Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Facile access to benzofuran-fused tetrahydropyridines via catalytic asymmetric [4 + 2] cycloaddition of aurone-derived 1-azadienes with 3-vinylindoles

Wai Lean Koay,[ab] Guang-Jian Mei,*[a] and Yixin Lu*[abc]

a. Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543, Singapore. E-mail: mgjx1x2x3@163.com; chmlyx@nus.edu.sg.

b. NUS Graduate School for Integrative Sciences & Engineering (NGS), National University of Singapore, University Hall, Tan Chin Tuan Wing #04-02, 21 Lower Kent Ridge Road, Singapore, 119077, Singapore

c. Joint School of National University of Singapore and Tianjin University, International Campus of Tianjin University, Binhai New City, Fuzhou, Fujian, 350207, China

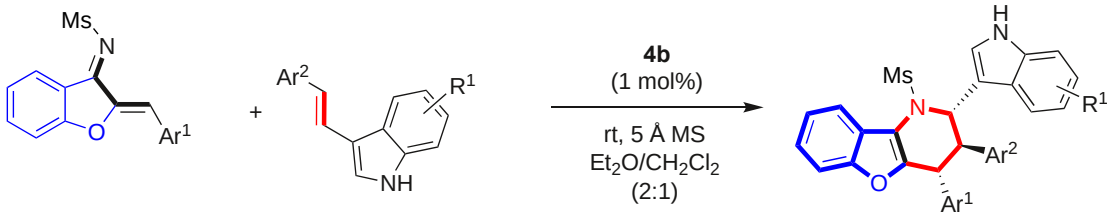
Supporting Information

A. General Information

Unless otherwise specified, all reactions were conducted under an inert atmosphere and anhydrous conditions. All the solvents were purified according to the standard procedures. All chemicals which are commercially available were employed without further purification. Thin-layer chromatography (TLC) was performed on silica gel plates (60F-254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (200–300 mesh). ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature in $CDCl_3$ on a Bruker AMX500 (500 MHz) or AMX400 (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm). The data are reported as follows: for ^{1}H NMR, chemical shift in ppm from tetramethylsilane with the solvent as internal standard ($CDCl_3$ δ 7.26 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of non-equivalent resonances), integration; for ^{13}C NMR, chemical shift in ppm from tetramethylsilane with the solvent as internal indicator ($CDCl_3$ δ 77.1 ppm), multiplicity with respect to protons. All high-resolution mass spectra were performed by the MS service at the chemistry department, National University of Singapore, and were obtained on a Finnigan/MAT 95XL-T spectrometer to be given in m/z. Optical rotations were measured using an Anton Paar MCP-100 digital polarimeter using a 1 cm glass cell. Enantiomeric excesses were determined by HPLC analysis on a chiral stationary phase using CHIRALPAK® columns (IE, ID & IC) eluting with hexane/isopropanol mixtures as indicated. Aurone-derived 1-azadienes **1**[1] and 3-vinylindoles **2**[2] were synthesized according to literature-reported procedures respectively.

B. Representative Procedures

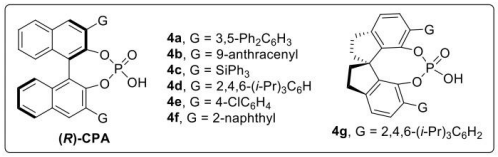
General Procedure for chiral phosphoric acid catalyzed dearomative [3 + 2] cycloaddition reaction of *α*-naphthols with azoalkenes:



1 (0.1 mmol) **2** (0.18 mmol) **3**

To a stirring anhydrous Et_2O:CH_2Cl_2 (2:1) solution (1 ml) of aurone-derived 1-azadienes **1** (0.1 mmol) and 3-vinylindoles **2** (0.18 mmol) was added 5Å MS (100 mg) and CPA **4b** (1 mol%) at rt. The reaction mixture was stirred until completion of reaction (as monitored by TLC). After which, the mixture was filtered and the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (Hexane: CH_2Cl_2 = 2:1) to afford cycloadducts **3**.

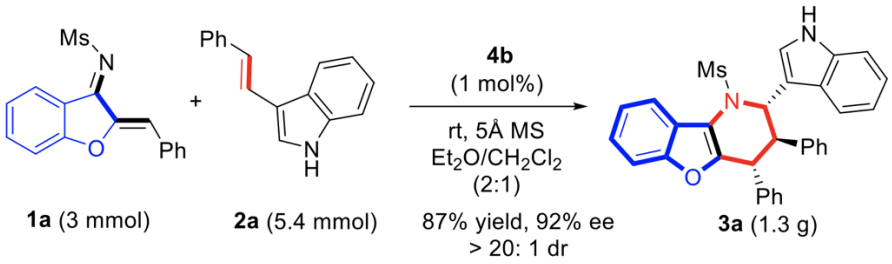
Table 1. Optimization of reaction conditions[a]



Entry	Cat.	Solvent	dr[b]	Yield (%)[c]	*ee* (%)[d]
1	**4a**	DCE	>20:1	90	72
2	**4b**	DCE	>20:1	95	72
3	**4c**	DCE	>20:1	45	3
4	**4d**	DCE	>20:1	72	46
5	**4e**	DCE	>20:1	99	34
6	**4f**	DCE	>20:1	98	46
7	**4g**	DCE	>20:1	97	61
8	**4b**	$CHCl_3$	>20:1	86	25
9	**4b**	CH_2Cl_2	>20:1	98	83
10	**4b**	toluene	>20:1	90	46
11	**4b**	Et_2O	>20:1	90	94
12[e]	**4b**	Et_2O/CH_2Cl_2	>20:1	98	93

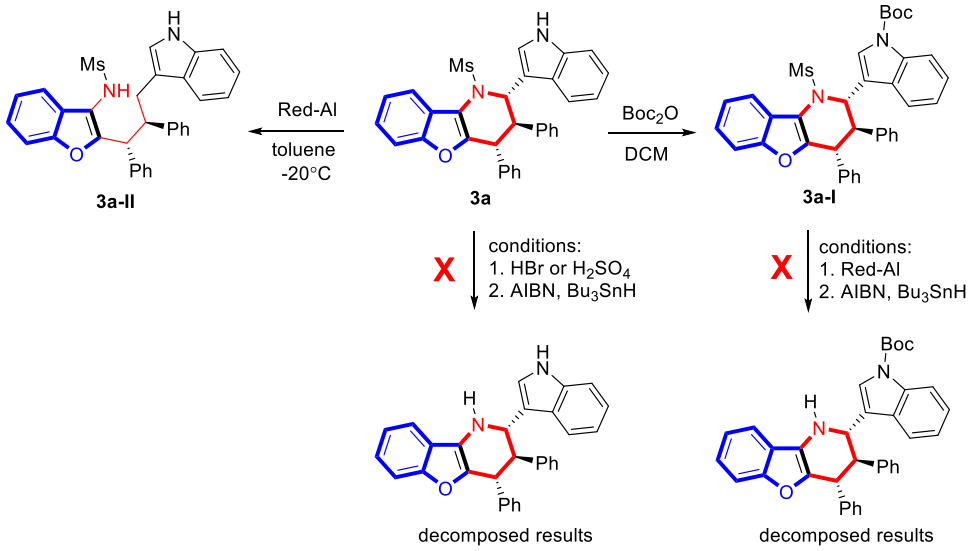
[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.18 mmol), and catalyst **4** (1 mol%), 5Å MS (100 mg) in the solvent specified (1 mL) at RT for 20 h. [b]The diastereomeric ratio (dr) value was determined by crude ^1H NMR. [c]Isolated yield. [d]The *ee* value was determined by HPLC analysis using a chiral stationary phase. [e]Et_2O:CH_2Cl_2 = 2:1.

Synthesis of 3a at a gram-scale:



To a stirring anhydrous Et_2O:CH_2Cl_2 (2:1) solution (15 ml) of aurone-derived 1-azadienes **1a** (3 mmol) and 3-vinylindoles **2a** (5.4 mmol) was added 5Å MS (3 g) and CPA **4b** (1 mol%) at rt. The reaction mixture was stirred until completion of reaction (as monitored by TLC). Then, the reaction mixture was vacuum filtered through Celite and water was added to the filtrate followed by extraction with AcOEt (2 × 20 mL). The combined organic layer was washed with brine, separated, dried over Na_2SO_4 and filtered. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (Hexane: CH_2Cl_2 = 2:1) to afford product **3a** (1.3 g) in 87% yield with 92% *ee*.

Further elaborations of 3a:

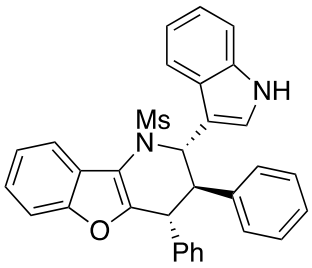


For **3a-I**: To a stirring anhydrous CH_2Cl_2 solution (1 ml) of **3a** (0.1 mmol) was added Et_3N (0.2 mmol) and Boc_2O (0.15 mmol) at rt. The reaction mixture was stirred until completion of reaction (as monitored by TLC). Then, the reaction was quenched by adding the NH_4Cl aqueous solution followed by extraction with AcOEt (2 × 2 mL). The combined organic layer was washed with brine, separated, dried over Na_2SO_4 and filtered. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (Hexane: CH_2Cl_2 = 2:1) to afford product **3a-I** (58 mg) in 96% yield.

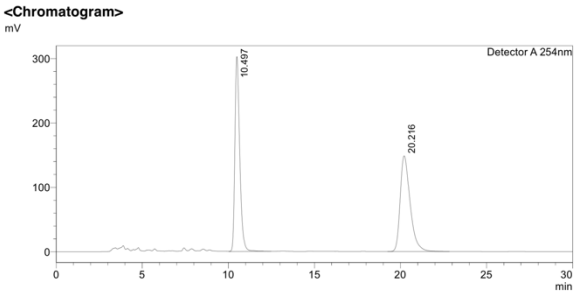
For **3a-II**: To a stirring anhydrous toluene solution (1 ml) of **3a** (0.1 mmol) was added Red-Al (1 mmol) at-20 ^{o}C. The reaction mixture was stirred until completion of reaction (as monitored by TLC). Then, the reaction was quenched by adding the NH_4Cl aqueous solution followed by extraction with AcOEt (2 × 2 mL). The combined organic layer was washed with brine, separated, dried over Na_2SO_4 and filtered. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on basic alumina (Hexane: AcOEt = 8:1) to afford product **3a-II** (48 mg) in 93% yield

C. Analytical Data and HPLC Chromatograms of the Products

(2*S*,3*R*,4*R*)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-3,4-diphenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3a**



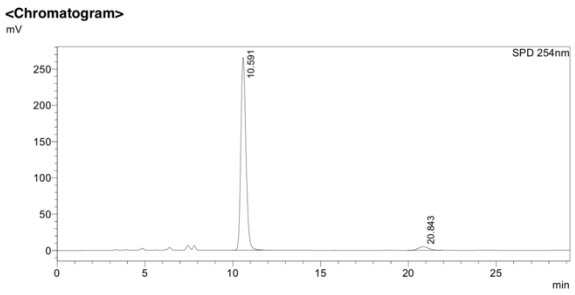
Yellowish oil; isolated yield = 98%; $[a]_D^{25}$ = –55.2 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 1H), 7.90 (s, 1H), 7.58 – 7.31 (m, 4H), 7.25 – 7.13 (m, 5H), 7.11 – 6.88 (m, 5H), 6.85 – 6.73 (m, 3H), 5.86 (d, *J* = 7.1 Hz, 1H), 4.58 (d, *J* = 5.6 Hz, 1H), 4.43 – 4.40 (m, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.0, 146.3, 141.8, 139.3, 135.9, 128.6, 128.0, 127.9, 127.8, 127.1, 126.3, 126.1, 124.9, 124.6, 123.3, 123.1, 122.1, 121.4, 120.0, 119.9, 118.5, 112.0, 111.8, 111.3, 61.4, 51.5, 45.7, 41.6. HRMS (ESI) m/z calcd for $C_{32}H_{26}N_2O_3S$ $[M - H]^-$ = 517.1591, found = 517.1589; HRMS (ESI) m/z calcd for $C_{32}H_{25}FN_2O_3S$ $[M - H]^-$ = 535.1497, found = 535.1502; the *ee* value was 93%, t_R (major) = 10.6 min, t_R (minor) = 20.8 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.497	5947393	302576	49.927	67.045
2	20.216	5964738	148730	50.073	32.955
Total		11912131	451306	100.000	100.000

Racemic **3a**

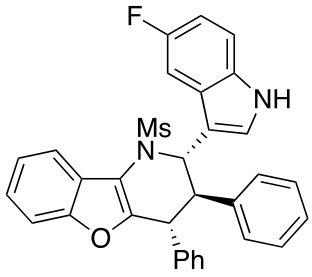


<Peak Table>
SPD 254nm

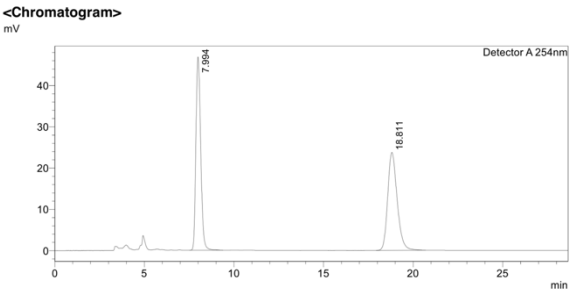
Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.591	5354412	265544	96.406	98.166
2	20.843	199620	4962	3.594	1.834
Total		5554032	270506	100.000	100.000

Enantioenriched **3a**

(2S,3R,4R)-2-(5-fluoro-1*H*-indol-3-yl)-1-(methylsulfonyl)-3,4-diphenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3b**



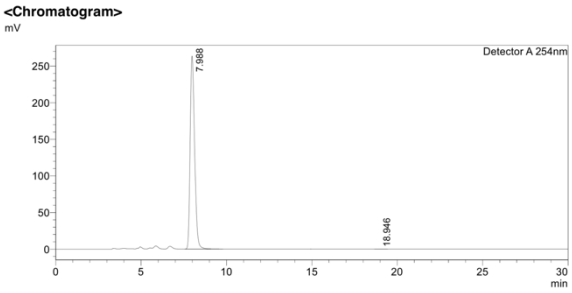
Yellowish oil; isolated yield = 93%; $[a]_D^{25}$ = –156 (c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.04 (m, 1H), 7.88 (s, 1H), 7.51 – 7.43 (m, 1H), 7.41 – 7.30 (m, 2H), 7.30 – 7.17 (m, 5H), 7.15 – 7.12 (m, 1H), 7.07 – 7.04 (m, 1H), 6.94 – 6.81 (m, 3H), 6.81 – 6.78 (m, 1H), 6.73 – 6.66 (m, 2H), 5.84 (d, *J* = 6.2 Hz, 1H), 4.62 (d, *J* = 4.8 Hz, 1H), 4.37 – 4.34 (m, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.7 (d, *J* = 234 Hz), 154.1, 145.4, 141.7, 139.4, 132.5, 128.8, 128.0, 127.8, 127.7, 127.4, 126.4, 126.2, 124.8, 123.3, 122.9, 121.6, 119.8, 112.0, 111.9, 111.8, 110.5 (d, *J* = 26 Hz), 103.7 (d, *J* = 24 Hz), 61.3, 50.9, 44.6, 41.2; HRMS (ESI) m/z calcd for $C_{32}H_{25}FN_2O_3S$ $[M - H]^-$ = 535.1497, found = 535.1502; the *ee* value was 99%, t_R (major) = 8.0 min, t_R (minor) = 18.9 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.994	877195	46844	50.191	66.358
2	18.811	870532	23749	49.809	33.642
Total		1747728	70592	100.000	100.000

Racemic **3b**

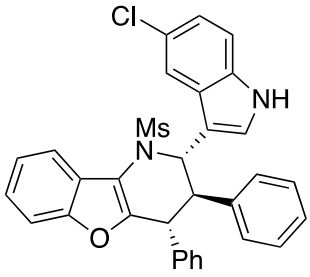


<Peak Table>
Detector A 254nm

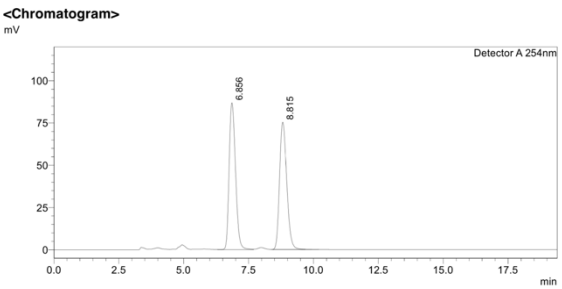
Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.988	4772825	263455	99.974	99.980
2	18.946	1223	52	0.026	0.020
Total		4774048	263507	100.000	100.000

Enantioenriched **3b**

(2S,3R,4R)-2-(5-chloro-1*H*-indol-3-yl)-1-(methylsulfonyl)-3,4-diphenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3c**



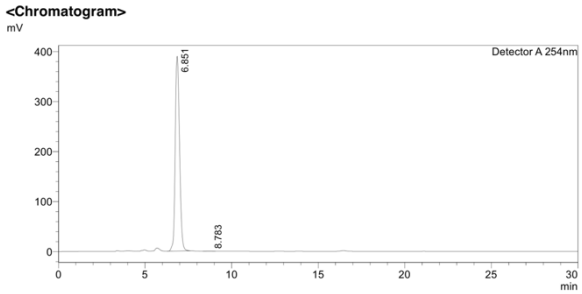
Yellowish oil; isolated yield = 92%; $[a]_D^{25}$ = –171 (c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.13 (m, 1H), 7.93 (s, 1H), 7.52 – 7.43 (m, 1H), 7.43 (s, 1H), 7.41 – 7.27 (m, 2H), 7.30 – 7.15 (m, 4H), 7.07 – 6.96 (m, 2H), 6.93 – 6.80 (m, 4H), 6.71 – 6.64 (m, 2H), 5.86 (d, *J* = 6.2 Hz, 1H), 4.64 (d, *J* = 4.6 Hz, 1H), 4.39 – 4.36 (m, 1H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 145.2, 141.6, 139.4, 134.4, 128.8, 128.0, 127.7, 127.6, 127.4, 126.9, 126.1, 125.9, 125.4, 124.7, 123.2, 122.7, 122.3, 121.6, 119.7, 118.1, 112.4, 112.2, 111.8, 61.2, 50.7, 44.3, 41.1; HRMS (ESI) m/z calcd for $C_{32}H_{25}ClN_2O_3S$ [M - H]$^-$ = 551.1202, found = 551.1204; the *ee* value was 99%, t_R (major) = 6.9 min, t_R (minor) = 8.8min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.856	1489142	86913	50.490	53.561
2	8.815	1460267	75356	49.510	46.439
Total		2949409	162269	100.000	100.000

Racemic **3c**

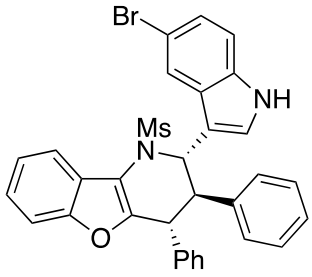


<Peak Table>
Detector A 254nm

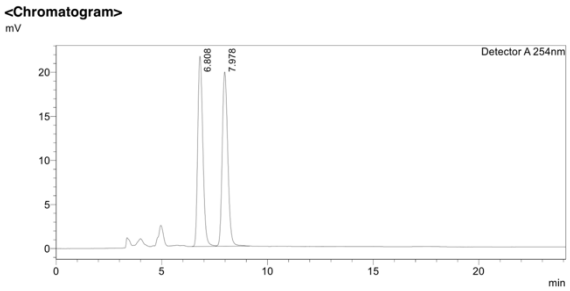
Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.851	6624356	389247	99.931	99.949
2	8.783	4605	200	0.069	0.051
Total		6628961	389447	100.000	100.000

Enantioenriched **3c**

(2S,3R,4R)-2-(5-bromo-1*H*-indol-3-yl)-1-(methylsulfonyl)-3,4-diphenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3d**



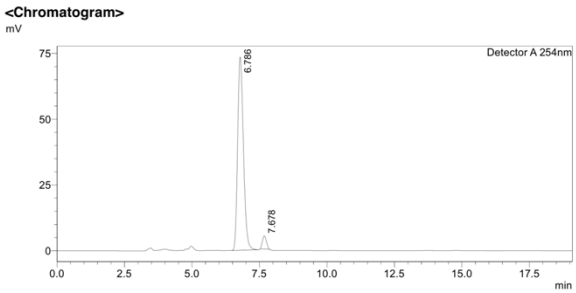
Yellowish oil; isolated yield = 84%; $[a]_D^{25}$ = –188 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 – 8.16 (m, 1H), 7.98 (s, 1H), 7.61 (s, 1H), 7.53 – 7.48 (m, 1H), 7.43 – 7.34 (m, 2H), 7.33 – 7.21 (m, 3H), 7.16 – 7.14 (m, 1H), 7.02 (d, *J* = 8.6 Hz, 1H), 6.95 – 6.83 (m, 5H), 6.71 (d, *J* = 7.0 Hz, 2H), 5.89 (d, *J* = 6.0 Hz, 1H), 4.67 (d, *J* = 4.6 Hz, 1H), 4.43 – 4.37 (m, 1H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 145.3, 141.6, 139.4, 134.7, 128.8, 128.0, 127.8, 127.7, 127.6, 127.4, 126.2, 125.8, 124.9, 124.8, 123.3, 122.8, 121.6, 121.2, 119.7, 113.1, 112.7, 112.3, 111.9, 61.3, 50.7, 44.4, 41.1; HRMS (ESI) m/z calcd for $C_{32}H_{25}BrN_2O_3S$ [M - H]$^-$ = 595.0696, found = 595.0682; the *ee* value was 91%, t_R (major) = 6.8 min, t_R (minor) = 7.7 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.808	363457	21576	50.120	52.190
2	7.978	361722	19765	49.880	47.810
Total		725180	41341	100.000	100.000

Racemic **3d**

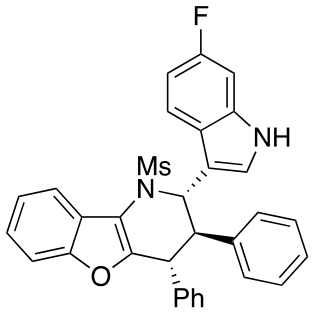


<Peak Table>
Detector A 254nm

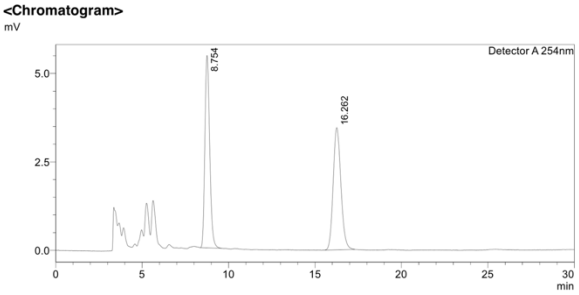
Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.786	1097367	73450	95.471	93.632
2	7.678	52062	4996	4.529	6.368
Total		1149429	78446	100.000	100.000

Enantioenriched **3d**

(2S,3R,4R)-2-(6-fluoro-1*H*-indol-3-yl)-1-(methylsulfonyl)-3,4-diphenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3e**



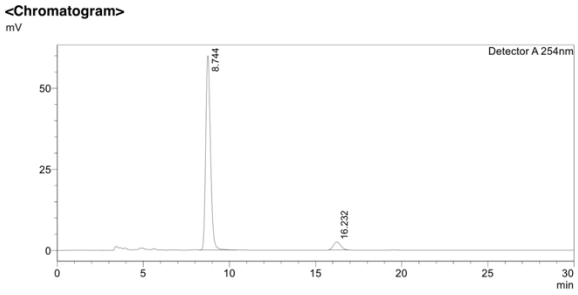
Yellowish oil; isolated yield = 84%; $[\alpha]_D^{25}$ = –128 (c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.11 (m, 1H), 7.83 (s, 1H), 7.50 – 7.45 (m, 1H), 7.43 – 7.30 (m, 3H), 7.25 – 7.21 (m, 4H), 6.90 – 6.63 (m, 8H), 5.89 (d, *J* = 6.0 Hz, 1H), 4.64 (d, *J* = 4.6 Hz, 1H), 4.40 – 4.33 (m, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8 (d, *J* = 237 Hz) , 154.1, 145.2, 141.8, 139.5, 136.2, 136.1, 128.8, 128.0, 127.8, 127.7, 127.4, 126.2, 124.8, 124.7, 123.3, 122.8, 122.4, 121.6, 119.8, 119.4, 119.3, 113.0, 111.9, 108.6 (d, *J* = 25 Hz), 97.5 (d, *J* = 26 Hz), 61.4, 51.2, 44.3, 41.1; HRMS (ESI) m/z calcd for $C_{32}H_{25}FN_2O_3S$ [M - H]$^-$ = 535.1497, found = 535.1496; the *ee* value was 88%, t_R (major) = 8.7 min, t_R (minor) = 16.2 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.754	106173	5438	49.877	61.141
2	16.262	106698	3456	50.123	38.859
Total		212872	8893	100.000	100.000

Racemic **3e**

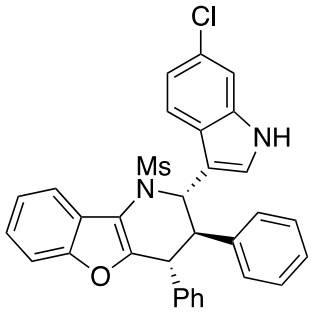


<Peak Table>
Detector A 254nm

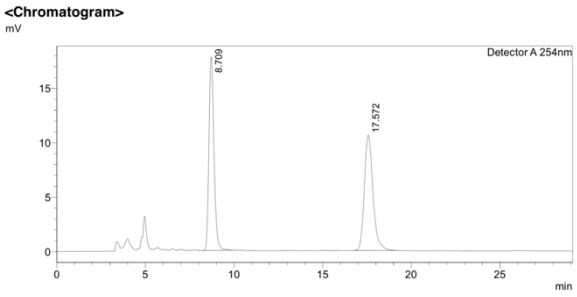
Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.744	1161215	59871	94.163	96.051
2	16.232	71987	2462	5.837	3.949
Total		1233202	62332	100.000	100.000

Enantioenriched **3e**

(2S,3R,4R)-2-(6-chloro-1*H*-indol-3-yl)-1-(methylsulfonyl)-3,4-diphenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3f**

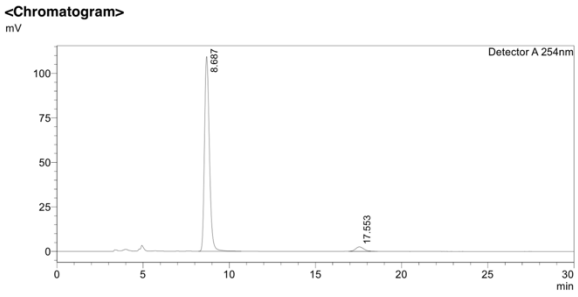


Yellowish oil; isolated yield = 92%; $[\alpha]_D^{25}$ = –100 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.10 (m, 1H), 7.87 (s, 1H), 7.52 – 7.43 (m, 1H), 7.41 – 7.30 (m, 3H), 7.30 – 7.16 (m, 4H), 7.14 – 7.13 (m, 1H), 6.96 – 6.94 (m, 1H), 6.89 – 6.88 (m, 3H), 6.81 – 6.80 (m, 1H), 6.69 – 6.67 (m, 2H), 5.87 (d, *J* = 5.5 Hz, 1H), 4.63 (d, *J* = 4.8 Hz, 1H), 4.38 – 4.31 (m, 1H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.1, 145.3, 141.6, 139.3, 136.4, 128.8, 128.0, 127.8, 127.4, 126.3, 125.1, 124.8, 124.4, 123.3, 122.8, 121.6, 120.6, 119.7, 119.5, 113.0, 111.9, 111.2, 61.3, 51.2, 44.4, 41.1; HRMS (ESI) m/z calcd for $C_{32}H_{25}ClN_2O_3S$ $[M - H]^-$ = 551.1202, found = 551.1197; the *ee* value was 92%, t_R (major) = 8.7 min, t_R (minor) = 17.6 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	8.709	355458	17785	62.642	49.716
2	17.572	359523	10606	37.358	50.284
Total		714981	28391	100.000	100.000



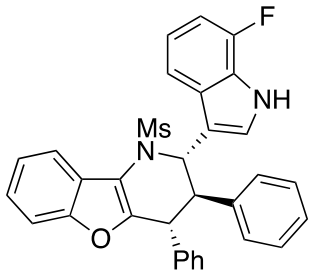
<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.687	2176324	109331	96.232	97.710
2	17.553	85224	2562	3.768	2.290
Total		2261548	111893	100.000	100.000

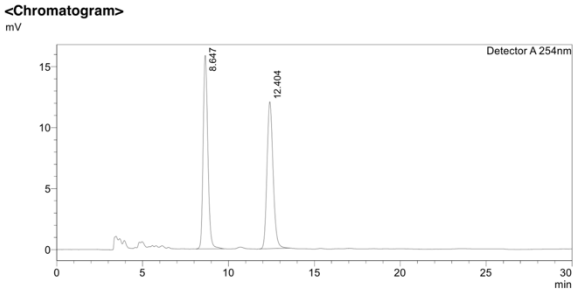
Racemic **3f**

Enantioenriched **3f**

(2S,3R,4R)-2-(7-fluoro-1*H*-indol-3-yl)-1-(methylsulfonyl)-3,4-diphenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3g**



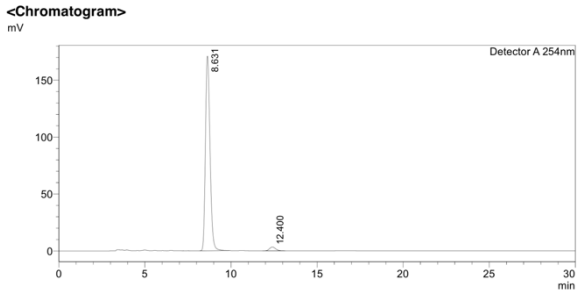
Yellowish oil; isolated yield = 97%; $[a]_D^{25}$ = –131 (c 2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.15 (m, 1H), 8.05 (s, 1H), 7.52 – 7.45 (m, 1H), 7.41 – 7.32 (m, 2H), 7.32 – 7.18 (m, 5H), 6.94 – 6.83 (m, 5H), 6.80 – 6.76 (m, 1H), 6.70 – 6.67 (m, 2H), 5.91 (d, *J* = 6.1 Hz, 1H), 4.65 (d, *J* = 4.6 Hz, 1H), 4.42 – 4.36 (m, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 149.3 (d, *J* = 243 Hz), 145.2, 141.7, 139.4, 129.4 (d, *J* = 5 Hz), 128.8, 128.0, 127.8, 127.6, 127.4, 126.2, 125.0, 124.8, 124.5 (d, *J* = 14 Hz), 123.2, 122.7, 121.6, 120.2, 120.1, 119.7, 114.5 (d, *J* = 4 Hz), 113.7, 111.9, 106.9 (d, *J* = 16 Hz), 61.3, 51.0, 44.3, 41.1; HRMS (ESI) m/z calcd for $C_{32}H_{25}FN_2O_3S$ $[M - H]^-$ = 535.1497, found = 535.1500; the *ee* value was 95%, t_R (major) = 8.6 min, t_R (minor) = 12.4 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.647	303651	15863	50.731	56.839
2	12.404	294899	12045	49.269	43.161
Total		598550	27908	100.000	100.000

Racemic **3g**

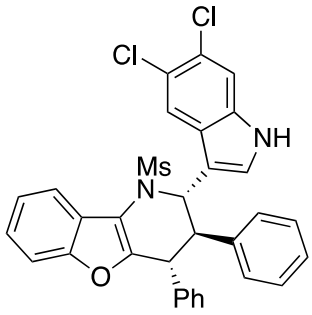


<Peak Table>
Detector A 254nm

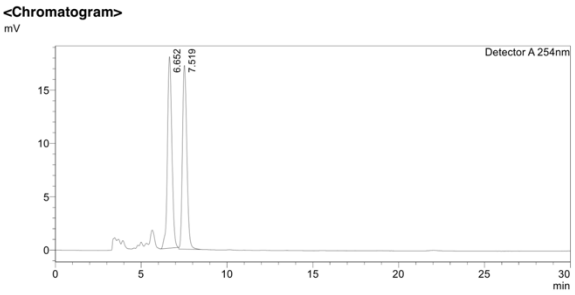
Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.631	3184704	170874	97.472	98.050
2	12.400	82588	3399	2.528	1.950
Total		3267292	174273	100.000	100.000

Enantioenriched **3g**

(2S,3R,4R)-2-(5,6-dichloro-1*H*-indol-3-yl)-1-(methylsulfonyl)-3,4-diphenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3h**



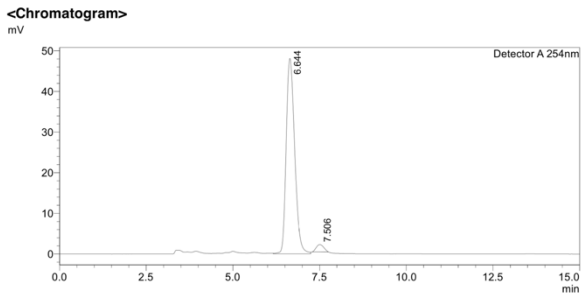
Yellowish oil; isolated yield = 98%; $[a]_D^{25}$ = –158 (c 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 – 8.23 (m, 1H), 7.91 (s, 1H), 7.52 – 7.42 (m, 2H), 7.41 – 7.18 (m, 7H), 6.88 – 6.77 (m, 4H), 6.64 – 6.58 (m, 2H), 5.87 (d, *J* = 6.2 Hz, 1H), 4.68 (d, *J* = 3.8 Hz, 1H), 4.36 – 4.29 (m, 1H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 144.5, 141.5, 139.5, 135.0, 129.0, 128.0, 127.7, 127.6, 126.1, 125.8, 125.3, 125.0, 123.7, 123.4, 122.4, 121.7, 119.8, 119.5, 113.1, 112.6, 111.9, 61.3, 50.5, 43.3, 40.7; HRMS (ESI) m/z calcd for $C_{32}H_{24}Cl_2N_2O_3S$ $[M - H]^-$ = 585.0812, found = 585.0811; the *ee* value was 94%, t_R (major) = 6.6 min, t_R (minor) = 7.5 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.652	319894	17931	50.918	51.012
2	7.519	308357	17220	49.082	48.988
Total		628252	35151	100.000	100.000

Racemic **3h**

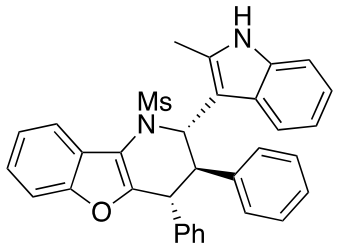


<Peak Table>
Detector A 254nm

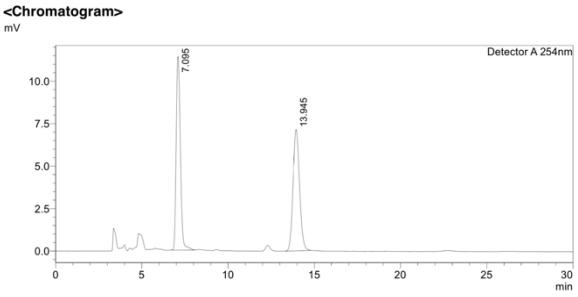
Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.644	819835	48070	96.803	96.378
2	7.506	27075	1807	3.197	3.622
Total		846910	49877	100.000	100.000

Enantioenriched **3h**

(2S,3R,4R)-2-(2-methyl-1*H*-indol-3-yl)-1-(methylsulfonyl)-3,4-diphenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3i**



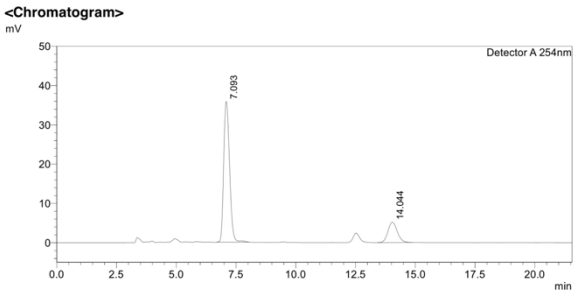
Brownish oil; isolated yield = 97%; $[a]_D^{25}$ = –12 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 1H), 7.62 (s, 1H), 7.46 – 7.35 (m, 2H), 7.34 – 7.21 (m, 2H), 7.20 – 6.94 (m, 10H), 6.82 – 6.77 (m, 2H), 5.60 (d, *J* = 11.0 Hz, 1H), 4.69 (d, *J* = 11.0 Hz, 1H), 3.89 – 3.84 (m, 1H), 2.61 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.0, 146.6, 139.0, 136.8, 135.3, 134.2, 129.1, 128.7, 128.3, 128.1, 127.2, 127.0, 126.3, 124.1, 123.7, 122.9, 121.3, 121.1, 120.0, 118.9, 118.7, 111.9, 110.8, 108.8, 61.1, 57.7, 46.1, 41.9, 11.2; HRMS (ESI) m/z calcd for $C_{33}H_{28}N_2O_3S$ $[M - H]^-$ = 531.1748, found = 531.1751; the *ee* value was 63%, t_R (major) = 7.1 min, t_R (minor) = 14.0 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.095	194009	11405	50.813	61.472
2	13.945	187799	7148	49.187	38.528
Total		381808	18554	100.000	100.000

Racemic **3i**

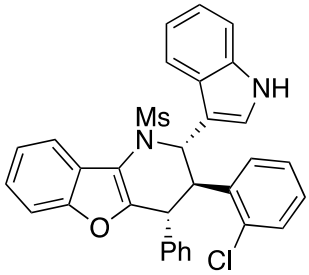


<Peak Table>
Detector A 254nm

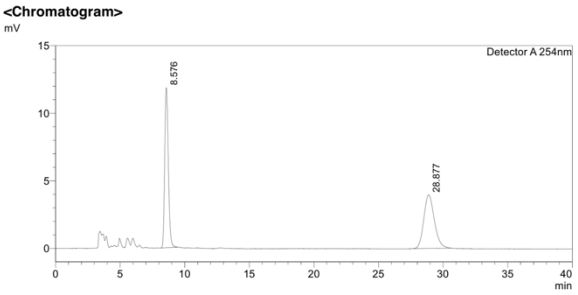
Peak#	Ret. Time	Area	Height	Area%	Height%
1	7.093	612185	35800	81.330	87.342
2	14.044	140535	5188	18.670	12.658
Total		752719	40988	100.000	100.000

Enantioenriched **3i**

(2S,3R,4R)-3-(2-chlorophenyl)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-4-phenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3j**

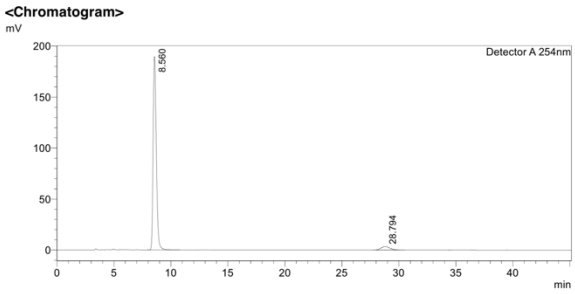


Yellowish oil; isolated yield = 94%; $[\alpha]_D^{25}$ = −142 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.92 (s, 1H), 7.69 – 7.67 (m, 1H), 7.48 – 7.46 (m, 1H), 7.37 – 7.35 (m, 3H), 7.17 – 7.06 (m, 4H), 7.01 – 6.90 (m, 5H), 6.73 (s, 2H), 5.94 (s, 1H), 4.97 (s, 1H), 4.58 (s, 1H), 2.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 139.2, 135.9, 134.4, 130.0, 128.5, 127.9, 127.3, 126.4, 124.7, 123.2, 122.2, 121.4, 120.5, 120.0, 119.1, 111.9, 111.1, 59.4, 45.7, 42.1, 29.8; HRMS (ESI) m/z calcd for $C_{32}H_{25}ClN_2O_3S$ [M - H]$^-$ = 551.1202, found = 551.1191; the *ee* value was 90%, t_R (major) = 8.6 min, t_R (minor) = 28.8 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.576	229453	11843	50.483	74.899
2	28.877	225063	3969	49.517	25.101
Total		454516	15813	100.000	100.000



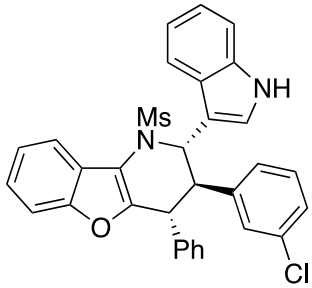
<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.560	3687074	189620	95.094	98.241
2	28.794	190221	3394	4.906	1.759
Total		3877296	193015	100.000	100.000

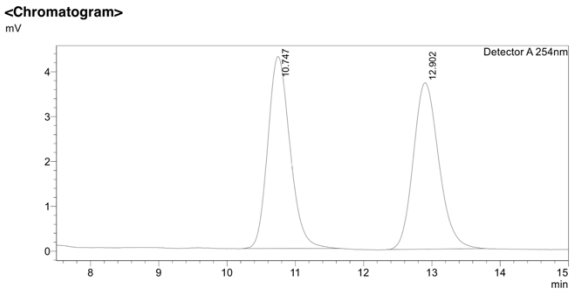
Racemic **3j**

Enantioenriched **3j**

(2S,3R,4R)-3-(3-chlorophenyl)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-4-phenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3k**



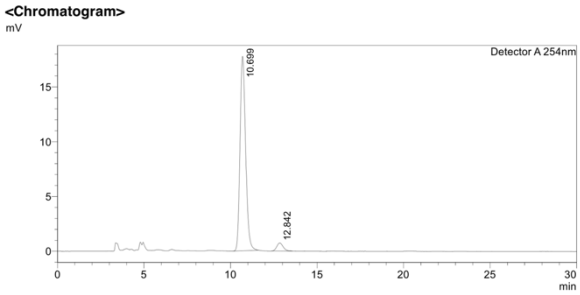
Yellowish oil; isolated yield = 92%; $[a]_D^{25}$ = –105 (c 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 2H), 7.56 – 7.54 (m, 1H), 7.46 – 7.44 (m, 1H), 7.36 – 7.33 (m, 2H), 7.23 – 7.22 (m, 1H), 7.14 – 6.97 (m, 9H), 6.86 – 6.80 (m, 2H), 5.75 (d, *J* = 7.9 Hz, 1H), 4.48 (d, *J* = 6.6 Hz, 1H), 4.40 – 4.33 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 143.9, 138.9, 135.8, 134.4, 130.0, 128.2, 128.1, 127.4, 126.8, 126.3, 125.4, 124.7, 123.6, 123.2, 122.5, 121.2, 120.2, 118.5, 111.9, 111.5, 111.3, 60.9, 52.1, 46.8, 42.1; HRMS (ESI) m/z calcd for $C_{32}H_{25}ClN_2O_3S$ $[M - H]^-$ = 551.1202, found = 551.1199; the *ee* value was 91%, t_R (major) = 10.7 min, t_R (minor) = 12.8 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.747	96882	4278	50.117	53.569
2	12.902	96431	3708	49.883	46.431
Total		193313	7987	100.000	100.000

Racemic **3k**

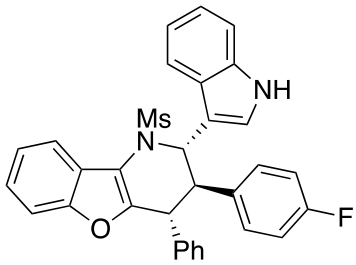


<Peak Table>
Detector A 254nm

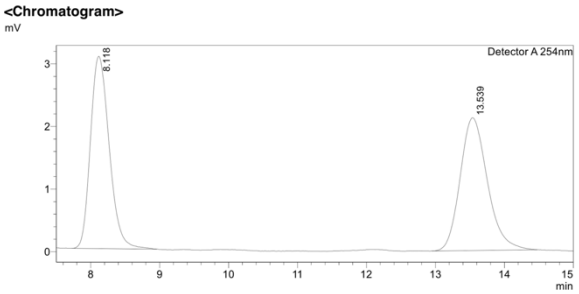
Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.699	399717	17741	95.477	96.018
2	12.842	18935	736	4.523	3.982
Total		418652	18477	100.000	100.000

Enantioenriched **3k**

(2S,3R,4R)-3-(4-fluorophenyl)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-4-phenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3l**



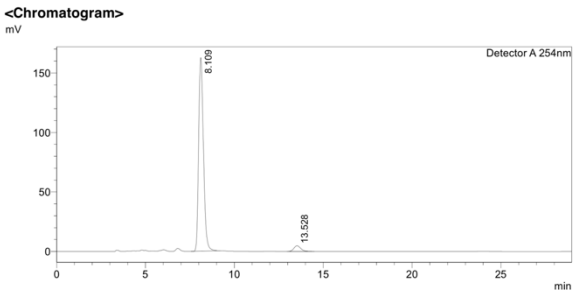
Yellowish oil; isolated yield = 99%; $[\alpha]_D^{25}$ = –152 (c 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.88 (m, 2H), 7.56 – 7.54 (m, 1H), 7.45 – 7.43 (m, 1H), 7.35 – 7.32 (m, 2H), 7.24 – 7.22 (m, 1H), 7.14 – 7.11 (m, 1H), 7.09 – 6.97 (m, 5H), 6.89 – 6.79 (m, 5H), 5.73 (d, *J* = 8.1 Hz, 1H), 4.46 (d, *J* = 6.8 Hz, 1H), 4.38 – 4.35 (m, 1H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7 (d, *J* = 245 Hz), 154.1, 146.9, 139.0, 137.4, 137.4, 135.7, 129.5 (d, *J* = 7 Hz), 128.2, (d, *J* = 13 Hz), 126.8, 126.3, 125.6, 124.7, 123.6, 123.1, 122.4, 121.2, 120.2, 118.5, 115.5 (d, *J* = 21 Hz), 111.9, 111.5, 111.3, 61.2, 51.7, 47.2, 42.2; HRMS (ESI) m/z calcd for $C_{32}H_{25}FN_2O_3S$ [M - H]$^-$ = 535.1497, found = 535.1500; the *ee* value was 92%, t_R (major) = 8.1 min, t_R (minor) = 13.5 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.118	58153	3070	49.926	59.149
2	13.539	58325	2120	50.074	40.851
Total		116478	5190	100.000	100.000

Racemic **3l**

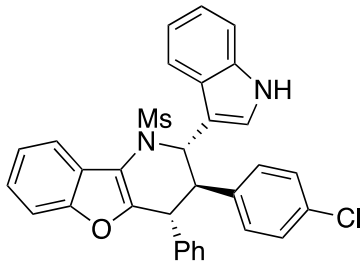


<Peak Table>
Detector A 254nm

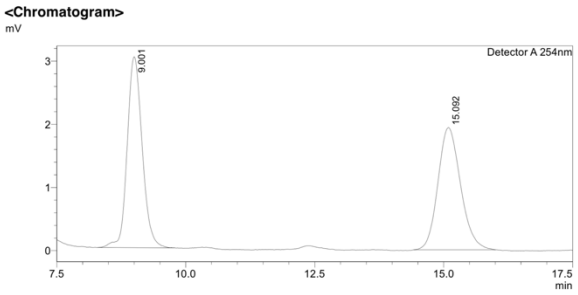
Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.109	3071070	162573	95.978	97.166
2	13.528	128696	4741	4.022	2.834
Total		3199766	167314	100.000	100.000

Enantioenriched **3l**

(2S,3R,4R)-3-(4-chlorophenyl)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-4-phenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3m**

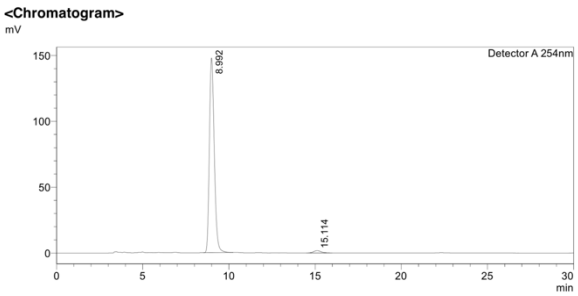


Yellowish oil; isolated yield = 96%; $[a]_D^{25}$ = –152 (c 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.89 – 7.87 (m, 1H), 7.57 – 7.55 (m, 1H), 7.44 – 7.42 (m, 1H), 7.35 – 7.31 (m, 2H), 7.25 – 7.23 (m, 1H), 7.18 – 6.93 (m, 8H), 6.85 – 6.83 (m, 3H), 5.71 (d, *J* = 8.4 Hz, 1H), 4.44 (d, *J* = 7.1 Hz, 1H), 4.38 – 4.35 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 147.1, 140.1, 138.8, 135.7, 132.8, 129.4, 128.8, 128.3, 128.2, 126.9, 126.4, 125.8, 124.7, 123.8, 123.1, 122.5, 121.1, 120.3, 120.2, 118.5, 111.9, 111.5, 111.0, 61.0, 51.9, 47.4, 42.3; HRMS (ESI) m/z calcd for $C_{32}H_{25}ClN_2O_3S$ $[M - H]^-$ = 551.1202, found = 551.1192; the *ee* value was 96%, t_R (major) = 9.0 min, t_R (minor) = 15.1 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.001	61278	3023	50.880	60.956
2	15.092	59157	1936	49.120	39.044
Total		120435	4959	100.000	100.000



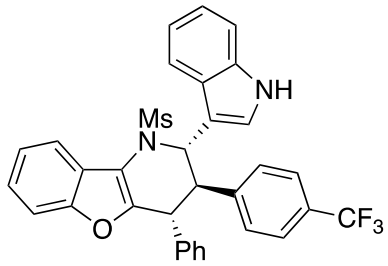
<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.992	2930349	147782	98.246	98.850
2	15.114	52316	1720	1.754	1.150
Total		2982665	149502	100.000	100.000

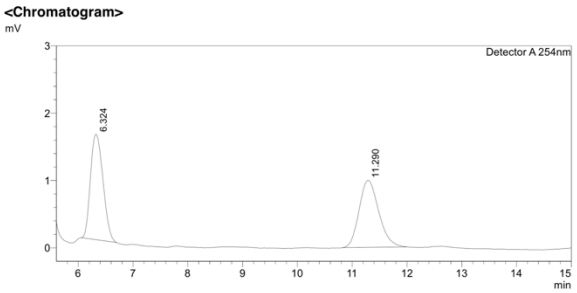
Racemic **3m**

Enantioenriched **3m**

(2S,3R,4R)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-4-phenyl-3-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3n**



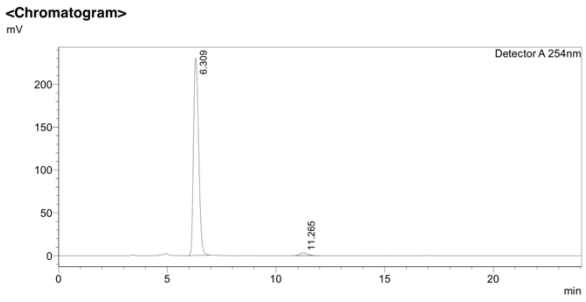
Yellowish oil; isolated yield = 98%; $[a]_D^{25}$ = –132 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.86 – 7.84 (m, 1H), 7.60 – 7.58 (m, 1H), 7.48 – 7.38 (m, 3H), 7.35 – 7.32 (m, 2H), 7.25 (s, 1H), 7.19 – 7.03 (m, 7H), 6.90 – 6.80 (m, 2H), 5.75 (d, *J* = 8.1 Hz, 1H), 4.51 – 4.39 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 147.2, 145.7, 138.6, 135.6, 129.4, 129.1, 128.4, 128.3, 128.3, 127.1, 126.5, 126.0, 125.5, 125.5, 124.7, 124.0 (q, *J* = 271 Hz), 123.8, 123.2, 122.6, 121.1, 120.4, 120.3, 118.4, 111.9, 111.6, 110.6, 60.7, 52.4, 47.7, 42.4; HRMS (ESI) m/z calcd for $C_{33}H_{25}F_3N_2O_3S$ [M - H]$^-$ = 585.1465, found = 585.1446; the *ee* value was 96%, t_R (major) = 6.3 min, t_R (minor) = 11.3 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.324	24888	1567	50.112	61.164
2	11.290	24776	995	49.888	38.836
Total		49664	2562	100.000	100.000

Racemic **3n**

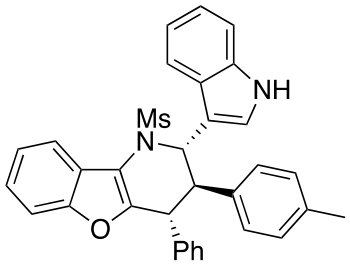


<Peak Table>
Detector A 254nm

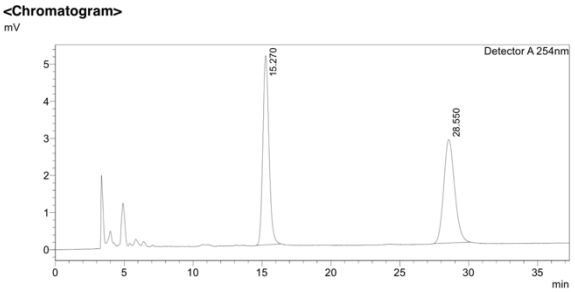
Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.309	3751811	229972	97.865	98.576
2	11.265	81855	3321	2.135	1.424
Total		3833666	233293	100.000	100.000

Enantioenriched **3n**

(2S,3R,4R)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-4-phenyl-3-(p-tolyl)-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3o**



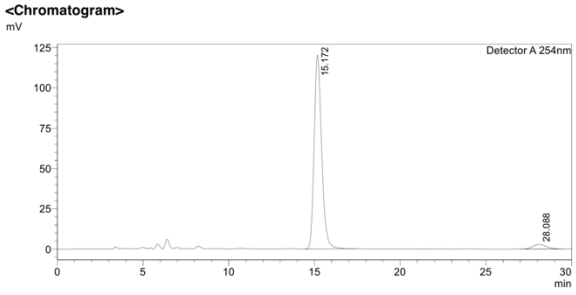
Yellowish oil; isolated yield = 98%; $[a]_D^{25}$ = –112 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.05 (m, 1H), 7.89 (s, 1H), 7.55 – 7.53 (m, 1H), 7.47 – 7.44 (m, 1H), 7.36 – 7.32 (m, 2H), 7.18 – 7.15 (m, 1H), 7.12 – 6.97 (m, 6H), 6.97 – 6.86 (m, 2H), 6.83 – 6.82 (m, 1H), 6.78 – 6.71 (m, 2H), 5.84 (d, *J* = 7.0 Hz, 1H), 4.56 (d, *J* = 5.5 Hz, 1H), 4.41 – 4.34 (m, 1H), 2.35 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 146.3, 139.5, 138.8, 136.8, 135.9, 129.4, 128.0, 127.9, 127.8, 126.3, 126.1, 124.9, 124.6, 123.3, 123.1, 122.1, 121.5, 119.9, 118.6, 112.2, 111.8, 111.3, 61.5, 51.1, 45.6, 41.5; HRMS (ESI) m/z calcd for $C_{33}H_{28}N_2O_3S$ $[M - H]^-$ = 531.1748, found = 531.1759; the *ee* value was 92%, t_R (major) = 15.2 min, t_R (minor) = 28.1 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	15.270	156771	5099	50.463	64.661
2	28.550	153893	2787	49.537	35.339
Total		310664	7885	100.000	100.000

Racemic **3o**

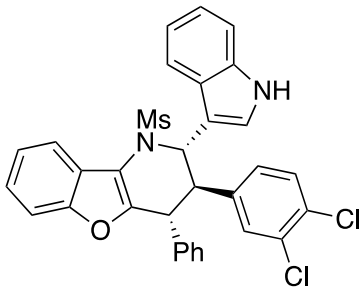


<Peak Table>
Detector A 254nm

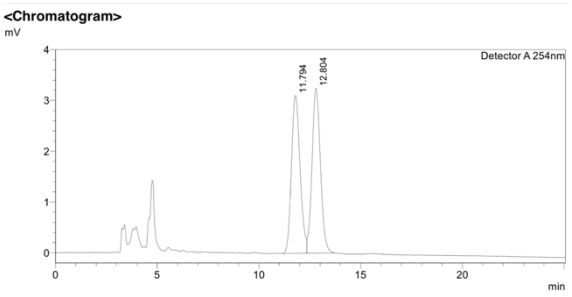
Peak#	Ret. Time	Area	Height	Area%	Height%
1	15.172	3655983	120257	95.859	97.648
2	28.088	157931	2897	4.141	2.352
Total		3813914	123154	100.000	100.000

Enantioenriched **3o**

(2S,3R,4R)-3-(3,4-dichlorophenyl)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-4-phenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3p**

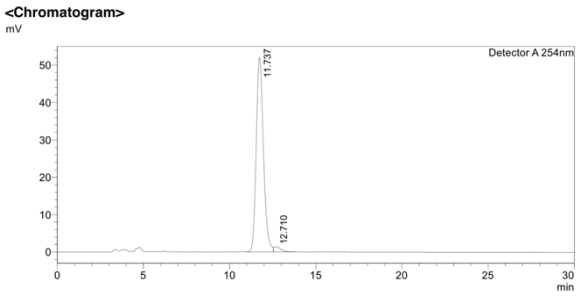


Yellowish oil; isolated yield = 98%; $[a]_D^{25}$ = –138 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.84 – 7.82 (m, 1H), 7.57 – 7.55 (m, 1H), 7.44 – 7.42 (m, 1H), 7.37 – 7.26 (m, 2H), 7.23 – 7.13 (m, 2H), 7.13 – 7.05 (m, 5H), 6.91 – 6.81 (m, 4H), 5.66 (d, *J* = 8.6 Hz, 1H), 4.43 – 4.29 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 147.1, 141.9, 138.5, 135.6, 132.5, 131.0, 130.6, 130.0, 128.4, 128.3, 127.4, 127.2, 126.4, 125.9, 124.7, 123.8, 123.2, 122.7, 121.0, 120.5, 120.3, 118.4, 111.9, 111.6, 110.5, 60.6, 52.1, 47.9, 42.5; HRMS (ESI) m/z calcd for $C_{32}H_{24}Cl_2N_2O_3S$ $[M - H]^-$ = 585.0812, found = 585.0804; the *ee* value was 95%, t_R (major) = 11.7 min, t_R (minor) = 12.7 min (Chiralpak ID, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.794	91313	3110	49.422	48.933
2	12.804	93451	3246	50.578	51.067
Total		184764	6357	100.000	100.000

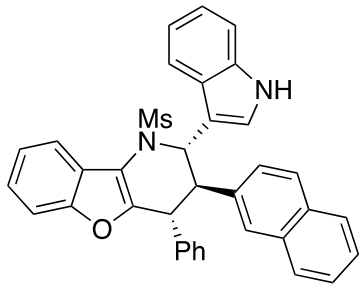


<Peak Table>
Detector A 254nm

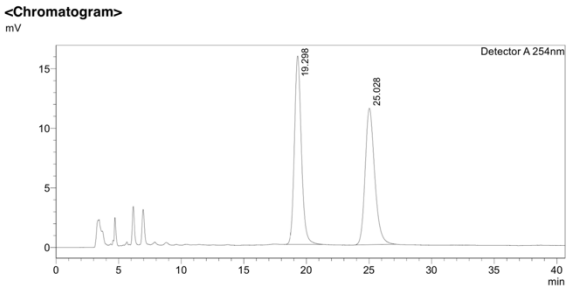
Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.737	1518397	52010	97.570	97.457
2	12.710	37819	1357	2.430	2.543
Total		1556216	53367	100.000	100.000

Racemic **3p** Enantioenriched **3p**

(2S,3R,4R)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-3-(naphthalen-2-yl)-4-phenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3q**



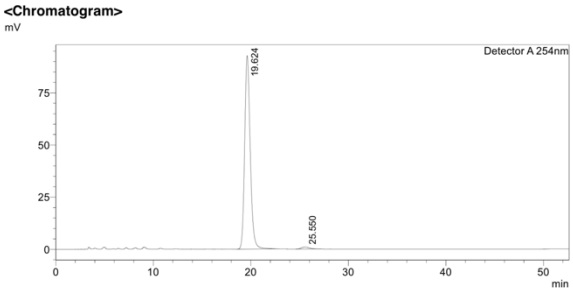
Brownish oil; isolated yield = 99%; $[a]_D^{25}$ = –139 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 1H), 7.90 – 7.85 (m, 1H), 7.78 – 7.65 (m, 2H), 7.64 – 7.61 (m, 2H), 7.51 – 7.31 (m, 5H), 7.35 – 7.25 (m, 1H), 7.22 – 7.15 (m, 1H), 7.15 – 7.03 (m, 2H), 7.02 – 6.94 (m, 3H), 6.87 – 6.77 (m, 3H), 5.92 (d, *J* = 8.0 Hz, 1H), 4.65 (d, *J* = 6.6 Hz, 1H), 4.59 – 4.55 (m, 1H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 147.3, 139.3, 139.0, 135.7, 133.2, 132.4, 128.6, 128.2, 128.1, 127.8, 127.6, 127.1, 126.7, 126.5, 126.2, 125.9, 125.7, 124.6, 123.8, 123.1, 122.3, 121.3, 120.2, 120.1, 118.6, 111.9, 111.4, 61.2, 52.3, 46.9, 42.0; HRMS (ESI) m/z calcd for $C_{36}H_{28}N_2O_3S$ [M - H]$^-$ = 567.1748, found = 567.1752; the *ee* value was 97%, t_R (major) = 19.6 min, t_R (minor) = 25.6 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	19.298	613572	15801	50.273	58.007
2	25.028	606897	11439	49.727	41.993
Total		1220468	27240	100.000	100.000

Racemic **3q**

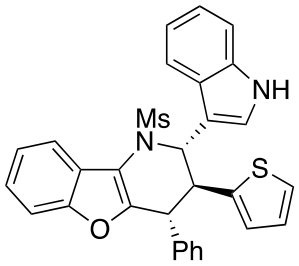


<Peak Table>
Detector A 254nm

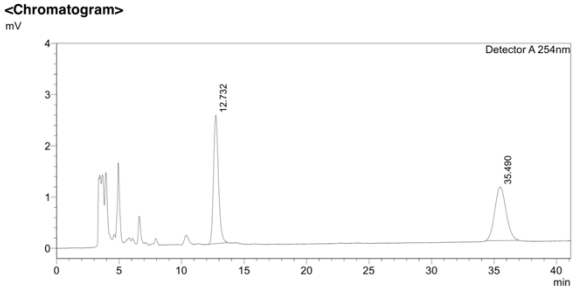
Peak#	Ret. Time	Area	Height	Area%	Height%
1	19.624	3688664	92735	98.480	98.965
2	25.550	56933	969	1.520	1.035
Total		3745597	93704	100.000	100.000

Enantioenriched **3q**

(2S,3S,4R)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-4-phenyl-3-(thiophen-2-yl)-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3r**

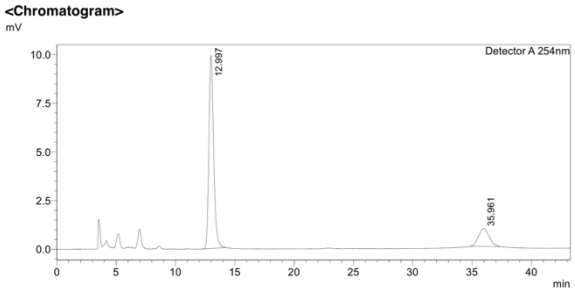


Brownish oil; isolated yield = 98%; $[\alpha]_D^{25}$ = –60 (c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.14 (m, 1H), 7.85 (s, 1H), 7.52 – 7.43 (m, 2H), 7.40 – 7.30 (m, 2H), 7.19 – 6.93 (m, 4H), 6.92 – 6.79 (m, 5H), 6.78 – 6.67 (m, 2H), 5.98 (d, *J* = 5.3 Hz, 1H), 4.71 – 4.68 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 145.4, 139.2, 136.2, 127.6, 126.9, 126.2, 125.6, 124.8, 124.4, 124.1, 123.2, 122.7, 122.1, 121.7, 119.8, 119.3, 118.6, 112.4, 111.9, 111.2, 61.8, 46.7, 45.9, 41.1; HRMS (ESI) m/z calcd for $C_{30}H_{24}N_2O_3S_2$ $[M - H]^-$ = 523.1156, found = 523.1144; the *ee* value was 65%, t_R (major) = 12.9 min, t_R (minor) = 35.9 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.732	68577	2509	50.960	70.531
2	35.490	65994	1048	49.040	29.469
Total		134571	3557	100.000	100.000

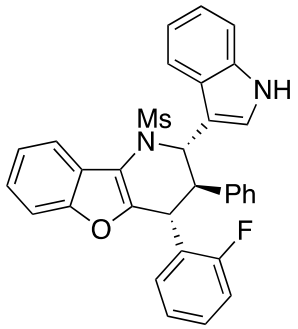


<Peak Table>
Detector A 254nm

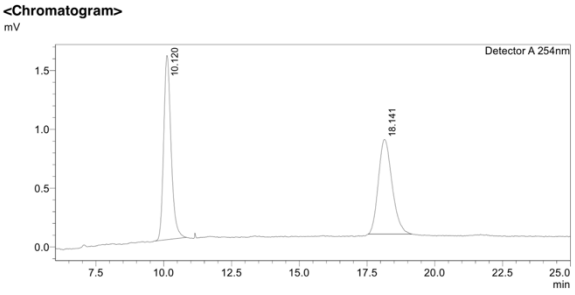
Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.997	274824	9904	82.717	91.501
2	35.961	57423	920	17.283	8.499
Total		332246	10824	100.000	100.000

Racemic **3r** Enantioenriched **3r**

(2S,3R,4R)-4-(2-fluorophenyl)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-3-phenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3s**



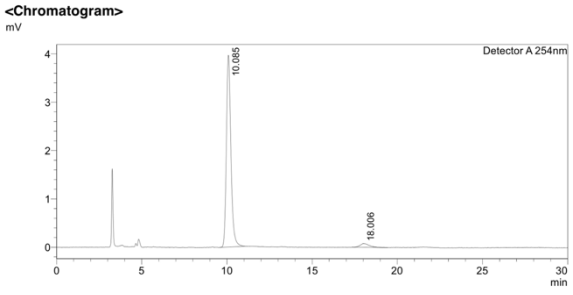
Yellowish oil; isolated yield = 90%; $[a]_D^{25}$ = –117 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 – 8.23 (m, 1H), 7.84 (s, 1H), 7.55 – 7.46 (m, 2H), 7.41 – 7.20 (m, 6H), 7.13 – 6.93 (m, 3H), 6.83 – 6.71 (m, 2H), 6.68 – 6.60 (m, 1H), 6.48 – 6.45 (m, 1H), 6.25 (s, 1H), 5.98 (d, *J* = 5.3 Hz, 1H), 4.93 (d, *J* = 3.9 Hz, 1H), 4.53 – 4.48 (m, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5 (d, *J* = 244 Hz), 154.1, 141.6, 136.5, 129.2 (d, *J* = 4 Hz), 128.8, 127.9, 127.7, 127.7, 127.4, 126.2 (d, *J* = 13 Hz), 125.4, 124.8, 123.6, 123.3, 122.8, 122.8, 122.5, 122.0, 121.8, 120.1, 119.7, 118.6, 114.7 (d, *J* = 22 Hz), 113.3, 111.9, 111.2, 61.7, 48.6, 40.9, 37.6; HRMS (ESI) m/z calcd for $C_{32}H_{25}FN_2O_3S$ $[M - H]^-$ = 535.1497, found = 535.1487; the *ee* value was 92%, t_R (major) = 10.1 min, t_R (minor) = 18.0 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.120	29655	1566	51.082	66.052
2	18.141	28398	805	48.918	33.948
Total		58053	2370	100.000	100.000

Racemic **3s**

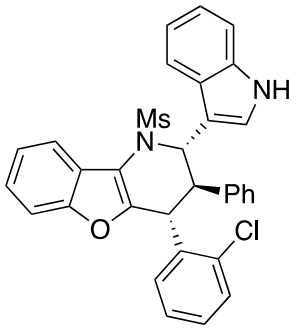


<Peak Table>
Detector A 254nm

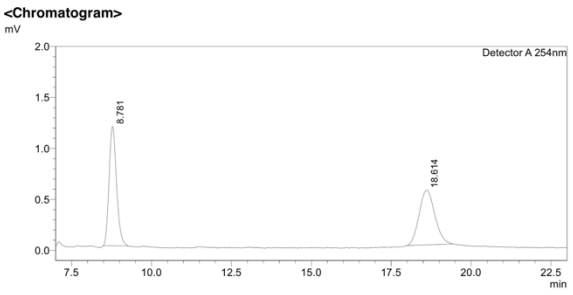
Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.085	73452	3964	96.243	98.053
2	18.006	2868	79	3.757	1.947
Total		76320	4043	100.000	100.000

Enantioenriched **3s**

(2S,3R,4R)-4-(2-chlorophenyl)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-3-phenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3t**



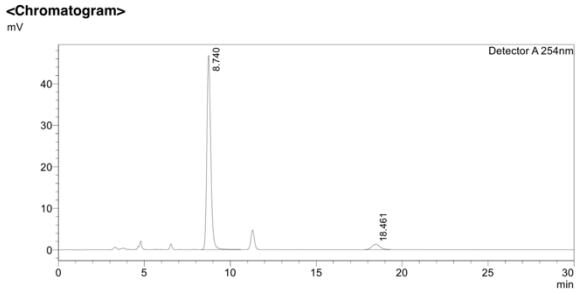
Yellowish oil; isolated yield = 82%; $[a]_D^{25}$ = –26 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.80 (s, 1H), 7.53 – 7.21 (m, 9H), 7.10 – 6.83 (m, 5H), 6.60 – 6.41 (m, 2H), 6.05 – 6.00 (m, 1H), 5.02 (s, 1H), 4.62 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 142.0, 136.7, 133.1, 131.6, 129.2, 128.9, 127.9, 127.6, 127.0, 125.2, 125.1, 125.0, 123.4, 123.0, 122.1, 121.9, 120.3, 119.6, 118.5, 114.0, 112.4, 111.9, 111.0, 61.9, 47.1, 40.6, 39.6; HRMS (ESI) m/z calcd for $C_{32}H_{25}ClN_2O_3S$ [M - H]$^-$ = 551.1202, found = 551.1191; the *ee* value was 89%, t_R (major) = 8.7 min, t_R (minor) = 18.5 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.781	18971	1172	50.808	68.603
2	18.614	18368	536	49.192	31.397
Total		37339	1708	100.000	100.000

Racemic **3t**

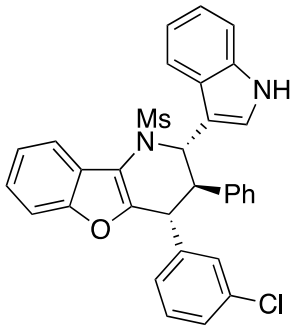


<Peak Table>
Detector A 254nm

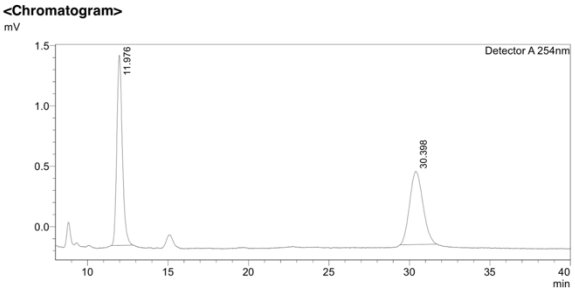
Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.740	746681	46766	94.460	97.298
2	18.461	43793	1299	5.540	2.702
Total		790474	48064	100.000	100.000

Enantioenriched **3t**

(2S,3R,4R)-4-(3-chlorophenyl)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-3-phenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3u**



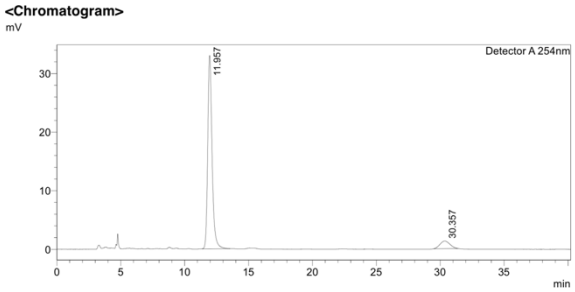
Yellowish oil; isolated yield = 84%; $[a]_D^{25}$ = –51 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 – 8.18 (m, 1H), 7.86 (s, 1H), 7.52 – 7.24 (m, 8H), 7.15 – 6.91 (m, 3H), 6.82 – 6.58 (m, 4H), 6.36 (s, 1H), 5.94 (d, *J* = 5.1 Hz, 1H), 4.59 (d, *J* = 3.6 Hz, 1H), 4.39 – 4.37 (m, 1H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3, 143.4, 141.8, 136.4, 133.2, 129.5, 129.0, 128.9, 128.0, 127.8, 127.7, 126.2, 126.1, 125.5, 125.1, 124.1, 123.4, 122.4, 122.2, 122.0, 120.2, 119.9, 118.6, 112.8, 112.1, 111.3, 61.5, 50.3, 43.2, 41.2; HRMS (ESI) m/z calcd for $C_{32}H_{25}ClN_2O_3S$ [M - H]$^-$ = 551.1202, found = 551.1197; the *ee* value was 83%, t_R (major) = 12.0 min, t_R (minor) = 30.4 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.976	37582	1575	51.841	72.175
2	30.398	34913	607	48.159	27.825
Total		72495	2182	100.000	100.000

Racemic **3u**

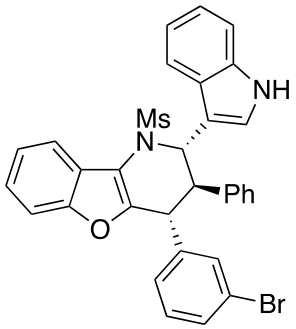


<Peak Table>
Detector A 254nm

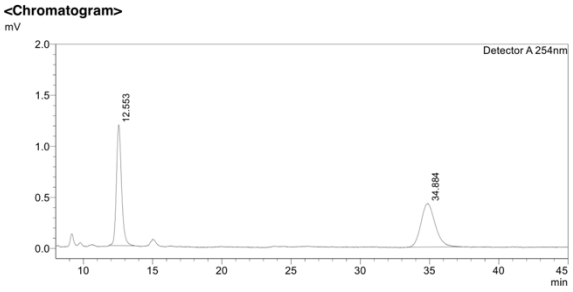
Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.957	779281	32991	91.617	96.175
2	30.357	71308	1312	8.383	3.825
Total		850589	34303	100.000	100.000

Enantioenriched **3u**

(2S,3R,4R)-4-(3-bromophenyl)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-3-phenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3v**



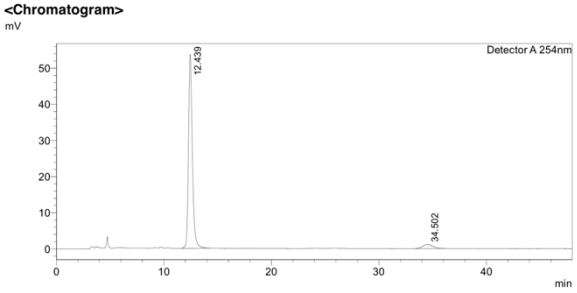
Yellowish oil; isolated yield = 80%; $[a]_D^{25}$ = –116 (c 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 – 8.25 (m, 1H), 7.89 (s, 1H), 7.55 – 7.29 (m, 8H), 7.19 – 6.93 (m, 3H), 6.84 (s, 2H), 6.70 – 6.67 (m, 2H), 6.51 (s, 1H), 5.99 (d, *J* = 4.6 Hz, 1H), 4.63 (s, 1H), 4.42 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 142.0, 141.7, 136.3, 130.5, 129.1, 129.0, 127.9, 127.6, 126.4, 125.3, 125.0, 123.8, 123.4, 122.1, 122.0, 121.4, 120.0, 119.8, 118.5, 112.0, 111.2, 61.4, 50.0, 42.8, 41.1; HRMS (ESI) m/z calcd for $C_{32}H_{25}BrN_2O_3S$ $[M - H]^-$ = 595.0696, found = 595.0698; the *ee* value was 89%, t_R (major) = 12.4 min, t_R (minor) = 34.5 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.553	30582	1183	50.093	73.475
2	34.884	30468	427	49.907	26.525
Total		61050	1610	100.000	100.000

Racemic **3v**

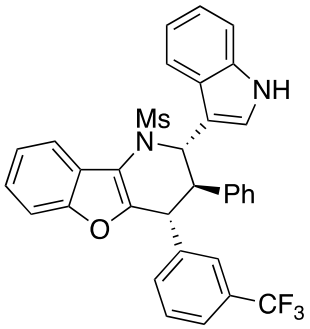


<Peak Table>
Detector A 254nm

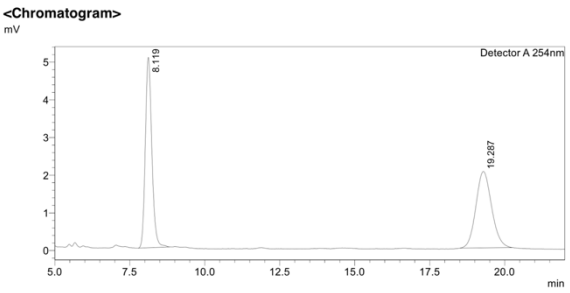
Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.439	1347684	53677	94.615	97.916
2	34.502	76705	1142	5.385	2.084
Total		1424390	54819	100.000	100.000

Enantioenriched **3v**

(2S,3R,4R)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-3-phenyl-4-(3-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3w**



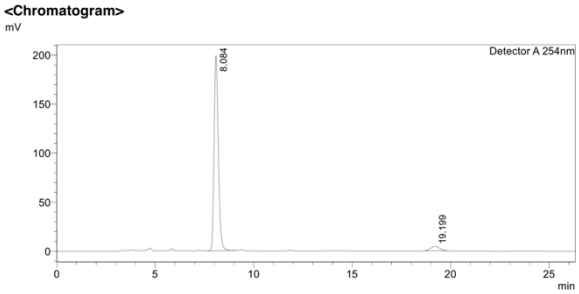
Yellowish oil; isolated yield = 92%; $[\alpha]_D^{25}$ = –93 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 – 8.28 (m, 1H), 7.84 (s, 1H), 7.55 – 7.24 (m, 8H), 7.09 – 6.70 (m, 8H), 6.02 (d, *J* = 4.7 Hz, 1H), 4.72 (d, *J* = 2.8 Hz, 1H), 4.48 – 4.43 (m, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 141.6, 140.8, 136.3, 130.8, 129.6, 129.3, 129.0, 127.9, 127.9, 127.7, 125.1, 124.1, 123.9 (q, *J* = 271 Hz), 123.5, 123.4, 122.7, 122.1, 122.0, 120.2, 119.7, 118.4, 112.8, 111.9, 111.3, 61.4, 49.9, 42.7, 41.0; HRMS (ESI) m/z calcd for $C_{33}H_{25}F_3N_2O_3S$ $[M - H]^-$ = 585.1465, found = 585.1470; the *ee* value was 90%, t_R (major) = 8.1 min, t_R (minor) = 19.2 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.119	76437	5052	50.898	71.367
2	19.287	73739	2027	49.102	28.633
Total		150176	7079	100.000	100.000

Racemic **3w**

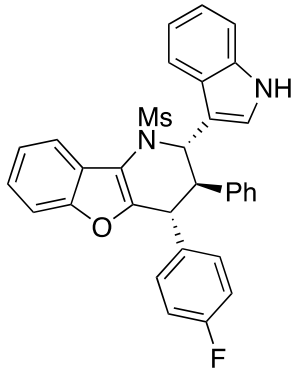


<Peak Table>
Detector A 254nm

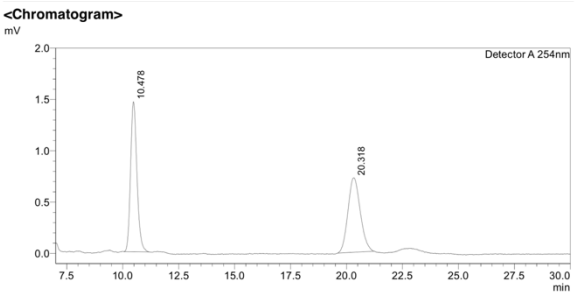
Peak#	Ret. Time	Area	Height	Area%	Height%
1	8.084	2979829	198966	95.199	97.808
2	19.199	150289	4460	4.801	2.192
Total		3130119	203425	100.000	100.000

Enantioenriched **3w**

(2S,3R,4R)-4-(4-fluorophenyl)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-3-phenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3x**



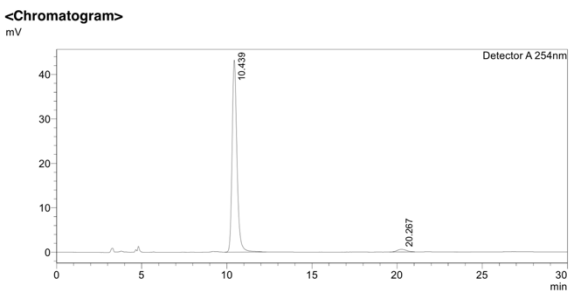
Yellowish oil; isolated yield = 93%; $[\alpha]_D^{25}$ = –113 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 1H), 7.93 (s, 1H), 7.56 – 7.32 (m, 6H), 7.25 – 7.14 (m, 9H), 7.14 – 7.00 (m, 4H), 6.82 – 6.81 (m,1H), 6.72 – 6.56 (m, 5H), 5.88 (d, *J* = 6.8 Hz, 1H), 4.57 (d, *J* = 5.4 Hz, 1H), 4.41 – 4.35 (m, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.3 (d, *J* = 244 Hz), 154.1, 145.7, 141.6, 136.0, 135.2 (d, *J* = 3 Hz), 129.4 (d, *J* = 8 Hz), 128.8, 128.0, 127.3, 126.0, 124.8, 123.2, 123.1, 122.3, 121.6, 120.1, 112.0, 118.5, 114.6 (d, *J* = 22 Hz), 112.0, 111.8, 111.4, 61.4, 51.4, 44.7, 41.5; HRMS (ESI) m/z calcd for $C_{32}H_{25}FN_2O_3S$ [M - H]$^-$ = 535.1497, found = 535.1492; the *ee* value was 95%, t_R (major) = 10.4 min, t_R (minor) = 20.3 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.478	29000	1462	51.042	66.837
2	20.318	27816	725	48.958	33.163
Total		56815	2187	100.000	100.000

Racemic **3x**

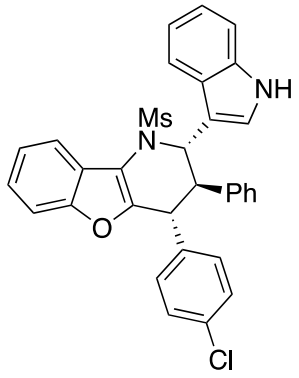


<Peak Table>
Detector A 254nm

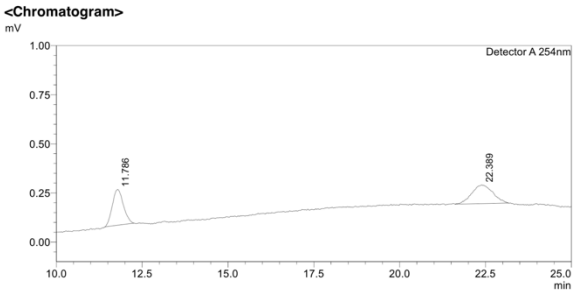
Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.439	857800	43232	97.470	98.656
2	20.267	22270	589	2.530	1.344
Total		880069	43821	100.000	100.000

Enantioenriched **3x**

(2S,3R,4R)-4-(4-chlorophenyl)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-3-phenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3y**



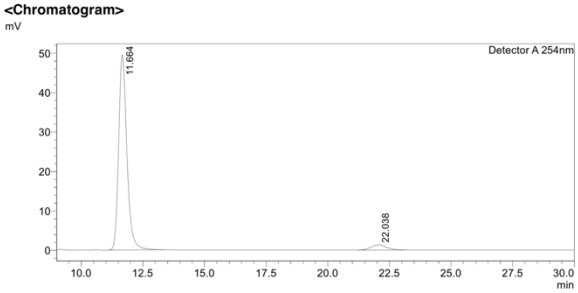
Yellowish oil; isolated yield = 83%; $[a]_D^{25}$ = –50 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.08 (m, 1H), 7.90 (s, 1H), 7.59 – 7.31 (m, 4H), 7.28 – 6.99 (m, 7H), 6.86 – 6.84 (m, 3H), 6.64 – 6.62 (m, 2H), 5.89 (d, *J* = 6.5 Hz, 1H), 4.57 (d, *J* = 4.9 Hz, 1H), 4.40 – 4.37 (m,1H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 141.6, 138.0, 136.0, 132.1, 129.1, 128.8, 128.3, 128.0, 127.9, 127.4, 125.9, 125.4, 124.9, 124.7, 123.3, 123.0, 122.4, 121.7, 120.2, 120.0, 118.6, 111.8, 111.4, 61.4, 53.5, 51.0, 41.5; HRMS (ESI) m/z calcd for $C_{32}H_{25}ClN_2O_3S$ $[M - H]^-$ = 551.1202, found = 551.1204; the *ee* value was 91%, t_R (major) = 11.7 min, t_R (minor) = 22.0 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.786	4103	183	50.335	65.636
2	22.389	4048	96	49.665	34.364
Total		8151	278	100.000	100.000

Racemic **3y**

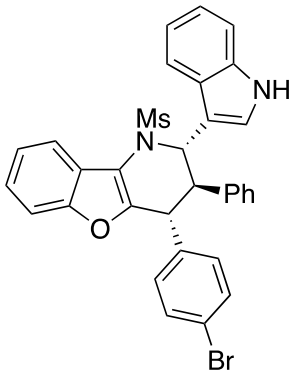


<Peak Table>
Detector A 254nm

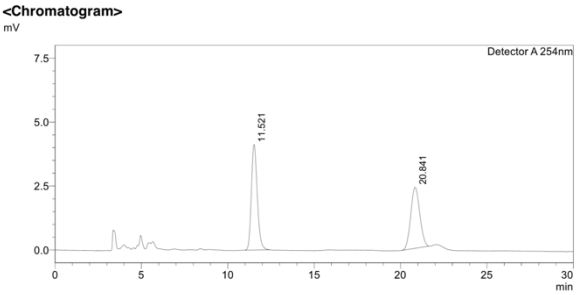
Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.664	1154114	49521	95.287	97.466
2	22.038	57087	1287	4.713	2.534
Total		1211201	50808	100.000	100.000

Enantioenriched **3y**

(2S,3R,4R)-4-(4-bromophenyl)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-3-phenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3z**



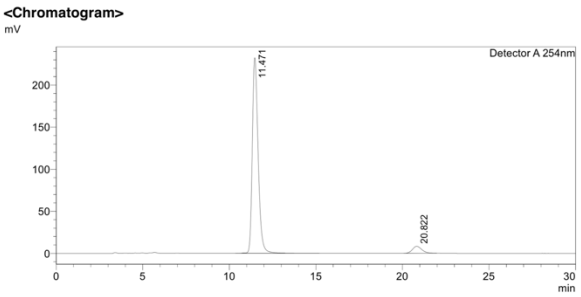
Yellowish oil; isolated yield = 80%; $[\alpha]_D^{25}$ = –160 (c 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.09 (m, 1H), 7.88 (s, 1H), 7.54 – 7.44 (m, 2H), 7.40 – 7.31 (m, 2H), 7.31 – 7.15 (m, 5H), 7.13 – 7.10 (m, 1H), 7.05 – 6.95 (m, 3H), 6.84 – 6.80 (m, 1H), 6.57 – 6.55 (m, 2H), 5.90 (d, *J* = 6.6 Hz, 1H), 4.55 (d, *J* = 5.0 Hz, 1H), 4.40 – 4.38 (m, 1H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 141.5, 138.6, 136.1, 130.8, 129.5, 128.9, 128.0, 127.4, 124.9, 124.6, 123.3, 122.9, 122.4, 121.7, 120.2, 120.0, 118.5, 112.2, 111.8, 111.5, 61.4, 50.8, 44.4, 41.5; HRMS (ESI) m/z calcd for $C_{32}H_{25}BrN_2O_3S$ [M - H]$^-$ = 595.0696, found = 595.0685; the *ee* value was 89%, t_R (major) = 11.5 min, t_R (minor) = 20.8 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.521	98519	4121	53.026	63.286
2	20.841	87274	2391	46.974	36.714
Total		185793	6512	100.000	100.000

Racemic **3z**

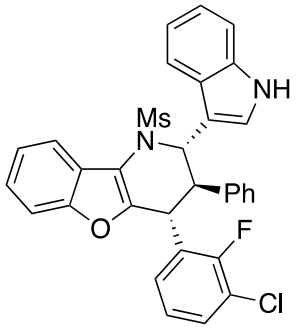


<Peak Table>
Detector A 254nm

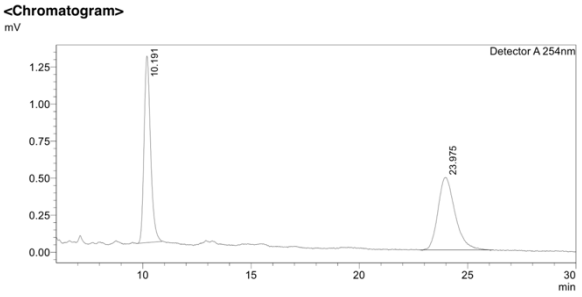
Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.471	5486626	232360	94.615	96.564
2	20.822	312259	8267	5.385	3.436
Total		5798885	240627	100.000	100.000

Enantioenriched **3z**

(2S,3R,4R)-4-(3-chloro-2-fluorophenyl)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-3-phenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3a'**



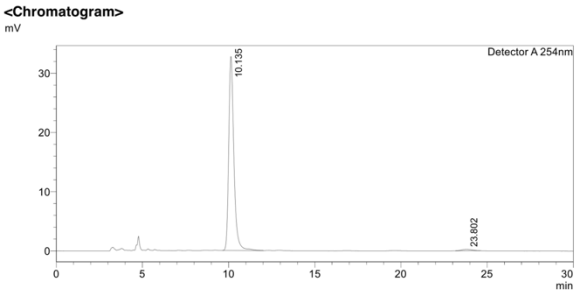
Yellowish oil; isolated yield = 90%; $[\alpha]_D^{25}$ = –75 (c 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 – 8.28 (m, 1H), 7.81 (s, 1H), 7.53 – 7.47 (m, 2H), 7.43 – 7.20 (m, 6H), 7.12 – 6.97 (m, 3H), 6.85 – 6.68 (m, 2H), 6.31 – 6.28 (m, 1H), 6.06 – 5.90 (m, 2H), 4.92 (d, *J* = 3.1 Hz, 1H), 4.58 – 4.53 (m, 1H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.8 (d, *J* = 247 Hz), 154.2, 141.4, 136.7, 129.0, 128.1, 128.0, 127.8, 127.6 (d, *J* = 4 Hz), 125.2, 123.6, 123.4, 123.0 (d, *J* = 5 Hz), 122.2 (d, *J* = 8 Hz), 120.3, 119.9, 118.6, 113.7, 112.0, 111.2, 61.8, 47.5, 40.8, 37.2; HRMS (ESI) m/z calcd for $C_{32}H_{24}ClFN_2O_3S$ [M - H]$^-$ = 569.1107, found = 569.1105; the *ee* value was 97%, t_R (major) = 10.1 min, t_R (minor) = 23.8 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.191	26299	1260	49.546	72.042
2	23.975	26781	489	50.454	27.958
Total		53080	1749	100.000	100.000

Racemic **3a'**

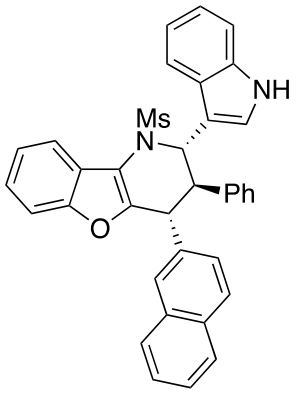


<Peak Table>
Detector A 254nm

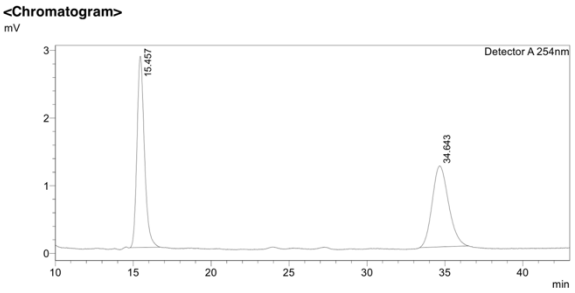
Peak#	Ret. Time	Area	Height	Area%	Height%
1	10.135	685010	32745	98.549	99.302
2	23.802	10089	230	1.451	0.698
Total		695099	32976	100.000	100.000

Enantioenriched **3a'**

(2S,3R,4R)-2-(1*H*-indol-3-yl)-1-(methylsulfonyl)-4-(naphthalen-2-yl)-3-phenyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine **3b'**



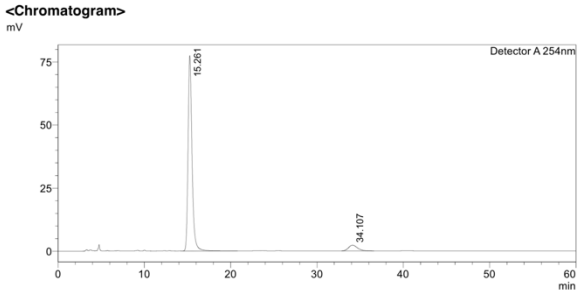
Yellowish oil; isolated yield = 85%; $[a]_D^{25}$ = –135 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 1H), 7.81 (s, 1H), 7.64 – 7.51 (m, 2H), 7.48 – 7.29 (m, 6H), 7.21 – 7.17 (m, 5H), 7.07 (s, 1H), 7.03 – 6.85 (m, 5H), 5.90 (d, *J* = 7.1 Hz, 1H), 4.74 (d, *J* = 5.6 Hz, 1H), 4.56 – 4.50 (m, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 141.8, 136.8, 135.8, 133.0, 132.2, 128.7, 128.1, 127.8, 127.6, 127.4, 127.2, 127.2, 126.1, 125.9, 125.7, 125.4, 125.1, 124.6, 123.4, 123.2, 122.14 121.5, 120.1, 119.9, 118.5, 111.9, 111.1, 61.5, 51.1, 46.0, 41.7; HRMS (ESI) m/z calcd for $C_{36}H_{28}N_2O_3S$ [M - H]$^-$ = 567.1748, found = 567.1754; the *ee* value was 87%, t_R (major) = 15.3 min, t_R (minor) = 34.1 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	15.457	93162	2825	51.645	70.257
2	34.643	87227	1196	48.355	29.743
Total		180389	4021	100.000	100.000

Racemic **3b'**

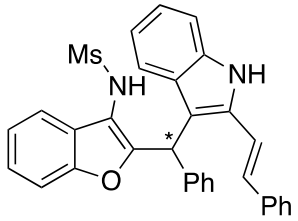


<Peak Table>
Detector A 254nm

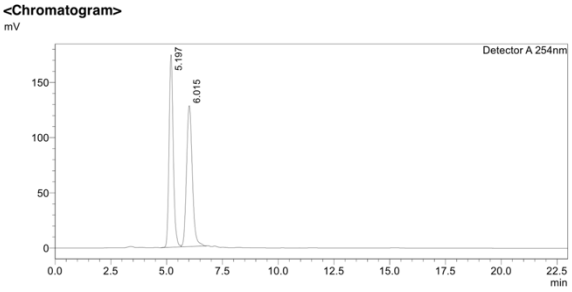
Peak#	Ret. Time	Area	Height	Area%	Height%
1	15.261	2472680	77426	93.711	97.130
2	34.107	165955	2288	6.289	2.870
Total		2638635	79714	100.000	100.000

Enantioenriched **3b'**

(*E*)-N-(2-(phenyl(2-styryl-1*H*-indol-3-yl)methyl)benzofuran-3-yl)methanesulfonamide **5**



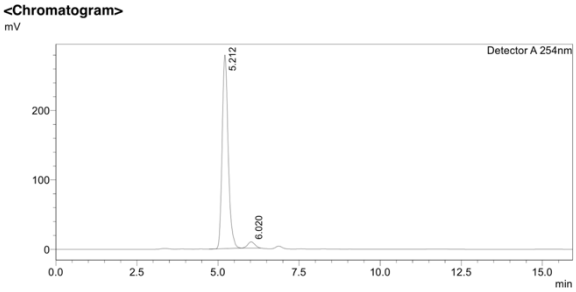
Yellowish oil; isolated yield = 95%; $[a]_D^{25}$ = +75 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.58 – 7.56 (m, 1H), 7.49 – 7.34 (m, 4H), 7.34 – 7.14 (m, 13H), 7.02 – 6.99 (m, 1H), 6.83 (d, *J* = 16.3 Hz, 1H), 6.49 (s, 1H), 6.09 (d, *J* = 13.3 Hz, 1H), 2.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2, 153.3, 139.9, 136.7, 136.6, 133.8, 128.9, 128.6, 128.5, 128.3, 127.9, 127.9, 127.0, 126.5, 125.8, 124.8, 123.6, 123.4, 120.6, 120.2, 118.7, 117.0, 114.2, 113.5, 112.2, 110.7, 40.3, 38.9; HRMS (ESI) m/z calcd for $C_{32}H_{26}N_2O_3S$ $[M - H]^-$ = 517.1591, found = 517.1590; the *ee* value was 92%, t_R (major) = 5.2 min, t_R (minor) = 6.0 min (Chiralpak IC, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	5.197	2278979	174355	49.664	57.728
2	6.015	2309771	127674	50.336	42.272
Total		4588750	302030	100.000	100.000

Racemic **5**

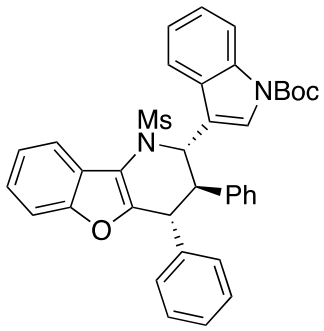


<Peak Table>
Detector A 254nm

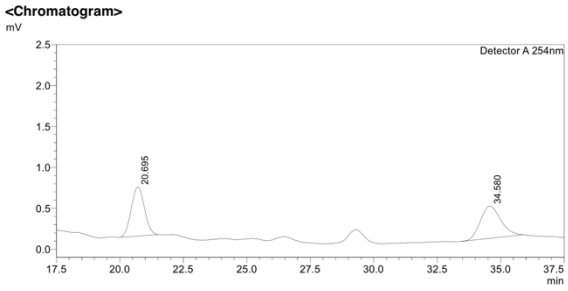
Peak#	Ret. Time	Area	Height	Area%	Height%
1	5.212	3605079	279142	96.293	96.905
2	6.020	138788	8916	3.707	3.095
Total		3743868	288057	100.000	100.000

Enantioenriched **5**

3a-I

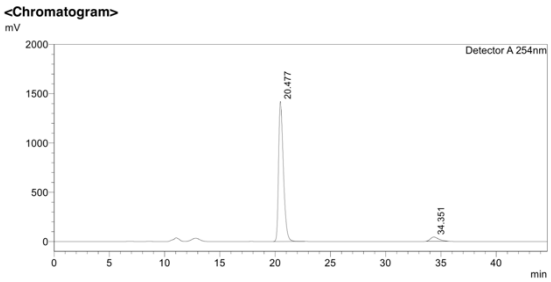


Off white oil; isolated yield = 96%; $[\alpha]_D^{25}$ = –35.5 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.20 (m, 1H), 7.88 – 7.86 (m, 1H), 7.57 – 7.06 (m, 12H), 6.82 – 6.79 (m, 3H), 6.71 – 6.61 (m, 2H), 5.92 – 5.91 (m, 1H), 4.71 (d, *J* = 3.6 Hz, 1H), 4.35 – 4.32 (m, 1H), 2.41 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.10, 149.27, 143.98, 141.49, 139.22, 135.47, 128.94, 128.37, 128.02, 127.99, 127.69, 127.63, 127.41, 126.12, 126.08, 125.15, 124.88, 124.77, 124.21, 123.34, 122.40, 122.21, 121.80, 119.60, 118.75, 117.55, 115.19, 111.77, 83.61, 60.83, 50.27, 42.69, 40.71, 28.03, 27.95, 27.72; HRMS (ESI) m/z calcd for $C_{37}H_{35}N_2O_5S$ $[M + H]^+$ = 619.2261, found = 619.2278; the *ee* value was 90%, t_R (major) = 20.5 min, t_R (minor) = 34.4 min (Chiralpak IE, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 0.5 mL/min).



<Peak Table>
Detector A 254nm

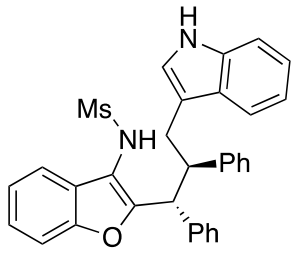
Peak#	Ret. Time	Area	Height	Area%	Height%
1	20.695	21735	600	49.739	60.351
2	34.580	21963	394	50.261	39.649
Total		43697	994	100.000	100.000



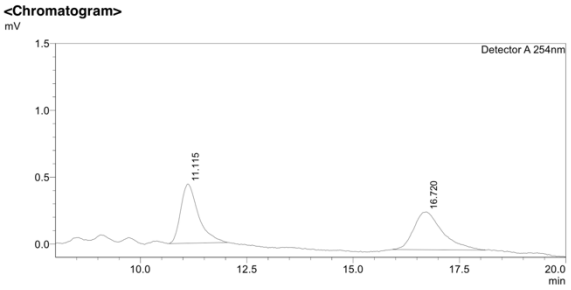
<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	20.477	42860533	1421595	94.935	97.047
2	34.351	2286655	43250	5.065	2.953
Total		45147188	1464845	100.000	100.000

3a-II

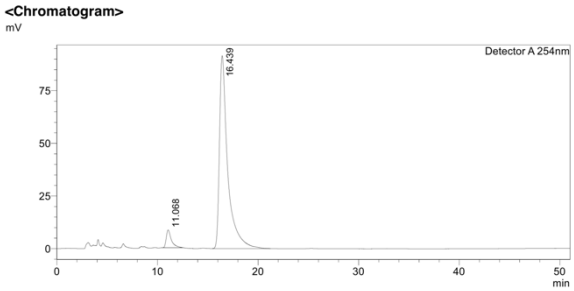


Pale yellow oil; isolated yield = 93%; $[a]_D^{25}$ = –33.8 (c 1.0, MeOH); ^{1}H NMR (400 MHz, CD_3CN) δ 8.68 (s, 1H), 7.63 – 7.53 (m, 2H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.32 – 7.21 (m, 5H), 7.19 – 7.14 (m, 1H), 7.04 – 6.90 (m, 9H), 6.40 (d, *J* = 2.2 Hz, 1H), 4.81 (d, *J* = 11.4 Hz, 1H), 3.92 (td, *J* = 11.4, 3.3 Hz, 1H), 3.02 (dd, *J* = 14.5, 11.4 Hz, 1H), 2.90 – 2.82 (m, 4H); ^{13}C NMR (100 MHz, CD_3CN) δ 156.9, 153.8, 143.4, 140.7, 136.7, 129.4, 129.3, 128.6, 128.3, 127.9, 127.1, 126.6, 125.3, 124.0, 123.2, 121.7, 119.9, 119.2, 118.8, 115.2, 113.6, 112.0, 111.7, 51.3, 49.0, 40.5, 31.1; HRMS (ESI) m/z calcd for $C_{32}H_{27}N_2O_3S$ [M - H]$^-$ = 519.1748, found = 519.1760; the *ee* value was 89%, t_R (major) = 16.4 min, t_R (minor) = 11.1 min (Chiralpak AD-H, λ = 254 nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.115	12815	443	49.158	60.998
2	16.720	13254	283	50.842	39.002
Total		26069	727	100.000	100.000



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.068	304095	8475	5.501	8.471
2	16.439	5223845	91565	94.499	91.529
Total		5527940	100040	100.000	100.000

D. X-Ray Crystallographic Analysis and Determination of the Absolute Configurations of Product 3b

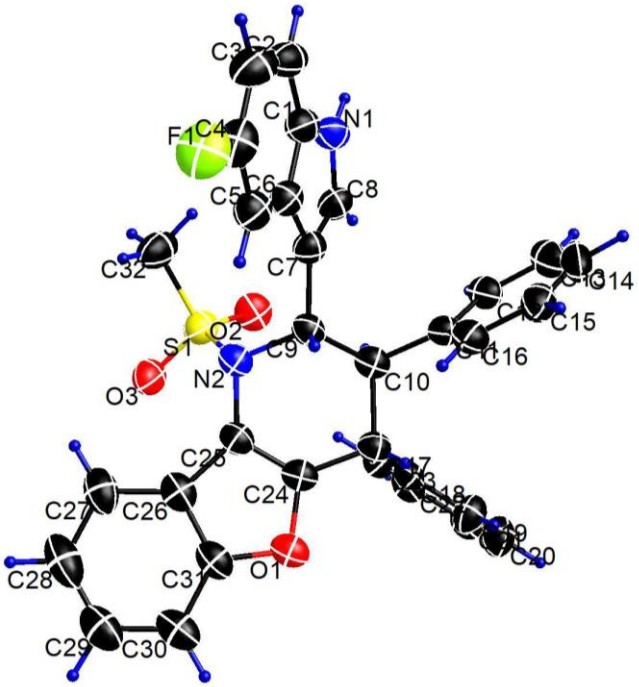


Figure 1. X-ray structure of **3b** (CCDC 2027692)

Table 1. Crystal data and structure refinement for K255.

Identification code	K255	
Empirical formula	C35 H32 F N2 O3 S	
Formula weight	579.68	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.8396(7) Å	a= 90°.
	b = 14.8000(10) Å	b= 90°.
	c = 20.0419(13) Å	g = 90°.
Volume	3215.2(4) $Å^3$	
Z	4	
Density (calculated)	1.198 Mg/m^3	

Absorption coefficient	0.142 mm^{-1}

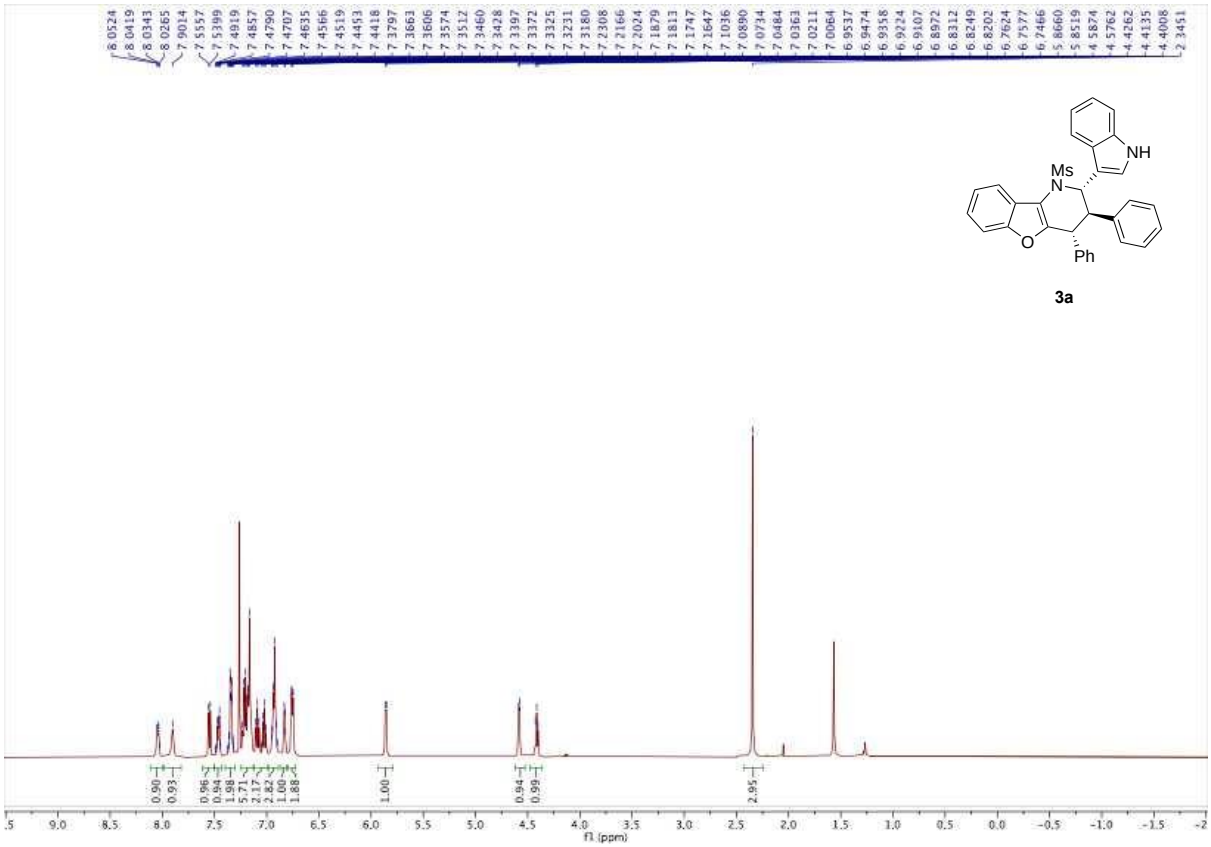
F(000)	1220
Crystal size	0.340 x 0.272 x 0.051 mm^3
Theta range for data collection	2.753 to 29.756°.
Index ranges	-15<=h<=15, -20<=k<=20, -25<=l<=27
Reflections collected	46293
Independent reflections	9075 [R(int) = 0.0911]
Completeness to theta = 25.242°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7459 and 0.5968
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9075 / 49 / 409
Goodness-of-fit on F^2	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0703, wR2 = 0.1644
R indices (all data)	R1 = 0.1416, wR2 = 0.2051
Absolute structure parameter	-0.03(5)
Extinction coefficient	0.025(3)
Largest diff. peak and hole	0.730 and -0.534 e.$Å^{-3}$

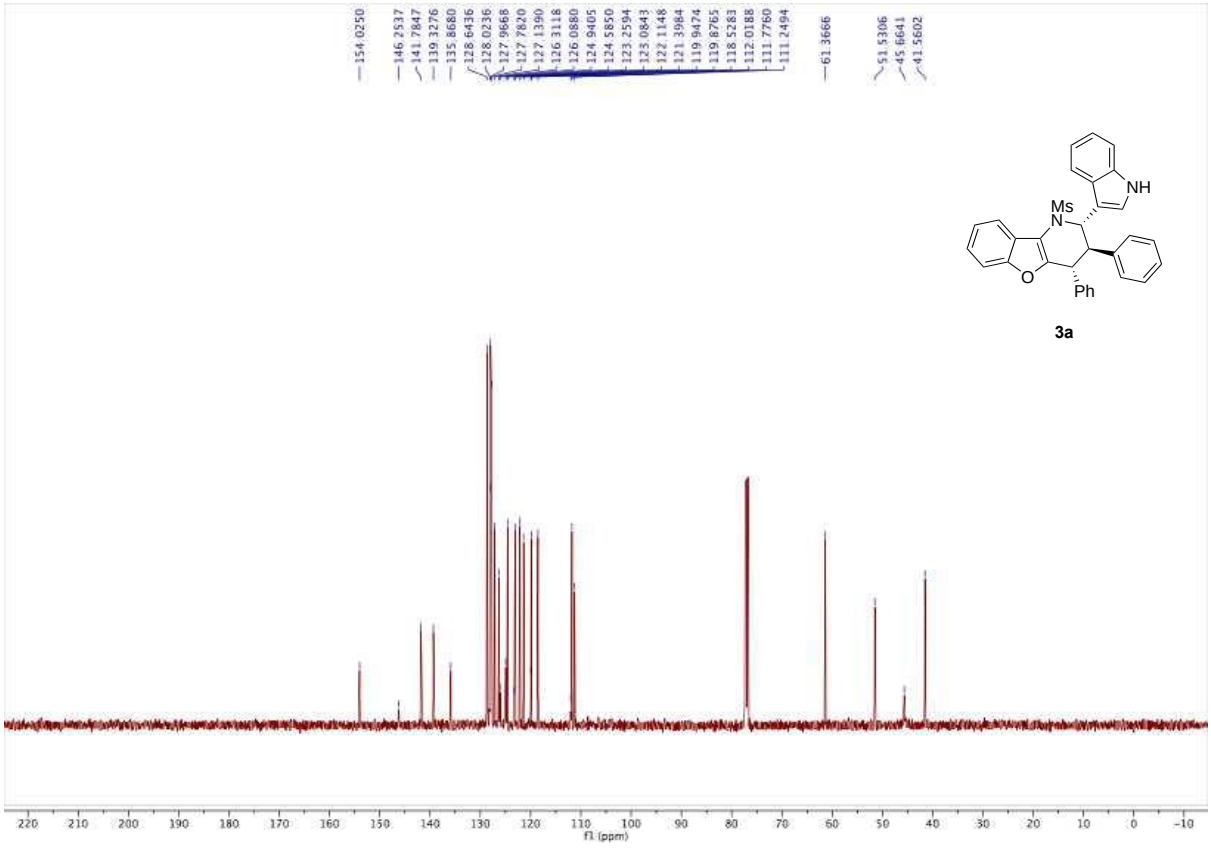
E. References

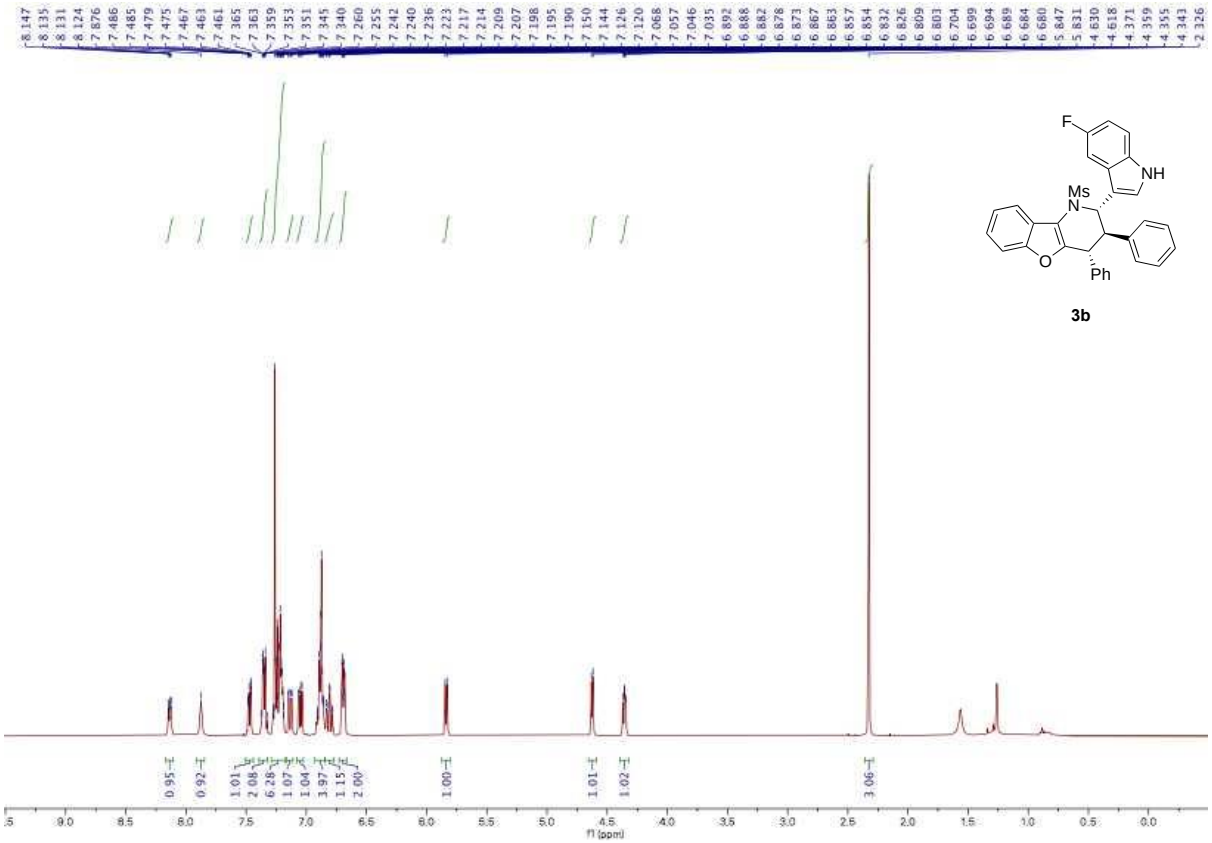
[1] H. Ni, X. Tang, W. Zheng, W. Yao, N. Ullah and Y. Lu, *Angew. Chem. Int. Ed.*, 2017, **56**, 14222-14226.

[2] X.-K. Guan, G.-F. Liu, D. An, H. Zhang and S.-Q. Zhang, *Org. Lett.*, 2019, **21**, 5438-5422.

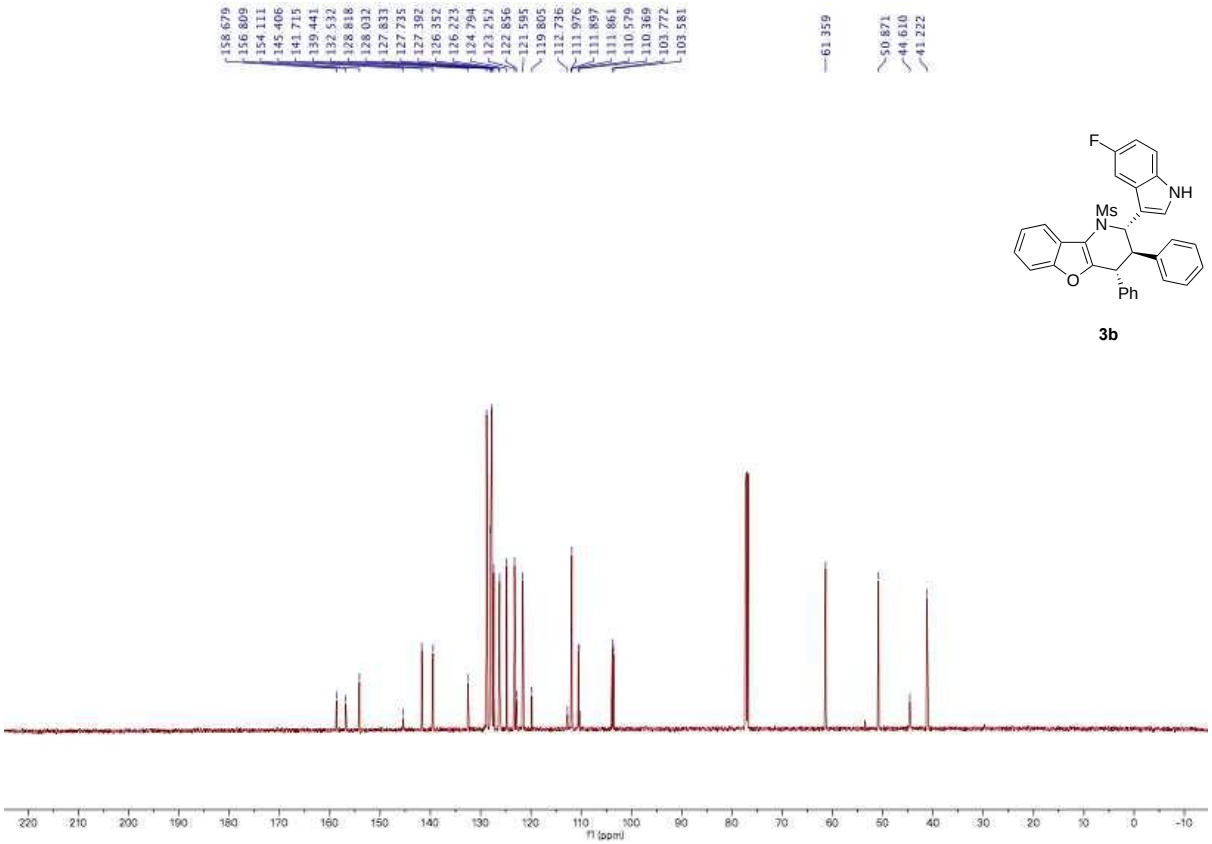
F. ^{1}H and ^{13}C NMR Spectra of Products



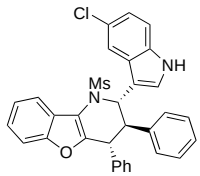




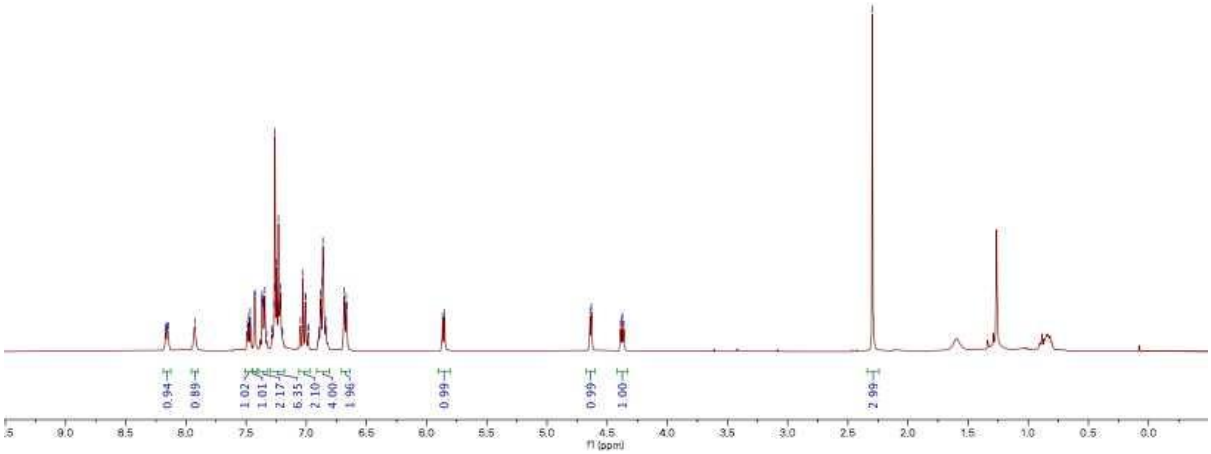
3b

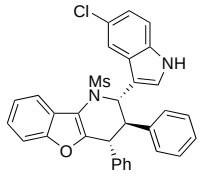


3b

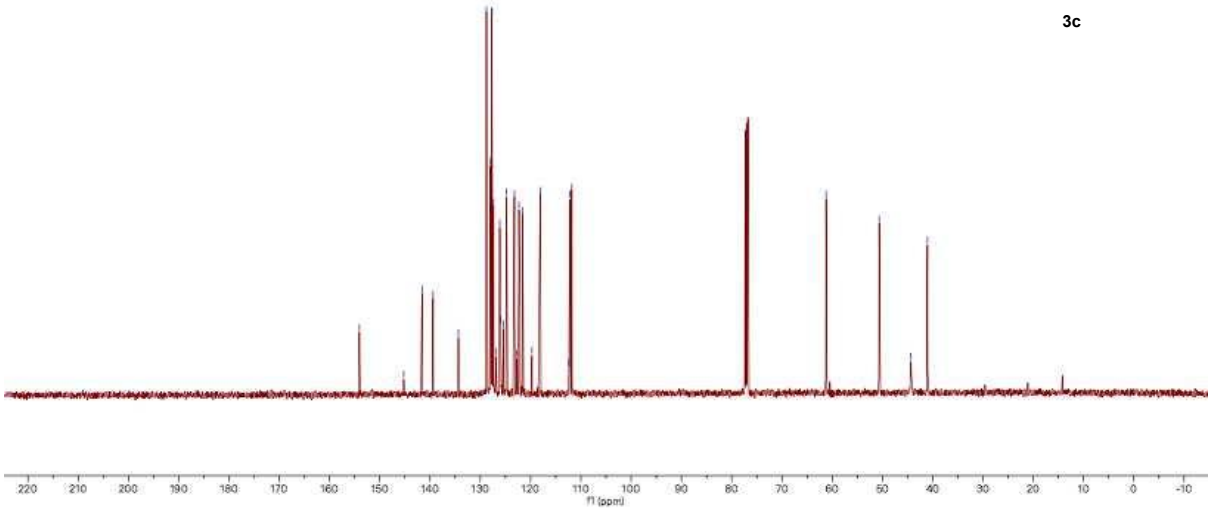


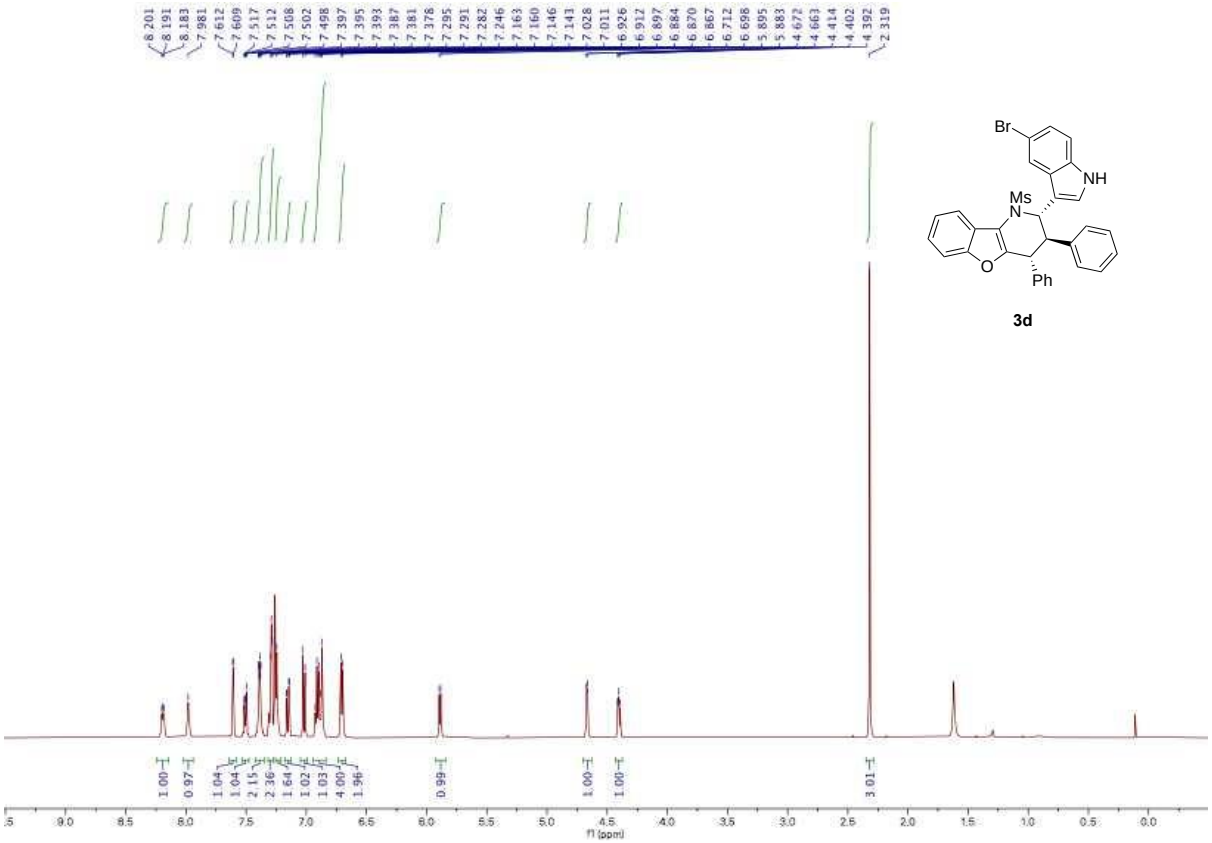
3c



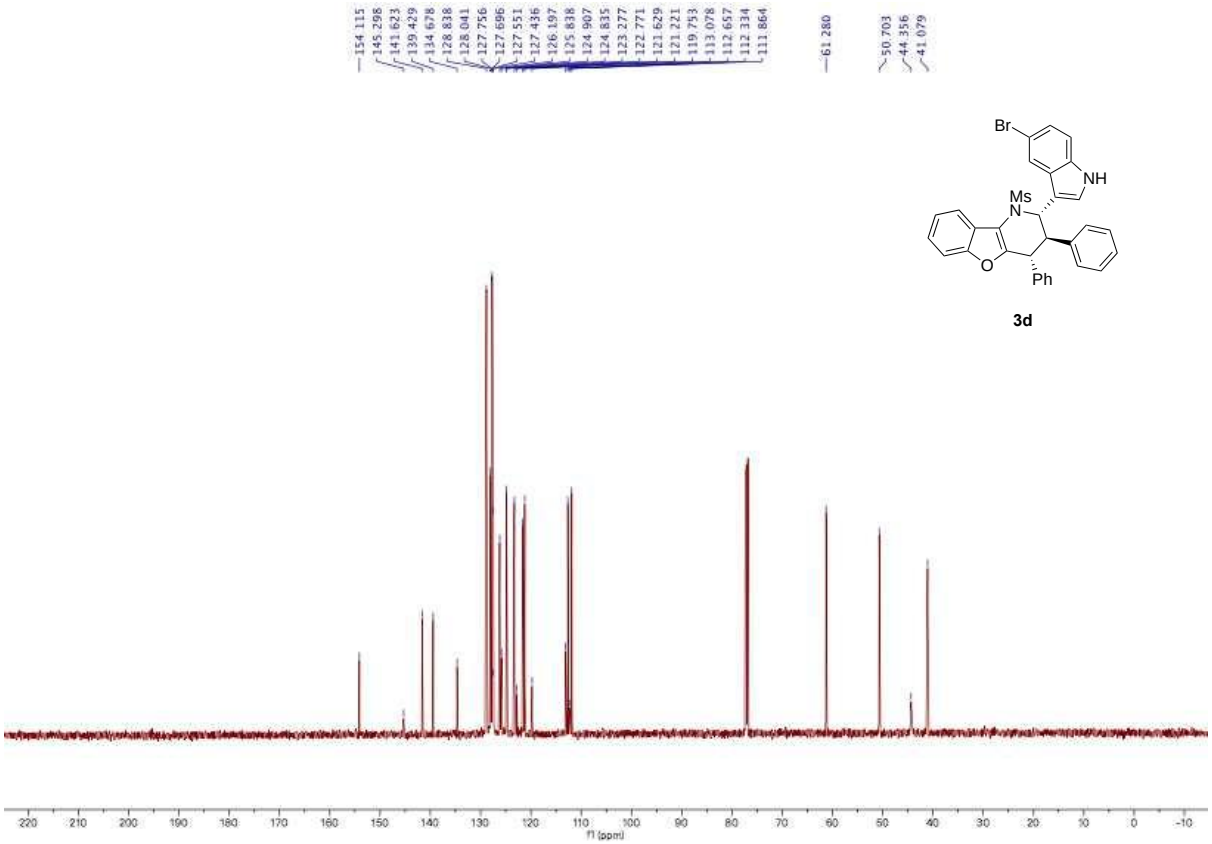


3c

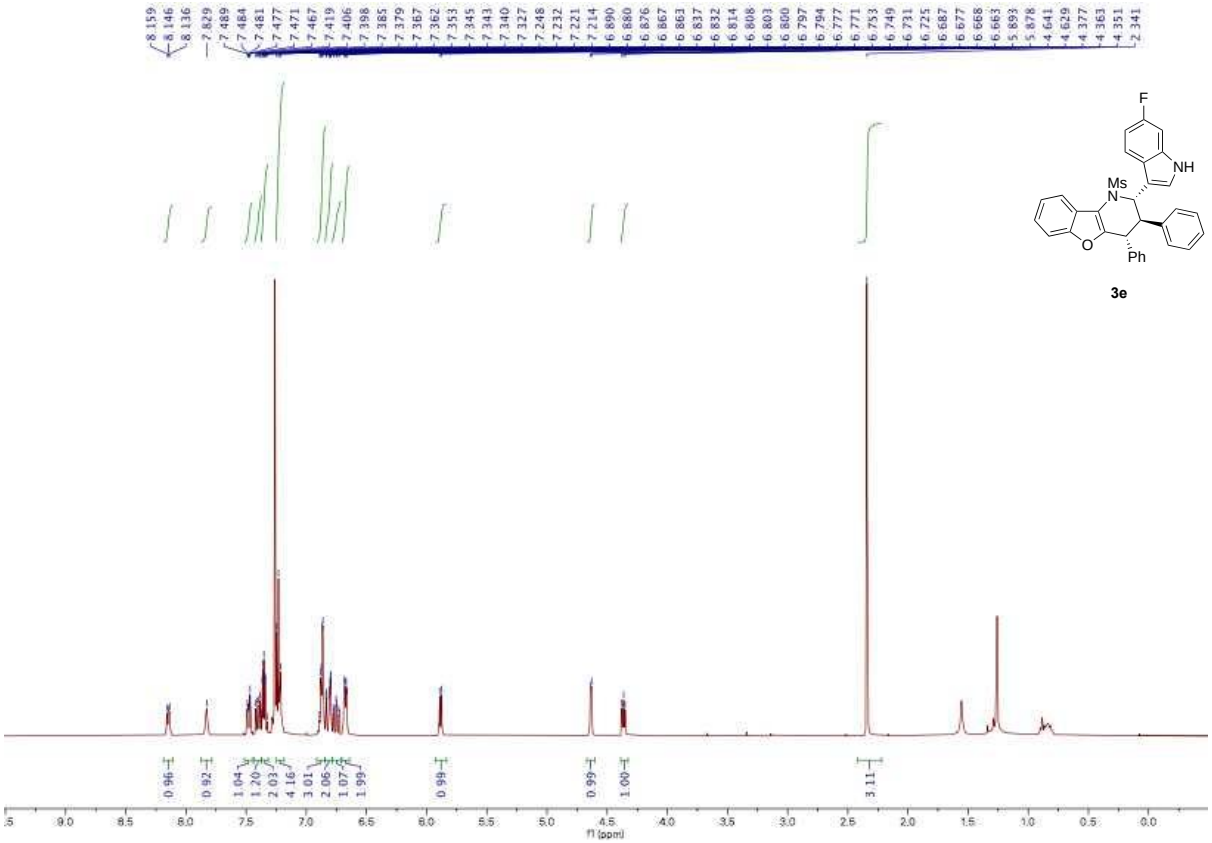




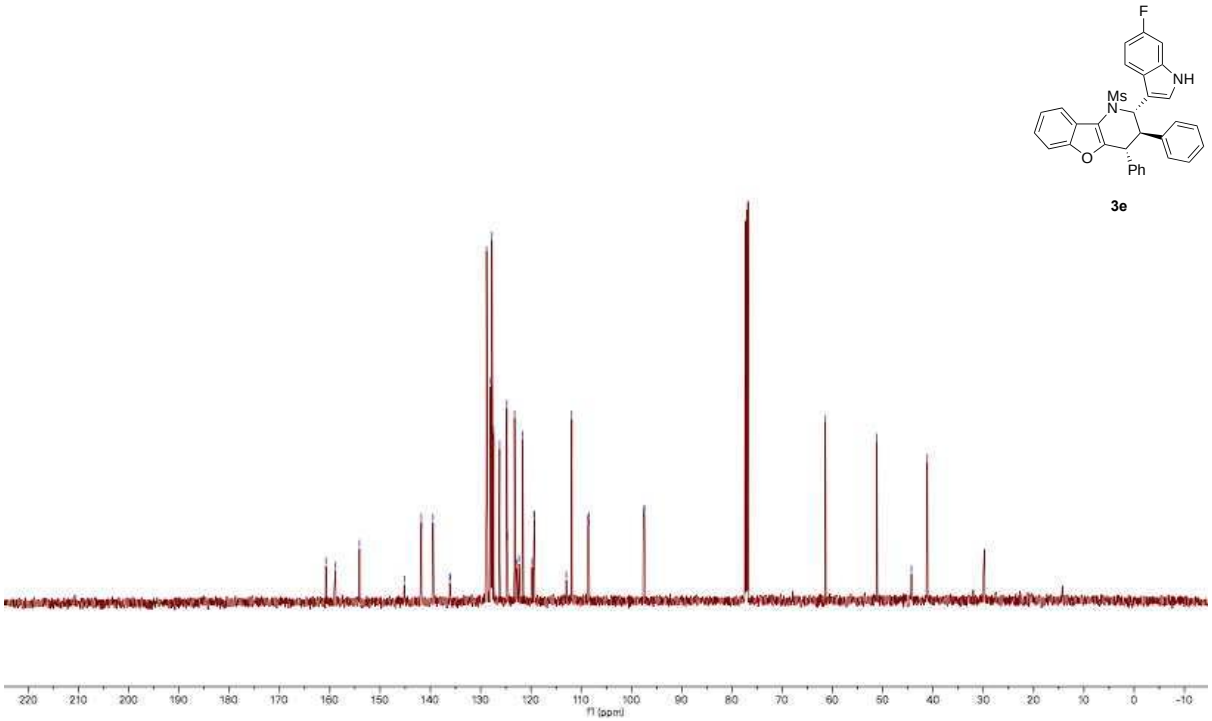
3d



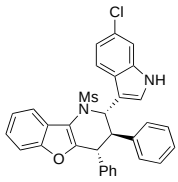
3d



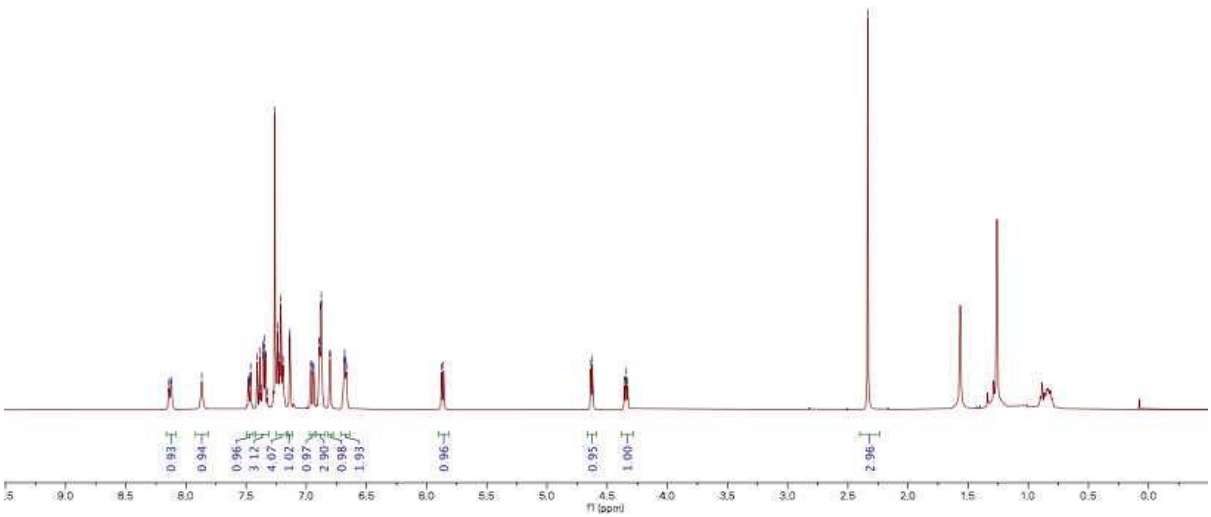
3e

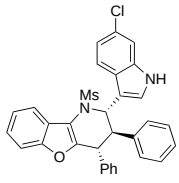


3e



3f





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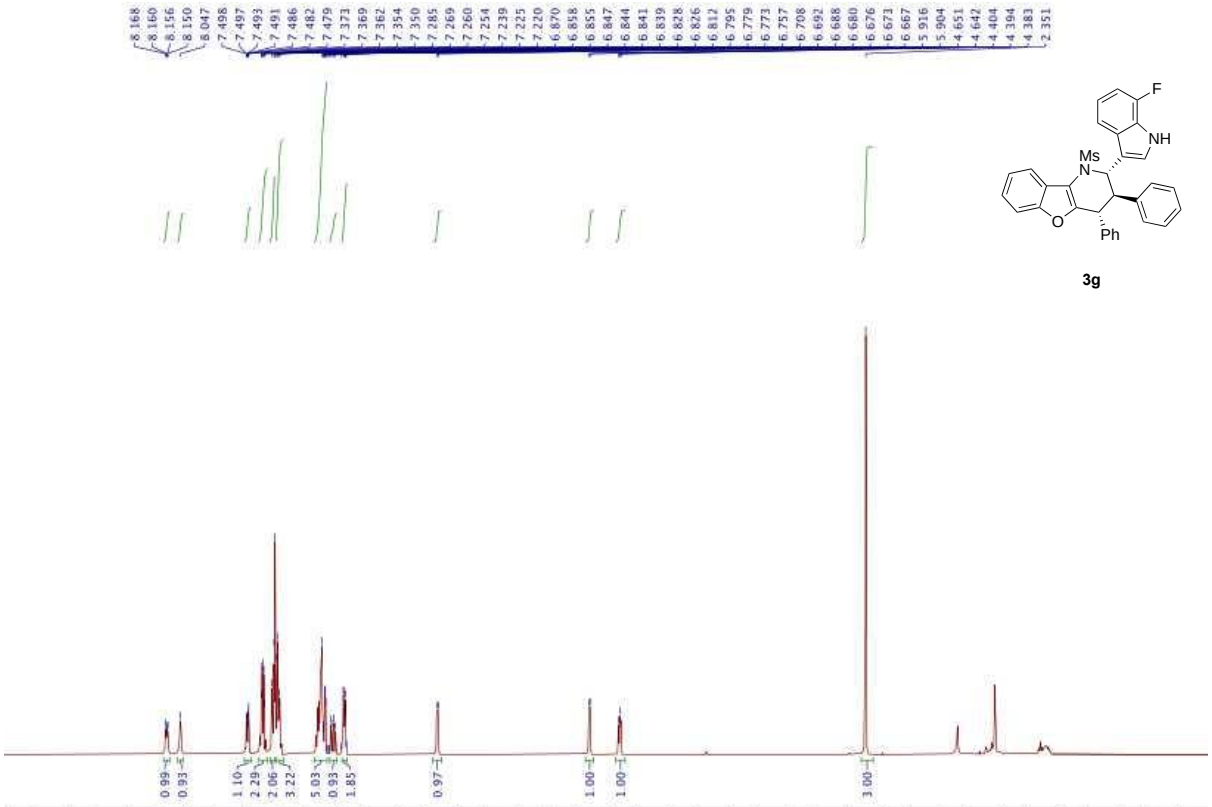
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7.493
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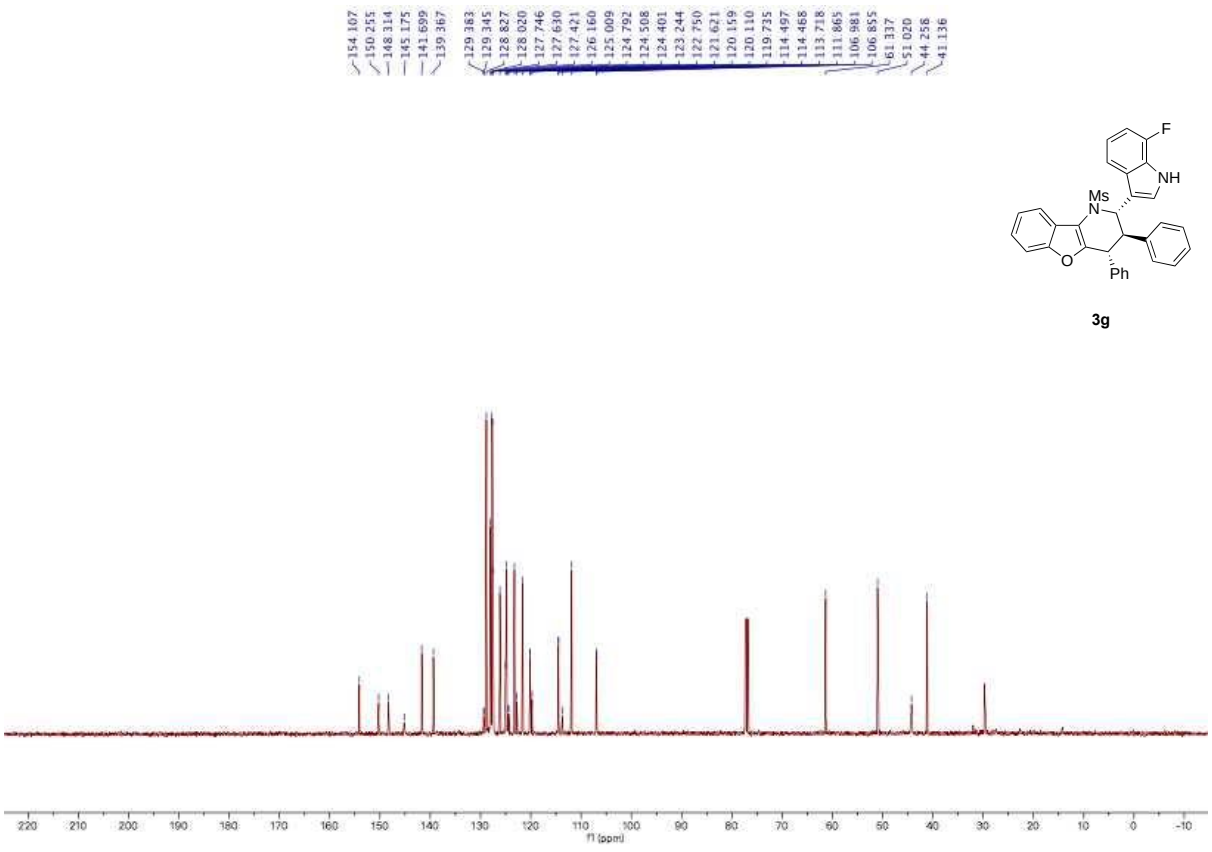
7.486
7.482
7.479
7.373
7.369
7.362
7.354
7.350
7.285
7.269
7.260
7.254
7.239
7.225
7.220
6.870
6.858
6.855
6.847
6.844
6.841
6.839
6.828
6.826
6.812
6.795
6.779
6.773
6.757
6.708
6.692
6.688
6.680
6.676
6.671
6.667
5.916
5.904
4.651
4.642
4.404
4.394
4.383
2.351
F
NH
Ms
N
O
Ph
3g
0.99
0.93
1.10
2.29
2.06
3.22
5.03
0.93
1.85
0.97
1.00
1.00
3.00
f1 (ppm)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150.255
148.314
145.175
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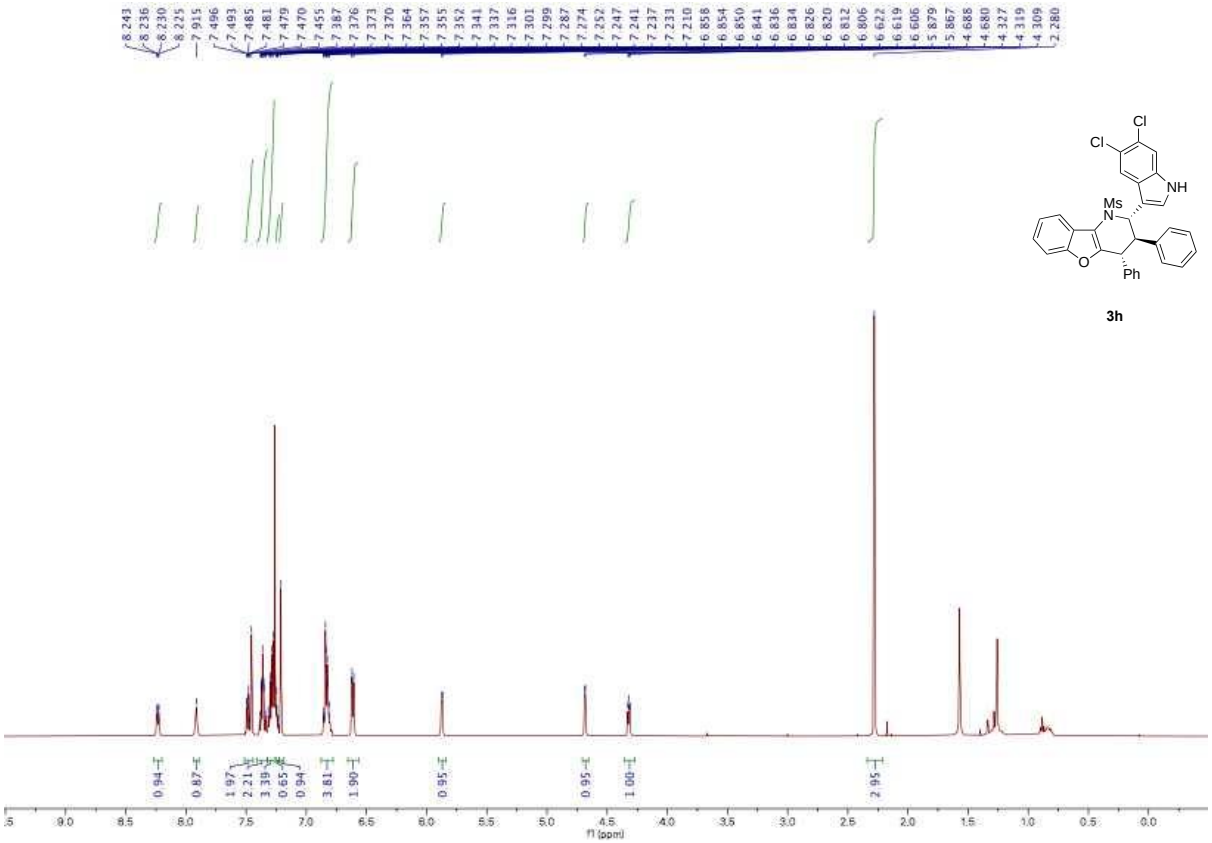
139.367
129.383
129.345
128.827
128.020
127.746
127.630
127.421
126.160
125.009
124.792
124.508
124.401
123.244
122.750
121.621
120.159
120.110
119.735
114.497
114.468
113.718
111.865
106.981
106.855
61.337
51.020
44.258
41.136
F
NH
Ms
N
O
Ph
3g
f1 (ppm)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8.225
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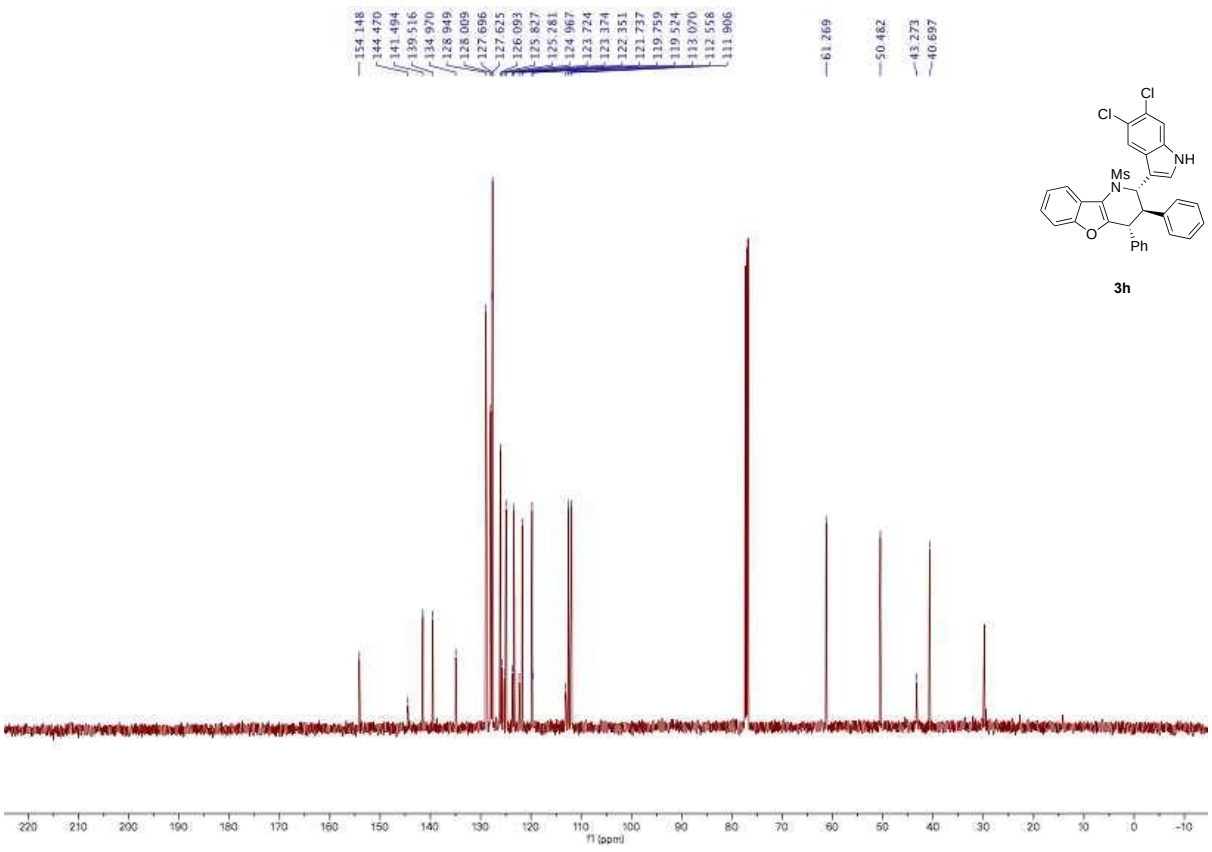
7.496
7.493
7.485
7.481
7.479
7.470
7.455
7.387
7.376
7.373
7.370
7.364
7.357
7.355
7.352
7.341
7.337
7.316
7.301
7.299
7.287
7.274
7.252
7.247
7.241
7.237
7.233
7.210
6.858
6.854
6.850
6.841
6.836
6.834
6.826
6.820
6.812
6.806
6.622
6.619
6.606
5.879
5.867
4.688
4.680
4.327
4.319
4.309
2.280
Cl
Cl
NH
Ms
N
O
Ph
0.94
0.87
1.97
2.21
3.39
0.65
0.94
3.81
1.90
0.95
0.95
1.00
2.95
f1 (ppm)

3h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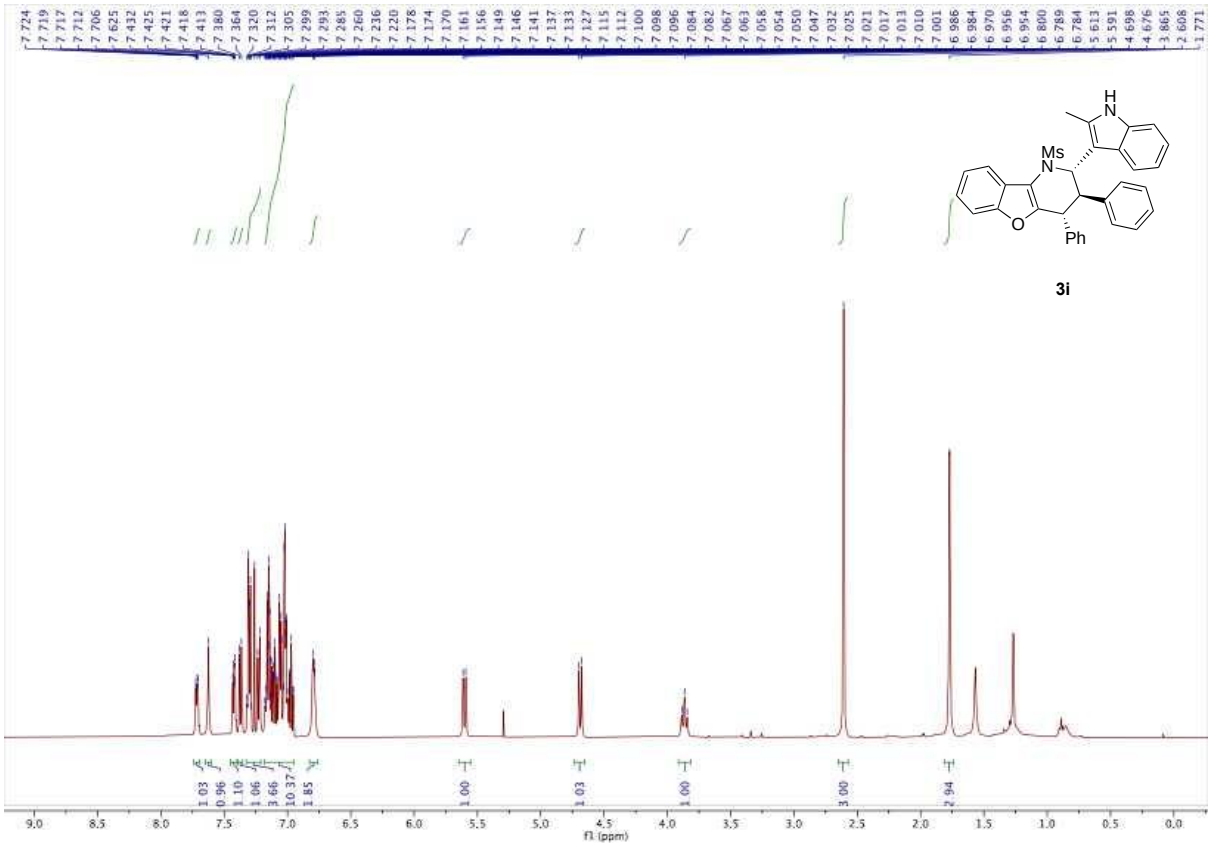
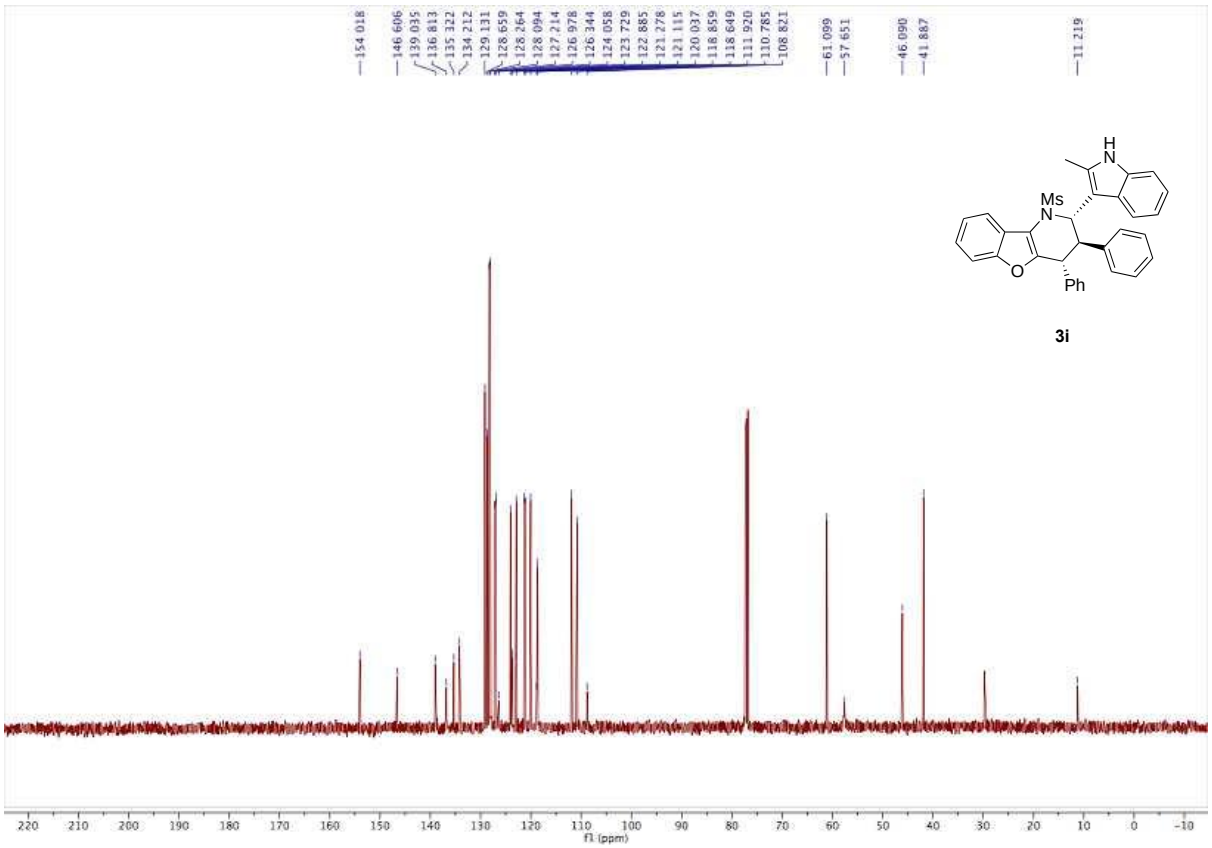
144.470
141.494
139.516
134.970
128.949
128.009
127.696
127.625
126.093
125.827
125.281
124.967
123.724
123.374
122.351
121.737
119.759
119.524
113.070
112.558
111.906
61.269
50.482
43.273
40.697
Cl
Cl
NH
Ms
N
O
Ph
f1 (ppm)

3h



3i



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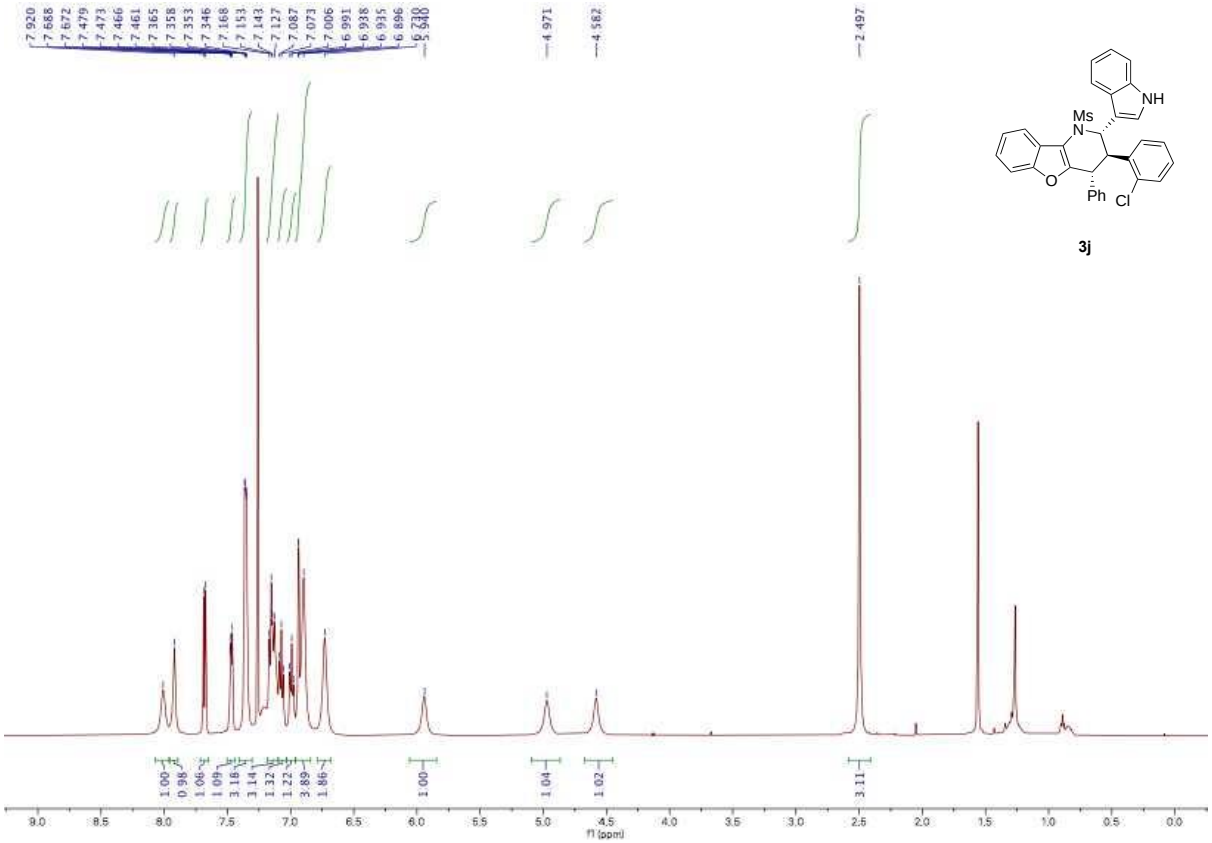
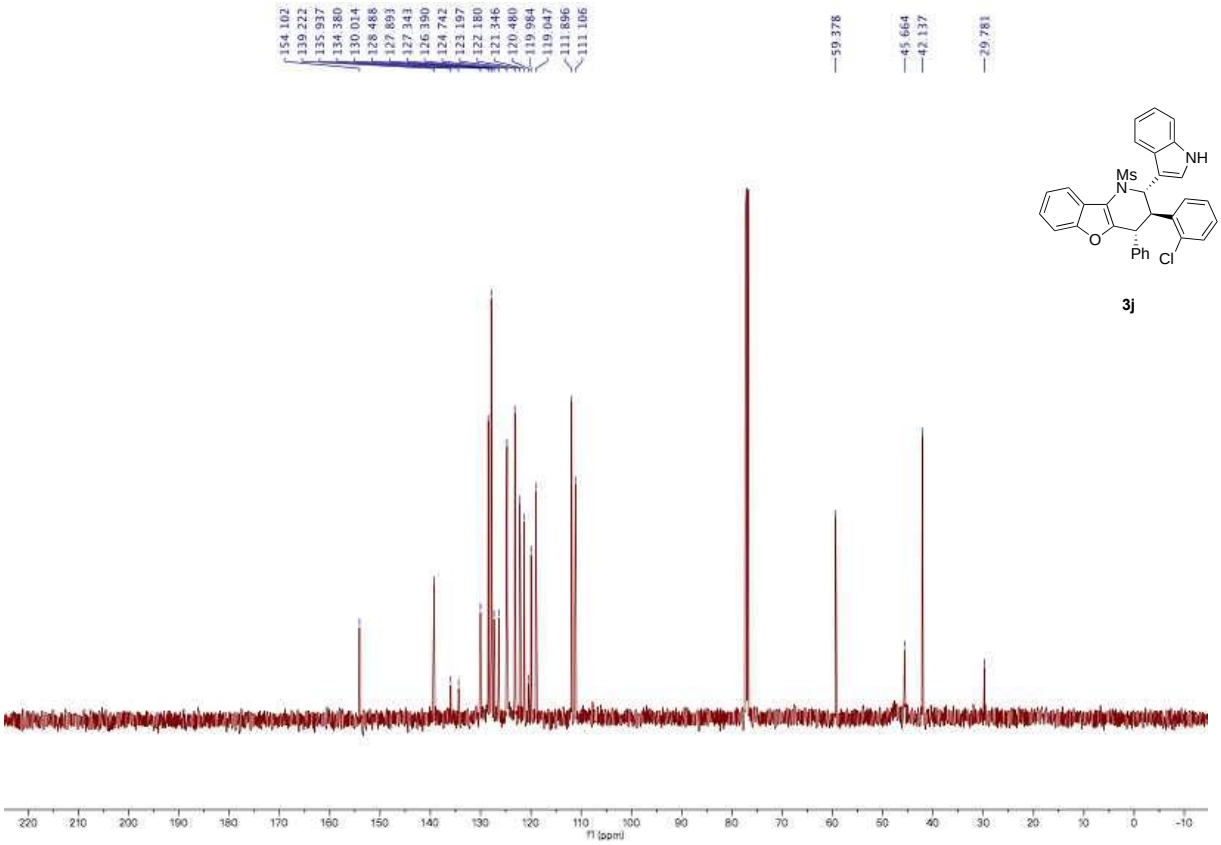

7.920
7.688
7.672
7.479
7.473
7.466
7.461
7.365
7.358
7.353
7.346
7.168
7.153
7.143
7.127
7.087
7.073
7.006
6.991
6.938
6.935
6.896
6.880
6.840
4.971
4.582
2.497
1.00
0.98
1.06
1.09
3.18
3.14
1.32
1.22
3.89
1.86
1.00
1.04
1.02
3.11
f1 (ppm)

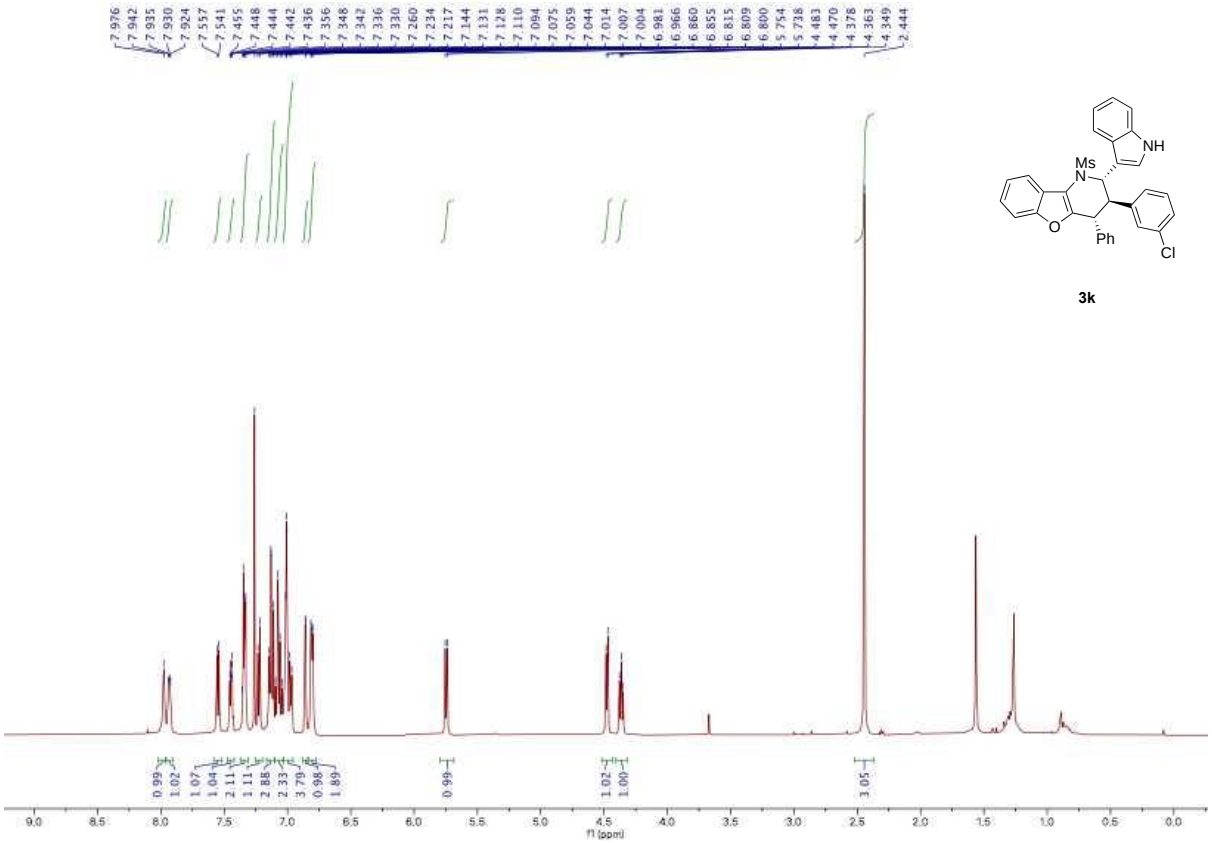
NH
Ms
N
O
Ph
Cl

3j


154.102
139.222
135.937
134.380
130.014
128.488
127.893
127.343
126.390
124.742
123.197
122.180
121.346
120.480
119.984
119.047
111.896
111.106
59.378
45.664
42.137
29.781
f1 (ppm)

NH
Ms
N
O
Ph
Cl

3j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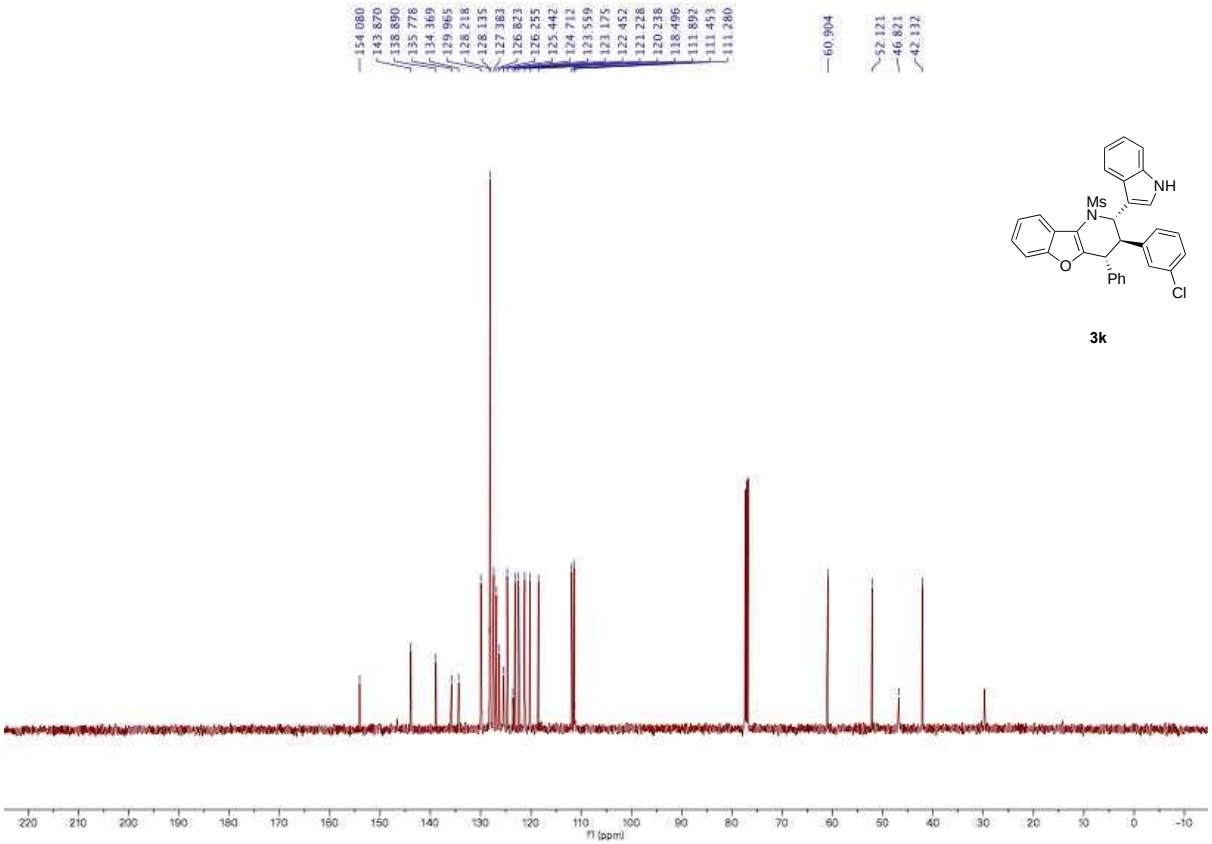
7.942
7.935
7.930
7.924
7.557
7.541
7.455
7.448
7.444
7.442
7.436
7.356
7.348
7.342
7.336
7.330
7.260
7.234
7.217
7.144
7.131
7.128
7.110
7.094
7.075
7.059
7.044
7.014
7.007
7.004
6.981
6.966
6.860
6.855
6.815
6.809
6.800
5.754
5.738
4.483
4.470
4.378
4.363
4.349
2.444
0.99
1.02
1.07
1.04
2.11
1.11
2.88
2.33
3.79
0.98
1.89
0.99
1.02
1.00
3.05
f1 (ppm)
NH
Ms
N
O
Ph
Cl

3k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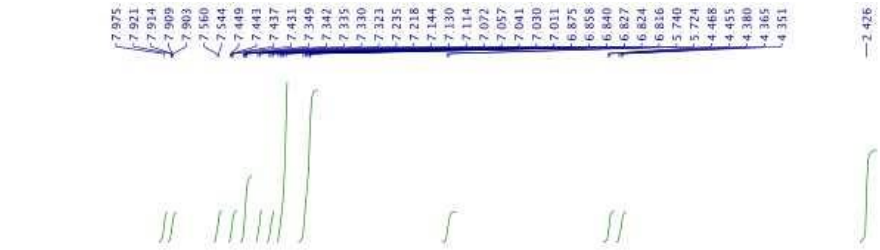
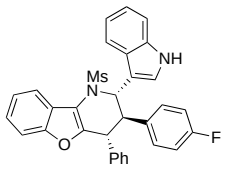
143.870
138.890
135.778
134.369
129.965
128.218
128.135
127.383
126.823
126.255
125.442
124.712
123.559
123.175
122.452
121.228
120.238
118.496
111.892
111.453
111.280
60.904
52.121
46.821
42.132
f1 (ppm)
NH
Ms
N
O
Ph
Cl

3k





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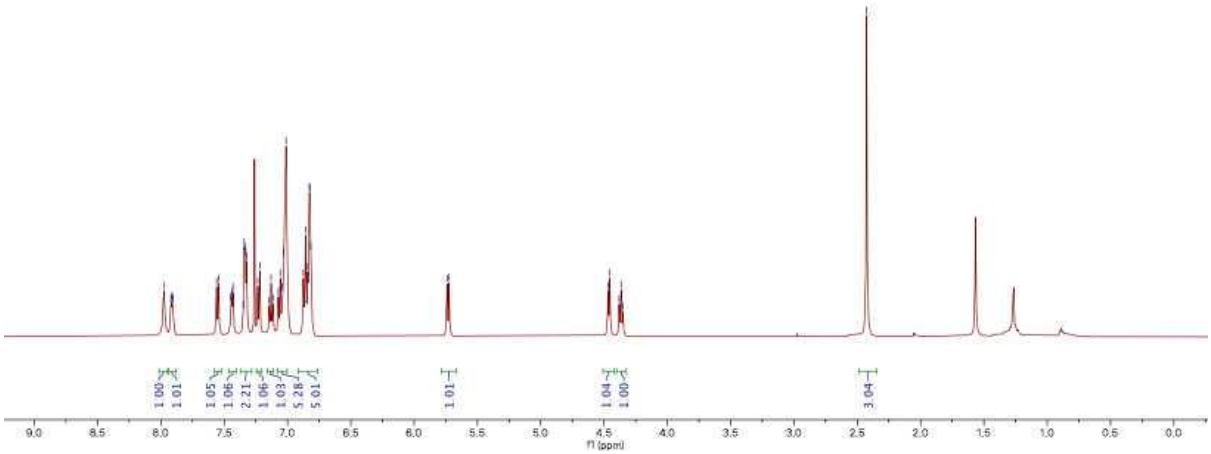
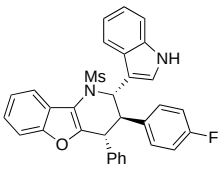
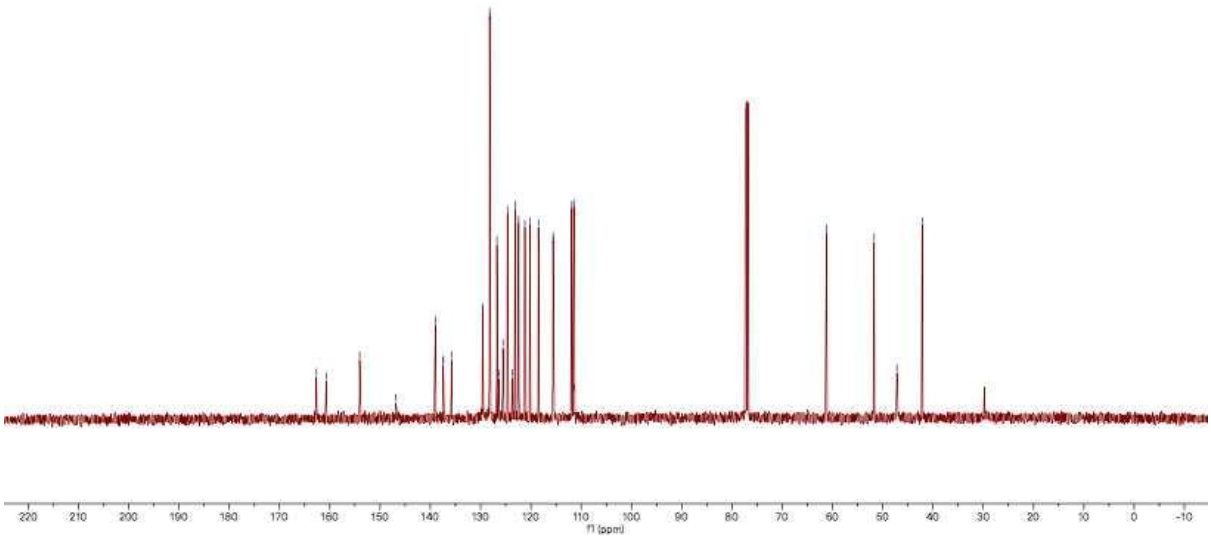
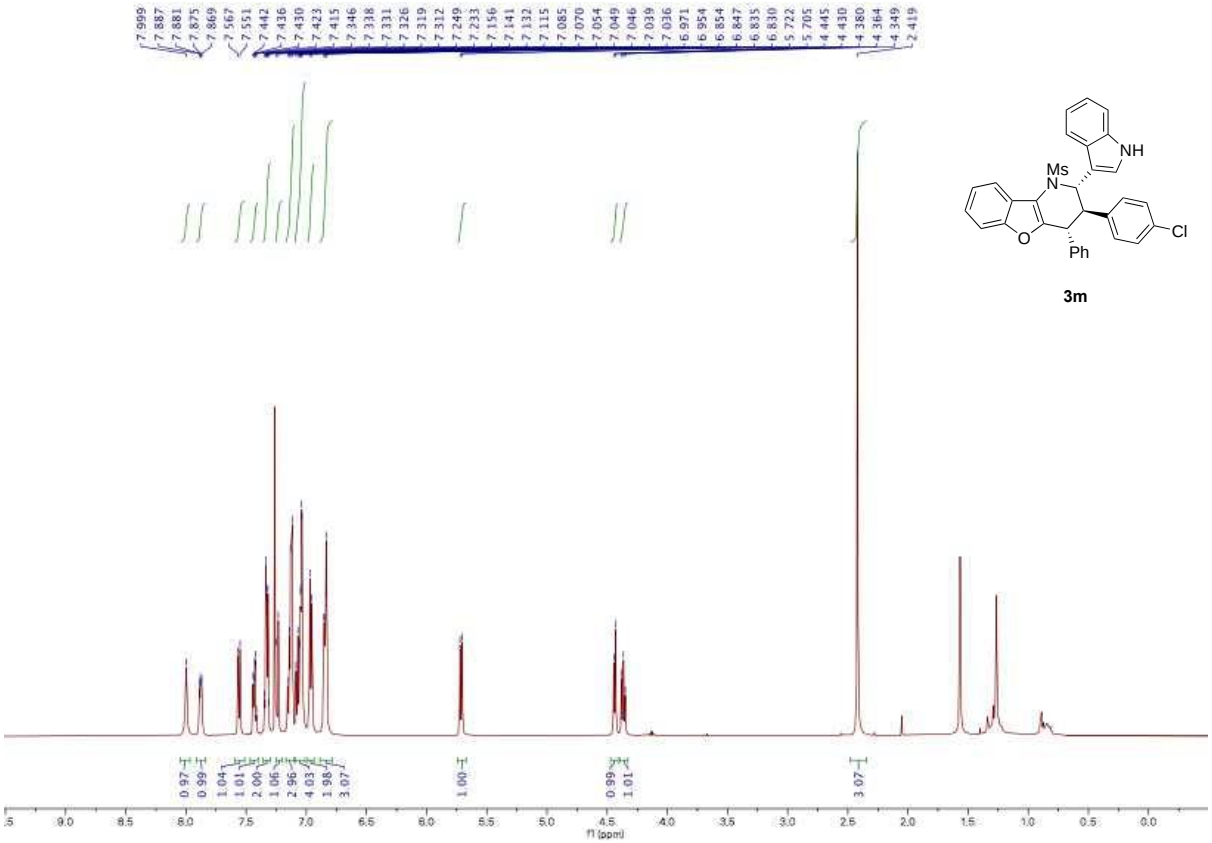




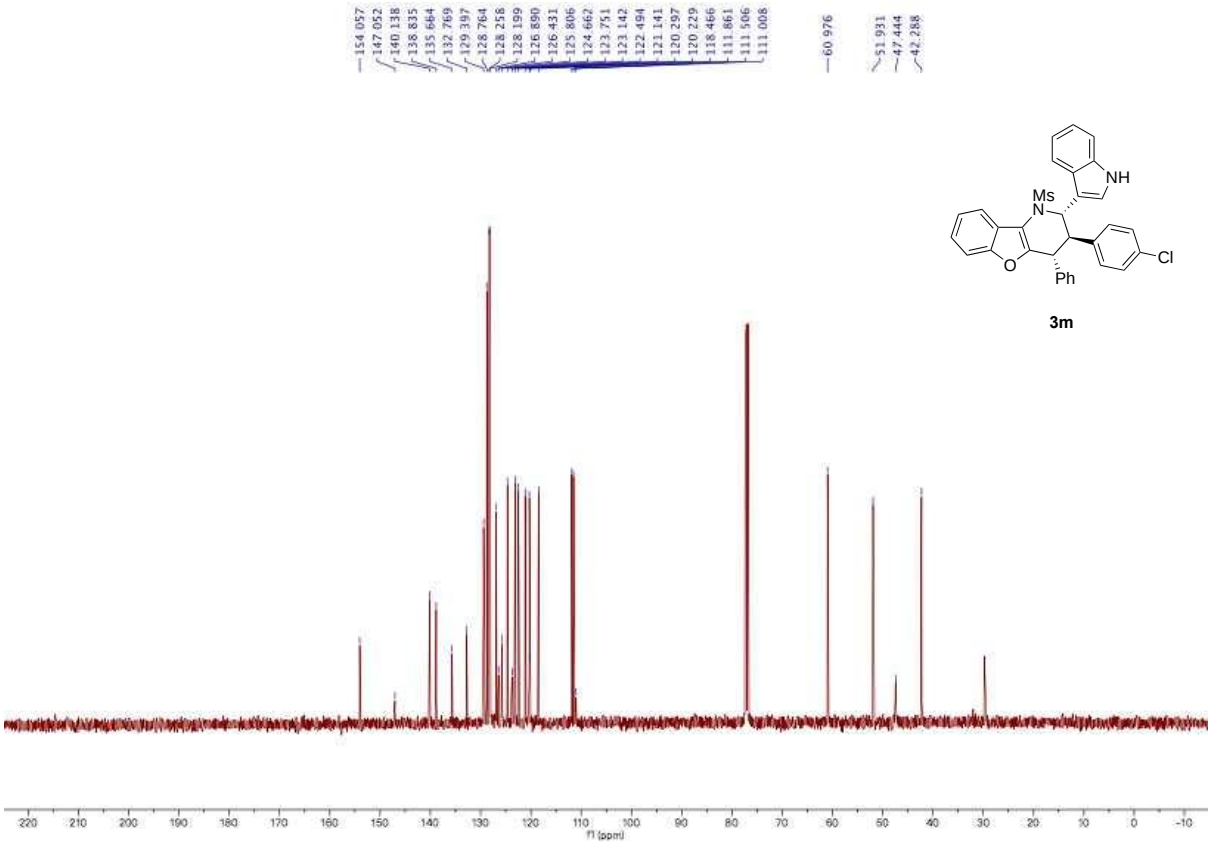
3l




7.999
7.887
7.881
7.875
7.869
7.567
7.551
7.442
7.436
7.430
7.423
7.415
7.346
7.338
7.331
7.326
7.319
7.312
7.249
7.233
7.156
7.141
7.132
7.115
7.085
7.070
7.054
7.049
7.046
7.039
7.036
6.971
6.954
6.854
6.847
6.835
6.830
5.722
5.705
4.445
4.430
4.380
4.364
4.349
2.419
0.97
0.99
1.04
1.01
2.00
1.06
2.96
4.03
1.98
3.07
1.00
0.99
1.01
3.07
f1 (ppm)

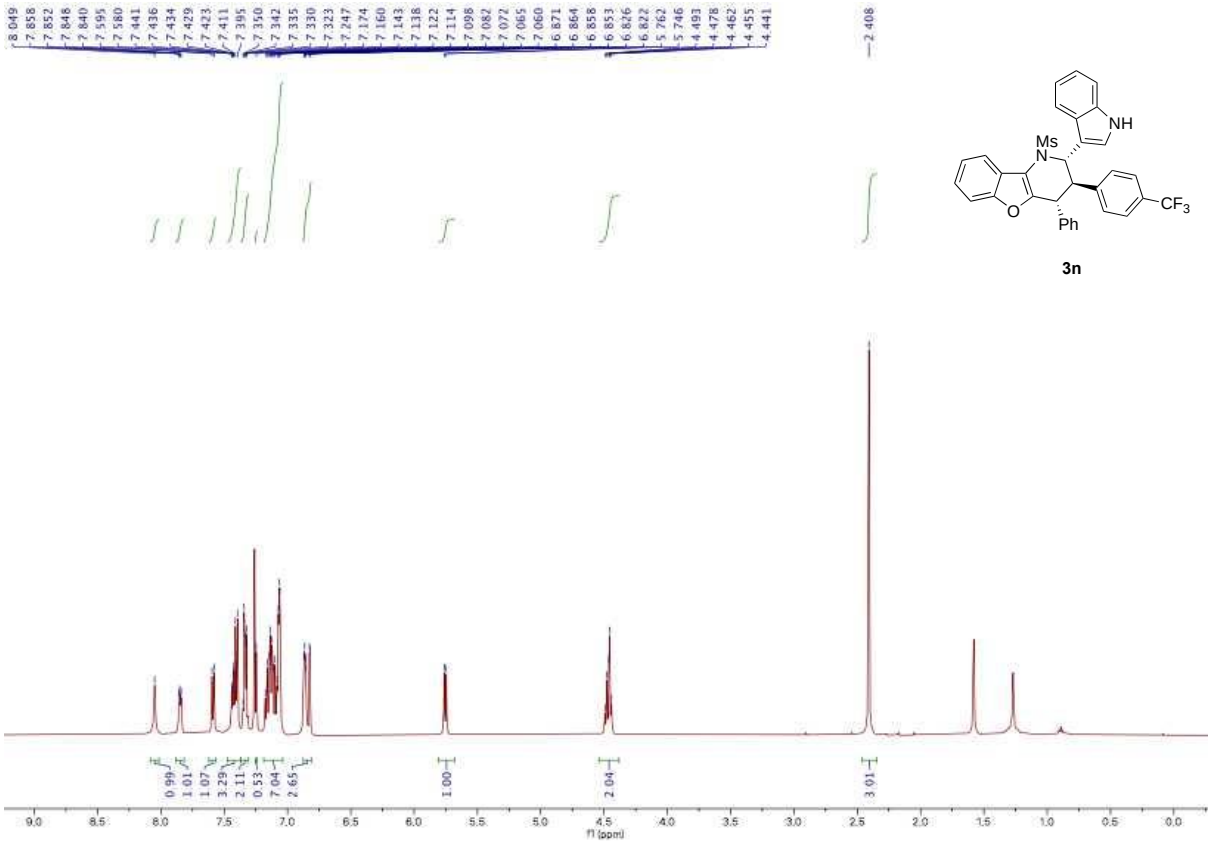
NH
Ms
N
O
Cl
Ph

3m

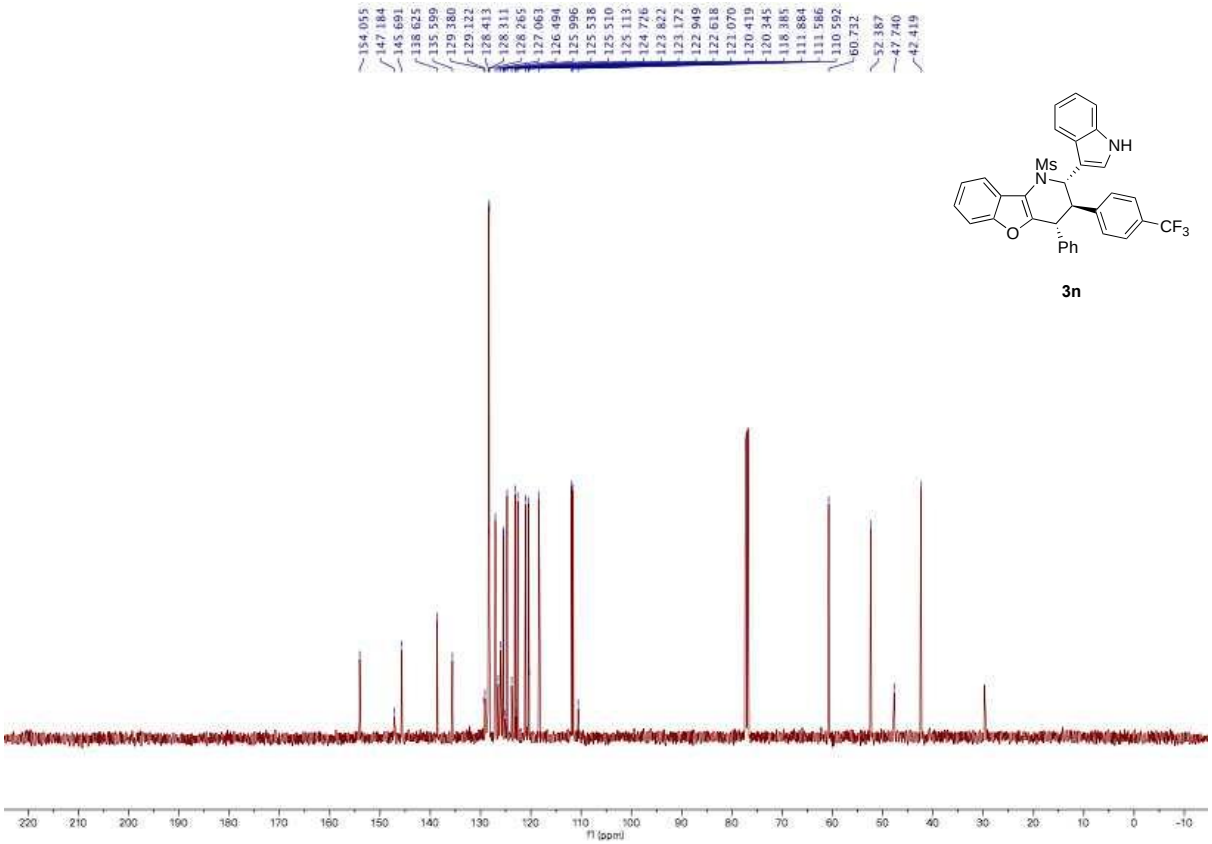

154.057
147.052
140.138
138.835
135.684
132.769
129.397
128.764
128.256
128.199
126.890
126.431
125.806
124.662
123.751
123.142
122.494
121.141
120.297
120.229
118.466
111.861
111.506
111.008
60.976
51.931
47.444
42.288
f1 (ppm)

NH
Ms
N
O
Cl
Ph

3m


8.049
7.858
7.852
7.848
7.840
7.595
7.580
7.441
7.436
7.434
7.429
7.423
7.411
7.395
7.350
7.342
7.335
7.330
7.323
7.247
7.174
7.160
7.143
7.138
7.122
7.114
7.098
7.082
7.072
7.065
7.060
6.871
6.864
6.858
6.853
6.826
6.822
5.762
5.746
4.493
4.478
4.462
4.455
4.441
2.408
0.99
1.01
1.07
3.29
2.11
0.53
7.04
2.65
1.00
2.04
3.01
f1 (ppm)
NH
Ms
N
O
Ph
CF3

3n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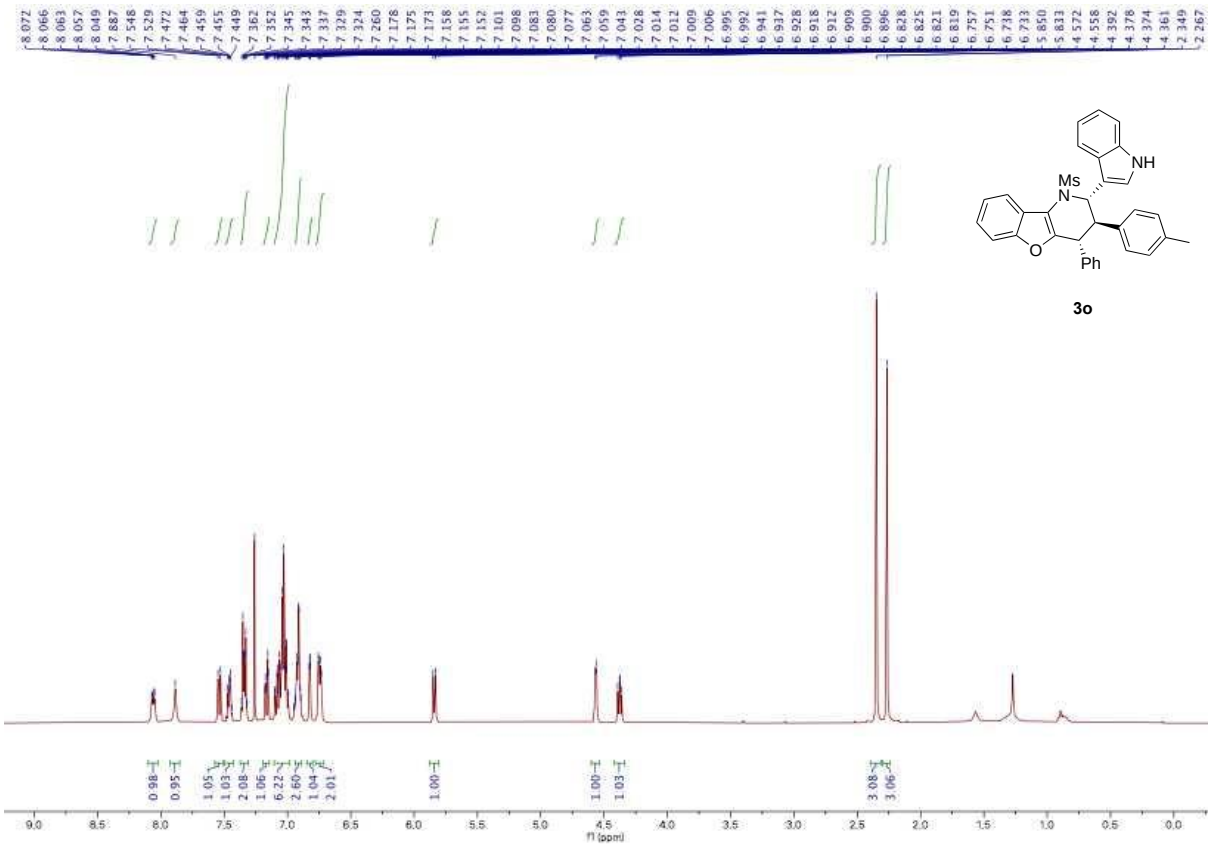
147.184
145.691
138.625
135.599
129.380
129.122
128.413
128.311
128.265
127.063
126.494
125.996
125.538
125.510
125.113
124.726
123.822
123.172
122.949
122.618
121.070
120.419
120.345
118.385
111.884
111.586
110.592
60.732
52.387
47.740
42.419
f1 (ppm)
NH
Ms
N
O
Ph
CF3

3n



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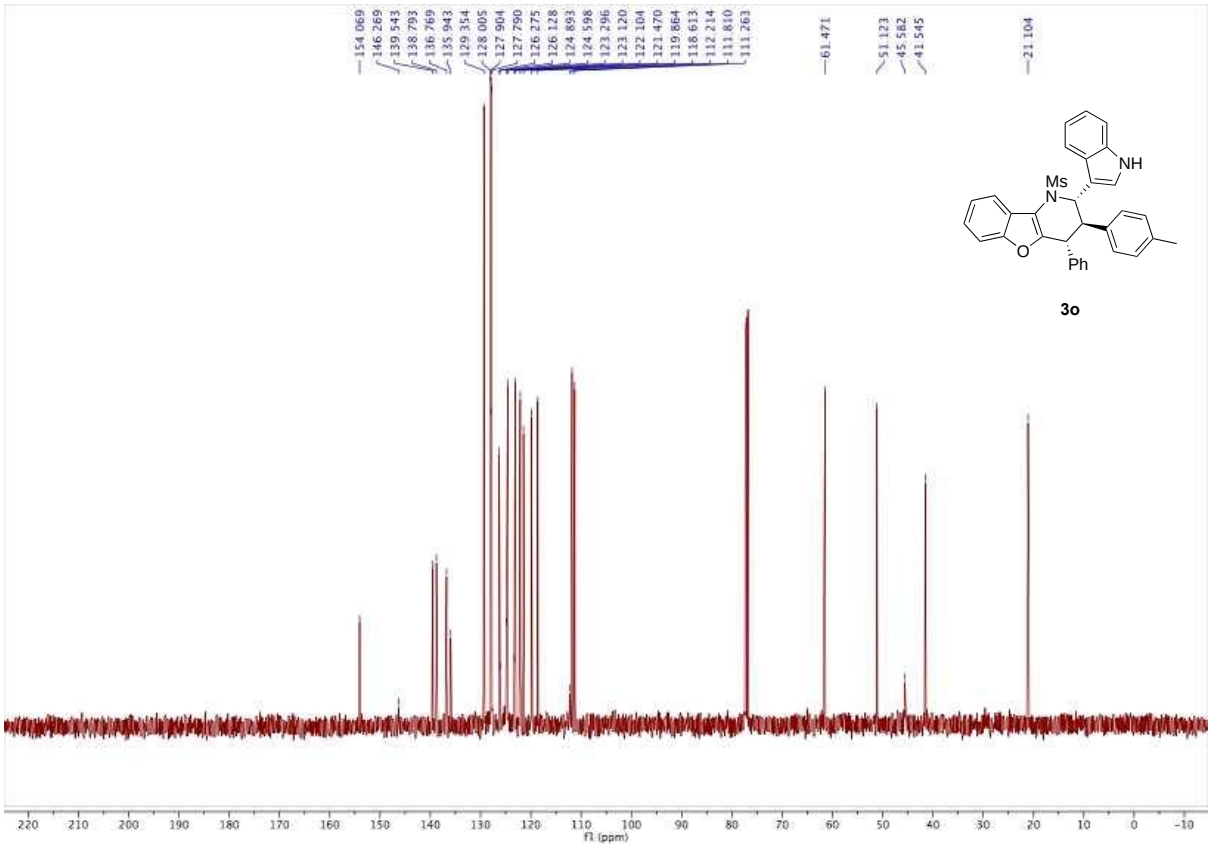

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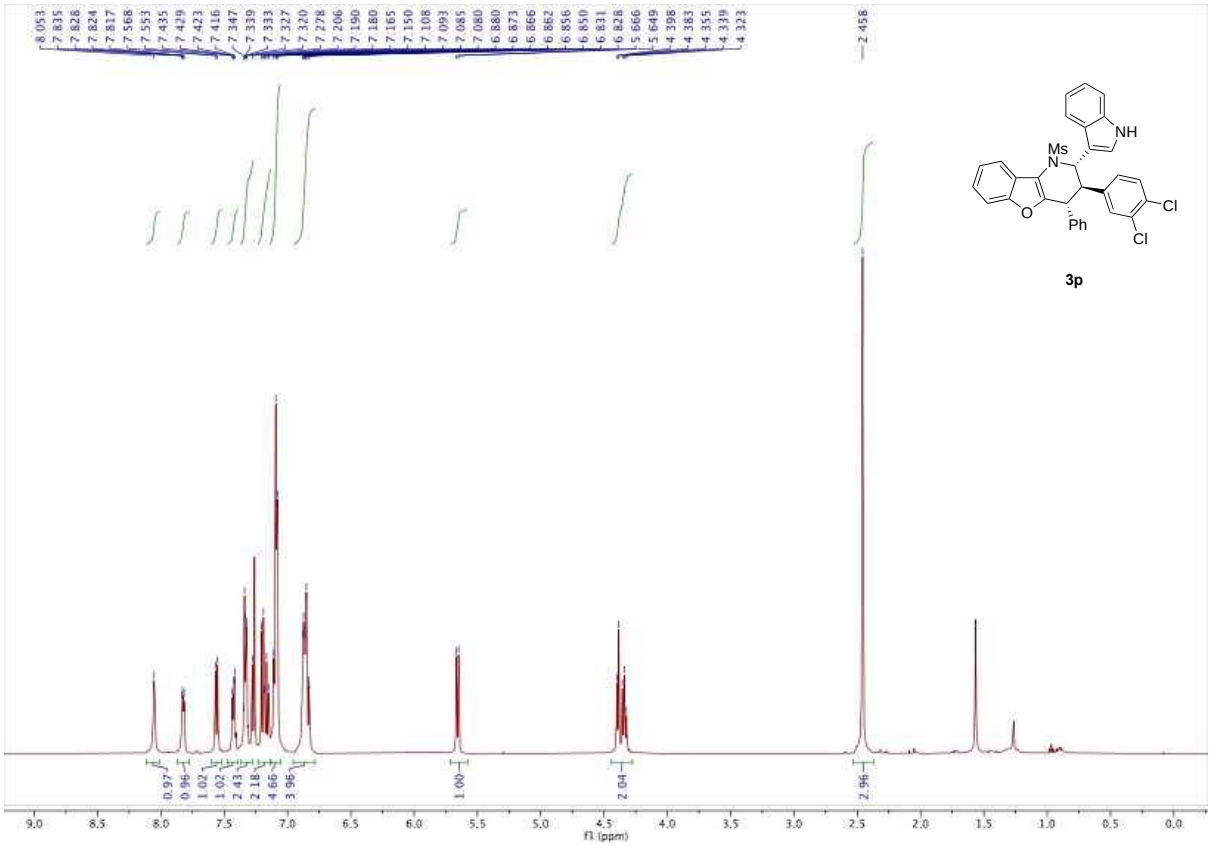
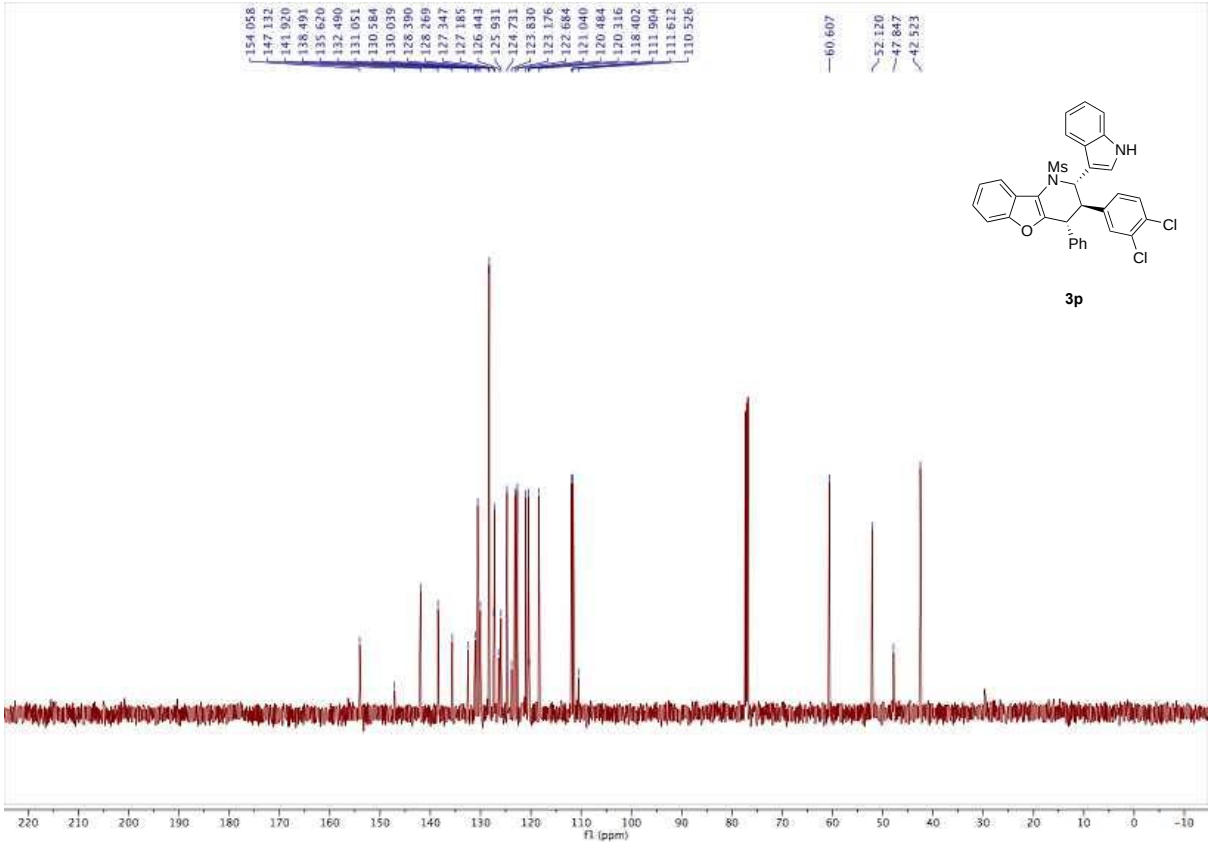
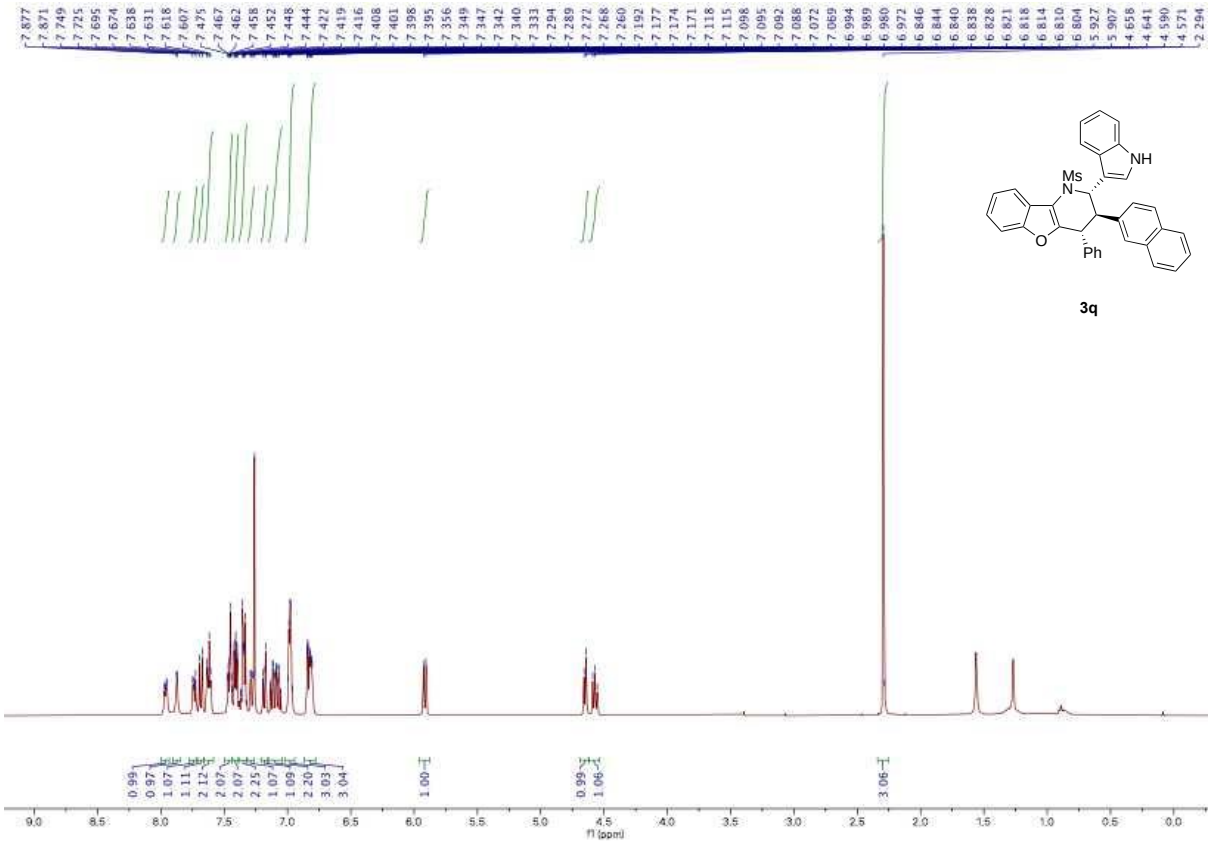
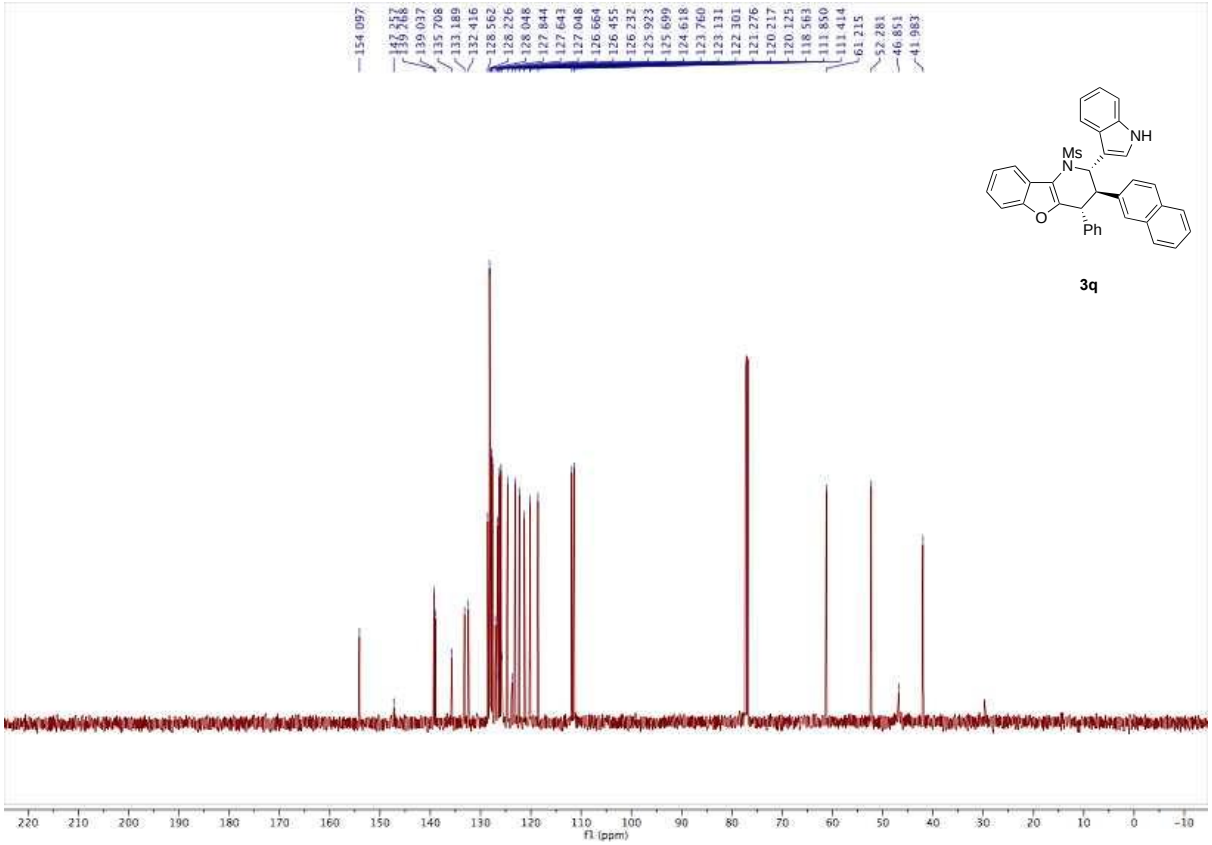

NH
Ms
N
O
Ph
Cl
Cl
3p

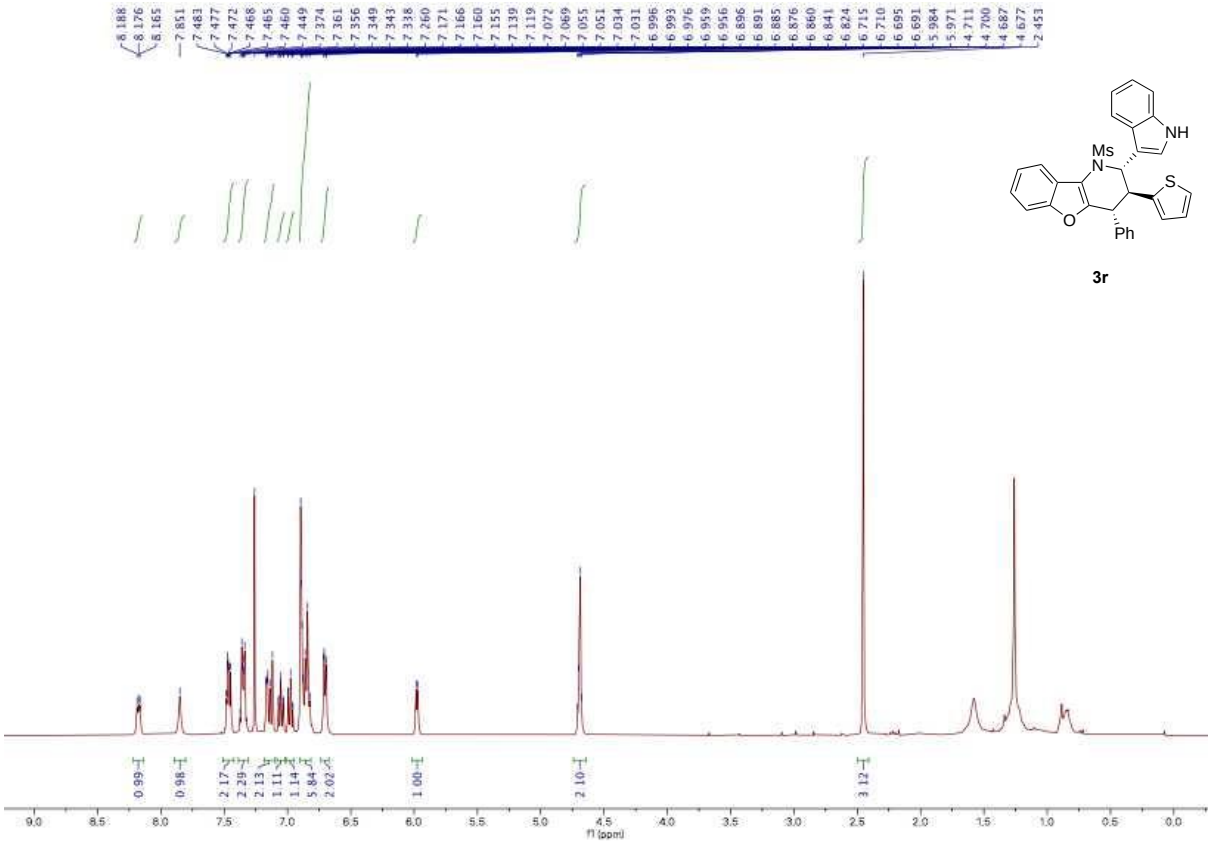

NH
Ms
N
O
Ph
Cl
Cl
3p



3q



3q



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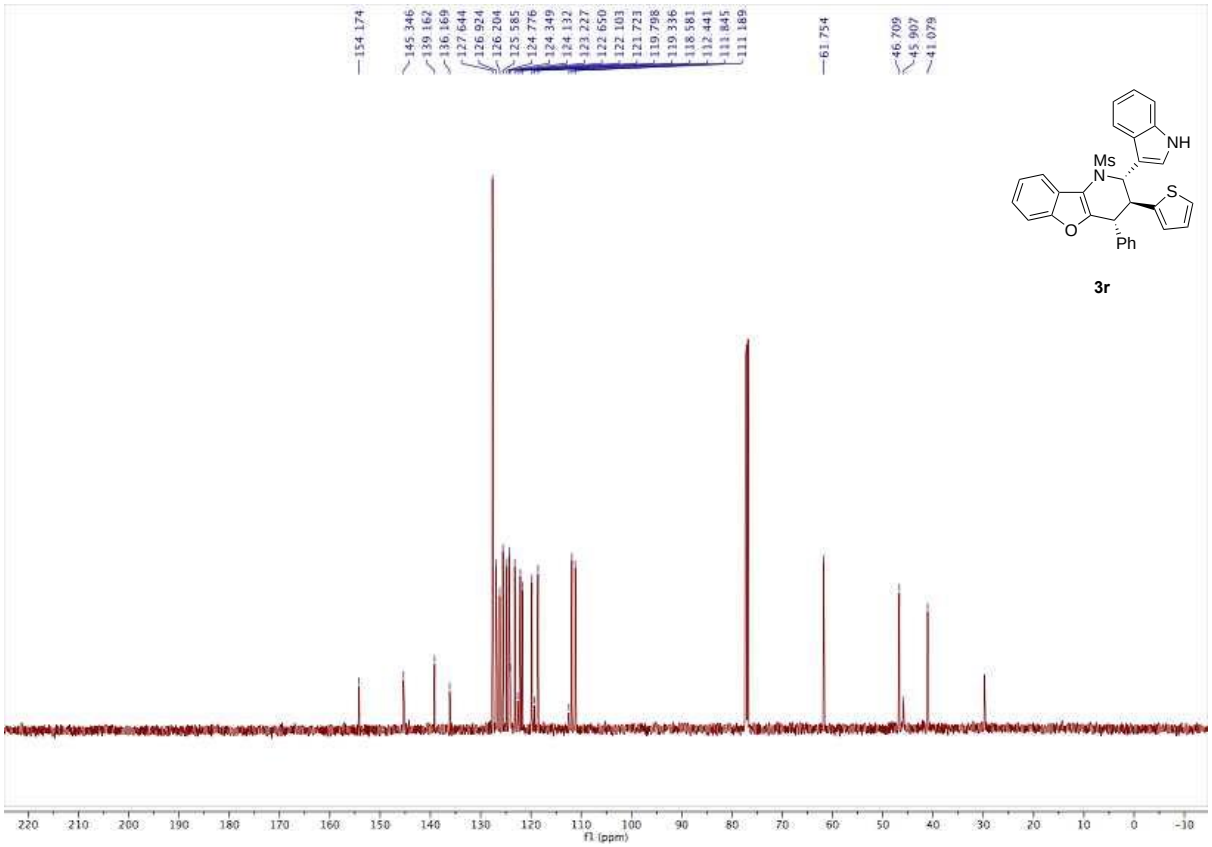
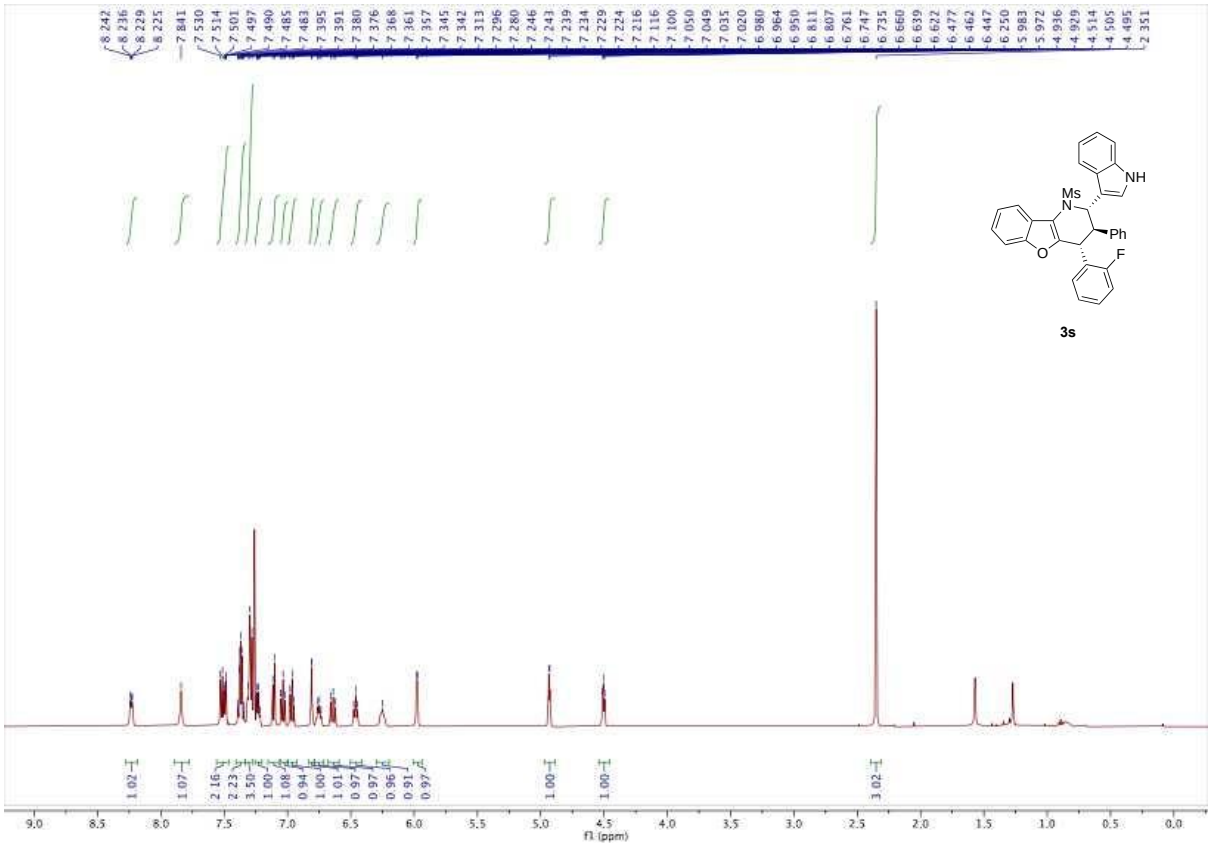
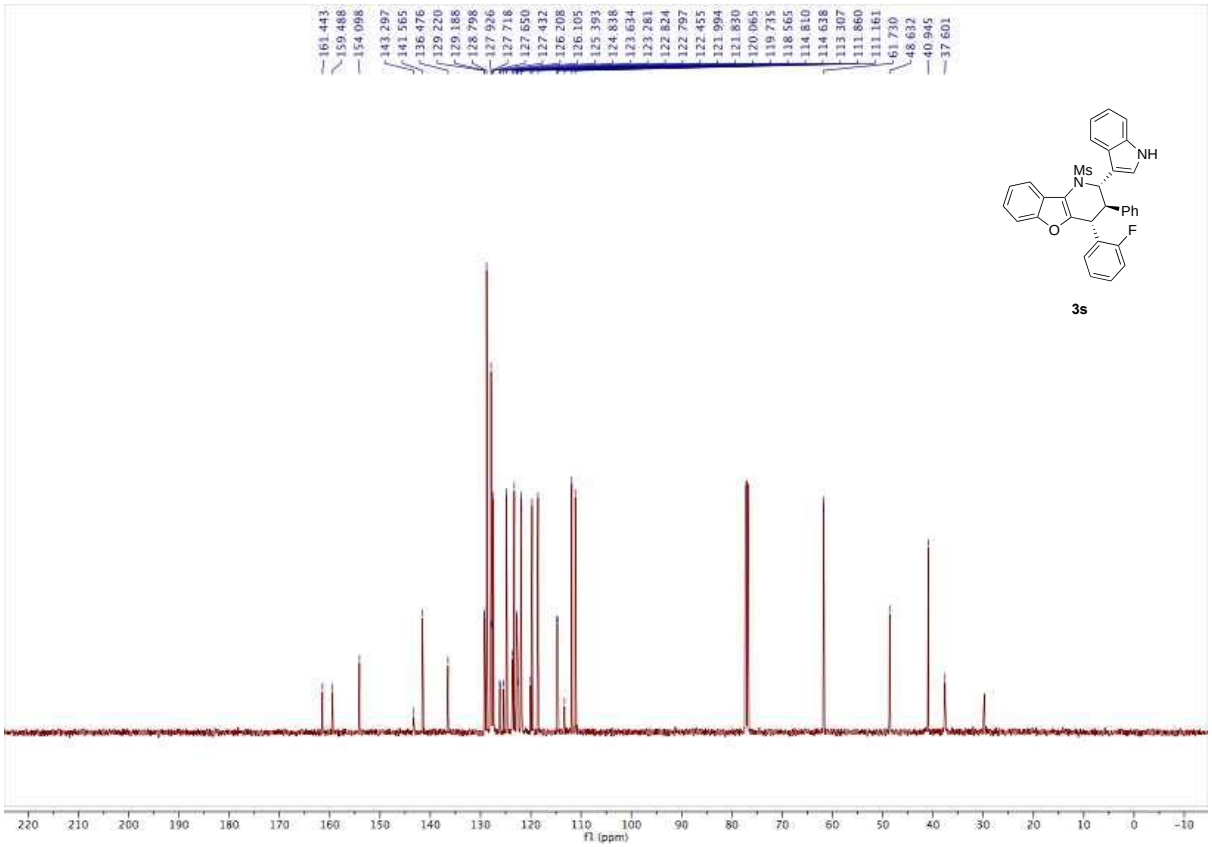
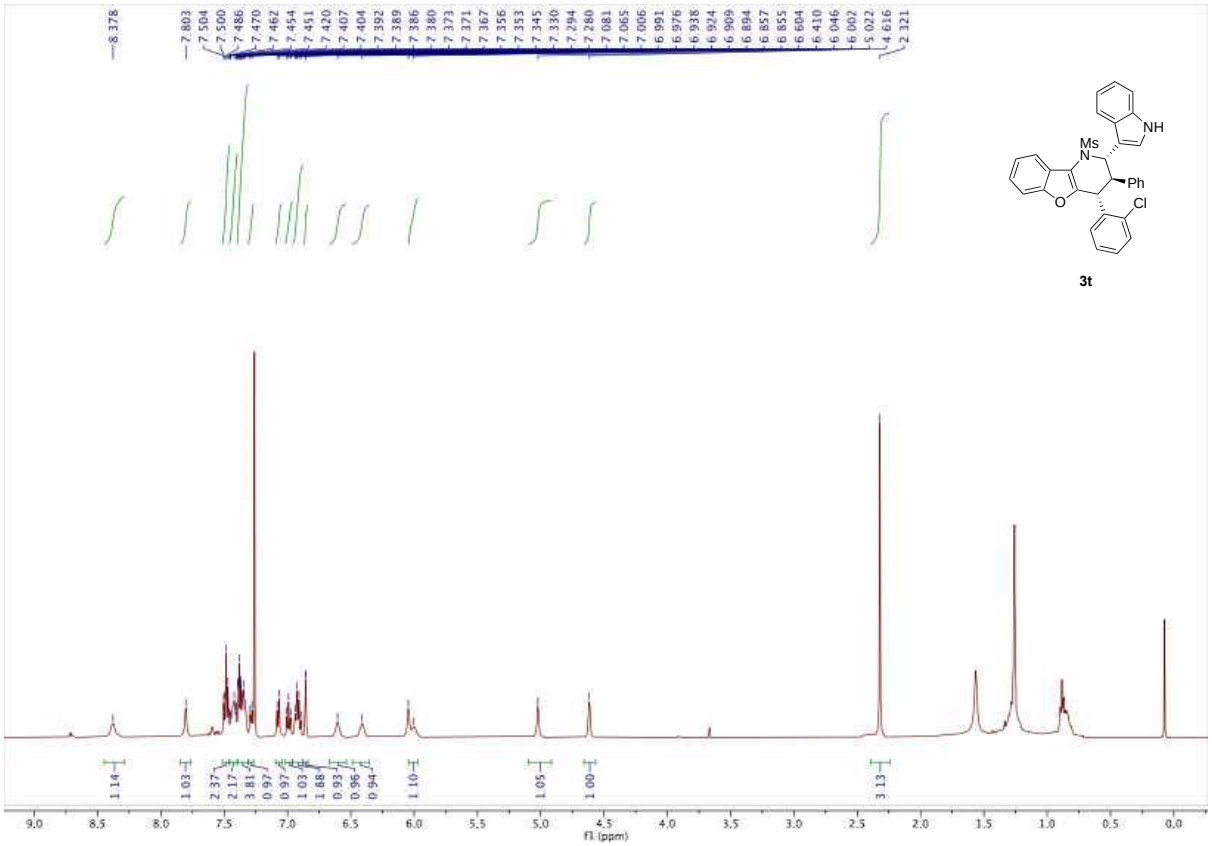


3r


NH
Ms
N
Ph
F
O
3s
f1 (ppm)


NH
Ms
N
Ph
F
O
3s
f1 (ppm)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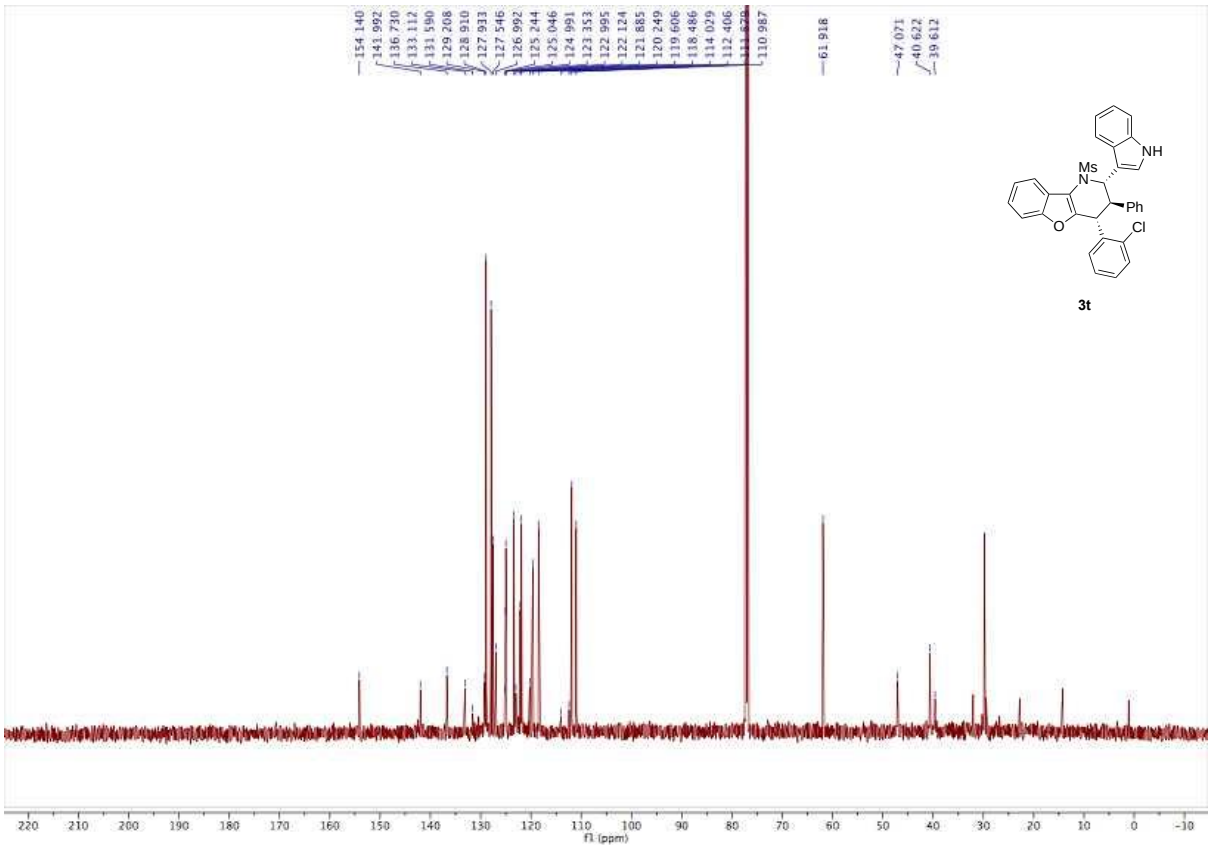
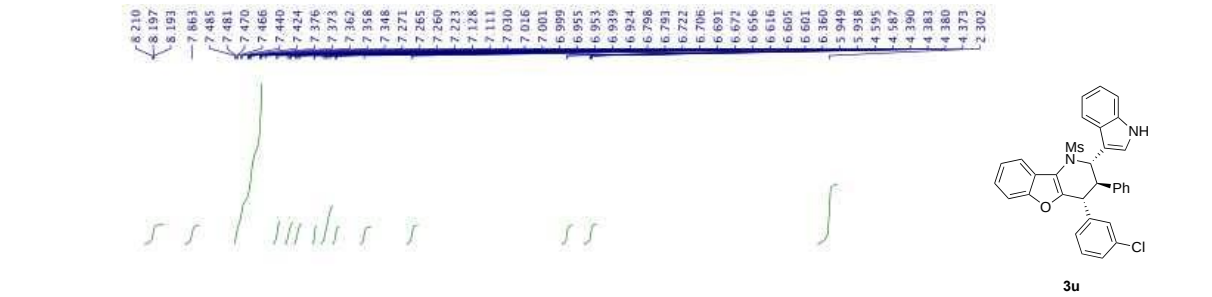
7.803
7.504
7.500
7.486
7.470
7.462
7.454
7.451
7.420
7.407
7.404
7.392
7.389
7.386
7.380
7.373
7.371
7.367
7.356
7.353
7.345
7.330
7.294
7.280
7.081
7.065
7.006
6.991
6.976
6.938
6.924
6.909
6.894
6.857
6.855
6.604
6.410
6.046
6.002
5.022
4.616
2.321
NH
Ms
N
Ph
Cl
O
3t
1.14
1.03
2.37
2.17
3.81
0.97
0.97
1.03
1.88
0.93
0.96
0.94
1.10
1.05
1.00
3.13
f1 (ppm)


154.140
141.992
136.730
133.112
131.580
129.208
128.910
127.933
127.546
126.992
125.244
125.046
124.991
123.353
122.995
122.124
121.885
120.249
119.606
118.486
114.029
112.406
111.628
110.987
61.918
47.071
40.622
39.612
NH
Ms
N
Ph
Cl
O
3t
f1 (ppm)


8.210
8.197
8.193
7.863
7.485
7.481
7.470
7.466
7.440
7.424
7.376
7.373
7.362
7.358
7.348
7.271
7.265
7.260
7.223
7.128
7.111
7.030
7.016
7.001
6.999
6.955
6.953
6.939
6.924
6.798
6.793
6.722
6.706
6.691
6.672
6.656
6.616
6.605
6.601
6.360
5.949
5.938
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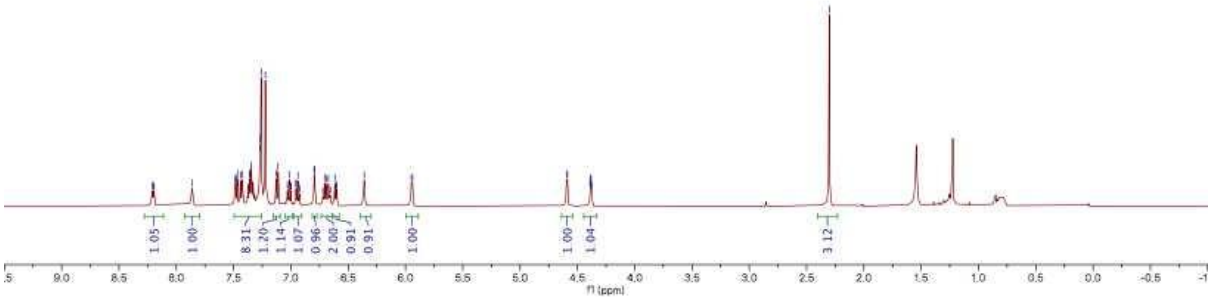
4.587
4.390
4.383
4.380
4.373
2.302
NH
Ms
N
Ph
O
Cl

3u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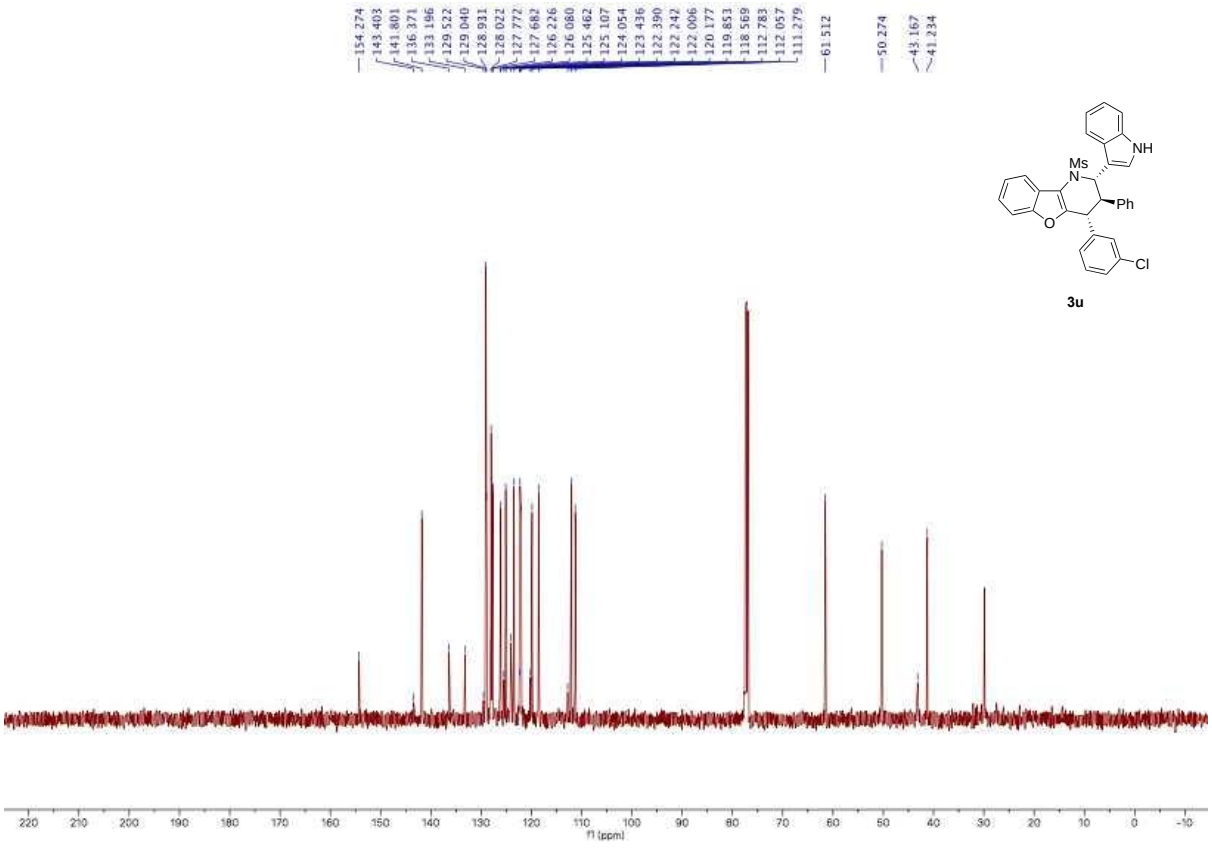
1.00
8.31
1.20
1.14
1.07
0.96
2.00
0.91
0.91
1.00
1.00
1.04
3.12
f1 (ppm)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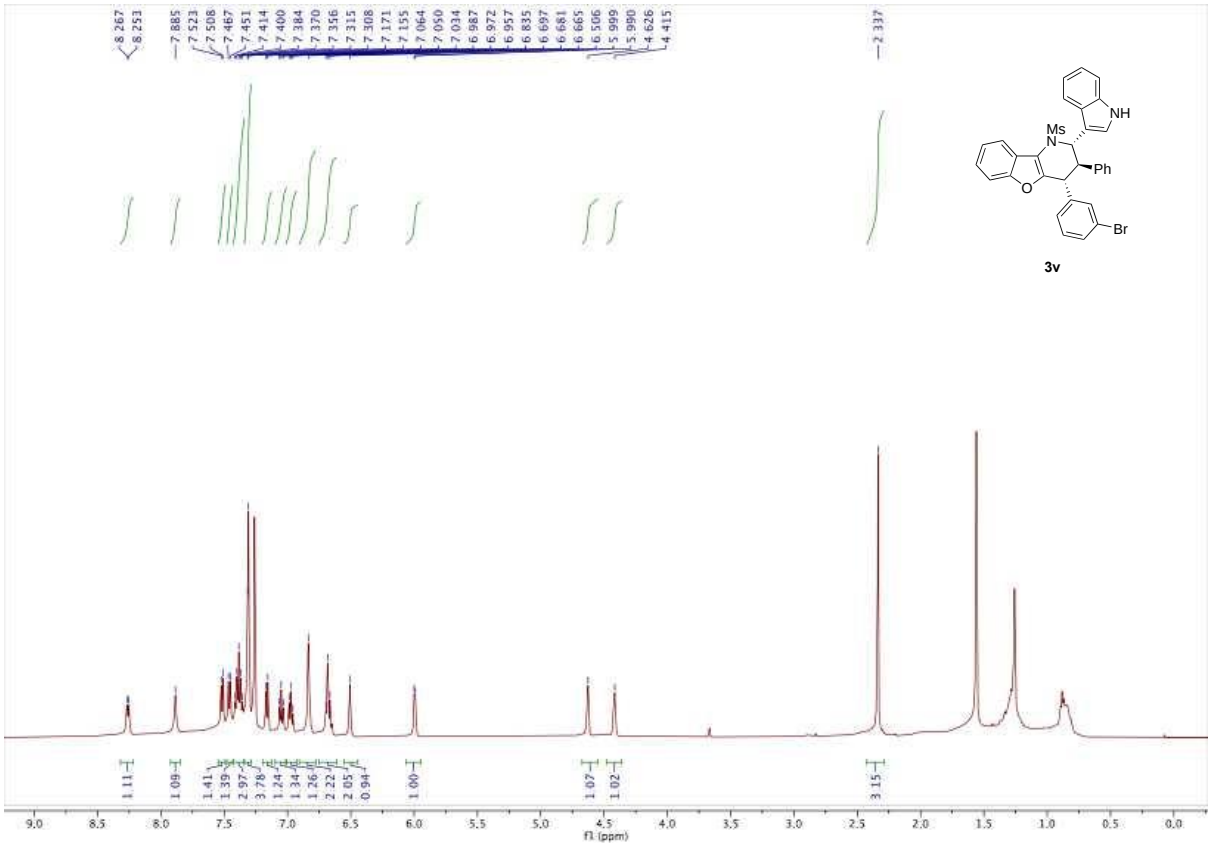
143.403
141.801
136.371
133.196
129.522
129.040
128.931
128.022
127.772
127.682
126.226
126.080
125.462
125.107
124.054
123.436
122.390
122.242
122.006
120.177
119.853
118.569
112.783
112.057
111.279
61.512
50.274
43.167
41.234
NH
Ms
N
Ph
O
Cl
f1 (ppm)

3u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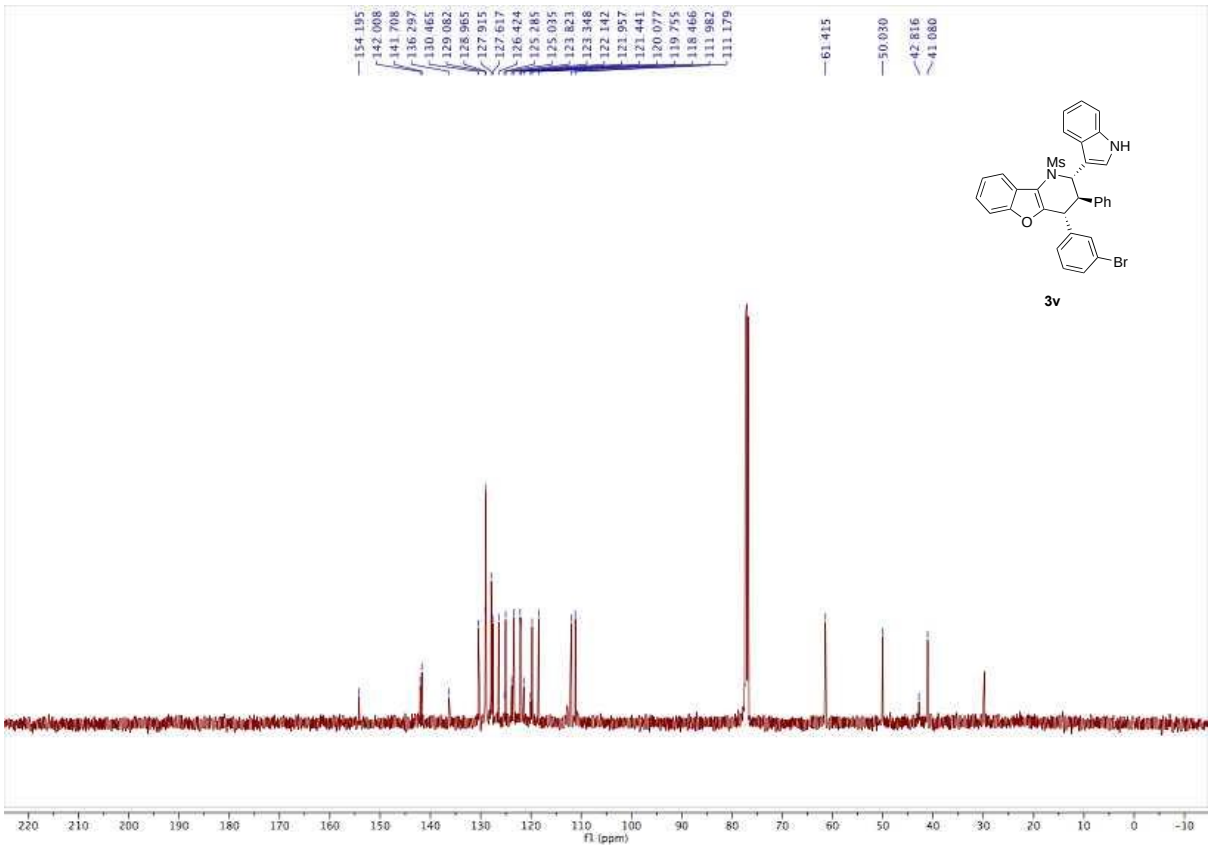
8.253
7.885
7.523
7.508
7.467
7.451
7.414
7.400
7.384
7.370
7.356
7.315
7.308
7.171
7.155
7.064
7.050
7.034
6.987
6.972
6.957
6.835
6.697
6.681
6.665
6.506
5.999
5.990
4.626
4.415
2.337
NH
Ms
N
Ph
O
Br
3v
1.11
1.09
1.41
1.39
2.97
3.78
1.24
1.34
1.26
2.22
2.05
0.94
1.00
1.07
1.02
3.15
f1 (ppm)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141.708
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130.465
129.082
128.965
127.915
127.617
126.424
125.285
125.035
123.823
123.348
122.142
121.957
121.441
120.077
119.755
118.466
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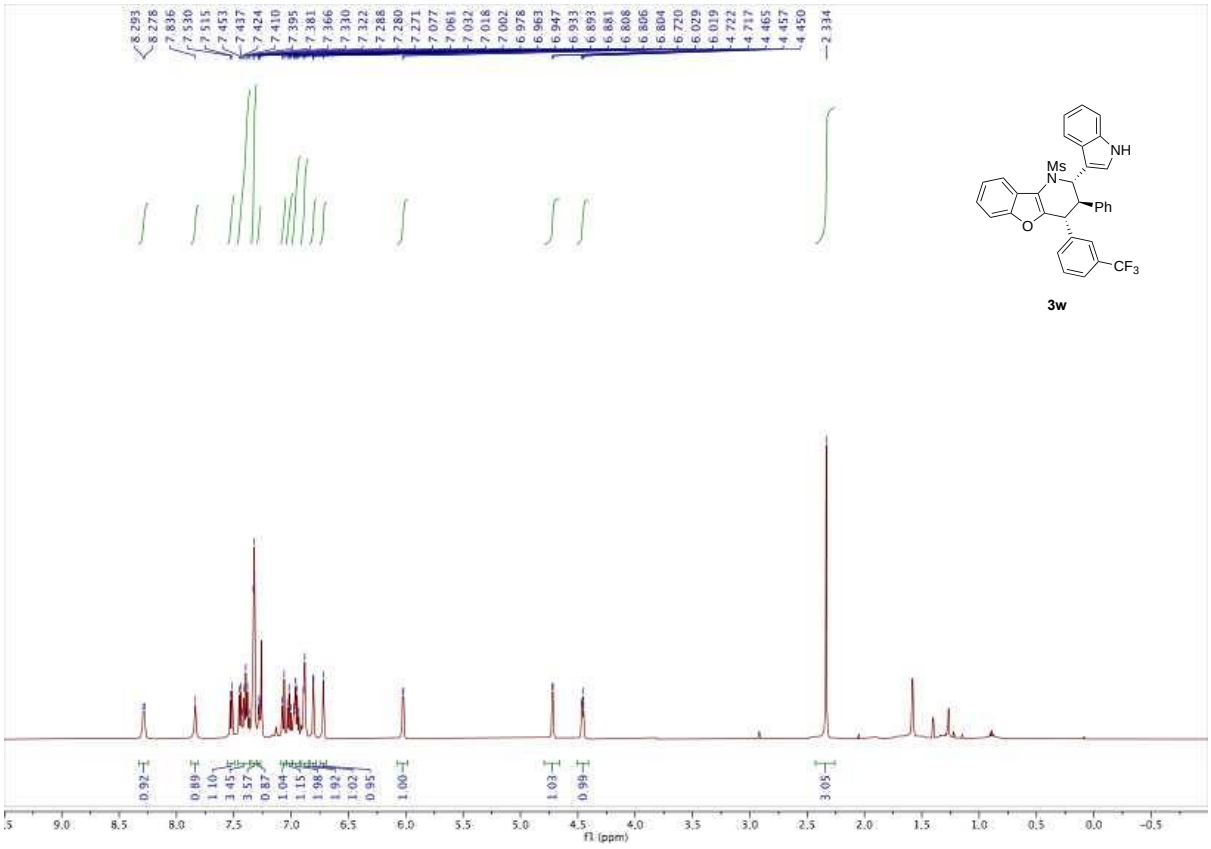
111.179
61.415
50.030
42.816
41.080
NH
Ms
N
Ph
O
Br
3v
f1 (ppm)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7.836
7.530
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7.437
7.424
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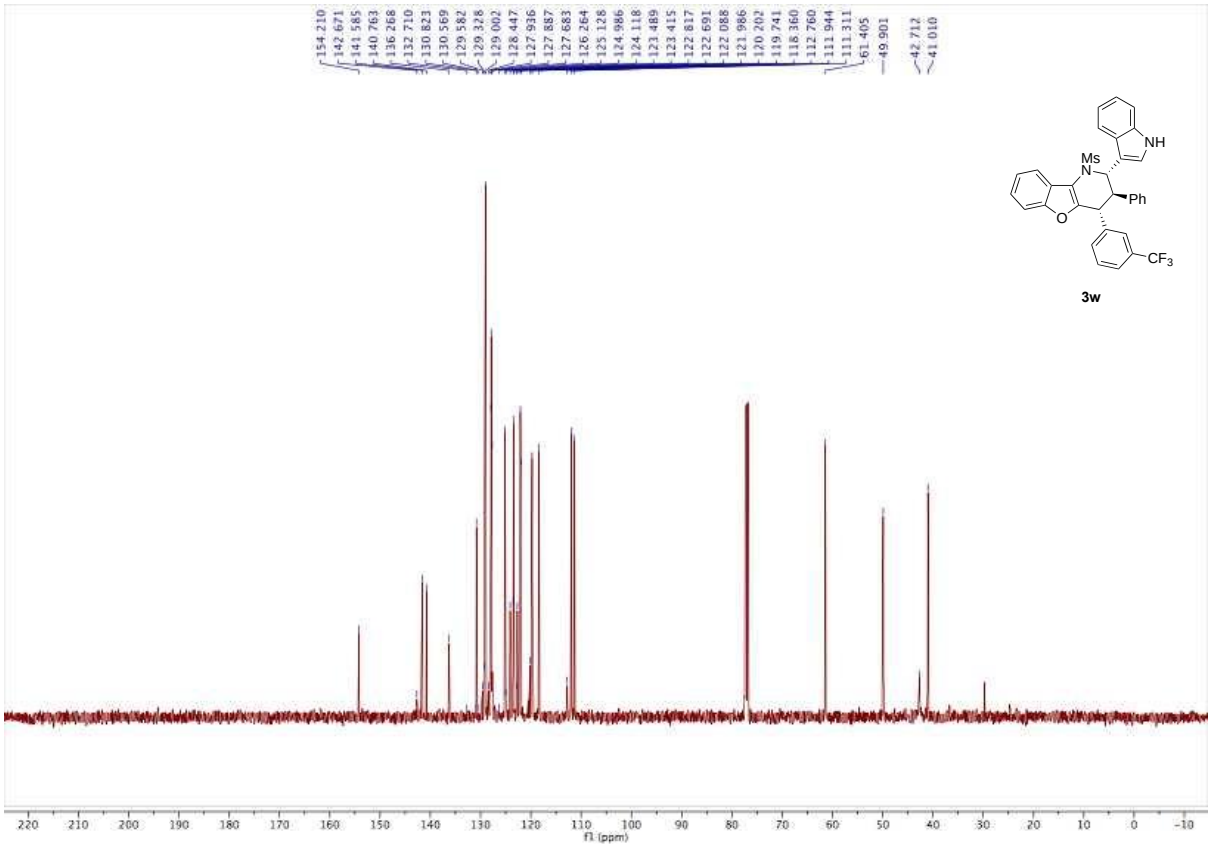
7.395
7.381
7.366
7.330
7.322
7.288
7.280
7.271
7.077
7.061
7.032
7.018
7.002
6.978
6.963
6.947
6.933
6.893
6.881
6.808
6.806
6.804
6.730
6.029
6.019
4.722
4.717
4.465
4.457
4.450
2.334
NH
Ms
N
Ph
O
CF3
3w
0.92
0.89
1.10
3.45
3.57
0.87
1.04
1.15
1.98
1.92
1.02
0.95
1.00
1.03
0.99
3.05
f1 (ppm)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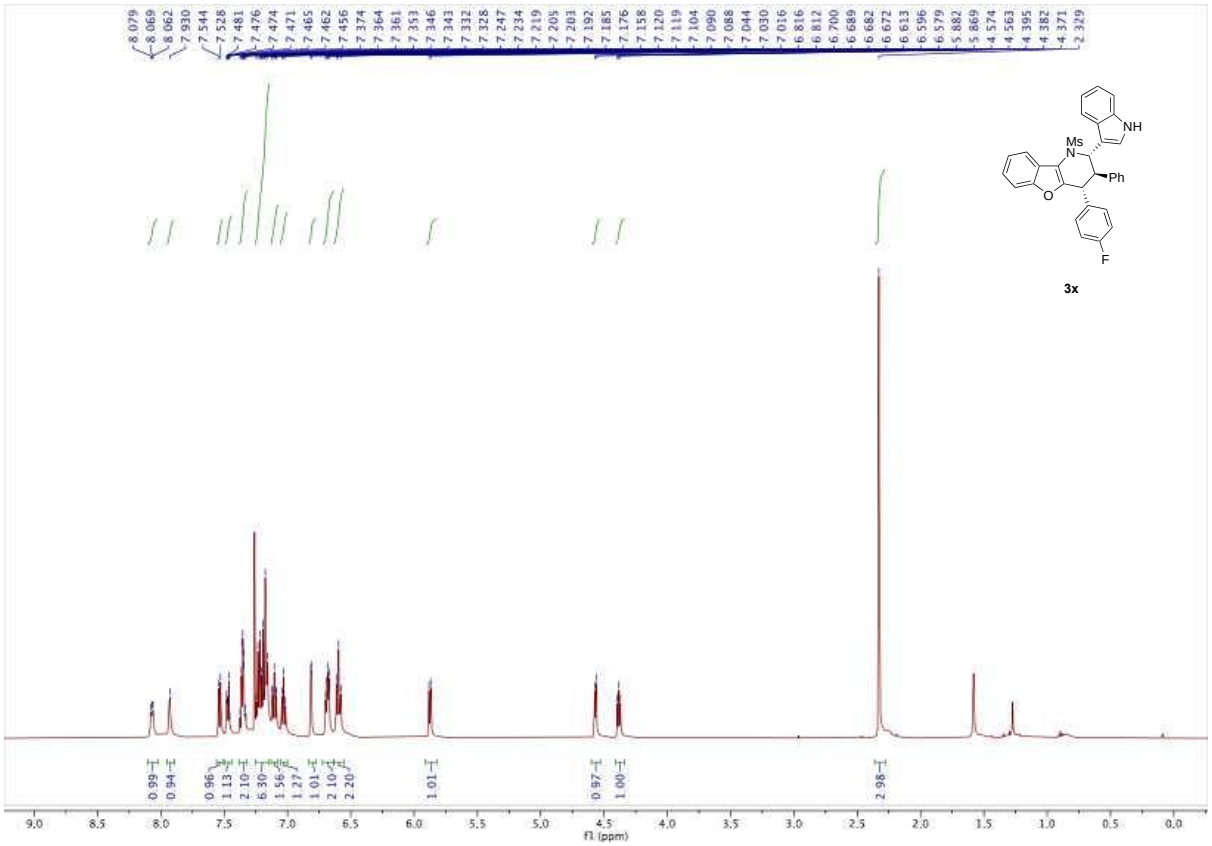
142.671
141.585
140.763
136.268
132.710
130.823
130.569
129.582
129.328
129.002
128.447
127.936
127.887
127.683
126.264
125.128
124.986
124.118
123.489
123.415
122.817
122.691
122.088
121.986
120.202
119.741
118.360
112.760
111.944
111.311
61.405
49.901
42.712
41.010
NH
Ms
N
Ph
O
CF3
3w
f1 (ppm)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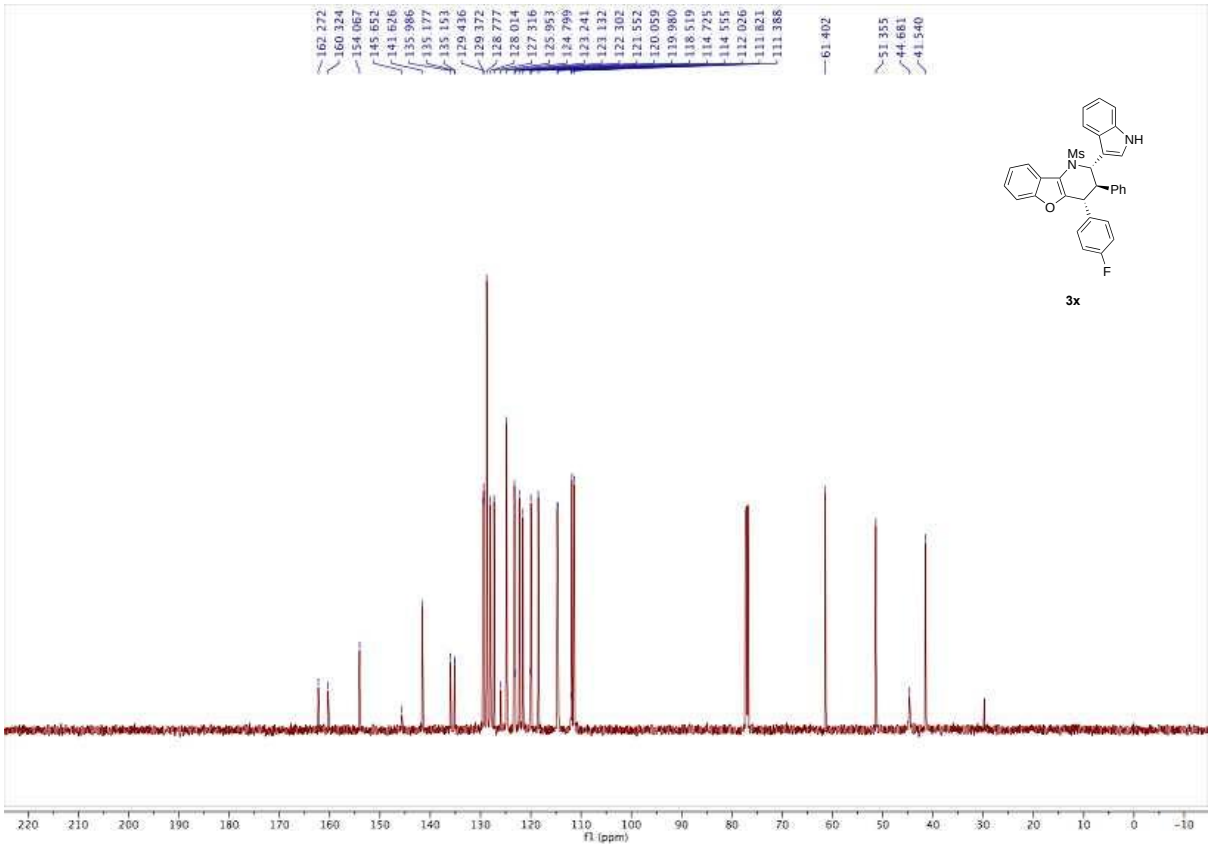
8.069
8.062
7.930
7.544
7.528
7.481
7.476
7.474
7.471
7.465
7.462
7.456
7.374
7.364
7.361
7.353
7.346
7.343
7.332
7.328
7.247
7.234
7.219
7.205
7.203
7.192
7.185
7.176
7.158
7.120
7.119
7.104
7.090
7.088
7.044
7.030
7.016
6.816
6.812
6.700
6.689
6.682
6.672
6.613
6.596
6.579
5.882
5.869
4.574
4.563
4.395
4.382
4.371
2.329
NH
Ms
N
Ph
O
F
3x
0.99
0.94
0.96
1.13
2.10
6.30
1.56
1.27
1.01
2.10
2.20
1.01
0.97
1.00
2.98
f1 (ppm)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154.067
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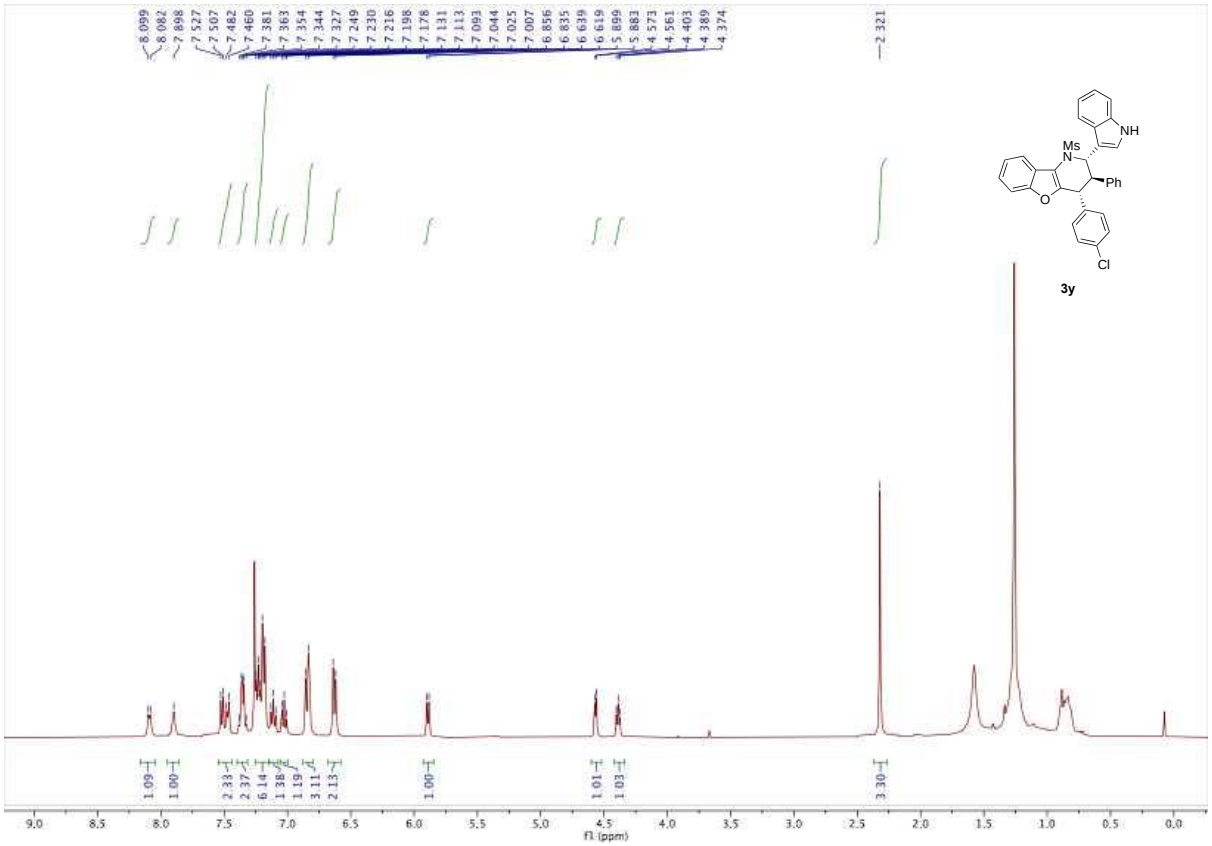
141.626
135.986
135.177
135.153
129.436
129.372
128.777
128.014
127.316
125.953
124.799
123.241
123.132
122.302
121.552
120.059
119.980
118.519
114.725
114.555
112.026
111.821
111.388
61.402
51.355
44.681
41.540
NH
Ms
N
Ph
O
F
3x
f1 (ppm)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7.482
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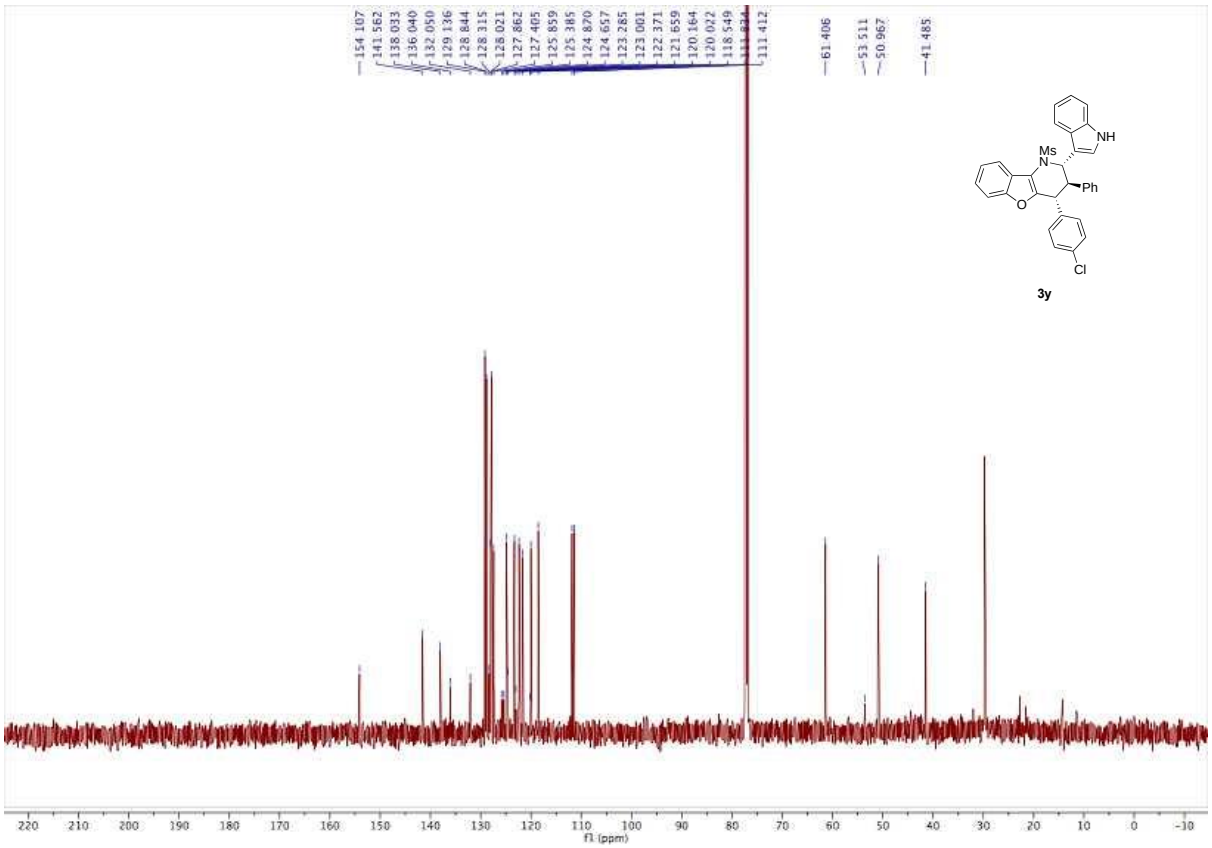
7.381
7.363
7.354
7.344
7.327
7.249
7.230
7.216
7.198
7.178
7.131
7.113
7.093
7.044
7.025
7.007
6.856
6.835
6.639
6.619
5.899
5.883
4.573
4.561
4.403
4.389
4.374
2.321
1.09
1.00
2.33
2.37
6.14
1.38
1.19
3.11
2.13
1.00
1.01
1.03
3.30
NH
Ms
N
Ph
O
Cl
3y
f1 (ppm)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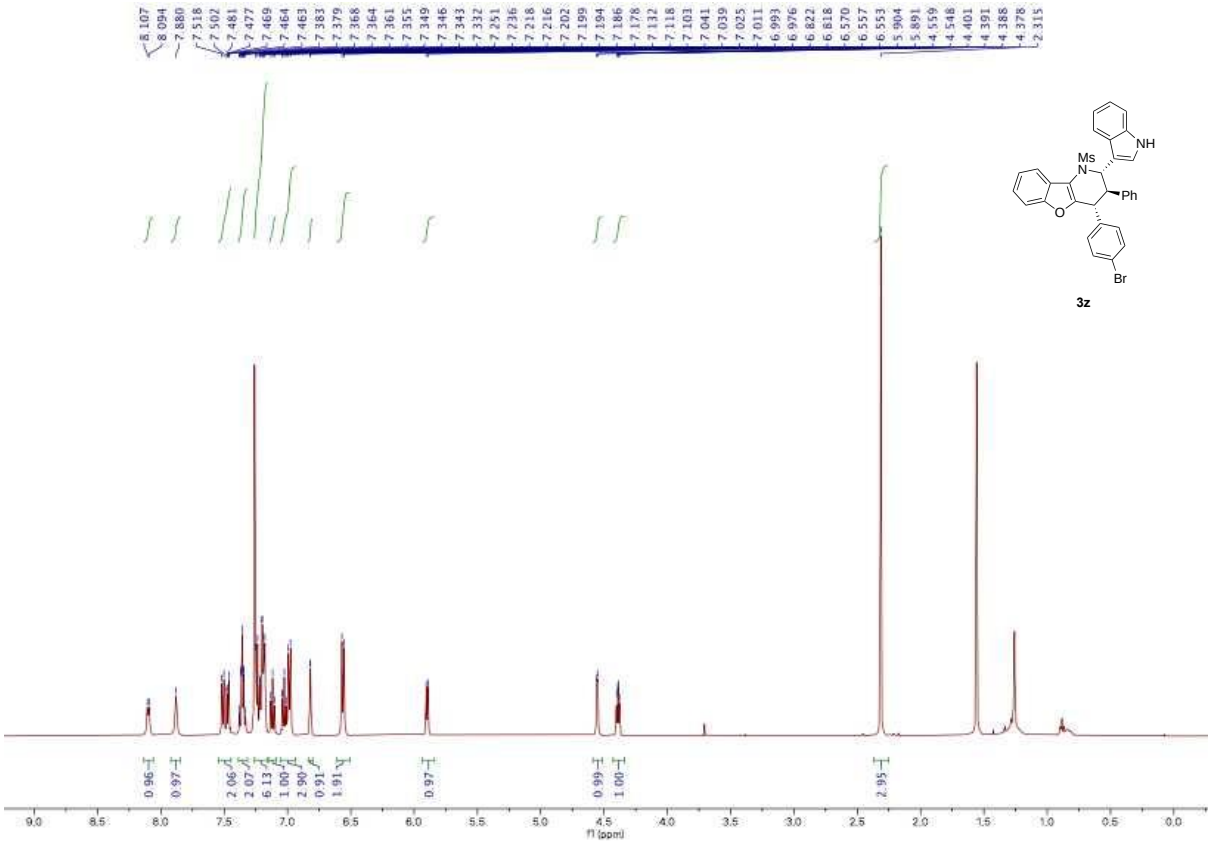
141.562
138.033
136.040
132.050
129.136
128.844
128.315
128.021
127.862
127.405
125.859
125.385
124.870
124.657
123.285
123.001
122.371
121.659
120.164
120.022
118.549
111.834
111.412
61.406
53.511
50.967
41.485
NH
Ms
N
Ph
O
Cl
3y
f1 (ppm)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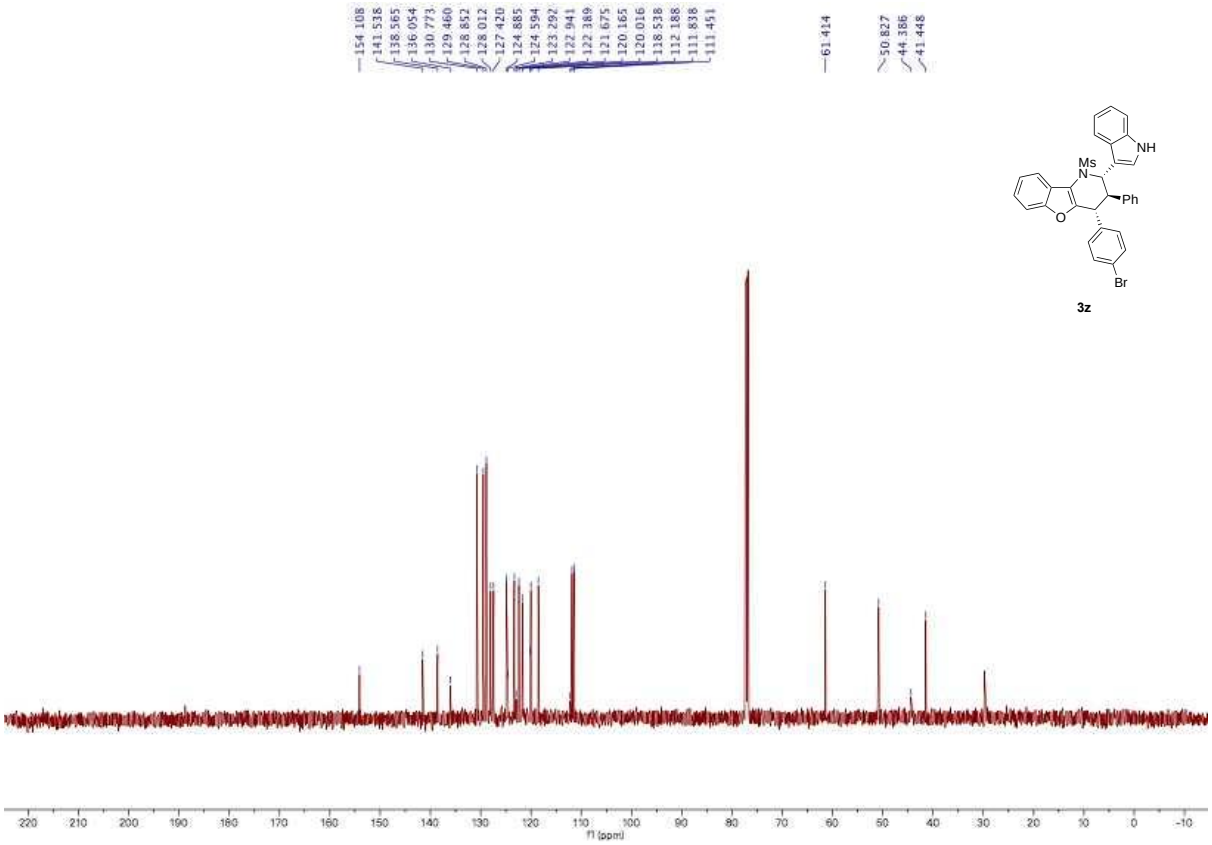
7.518
7.502
7.481
7.477
7.469
7.464
7.463
7.383
7.379
7.368
7.364
7.361
7.355
7.349
7.346
7.343
7.332
7.251
7.236
7.218
7.216
7.202
7.199
7.194
7.186
7.178
7.132
7.118
7.103
7.041
7.039
7.025
7.011
6.993
6.976
6.822
6.818
6.570
6.557
6.553
5.904
5.891
4.559
4.548
4.401
4.391
4.388
4.378
2.315
NH
Ms
N
Ph
O
Br
3z
0.96
0.97
2.06
2.07
6.13
1.00
2.90
0.91
1.91
0.97
0.99
1.00
2.95
f1 (ppm)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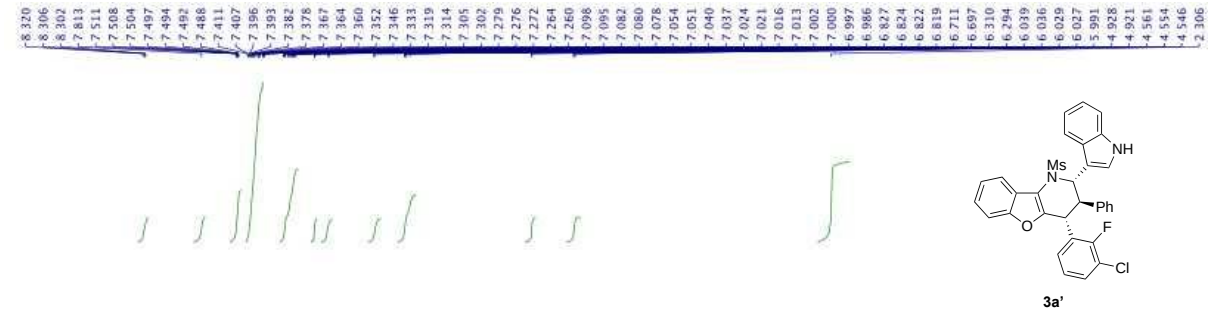
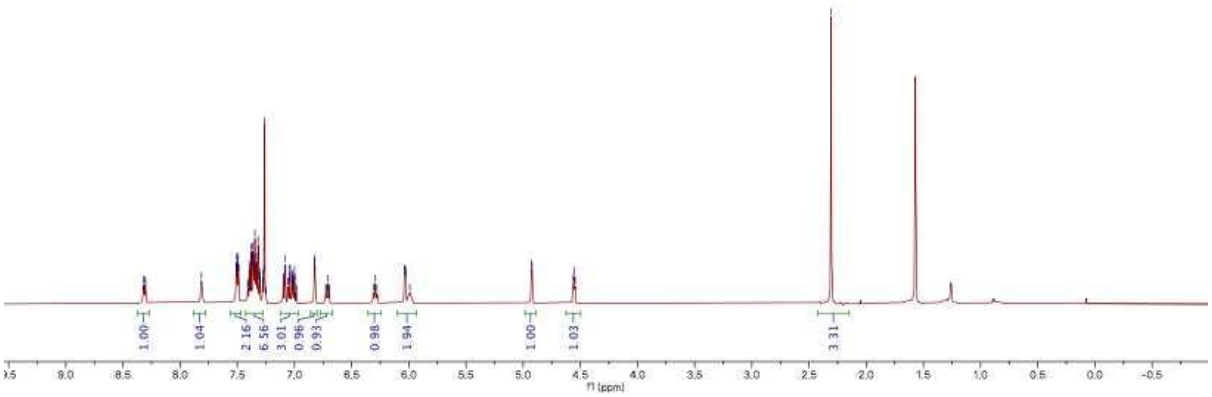
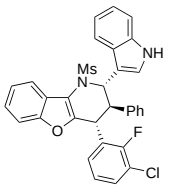
136.054
130.773
129.460
128.852
128.012
127.420
124.885
124.594
123.292
122.941
122.389
121.675
120.165
120.016
118.538
112.188
111.838
111.451
61.414
50.827
44.386
41.448
NH
Ms
N
Ph
O
Br
3z
f1 (ppm)



3a'





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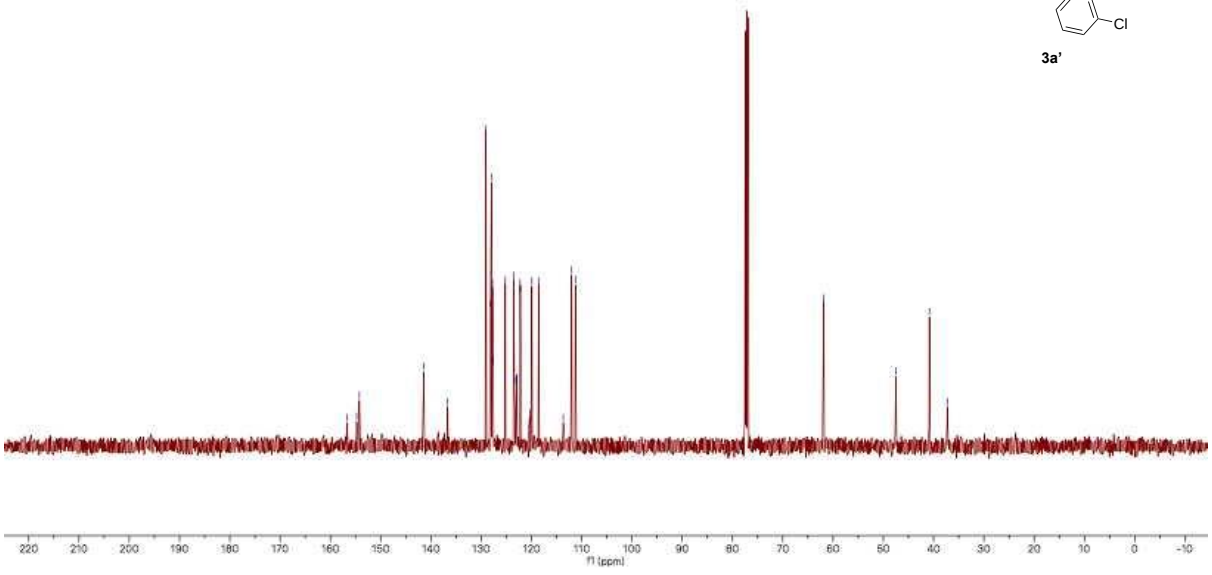

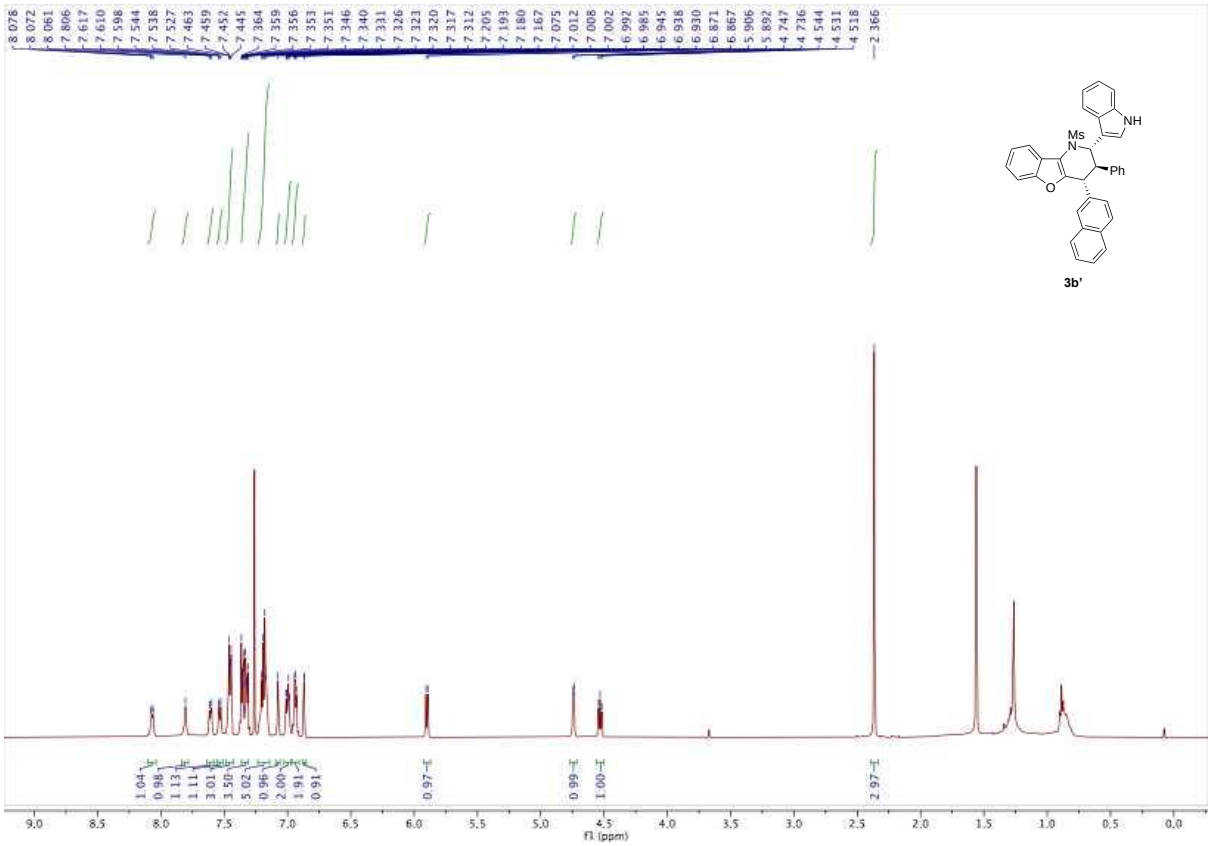
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7.617
7.610
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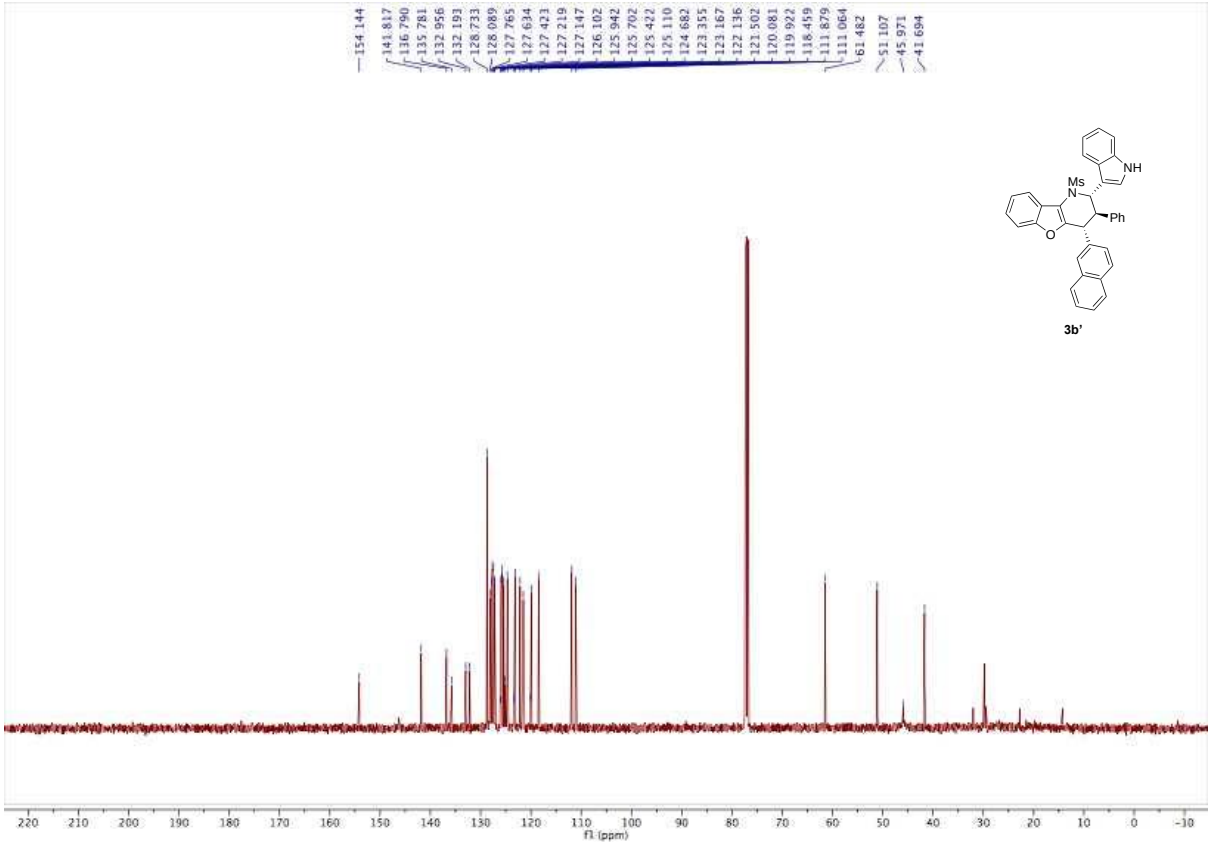
7.544
7.538
7.527
7.463
7.459
7.452
7.445
7.364
7.359
7.356
7.353
7.351
7.346
7.340
7.331
7.326
7.323
7.320
7.317
7.312
7.205
7.193
7.180
7.167
7.075
7.012
7.008
7.002
6.992
6.985
6.945
6.938
6.930
6.871
6.867
5.906
5.892
4.747
4.736
4.544
4.531
4.518
2.366
NH
Ms
N
Ph
O
3b'
1.04
0.98
1.13
1.11
3.01
3.50
5.02
0.96
2.00
1.91
0.91
0.97
0.99
1.00
2.97
f1 (ppm)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136.790
135.781
132.956
132.193
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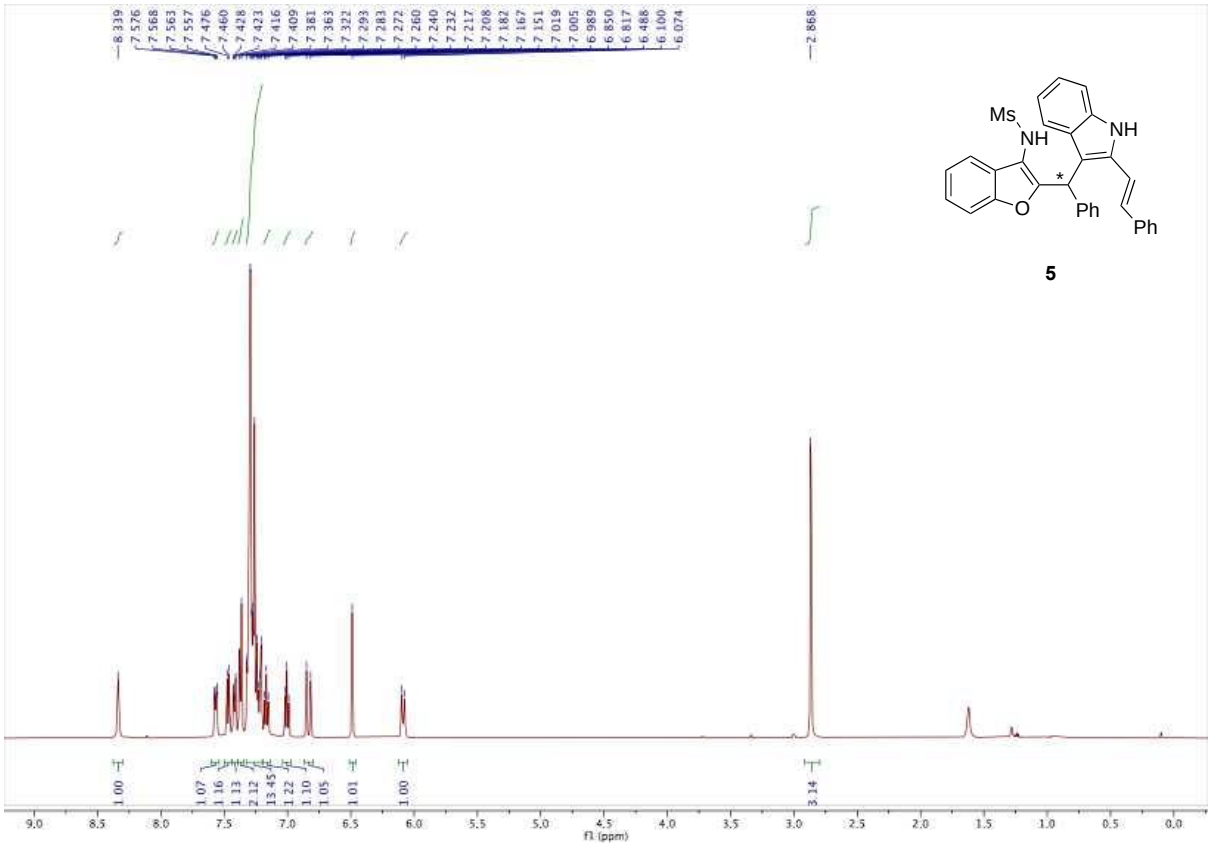
128.089
127.765
127.634
127.423
127.219
127.147
126.102
125.942
125.702
125.422
125.110
124.682
123.355
123.167
122.136
121.502
120.081
119.922
118.459
111.879
111.064
61.482
51.107
45.971
41.694
NH
Ms
N
Ph
O
3b'
f1 (ppm)



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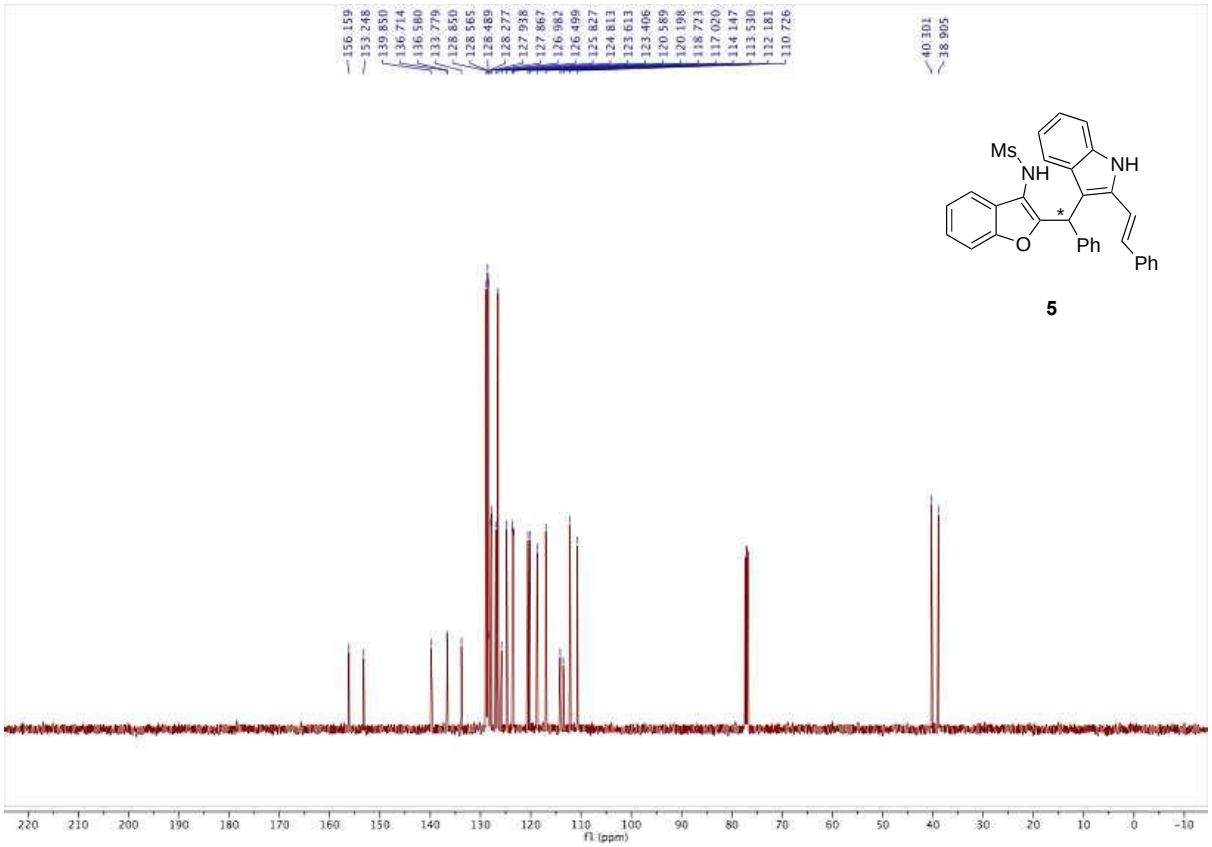
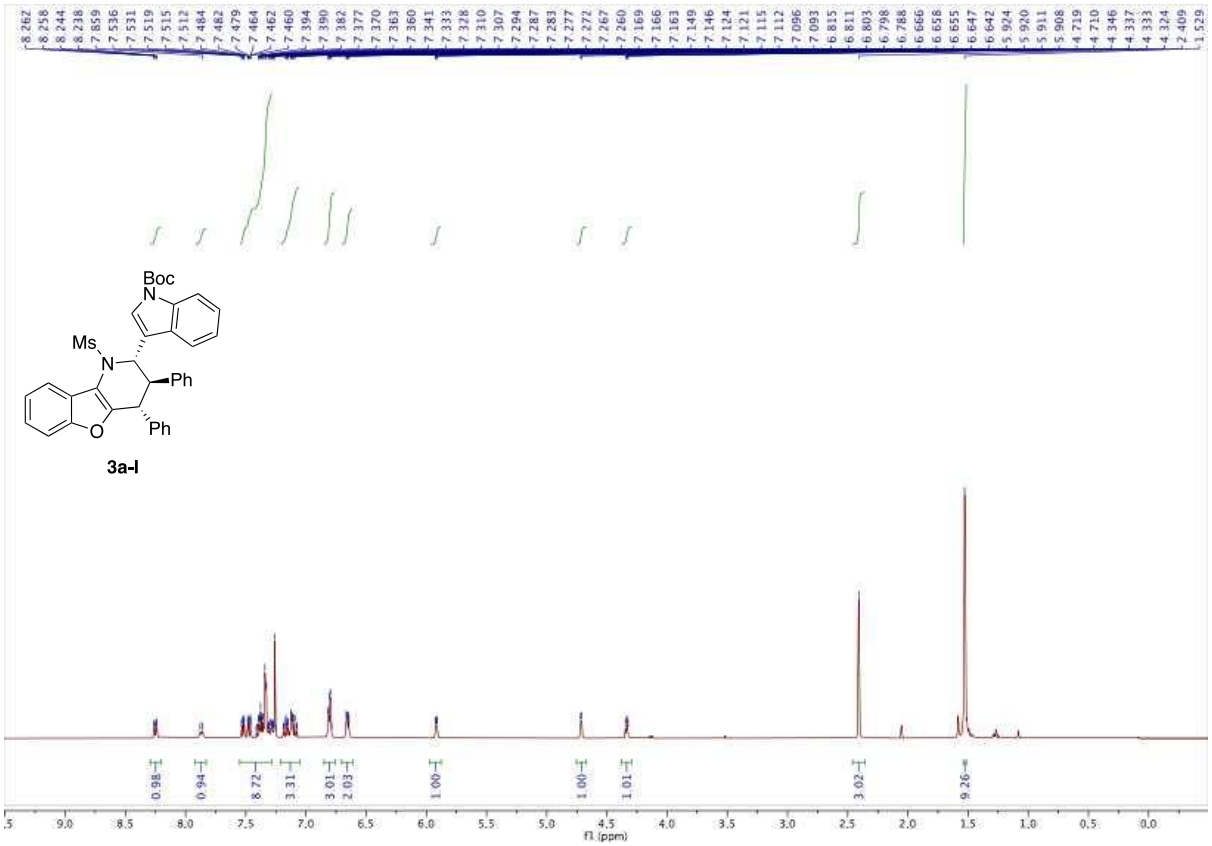
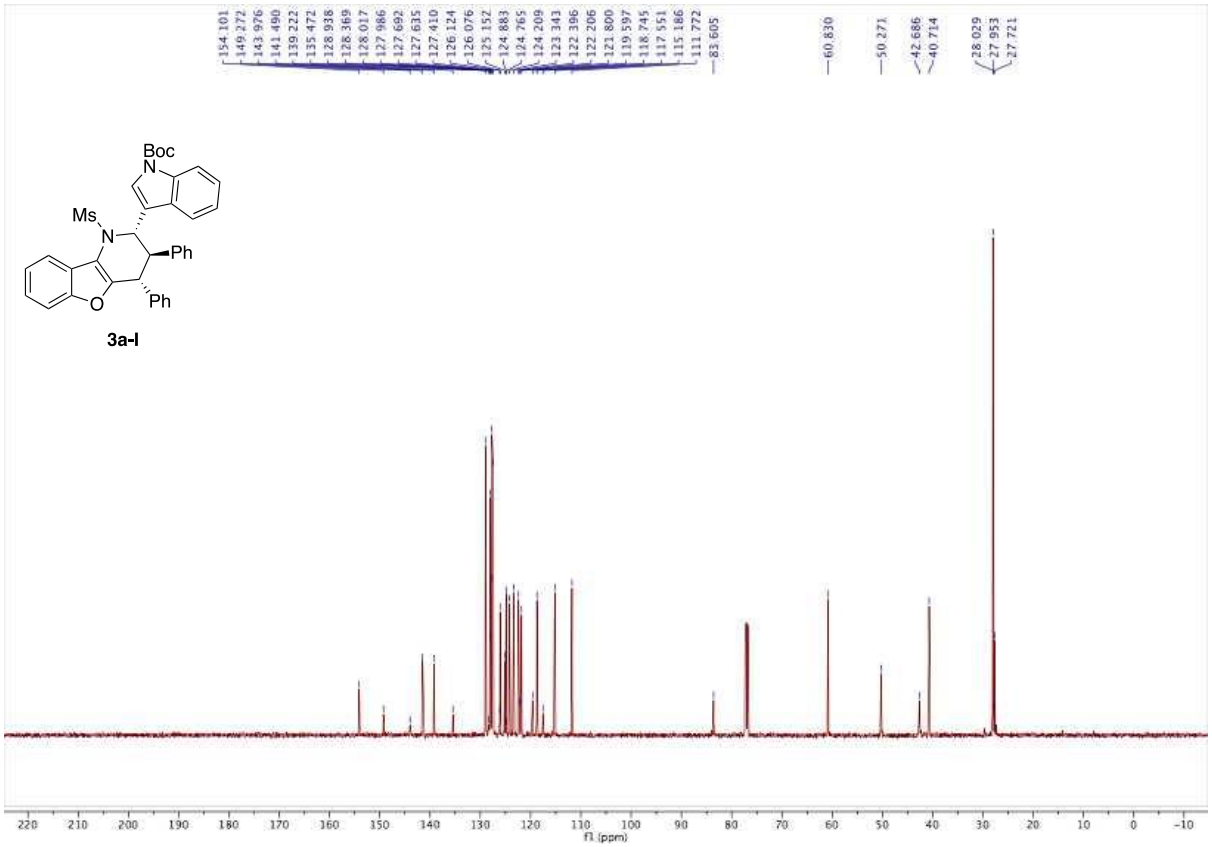
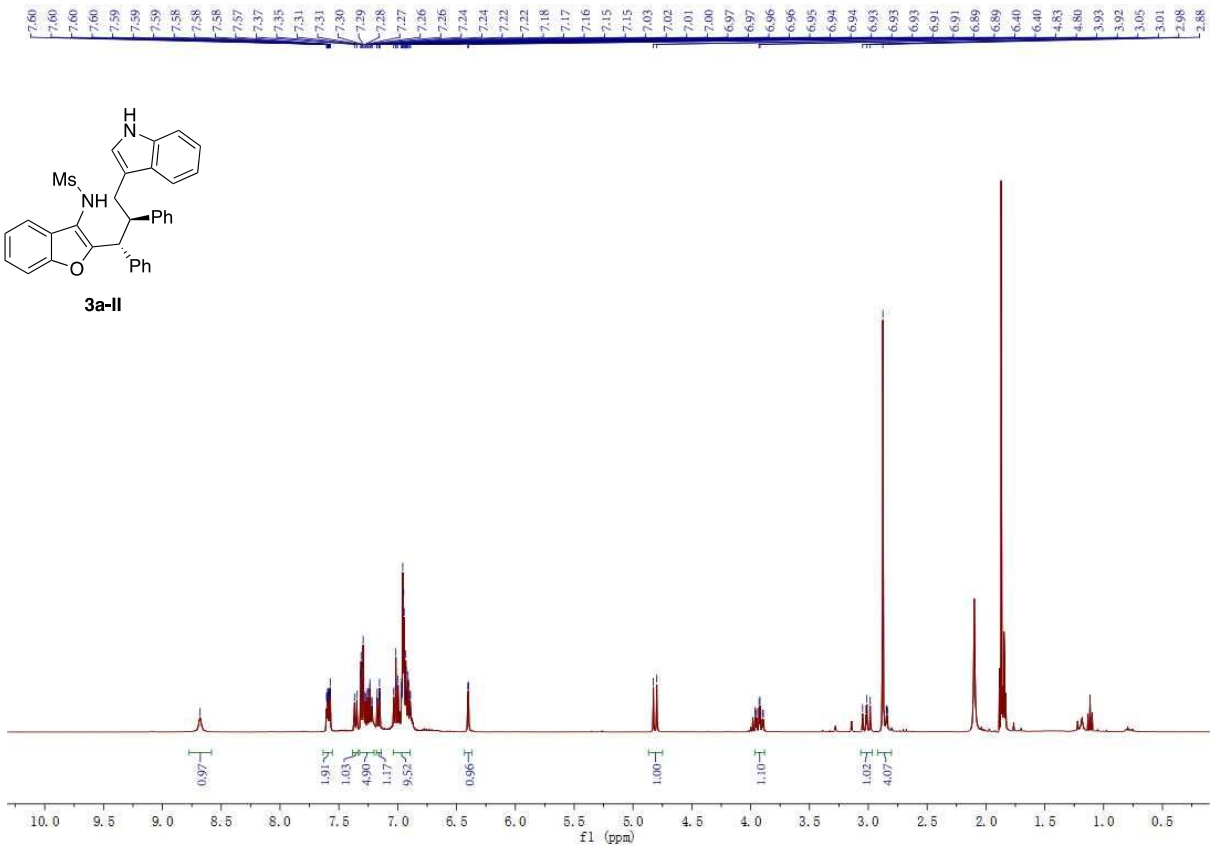
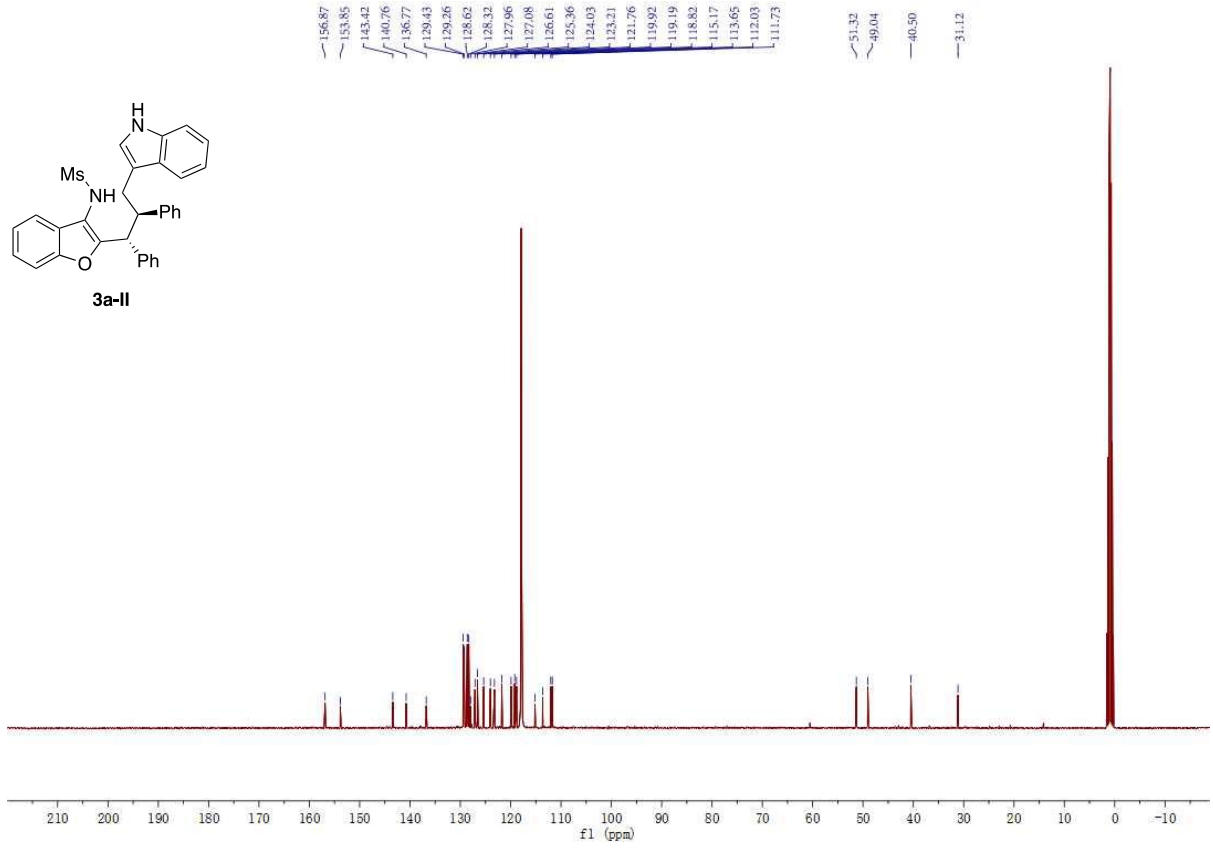


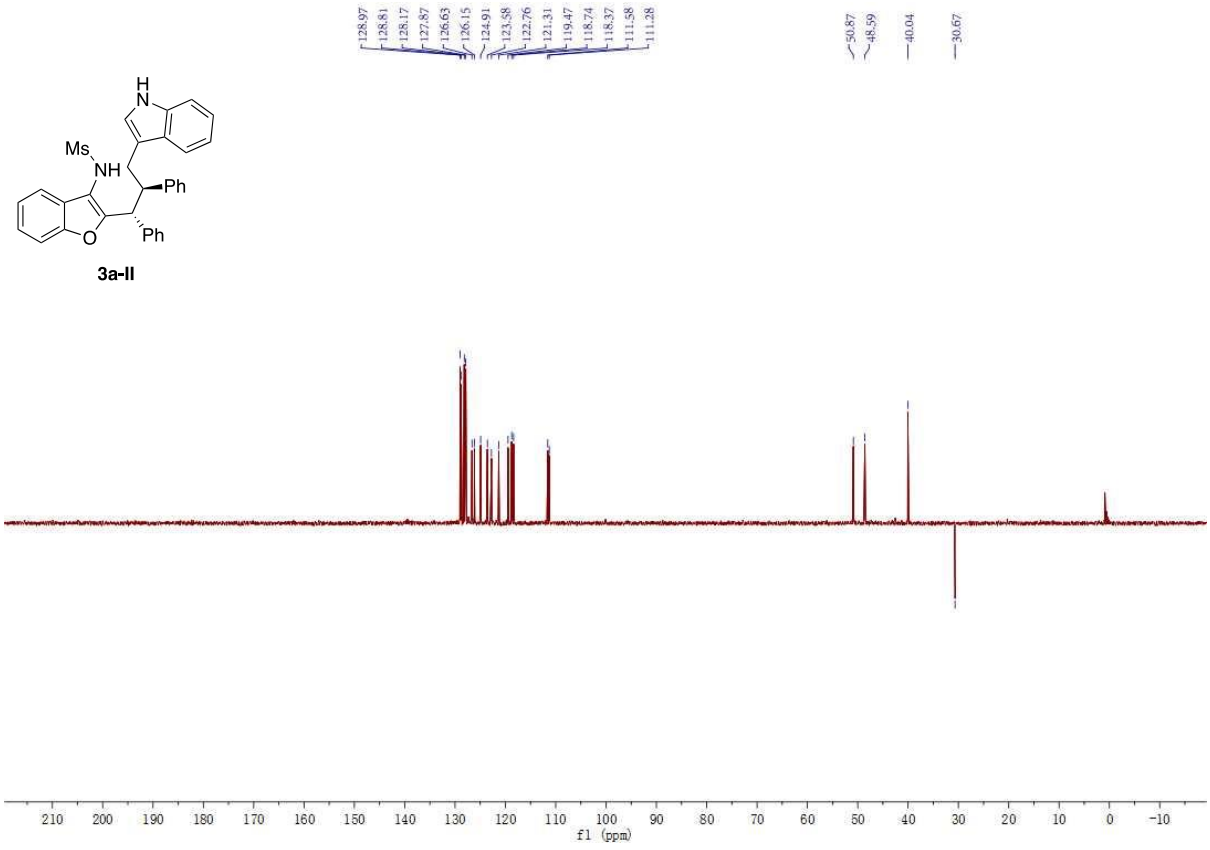
5


Boc
N
Ms
N
Ph
Ph
O
3a-l
f1 (ppm)


Boc
N
Ms
N
Ph
Ph
O
3a-l
f1 (ppm)


Ms
NH
Ph
Ph
O
H
N
3a-II
f1 (ppm)


Ms
NH
Ph
Ph
O
H
N
3a-II
f1 (ppm)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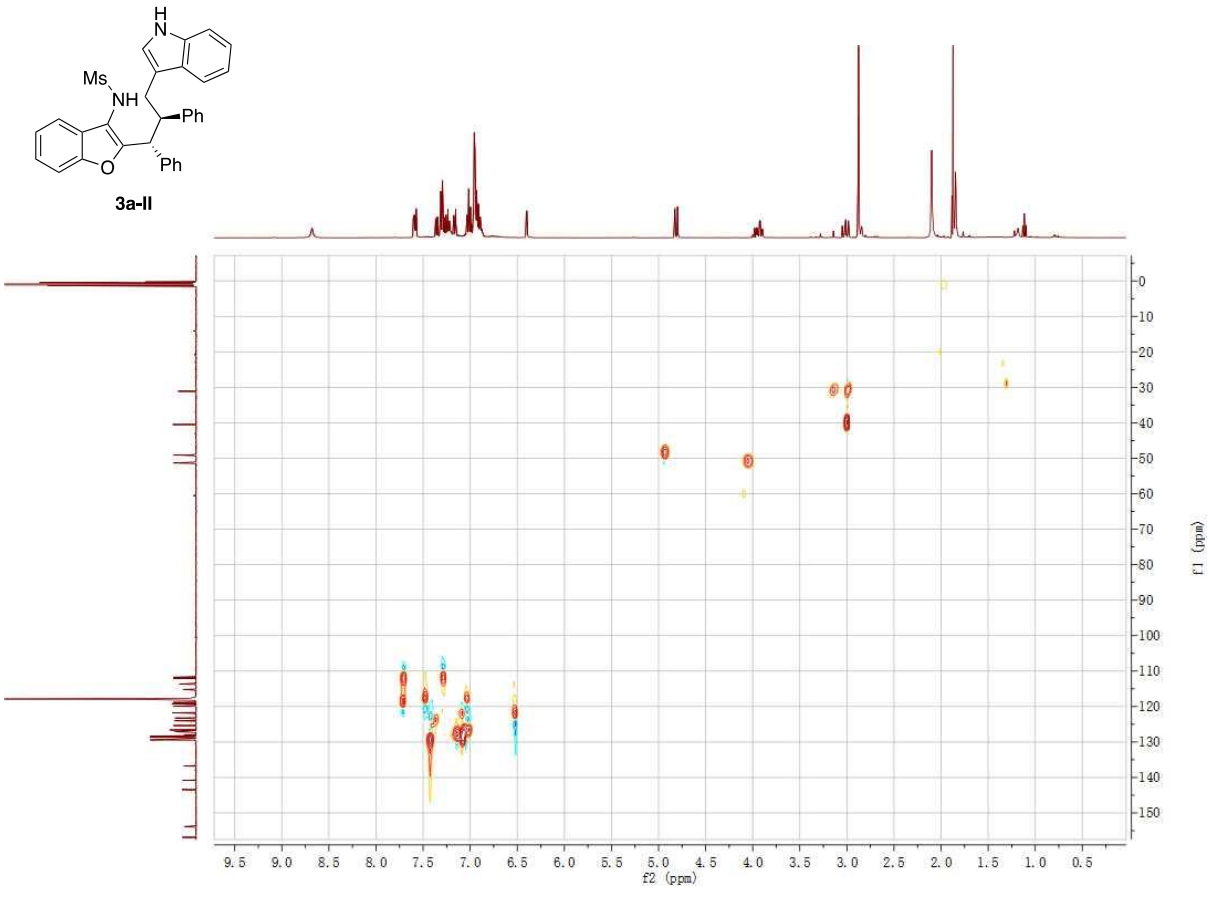
128.17
127.87
126.63
126.15
124.91
123.58
122.76
121.31
119.47
118.74
118.37
111.58
111.38
50.87
48.59
40.04
30.67
H
N
Ms
NH
Ph
Ph
O
3a-II
f1 (ppm)

HSQC


H
N
Ms
NH
Ph
Ph
O
3a-II
f2 (ppm)
f1 (ppm)