

Supporting Information

Copper(I)-Catalyzed Asymmetric [3 + 3] Annulation Involving Aziridines to Construct Tetrahydro- β -carbolines

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† These authors contributed equally to this work.

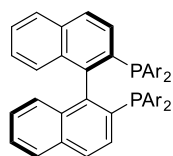
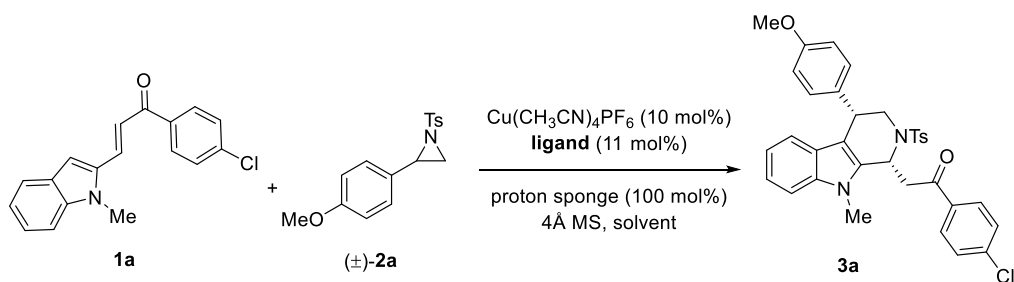
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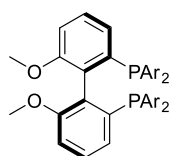
1. General information

¹H NMR spectrum were recorded on a Bruker DPX 400 MHz spectrometer in CDCl₃. Chemical shifts were reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The spectra are interpreted as: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, coupling constant (s) J are reported in Hz and relative integrations are reported. ¹³C NMR (100 MHz) spectrum were recorded on a Bruker DPX 400 MHz spectrometer in CDCl₃. Chemical shifts were reported in ppm with the internal chloroform signal at 77.06 ppm as a standard. Optical rotations were measured on an AUTOPOL V. Diastereomeric ratios were determined by analysis of ¹H NMR spectroscopy. Enantiomeric excesses were determined by analysis of HPLC traces, obtained by using Chiralpak IA columns with hexane and isopropanol or ethyl acetate as solvents. (Chiralpak IA columns were purchased from Daicel Chemical Industries, LTD.) Melting points were obtained in open capillary tubes using SGW X-4 micro melting point apparatus which were uncorrected. High-resolution mass spectra (HRMS) were recorded on a Waters GCT Premier mass spectrometer using EI-TOF (electron ionization-time of flight). Commercially available materials purchased from Adamas-beta, TCI or Energy Chemical and were used as received. Substituted 2-vinylindoles¹ and aziridines² were prepared according to the literature procedures.

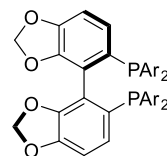
2. Optimization study



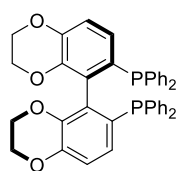
L1: Ar = C₆H₅
L2: Ar = 3,5-Me₂C₆H₃



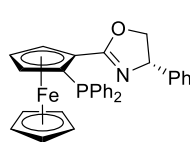
L3: Ar = C₆H₅
L4: Ar = 3,5-(tBu)₂-4-OMeC₆H₂



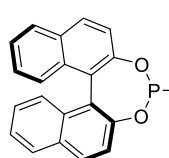
L5: Ar = C₆H₅
L6: Ar = 3,5-(tBu)₂-4-OMeC₆H₂



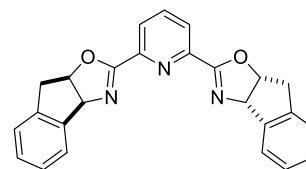
L7



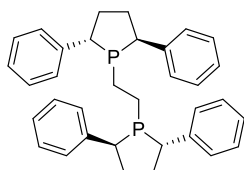
L8



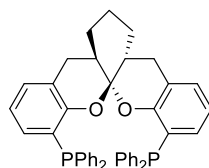
L9



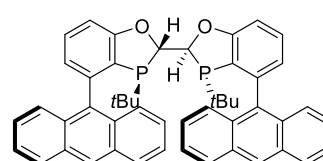
L10



L11



L12



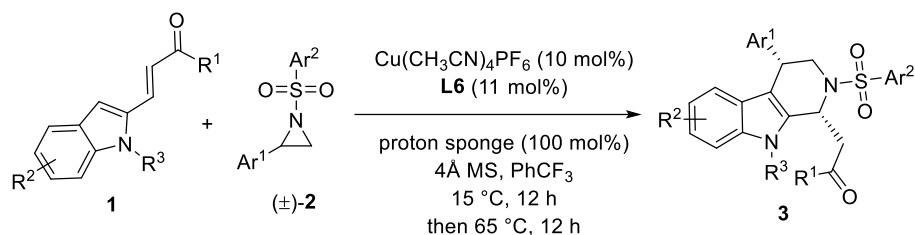
L13

entry	ligand	solvent	yield (%) ^[b]	dr ^[c]	ee (%) ^[d]
1	L1	toluene	60	3.4:1	68
2	L2	toluene	62	11.1:1	73
3	L3	toluene	38	5.6:1	55
4	L4	toluene	84	>20:1	68
5	L5	toluene	47	5:1	45
6	L6	toluene	80	>20:1	84
7	L7	toluene	57	13:1	25
8	L8	toluene	27	>20:1	-10
9	L9	toluene	34	6:1	-10
10	L10	toluene	12	20:1	-10
11	L11	toluene	38	11.7:1	64
12	L12	toluene	19	10:1	11

13	L13	toluene	17	9:1	-33
14 ^[e]	L6	toluene	68	>20:1	91
15 ^[f]	L6	toluene	93	>20:1	90
16 ^[g]	L6	toluene	57	>20:1	94
17 ^[h]	L6	toluene	75	>20:1	93
18 ^[i]	L6	toluene	N.P.	/	/
19	L6	DCE	67	12.5:1	92
20	L6	MeCN	N.P.	/	/
21	L6	Mesitylene	72	>20:1	82
22	L6	CHCl ₃	66	>20:1	88
23	L6	CH ₂ Cl ₂	63	13:1	89
24	L6	THF	N.P.	/	/
25	L6	xylene	74	>20:1	82
26	L6	PhCF ₃	95	12:1	92
27 ^[g]	L6	PhCF ₃	62	>20:1	95
28 ^[h]	L6	PhCF ₃	95	>20:1	94
29 ^[i]	L6	PhCF ₃	N.P.	/	/

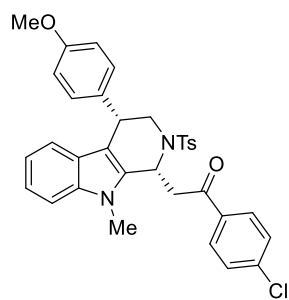
[a] Unless others stated, reactions were performed with **1a** (0.10 mmol), **2a** (0.20 mmol) in 1.0 mL of solvent with activated powdered 4Å molecular sieves (100 mg) added at 65 °C for 24 h. [b] Isolated yield. [c] Determined by ¹H NMR analysis. [d] Determined by chiral HPLC analysis. [e] Reaction was conducted at 25 °C for 24 h. [f] Reaction was conducted at 25 °C for 12 h, then at 65 °C for 12 h. [g] Reaction was conducted at 15 °C for 24 h. [h] Reaction was conducted at 15 °C for 12 h, then at 65 °C for 12 h. [i] Reaction was conducted at 0 °C for 24 h. N.P. = no product.

3. Preparation and characterization data of chiral tetrahydro- β -carbolines



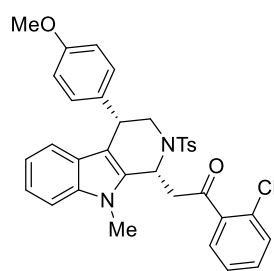
Under a nitrogen atmosphere, $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (0.01 mmol), ligand **L6** (0.011 mmol) and activated powdered 4Å molecular sieves (100 mg) were dissolved in 1.0 mL of dry PhCF_3 and stirred at room temperature for about 30 min. Then, substituted 2-vinylindoles **1** (0.1 mmol), aziridines **2** (0.2 mmol), and proton sponge (21.4 mg, 0.1 mmol) were added to the resulting mixture, and the mixture was stirred at 15 °C for 12 h, then stirred at 65 °C for 12 h. The solvent was evaporated and the residue was purified by column chromatography on silica gel to afford products **3**.

1-(4-Chlorophenyl)-2-((1*R*,4*S*)-4-(4-methoxyphenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)ethan-1-one (**3a**)



56.9 mg, 95% yield, light yellow solid, m.p. 164–166 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.6$ Hz, 2H), 7.58 (d, $J = 8.3$ Hz, 2H), 7.41 (d, $J = 8.6$ Hz, 2H), 7.25 (m, 1H), 7.17 – 7.11 (m, 3H), 7.02 (d, $J = 8.1$ Hz, 2H), 6.89 – 6.82 (m, 3H), 6.66 (d, $J = 7.9$ Hz, 1H), 6.00 (dd, $J = 7.6, 2.9$ Hz, 1H), 4.24 – 4.14 (m, 2H), 3.81 (s, 3H), 3.72 (s, 3H), 3.71 – 3.66 (m, 1H), 3.21 – 3.07 (m, 2H), 2.23 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 195.1, 158.8, 143.4, 140.1, 137.5, 137.3, 135.1, 135.0, 133.2, 129.7 (2C), 129.4 (2C), 129.3 (2C), 129.0 (2C), 127.0 (2C), 125.8, 121.9, 120.2, 119.3, 114.1 (2C), 110.3, 108.9, 55.3, 48.4, 48.3, 43.9, 39.0, 30.0, 21.4; **HRMS** (EI, m/z): calcd for $\text{C}_{34}\text{H}_{31}\text{ClN}_2\text{O}_4\text{S} [\text{M}]^+$: 598.1688, found: 598.1697; $[\alpha]_D^{25} = +17.2$ (c 1.00, CH_2Cl_2); 94% ee, >20:1 dr; **HPLC** (Chiralpak IA, hexane/isopropanol = 70/30, 1.0 mL/min, 254 nm) $t_R = 11.30$ min (major), 18.52 min (minor).

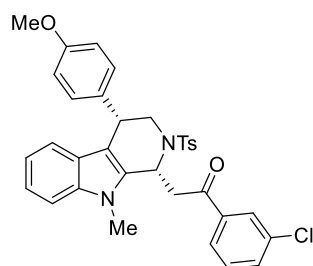
1-(2-Chlorophenyl)-2-((1*R*,4*S*)-4-(4-methoxyphenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)ethan-1-one (**3b**)



34.2 mg, 57% yield, light yellow solid, m.p. 133–135 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.71 – 7.64 (m, 2H), 7.47 – 7.43 (m, 1H), 7.42 – 7.37 (m, 2H), 7.34 – 7.30 (m, 1H), 7.27 – 7.24 (m, 1H), 7.15 – 7.06 (m, 5H), 6.86 – 6.79 (m, 3H), 6.62 (d, $J = 7.9$ Hz, 1H), 5.96 (dd, $J = 8.3, 3.1$ Hz, 1H), 4.15 (dd, $J = 14.3, 6.1$ Hz, 1H), 4.05 (dd, $J = 10.7, 6.1$ Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.73 – 3.67 (m, 1H), 3.34 (dd, $J = 17.0, 3.2$ Hz, 1H), 3.13 (dd, $J = 14.3, 10.8$ Hz, 1H), 2.26 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 199.1, 158.7, 143.5, 138.9, 137.4, 137.2, 134.9, 133.2, 132.3, 130.8, 130.4, 129.8, 129.5 (2C), 129.3 (2C), 127.2(4), 127.1(6) (2C), 125.8, 121.8, 120.1, 119.2,

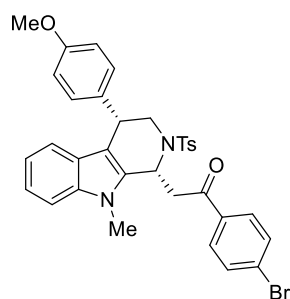
114.1 (2C), 110.2, 108.9, 55.3, 48.5, 48.2, 48.1, 38.6, 30.0, 21.4; **HRMS** (EI, m/z): calcd for C₃₄H₃₁ClN₂O₄S [M]⁺: 598.1688, found: 598.1696; [α]_D²⁵ = +19.8 (c 1.00, CH₂Cl₂); 91% ee, >20:1 dr; **HPLC** (Chiralpak IA, hexane/ethyl acetate = 70/30, 1.0 mL/min, 254 nm) t_R = 8.23 min (major), 11.00 min (minor).

1-(3-Chlorophenyl)-2-((1*R*,4*S*)-4-(4-methoxyphenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)ethan-1-one (3c)



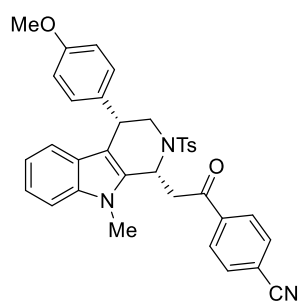
55.7 mg, 93% yield, light yellow oil; **¹H NMR** (400 MHz, CDCl₃) δ 7.77 (t, *J* = 1.9 Hz, 1H), 7.71 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.53 (ddd, *J* = 8.0, 2.2, 1.0 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.18 – 7.10 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.91 – 6.83 (m, 3H), 6.67 (d, *J* = 7.9 Hz, 1H), 6.01 (dd, *J* = 7.7, 3.1 Hz, 1H), 4.26 – 4.18 (m, 2H), 3.81 (s, 3H), 3.72 (s, 3H), 3.69 – 3.62 (m, 1H), 3.22 – 3.07 (m, 2H), 2.23 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 195.0, 158.7, 143.4, 138.1, 137.5, 137.3, 135.1, 135.0, 133.5, 133.1, 130.0, 129.5 (2C), 129.3 (2C), 128.4, 127.0 (2C), 126.4, 125.8, 121.9, 120.2, 119.3, 114.1 (2C), 110.4, 108.9, 55.3, 48.4, 48.1, 44.0, 39.2, 30.0, 21.4; **HRMS** (EI, m/z): calcd for C₃₄H₃₁ClN₂O₄S [M]⁺: 598.1688, found: 598.1688; [α]_D²⁵ = +21.2 (c 1.00, CH₂Cl₂); 94% ee, 10:1 dr; **HPLC** (Chiralpak IA, hexane/ethyl acetate = 70/30, 1.0 mL/min, 254 nm) t_R = 8.22 min (major), 12.43 min (minor).

1-(4-Bromophenyl)-2-((1*R*,4*S*)-4-(4-methoxyphenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)ethan-1-one (3d)



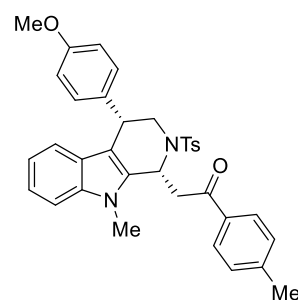
50.2 mg, 78% yield, light yellow solid, m.p. 140–142 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.75 – 7.67 (m, 2H), 7.61 – 7.54 (m, 3H), 7.27 (s, 1H), 7.28 – 7.24 (s, 1H), 7.17 – 7.10 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.90 – 6.78 (m, 3H), 6.66 (d, *J* = 7.9 Hz, 1H), 6.00 (dd, *J* = 7.7, 3.1 Hz, 1H), 4.26 – 4.13 (m, 2H), 3.81 (s, 3H), 3.72 (s, 3H), 3.72 – 3.61 (m, 1H), 3.22 – 3.05 (m, 2H), 2.23 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 195.3, 158.7, 143.4, 137.5, 137.3, 135.3, 135.1, 133.1, 132.0 (2C), 129.8 (2C), 129.4 (2C), 129.3 (2C), 128.9, 127.0 (2C), 125.8, 121.8, 120.2, 119.3, 114.1 (2C), 110.3, 108.9, 55.3, 48.4, 48.3, 43.8, 39.0, 30.0, 21.4; **HRMS** (EI, m/z): calcd for C₃₄H₃₁⁷⁹BrN₂O₄S [M]⁺: 642.1182, found: 642.1184; calcd for C₃₄H₃₁⁸¹BrN₂O₄S [M]⁺: 644.1162, found: 644.1168; [α]_D²⁵ = +24.2 (c 1.00, CH₂Cl₂); 94% ee, 6:1 dr; **HPLC** (Chiralpak IA, hexane/ethyl acetate = 70/30, 1.0 mL/min, 254 nm) t_R = 9.45 min (major), 15.25 min (minor).

4-((1*R*,4*S*)-4-(4-Methoxyphenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)acetyl)benzonitrile (3e)



24.8 mg, 42% yield, light yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.3$ Hz, 2H), 7.79 – 7.72 (m, 2H), 7.59 (d, $J = 8.3$ Hz, 2H), 7.28 – 7.24 (m, 1H), 7.17 – 7.09 (m, 3H), 7.05 (d, $J = 8.2$ Hz, 2H), 6.85 (dd, $J = 8.1, 5.8$ Hz, 3H), 6.65 (d, $J = 7.7$ Hz, 1H), 5.96 (dd, $J = 8.0, 2.9$ Hz, 1H), 4.20 (dd, $J = 14.2, 6.0$ Hz, 1H), 4.08 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.81 (s, 3H), 3.79 – 3.75 (m, 1H), 3.73 (s, 3H), 3.22 – 3.13 (m, 2H), 2.24 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 195.3, 158.8, 143.6, 139.6, 137.5, 137.1, 134.6, 132.9, 132.6 (2C), 129.5 (2C), 129.3 (2C), 128.7 (2C), 127.0 (2C), 125.7, 122.0, 120.2, 119.4, 117.8, 116.7, 114.1 (2C), 110.4, 108.9, 55.3, 48.4, 48.3, 44.2, 38.8, 30.0, 21.4; **HRMS** (EI, m/z): calcd for $\text{C}_{35}\text{H}_{31}\text{N}_3\text{O}_4\text{S} [\text{M}]^+$: 589.2030, found: 589.2036; $[\alpha]_{\text{D}}^{25} = +53.5$ (c 1.00, CH_2Cl_2); 95% ee, 12.5:1 dr; **HPLC** (Chiralpak IA, hexane/ isopropanol = 70/30, 1.0 mL/min, 254 nm) $t_{\text{R}} = 18.09$ min (major), 31.84 min (minor).

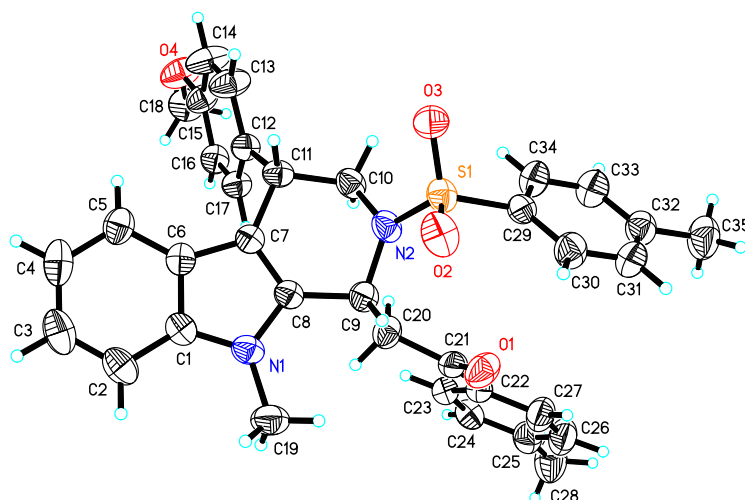
2-((1*R*,4*S*)-4-(4-Methoxyphenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)-1-(*p*-tolyl)ethan-1-one (3f)



49.2 mg, 85% yield, light yellow solid, m.p. 167–169 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 (d, $J = 8.2$ Hz, 2H), 7.59 (d, $J = 8.3$ Hz, 2H), 7.27 – 7.21 (m, 3H), 7.18 – 7.10 (m, 3H), 7.00 (d, $J = 8.0$ Hz, 2H), 6.88 – 6.81 (m, 3H), 6.66 (d, $J = 7.9$ Hz, 1H), 6.04 (dd, $J = 7.6, 3.3$ Hz, 1H), 4.25 – 4.17 (m, 2H), 3.81 (s, 3H), 3.71 (s, 3H), 3.70 – 3.65 (m, 1H), 3.22 – 3.09 (m, 2H), 2.41 (s, 3H), 2.20 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 195.6, 158.7, 144.5, 143.2, 137.4, 137.3, 135.5, 134.1, 133.3, 129.4 (2C), 129.4 (2C), 129.3 (2C), 128.5 (2C), 127.1 (2C), 125.8, 121.7, 120.1, 119.2, 114.1 (2C), 110.1, 108.9, 55.3, 48.4, 48.1, 43.8, 39.1, 30.0, 21.7, 21.4; **HRMS** (EI, m/z): calcd for $\text{C}_{35}\text{H}_{34}\text{N}_2\text{O}_4\text{S} [\text{M}]^+$: 578.2234, found: 578.2238; $[\alpha]_{\text{D}}^{25} = +31.9$ (c 1.00, CH_2Cl_2); 93% ee, 14:1 dr; **HPLC** (Chiralpak IA, hexane/ethyl acetate = 70/30, 1.0 mL/min, 254 nm) $t_{\text{R}} = 9.93$ min (major), 13.94 min (minor).

The X-ray data for compound 3f

Compound **3f** with 96% ee was obtained by recrystallization from ethyl acetate and petroleum ether, which was suspended in hexane in a screw-top vial. Drops of DCE were added with shaking until all the compound has dissolved. The lid was then loosely screwed on the vial, and a single crystal was obtained by natural volatilization at room temperature. The data set was collected by a Bruker APEX-II CCD at 293(2) K equipped with micro-focus Mo radiation source ($K\alpha = 0.71073$ Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL program package. Details of the X-ray experiments and crystal data are summarized below. CCDC 2007786 contains the supplementary crystallographic data, and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

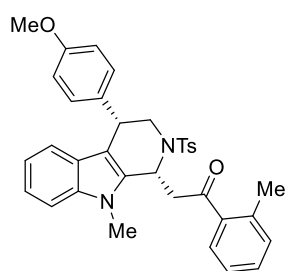


ellipsoid contour at 30% probability level

Identification code	mo_d8v20175_0m	
Empirical formula	C ₃₅ H ₃₄ N ₂ O ₄ S	
Formula weight	578.70	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 8.9637(3) Å	α = 90°.
	b = 14.9790(6) Å	β = 100.0870(10)°.
	c = 11.5706(5) Å	γ = 90°.
Volume	1529.54(10) Å ³	
Z	2	
Density (calculated)	1.257 Mg/m ³	
Absorption coefficient	0.147 mm ⁻¹	
F(000)	612	
Crystal size	0.200 x 0.160 x 0.130 mm ³	
Theta range for data collection	2.246 to 25.999°.	
Index ranges	-11 ≤ h ≤ 11, -18 ≤ k ≤ 18, -13 ≤ l ≤ 14	
Reflections collected	15690	
Independent reflections	5948 [R(int) = 0.0276]	
Completeness to theta = 25.242°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6430	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5948 / 1 / 384	

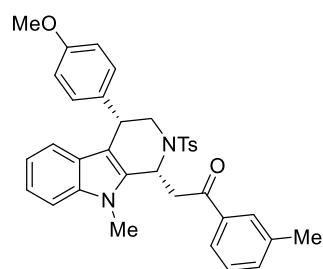
Goodness-of-fit on F^2	1.028
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0400$, $wR2 = 0.0980$
R indices (all data)	$R1 = 0.0517$, $wR2 = 0.1087$
Absolute structure parameter	-0.03(2)
Extinction coefficient	0.054(12)
Largest diff. peak and hole	0.139 and -0.158 e.Å ⁻³

2-((1*R*,4*S*)-4-(4-Methoxyphenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)-1-(*o*-tolyl)ethan-1-one (3g)



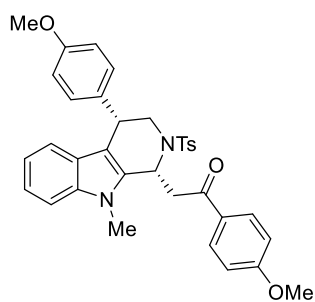
49.8 mg, 86% yield, light yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.63 (d, $J = 8.3$ Hz, 2H), 7.51 (d, $J = 7.7$ Hz, 1H), 7.38 (td, $J = 7.5$, 1.4 Hz, 1H), 7.28 – 7.24 (s, 1H), 7.25 – 7.18 (m, 2H), 7.16 – 7.08 (m, 3H), 7.04 (d, $J = 8.1$ Hz, 2H), 6.89 – 6.81 (m, 3H), 6.64 (d, $J = 8.0$ Hz, 1H), 6.02 (dd, $J = 8.0$, 3.0 Hz, 1H), 4.21 (dd, $J = 14.1$, 6.1 Hz, 1H), 4.13 (dd, $J = 10.7$, 6.1 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 3.66 (dd, $J = 16.7$, 7.9 Hz, 1H), 3.22 – 3.09 (m, 2H), 2.53 (s, 3H), 2.22 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 199.3, 158.7, 143.4, 139.2, 137.4, 137.3, 137.0, 135.4, 133.3, 132.2, 131.9, 129.4 (2C), 129.3 (2C), 128.8, 127.1 (2C), 125.8(2), 125.7(6), 121.7, 120.1, 119.2, 114.1 (2C), 110.1, 108.9, 55.3, 48.3(2), 48.3(0), 46.7, 38.8, 30.0, 21.5, 21.4; **HRMS** (EI, m/z): calcd for $\text{C}_{35}\text{H}_{34}\text{N}_2\text{O}_4\text{S}$ [M]⁺: 578.2234, found: 578.2233; $[\alpha]_{\text{D}}^{25} = +19.0$ (c 1.00, CH_2Cl_2); 92% ee, 20:1 dr; **HPLC** (Chiralpak IA, hexane/ethyl acetate = 70/30, 1.0 mL/min, 254 nm) $t_{\text{R}} = 7.47$ min (major), 10.87 min (minor).

2-((1*R*,4*S*)-4-(4-Methoxyphenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)-1-(*m*-tolyl)ethan-1-one (3h)



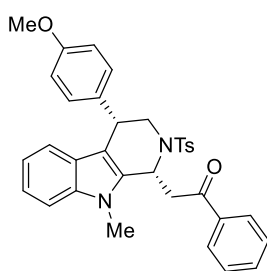
56.7 mg, 98% yield, light yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 – 7.58 (m, 4H), 7.38 (d, $J = 7.6$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.27 – 7.23 (s, 1H), 7.18 – 7.10 (m, 3H), 7.02 (d, $J = 8.0$ Hz, 2H), 6.88 – 6.82 (m, 3H), 6.66 (d, $J = 7.8$ Hz, 1H), 6.05 (dd, $J = 7.5$, 3.3 Hz, 1H), 4.25 – 4.18 (m, 2H), 3.81 (s, 3H), 3.71 (s, 3H), 3.69 – 3.62 (m, 1H), 3.23 – 3.10 (m, 2H), 2.38 (s, 3H), 2.21 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 196.2, 158.7, 143.2, 138.5, 137.4, 137.3, 136.6, 135.5, 134.3, 133.3, 129.3(9) (2C), 129.3(5) (2C), 128.8, 128.6, 127.1 (2C), 125.8, 125.5, 121.7, 120.2, 119.2, 114.1 (2C), 110.1, 108.9, 55.3, 48.4, 48.0, 44.0, 39.1, 30.0, 21.3(9), 21.3(7); **HRMS** (EI, m/z): calcd for $\text{C}_{35}\text{H}_{34}\text{N}_2\text{O}_4\text{S}$ [M]⁺: 578.2234, found: 578.2242; $[\alpha]_{\text{D}}^{25} = +21.9$ (c 1.00, CH_2Cl_2); 91% ee, 14:1 dr; **HPLC** (Chiralpak IA, hexane/ethyl acetate = 70/30, 1.0 mL/min, 254 nm) $t_{\text{R}} = 8.47$ min (major), 11.54 min (minor).

1-(4-Methoxyphenyl)-2-((1*R*,4*S*)-4-(4-methoxyphenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)ethan-1-one (3i)



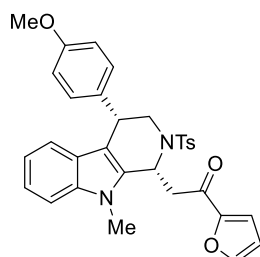
53.5 mg, 90% yield, light yellow solid, m.p. 172–174 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.9 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.22 (m, 1H), 7.17 – 7.10 (m, 3H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.92 – 6.82 (m, 5H), 6.66 (d, *J* = 7.9 Hz, 1H), 6.06 – 6.01 (m, 1H), 4.25 – 4.16 (m, 2H), 3.86 (s, 3H), 3.81 (s, 3H), 3.72 (s, 3H), 3.70 – 3.63 (m, 1H), 3.24 – 3.04 (m, 2H), 2.21 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 194.5, 163.9, 158.7, 143.2, 137.4, 137.3, 135.5, 133.3, 130.7 (2C), 129.7, 129.3(5) (2C), 129.3(3) (2C), 127.0 (2C), 125.8, 121.7, 120.1, 119.2, 114.1 (2C), 113.8 (2C), 110.1, 108.9, 55.5, 55.3, 48.4, 48.3, 43.5, 39.1, 30.0, 21.4; HRMS (EI, m/z): calcd for C₃₅H₃₄N₂O₅S [M]⁺: 594.2183, found: 594.2190; [α]_D²⁵ = +51.1 (*c* 1.00, CH₂Cl₂); 94% ee, 11:1 dr; HPLC (Chiralpak IA, hexane/ethyl acetate = 70/30, 1.0 mL/min, 254 nm) t_R = 12.75 min (major), 17.90 min (minor).

2-((1*R*,4*S*)-4-(4-Methoxyphenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)-1-phenylethan-1-one (3j)



50.3 mg, 89% yield, light yellow solid, m.p. 124–126 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 7.2 Hz, 2H), 7.63 – 7.53 (m, 3H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.23 (m, 1H), 7.18 – 7.10 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 3H), 6.66 (d, *J* = 7.9 Hz, 1H), 6.05 (dd, *J* = 7.6, 3.2 Hz, 1H), 4.25 – 4.17 (m, 2H), 3.81 (s, 3H), 3.76 – 3.68 (m, 4H), 3.22 – 3.08 (m, 2H), 2.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 196.0, 158.7, 143.3, 137.5, 137.3, 136.6, 135.4, 133.6, 133.3, 129.4 (2C), 129.3 (2C), 128.7 (2C), 128.3 (2C), 127.1 (2C), 125.8, 121.8, 120.2, 119.2, 114.1 (2C), 110.2, 108.9, 55.3, 48.4, 48.1, 43.9, 39.1, 30.0, 21.4; HRMS (EI, m/z): calcd for C₃₄H₃₂N₂O₄S [M]⁺: 564.2077, found: 564.2078; [α]_D²⁵ = +17.1 (*c* 1.00, CH₂Cl₂); 93% ee, 12.5:1 dr; HPLC (Chiralpak IA, hexane/ethyl acetate = 70/30, 1.0 mL/min, 254 nm) t_R = 9.26 min (major), 13.62 min (minor).

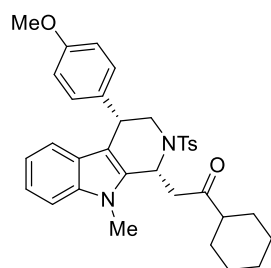
1-(Furan-2-yl)-2-((1*R*,4*S*)-4-(4-methoxyphenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)ethan-1-one (3k)



48.3 mg, 87% yield, light yellow solid, m.p. 125–127 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.55 (m, 3H), 7.28 – 7.25 (m, 1H), 7.19 – 7.10 (m, 4H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.87 – 6.82 (m, 3H), 6.65 (d, *J* = 7.9 Hz, 1H), 6.53 (dd, *J* = 3.6, 1.7 Hz, 1H), 5.94 (dd, *J* = 8.9, 3.3 Hz, 1H), 4.20 – 4.12 (m, 2H), 3.81 (s, 3H), 3.77 (s, 3H), 3.55 (dd, *J* = 15.4, 8.8 Hz, 1H), 3.24 (dd, *J* = 16.1, 12.7 Hz, 1H), 3.09 (dd, *J* = 15.4, 3.3 Hz, 1H), 2.26 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 185.1, 158.7, 152.7, 146.7, 143.3, 137.4, 137.2, 135.0, 133.3, 129.4 (2C), 129.3 (2C), 127.1 (2C), 125.8, 121.8, 120.2, 119.2, 117.8, 114.1 (2C), 112.7, 110.3, 108.9, 55.3, 48.3, 48.0, 44.0, 38.9, 30.0, 21.4; HRMS (EI, m/z): calcd for C₃₂H₃₀N₂O₅S [M]⁺: 554.1870, found: 554.1878; [α]_D²⁵ = +28.6 (*c* 1.00, CH₂Cl₂); 91% ee, 14:1 dr; HPLC (Chiralpak IA, hexane/ isopropanol = 70/30, 1.0

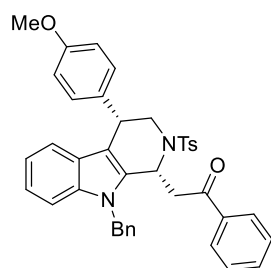
mL/min, 254 nm) t_R = 12.82 min (major), 18.14 min (minor).

1-Cyclohexyl-2-((1*R*,4*S*)-4-(4-methoxyphenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)ethan-1-one (3l)



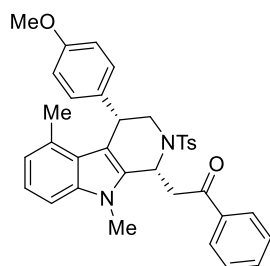
52.5 mg, 92% yield, light yellow solid, m.p. 147–149 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 (d, J = 8.3 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.17 – 7.07 (m, 5H), 6.85 – 6.80 (m, 3H), 6.62 (d, J = 7.9 Hz, 1H), 5.82 (dd, J = 7.9, 3.0 Hz, 1H), 4.23 – 4.17 (m, 1H), 4.09 (dd, J = 10.8, 6.1 Hz, 1H), 3.80 (s, 3H), 3.66 (s, 3H), 3.14 (m, 2H), 2.70 (dd, J = 16.8, 3.1 Hz, 1H), 2.34 – 2.24 (m, 4H), 1.84 – 1.71 (m, 4H), 1.67 – 1.61 (m, 1H), 1.32 – 1.15 (m, 5H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 209.4, 158.7, 143.4, 137.4, 137.4, 135.4, 133.3, 129.4 (2C), 129.3 (2C), 127.1 (2C), 125.8, 121.7, 120.1, 119.2, 114.0 (2C), 109.9, 108.8, 55.3, 51.3, 48.2, 47.7, 46.1, 38.8, 29.8, 28.1, 27.8, 25.8, 25.6, 25.5, 21.4; **HRMS** (EI, m/z): calcd for $\text{C}_{34}\text{H}_{38}\text{N}_2\text{O}_4\text{S}$ $[\text{M}]^+$: 570.2547, found: 570.2551; $[\alpha]_{\text{D}}^{25}$ = +21.1 (c 1.00, CH_2Cl_2); 92% ee, 17:1 dr; **HPLC** (Chiralpak IA, hexane/ethyl acetate = 70/30, 1.0 mL/min, 254 nm) t_R = 6.97 min (major), 10.83 min (minor).

2-((1*R*,4*S*)-9-Benzyl-4-(4-methoxyphenyl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)-1-phenylethan-1-one (3m)



38.4 mg, 60% yield, light yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.68 (d, J = 7.3 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.45 (d, J = 8.3 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.23 – 7.14 (m, 6H), 7.13 – 7.05 (m, 1H), 6.99 (dd, J = 10.7, 7.7 Hz, 4H), 6.88 (dd, J = 8.4, 3.1 Hz, 3H), 6.70 (d, J = 7.9 Hz, 1H), 5.97 (dd, J = 7.8, 2.9 Hz, 1H), 5.40 (d, J = 3.8 Hz, 2H), 4.27 – 4.16 (m, 2H), 3.82 (s, 3H), 3.58 (dd, J = 16.7, 7.7 Hz, 1H), 3.21 (dd, J = 14.0, 10.6 Hz, 1H), 2.96 (dd, J = 16.7, 3.0 Hz, 1H), 2.23 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 196.1, 158.7, 143.2, 137.4, 137.3, 137.2, 136.5, 135.4, 133.3, 133.2, 129.3(9) (2C), 129.3(6) (2C), 128.9 (2C), 128.5 (2C), 128.2 (2C), 127.5 (2C), 127.1 (2C), 126.2, 126.0, 122.1, 120.4, 119.4, 114.1 (2C), 111.1, 109.7, 55.3, 48.3, 48.1, 46.7, 44.1, 39.1, 21.4; **HRMS** (EI, m/z): calcd for $\text{C}_{40}\text{H}_{36}\text{N}_2\text{O}_4\text{S}$ $[\text{M}]^+$: 640.2390, found: 640.2393; $[\alpha]_{\text{D}}^{25}$ = +36.3 (c 1.00, CH_2Cl_2); 89% ee, 6:1 dr; **HPLC** (Chiralpak IA, hexane/ethyl acetate = 70/30, 1.0 mL/min, 254 nm) t_R = 8.84 min (major), 12.53 min (minor).

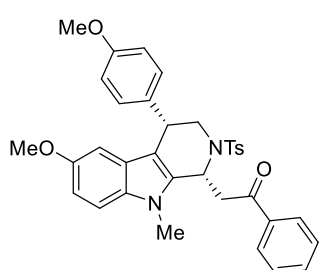
2-((1*R*,4*S*)-4-(4-Methoxyphenyl)-5,9-dimethyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)-1-phenylethan-1-one (3n)



50.9 mg, 88% yield, light yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.87 (d, J = 7.8 Hz, 2H), 7.55 (t, J = 7.7 Hz, 3H), 7.44 (t, J = 7.7 Hz, 2H), 7.10 – 7.01 (m, 4H), 6.93 (d, J = 8.1 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 6.65 (d, J = 6.9 Hz, 1H), 5.95 (dd, J = 7.6, 3.6 Hz, 1H), 4.37 (dd, J = 9.5, 6.8 Hz, 1H), 4.14 (dd, J = 14.5, 6.8 Hz, 1H), 3.79 (s, 4H), 3.70 (s, 3H), 3.27 – 3.14 (m, 2H), 2.12 (s, 3H), 1.82 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 196.1, 158.5, 143.4, 137.7, 136.9, 136.6, 136.4, 135.4, 133.6, 130.9, 129.1 (2C), 128.7 (2C), 128.6 (2C), 128.3 (2C), 127.1 (2C), 125.2, 122.0, 121.2, 114.2 (2C), 109.9, 106.6, 55.3, 49.0, 48.5, 43.9, 39.1, 30.0, 21.3, 20.4; **HRMS** (EI, m/z):

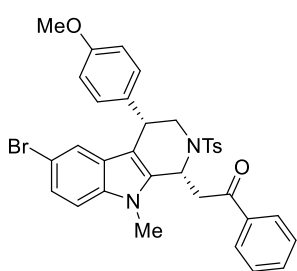
calcd for $C_{35}H_{34}N_2O_4S$ $[M]^+$: 578.2234, found: 578.2237; $[\alpha]_D^{25} = +18.0$ (c 1.00, CH_2Cl_2); 93% ee, >20:1 dr; **HPLC** (Chiralpak IA, hexane/ethyl acetate = 70/30, 1.0 mL/min, 254 nm) $t_R = 8.91$ min (major), 13.28 min (minor).

2-((1*R*,4*S*)-6-Methoxy-4-(4-methoxyphenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)-1-phenylethan-1-one (3o)



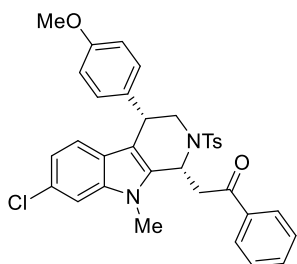
56.5 mg, 95% yield, light yellow oil, m.p. 146–148 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H), 7.63 – 7.53 (m, 3H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.17 – 7.11 (m, 3H), 7.00 (d, $J = 8.0$ Hz, 2H), 6.88 – 6.83 (m, 2H), 6.78 (dd, $J = 8.8, 2.5$ Hz, 1H), 6.11 (d, $J = 2.4$ Hz, 1H), 6.03 (dd, $J = 7.6, 3.3$ Hz, 1H), 4.25 – 4.16 (m, 2H), 3.80 (s, 3H), 3.73 – 3.66 (m, 4H), 3.54 (s, 3H), 3.22 – 3.08 (m, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 158.7, 153.6, 143.2, 137.3, 136.5, 136.0, 133.5, 133.1, 132.8, 129.4 (2C), 129.3 (2C), 128.7 (2C), 128.3 (2C), 127.0 (2C), 126.2, 114.1 (2C), 111.2, 109.7, 109.5, 102.7, 55.7, 55.3, 48.4, 48.1, 43.9, 39.1, 30.1, 21.4.; **HRMS** (EI, m/z): calcd for $C_{35}H_{34}N_2O_5S$ $[M]^+$: 594.2183, found: 594.2186; $[\alpha]_D^{25} = -10.4$ (c 1.00, CH_2Cl_2); 94% ee, 10:1 dr; **HPLC** (Chiralpak IA, hexane/ethyl acetate = 70/30, 1.0 mL/min, 254 nm) $t_R = 11.09$ min (major), 15.22 min (minor).

2-((1*R*,4*S*)-6-Bromo-4-(4-methoxyphenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)-1-phenylethan-1-one (3p)



56.0 mg, 87% yield, light yellow solid, m.p. 167–169 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 2H), 7.61 – 7.53 (m, 3H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.20 (dd, $J = 8.6, 1.9$ Hz, 1H), 7.11 (d, $J = 8.8$ Hz, 3H), 6.99 (d, $J = 8.1$ Hz, 2H), 6.86 (d, $J = 8.6$ Hz, 2H), 6.78 (d, $J = 1.9$ Hz, 1H), 6.04 (dd, $J = 7.5, 3.3$ Hz, 1H), 4.22 – 4.11 (m, 2H), 3.82 (s, 3H), 3.74 – 3.66 (m, 4H), 3.20 – 3.05 (m, 2H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 158.8, 143.4, 137.1, 136.7, 136.4, 136.1, 133.7, 132.7, 129.4 (2C), 129.1 (2C), 128.7 (2C), 128.3 (2C), 127.5, 127.0 (2C), 124.6, 122.4, 114.3 (2C), 112.6, 110.4, 109.8, 55.3, 48.4, 47.9, 43.7, 38.8, 30.1, 21.4; **HRMS** (EI, m/z): calcd for $C_{34}H_{31}^{79}BrN_2O_4S$ $[M]^+$: 642.1182, found: 642.1190; calcd for $C_{34}H_{31}^{81}BrN_2O_4S$ $[M]^+$: 644.1162, found: 644.1161; $[\alpha]_D^{25} = -33.7$ (c 1.00, CH_2Cl_2); 93% ee, 11:1 dr; **HPLC** (Chiralpak IA, hexane/ethyl acetate = 70/30, 1.0 mL/min, 254 nm) $t_R = 9.56$ min (major), 15.28 min (minor).

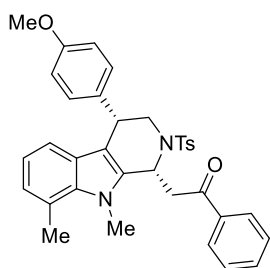
2-((1*R*,4*S*)-7-Chloro-4-(4-methoxyphenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)-1-phenylethan-1-one (3q)



46.1 mg, 77% yield, light yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H), 7.60 – 7.55 (m, 3H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.24 (d, $J = 1.8$ Hz, 1H), 7.12 (d, $J = 8.6$ Hz, 2H), 7.01 (d, $J = 8.1$ Hz, 2H), 6.85 (d, $J = 8.6$ Hz, 2H), 6.80 (dd, $J = 8.4, 1.8$ Hz, 1H), 6.55 (d, $J = 8.5$ Hz, 1H), 6.04 (dd, $J = 7.6, 3.2$ Hz, 1H), 4.25 – 4.16 (m, 2H), 3.81 (s, 3H), 3.73 – 3.66 (m, 4H), 3.19 – 3.07 (m, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 158.8, 143.4,

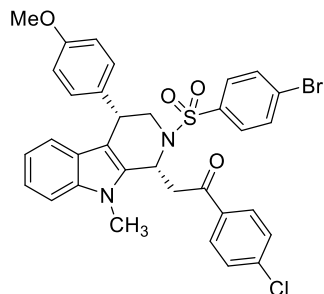
137.9, 137.2, 136.4, 136.2, 133.6, 132.9, 129.4 (2C), 129.3 (2C), 128.7 (2C), 128.3 (2C), 127.8, 127.1 (2C), 124.4, 120.9, 119.9, 114.2 (2C), 110.5, 109.1, 55.3, 48.3, 47.9, 43.7, 39.0, 30.1, 21.4; **HRMS** (EI, m/z): calcd for C₃₄H₃₁ClN₂O₄S [M]⁺: 598.1688, found: 598.1691; [α]_D²⁵ = +18.8 (c 1.00, CH₂Cl₂); 91% ee, 10:1 dr; **HPLC** (Chiralpak IA, hexane/ethyl acetate = 70/30, 1.0 mL/min, 254 nm) t_R = 8.86 min (major), 15.49 min (minor).

2-((1*R*,4*S*)-4-(4-Methoxyphenyl)-8,9-dimethyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)-1-phenylethan-1-one (3r)



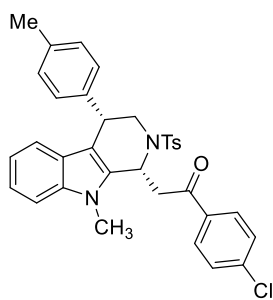
52.7 mg, 91% yield, light yellow solid, m.p. 130–132 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.84 (d, *J* = 7.3 Hz, 2H), 7.63 – 7.54 (m, 3H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.88 – 6.79 (m, 3H), 6.69 (t, *J* = 7.5 Hz, 1H), 6.48 (d, *J* = 7.9 Hz, 1H), 6.02 (dd, *J* = 7.9, 3.0 Hz, 1H), 4.24 – 4.15 (m, 2H), 3.96 (s, 3H), 3.80 (s, 3H), 3.72 (dd, *J* = 16.7, 7.8 Hz, 1H), 3.21 – 3.06 (m, 2H), 2.73 (s, 3H), 2.21 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 196.1, 158.6, 143.3, 137.3, 136.6, 136.5, 136.0, 133.5, 133.4, 129.4 (2C), 129.3 (2C), 128.7 (2C), 128.3 (2C), 127.1 (2C), 126.7, 124.9, 120.9, 119.3, 118.3, 114.1 (2C), 110.3, 55.3, 48.3, 48.1, 43.8, 39.1, 33.1, 21.4, 20.3; **HRMS** (EI, m/z): calcd for C₃₅H₃₄N₂O₄S [M]⁺: 578.2234, found: 578.2237; [α]_D²⁵ = +42.0 (c 1.00, CH₂Cl₂); 94% ee, 11:1 dr; **HPLC** (Chiralpak IA, hexane/ethyl acetate = 70/30, 1.0 mL/min, 254 nm) t_R = 9.20 min (major), 13.87 min (minor).

2-((1*R*,4*S*)-2-((4-Bromophenyl)sulfonyl)-4-(4-methoxyphenyl)-9-methyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)-1-(4-chlorophenyl)ethan-1-one (3s)



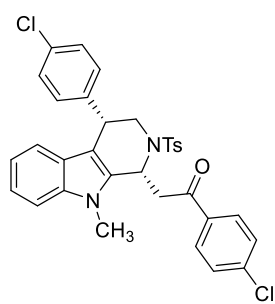
57.8 mg, 87% yield, light yellow solid, m.p. 171–173 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.78 – 7.71 (m, 2H), 7.58 – 7.53 (m, 2H), 7.43 – 7.34 (m, 4H), 7.29 – 7.23 (m, 1H), 7.23 – 7.09 (m, 3H), 6.89 – 6.83 (m, 3H), 6.68 (d, *J* = 7.92 Hz, 1H), 6.00 (dd, *J* = 8.07, 2.83 Hz, 1H), 4.29 – 4.17 (m, 2H), 3.80 (s, 3H), 3.71 (s, 3H), 3.68 (d, *J* = 2.32 Hz, 1H), 3.25 – 3.14 (m, 1H), 3.09 (dd, *J* = 16.67, 2.94 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 194.9, 158.9, 140.5, 139.5, 137.5, 134.8, 134.7, 132.9, 132.1 (2C), 129.7 (2C), 129.4 (2C), 129.2 (2C), 128.6 (2C), 127.6, 125.7, 122.1, 120.3, 119.5, 114.2 (2C), 110.4, 109.0, 55.4, 48.6, 48.4, 43.6, 39.4, 30.1.; **HRMS** (EI, m/z): calcd for C₃₃H₂₈⁷⁹BrClN₂O₄S [M]⁺: 662.0636, found: 662.0643; calcd for C₃₃H₂₈⁸¹BrClN₂O₄S [M]⁺: 664.0616, found: 664.0613; [α]_D²⁵ = +33.5 (c 0.20, CH₂Cl₂); 94% ee, 5:1 dr; **HPLC** (Chiralpak IA, hexane/isopropanol = 70/30, 1.0 mL/min, 254 nm) t_R = 12.44 min (major), 22.88 min (minor).

1-(4-Chlorophenyl)-2-((1*R*,4*S*)-9-methyl-4-(*p*-tolyl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)ethan-1-one (3t)



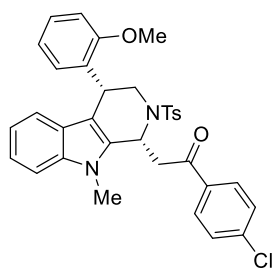
52.4 mg, 90% yield, light yellow solid, m.p. 183-185 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 – 7.76 (m, 2H), 7.57 (d, J = 8.21 Hz, 2H), 7.43 – 7.36 (m, 2H), 7.29 – 7.22 (m, 1H), 7.18 – 7.07 (m, 5H), 7.01 (d, J = 8.08 Hz, 2H), 6.89 – 6.80 (m, 1H), 6.66 (d, J = 7.90 Hz, 1H), 6.00 (dd, J = 7.78, 3.11 Hz, 1H), 4.27 – 4.14 (m, 2H), 3.73 (s, 3H), 3.71 – 3.66 (m, 1H), 3.24 – 3.08 (m, 2H), 2.35 (s, 3H), 2.22 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 195.2, 143.5, 140.2, 138.2, 137.6, 137.3, 136.9, 135.2, 135.0, 129.8 (2C), 129.5(3) (2C), 129.5(1) (2C), 129.1 (2C), 128.8, 128.3 (2C), 127.1 (2C), 121.9, 120.3, 119.4, 110.2, 109.0, 48.5, 48.4, 43.9, 39.5, 30.1, 21.5, 21.3; **HRMS** (EI, m/z): calcd for $\text{C}_{34}\text{H}_{31}\text{ClN}_2\text{O}_3\text{S}$ $[\text{M}]^+$: 582.1738, found: 582.1747; $[\alpha]_{\text{D}}^{25} = +30.0$ (c 0.20, CH_2Cl_2); 87% ee, 10:1 dr; **HPLC** (Chiralpak IA, hexane/isopropanol = 70/30, 1.0 mL/min, 254 nm) $t_{\text{R}} = 9.15$ min (major), 13.02 min (minor).

1-(4-Chlorophenyl)-2-((1R,4S)-4-(4-chlorophenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indol-1-yl)ethan-1-one (3u)



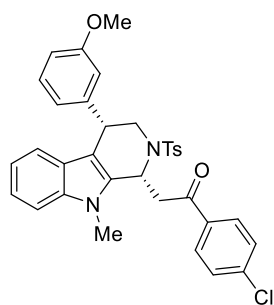
36.2 mg, 60% yield, light yellow solid, m.p. 225-227 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 7.30 – 7.24 (m, 3H), 7.20 – 7.10 (m, 3H), 7.02 (d, J = 8.0 Hz, 2H), 6.91 – 6.82 (m, 1H), 6.66 – 6.59 (m, 1H), 6.01 (dd, J = 7.7, 3.0 Hz, 1H), 4.21 (dt, J = 10.8, 6.0 Hz, 2H), 3.72 (s, 3H), 3.66 (d, J = 7.6 Hz, 1H), 3.22 – 3.03 (m, 2H), 2.22 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 195.0, 143.6, 140.3, 139.8, 137.6, 137.2, 135.4, 134.9, 133.0, 129.8 (2C), 129.8 (2C), 129.5 (2C), 129.1 (2C), 129.0 (2C), 127.1 (2C), 125.6, 122.1, 120.0, 119.5, 109.5, 109.1, 48.3, 48.3, 43.8, 39.5, 30.1, 21.5; **HRMS** (EI, m/z): calcd for $\text{C}_{33}\text{H}_{28}\text{Cl}_2\text{N}_2\text{O}_3\text{S}$ $[\text{M}]^+$: 602.1192, found: 602.1201; $[\alpha]_{\text{D}}^{25} = +37.0$ (c 0.20, CH_2Cl_2); 96% ee, 12:1 dr; **HPLC** (Chiralpak IA, hexane/isopropanol = 70/30, 1.0 mL/min, 254 nm) $t_{\text{R}} = 11.30$ min (major), 17.83 min (minor).

1-(4-Chlorophenyl)-2-((1R,4R)-4-(2-methoxyphenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indol-1-yl)ethan-1-one (3v)



28.8 mg, 48% yield, light yellow solid, m.p. 175–177 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.83 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 1.8 Hz, 1H), 7.24 (d, J = 5.6 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 7.03 – 6.92 (m, 4H), 6.87 – 6.79 (m, 2H), 6.67 (d, J = 7.9 Hz, 1H), 5.97 (dd, J = 7.8, 3.4 Hz, 1H), 4.53 (dd, J = 10.7, 6.2 Hz, 1H), 4.39 (dd, J = 14.3, 6.2 Hz, 1H), 3.88 (s, 3H), 3.74 (s, 3H), 3.70 (t, J = 7.0 Hz, 1H), 3.21 – 3.09 (m, 2H), 2.19 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 195.3, 157.6, 143.3, 140.1, 137.4, 137.2, 135.3, 135.1, 129.8 (2C), 129.3 (2C), 129.0 (2C), 128.9, 128.9, 128.1, 127.0 (2C), 125.7, 121.7, 120.7, 120.3, 119.1, 110.6, 109.5, 108.9, 55.6, 48.6, 46.0, 43.9, 32.4, 30.0, 21.4; **HRMS** (EI, m/z): calcd for $\text{C}_{34}\text{H}_{31}\text{ClN}_2\text{O}_4\text{S}$ $[\text{M}]^+$: 598.1688, found: 598.1690; $[\alpha]_{\text{D}}^{25} = +17.8$ (c 1.00, CH_2Cl_2); 60% ee, 20:1 dr; **HPLC** (Chiralpak IA, hexane/isopropanol = 70/30, 1.0 mL/min, 254 nm) $t_{\text{R}} = 9.72$ min (major), 19.97 min (minor).

1-(4-Chlorophenyl)-2-((1*R*,4*S*)-4-(3-methoxyphenyl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-1-yl)ethan-1-one (3w)



30.0 mg, 50% yield, light yellow solid, m.p. 191–193 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.87 – 6.78 (m, 4H), 6.69 (d, *J* = 7.9 Hz, 1H), 6.01 (dd, *J* = 7.8, 3.1 Hz, 1H), 4.28 – 4.16 (m, 2H), 3.78 (s, 3H), 3.72 (s, 3H), 3.71 – 3.66 (m, 1H), 3.22 (dd, *J* = 13.5, 10.2 Hz, 1H), 3.11 (dd, *J* = 16.5, 3.2 Hz, 1H), 2.22 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 195.0, 159.9, 143.5, 142.9, 140.1, 137.5, 137.2, 135.1, 134.9, 129.7,

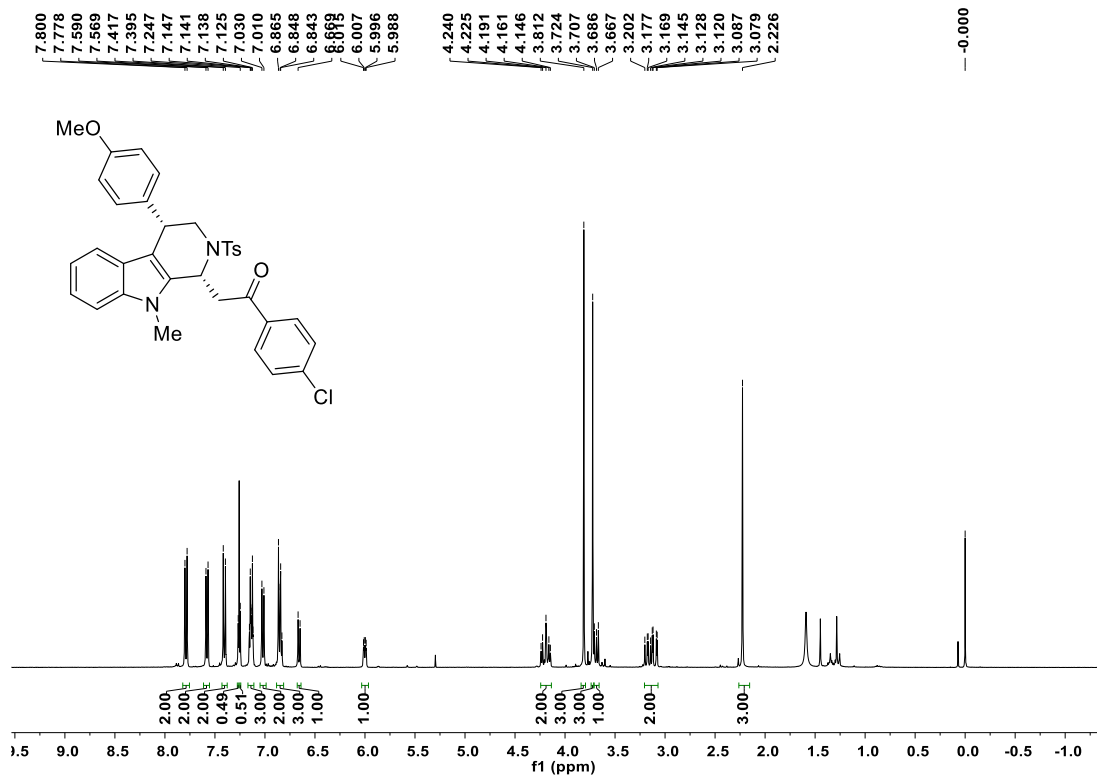
129.7 (2C), 129.4 (2C), 129.0 (2C), 127.0 (2C), 125.7, 121.9, 120.7, 120.2, 119.3, 114.5, 112.1, 109.8, 108.9, 55.3, 48.3, 48.2, 43.8, 39.9, 30.0, 21.4; HRMS (EI, m/z): calcd for C₃₄H₃₁ClN₂O₄S [M]⁺: 598.1688, found: 598.1692; [α]_D²⁵ = +22.3 (*c* 1.00, CH₂Cl₂); 69% ee, 10:1 dr; HPLC (Chiralpak IA, hexane/isopropanol = 70/30, 1.0 mL/min, 254 nm) t_R = 11.15 min (major), 18.38 min (minor).

4. References

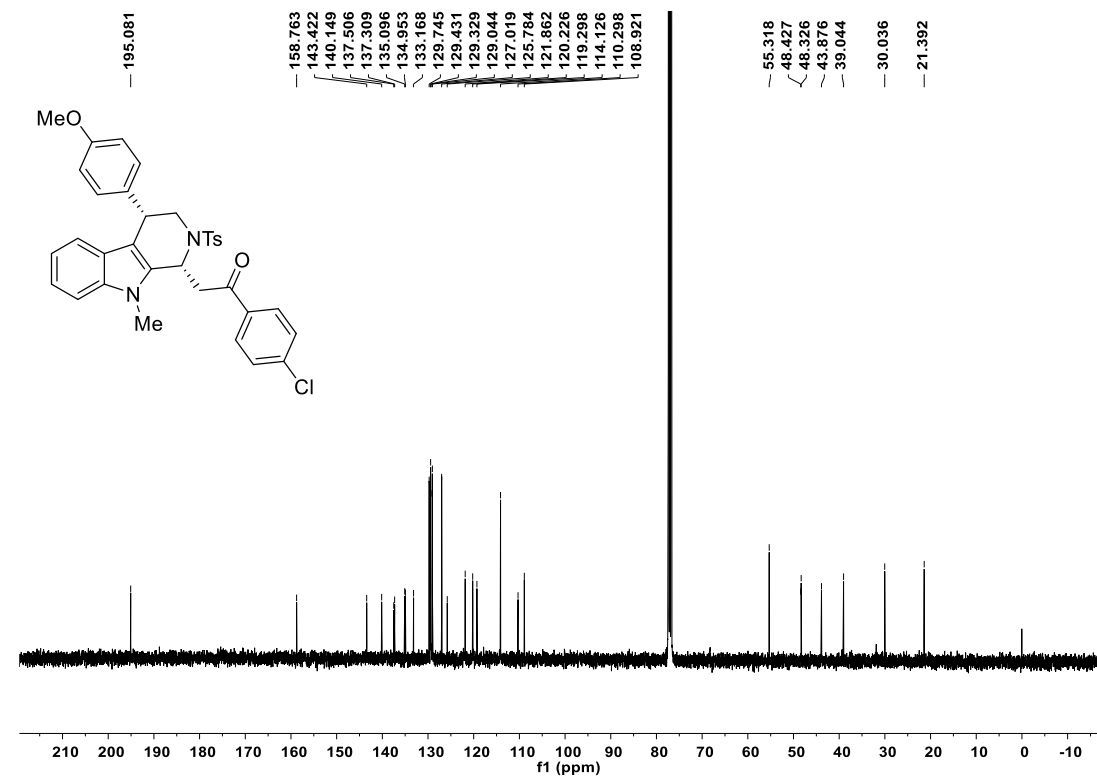
- [1] S. K. Davidsen, G. W. Phillips, S. F. Martin, *Org. Synth.*, 1987, **65**, 119.
- [2] C.-P. Yu, Y. Tang, L. Cha, S. Milikisiyants, T. I. Smirnova, A. I. Smirnov, Y. Guo, W.-C. Chang, *J. Am. Chem. Soc.*, 2018, **140**, 15190.

5. ^1H NMR and ^{13}C NMR spectra

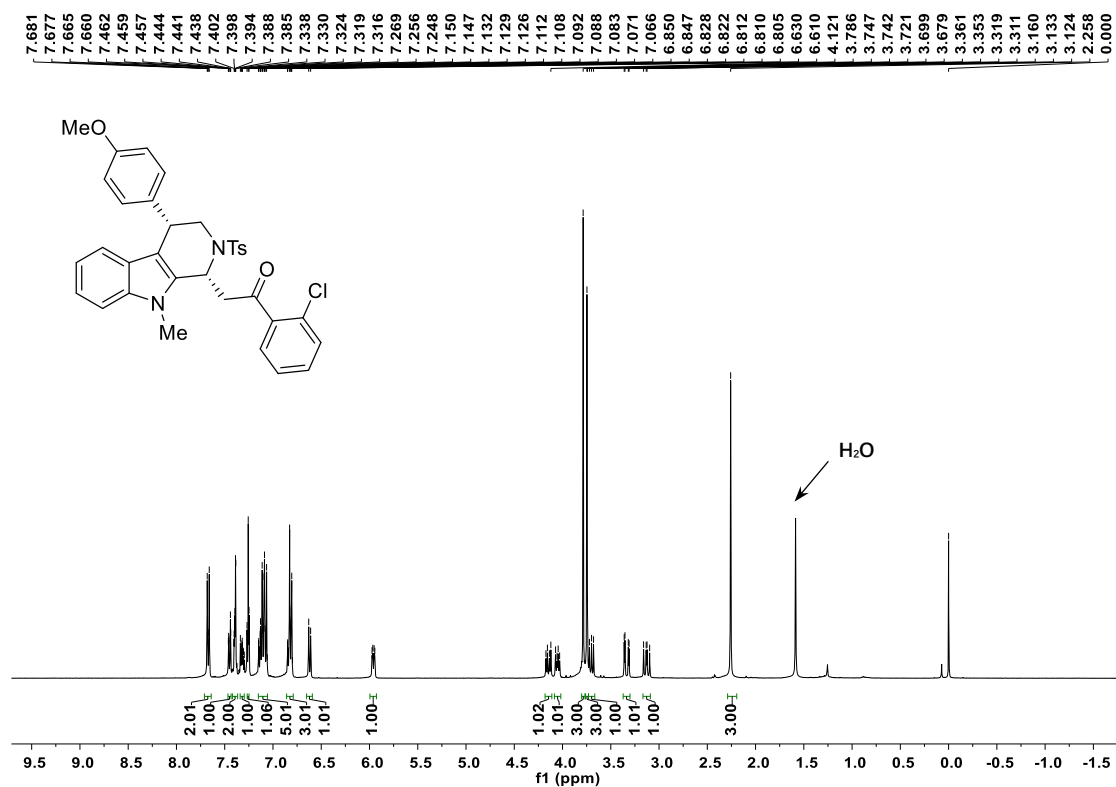
^1H NMR of **3a** in CDCl_3



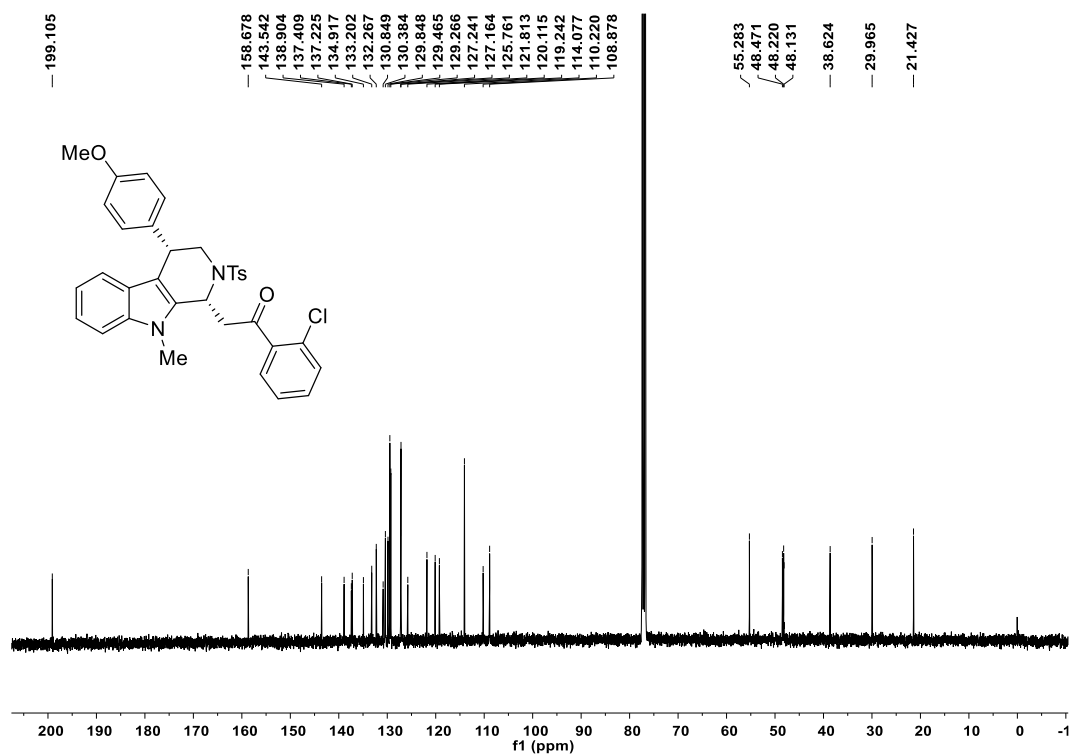
^{13}C NMR of **3a** in CDCl_3



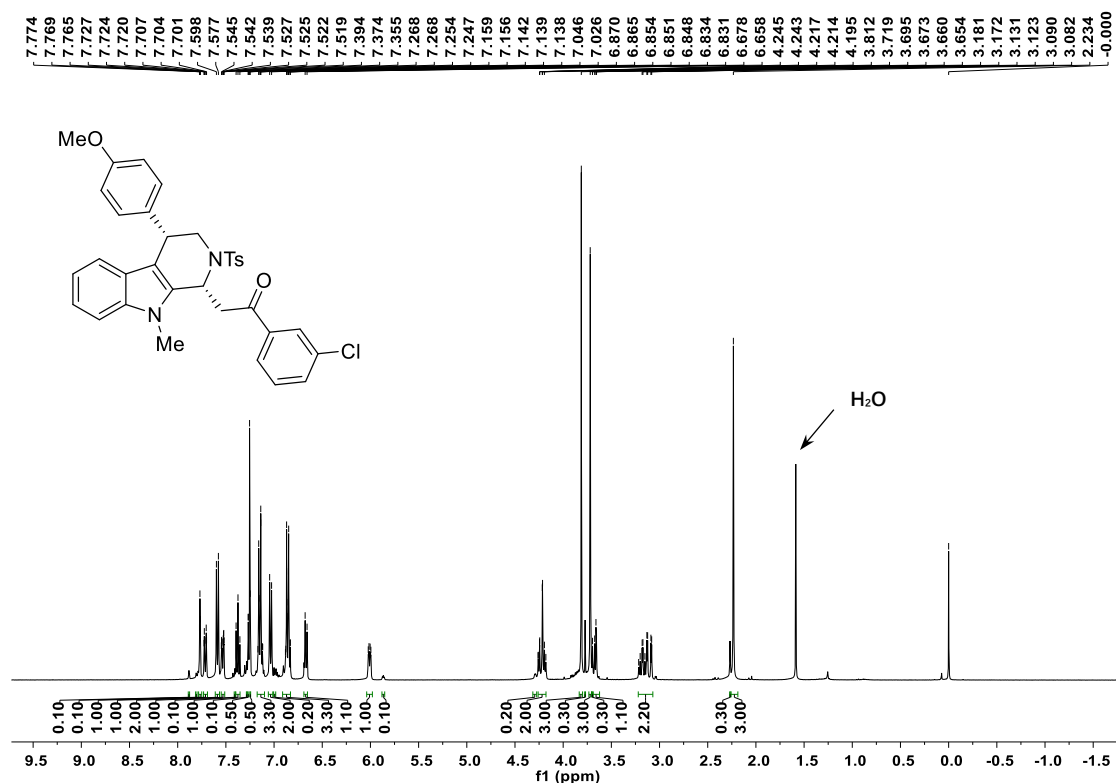
^1H NMR of **3b** in CDCl_3



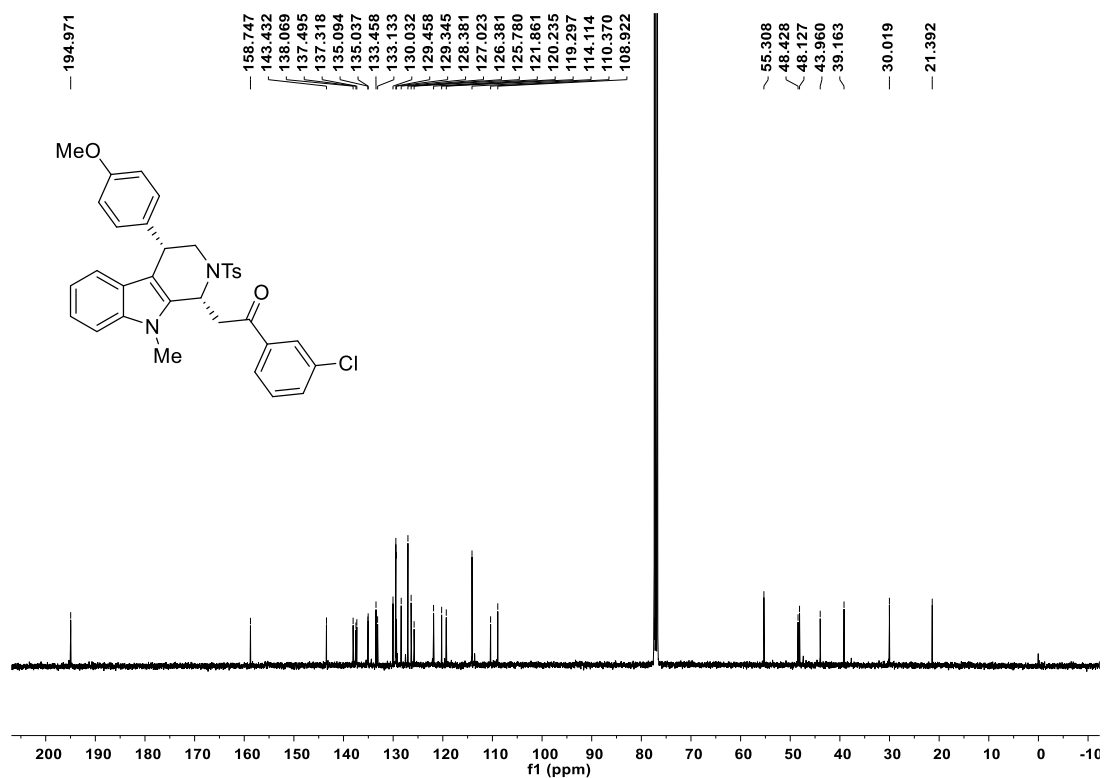
^{13}C NMR of **3b** in CDCl_3



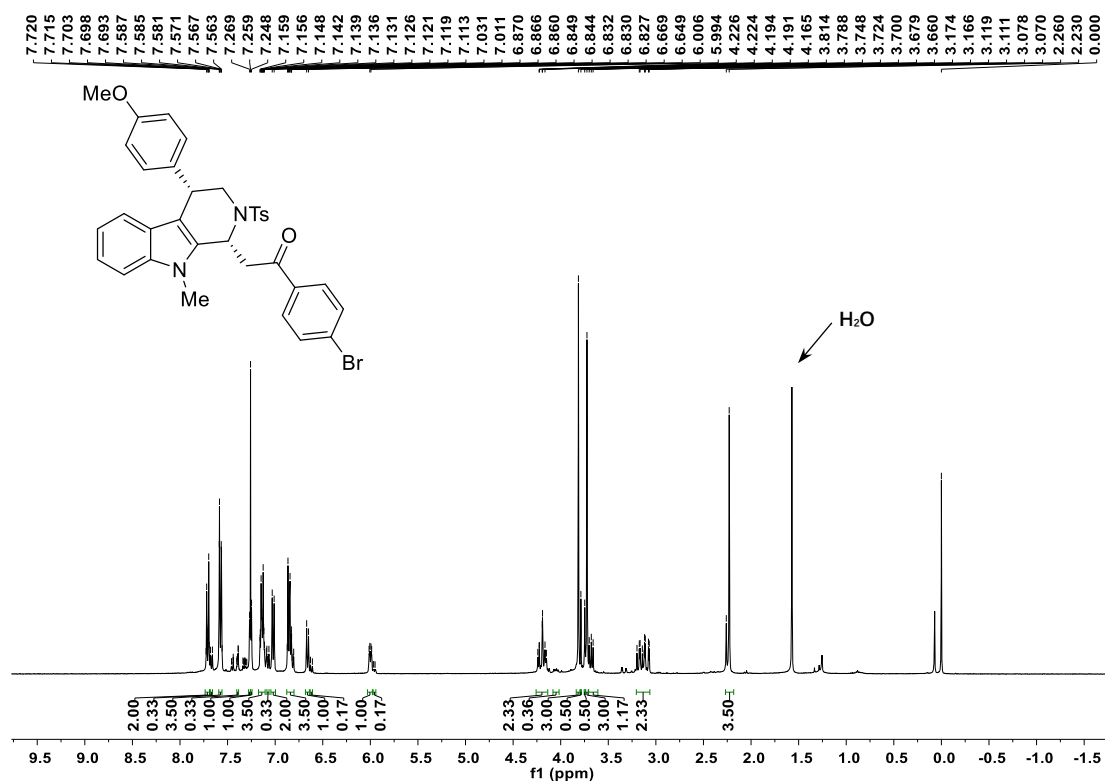
^1H NMR of **3c** in CDCl_3 (a mixture of diastereomers, 10:1 dr)



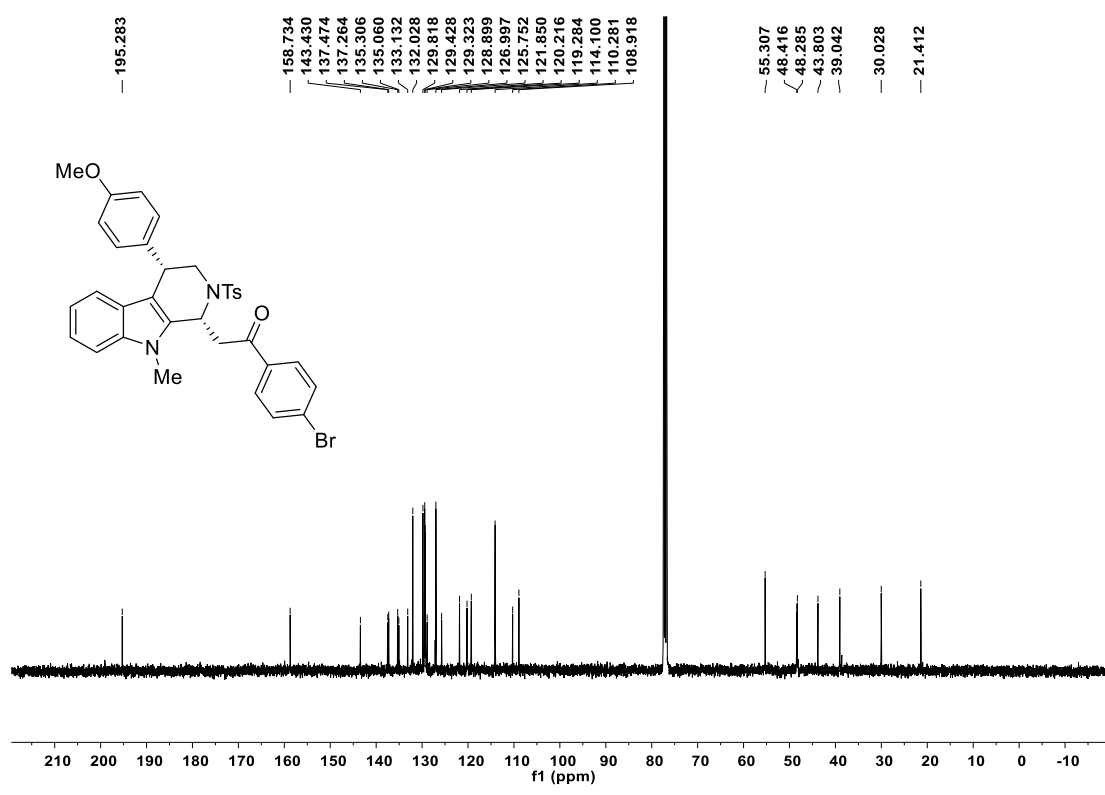
^{13}C NMR of **3c** in CDCl_3 (a mixture of diastereomers, 10:1 dr)



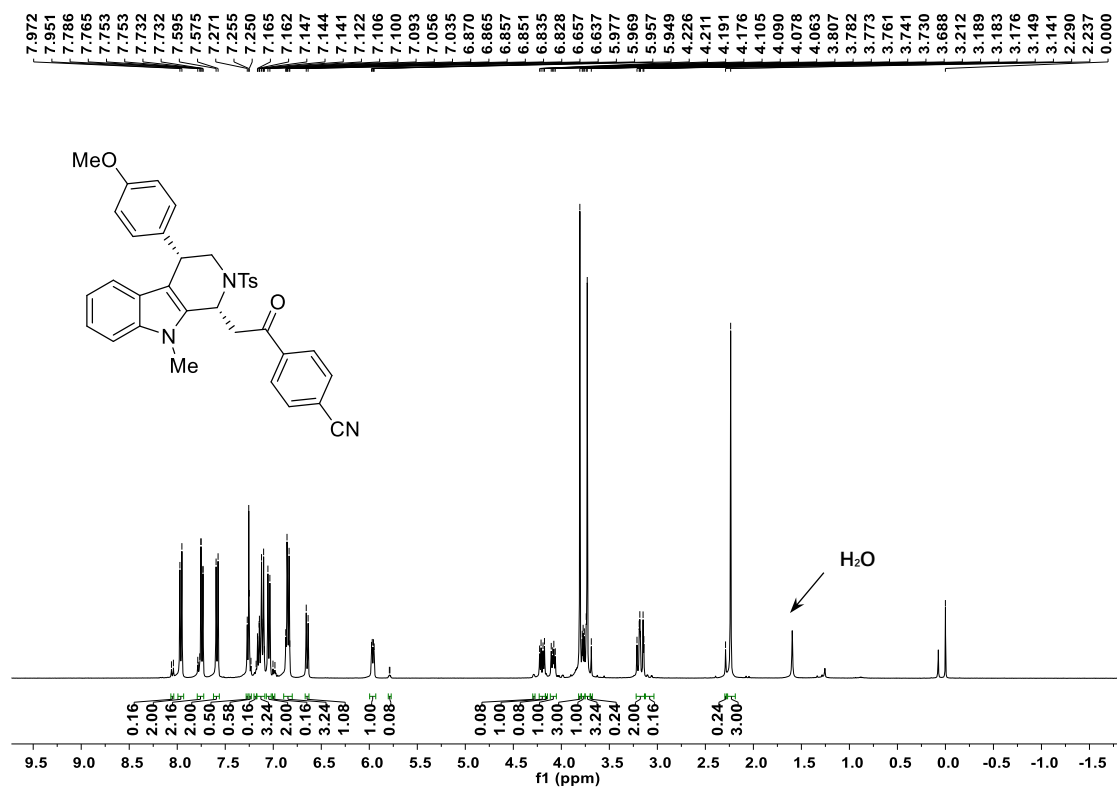
^1H NMR of **3d** in CDCl_3 (a mixture of diastereomers, 6:1 dr)



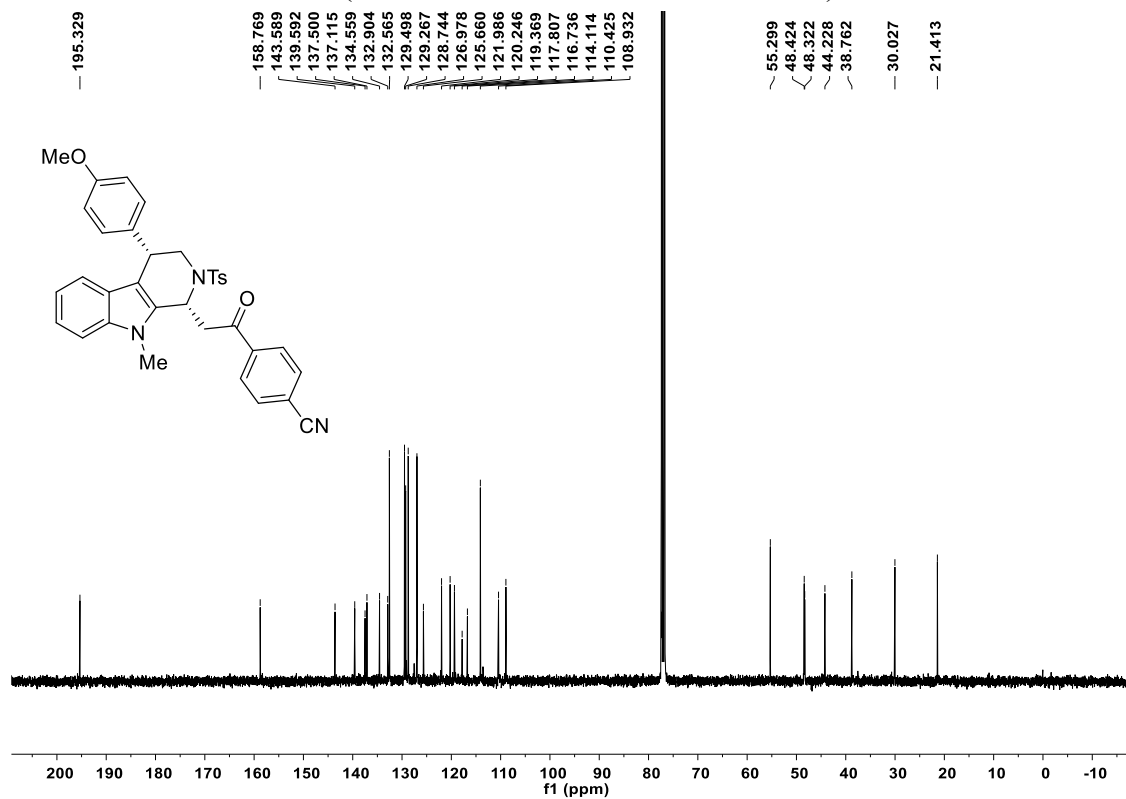
^{13}C NMR of **3d** in CDCl_3 (a mixture of diastereomers, 6:1 dr)



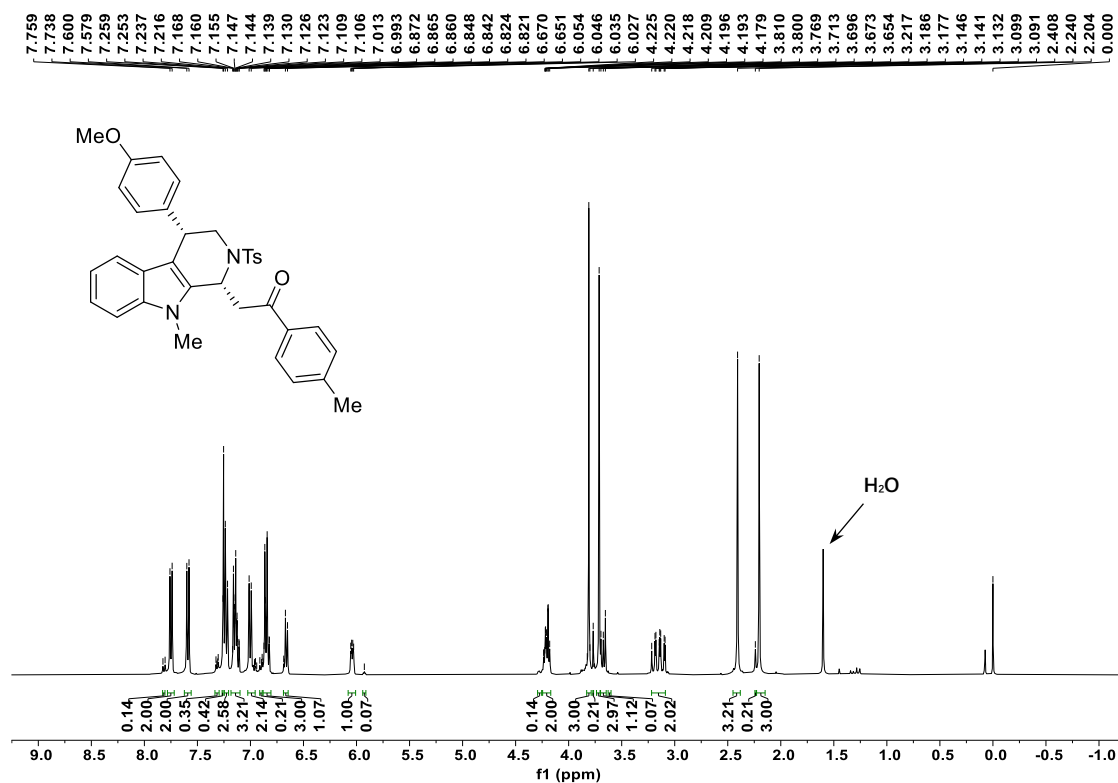
^1H NMR of **3e** in CDCl_3 (a mixture of diastereomers, 12.5:1 dr)



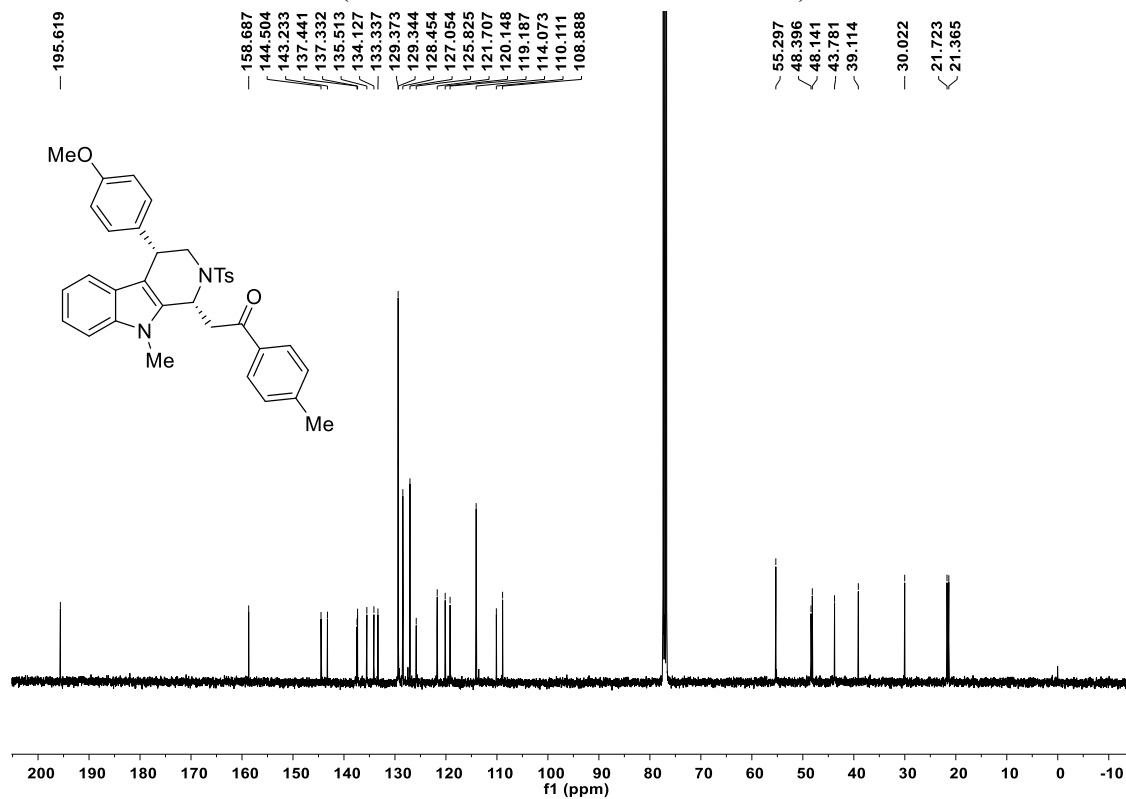
^{13}C NMR of **3e** in CDCl_3 (a mixture of diastereomers, 12.5:1 dr)



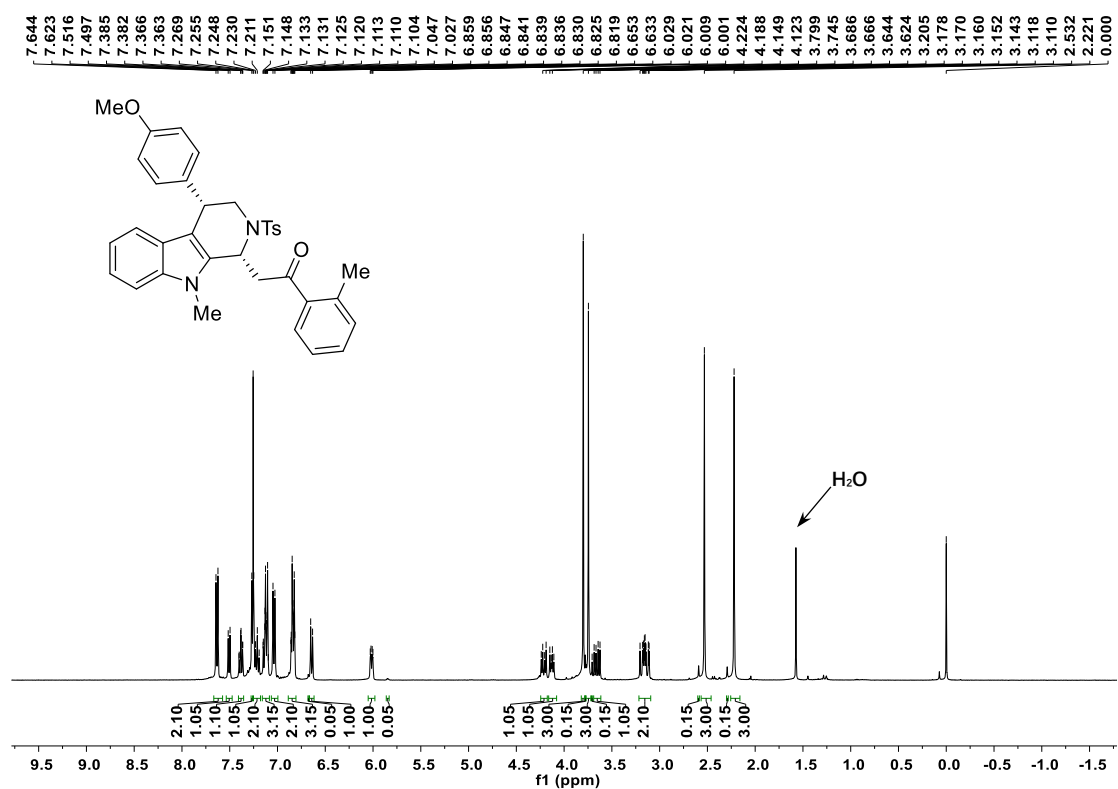
^1H NMR of **3f** in CDCl_3 (a mixture of diastereomers, 14:1 dr)



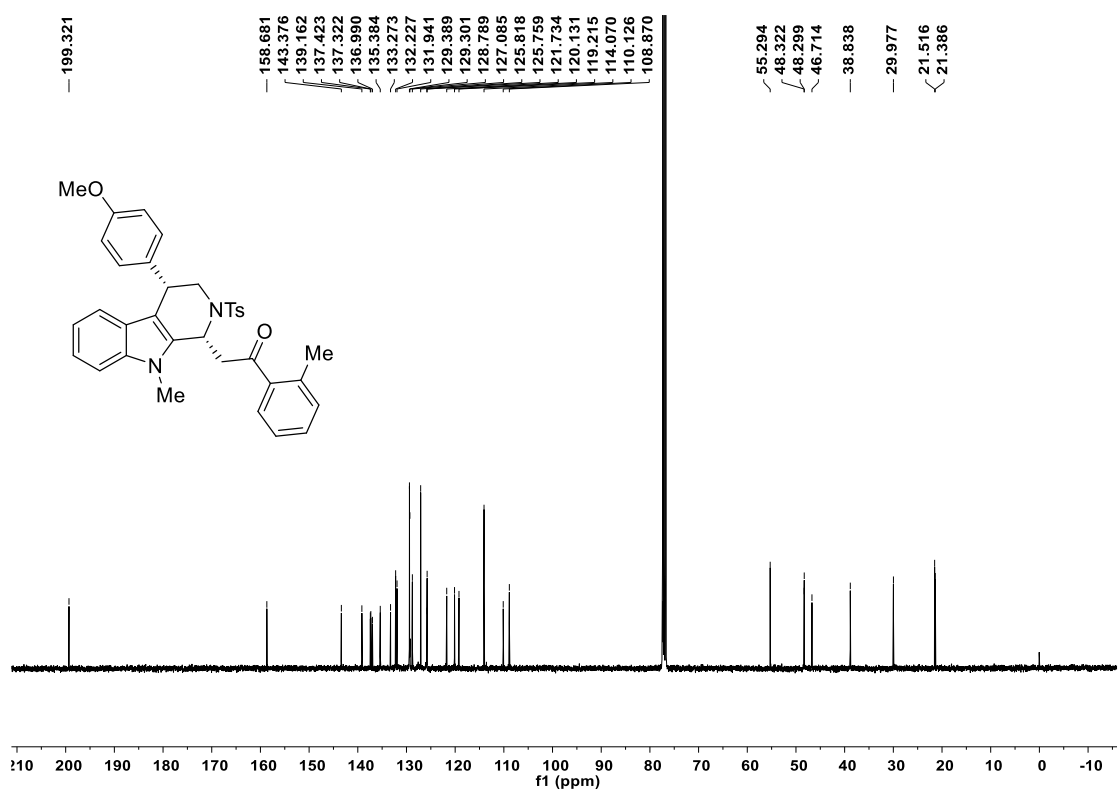
^{13}C NMR of **3f** in CDCl_3 (a mixture of diastereomers, 14:1 dr)



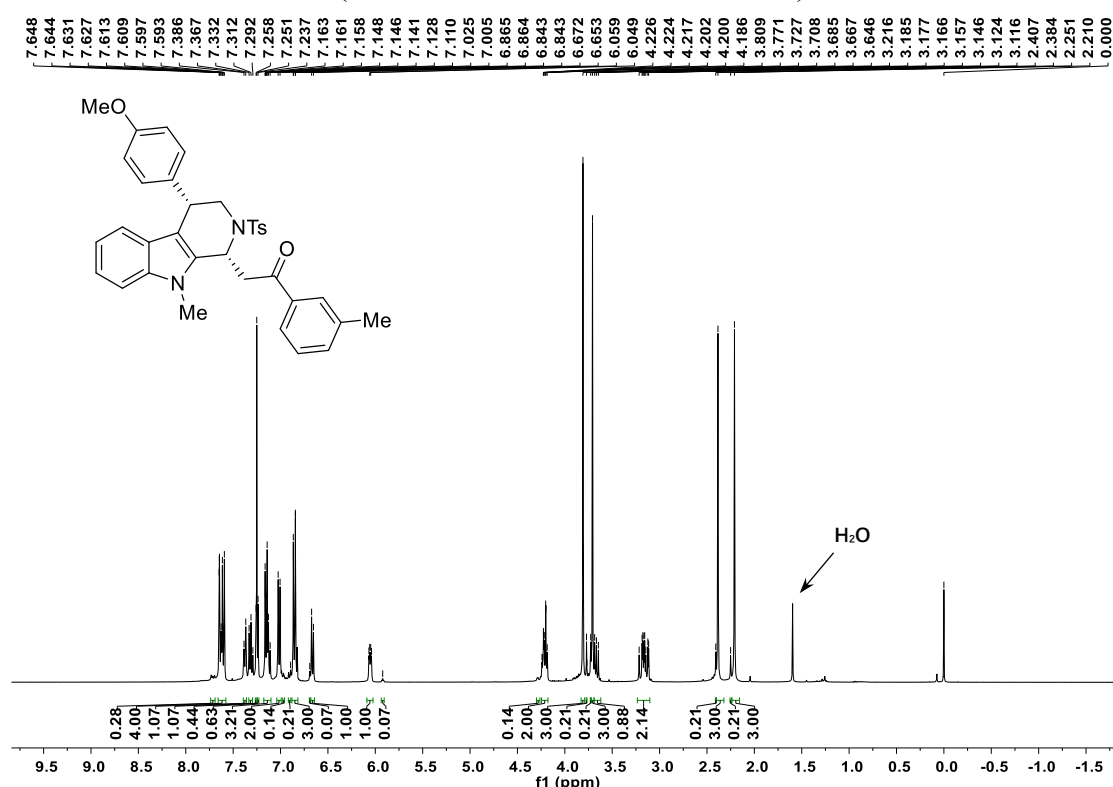
^1H NMR of **3g** in CDCl_3 (a mixture of diastereomers, 20:1 dr)



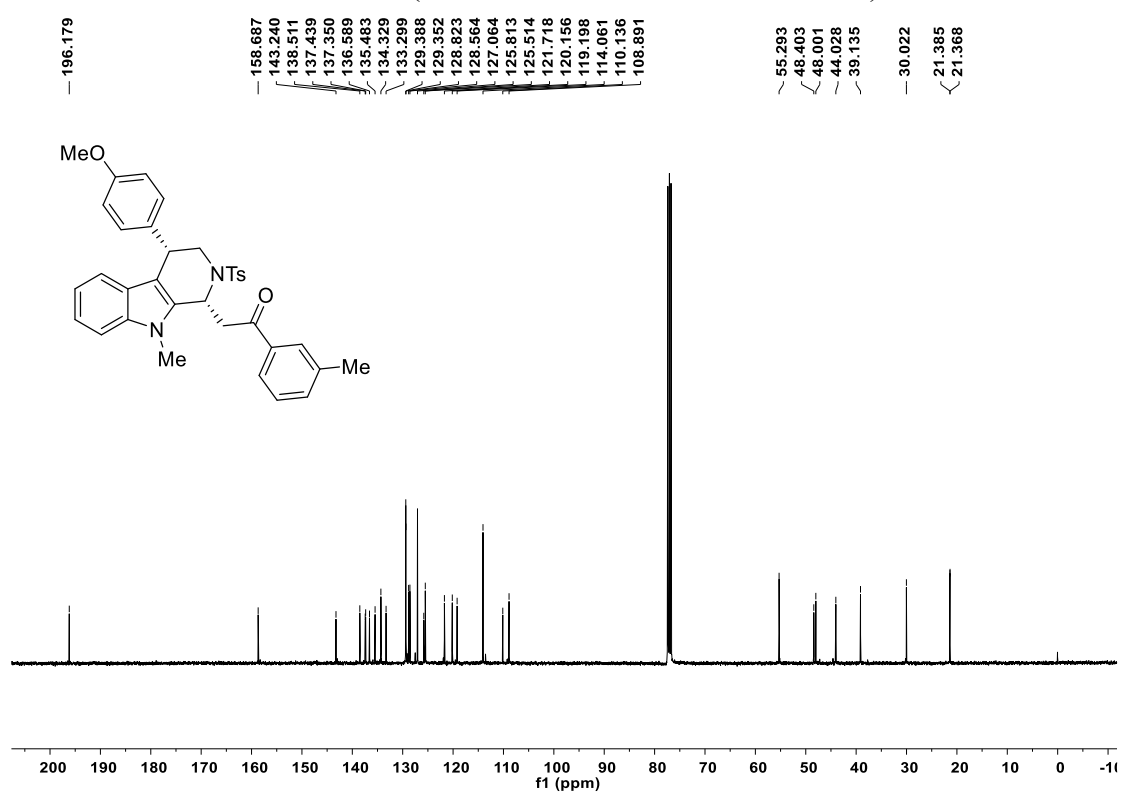
^{13}C NMR of **3g** in CDCl_3 (a mixture of diastereomers, 20:1 dr)



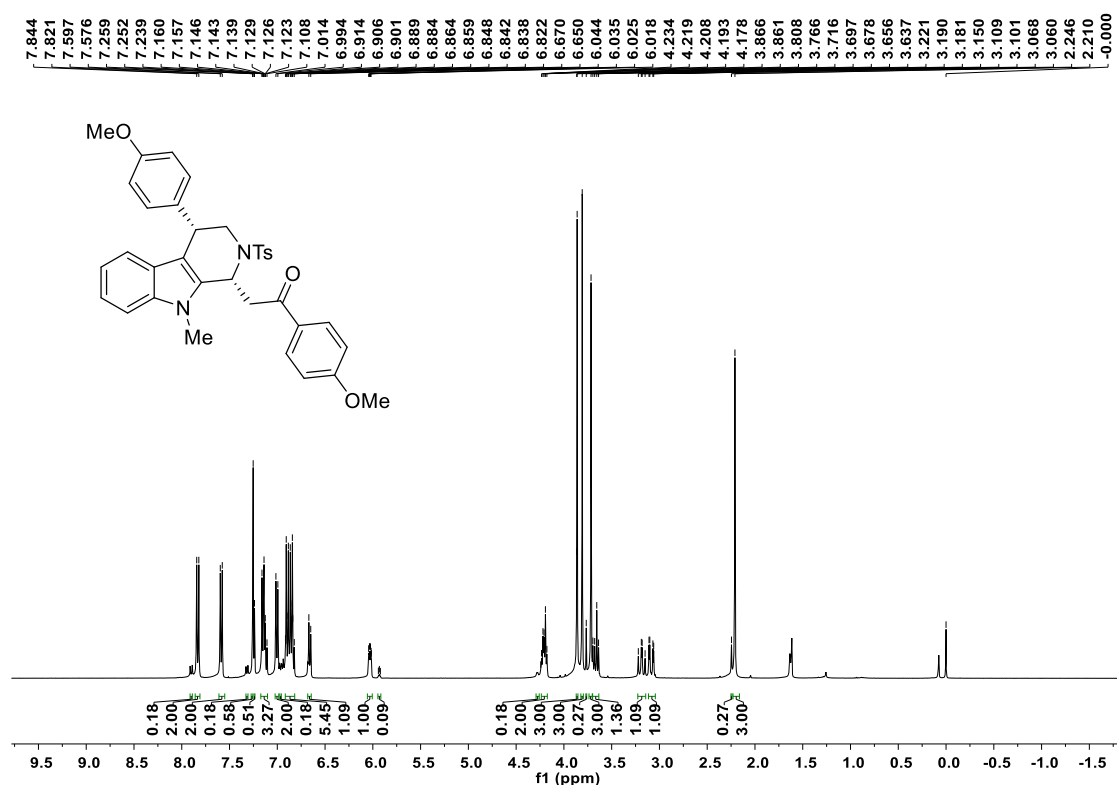
¹H NMR of **3h** in CDCl₃ (a mixture of diastereomers, 14:1 dr)



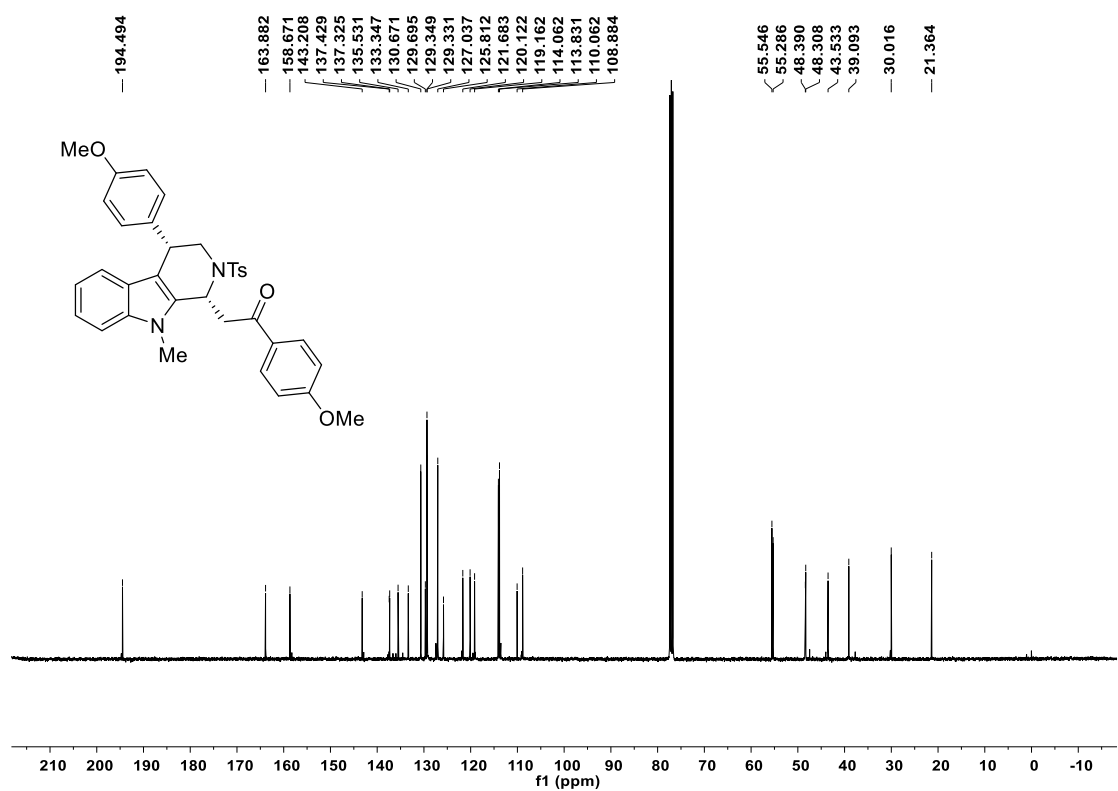
¹³C NMR of **3h** in CDCl₃ (a mixture of diastereomers, 14:1 dr)



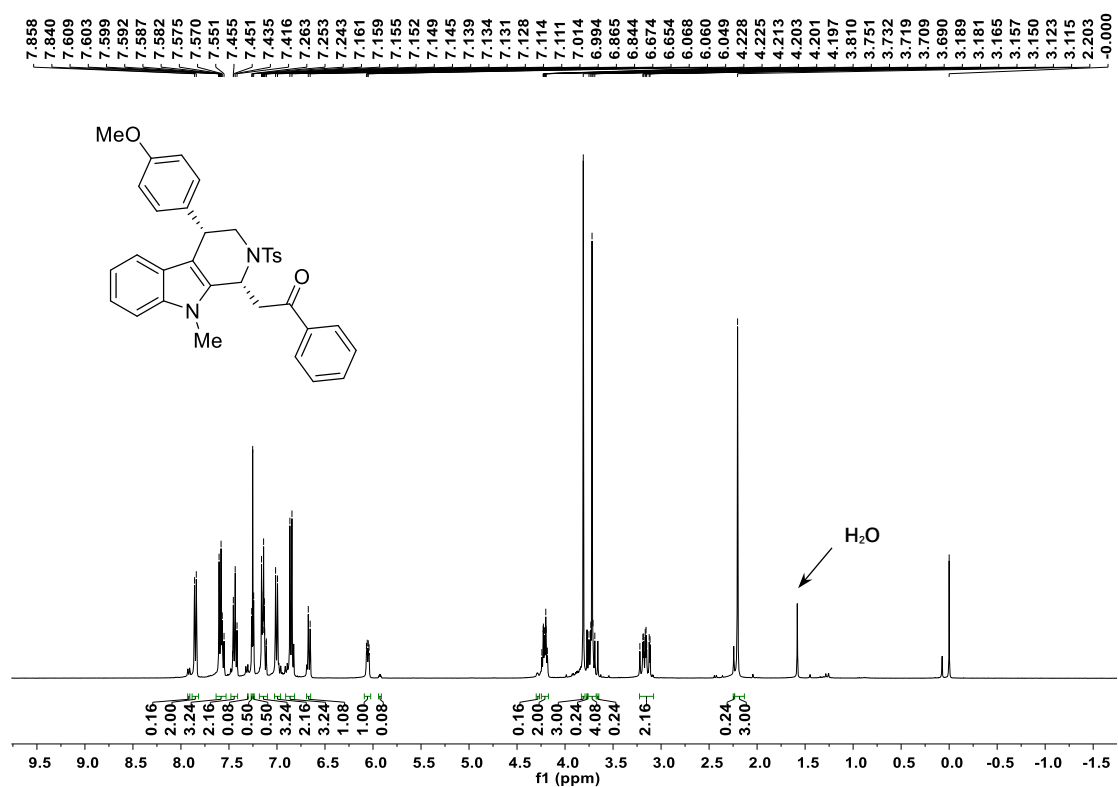
^1H NMR of **3i** in CDCl_3 (a mixture of diastereomers, 11:1 dr)



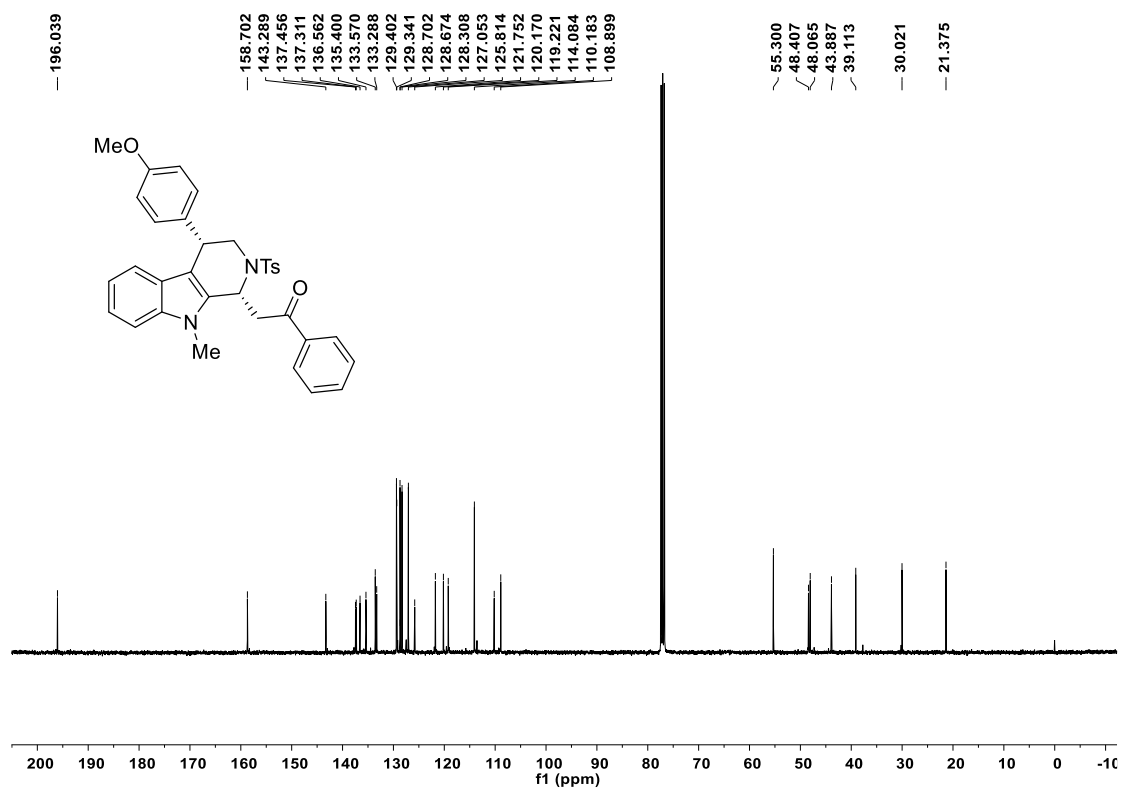
^{13}C NMR of **3i** in CDCl_3 (a mixture of diastereomers, 11:1 dr)



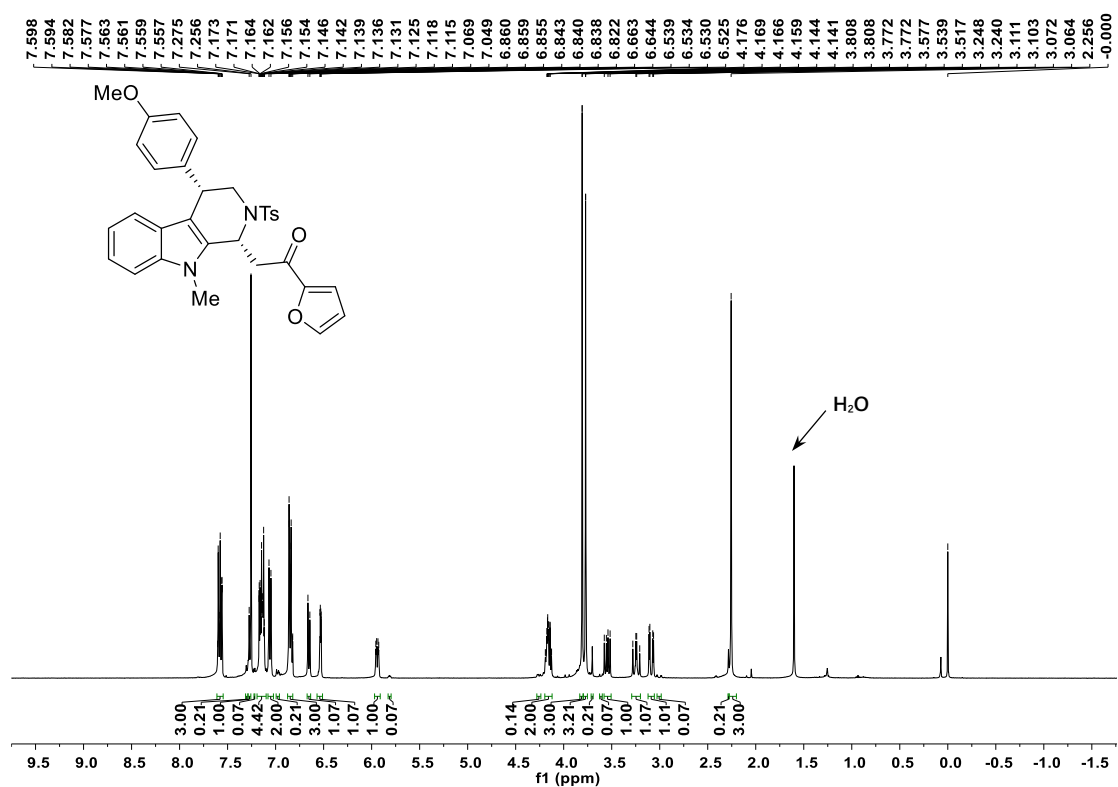
^1H NMR of **3j** in CDCl_3 (a mixture of diastereomers, 12.5:1 dr)



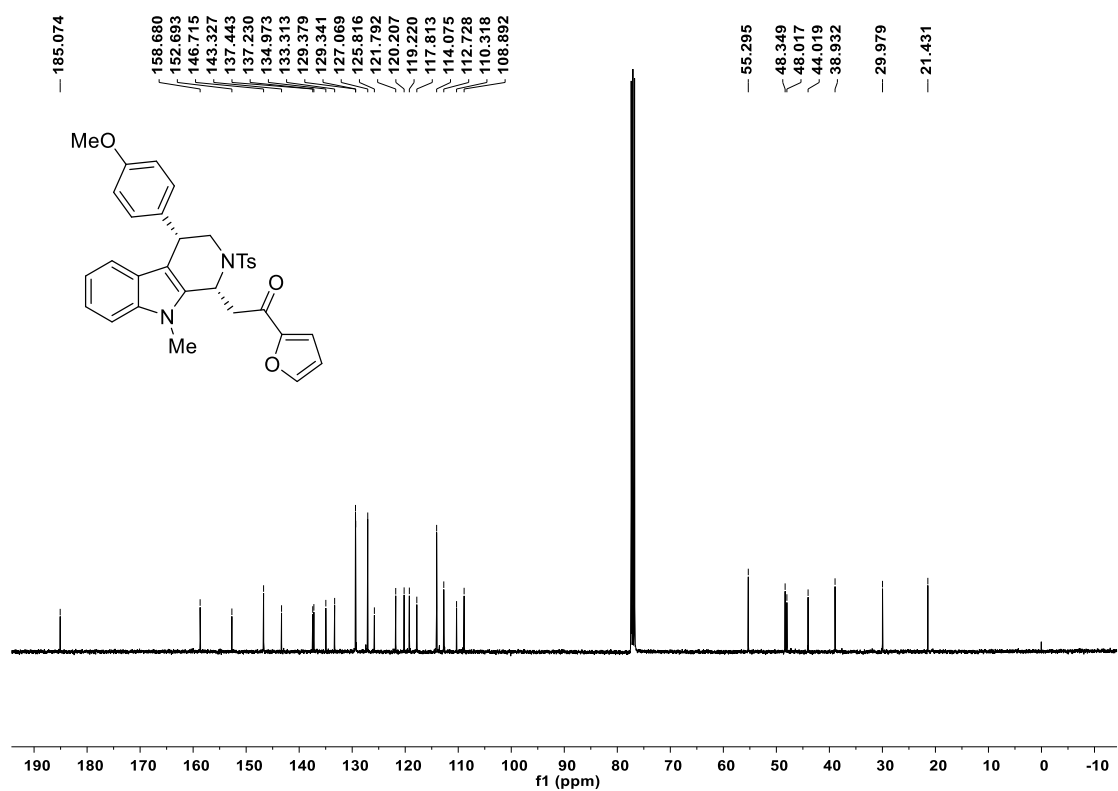
^{13}C NMR of **3j** in CDCl_3 (a mixture of diastereomers, 12.5:1 dr)



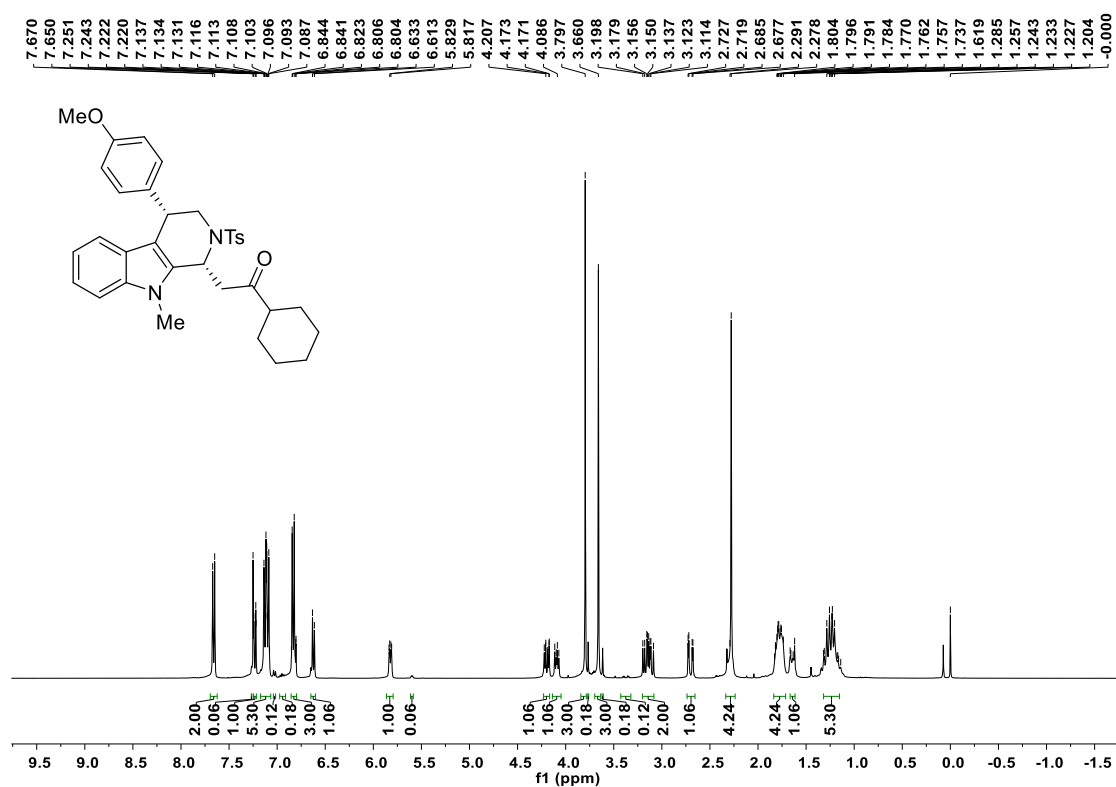
^1H NMR of **3k** in CDCl_3 (a mixture of diastereomers, 14:1 dr)



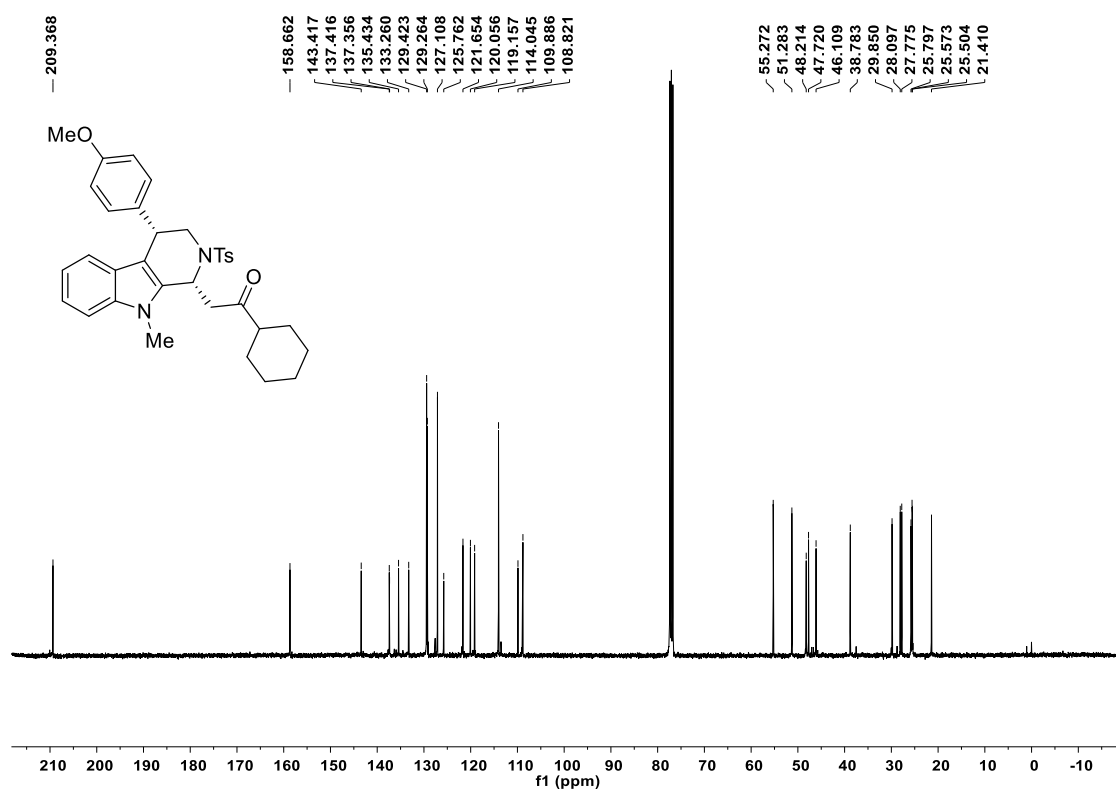
^{13}C NMR of **3k** in CDCl_3 (a mixture of diastereomers, 14:1 dr)



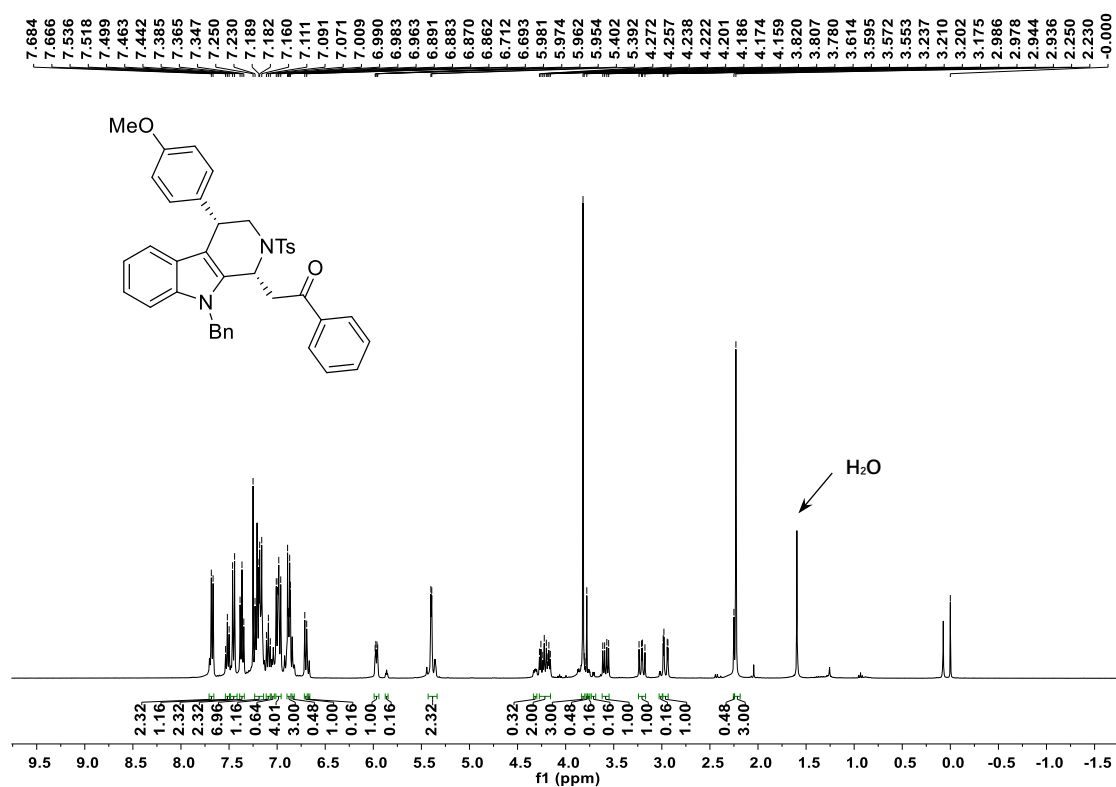
^1H NMR of **31** in CDCl_3 (a mixture of diastereomers, 17:1 dr)



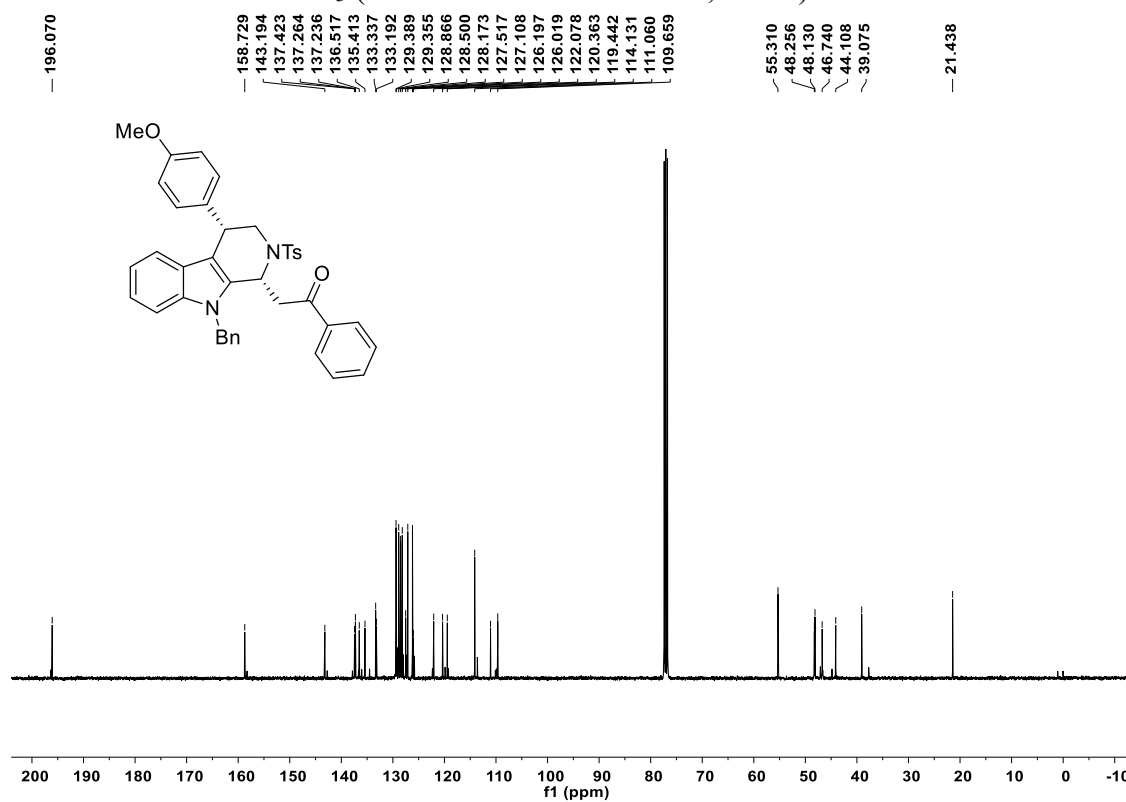
^{13}C NMR of **31** in CDCl_3 (a mixture of diastereomers, 17:1 dr)



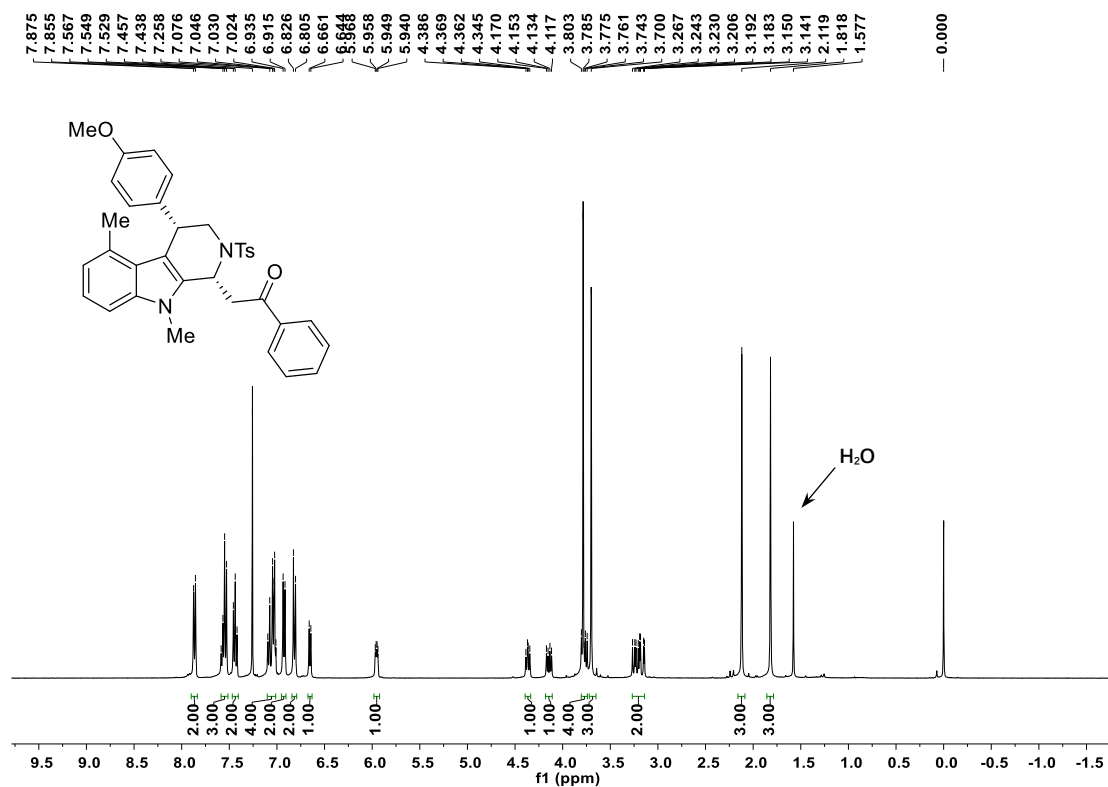
^1H NMR of **3m** in CDCl_3 (a mixture of diastereomers, 6:1 dr)



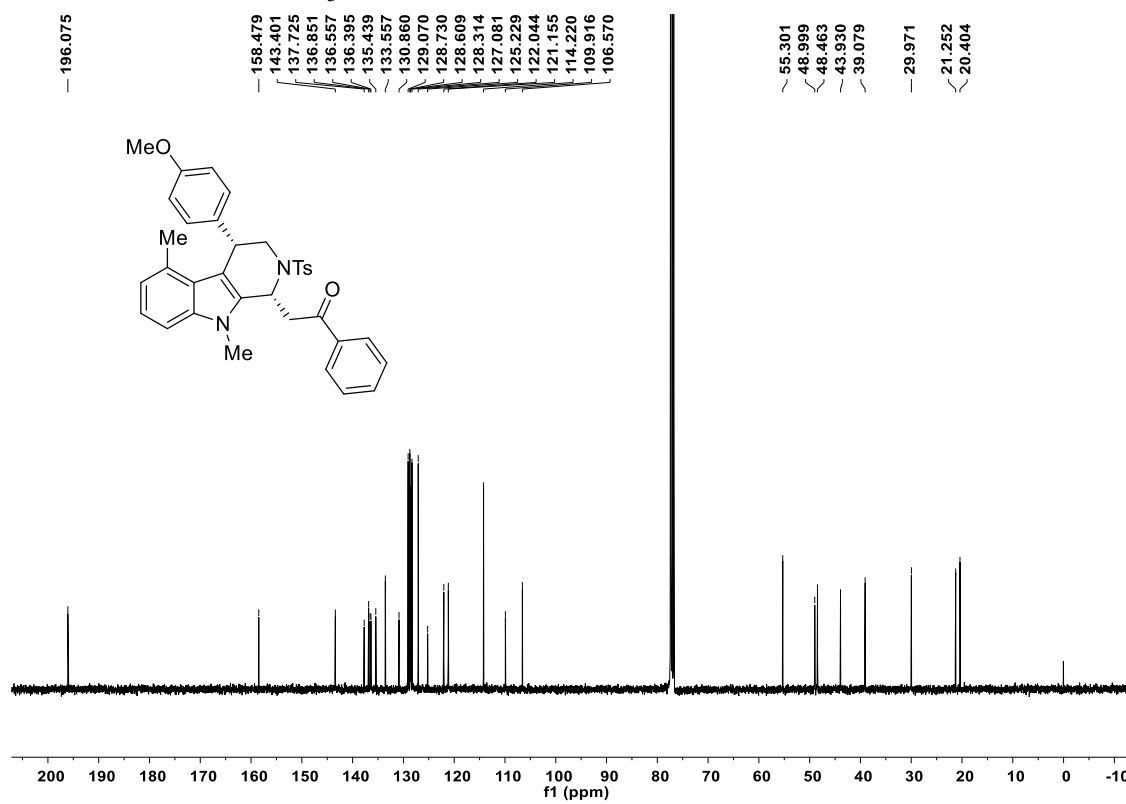
^{13}C NMR of **3m** in CDCl_3 (a mixture of diastereomers, 6:1 dr)



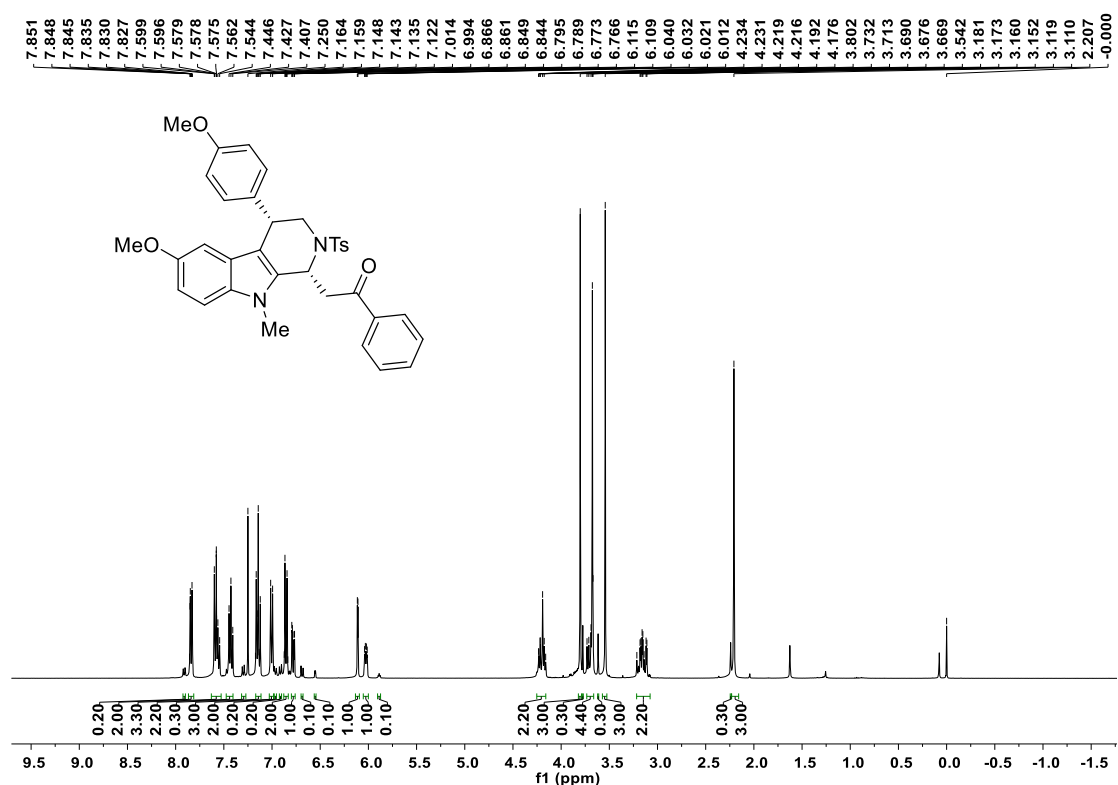
^1H NMR of **3n** in CDCl_3



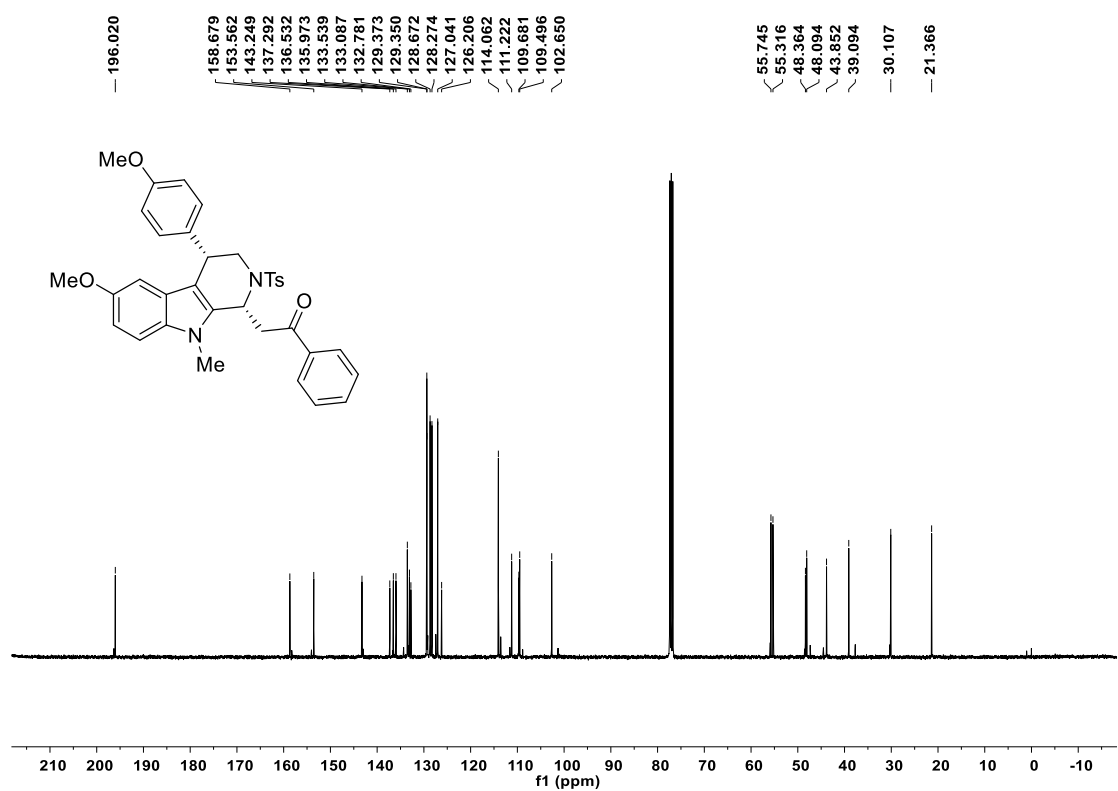
^{13}C NMR of **3n** in CDCl_3



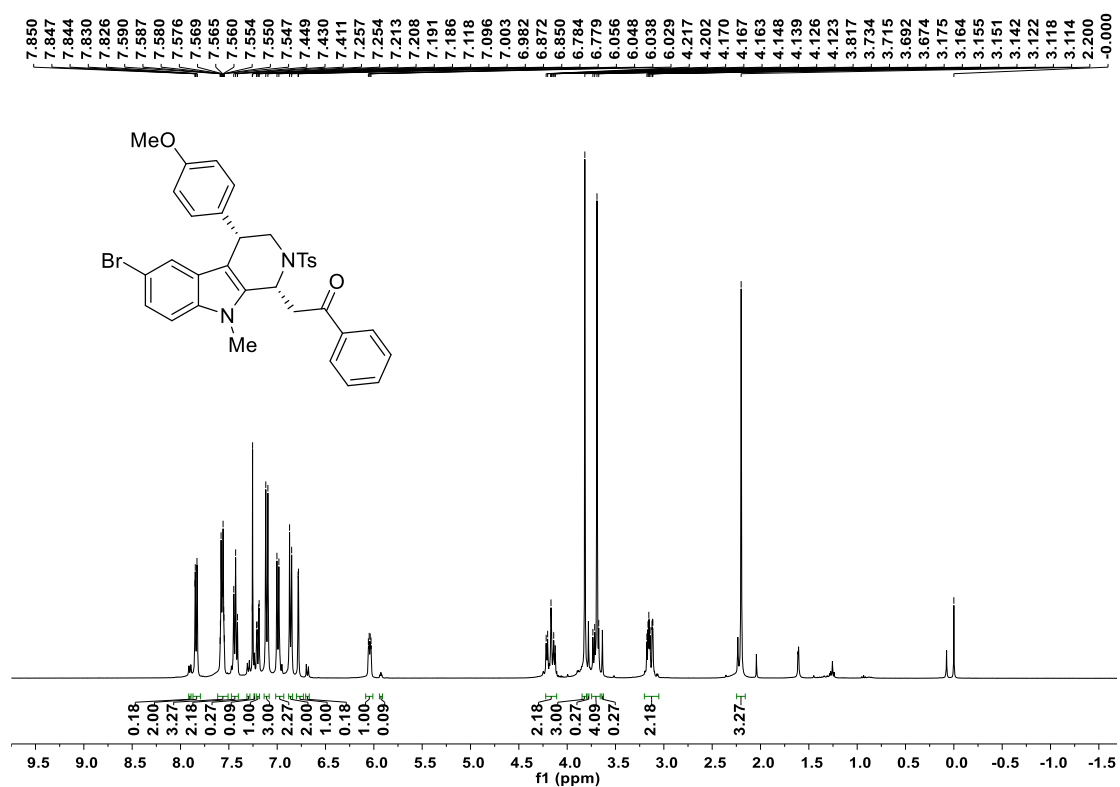
^1H NMR of **3o** in CDCl_3 (a mixture of diastereomers, 10:1 dr)



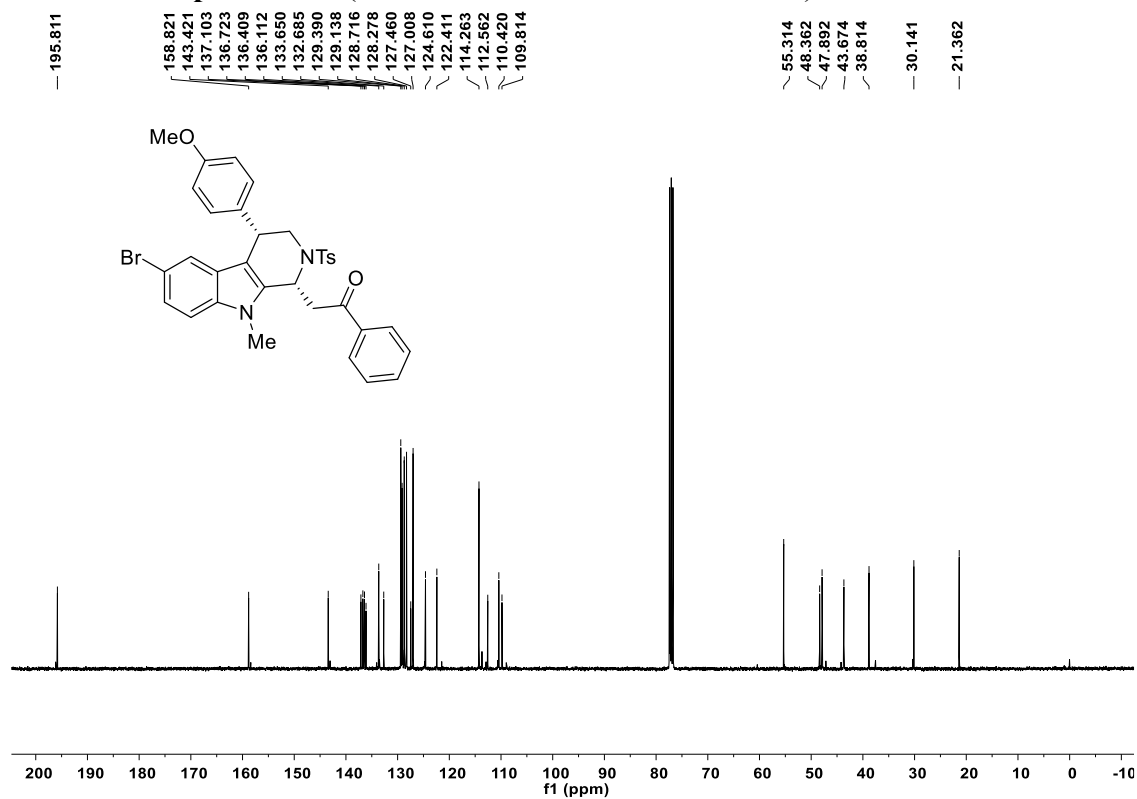
^{13}C NMR of **3o** in CDCl_3 (a mixture of diastereomers, 10:1 dr)



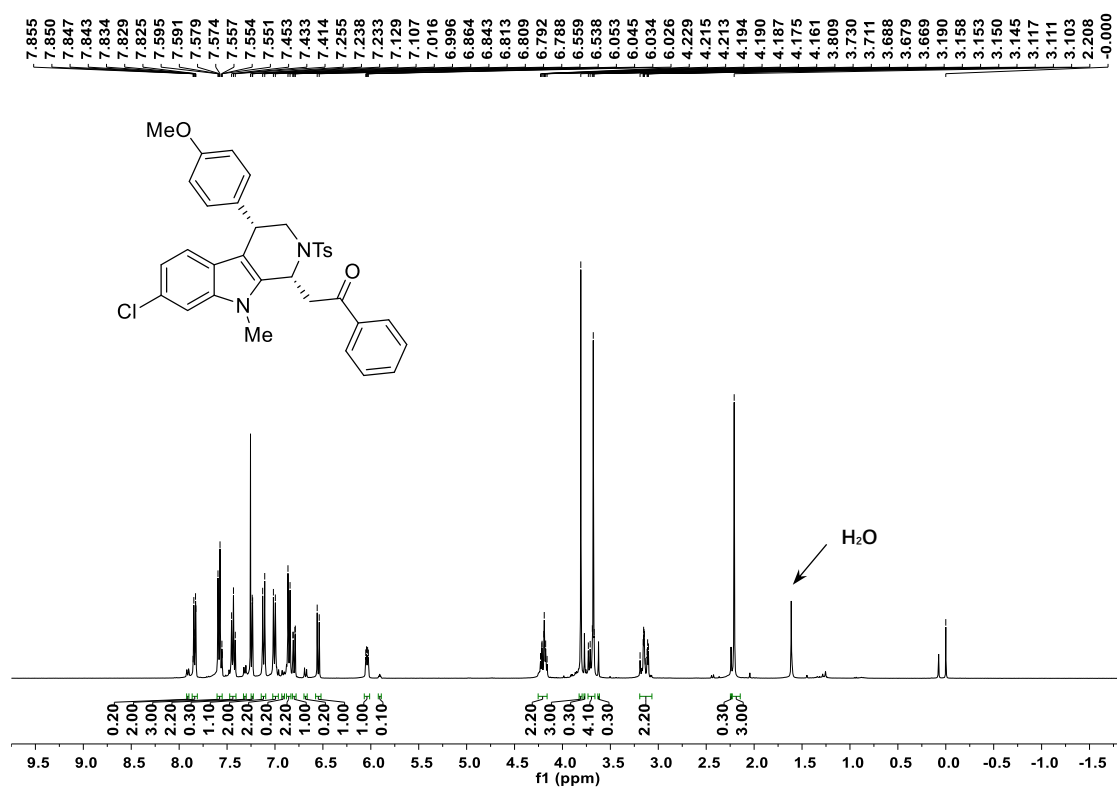
^1H NMR of **3p** in CDCl_3 (a mixture of diastereomers, 11:1 dr)



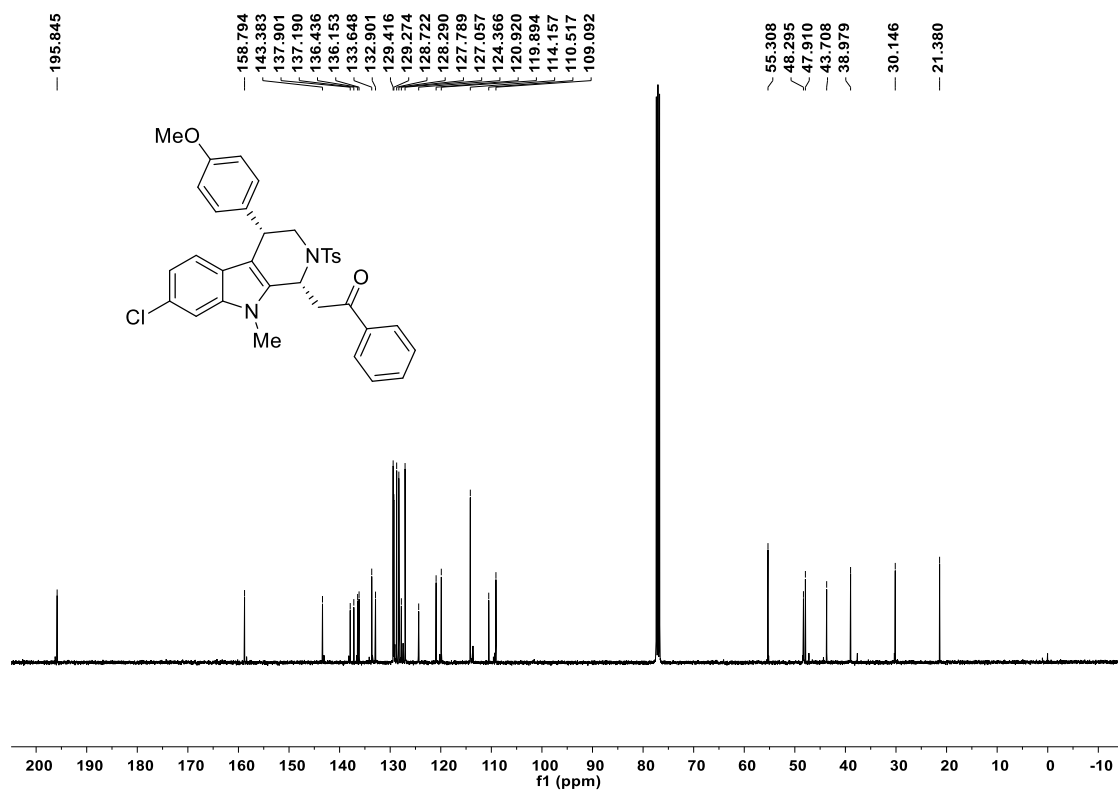
^{13}C NMR of **3p** in CDCl_3 (a mixture of diastereomers, 11:1 dr)



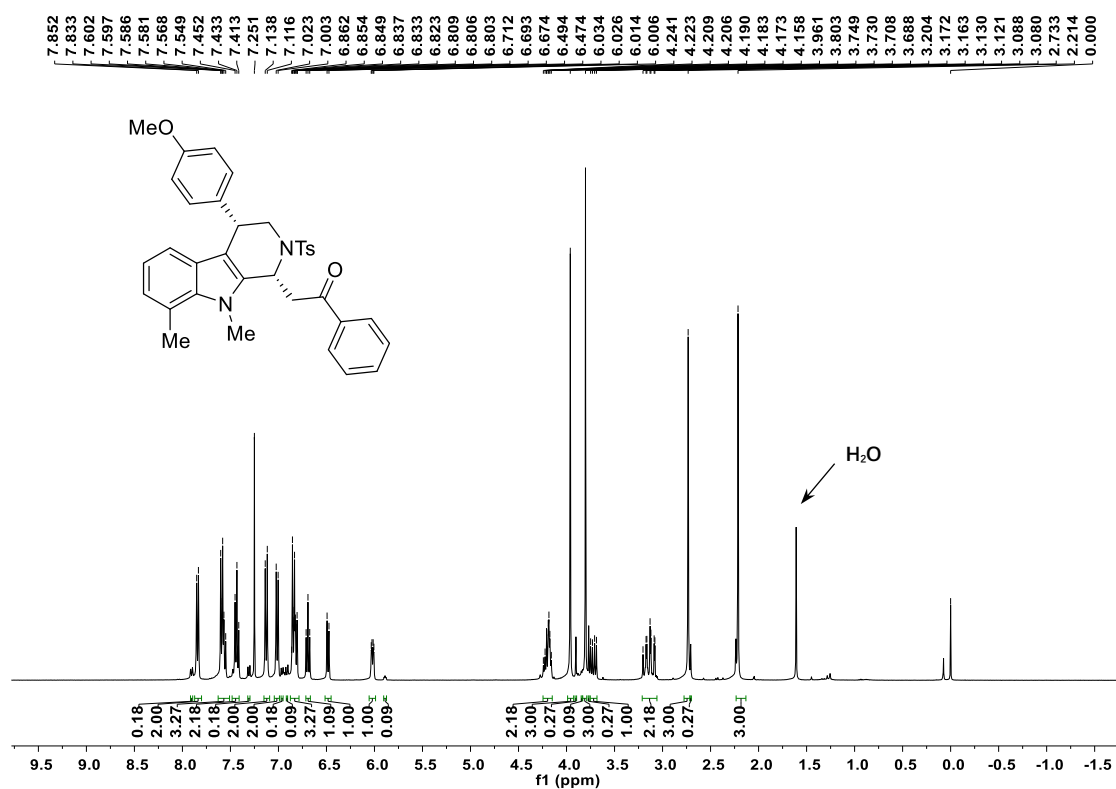
^1H NMR of **3q** in CDCl_3 (a mixture of diastereomers, 10:1 dr)



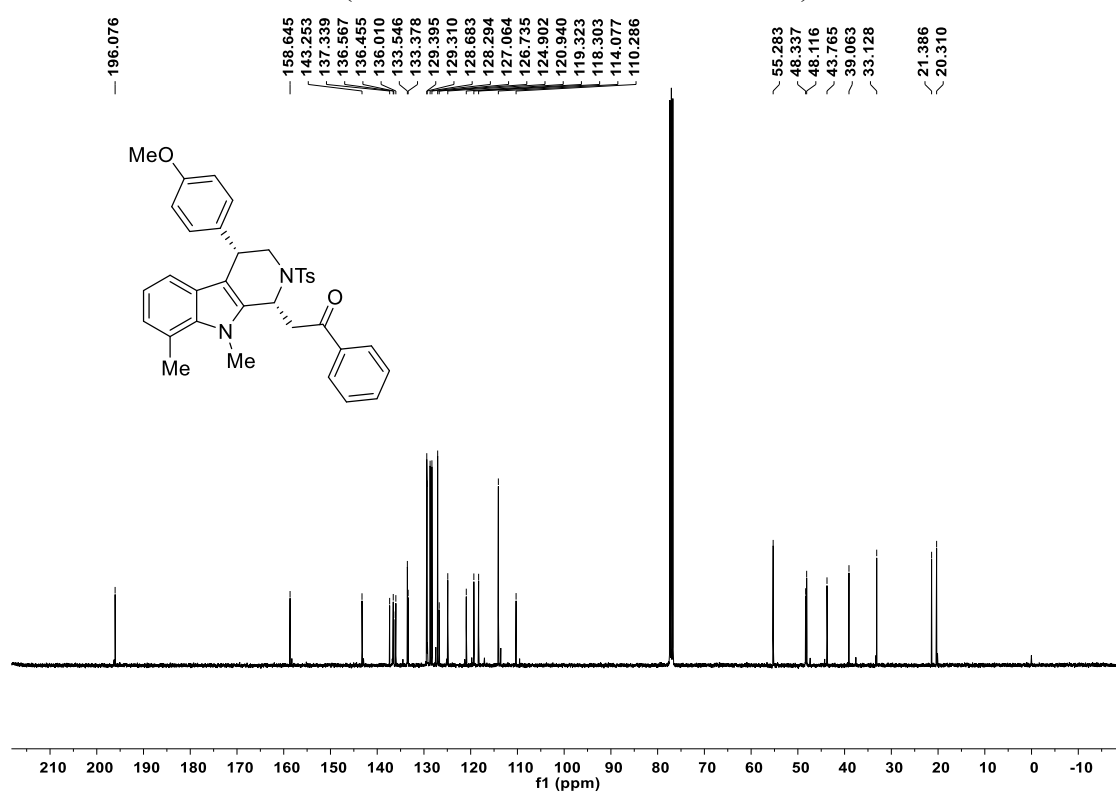
^{13}C NMR of **3q** in CDCl_3 (a mixture of diastereomers, 10:1 dr)



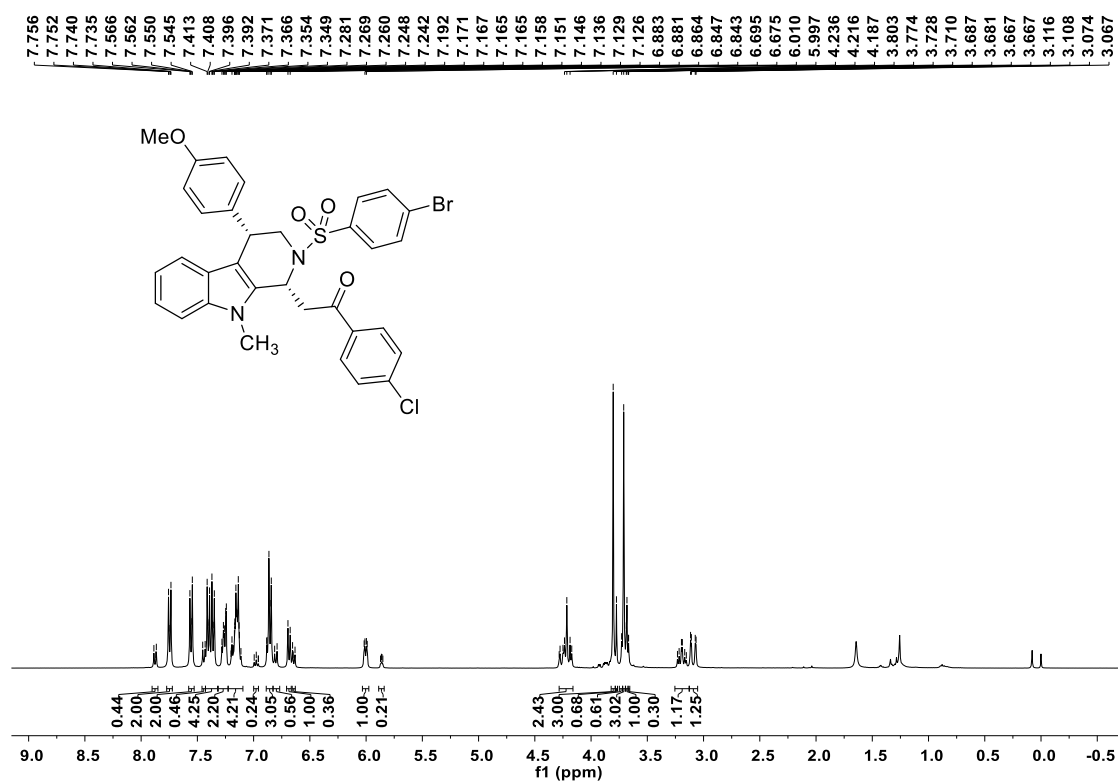
^1H NMR of **3r** in CDCl_3 (a mixture of diastereomers, 11:1 dr)



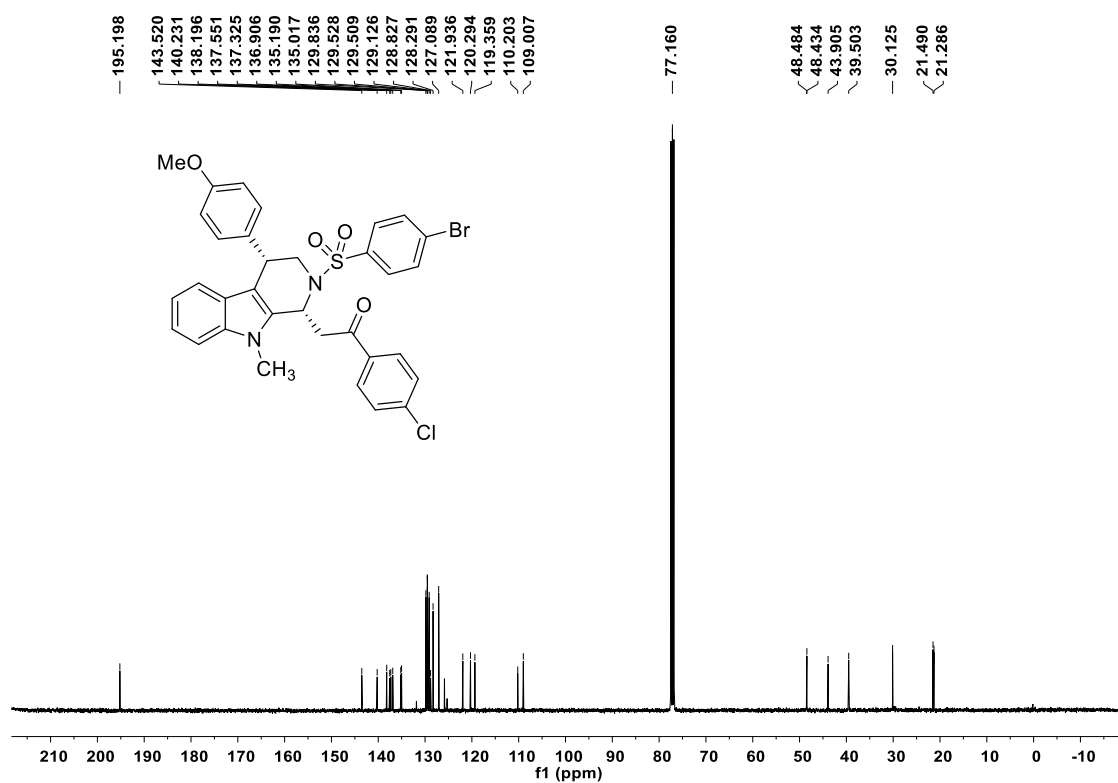
^{13}C NMR of **3r** in CDCl_3 (a mixture of diastereomers, 11:1 dr)



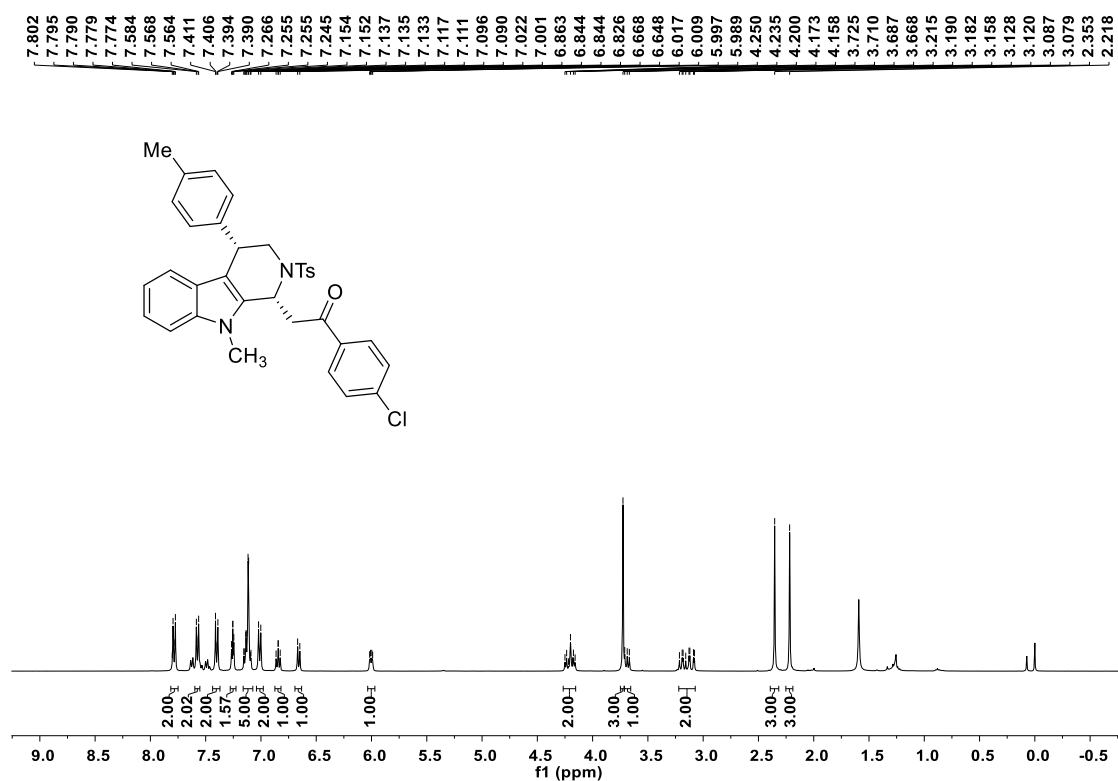
^1H NMR of **3s** in CDCl_3 (a mixture of diastereomers, 5:1 dr)



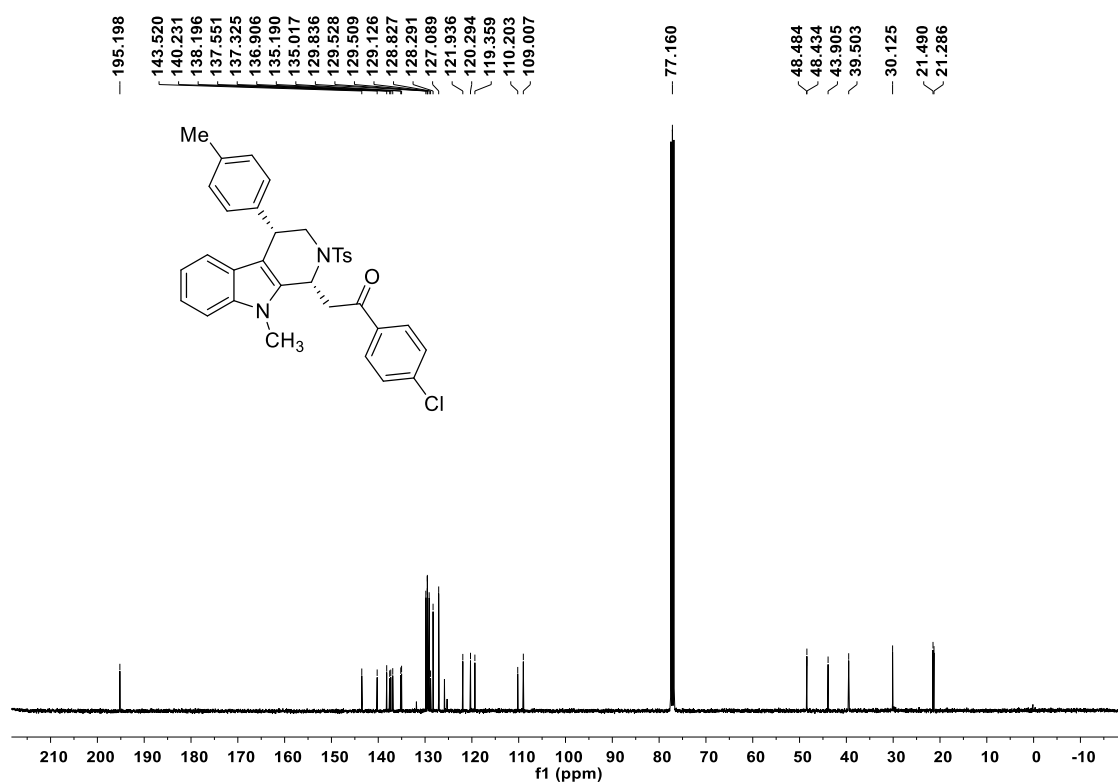
^{13}C NMR of **3s** in CDCl_3 (a mixture of diastereomers, 5:1 dr)



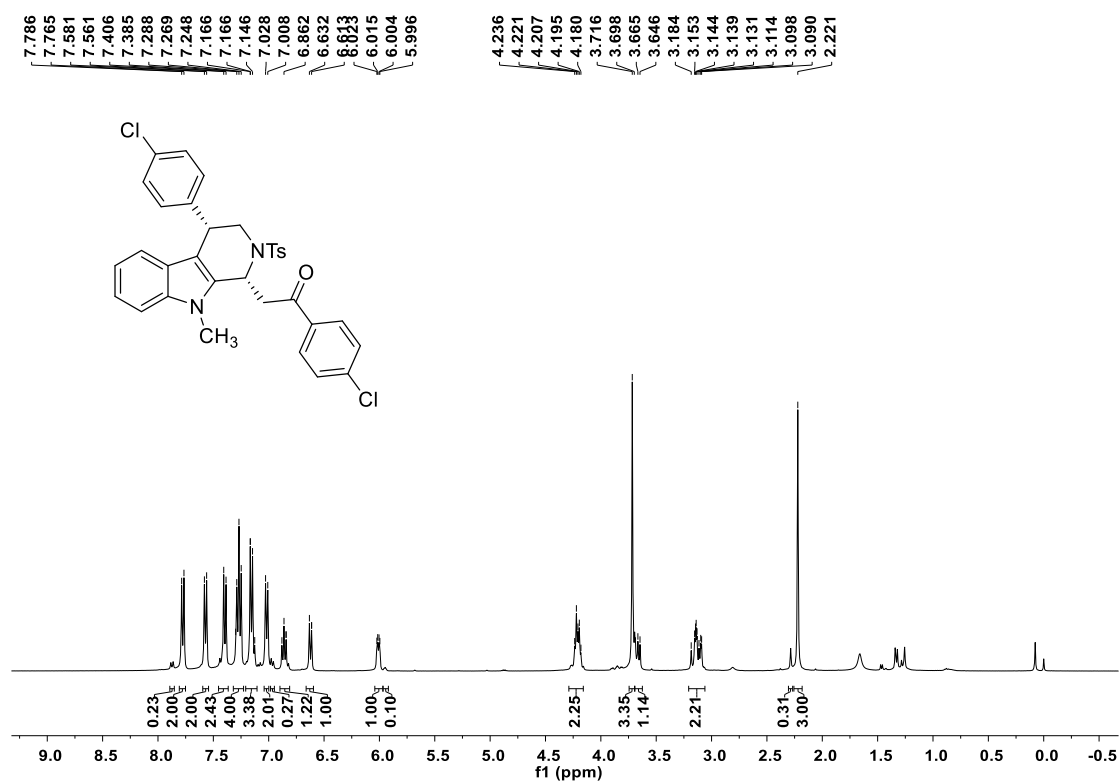
¹H NMR of **3t** in CDCl₃



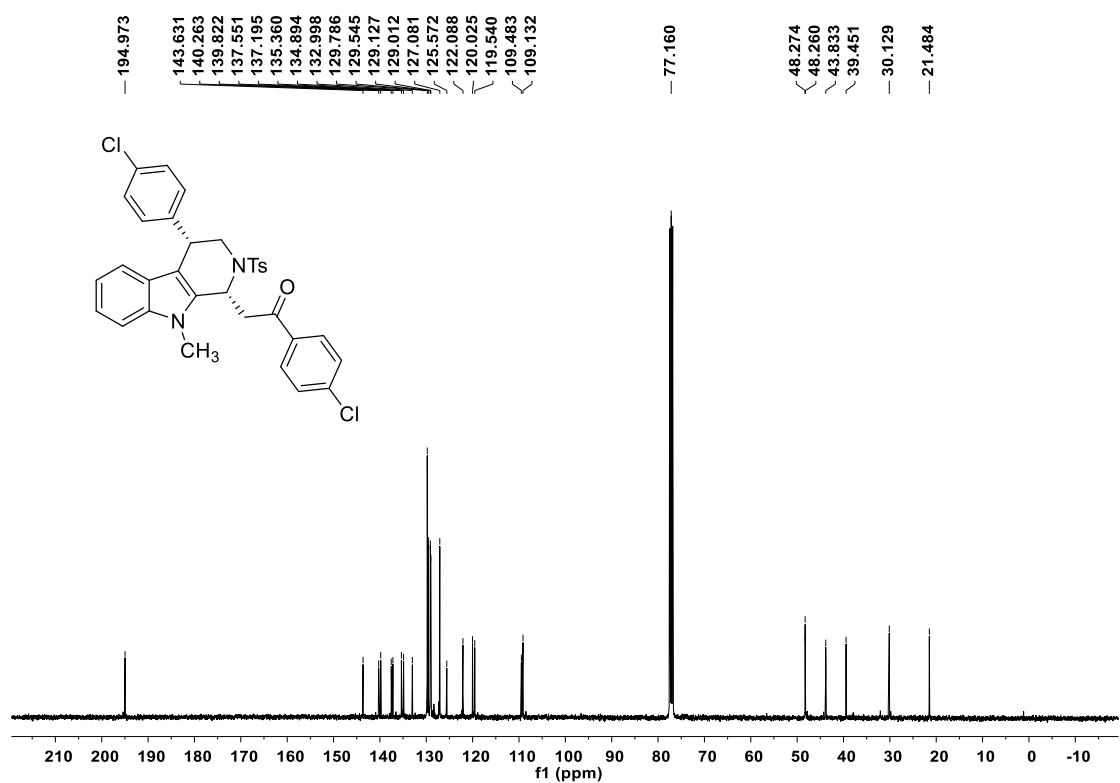
¹³C NMR of **3t** in CDCl₃



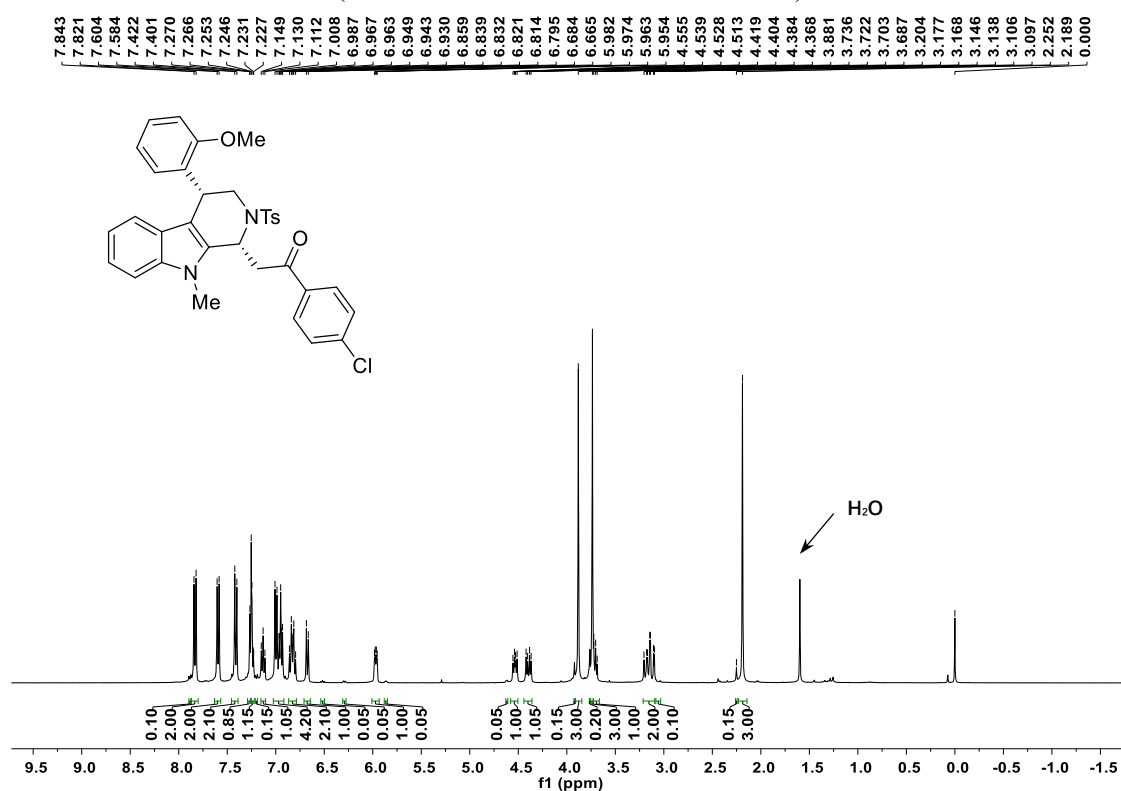
^1H NMR of **3u** in CDCl_3 (a mixture of diastereomers, 12:1 dr)



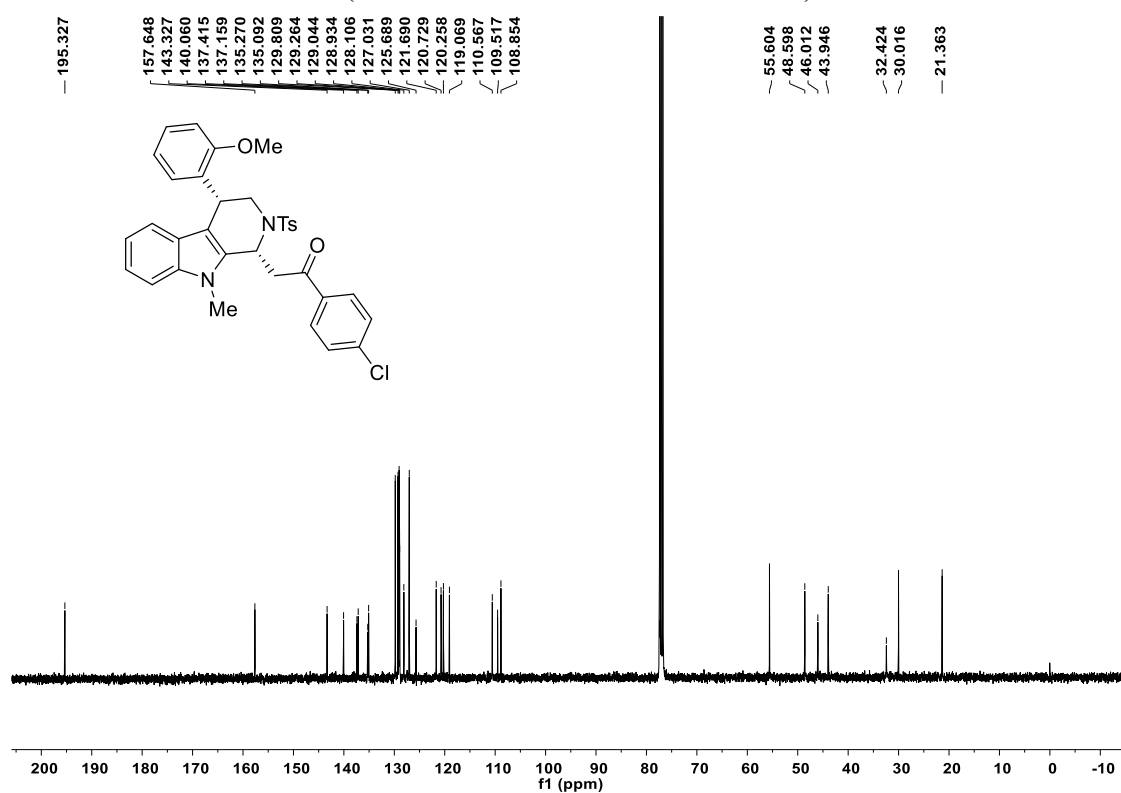
^{13}C NMR of **3u** in CDCl_3 (a mixture of diastereomers, 12:1 dr)



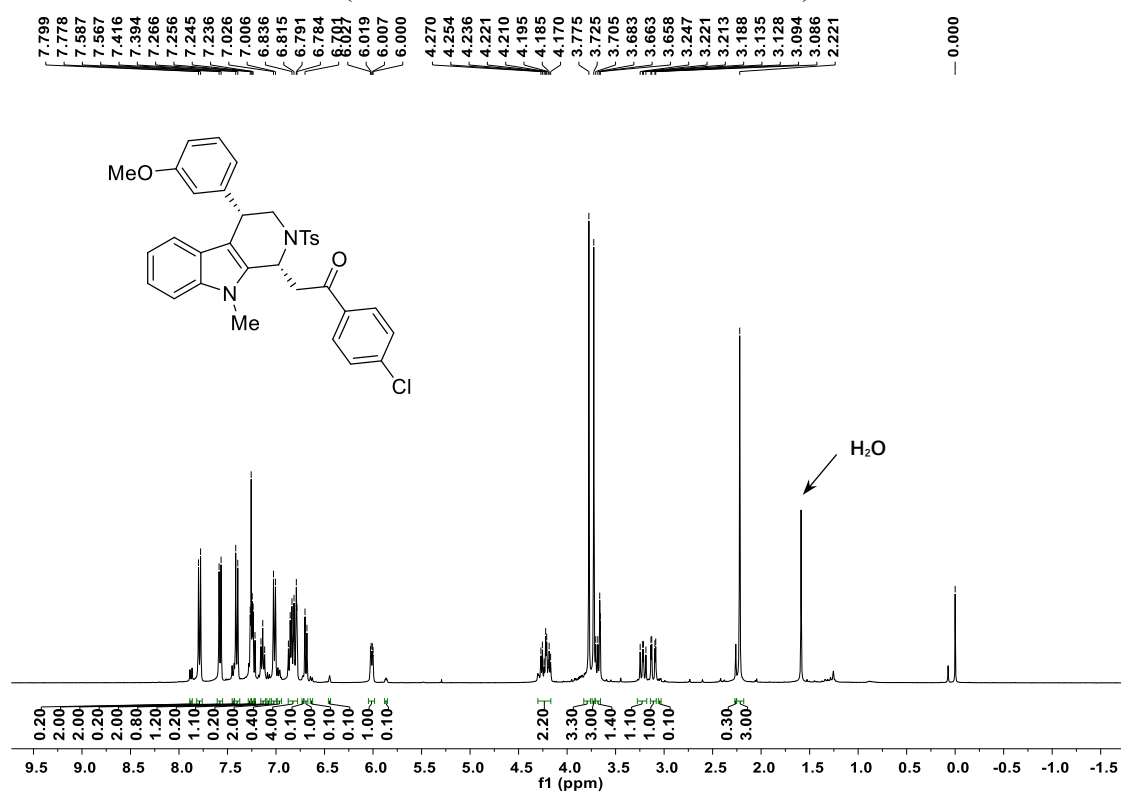
¹H NMR of **3v** in CDCl₃ (a mixture of diastereomers, 20:1 dr)



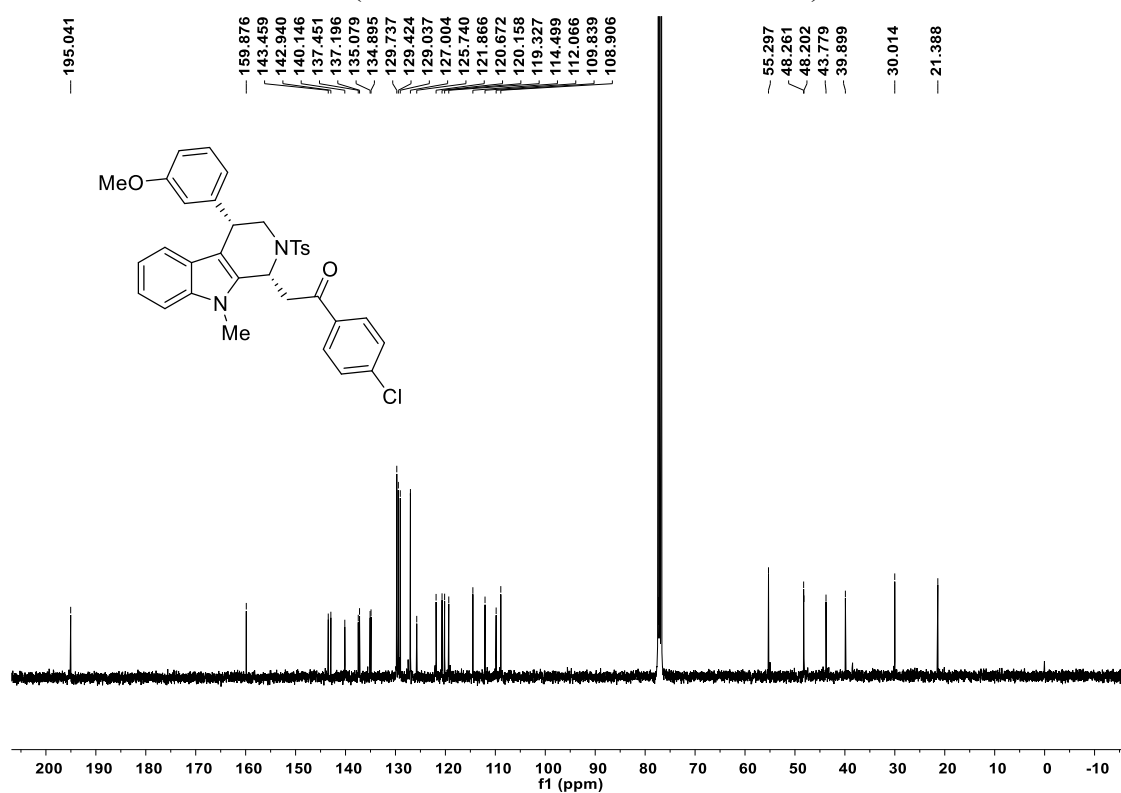
¹³C NMR of **3v** in CDCl₃ (a mixture of diastereomers, 20:1 dr)



^1H NMR of **3w** in CDCl_3 (a mixture of diastereomers, 10:1 dr)

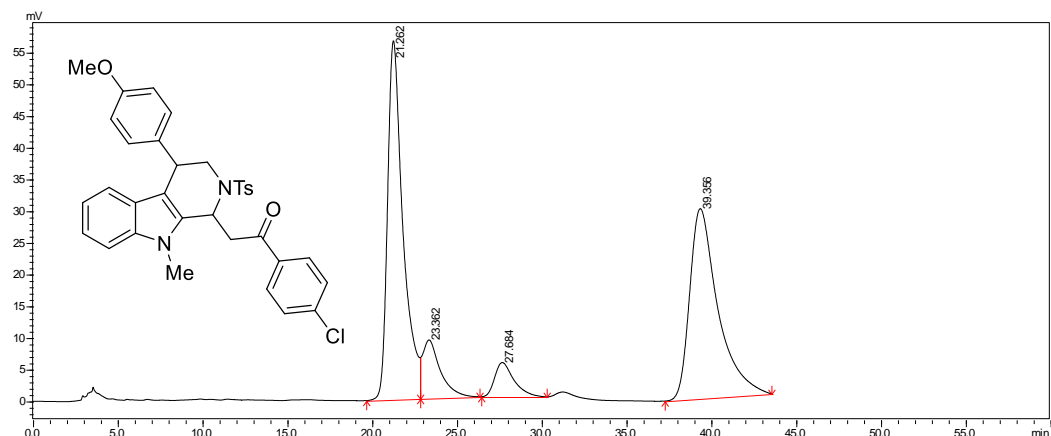


^{13}C NMR of **3w** in CDCl_3 (a mixture of diastereomers, 10:1 dr)

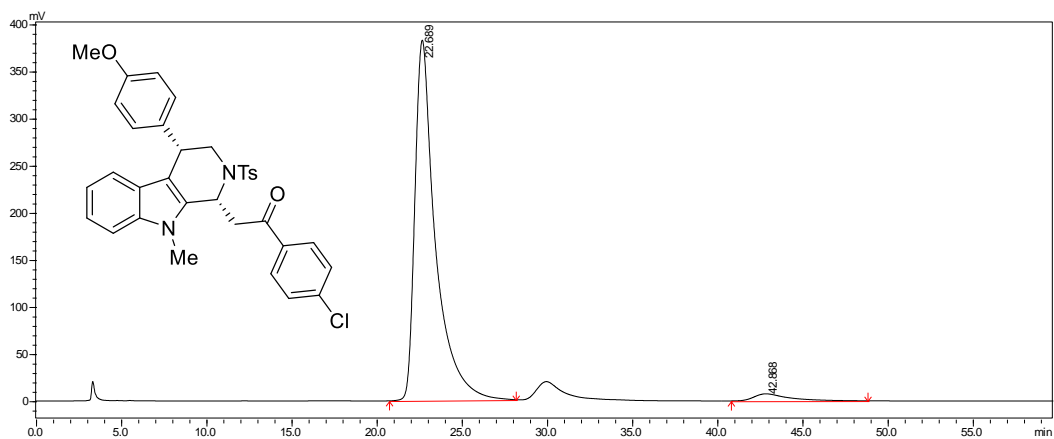


6. HPLC chromatograms

HPLC chromatogram of compound **3a** (94% ee)

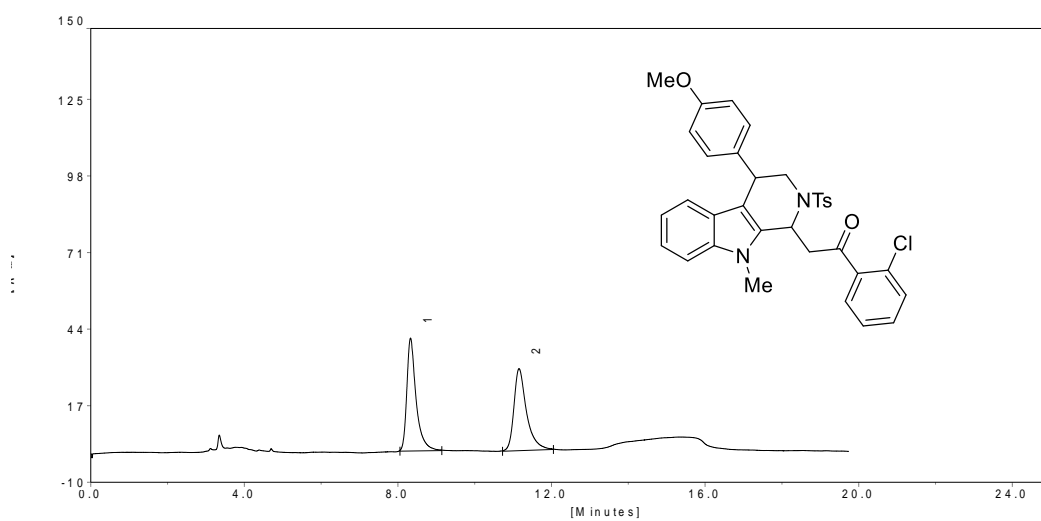


	Ret Time (min)	Height (μ V)	Area (μ V.sec)	Area (%)
1	21.262	56589	3572754	43.845
2	23.362	9229	686093	8.420
3	27.684	5401	424928	5.215
4	39.356	29961	3464855	42.521

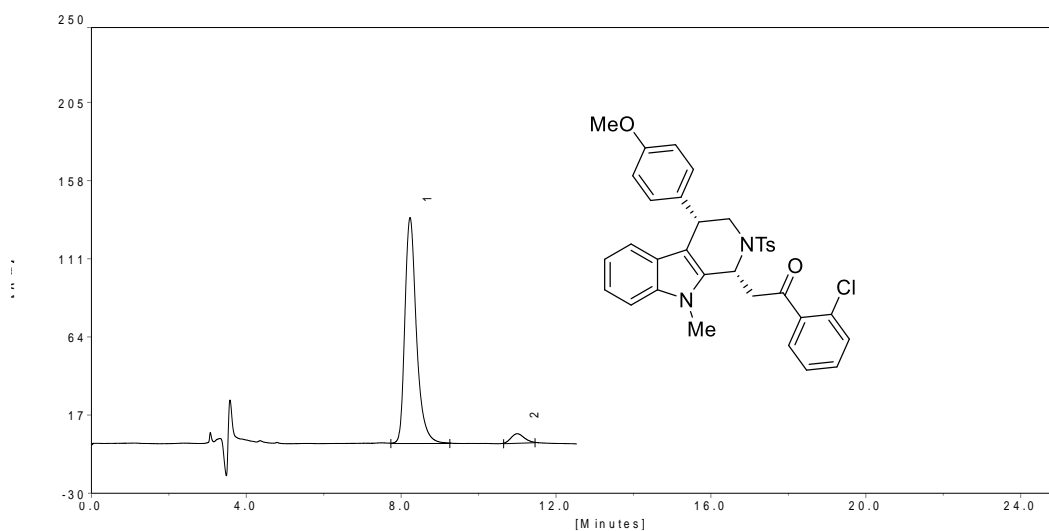


	Ret Time (min)	Height (μ V)	Area (μ V.sec)	Area (%)
1	22.689	382602	32072955	96.808
2	42.868	7523	1057681	3.192

HPLC chromatogram of compound **3b** (91% ee)

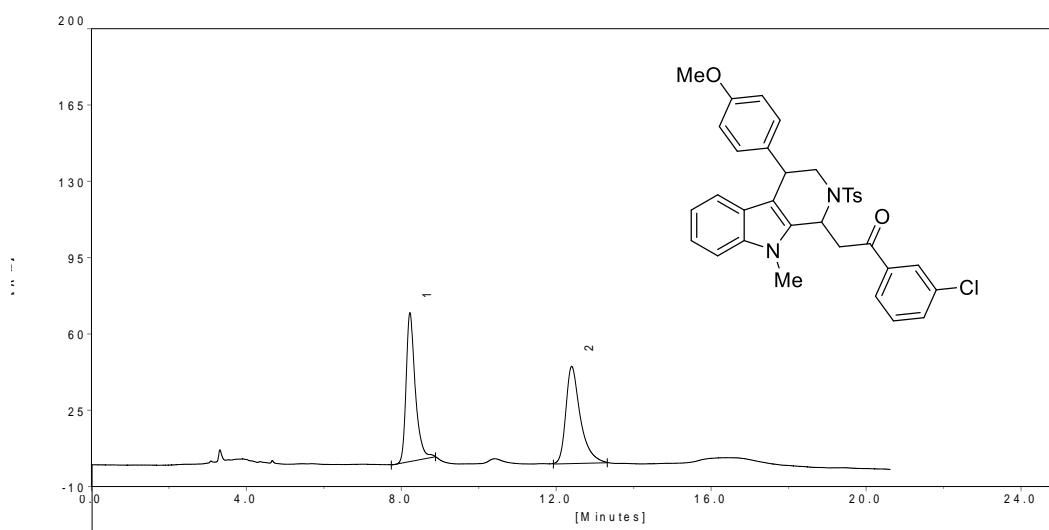


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	8.32833	39.68	658.64	50.4002
2	11.15500	28.79	648.18	49.5998

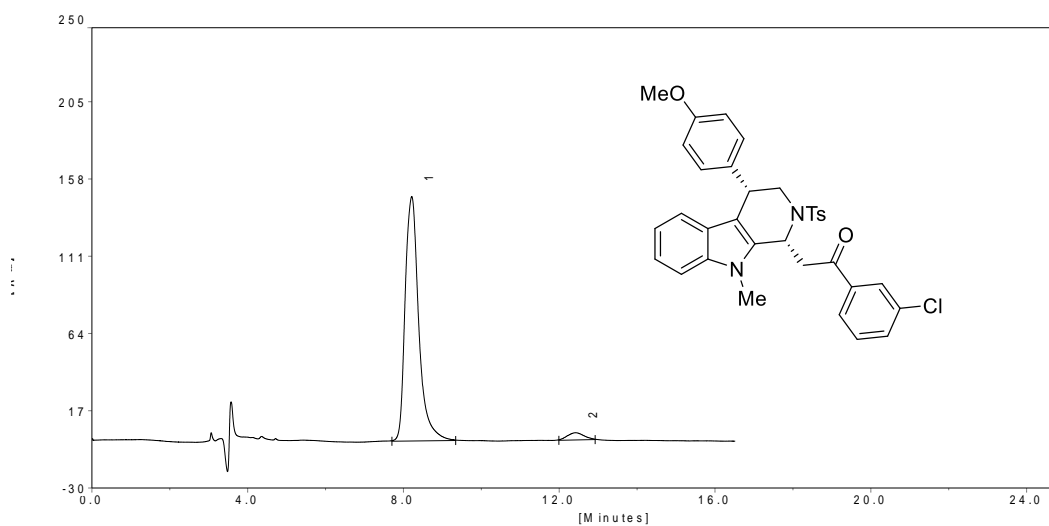


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	8.23083	135.66	2797.19	95.7101
2	10.99667	5.49	125.38	4.2899

HPLC chromatogram of compound **3c** (94% ee)

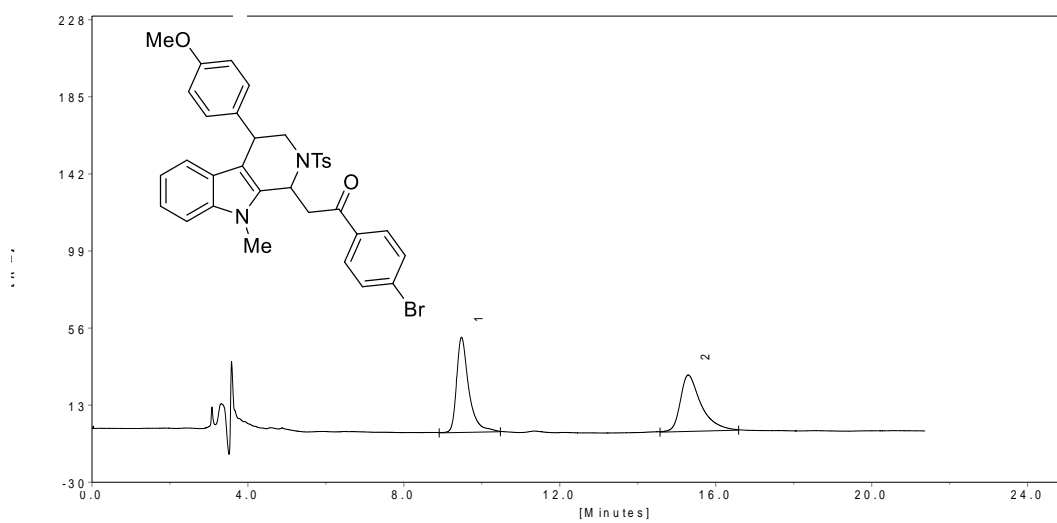


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	8.22167	68.12	1106.63	49.2063
2	12.39750	44.42	1142.33	50.7937

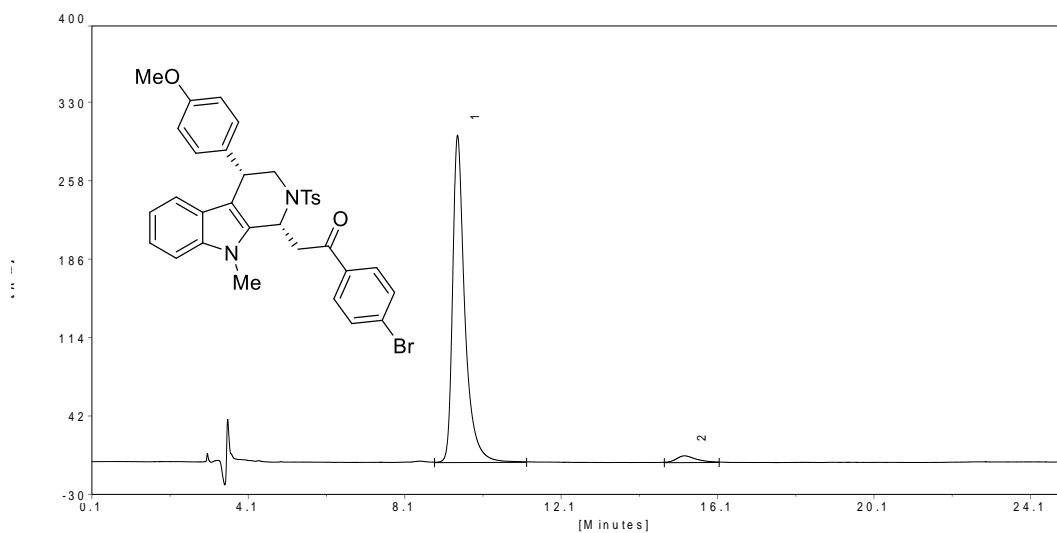


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	8.21500	148.50	3582.91	96.8629
2	12.42667	4.1	116.04	3.1371

HPLC chromatogram of compound **3d** (94% ee)

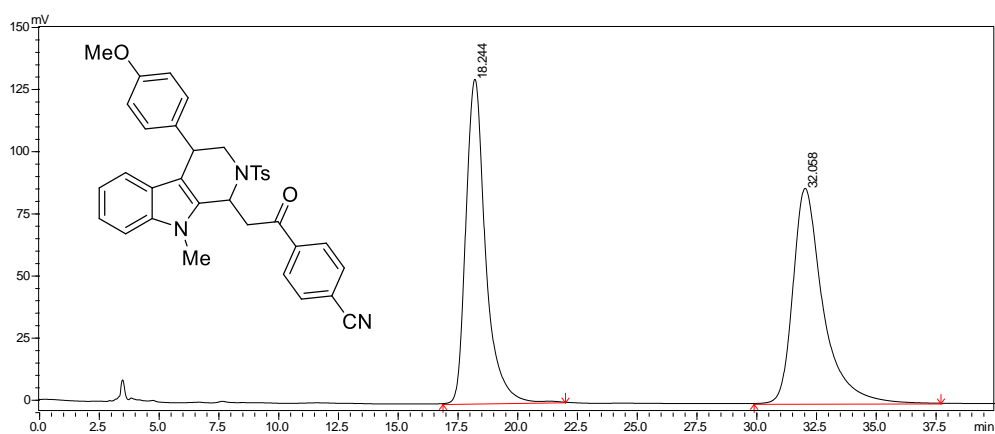


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	9.47750	52.96	1136.40	50.0876
2	15.29000	31.22	1132.42	49.9124

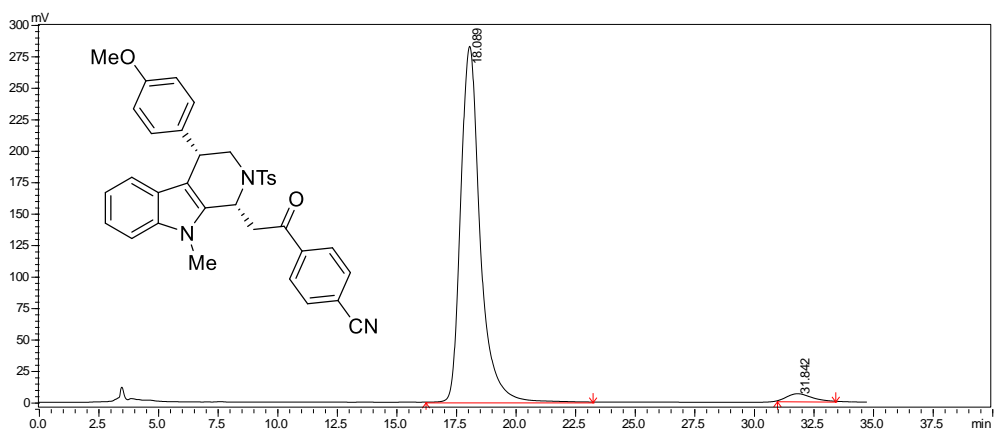


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	9.45250	300.14	6490.53	97.1084
2	15.25167	5.83	193.27	2.8916

HPLC chromatogram of compound **3e** (95% ee)

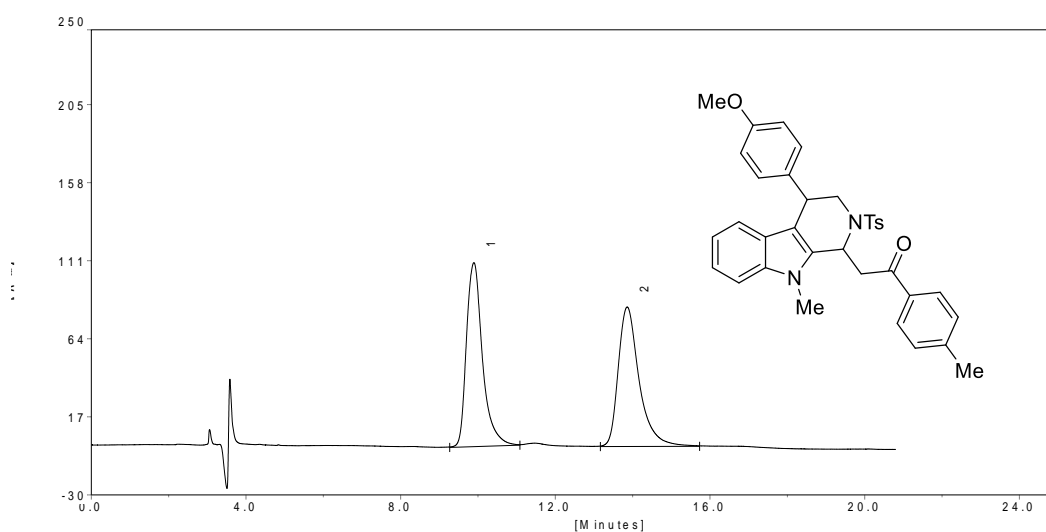


	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	18.244	130332	7434994	49.671
2	32.058	86542	7533450	50.329

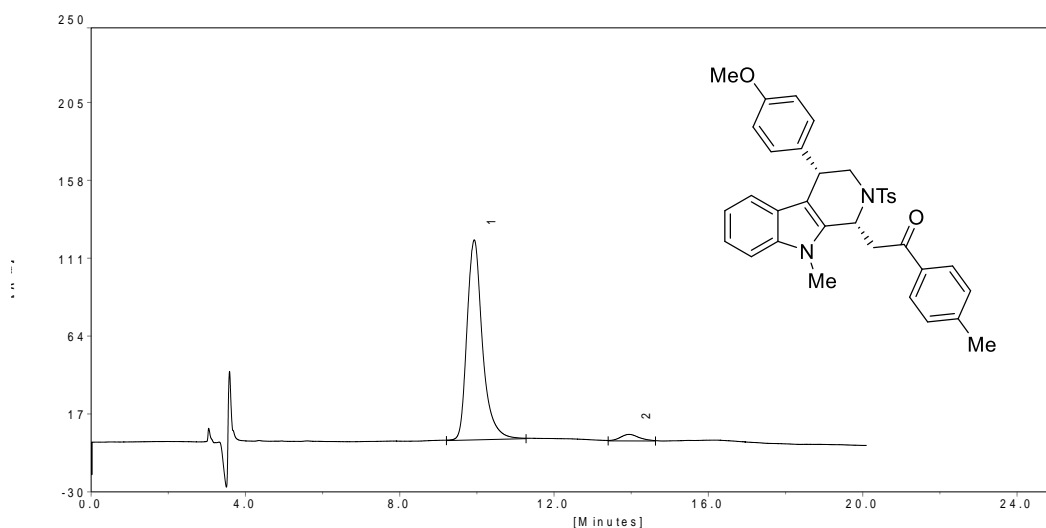


	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	18.089	282680	16017871	97.583
2	31.842	5808	396730	2.417

HPLC chromatogram of compound **3f** (93% ee)

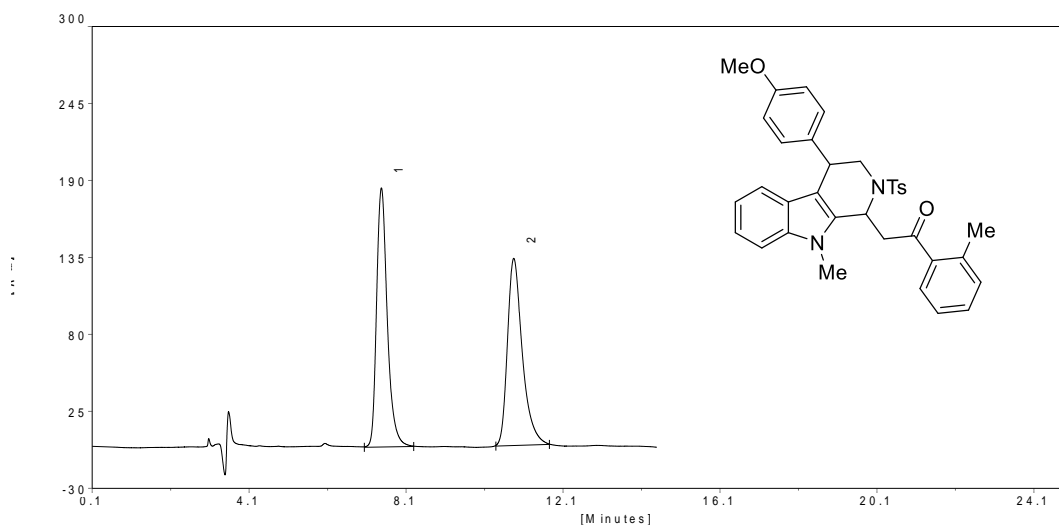


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	9.89500	110.51	3159.43	50.3766
2	13.86000	83.76	3112.20	49.6234

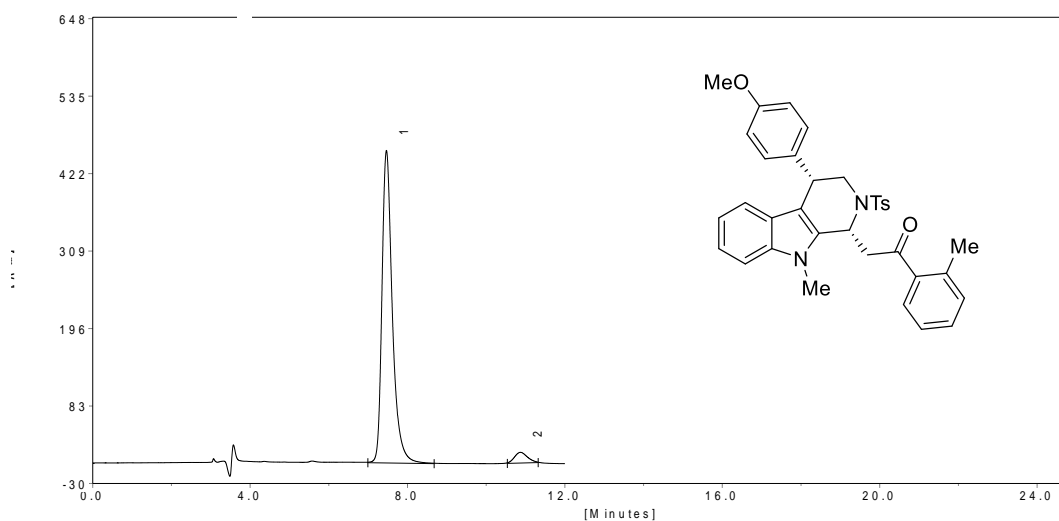


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	9.93250	120.50	3332.84	96.6480
2	13.93750	3.69	115.59	3.3520

HPLC chromatogram of compound **3g** (92% ee)

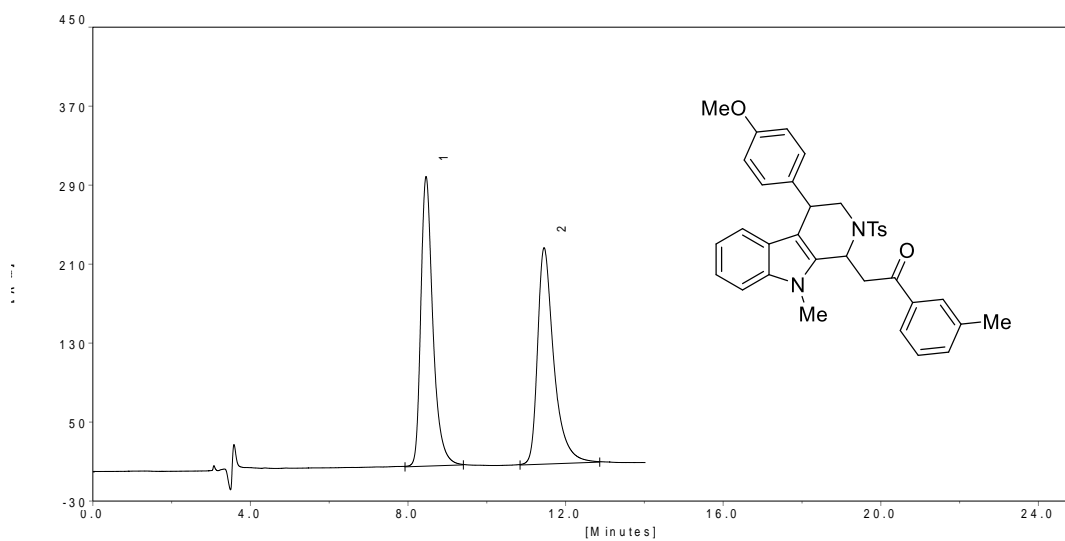


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	7.47167	184.83	3480.32	49.9441
2	10.84667	133.45	3488.11	50.0559

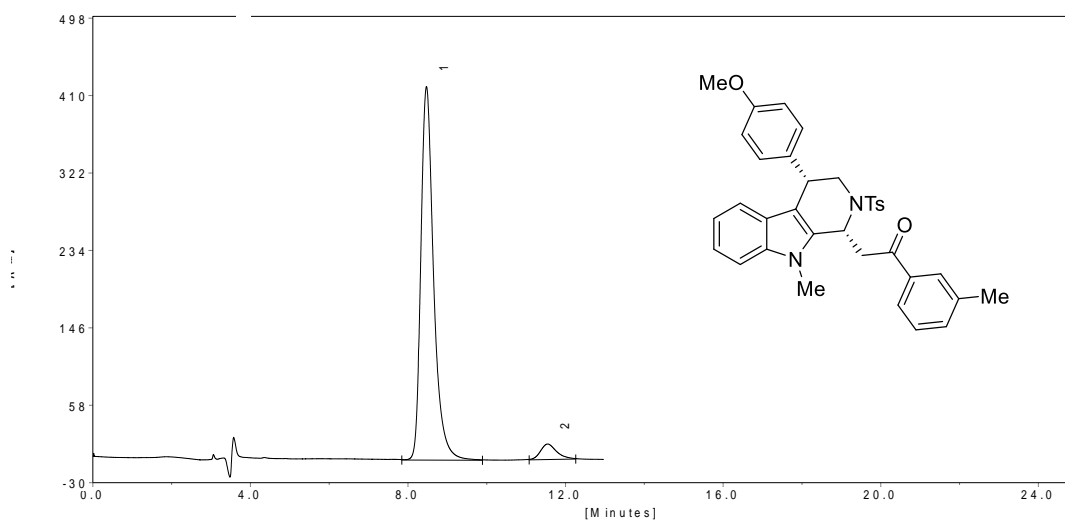


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	7.46500	455.20	8297.99	96.1813
2	10.86500	15.01	329.46	3.8187

HPLC chromatogram of compound **3h** (91% ee)

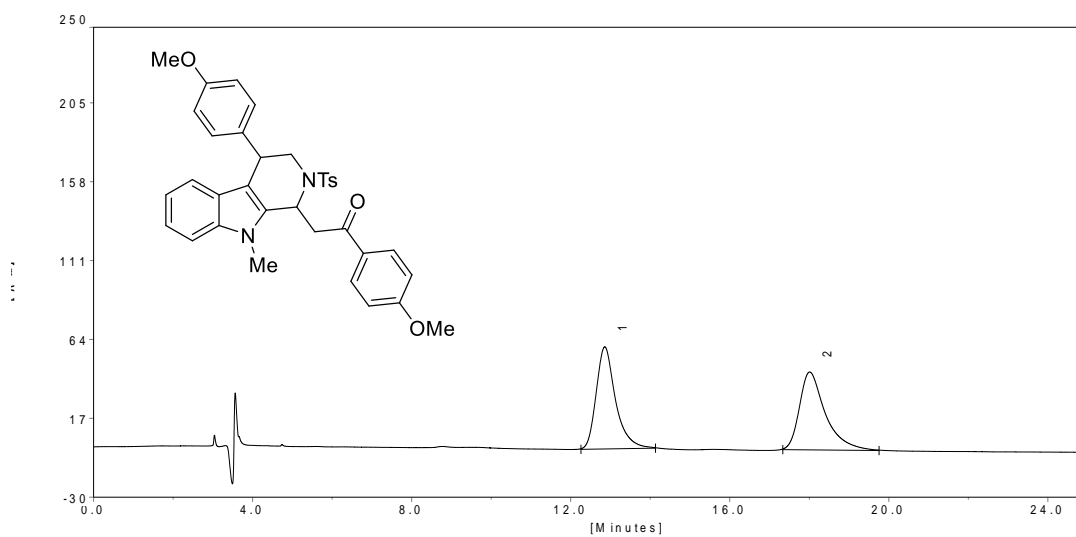


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	8.45833	293.00	6201.94	49.8837
2	11.45417	218.85	6230.85	50.1163

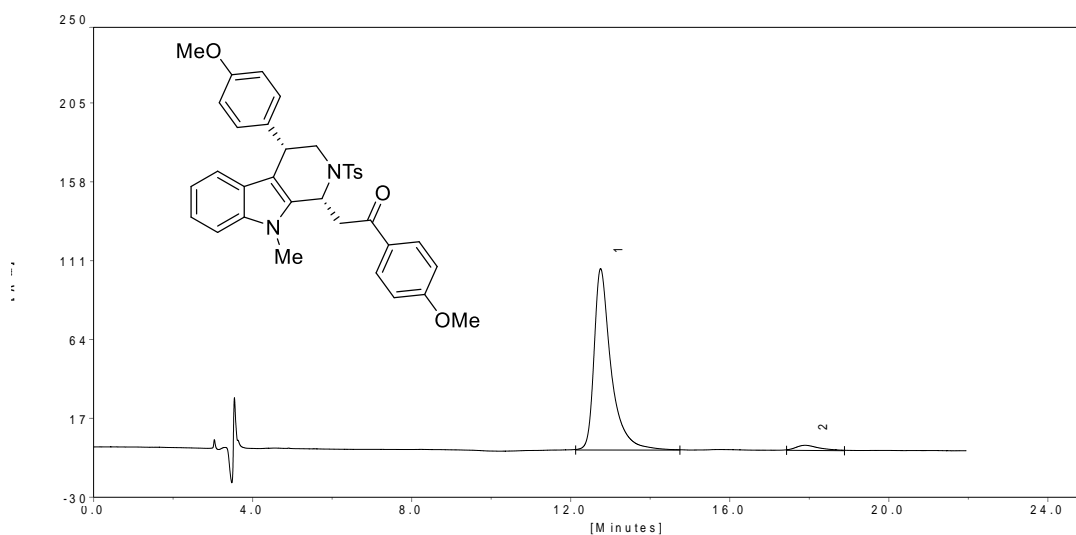


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	8.46833	424.07	9505.45	95.2914
2	11.54083	17.13	469.69	4.7086

HPLC chromatogram of compound **3i** (94% ee)

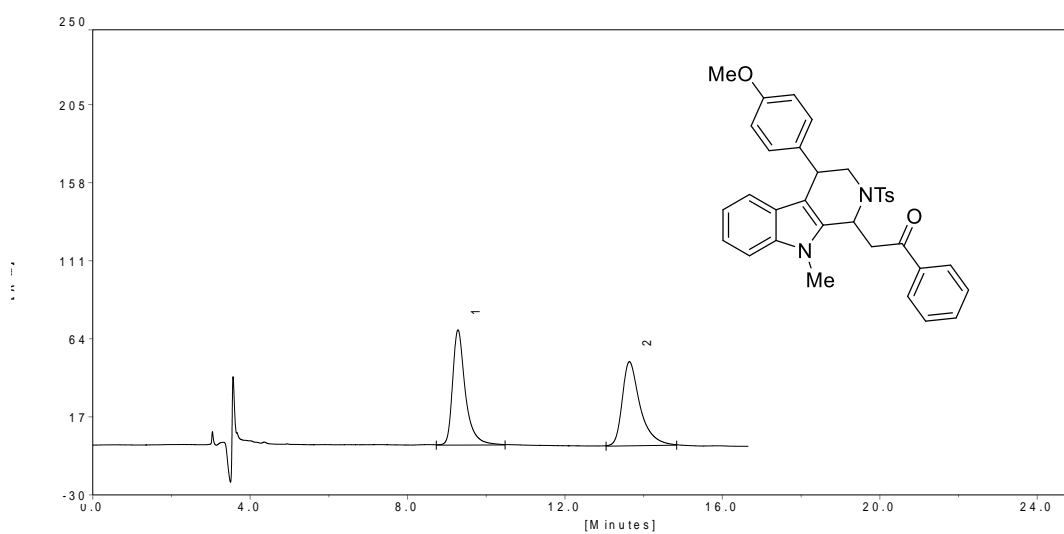


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	12.85917	60.62	2024.33	49.5881
2	18.00833	46.16	2057.96	50.4119

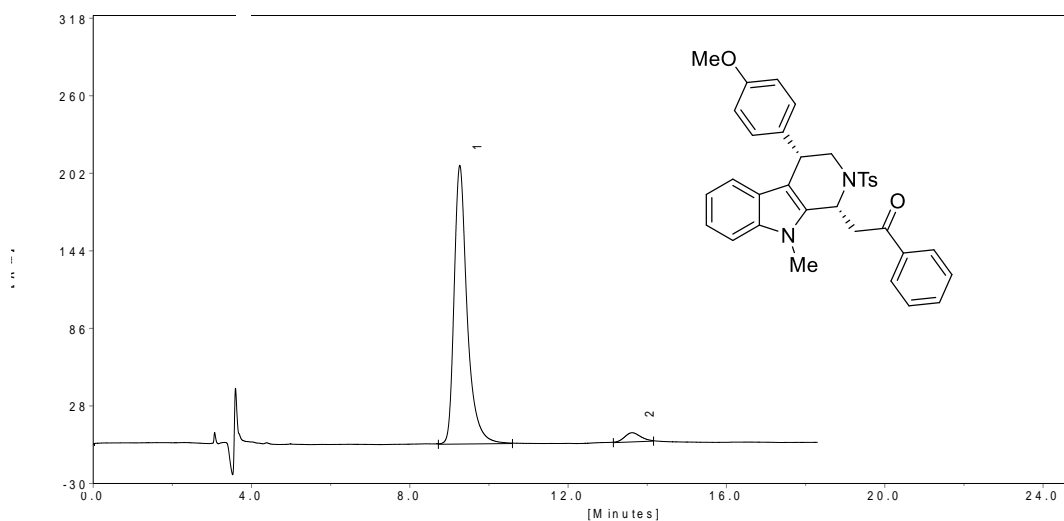


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	12.75167	107.89	3178.17	96.8045
2	17.90167	2.80	104.91	3.1955

HPLC chromatogram of compound **3j** (93% ee)

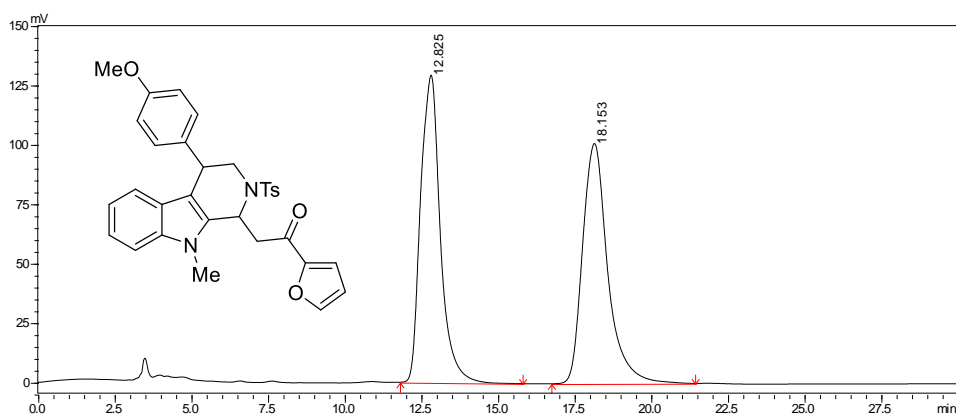


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	9.28167	69.14	1538.36	49.4357
2	13.63667	50.45	1573.48	50.5643

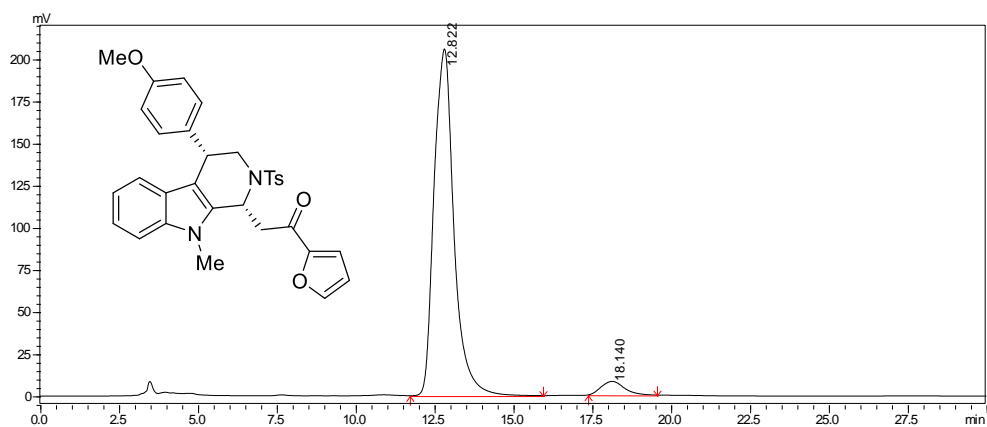


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	9.26333	208.21	4730.25	96.4141
2	13.61833	6.56	175.93	3.5859

HPLC chromatogram of compound **3k** (91% ee)

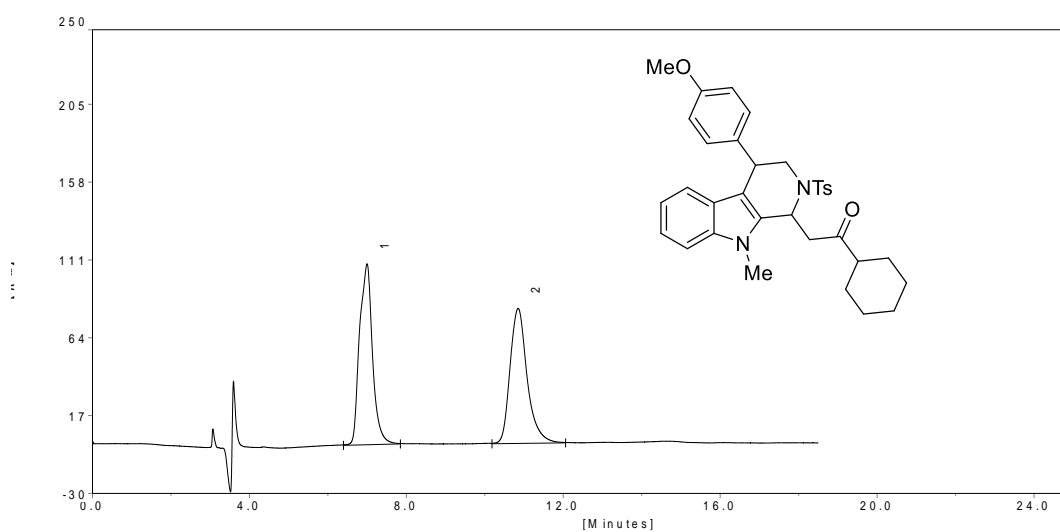


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	12.825	129308	5772123	50.010
2	18.153	101023	5769740	49.990

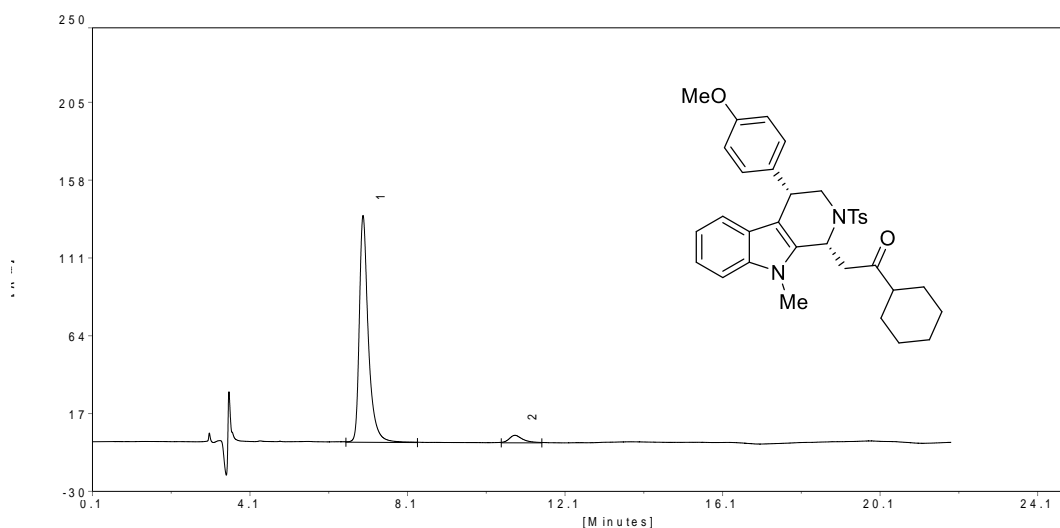


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	12.822	205734	9017998	95.648
2	18.140	8061	410359	4.352

HPLC chromatogram of compound **31** (92% ee)

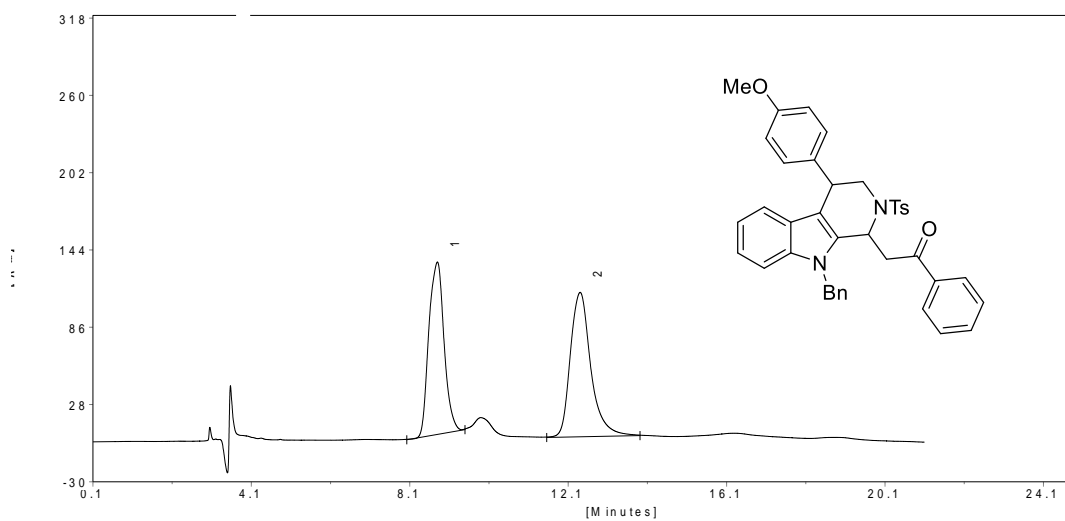


	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.99917	109.01	2479.51	50.4105
2	10.85167	81.31	2439.12	49.5895

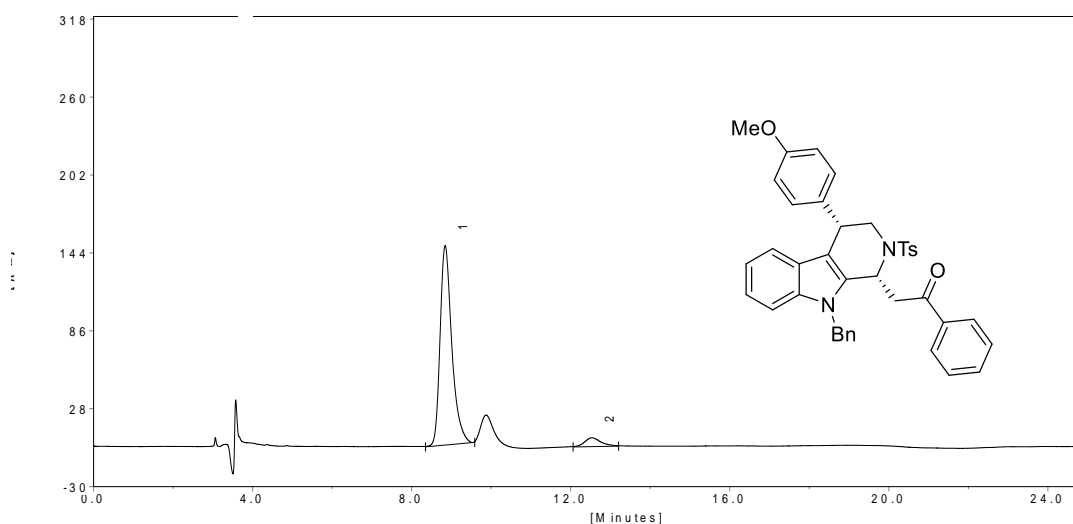


	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.97250	136.80	2153.41	95.7685
2	10.82583	4.30	95.15	4.2315

HPLC chromatogram of compound **3m** (89% ee)

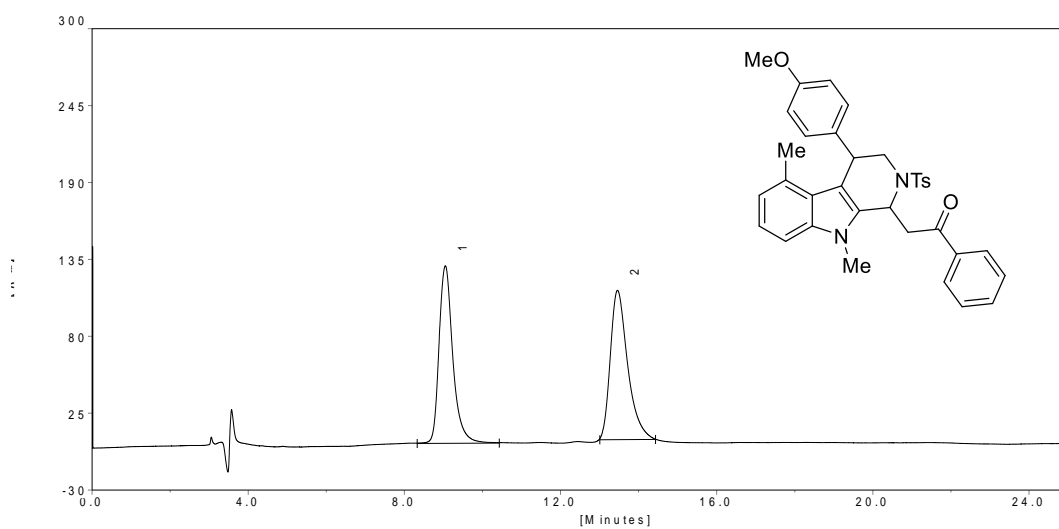


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	8.80000	129.05	3414.62	47.0523
2	12.40167	108.07	3842.46	52.9477

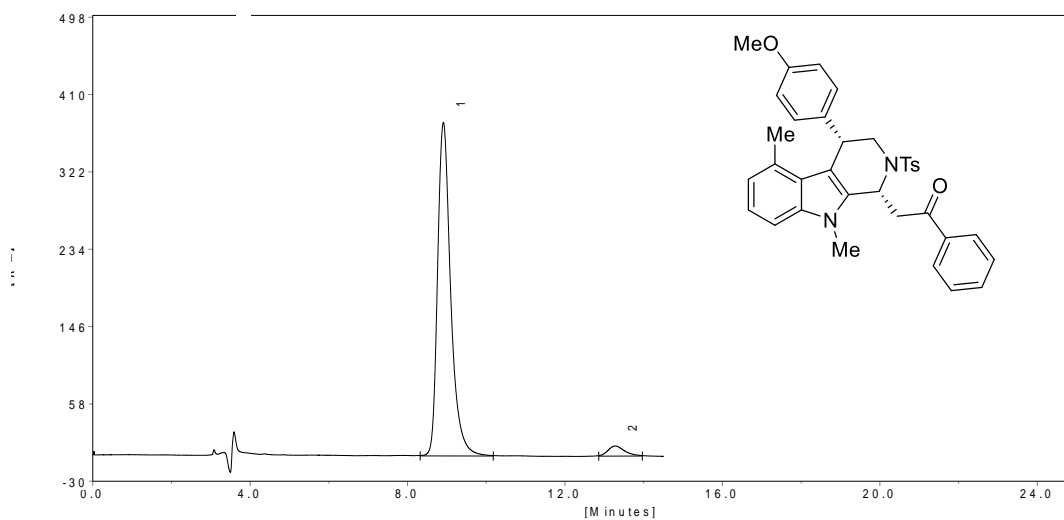


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	8.84167	148.21	3011.36	94.7043
2	12.53000	6.25	168.39	5.2957

HPLC chromatogram of compound **3n** (93% ee)

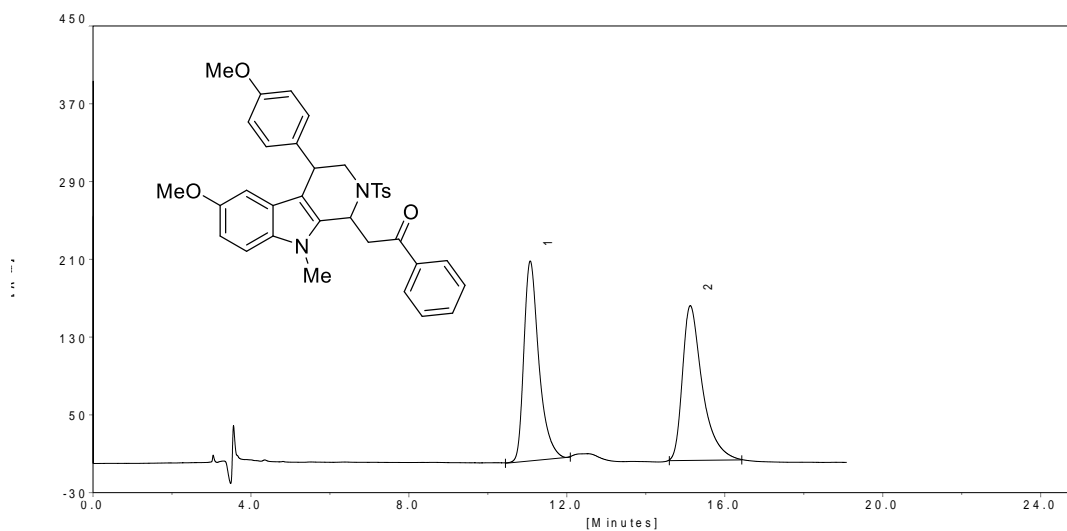


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	9.05000	126.73	3080.35	
	48.5193			
2	13.45917	106.55	3268.36	
	51.4807			

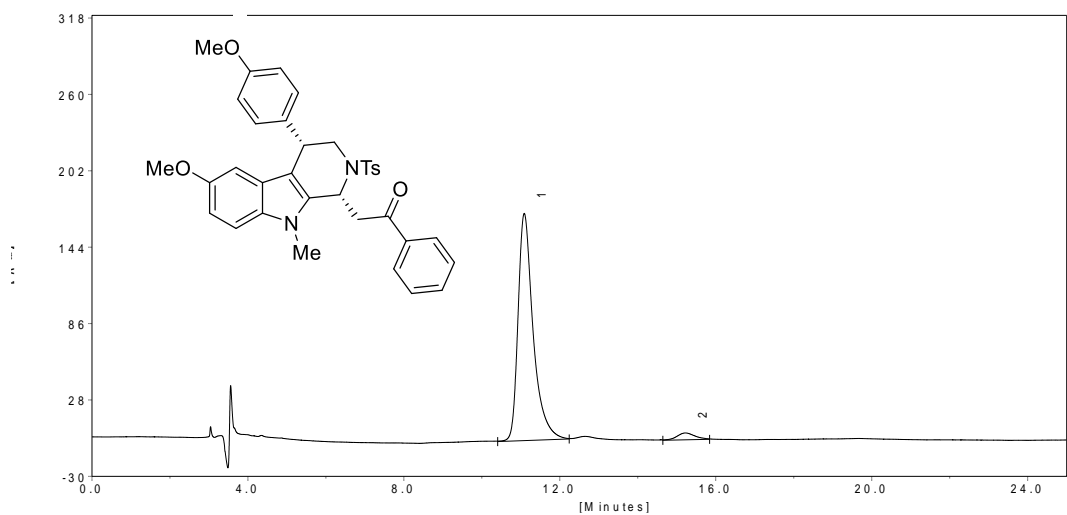


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	8.91083	379.09	8725.42	96.6102
2	13.27583	11.03	306.16	3.3898

HPLC chromatogram of compound **3o** (94% ee)

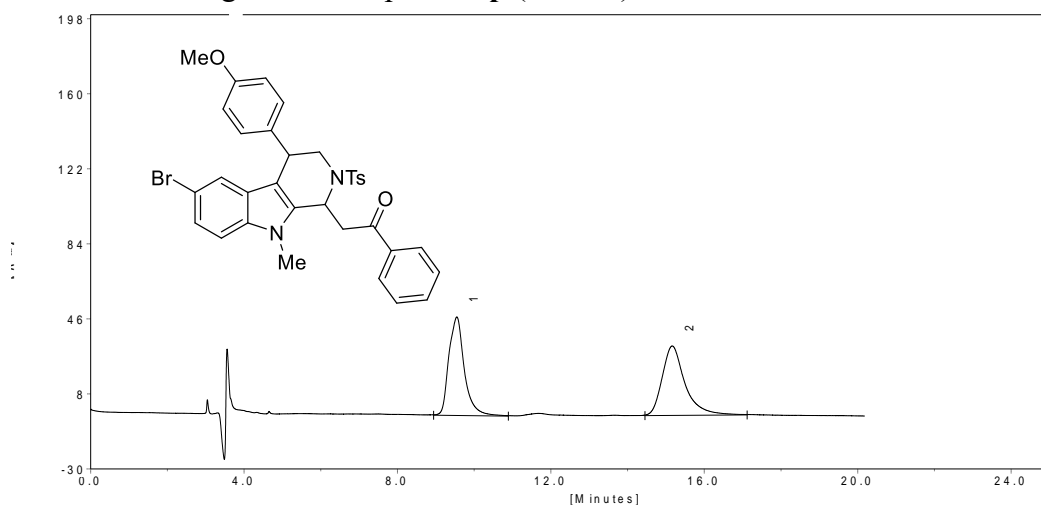


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	11.07333	205.22	5380.43	49.3030
2	15.12667	158.83	5532.54	50.6970

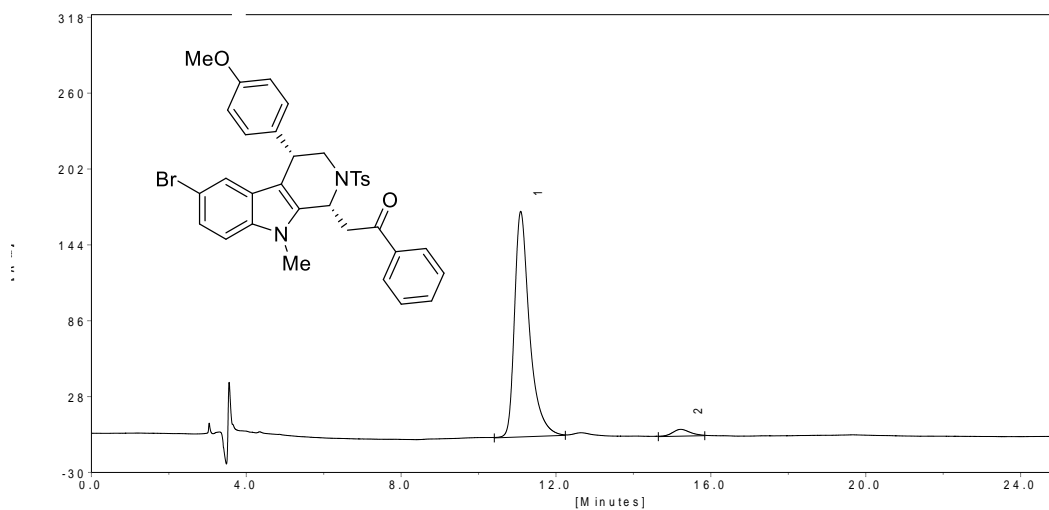


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	11.08917	172.22	4602.48	96.9515
2	15.22167	4.89	144.72	3.0485

HPLC chromatogram of compound **3p** (93% ee)

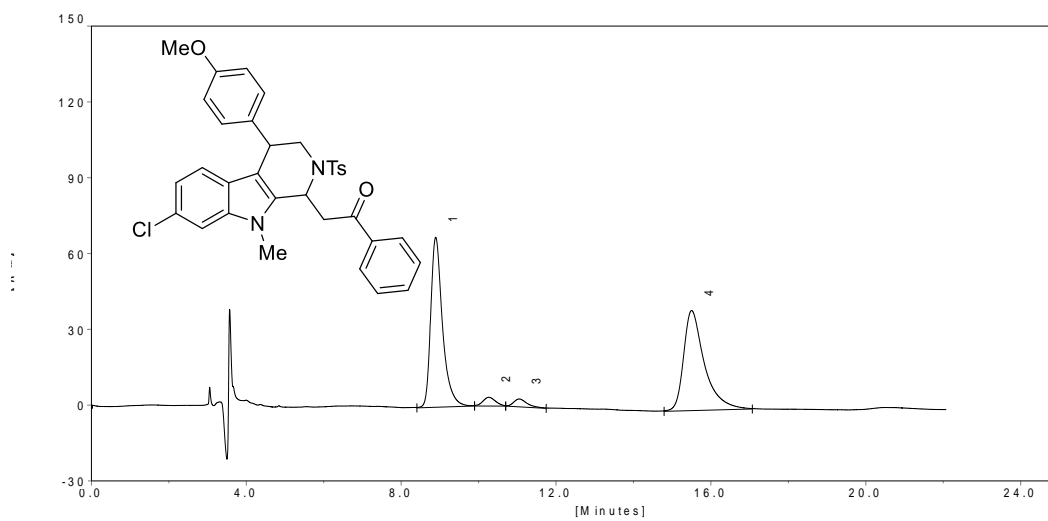


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	9.54917	49.73	1374.23	49.2150
2	15.16083	34.99	1418.07	50.7850

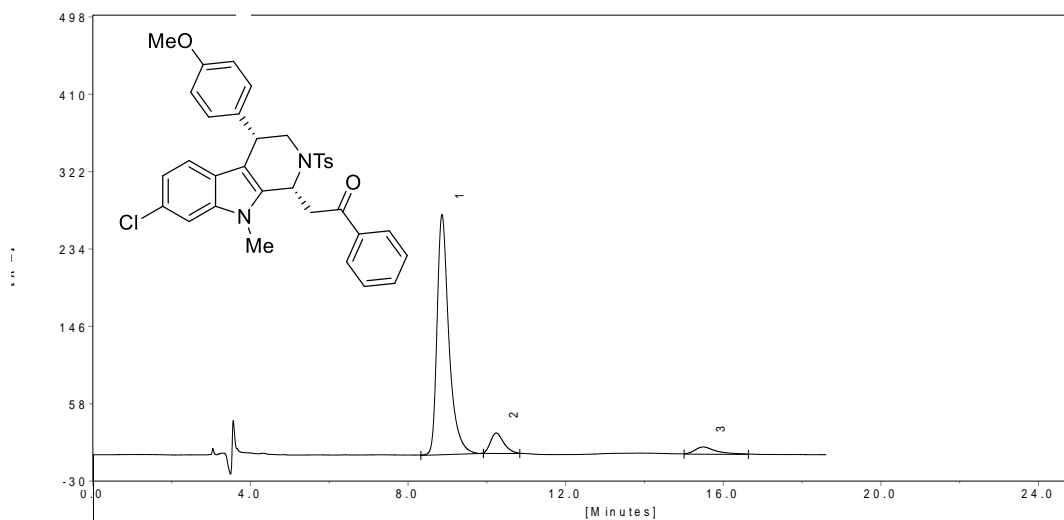


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	9.56250	181.24	3943.55	96.3499
2	15.28083	4.58	149.40	3.6501

HPLC chromatogram of compound **3q** (91% ee)

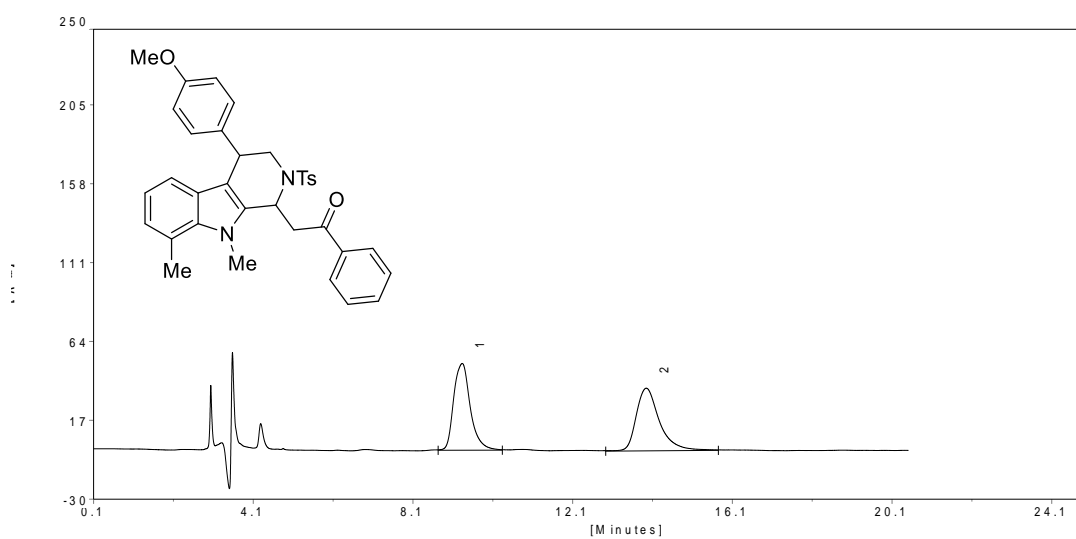


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	8.89333	67.15	1405.87	46.8250
2	10.26000	3.30	70.46	2.3469
3	11.04583	2.97	66.64	2.2195
4	15.50500	39.44	1459.42	48.6086

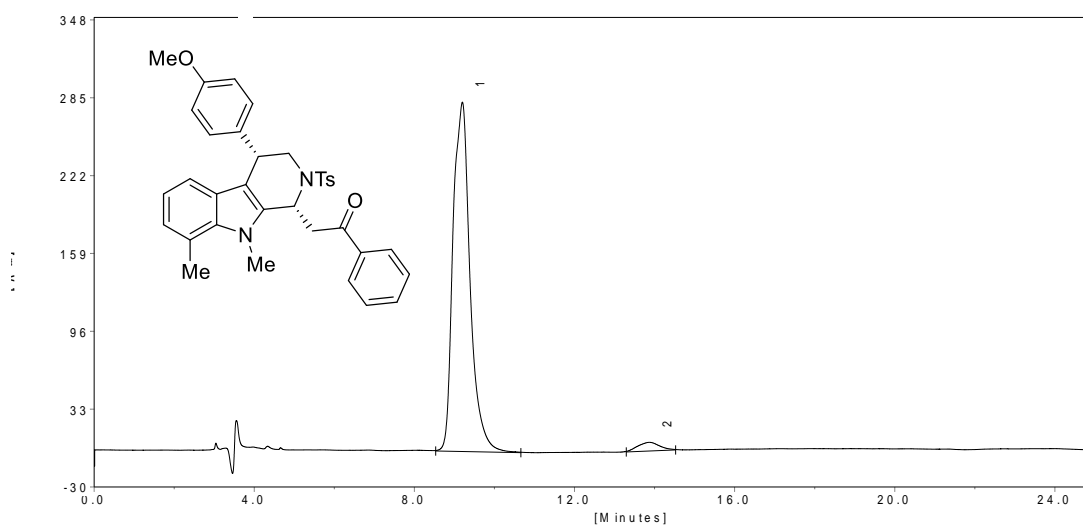


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	8.86167	272.78	5663.76	87.6911
2	10.23750	22.82	521.43	8.0733
3	15.48500	7.82	273.57	4.2357

HPLC chromatogram of compound **3r** (94% ee)

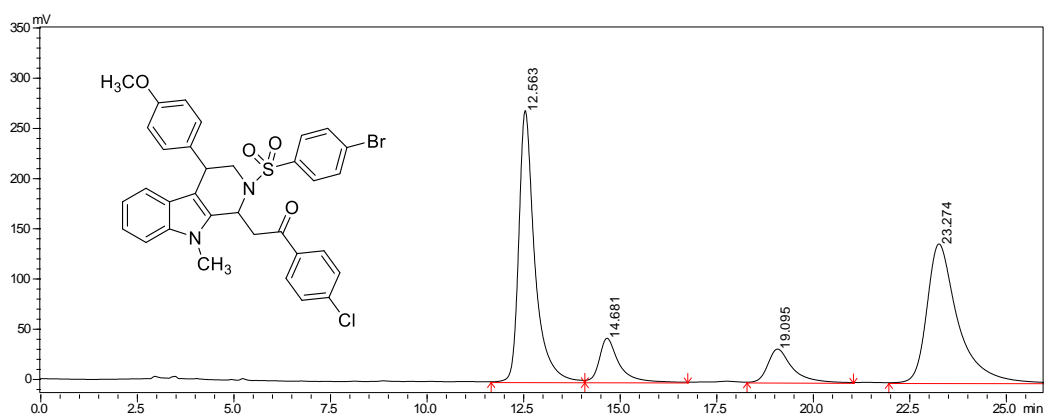


	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.33333	51.45	1470.74	50.1814
2	13.94750	37.11	1460.11	49.8186

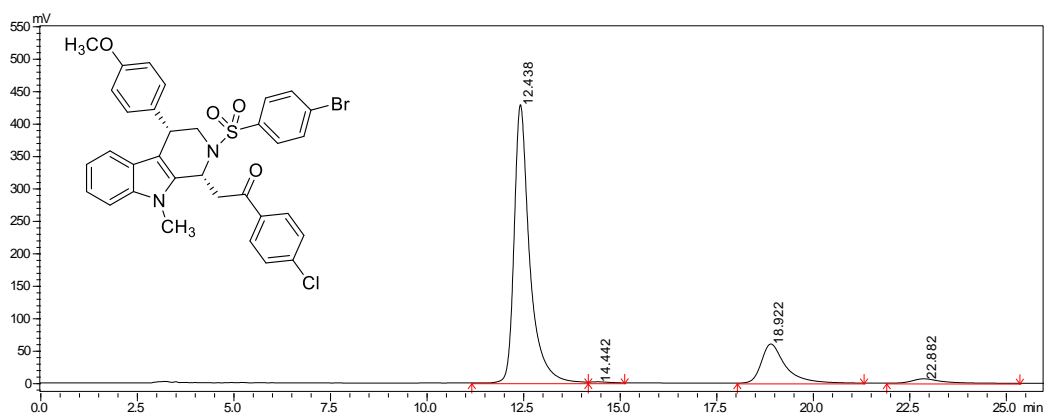


	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.20000	282.39	8316.58	97.1949
2	13.87417	6.64	240.02	2.8051

HPLC chromatogram of compound **3s** (94% ee)

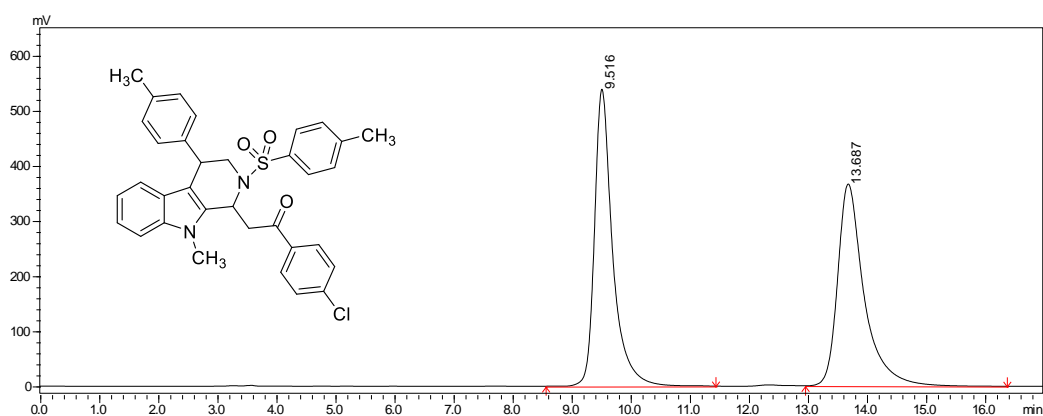


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	12.563	270057	7723129	42.202
2	14.681	43578	1522921	8.322
3	19.095	33047	1411586	7.713
4	23.274	138222	7642778	41.763

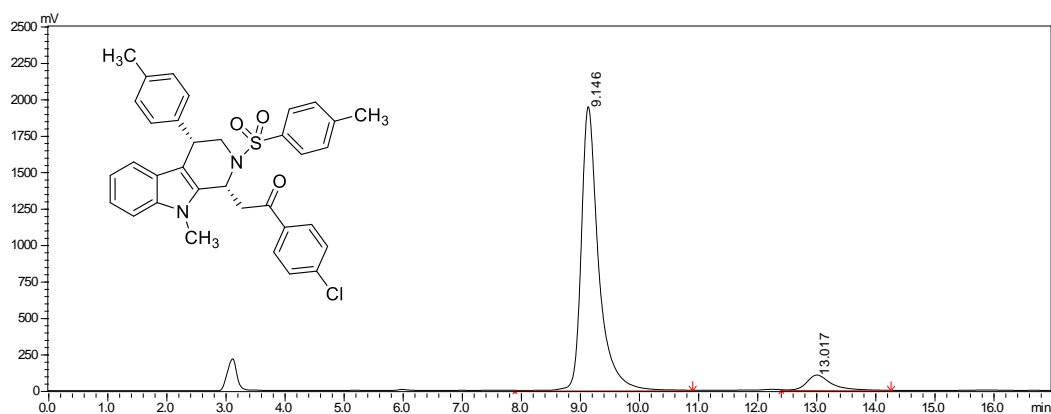


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	12.438	428797	11949014	79.972
2	14.442	1628	52128	0.349
3	18.922	60262	2595801	17.373
4	22.882	6704	344562	2.306

HPLC chromatogram of compound **3t** (87% ee)

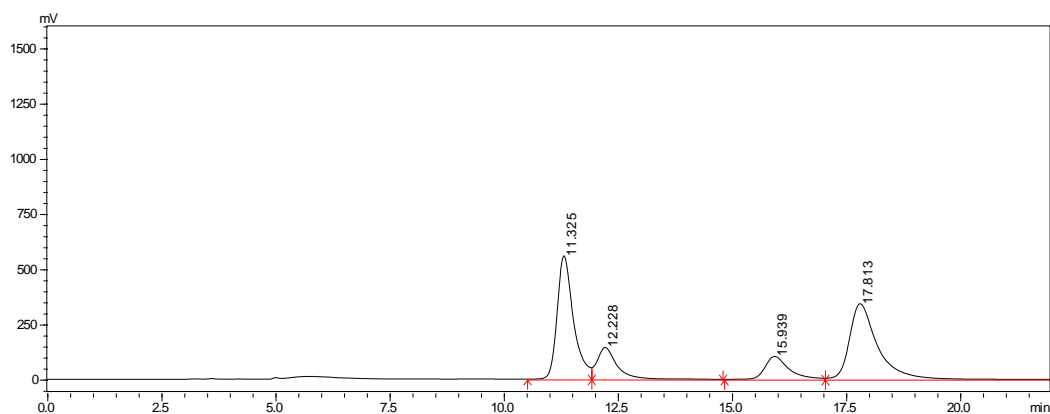


	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.516	538982	11498837	50.285
2	13.687	366432	11368453	49.715

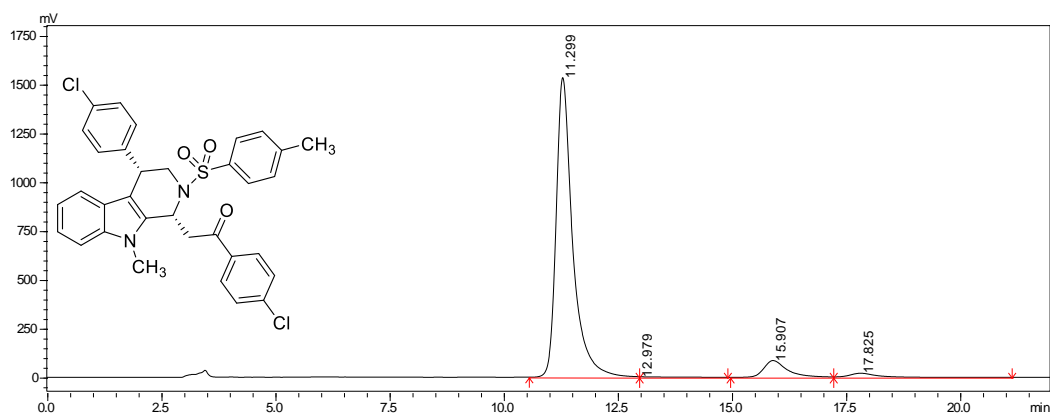


	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.146	1945246	39349885	93.348
2	13.017	102029	2804260	6.652

HPLC chromatogram of compound **3u** (96% ee)

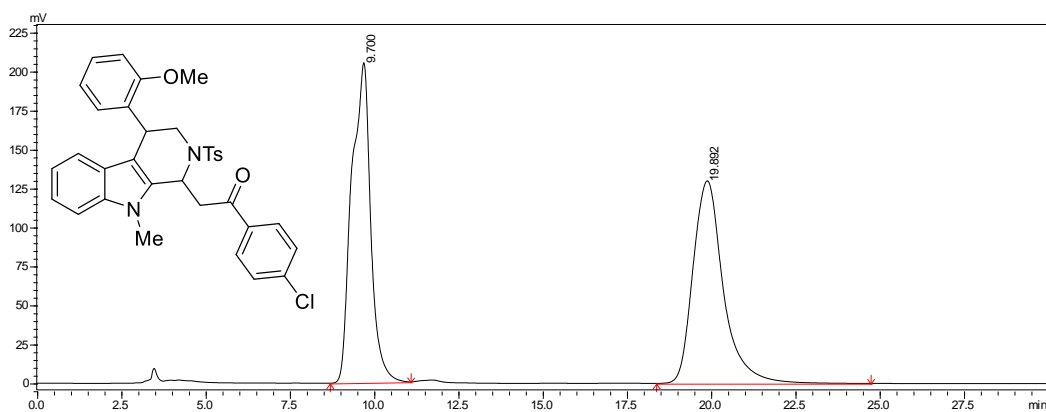


	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	11.325	558311	13892261	37.929
2	12.228	144130	4407309	12.033
3	15.939	103685	3742353	10.217
4	17.813	342323	14585379	39.821

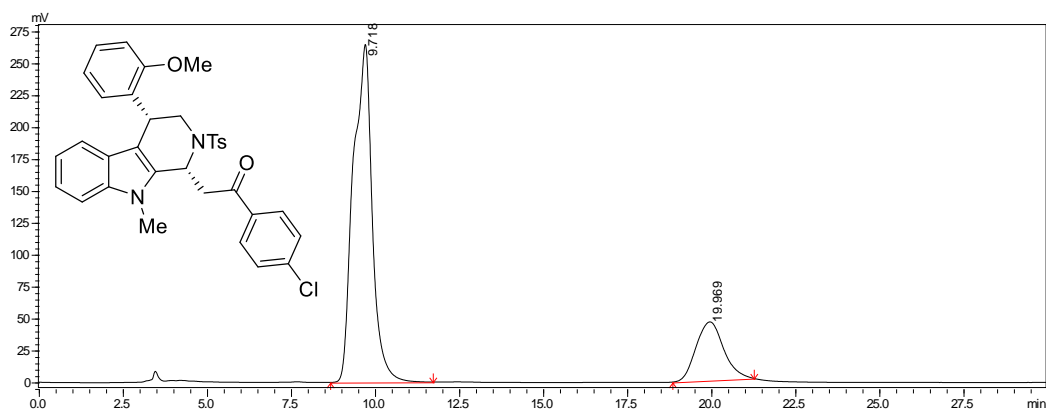


	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	11.299	1534316	38639559	90.527
2	12.979	2744	90162	0.211
3	15.907	85838	3064569	7.180
4	17.825	21002	888480	2.082

HPLC chromatogram of compound **3v** (60% ee)

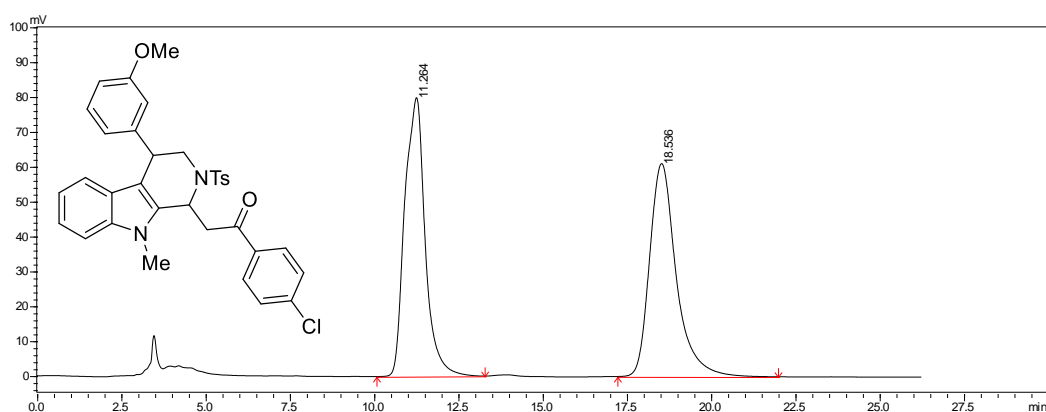


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	9.700	205276	8042339	49.737
2	19.892	129951	8127300	50.263

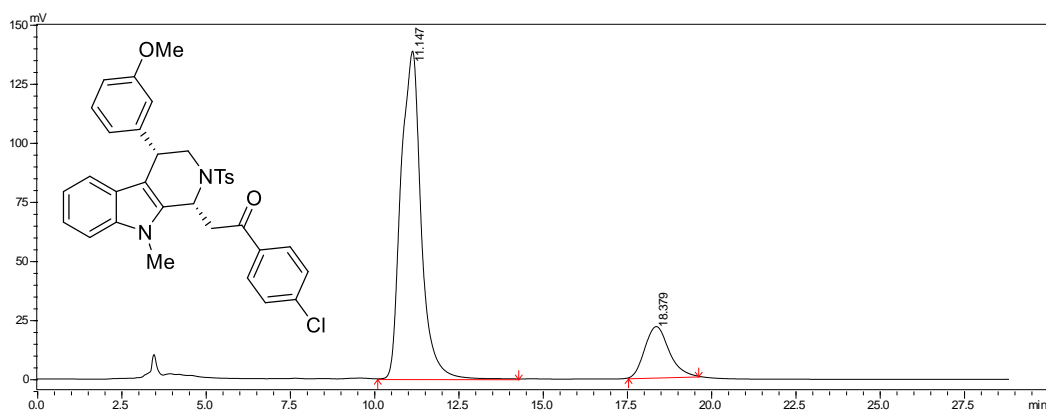


	Ret Time (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{sec}$)	Area (%)
1	9.718	264594	10388270	79.880
2	19.969	45795	2616553	20.120

HPLC chromatogram of compound **3w** (69% ee)



	Ret Time (min)	Height (μ V)	Area (μ V.sec)	Area (%)
1	11.264	79907	3362735	50.063
2	18.536	61047	3354223	49.937



	Ret Time (min)	Height (μ V)	Area (μ V.sec)	Area (%)
1	11.147	138667	5730010	84.306
2	18.379	21434	1066661	15.694