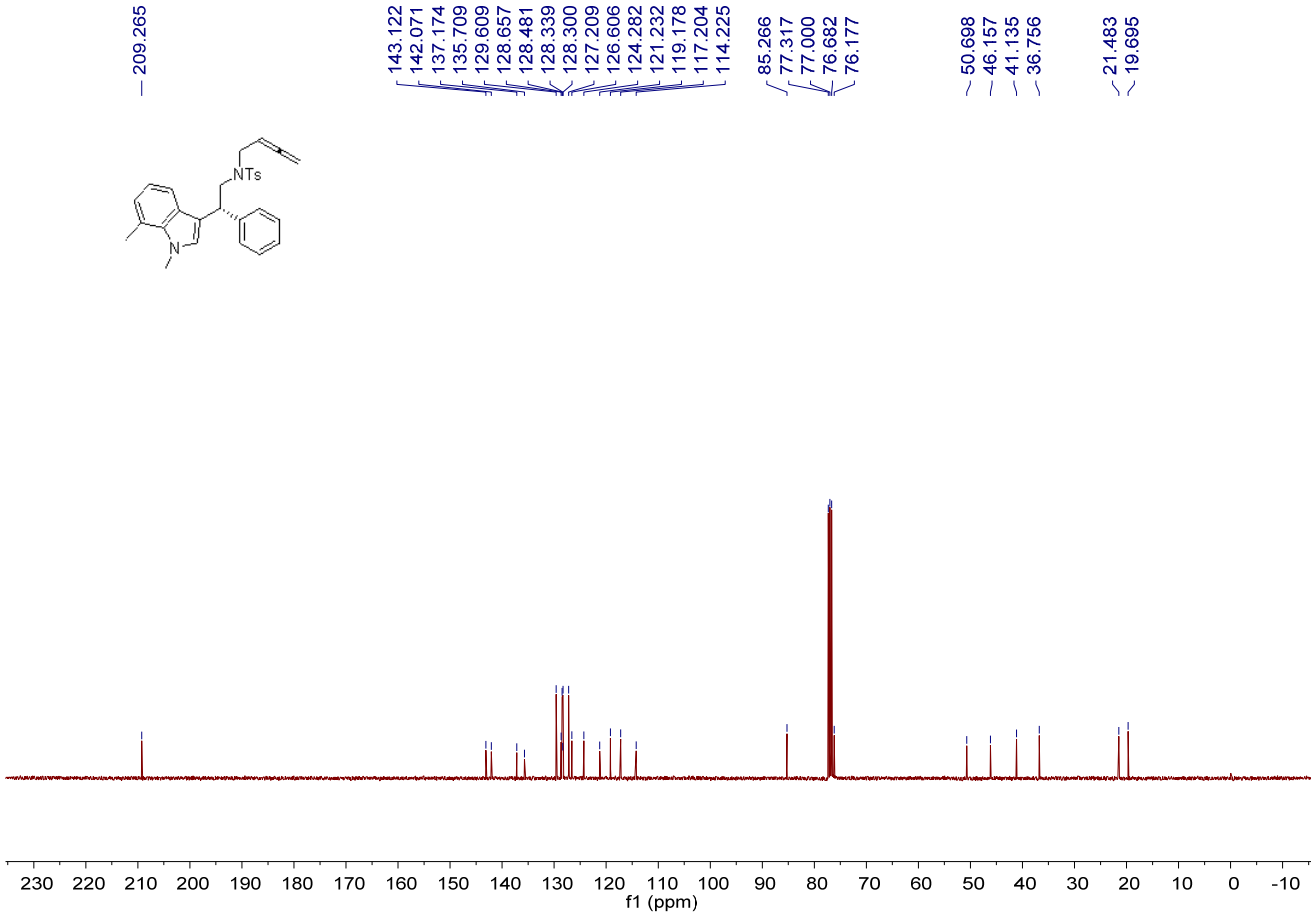
4.713
4.701
4.694
4.688
4.671
4.653
4.640
4.598
4.578
4.558
4.011
3.997
3.982
3.963
3.911
3.905
3.888
3.865
3.849
3.841
3.647
3.626
3.613
3.592
3.579
3.558
3.540
3.533
2.735
2.394
0.000
NTs
2.00
8.23
2.98
2.96
1.00
3.02
0.92
1.03
2.02
3.00
2.98
f1 (ppm)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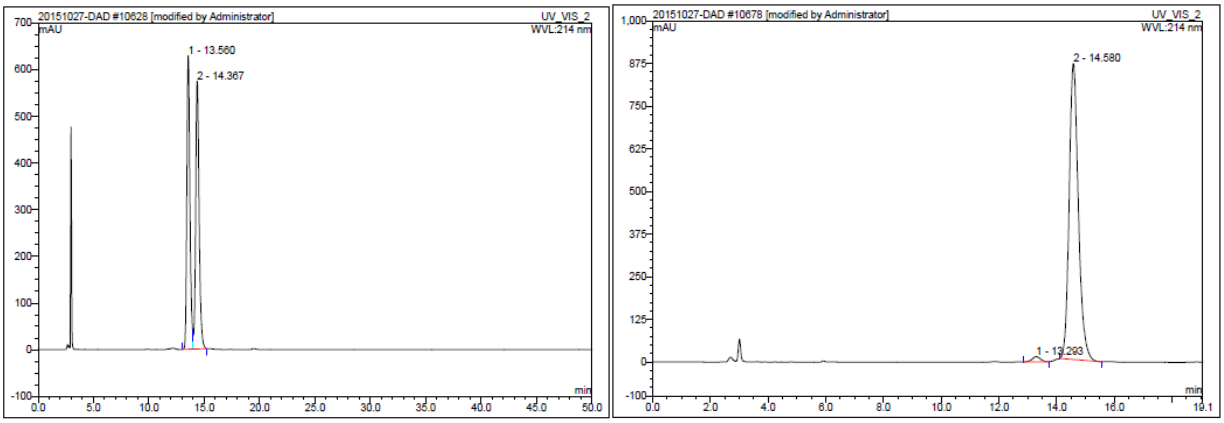
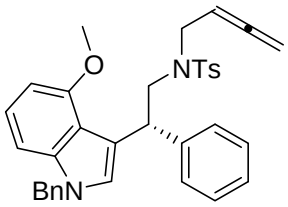
137.174
135.709
129.609
128.657
128.481
128.339
128.300
127.209
126.606
124.282
121.232
119.178
117.204
114.225
85.266
77.317
77.000
76.682
76.177
50.698
46.157
41.135
36.756
21.483
19.695
NTs
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.56	n.a.	628.573	202.970	49.66	n.a.	BM
2	14.37	n.a.	573.219	205.712	50.34	n.a.	MB
Total:			1201.792	408.682	100.00	0.000	

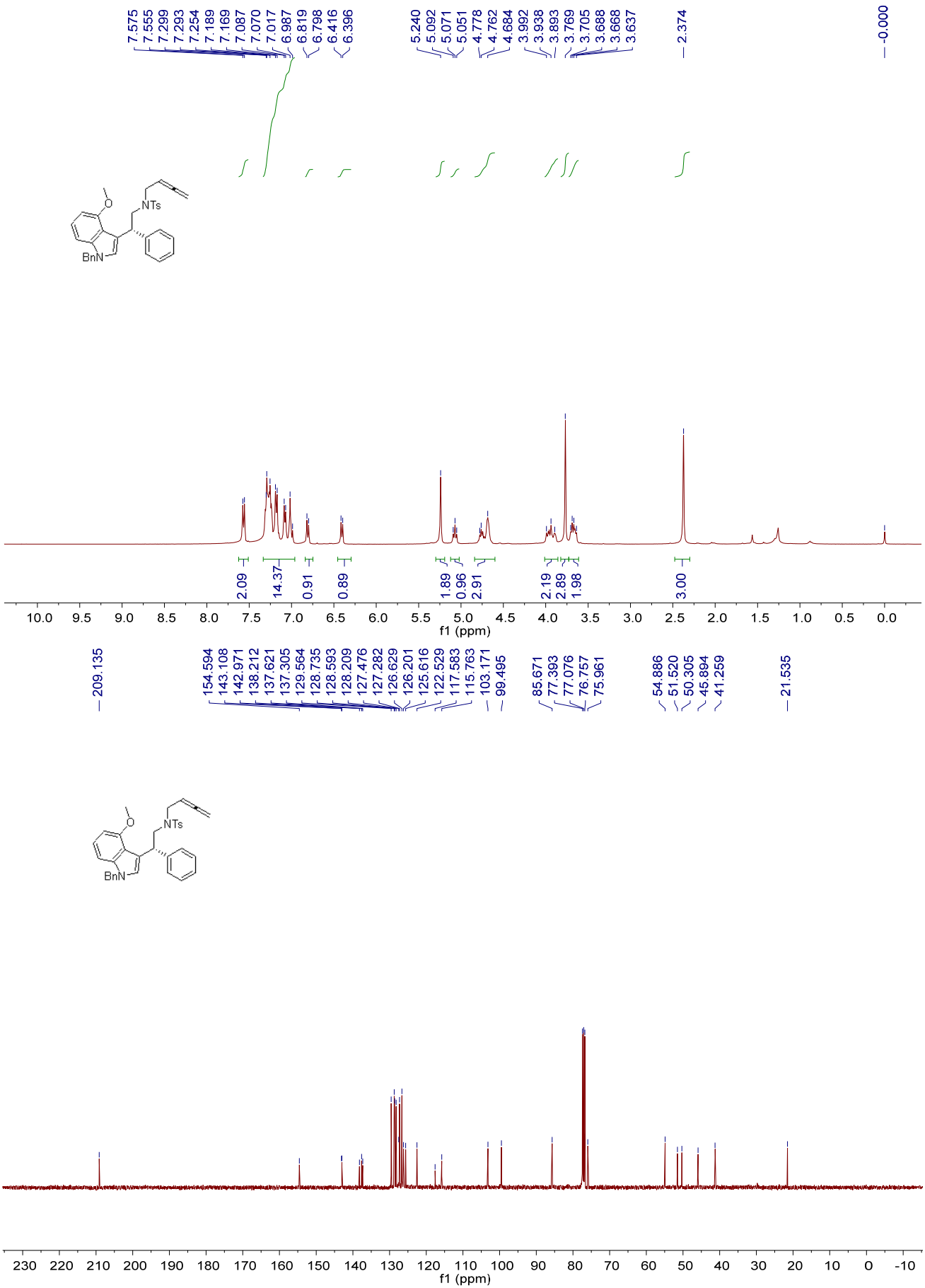
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.29	n.a.	15.367	5.076	1.56	n.a.	BMB
2	14.58	n.a.	867.839	320.531	98.44	n.a.	BMB*
Total:			883.206	325.607	100.00	0.000	

Translation: Chiralcel ID3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_{minor} = 13.29 min, t_{major} = 14.58 min; ee% = 97%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(*R*)-*N*-(2-(1-benzyl-4-methoxy-1*H*-indol-3-yl)-2-phenylethyl)-*N*-(buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide 1k

A white solid, 47% yield (26.4 mg). M.p.: 107-110 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.37 (s, 3H), 3.63-3.71 (m, 2H), 3.77 (s, 3H), 3.89-4.00 (m, 2H), 4.68-4.78 (m, 3H), 5.07 (t, *J* = 8.0 Hz, 1H), 5.24 (s, 2H), 6.40 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.98-7.30 (m, 14H), 7.56 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 41.3, 45.9, 50.3, 51.5, 54.9, 76.0, 85.7, 99.5, 103.2, 115.8, 117.6, 122.5, 125.6, 126.2, 126.6, 127.3, 127.5, 128.2, 128.6, 128.7, 129.6, 137.3, 137.6, 138.2, 143.0, 143.1, 154.6, 209.1. IR (CH_2Cl_2) ν 3027, 2925, 1954, 1578, 1497, 1338, 1257, 1156, 1091, 940, 850, 730, 699 cm^{-1}. MS (ESI) *m/z* (%): 563.23 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{35}H_{35}N_2O_3S^{+1}$ $[M+H]^+$ requires 563.2363, found: 563.2355. Enantiomeric excess was determined by HPLC with a Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 21.02 min, t_{major} = 18.78 min; ee% = 96%; $[\alpha]_D^{25}$ = -80.0 (c 0.10, CH_2Cl_2)].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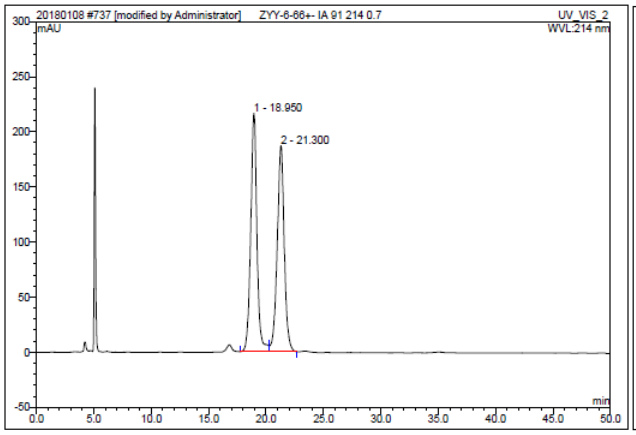
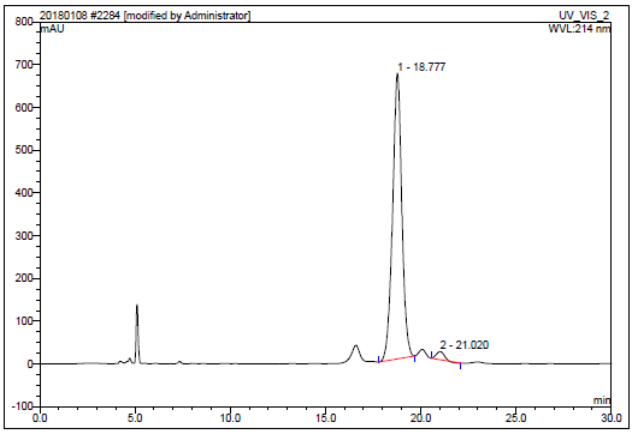
7.555
7.299
7.293
7.254
7.189
7.169
7.087
7.070
7.017
6.987
6.819
6.798
6.416
6.396
5.240
5.092
5.071
5.051
4.778
4.762
4.684
3.992
3.938
3.893
3.769
3.705
3.688
3.668
3.637
2.374
-0.000
NTs
BnN
2.09
14.37
0.91
0.89
1.89
0.96
2.91
2.19
2.89
1.98
3.00
f1 (ppm)
209.135
154.594
143.108
142.971
138.212
137.621
137.305
129.564
128.735
128.593
128.209
127.476
127.282
126.629
126.201
125.616
122.529
117.583
115.763
103.171
99.495
85.671
77.393
77.076
76.757
75.961
54.886
51.520
50.305
45.894
41.259
21.535
NTs
BnN
f1 (ppm)

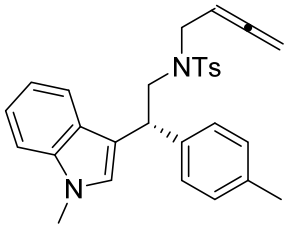




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.95	n.a.	216.342	136.453	50.61	n.a.	BM *
2	21.30	n.a.	186.708	133.150	49.39	n.a.	MB*
Total:			403.050	269.603	100.00	0.000	

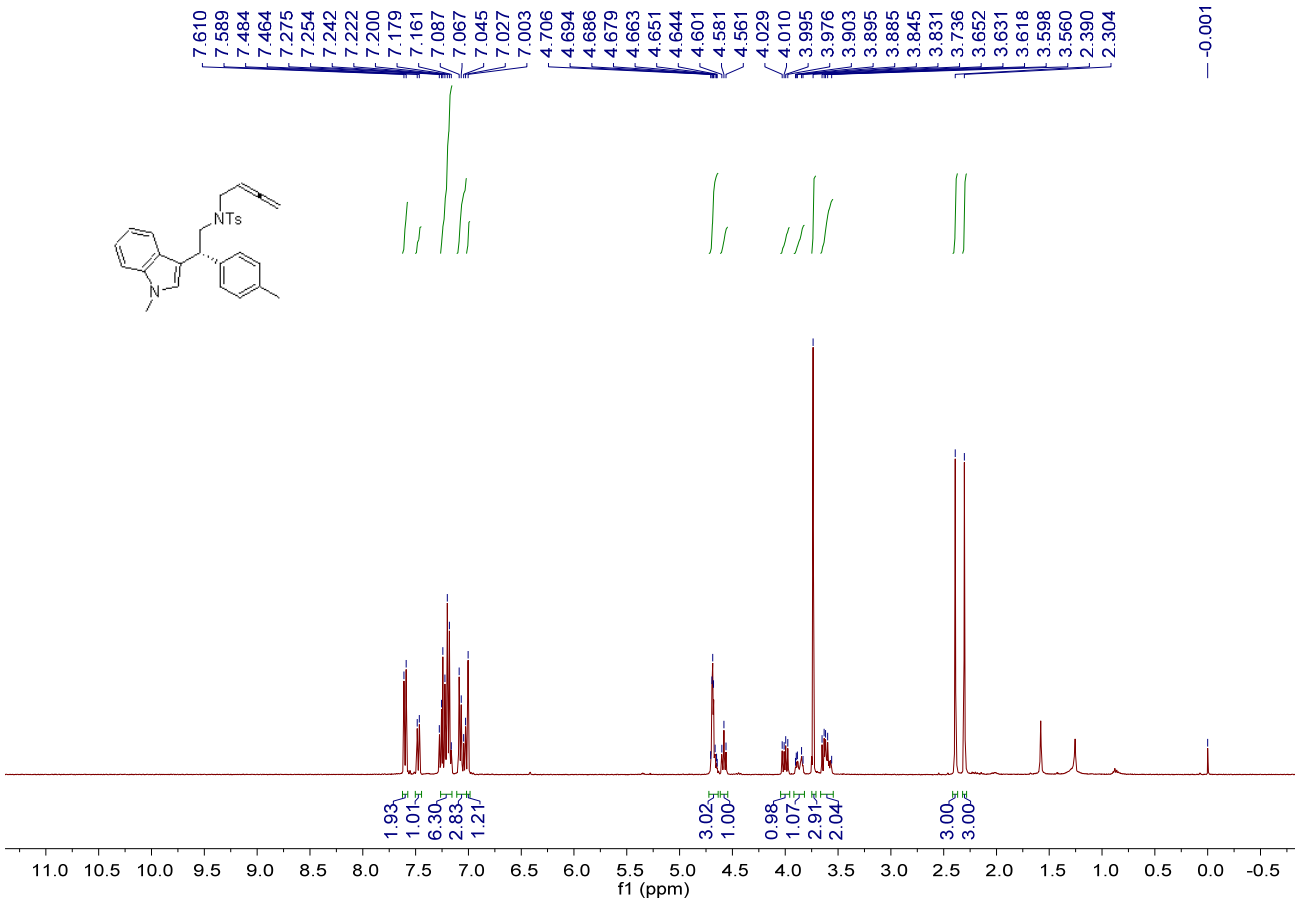
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.78	n.a.	668.476	376.016	97.79	n.a.	BMB*
2	21.02	n.a.	19.023	8.489	2.21	n.a.	BMB*
Total:			687.499	384.506	100.00	0.000	

Translation: Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 21.02 min, t_{major} = 18.78 min; ee% = 96%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(*R*)-*N*-(buta-2,3-dien-1-yl)-4-methyl-*N*-(2-(1-methyl-1*H*-indol-3-yl)-2-(*p*-tolyl)ethyl)benzenesulfonamide 1l

A white solid, 48% yield (22.6 mg). M.p.: 66-69 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.30 (s, 3H), 2.39 (s, 3H), 3.56-3.66 (m, 2H), 3.74 (s, 3H), 3.83-3.91 (m, 1H), 4.00 (dd, *J* = 13.6, 7.6 Hz, 1H), 4.58 (t, *J* = 8.0 Hz, 1H), 4.64-4.71 (m, 3H), 7.00 (s, 1H), 7.02-7.09 (m, 3H), 7.16-7.26 (m, 6H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.0, 21.5, 32.8, 40.9, 46.2, 50.8, 76.1, 85.3, 109.2, 114.9, 118.8, 119.2, 121.6, 126.9, 127.2, 127.3, 128.1, 129.2, 129.6, 136.1, 137.0, 137.2, 139.0, 143.1, 209.3. IR (CH_2Cl_2) ν 2923, 1953, 1325, 1155, 1092, 812, 739, 656 cm^{-1}. MS (ESI) *m/z* (%): 471.20 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{29}H_{31}N_2O_2S^{+1}$ $[M+H]^+$ requires 471.2101, found: 471.2096. Enantiomeric excess was determined by HPLC with a Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.70 mL/min; t_{minor} = 24.13 min, t_{major} = 21.33 min; ee% = 98%; $[\alpha]_D^{25}$ = -35.3 (c 0.10, CH_2Cl_2)].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7.254
7.242
7.222
7.200
7.179
7.161
7.087
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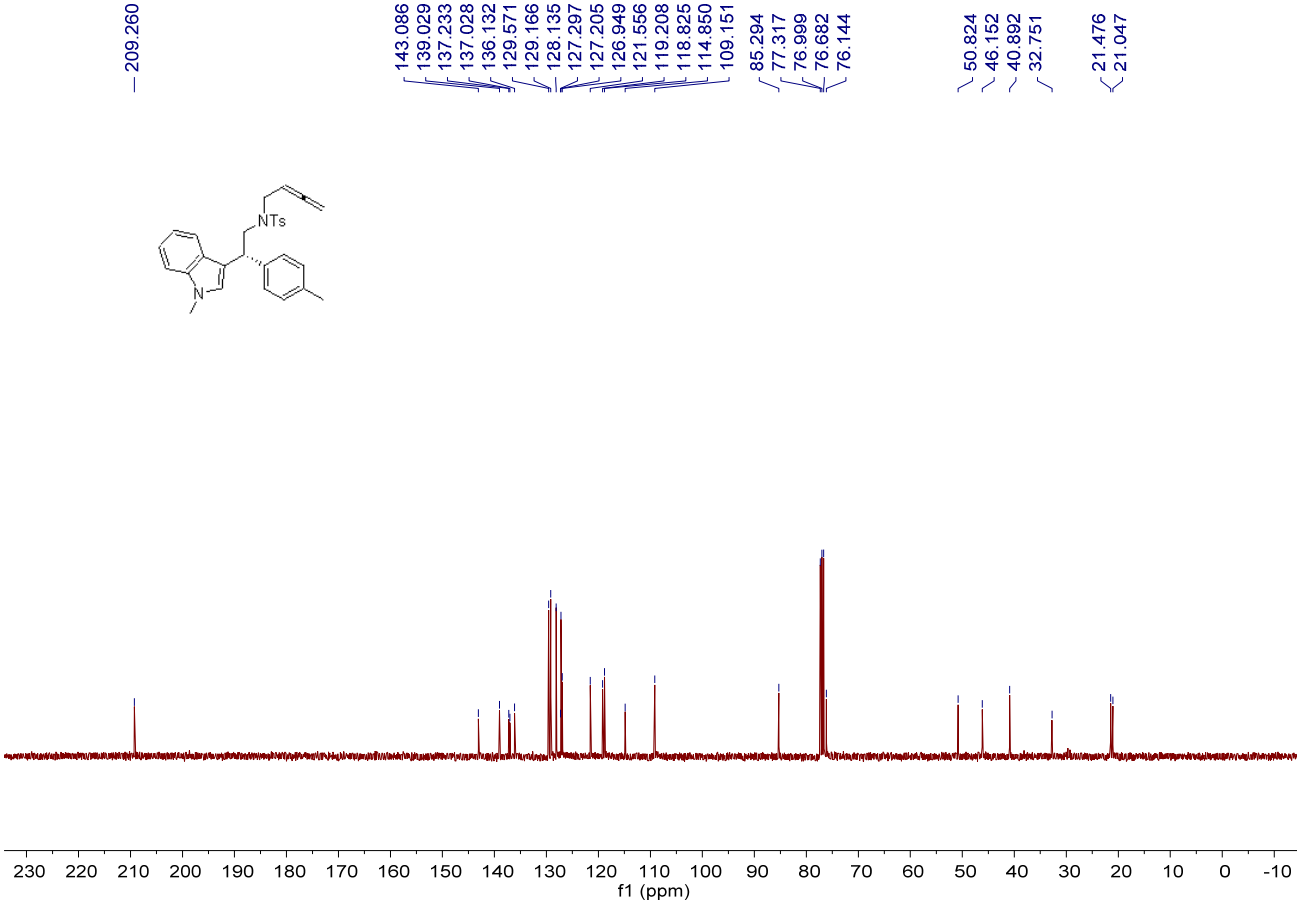
7.045
7.027
7.003
4.706
4.694
4.686
4.679
4.663
4.651
4.644
4.601
4.581
4.561
4.029
4.010
3.995
3.976
3.903
3.895
3.885
3.845
3.831
3.736
3.652
3.631
3.618
3.598
3.560
2.390
2.304
-0.001
NTs
1.93
1.01
6.30
2.83
1.21
3.02
1.00
0.98
1.07
2.91
2.04
3.00
3.00
f1 (ppm)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137.028
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127.297
127.205
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119.208
118.825
114.850
109.151
85.294
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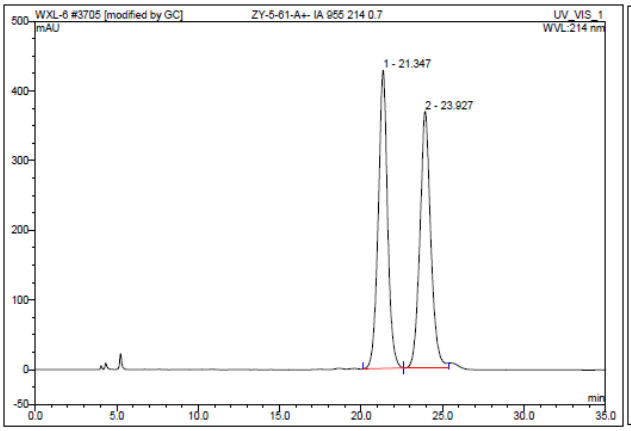
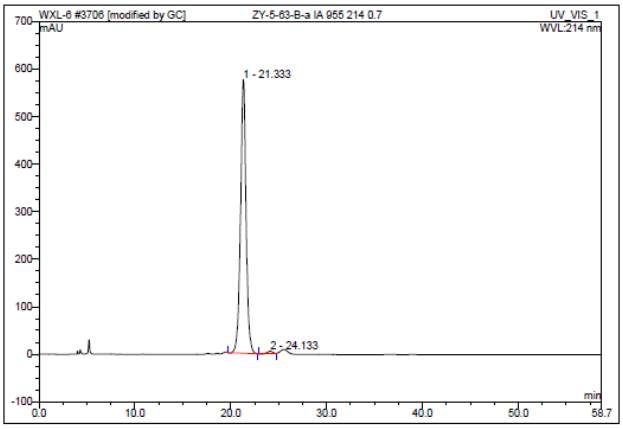
32.751
21.476
21.047
NTs
f1 (ppm)

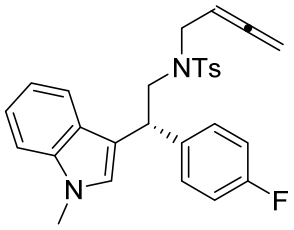




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.35	n.a.	427.956	283.865	49.91	n.a.	BMB*
2	23.93	n.a.	368.687	284.928	50.09	n.a.	BM *
Total:			796.643	568.793	100.00	0.000	

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.33	n.a.	575.212	383.338	98.93	n.a.	BMB*
2	24.13	n.a.	5.969	4.143	1.07	n.a.	BM *
Total:			581.180	387.480	100.00	0.000	

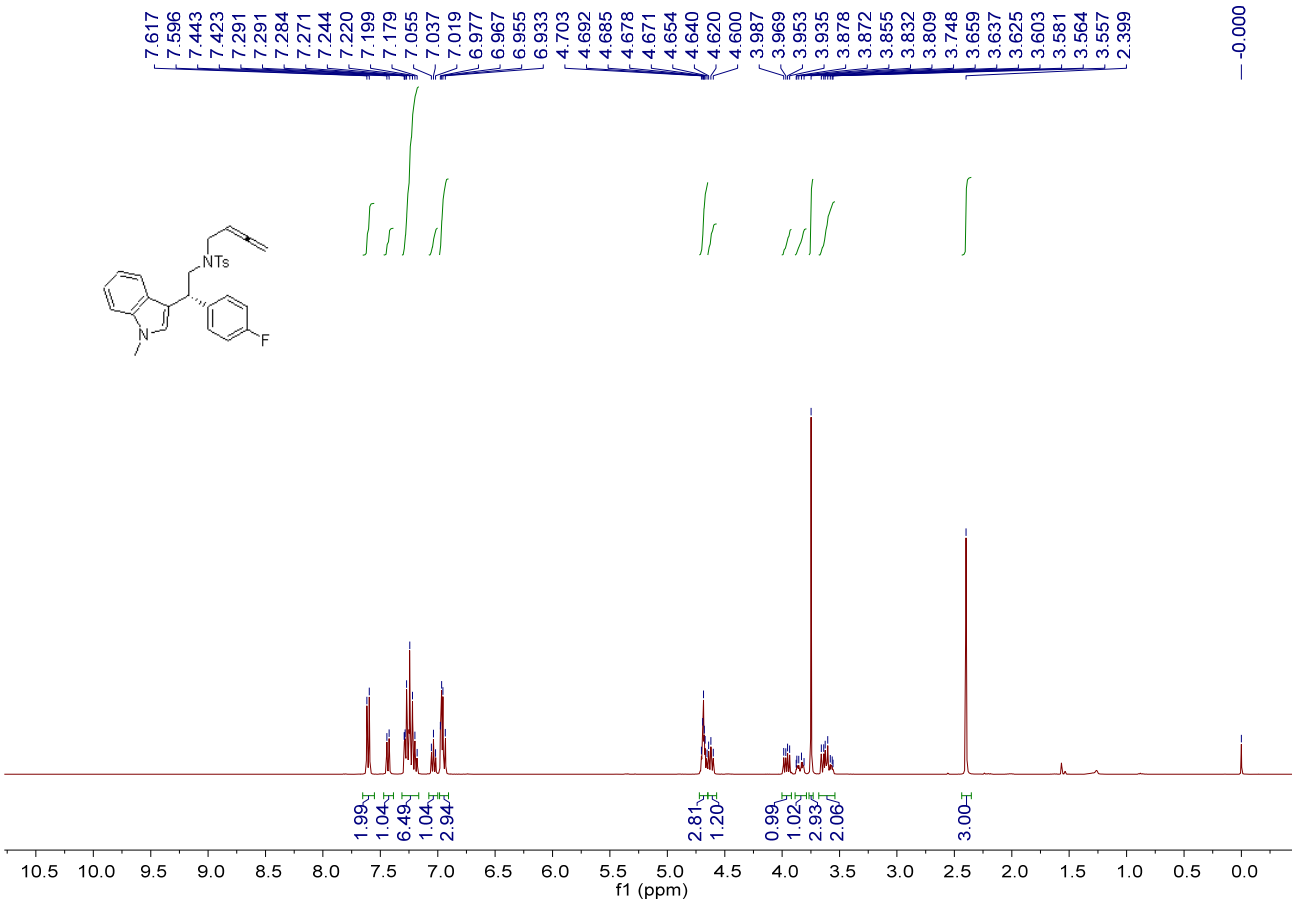
Translation: Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.70 mL/min; t_{minor} = 24.13 min, t_{major} = 21.33 min; ee% = 98%]. (*Note*: *In the 5-minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(*R*)-*N*-(buta-2,3-dien-1-yl)-*N*-(2-(4-fluorophenyl)-2-(1-methyl-1*H*-indol-3-yl)ethyl)-4-methylbenzenesulfonamide 1m

A white solid, 44% yield (20.9 mg). M.p.: 109-112 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 3.55-3.66 (m, 2H), 3.75 (s, 3H), 3.80-3.88 (m, 1H), 3.96 (dd, *J* = 13.6, 7.2 Hz, 1H), 4.62 (t, *J* = 8.0 Hz, 1H), 4.65-4.71 (m, 3H), 6.93-6.98 (m, 3H), 7.01-7.06 (m, 1H), 7.17-7.30 (m, 6H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 32.8, 40.7, 46.4, 50.9, 76.2, 85.3, 109.3, 114.6, 115.2 (d, *J* = 21.2 Hz), 119.0 (d, *J* = 16.9 Hz), 121.8, 126.8, 127.1, 127.2, 129.6, 129.7 (d, *J* = 7.9 Hz), 137.1, 137.7 (d, *J* = 3.0 Hz), 143.2, 161.6 (d, *J* = 243.3 Hz), 209.3. ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -116.3. IR (CH_2Cl_2) ν 2920, 2854, 1951, 1599, 1503, 1336, 1154, 1100, 1090, 969, 837, 747, 658 cm^{-1}. MS (ESI) *m/z* (%): 475.18 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{28}H_{28}N_2O_2FS^{+1}$ $[M+H]^+$ requires 475.1850, found: 475.1846. Enantiomeric excess was determined by HPLC with a Chiralcel IG column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 49.95 min, t_{major} = 44.47 min; ee% = 98%; $[\alpha]_D^{25}$ = -41.5 (c 0.20,

CH_2Cl_2)].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7.291
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7.271
7.244
7.220
7.199
7.179
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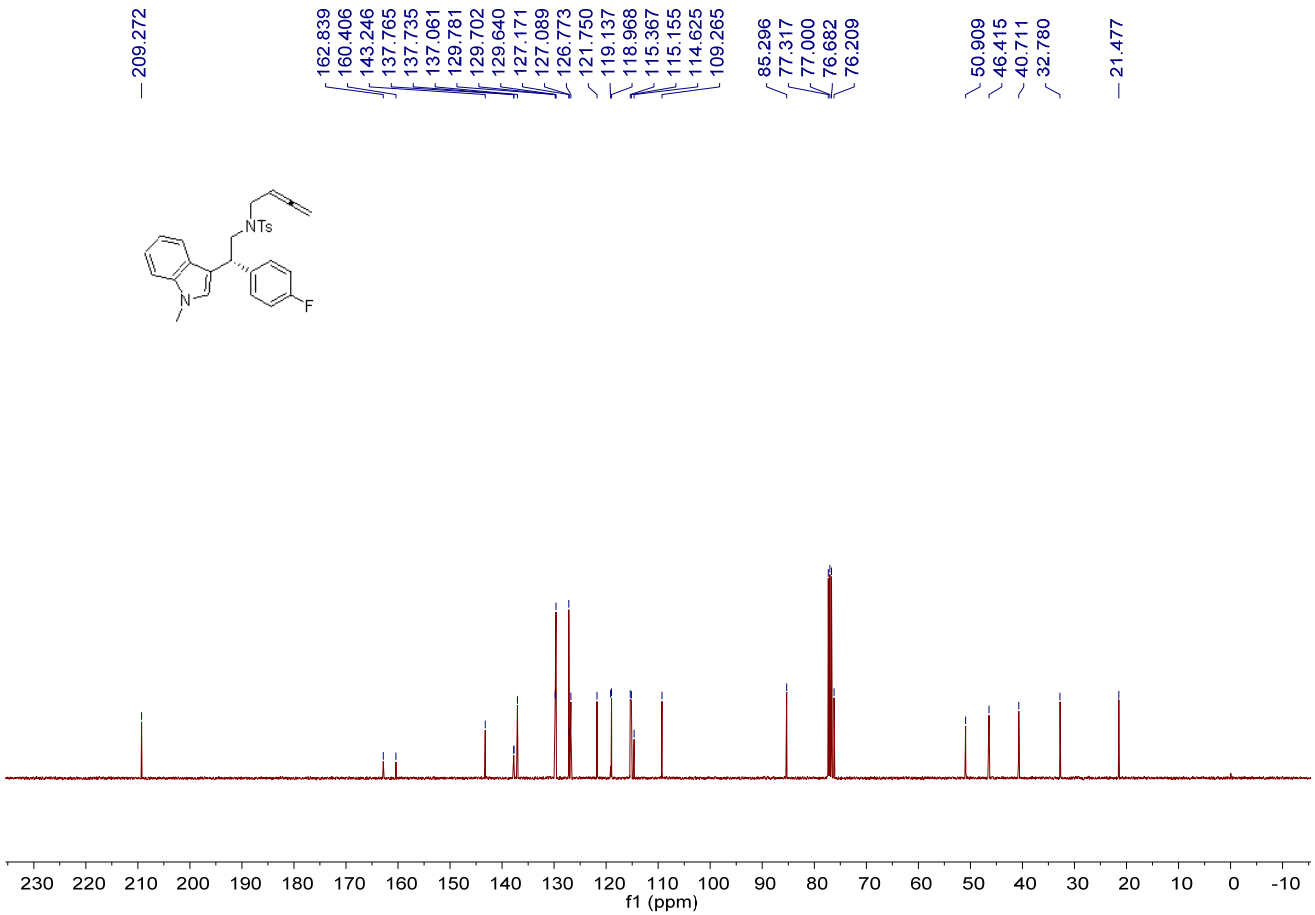
7.037
7.019
6.977
6.967
6.955
6.933
4.703
4.692
4.685
4.678
4.671
4.654
4.640
4.620
4.600
3.987
3.969
3.953
3.935
3.878
3.872
3.855
3.832
3.809
3.748
3.659
3.637
3.625
3.603
3.581
3.564
3.557
2.399
-0.000
NTs
N
F
1.99
1.04
6.49
1.04
2.94
2.81
1.20
0.99
1.02
2.93
2.06
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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160.406
143.246
137.765
137.735
137.061
129.781
129.702
129.640
127.171
127.089
126.773
121.750
119.137
118.968
115.367
115.155
114.625
109.265
85.296
77.317
77.000
76.682
76.209
50.909
46.415
40.711
32.780
21.477
NTs
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F
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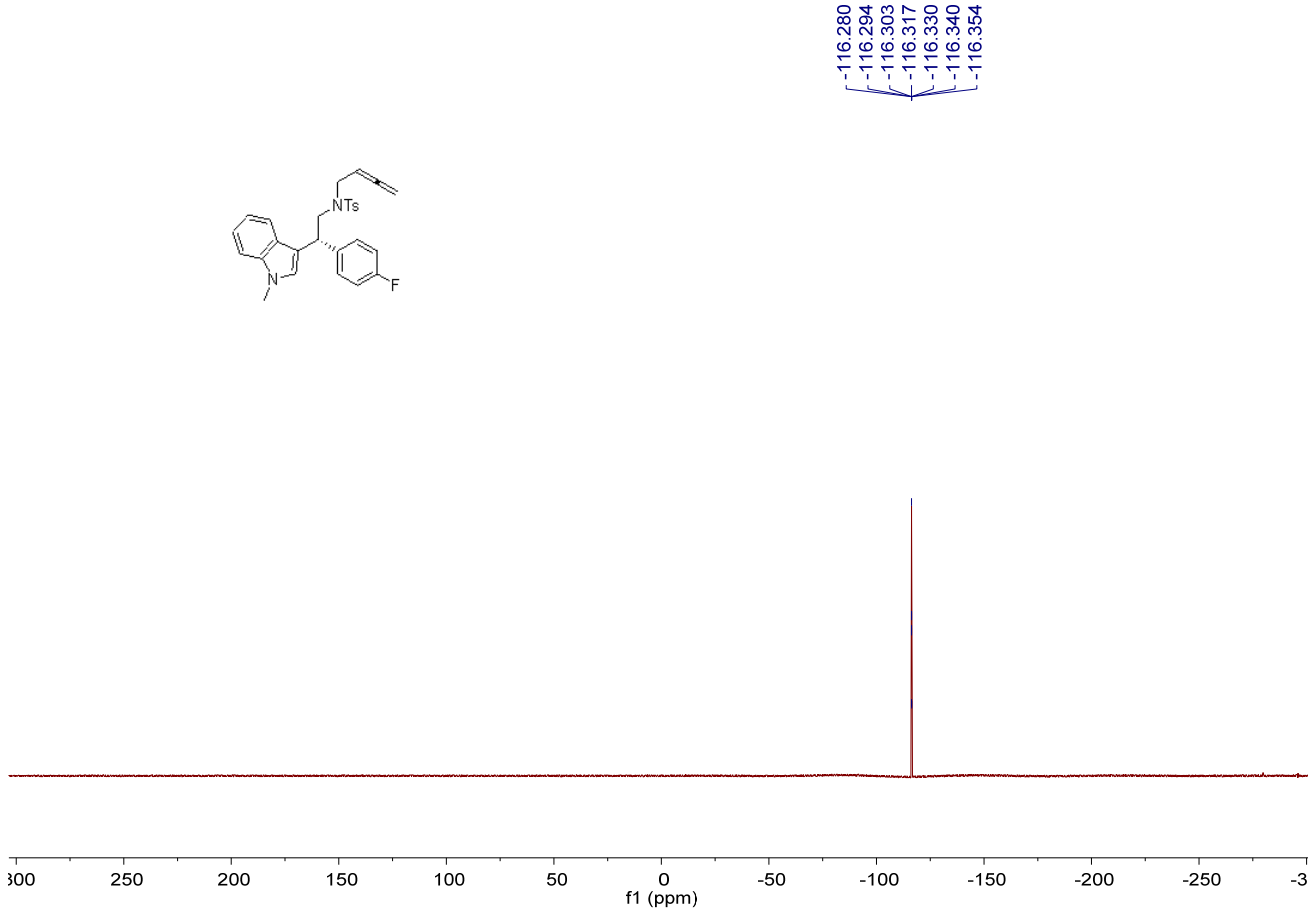
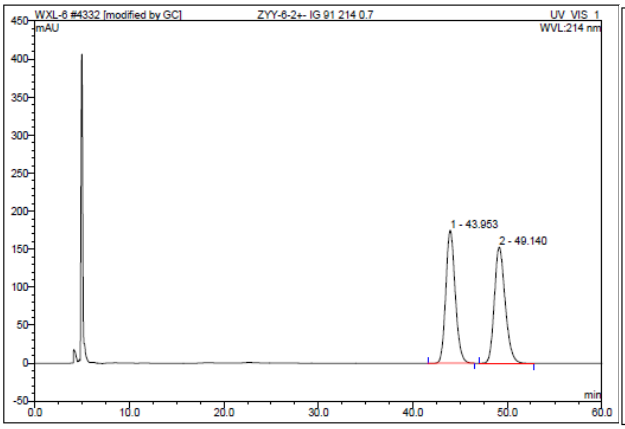
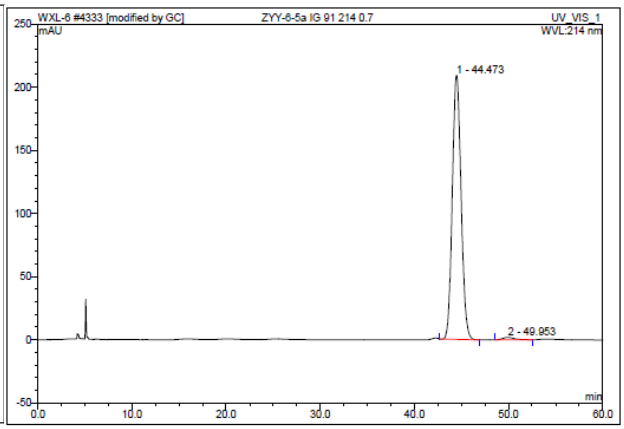
f1 (ppm)


-116.280
-116.294
-116.303
-116.317
-116.330
-116.340
-116.354
NTs
N
F
300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -3
f1 (ppm)

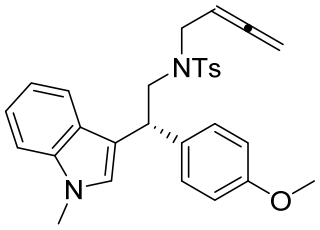




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	43.95	n.a.	174.961	202.087	49.99	n.a.	BMB*
2	49.14	n.a.	152.894	202.206	50.01	n.a.	BMB*
Total:			327.855	404.293	100.00	0.000	

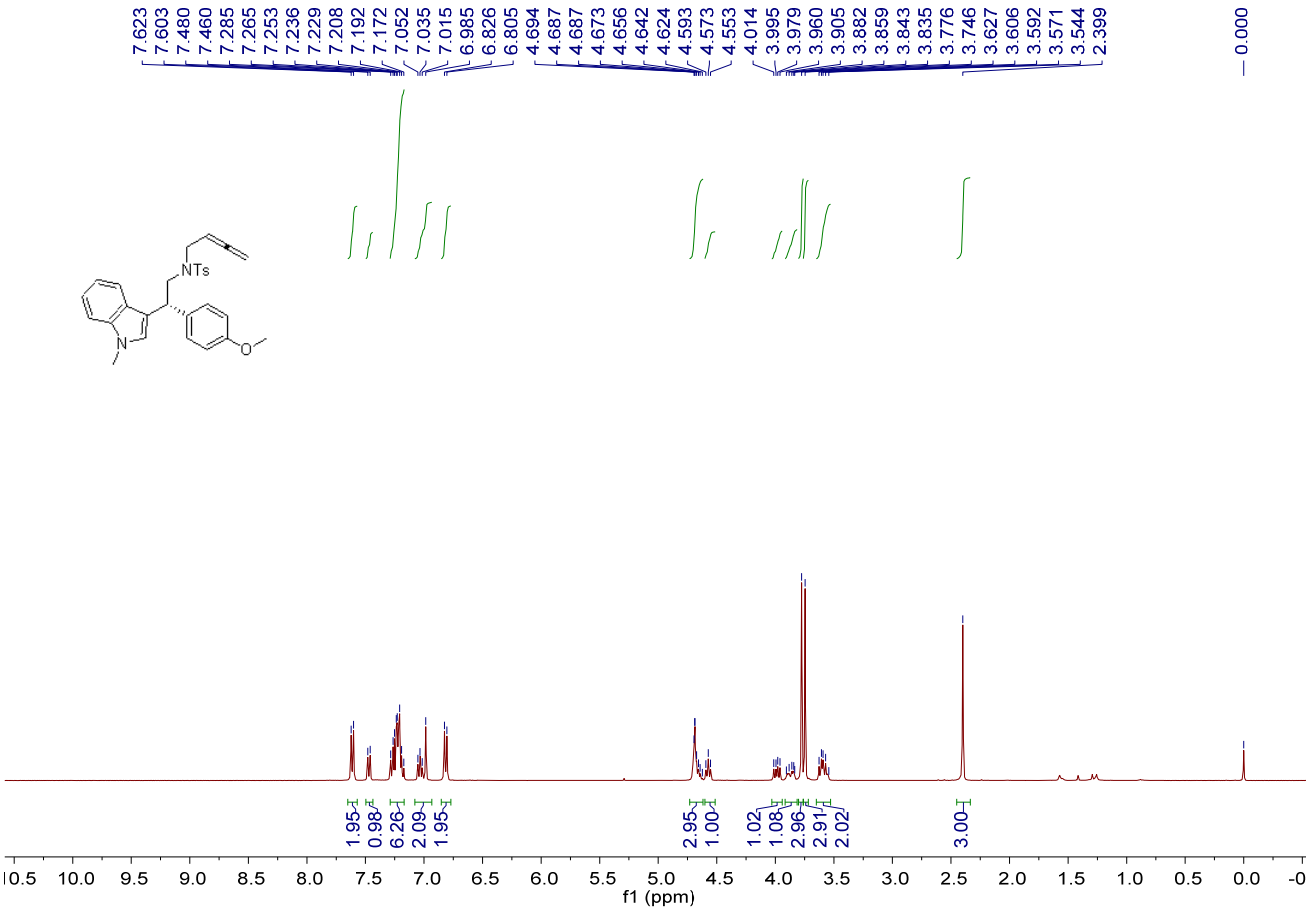
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	44.47	n.a.	209.112	225.810	98.76	n.a.	BMB*
2	49.95	n.a.	1.961	2.842	1.24	n.a.	BMB*
Total:			211.073	228.652	100.00	0.000	

Translation: Chiralcel IG column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 49.95 min, t_{major} = 44.47 min; ee% = 98%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(*R*)-*N*-(buta-2,3-dien-1-yl)-*N*-(2-(4-methoxyphenyl)-2-(1-methyl-1*H*-indol-3-yl)ethyl)-4-methylbenzenesulfonamide 1n

A white solid, 46% yield (22.3 mg). M.p.: 61-64 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 3.54-3.63 (m, 2H), 3.75 (s, 3H), 3.78 (s, 3H), 3.83-3.91 (m, 1H), 3.98 (dd, *J* = 14.0, 7.6 Hz, 1H), 4.57 (t, *J* = 8.0 Hz, 1H), 4.62-4.70 (m, 3H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.98-7.06 (m, 2H), 7.17-7.29 (m, 6H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 32.7, 40.5, 46.2, 50.9, 55.1, 76.1, 85.3, 109.1, 113.8, 115.0, 118.8, 119.2, 121.5, 126.8, 127.1, 127.2, 129.2, 129.6, 134.1, 137.0, 137.1, 143.1, 158.2, 209.2. IR (CH_2Cl_2) ν 2931, 1953, 1610, 1510, 1325, 1248, 1154, 1092, 814, 739, 656 cm^{-1}. MS (ESI) *m/z* (%): 487.20 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{29}H_{31}N_2O_3S^{+1}$ $[M+H]^+$ requires 487.2050, found: 487.2046. Enantiomeric excess was determined by HPLC with a Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 25.87 min, t_{major} = 22.80 min; ee% = 97%; $[\alpha]_D^{25}$ = -71.6 (c 0.70, CH_2Cl_2)].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7.208
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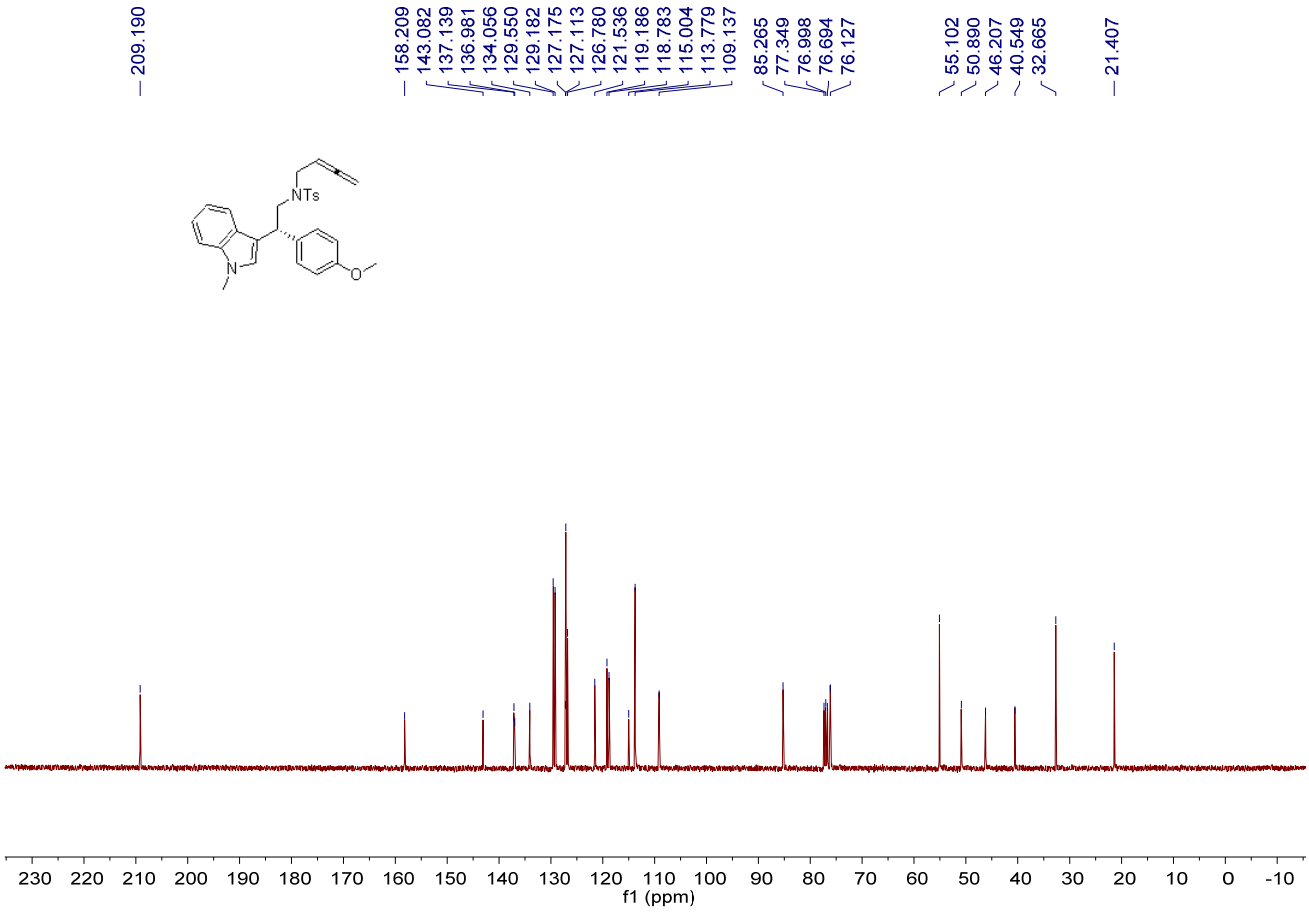
7.035
7.015
6.985
6.826
6.805
4.694
4.687
4.687
4.673
4.656
4.642
4.624
4.593
4.573
4.553
4.014
3.995
3.979
3.960
3.905
3.882
3.859
3.843
3.835
3.776
3.746
3.627
3.606
3.592
3.571
3.544
2.399
0.000
NTs
N
O
1.95
0.98
6.26
2.09
1.95
2.95
1.00
1.02
1.08
2.96
2.91
2.02
3.00
f1 (ppm)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158.209
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134.056
129.550
129.182
127.175
127.113
126.780
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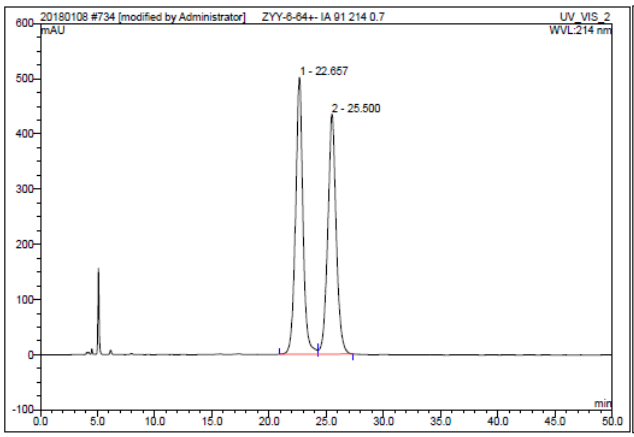
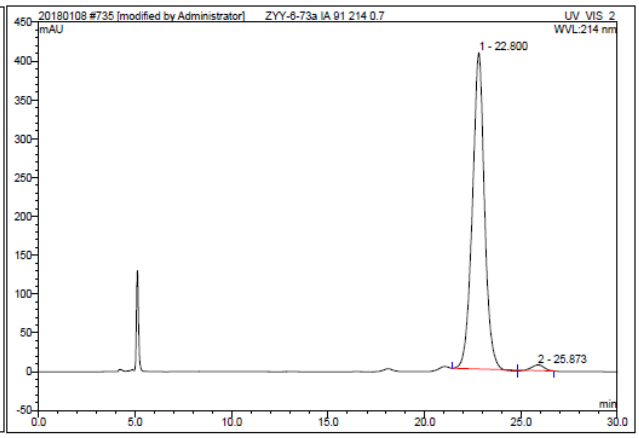
115.004
113.779
109.137
85.265
77.349
76.998
76.694
76.127
55.102
50.890
46.207
40.549
32.665
21.407
NTs
N
O
f1 (ppm)

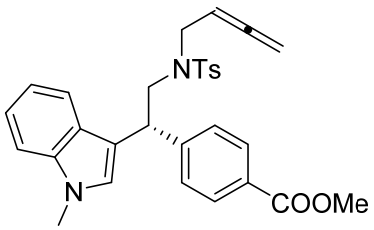




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.66	n.a.	501.120	376.071	50.30	n.a.	BM
2	25.50	n.a.	434.794	371.541	49.70	n.a.	MB
Total:			935.914	747.611	100.00	0.000	

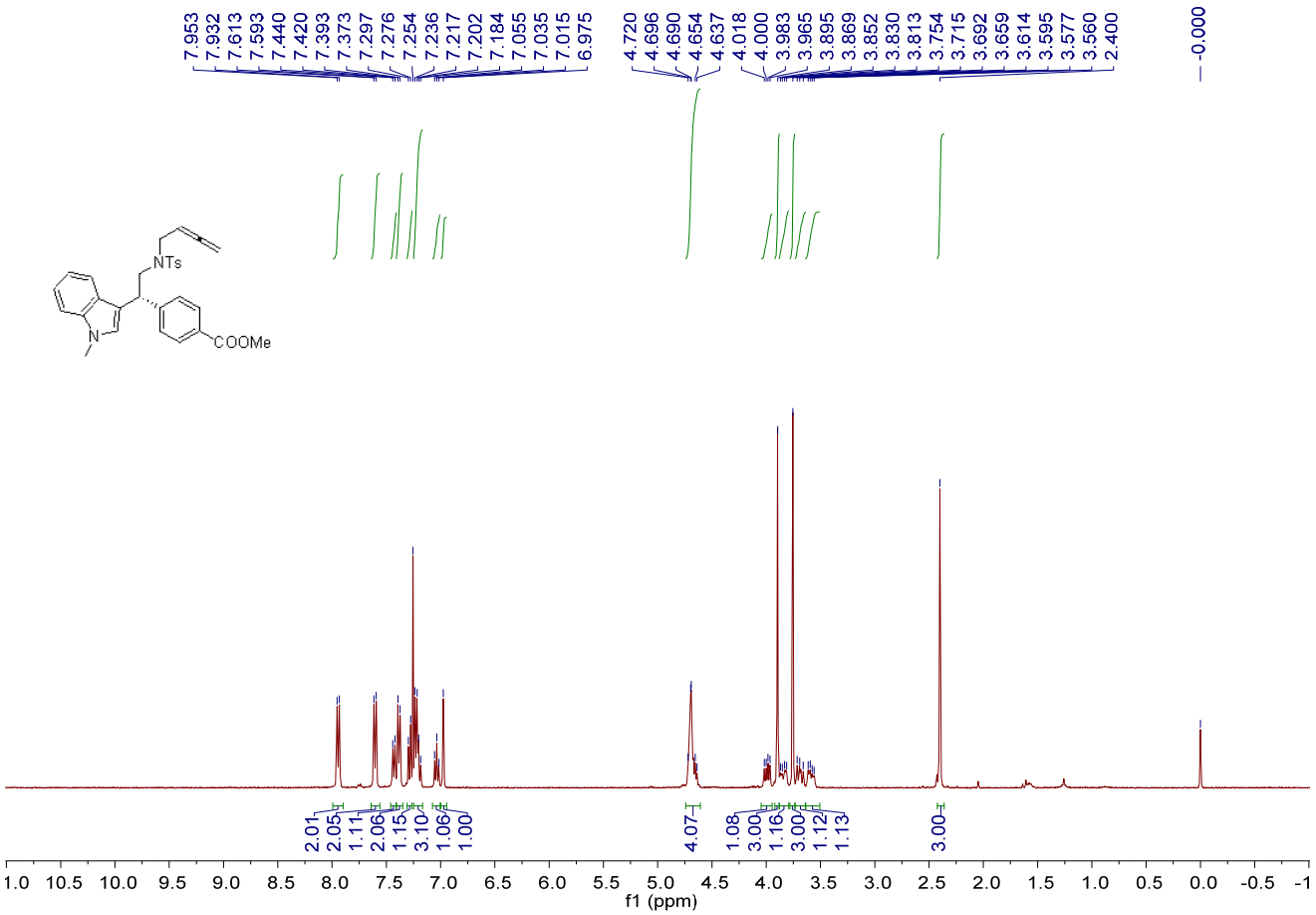
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.80	n.a.	407.350	296.459	98.27	n.a.	BM *
2	25.87	n.a.	7.537	5.212	1.73	n.a.	MB*
Total:			414.887	301.672	100.00	0.000	

Translation: Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 25.87 min, t_{major} = 22.80 min; ee% = 97%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(*R*)-methyl 4-(2-(*N*-(buta-2,3-dien-1-yl)-4-methylphenylsulfonamido)-1-(1-methyl-1*H*-indol-3-yl) ethyl)benzoate 1o

A white solid, 44% yield (22.8 mg). M.p.: 152-155 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 3.56-3.62 (m, 1H), 3.65-3.72 (m, 1H), 3.75 (s, 3H), 3.84 (dd, *J* = 15.6, 6.8 Hz, 1H), 3.90 (s, 3H), 3.99 (dd, *J* = 14.0, 7.2 Hz, 1H), 4.63-4.72 (m, 4H), 6.98 (s, 1H), 7.01-7.06 (m, 1H), 7.18-7.24 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 32.8, 41.6, 46.5, 50.6, 52.0, 76.3, 85.3, 109.3, 114.0, 119.0, 119.1, 121.8, 126.8, 127.0, 127.2, 128.4, 128.6, 129.7, 129.8, 136.97, 137.02, 143.3, 147.5, 166.9, 209.3. IR (CH_2Cl_2) ν 2948, 1954, 1716, 1610, 1435, 1328, 1278, 1158, 1018, 936, 852, 741, 658 cm^{-1}. MS (ESI) *m/z* (%): 515.19 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{30}H_{31}N_2O_4S^{+1}$ $[M+H]^+$ requires 515.1999, found: 515.1993. (*Note: compound **3o** was reduced to the corresponding alcohol **3o'** to determine enantiomeric excess*.)


7.953
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7.593
7.440
7.420
7.393
7.373
7.297
7.276
7.254
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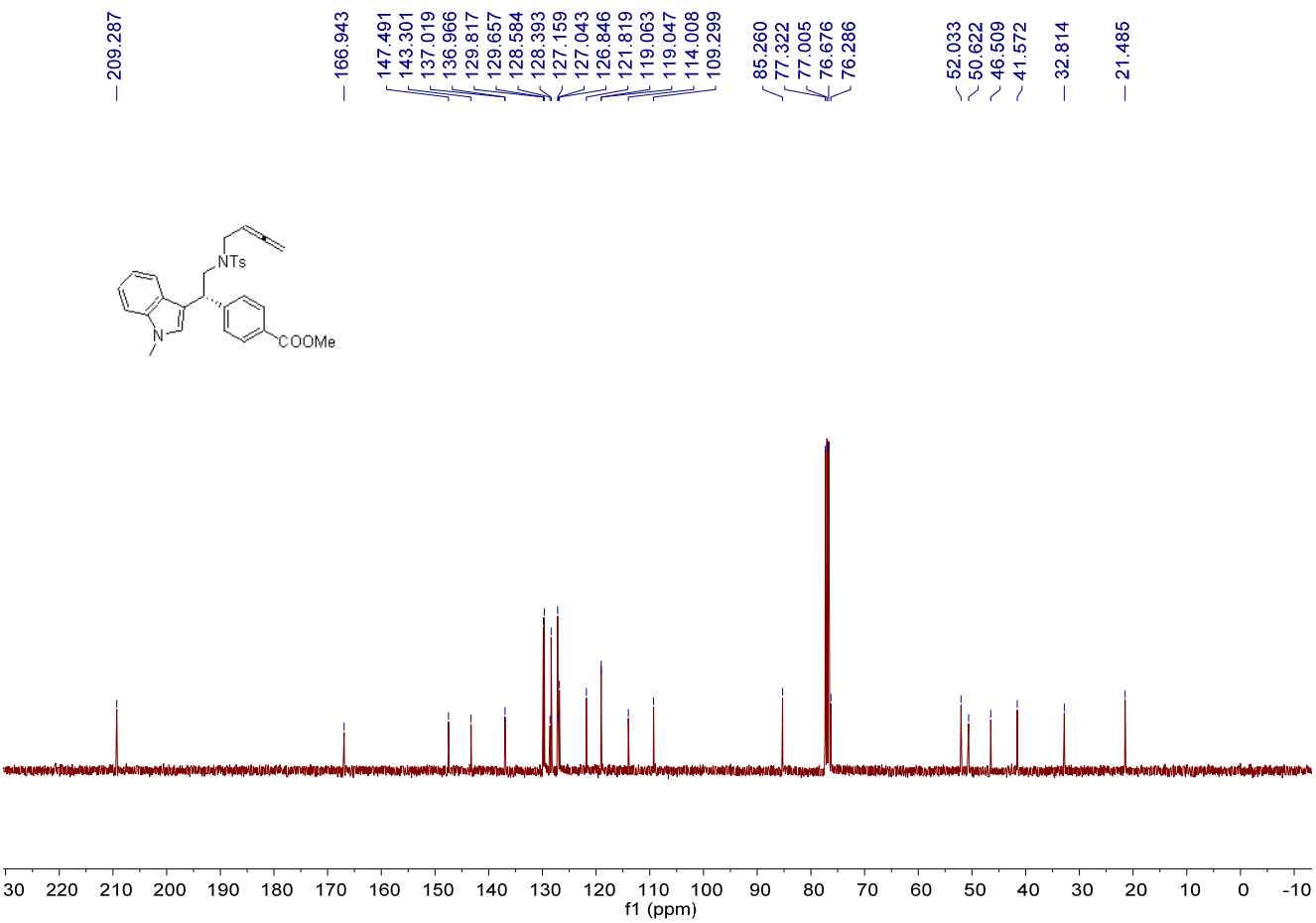
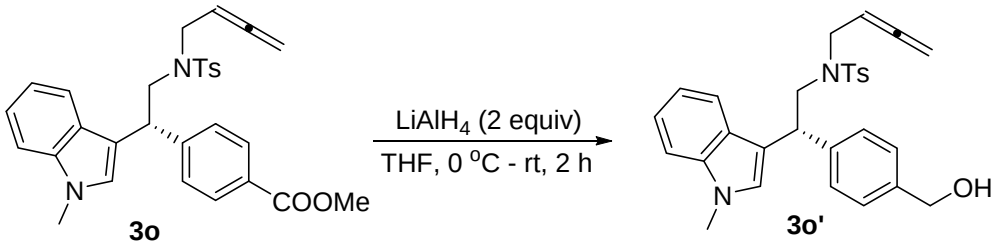
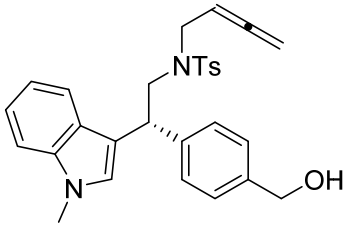
7.217
7.202
7.184
7.055
7.035
7.015
6.975
4.720
4.696
4.690
4.654
4.637
4.018
4.000
3.983
3.965
3.895
3.869
3.852
3.830
3.813
3.754
3.715
3.692
3.659
3.614
3.595
3.577
3.560
2.400
-0.000
NTs
COOMe
2.01
2.05
1.11
2.06
1.15
3.10
1.06
1.00
4.07
1.08
3.00
1.16
3.00
1.12
1.13
3.00
f1 (ppm)


209.287
166.943
147.491
143.301
137.019
136.966
129.817
129.657
128.584
128.393
127.159
127.043
126.846
121.819
119.063
119.047
114.008
109.299
85.260
77.322
77.005
76.676
76.286
52.033
50.622
46.509
41.572
32.814
21.485
NTs
COOMe
f1 (ppm)

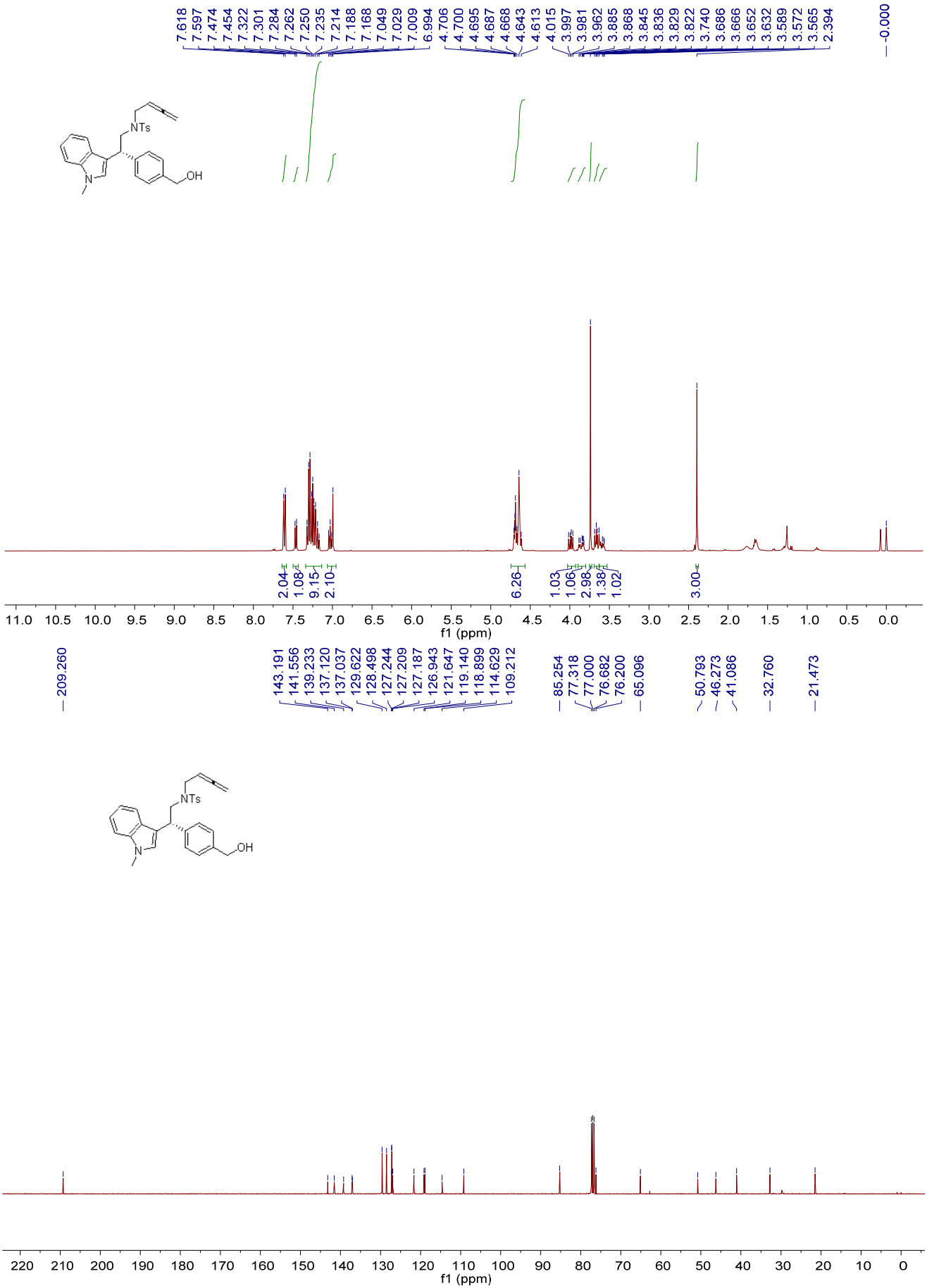


To an oven-dried reaction tube was added $LiAlH_4$ (3.3 mg, 0.088 mmol) and anhydrous THF (0.8 mL). The tube was cooled to 0 °C, and **3o** (22.8 mg, 0.044 mmol) was added into tube at 0 °C. The resulting mixture was stirred at room temperature for 2 h. The solution was filtered through a short column of silica gel eluting with ethyl acetate, and then the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 4/1) to give the corresponding product **3o'**.



(*R*)-*N*-(buta-2,3-dien-1-yl)-*N*-(2-(4-(hydroxymethyl)phenyl)-2-(1-methyl-1*H*-indol-3-yl)ethyl)-4-methylbenzenesulfonamide 1o'

A white liquid, 86% yield (18.4 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.39 (s, 3H), 3.56-3.63 (m, 1H), 3.63-3.69 (m, 1H), 3.74 (s, 3H), 3.82-3.89 (m, 1H), 3.99 (dd, *J* = 14.0, 7.2 Hz, 1H), 4.61-4.71 (m, 6H), 6.99-7.05 (m, 2H), 7.16-7.33 (m, 9H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 32.8, 41.1, 46.3, 50.8, 65.1, 76.2, 85.3, 109.2, 114.6, 118.9, 119.1, 121.6, 126.9, 127.2, 127.21, 127.24, 128.5, 129.6, 137.0, 137.1, 139.2, 141.6, 143.2, 209.3. MS (ESI) *m/z* (%): 504.23 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{29}H_{34}N_3O_3S^{+1}$ $[M+NH_4]^+$ requires 504.2315, found: 504.2308. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 23.41 min, t_{major} = 26.74 min; ee% = 96%; $[\alpha]_D^{25}$ = -81.5 (c 0.10, CH_2Cl_2)].


7.618
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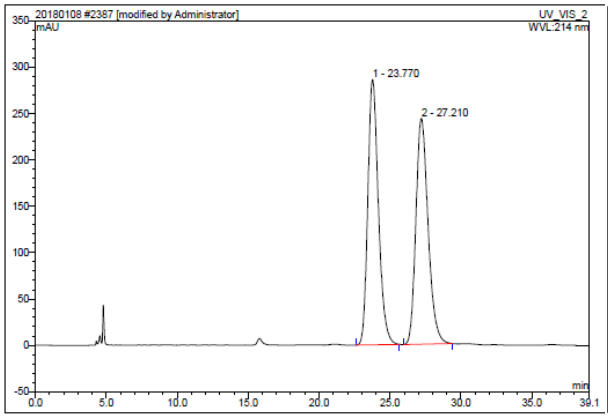
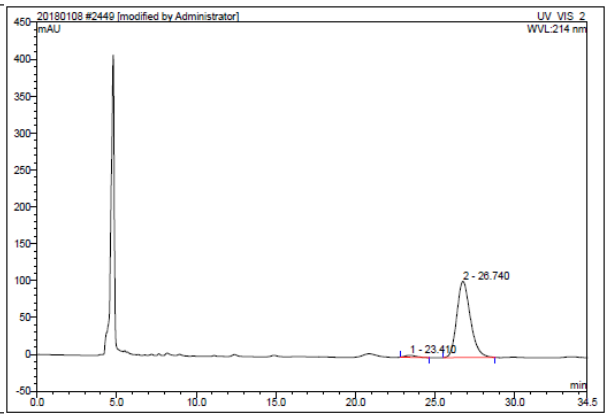
7.474
7.454
7.322
7.301
7.284
7.262
7.250
7.235
7.214
7.188
7.168
7.049
7.029
7.009
6.994
4.706
4.700
4.695
4.687
4.668
4.643
4.613
4.015
3.997
3.981
3.962
3.885
3.868
3.845
3.836
3.829
3.822
3.740
3.686
3.666
3.652
3.632
3.589
3.572
3.565
2.394
-0.000
NTs
OH
2.04
1.08
9.15
2.10
6.26
1.03
1.06
2.98
1.38
1.02
3.00
f1 (ppm)
209.260
143.191
141.556
139.233
137.120
137.037
129.622
128.498
127.244
127.209
127.187
126.943
121.647
119.140
118.899
114.629
109.212
85.254
77.318
77.000
76.682
76.200
65.096
50.793
46.273
41.086
32.760
21.473
NTs
OH
f1 (ppm)

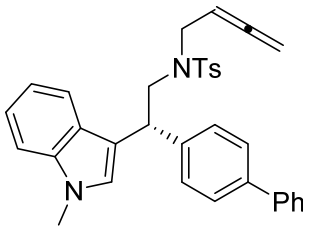


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	23.77	n.a.	285.919	246.986	50.44	n.a.	BMB
2	27.21	n.a.	243.307	242.714	49.56	n.a.	BMB
Total:			529.226	489.700	100.00	0.000	



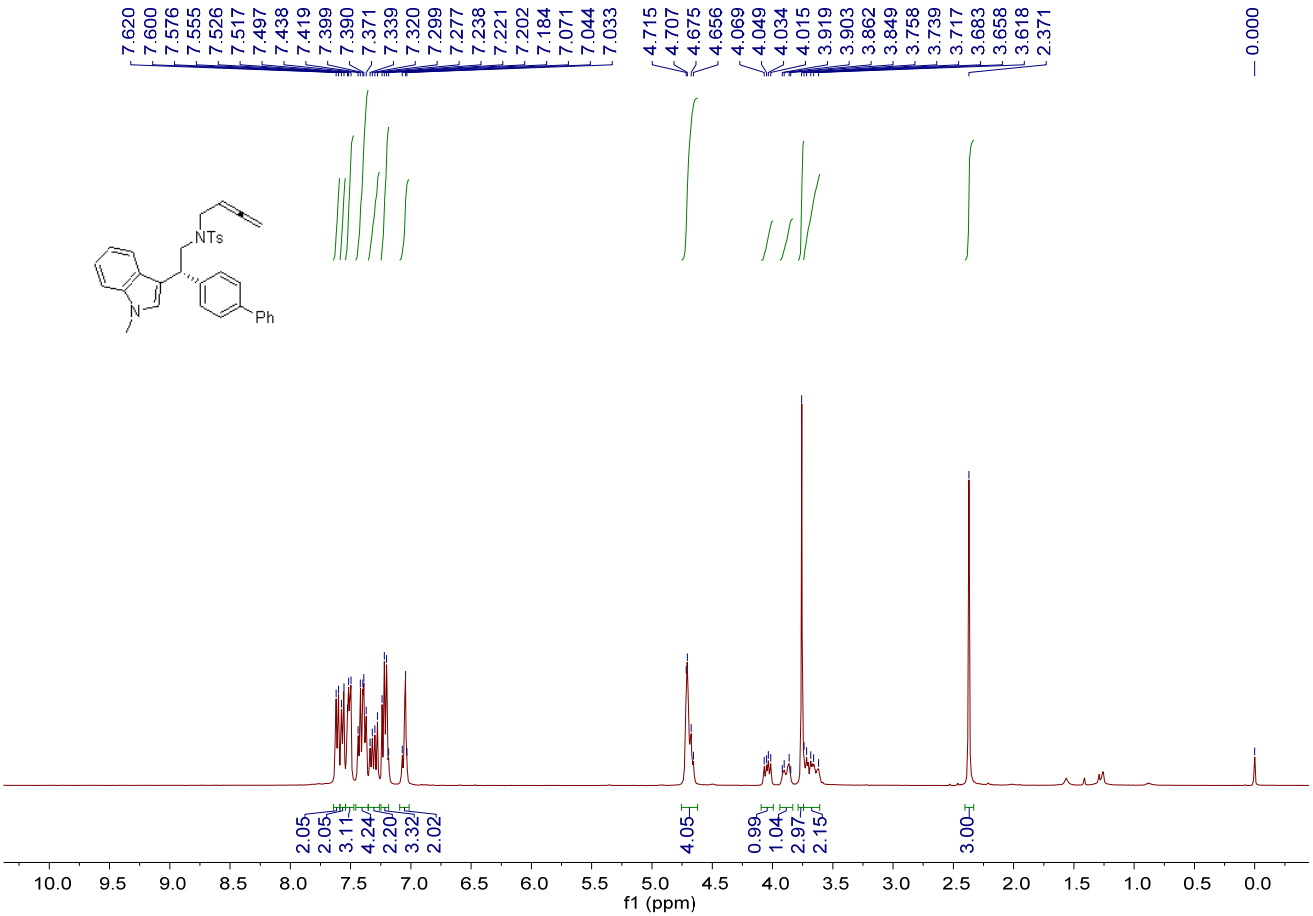
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	23.41	n.a.	2.649	2.045	1.97	n.a.	BMB*
2	26.74	n.a.	103.296	101.903	98.03	n.a.	BMB
Total:			105.945	103.948	100.00	0.000	

Translation: Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 23.41 min, t_{major} = 26.74 min; ee% = 96%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(*R*)-*N*-(2-([1,1'-biphenyl]-4-yl)-2-(1-methyl-1*H*-indol-3-yl)ethyl)-*N*-(buta-2,3-dien-1-yl)-4-methyl benzenesulfonamide 1p

A white solid, 44% yield (25.4 mg). M.p.: 43-46 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.37 (s, 3H), 3.61-3.74 (m, 2H), 3.76 (s, 3H), 3.84-3.92 (m, 1H), 4.04 (dd, *J* = 13.6, 7.6 Hz, 1H), 4.65-4.72 (m, 4H), 7.03-7.08 (m, 2H), 7.18-7.24 (m, 3H), 7.27-7.34 (m, 2H), 7.37-7.44 (m, 4H), 7.49-7.53 (m, 3H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 32.8, 41.0, 46.3, 50.7, 76.2, 85.3, 109.2, 114.6, 118.9, 119.2, 121.7, 126.9, 127.0, 127.10, 127.17, 127.19, 127.2, 128.7, 129.6, 137.0, 137.1, 139.4, 140.8, 141.2, 143.2, 209.3. IR (CH_2Cl_2) ν 3027, 2923, 1954, 1598, 1485, 1326, 1154, 1092, 936, 814, 738, 656 cm^{-1}. MS (ESI) *m/z* (%): 533.22 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{34}H_{33}N_2O_2S^{+1}$ $[M+H]^+$ requires 533.2257, found: 533.2252. Enantiomeric excess was determined by HPLC with a Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 16.43 min, t_{major} = 12.29 min; ee% = 89%; $[\alpha]_D^{25}$ = -12.7 (c 0.10, CH_2Cl_2)].


7.620
7.600
7.576
7.555
7.526
7.517
7.497
7.438
7.419
7.399
7.390
7.371
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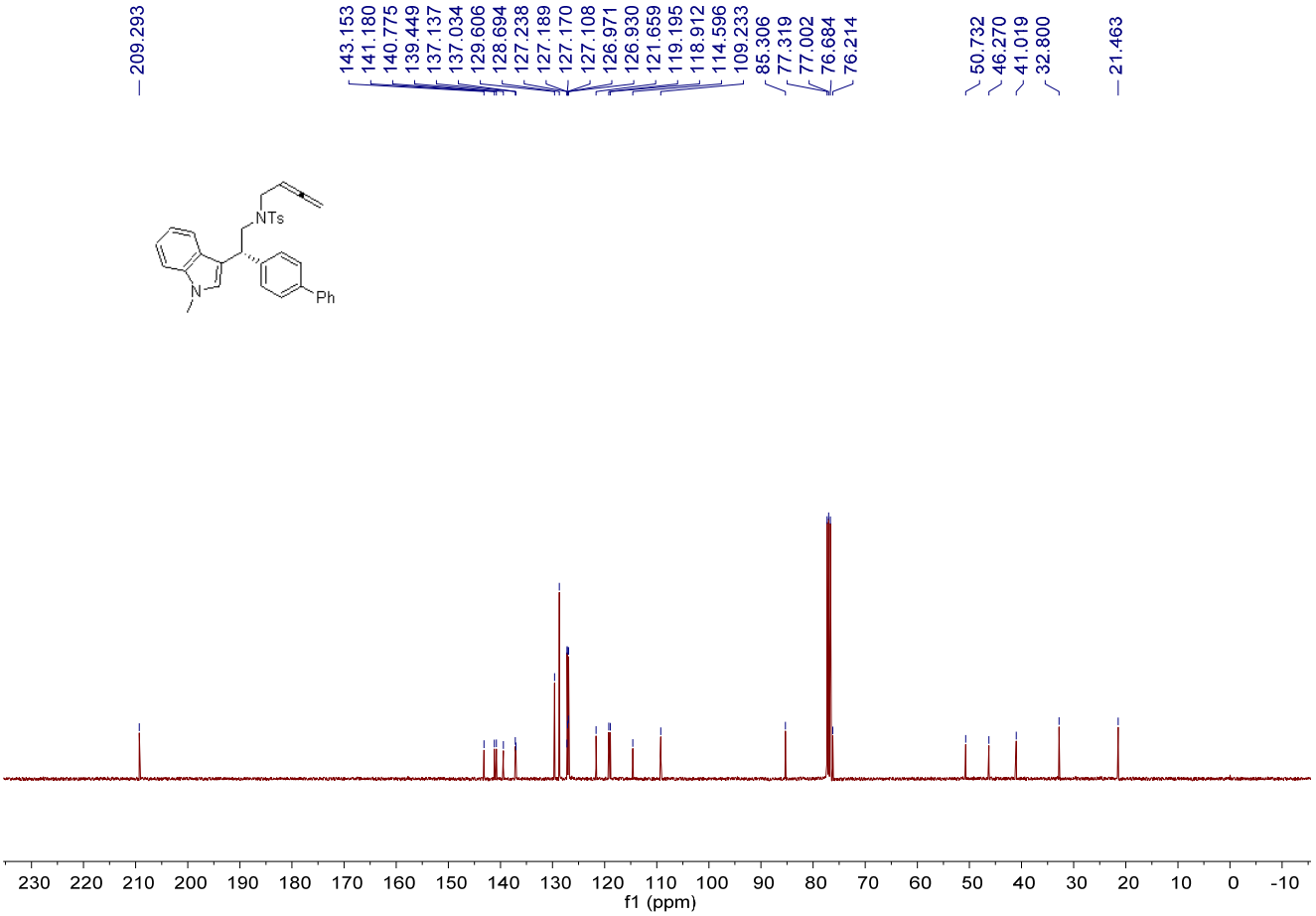
7.320
7.299
7.277
7.238
7.221
7.202
7.184
7.071
7.044
7.033
4.715
4.707
4.675
4.656
4.069
4.049
4.034
4.015
3.919
3.903
3.862
3.849
3.758
3.739
3.717
3.683
3.658
3.618
2.371
0.000
NTs
Ph
2.05
2.05
3.11
4.24
2.20
3.32
2.02
4.05
0.99
1.04
2.97
2.15
3.00
f1 (ppm)


209.293
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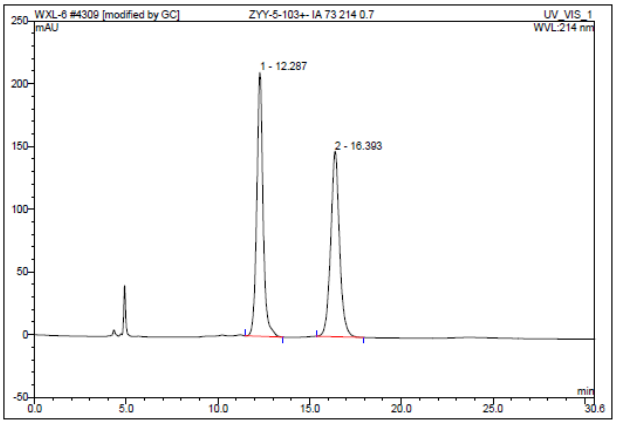
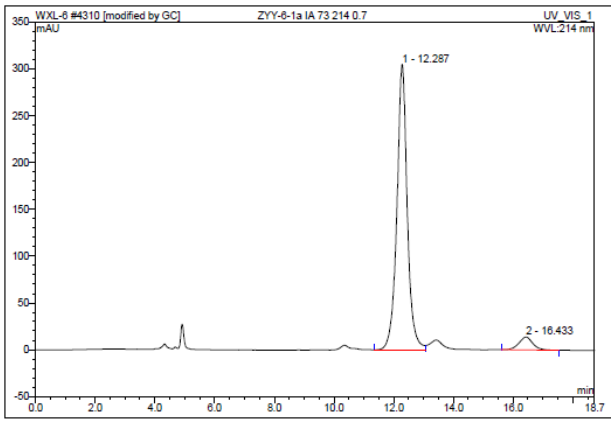
141.180
140.775
139.449
137.137
137.034
129.606
128.694
127.238
127.189
127.170
127.108
126.971
126.930
121.659
119.195
118.912
114.596
109.233
85.306
77.319
77.002
76.684
76.214
50.732
46.270
41.019
32.800
21.463
NTs
Ph
f1 (ppm)

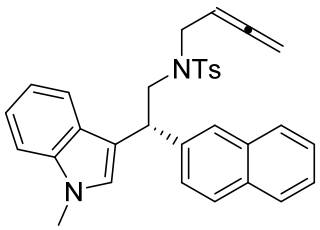


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.29	n.a.	210.240	83.760	50.40	n.a.	BMB*
2	16.39	n.a.	147.656	82.441	49.60	n.a.	BMB*
Total:			357.896	166.201	100.00	0.000	



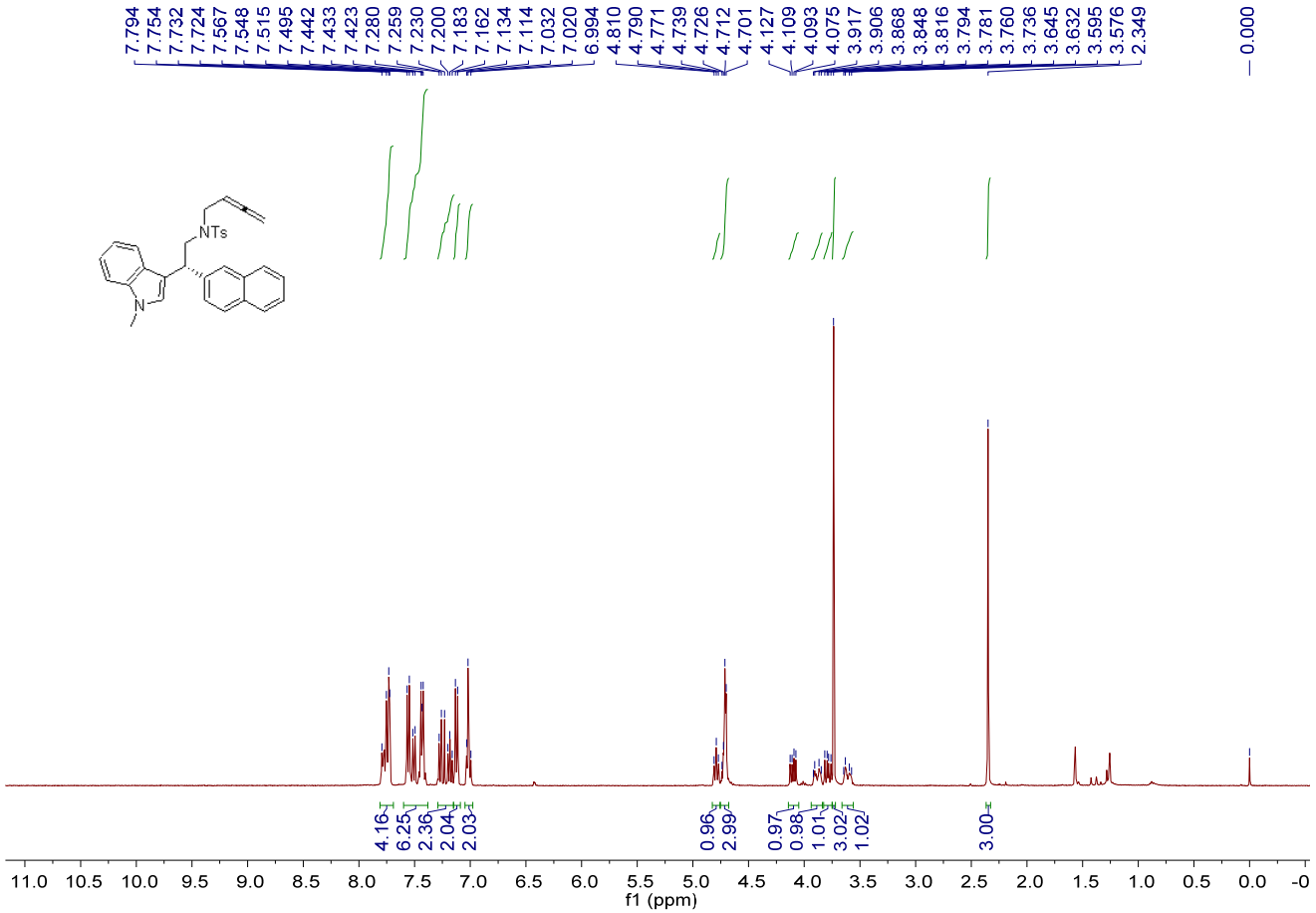
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.29	n.a.	304.735	122.728	94.29	n.a.	BM *
2	16.43	n.a.	13.768	7.430	5.71	n.a.	BMB*
Total:			318.502	130.159	100.00	0.000	

Translation: Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 16.43 min, t_{major} = 12.29 min; ee% = 89%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(*R*)-*N*-(buta-2,3-dien-1-yl)-4-methyl-*N*-(2-(1-methyl-1*H*-indol-3-yl)-2-(naphthalen-2-yl)ethyl)benzenesulfonamide 1q

A white solid, 50% yield (25.3 mg). M.p.: 80-83 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.35 (s, 3H), 3.57-3.65 (m, 1H), 3.74 (s, 3H), 3.78 (dd, *J* = 13.6, 8.4 Hz, 1H), 3.84-3.92 (m, 1H), 4.10 (dd, *J* = 13.6, 7.2 Hz, 1H), 4.70-4.74 (m, 3H), 4.79 (t, *J* = 8.0 Hz, 1H), 6.99-7.04 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.16-7.28 (m, 2H), 7.42-7.57 (m, 6H), 7.72-7.80 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 32.8, 41.5, 46.3, 50.7, 76.2, 85.4, 109.2, 114.7, 118.9, 119.2, 121.7, 125.5, 125.9, 126.6, 126.9, 127.0, 127.1, 127.3, 127.5, 127.7, 128.2, 129.5, 132.4, 133.4, 137.0, 137.2, 139.5, 143.1, 209.3. IR (CH_2Cl_2) ν 3051, 2923, 1952, 1598, 1328, 1155, 1092, 934, 813, 739, 657 cm^{-1}. MS (ESI) *m/z* (%): 507.20 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{32}H_{31}N_2O_2S^{+1}$ $[M+H]^+$ requires 507.2101, found: 507.2095. Enantiomeric excess was determined by HPLC with a Chiralcel IG column [λ = 214 nm; eluent: Hexane/Isopropanol = 50/50; Flow rate: 0.70 mL/min; t_{minor} = 21.60 min, t_{major} = 18.32 min; ee% = 80%; $[\alpha]_D^{25}$ = -86.3 (c 0.08, CH_2Cl_2)].


7.794
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7.724
7.567
7.548
7.515
7.495
7.442
7.433
7.423
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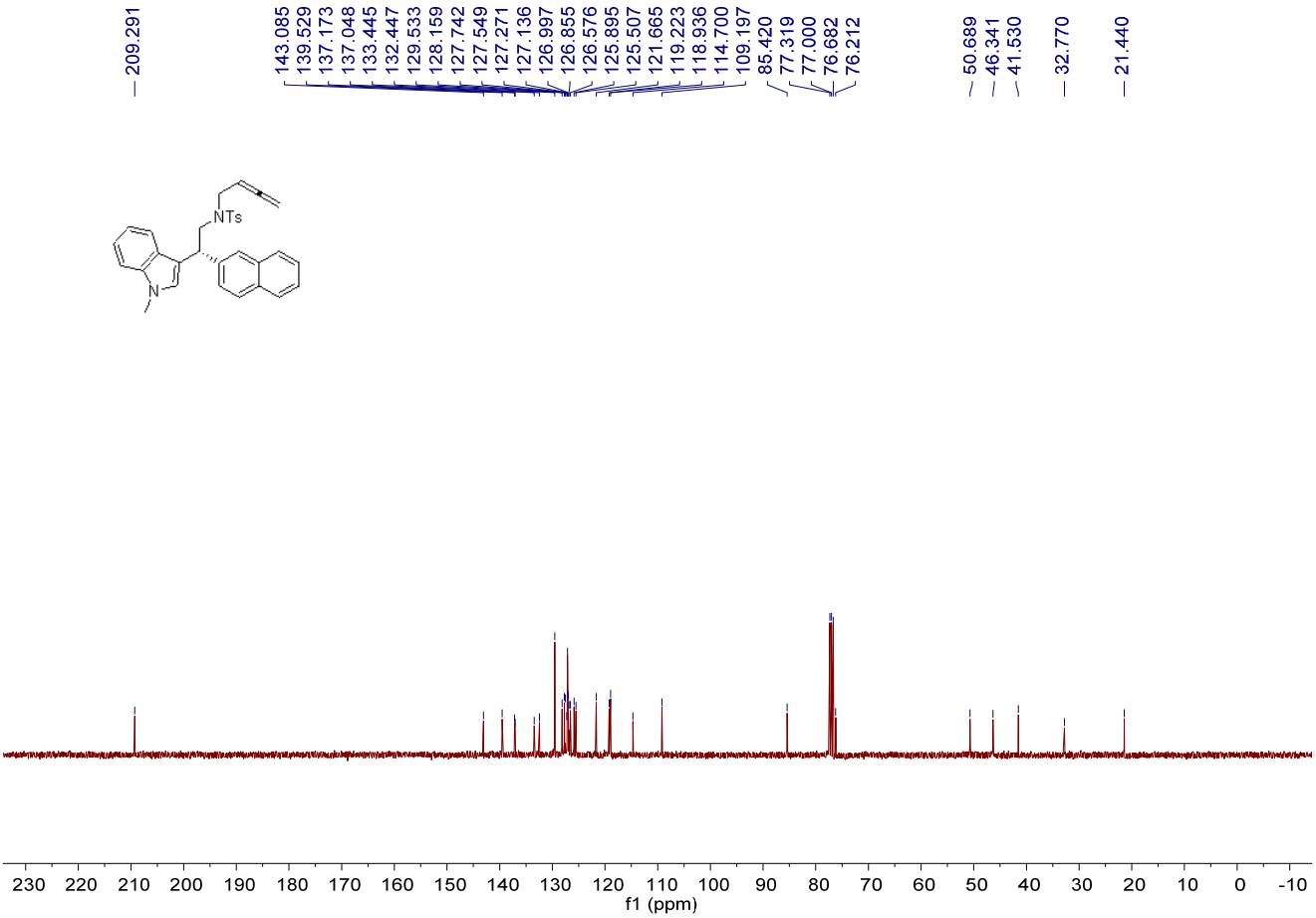
7.259
7.230
7.200
7.183
7.162
7.134
7.114
7.032
7.020
6.994
4.810
4.790
4.771
4.739
4.726
4.712
4.701
4.127
4.109
4.093
4.075
3.917
3.906
3.868
3.848
3.816
3.794
3.781
3.760
3.736
3.645
3.632
3.595
3.576
2.349
0.000
NTs
4.16
6.25
2.36
2.04
2.03
0.96
2.99
0.97
0.98
1.01
3.02
1.02
3.00
f1 (ppm)


209.291
143.085
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137.173
137.048
133.445
132.447
129.533
128.159
127.742
127.549
127.271
127.136
126.997
126.855
126.576
125.895
125.507
121.665
119.223
118.936
114.700
109.197
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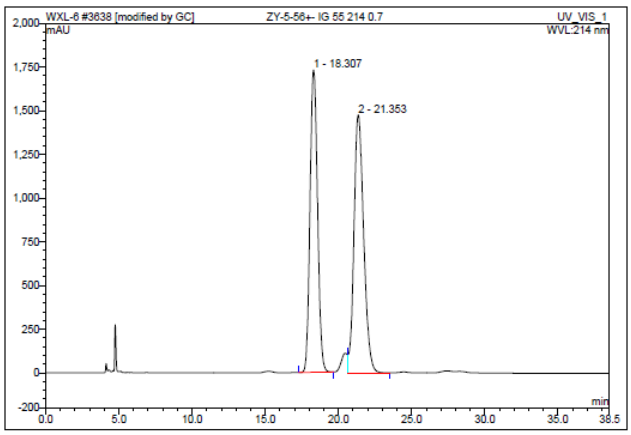
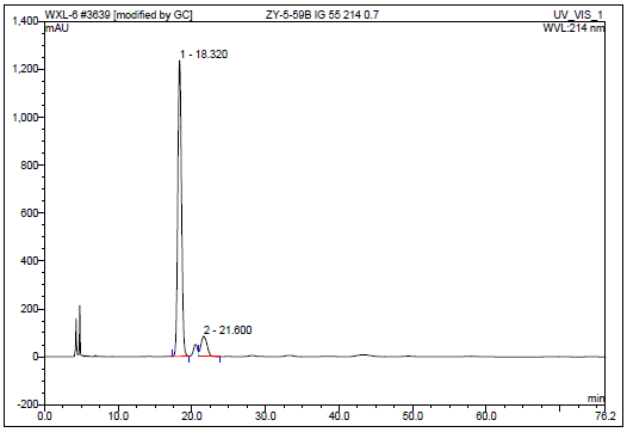
46.341
41.530
32.770
21.440
NTs
f1 (ppm)

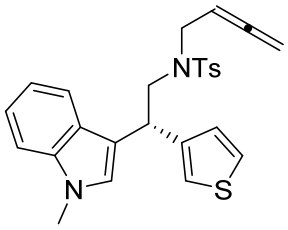


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.31	n.a.	1729.879	1029.519	47.56	n.a.	BMB*
2	21.35	n.a.	1475.673	1134.967	52.44	n.a.	MB*
Total:			3205.552	2164.486	100.00	0.000	



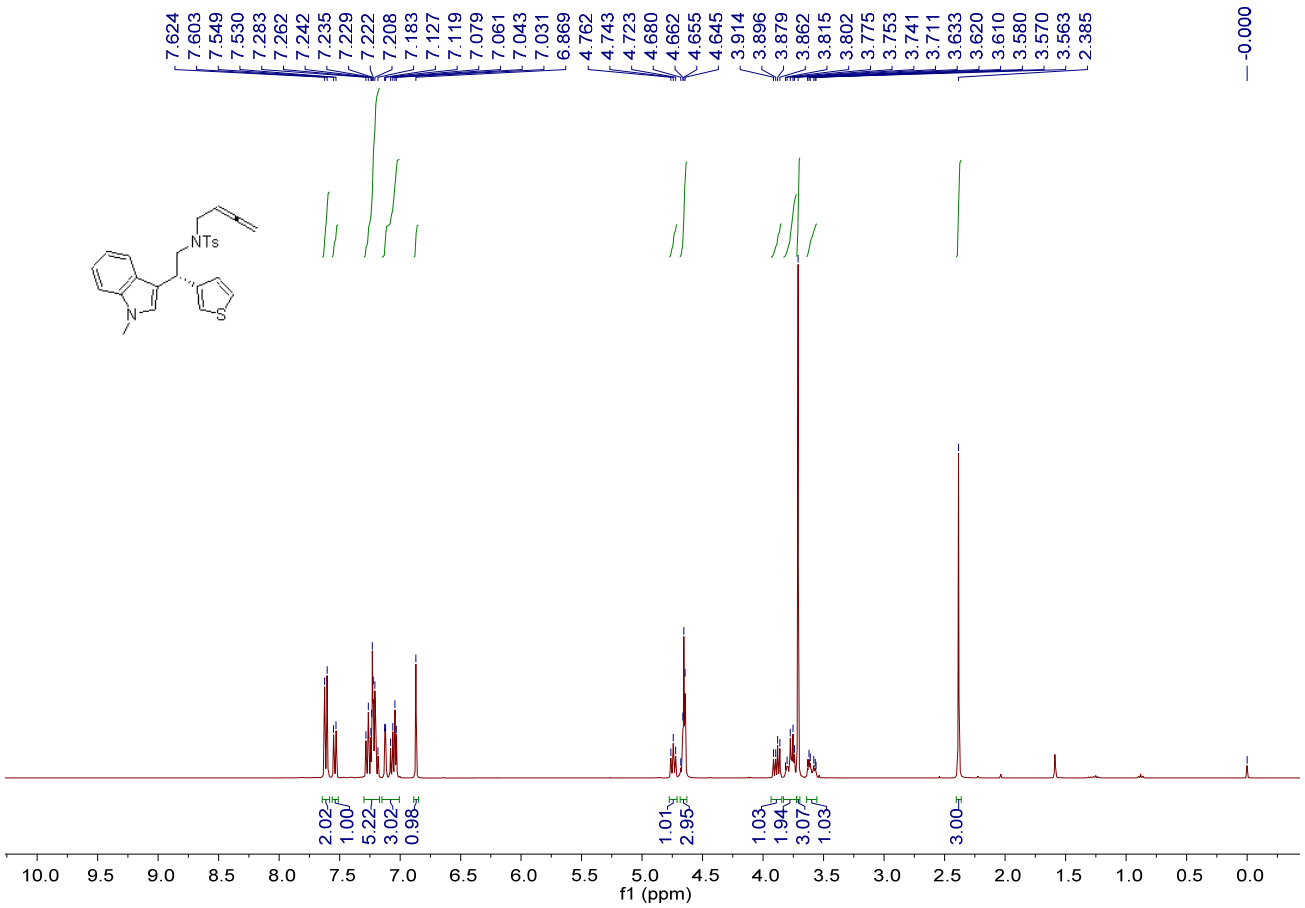
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.32	n.a.	1234.597	727.954	89.98	n.a.	BMB*
2	21.60	n.a.	84.422	81.077	10.02	n.a.	MB*
Total:			1319.020	809.030	100.00	0.000	

Translation: Chiralcel IG column [λ = 214 nm; eluent: Hexane/Isopropanol = 50/50; Flow rate: 0.70 mL/min; t_{minor} = 21.60 min, t_{major} = 18.32 min; ee% = 80%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(*S*)-*N*-(buta-2,3-dien-1-yl)-4-methyl-*N*-(2-(1-methyl-1*H*-indol-3-yl)-2-(thiophen-3-yl)ethyl)benzenesulfonamide 1r

A white solid, 48% yield (22.2 mg). M.p.: 101-104 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.39 (s, 3H), 3.56-3.64 (m, 1H), 3.71 (s, 3H), 3.74-3.82 (m, 2H), 3.88 (dd, *J* = 13.6, 6.8 Hz, 1H), 4.64-4.68 (m, 3H), 4.74 (t, *J* = 8.0 Hz, 1H), 6.87 (s, 1H), 7.03-7.13 (m, 3H), 7.18-7.29 (m, 5H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 32.7, 37.2, 46.6, 51.0, 76.1, 85.4, 109.3, 114.8, 118.9, 119.2, 121.55, 121.63, 125.4, 126.9, 127.0, 127.2, 127.8, 129.6, 137.0, 137.2, 142.7, 143.1, 209.2. IR (CH_2Cl_2) ν 2919, 2858, 1952, 1455, 1337, 1155, 1098, 837, 747, 667 cm^{-1}. MS (ESI) *m/z* (%): 463.15 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{26}H_{27}N_2O_2S_2^{+1}$ $[M+H]^+$ requires 463.1508, found: 463.1507. Enantiomeric excess was determined by HPLC with a Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 85/15; Flow rate: 0.70 mL/min; t_{minor} = 35.81 min, t_{major} = 39.73 min; ee% = 95%; $[\alpha]_D^{25}$ = -115.3 (c 0.12, CH_2Cl_2)].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7.603
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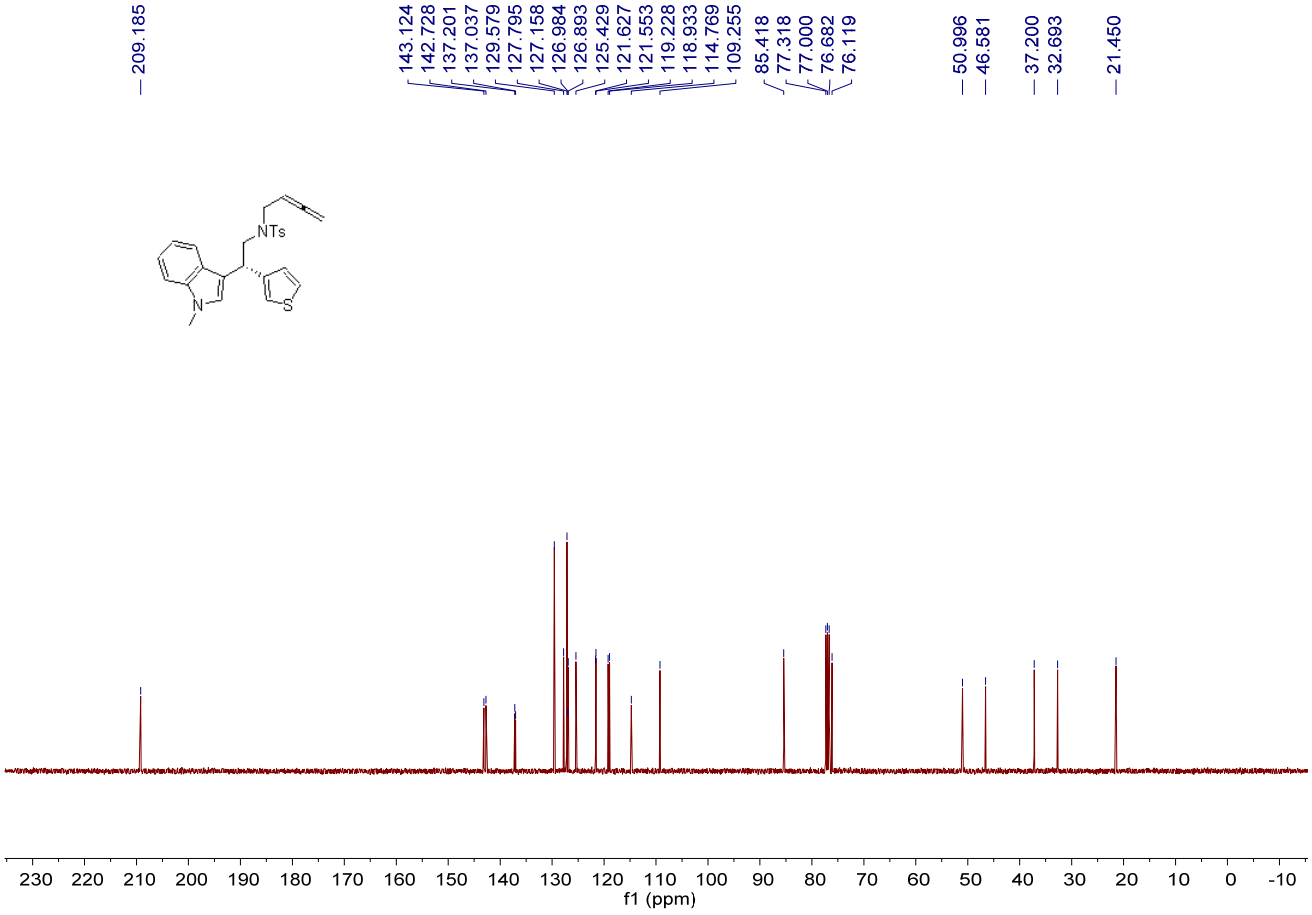
7.262
7.242
7.235
7.229
7.222
7.208
7.183
7.127
7.119
7.079
7.061
7.043
7.031
6.869
4.762
4.743
4.723
4.680
4.662
4.655
4.645
3.914
3.896
3.879
3.862
3.815
3.802
3.775
3.753
3.741
3.711
3.633
3.620
3.610
3.580
3.570
3.563
2.385
-0.000
NTs
N
S
2.02
1.00
5.22
3.02
0.98
1.01
2.95
1.03
1.94
3.07
1.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


209.185
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142.728
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137.037
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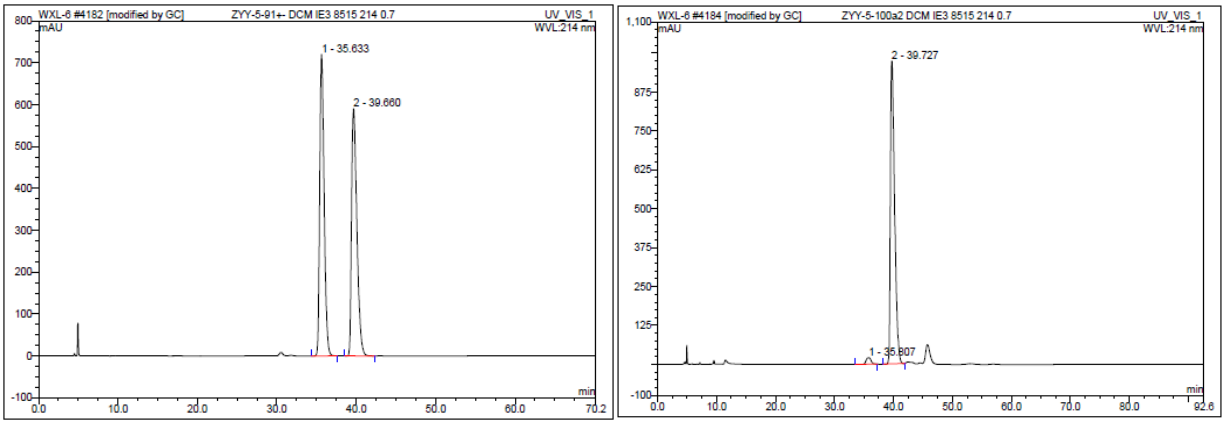
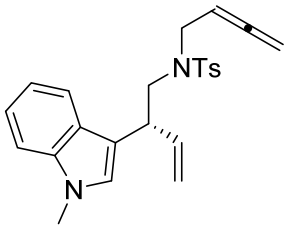
127.158
126.984
126.893
125.429
121.627
121.553
119.228
118.933
114.769
109.255
85.418
77.318
77.000
76.682
76.119
50.996
46.581
37.200
32.693
21.450
NTs
N
S
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	35.63	n.a.	720.171	465.122	50.36	n.a.	BMB*
2	39.66	n.a.	590.610	458.454	49.64	n.a.	BMB*
Total:			1310.781	923.576	100.00	0.000	

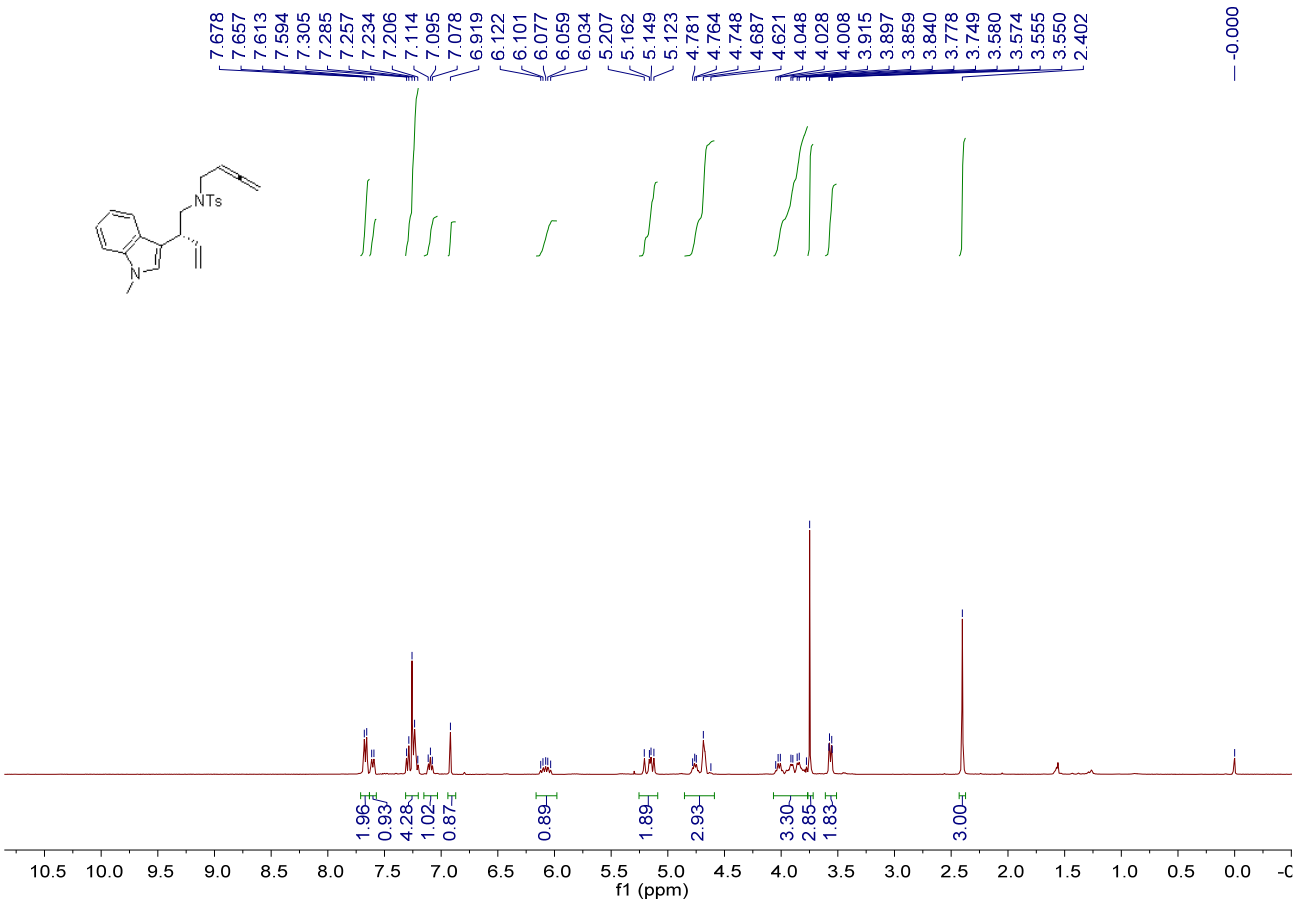
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	35.81	n.a.	20.737	19.844	2.40	n.a.	BMB*
2	39.73	n.a.	972.766	807.807	97.60	n.a.	BMB*
Total:			993.503	827.651	100.00	0.000	

Translation: Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 85/15; Flow rate: 0.70 mL/min; t_{minor} = 35.81 min, t_{major} = 39.73 min; ee% = 95%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(*R*)-*N*-(buta-2,3-dien-1-yl)-4-methyl-*N*-(2-(1-methyl-1*H*-indol-3-yl)but-3-en-1-yl)benzenesulfonamide 1s

A white liquid, 48% yield (19.4 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 3.55-3.58 (m, 2H), 3.75 (s, 3H), 3.77-4.05 (m, 3H), 4.62-4.79 (m, 3H), 5.12-5.21 (m, 2H), 6.03-6.13 (m, 1H), 6.92 (s, 1H), 7.07-7.12 (m, 1H), 7.20-7.31 (m, 4H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 32.7, 40.1, 46.7, 50.6, 76.1, 85.5, 109.3, 114.0, 116.2, 118.9, 119.3, 121.7, 126.3, 126.9, 127.2, 129.6, 137.0, 137.4, 138.7, 143.1, 209.3. IR (CH_2Cl_2) ν 2924, 1954, 1597, 1328, 1155, 1090, 848, 739, 657 cm^{-1}. MS (ESI) *m/z* (%): 407.17 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{24}H_{27}N_2O_2S^{+1}$ $[M+H]^+$ requires 407.1788, found: 407.1782. Enantiomeric excess was determined by HPLC with a Chiralcel IB column [λ = 214 nm; eluent: Hexane/Isopropanol = 96/4; Flow rate: 0.70 mL/min; t_{minor} = 21.41 min, t_{major} = 19.79 min; ee% = 84%; $[\alpha]_D^{25}$ = -23.0 (c 0.10, CH_2Cl_2)].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7.285
7.257
7.234
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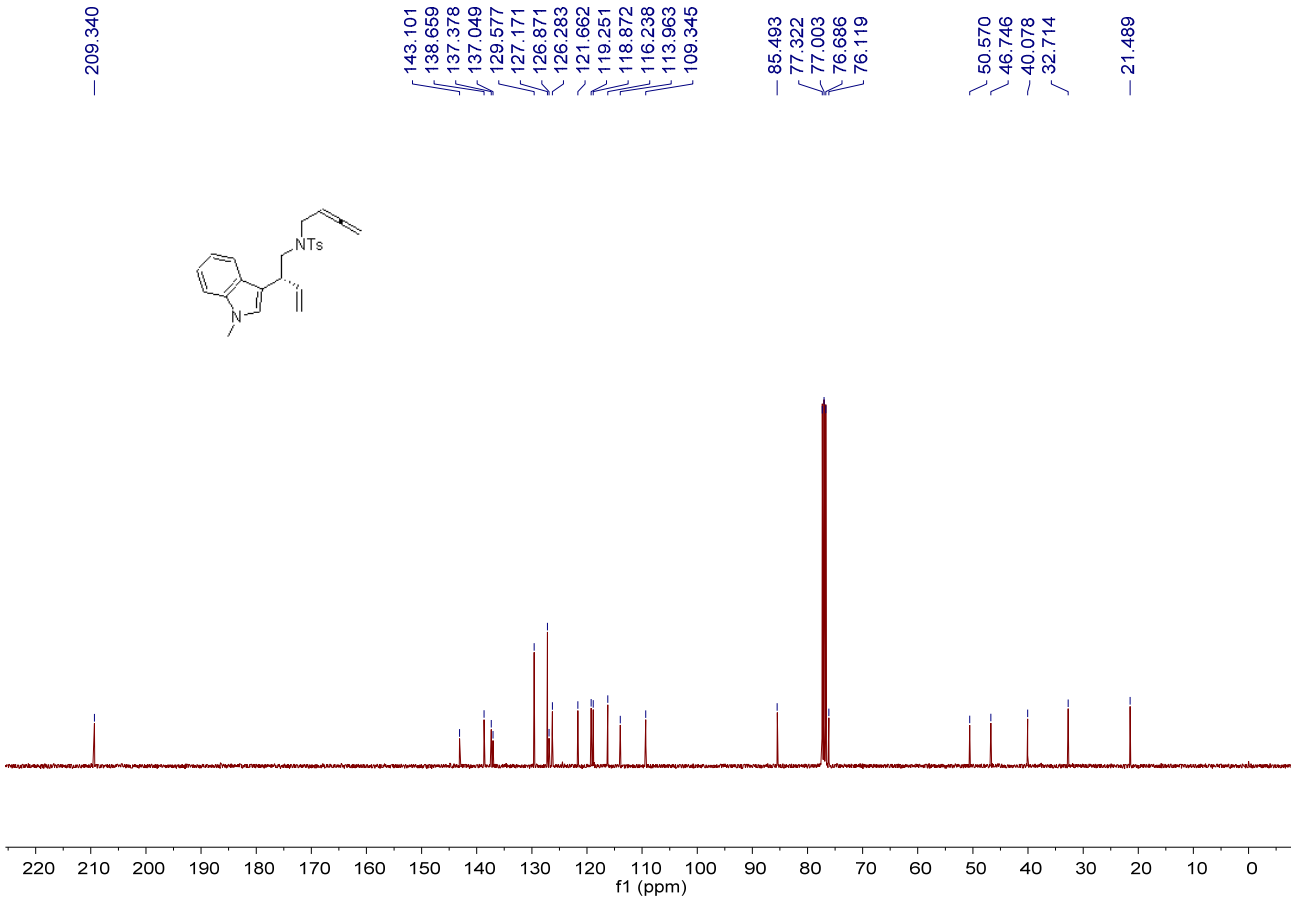
7.114
7.095
7.078
6.919
6.122
6.101
6.077
6.059
6.034
5.207
5.162
5.149
5.123
4.781
4.764
4.748
4.687
4.621
4.048
4.028
4.008
3.915
3.897
3.859
3.840
3.778
3.749
3.580
3.574
3.555
3.550
2.402
-0.000
NTs
1.96
0.93
4.28
1.02
0.87
0.89
1.89
2.93
3.30
2.85
1.83
3.00
f1 (ppm)


209.340
143.101
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137.378
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129.577
127.171
126.871
126.283
121.662
119.251
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113.963
109.345
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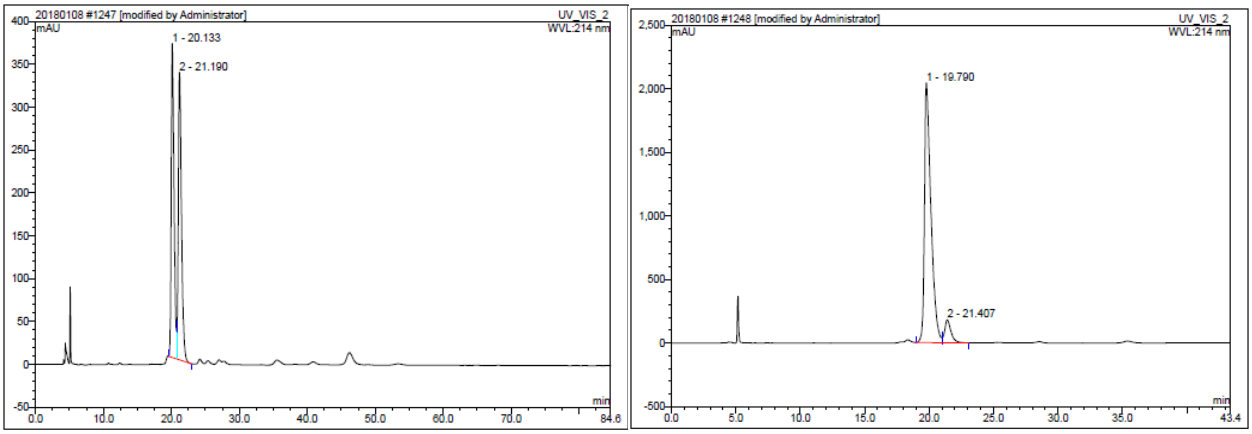
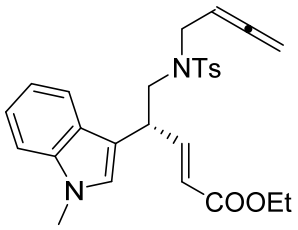
40.078
32.714
21.489
NTs
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.13	n.a.	366.103	175.206	49.25	n.a.	BM *
2	21.19	n.a.	335.230	180.523	50.75	n.a.	MB*
Total:			701.333	355.729	100.00	0.000	

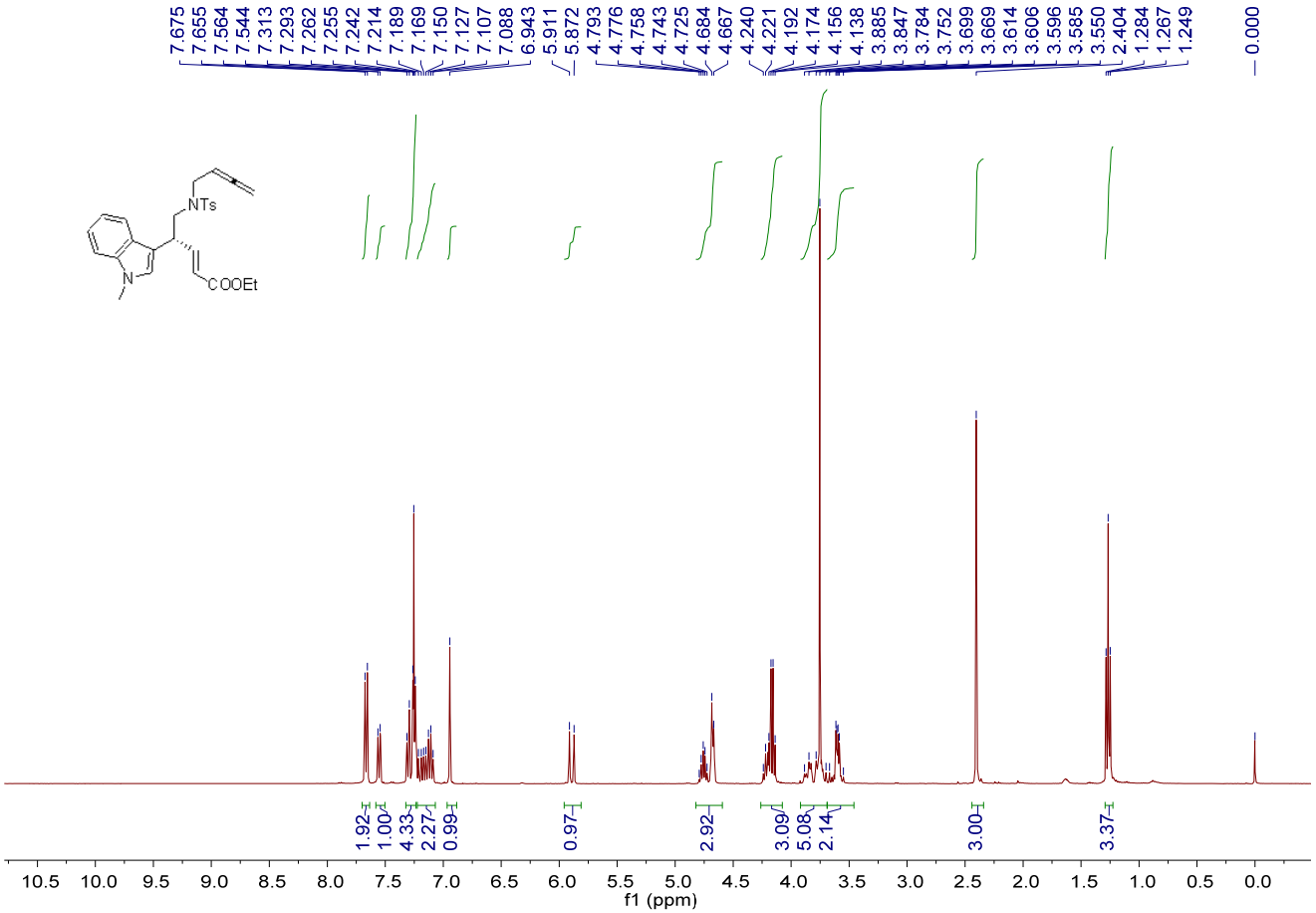
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.79	n.a.	2042.766	1194.206	92.07	n.a.	BM *
2	21.41	n.a.	180.355	102.871	7.93	n.a.	MB*
Total:			2223.122	1297.078	100.00	0.000	

Translation: Chiralcel IB column [λ = 214 nm; eluent: Hexane/Isopropanol = 96/4; Flow rate: 0.70 mL/min; t_{minor} = 21.41 min, t_{major} = 19.79 min; ee% = 84%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(*R*,*E*)-ethyl 5-(*N*-(buta-2,3-dien-1-yl)-4-methylphenylsulfonamido)-4-(1-methyl-1H-indol-3-yl) pent-2-enoate 1t

A white liquid, 44% yield (20.9 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.27 (t, *J* = 7.2 Hz, 3H), 2.40 (s, 3H), 3.55-3.67 (m, 2H), 3.69-3.89 (m, 5H), 4.13-4.24 (m, 3H), 4.66-4.80 (m, 3H), 5.89 (d, *J* = 15.6 Hz, 1H), 6.94 (s, 1H), 7.08-7.22 (m, 2H), 7.24-7.32 (m, 4H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.2, 21.5, 32.8, 39.0, 47.3, 50.2, 60.3, 76.3, 85.4, 109.5, 111.9, 119.0, 119.2, 121.9, 122.4, 126.6, 127.2, 129.7, 136.9, 137.0, 143.3, 148.0, 166.4, 209.4. IR (CH_2Cl_2) ν 2924, 1954, 1712, 1597, 1470, 1328, 1155, 1090, 981, 853, 741, 657 cm^{-1}. MS (ESI) *m/z* (%): 496.22 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{27}H_{34}N_3O_4S^{+1}$ $[M+NH_4]^+$ requires 496.2265, found: 496.2254. Enantiomeric excess was determined by HPLC with a Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 27.91 min, t_{major} = 24.09 min; ee% = 91%; $[\alpha]_D^{25}$ = 3.5 (c 0.08, CH_2Cl_2)].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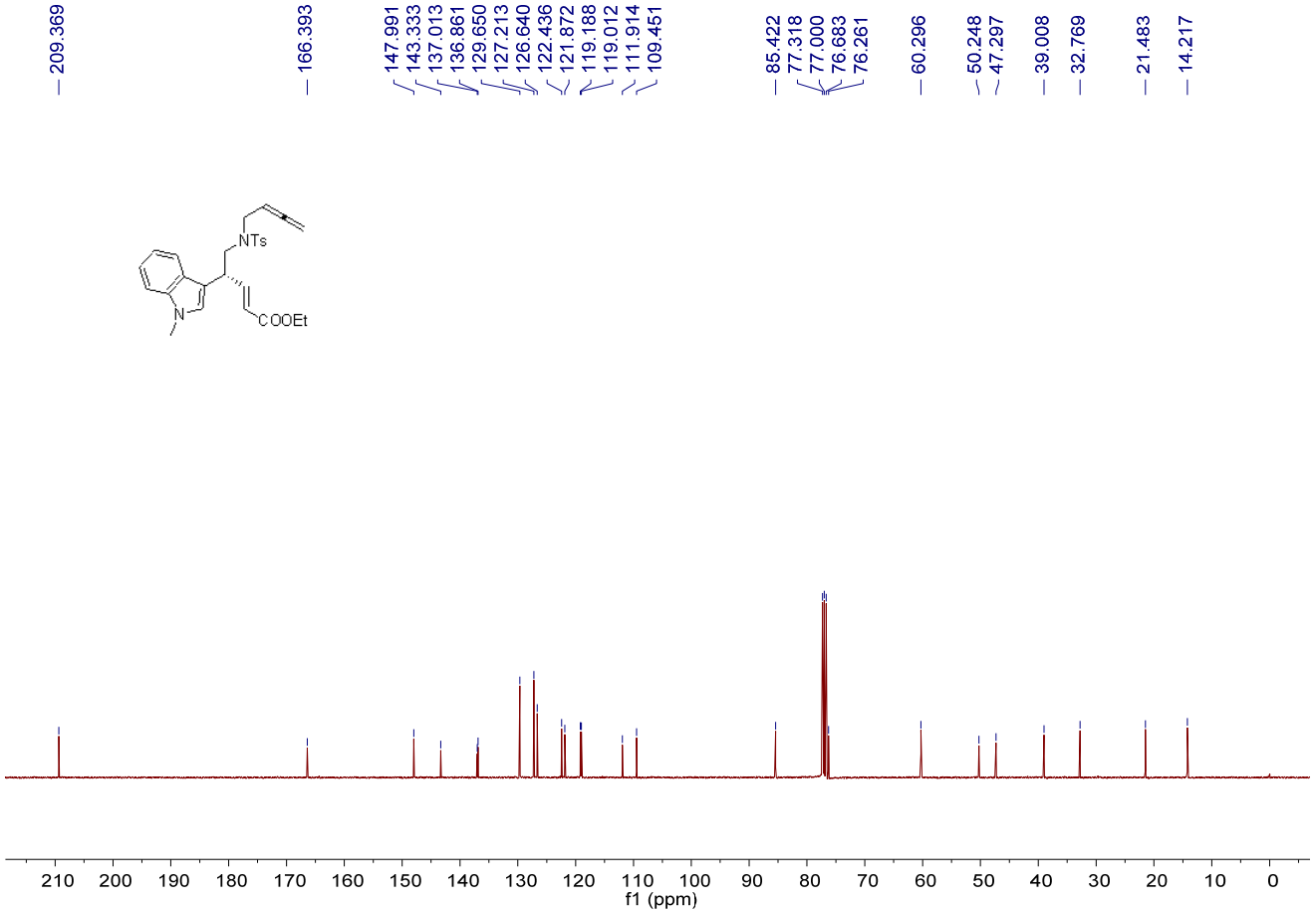
7.293
7.262
7.255
7.242
7.214
7.189
7.169
7.150
7.127
7.107
7.088
6.943
5.911
5.872
4.793
4.776
4.758
4.743
4.725
4.684
4.667
4.240
4.221
4.192
4.174
4.156
4.138
3.885
3.847
3.784
3.752
3.699
3.669
3.614
3.606
3.596
3.585
3.550
2.404
1.284
1.267
1.249
0.000
NTs
COOEt
1.92
1.00
4.33
2.27
0.99
0.97
2.92
3.09
5.08
2.14
3.00
3.37
f1 (ppm)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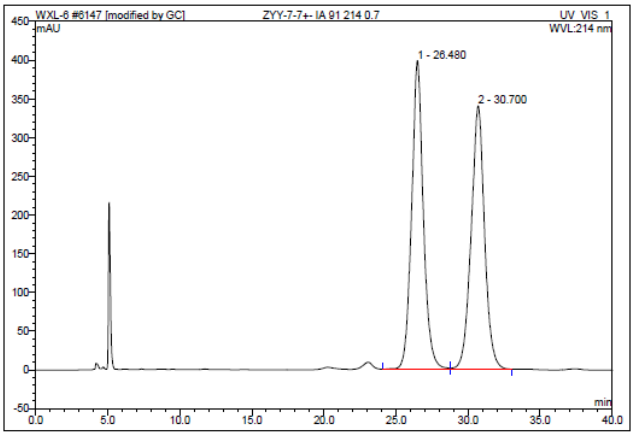
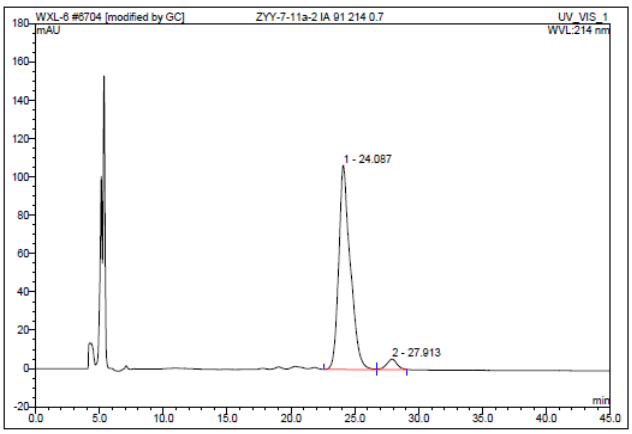
143.333
137.013
136.861
129.650
127.213
126.640
122.436
121.872
119.188
119.012
111.914
109.451
85.422
77.318
77.000
76.683
76.261
60.296
50.248
47.297
39.008
32.769
21.483
14.217
NTs
COOEt
f1 (ppm)

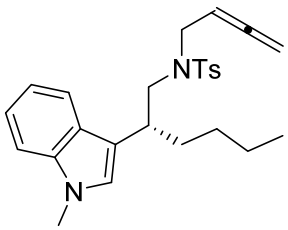




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	26.48	n.a.	398.830	376.301	50.59	n.a.	BM *
2	30.70	n.a.	340.342	367.554	49.41	n.a.	MB*
Total:			739.172	743.856	100.00	0.000	

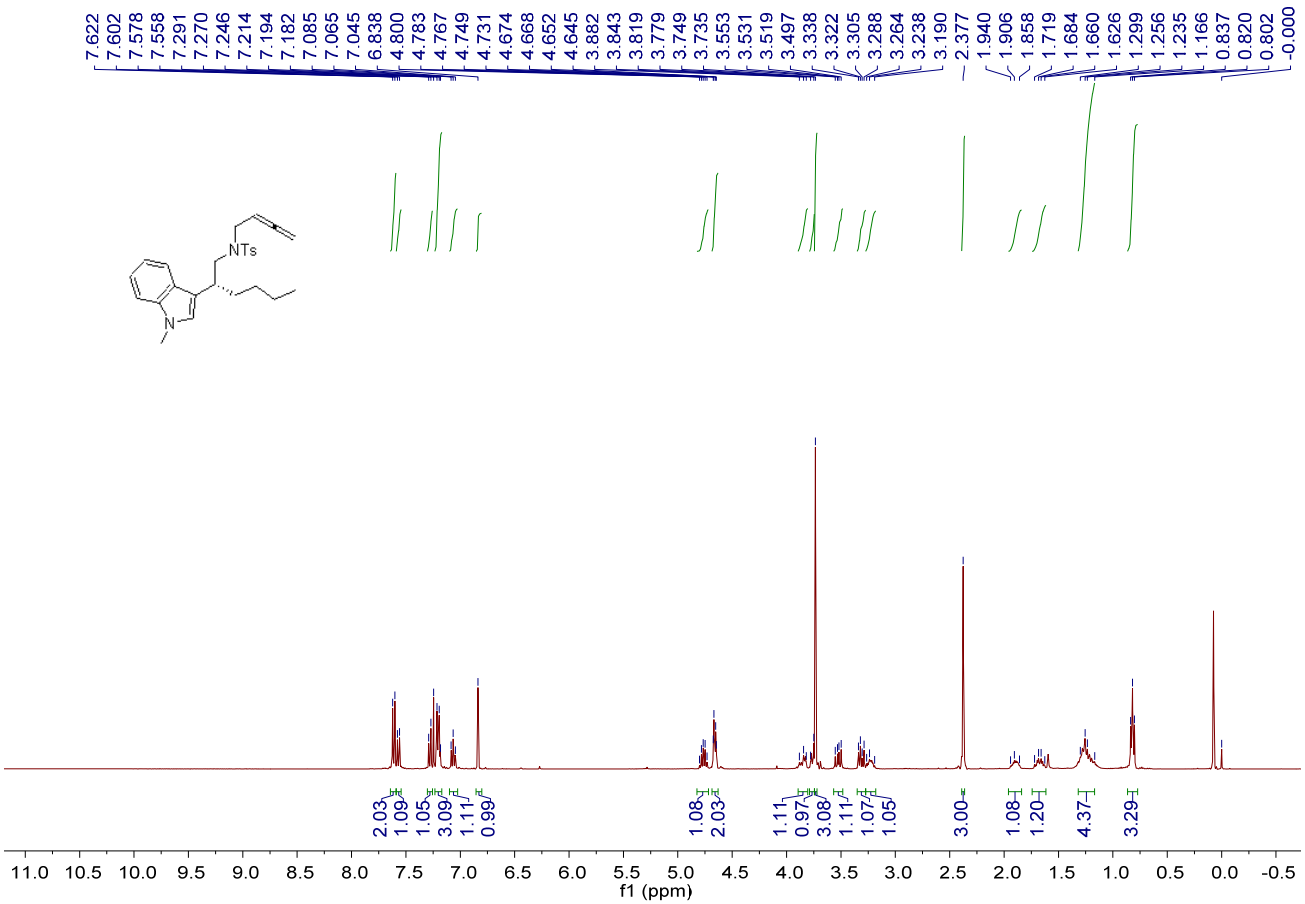
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	24.09	n.a.	106.456	111.558	95.66	n.a.	BM
2	27.91	n.a.	5.424	5.062	4.34	n.a.	MB
Total:			111.880	116.620	100.00	0.000	

Translation: Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 27.91 min, t_{major} = 24.09 min; ee% = 91%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(*R*)-*N*-(buta-2,3-dien-1-yl)-4-methyl-*N*-(2-(1-methyl-1*H*-indol-3-yl)hexyl)benzenesulfonamide 1u

A white liquid, 43% yield (18.8 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.82 (t, *J* = 7.2 Hz, 3H), 1.16-1.30 (m, 4H), 1.62-1.72 (m, 1H), 1.85-1.94 (m, 1H), 2.38 (s, 3H), 3.19-3.27 (m, 1H), 3.31 (dd, *J* = 13.2, 6.8 Hz, 1H), 3.52 (dd, *J* = 13.6, 8.8 Hz, 1H), 3.74 (s, 3H), 3.74-3.78 (m, 1H), 3.81-3.89 (m, 1H), 4.64-4.68 (m, 2H), 4.73-4.80 (m, 1H), 6.84 (s, 1H), 7.04-7.09 (m, 1H), 7.18-7.22 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.0, 14.0, 21.4, 22.8, 29.7, 32.3, 32.7, 35.3, 46.9, 52.2, 76.0, 85.7, 109.3, 115.4, 118.6, 119.1, 121.4, 126.3, 127.1, 127.4, 129.5, 137.0, 137.3, 143.0, 209.2. IR (CH_2Cl_2) ν 3288, 2954, 2921, 2851, 1735, 1597, 1494, 1349, 1185, 1161, 1092, 929, 898, 750, 658 cm^{-1}. MS (ESI) *m/z* (%): 437.22 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{26}H_{33}N_2O_2S^{+1}$ $[M+H]^+$ requires 437.2257, found: 437.2256. Enantiomeric excess was determined by HPLC with a Chiralcel AD column [λ = 254 nm; eluent: Hexane/Isopropanol = 100/1; Flow rate: 0.30 mL/min; t_{minor} = 93.49 min, t_{major} = 99.29 min; ee% = 94%; $[\alpha]_D^{25}$ = 9.1 (c 0.15, CH_2Cl_2)].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7.214
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7.182
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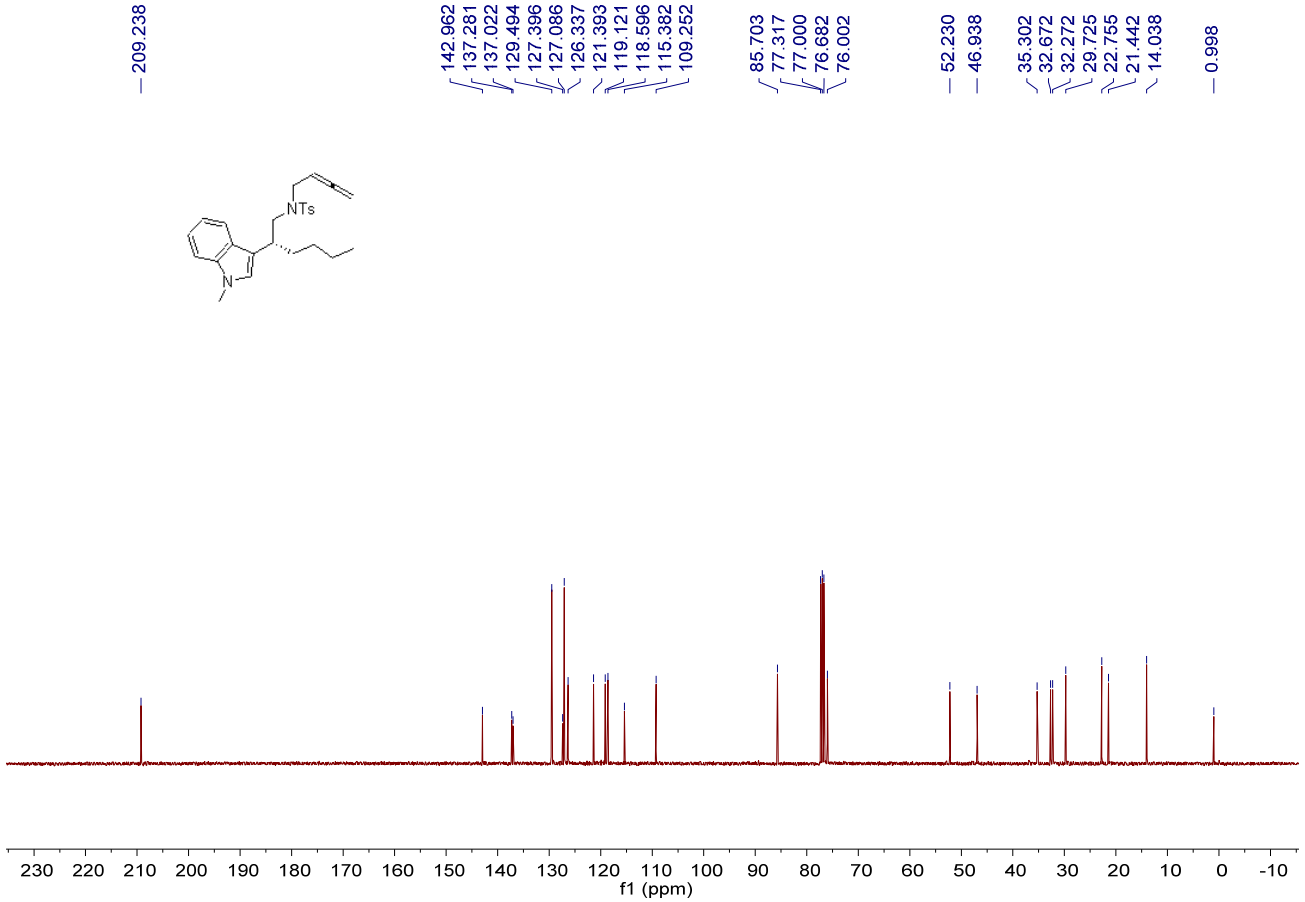
6.838
4.800
4.783
4.767
4.749
4.731
4.674
4.668
4.652
4.645
3.882
3.843
3.819
3.779
3.749
3.735
3.553
3.531
3.519
3.497
3.338
3.322
3.305
3.288
3.264
3.238
3.190
2.377
1.940
1.906
1.858
1.719
1.684
1.660
1.626
1.299
1.256
1.235
1.166
0.837
0.820
0.802
-0.000
NTs
N
2.03
1.09
1.05
3.09
1.11
0.99
1.08
2.03
1.11
0.97
3.08
1.11
1.07
1.05
3.00
1.08
1.20
4.37
3.29
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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127.396
127.086
126.337
121.393
119.121
118.596
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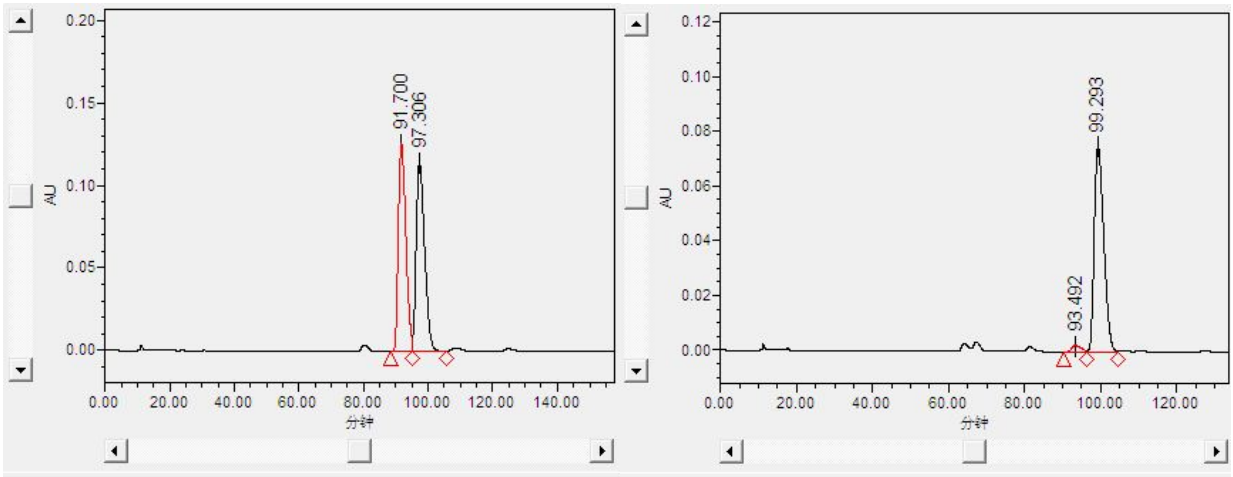
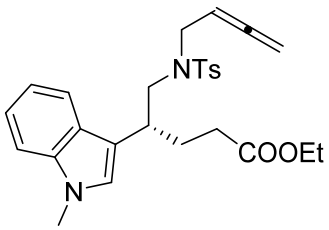
77.000
76.682
76.002
52.230
46.938
35.302
32.672
32.272
29.725
22.755
21.442
14.038
0.998
NTs
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		91.700	20536783	49.66	125765	Bv	88.417	95.233
2		97.306	20820759	50.34	114397	vV	95.233	105.767

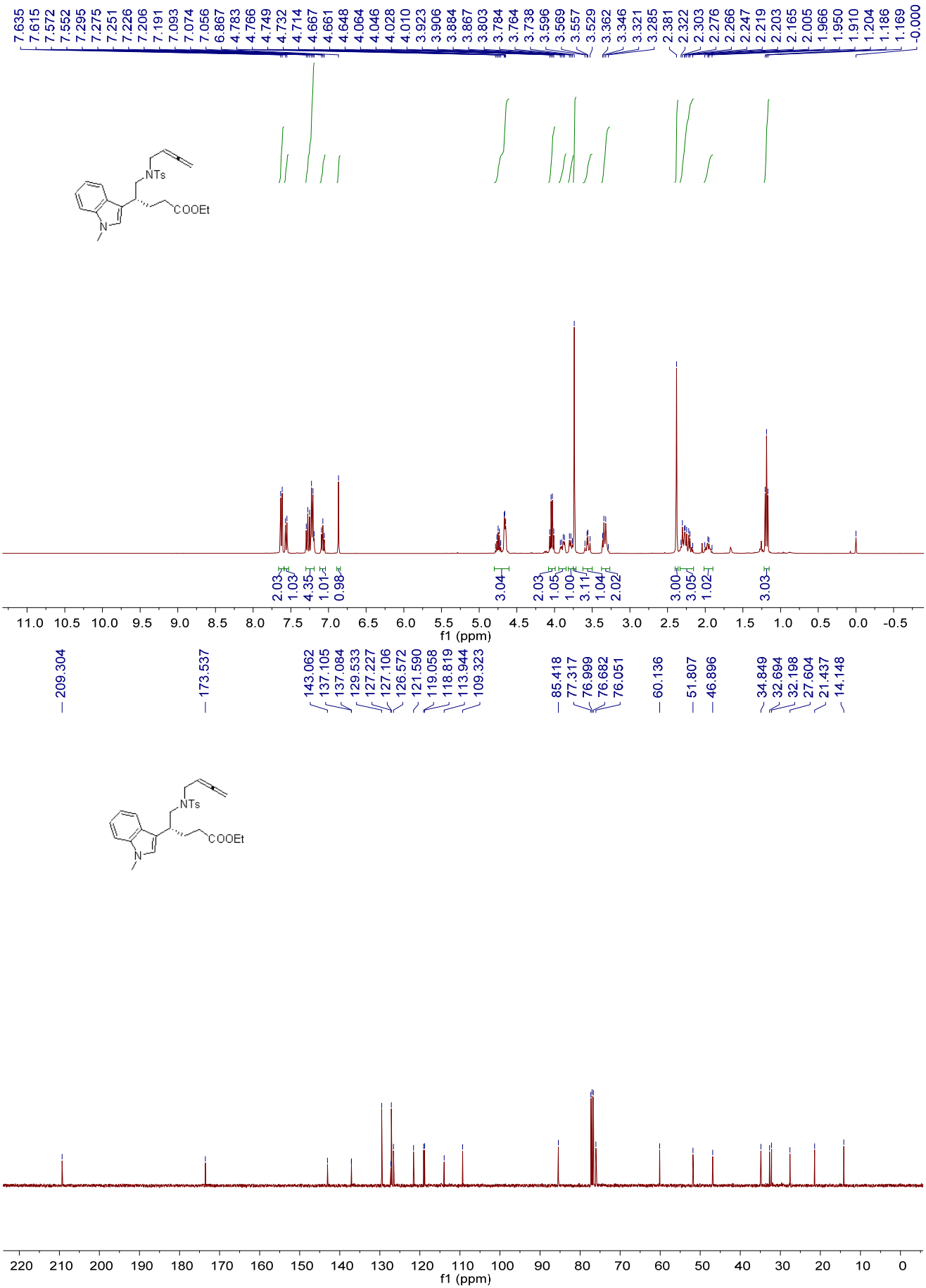
	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		93.492	430169	3.17	2417	BV	90.233	96.433
2		99.293	13157534	96.83	75411	VV	96.433	104.667

Translation: Chiralcel AD column [λ = 254 nm; eluent: Hexane/Isopropanol = 100/1; Flow rate: 0.30 mL/min; t_{minor} = 93.49 min, t_{major} = 99.29 min; ee% = 94%].



(*R*)-ethyl 5-(*N*-(buta-2,3-dien-1-yl)-4-methylphenylsulfonamido)-4-(1-methyl-1*H*-indol-3-yl) Pentanoate 1v

A white liquid, 43% yield (20.5 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.87 (t, *J* = 7.2 Hz, 3H), 1.91-2.01 (m, 1H), 2.16-2.33 (m, 3H), 2.38 (s, 3H), 3.28-3.37 (m, 2H), 3.52-3.60 (m, 1H), 3.74 (s, 3H), 3.76-3.81 (m, 1H), 3.86-3.93 (m, 1H), 4.03 (q, *J* = 7.2 Hz, 2H), 4.64-4.79 (m, 3H), 6.87 (s, 1H), 7.05-7.10 (m, 1H), 7.19-7.30 (m, 4H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 21.4, 27.6, 32.2, 32.7, 34.8, 46.9, 51.8, 60.1, 76.1, 85.4, 109.3, 113.9, 118.8, 119.1, 121.6, 126.6, 127.1, 127.2, 129.5, 137.08, 137.11, 143.1, 173.5, 209.3. IR (CH_2Cl_2) ν 2929, 1954, 1727, 1327, 1155, 1090, 971, 852, 739, 658 cm^{-1}. MS (ESI) *m/z* (%): 498.24 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{27}H_{36}N_3O_4S^{+1}$ $[M+NH_4]^+$ requires 498.2421, found: 498.2410. Enantiomeric excess was determined by HPLC with a Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_{minor} = 51.95 min, t_{major} = 48.65 min; ee% = 99%; $[\alpha]_D^{25}$ = 10.0 (c 0.08, CH_2Cl_2)].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7.615
7.572
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7.295
7.275
7.251
7.226
7.206
7.191
7.093
7.074
7.056
6.867
4.783
4.766
4.749
4.732
4.714
4.667
4.661
4.648
4.064
4.046
4.028
4.010
3.923
3.906
3.884
3.867
3.803
3.784
3.764
3.738
3.596
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3.529
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3.321
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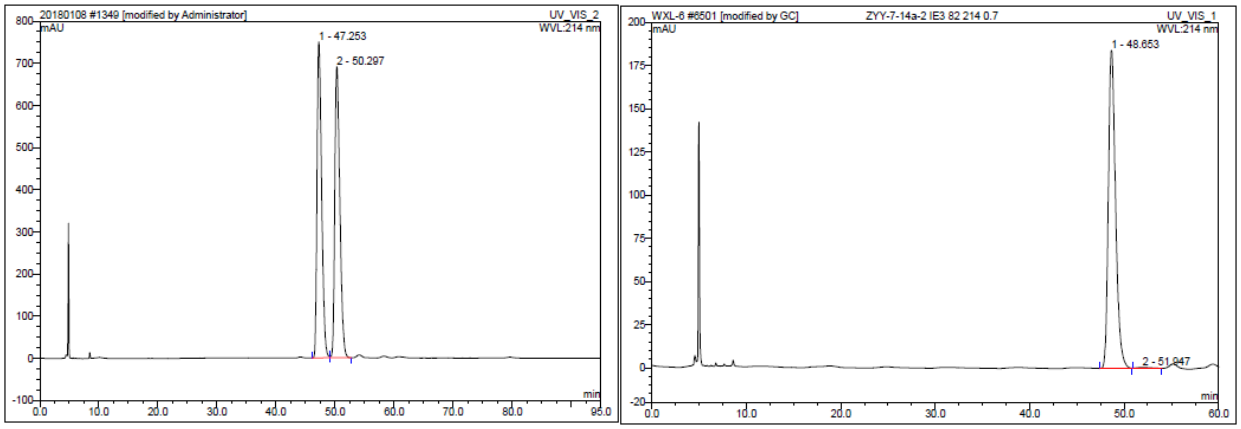
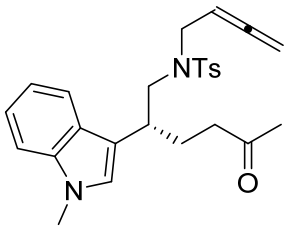
2.322
2.303
2.276
2.266
2.247
2.219
2.203
2.165
2.005
1.966
1.950
1.910
1.204
1.186
1.169
-0.000
NTs
COOEt
N
2.03
1.03
4.35
1.01
0.98
3.04
2.03
1.05
1.00
3.11
1.04
2.02
3.00
3.05
1.02
3.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
209.304
173.537
143.062
137.105
137.084
129.533
127.227
127.106
126.572
121.590
119.058
118.819
113.944
109.323
85.418
77.317
76.999
76.682
76.051
60.136
51.807
46.896
34.849
32.694
32.198
27.604
21.437
14.148
NTs
COOEt
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	47.25	n.a.	749.902	683.112	49.93	n.a.	BM *
2	50.30	n.a.	690.782	684.985	50.07	n.a.	MB*
Total:			1440.684	1368.097	100.00	0.000	

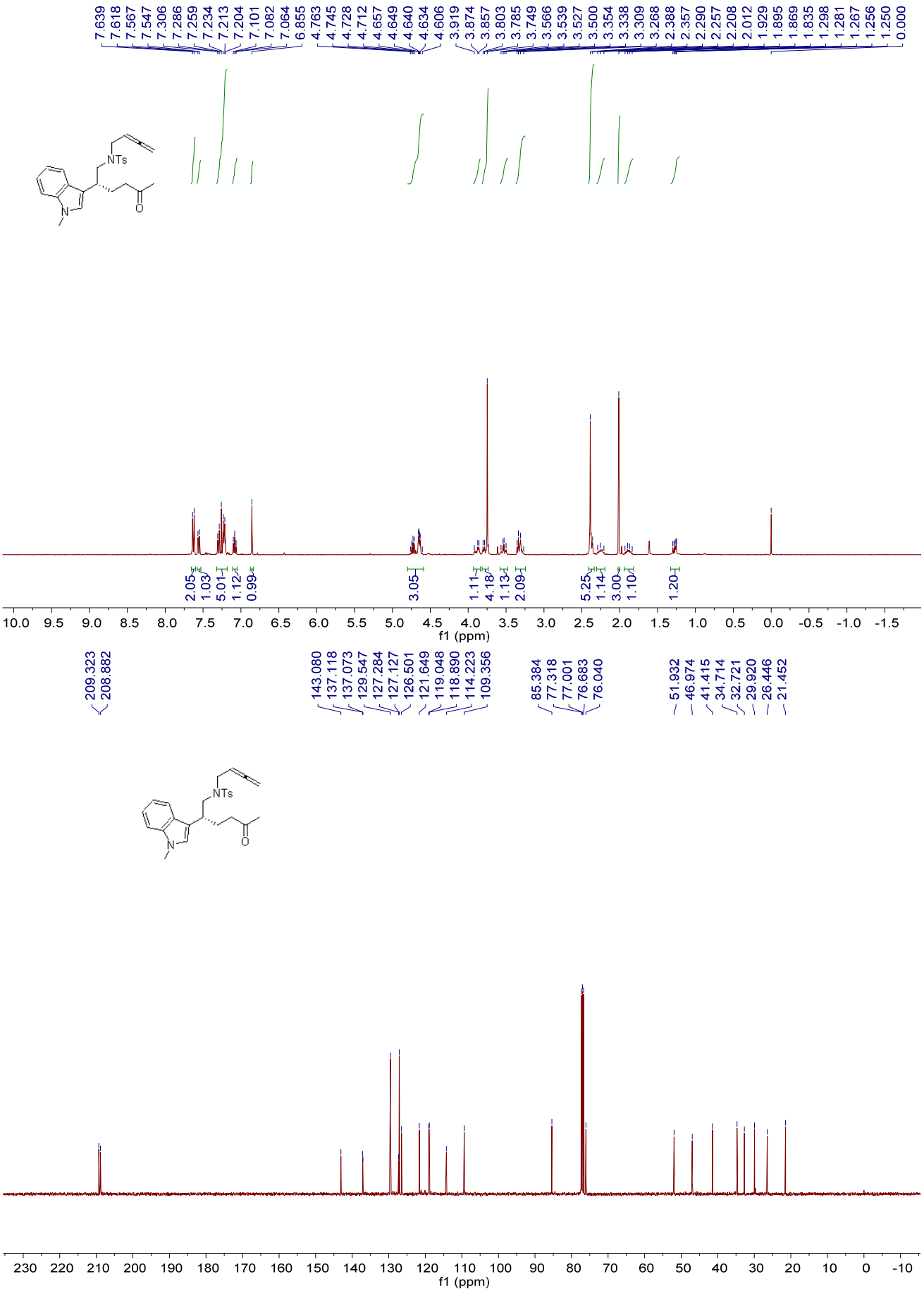
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	48.65	n.a.	184.039	163.076	99.43	n.a.	BMB
2	51.95	n.a.	0.589	0.928	0.57	n.a.	BMB*
Total:			184.628	164.005	100.00	0.000	

Translation: Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_{minor} = 51.95 min, t_{major} = 48.65 min; ee% = 99%]. (*Note*: *In the 5-minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(*R*)-*N*-(buta-2,3-dien-1-yl)-4-methyl-*N*-(2-(1-methyl-1*H*-indol-3-yl)-5-oxohexyl)benzenesulfonamide 1w

A white liquid, 42% yield (18.8 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.25-1.30 (m, 1H), 1.83-1.93 (m, 1H), 2.01 (s, 3H), 2.20-2.29 (m, 1H), 2.35-2.39 (m, 5H), 3.26-3.36 (m, 2H), 3.50-3.57 (m, 1H), 3.74-3.81 (m, 4H), 3.85-3.92 (m, 1H), 4.60-4.77 (m, 3H), 6.86 (s, 1H), 7.06-7.11 (m, 1H), 7.20-7.31 (m, 5H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 26.4, 29.9, 32.7, 34.7, 41.4, 47.0, 51.9, 76.0, 85.4, 109.4, 114.2, 118.9, 119.0, 121.6, 126.5, 127.1, 127.3, 129.5, 137.07, 137.12, 143.1, 208.9, 209.3. IR (CH_2Cl_2) ν 2921, 1954, 1711, 1597, 1471, 1327, 1155, 1089, 964, 897, 740, 657 cm^{-1}. MS (ESI) *m/z* (%): 468.23 (100) $[M+NH_4]^+$; HRMS (ESI) Calcd. For $C_{26}H_{34}N_3O_3S^{+1}$ $[M+NH_4]^+$ requires 468.2315, found: 468.2305. Enantiomeric excess was determined by HPLC with a Chiralcel IF3 column [λ = 286 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 65.64 min, t_{major} = 62.59 min; ee% = 80%; $[\alpha]_D^{25}$ = -6.0 (c 0.05, CH_2Cl_2)].


7.639
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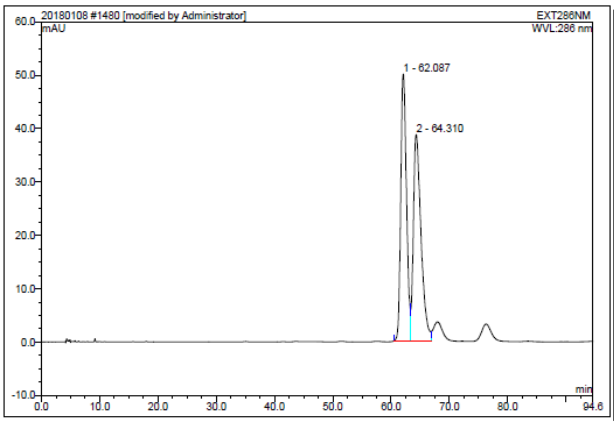
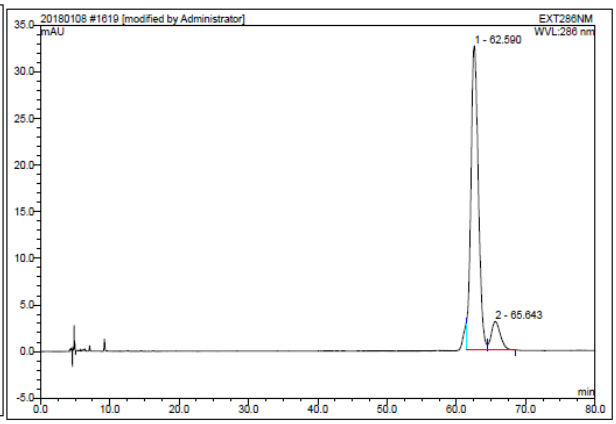
7.567
7.547
7.306
7.286
7.259
7.234
7.213
7.204
7.101
7.082
7.064
6.855
4.763
4.745
4.728
4.712
4.657
4.649
4.640
4.634
4.606
3.919
3.874
3.857
3.803
3.785
3.749
3.566
3.539
3.527
3.500
3.354
3.338
3.309
3.268
2.388
2.357
2.290
2.257
2.208
2.012
1.929
1.895
1.869
1.835
1.298
1.281
1.267
1.256
1.250
0.000
NTs
O
2.05
1.03
5.01
1.12
0.99
3.05
1.11
4.18
1.13
2.09
5.25
1.14
3.00
1.10
1.20
f1 (ppm)
209.323
208.882
143.080
137.118
137.073
129.547
127.284
127.127
126.501
121.649
119.048
118.890
114.223
109.356
85.384
77.318
77.001
76.683
76.040
51.932
46.974
41.415
34.714
32.721
29.920
26.446
21.452
NTs
O
f1 (ppm)

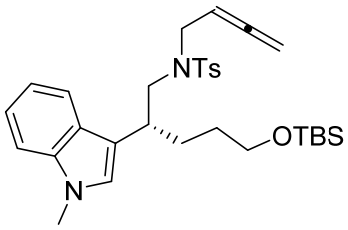


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	62.09	n.a.	49.911	56.585	49.23	n.a.	BM *
2	64.31	n.a.	38.558	58.363	50.77	n.a.	M *
Total:			88.469	114.948	100.00	0.000	



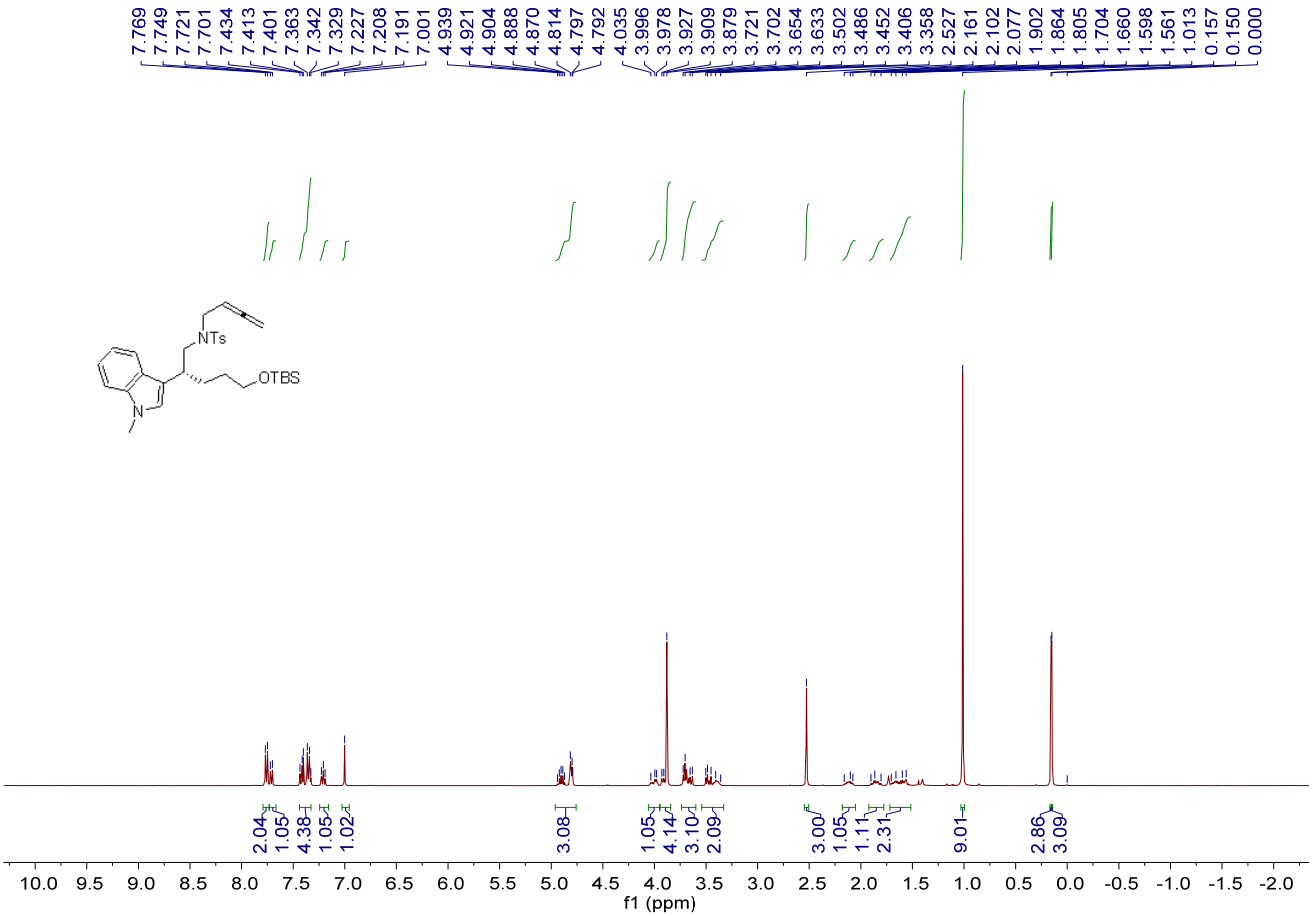
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	62.59	n.a.	32.555	40.753	90.01	n.a.	M *
2	65.64	n.a.	3.038	4.524	9.99	n.a.	MB*
Total:			35.593	45.277	100.00	0.000	

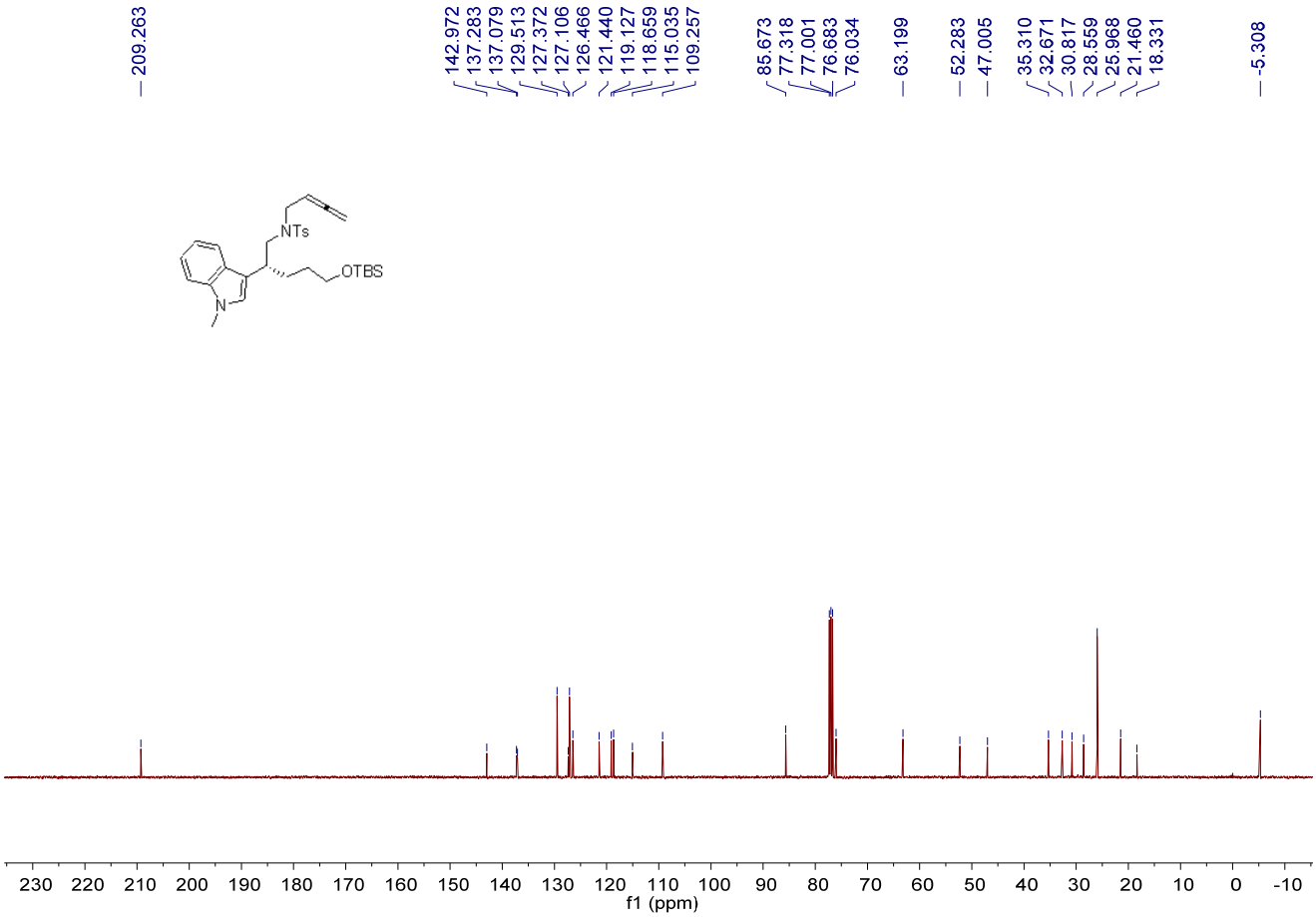
Translation: Chiralcel IF3 column [λ = 286 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 65.64 min, t_{major} = 62.59 min; ee% = 80%].

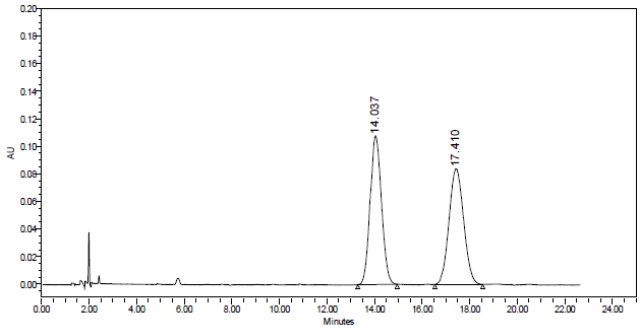


(*R*)-*N*-(buta-2,3-dien-1-yl)-*N*-(5-((tert-butyldimethylsilyl)oxy)-2-(1-methyl-1*H*-indol-3-yl)pentyl)-4-methylbenzenesulfonamide 1x

A white liquid, 43% yield (23.9 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.15 (s, 3H), 0.16 (s, 3H), 1.01 (s, 9H), 1.56-1.71 (m, 2H), 1.80-1.91 (m, 1H), 2.07-2.17 (m, 1H), 2.53 (s, 3H), 3.35-3.51 (m, 2H), 3.63-3.73 (m, 3H), 3.87-3.93 (m, 4H), 3.97-4.04 (m, 1H), 4.79-4.94 (m, 3H), 7.00 (s, 1H), 7.19-7.23 (m, 1H), 7.32-7.44 (m, 4H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ -5.3, 18.3, 21.5, 26.0, 28.6, 30.8, 32.7, 35.3, 47.0, 52.3, 63.2, 76.0, 85.7, 109.3, 115.0, 118.7, 119.1, 121.4, 126.5, 127.1, 127.4, 129.5, 137.1, 137.3, 143.0, 209.3. IR (CH_2Cl_2) ν 2927, 2855, 1954, 1598, 1471, 1327, 1158, 1090, 834, 737, 658 cm^{-1}. MS (ESI) *m/z* (%): 553.29 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{31}H_{45}N_2O_3SSi^{+1}$ $[M+H]^+$ requires 553.2915, found: 553.2900. Enantiomeric excess was determined by HPLC with a Chiralcel PC1 column [λ = 214 nm; eluent: CO_2 / MeOH = 95/5; Flow rate: 2.20 mL/min; t_{minor} = 17.44 min, t_{major} = 14.00 min; ee% = 98%; $[\alpha]_D^{25}$ = 31.8 (c 0.3, CH_2Cl_2)].

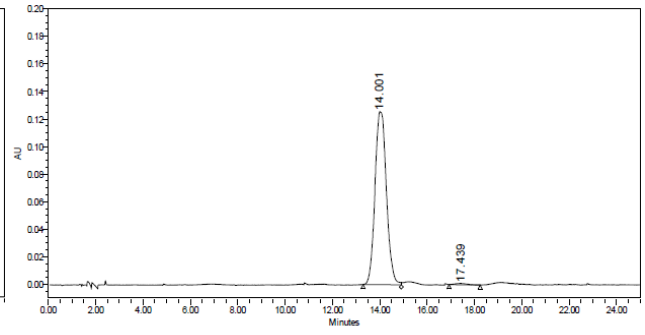

7.769
7.749
7.721
7.701
7.434
7.413
7.401
7.363
7.342
7.329
7.227
7.208
7.191
7.001
4.939
4.921
4.904
4.888
4.870
4.814
4.797
4.792
4.035
3.996
3.978
3.927
3.909
3.879
3.721
3.702
3.654
3.633
3.502
3.486
3.452
3.406
3.358
2.527
2.161
2.102
2.077
1.902
1.864
1.805
1.704
1.660
1.598
1.561
1.013
0.157
0.150
0.000
NTs
OTBS
N
2.04
1.05
4.38
1.05
1.02
3.08
1.05
4.14
3.10
2.09
3.00
1.05
1.11
2.31
9.01
2.86
3.09
f1 (ppm)


209.263
142.972
137.283
137.079
129.513
127.372
127.106
126.466
121.440
119.127
118.659
115.035
109.257
85.673
77.318
77.001
76.683
76.034
63.199
52.283
47.005
35.310
32.671
30.817
28.559
25.968
21.460
18.331
-5.308
NTs
OTBS
N
f1 (ppm)



Peak Results

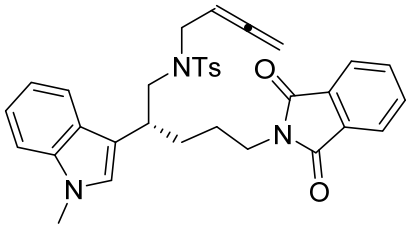
	RT	Area	Height	% Area
1	14.037	3587056	108195	50.01
2	17.410	3585090	83945	49.99



Peak Results

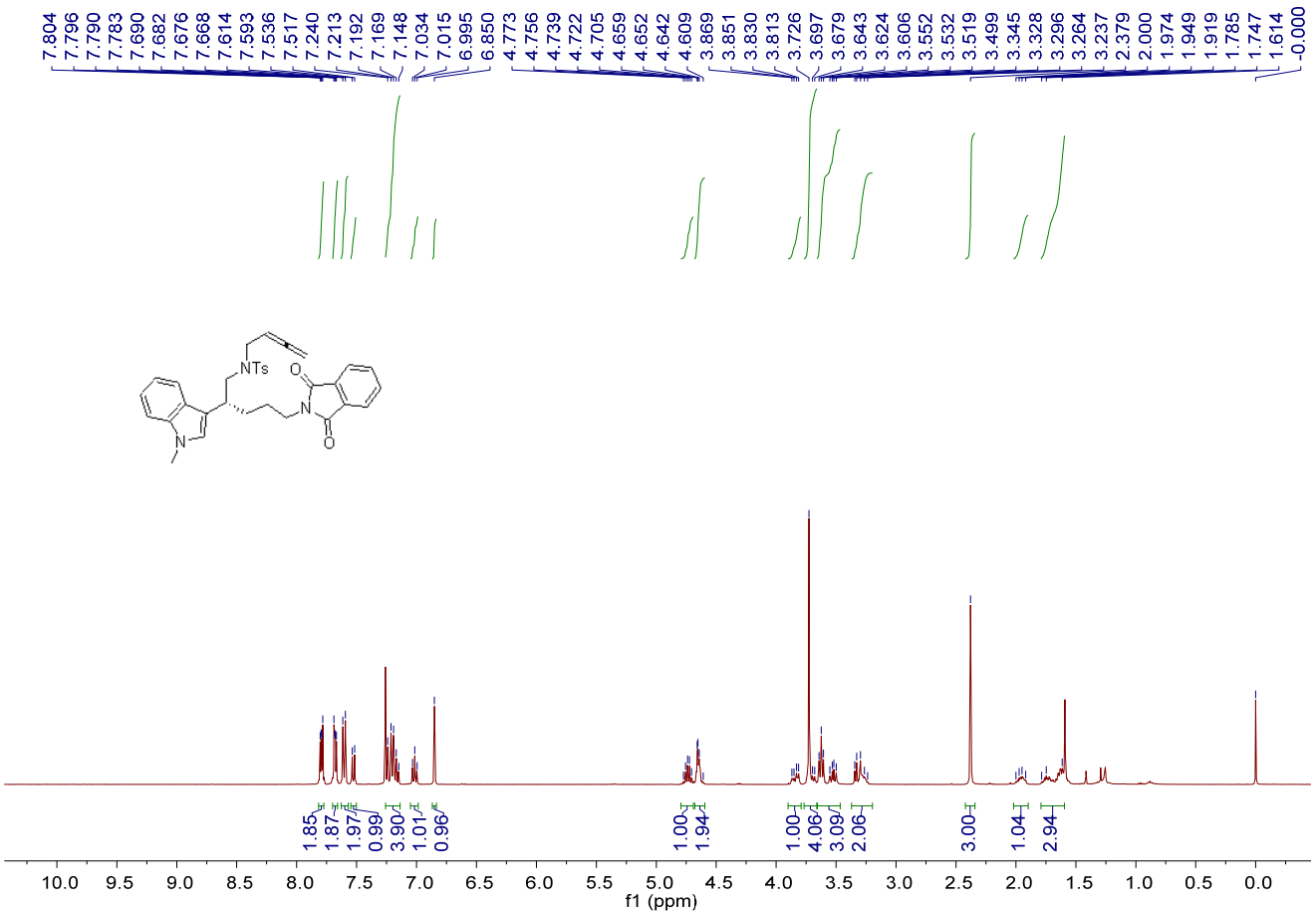
	RT	Area	Height	% Area
1	14.001	4205440	125476	99.21
2	17.439	33569	1080	0.79

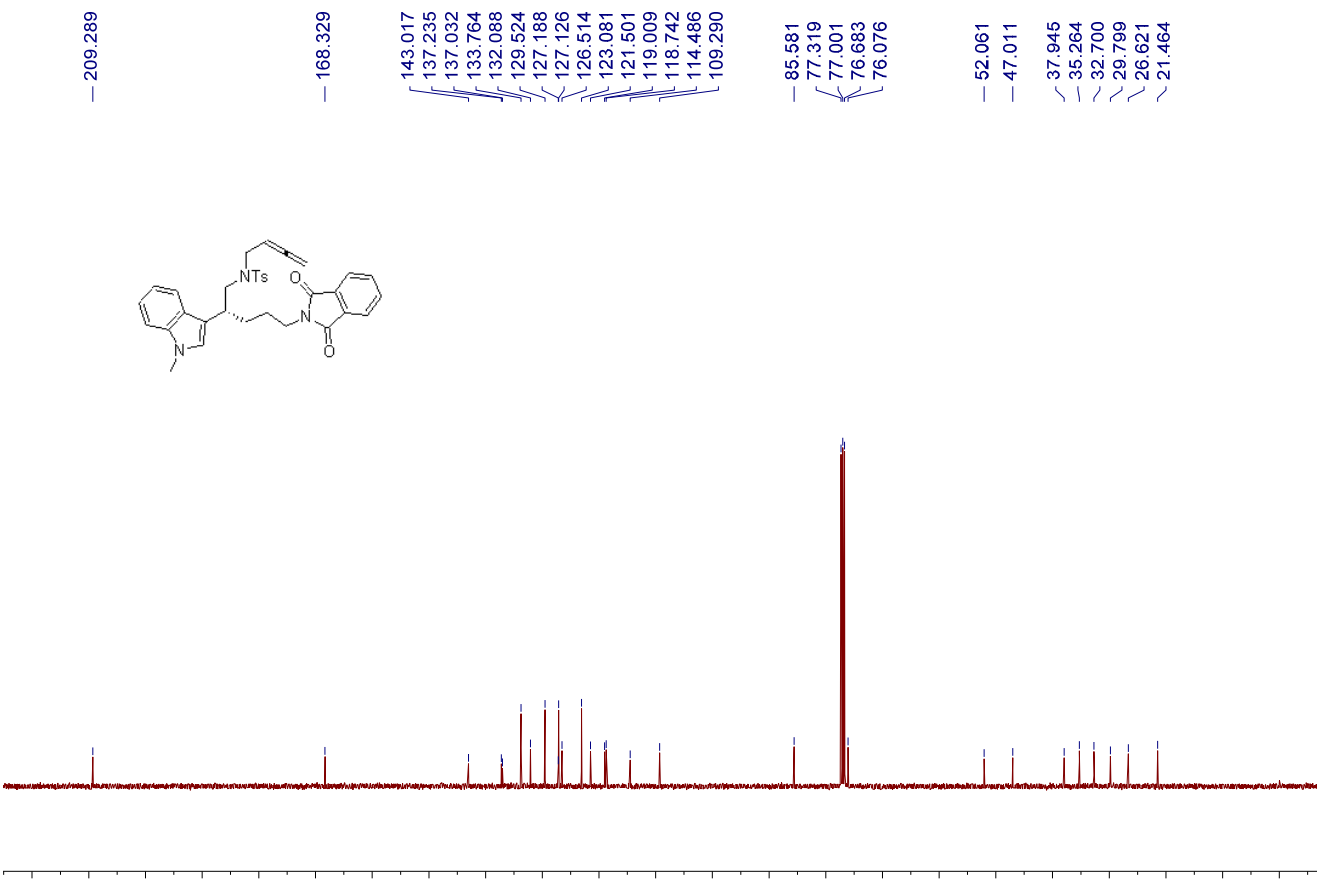
Translation: Chiralcel PC1 column [λ = 214 nm; eluent: CO_2 / MeOH = 95/5; Flow rate: 2.20 mL/min; t_{minor} = 17.44 min, t_{major} = 14.00 min; ee% = 98%].

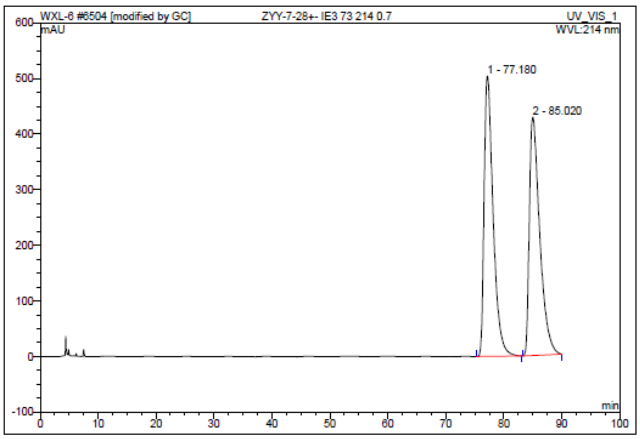


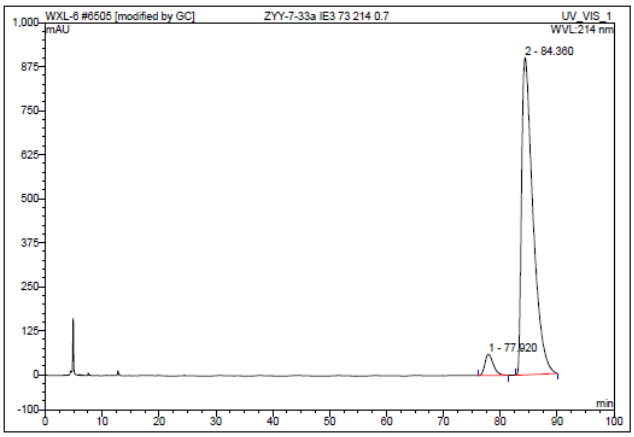
(*R*)-*N*-(buta-2,3-dien-1-yl)-*N*-(5-(1,3-dioxoisoindolin-2-yl)-2-(1-methyl-1*H*-indol-3-yl)pentyl)-4-methylbenzenesulfonamide 1y

A white solid, 42% yield (23.2 mg). M.p.: 88-91 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.61-1.79 (m, 3H), 1.91-2.00 (m, 1H), 2.38 (s, 3H), 3.23-3.35 (m, 2H), 3.49-3.65 (m, 3H), 3.67-3.73 (m, 4H), 3.81-3.87 (m, 1H), 4.60-4.66 (m, 2H), 4.70-4.78 (m, 1H), 6.85 (s, 1H), 6.99-7.04 (m, 1H), 7.14-7.24 (m, 4H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.66-7.69 (m, 2H), 7.78-7.81 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 26.6, 29.8, 32.7, 35.3, 37.9, 47.0, 52.1, 76.1, 85.6, 109.3, 114.5, 118.7, 119.0, 121.5, 123.1, 126.5, 127.1, 127.2, 129.5, 132.1, 133.8, 137.0, 137.2, 143.0, 168.3, 209.3. IR (CH_2Cl_2) ν 3242, 2933, 1953, 1706, 1395, 1185, 1155, 1090, 852, 741, 656 cm^{-1}. MS (ESI) *m/z* (%): 568.22 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{33}H_{34}N_3O_4S^{+1}$ $[M+H]^+$ requires 568.2265, found: 568.2257. Enantiomeric excess was determined by HPLC with a Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 77.92 min, t_{major} = 84.36 min; ee% = 91%; $[\alpha]_D^{25}$ = 36.0 (c 1.1, CH_2Cl_2)].


7.804 7.796 7.790 7.783 7.690 7.682 7.676 7.668 7.614 7.593 7.536 7.517 7.240 7.213 7.192 7.169 7.148 7.034 7.015 6.995 6.850
4.773 4.756 4.739 4.722 4.705 4.659 4.652 4.642 4.609 3.869 3.851 3.830 3.813 3.726 3.697 3.679 3.643 3.624 3.606 3.552 3.532 3.519 3.499 3.345 3.328 3.296 3.264 3.237 2.379 2.000 1.974 1.949 1.919 1.785 1.747 1.614 -0.000
NTs
O
N
O
N
1.85 1.87 1.97 0.99 3.90 1.01 0.96 1.00 1.94 1.00 4.06 3.09 2.06 3.00 1.04 2.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


209.289
168.329
143.017 137.235 137.032 133.764 132.088 129.524 127.188 127.126 126.514 123.081 121.501 119.009 118.742 114.486 109.290
85.581 77.319 77.001 76.683 76.076
52.061
47.011
37.945 35.264 32.700 29.799 26.621 21.464
NTs
O
N
O
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



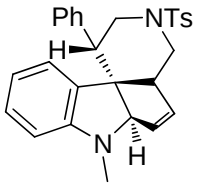


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	77.18	n.a.	504.083	910.030	50.55	n.a.	BMB
2	85.02	n.a.	428.538	890.212	49.45	n.a.	BMB
Total:			932.621	1800.242	100.00	0.000	

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	77.92	n.a.	60.561	102.862	4.70	n.a.	BMB
2	84.36	n.a.	901.414	2085.839	95.30	n.a.	BMB
Total:			961.975	2188.700	100.00	0.000	

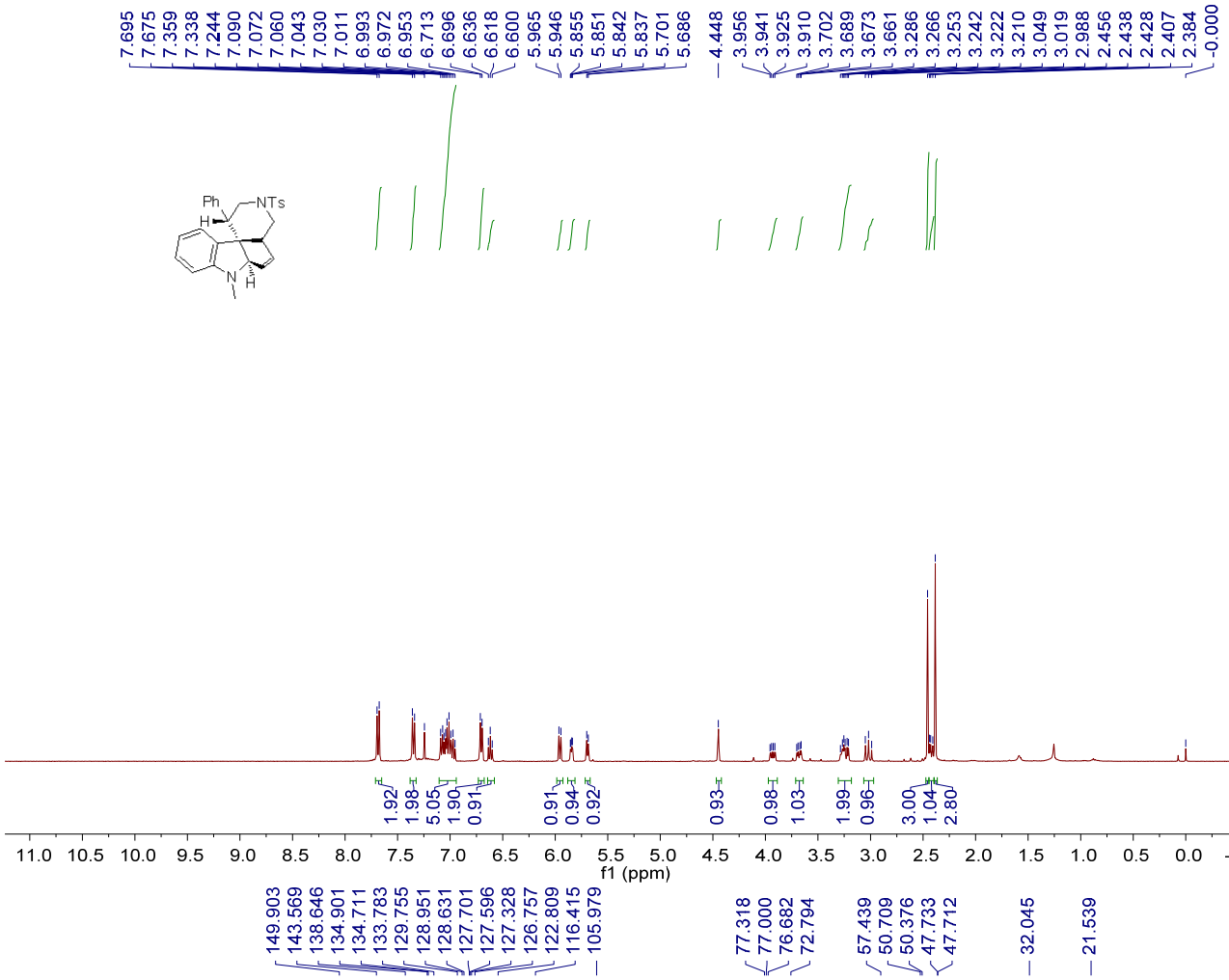
Translation: Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 77.92 min, t_{major} = 84.36 min; ee% = 91%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).

7. Characterization and spectra charts for compounds 2.



(1*S*,4a*R*,6a*R*,11b*S*)-7-methyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclo penta[1,2-*b*]indole 2a

A white solid, 49% yield (22.3 mg). M.p.: 183-186 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.38 (s, 3H), 2.40-2.44 (m, 1H), 2.46 (s, 3H), 3.02 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.21-3.29 (m, 2H), 3.68 (dd, *J* = 11.2, 4.8 Hz, 1H), 3.93 (dd, *J* = 12.4, 6.0 Hz, 1H), 4.45 (s, 1H), 5.69 (d, *J* = 6.0 Hz, 1H), 5.83-5.86 (m, 1H), 5.95 (d, *J* = 7.6 Hz, 1H), 6.60-6.64 (m, 1H), 6.69-6.72 (m, 2H,), 6.95-7.09 (m, 5H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 32.0, 47.71, 47.73, 50.4, 50.7, 57.4, 72.8, 106.0, 116.4, 122.8, 126.8, 127.3, 127.6, 127.7, 128.6, 129.0, 129.8, 133.8, 134.7, 134.9, 138.6, 143.6, 149.9. IR (CH_2Cl_2) ν 3054, 2920, 2852, 1604, 1494, 1339, 1161, 937, 860, 733, 662 cm^{-1}. MS (ESI) *m/z* (%): 457.19 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{28}H_{29}N_2O_2S^{+1}[M+H]^+$ requires 457.1944, found: 457.1940. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70 mL/min; t_{minor} = 41.05 min, t_{major} = 37.92 min; ee% = 91%; $[\alpha]_D^{25}$ = -162.9 (c 0.1, CH_2Cl_2)].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7.030
7.011
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6.972
6.953
6.713
6.696
6.636
6.618
6.600
5.965
5.946
5.855
5.851
5.842
5.837
5.701
5.686
4.448
3.956
3.941
3.925
3.910
3.702
3.689
3.673
3.661
3.286
3.266
3.253
3.242
3.222
3.210
3.049
3.019
2.988
2.456
2.438
2.428
2.407
2.384
-0.000
Ph
NTs
H
N
H
1.92
1.98
5.05
1.90
0.91
0.91
0.94
0.92
0.93
0.98
1.03
1.99
0.96
3.00
1.04
2.80
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
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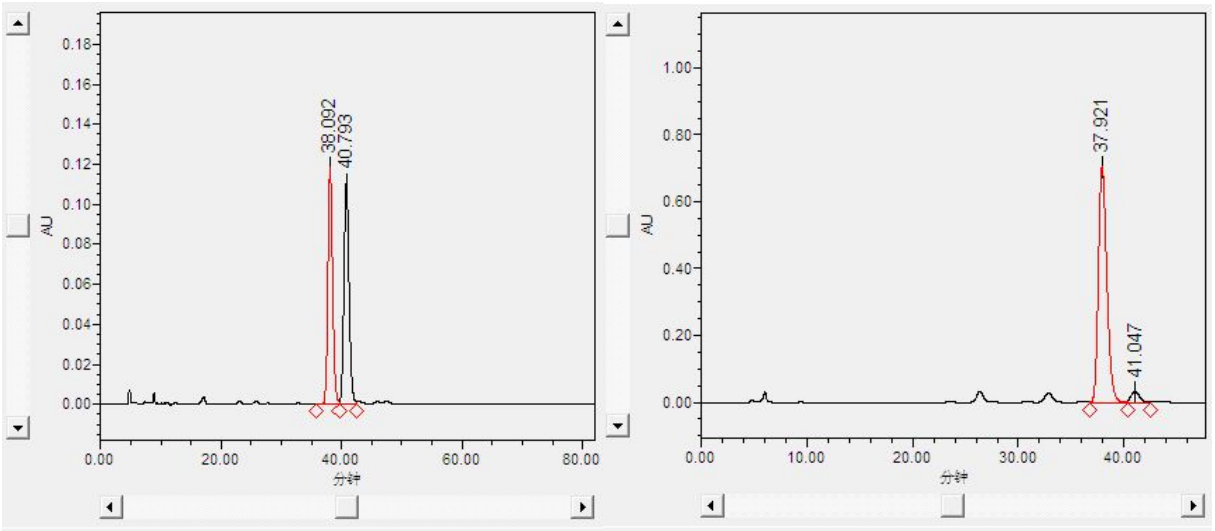
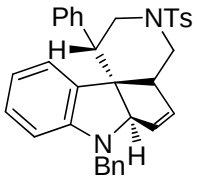
143.569
138.646
134.901
134.711
133.783
129.755
128.951
128.631
127.701
127.596
127.328
126.757
122.809
116.415
105.979
77.318
77.000
76.682
72.794
57.439
50.709
50.376
47.733
47.712
32.045
21.539
Ph
NTs
H
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		38.092	6562538	50.21	118639	VV	35.783	39.617
2		40.793	6507006	49.79	110760	VV	39.617	42.417

	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		37.921	39133451	95.48	705536	Vv	36.717	40.367
2		41.047	1853650	4.52	32263	vV	40.367	42.483

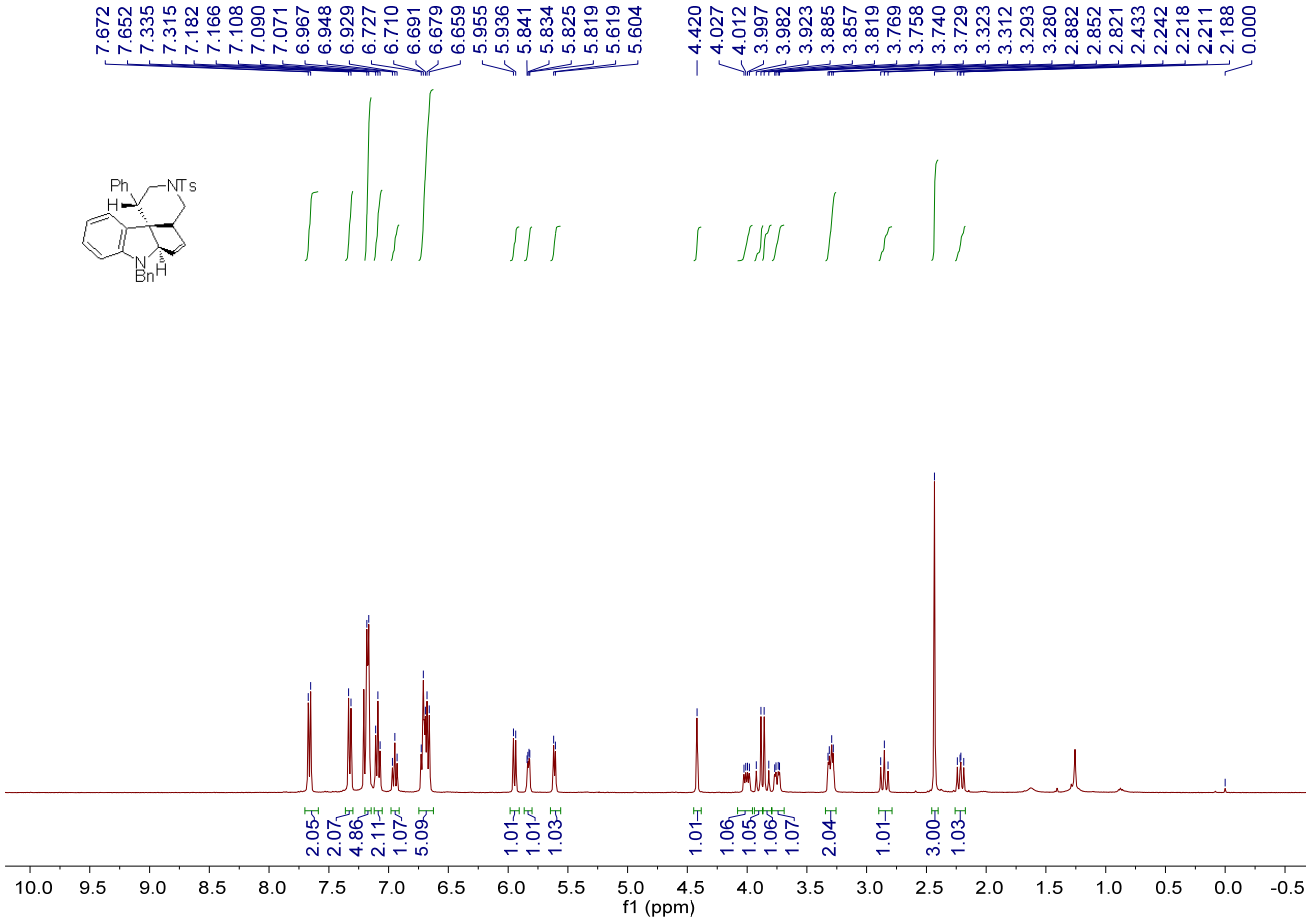
Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70 mL/min; t_{minor} = 41.05 min, t_{major} = 37.92 min; ee% = 91%].

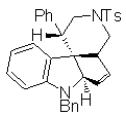


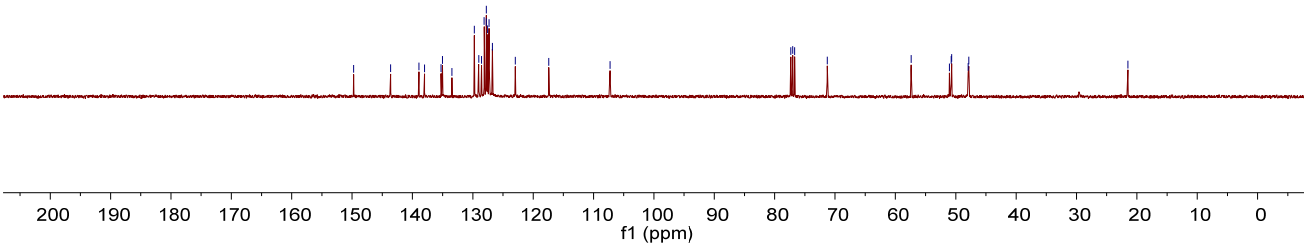
(1*S*,4a*R*,6a*R*,11b*S*)-7-benzyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 2b

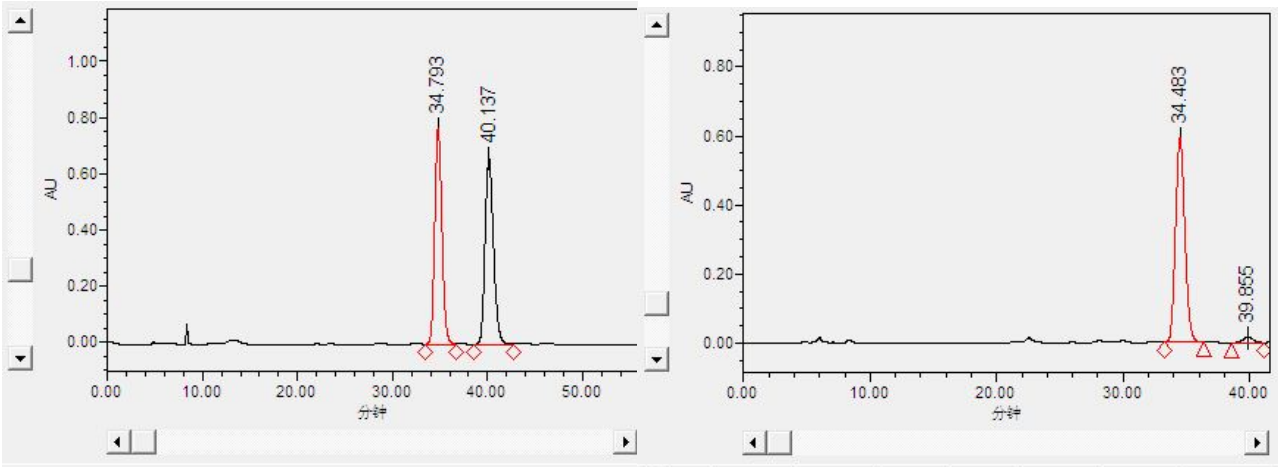
A white solid, 34% yield (18.1 mg). M.p.: 117-120 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.21 (dd, *J* = 12.0, 9.6 Hz, 1H), 2.43 (s, 3H), 2.85 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.28-3.33 (m, 2H), 3.75 (dd, *J* = 11.6, 4.4 Hz, 1H), 3.84 (d, *J* = 15.2 Hz, 1H), 3.90 (d, *J* = 15.2 Hz, 1H), 4.00 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.42 (s, 1H), 5.61 (d, *J* = 6.0 Hz, 1H), 5.83 (dd, *J* = 6.0, 2.4 Hz, 1H), 5.94 (d, *J* = 7.6 Hz, 1H), 6.65-6.73 (m, 5H), 6.92-6.97 (m, 1H), 7.07-7.11 (m, 2H), 7.16-7.19 (m, 5H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 47.8, 47.9, 50.7, 50.8, 51.1, 57.4, 71.3, 107.3, 117.4, 123.0, 126.7, 127.3, 127.5, 127.7, 127.8, 128.1, 128.6, 129.0, 129.8, 133.5, 135.0, 135.3, 138.0, 138.9, 143.6, 149.7. IR (CH_2Cl_2) ν 3058, 2920, 1600, 1484, 1344, 1162, 1089, 936, 859, 729, 659 cm^{-1}. MS (ESI) *m/z* (%): 533.22 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{34}H_{33}N_2O_2S^{+1}[M+H]^+$ requires 533.2257, found: 533.2251. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70

mL/min; t_{minor} = 39.86 min, t_{major} = 34.48 min; ee% = 94%; $[\alpha]_D^{25}$ = -129.4 (c 0.4, CH_2Cl_2)].





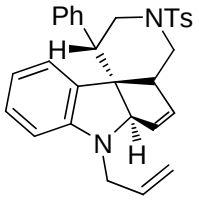




	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		34.793	40703197	49.86	769500	VV	33.467	36.650
2		40.137	40935313	50.14	663426	VV	38.550	42.717

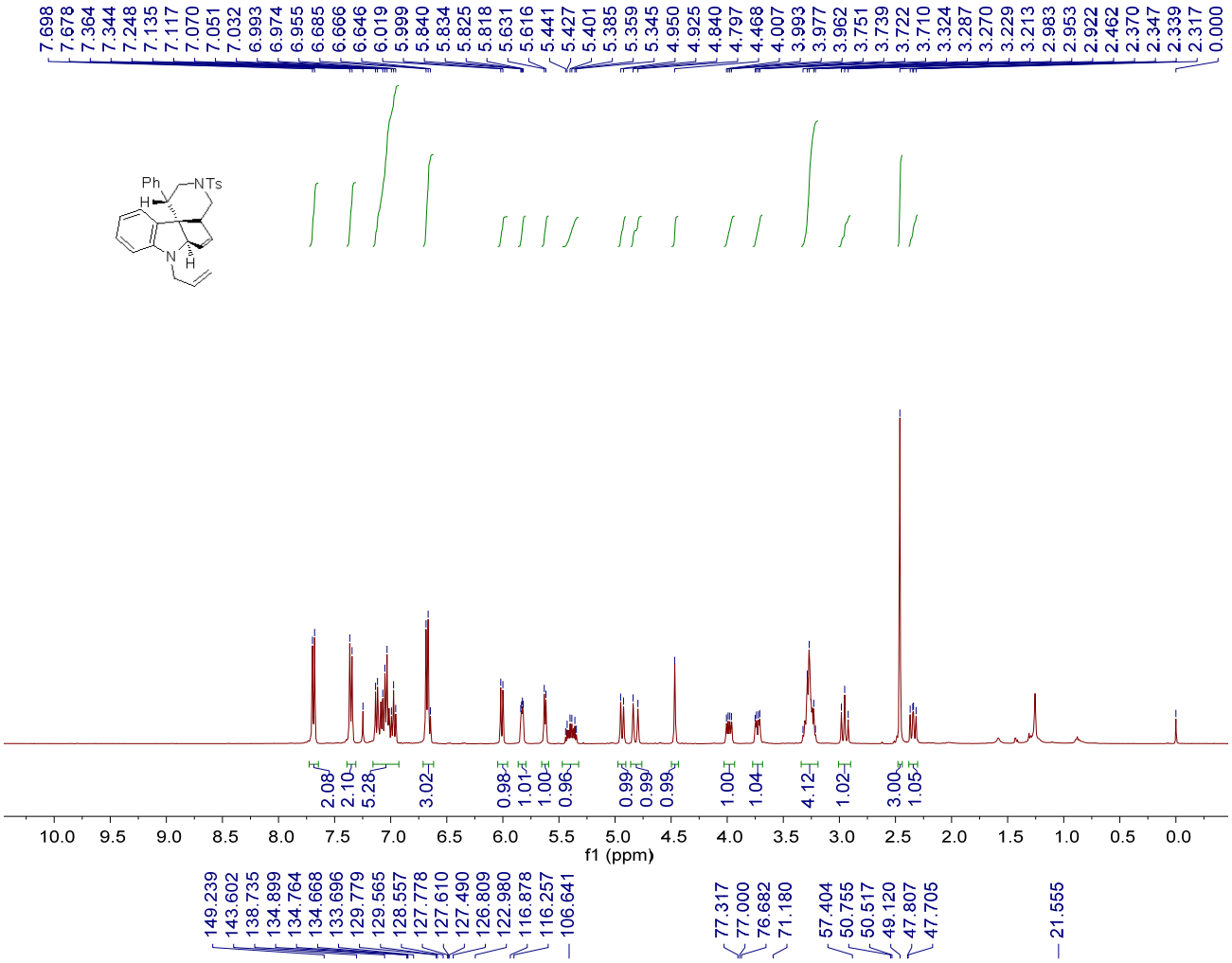
	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		34.483	30325837	97.02	592462	VB	33.283	36.383
2		39.855	930795	2.98	15877	BV	38.600	41.117

Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70 mL/min; t_{minor} = 39.86 min, t_{major} = 34.48 min; ee% = 94%].



(1*S*,4a*R*,6a*R*,11b*S*)-7-allyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 2c

A white solid, 45% yield (21.7 mg). M.p.: 107-110 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.34 (dd, *J* = 12.0, 8.8 Hz, 1H), 2.46 (s, 3H), 2.95 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.21-3.33 (m, 4H), 3.73 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.98 (dd, *J* = 12.0, 5.6 Hz, 1H), 4.47 (s, 1H), 4.82 (d, *J* = 17.2 Hz, 1H), 4.94 (d, *J* = 10.0 Hz, 1H), 5.34-5.45 (m, 1H), 5.62 (d, *J* = 6.0 Hz, 1H), 5.83 (dd, *J* = 6.0, 2.4 Hz, 1H), 6.01 (d, *J* = 8.0 Hz, 1H), 6.64-6.69 (m, 3H), 6.95-7.14 (m, 5H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 47.7, 47.8, 49.1, 50.5, 50.8, 57.4, 71.2, 106.6, 116.3, 116.9, 123.0, 126.8, 127.5, 127.6, 127.8, 128.6, 129.6, 129.8, 133.7, 134.7, 134.8, 134.9, 138.7, 143.6, 149.2. IR (CH_2Cl_2) ν 3053, 2921, 2850, 1601, 1485, 1343, 1161, 1089, 934, 858, 730, 659 cm^{-1}. MS (ESI) *m/z* (%): 483.20 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{30}H_{31}N_2O_2S^{+1}[M+H]^+$ requires 483.2101, found: 483.2092. Enantiomeric excess was determined by HPLC with a Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 16.34 min, t_{major} = 14.46 min; ee% = 94%; $[\alpha]_D^{25}$ = -102.5 (c 0.08, CH_2Cl_2)].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6.646
6.019
5.999
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5.834
5.825
5.818
5.631
5.616
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5.427
5.401
5.385
5.359
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3.287
3.270
3.229
3.213
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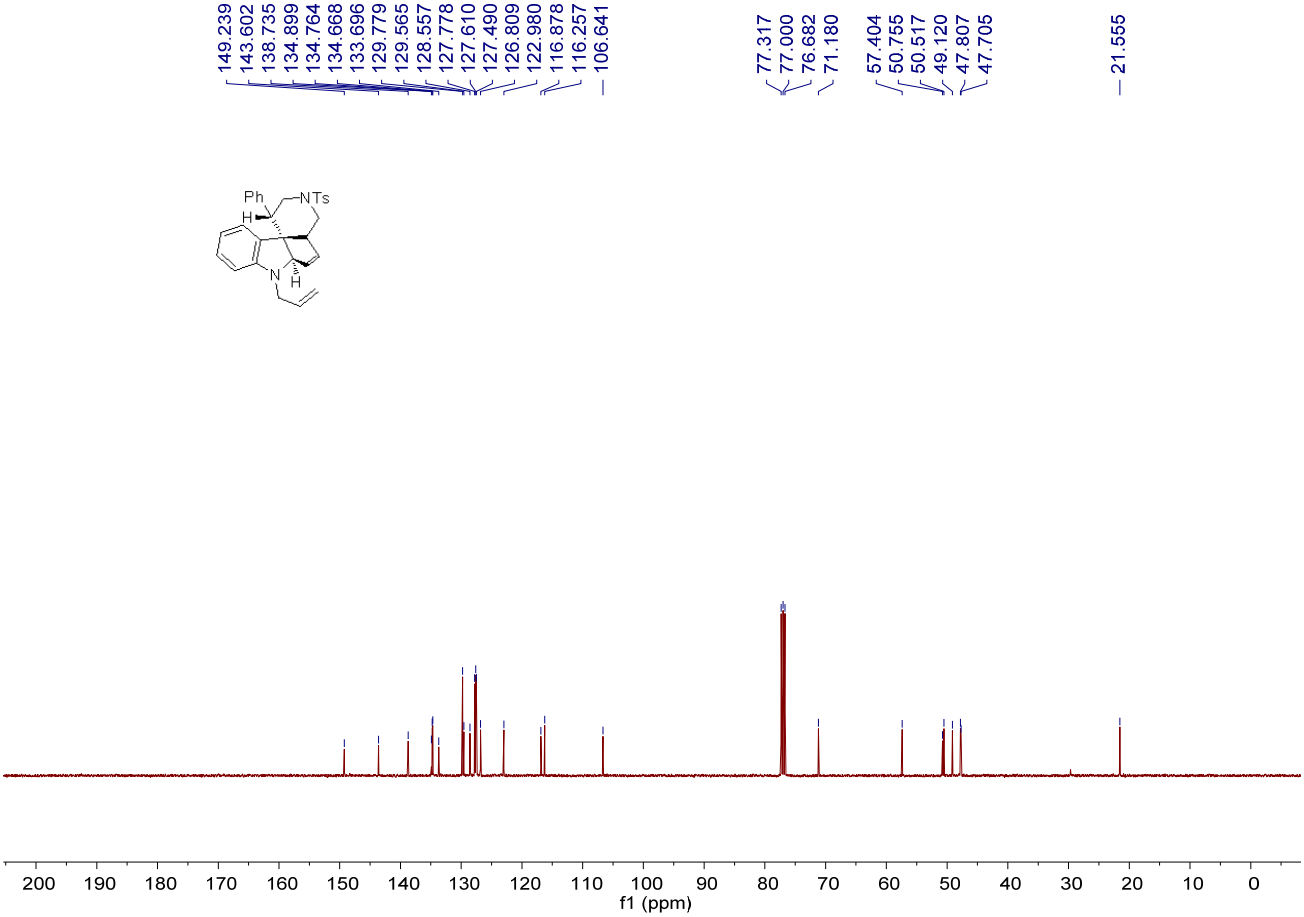
2.922
2.462
2.370
2.347
2.339
2.317
0.000
Ph
NTs
H
N
H
2.08
2.10
5.28
3.02
0.98
1.01
1.00
0.96
0.99
0.99
0.99
1.00
1.04
4.12
1.02
3.00
1.05
f1 (ppm)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77.000
76.682
71.180
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47.807
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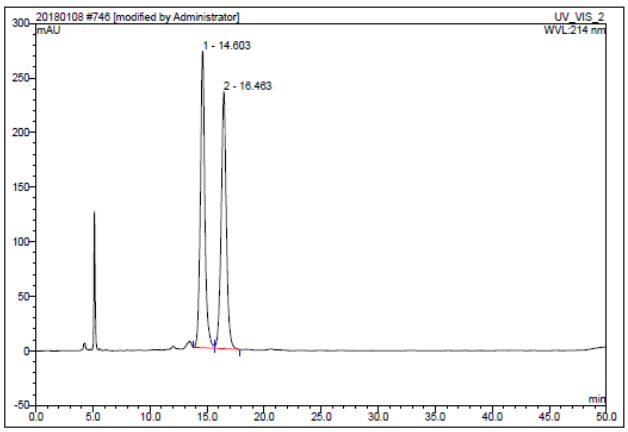
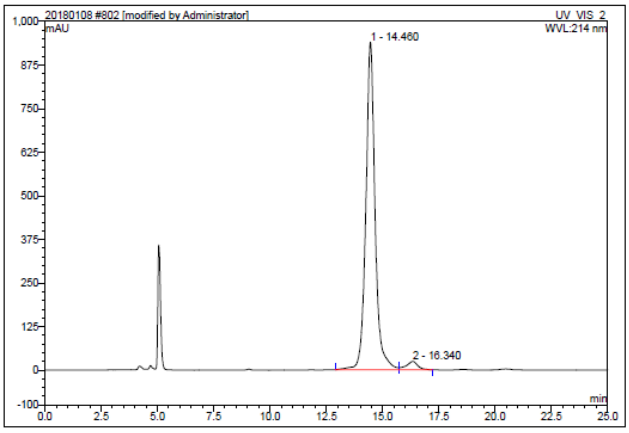
Ph
NTs
H
N
H
f1 (ppm)

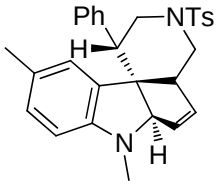


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.60	n.a.	271.741	124.854	50.26	n.a.	BM *
2	16.46	n.a.	235.630	123.571	49.74	n.a.	MB*
Total:			507.371	248.425	100.00	0.000	



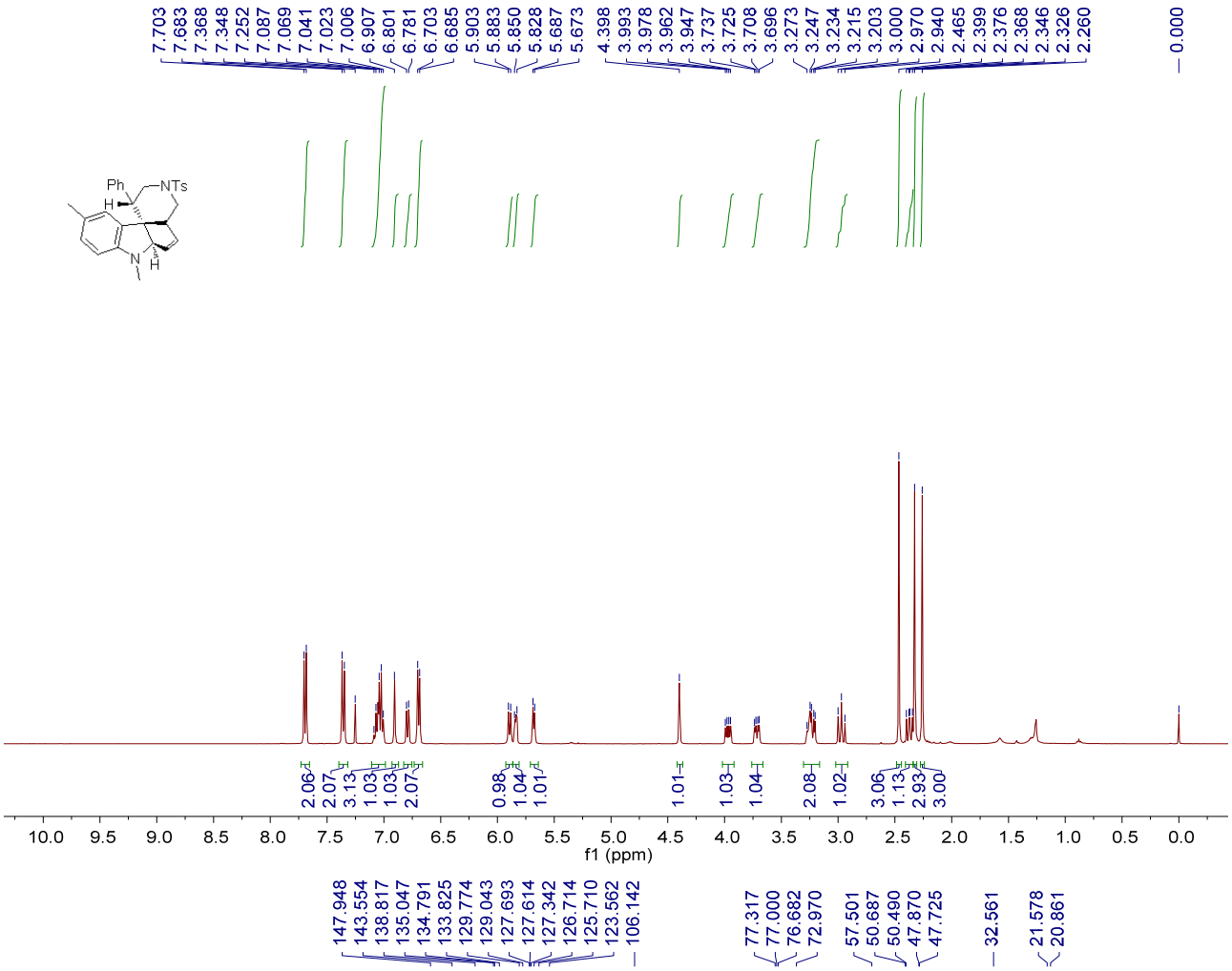
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.46	n.a.	939.600	446.250	96.94	n.a.	BM
2	16.34	n.a.	23.809	14.063	3.06	n.a.	MB
Total:			963.409	460.313	100.00	0.000	

Translation: Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 16.34 min, t_{major} = 14.46 min; ee% = 94%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(1*S*,4a*R*,6a*R*,11b*S*)-7,10-dimethyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 2d

A white solid, 49% yield (23.0 mg). M.p.: 89-92 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.26 (s, 3H), 2.33 (s, 3H), 2.37 (dd, *J* = 12.0, 8.8 Hz, 1H), 2.47 (s, 3H), 2.97 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.20-3.28 (m, 2H), 3.71 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.97 (dd, *J* = 12.4, 6.0 Hz, 1H), 4.40 (s, 1H), 5.68 (d, *J* = 5.6 Hz, 1H), 5.82-5.85 (m, 1H), 5.89 (d, *J* = 8.0 Hz, 1H), 6.68-6.71 (m, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.91 (s, 1H), 7.00-7.09 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.9, 21.6, 32.6, 47.7, 47.9, 50.5, 50.7, 57.5, 73.0, 106.1, 123.6, 125.7, 126.7, 127.3, 127.6, 127.7, 129.0, 129.8, 133.8, 134.8, 135.0, 138.8, 143.6, 147.9. IR (CH_2Cl_2) ν 2962, 2852, 1496, 1341, 1259, 1016, 865, 795, 696 cm^{-1}. MS (ESI) *m/z* (%): 471.20 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{29}H_{31}N_2O_2S^{+1}[M+H]^+$ requires 471.2101, found: 471.2092. Enantiomeric excess was determined by HPLC with a Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 50/50; Flow rate: 0.70 mL/min; t_{minor} = 7.65 min, t_{major} = 7.02 min; ee% = 92%; $[\alpha]_D^{25}$ = -132.5 (c 0.12, CH_2Cl_2)].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7.023
7.006
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6.703
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5.903
5.883
5.850
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5.673
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3.993
3.978
3.962
3.947
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3.725
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3.696
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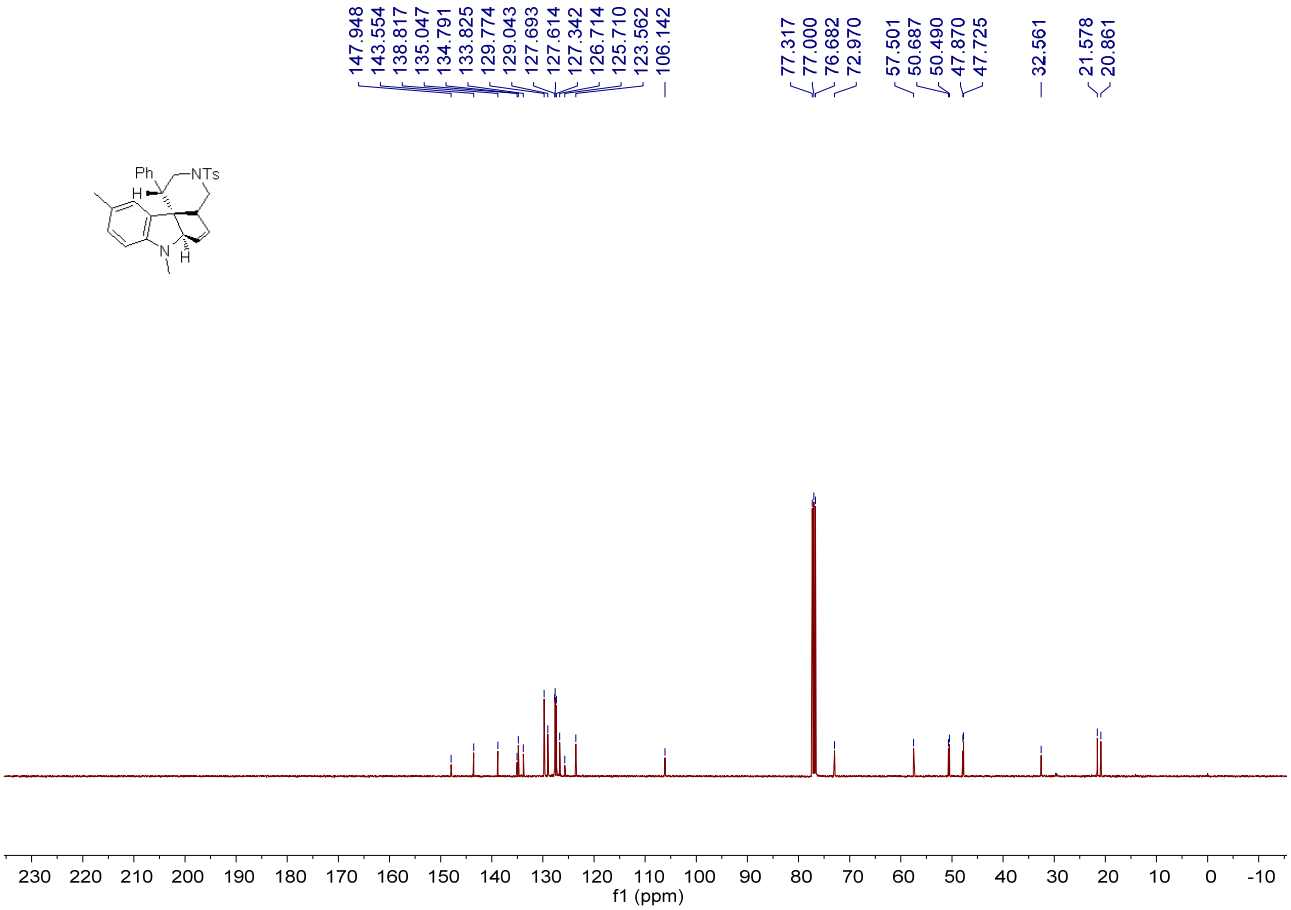
3.215
3.203
3.000
2.970
2.940
2.465
2.399
2.376
2.368
2.346
2.326
2.260
0.000
Ph
NTs
H
N
H
2.06
2.07
3.13
1.03
1.03
2.07
0.98
1.04
1.01
1.01
1.03
1.04
2.08
1.02
3.06
1.13
2.93
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


147.948
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129.774
129.043
127.693
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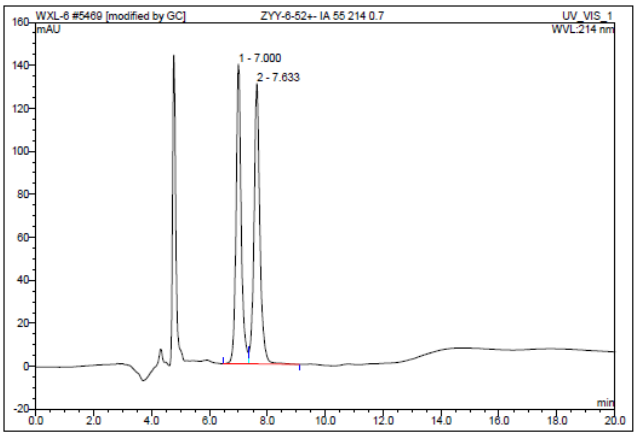
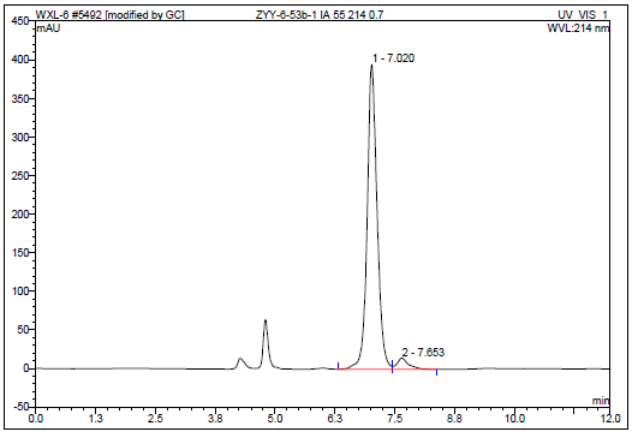
123.562
106.142
77.317
77.000
76.682
72.970
57.501
50.687
50.490
47.870
47.725
32.561
21.578
20.861
Ph
NTs
H
N
H
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

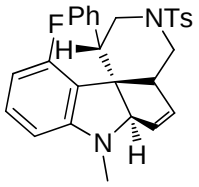




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.00	n.a.	139.426	28.740	48.30	n.a.	BM *
2	7.63	n.a.	130.503	30.761	51.70	n.a.	MB*
Total:			269.928	59.501	100.00	0.000	

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.02	n.a.	394.772	95.078	95.97	n.a.	BM
2	7.65	n.a.	14.413	3.994	4.03	n.a.	MB
Total:			409.186	99.071	100.00	0.000	

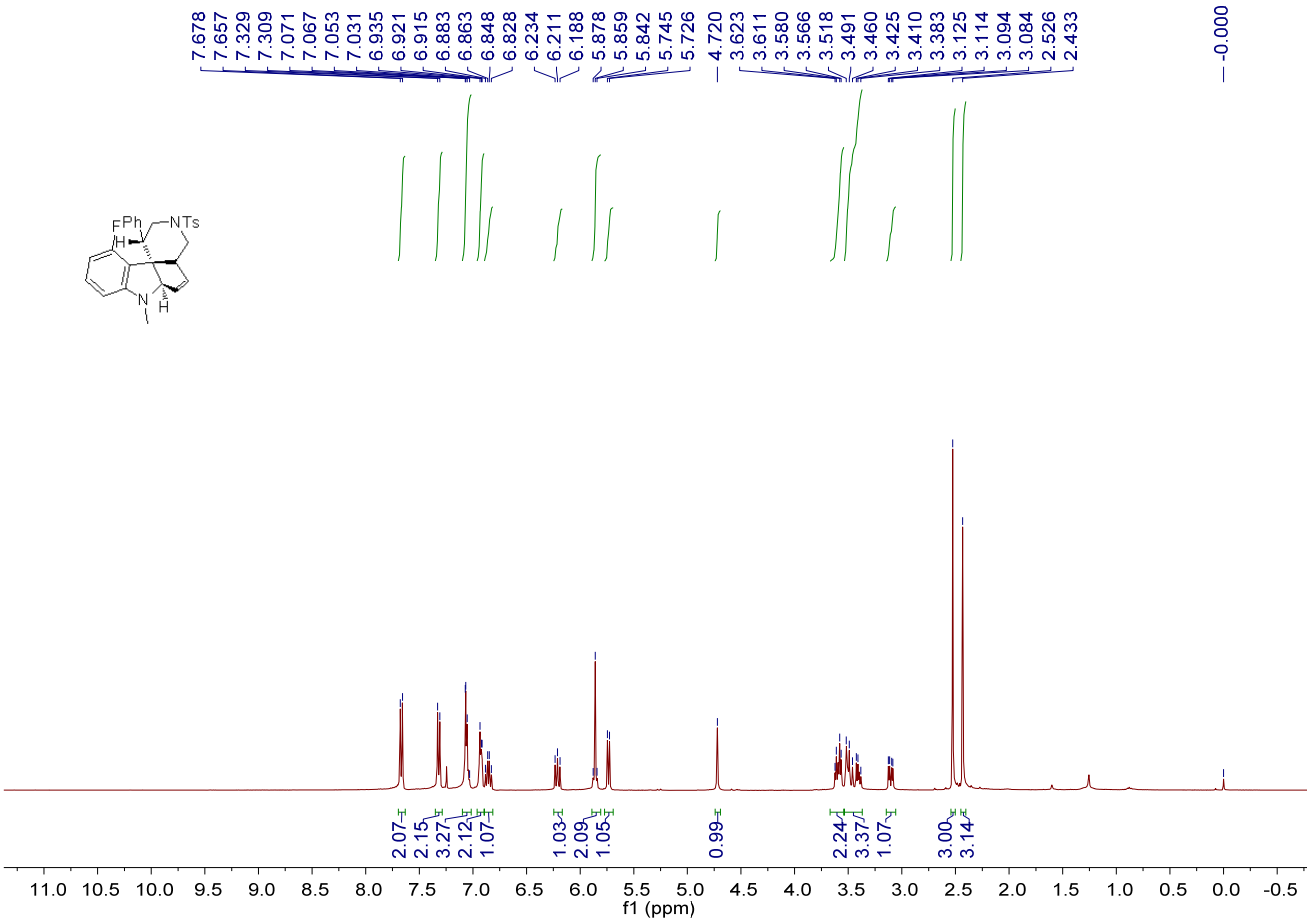
Translation: Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 50/50; Flow rate: 0.70 mL/min; t_{minor} = 7.65 min, t_{major} = 7.02 min; ee% = 92%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).

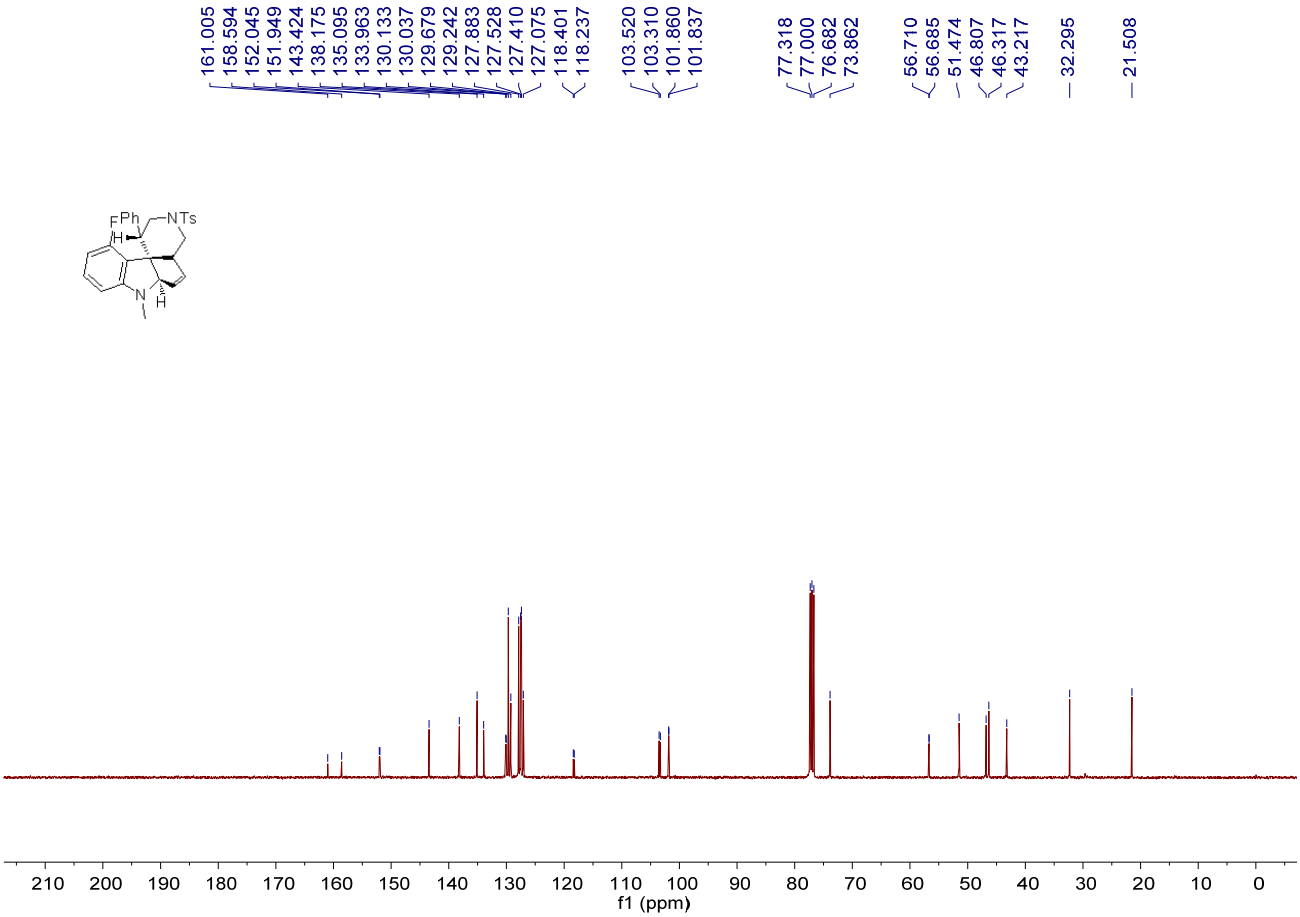


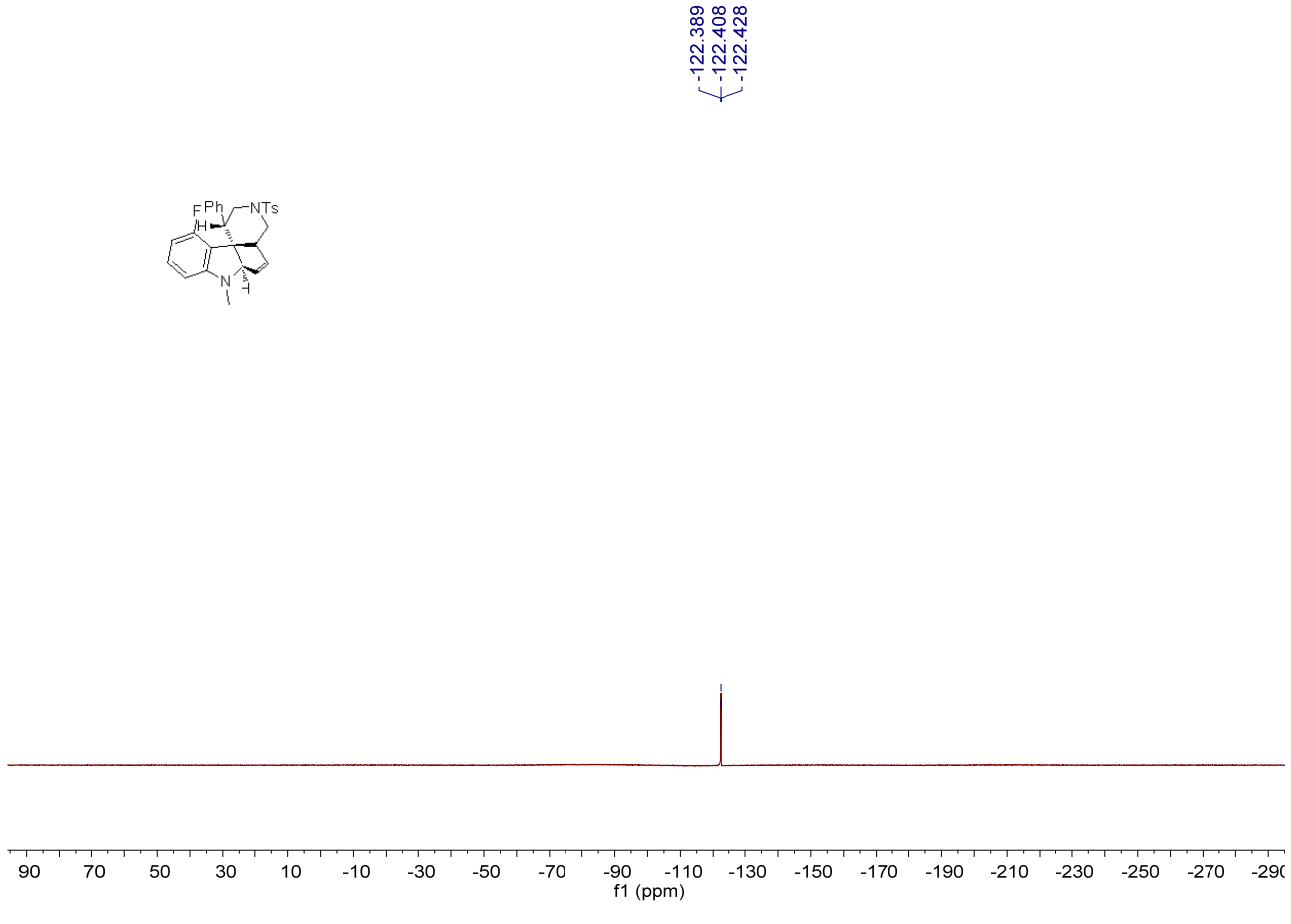
(1*S*,4a*R*,6a*R*,11b*S*)-11-fluoro-7-methyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 2e

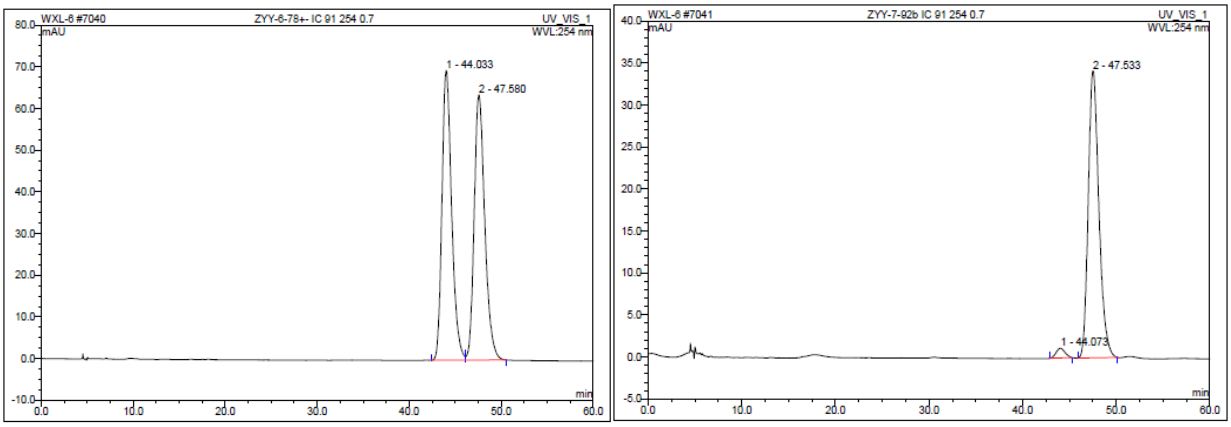
A white solid, 46% yield (21.9 mg). M.p.: 176-179 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.43 (s, 3H), 2.53 (s, 3H), 3.10 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.38-3.52 (m, 3H), 3.56-3.63 (m, 2H), 4.72 (s, 1H), 5.73 (d, *J* = 8.0 Hz, 1H), 5.84-5.88 (m, 2H), 6.18-6.24 (m, 1H), 6.82-6.89 (m, 1H), 6.91-6.94 (m, 2H), 7.03-7.08 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 32.3, 43.2, 46.3, 46.8, 51.5, 56.69, 56.71, 73.9, 101.8 (d, *J* = 2.3 Hz), 103.4 (d, *J* = 21.0 Hz), 118.3 (d, *J* = 16.4 Hz), 127.1, 127.4, 127.5, 127.9, 129.2, 129.7, 130.1 (d, *J* = 9.6 Hz), 134.0, 135.1, 138.2, 143.4, 152.0 (d, *J* = 9.6 Hz), 159.8 (d, *J* = 241.1 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -122.4. IR (CH_2Cl_2) ν 3059, 2901, 1913, 1627, 1467, 1159, 1087, 958, 860, 782, 661 cm^{-1}. MS (ESI) *m/z* (%): 475.18 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{28}H_{28}N_2O_2FS^{+1}$ $[M+H]^+$ requires 475.1850, found: 475.1841. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 44.07 min,

t_{major} = 47.53 min; ee% = 95%; $[\alpha]_D^{25}$ = -62.3 (c 0.10, CH_2Cl_2)].




161.005
158.594
152.045
151.949
143.424
138.175
135.095
133.963
130.133
130.037
129.679
129.242
127.883
127.528
127.410
127.075
118.401
118.237
103.520
103.310
101.860
101.837
77.318
77.000
76.682
73.862
56.710
56.685
51.474
46.807
46.317
43.217
32.295
21.508
F
Ph
NTs
H
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

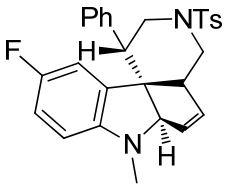

-122.389
-122.408
-122.428
F
Ph
NTs
H
N
H
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	44.03	n.a.	69.525	84.958	49.96	n.a.	BM
2	47.58	n.a.	63.664	85.089	50.04	n.a.	MB
Total:			133.189	170.047	100.00	0.000	

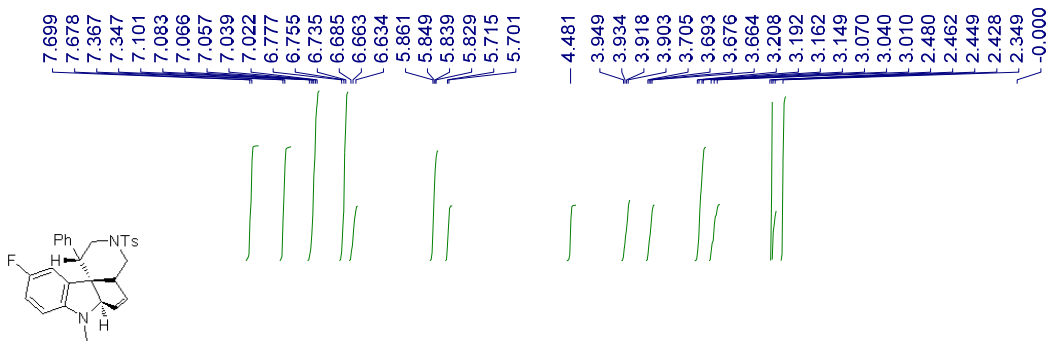
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	44.07	n.a.	1.150	1.254	2.71	n.a.	BMB
2	47.53	n.a.	34.163	45.055	97.29	n.a.	BMB
Total:			35.313	46.309	100.00	0.000	

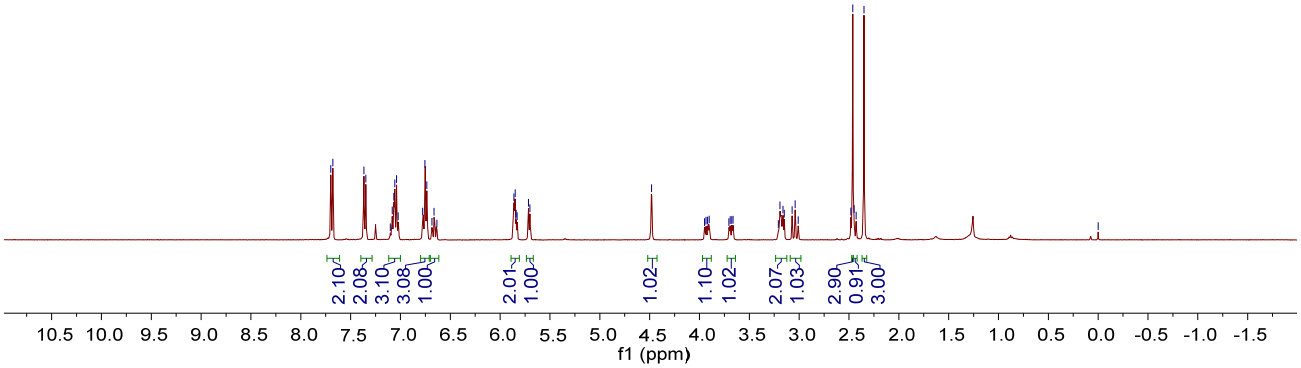
Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 44.07 min, t_{major} = 47.53 min; ee% = 95%].



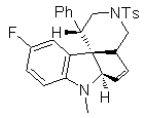
(1*S*,4a*R*,6a*R*,11b*S*)-10-fluoro-7-methyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 2f

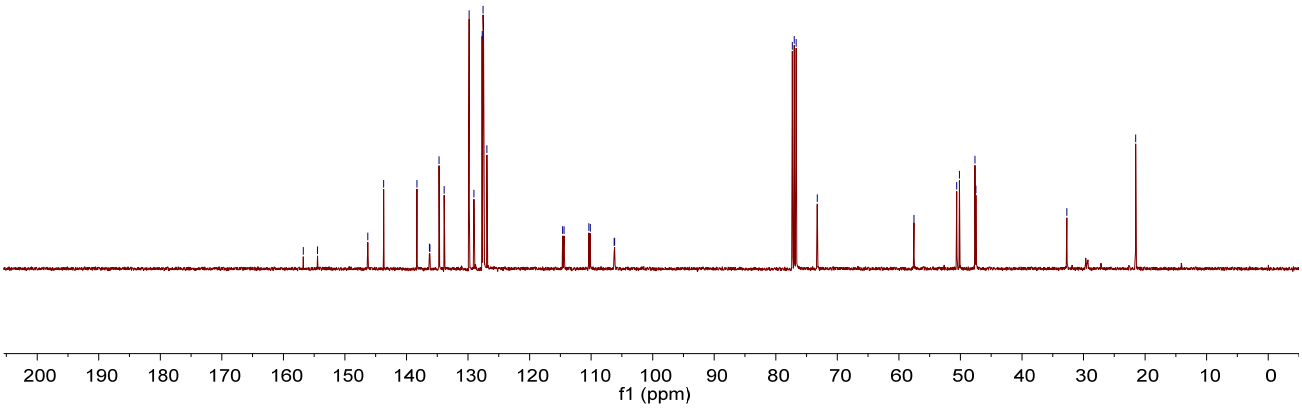
A white solid, 49% yield (23.3 mg). M.p.: 142-145 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.35 (s, 3H), 2.45 (dd, *J* = 12.0, 8.8 Hz, 1H), 2.46 (s, 3H), 3.04 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.14-3.21 (m, 2H), 3.68 (dd, *J* = 12.0, 4.8 Hz, 1H), 3.92 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.48 (s, 1H), 5.71 (d, *J* = 5.6 Hz, 1H), 5.82-5.87 (m, 2H), 6.63-6.69 (m, 1H), 6.73-6.78 (m, 3H), 7.02-7.11 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 32.7, 47.5, 47.6, 50.2, 50.6, 57.5, 73.3, 106.2 (d, *J* = 8.0 Hz), 110.2 (d, *J* = 23.8 Hz), 114.5 (d, *J* = 22.8 Hz), 126.9, 127.5, 127.6, 127.7, 129.0, 129.8, 133.9, 136.2 (d, *J* = 7.1 Hz), 138.3, 143.7, 146.3, 155.4 (d, *J* = 232.3 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -128.3. IR (CH_2Cl_2) ν 3029, 2920, 2849, 1646, 1492, 1337, 1164, 988, 960, 860, 771, 658 cm^{-1}. MS (ESI) *m/z* (%): 475.18 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{28}H_{28}N_2O_2FS^{+1}$ $[M+H]^+$ requires 475.1850, found: 475.1846. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70 mL/min; t_{minor} = 87.93 min, t_{major} = 53.11 min; ee% = 99%; $[\alpha]_D^{25}$ = -80.1 (c 0.20, CH_2Cl_2)].

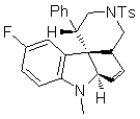

7.699
7.678
7.367
7.347
7.101
7.083
7.066
7.057
7.039
7.022
6.777
6.755
6.735
6.685
6.663
6.634
5.861
5.849
5.839
5.829
5.715
5.701
4.481
3.949
3.934
3.918
3.903
3.705
3.693
3.676
3.664
3.208
3.192
3.162
3.149
3.070
3.040
3.010
2.480
2.462
2.449
2.428
2.349
-0.000
Ph
NTs
F
H
N
H

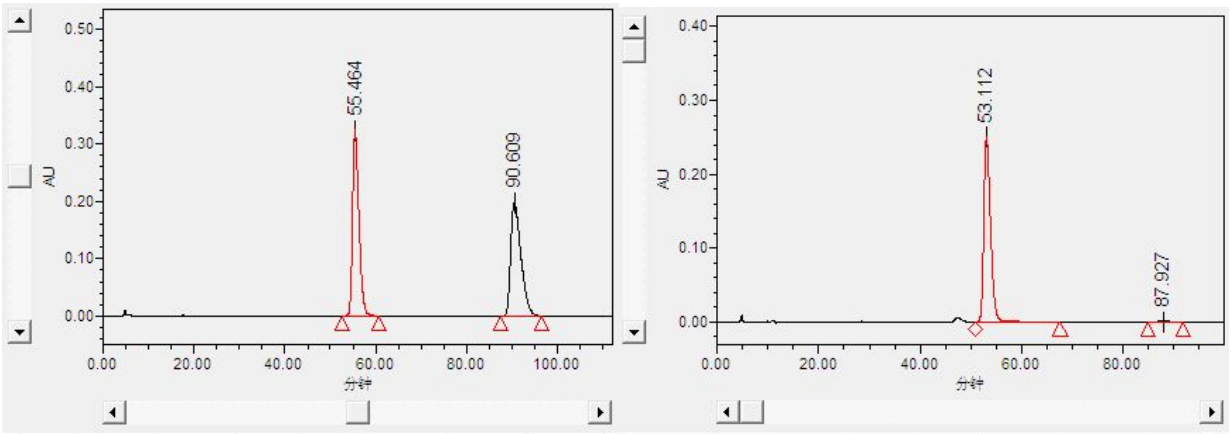

2.10
2.08
3.10
3.08
1.00
2.01
1.00
1.02
1.10
1.02
2.07
1.03
2.90
0.91
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


156.770
154.447
146.289
143.712
138.298
136.273
136.202
134.711
133.865
129.812
129.047
127.699
127.563
127.473
126.931
114.621
114.393
110.368
110.130
106.248
106.168
77.318
77.000
76.682
73.265
57.543
50.589
50.156
47.640
47.469
32.708
21.526


Ph
NTs
F
H
N
H


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

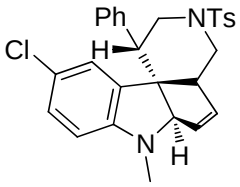




	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		55.464	31801376	50.22	324002	BB	52.633	60.767
2		90.609	31522197	49.78	198436	BB	87.650	96.767

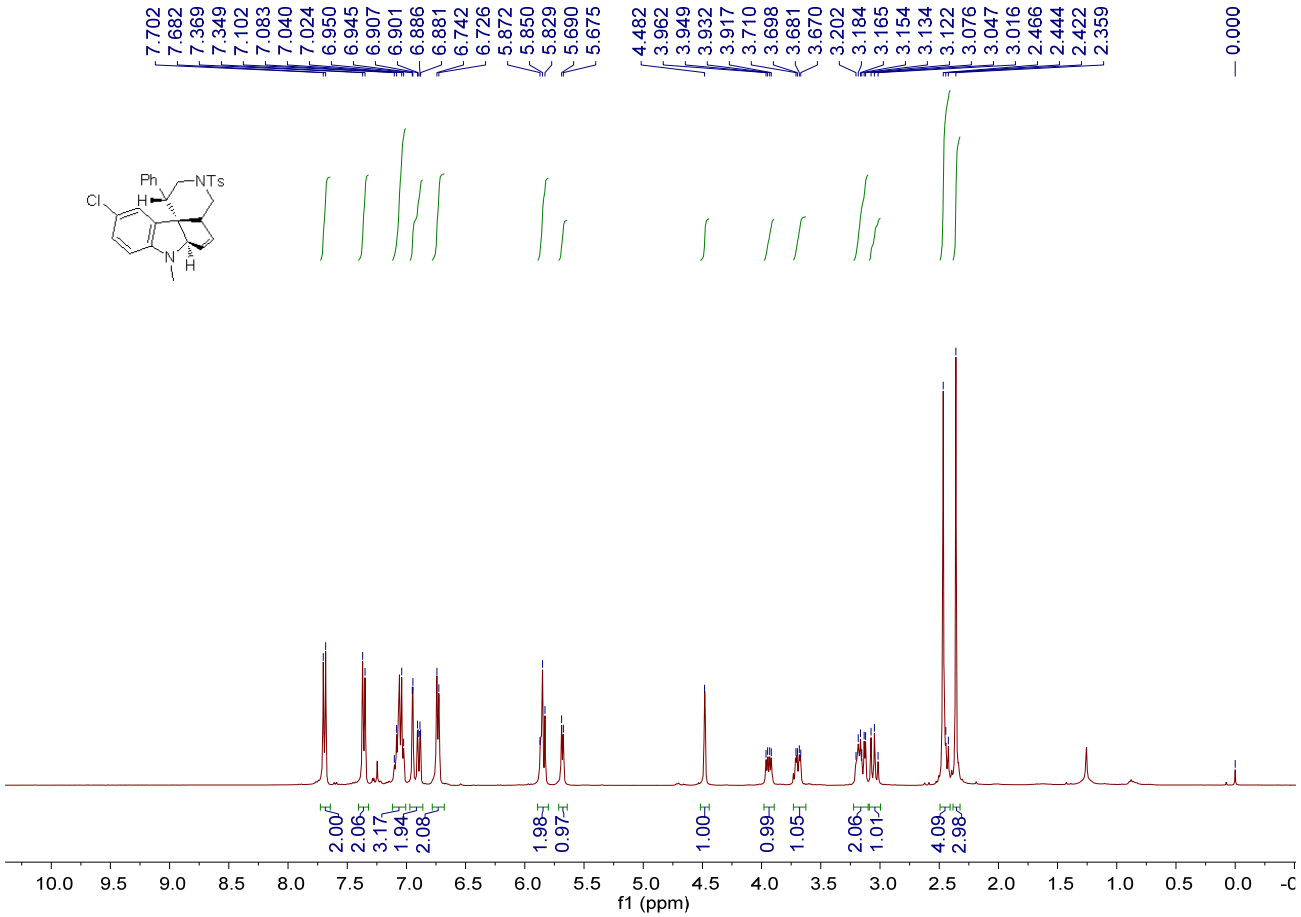
	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		53.112	23108359	99.38	250655	VB	50.950	67.683
2		87.927	144642	0.62	1011	BB	84.933	92.000

Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70 mL/min; t_{minor} = 87.93 min, t_{major} = 53.11 min; ee% = 99%].



(1*S*,4a*R*,6a*R*,11b*S*)-10-chloro-7-methyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 2g

A white solid, 45% yield (22.1 mg). M.p.: 183-186 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.36 (s, 3H), 2.42-2.47 (m, 4H), 3.05 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.12-3.21 (m, 2H), 3.69 (dd, *J* = 11.2, 4.4 Hz, 1H), 3.94 (dd, *J* = 12.4, 6.0 Hz, 1H), 4.48 (s, 1H), 5.68 (d, *J* = 6.0 Hz, 1H), 5.82-5.88 (m, 2H), 6.72-6.75 (m, 2H), 6.88-6.95 (m, 2H), 7.02-7.11 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 32.0, 47.5, 47.6, 50.2, 50.3, 57.5, 73.1, 106.6, 120.6, 123.0, 126.9, 127.48, 127.52, 127.6, 128.3, 128.7, 129.8, 134.0, 134.9, 136.7, 138.2, 143.7, 148.4. IR (CH_2Cl_2) ν 2923, 1597, 1492, 1342, 1153, 1058, 935, 814, 730, 658 cm^{-1}. MS (ESI) *m/z* (%): 491.15 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{28}H_{28}N_2O_2ClS^{+1}[M+H]^+$ requires 491.1555, found: 491.1552. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_{minor} = 45.89 min, t_{major} = 35.44 min; ee% = 98%; $[\alpha]_D^{25}$ = -111.1 (c 0.12, CH_2Cl_2)].


7.702
7.682
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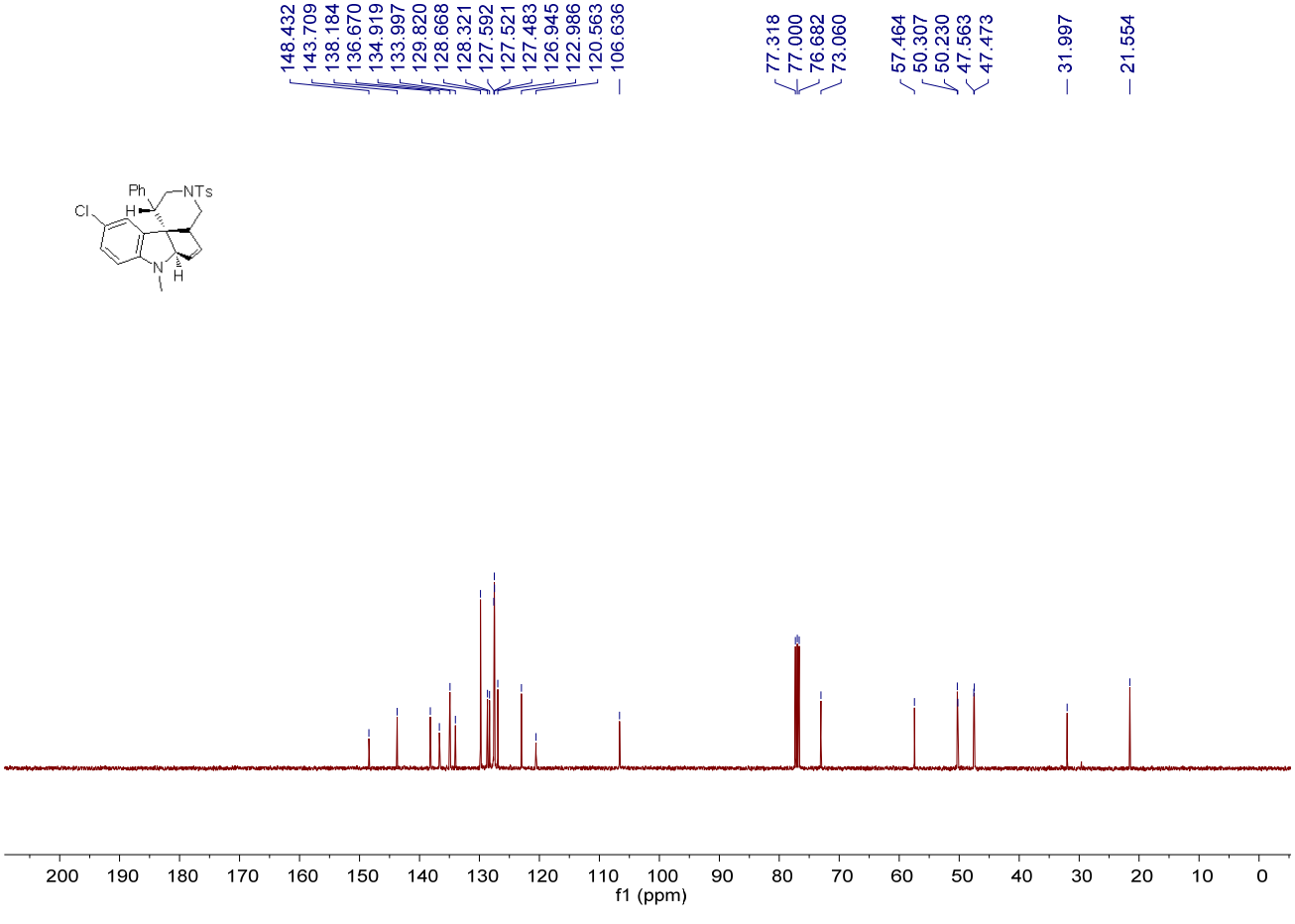
7.083
7.040
7.024
6.950
6.945
6.907
6.901
6.886
6.881
6.742
6.726
5.872
5.850
5.829
5.690
5.675
4.482
3.962
3.949
3.932
3.917
3.710
3.698
3.681
3.670
3.202
3.184
3.165
3.154
3.134
3.122
3.076
3.047
3.016
2.466
2.444
2.422
2.359
0.000
Ph
NTs
H
Cl
N
H
2.00
2.06
3.17
1.94
2.08
1.98
0.97
1.00
0.99
1.05
2.06
1.01
4.09
2.98
f1 (ppm)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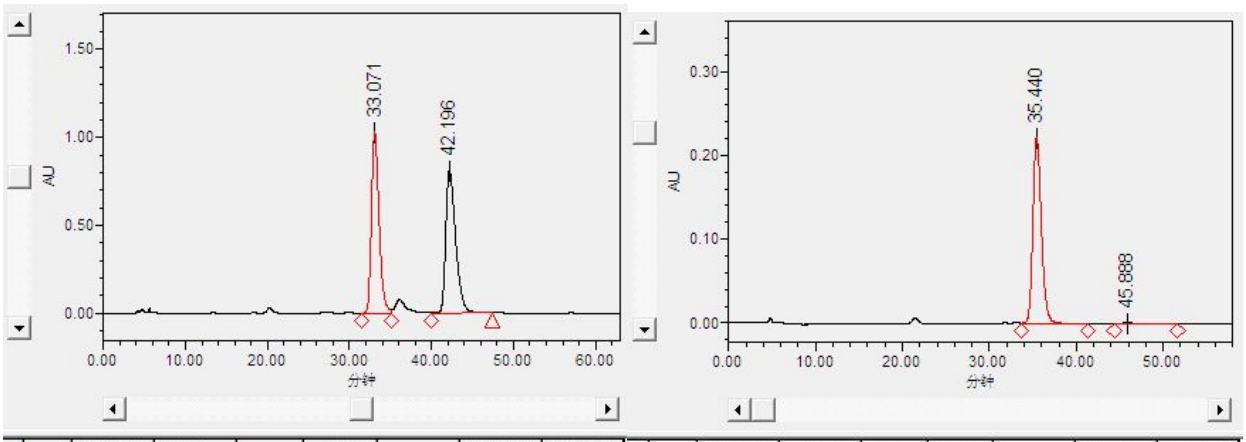
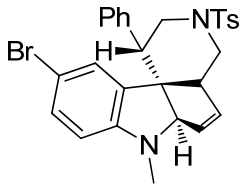
128.321
127.592
127.521
127.483
126.945
122.986
120.563
106.636
77.318
77.000
76.682
73.060
57.464
50.307
50.230
47.563
47.473
31.997
21.554
Ph
NTs
H
Cl
N
H
f1 (ppm)



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		33.071	66959496	49.60	1032070	VV	31.417	35.133
2		42.196	68032895	50.40	809323	VB	40.000	47.350

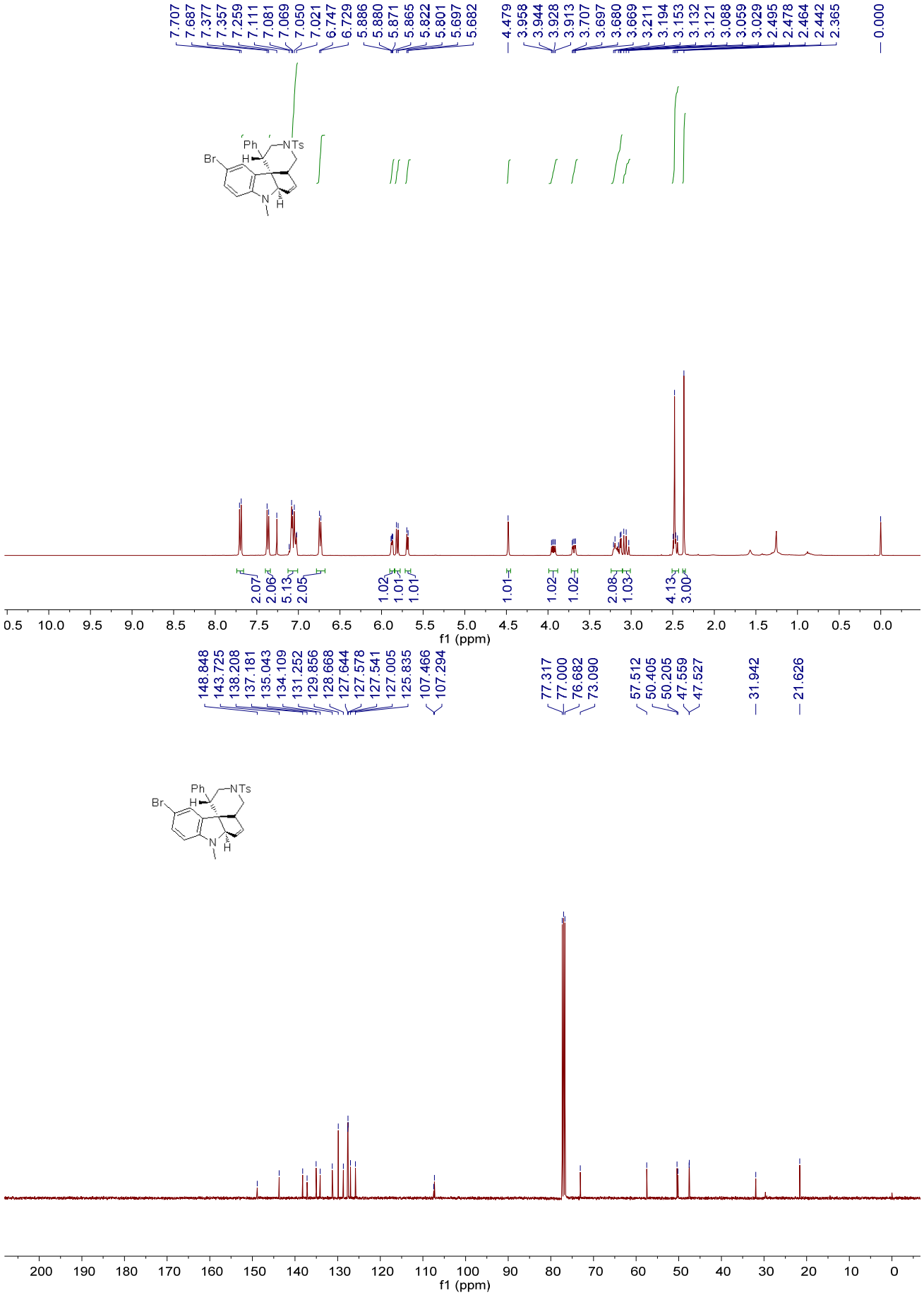
	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		35.440	15298789	98.99	222218	VV	33.683	41.283
2		45.888	156684	1.01	1180	VV	44.350	51.667

Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_{minor} = 45.89 min, t_{major} = 35.44 min; ee% = 98%].



(1*S*,4a*R*,6a*R*,11b*S*)-10-bromo-7-methyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 2h

A white solid, 47% yield (24.9 mg). M.p.: 199-202 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.37 (s, 3H), 2.44-2.50 (m, 4H), 3.06 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.12-3.22 (m, 2H), 3.69 (dd, *J* = 10.8, 4.0 Hz, 1H), 3.93 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.48 (s, 1H), 5.69 (d, *J* = 6.0 Hz, 1H), 5.81 (d, *J* = 8.0 Hz, 1H), 5.86-5.89 (m, 1H), 6.72-6.75 (m, 2H), 7.02-7.11 (m, 5H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 31.9, 47.5, 47.6, 50.2, 50.4, 57.5, 73.1, 107.3, 107.5, 125.8, 127.0, 127.5, 127.6, 127.7, 128.7, 129.9, 131.3, 134.1, 135.0, 137.2, 138.2, 143.7, 148.8. IR (CH_2Cl_2) ν 2918, 2852, 1595, 1481, 1343, 1169, 938, 861, 730, 658 cm^{-1}. MS (ESI) *m/z* (%): 535.10 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{28}H_{28}N_2O_2BrS^{+1}[M+H]^+$ requires 535.1049, found: 535.1048. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 30.13 min, t_{major} = 24.97 min; ee% = 91%; $[\alpha]_D^{25}$ = -111.1 (c 0.30, CH_2Cl_2)].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7.377
7.357
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7.111
7.081
7.069
7.050
7.021
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5.880
5.871
5.865
5.822
5.801
5.697
5.682
4.479
3.958
3.944
3.928
3.913
3.707
3.697
3.680
3.669
3.211
3.194
3.153
3.132
3.121
3.088
3.059
3.029
2.495
2.478
2.464
2.442
2.365
0.000
Ph
NTs
H
Br
N
H
2.07
2.06
5.13
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1.01
1.01
1.01
1.02
1.02
2.08
1.03
4.13
3.00
f1 (ppm)
148.848
143.725
138.208
137.181
135.043
134.109
131.252
129.856
128.668
127.644
127.578
127.541
127.005
125.835
107.466
107.294
77.317
77.000
76.682
73.090
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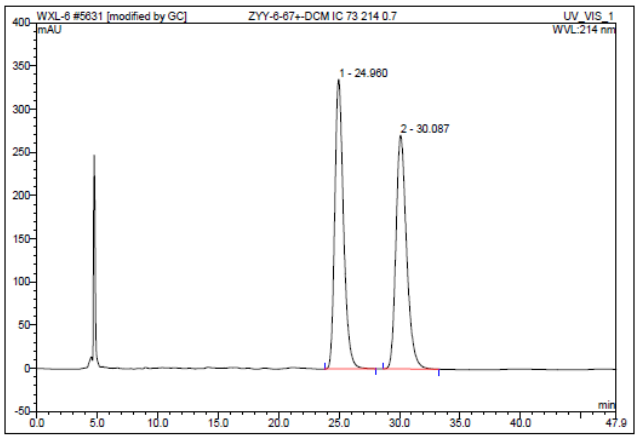
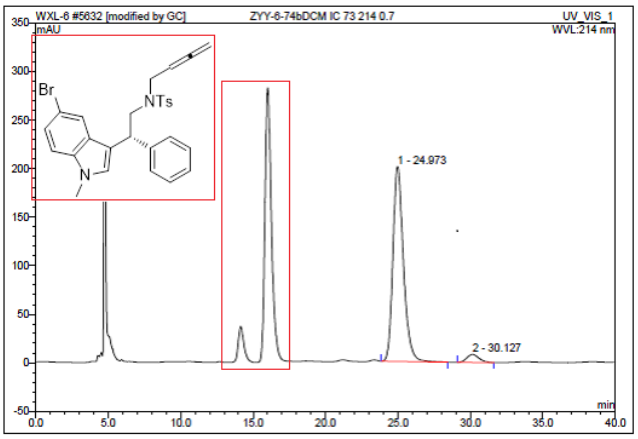
47.527
31.942
21.626
f1 (ppm)

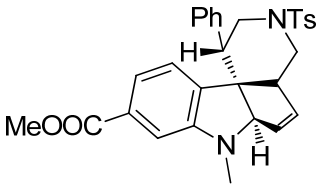




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	24.96	n.a.	335.195	280.655	50.47	n.a.	BMB
2	30.09	n.a.	270.368	275.457	49.53	n.a.	BMB
Total:			605.563	556.112	100.00	0.000	

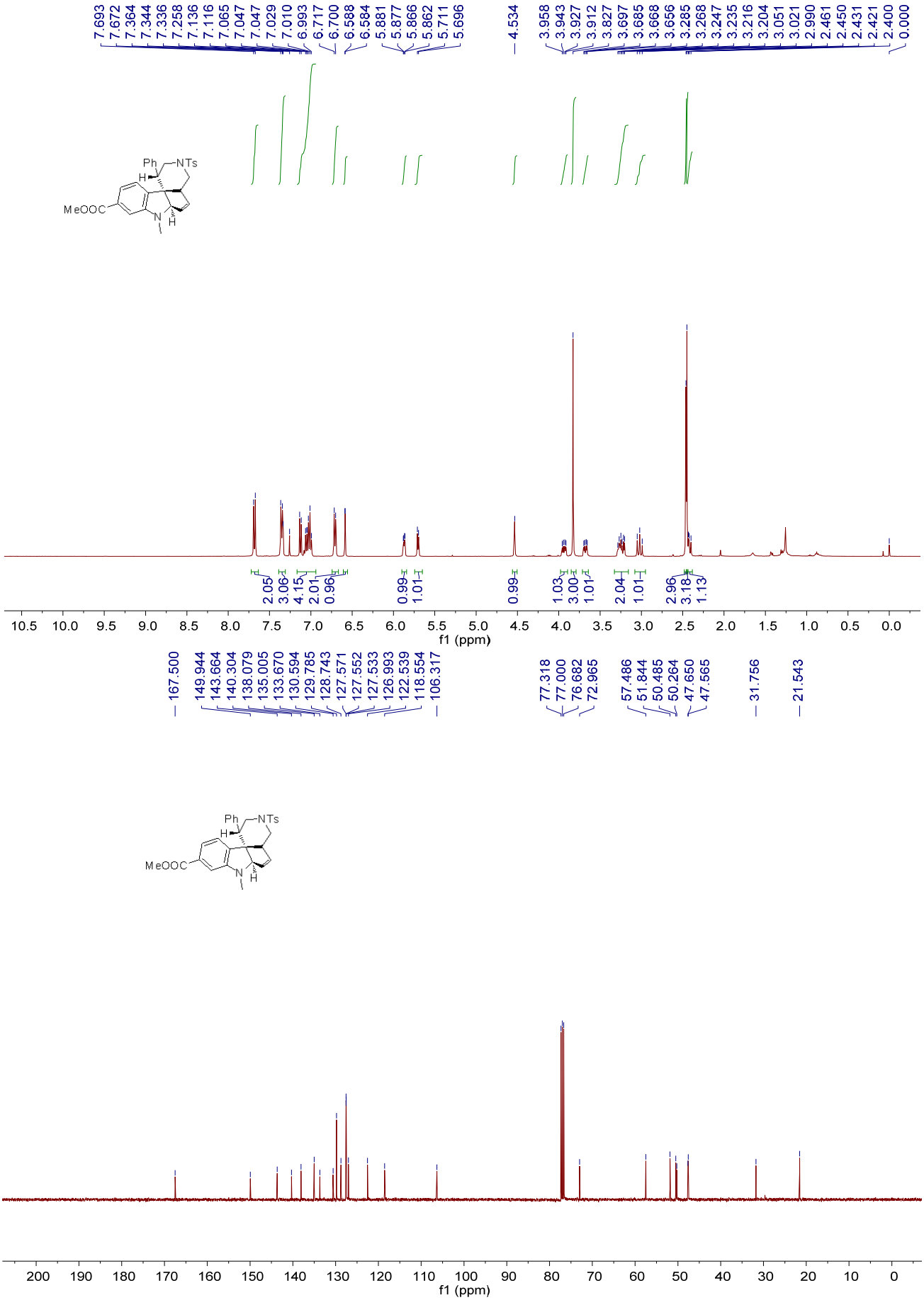
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	24.97	n.a.	200.400	169.044	95.44	n.a.	BMB*
2	30.13	n.a.	8.225	8.079	4.56	n.a.	BMB
Total:			208.625	177.123	100.00	0.000	

Translation: Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 30.13 min, t_{major} = 24.97 min; ee% = 91%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(1*S*,4a*R*,6a*R*,11b*S*)-methyl 7-methyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido [4',3':2,3]cyclopenta[1,2-*b*]indole-9-carboxylate 2i

A white solid, 48% yield (24.6 mg). M.p.: 142-145 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40-2.44 (m, 1H), 2.45 (s, 3H), 2.46 (s, 3H), 3.02 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.20-3.29 (m, 2H), 3.67 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.83 (s, 3H), 3.93 (dd, *J* = 12.4, 6.0 Hz, 1H), 4.53 (s, 1H), 5.69-5.72 (m, 1H), 5.86-5.89 (m, 1H), 6.58-6.59 (m, 1H), 6.70-6.72 (m, 2H), 6.99-7.14 (m, 4H), 7.33-7.37 (m, 3H), 7.68 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 31.8, 47.6, 47.7, 50.3, 50.5, 51.8, 57.5, 73.0, 106.3, 118.6, 122.5, 127.0, 127.53, 127.55, 127.57, 128.7, 129.8, 130.6, 133.7, 135.0, 138.1, 140.3, 143.7, 149.9, 167.5. IR (CH_2Cl_2) ν 2918, 2847, 1712, 1496, 1345, 1164, 1090, 931, 859, 730, 662 cm^{-1}. MS (ESI) *m/z* (%): 515.19 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{30}H_{31}N_2O_4S^{+1}[M+H]^+$ requires 515.1999, found: 515.1990. Enantiomeric excess was determined by HPLC with a Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 39.07 min, t_{major} = 35.57 min; ee% = 98%; $[\alpha]_D^{25}$ = -43.0 (c 0.10, CH_2Cl_2)].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7.672
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7.344
7.336
7.258
7.136
7.116
7.065
7.047
7.047
7.029
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6.993
6.717
6.700
6.588
6.584
5.881
5.877
5.866
5.862
5.711
5.696
4.534
3.958
3.943
3.927
3.912
3.827
3.697
3.685
3.668
3.656
3.285
3.268
3.247
3.235
3.216
3.204
3.051
3.021
2.990
2.461
2.450
2.431
2.421
2.400
0.000
Ph
NTs
H
MeOOC
N
H
2.05
3.06
4.15
2.01
0.96
0.99
1.01
0.99
1.03
3.00
1.01
2.04
1.01
2.96
3.18
1.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
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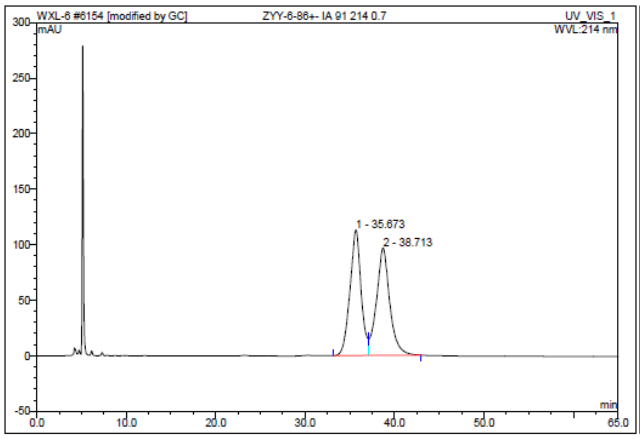
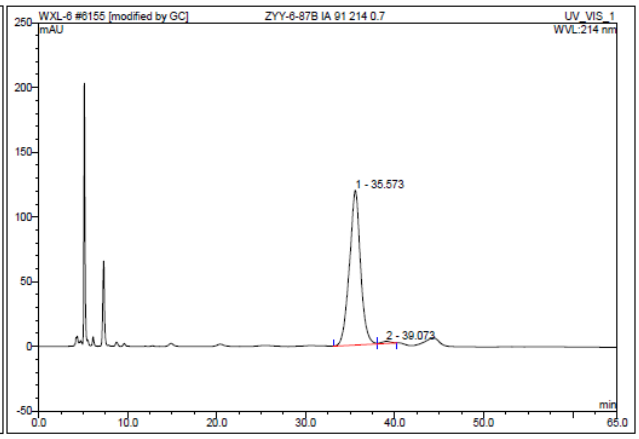
149.944
143.664
140.304
138.079
135.005
133.670
130.594
129.785
128.743
127.571
127.552
127.533
126.993
122.539
118.554
106.317
77.318
77.000
76.682
72.965
57.486
51.844
50.485
50.264
47.650
47.565
31.756
21.543
Ph
NTs
H
MeOOC
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

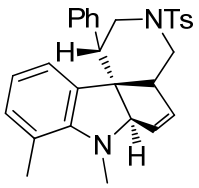




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	35.67	n.a.	113.031	162.898	49.46	n.a.	BM
2	38.71	n.a.	96.574	166.444	50.54	n.a.	MB
Total:			209.605	329.342	100.00	0.000	

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	35.57	n.a.	119.474	172.299	98.91	n.a.	BM
2	39.07	n.a.	1.590	1.895	1.09	n.a.	MB
Total:			121.064	174.194	100.00	0.000	

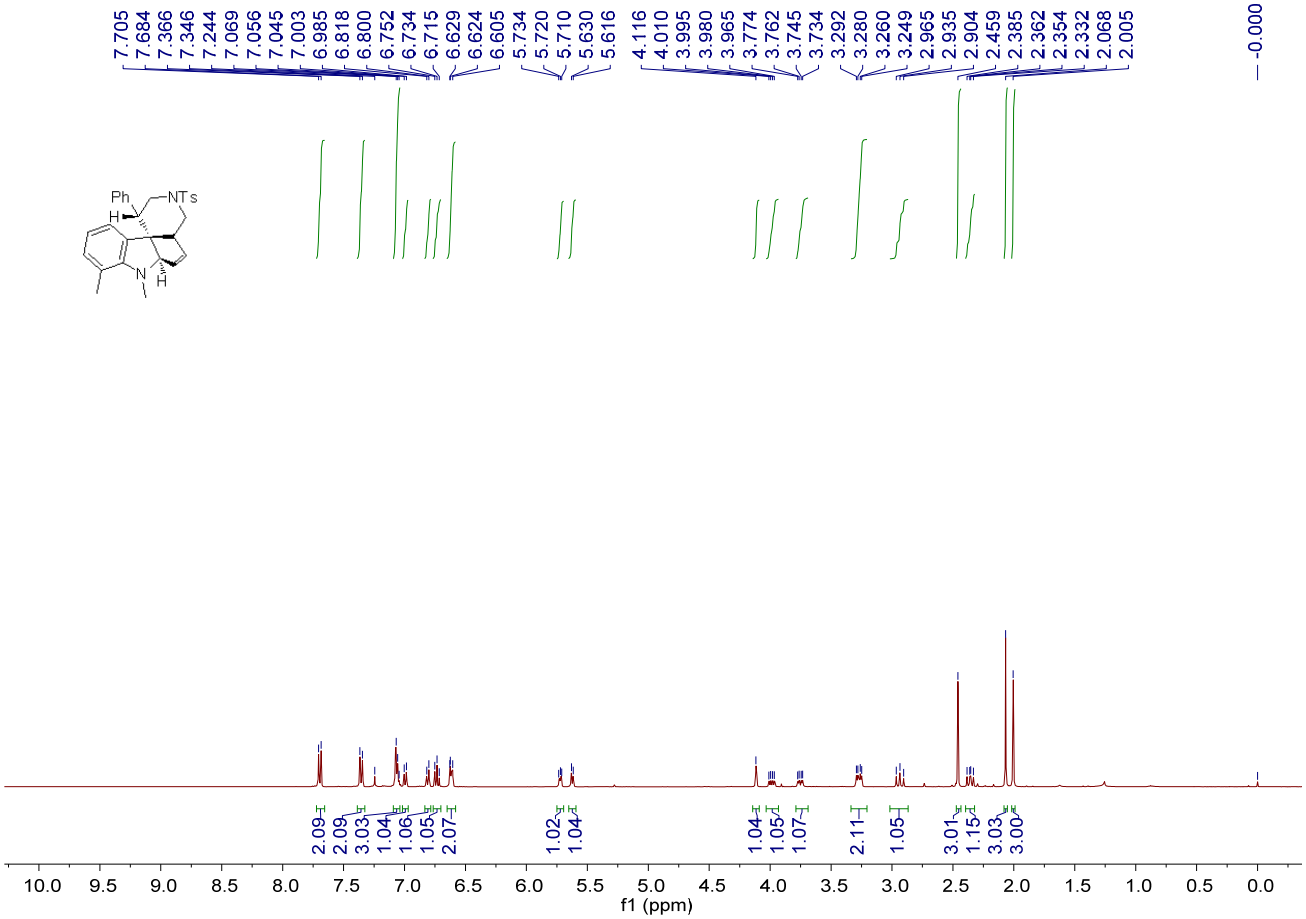
Translation: Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 39.07 min, t_{major} = 35.57 min; ee% = 98%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(1*S*,4a*R*,6a*R*,11b*S*)-7,8-dimethyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 2j

A white solid, 46% yield (21.6 mg). M.p.: 85-88 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.01 (s, 3H), 2.07 (s, 3H), 2.36 (dd, *J* = 12.0, 8.8 Hz, 1H), 2.46 (s, 3H), 2.94 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.24-3.30 (m, 2H), 3.75 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.99 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.12 (s, 1H), 5.62 (d, *J* = 5.6 Hz, 1H), 5.71-5.74 (m, 1H), 6.60-6.63 (m, 2H), 6.71-6.76 (m, 1H), 6.80-6.82 (m, 1H), 6.98-7.01 (m, 1H), 7.04-7.07 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.8, 21.5, 37.9, 47.6, 47.7, 50.5, 51.0, 58.8, 75.6, 119.4, 120.9, 121.2, 126.9, 127.6, 127.9, 129.8, 131.2, 132.0, 133.5, 133.7, 136.9, 139.3, 143.6, 149.2. IR (CH_2Cl_2) ν 2920, 1598, 1467, 1343, 1162, 1089, 937, 855, 744, 659 cm^{-1}. MS (ESI) *m/z* (%): 471.20 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{29}H_{31}N_2O_2S^{+1}[M+H]^+$ requires 471.2101, found: 471.2097. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.50 mL/min; t_{minor} = 78.59 min, t_{major} = 85.21 min; ee% = 97%; $[\alpha]_D^{25}$ = -77.7 (c 0.20,

CH_2Cl_2)].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7.056
7.045
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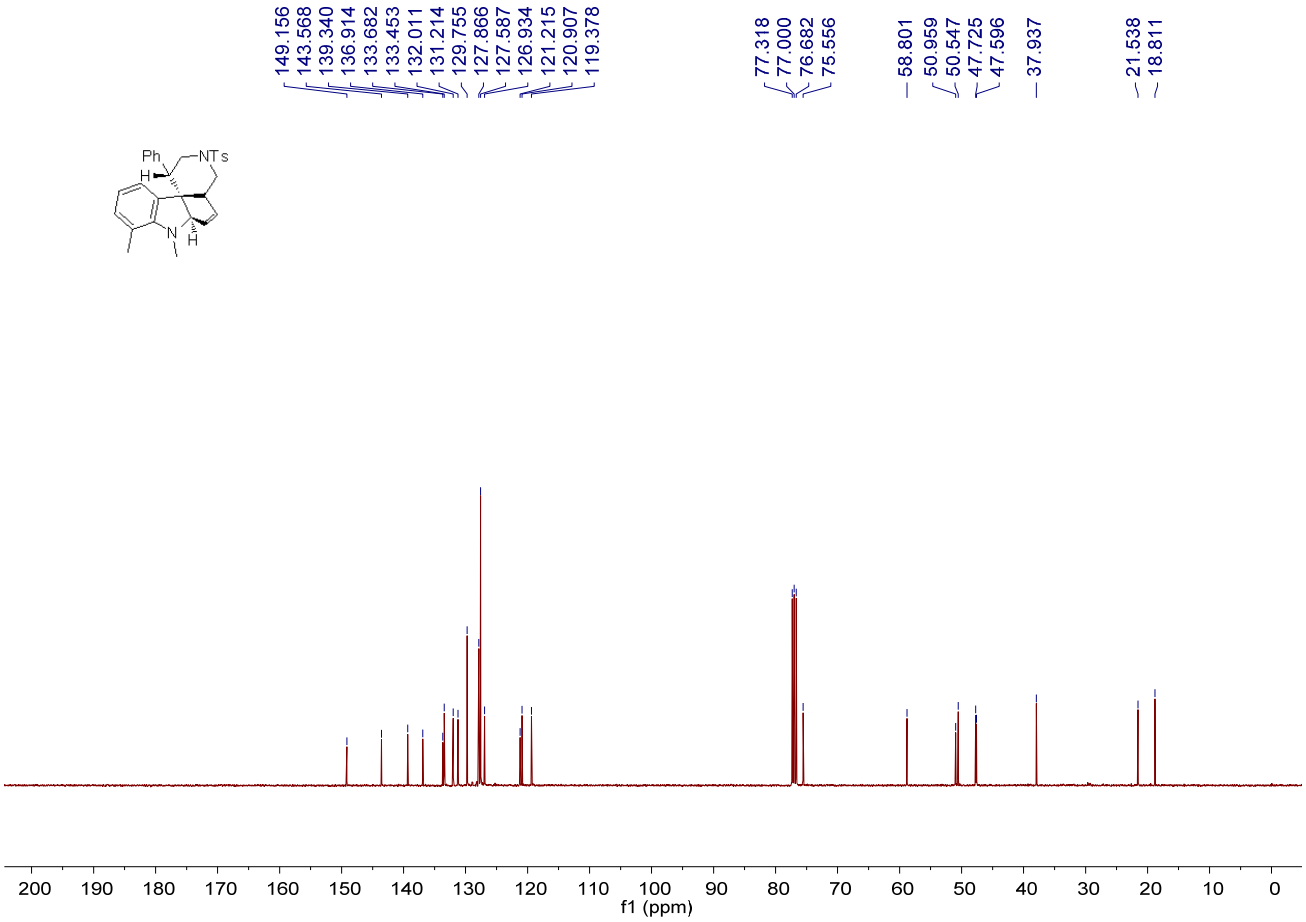
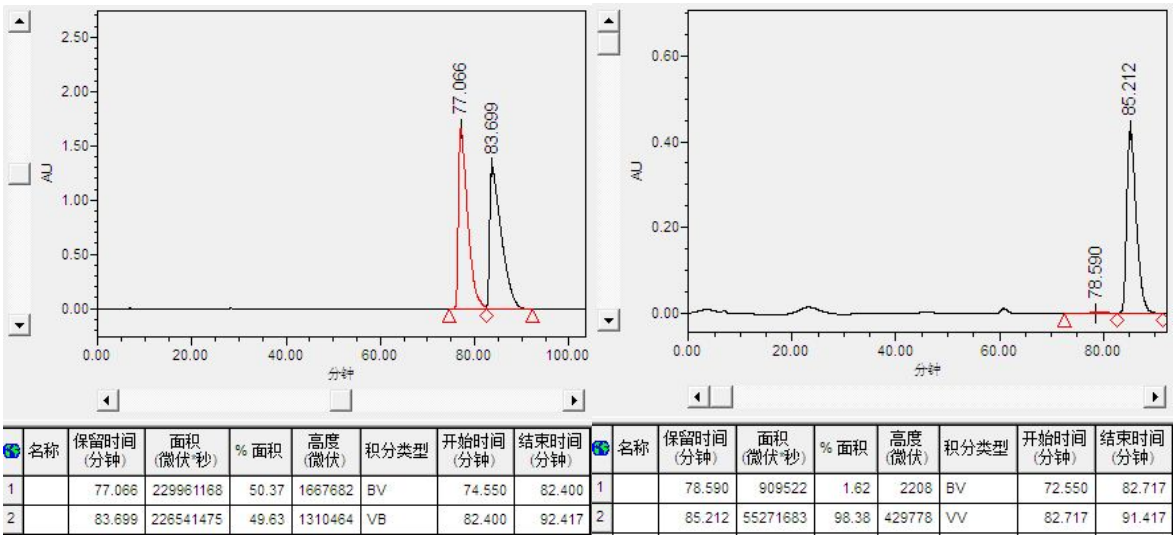
6.752
6.734
6.715
6.629
6.624
6.605
5.734
5.720
5.710
5.630
5.616
4.116
4.010
3.995
3.980
3.965
3.774
3.762
3.745
3.734
3.292
3.280
3.260
3.249
2.965
2.935
2.904
2.459
2.385
2.362
2.354
2.332
2.068
2.005
-0.000
Ph
NTs
H
N
H
2.09
2.09
3.03
1.04
1.06
1.05
2.07
1.02
1.04
1.04
1.05
1.07
2.11
1.05
3.01
1.15
3.03
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

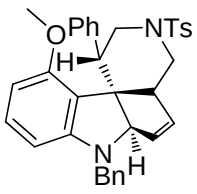




	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		77.066	229961168	50.37	1667682	BV	74.550	82.400
2		83.699	226541475	49.63	1310464	VB	82.400	92.417

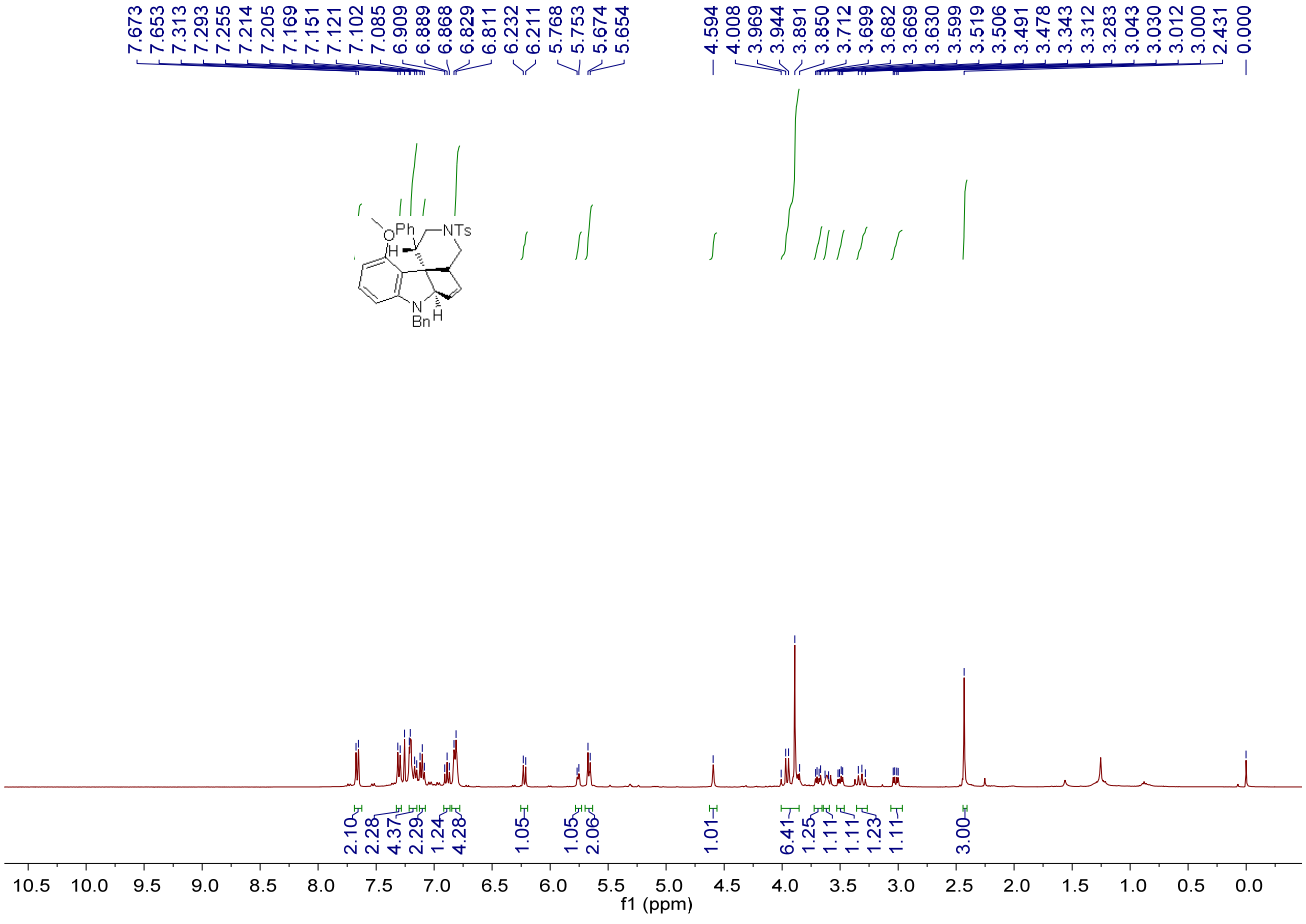
	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		78.590	909522	1.62	2208	BV	72.550	82.717
2		85.212	55271683	98.38	429778	VV	82.717	91.417

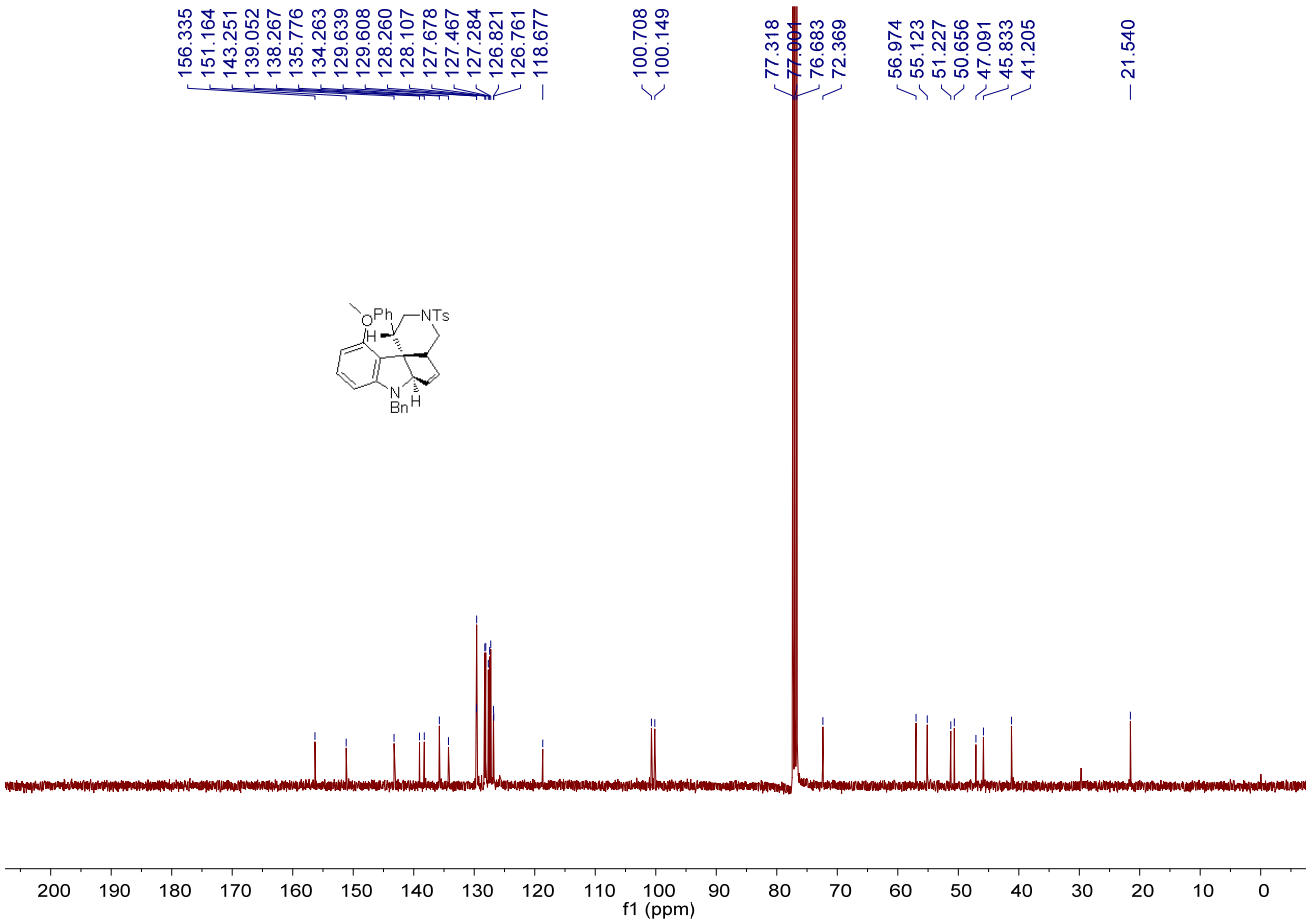
Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.50 mL/min; t_{minor} = 78.59 min, t_{major} = 85.21 min; ee% = 97%].

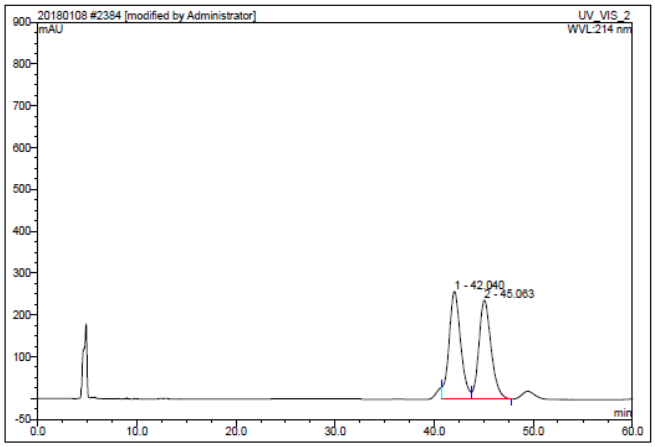


(1*S*,4a*R*,6a*R*,11b*S*)-7-benzyl-11-methoxy-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4', 3':2,3]cyclopenta[1,2-*b*]indole 2k

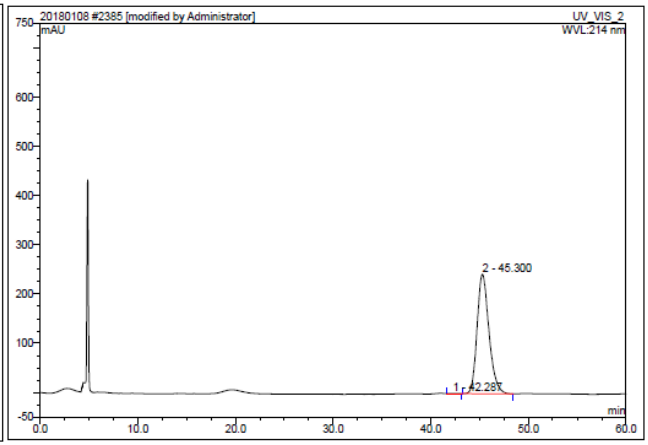
A white solid, 46% yield (25.9 mg). M.p.: 90-93 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.43 (s, 3H), 3.02 (dd, *J* = 12.0, 4.8 Hz, 1H), 3.31 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.50 (dd, *J* = 11.2, 5.2 Hz, 1H), 3.59-3.63 (m, 1H), 3.69 (dd, *J* = 12.0, 5.2 Hz, 1H), 3.85-4.01 (m, 6H), 4.59 (s, 1H), 5.65-5.68 (m, 2H), 5.75-5.77 (m, 1H), 6.22 (d, *J* = 8.4 Hz, 1H), 6.81-6.83 (m, 4H), 6.86-6.91 (m, 1H), 7.08-7.13 (m, 2H), 7.15-7.22 (m, 4H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 41.2, 45.8, 47.1, 50.7, 51.2, 55.1, 57.0, 72.3, 100.1, 100.7, 118.7, 126.7, 126.8, 127.3, 127.5, 127.7, 128.1, 128.3, 129.61, 129.64, 134.3, 135.8, 138.3, 139.1, 143.3, 151.2, 156.3. IR (CH_2Cl_2) ν 3028, 2919, 2842, 1599, 1494, 1338, 1166, 941, 859, 729, 662 cm^{-1}. MS (ESI) *m/z* (%): 563.23 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{35}H_{35}N_2O_3S^{+1}[M+H]^+$ requires 563.2363, found: 563.2358. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 85/15; Flow rate: 0.70 mL/min; t_{minor} = 42.29 min, t_{major} = 45.30 min; ee% = 99%; $[\alpha]_D^{25}$ = -25.0 (c 0.70, CH_2Cl_2)].





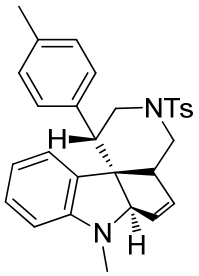


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	42.04	n.a.	256.915	347.820	50.75	n.a.	M *
2	45.06	n.a.	236.220	337.479	49.25	n.a.	MB*
Total:			493.135	685.299	100.00	0.000	



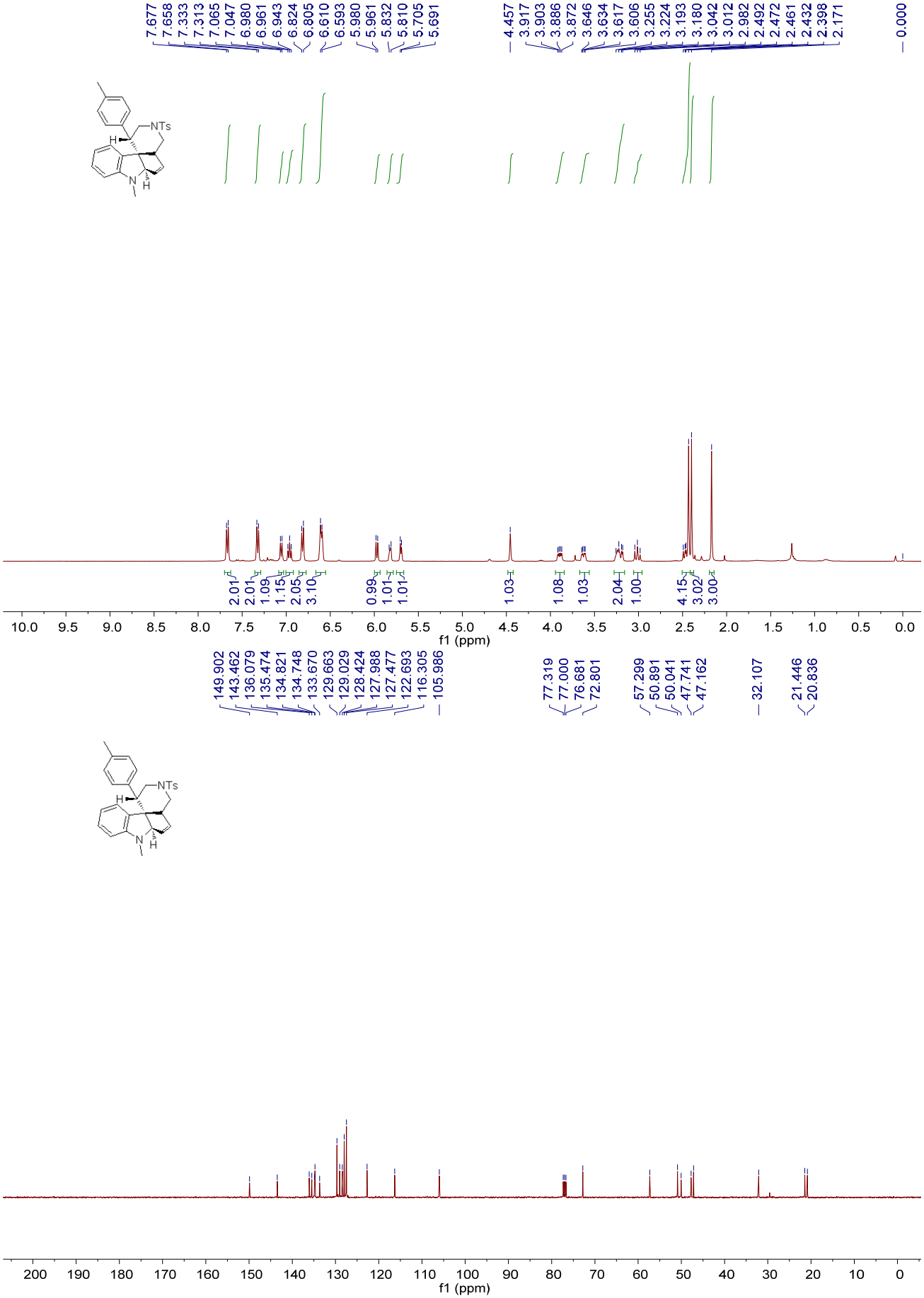
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	42.29	n.a.	0.382	0.258	0.08	n.a.	BMB*
2	45.30	n.a.	242.532	342.210	99.92	n.a.	BMB*
Total:			242.915	342.468	100.00	0.000	

Translation: Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 85/15; Flow rate: 0.70 mL/min; t_{minor} = 42.29 min, t_{major} = 45.30 min; ee% = 99%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(1*S*,4a*R*,6a*R*,11b*S*)-7-methyl-1-(*p*-tolyl)-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 2l

A white solid, 47% yield (22.1 mg). M.p.: 50-53 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.17 (s, 3H), 2.40 (s, 3H), 2.43-2.50 (m, 4H), 3.01 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.18-3.26 (m, 2H), 3.62 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.89 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.46 (s, 1H), 5.70 (d, *J* = 5.6 Hz, 1H), 5.81-5.84 (m, 1H), 5.97 (d, *J* = 8.0 Hz, 1H), 6.59-6.61 (m, 3H), 6.80-6.83 (m, 2H), 6.94-6.98 (m, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.8, 21.4, 32.1, 47.2, 47.7, 50.0, 50.9, 57.3, 72.8, 106.0, 116.3, 122.7, 127.5, 128.0, 128.4, 129.0, 129.7, 133.7, 134.7, 134.8, 135.5, 136.1, 143.5, 149.9. IR (CH_2Cl_2) ν 2921, 2851, 1603, 1489, 1341, 1159, 1089, 933, 815, 719, 657 cm^{-1}. MS (ESI) *m/z* (%): 471.20 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{29}H_{31}N_2O_2S^{+1}[M+H]^+$ requires 471.2101, found: 471.2098. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 54.57 min, t_{major} = 49.77 min; ee% = 90%; $[\alpha]_D^{25}$ = -22.0 (c 0.10, CH_2Cl_2)].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7.313
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7.047
6.980
6.961
6.943
6.824
6.805
6.610
6.593
5.980
5.961
5.832
5.810
5.705
5.691
4.457
3.917
3.903
3.886
3.872
3.646
3.634
3.617
3.606
3.255
3.224
3.193
3.180
3.042
3.012
2.982
2.492
2.472
2.461
2.432
2.398
2.171
0.000
NTs
H
N
H
2.01
2.01
1.09
1.15
2.05
3.10
0.99
1.01
1.01
1.03
1.08
1.03
2.04
1.00
4.15
3.02
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
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135.474
134.821
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129.663
129.029
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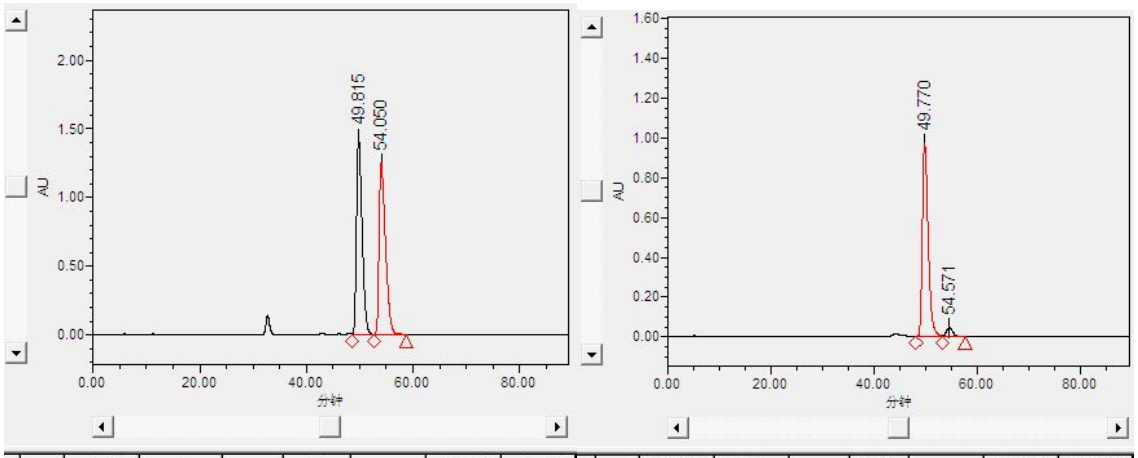
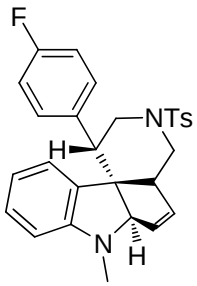
127.477
122.693
116.305
105.986
77.319
77.000
76.681
72.801
57.299
50.891
50.041
47.741
47.162
32.107
21.446
20.836
NTs
H
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		49.815	104921549	49.82	1431410	VV	48.567	52.617
2		54.050	105667334	50.18	1249338	VB	52.617	58.867

	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		49.770	76684945	95.06	972475	VV	48.100	53.150
2		54.571	3988687	4.94	45724	VB	53.150	57.617

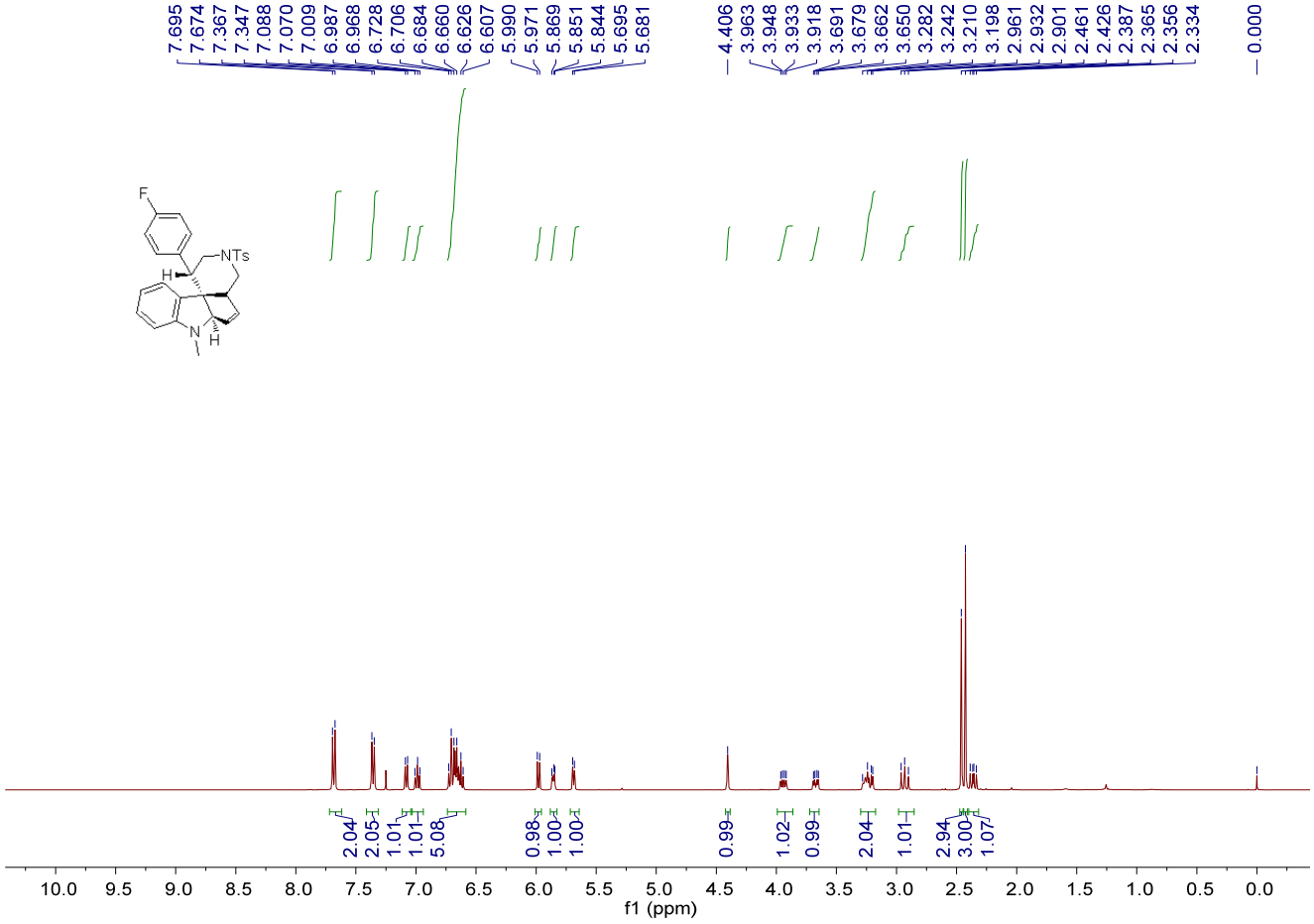
Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 54.57 min, t_{major} = 49.77 min; ee% = 90%].

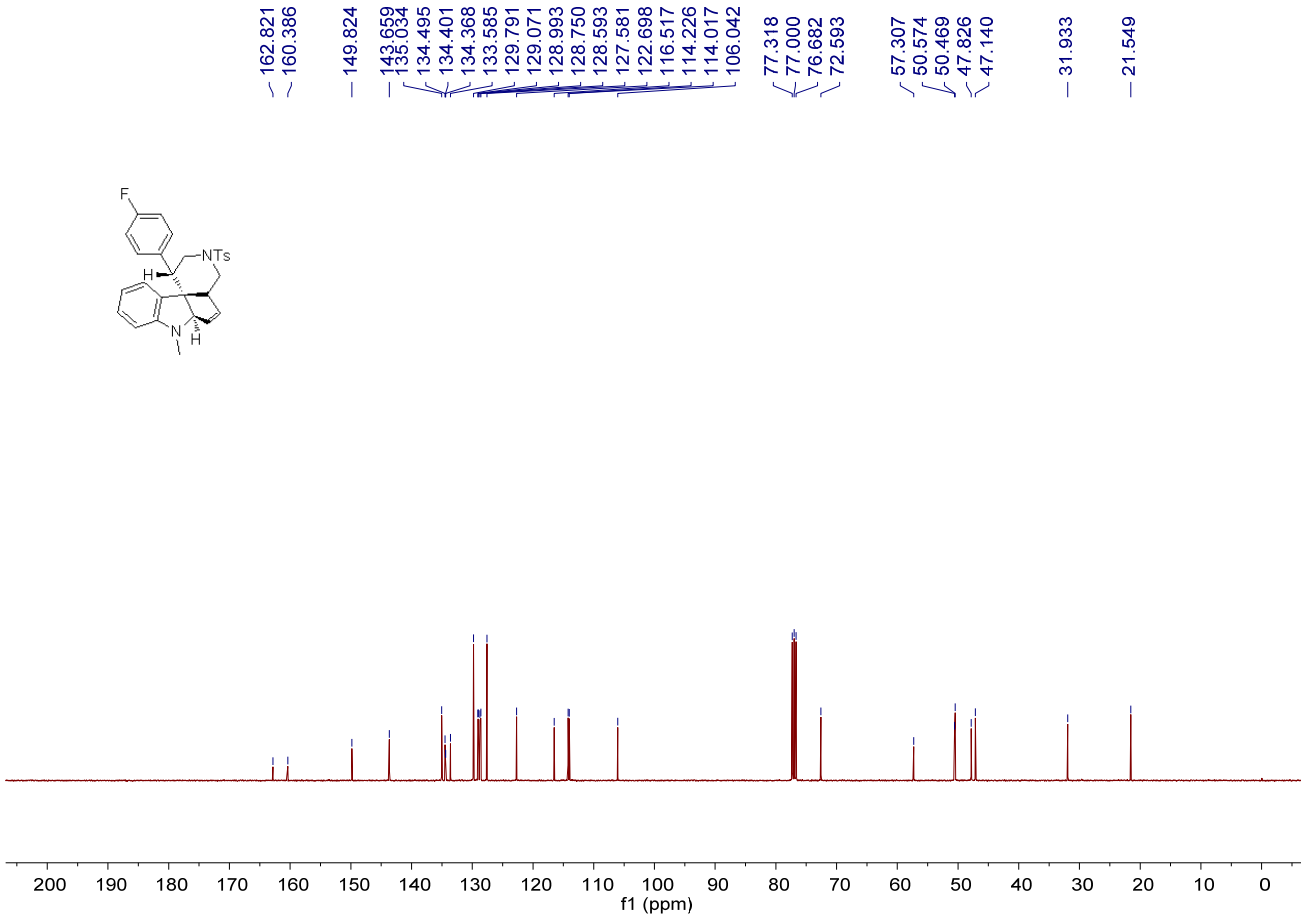


(1*S*,4a*R*,6a*R*,11b*S*)-1-(4-fluorophenyl)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 2m

A white solid, 46% yield (21.8 mg). M.p.: 91-94 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.36 (dd, *J* = 12.4, 8.8 Hz, 1H), 2.43 (s, 3H), 2.46 (s, 3H), 2.93 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.19-3.29 (m, 2H), 3.67 (dd, *J* = 12.0, 4.8 Hz, 1H), 3.94 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.41 (s, 1H), 5.69 (d, *J* = 5.6 Hz, 1H), 5.84-5.87 (m, 1H), 5.98 (d, *J* = 7.6 Hz, 1H), 6.60-6.73 (m, 5H), 6.96-7.01 (m, 1H), 7.07-7.09 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 31.9, 47.1, 47.8, 50.5, 50.6, 57.3, 72.6, 106.0, 114.1 (d, *J* = 20.9 Hz), 116.5, 122.7, 127.6, 128.6 (d, *J* = 15.7 Hz), 129.0 (d, *J* = 7.8 Hz), 129.8, 133.6, 134.4 (d, *J* = 3.3 Hz), 134.5, 135.0, 143.7, 149.8, 161.6 (d, *J* = 243.5 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -115.9. IR (CH_2Cl_2) ν 3049, 2919, 1602, 1509, 1341, 1158, 935, 833, 770, 657 cm^{-1}. MS (ESI) *m/z* (%): 475.18 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{28}H_{28}N_2O_2FS^{+1}$ $[M+H]^+$ requires 475.1850, found: 475.1839. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 94/6;

Flow rate: 0.70 mL/min; t_{minor} = 100.31 min, t_{major} = 83.00 min; ee% = 87%; $[\alpha]_D^{25}$ = -106.2 (c 0.50, CH_2Cl_2)].

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134.495
134.401
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129.791
129.071
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128.750
128.593
127.581
122.698
116.517
114.226
114.017
106.042
77.318
77.000
76.682
72.593
57.307
50.574
50.469
47.826
47.140
31.933
21.549
F
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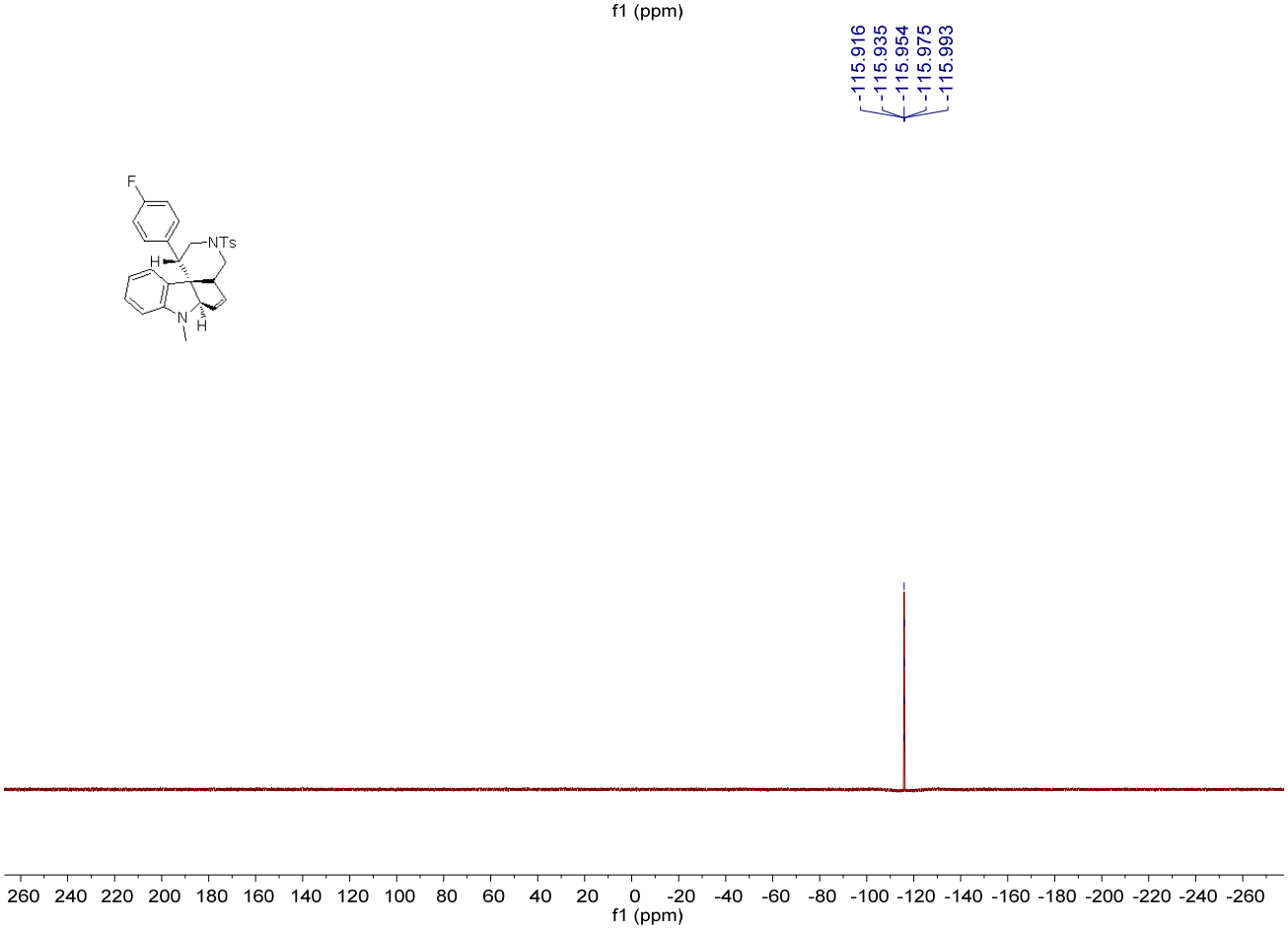
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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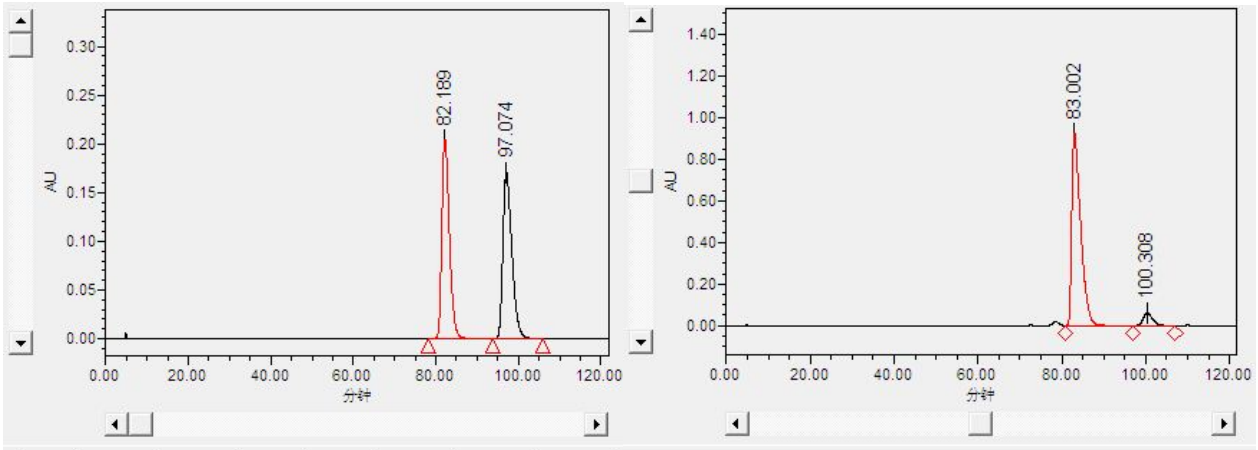
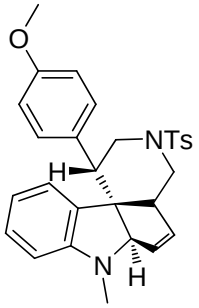
-115.935
-115.954
-115.975
-115.993
F
NTs
H
N
H
260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		82.189	25944513	50.09	204393	BB	78.350	93.800
2		97.074	25854282	49.91	170797	BB	93.817	105.950

	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		83.002	136048928	93.34	922022	VV	80.867	96.967
2		100.308	9708292	6.66	61958	VV	96.967	107.033

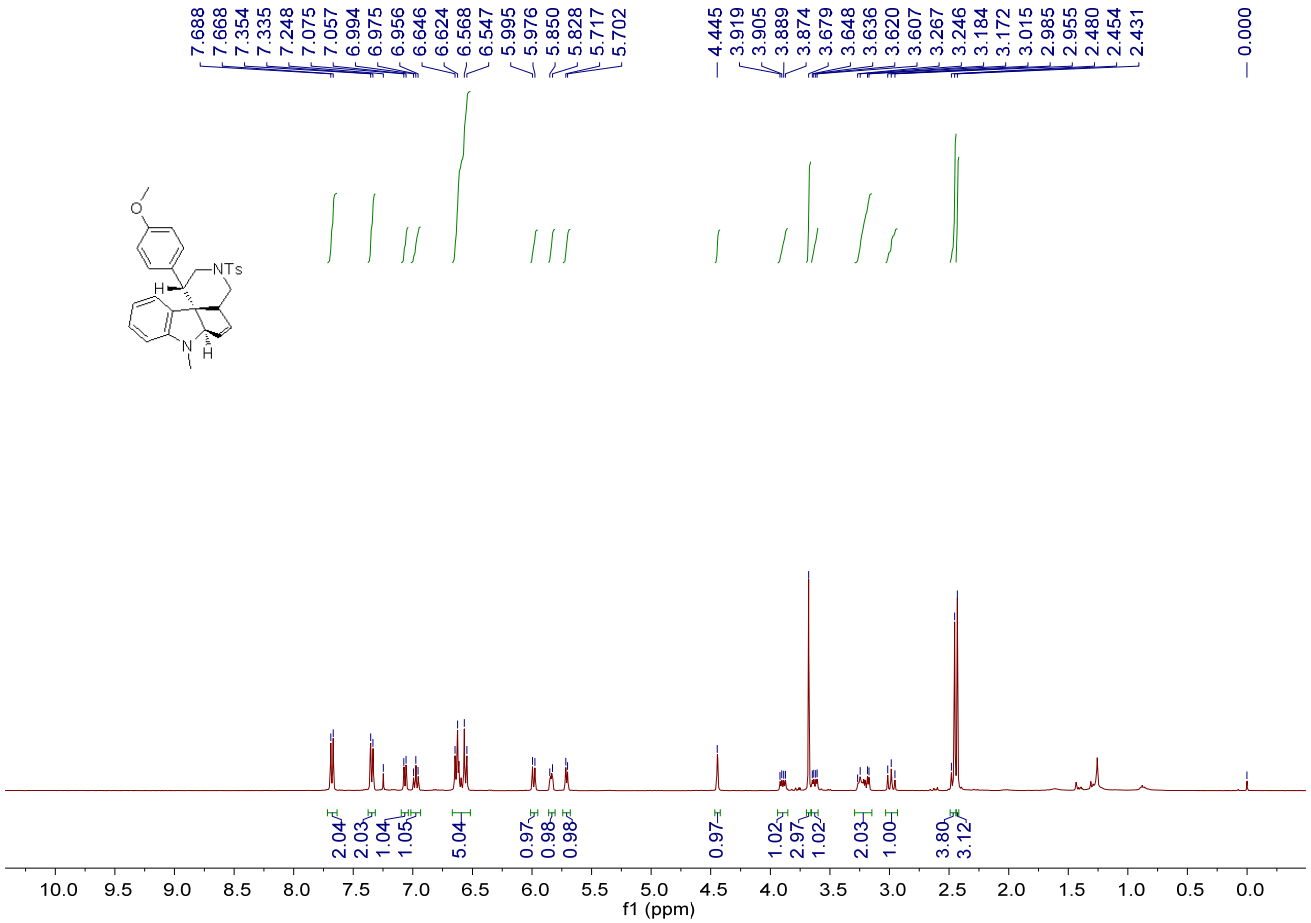
Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 94/6; Flow rate: 0.70 mL/min; t_{minor} = 100.31 min, t_{major} = 83.00 min; ee% = 87%].

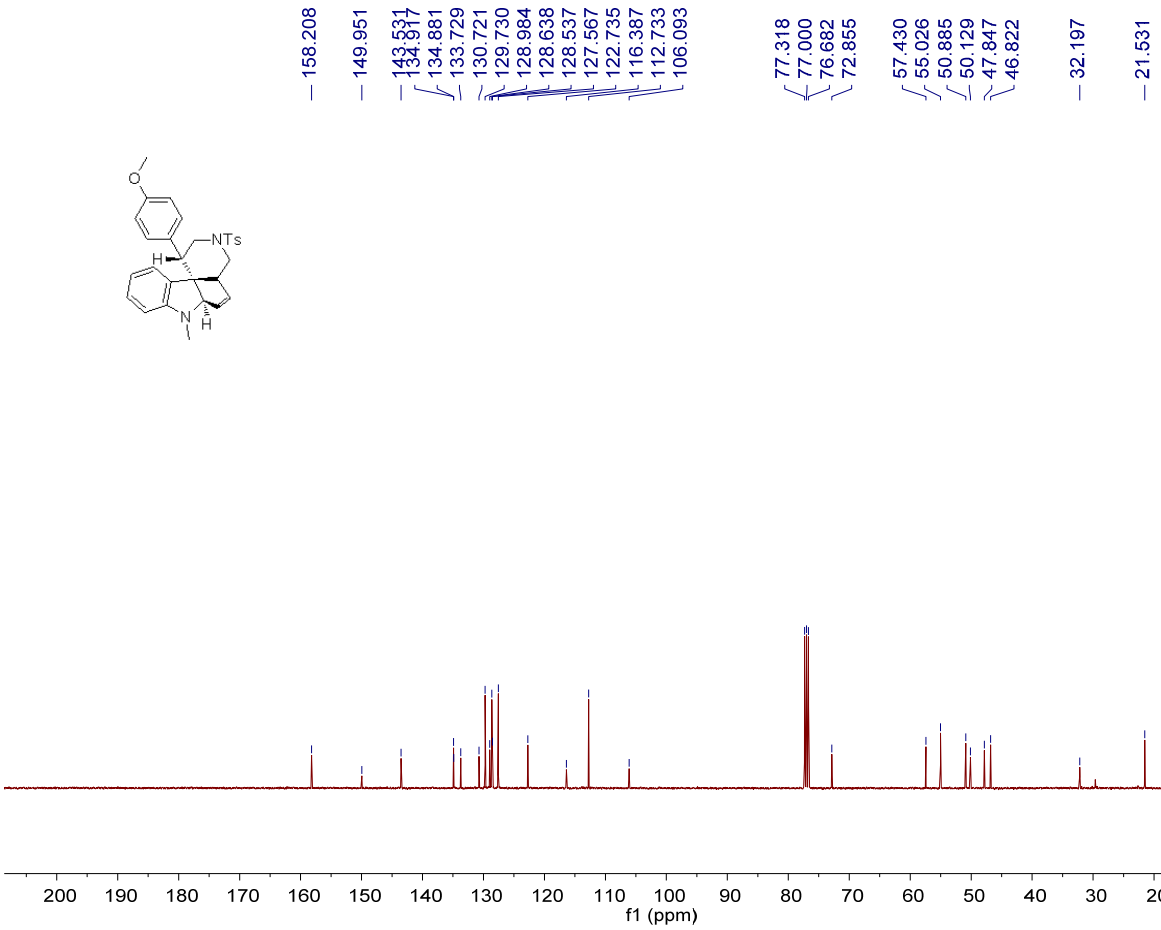


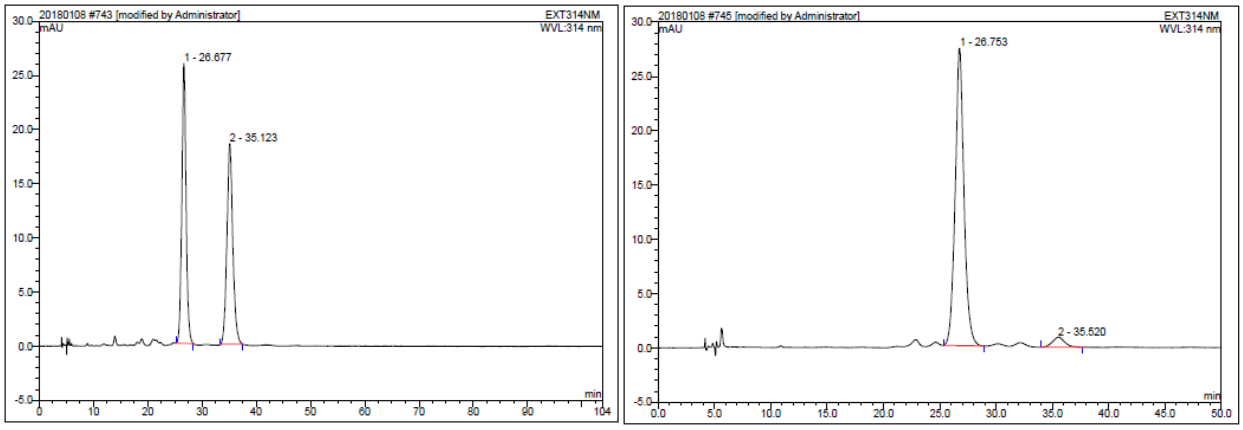
(1*S*,4a*R*,6a*R*,11b*S*)-1-(4-methoxyphenyl)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 2n

A white solid, 46% yield (22.5 mg). M.p.: 77-80 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.43 (s, 3H), 2.45-2.48 (m, 4H), 2.99 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.17-3.27 (m, 2H), 3.63 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.68 (s, 3H), 3.89 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.45 (s, 1H), 5.71 (d, *J* = 6.0 Hz, 1H), 5.82-5.85 (m, 1H), 5.98 (d, *J* = 8.0 Hz, 1H), 6.54-6.65 (m, 5H), 6.95-7.00 (m, 1H), 7.05-7.08 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 32.2, 46.8, 47.8, 50.1, 50.9, 55.0, 57.4, 72.9, 106.1, 112.7, 116.4, 122.7, 127.6, 128.5, 128.6, 129.0, 129.7, 130.7, 133.7, 134.8, 134.9, 143.5, 150.0, 158.2. IR (CH_2Cl_2) ν 2920, 2852, 1602, 1514, 1340, 1161, 935, 833, 729, 658 cm^{-1}. MS (ESI) *m/z* (%): 487.20 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{29}H_{31}N_2O_3S^{+1}[M+H]^+$ requires 487.2050, found: 487.2042. Enantiomeric excess was determined by HPLC with a Chiralcel IA column [λ = 314 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 35.52

min, t_{major} = 26.75 min; ee% = 91%; $[\alpha]_D^{25}$ = -118.4 (c 0.70, CH_2Cl_2)].



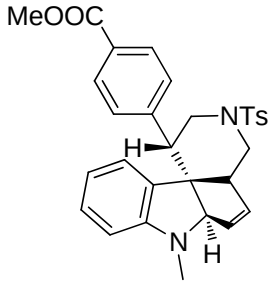




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	26.68	n.a.	25.848	23.382	50.13	n.a.	BMB
2	35.12	n.a.	18.506	23.257	49.87	n.a.	BMB
Total:			44.354	46.639	100.00	0.000	

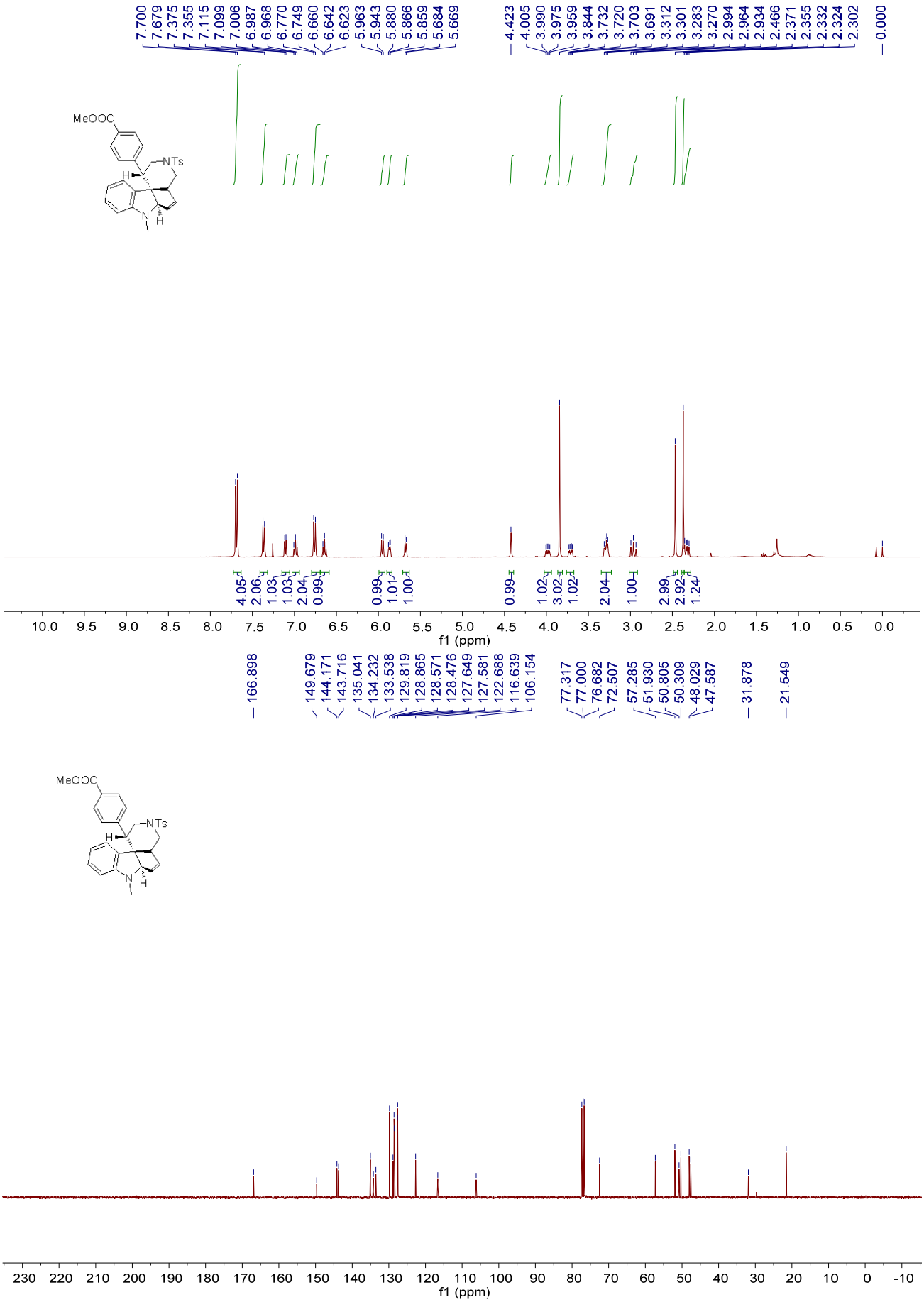
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	26.75	n.a.	27.395	24.913	95.49	n.a.	BMB*
2	35.52	n.a.	0.937	1.176	4.51	n.a.	BMB*
Total:			28.332	26.089	100.00	0.000	

Translation: Chiralcel IA column [λ = 314 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 35.52 min, t_{major} = 26.75 min; ee% = 91%].



Methyl 4-((1*S*,4a*R*,6a*R*,11b*S*)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3] cyclopenta[1,2-*b*]indol-1-yl)benzoate 2o

A white solid, 45% yield (23.3 mg). M.p.: 88-92 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.33 (dd, *J* = 12.4, 8.8 Hz, 1H), 2.37 (s, 3H), 2.47 (s, 3H), 2.96 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.27-3.32 (m, 2H), 3.71 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.84 (s, 3H), 3.98 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.42 (s, 1H), 5.67 (d, *J* = 6.0 Hz, 1H), 5.85-5.88 (m, 1H), 5.95 (d, *J* = 8.0 Hz, 1H), 6.62-6.66 (m, 1H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.96-7.01 (m, 1H), 7.09-7.12 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.67-7.70 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 31.9, 47.6, 48.0, 50.3, 50.8, 51.9, 57.3, 72.5, 106.2, 116.6, 122.7, 127.6, 127.7, 128.5, 128.6, 128.9, 129.8, 133.5, 134.2, 135.0, 143.7, 144.2, 149.7, 166.9. IR (CH_2Cl_2) ν 2923, 2852, 1717, 1603, 1488, 1208, 1164, 935, 779, 674 cm^{-1}. MS (ESI) *m/z* (%): 515.19 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{30}H_{31}N_2O_4S^{+1}[M+H]^+$ requires 515.1999, found: 515.1994. Enantiomeric excess was determined by HPLC with a Chiralcel IF3 column [λ = 317 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 37.91 min, t_{major} = 33.82 min; ee% = 88%; $[\alpha]_D^{25}$ = -108.1 (c 0.10, CH_2Cl_2)].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3.844
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H
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1.03
2.04
0.99
0.99
1.01
1.00
0.99
1.02
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1.02
2.04
1.00
2.99
2.92
1.24
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8.5
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6.5
6.0
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3.0
2.5
2.0
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0.0
f1 (ppm)
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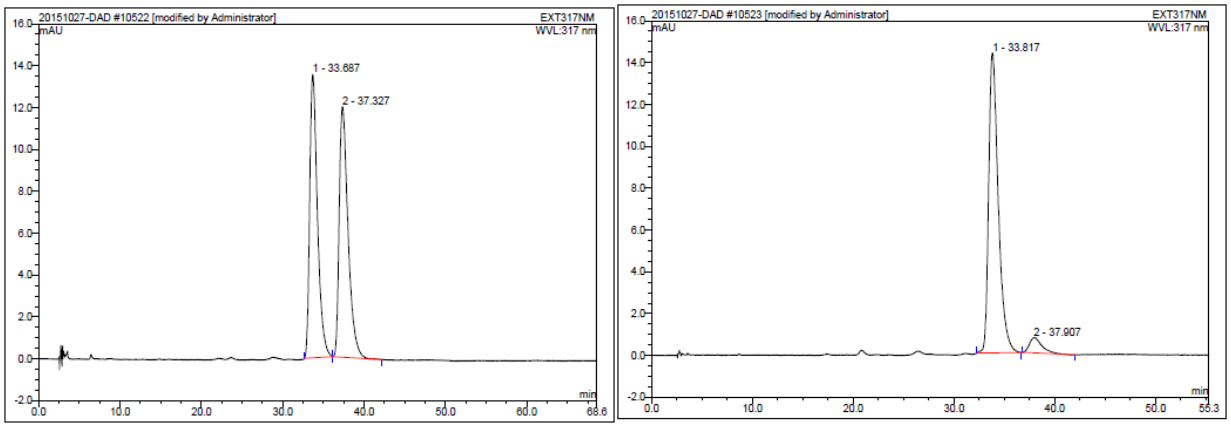
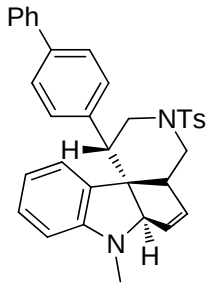
106.154
77.317
77.000
76.682
72.507
57.285
51.930
50.805
50.309
48.029
47.587
31.878
21.549
MeOOC
NTs
H
N
H
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	33.69	n.a.	13.547	14.886	49.73	n.a.	BMb*
2	37.33	n.a.	11.972	15.049	50.27	n.a.	bMB*
Total:			25.519	29.935	100.00	0.000	

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	33.82	n.a.	14.345	15.857	93.97	n.a.	BMB*
2	37.91	n.a.	0.725	1.017	6.03	n.a.	BMB*
Total:			15.070	16.873	100.00	0.000	

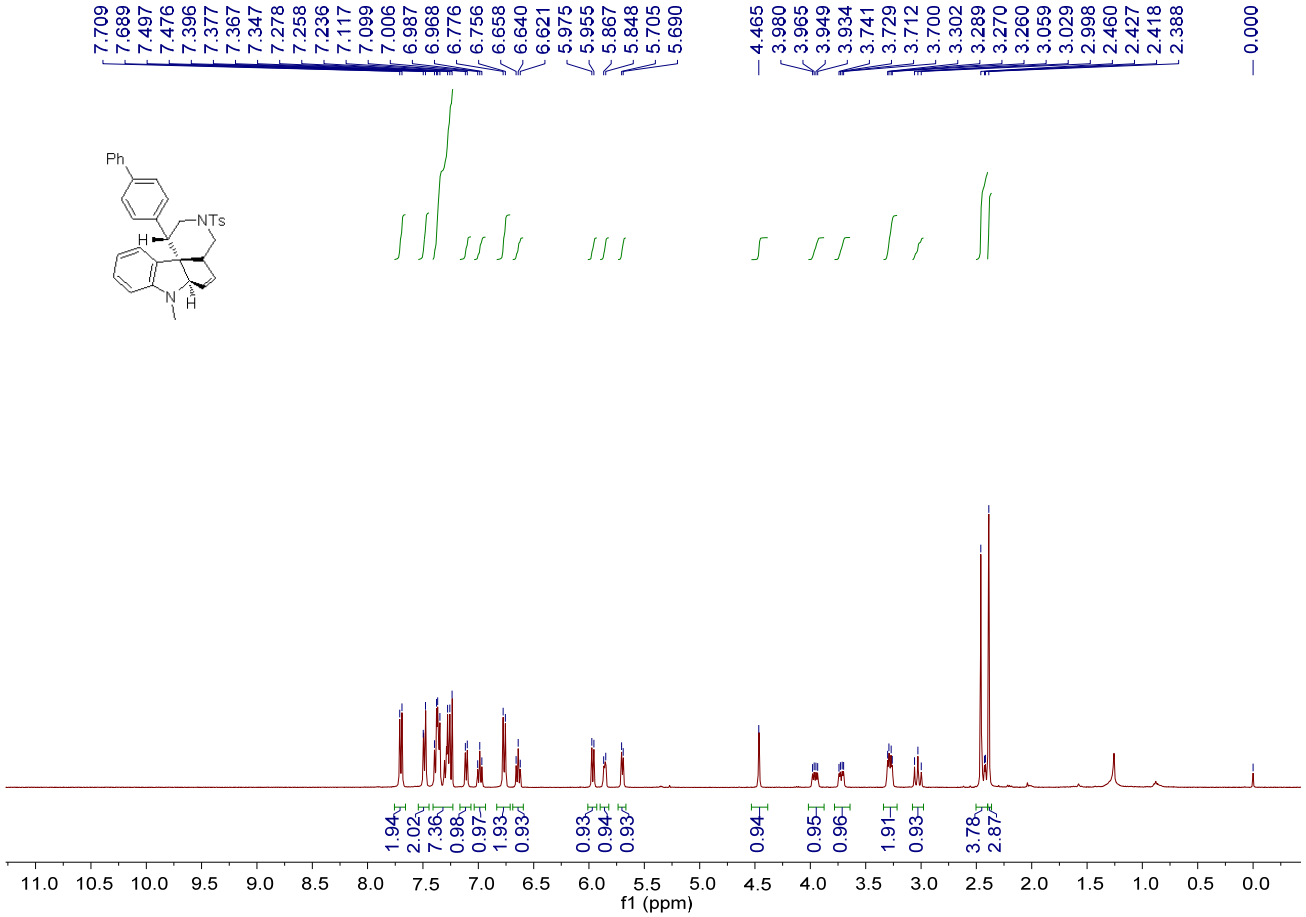
Translation: Chiralcel IF3 column [λ = 317 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 37.91 min, t_{major} = 33.82 min; ee% = 88%].

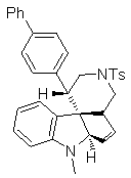


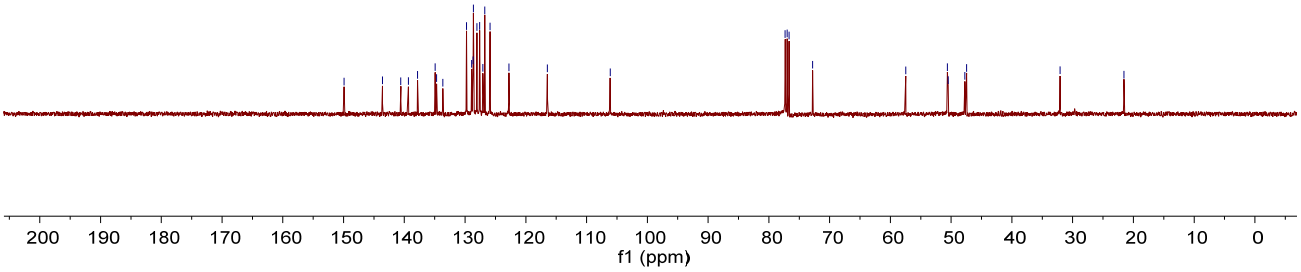
(1*S*,4a*R*,6a*R*,11b*S*)-1-([1,1'-biphenyl]-4-yl)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 2p

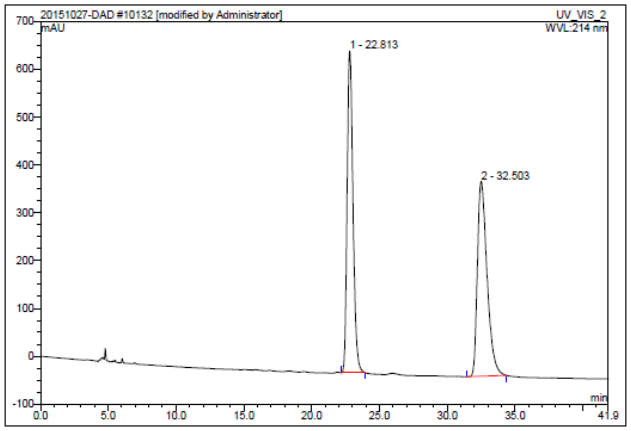
A white solid, 45% yield (23.9 mg). M.p.: 124-127 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.38 (s, 3H), 2.41-2.46 (m, 4H), 3.03 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.26-3.31 (m, 2H), 3.71 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.95 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.47 (s, 1H), 5.70 (d, *J* = 6.0 Hz, 1H), 5.84-5.87 (m, 1H), 5.96 (d, *J* = 8.0 Hz, 1H), 6.62-6.66 (m, 1H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.96-7.01 (m, 1H), 7.09-7.12 (m, 1H), 7.23-7.50 (m, 7H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 32.1, 47.5, 47.7, 50.5, 50.6, 57.5, 72.8, 106.1, 116.5, 122.8, 125.9, 126.8, 127.1, 127.6, 128.1, 128.6, 128.7, 128.9, 129.8, 133.7, 134.7, 134.9, 137.8, 139.3, 140.6, 143.6, 149.9. IR (CH_2Cl_2) ν 3051, 2920, 2847, 1602, 1488, 1340, 1160, 929, 838, 722, 659 cm^{-1}. MS (ESI) *m/z* (%): 533.22 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{34}H_{33}N_2O_2S^{+1}[M+H]^+$ requires 533.2257, found: 533.2256. Enantiomeric excess was determined by HPLC with a Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.70 mL/min; t_{minor} = 32.91 min, t_{major} = 22.85 min; ee% =

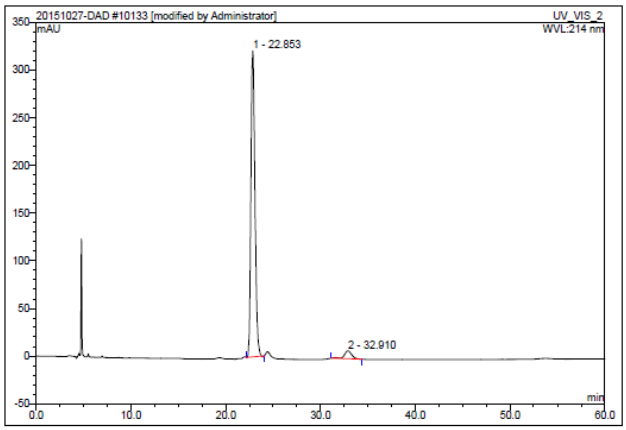
91%; $[\alpha]_D^{25}$ = -63.8 (c 0.08, CH_2Cl_2)].







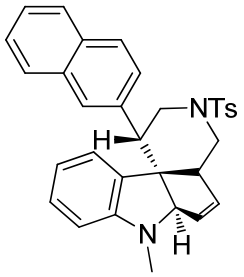




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.81	n.a.	671.875	336.707	50.02	n.a.	BMB*
2	32.50	n.a.	406.946	336.426	49.98	n.a.	BMB*
Total:			1078.821	673.133	100.00	0.000	

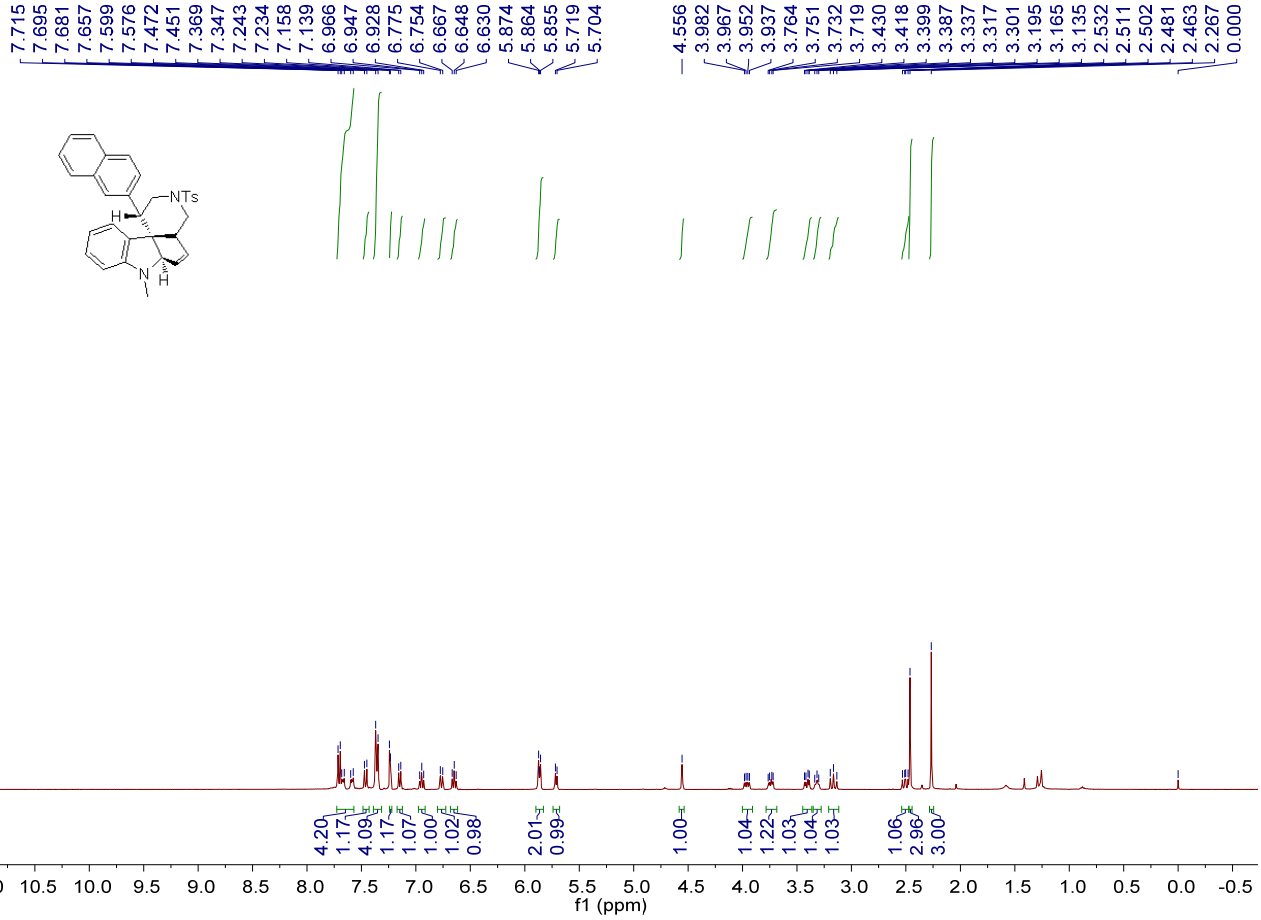
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.85	n.a.	320.726	158.499	95.51	n.a.	BMB*
2	32.91	n.a.	8.262	7.453	4.49	n.a.	BMB*
Total:			328.987	165.952	100.00	0.000	

Translation: Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.70 mL/min; t_{minor} = 32.91 min, t_{major} = 22.85 min; ee% = 91%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



(1*S*,4a*R*,6a*R*,11b*S*)-7-methyl-1-(naphthalen-2-yl)-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 2q

A white solid, 49% yield (24.7 mg). M.p.: 153-156 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.27 (s, 3H), 2.46 (s, 3H), 2.51 (dd, *J* = 12.0, 8.8 Hz, 1H), 3.17 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.30-3.34 (m, 1H), 3.40 (dd, *J* = 12.0, 4.8 Hz, 1H), 3.74 (dd, *J* = 12.8, 5.2 Hz, 1H), 3.96 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.56 (s, 1H), 5.71 (d, *J* = 6.0 Hz, 1H), 5.85-5.88 (m, 2H), 6.63-6.67 (m, 1H), 6.75-6.78 (m, 1H), 6.92-6.97 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.23-7.24 (m, 1H), 7.34-7.37 (m, 4H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.57-7.72 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 32.1, 47.79, 47.81, 50.3, 50.9, 57.5, 72.9, 106.2, 116.5, 122.8, 125.4, 125.6, 126.1, 126.5, 126.6, 127.3, 127.55, 127.61, 128.7, 129.0, 129.8, 132.3, 132.8, 133.8, 134.7, 134.9, 136.4, 143.6, 149.9. IR (CH_2Cl_2) ν 3050, 2920, 1602, 1489, 1338, 1158, 934, 816, 723, 657 cm^{-1}. MS (ESI) *m/z* (%): 507.20 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{32}H_{31}N_2O_2S^{+1}[M+H]^+$ requires 507.2101, found: 507.2094. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 68.13 min, t_{major} = 62.80 min; ee% = 90%; $[\alpha]_D^{25}$ = -187.7 (c 2.00, CH_2Cl_2)].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7.451
7.369
7.347
7.243
7.234
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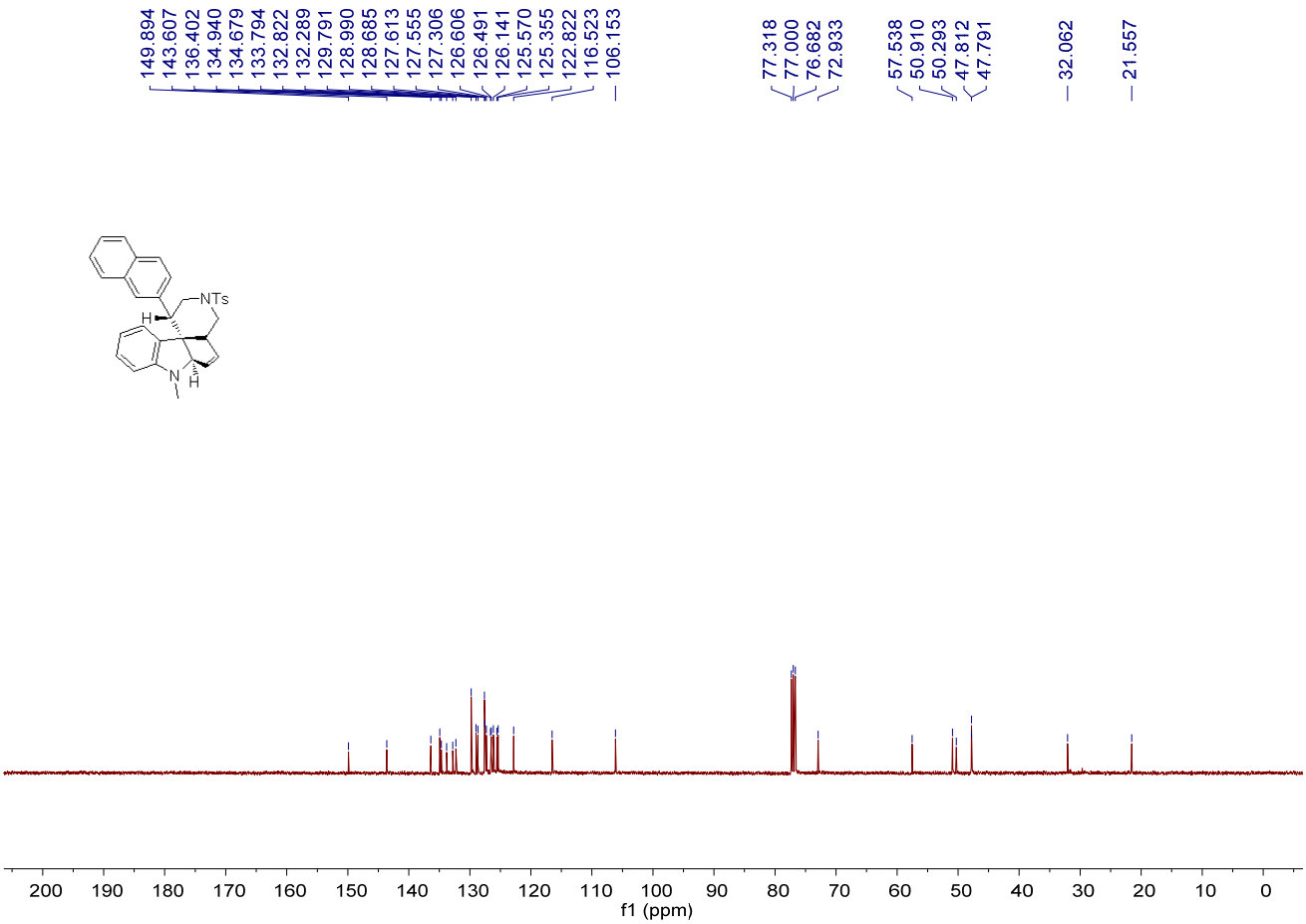
7.139
6.966
6.947
6.928
6.775
6.754
6.667
6.648
6.630
5.874
5.864
5.855
5.719
5.704
4.556
3.982
3.967
3.952
3.937
3.764
3.751
3.732
3.719
3.430
3.418
3.399
3.387
3.337
3.317
3.301
3.195
3.165
3.135
2.532
2.511
2.502
2.481
2.463
2.267
0.000
NTs
H
N
H
4.20
1.17
4.09
1.17
1.07
1.00
1.02
0.98
2.01
0.99
1.00
1.04
1.22
1.03
1.04
1.03
1.06
2.96
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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134.679
133.794
132.822
132.289
129.791
128.990
128.685
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127.306
126.606
126.491
126.141
125.570
125.355
122.822
116.523
106.153
77.318
77.000
76.682
72.933
57.538
50.910
50.293
47.812
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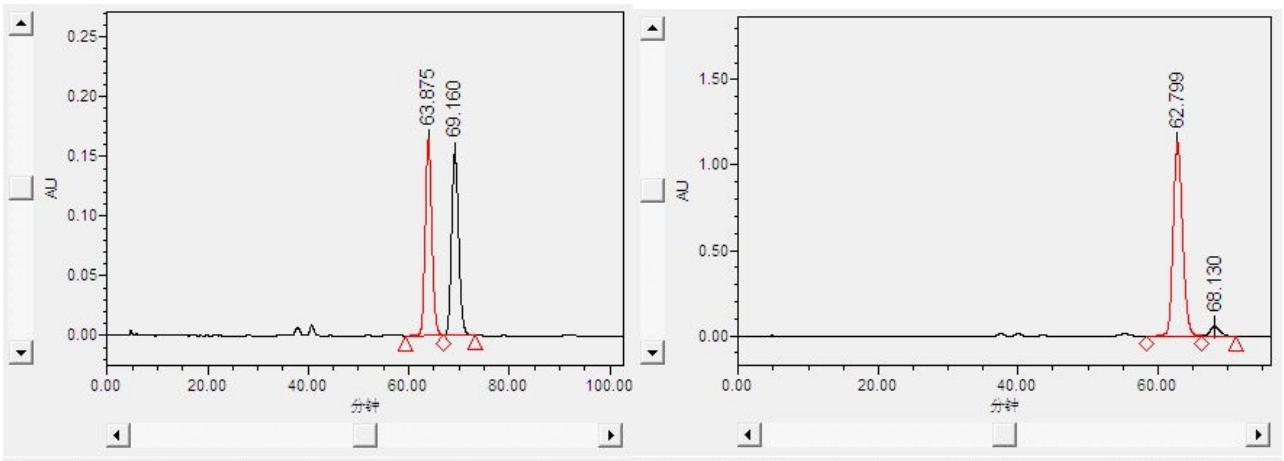
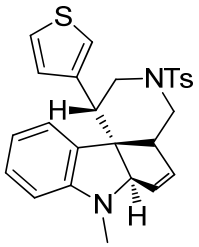
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		63.875	15232619	50.29	164097	BV	59.517	66.950
2		69.160	15056418	49.71	153245	VB	66.950	73.283

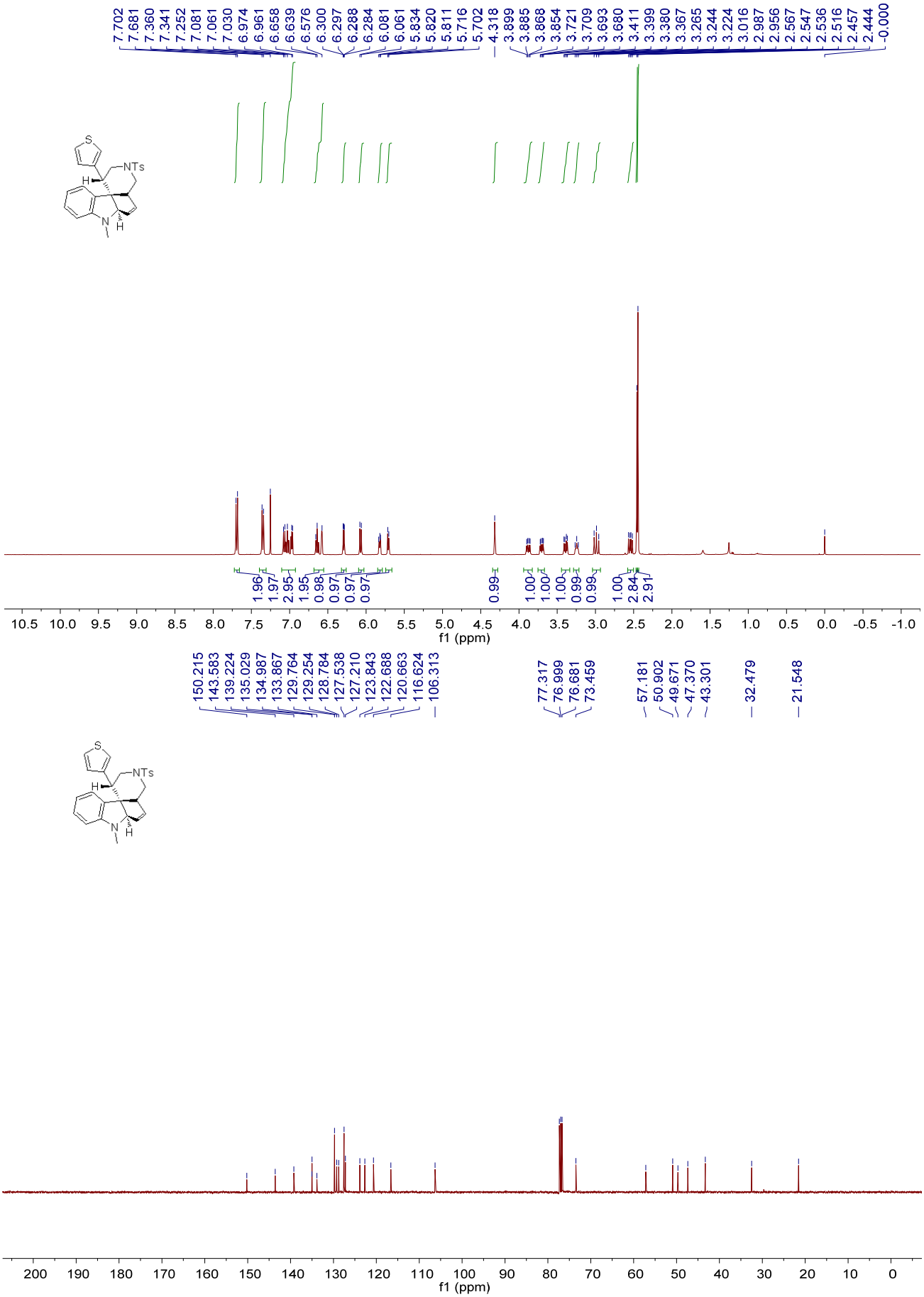
	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		62.799	105694648	95.01	1130949	VV	58.417	66.267
2		68.130	5546331	4.99	56450	VB	66.267	71.183

Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 68.13 min, t_{major} = 62.80 min; ee% = 90%].



(1*R*,4a*R*,6a*R*,11b*S*)-7-methyl-1-(thiophen-3-yl)-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 2r

A white solid, 48% yield (22.1 mg). M.p.: 145-148 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.44 (s, 3H), 2.46 (s, 3H), 2.54 (dd, *J* = 12.0, 8.0 Hz, 1H), 2.99 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.22-3.27 (m, 1H), 3.39 (dd, *J* = 12.4, 5.2 Hz, 1H), 3.70 (dd, *J* = 11.6, 5.2 Hz, 1H), 3.87 (dd, *J* = 12.4, 5.6 Hz, 1H), 4.32 (s, 1H), 5.71 (d, *J* = 6.0 Hz, 1H), 5.81-5.84 (m, 1H), 6.07 (d, *J* = 8.0 Hz, 1H), 6.29 (dd, *J* = 4.8, 1.6 Hz, 1H), 6.57-6.66 (m, 2H), 6.96-7.09 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 32.5, 43.3, 47.4, 49.7, 50.9, 57.2, 73.5, 116.6, 120.7, 122.7, 123.8, 127.2, 127.5, 128.8, 129.3, 129.8, 133.9, 134.98, 135.03, 139.2, 143.6, 150.2. IR (CH_2Cl_2) ν 3047, 2922, 1600, 1493, 1335, 1161, 935, 812, 732, 657 cm^{-1}. MS (ESI) *m/z* (%): 463.15 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{26}H_{27}N_2O_2S_2^{+1}[M+H]^+$ requires 463.1508, found: 463.1505. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 94/6; Flow rate: 0.70 mL/min; t_{minor} = 133.59 min, t_{major} = 121.45 min; ee% = 95%; $[\alpha]_D^{25}$ = -104.7 (c 0.15, CH_2Cl_2)].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7.341
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7.081
7.061
7.030
6.974
6.961
6.658
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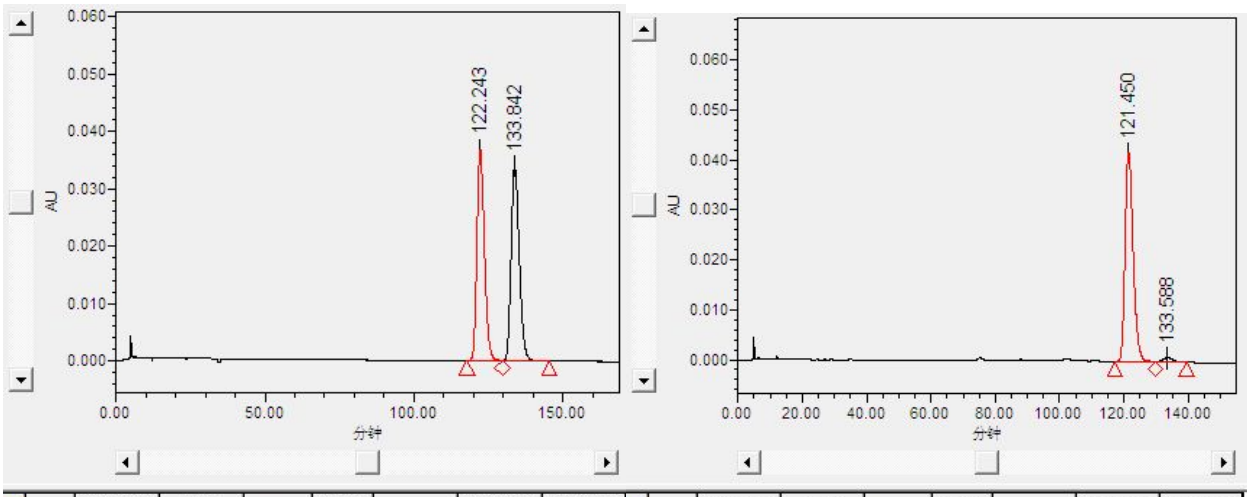
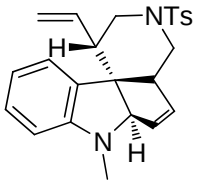
6.300
6.297
6.288
6.284
6.081
6.061
5.834
5.820
5.811
5.716
5.702
4.318
3.899
3.885
3.868
3.854
3.721
3.709
3.693
3.680
3.411
3.399
3.380
3.367
3.265
3.244
3.224
3.016
2.987
2.956
2.567
2.547
2.536
2.516
2.457
2.444
-0.000
NTs
1.96
1.97
2.95
1.95
0.98
0.97
0.97
0.97
0.99
1.00
1.00
1.00
0.99
0.99
1.00
2.84
2.91
f1 (ppm)
150.215
143.583
139.224
135.029
134.987
133.867
129.764
129.254
128.784
127.538
127.210
123.843
122.688
120.663
116.624
106.313
77.317
76.999
76.681
73.459
57.181
50.902
49.671
47.370
43.301
32.479
21.548
NTs
f1 (ppm)



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		122.243	6454659	49.97	36837	BV	117.867	129.667
2		133.842	6462050	50.03	34077	VB	129.667	145.433

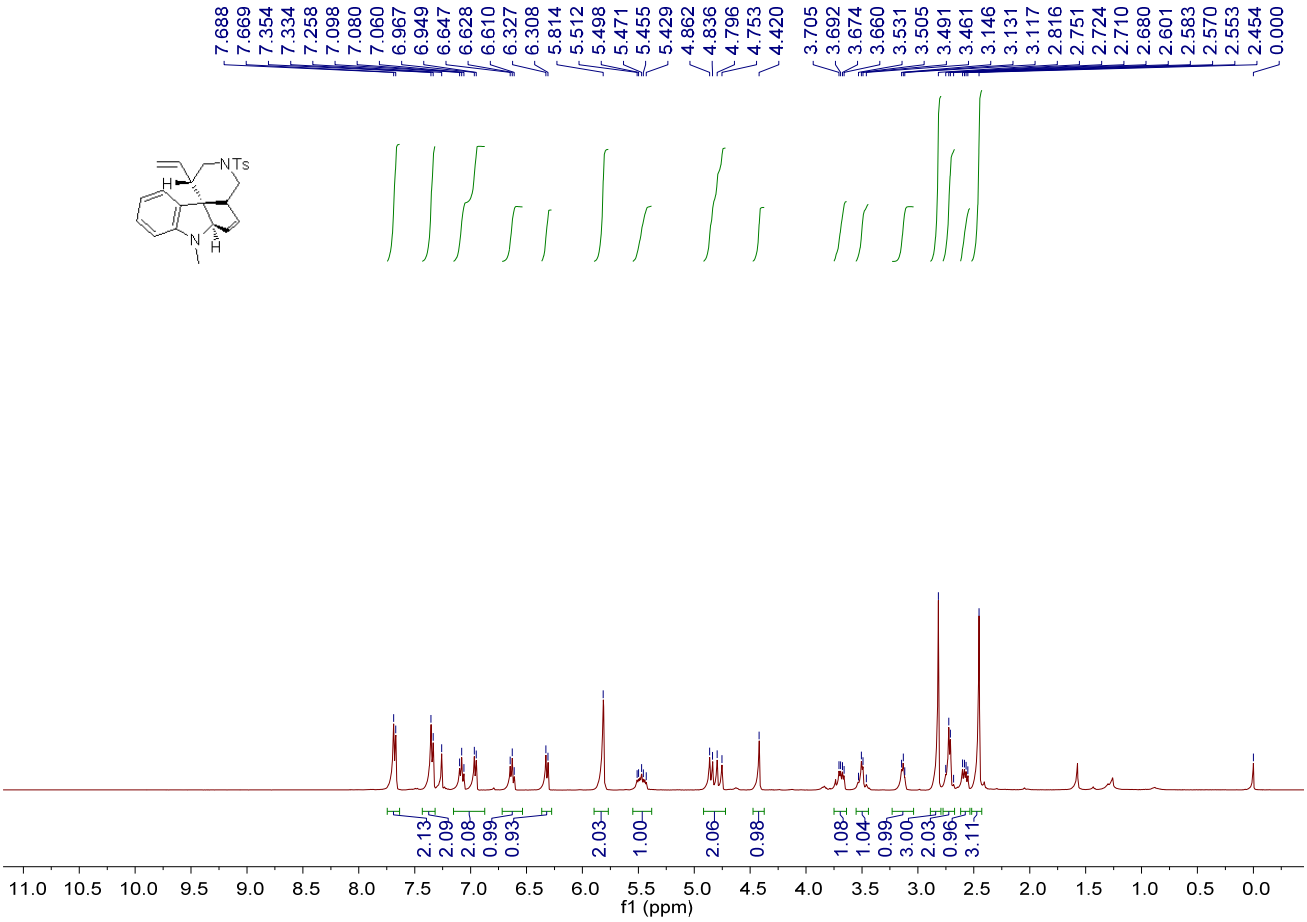
	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		121.450	7311369	97.64	41782	BV	117.433	129.767
2		133.588	176549	2.36	909	VB	129.767	139.433

Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 94/6; Flow rate: 0.70 mL/min; t_{minor} = 133.59 min, t_{major} = 121.45 min; ee% = 95%].



(1*S*,4a*R*,6a*R*,11b*R*)-7-methyl-3-tosyl-1-vinyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 2s

A white solid, 48% yield (19.4 mg). M.p.: 92-95 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.45 (s, 3H), 2.55-2.61 (m, 1H), 2.68-2.76 (m, 2H), 2.82 (s, 3H), 3.11-3.15 (m, 1H), 3.46-3.54 (m, 1H), 3.66-3.71 (m, 1H), 4.42 (s, 1H), 4.75-4.87 (m, 2H), 5.42-5.52 (m, 1H), 5.81 (s, 2H), 6.31 (d, *J* = 7.6 Hz, 1H), 6.61-6.65 (m, 1H), 6.94-7.10 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 32.6, 45.3, 46.9, 48.8, 51.5, 55.5, 73.2, 106.4, 116.6, 117.1, 122.6, 127.5, 128.6, 128.8, 129.7, 133.9, 135.1, 135.4, 135.5, 143.5, 150.4. IR (CH_2Cl_2) ν 2922, 2852, 2360, 1747, 1463, 1162, 1089, 937, 815, 747, 658 cm^{-1}. MS (ESI) *m/z* (%): 407.17 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{24}H_{27}N_2O_2S^{+1}$ $[M+H]^+$ requires 407.1788, found: 407.1775. Enantiomeric excess was determined by HPLC with a Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_{minor} = 29.53 min, t_{major} = 27.93 min; ee% = 95%; $[\alpha]_D^{25}$ = 17.3 (c 0.10, CH_2Cl_2)].


7.688
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7.098
7.080
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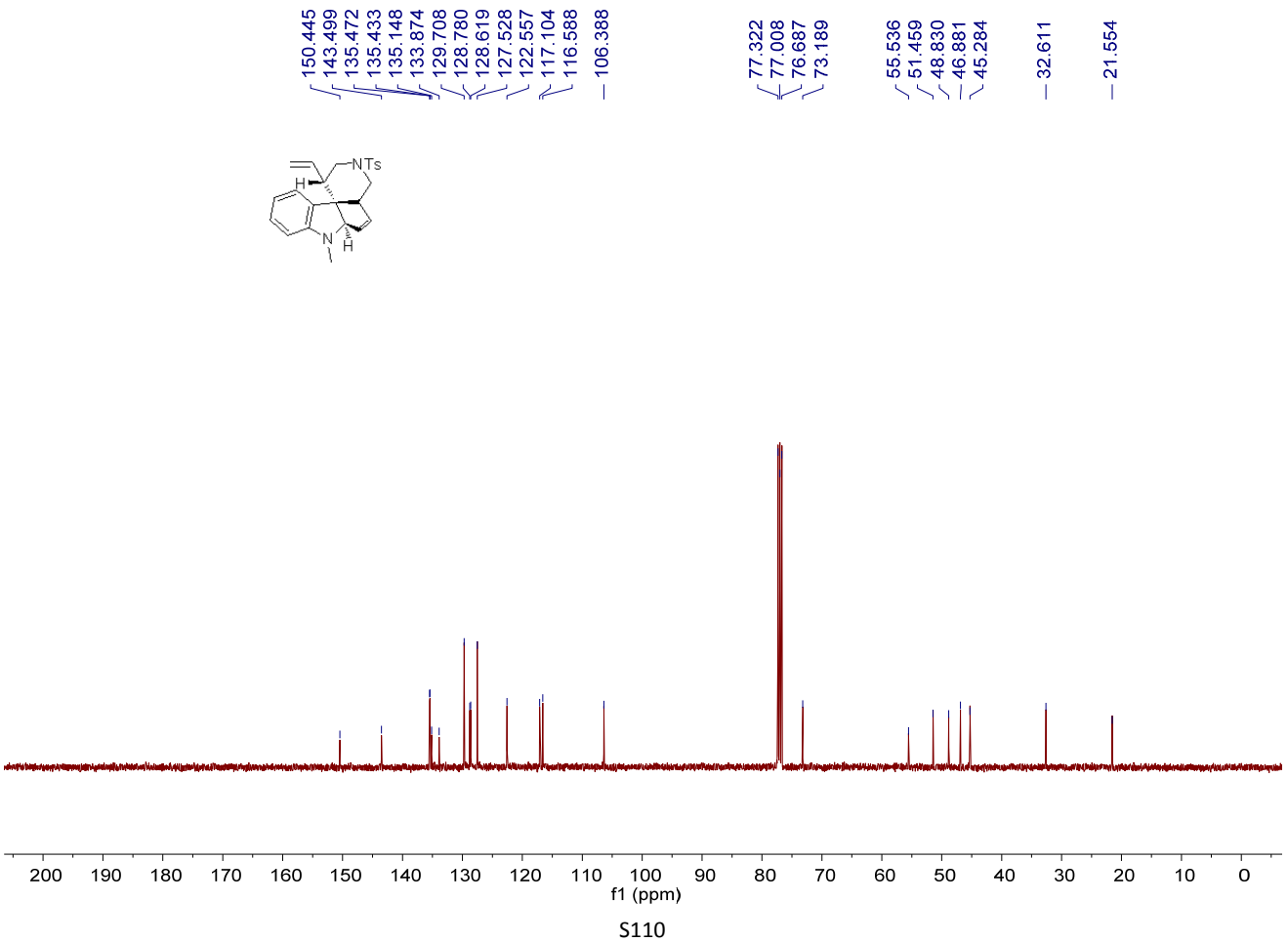
6.949
6.647
6.628
6.610
6.327
6.308
5.814
5.512
5.498
5.471
5.455
5.429
4.862
4.836
4.796
4.753
4.420
3.705
3.692
3.674
3.660
3.531
3.505
3.491
3.461
3.146
3.131
3.117
2.816
2.751
2.724
2.710
2.680
2.601
2.583
2.570
2.553
2.454
0.000
NTs
H
N
H
2.13
2.09
2.08
0.99
0.93
2.03
1.00
2.06
0.98
1.08
1.04
0.99
3.00
2.03
0.96
3.11
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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135.433
135.148
133.874
129.708
128.780
128.619
127.528
122.557
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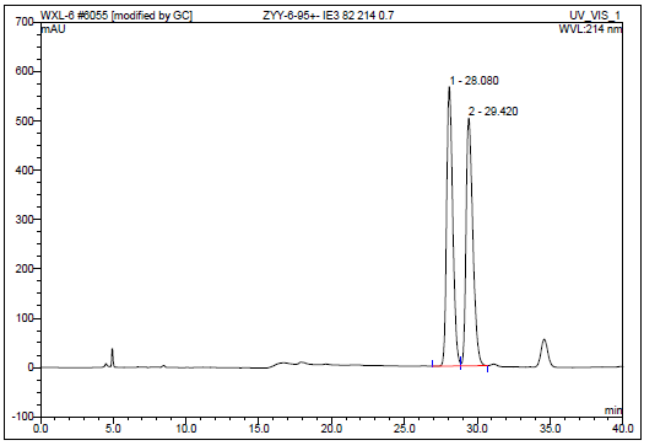
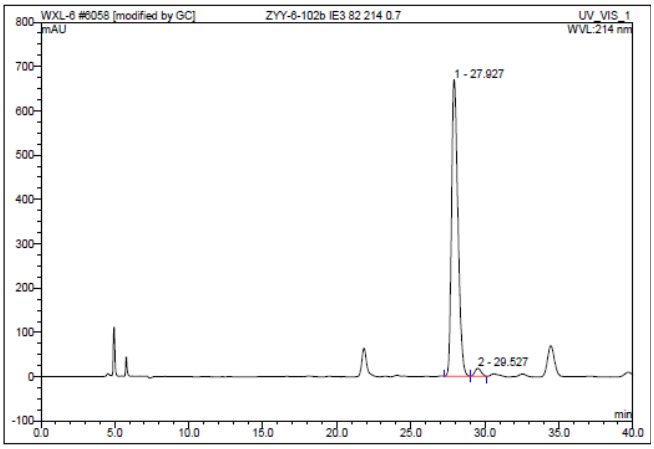
106.388
77.322
77.008
76.687
73.189
55.536
51.459
48.830
46.881
45.284
32.611
21.554
NTs
H
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

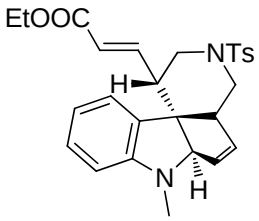




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	28.08	n.a.	566.216	275.814	50.46	n.a.	BM *
2	29.42	n.a.	502.088	270.735	49.54	n.a.	MB*
Total:			1068.304	546.549	100.00	0.000	

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	27.93	n.a.	669.261	335.403	97.46	n.a.	BM
2	29.53	n.a.	17.800	8.727	2.54	n.a.	MB
Total:			687.061	344.131	100.00	0.000	

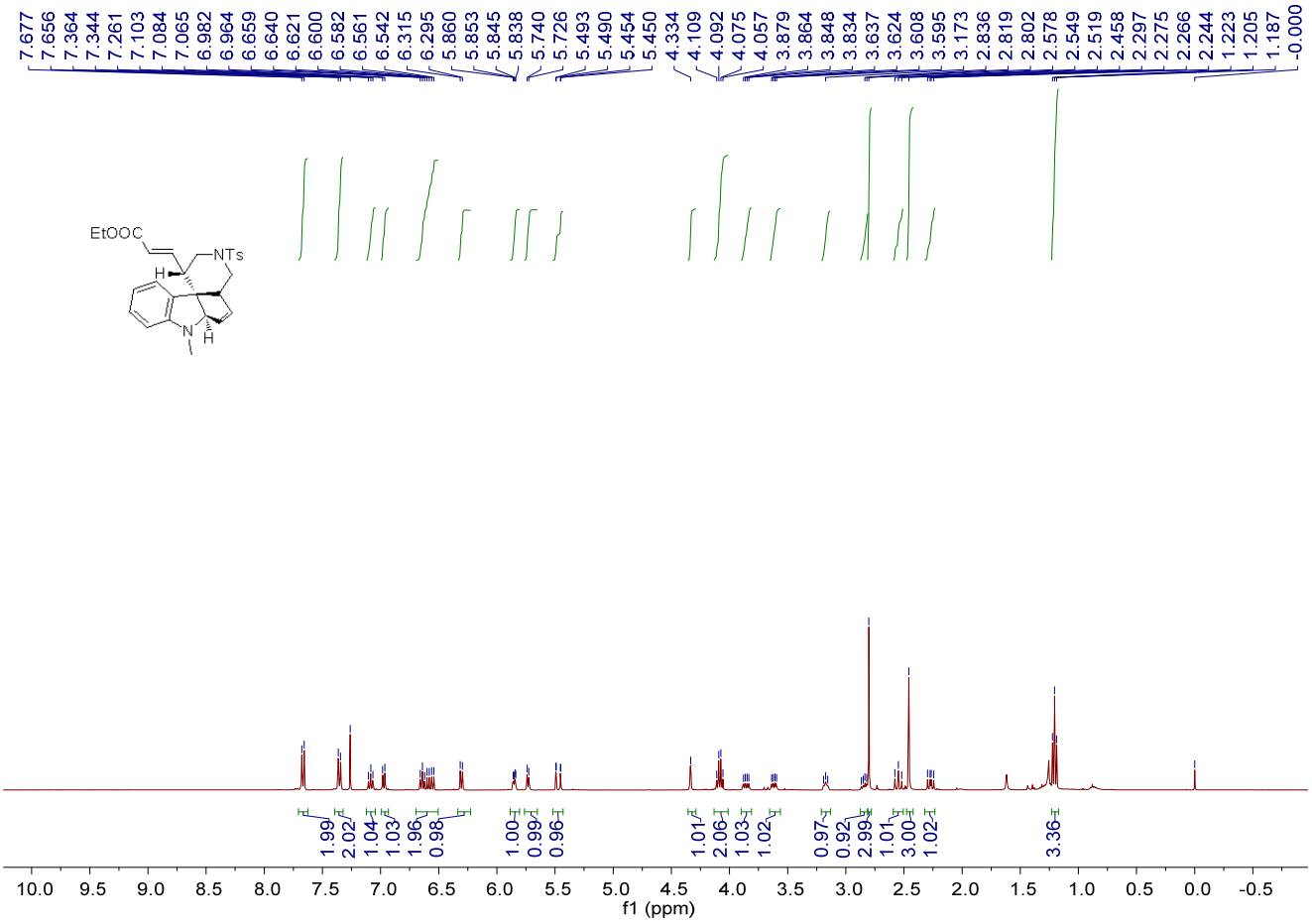
Translation: Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_{minor} = 29.53 min, t_{major} = 27.93 min; ee% = 95%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).

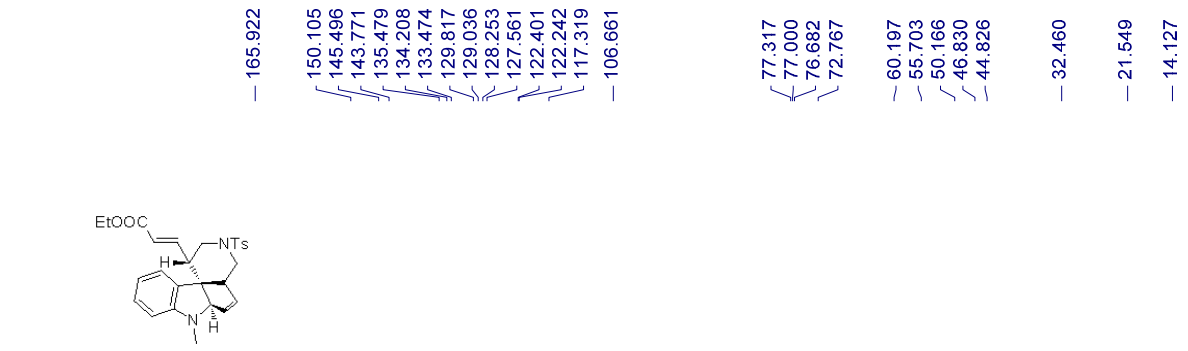


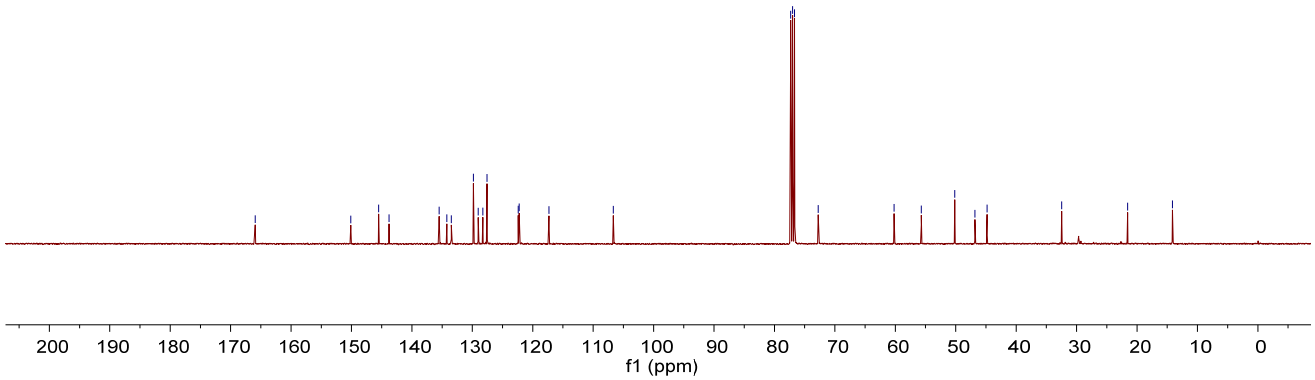
(E)-ethyl 3-((1S,4aR,6aR,11bS)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3] cyclopenta[1,2-b]indol-1-yl)acrylate 2t

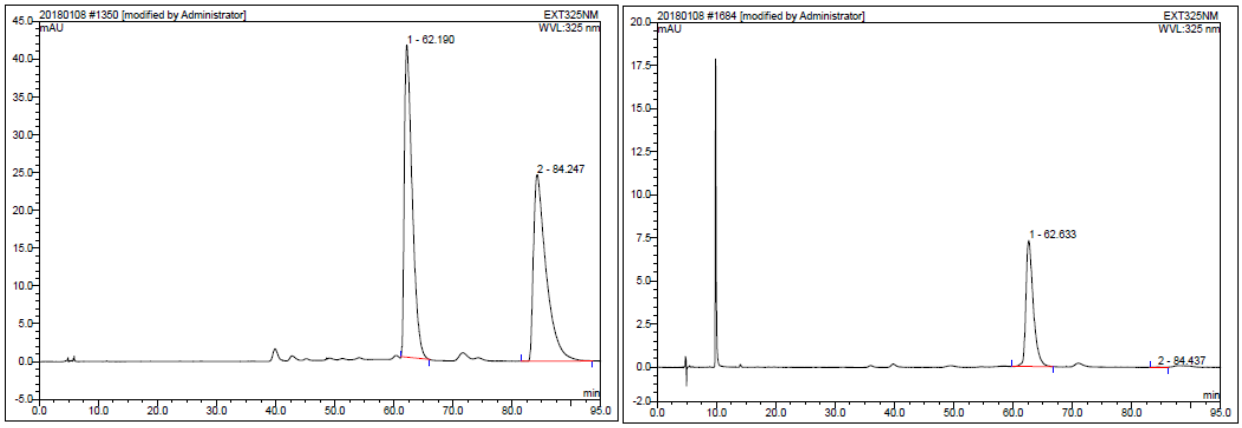
A white solid, 43% yield (20.8 mg). M.p.: 66-69 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.21 (t, *J* = 7.2 Hz, 3H), 2.27 (dd, *J* = 12.0, 8.8 Hz, 1H), 2.46 (s, 3H), 2.55 (dd, *J* = 12.0, 12.0 Hz, 1H), 2.80 (s, 3H), 2.81-2.87 (m, 1H), 3.15-3.20 (m, 1H), 3.61 (dd, *J* = 12.0, 5.2 Hz, 1H), 3.85 (dd, *J* = 12.0, 5.6 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 4.33 (s, 1H), 5.45-5.50 (m, 1H), 5.72-5.74 (m, 1H), 5.83-5.86 (m, 1H), 6.30 (d, *J* = 8.0 Hz, 1H), 6.54-6.66 (m, 2H), 6.96-6.99 (m, 1H), 7.06-7.11 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 21.5, 32.5, 44.8, 46.8, 50.2, 55.7, 60.2, 72.8, 106.7, 117.3, 122.2, 122.4, 127.6, 128.3, 129.0, 129.8, 133.5, 134.2, 135.5, 143.8, 145.5, 150.1, 165.9. IR (CH_2Cl_2) ν 3052, 2933, 1721, 1601, 1342, 1168, 1011, 932, 822, 750, 662 cm^{-1}. MS (ESI) *m/z* (%): 479.19 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{27}H_{31}N_2O_4S^{+1}$ $[M+H]^+$ requires 479.1999, found: 479.1985. Enantiomeric excess was determined by HPLC with a Chiralcel

IE3 column [λ = 325 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_{minor} = 82.44 min, t_{major} = 62.63 min; ee% = 99%; $[\alpha]_D^{25}$ = -31.2 (c 0.08, CH_2Cl_2)].





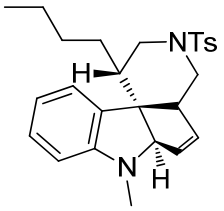




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	62.19	n.a.	41.267	63.832	50.98	n.a.	BMB*
2	84.25	n.a.	24.632	61.384	49.02	n.a.	BMB*
Total:			65.899	125.216	100.00	0.000	

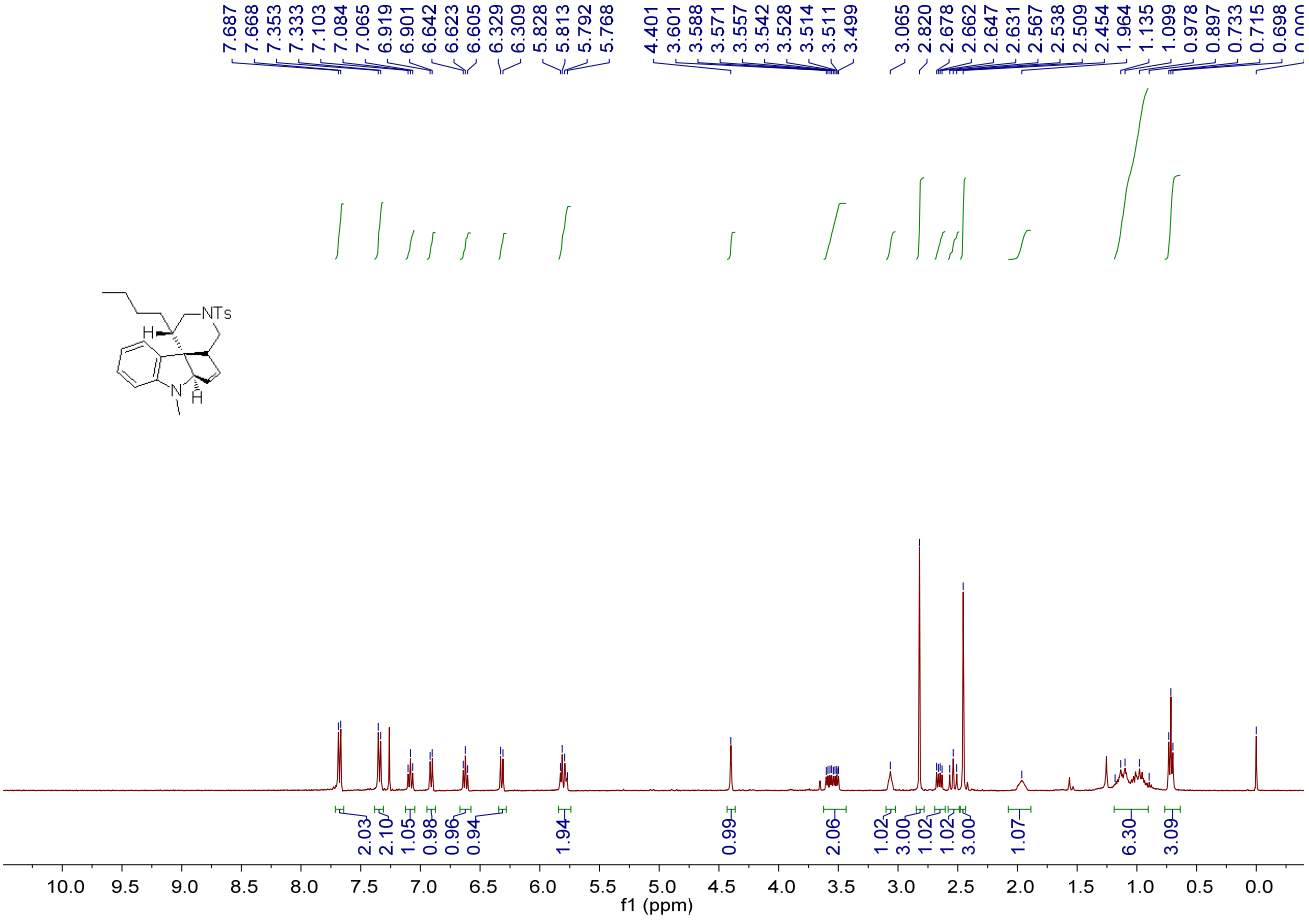
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	62.63	n.a.	7.296	10.465	99.82	n.a.	BMB*
2	84.44	n.a.	0.023	0.019	0.18	n.a.	BM *
Total:			7.319	10.484	100.00	0.000	

Translation: Chiralcel IE3 column [λ = 325 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_{minor} = 84.44 min, t_{major} = 62.63 min; ee% = 99%].



(1*S*,4a*R*,6a*R*,11b*R*)-1-butyl-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 2u

A white solid, 44% yield (19.2 mg). M.p.: 43-46 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.72 (t, *J* = 7.2 Hz, 3H), 0.89-1.19 (m, 6H), 1.96 (br, 1H), 2.45 (s, 3H), 2.54 (dd, *J* = 12.0, 12.0 Hz, 1H), 2.65 (dd, *J* = 12.4, 6.4 Hz, 1H), 2.82 (s, 3H), 3.07 (br, 1H), 3.49-3.61 (m, 2H), 4.40 (s, 1H), 5.76-5.83 (m, 2H), 6.31 (d, *J* = 8.0 Hz, 1H), 6.60-6.65 (m, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 7.06-7.11 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 21.6, 22.4, 28.4, 29.4, 32.6, 40.6, 47.4, 48.4, 52.4, 55.8, 73.2, 106.3, 117.1, 122.5, 127.5, 128.5, 129.0, 129.7, 134.0, 135.5, 135.6, 143.4, 150.6. IR (CH_2Cl_2) ν 2920, 1794, 1601, 1407, 1169, 1090, 965, 871, 712, 661 cm^{-1}. MS (ESI) *m/z* (%): 437.22 (100) $[M+H]^+$; HRMS (DART) Calcd. For $C_{26}H_{33}N_2O_2S^{+1}$ $[M+H]^+$ requires 437.2257, found: 437.2254. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 94/6; Flow rate: 0.70 mL/min; t_{minor} = 64.48 min, t_{major} = 78.27 min; ee% = 92%; $[\alpha]_D^{25}$ = -12.3 (c 0.10, CH_2Cl_2)].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6.901
6.642
6.623
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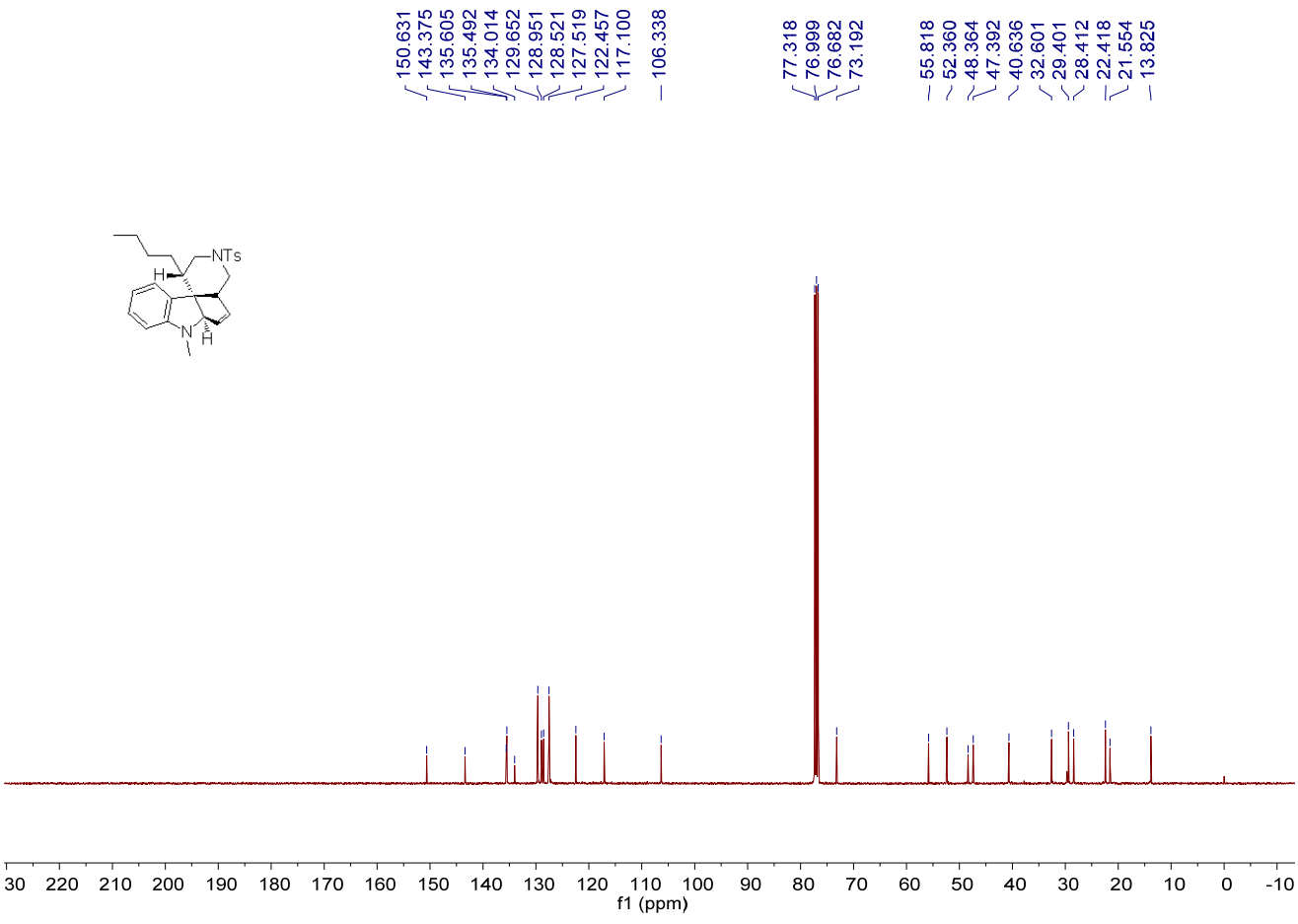
6.329
6.309
5.828
5.813
5.792
5.768
4.401
3.601
3.588
3.571
3.557
3.542
3.528
3.514
3.511
3.499
3.065
2.820
2.678
2.662
2.647
2.631
2.567
2.538
2.509
2.454
1.964
1.135
1.099
0.978
0.897
0.733
0.715
0.698
NTs
H
N
H
2.03
2.10
1.05
0.98
0.96
0.94
1.94
0.99
2.06
1.02
3.00
1.02
1.02
3.00
1.07
6.30
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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135.492
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129.652
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128.521
127.519
122.457
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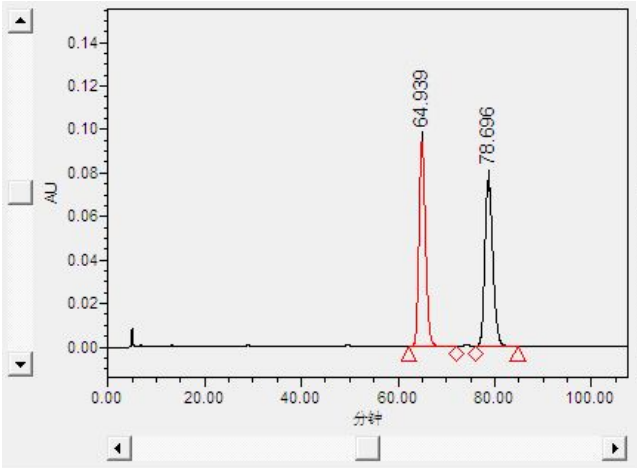
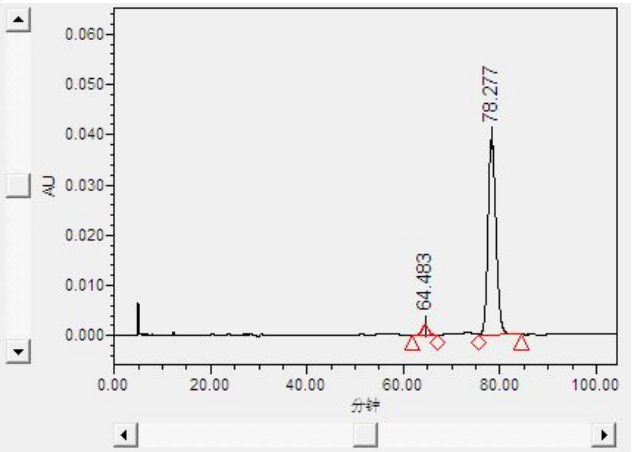
76.999
76.682
73.192
55.818
52.360
48.364
47.392
40.636
32.601
29.401
28.412
22.418
21.554
13.825
NTs
H
N
H
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

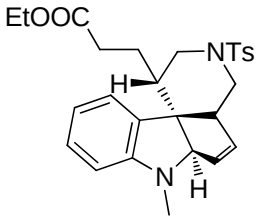




	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		64.939	8888160	50.11	93830	BV	62.250	72.083
2		78.696	8848431	49.89	76694	VB	76.050	84.767

	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	开始时间 (分钟)	结束时间 (分钟)
1		64.483	176135	3.77	1881	BV	61.767	67.033
2		78.277	4495486	96.23	39272	VB	75.617	84.317

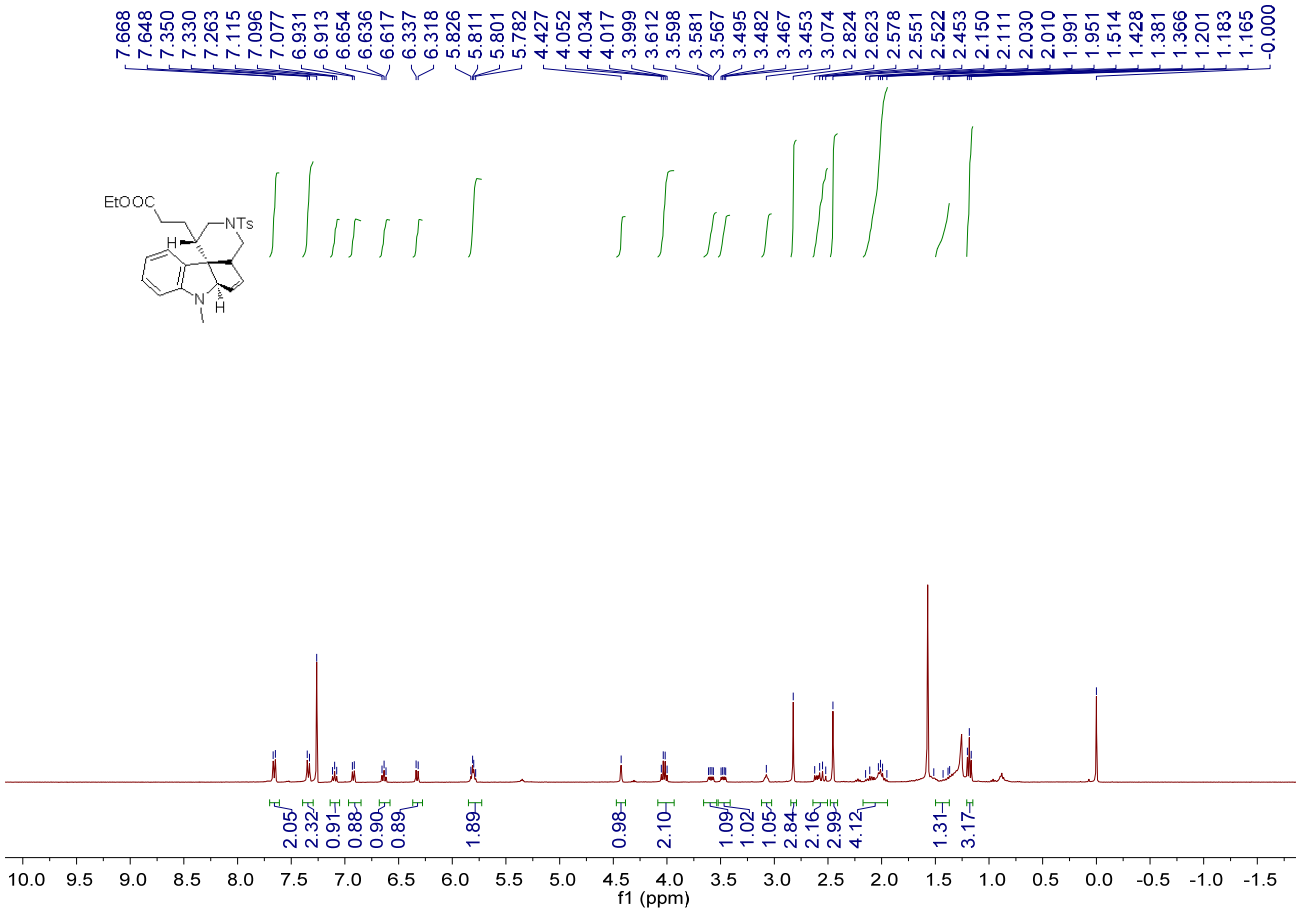
Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 94/6; Flow rate: 0.70 mL/min; t_{minor} = 64.48 min, t_{major} = 78.27 min; ee% = 92%].



ethyl 3-((1*S*,4a*R*,6a*R*,11b*R*)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3] cyclopenta[1,2-*b*]indol-1-yl)propanoate 2v

A white solid, 43% yield (20.8 mg). M.p.: 55-58 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.18 (t, *J* = 7.2 Hz, 3H), 1.36-1.52 (m, 1H), 1.95-2.15 (m, 4H), 2.45 (s, 3H), 2.52-2.63 (m, 2H), 2.82 (s, 3H), 3.07 (br, 1H), 3.47 (dd, *J* = 12.0, 5.6 Hz, 1H), 3.58 (dd, *J* = 12.0, 5.6 Hz, 1H), 4.02 (q, *J* = 7.2 Hz, 2H), 4.43 (s, 1H), 5.78-5.83 (m, 2H), 6.32 (d, *J* = 8.0 Hz, 1H), 6.61-6.66 (m, 1H), 6.91-6.93 (m, 1H), 7.07-7.12 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 21.6, 24.3, 32.2, 32.5, 40.6, 47.3, 48.5, 52.2, 55.7, 60.3, 73.1, 106.6, 117.3, 122.6, 127.5, 128.7, 128.8, 129.7, 133.9, 135.1, 135.4, 143.5, 150.5, 173.1. IR (CH_2Cl_2) ν 2922, 2852, 1730, 1602, 1486, 1344, 1160, 1089, 930, 816, 739, 659 cm^{-1}. MS (ESI) *m/z* (%): 481.21 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{27}H_{33}N_2O_4S^{+1}$ $[M+H]^+$ requires 481.2156, found: 481.2145. Enantiomeric excess was determined by HPLC with a Chiralcel IE3 column [λ = 309 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_{minor} = 65.21 min, t_{major} = 58.03 min; ee% = 93%; $[\alpha]_D^{25}$ = -58.8 (c

0.08, CH_2Cl_2)].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7.077
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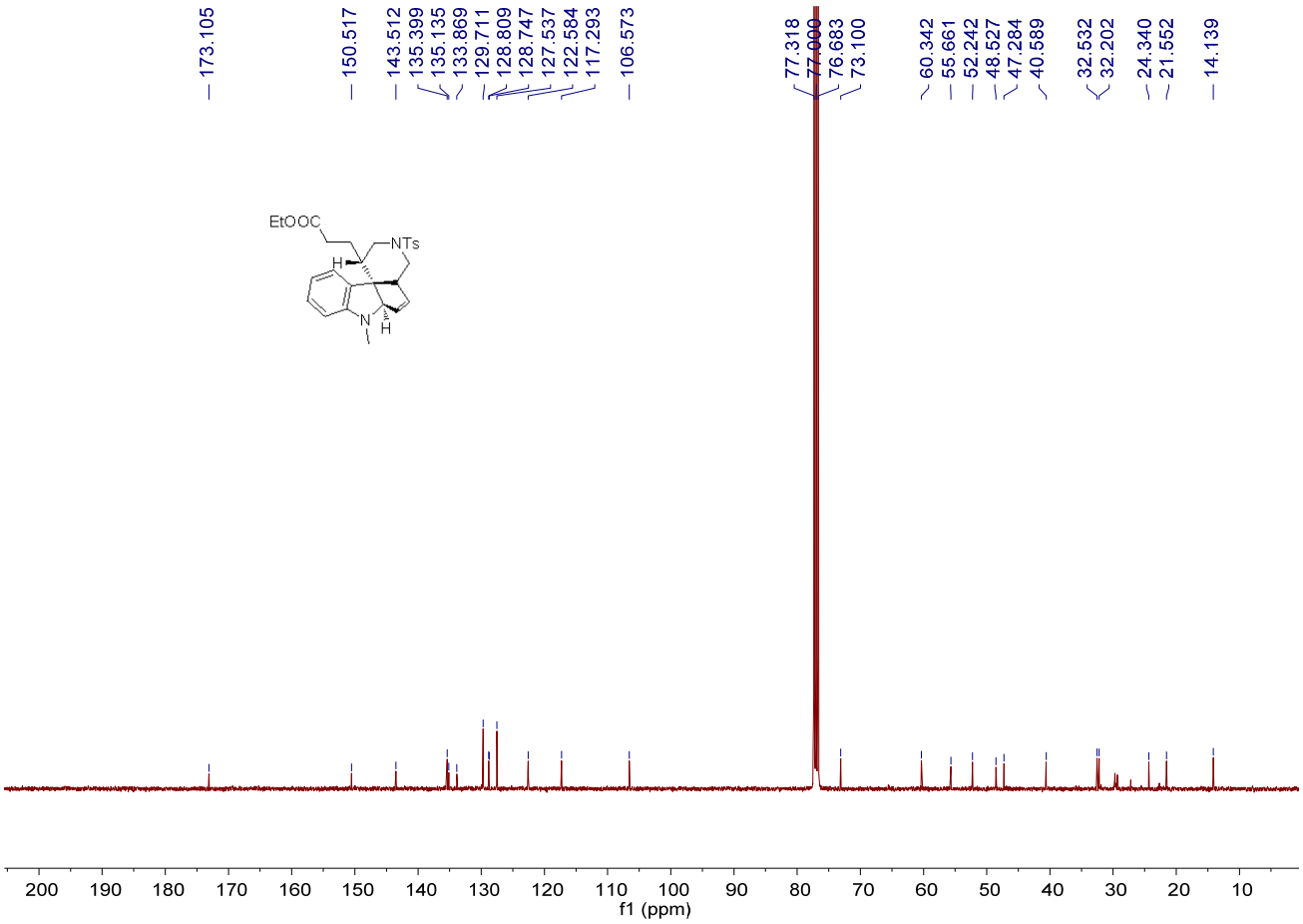
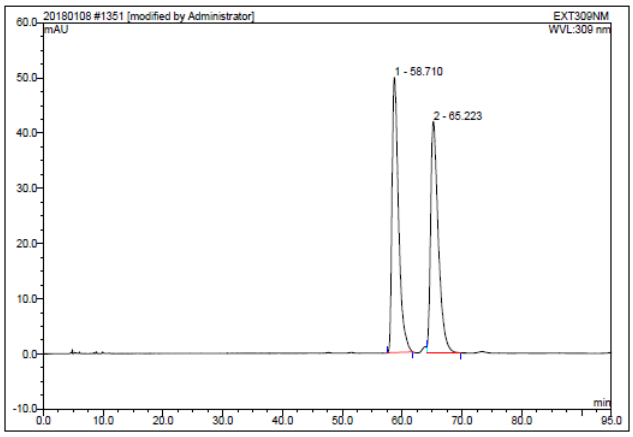
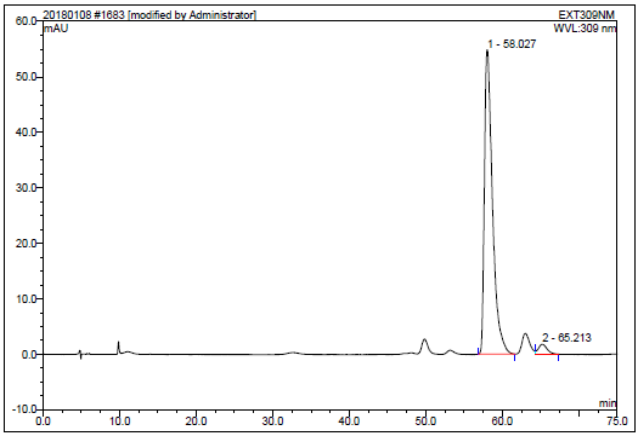
6.636
6.617
6.337
6.318
5.826
5.811
5.801
5.782
4.427
4.052
4.034
4.017
3.999
3.612
3.598
3.581
3.567
3.495
3.482
3.467
3.453
3.074
2.824
2.623
2.578
2.551
2.522
2.453
2.150
2.111
2.030
2.010
1.991
1.951
1.514
1.428
1.381
1.366
1.201
1.183
1.165
-0.000
EtOOC
NTs
H
N
H
2.05
2.32
0.91
0.88
0.90
0.89
1.89
0.98
2.10
1.09
1.02
1.05
2.84
2.16
2.99
4.12
1.31
3.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)



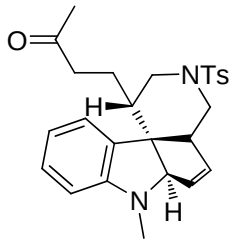




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	58.71	n.a.	49.809	63.255	50.26	n.a.	BMB
2	65.22	n.a.	41.908	62.591	49.74	n.a.	MB*
Total:			91.717	125.846	100.00	0.000	

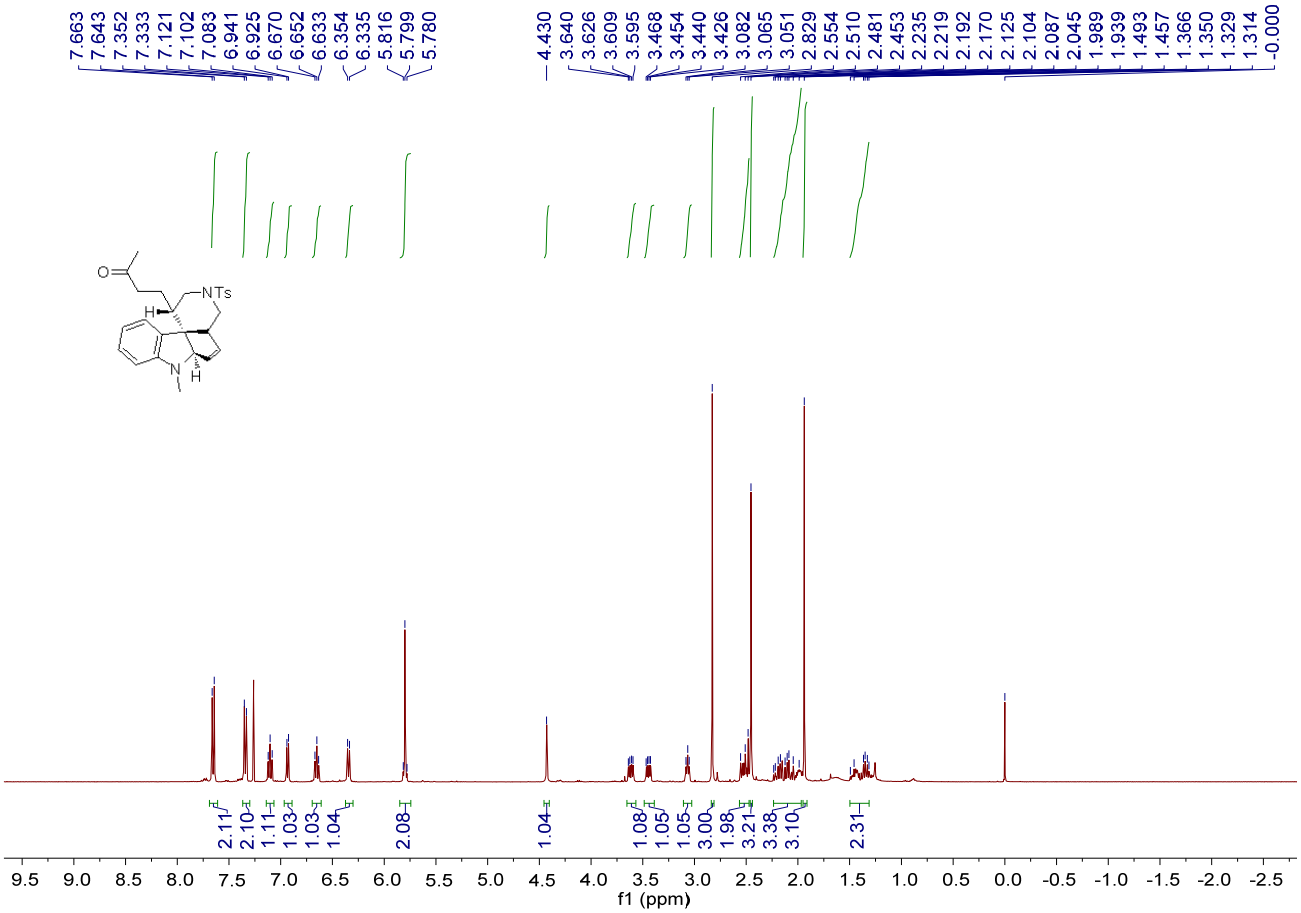
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	58.03	n.a.	54.873	67.230	96.61	n.a.	BMB*
2	65.21	n.a.	1.794	2.362	3.39	n.a.	MB*
Total:			56.667	69.591	100.00	0.000	

Translation: Chiralcel IE3 column [λ = 309 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_{minor} = 65.21 min, t_{major} = 58.03 min; ee% = 93%].



4-((1*S*,4a*R*,6a*R*,11b*R*)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indol-1-yl)butan-2-one 2w

A white liquid, 43% yield (19.4 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.31-1.50 (m, 2H), 1.94 (s, 3H), 1.98-2.24 (m, 3H), 2.45 (s, 3H), 2.48-2.56 (m, 2H), 2.83 (s, 3H), 3.05-3.09 (m, 1H), 3.45 (dd, *J* = 11.6, 5.6 Hz, 1H), 3.61 (dd, *J* = 12.4, 5.6 Hz, 1H), 4.43 (s, 1H), 5.78-5.82 (m, 2H), 6.34 (d, *J* = 7.6 Hz, 1H), 6.63-6.67 (m, 1H), 6.92-6.95 (m, 1H), 7.08-7.13 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 23.1, 29.7, 32.6, 40.7, 41.6, 47.6, 48.8, 52.1, 55.7, 73.0, 106.7, 117.3, 122.6, 127.5, 128.6, 128.8, 129.7, 133.8, 135.4, 135.5, 143.5, 150.5, 208.4. IR (CH_2Cl_2) ν 2921, 1716, 1600, 1485, 1340, 1164, 1091, 937, 815, 786, 660 cm^{-1}. MS (ESI) *m/z* (%): 451.20 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{26}H_{31}N_2O_3S^{+1}$ $[M+H]^+$ requires 451.2050, found: 451.2035. Enantiomeric excess was determined by HPLC with a Chiralcel IE3 column [λ = 311 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 57.19 min, t_{major} = 51.27 min; ee% = 94%; $[\alpha]_D^{25}$ = -17.8 (c 1.10, CH_2Cl_2)].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6.670
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6.335
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3.640
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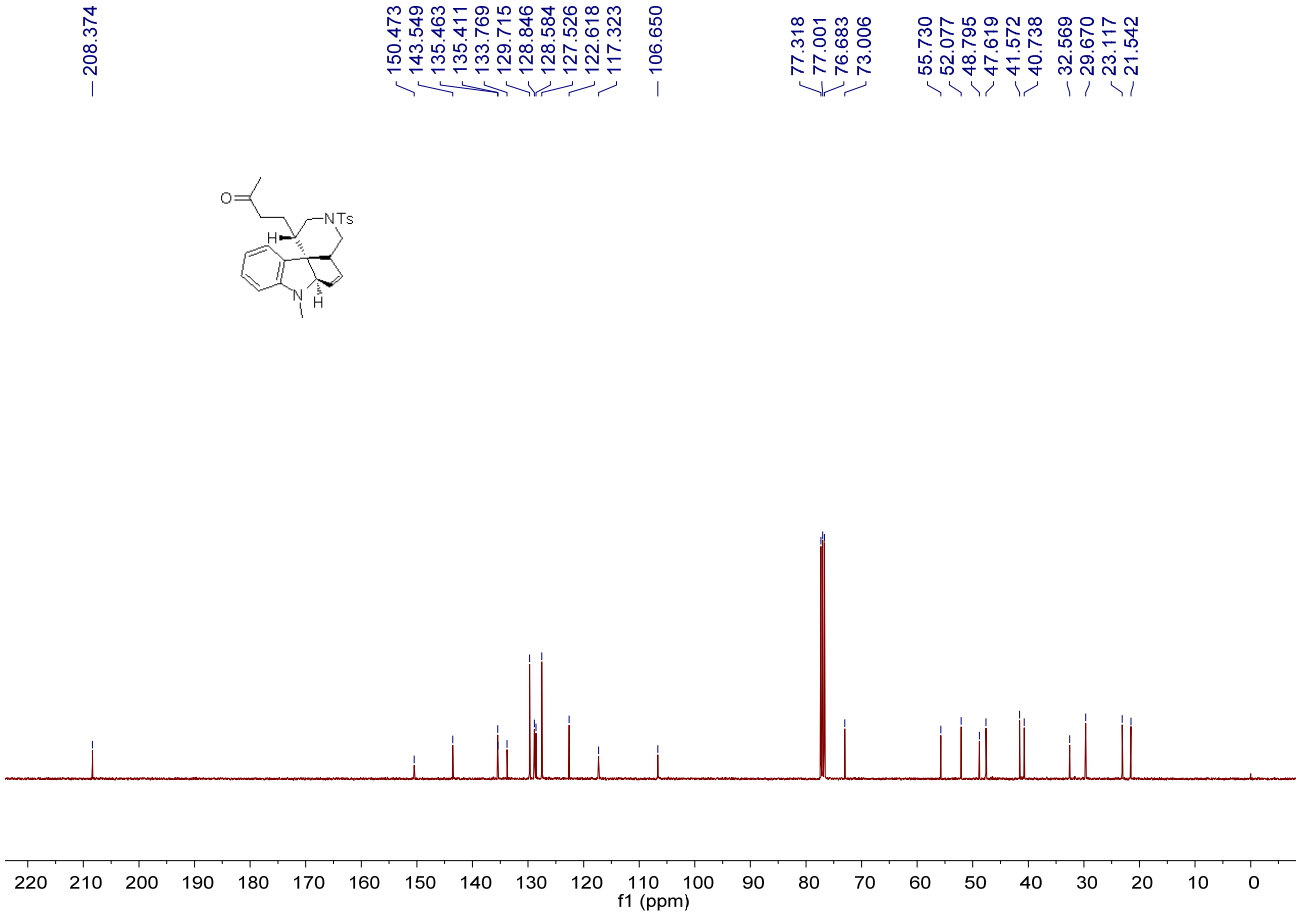
2.125
2.104
2.087
2.045
1.989
1.939
1.493
1.457
1.366
1.350
1.329
1.314
-0.000
NTs
H
N
H
2.11
2.10
1.11
1.03
1.03
1.04
2.08
1.04
1.08
1.05
1.05
3.00
1.98
3.21
3.38
3.10
2.31
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5
f1 (ppm)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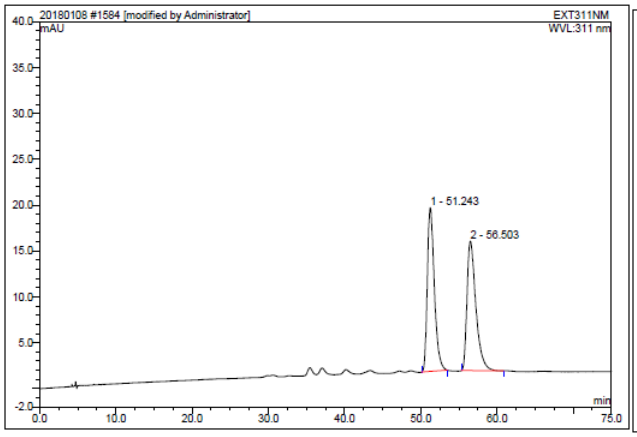
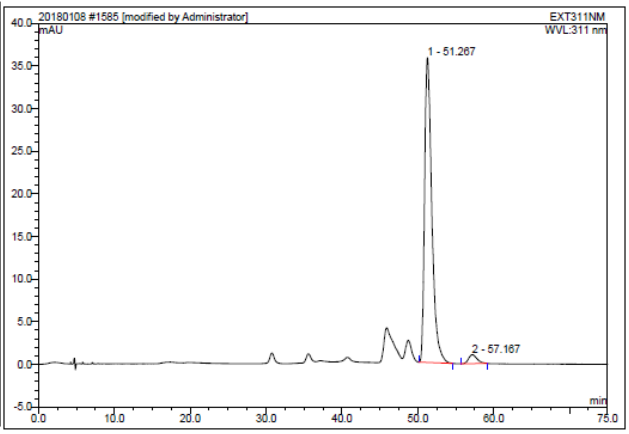
77.318
77.001
76.683
73.006
55.730
52.077
48.795
47.619
41.572
40.738
32.569
29.670
23.117
21.542
NTs
H
N
H
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

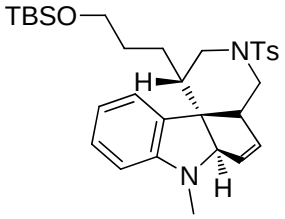


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	51.24	n.a.	17.827	19.018	50.02	n.a.	BMB
2	56.50	n.a.	14.120	19.006	49.98	n.a.	BMB*
Total:			31.947	38.024	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	51.27	n.a.	35.723	39.471	96.75	n.a.	BMB*
2	57.17	n.a.	1.046	1.327	3.25	n.a.	BMB*
Total:			36.770	40.798	100.00	0.000	

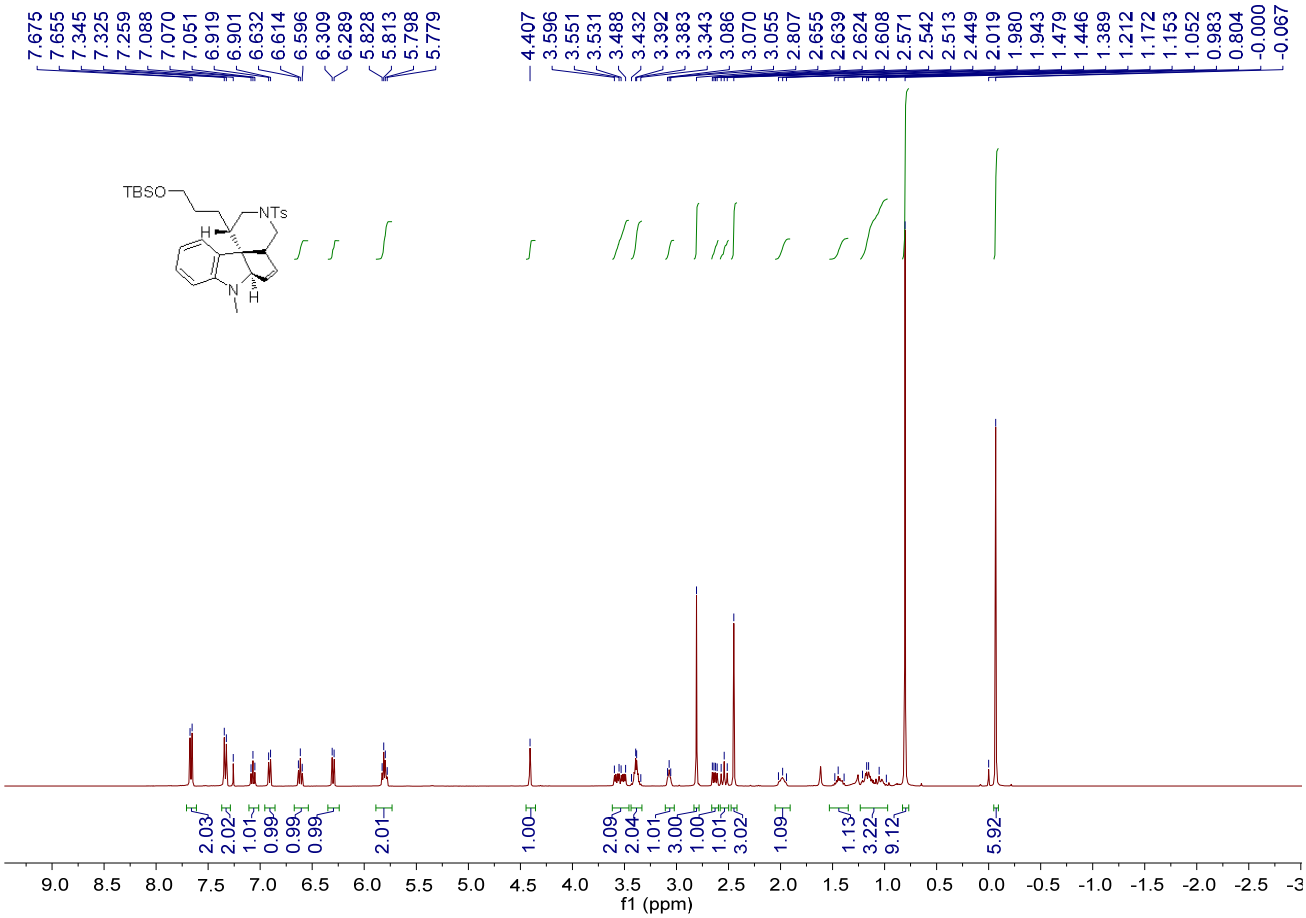
Translation: Chiralcel IE3 column [λ = 311 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 57.19 min, t_{major} = 51.27 min; ee% = 94%].

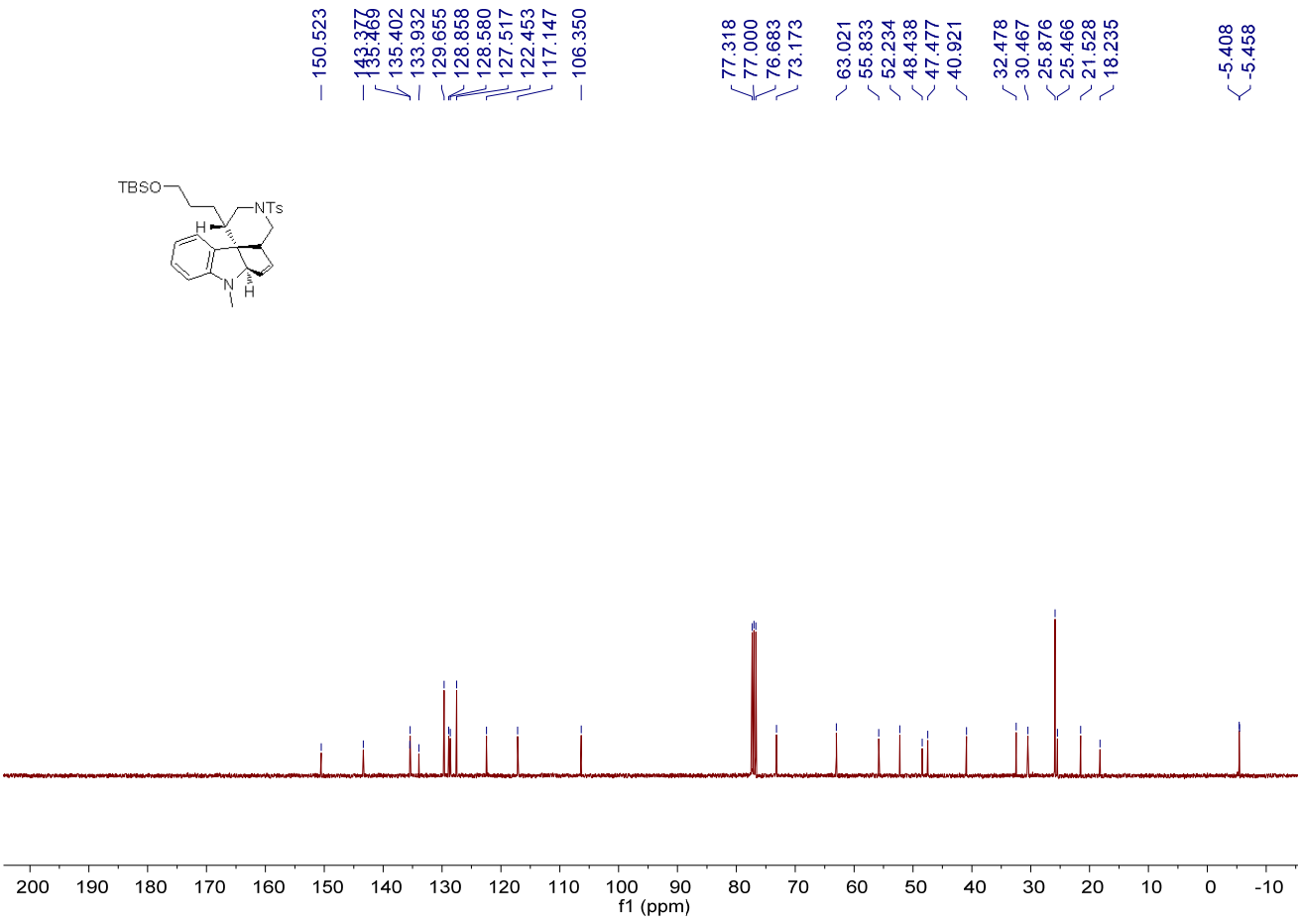


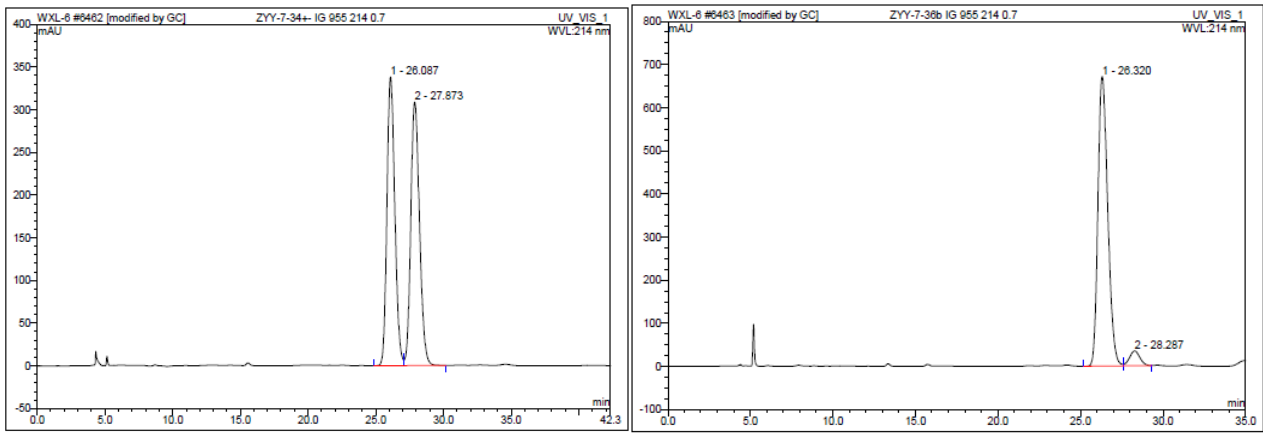
(1*S*,4a*R*,6a*R*,11b*R*)-1-(3-((tert-butyldimethylsilyl)oxy)propyl)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 2x

A white liquid, 44% yield (24.2 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ -0.07 (s, 6H), 0.80 (s, 9H), 0.98-1.22 (m, 3H), 1.38-1.48 (m, 1H), 1.94-2.02 (m, 1H), 2.45 (s, 3H), 2.54 (dd, *J* = 11.6, 11.6 Hz, 1H), 2.63 (dd, *J* = 12.0, 6.4 Hz, 1H), 2.81 (s, 3H), 3.05-3.09 (m, 1H), 3.34-3.44 (m, 2H), 3.48-3.60 (m, 2H), 4.41 (s, 1H), 5.77-5.83 (m, 2H), 6.29 (d, *J* = 8.0 Hz, 1H), 6.59-6.64 (m, 1H), 6.90-6.92 (m, 1H), 7.05-7.09 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ -5.46, -5.41, 18.2, 21.5, 25.5, 25.9, 30.5, 32.5, 40.9, 47.5, 48.4, 52.2, 55.8, 63.0, 73.2, 106.4, 117.1, 122.5, 127.5, 128.6, 128.9, 129.7, 133.9, 135.4, 135.5, 143.4, 150.5. IR (CH_2Cl_2) ν 3041, 2927, 2853, 1603, 1491, 1346, 1248, 1157, 1090, 945, 833, 737, 668 cm^{-1}. MS (ESI) *m/z* (%): 553.28 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{31}H_{45}N_2O_3SSi^{+1}$ $[M+H]^+$ requires 553.2915, found: 553.2898. Enantiomeric excess was determined by HPLC with a Chiralcel IG column [λ = 214 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.70 mL/min; t_{minor} = 28.29 min, t_{major} = 26.32 min; ee% =

90%; $[\alpha]_D^{25}$ = -183.1 (c 0.12, CH_2Cl_2)].



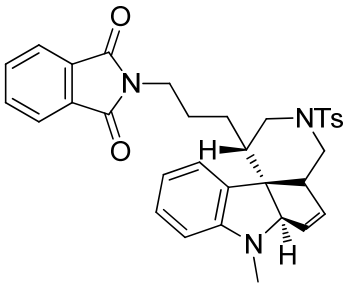




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	26.09	n.a.	338.079	228.699	49.71	n.a.	BM
2	27.87	n.a.	308.778	231.332	50.29	n.a.	MB
Total:			646.857	460.031	100.00	0.000	

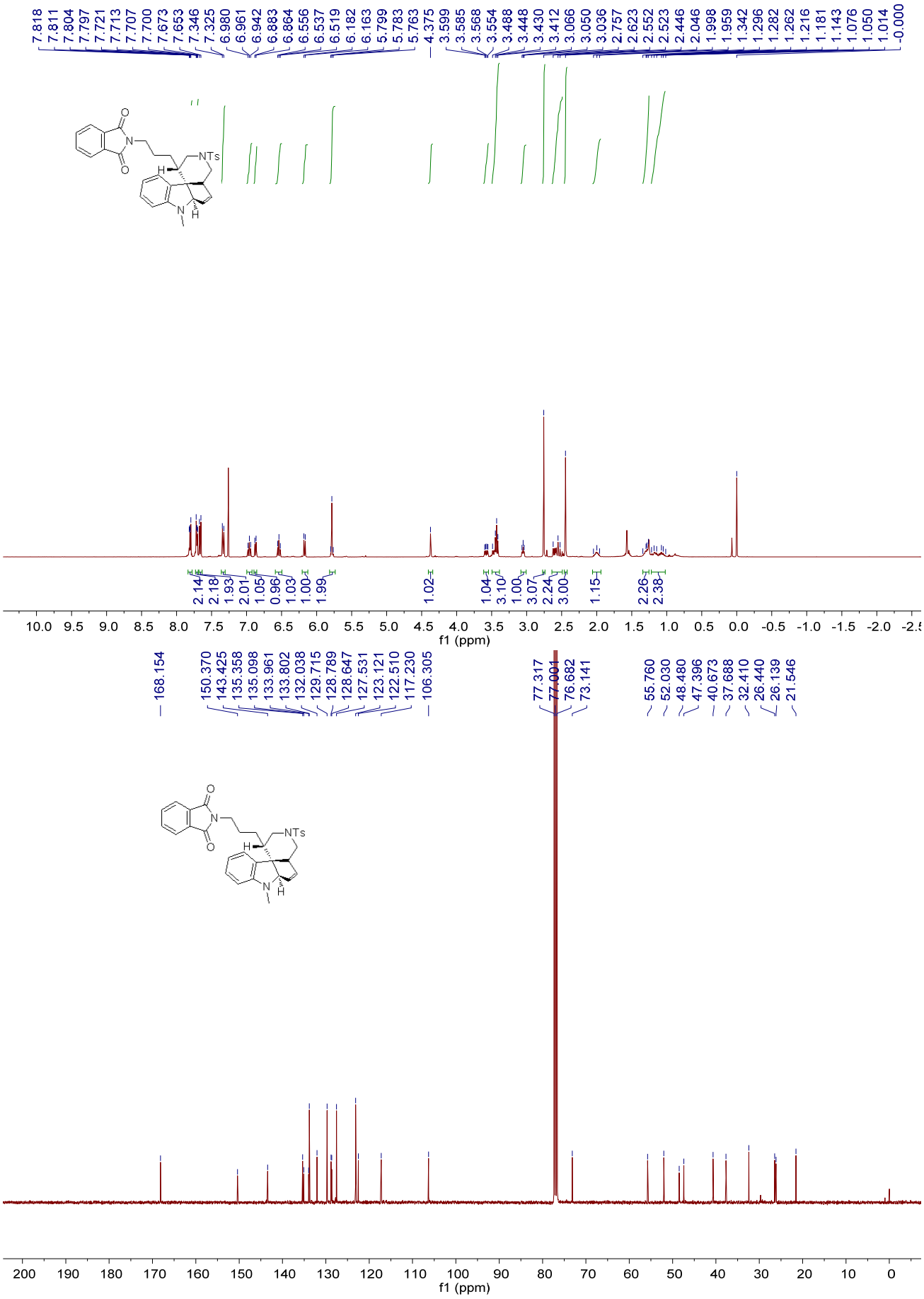
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	26.32	n.a.	671.712	463.259	94.89	n.a.	BM *
2	28.29	n.a.	34.215	24.970	5.11	n.a.	MB*
Total:			705.927	488.228	100.00	0.000	

Translation: Chiralcel IG column [λ = 214 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.70 mL/min; t_{minor} = 28.29 min, t_{major} = 26.32 min; ee% = 90%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



2-(3-((1*S*,4a*R*,6a*R*,11b*R*)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indol-1-yl)propyl)isoindoline-1,3-dione 2y

A white solid, 44% yield (24.9 mg). M.p.: 163-166 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.01-1.22 (m, 2H), 1.26-1.35 (m, 2H), 1.95-2.05 (m, 1H), 2.45 (s, 3H), 2.52-2.63 (m, 2H), 2.76 (s, 3H), 3.03-3.07 (m, 1H), 3.41-3.49 (m, 3H), 3.57 (dd, *J* = 12.4, 5.6 Hz, 1H), 4.38 (s, 1H), 5.76-5.80 (m, 2H), 6.17 (d, *J* = 7.6 Hz, 1H), 6.51-6.56 (m, 1H), 6.86-6.89 (m, 1H), 6.94-6.98 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.70-7.73 (m, 2H), 7.79-7.82 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 26.1, 26.4, 32.4, 37.7, 40.7, 47.4, 48.5, 52.0, 55.8, 73.1, 106.3, 117.2, 122.5, 123.1, 127.5, 128.6, 128.8, 129.7, 132.0, 133.8, 134.0, 135.1, 135.4, 143.4, 150.4, 168.2. IR (CH_2Cl_2) ν 2924, 2849, 1770, 1601, 1397, 1161, 1090, 934, 877, 786, 660 cm^{-1}. MS (ESI) *m/z* (%): 568.22 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{33}H_{34}N_3O_4S^{+1}$ $[M+H]^+$ requires 568.2265, found: 568.2252. Enantiomeric excess was determined by HPLC with a Chiralcel IG column [λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.70 mL/min; t_{minor} = 79.14 min, t_{major} = 66.33 min; ee% = 91%; $[\alpha]_D^{25}$ = -15.1 (c 0.5, CH_2Cl_2)].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6.883
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3.050
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2.623
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2.523
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1.998
1.959
1.342
1.296
1.282
1.262
1.216
1.181
1.143
1.076
1.050
1.014
-0.000
NTs
H
N
H
2.14
2.18
1.93
2.01
1.05
0.96
1.03
1.00
1.99
1.02
1.04
3.10
1.00
3.07
2.24
3.00
1.15
2.26
2.38
f1 (ppm)
168.154
150.370
143.425
135.358
135.098
133.961
133.802
132.038
129.715
128.789
128.647
127.531
123.121
122.510
117.230
106.305
77.317
77.001
76.682
73.141
55.760
52.030
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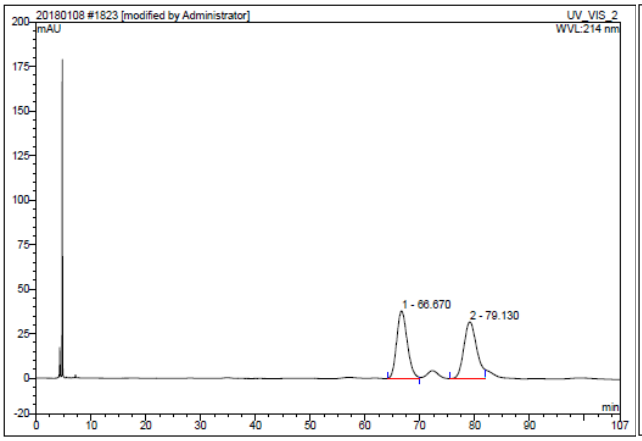
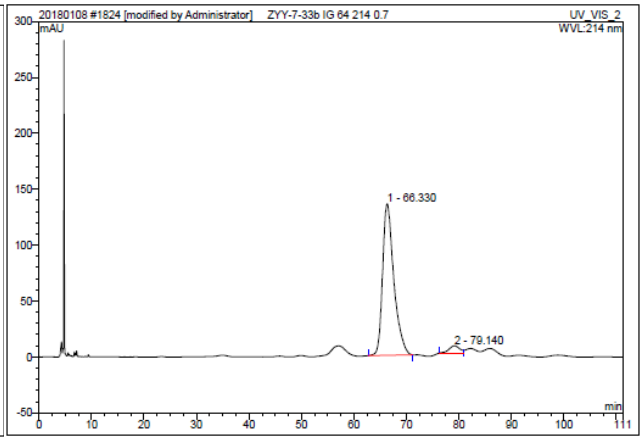
40.673
37.688
32.410
26.440
26.139
21.546
NTs
H
N
H
f1 (ppm)



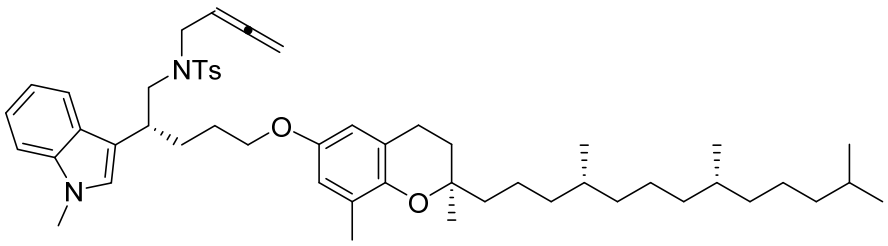
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	66.67	n.a.	37.930	84.652	49.37	n.a.	BM *
2	79.13	n.a.	31.931	86.822	50.63	n.a.	BM *
Total:			69.861	171.474	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	66.33	n.a.	135.482	336.292	95.67	n.a.	BMB
2	79.14	n.a.	6.446	15.219	4.33	n.a.	BM *
Total:			141.927	351.511	100.00	0.000	

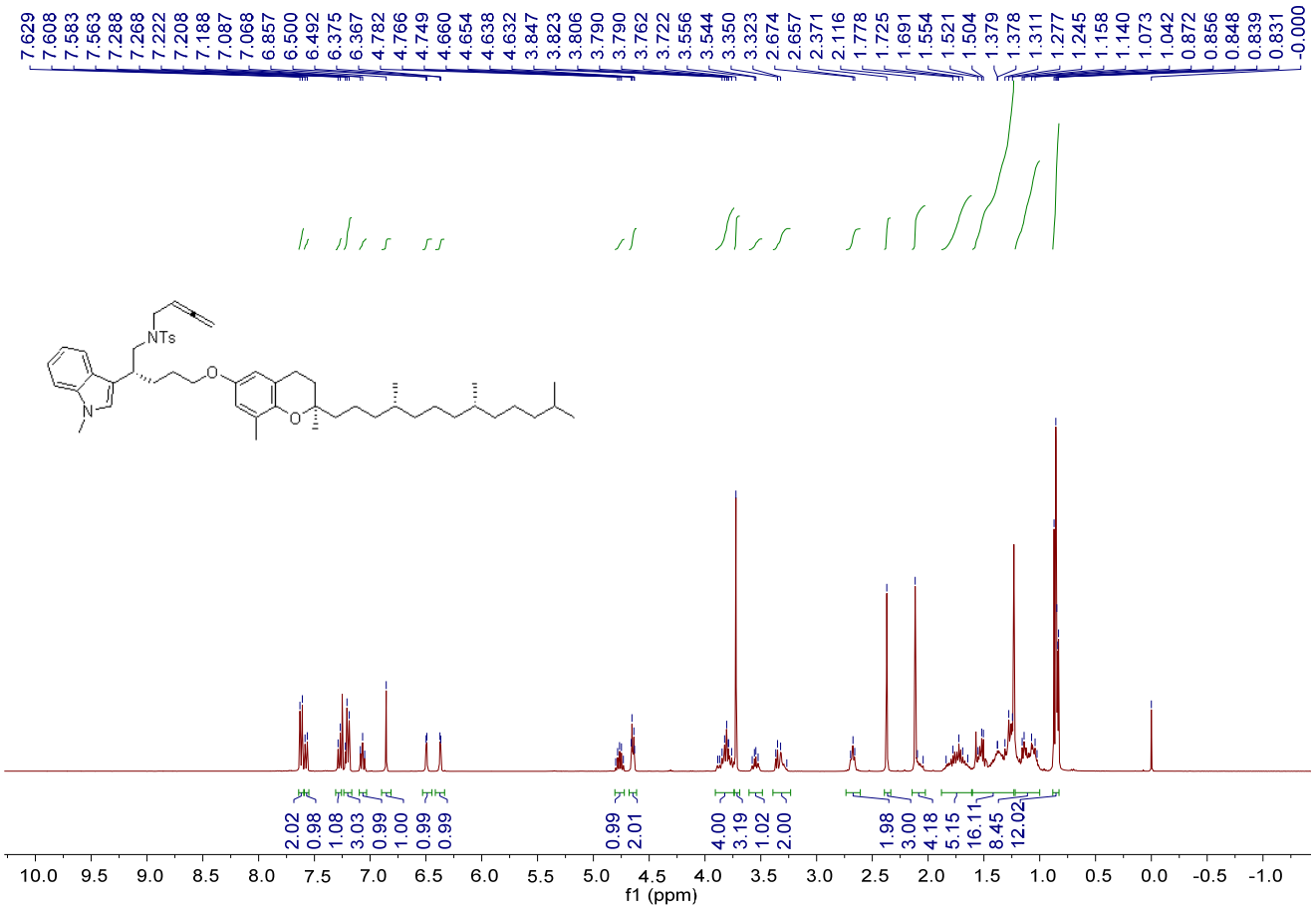
Translation: Chiralcel IG column [λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.70 mL/min; t_{minor} = 79.14 min, t_{major} = 66.33 min; ee% = 91%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).

8. Characterization and spectra charts for compounds 3 and 4



***N*-(buta-2,3-dien-1-yl)-*N*-((*R*)-5-(((*R*)-2,8-dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)-2-(1-methyl-1*H*-indol-3-yl)pentyl)-4-methylbenzenesulfonamide 3**

A white liquid, 43% yield (35.6 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.83-0.88 (m, 12H), 1.02-1.16 (m, 8H), 1.24-1.56 (m, 16H), 1.64-1.84 (m, 5H), 2.04-2.12 (m, 4H), 2.37 (s, 3H), 2.65-2.70 (m, 2H), 3.26-3.37 (m, 2H), 3.52-3.58 (m, 1H), 3.72 (s, 3H), 3.76-3.89 (m, 4H), 4.63-4.66 (m, 2H), 4.73-4.80 (m, 1H), 6.37 (d, *J* = 3.2 Hz, 1H), 6.50 (d, *J* = 3.2 Hz, 1H), 6.86 (s, 1H), 7.04-7.09 (m, 1H), 7.18-7.23 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.2, 19.6, 19.7, 21.0, 21.5, 22.6, 22.7, 24.1, 24.4, 24.8, 27.4, 28.0, 28.8, 31.4, 32.68, 32.7, 32.8, 35.3, 37.3, 37.4, 37.5, 39.3, 40.0, 47.1, 52.3, 68.3, 75.5, 76.1, 85.7, 109.3, 111.8, 114.8, 115.4, 118.7, 119.1, 120.9, 121.5, 126.5, 127.0, 127.1, 127.3, 129.5, 137.1, 137.2, 143.0, 146.0, 151.4, 209.3. IR (CH_2Cl_2) ν 2924, 2866, 1954, 1599, 1469, 1327, 1156, 1090, 1055, 850, 737, 659 cm^{-1}. MS (ESI) *m/z* (%): 823.54 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{52}H_{75}N_2O_4S^{+1}$ $[M+H]^+$ requires 823.5442, found: 823.5442. Enantiomeric excess was determined by HPLC with a Chiralcel IF3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 19.95 min, t_{major} = 18.56 min; ee% = 96%; $[\alpha]_D^{25}$ = 35.3 (c 0.1, CH_2Cl_2)].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7.268
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7.208
7.188
7.087
7.068
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6.492
6.375
6.367
4.782
4.766
4.749
4.660
4.654
4.638
4.632
3.847
3.823
3.806
3.790
3.790
3.762
3.722
3.556
3.544
3.350
3.323
2.674
2.657
2.371
2.116
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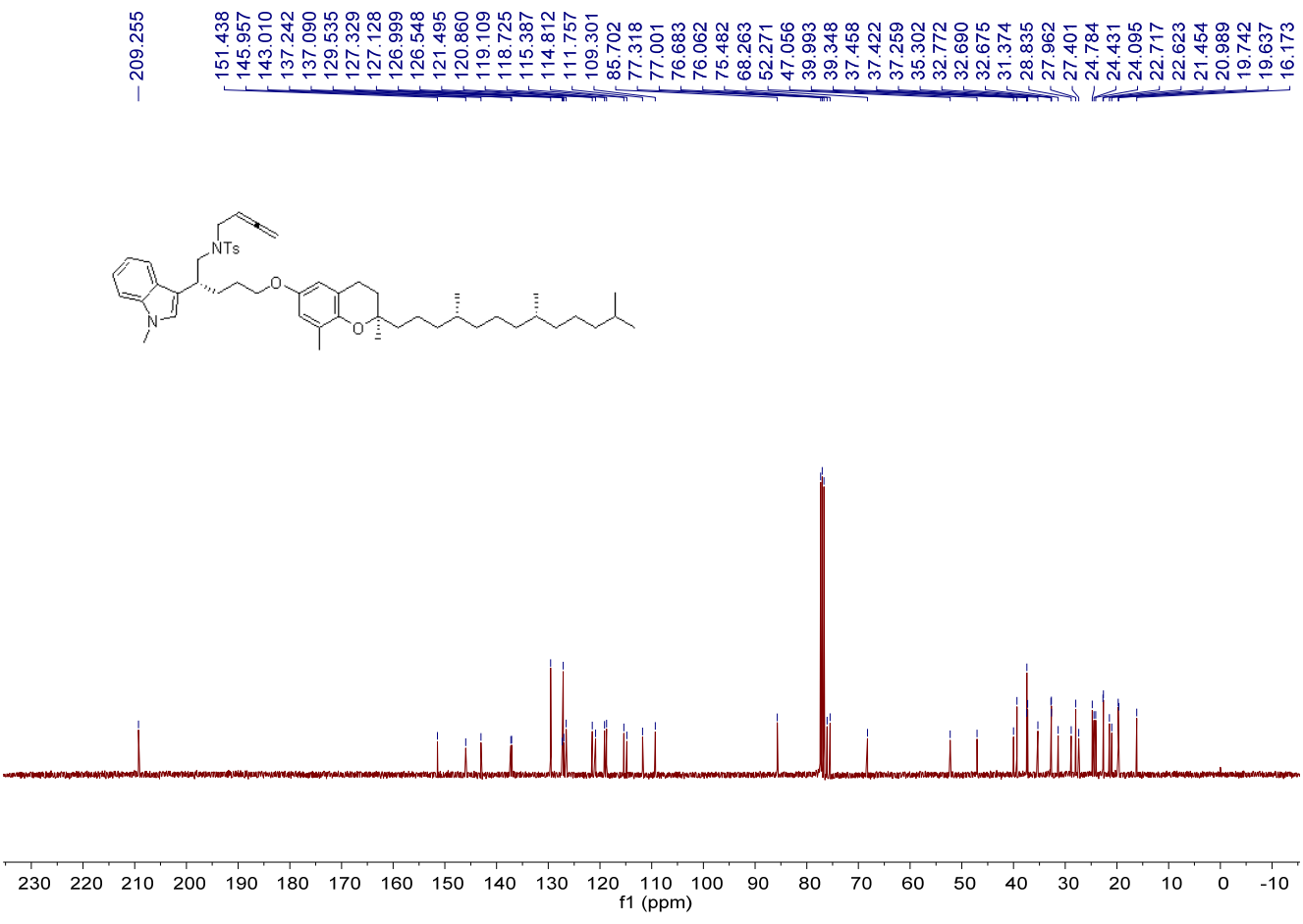
1.521
1.504
1.379
1.378
1.311
1.277
1.245
1.158
1.140
1.073
1.042
0.872
0.856
0.848
0.839
0.831
-0.000
NTs
O
N
O
2.02
0.98
1.08
3.03
0.99
1.00
0.99
0.99
0.99
2.01
4.00
3.19
1.02
2.00
1.98
3.00
4.18
5.15
16.11
8.45
12.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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137.090
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126.548
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27.401
24.784
24.431
24.095
22.717
22.623
21.454
20.989
19.742
19.637
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NTs
O
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O
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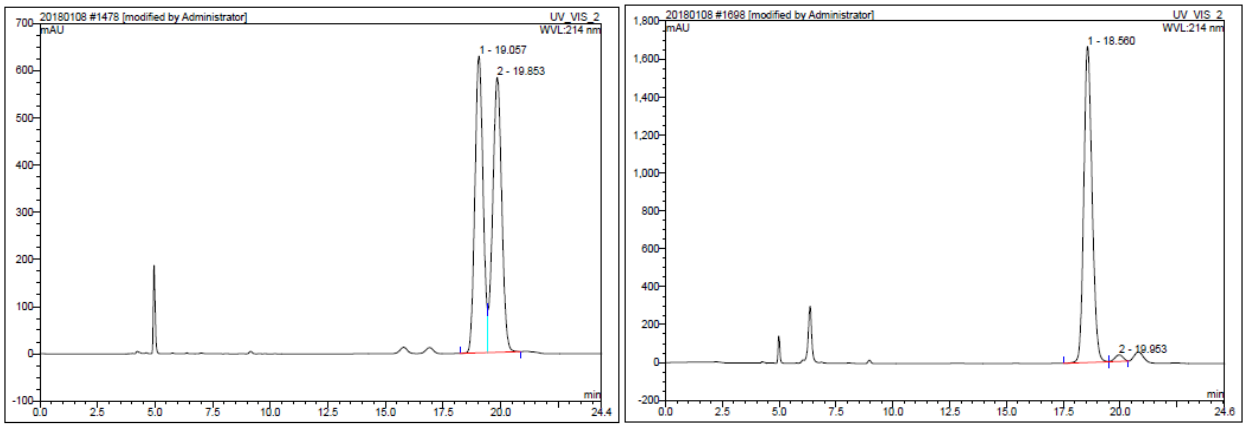
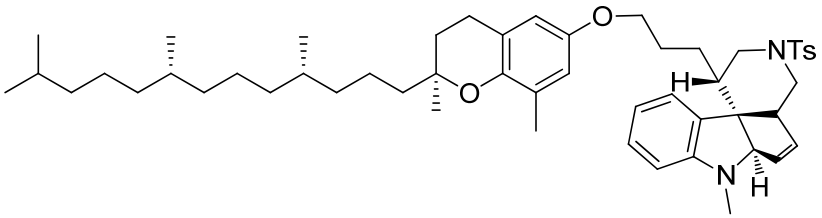
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.06	n.a.	628.565	257.893	49.49	n.a.	BM *
2	19.85	n.a.	582.282	263.244	50.51	n.a.	MB*
Total:			1210.847	521.137	100.00	0.000	

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.56	n.a.	1665.647	703.881	98.03	n.a.	BM *
2	19.95	n.a.	34.058	14.142	1.97	n.a.	MB*
Total:			1699.705	718.023	100.00	0.000	

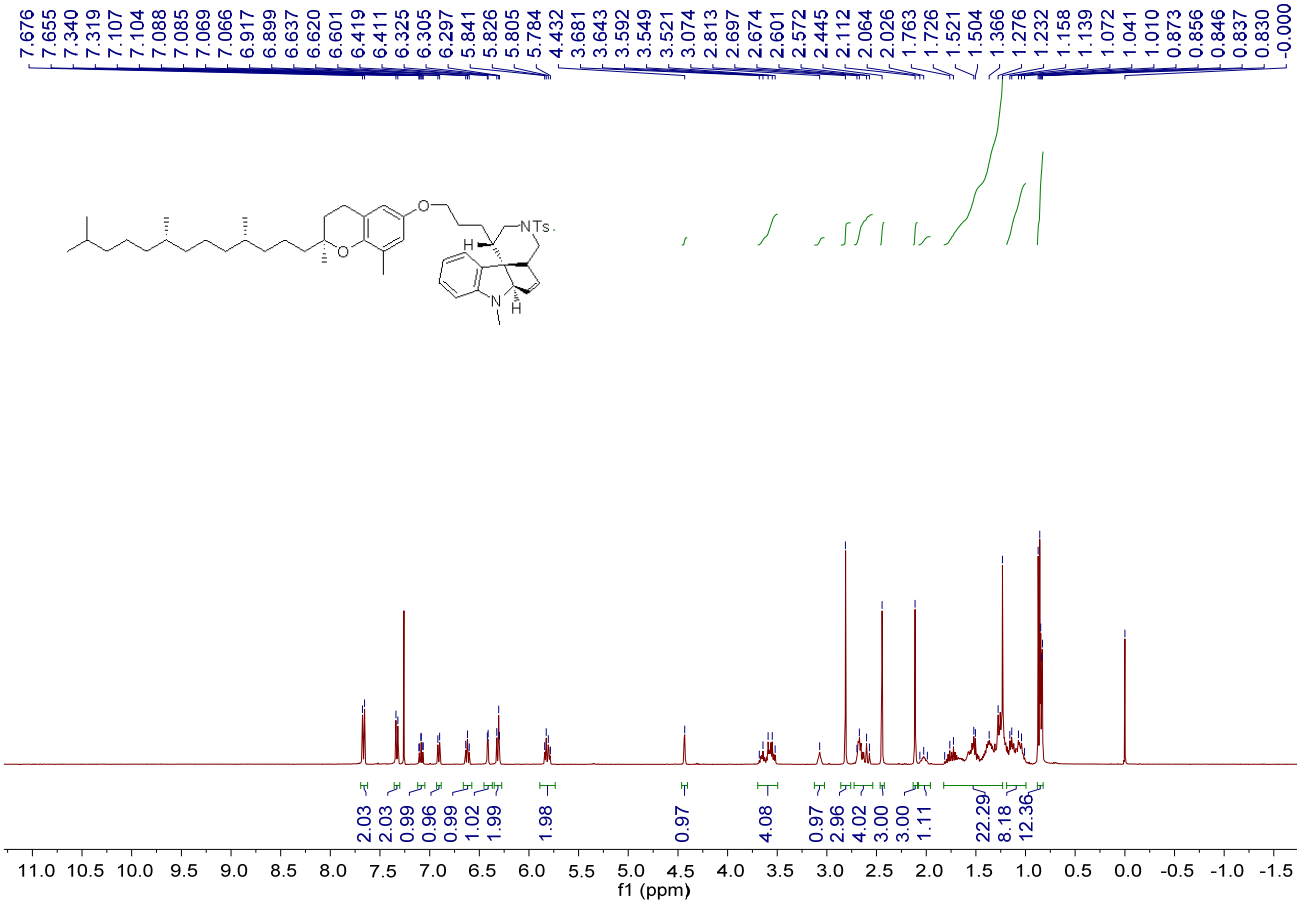
Translation: Chiralcel IF3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 19.95 min, t_{major} = 18.56 min; ee% = 96%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).

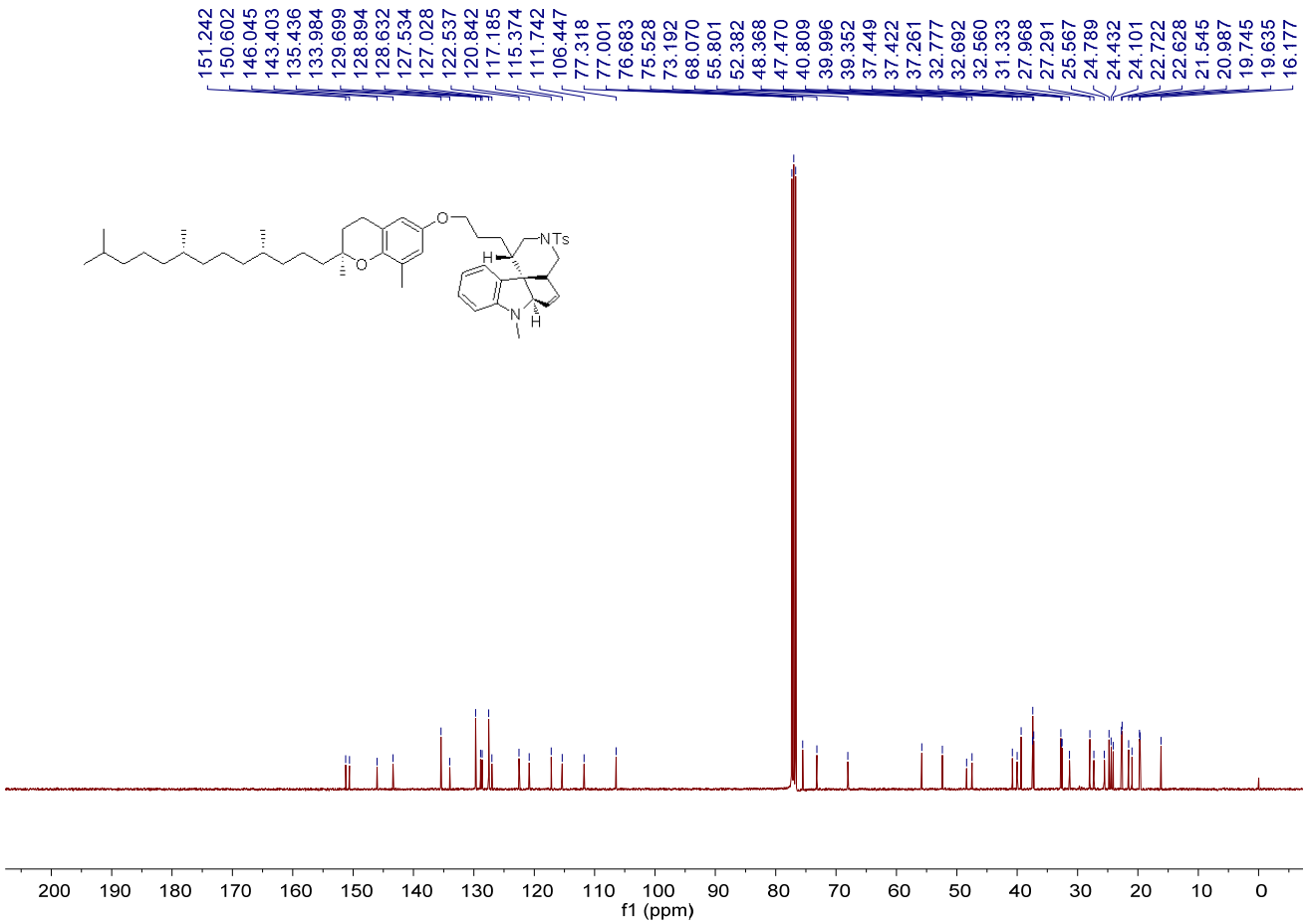


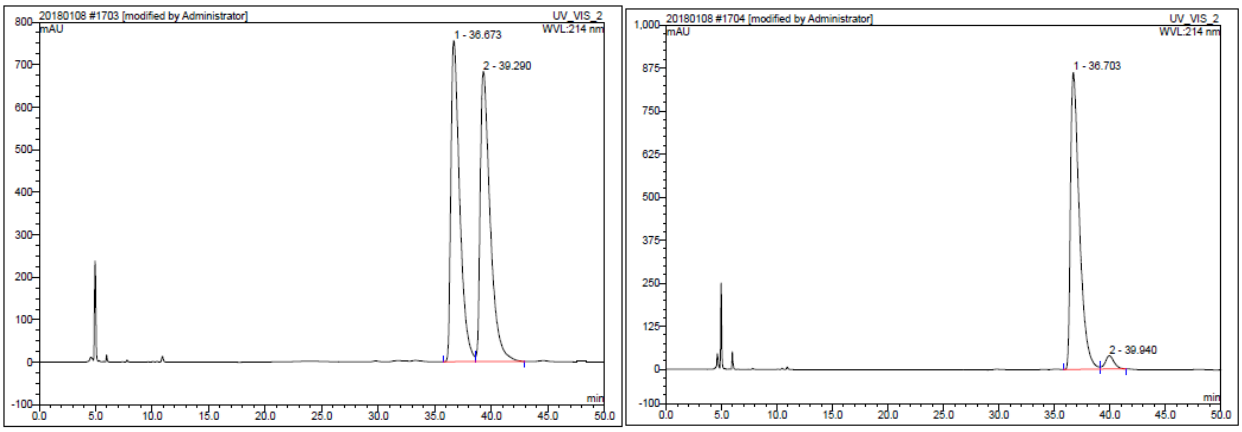
(1*S*,4a*R*,6a*R*,11b*R*)-1-(3-(((*S*)-2,8-dimethyl-2-((4*S*,8*S*)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)propyl)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 4

A white solid, 43% yield (35.5 mg). M.p.: 127-130 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.83-0.88 (m, 12H), 1.01-1.16 (m, 8H), 1.23-1.82 (m, 22H), 1.98-2.07 (m, 1H), 2.11 (s, 3H), 2.45 (s, 3H), 2.57-2.70 (m, 4H), 2.81 (s, 3H), 3.07 (br, 1H), 3.52-3.69 (m, 4H), 4.43 (s, 1H), 5.78-5.85 (m, 2H), 6.29-6.33 (m, 2H), 6.41-6.42 (m, 1H), 6.60-6.64 (m, 1H), 6.89-6.92 (m, 1H), 7.06-7.11 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.2, 19.6, 19.7, 21.0, 21.5, 22.6, 22.7, 24.1, 24.4, 24.8, 25.6, 27.3, 28.0, 31.3, 32.6, 32.7, 32.8, 37.3, 37.42, 37.45, 39.4, 40.0, 40.8, 47.5, 48.4, 52.4, 55.8, 68.1, 73.2, 75.5, 106.4, 111.7, 115.4, 117.2, 120.8, 122.5, 127.0, 127.5, 128.6, 128.9, 129.7, 134.0, 135.4, 143.4, 146.0, 150.6, 151.2. IR (CH_2Cl_2) ν 2922, 2849, 1603, 1486, 1468, 1338, 1260, 1156, 1012, 935, 812, 738, 659 cm^{-1}. MS (ESI) *m/z* (%): 823.54 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{52}H_{75}N_2O_4S^{+1}$ $[M+H]^+$ requires 823.5442, found: 823.5445.

Enantiomeric excess was determined by HPLC with a Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 39.94 min, t_{major} = 36.70 min; ee% = 92%; $[\alpha]_D^{25}$ = -153.8 (c 0.20, CH_2Cl_2)].





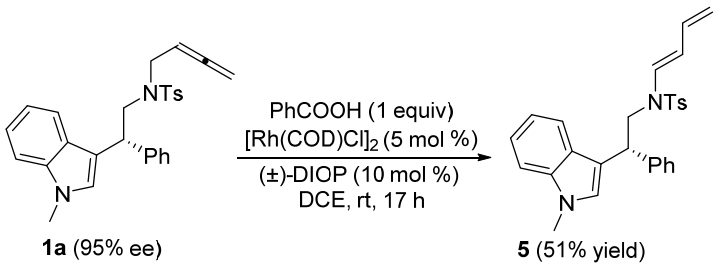


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	36.67	n.a.	755.397	682.374	49.53	n.a.	BM
2	39.29	n.a.	682.851	695.263	50.47	n.a.	MB
Total:			1438.248	1377.638	100.00	0.000	

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	36.70	n.a.	862.582	804.672	95.76	n.a.	BM
2	39.94	n.a.	36.603	35.589	4.24	n.a.	MB
Total:			901.185	840.261	100.00	0.000	

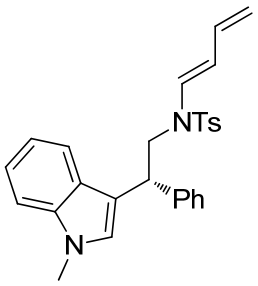
Translation: Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 39.94 min, t_{major} = 36.70 min; ee% = 92%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).

9. General procedure for the synthesis of 5, 6, 7 and 8 and their characterization and spectra Charts



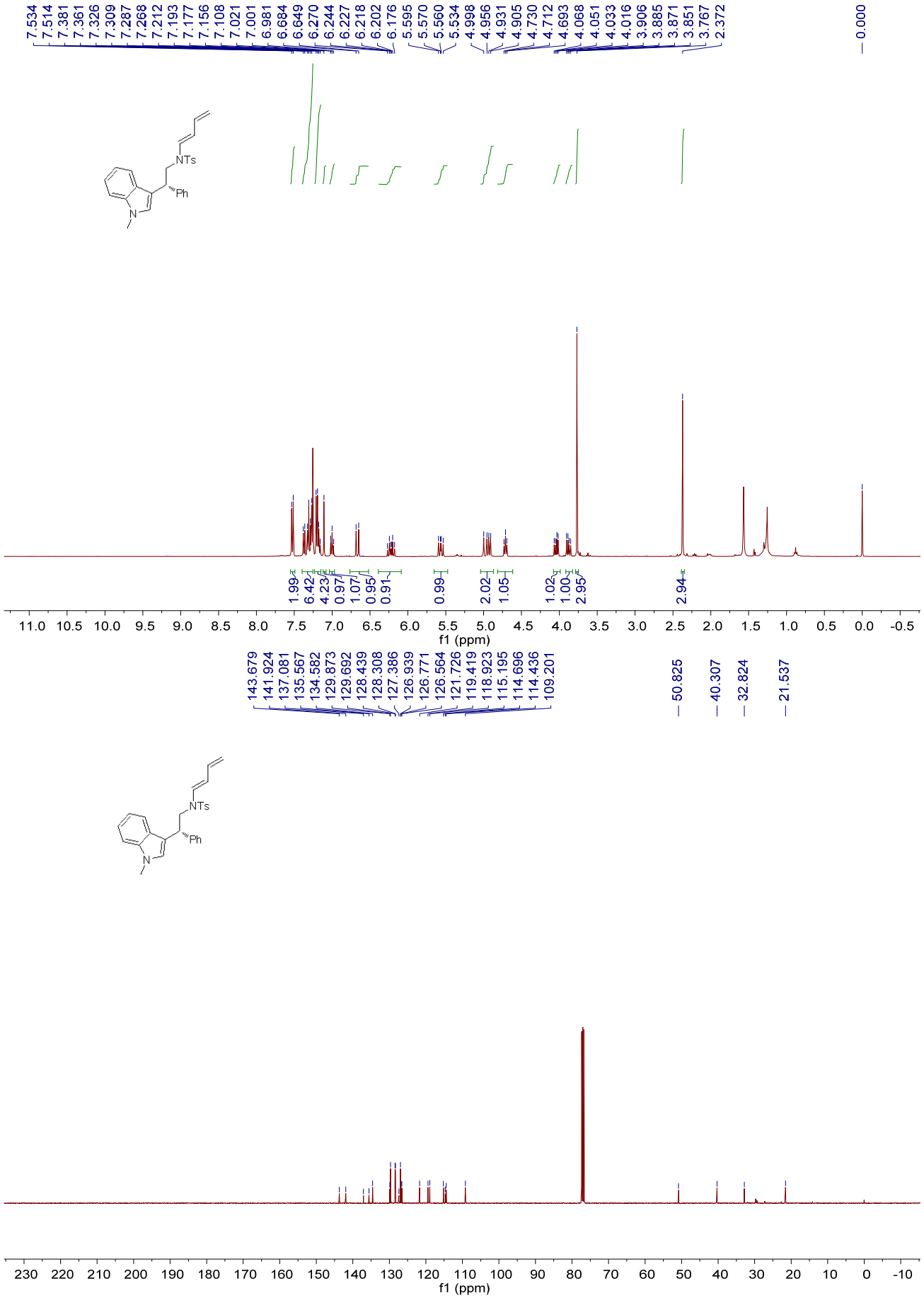
1a (95% ee) **5** (51% yield)

To an oven-dried reaction tube was sequentially added $[Rh(COD)Cl]_2$ (0.005 mmol), (±)-DIOP (0.01 mmol) and benzoic acid (0.1 mmol), and the tube was evacuated and backfilled with argon for three times. Then, **1a** (0.10 mmol) in 1,2-dichloroethane (1.00 mL) was added into tube under an argon atmosphere. The resulting mixture was stirred at room temperature. When the reaction was complete as monitored by TLC, the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 10/1) to give the corresponding product **5**.



(*R*,*E*)-*N*-(buta-1,3-dien-1-yl)-4-methyl-*N*-(2-(1-methyl-1*H*-indol-3-yl)-2-phenylethyl)benzenesulfonamide 5

A white liquid, 51% yield (23.2 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.37 (s, 3H), 3.77 (s, 3H), 3.88 (dd, J = 14.0, 8.0 Hz, 1H), 4.04 (dd, J = 14.0, 8.0 Hz, 1H), 4.71 (t, J = 7.6 Hz, 1H), 4.90-5.00 (m, 2H), 5.57 (dd, J = 14.0, 10.0 Hz, 1H), 6.17-6.27 (m, 1H), 6.67 (d, J = 14.0 Hz, 1H), 6.98-7.03 (m, 1H), 7.11 (s, 1H), 7.15-7.22 (m, 4H), 7.26-7.39 (m, 6H), 7.52 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 32.8, 40.3, 50.8, 109.2, 114.4, 114.7, 115.2, 118.9, 119.4, 121.7, 126.6, 126.7, 126.9, 127.4, 128.3, 128.4, 129.7, 129.9, 134.6, 135.6, 137.1, 141.9, 143.7. IR (CH_2Cl_2) ν 2920, 1949, 1599, 1474, 1334, 1160, 1093, 1010, 903, 858, 750, 659 cm^{-1}. MS (ESI) *m/z* (%): 457.19 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{28}H_{29}N_2O_2S^{+1}$ $[M+H]^+$ requires 457.1944, found: 457.1941.


7.534
7.514
7.381
7.361
7.326
7.309
7.287
7.268
7.212
7.193
7.177
7.156
7.108
7.021
7.001
6.981
6.684
6.649
6.270
6.244
6.227
6.218
6.202
6.176
5.595
5.570
5.560
5.534
4.998
4.956
4.931
4.905
4.730
4.712
4.693
4.068
4.051
4.033
4.016
3.906
3.885
3.871
3.851
3.767
2.372
0.000
NTs
Ph
N
1.99
6.42
4.23
0.97
1.07
0.95
0.91
0.99
2.02
1.05
1.02
1.00
2.95
2.94
f1 (ppm)
143.679
141.924
137.081
135.567
134.582
129.873
129.692
128.439
128.308
127.386
126.939
126.771
126.564
121.726
119.419
118.923
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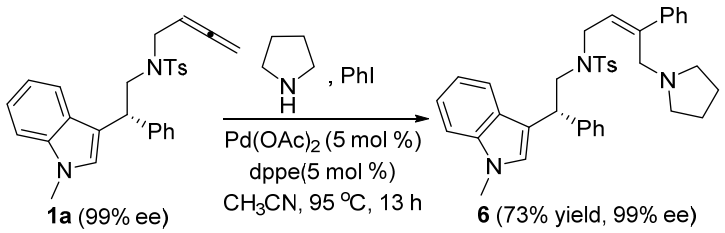
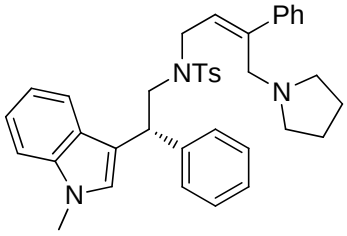
32.824
21.537
NTs
Ph
N
f1 (ppm)

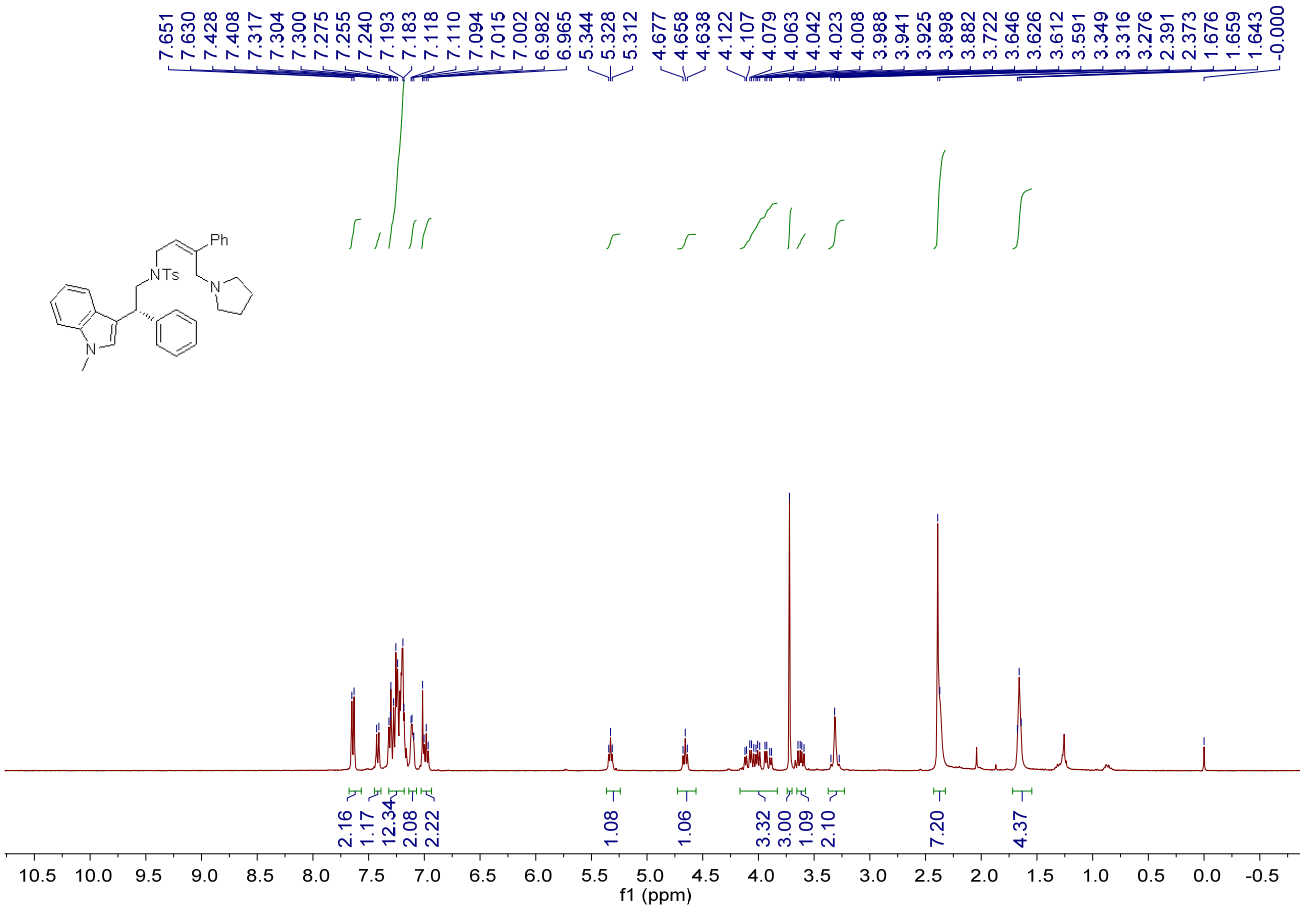


To an oven-dried reaction tube was sequentially added $Pd(OAc)_2$ (0.005 mmol), dppe (0.005 mmol), **1a** and acetonitrile (1.00 mL). Then, iodobenzene (0.125 mmol) and pyrrolidine (0.6 mmol) were added into tube under an argon atmosphere. The resulting mixture was stirred at 95 °C. When the reaction was complete as monitored by TLC, the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 10/1-5/1) to give the corresponding product **6**.



(*R*,*Z*)-4-methyl-*N*-(2-(1-methyl-1*H*-indol-3-yl)-2-phenylethyl)-*N*-(3-phenyl-4-(pyrrolidin-1-yl)but-2-en-1-yl)benzenesulfonamide 6

A white solid, 73% yield (44.1 mg). M.p.: 111-114 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.64-1.68 (m, 4H), 2.37-2.40 (m, 7H), 3.27-3.35 (m, 2H), 3.59-3.65 (m, 1H), 3.72 (s, 3H), 3.88-4.13 (m, 3H), 4.66 (t, *J* = 8.0 Hz, 1H), 5.33 (t, *J* = 6.4 Hz, 1H), 6.96-7.02 (m, 2H), 7.09-7.12 (m, 2H), 7.18-7.32 (m, 12H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 23.4, 32.7, 42.2, 46.5, 52.4, 53.9, 109.2, 114.8, 118.9, 119.3, 121.6, 126.3, 126.6, 127.0, 127.1, 127.2, 127.3, 128.0, 128.3, 128.5, 129.6, 137.0, 137.1, 141.8, 142.2, 143.2. IR (CH_2Cl_2) ν 3394, 2922, 2851, 1646, 1454, 1327, 1155, 1090, 922, 814, 738, 699, 653 cm^{-1}. MS (ESI) *m/z* (%): 604.29 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{38}H_{42}N_3O_2S^{+1}$ $[M+H]^+$ requires 604.2992, found: 604.2978. Enantiomeric excess was determined by HPLC with a Chiralcel ID3 column [λ = 254 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.70 mL/min; t_{minor} = 30.71 min, t_{major} = 32.46 min; ee% = 99%; $[\alpha]_D^{25}$ = -106.5 (c 0.10, CH_2Cl_2)].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7.304
7.300
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7.110
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7.015
7.002
6.982
6.965
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5.312
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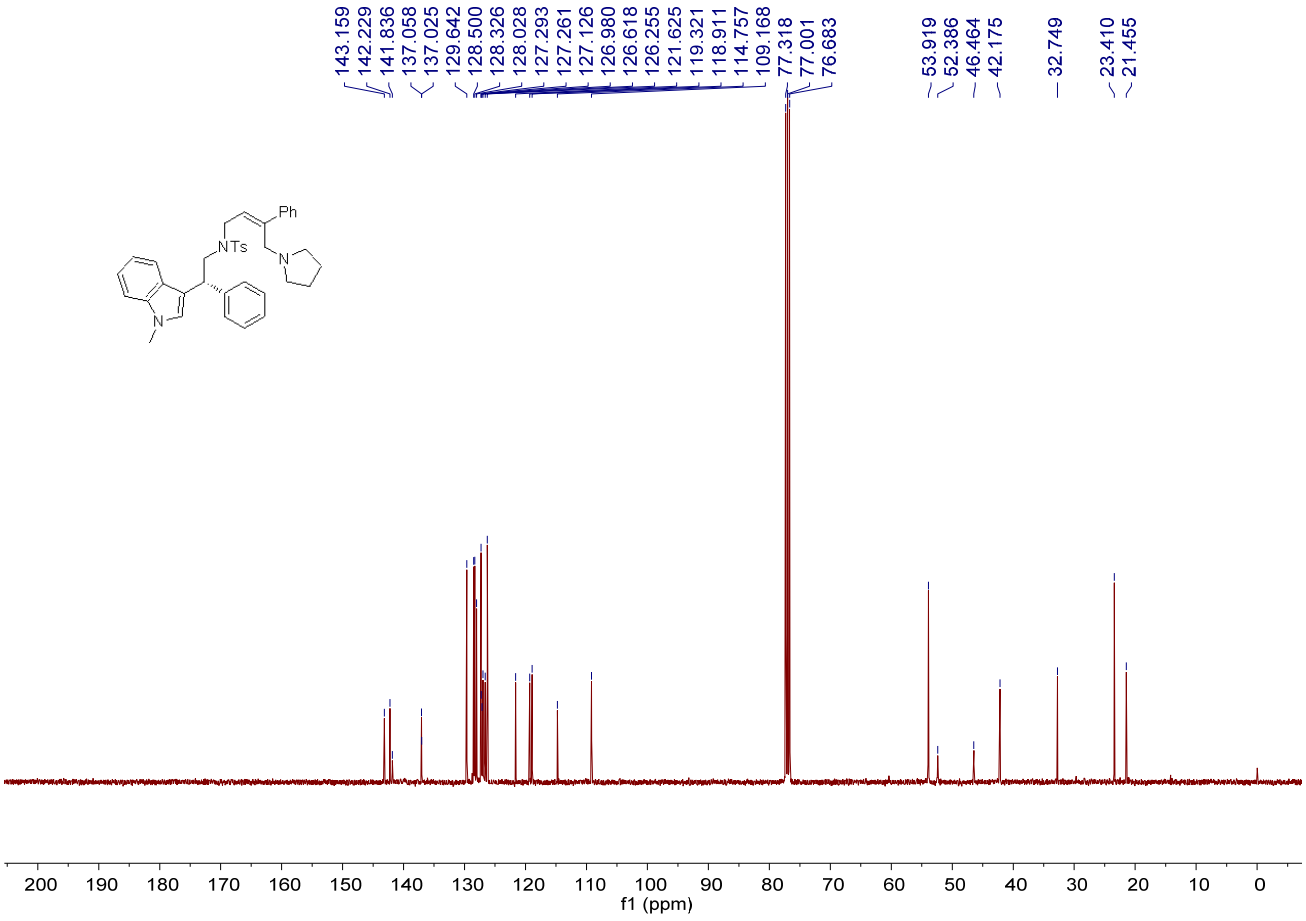
4.658
4.638
4.122
4.107
4.079
4.063
4.042
4.023
4.008
3.988
3.941
3.925
3.898
3.882
3.722
3.646
3.626
3.612
3.591
3.349
3.316
3.276
2.391
2.373
1.676
1.659
1.643
-0.000
Ph
NTs
N
N
2.16
1.17
12.34
2.08
2.22
1.08
1.06
3.32
3.00
1.09
2.10
7.20
4.37
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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141.836
137.058
137.025
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128.500
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127.293
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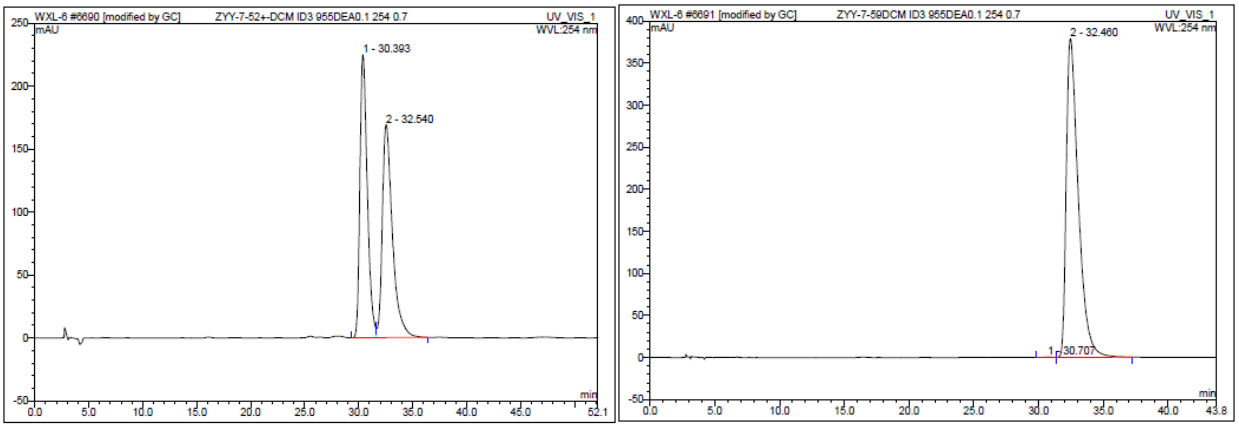
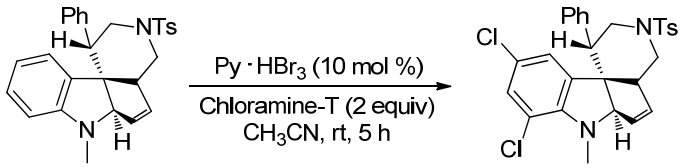
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	30.39	n.a.	224.713	178.716	49.24	n.a.	BM
2	32.54	n.a.	168.901	184.259	50.76	n.a.	MB
Total:			393.613	362.975	100.00	0.000	

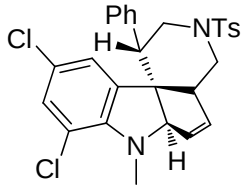
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	30.71	n.a.	0.554	0.349	0.09	n.a.	BMB*
2	32.46	n.a.	378.706	408.423	99.91	n.a.	BMB
Total:			379.260	408.772	100.00	0.000	

Translation: Chiralcel ID3 column [λ = 254 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.70 mL/min; t_{minor} = 30.71 min, t_{major} = 32.46 min; ee% = 99%].



2a (95% ee) **7** (52% yield, 95% ee)

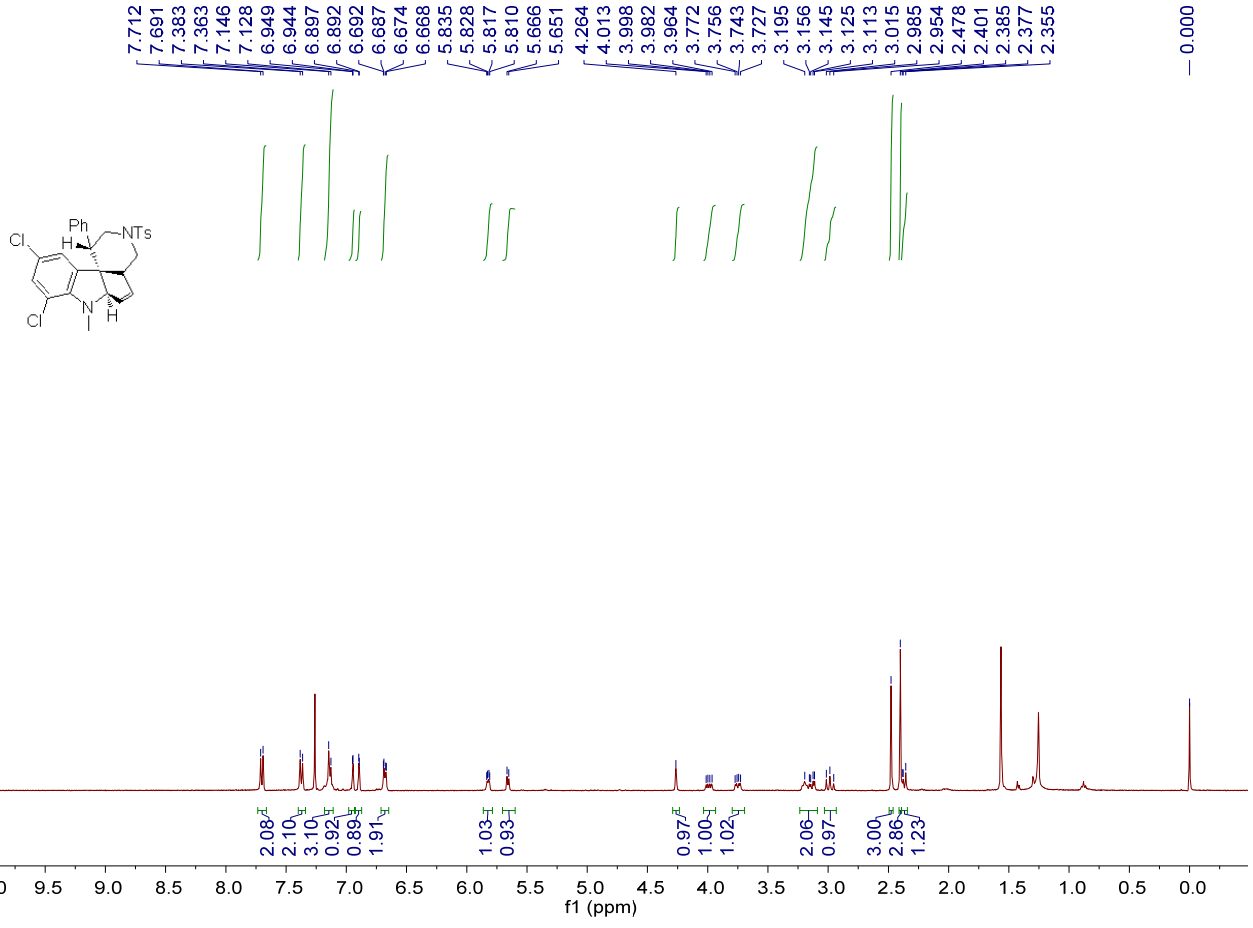
To an oven-dried reaction tube was sequentially added **2a** (0.10 mmol), Py·HBr_3 (0.01 mmol), and Chloramine-T (0.20 mmol) in acetonitrile (1.00 mL) under an argon atmosphere. The resulting mixture was stirred at room temperature. When the reaction was complete as monitored by TLC, water (5.00 mL) and ethyl acetate (5.00 mL) were added and then the aqueous solution was separated and extracted with ethyl acetate (3 × 5 mL). The organic layer was then washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 10/1) to give the corresponding product **7**.

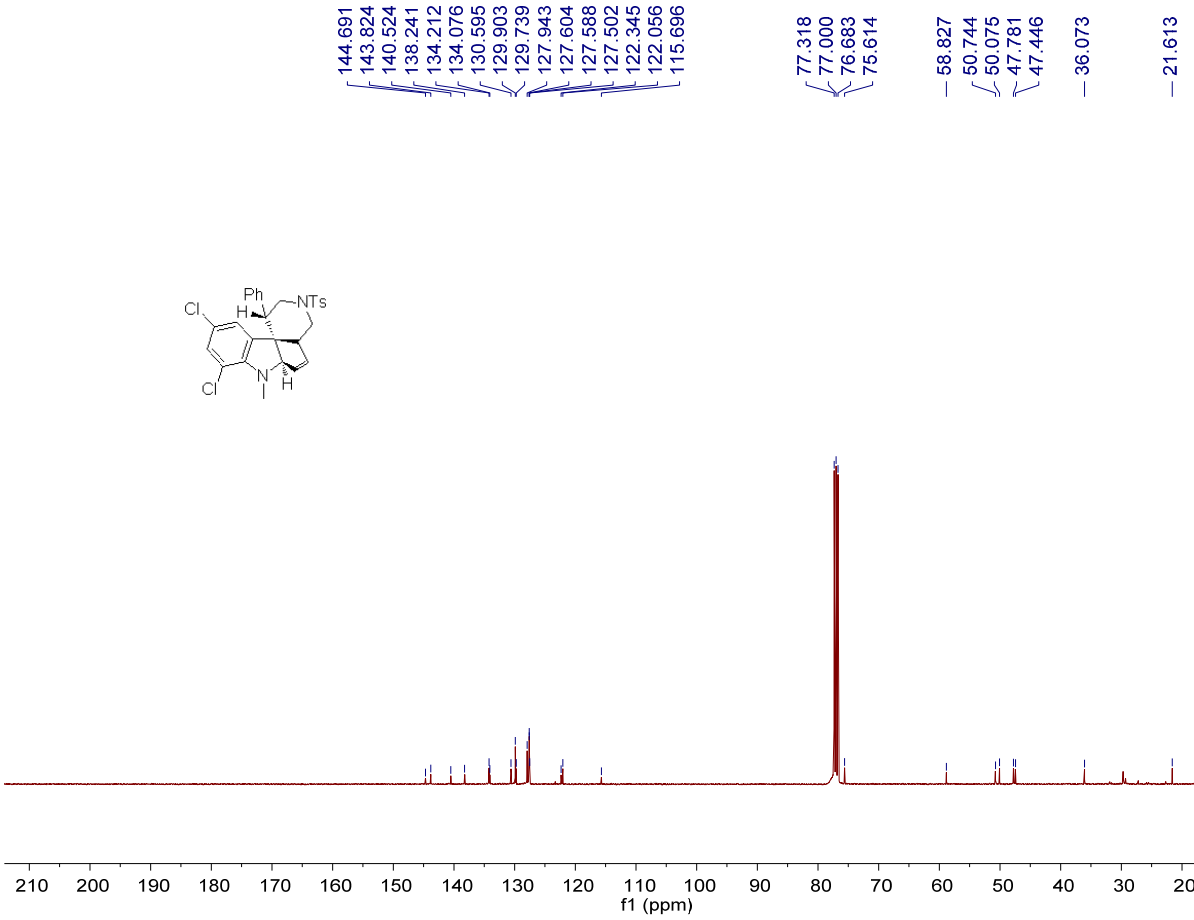


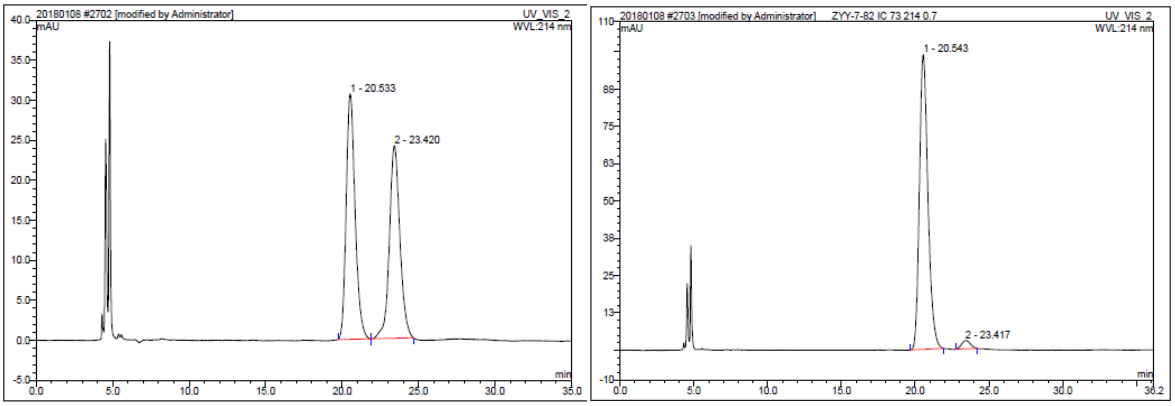
(1*S*,4a*R*,6a*R*,11b*S*)-8,10-dichloro-7-methyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 7

A white solid, 52% yield (27.1 mg). M.p.: 166-169 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.36 (s,

3H), 2.42-2.47 (m, 4H), 3.05 (dd, *J* = 12.0, 12.0 Hz, 1H), 3.12-3.21 (m, 2H), 3.69 (dd, *J* = 11.2, 4.4 Hz, 1H), 3.94 (dd, *J* = 12.4, 6.0 Hz, 1H), 4.48 (s, 1H), 5.68 (d, *J* = 6.0 Hz, 1H), 5.82-5.88 (m, 2H), 6.72-6.75 (m, 2H), 6.88-6.95 (m, 2H), 7.02-7.11 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 36.1, 47.4, 47.8, 50.1, 50.7, 58.8, 75.6, 115.7, 122.1, 122.3, 127.50, 127.59, 127.6, 127.9, 129.7, 129.9, 130.6, 134.1, 134.2, 138.2, 140.5, 143.8, 144.7. IR (CH_2Cl_2) ν 2923, 1597, 1492, 1342, 1153, 1058, 935, 814, 730, 658 cm^{-1}. MS (ESI) *m/z* (%): 525.11 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{28}H_{27}N_2O_2Cl_2S^{+1}[M+H]^+$ requires 525.1165, found: 525.1165. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 23.42 min, t_{major} = 20.54 min; ee% = 95%; $[\alpha]_D^{25}$ = -263.8 (c 0.20, CH_2Cl_2)].



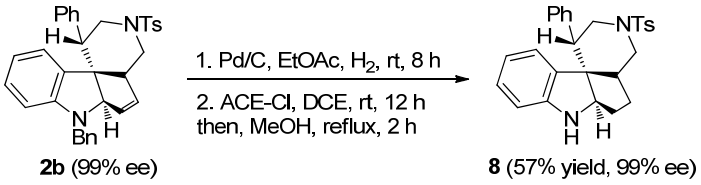




No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.53	n.a.	30.680	20.753	51.95	n.a.	BM
2	23.42	n.a.	24.051	19.193	48.05	n.a.	MB
Total:			54.731	39.946	100.00	0.000	

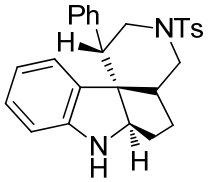
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.54	n.a.	98.771	66.514	97.25	n.a.	BMB
2	23.42	n.a.	2.777	1.880	2.75	n.a.	BMB
Total:			101.549	68.394	100.00	0.000	

Translation: Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 23.42 min, t_{major} = 20.54 min; ee% = 95%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



2b (99% ee) **8** (57% yield, 99% ee)

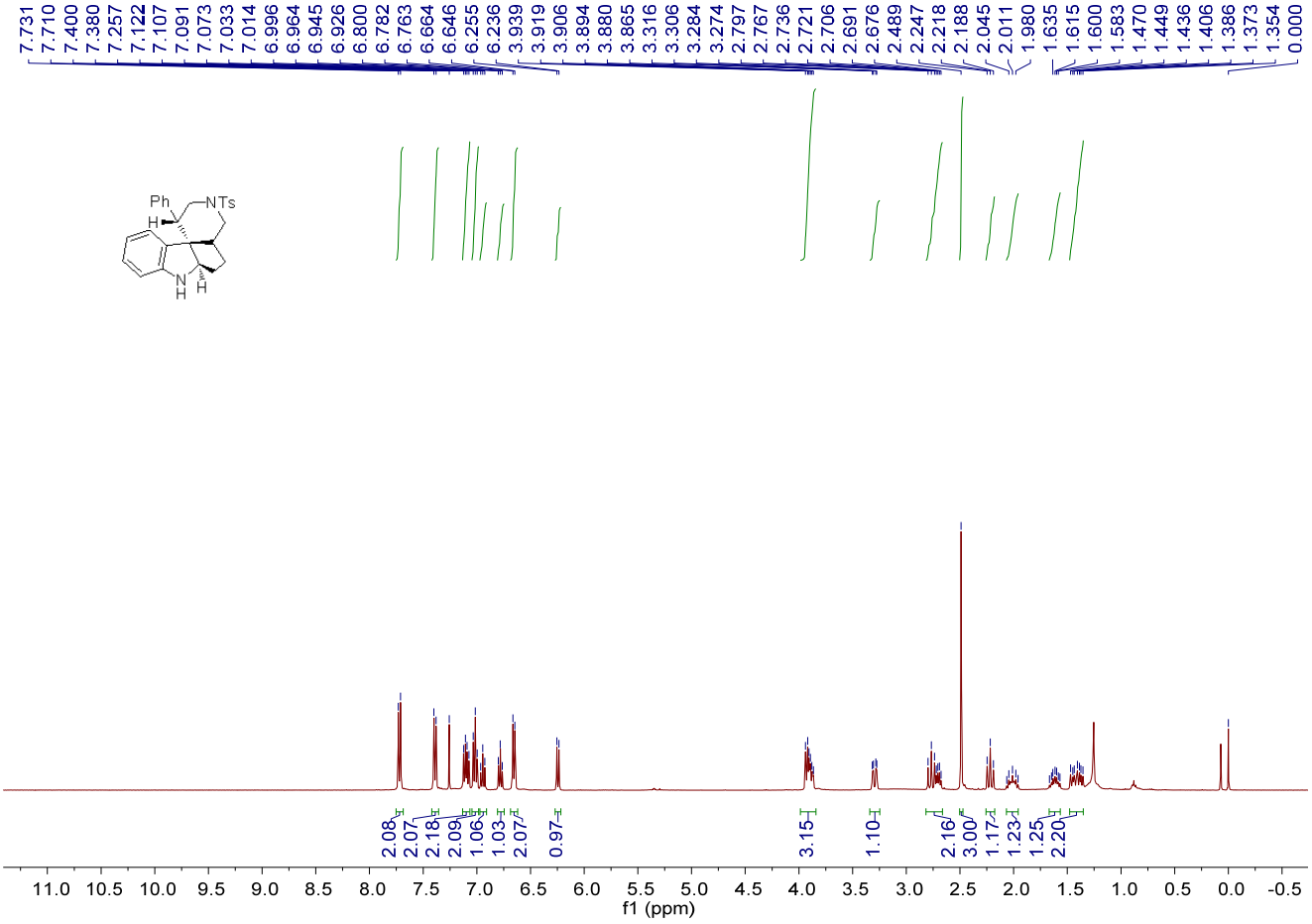
To an oven-dried reaction tube was sequentially added **2b** (0.10 mmol) and Pd/C (0.01 mmol) in ethyl acetate (2.00 mL). The resulting mixture was stirred at room temperature under H_2 atmosphere. When the reaction was complete as monitored by TLC, the Pd/C was removed, and then the solution was concentrated under reduced pressure to give the crude residue. Then, ACE-Cl (0.2 mmol) in DCE (1.0 mL) was added into crude residue. The resulting mixture was stirred at room temperature for 12 h. After that, DCE was removed under reduced pressure and MeOH (1.0 mL) was added into bottle. The bottle was stirred at reflux for 2 h. When the reaction was complete as monitored by TLC, the mixture was based with saturated $NaHCO_3$ solution, and extracted with ethyl acetate (3 × 5 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the residue. Then, the crude residue was purified via a silica gel flash column chromatography (PE/EA = 6/1) to give the corresponding product **8**.

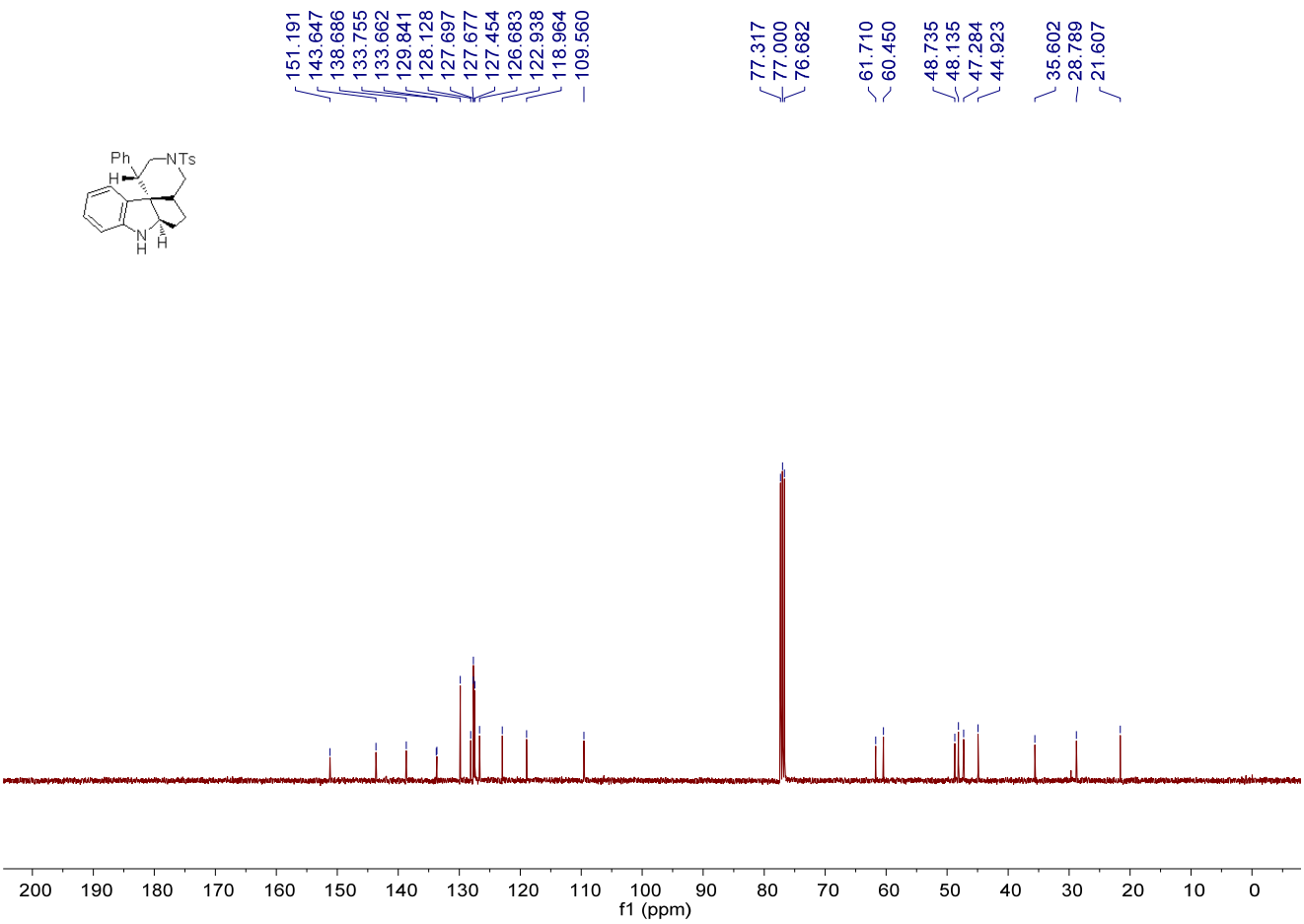


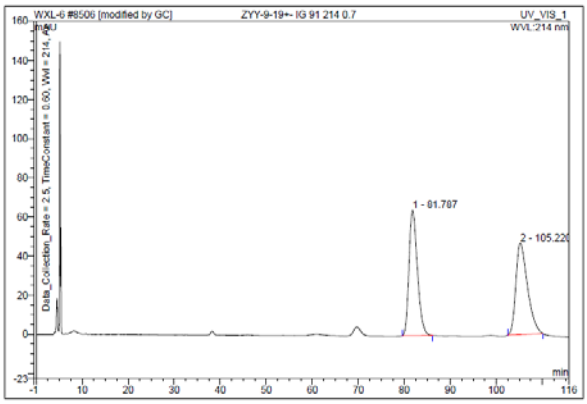
(1*S*,4a*R*,6a*R*,11b*S*)-1-phenyl-3-tosyl-2,3,4,4a,5,6,6a,7-octahydro-1*H*-pyrido[4',3':2,3]cyclopenta[1,2-*b*]indole 8

A white solid, 57% yield for two steps (25.3 mg). M.p.: 59-62 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.35-1.47 (m, 2H), 1.56-1.67 (m, 1H), 1.95-2.07 (m, 1H), 2.18-2.25 (m, 1H), 2.49 (s, 3H), 2.67-2.80 (m, 2H), 3.27-3.32 (m, 1H), 3.86-3.94 (m, 3H), 6.24 (d, *J* = 7.6 Hz, 1H), 6.64-6.67 (m, 2H), 6.76-6.80 (m, 1H), 6.92-6.97 (m, 1H), 6.99-7.04 (m, 2H), 7.07-7.13 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 28.8, 35.6, 44.9, 47.3, 48.1, 48.7, 60.5, 61.7, 109.6, 119.0, 122.9, 126.7, 127.5, 127.68, 127.70, 128.1, 129.8, 133.7, 133.8, 138.7, 143.6, 151.2. IR (CH_2Cl_2) ν 3380, 3030, 2936, 2867, 1603, 1344, 1161, 1089, 934, 815, 700, 662 cm^{-1}. MS (ESI) *m/z* (%): 445.19 (100) $[M+H]^+$; HRMS (ESI) Calcd. For $C_{27}H_{29}N_2O_2S^{+1}[M+H]^+$ requires 445.1944, found: 445.1940. Enantiomeric excess was determined by HPLC with a Chiralcel IG column [λ = 214 nm;

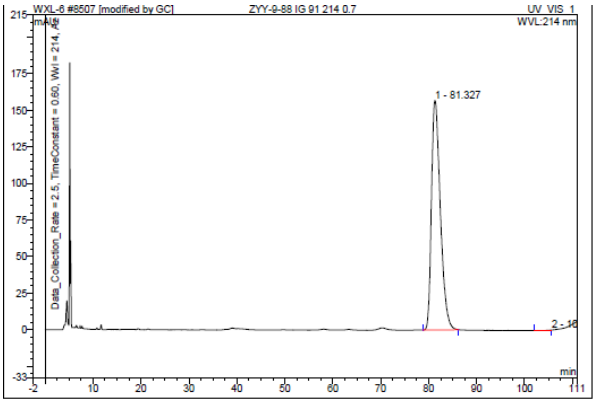
eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 105.67 min, t_{major} = 81.33 min; ee% = 99%; $[\alpha]_D^{25}$ = -42.1 (c 0.20, CH_2Cl_2)].





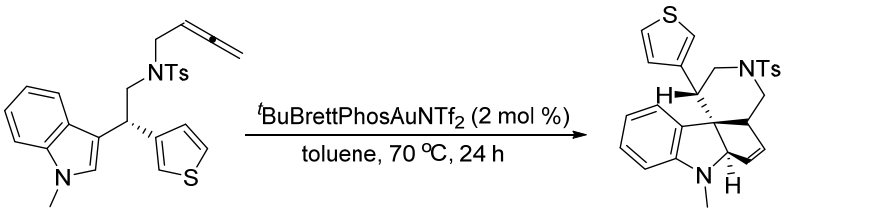


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	81.79	n.a.	64.265	135.815	49.93	n.a.	BMB*
2	105.22	n.a.	46.722	136.220	50.07	n.a.	BMB*
Total:			110.986	272.035	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	81.33	n.a.	156.976	336.612	99.96	n.a.	BMB
2	105.67	n.a.	0.227	0.119	0.04	n.a.	BM *
Total:			157.202	336.730	100.00	0.000	

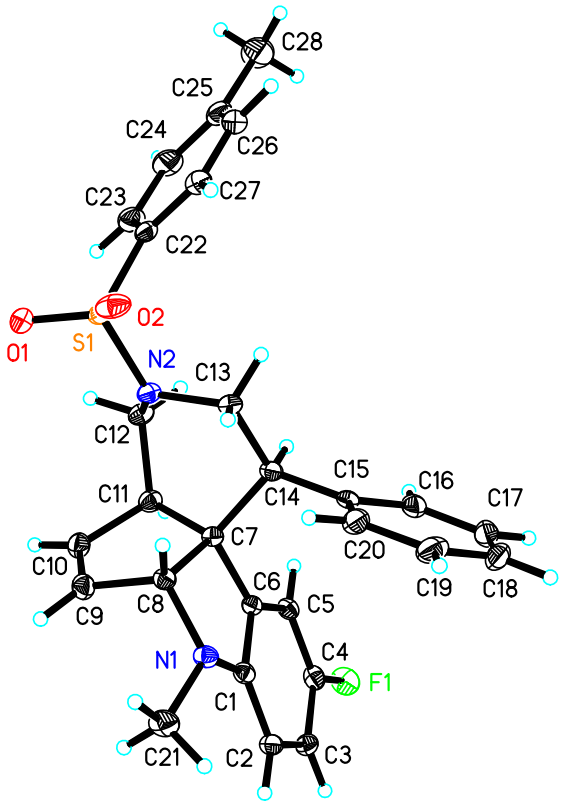
Translation: Chiralcel IG column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 105.67 min, t_{major} = 81.33 min; ee% = 99%]. (*Note*: *In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring*).



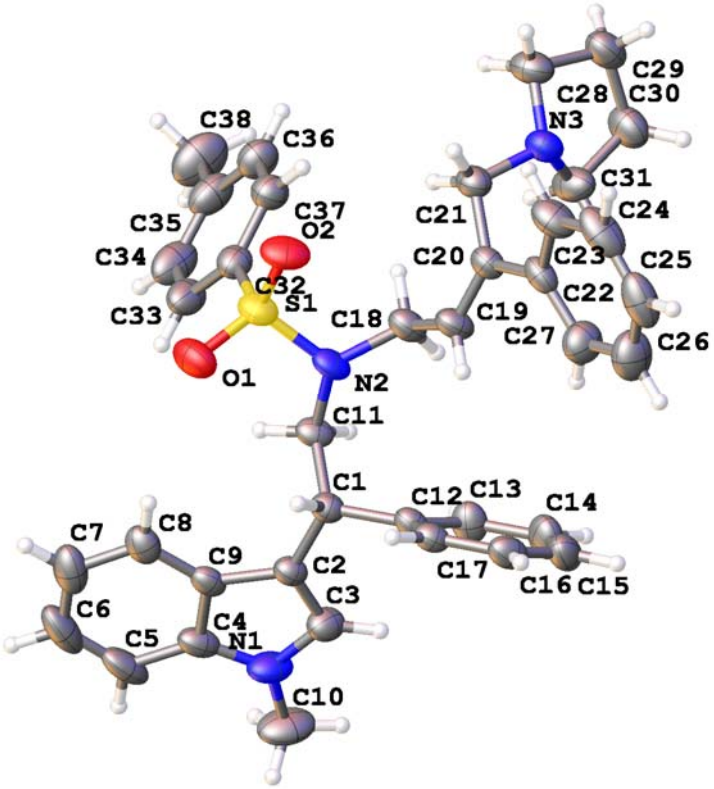
1r (95% ee) **2r'**, 82% yield (30% ee)

To a flame dried Schlenk tube was added chiral compound **1r** (0.1 mmol), ^{t}BuBrettphosAuNTf$_2$ (2.0 mol %) and the tube was evacuated and backfilled with argon for three times. Then, anhydrous toluene (1.0 mL) was added into tube under argon atmosphere. The reaction mixture was allowed to stir at 70 ^{o}C. The solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography on silica gel to give the desired product **2r'**.

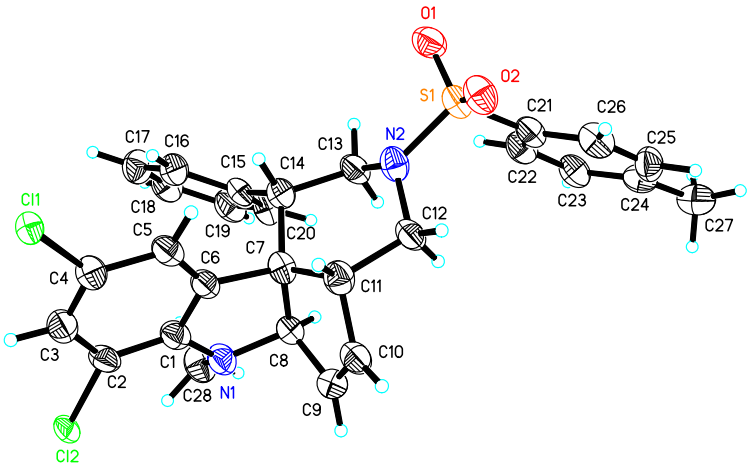
10. X-ray crystallographic information of products 2f, 6, 7 and 2r'.



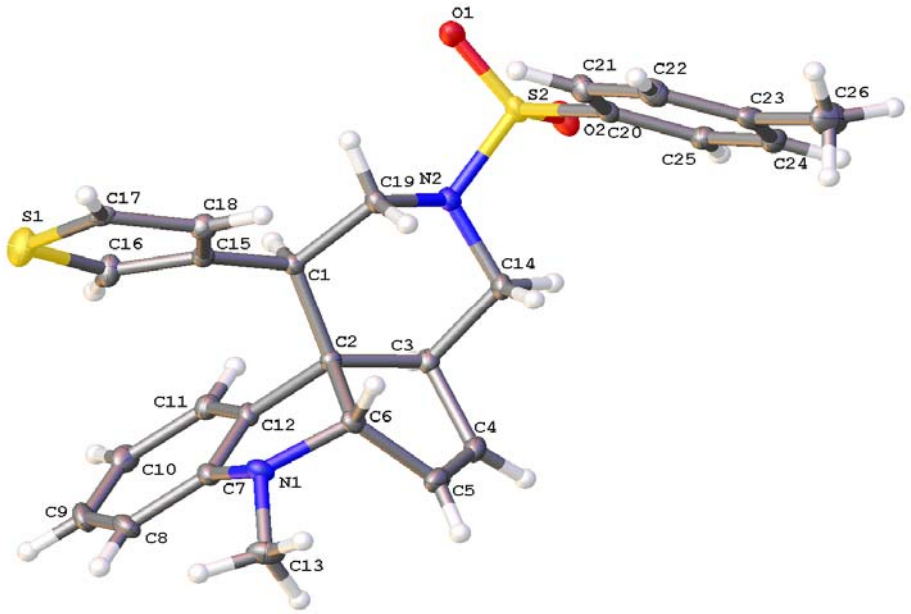
The crystal data of **2f** have been deposited in CCDC with number 1816191. Empirical Formula: $C_{28}H_{27}FN_2O_2S$; Formula Weight: 474.57; Crystal Color, colorless; Crystal Dimensions: 0.180 x 0.140 x 0.100 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 9.8347(3)Å, b = 10.2954(3)Å, c = 12.0508(4)Å, $\alpha = 90^o$, $\beta = 105.0320(10)^o$, $\gamma = 90^o$, V = 1178.42(6)$Å^3$; Space group: P 21; Z = 2; D_{calc} = 1.337 g/cm^3; F_{000} = 500; Final R indices [I>2sigma(I)] R1 = 0.0321, wR2 = 0.0830.



The crystal data of **6** have been deposited in CCDC with number 1851028. Empirical Formula: $C_{38}H_{41}N_3O_2S$; Formula Weight: 603.80; Crystal Color, colorless; Crystal Dimensions: 0.1 x 0.03 x 0.02 mm^3; Crystal System: Orthorhombic; Lattice Parameters: a = 9.7314(4)Å, b = 11.3674(5)Å, c = 29.2938(12)Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 3240.5(2)$Å^3$; Space group: $P2_12_12_1$; Z = 4; D_{calc} = 1.238 g/cm^3; F_{000} = 1288; Final R indices [I>2sigma(I)] R1 = 0.0459, wR2 = 0.1111.



The crystal data of **7** have been deposited in CCDC with number 1846480. Empirical Formula: $C_{28}H_{26}Cl_2N_2O_2S$; Formula Weight: 525.47; Crystal Color, colorless; Crystal Dimensions: 0.160 x 0.130 x 0.080 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 8.5142(5)Å, b = 11.8312(8)Å, c = 13.0004(8)Å, $\alpha = 90^o$, $\beta = 106.969(3)^o$, $\gamma = 90^o$, V = 1252.56(14)$Å^3$; Space group: P 21; Z = 2; D_{calc} = 1.393 g/cm^3; F_{000} = 548; Final R indices [I>2sigma(I)] R1 = 0.0862, wR2 = 0.2346.



The crystal data of **2r'** have been deposited in CCDC with number 1838571. Empirical Formula: $C_{26}H_{26}N_2O_2S_2$; Formula Weight: 462.61; Crystal Color, colorless; Crystal Dimensions: 0.1 x 0.08 x 0.05 mm^3; Crystal System: Triclinic; Lattice Parameters: a = 6.42400(10)Å, b = 8.1480(2)Å, c = 11.8965(3)Å, α = 108.3570(10)°, β = 103.5550(10)°, γ = 93.6680(10)°, V = 568.10(2)$Å^3$; Space group: P1; Z = 1; D_{calc} = 1.352 g/cm^3; F_{000} = 244; Final R indices [I>2sigma(I)] R1 = 0.0369, wR2 = 0.1009.

11. References

[1] Rajasekar, S.; Yadagiri, D.; Anbarasan, P. *Chem. - Eur. J*. **2015**, *21*, 17079.

[2] Lin, T.-Y.; Wu, H.-H.; Feng, J.-J.; Zhang, J.-L. *ACS Catal*. **2017**, *7*, 4047.