

Supporting Information

Rhodium-Catalyzed Intermolecular [3+3] Cycloaddition of Vinyl Aziridines with C,N-Cyclic Azomethine Imines: Stereospecific Synthesis of Chiral Fused Tricyclic 1,2,4-Hexahydrotriazines

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1. General Information

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen. ^1H NMR, ^{13}C NMR spectra were measured at 400 MHz (or 500 MHz) and 100 MHz (or 125 MHz) in CDCl_3 using TMS signal (δ 0.00 ppm) and the residual signals from CHCl_3 (δ 77.0 ppm) as internal references for ^1H and ^{13}C NMR respectively. Data for ^1H NMR spectra are reported as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, qd = quartet of doublets, ddd = doublet of doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Tetrahydrofuran and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane and 1,2-dichloroethane (DCE) was distilled from CaH_2 prior to use.

The catalysts $[\text{Rh}(\eta^6\text{-C}_{10}\text{H}_8)(\text{COD})]\text{SbF}_6$,^[1] $[\text{Rh}(\text{dnCOT})(\text{MeCN})_2]\text{SbF}_6$,^[2] $\text{RhCl}(\text{IPr})(\text{COD})$,^[3] chiral vinylaziridines **1a-1h**^[4] and *C,N*-cyclic *N'*-acyl azomethine imine **2**^[5] were synthesized according to the reported procedure. All other chemicals and solvents were purchased from commercial company and used as received.

2. Figure S1. Other Attempted Dipoles

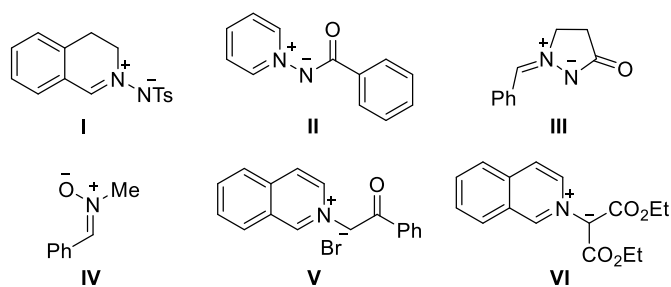
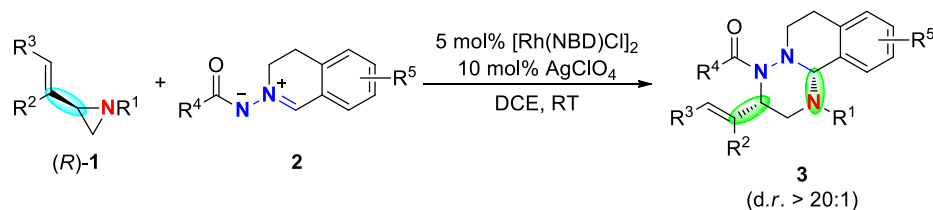


Figure S1. Other Attempted Dipoles

The 1,3-dipolar cycloadditions of vinylaziridine (*R*)-**1a** (98% *ee*) with other dipoles (Figure S1, **I-VI**) have been examined. However, subjecting (*R*)-**1a** and dipoles **I-VI** to a solution of various rhodium-catalysts did not give the desired [3+3] cycloadducts.

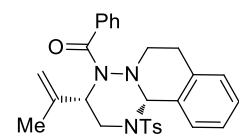
3. Experimental Procedures and Characterization Data

General Procedure for [Rh(NBD)Cl]₂/AgClO₄ Catalyzed Intermolecular [3+3] Cycloaddition Reaction of Vinyl Aziridines **1** and Dipoles **2**.



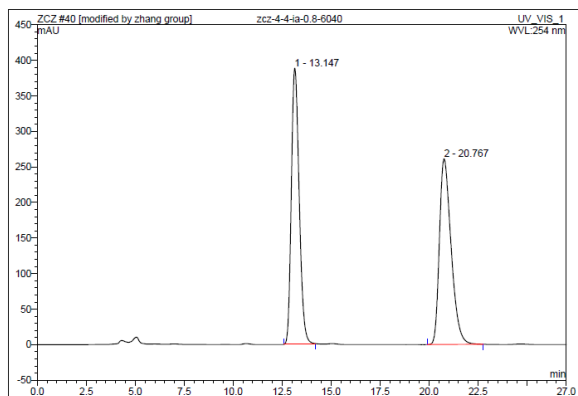
A mixture of [Rh(NBD)Cl]₂ (5.0 mg, 5 mol%) and AgClO₄ (5.0 mg, 10 mol%) in DCE (0.5 mL) was stirred at room temperature under argon atmosphere for 30 min. Then a solution of vinylaziridine **1** (0.20 mmol) and dipoles **2** (0.3 mmol) in DCE (1.5 mL) was added dropwise over a period of 3 mins at room temperature. The resulting mixture was then stirred at RT for about 0.5-14 h. Upon complete consumption of **1** (TLC monitoring), the solvent was removed under reduced pressure, and the residue was purified by chromatography on a silica gel column, eluting with hexane:EtOAc:DCM (5:1:1 to 3:1:1) to afford the desired [3+3] cycloadduct **3**.

phenyl((3*S*,11*bS*)-3-(prop-1-en-2-yl)-1-tosyl-2,3,6,7-tetrahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11*bH*)-yl)methanone: (*S,S*)-**3aa**

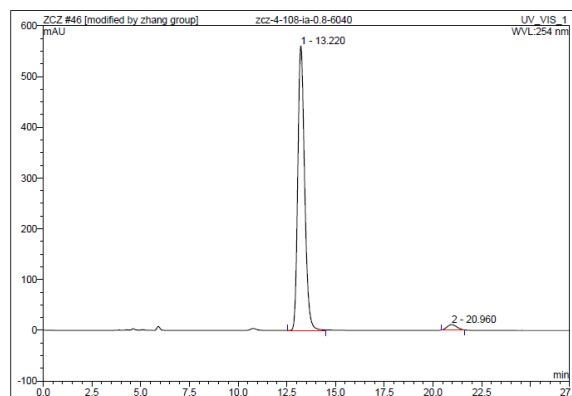


White solid. m.p. 127.5-129.1 °C. 80% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.39-7.29 (m, 5H), 7.24-7.19 (m, 2H), 7.01 (d, *J* = 6.8 Hz, 1H), 5.95 (s, 1H), 4.92 (s, 1H), 4.86 (s, 1H), 4.80 (t, *J* = 8.8 Hz, 1H), 4.16 (dd, *J* = 15.2 and 7.2 Hz, 1H), 3.43-3.37 (m, 1H), 3.32 (dd, *J* = 15.2 and 11.2 Hz, 1H), 3.24-3.21 (m, 1H), 2.70-2.59 (m, 2H), 2.41 (s, 3H), 1.76 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 171.5, 144.5, 142.3, 137.0, 135.4, 135.1, 133.0, 130.3, 129.9, 129.5, 128.2, 127.7, 127.5, 127.2, 126.8, 111.3, 71.5, 55.6, 50.1, 41.8, 30.1, 21.6, 20.2. HRMS (ESI) calcd for C₂₈H₂₉N₃NaO₃S [(M+Na⁺)]: 510.1822, found:510.1828. [α]_D²² = +133.7 (*c* 1.0, CHCl₃). 95% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 13.22 min (major), 20.96 min (minor).

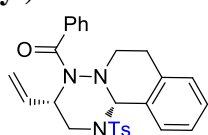


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.15	n.a.	388.426	180.377	49.95	n.a.	BM*
2	20.77	n.a.	261.142	180.716	50.05	n.a.	BMB*
Total:			649.568	361.092	100.00	0.000	



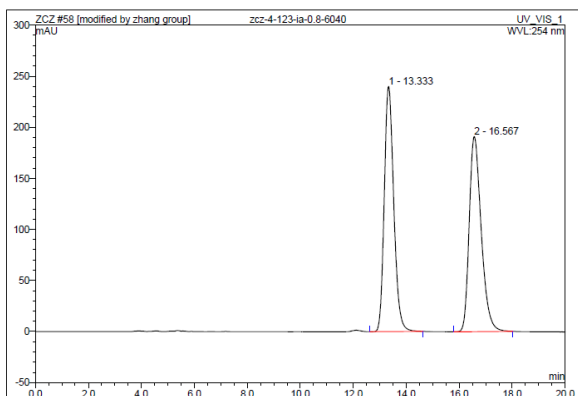
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.22	n.a.	560.065	227.432	97.44	n.a.	BM*
2	20.96	n.a.	10.559	5.971	2.56	n.a.	BMB*
Total:			570.624	233.403	100.00	0.000	

phenyl((3*S*,11*bS*)-1-tosyl-3-vinyl-2,3,6,7-tetrahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11*bH*)-yl)methanone: (*S,S*)-3ba

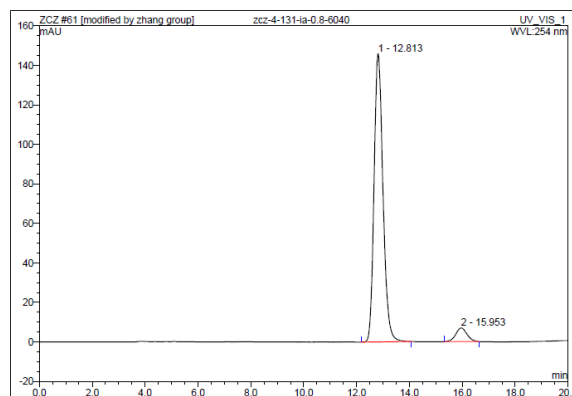


White solid. m.p. 143.8-145.1 °C. 60% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, *J* = 6.8 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 2H), 7.29-7.22 (m, 4H), 7.03 (d, *J* = 6.4 Hz, 1H), 6.03 (s, 1H), 5.93-5.85 (m, 1H), 5.28-5.21 (m, 2H), 4.79-4.73 (m, 1H), 4.10 (dd, *J* = 15.2 and 7.6 Hz, 1H), 3.48-3.35 (m, 2H), 3.06-3.03 (m, 1H), 2.67-2.60 (m, 2H), 2.36 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 170.5, 144.4, 137.0, 135.7, 135.1, 134.7, 132.6, 130.2, 130.1, 129.6, 128.3, 127.7, 127.64, 127.57, 127.5, 126.8, 118.0, 71.6, 53.4, 50.7, 42.7, 30.3, 21.6. HRMS (ESI) calcd for C₂₇H₂₇N₃NaO₃S [(M+Na⁺)]: 496.1665, found: 496.1678. [α]_D²² = +94.3 (*c* 1.0, CHCl₃). 89% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 12.81 min (major), 15.95 min (minor).

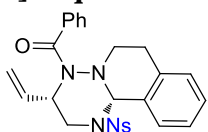


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.33	n.a.	240.222	99.755	49.86	n.a.	BMB*
2	16.57	n.a.	191.055	100.331	50.14	n.a.	BMB*
Total:			431.278	200.087	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.81	n.a.	145.812	56.997	94.42	n.a.	BMB*
2	15.95	n.a.	6.898	3.370	5.58	n.a.	BMB*
Total:			152.710	60.367	100.00	0.000	

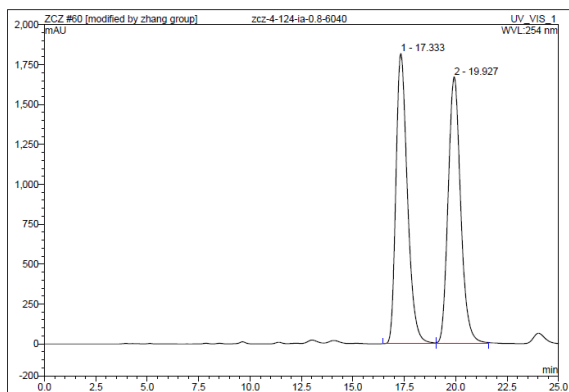
((3*S*,11*bS*)-1-((4-nitrophenyl)sulfonyl)-3-vinyl-2,3,6,7-tetrahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11*bH*)-yl)(phenyl)methanone: (*S,S*)-3ca



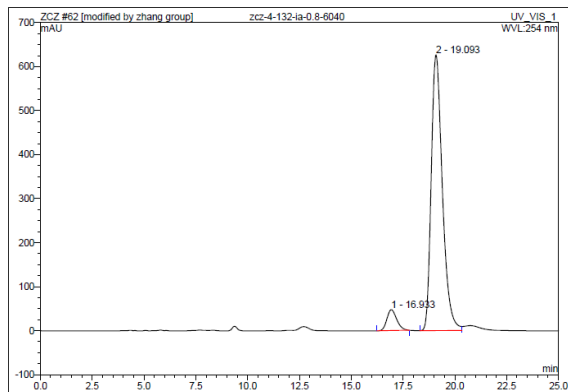
White solid. m.p. 110.5-112.9 °C. 76% yield.

¹H NMR (400 MHz, CDCl₃): δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.56-7.54 (m, 2H), 7.43-7.39 (m, 1H), 7.35-7.20 (m, 4H), 7.07 (d, *J* = 7.2 Hz, 1H), 5.99-5.91 (m, 2H), 5.35-5.27 (m, 2H), 4.89-4.88 (m, 1H), 4.13 (dd, *J* = 15.2 and 7.2 Hz,

1H), 3.64 (dd, $J = 14.4$ and 9.2 Hz, 1H), 3.58-3.51 (m, 1H), 3.11-3.09 (m, 1H), 2.76-2.64 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 169.9, 150.2, 146.0, 135.3, 135.2, 133.7, 131.1, 130.7, 129.2, 128.8, 128.6, 128.1, 128.0, 127.8, 126.7, 124.6, 118.5, 72.9, 52.8, 50.2, 43.9, 29.9. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{24}\text{N}_4\text{NaO}_5\text{S}$ [(M+Na⁺)]: 527.1360, found: 527.1370. $[\alpha]_D^{22} = +82.7$ (c 1.0, CHCl_3). 87% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 16.93 min (minor), 19.09 min (major).

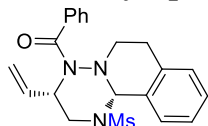


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.33	n.a.	1816.916	1180.892	49.89	n.a.	BM *
2	19.93	n.a.	1671.990	1186.008	50.11	n.a.	M *
Total:			3488.906	2366.900	100.00	0.000	



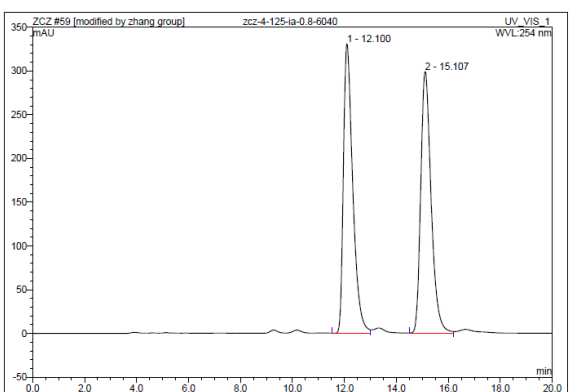
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.93	n.a.	47.535	26.073	6.26	n.a.	BMB*
2	19.09	n.a.	626.407	390.555	93.74	n.a.	BM *
Total:			673.943	416.627	100.00	0.000	

((3*S*,11*bS*)-1-(methylsulfonyl)-3-vinyl-2,3,6,7-tetrahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11*bH*)-yl)(phenyl)methanone: (*S,S*)-3da

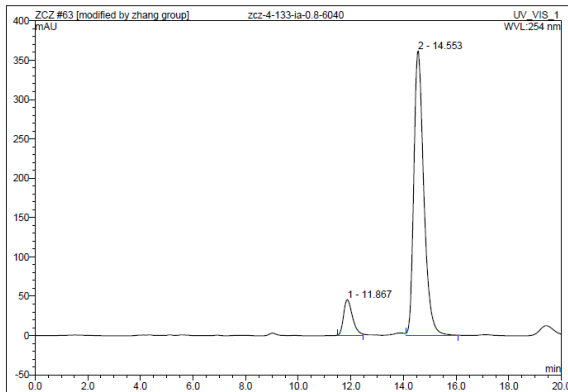


White solid. m.p. 199.7-200.9 °C. 67% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.80 (d, $J = 7.2$ Hz, 1H), 7.62 (d, $J = 6.8$ Hz, 2H), 7.43-7.35 (m, 3H), 7.28-7.22 (m, 2H), 7.07 (d, $J = 6.0$ Hz, 1H), 6.03-5.95 (m, 1H), 5.79 (s, 1H), 5.44-5.35 (m, 2H), 5.32 (d, $J = 10.8$ Hz, 1H), 4.11 (dd, $J = 15.2$ and 7.2 Hz, 1H), 3.57-3.50 (m, 1H), 3.35 (dd, $J = 15.2$ and 10.8 Hz, 1H), 3.28-3.26 (m, 1H), 3.04 (s, 3H), 2.79-2.68 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 172.0, 135.1, 134.7, 132.2, 130.5, 129.2, 128.5, 128.0, 127.7, 127.5, 126.9, 118.8, 71.7, 53.9, 50.7, 42.5, 40.6, 30.2. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{23}\text{N}_3\text{NaO}_3\text{S}$ [(M+Na⁺)]: 420.1352, found: 420.1360. $[\alpha]_D^{22} = +56.8$ (c 1.0, CHCl_3). 80% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 11.87 min (minor), 14.55 min (major).

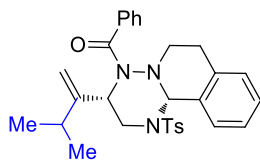


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.10	n.a.	330.608	137.704	49.94	n.a.	BM *
2	15.11	n.a.	298.829	138.047	50.06	n.a.	BM *
Total:			629.436	275.750	100.00	0.000	



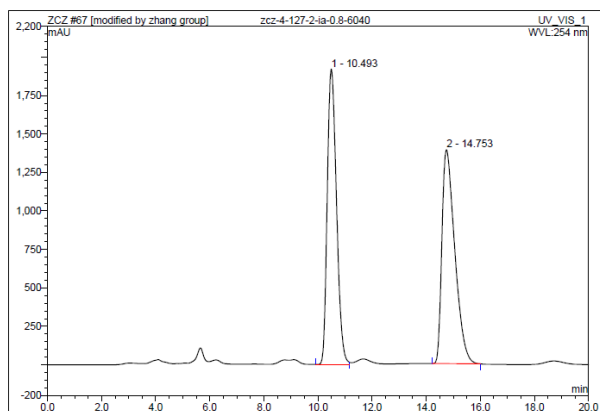
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.87	n.a.	45.193	17.707	10.04	n.a.	BM *
2	14.55	n.a.	361.306	158.687	89.96	n.a.	M *
Total:			406.499	176.394	100.00	0.000	

((3*S*,11*bS*)-3-(3-methylbut-1-en-2-yl)-1-tosyl-2,3,6,7-tetrahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11*bH*)-yl)(phenyl)methanone: (*S,S*)-3ea

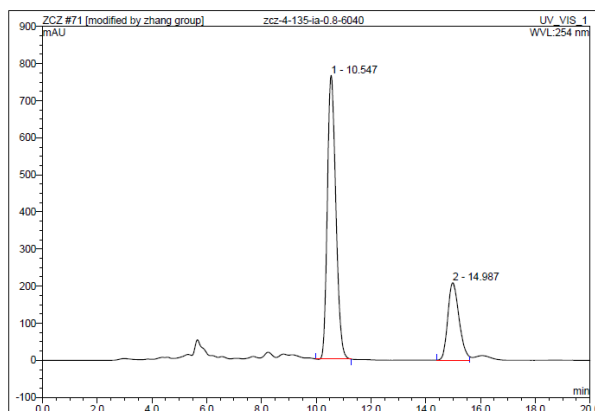


White solid. m.p. 130.8-132.4 °C. 40% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.82-7.78 (m, 3H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.38-7.29 (m, 5H), 7.24-7.19 (m, 2H), 7.01 (d, *J* = 6.8 Hz, 1H), 5.97 (s, 1H), 4.96 (s, 2H), 4.83-4.79 (m, 1H), 4.13 (dd, *J* = 15.2 and 6.8 Hz, 1H), 3.42-3.36 (m, 1H), 3.31-3.22 (m, 2H), 2.70-2.61 (m, 2H), 2.41 (s, 3H), 2.25-2.17 (m, 1H), 1.09 (d, *J* = 7.2 Hz, 3H), 1.07 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 171.3, 152.5, 144.4, 137.0, 135.5, 135.0, 133.1, 130.2, 129.8, 129.4, 128.1, 127.6, 127.4, 127.2, 126.7, 107.6, 71.7, 55.1, 50.5, 42.2, 30.4, 30.1, 22.3, 22.0, 21.5. HRMS (ESI) calcd for C₃₀H₃₃N₃NaO₃S [(M+Na⁺)]: 538.2135, found: 538.2143. [α]²²_D = +58.2 (*c* 1.0, CHCl₃). 47% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 10.55 min (major), 14.99 min (minor).

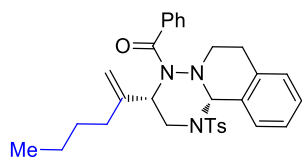


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.49	n.a.	1921.187	760.639	49.80	n.a.	BM*
2	14.75	n.a.	1390.251	766.852	50.20	n.a.	BMB*
Total:			3311.438	1527.491	100.00	0.000	



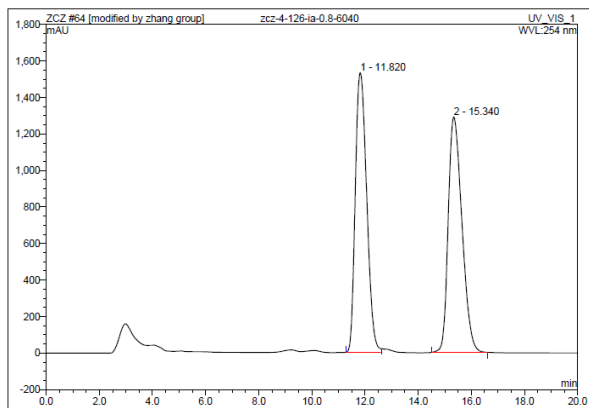
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.55	n.a.	764.633	274.893	73.47	n.a.	BMB*
2	14.99	n.a.	208.537	99.276	26.53	n.a.	BM*
Total:			973.170	374.169	100.00	0.000	

((3*S*,11*bS*)-3-(hex-1-en-2-yl)-1-tosyl-2,3,6,7-tetrahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11*bH*)-yl)(phenyl)methanone: (*S,S*)-3fa

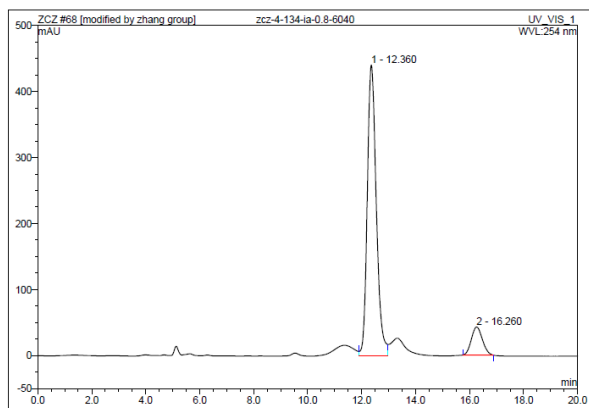


Colorless oil. 73% yield.

¹H NMR (500 MHz, CDCl₃): δ 7.87 (d, *J* = 7.5 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 7.0 Hz, 2H), 7.40 (d, *J* = 7.0 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.28-7.18 (m, 2H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.00 (s, 1H), 4.96 (s, 1H), 4.95 (s, 1H), 4.75-4.72 (m, 1H), 4.14 (dd, *J* = 15.5 and 7.0 Hz, 1H), 3.40-3.35 (m, 1H), 3.31-3.22 (m, 2H), 2.69-2.60 (m, 2H), 2.44 (s, 3H), 2.07-1.98 (m, 2H), 1.49-1.41 (m, 2H), 1.38-1.30 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 171.3, 146.0, 144.5, 137.1, 135.5, 135.1, 133.1, 130.3, 129.8, 129.5, 128.2, 127.7, 127.5, 127.2, 126.8, 109.8, 71.6, 55.3, 50.4, 41.9, 32.8, 30.2, 29.8, 22.4, 21.6, 14.0. HRMS (ESI) calcd for C₃₁H₃₅N₃NaO₃S [(M+Na⁺)]: 552.2291, found: 552.2300. [α]²²_D = +81.0 (*c* 1.0, CHCl₃). 79% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 12.36 min (major), 16.26 min (minor).

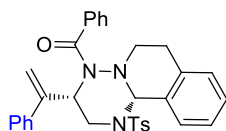


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.82	n.a.	1530.643	759.664	49.64	n.a.	BM*
2	15.34	n.a.	1288.456	770.836	50.36	n.a.	BMB*
Total:			2819.099	1530.499	100.00	0.000	



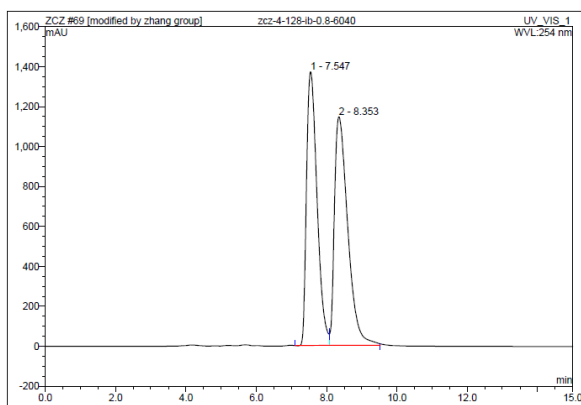
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.36	n.a.	440.286	170.362	89.49	n.a.	M*
2	16.26	n.a.	42.420	20.001	10.51	n.a.	BMB*
Total:			482.706	190.364	100.00	0.000	

phenyl((3*S*,11*BS*)-3-(1-phenylvinyl)-1-tosyl-2,3,6,7-tetrahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11*B**H*)-yl)methanone: (*S,S*)-3ga**

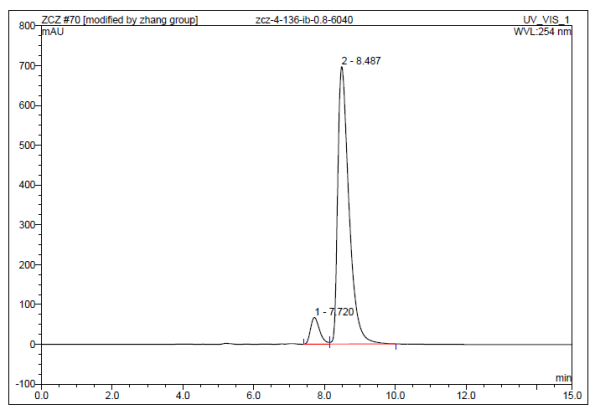


White solid. m.p. 104.3-105.9 °C. 74% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.80-7.78 (m, 3H), 7.54 (d, *J* = 6.8 Hz, 2H), 7.41-7.30 (m, 8H), 7.24-7.20 (m, 4H), 7.02-7.01 (m, 1H), 6.01 (s, 1H), 5.25 (s, 2H), 5.23-5.19 (m, 1H), 3.91 (dd, *J* = 15.6 and 6.8 Hz, 1H), 3.42-3.35 (m, 1H), 3.24-3.20 (m, 1H), 3.11 (dd, *J* = 15.6 and 11.2 Hz, 1H), 2.72-2.61 (m, 2H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 171.4, 146.1, 144.7, 139.2, 137.1, 135.3, 134.9, 133.1, 130.4, 130.0, 129.5, 128.6, 128.2, 128.1, 127.8, 127.49, 127.46, 127.3, 127.0, 126.9, 113.6, 71.8, 55.4, 50.7, 42.2, 30.3, 21.7. HRMS (ESI) calcd for C₃₃H₃₁N₃NaO₃S [(M+Na⁺)]: 572.1978, found: 572.1988. [α]²²_D = +0.3 (*c* 1.0, CHCl₃). 85% *ee*. HPLC analysis of the product: Daicel Chiralpak IB column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 7.72 min (minor), 8.49 min (major)

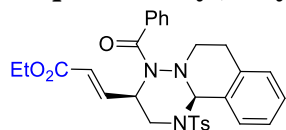


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.55	n.a.	1370.186	475.345	48.64	n.a.	BM*
2	8.35	n.a.	1143.357	501.977	51.36	n.a.	M*
Total:			2513.543	977.322	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.72	n.a.	66.993	20.148	7.29	n.a.	BM*
2	8.49	n.a.	696.718	256.218	92.71	n.a.	MB*
Total:			763.712	276.366	100.00	0.000	

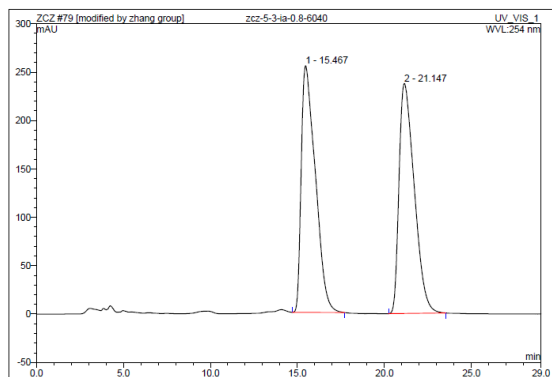
(*E*)-ethyl-3-((3*R*,11*BR*)-4-benzoyl-1-tosyl-2,3,4,6,7,11*b*-hexahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-3-yl)acrylate: (*R,R*)-3ha**



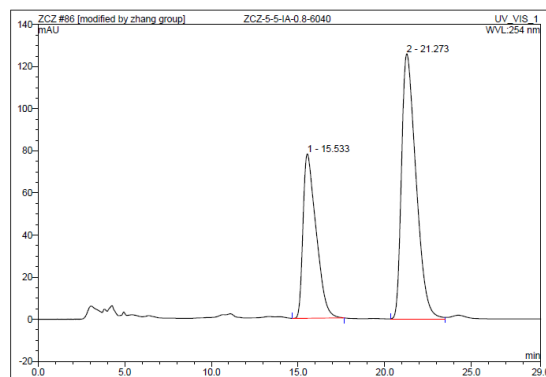
Yellow oil. 50% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.54-7.52 (m, 2H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.35-7.31 (m, 2H), 7.26-7.22 (m, 4H), 7.04 (d, *J* = 6.8 Hz, 1H), 6.88 (dd, *J* = 16.0 and 5.6 Hz, 1H), 6.08 (s, 1H), 5.97 (dd, *J* = 16.4

and 2.0 Hz, 1H), 4.93-4.88 (m, 1H), 4.19-4.10 (m, 3H), 3.39-3.33 (m, 2H), 3.10-3.08 (m, 1H), 2.70-2.60 (m, 2H), 2.37 (s, 3H), 1.26 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.6, 165.7, 144.7, 144.0, 136.7, 134.9, 134.0, 132.4, 130.4, 130.3, 129.5, 128.4, 127.9, 127.7, 127.5, 126.9, 123.7, 71.4, 60.7, 52.1, 50.8, 42.0, 30.2, 21.6, 14.2. HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{31}\text{N}_3\text{NaO}_5\text{S}$ [(M+Na⁺)]: 568.1877, found: 568.1883. $[\alpha]^{22}_{\text{D}} = -11.5$ (c 1.0, CHCl_3). 28% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 15.53 min (minor), 21.27 min (major).

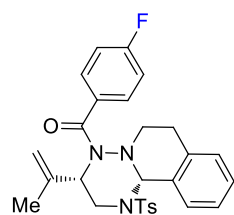


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.47	n.a.	255.023	239.392	49.84	n.a.	BMB*
2	21.15	n.a.	237.777	240.922	50.16	n.a.	BMB*
Total:			492.800	480.314	100.00	0.000	



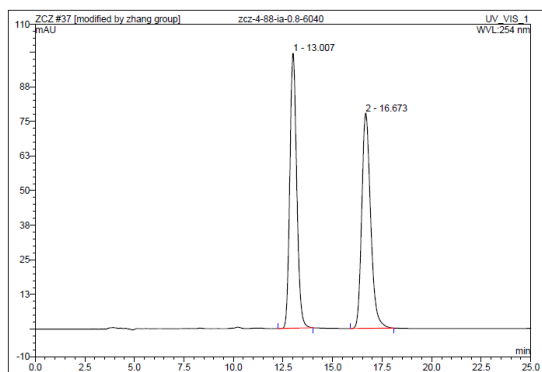
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.53	n.a.	78.019	68.075	35.89	n.a.	BMB*
2	21.27	n.a.	125.830	121.586	64.11	n.a.	BM*
Total:			203.849	189.661	100.00	0.000	

(4-fluorophenyl)((3*S*,11*bS*)-3-(prop-1-en-2-yl)-1-tosyl-2,3,6,7-tetrahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11*bH*)-yl)methanone: (*S,S*)-3ab

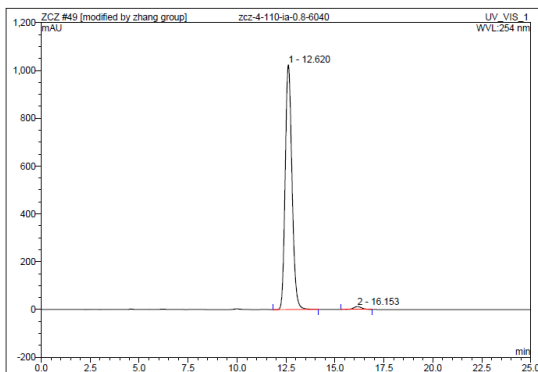


White solid. m.p. 132.2-135.1 °C. 82% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.77-7.75 (m, 3H), 7.57 (dd, $J = 9.2$ and 5.6 Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 7.24-7.20 (m, 2H), 7.04-7.00 (m, 3H), 5.95 (s, 1H), 4.92 (s, 1H), 4.88-4.85 (m, 2H), 4.16 (dd, $J = 15.2$ and 7.2 Hz, 1H), 3.46-3.39 (m, 1H), 3.33 (dd, $J = 15.2$ and 11.2 Hz, 1H), 3.23-3.21 (m, 1H), 2.76-2.64 (m, 2H), 2.40 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.0, 163.5 (d, $J = 247.1$ Hz), 144.4, 142.2, 136.8, 134.9, 132.7, 131.0 (d, $J = 3.1$ Hz), 130.1, 129.9 (d, $J = 8.2$ Hz), 129.3, 128.2, 127.5, 127.4, 126.8, 114.6 (d, $J = 22.2$ Hz), 111.2, 71.2, 55.7, 49.9, 41.7, 30.0, 21.5, 20.1. ^{19}F NMR (376 MHz, CDCl_3): δ -109.9. HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{28}\text{FN}_3\text{NaO}_3\text{S}$ [(M+Na⁺)]: 528.1728, found: 528.1737. $[\alpha]^{22}_{\text{D}} = +135.6$ (c 1.0, CHCl_3). 97% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 12.62 min (major), 16.15 min (minor).

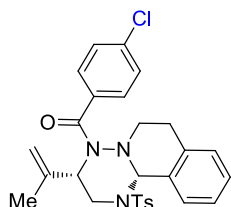


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.01	n.a.	99.370	40.071	49.75	n.a.	BMB*
2	16.67	n.a.	77.766	40.475	50.25	n.a.	BMB*
Total:			177.136	80.546	100.00	0.000	



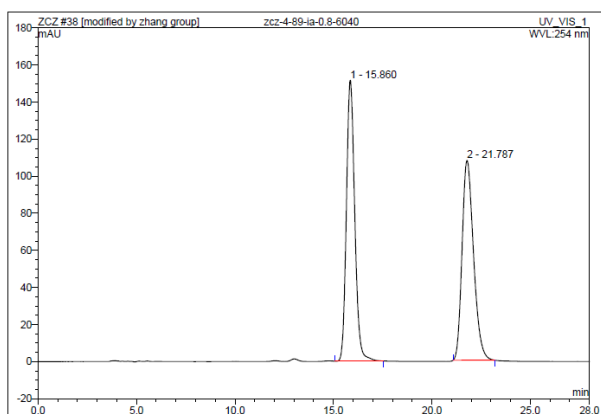
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.62	n.a.	1023.475	410.321	98.61	n.a.	BMB*
2	16.15	n.a.	11.993	5.798	1.39	n.a.	BMB*
Total:			1035.468	416.119	100.00	0.000	

(4-chlorophenyl)((3*S*,11*bS*)-3-(prop-1-en-2-yl)-1-tosyl-2,3,6,7-tetrahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11*bH*)-yl)methanone: (*S,S*)-3ac

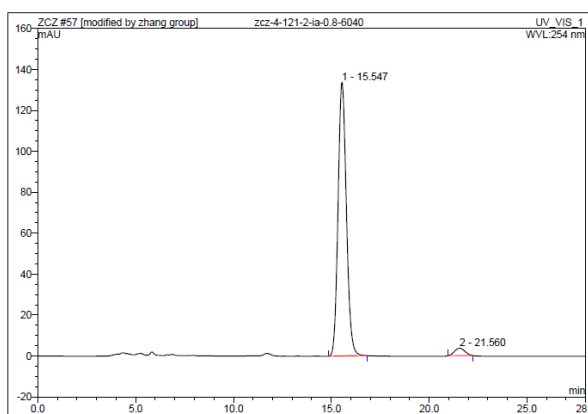


Yellow solid. m.p. 173.2-174.6 °C. 88% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.77-7.75 (m, 3H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.23-7.21 (m, 2H), 7.04-7.02 (m, 1H), 5.93 (s, 1H), 4.92 (s, 1H), 4.89-4.85 (m, 2H), 4.15 (dd, $J = 15.2$ and 7.2 Hz, 1H), 3.45-3.39 (m, 1H), 3.33 (dd, $J = 14.8$ and 10.8 Hz, 1H), 3.22-3.20 (m, 1H), 2.75-2.62 (m, 2H), 2.40 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.3, 144.5, 142.3, 136.9, 136.0, 135.0, 133.6, 132.8, 130.2, 129.4, 129.0, 128.3, 127.9, 127.6, 127.5, 126.9, 111.4, 71.3, 55.8, 50.0, 41.9, 30.1, 21.6, 20.2. HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{28}\text{ClN}_3\text{NaO}_3\text{S}$ [(M+Na⁺)]: 544.1432, found: 544.1440. $[\alpha]_D^{22} = +131.3$ (c 1.0, CHCl_3). 93% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 15.55 min (major), 21.56 min (minor).

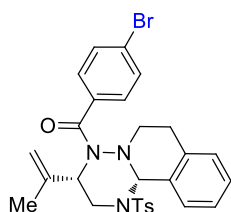


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.86	n.a.	151.340	74.197	50.52	n.a.	MB*
2	21.79	n.a.	107.745	72.666	49.48	n.a.	MB*
Total:			259.085	146.863	100.00	0.000	



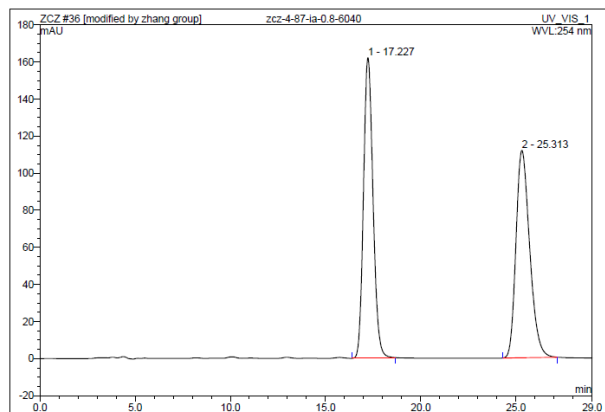
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.55	n.a.	133.744	65.845	96.67	n.a.	BMB*
2	21.56	n.a.	3.680	2.265	3.33	n.a.	BMB*
Total:			137.424	68.110	100.00	0.000	

(4-bromophenyl)((3*S*,11*bS*)-3-(prop-1-en-2-yl)-1-tosyl-2,3,6,7-tetrahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11*bH*)-yl)methanone: (*S,S*)-3ad

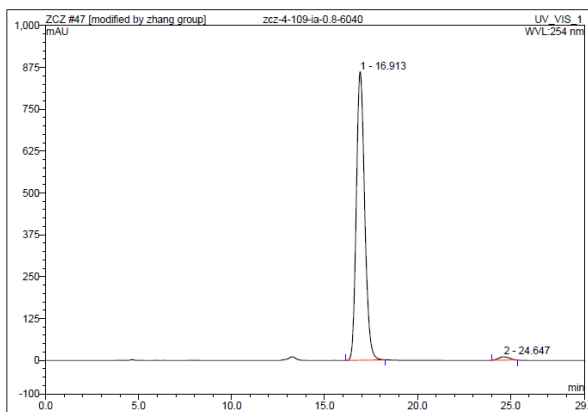


White solid. m.p. 176.2-178.5 °C. 84% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, $J = 8.0$ Hz, 2H), 7.74-7.73 (m, 1H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.23-7.21 (m, 2H), 7.04-7.02 (m, 1H), 5.93 (s, 1H), 4.92 (s, 1H), 4.89-4.84 (m, 2H), 4.15 (dd, $J = 14.8$ and 7.2 Hz, 1H), 3.45-3.38 (m, 1H), 3.33 (dd, $J = 14.8$ and 10.4 Hz, 1H), 3.22-3.19 (m, 1H), 2.73-2.62 (m, 2H), 2.40 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.5, 144.5, 142.3, 136.9, 135.0, 134.1, 132.8, 130.9, 130.3, 129.4, 129.2, 128.3, 127.6, 127.5, 126.9, 124.3, 111.4, 71.3, 55.8, 50.0, 41.8, 30.1, 21.6, 20.2. HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{28}\text{BrN}_3\text{NaO}_3\text{S}$ [(M+Na⁺)]: 588.0927, found: 588.0936. $[\alpha]_D^{22} = +129.1$ (c 1.0, CHCl_3). 97% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 16.91 min (major), 24.65 min (minor).

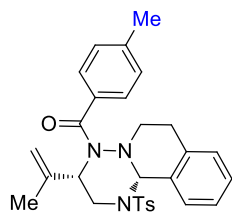


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.23	n.a.	162.103	94.139	50.23	n.a.	BM*
2	25.31	n.a.	111.806	93.263	49.77	n.a.	BMB*
Total:			273.909	187.402	100.00	0.000	



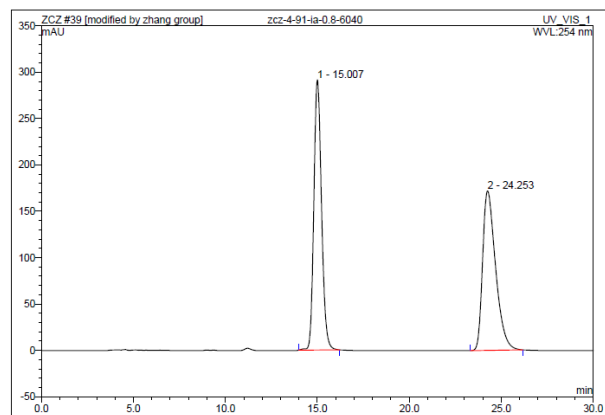
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.91	n.a.	861.087	448.262	98.52	n.a.	BMB*
2	24.65	n.a.	9.908	6.741	1.48	n.a.	BMB*
Total:			870.995	455.003	100.00	0.000	

((3*S*,11*bS*)-3-(prop-1-en-2-yl)-1-tosyl-2,3,6,7-tetrahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11*bH*)-yl)(*p*-tolyl)methanone: (*S,S*)-3ae

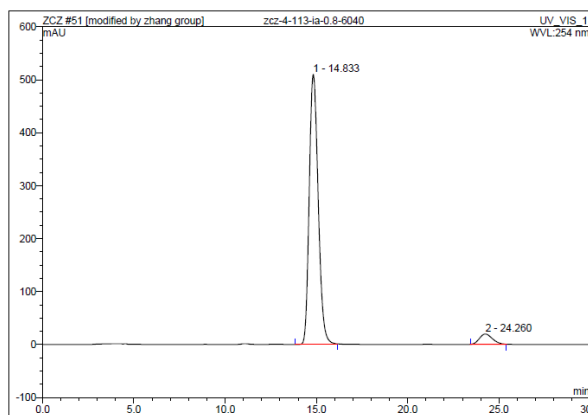


Colorless oil. 88% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.25-7.19 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 6.8 Hz, 1H), 5.96 (s, 1H), 4.90 (s, 1H), 4.84 (s, 1H), 4.77 (t, *J* = 8.8 Hz, 1H), 4.16 (dd, *J* = 15.2 and 7.2 Hz, 1H), 3.43-3.38 (m, 1H), 3.32 (dd, *J* = 15.2 and 11.2 Hz, 1H), 3.25-3.23 (m, 1H), 2.79-2.71 (m, 1H), 2.66-2.62 (m, 1H), 2.40 (s, 3H), 2.35 (s, 3H), 1.75 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 171.1, 144.4, 142.4, 140.2, 137.0, 135.1, 133.1, 132.0, 130.3, 129.6, 128.3, 128.2, 127.7, 127.5, 126.8, 111.2, 71.5, 55.6, 50.1, 41.8, 30.2, 21.6, 21.4, 20.2. HRMS (ESI) calcd for C₂₉H₃₁N₃NaO₃S [(M+Na⁺)]: 524.1978, found:524.1990. [α]_D²² = +125.8 (*c* 1.0, CHCl₃). 90% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 14.83 min (major), 24.26 min (major).



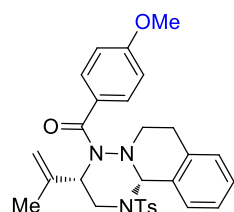
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.01	n.a.	291.288	141.065	50.08	n.a.	BMB*
2	24.25	n.a.	172.017	140.615	49.92	n.a.	BMB*
Total:			463.306	281.680	100.00	0.000	



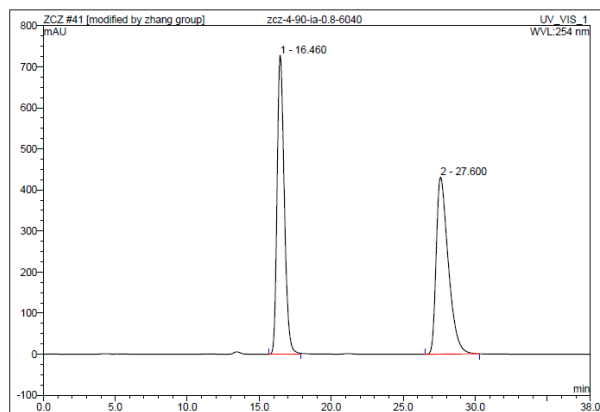
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.83	n.a.	509.901	290.235	94.79	n.a.	BM*
2	24.26	n.a.	19.429	15.943	5.21	n.a.	BMB*
Total:			529.329	306.178	100.00	0.000	

(4-methoxyphenyl)((3*S*,11*bS*)-3-(prop-1-en-2-yl)-1-tosyl-2,3,6,7-tetrahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11*bH*)-yl)methanone: (*S,S*)-3af

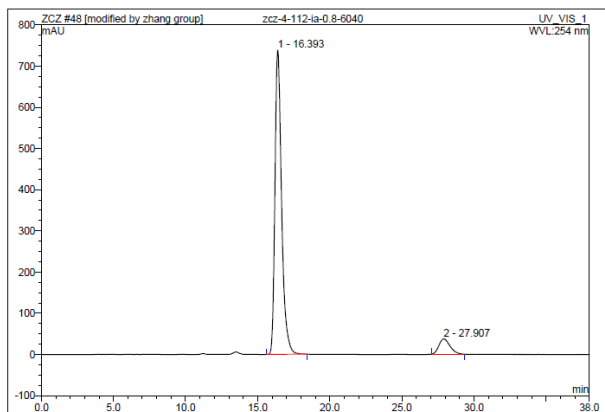
Yellow solid. m.p. 165.1-167.8 °C. 90% yield.



^1H NMR (400 MHz, CDCl_3): δ 7.89 (d, $J = 6.4$ Hz, 1H), 7.74 (d, $J = 7.6$ Hz, 2H), 7.60 (d, $J = 8.0$ Hz, 2H), 7.25-7.20 (m, 4H), 7.05 (d, $J = 6.4$ Hz, 1H), 6.83 (d, $J = 8.8$ Hz, 2H), 5.99 (s, 1H), 4.90 (s, 1H), 4.83 (s, 1H), 4.80-4.78 (m, 1H), 4.20-4.14 (m, 1H), 3.81 (s, 3H), 3.46-3.40 (m, 1H), 3.35-3.19 (m, 2H), 2.87-2.81 (m, 1H), 2.69-2.65 (m, 1H), 2.39 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 169.7, 161.0, 144.2, 142.4, 137.0, 135.0, 132.9, 130.2, 129.6, 128.2, 127.5, 127.4, 126.9, 126.6, 112.8, 111.2, 71.4, 55.7, 55.2, 50.1, 41.8, 30.2, 21.6, 20.2. HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{31}\text{N}_3\text{NaO}_4\text{S}$ [(M+Na $^+$)]: 540.1927, found: 540.1943. $[\alpha]^{22}_{\text{D}} = +117.7$ (c 1.0, CHCl_3). 85% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 16.39 min (major), 27.91 min (minor).

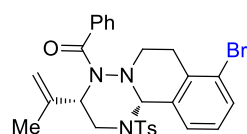


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.46	n.a.	727.855	420.657	50.19	n.a.	BM*
2	27.60	n.a.	430.972	417.478	49.81	n.a.	BMB*
Total:			1158.827	838.135	100.00	0.000	



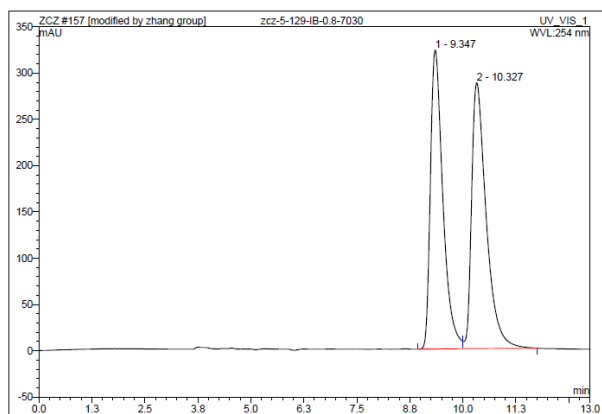
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.39	n.a.	738.175	394.228	92.41	n.a.	BMB*
2	27.91	n.a.	36.812	32.377	7.59	n.a.	BMB*
Total:			774.987	426.605	100.00	0.000	

((3*S*,11*bS*)-8-bromo-3-(prop-1-en-2-yl)-1-tosyl-2,3,6,7-tetrahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11*bH*)-yl)(phenyl)methanone: (*S,S*)-3ag

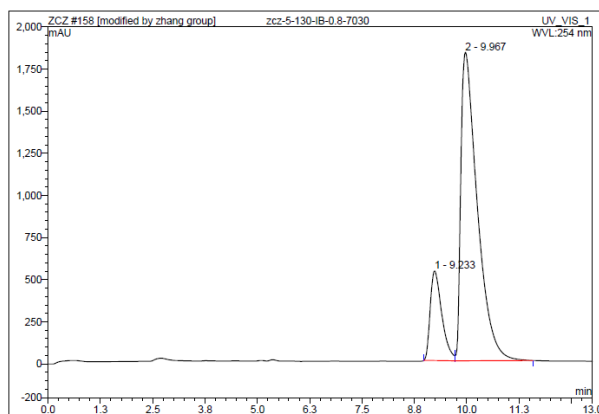


Colorless oil. 60% yield.

^1H NMR (500 MHz, CDCl_3): δ 7.79 (d, $J = 7.5$ Hz, 1H), 7.73 (d, $J = 7.5$ Hz, 2H), 7.51-7.48 (m, 3H), 7.38-7.37 (m, 1H), 7.36 (d, $J = 6.5$ Hz, 2H), 7.30-7.28 (m, 2H), 7.12-7.08 (m, 1H), 5.85 (s, 1H), 4.99-4.97 (m, 2H), 4.90-4.85 (m, 1H), 4.12 (dd, $J = 14.0$ and 7.0 Hz, 1H), 3.56-3.51 (m, 1H), 3.47-3.43 (m, 1H), 3.30-3.24 (m, 1H), 2.92-2.89 (m, 1H), 2.50-2.45 (m, 1H), 2.44 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 171.3, 144.5, 142.4, 136.8, 135.1, 134.8, 134.7, 132.3, 130.2, 129.9, 129.1, 127.8, 127.7, 127.5, 127.2, 123.7, 111.5, 71.8, 54.8, 49.2, 42.2, 30.3, 21.6, 20.2. HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{28}\text{BrN}_3\text{NaO}_3\text{S}$ [(M+Na $^+$)]: 588.0927, found: 588.0926. $[\alpha]^{21}_{\text{D}} = +66.1$ (c 1.0, CHCl_3). 66% *ee*. HPLC analysis of the product: Daicel Chiralpak IB column; hexane/2-propanol = 70/30, 0.8 mL/min. Retention times: 9.23 min (minor), 9.97 min (major).

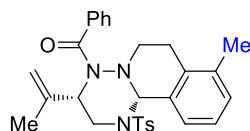


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.35	n.a.	322.964	110.207	48.98	n.a.	BM*
2	10.33	n.a.	287.158	114.815	51.02	n.a.	MB*
Total:			610.122	225.022	100.00	0.000	



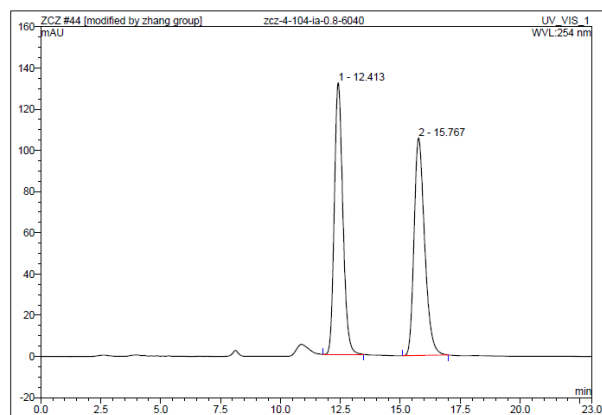
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.23	n.a.	530.761	170.804	17.02	n.a.	BM*
2	9.97	n.a.	1830.292	832.970	82.98	n.a.	MB*
Total:			2361.054	1003.774	100.00	0.000	

((3*S*,11*bS*)-8-methyl-3-(prop-1-en-2-yl)-1-tosyl-2,3,6,7-tetrahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11*bH*)-yl)(phenyl)methanone: (*S,S*)-3ah

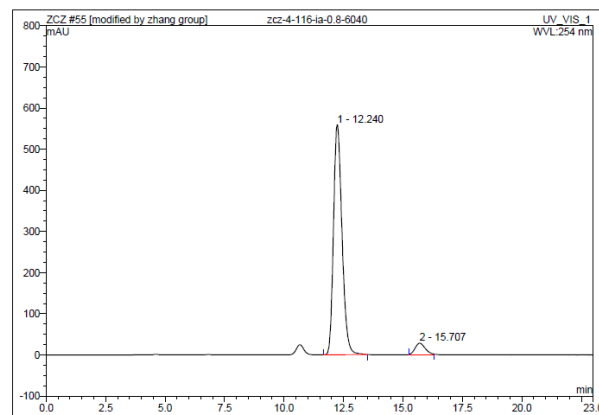


White solid. m.p. 184.8-187.1 °C. 89% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.36-7.30 (m, 3H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.12-7.06 (m, 2H), 5.87 (s, 1H), 4.95 (s, 2H), 4.89 (t, *J* = 8.0 Hz, 1H), 4.11 (dd, *J* = 14.8 and 7.2 Hz, 1H), 3.52 (dd, *J* = 14.8 and 10.4 Hz, 1H), 3.45-3.42 (m, 1H), 3.25-3.22 (m, 1H), 2.66-2.62 (m, 1H), 2.46-2.42 (m, 1H), 2.39 (s, 3H), 2.15 (s, 3H), 1.79 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 171.5, 144.2, 142.6, 137.1, 135.5, 134.9, 133.7, 132.6, 130.1, 129.8, 129.7, 127.7, 127.54, 127.49, 127.3, 126.4, 111.4, 72.2, 55.2, 49.4, 42.2, 26.8, 21.6, 20.3, 19.3. HRMS (ESI) calcd for C₂₉H₃₁N₃NaO₃S [(M+Na)⁺]: 524.1978, found: 524.1988. [α]_D²² = +97.2 (*c* 1.0, CHCl₃). 89% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 12.24 min (major), 15.71 min (minor).



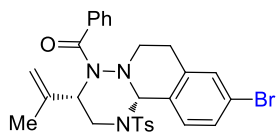
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.41	n.a.	131.860	54.290	50.05	n.a.	BMB*
2	15.77	n.a.	105.546	54.192	49.95	n.a.	BMB*
Total:			237.406	108.481	100.00	0.000	



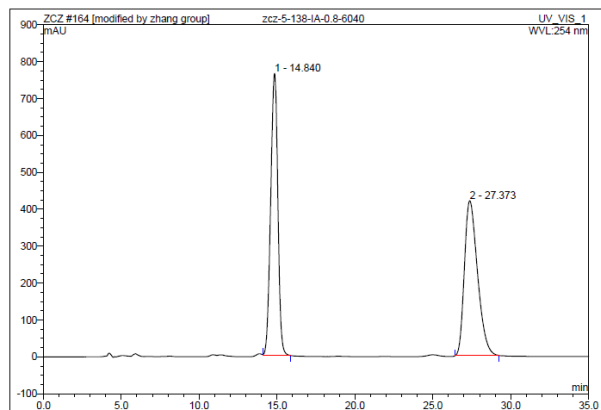
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.24	n.a.	558.955	231.328	94.50	n.a.	BMB*
2	15.71	n.a.	27.559	13.458	5.50	n.a.	BM*
Total:			586.514	244.785	100.00	0.000	

((3*S*,11*bS*)-9-bromo-3-(prop-1-en-2-yl)-1-tosyl-2,3,6,7-tetrahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11*bH*)-yl)(phenyl)methanone: (*S,S*)-3ai

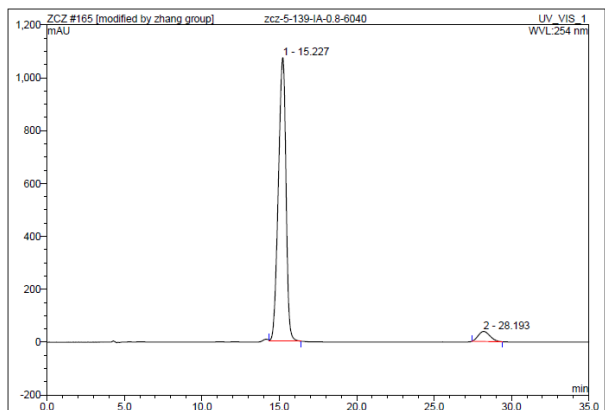
Yellow solid. m.p. 106.8-107.4 °C. 79% yield.



^1H NMR (400 MHz, CDCl_3): δ 7.77 (d, $J = 8.4$ Hz, 2H), 7.71 (d, $J = 8.8$ Hz, 1H), 7.47 (d, $J = 7.2$ Hz, 2H), 7.39-7.28 (m, 6H), 7.16 (s, 1H), 5.85 (s, 1H), 4.93 (s, 1H), 4.87 (s, 1H), 4.79-4.74 (m, 1H), 4.16 (dd, $J = 15.2$ and 7.6 Hz, 1H), 3.41-3.30 (m, 2H), 3.22-3.20 (m, 1H), 2.67-2.56 (m, 2H), 2.42 (s, 3H), 1.76 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 171.2, 144.6, 142.2, 137.1, 136.7, 135.1, 131.9, 131.4, 130.34, 130.30, 130.0, 127.7, 127.5, 127.2, 122.3, 111.4, 71.3, 55.3, 49.6, 41.9, 29.9, 21.7, 20.2. HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{28}\text{BrN}_3\text{NaO}_3\text{S}$ [(M+Na) $^+$]: 588.0927, found: 588.0932. $[\alpha]_D^{21} = +107.2$ (c 1.0, CHCl_3). 90% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 15.23 min (major), 28.19 min (minor).

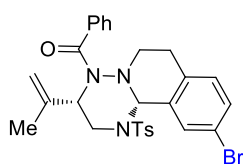


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.84	n.a.	764.227	407.398	49.90	n.a.	MB*
2	27.37	n.a.	419.757	408.970	50.10	n.a.	BM*
Total:			1183.984	816.368	100.00	0.000	



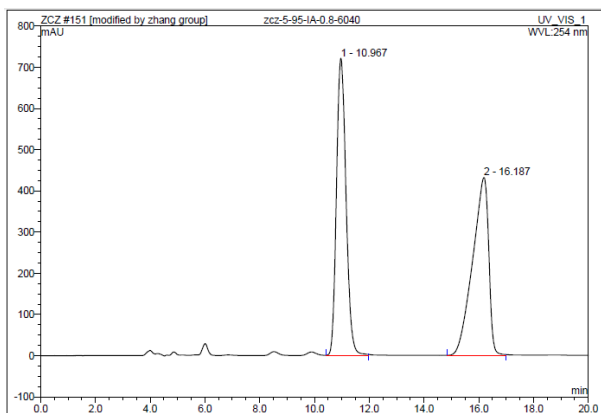
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.23	n.a.	1072.017	611.312	94.86	n.a.	MB*
2	28.19	n.a.	38.012	33.096	5.14	n.a.	BMB*
Total:			1110.028	644.408	100.00	0.000	

((3S,11bS)-10-bromo-3-(prop-1-en-2-yl)-1-tosyl-2,3,6,7-tetrahydro-1H-[1,2,4]triazino[3,2-a]isoquinolin-4(11bH)-yl(phenyl)methanone: (S,S)-3aj

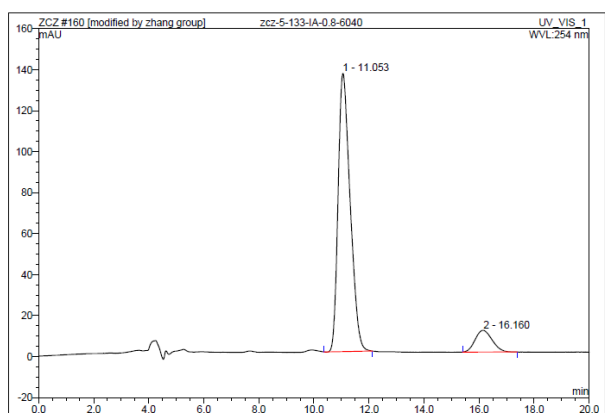


White solid. m.p. 119.3-120.4 °C. 82% yield.

^1H NMR (500 MHz, CDCl_3): δ 7.80 (d, $J = 8.0$ Hz, 2H), 7.63 (s, 1H), 7.52-7.51 (m, 2H), 7.37-7.31 (m, 6H), 6.88 (d, $J = 8.0$ Hz, 1H), 5.85 (s, 1H), 4.99-4.98 (m, 2H), 4.94 (s, 1H), 4.18 (dd, $J = 15.0$ and 7.0 Hz, 1H), 3.43-3.35 (m, 2H), 3.24-3.22 (m, 1H), 2.59-2.55 (m, 2H), 2.45 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 171.8, 144.6, 142.4,



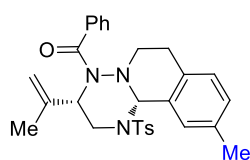
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.97	n.a.	720.486	291.203	49.80	n.a.	BM*
2	16.19	n.a.	431.435	293.566	50.20	n.a.	BM*
Total:			1151.921	584.769	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.05	n.a.	135.681	68.601	90.06	n.a.	BMB*
2	16.16	n.a.	10.587	7.570	9.94	n.a.	BMB*
Total:			146.268	76.170	100.00	0.000	

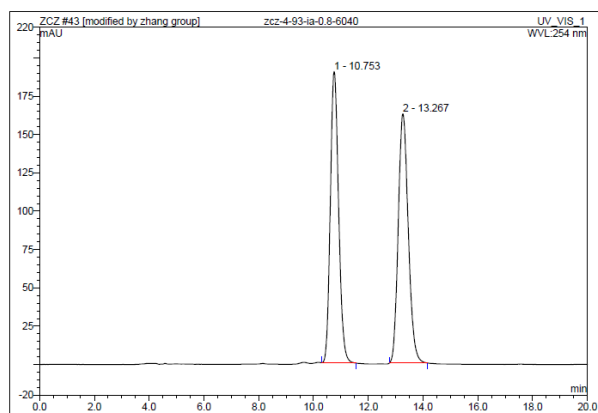
136.9, 135.5, 135.0, 134.1, 132.0, 131.3, 130.3, 129.8, 129.2, 127.7, 127.5, 127.1, 120.4, 111.4, 71.0, 55.5, 49.5, 42.3, 29.6, 21.6, 20.2. HRMS (ESI) calcd for C₂₈H₂₈BrN₃NaO₃S [(M+Na⁺)]: 588.0927, found: 588.0927. [α]²¹_D = +153.2 (*c* 1.0, CHCl₃). 80% *ee*, HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 11.05 min (major), 16.16 min (minor).

((3*S*,11*bS*)-10-methyl-3-(prop-1-en-2-yl)-1-tosyl-2,3,6,7-tetrahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11*bH*)-yl)(phenyl)methanone: (*S,S*)-3ak

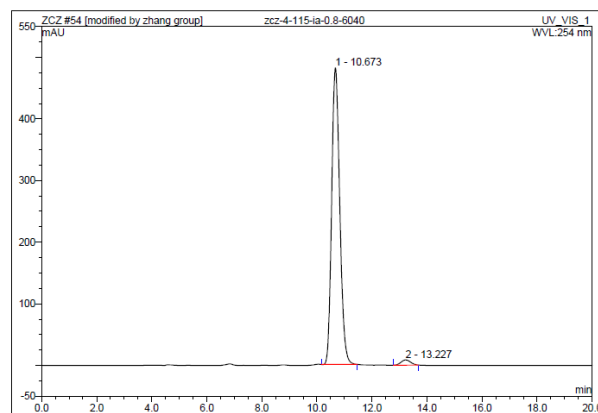


Yellow solid. m.p. 159.5-161.2 °C. 93% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 6.8 Hz, 2H), 7.39-7.29 (m, 6H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 5.90 (s, 1H), 4.93 (s, 1H), 4.88 (s, 2H), 4.19 (dd, *J* = 14.8 and 7.2 Hz, 1H), 3.43-3.31 (m, 2H), 3.23-3.20 (m, 1H), 2.62-2.56 (m, 2H), 2.41 (s, 3H), 2.24 (s, 3H), 1.79 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 171.7, 144.4, 142.5, 137.3, 136.3, 135.6, 132.7, 132.2, 130.2, 129.8, 129.6, 129.0, 127.62, 127.55, 127.4, 127.2, 111.3, 71.5, 55.8, 50.1, 42.1, 29.7, 21.6, 21.2, 20.2. HRMS (ESI) calcd for C₂₉H₃₁N₃NaO₃S [(M+Na⁺)]: 524.1978, found: 524.1990. [α]²²_D = +119.6 (*c* 1.0, CHCl₃). 96% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 10.67 min (major), 13.23 min (minor).

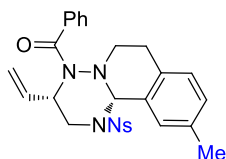


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.75	n.a.	190.205	66.654	49.17	n.a.	MB*
2	13.27	n.a.	162.710	68.916	50.83	n.a.	BMB*
Total:			352.916	135.570	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.67	n.a.	481.472	163.750	97.98	n.a.	BMB*
2	13.23	n.a.	8.448	3.369	2.02	n.a.	BMB*
Total:			489.920	167.120	100.00	0.000	

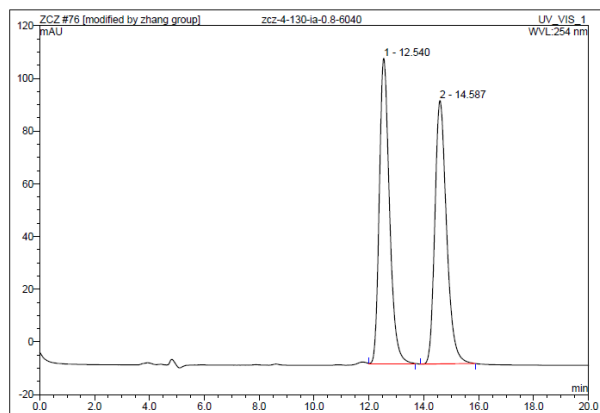
((3*S*,11*bS*)-10-methyl-1-((4-nitrophenyl)sulfonyl)-3-vinyl-2,3,6,7-tetrahydro-1*H*-[1,2,4]triazino[3,2-*a*]isoquinolin-4(11*bH*)-yl)(phenyl)methanone: (*S,S*)-3ck



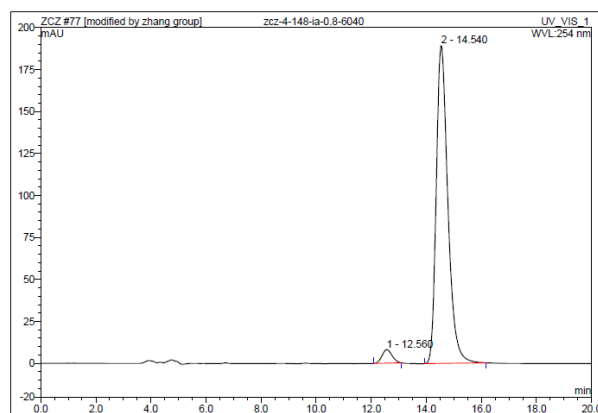
White solid. m.p. 150.7-151.9 °C. 70% yield.

¹H NMR (400 MHz, CDCl₃): δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.42-7.38 (m, 1H), 7.34-7.30 (m, 2H), 7.22 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.03-5.94 (m, 1H), 5.90 (s, 1H), 5.36 (d, *J* = 17.2 Hz, 1H), 5.29 (d, *J* = 10.4 Hz, 1H), 4.94-4.93 (m, 1H), 4.11 (dd, *J* = 14.8 and 6.0 Hz, 1H), 3.72 (dd, *J* = 14.4 and 8.8 Hz, 1H), 3.59-3.53 (m, 1H), 3.07-3.05 (m, 1H), 2.70-2.54 (m, 2H), 2.24 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 170.0, 150.1, 146.4, 135.9, 135.2, 133.9, 132.2, 130.6, 130.5, 129.7, 128.6, 128.1, 128.0, 127.8, 124.5, 118.6, 73.2, 52.8, 50.2, 44.4, 29.5, 21.2. HRMS (ESI) calcd for C₂₇H₂₆N₄NaO₅S [(M+Na⁺)]: 541.1516, found: 541.1524. [α]²²_D = +84.1 (*c* 1.0, CHCl₃). 93% *ee*. HPLC

analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 12.56 min (minor), 14.54 min (major).

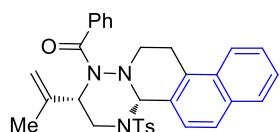


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.54	n.a.	115.766	49.675	50.13	n.a.	MBB*
2	14.59	n.a.	99.911	49.417	49.87	n.a.	MBB*
Total:			215.677	99.092	100.00	0.000	



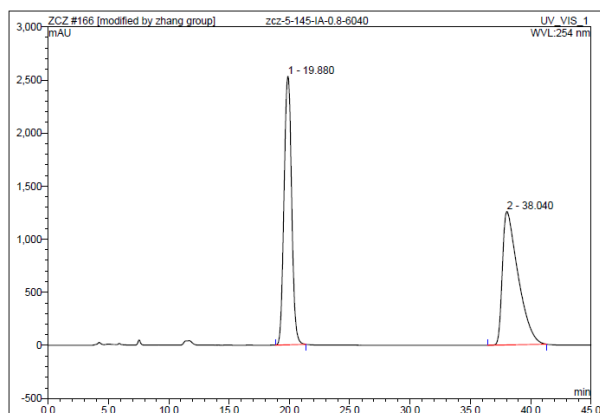
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.56	n.a.	8.054	3.379	3.53	n.a.	MBB*
2	14.54	n.a.	189.187	92.275	96.47	n.a.	MBB*
Total:			197.241	95.654	100.00	0.000	

phenyl((2*S*,4*aS*)-2-(prop-1-en-2-yl)-4-tosyl-2,3,4,4*a*,11,12-hexahydro-1*H*-benzo[*f*][1,2,4]triazino[3,2-*a*]isoquinolin-1-yl)methanone: (*S,S*)-3a

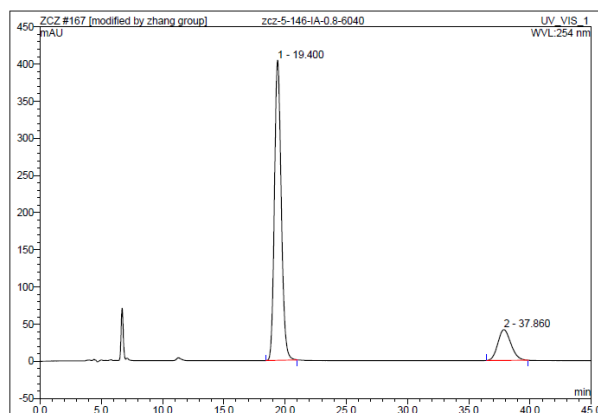


Yellow solid. m.p. 187.6-188.8 °C. 93% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, *J* = 8.8 Hz, 1H), 7.83-7.79 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.56-7.54 (m, 2H), 7.49-7.47 (m, 2H), 7.35-7.29 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.00 (s, 1H), 4.96 (s, 2H), 4.93-4.90 (m, 1H), 4.13 (dd, *J* = 15.2 and 6.8 Hz, 1H), 3.59-3.53 (m, 2H), 3.39-3.36 (m, 1H), 3.22-3.18 (m, 1H), 2.83-2.75 (m, 1H), 2.36 (s, 3H), 1.81 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 171.4, 144.4, 142.6, 136.9, 135.4, 132.9, 131.4, 130.6, 130.1, 129.9, 129.7, 128.5, 127.7, 127.6, 127.4, 126.9, 126.6, 126.5, 126.4, 123.2, 111.4, 72.4, 55.1, 49.2, 42.2, 25.7, 21.6, 20.4. HRMS (ESI) calcd for C₃₂H₃₁N₃NaO₃S [(M+Na)⁺]: 560.1978, found: 560.1983. [α]_D²¹ = +45.1 (*c* 1.0, CHCl₃). 67% *ee*. HPLC analysis of the product: Daicel Chiralpak IA column; hexane/2-propanol = 60/40, 0.8 mL/min. Retention times: 19.40 min (major), 37.86 min (minor).



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.88	n.a.	2529.936	1838.158	49.26	n.a.	MBB*
2	38.04	n.a.	1256.412	1893.204	50.74	n.a.	MBB*
Total:			3786.348	3731.362	100.00	0.000	

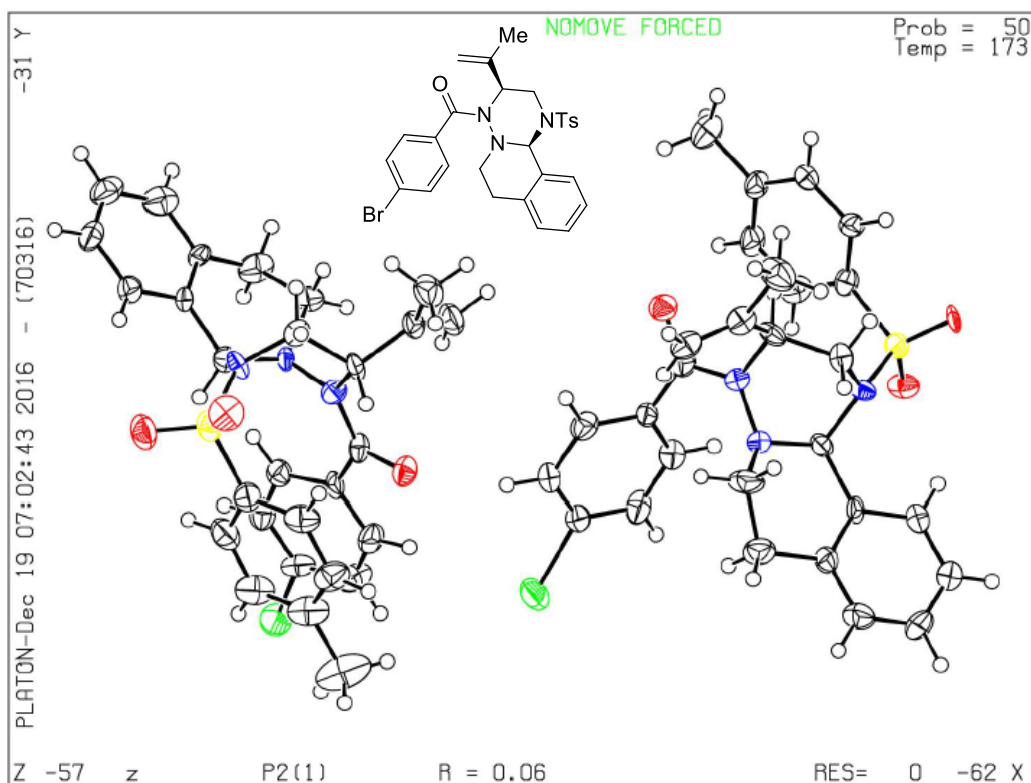


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.40	n.a.	403.974	260.008	83.58	n.a.	MBB*
2	37.86	n.a.	41.349	51.071	16.42	n.a.	MBB*
Total:			445.323	311.079	100.00	0.000	

4. References:

- [1] Wender, P. A.; Williams, T. J. *Angew. Chem. Int. Ed.* **2002**, *41*, 4550.
- [2] Wender, P. A.; Lesser, A. B.; Sirois, L. E. *Angew. Chem. Int. Ed.* **2012**, *51*, 2736.
- [3] Lee, S. I.; Park, S. Y.; Park, J. H.; Jung, I. G.; Choi, S. Y.; Chung, Y. K.; Lee, B. Y. *J. Org. Chem.* **2006**, *71*, 91.
- [4] a) Feng, J.-J.; Lin, T.-Y.; Zhu, C.-Z.; Wang, H.; Wu, H.-H.; Zhang, J. *J. Am. Chem. Soc.* **2016**, *138*, 2178. b) Zuo, G.; Zhang, K.; Louie, J. *Tetrahedron Lett.* **2008**, *49*, 6797. c) Brichacek, M.; Lee, D.; Njardarson, J. T. *Org. Lett.* **2008**, *10*, 5023. d) Lam, S. K.; Lam, S.; Wong, W.-T.; Chiu, P. *Chem. Comm.* **2014**, *50*, 1738.
- [5] a) Hashimoto, T.; Maeda, Y.; Omote, M.; Nakatsu, H.; Maruoka, K. *J. Am. Chem. Soc.* **2010**, *132*, 4076. b) Zhang, L.; Liu, H.; Qiao, G.; Hou, Z.; Liu, Y.; Xiao, Y.; Guo, H. *J. Am. Chem. Soc.* **2015**, *137*, 4316.

5. Crystal Structure of (S,S)-3ad.



Datablock: z

Bond precision:	C-C = 0.0129 Å	Wavelength=0.71073
Cell:	a=9.2518 (12) b=18.883 (3) c=15.178 (2)	alpha=90 beta=94.143 (5) gamma=90
Temperature:	173 K	
Volume	Calculated 2644.7 (6)	Reported 2644.7 (6)
Space group	P 21	P2 (1)
Hall group	P 2yb	?
Moiety formula	C28 H28 Br N3 O3 S	?
Sum formula	C28 H28 Br N3 O3 S	C28 H28 Br N3 O3 S
Mr	566.49	566.50
Dx, g cm ⁻³	1.423	1.423
Z	4	4
Mu (mm ⁻¹)	1.668	1.668
F000	1168.0	1168.0
F000'	1167.76	
h, k, lmax	11, 22, 18	11, 22, 18
Nref	9309 [4809]	9164
Tmin, Tmax	0.612, 0.792	0.609, 0.800
Tmin'	0.571	
Correction method=	# Reported T Limits: Tmin=0.609 Tmax=0.800	
AbsCorr =	MULTI-SCAN	
Data completeness=	1.91/0.98	Theta(max)= 25.010
R(reflections)=	0.0635 (5787)	wR2(reflections)= 0.1724 (9164)
S =	1.012	Npar= 649

6. ¹H and ¹³C NMR Spectra for New Compounds

