Supporting Information

Rh(I)-Catalyzed stereoselective intramolecular cycloaddition reactions of ene-vinylidenecyclopropanes for the construction of fused 6,5-bicyclic skeletons with a quaternary all carbon stereocenter

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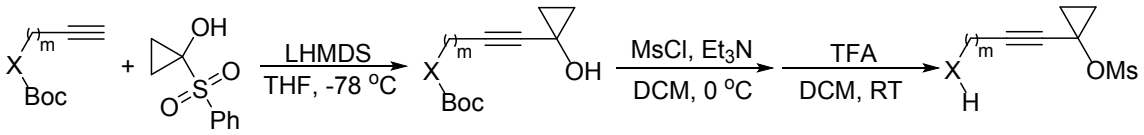
CONTENTS

1. General Remarks.

Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_D$-values are given in unit of 10 deg^{-1} cm^2 g^{-1}. ^1H NMR spectra were recorded on a Varian Mercury-300 and 400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; coupling constants *J* are given in Hz. ^{13}C NMR spectra were recorded on a Varian Mercury-300 and 400 spectrophotometers (75 or 100 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Chiral HPLC was performed on a SHIMADZU SPD-10A *vp* series with chiral columns (Chiralpak AD-H, AS-H, and IC columns 4.6 × 250 mm, (Daicel Chemical Ind., Ltd.)) and chiral column (Phenomenex Lux 5μ Amylose-2 column 4.6 × 250 mm (PA-2), Phenomenex Lux 5μ Cellulose-2 column 4.6 × 250 mm (PC-2), (Phenomenex Ind., Ltd.)). Mass spectra were recorded by EI, ESI and HRMS was measured on a HP-5989 instrument.

2. Representative procedure for the preparation of compounds S3~1:



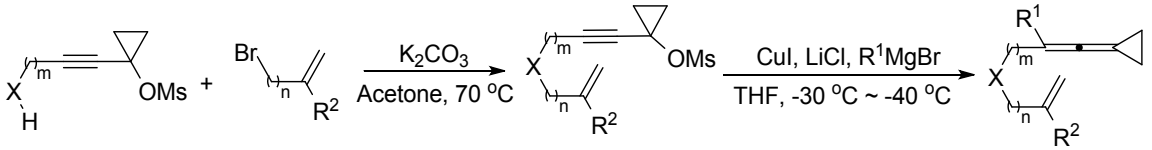
S1 **S2** **S3** **S4**

m = 1, 2; X = NTs, NBs

To the solution of compound **S1** (20 mmol) in THF (30 mL) was added LMHDS (22 mmol, 1.0 M in THF) within 20 min at -78 °C under argon. The resulting solution was allowed to stir at -78 °C for 0.5 h before a solution of **S2** (10 mmol) in THF (10 mL) was added into the above mixture. Consequently, the reaction mixture was allowed to warm up to room temperature and was stirred for 8 h. Then, saturated NH_4Cl solution was added to quench the reaction. Extracted with ethyl ether, dried over anhydrous Na_2SO_4, filtered, the organic phase was purified by a flash column chromatography on silica gel to give the corresponding products **S3** (PE/EA: 4:1~2:1).

Under argon atmosphere, compound **S3** (4.0 mmol) was dissolved in DCM (10.0 mL) at 0 °C, Et_3N (8.0 mmol) and MsCl (6.0 mmol) was added. After stirring for 1 h, the reaction was quenched with H_2O (10.0 mL), extracted with DCM (10 mL x 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was transferred into a 50 mL flask with 10 mL DCM. Then, trifluoroacetic acid (TFA, 40 mmol) was added dropwise. After stirring for 12 h, the reaction was quenched with saturated $NaCO_3$ solution, extracted with DCM (10 mL x 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **S4** (PE/EA: 4:1~1:1).

To the solution of **S4** (1.5 mmol) and K_2CO_3 (1.8 mmol) in acetone (10 ml) was added **S5** (1.8 mmol). The resulting solution was allowed to stir at 70 °C for 8 h. Then, the reaction was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **S6** (PE/EA: 4:1~2:1).



S4 **S5** **S6** **1**

m = 1, 2
X = NTs, NBs

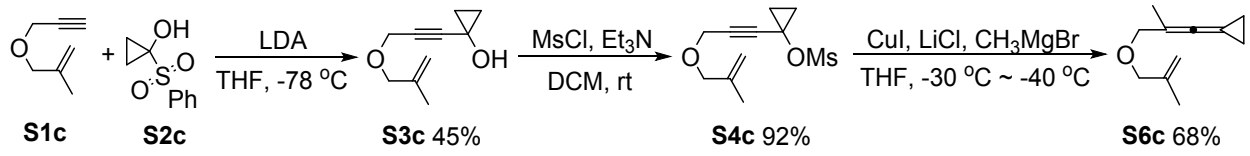
n= 1, 2
R^2 *= Alkyl, Ar*

m = 1, 2
n = 1, 2
X = NTs, NBs
R^2 *= Alkyl, Ar*

m = 1, 2
n = 1, 2
X = NTs, NBs
R^1 *= Alkyl, Ar*
R^2 *= Alkyl, Ar*

Under argon atmosphere, CuI (2.2 mmol) and LiCl (2.2 mmol) in a three-necked bottle was dried upon heating. Then THF (10 mL) was added. At -15 °C, R^3MgBr (1.0 mol/L in THF, 2.0 mmol, 2.0 mL) was added to the reaction. 10 minutes later, the flask was moved into a -40 °C bath and stirred for a while before a solution of **S6** (1.0 mmol) in THF (10 mL) was added dropwise into the above flask. After stirring at -40 °C for 8 h, the reaction was quenched with saturated NH_4Cl solution, extracted with EA (10 mL x 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **1** (PE/EA: 10:1).

3. Typical procedure for the preparation of compounds S6c .

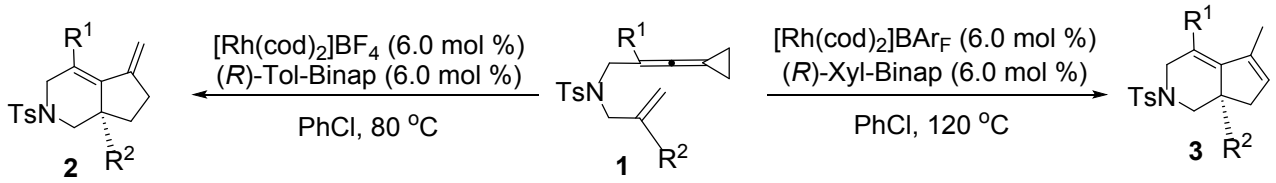


S1c **S2c** **S3c** 45% **S4c** 92% **S6c** 68%

20 mmol

The synthesis of compounds **S6c** have been presented in our previous work.[1]

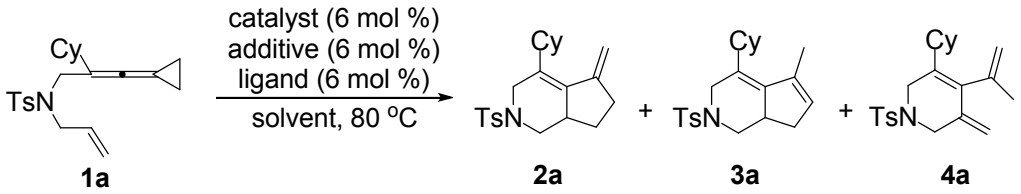
4. General procedure for the rhodium-catalyzed enantioselective cycloisomerization of ene-vinylidenecyclopropanes 1.



To a 10 mL dried tube was charged with ene-VDCP **1** (0.1 mmol, 1.0 equiv), $[Rh(COD)_2]BF_4$ (6.0 mol %) and (*R*)-Tol-Binap (6.0 mol %). The reaction tube was evacuated and backfilled with argon (repeated three times). Then, PhCl (2.0 mL) was added into the tube. The reaction mixture was stirred at 80 °C for 12-18 h. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **2**.

To a 10 mL dried tube was charged with ene-VDCPs **1** (0.1 mmol, 1.0 equiv), $[Rh(COD)_2]BAr_F$ (6.0 mol %) and (*R*)-Xyl-Binap (6.0 mol %). The reaction tube was evacuated and backfilled with argon (repeated three times). Then, PhCl (2.0 mL) was added into the tube. The reaction mixture was stirred at 120 °C for 3-4 h. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **3**.

5. Table S1. Optimization of the reaction conditions

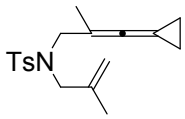


1a **2a** **3a** **4a**

entry[a]	catalyst	additive	ligand	solvent	yield/[%][b]/**2a**:**3a**:**4a**/[%]
1	$[Rh(cod)_2]BF_4$	-	(*rac*)-Binap	DCE	94 (82:7:11)
2	$[Rh(cod)Cl]_2$	$AgNTf_2$	(*rac*)-Binap	DCE	complex
3	$[Rh(cod)Cl]_2$	-	(*rac*)-Binap	DCE	-
4	$[Rh(cod)_2]BF_4$	-	-	DCE	-
5	$[Rh(cod)_2]BF_4$	-	DPEPhos	DCE	-
6	$[Rh(cod)_2]BF_4$	-	dppe	DCE	-
7	$[Rh(cod)_2]BF_4$	-	dppf	DCE	-
8	$[Rh(cod)_2]BF_4$	-	(*rac*)-Binap	dioxane	complex
9	$[Rh(cod)_2]BF_4$	-	(*rac*)-Binap	MeCN	-
10	$[Rh(cod)_2]BF_4$	-	(*rac*)-Binap	PhMe	92 (77:11:12)
11	$[Rh(cod)_2]BF_4$	-	(*rac*)-Binap	PhCl	88 (91:4:5)
12	$[Rh(cod)_2]BAr_F$	-	(*rac*)-Binap	DCE	81 (83:6:11)
13	$[Rh(cod)_2]BAr_F$	-	(*rac*)-Binap	PhMe:MeCN = 3:1	85 (38:15:47)
14[c]	$[Rh(cod)_2]BAr_F$	-	(*rac*)-Binap	PhCl	93 (6:82:12)
15[d]	$[Rh(cod)_2]BAr_F$	LiCl	(*rac*)-Binap	DCE	complex
16[e]	$[Rh(cod)_2]BAr_F$	4Å MS	(*rac*)-Binap	DCE	85 (79:10:11)

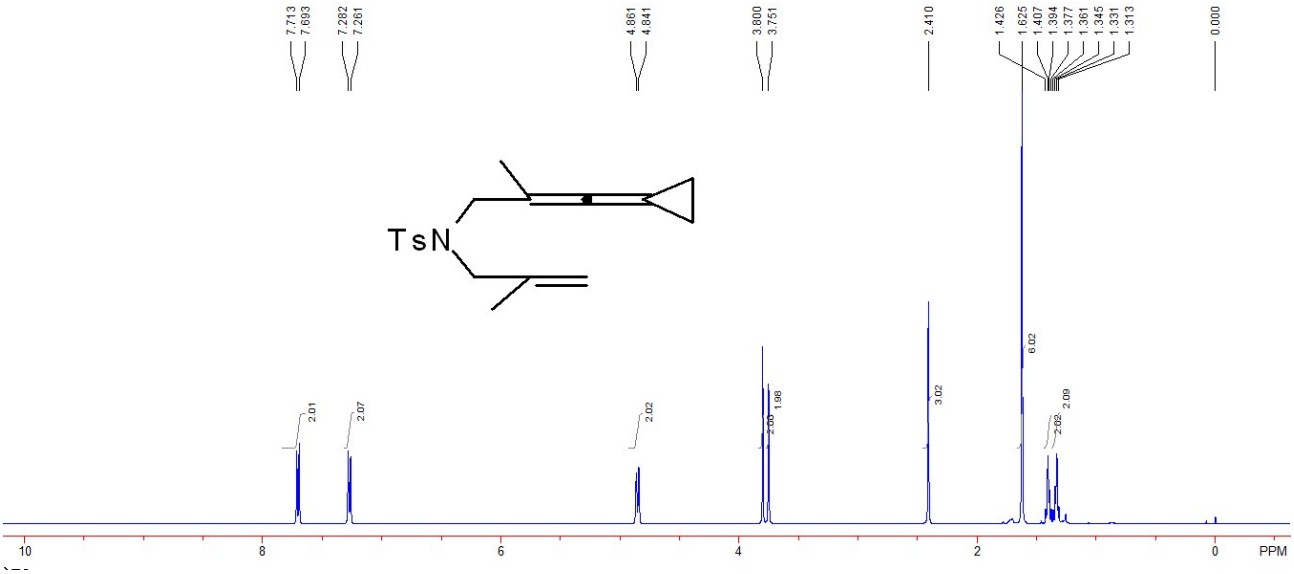
[a]Reaction conditions: **1a** (0.1 mmol), catalyst (6 mol %), additive (6 mol %), ligand (6 mol %), and solvent (2 mL) were added and the reaction mixture was stirred at 80 °C for 12-18 h. [b]Isolated yield. [c]The reaction was conducted at 120 °C. [d]LiCl (2.0 equiv) was added. [e]4Å molecular sieve (50 mg) was added.

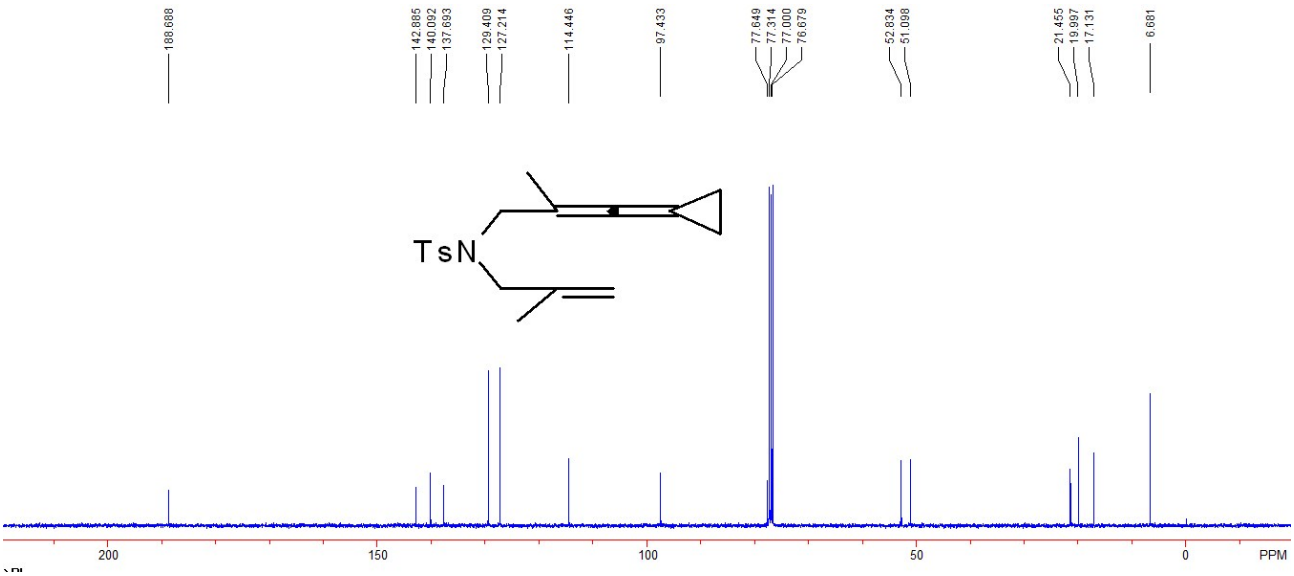
6. Characterization and spectra charts for compounds 1

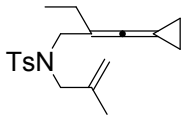


N-(3-cyclopropylidene-2-methylallyl)-4-methyl-N-(2-methylallyl)benzenesulfonamide (1b)

2 mmol scale, a light yellow oil, 87% yield (615 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.31-1.36 (m, 2H), 1.38-1.43 (m, 2H), 1.63 (s, 6H), 2.41 (s, 3H), 3.75 (s, 2H), 3.80 (s, 2H), 4.85 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.7, 17.1, 20.0, 21.5, 51.1, 52.8, 77.6, 97.4, 114.4, 127.2, 129.4, 137.7, 140.1, 142.9, 188.7. IR (CH_2Cl_2): ν 3060, 2980, 2853, 2024, 1655, 1598, 1495, 1442, 1373, 1336, 1304, 1287, 1156, 1102, 1089, 1065, 1006, 904, 814, 802, 770, 708 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{24}NO_2S$ $(M+H)^+$: 318.1522, Found: 318.1523.

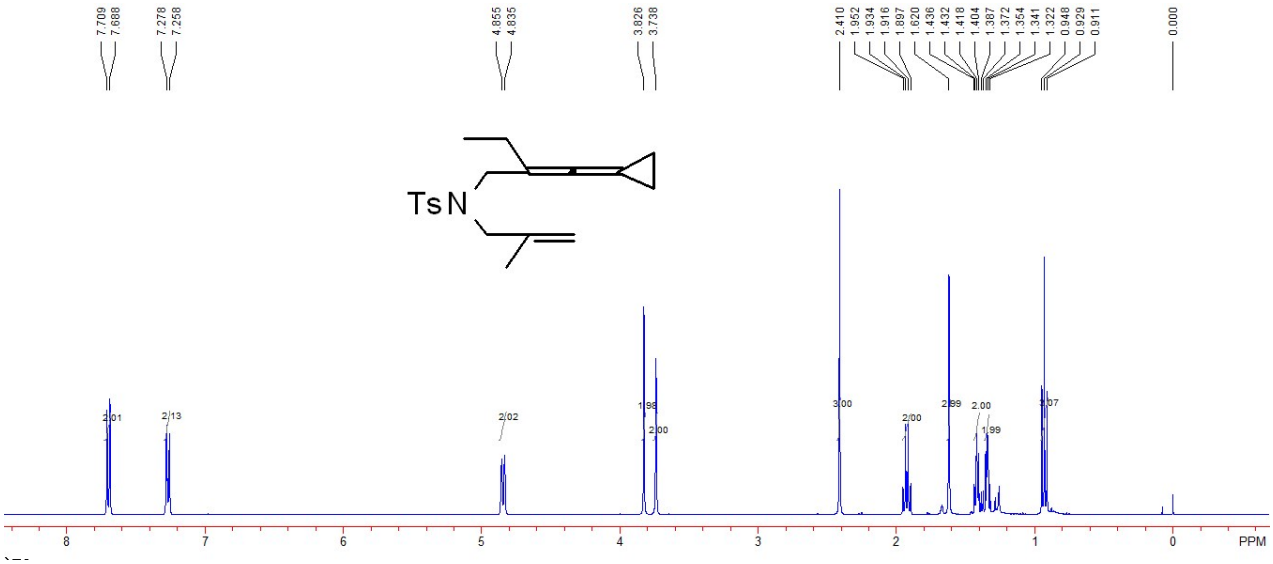


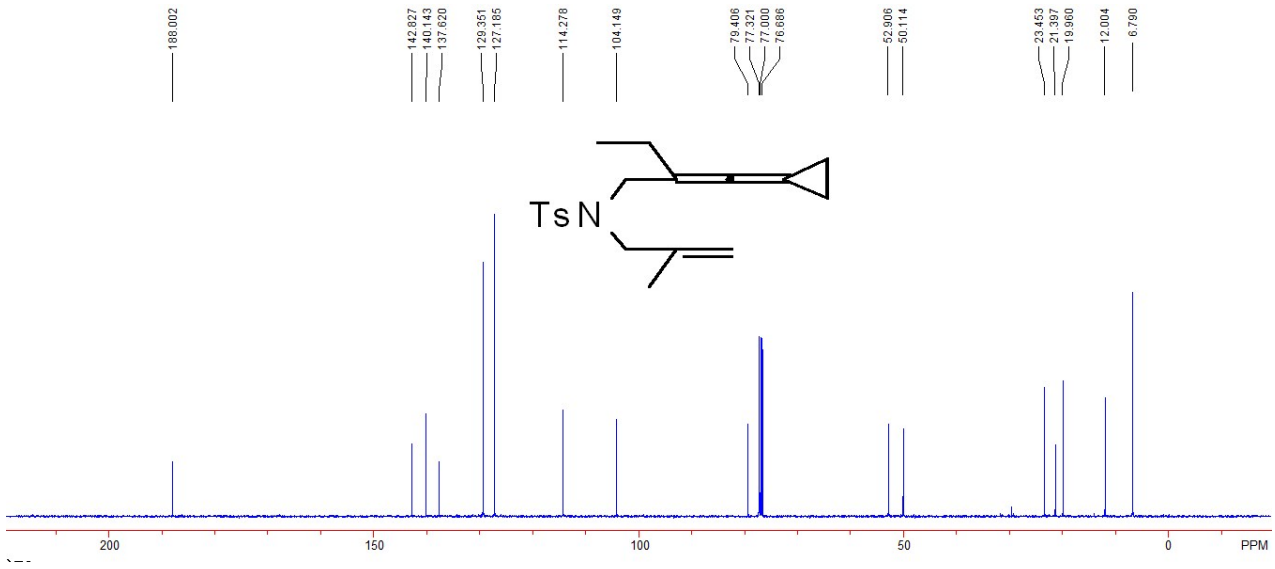


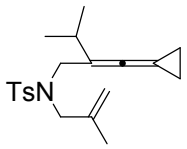


N-(2-(cyclopropylidene-λ^5-methylene)butyl)-4-methyl-N-(2-methylallyl)benzenesulfonamide (1c)

2.0 mmol scale, a light yellow oil, 78% yield (662 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.93 (t, *J* = 7.2 Hz, 3H), 1.32-1.37 (m, 2H), 1.39-1.44 (m, 2H), 1.62 (s, 3H), 1.93 (q, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 3.74 (s, 2H), 3.83 (s, 2H), 4.85 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.8, 12.0, 20.0, 21.4, 23.5, 50.1, 52.9, 79.4, 104.1, 114.3, 127.2, 129.4, 137.6, 140.1, 142.8, 188.0. IR (neat): ν 3064, 2966, 2927, 2867, 2017, 1594, 1435, 1335, 1155, 1090, 1010, 993, 904, 814, 763, 708, 657 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{26}NO_2S$ $(M+H)^+$: 332.1679, Found: 332.1672.

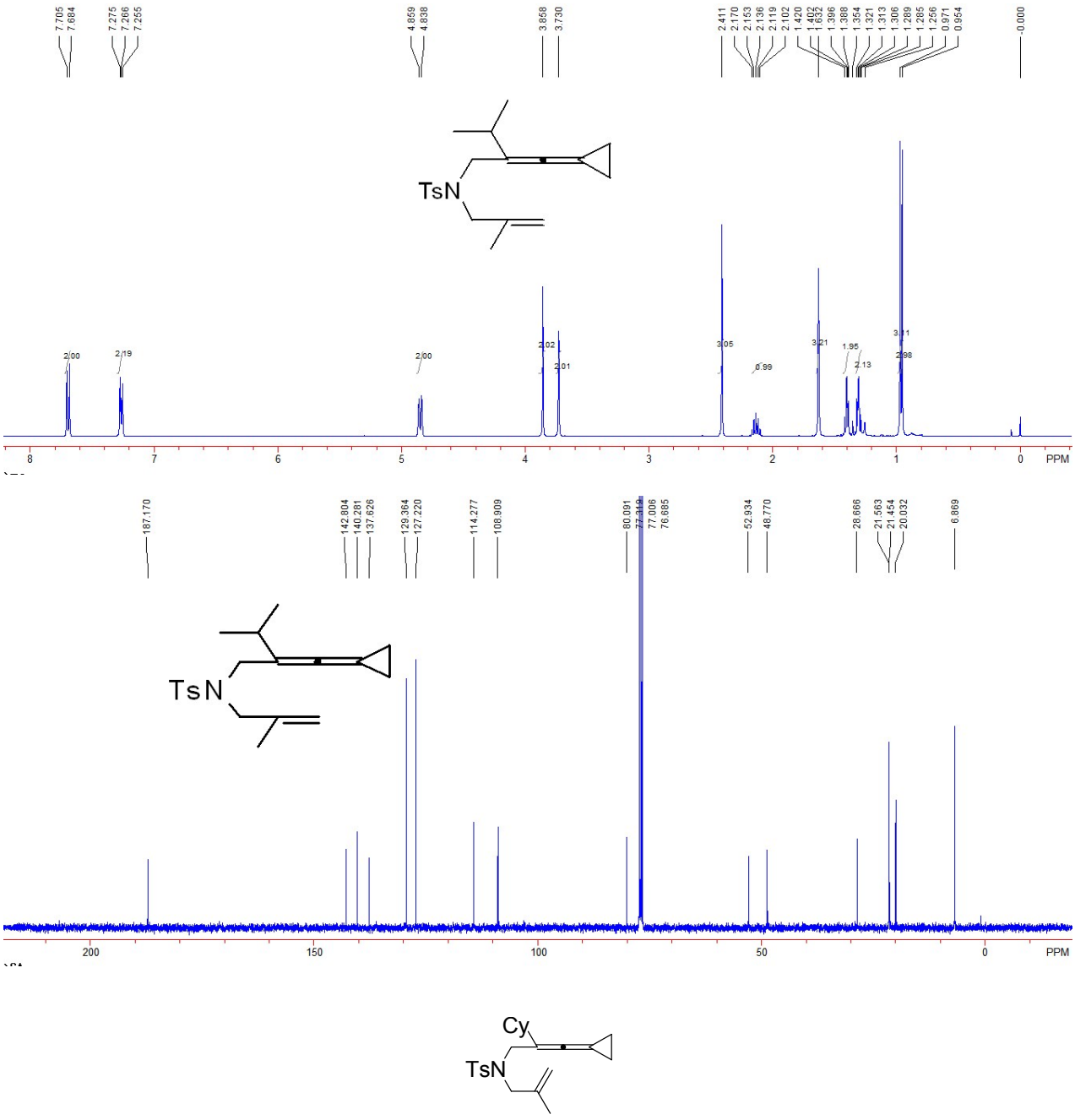






N-(2-(cyclopropylidene-λ^5-methylene)-3-methylbutyl)-4-methyl-N-(2-methylallyl)benzenesulfonamide (1d)

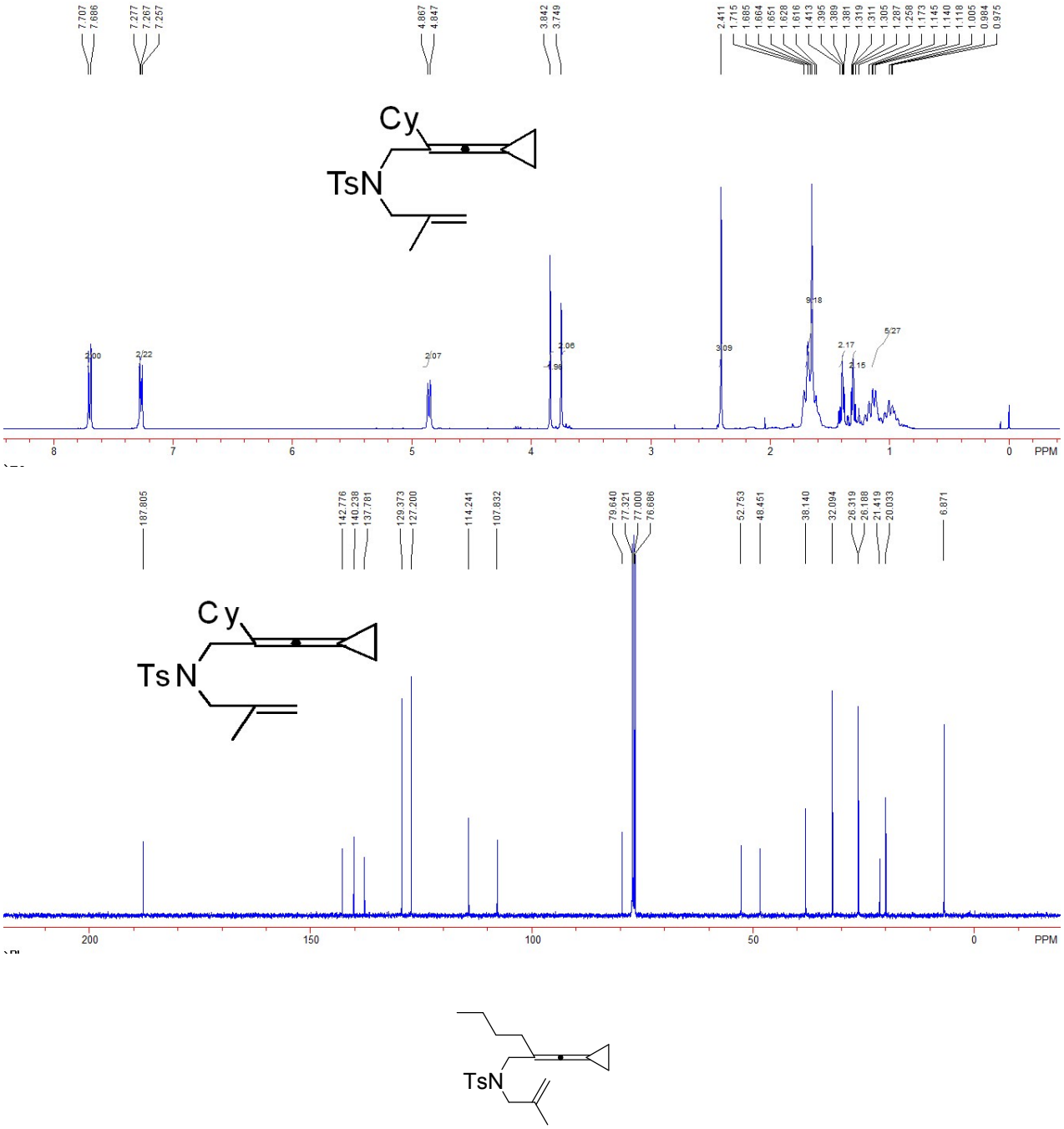
1.0 mmol scale, A white solid, 53% yield (183 mg). M. P. 99-103 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.96 (d, *J* = 6.8 Hz, 6H),1.26-1.32 (m, 2H), 1.35-1.42 (m, 2H), 1.63 (s, 3H), 2.10-2.17 (m, 1H), 2.41 (s, 3H), 3.73 (s, 2H), 3.86 (s, 2H), 4.85 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.9, 20.0, 21.5, 21.6, 28.7, 48.8, 52.9, 80.1, 108.9, 114.3, 127.2, 129.4, 137.6, 140.3, 142.8, 187.2. IR (neat): ν 3064, 2966, 2927, 2867, 2010, 1634, 1441, 1340, 1105, 1085, 1001, 983, 883, 814, 773, 708, 667 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{28}NO_2S$ $(M+H)^+$:346.1835, Found: 346.1829.



N-(2-cyclohexyl-3-cyclopropylidene-3λ^5-allyl)-4-methyl-N-(2-methylallyl)benzenesulfonamide (1e)

1.0 mmol scale, a light yellow oil, 58% yield (223mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.98-1.17 (m, 5H), 1.26-1.32 (m, 2H), 1.38-1.41 (m, 2H), 1.62-1.72 (m, 9H), 2.41 (s, 3H), 3.75 (s, 2H), 3.84 (s, 2H), 4.86 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H).^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.9, 20.0, 21.4, 26.2, 26.3, 32.1, 38.1, 48.5, 52.8, 79.6, 107.8, 114.2, 127.2, 129.4, 137.8, 140.2, 142.8, 187.8. IR (neat): ν 2924, 2846, 2019, 1597, 1447, 1337, 1156, 1096, 1014, 991, 907, 814, 766, 706, 665 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{32}NO_2S$ $(M+H)^+$:

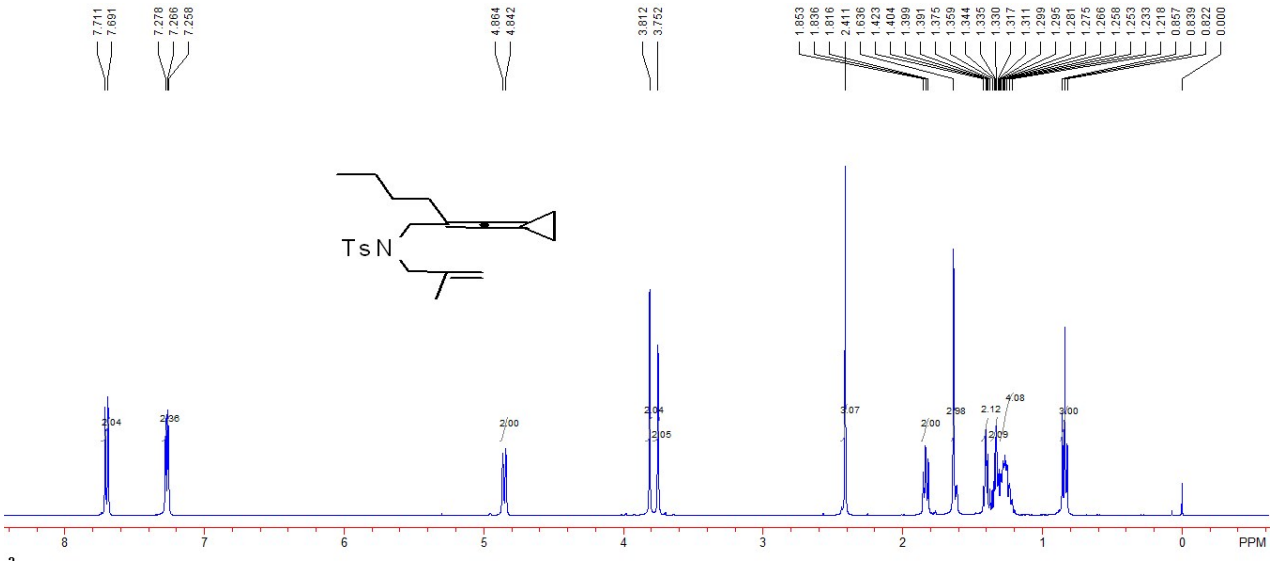
386.2148, Found: 386.2142.

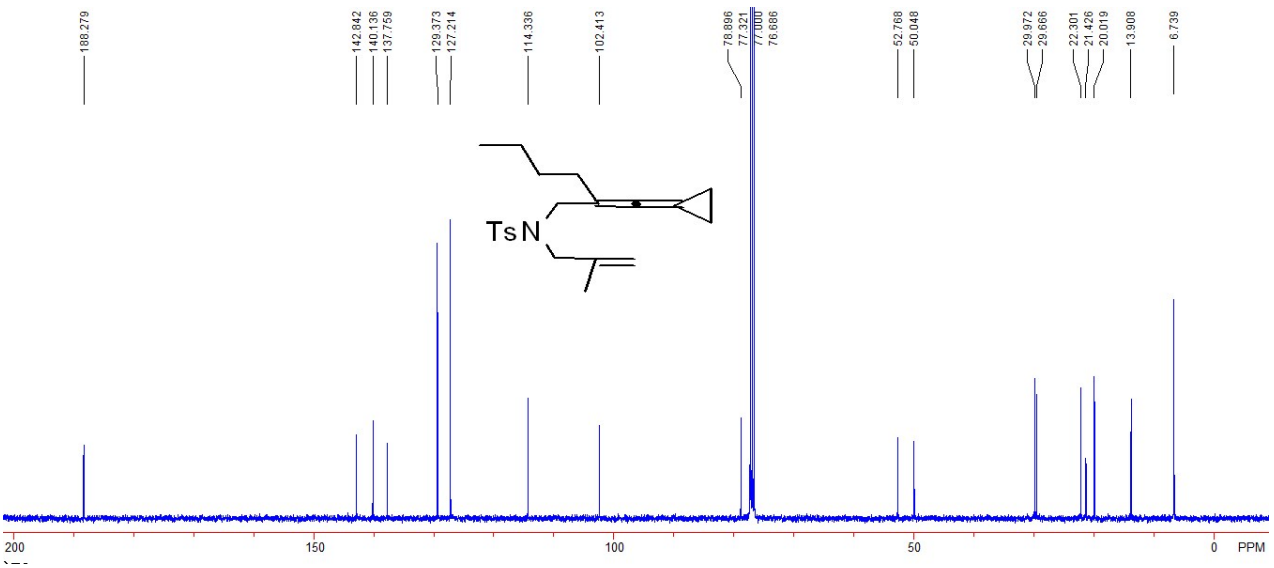


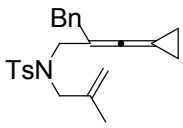
N-(2-(cyclopropylidene-λ^5-methylene)hexyl)-4-methyl-N-(2-methylallyl)benzenesulfonamide (1f)

1.0 mmol scale, a light yellow oil, 60% yield (215 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.84 (t, *J* = 6.8 Hz, 3H), 1.22-1.30 (m, 4H), 1.31-1.36 (m, 2H), 1.38-1.42 (m, 2H), 1.64 (s, 3H), 1.84 (t, *J* = 8.0 Hz, 2H), 2.41 (s, 3H), 3.75 (s, 2H), 3.81 (s, 2H), 4.85 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.7, 13.9, 20.0, 21.4, 22.3 29.7, 30.0, 50.0, 52.8, 78.9, 102.4, 114.3, 127.2, 129.4, 137.8, 140.1, 142.8, 188.3. IR (neat): ν

2956, 2925, 2855, 2020, 1437, 1340, 1340, 1305, 1156, 1093, 1005, 905, 814, 768, 708, 659 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{30}NO_2S$ $(M+H)^+$: 360.1984, Found: 360.1992.



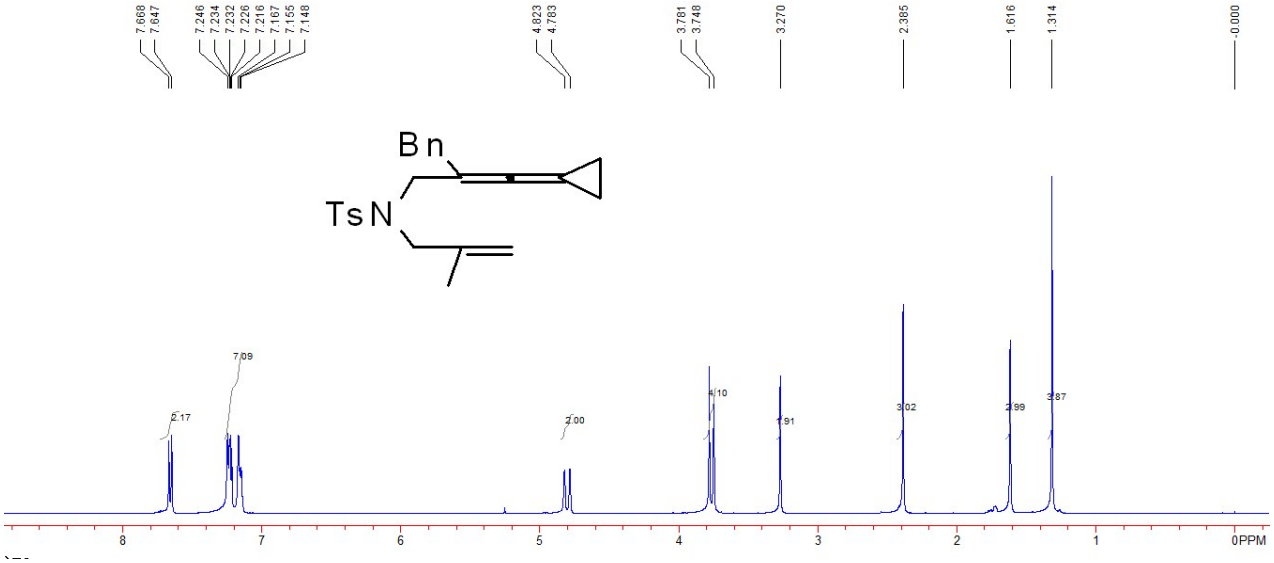


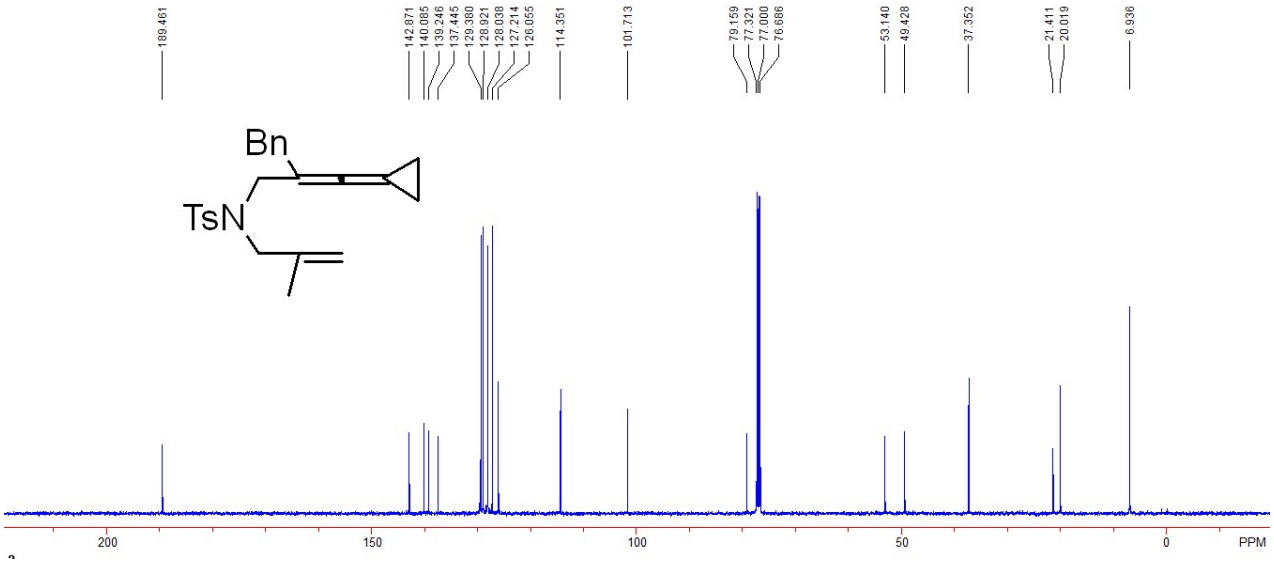


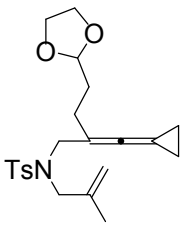
N-(2-benzyl-3-cyclopropylidene-3λ^5-allyl)-4-methyl-N-(2-methylallyl)benzenesulfonamide (1g)

1.0 mmol scale, a light yellow oil, 52% yield (204 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.31 (s, 4H), 1.62 (s, 3H), 2.39 (s, 3H), 3.27 (s, 2H), 3.75 (s, 2H), 3.78 (s, 2H), 4.80 (d, J = 16.0 Hz, 2H), 7.15-7.25 (m, 7H),, 7.66 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.9, 20.0, 21.4, 37.4, 49.4, 53.1, 79.2, 101.7, 114.4, 126.1, 127.2, 128.0, 128.9, 129.4, 137.4, 139.2, 140.1,

142.9, 189.5. IR (neat): ν 3027, 2915, 2024, 1728, 1597, 1495, 1443, 1355, 1331, 1159, 1090, 918, 813, 799, 651 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{28}NO_2S$ $(M+H)^+$: 394.1835, Found: 394.1828.



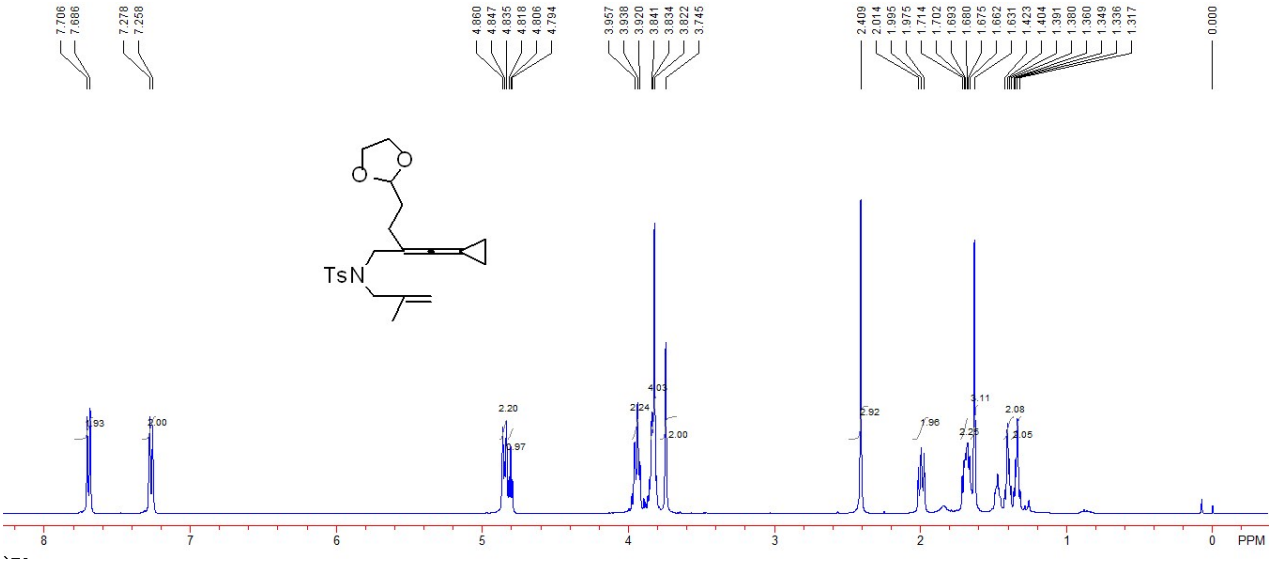


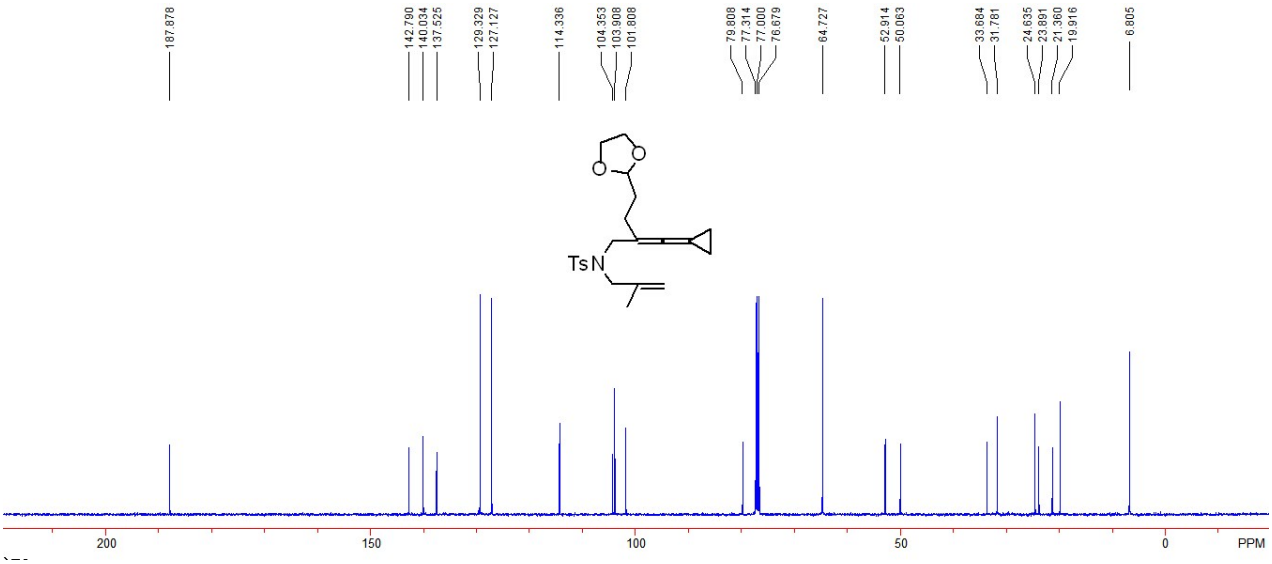


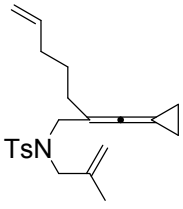
N-(2-(cyclopropylidene-λ^5-methylene)-4-(1,3-dioxolan-2-yl)butyl)-4-methyl-N-(2-methylallyl)benzenesulfonamide (1h)

1.0 mmol scale, a light yellow oil, 68% yield (274 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.32-1.36 (m, 2H), 1.38-1.42 (m, 2H), 1.63 (s, 3H), 1.66-1.71 (m, 2H), 2.00 (t, J = 8.0 Hz, 3H), 2.41 (s,

3H), 3.75 (s, 2H), 3.82-3.84 (m, 4H), 3.92-3.96 (m, 2H), 4.81(t, J = 4.8 Hz, 1H), 4.84-4.86 (m, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.8, 19.9, 21.4, 23.9, 24.6, 31.8, 33.7, 50.1, 52.9, 64.7, 79.8, 101.8, 103.9, 104.4, 114.3, 127.1, 129.3, 137.5, 140.0, 142.8, 187.9. IR (CH_2Cl_2): ν 2946, 2924, 2910, 2022, 1443, 1410, 1334, 1305, 1156, 1101, 1019, 906, 815, 803, 768, 708, 659 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{33}N_2O_4S$ $(M+NH_4)^+$: 421.2156, Found: 421.2147.

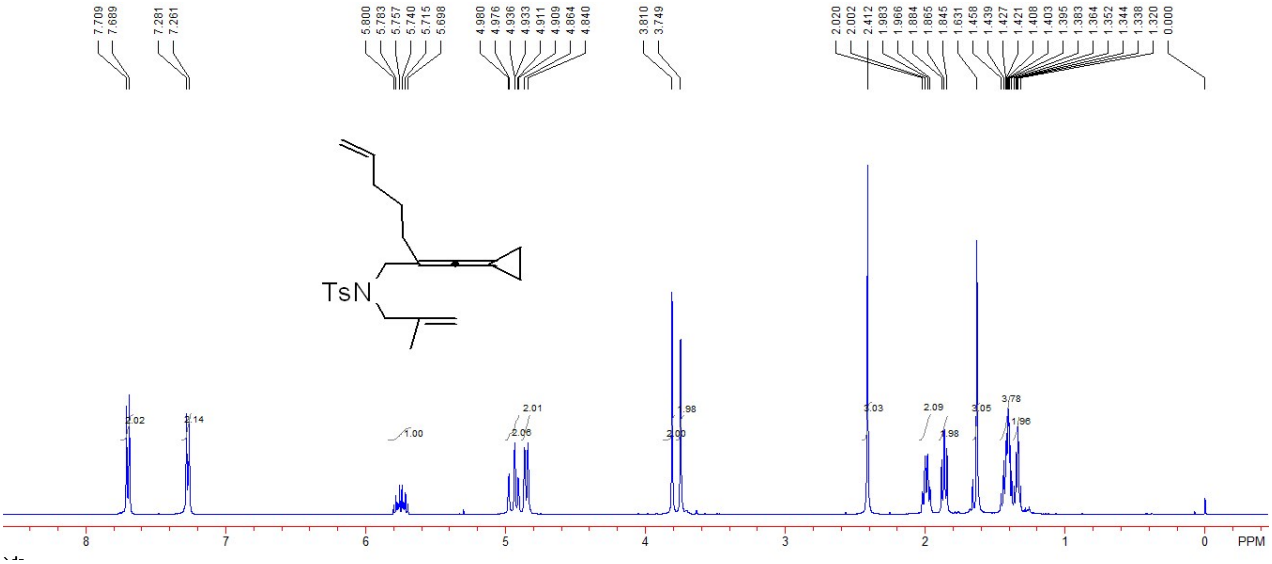


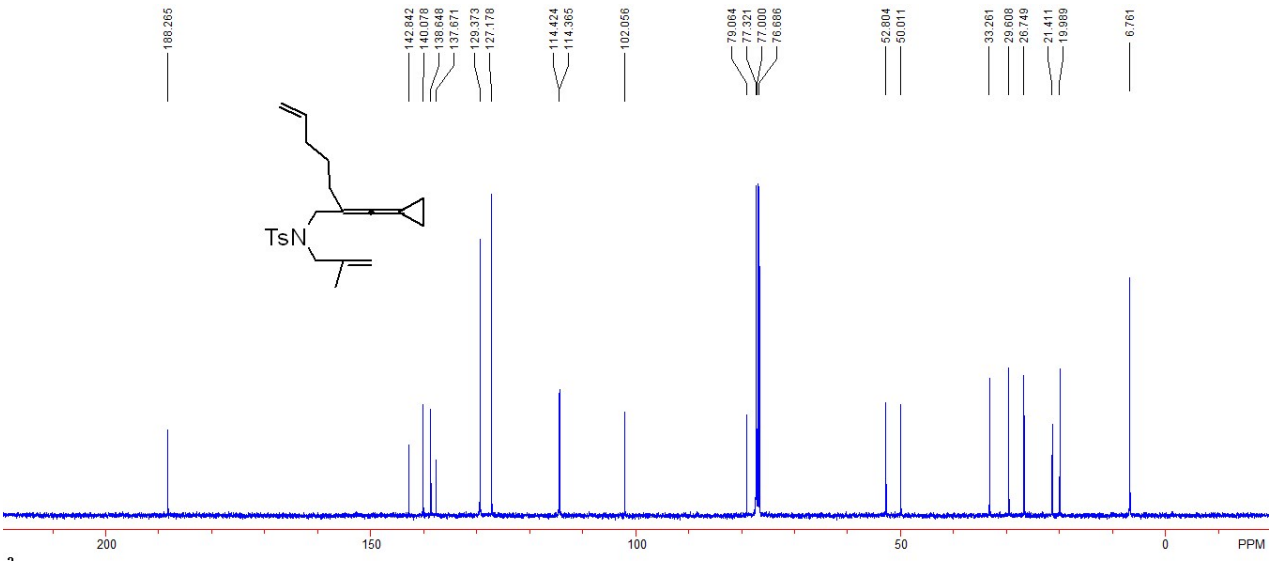


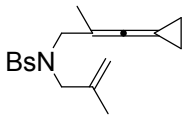


N-(2-(cyclopropylidene-λ^5-methylene)hept-6-en-1-yl)-4-methyl-N-(2-methylallyl)benzenesulfonamide(1i)

1.0 mmol scale, a light yellow oil, 67% yield (249 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.32-1.46 (m, 6H), 1.63 (s, 3H), 1.87 (t, *J* = 8.0 Hz, 2H), 1.99 (q, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 3.75 (s, 2H), 3.81 (s, 2H), 4.85 (d, *J* = 9.6 Hz, 2H), 4.91-4.98 (m, 2H), 5.70-5.80 (m, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.8, 20.0, 21.4, 26.7, 29.6, 33.3, 50.0, 52.8, 79.1, 102.1, 114.3, 114.4, 127.2, 129.4, 137.6, 138.6, 140.1, 142.8, 188.3. IR (neat) 3074, 2982, 2920, 2849, 2017, 1636, 1594, 1440, 1343, 1157, 1094, 905, 813, 656 cm^{-1}.HRMS (ESI) calcd. for $C_{22}H_{30}NO_2S$ $(M+H)^+$: 372.1992, Found: 372.1986.

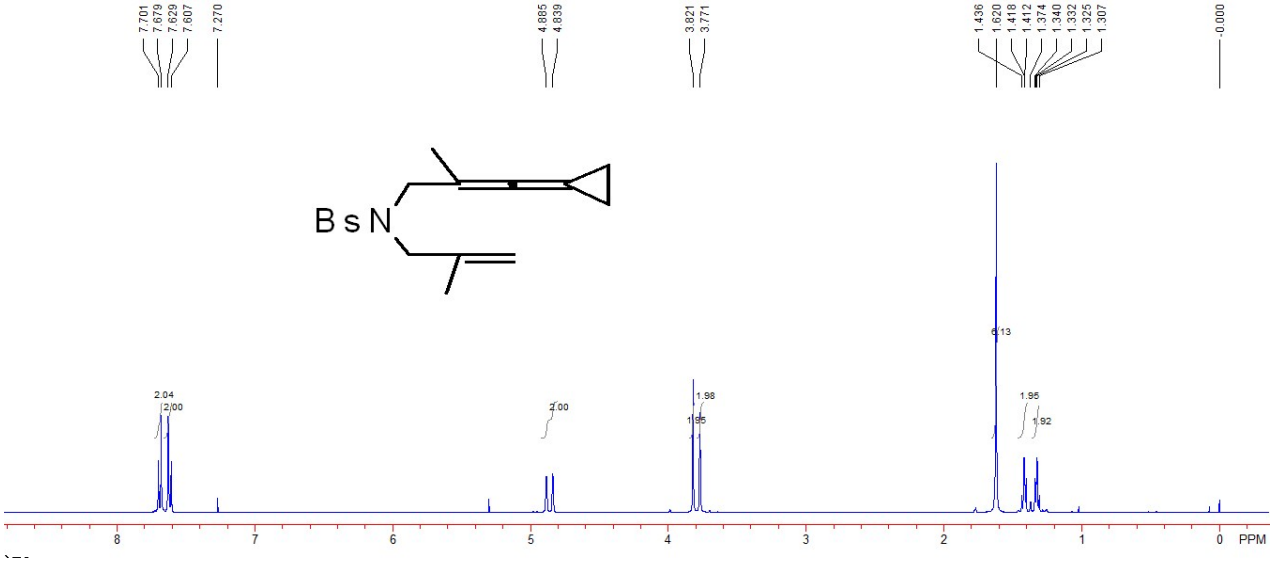


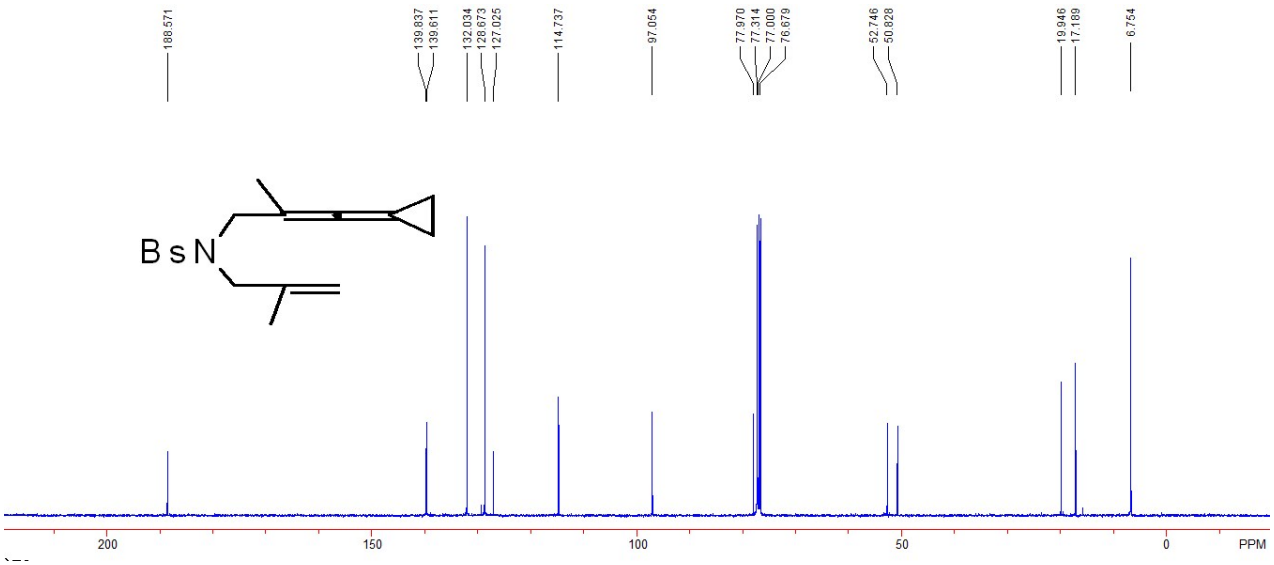


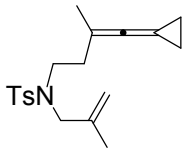


4-bromo-N-(3-cyclopropylidene-2-methyl-3λ^5-allyl)-N-(2-methylallyl)benzenesulfonamide (1j)

1.0 mmol scale, a light yellow oil, 62% yield (236 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.31-1.34 (m, 2H), 1.37-1.44 (m, 2H), 1.62 (s, 6H), 3.77 (s, 2H), 3.82 (s, 2H), 4.86 (d, *J* = 18.4 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.8, 17.2, 19.9, 50.8, 52.7, 78.0, 97.1, 114.7, 127.0, 128.7, 132.0, 139.6, 139.8, 188.6. IR (neat): ν 3094, 2985, 2912, 2839, 2027, 1573, 1440, 1388, 1344, 1159, 1099, 1086, 1067, 1004, 903, 822, 779, 703, 661 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{21}BrNO_2S$ $(M+H)^+$: 382.0471, Found: 382.0466.

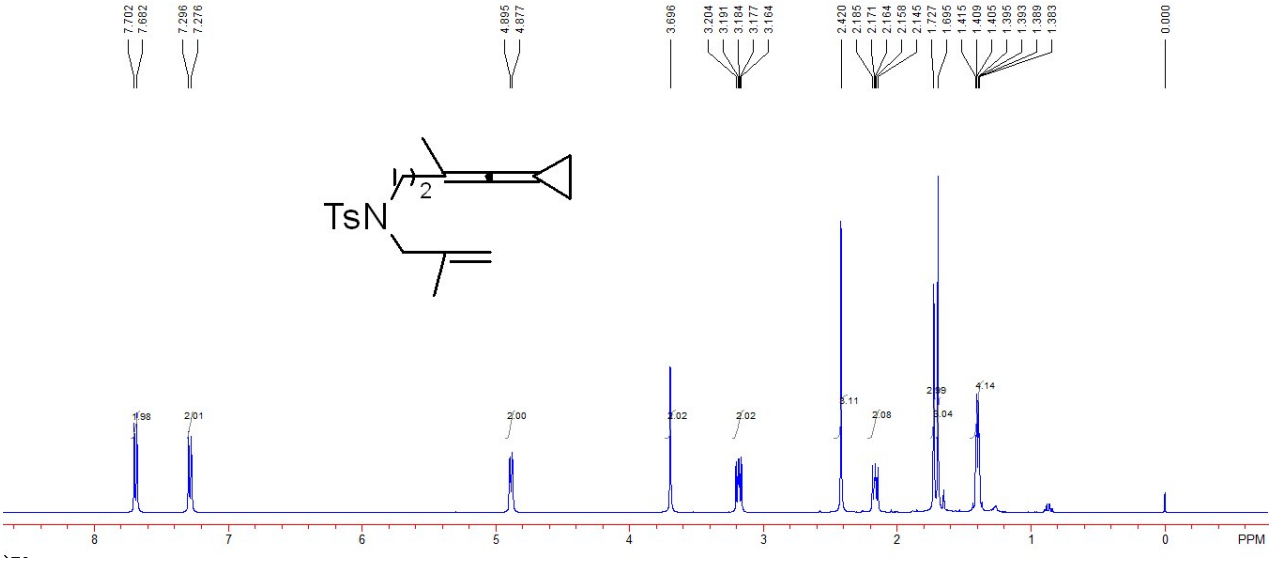


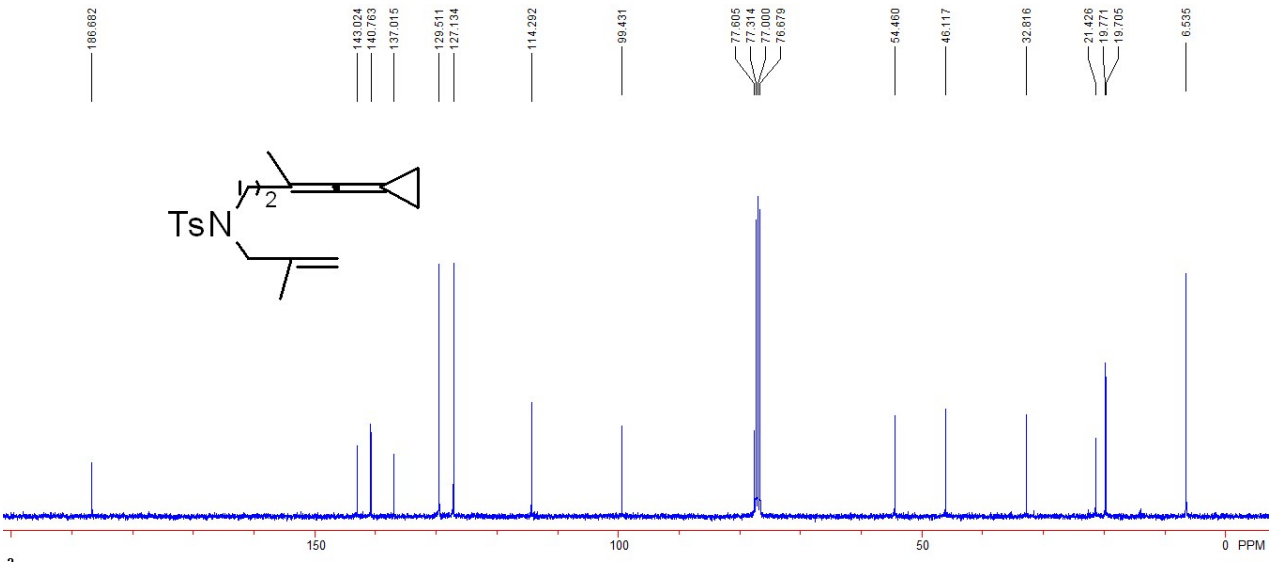


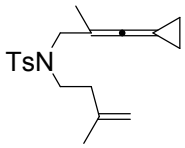


N-(4-cyclopropylidene-3-methyl-4λ^5-but-3-en-1-yl)-4-methyl-N-(2-methylallyl)benzenesulfonamide (1k)

1.0 mmol scale, a light yellow oil, 65% yield (215 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.38-1.42 (m, 4H), 1.70 (s, 3H), 1.73 (s, 3H), 2.15-2.19 (m, 2H), 2.42 (s, 3H), 3.16-3.20 (m, 2H), 3.70 (s, 2H), 4.89 (d, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.5, 19.7, 19.8, 21.4, 32.8, 46.1, 54.5, 77.6, 99.4, 114.3, 127.1, 129.5, 137.0, 140.8, 143.0, 186.7. IR (CH_2Cl_2): ν 3060, 2928, 2831, 2014, 1755, 1698, 1595, 1442, 1373, 1346, 1314, 1277, 1246, 1006, 914, 834, 812, 761, 708 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{26}NO_2S$ $(M+H)^+$: 332.1679, Found: 332.1673.

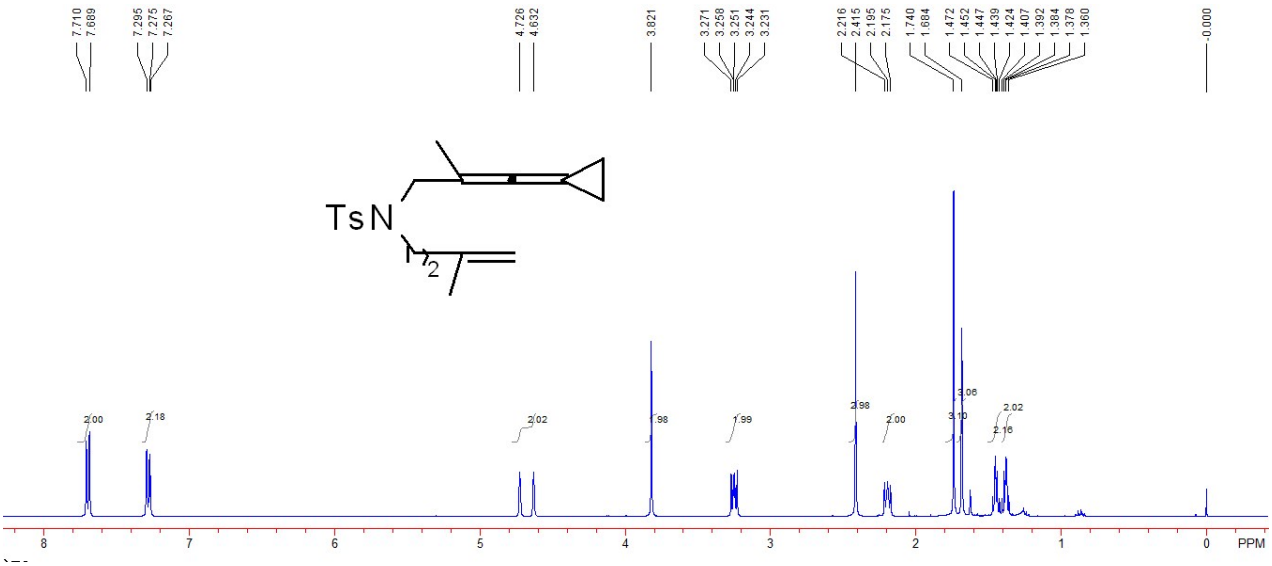


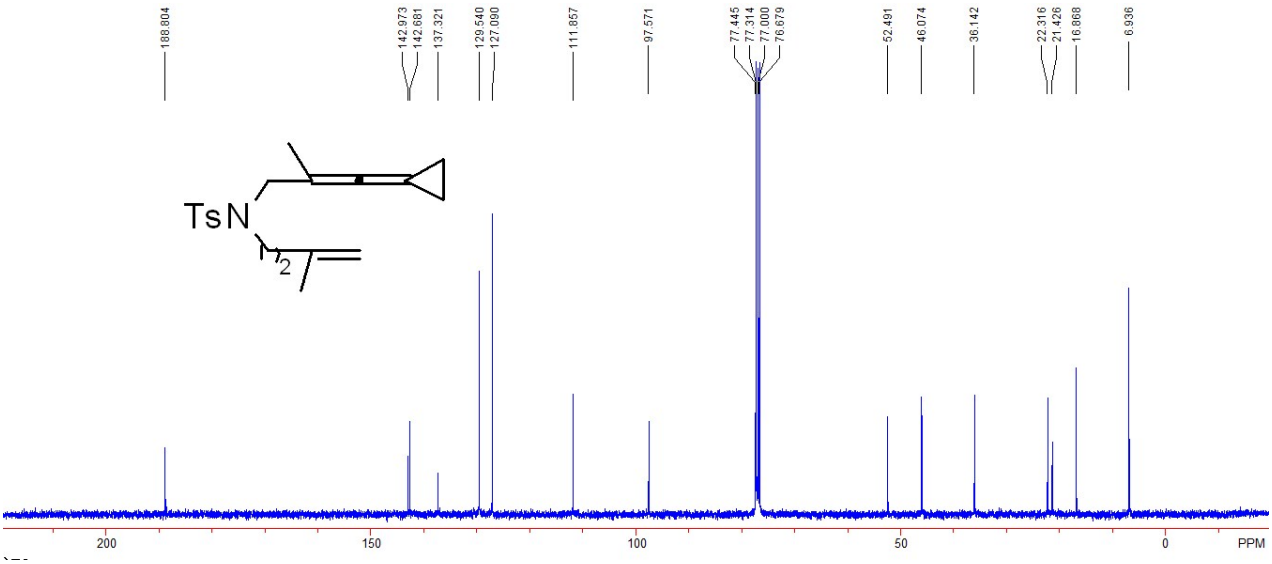


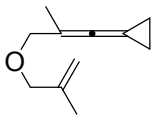


N-(3-cyclopropylidene-2-methyl-3λ^5-allyl)-4-methyl-N-(3-methylbut-3-en-1-yl)benzenesulfonamide (1l)

1.0 mmol scale, a light yellow oil, 63% yield (208 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.36-1.41 (m, 2H), 1.42-1.47 (m, 2H), 1.68 (s, 3H), 1.74 (s, 3H), 2.18-2.22 (m, 2H), 2.42 (s, 3H), 3.23-3.27 (m, 2H), 3.82 (s, 2H), 4.63 (s, 1H), 4.73 (s, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.9, 16.9, 21.4, 22.3, 36.1, 46.1, 52.5, 77.4, 97.6, 111.9, 127.1, 129.5, 137.3, 142.7, 143.0, 188.8. IR (CH_2Cl_2): ν 3060, 2980, 2853, 2024, 1655, 1598, 1495, 1442, 1373, 1336, 1304, 1287, 1156, 1102, 1089, 1065, 1006, 904, 814, 802, 770, 708 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{26}NO_2S$ $(M+H)^+$: 322.1679, Found: 332.1672.

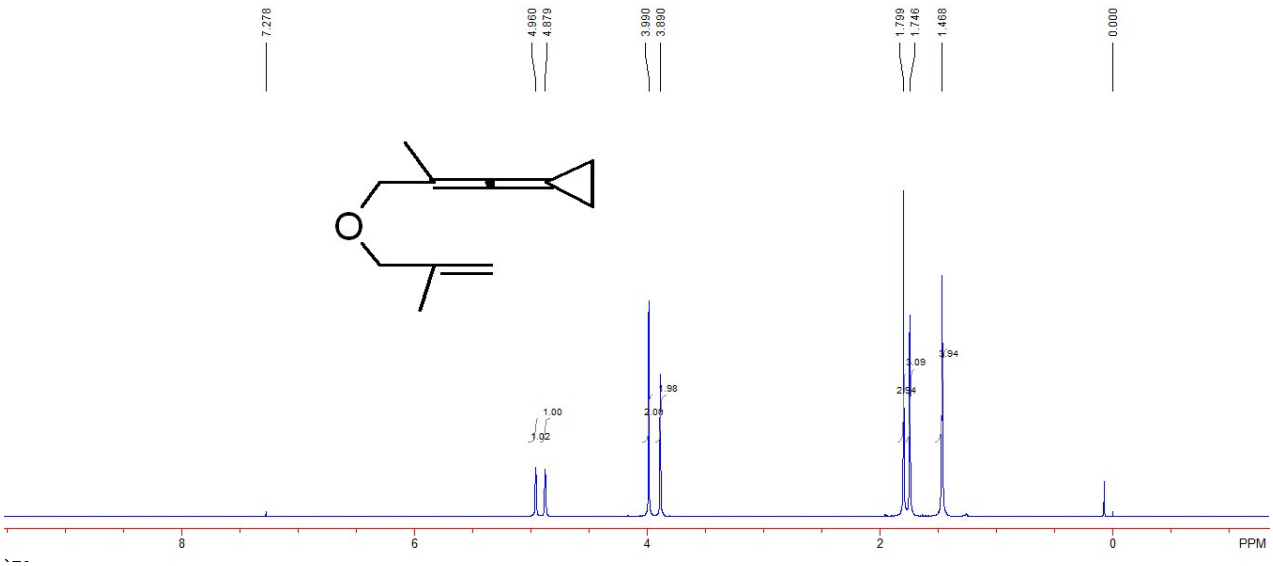


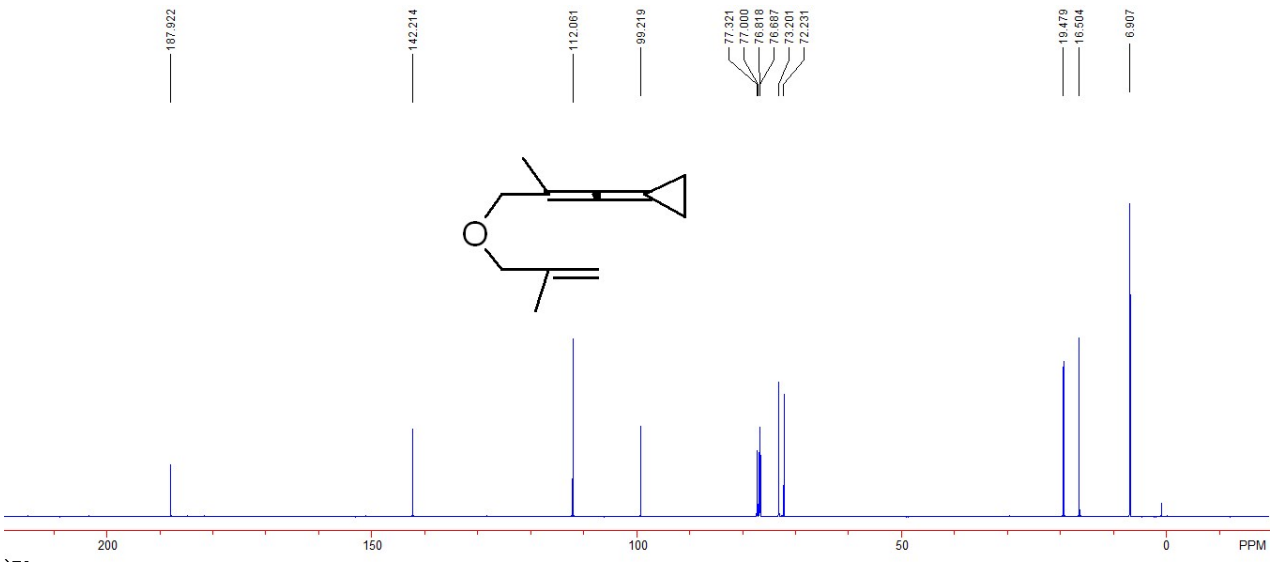


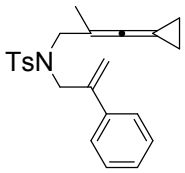


(2-methyl-3-((2-methylallyl)oxy)-1λ^5-prop-1-en-1-ylidene)cyclopropane (1m)

1.0 mmol scale, a light yellow oil, 50% yield (218 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.47 (s, 4H), 1.75 (s, 3H), 1.80 (s, 3H), 3.89 (s, 2H), 3.99 (s, 2H), 4.88 (s, 1H), 4.96 (s, 1H) . ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.9, 16.5, 19.5, 72.2, 73.2, 76.8, 99.2, 112.1, 142.2, 187.9. IR (CH_2Cl_2): ν 2963, 1737, 1566, 1453, 1375, 1144, 1088, 1015, 912, 798, 662 cm^{-1}. Mass (EI) (M^+-H): 163.1, HRMS (EI) calcd. for $C_{11}H_{16}O$ (M^+): 164.1201, Found: 164.1201.



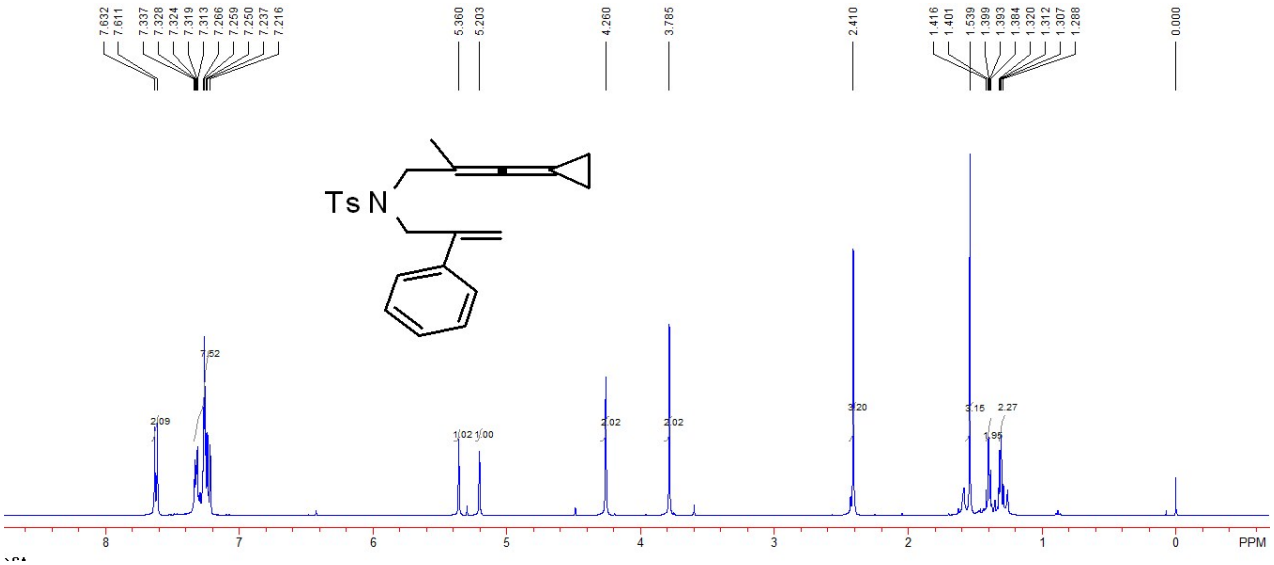


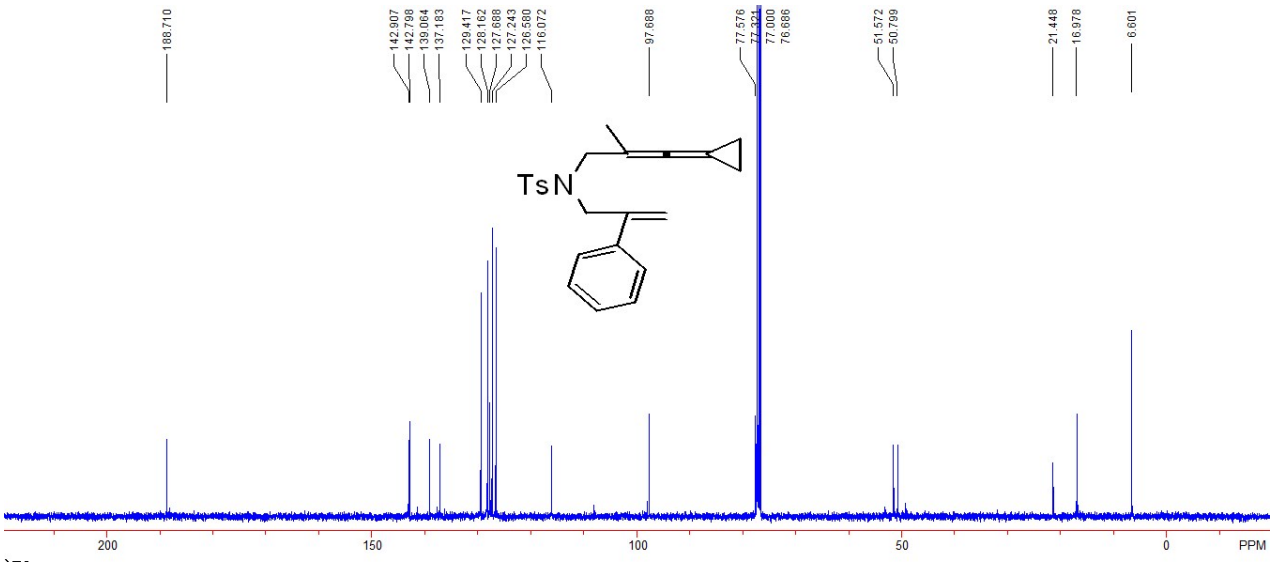


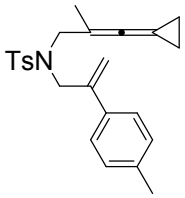
N-(3-cyclopropylidene-2-methyl-3λ^5-allyl)-4-methyl-N-(2-phenylallyl)benzenesulfonamide (1n)

1.0 mmol scale, a light yellow oil, 66% yield (250 mg).^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.29-1.32 (m, 2H), 1.38-1.42 (m, 2H), 1.54 (s, 3H), 2.41 (s, 3H), 3.79 (s, 2H), 4.26 (s, 2H), 5.20 (s, 1H), 5.36 (s, 1H), 7.22-7.34 (m, 7H), 7.62 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.6, 17.0, 21.4, 50.8, 51.6, 51.1, 77.6, 97.7, 116.1, 126.6, 127.2, 127.7, 128.2, 129.4, 137.2, 139.1, 142.8, 142.9, 188.7. IR (CH_2Cl_2): ν 2951, 2792, 2369, 2001, 1665, 1592, 1270, 1163, 1090, 1057,

959, 804, 789, 775, 659 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{26}NO_2S$ $(M+H)^+$: 380.1679, Found: 380.1672.



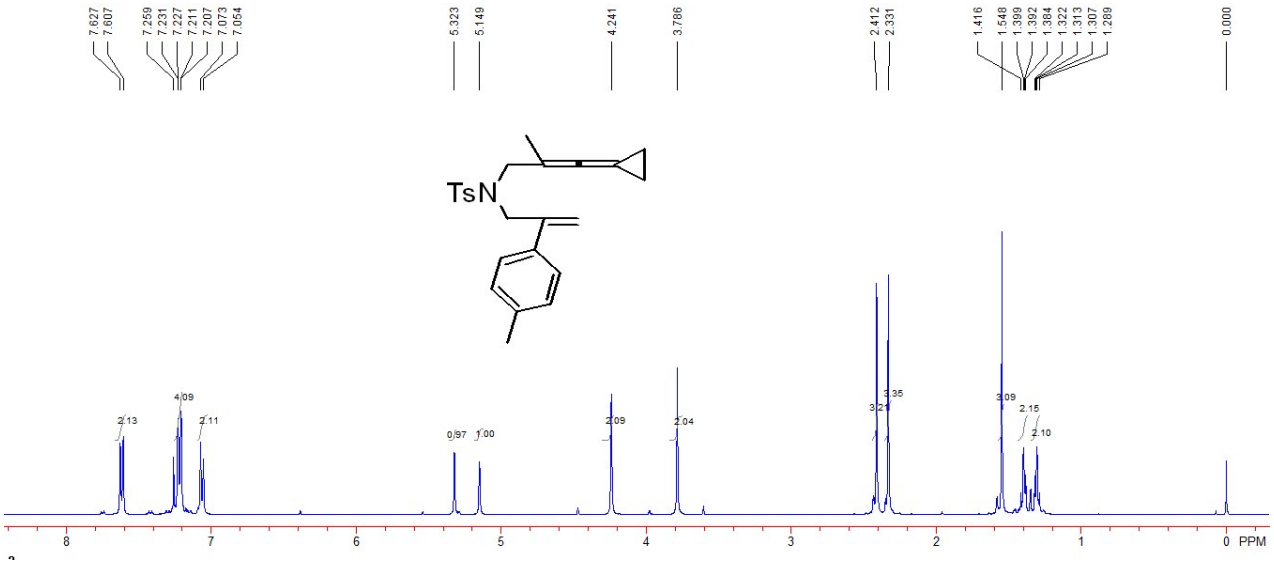


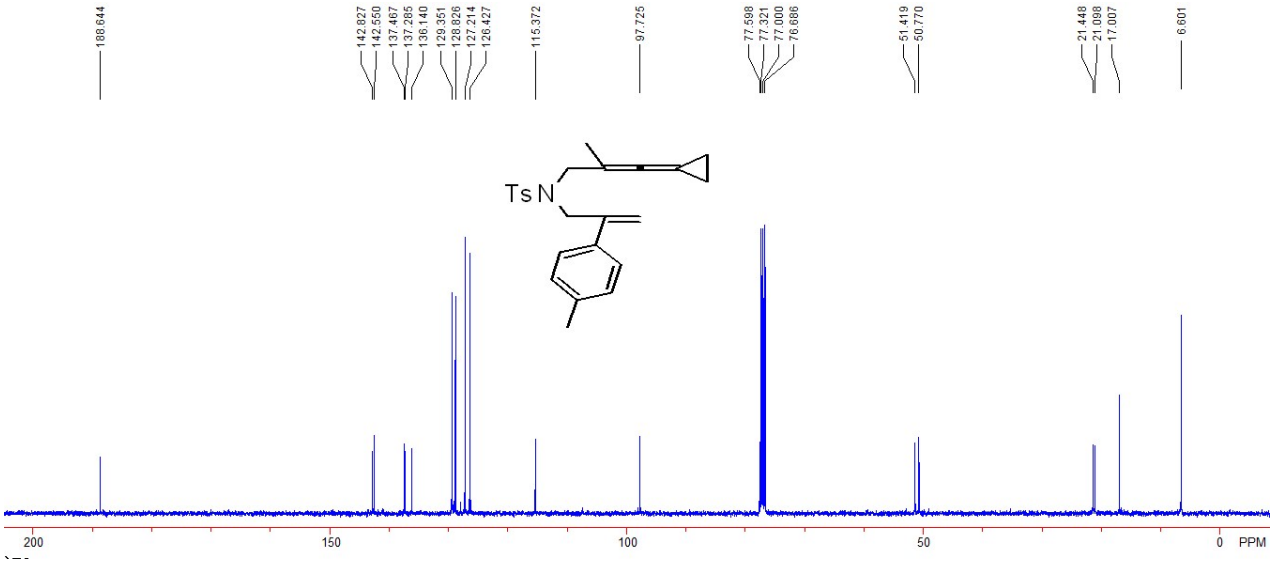


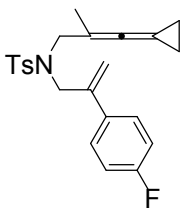
N-(3-cyclopropylidene-2-methyl-3λ^5-allyl)-4-methyl-N-(2-methylenehexyl)benzenesulfonamide (1o)

1.0 mmol scale, a light yellow oil, 65% yield (255 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.29-1.35 (m, 2H), 1.38-1.42 (m, 2H), 1.55 (s, 3H), 2.33 (s, 3H), 2.41 (s, 3H), 3.79 (s, 2H), 4.24 (s, 2H), 5.15 (s, 1H), 5.32 (s, 1H), 7.06 (d, J = 8.0 Hz, 2H), 7.22 (dd, J_1 = 2.0 Hz, J_2 = 8.0 Hz, 4H) 7.62 (d,

J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.6, 17.0, 21.1, 21.4, 50.8, 51.4, 77.6, 97.7, 115.4, 126.4, 127.2, 128.8, 129.4, 136.1, 137.3, 137.5, 142.6, 142.8, 188.6. IR (CH_2Cl_2): ν 2938, 2909, 2019, 1646, 1440, 1352, 1152, 1087, 1049, 1017, 902, 805, 775, 622 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{28}NO_2S$ $(M+H)^+$: 394.1835, Found: 394.1826.

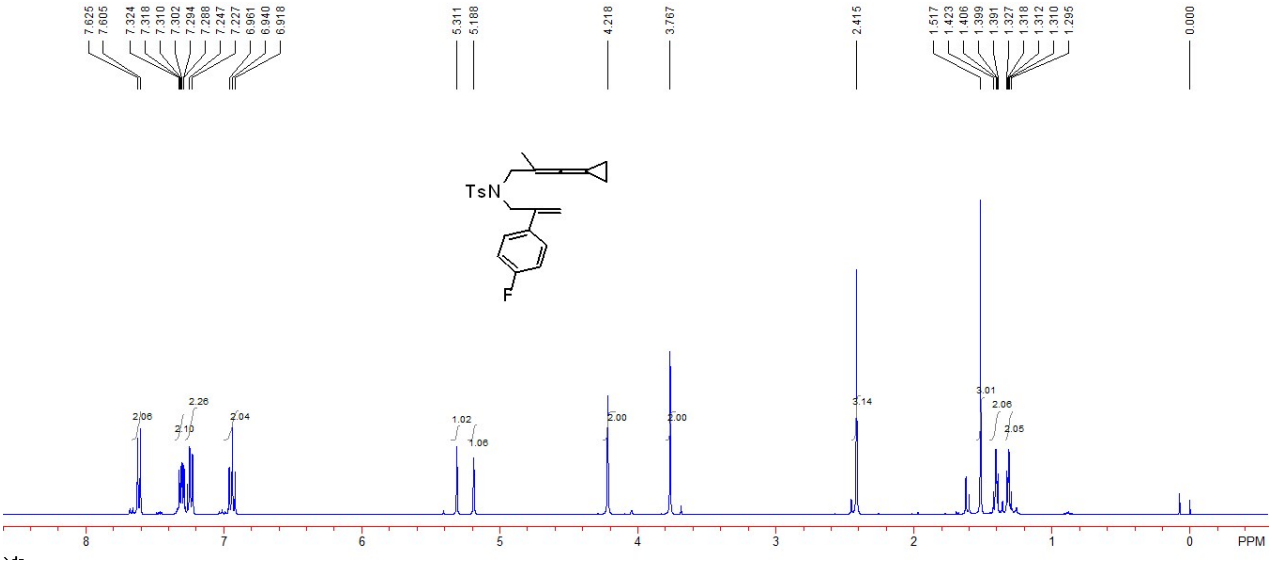


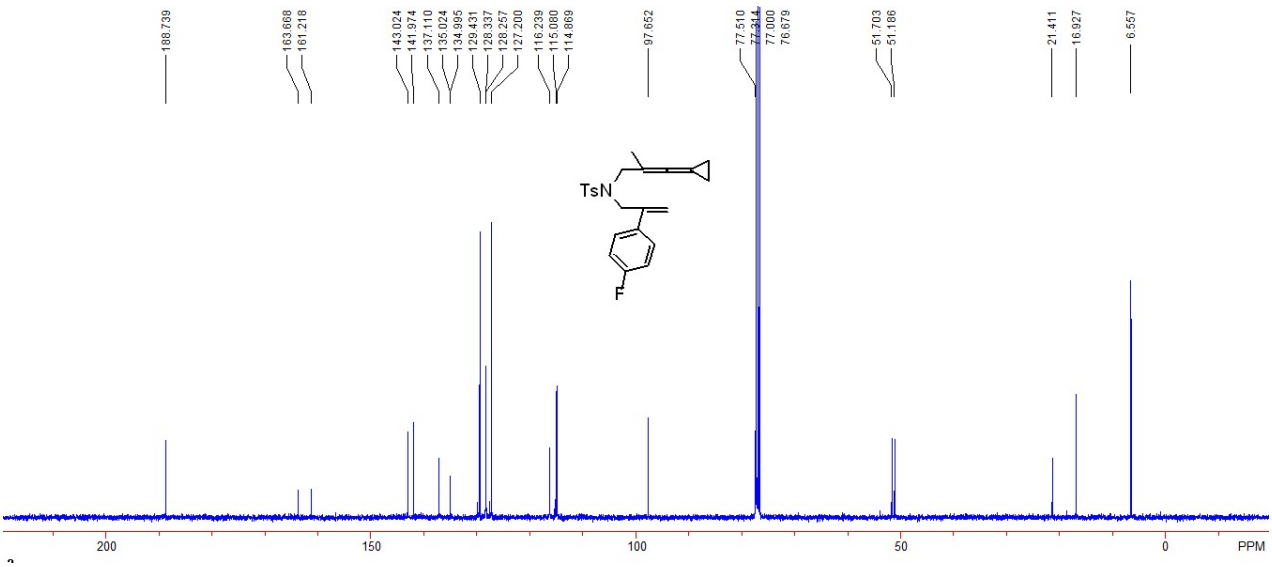


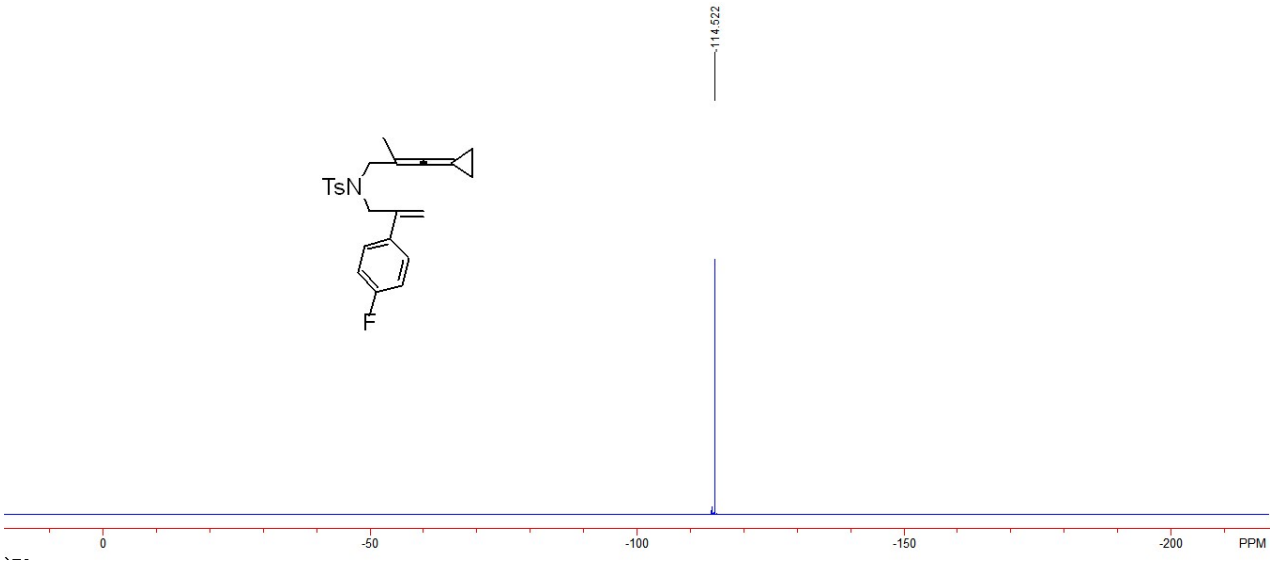


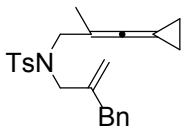
N-(3-cyclopropylidene-2-methyl-3λ^5-allyl)-N-(2-(4-fluorophenyl)allyl)-4-methylbenzenesulfonamide (1p)

1.0 mmol scale, a light yellow oil, 65% yield (258 mg).^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.30-1.33 (m, 2H), 1.39-1.42 (m, 2H), 1.52 (s, 3H), 2.42 (s, 3H), 3.77 (s, 2H), 4.22 (s, 2H), 5.19 (s, 1H), 5.31 (s, 1H), 6.94 (t, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.29-7.32 (m, 2H), 7.62 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.6, 16.9, 21.4, 51.2, 51.7, 77.5, 97.7, 115.0 (d, *J* = 20.0 Hz), 116.2, 127.2, 128.3 (d, *J* = 8.0 Hz), 129.4, 135.0 (d, *J* = 2.9 Hz), 137.1, 142.0, 143.0, 162.4 (d, *J* = 245.0 Hz), 188.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.5 (s, 1F). IR (CH_2Cl_2): ν 3011, 2923, 2876, 2350, 2341, 2035, 1801, 1697, 1440, 1417, 1352, 1330, 1272, 1225, 1155, 1091, 1043, 978, 916, 786, 671 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{25}FNO_2S$ $(M+H)^+$: 398.1583, Found: 398.1577.



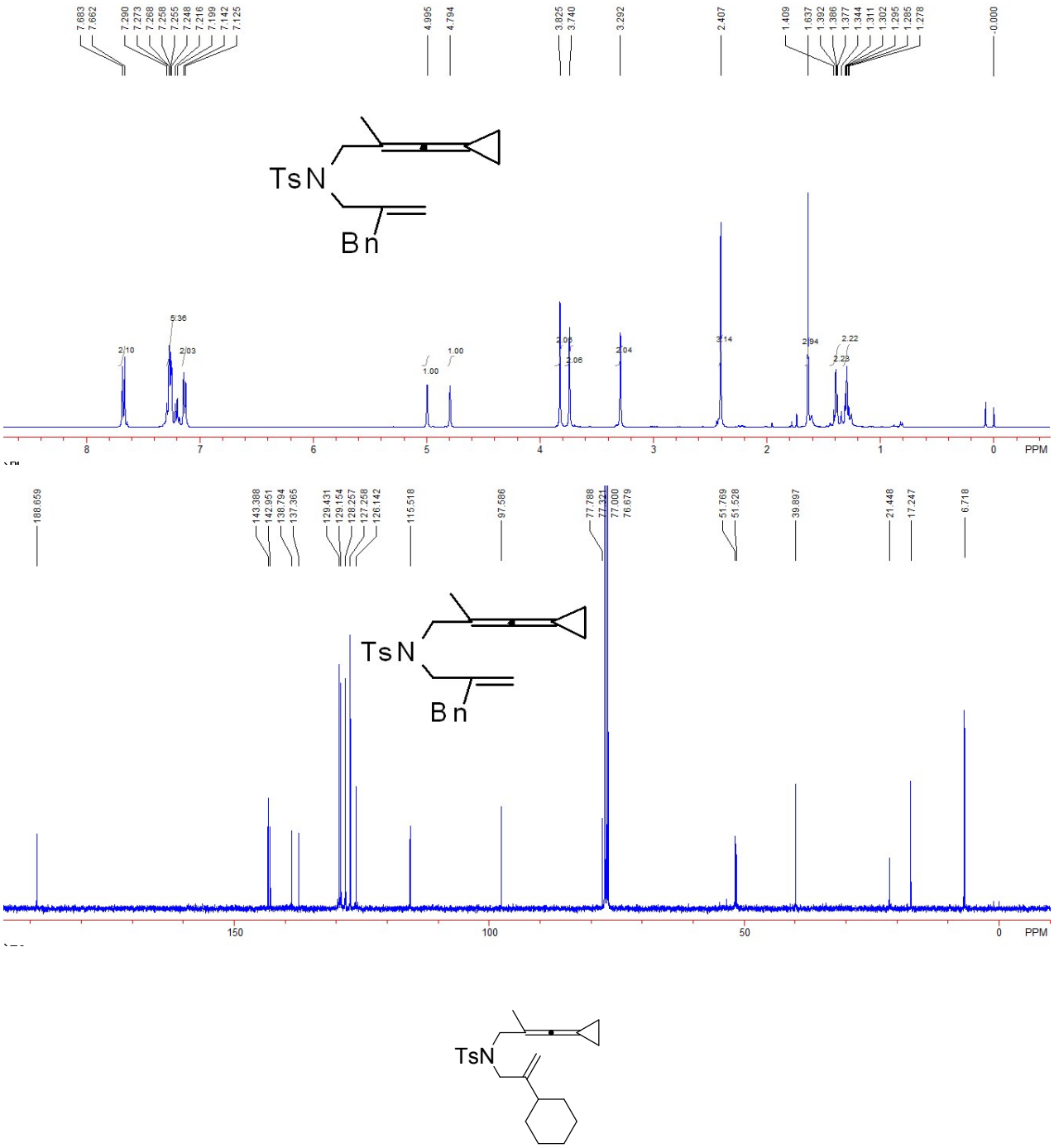






N-(2-benzylallyl)-N-(3-cyclopropylidene-2-methyl-3λ^5-allyl)-4-methylbenzenesulfonamide (1q)

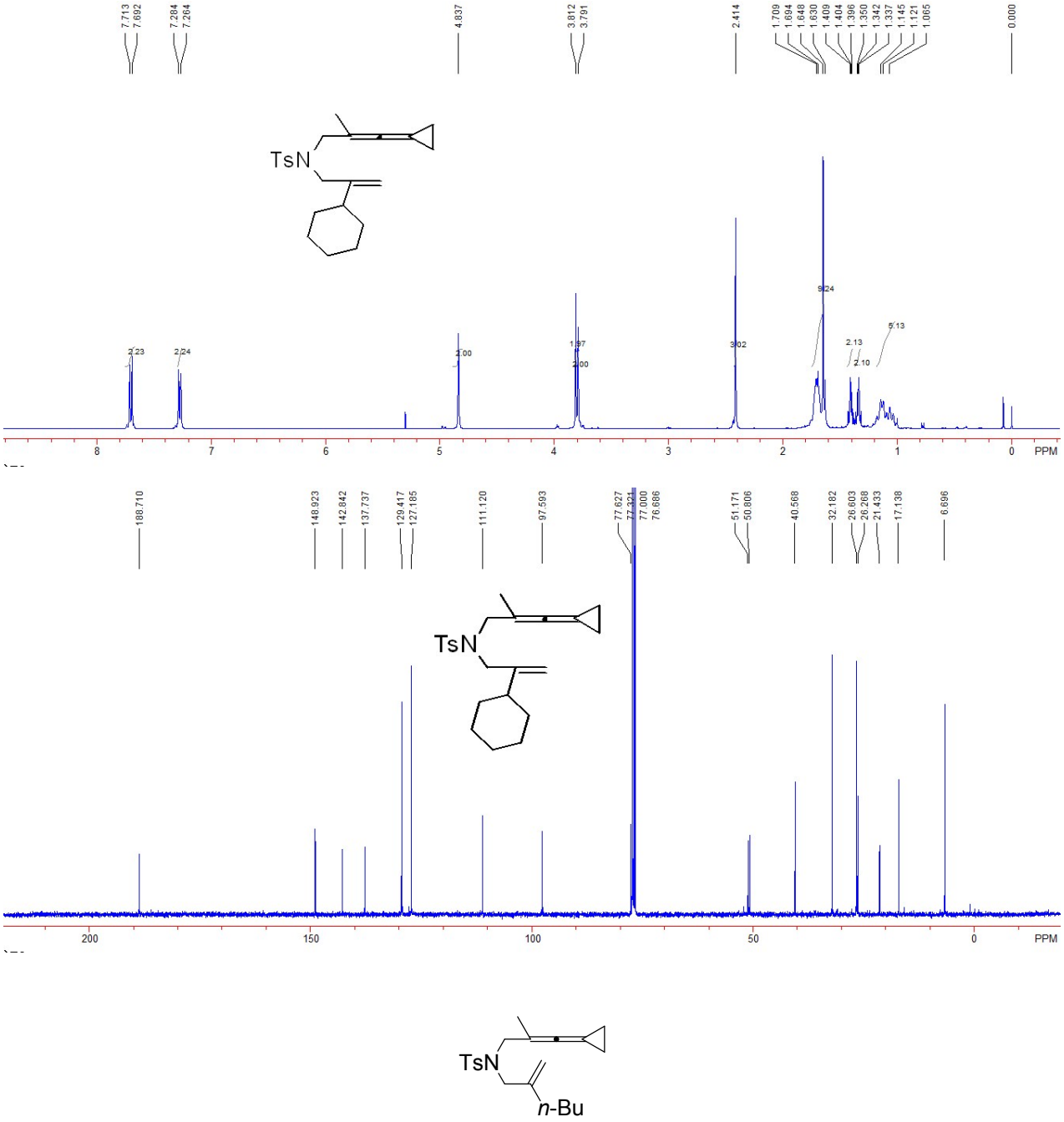
1.0 mmol scale, a light yellow oil, 68% yield (268 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.28-1.31 (m, 2H), 1.38-1.41 (m, 2H), 1.64 (s, 3H), 2.41 (s, 3H), 3.29 (s, 2H), 3.74 (s, 2H), 3.83 (s, 2H), 4.79 (s, 1H), 5.00 (s, 1H), 7.13 (d, *J* = 6.8 Hz, 2H), 7.20-7.29 (m, 5H), 7.67 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.7, 17.2, 21.4, 39.9, 51.5, 51.8, 77.8, 97.6, 115.5, 126.1, 127.3, 128.3, 129.2, 129.4, 137.4, 138.8, 143.0, 143.4, 188.7. IR (CH_2Cl_2): ν 3011, 2975, 2919, 2238, 2019, 1597, 1492, 1346, 1158, 1091, 902, 813, 765, 740, 699 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{28}NO_2S$ $(M+H)^+$: 394.1835, Found: 394.1826.



N-(2-cyclohexylallyl)-N-(3-cyclopropylidene-2-methyl-3λ^5-allyl)-4-methylbenzenesulfonamide (1r)

1.0 mmol scale, a light yellow oil, 75% yield (289 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.07-1.15 (m, 5H), 1.34-1.35 (m, 2H), 1.40-1.41 (m, 2H), 1.63-1.71 (m, 9H), 2.41 (s, 3H), 3.79 (s, 2H), 3.81 (s, 2H), 4.84 (s, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.7, 17.1, 21.4, 26.3, 26.6, 32.2, 40.6, 50.8, 51.1, 77.4, 97.6, 111.1, 127.2, 129.4, 137.7, 142.8, 148.9, 188.7. IR (CH_2Cl_2): ν 2930, 2849, 2022, 1592, 1438, 1322, 1312, 1155,

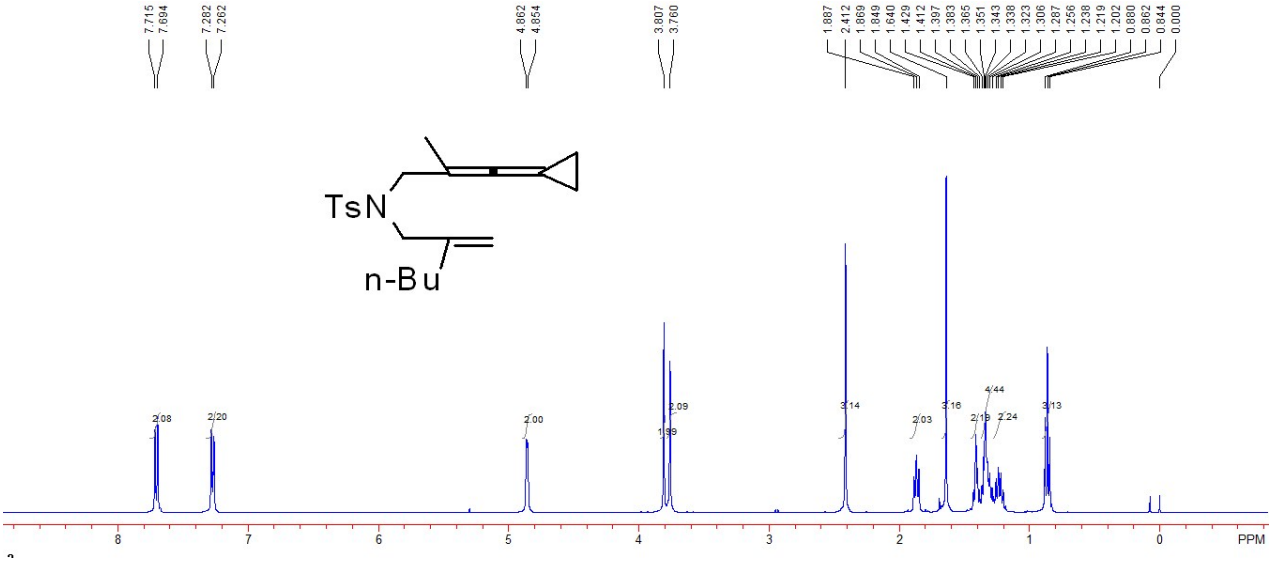
1110, 1087, 906, 891, 813, 806, 768, 662 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{32}NO_2S$ $(M+H)^+$: 386.2148, Found: 386.2139.

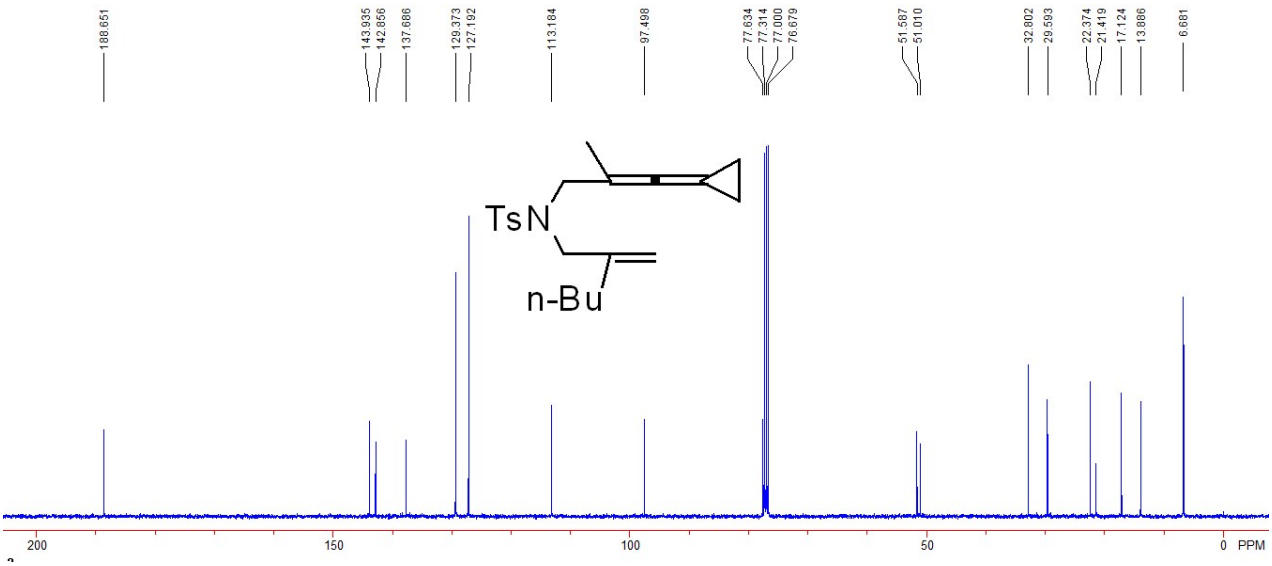


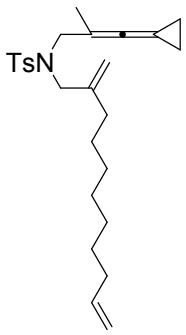
N-(3-cyclopropylidene-2-methyl-3λ^5-allyl)-4-methyl-N-(2-methylenehexyl)benzenesulfonamide (1s)

1.0 mmol scale, a light yellow oil, 74% yield (266 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.86 (t, *J* = 7.2 Hz, 3H), 1.20-1.26 (m, 2H), 1.29-1.37 (m, 4H), 1.38-1.43 (m, 2H), 1.64 (s, 3H), 1.87 (t, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 3.76 (s, 2H), 3.81 (s, 2H), 4.85 (d, *J* = 3.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.7, 13.9, 17.1, 21.4, 22.4,

29.6, 32.8, 51.0, 51.6, 77.6, 97.5, 113.2, 127.2, 129.4, 137.7, 142.9, 143.9, 188.7. IR (neat): ν 2985, 2956, 2923, 2857, 2022, 1646,1431, 1341, 1156, 1116, 1089, 1048, 1019, 905, 813, 754, 658 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{30}NO_2S$ $(M+H)^+$: 360.1992, Found: 360.1984.



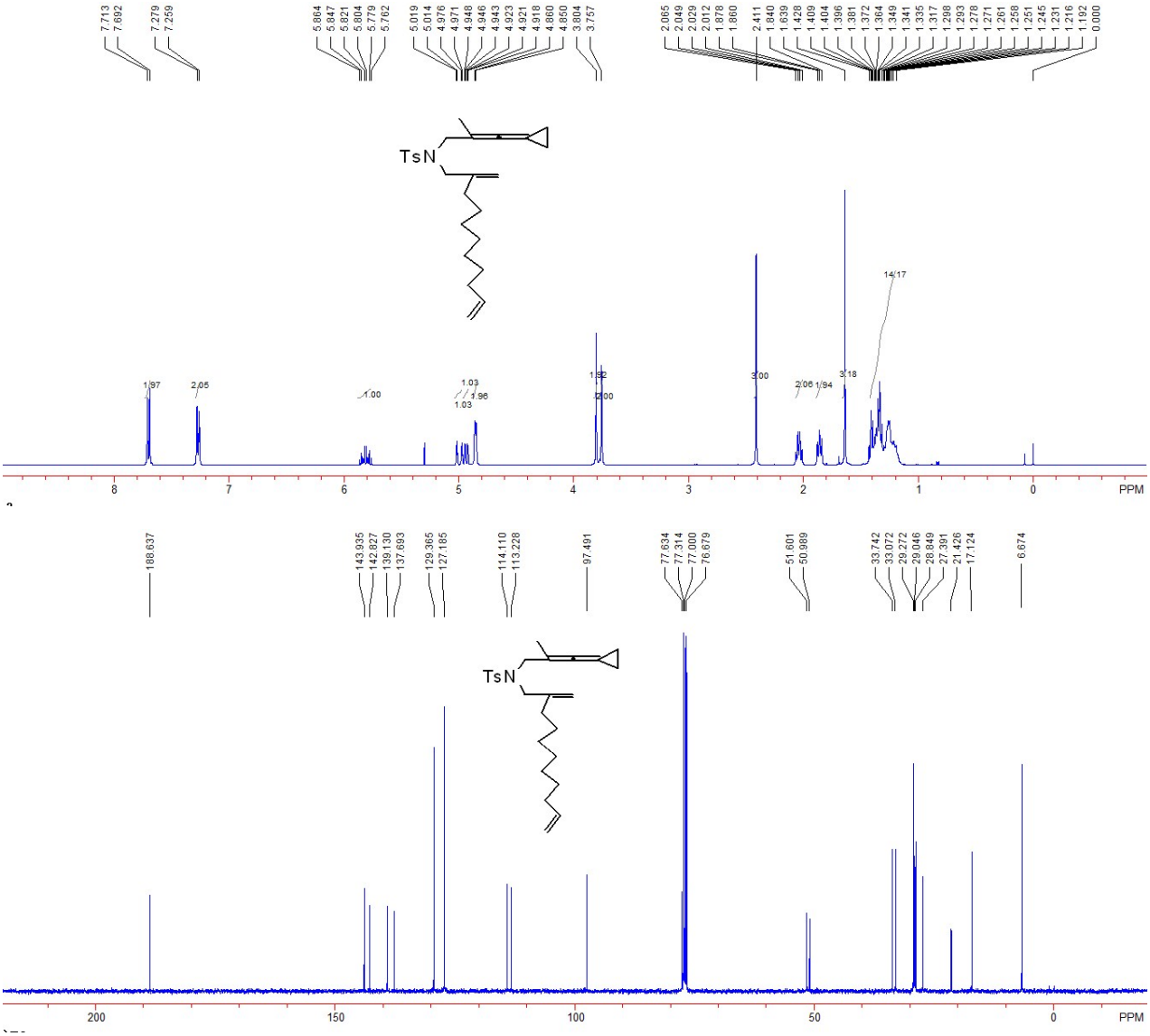


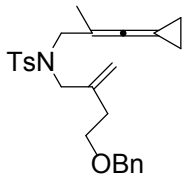


N-(3-cyclopropylidene-2-methyl-3λ^5-allyl)-4-methyl-N-(2-methyleneundec-10-en-1-

yl)benzenesulfonamide (1t)

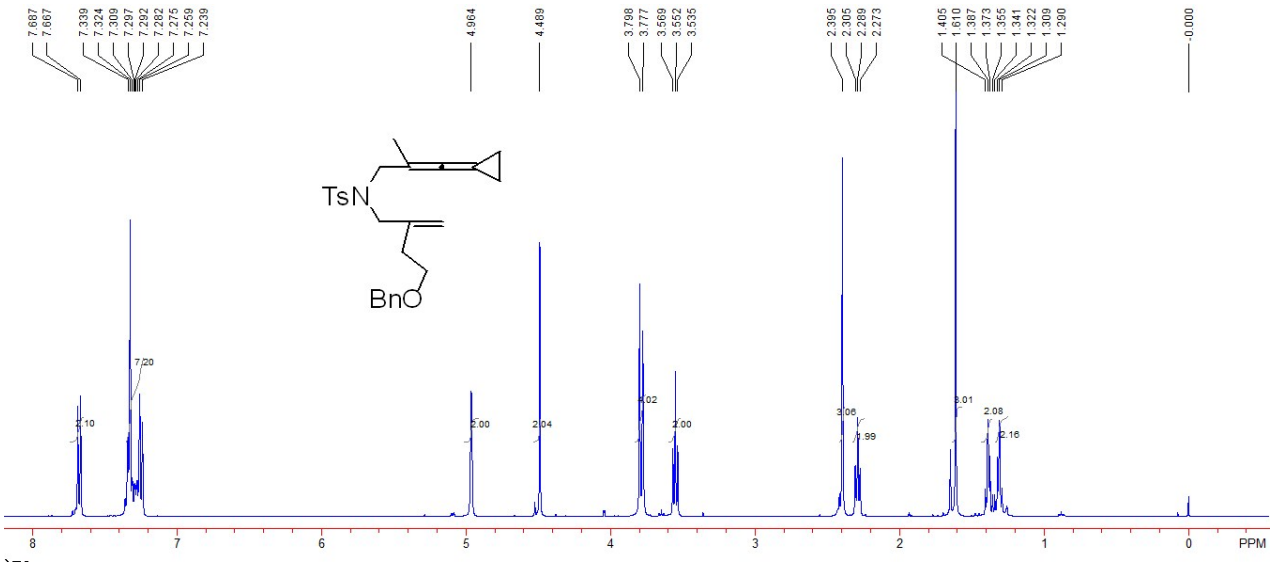
1.0 mmol scale, a light yellow oil, 59% yield (252 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.19-1.43 (m, 14H), 1.64 (s, 3H), 1.86 (t, *J* = 8.0 Hz, 2H), 2.04 (q, *J* = 6.4 Hz, 2H), 2.41 (s, 3H), 3.76 (s, 2H), 3.80 (s, 2H), 4.86 (d, *J* = 4.0 Hz, 2H), 4.92-4.95 (m, 1H), 4.97-5.02 (m, 1H), 5.76-5.86 (m, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.7, 17.1, 21.4, 27.4, 28.8, 29.0, 29.2, 33.1, 33.7, 51.0, 51.6, 77.6, 97.5, 113.2, 114.1, 127.2, 129.4, 137.7, 139.1, 142.8, 143.9, 188.6. IR (CH_2Cl_2): ν 2925, 2849, 2027, 1646, 1592, 1448, 1343, 1156, 1089, 1049, 905, 813, 809, 770, 658 cm^{-1}. HRMS (ESI) calcd. for $C_{26}H_{38}NO_2S$ $(M+H)^+$: 428.2618, Found: 428.2607.

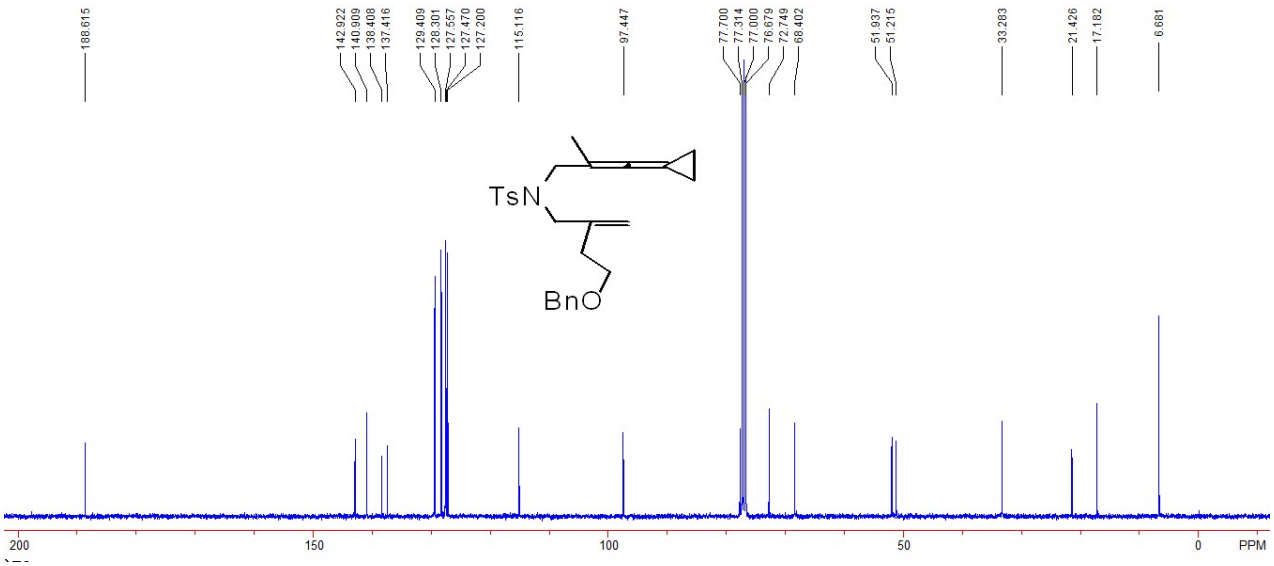


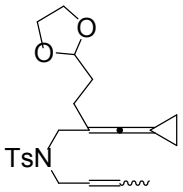


N-(4-(benzyloxy)-2-methylenebutyl)-N-(3-cyclopropylidene-2-methyl-3λ^5-allyl)-4-methylbenzenesulfonamide (1u)

1.0 mmol scale, a light yellow oil, 67% yield (292 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.29-1.34 (m, 2H), 1.36-1.41 (m, 2H), 1.61 (s, 3H), 2.29 (t, *J* = 6.4 Hz, 2H), 2.40 (s, 3H), 3.55 (t, *J* = 6.8 Hz, 2H), 3.78 (s, 2H), 3.80 (s, 2H), 4.49 (s, 2H), 4.96 (s, 2H), 7.24-7.34 (m, 7H), 7.68 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.7, 17.2, 21.4, 33.3, 51.2, 51.9, 68.4, 72.7, 77.7, 97.4, 115.1, 127.2, 127.4, 127.6, 128.3, 129.4, 137.4, 138.4, 140.9, 142.9, 188.6. IR (CH_2Cl_2): ν 2980, 2912, 2842, 2012, 1712, 1600, 1338, 1156, 1089, 1012, 939, 919, 905, 792, 767, 704, 667, 659 cm^{-1}. HRMS (ESI) calcd. for $C_{26}H_{35}N_2O_3S$ $(M+NH)^+$: 455.2363, Found: 455.2351.



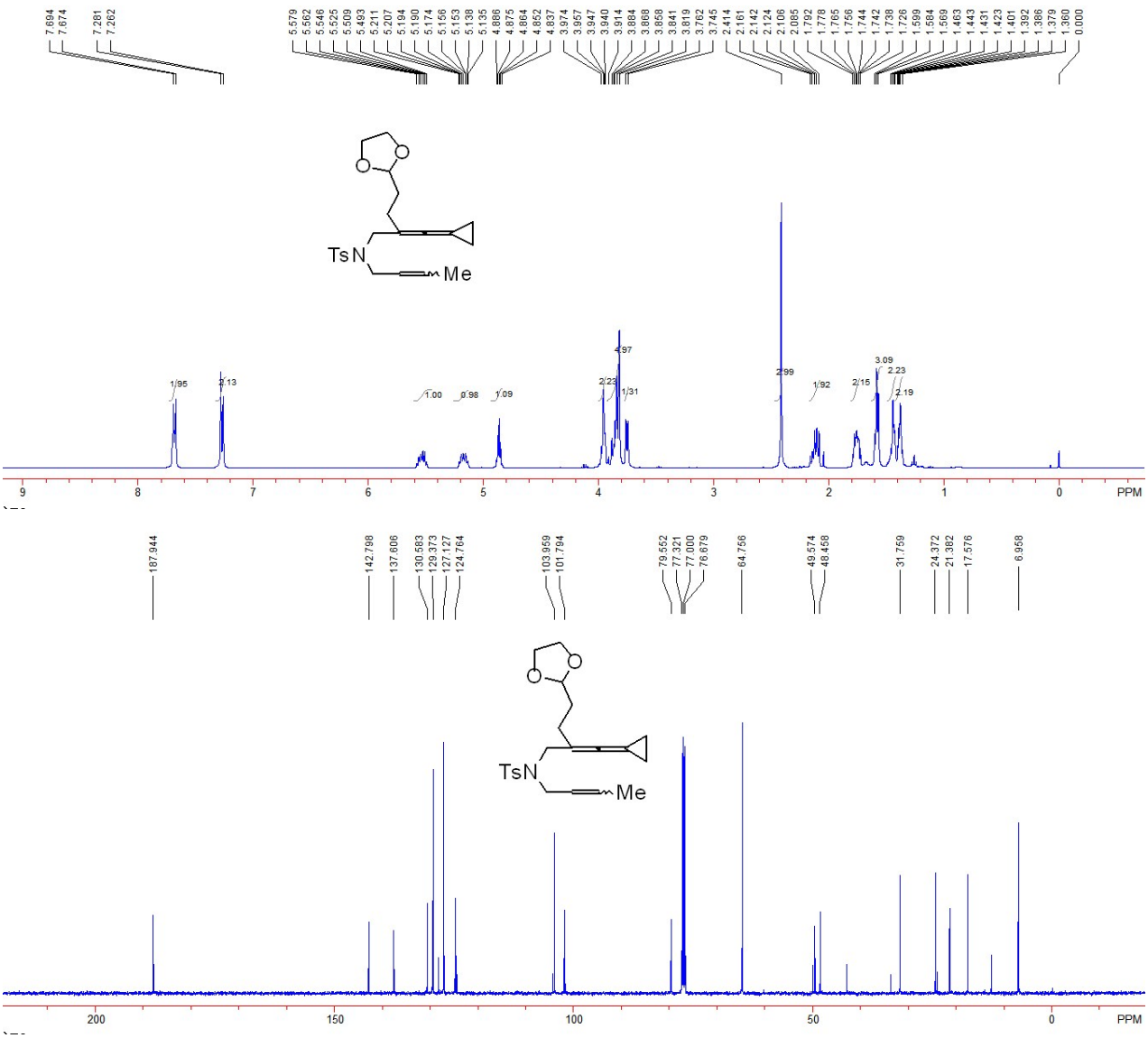




(E:Z = 5:1)

N-(but-2-en-1-yl)-N-(2-(cyclopropylidene-l5-methylene)-4-(1,3-dioxolan-2-yl)butyl)-4-methylbenzenesulfonamide (5a)

1.0 mmol scale, a light yellow oil, 77% yield (310 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.36-1.40 (m, 2H), 1.42-1.46 (m, 2H), 1.57-1.60 (m, 3H), 1.73-1.79 (m, 2H), 2.09-2.16 (m, 2H), 2.41 (s, 3H), 3.75 (d, *J* = 6.8 Hz, 1H), 3.82-3.88 (m, 4H), 3.91-3.97 (m, 2H), 4.84-4.89 (m, 1H), 5.14-5.21 (m, 1H), 5.49-5.58 (m, 1H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 7.0, 17.6, 21.4, 24.4, 31.8, 48.5, 49.6, 64.8, 79.6, 101.8, 104.0, 124.8, 127.2, 129.4, 130.6, 137.6, 142.8, 187.9. IR (CH_2Cl_2): ν 3019, 2925, 2878, 2017, 1438, 1337, 1155, 1090, 1030, 967, 912, 814, 802, 773, 689, 658 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{30}NO_4S$ $(M+H)^+$: 404.1817, Found: 404.1885.


7.694
7.674
7.281
7.262
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5.562
5.546
5.525
5.509
5.493
5.211
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5.190
5.174
5.156
5.153
5.138
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4.852
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3.974
3.957
3.947
3.940
3.914
3.884
3.868
3.858
3.841
3.819
3.762
3.745
2.414
2.161
2.142
2.124
2.108
2.085
1.792
1.778
1.765
1.756
1.744
1.742
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1.726
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1.584
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1.423
1.401
1.392
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TsN
Me
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2.13
1.00
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1.09
2.23
4.97
1.31
2.99
1.92
2.15
3.09
2.23
2.19
9
8
7
6
5
4
3
2
1
0
PPM
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130.583
129.373
127.127
124.764
103.959
101.794
79.552
77.321
77.000
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64.756
49.574
48.458
31.759
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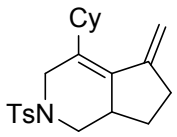
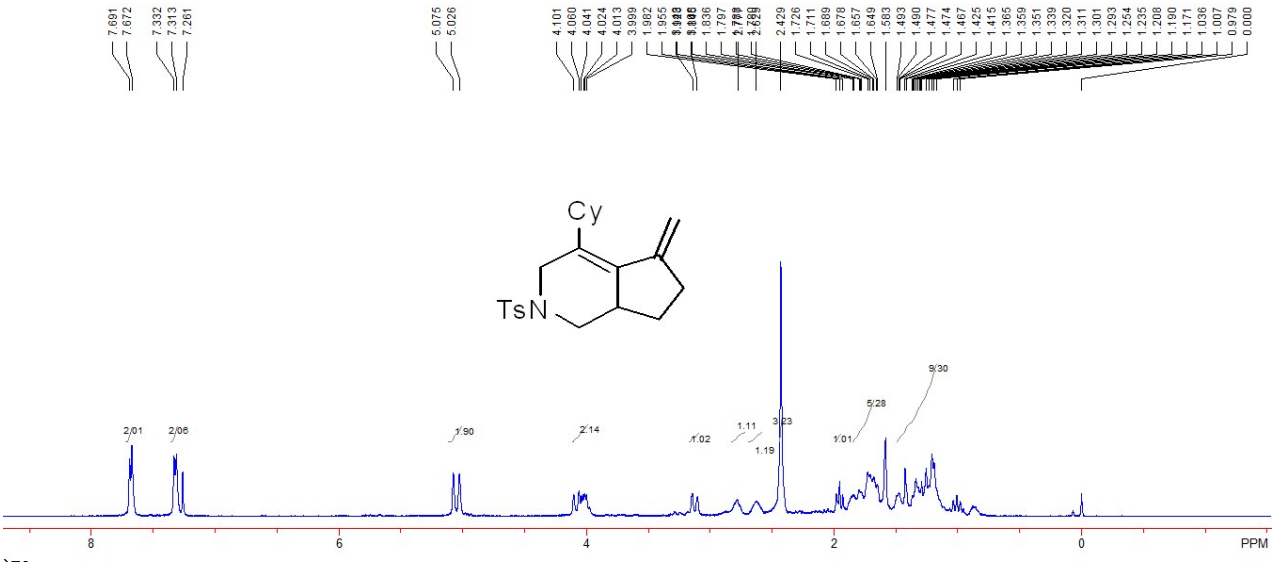
17.576
6.958
TsN
Me
200
150
100
50
0
PPM

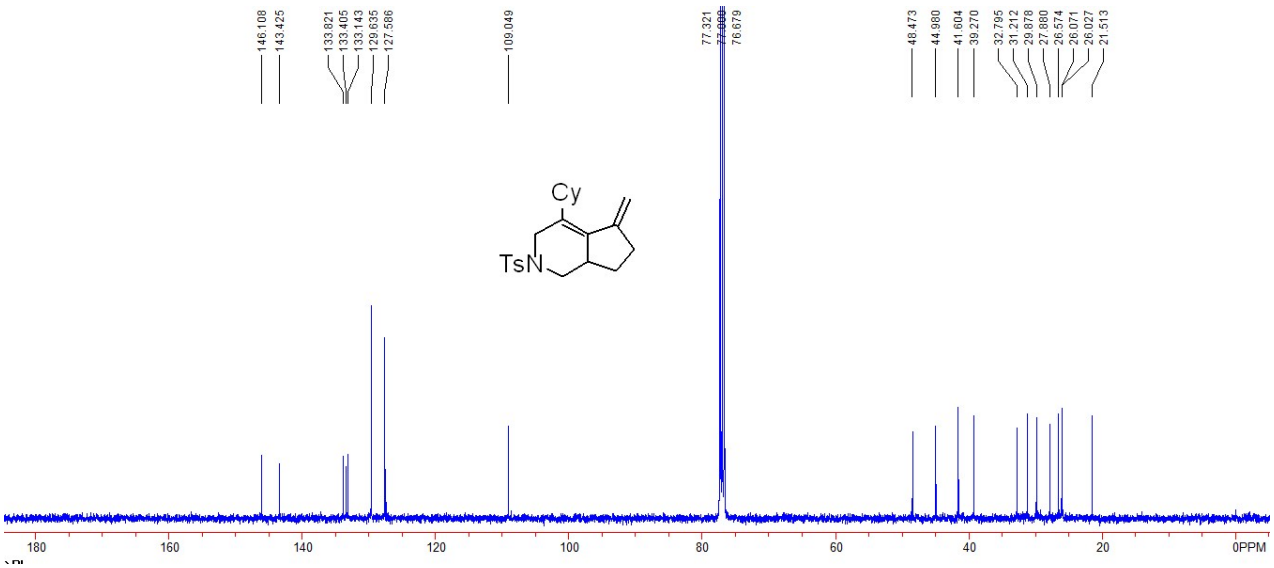
7. Characterization and spectra charts for product

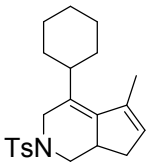


4-cyclohexyl-5-methylene-2-tosyl-2,3,5,6,7,7a-hexahydro-1H-cyclopenta[c]pyridine (2a)

A white solid. 77% yield (28 mg). M. P. 89-92 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.98-1.49 (m, 9H), 1.59-1.85 (m, 5H), 1.93-1.98 (m, 1H), 2.43 (s, 3H), 2.63 (s, 1H), 2.78 (s, 1H), 3.13 (d, J = 14.0 Hz, 2H), 4.00-4.10 (m, 2H), 5.03 (s, 1H), 5.08 (s, 1H), 7.32 (d, J = 7.6 Hz, 2H), 7.68 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.5, 26.03, 26.07, 26.6, 27.9, 29.9, 31.2, 32.8, 39.3, 41.6, 45.0, 48.5, 109.0, 127.6, 129.6, 133.1, 133.4, 133.8, 143.4, 146.1. IR (CH_2Cl_2): ν 3014, 2922, 1627, 1477, 1403, 1326, 1278, 1125, 969, 948, 822, 671, 662 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{30}NO_2S$ $(M+H)^+$: 372.1992, Found: 372.1992.

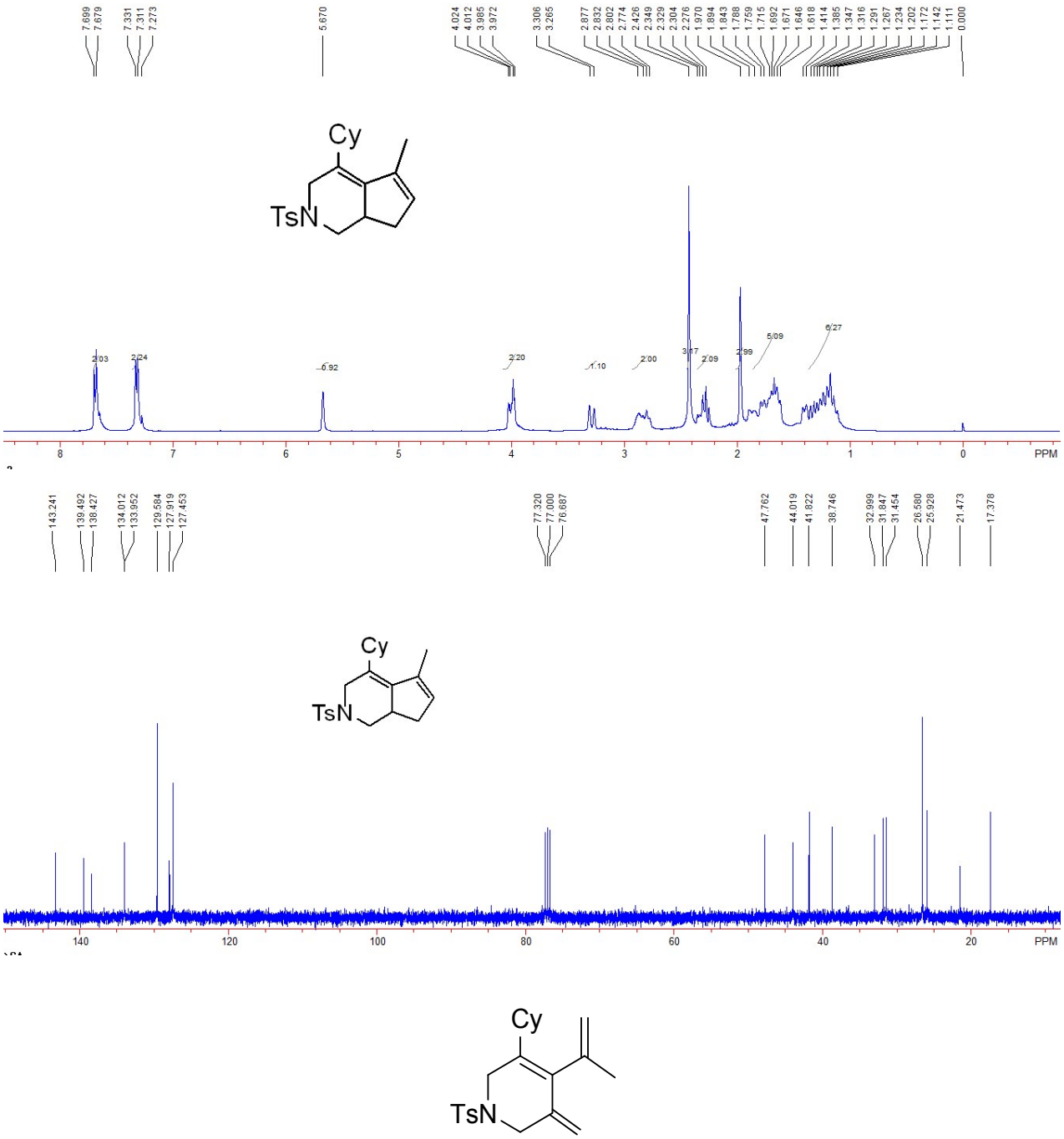






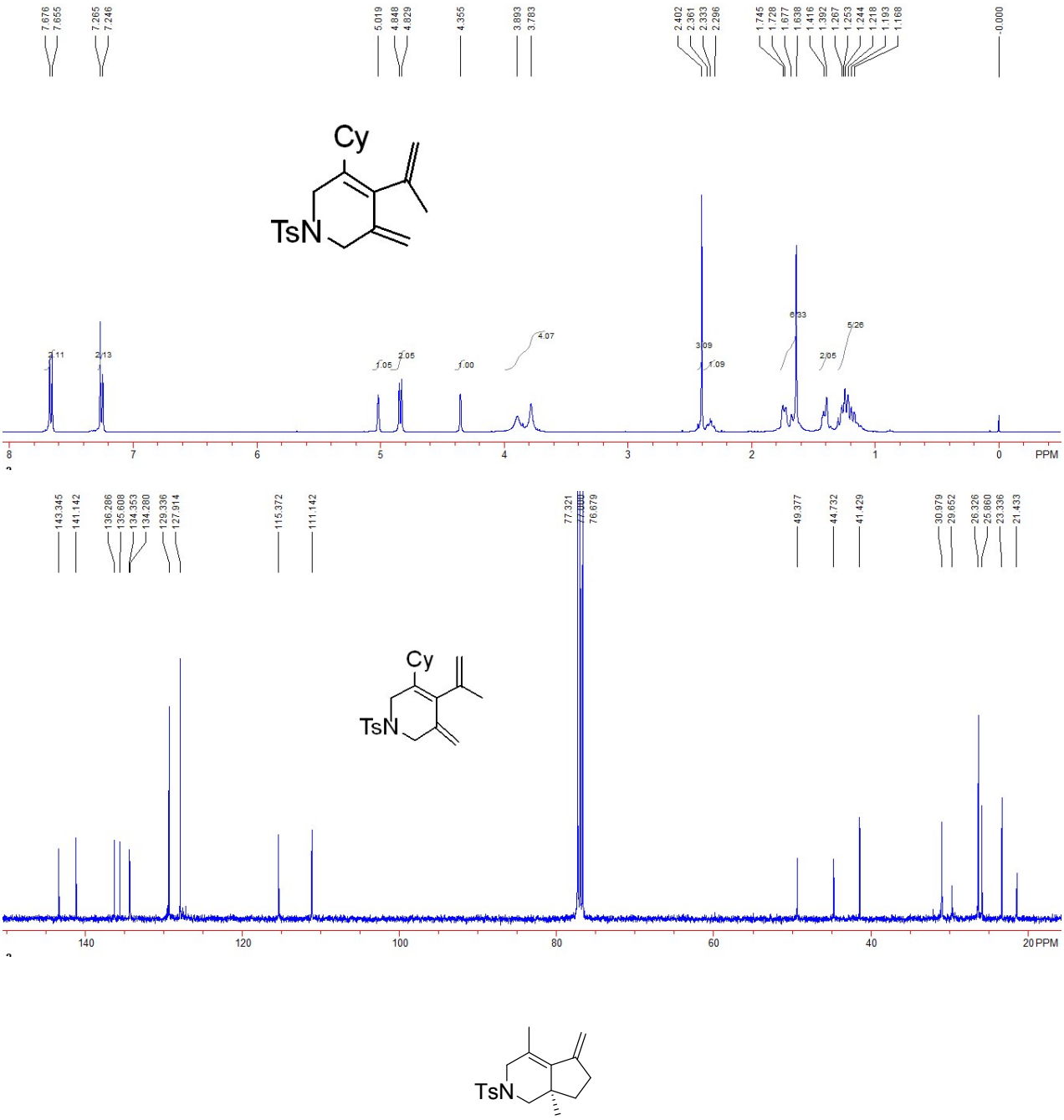
4-cyclohexyl-5-methyl-2-tosyl-2,3,7,7a-tetrahydro-1H-cyclopenta[c]pyridine (3a)

A white solid. 67% yield (25 mg). M. P. 93-95 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.11-1.41 (m, 6H), 1.62-1.89 (m, 5H), 1.97 (s, 3H), 2.28-2.35 (m, 2H), 2.43 (s, 3H), 2.77-2.88 (m, 2H), 3.29 (d, J = 16.4 Hz, 1H), 3.97-4.02 (m, 2H), 5.67 (s, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 17.4, 21.5, 25.9, 26.6, 31.5, 31.8, 33.0, 38.7, 41.8, 44.0, 47.8, 127.5, 127.9, 129.6, 133.95, 134.01, 138.4, 139.5, 143.2. IR (CH_2Cl_2): ν 3102, 2972, 1607, 1558, 1493, 1460, 1430, 1389, 1324, 1259, 1135, 979, 938, 832, 682, 664 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{30}NO_2S$ $(M+H)^+$: 372.1992, Found: 372.1992.



5-cyclohexyl-3-methylene-4-(prop-1-en-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine (4a)

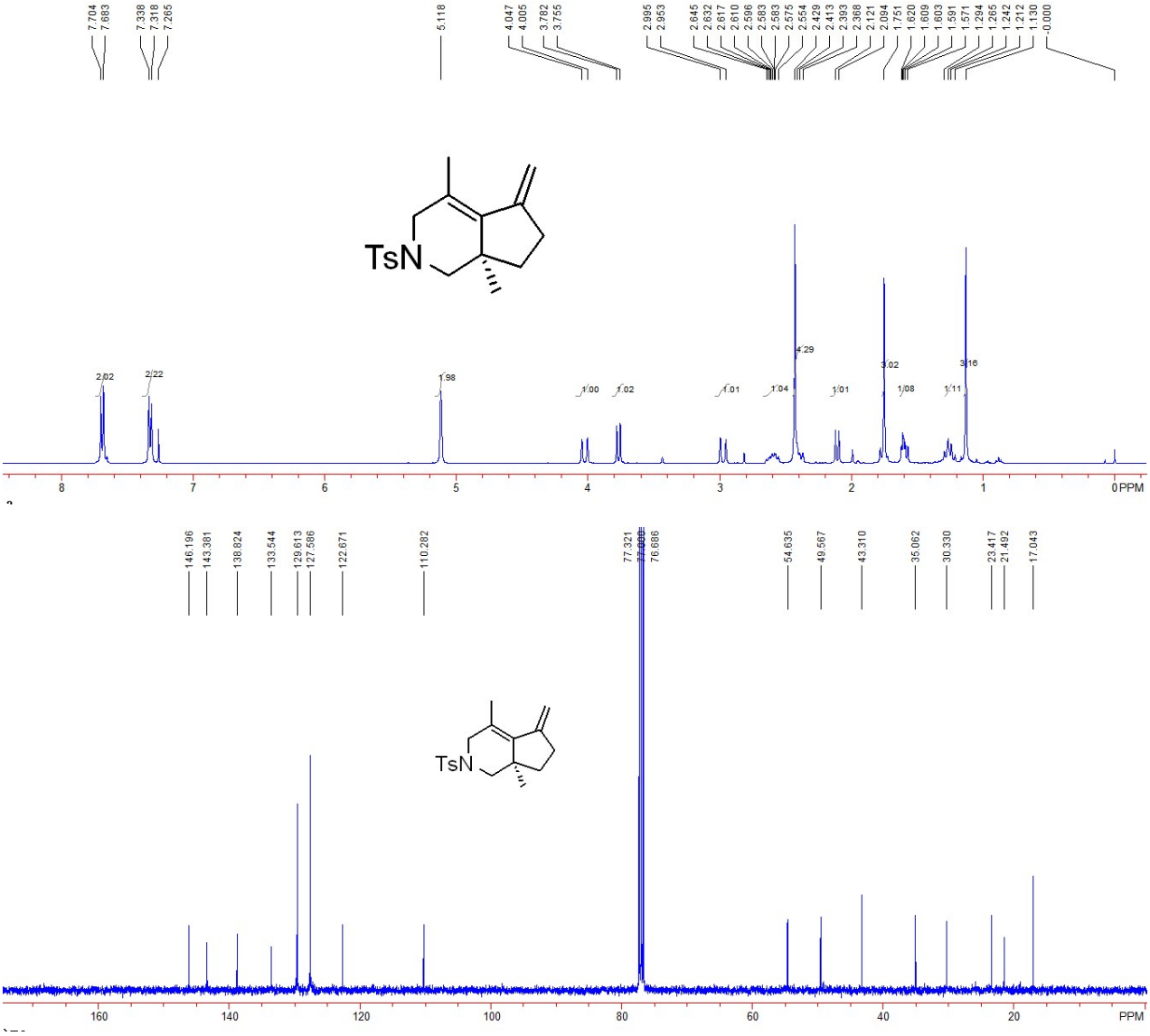
A white solid. 45% yield (17 mg). M. P. 79-82 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.17-1.27 (m, 5H), 1.39-1.42 (m, 2H), 1.64-1.75 (m, 6H), 2.33 (t, J = 14.8 Hz, 1H), 2.40 (s, 3H), 3.79-3.89 (m, 4H), 4.36 (s, 1H), 4.84 (d, J = 7.6 Hz, 2H), 5.02 (s, 1H), 7.26 (d, J = 7.6 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.4, 23.3, 25.9, 26.3, 29.7, 31.0, 41.4, 44.7, 49.4, 111.1, 115.4, 127.9, 129.3, 134.3, 134.4, 135.6, 136.3, 141.1, 143.3. IR (CH_2Cl_2): ν 2967, 2923, 1662, 1623, 1449, 1346, 1162, 1093, 1050, 977, 905, 871, 816, 793, 765, 712, 666 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{30}NO_2S$ $(M+H)^+$: 372.1992, Found: 372.1991.

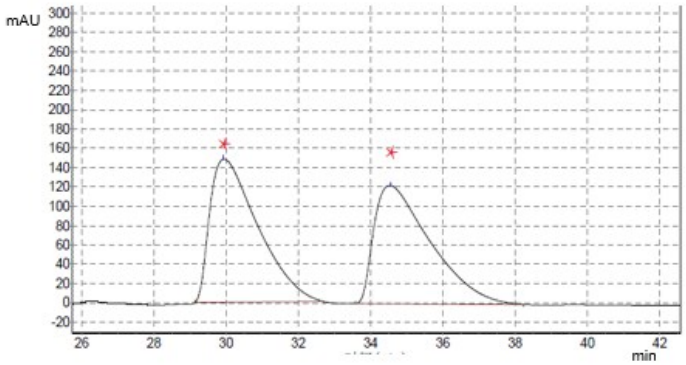


(*R*)-4,7a-dimethyl-5-methylene-2-tosyl-2,3,5,6,7,7a-hexahydro-1*H*-cyclopenta[*c*]pyridine (2b)

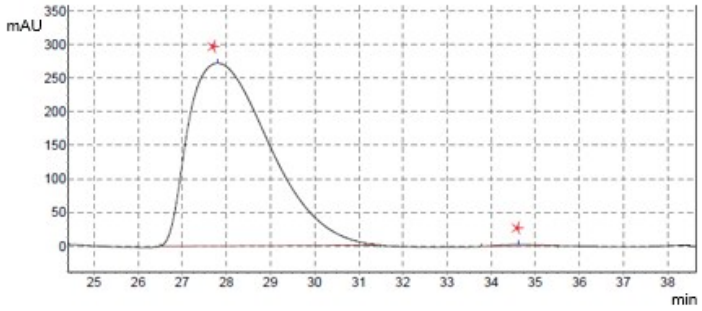
A white solid, 91% yield (29 mg). M. P. 83-88 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.13 (s, 3H), 1.21-1.29 (m, 1H), 1.57-1.62 (m, 1H), 1.75 (s, 3H), 2.11 (d, *J* = 10.8 Hz, 1H), 2.37-2.43 (m, 4H), 2.56-2.65 (m, 1H), 2.97 (d, *J* = 16.8 Hz, 1H), 3.77 (d, *J* = 10.4 Hz, 1H), 4.03 (d, *J* = 16.8 Hz, 1H), 5.12 (s, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 17.0, 21.5, 23.4, 30.3, 35.1, 43.3, 49.6, 54.6, 110.3, 122.7, 127.6, 129.6, 133.5, 138.9, 143.4, 146.2. IR (CH_2Cl_2): ν 3052, 2934,1697, 1590, 1344, 1258, 1123, 1031, 977, 901, 841, 811, 794, 767, 712, 663 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{24}NO_2S$ $(M+H)^+$: 318.1522, Found:

318.1513. Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 25/1; Flow rate: 0.80 mL/min; t_{minor} = 27.80 min, t_{major} = 34.63 min; ee% > 99%; $[\alpha]^{20}_D$ = +58.3 (c 1.00, CH_2Cl_2)].



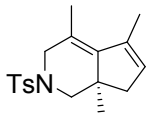


Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	29.933	148179.438	13661397.000	50.7596
2	34.542	122500.766	13252510.000	49.2404
Totals:		270680.203	26913907.000	100.0000



Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	27.795	272297.813	34762648.000	99.6449
2	34.625	2037.162	123894.500	0.3551
Totals:		274334.974	34886542.500	100.0000

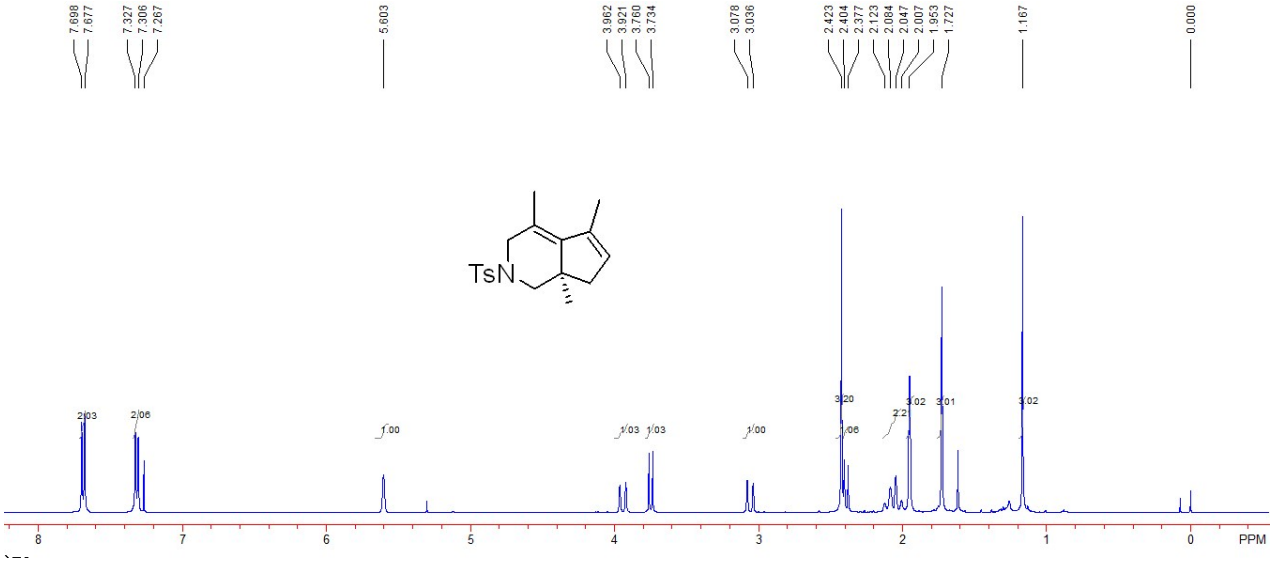
Translation: Chiralcel AS-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 25/1; Flow rate: 0.8 mL/min; t_{minor} = 27.80 min, t_{major} = 34.63 min; ee% > 99%].

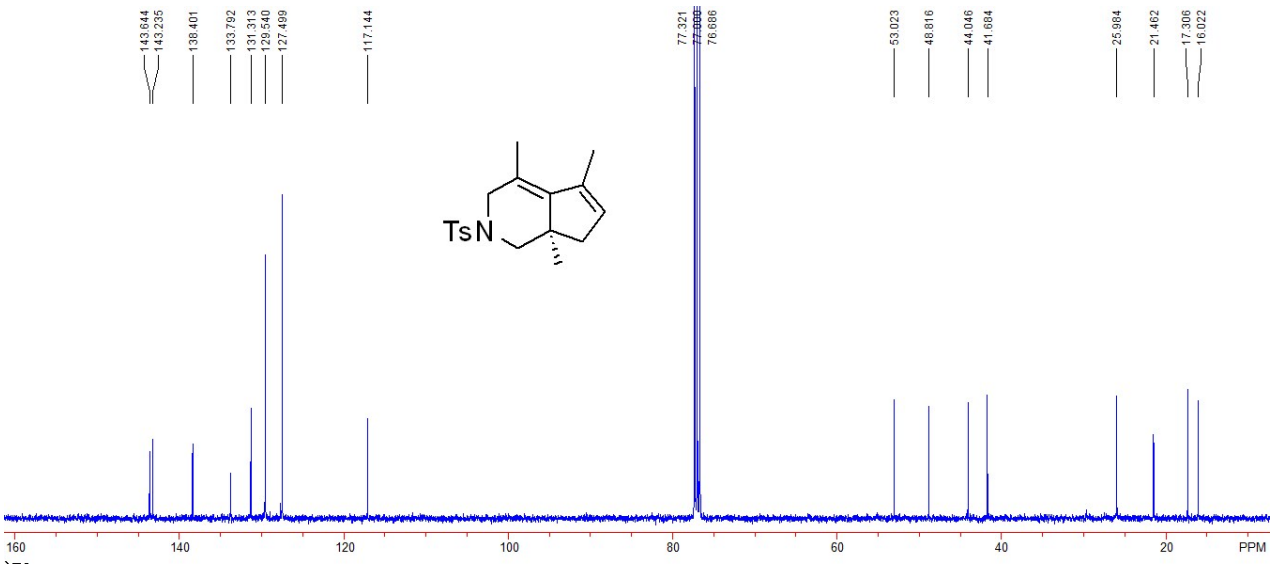


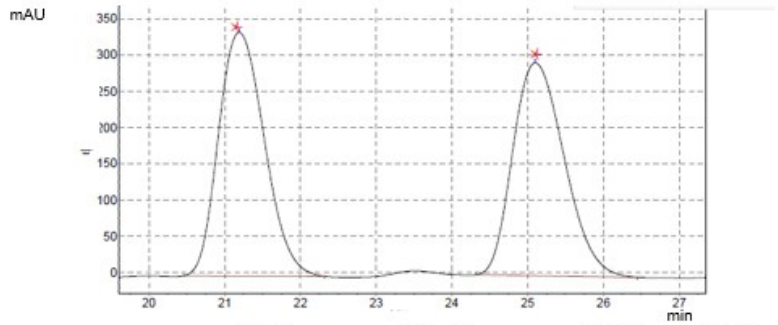
(*R*)-4,5,7a-trimethyl-2-tosyl-2,3,7,7a-tetrahydro-1*H*-cyclopenta[*c*]pyridine (3b)

A white solid, 93% yield (30 mg). M. P. 86-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.17 (s, 3H),1.73 (s, 3H), 1.95 (s, 3H), 2.07 (q, *J* = 15.6 Hz, 2H), 2.39 (d, *J* = 10.4 Hz, 1H), 2.42 (s, 3H), 3.06 (d, *J* = 16.0 Hz, 1H), 3.55 (d, *J* = 10.8 Hz, 1H), 3.94 (d, *J* = 16.4 Hz, 1H), 5.60 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 16.0, 17.3, 21.5, 26.0, 41.7, 44.0, 48.8, 53.0, 117.1, 127.5, 129.5, 131.3, 133.8, 138.4, 143.2, 143.6. IR (CH_2Cl_2): ν 3041, 2833, 2959, 2849, 1697, 1591, 1334, 1258, 1158, 1090, 1011, 977, 901, 841, 811, 794, 767, 712, 663 cm^{-1}. Mass (ESI) $(M+H)^+$: 318.1, HRMS (ESI) calcd. for $C_{18}H_{24}NO_2S$

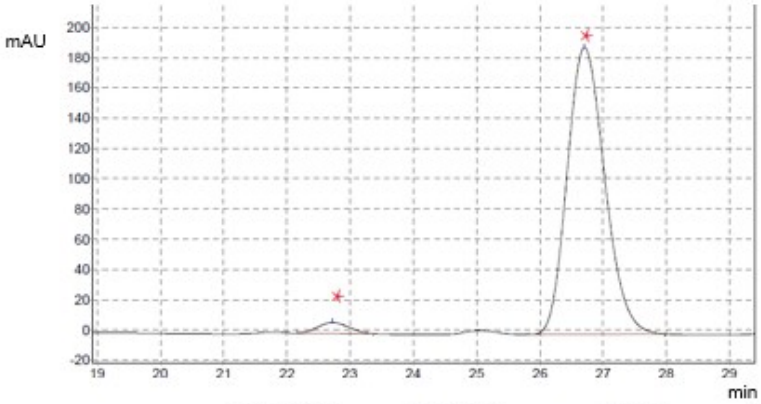
$(M+H)^+$: 318.1522, Found: 318.1514. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 25/1; Flow rate: 0.80 mL/min; t_{minor} = 22.72 min, t_{major} = 26.71 min; ee% = 94%; $[\alpha]^{20}_D$ = +250.4 (c 1.00, CH_2Cl_2)].





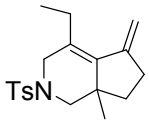


Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	21.192	336106.938	14127385.000	50.4969
2	25.100	293683.875	13849344.000	49.5031
Totals:		629790.813	27976729.000	100.0000



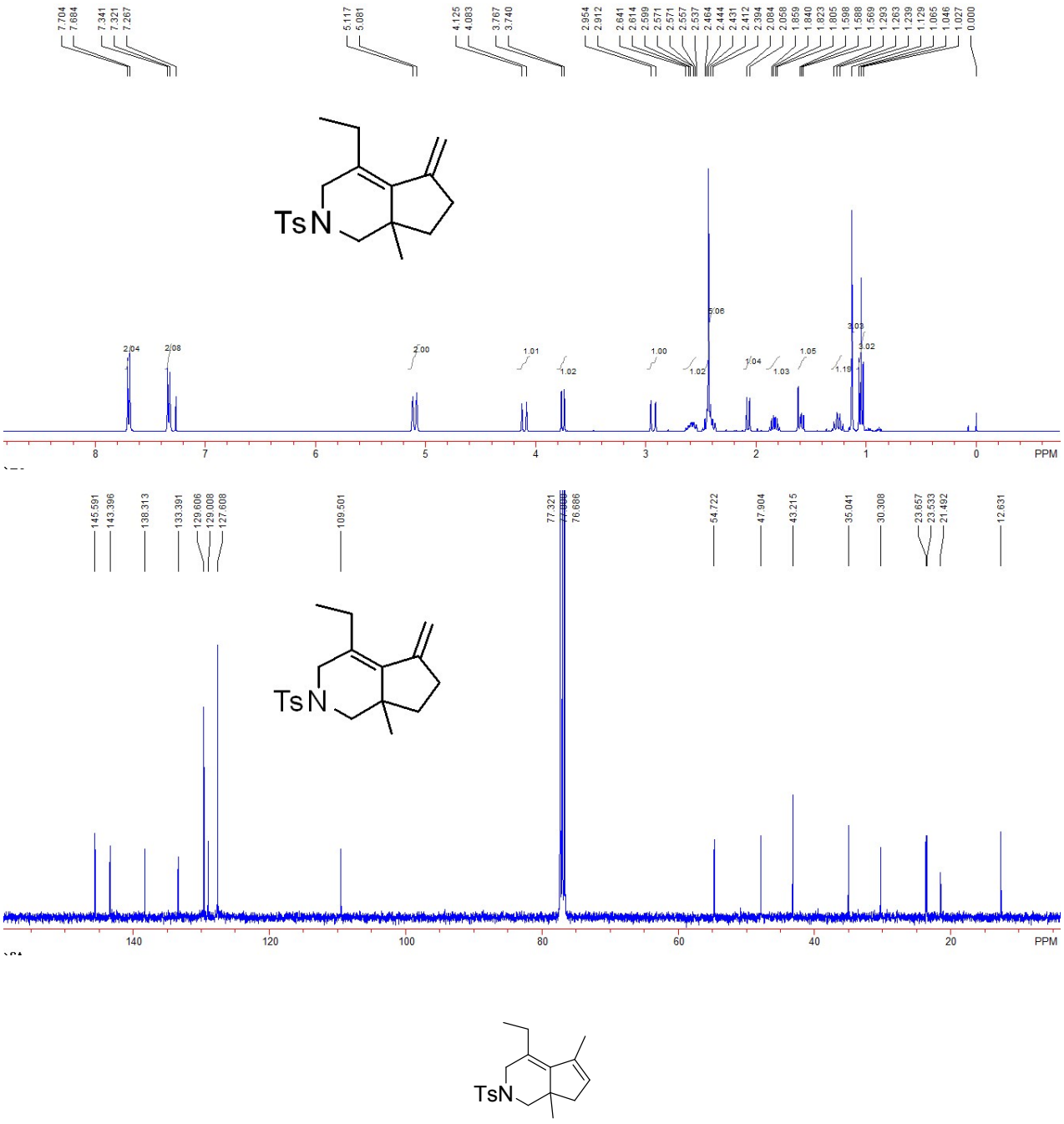
Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	22.718	7071.564	238602.641	2.9561
2	26.705	189770.375	7833047.500	97.0439
Totals:		196841.939	8071650.141	100.0000

Translation: Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 25/1; Flow rate: 0.8 mL/min; t_{minor} = 22.72 min, t_{major} = 26.71 min; ee% = 94%].



4-ethyl-7a-methyl-5-methylene-2-tosyl-2,3,5,6,7,7a-hexahydro-1*H*-cyclopenta[*c*]pyridine (2c)

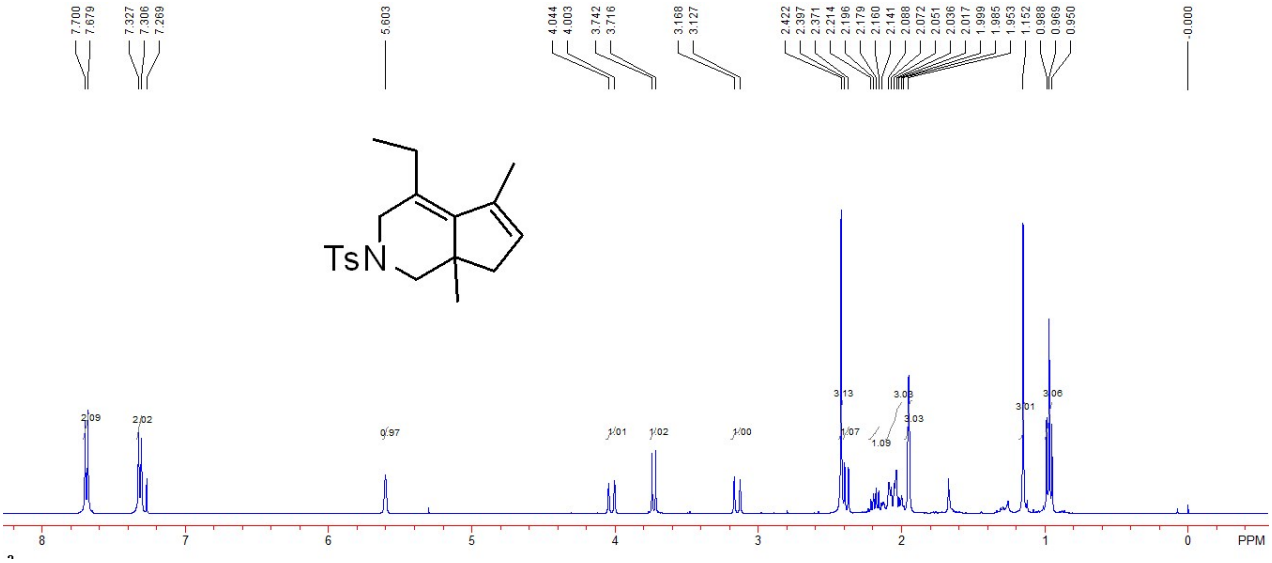
A white solid. 89% yield (30 mg). M. P. 90-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.05 (t, *J* = 7.6 Hz, 3H), 1.13 (s, 3H), 1.25 (q, *J* = 12.0 Hz, 1H), 1.57-1.60 (m, 1H), 1.79-1.88 (m, 1H), 2.07 (d, *J* = 10.4 Hz, 1H), 2.39-2.46 (m, 5H), 2.54-2.64 (m, 1H), 2.93 (d, *J* = 16.8 Hz, 1H), 3.75 (d, *J* = 10.8 Hz, 1H), 4.10 (d, *J* = 16.8 Hz, 1H), 5.10 (d, *J* = 14.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 12.6, 21.5, 23.5, 23.7, 30.3, 35.0, 43.2, 47.9, 54.7, 109.5, 127.6, 129.0, 129.6, 133.4, 138.3, 143.4, 145.6. IR (CH_2Cl_2): ν 2956, 2912, 2833, 1654, 1328, 1161, 1083, 812, 757, 703, 691, 662 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{26}NO_2S$ $(M+H)^+$: 332.1678, Found: 332.1675.

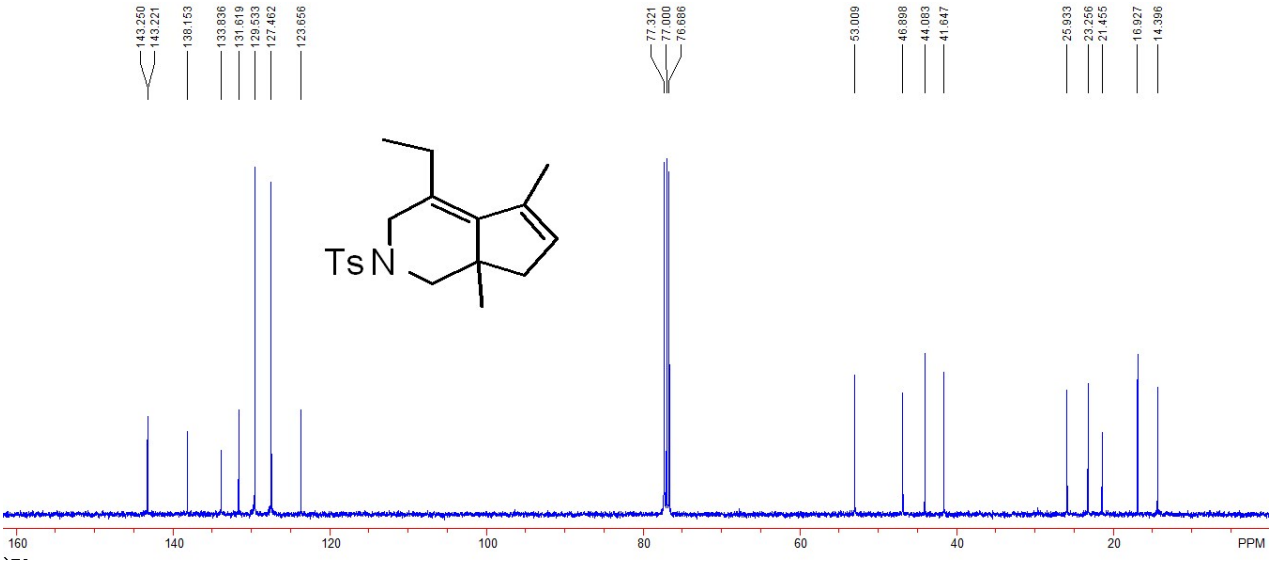


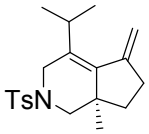
4-ethyl-5,7a-dimethyl-2-tosyl-2,3,7,7a-tetrahydro-1*H*-cyclopenta[*c*]pyridine (3c)

A white solid. 89% yield (30 mg). M. P. 92-95 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.97 (t, *J* = 7.6 Hz, 3H), 1.15 (s, 3H), 1.95 (s, 3H), 1.99-2.09 (m, 3H), 2.14-2.21 (m, 1H), 2.38 (d, *J* = 10.4 Hz, 1H), 2.42 (s, 3H), 3.15 (d, *J* = 16.4 Hz, 1H), 3.73 (d, *J* = 10.4 Hz, 1H), 4.02 (d, *J* = 16.4 Hz, 1H), 5.06 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.4, 16.9, 21.5, 23.3, 25.9, 41.6, 44.1, 46.9, 53.0, 123.7, 127.5, 129.5, 131.6, 133.8, 138.1, 143.2, 143.3. IR (CH_2Cl_2): ν 2959, 2922, 2862, 1709, 1631, 1600, 1508, 1454, 1335, 1160, 1091, 1047, 1023, 952, 934, 814, 660 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{26}NO_2S$ $(M+H)^+$:

332.1679, Found: 332.1675.



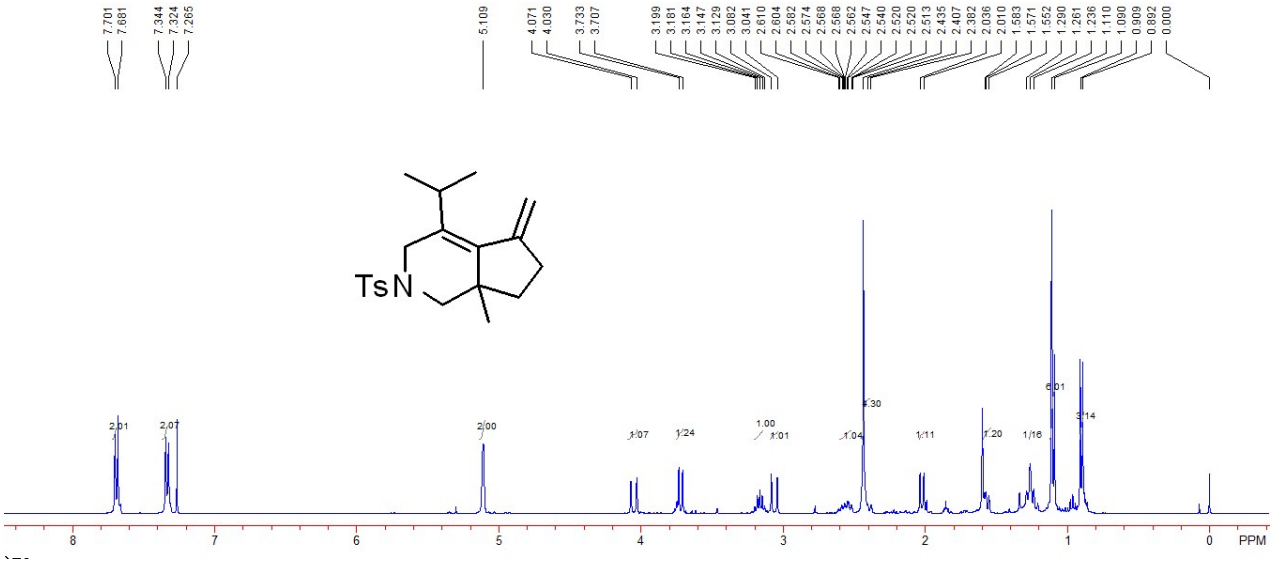


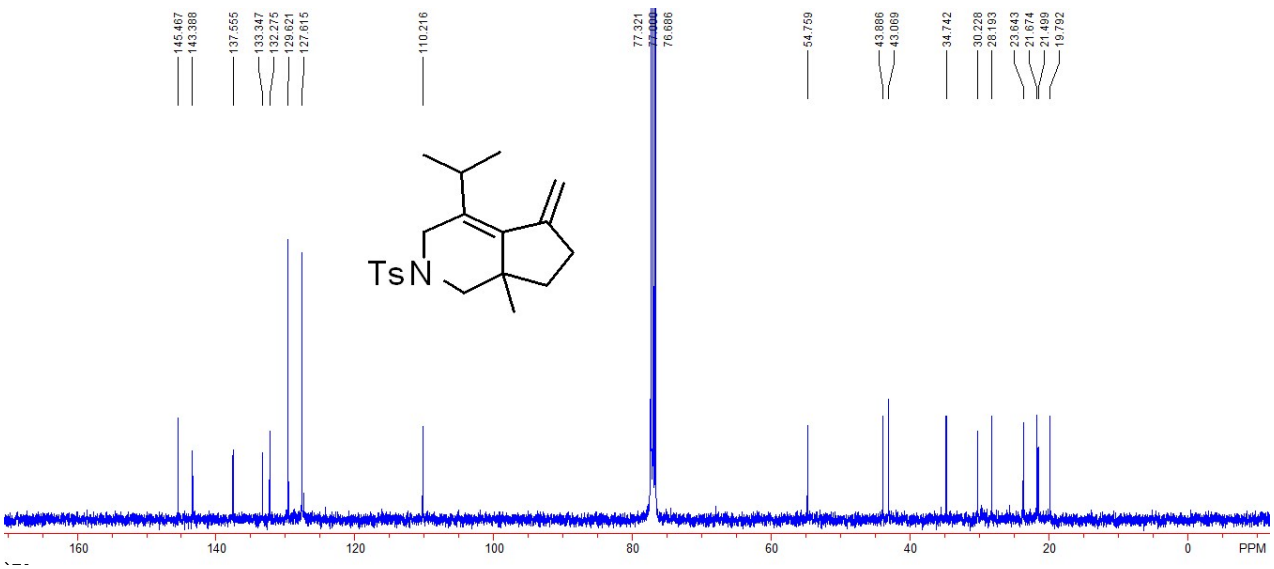


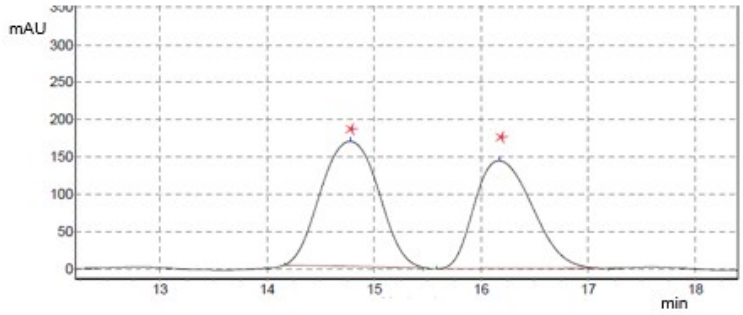
(R)-4-isopropyl-7a-methyl-5-methylene-2-tosyl-2,3,5,6,7,7a-hexahydro-1H-cyclopenta[c]pyridine (2d)

A white solid. 73% yield (26 mg). M. P. 99-103 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.90 (d, *J* = 6.8 Hz, 3H), 1.09-1.11 (m, 6H), 1.24-1.29 (m, 1H), 1.55-1.58 (m, 1H), 2.02 (d, *J* = 10.4 Hz, 1H), 2.38-2.44 (m, 4H), 2.51-2.61 (m, 1H), 3.06 (d, *J* = 16.4 Hz, 1H), 3.13-3.20 (m, 1H), 3.72 (d, *J* = 10.4 Hz, 1H), 4.05 (d, *J* = 16.4 Hz, 1H), 5.11 (s, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 19.8, 21.5, 21.7, 23.6, 28.2, 30.2, 34.7, 43.1, 43.9,

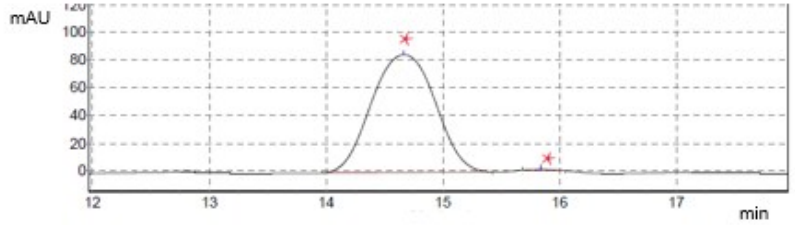
54.8, 110.2, 127.6, 129.6, 132.3, 133.3, 137.6, 143.4, 145.5. IR (CH_2Cl_2): ν 3073, 2961, 2926, 2863, 1709, 1598, 1460, 1338, 1202, 1113, 1090, 1037, 994, 966, 938, 808, 782, 736, 707, 659 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{28}NO_2S$ $(M+H)^+$: 346.1835, Found: 346.1833. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 50/1; Flow rate: 0.80 mL/min; t_{minor} = 15.84 min, t_{major} = 14.67 min; ee% > 99%; $[\alpha]^{20}_D$ = +73.5 (c 1.00, CH_2Cl_2)].





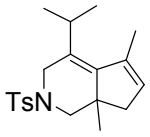


Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	14.775	167372.547	6270584.500	53.7480
2	16.165	144651.563	5396044.500	46.2520
Totals:		312024.109	11666629.000	100.0000



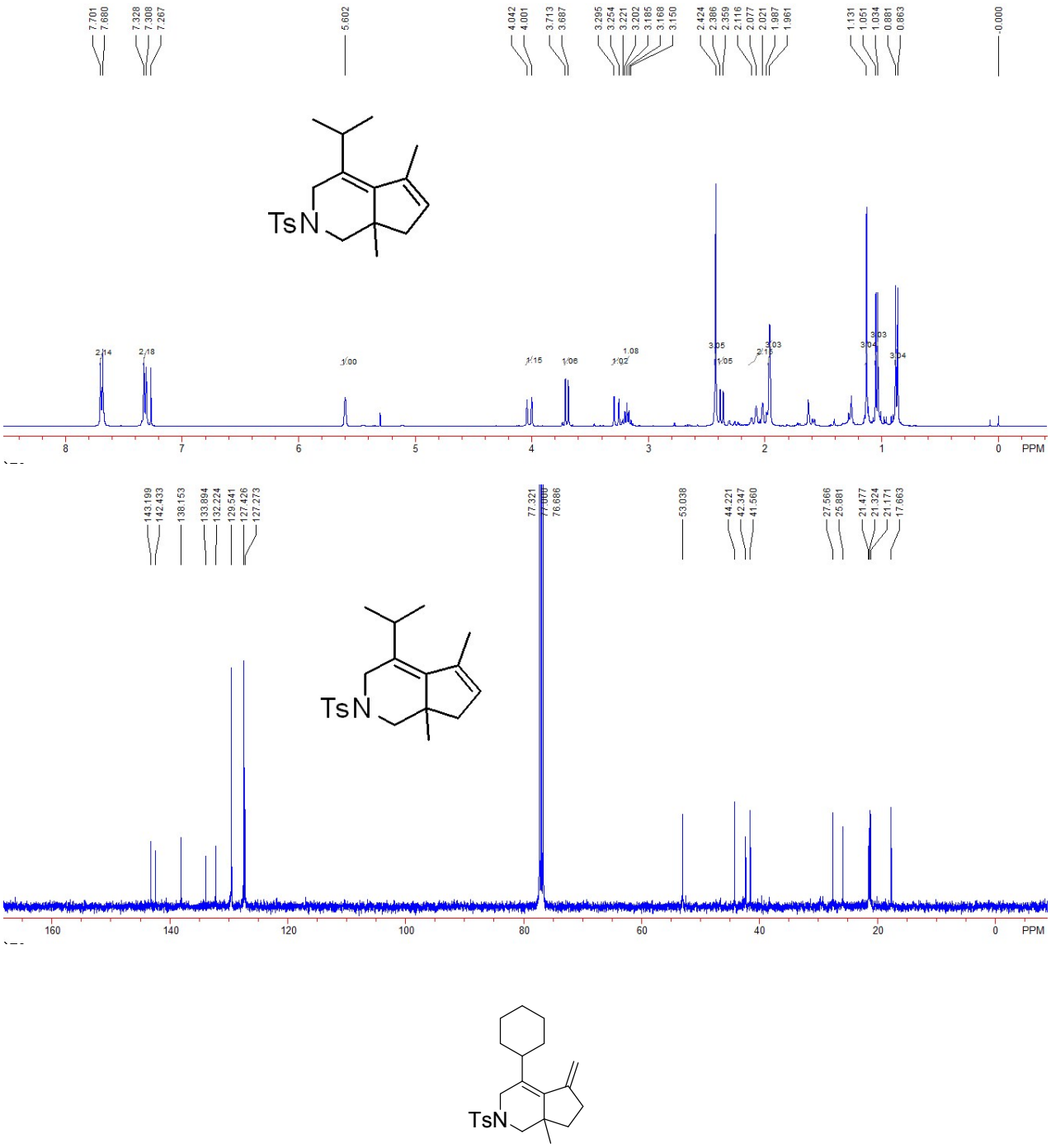
Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	14.668	84939.672	3217028.000	99.6910
2	15.838	693.539	9971.501	0.3090
Totals:		85633.211	3226999.501	100.0000

Translation: Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 50/1; Flow rate: 0.8 mL/min; t_{minor} = 15.84 min, t_{major} = 14.67 min; ee% > 99%].



4-isopropyl-5,7a-dimethyl-2-tosyl-2,3,7,7a-tetrahydro-1*H*-cyclopenta[*c*]pyridine (3d)

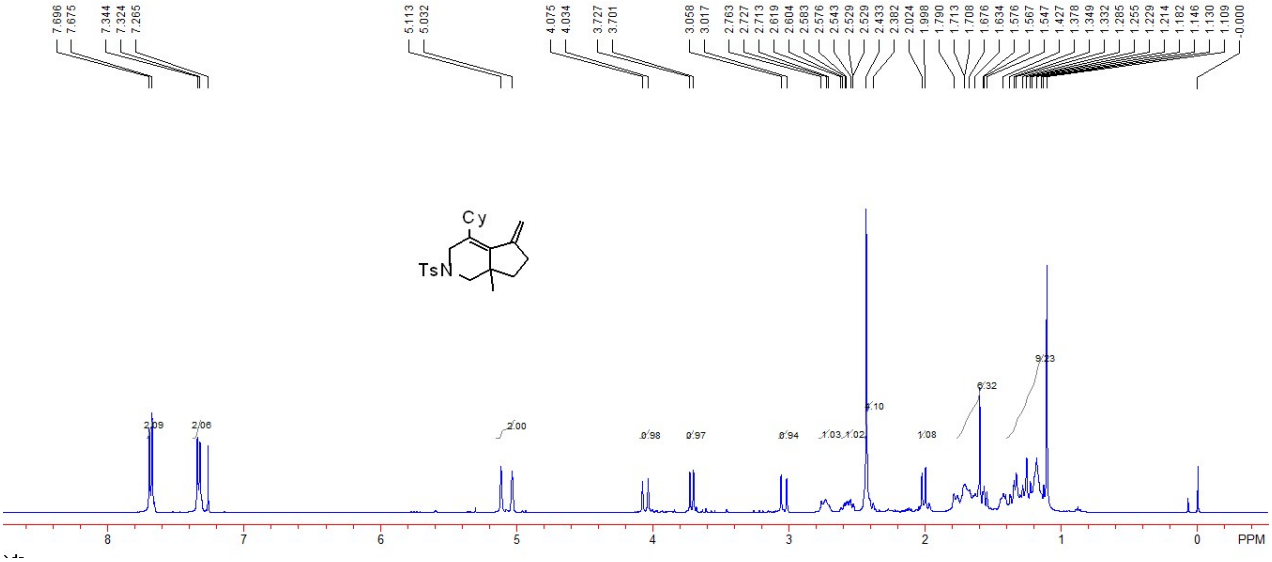
A white solid. 77% yield (27 mg). M. P. 105-108 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.87 (d, *J* = 7.2 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 1.13 (s, 3H), 1.96 (s, 3H), 1.99-2.12 (m, 2H), 2.37 (d, *J* = 10.8 Hz, 1H), 2.42 (s, 3H), 3.15-3.22 (m, 1H), 3.27 (d, *J* = 16.4 Hz, 1H), 3.70 (d, *J* = 10.8 Hz, 1H) ,4.02 (d, *J* = 16.4 Hz, 1H), 5.60 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 17.7, 21.2, 21.3, 21.5, 25.9, 27.6, 41.6, 42.3, 44.2, 53.0, 127.3, 127.4, 129.5, 132.2, 133.9, 138.2, 142.4, 143.1. IR (CH_2Cl_2): ν 2964, 2925, 1707, 1598, 1460, 1338, 1201, 1118, 1089, 1037, 994, 966, 911, 808, 781, 707 cm^{-1}. Mass (ESI) $(M+H)^+$: 346.1. HRMS (ESI) calcd. for $C_{20}H_{28}NO_2S$ $(M+H)^+$: 346.1825, Found: 346.1835.

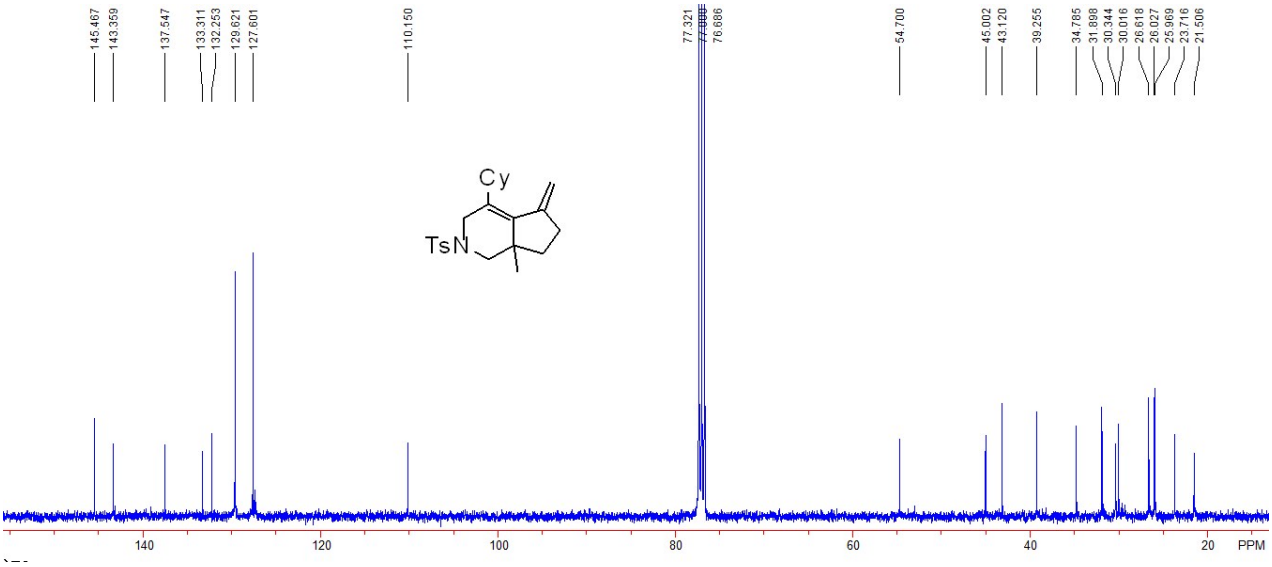


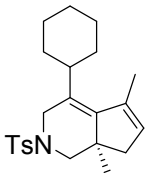
4-cyclohexyl-7a-methyl-5-methylene-2-tosyl-2,3,5,6,7,7a-hexahydro-1*H*-cyclopenta[*c*]pyridine (2e)

A white solid, 73% yield (28 mg). M. P. 124-127 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11-1.43 (m, 9H), 1.55-1.79 (m, 6H), 2.01 (d, J = 10.4 Hz, 1H), 2.38-2.43 (m, 4H), 2.53-2.62 (m, 1H), 2.71-2.76 (m, 1H), 3.04 (d, J = 16.4 Hz, 1H), 3.71 (d, J = 10.4 Hz, 1H) ,4.05 (d, J = 16.4 Hz, 1H), 5.03 (s, 1H), 5.11 (s, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.5, 23.7, 25.97, 26.03, 26.6, 30.0, 30.3, 31.9, 34.8, 39.3, 43.1, 45.0, 54.7, 110.2,

127.6, 129.6, 132.3, 133.3, 137.5, 143.4, 145.5. IR (CH_2Cl_2): ν 2925, 2844, 1707, 1549, 1446, 1411, 1337, 1249, 1161, 1090, 1058, 1027, 913, 806, 814, 736, 664 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{32}NO_2S$ $(M+H)^+$: 386.2148, Found: 386.2143.



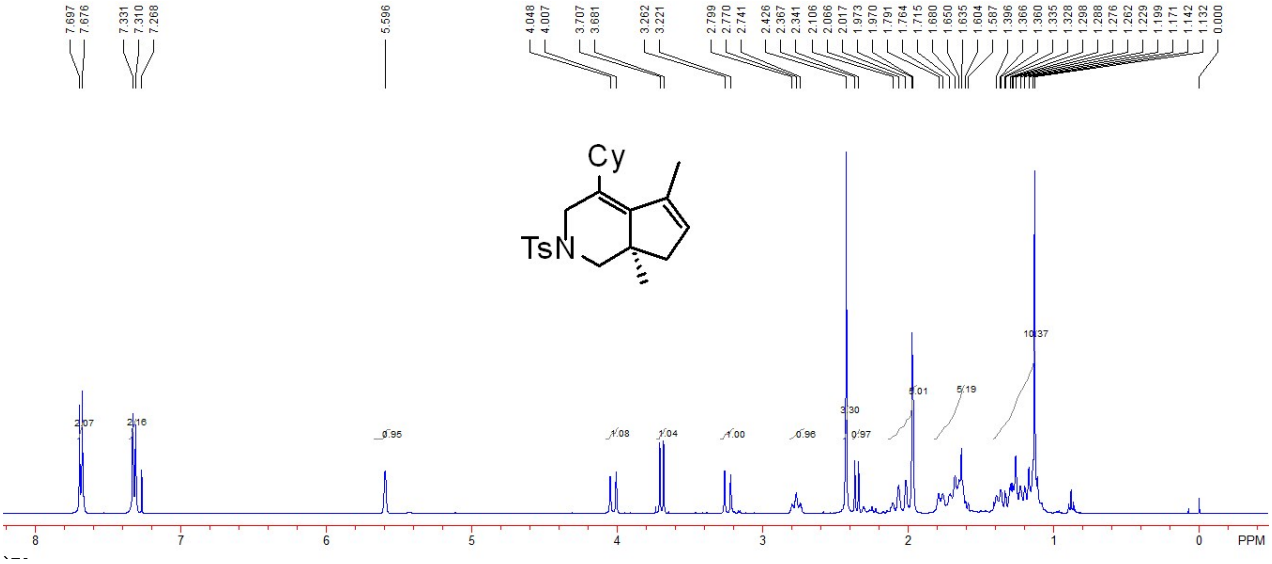


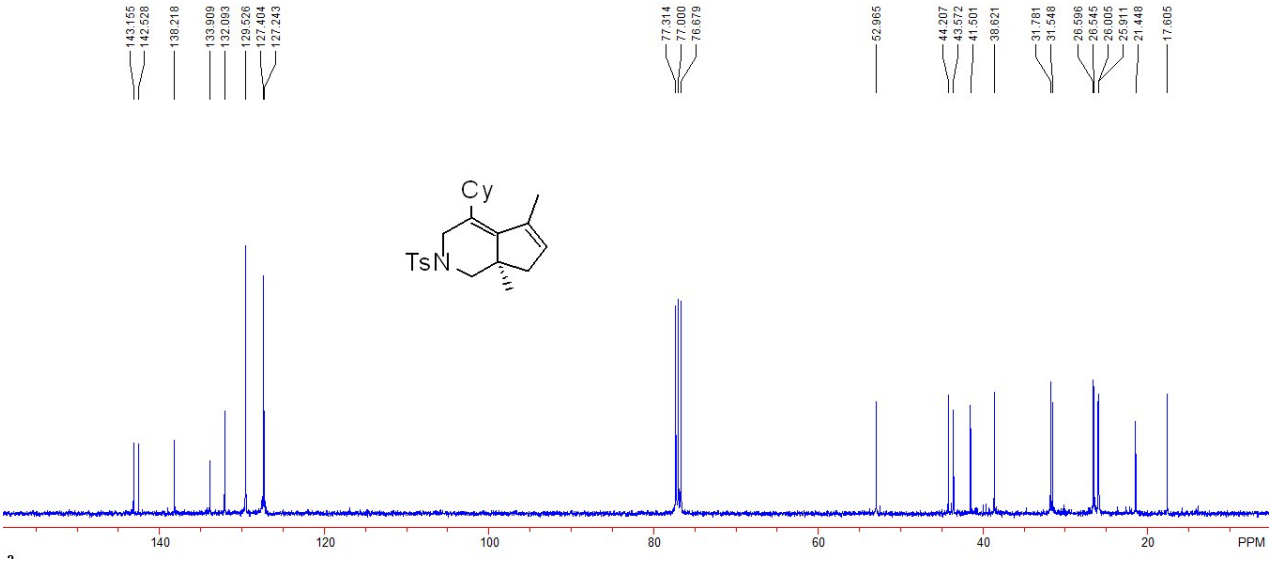


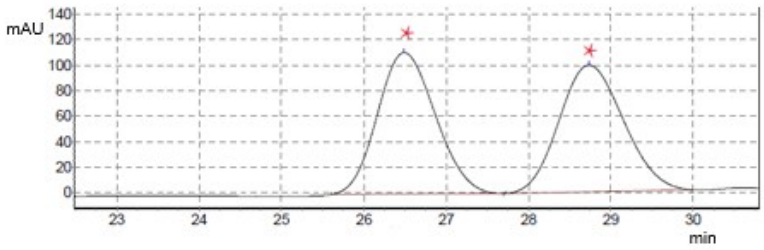
4-cyclohexyl-5,7a-dimethyl-2-tosyl-2,3,7,7a-tetrahydro-1*H*-cyclopenta[*c*]pyridine (3e)

A light yellow oil, 88% yield (35 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.13-1.40 (m, 10H), 1.57-1.79 (m, 5H), 1.97-2.11 (m, 5H), 2.35 (d, *J* = 10.4 Hz, 1H), 2.43 (s, 3H), 2.77 (t, *J* = 11.6 Hz, 1H), 3.24 (d, *J* = 16.0 Hz, 1H), 3.69 (d, *J* = 10.4 Hz, 1H) ,4.03 (d, *J* = 16.4 Hz, 1H), 5.60 (s, 1H),

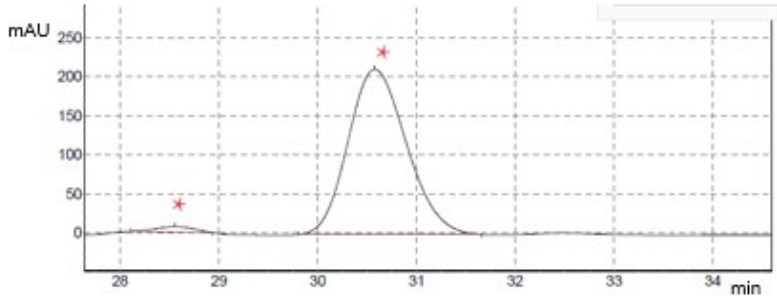
7.32 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 17.6, 21.4, 25.9, 26.0, 26.5, 26.6, 31.5, 31.8 38.6, 41.5, 43.6, 44.2, 53.0, 127.2, 127.4, 129.5, 132.1, 133.9, 138.2, 142.5, 143.2. IR (CH_2Cl_2): ν 2912, 2842, 1587, 1489, 1441, 1349, 1337, 1161, 1089, 967, 821, 814, 787, 756, 701, 659 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{32}NO_2S$ $(M+H)^+$: 386.2148, Found: 386.2144. Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 25/1; Flow rate: 0.80 mL/min; t_{minor} = 30.58 min, t_{major} = 28.55 min; ee% = 96%; $[\alpha]^{20}_D$ = +80.1 (c 1.00, CH_2Cl_2)].





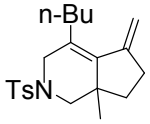


Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	26.490	110982.781	5422091.000	50.1231
2	28.733	99315.570	5395454.000	49.8769
Totals:		210298.352	10817545.000	100.0000



Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	28.553	6586.338	175362.109	1.9771
2	30.578	211388.734	8694290.000	98.0229
Totals:		217975.072	8869652.109	100.0000

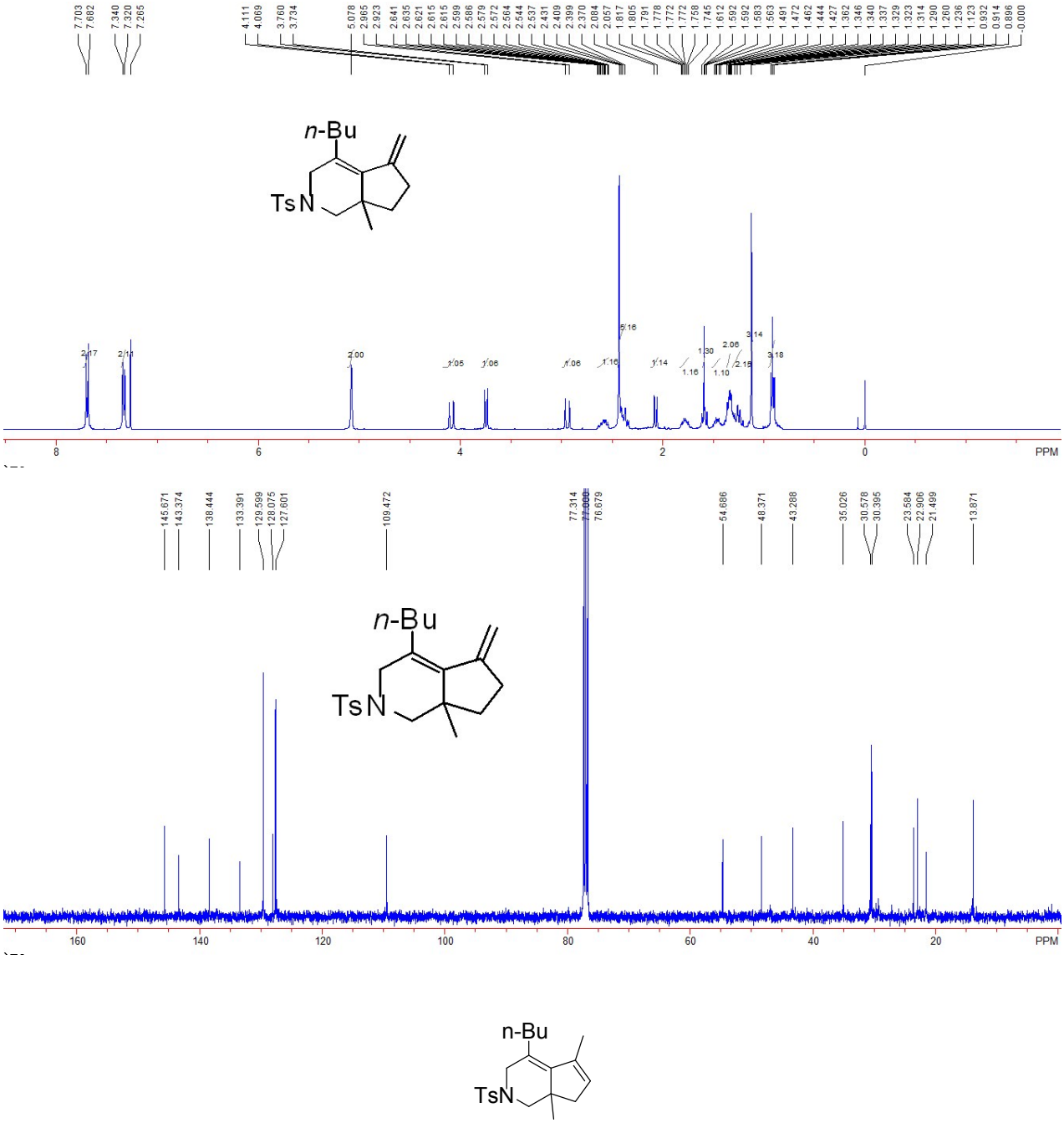
Translation: Chiralcel IC-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 25/1; Flow rate: 0.8 mL/min; t_{minor} = 30.58 min, t_{major} = 28.55 min; ee% = 96%].



4-butyl-7a-methyl-5-methylene-2-tosyl-2,3,5,6,7,7a-hexahydro-1*H*-cyclopenta[*c*]pyridine (2f)

A light yellow oil. 86% yield (31 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.12 (s, 3H), 1.24-1.31 (m, 2H), 1.32-1.36 (m, 2H), 1.43-1.49 (m, 1H), 1.56-1.61 (m, 1H), 1.75-1.82 (m, 1H), 2.07 (d, *J* = 10.8 Hz, 1H), 2.37-2.43 (m, 5H), 2.54-2.64 (m, 1H), 2.94 (d, *J* = 16.8 Hz, 1H), 3.75 (d, *J* = 10.8 Hz, 1H) ,4.09 (d, *J* = 16.4 Hz, 1H), 5.08 (s, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 13.9, 21.5, 22.9, 23.6, 30.4, 30.6, 35.0, 43.3, 48.4, 54.7, 109.5, 127.6, 128.1, 129.6, 133.4, 138.4, 143.4, 145.7. IR (CH_2Cl_2): ν 2962, 2928, 2873, 1707, 1592, 1454, 1336, 1247, 1160, 1090, 1071, 814, 735, 705, 663 cm^{-1}. Mass (ESI) $(M+H)^+$: 360.2, HRMS (ESI) calcd. for $C_{21}H_{30}NO_2S$ $(M+H)^+$: 360.1992,

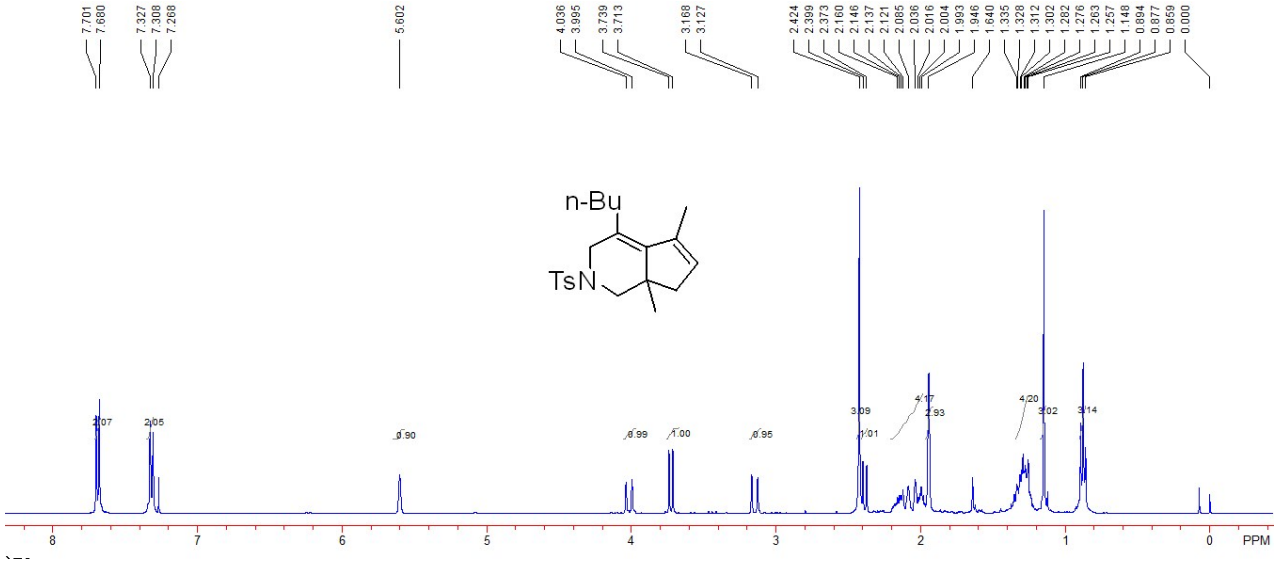
Found: 360.1981.

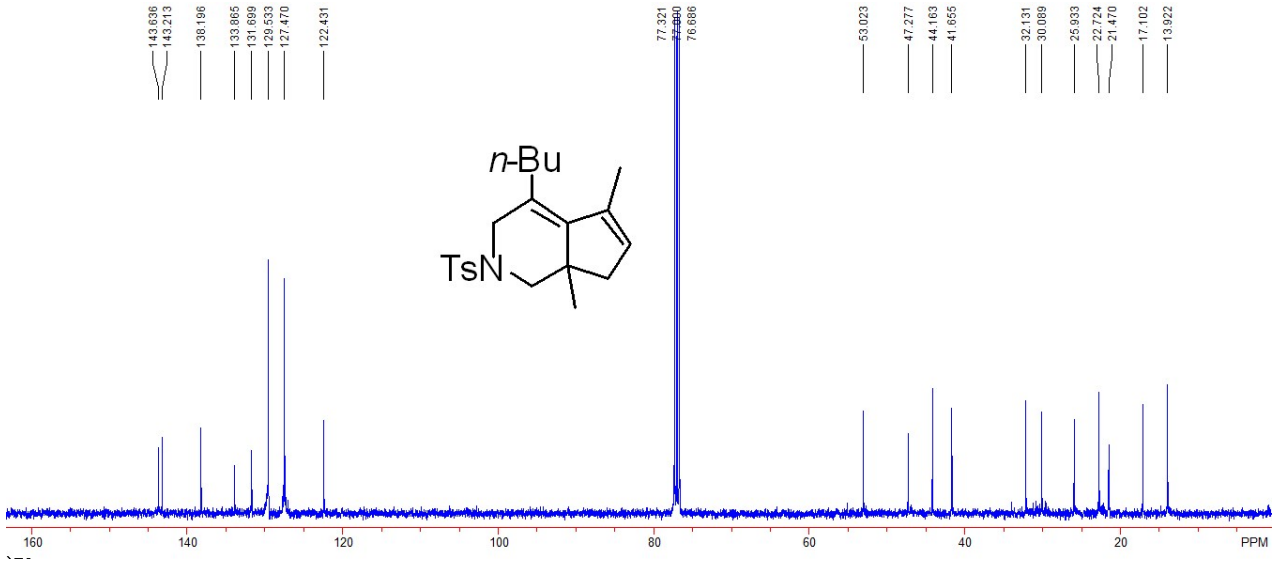


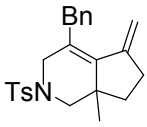
4-butyl-5,7a-dimethyl-2-tosyl-2,3,7,7a-tetrahydro-1*H*-cyclopenta[*c*]pyridine (3f)

A white solid, 86% yield (31 mg). M. P. 116-119 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.15 (s, 3H), 1.26-1.33 (m, 4H), 1.95 (s, 3H), 1.99-2.15 (m, 4H), 2.39 (d, *J* = 10.4 Hz, 1H), 2.42 (s, 3H), 3.15 (d, *J* = 16.4 Hz, 1H), 3.73 (d, *J* = 10.4 Hz, 1H) ,4.02 (d, *J* = 16.4 Hz, 1H), 5.60 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 13.9, 17.1, 21.5, 22.7, 25.9, 30.1, 32.1, 41.7, 44.2, 47.3, 53.0, 122.4, 127.5, 129.5, 131.7, 133.9, 138.2, 143.2, 143.6. IR (CH_2Cl_2): ν 2901, 1680, 1523, 1458, 1121, 1091, 1167, 1027, 978,

917, 865, 835, 814, 736, 667 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{30}NO_2S$ $(M+H)^+$: 360.1992, Found: 360.1981.



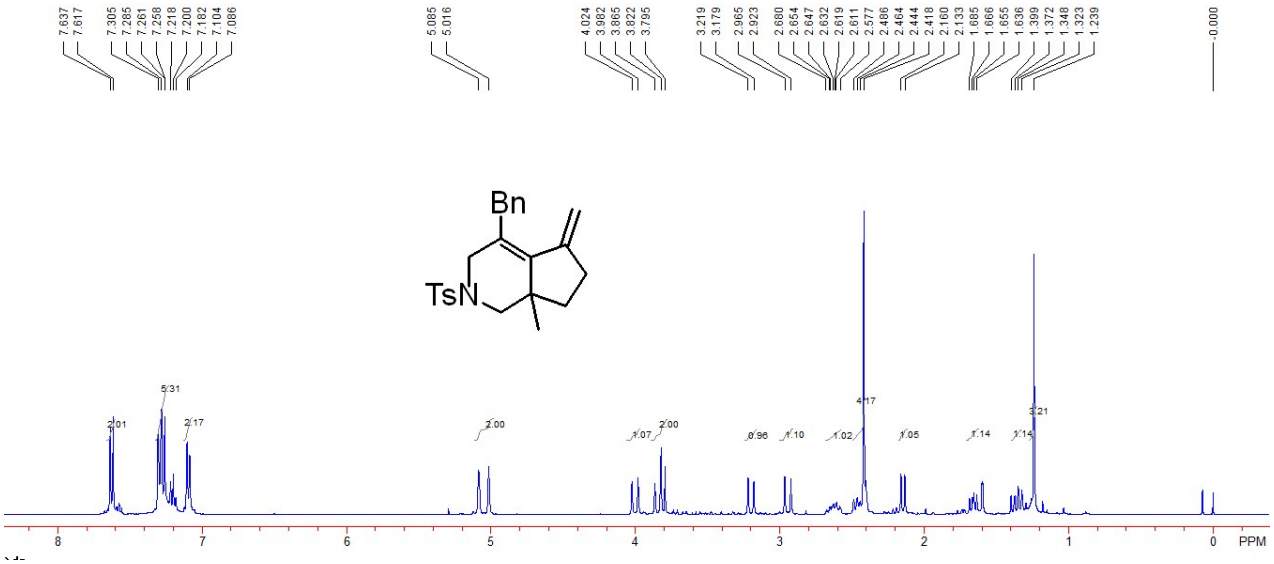


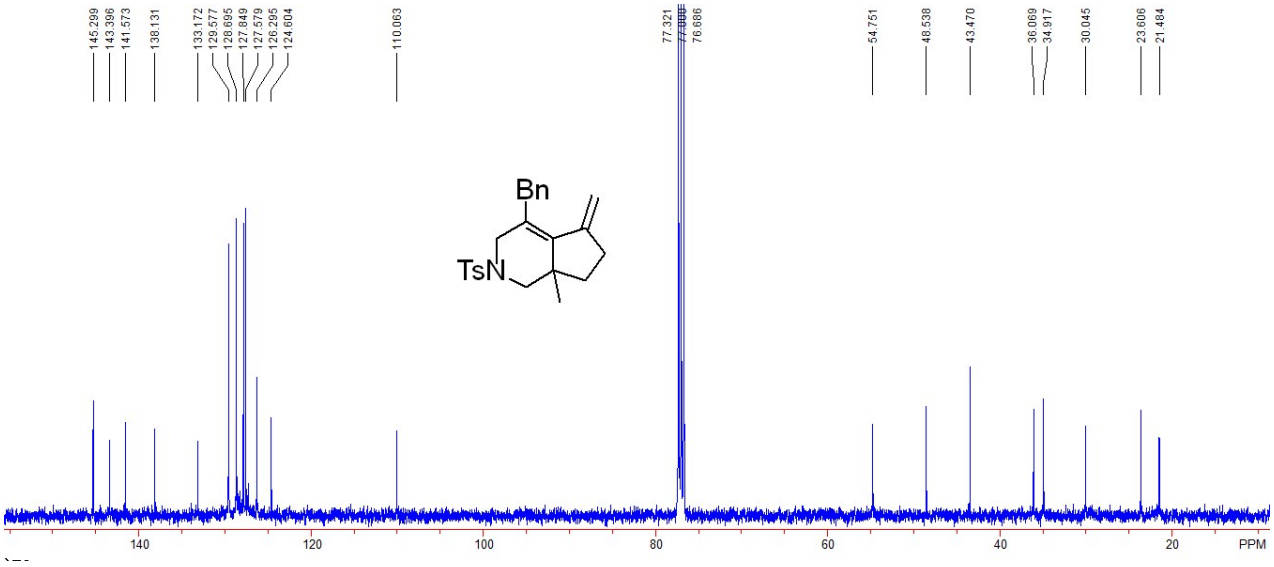


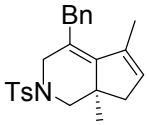
4-benzyl-7a-methyl-5-methylene-2-tosyl-2,3,5,6,7,7a-hexahydro-1*H*-cyclopenta[*c*]pyridine (2g)

A white solid, 82% yield (33 mg). M. P. 106-108 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (s, 3H), 1.32-1.40 (m, 1H), 1.64-1.69 (m, 1H), 2.15 (d, *J* = 10.8 Hz, 1H), 2.42-2.49 (m, 4H), 2.58-2.68 (m, 1H), 2.94 (d, *J* = 16.8 Hz, 1H), 3.20 (d, *J* = 16.0 Hz, 1H), 3.80-3.87 (m, 2H), 4.00 (d, *J* = 16.8 Hz, 1H), 5.02 (s, 1H), 5.09 (s, 1H), 7.10 (d, *J* = 7.2 Hz, 2H), 7.18-7.31 (m, 5H), 7.63 (d, *J* =

8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 23.6, 30.0, 34.9, 36.1, 43.5, 48.5, 54.8, 110.1, 124.6, 126.3, 127.6, 127.8, 128.7, 129.6, 133.2, 138.1, 141.6, 143.4, 145.3. IR (CH_2Cl_2): ν 2959, 2924, 2849, 1607, 1495, 1452, 1350, 1328, 1203, 1162, 1091, 1003, 941, 815, 731, 678, 663 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{28}NO_2S$ $(M+H)^+$: 394.1835, Found: 394.1829.



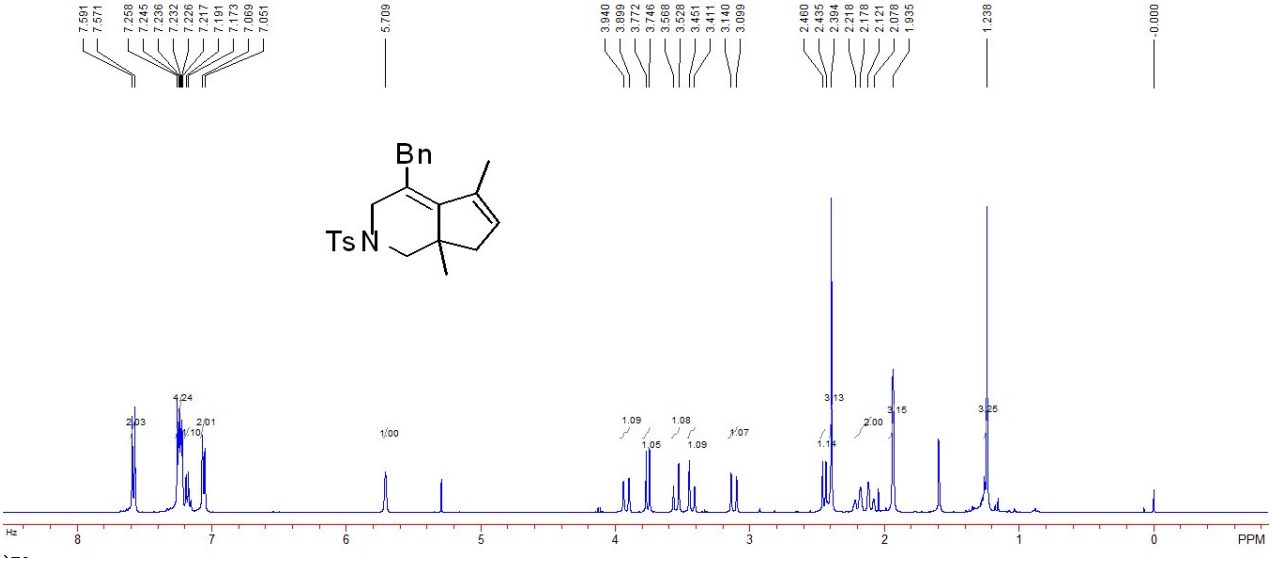


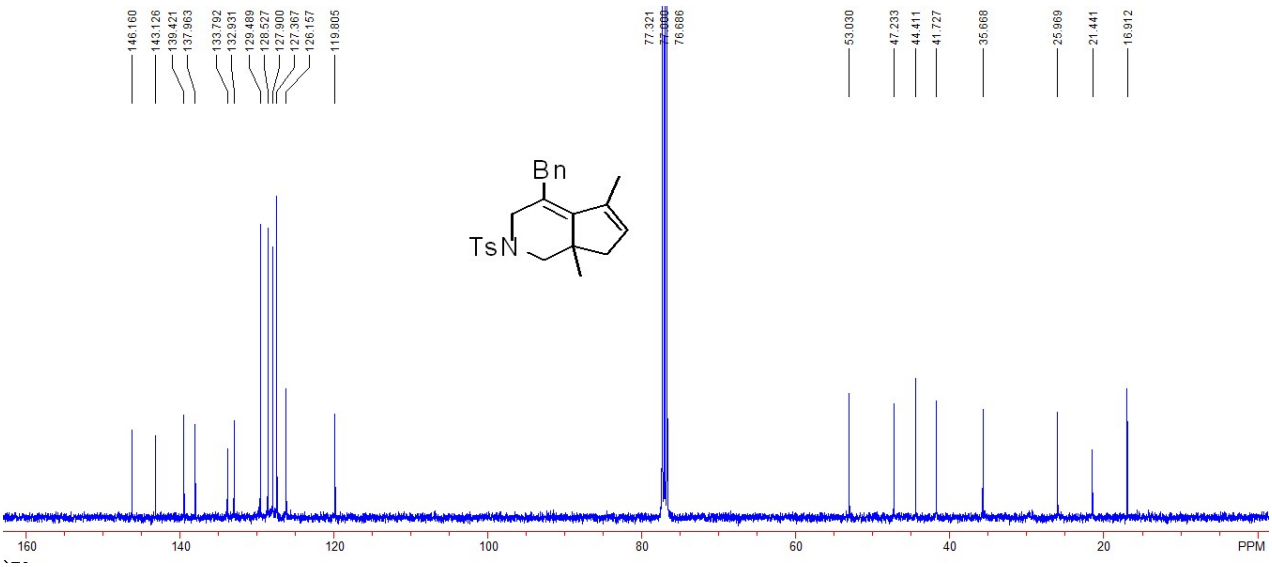


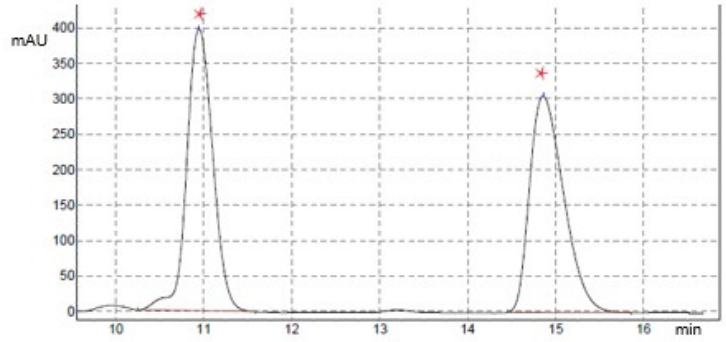
4-benzyl-5,7a-dimethyl-2-tosyl-2,3,7,7a-tetrahydro-1*H*-cyclopenta[*c*]pyridine (3g)

A white solid, 84% yield (33 mg). M. P. 110-112 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (s, 3H), 1.94 (s, 3H), 2.08-2.22 (m, 2H), 2.39 (s, 3H), 2.45 (d, J = 10.0 Hz, 1H), 3.12 (d, J = 16.4 Hz,

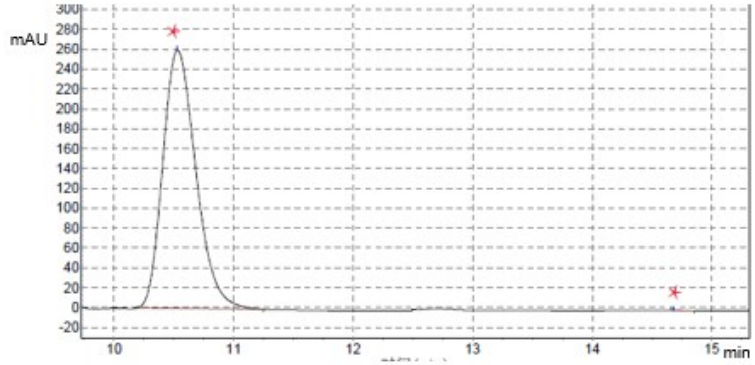
1H), 3.43 (d, J = 16.0 Hz, 1H), 3.55 (d, J = 16.0 Hz, 1H), 3.76 (d, J = 10.4 Hz, 1H), 3.92 (d, J = 16.0 Hz, 1H), 5.71 (s, 1H), 7.06 (d, J = 7.2 Hz, 2H), 7.17-7.19 (m, 1H), 7.22-7.26 (m, 4H), 7.58 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.9, 21.4, 26.0, 35.7, 41.7, 44.4, 47.2, 53.0, 119.8, 126.2, 127.4, 127.9, 128.5, 129.5, 132.9, 133.8, 138.0, 139.4, 143.1, 146.2. IR (CH_2Cl_2): ν 2939, 2908, 1657, 1575, 1412, 1367, 1318, 1102, 1012, 915, 834, 752, 683 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{28}NO_2S$ $(M+H)^+$: 394.1835, Found: 394.1825. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 10/1; Flow rate: 0.80 mL/min; t_{minor} = 14.68 min, t_{major} = 10.53 min; ee% > 99%; $[\alpha]^{20}_D$ = +53.7 (c 1.00, CH_2Cl_2)]





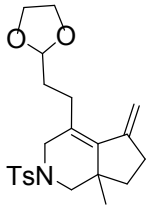


Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	10.943	397301.000	8204983.500	50.0916
2	14.857	304708.344	8174967.500	49.9084
Totals:		702009.344	16379951.000	100.0000



Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	10.532	259797.172	5002751.000	99.9920
2	14.678	24.400	398.300	0.0080
Totals:		259821.572	5003149.300	100.0000

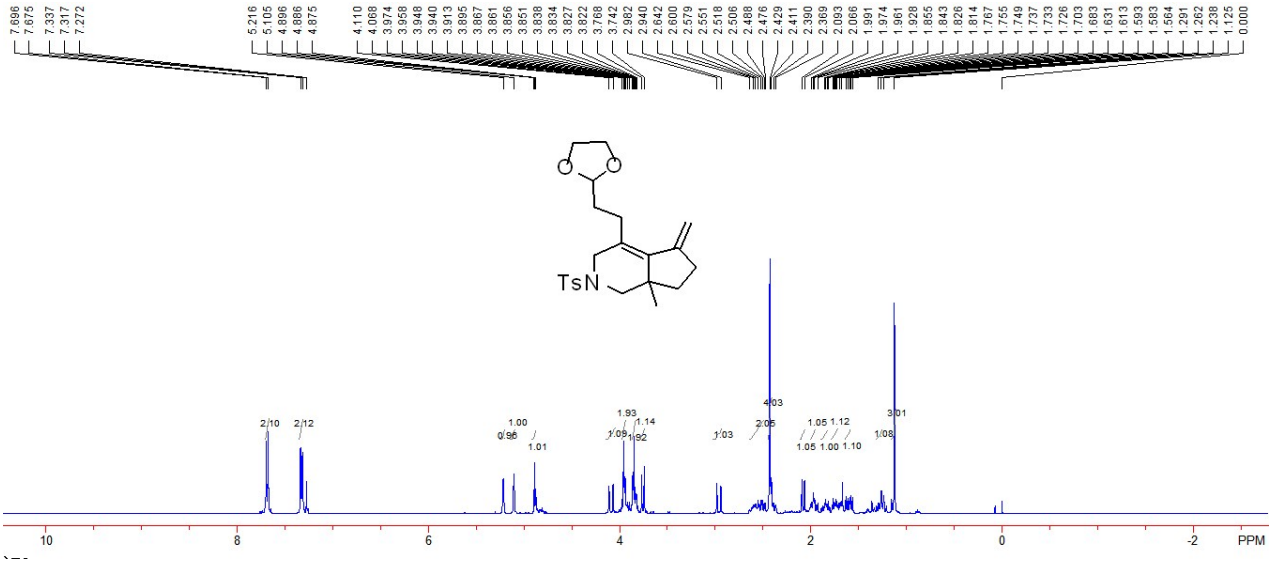
Translation: Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 10/1; Flow rate: 0.8 mL/min;t_{minor} = 14.68 min, t_{major} = 10.53 min; ee% > 99%].

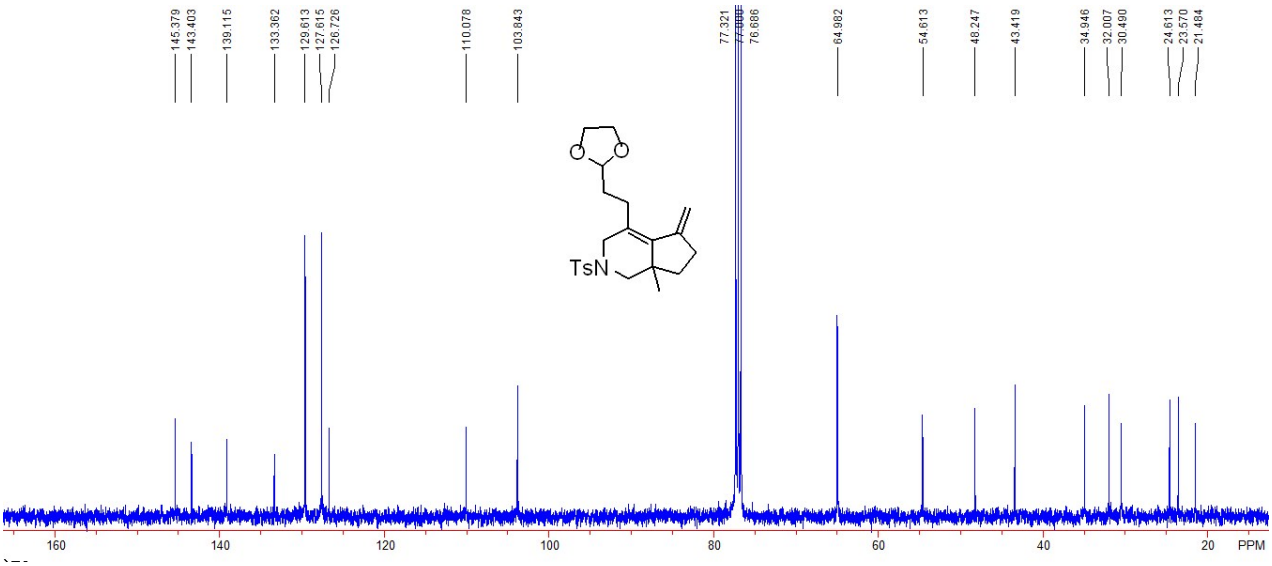


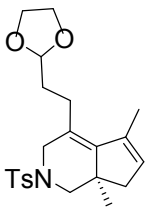
4-(2-(1,3-dioxolan-2-yl)ethyl)-7a-methyl-5-methylene-2-tosyl-2,3,5,6,7,7a-hexahydro-1*H*-cyclopenta[*c*]pyridine (2h)

A light yellow oil, 81% yield (33 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.13 (s, 3H), 1.24-1.29 (m, 1H), 1.56-1.63 (m, 1H), 1.68-1.77 (m, 1H), 1.81-1.86 (m, 1H), 1.93-1.99 (m, 1H), 2.08 (d, *J* = 10.4 Hz, 1H), 2.37-2.43 (m, 4H), 2.48-2.64 (m, 2H), 2.96 (d, *J* = 16.8 Hz, 1H), 3.76 (d, *J* =

10.8 Hz, 1H), 3.83-3.87 (m, 2H), 3.91-3.97 (m, 2H), 4.09 (d, J = 16.8 Hz, 1H), 4.89 (t, J = 4.0 Hz, 1H), 5.11 (s, 1H), 5.22 (s, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 23.6, 24.6, 30.5, 32.0, 34.9, 43.4, 48.2, 54.6, 65.0, 103.8, 110.1, 126.7, 127.6, 129.6, 133.4, 139.1, 143.4, 145.4. IR (CH_2Cl_2): ν 2991, 1747, 1651, 1580, 1453, 1406, 1151, 1060, 1001, 994, 954, 919, 873, 847, 810, 763, 681, 651 cm^{-1}. Mass (ESI) $(M+H)^+$: 404.1, HRMS (ESI) calcd. for $C_{22}H_{33}N_2O_4S$ $(M+NH_4)^+$: 421.2156, Found: 421.2144.

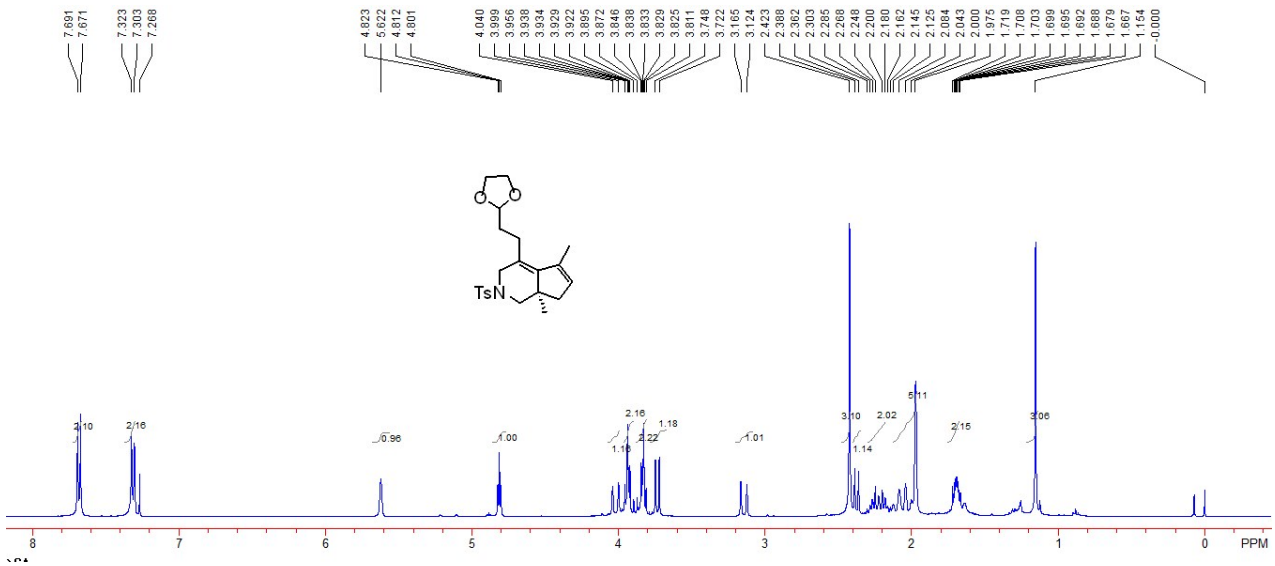


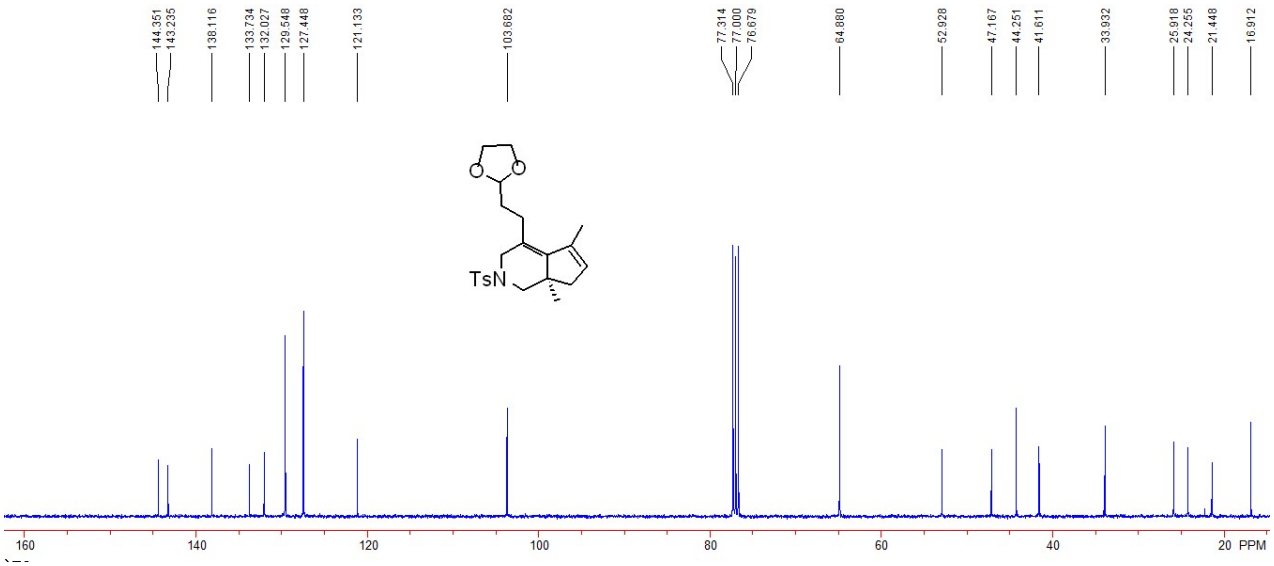


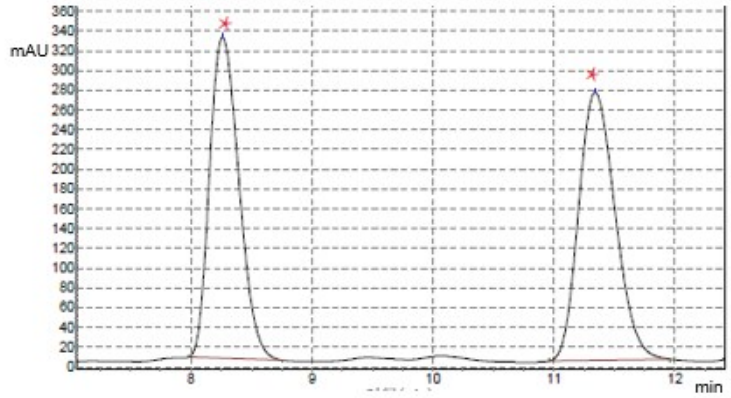


(R)-4-(2-(1,3-dioxolan-2-yl)ethyl)-5,7a-dimethyl-2-tosyl-2,3,7,7a-tetrahydro-1H-cyclopenta[c]pyridine (3h)

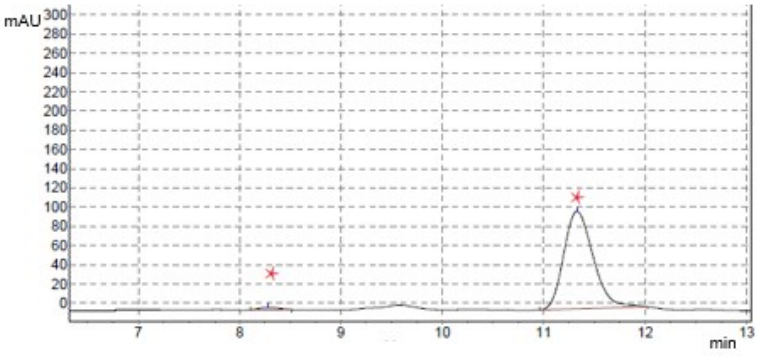
A light yellow oil, 86% yield (35 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.15 (s, 3H), 1.67-1.72 (m, 2H), 1.97-2.13 (m, 5H), 2.15-2.30 (m, 2H), 2.37 (d, *J* = 10.4 Hz, 1H), 2.42 (s, 3H), 3.14 (d, *J* = 16.4 Hz, 1H), 3.73 (d, *J* = 10.4 Hz, 1H), 3.81-3.87 (m, 2H), 3.90-3.96 (m, 2H), 4.02 (d, *J* = 16.4 Hz, 1H), 4.81 (t, *J* = 4.8 Hz, 1H), 5.62 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.9, 21.4, 24.3, 25.9, 33.9, 41.6, 44.3, 47.2, 52.9, 64.9, 103.7, 121.1, 127.4, 129.5, 132.0, 133.7, 138.1, 143.2, 144.4. IR (CH_2Cl_2): ν 2950, 1697, 1530, 1463, 1207, 1120, 1003, 947, 816, 767, 681, 649 cm^{-1}. Mass (ESI) $(M+H)^+$: 404.1, HRMS (ESI) calcd. for $C_{22}H_{33}N_2O_4S$ $(M+NH_4)^+$: 421.2156, Found: 421.2149. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 3/1; Flow rate: 0.80 mL/min; t_{minor} = 8.28 min, t_{major} = 11.33 min; ee% = 97%; $[\alpha]^{20}_D$ = +87.5 (c 1.00, CH_2Cl_2)].





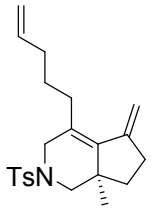


Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	8.258	325313.438	5475935.000	49.0528
2	11.340	271471.875	5687403.000	50.9472
Totals:		596785.313	11163338.000	100.0000



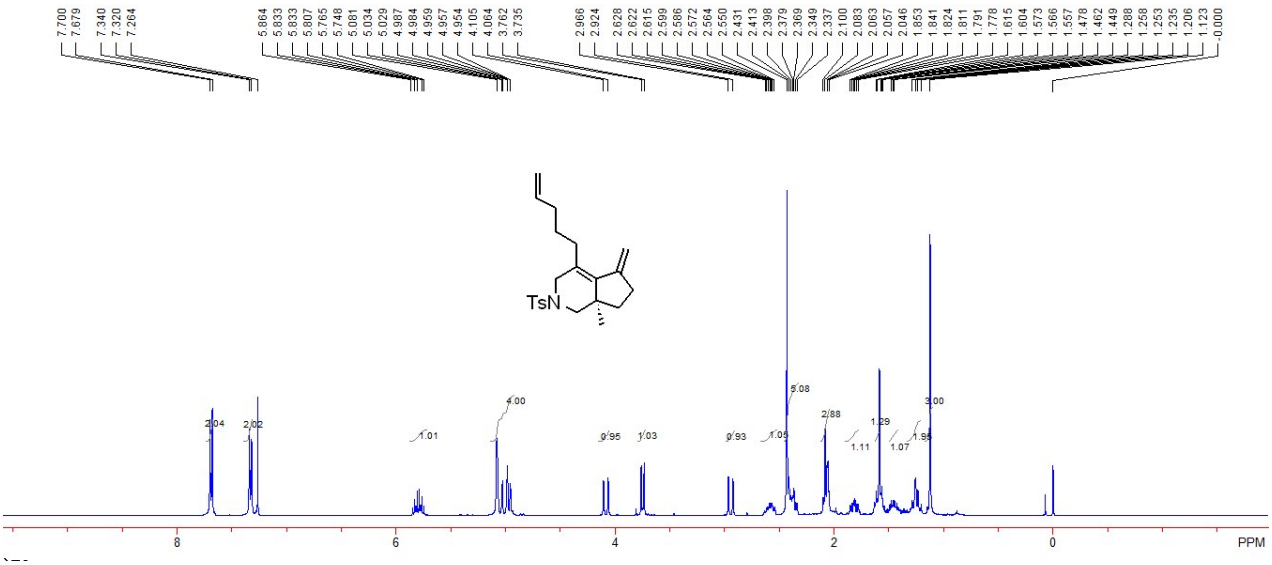
Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	8.278	2293.129	31644.902	1.5268
2	11.327	101347.859	2040947.125	98.4732
Totals:		103640.989	2072592.027	100.0000

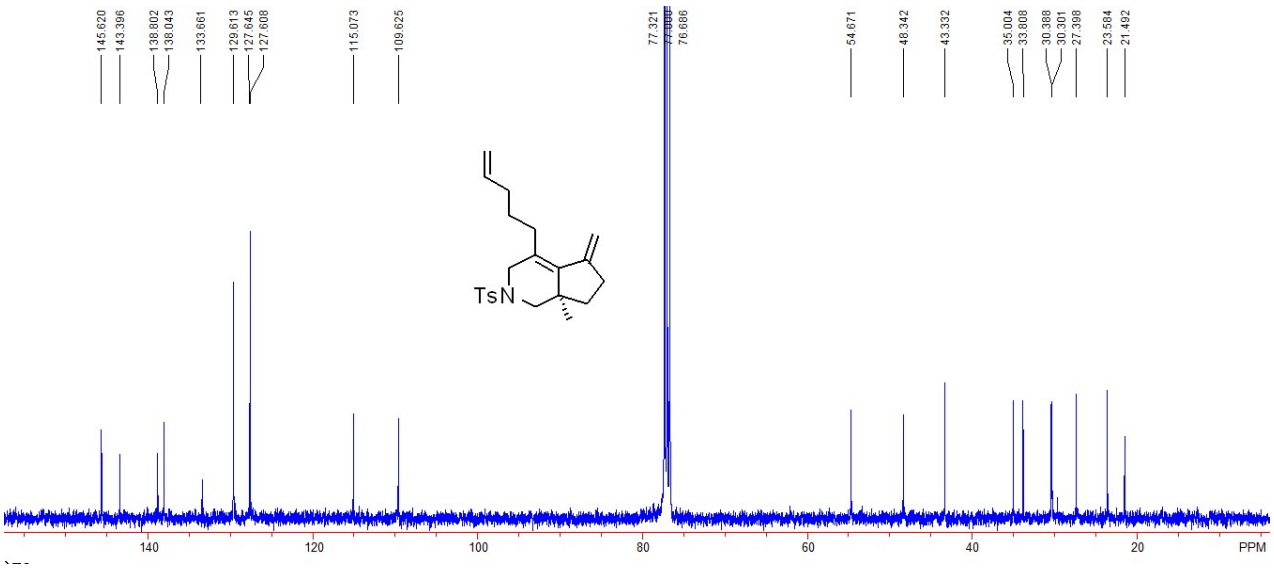
Translation: Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 3/1; Flow rate: 0.8 mL/min; t_{minor} = 8.28 min, t_{major} = 11.33 min; ee% = 97%].

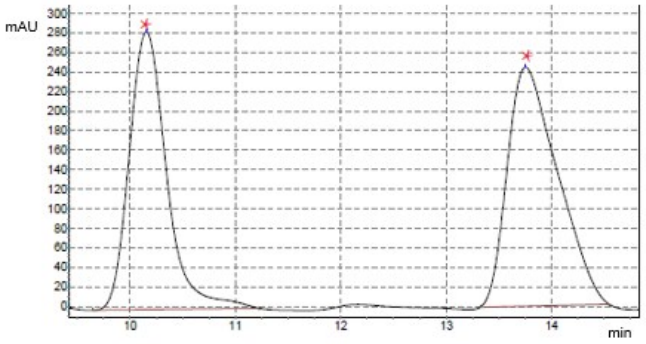


(*R*)-7a-methyl-5-methylene-4-(pent-4-en-1-yl)-2-tosyl-2,3,5,6,7,7a-hexahydro-1*H*-cyclopenta[*c*]pyridine (2i)

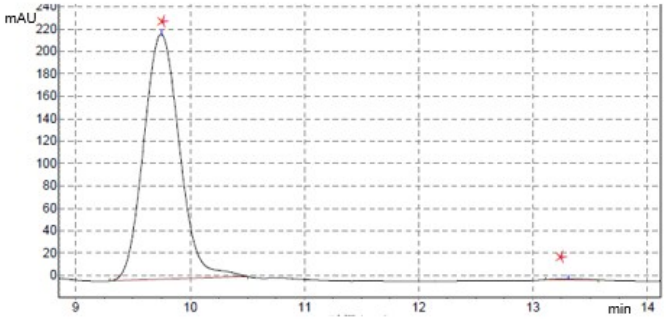
A light yellow oil. 51% yield (20 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.12 (s, 3H), 1.21-1.29 (m, 2H), 1.45-1.48 (m, 1H), 1.56-1.62 (m, 1H), 1.78-1.85 (m, 1H), 2.05-2.10 (m, 2H), 2.34-2.43 (m, 5H), 2.55-2.63 (m, 1H), 2.95 (d, *J* = 16.8 Hz, 1H), 3.75 (d, *J* = 10.8 Hz, 1H), 4.08 (d, *J* = 16.4 Hz, 1H), 4.95-5.03 (m, 2H), 5.08 (s, 2H), 5.75-5.86 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.5, 23.6, 27.4, 30.3, 30.4, 33.8, 35.0, 43.3, 48.3, 54.7, 109.6, 115.1, 127.61, 127.65, 133.7, 138.0, 138.8, 143.4, 145.6. IR (CH_2Cl_2): ν 2956, 2930, 2849, 1722, 1597, 1456, 1348, 1248, 1161, 1094, 1018, 987, 906, 861, 813, 790, 757, 731, 692, 662 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{30}NO_2S$ $(M+H)^+$: 372.1992, Found: 372.1990. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 25/1; Flow rate: 0.80 mL/min; t_{minor} = 13.31 min, t_{major} = 9.75 min; ee% > 99%; $[\alpha]^{20}_D$ = +71.2 (c 1.00, CH_2Cl_2)].





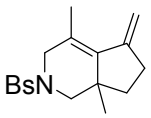


Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	10.155	284749.781	7011692.000	46.3651
2	13.752	244574.766	8111094.500	53.6349
Totals:		529324.547	15122786.500	100.0000



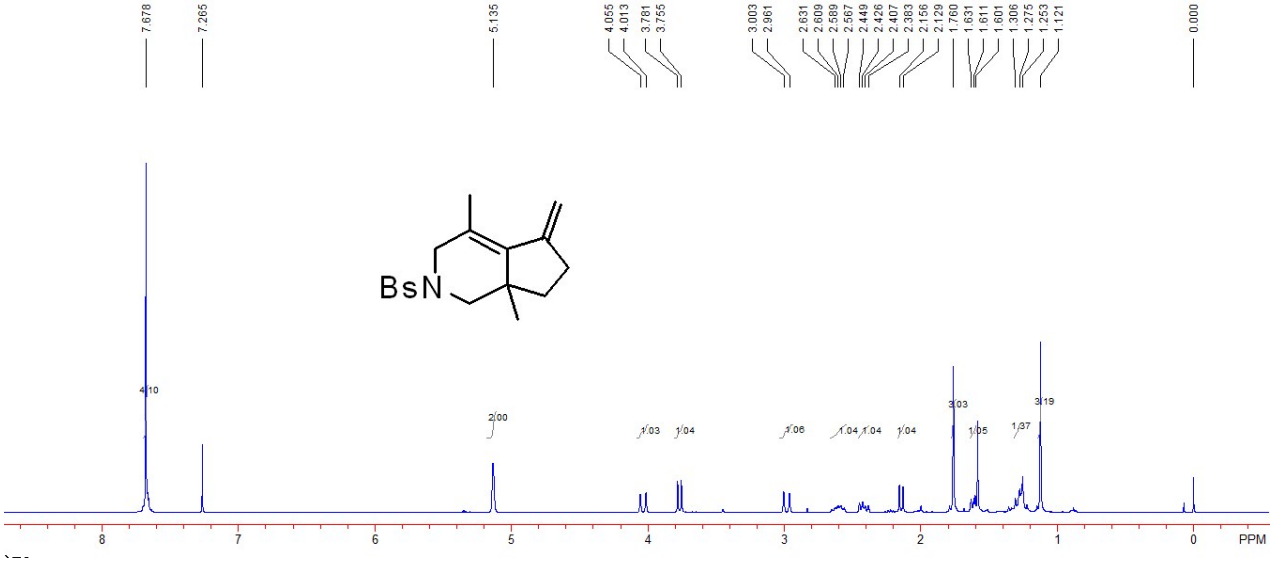
Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	9.747	218893.547	4753898.500	99.6222
2	13.305	1054.419	18028.549	0.3778
Totals:		219947.966	4771927.049	100.0000

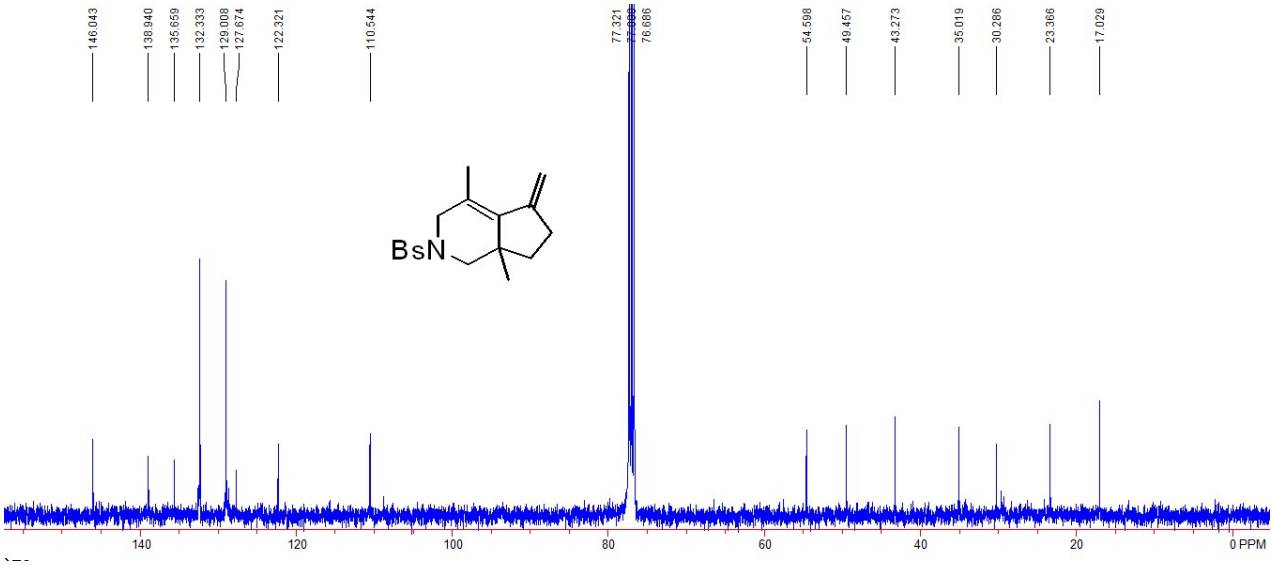
Translation: Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 25/1; Flow rate: 0.80 mL/min; t_{minor} = 13.31 min, t_{major} = 9.75 min; ee% > 99%].

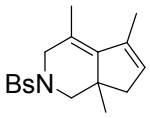


2-((4-bromophenyl)sulfonyl)-4,7a-dimethyl-5-methylene-2,3,5,6,7,7a-hexahydro-1*H*-cyclopenta[*c*]pyridine (2j)

A light yellow oil, 88% yield (34 mg). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.12 (s, 3H), 1.25-1.31 (m, 1H), 1.60-1.63 (m, 1H), 1.76 (s, 3H), 2.14 (d, *J* = 10.8 Hz, 1H), 2.38-2.45 (m, 1H), 2.57-2.63 (m, 1H), 2.98 (d, *J* = 16.8 Hz, 1H), 3.77 (d, *J* = 10.8 Hz, 1H), 4.03 (d, *J* = 16.8 Hz, 1H), 5.14 (s, 2H), 7.68 (s, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 17.0, 23.4, 30.3, 35.0, 43.3, 49.5, 54.6, 110.5 , 122.3, 127.7, 129.0, 132.3, 135.7, 138.9, 146.0. IR (CH_2Cl_2): ν 2962, 2930, 2847, 1707, 1651, 1574, 1389, 1351, 1207, 1089, 1069, 1009, 738 cm^{-1}. Mass (ESI) $(M+H)^+$: 382.0, HRMS (ESI) calcd. for $C_{17}H_{21}BrNO_2S$ $(M+H)^+$: 382.0471, Found: 382.0463.

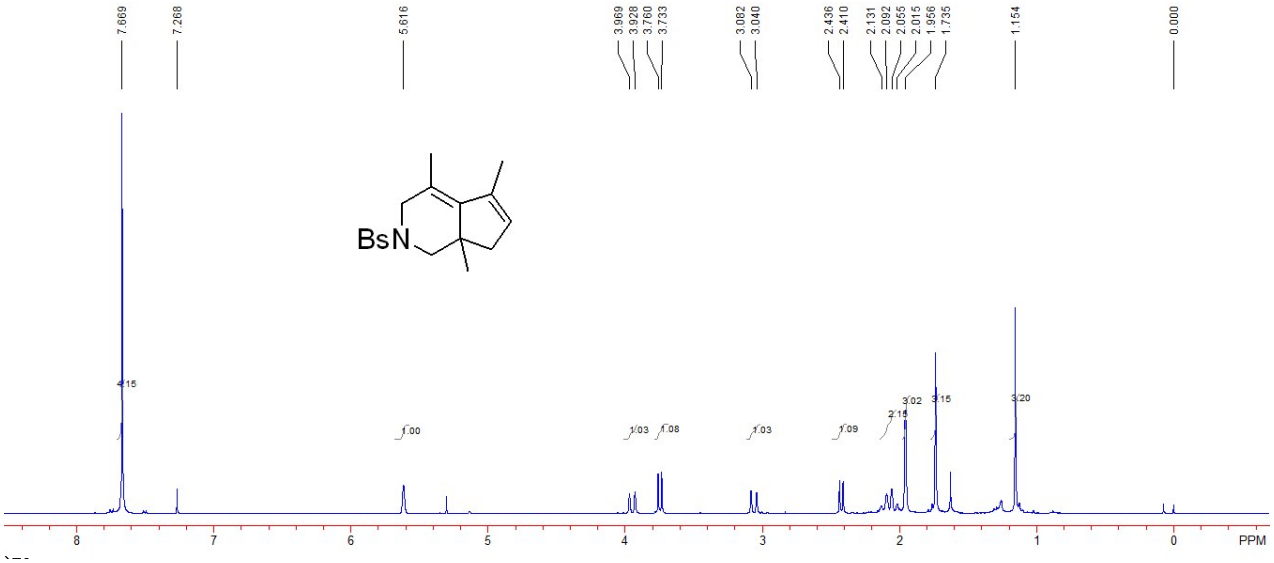


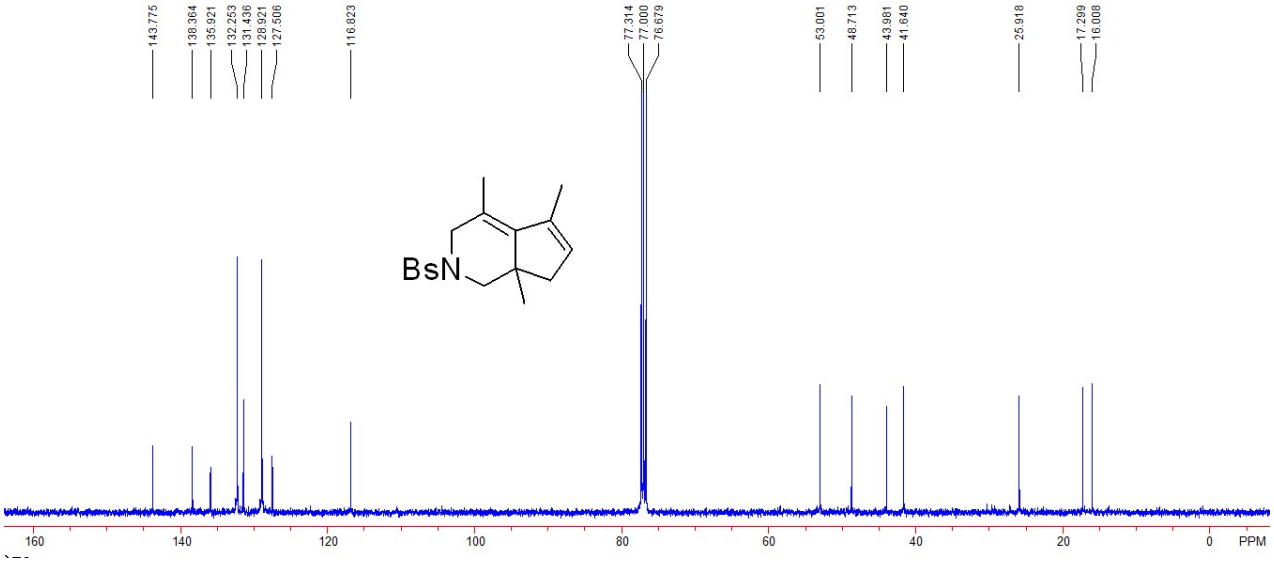


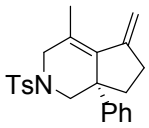


2-((4-bromophenyl)sulfonyl)-4,5,7a-trimethyl-2,3,7,7a-tetrahydro-1*H*-cyclopenta[*c*]pyridine (3j)

A white solid, 88% yield (33 mg). M. P. 110-113 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.15 (s, 3H), 1.74 (s, 3H), 1.96 (s, 3H), 2.07 (q, *J* = 14.8 Hz, 2H), 2.42 (d, *J* = 10.4 Hz, 1H), 3.06 (d, *J* = 16.8 Hz, 1H), 3.74 (d, *J* = 10.4 Hz, 1H) 3.95 (d, *J* = 16.8 Hz, 1H), 5.62 (s, 1H), 7.67 (s, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.0, 17.3, 25.9, 41.6, 44.0, 48.7, 53.0, 116.8, 127.5, 128.9, 131.4, 132.3, 135.9, 138.4, 143.8. IR (CH_2Cl_2): ν 2950, 2915, 1797, 1590, 1439, 1368, 1255, 1164, 1153, 1093, 1049, 1029, 993, 967, 916, 825, 764, 651, 621 cm^{-1}. HRMS (ESI) calcd. for $C_{17}H_{21}BrNO_2S$ $(M+H)^+$: 382.0471, Found: 382.0468.

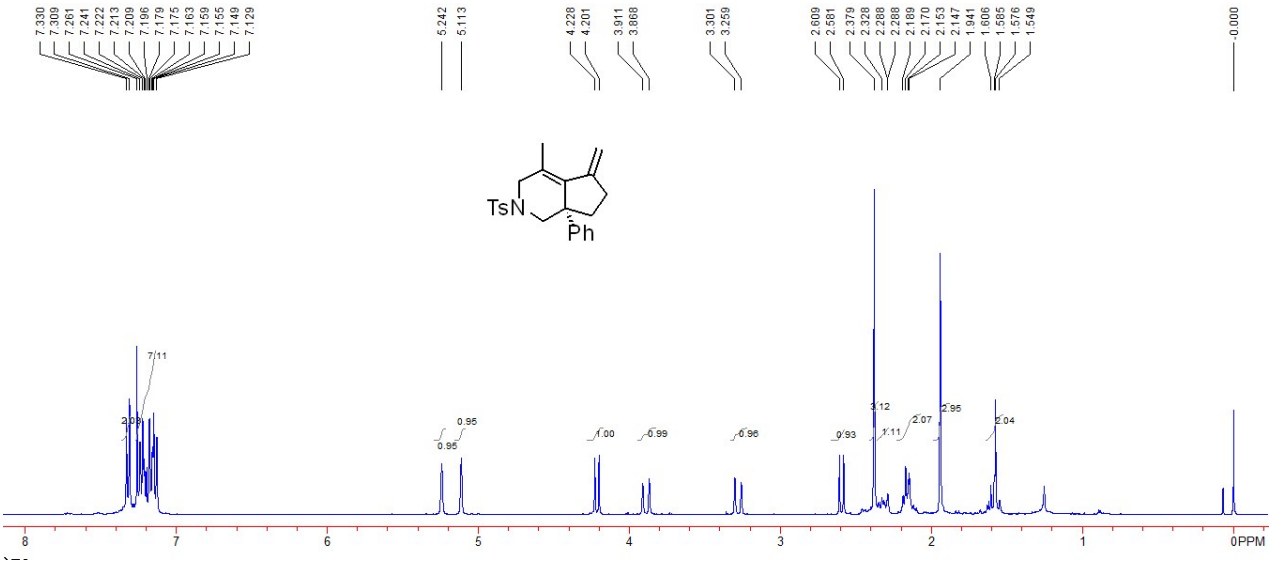


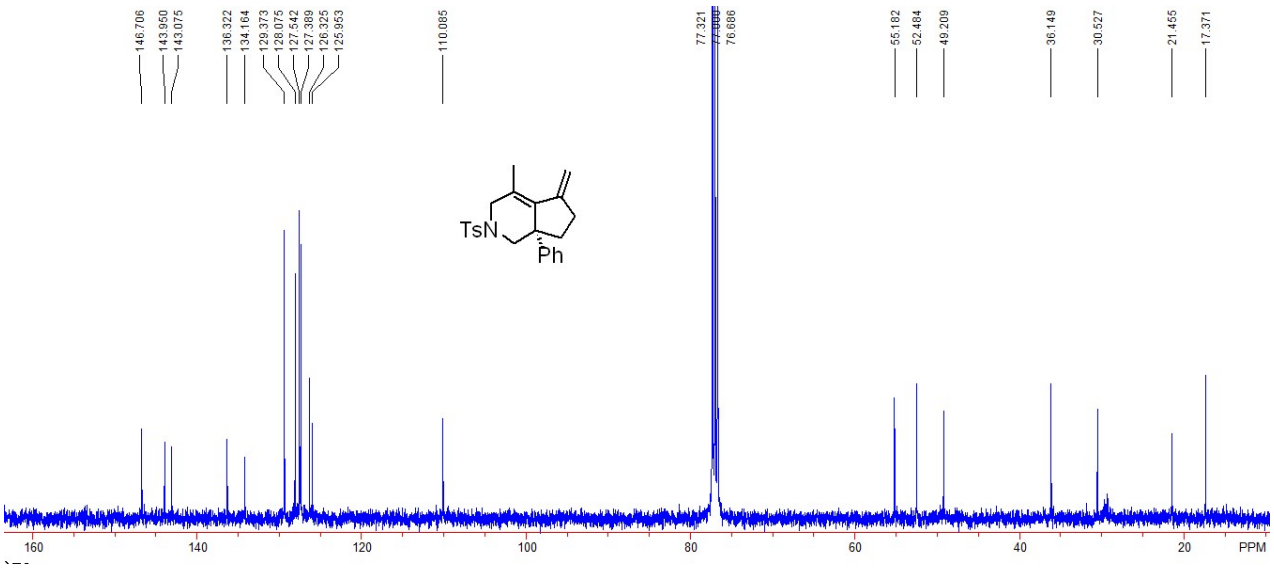


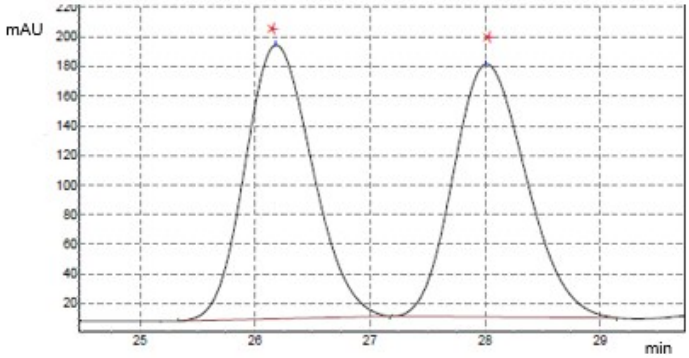


(*S*)-4-methyl-5-methylene-7a-phenyl-2-tosyl-2,3,5,6,7,7a-hexahydro-1H-cyclopenta[c]pyridine (2n)

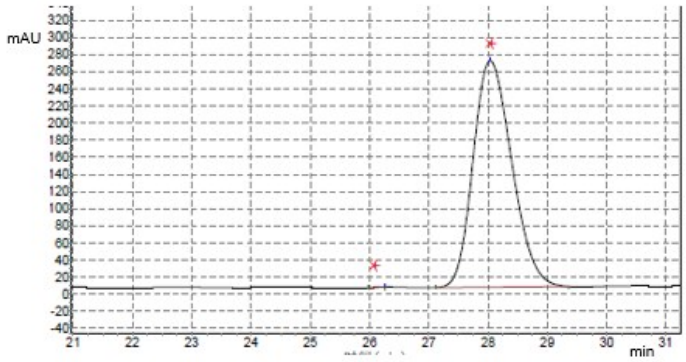
A white solid. 76% yield (29 mg). M. P. 118-122 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.55-1.61 (m, 2H), 1.94 (s, 3H), 2.15-2.19 (m, 2H), 2.29-2.38 (m, 4H), 2.60 (d, *J* = 11.2 Hz, 1H), 3.28 (d, *J* = 16.8 Hz, 1H), 3.89 (d, *J* = 17.2 Hz, 1H), 4.21 (d, *J* = 10.8 Hz, 1H), 5.11 (s, 1H), 5.24 (s, 1H), 7.13-7.26 (m, 7H), 7.32 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 17.4, 21.5, 30.5, 36.1, 49.2, 52.5, 55.2, 110.1, 126.0, 127.4, 127.5, 128.1, 129.4, 134.1, 136.3, 143.1, 144.0, 146.7. IR (CH_2Cl_2): ν 2951, 2923, 2852, 2342, 1665, 1592, 1493, 1443, 1350, 1163, 1090, 1057, 959, 812, 820, 766, 701, 662 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{26}NO_2S$ $(M+H)^+$: 380.1679, Found: 380.1676. Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 3/1; Flow rate: 0.80 mL/min; t_{minor} = 26.27 min, t_{major} = 28.04 min; ee% > 99%; $[\alpha]^{20}_D$ = +133.7 (c 1.00, CH_2Cl_2)].





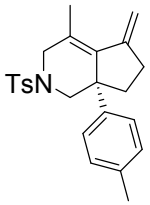


Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	26.185	184914.734	7502388.500	49.9346
2	28.013	170859.156	7522049.500	50.0654
Totals:		355773.891	15024438.000	100.0000



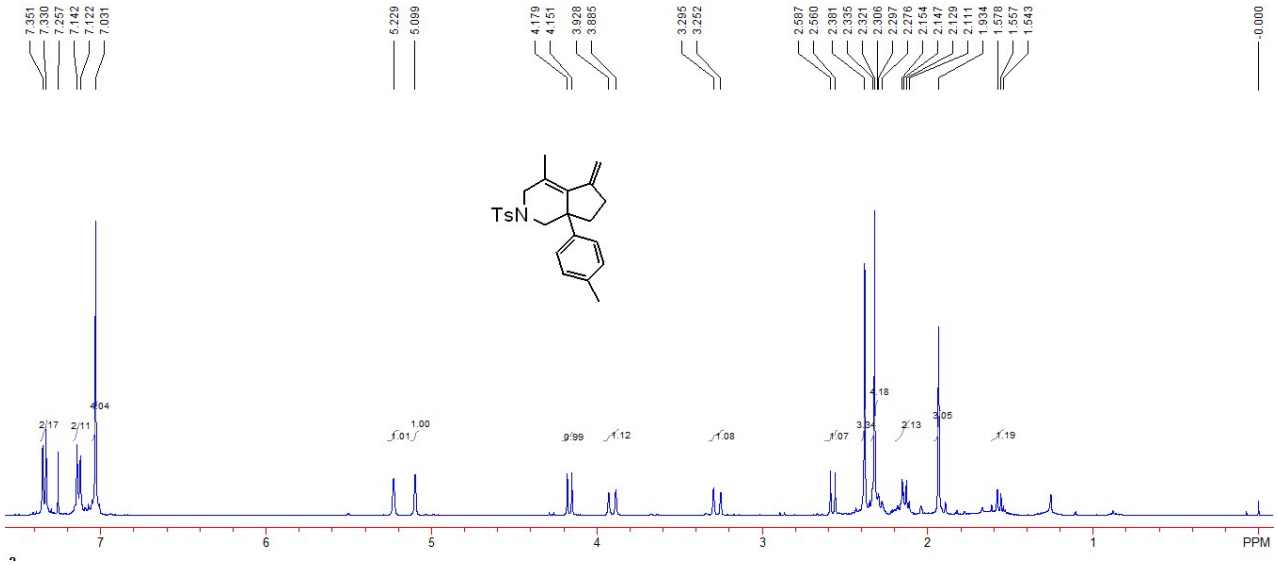
Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	26.272	2.078	338.515	0.0028
2	28.035	264290.563	11969334.000	99.9972
Totals:		264292.640	11969672.515	100.0000

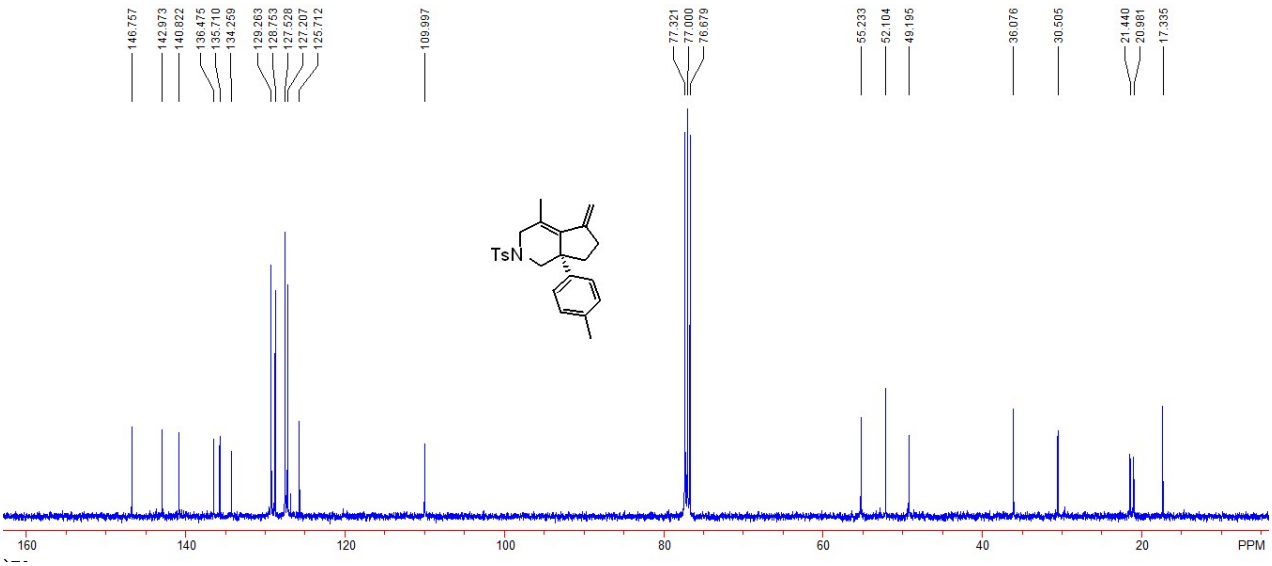
Translation: Chiralcel IC-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 3/1; Flow rate: 0.80 mL/min; t_{minor} = 26.27 min, t_{major} = 28.04 min; ee% > 99%].

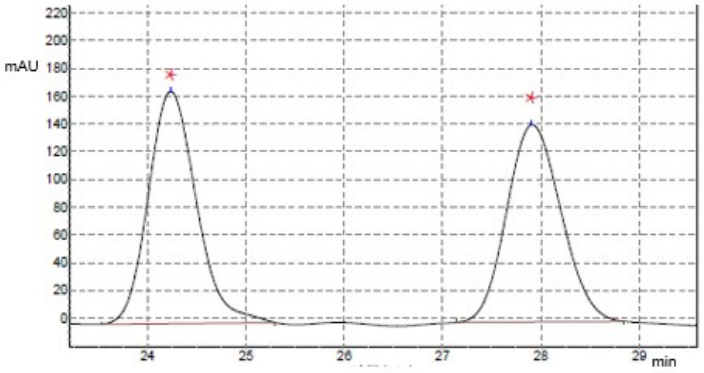


(*S*)-4-methyl-5-methylene-7a-(p-tolyl)-2-tosyl-2,3,5,6,7,7a-hexahydro-1*H*-cyclopenta[*c*]pyridine (2o)

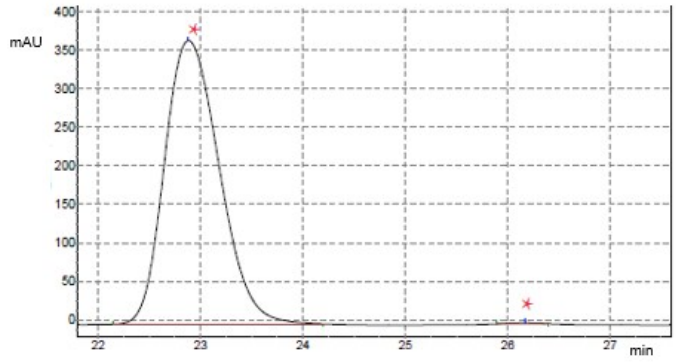
A light yellow oil. 74% yield (29 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.54-1.58 (m, 1H), 1.93 (s, 3H), 2.11-2.15 (m, 2H), 2.28-2.35 (m, 4H), 2.38 (s, 3H), 2.57 (d, *J* = 11.2 Hz, 1H), 3.27 (d, *J* = 16.8 Hz, 1H), 3.91 (d, *J* = 17.2 Hz, 1H), 4.17 (d, *J* = 11.2 Hz, 1H), 5.10 (s, 1H), 5.23 (s, 1H), 7.03 (s, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 17.3, 21.0, 21.4, 30.5, 36.1, 49.2, 52.1, 55.2, 110.0, 125.7, 127.2, 127.5, 128.8, 129.3, 134.2, 135.7, 136.5, 140.8, 143.0, 146.8. IR (CH_2Cl_2): ν 2956, 2924, 2849, 1714, 1675, 1591, 1448, 1354, 1331, 1165, 1090, 1019, 958, 813, 661 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{28}NO_2S$ $(M+H)^+$: 394.1835, Found: 394.1832. Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 3/1; Flow rate: 0.80 mL/min; t_{minor} = 26.17 min, t_{major} = 22.88 min; ee% > 99%; $[\alpha]^{20}_D$ = +138.5 (c 1.00, CH_2Cl_2)].





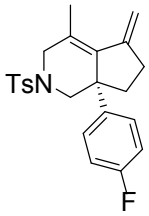


Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	24.233	167201.234	5659592.500	50.9279
2	27.912	142041.578	5453362.500	49.0721
Totals:		309242.813	11112955.000	100.0000



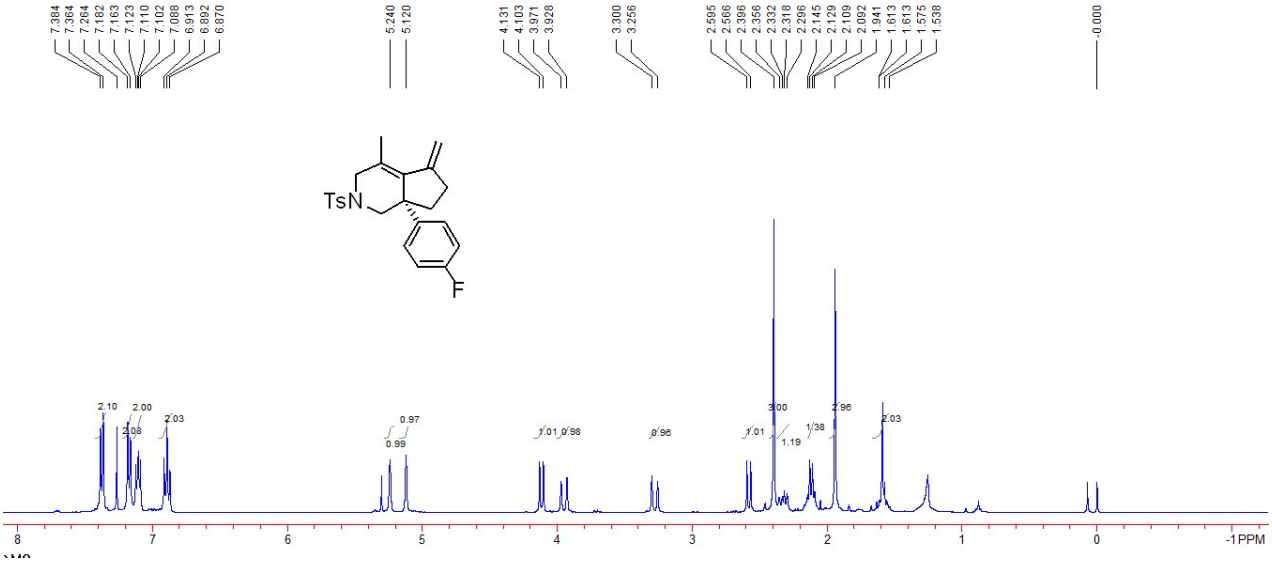
Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	22.882	367884.500	13639503.000	99.8525
2	26.165	1031.061	20145.547	0.1475
Totals:		368915.561	13659648.547	100.0000

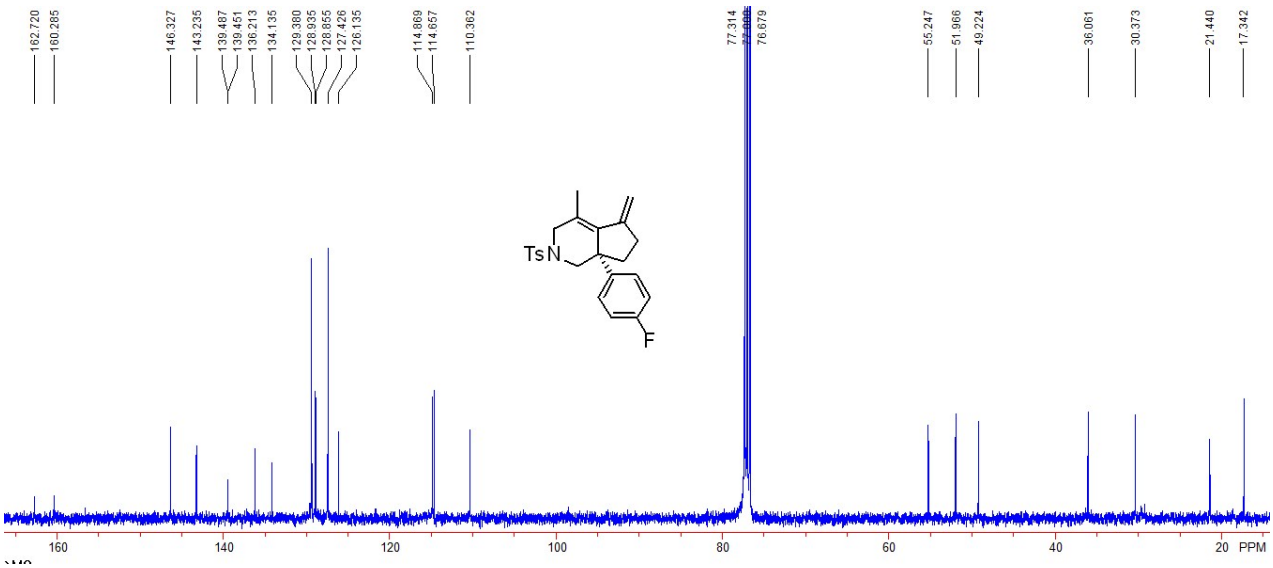
Translation: Chiralcel IC-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 3/1; Flow rate: 0.80 mL/min; t_{minor} = 26.17 min, t_{major} = 22.88 min; ee% > 99%].

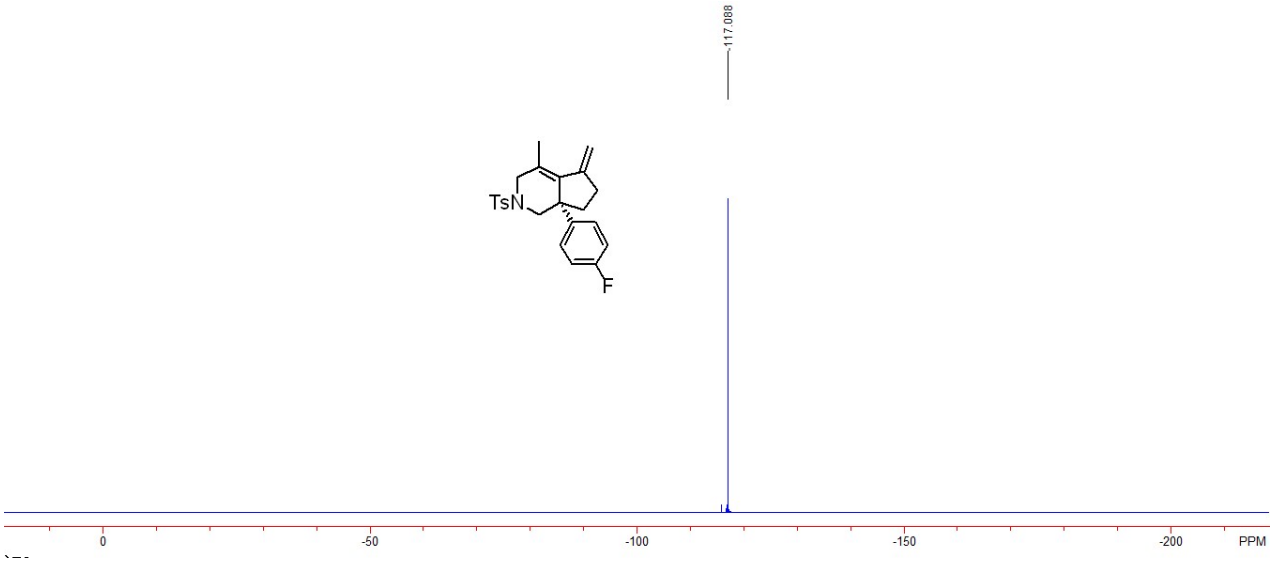


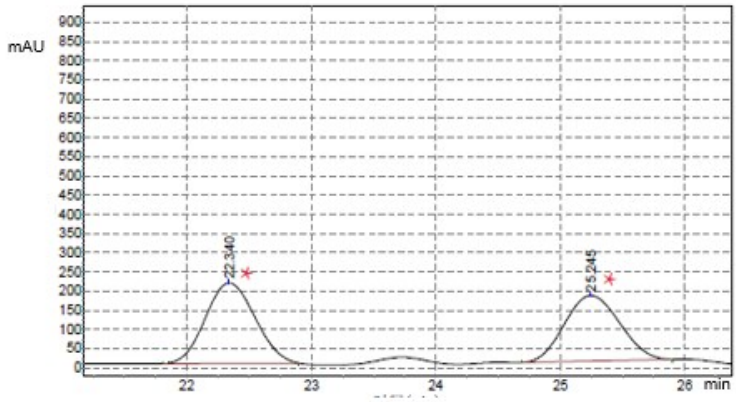
(*S*)-7a-(4-fluorophenyl)-4-methyl-5-methylene-2-tosyl-2,3,5,6,7,7a-hexahydro-1*H*-cyclopenta[*c*]pyridine (2p)

A light yellow oil. 70% yield (29 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.54-1.61 (m, 2H), 1.94 (s, 3H), 2.09-2.14 (m, 2H), 2.30-2.36 (m, 2H), 2.40 (s, 3H), 2.58 (d, *J* = 11.6 Hz, 1H), 3.28 (d, *J* = 17.6 Hz, 1H), 3.95 (d, *J* = 11.6 Hz, 1H), 4.12 (d, *J* = 10.8 Hz, 1H), 5.12 (s, 1H), 5.24 (s, 1H), 6.89 (t, *J* = 8.4 Hz, 2H), 7.09-7.12 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 17.3, 21.4, 30.4, 36.1, 49.2, 52.0, 55.2, 110.4, 114.8 (d, *J* = 21.2 Hz), 126.1, 127.4, 128.9 (d, *J* = 8.0 Hz), 129.4, 134.1, 136.2, 139.4 (d, *J* = 3.6 Hz), 143.2, 146.3, 161.5 (d, *J* = 243.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.1 (s, 1F). IR (CH_2Cl_2): ν 2920, 2852, 1599, 1507, 1443, 1349, 1161, 1090, 1015, 958, 833, 806, 791, 662 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{25}FNO_2S$ $(M+H)^+$: 398.1585. Found: 398.1578. Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 3/1; Flow rate: 0.80 mL/min; t_{minor} = 23.08 min, t_{major} = 25.77 min; ee% > 99%; $[\alpha]^{20}_D$ = +141.3 (c 1.00, CH_2Cl_2)].

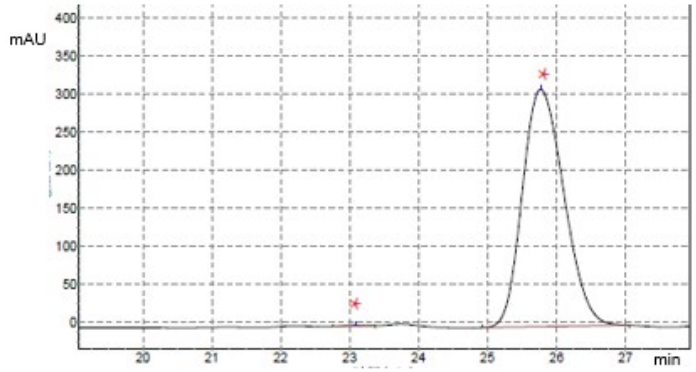






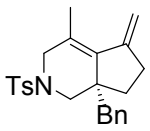


Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	22.340	209359.016	5789647.500	52.5603
2	25.245	170555.859	5225606.000	47.4397
Totals:		379914.875	11015253.500	100.0000



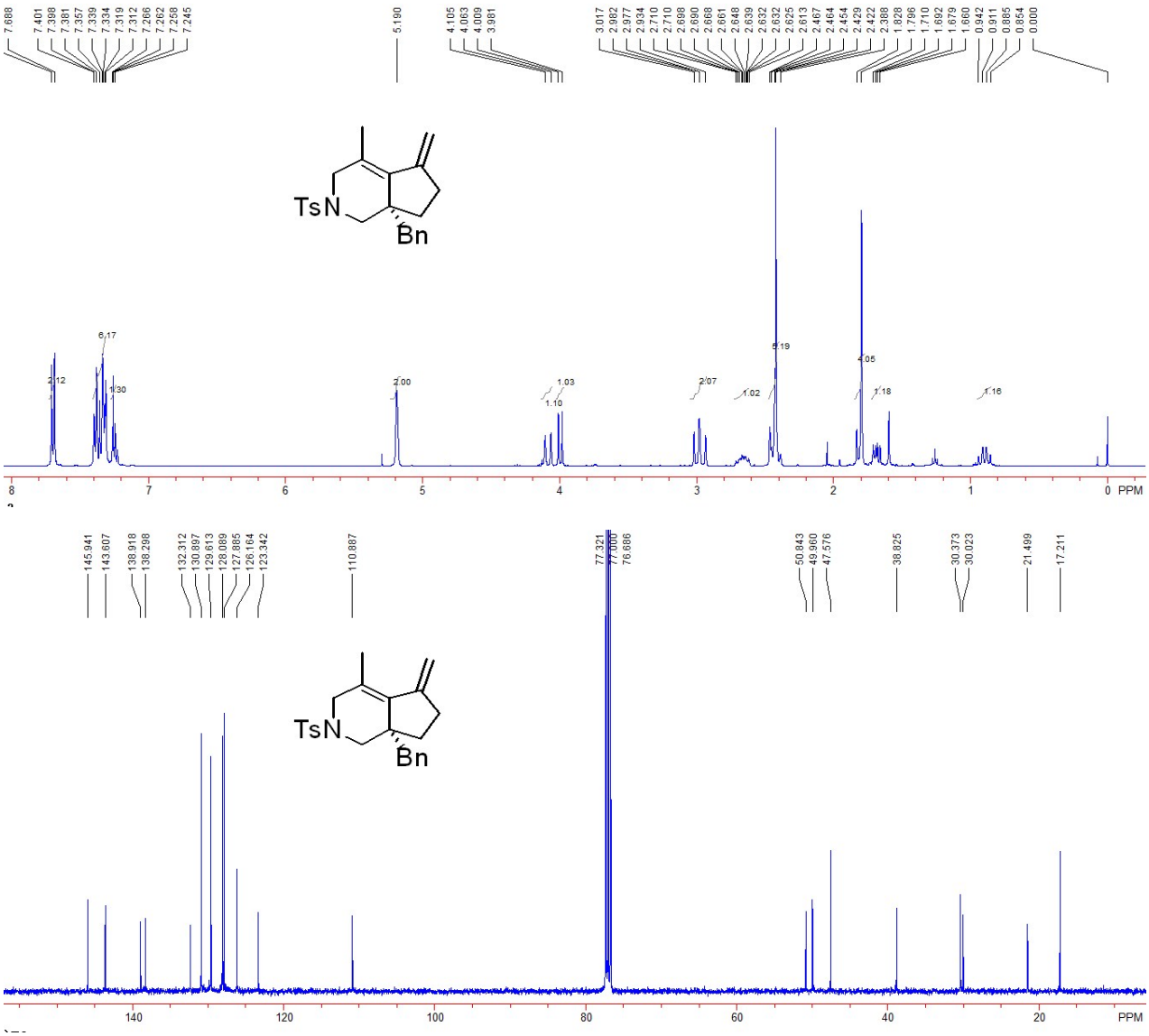
Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	23.082	1018.520	21474.455	0.1638
2	25.773	312082.156	13088359.000	99.8362
Totals:		313100.676	13109833.455	100.0000

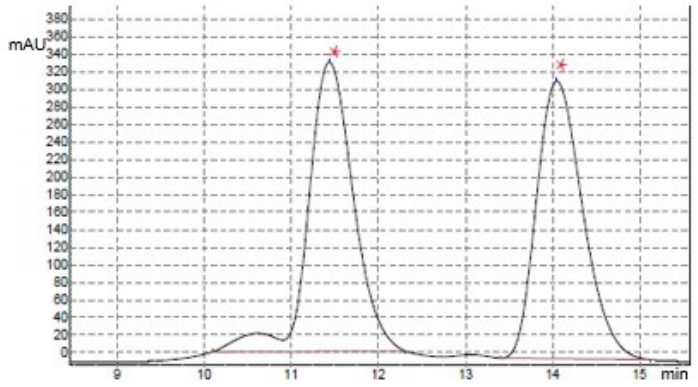
Translation: Chiralcel IC-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 3/1; Flow rate: 0.80 mL/min; t_{minor} = 23.08 min, t_{major} = 25.77 min; ee% > 99%].



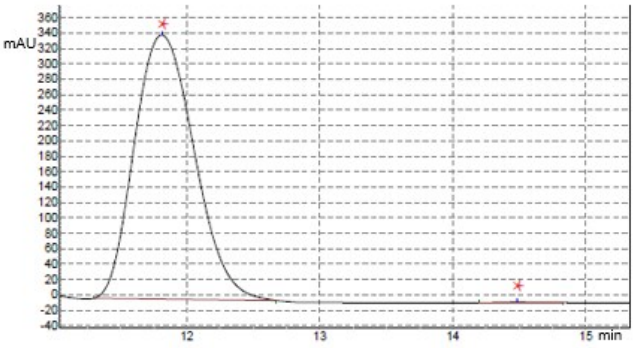
(*S*)-7a-benzyl-4-methyl-5-methylene-2-tosyl-2,3,5,6,7,7a-hexahydro-1*H*-cyclopenta[*c*]pyridine (2q)

A white solid. 87% yield (34 mg). M. P. 119-122 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.90 (q, *J* = 10.4 Hz, 1H), 1.66-1.71 (m, 1H), 1.80-1.83 (m, 4H), 2.39-2.47 (m, 5H), 2.61-2.71 (m, 1H), 2.93-3.02 (m, 2H), 4.00 (d, *J* = 11.2 Hz, 1H), 4.08 (d, *J* = 16.8 Hz, 1H), 5.19 (s, 2H), 7.25-7.27 (m, 1H), 7.31-7.40 (m, 6H), 7.70 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 17.2, 21.5, 30.0, 30.4, 38.8, 47.6, 50.0, 50.8, 110.9, 123.3, 126.2, 127.9, 128.1, 129.6, 130.9, 132.3, 138.3, 138.9, 143.6, 145.9. IR (CH_2Cl_2): ν 3029, 2923, 2849,1599, 1492, 1448, 1344, 1165, 1089, 960, 813, 706, 691, 678 cm^{-1}. Mass (ESI) $(M+H)^+$: 394.1, HRMS (ESI) calcd. for $C_{24}H_{28}NO_2S$ $(M+H)^+$: 394.1835, Found: 394.1824. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 25/1; Flow rate: 0.80 mL/min; t_{minor} = 14.49 min, t_{major} = 11.81 min; ee% > 99%; $[\alpha]^{20}_D$ = +280.1 (c 1.00, CH_2Cl_2)].



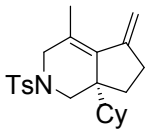


Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	11.438	329222.906	11897776.000	50.6639
2	14.050	316007.969	11585942.000	49.3361
Totals:		645230.875	23483718.000	100.0000



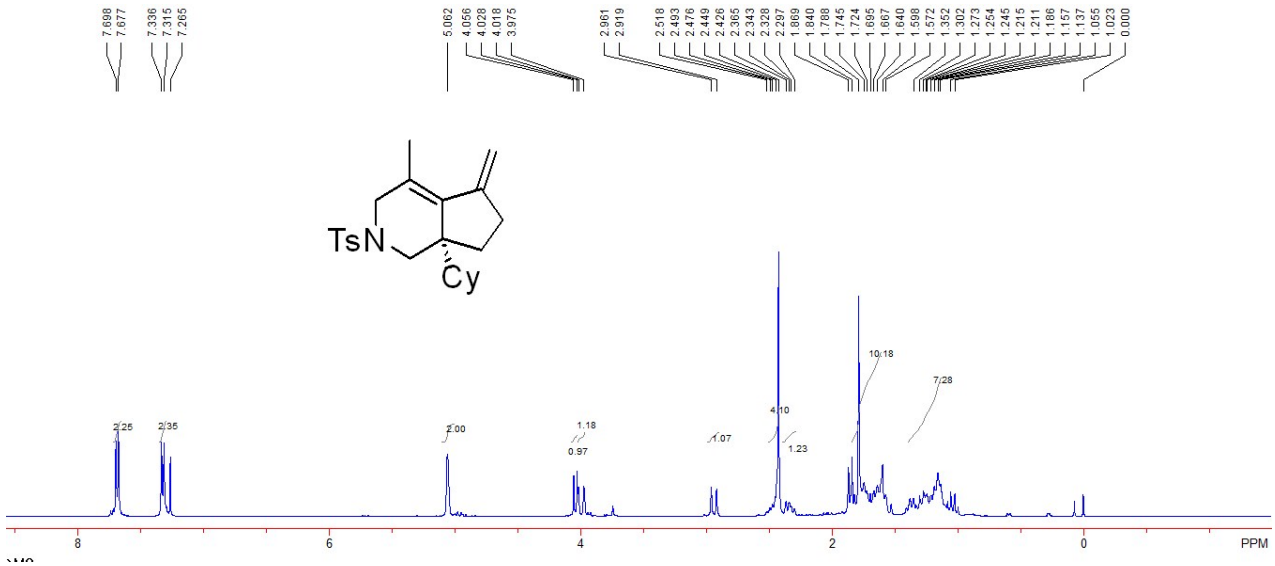
Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	11.810	343007.500	10740846.000	99.9402
2	14.485	574.000	6429.001	0.0598
Totals:		343581.500	10747275.001	100.0000

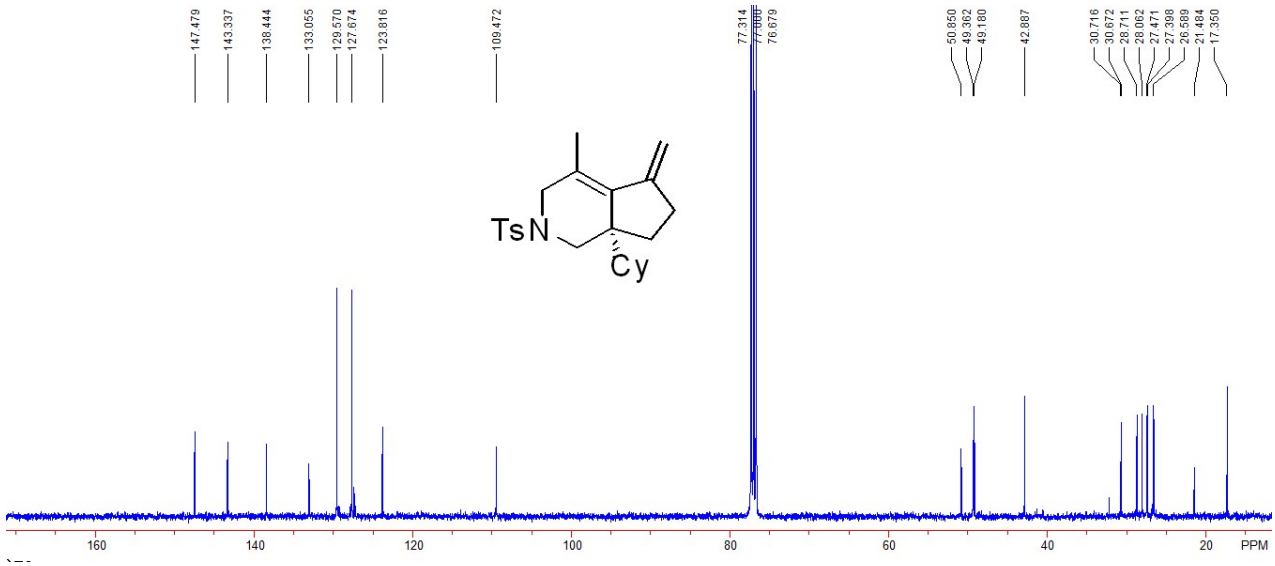
Translation: Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 25/1; Flow rate: 0.80 mL/min; t_{minor} = 14.49 min, t_{major} = 11.81 min; ee% > 99%].

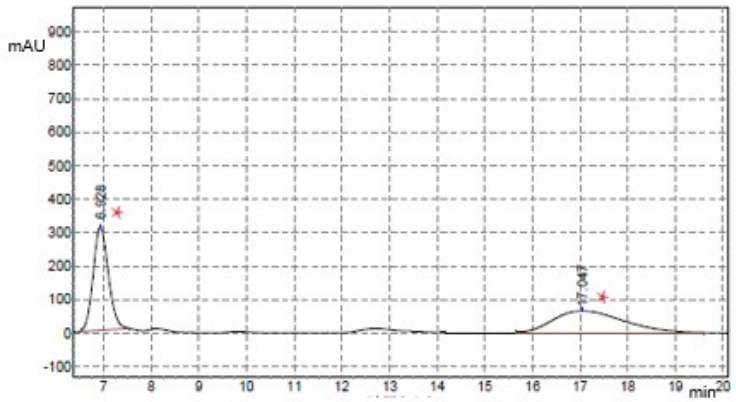


(*S*)-7a-cyclohexyl-4-methyl-5-methylene-2-tosyl-2,3,5,6,7,7a-hexahydro-1*H*-cyclopenta[*c*]pyridine (2r)

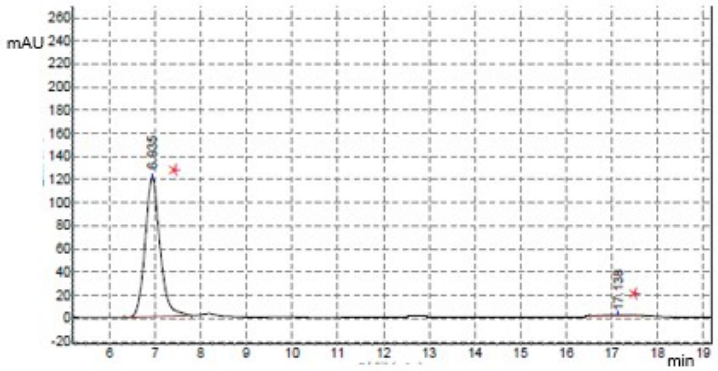
A light yellow oil. 67% yield (26 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.00-1.41 (m, 7H), 1.58-1.87 (m, 10H), 2.30-2.37 (m, 1H), 2.42-2.51 (m, 4H), 2.95 (d, *J* = 16.8 Hz, 1H), 4.00 (d, *J* = 16.8 Hz, 1H), 4.04 (d, *J* = 10.8 Hz, 1H), 5.06 (s, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 17.4, 21.5, 26.6, 27.4, 27.5, 28.1, 28.7, 30.67, 30.72, 42.9, 49.2, 49.4, 50.9, 109.5, 123.8, 127.7, 129.6, 133.1, 138.4, 143.4, 147.5. IR (CH_2Cl_2): ν 2938, 1697, 1547, 1450, 1315, 1219, 1165, 1080, 1048, 975, 916, 854, 819, 771, 726, 661, 633 cm^{-1}. Mass (ESI) $(M+H)^+$: 386.2, HRMS (ESI) calcd. for $C_{23}H_{32}NO_2S$ $(M+H)^+$: 386.2148, Found: 386.2137. Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 10/1; Flow rate: 0.80 mL/min; t_{minor} = 17.14 min, t_{major} = 6.94 min; ee% = 97%; $[\alpha]^{20}_D$ = +222.7 (c 1.00, CH_2Cl_2)].





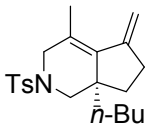


Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	6.928	307478.438	6790574.500	50.7154
2	17.047	65205.879	6598984.500	49.2846
Totals:		372684.316	13389559.000	100.0000



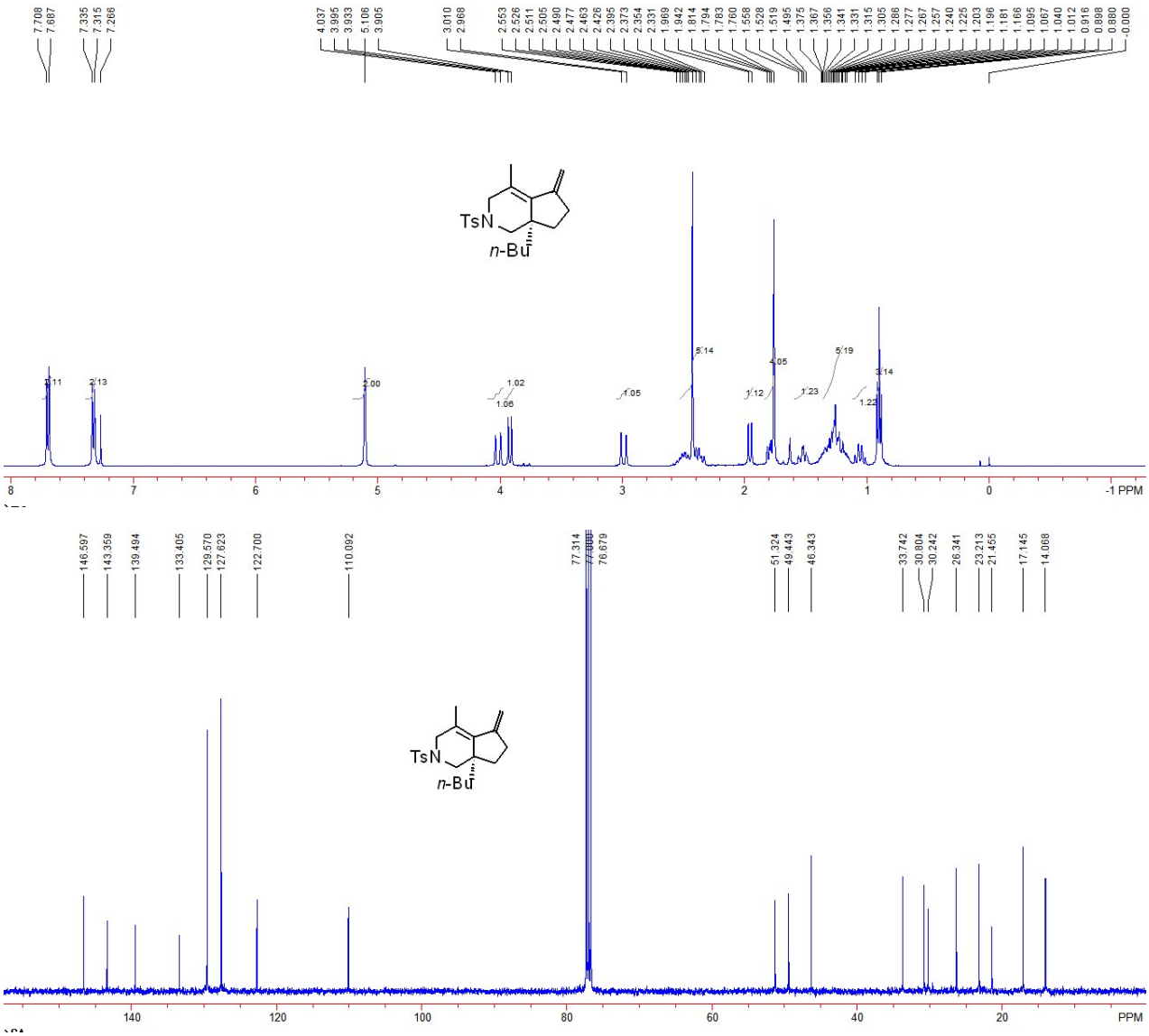
Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	6.935	120633.813	2721597.250	98.5268
2	17.138	904.231	40693.156	1.4732
Totals:		121538.043	2762290.406	100.0000

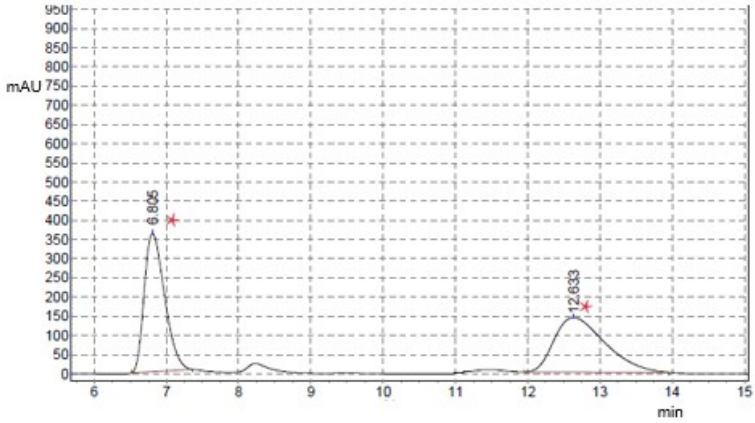
Translation: Chiralcel AS-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 10/1; Flow rate: 0.8 mL/min; t_{minor} = 17.14 min, t_{major} = 6.94 min; ee% = 97%].



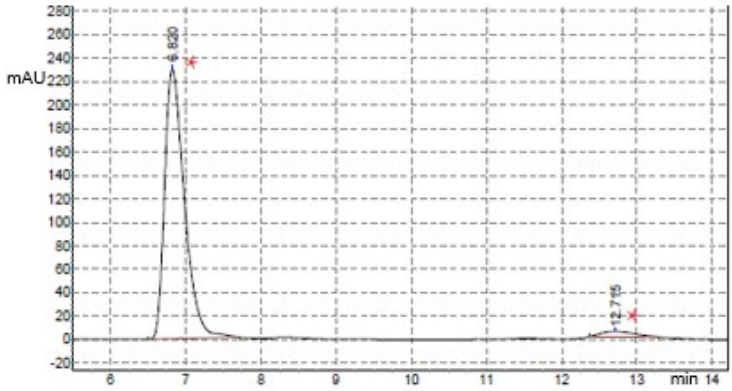
(*R*)-7a-butyl-4-methyl-5-methylene-2-tosyl-2,3,5,6,7,7a-hexahydro-1*H*-cyclopenta[*c*]pyridine (2s)

A light yellow oil. 86% yield (31 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.90 (t, *J* = 6.8 Hz, 3H), 1.05 (q, *J* = 11.6 Hz, 1H), 1.17-1.38 (m, 5H), 1.50-1.56 (m, 1H), 1.76-1.82 (m, 4H), 1.95 (d, *J* = 10.8 Hz, 1H), 2.33-2.55 (m, 5H), 2.98 (d, *J* = 16.8 Hz, 1H), 3.92 (d, *J* = 10.8 Hz, 1H), 4.02 (d, *J* = 17.2 Hz, 1H), 5.11 (s, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.1, 17.1, 21.5, 23.2, 26.3, 30.2, 30.8, 33.7, 46.3, 49.4, 51.3, 110.1, 122.7, 127.6, 129.6, 133.4, 139.5, 143.4, 146.6. IR (CH_2Cl_2): ν 2951, 1667, 1637, 1549, 1479, 1314, 1126, 1071, 976, 942, 841, 815, 712, 669 cm^{-1}. Mass (ESI) $(M+H)^+$: 360.2, HRMS (ESI) calcd. for $C_{21}H_{30}NO_2S$ $(M+H)^+$: 360.1992, Found: 360.1981. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 10/1; Flow rate: 0.80 mL/min; t_{minor} = 12.72 min, t_{major} = 6.82 min; ee% = 93%; $[\alpha]^{20}_D$ = +65.7 (c 1.00, CH_2Cl_2)].



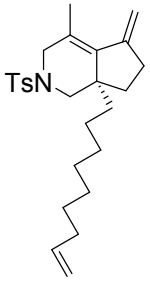


Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	6.805	360283.469	7038690.500	50.3488
2	12.633	142154.063	6941178.500	49.6512
Totals:		502437.531	13979869.000	100.0000



Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	6.820	230092.219	4208874.000	96.7443
2	12.715	4560.075	141637.906	3.2557
Totals:		234652.293	4350511.906	100.0000

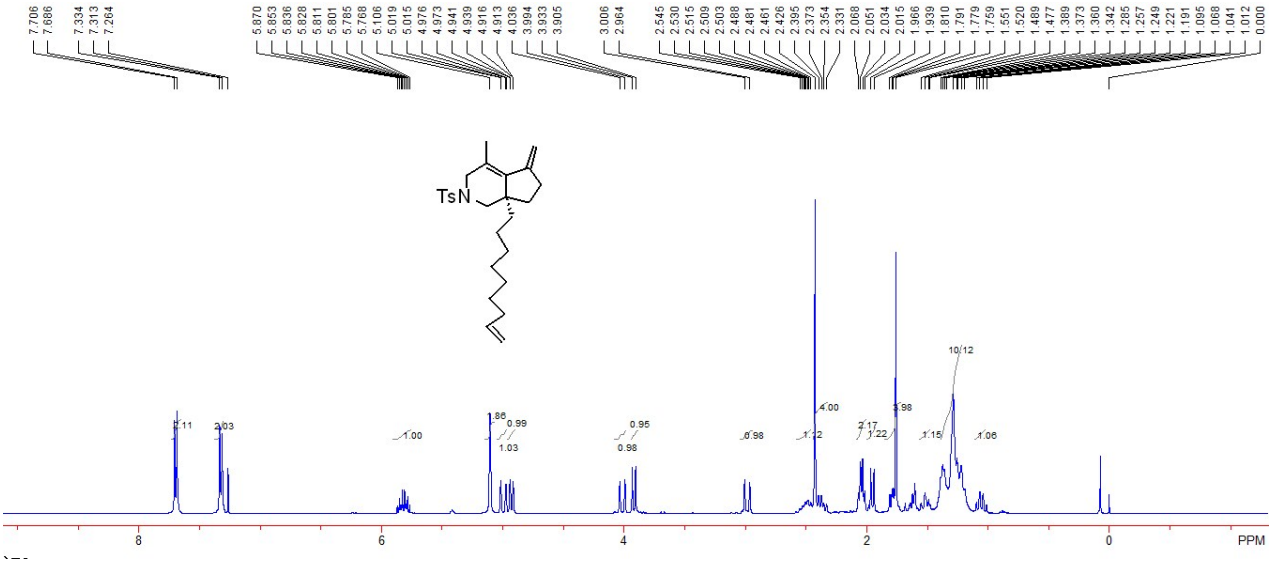
Translation: Chiralcel IC-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 10/1; Flow rate: 0.80 mL/min; t_{minor} = 12.72 min, t_{major} = 6.82 min; ee% = 93%].

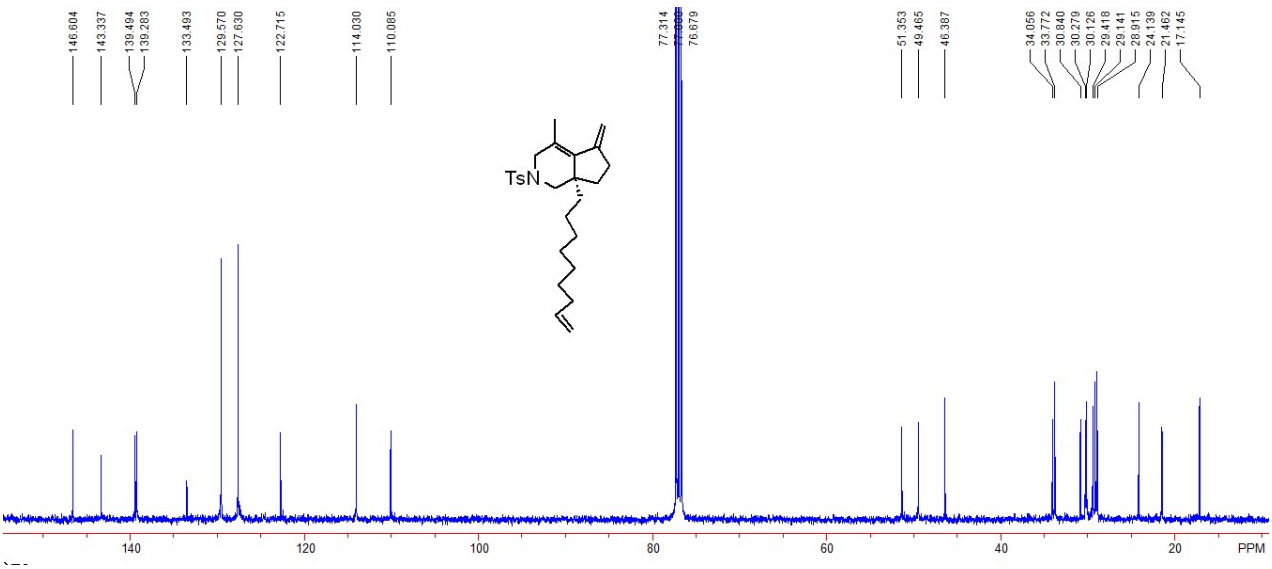


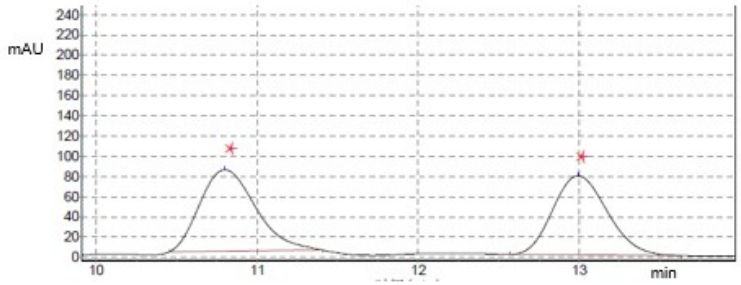
(*R*)-4-methyl-5-methylene-7a-(non-8-en-1-yl)-2-tosyl-2,3,5,6,7,7a-hexahydro-1*H*-cyclopenta[*c*]pyridine (2t)

A light yellow oil. 83% yield (35 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.05 (t, *J* = 10.8 Hz, 1H), 1.19-1.39 (m, 10H), 1.48-1.55 (m, 1H), 1.76-1.81 (m, 4H), 1.95 (d, *J* = 10.8 Hz, 1H), 2.04 (q, *J* = 6.8 Hz, 2H), 2.33-2.55 (m, 5H), 2.99 (d, *J* = 16.8 Hz, 1H), 3.92 (d, *J* = 10.8 Hz, 1H), 4.02 (d, *J* = 16.8 Hz, 1H), 4.93 (dd, J_1 = 0.8 Hz, J_2 = 10.0 Hz, 1H), 5.00 (dd, J_1 = 1.6 Hz, J_2 = 17.2 Hz, 1H), 5.11 (s, 2H), 5.77-5.87 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 17.1, 21.5, 24.1, 28.9, 29.1, 29.4, 30.1, 30.3, 30.8, 33.8, 34.1, 46.4, 49.5, 51.4, 110.1, 114.0, 122.7, 127.6, 129.6, 133.5, 139.3, 139.5, 143.3, 146.6. IR (CH_2Cl_2): ν 2953, 2923, 2852, 2342, 1724, 1637, 1611, 1517, 1461, 1370, 1163, 1091, 1028, 1013, 945, 920, 766, 723, 714, 684, 671 cm^{-1}. HRMS (ESI) calcd. for $C_{26}H_{38}NO_2S$ $(M+H)^+$: 428.2618, Found: 428.2605. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 50/1; Flow rate: 0.80 mL/min; t_{minor} = 12.84 min, t_{major} = 10.70

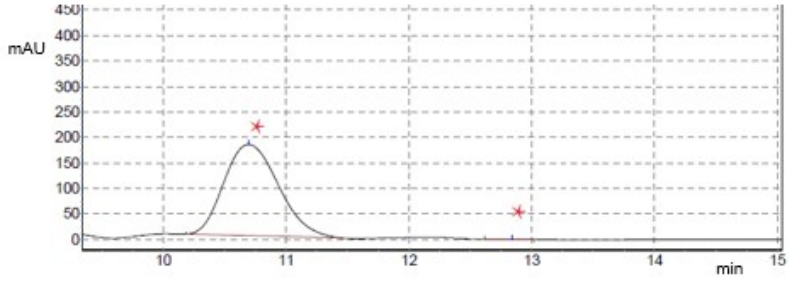
min; ee% > 99%; $[\alpha]^{20}_{D}$ = +48.2 (c 1.00, CH_2Cl_2)].





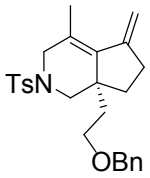


Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	10.800	80524.445	1932610.250	51.2675
2	12.993	78302.172	1837046.375	48.7325
Totals:		158826.617	3769656.625	100.0000



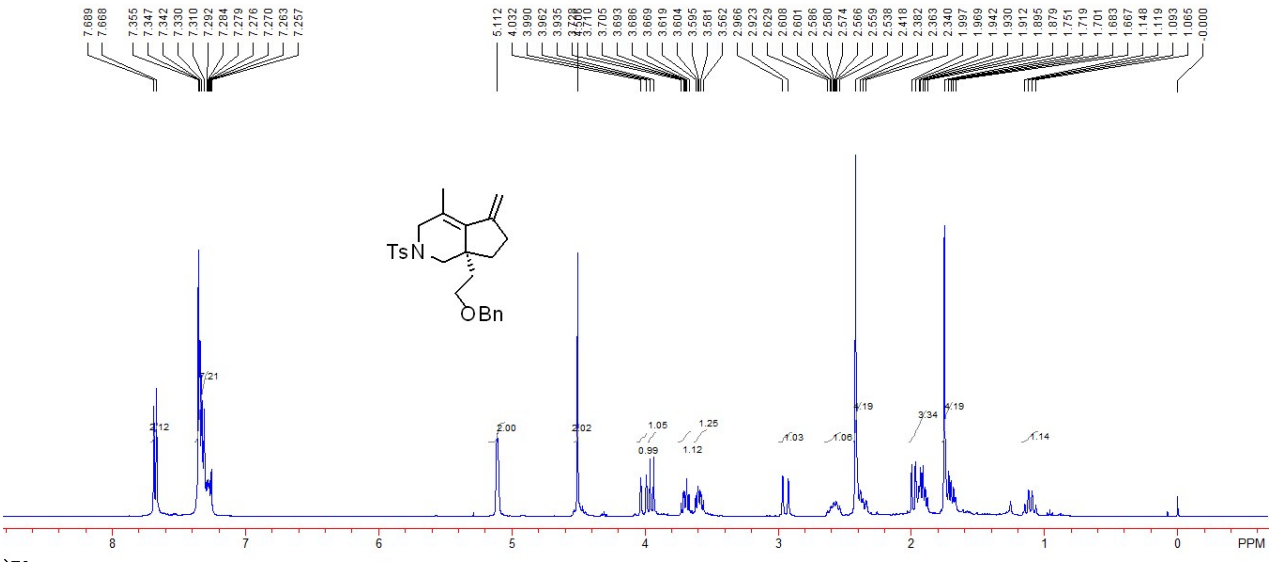
Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	10.695	178728.359	5497522.000	99.8374
2	12.837	618.000	8952.000	0.1626
Totals:		179346.360	5506474.000	100.0000

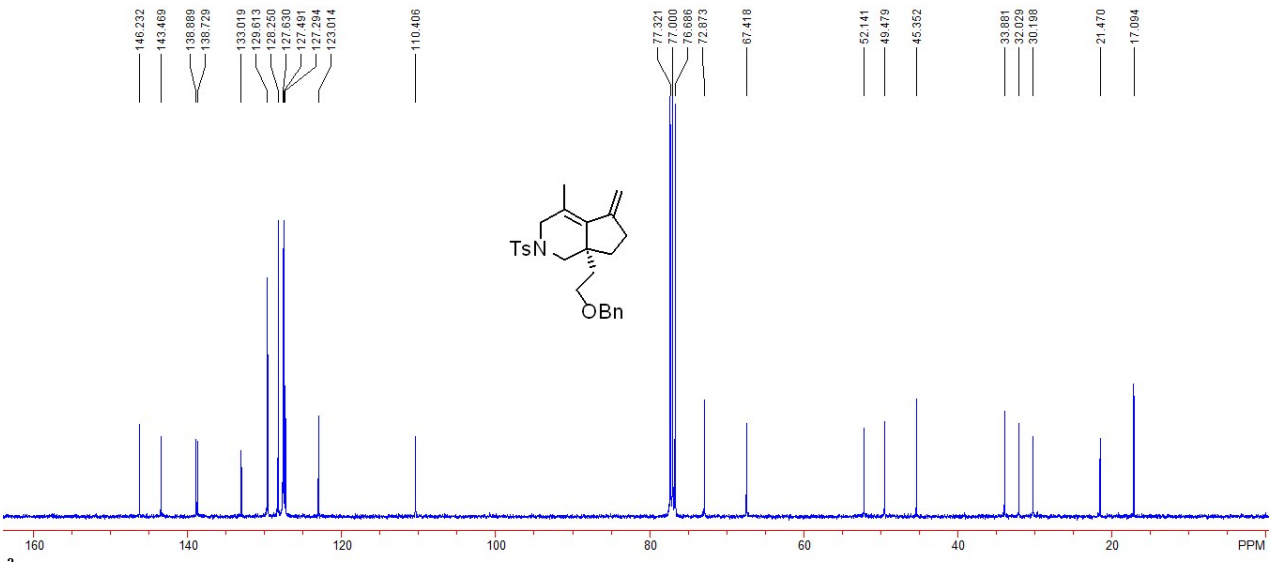
Translation: Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 50/1; Flow rate: 0.80 mL/min; t_{minor} = 12.84 min, t_{major} = 10.70 min; ee% > 99%].

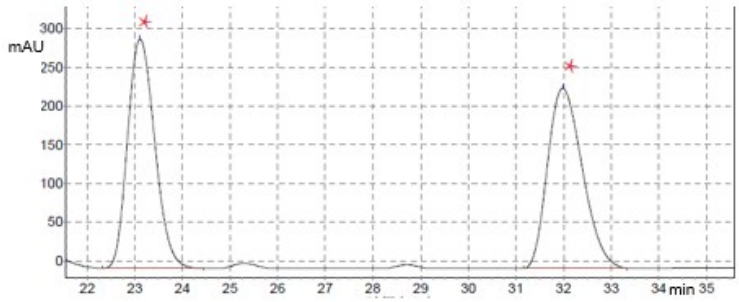


(*S*)-7a-(2-(benzyloxy)ethyl)-4-methyl-5-methylene-2-tosyl-2,3,5,6,7,7a-hexahydro-1*H*-cyclopenta[*c*]pyridine (2u)

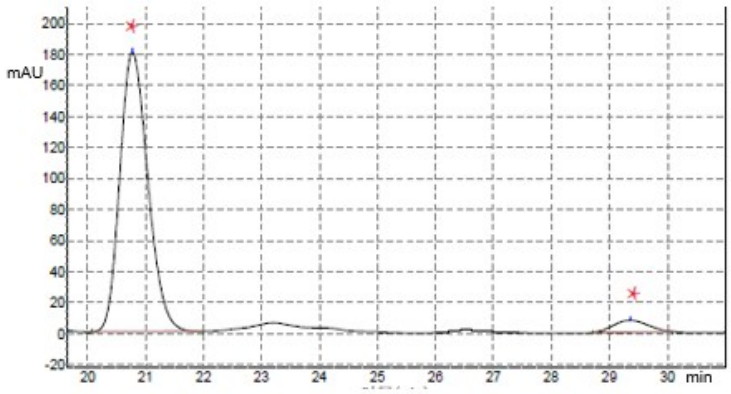
A white solid. 91% yield (40 mg). M. P. 122-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.11 (q, *J* = 10.4 Hz, 1H), 1.67-1.75 (m, 4H), 1.88-2.00 (m, 3H), 2.34-2.42 (m, 4H), 2.54-2.63 (m, 1H), 2.94 (d, *J* = 16.0 Hz, 1H), 3.56-3.62 (m, 1H), 3.67-3.73 (m, 1H), 3.95 (d, *J* = 10.8 Hz, 1H), 4.02 (d, *J* = 16.8 Hz, 1H), 4.51 (s, 2H), 5.11 (s, 2H), 7.26-7.36 (m, 7H), 7.68 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 17.1, 21.5, 30.2, 32.0, 33.9, 45.4, 49.5, 52.1, 67.4, 72.9, 110.4, 123.0, 127.3, 127.5, 127.6, 128.3, 129.6, 133.0, 138.7, 138.9, 143.5, 146.2. IR (CH_2Cl_2): ν 2923, 2852, 1712, 1594, 1451, 1334, 1158, 1090, 864, 817, 743, 706, 699, 661 cm^{-1}. HRMS (ESI) calcd. for $C_{26}H_{32}NO_3S$ $(M+H)^+$: 438.2097, Found: 438.2090. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 25/1; Flow rate: 0.80 mL/min; t_{minor} = 20.78 min, t_{major} = 29.35 min; ee% = 90.0%; $[\alpha]^{20}_D$ = +83.8 (c 1.00, CH_2Cl_2)].





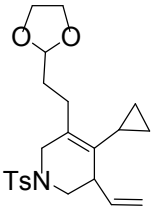


Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	23.115	296708.000	11746904.000	49.8884
2	31.982	233140.875	11799467.000	50.1116
Totals:		529848.875	23546371.000	100.0000



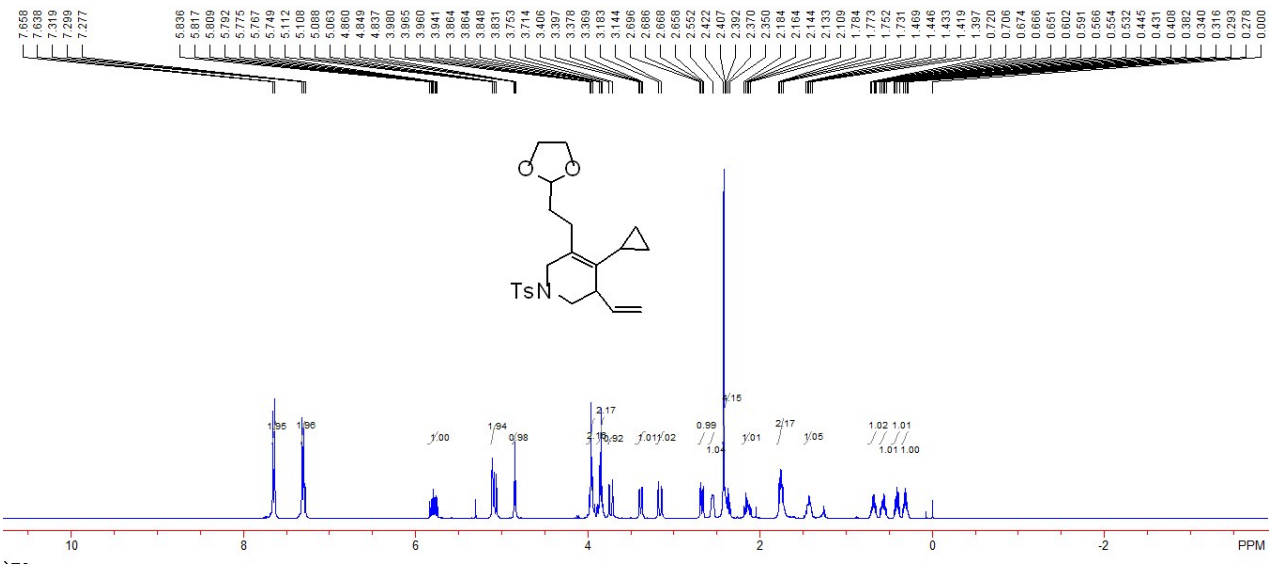
Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	20.775	180160.719	6042474.000	95.0482
2	29.352	7662.235	314796.906	4.9518
Totals:		187822.954	6357270.906	100.0000

Translation: Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 25/1; Flow rate: 0.80 mL/min; t_{minor} = 20.78 min, t_{major} = 29.35 min; ee% = 90.0%].



5-(2-(1,3-dioxolan-2-yl)ethyl)-4-cyclopropyl-1-tosyl-3-vinyl-1,2,3,6-tetrahydropyridine (6a)

A light yellow oil. 93% yield (37 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.27-0.34 (m, 1H), 0.38-0.45 (m, 1H), 0.53-0.60 (m, 1H), 0.65-0.72 (m, 1H), 1.40-1.47 (m, 1H), 1.73-1.78 (m, 2H), 2.11-2.16 (m, 1H), 2.35-2.42 (m, 4H), 2.55 (s, 1H), 2.68 (dd, J_1 = 4.0 Hz, J_1 =11.2 Hz, 1H), 3.16 (d, J = 15.6 Hz, 1H), 3.39 (dd, J_1 = 3.6 Hz, J_1 =11.2 Hz, 1H), 3.73 (d, J = 15.6 Hz, 1H), 3.83-3.86 (m, 2H), 3.94-3.98 (m, 2H), 4.85 (t, J = 4.8 Hz, 1H), 5.06-5.11 (m, 2H), 5.75-5.84 (m, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 4.7, 5.9, 11.8, 21.4, 25.1, 32.2, 40.1, 47.7, 48.3, 64.87, 64.88, 103.9, 116.6, 127.7, 129.3, 129.5, 130.9, 133.0, 138.5, 143.4. IR (CH_2Cl_2): ν 2951, 2923, 2883, 1728, 1594, 1451, 1340, 1162, 1091, 1086, 992, 957, 910, 842, 815, 788, 692 cm^{-1}. HRMS (ESI) calcd. For $C_{22}H_{30}NO_4S$ $(M+H)^+$: 404.1890. Found: 404.1882.


7.658
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7.319
7.299
7.277
5.836
5.817
5.809
5.792
5.775
5.767
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5.108
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4.837
3.980
3.965
3.960
3.941
3.864
3.864
3.848
3.831
3.753
3.714
3.406
3.397
3.378
3.369
3.183
3.144
2.696
2.686
2.668
2.658
2.552
2.422
2.407
2.392
2.370
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1.397
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0.651
0.602
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0.566
0.554
0.532
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0.431
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0.382
0.340
0.316
0.293
0.278
0.000

TsN
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1.96
1.00
1.94
0.98
2.17
2.15
0.92
1.01
1.02
0.99
1.04
3.15
1.01
2.17
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1.02
1.01
1.01
1.00
10
8
6
4
2
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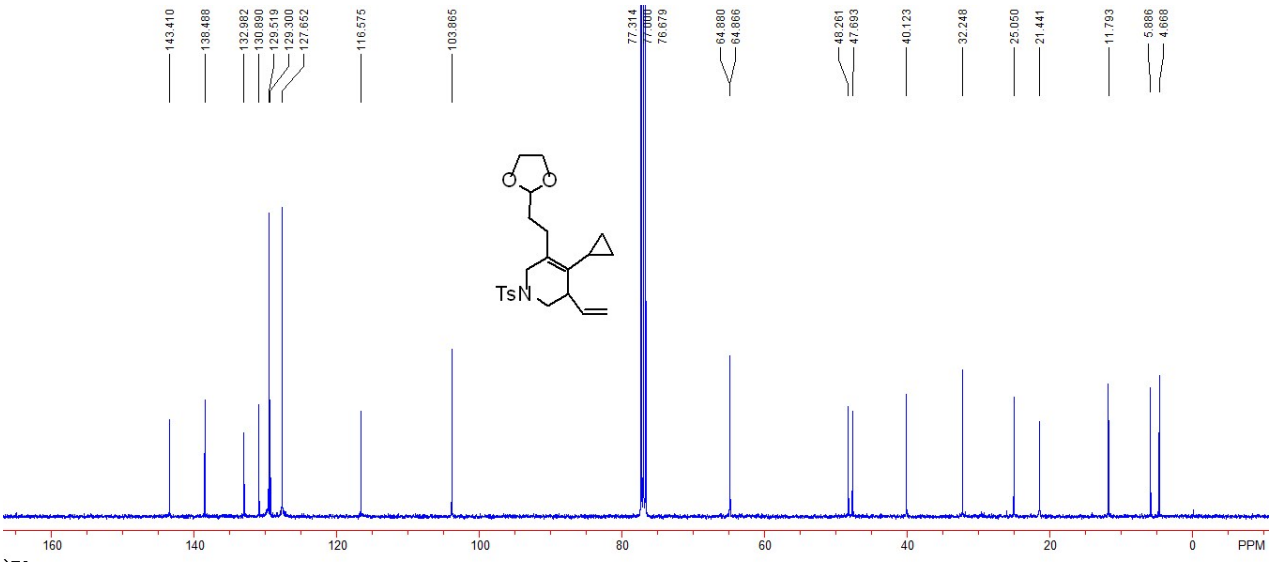
PPM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116.575
103.865
77.314
77.000
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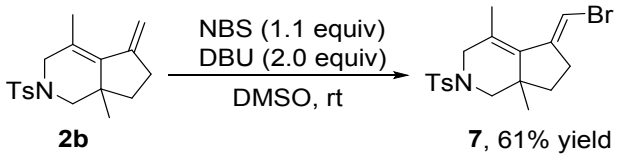
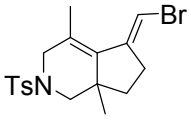
64.880
64.866
48.261
47.693
40.123
32.248
25.050
21.441
11.793
5.886
4.668
TsN
160
140
120
100
80
60
40
20
0
PPM

8. Transformations of products 2 and 3



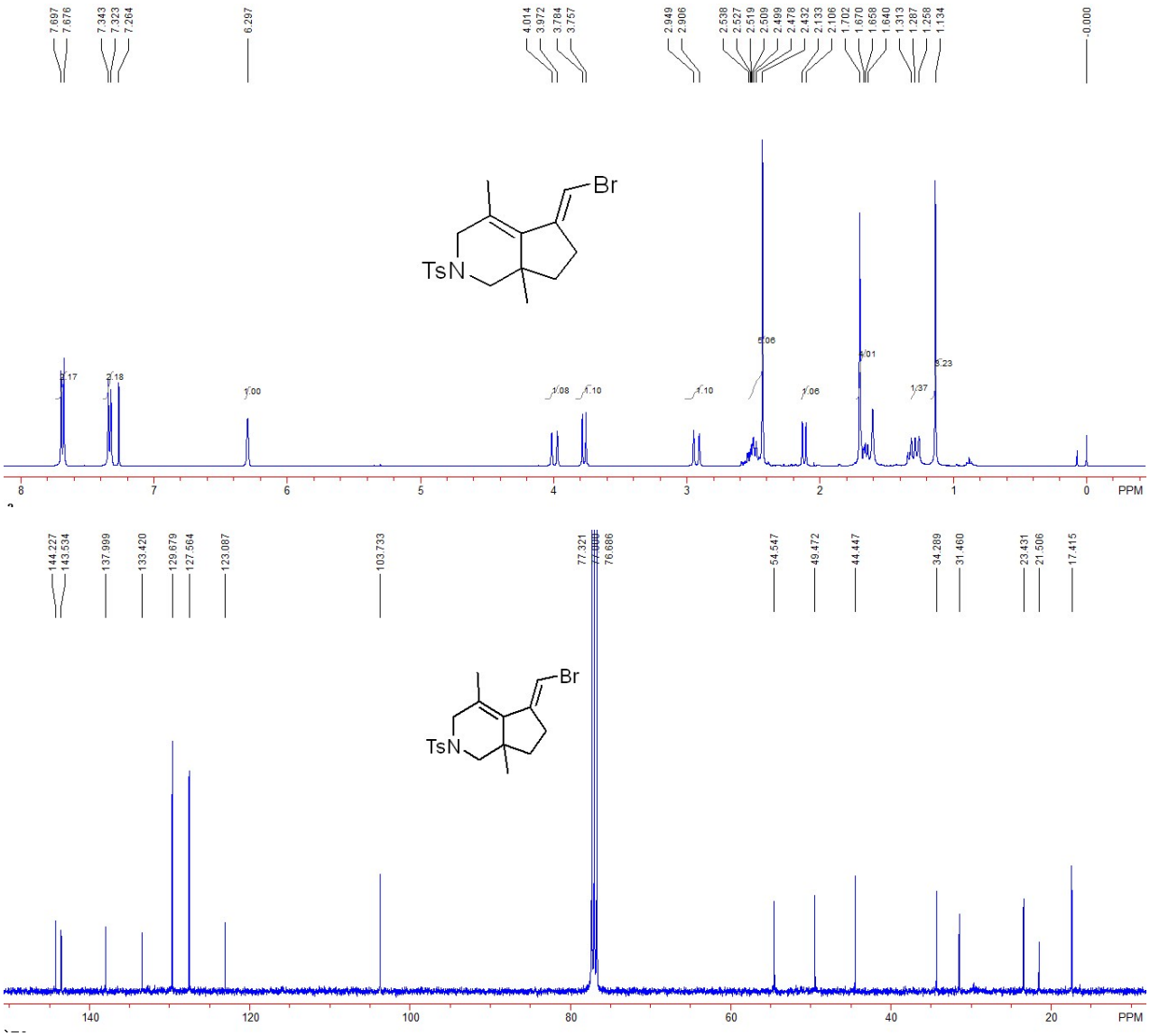
2b **7**, 61% yield

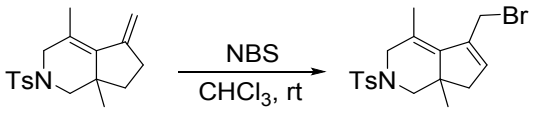
To a solution of compound **2b** (0.1 mmol, 1.0 equiv) in DMSO was added NBS (1.1 equiv), and the reaction mixture was stirred at room temperature. After 30 min, the mixture was added DBU (2.0 equiv). Then, the mixture was concentrated under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **7** (PE/EA: 30:1~20:1), yield: 61%.



(E)-5-(bromomethylene)-4,7a-dimethyl-2-tosyl-2,3,5,6,7,7a-hexahydro-1H-cyclopenta[c]pyridine (7)

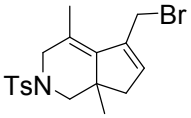
A white solid. 68% yield (27 mg). M. P. 108-111 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.13 (s, 3H), 1.29 (t, *J* = 10.8 Hz, 1H), 1.64-1.70 (m, 4H), 2.12 (d, *J* = 10.8 Hz, 1H), 2.43-2.54 (m, 5H), 2.93 (d, *J* = 17.2Hz, 1H), 3.77 (d, *J* = 10.8 Hz, 1H), 3.99 (d, *J* = 10.8 Hz, 1H), 6.30 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 17.4, 21.5, 23.4, 31.5, 34.3, 44.4, 49.5, 54.5, 103.7, 123.1, 127.6, 129.7, 133.4, 138.0, 143.5, 144.2. IR (CH_2Cl_2): ν 2958, 1977, 1662, 1628, 1474, 1371, 1346, 1168, 1080, 713, 685, 660 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{23}BrNO_2S$ $(M+H)^+$: 396.0624, Found: 396.0627.





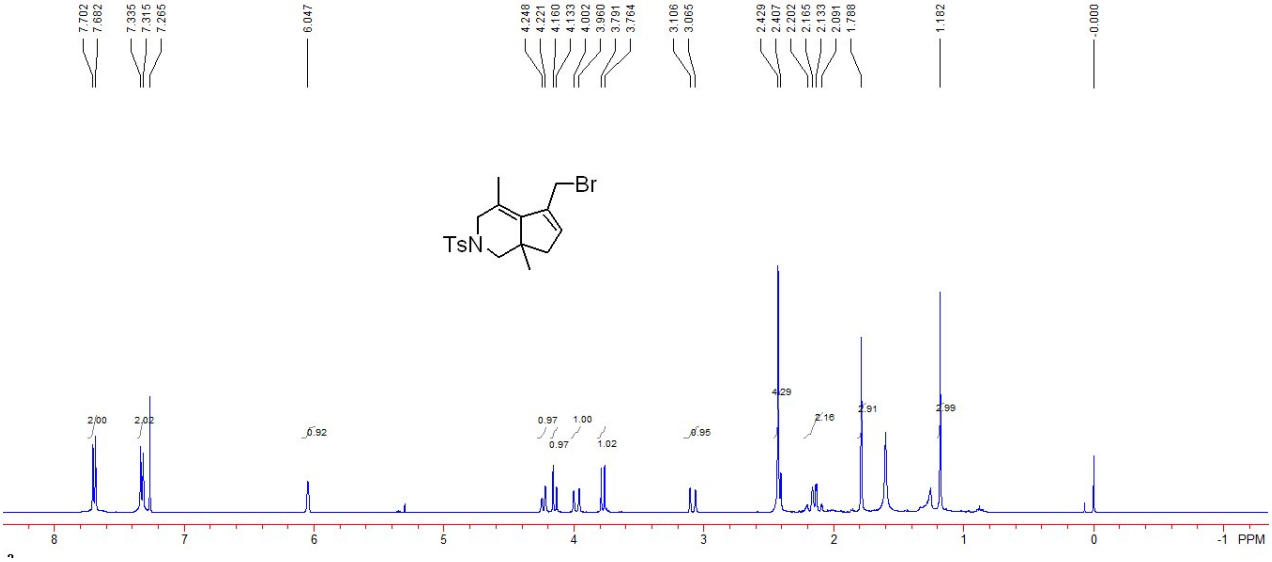
2b **8**, 53% yield

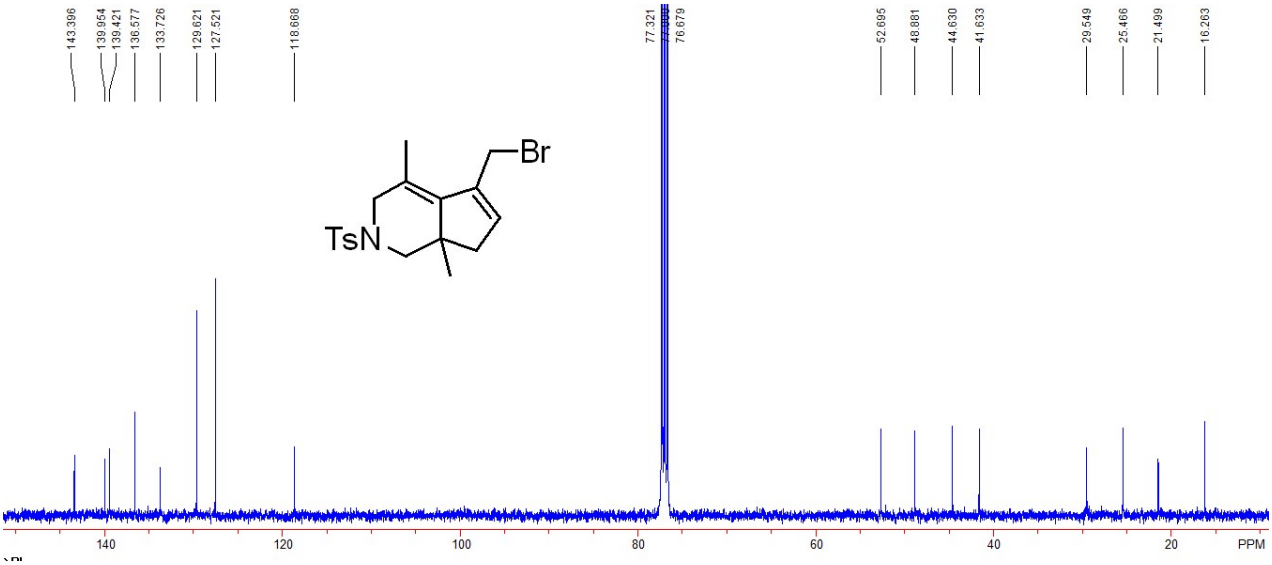
To a solution of **2b** (0.1 mmol, 1.0 equiv) in $CHCl_3$ was added NBS (1.1 equiv), and the reaction mixture was stirred at room temperature overnight. The mixture was concentrated under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **8** (PE/EA: 30:1~20:1), yield: 53%.[2]

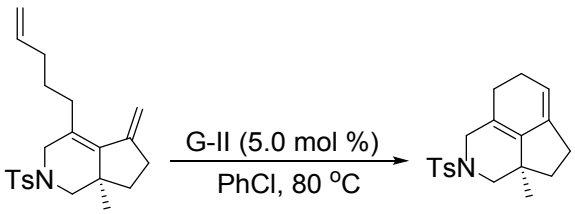


5-(bromomethyl)-4,7a-dimethyl-2-tosyl-2,3,7,7a-tetrahydro-1H-cyclopenta[c]pyridine (8)

A white solid. 61% yield (25 mg). M. P. 86-89 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.18 (s, 3H), 1,79 (s, 3H), 2.09-2.20 (m, 2H), 2.41-2.43 (m, 4H), 3.09 (d, *J* = 16.4 Hz, 1H), 3.78 (d, *J* = 10.8 Hz, 1H), 3.98 (d, *J* = 16.8 Hz, 1H), 4.15 (d, *J* = 10.8 Hz, 1H), 4.23 (d, *J* = 10.8 Hz, 1H), 6.05 (s, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 16.3, 21.5, 25.5, 29.5, 41.6, 44.6, 48.9, 52.7, 118.7, 127.5, 129.6, 133.7, 136.6, 139.4, 140.0, 143.4. IR (CH_2Cl_2): ν 2972, 1463, 1370, 1343, 1263, 1161, 1088, 1046, 1009, 976, 905, 851, 818, 804, 781, 753, 711, 664 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{23}BrNO_2S$ $(M+H)^+$: 396.0621, Found: 396.0624.

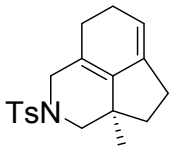






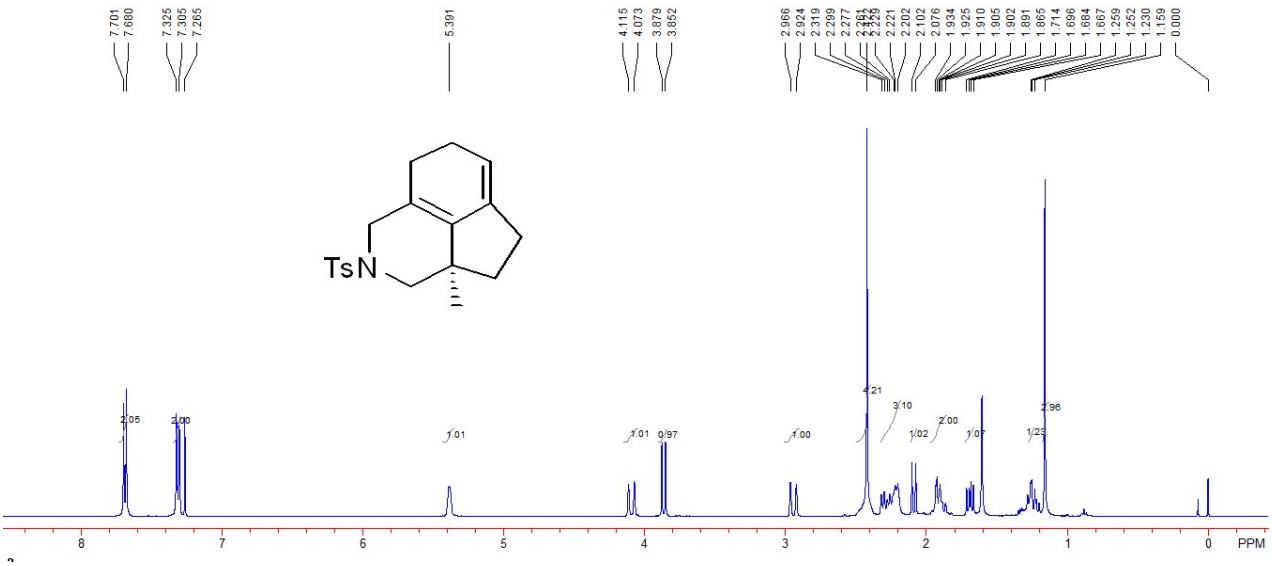
2t, > 99% ee **9**, 72% yield, > 99% ee

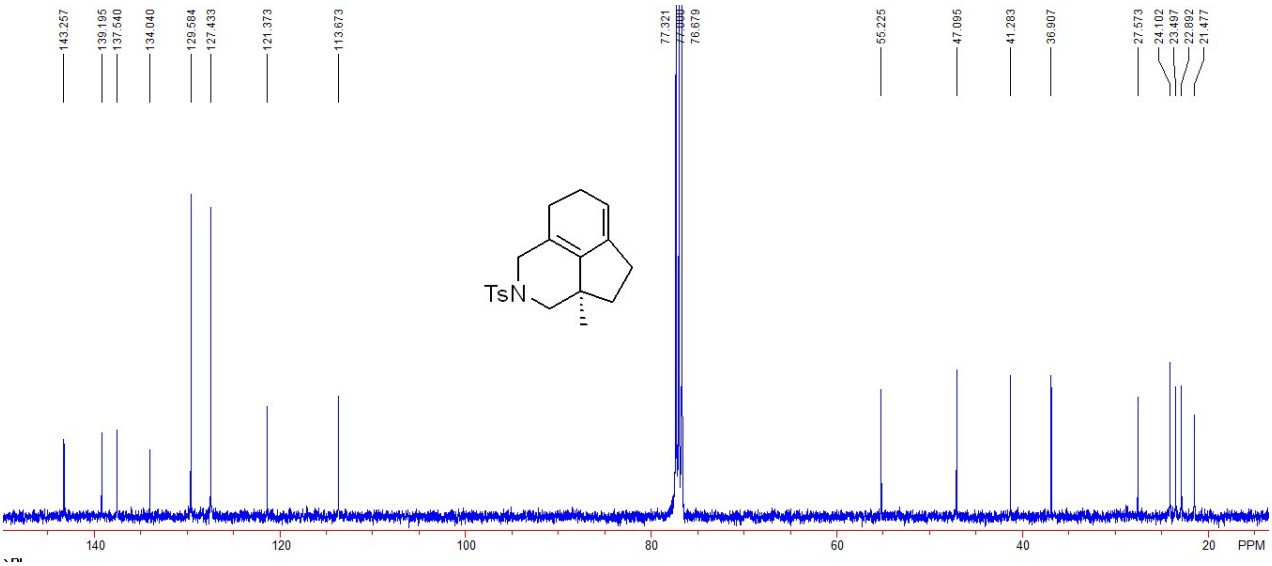
Under argon atmosphere, compound **2t** (0.1 mmol, 1.0 equiv), Grubbs II (5.0 mol %) and PhCl (2 mL) were added and then the mixture was stirred and heated at 80 °C for 12 h. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **9**.

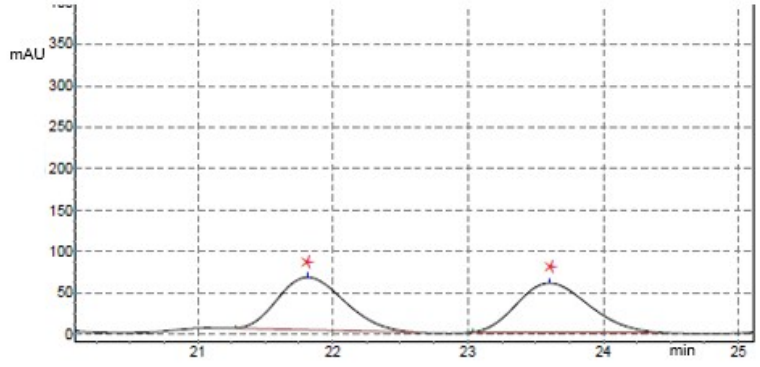


(R)-3a-methyl-2-tosyl-1,2,3,3a,4,5,7,8-octahydrocyclopenta[*de*]isoquinoline (9)

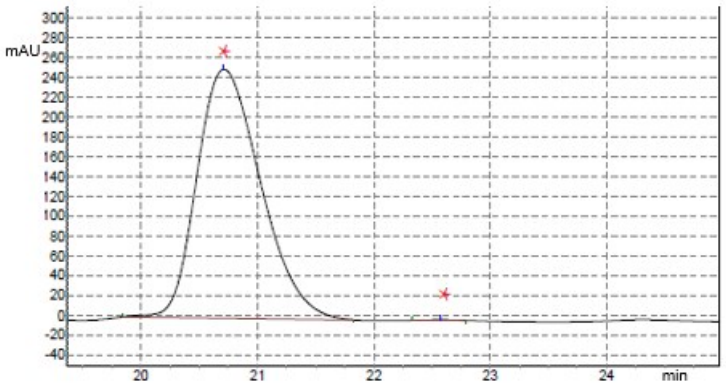
A white solid. 72% yield (26 mg). M. P. 107-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.16 (s, 3H), 1.23-1.26 (m, 1H), 1.67-1.71 (m, 1H), 1.87-1.93 (m, 2H), 2.09 (d, *J* = 10.4 Hz, 1H), 2.20-2.32 (m, 3H), 2.42 (s, 4H), 2.95 (d, *J* = 16.8 Hz, 1H), 3.87 (d, *J* = 10.8 Hz, 1H), 4.09 (d, *J* = 16.2 Hz, 1H), 5.39 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.5, 22.9, 23.5, 24.1, 27.6, 36.9, 41.3, 47.1, 55.2, 113.7, 121.4, 127.4, 129.6, 134.0, 137.5, 139.2, 143.3. IR (CH_2Cl_2): ν 3021, 2915, 1617, 1535, 1478, 1255, 1191, 1074, 1021, 983, 902, 837, 792, 667 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{24}NO_2S$ $(M+H)^+$: 330.1522, Found: 330.1521 Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 50/1; Flow rate: 0.80 mL/min; t_{minor} = 22.57 min, t_{major} = 20.71 min; ee% > 99%; $[\alpha]^{20}_D$ = +84.9 (c 1.00, CH_2Cl_2)].





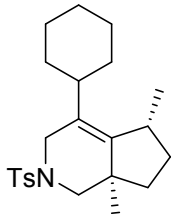


Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	21.813	63435.453	2177304.000	50.0201
2	23.603	59254.078	2175551.500	49.9799
Totals:		122689.531	4352855.500	100.0000



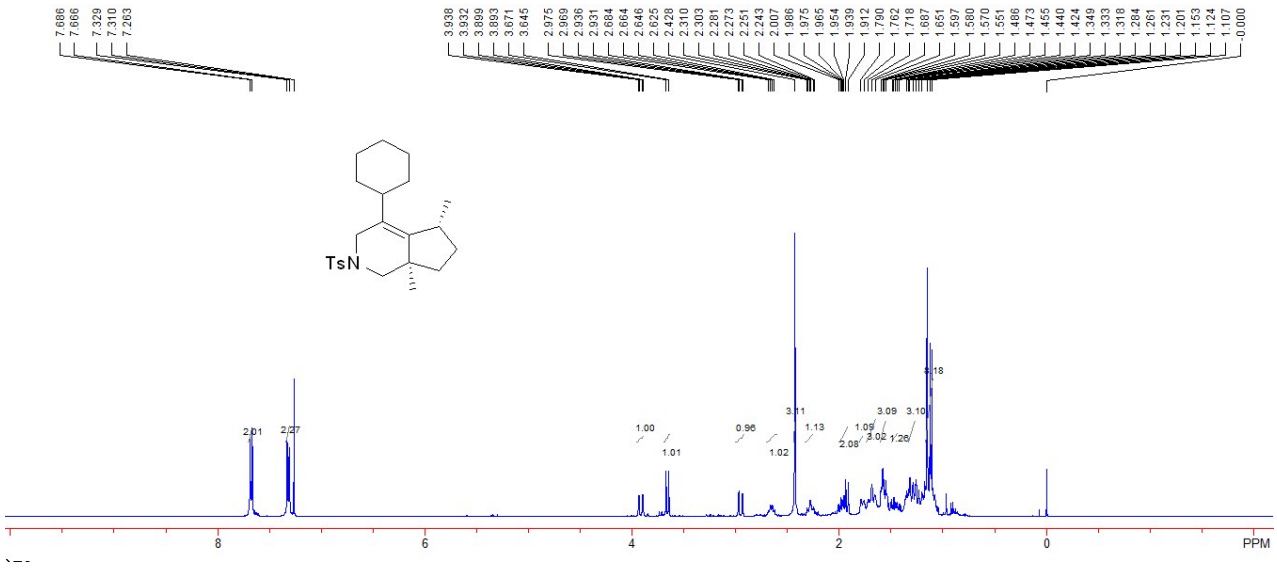
Peak	RetTime (min)	Height (mAU)	Area (mAU*S)	Area %
1	20.710	251271.359	9558852.000	99.9072
2	22.568	506.696	8874.199	0.0928
Totals:		251778.055	9567726.199	100.0000

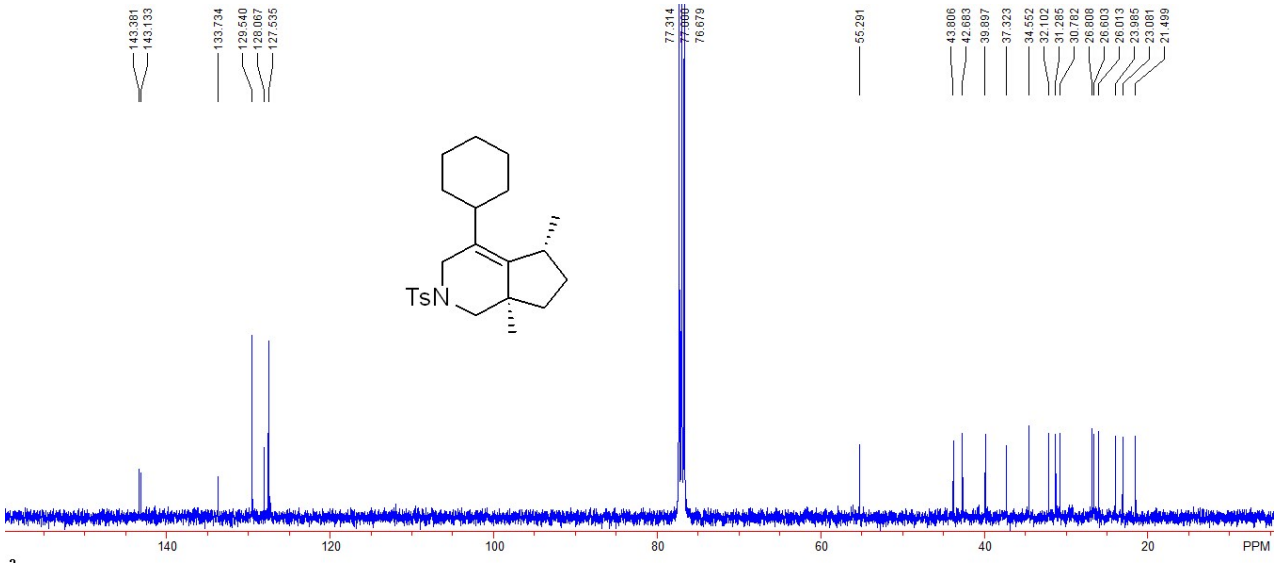
Translation: Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 50/1; Flow rate: 0.80 mL/min; t_{minor} = 22.57 min, t_{major} = 20.71 min; ee% > 99%].

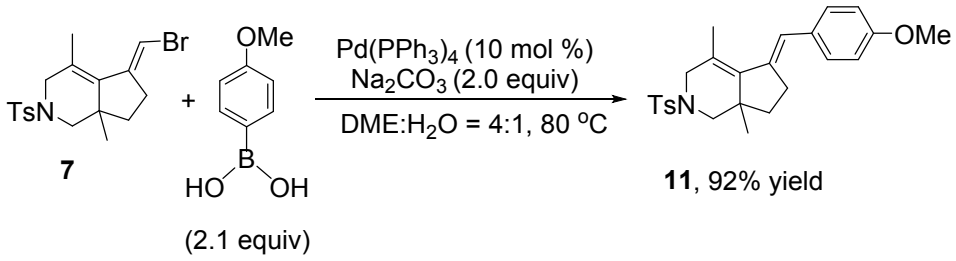


4-cyclohexyl-5,7a-dimethyl-2-tosyl-2,3,5,6,7,7a-hexahydro-1H-cyclopenta[c]pyridine (10)

A white solid. 83% yield (32 mg). M. P. 99-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) □ 1.11-1.15 (m, 8H), 1.20-1.35 (m, 3H), 1.42-1.49 (m, 1H), 1.55-1.60 (m, 3H), 1.65-1.72 (m, 3H), 1.76-1.79 (m, 1H), 1.91-2.00 (m, 2H), 2.24-2.31 (m, 1H), 2.43 (s, 3H), 2.63-2.68 (m, 1H), 2.95 (dd, J_1 = 2.4 Hz, J_2 = 15.6 Hz, 1H), 3.66 (d, J = 10.4 Hz, 1H), 3.92 (dd, J_1 = 2.4 Hz, J_2 = 15.6 Hz, 1H), 7.32 (d, J = 7.6 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) 21.5, 23.1, 24.0, 26.0, 26.6, 26.8, 30.8, 31.3, 32.1, 34.6, 37.3, 39.9, 42.7, 43.8, 55.3, 127.5, 128.1, 129.5, 133.7, 143.1, 143.4. IR (CH_2Cl_2): ν 2924, 2851, 1449, 1350, 1337, 1305, 1268, 1117, 1092, 970, 945, 831, 788, 708, 673, 654 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{34}NO_2S$ $(M+H)^+$: 388.2305, Found: 388.2302.

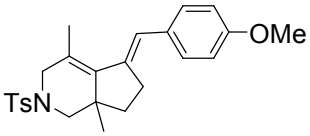






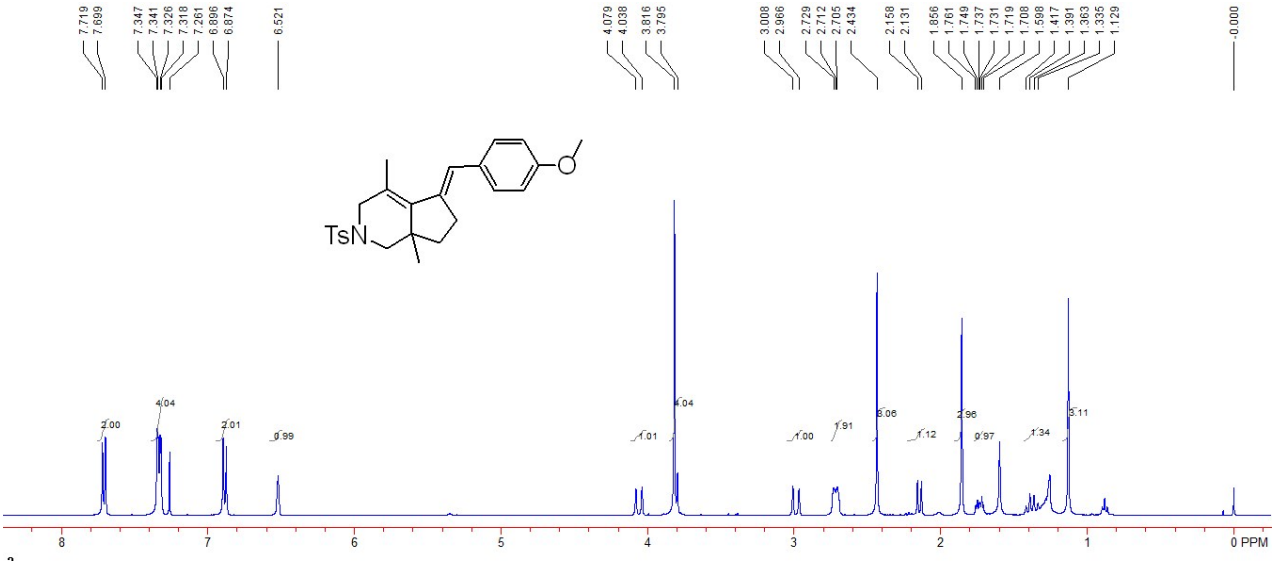
Compound **7** (1.0 equiv) and $Pd(PPh_3)_4$ (10 mol %) were added to a Schlenk tube. The tube was evacuated and refilled with argon for three times, and then DME (1,2-dimethoxyethane, 2.0 mL) was added. The reaction mixture was stirred at room temperature for 20 minutes. Sodium carbonate (2.0 equiv), water (0.5 mL), and the *para*-methoxyphenylboronic acid (2.1 equiv) were added, and the reaction mixture was heated under reflux for 18 h. The reaction mixture was dried

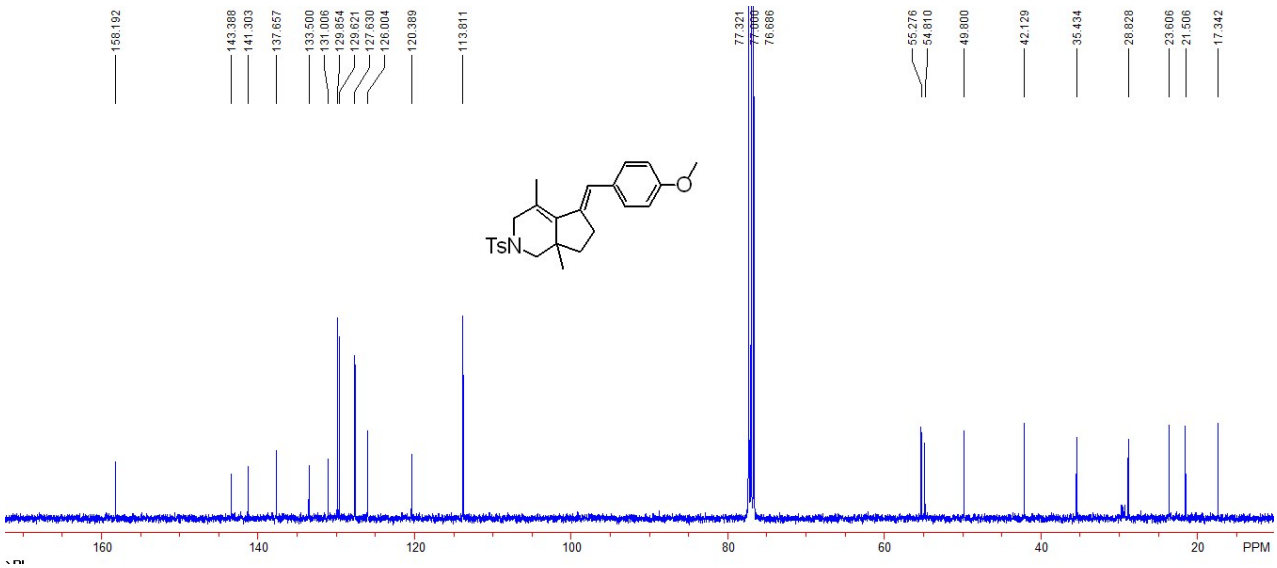
over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **11** in 92% yield using PE/EA = 15:1 as eluent.[3]

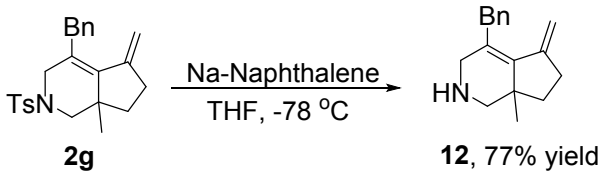


(E)-5-(4-methoxybenzylidene)-4,7a-dimethyl-2-tosyl-2,3,5,6,7,7a-hexahydro-1H-cyclopenta[c]pyridine (11)

A white solid. 92% yield (39 mg). M. P. 128-131 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.13 (s, 3H), 1.38 (q, *J* = 11.2 Hz, 1H), 1.71-1.76 (m, 1H), 1.86 (s, 3H), 2.14 (d, *J* = 10.8 Hz, 1H), 2.43 (s, 3H), 2.71-2.73 (m, 2H), 2.99 (d, *J* = 16.8 Hz, 1H), 3.80-3.82 (m, 4H), 4.06 (d, *J* = 16.4 Hz, 1H), 6.52 (s, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 7.32-7.35 (m, 4H), 7.71 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 17.3, 21.5, 23.6, 28.8, 35.4, 42.1, 49.8, 54.8, 55.3, 113.8, 120.4, 126.0, 127.6, 129.6, 129.9, 131.0, 133.5, 137.7, 141.3, 143.4, 158.2. IR (CH_2Cl_2): ν 2958, 2943, 2872, 2332, 1675, 1492, 1443, 1320, 1173, 1071, 1019, 949, 832, 811, 763, 711, 667 cm^{-1}. HRMS (ESI) calcd. for $C_{25}H_{30}NO_3S$ $(M+H)^+$: 424.1941, Found: 424.1936.

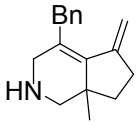






2g **12**, 77% yield

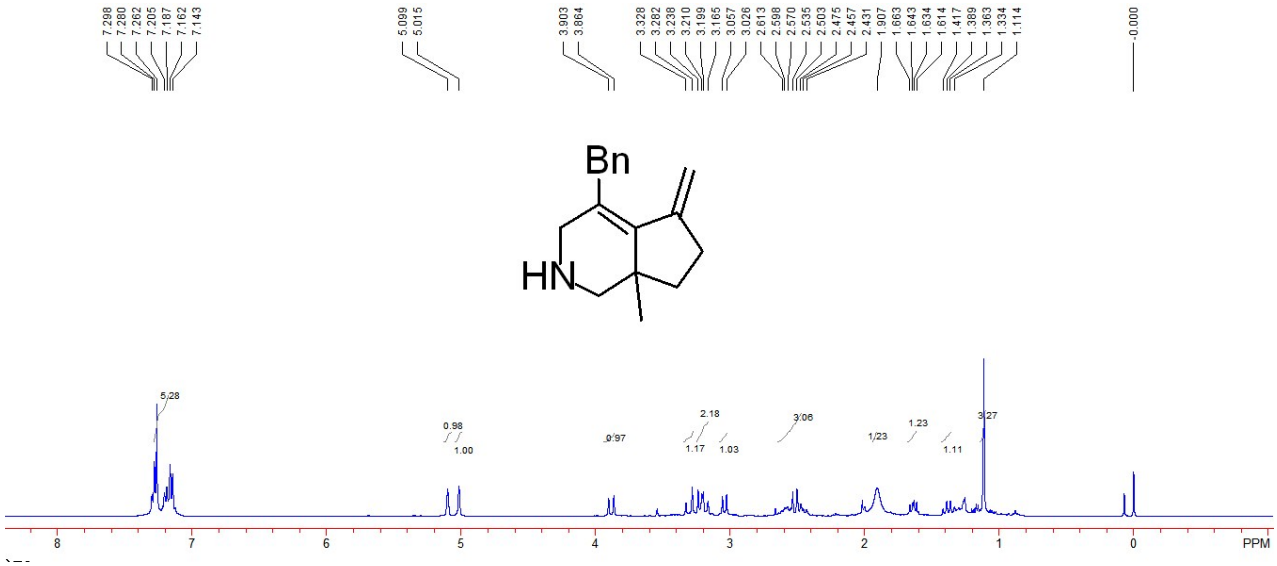
A solution 1 M of sodium naphthalide in THF was prepared as follows: to a stirred solution of naphthalene (5 g, 39 mmol) in 39 mL of THF, sodium metal (1.1 g, 47 mmol) was added under nitrogen atmosphere, and the solution was stirred for 1 h. A solution of **2g** (39 mg, 0.1 mmol) in anhydrous THF (2.0 mL) was cooled to -78 °C under nitrogen atmosphere and 1.0 mL (1.0 mmol) of 1 M sodium naphthalenide in THF was added dropwise. The mixture was stirred for 40 min at this temperature and then 15 mL of saturated NH_4Cl aqueous solution was added. The solution was left to warm up to room temperature and the aqueous layer was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4. Then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **12** in 77% yield using EA/Et_3N = 25:1 as eluent.[4]

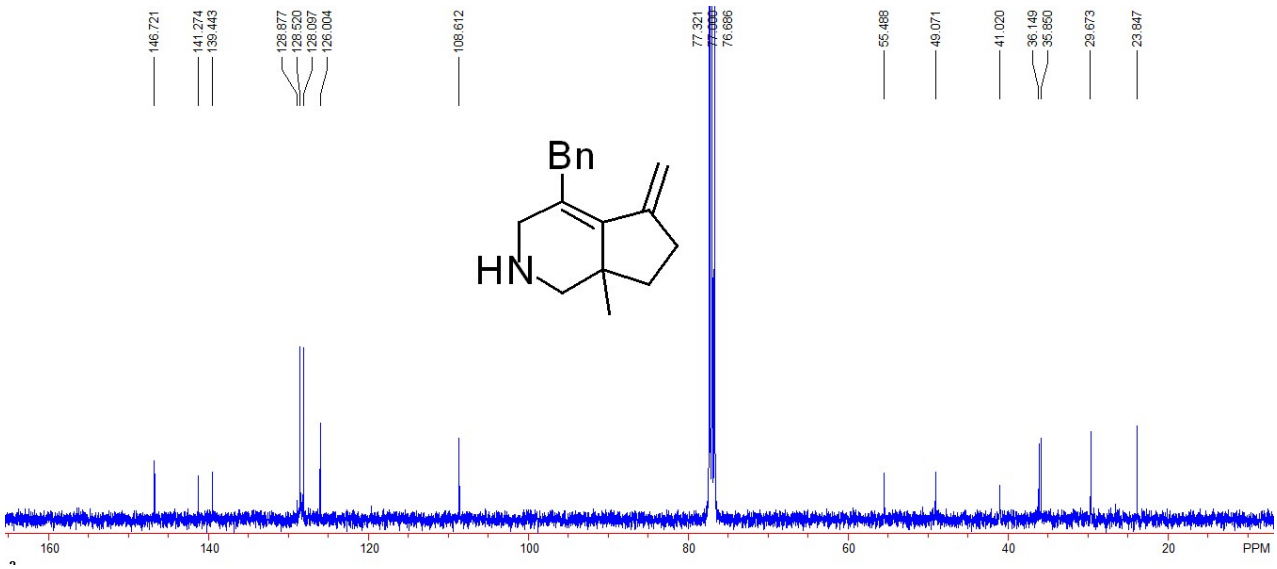


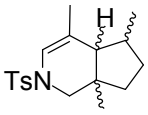
4-benzyl-7a-methyl-5-methylene-2,3,5,6,7,7a-hexahydro-1H-cyclopenta[c]pyridine (12)

A light yellow oil. 76% yield (18 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.11 (s, 3H), 1.33-

1.42 (m, 1H), 1.61-1.66 (m, 1H), 1.91 (brs, 1H), 2.43-2.61 (m, 3H), 3.04 (d, J = 12.4 Hz, 1H), 3.17-3.24 (m, 2H), 3.31 (d, J = 18.4 Hz, 1H), 3.88 (d, J = 15.6 Hz, 1H), 5.02 (s, 1H), 5.10 (s, 1H), 7.14-7.30 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 23.8, 29.7, 35.9, 36.1, 41.0, 49.0, 55.5, 108.6, 126.0, 128.1, 128.5, 128.9, 139.4, 141.3, 146.7. IR (CH_2Cl_2): ν 3310, 3060, 3025, 2923, 2857, 1600, 1493, 1370, 1118, 1029, 911, 799 cm^{-1}. Mass (EI) $(M)^+$: 239.2, HRMS (EI) calcd calcd. for $C_{17}H_{21}N$ $(M)^+$: 239.1674, Found: 239.1672.

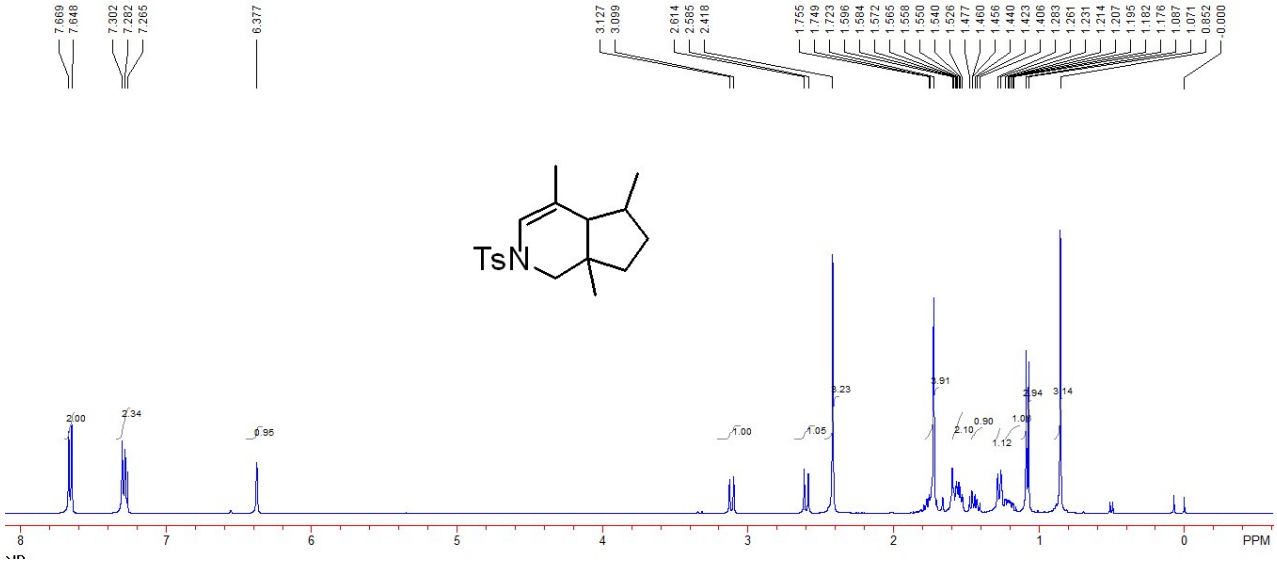


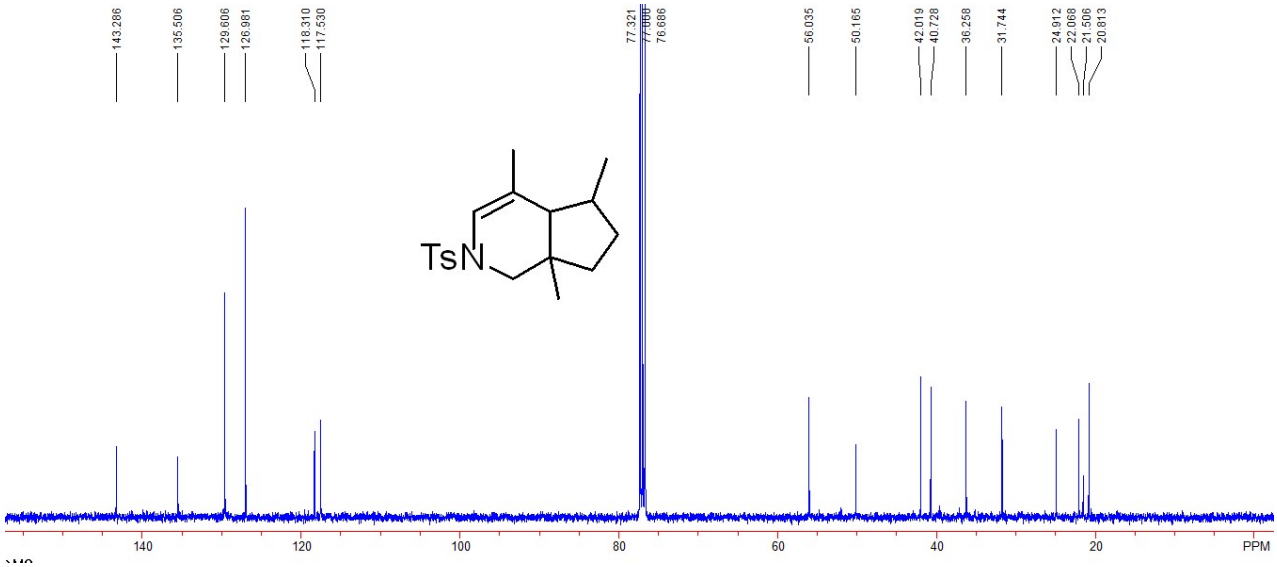




4,5,7a-trimethyl-2-tosyl-2,4a,5,6,7,7a-hexahydro-1H-cyclopenta[c]pyridine (13)

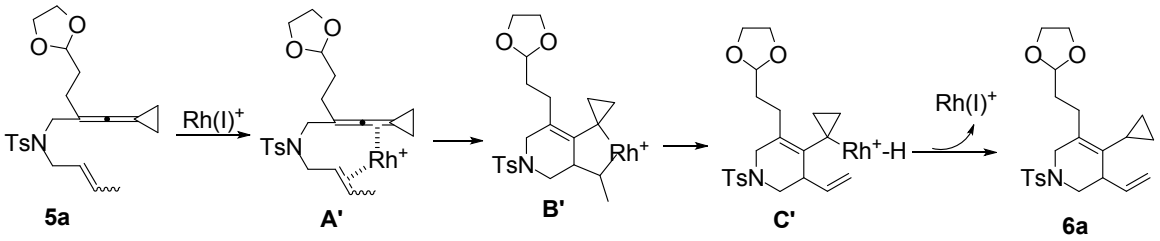
A light yellow oil. 78% yield (25 mg). M. P. 93-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.85 (s, 3H), 1.08 (d, *J* = 6.4 Hz, 3H), 1.18-1.23 (m, 1H), 1.26-1.28 (m, 1H), 1.18-1.23 (m, 1H), 1.26-1.28 (m, 1H), 1.41-1.48 (m, 1H), 1.53-1.60 (m, 2H), 1.72-1.76 (m, 4H), 2.42 (s, 3H), 2.60 (d, *J* = 11.6 Hz, 1H), 3.11 (d, *J* = 11.2 Hz, 1H), 6.38 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 20.8, 21.5, 22.1, 24.9, 31.7, 36.3, 40.7, 42.0, 50.2, 56.0, 117.5, 118.3, 127.0, 129.6, 135.5, 143.3. IR (CH_2Cl_2): ν 2973, 2830, 1371, 1336, 1108, 1075, 813, 692, 663 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{26}NO_2S$ $(M+H)^+$: 320.1677, Found: 320.1679.





9. Plausible mechanism for the formation of product 6a

A plausible reaction mechanism for the formation of product **6a** has been shown in Scheme S1 using **5a** as the model substrate. At first, the coordination of $Rh(I)^+$ with alkene and allene moieties in VDCP leads to the formation of intermediate **A'**, which then undergoes a cyclometallation to give the corresponding rhodacyclic intermediate **B'**. The β-hydride elimination from intermediate **B'** affords the rhodium hydride species **C** and the subsequent reductive elimination from species **C** gives the desired product **6a**.



Scheme S1. A plausible mechanism for the formation of product **6a**

10. **X-ray crystallographic information of products 2a'**, **3a**, **4a**, **2d**, **7**, **9** and **10**.

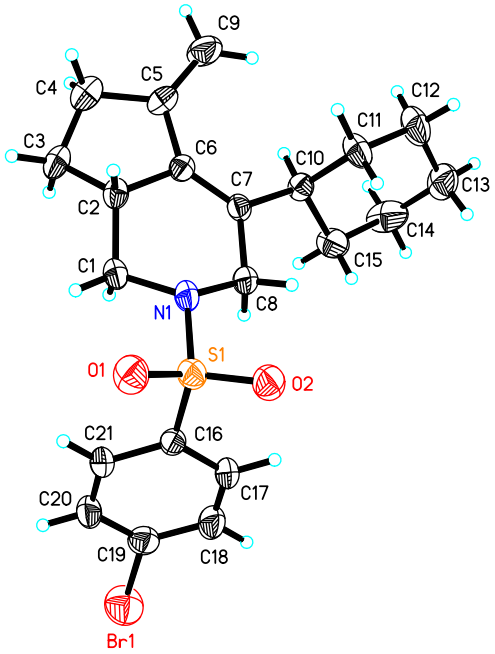


Figure S1. The crystal data of **2a'** have been deposited in CCDC with number 1540623. Empirical Formula: $C_{21}H_{26}BrNO_2S$; Formula Weight: 436.40; Crystal Color, Habit: colorless; Crystal Dimensions: 0.200 x 0.170 x 0.130 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 10.888(3) Å, alpha = 90 deg. b = 8.651(2) Å, beta = 97.500(5) deg. c = 10.910(3) Å, gamma = 90 deg.; V = 1018.9(4) $Å^3$; Space group: P 21; Z = 2; D_{calc} = 1.422 g/cm^3; F_{000} = 452; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0461, 0.1074.

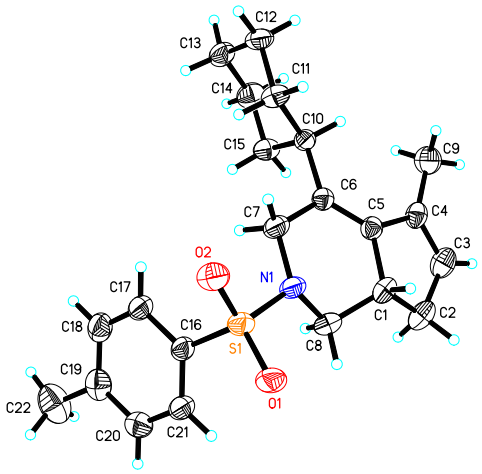


Figure S2. The crystal data of **3a** have been deposited in CCDC with number 1549540. Empirical Formula: $C_{22}H_{29}NO_2S$; Formula Weight: 371.52; Crystal Color, Habit: colorless; Crystal Dimensions: 0.200 x 0.170 x 0.130 mm^3; Crystal System: Orthorhombic; Lattice Parameters: a = 8.8700(16) Å, alpha = 90 deg. b = 10.6671(18) Å, beta = 90 deg. c = 21.508(4) Å, gamma = 90 deg.; V = 2035.1(6) $Å^3$; Space group: P 21 21 21; Z = 4; D_{calc} = 1.213 g/cm^3; F_{000} = 800; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0496, 0.1022.

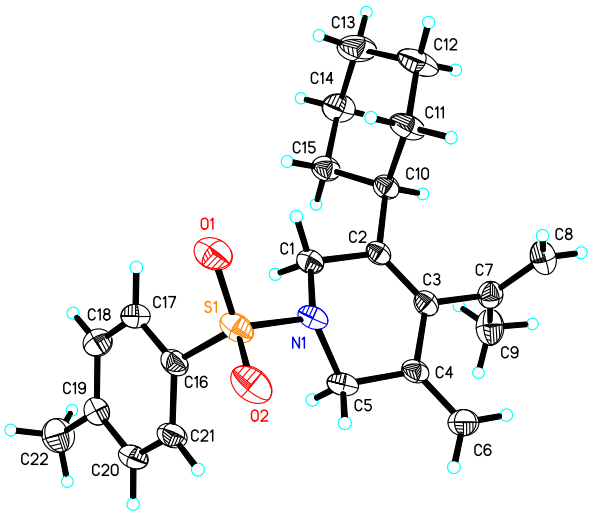


Figure S3. The crystal data of **4a** have been deposited in CCDC with number 1532042. Empirical Formula: $C_{30}H_{29}NO_3S$; Formula Weight: 483.60; Crystal Color, Habit: colorless; Crystal Dimensions: 0.220 x 0.160 x 0.110 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 9.8296(13)Å, b = 13.4413(17)Å, c = 22.608(3)Å, α = 90°, β = 94.433(3)°, □ = 90°, V = 2978.1(7)$Å^3$; Space group: P 21/n; Z = 4; D_{calc} = 1.079 g/cm^3; F_{000} = 1024; Final R indices [I>2sigma(I)] R1 = 0.0682, wR2 = 0.1582.

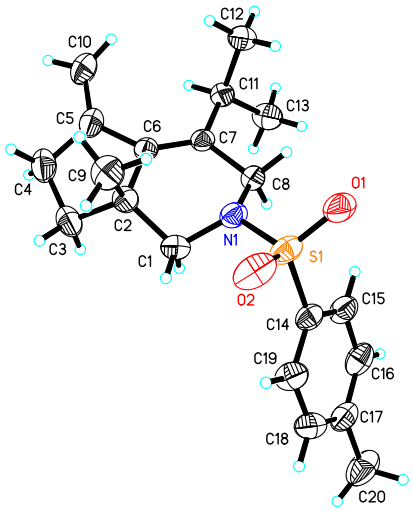


Figure S4. The crystal data of **2d** have been deposited in CCDC with number 1823053. Empirical Formula: $C_{20}H_{27}NO_2S$; Formula Weight: 345.48; Crystal Color, Habit: colorless; Crystal Dimensions: 0.200 x 0.170 x 0.110 mm^3; Crystal System: Orthorhombic; Lattice Parameters: a = 5.8832(2) Å, alpha = 90 deg. b = 8.7875(2) Å, beta = 90 deg. c = 37.5443(11) Å, gamma = 90 deg.; V = 1940.99(10) $Å^3$; Space group: P 21 21 21; Z = 4; D_{calc} = 1.182 g/cm^3; F_{000} = 744; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0415, 0.1086.

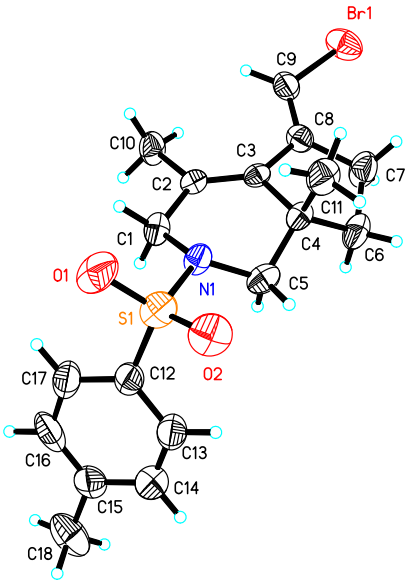


Figure S5.The crystal data of **7** have been deposited in CCDC with number 1842625. Empirical Formula: $C_{18}H_{22}BrNO_2S$; Formula Weight: 396.33; Crystal Color, Habit: colorless; Crystal Dimensions: 0.150 x 0.100 x 0.030 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 12.551(3) Å, alpha = 90 deg. b = 8.7875(2) Å, beta = 113.904(5) deg. c = 14.276(3) Å, gamma = 90 deg.; V = 1804.0(7) $Å^3$; Space group: P 21/c; Z = 4; D_{calc} = 1.459 g/cm^3; F_{000} = 816; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0841, 0.1987.

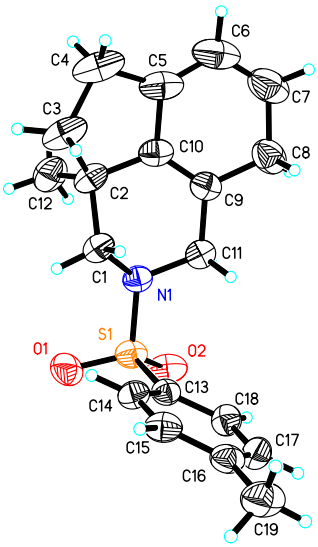


Figure S6. The crystal data of **9** have been deposited in CCDC with number 1845295. Empirical Formula: $C_{19}H_{23}NO_2S$; Formula Weight: 329.44; Crystal Color, Habit: colorless; Crystal Dimensions: 0.20 x 0.17 x 0.10 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 35.164(3) Å, alpha = 90 deg. b = 8.6573(6) Å, beta = 94.241(2) deg. c = 11.5114(9) Å, gamma = 90 deg.; V = 3494.7(5) $Å^3$; Space group: C 2/c; Z = 8; D_{calc} = 1.252 g/cm^3; F_{000} = 1408; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0583, 0.1308.

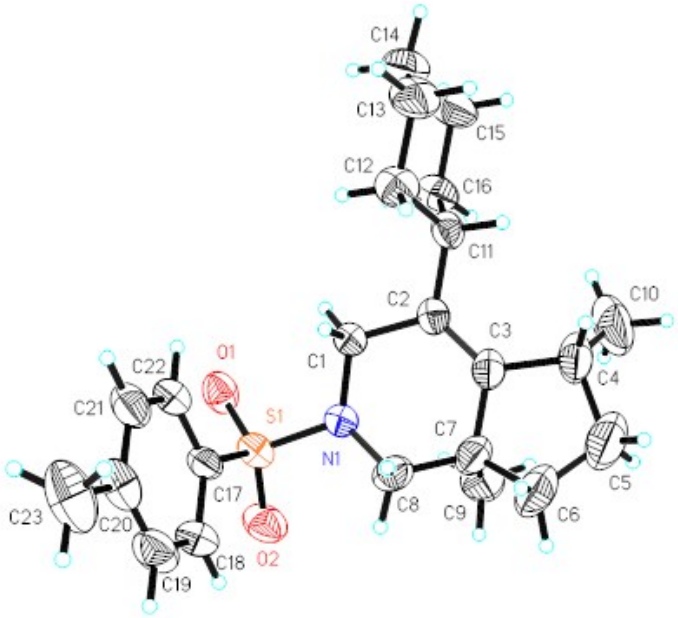
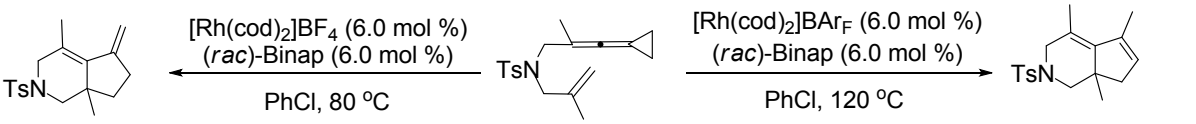


Figure S7. The crystal data of **10** have been deposited in CCDC with number 1875219. Empirical Formula: $C_{23}H_{33}NO_2S$; Formula Weight: 387.56; Crystal Color, Habit: colorless; Crystal Dimensions: 0.200 x 0.180 x 0.070 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 19.505(3) Å, alpha = 90 deg. b = 8.6857(13) Å, beta = 92.309(4) deg. c = 13.1687(16) Å, gamma = 90 deg.; V = 2229.2(5) $Å^3$; Space group: P 21/c; Z = 4; D_{calc} = 1.155 g/cm^3; F_{000} = 840; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0661, 0.1559.

11. Gram-scale synthesis



2b, 1.027 g, 81% yield **1b**, (4.0 mmol) **3b**, 1.115 g, 88% yield

Scheme S2. Gram-scale synthesis of products **2b** and **3b** under the corresponding optimal conditions.

13. **References**

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