Supporting Information

Copper-Catalyzed (4+3)-Cycloaddition of 4-Indolylcarbinols with Aziridines: Stereoselective Synthesis of Azepinoindoles

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General Information. 1*H*-Indole-4-carbaldehyde, styrenes, $Cu(CH_3CN)_4BF_4$, $LiAlH_4$, $NaCNBH_3$ and oxone were purchased from Aldrich and used as received. Chloramine-T hydrate was purchased from Merck, and used as received. The solvents were dried prior to use according to the standard procedure. SRL silica gel G/GF 254 plates were used for analytical TLC and SRL silica gel (100-200 mesh) was used for column chromatography. NMR (^1H, ^{13}C and ^{19}F) spectra were recorded with Bruker Avance III 600, 500 and 400 MHz spectrometers using $CDCl_3$ as solvent and Me_4Si as an internal standard. Chemical shifts (δ) and spin-spin coupling constant (*J*) are reported in ppm and in Hz, respectively, and other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dd = doublet of doublets. Melting points were determined using a Büchi B-540 apparatus and are uncorrected. FT-IR spectra were collected on Perkin Elmer IR spectrometer. Q-Tof ESI-MS instrument was used for recording mass spectra. Single crystal X-ray data of **3aa** and **3pa-major** were collected on a Bruker SMART APEX equipped with a CCD area detector using Mo/Kα radiation and the structure was solved by direct method using *SHELXL-2018/3* (Göttingen, Germany).

Sample Preparation for Crystal Growth. The compound **3aa** and **3pa-major** were dissolved in minimum volume of acetonitrile and kept at room temperature for slow evaporation (3 days). Block shaped crystal were formed in either case which was further subjected to X-ray diffraction analysis.

Crystal Structure and Data of 3aa

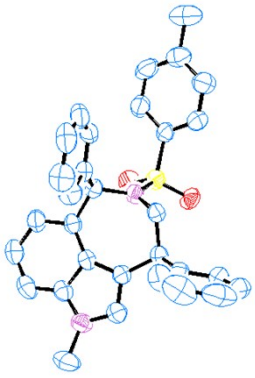


Figure S1. ORTEP diagram of 6-Methyl-1,4-diphenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole **3aa** with 50% ellipsoid (CCDC 2368687). H-Omitted for clarity.

Identification code	**3aa**
Empirical formula	'C31H28N2O2S'
Formula weight	492.61
Crystal habit, colour	block/Colorless
Temperature, *T*/K	294 K
Wavelength, λ/Å	0.71073
Crystal system	'monoclinic'
Space group	'C 2/c'
Unit cell dimensions	a = 28.290(4) Å b = 9.2132(14) Å c = 20.312(3) Å α = 90 β = 103.531(4) γ = 90
Volume, *V*/Å^3	5147.1(14)
Z	8
Calculated density, Mg·m^{-3}	1.271
Absorption coefficient, μ/mm^{-1}	0.157
F(000)	2080
θ range for data collection	2.24 to 22.28°
Limiting indices	-33 ≤ h ≤ 33, –10 ≤ k ≤ 10, –24 ≤ l ≤ 24
Reflection collected / unique	4536/2950
Completeness to θ	100%
Absorption correction	None
Max. and min. transmission	0.969 and 0.962
Refinement method	'SHELXL-2018/3 (Sheldrick, 2018)'
Data / restraints / parameters	4536/0/327
Goodness–of–fit on F^2	1.131
Final *R* indices [*I*>2sigma(*I*)]	R1 = 0.0570, wR2 = 0.1166
R indices (all data)	R1 = 0.1057, wR2 = 0.1526

Crystal Structure and Data of 3pa-major

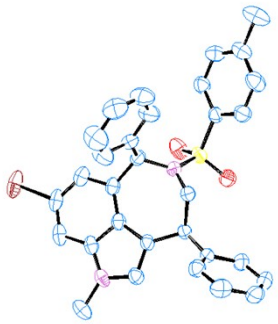
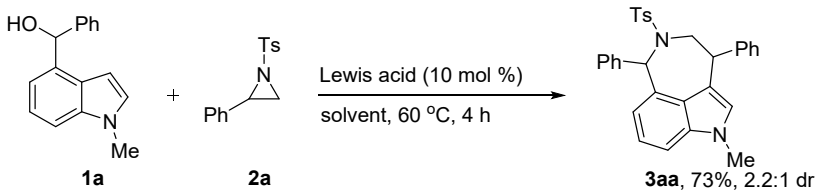


Figure S2. ORTEP diagram of 8-Bromo-6-methyl-1,4-diphenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole **3pa-major** with 50% ellipsoid (CCDC 2368691). H-Omitted for clarity.

Identification code	**3pa-major**
Empirical formula	'C31H27BrN2O2S'
Formula weight	571.51
Crystal habit, colour	block/Colorless
Temperature, *T*/K	296 K
Wavelength, λ/Å	0.71073
Crystal system	'triclinic'
Space group	'P -1'
Unit cell dimensions	a = 8.3606(12) Å b = 10.4276(16) Å c = 15.974(2) Å α = 92.585(4) β = 105.246(4) γ = 95.304(4)
Volume, *V*/Å^3	1334.4(3)
Z	2
Calculated density, Mg·m^{-3}	1.422
Absorption coefficient, μ/mm^{-1}	1.650
F(000)	588
θ range for data collection	1.967 to 24.999°
Limiting indices	$-9 \le h \le 9$, $-12 \le k \le 12$, $-18 \le l \le 18$
Reflection collected / unique	4656/4039
Completeness to θ	99.2%
Absorption correction	Multi scan

Max. and min. transmission	0.7452 and 0.6324
Refinement method	'SHELXL-2018/3 (Sheldrick, 2018)'
Data / restraints / parameters	4656/0/336
Goodness−of−fit on F^2	0.763
Final *R* indices [*I*>2sigma(*I*)]	R1 = 0.0329, wR2 = 0.1025
R indices (all data)	R1 = 0.0403, wR2 = 0.1149

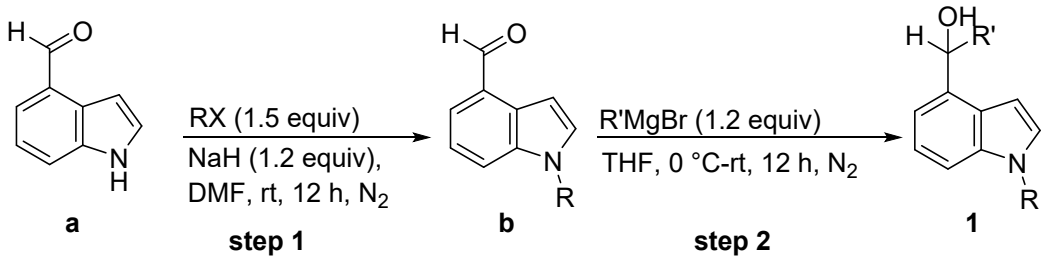
Table S1. Optimization of the reaction conditions[a]



Entry	Lewis acid	Ligand	Solvent	Yield (%)[b]
8	$[Cu(CH_3CN)_4]PF_6$	-	$(CH_2Cl)_2$	45
[c]9	$[Cu(CH_3CN)_4]BF_4$	-	CH_2Cl_2	25
10	$[Cu(CH_3CN)_4]BF_4$	-	CH_3CN	n.r.
11	**$[Cu(CH_3CN)_4]BF_4$**	**-**	**toluene**	**73**
12	$[Cu(CH_3CN)_4]BF_4$	-	THF	41
13	$[Cu(CH_3CN)_4]BF_4$	-	CH_3OH	n.r.
14	$[Cu(CH_3CN)_4]BF_4$	-	*m*-xylene	54
15	$[Cu(CH_3CN)_4]BF_4$	dppe	toluene	63
16	$[Cu(CH_3CN)_4]BF_4$	dppb	toluene	25
17	$[Cu(CH_3CN)_4]BF_4$	PPh_3	toluene	n.r.
18	$[Cu(CH_3CN)_4]BF_4$	2,2'-bipyridyl	toluene	n.r.
[d]19	$[Cu(CH_3CN)_4]BF_4$	-	toluene	31
[e]20	$[Cu(CH_3CN)_4]BF_4$	-	toluene	62
21	-	-	toluene	n.r.

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), Lewis acid (10 mol %), Ligand (10 mol %), solvent (1 mL), 60 °C, 4 h. [b]Isolated yield. n.r. = no reaction. [c]Reaction temperature 40 °C. [d]Reaction temperature 50 °C. [e]Reaction temperature 100 °C.

General Procedure for the Synthesis of 1a-o.[1b, 1c]

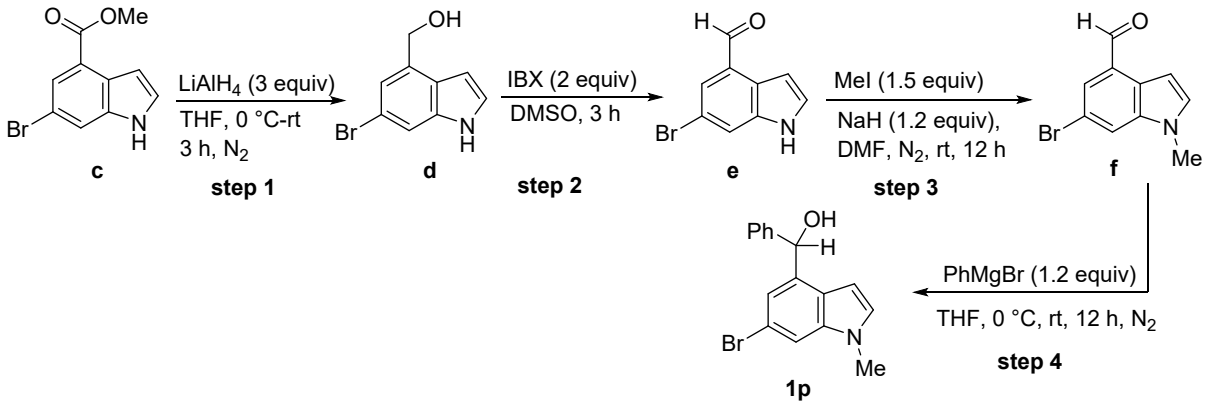


Step 1: To a suspension of NaH (3.6 mmol, 60% dispersion in mineral oil, 1.2 equiv) in DMF (10 mL) at 0 °C, was added 1*H*-Indole-4-carbaldehyde **a** (3 mmol, 1 equiv), under nitrogen atmosphere. The reaction mixture was allowed to stir at the same temperature for 30 minutes and then alkyl halide (4.5 mmol, 1.5 equiv) was added dropwise. The mixture was then stirred at room temperature for 12 h. After completion, the reaction mixture was diluted with ethyl acetate (30 mL), washed with brine (2 x 10 mL) and ice-water (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using hexane and ethyl acetate as eluent to give **b**.

Step 2: To a stirring solution of **b** (2 mmol, 1 equiv) in THF (1.0 M), under a nitrogen atmosphere at 0 °C, was added the alkyl/aryl magnesium halide (freshly prepared from alkyl/aryl halide (1.2 equiv) and magnesium turnings (1.2 equiv) in THF (2 mL/mmol)) dropwise after 3 h. The reaction mixture was then allowed to stir at room temperature for another 12 h. The reaction was then quenched with saturated NH_4Cl and extracted with ethyl acetate (30 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using hexane and ethyl acetate as eluent to give **1**.

Procedure for the Synthesis of 1p.

Step-1: To a solution of **c** (5 mmol, 1 equiv) in THF (20 mL) at 0 °C under nitrogen atmosphere, $LiAlH_4$ (15 mmol, 3 equiv) was added portion wise. The reaction mixture was then gradually moved to room temperature and allowed to stir for 3 h. After completion, the reaction mixture was quenched with saturated NH_4Cl (30 mL) and extracted with ethyl acetate (3 x 20 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using ethyl acetate and hexane as an eluent to afford **d**.

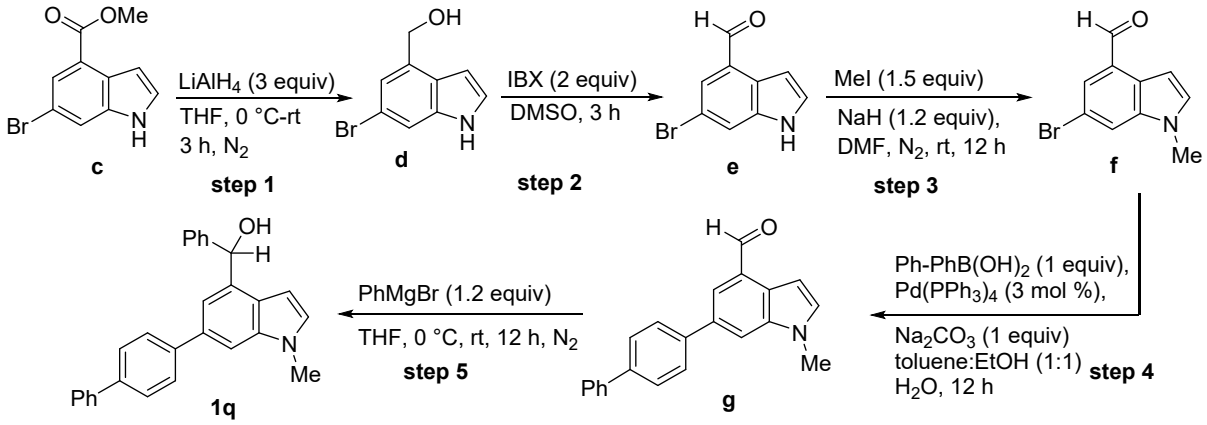


Step-2: To a suspension of IBX (8 mmol, 2 equiv) in DMSO (15 mL), was added (6-bromo-1*H*-indol-4-yl)methanol **d** (4 mmol, 1 equiv) and the resulting mixture was allowed to stir at room temperature for 3 h under air. After 3 h, the reaction mixture was diluted with ethyl acetate (30 mL), washed with brine (1 x 10 mL) and ice-water (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using hexane and ethyl acetate as eluent to give **e**.

Step-3: To a suspension of NaH (3.6 mmol, 60% dispersion in mineral oil, 1.2 equiv) in DMF (10 mL) at 0 °C, was added 6-bromo-1*H*-indole-4-carbaldehyde **e** (3 mmol, 1 equiv), under nitrogen atmosphere. The reaction mixture was allowed to stir at the same temperature for 30 minutes and then methyl iodide (4.5 mmol, 1.5 equiv) was added dropwise. The mixture was then allowed to stir at room temperature for 12 h. After completion, as monitored by TLC, the reaction mixture was diluted with ethyl acetate (30 mL), washed with brine (1 x 10 mL) and ice-water (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using hexane and ethyl acetate as eluent to give **f**.

Step 4: To a stirring solution of **f** (2 mmol, 1 equiv) in THF (1.0 M), under a nitrogen atmosphere at 0 °C, was added PhMgBr (2.4 mmol, 1.2 equiv) (freshly prepared from bromo benzene (1.2 equiv) and magnesium turnings (1.2 equiv) in THF (2 mL/mmol)) dropwise after 3 h. The reaction mixture was then allowed to stir at room temperature for another 12 h. The reaction was then quenched with saturated NH_4Cl and extracted with ethyl acetate (30 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using hexane and ethyl acetate as eluent to give **1p**.

Procedure for the Synthesis of 1q.



Step-1: To a solution of **c** (5 mmol, 1 equiv) in THF (20 mL) at 0 °C under nitrogen atmosphere, $LiAlH_4$ (15 mmol, 3 equiv) was added portion wise. The reaction mixture was then gradually moved to room temperature and allowed to stir for 3 h. After completion, the reaction mixture was quenched with saturated NH_4Cl (30 mL) and extracted with ethyl acetate (3 x 20 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using ethyl acetate and hexane as an eluent to afford **d**.

Step-2: To a suspension of IBX (8 mmol, 2 equiv) in DMSO (15 mL), was added (6-bromo-1*H*-indol-4-yl)methanol **d** (4 mmol, 1 equiv) and the resulting mixture was allowed to stir at room temperature for 3 h under air. After 3 h, the reaction mixture was diluted with ethyl acetate (30 mL), washed with brine (1 x 10 mL) and ice-water (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using hexane and ethyl acetate as eluent to give **e**.

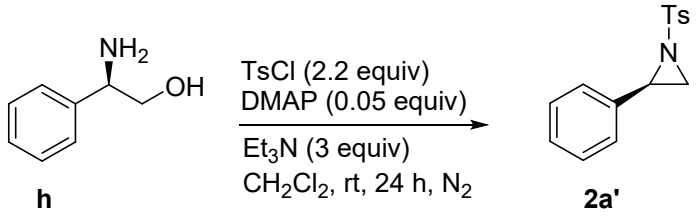
Step-3: To a suspension of NaH (3.6 mmol, 60% dispersion in mineral oil, 1.2 equiv) in DMF (10 mL) at 0 °C, was added 6-bromo-1*H*-indole-4-carbaldehyde **e** (3 mmol, 1 equiv), under nitrogen atmosphere. The reaction mixture was allowed to stir at the same temperature for 30 minutes and then methyl iodide (4.5 mmol, 1.5 equiv) was added dropwise. The mixture was then allowed to stir at room temperature for 12 h. After completion, as monitored by TLC, the reaction mixture was diluted with ethyl acetate (30 mL), washed with brine (1 x 10 mL) and ice-water (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using hexane and ethyl acetate as eluent to give **f**.

Step-4: To a solution of **f** (2 mmol, 1 equiv) in toluene/EtOH (1:1, 6 mL), was added the 4-biphenyl boronic acid (2 mmol, 1 equiv), $Pd(PPh_3)_4$ (3 mol %), Na_2CO_3 (2 mmol, 1 equiv) and H_2O (100 µL). The mixture was stirred at 100 °C for 12 h under nitrogen atmosphere. After 12 h, the reaction mixture was cooled to room temeprature and diluted with ethyl acetate (10 mL) and washed with brine (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using hexane and ethyl acetate as eluent to give **g**.

Step-5: To a stirring solution of **g** (1 mmol, 1 equiv) in THF (1.0 M), under a nitrogen atmosphere at 0 °C, was added PhMgBr (2.4 mmol, 1.2 equiv) (freshly prepared from bromo benzene (1.2 equiv) and magnesium turnings (1.2 equiv) in THF (2 mL/mmol)) dropwise after 3 h. The reaction mixture was then allowed to stir at room temperature for another 12 h. The reaction was then quenched with saturated NH_4Cl and extracted with ethyl acetate (30 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using hexane and ethyl acetate as eluent to give **1q**.

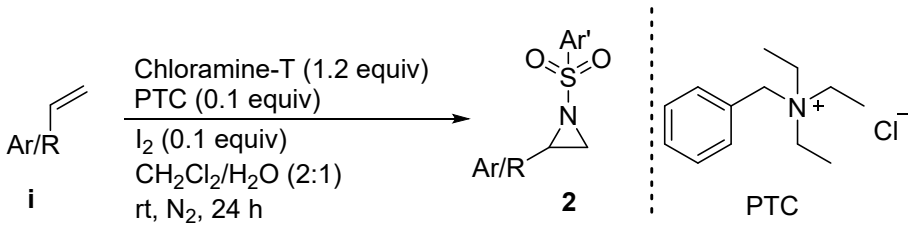
Indole **1r** was prepared according to the reported procedure.[1a]

Procedure for the Synthesis of 2a'.[2d]



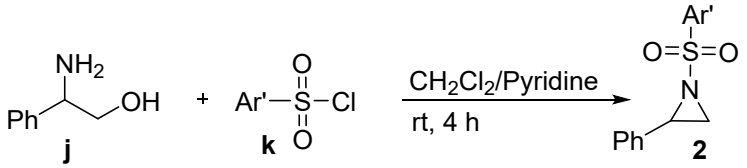
To a stirring solution of (*R*)-(−)-2-phenylglycinol **h** (2 mmol, 1 equiv, 274 mg), TsCl (4.4 mmol, 2.2 equiv, 836 mg) and DMAP (0.1 mmol, 0.05 equiv, 12 mg) in CH_2Cl_2 (20 mL) at 0 °C was added a solution of Et_3N (6.0 mmol, 3 equiv, 606 mg) in dry CH_2Cl_2 (10 mL). The resultant mixture was warmed to room temperature and allowed to stir for 24 h under nitrogen atmosphere. The mixture was then treated with a saturated NH_4Cl (20 mL) and extracted with CH_2Cl_2 (3 × 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on a silica gel column chromatography using hexane and ethyl acetate as eluent to give **2a'**.

General Procedure for the Synthesis of 2b-m and 2t.[2]



To a stirring solution of the alkene **i** (2 mmol, 1 equiv) and benzyltriethylammonium chloride (PTC) (0.2 mmol, 0.1 equiv) in CH_2Cl_2/H_2O (2:1, 15 mL) were added chloramine-T (2.4 mmol, 1.2 equiv) and iodine (0.2 mmol, 0.1 equiv) at room temperature under nitrogen. The reaction mixture was allowed to stir for 24 h and then washed with saturated $Na_2S_2O_3$ (2 x 10 mL) and extracted with CH_2Cl_2 (3 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and ethyl acetate as eluent to give **2**.

General Procedure for the Synthesis of 2n-r.[2b]



To a stirring solution of 2-phenylglycinol **j** (2 mmol, 1 equiv) in CH_2Cl_2/pyridine (1.4:0.7 mL) was added the appropriate sulfonyl chloride **k** (6 mmol, 3 equiv) in one portion at 0 ^oC. The reaction mixture was then allowed to stir for 4 h at room temperature. After completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL), and washed with aqueous 2 N HCl (3 x 10 mL). The combined acidic aqueous layers were then extracted with CH_2Cl_2 (1 x 20 mL). The organic layer was then washed with aqueous 2 N KOH (3 x 20 mL). The combined basic layers were then extracted with CH_2Cl_2 (1 x 20 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and ethyl acetate as eluent to give **2**.

Aziridine **2s**, **2u** and **2v** were prepared according to the reported procedure.[2a, 2c, 2d]

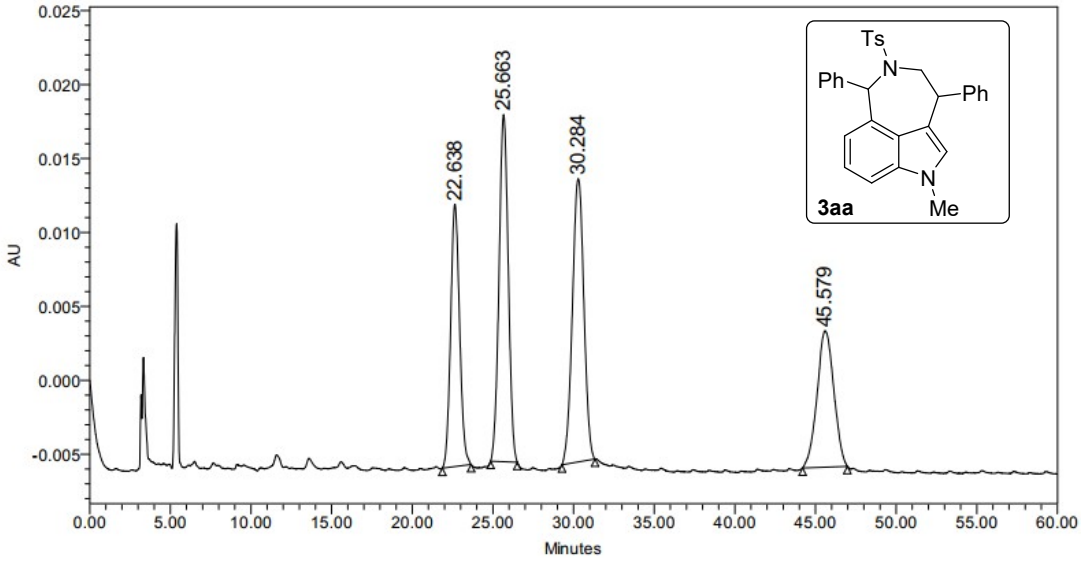
General Procedure for the Synthesis of 3aa-qa. Indole **1** (0.1 mmol, 1 equiv), aziridine **2** (0.12 mmol, 1.2 equiv) and $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 0.10 equiv) were stirred in toluene (2 mL) at

60 °C for 4 h under calcium chloride tube. After completion, as monitored by TLC, the reaction mixture was allowed to cool to room temperature and diluted with ethyl acetate (5 mL) and passed through a short pad of celite using ethyl acetate (10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent to afford **3**.

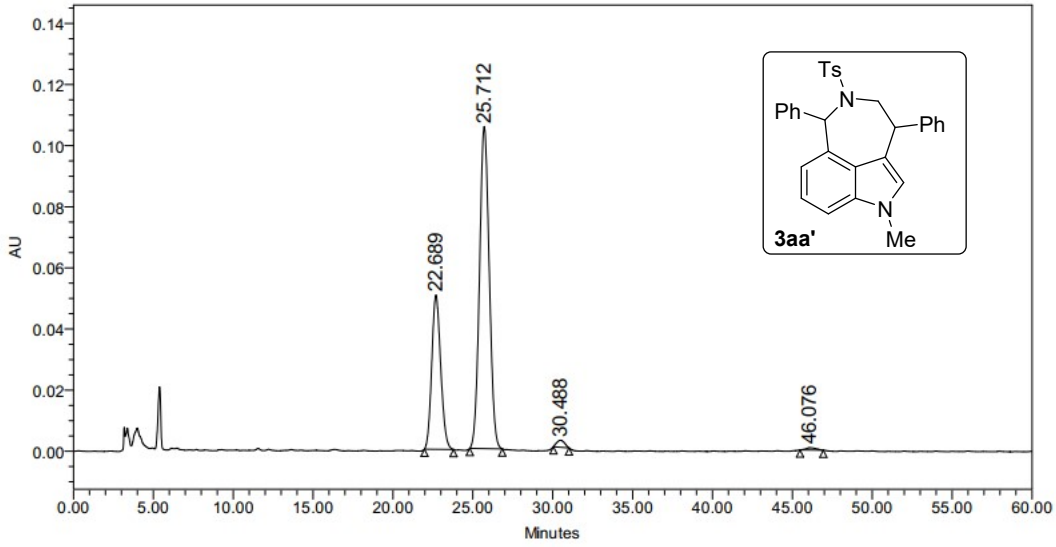
General Procedure for the Stereoselective Synthesis of 3aa', 3ha' and 3pa'. Indole **1** (0.1 mmol, 1 equiv), (*R*)-2-phenyl-1-tosylaziridine **2a'** (0.12 mmol, 1.2 equiv) and $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 0.10 equiv) were stirred in toluene (2 mL) at 60 °C for 4 h under calcium chloride tube. The purification was performed as above presented general procedure. The enantiomeric excess was determined using chiral HPLC.

Scale-up Synthesis of 3af. Indole **1a** (2 mmol, 1 equiv, 474 mg), aziridine **2f** (2.4 mmol, 1.2 equiv, 840 mg) and $Cu(CH_3CN)_4BF_4$ (0.2 mmol, 0.10 equiv, 63 mg) were stirred in toluene (5 mL) at 60 °C for 4 h under calcium chloride tube. After completion, as monitored by TLC, the reaction mixture was allowed to cool to room temperature and diluted with ethyl acetate (10 mL) and passed through a short pad of celite using ethyl acetate (15 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent to afford **3af**.

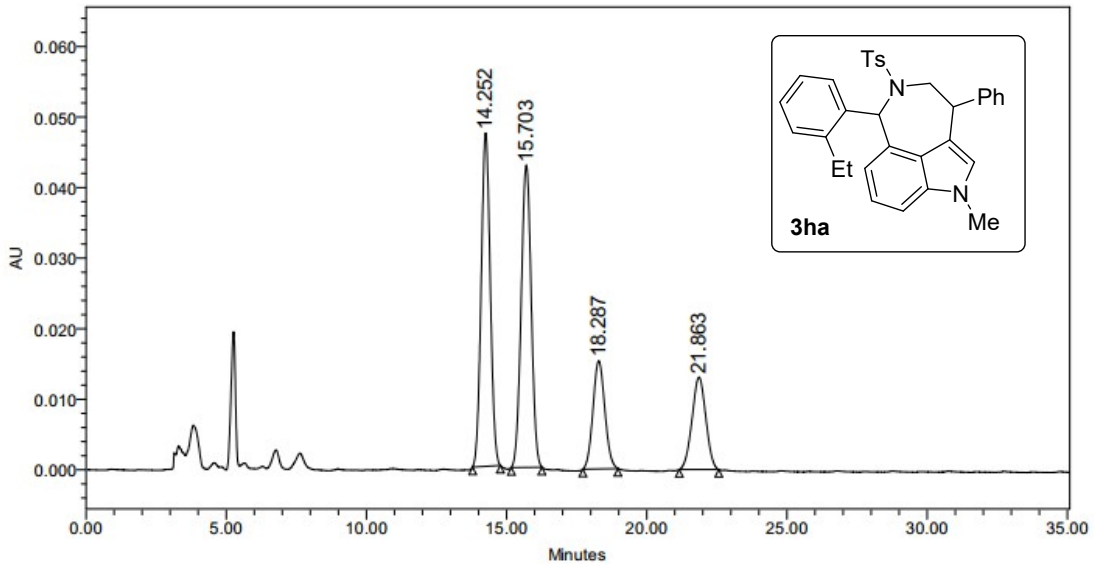
HPLC chromatograms



	RT	Area	% Area	Height
1	22.638	680784	21.13	17740
2	25.663	930497	28.88	23462
3	30.284	945526	29.35	19138
4	45.579	664697	20.63	9211



	RT	Area	% Area	Height
1	22.689	1966156	30.08	50431
2	25.712	4457591	68.21	105370
3	30.488	78877	1.21	2285
4	46.076	32900	0.50	750



	RT	Area	% Area	Height
1	14.252	1056579	35.01	47244
2	15.703	1064087	35.26	42848
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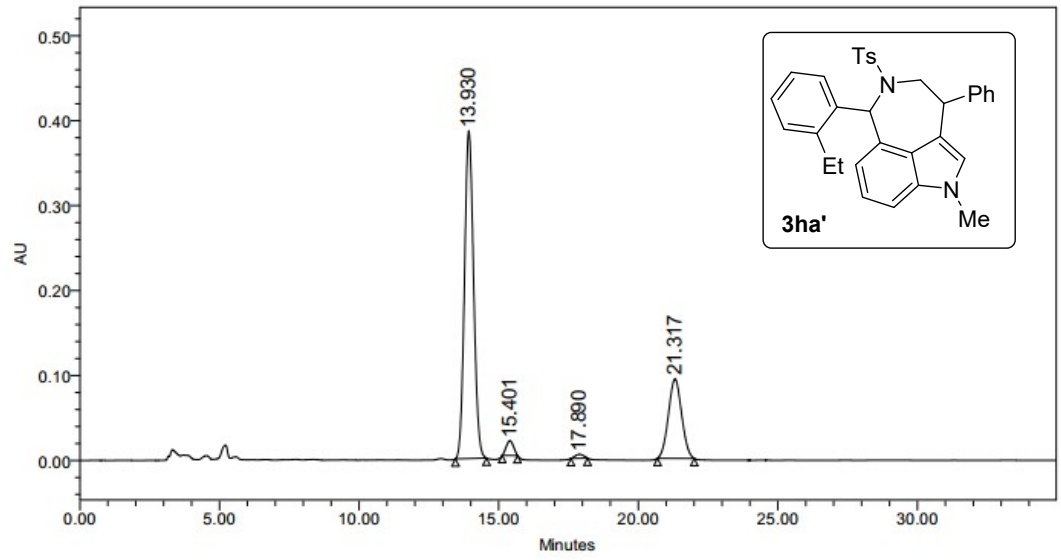
4	21.863	447413	14.83	13082



	RT	Area	% Area	Height
1	13.930	8675663	71.36	385831
2	15.401	314290	2.59	17291
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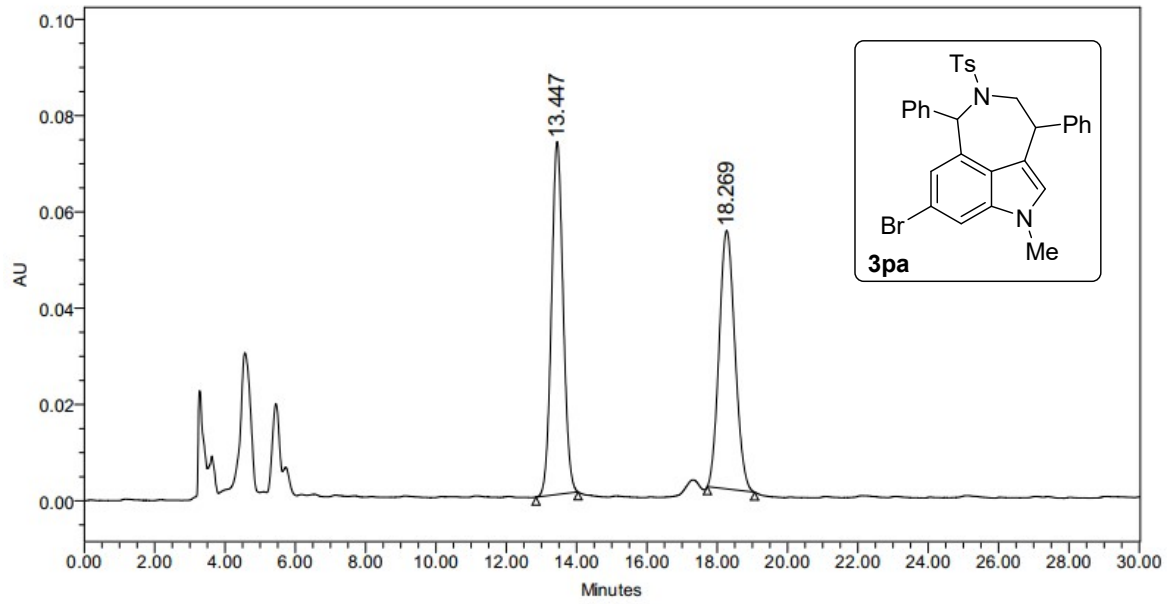
4	21.317	3071005	25.26	93646



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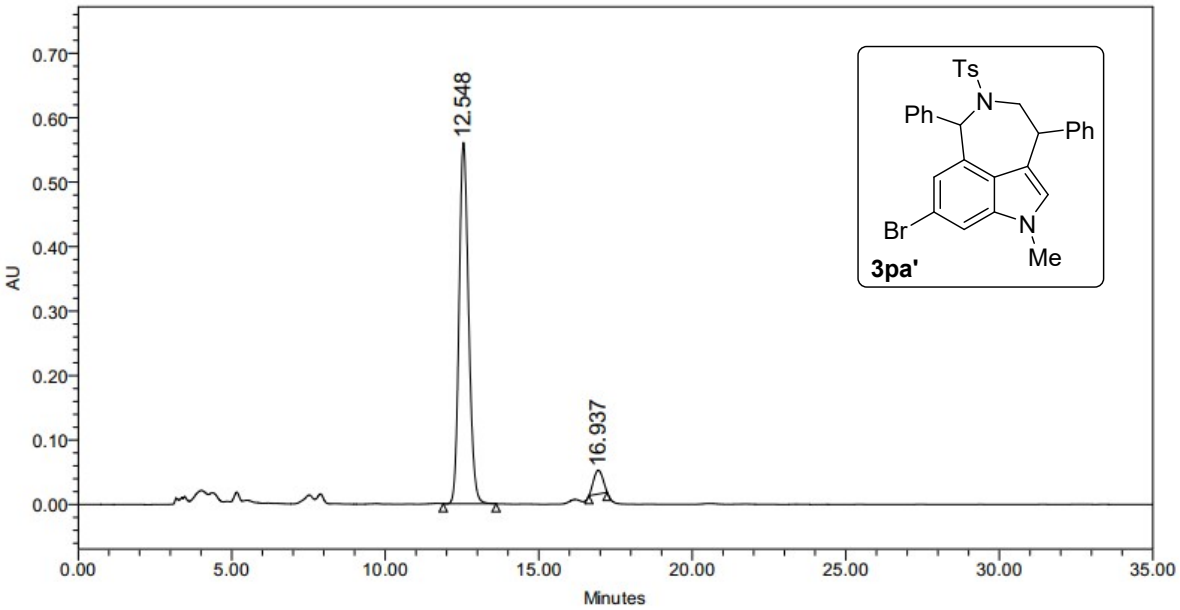
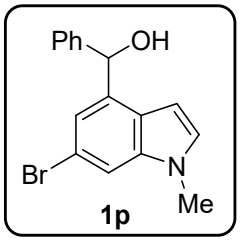


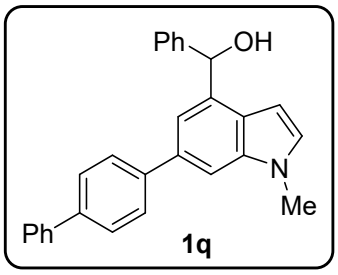
	RT	Area	% Area	Height
1	12.548	12074016	94.09	560171
2	16.937	758019	5.91	36971

Characterization Data



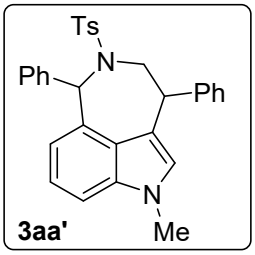
1p

(6-Bromo-1-methyl-1H-indol-4-yl)(phenyl)methanol 1p. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.42; sticky liquid; yield 61% (384 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 3H), 7.38-7.37 (m, 1H), 7.33-7.30 (m, 2H), 7.26-7.23 (m, 2H), 6.97-6.96 (m, 1H), 6.41-6.40 (m, 1H), 6.17 (s, 1H), 3.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 137.8, 137.2, 129.4, 128.5, 127.7, 126.7, 125.0, 120.1, 115.3, 111.9, 100.0, 74.5, 33.0; FT-IR (neat) 3024, 1735, 1293, 1178, 1045, 751 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{15}BrNO$: 316.0332, found: 316.0323.



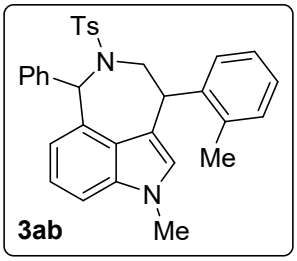
1q

(6-([1,1'-Biphenyl]-4-yl)-1-methyl-1H-indol-4-yl)(phenyl)methanol 1q. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.44; sticky liquid; yield 58% (225 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8 Hz, 2H), 7.68-7.64 (m, 4H), 7.55 (s, 1H), 7.51 (t, *J*= 4 Hz, 3H), 7.46 (t, *J* =7.5 Hz, 2H), 7.37-7.30 (m, 3H), 7.25-7.22 (m, 2H), 7.04 (d, *J* = 3 Hz, 1H), 6.48 (d, J = 3.5 Hz, 1H), 6.28 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.5, 141.4, 140.9, 139.6, 137.7, 136.1, 134.7, 129.7, 128.9, 128.5, 127.9, 127.57, 127.53, 127.3, 127.1, 126.7, 125.5, 116.9, 107.4, 99.7, 75.3, 33.1; FT-IR (neat) 3024, 1732, 1374, 1215, 1045, 748 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{28}H_{24}NO$: 390.1852, found: 390.1840.



3aa'

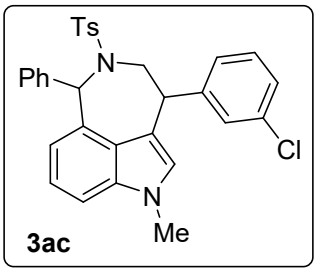
6-Methyl-1,4-diphenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3aa'. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.60; colorless solid; mp 154-155 °C; yield 73% (36 mg); mixture of diastereomers (dr = 2.2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8 Hz, 2H), 7.31-7.30 (m, 1H), 7.25-7.19 (m, 6.20H), 7.16-7.15 (m, 7.17H), 7.12-7.10 (m, 2.70H), 7.00-6.99 (m, 1H), 6.89-6.86 (m, 3.21H), 6.83-6.82 (m, 0.73H), 6.73 (s, 1H), 6.67 (s, 0.39H), 6.35 (s, 1H), 5.92 (s, 0.38H), 4.52-4.49 (m, 1H), 4.15-4.10 (m, 0.43H), 3.78-3.74 (m, 1.41H), 3.66 (s, 3H), 3.63-3.61 (m, 0.41H), 3.53 (s, 1H), 3.38-3.32 (m, 1H), 2.33 (s, 3H), 2.26 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 142.8, 141.8, 141.1, 140.6, 140.3, 138.8, 137.7, 137.6, 136.9, 133.3, 132.5, 129.4, 129.1, 129.0, 128.7, 128.69, 128.60, 128.3, 128.0, 127.6, 127.5, 127.3, 126.9, 126.7, 126.6, 126.1, 125.8, 121.9, 121.2, 119.6, 119.1, 117.17, 117.13, 108.6, 108.2, 65.1, 63.4, 53.0, 50.5, 46.4, 42.9, 32.9, 32.6, 21.58, 21.51; FT-IR (KBr) 2924, 1733, 1343, 1156, 1091, 660, 545 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{31}H_{29}N_2O_2S$: 493.1944, found: 493.1956; $[\alpha]_D^{25}$ = +100 (c = 0.01, $CHCl_3$); HPLC: *ee* for major diastereomer = >96% *ee* [YMC Chiral ART Cellulose-SC column, hexane/^{i}PrOH = 90:10, flow rate: 1 mL/min, λ= 254 nm, t_R = 25.71 min (major), 30.48 min (minor)].



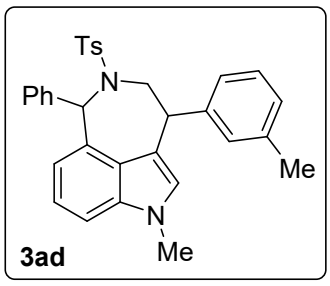
3ab

6-Methyl-1-phenyl-4-(*o*-tolyl)-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3ab. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.54; colorless solid; mp 157-158 °C; yield 68% (34 mg); major diastereomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.68 (m, 2H), 7.23-7.18 (m, 2H), 7.16-7.15 (m, 5H), 7.10-7.08 (m, 3H), 7.03-6.96 (m, 2H), 6.90-6.88 (m, 3H), 6.77

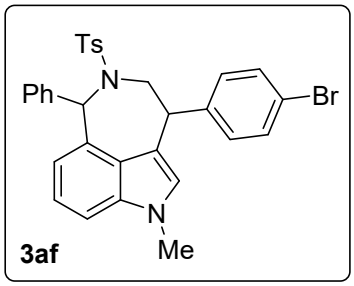
(s, 1H), 6.31 (s, 1H), 4.81-4.77 (m, 1H), 3.72-3.68 (m, 1H), 3.66 (s, 3H), 3.34-3.27 (m, 1H), 2.41 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 142.1, 141.2, 138.9, 137.7, 136.3, 133.3, 130.2, 129.3, 129.1, 128.6, 128.3, 128.2, 127.6, 127.3, 126.6, 126.2, 126.0, 121.2, 119.1, 117.0, 108.2, 65.2, 49.6, 41.1, 32.9, 21.5, 19.6; FT-IR (KBr) 2982, 1732, 1373, 1241, 1045, 755 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{32}H_{31}N_2O_2S$: 507.2101, found: 507.2104.



4-(3-Chlorophenyl)-6-methyl-1-phenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3ac. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.52; colorless solid; mp 161-162 °C; yield 62% (32 mg); mixture of diastereomers (dr = 2.2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.69 (m, 0.81H), 7.31-7.29 (m, 3.29H), 7.20-7.10 (m, 11.48H), 7.06-7.04 (m, 0.61H), 7.00-6.98 (m, 1H), 6.93-6.83 (m, 4.50H), 6.71 (s, 0.41H), 6.67 (s, 1H), 6.36 (0.42H), 5.96 (s, 1H), 4.52-4.48 (m, 0.44H), 4.11-4.05 (m, 1H), 3.80-3.76 (m, 1H), 3.73-3.72 (m, 0.35H), 3.68 (s, 1H), 3.66-3.61 (m, 1H), 3.57 (s, 3H), 3.35-3.28 (m, 0.45H), 2.34 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7, 143.1, 143.0, 142.0, 141.0, 140.2, 138.7, 137.7, 137.6, 136.9, 134.3, 133.2, 132.5, 129.94, 129.92, 129.4, 129.1, 128.9, 128.8, 128.74, 128.70, 128.5, 128.4, 128.1, 127.73, 127.71, 127.5, 127.3, 127.2, 127.0, 126.9, 126.7, 126.4, 126.2, 125.73, 125.70, 122.1, 121.4, 119.7, 119.2, 116.4, 116.2, 108.7, 108.3, 65.1, 63.5, 52.5, 50.3, 46.2, 42.9, 32.9, 32.7, 21.59, 21.53; FT-IR (KBr) 2926, 1733, 1343, 1256, 1090, 666, 593, 546 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{31}H_{28}ClN_2O_2S$: 527.1555, found: 527.1563.

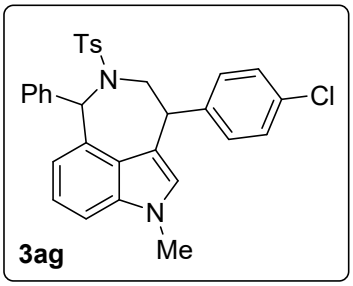


6-Methyl-1-phenyl-4-(*m*-tolyl)-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3ad. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.56; colorless solid; mp 171-172 °C; yield 65% (33 mg); mixture of diastereomers (dr = 2.5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.32-7.29 (m, 1.29H), 7.24-7.21 (m, 2H), 7.18-7.16 (m, 5H), 7.14-7.09 (m, 3.68H), 7.06-7.03 (m, 1H), 7.01-7.00 (m, 0.70H), 6.98 (s, 1.17H), 6.95-6.93 (m, 1.11H), 6.91-6.86 (m, 3H), 6.84-6.82 (m, 1.16H), 6.77 (s, 0.40H), 6.73 (s, 1H), 6.67 (s, 0.39H), 6.38 (s, 1H), 5.93 (s, 0.38H), 4.50-4.46 (m, 1H), 4.17-4.10 (m, 0.41H), 3.79-3.74 (m, 1.43H), 3.67 (s, 3H), 3.63-3.59 (m, 0.40H), 3.54 (s, 1.20H), 3.38-3.32 (m, 1H), 2.33 (s, 3H), 2.29-2.27 (m, 5.24H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 142.8, 141.8, 141.1, 140.5, 140.3, 138.8, 138.2, 138.1, 137.69, 137.65, 136.9, 133.3, 132.5, 129.49, 129.44, 129.3, 129.1, 129.0, 128.6, 128.5, 128.4, 128.3, 128.07, 128.04, 127.7, 127.6, 127.5, 127.3, 126.7, 126.5, 126.1, 125.8, 125.69, 125.66, 121.9, 121.2, 119.6, 119.1, 117.2, 117.1, 108.6, 108.1, 65.1, 63.3, 52.9, 50.6, 46.3, 42.8, 32.9, 32.6, 21.56, 21.50; FT-IR (KBr) 2985, 1734, 1370, 1242, 1045, 750 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{32}H_{31}N_2O_2S$: 507.2101, found: 507.2105.

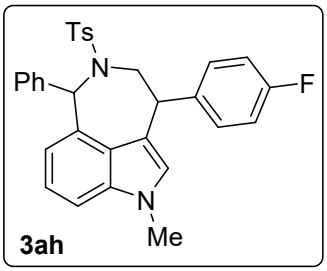


4-(4-Bromophenyl)-6-methyl-1-phenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3af. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; colorless solid; mp 174-175 °C; yield 75% (42 mg); mixture of diastereomers (dr = 2.1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8 Hz, 2H), 7.38-7.36 (m, 2H), 7.35-7.32 (m, 1H), 7.30-7.28 (m, 1.51H), 7.22-7.19 (m, 1.50H), 7.18-7.10 (m, 8.57H), 7.05-7.02 (m, 1.94H), 7.00-6.98 (m, 0.52H), 6.87-6.83 (m, 5H), 6.70-6.69 (m, 1.38H), 6.34 (s, 1H), 5.97 (s, 0.47H), 4.52-4.48 (m, 1H), 4.11-4.05 (m, 0.51H), 3.82-3.77 (m, 0.51H), 3.75-3.70 (m, 1.10H), 3.67 (s, 3H), 3.64-3.60 (m, 0.52H), 3.56 (s, 1.49H), 3.32-3.25 (m, 1H), 2.33 (s, 3H), 2.27 (s, 1.50H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 142.7, 142.0, 140.9, 140.3, 140.2, 138.6, 137.7, 137.6, 137.1, 133.3, 132.5, 131.7, 130.44, 130.40, 129.4, 129.1, 128.9, 128.6, 128.5, 128.4, 128.1, 127.7, 127.6, 127.3, 126.6, 126.4, 126.2, 125.7,

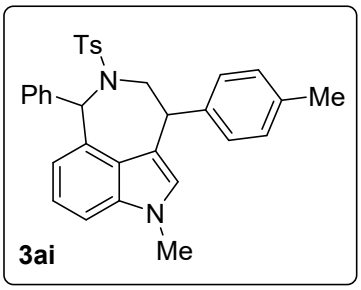
122.1, 121.4, 121.0, 120.7, 119.7, 119.2, 116.6, 116.4, 108.7, 108.2, 65.0, 63.6, 52.5, 50.3, 45.9, 42.6, 32.9, 32.7, 21.58, 21.52; FT-IR (KBr) 2984, 1732, 1373, 1241, 1045, 748, 667 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{31}H_{28}BrN_2O_2S$: 571.1049, found: 571.1043.



4-(4-Chlorophenyl)-6-methyl-1-phenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3ag. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.51; colorless solid; mp 172-173 °C; yield 74% (39 mg); mixture of diastereomers (dr = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.29-7.28 (m, 1.54H), 7.25-7.23 (m, 2H), 7.20-7.17 (m, 4.24H), 7.16-7.14 (m, 5H), 7.12-7.08 (m, 4H), 7.00-6.98 (m, 0.49H), 6.91-6.83 (m, 4.92H), 6.70-6.68 (m, 1.51H), 6.33 (s, 1H), 5.96 (s, 0.49H), 4.53-4.49 (m, 1H), 4.11-4.05 (m, 0.53H), 3.82-3.78 (m, 0.50H), 3.75-3.70 (m, 1H), 3.67 (s, 3H), 3.64-3.60 (m, 0.52H), 3.56 (s, 1.49H), 3.32-3.26 (m, 1H), 2.33 (s, 3H), 2.27 (s, 1.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 142.2, 142.0, 141.0, 140.3, 139.6, 138.7, 137.7, 137.6, 137.1, 133.3, 132.9, 132.6, 132.5, 130.05, 130.01, 129.4, 129.1, 128.9, 128.7, 128.5, 128.4, 128.1, 127.7, 127.6, 127.3, 126.6, 126.4, 126.2, 125.7, 122.1, 121.4, 119.7, 119.2, 116.7, 116.5, 108.7, 108.2, 65.0, 63.6, 52.6, 50.4, 45.9, 42.5, 32.9, 32.7, 21.58, 21.51; FT-IR (KBr) 2925, 1733, 1340, 1255, 1090, 670, 593, 546 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{31}H_{28}ClN_2O_2S$: 527.1555, found: 527.1552.

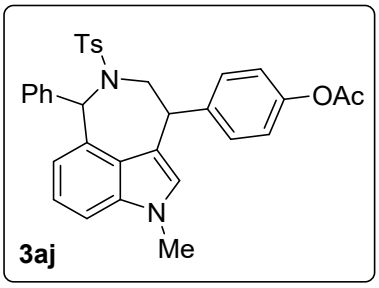


4-(4-Fluorophenyl)-6-methyl-1-phenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3ah. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 170-171 °C; yield 71% (36 mg); mixture of diastereomers (dr = 2.8:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.31-7.29 (m, 1.11H), 7.23-7.21 (m, 1.50H), 7.19-7.10 (m, 9.13H), 7.01-6.99 (m, 0.47H), 6.96-6.92 (m, 3.38H), 6.88-6.83 (m, 3.62H), 6.71 (s, 1H), 6.68 (s, 0.40H), 6.34 (s, 1H), 5.94 (s, 0.35H), 4.53-4.49 (m, 1H), 4.11-4.05 (m, 0.39H), 3.82-3.79 (m, 0.35H), 3.77-3.72 (m, 1H), 3.67 (s, 3H), 3.64-3.61 (m, 0.36H), 3.56 (s, 1H), 3.34-3.27 (m, 1H), 2.34 (s, 3H), 2.27 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9, 162.8 (d, J_{C-F} = 243.6 Hz), 160.9, 142.9, 142.0, 141.0, 140.3, 139.4 (d, J_{C-F} = 3.2 Hz), 138.7, 137.7, 137.6, 136.9, 136.64, 136.61, 133.3, 132.5, 130.19, 130.13, 130.1 (d, J_{C-F} = 7.8 Hz), 129.4, 129.1, 128.9, 128.6, 128.46, 128.40, 128.0, 127.67, 127.62, 127.3, 126.6, 126.4, 126.1, 125.7, 122.0, 121.3, 119.6, 119.1, 117.0, 116.9, 115.5, 115.4 (d, J_{C-F} = 21 Hz), 115.3, 108.7, 108.2, 65.0, 63.4, 52.9, 50.5, 45.7, 42.3, 32.9, 32.6, 21.5, 21.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ -115.3, -115.9; FT-IR (KBr) 2924, 1736, 1507, 1340, 1155, 744, 543 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{31}H_{28}FN_2O_2S$: 511.1850, found: 511.1843.

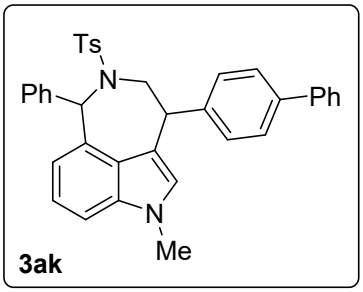


6-Methyl-1-phenyl-4-(*p*-tolyl)-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3ai. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.51; colorless solid; mp 179-180 °C; yield 72% (36 mg); mixture of diastereomers (dr = 2.1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8 Hz, 2H), 7.30-7.29 (m, 1.46H), 7.22-7.20 (m, 2H), 7.17-7.13 (m, 4.91H), 7.12-7.07 (m, 3.34H), 7.05-7.04 (m, 3.28H), 7.02-6.98 (m, 0.90H), 6.89-6.87 (m, 3H), 6.85-6.80 (m, 1.35H), 6.72 (s, 1H) 6.66 (s, 0.42H), 6.37 (s, 1H), 5.93 (s, 0.46H), 4.49-4.45 (m, 1H), 4.14-4.07 (m, 0.50H), 3.75-3.70 (m, 1.56H), 3.66 (s, 3H), 3.62-3.59 (m, 0.56H), 3.53 (s, 1.31H), 3.35-3.28 (m, 1H), 2.33-2.31 (m, 3.48H), 2.30 (s, 3H), 2.26 (s, 1.22H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 141.8, 141.1, 140.7, 140.3, 138.8, 137.7, 136.9, 136.5, 133.3, 132.6, 129.38, 129.34, 129.2, 129.1, 129.0, 128.6,

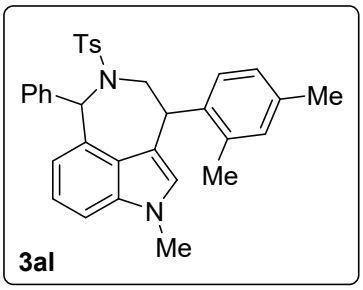
128.59, 128.55, 128.3, 127.6, 127.5, 127.3, 126.7, 126.6, 126.1, 125.8, 121.9, 121.2, 119.6, 119.1, 117.3, 108.6, 108.1, 65.1, 63.4, 53.0, 50.6, 45.9, 42.5, 32.9, 32.6, 21.57, 21.51, 21.2, 21.1; FT-IR (KBr) 2979, 1736, 1368, 1241, 1048, 751 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{32}H_{31}N_2O_2S$: 507.2101, found: 507.2097.



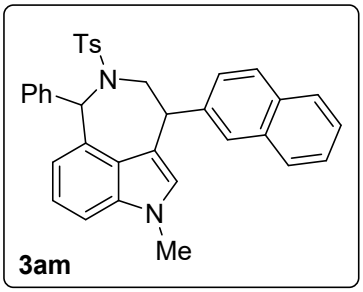
4-(6-Methyl-1-phenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indol-4-yl)phenyl acetate 3aj. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.45; colorless solid; mp 169-170 °C; yield 69% (38 mg); mixture of diastereomers (dr = 2.1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8 Hz, 2H), 7.33-7.29 (m, 1.51H), 7.23-7.11 (m, 12H), 7.01-6.95 (m, 4.36H), 6.88-6.82 (m, 4H), 6.71 (s, 1H) 6.67 (s, 0.45H), 6.41 (s, 1H), 5.96 (s, 0.46H), 4.56-4.52 (m, 1H), 4.13-4.06 (m, 0.48H), 3.81-3.72 (m, 1.49H), 3.67 (s, 3H), 3.64-3.62 (m, 0.49H), 3.55 (s, 1.44H), 3.34-3.27 (m, 1H), 2.34 (s, 3H), 2.29 (s, 1.44H), 2.27-2.26 (m, 4.48H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 169.6, 149.7, 149.5, 142.9, 141.9, 141.2, 141.0, 140.2, 133.3, 132.5, 129.66, 129.62, 129.4, 129.14, 129.11, 128.6, 128.44, 128.40, 128.0, 127.67, 127.61, 127.3, 126.7, 126.5, 126.2, 125.7, 122.0, 121.7, 121.6, 121.3, 119.6, 119.1, 108.7, 108.2, 65.0, 63.4, 52.8, 50.6, 45.9, 42.4, 32.9, 32.6, 21.57, 21.51, 21.29, 21.26; FT-IR (KBr) 2924, 2854, 1761, 1504, 1370, 1340, 1201, 1157, 748, 543 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{33}H_{31}N_2O_4S$: 551.1999, found: 551.1990.



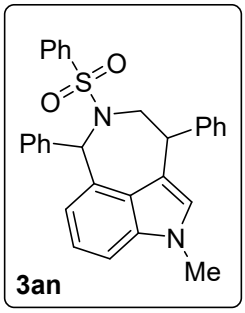
4-([1,1'-Biphenyl]-4-yl)-6-methyl-1-phenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3ak. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 173-174 °C; yield 77% (43 mg); mixture of diastereomers (dr = 3.3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8 Hz, 2H), 7.57-7.53 (m, 2.68H), 7.48-7.46 (m, 2.50H), 7.42-7.38 (m, 2.34H), 7.33-7.30 (m, 2.31H), 7.24-7.21 (m, 4.02H), 7.18-7.14 (m, 4.85H), 7.12-7.10 (m, 2.20H), 7.07-7.05 (m, 0.68H), 7.01-6.99 (m, 0.32H), 6.91-6.87 (m, 3H), 6.83-6.81 (m, 0.66H), 6.73 (s, 1H), 6.69 (s, 0.33H), 6.43 (s, 1H), 6.01 (s, 0.30H), 4.59-4.55 (m, 1H), 4.20-4.14 (m, 0.32H), 3.85-3.77 (m, 1.33H), 3.70-3.67 (m, 3.33H), 3.54 (s, 1H), 3.41-3.34 (m, 1H), 2.33 (s, 3H), 2.24 (s, 0.91H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9, 142.8, 141.8, 141.1, 140.9, 140.8, 140.3, 140.1, 139.9, 139.8, 138.8, 137.7, 137.6, 137.0, 133.3, 132.5, 129.4, 129.17, 129.13, 129.10, 129.0, 128.9, 128.8, 128.6, 128.4, 128.0, 127.64, 127.61, 127.4, 127.35, 127.32, 127.1, 126.6, 126.5, 126.2, 125.8, 122.0, 121.2, 119.6, 119.1, 117.0, 116.9, 108.7, 108.2, 65.1, 63.4, 52.9, 50.5, 46.1, 42.6, 32.9, 32.6, 21.5, 21.4; FT-IR (KBr) 2925, 1733, 1485, 1342, 1241, 1156, 1092, 757, 660, 548 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{37}H_{33}N_2O_2S$: 569.2257, found: 569.2261.



4-(2,4-Dimethylphenyl)-6-methyl-1-phenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3al. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 182-183 °C; yield 69% (36 mg); major diastereomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.6 Hz, 2H), 7.16-7.14 (m, 4H), 7.09-7.07 (m, 2H), 6.98 (s, 1H), 6.90-6.84 (m, 5H), 6.77 (s, 1H), 6.33 (s, 1H), 4.77-4.73 (m, 1H), 3.73-3.68 (m, 1H), 3.66 (s, 3H), 3.31-3.24 (m, 1H), 2.38 (s, 3H), 2.32 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 141.2, 139.1, 138.9, 136.18, 136.13, 133.3, 130.9, 129.3, 129.1, 128.69, 128.61, 128.3, 128.2, 127.8, 127.5, 127.3, 126.9, 126.7, 121.2, 119.0, 108.1, 65.1, 49.7, 40.7, 32.8, 21.5, 21.0, 19.5; FT-IR (KBr) 2923, 1735, 1451, 1239, 1156, 1091, 747, 657, 543 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{33}H_{33}N_2O_2S$: 521.2257, found: 521.2257.

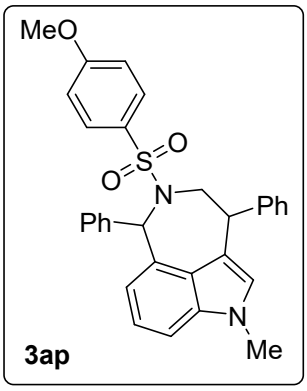


6-Methyl-4-(naphthalen-2-yl)-1-phenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3am. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.46; colorless solid; mp 168-169 ^{o}C; yield 75% (40 mg); mixture of diastereomers (dr = 2.7:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.75 (m, 4H), 7.73-7.72 (m, 1.52H), 7.70-7.67 (m, 1.93H), 7.48-7.42 (m, 2.97H), 7.35-7.33 (m, 1.22H), 7.27-7.26 (m, 0.42H), 7.248-7.245 (m, 0.71H), 7.22-7.21 (m, 1.61H), 7.20-7.16 (m, 5.46H), 7.14-7.12 (m, 2H), 7.04-7.02 (m, 0.4H), 6.94-6.89 (m, 2.98H), 6.83-6.81 (m, 0.72H), 6.76 (s, 1H), 6.73 (s, 0.38H), 6.368-6.365 (m, 1H), 5.95-5.94 (m, 0.36H), 4.75-4.70 (m, 1H), 4.34-4.28 (m, 0.40H), 4.01-3.96 (m, 0.38H), 3.88-3.83 (m, 1H), 3.75-3.70 (m, 0.40H), 3.64 (s, 3H), 3.53 (s, 1.14H), 3.51-3.44 (m, 1H), 2.34 (s, 3H), 2.25 (s, 1.20H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9, 141.9, 141.1, 140.9, 140.3, 138.7, 138.3, 137.7, 137.6, 137.0, 133.5, 133.3, 132.7, 132.68, 132.61, 129.4, 129.2, 129.1, 128.7, 128.4, 128.3, 128.2, 128.1, 127.8, 127.79, 127.74, 127.67, 127.65, 127.4, 127.3, 127.2, 126.8, 126.7, 126.67, 126.61, 126.4, 126.2, 126.1, 125.9, 125.8, 125.7, 122.0, 121.3, 119.6, 119.1, 117.08, 117.00, 108.7, 108.2, 65.1, 63.5, 52.5, 50.3, 46.6, 43.1, 32.9, 32.6, 21.58, 21.51; FT-IR (KBr) 2923, 1733, 1456, 1341, 1241, 1153, 745, 660, 548 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{35}H_{31}N_2O_2S$: 543.2101, found: 543.2107.



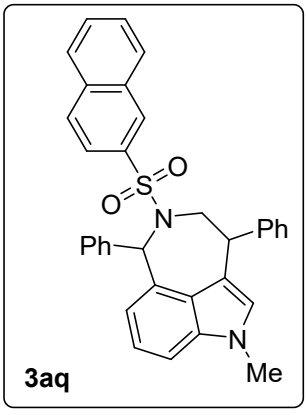
6-Methyl-1,4-diphenyl-2-(phenylsulfonyl)-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3an. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.49; colorless solid; mp 152-153

°C; yield 74% (35 mg); mixture of diastereomers (dr = 2.2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.82 (m, 2H), 7.44-7.39 (m, 1.11H), 7.33-7.27 (m, 5.19H), 7.25-7.19 (m, 5.88H), 7.18-7.10 (m, 6.67H), 7.05-6.98 (m, 2.37H), 6.90-6.87 (m, 3H), 6.76 (s, 1H), 6.70 (s, 0.47H), 6.356-6.353 (m, 1H), 5.916-5.913 (m, 0.45H), 4.52-4.47 (m, 1H), 4.17-4.10 (m, 0.48H), 3.82-3.75 (m, 1.48H), 3.69-3.67 (m, 0.36H), 3.65 (s, 3H), 3.52 (s, 1.42H), 3.40-3.33 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 141.7, 141.0, 140.5, 140.1, 139.7, 137.6, 133.1, 132.3, 132.2, 131.2, 129.1, 129.0, 128.8, 128.7, 128.69, 128.68, 128.65, 128.61, 128.4, 128.0, 127.8, 127.67, 127.64, 127.3, 127.2, 127.0, 126.7, 126.5, 126.2, 125.8, 121.9, 121.2, 119.6, 119.1, 117.0, 116.8, 108.8, 108.2, 65.1, 63.4, 53.0, 50.5, 46.3, 42.9, 32.9, 32.6; FT-IR (KBr) 3026, 1733, 1447, 1342, 1306, 1157, 1047, 745, 605 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{30}H_{27}N_2O_2S$: 479.1788, found: 479.1772.

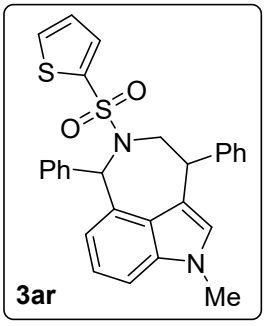


2-((4-Methoxyphenyl)sulfonyl)-6-methyl-1,4-diphenyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3ap. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.45; colorless solid; mp 149-150 °C; yield 78% (39 mg); mixture of diastereomers (dr = 2.6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.35-7.27 (m, 2.44H), 7.25-7.19 (m, 5.23H), 7.18-7.11 (m, 6.94H), 7.02-6.99 (m, 1.15H), 6.94-6.92 (m, 2H), 6.88-6.86 (m, 1H), 6.78 (d, *J* = 9.2 Hz, 2H), 6.74 (s, 1H), 6.67 (s, 0.40H), 6.50-6.47 (m, 0.79H), 6.364-6.360 (m, 1H), 5.935-5.932 (m, 0.38H), 4.52-4.47 (m, 1H), 4.16-4.09 (m, 0.44H), 3.79-3.78 (m, 3.73H), 3.76-3.74 (m, 2.08H), 3.66 (s, 3H), 3.64-3.61 (m, 0.42H), 3.53 (s, 1.13H), 3.39-3.32 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 161.9, 143.7, 141.2, 140.6, 140.3, 137.7, 133.5, 133.2, 132.4, 131.7, 129.4, 129.1, 129.0, 128.7, 128.69, 128.66, 128.62, 128.5, 128.4, 128.0, 127.6, 127.5, 127.3, 126.9, 126.5, 126.1, 125.8, 122.0, 121.2, 119.6, 119.1, 117.12, 117.10, 113.9, 112.8, 108.7, 108.2, 65.0, 63.3, 55.6, 55.5, 52.9, 50.4,

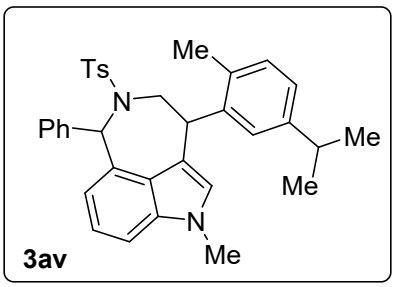
46.2, 42.9, 32.9, 32.5; FT-IR (KBr) 2924, 2854, 1736, 1458, 1341, 1153, 1093, 557 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{31}H_{29}N_2O_3S$: 509.1893, found: 509.1893.



6-Methyl-2-(naphthalen-2-ylsulfonyl)-1,4-diphenyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3aq. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; colorless solid; mp 155-156 °C; yield 71% (37 mg); mixture of diastereomers (dr = 2.5:1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.90-7.88 (m, 1H), 7.86-7.83 (m, 2.19H), 7.81-7.79 (m, 1.21H), 7.76-7.70 (m, 1H), 7.69-7.64 (m, 1.54H), 7.63-7.57 (m, 1.44H), 7.54-7.52 (m, 0.45H), 7.44-7.39 (m, 2.37H), 7.36-7.29 (m, 4.42H), 7.27-7.26 (m, 1.95H), 7.25-7.21 (m, 3.83H), 7.16-7.14 (m, 0.41H), 7.11-7.09 (m, 0.85H), 7.07-7.04 (m, 1.94H), 7.02-7.00 (m, 0.93H), 6.95 (s, 1H), 6.88 (s, 0.40H), 6.37-6.36 (m, 1H), 5.808-5.804 (m, 0.40H), 4.63-4.58 (m, 1H), 4.41-4.35 (m, 0.41H), 4.00-3.95 (m, 1H), 3.88-3.77 (m, 0.90H), 3.65 (s, 3H), 3.55-3.48 (m, 1H), 3.19 (s, 1.18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 141.0, 140.3, 139.9, 138.5, 137.5, 137.3, 136.7, 134.5, 134.1, 133.0, 132.0, 131.7, 131.6, 129.4, 129.2, 129.1, 129.0, 128.9, 128.7, 128.68, 128.62, 128.59, 128.50, 128.49, 128.43, 128.2, 128.08, 128.04, 127.7, 127.6, 127.4, 127.39, 127.37, 127.33, 127.1, 126.9, 126.5, 126.4, 125.9, 125.84, 122.80, 122.5, 121.9, 121.2, 119.7, 119.1, 116.8, 116.6, 108.9, 108.2, 65.4, 63.6, 53.0, 50.6, 46.2, 43.1, 32.7, 32.0; FT-IR (KBr) 3027, 2935, 1735, 1493, 1451, 1339, 1154, 1131, 745, 701, 665, 545 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{34}H_{29}N_2O_2S$: 529.1944, found: 529.1947.

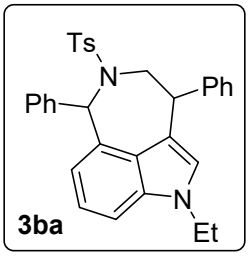


6-Methyl-1,4-diphenyl-2-(thiophen-2-ylsulfonyl)-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3ar. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.47; colorless solid; mp 149-150 °C; yield 72% (35 mg); mixture of diastereomers (dr = 2.1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.48 (m, 1H), 7.38-7.36 (m, 1H), 7.32-7.28 (m, 1.78H), 7.28-7.24 (m, 3.64H), 7.23-7.20 (m, 4.50H), 7.18-7.12 (m, 6.21H), 7.06-7.01 (m, 1.49H), 6.92-6.90 (m, 2H), 6.87-6.85 (m, 2H), 6.76 (s, 1H), 6.73-6.72 (m, 0.49H), 6.69 (s, 0.49H), 6.61-6.59 (m, 0.48H), 6.399-6.396 (m, 1H), 5.977-5.974 (m, 0.47H), 4.68-4.63 (m, 1H), 4.23-4.17 (m, 0.47H), 3.82-3.78 (m, 1.48H), 3.73-3.69 (m, 0.50H), 3.66 (s, 3H), 3.54 (s, 1.50H), 3.41-3.34 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 142.7, 140.8, 140.4, 140.27, 140.23, 137.71, 137.70, 132.8, 131.89, 131.81, 131.3, 131.1, 130.3, 129.1, 128.77, 128.71, 128.6, 128.4, 127.8, 127.7, 127.6, 127.4, 127.05, 127.01, 126.5, 126.4, 126.3, 125.7, 121.9, 121.2, 119.7, 119.1, 117.08, 117.00, 109.0, 108.3, 65.3, 63.7, 53.4, 50.6, 46.2, 42.7, 32.9, 32.7; FT-IR (KBr) 3027, 2938, 1734, 1451, 1345, 1152, 1013, 744, 701, 607, 574 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{28}H_{25}N_2O_2S_2$: 485.1352, found: 485.1351.

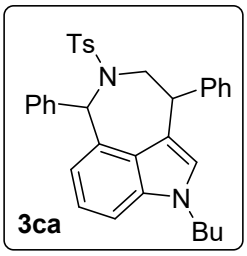


4-(5-Isopropyl-2-methylphenyl)-6-methyl-1-phenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3av. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; colorless solid; mp 173-174 °C; yield 63% (34 mg); major diastereomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.24-7.19 (m, 2H), 7.17-7.13 (m, 4H), 7.09-7.07 (m, 2H), 6.97-

6.89 (m, 4H), 6.81-6.80 (m, 1H), 6.77 (s, 1H), 6.349-6.345 (m, 1H), 4.80-4.75 (m, 1H), 3.71-3.64 (m, 4H), 3.32-3.25 (m, 1H), 2.70-2.63 (m, 1H), 2.36-2.32 (m, 6H), 1.07-1.04 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 142.8, 142.0, 141.2, 138.9, 137.7, 133.6, 133.5, 130.1, 129.3, 129.2, 128.6, 128.3, 127.6, 127.3, 126.5, 126.2, 124.3, 121.2, 119.0, 117.1, 108.1, 65.2, 49.6, 41.2, 33.6, 32.8, 24.1, 23.9, 21.5, 19.1; FT-IR (KBr) 2925, 1735, 1456, 1343, 1158, 1092, 747, 660, 549 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{35}H_{37}N_2O_2S$: 549.2570, found: 549.2576.

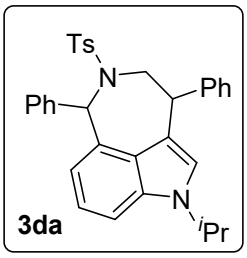


6-Ethyl-1,4-diphenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3ba. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.52; colorless solid; mp 187-188 °C; yield 74% (37 mg); major diastereomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8 Hz, 2H), 7.24-7.19 (m, 4H), 7.16-7.11 (m, 6H), 7.08-7.06 (m, 2H), 6.92-6.90 (m, 2H), 6.86-6.84 (m, 1H), 6.72 (s, 1H), 6.41 (s, 1H), 4.55-4.51 (m, 1H), 4.13-4.04 (m, 1H), 4.03-3.96 (m, 1H), 3.78-3.73 (m, 1H), 3.36-3.30 (m, 1H), 2.31 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 142.7, 141.1, 138.7, 136.6, 133.3, 129.28, 129.21, 128.7, 128.5, 128.3, 127.6, 127.38, 127.30, 126.9, 126.0, 121.0, 119.1, 117.1, 108.2, 65.2, 50.6, 46.3, 41.0, 21.5, 15.4; FT-IR (KBr) 2923, 1731, 1485, 1341, 1156, 1092, 663, 545 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{32}H_{31}N_2O_2S$: 507.2101, found: 507.2106.



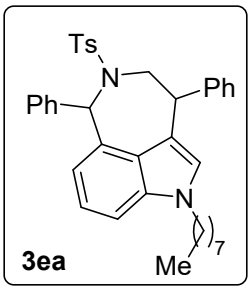
6-Butyl-1,4-diphenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3ca. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.54; colorless solid; mp 201-202 °C; yield 76%

(40 mg); mixture of diastereomers (dr = 2.7:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.66 (m, 2H), 7.33-7.27 (m, 1.45H), 7.25-7.19 (m, 6H), 7.15-7.12 (m, 7.61H), 7.05-7.03 (m, 2H), 6.99-6.92 (m, 3H), 6.85-6.81 (m, 1.70H), 6.74 (s, 1H), 6.69 (s, 0.39H), 6.38 (s, 1H), 5.96 (s, 0.37H), 4.53-4.49 (m, 1H), 4.11-4.00 (m, 1.41H), 3.93-3.84 (m, 1.36H), 3.83-3.81 (m, 0.37H), 3.78-3.73 (m, 1.36H), 3.66-3.61 (m, 0.39H), 3.36-3.29 (m, 1H), 2.29 (s, 3H), 2.24 (s, 1.18H), 1.71-1.60 (m, 2.77H), 1.25-1.21 (m, 2.79H), 0.94-0.88 (m, 4.13H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 142.7, 141.8, 141.1, 140.7, 140.4, 138.8, 136.99, 136.97, 136.93, 133.1, 132.7, 129.24, 129.20, 128.75, 128.70, 128.6, 128.5, 128.4, 128.3, 128.0, 127.6, 127.5, 127.34, 127.31, 126.9, 126.8, 126.5, 125.9, 125.0, 121.7, 121.0, 119.5, 119.0, 116.87, 116.83, 108.8, 108.3, 65.2, 63.3, 53.1, 50.6, 46.2, 46.1, 46.0, 42.9, 32.6, 32.2, 21.5, 20.2, 20.1, 13.87, 13.85; FT-IR (KBr) 2925, 1733, 1487, 1431, 1340, 1155, 1093, 1009, 665, 544 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{34}H_{35}N_2O_2S$: 535.2414, found: 535.2402.

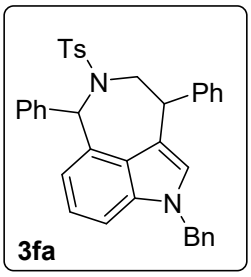


6-Isopropyl-1,4-diphenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3da. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.51; colorless solid; mp 199-200 °C; yield 71% (37 mg); mixture of diastereomers (dr = 1.3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.38-7.30 (m, 2.82H), 7.29-7.26 (m, 3H), 7.25-7.23 (m, 4H), 7.21-7.19 (m, 1.33H), 7.17-7.14 (m, 6.74H), 7.13-7.10 (m, 2.13H), 7.05-7.03 (m, 2.14H), 7.01-6.97 (m, 1.44H), 6.96-6.93 (m, 2.61H), 6.86-6.84 (m, 1H), 6.82-6.80 (m, 1.13H), 6.73 (s, 1H), 6.70 (s, 0.74H), 6.508-6.505 (m, 1H), 6.05-6.04 (m, 0.72H), 4.63-4.58 (m, 1.16H), 4.57-4.53 (m, 1H), 4.46-4.39 (m, 0.76H), 4.11-4.05 (m, 0.76H), 3.79-3.72 (m, 1.76H), 3.65-3.60 (m, 0.76H), 3.34-3.28 (m, 1H), 2.29 (s, 3H), 2.22 (s, 2.16H), 1.41 (d, *J* = 6.8 Hz, 3H), 1.36 (d, J = 6.4 Hz, 3H), 1.33-1.29 (m, 4.56H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 142.6, 141.7, 141.1, 140.6, 140.3, 138.7, 136.9, 136.5, 133.1, 132.6, 129.2, 129.1, 128.79, 128.70, 128.68, 128.66, 128.5, 128.4, 128.3, 128.0, 127.6, 127.5, 127.35, 127.31, 126.88, 126.82, 126.7, 126.6, 126.0, 123.8, 121.5, 120.9, 120.8,

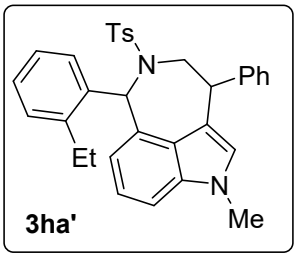
119.6, 119.1, 116.89, 116.81, 108.9, 108.2, 65.3, 63.3, 53.2, 50.8, 47.1, 46.9, 46.3, 43.1, 22.98, 22.97, 22.6, 22.5, 21.5, 21.4; FT-IR (KBr) 3066, 2977, 2929, 1734, 1372, 1287, 1242, 1157, 1092, 1046, 747, 701, 666, 544 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{33}H_{33}N_2O_2S$: 521.2257, found: 521.2256.



6-Octyl-1,4-diphenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3ea. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.51; colorless solid; mp 207-208 °C; yield 78% (46 mg); mixture of diastereomers (dr = 2.7:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8 Hz, 2H), 7.34-7.28 (m, 1.41H), 7.24-7.20 (m, 5.40H), 7.16-7.14 (m, 7H), 7.12-7.10 (m, 1H), 7.07-7.05 (m, 2.12H), 6.99-6.97 (m, 1.18H), 6.93-6.91 (m, 2.15H), 6.86-6.82 (m, 1.88H), 6.74 (s, 1H), 6.69 (s, 0.42H), 6.39 (s, 1H), 5.97 (s, 0.36H), 4.55-4.51 (m, 1H), 4.12-4.06 (m, 0.60H), 4.03-3.89 (m, 2H), 3.88-3.81 (m, 0.86H), 3.79-3.74 (m, 1.70H), 3.67-3.62 (m, 0.42H), 3.36-3.29 (m, 1H), 2.31 (s, 3H), 2.24 (s, 1.15H), 1.75-1.70 (m, 2.15H), 1.67-1.62 (m, 0.84H), 1.31-1.26 (m, 13.80H), 0.88 (t, *J* = 6.4 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 142.7, 141.8, 141.1, 140.7, 140.4, 138.8, 136.97, 136.91, 133.2, 132.6, 129.2, 129.1, 128.76, 128.71, 128.66, 128.65, 128.5, 128.4, 128.3, 128.05, 128.02, 127.6, 127.5, 127.35, 127.30, 126.9, 126.8, 126.5, 125.9, 125.1, 121.7, 121.0, 119.5, 119.0, 116.85, 116.82, 108.8, 108.3, 65.2, 63.3, 53.1, 50.6, 46.4, 46.34, 46.30, 42.9, 31.8, 30.5, 30.1, 29.8, 29.35, 29.32, 29.2, 27.05, 27.01, 22.7, 21.5, 14.2; FT-IR (KBr) 2925, 2854, 1600, 1493, 1342, 1158, 1092, 743, 701, 665, 544 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{38}H_{43}N_2O_2S$: 591.3040, found: 591.3030.

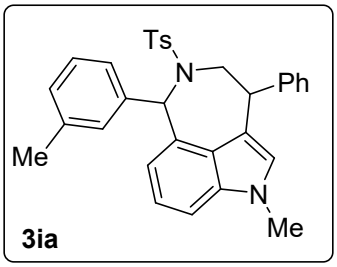


6-Benzyl-1,4-diphenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3fa. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 197-198 °C; yield 72% (41 mg); mixture of diastereomers (dr = 2.1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8 Hz, 2H), 7.32-7.27 (m, 5.12H), 7.24-7.21 (m, 6.12H), 7.19-7.15 (m, 7H), 7.11-7.06 (m, 4.56H), 7.03-6.99 (m, 4.60H), 6.96-6.94 (m, 2.24H), 6.88-6.86 (m, 2H), 6.77 (s, 1H), 6.69 (s, 0.53H), 6.47 (s, 1H), 6.11 (s, 0.46H), 5.29-5.25 (m, 1H), 5.13-5.09 (m, 1H), 4.55-4.51 (m, 1H), 4.09 (t, *J* = 12 Hz, 0.48H), 3.84-3.76 (m, 1.45H), 3.69-3.64 (m, 0.48H), 3.39-3.33 (m, 1H), 2.31 (s, 3H), 2.26 (s, 1.51H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 142.8, 142.1, 141.1, 140.6, 140.5, 138.9, 137.5, 137.4, 137.3, 137.0, 133.3, 132.9, 129.3, 129.1, 128.8, 128.74, 128.71, 128.69, 128.67, 128.61, 128.5, 128.4, 127.9, 127.75, 127.70, 127.6, 127.5, 127.3, 126.99, 126.94, 126.7, 126.5, 126.1, 125.8, 122.1, 121.4, 119.8, 119.4, 117.75, 117.72, 109.2, 108.7, 65.1, 63.2, 53.1, 50.6, 50.1, 50.0, 46.2, 42.8, 21.6; FT-IR (KBr) 2924, 1735, 1451, 1339, 1155, 745, 698, 665, 544 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{37}H_{33}N_2O_2S$: 569.2257, found: 569.2253.



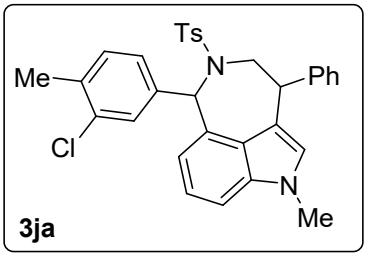
6-Methyl-1-(2-ethylphenyl)-4-phenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3ha'. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.60; colorless solid; mp 143-144 °C; yield 83% (43 mg); mixture of diastereomers (dr = 2.0:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8 Hz, 2H), 7.38 (d, *J* = 8 Hz, 0.51H), 7.32-7.27 (m, 1.67H), 7.25-7.23 (m, 2.40H), 7.21-7.20 (m, 1.64H), 7.19-7.15 (m, 2.67H), 7.13-7.10 (m, 4H), 7.07-7.02 (m, 2H), 7.01-6.99 (m, 2H),

6.97-6.90 (m, 2.36H), 6.85-6.84 (m, 1H), 6.78-6.75 (m, 2.48H), 6.68-6.63 (m, 2H), 6.22 (s, 1H), 5.77 (s, 0.48H), 4.53-4.49 (m, 1H), 4.18-4.12 (m, 0.53H), 4.02-3.99 (m, 0.52H), 3.75-3.71 (m, 1H), 3.58 (s, 3H), 3.46 (s, 1.47H), 3.44-3.39 (m, 1H), 3.30-3.25 (m, 0.52H), 3.20-3.15 (m, 0.50H), 3.11-2.96 (m, 2.49H), 2.22 (s, 1.48H), 2.17 (s, 3H), 1.43 (t, J = 7.5 Hz, 1.50H), 1.34 (t, J = 7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 144.38, 144.31, 142.1, 141.2, 140.7, 137.9, 137.7, 137.5, 137.0, 136.8, 136.0, 134.6, 133.3, 131.3, 130.4, 129.5, 129.0, 128.9, 128.7, 128.6, 128.5, 128.3, 128.2, 127.6, 127.5, 127.36, 127.33, 126.8, 126.7, 126.3, 126.2, 125.4, 125.3, 122.1, 121.4, 119.3, 118.8, 117.0, 116.6, 108.3, 107.8, 63.2, 61.8, 52.5, 49.7, 44.5, 44.2, 32.7, 32.4, 25.0, 24.6, 21.5, 21.3, 15.8, 14.6; FT-IR (KBr) 2924, 1734, 1486, 1345, 1151, 1094, 669, 547 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{33}H_{33}N_2O_2S$: 521.2257, found: 521.2257; $[\alpha]_D^{25}$ = +32.86 (c = 0.07, $CHCl_3$); HPLC: *ee* for major diastereomer = 93% *ee* [YMC Chiral ART Cellulose-SC column, hexane/^{i}PrOH = 90:10, flow rate: 1 mL/min, λ= 254 nm, t_R = 13.93 min (major), 15.40 min (minor)].

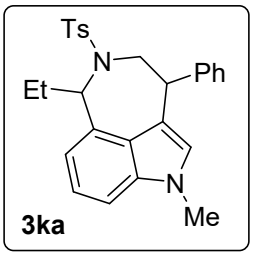


6-Methyl-4-phenyl-1-(*m*-tolyl)-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3ia. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; colorless solid; mp 140-141 °C; yield 79% (40 mg); mixture of diastereomers (dr = 1.3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2H), 7.30-7.27 (m, 1.95H), 7.24-7.22 (m, 2.84H), 7.20-7.14 (m, 6.41H), 7.13-7.08 (m, 3.84H), 7.04-7.01 (m, 2.55H), 6.99-6.93 (m, 2.72H), 6.87-6.82 (m, 2.21H), 6.65-6.62 (m, 2.53H), 6.59-6.57 (m, 1H), 6.376-6.372 (m, 1H), 5.92-5.91 (m, 0.77H), 4.58-4.53 (m, 1H), 4.18-4.12 (m, 0.72H), 3.84-3.80 (m, 0.76H), 3.78-3.73 (m, 1H), 3.66 (s, 3H), 3.64-3.59 (m, 0.80H), 3.53 (s, 2.31H), 3.40-3.33 (m, 1H), 2.34 (s, 3H), 2.27-2.26 (m, 4.30H), 2.14(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 142.8, 141.8, 141.0, 140.7, 140.1, 139.0, 138.3, 138.0, 137.7, 137.6, 137.0, 133.5, 132.7, 129.7, 129.4, 129.0, 128.7, 128.6, 128.59, 128.50, 128.4, 128.3, 128.1, 127.3, 126.9, 126.6, 126.3, 126.1, 125.8, 125.2, 121.9, 121.2, 119.6, 119.0, 117.1, 108.5, 108.1, 65.1, 63.3, 52.8, 50.7,

46.7, 43.0, 32.9, 32.6, 21.6, 21.56, 21.50, 21.4; FT-IR (KBr) 2924, 1729, 1484, 1342, 1159, 1096, 660, 543 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{32}H_{31}N_2O_2S$: 507.2101, found: 507.2110.

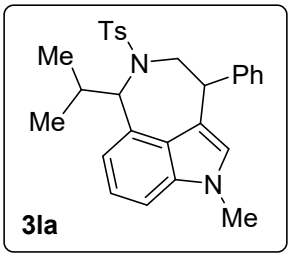


1-(3-Chloro-4-methylphenyl)-6-methyl-4-phenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3ja. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; colorless solid; mp 144-145 °C; yield 72% (39 mg); mixture of diastereomers (dr = 1.5:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.30-7.27 (m, 2.93H), 7.24-7.21 (m, 2.41H), 7.19-7.11 (m, 8H), 7.08-7.02 (m, 2.14H), 7.01-6.95 (m, 2H), 6.85-6.83 (m, 2H), 6.66-6.65 (m, 2H), 6.61 (s, 1H), 6.58 (s, 0.62H), 6.385-6.381 (m, 1H), 5.95-5.94 (m, 0.64H), 4.56-4.51 (m, 1H), 4.19-4.12 (m, 0.64H), 3.87-3.83 (m, 0.64H), 3.81-3.76 (m, 1.64H), 3.67 (s, 3H), 3.54 (s, 1.94H), 3.35-3.28 (m, 1H), 2.36-2.35 (m, 4.86H), 2.27-2.25 (m, 4.91H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 143.2, 142.1, 140.7, 140.4, 139.8, 138.7, 137.7, 137.0, 136.8, 135.4 135.3, 134.7, 134.5, 132.8, 131.9, 131.1, 130.7, 129.5, 129.1, 128.7, 128.54, 128.51, 127.4, 127.2, 127.0, 126.6, 126.3, 125.7, 122.0, 121.3, 119.6, 119.0, 117.0, 108.8, 108.4, 64.5, 62.8, 52.8, 50.7, 46.7, 43.0, 32.9, 32.6, 21.6, 21.5, 19.8, 19.7; FT-IR (KBr) 2926, 1745, 1490, 1351, 1155, 1090, 745, 548 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{32}H_{30}ClN_2O_2S$: 541.1711, found: 541.1715.

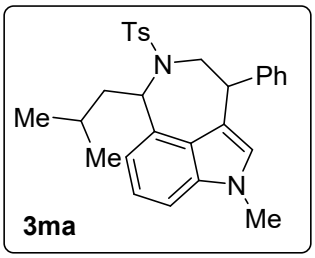


1-Ethyl-6-methyl-4-phenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3ka. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; colorless solid; mp 182-183 °C; yield 75% (33 mg); major diastereomer; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8 Hz, 2H),

7.36-7.28 (m, 5H), 7.15-7.10 (m, 4H), 6.90-6.88 (m, 1H), 6.338-6.334 (m, 1H), 5.28-5.24 (m, 1H), 4.54-4.50 (m, 1H), 4.02-3.97 (m, 1H), 3.62 (s, 3H), 3.59-3.52 (m, 1H), 2.32 (s, 3H), 1.92-1.78 (m, 2H), 0.75 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 142.7, 138.8, 137.7, 137.4, 129.3, 128.8, 128.7, 127.2, 127.1, 124.0, 121.1, 117.4, 116.8, 107.7, 63.5, 49.2, 46.8, 32.8, 29.6, 21.5, 11.6; FT-IR (KBr) 2926, 1736, 1454, 1340, 1155, 1032, 749, 703, 657, 583 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{27}H_{29}N_2O_2S$: 445.1944, found: 445.1950.

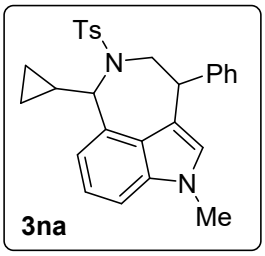


1-Isopropyl-6-methyl-4-phenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3la. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; colorless solid; mp 183-184 °C; yield 63% (29 mg); major diastereomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.4 Hz, 2H), 7.35-7.34 (m, 3H), 7.31-7.27 (m, 2H), 7.16-7.05 (m, 4H), 6.89-6.87 (m, 1H), 6.337-6.333 (m, 1H), 4.82 (d, J = 10 Hz, 1H), 4.50-4.45 (m, 1H), 4.04-3.99 (m, 1H), 3.64-3.57 (m, 4H), 2.30 (s, 3H), 2.10-2.06 (m, 1H), 0.90 (d, J = 6.8 Hz, 3H), 0.77 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 142.5, 138.6, 137.8, 135.0, 129.2, 128.8, 128.7, 127.3, 127.1, 124.6, 120.3, 119.3, 116.8, 108.1, 68.5, 49.8, 46.6, 32.8, 31.7, 21.56, 21.54, 20.9; FT-IR (KBr) 2928, 1456, 1341, 1302, 1150, 751, 699, 652, 543 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{28}H_{31}N_2O_2S$: 459.2101, found: 459.2101.



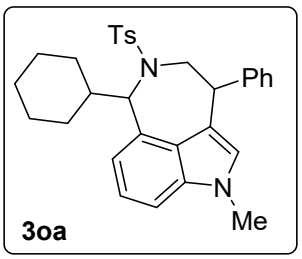
1-Isobutyl-6-methyl-4-phenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3ma. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; colorless solid; mp 179-180 °C;

yield 61% (29 mg); major diastereomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.4 Hz, 2H), 7.36-7.28 (m, 5H), 7.16-7.10 (m, 2H), 7.07-7.05 (m, 2H), 6.87-6.85 (m, 1H), 6.306-6.302 (m, 1H), 5.47-5.43 (m, 1H), 4.50-4.45 (m, 1H), 4.01-3.96 (m, 1H), 3.66-3.62 (m, 1H), 3.60 (s, 3H), 2.30 (s, 3H), 1.85 (t, J = 10 Hz, 1H), 1.54-1.49 (m, 2H), 0.90-0.85 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 142.6, 138.7, 137.7, 137.6, 129.2, 128.8, 128.7, 128.6, 127.4, 127.1, 124.2, 121.1, 117.3, 116.6, 107.6, 59.8, 49.3, 46.4, 46.0, 32.8, 24.7, 23.2, 21.9, 21.5; FT-IR (KBr) 2936, 1457, 1339, 1305, 1150, 980, 751, 703, 657, 546 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{29}H_{33}N_2O_2S$: 473.2257, found: 473.2281.

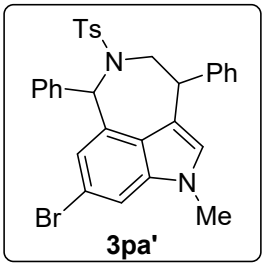


1-Cyclopropyl-6-methyl-4-phenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole

3na. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; colorless solid; mp 177-178 °C; yield 69% (31 mg); major diastereomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.4 Hz, 2H), 7.37-7.27 (m, 5H), 7.18-7.12 (m, 4H), 6.90-6.88 (m, 1H), 6.365-6.361 (m, 1H), 4.91 (d, J = 7.2 Hz, 1H), 4.54-4.49 (m, 1H), 4.13-4.01 (m, 2H), 3.63 (s, 3H), 2.33 (s, 3H), 1.15-1.06 (m, 1H), 0.59-0.54 (m, 1H), 0.40-0.32 (m, 2H), 0.13-0.06 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 142.7, 138.9, 137.6, 134.9, 129.4, 128.9, 128.8, 128.7, 127.1, 127.0, 124.7, 120.9, 117.7, 117.1, 108.1, 65.8, 50.4, 47.3, 32.8, 21.5, 16.9, 6.5, 3.2; FT-IR (KBr) 2924, 1454, 1338, 1305, 1154, 1093, 981, 752, 703, 659, 548 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{28}H_{29}N_2O_2S$: 457.1944, found: 457.1947.

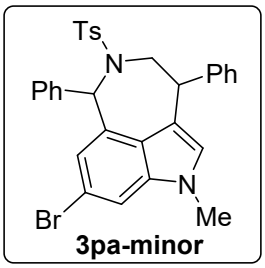


1-Cyclohexyl-6-methyl-4-phenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3oa. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; colorless solid; mp 188-189 °C; yield 72% (36 mg); mixture of diastereomers (dr = 2.8:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.40-7.27 (m, 6.72H), 7.16-7.03 (m, 5H), 6.85-6.79 (m, 1.80H), 6.337-6.333 (m, 1H), 5.926-5.922 (m, 0.35H), 5.03 (d, *J* = 11.2 Hz, 0.35H), 4.90 (d, *J* = 9.6 Hz, 1H), 4.63-4.58 (m, 0.36H), 4.46-4.41(m, 1H), 4.11-4.05 (m, 0.42H), 4.03-3.98 (m, 1H), 3.94-3.89 (m, 0.39H), 3.62 (s, 3H), 3.60-3.53 (m, 1H), 3.50 (s, 1H), 2.29 (s, 3H), 2.22 (s, 1H), 1.68-1.60 (m, 4.05H), 1.13-0.76 (m, 10.81H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 142.5, 138.7, 137.8, 134.5, 133.6, 129.1, 128.9, 128.8, 128.7, 128.6, 128.3, 127.5, 127.3, 127.1, 126.7, 124.7, 121.3, 120.3, 120.2, 119.5, 117.4, 116.7, 108.1, 108.0, 67.5, 67.0, 53.0, 49.8, 46.4, 43.4, 40.3, 32.8, 32.6, 31.9, 31.7, 31.4, 31.0, 29.8, 26.5, 26.3, 26.2, 21.5, 21.4; FT-IR (KBr) 2848, 1736, 1493, 1445, 1417, 1239, 1046, 747 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{31}H_{35}N_2O_2S$: 499.2414, found: 499.2415.



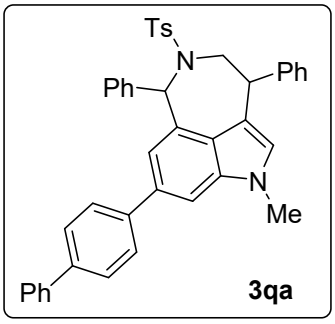
3pa'

8-Bromo-6-methyl-1,4-diphenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3pa'. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 170-171 °C; yield 56% (32 mg); major diastereomer; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8 Hz, 2H), 7.36 (s, 1H), 7.27 (s, 1H), 7.24-7.19 (m, 2H), 7.17-7.13 (m, 7H), 6.99 (s, 1H), 6.85-6.83 (m, 2H), 6.62 (s, 1H), 6.35 (s, 1H), 4.53-4.50 (m, 1H), 3.75-3.72 (m, 1H), 3.63 (s, 3H), 3.34-3.29 (m, 1H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 143.1, 140.3, 138.5, 138.4, 135.2, 129.7, 129.5, 129.1, 128.69, 128.64, 128.5, 127.8, 127.3, 127.1, 124.9, 121.8, 117.6, 114.7, 111.3, 64.6, 50.3, 46.4, 33.0, 21.6; FT-IR (KBr) 2924, 1735, 1457, 1346, 1154, 1092, 680, 550 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{31}H_{28}BrN_2O_2S$: 571.1049, found: 571.1039; $[\alpha]_D^{25}$ = +15 (c = 0.02, $CHCl_3$); HPLC: *ee* for major diastereomer = >88% *ee* [YMC Chiral ART Cellulose-SC column, hexane/^{i}PrOH = 90:10, flow rate: 1 mL/min, λ= 254 nm, t_R = 12.54 min (major), 16.93 min (minor)].



3pa-minor

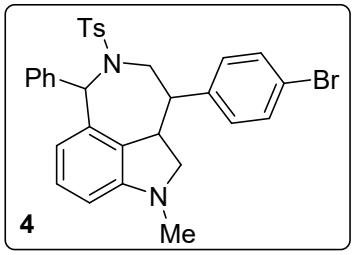
8-Bromo-6-methyl-1,4-diphenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3pa. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.46; colorless solid; mp 170-171 °C; yield 28% (16 mg); minor diastereomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 6H), 7.25-7.21 (m, 3H), 7.20-7.17 (m, 2H), 7.065-7.061 (m, 1H), 7.02-6.99 (m, 2H), 6.89 (d, *J* = 8 Hz, 2H), 6.54 (s, 1H), 5.934-5.930 (m, 1H), 4.22-4.16 (m, 1H), 3.74-3.69 (m, 1H), 3.64-3.59 (m, 1H), 3.50 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 140.2, 139.4, 138.3, 136.9, 134.2, 128.78, 128.72, 128.4, 127.9, 127.8, 127.5, 126.8, 126.7, 125.4, 122.6, 117.6, 115.2, 111.5, 62.7, 52.8, 42.9, 32.7, 21.5; FT-IR (KBr) 2926, 1735, 1459, 1347, 1154, 1092, 683, 549 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{31}H_{28}BrN_2O_2S$: 571.1049, found: 571.1039.



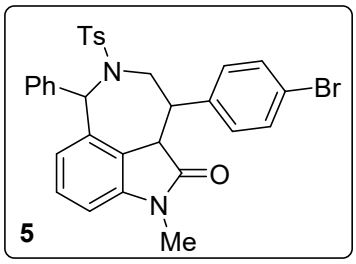
3qa

8-([1,1'-Biphenyl]-4-yl)-6-methyl-1,4-diphenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 3qa. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.51; colorless solid; mp 174-175 °C; yield 77% (49 mg); mixture of diastereomers (dr = 2.2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.72 (m, 5H), 7.70-7.63 (m, 5H), 7.50-7.43 (m, 4H), 7.38-7.27 (m, 5.89H), 7.24-7.13 (m, 8.70H), 7.07-7.04 (m, 0.69H), 6.96-6.94 (m, 1.46H), 6.83-6.80 (m, 1.44H), 6.71 (s, 0.42H), 6.417-6.414 (m, 1H), 6.00-5.99 (m, 0.45H), 4.58-4.54 (m, 1H), 4.27-4.21 (m, 0.45H), 3.81-3.76 (m, 1.47H), 3.73 (s, 3H), 3.70-3.66 (m, 0.50H), 3.60 (s, 1.34H), 3.42-3.35 (m, 1H), 2.35 (s, 3H), 2.25 (s, 1.31H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 143.0, 141.9, 141.1, 140.98, 140.95,

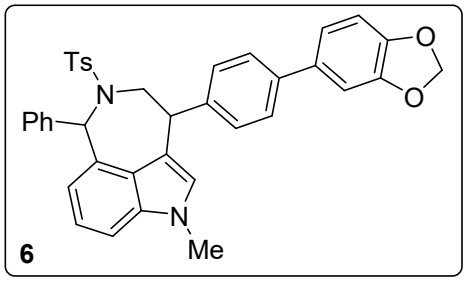
140.8, 140.5, 140.0, 139.8, 139.7, 138.7, 138.3, 138.2, 137.0, 135.1, 134.1, 133.7, 132.8, 129.7, 129.4, 129.2, 128.97, 128.94, 128.69, 128.64, 128.4, 128.3, 128.1, 127.79, 127.71, 127.6, 127.5, 127.4, 127.18, 127.15, 127.0, 126.8, 126.6, 126.0, 125.4, 119.4, 118.6, 117.25, 117.23, 106.9, 106.5, 65.2, 63.4, 53.1, 50.6, 46.4, 42.9, 33.0, 32.7, 21.6, 21.5; FT-IR (KBr) 2984, 1733, 1462, 1418, 1240, 1045, 752 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{43}H_{37}N_2O_2S$: 645.2570, found: 645.2575.



4-(4-Bromophenyl)-6-methyl-1-phenyl-2-tosyl-2,3,4,4a,5,6-hexahydro-1H-azepino[5,4,3-cd]indole 4.[3] To a solution of **3af** (0.1 mmol, 1 equiv, 57 mg) in AcOH (5 mL) at 0 °C was added $NaBH_3CN$ (0.5 mmol, 5 equiv, 31 mg) portion wise. The reaction was allowed to stir at room temperature for 12 h. After complete consumption of the starting material, saturated aq. NaOH (5 mL) was added slowly to the reaction mixture at 0 °C and extracted with ethyl acetate (3 x 10 mL). Subsequently, the combined organic layers were washed with brine (5 mL) and water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using hexane and ethyl acetate as an eluent to afford **4**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 165-166 °C; yield 85% (48 mg); major diastereomer; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.24-7.21 (m, 5H), 7.16-7.12 (m, 1H), 6.89-6.87 (m, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.49 (d, *J* = 7.6 Hz, 1H), 6.33 (s, 1H), 3.75-3.70 (m, 1H), 3.57-3.47 (m, 1H), 3.13-3.06 (m, 2H), 2.78-2.71 (m, 1H), 2.64 (s, 3H), 2.41 (s, 3H), 2.40-2.35 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 143.2, 140.2, 138.4, 137.7, 132.0, 129.6, 129.4, 128.9, 128.77, 128.70, 128.4, 128.2, 127.7, 127.4, 119.1, 107.4, 64.2, 61.5, 50.1, 49.0, 46.2, 35.9, 21.6; FT-IR (KBr) 2924, 1735, 1597, 1486 1339, 1156, 1008, 661, 601, 543 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{31}H_{30}BrN_2O_2S$: 573.1206, found: 573.1205.



4-(4-Bromophenyl)-6-methyl-1-phenyl-2-tosyl-1,2,3,4,4a,6-hexahydro-5H-azepino[5,4,3-cd]indol-5-one 5.[4] To a solution of **3af** (0.1 mmol, 1 equiv, 57 mg) and KBr (0.01 mmol, 0.1 equiv, 2 mg) in ^{t}BuOH/H_2O (v/v 20:1) (2 mL) at room temperature, was added oxone (0.12 mmol, 1.2 equiv, 37 mg) and allowed to stir for 4 h. After completion, as monitored by TLC, the reaction mixture was quenched with saturated aq. $Na_2S_2O_3$ (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine (5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using hexane and ethyl acetate as an eluent to afford **5**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.41; colorless solid; mp 179-180 ^{o}C; yield 77% (45 mg); major diastereomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.38 (m, 3H), 7.25-7.23 (m, 3H), 7.12-7.10 (m, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.87-6.82 (m, 3H), 6.56 (s, 1H), 6.41 (d, *J* = 8.8 Hz, 2H), 4.37-4.32 (m, 1H), 3.67-3.62 (m, 2H), 3.44-3.41 (m, 1H), 3.01 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9, 144.8, 143.2, 138.6, 137.4, 136.7, 135.9, 131.2, 130.0, 129.7, 129.3, 129.0, 128.16, 128.11, 126.7, 126.2, 122.8, 121.2, 108.2, 64.4, 50.3, 49.2, 42.9, 26.4, 21.7; FT-IR (KBr) 2922, 2851, 1715, 1608, 1470, 1331, 1156, 1009, 600, 597, 541 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{31}H_{28}BrN_2O_3S$: 587.0999, found: 587.1001.



4-(4-(benzo[d][1,3]dioxol-5-yl)phenyl)-6-methyl-1-phenyl-2-tosyl-2,3,4,6-tetrahydro-1H-azepino[5,4,3-cd]indole 6.[5] To a solution of **3af** (0.1 mmol, 1 equiv, 57 mg) in toluene/EtOH (1:1,

3 mL), was added the benzo[d][1,3]dioxol-5-ylboronic acid (0.1 mmol, 1 equiv, 16 mg), $Pd(PPh_3)_4$ (3 mol %, 3 mg), Na_2CO_3 (0.1 mmol, 1 equiv, 11 mg) and H_2O (100 µL). The mixture was stirred at 100 °C for 12 h under a nitrogen atmosphere. After 12 h, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (10 mL) and washed with brine (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using hexane and ethyl acetate as eluent to give **6**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.49; colorless solid; mp 149-150 °C; yield 90% (55 mg); mixture of diastereomers (dr = 1.6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8 Hz, 2.96H), 7.35-7.27 (m, 2H), 7.25-7.14 (m, 10.32H), 7.13-7.11 (m, 2.20H), 7.04-7.00 (m, 4.63H), 6.91-6.82 (m, 5.55H), 6.74 (s, 1H), 6.69 (s, 0.58H), 6.433-6.430 (m, 1H), 6.00 (s, 1.27H), 5.98 (s, 2H), 4.58-4.54 (m, 1H), 4.19-4.13 (m, 0.60H), 3.85-3.76 (m, 1.60H), 3.69-3.64 (m, 3.60H), 3.55 (s, 1.79H), 3.40-3.33 (m, 1H), 2.34 (s, 3H), 2.26 (s, 1.81H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.28, 148.23, 147.2, 147.1, 142.9, 142.4, 141.8, 141.1, 140.3, 139.8, 139.6, 139.4, 138.8, 137.7, 137.6, 137.0, 135.3, 135.2, 133.3, 132.6, 129.4, 129.17, 129.11, 129.08, 129.06, 128.6, 128.41, 128.40, 128.0, 127.64, 127.60, 127.3, 127.0, 126.6, 126.5, 126.2, 125.8, 122.0, 121.2, 120.5, 119.6, 119.1, 117.02, 117.00, 108.7, 108.6, 108.2, 107.63, 107.61, 101.29, 101.26, 65.1, 63.4, 52.9, 50.5, 46.0, 42.5, 32.9, 32.6, 21.58, 21.51; FT-IR (KBr) 2922, 1735, 1481, 1340, 1224, 1156, 1039, 808, 544 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{38}H_{33}N_2O_4S$: 613.2156, found: 613.2153.

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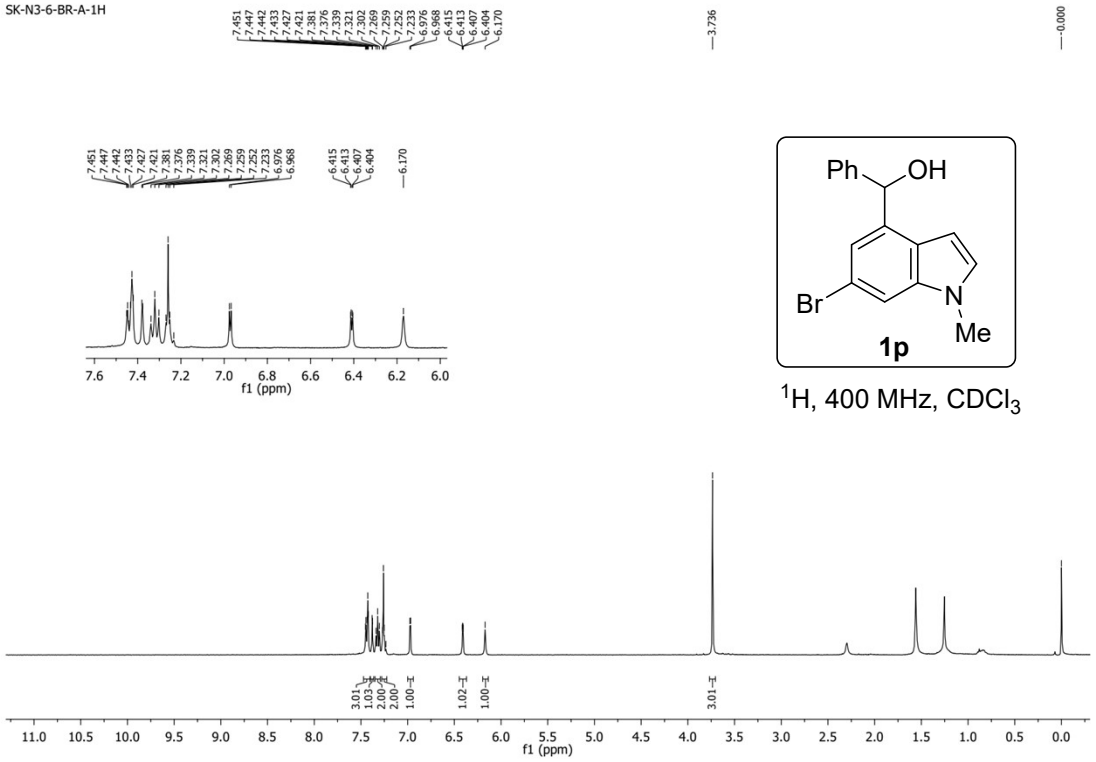
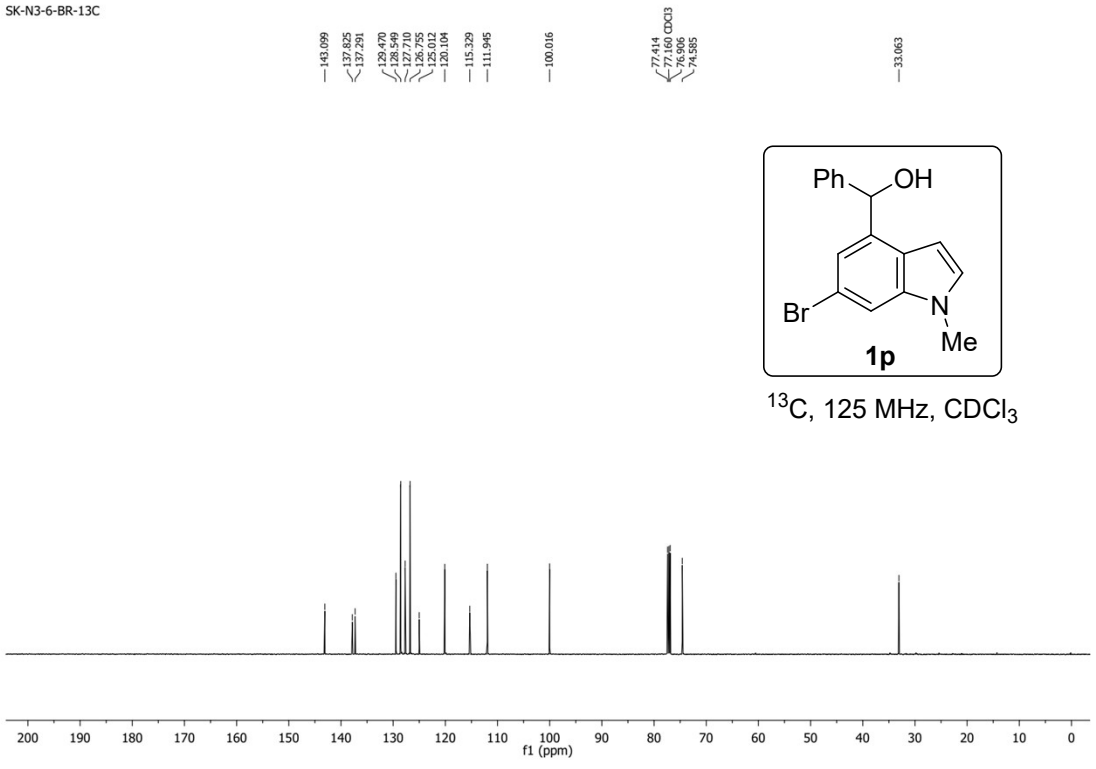
^{1}H ,^{13}C and ^{19}F NMR spectra



^{1}H, 400 MHz, $CDCl_3$



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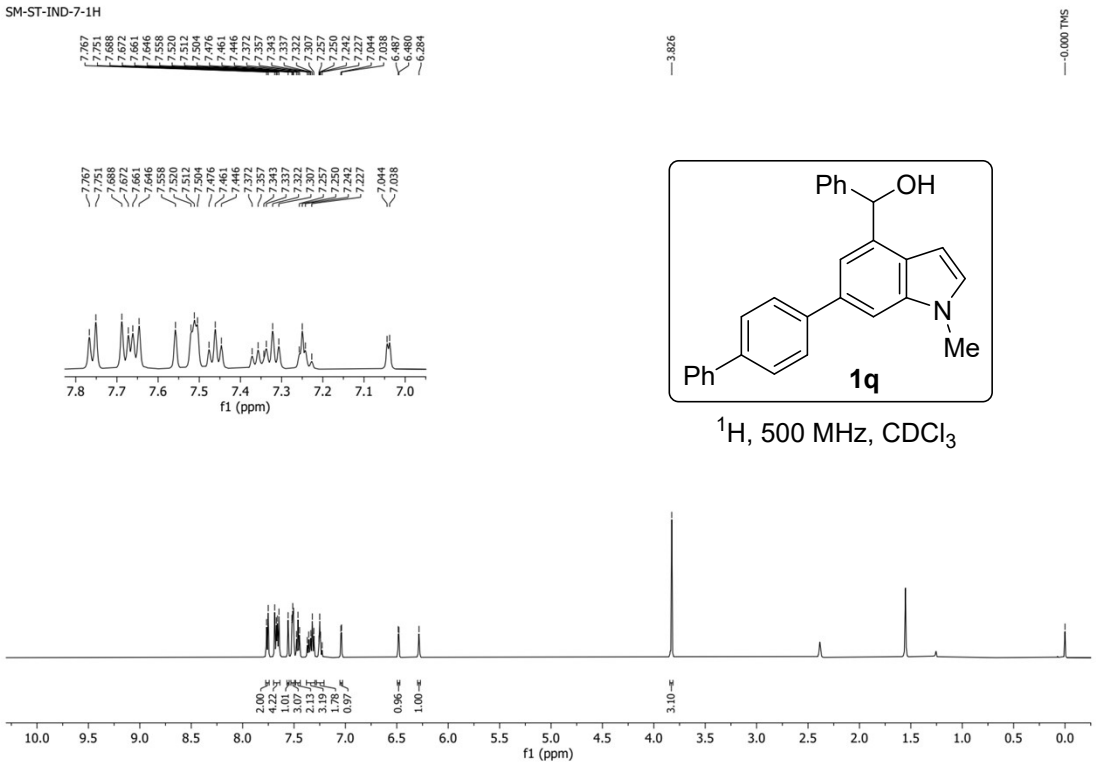
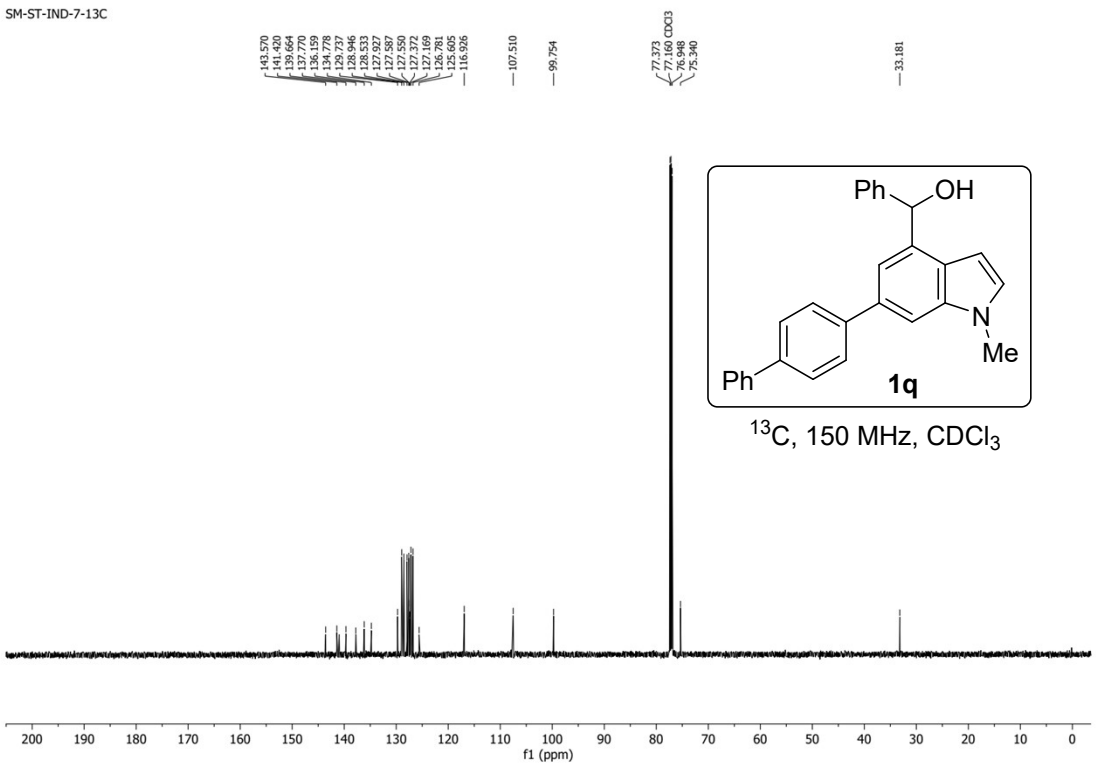
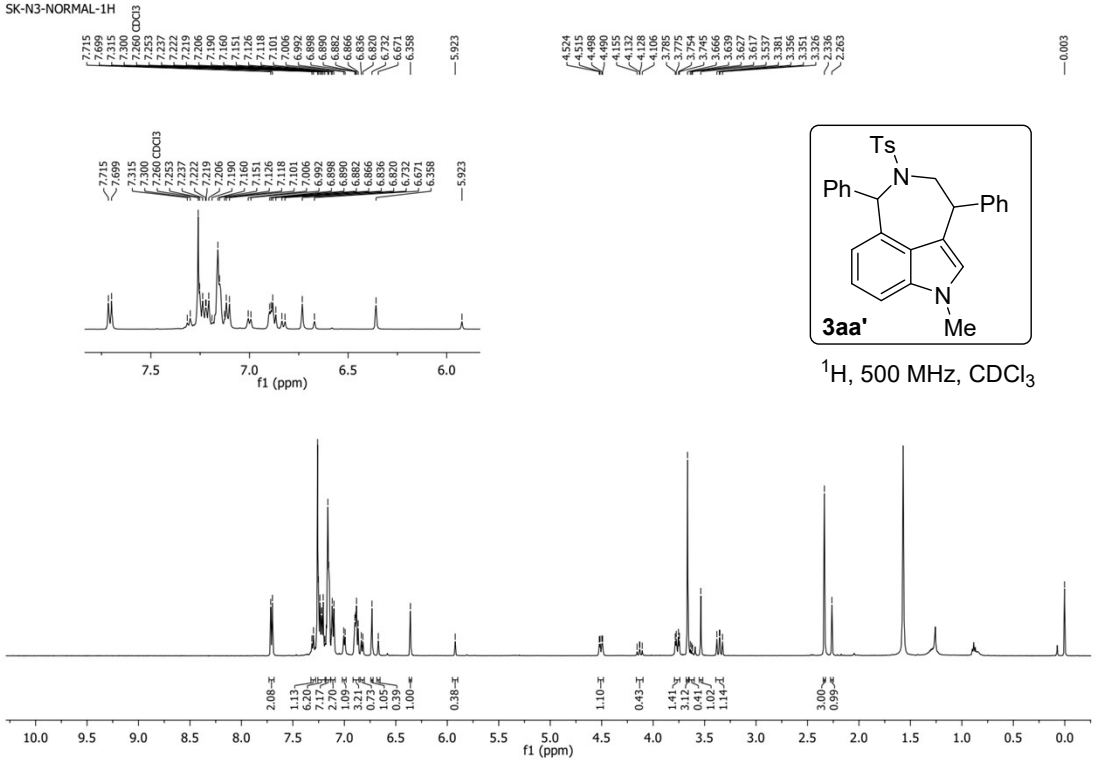


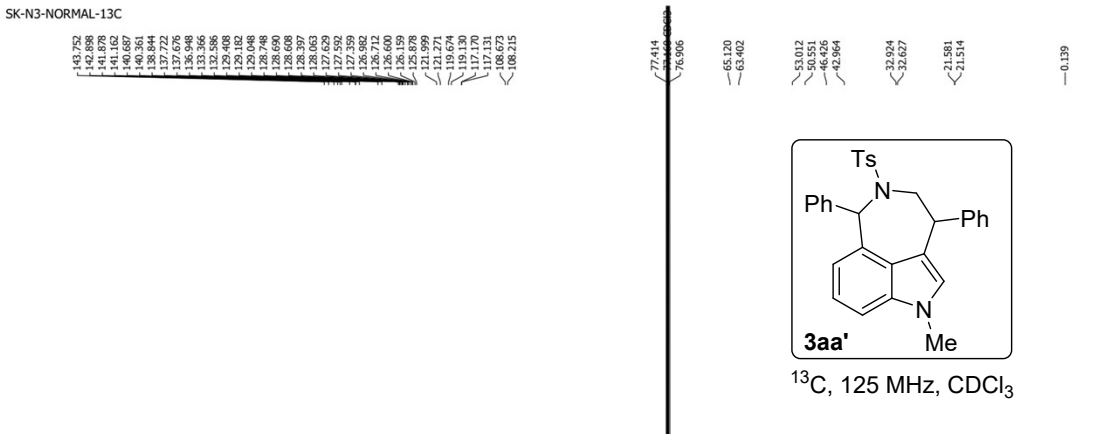
^{1}H, 500 MHz, $CDCl_3$



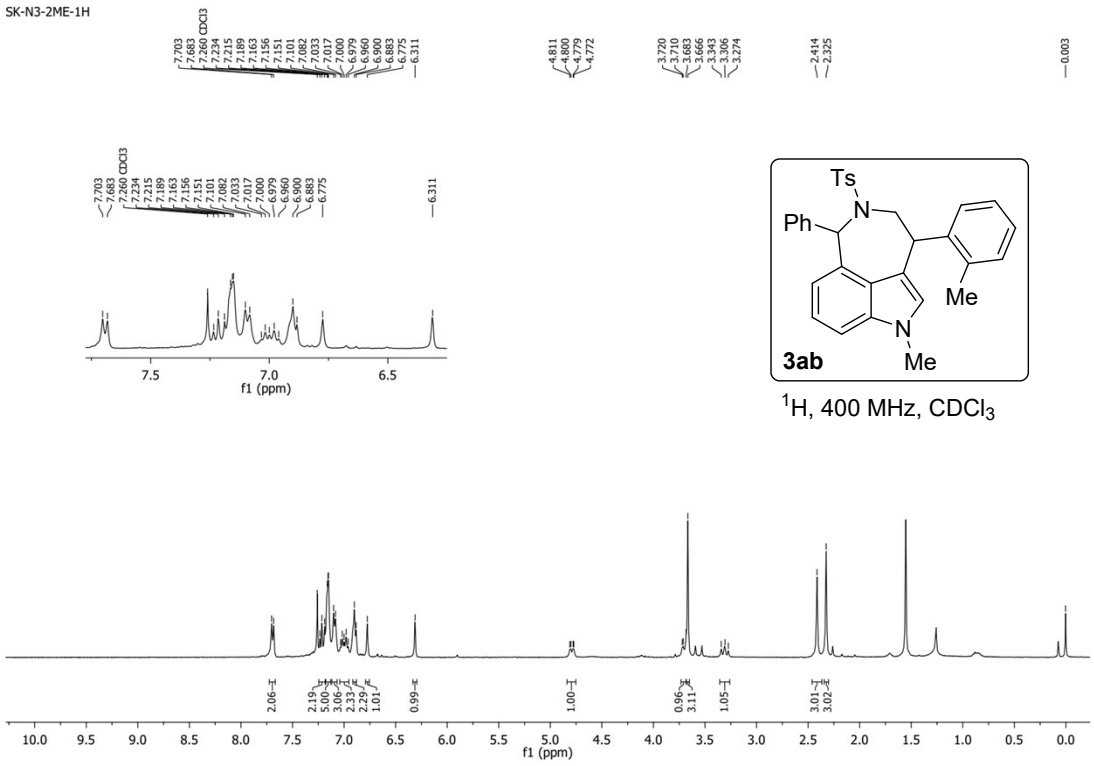
^{13}C, 150 MHz, $CDCl_3$



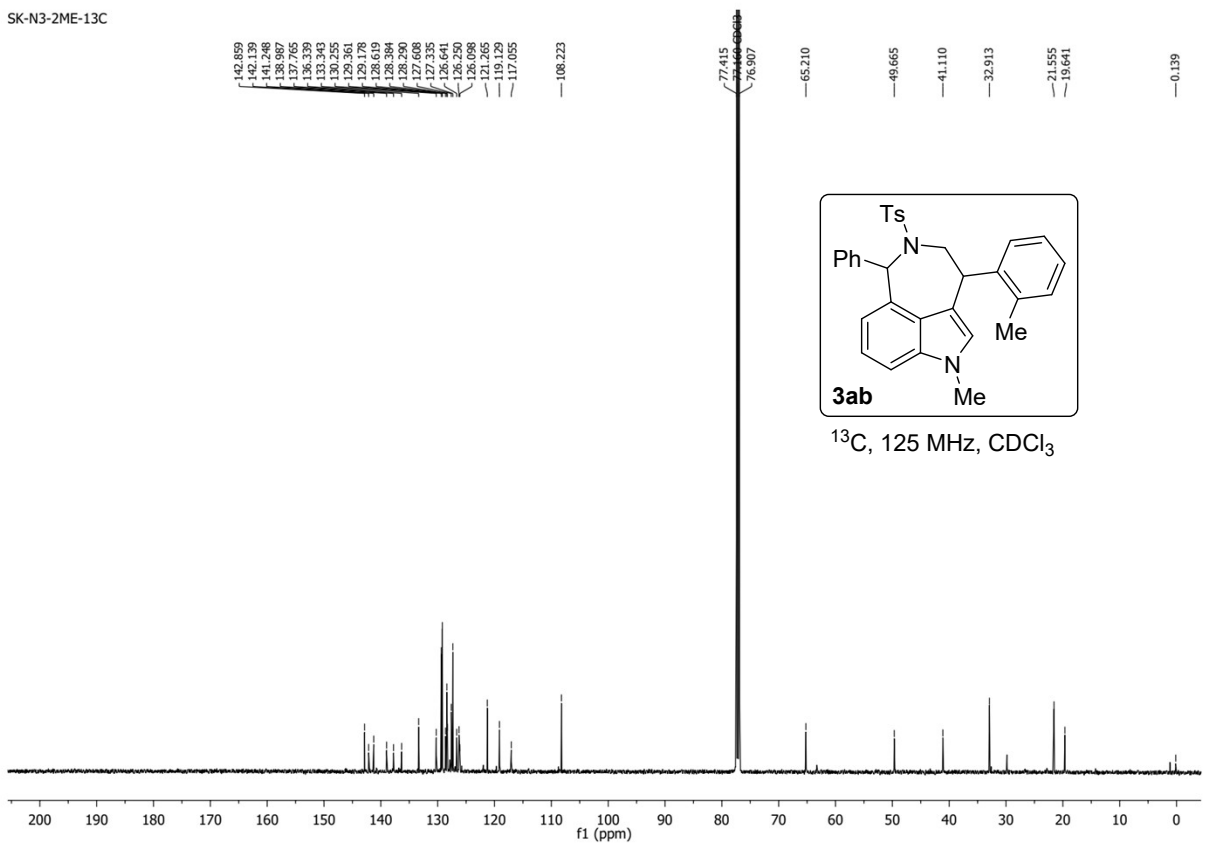
^{1}H, 500 MHz, $CDCl_3$



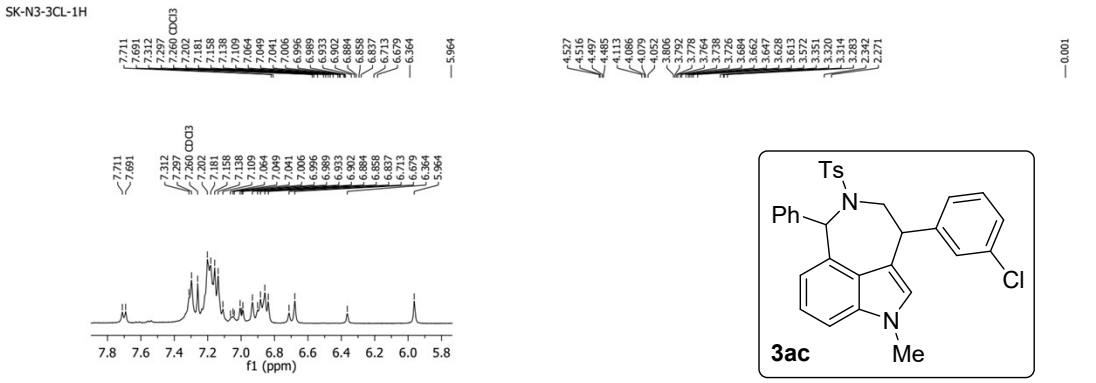
^{13}C, 125 MHz, $CDCl_3$



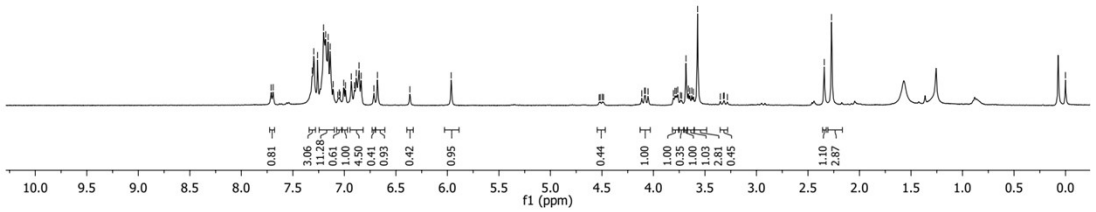
^{1}H, 400 MHz, $CDCl_3$

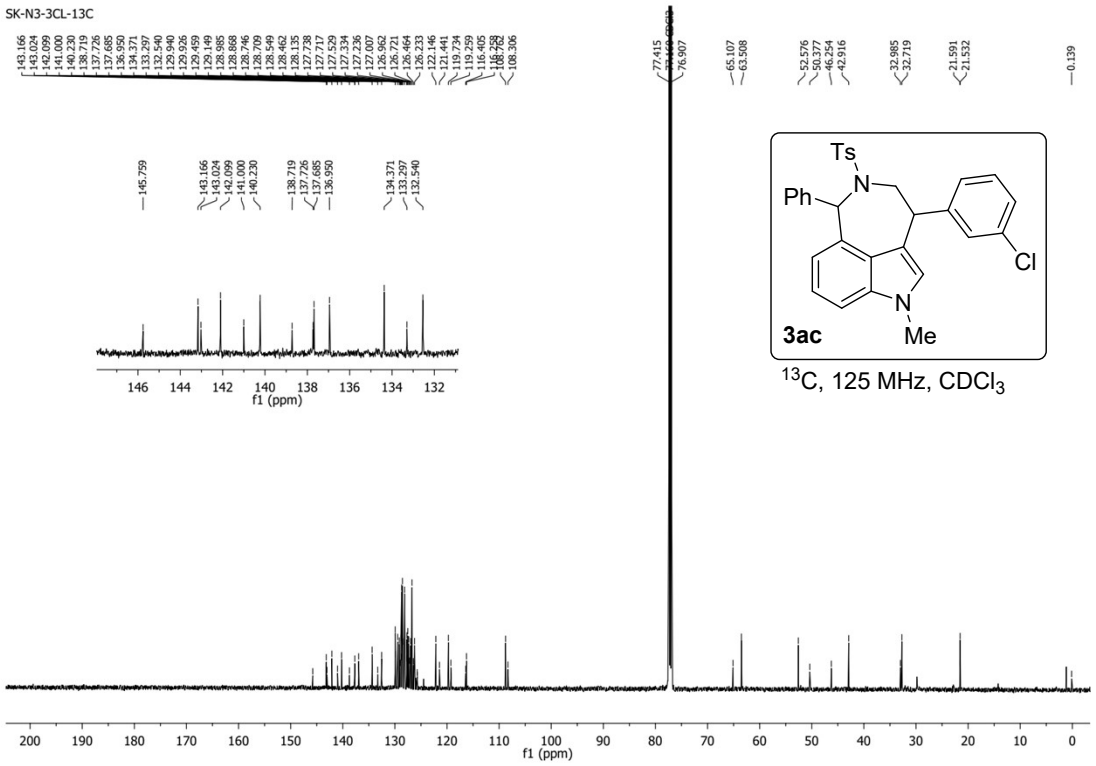


^{13}C, 125 MHz, $CDCl_3$

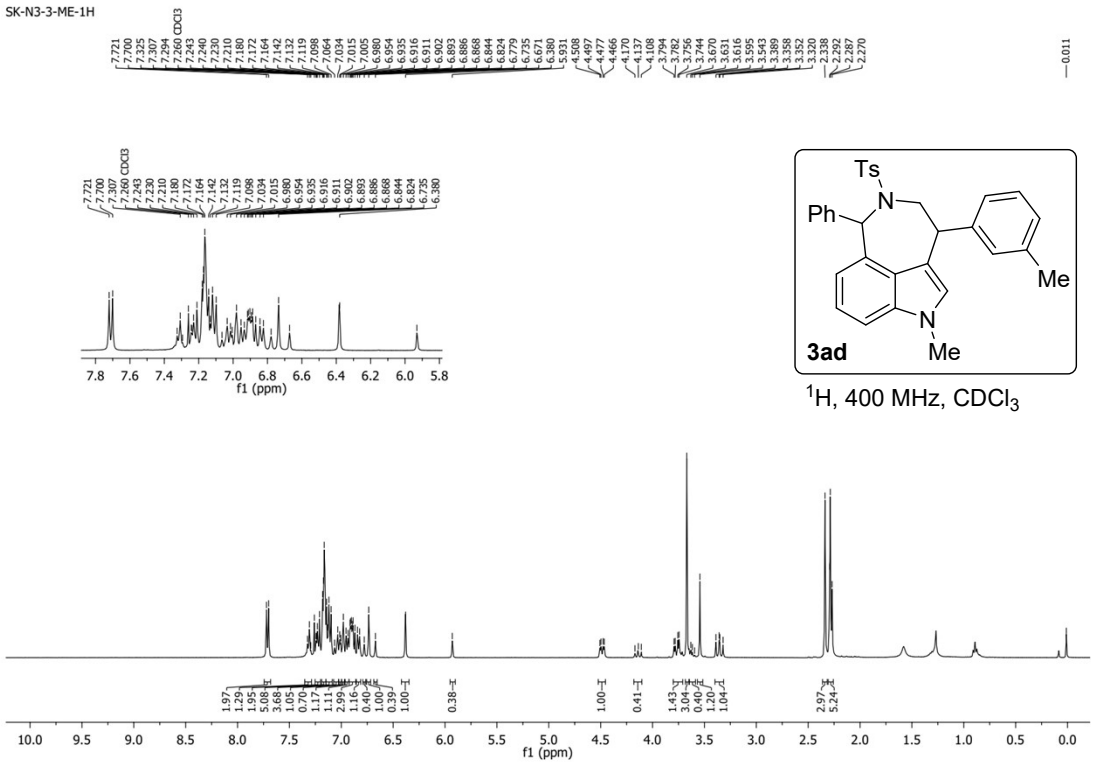


^{1}H, 400 MHz, $CDCl_3$

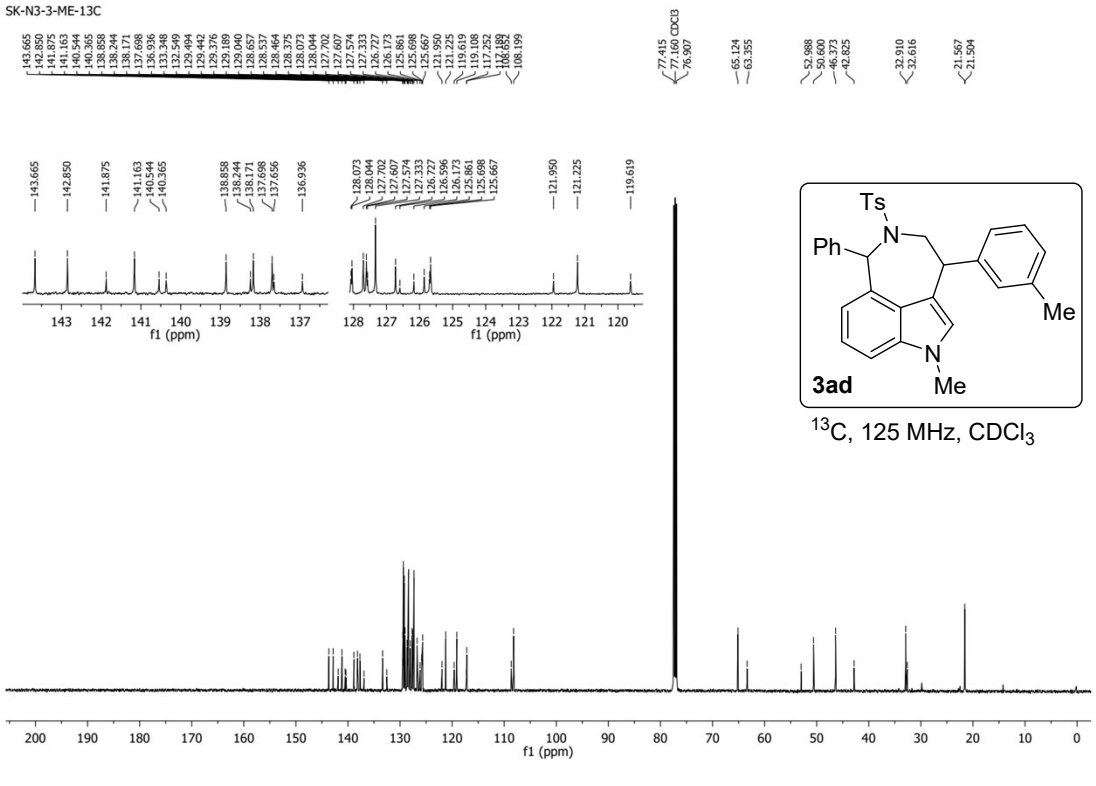




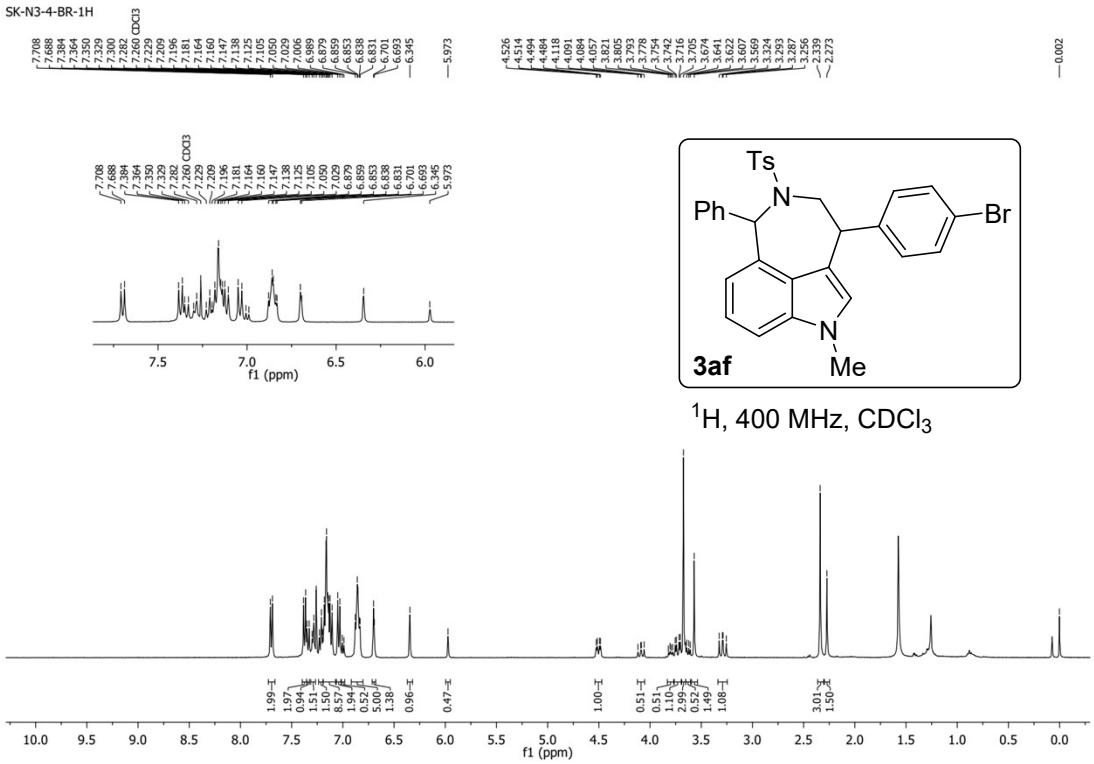
^{13}C, 125 MHz, $CDCl_3$



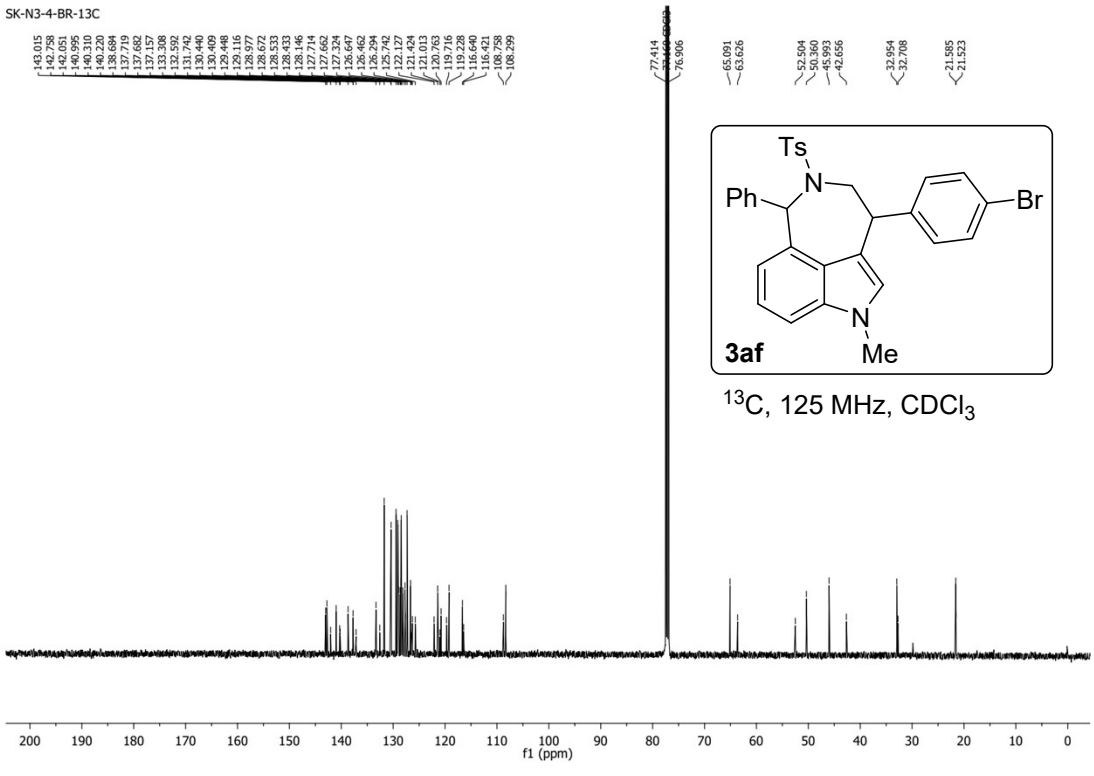
^{1}H, 400 MHz, $CDCl_3$



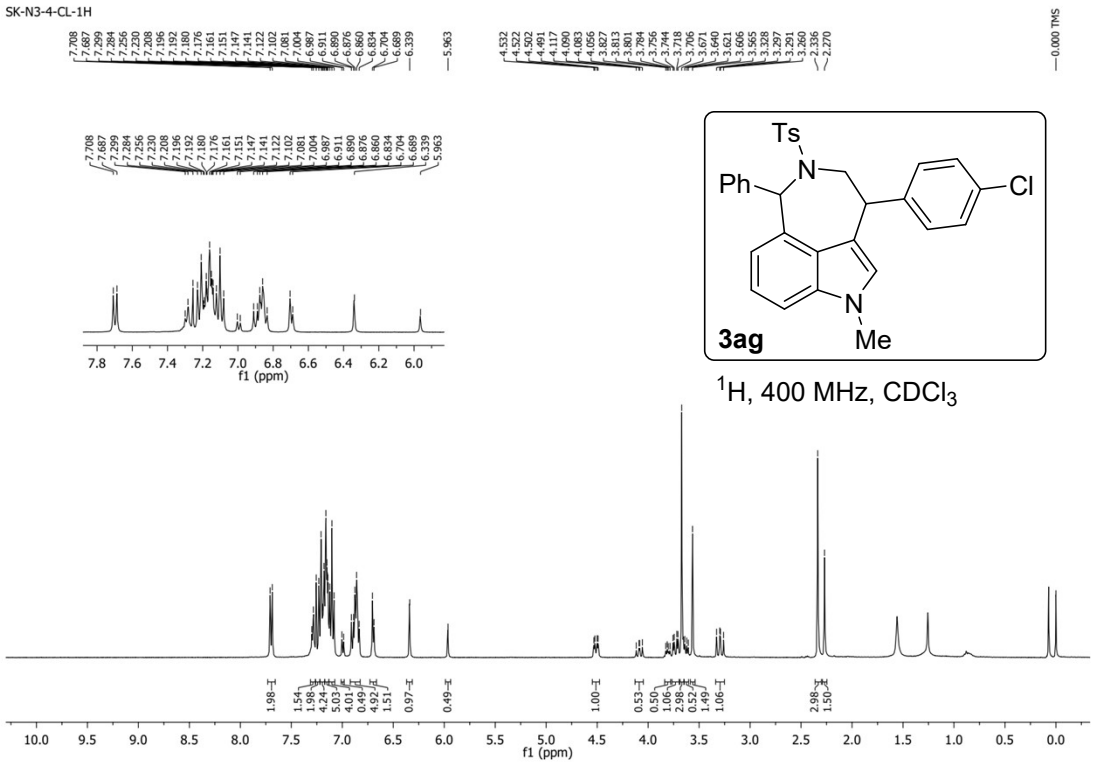
^{13}C, 125 MHz, $CDCl_3$



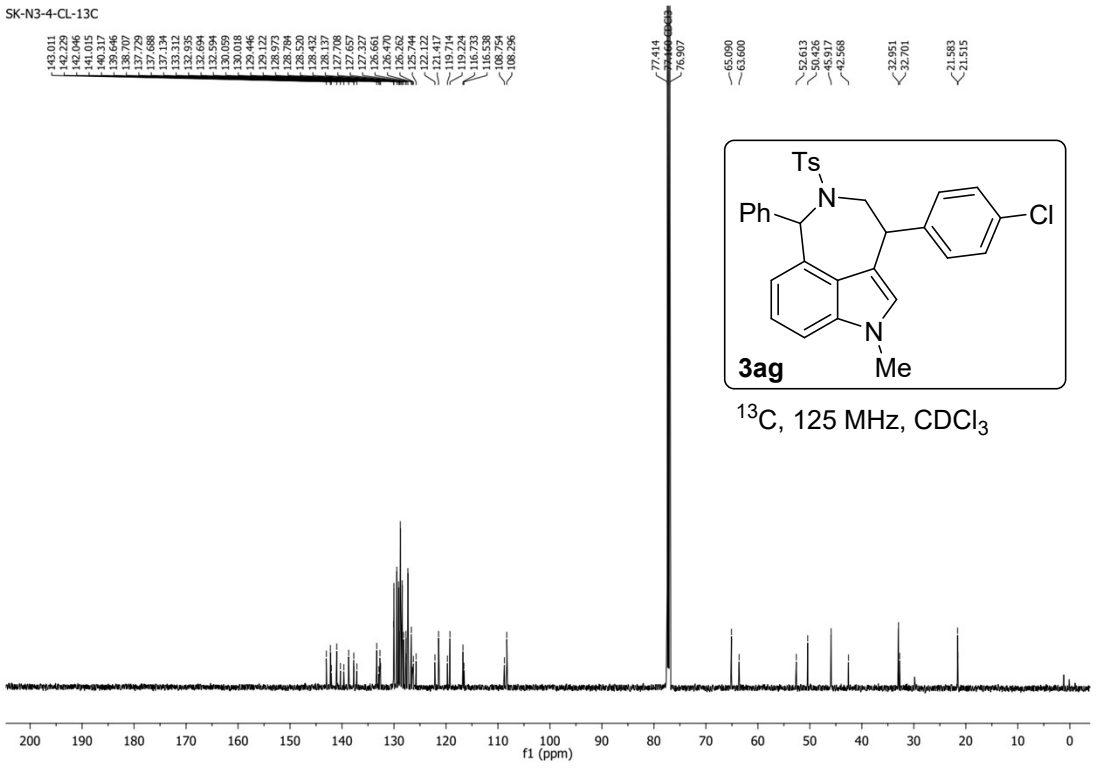
^{1}H, 400 MHz, $CDCl_3$



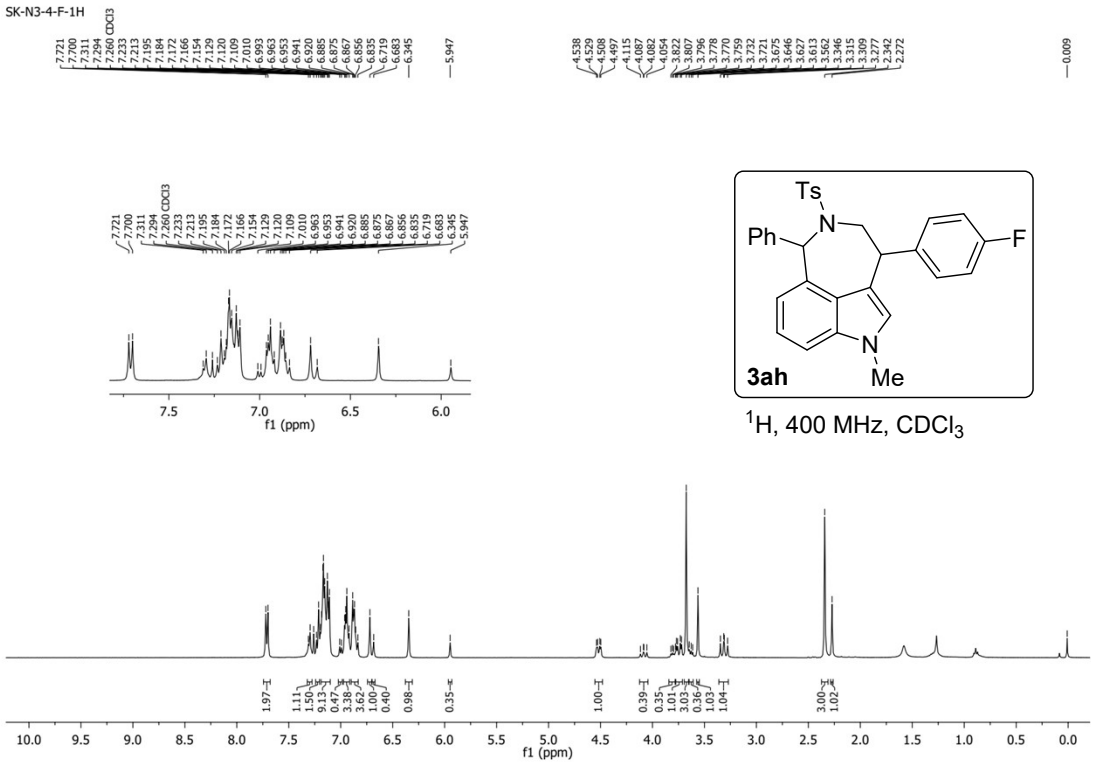
^{13}C, 125 MHz, $CDCl_3$



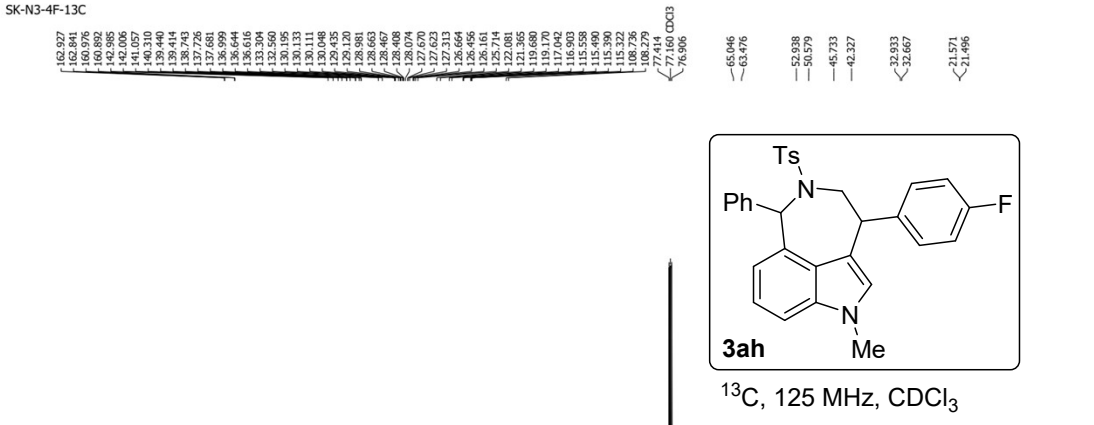
^{1}H, 400 MHz, $CDCl_3$



^{13}C, 125 MHz, $CDCl_3$

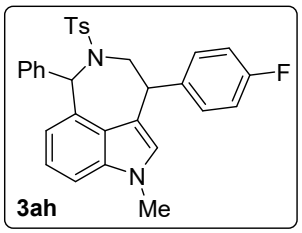


^{1}H, 400 MHz, $CDCl_3$



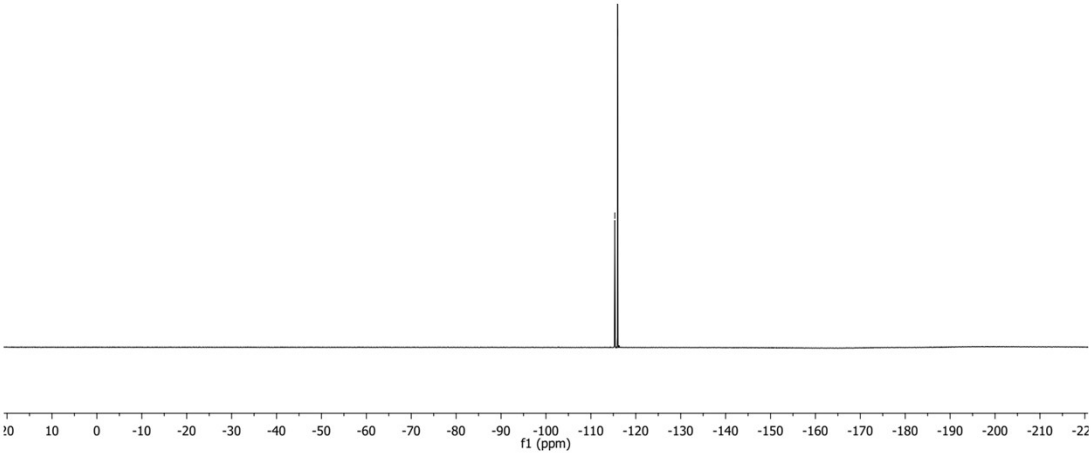
^{13}C, 125 MHz, $CDCl_3$

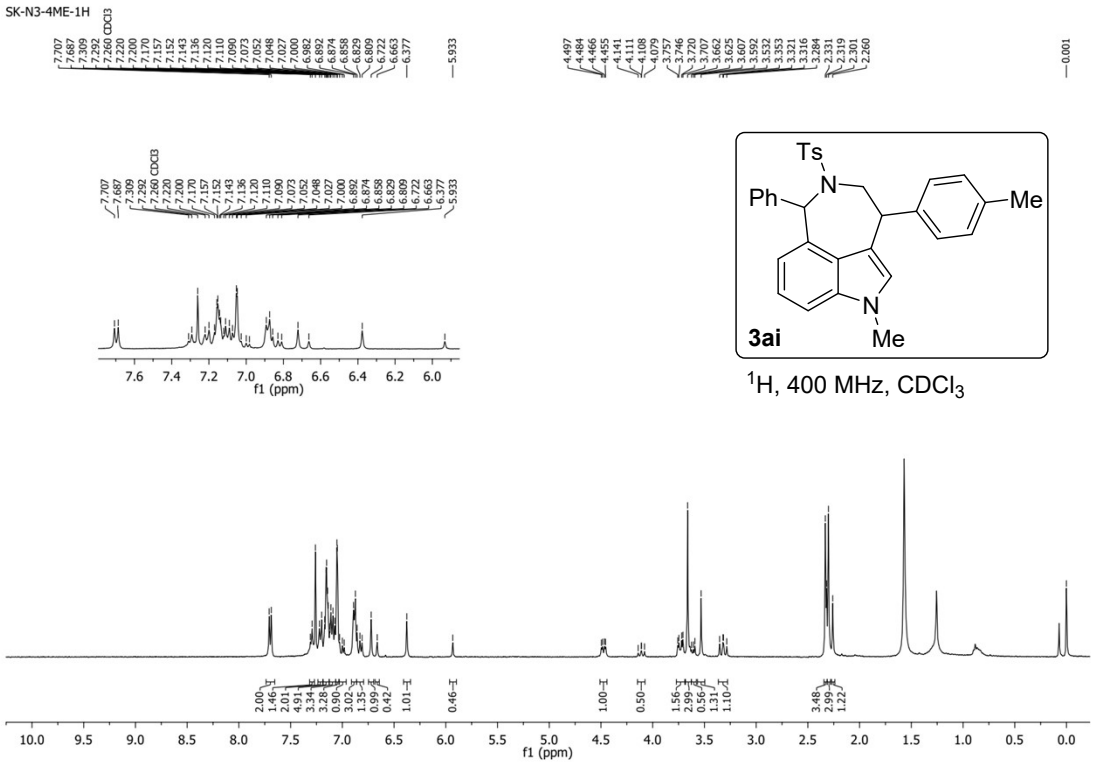
SK-N3-4F-19F



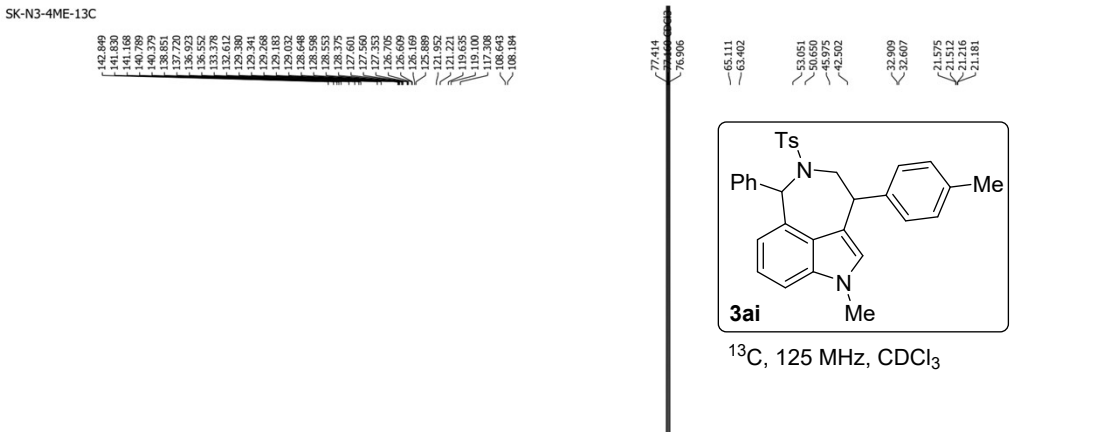
3ah

^{19}F, 470 MHz, $CDCl_3$

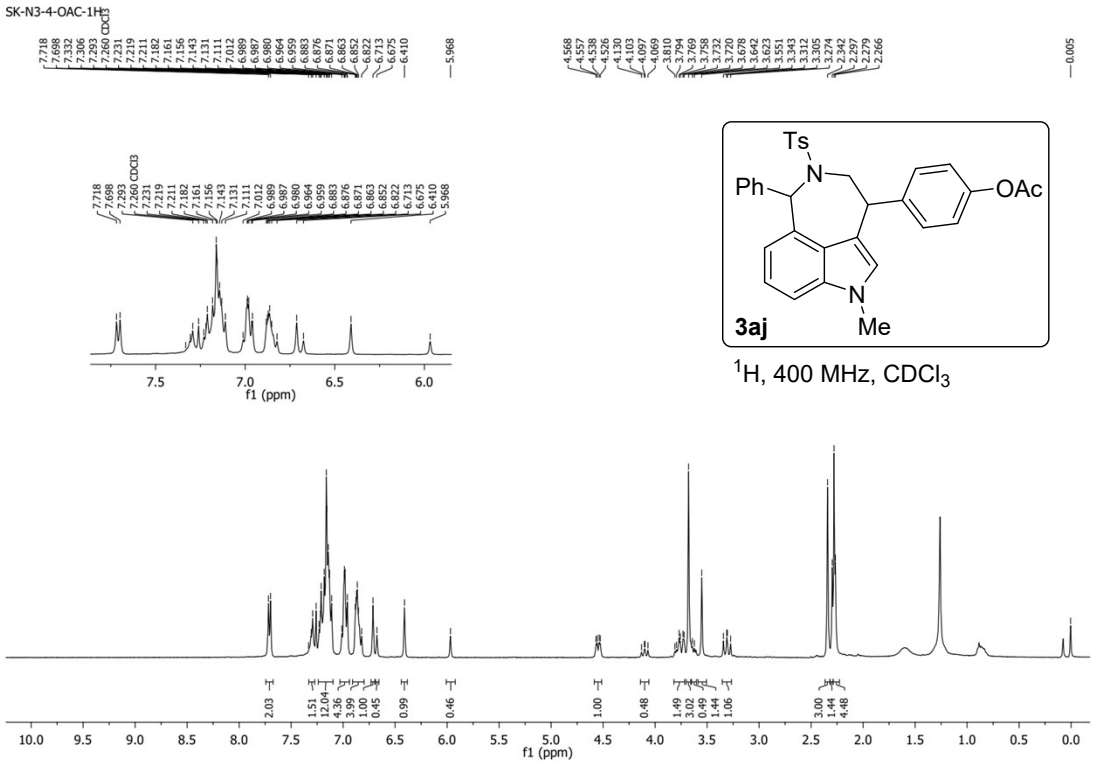




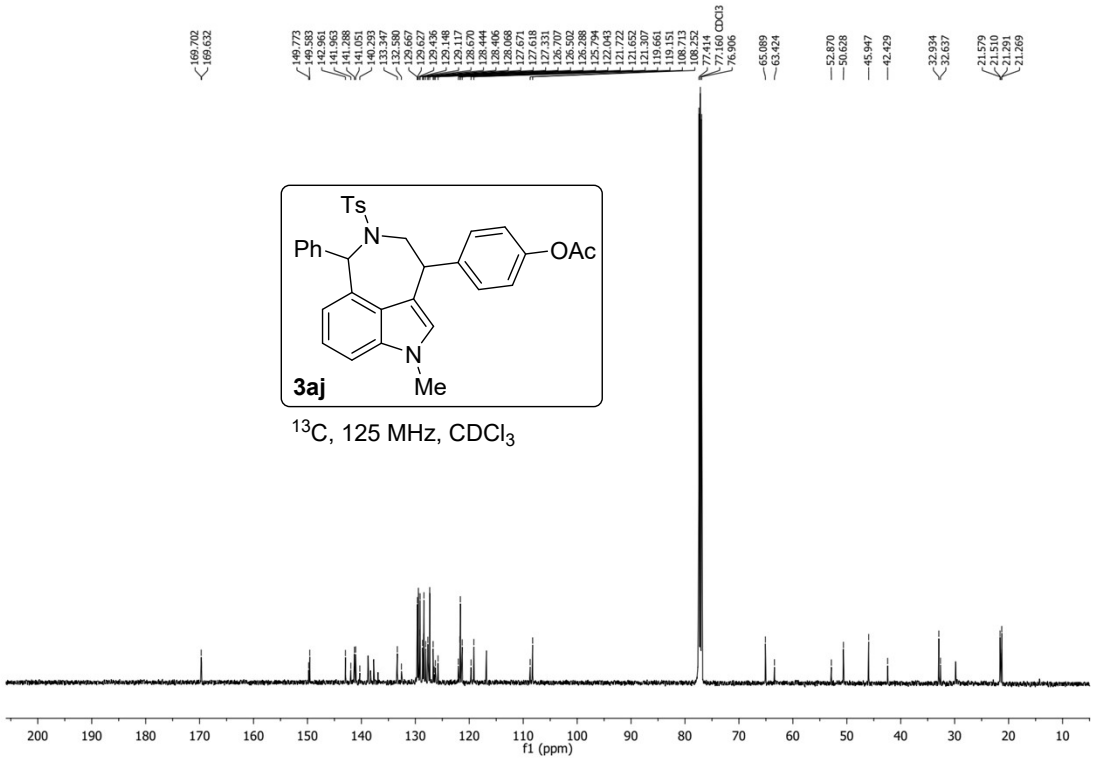
^{1}H, 400 MHz, $CDCl_3$



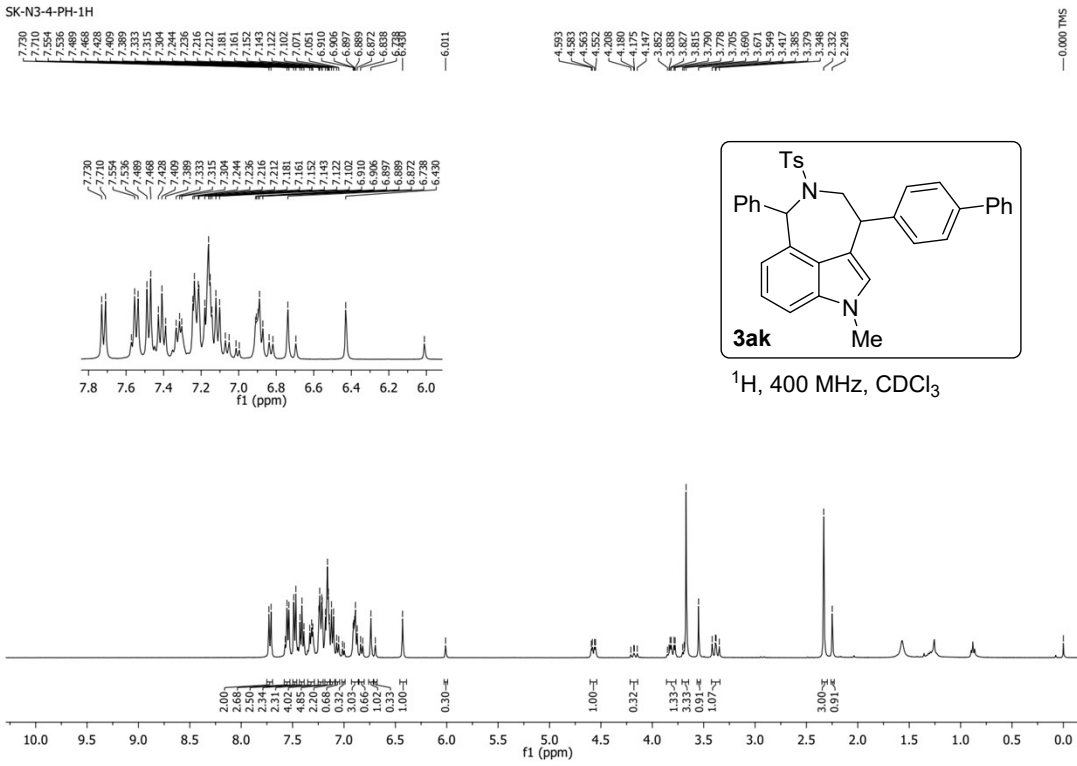
^{13}C, 125 MHz, $CDCl_3$



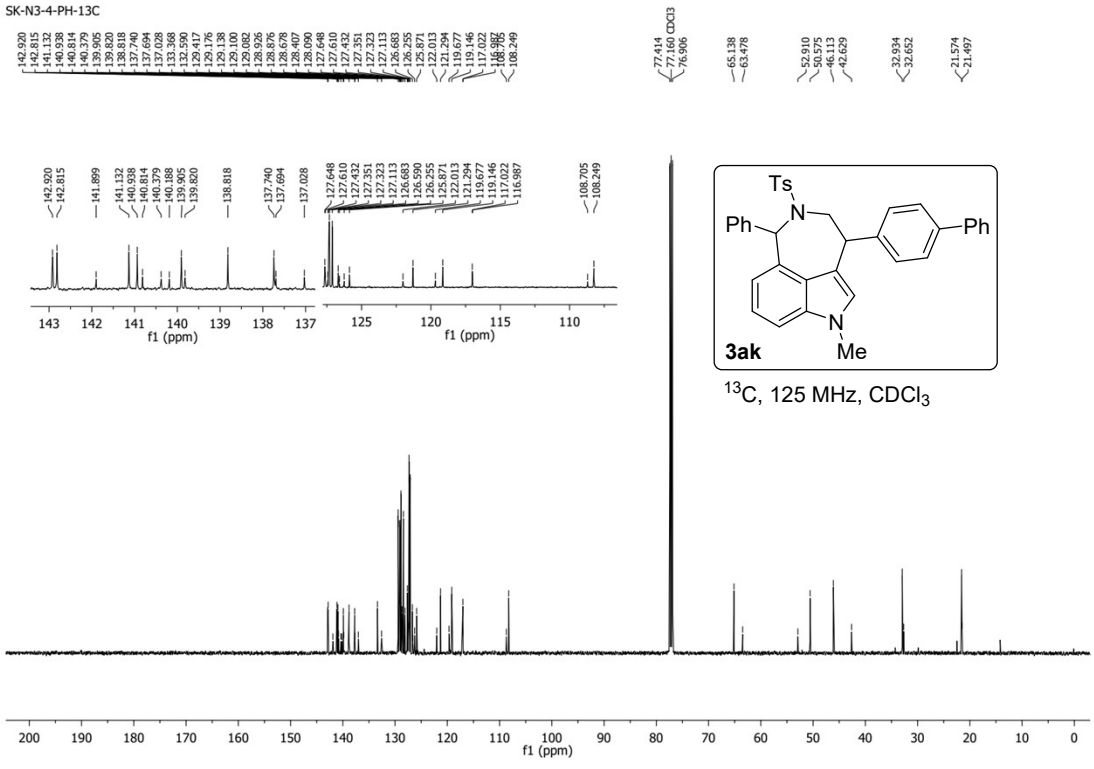
^{1}H, 400 MHz, $CDCl_3$



^{13}C, 125 MHz, $CDCl_3$

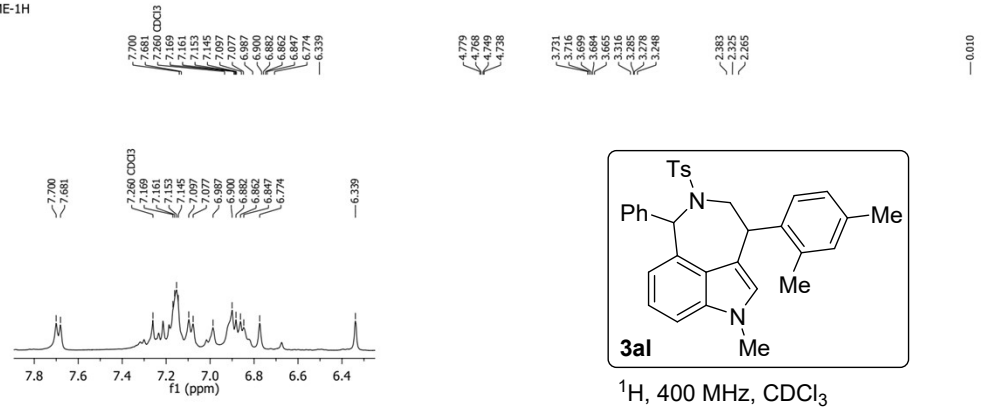


^{1}H, 400 MHz, $CDCl_3$

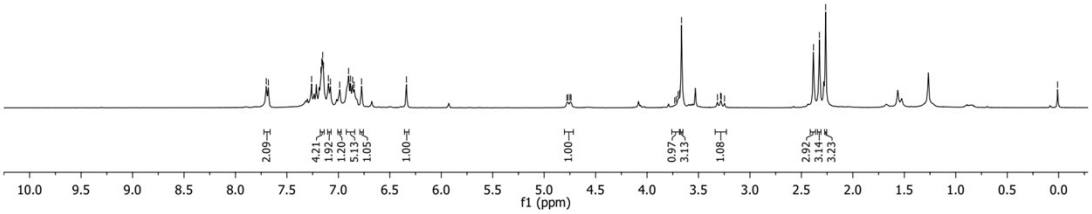


^{13}C, 125 MHz, $CDCl_3$

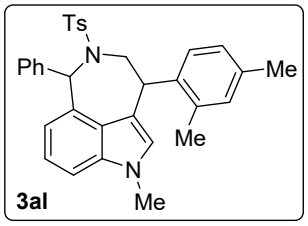
SK-N3-2,4-DIME-1H



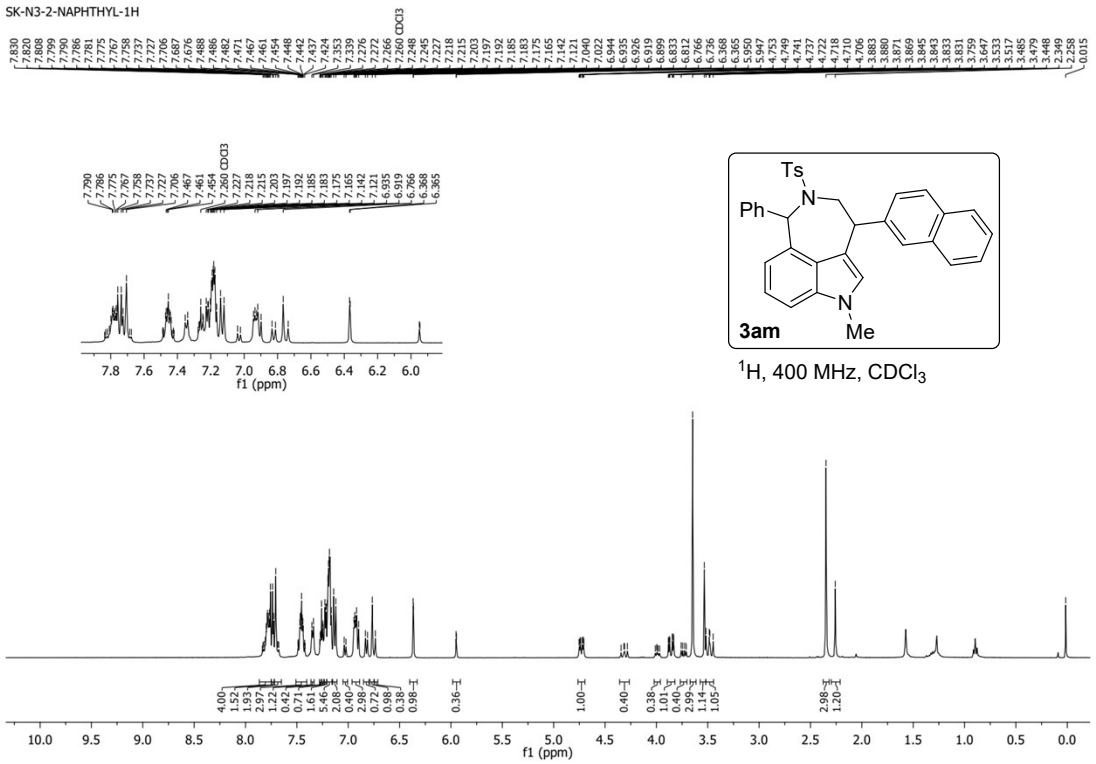
^{1}H, 400 MHz, $CDCl_3$



SK-N3-2,4-DIME-13C



^{13}C, 125 MHz, $CDCl_3$



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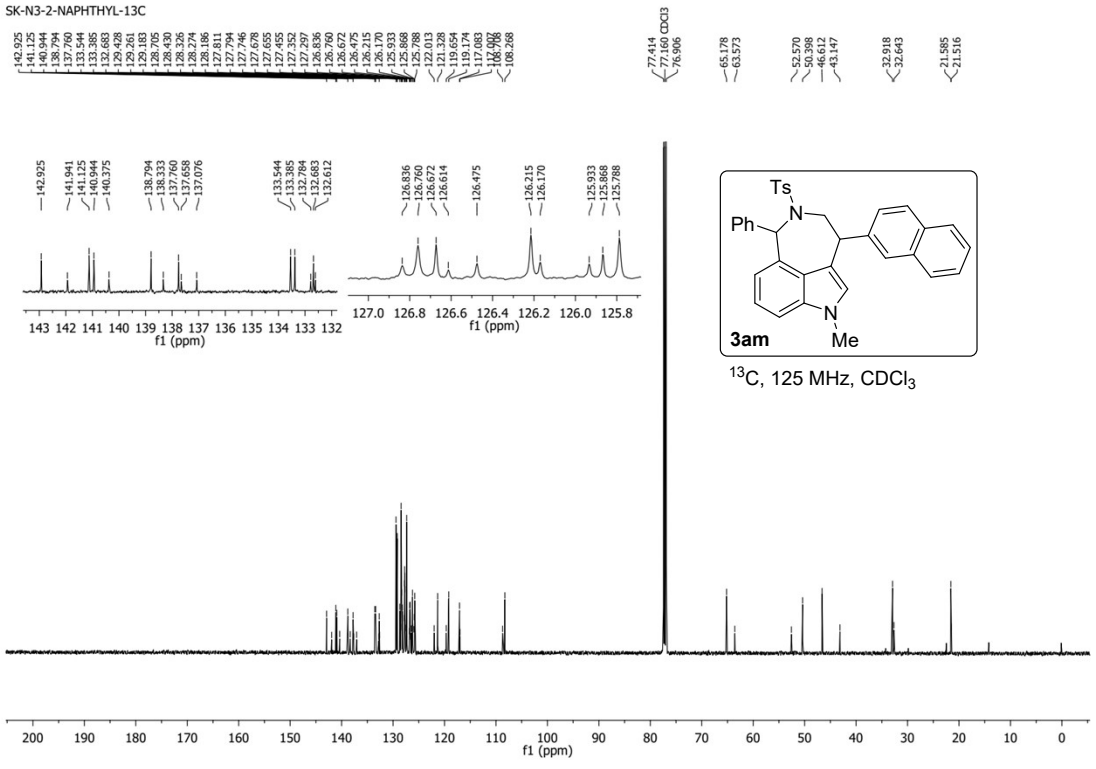
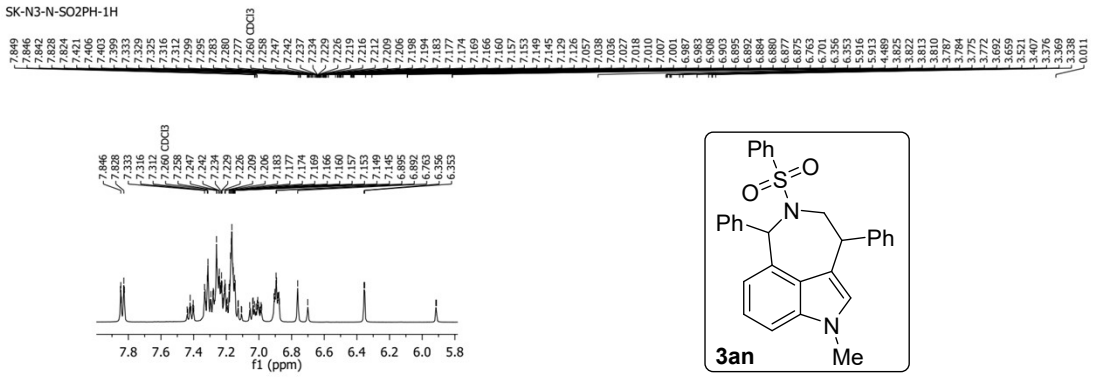
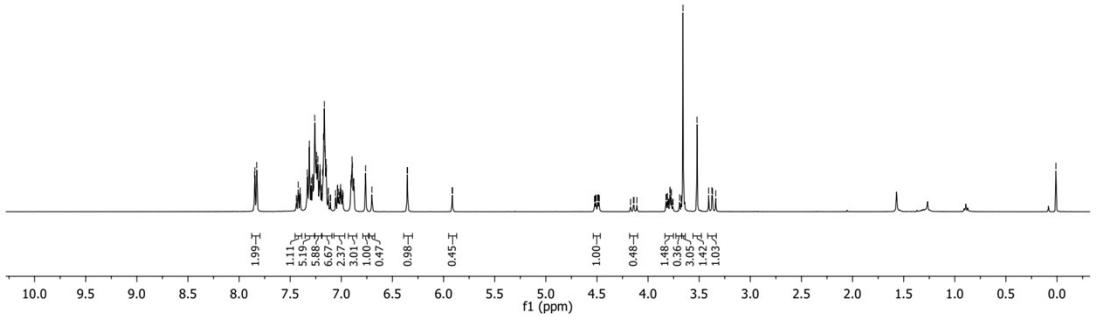
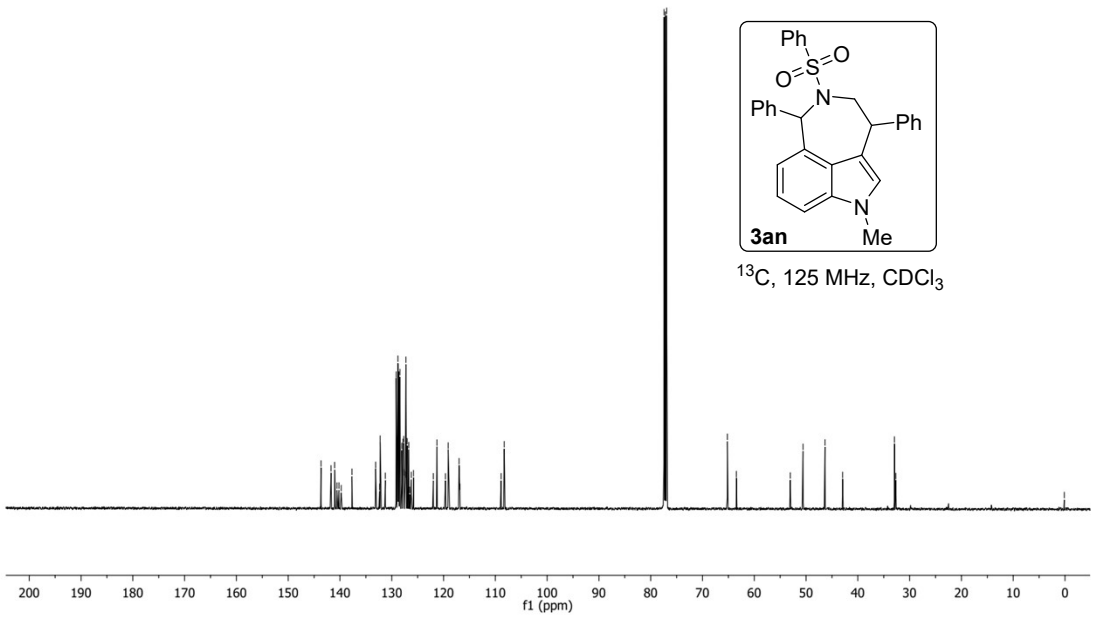


^{13}C, 125 MHz, $CDCl_3$

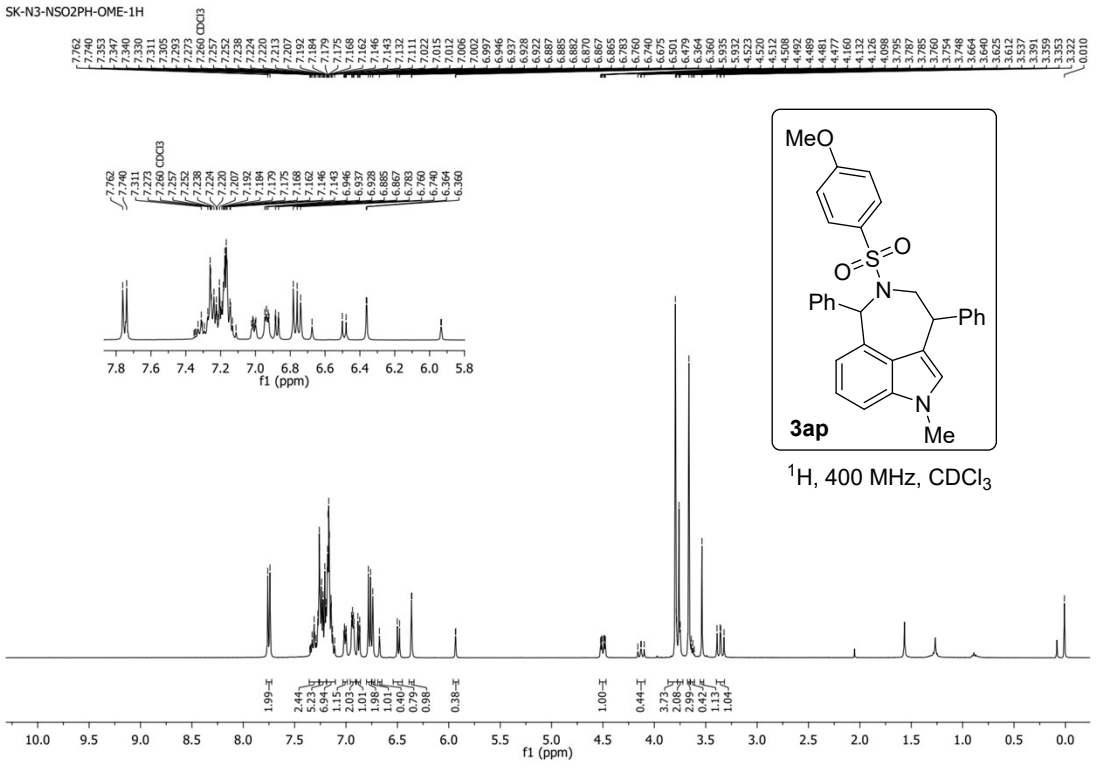


^{1}H, 400 MHz, $CDCl_3$

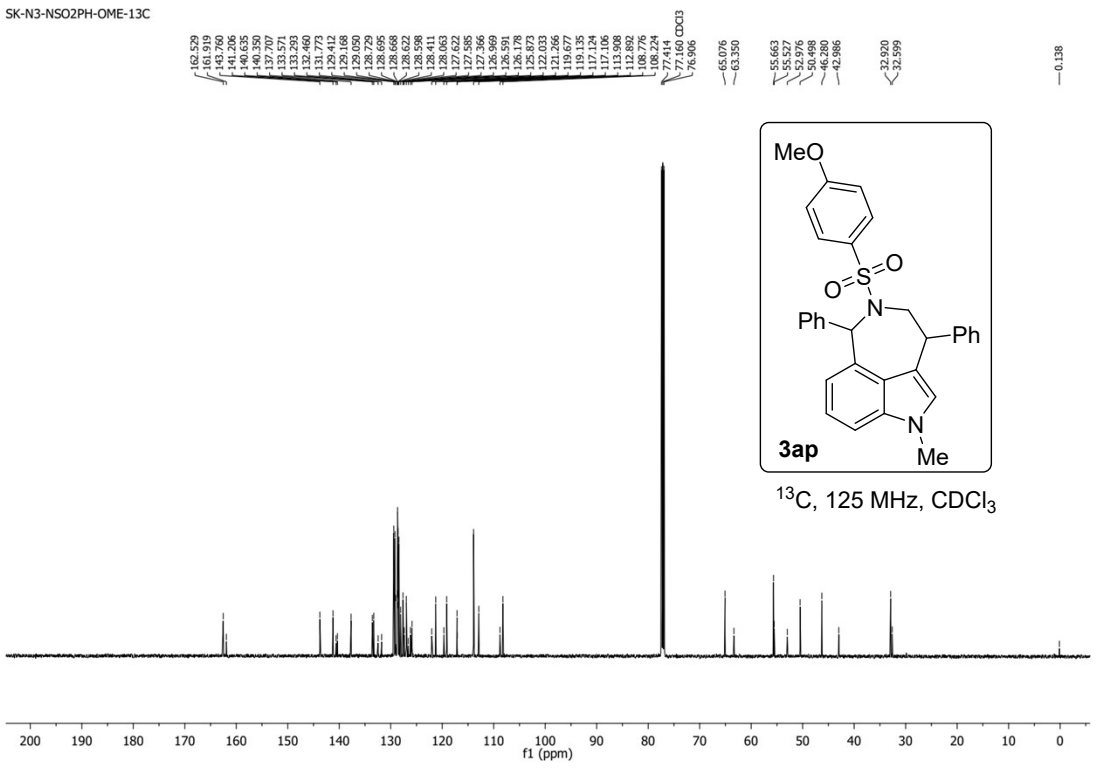




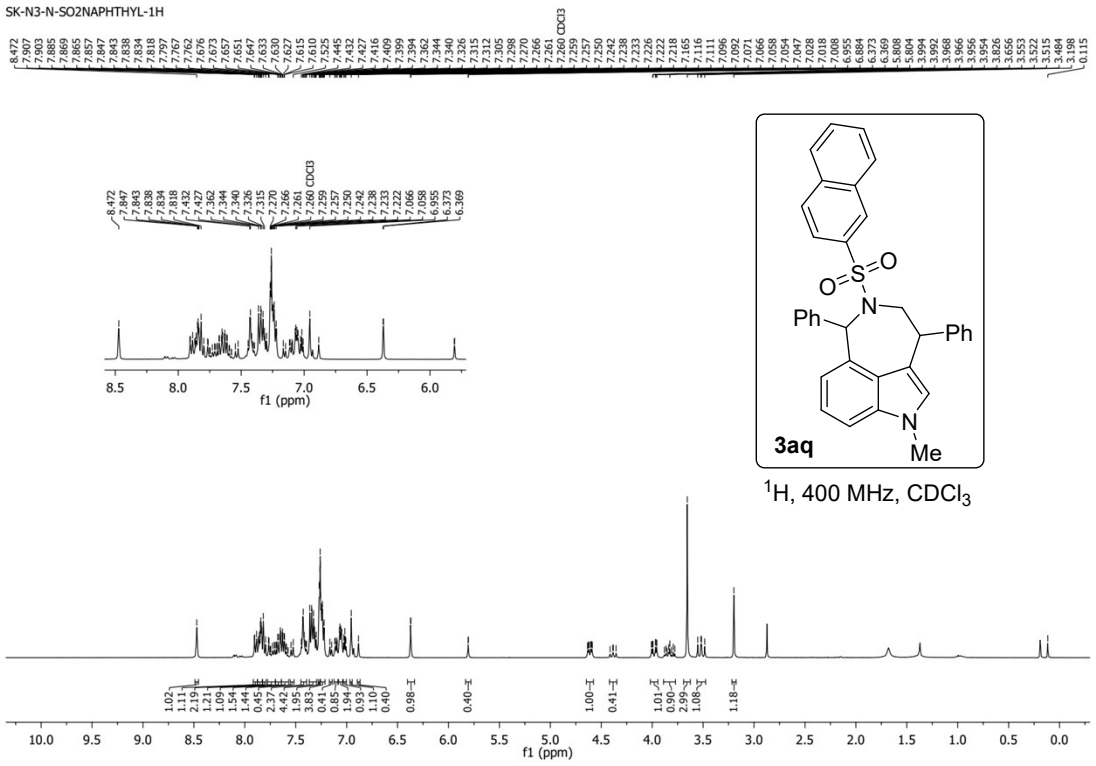
^{13}C, 125 MHz, $CDCl_3$



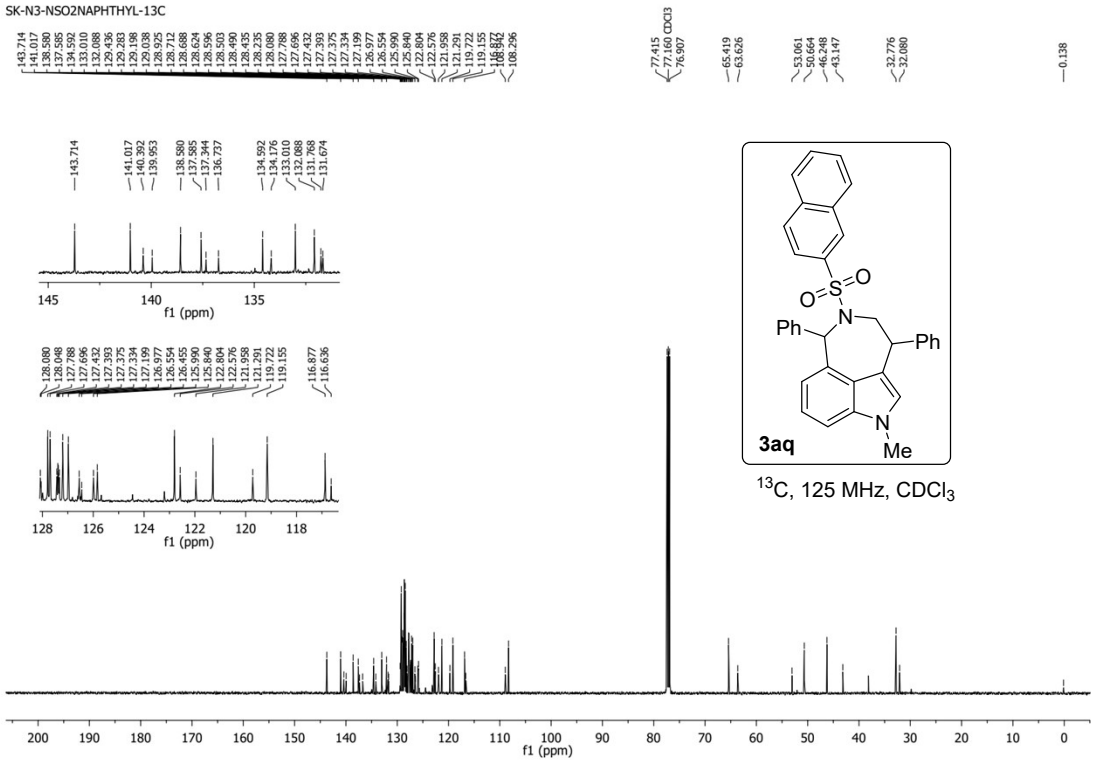
^{1}H, 400 MHz, $CDCl_3$



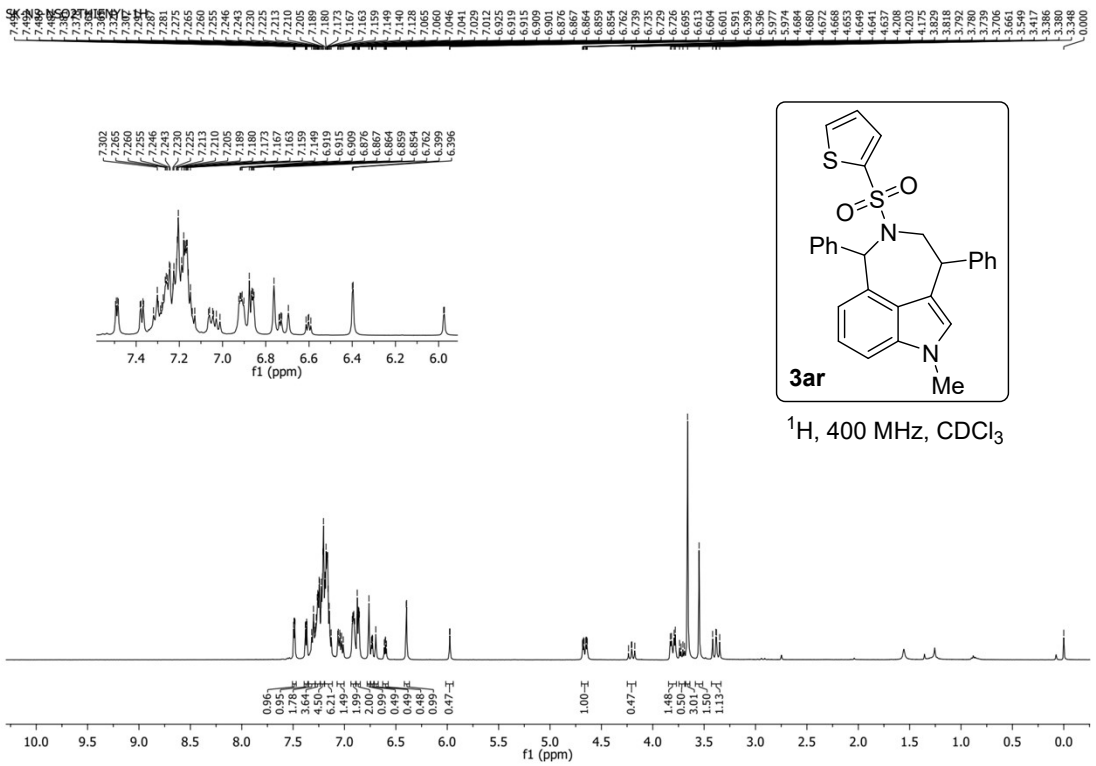
^{13}C, 125 MHz, $CDCl_3$



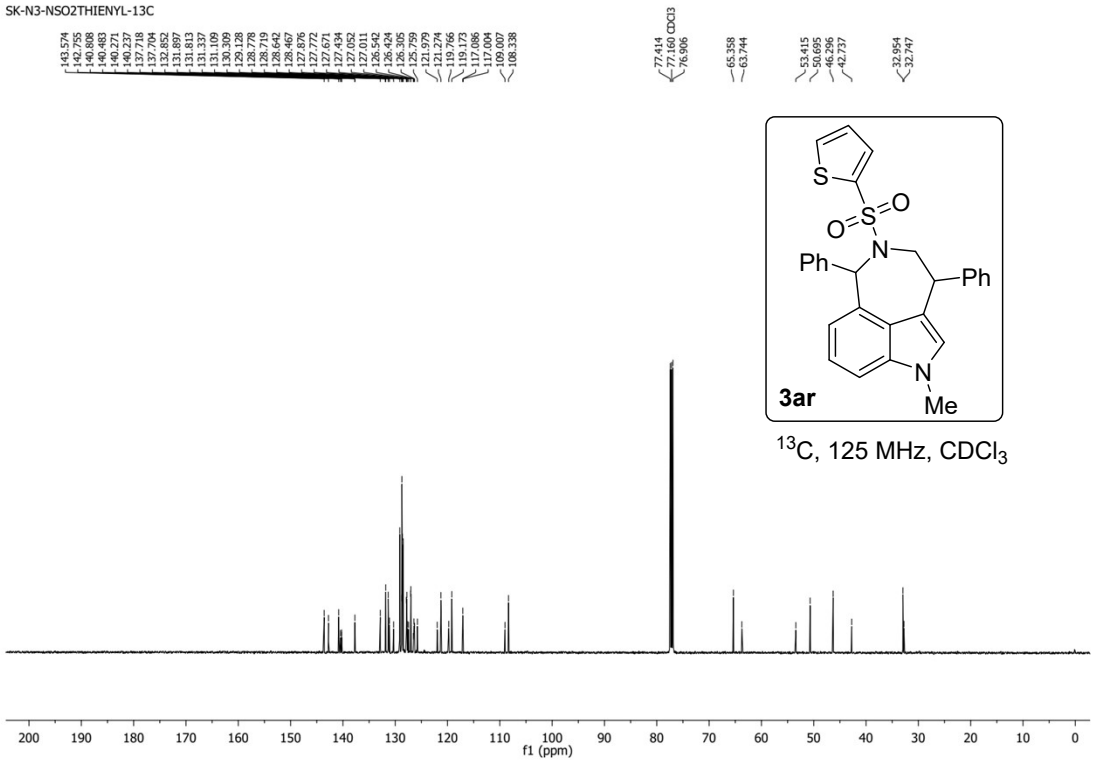
^{1}H, 400 MHz, $CDCl_3$



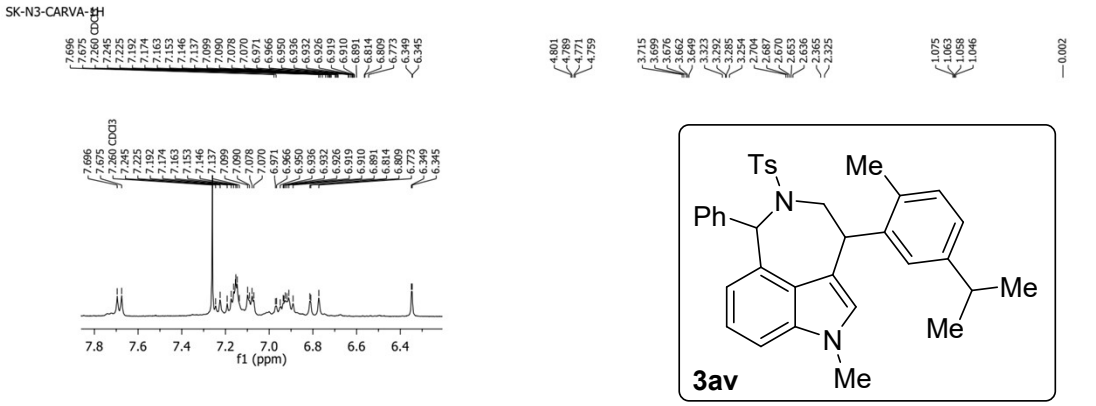
^{13}C, 125 MHz, $CDCl_3$



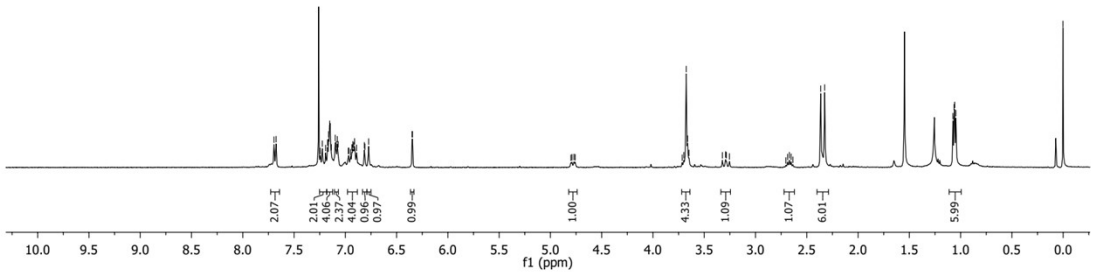
^{1}H, 400 MHz, $CDCl_3$

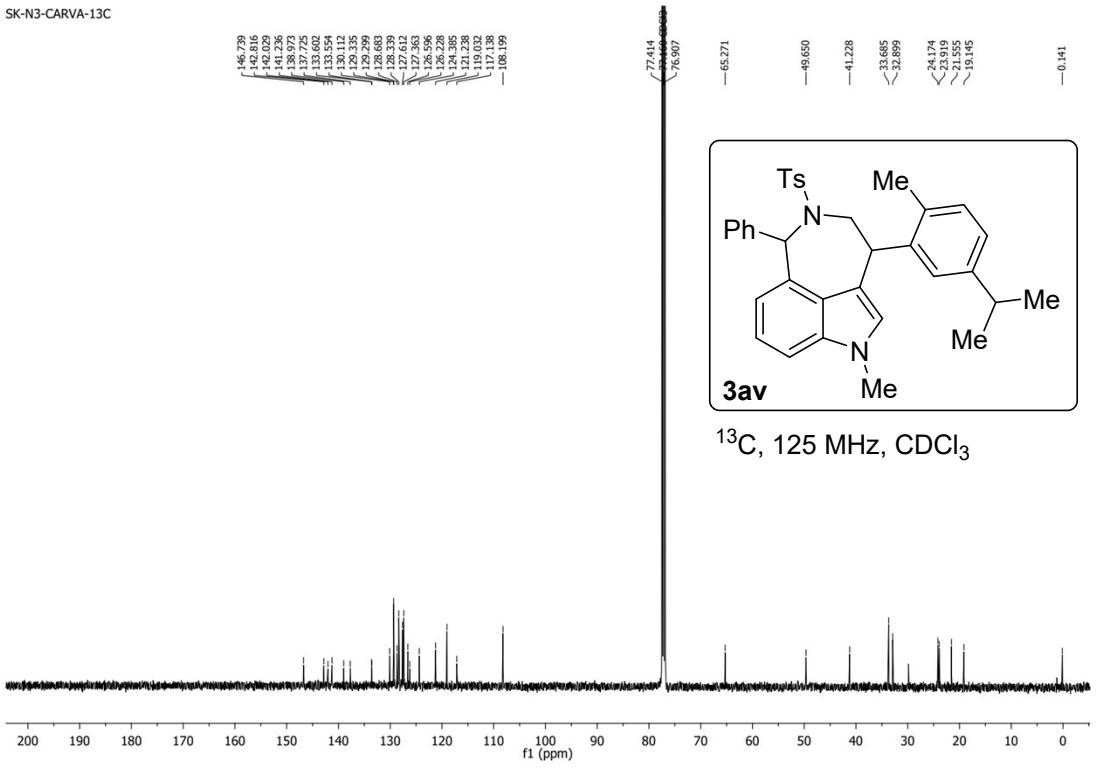


^{13}C, 125 MHz, $CDCl_3$

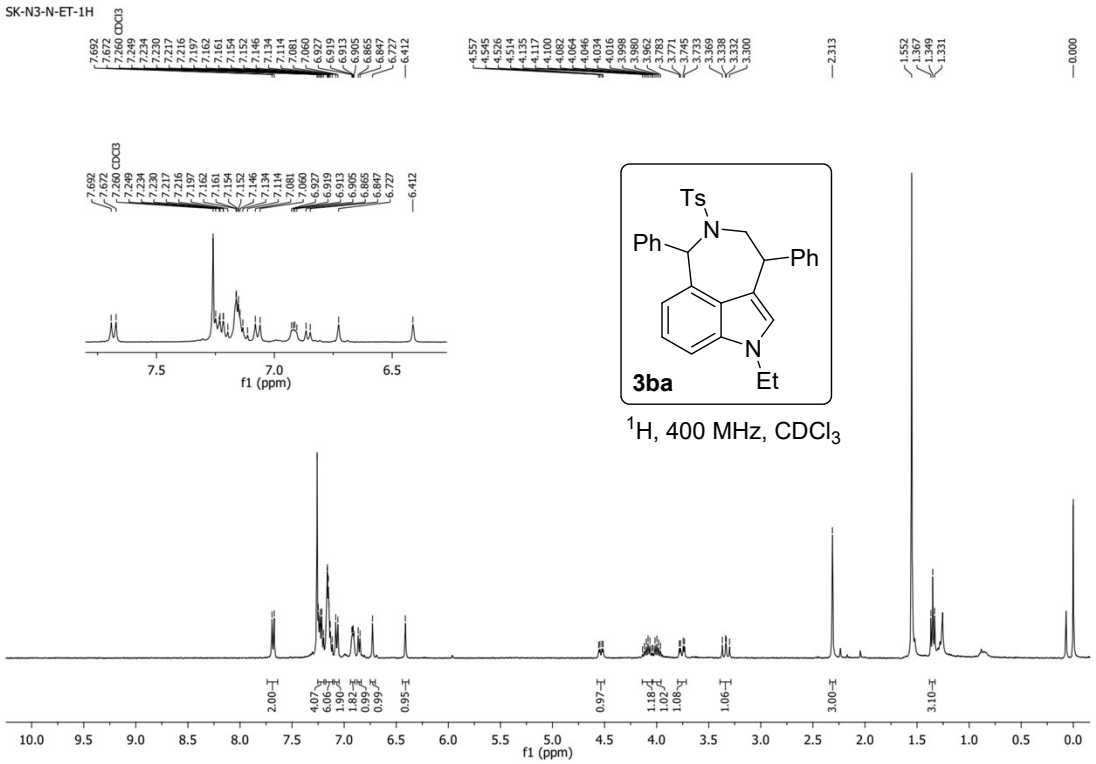


^{1}H, 400 MHz, $CDCl_3$

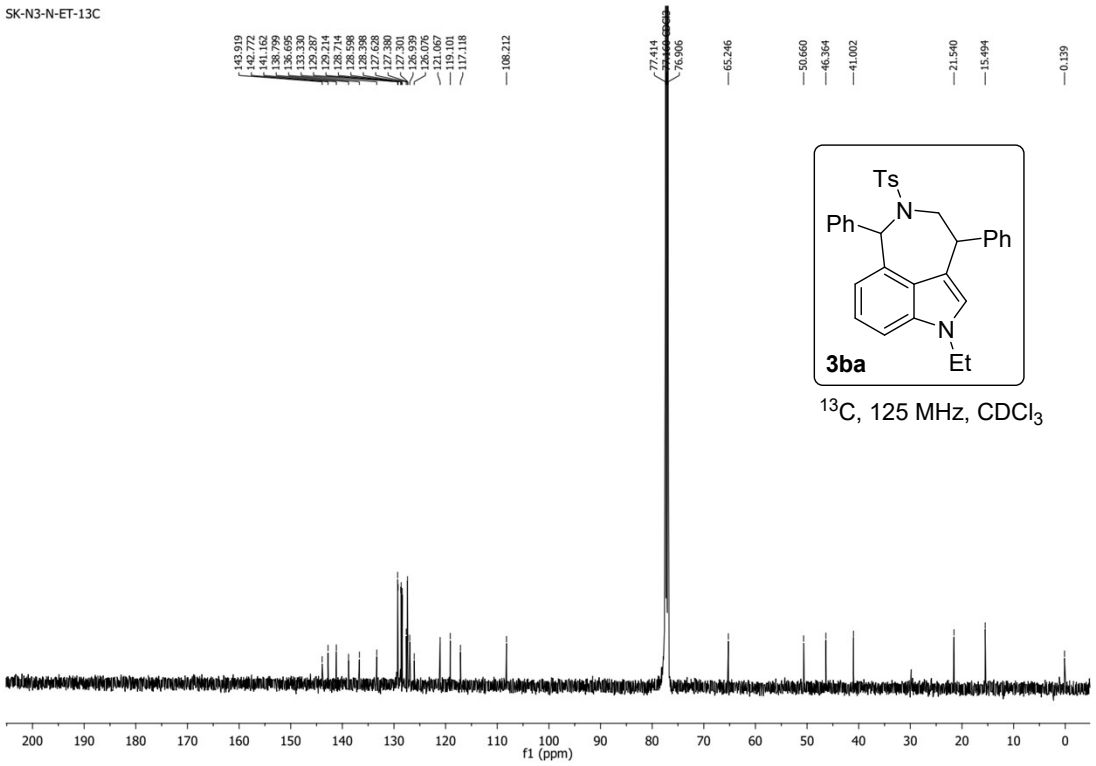




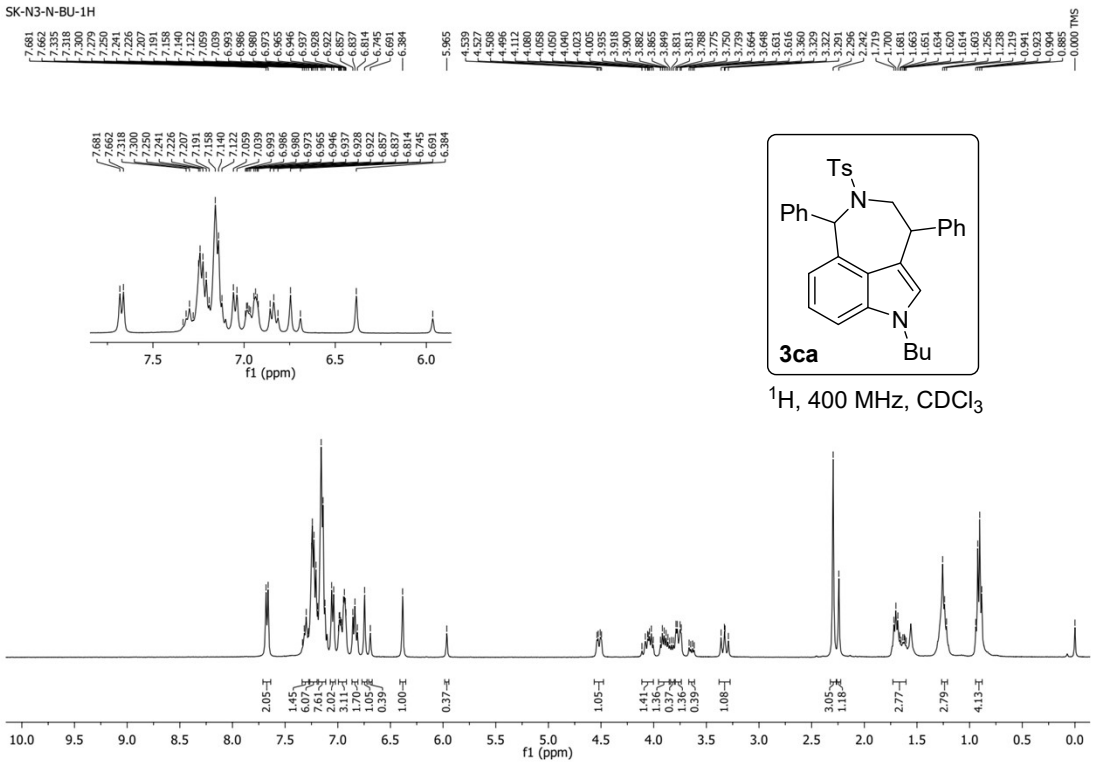
^{13}C, 125 MHz, $CDCl_3$



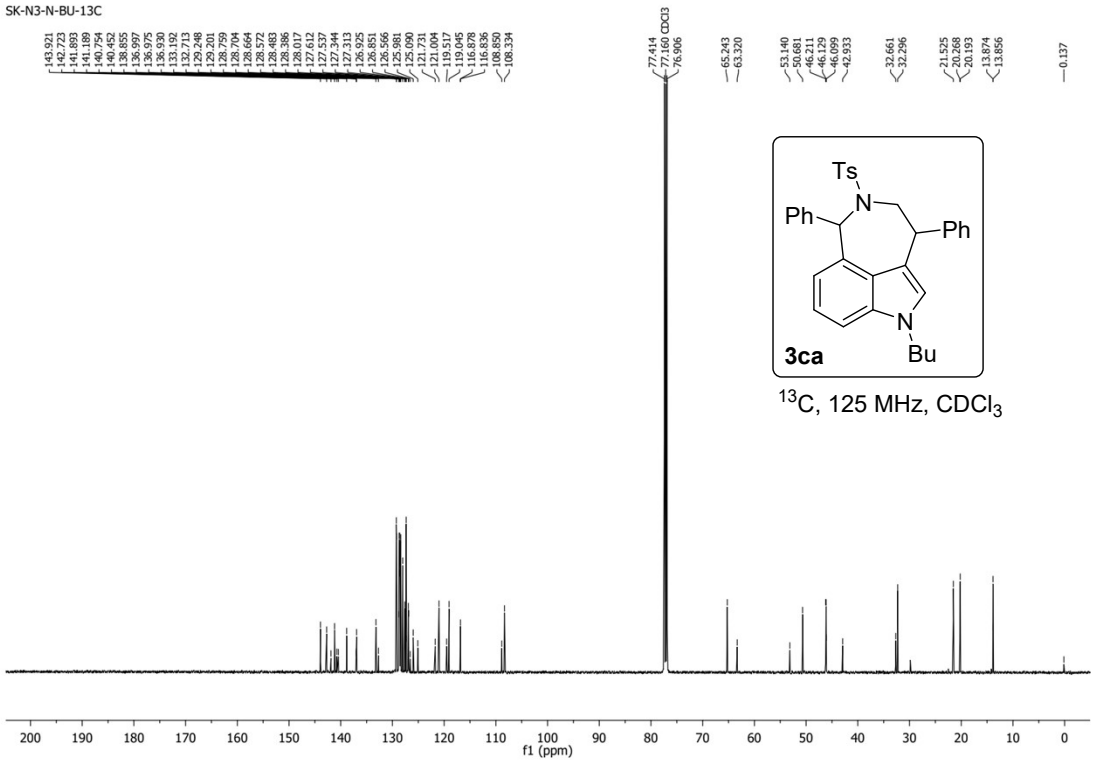
^{1}H, 400 MHz, $CDCl_3$



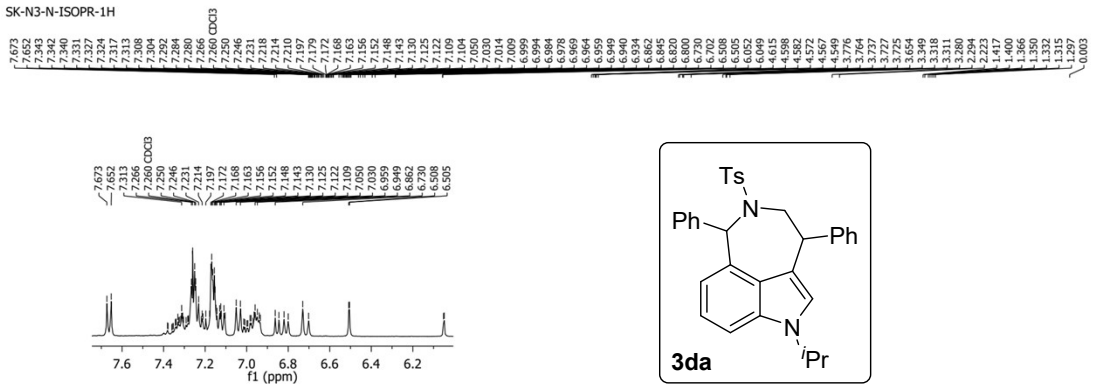
^{13}C, 125 MHz, $CDCl_3$



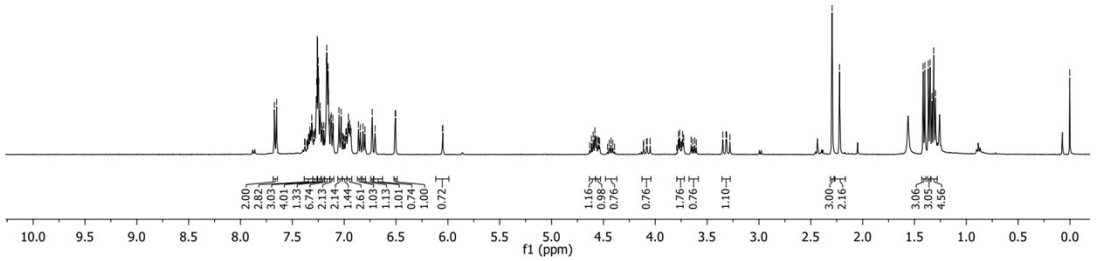
^{1}H, 400 MHz, $CDCl_3$

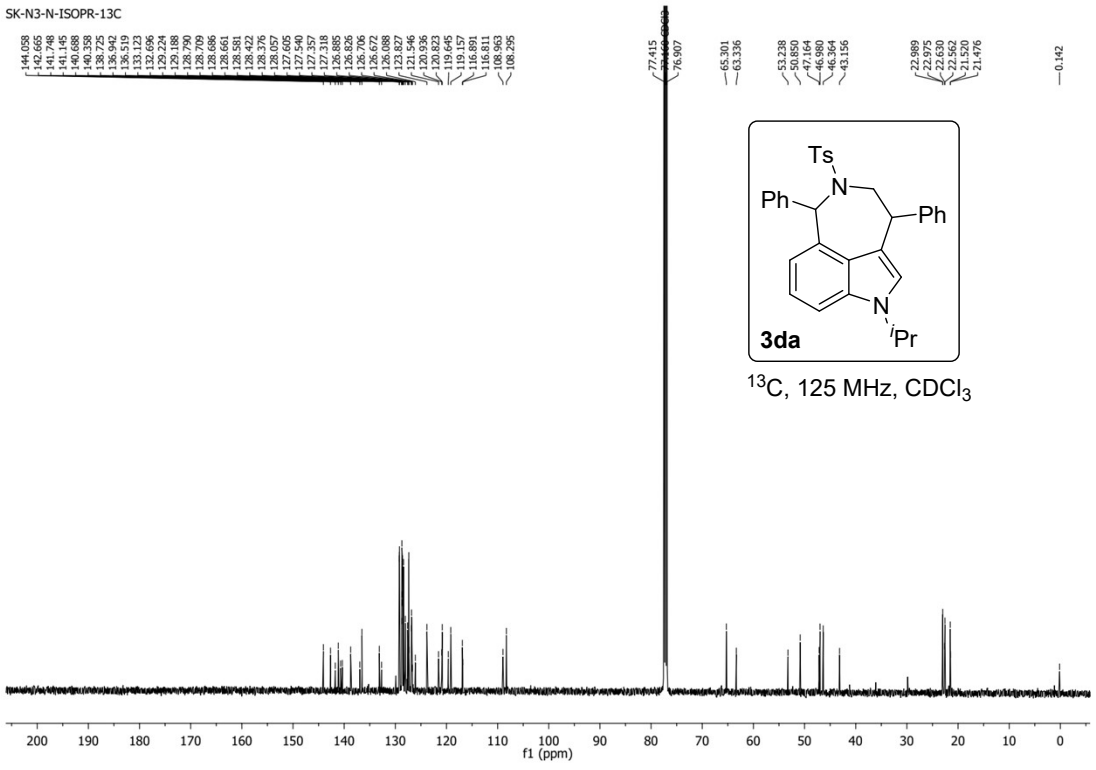


^{13}C, 125 MHz, $CDCl_3$

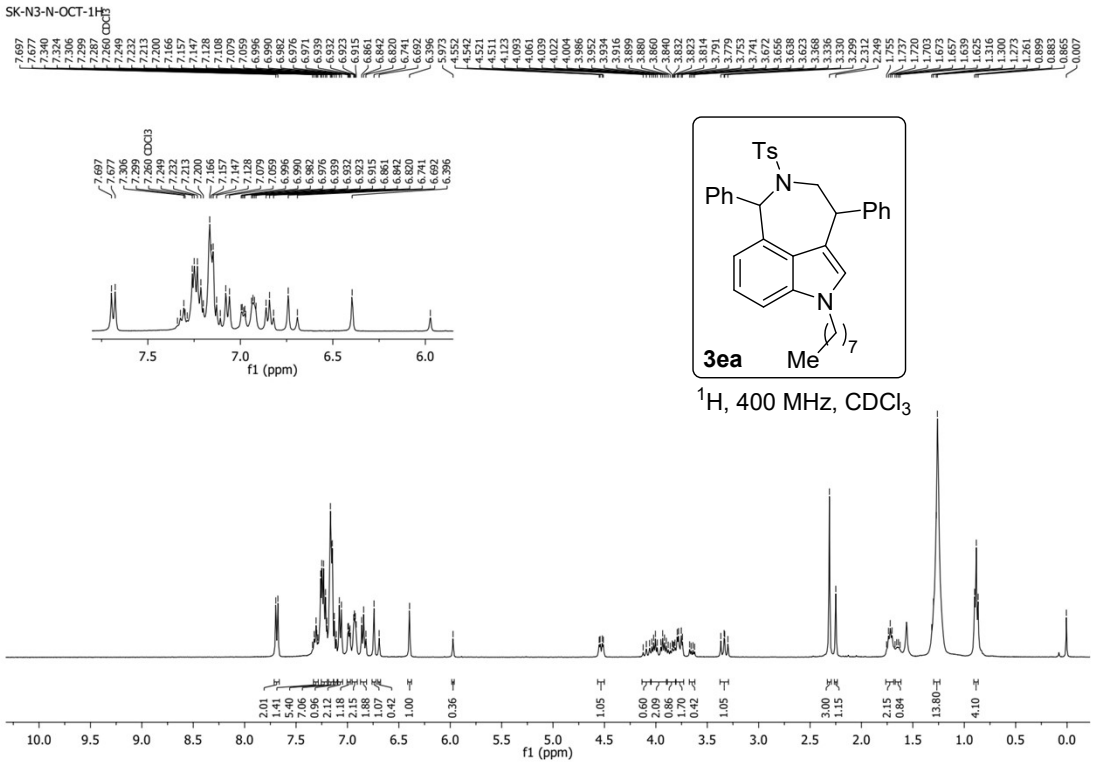


^{1}H, 400 MHz, $CDCl_3$

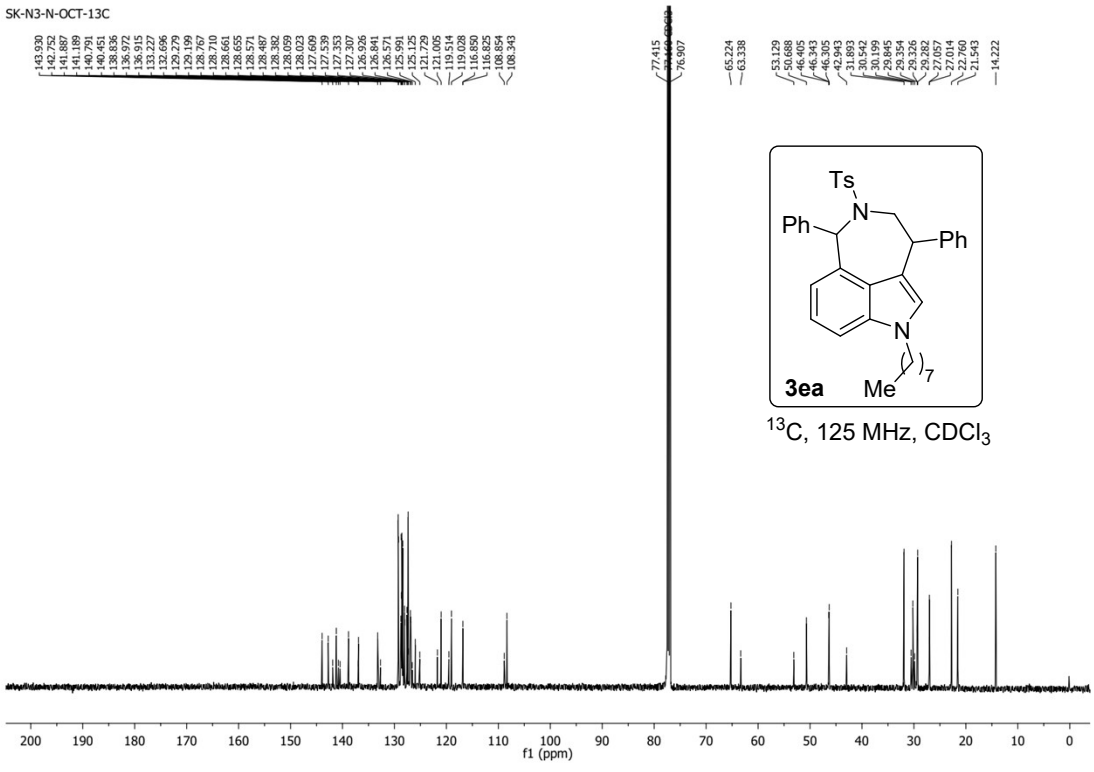




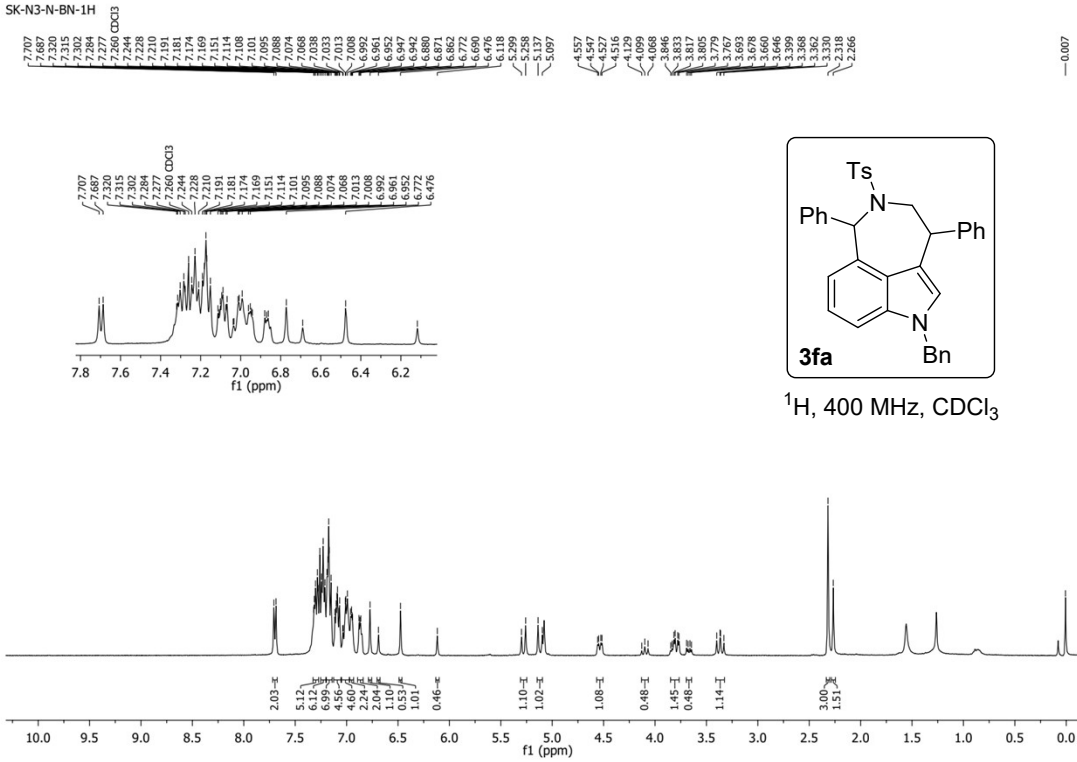
^{13}C, 125 MHz, $CDCl_3$



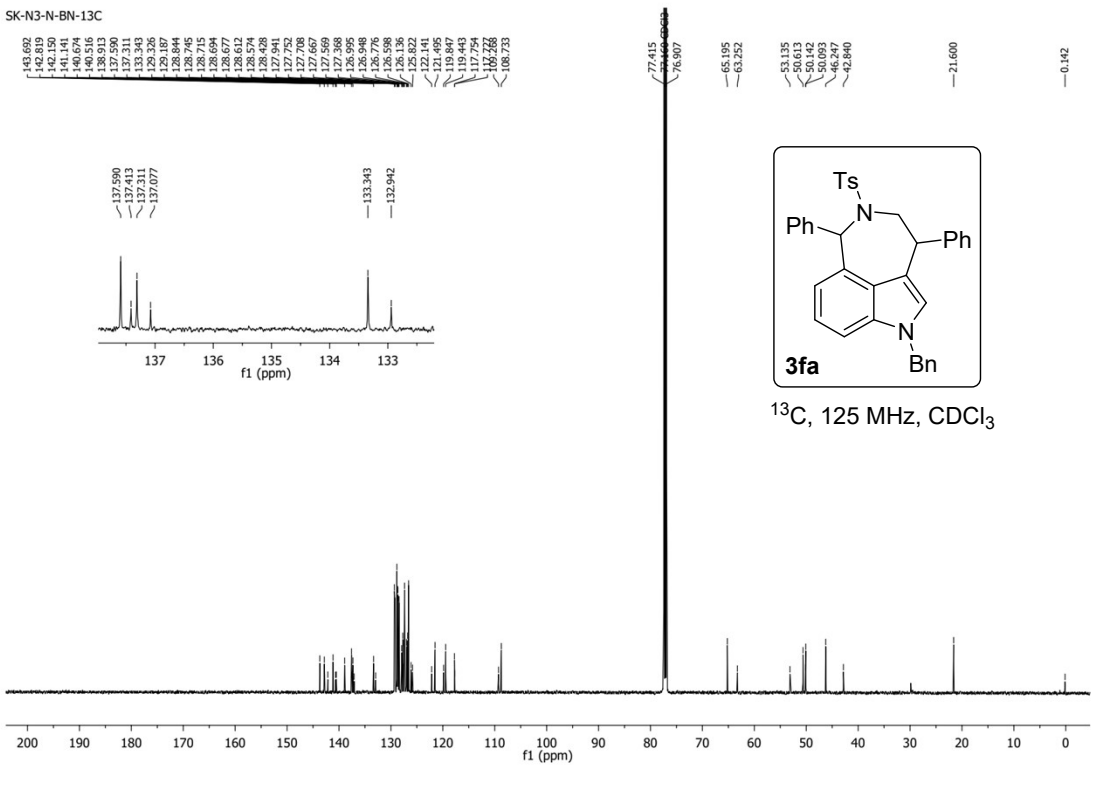
^{1}H, 400 MHz, $CDCl_3$



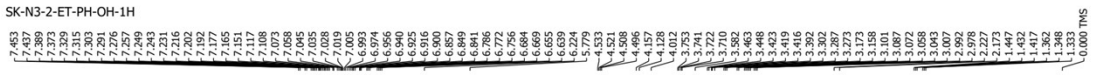
^{13}C, 125 MHz, $CDCl_3$

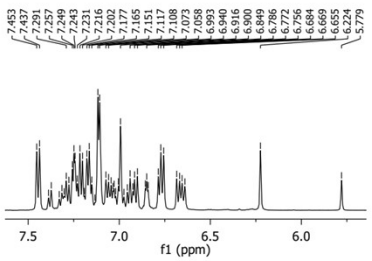


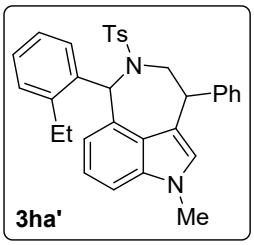
^{1}H, 400 MHz, $CDCl_3$



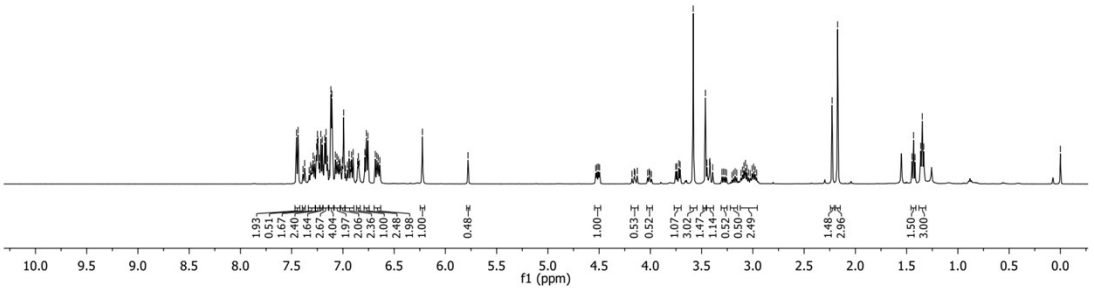
^{13}C, 125 MHz, $CDCl_3$

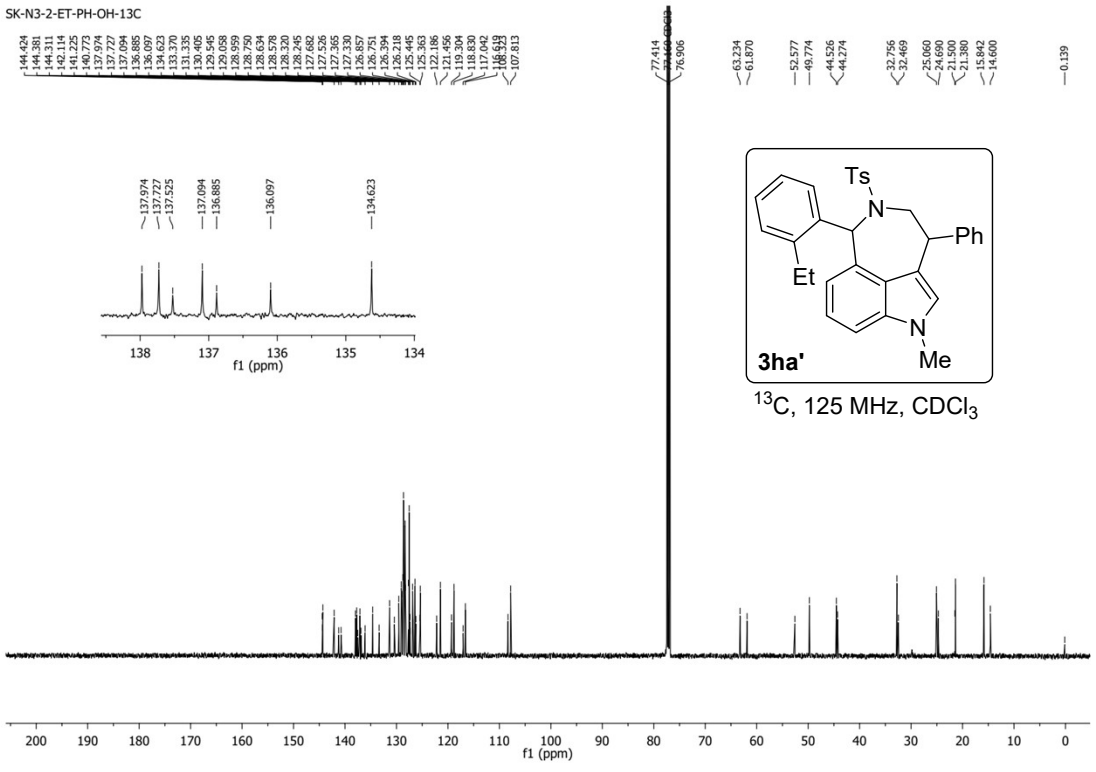




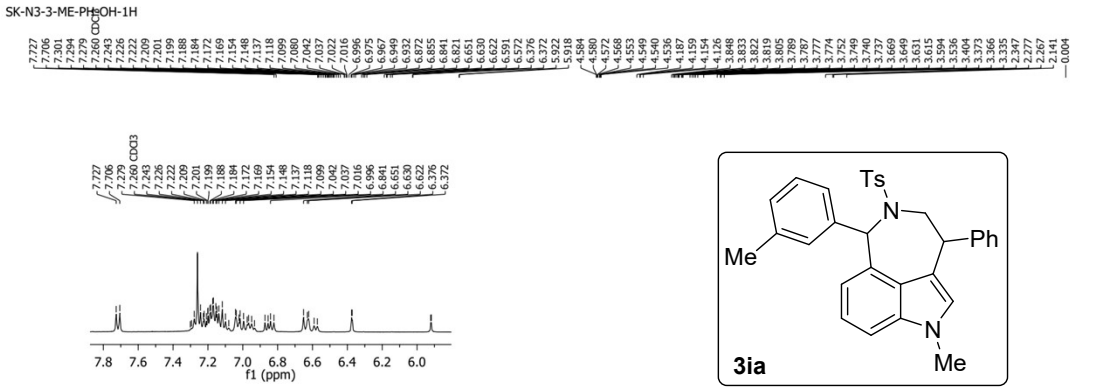


^{1}H, 400 MHz, $CDCl_3$

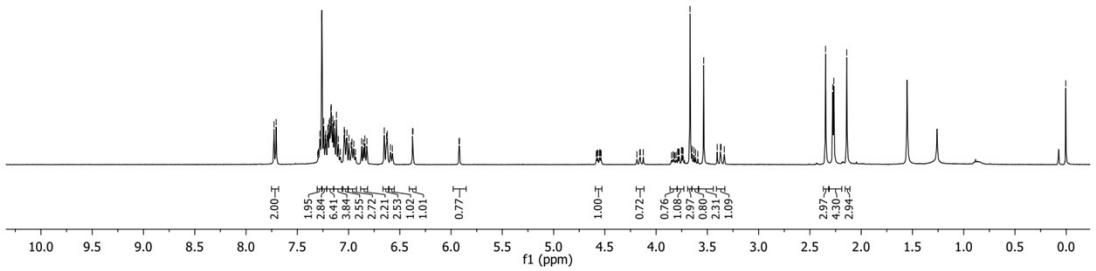


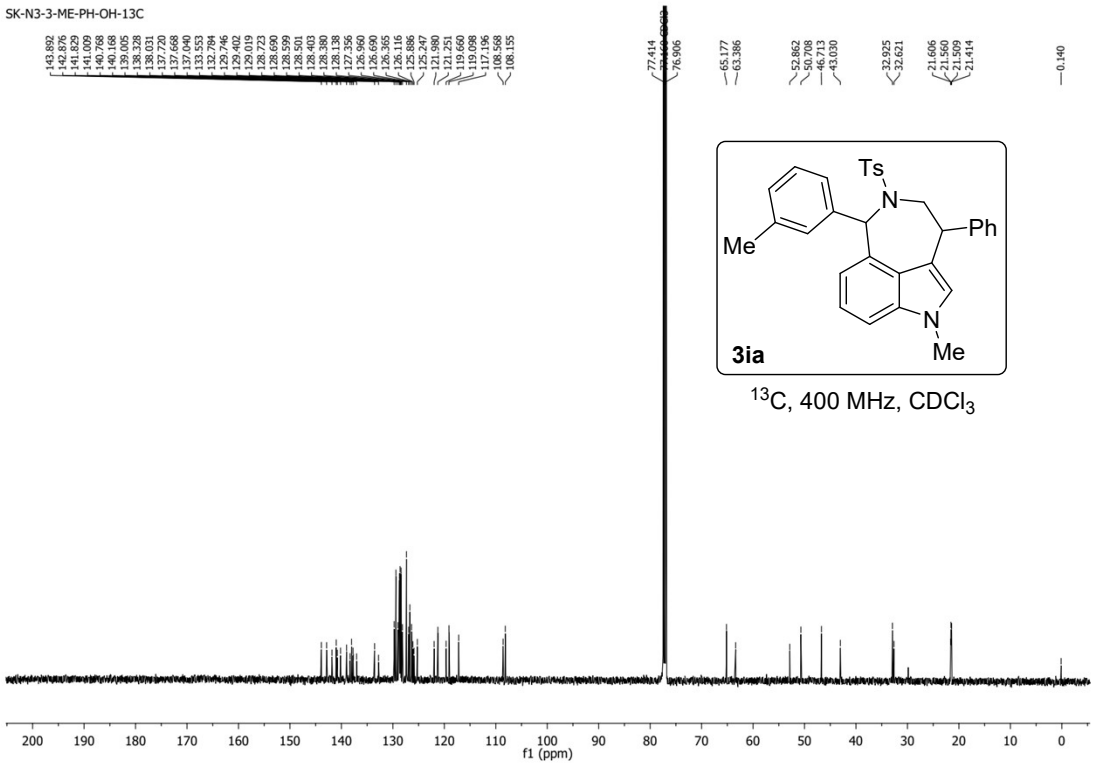


^{13}C, 125 MHz, $CDCl_3$

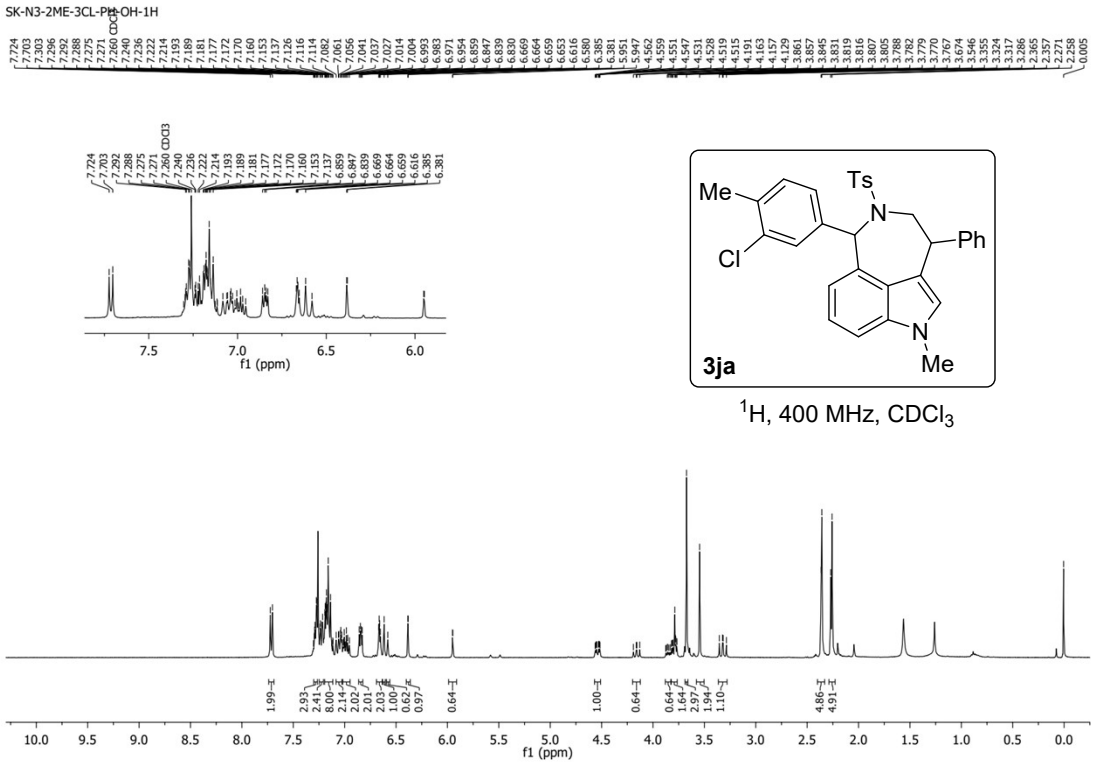


^{1}H, 400 MHz, $CDCl_3$

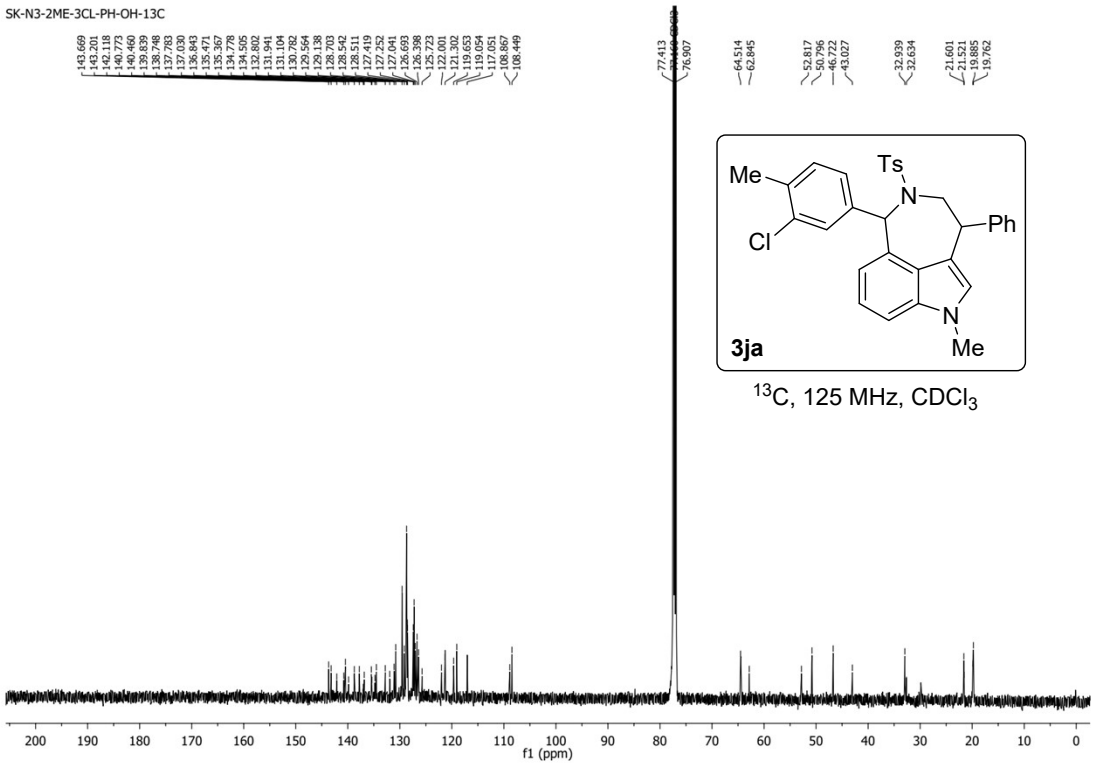




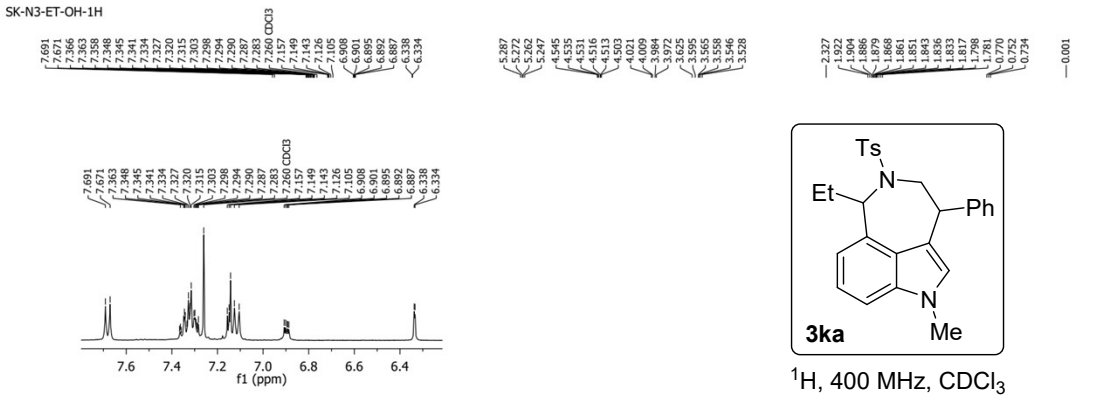
^{13}C, 400 MHz, $CDCl_3$



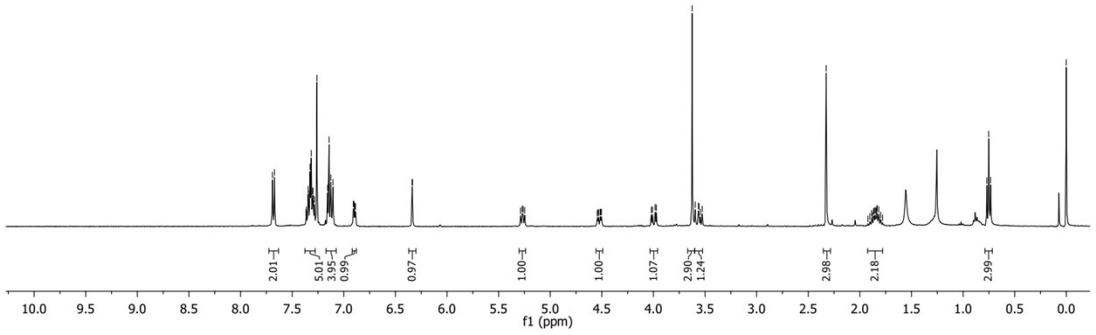
^{1}H, 400 MHz, $CDCl_3$

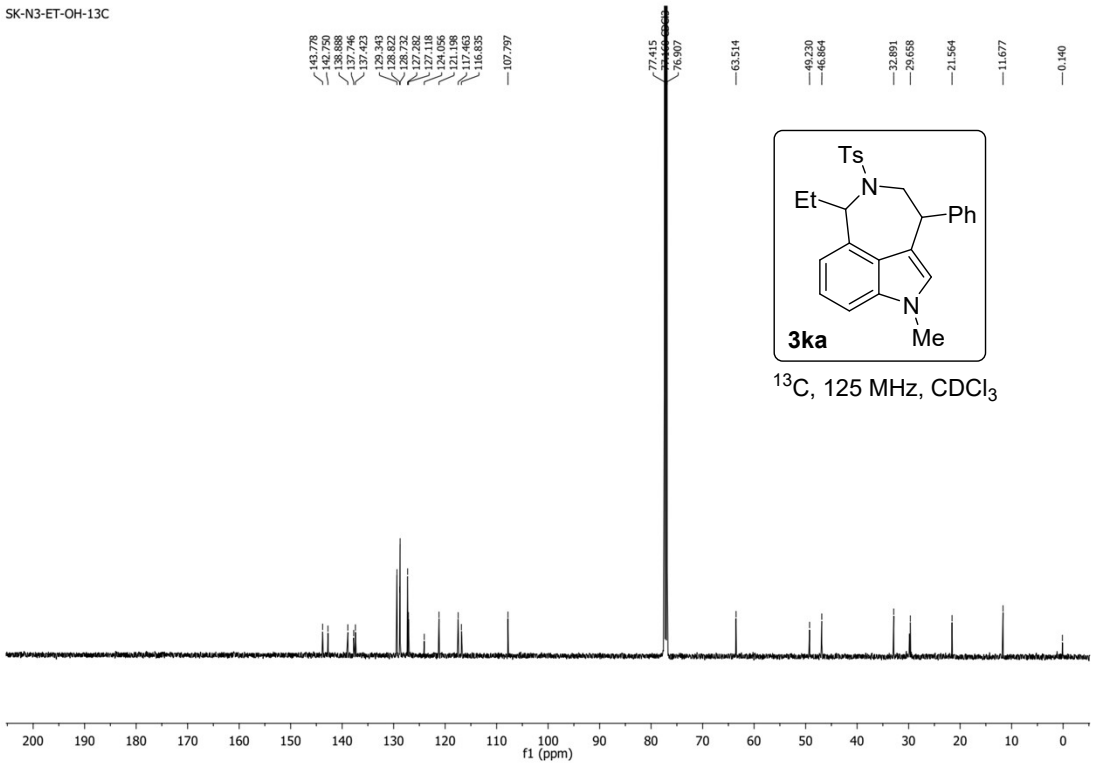


^{13}C, 125 MHz, $CDCl_3$

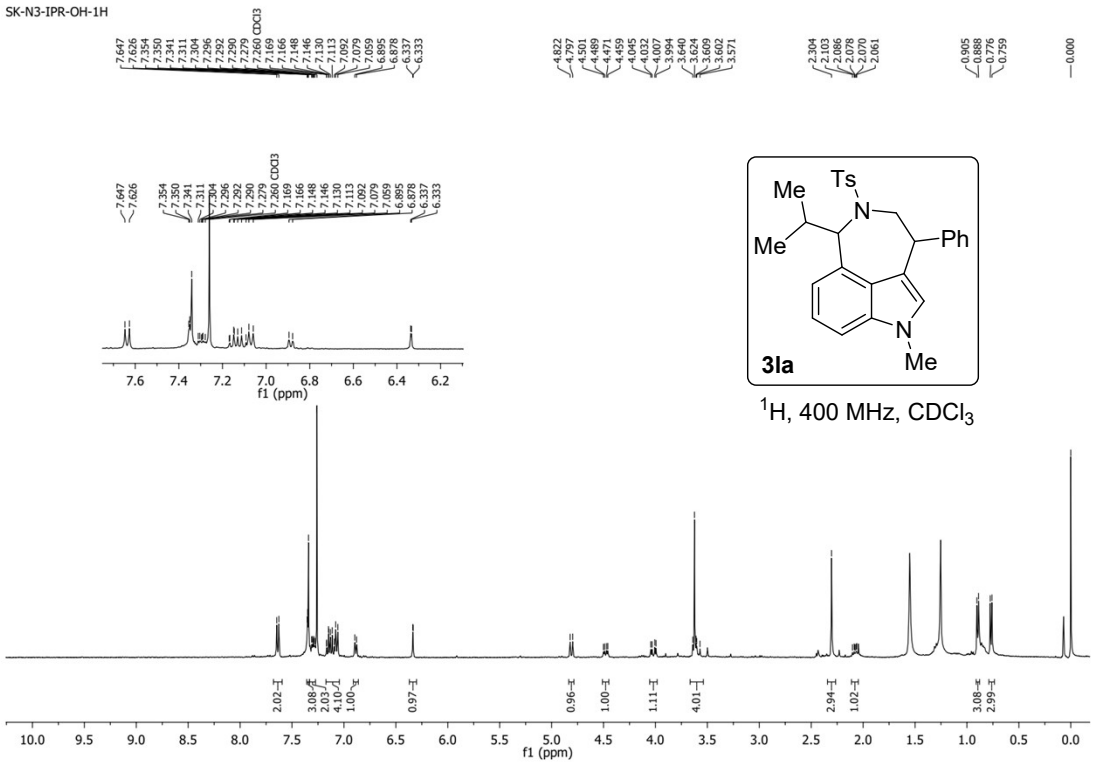


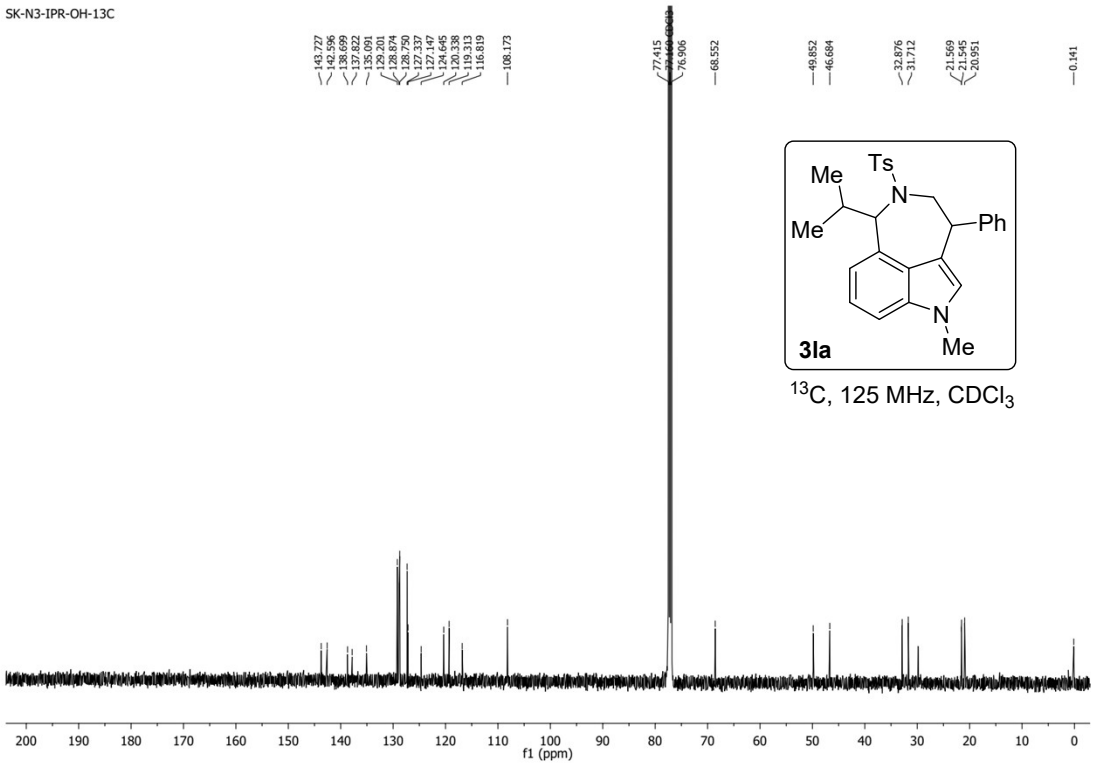
^{1}H, 400 MHz, $CDCl_3$

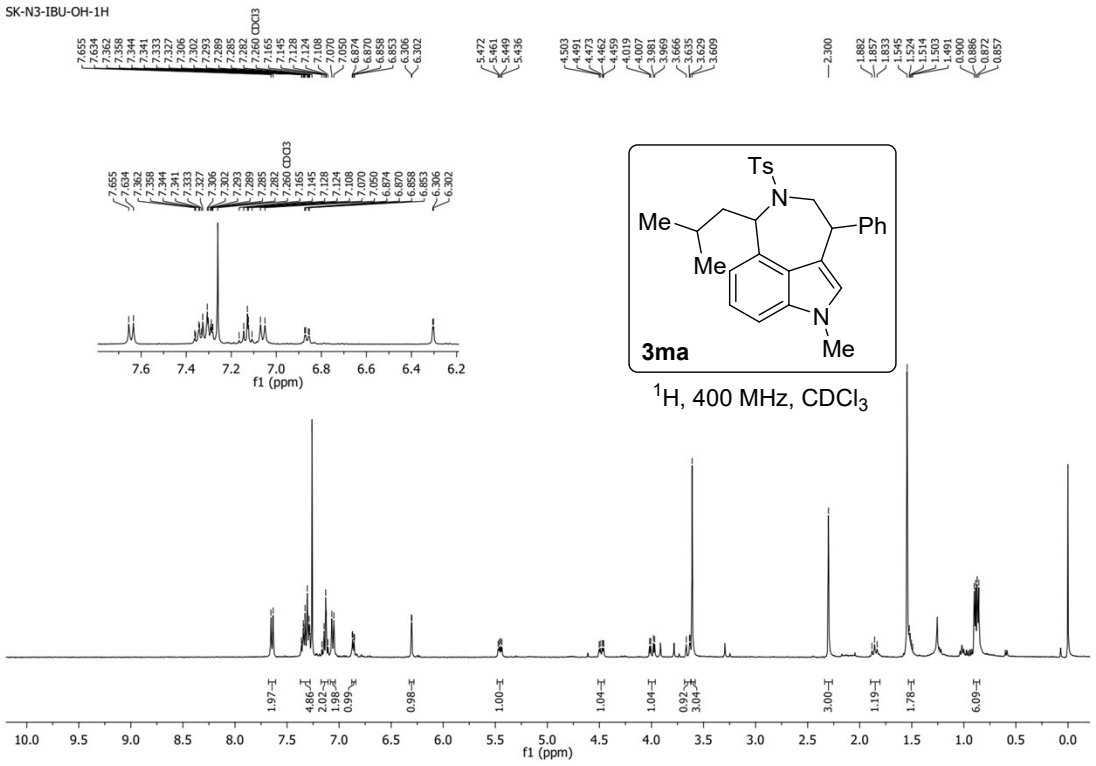


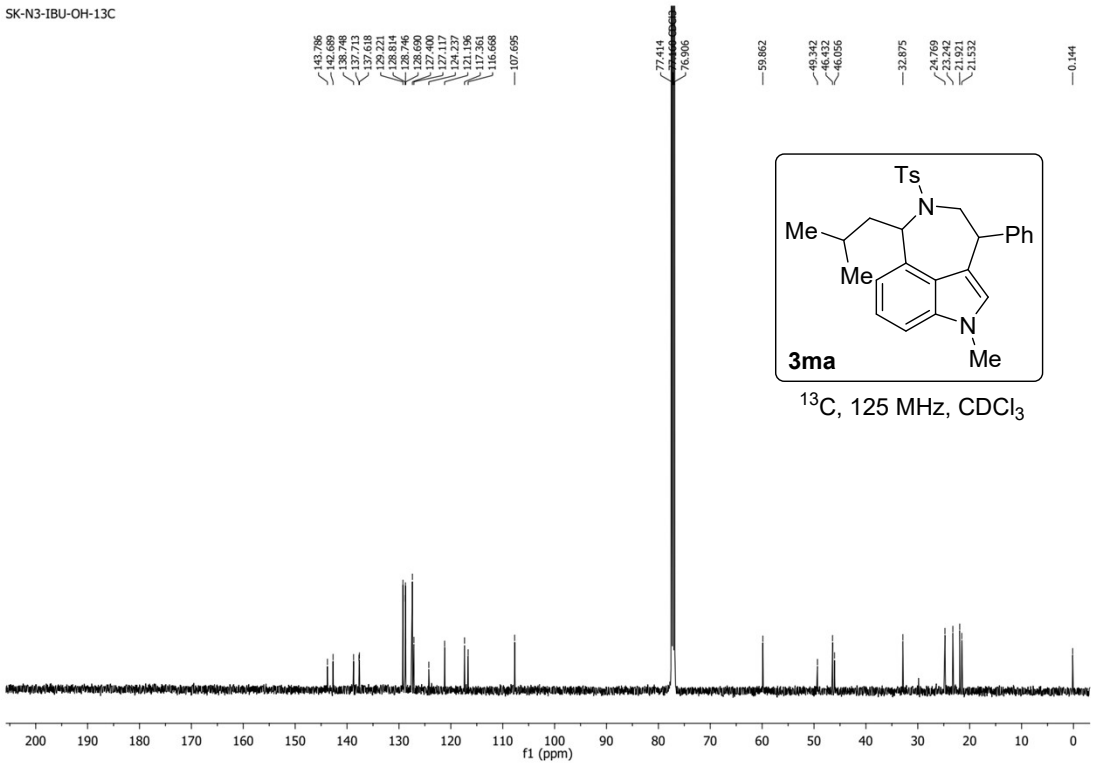


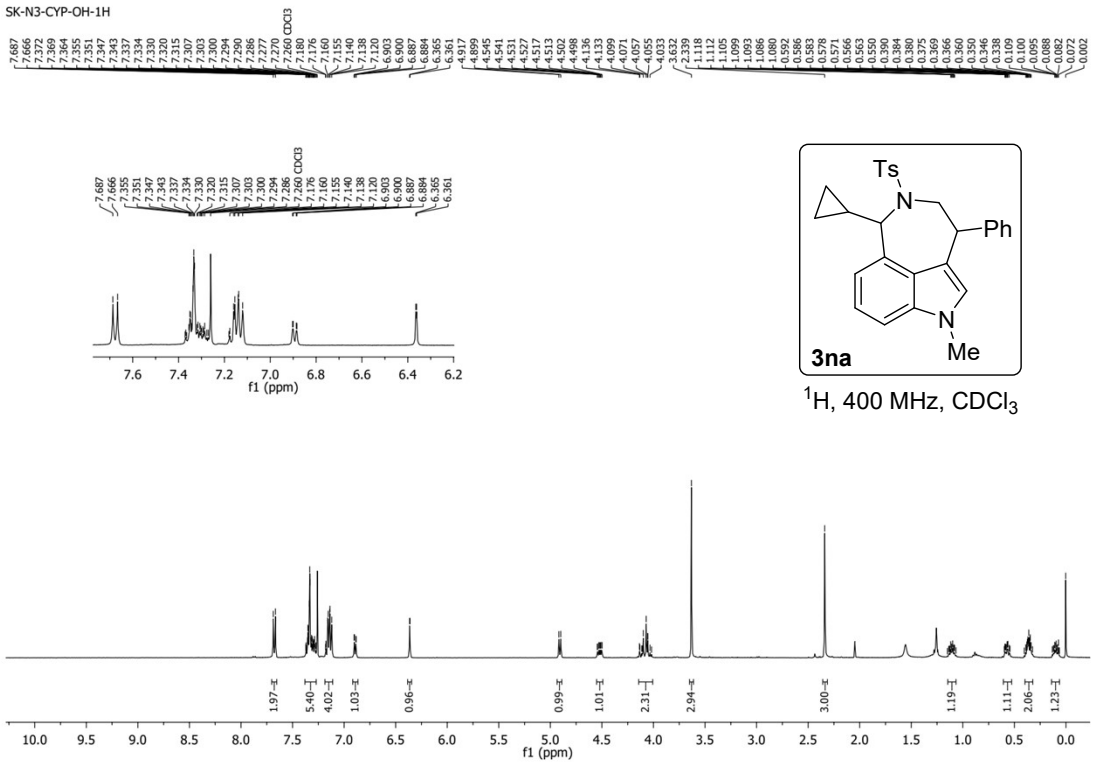
^{13}C, 125 MHz, $CDCl_3$


SK-N3-IPR-OH-1H
Me
Ts
N
Ph
Me
N
Me
3la
1H, 400 MHz, CDCl3
f1 (ppm)

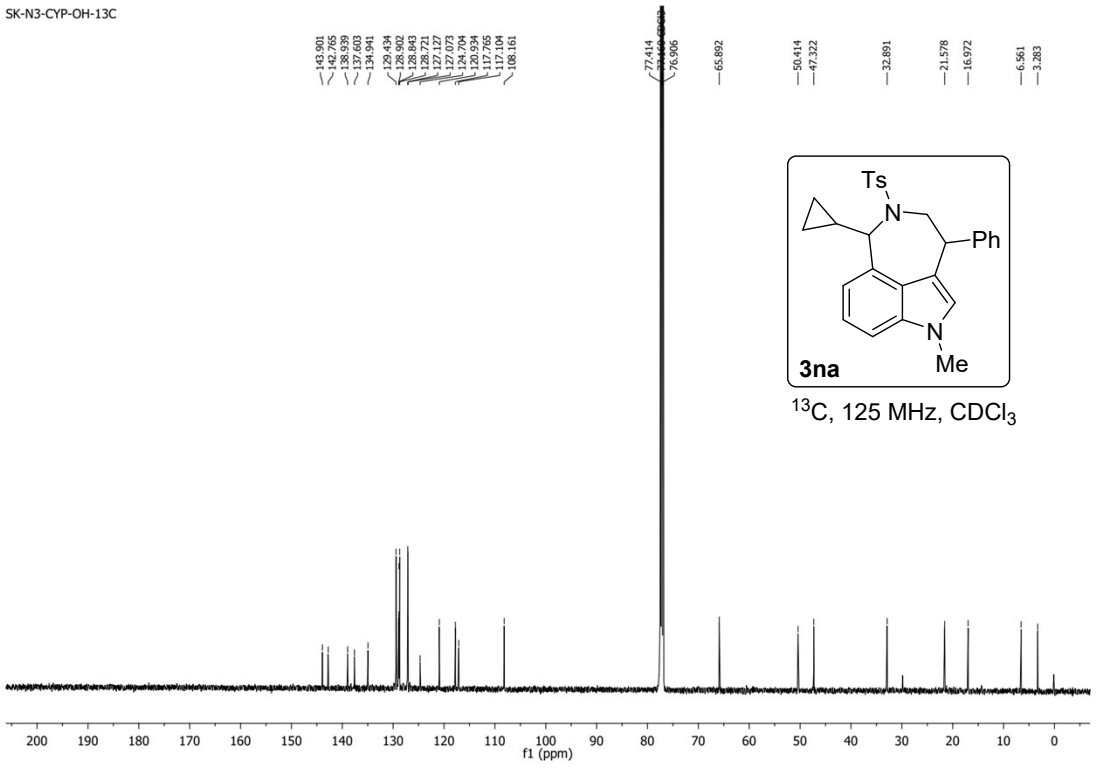

SK-N3-IPR-OH-13C
Me
Ts
N
Ph
Me
N
Me
3la
13C, 125 MHz, CDCl3
f1 (ppm)


SK-N3-IBU-OH-1H
Ts
N
Me
Ph
Me
N
Me
3ma
^{1}H, 400 MHz, CDCl$_3$
f1 (ppm)

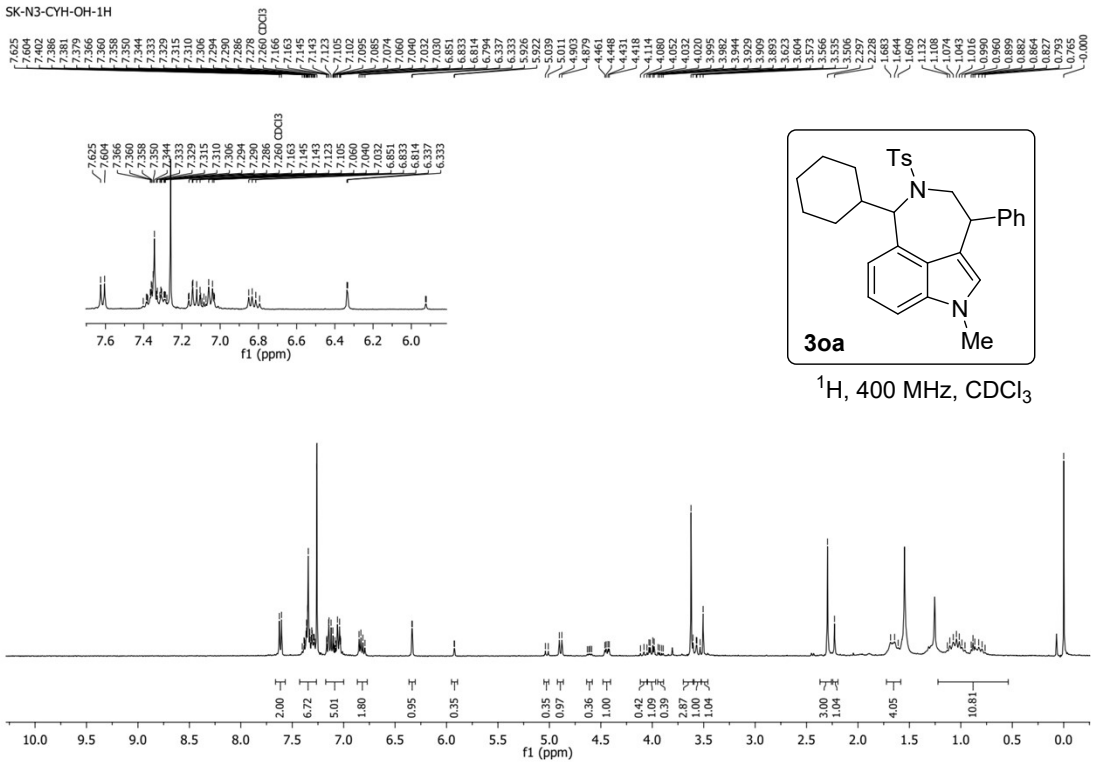

SK-N3-IBU-OH-13C
Ts
N
Me
Ph
Me
N
Me
3ma
^{13}C, 125 MHz, CDCl$_3$
f1 (ppm)



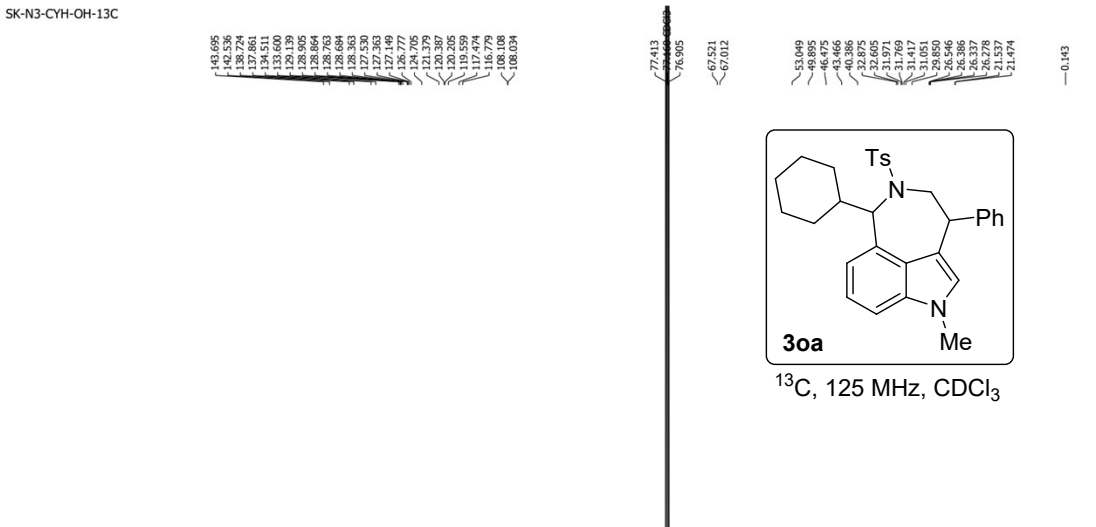
^{1}H, 400 MHz, $CDCl_3$



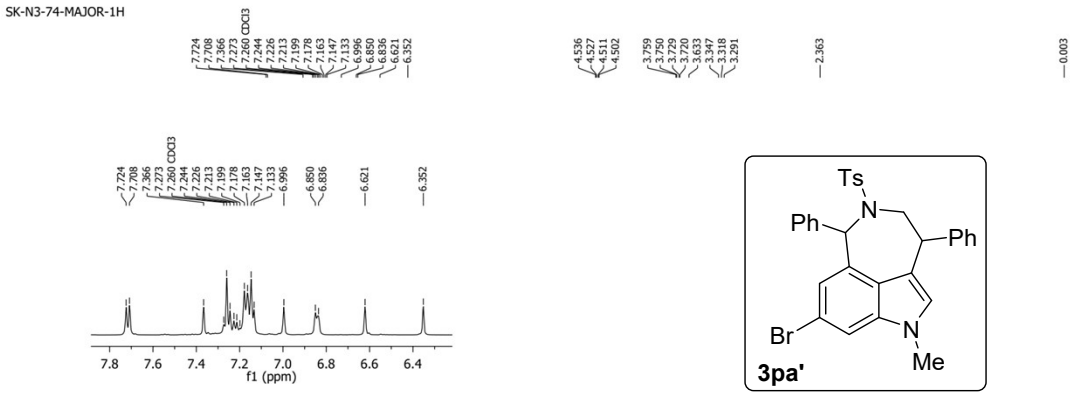
^{13}C, 125 MHz, $CDCl_3$



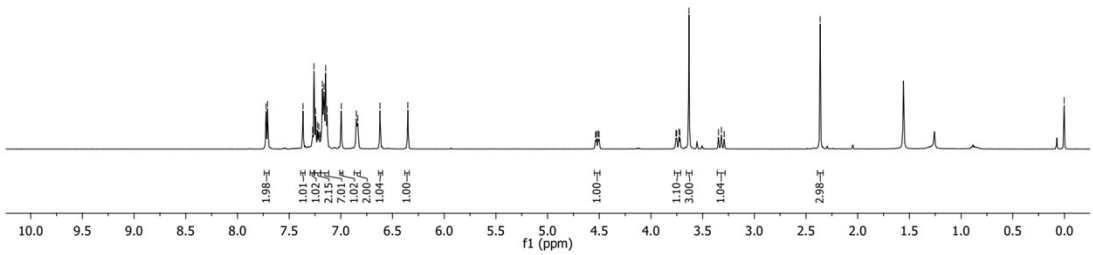
^{1}H, 400 MHz, $CDCl_3$

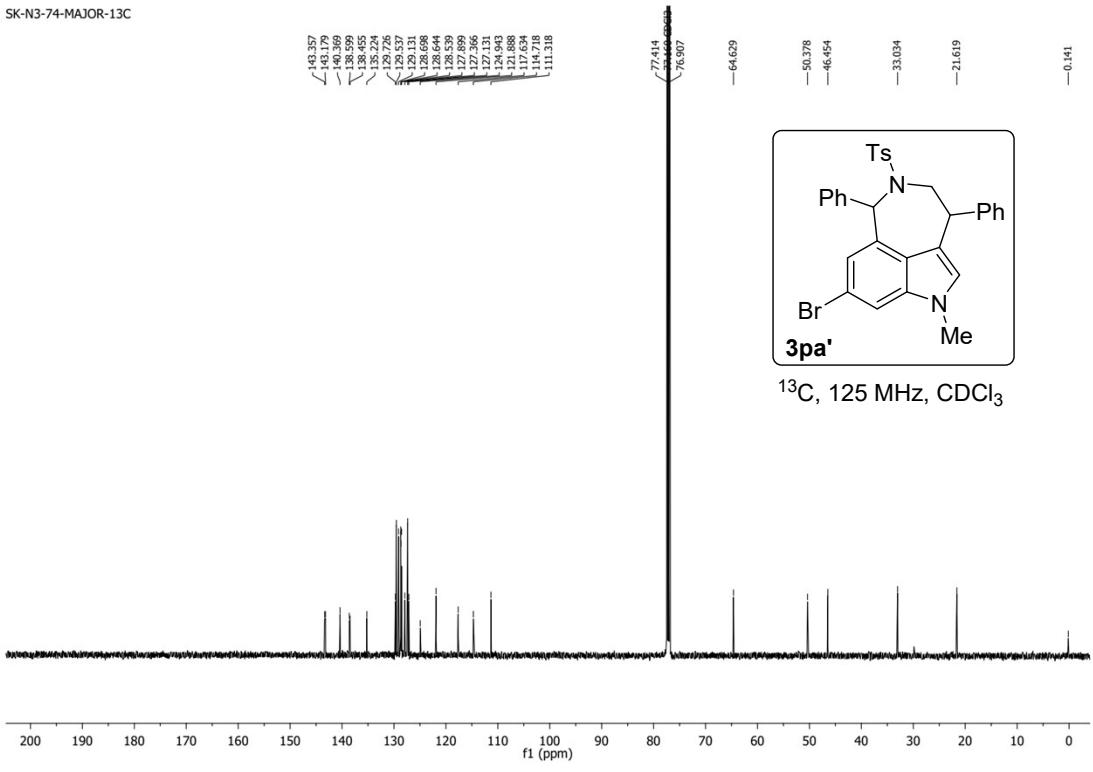


^{13}C, 125 MHz, $CDCl_3$

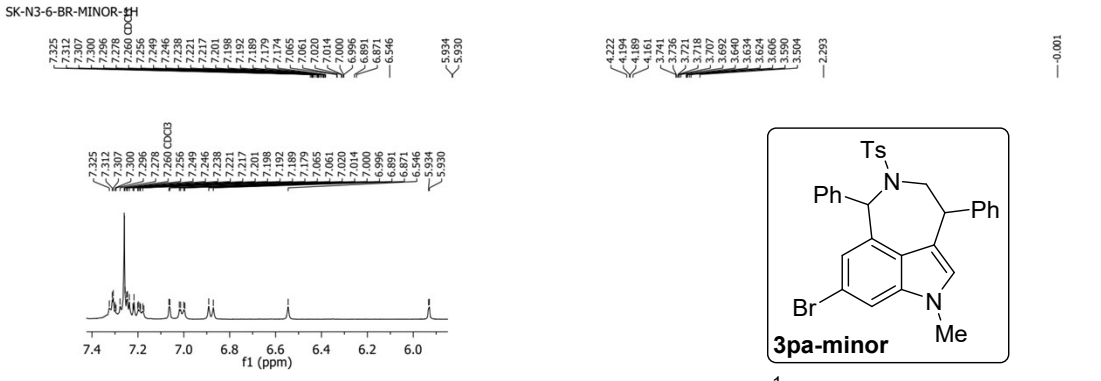


^{1}H, 400 MHz, $CDCl_3$

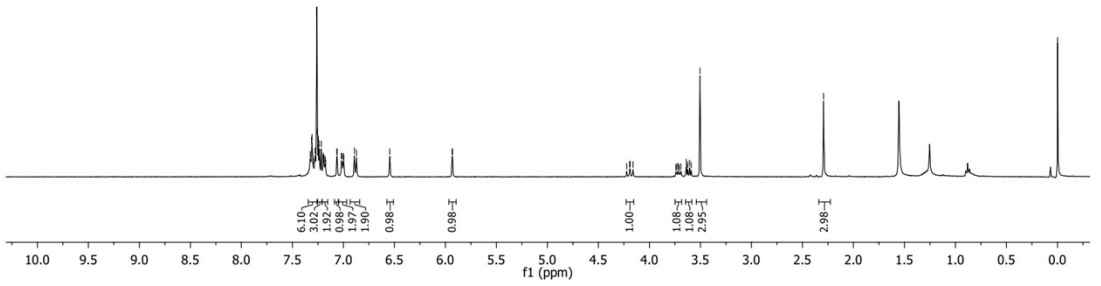


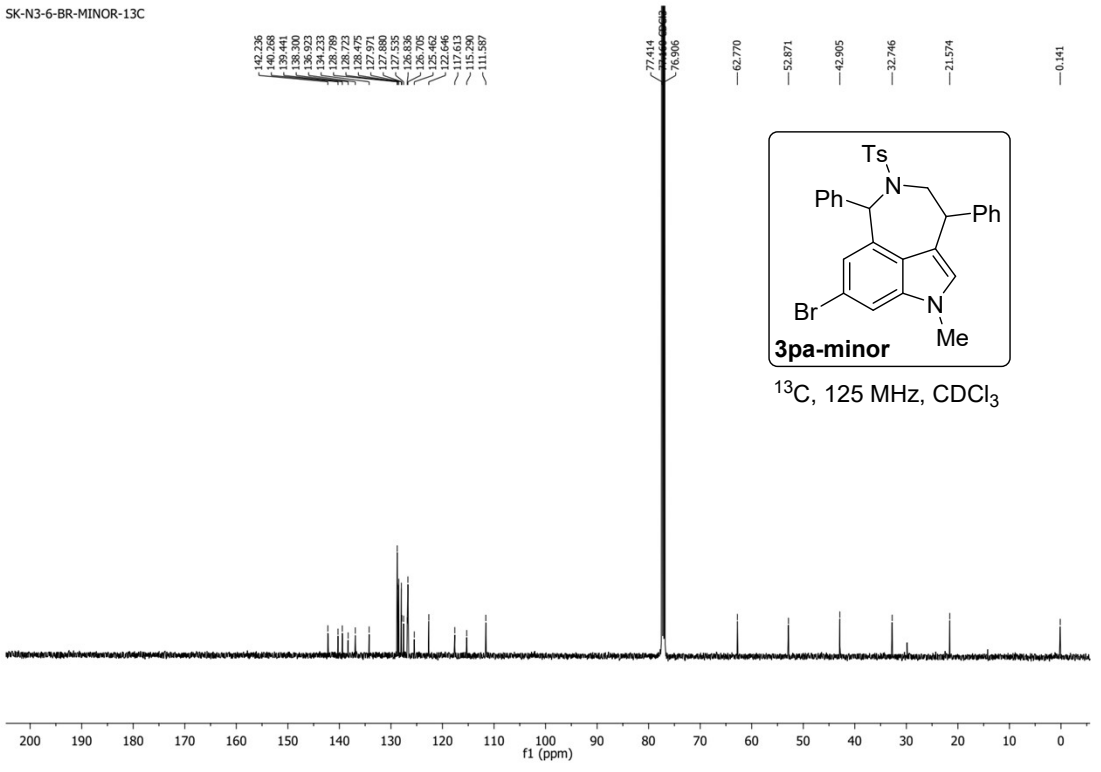


^{13}C, 125 MHz, $CDCl_3$

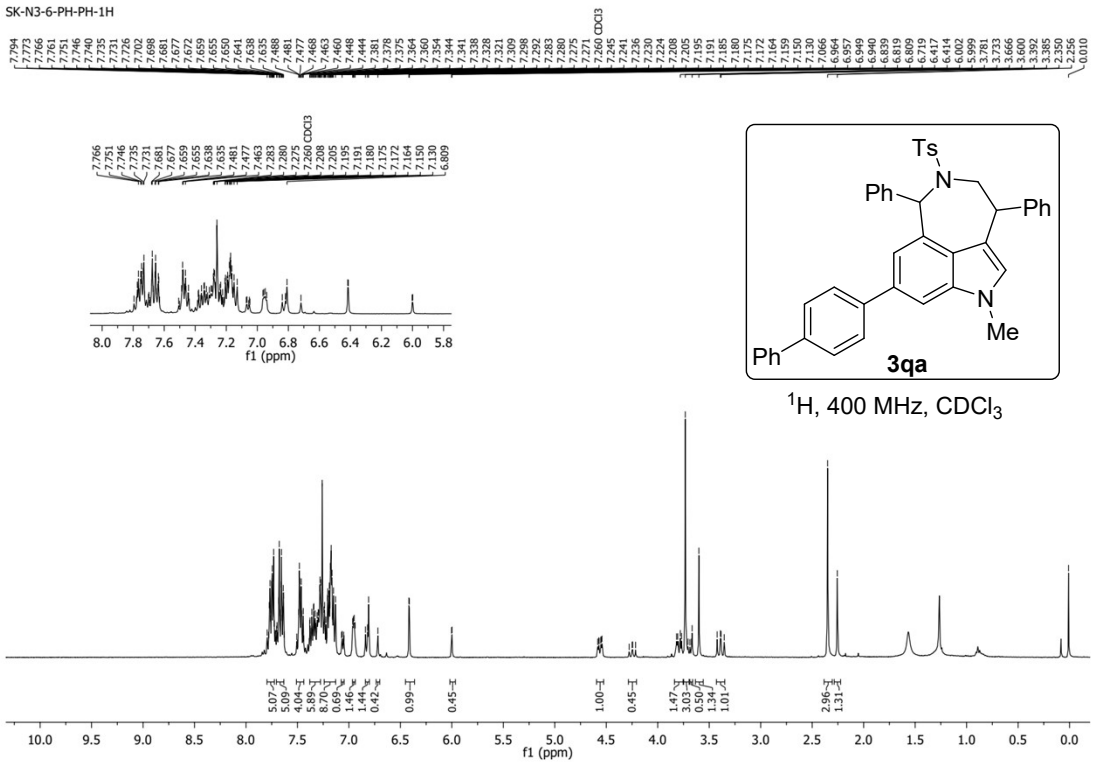


^{1}H, 400 MHz, $CDCl_3$

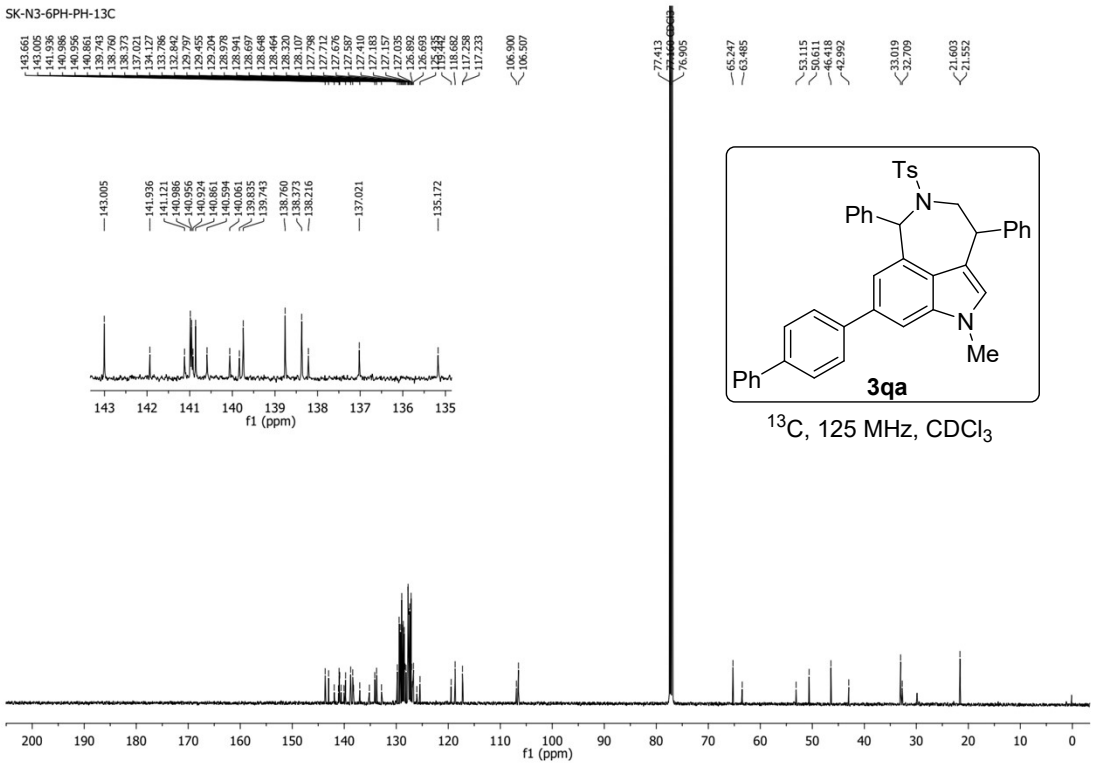




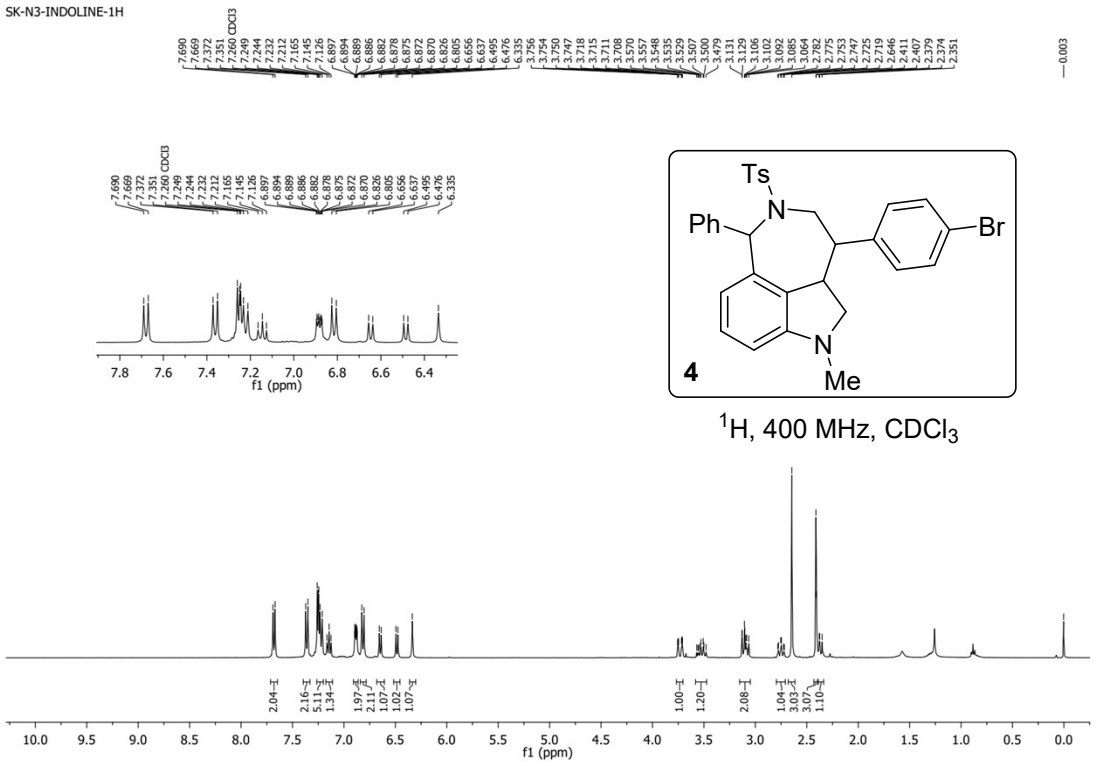
^{13}C, 125 MHz, $CDCl_3$



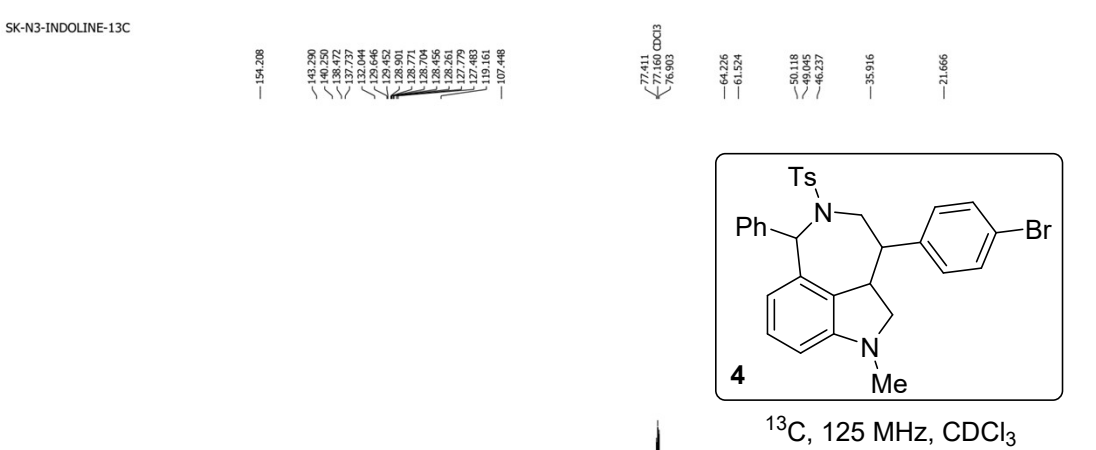
^{1}H, 400 MHz, $CDCl_3$



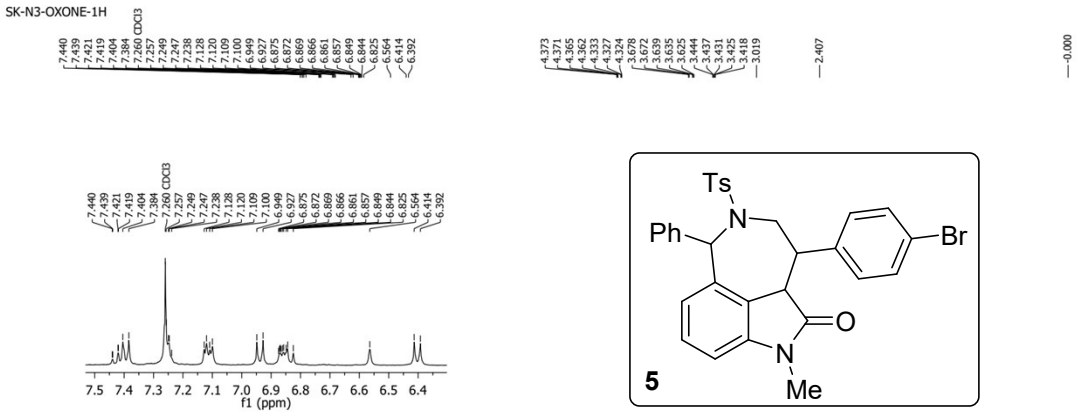
^{13}C, 125 MHz, $CDCl_3$



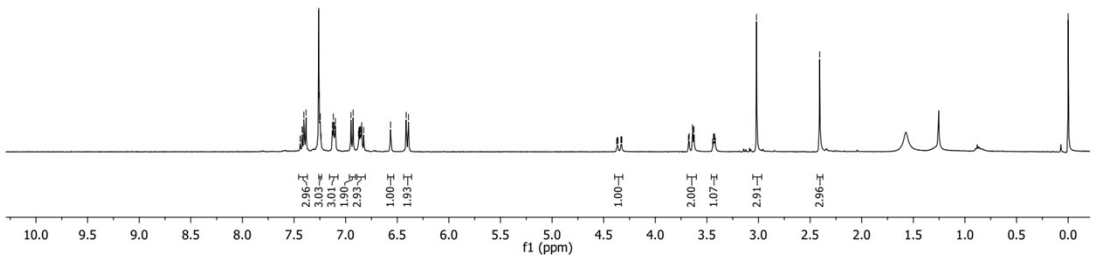
^{1}H, 400 MHz, $CDCl_3$

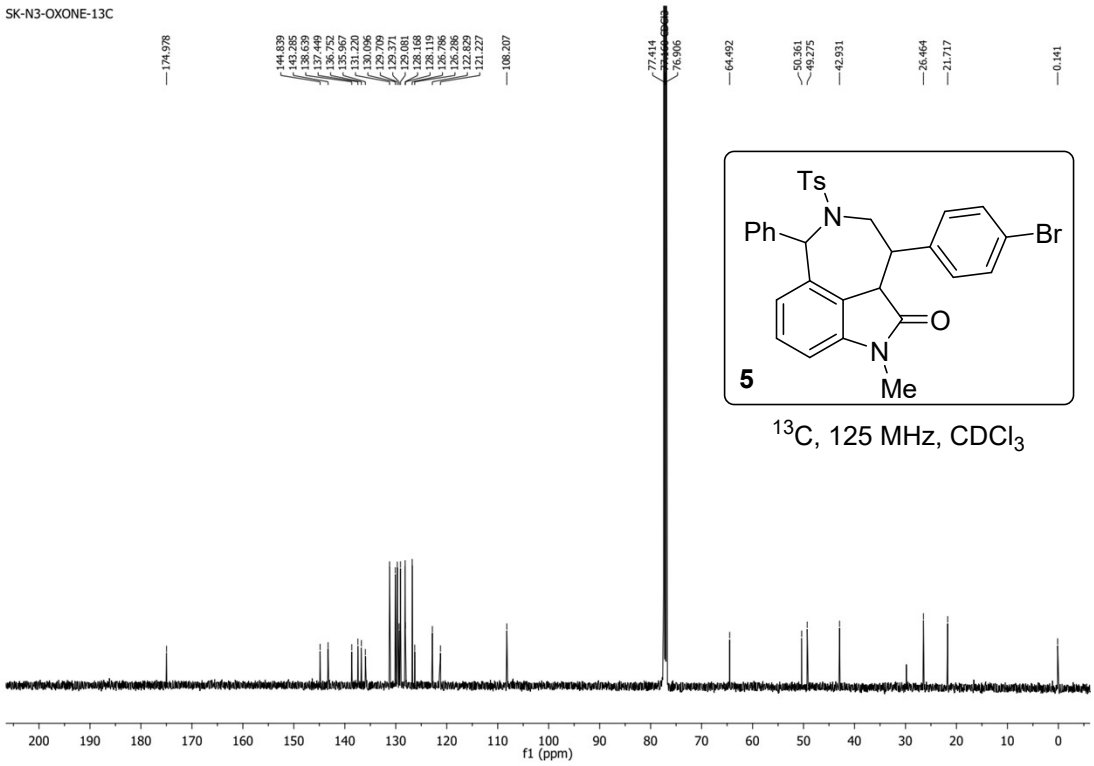


^{13}C, 125 MHz, $CDCl_3$

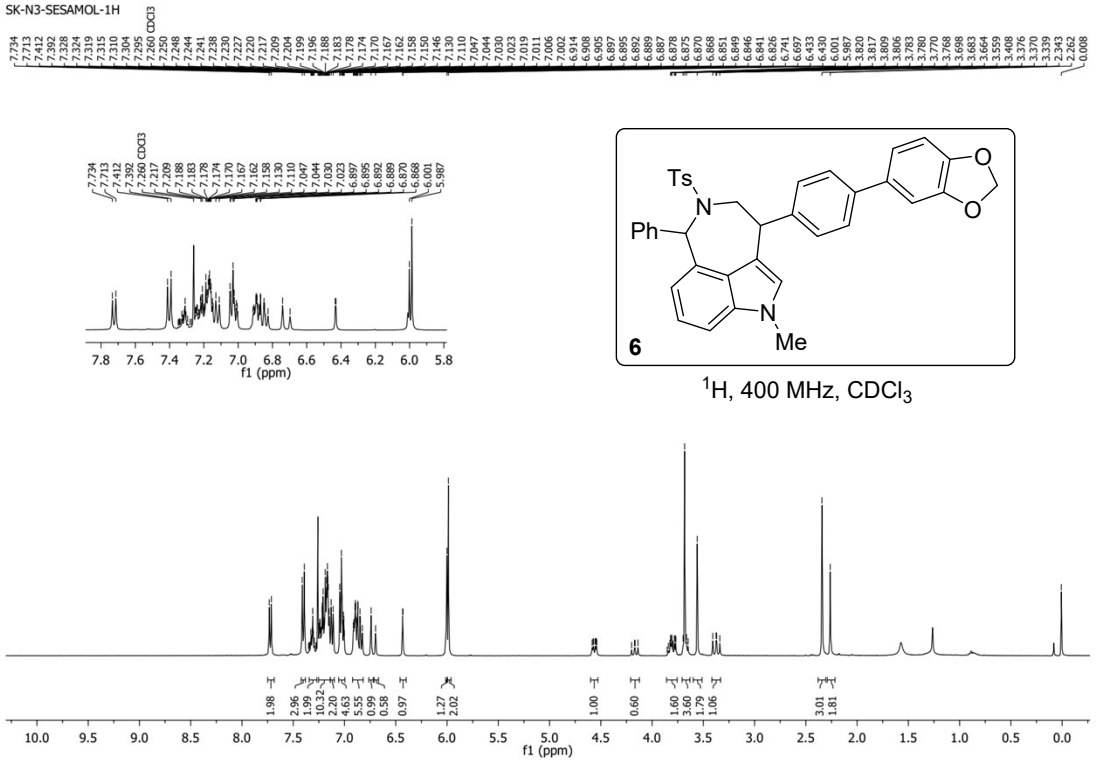


^{1}H, 400 MHz, $CDCl_3$

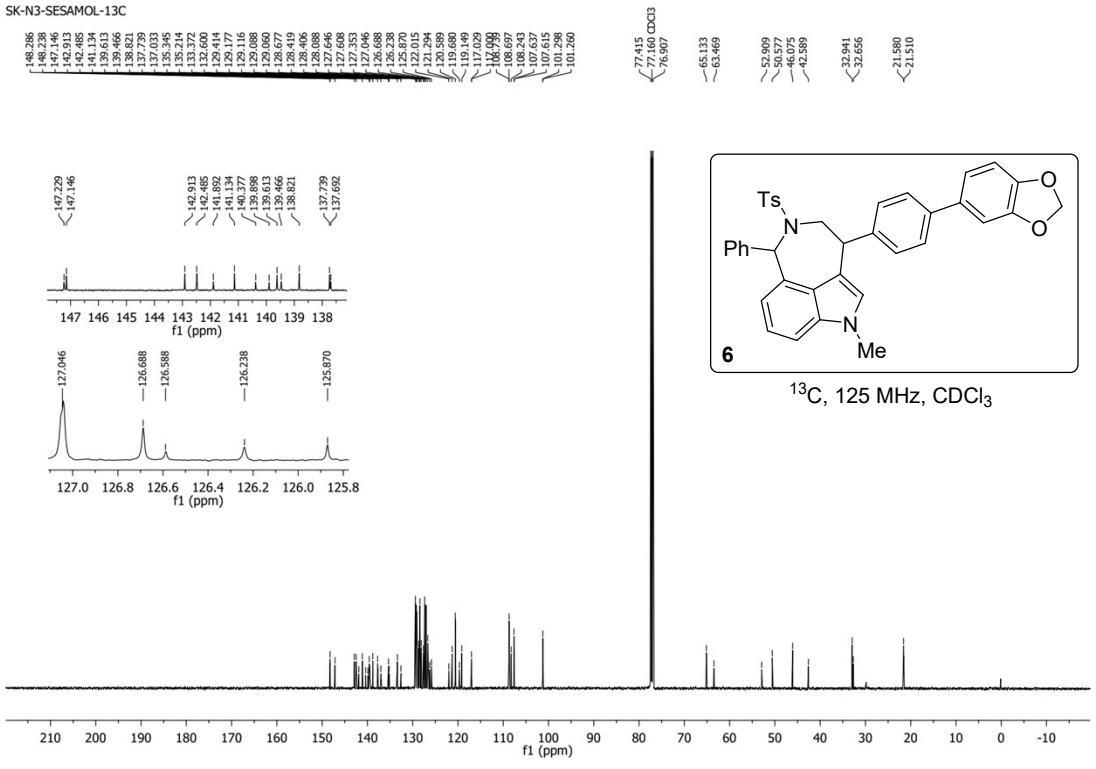




^{13}C, 125 MHz, $CDCl_3$



^{1}H, 400 MHz, $CDCl_3$



^{13}C, 125 MHz, $CDCl_3$