Supporting Information

Pd/Xiang-Phos-catalyzed Enantioselective Intermolecular Carboheterofunctionalization of Norbornene and Norbornadiene

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1. General Information

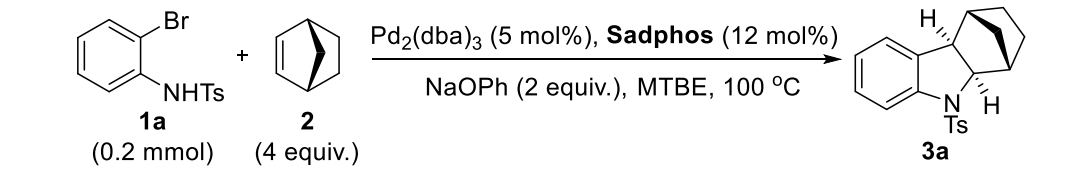
Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere; materials obtained from commercial suppliers were used directly without further purification. The $[\alpha]_D$ was recorded using PolAAr 3005 High Accuracy Polarimeter. ^{1}H NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in chloroform-d_3; ^{13}C NMR spectra were recorded on a Bruker 101 MHz or 126 MHz spectrometer in chloroform-d_3; ^{19}F NMR spectra were recorded on a Bruker 376 MHz spectrometer in chloroform-d_3. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. The data is being reported as (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration).

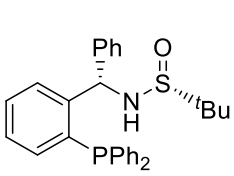
Trichloromethane ($CHCl_3$)， dichloromethane, 1,2-dichloroethane and acetonitrile were freshly distilled from CaH_2; tetrahydrofuran (THF), toluene and ether were dried with sodium and benzophenone, and distilled before use.

Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 200-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate. 2-Br-aniline derivatives **1a-1t** were synthesized according to the corresponding literature[1]. Other reagents and solvents were used as received from commercial sources (*Energy Chemical, J&K®, Adamas-beta®, Bidepharm*) without further purification. The enantionmeric excesses of the products were determined by chiral stationary phase HPLC using a Chiralpak IB, IC, IF, OJ-H.

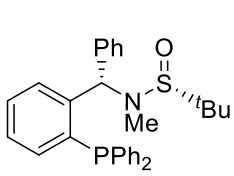
2. Optimization of the intermolecular carboheterofunctionalizations

2.1 Scheme S1. Screened representative **Sadphos** ligands on the intermolecular carboamination of norbornene and **1a**

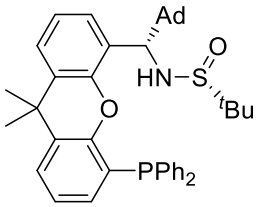




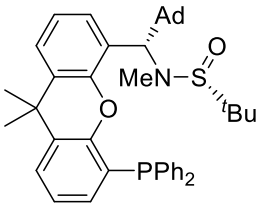
(*S*, R_S)-**M1**
N.D.



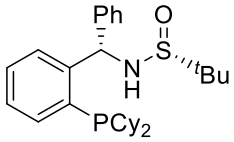
(*S*, R_S)-***N*-Me-M1**
N.D.



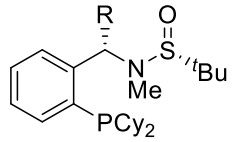
(*S*, R_S)-**PC1**
N.D.



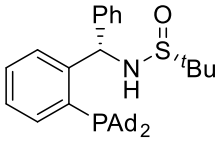
(*S*, R_S)-***N*-Me-PC1**
N.D.



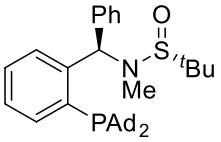
(*S*, R_S)-**Xu1**
N.D.



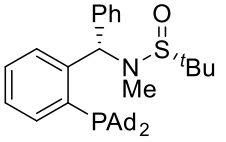
R = 3,5-^{t}Bu$_2$-4-MeOC$_6$H$_2$
(*S*, R_S)-***N*-Me-Xu2**
N.D.



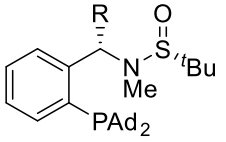
(*S*, R_S)-**X1**
N.D.



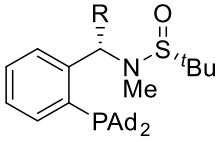
(*R*, R_S)-***N*-Me-X1** (**L1**)
33% yield, -8% *ee*



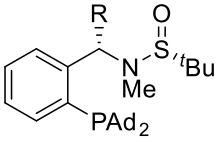
(*S*, R_S)-***N*-Me-X1** (**L2**)
58% yield, 48% *ee*



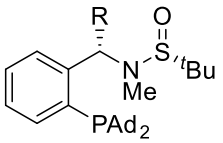
R = 1-naphthyl
(*S*, R_S)-***N*-Me-X2** (**L3**)
44% yield, 31% *ee*



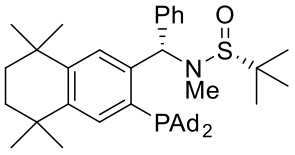
R = 3,5-^{t}Bu$_2$-4-MeOC$_6$H$_2$
(*S*, R_S)-***N*-Me-X3** (**L4**)
52% yield, 39% *ee*



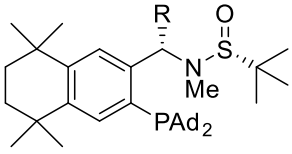
R = Me
(*S*, R_S)-***N*-Me-X4** (**L5**)
21% yield, 54% *ee*



R = $(CH_2)_2(CH)(CH_3)_2$
(*S*, R_S)-***N*-Me-X5** (**L6**)
27% yield, 52% *ee*

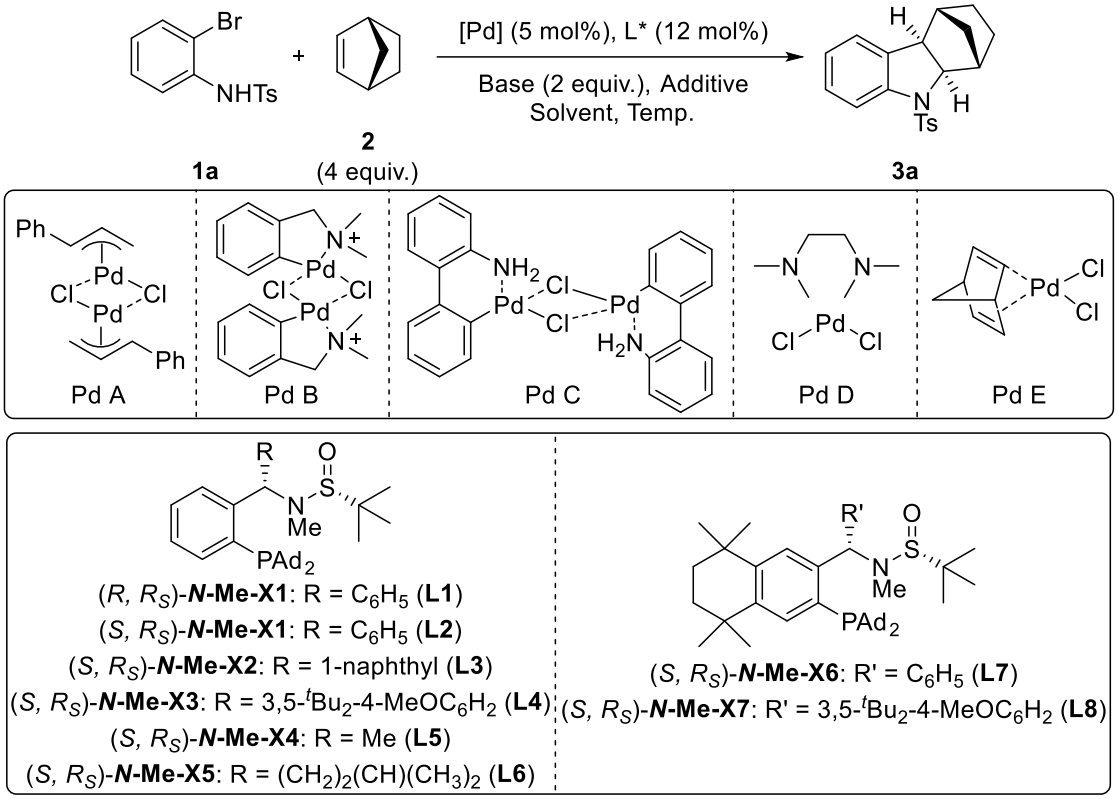


(*S*, R_S)-***N*-Me-X6** (**L7**)
71% yield, 56% *ee*



R = 3,5-^{t}Bu$_2$-4-MeOC$_6$H$_2$
(*S*, R_S)-***N*-Me-X7** (**L8**)
66% yield, 48% *ee*

2.2 Table S1. Detailed optimization of the enantioselective intermolecular carboamination of norbornene and **1a**[a]

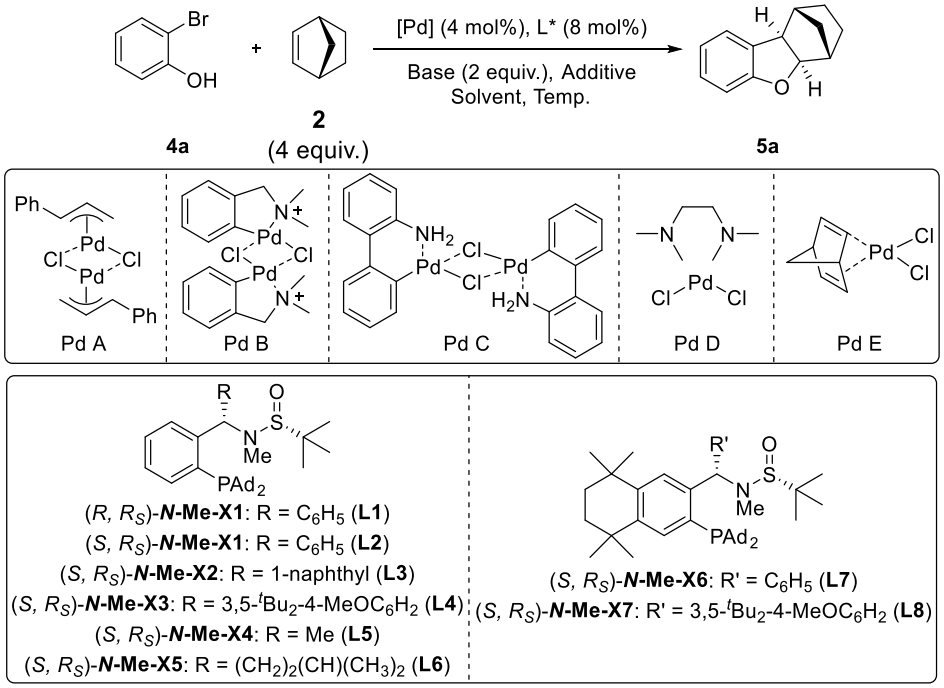


Entry	Pd	L*	Base	Additive	Solvent	Temp. (°C)	Yield (Ee) (%)[b,c]
1	$Pd_2(dba)_3$	**L7**	CH_3OLi	-	MTBE	100	33(18)
2	$Pd_2(dba)_3$	**L7**	LiO^{t}Bu	-	MTBE	100	51(16)
3	$Pd_2(dba)_3$	**L7**	EtONa	-	MTBE	100	49(39)
4	$Pd_2(dba)_3$	**L7**	NaO^{t}Bu	-	MTBE	100	65(26.2)
5	$Pd_2(dba)_3$	**L7**	KO^{t}Bu	-	MTBE	100	52(31)
6	$Pd_2(dba)_3$	**L7**	CsF	-	MTBE	100	37(38.6)
7	$Pd_2(dba)_3$	**L7**	Na_2CO_3	-	MTBE	100	29(-9)
8	$Pd_2(dba)_3$	**L7**	K_3PO_4	-	MTBE	100	55(43.4)
9	$Pd_2(dba)_3$	**L7**	DABCO	-	MTBE	100	0
10	$Pd_2(dba)_3$	**L7**	*i*Pr$_2$NEt	-	MTBE	100	0
11	$Pd_2(dba)_3$	**L7**	NaOPh	-	MTBE	100	71(55.5)
12	$Pd_2(dba)_3$	**L7**	NaOPh	-	2-Me-THF	100	42(22.7)
13	$Pd_2(dba)_3$	**L7**	NaOPh	-	1,4-dioxane	100	34(12.5)
14	$Pd_2(dba)_3$	**L7**	NaOPh	-	DCM	100	82(79.7)
15	$Pd_2(dba)_3$	**L7**	NaOPh	-	DCE	100	84(77.9)
16	$Pd_2(dba)_3$	**L7**	NaOPh	-	$CHCl_3$	100	75(59.8)
17	$Pd_2(dba)_3$	**L7**	NaOPh	-	Toluene	100	79(66.9)
18	$Pd_2(dba)_3$	**L7**	NaOPh	-	$PhCF_3$	100	80(75.6)

19	$Pd_2(dba)_3$	**L7**	NaOPh	-	MeOH	100	63(57.1)
20	$Pd(dba)_2$	**L7**	NaOPh	-	DCM	100	66(75)
21	$Pd_2(dba)_3$•$CHCl_3$	**L7**	NaOPh	-	DCM	100	77(75)
22	$Pd(OAc)_2$	**L7**	NaOPh	-	DCM	100	69(71)
23	Pd A	**L7**	NaOPh	-	DCM	100	73(75)
24	Pd B	**L7**	NaOPh	-	DCM	100	82(77)
25	Pd C	**L7**	NaOPh	-	DCM	100	77(71.7)
26	Pd D	**L7**	NaOPh	-	DCM	100	25(83.3)
27	Pd E	**L7**	NaOPh	-	DCM	100	59(72.3)
28	Pd B	**L7**	NaOPh	3 Å	DCM	100	75(83.5)
29	Pd B	**L7**	NaOPh	4 Å	DCM	100	78(89.1)
30	Pd B	**L7**	NaOPh	5 Å	DCM	100	69(69.3)
31	Pd B	**L1**	NaOPh	4 Å	DCM	100	53(-8.4)
32	Pd B	**L2**	NaOPh	4 Å	DCM	100	73(66.1)
33	Pd B	**L3**	NaOPh	4 Å	DCM	100	54(51.7)
34	Pd B	**L4**	NaOPh	4 Å	DCM	100	66(56.5)
35	Pd B	**L5**	NaOPh	4 Å	DCM	100	33(81.3)
36	Pd B	**L6**	NaOPh	4 Å	DCM	100	41(80.8)
37	Pd B	**L8**	NaOPh	4 Å	DCM	100	71(78.6)
38[d]	Pd B	**L7**	NaOPh	4 Å	DCM	80	79(92)
39[e]	Pd B	**L7**	NaOPh	4 Å	DCM	80	41(94.5)
40[d]	Pd B	**L7**	NaOPh	4 Å	DCM	60	50(97)
41[d]	Pd B	**L7**	NaOPh	4 Å	DCM	50	27(98)
42[d]	Pd B	**L7**	NaOPh	4 Å	DCM	25	trace

[a] Unless otherwise specified, all reactions were carried out with **1a** (0.2 mmol), **2** (4 equiv.), [Pd] source (5 mol%), ***N*-Me-Xiang-Phos** (12 mol%), Base (2 equiv.), additive (50 mg) in solvent (0.2 M) for 24 hours. [b] Yield of isolated product. [c] Determined by chiral HPLC. [d] **L7** was added to 20 mol%. [e] 2 mol% [Pd] and 10 mol% **L7** were employed.

2.3 Table S2. Detailed optimization of the enantioselective intermolecular carbo-etherification of norbornene and **4a**[a]



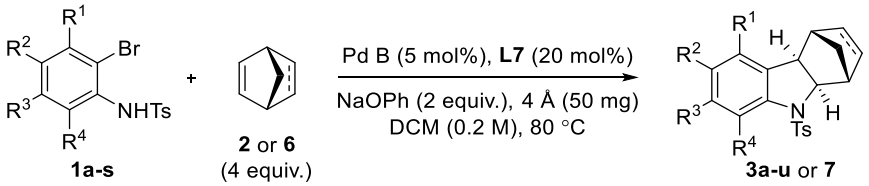
Entry	Pd	L*	Base	Additive	Solvent	Temp. (°C)	Yield (Ee) (%)[b,c]
1	$Pd_2(dba)_3$	**L1**	NaOPh	-	MTBE	100	trace
2	$Pd_2(dba)_3$	**L2**	NaOPh	-	MTBE	100	64(70)
3	$Pd_2(dba)_3$	**L3**	NaOPh	-	MTBE	100	44(62)
4	$Pd_2(dba)_3$	**L4**	NaOPh	-	MTBE	100	70(61)
5	$Pd_2(dba)_3$	**L5**	NaOPh	-	MTBE	100	trace
6	$Pd_2(dba)_3$	**L6**	NaOPh	-	MTBE	100	trace
7	$Pd_2(dba)_3$	**L7**	NaOPh	-	MTBE	100	45(72)
8	$Pd_2(dba)_3$	**L8**	NaOPh	-	MTBE	100	51(64)
9	$Pd_2(dba)_3$	**L2**	CH_3ONa	-	MTBE	100	11(58)
10	$Pd_2(dba)_3$	**L2**	EtONa	-	MTBE	100	trace
11	$Pd_2(dba)_3$	**L2**	NaO^{t}Bu	-	MTBE	100	15(89)
12	$Pd_2(dba)_3$	**L2**	HCOONa	-	MTBE	100	trace
13	$Pd_2(dba)_3$	**L2**	CH_3OLi	-	MTBE	100	trace
14	$Pd_2(dba)_3$	**L2**	LiO^{t}Bu	-	MTBE	100	trace
15	$Pd_2(dba)_3$	**L2**	KO^{t}Bu	-	MTBE	100	N.D.
16	$Pd_2(dba)_3$	**L2**	Na_2CO_3	-	MTBE	100	N.D.
17	$Pd_2(dba)_3$	**L2**	K_3PO_4	-	MTBE	100	42(50)
18	$Pd_2(dba)_3$	**L2**	K_2CO_3	-	MTBE	100	45(49)
19	$Pd_2(dba)_3$	**L2**	Cs_2CO_3	-	MTBE	100	50(44)
20	$Pd_2(dba)_3$	**L2**	CsF	-	MTBE	100	49(48)

21	$Pd_2(dba)_3$	**L2**	DABCO	-	MTBE	100	N.D.
22	$Pd_2(dba)_3$	**L2**	*i*Pr_2NEt	-	MTBE	100	N.D.
23	$Pd_2(dba)_3$	**L2**	NaO*t*Bu	-	THF	100	N.D.
24	$Pd_2(dba)_3$	**L2**	NaO*t*Bu	-	2-Me-THF	100	N.D.
25	$Pd_2(dba)_3$	**L2**	NaO*t*Bu	-	1,4-dioxane	100	N.D.
26	$Pd_2(dba)_3$	**L2**	NaO*t*Bu	-	DME	100	29(25)
27	$Pd_2(dba)_3$	**L2**	NaO*t*Bu	-	DCM	100	18(83)
28	$Pd_2(dba)_3$	**L2**	NaO*t*Bu	-	DCE	100	22(80)
29	$Pd_2(dba)_3$	**L2**	NaO*t*Bu	-	$CHCl_3$	100	15(74)
30	$Pd_2(dba)_3$	**L2**	NaO*t*Bu	-	Toluene	100	16(85)
31	$Pd_2(dba)_3$	**L2**	NaO*t*Bu	-	$PhCF_3$	100	14(77.7)
32	$Pd_2(dba)_3$	**L2**	NaO*t*Bu	-	MeOH	100	trace
33	$Pd_2(dba)_3$	**L2**	NaO*t*Bu	3 Å	MTBE	100	40(86)
34	$Pd_2(dba)_3$	**L2**	NaO*t*Bu	4 Å	MTBE	100	38(87)
35	$Pd_2(dba)_3$	**L2**	NaO*t*Bu	5 Å	MTBE	100	45(64)
36	$Pd(dba)_2$	**L2**	NaO*t*Bu	4 Å	MTBE	100	29(86)
37	$Pd_2(dba)_3$•$CHCl_3$	**L2**	NaO*t*Bu	4 Å	MTBE	100	41(83)
38	$Pd(OAc)_2$	**L2**	NaO*t*Bu	4 Å	MTBE	100	23(85)
39	Pd A	**L2**	NaO*t*Bu	4 Å	MTBE	100	trace
40	Pd B	**L2**	NaO*t*Bu	4 Å	MTBE	100	60(90)
41	Pd C	**L2**	NaO*t*Bu	4 Å	MTBE	100	55(83)
42	Pd D	**L2**	NaO*t*Bu	4 Å	MTBE	100	N.D.
43	Pd E	**L2**	NaO*t*Bu	4 Å	MTBE	100	26(86)
44	Pd B	**L7**	NaO*t*Bu	4 Å	MTBE	100	56(93)
45[d]	Pd B	**L7**	NaO*t*Bu	4 Å	MTBE	100	50(86)
46[e]	Pd B	L7	NaO*t*Bu	4 Å	MTBE	100	68(93)

[a] Unless otherwise specified, all reactions were carried out with **4a** (0.2 mmol), **2** (4 equiv.), [Pd] source (4 mol%), ***N*-Me-Xiang-Phos** (8 mol%), Base (2 equiv.), additive (50 mg) in solvent (0.2 M) for 36 hours. [b] Yield of isolated product. [c] Determined by chiral HPLC. [d] 4 mol% [Pd] and 10 mol% **L7** were employed. [e] 5 mol% [Pd] and 12 mol% **L7** were employed.

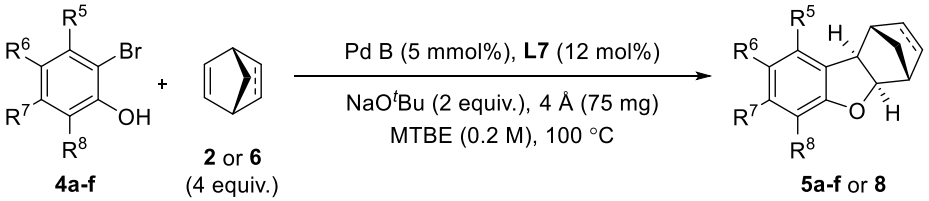
3. Experimental procedures [2]

3.1 General procedure for the intermolecular carboamination using 2-bromoaniline derivatives (GP1)



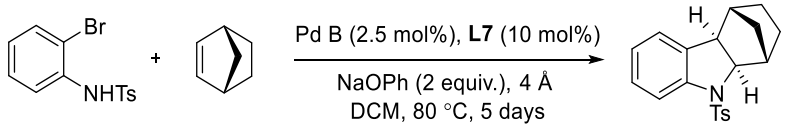
Activated 4 Å (50 mg), Pd B (5 mol%) and (*S*, *R*$_S$)-***N*-Me-X6** (20 mol%) were added in a sealed tube. The flask was evacuated and refilled with argon. Then 2-Br-anilines **1** (0.2 mmol) and dry DCM (1 mL) were added to the tube. NaOPh (2 equiv.) was subsequently added under a flow of argon, followed by **2** or **6** (4 equiv.). The mixture was stirred at 80 °C for 24-36 h. After the reaction was completed (monitored by TLC), solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel using hexane/EtOAc as the eluent to afford the desired product **3** or **7**.

3.2 General procedure for the intermolecular carboetherification using 2-bromophenol derivatives (GP2)



Activated 4 Å (75 mg), Pd **B** (5 mol%), (*S*, *R*$_S$)-***N*-Me-X6** (12 mol%) were added in a sealed tube. The flask was evacuated and refilled with argon. Then 2-Br-phenols **4** (0.3 mmol) and dry MTBE (1.5 mL) were added to the tube. NaO^{t}Bu (2 equiv.) was subsequently added under a flow of argon, followed by **2** or **6** (4 equiv.). The mixture was stirred at 100 °C for 36-48 h. After the reaction was completed (monitored by TLC), solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel using hexane/Et_2O as the eluent to afford the desired product **5** or **8**.

4. Gram Scale Preparation of 3a



1a 5 mmol, 1.63 g

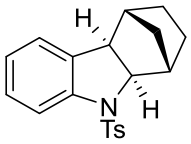
2 (4 equiv.)

3a, 1.27 g
75% yield, 89% *ee*

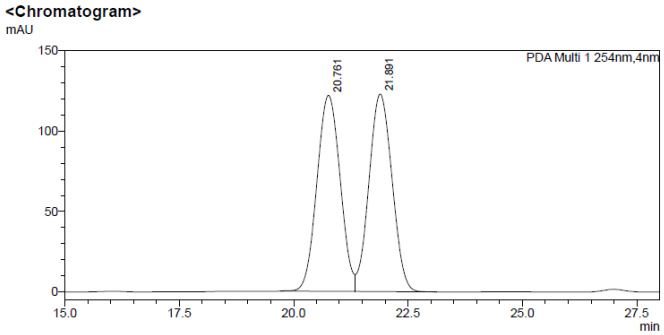
Activated 4 Å (500 mg), Pd B (2.5 mol%, 69 mg) and (*S*, R_S)-***N*-Me-X6** (10 mol%, 356 mg) were added in a sealed tube. The flask was evacuated and refilled with argon. Then *N*-(2-bromophenyl)-4-methylbenzenesulfonamide **1a** (5 mmol, 1.63 g) and dry DCM (10 mL) were added to the tube. NaOPh (2 equiv., 1.16 g) was subsequently added under a flow of argon, followed by **2** (4 equiv., 1.88 g). The mixture was stirred at 80 ^{o}C for 5 days. After the reaction was completed (monitored by TLC), solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel using hexane/EtOAc (8:1) as the eluent to afford the desired product **3a** (1.27 g, 75% yield, 89% *ee*).

5. General Data for 3, 5, 7 and 8

(1*S*,4*R*,4a*R*,9a*R*)-9-tosyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole

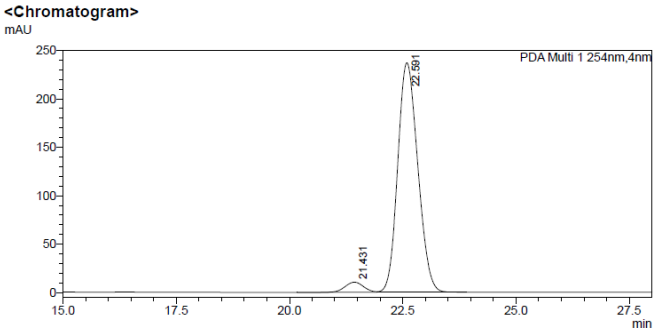


3a; white solid (hexane/EtOAc = 8:1, 54 mg, 79% isolated yield); m.p. = 165-167 ºC; $[\alpha]_D^{20}$ = 110.018 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.15-7.11 (m, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.94 (td, *J* = 7.4, 0.9 Hz, 1H), 3.96 (d, *J* = 8.1 Hz, 1H), 3.08 (d, *J* = 8.1 Hz, 1H), 2.75 (d, *J* = 1.6 Hz, 1H), 2.34 (s, 3H), 2.24 (s, 1H), 1.60-1.58 (m, 2H), 1.37-1.35 (m, 1H), 1.30-1.27 (m, 2H), 1.15-1.12 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.72, 143.37, 134.95, 133.96, 129.55, 127.73, 127.06, 124.84, 123.63, 114.14, 69.78, 50.42, 43.89, 43.05, 32.22, 28.33, 25.29, 21.44. Enantiomeric excess: 92%, determined by HPLC (Chiralpak IC, hexane/*i*-PrOH = 93/7; flow rate 0.8 ml/min; 25 ℃; 254 nm), first peak: t_R = 21.4 min, second peak: t_R = 22.6 min; HRMS (ESI) m/z calcd. for $C_{20}H_{21}NNaO_2S$ $[M+Na]^+$ = 362.1185, found = 362.1186.



<Peak Table>
PDA Ch1 254nm

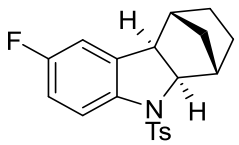
Peak#	Ret. Time	Height	Height%	Area	Area%
1	20.761	121880	49.807	4303556	49.969
2	21.891	122826	50.193	4308825	50.031
Total		244706	100.000	8612381	100.000



<Peak Table>
PDA Ch1 254nm

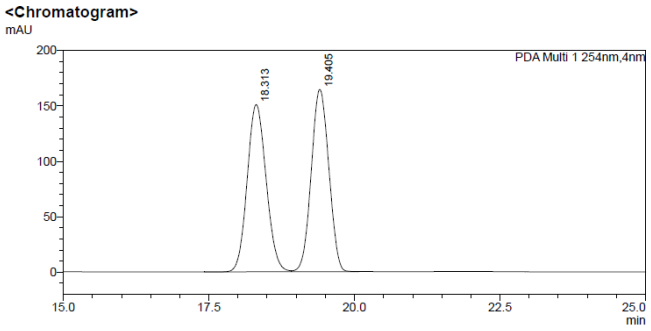
Peak#	Ret. Time	Height	Height%	Area	Area%
1	21.431	10462	4.227	298469	3.926
2	22.591	237040	95.773	7303240	96.074
Total		247502	100.000	7601709	100.000

(1*S*,4*R*,4a*R*,9a*R*)-6-fluoro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole



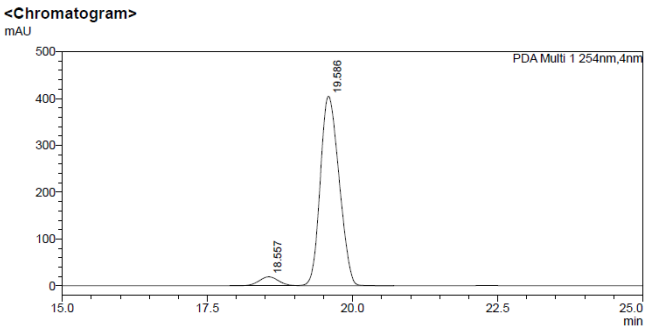
3b; white solid (hexane/EtOAc = 8:1, 70 mg, 98% isolated yield); m.p. = 135-136 ºC; $[\alpha]_D^{20}$ = 181.052 (*c* = 0.625, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.54 (dd, *J* = 8.9, 4.6 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.83 (td, *J* = 8.8, 2.7 Hz, 1H), 6.71 (dd, *J* = 8.1, 2.5 Hz, 1H), 3.96 (d, *J* = 8.1 Hz, 1H), 3.04 (d, *J* = 8.1 Hz, 1H), 2.73 (s, 1H), 2.37 (s, 3H), 2.22 (s, 1H), 1.61-1.58 (m, 2H), 1.37-1.34 (m, 1H), 1.29-1.26 (m, 2H), 1.18-1.15 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.69 (d, *J* =243.4 Hz), 143.92, 139.45 (d, *J* = 2.0 Hz), 136.11 (d, *J* = 8.1 Hz), 134.56, 129.63, 127.14, 115.25 (d, *J* = 8.1 Hz), 114.29 (d, *J* = 23.2 Hz), 111.91 (d, *J* = 24.2 Hz), 70.29, 50.38, 43.96, 42.98, 32.32, 28.27, 25.24,

21.49. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.80. Enantiomeric excess: 91%, determined by HPLC (Chiralpak IC, hexane/*i*-PrOH = 95/5; flow rate 0.8 ml/min; 25 ℃; 254 nm), first peak: t_R = 18.6 min, second peak: t_R = 19.6 min; HRMS (ESI) m/z calcd. for $C_{20}H_{20}FNNaO_2S$ $[M+Na]^+$ = 380.1091, found = 380.1078.



<Peak Table>
PDA Ch1 254nm

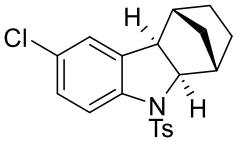
Peak#	Ret. Time	Height	Height%	Area	Area%
1	18.313	150858	47.849	3421135	49.753
2	19.405	164423	52.151	3455128	50.247
Total		315281	100.000	6876263	100.000



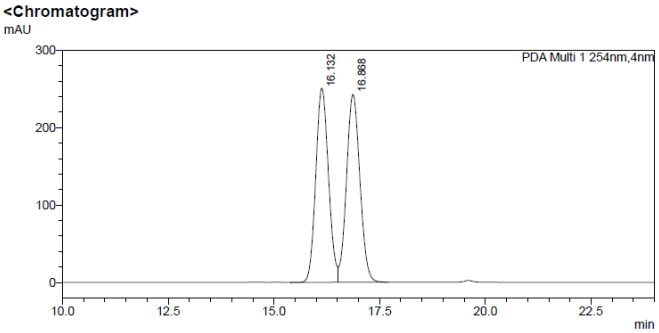
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	18.557	19116	4.512	450847	4.713
2	19.586	404523	95.488	9114759	95.287
Total		423638	100.000	9565606	100.000

(1*S*,4*R*,4a*R*,9a*R*)-6-chloro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole

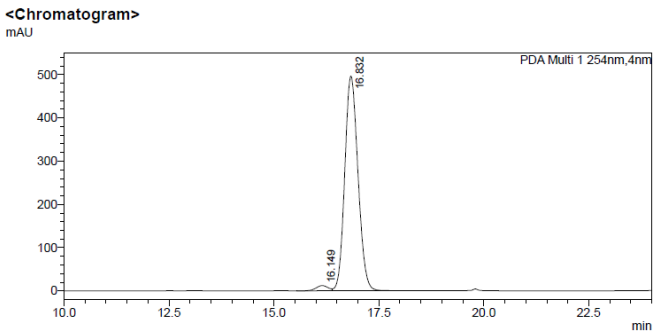


3c; white solid (hexane/EtOAc = 8:1, 64 mg, 86% isolated yield); m.p. = 112-113 ºC; $[\alpha]_D^{20}$ = 189.059 (*c* = 0.542, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.10 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.98 (d, *J* = 1.4 Hz, 1H), 3.96 (d, *J* = 8.1 Hz, 1H), 3.04 (d, *J* = 8.1 Hz, 1H), 2.74 (s, 1H), 2.37 (s, 3H), 2.23 (s, 1H), 1.61-1.59 (m, 2H), 1.37-1.34 (m, 1H), 1.29-1.26 (m, 2H), 1.18-1.16 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.04, 142.19, 136.00, 134.61, 129.70, 128.69, 127.77, 127.08, 125.06, 115.17, 70.22, 50.22, 43.91, 43.03, 32.30, 28.27, 25.23, 21.50. Enantiomeric excess: 96%, determined by HPLC (Chiralpak IC, hexane/*i*-PrOH = 95/5; flow rate 0.8 ml/min; 25 ℃; 254 nm), first peak: t_R = 16.1 min, second peak: t_R = 16.8 min; HRMS (ESI) m/z calcd. for $C_{20}H_{20}ClNNaO_2S$ $[M+Na]^+$ = 396.0795, found = 396.0788.



<Peak Table>
PDA Ch1 254nm

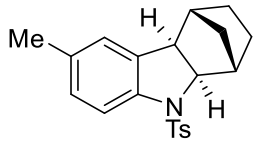
Peak#	Ret. Time	Height	Height%	Area	Area%
1	16.132	251121	50.847	5243578	49.467
2	16.868	242755	49.153	5356585	50.533
Total		493875	100.000	10600164	100.000



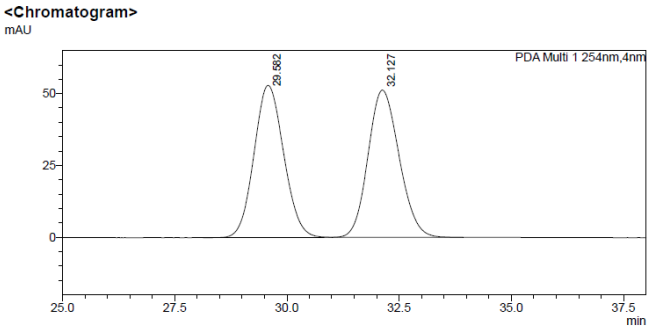
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	16.149	12013	2.363	240238	2.160
2	16.832	496317	97.637	10883673	97.840
Total		508330	100.000	11123911	100.000

(1*S*,4*R*,4a*R*,9a*R*)-6-methyl-9-tosyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole

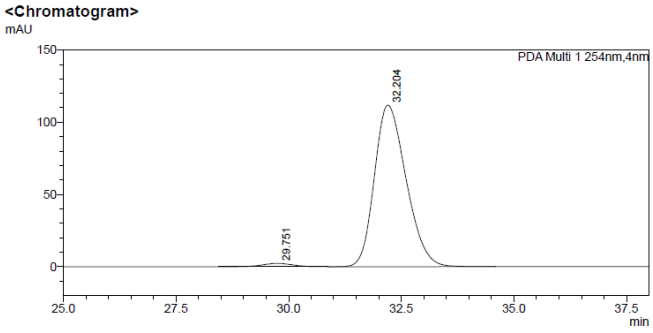


3d; white solid (hexane/EtOAc = 8:1, 39 mg, 55% isolated yield); m.p. = 111-112 °C; $[\alpha]_D^{20}$ = 137.697 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.82 (s, 1H), 3.92 (d, *J* = 8.1 Hz, 1H), 3.02 (d, *J* = 8.1 Hz, 1H), 2.72 (s, 1H), 2.35 (s, 3H), 2.25 (s, 3H), 2.22 (s, 1H), 1.60-1.57 (m, 2H), 1.36 (d, *J* = 10.8 Hz, 1H), 1.29-1.25 (m, 2H), 1.13 (d, *J* = 10.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.60, 141.05, 134.88, 134.09, 133.26, 129.53, 128.35, 127.12, 125.46, 114.02, 69.93, 50.43, 43.92, 43.01, 32.28, 28.34, 25.31, 21.46, 20.81. Enantiomeric excess: 96%, determined by HPLC (Chiralpak IC, hexane/*i*-PrOH = 95/5; flow rate 0.8 ml/min; 25 ℃; 254 nm), first peak: t_R = 29.8 min, second peak: t_R = 32.2 min; HRMS (ESI) m/z calcd. for $C_{21}H_{23}NNaO_2S$ $[M+Na]^+$ = 376.1342, found = 376.1340.



<Peak Table>
PDA Ch1 254nm

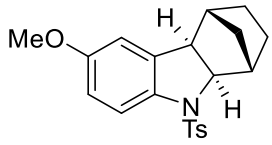
Peak#	Ret. Time	Height	Height%	Area	Area%
1	29.582	52964	50.795	2443237	49.610
2	32.127	51307	49.205	2481671	50.390
Total		104271	100.000	4924907	100.000



<Peak Table>
PDA Ch1 254nm

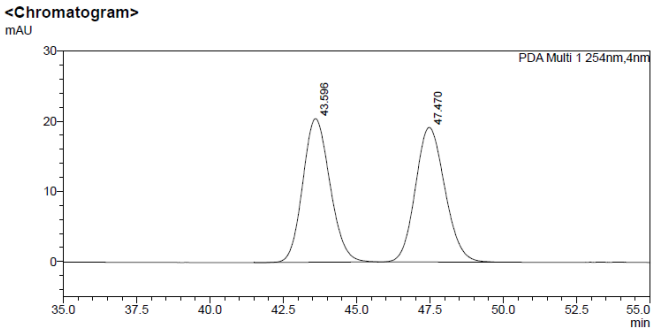
Peak#	Ret. Time	Height	Height%	Area	Area%
1	29.751	2290	2.007	105788	1.900
2	32.204	111769	97.993	5463247	98.100
Total		114059	100.000	5569036	100.000

(1*S*,4*R*,4a*R*,9a*R*)-6-methoxy-9-tosyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole



3e; white solid (hexane/EtOAc = 4:1, 48 mg, 65% isolated yield); m.p. = 189-191 °C; $[\alpha]_D^{20}$ = 180.211 (*c* = 0.56, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.69 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.57 (d, *J* = 2.5 Hz, 1H), 3.91 (d, *J* = 8.0 Hz, 1H), 3.74 (s, 3H), 3.01 (d, *J* = 8.0 Hz, 1H), 2.70 (s, 1H), 2.35 (s, 3H), 2.22 (s, 1H), 1.59-1.56 (m, 2H), 1.35 (d, *J* = 10.6 Hz, 1H), 1.28-1.25 (m, 2H), 1.13 (d, *J* = 10.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.56, 143.60, 136.81, 135.66, 134.52, 129.50, 127.13, 115.22, 112.72, 110.50, 70.03, 55.47, 50.57, 43.90, 42.88, 32.30, 28.25, 25.25, 21.44. Enantiomeric excess: 94%, determined by HPLC (Chiralpak IC, hexane/*i*-PrOH =

95/5; flow rate 0.8 ml/min; 25 ℃; 254 nm), first peak: t_R = 43.5 min, second peak: t_R = 47.0 min; HRMS (ESI) m/z calcd. for $C_{21}H_{23}NNaO_3S$ $[M+Na]^+$ = 392.1291, found = 392.1285.



<Peak Table>
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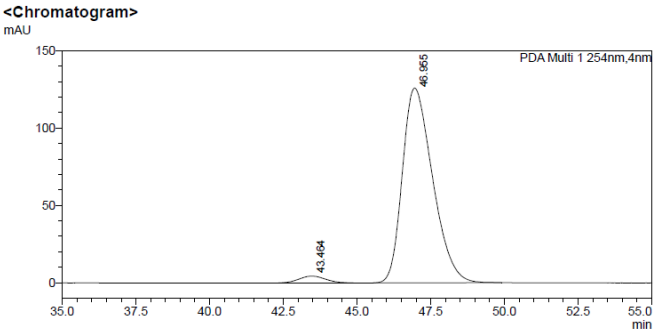
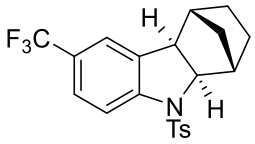
Peak#	Ret. Time	Height	Height%	Area	Area%
1	43.596	20459	51.625	1321443	49.625
2	47.470	19171	48.375	1341394	50.375
Total		39631	100.000	2662837	100.000



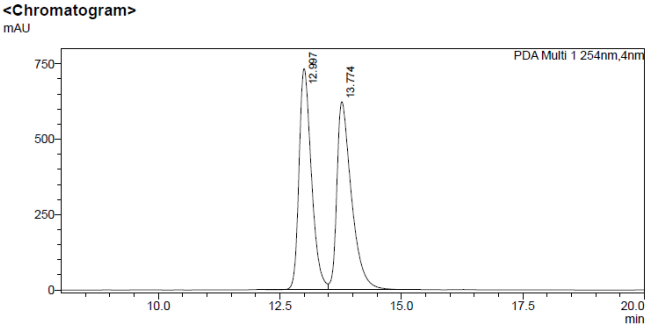
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	43.464	4454	3.413	279049	3.005
2	46.955	126049	96.587	9005689	96.995
Total		130503	100.000	9284737	100.000

(1*S*,4*R*,4a*R*,9a*R*)-9-tosyl-6-(trifluoromethyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole



3f; white solid (hexane/EtOAc = 8:1, 55 mg, 67% isolated yield); m.p. = 131-132 ºC; $[\alpha]_D^{20}$ = 131.181 (*c* = 0.625, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.26-7.23 (m, 3H), 4.04 (d, *J* = 8.1 Hz, 1H), 3.13 (d, *J* = 8.1 Hz, 1H), 2.79 (s, 1H), 2.38 (s, 3H), 2.29 (s, 1H), 1.64-1.59 (m, 2H), 1.37-1.29 (m, 3H), 1.20 (d, *J* = 10.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.47, 144.31, 134.77, 134.61, 129.82, 127.02, 125.62 (q, *J* = 32.3 Hz), 125.46 (q, *J* = 3.7 Hz), 124.19 (q, *J* = 271.7 Hz), 122.08 (q, *J* = 3.7 Hz), 113.55, 70.37, 50.09, 43.84, 43.19, 32.28, 28.28, 25.23, 21.52. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.62. Enantiomeric excess: 99%, determined by HPLC (Chiralpak IB, hexane/*i*-PrOH = 97/3; flow rate 0.5 ml/min; 25 ℃; 254 nm), first peak: t_R = 13.2 min, second peak: t_R = 14.3 min; HRMS (ESI) m/z calcd. for $C_{21}H_{20}F_3NNaO_2S$ $[M+Na]^+$ = 430.1059, found = 430.1045.



<Peak Table>
PDA Ch1 254nm

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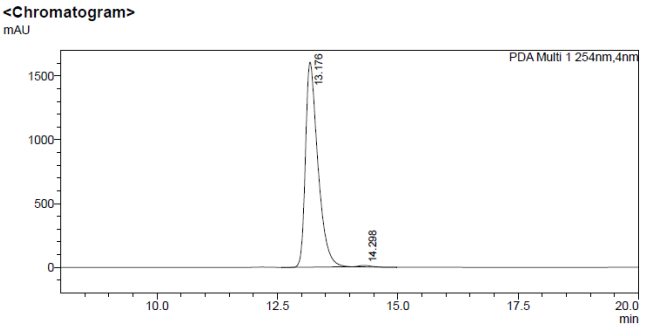
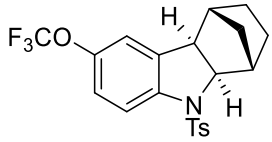
1	12.997	732675	54.040	12928407	49.854
2	13.774	623138	45.960	13004154	50.146
Total		1355813	100.000	25932562	100.000



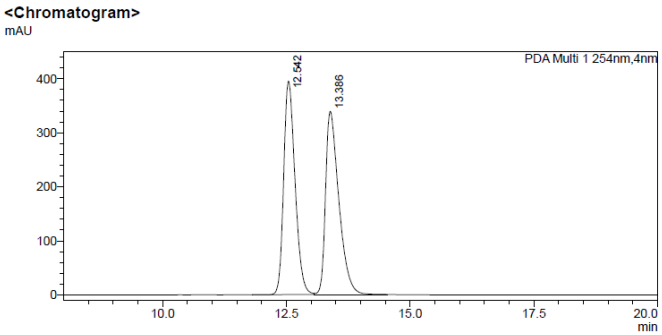
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.176	1606732	99.328	28790829	99.396
2	14.298	10877	0.672	175021	0.604
Total		1617609	100.000	28965850	100.000

(1*S*,4*R*,4a*R*,9a*R*)-9-tosyl-6-(trifluoromethoxy)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole

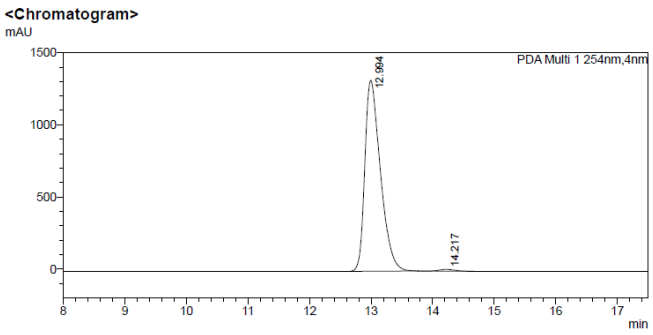


3g; white solid (hexane/EtOAc = 8:1, 61 mg, 72% isolated yield); m.p. = 119-120 °C; $[\alpha]_D^{20}$ = 138.749 (*c* = 0.625, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 1H), 6.88 (s, 1H), 4.00 (d, *J* = 8.1 Hz, 1H), 3.08 (d, *J* = 8.1 Hz, 1H), 2.76 (s, 1H), 2.38 (s, 3H), 2.25 (s, 1H), 1.62-1.59 (m, 2H), 1.38-1.35 (m, 1H), 1.30-1.27 (m, 2H), 1.20-1.17 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.31, 144.11, 142.08, 135.80, 134.72, 129.73, 127.10, 120.58, 120.42 (q, *J* = 257.04 Hz), 117.90, 114.63, 70.36, 50.26, 43.88, 43.10, 32.32, 28.28, 25.20, 21.50. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.12. Enantiomeric excess: 98%, determined by HPLC (Chiralpak IB, hexane/*i*-PrOH = 97/3; flow rate 0.5 ml/min; 25 ℃; 254 nm), first peak: t_R = 13.0 min, second peak: t_R = 14.2 min; HRMS (ESI) m/z calcd. for $C_{21}H_{20}F_3NNaO_3S$ $[M+Na]^+$ = 446.1008, found = 446.1001.



<Peak Table>
PDA Ch1 254nm

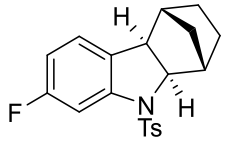
Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.542	395135	53.837	6289914	49.837
2	13.386	338817	46.163	6331109	50.163
Total		733952	100.000	12621023	100.000



<Peak Table>
PDA Ch1 254nm

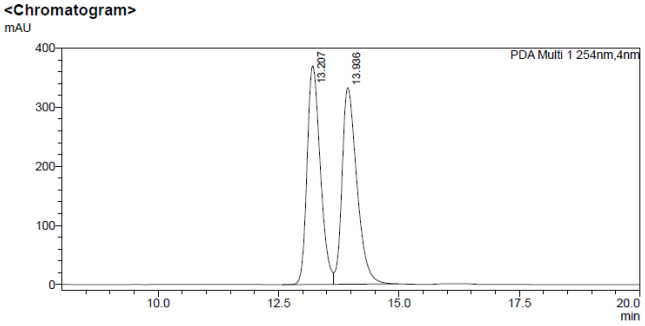
Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.994	1324678	99.106	23254990	99.135
2	14.217	11953	0.894	202981	0.865
Total		1336631	100.000	23457971	100.000

(1*S*,4*R*,4a*R*,9a*R*)-7-fluoro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole



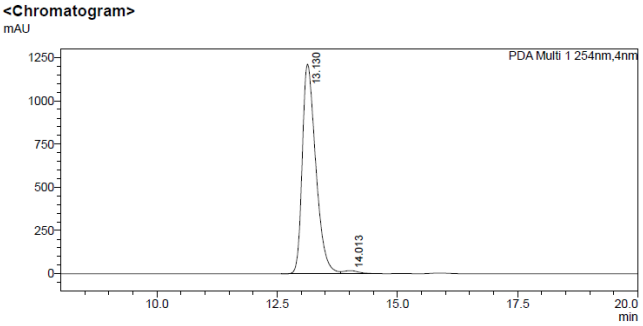
3h; white solid (hexane/EtOAc = 8:1, 64 mg, 90% isolated yield); m.p. = 160-162 °C; $[\alpha]_D^{20}$ = 165.809 (*c* = 0.542, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.33 (dd, *J* = 10.3, 2.3 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.93 (dd, *J* = 7.7, 5.7 Hz, 1H), 6.63 (td, *J* = 8.6, 2.4 Hz, 1H), 3.99 (d, *J* = 8.1 Hz, 1H), 3.03 (d, *J* = 8.1 Hz, 1H), 2.75 (s, 1H), 2.37 (s, 3H), 2.21 (s, 1H), 1.61-1.57 (m, 2H), 1.36 (d, *J* = 9.7 Hz, 1H), 1.29-1.25 (m, 2H), 1.18-1.14 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.63 (d, *J* = 244.4 Hz), 144.77 (d, *J* = 11.1 Hz), 144.08, 134.77, 129.72, 129.41 (d, *J* = 3.0 Hz), 127.08, 125.39 (d, *J* = 10.1 Hz), 110.20 (d, *J* = 22.2 Hz), 102.19 (d, *J* = 28.3 Hz), 70.78, 49.83, 43.87, 43.07, 32.17, 28.22, 25.20, 21.49. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.74. Enantiomeric excess: 97%, determined by HPLC

(Chiralpak IB, hexane/*i*-PrOH = 97/3; flow rate 0.5 ml/min; 25 ℃; 254 nm), first peak: t_R = 13.1 min, second peak: t_R = 14.0 min; HRMS (ESI) m/z calcd. for $C_{20}H_{20}FNNaO_2S$ $[M+Na]^+$ = 380.1091, found = 380.1080.



<Peak Table>
PDA Ch1 254nm

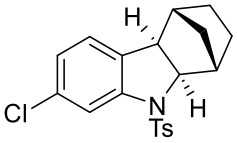
Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.207	370264	52.663	7053945	49.777
2	13.936	332816	47.337	7117230	50.223
Total		703081	100.000	14171175	100.000



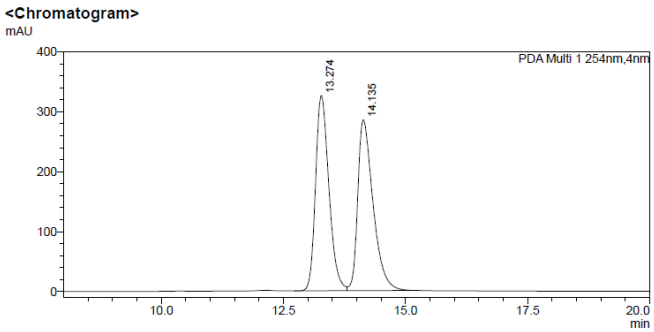
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.130	1212280	98.588	23656937	98.484
2	14.013	17362	1.412	364268	1.516
Total		1229641	100.000	24021205	100.000

(1*S*,4*R*,4a*R*,9a*R*)-7-chloro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole

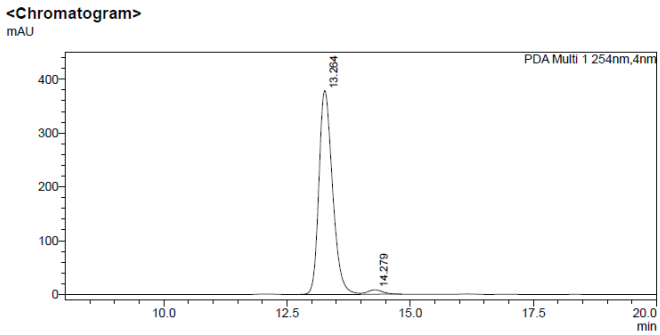


3i; white solid (hexane/EtOAc = 8:1, 56 mg, 75% isolated yield); m.p. = 197-199 ºC; $[\alpha]_D^{20}$ = 285.882 (*c* = 0.625, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 0.9 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.94-6.90 (m, 2H), 3.97 (d, *J* = 8.1 Hz, 1H), 3.03 (d, *J* = 8.1 Hz, 1H), 2.74 (s, 1H), 2.38 (s, 3H), 2.22 (s, 1H), 1.61-1.57 (m, 2H), 1.37-1.34 (m, 1H), 1.29-1.26 (m, 2H), 1.18-1.14 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.64, 144.11, 134.73, 133.45, 132.54, 129.75, 127.06, 125.57, 123.68, 114.37, 70.46, 49.97, 43.84, 43.05, 32.22, 28.26, 25.21, 21.51. Enantiomeric excess: 95%, determined by HPLC (Chiralpak IB, hexane/*i*-PrOH = 97/3; flow rate 0.5 ml/min; 25 ℃; 254 nm), first peak: t_R = 13.3 min, second peak: t_R = 14.3 min; HRMS (ESI) m/z calcd. for $C_{20}H_{20}ClNNaO_2S$ $[M+Na]^+$ = 396.0795, found = 396.0786.



<Peak Table>
PDA Ch1 254nm

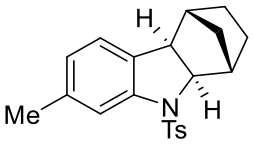
Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.274	325860	53.323	6198419	49.946
2	14.135	285251	46.677	6211938	50.054
Total		611111	100.000	12410358	100.000



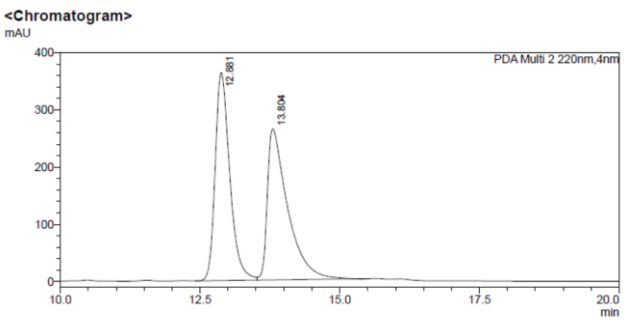
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.264	378540	97.880	7262602	97.616
2	14.279	8199	2.120	177403	2.384
Total		386739	100.000	7440005	100.000

(1*S*,4*R*,4a*R*,9a*R*)-7-methyl-9-tosyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole

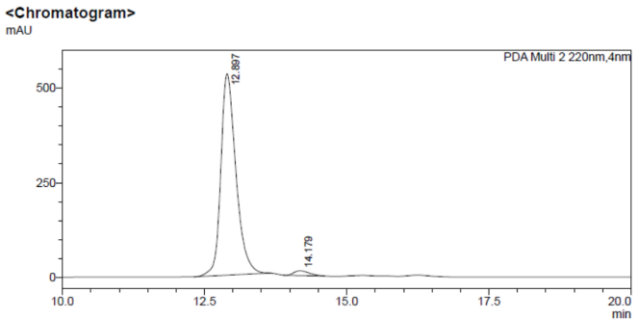


3j; white solid (hexane/EtOAc = 8:1, 46 mg, 65% isolated yield); m.p. = 224-225 °C; $[\alpha]_D^{20}$ = 180.176 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.43 (s, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 3.94 (d, *J* = 8.1 Hz, 1H), 3.03 (d, *J* = 8.1 Hz, 1H), 2.72 (s, 1H), 2.35 (s, 3H), 2.33 (s, 3H), 2.21 (s, 1H), 1.58-1.56 (m, 2H), 1.37-1.34 (m, 1H), 1.28-1.25 (m, 2H), 1.12 (d, *J* = 10.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.65, 143.54, 137.76, 135.06, 131.11, 129.56, 127.04, 124.40, 114.81, 70.11, 50.11, 43.85, 43.03, 32.19, 28.28, 25.31, 21.49. Enantiomeric excess: 95%, determined by HPLC (Chiralpak IB, hexane/*i*-PrOH = 97/3; flow rate 0.5 ml/min; 25 ℃; 254 nm), first peak: t_R = 12.9 min, second peak: t_R = 14.2 min; HRMS (ESI) m/z calcd. for $C_{21}H_{23}NNaO_2S$ $[M+Na]^+$ = 376.1342, found = 376.1334.



<Peak Table>
PDA Ch2 220nm

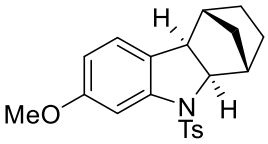
Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.881	363425	57.902	6608538	49.781
2	13.804	264226	42.098	6666770	50.219
Total		627652	100.000	13275308	100.000



<Peak Table>
PDA Ch2 220nm

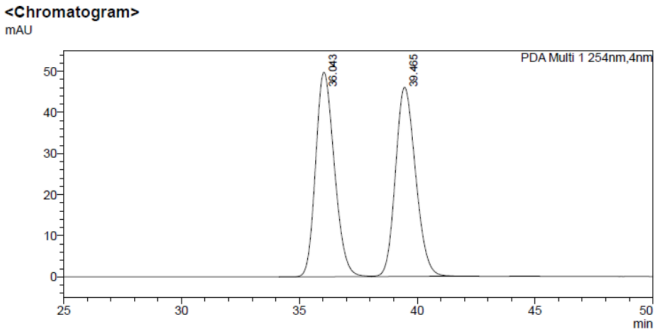
Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.897	532742	97.712	9839037	97.671
2	14.179	12475	2.288	234566	2.329
Total		545218	100.000	10073603	100.000

(1*S*,4*R*,4a*R*,9a*R*)-7-methoxy-9-tosyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole



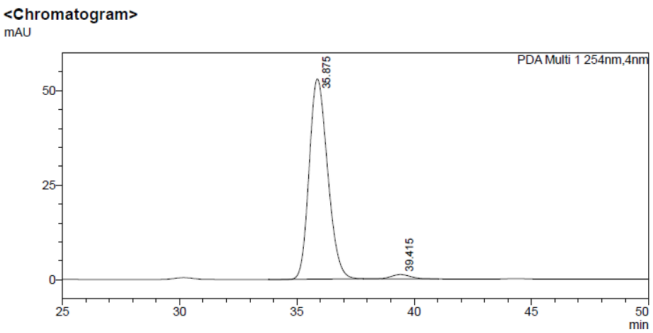
3k; white solid (hexane/EtOAc = 5:1, 55 mg, 74% isolated yield); m.p. = 171-173 °C; $[\alpha]_D^{20}$ = 274.139 (*c* = 0.625, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.22-7.20 (m, 3H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.50 (dd, *J* = 8.2, 2.3 Hz, 1H), 3.96 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 3.01 (d, *J* = 8.1 Hz, 1H), 2.72 (s, 1H), 2.36 (s, 3H), 2.19 (s, 1H), 1.58-1.56 (m, 2H), 1.36 (d, *J* = 9.9 Hz, 1H), 1.29-1.24 (m, 2H), 1.13 (d, *J* = 10.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.71, 144.57, 143.77, 134.97, 129.60, 127.11, 126.07, 125.05, 109.57, 100.33, 70.65, 55.53, 49.77, 43.88, 43.03, 32.14, 28.19, 25.28, 21.49. Enantiomeric excess: 96%, determined by HPLC (Chiralpak IC, hexane/*i*-PrOH = 95/5; flow rate 0.8

ml/min; 25 ℃; 254 nm), first peak: t_R = 35.9 min, second peak: t_R = 39.4 min; HRMS (ESI) m/z calcd. for $C_{21}H_{23}NNaO_3S$ $[M+Na]^+$ = 392.1291, found = 392.1283.



<Peak Table>
PDA Ch1 254nm

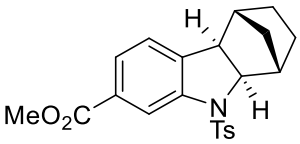
Peak#	Ret. Time	Height	Height%	Area	Area%
1	36.043	49735	51.949	2752913	50.191
2	39.465	46003	48.051	2731976	49.809
Total		95737	100.000	5484888	100.000



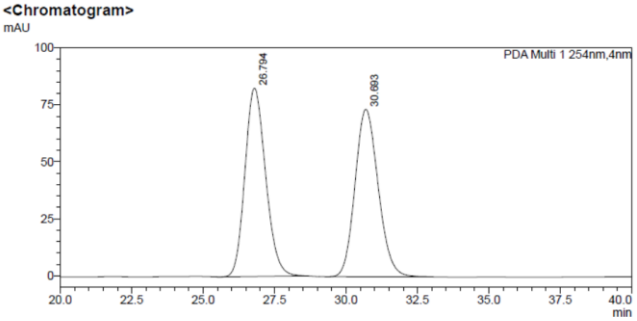
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	35.875	53003	97.903	2905998	97.876
2	39.415	1135	2.097	63053	2.124
Total		54138	100.000	2969051	100.000

methyl (1*S*,4*R*,4a*R*,9a*R*)-9-tosyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole-7-carboxylate

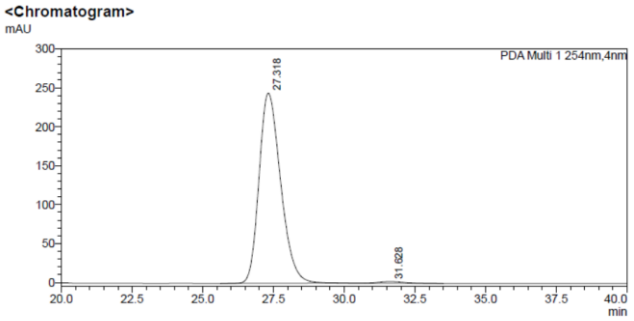


3l; white solid (hexane/EtOAc = 4:1, 46 mg, 58% isolated yield); m.p. = 166-167 ºC; $[\alpha]_D^{20}$ = 296.895 (*c* = 0.313, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 4.0 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 3H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 1H), 4.02 (d, *J* = 8.1 Hz, 1H), 3.92 (s, 3H), 3.11 (d, *J* = 8.1 Hz, 1H), 2.77 (s, 1H), 2.36 (s, 3H), 2.27 (s, 1H), 1.63-1. 60 (m, 2H), 1.35-1.26 (m, 3H), 1.17 (d, *J* = 10.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.78, 144.02, 143.82, 139.32, 134.77, 130.13, 129.69, 127.10, 125.55, 124.72, 114.80, 70.15, 52.17, 50.39, 43.92, 43.09, 32.31, 28.40, 25.21, 21.49. Enantiomeric excess: 98%, determined by HPLC (Chiralpak IC, hexane/*i*-PrOH = 70/30; flow rate 0.8 ml/min; 25 ℃; 254 nm), first peak: t_R = 27.3 min, second peak: t_R = 31.6 min; HRMS (ESI) m/z calcd. for $C_{22}H_{23}NNaO_4S$ $[M+Na]^+$ = 420.1240, found = 420.1236.



<Peak Table>
PDA Ch1 254nm

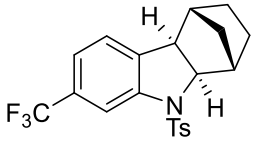
Peak#	Ret. Time	Height	Height%	Area	Area%
1	26.794	82584	52.931	4165127	50.113
2	30.693	73438	47.069	4146387	49.887
Total		156023	100.000	8311514	100.000



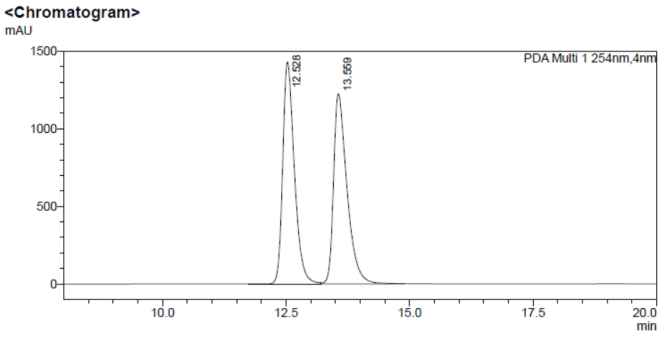
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	27.318	244246	99.085	12971409	99.088
2	31.628	2256	0.915	119407	0.912
Total		246503	100.000	13090816	100.000

(1*S*,4*R*,4a*R*,9a*R*)-9-tosyl-7-(trifluoromethyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole

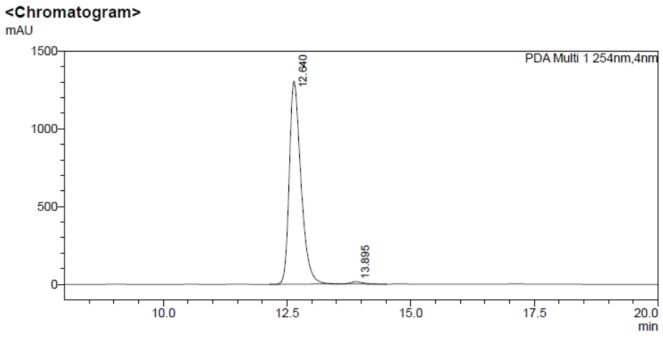


3m; white solid (hexane/EtOAc = 8:1, 59 mg, 72% isolated yield); m.p. = 164-165 °C; $[\alpha]_D^{20}$ = 166.333 (*c* = 0.625, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.24-7.20 (m, 3H), 7.11 (d, *J* = 7.8 Hz, 1H), 4.03 (d, *J* = 8.1 Hz, 1H), 3.12 (d, *J* = 8.0 Hz, 1H), 2.78 (s, 1H), 2.37 (s, 3H), 2.27 (s, 1H), 1.63-1.60 (m, 2H), 1.37-1.26 (m, 3H), 1.19 (d, *J* = 10.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.27, 143.99, 137.95, 134.54, 130.28 (q, *J* = 32.2 Hz), 129.78, 127.05, 125.16, 124.01 (q, *J* = 272.3 Hz), 120.67 (q, *J* = 3.8 Hz), 110.88 (q, *J* = 3.9 Hz), 70.23, 50.24, 43.91, 43.11, 32.30, 28.36, 25.19, 21.49. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.18. Enantiomeric excess: 98%, determined by HPLC (Chiralpak IB, hexane/*i*-PrOH = 97/3; flow rate 0.5 ml/min; 25 ℃; 254 nm), first peak: t_R = 12.6 min, second peak: t_R = 13.9 min; HRMS (ESI) m/z calcd. for $C_{21}H_{20}F_3NNaO_2S$ $[M+Na]^+$ = 430.1059, found = 430.1047.



<Peak Table>
PDA Ch1 254nm

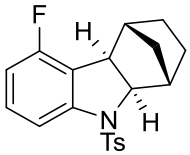
Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.528	1430130	53.846	23473670	50.303
2	13.559	1225840	46.154	23191059	49.697
Total		2655969	100.000	46664729	100.000



<Peak Table>
PDA Ch1 254nm

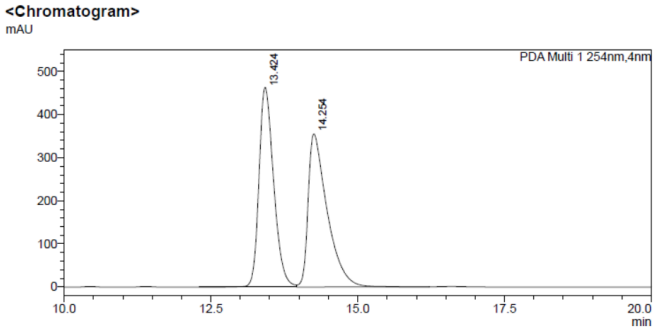
Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.640	1306422	98.834	21467051	98.790
2	13.895	15412	1.166	263041	1.210
Total		1321834	100.000	21730092	100.000

(1*S*,4*R*,4a*R*,9a*R*)-5-fluoro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole



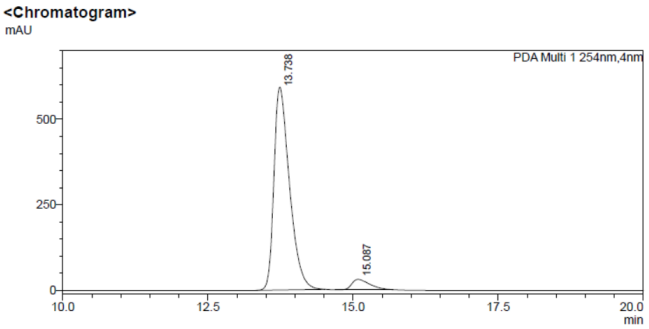
3n; white solid (hexane/EtOAc = 8:1, 46 mg, 65% isolated yield); m.p. = 118-120 °C; $[\alpha]_D^{20}$ = 6.840 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.11 (td, *J* = 8.2, 6.0 Hz, 1H), 6.63 (t, *J* = 8.5 Hz, 1H), 4.00 (d, *J* = 8.1 Hz, 1H), 3.18 (d, *J* = 8.1 Hz, 1H), 2.76 (s, 1H), 2.43 (s, 1H), 2.37 (s, 3H), 1.62-1.59 (m, 2H), 1.40 (d, *J* = 10.7 Hz, 1H), 1.32-1.26 (m, 2H), 1.20 (d, *J* = 10.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.17 (d, *J* = 247.0 Hz), 145.87 (d, *J* = 8.4 Hz), 144.05, 134.72, 129.67, 129.59 (d, *J* = 8.2 Hz), 127.08, 120.21 (d, *J* = 21.4 Hz), 110.44 (d, *J* = 20.2 Hz), 109.92 (d, *J* = 3.3 Hz), 70.57, 47.62, 43.88, 40.89, 32.40, 28.29, 25.05, 21.49. ^{19}F NMR

(376 MHz, $CDCl_3$) δ -118.65. Enantiomeric excess: 89%, determined by HPLC (Chiralpak IB, hexane/*i*-PrOH = 97/3; flow rate 0.5 ml/min; 25 ℃; 254 nm), first peak: t_R = 13.7 min, second peak: t_R = 15.1 min; HRMS (ESI) m/z calcd. for $C_{20}H_{20}FNNaO_2S$ $[M+Na]^+$ = 380.1091, found = 380.1086.



<Peak Table>
PDA Ch1 254nm

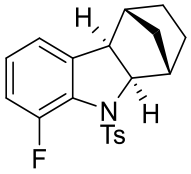
Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.424	463371	56.616	8023210	50.027
2	14.254	355069	43.384	8014477	49.973
Total		818440	100.000	16037687	100.000



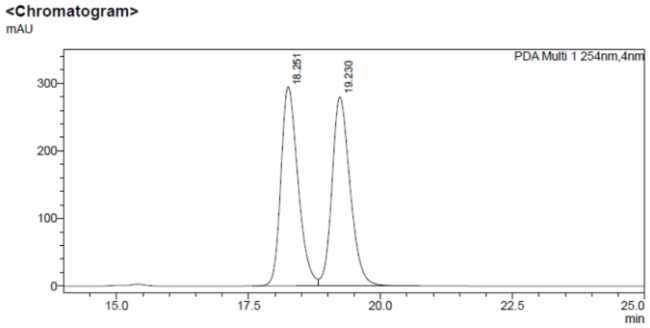
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.738	592298	95.120	11048763	94.440
2	15.087	30385	4.880	650449	5.560
Total		622683	100.000	11699212	100.000

(1*S*,4*R*,4a*R*,9a*R*)-8-fluoro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole

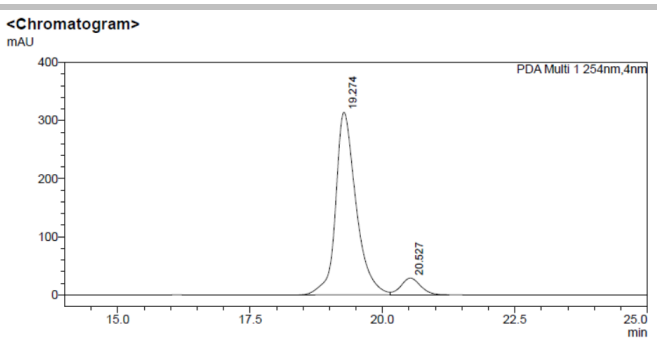


3o; white solid (hexane/EtOAc = 8:1, 38 mg, 53% isolated yield); m.p. = 138-139 ºC; $[\alpha]_D^{20}$ = 28.051 (*c* = 0.313, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 9.5 Hz, 2H), 6.93-6.88 (m, 1H), 6.85-6.79 (m, 2H), 4.52 (d, *J* = 8.0 Hz, 1H), 3.27 (d, *J* = 8.0 Hz, 1H), 2.70 (s, 1H), 2.39 (s, 3H), 2.25 (s, 1H), 1.62-1.60 (m, 2H), 1.36-1.26 (m, 3H), 1.16 (d, *J* = 10.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.19 (d, *J* = 252.0 Hz), 143.51, 138.96 (d, *J* = 2.5 Hz), 136.70 (d, *J* = 1.3 Hz), 130.36 (d, *J* = 8.82 Hz), 129.42, 127.27 (d, *J* = 1.3 Hz), 125.07 (d, *J* = 6.3 Hz), 120.39 (d, *J* = 3.8 Hz), 115.81 (d, *J* = 21.4 Hz), 71.05, 50.77, 43.73, 43.31, 32.24, 28.07, 25.49, 21.51. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.17. Enantiomeric excess: 84%, determined by HPLC (Chiralpak IF, hexane/*i*-PrOH = 90/10; flow rate 0.8 ml/min; 25 ℃; 254 nm), first peak: t_R = 19.3 min, second peak: t_R = 20.5 min; HRMS (ESI) m/z calcd. For $C_{20}H_{20}FNNaO_2S$ $[M+Na]^+$ = 380.1091, found = 380.1086.



<Peak Table>
PDA Ch1 254nm

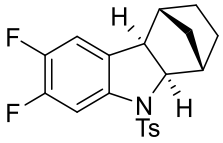
Peak#	Ret. Time	Height	Height%	Area	Area%
1	18.251	294897	51.321	6629511	49.858
2	19.230	279721	48.679	6667317	50.142
Total		574617	100.000	13296829	100.000



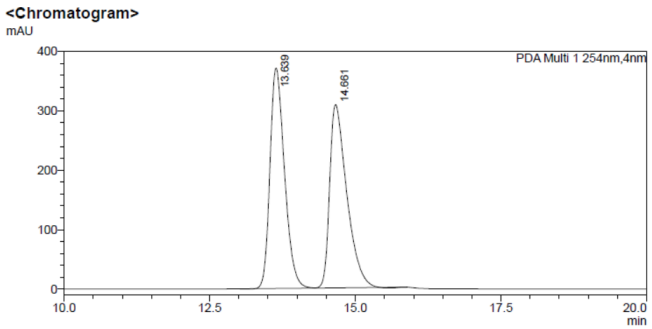
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	19.274	314351	91.612	8472649	91.950
2	20.527	28781	8.388	741782	8.050
Total		343132	100.000	9214432	100.000

(1*S*,4*R*,4a*R*,9a*R*)-6,7-difluoro-9-tosyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole

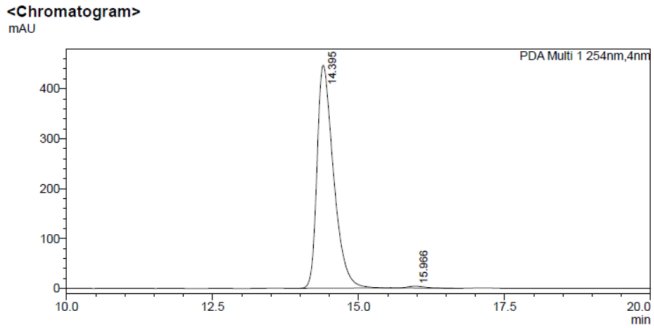


3p; white solid (hexane/EtOAc = 8:1, 70 mg, 93% isolated yield); m.p. = 144-145 ºC; $[\alpha]_D^{20}$ = 93.154 (*c* = 0.583, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.46 (dd, *J* = 11.4, 6.9 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 6.80 (t, *J* = 8 Hz, 1H), 3.95 (d, *J* = 8.1 Hz, 1H), 3.02 (d, *J* = 8.1 Hz, 1H), 2.73 (s, 1H), 2.38 (s, 3H), 2.20 (s, 1H), 1.59 (d, *J* = 8.2 Hz, 2H), 1.37-1.33 (m, 1H), 1.28-1.24 (m, 2H), 1.18 (d, *J* = 10.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.36 (dd, *J* = 13.9, 323.8 Hz), 147.42 (dd, *J* = 13.9, 322.6 Hz), 144.24, 139.42 (dd, *J* = 9.4, 2.2 Hz), 134.38, 129.78, 129.63 (dd, *J* = 5.8, 3.2 Hz), 127.12, 113.17 (d, *J* = 19.0 Hz), 103.98 (d, *J* = 23.6 Hz), 70.50, 50.06, 43.91, 42.96, 32.23, 28.15, 25.13, 21.51. ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.15 (d, *J* = 20.6 Hz), -143.40 (d, *J* = 20.6 Hz). Enantiomeric excess: 98%, determined by HPLC (Chiralpak IB, hexane/*i*-PrOH = 97/3; flow rate 0.5 ml/min; 25 ℃; 254 nm), first peak: t_R = 14.4 min, second peak: t_R = 16.0 min; HRMS (ESI) m/z calcd. For $C_{20}H_{19}F_2NNaO_2S$ $[M+Na]^+$ = 398.0997, found = 398.0990.



<Peak Table>
PDA Ch1 254nm

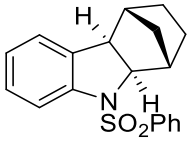
Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.639	371085	54.597	6441584	50.518
2	14.661	308592	45.403	6309566	49.482
Total		679677	100.000	12751150	100.000



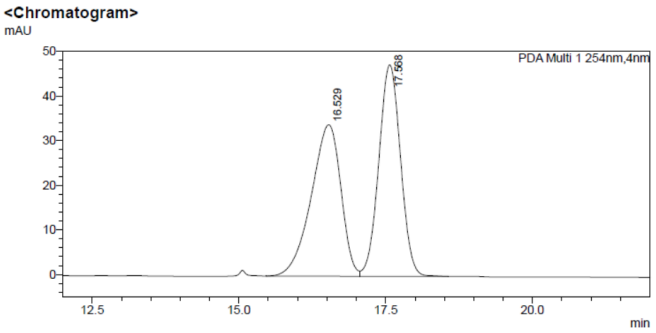
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	14.395	446814	99.184	8783804	99.134
2	15.966	3678	0.816	76754	0.866
Total		450492	100.000	8860557	100.000

(1*S*,4*R*,4a*R*,9a*R*)-9-(phenylsulfonyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole

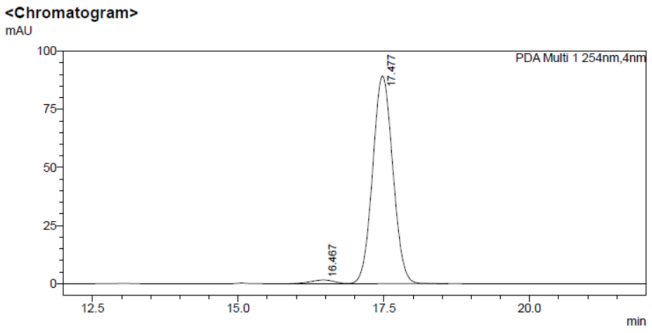


3q; white solid (hexane/EtOAc = 8:1, 50 mg, 77% isolated yield); m.p. = 115-117 ºC; $[\alpha]_D^{20}$ = 162.429 (*c* = 0.625, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.76 (m, 2H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.51 (dt, *J* = 14.9, 1.2 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.16-7.12 (m, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.95 (td, *J* = 7.4, 0.9 Hz, 1H), 3.97 (d, *J* = 8.1 Hz, 1H), 3.08 (d, *J* = 8.1 Hz, 1H), 2.75 (s, 1H), 2.24 (s, 1H), 1.61-1.58 (m, 2H), 1.37-1.34 (m, 1H), 1.30-1.27 (m, 2H), 1.16-1.12 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.24, 137.86, 133.95, 132.92, 128.94, 127.77, 127.02, 124.89, 123.75, 114.11, 69.80, 50.40, 43.88, 43.03, 32.20, 28.29, 25.29. Enantiomeric excess: 96%, determined by HPLC (Chiralpak IC, hexane/*i*-PrOH = 93/7; flow rate 0.8 ml/min; 25 ℃; 254 nm), first peak: t_R = 16.5 min, second peak: t_R = 17.5 min; HRMS (ESI) m/z calcd. For $C_{19}H_{19}NNaO_2S$ $[M+Na]^+$ = 348.1029, found = 348.1026.



<Peak Table>
PDA Ch1 254nm

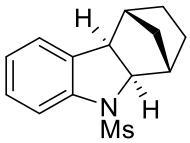
Peak#	Ret. Time	Height	Height%	Area	Area%
1	16.529	33925	41.725	1190992	49.414
2	17.568	47381	58.275	1219258	50.586
Total		81306	100.000	2410249	100.000



<Peak Table>
PDA Ch1 254nm

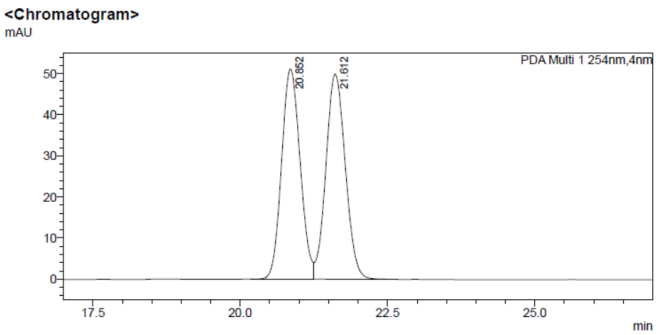
Peak#	Ret. Time	Height	Height%	Area	Area%
1	16.467	1659	1.823	48009	2.178
2	17.477	89383	98.177	2155805	97.822
Total		91043	100.000	2203814	100.000

(1*S*,4*R*,4a*R*,9a*R*)-9-(methylsulfonyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole



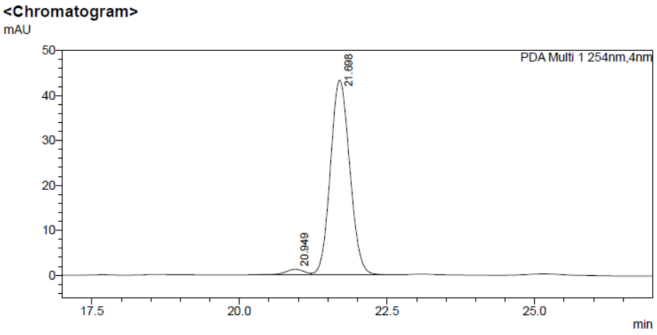
3r; white solid (hexane/EtOAc = 8:1, 43 mg, 82% isolated yield); m.p. = 59-60 ºC; $[\alpha]_D^{20}$ = 28.219 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.7 Hz, 1H), 7.17-7.14 (m, 2H), 7.03-6.99 (m, 1H), 4.08 (d, *J* = 8.1 Hz, 1H), 3.34 (d, *J* = 8.1 Hz, 1H), 2.85 (s, 3H), 2.67 (d, *J* = 2.2 Hz, 1H), 2.33 (s, 1H), 1.66-1.56 (m, 2H), 1.37-1.36 (m, 2H), 1.30-1.26 (m, 1H), 1.17 (d, *J* = 10.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.15, 133.74, 128.04, 125.17, 123.76, 113.16, 70.20, 50.52, 43.69, 43.18, 35.57, 31.97, 28.35, 25.11. Enantiomeric excess: 95%, determined by HPLC (Chiralpak IF, hexane/*i*-PrOH = 92/8; flow rate

0.5 ml/min; 25 ℃; 254 nm), first peak: t_R = 20.9min, second peak: t_R = 21.7 min; HRMS (ESI) m/z calcd. For $C_{14}H_{17}NNaO_2S$ $[M+Na]^+$ = 286.0872, found = 286.0868.



<Peak Table>
PDA Ch1 254nm

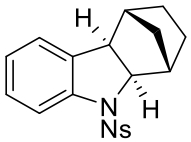
Peak#	Ret. Time	Height	Height%	Area	Area%
1	20.852	51123	50.602	1119728	49.463
2	21.612	49906	49.398	1144021	50.537
Total		101029	100.000	2263749	100.000



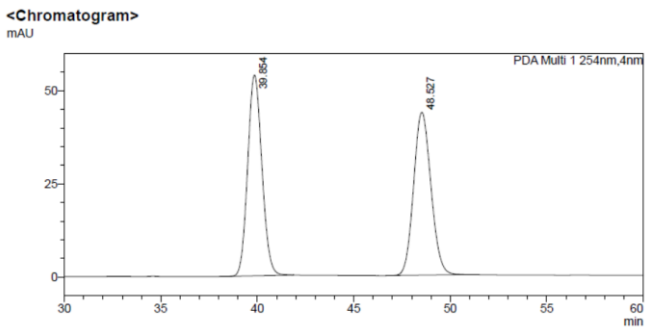
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	20.949	1213	2.726	26097	2.578
2	21.698	43259	97.274	986315	97.422
Total		44472	100.000	1012413	100.000

(1*S*,4*R*,4a*R*,9a*R*)-9-((4-nitrophenyl)sulfonyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole

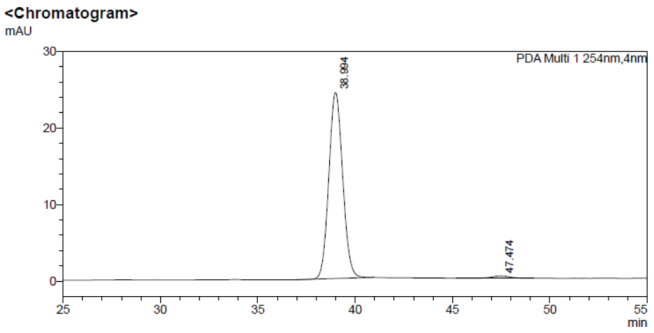


3s; white solid (hexane/EtOAc = 5:1, 40 mg, 54% isolated yield); m.p. = 189-191 °C; $[\alpha]_D^{20}$ = 192.648 (*c* = 0.313, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-8.24 (m, 2H), 7.98-7.94 (m, 2H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.20-7.16 (m, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 7.01 (td, *J* = 7.4, 0.9 Hz, 1H), 3.95 (d, *J* = 8.0 Hz, 1H), 3.11 (d, *J* = 8.0 Hz, 1H), 2.75 (d, *J* = 2.5 Hz, 1H), 2.27 (s, 1H), 1.63-1.59 (m, 2H), 1.35-1.26 (m, 3H), 1.17 (dd, *J* = 10.5, 1.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.21, 143.30, 142.37, 134.02, 128.21, 128.06, 125.25, 124.55, 124.21, 114.01, 70.09, 50.39, 43.92, 43.01, 32.15, 28.19, 25.26. Enantiomeric excess: 97%, determined by HPLC (Chiralpak IC, hexane/*i*-PrOH = 93/7; flow rate 0.8 ml/min; 25 ℃; 254 nm), first peak: t_R = 20.9min, second peak: t_R = 21.7 min; HRMS (ESI) m/z calcd. For $C_{19}H_{18}N_2NaO_4S$ $[M+Na]^+$ = 393.0879, found = 393.0885.



<Peak Table>
PDA Ch1 254nm

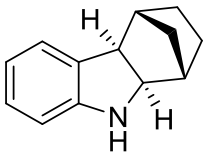
Peak#	Ret. Time	Height	Height%	Area	Area%
1	39.854	53947	55.199	2766414	50.221
2	48.527	43785	44.801	2742113	49.779
Total		97732	100.000	5508527	100.000



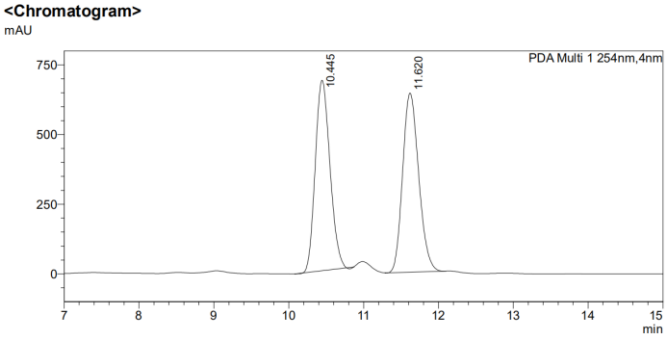
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	38.994	24322	98.743	1201656	98.494
2	47.474	310	1.257	18372	1.506
Total		24631	100.000	1220028	100.000

(1*S*,4*R*,4a*R*,9a*R*)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole

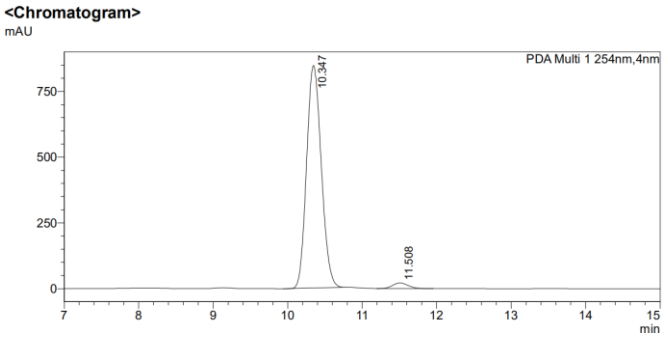


3t; brown solid (hexane/EtOAc = 20:1, 20 mg, 63% isolated yield); $[\alpha]_D^{20}$ = -7.0841 (*c* = 0.95, CH_2Cl_2); ^{1}H NMR (500 MHz, C_6D_6) δ 7.00 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.70 (td, *J* = 7.3, 0.5 Hz, 1H), 6.35 (d, *J* = 7.8 Hz, 1H), 3.38 (d, *J* = 8.2 Hz, 1H), 3.04 (d, *J* = 8.2 Hz, 1H), 2.89 (s, 1H), 2.12 (d, *J* = 3.5 Hz, 1H), 1.87 (d, *J* = 4.2 Hz, 1H), 1.56 (d, *J* = 10.1 Hz, 1H), 1.37-1.24 (m, 2H), 1.11-1.06 (m, 1H), 0.95-0.90 (m, 2H); ^{13}C NMR (126 MHz, C_6D_6) δ 153.13, 131.70, 124.77, 118.08, 108.16, 65.52, 52.61, 44.58, 43.51, 32.43, 28.86, 25.54. Enantiomeric excess: 95%, determined by HPLC (Chiralpak IC, hexane/*i*-PrOH = 97/3; flow rate 0.5 ml/min; 25 ℃; 254 nm), first peak: t_R = 10.4 min, second peak: t_R = 11.6 min; HRMS (ESI) m/z calcd. For $C_{13}H_{16}N$ $[M+H]^+$ = 186.1277, found = 186.1272.



<Peak Table>
PDA Ch1 254nm

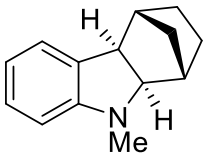
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.445	683528	51.546	9313181	49.275
2	11.620	642516	48.454	9587299	50.725
Total		1326044	100.000	18900481	100.000



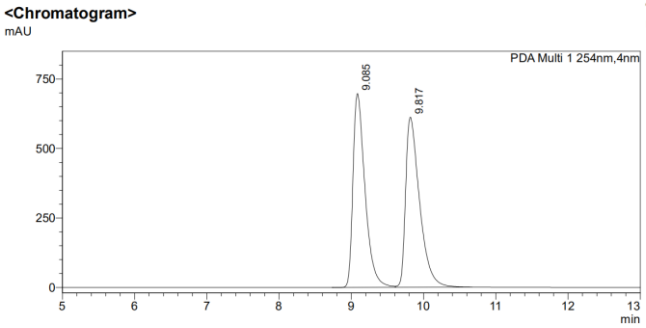
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.347	845902	97.545	11594081	97.404
2	11.508	21287	2.455	308980	2.596
Total		867188	100.000	11903061	100.000

(1*S*,4*R*,4a*R*,9a*R*)-9-methyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole

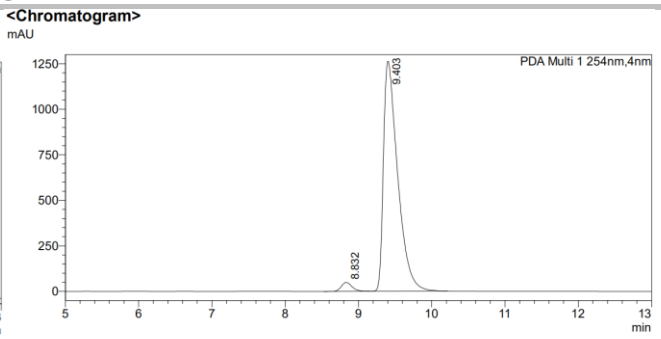


3u; brown oil (hexane/EtOAc = 50:1, 38 mg, 85% isolated yield); $[\alpha]_D^{20}$ = -169.7366 (*c* = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, C_6D_6) δ 7.09 (t, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.70-6.66 (m, 1H), 6.20 (d, *J* = 7.8 Hz, 1H), 3.17 (d, *J* = 8.3 Hz, 1H), 3.02 (d, *J* = 8.3 Hz, 1H), 2.44 (s, 3H), 2.15 (s, 1H), 2.10 (d, *J* = 3.0 Hz, 1H), 1.56-1.54 (m, 1H), 1.34-1.27 (m, 2H), 1.10-1.06 (m, 1H), 0.94-0.88 (m, 2H); ^{13}C NMR (126 MHz, C_6D_6) δ 154.21, 131.79, 124.46, 116.66, 104.79, 73.01, 51.18, 43.47, 40.85, 32.74, 29.01, 25.22; Enantiomeric excess: 94%, determined by HPLC (Chiralpak IF, hexane/*i*-PrOH = 100/0; flow rate 0.8 ml/min; 25 ℃; 254 nm), first peak: t_R = 9.1 min, second peak: t_R = 9.8 min; HRMS (ESI) m/z calcd. For $C_{14}H_{18}N$ $[M+H]^+$ = 200.1434, found = 200.1430.



<Peak Table>
PDA Ch1 254nm

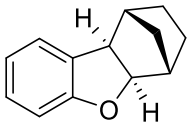
Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.085	698065	53.272	8099540	49.622
2	9.817	612319	46.728	8222798	50.378
Total		1310383	100.000	16322339	100.000



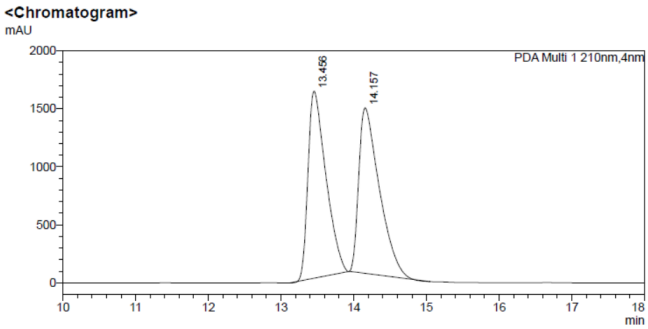
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.832	49247	3.757	495371	2.822
2	9.403	1261633	96.243	17057242	97.178
Total		1310880	100.000	17552613	100.000

(1*R*,4*S*,4a*R*,9b*R*)-1,2,3,4,4a,9b-hexahydro-1,4-methanodibenzo[*b*,*d*]furan

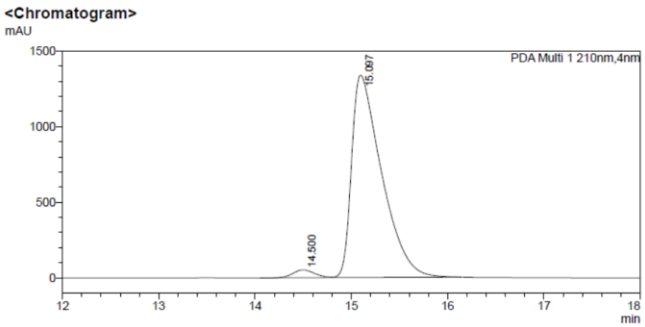


5a; pale yellow oil (hexane/Et_2O = 20:1, 39 mg, 70% isolated yield); $[\alpha]_D^{20}$ = 25.120 (*c* = 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 7.3 Hz, 1H), 7.08-7.04 (m, 1H), 6.80 (td, *J* = 7.4, 0.7 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 4.68 (d, *J* = 7.2 Hz, 1H), 3.27 (d, *J* = 7.2 Hz, 1H), 2.53 (d, *J* = 3.1 Hz, 1H), 2.33 (s, 1H), 1.59-1.53 (m, 2H), 1.46-1.43 (m, 1H), 1.34-1.30 (m, 1H), 1.19-1.13 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.33, 129.61, 128.00, 124.70, 120.03, 108.44, 89.21, 51.61, 42.56, 42.24, 32.07, 27.89, 23.50. Enantiomeric excess: 95%, determined by HPLC (Chiralpak IB, hexane/*i*-PrOH = 100/0; flow rate 0.5 ml/min; 25 ℃; 210 nm), first peak: t_R = 14.5 min, second peak: t_R = 15.1 min; HRMS (ESI) m/z calcd. For $C_{13}H_{14}NaO$ $[M+Na]^+$ = 209.0937, found = 209.0925.



<Peak Table>
PDA Ch1 210nm

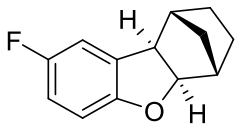
Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.456	1611797	53.033	27600885	49.543
2	14.157	1427465	46.967	28109978	50.457
Total		3039262	100.000	55710863	100.000



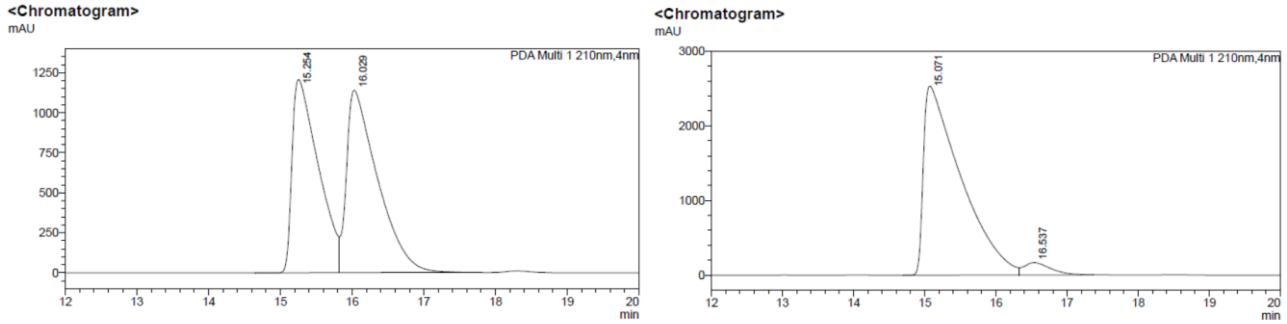
<Peak Table>
PDA Ch1 210nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	14.500	52197	3.752	824393	2.760
2	15.097	1338950	96.248	29045924	97.240
Total		1391147	100.000	29870317	100.000

(1*R*,4*S*,4a*R*,9b*R*)-8-fluoro-1,2,3,4,4a,9b-hexahydro-1,4-methanodibenzo[*b*,*d*]furan



5b; pale yellow oil (hexane/Et_2O = 20:1, 31 mg, 51% isolated yield); $[\alpha]_D^{20}$ = 30.649 (*c* = 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.80 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.73 (td, *J* = 8.8, 2.7 Hz, 1H), 6.57 (dd, *J* = 8.7, 4.1 Hz, 1H), 4.69 (d, *J* = 7.3 Hz, 1H), 3.25 (d, *J* = 7.3 Hz, 1H), 2.51 (d, *J* = 2.3 Hz, 1H), 2.28 (s, 1H), 1.61-1.51 (m, 2H), 1.46-1.43 (m, 1H), 1.33-1.26 (m, 1H), 1.18-1.13 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ157.30 (d, *J* = 1.3 Hz), 157.20 (d, *J* = 236.2 Hz), 130.91 (d, *J* = 8.3 Hz), 113.99 (d, *J* = 24.1 Hz), 111.63 (d, *J* = 24.3 Hz), 108.33 (d, *J* = 8.5 Hz), 89.92, 51.85, 42.45, 42.30, 32.07, 27.80, 23.36. ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.25. Enantiomeric excess: 91%, determined by HPLC (Chiralpak IB, hexane/*i*-PrOH = 100/0; flow rate 0.5 ml/min; 25 ℃; 210 nm), first peak: t_R = 15.1 min, second peak: t_R = 16.5 min; HRMS (ESI) m/z calcd. For $C_{13}H_{13}FNaO$ $[M+Na]^+$ = 227.0843, found = 227.0839.



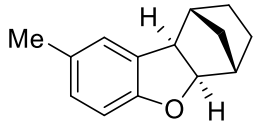
<Peak Table>
PDA Ch1 210nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	15.254	1208275	51.473	30700528	47.235
2	16.029	1139132	48.527	34294798	52.765
Total		2347407	100.000	64995326	100.000

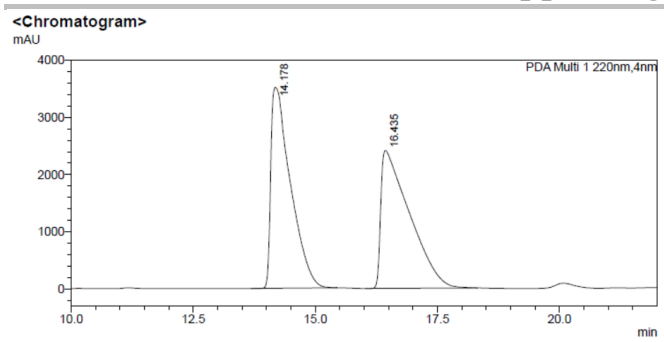
<Peak Table>
PDA Ch1 210nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	15.071	2535800	93.858	93152861	95.585
2	16.537	165928	6.142	4302529	4.415
Total		2701729	100.000	97455390	100.000

(1*R*,4*S*,4a*R*,9b*R*)-8-methyl-1,2,3,4,4a,9b-hexahydro-1,4-methanodibenzo[*b*,*d*]furan

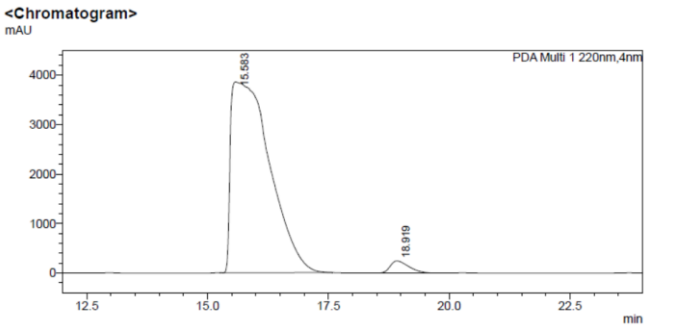


5c; amorphous solid (hexane/Et_2O = 20:1, 39 mg, 65% isolated yield); $[\alpha]_D^{20}$ = 48.527 (*c* = 0.625, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 6.92 (s, 1H), 6.86 (dd, *J* = 8.1, 0.6 Hz, 1H), 6.58 (d, *J* = 8.1 Hz, 1H), 4.66 (d, *J* = 7.2 Hz, 1H), 3.23 (d, *J* = 7.2 Hz, 1H), 2.51 (d, *J* = 2.9 Hz, 1H), 2.28 (s, 1H), 2.26 (s, 3H), 1.57-1.54 (m, 2H), 1.46-1.44 (m, 1H), 1.33-1.29 (m, 1H), 1.18-1.12 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.24, 129.59, 129.23, 128.34, 125.30, 107.92, 89.29, 51.69, 42.52, 42.27, 32.09, 27.90, 23.48, 20.71. Enantiomeric excess: 94%, determined by HPLC (Chiralpak IB, hexane/*i*-PrOH = 100/0; flow rate 0.5 ml/min; 25 ℃; 220 nm), first peak: t_R = 15.6 min, second peak: t_R = 18.9 min; HRMS (ESI) m/z calcd. For $C_{14}H_{16}NaO$ $[M+Na]^+$ = 223.1093, found = 223.1091.



<Peak Table>
PDA Ch1 220nm

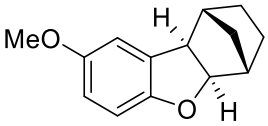
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.178	98362615	3514636	0.000		M	
2	16.435	98600409	2413513	0.000		M	
Total		196963024	5928149				



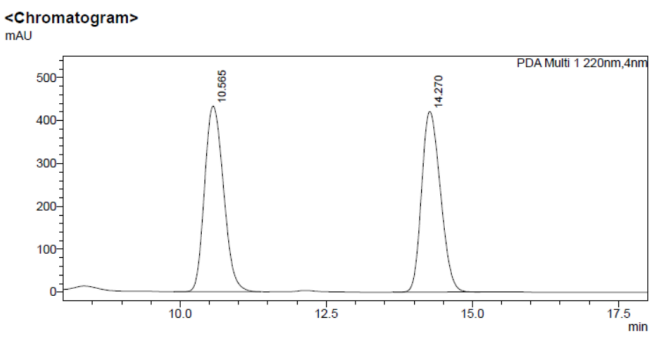
<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	15.583	3855261	94.004	217667587	97.051
2	18.919	245920	5.996	6613698	2.949
Total		4101181	100.000	224281285	100.000

(1*R*,4*S*,4a*R*,9b*R*)-8-methoxy-1,2,3,4,4a,9b-hexahydro-1,4-methanodibenzo[*b*,*d*]furan

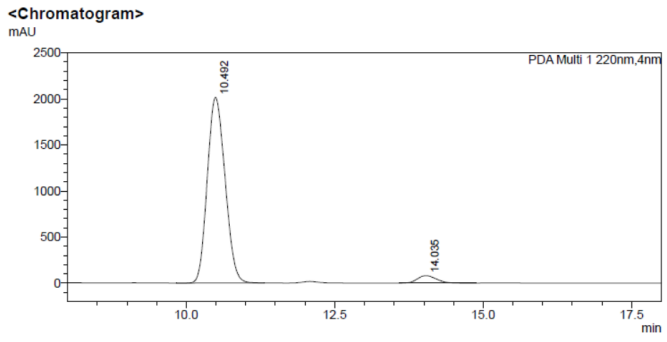


5d; amorphous solid (hexane/Et_2O = 10:1, 40 mg, 61% isolated yield); $[\alpha]_D^{20}$ = 49.599 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.71-6.70 (m, 1H), 6.62-6.58 (m, 2H), 4.66 (d, *J* = 7.2 Hz, 1H), 3.75 (s, 3H), 3.25 (d, *J* = 7.2 Hz, 1H), 2.51 (s, 1H), 2.30 (s, 1H), 1.57-1.52 (m, 2H), 1.48-1.45 (m, 1H), 1.33-1.26 (m, 1H), 1.17-1.14 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.49, 153.78, 130.55, 112.78, 110.99, 108.16, 89.50, 55.97, 52.09, 42.43, 42.32, 32.11, 27.87, 23.42. Enantiomeric excess: 92%, determined by HPLC (Chiralpak IB, hexane/*i*-PrOH = 99/1; flow rate 0.5 ml/min; 25 ℃; 220 nm), first peak: t_R = 10.5 min, second peak: t_R = 14.0 min; HRMS (ESI) m/z calcd. For $C_{14}H_{16}NaO_2$ $[M+Na]^+$ = 239.1043, found = 239.1040.



<Peak Table>
PDA Ch1 220nm

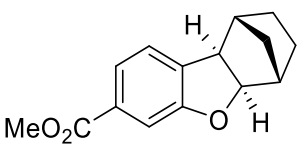
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.565	432942	50.686	9784679	50.842
2	14.270	421221	49.314	9460641	49.158
Total		854162	100.000	19245320	100.000



<Peak Table>
PDA Ch1 220nm

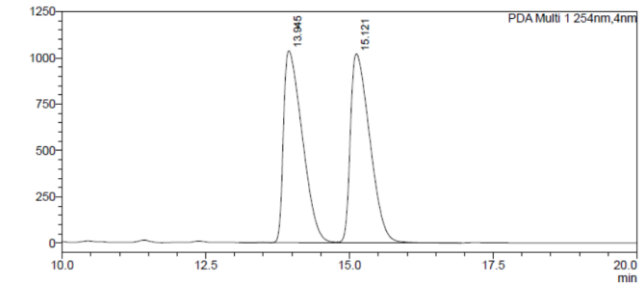
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.492	2014582	96.201	41942531	96.010
2	14.035	79559	3.799	1742864	3.990
Total		2094140	100.000	43685394	100.000

methyl (1*R*,4*S*,4a*R*,9b*R*)-1,2,3,4,4a,9b-hexahydro-1,4-methanodibenzo[*b*,*d*]furan-7-carboxylate



5e; white solid (hexane/Et_2O = 10:1, 32 mg, 44% isolated yield); m.p. = 132-133 ºC; $[\alpha]_D^{20}$ = 67.582 (*c* = 0.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.31 (d, *J* = 1.2 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 4.73 (d, *J* = 7.2 Hz, 1H), 3.87 (s, 3H), 3.29 (d, *J* = 7.2 Hz, 1H), 2.55 (d, *J* = 3.0 Hz, 1H), 2.31 (s, 1H), 1.62-1.54 (m, 2H), 1.40 (d, *J* = 10.6 Hz, 1H), 1.35-1.31 (m, 1H), 1.19-1.15 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.97, 161.52, 135.28, 130.26, 124.32, 122.12, 109.16, 89.76, 51.97, 51.45, 42.50, 42.21, 32.07, 27.85, 23.34. Enantiomeric excess: 91%, determined by HPLC (Chiralpak IB, hexane/*i*-PrOH = 99/1; flow rate 0.5 ml/min; 25 ℃; 254 nm), first peak: t_R = 14.2 min, second peak: t_R = 14.9 min; HRMS (ESI) m/z calcd. For $C_{15}H_{16}NaO_3$ $[M+Na]^+$ = 267.0992, found = 267.0991.

<Chromatogram>



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.945	1036221	50.383	23577784	49.627
2	15.121	1020486	49.617	23932663	50.373
Total		2056707	100.000	47510447	100.000

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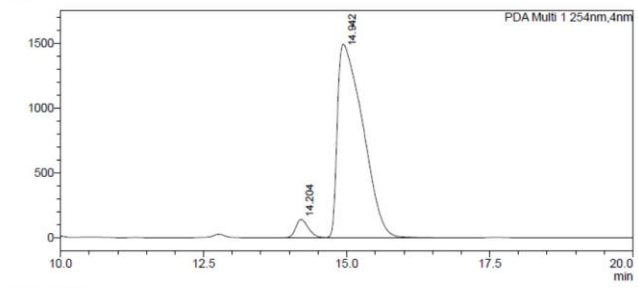
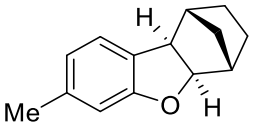


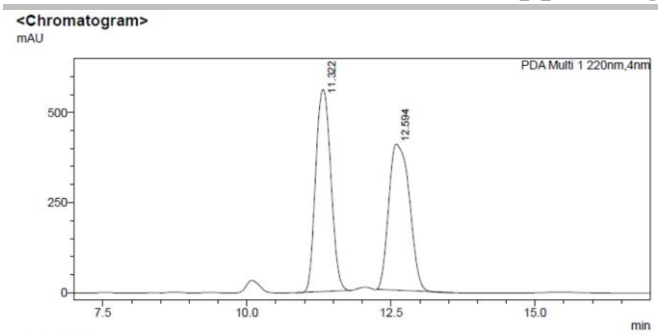
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	14.204	140340	8.605	2165988	4.507
2	14.942	1490656	91.395	45897096	95.493
Total		1630996	100.000	48063085	100.000

(1*R*,4*S*,4a*R*,9b*R*)-7-methyl-1,2,3,4,4a,9b-hexahydro-1,4-methanodibenzo[*b*,*d*]furan

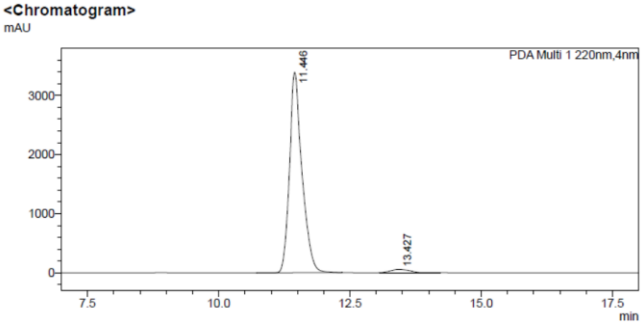


5f; amorphous solid (hexane/Et_2O = 20:1, 40 mg, 66% isolated yield); $[\alpha]_D^{20}$ = 33.151 (*c* = 0.625, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.25 (s, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 7.4 Hz, 1H), 4.66 (d, *J* = 7.0 Hz, 1H), 3.22 (d, *J* = 7.2 Hz, 1H), 2.51 (s, 1H), 2.27 (s, 4H), 1.56-1.51 (m, 2H), 1.44 (d, *J* = 10.8 Hz, 1H), 1.34-1.28 (m, 1H), 1.17-1.10 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.59, 138.14, 126.68, 124.22, 120.74, 109.18, 89.51, 51.34, 42.53, 42.21, 32.03, 27.85, 23.49, 21.46. Enantiomeric excess: 95%, determined by HPLC (Chiralpak IB, hexane/*i*-PrOH = 100/0; flow rate 0.5 ml/min; 25 ℃; 220 nm), first peak: t_R = 11.4 min, second peak: t_R = 13.4 min; HRMS (ESI) m/z calcd. For $C_{14}H_{16}NaO$ $[M+Na]^+$ = 223.1093, found = 223.1089.



<Peak Table>
PDA Ch1 220nm

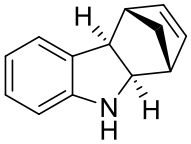
Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.322	560999	58.043	10289908	50.407
2	12.594	405522	41.957	10123688	49.593
Total		966521	100.000	20413596	100.000



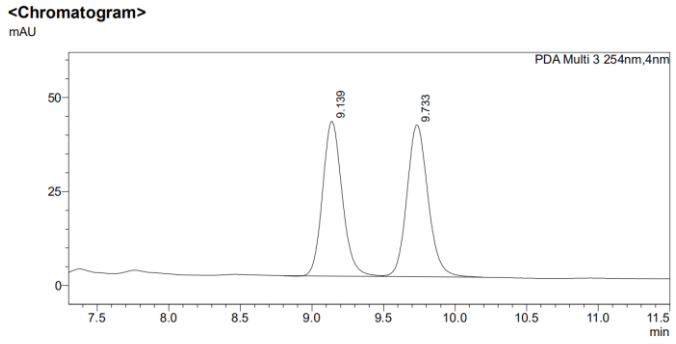
<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.446	3394776	98.435	56243297	97.630
2	13.427	53965	1.565	1365392	2.370
Total		3448742	100.000	57608688	100.000

(1*R*,4*S*,4a*R*,9a*R*)-4,4a,9,9a-tetrahydro-1H-1,4-methanocarbazole

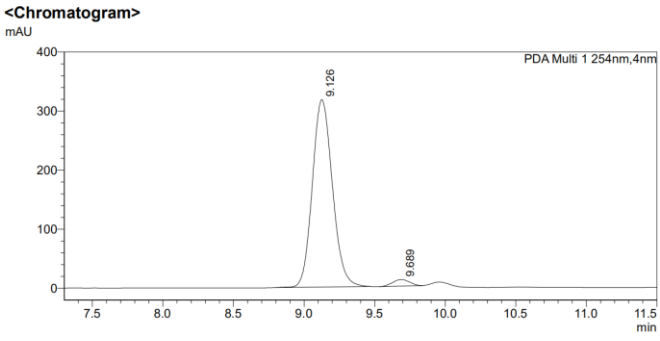


7; yellow oil (hexane/EtOAc = 20:1, 28 mg, 73% isolated yield); $[\alpha]_D^{20}$ = -20.1196 (*c* = 0.25, CH_2Cl_2); ^{1}H NMR (500 MHz, C_6D_6) δ 7.03 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.72 (td, *J* = 7.4, 0.8 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 1H), 6.05 (dd, *J* = 5.8, 2.9 Hz, 1H), 5.82 (dd, *J* = 5.8, 3.0 Hz, 1H), 3.55 (d, *J* = 8.1 Hz, 1H), 3.24 (d, *J* = 8.1 Hz, 1H), 2.88 (s, 1H), 2.70 (s, 1H), 2.48 (s, 1H), 1.67 (d, *J* = 8.8 Hz, 1H), 1.42-1.40 (m, 1H); ^{13}C NMR (126 MHz, C_6D_6) δ 154.76, 139.77, 135.41, 129.60, 128.04, 124.42, 118.20, 108.85, 64.27, 50.69, 50.63, 48.75, 42.50; Enantiomeric excess: 94%, determined by HPLC (Chiralpak IF, hexane/*i*-PrOH = 99/1; flow rate 0.8 ml/min; 25 ℃; 254 nm), first peak: t_R = 9.1 min, second peak: t_R = 9.7 min; HRMS (ESI) m/z calcd. For $C_{13}H_{14}N$ $[M+H]^+$ = 184.1121, found = 184.1113.



<Peak Table>
PDA Ch3 254nm

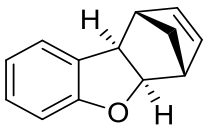
Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.139	41198	50.527	392491	48.625
2	9.733	40338	49.473	414695	51.375
Total		81536	100.000	807186	100.000



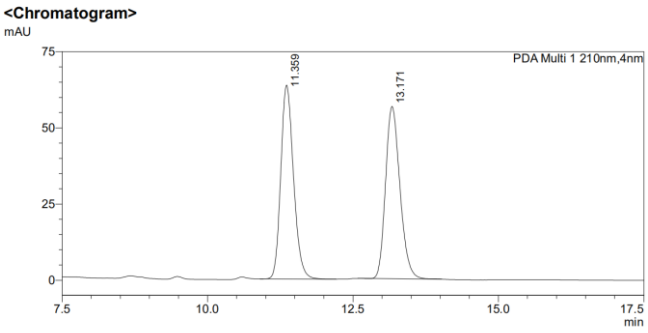
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.126	316994	96.661	3142430	97.153
2	9.689	10950	3.339	92076	2.847
Total		327944	100.000	3234506	100.000

(1*S*,4*R*,4a*R*,9b*R*)-1,4,4a,9b-tetrahydro-1,4-methanodibenzo[*b*,*d*]furan

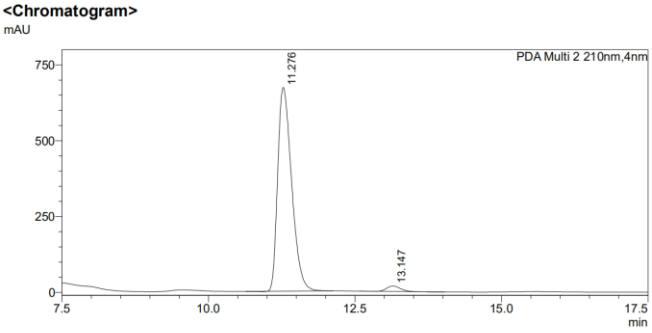


8; yellow oil (hexane/EtOAc = 100:0, 25 mg, 45% isolated yield); $[\alpha]_D^{20}$ = 40.5192 (*c* = 0.25, $CHCl_3$); Enantiomeric excess: 95%, determined by HPLC (Chiralpak OJ-H, hexane/*i*-PrOH = 100/0; flow rate 0.8 ml/min; 25 ℃; 210 nm), first peak: t_R = 11.4 min, second peak: t_R = 13.2 min; HRMS (ESI) m/z calcd. For $C_{13}H_{13}O$ $[M+H]^+$ = 185.0961, found = 185.0957. (Please refer to Catellani's work for ^1H and ^{13}C NMR)[3]



<Peak Table>
PDA Ch1 210nm

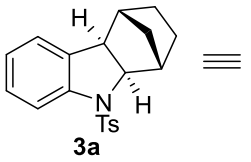
Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.359	63653	52.951	971099	49.893
2	13.171	56559	47.049	975250	50.107
Total		120212	100.000	1946349	100.000



<Peak Table>
PDA Ch2 210nm

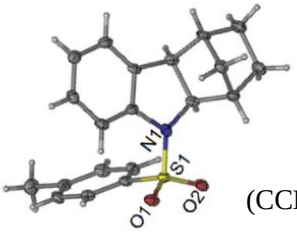
Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.276	672313	97.404	11128515	97.512
2	13.147	17918	2.596	283922	2.488
Total		690231	100.000	11412438	100.000

6. X-ray structure of 3a and 5e

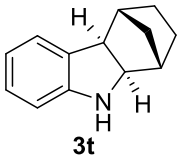


3a

≡

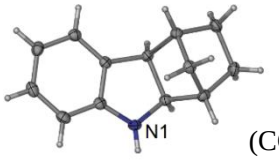


(CCDC: 1981383)

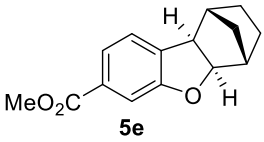


3t

≡

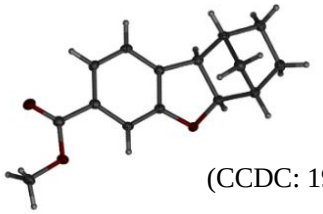


(CCDC: 2032220)



5e

≡

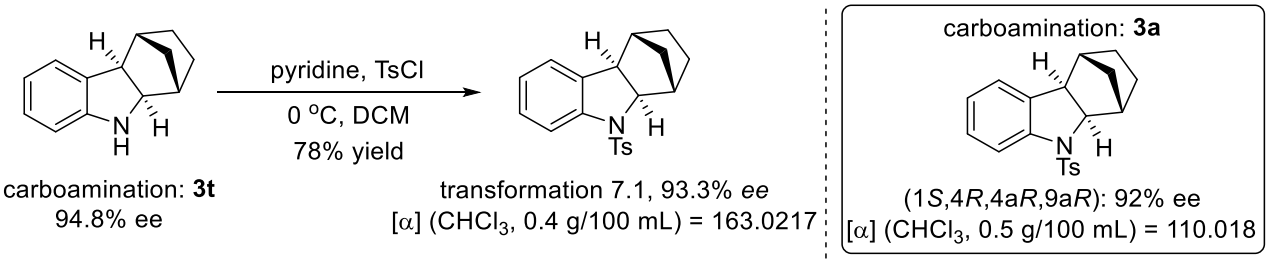


(CCDC: 1981385)

7. Confirmation of the absolute configuration of 3t, 3u, 7 and 8

The absolute configuration of compounds **3t**, **3u**, **7** and **8** was confirmed by comparing the rotational value of a series of transformed products with the previous products **3a** and **5a**.

7.1 Confirmation of the absolute configuration of **3t**

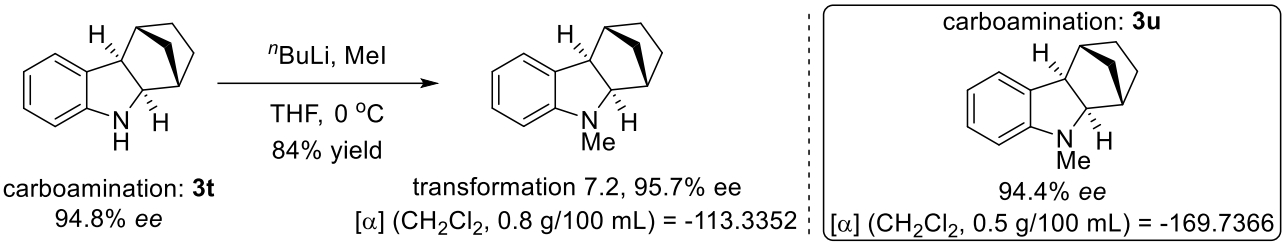


carboamination: **3t**
94.8% ee

transformation 7.1, 93.3% *ee*
[α] ($CHCl_3$, 0.4 g/100 mL) = 163.0217

carboamination: **3a**
(1*S*,4*R*,4a*R*,9a*R*): 92% ee
[α] ($CHCl_3$, 0.5 g/100 mL) = 110.018

7.2 Confirmation of the absolute configuration of **3u**

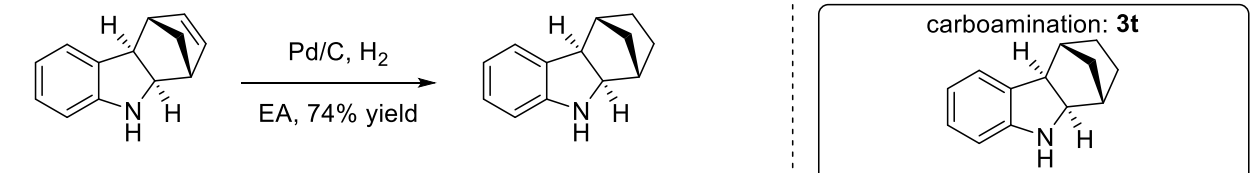


carboamination: **3t**
94.8% *ee*

transformation 7.2, 95.7% ee
[α] (CH_2Cl_2, 0.8 g/100 mL) = -113.3352

carboamination: **3u**
94.4% *ee*
[α] (CH_2Cl_2, 0.5 g/100 mL) = -169.7366

7.3 Confirmation of the absolute configuration of **7**

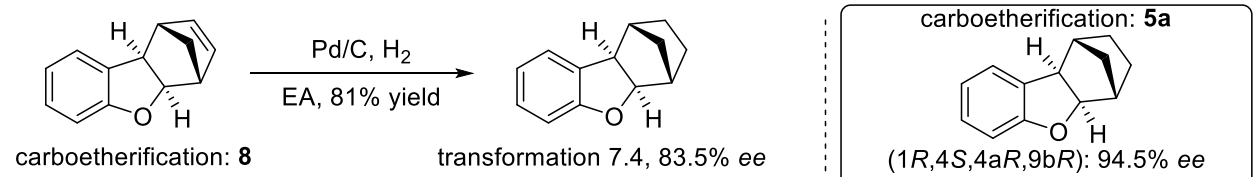


carboamination: **7**
94.3% *ee*

transformation 7.3, 93.2% *ee*
[α] ($CHCl_3$, 0.5 g/100 mL) = -8.3398

carboamination: **3t**
94.8% ee
[α] ($CHCl_3$, 0.33 g/100 mL) = -5.0302

7.4 Confirmation of the absolute configuration of **8**



carboetherification: **8**
95.1% *ee*

transformation 7.4, 83.5% *ee*
[α] ($CHCl_3$, 0.25 g/100 mL) = 11.9998

carboetherification: **5a**
(1*R*,4*S*,4a*R*,9b*R*): 94.5% *ee*
[α] ($CHCl_3$, 0.5 g/100 mL) = 25.120

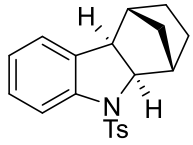
8. References

1 T. W. Liwosz and S. R. Chemler, *Chem. Eur. J.*, 2013, **19**, 12771.

2 M. Tao, Y. Tu, Y. Liu, H. Wu, L. Liu and J. Zhang, *Chem. Sci.*, 2020, **11**, 6283.

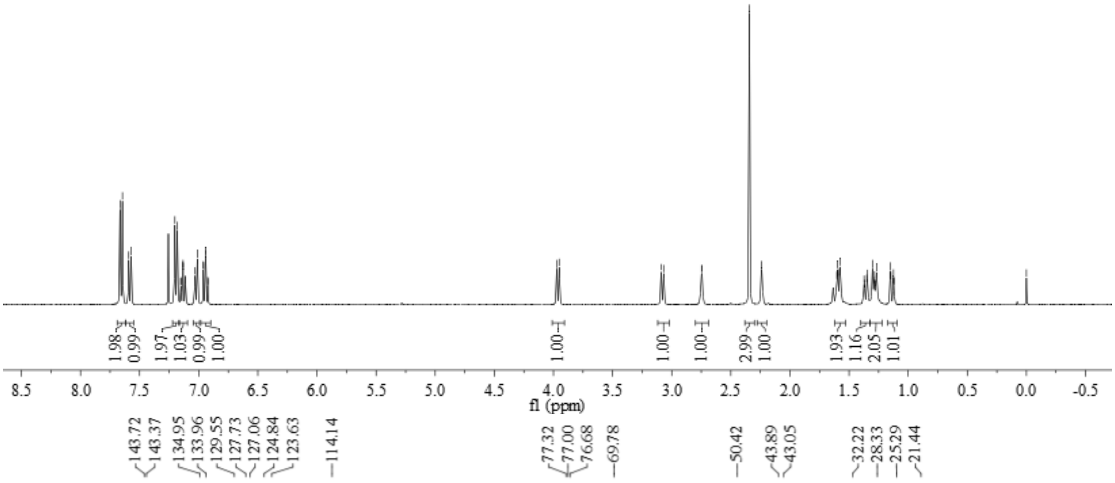
3 M. Catellani and A. Del Rio, *Russ. Chem. Bull.*, 1998, **47**, 928.

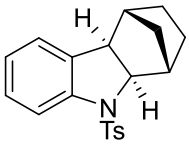
9. ^{1}H, ^{13}C, ^{19}F Spectra for 3, 5 and 7



3a

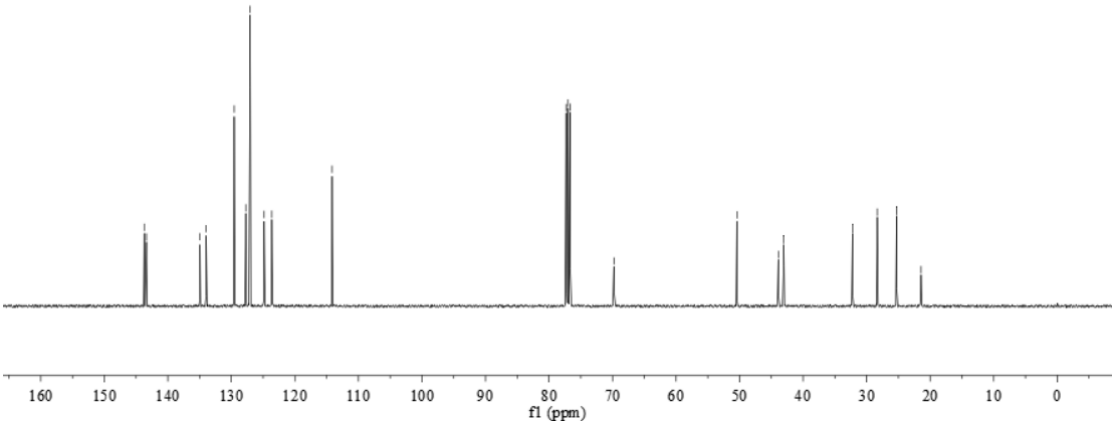
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

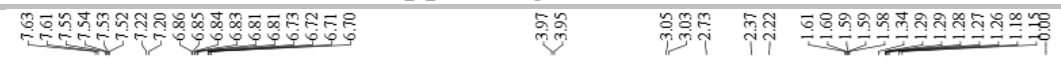


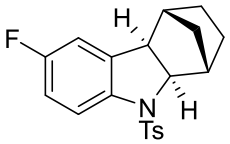


3a

^{13}C NMR (101 MHz, $CDCl_3$, 298 K)

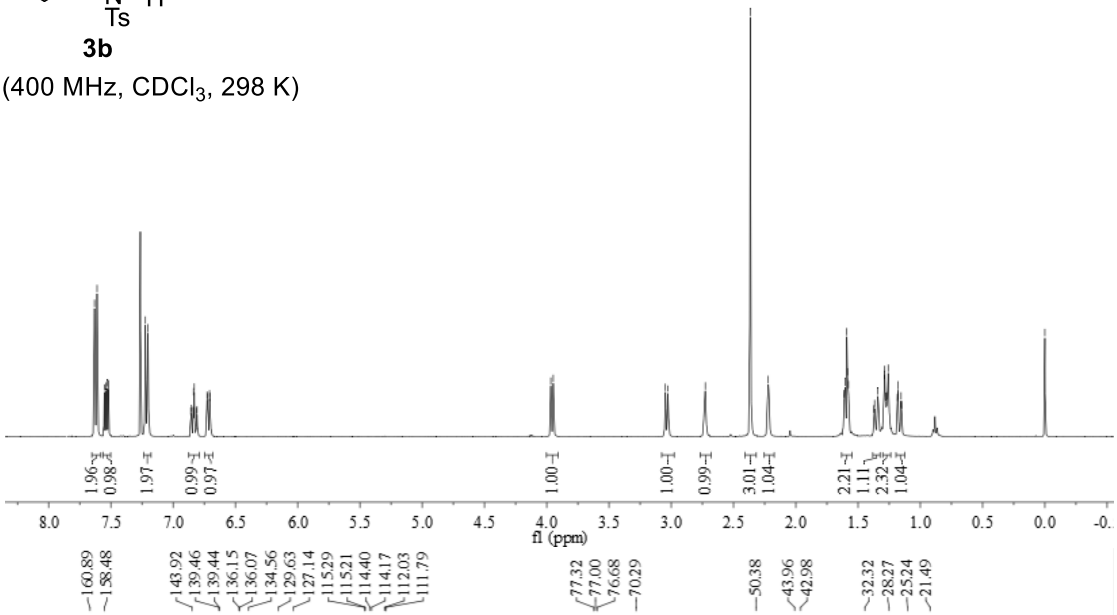


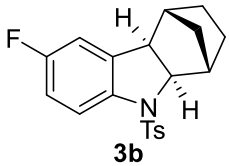




3b

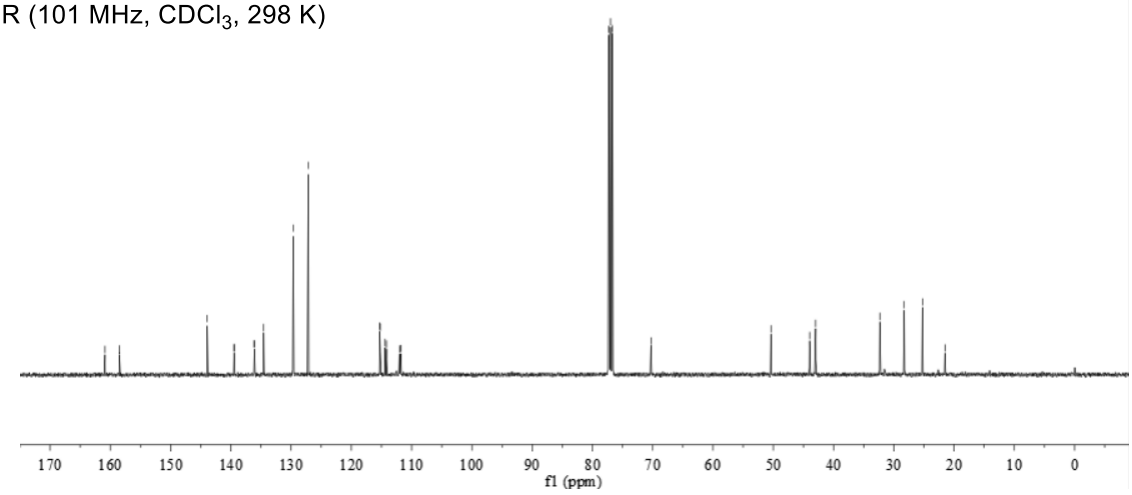
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

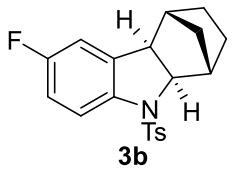




3b

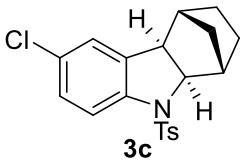
^{13}C NMR (101 MHz, $CDCl_3$, 298 K)





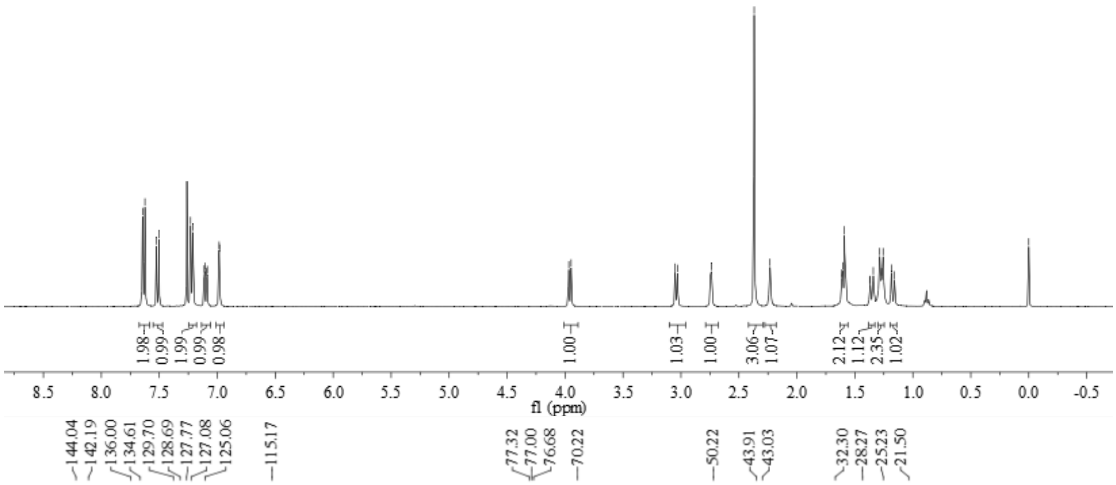
3b

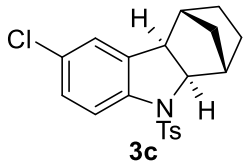
^{19}F NMR (376 MHz, $CDCl_3$, 298 K)



3c

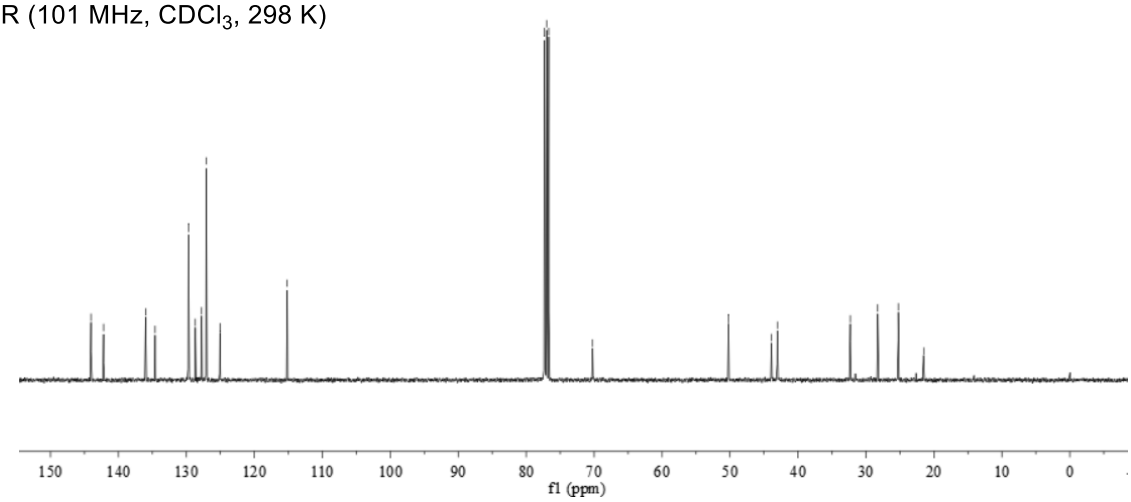
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

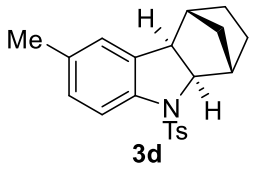




3c

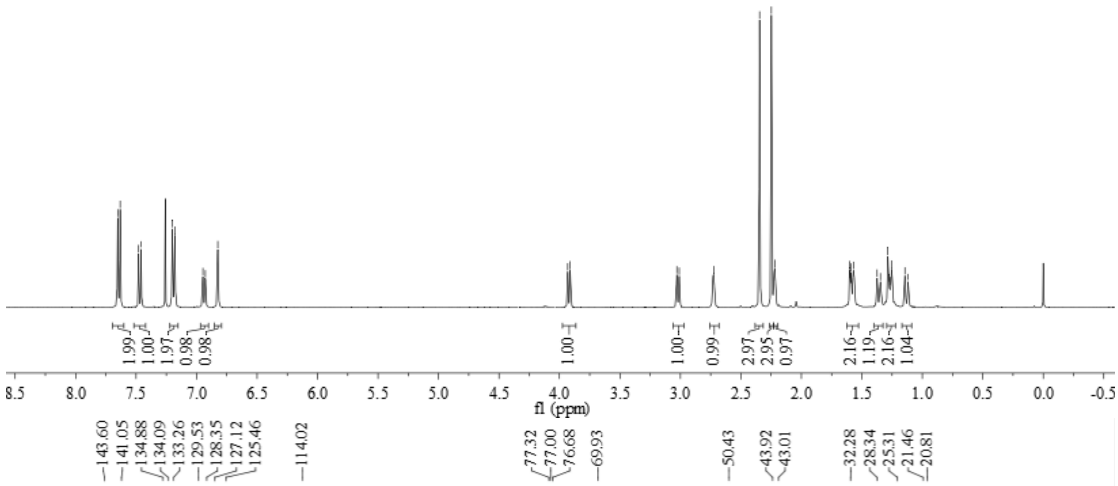
^{13}C NMR (101 MHz, $CDCl_3$, 298 K)

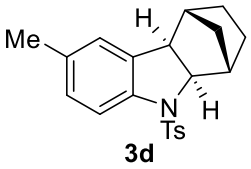




3d

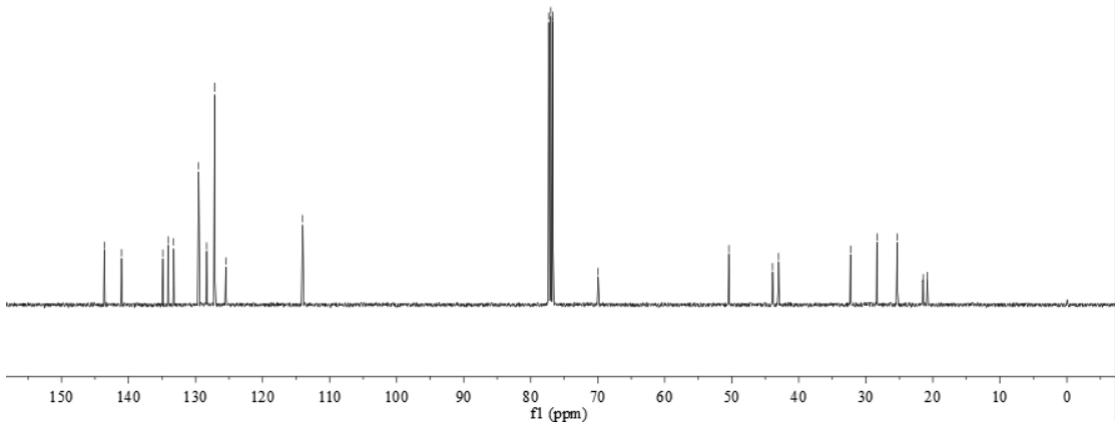
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

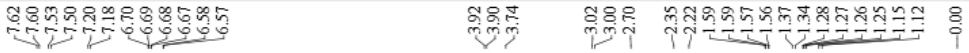


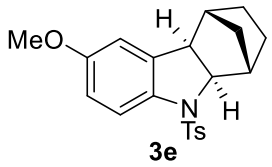


3d

^{13}C NMR (101 MHz, $CDCl_3$, 298 K)

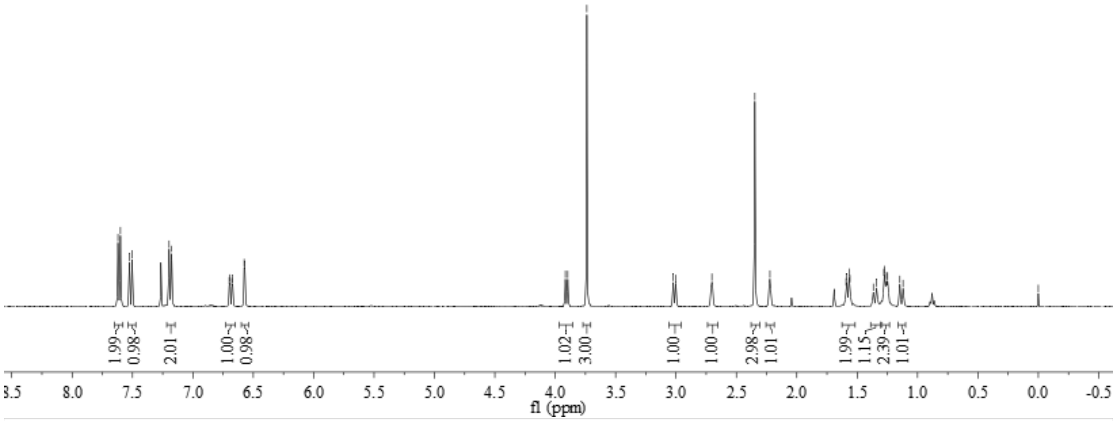


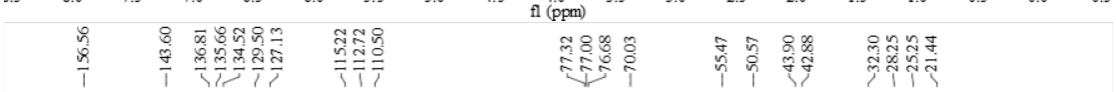


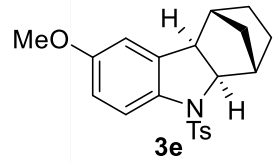


3e

^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

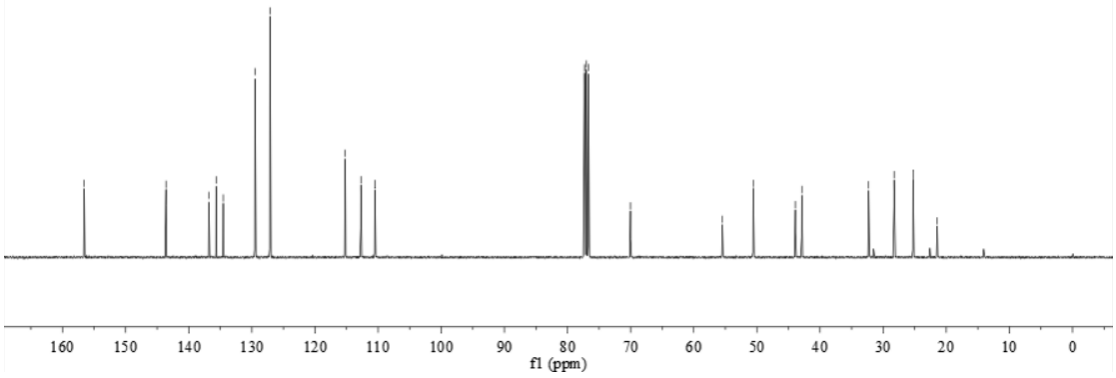


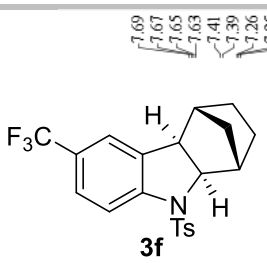




3e

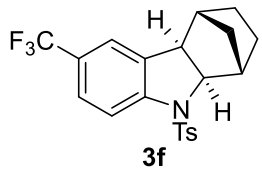
^{13}C NMR (101 MHz, $CDCl_3$, 298 K)





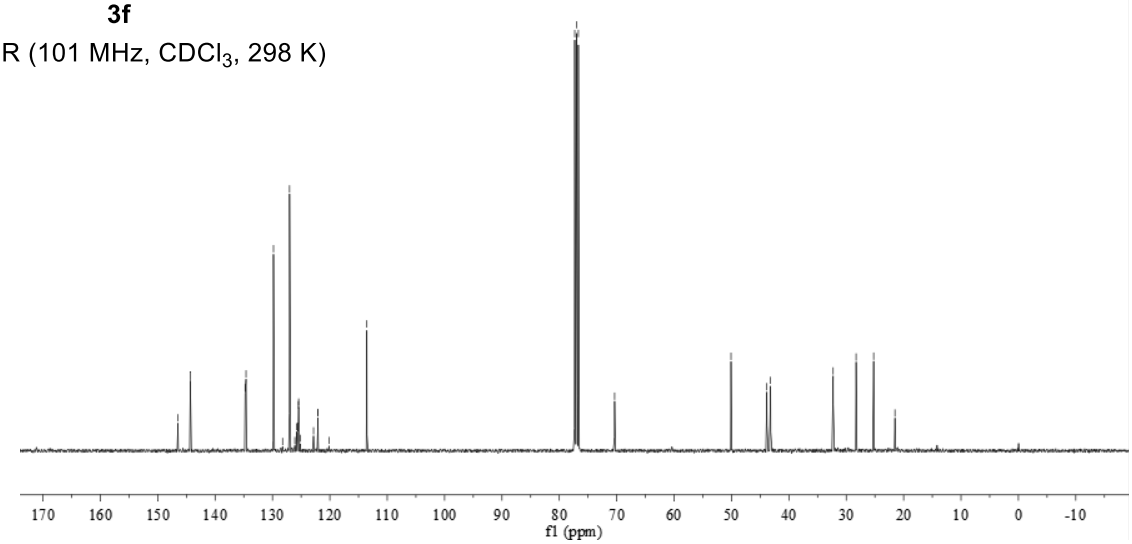
3f

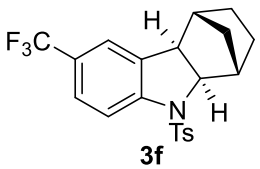
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



3f

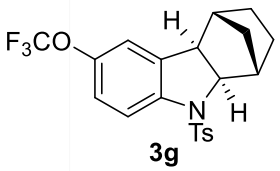
^{13}C NMR (101 MHz, $CDCl_3$, 298 K)





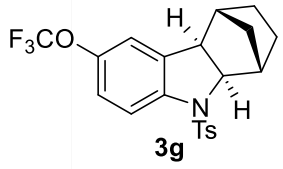
3f

^{19}F NMR (376 MHz, $CDCl_3$, 298 K)



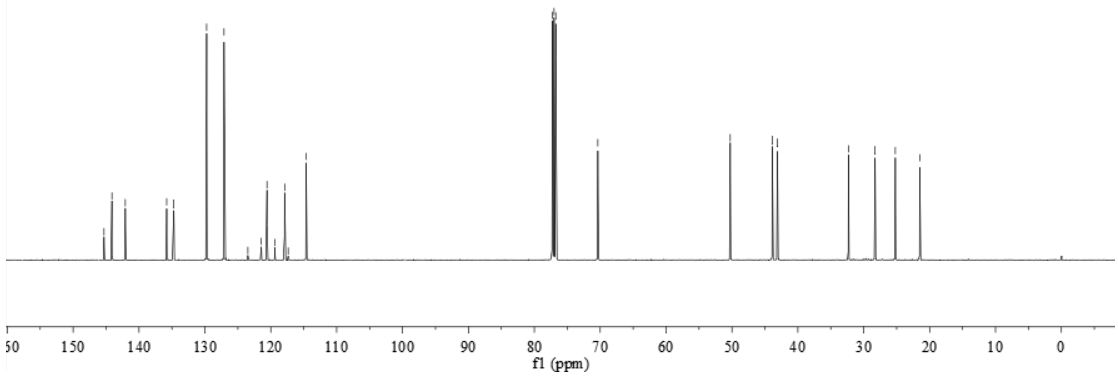
3g

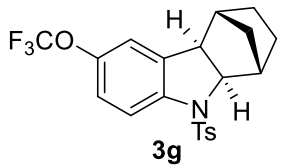
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



3g

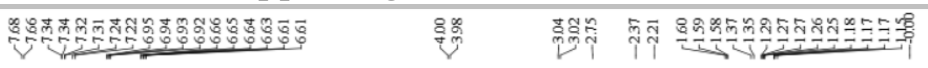
^{13}C NMR (101 MHz, $CDCl_3$, 298 K)

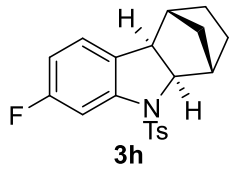




3g

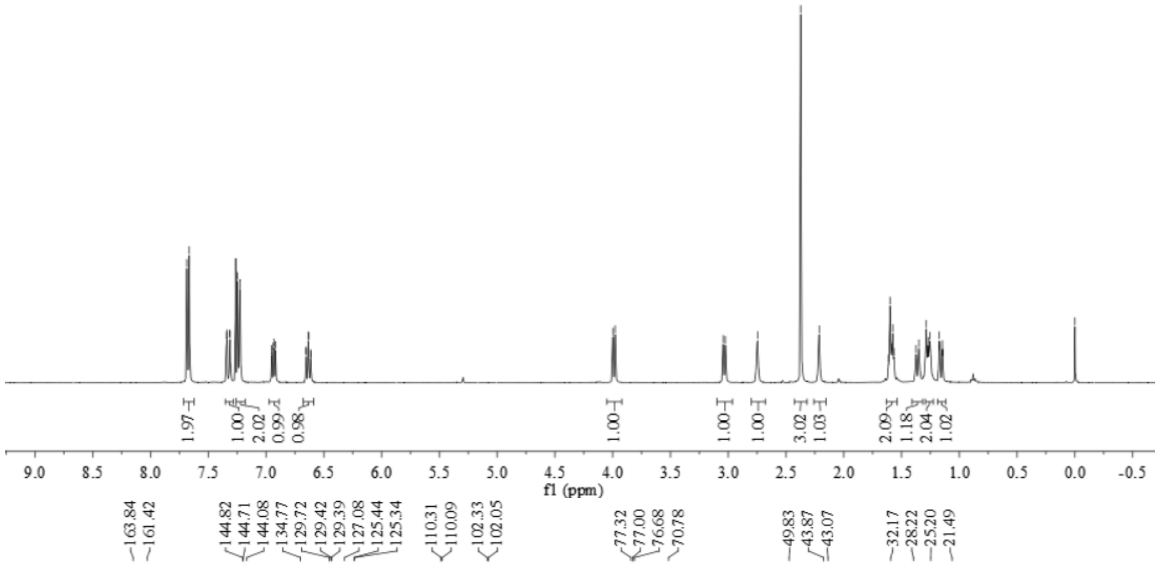
^{19}F NMR (376 MHz, $CDCl_3$, 298 K)

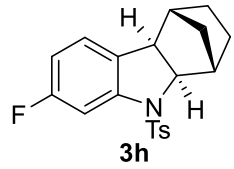




3h

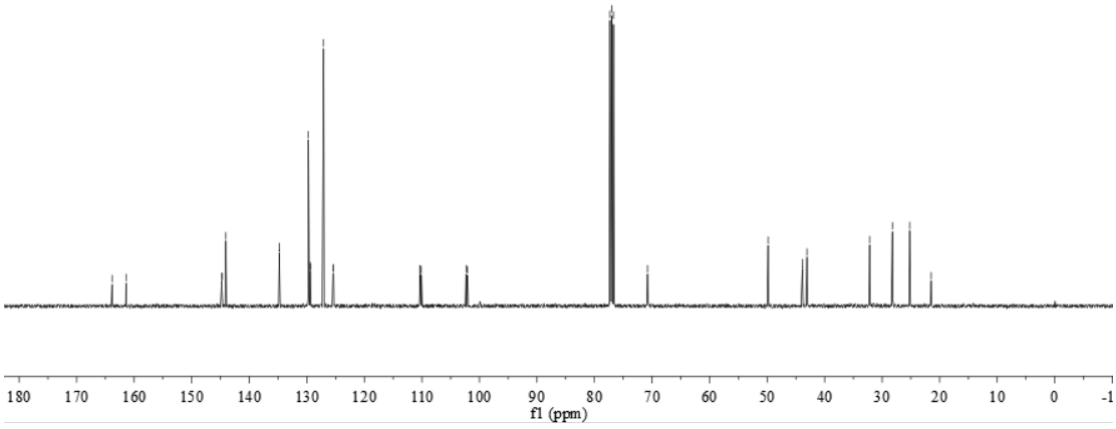
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

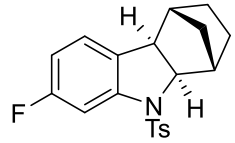




3h

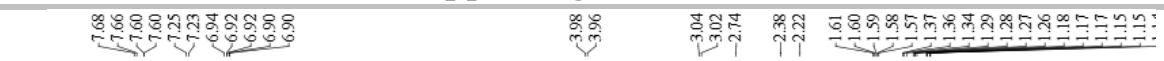
^{13}C NMR (101 MHz, $CDCl_3$, 298 K)

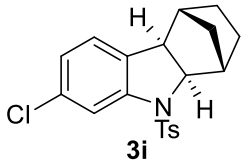




3h

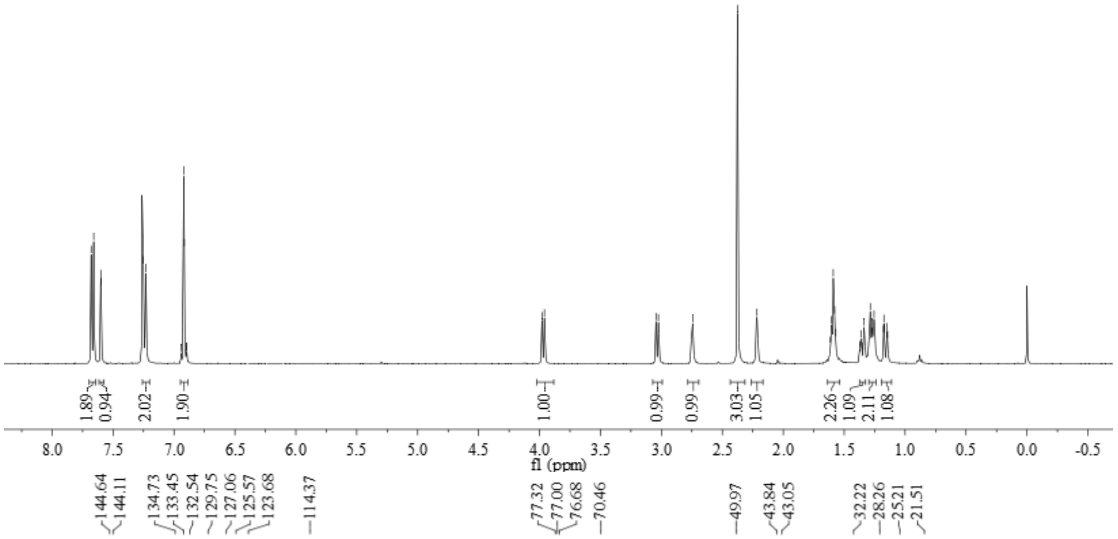
^{19}F NMR (376 MHz, $CDCl_3$, 298 K)

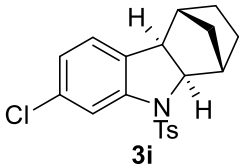




3i

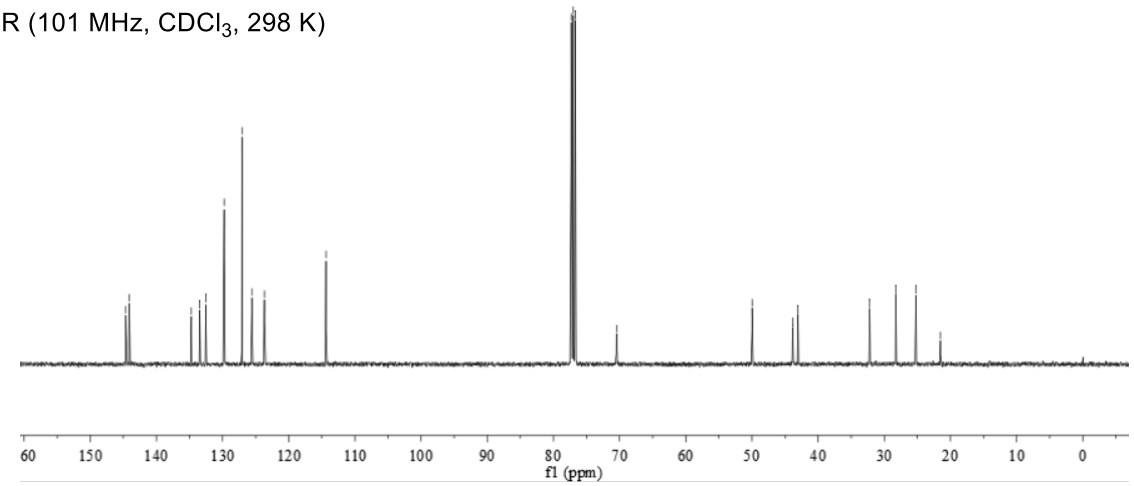
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

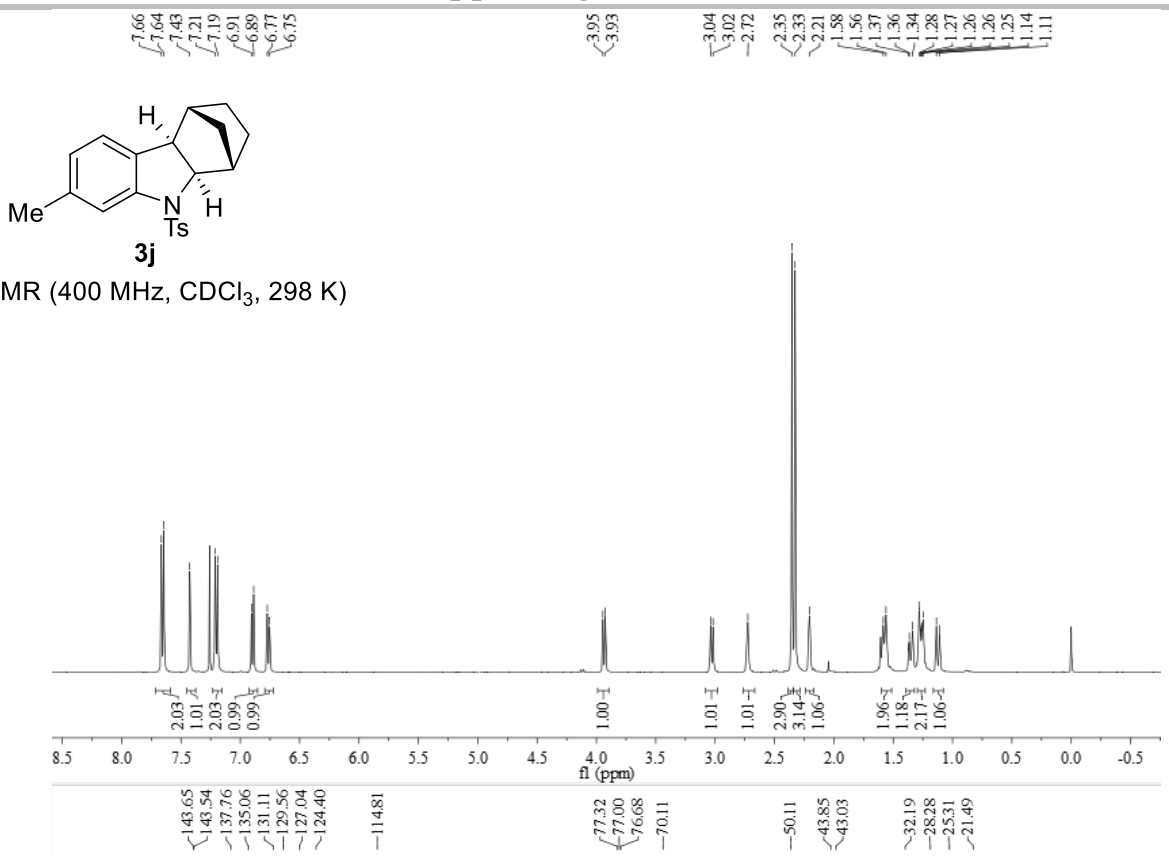




3i

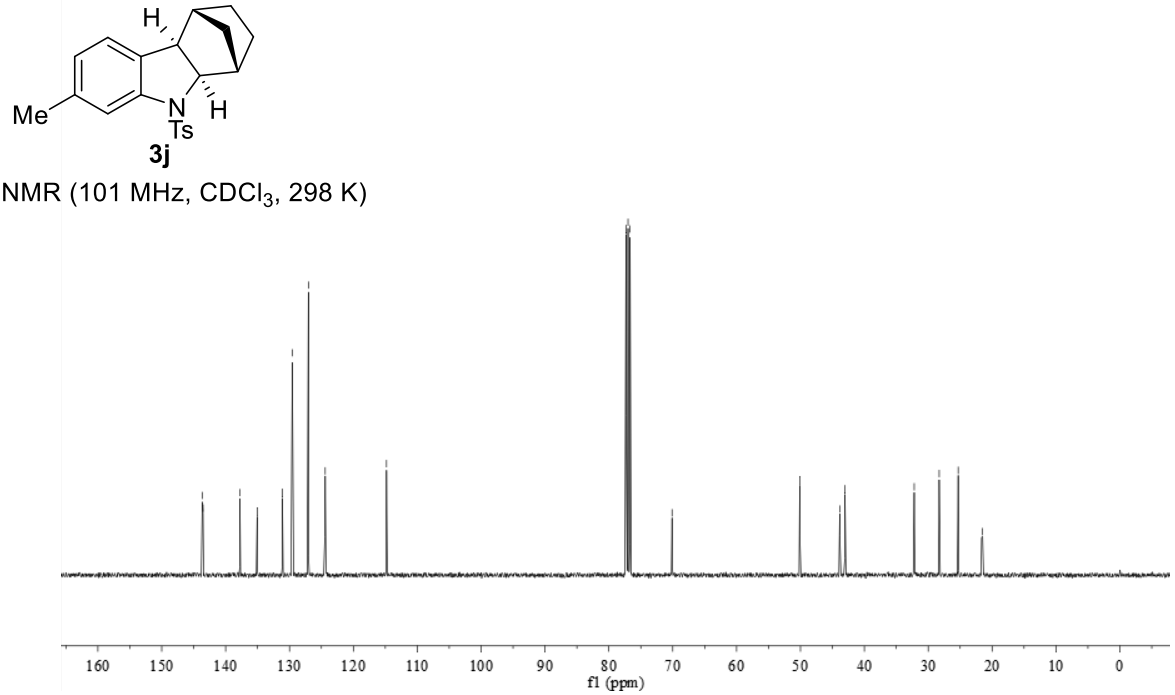
^{13}C NMR (101 MHz, $CDCl_3$, 298 K)





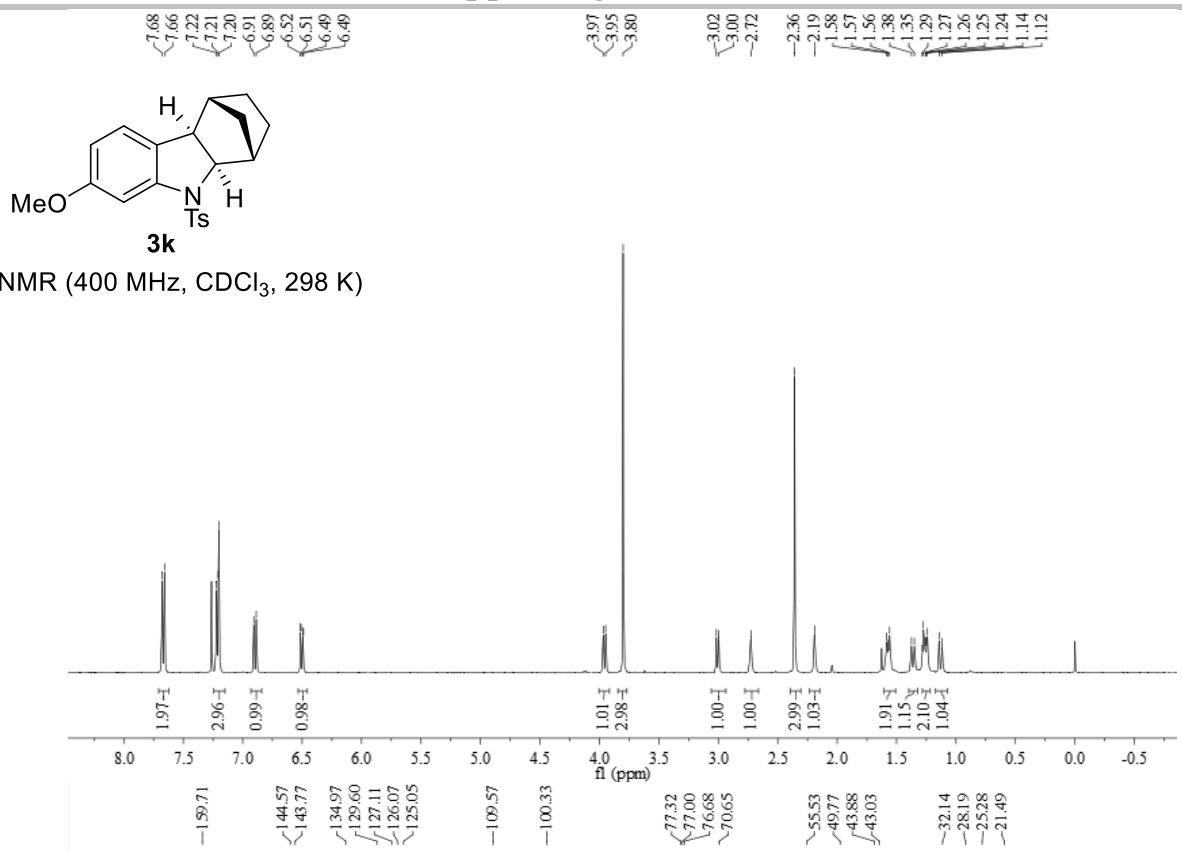
3j

^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



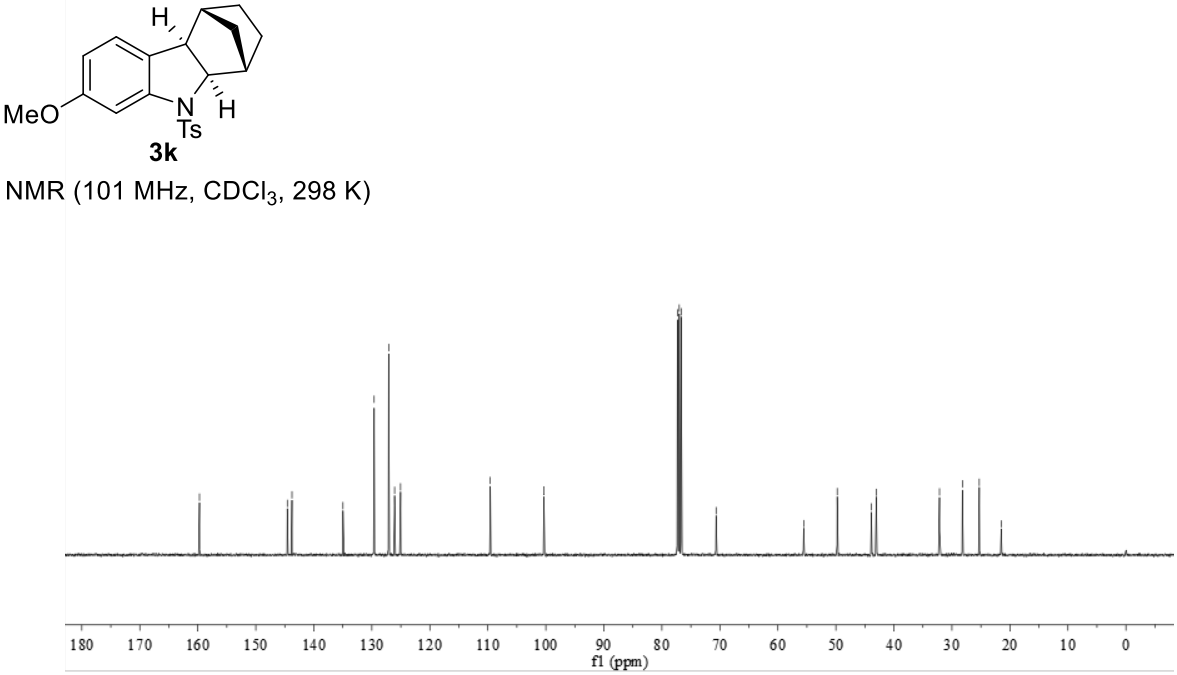
3j

^{13}C NMR (101 MHz, $CDCl_3$, 298 K)



3k

^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

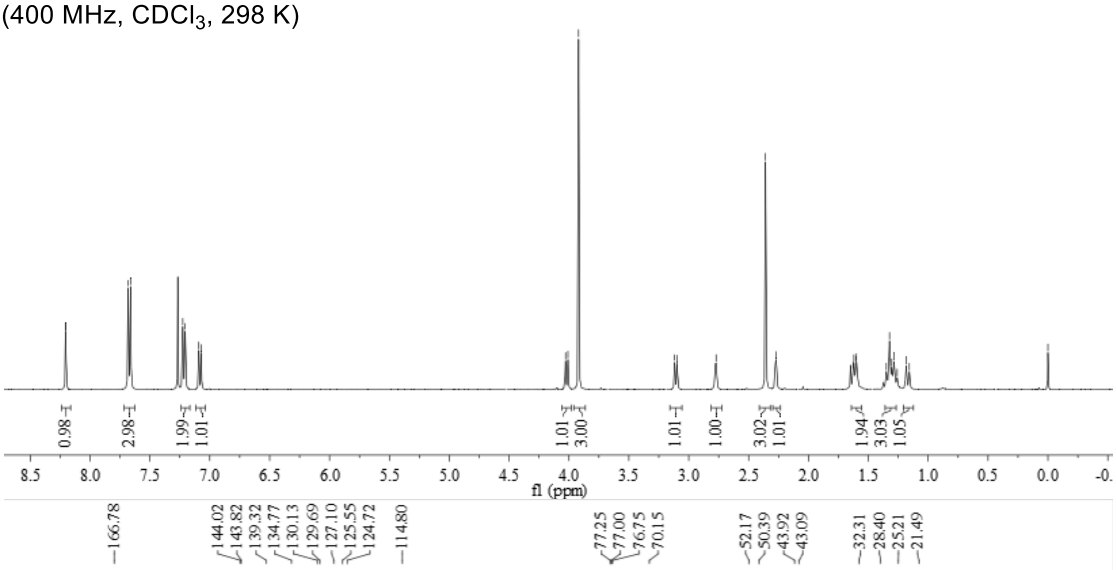


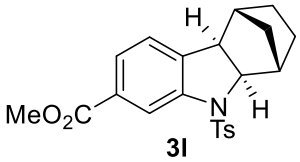
3k

^{13}C NMR (101 MHz, $CDCl_3$, 298 K)

3l

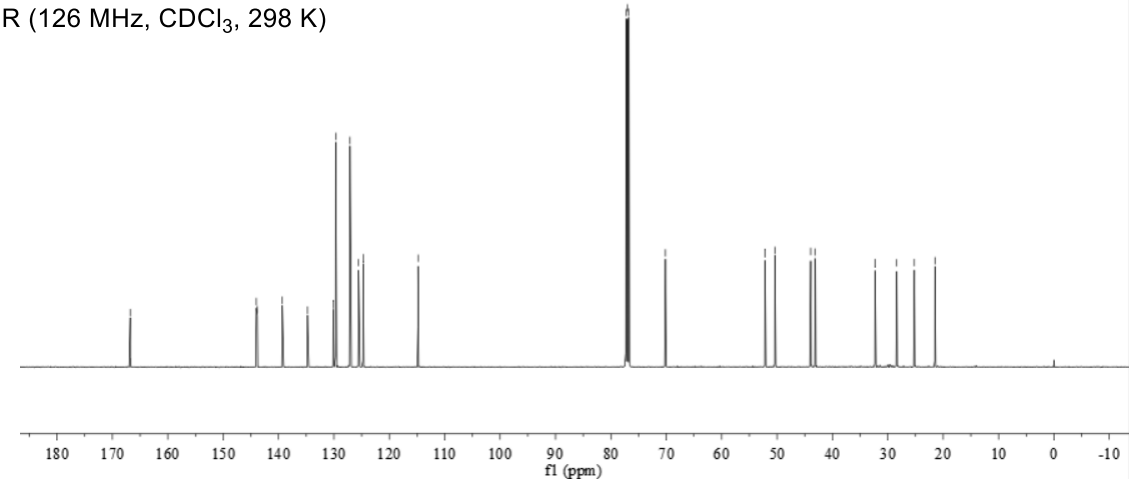
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

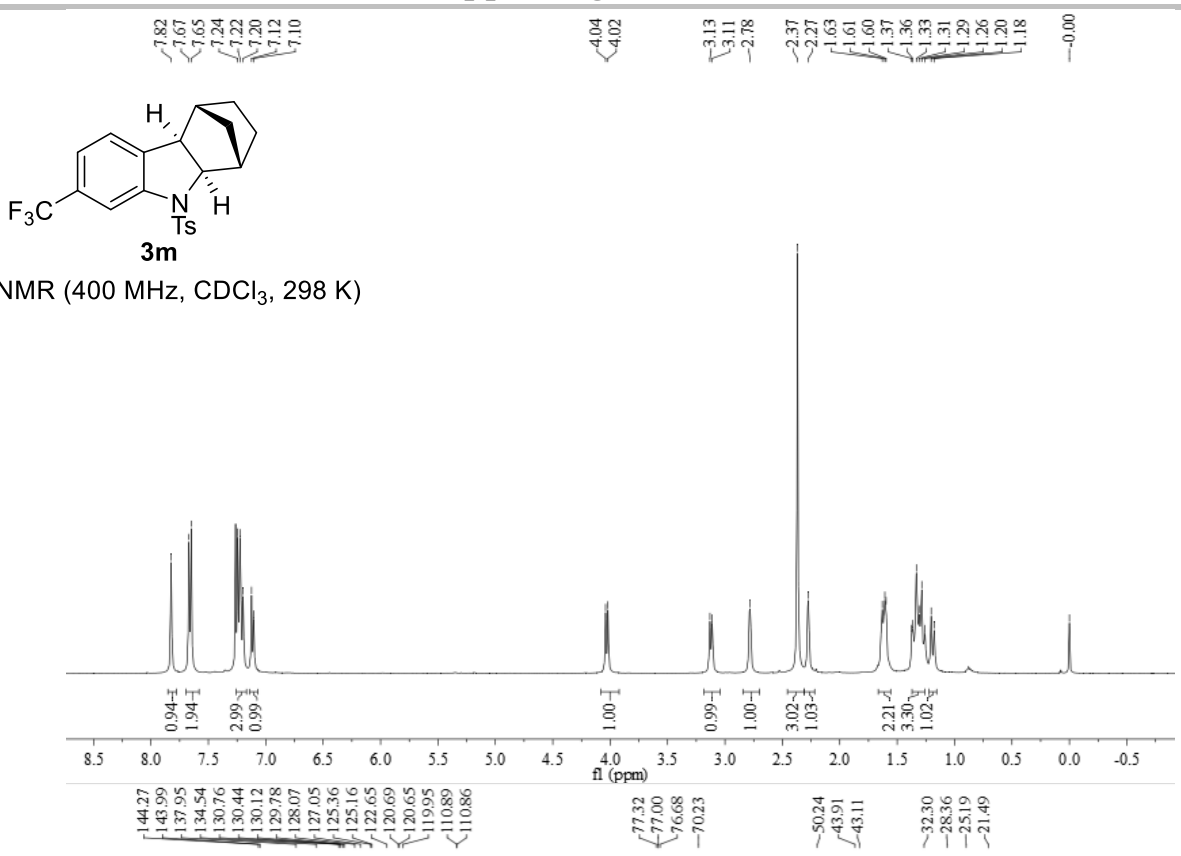




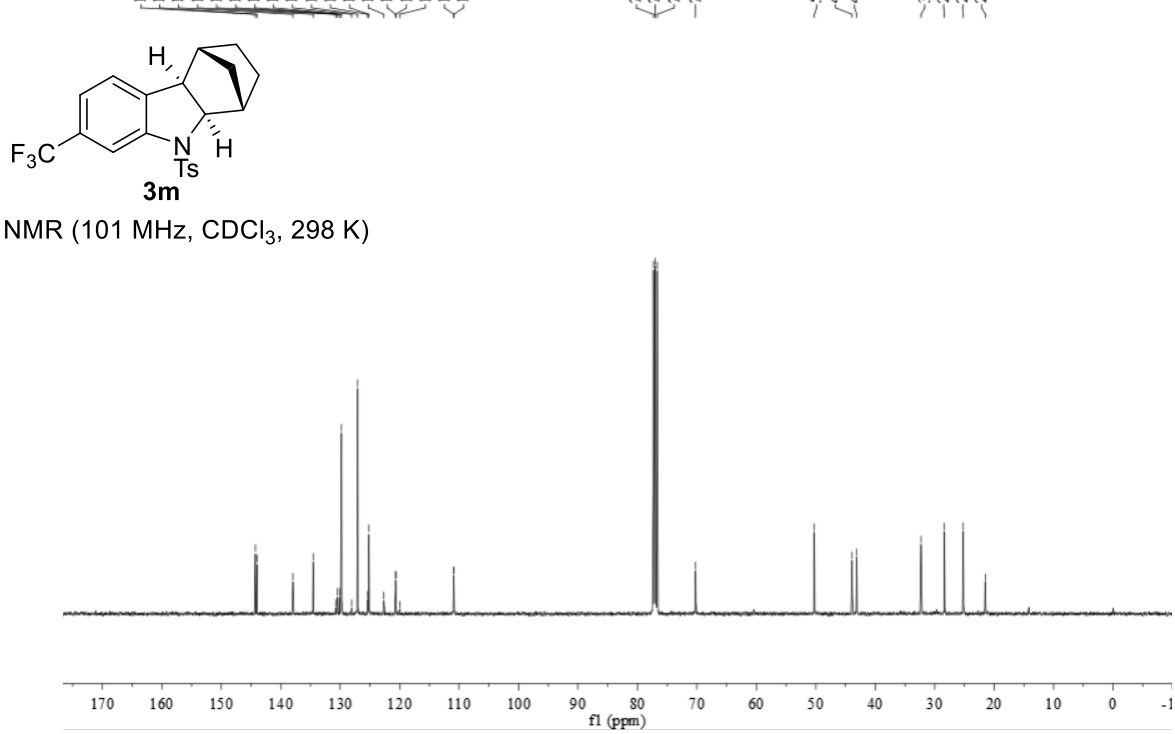
3l

^{13}C NMR (126 MHz, $CDCl_3$, 298 K)

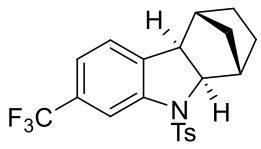




^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

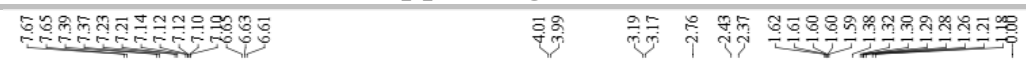


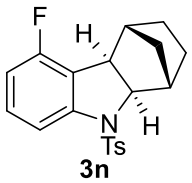
^{13}C NMR (101 MHz, $CDCl_3$, 298 K)



3m

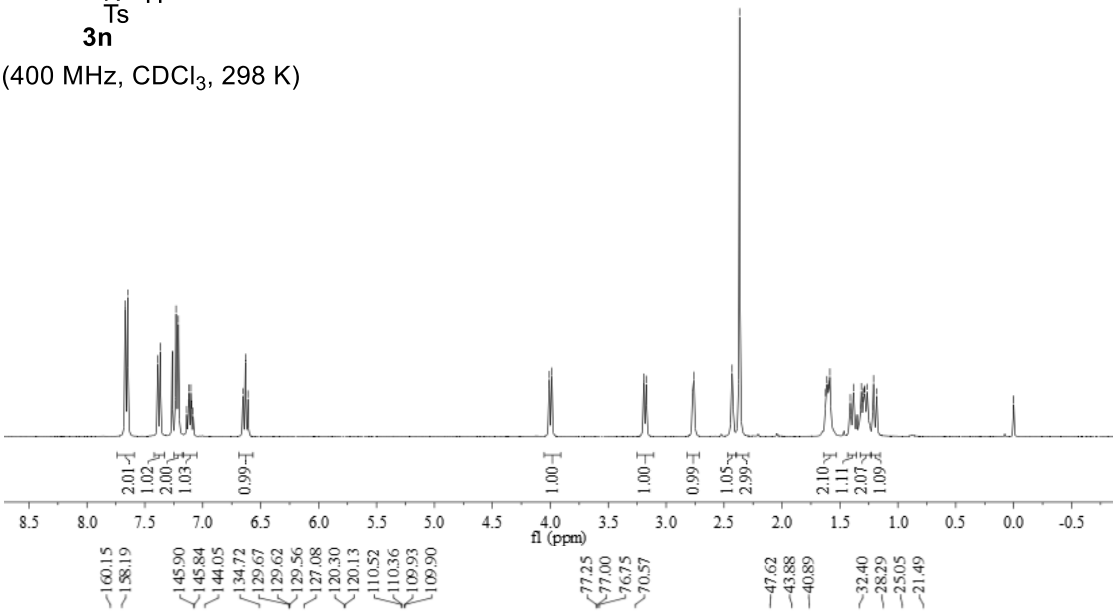
^{19}F NMR (376 MHz, $CDCl_3$, 298 K)

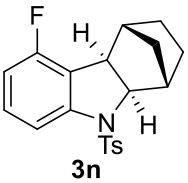




3n

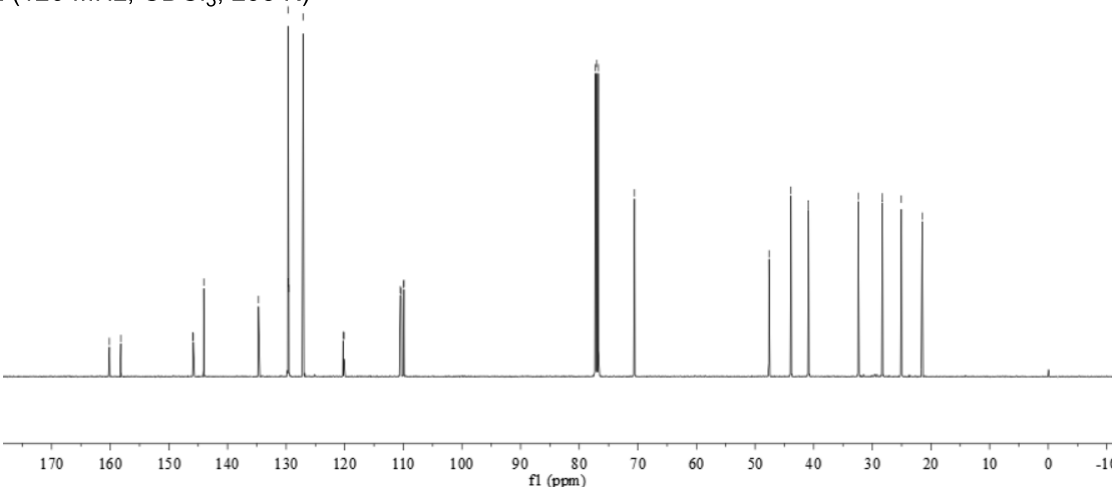
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

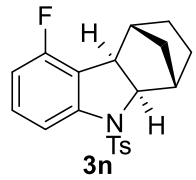




3n

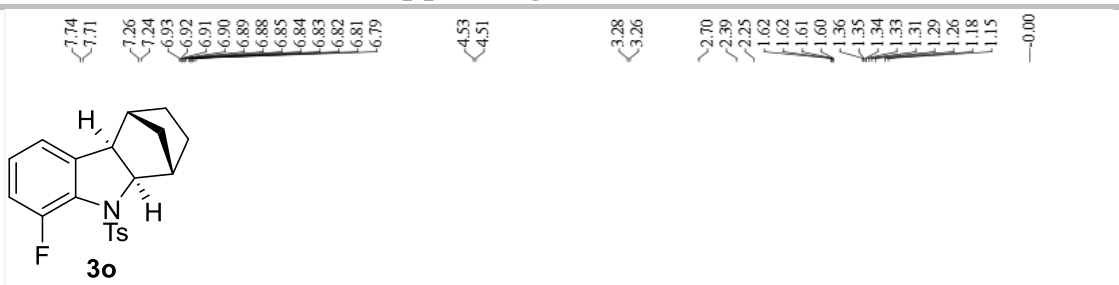
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)





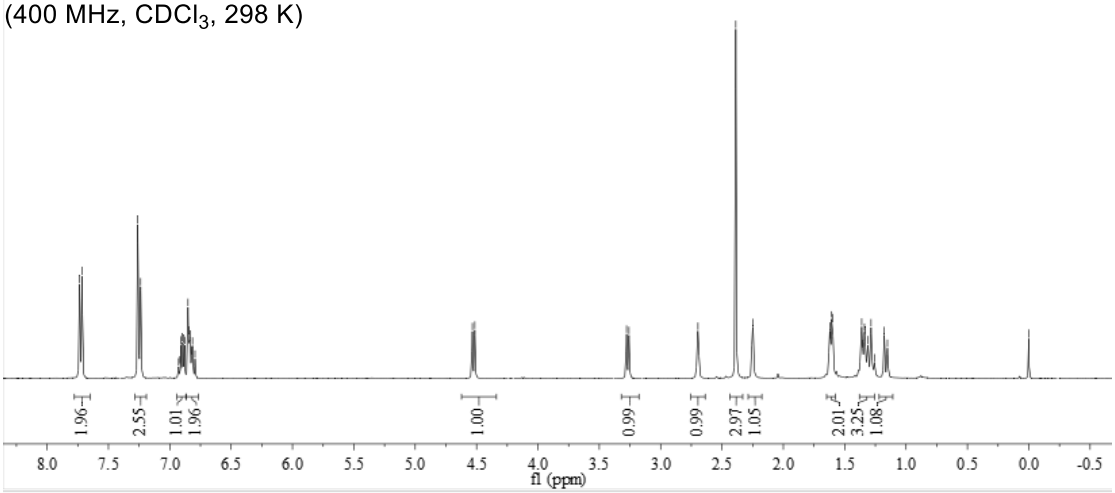
3n

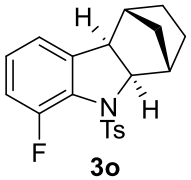
^{19}F NMR (376 MHz, $CDCl_3$, 298 K)



3o

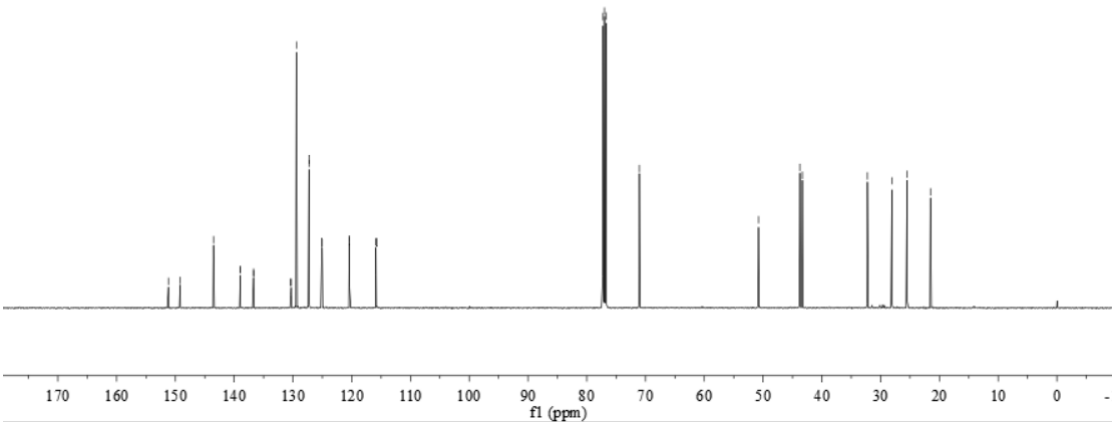
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

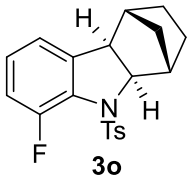




3o

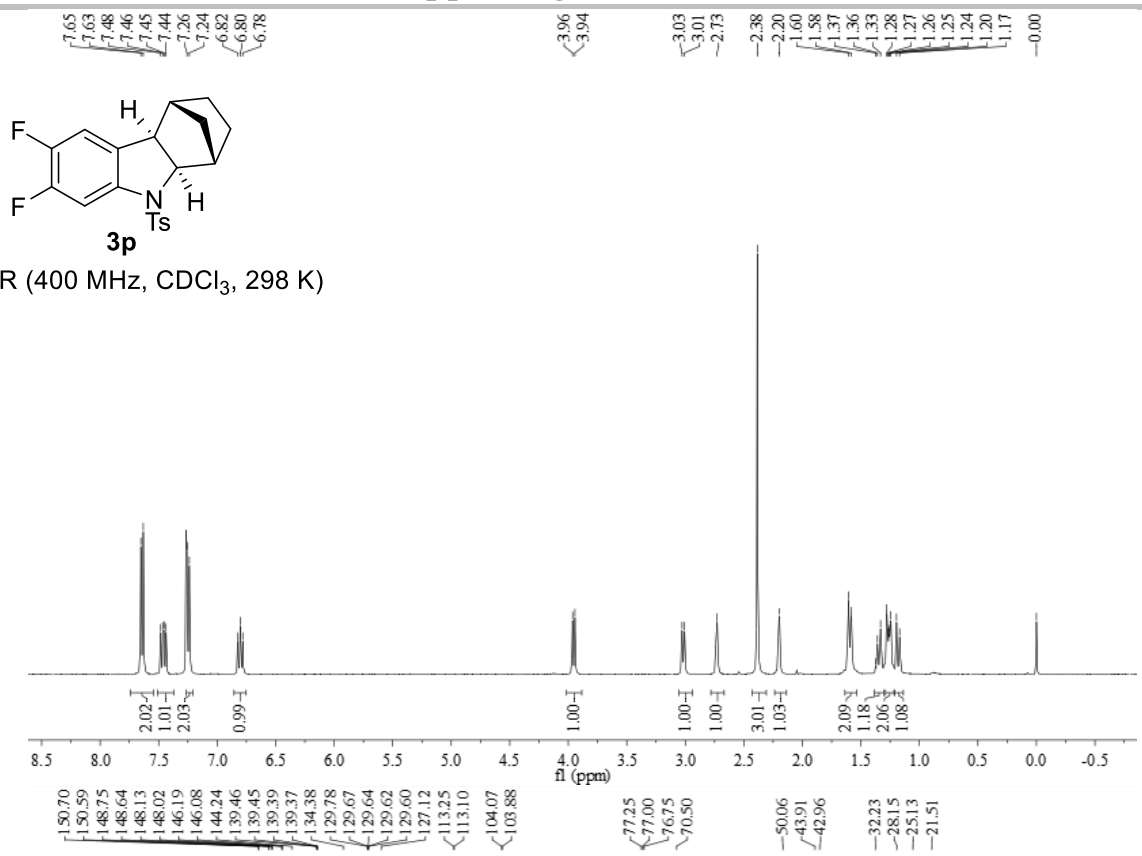
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)



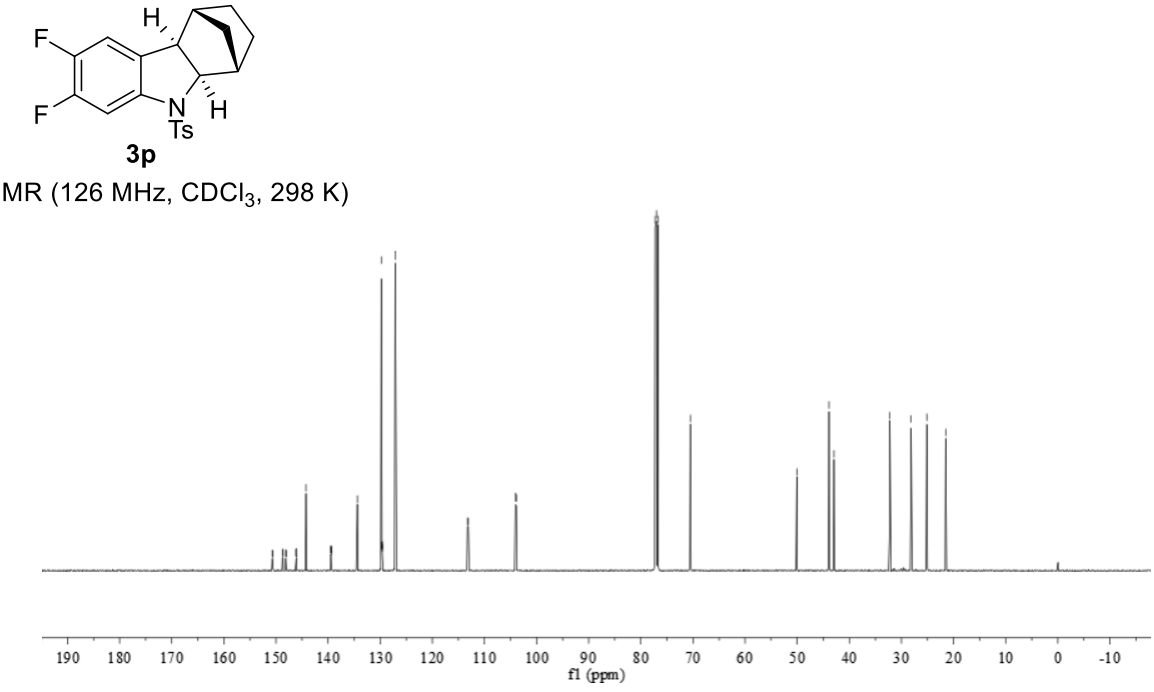


3o

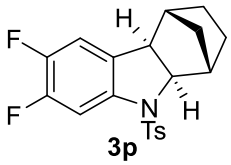
^{19}F NMR (376 MHz, $CDCl_3$, 298 K)



^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

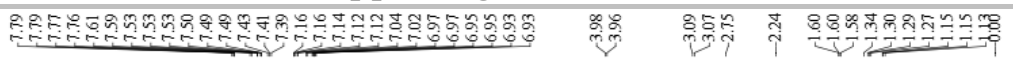


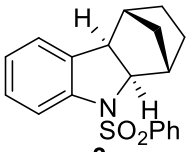
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)



3p

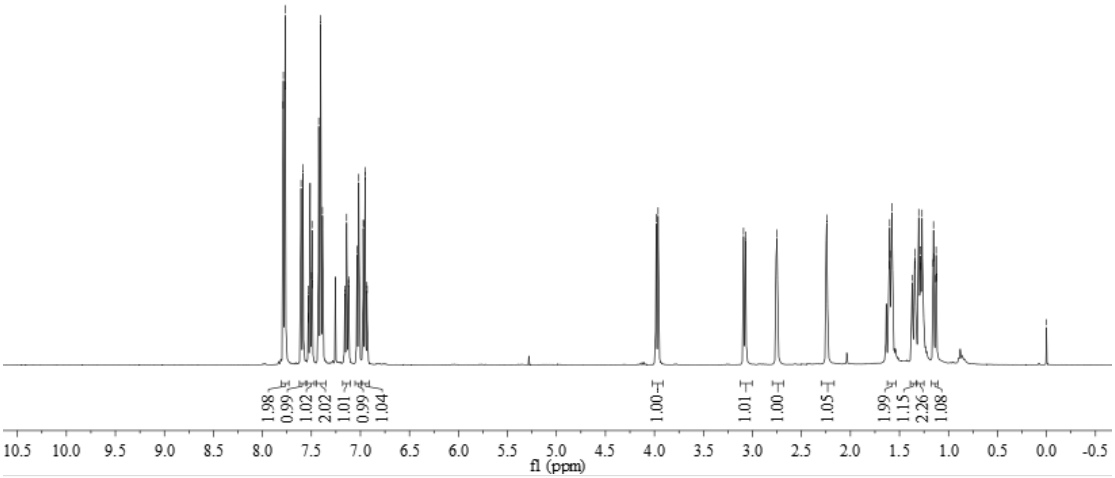
^{19}F NMR (376 MHz, $CDCl_3$, 298 K)

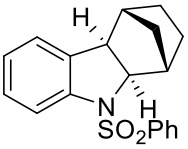




3q

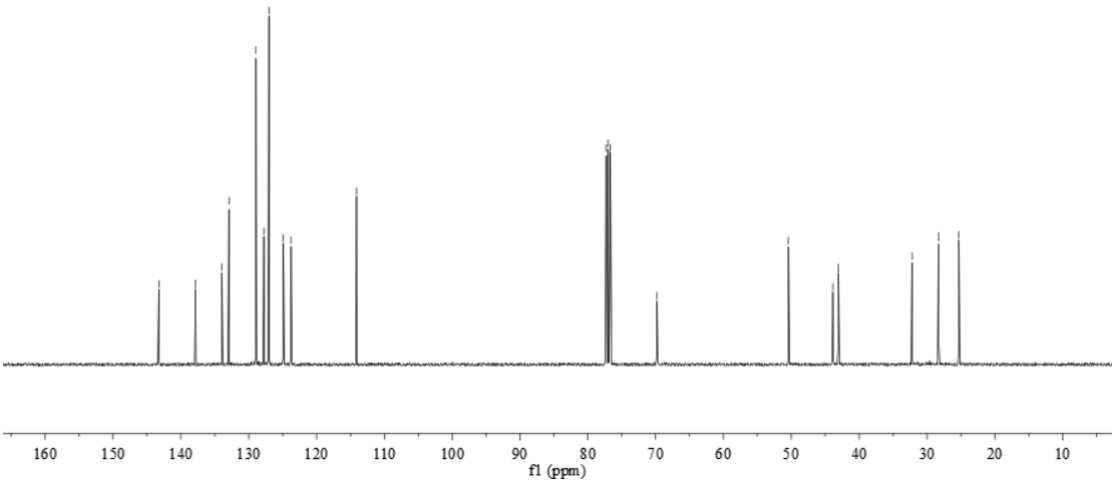
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

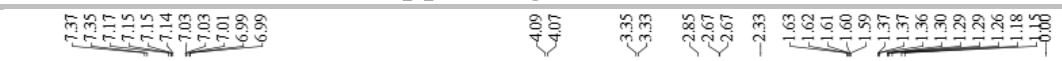


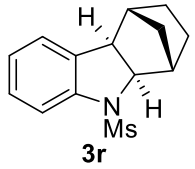


3q

^{13}C NMR (101 MHz, $CDCl_3$, 298 K)

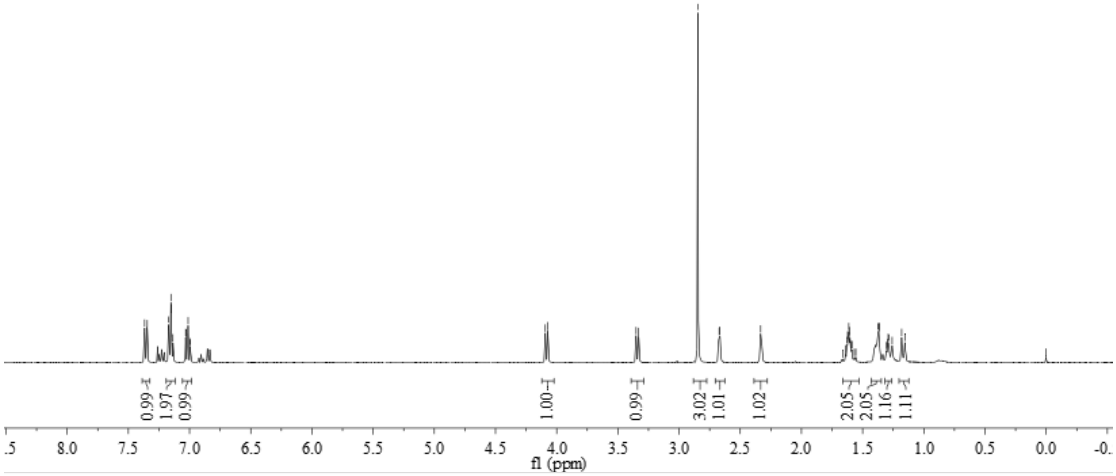


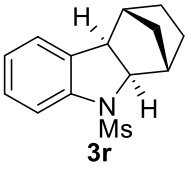




3r

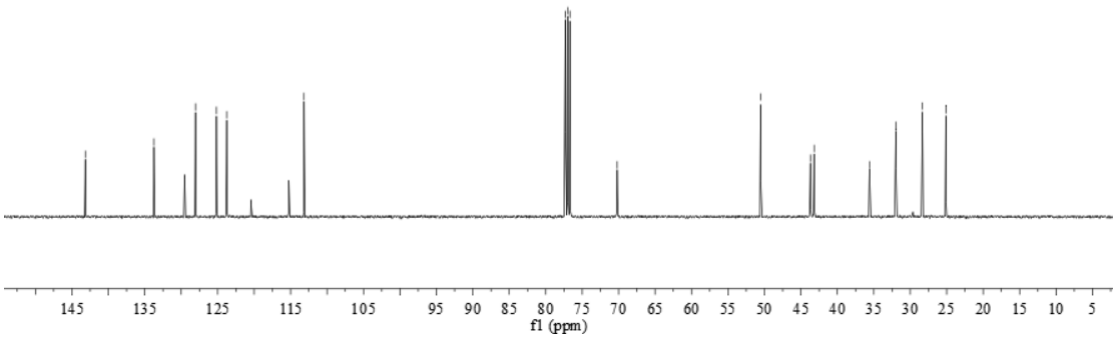
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

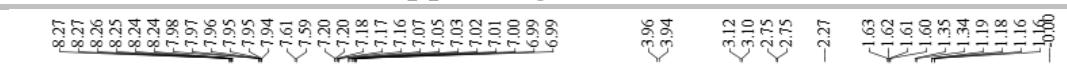


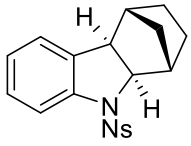


3r

^{13}C NMR (101 MHz, $CDCl_3$, 298 K)

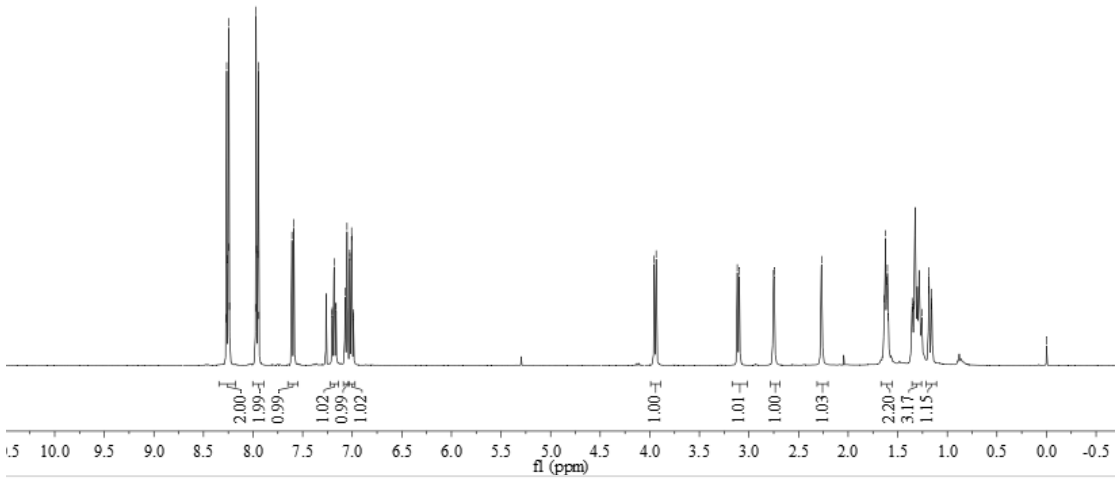


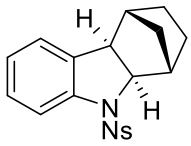




3s

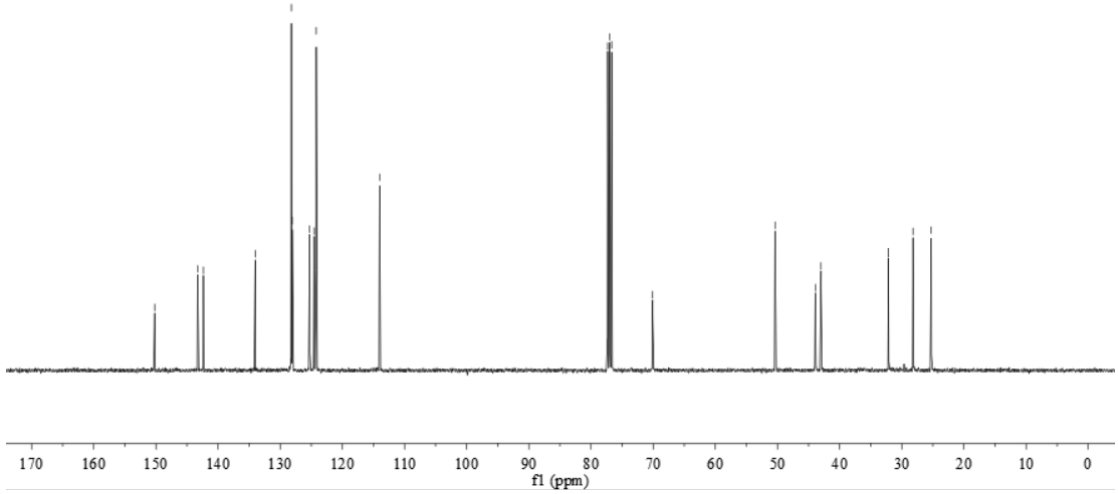
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)





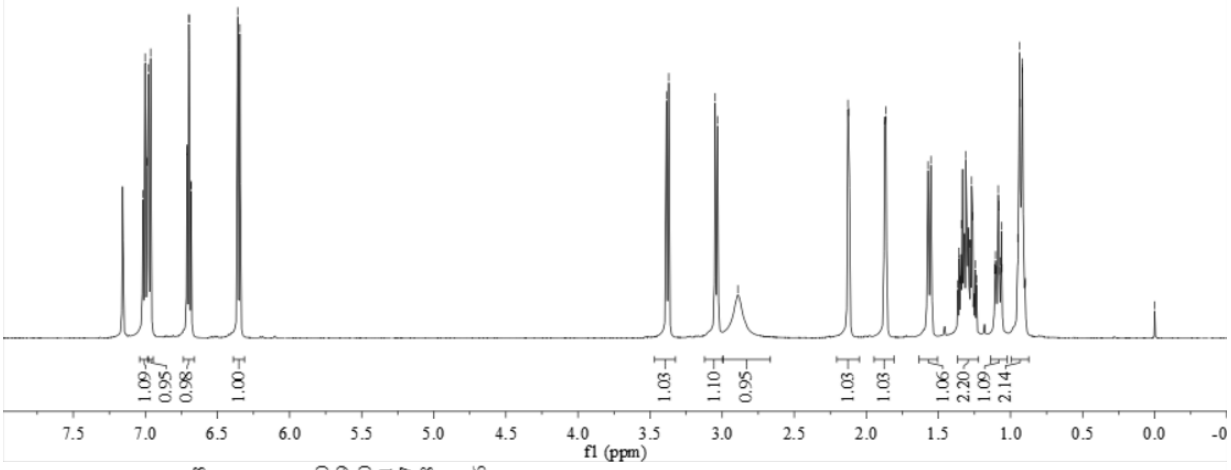
3s

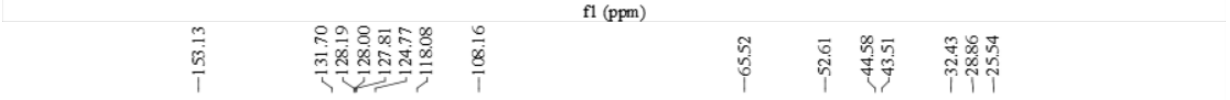
^{13}C NMR (101 MHz, $CDCl_3$, 298 K)



3t

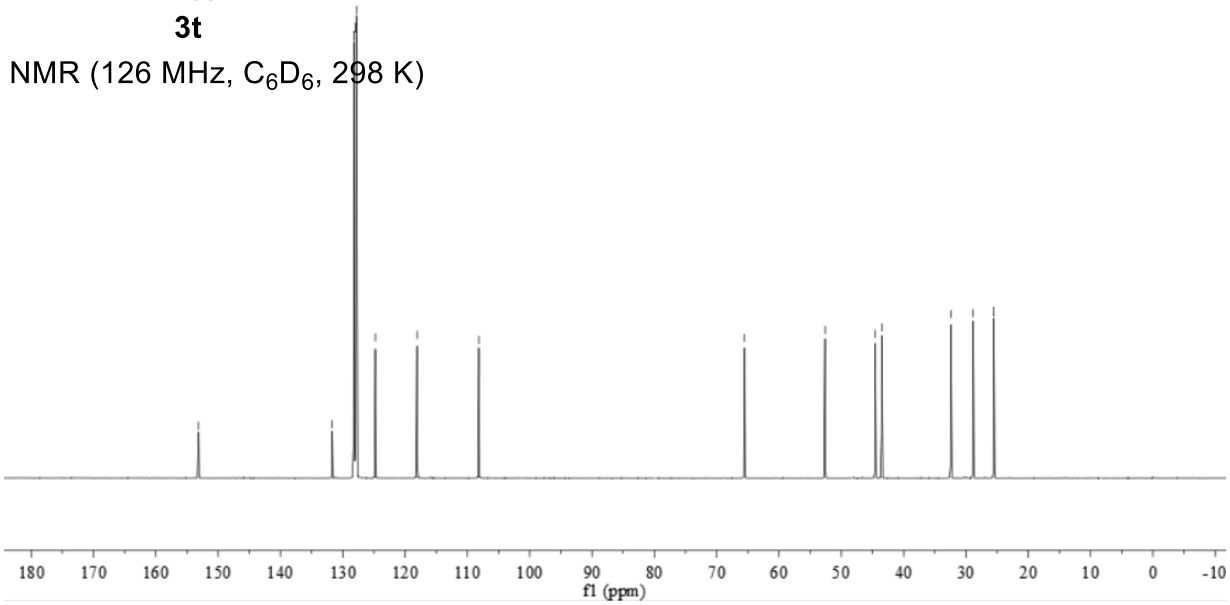
^{1}H NMR (500 MHz, C_6D_6, 298 K)

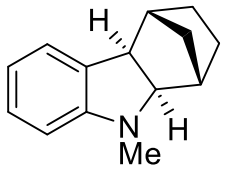




3t

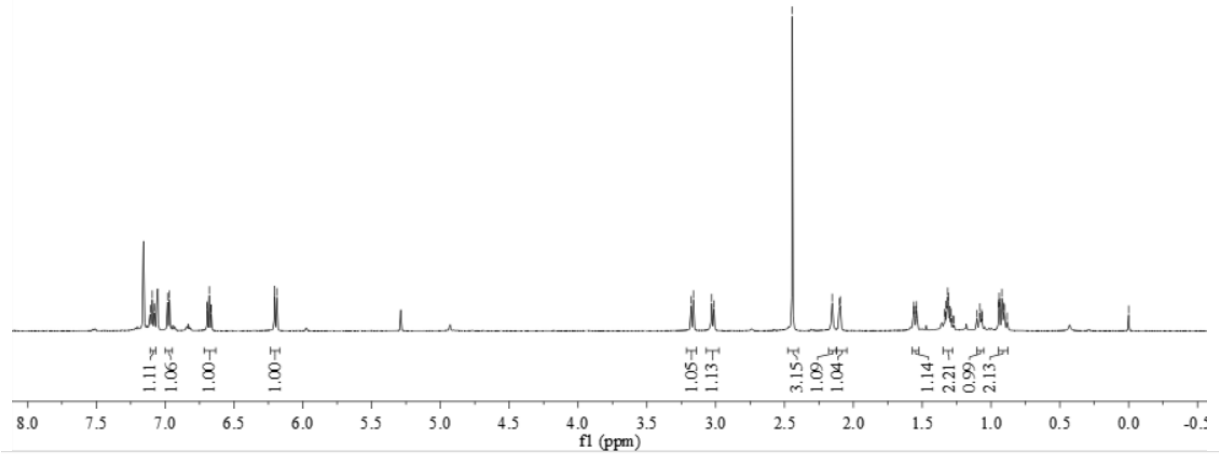
^{13}C NMR (126 MHz, C_6D_6, 298 K)

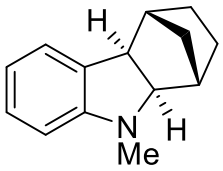




3u

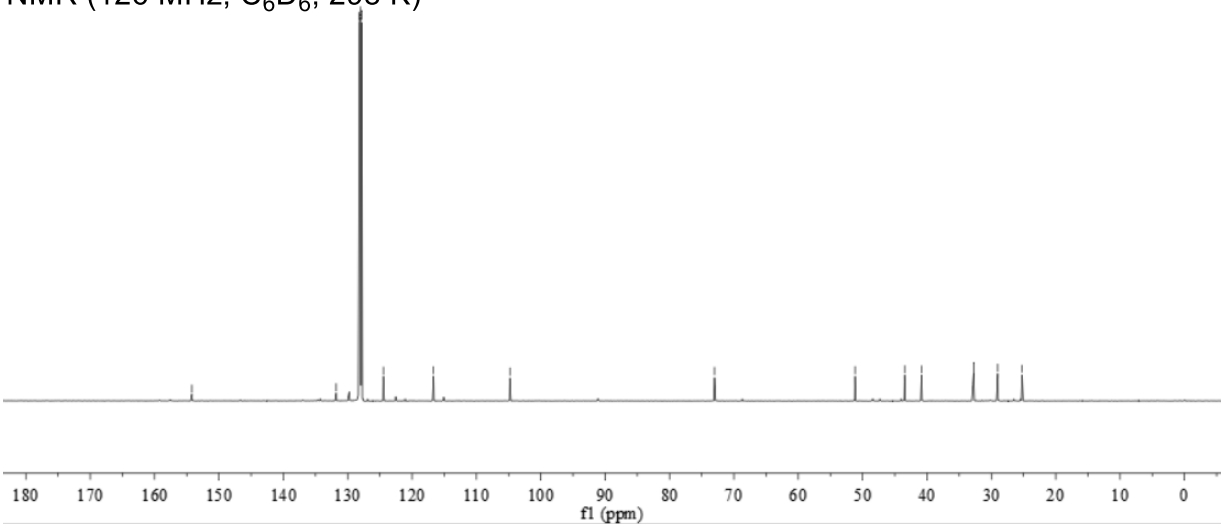
^{1}H NMR (500 MHz, C_6D_6, 298 K)





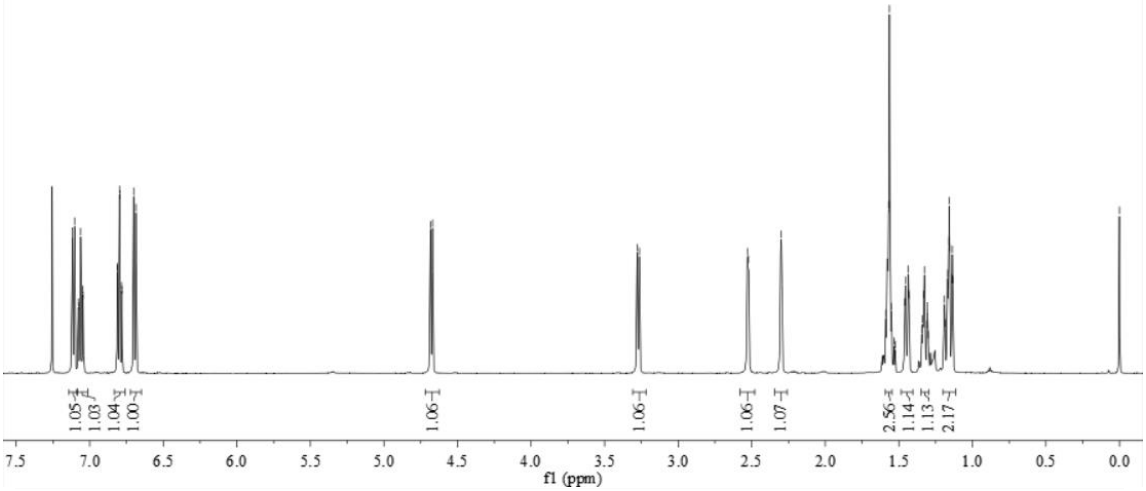
3u

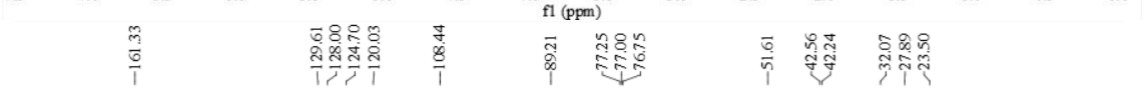
^{13}C NMR (126 MHz, C_6D_6, 298 K)

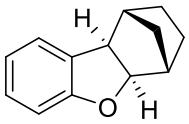


5a

^{1}H NMR (500 MHz, $CDCl_3$, 298 K)

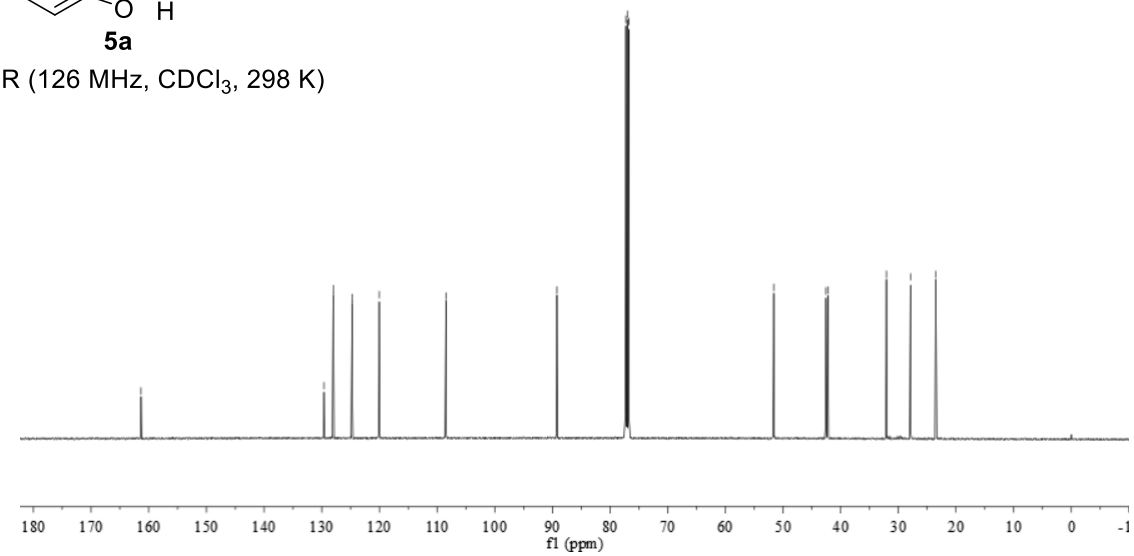






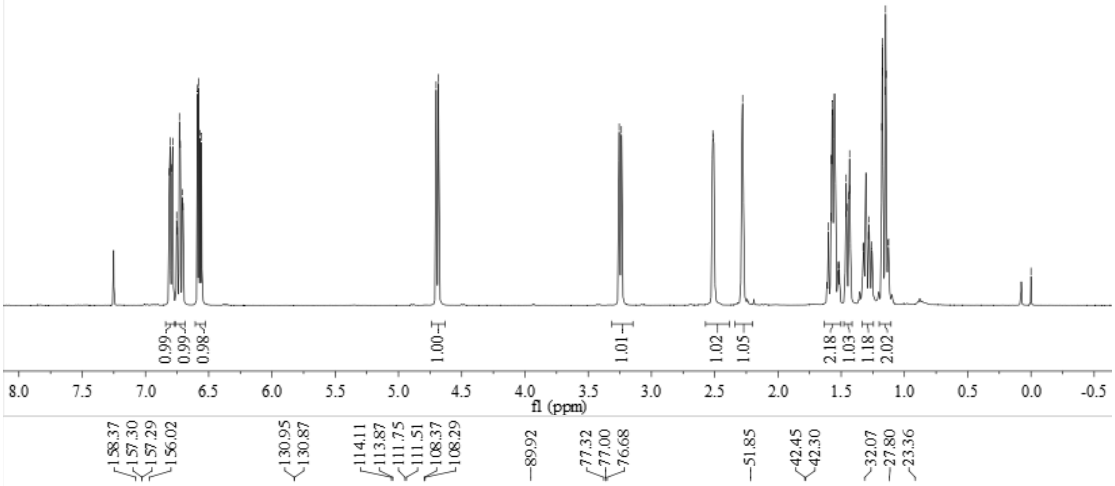
5a

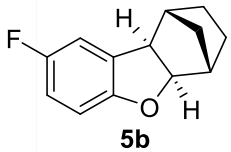
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)



5b

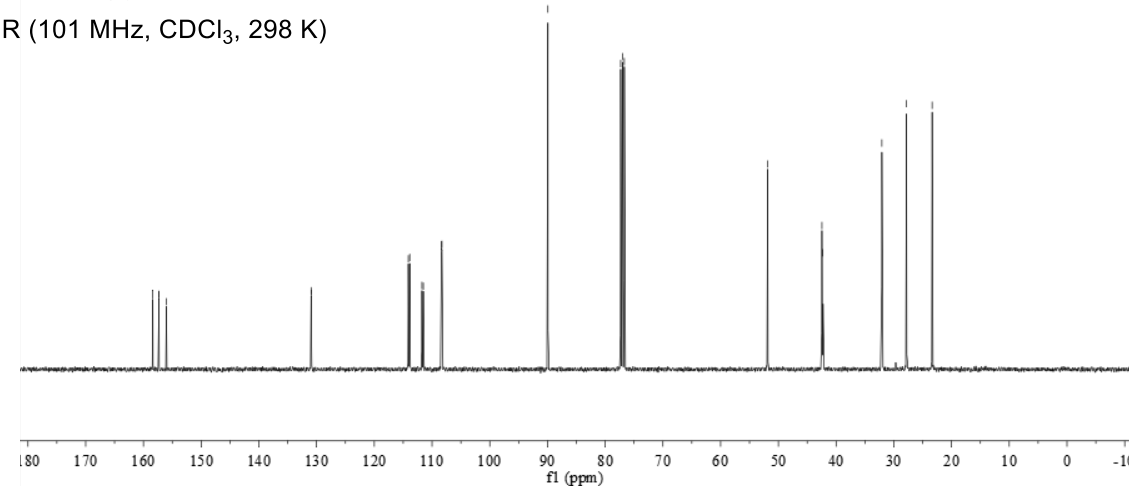
^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

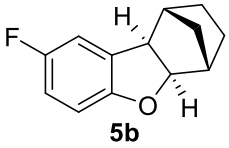




5b

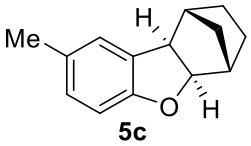
^{13}C NMR (101 MHz, $CDCl_3$, 298 K)





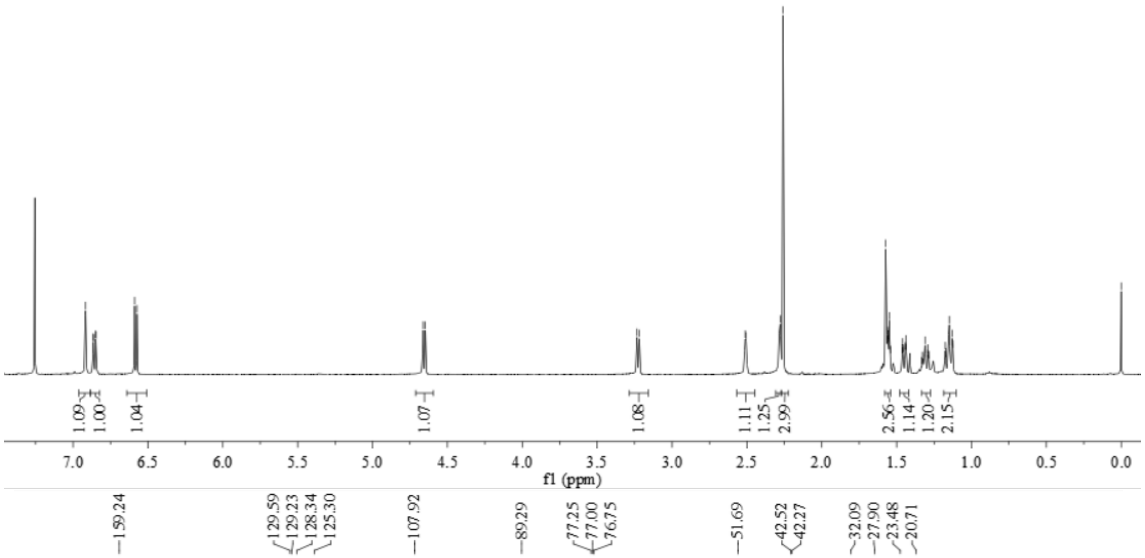
5b

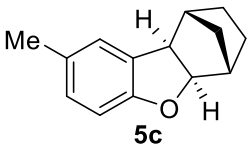
^{19}F NMR (376 MHz, $CDCl_3$, 298 K)



5c

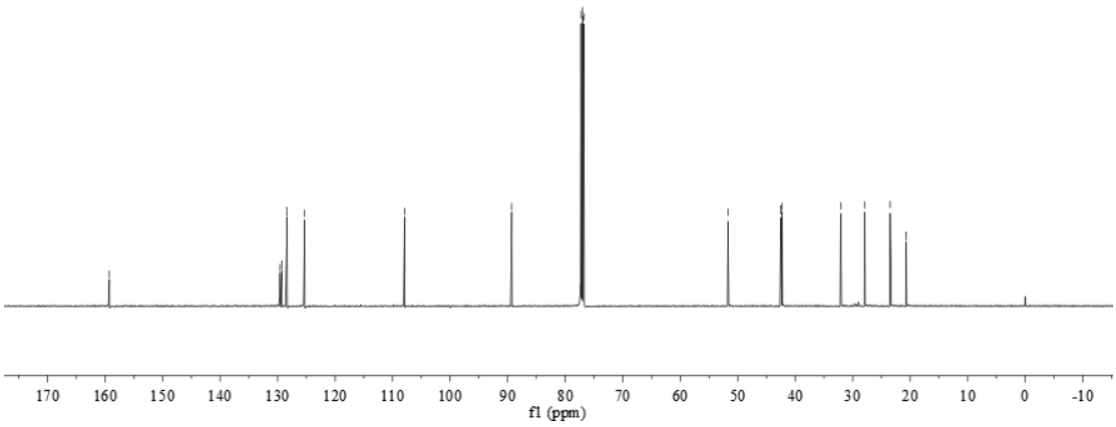
^{1}H NMR (500 MHz, $CDCl_3$, 298 K)

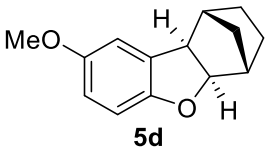




5c

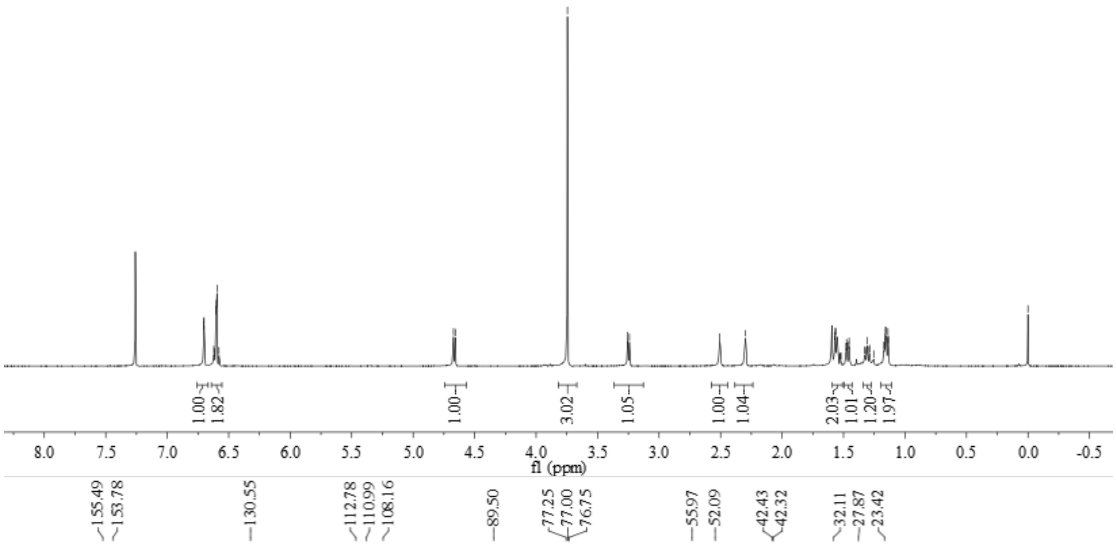
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)

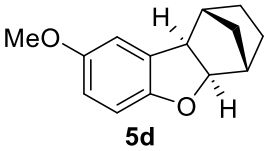




5d

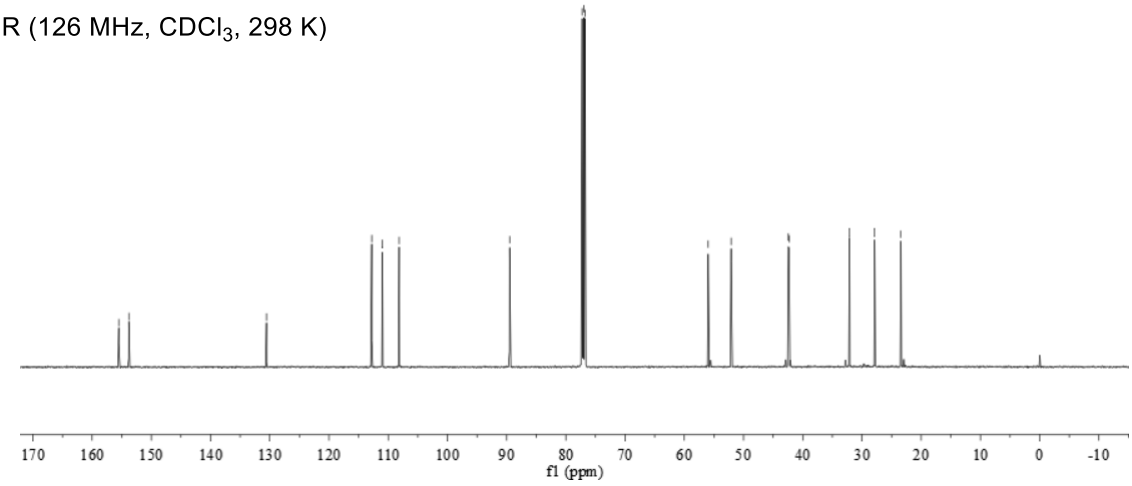
^{1}H NMR (500 MHz, $CDCl_3$, 298 K)

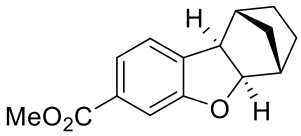




5d

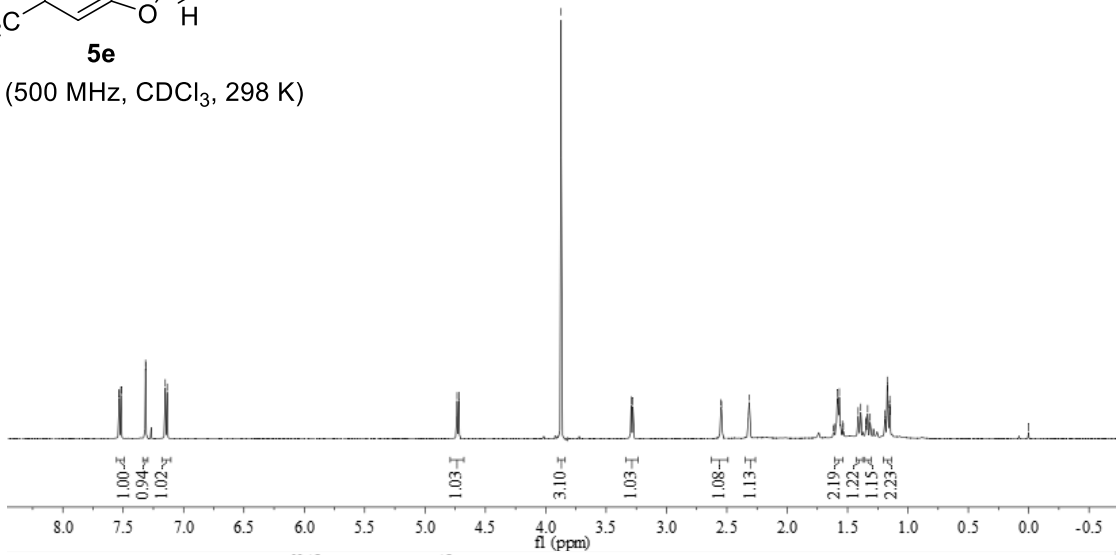
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)

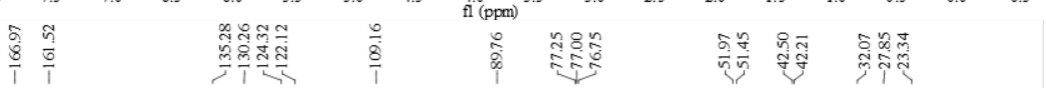


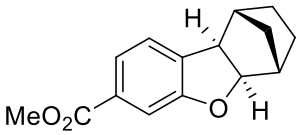


5e

^{1}H NMR (500 MHz, $CDCl_3$, 298 K)

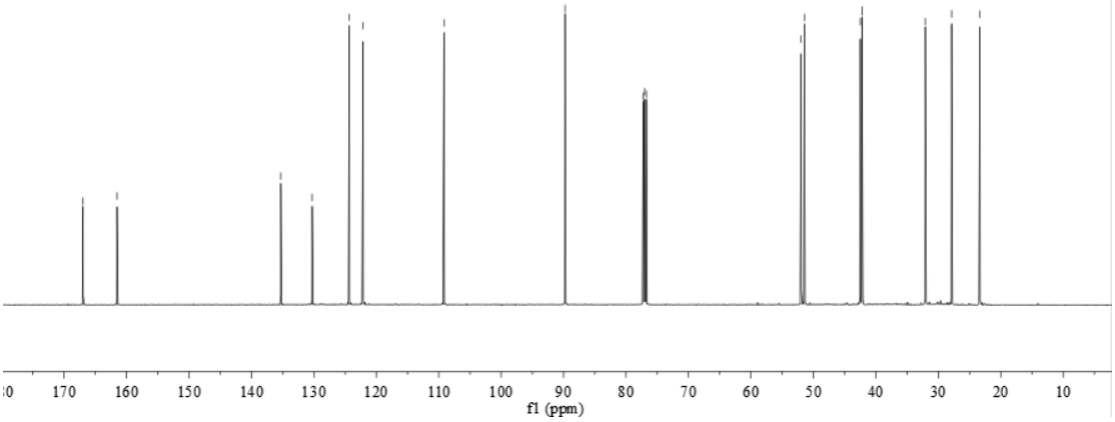


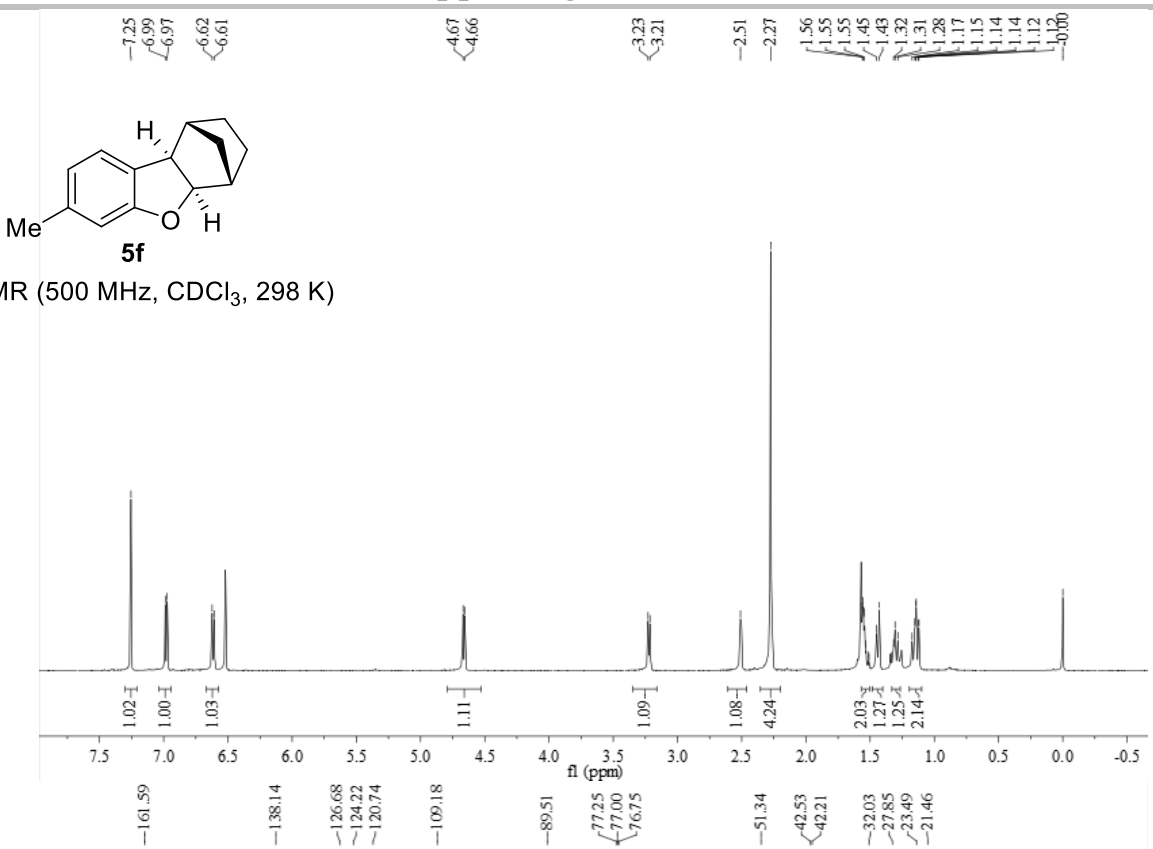




5e

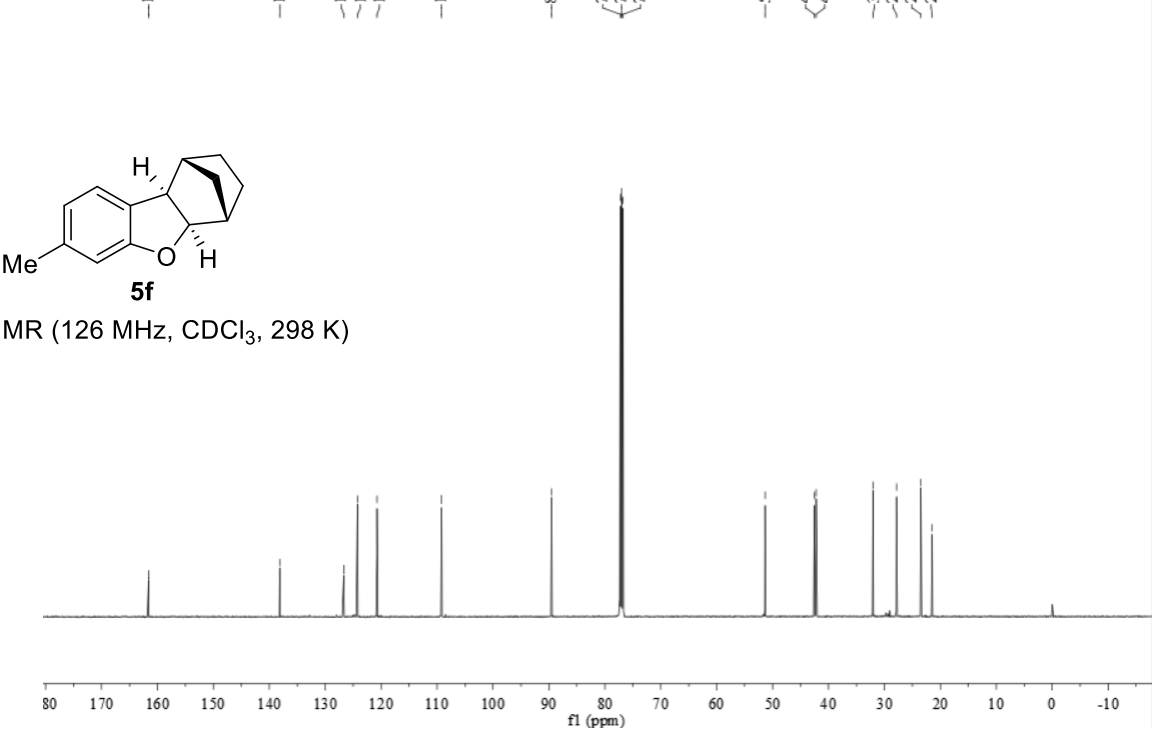
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)





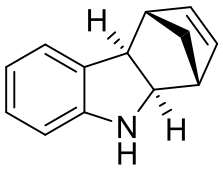
5f

^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



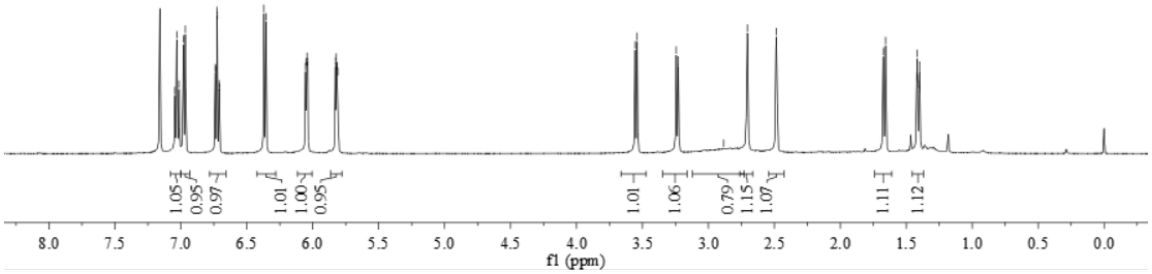
5f

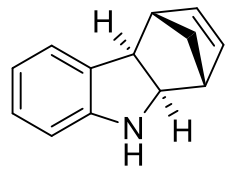
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)



7

^{1}H NMR (500 MHz, C_6D_6, 298 K)





7

^{13}C NMR (126 MHz, C_6D_6, 298 K)