Supporting Information

Integrating C-H activation/ 2-fold annulation: a modular access to heteroaryl-tethered oxazoloisoquinolinones

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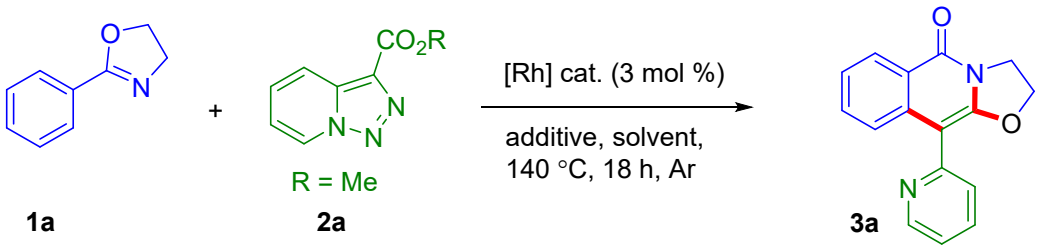
General Information. $[Cp^*RhCl_2]_2$ (>97%), $Rh_2(OAc)_4$ (>98%), AgOAc (≥99.99%), $Cu(OAc)_2$ (>98%), KOAc, NaOAc, CsOAc, Na_2CO_3, 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) of Aldrich and TCI Chemicals were used as received. Methanol, 1,2-dichloroethane, toluene and tetrahydrofuran were dried prior to use as per the standard procedure. Merck silica gel G/GF254 plates were used for analytical thin-layer chromatography (TLC). Column chromatography was carried out using Rankem silica gel (100-200 mesh). Bruker Avance III 400, 500 and 600 MHz NMR spectrometers were used to record spectra using $CDCl_3$ as the solvent and tetramethylsilane (Me_4Si) as an internal standard. Chemical shifts (δ) and spin-spin coupling constant (*J*) are reported in parts per million and hertz (Hz), respectively, and to describe peak patterns following abbreviations were used when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, m = multiplet. Melting points were determined using a Büchi B-540 apparatus and are uncorrected. FT-IR spectra were recorded on a PerkinElmer FT-IR spectrometer. Quadrupole time-of-flight electrospray ionization (ESI) mass spectrometer (Agilent 6546) was used for recording HRMS. Single crystal X-ray data was collected on a Bruker SMART APEX equipped with a CCD area detector using Mo/Kα radiation and the structure was solved by direct method using SHELXT-2018/2 (Göttingen, Germany).

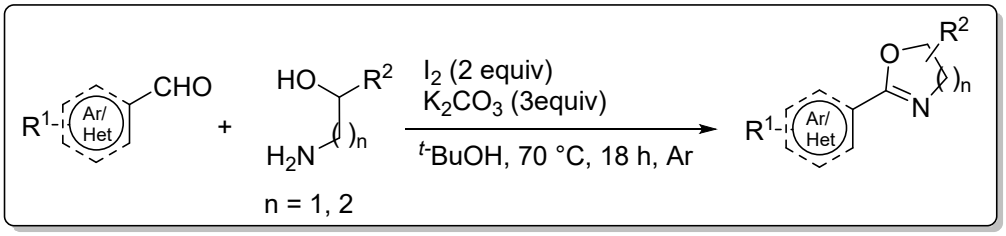
Tables S1. Optimization of the Reaction Conditions[a]



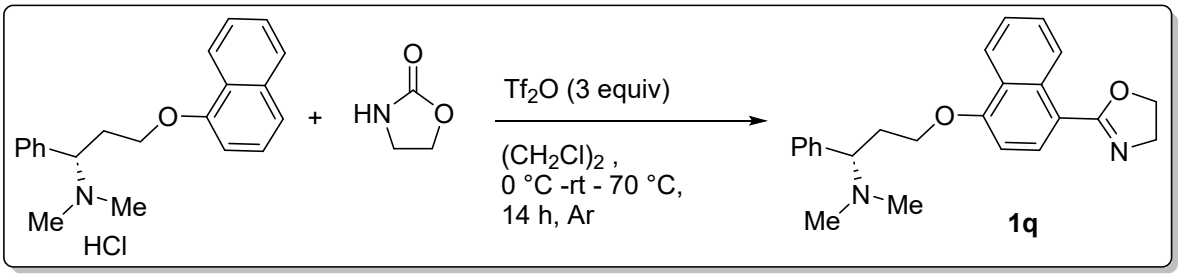
1a **2a** **3a**

entry	catalyst (3 mol %)	additive (50 mol %)	solvent	yield (%)
1	$[Cp^*RhCl_2]_2$	AgOAc	TFE	57
2	$[Cp^*RhCl_2]_2$	KOAc	TFE	72
3	**$[Cp^*RhCl_2]_2$**	**NaOAc**	**TFE**	**82**
4	$[Cp^*RhCl_2]_2$	CsOAc	TFE	55
5	$[Cp^*RhCl_2]_2$	Na_2CO_3	TFE	n.d.
6	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$	TFE	trace
7	$[Cp^*RhCl_2]_2$	AcOH	TFE	25
8	$[Cp^*RhCl_2]_2$	NaOAc	HFIP	54
9	$[Cp^*RhCl_2]_2$	NaOAc	MeOH	27
10	$[Cp^*RhCl_2]_2$	NaOAc	H_2O	n.d.
11	$[Cp^*RhCl_2]_2$	NaOAc	$(CH_2Cl)_2$	trace
12	$[Cp^*RhCl_2]_2$	NaOAc	PhMe	n.d.
13	$[Cp^*RhCl_2]_2$	NaOAc	THF	n.d.
14	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	NaOAc	TFE	59
15	$Rh_2(OAc)_4$	NaOAc	TFE	n.d.
16[c]	$[Cp^*RhCl_2]_2$	NaOAc	TFE	73
17[d]	$[Cp^*RhCl_2]_2$	NaOAc	TFE	21
18[e]	$[Cp^*RhCl_2]_2$	NaOAc	TFE	57
19	$[Cp^*RhCl_2]_2$	---	TFE	48
20	---	NaOAc	TFE	n.d.

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), [Rh] (3 mol %), additive (50 mol %), solvent (1 mL), 140 °C, 18 h, Ar, pressure tube. [b]Isolated yield. [c]With **2a′** (when R= Et). [d]Reaction at 70 °C. [e]Using 20 mol % NaOAc. n.d. = not detected.

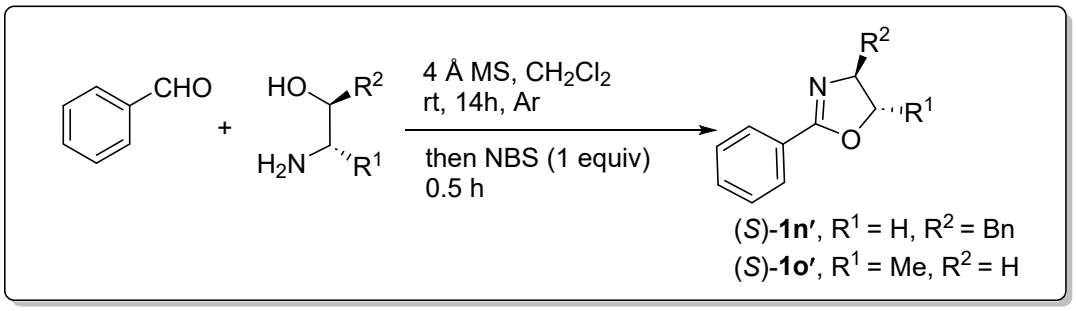


General Procedure for the Preparation of Substrates 1a-p, 1r-t and 1A-C.[1b] To a stirred solution of aldehyde (3 mmol) in *tert*-butyl alcohol (30 mL), amino alcohol (3.3 mmol, 1.1 equiv) was added. The resulting mixture was allowed to stir at room temperature for 30 min under argon atmosphere. Next, K_2CO_3 (9 mmol, 3 equiv, 1.24 g) and I_2 (6 mmol, 2 equiv, 1.51 g) were added and further stirred at the same temperature for 18 h. The progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was allowed to cool and quenched with saturated aqueous $Na_2S_2O_3$ until the color of iodine was disappeared. The mixture was extracted with EtOAc (2 x 20 mL). The combined organic layer was washed with brine (2 x 10 mL) and water (10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford **1a-p, 1r-t and 1A-C.**



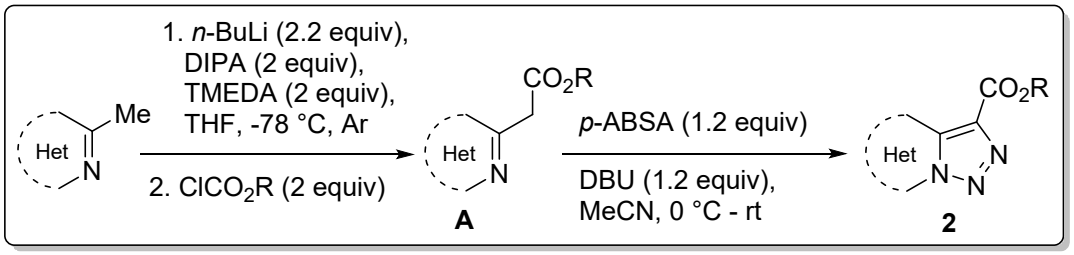
Preparation of (*S*)-3-((4-(4,5-Dihydrooxazol-2-yl)naphthalen-1-yl)oxy)-*N*,*N*-dimethyl-1-phenylpropan-1-amine 1q.[1j] To a stirred solution of oxazolidin-2-one (6 mmol, 3 equiv, 522 mg) in $(CH_2Cl)_2$ (8 mL), trifluoromethanesulfonic anhydride (6 mmol, 3 equiv, 1 mL) was added dropwise over 5 min *via* syringe at 0 ºC under argon atmosphere. The resulting solution was allowed to warm to room temperature and continued the stirring for an additional 20 min under the same temperature. Then, solution of (*S*)-*N*,*N*-dimethyl-3-(naphthalen-1-yloxy)-1-phenylpropan-1-amine hydrochloride (2 mmol, 1 equiv, 684 mg) in $(CH_2Cl)_2$ (2 mL) was added dropwise to the reaction mixture within 1 min and the resultant solution was stirred at 70 °C in a preheated oil bath for 14 h. Upon completion, monitored by TLC, the reaction mixture was allowed to cool to room temperature, and quenched with saturated aqueous K_2CO_3 and extracted with EtOAc (2 x 20 mL). The combined organic layer was washed with brine (2 x 10

mL) and water (10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate (70/30, v/v) as an eluent to afford **1q** in 65% (486 mg) yield**.**



Procedure for the Preparation of Optically Pure Substrates 1n′-o′.[1a] To a stirred solution of optically pure (*S*)-amino alcohol (3 mmol, 1 equiv) in CH_2Cl_2 (15 mL), benzaldehyde (3 mmol, 1 equiv, 0.3 mL) was added. The resulting mixture was allowed to stir at room temperature over 4 Å molecular sieves (4.5 g) for 14 h under argon atmosphere. Next, *N*-bromosuccinimide (3 mmol, 1 equiv, 531 mg) was added and further stirred at the same temperature for 0.5 h. Upon completion (monitored by TLC), the reaction mixture was filtered and the filtrate was washed with saturated aqueous $NaHCO_3$ (2 x 20 mL). The mixture was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layer was washed with brine (2 x 20 mL) and water (10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford **1n′-o′.**

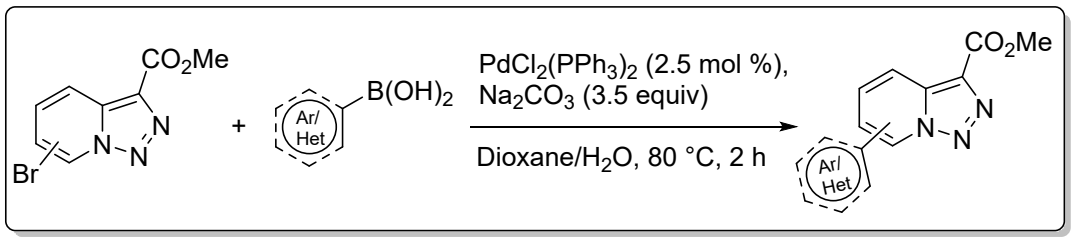
Substrates **1l** and **1r-t** are new, the complete characterization data are provided whereas **1a-k**,[1b,d-f,h] **1m-q**[1c,i-j], **1A-C**[1c-d] and **1n′-o′**[1a,g] are known, synthesized according to the reported procedure.



General Procedure for the Preparation of Substrates 2a-b, 2d-e and 2h-j.[2b] To a stirred solution of diisopropylamine (10 mmol, 2 equiv, 1.01g) in THF (20 mL), *n*-BuLi (11 mmol, 5.5 mL, 2M in hexane) was added dropwise at -78 °C and continued the stirring for 10 min

under argon atmosphere. The mixture was allowed to warm to 0 °C and further stirred for 30 min. Then, the solution of 2-methyl substituted *N*-heterocyles (5 mmol) in THF (10 mL) was added dropwise to the mixture at -78 °C for 10 min. *N,N,N',N'*-Tetramethylethylene diamine (10 mmol, 2equiv, 1.16 g) was then added and continued the stirring for 1 h at the same temperature. Corresponding alkyl chloroformate (10 mmol) was then added slowly and warmed to room temperature. Upon completion, monitored by TLC, the resultant mixture was quenched with H_2O and extracted using EtOAc (2 x 20 mL). The combined organic layer was washed with brine (2 x 10 mL) and water (10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford the ester **A**.

To the stirred solution of corresponding ester **A** (3 mmol) and *p*-acetamidobenzenesulfonyl azide (3.6 mmol, 864 mg) in CH_3CN (10 mL), 1,8-diazabicyclo[5.4.0]undec-7- ene (3.6 mmol, 537 μL) was added at 0 °C. The mixture was allowed to cool to room temperature and stirred for an appropriate time (10-12 h). The progress of reaction was monitored by TLC. Upon completion, the resultant mixture was quenched with saturated aqueous NH_4Cl solution and extracted with EtOAc (3 x 20 mL). The combined organic layer was washed with brine (2 x 10 mL) and water (10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford the corresponding (hetero)-aryl *N*-fused 1,2,3-triazoles **2**.



General Procedure for the Preparation of Pyridotriazoles 2c, 2f-g and 2k.[2b] Bromo-substituted pyridotriazoles (1 mmol), (hetero)aryl boronic acid (1.3 mmol), $PdCl_2(PPh_3)_2$ (2.5 mol %, 0.025 mmol, 18 mg) and Na_2CO_3 (3.5 mmol, 3.5 equiv, 371 mg) were stirred in dioxane/H_2O (10:10, v/v) at 80 °C in a preheated oil bath for 2 h under argon atmosphere. Upon completion, monitored by TLC, the resultant mixture was quenched with saturated aqueous NH_4Cl solution and extracted with EtOAc (3 x 20 mL). The combined organic layer was washed with brine (2 x 10 mL) and water (10 mL). Drying (Na_2SO_4) and evaporation of the

solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford the substituted pyridotriazoles **2c**, **2f-g** and **2k**.

Substrates **2c**, **2f-g** and **2k** are new, the complete characterization data are provided whereas **2a-b**,[2b-c] **2d-e**[2b] and **2h-j**[2a-b] are known, synthesized according to the reported procedure.

General Procedure for Rh(III)-Catalyzed C-H Activation/2-fold Annulation. In an oven-dried pressure tube, a mixture of aryl-/heteroaryl-oxazoline **1** (0.2 mmol), heteroaryl *N*-fused 1,2,3-triazole **2** (0.3 mmol, 1.5 equiv), $[Cp^*RhCl_2]_2$ (3 mol %, 0.006 mmol, 3.70 mg), NaOAc (0.1 mmol, 0.5 equiv, 8.2 mg) in TFE (1 mL) was stirred at 140 °C for 18 h under argon atmosphere. The progress of the reaction was monitored by TLC utilizing acetone and CH_2Cl_2 as an eluent. Upon completion, the resulting solution was cooled to room temperature, diluted with ethyl acetate (10 mL) and passed through a short celite pad. The filtrate was concentrated under reduced pressure and the residue was purified on silica gel column chromatography using acetone and CH_2Cl_2 as an eluent to afford the annulated product **3**.

Scale-up Synthesis of 3g. In an oven-dried pressure tube, a mixture of 2-(4-bromophenyl)-4,5-dihydrooxazole **1g** (3 mmol, 674 mg), methyl [1,2,3]triazolo[1,5-*a*]pyridine-3-carboxylate **2a** (4.5 mmol, 1.5 equiv, 796 mg), $[Cp^*RhCl_2]_2$ (3 mol %, 0.09 mmol, 55 mg), NaOAc (1.5 mmol, 0.5 equiv, 123 mg) in TFE (10 mL) was stirred at 140 °C for 18 h under argon atmosphere. The progress of the reaction was monitored by TLC utilizing acetone and CH_2Cl_2 as an eluent. Upon completion, the resulting solution was cooled to room temperature, diluted with ethyl acetate (20 mL) and passed through a short celite pad. The filtrate was concentrated under reduced pressure and the residue was purified on silica gel column chromatography using acetone and CH_2Cl_2 (10/90, v/v) as an eluent to afford the annulated product **3g** in 64% (0.65 g) yield.

Synthesis of 4.[2b] To an oven-dried round bottom flask, a mixture of compound **3g** (0.1 mmol, 34 mg), phenyl boronic acid (0.13 mmol, 1.3 equiv, 16 mg), $PdCl_2(PPh_3)_2$ (2.5 mol %, 0.0025 mmol, 1.75 mg) and Na_2CO_3 (0.35 mmol, 3.5 equiv, 37 mg) in dioxane/H_2O (1:1, v/v) was stirred at 80 °C in a preheated oil bath for 2 h under argon atmosphere. Upon completion, monitored by TLC, the resulting mixture was quenched with saturated aqueous NH_4Cl solution and extracted with EtOAc (3 x 10 mL). The combined organic layer was washed with brine (2 x 5 mL) and water (1 x 5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue

that was purified on silica gel column chromatography using acetone and CH_2Cl_2 (15/85, v/v) as an eluent to afford **4** in 86% (29 mg) yield.

Synthesis of 5.[3] In an oven-dried pressure tube, a mixture of **3g** (0.1 mmol, 34 mg), phenylacetylene (0.2 mmol, 2 equiv, 20.4 mg), $PdCl_2(PPh_3)_2$ (10 mol %, 0.01 mmol, 7.0 mg), CuI (0.01 mmol, 10 mol %, 1.9 mg) and Et_3N (0.5 mmol, 5 equiv, 70 μL) in DMF (1 mL) was stirred at 60 °C in a preheated oil bath for 30 h under argon atmosphere. Upon completion, monitored by TLC, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 10 mL). The combined organic layer was washed with brine (2 x 5 mL) and water (1 x 5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using acetone and CH_2Cl_2 (15/85, v/v) as an eluent to afford **5** in 88% (32 mg) yield.

Synthesis of 6.[4] To an oven-dried round bottom flask, a mixture of compound **3g** (0.1 mmol, 34 mg), diethyl phosphite (0.1 mmol, 1 equiv, 14 mg), $Pd(OAc)_2$ (5 mol %, 0.005 mmol, 1 mg mg), dppf (0.01 mmol, 10 mol %, 6 mg), NaOAc (0.012 mmol, 12 mol %, 1 mg) and DIPEA (0.12 mmol, 1.2 equiv, 16 mg) in THF (1 mL) was stirred at 70 °C in a preheated oil bath for 24 h under argon atmosphere. Upon completion, monitored by TLC, the resulting solution was cooled to room temperature, diluted with ethyl acetate (10 mL) and passed through a short celite pad. The filtrate was concentrated under reduced pressure and the residue was purified on silica gel column chromatography using acetone and CH_2Cl_2 (25/75, v/v) as an eluent to afford the phosphorylated **6** in 73% (29 mg) yield.

Synthesis of 7.[3] To an oven-dried round bottom flask, a mixture of compound **3g** (0.1 mmol, 34 mg), B_2pin_2 (0.4 mmol, 4 equiv, 101 mg), $Pd(dppf)Cl_2$ (10 mol %, 0.01 mmol, 7.3 mg) and KOAc (0.5 mmol, 5 equiv, 49 mg) in dioxane (1 mL) was stirred at 90 °C in a preheated oil bath for 12 h under argon atmosphere. Upon completion, monitored by TLC, the resulting solution was cooled to room temperature, diluted with ethyl acetate (10 mL) and passed through a short celite pad. The filtrate was concentrated under reduced pressure and the residue was purified on silica gel column chromatography using acetone and CH_2Cl_2 (20/80, v/v) as an eluent to afford the borylated **7** in 75% (29 mg) yield.

Photophysical Experiment Details: Absorption and emission spectra of some synthesized compounds were recorded in CH_2Cl_2 (1.0 x 10^{-5} M) at ambient temperature. The absorption and emission wavelengths are listed in the following.

entry	compound name	λ_{abs} (nm)	λ_{em} (nm)
1	**3m**	405	487
2	**3s**	381	460
3	**3t**	380	459
4	**3x**	345	406
5	**3l**	371	443

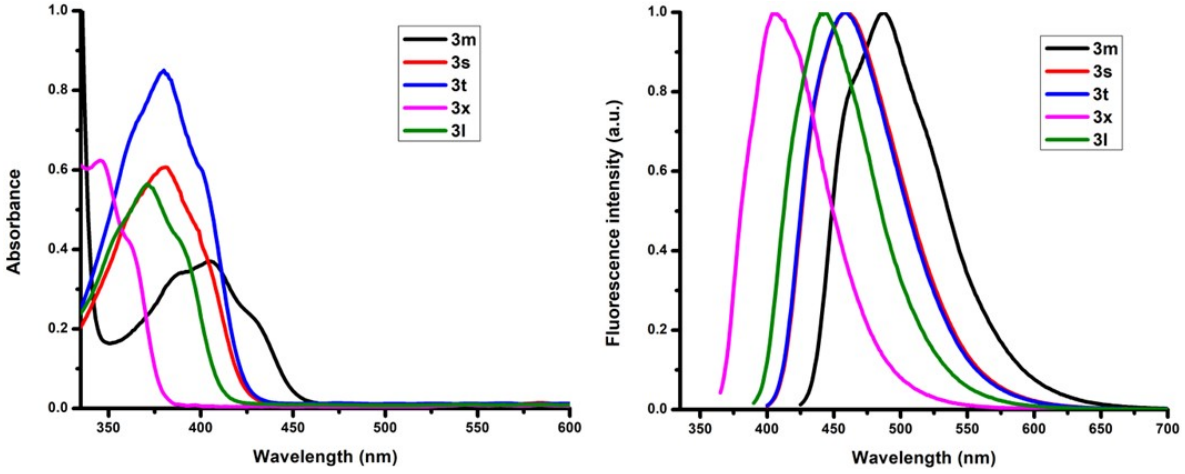
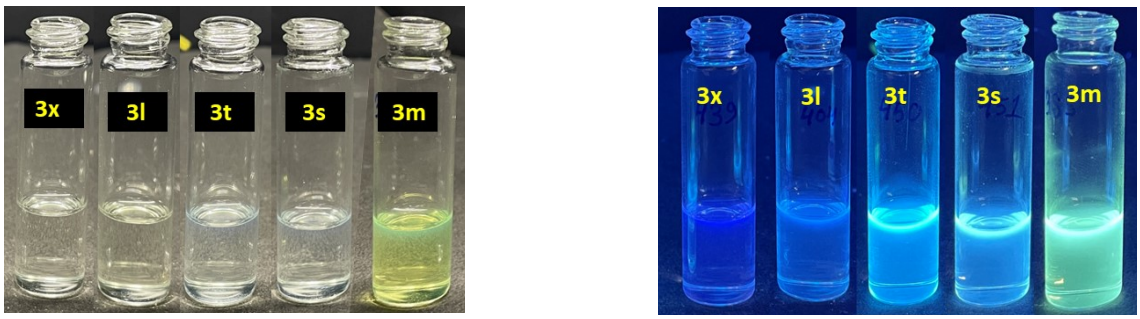


Figure S1: Normalized absorption (left) and emission (right) spectra of **3m**, **3s**, **3t**, **3x** and **3l** in CH_2Cl_2 (1.0 x 10^{-5} M)



under ambient light

under UV light

Figure S2: Fluorescence behaviour

Sample Preparation for Crystal Growth. The compound **3f** was dissolved in 1 mL of CH_2Cl_2/hexane(1:5) solution and kept at room temperature for slow evaporation (3 days). The block shaped crystal was then subjected to X-ray diffraction.

Crystal Data and Structure Refinement for 3f

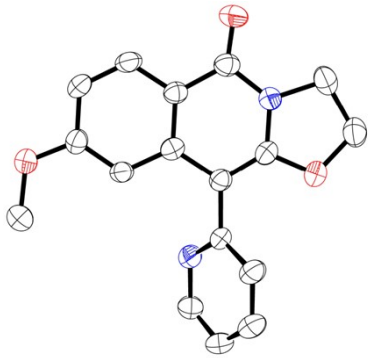
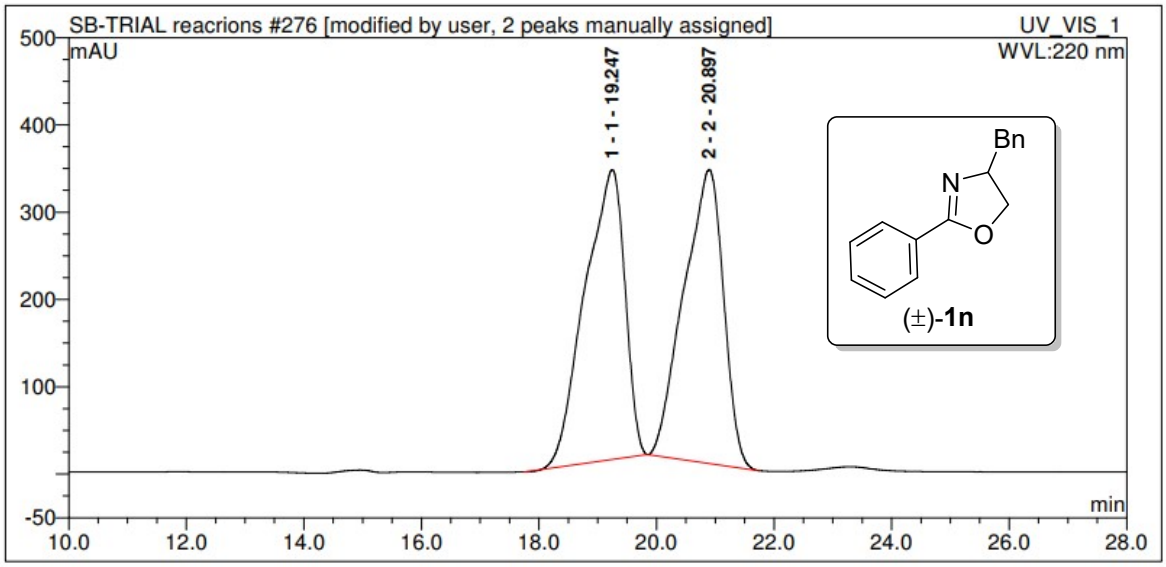


Figure S3. ORTEP diagram of 8-Methoxy-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one **3f** with 50% ellipsoid (CCDC 2382549). H-Atoms are omitted for clarity.

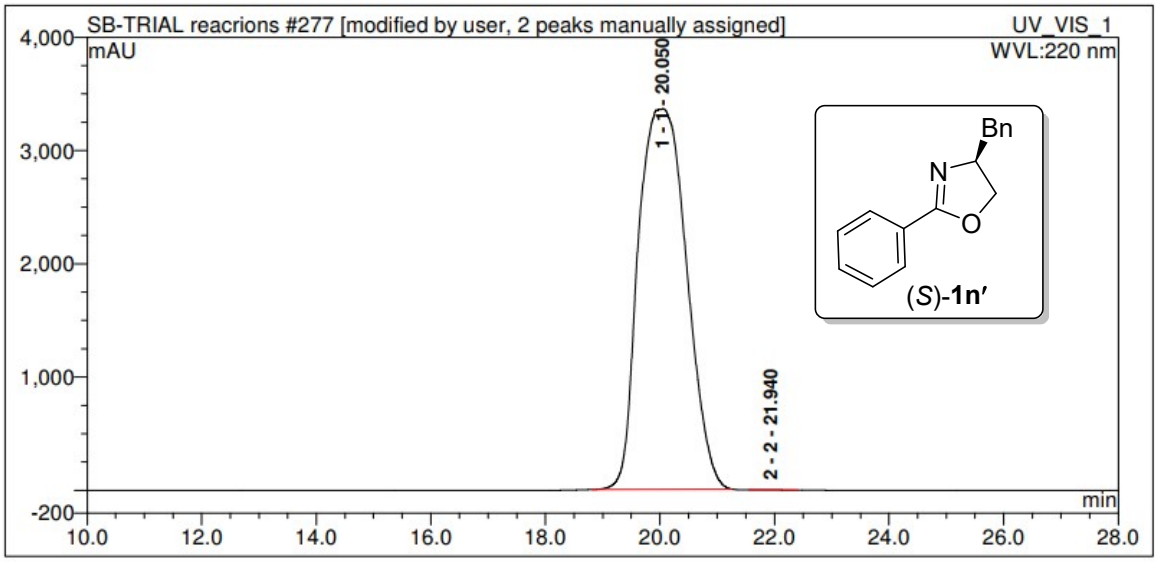
Identification code	**3f**
Empirical formula	$C_{17}H_{14}N_2O_3$
Formula weight	294.30
Crystal habit, color	block and colorless
Temperature, *T*/K	297 K
Wavelength, λ/Å	0.71073
Crystal system	triclinic
Space group	'P -1'
Unit cell dimensions	a = 8.7677(7) Å b = 9.1717(8) Å c = 10.1712(9) Å α = 64.119(2) β = 76.342(2) γ = 77.008(2)
Volume, *V*/Å^3	708.10(11)
Z	2
Calculated density, g·cm^{-3}	1.380
Absorption coefficient, μ/mm^{-1}	0.096

$F(000)$	308
θ range for data collection	2.414 to 24.998 °
Limiting indices	$-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-12 \leq l \leq 12$
Reflection collected / unique	2456 / 1921
Completeness to θ	98.40% (θ = 24.998 °)
Absorption correction	multi-scan
Refinement method	'SHELXT 2018/2 (Sheldrick, 2018)'
Data / restraints / parameters	2456/0/200
Goodness-of-fit on F^2	1.189
Final R indices [I >2sigma(I)]	$R1$ = 0.0605, $wR2$ = 0.1097
R indices (all data)	$R1$ = 0.0819, $wR2$ = 0.1161

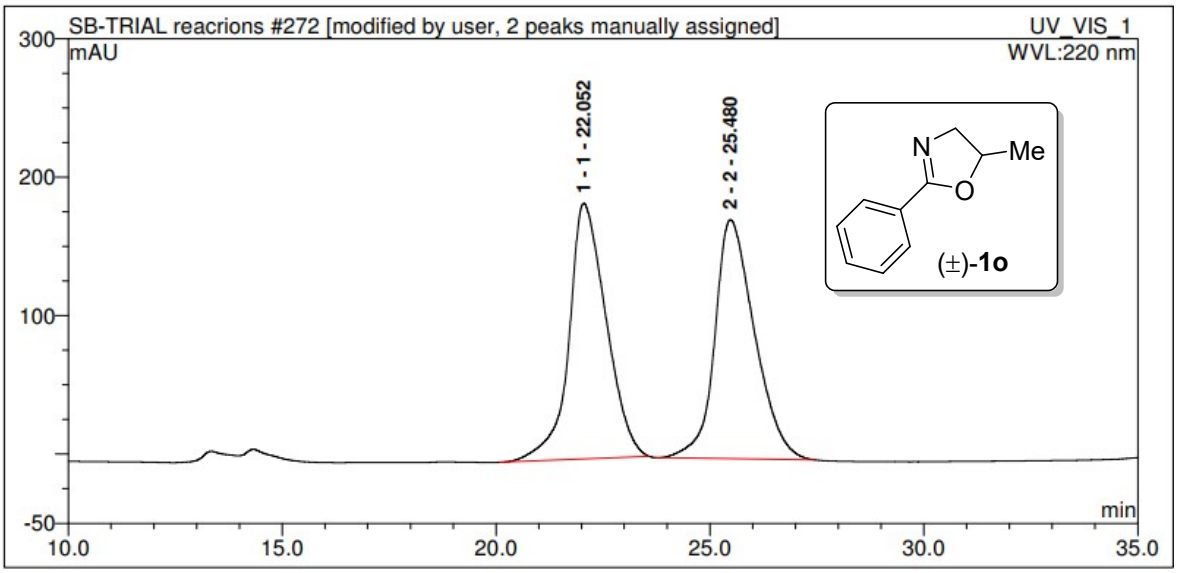
HPLC Chromatograms



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	19.24666667	261.9296	49.89092209	331.9948	n.a.
2	2	20.89666667	263.0749	50.10907791	336.9269	n.a.



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	20.05	3271.526	99.98327	3362.91	n.a.
2	2	21.94	0.547418	0.01672999907	1.13897	n.a.



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	22.05166667	186.4346	50.0064691	184.5683	n.a.
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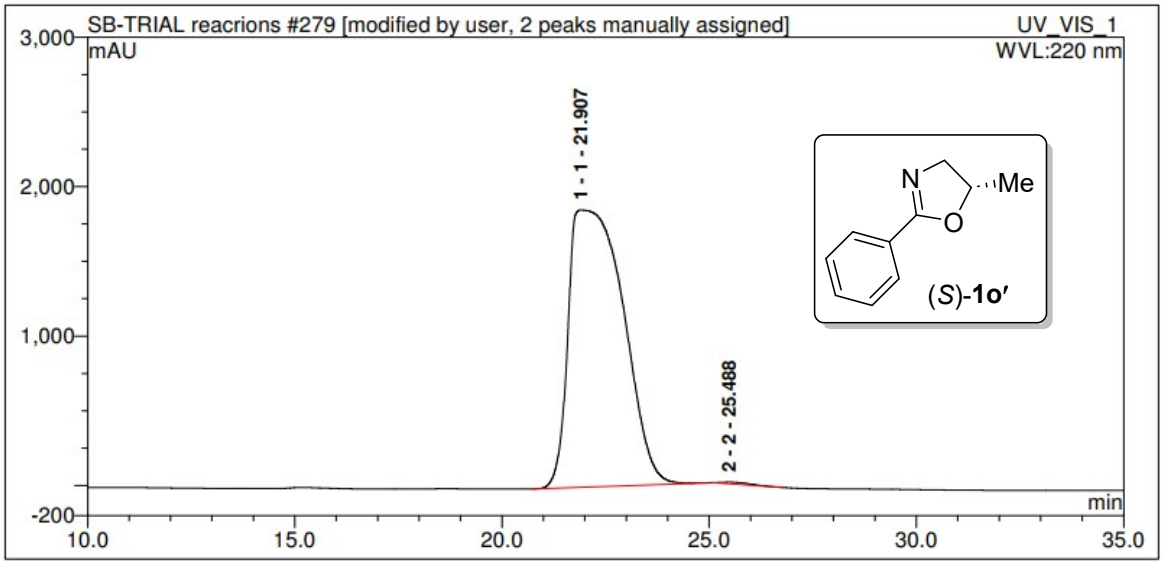
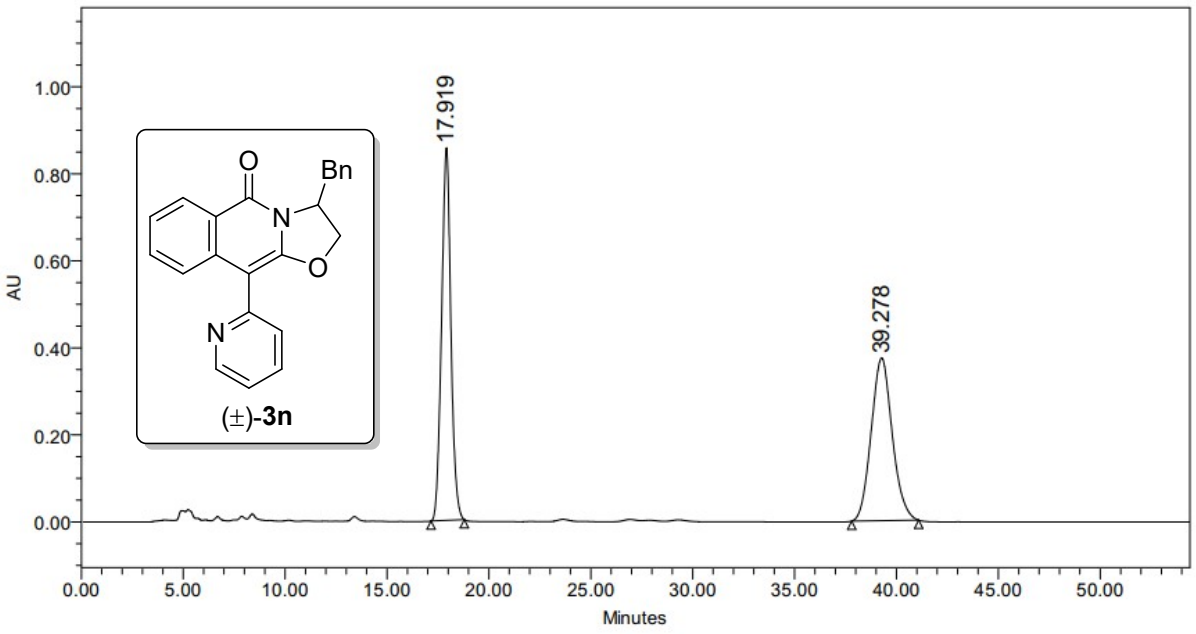
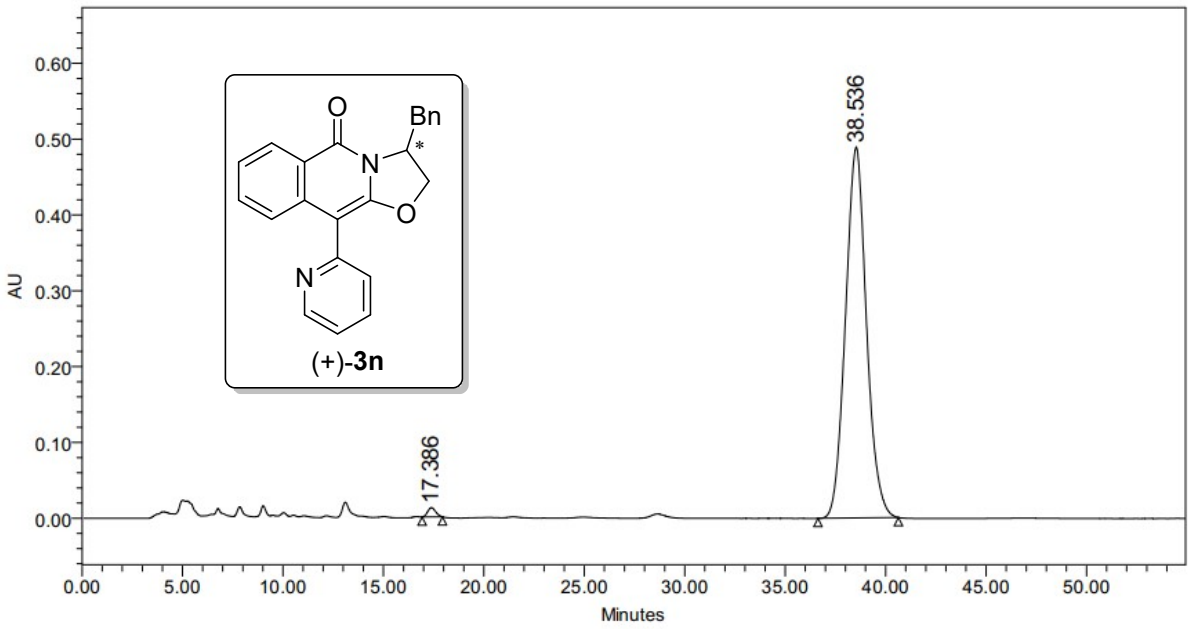


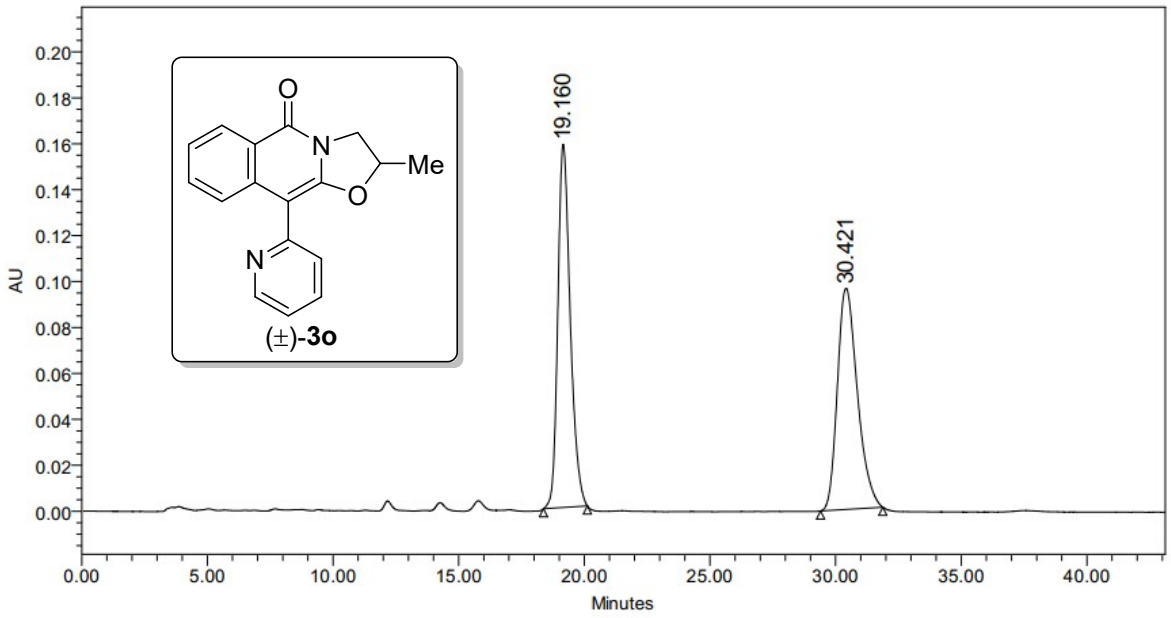
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	21.90666667	2843.078	99.63984724	1854.372	n.a.
2	2	25.48833333	10.27643	0.3601527569	11.53414	n.a.



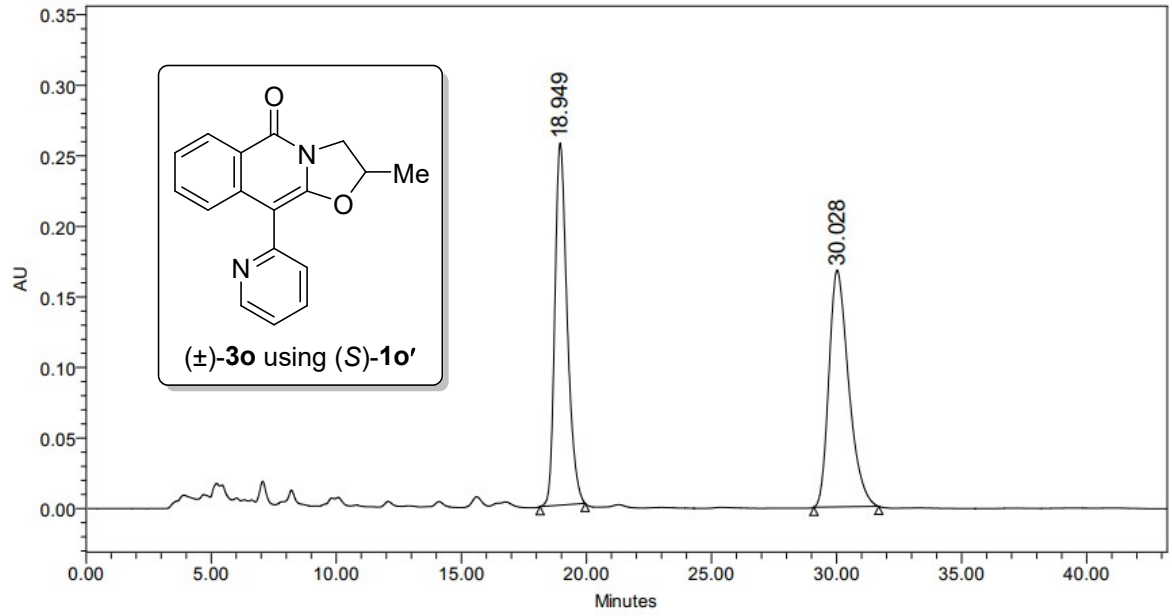
	RT	Area	% Area	Height
1	17.919	27118746	50.23	856049
2	39.278	26871875	49.77	374223



	RT	Area	% Area	Height
1	17.386	337003	0.94	12233
2	38.536	35420037	99.06	489286

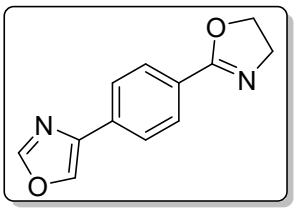


	RT	Area	% Area	Height
1	19.160	5433569	50.55	158077
2	30.421	5314729	49.45	96289

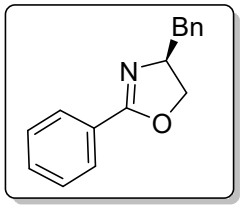


	RT	Area	% Area	Height
1	18.949	8778292	48.84	256668
2	30.028	9196816	51.16	167797

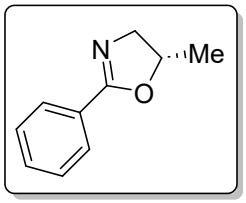
Characterization Data of 2-Aryloxazolines



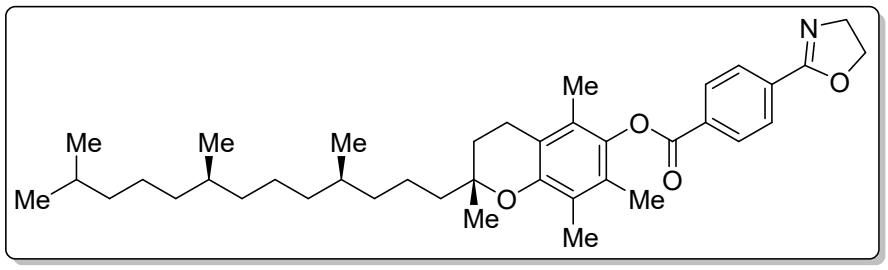
4-(4-(4,5-Dihydrooxazol-2-yl)phenyl)oxazole 1l. Analytical TLC on silica gel, 1:3 ethyl acetate/hexane R_f = 0.45; light yellow solid; mp 150-151 °C; yield 72% (462 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.95 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.44 (s, 1H), 4.45 (t, *J* = 9.6 Hz, 2H), 4.08 (t, *J* = 9.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.2, 151.0, 150.9, 130.3, 128.9, 127.8, 124.2, 122.9, 67.8, 55.0; FT-IR (KBr) 2924, 1645, 1484, 1412, 1357, 1317, 1261, 1071, 940, 830 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{12}H_{11}N_2O_2$: 215.0815, found 215.0818.



(*S*)-4-Benzyl-2-phenyl-4,5-dihydrooxazole 1n′.[1a] Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.48; colorless liquid; yield 75% (533 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.30-7.27 (m, 3H), 4.65-4.60 (m, 1H), 4.39 (t, *J* = 9.0 Hz, 1H), 4.18 (t, *J* = 7.8 Hz, 1H), 3.29 (dd, *J* = 13.8, 5.4 Hz, 1H), 2.78 (dd, *J* = 13.8, 9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.1, 138.1, 131.4, 129.3, 128.6, 128.4, 128.3, 127.9, 126.6, 71.9, 68.0, 41.9; $[\alpha]_D^{24.7}$ = + 26.72 (c = 1.27, MeOH); HPLC: >99% ee [CHIRALPAK ID, hexane/^{i}PrOH = 98:2, flow rate: 0.5 mL/min, λ = 220 nm, t_R = 20.05 min (major), 21.94 min (minor)].

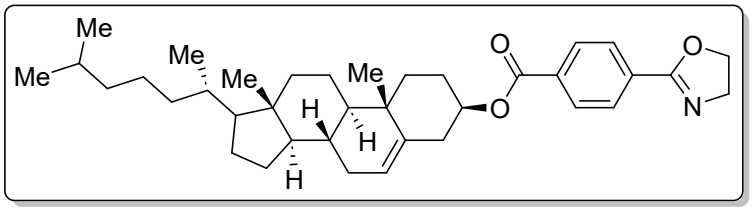


(*S*)-5-Methyl-2-phenyl-4,5-dihydrooxazole 1o′.[1g] Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.50; colorless liquid; yield 73% (352 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 4.86-4.80 (m, 1H), 4.13 (dd, *J* = 14.4, 9.0 Hz, 1H), 3.60 (dd, *J* = 14.4, 7.2 Hz, 1H), 1.41 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.9, 131.2, 128.3, 128.1, 76.3, 61.7, 21.2. $[\alpha]_D^{24.6}$ = + 25.40 (c = 0.50, $CHCl_3$); HPLC: >99% ee [CHIRALPAK IC, hexane/^{i}PrOH = 96:4, flow rate: 0.5 mL/min, λ = 220 nm, t_R = 21.90 min (major), 25.48 min (minor)].

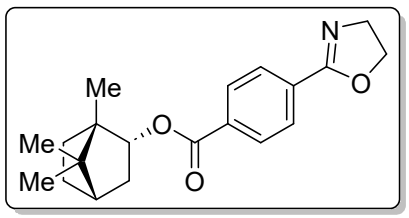


(*R*)-2,5,7,8-Tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl 4-(4,5-dihydrooxazol-2-yl)benzoate 1r. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.55; colorless solid; mp 95-96 °C; yield 70% (1.3 g); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 2H), 8.09 (d, *J* = 8.4 Hz, 2H), 4.49 (t, *J* = 9.6 Hz, 2H), 4.12 (t, *J* = 9.6 Hz, 2H), 2.62 (t, *J* = 6.6 Hz,

2H), 2.12 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.86-1.76 (m, 2H), 1.61-1.49 (m, 2H), 1.46-1.35 (m, 3H), 1.31-1.20 (m, 12H), 1.15-1.05 (m, 7H), 0.87-0.84 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.7, 164.0, 149.7, 140.6, 132.3, 132.0, 130.2, 128.4, 126.9, 125.1, 123.3, 117.6, 75.2, 68.0, 55.2, 39.5, 37.7, 37.6, 37.59, 37.53, 37.4, 32.9, 32.8, 28.1, 24.96, 24.95, 24.5, 22.8, 22.7, 21.1, 20.7, 19.89, 19.83, 19.81, 19.78, 19.74, 13.2, 12.3, 12.0; FT-IR (KBr) 2924, 1734, 1649, 1457, 1235, 1087, 941, 865, 707 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{39}H_{58}NO_4$: 604.4360, found 604.4365.



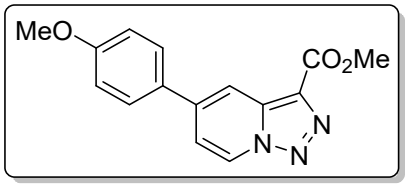
(3*R*,8*R*,9*R*,10*S*,13*S*,14*R*)-10,13-Dimethyl-17-((*S*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-(4,5-dihydrooxazol-2-yl)benzoate 1s. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 184-185 °C; yield 65% (1.1 g); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 2H), 5.42-5.41 (m, 1H), 4.89-4.84 (m, 1H), 4.46 (t, *J* = 9.6 Hz, 2H), 4.09 (t, *J* = 9.6 Hz, 2H), 2.47 (d, *J* = 7.8 Hz, 2H), 2.04-1.96 (m, 3H), 1.93-1.90 (m, 1H), 1.86-1.80 (m, 1H), 1.78-1.71 (m, 2H), 1.54-1.44 (m, 6H), 1.39-1.32 (m, 2H), 1.29-1.25 (m, 2H), 1.21-1.09 (m, 6H), 1.06 (s, 3H), 1.03-0.96 (m, 3H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.87-0.85 (m, 6H), 0.68 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.5, 164.1, 139.7, 133.3, 131.6, 129.6, 128.2, 123.0, 75.1, 67.9, 56.8, 56.3, 55.1, 50.2, 42.4, 39.9, 39.6, 38.3, 37.1, 36.8, 36.3, 35.9, 32.09, 32.04, 28.3, 28.1, 28.0, 24.4, 23.9, 22.9, 22.7, 21.2, 19.5, 18.8, 12.0; FT-IR (KBr) 2933, 1713, 1649, 1461, 1366, 1271, 1112, 1069, 945, 708 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{37}H_{54}NO_3$: 560.4098, found 560.4095.



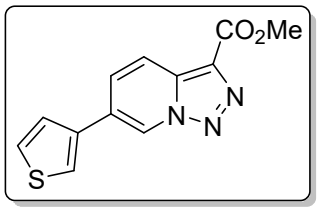
1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 4-(4,5-dihydro-oxazol-2-yl)benzoate 1t. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.45; brown solid; mp 106-107 °C; yield 75% (736 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.8 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 5.13-5.11 (m, 1H), 4.47 (t, *J* = 9.6 Hz, 2H), 4.09 (t, *J* =

9.6 Hz, 2H), 2.50-2.45 (m, 1H), 2.14-2.10 (m, 1H), 1.83-1.78 (m, 1H), 1.75-1.73 (m, 1H), 1.44-1.39 (m, 1H), 1.34-1.27 (m, 1H), 1.14-1.11 (m, 1H), 0.96 (s, 3H), 0.91 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 164.1, 133.3, 131.7, 129.6, 128.2, 81.1, 67.9, 55.2, 49.2, 48.0, 45.1, 37.0, 28.2, 27.5, 19.8, 19.0, 13.7; FT-IR (KBr) 2951, 1714, 1668, 1455, 1364, 1268, 1111, 1017, 867, 708 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{26}NO_3$: 328.1907, found 328.1910.

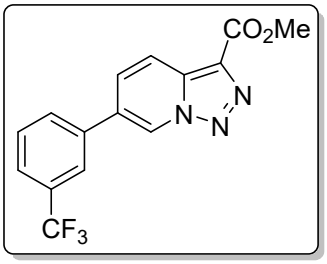
Characterization Data of Pyridotriazoles



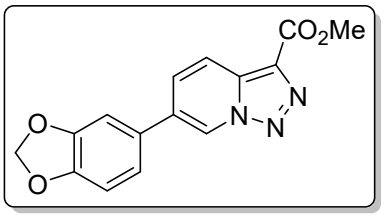
Methyl 5-(4-methoxyphenyl)-[1,2,3]triazolo[1,5-*a*]pyridine-3-carboxylate 2c. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.35; colorless solid; mp 155-156 °C; yield 85% (240 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83-8.81 (m, 1H), 8.37-8.36 (m, 1H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.40-7.37 (m, 1H), 7.06 (d, *J* = 8.8 Hz, 2H), 4.06 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.1, 161.0, 142.4, 135.9, 129.4, 129.2, 128.6, 125.8, 116.3, 114.9, 114.4, 55.6, 52.2; FT-IR (KBr) 2948, 1720, 1606, 1526, 1450, 1255, 1201, 1070, 804 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{15}H_{14}N_3O_3$: 284.1030, found 284.1034.



Methyl 6-(thiophen-3-yl)-[1,2,3]triazolo[1,5-*a*]pyridine-3-carboxylate 2f. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.53; colorless solid; mp 190-191 °C; yield 73% (189 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.29 (d, *J* = 9.0 Hz, 1H), 7.81-7.79 (m, 1H), 7.638-7.631 (m, 1H), 7.53-7.52 (m, 1H), 7.42-7.41 (m, 1H), 4.05 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.9, 136.2, 134.1, 129.6, 129.4, 128.1, 126.1, 125.6, 123.1, 122.1, 119.1, 52.2; FT-IR (KBr) 2923, 1728, 1511, 1441, 1309, 1182, 722 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{12}H_{10}N_3O_2S$: 260.0488, found 260.0483.

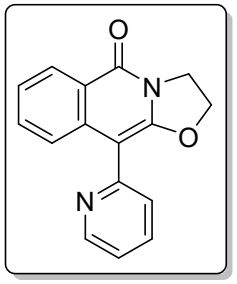


Methyl 6-(3-(trifluoromethyl)phenyl)-[1,2,3]triazolo[1,5-*a*]pyridine-3-carboxylate 2g. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.50; colorless solid; mp 197-198 °C; yield 70% (225 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.38 (d, *J* = 9.0 Hz, 1H), 7.88 (s, 1H), 7.83-7.79 (m, 2H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 4.07 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.8, 136.4, 134.4, 132.3 ($J_{C\text{-}F}$ = 32.4 Hz), 130.6, 130.3, 129.8, 129.7, 129.5, 126.0 ($J_{C\text{-}F}$ = 3.4 Hz), 124.7 ($J_{C\text{-}F}$ = 271.0 Hz), 124.3 ($J_{C\text{-}F}$ = 3.7 Hz), 123.3, 119.6, 52.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.74; FT-IR (KBr) 2922, 1703, 1457, 1334, 1269, 1175, 1110, 1075, 801 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{15}H_{11}F_3N_3O_2$: 322.0798, found 322.0799.

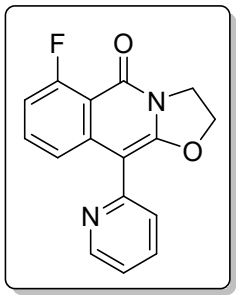


Methyl6-(benzo[*d*][1,3]dioxol-5-yl)-[1,2,3]triazolo[1,5-*a*]pyridine-3-carboxylate 2k. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.40; brown solid; mp 194-195 °C; yield 63% (187 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.29 (d, *J* = 9.0 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.10-7.08 (m, 2H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.06 (s, 2H), 4.06 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.9, 148.9, 148.8, 134.1, 131.0, 130.2, 129.4, 129.2, 122.3, 121.3, 119.0, 109.3, 107.6, 101.8, 52.3; FT-IR (KBr) 2922, 1722, 1481, 1237, 1037, 932, 809, 749 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{15}H_{12}N_3O_4$: 298.0822, found 298.0825.

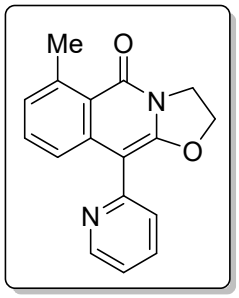
Characterization Data of the Products



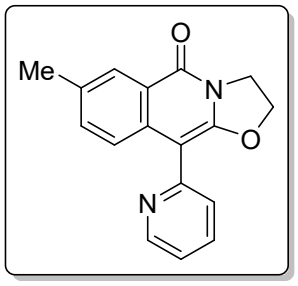
10-(Pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3a. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.50; light yellow solid; mp 180-181 °C; yield 82% (43.2 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.2 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.80-7.77 (m, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.54-7.52 (m, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.33-7.30 (m, 1H), 7.28-7.27 (m, 1H), 4.70 (t, *J* = 8.4 Hz, 2H), 4.41 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.2, 153.1, 150.1, 149.8, 138.3, 136.6, 132.9, 127.6, 126.4, 124.3, 123.6, 122.3, 122.0, 94.8, 68.2, 43.8; FT-IR (KBr) 2922, 2853, 1665, 1602, 1586, 1486, 1341, 1088, 1016, 983, 786, 764 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{13}N_2O_2$: 265.0972, found 265.0971.



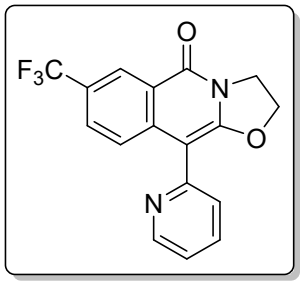
6-Fluoro-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3b. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.47; brown solid; mp 200-201 °C; yield 70% (39 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.2 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.44-7.40 (m, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.29-7.27 (m, 1H), 6.95-6.91 (m, 1H), 4.70 (t, *J* = 9.6 Hz, 2H), 4.38 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.9 ($J_{C\text{-}F}$ = 261.1 Hz), 157.5 ($J_{C\text{-}F}$ = 3.9 Hz), 152.9, 150.8, 149.9, 141.3, 136.7, 133.6 ($J_{C\text{-}F}$ = 10.3 Hz), 126.5, 122.3, 119.3 ($J_{C\text{-}F}$ = 4.2 Hz), 111.6 ($J_{C\text{-}F}$ = 6.3 Hz), 111.0 ($J_{C\text{-}F}$ = 21.1 Hz), 94.2, 68.3, 43.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -111.52; FT-IR (KBr) 2923, 2853, 1669, 1628, 1585, 1547, 1487, 1246, 1111, 1061, 808, 751 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{12}FN_2O_2$: 283.0877, found 283.0870.



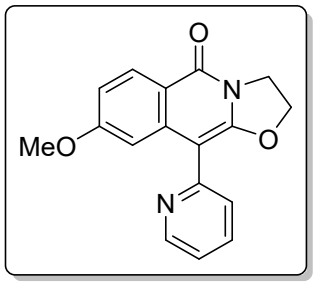
6-Methyl-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3c. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.55; light yellow solid; mp 160-161 °C; yield 81% (45 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.2 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.36-7.32 (m, 2H), 7.28-7.27 (m, 1H), 7.06 (d, *J* = 6.6 Hz, 1H), 4.67 (t, *J* = 8.4 Hz, 2H), 4.36 (t, *J* = 8.4 Hz, 2H), 2.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.1, 153.7, 149.9, 149.7, 141.9, 140.3, 136.6, 131.9, 127.5, 126.6, 122.0, 121.7, 120.8, 94.7, 68.1, 43.9, 23.9; FT-IR (KBr) 2919, 2851, 1731, 1667, 1601, 1586, 1483, 1376, 1405, 1109, 1059, 802 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}N_2O_2$: 279.1128, found 279.1132.



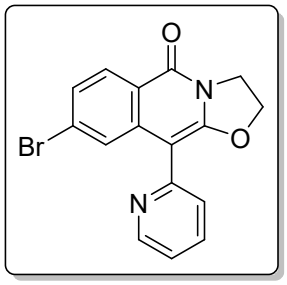
7-Methyl-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3d. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.54; colorless solid; mp 156-157 °C; yield 79% (43.9 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76-8.74 (m, 1H), 8.17 (s, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.27-7.25 (m, 1H), 4.69 (t, *J* = 7.8 Hz, 2H), 4.41 (t, *J* = 7.8 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.2, 153.3, 149.7, 149.4, 136.5, 135.9, 134.4, 134.1, 127.1, 126.3, 123.5, 122.2, 121.9, 94.7, 68.1, 43.8, 21.1; FT-IR (KBr) 2921, 1662, 1629, 1586, 1499, 1468, 1434, 1348, 1104, 1017, 824, 609 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}N_2O_2$: 279.1128, found 279.1130.



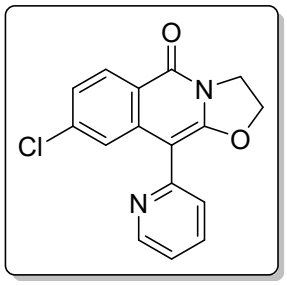
10-(Pyridin-2-yl)-7-(trifluoromethyl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3e. Analytical TLC on silica gel, 1:6 acetone/CH_2Cl_2 R_f = 0.56; colorless solid; mp 176-177 °C; yield 61% (40 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.8 Hz, 1H), 8.64 (s, 1H), 7.83-7.78 (m, 2H), 7.71-7.69 (m, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.31-7.29 (m, 1H), 4.76 (t, *J* = 8.4 Hz, 2H), 4.45 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 152.4, 151.8, 149.9, 141.0, 136.8, 128.9 ($J_{C\text{-}F}$ = 3.4 Hz), 126.4 ($J_{C\text{-}F}$ = 277.2 Hz), 126.1, 125.4 ($J_{C\text{-}F}$ = 4.3 Hz), 122.3, 121.9, 94.7, 68.6, 43.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.22; FT-IR (KBr) 2922, 1670, 1626, 1586, 1507, 1469, 1435, 1325, 1166, 1121, 1017, 952 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{12}F_3N_2O_2$: 333.0845, found 333.0848.



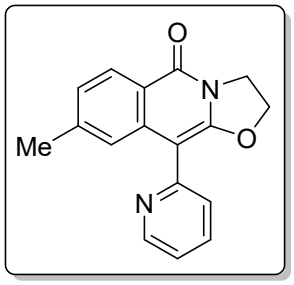
8-Methoxy-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3f. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.42; colorless solid; mp 196-197 °C; yield 80% (47 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.2 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 7.80-7.77 (m, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.28-7.26 (m, 1H), 7.08-7.07 (m, 1H), 6.91 (dd, *J* = 9.0, 2.4 Hz, 1H), 4.69 (t, *J* = 8.4 Hz, 2H), 4.39 (t, *J* = 8.4 Hz, 2H), 3.77 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.4, 159.8, 153.3, 150.7, 149.7, 140.5, 136.6, 129.7, 126.4, 122.0, 116.2, 113.2, 105.6, 94.5, 68.3, 55.4, 43.7; FT-IR (KBr) 2923, 1661, 1606, 1489, 1469, 1434, 1339, 1235, 1111, 1021, 774, 683 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}N_2O_3$: 295.1077, found 295.1072.



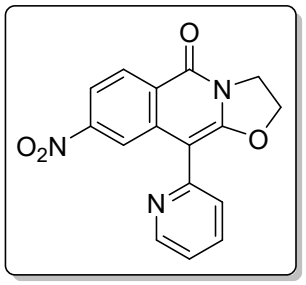
8-Bromo-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3g. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.55; light yellow solid; mp 190-191 °C; yield 72% (49.2 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.8 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.81-7.79 (m, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.30-7.28 (m, 1H), 4.72 (t, *J* = 8.4 Hz, 2H), 4.40 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 152.4, 151.0, 149.9, 139.8, 136.8, 129.3, 128.6, 127.6, 126.3, 126.2, 122.3, 120.9, 94.1, 68.4, 43.8; FT-IR (KBr) 2922, 1660, 1627, 1588, 1536, 1478, 1433, 1334, 1296, 1207, 1099, 865 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{12}BrN_2O_2$: 343.0077, found 343.0072.



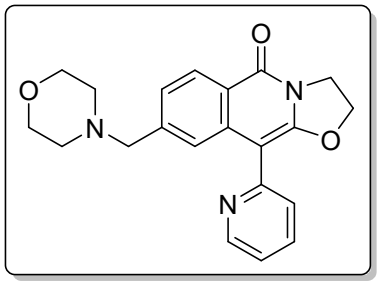
8-Chloro-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3h. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.53; colorless solid; mp 195-196 °C; yield 70% (41.7 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.2 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 7.82-7.79 (m, 1H), 7.65 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.30-7.27 (m, 2H), 4.72 (t, *J* = 8.4 Hz, 2H), 4.41 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 152.5, 151.1, 149.9, 139.75, 139.73, 136.8, 129.3, 126.3, 124.9, 123.2, 122.2, 120.6, 94.2, 68.4, 43.8; FT-IR (KBr) 2921, 1664, 1627, 1597, 1482, 1434, 1208, 1100, 948, 869 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{12}ClN_2O_2$: 299.0582, found 299.0586.



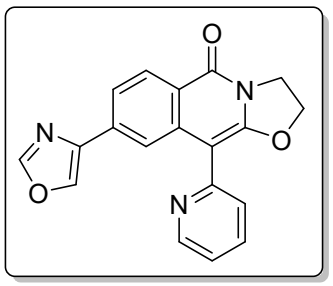
8-Methyl-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3i. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.56; yellow solid; mp 150-151 °C; yield 77% (42.8 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.2 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.37 (s, 1H), 7.29-7.27 (m, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 4.68 (t, *J* = 8.4 Hz, 2H), 4.39 (t, *J* = 8.4 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.2, 153.2, 150.1, 149.7, 143.6, 138.4, 136.6, 127.6, 126.5, 126.0, 123.2, 122.0, 120.0, 94.6, 68.2, 43.7, 22.2; FT-IR (KBr) 2920, 2848, 1662, 1626, 1586, 1486, 1276, 1102, 750 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}N_2O_2$: 279.1128, found 279.1132.



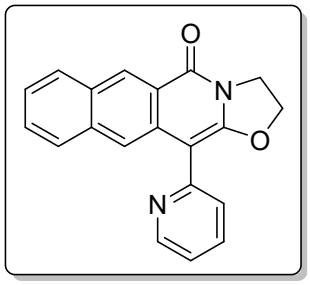
8-Nitro-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3j. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.44; orange solid; mp 245-246 °C; yield 55% (34 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 4.2 Hz, 1H), 8.66 (s, 1H), 8.51 (d, *J* = 9.0 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 1H), 7.84 (t, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.34-7.32 (m, 1H), 4.79 (t, *J* = 8.4 Hz, 2H), 4.46 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.0, 151.9, 151.8, 150.9, 150.0, 139.2, 137.0, 129.5, 126.2, 125.8, 122.5, 119.8, 117.9, 95.0, 68.7, 44.0; FT-IR (KBr) 2922, 2854, 1665, 1619, 1585, 1523, 1483, 1346, 1083, 1021, 835, 786 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{12}N_3O_4$: 310.0822, found 310.0823.



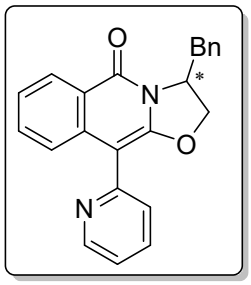
8-(Morpholinomethyl)-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3k. Analytical TLC on silica gel, 1:2 acetone/CH_2Cl_2 R_f = 0.35; brown solid; mp 146-147 °C; yield 75% (54.4 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.8 Hz, 1H), 8.31 (d, *J* = 7.8 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.55 (s, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.29-7.27 (m, 1H), 4.69 (t, *J* = 8.4 Hz, 2H), 4.40 (t, *J* = 7.8 Hz, 2H), 3.67-3.66 (m, 4H), 3.51 (s, 2H), 2.42-2.41 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.0, 153.1, 150.3, 149.7, 143.2, 138.3, 136.6, 127.7, 126.4, 125.2, 123.5, 122.0, 121.4, 94.7, 68.2, 67.0, 63.3, 53.7, 43.7; FT-IR (KBr) 2921, 2853, 1662, 1628, 1586, 1549, 1348, 1172, 1115, 914, 864, 782 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{21}H_{22}N_3O_3$: 364.1656, found 364.1654.



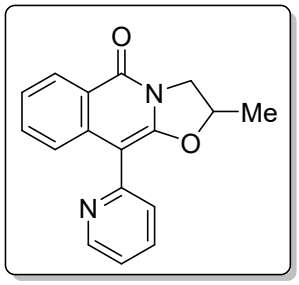
8-(Oxazol-4-yl)-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3l. Analytical TLC on silica gel, 1:4 acetone/CH_2Cl_2 R_f = 0.38; brown solid; mp 178-179 °C; yield 73% (48.3 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.2 Hz, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 7.97 (s, 1H), 7.90 (s, 1H), 7.83 (t, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.40 (s, 1H), 7.33-7.31 (m, 1H), 4.73 (t, *J* = 7.8 Hz, 2H), 4.43 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 152.8, 151.2, 151.1, 150.8, 149.9, 138.9, 136.7, 131.6, 128.6, 126.4, 123.5, 122.2, 121.9, 120.2, 119.1, 94.7, 68.3, 43.8; FT-IR (KBr) 2920, 2852, 1661, 1626, 1585, 1549, 1489, 1341, 1199, 1104, 1020, 867 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{14}N_3O_3$: 332.1030, found 332.1022.



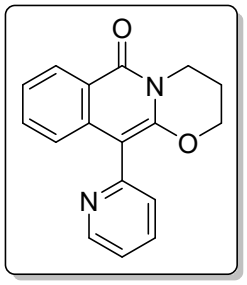
12-(Pyridin-2-yl)-2,3-dihydro-5*H*-benzo[*g*]oxazolo[3,2-*b*]isoquinolin-5-one 3m. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.51; yellow solid; mp 210-211 °C; yield 68% (42.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.82 (d, *J* = 4.8 Hz, 1H), 8.02 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.85-7.81 (m, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.50-7.46 (m, 1H), 7.43-7.39 (m, 1H), 7.33-7.30 (m, 1H), 4.69 (t, *J* = 8.0 Hz, 2H), 4.41 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.9, 153.5, 149.8, 149.3, 136.7, 136.0, 133.8, 130.2, 129.4, 129.1, 128.2, 127.7, 126.6, 125.3, 122.1, 121.9, 121.4, 93.9, 68.2, 43.6; FT-IR (KBr) 2923, 1663, 1586, 1497, 1469, 1432, 1358, 1183, 1017, 896, 780 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{15}N_2O_2$: 315.1128, found 315.1127.



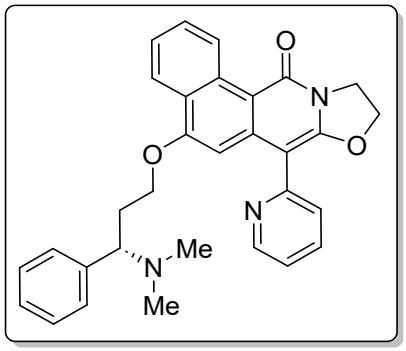
3-Benzyl-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one (+)-3n. Analytical TLC on silica gel, 1:6 acetone/CH_2Cl_2 R_f = 0.52; brown solid; mp 140-141 °C; yield 77% (54 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.8 Hz, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.35-7.28 (m, 4H), 7.24-7.22 (m, 4H), 5.12-5.09 (m, 1H), 4.48-4.46 (m, 1H), 4.41 (t, *J* = 8.4 Hz, 1H), 3.61-3.59 (m, 1H), 2.97-2.94 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.1, 153.2, 150.1, 149.7, 138.3, 136.5, 136.0, 132.9, 129.6, 129.0, 127.7, 127.3, 126.5, 124.3, 123.7, 122.6, 121.9, 94.7, 71.8, 57.3, 37.0; FT-IR (KBr) 2919, 2851, 1665, 1629, 1585, 1549, 1485, 1434, 1334, 1086, 994, 749 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{19}N_2O_2$: 355.1441, found 355.1443; $[\alpha]_D^{23.4}$ = + 44.62 (c = 0.13, $CHCl_3$); HPLC: >99% ee [CHIRALCEL AD-H, hexane/^{i}PrOH = 70:30, flow rate: 1 mL/min, λ = 254 nm, t_R = 17.38 min (minor), 38.53 min (major)].



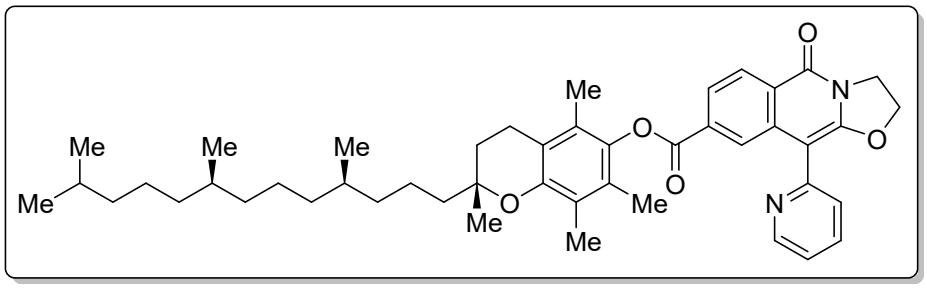
2-Methyl-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one (±)-3o. Analytical TLC on silica gel, 1:6 acetone/CH_2Cl_2 R_f = 0.55; colorless solid; mp 149-150 °C; yield 59% (32 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 4.2 Hz, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.57-7.52 (m, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.30-7.29 (m, 1H), 5.11-5.05 (m, 1H), 4.57-4.54 (m, 1H), 3.98-3.95 (m, 1H), 1.60 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.3, 153.3, 150.0, 149.7, 138.4, 136.6, 132.9, 127.6, 126.5, 124.2, 123.6, 122.2, 121.9, 94.5, 77.4, 50.0, 20.1; FT-IR (KBr) 2921, 2853, 1666, 1630, 1586, 1486, 1377, 1049, 823, 787, 695 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}N_2O_2$: 279.1128, found 279.1135; HPLC: [CHIRALCEL AD-H, hexane/^{i}PrOH = 70:30, flow rate: 1 mL/min, λ = 254 nm, t_R = 18.94 min, 30.02 min].



11-(Pyridin-2-yl)-3,4-dihydro-2*H*,6*H*-[1,3]oxazino[3,2-*b*]isoquinolin-6-one 3p. Analytical TLC on silica gel, 1:6 acetone/CH_2Cl_2 R_f = 0.53; light yellow solid; mp 190-191 °C; yield 54% (30 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.8 Hz, 1H), 8.37 (d, *J* = 7.8 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.30-7.27 (m, 2H), 7.20 (d, *J* = 7.8 Hz, 1H), 4.24-4.19 (m, 4H), 2.28-2.24 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.2, 154.3, 149.8, 147.4, 137.6, 136.5, 132.7, 127.9, 127.3, 124.2, 123.2, 122.0, 121.0, 97.3, 65.5, 39.8, 22.1; FT-IR (KBr) 2922, 1654, 1610, 1586, 1549, 1492, 1337, 1143, 700 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}N_2O_2$: 279.1128, found 279.1125.

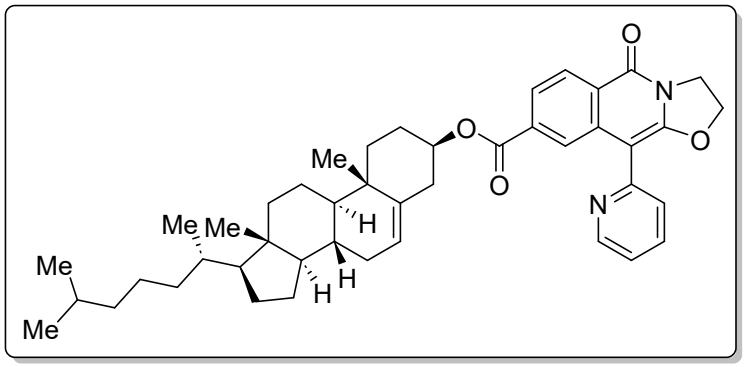


5-(3-(Dimethylamino)-3-phenylpropoxy)-7-(pyridin-2-yl)-9,10-dihydro-12*H*-benzo[*h*]oxazolo[3,2-*b*]isoquinolin-12-one 3q. Analytical TLC on silica gel, 1:1 acetone/CH_2Cl_2 R_f = 0.35; brown solid; mp 126-127 °C; yield 73% (71.6 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.08 (d, *J* = 9.0 Hz, 1H), 8.72 (d, *J* = 4.8 Hz, 1H), 8.24 (d, *J* = 7.8 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 8.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.30-7.25 (m, 4H), 7.21 (d, *J* = 7.2 Hz, 2H), 6.77 (s, 1H), 4.71 (t, *J* = 7.8 Hz, 2H), 4.49 (t, *J* = 8.4 Hz, 2H), 3.94-3.90 (m, 1H), 3.74-3.70 (m, 1H), 3.50-3.48 (m, 1H), 2.58-2.52 (m, 1H), 2.20 (s, 6H), 2.18-2.16 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.8, 157.9, 153.5, 151.2, 149.8, 142.4, 139.6, 136.6, 133.6, 128.8, 128.5, 128.3, 127.4, 126.7, 126.2, 125.0, 124.3, 122.0, 121.8, 109.0, 99.7, 95.7, 68.3, 67.8, 65.6, 44.4, 43.0, 32.8; FT-IR (KBr) 2923, 1756, 1661, 1589, 1544, 1468, 1439, 1241, 1154, 1089, 914, 772 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{31}H_{30}N_3O_3$: 492.2282, found 492.2286.

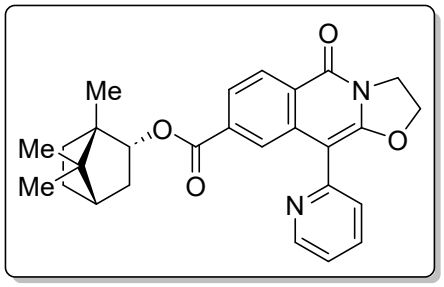


(*R*)-2,5,7,8-Tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl 5-oxo-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinoline-8-carboxylate 3r. Analytical TLC on silica gel, 1:6 acetone/CH_2Cl_2 R_f = 0.54; yellow solid; mp 153-154 °C; yield 77% (111 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.2 Hz, 1H), 8.59 (s, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.28-7.27 (m, 1H), 4.75 (t, *J* = 8.4 Hz, 2H), 4.46 (t, *J* = 8.4 Hz, 2H), 2.59 (t, *J* = 6.6 Hz, 2H), 2.10 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.84-1.73 (m, 2H), 1.55-1.49 (m, 2H), 1.46-1.36 (m, 3H), 1.31-1.21 (m, 12H), 1.15-1.03 (m, 7H), 0.86-0.83 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.9, 159.7, 152.5, 150.8, 149.9, 149.6, 140.7, 138.4, 136.7, 133.4, 128.2, 126.9, 126.5, 126.3, 125.3, 125.2, 124.7, 123.3,

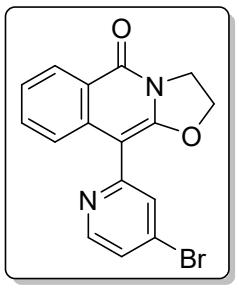
122.3, 117.6, 95.1, 75.2, 68.4, 43.9, 39.5, 37.69, 37.67, 37.58, 37.52, 37.4, 32.9, 32.8, 28.1, 24.95, 24.93, 24.5, 22.8, 22.7, 21.1, 20.7, 19.89, 19.82, 19.7, 13.2, 12.3, 11.9; FT-IR (KBr) 2923, 1734, 1665, 1585, 1549, 1465, 1376, 1230, 1199, 1093, 958, 751 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{46}H_{61}N_2O_5$: 721.4575, found 721.4568.



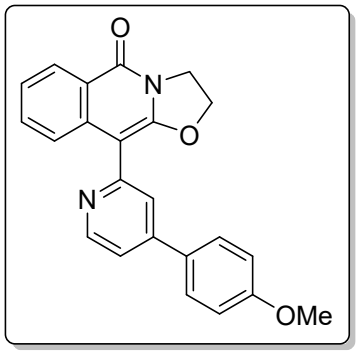
(3*R*,8*R*,9*R*,10*S*,13*S*,14*R*,17*S*)-10,13-Dimethyl-17-((*S*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 5-oxo-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinoline-8-carboxylate 3s. Analytical TLC on silica gel, 1:6 acetone/CH_2Cl_2 R_f = 0.51; light yellow solid; mp 230-231 °C; yield 75% (101 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.2 Hz, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.38 (s, 1H), 7.90-7.89 (m, 1H), 7.82-7.79 (m, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.30-7.28 (m, 1H), 5.40-5.39 (m, 1H), 4.83-4.77 (m, 1H), 4.73 (t, *J* = 8.4 Hz, 2H), 4.43 (t, *J* = 8.4 Hz, 2H), 2.43-2.41 (m, 2H), 2.02-1.95 (m, 3H), 1.91-1.87 (m, 1H), 1.85-1.79 (m, 1H), 1.72-1.66 (m, 2H), 1.60-1.54 (m, 2H), 1.53-1.48 (m, 2H), 1.47-1.42 (m, 2H), 1.37-1.30 (m, 2H), 1.28-1.24 (m, 2H), 1.20-1.07 (m, 6H), 1.04 (s, 3H), 1.02-0.95 (m, 3H), 0.91-0.90 (m, 3H), 0.86-0.85 (m, 6H), 0.67 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7, 159.7, 152.6, 150.6, 149.9, 139.7, 138.2, 136.7, 134.6, 127.9, 126.3, 125.8, 124.8, 124.2, 122.9, 122.2, 95.1, 75.3, 68.3, 56.8, 56.2, 50.1, 43.9, 42.4, 39.8, 39.6, 38.2, 37.1, 36.7, 36.3, 35.9, 32.06, 32.00, 28.3, 28.1, 27.8, 24.4, 23.9, 22.9, 22.7, 21.1, 19.5, 18.8, 12.0; FT-IR (KBr) 2926, 1716, 1664, 1630, 1585, 1550, 1468, 1252, 1204, 1107, 962, 756 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{44}H_{57}N_2O_4$: 677.4313, found 677.4306.



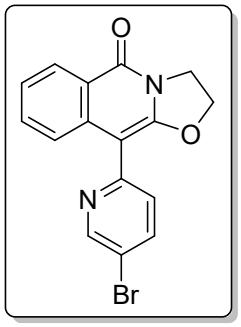
1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 5-oxo-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinoline-8-carboxylate 3t. Analytical TLC on silica gel, 1:6 acetone/CH_2Cl_2 R_f = 0.45; light yellow solid; mp 192-193 °C; yield 79% (70 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76-8.75 (m, 1H), 8.464-8.462 (m, 1H), 8.42 (d, *J* = 7.8 Hz, 1H), 7.92-7.90 (m, 1H), 7.80-7.78 (m, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.28-7.26 (m, 1H), 5.07-5.04 (m, 1H), 4.74 (t, *J* = 8.4 Hz, 2H), 4.44 (t, *J* = 8.4 Hz, 2H), 2.45-2.40 (m, 1H), 2.03-1.98 (m, 1H), 1.80-1.74 (m, 1H), 1.72-1.70 (m, 1H), 1.37-1.32 (m, 1H), 1.26-1.22 (m, 1H), 1.09-1.06 (m, 1H), 0.93 (s, 3H), 0.89 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 159.7, 152.6, 150.6, 149.8, 138.2, 136.6, 134.5, 127.9, 126.3, 125.9, 124.8, 124.1, 122.1, 95.0, 81.0, 68.4, 49.2, 47.9, 45.0, 43.8, 36.9, 28.1, 27.3, 19.8, 19.0, 13.6; FT-IR (KBr) 2923, 1715, 1664, 1630, 1585, 1551, 1485, 1255, 1203, 1108, 1016, 755 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{27}H_{29}N_2O_4$: 445.2122, found 445.2126.



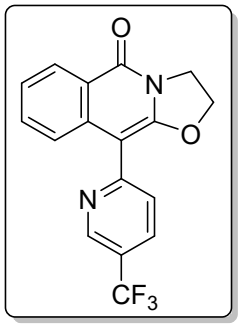
10-(4-Bromopyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3u. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.48; colorless solid; mp 164-165 °C; yield 70% (47.8 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.8 Hz, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.70-7.67 (m, 2H), 7.56-7.54 (m, 1H), 7.44-7.43 (m, 1H), 7.34-7.32 (m, 1H), 4.72 (t, *J* = 7.8 Hz, 2H), 4.41 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.2, 154.6, 150.5, 150.2, 137.8, 133.14, 133.12, 129.5, 127.7, 125.2, 124.5, 123.4, 122.2, 93.6, 68.4, 43.8; FT-IR (KBr) 2921, 1664, 1564, 1486, 1421, 1339, 1124, 1087, 1017, 984, 767 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{12}BrN_2O_2$: 343.0077, found 343.0074.



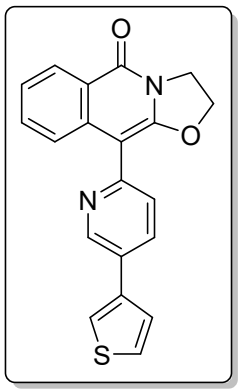
10-(4-(4-Methoxyphenyl)pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3v. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.40; brown solid; mp 222-223 °C; yield 75% (55.5 mg); ^{1}H NMR (600 MHz, $CDCl_3$) 8.75 (d, *J* = 4.8 Hz, 1H), 8.38 (d, *J* = 7.8 Hz, 1H), 7.68-7.67 (m, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.55-7.52 (m, 1H), 7.46-7.45 (m, 1H), 7.34-7.31 (m, 1H), 7.02 (d, *J* = 9.0 Hz, 2H), 4.70 (t, *J* = 8.4 Hz, 2H), 4.42 (t, *J* = 7.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.7, 160.2, 153.5, 150.2, 150.1, 148.6, 138.4, 132.9, 130.4, 128.3, 127.7, 124.3, 123.8, 123.6, 122.3, 119.5, 114.6, 94.9, 68.2, 55.5, 43.8; FT-IR (KBr) 2922, 1666, 1596, 1546, 1515, 1487, 1250, 1182, 1022, 826 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{19}N_2O_3$: 371.1390, found 371.1395.



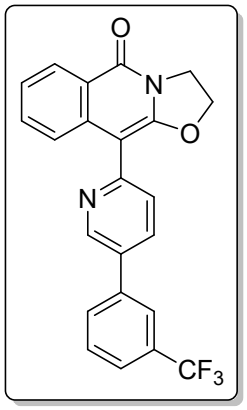
10-(5-Bromopyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3w. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.47; light brown solid; mp 154-155 °C; yield 73% (50 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80-8.79 (m, 1H), 8.37-8.35 (m, 1H), 7.90 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.56-7.53 (m, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.34-7.32 (m, 1H), 4.71 (t, *J* = 8.4 Hz, 2H), 4.41 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.1, 151.6, 150.7, 150.2, 139.2, 137.8, 133.0, 127.7, 127.6, 124.5, 123.4, 122.3, 118.9, 93.6, 68.3, 43.8; FT-IR (KBr) 2922, 1663, 1568, 1547, 1485, 1462, 1367, 1341, 1090, 1013, 864, 769 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{12}BrN_2O_2$: 343.0077, found 343.0083.



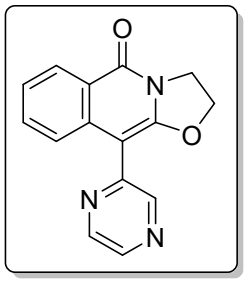
10-(5-(Trifluoromethyl)pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3x. Analytical TLC on silica gel, 1:6 acetone/CH_2Cl_2 R_f = 0.54; light yellow solid; mp 183-184 °C; yield 66% (43.8 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.99-8.98 (m, 1H), 8.37 (d, *J* = 7.2 Hz, 1H), 8.00-7.98 (m, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.57-7.54 (m, 1H), 7.35-7.32 (m, 1H), 4.71 (t, *J* = 8.4 Hz, 2H), 4.41 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.1, 157.0, 150.8, 146.4 ($J_{C\text{-}F}$ = 4.0 Hz), 137.5, 133.6 ($J_{C\text{-}F}$ = 3.3 Hz), 133.1, 127.7 ($J_{C\text{-}F}$ = 270.4 Hz), 124.6, 124.5 ($J_{C\text{-}F}$ = 33.0 Hz), 123.4, 122.8, 122.3, 93.7, 68.4, 43.7; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.26; FT-IR (KBr) 2923, 1662, 1603, 1488, 1329, 1125, 1081, 1017, 866, 762 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{12}F_3N_2O_2$: 333.0845, found 333.0847.



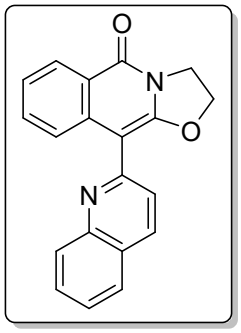
10-(5-(Thiophen-3-yl)pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3y. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.41; yellow solid; mp 209-210 °C; yield 69% (47.7 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.58 (s, 1H), 7.57-7.54 (m, 2H), 7.47-7.45 (m, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 4.73 (t, *J* = 7.8 Hz, 2H), 4.43 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.2, 151.5, 150.2, 147.5, 138.7, 138.3, 134.1, 133.0, 129.8, 127.7, 127.2, 126.3, 126.0, 124.4, 123.6, 122.3, 121.6, 94.5, 68.3, 43.8; FT-IR (KBr) 2923, 2855, 1663, 1629, 1549, 1486, 1334, 1089, 1017, 864, 787, 760 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{15}N_2O_2S$: 347.0849, found 347.0850.



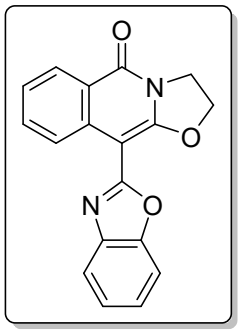
10-(5-(3-(Trifluoromethyl)phenyl)pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3z. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.48; light yellow solid; mp 217-218 °C; yield 68% (55.4 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.40 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.89 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.69-7.68 (m, 1H), 7.64 (t, *J* = 8.4 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 4.74 (t, *J* = 8.4 Hz, 2H), 4.44 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.2, 152.9, 150.4, 148.1, 138.6, 138.1, 135.0, 133.4, 133.0, 131.9 ($J_{C\text{-}F}$ = 32.1 Hz), 130.4, 129.8, 127.8 ($J_{C\text{-}F}$ = 210.4 Hz), 125.0, 124.9 ($J_{C\text{-}F}$ = 3.9 Hz), 124.5, 124.1 ($J_{C\text{-}F}$ = 3.7 Hz), 123.6, 123.2, 122.4, 94.3, 68.3, 43.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.65; FT-IR (KBr) 2919, 2851, 1729, 1664, 1550, 1486, 1335, 1266, 1166, 1124, 1016, 763 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{16}F_3N_2O_2$: 409.1158, found 409.1162.



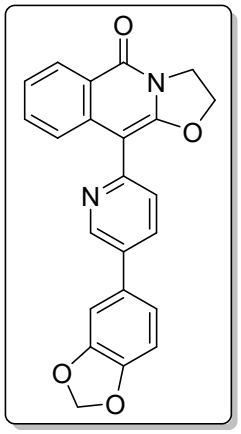
10-(Pyrazin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3aa. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.42; light yellow solid; mp 247-248 °C; yield 77% (40.8 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.70 (s, 1H), 8.50 (s, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 4.74 (t, *J* = 8.4 Hz, 2H), 4.43 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.2, 151.0, 149.6, 147.4, 144.1, 142.2, 137.5, 133.2, 127.9, 124.7, 123.1, 122.4, 91.3, 68.4, 43.8; FT-IR (KBr) 2922, 1668, 1626, 1548, 1486, 1423, 1341, 1121, 1092, 1015, 866, 761 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{15}H_{12}N_3O_2$: 266.0924, found 266.0928.



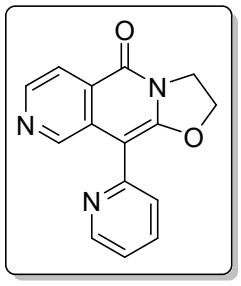
10-(Quinolin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3ab. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.43; light brown solid; mp 225-226 °C; yield 66% (41.4 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.8 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.76-7.73 (m, 2H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 4.72 (t, *J* = 8.4 Hz, 2H), 4.44 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.3, 153.6, 150.6, 148.3, 138.3, 136.4, 133.0, 129.8, 129.5, 127.7, 127.6, 127.0, 126.7, 124.4, 124.3, 123.8, 122.4, 95.1, 68.3, 43.8; FT-IR (KBr) 2919, 2850, 1736, 1664, 1596, 1486, 1459, 1089, 1019 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{15}N_2O_2$: 315.1128, found 315.1133.



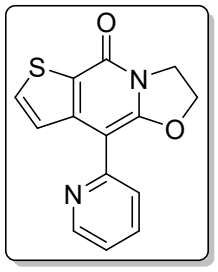
10-(Benzo[*d*]oxazol-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3ac. Analytical TLC on silica gel, 1:7 acetone/CH_2Cl_2 R_f = 0.49; brown solid; mp 230-231 °C; yield 70% (42.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.4 Hz, 1H), 8.40 (d, *J* = 8.0 Hz, 1H), 7.82-7.80 (m, 1H), 7.74-7.70 (m, 1H), 7.61-7.59 (m, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.37-7.33 (m, 2H), 4.91 (t, *J* = 8.4 Hz, 2H), 4.46 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.0, 159.5, 154.3, 149.9, 141.7, 135.9, 133.7, 127.7, 125.1, 124.8, 124.7, 124.4, 121.9, 119.7, 110.4, 83.6, 69.1, 43.7; FT-IR (KBr) 2921, 1664, 1624, 1534, 1488, 1454, 1337, 1246, 1092, 957, 690 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{13}N_2O_3$: 305.0921, found 305.0925.



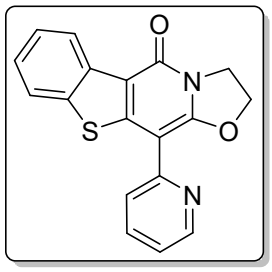
10-(5-(Benzo[*d*][1,3]dioxol-5-yl)pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 3ad. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.36; light brown solid; mp 235-236 °C; yield 68% (52.2 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.92 (d, *J* = 2.4 Hz, 1H), 8.39 (d, *J* = 7.8 Hz, 1H), 7.91 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.57-7.54 (m, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.13-7.12 (m, 2H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.04 (s, 2H), 4.73 (t, *J* = 7.8 Hz, 2H), 4.44 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.3, 151.5, 150.2, 148.6, 147.99, 147.91, 138.3, 134.67, 134.65, 133.0, 131.9, 127.7, 126.2, 124.4, 123.7, 122.3, 120.9, 109.1, 107.5, 101.5, 94.4, 68.3, 43.8; FT-IR (KBr) 2922, 1724, 1663, 1631, 1548, 1475, 1230, 1089, 1038, 862, 811 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{17}N_2O_4$: 385.1183, found 385.1177.



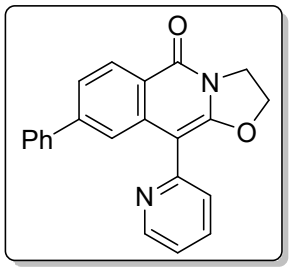
10-(Pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*][2,6]naphthyridin-5-one 3A. Analytical TLC on silica gel, 1:1 acetone/CH_2Cl_2 R_f = 0.40; brown solid; mp 197-198 °C; yield 70% (37 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.77 (d, *J* = 4.2 Hz, 1H), 8.54 (d, *J* = 4.8 Hz, 1H), 8.10 (d, *J* = 5.4 Hz, 1H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.31-7.29 (m, 1H), 4.76 (t, *J* = 8.4 Hz, 2H), 4.44 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.2, 151.7, 150.8, 149.9, 148.0, 144.0, 136.8, 132.5, 126.9, 126.1, 122.4, 119.4, 93.3, 68.4, 43.9; FT-IR (KBr) 2921, 1667, 1626, 1586, 1534, 1481, 1092, 1012, 984, 794 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{15}H_{12}N_3O_2$: 266.0924, found 266.0925.



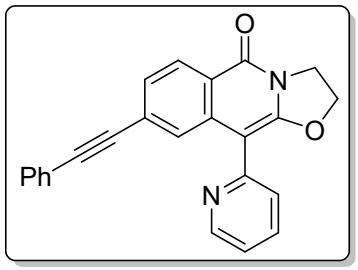
9-(Pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*a*]thieno[3,2-d]pyridin-5-one 3B. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.42; colorless solid; mp 186-187 °C; yield 68% (36.7 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.8 Hz, 1H), 7.76-7.72 (m, 2H), 7.68 (d, *J* = 5.4 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.21-7.19 (m, 1H), 4.81 (t, *J* = 8.4 Hz, 2H), 4.45 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.5, 153.3, 152.5, 149.4, 146.8, 136.4, 133.8, 124.9, 124.5, 123.6, 121.5, 95.6, 69.1, 43.8; FT-IR (KBr) 2921, 2850, 1659, 1586, 1514, 1467, 1059, 967, 852, 797 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{14}H_{11}N_2O_2S$: 271.0536, found 271.0544.



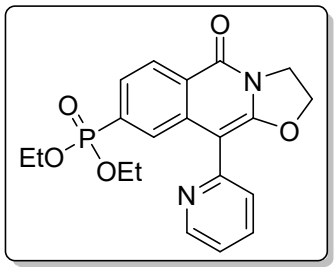
11-(Pyridin-2-yl)-2,3-dihydro-5*H*-benzo[4,5]thieno[2,3-d]oxazolo-[3,2-*a*]pyridin-5-one 3C. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.60; yellow solid; mp 225-226 °C; yield 79% (50.5 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (d, *J* = 8.4 Hz, 1H), 8.72-8.71 (m, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.75-7.72 (m, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.32-7.27 (m, 2H), 7.14-7.12 (m, 1H), 4.94 (t, *J* = 9.0 Hz, 2H), 4.45 (t, *J* = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.9, 153.7, 151.7, 146.4, 140.5, 136.2, 131.8, 129.8, 125.4, 125.1, 122.8, 121.7, 121.6, 120.3, 109.6, 101.2, 70.1, 44.3; FT-IR (KBr) 2923, 1722, 1651, 1584, 1516, 1465, 1257, 1097, 1002, 943, 793, 733 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{13}N_2O_2S$: 321.0692, found 321.0690.



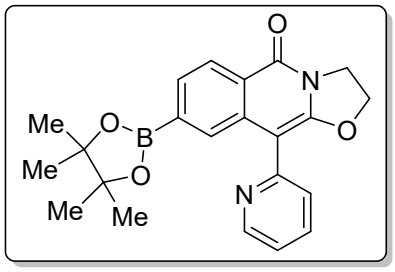
8-Phenyl-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 4. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.48; colorless solid; mp 238-239 °C; yield 86% (29 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.8 Hz, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 7.82-7.78 (m, 2H), 7.57-7.52 (m, 4H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.36-7.33 (m, 1H), 7.29-7.27 (m, 1H), 4.71 (t, *J* = 8.4 Hz, 2H), 4.43 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.1, 153.1, 150.5, 149.9, 145.6, 140.7, 138.7, 136.6, 128.8, 128.2, 128.0, 127.6, 126.4, 123.7, 122.1, 122.0, 121.2, 94.9, 68.3, 43.8; FT-IR (KBr) 2922, 2855, 1663, 1626, 1546, 1481, 1436, 1339, 1199, 1104, 760, 699 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{22}H_{17}N_2O_2$: 341.1285, found 341.1290.



8-(Phenylethynyl)-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo-[3,2-*b*]isoquinolin-5-one 5. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.50; light brown solid; mp 260-261 °C; yield 88% (32 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 4.8 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.83-7.80 (m, 1H), 7.77 (s, 1H), 7.52-7.49 (m, 3H), 7.45-7.43 (m, 1H), 7.33-7.32 (m, 3H), 7.31-7.29 (m, 1H), 4.71 (t, *J* = 8.4 Hz, 2H), 4.42 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.8, 152.8, 150.6, 150.0, 138.3, 136.7, 131.8, 128.7, 128.5, 127.9, 127.7, 127.2, 126.7, 126.5, 122.9, 122.2, 121.5, 94.5, 91.9, 89.4, 68.3, 43.8; FT-IR (KBr) 2920, 1661, 1539, 1478, 1336, 1206, 1100, 1024, 963, 884, 755 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{24}H_{17}N_2O_2$: 365.1285, found 365.1281.



Diethyl (5-oxo-10-(pyridin-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-8-yl)phosphonate 6. Analytical TLC on silica gel, 1:4 acetone/CH_2Cl_2 R_f = 0.34; brown solid; mp 140-141 °C; yield 73% (29 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.2 Hz, 1H), 8.43-8.41 (m, 1H), 8.16 (d, *J* = 15.6 Hz, 1H), 7.78 (t, *J* = 7.2 Hz, 1H), 7.65-6.62 (m, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.28-7.26 (m, 1H), 4.71 (t, *J* = 8.4 Hz, 2H), 4.41 (t, *J* = 8.4 Hz, 2H), 4.14-4.01 (m, 4H), 1.27 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 152.4, 150.8, 149.9, 138.1 ($J_{C\text{-}P}$ = 6.6 Hz), 136.7, 133.5 ($J_{C\text{-}P}$ = 183.6 Hz), 128.3 ($J_{C\text{-}P}$ = 12.1 Hz), 127.9 ($J_{C\text{-}P}$ = 14.8 Hz), 126.3, 126.0 ($J_{C\text{-}P}$ = 9.4 Hz), 124.5 ($J_{C\text{-}P}$ = 2.7 Hz), 122.3, 94.9, 68.3, 62.5 ($J_{C\text{-}P}$ = 5.4 Hz), 43.8, 16.3 ($J_{C\text{-}P}$ = 6.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 17.67; FT-IR (KBr) 2920, 1662, 1541, 1477, 1339, 1242, 1022, 966, 795, 686 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{22}N_2O_5P$: 401.1261, found 401.1268.



10-(Pyridin-2-yl)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-5*H*-oxazolo[3,2-*b*]isoquinolin-5-one 7. Analytical TLC on silica gel, 1:5 acetone/CH_2Cl_2 R_f = 0.42; colorless solid; mp 165-166 °C; yield 75% (29 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.8 Hz, 1H), 8.35 (d, *J* = 7.8 Hz, 1H), 8.04 (s, 1H), 7.81-7.78 (m, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.29-7.27 (m, 1H), 4.68 (t, *J* = 8.4 Hz, 2H), 4.41 (t, *J* = 8.4 Hz, 2H), 1.30 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.3, 153.1, 150.0, 149.8, 137.3, 136.5, 130.3, 129.9, 126.6, 126.5, 124.0, 122.0, 95.1, 84.2, 68.1, 43.8, 24.9; FT-IR (KBr) 2923, 1664, 1586, 1541, 1476, 1364, 1147, 1094, 967, 754 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{22}H_{24}BN_2O_4$: 391.1824, found 391.1816.

Mechanistic Investigations

Radical Trapping Experiments. In an oven-dried pressure tube, a mixture of 2-phenyl-4,5-dihydrooxazole **1a** (0.2 mmol, 29 mg), methyl [1,2,3]triazolo[1,5-*a*]pyridine-3-carboxylate **2a** (0.3 mmol, 1.5 equiv, 53 mg), $[Cp^*RhCl_2]_2$ (3 mol %, 0.006 mmol, 3.70 mg), NaOAc (0.1 mmol, 0.5 equiv, 8.2 mg) and) and TEMPO (0.2 mmol, 31.2 mg) or BHT (0.2 mmol, 44 mg) in TFE (1 mL) was stirred at 140 °C for 18 h under argon atmosphere. Upon completion, the resulting solution was cooled to room temperature, diluted with ethyl acetate (10 mL) and passed through a short celite pad. The purification was performed as described in the general procedure to afford **3a**.

H/D Exchange Experiment of 1a with CD_3OD in Absence of 2a. In an oven-dried pressure tube, a mixture of 2-phenyl-4,5-dihydrooxazole **1a** (0.2 mmol, 29 mg), $[Cp^*RhCl_2]_2$ (3 mol %, 0.006 mmol, 3.70 mg), NaOAc (0.1 mmol, 0.5 equiv, 8.2 mg) and CD_3OD (2 mmol, 10 equiv, 82 μL) in TFE (1 mL) was stirred at 140 °C for 18 h under argon atmosphere. The resulting solution was cooled to room temperature, diluted with ethyl acetate (10 mL) and passed through a short celite pad. The purification was performed as described in the general procedure to afford $[D_n]$-**1a**. The deuterium incorporation was observed as 25% at the *ortho*-position of aryl ring based on 600 MHz ^{1}H NMR spectrum.

H/D Exchange Experiment of 1a with CD_3OD in Presence of 2a. In an oven-dried pressure tube, a mixture of 2-phenyl-4,5-dihydrooxazole **1a** (0.2 mmol, 29 mg), methyl [1,2,3]triazolo[1,5-*a*]pyridine-3-carboxylate **2a** (0.3 mmol, 1.5 equiv, 53 mg), $[Cp^*RhCl_2]_2$ (3 mol %, 0.006 mmol, 3.70 mg), NaOAc (0.1 mmol, 0.5 equiv, 8.2 mg) and CD_3OD (2 mmol, 10 equiv, 82 μL) in TFE (1 mL) was stirred at 140 °C for 18 h under argon atmosphere. The resulting solution was cooled to room temperature, diluted with ethyl acetate (10 mL) and passed through a short celite pad. The purification was performed as described in the general procedure to afford $[D_n]$-**1a** and $[D_n]$-**3a**. The deuterium incorporation in $[D_n]$-**1a** was observed as 20% at the *ortho*-position of aryl ring based on 600 MHz ^{1}H NMR spectrum.

Preparation of 2-(Phenyl-d_5)-4,5-dihydrooxazole [D5]-**1a.**

Step-I:[5a] To a stirred solution of sulfuric acid (0.6 mL) in water (2 mL), benzene-d_6 (3 mmol, 265 μL) was added dropwise at 0 °C, which was treated with $NaBrO_3$ (3.3 mmol, 1.1 equiv, 498 mg) at the same temperature in two portions with an interval of 1 h and allowed to stir for another 10 h at room temperature. Upon completion, the mixture was quenched with ice water and extracted with diethyl ether (3 x 20 mL). The combined organic layer was washed with brine (15 mL) and water (15 mL). Drying (Na_2SO_4) and evaporation of the solvent gave crude 1-bromobenzene-d_5 that was used for the next step without further purification (73% yield, 353 mg).

Step-II:[5b] To a stirred solution of 1-bromobenzene-d_5 (2.0 mmol, 320 mg) in THF (10 mL), *n*-BuLi (2.4 mmol, 1.2 mL, 2M in hexane) was added dropwise at -78 °C for a period of 10 min under argon atmosphere. The solution was allowed to stir for 30 min and then *N*,*N*-dimethylformamide (20 mmol, 1.5 mL) was added and continued the stirring at the same temperature for 10 min. Upon completion, monitored by TLC, the resulting mixture was quenched with H_2O and extracted with EtOAc (3 x 20 mL). The combined organic layer was washed with brine (2 x 10 mL) and water (10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave crude bezaldehyde-d_5 that was used for the next step without further purification (55% yield, 122 mg).

Step-III:[1a] To a stirred solution of bezaldehyde-d_5 (1 mmol, 111 mg) in *tert*-butyl alcohol (10 mL), 2-aminoethan-1-ol (1.1 mmol, 1.1 equiv, 67 mg) was added. The resultant mixture was allowed to stir at room temperature for 30 min under argon atmosphere. K_2CO_3 (3 mmol, 3 equiv, 414 mg) and I_2 (2 mmol, 2 equiv, 506 mg) were then added and was further stirred at the same temperature for 18 h. The progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was allowed to cool and was quenched with saturated aqueous $Na_2S_2O_3$ solution until the color of iodine was disappeared. The mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was washed with brine (2 x 5 mL) and water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate (80/20, v/v) as an eluent to afford 2-(phenyl-d_5)-4,5-dihydrooxazole [D5]-**1a** in 75% (114 mg) yield.

Kinetic Isotope Effect Experiments.[5c]

Competitive Experiment. In an oven-dried pressure tube, a mixture of 2-phenyl-4,5-dihydrooxazole **1a** (0.1 mmol, 14.7 mg) and 2-(phenyl-d_5)-4,5-dihydrooxazole [D5]-**1a** (0.1

mmol, 17.6 mg) was reacted with methyl [1,2,3]triazolo[1,5-*a*]pyridine-3-carboxylate **2a** (0.15 mmol, 0.75 equiv, 26.5 mg) for 2 h under standard reaction conditions. The resulting mixture was cooled to room temperature, diluted with ethyl acetate (10 mL) and passed through a short pad of celite. The purification was performed as described in the general procedure to afford a mixture of **3a** and [D_4]-**3a** in 12% yield. The intermolecular k_H/k_D was found to be 2.2, based on 400 MHz ^{1}H NMR of the product **3a** and [D_4]-**3a**.

Parallel Experiments. Three sets of experiments were carried out, each having a mixture of 2-phenyl-4,5-dihydrooxazole **1a** (0.1 mmol, 14.7 mg) or 2-(phenyl-d_5)-4,5-dihydrooxazole [D_5]-**1a** (0.1 mmol, 17.6 mg) was reacted with methyl [1,2,3]triazolo[1,5-*a*]pyridine-3-carboxylate **2a** (0.075 mmol, 0.75 equiv, 13.3 mg) for 1 h (Set 1), 2h (Set 2) and 3h (Set 3), respectively, under standard reaction conditions. The resulting mixture was cooled to room temperature, diluted with ethyl acetate (10 mL) and passed through a short pad of celite. The purification was performed as described in the general procedure to afford a mixture of **3a** and [D_4]-**3a**. The KIE value was calculated using 600 MHz ^{1}H NMR spectroscopy.

Reaction Set	Time	k_H/k_D	Yield of **3a**/[D_4]-**3a**
Set 1	1h	2.3	10 %
Set 2	2h	2.3	14 %
Set 3	3h	2.4	19 %

Isotope Labelling Experiment. In an oven-dried pressure tube, a mixture of 2-phenyl-4,5-dihydrooxazole **1a** (0.2 mmol, 29 mg), methyl [1,2,3]triazolo[1,5-*a*]pyridine-3-carboxylate **2a** (0.3 mmol, 1.5 equiv, 53 mg), [Cp*$RhCl_2$]$_2$ (3 mol %, 0.006 mmol, 3.70 mg) and NaOAc (0.1 mmol, 0.5 equiv, 8.2 mg) was stirred in TFE/ $H_2{}^{18}O$ (9:1 , v/v) at 140 ^{o}C for 18 h under argon atmosphere. The resultant solution was cooled to room temperature, diluted with ethyl acetate (10 mL) and passed through a short celite pad. The formation of ^{18}O-**3a** was confirmed by HRMS. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{13}N_2O^{18}O$: 267.1015, found 267.1016.

Sample Name	SBT-431-RE	**Position**	P1-A1	**Instrument Name**	QTOF
User Name	SYSTEM (SYSTEM)	**Inj Vol**	5	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	SBT-431-RE.d
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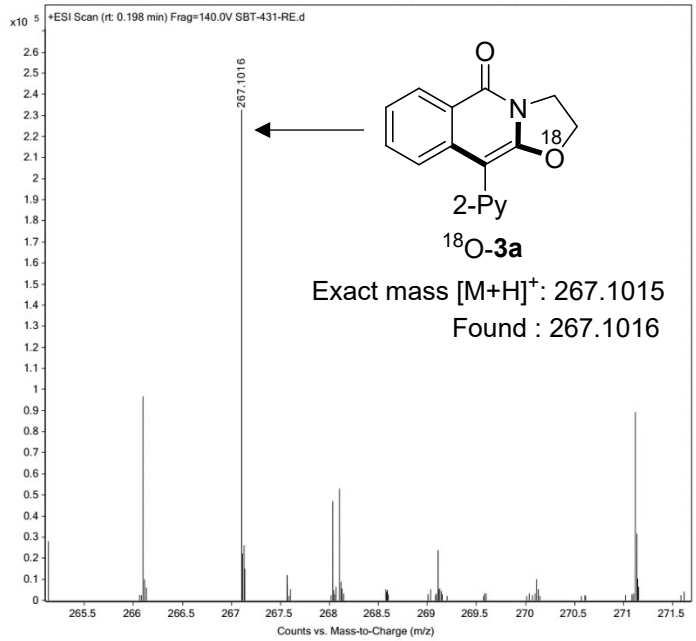


2-Py

^{18}O-**3a**

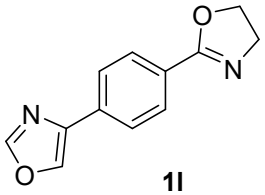
Exact mass $[M+H]^+$: 267.1015

Found : 267.1016

References

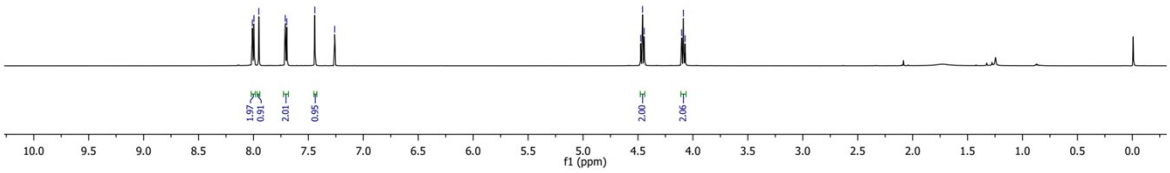
1. (*a*) K. Schwekendiek and F. Glorius, *Synthesis*, 2006, **2006**, 2996; (*b*) M. Ishihara and H. Togo, *Tetrahedron,* 2007, **63**, 1474; (*c*) X.-F. Wu, H. Neumann, S. Neumann and M. Beller, *Chem. - Eur. J.,* 2012, **18**, 13619; (*d*) P. Garg, S. Chaudhary and M. D. Milton, *J. Org. Chem.,* 2014, **79**, 8668; (*e*) R. Mei, J. Loup and L. Ackermann, *ACS Catal.,* 2016, **6**, 793; (*f*) D. Zell, S. Warratz, D. Gelman, S. J. Garden, and L. Ackermann, *Chem. -Eur. J.,* 2016, **22**, 1248; (*g*) M. C. Mollo and L. R. Orelli, *Org. Lett.*, 2016, **18**, 6116; (*h*) K. Korvorapun, N. Kaplaneris, T. Rogge, S. Warratz, A. C. Stückl and L. Ackermann, *ACS Catal.,* 2018, **8**, 886; (*i*) K. M. Nakafuku, S. C. Fosu and D. A. Nagib, *J. Am. Chem. Soc.,* 2018, **140**, 11202; (*j*) Q. Shi, Y. Huang and W. H. Liu, *Precis. Chem.,* 2023, **1**, 316.
2. (*a*) Y. Shi, A. V. Gulevich and V. Gevorgyan, *Angew. Chem., Int. Ed.,* 2014, **53**, 14191; (*b*) J. H. Kim, T. Gensch, D. Zhao, L. Stegemann, C. A. Strassert and F. Glorius, *Angew. Chem., Int. Ed.,* 2015, **54**, 10975; (*c*) X. Hou, R. Wang, F. Fang, Z. Qu, J. Zhou, T. Yu, D. Wang, H. Liu and Y. Zhou, *Org. Lett.,* 2024, **26**, 4451.
3. C. Chen, C. Ni, J.-H. Song, L.-Y. Ding, X.-X. Zhang, H. Guo, K. Wang, Z. Chen and B. Zhu, *ACS Catal.,* 2024, **14**, 12181.
4. M. Lilley, B. Mambwe, R. F. W. Jackson and R. Muimo, *Chem.Commun.,* 2014, **50**, 9343.
5. (*a*) L. Ackermann, S. I. Kozhushkov and D. S. Yufit, *Chem. - Eur. J.,* 2012, **18**, 12068; (*b*) C.-H. Hung, P. Gandeepan, C.-H. Cheng, *ChemCatChem,* 2014, **6**, 2692; (*c*) X. Wang, A. Lerchen, C. G. Daniliuc and F. Glorius, *Angew. Chem., Int. Ed.*, 2018, **57**, 1712.

SBT-4OXAZOLE-OX-DG-1H

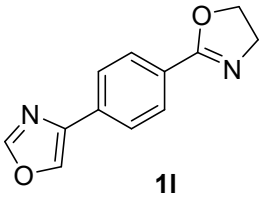


1l

^{1}H NMR (600 MHz, $CDCl_3$)

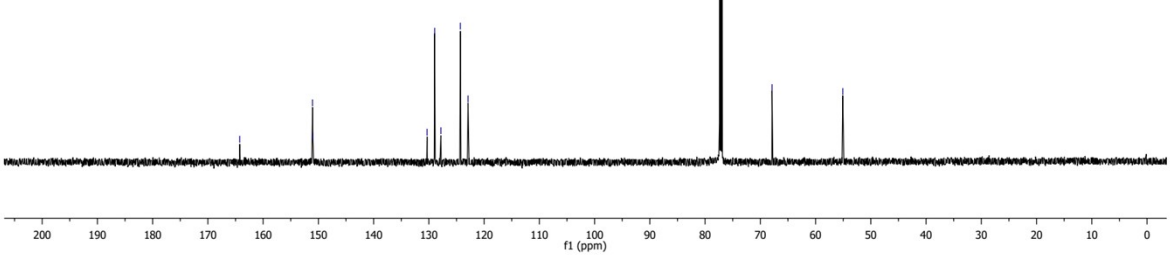


SBT-4OXAZOLE-OX-DG-13C

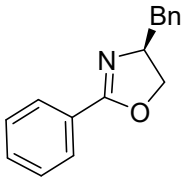


1l

^{13}C NMR (150 MHz, $CDCl_3$)



SBT-O-4Bn-OX-DG-CHI-1H



(*S*)-**1n′**

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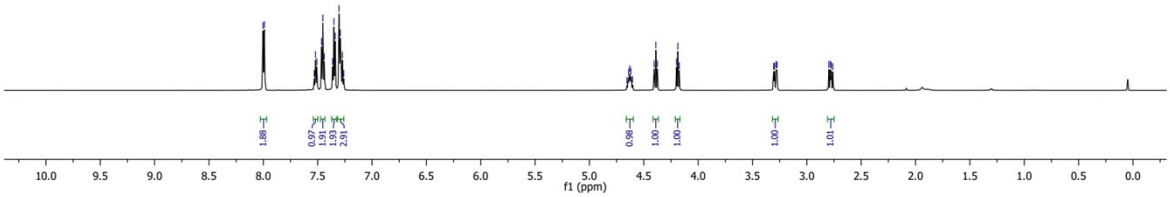

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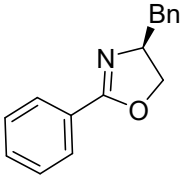

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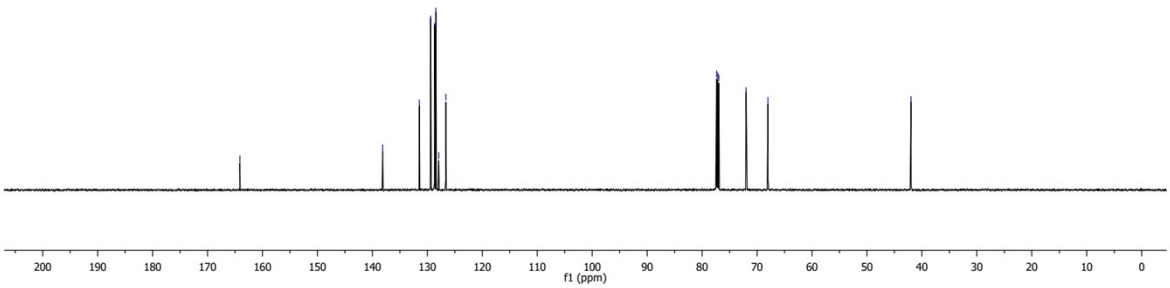

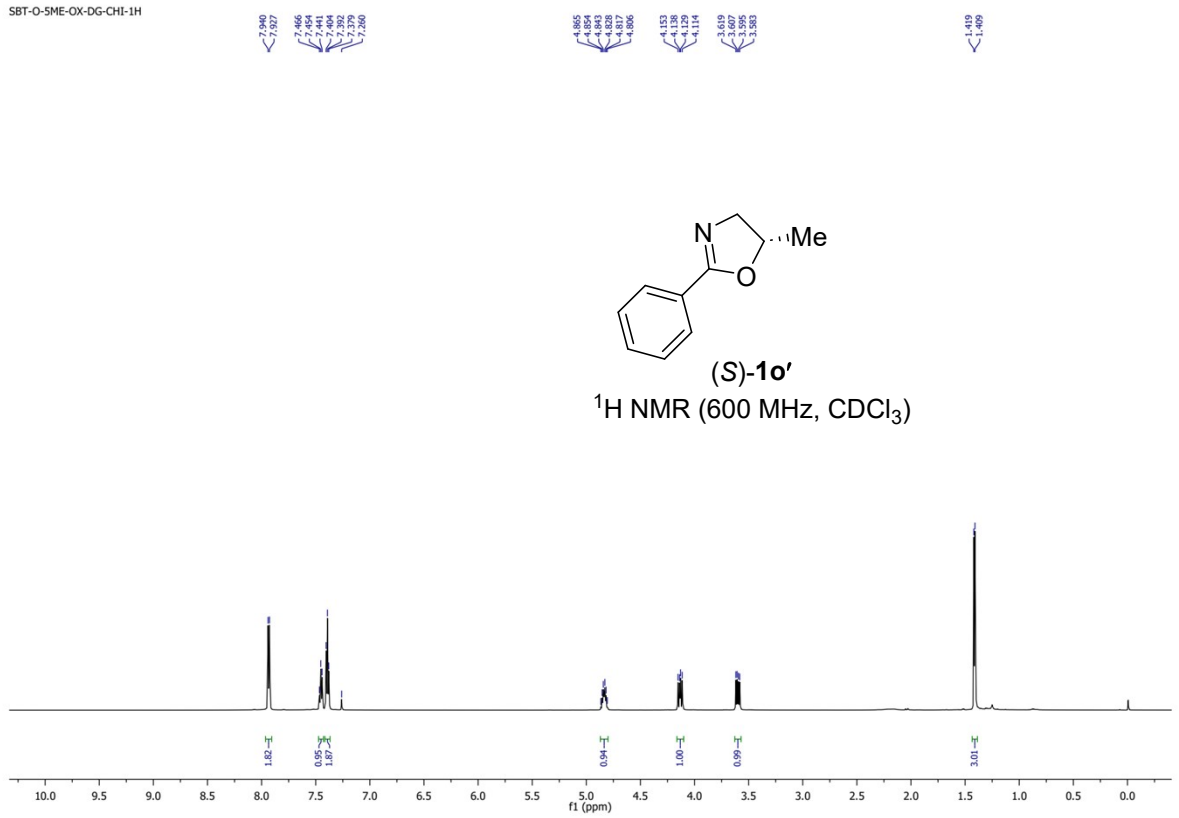

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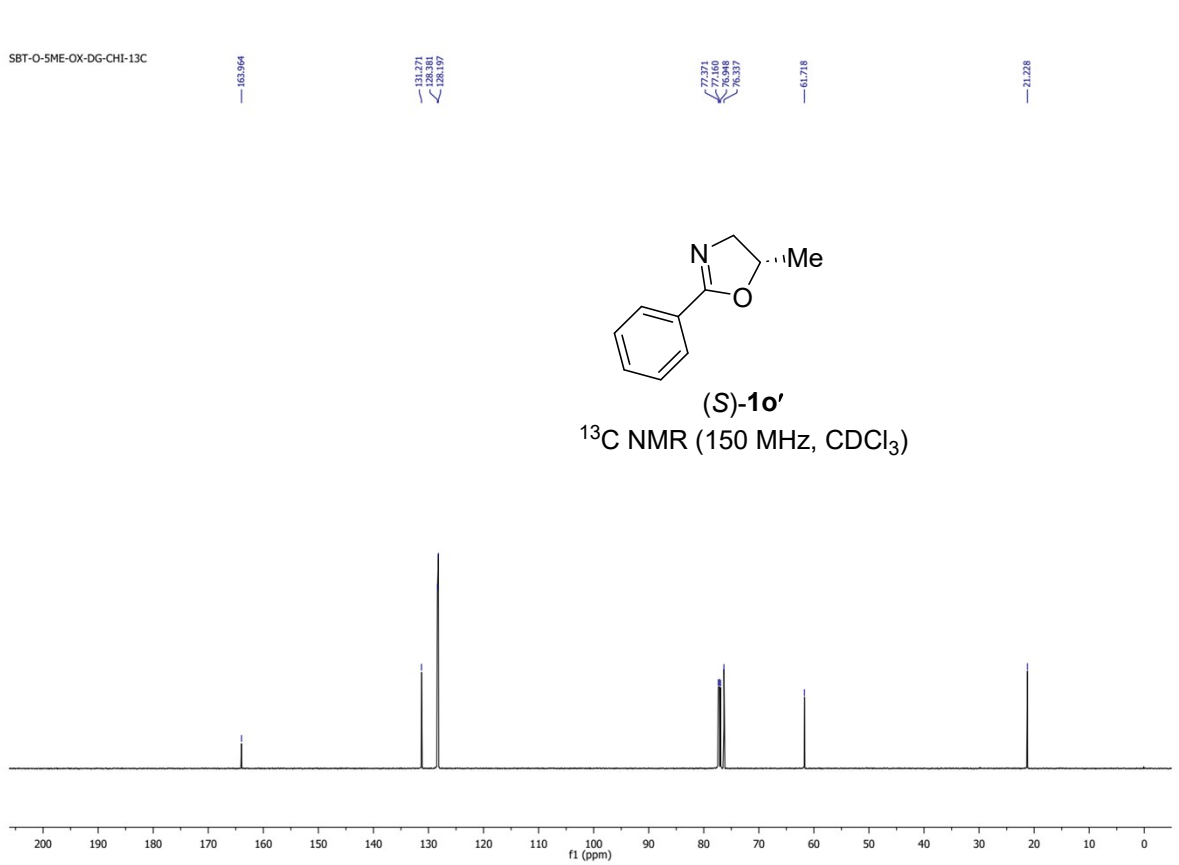

(*S*)-**1o′**

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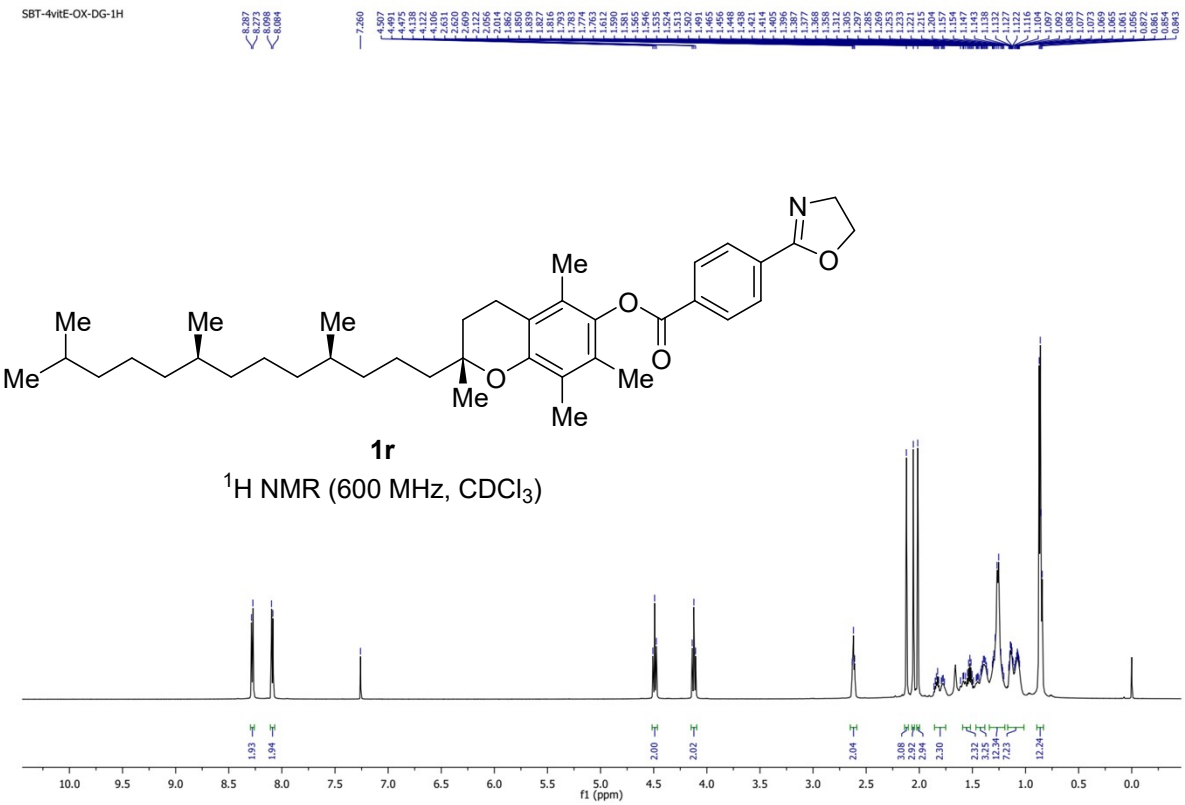

1r

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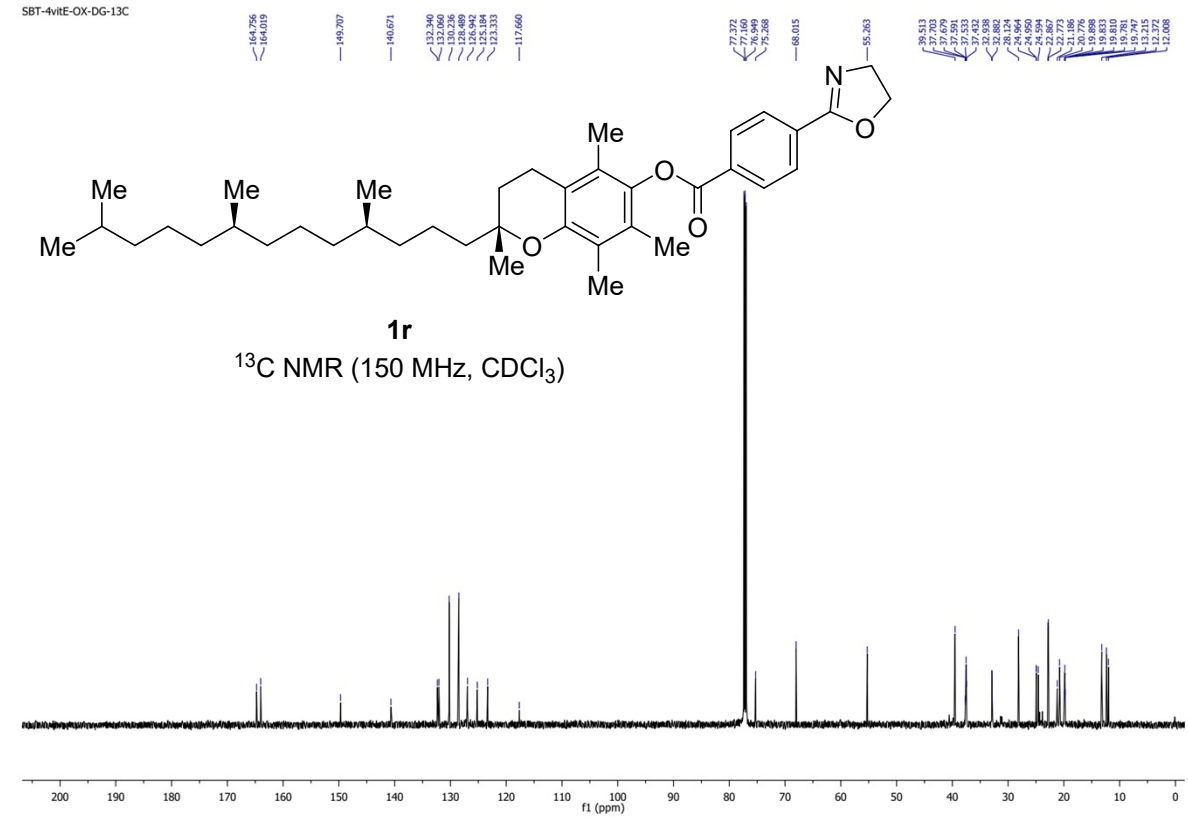

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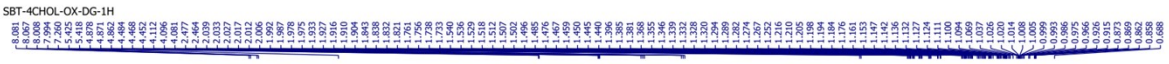

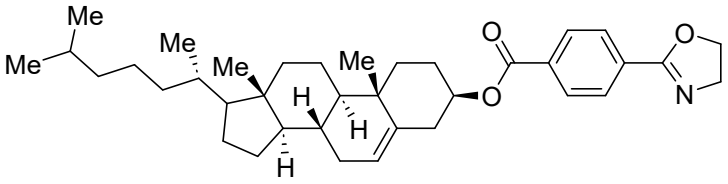

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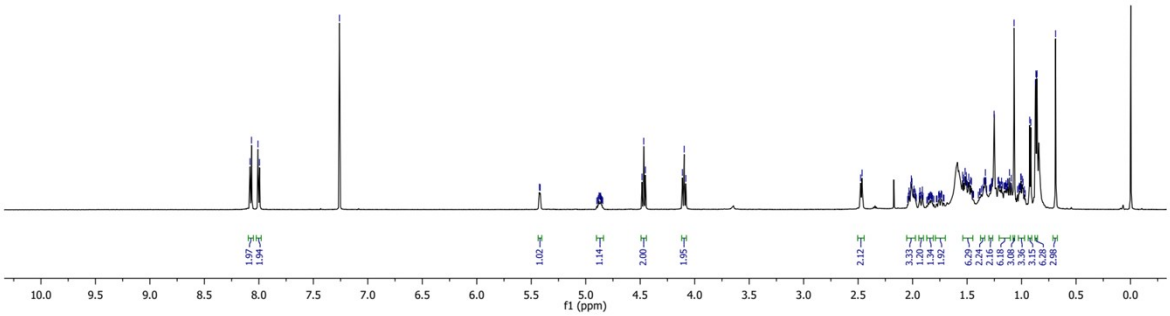
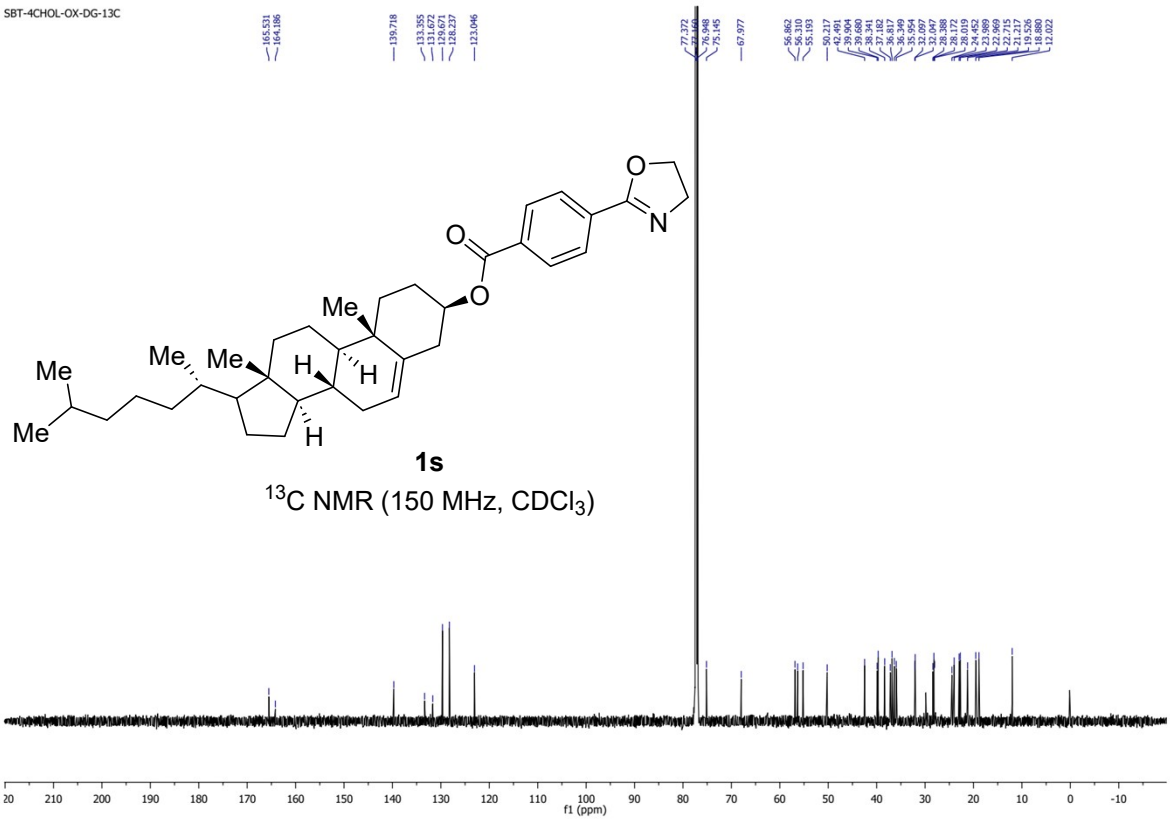
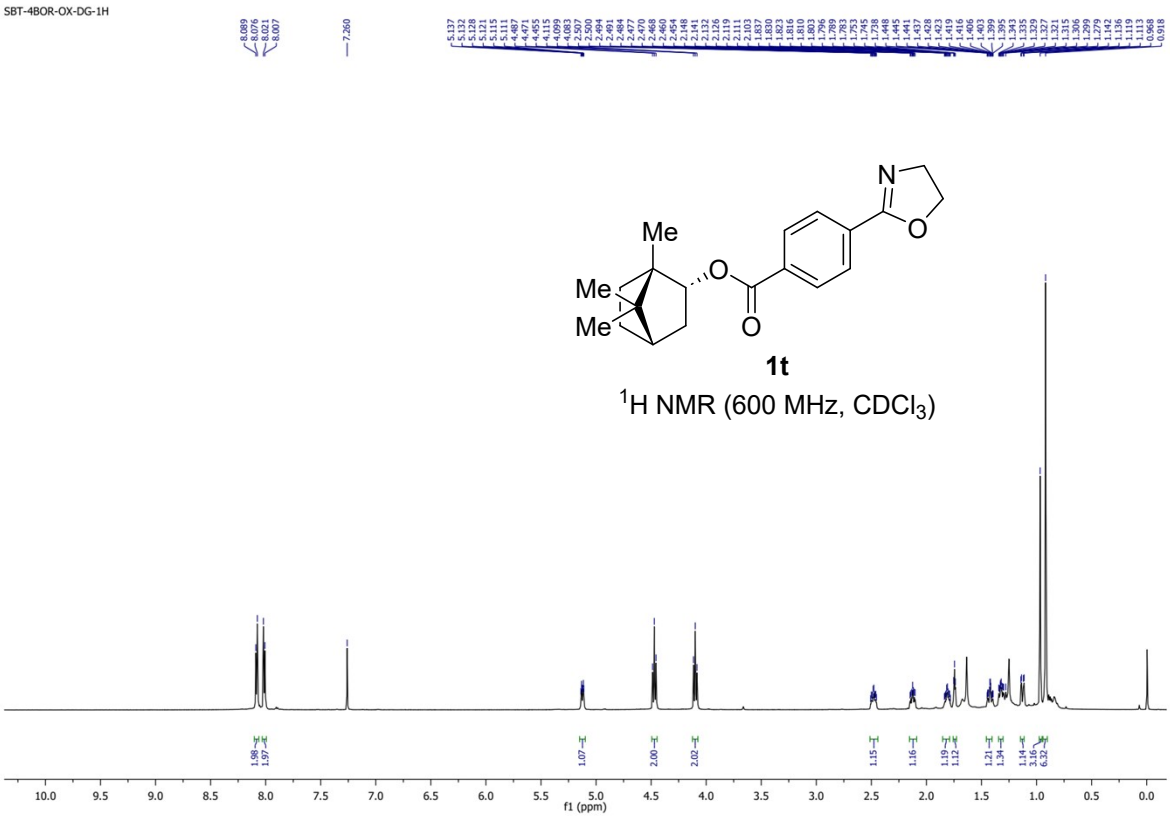




1s

^{13}C NMR (150 MHz, $CDCl_3$)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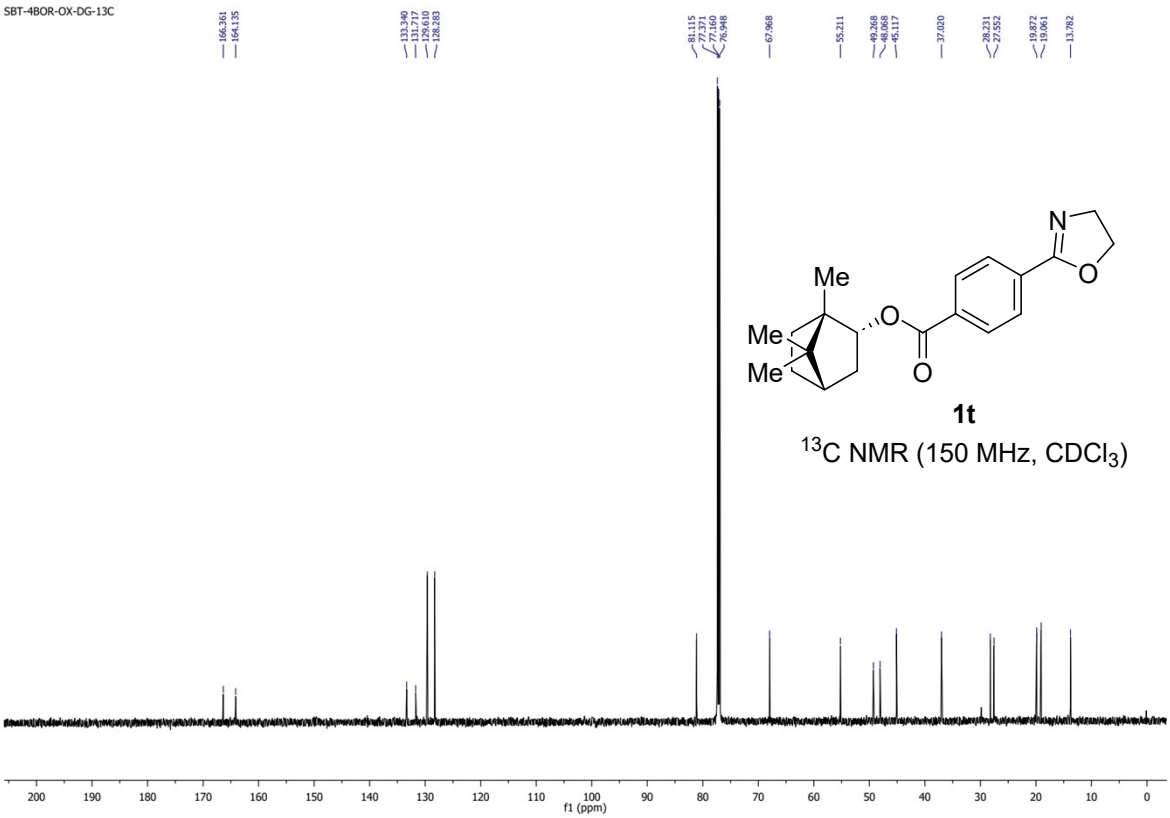
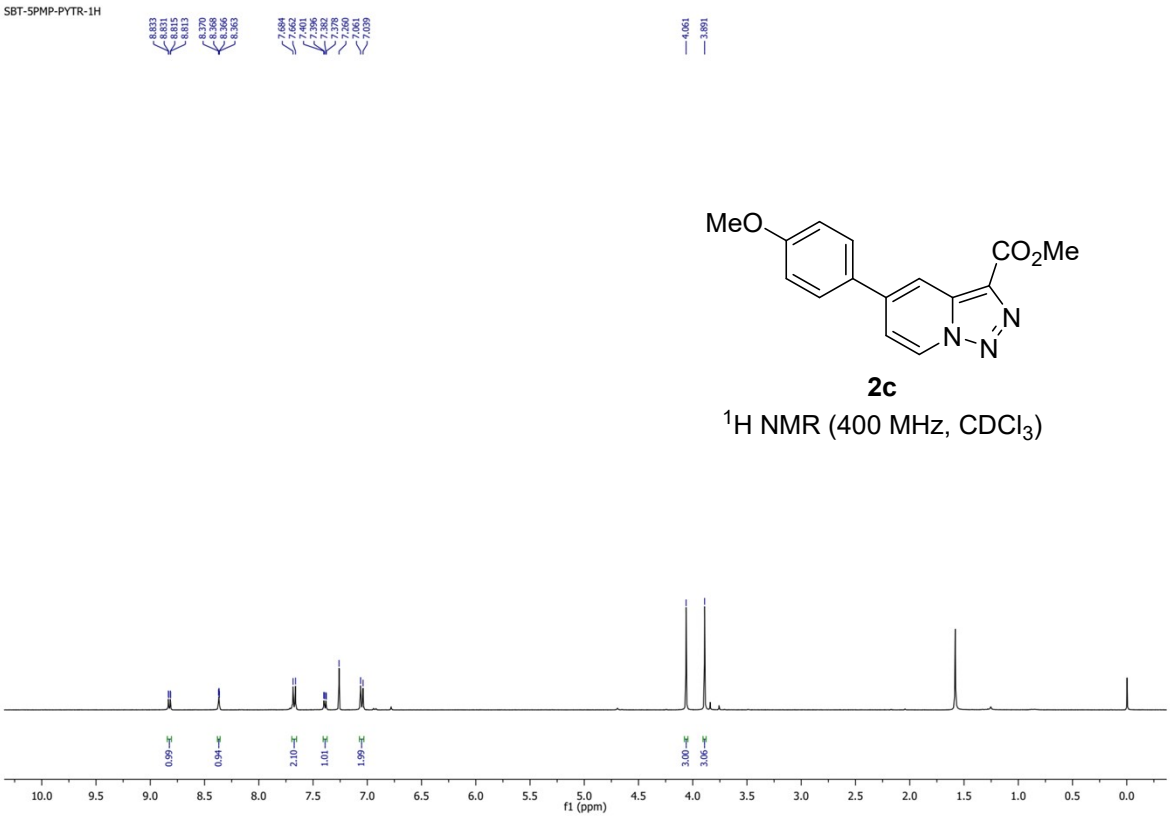
Me
Me
O
O
N
O
1t
1H NMR (600 MHz, CDCl3)
f1 (ppm)


SBT-4BOR-OX-DG-13C
Me
Me
Me
O
O
N
O
1t
13C NMR (150 MHz, CDCl3)
f1 (ppm)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8.833
8.831
8.815
8.813
8.370
8.368
8.366
8.363
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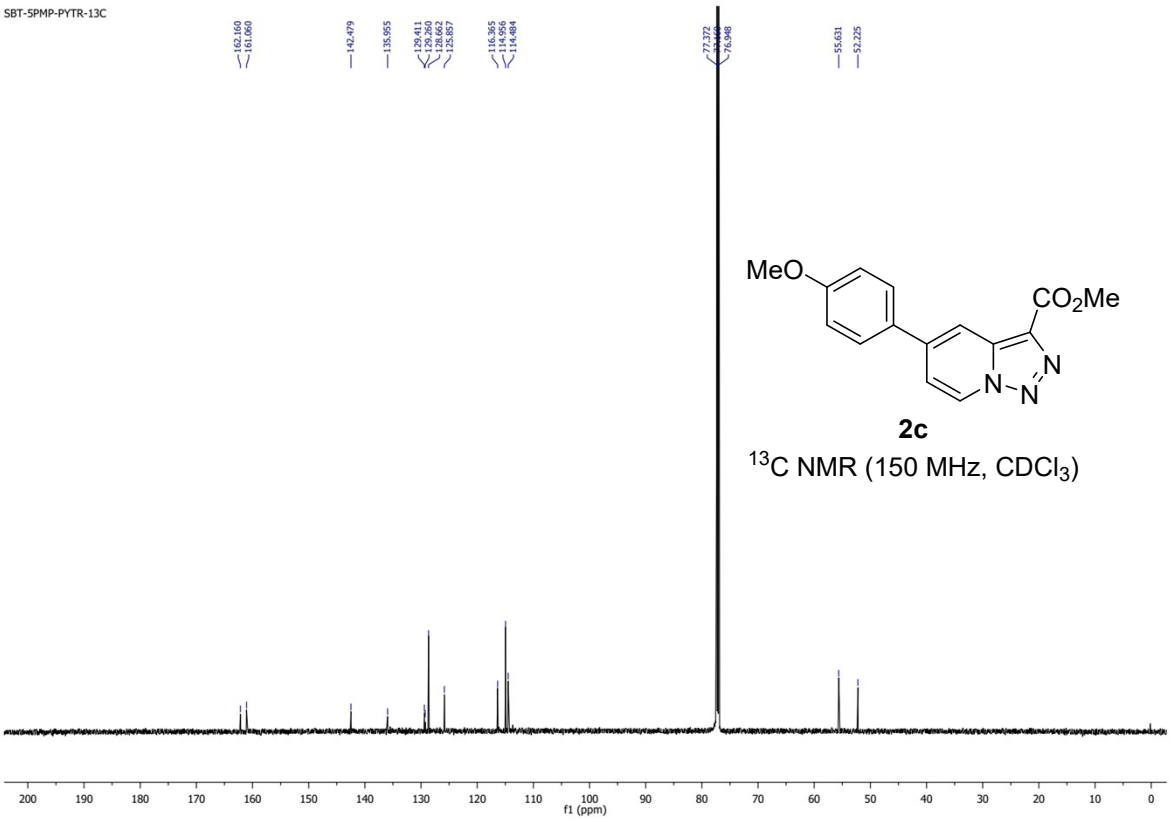
7.662
7.401
7.396
7.392
7.378
7.260
7.061
7.039
4.061
3.891
MeO
CO2Me
N
N
N
2c
1H NMR (400 MHz, CDCl3)
0.99
0.94
2.10
1.01
1.99
3.00
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


SBT-5PMP-PYTR-13C
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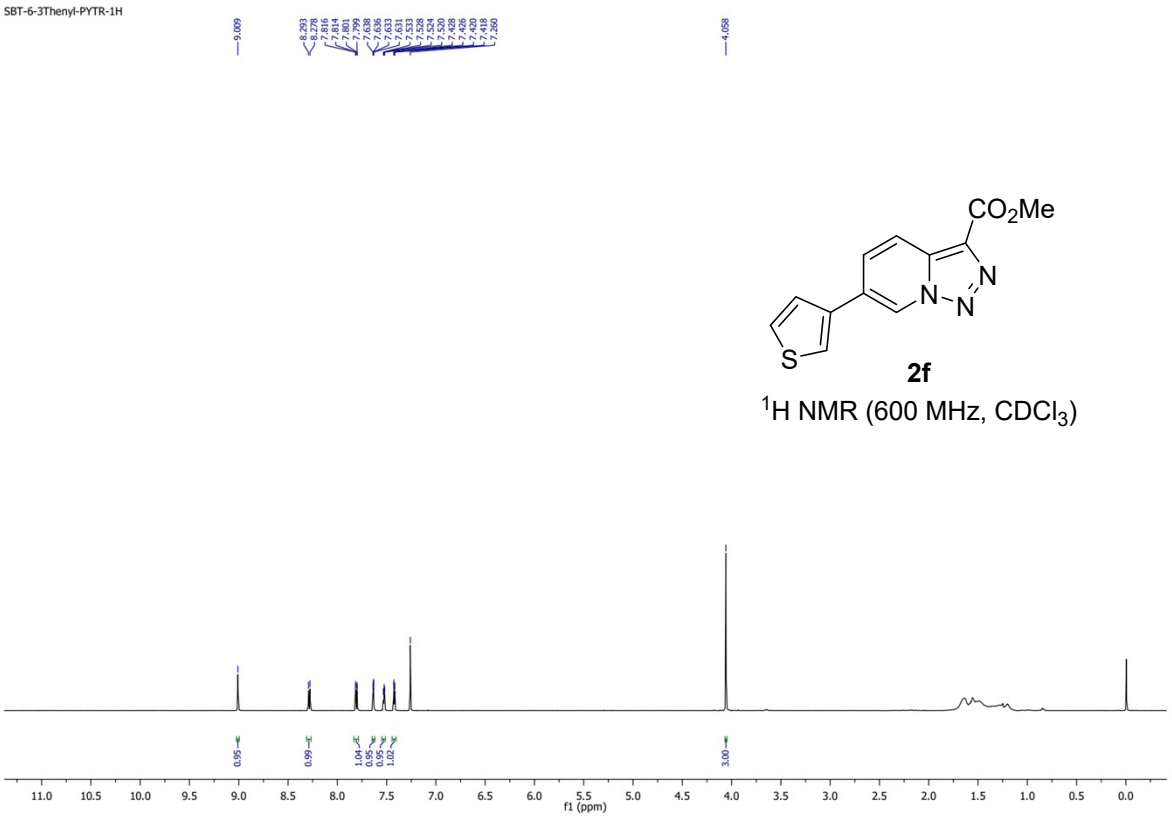
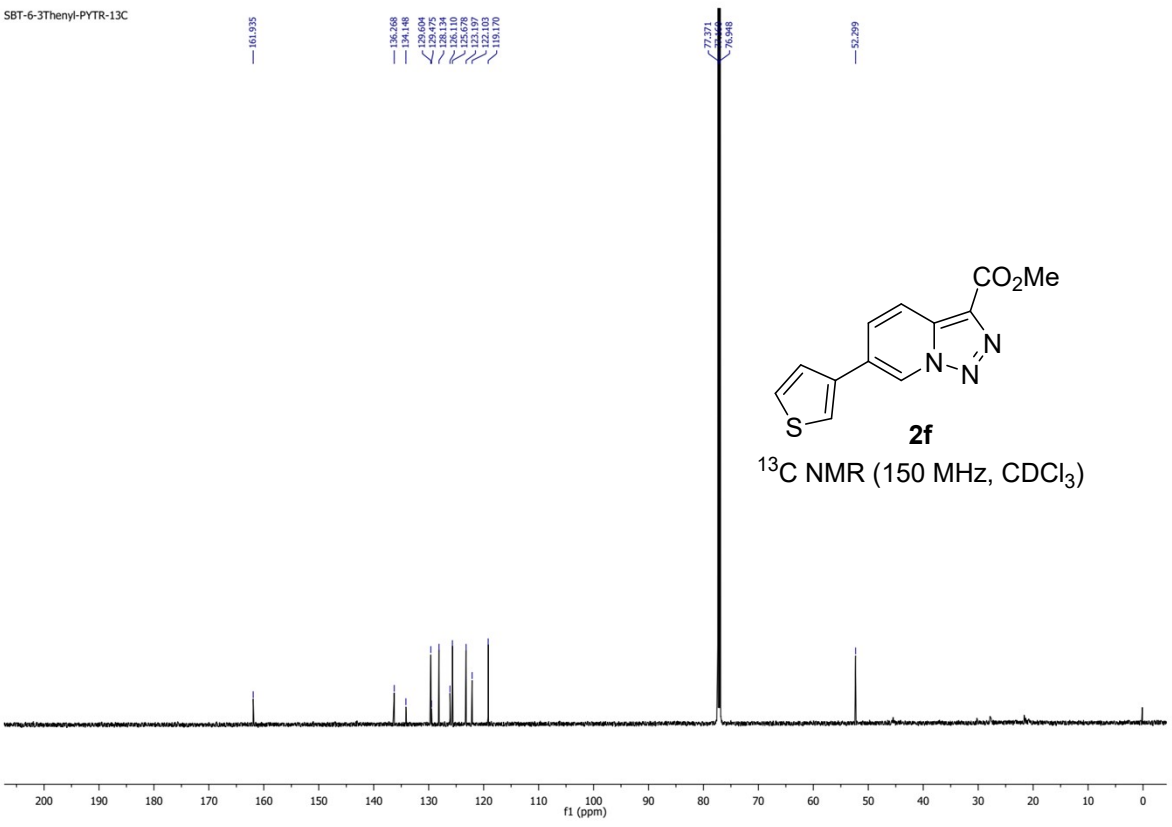
161.060
142.479
135.955
129.411
129.260
128.662
125.657
116.365
114.956
114.484
77.372
77.160
76.948
55.631
52.225
MeO
CO2Me
N
N
N
2c
13C NMR (150 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



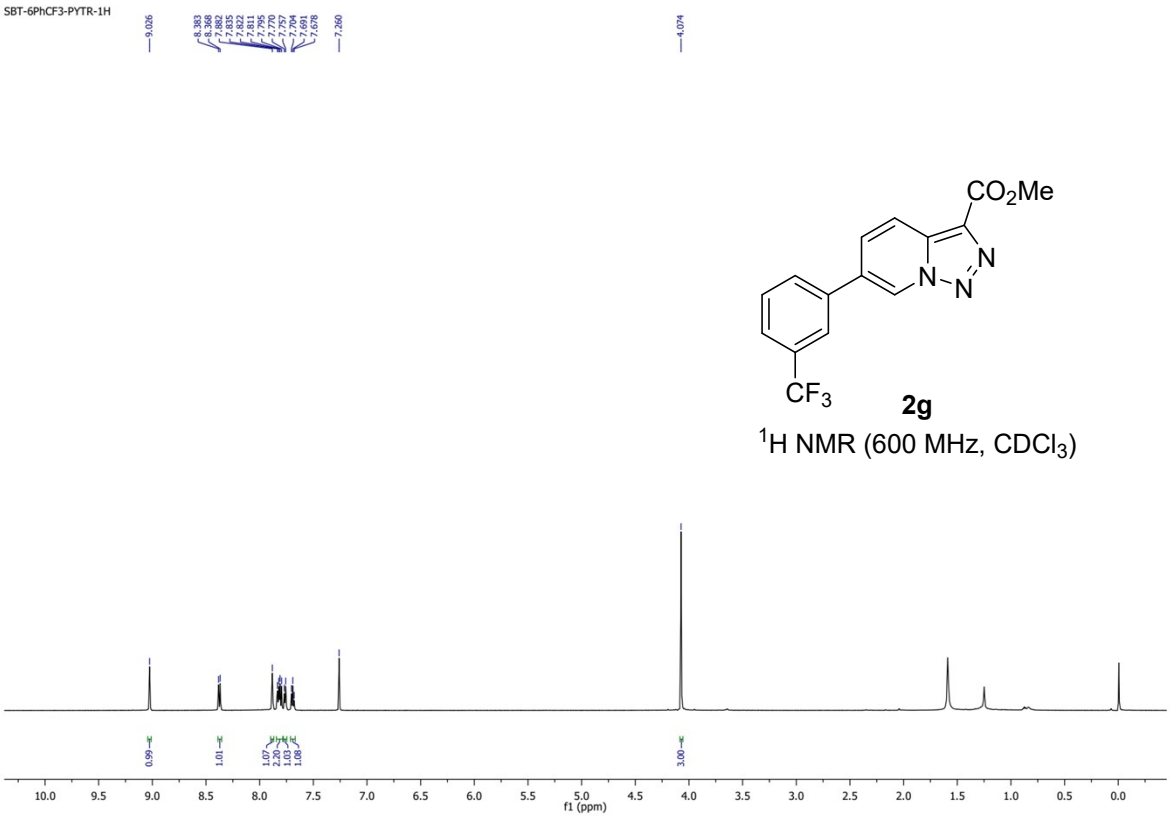
2f

^{1}H NMR (600 MHz, $CDCl_3$)



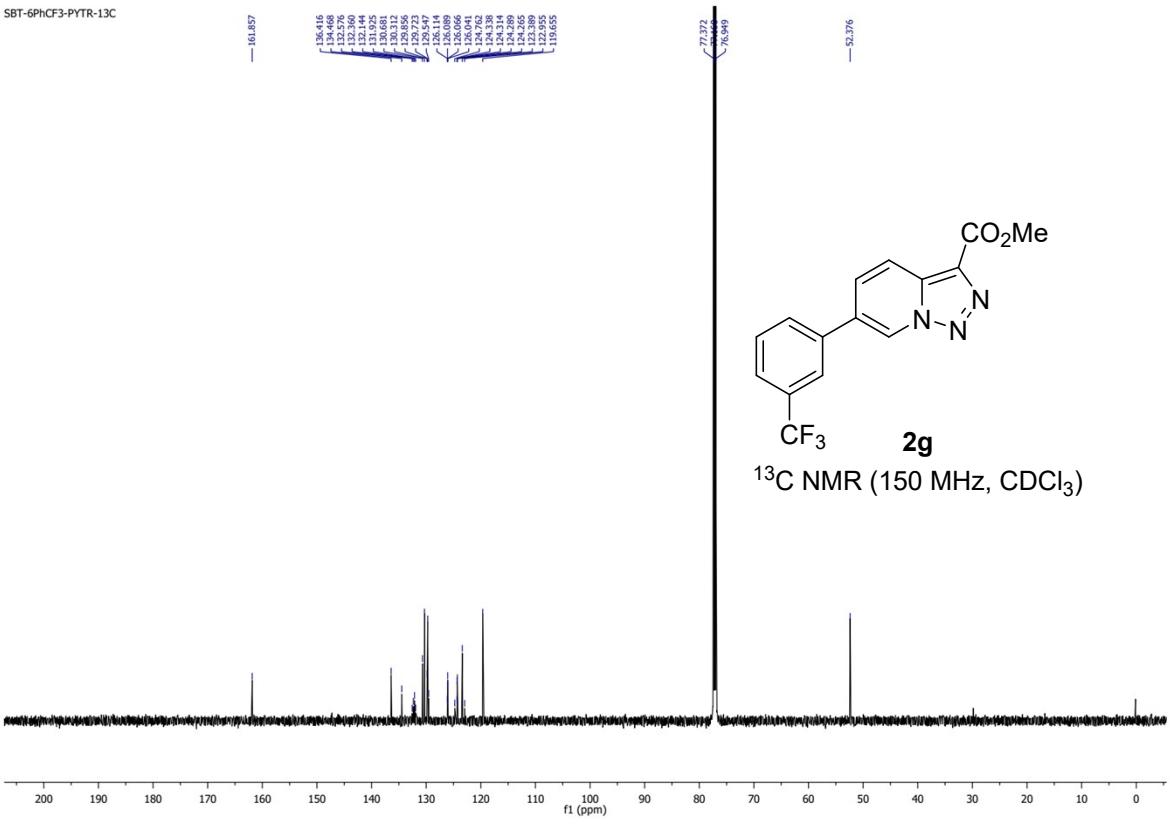
2f

^{13}C NMR (150 MHz, $CDCl_3$)



2g

^{1}H NMR (600 MHz, $CDCl_3$)



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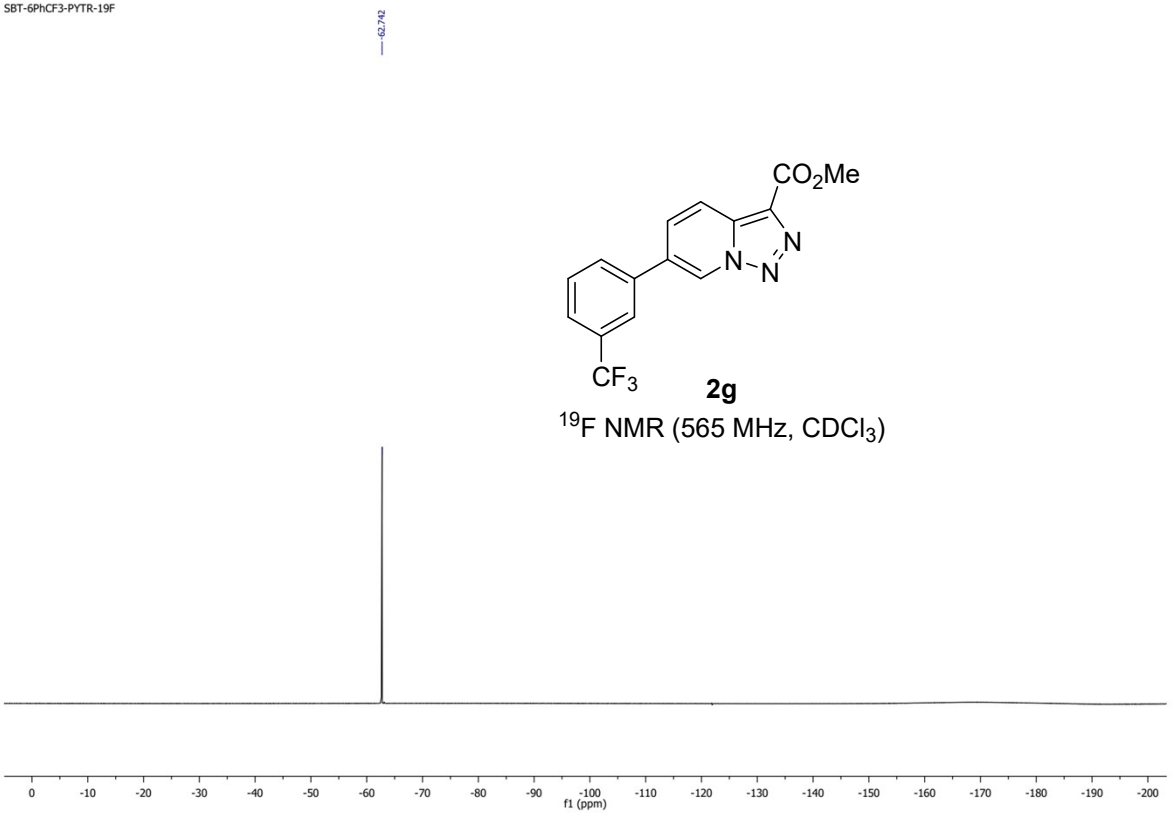
^{13}C NMR (150 MHz, $CDCl_3$)

SBT-6PhCF3-PYTR-19F



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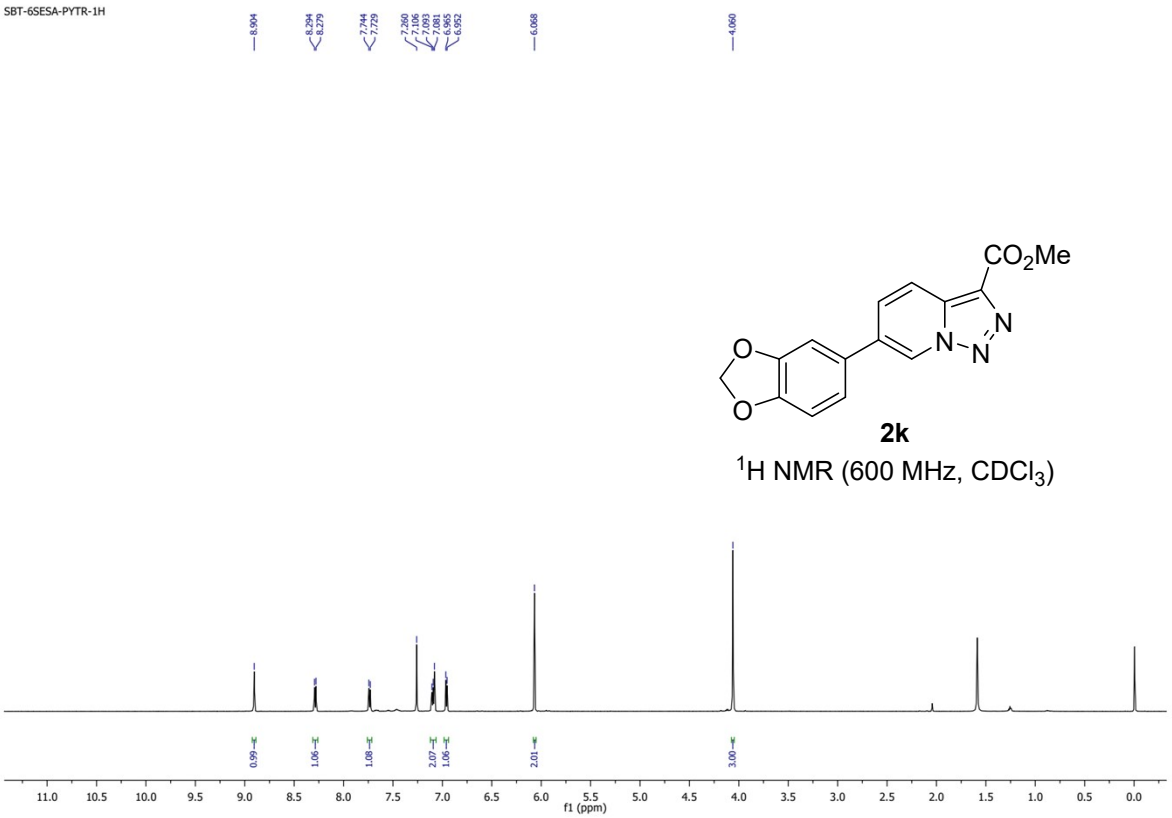
^{19}F NMR (565 MHz, $CDCl_3$)

SBT-6SESA-PYTR-1H



2k

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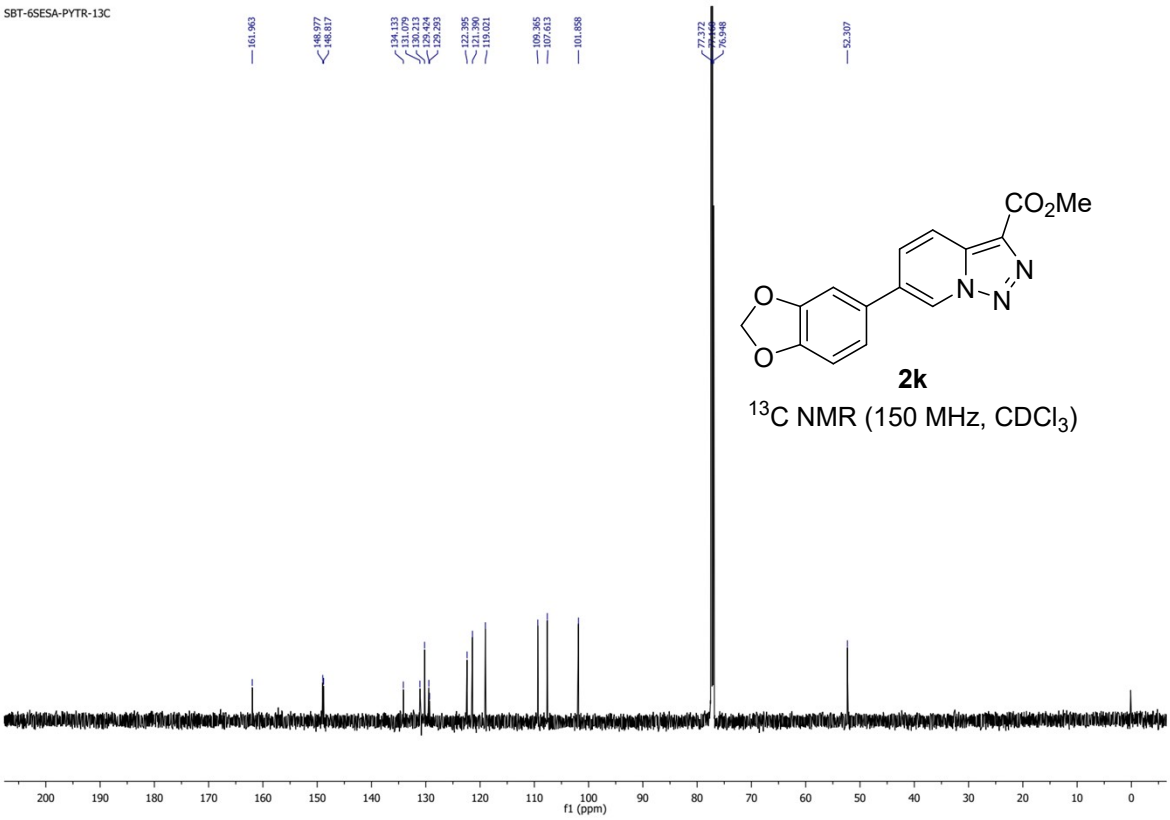

2k

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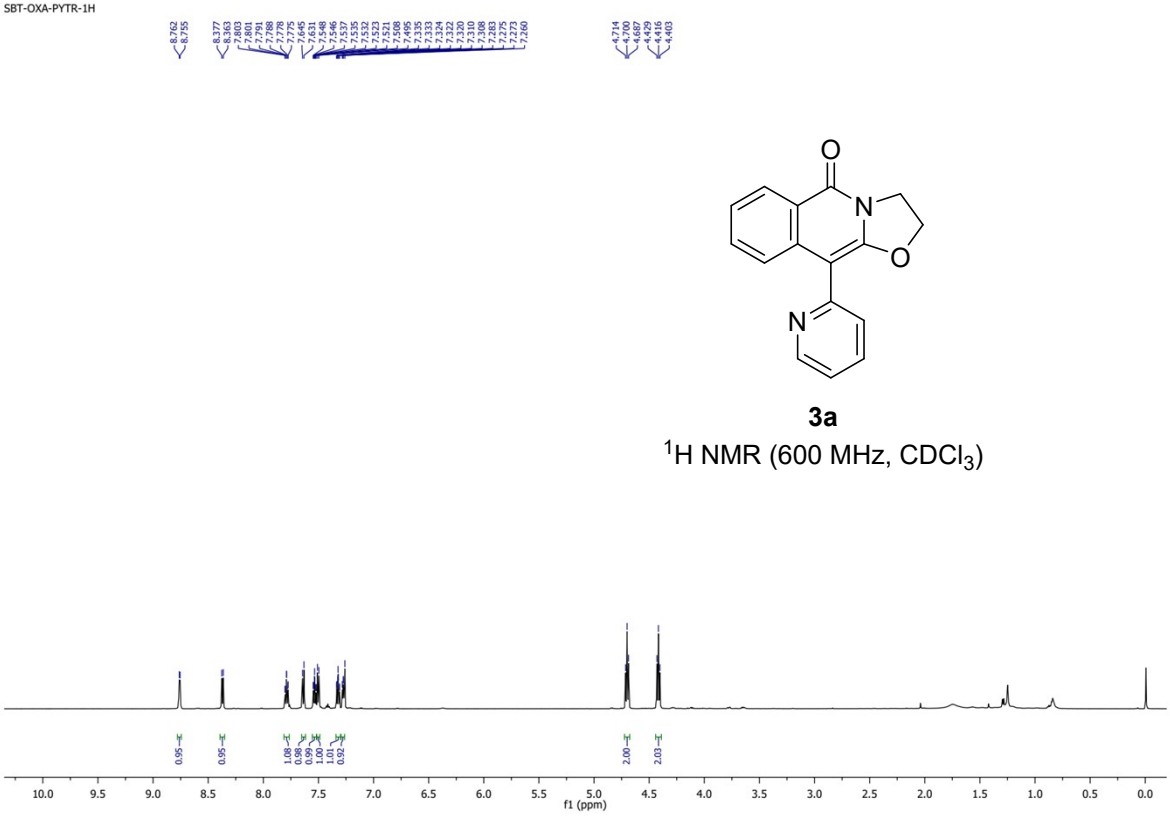
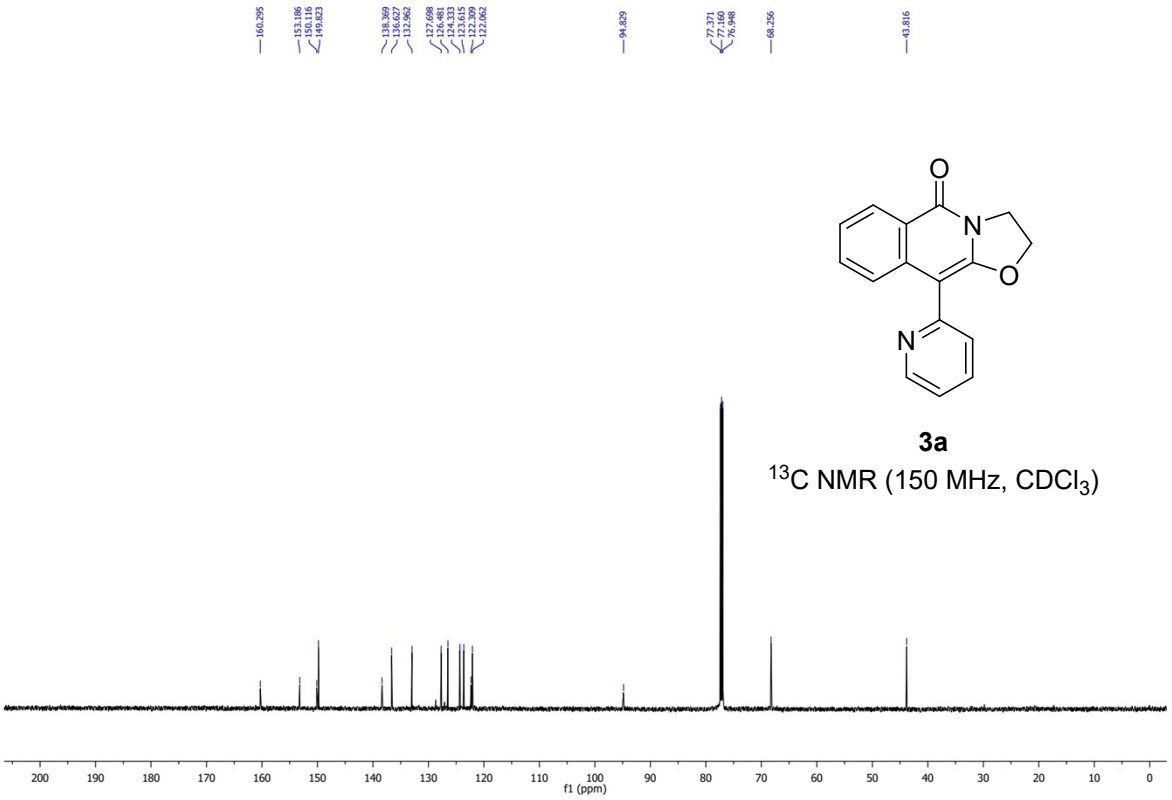


3a

^{1}H NMR (600 MHz, $CDCl_3$)

SBT-OXA-PYTR-13C



3a

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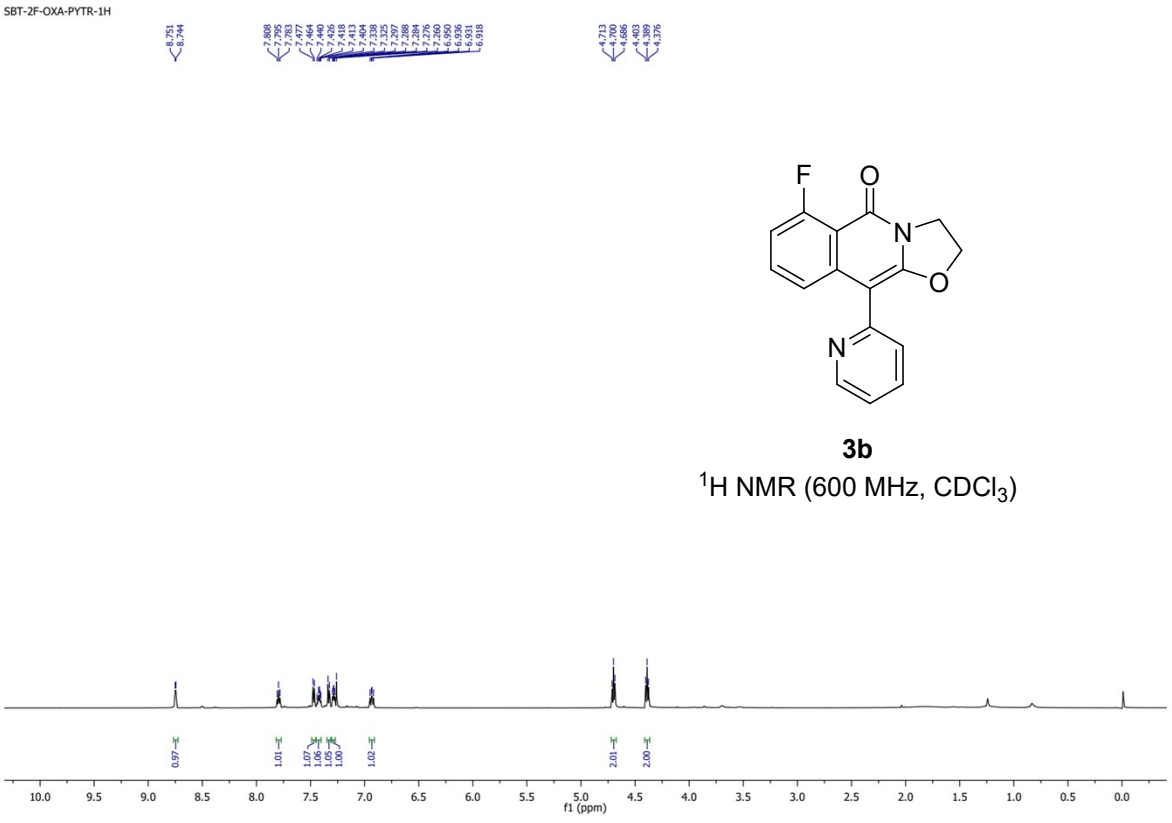
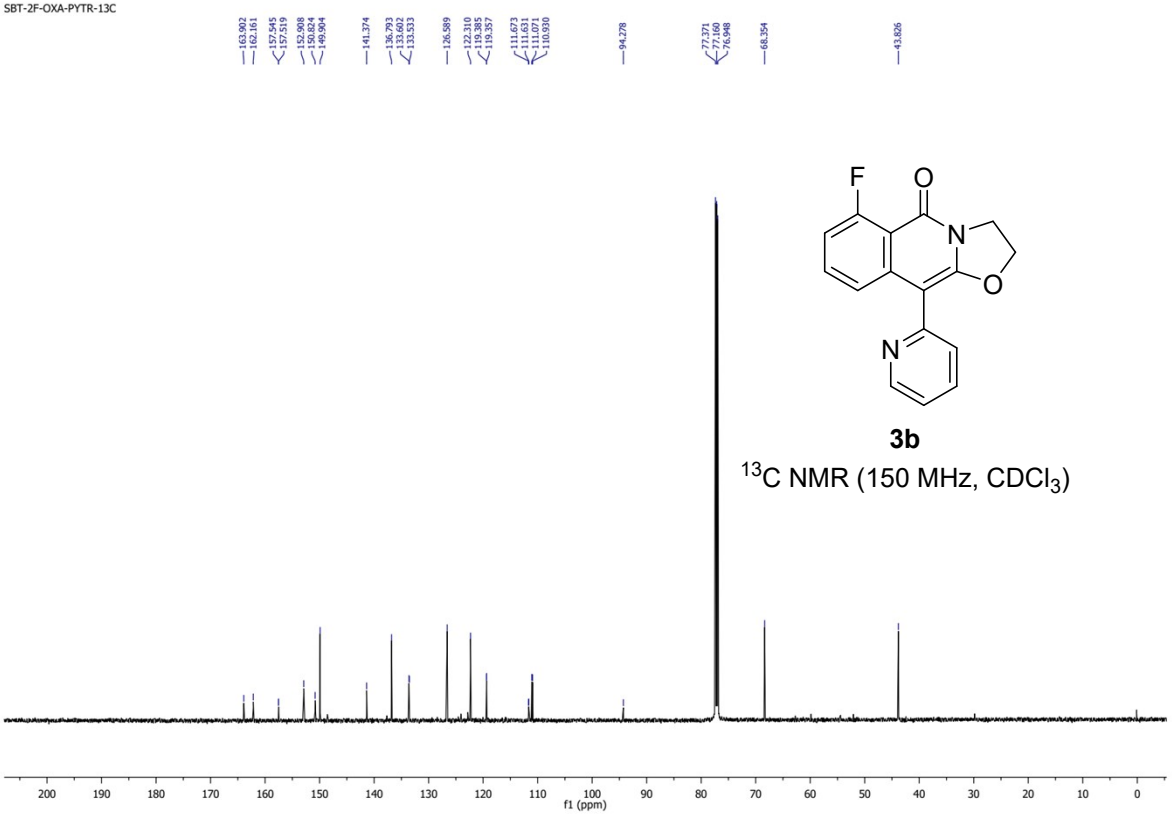
SBT-2F-OXA-PYTR-1H



3b

^{1}H NMR (600 MHz, $CDCl_3$)

SBT-2F-OXA-PYTR-13C



3b

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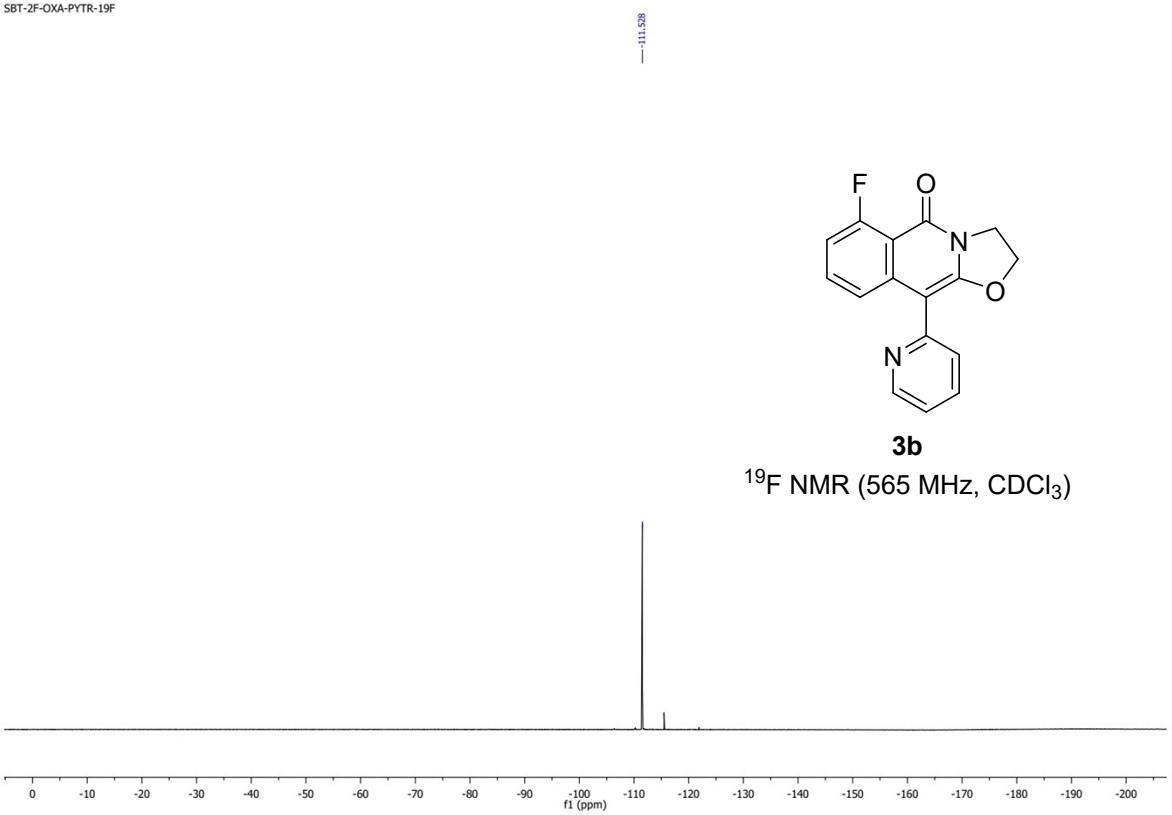

3b

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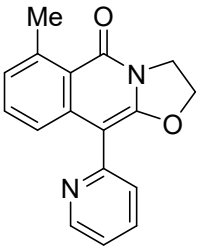

3c

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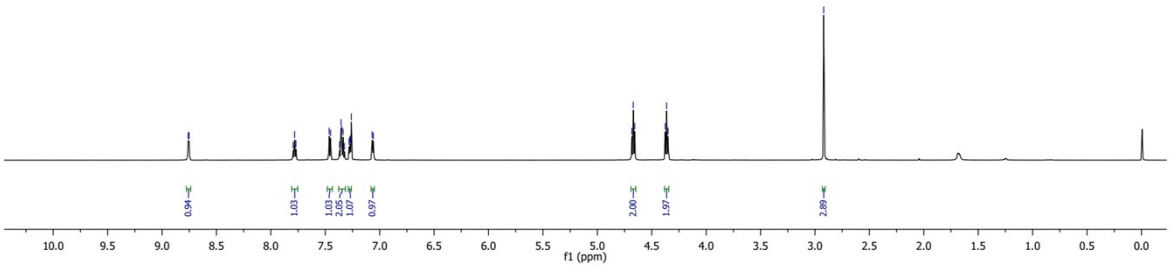
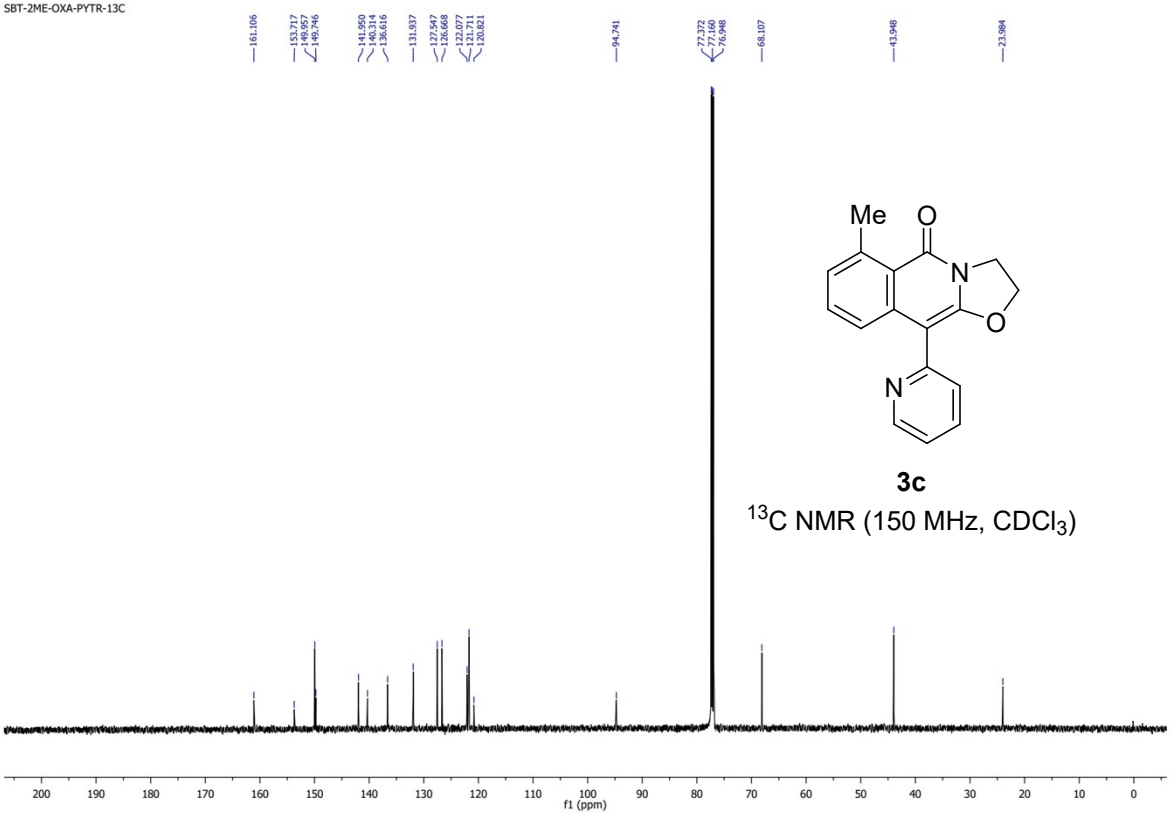


SBT-2ME-OXA-PYTR-13C



3c

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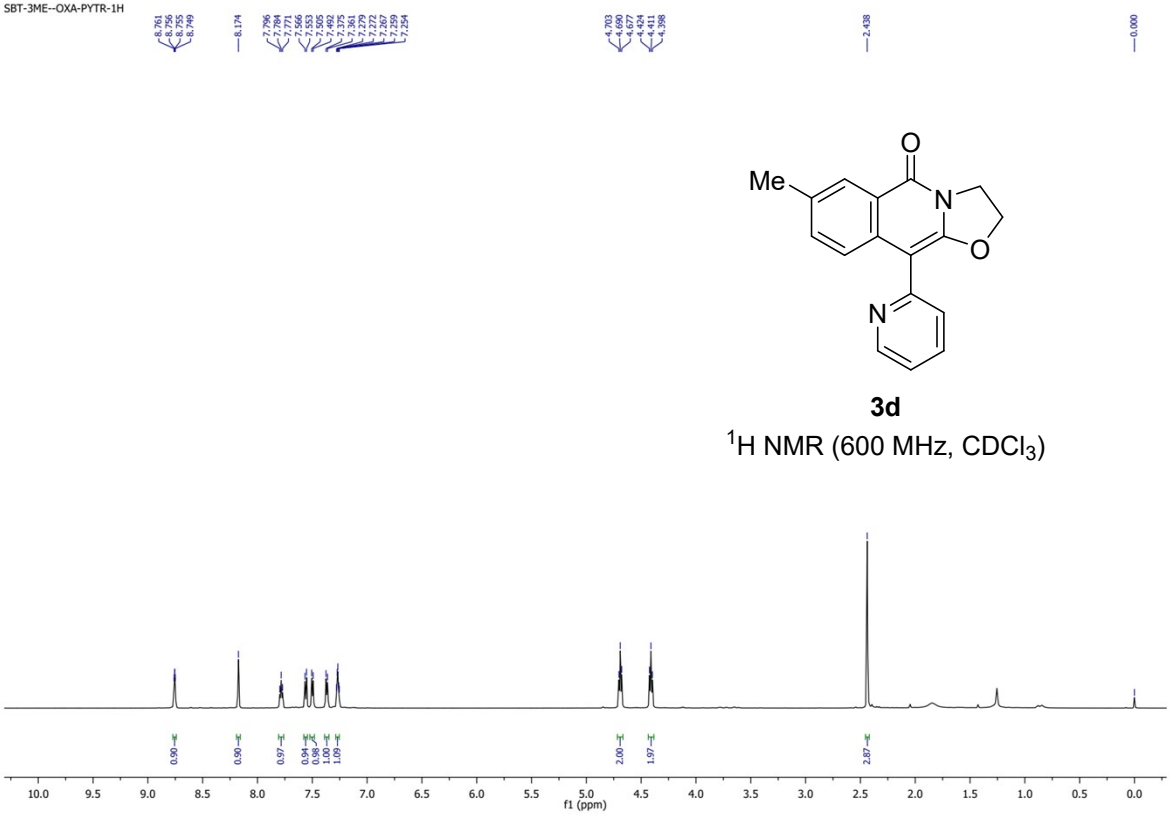

3d

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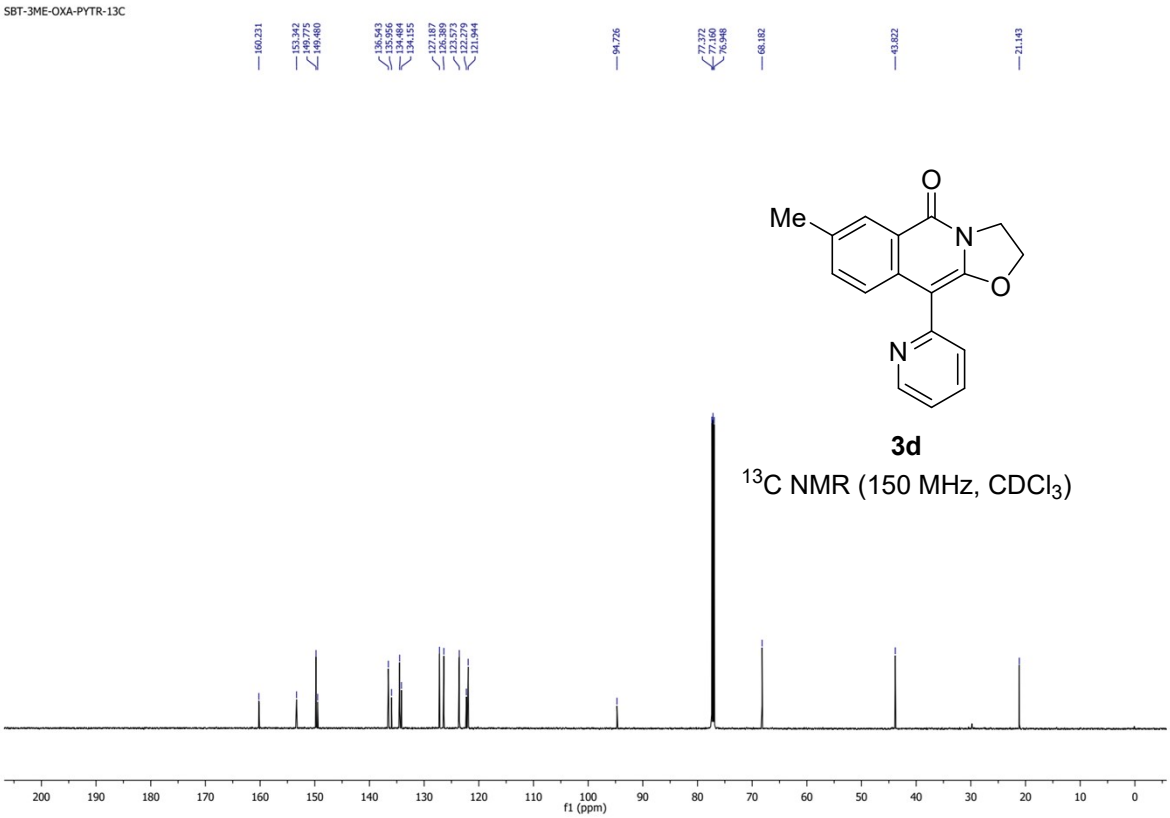
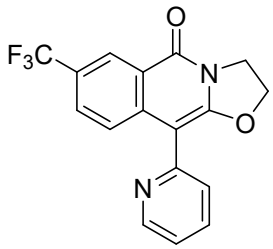


3d

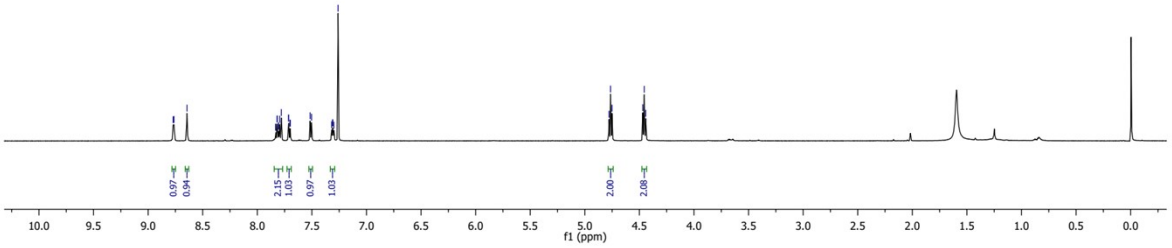
^{13}C NMR (150 MHz, $CDCl_3$)

SBT-3CF3-OXA-PYTR-1H

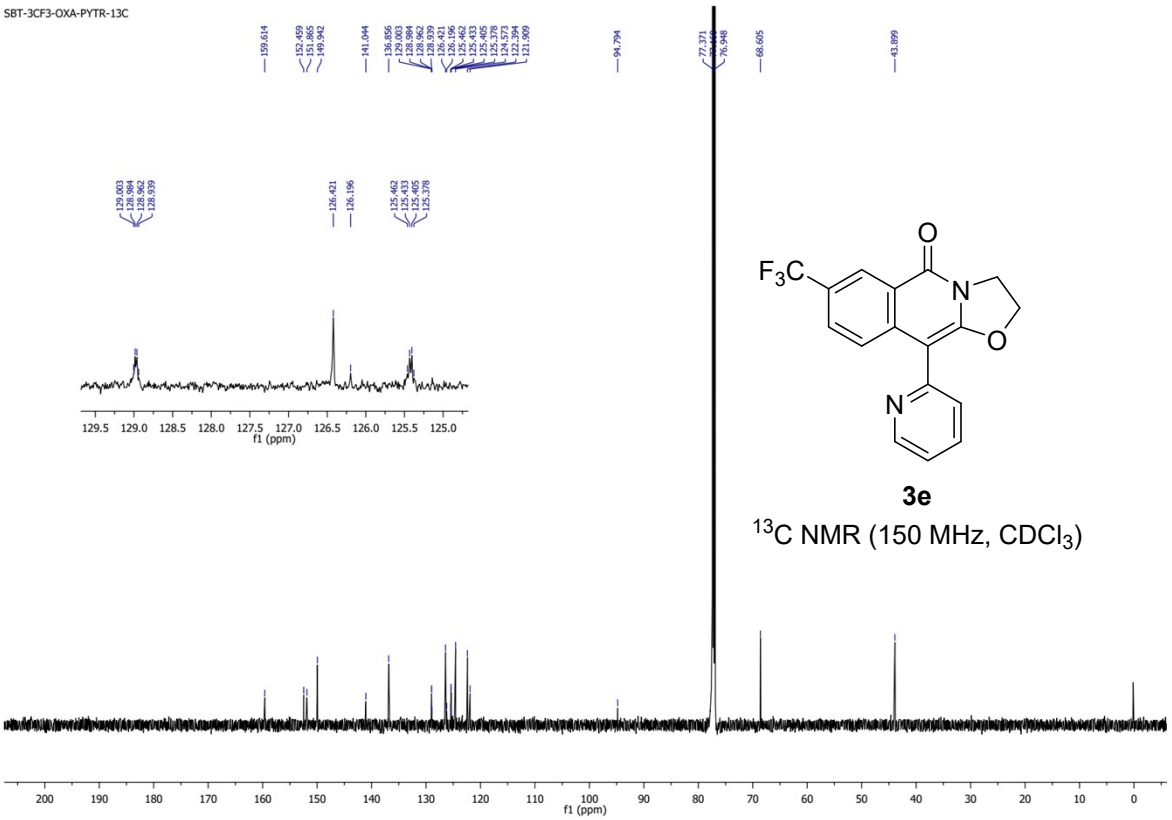


3e

^{1}H NMR (600 MHz, $CDCl_3$)



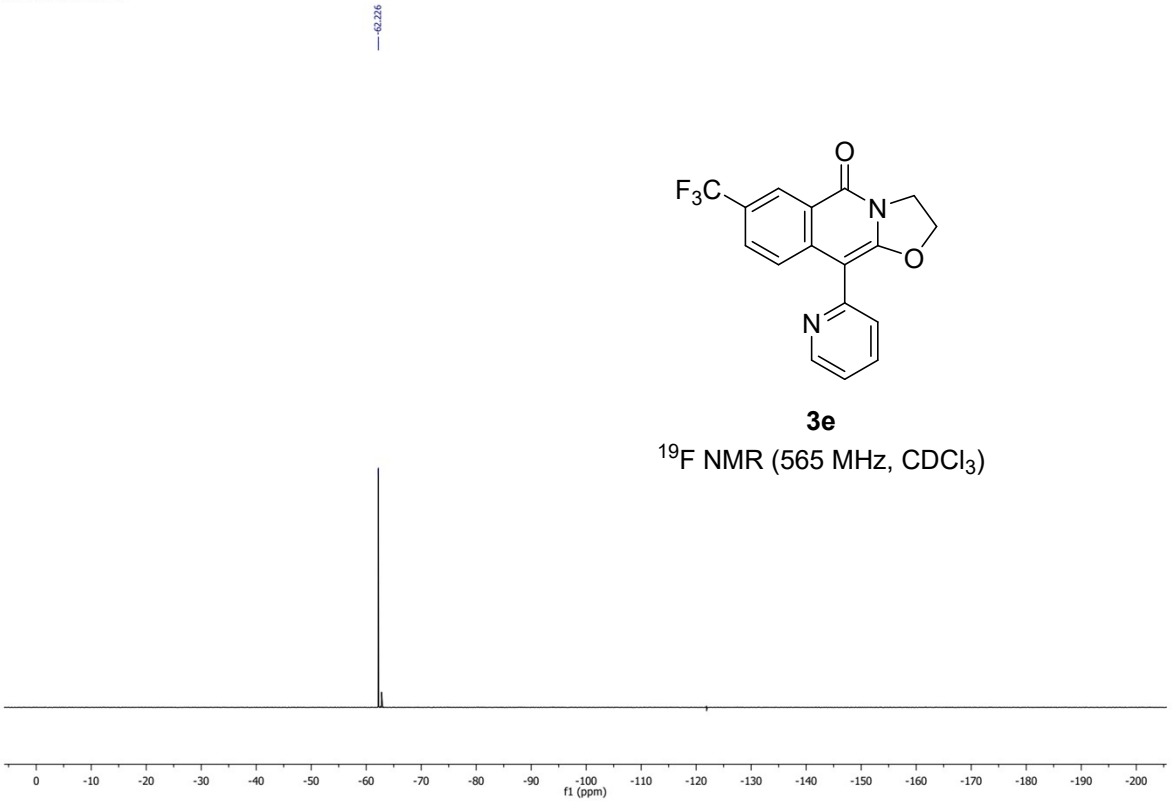
SBT-3CF3-OXA-PYTR-13C



3e

^{13}C NMR (150 MHz, $CDCl_3$)

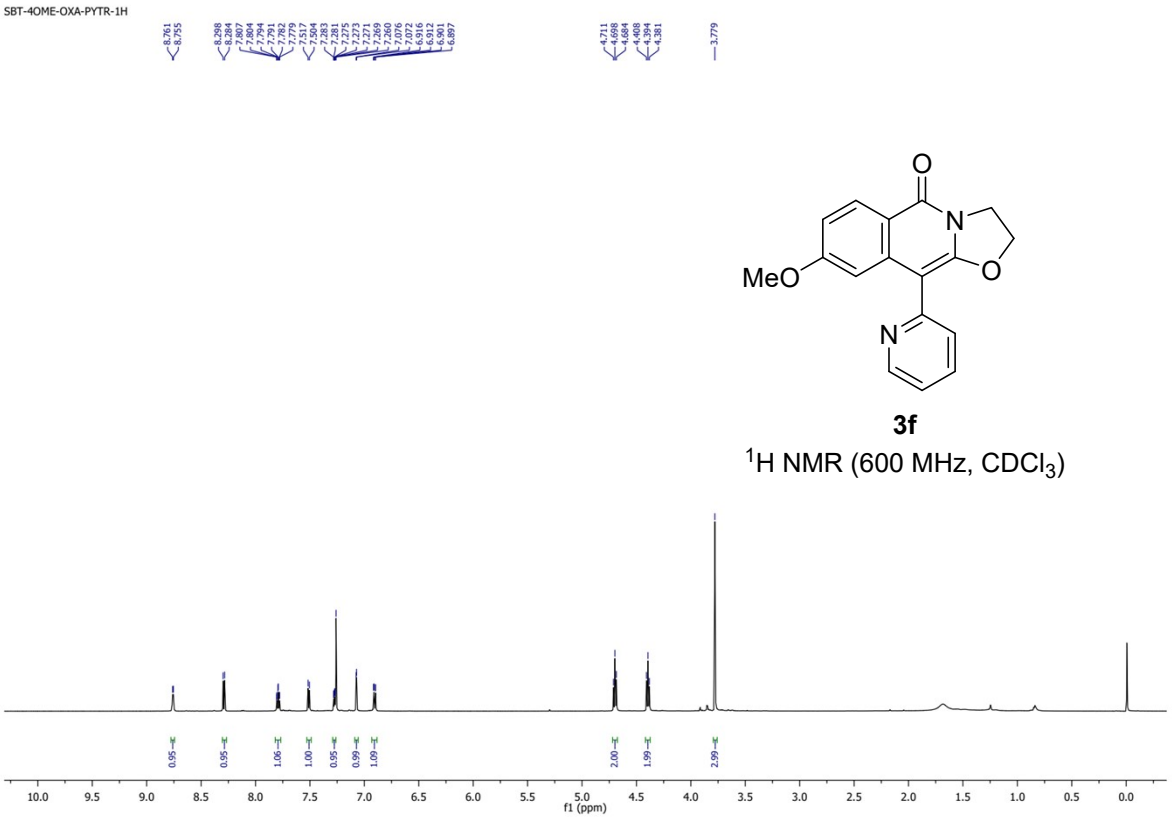
SBT-3CF3-OXA-PYTR-19F



3e

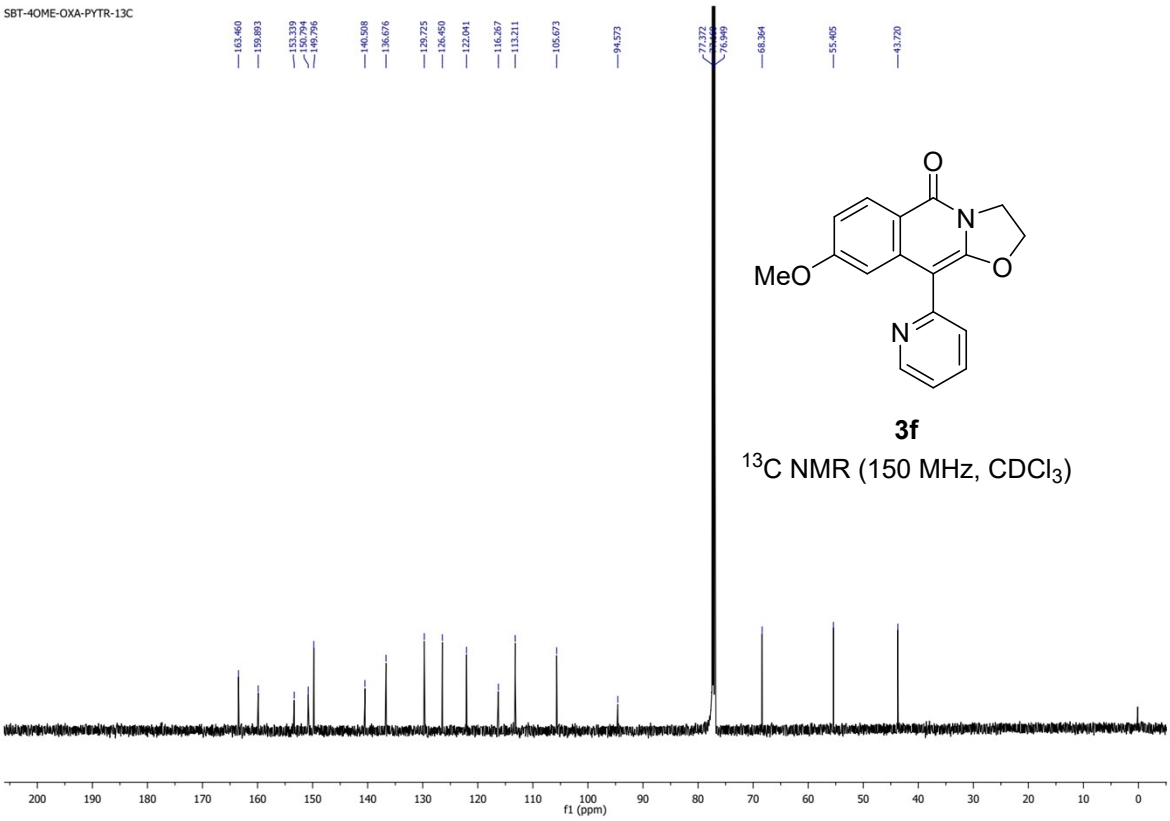
^{19}F NMR (565 MHz, $CDCl_3$)

SBT-4OME-OXA-PYTR-1H



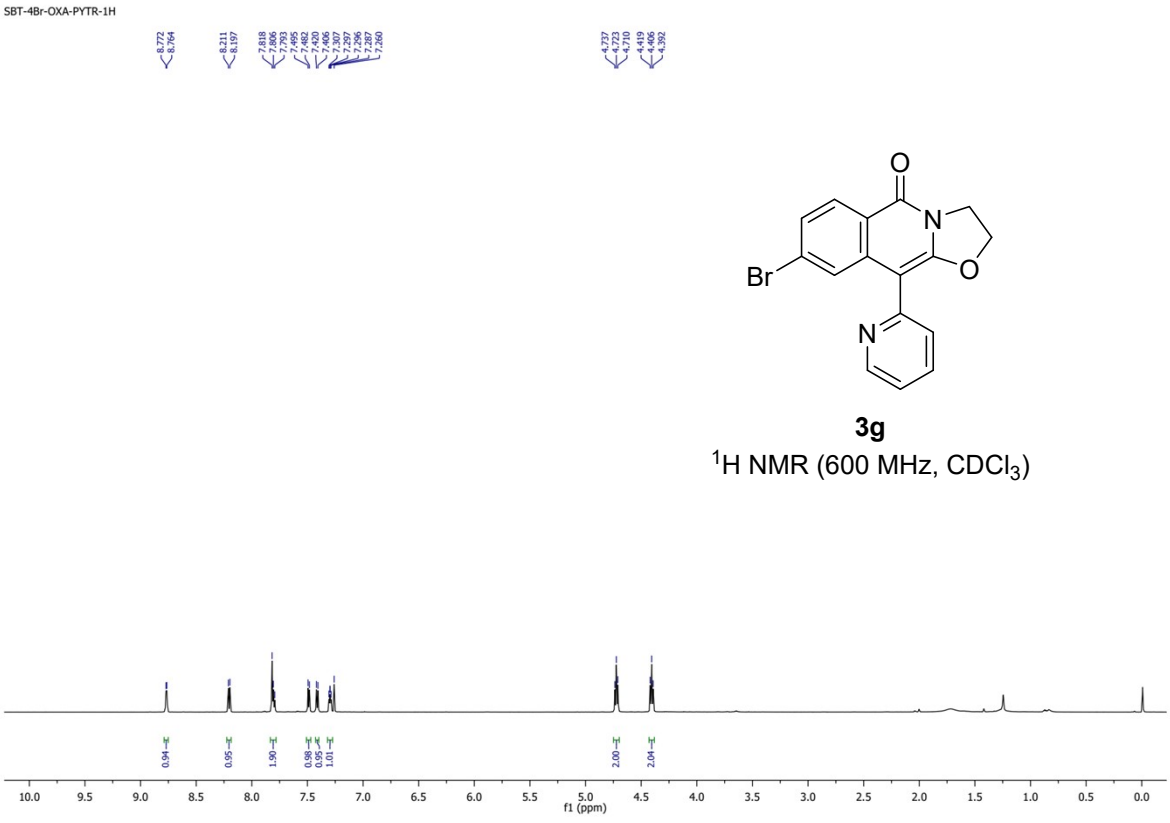
3f

^{1}H NMR (600 MHz, $CDCl_3$)



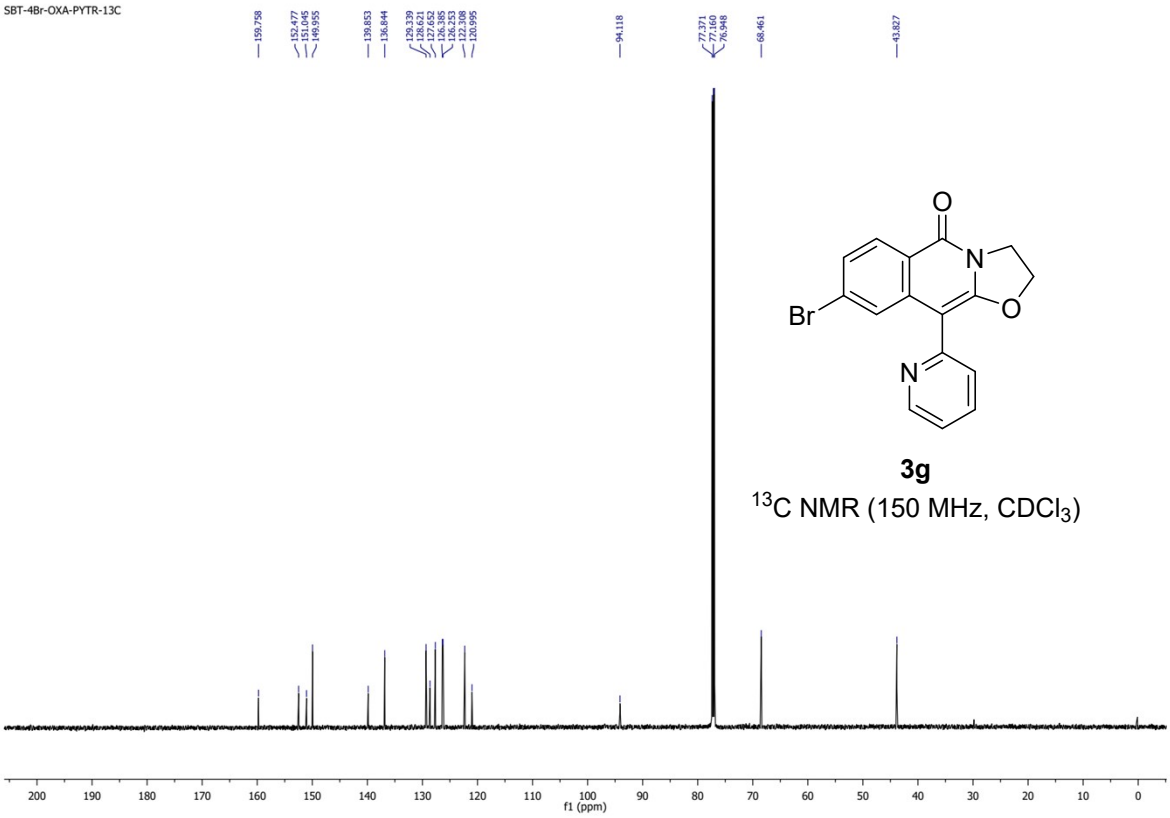
3f

^{13}C NMR (150 MHz, $CDCl_3$)



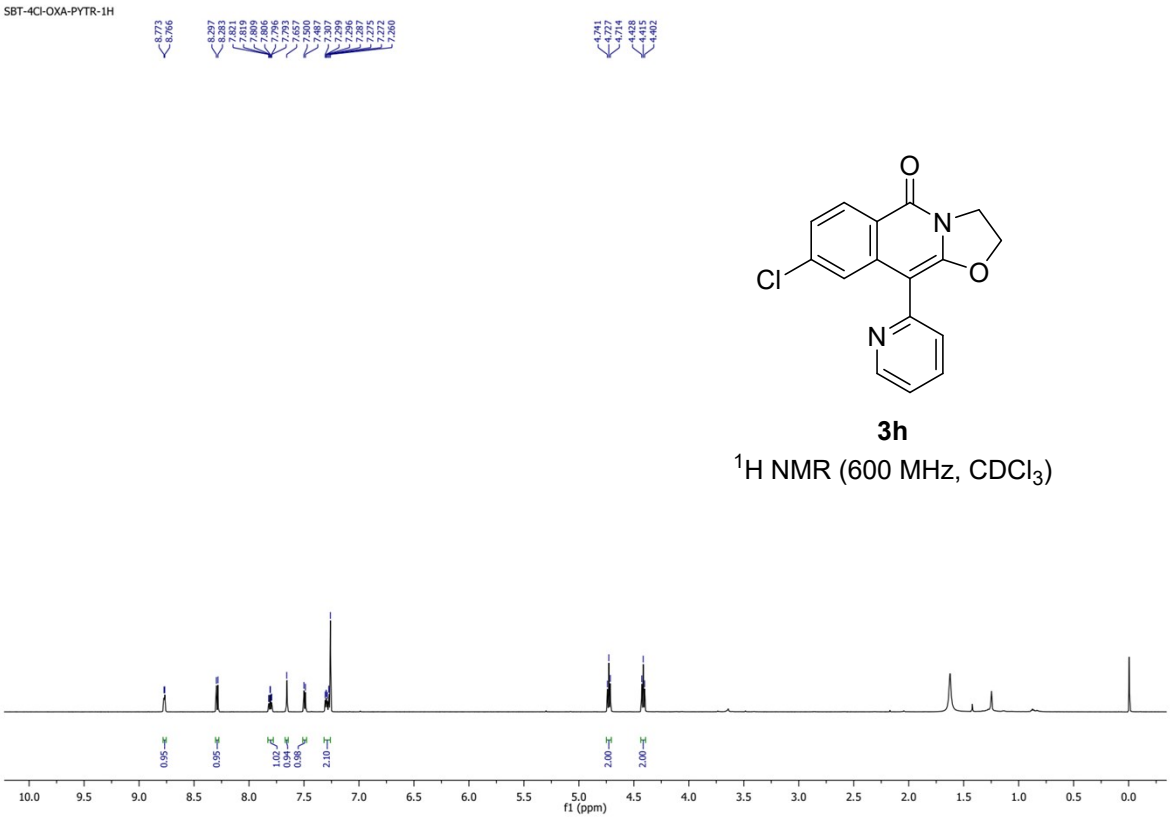
3g

^{1}H NMR (600 MHz, $CDCl_3$)



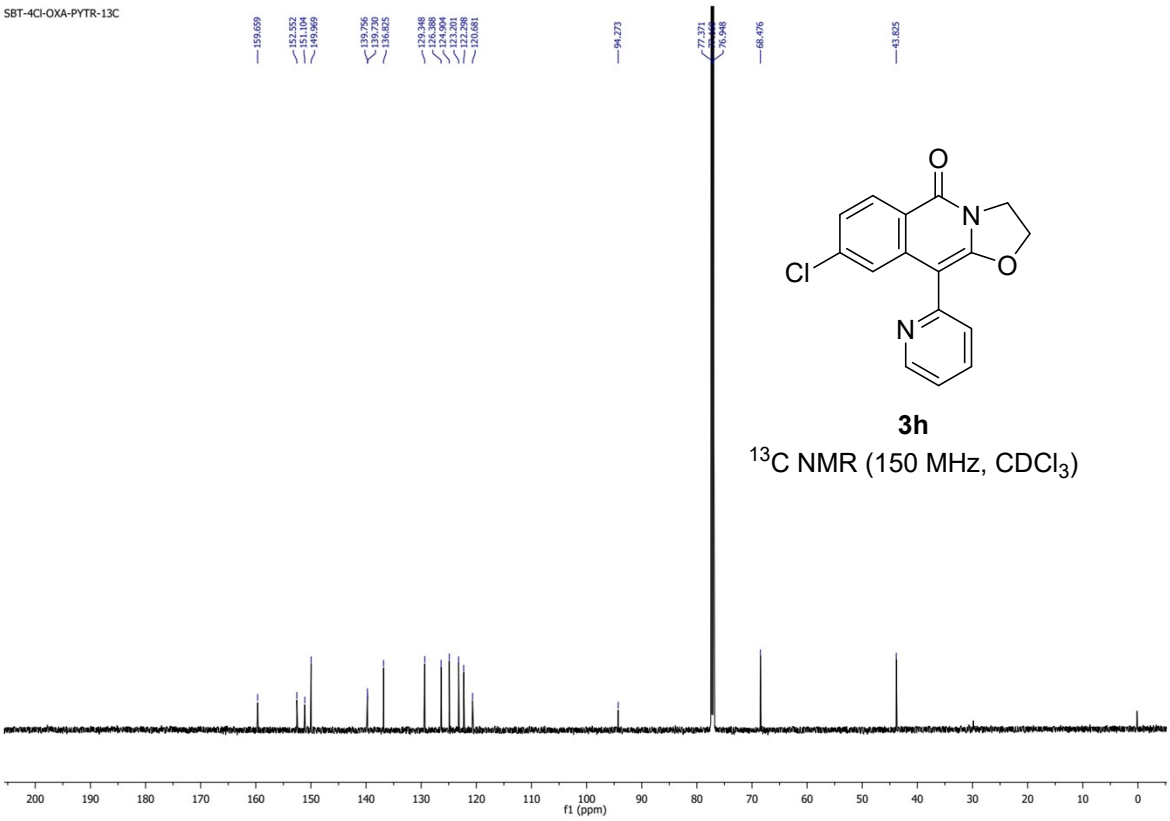
3g

^{13}C NMR (150 MHz, $CDCl_3$)



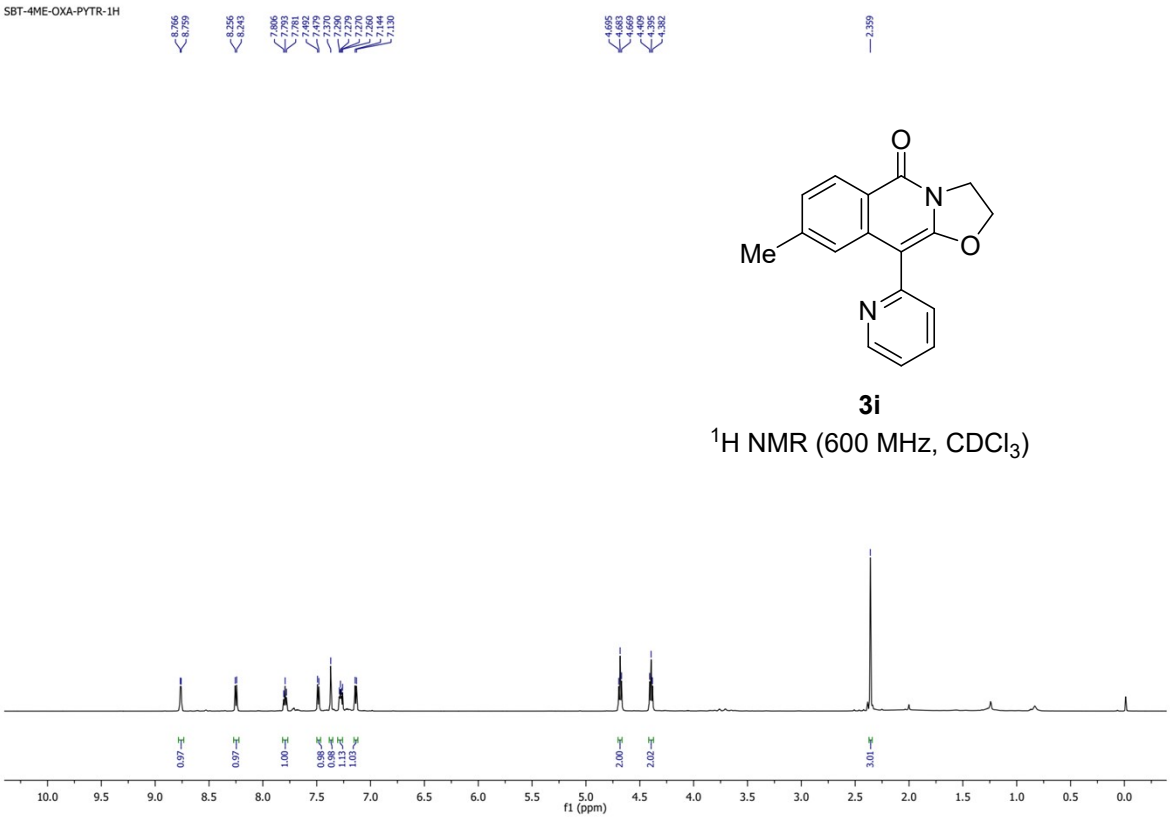
3h

^{1}H NMR (600 MHz, $CDCl_3$)



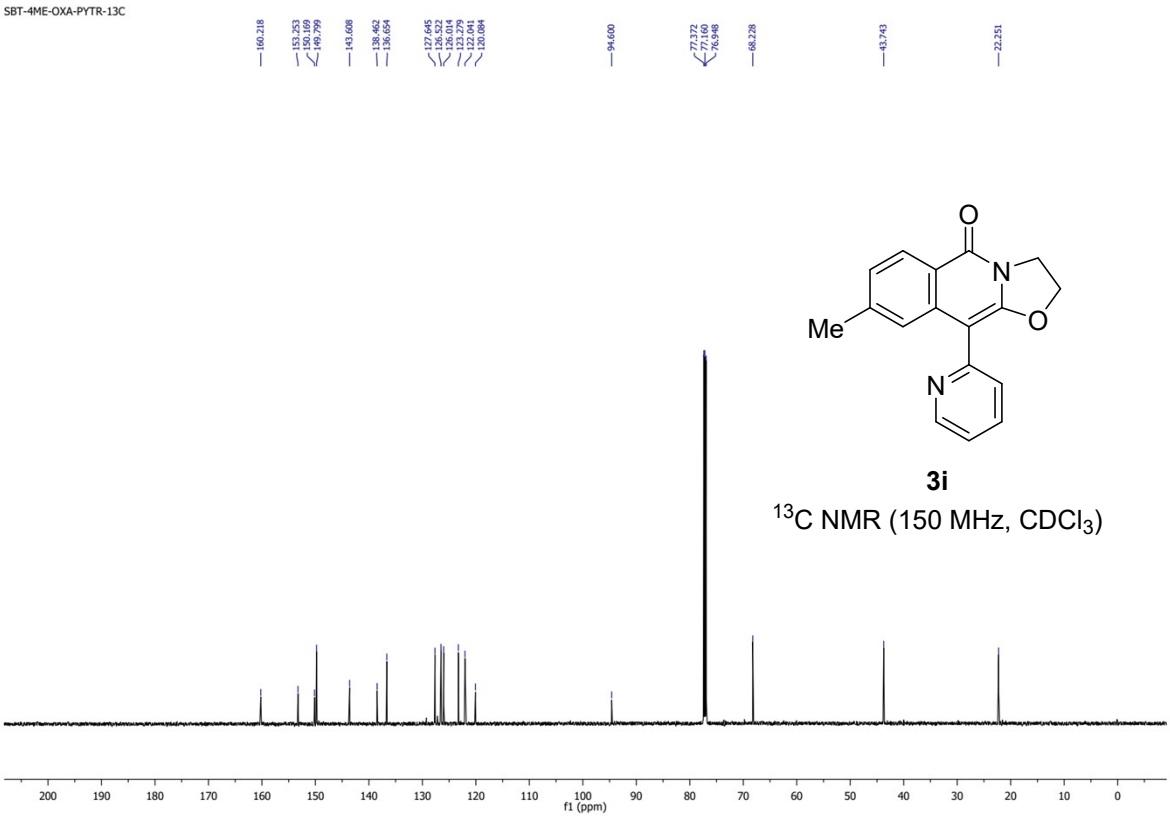
3h

^{13}C NMR (150 MHz, $CDCl_3$)



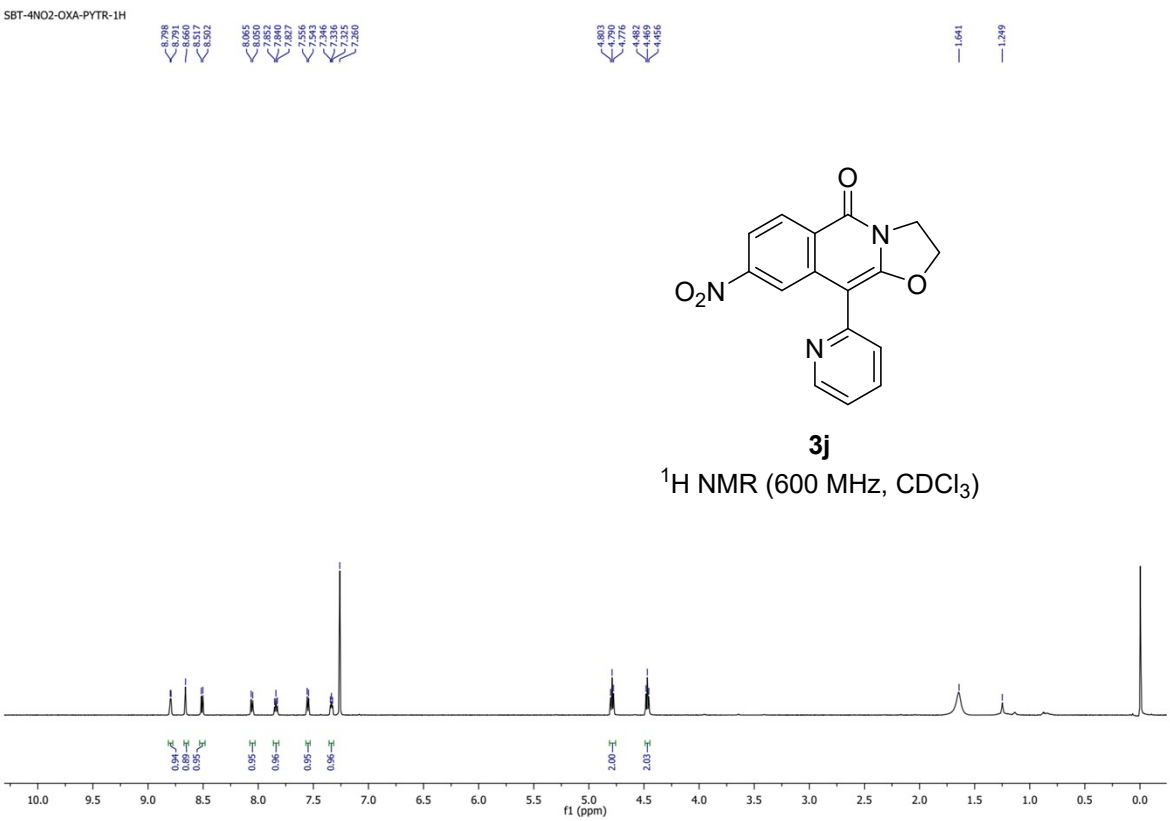
3i

^{1}H NMR (600 MHz, $CDCl_3$)



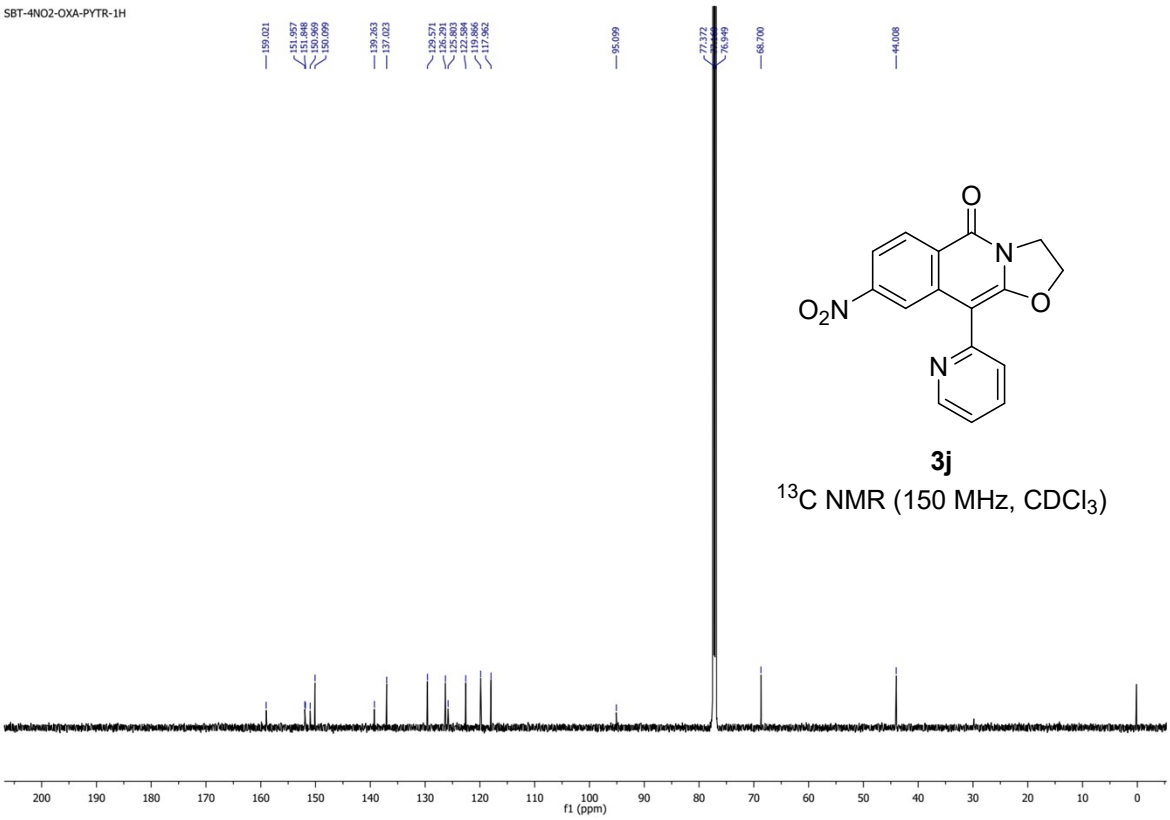
3i

^{13}C NMR (150 MHz, $CDCl_3$)



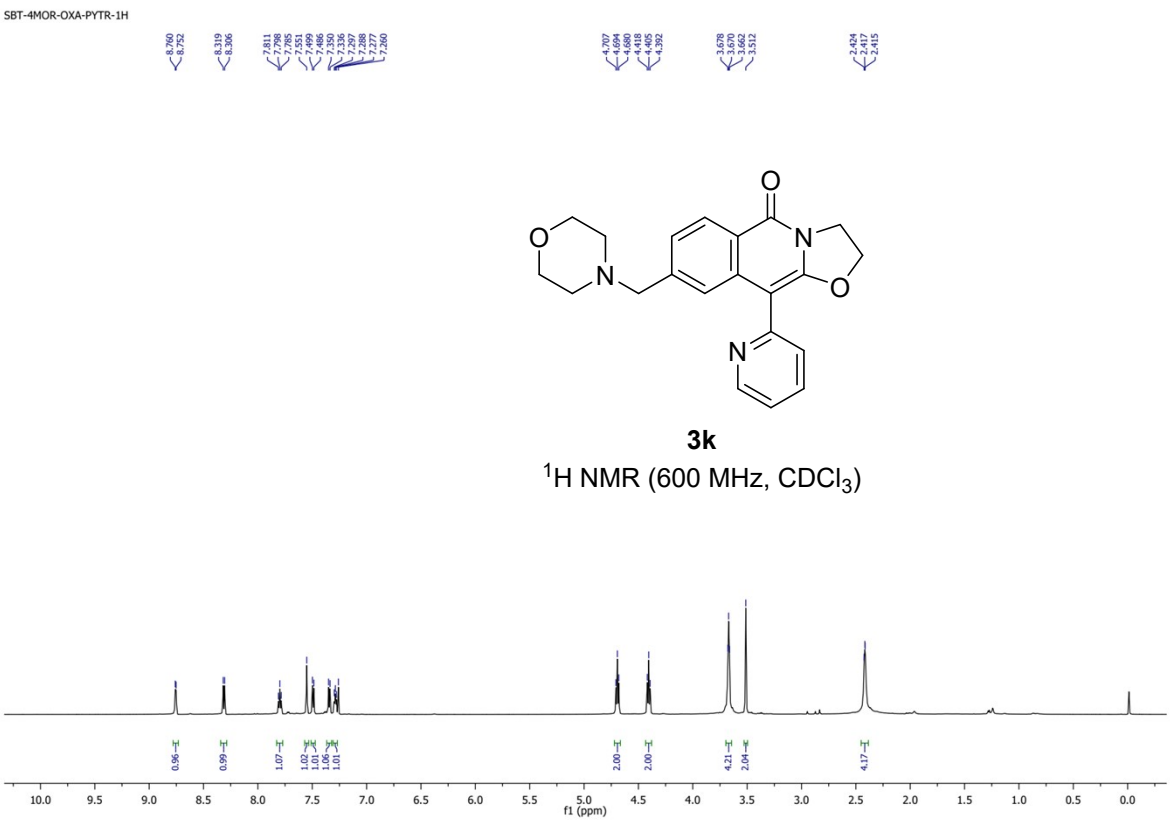
3j

^{1}H NMR (600 MHz, $CDCl_3$)



3j

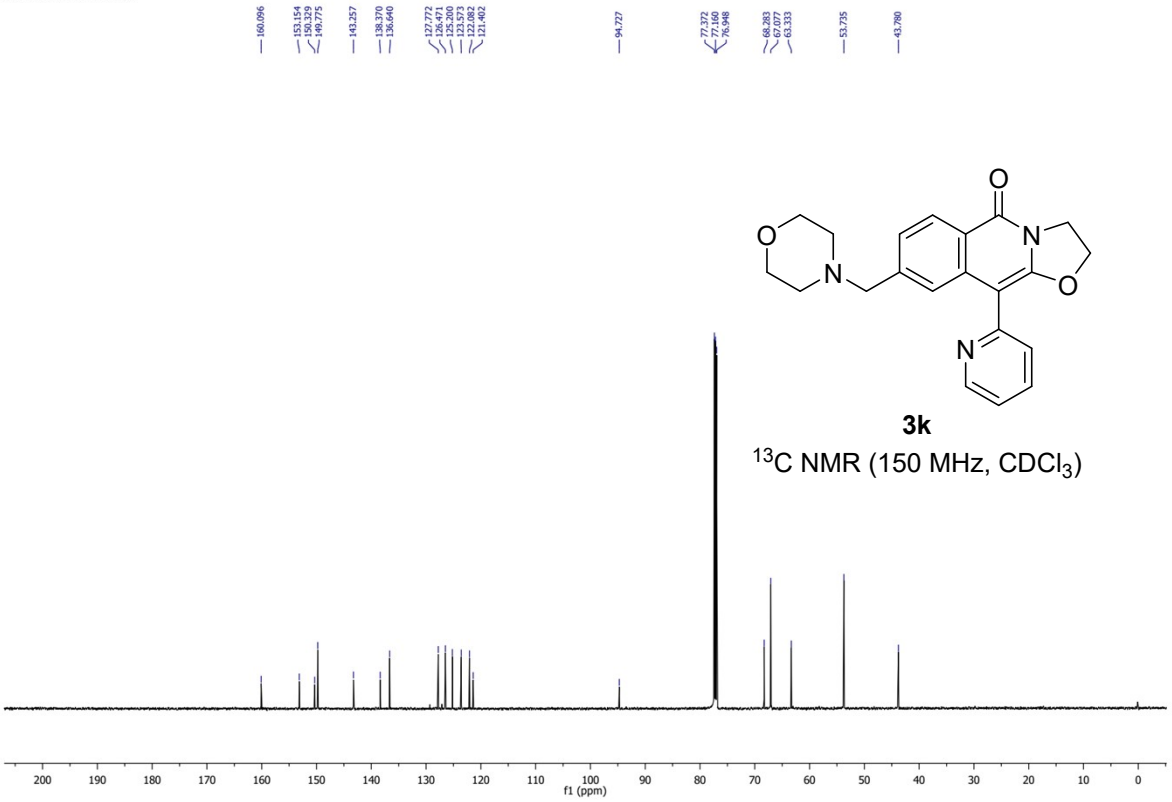
^{13}C NMR (150 MHz, $CDCl_3$)



3k

^{1}H NMR (600 MHz, $CDCl_3$)

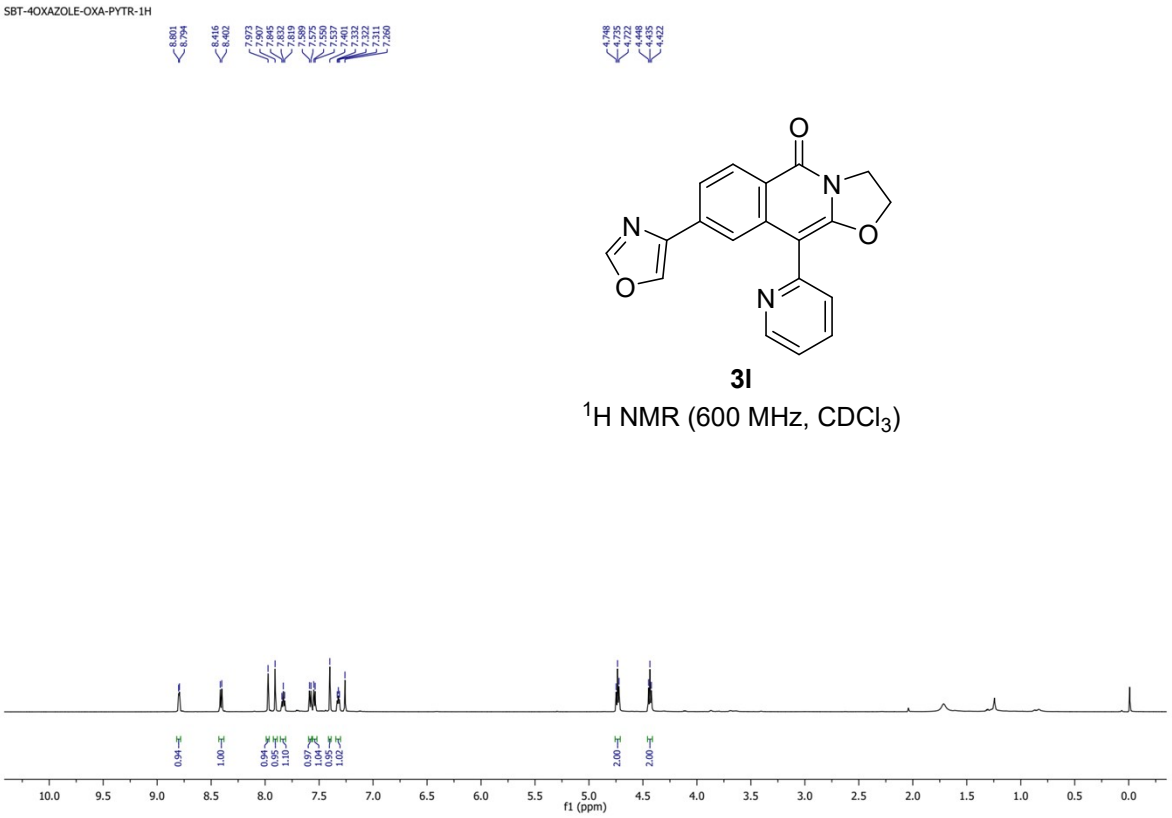
SBT-4MOR-OXA-PYTR-13C



3k

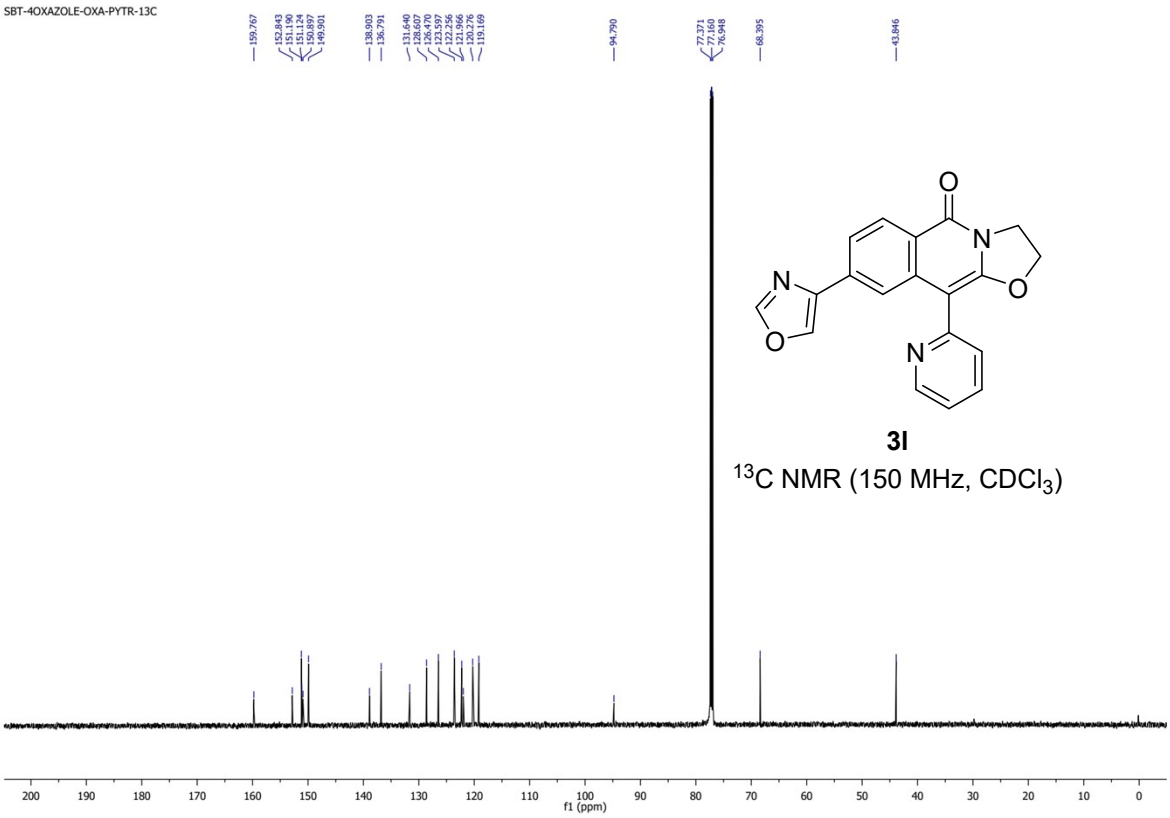
^{13}C NMR (150 MHz, $CDCl_3$)

SBT-4OXAZOLE-OXA-PYTR-1H



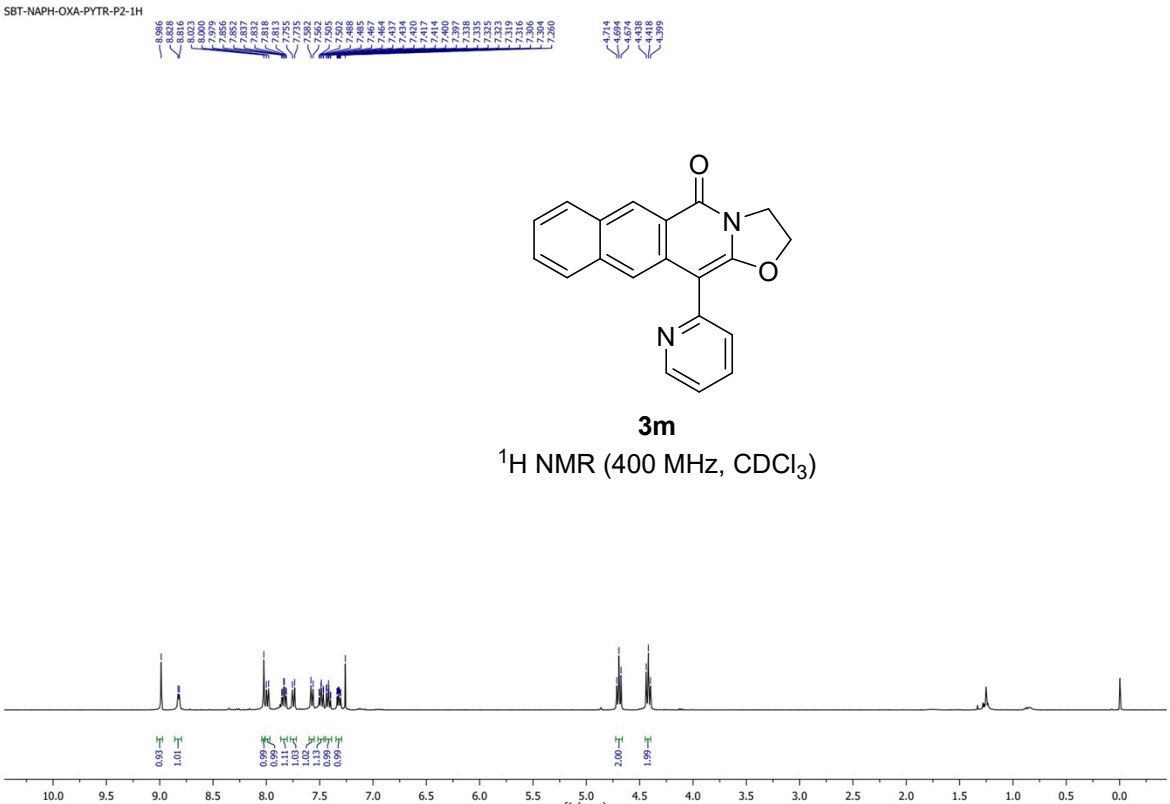
3l

^{1}H NMR (600 MHz, $CDCl_3$)



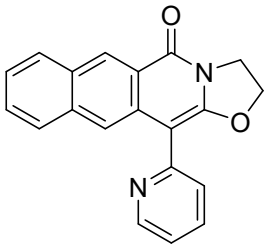
3l

^{13}C NMR (150 MHz, $CDCl_3$)



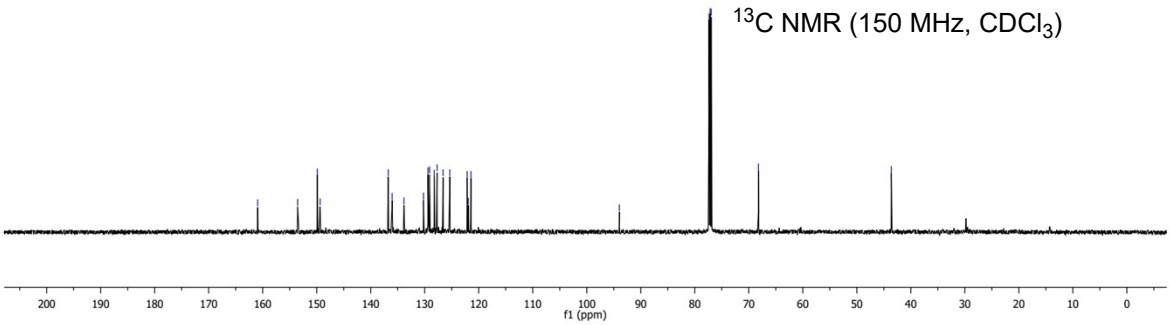
3m

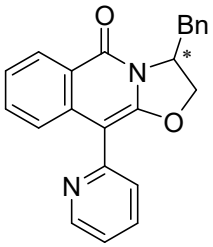
^{1}H NMR (400 MHz, $CDCl_3$)



3m

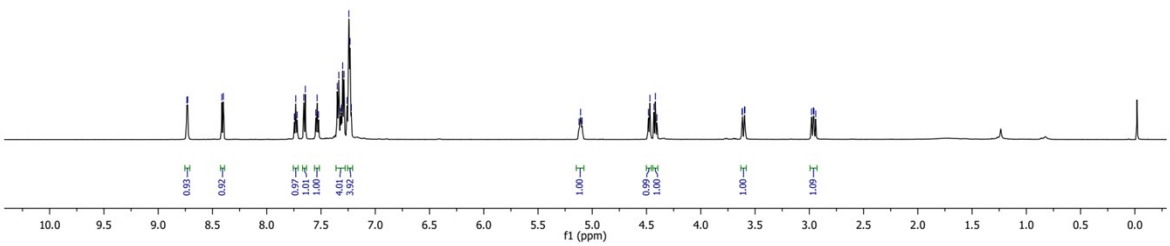
^{13}C NMR (150 MHz, $CDCl_3$)



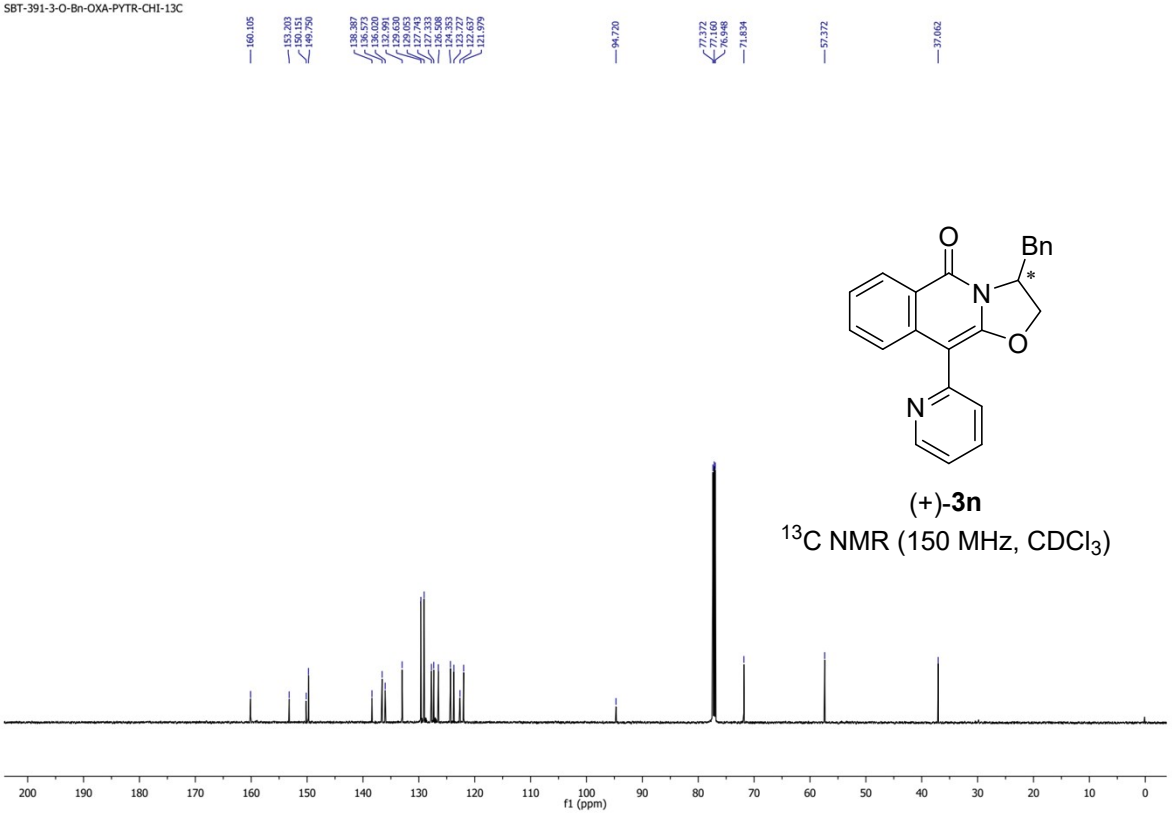


(+)-**3n**

^{1}H NMR (600 MHz, $CDCl_3$)



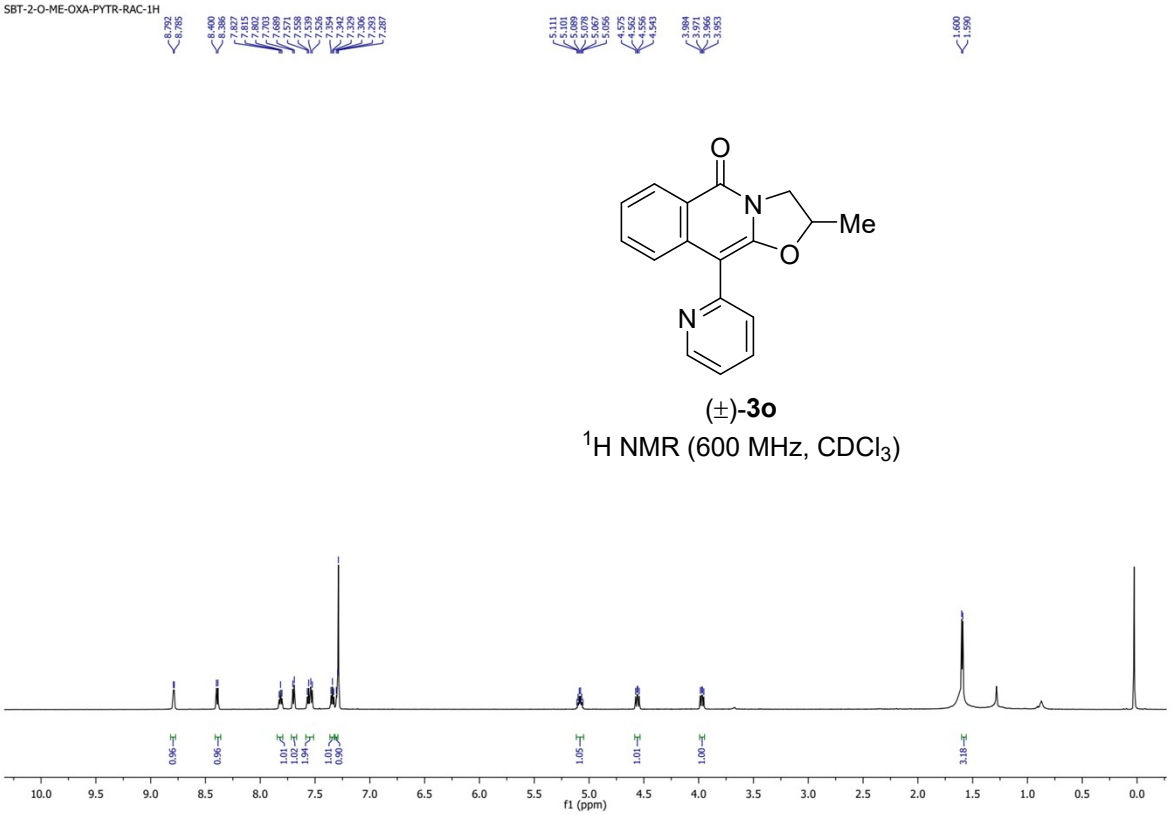
SBT-391-3-O-Bn-OXA-PYTR-CHI-13C



(+)-**3n**

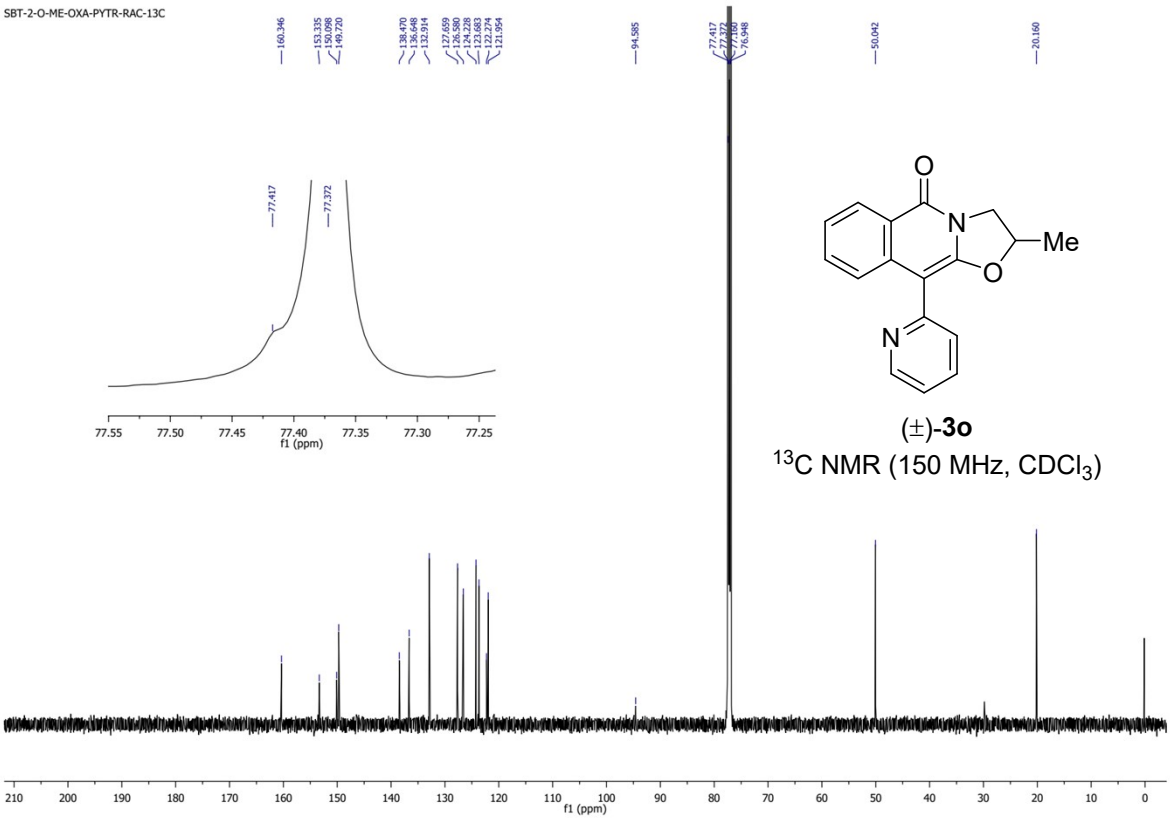
^{13}C NMR (150 MHz, $CDCl_3$)

SBT-2-O-ME-OXA-PYTR-RAC-1H



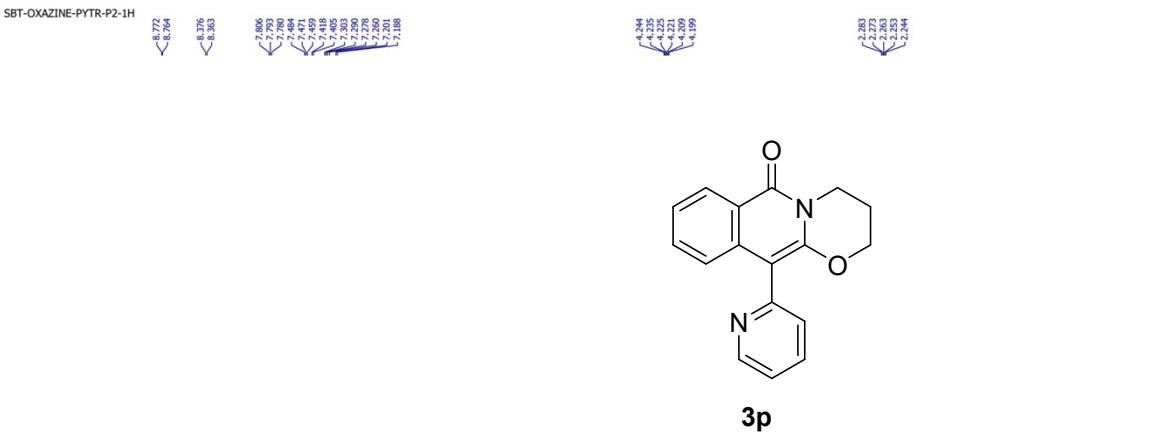
(±)-**3o**

^{1}H NMR (600 MHz, $CDCl_3$)



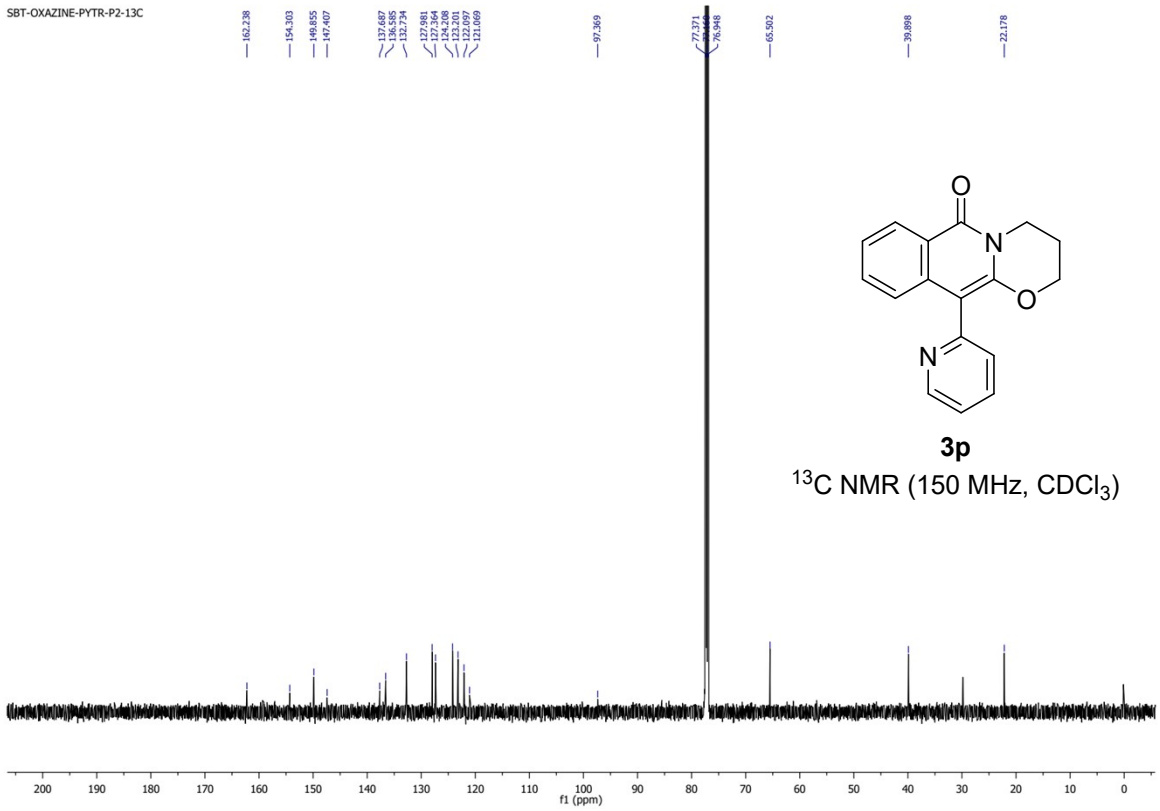
(±)-**3o**

^{13}C NMR (150 MHz, $CDCl_3$)



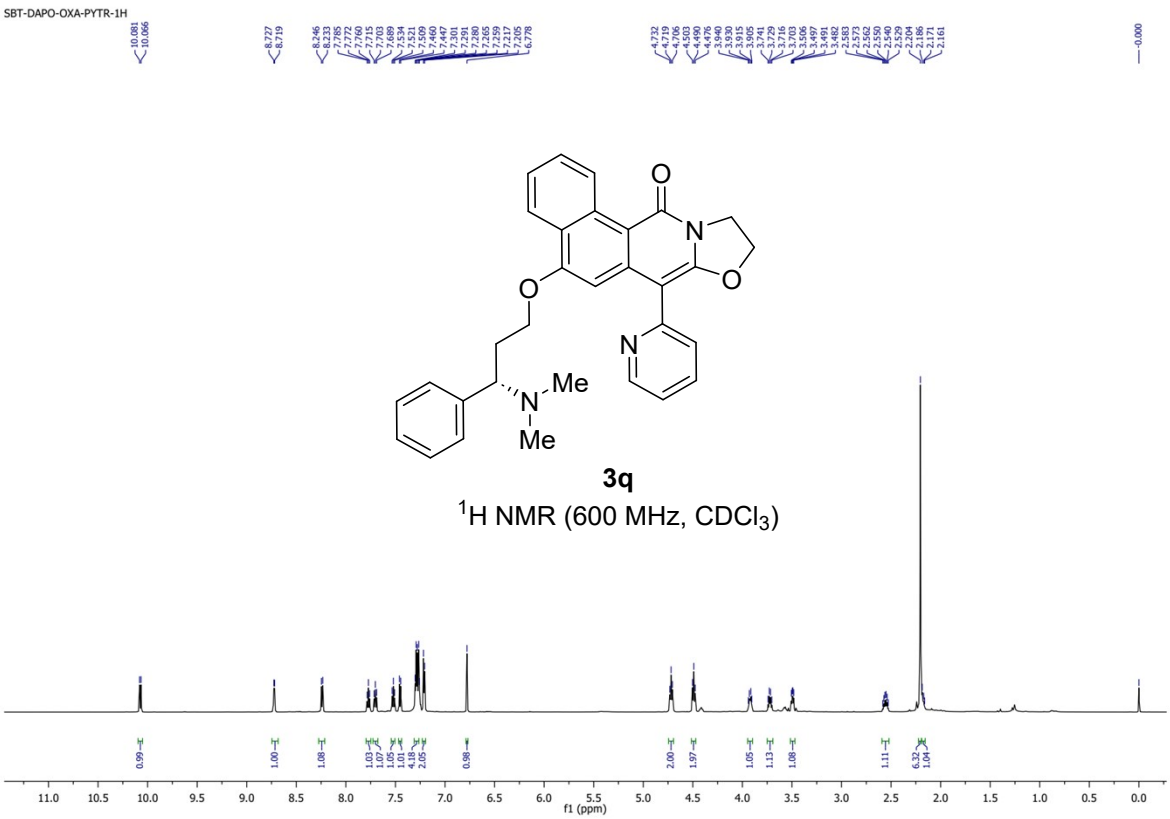
3p

^{1}H NMR (600 MHz, $CDCl_3$)



3p

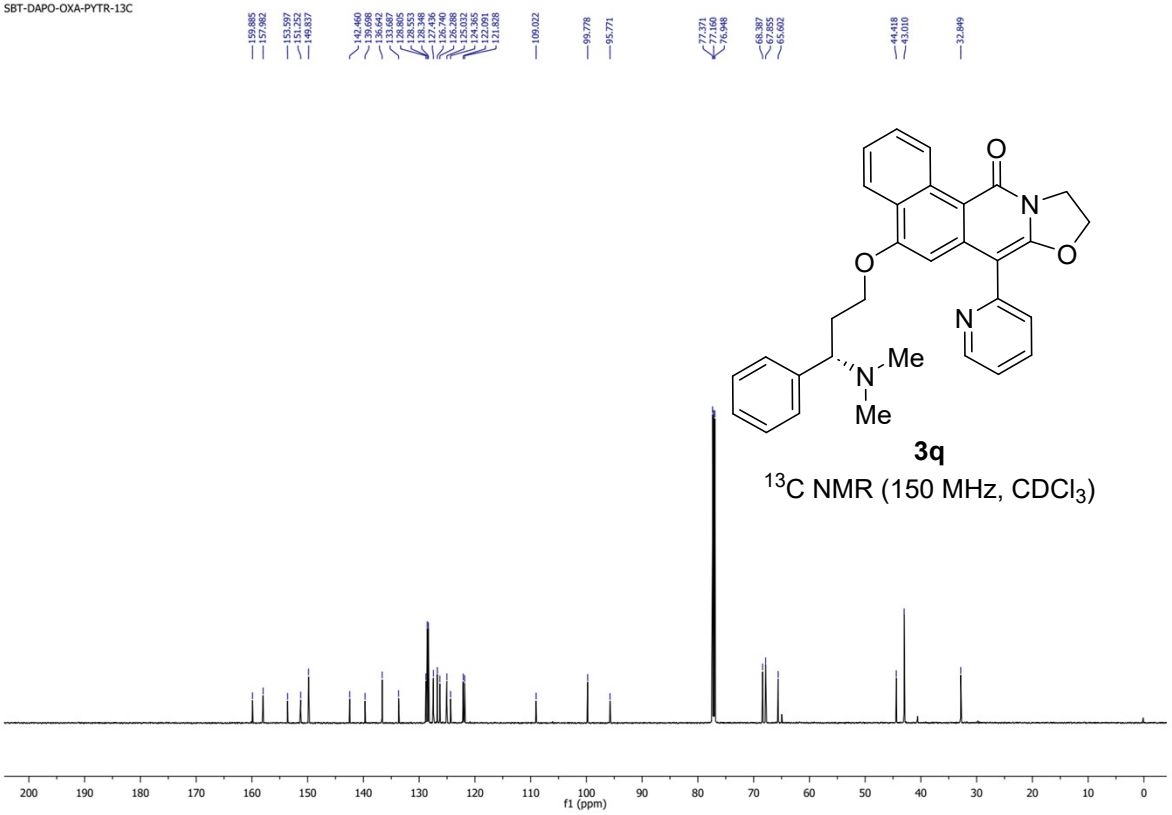
^{13}C NMR (150 MHz, $CDCl_3$)



3q

^{1}H NMR (600 MHz, $CDCl_3$)

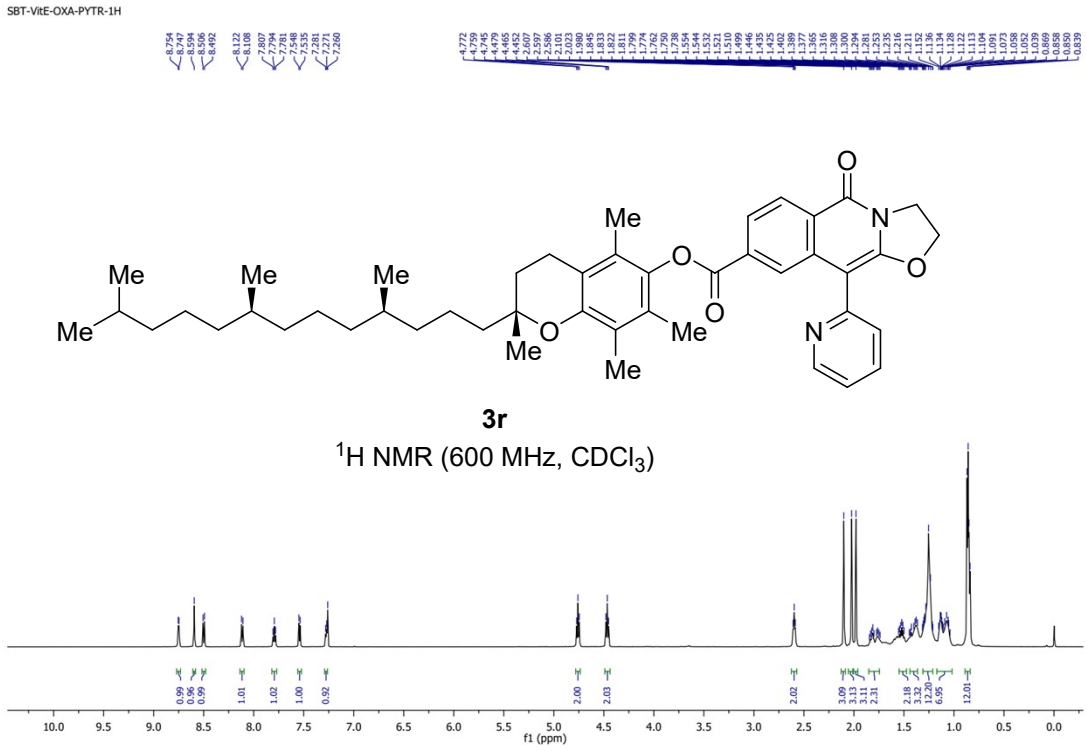
SBT-DAPO-OXA-PYTR-13C



3q

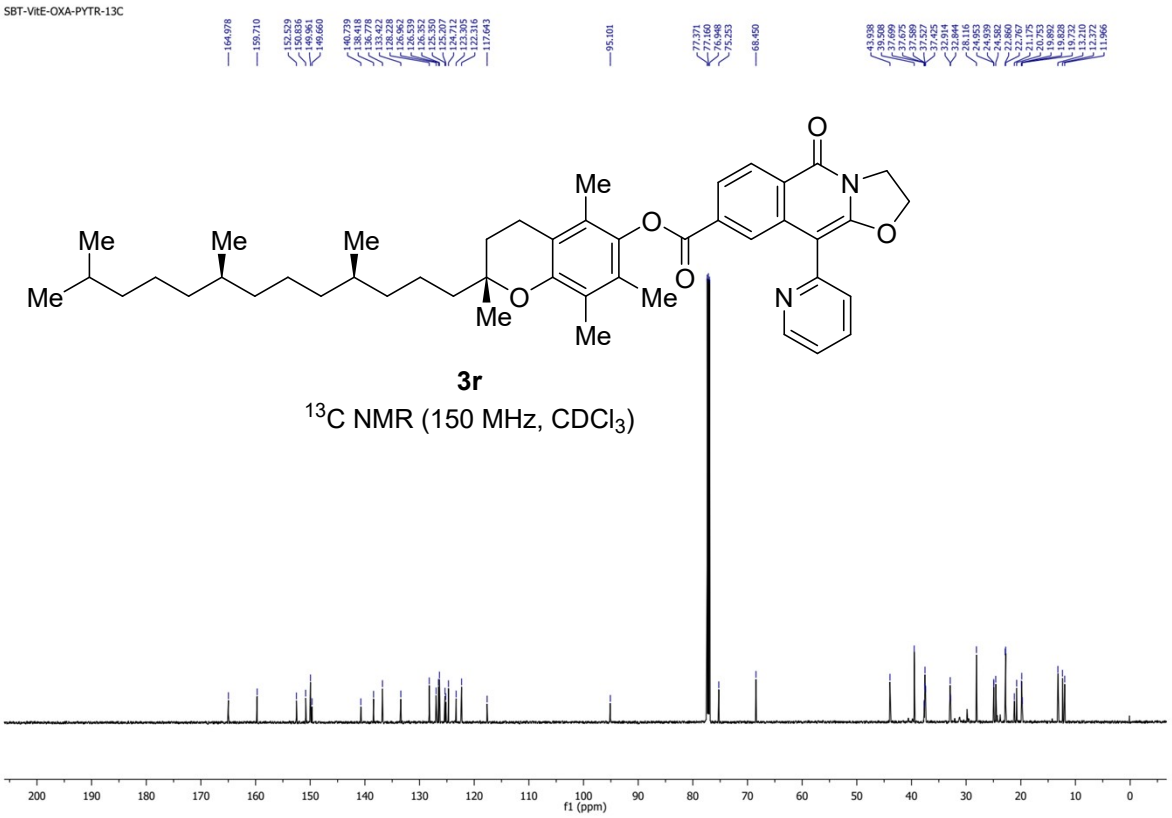
^{13}C NMR (150 MHz, $CDCl_3$)

SBT-VitE-OXA-PYTR-1H



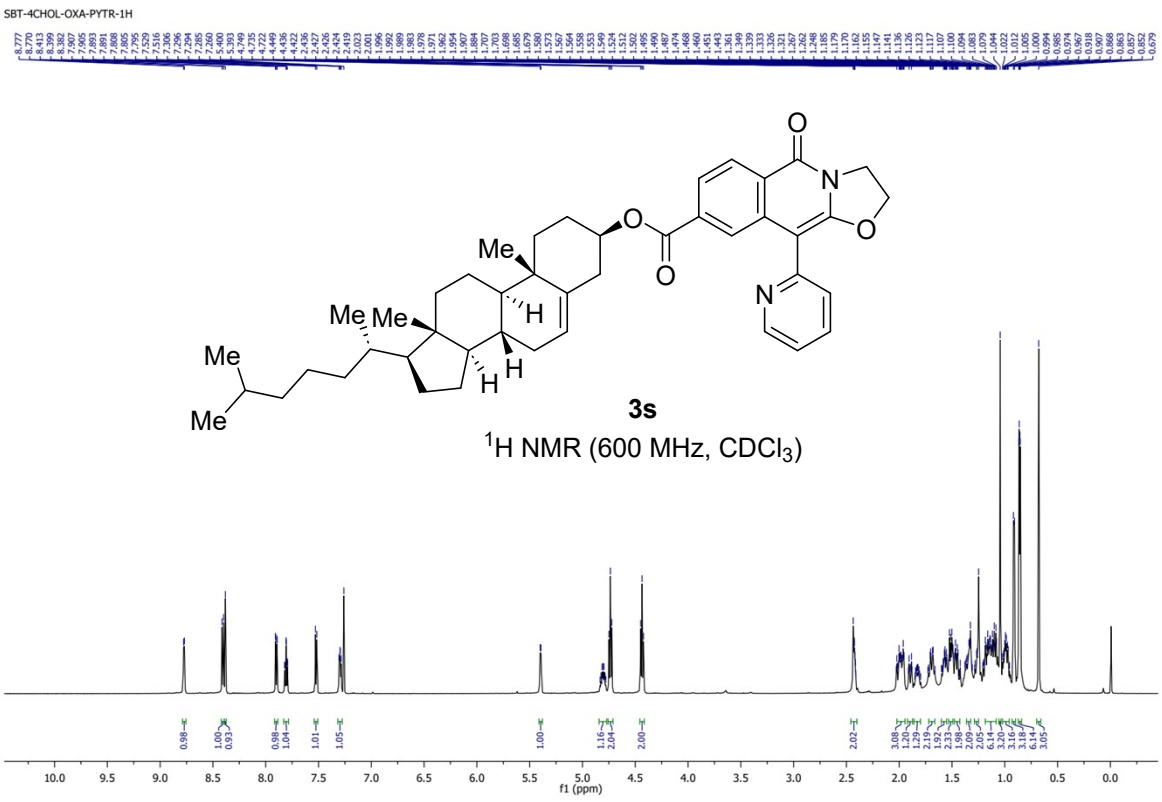
3r

^{1}H NMR (600 MHz, $CDCl_3$)



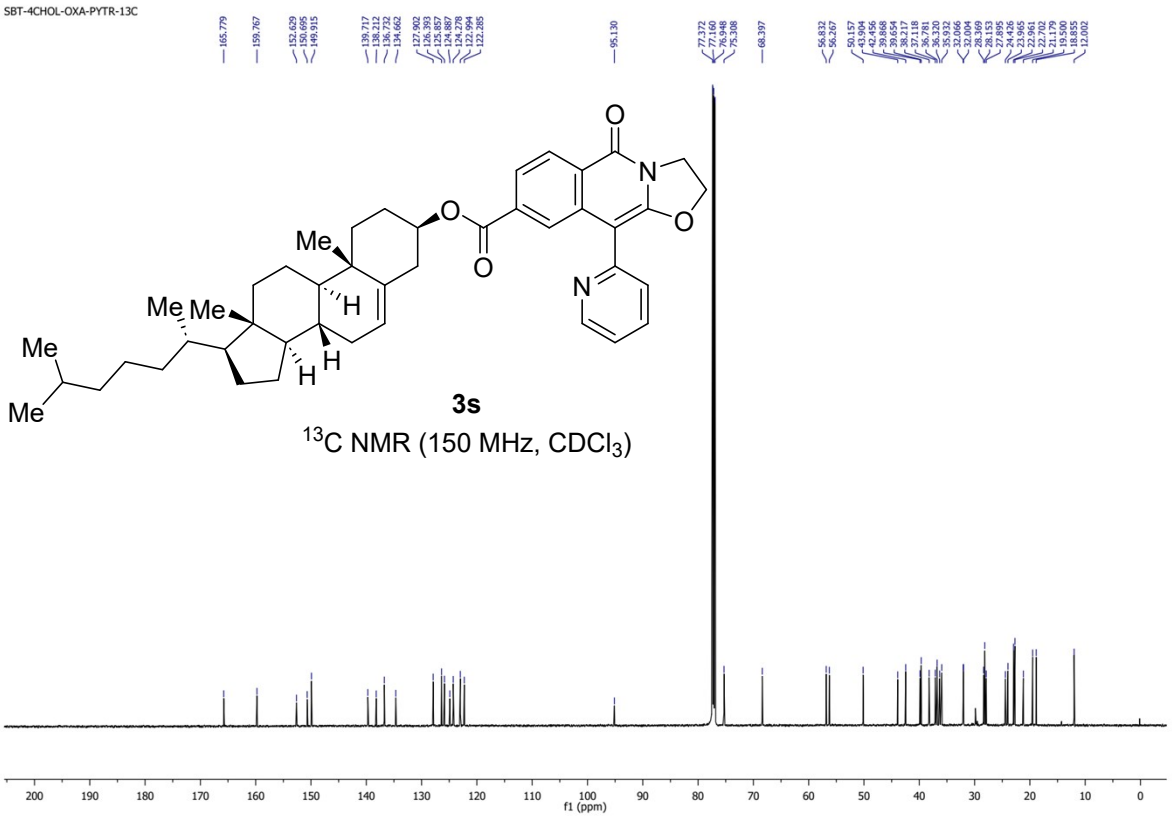
3r

^{13}C NMR (150 MHz, $CDCl_3$)



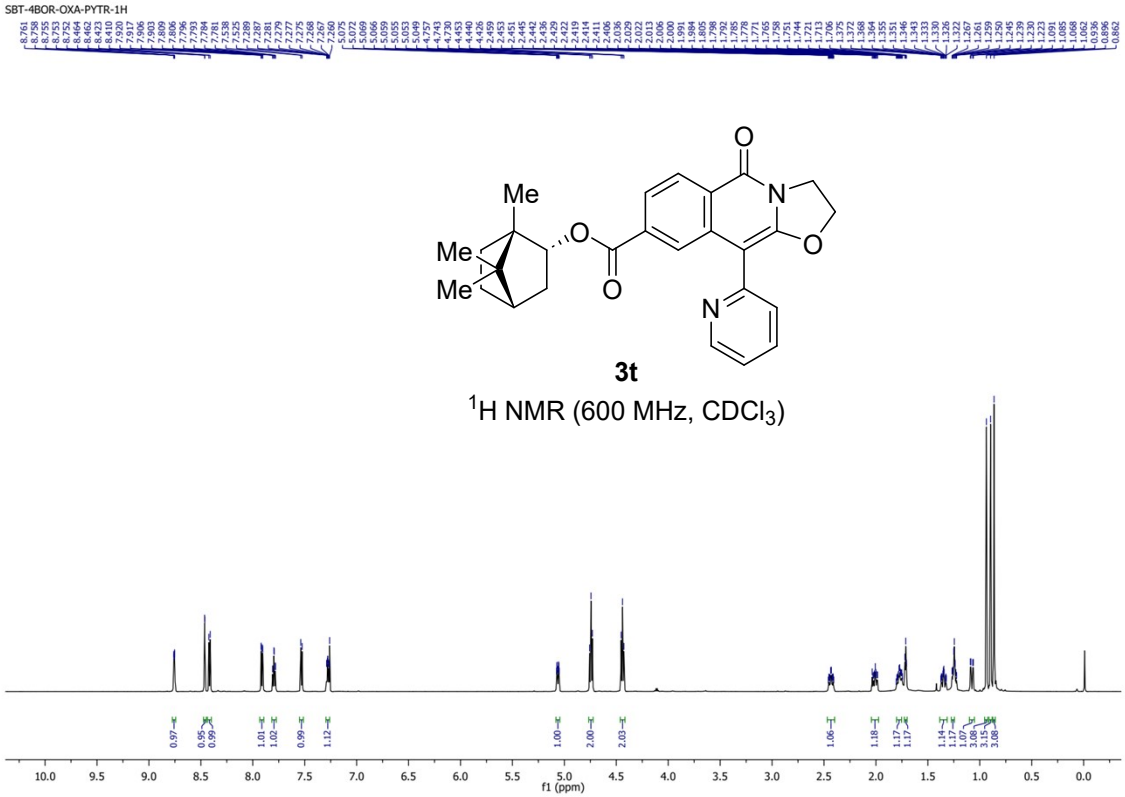
3s

^{1}H NMR (600 MHz, $CDCl_3$)



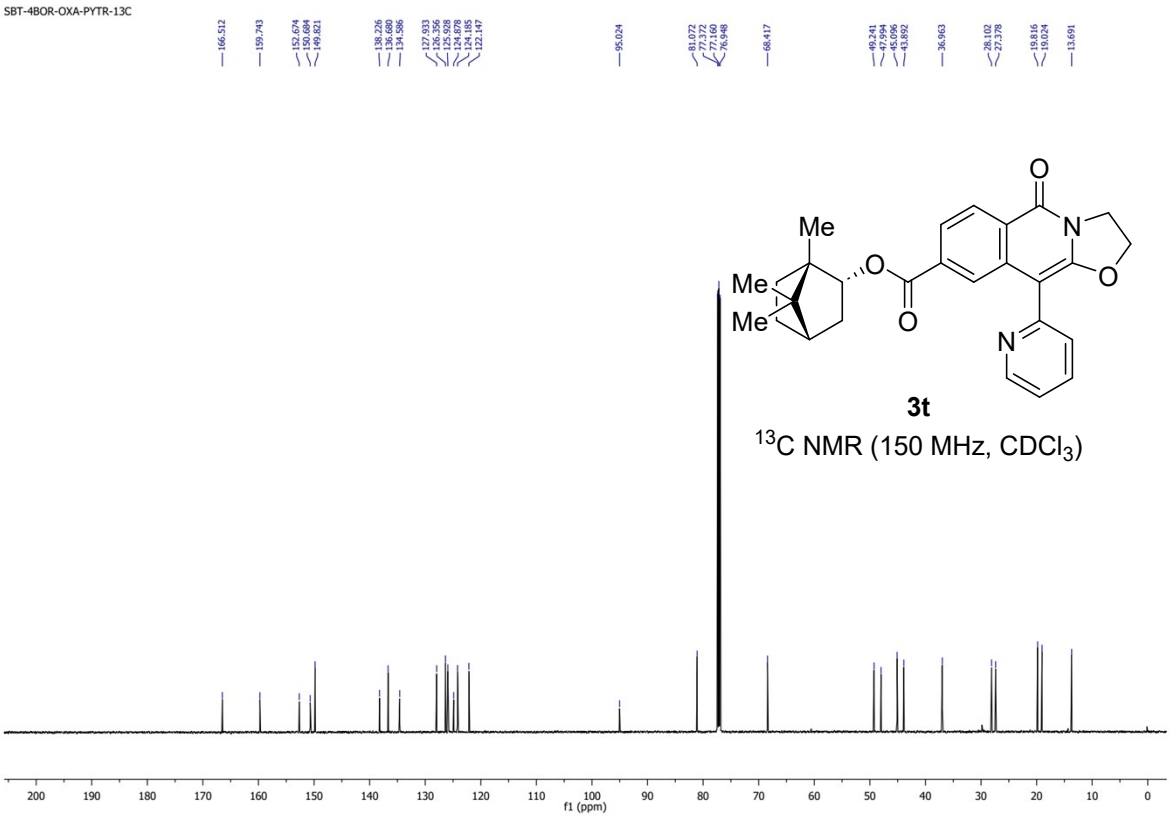
3s

^{13}C NMR (150 MHz, $CDCl_3$)



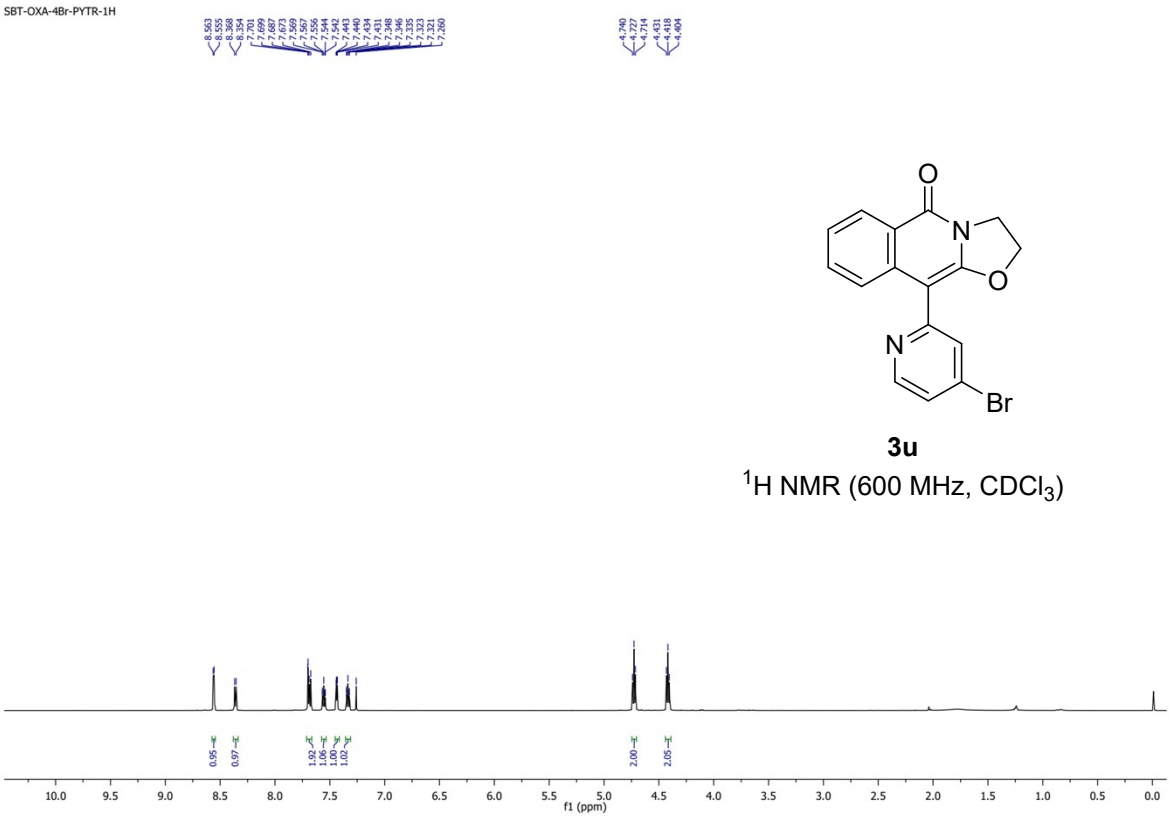
3t

^{1}H NMR (600 MHz, $CDCl_3$)



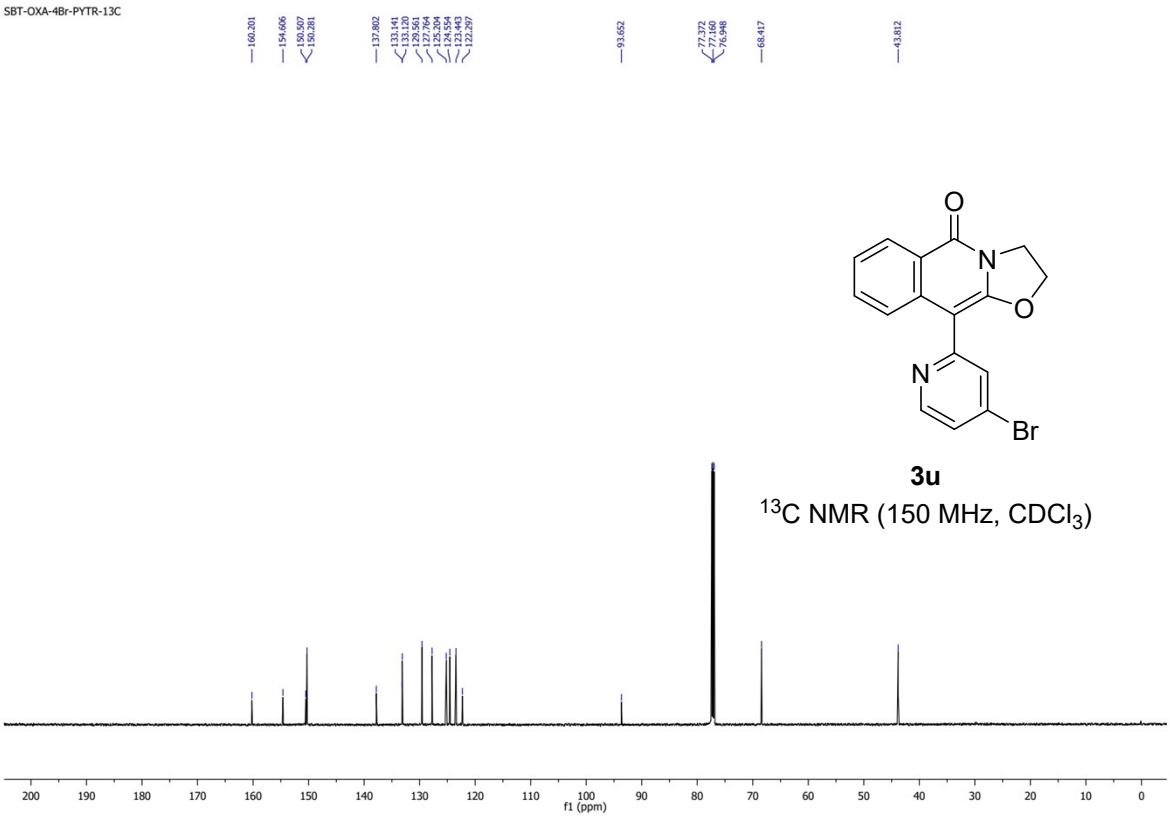
3t

^{13}C NMR (150 MHz, $CDCl_3$)



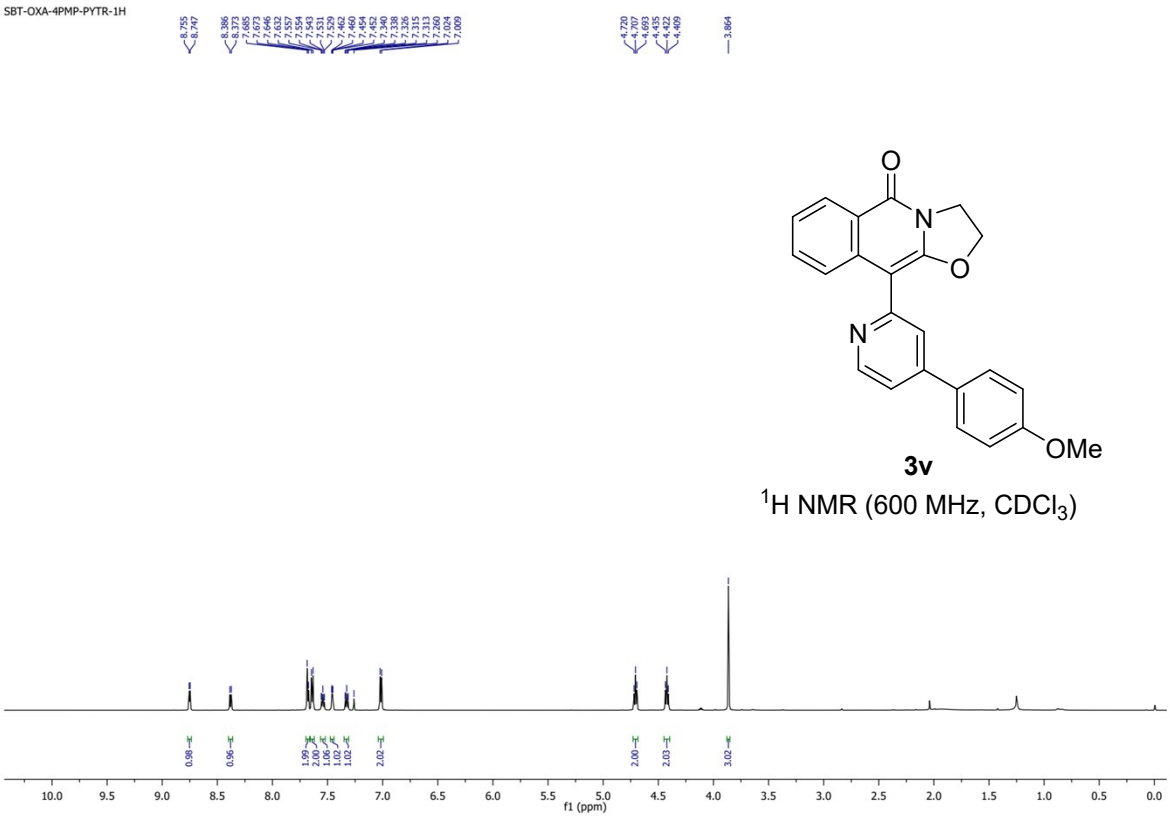
3u

^{1}H NMR (600 MHz, $CDCl_3$)



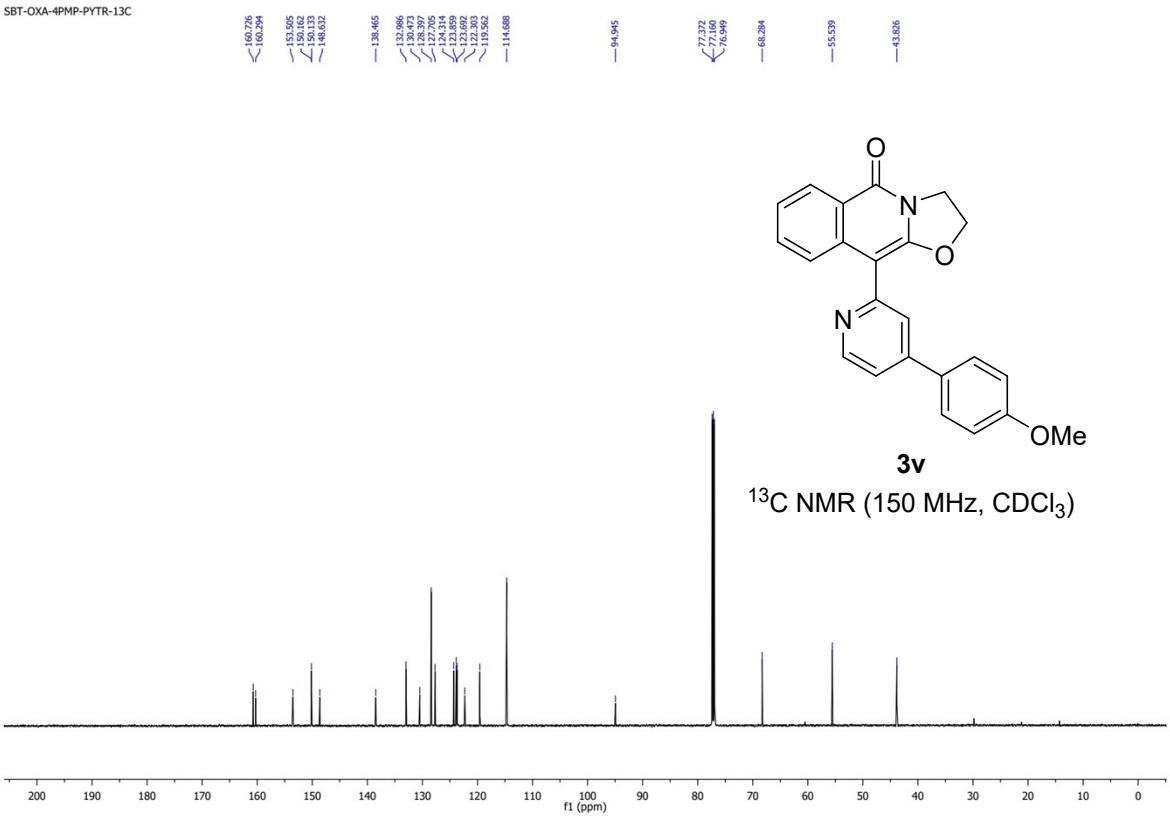
3u

^{13}C NMR (150 MHz, $CDCl_3$)



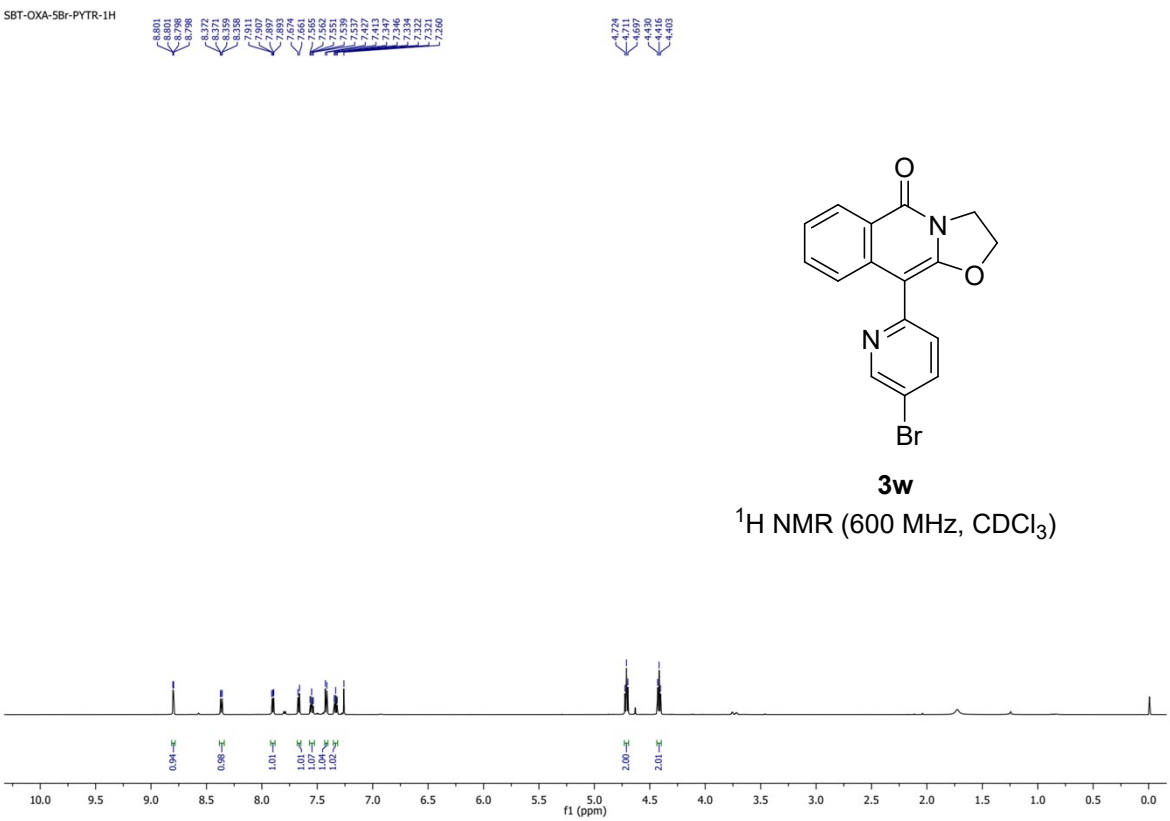
3v

^{1}H NMR (600 MHz, $CDCl_3$)



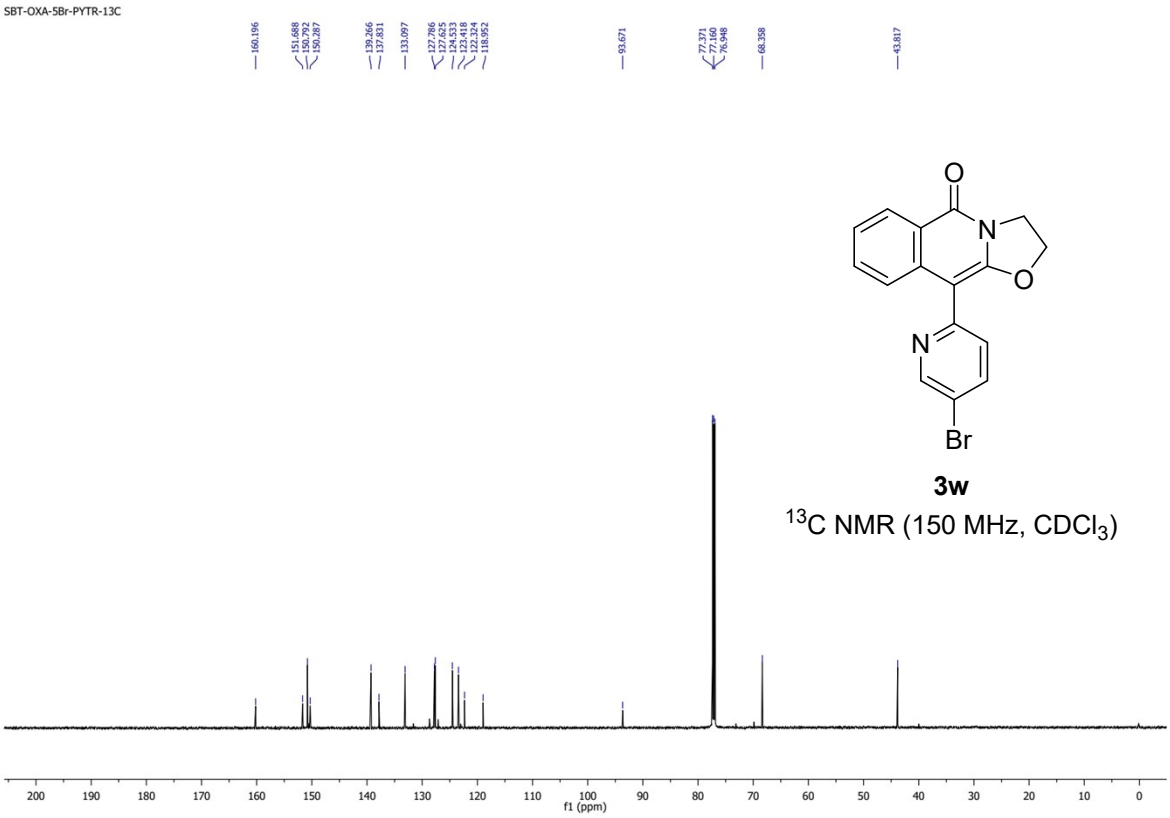
3v

^{13}C NMR (150 MHz, $CDCl_3$)



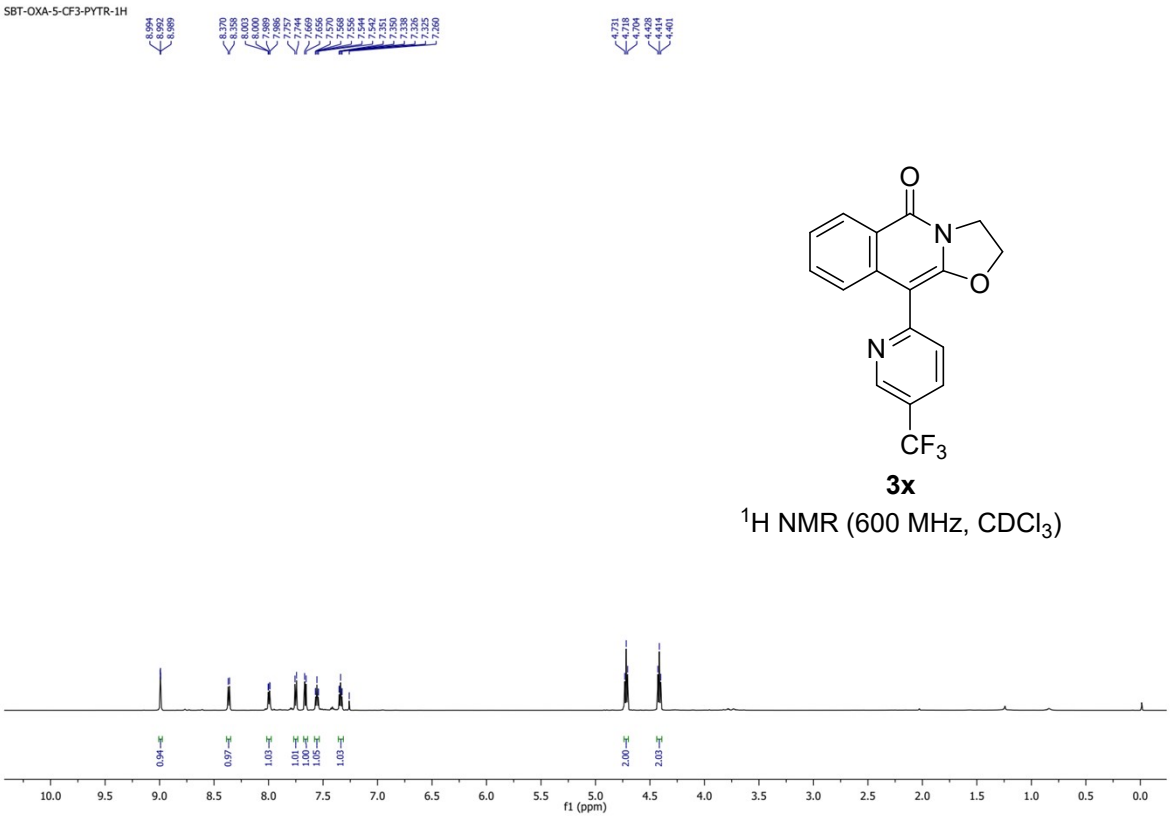
3w

^{1}H NMR (600 MHz, $CDCl_3$)



3w

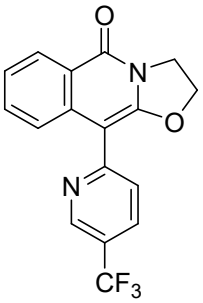
^{13}C NMR (150 MHz, $CDCl_3$)



3x

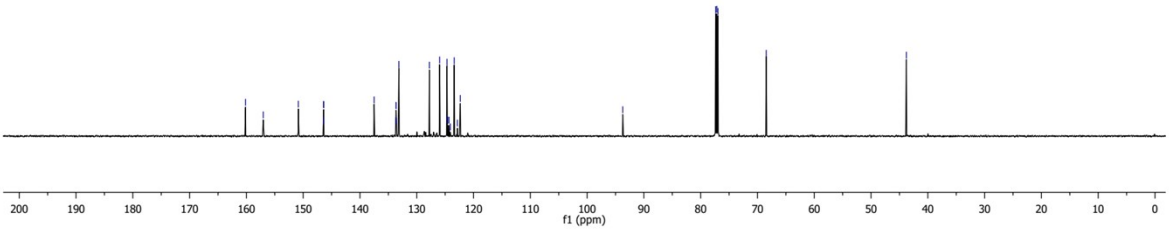
^{1}H NMR (600 MHz, $CDCl_3$)

SBT-OXA-5-CF3-PYTR-13C

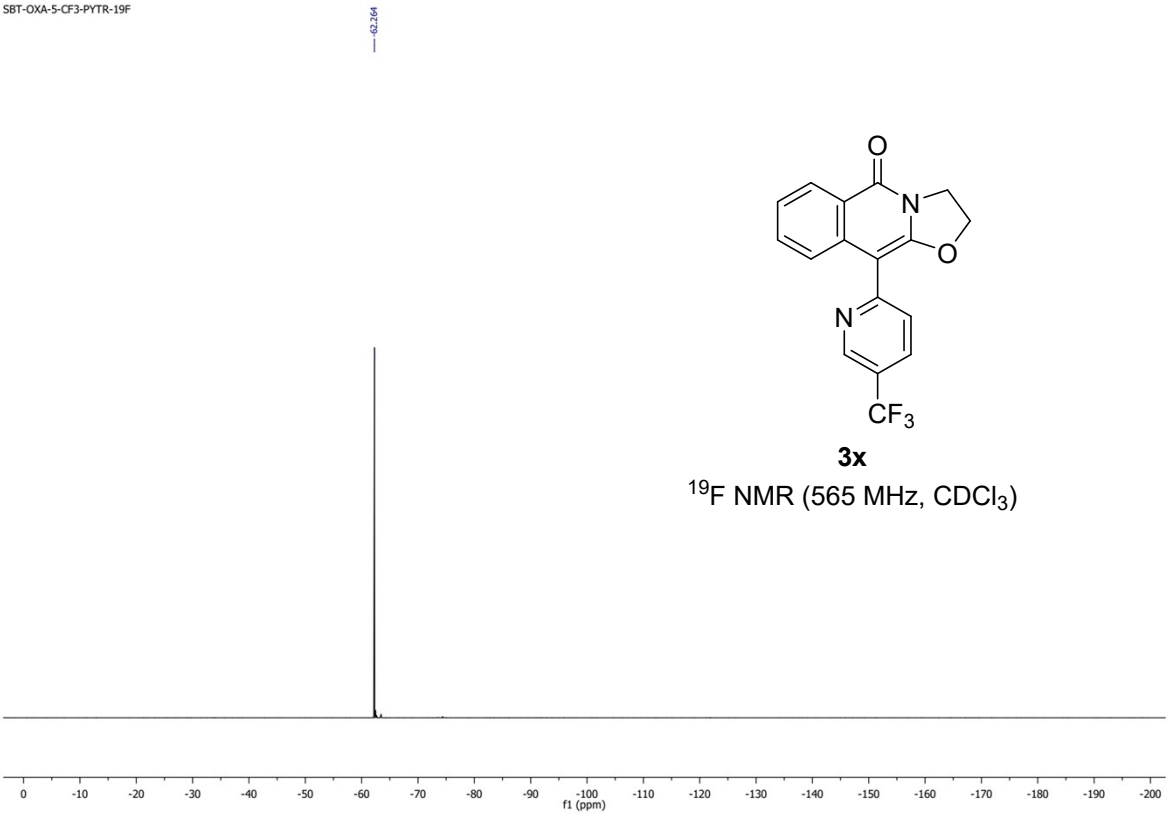


3x

^{13}C NMR (150 MHz, $CDCl_3$)

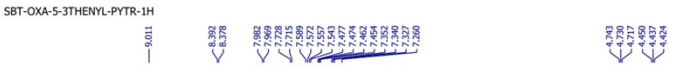


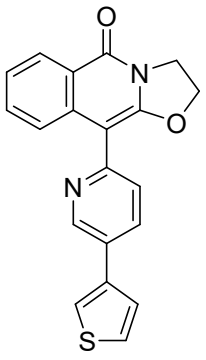
SBT-OXA-5-CF3-PYTR-19F



3x

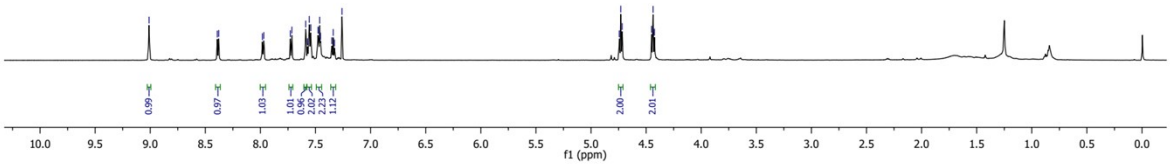
^{19}F NMR (565 MHz, $CDCl_3$)

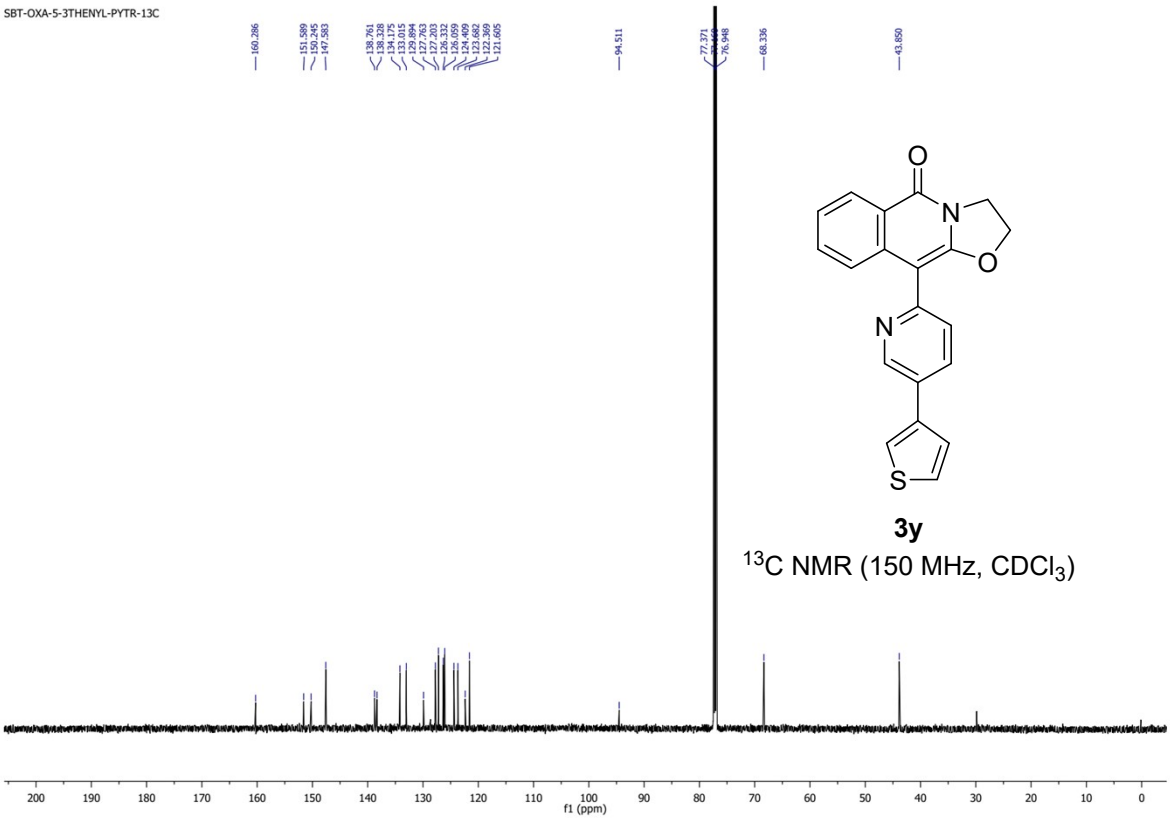




3y

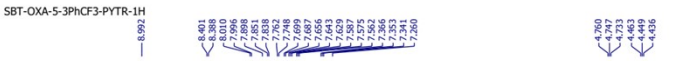
^{1}H NMR (600 MHz, $CDCl_3$)

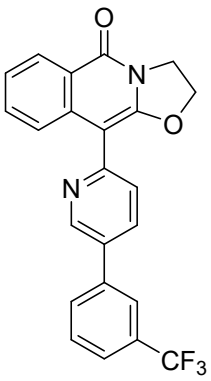




3y

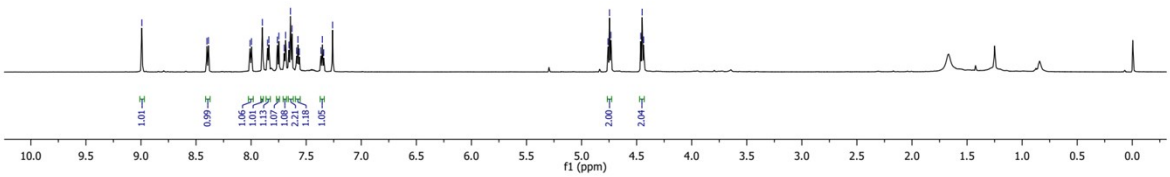
^{13}C NMR (150 MHz, $CDCl_3$)

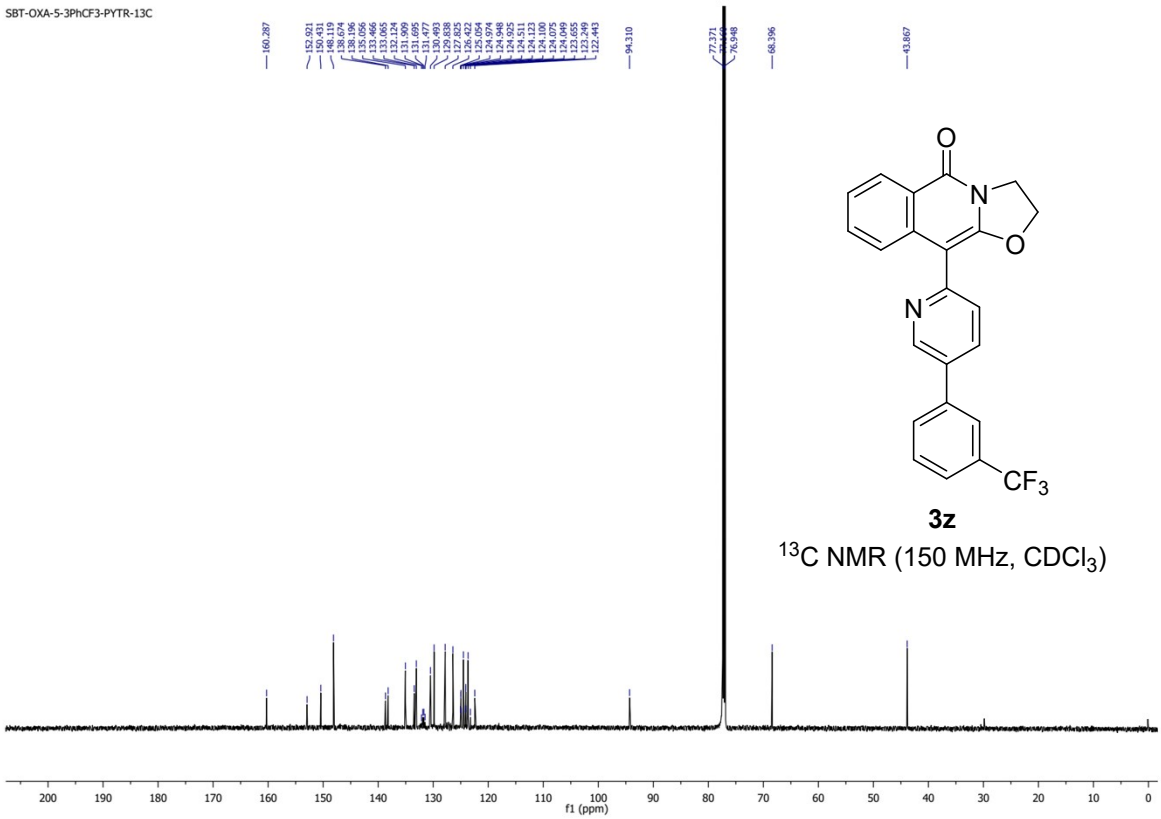




3z

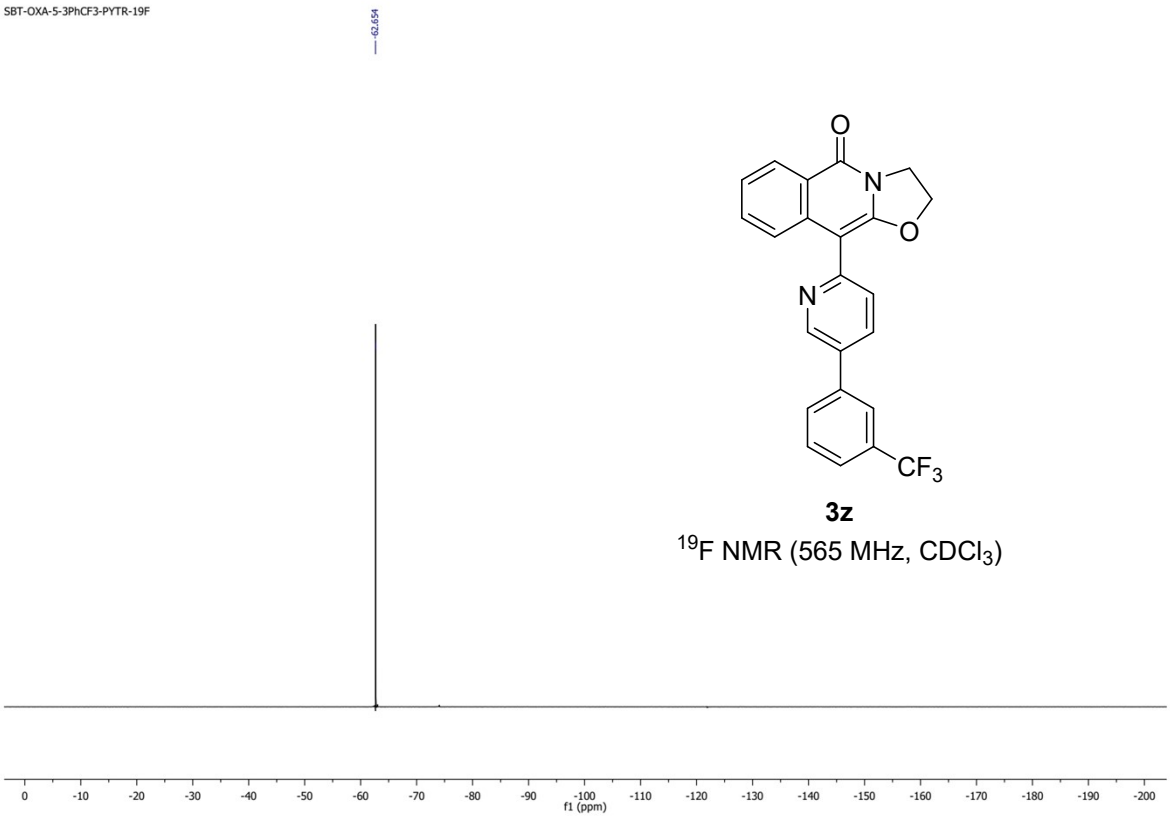
^{1}H NMR (600 MHz, $CDCl_3$)





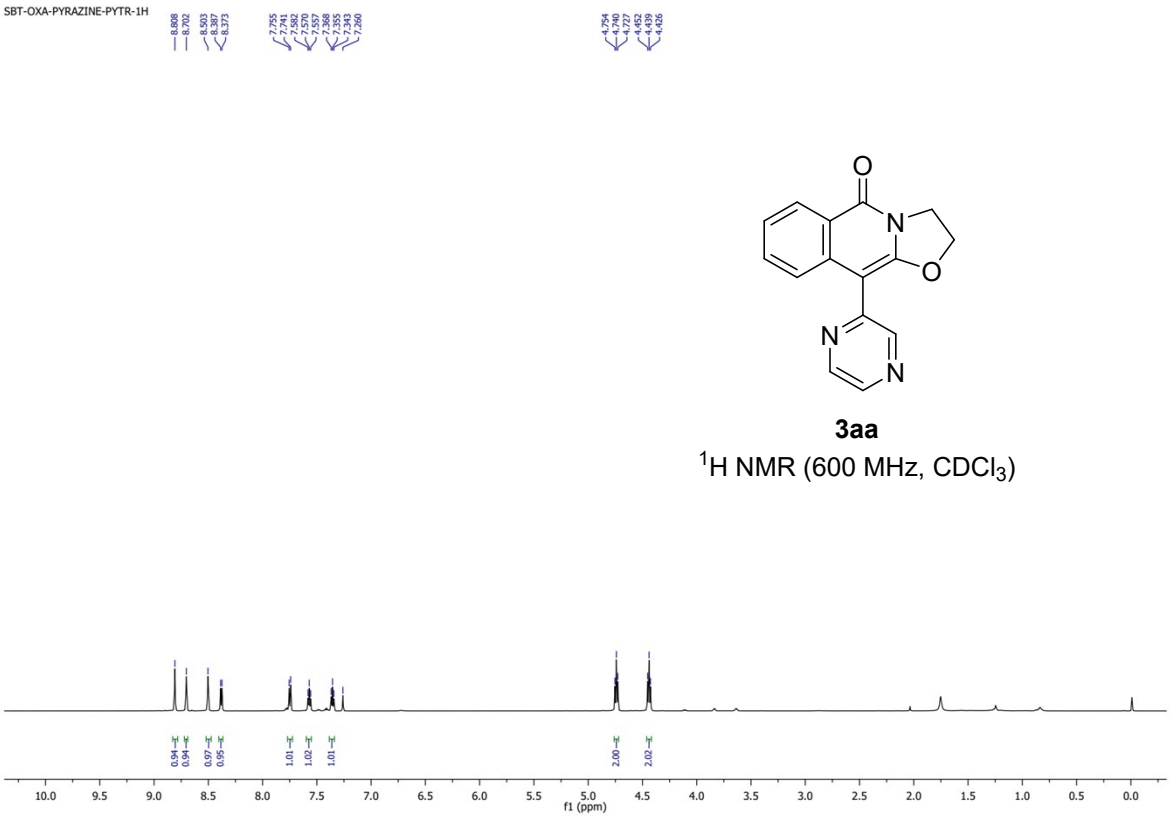
3z

^{13}C NMR (150 MHz, $CDCl_3$)



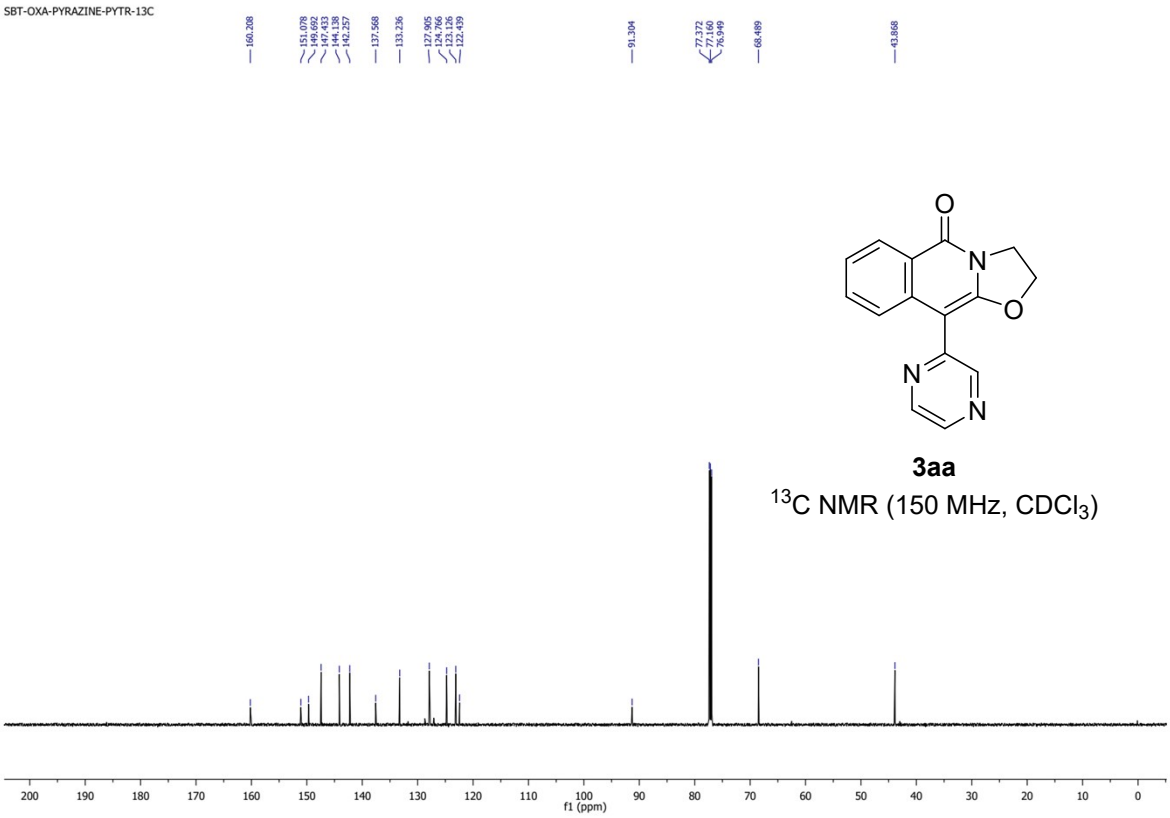
3z

^{19}F NMR (565 MHz, $CDCl_3$)



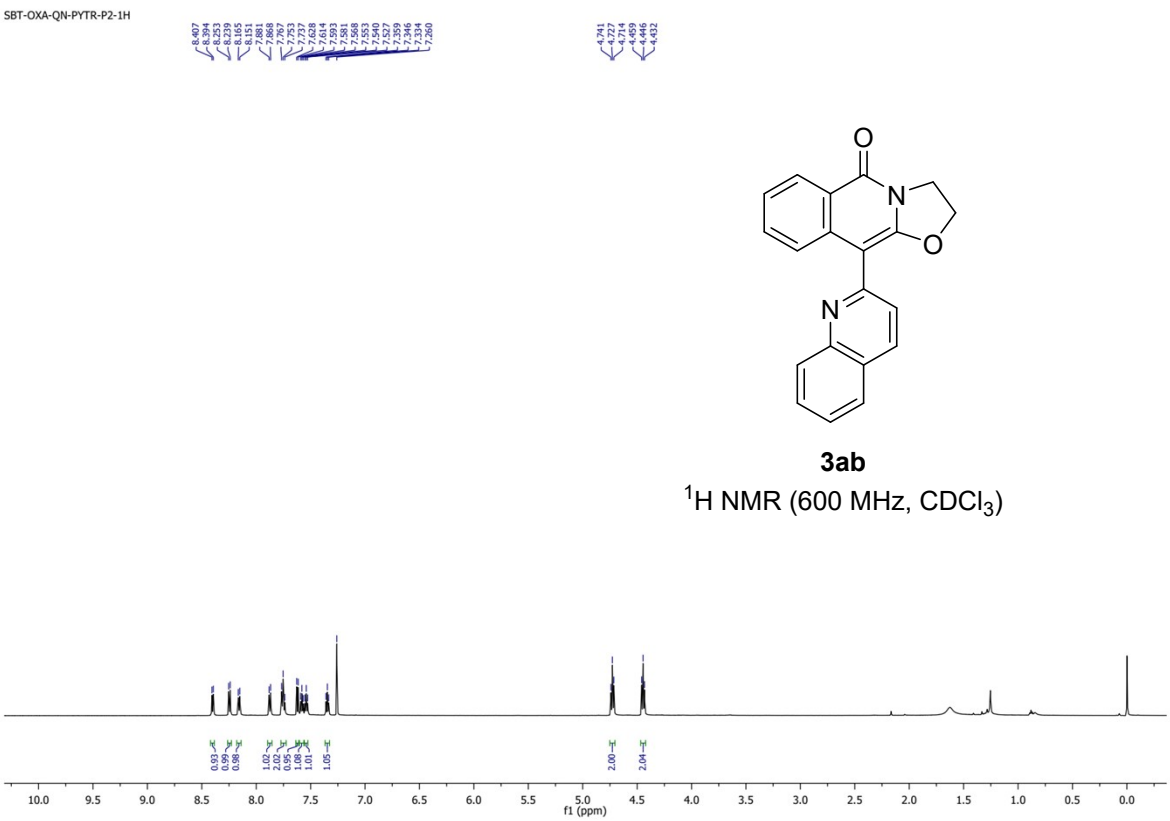
3aa

^{1}H NMR (600 MHz, $CDCl_3$)



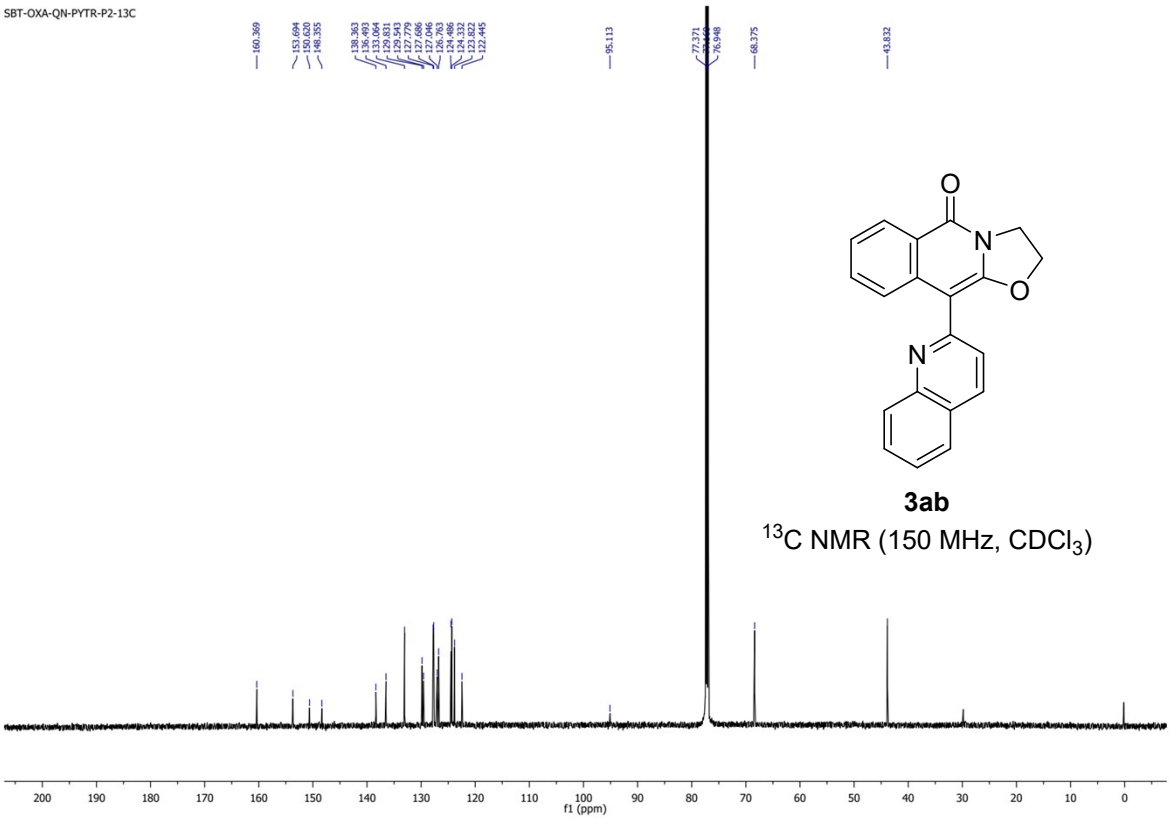
3aa

^{13}C NMR (150 MHz, $CDCl_3$)



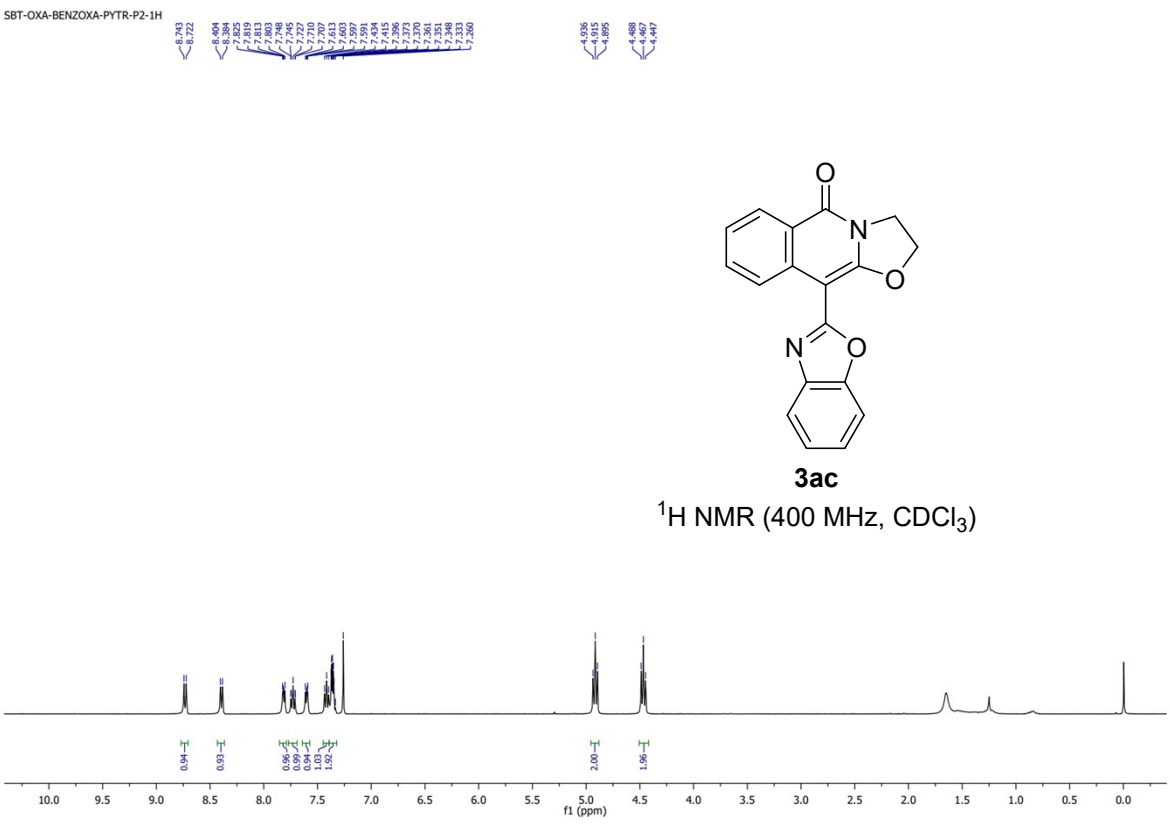
3ab

^{1}H NMR (600 MHz, $CDCl_3$)



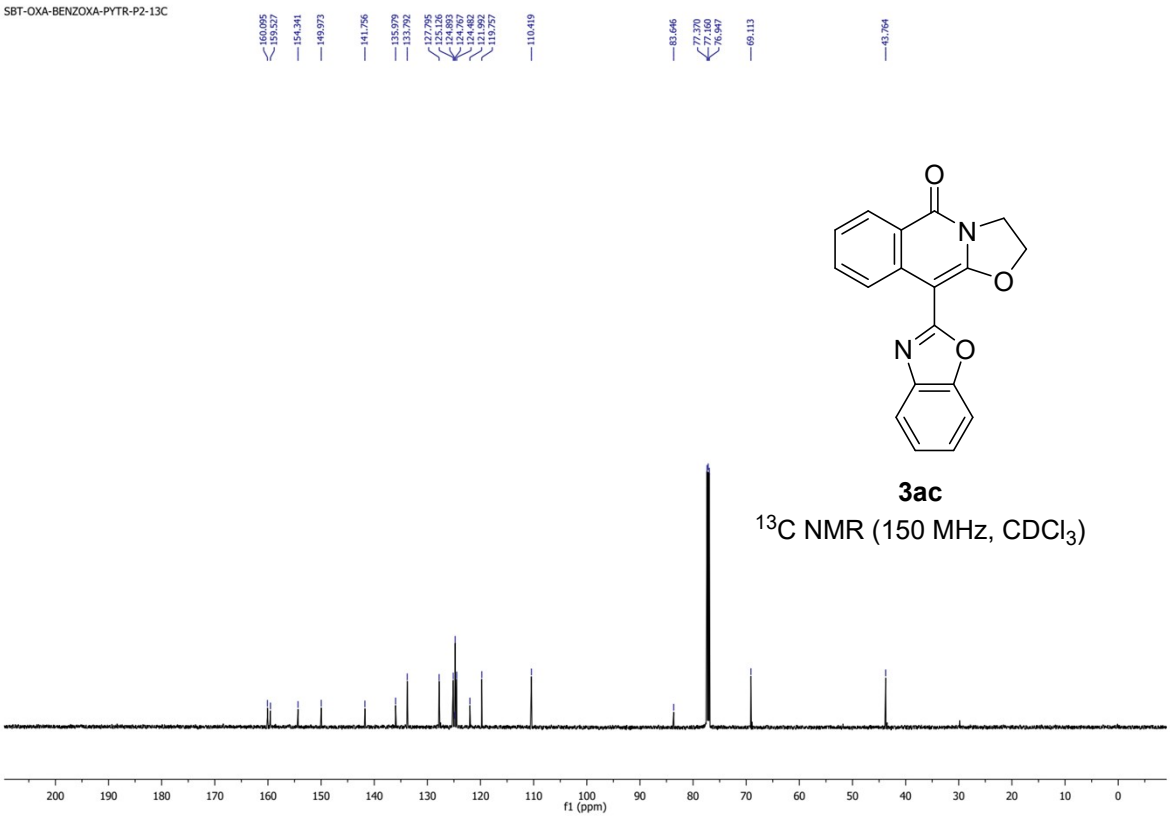
3ab

^{13}C NMR (150 MHz, $CDCl_3$)



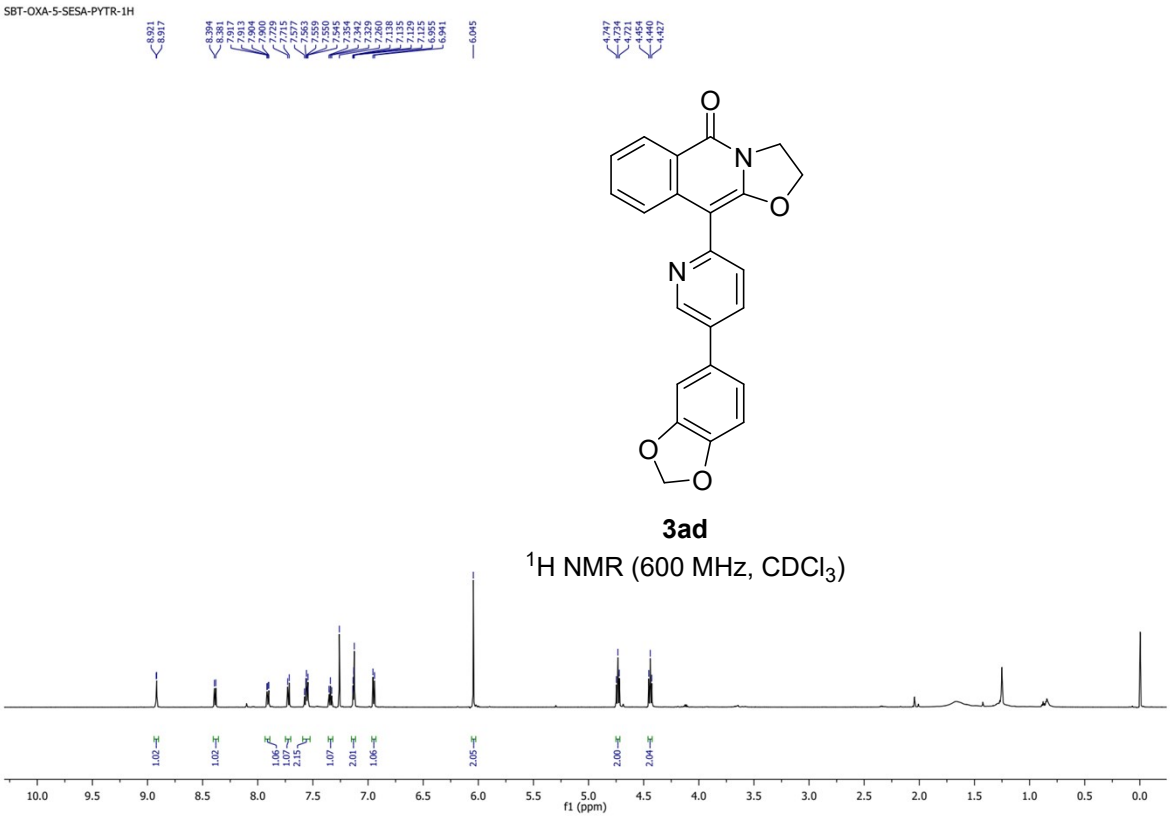
3ac

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



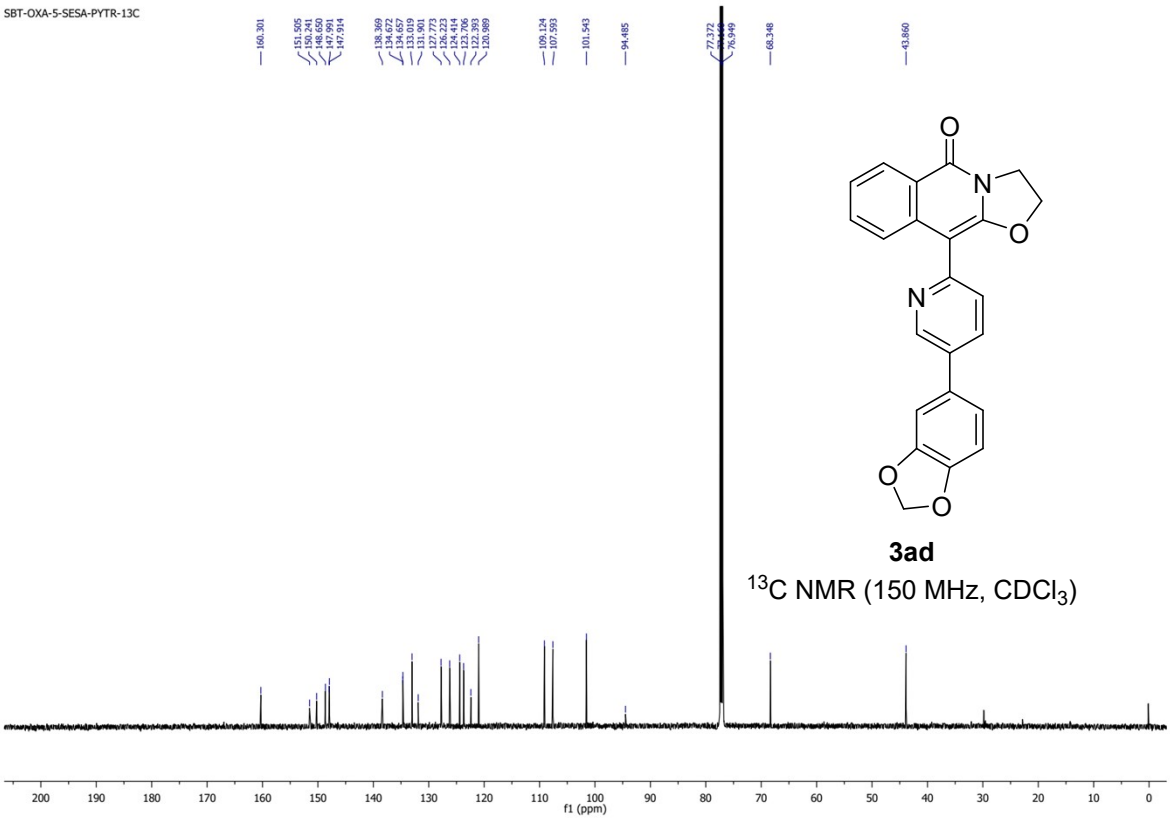
3ac

^{13}C NMR (150 MHz, $CDCl_3$)



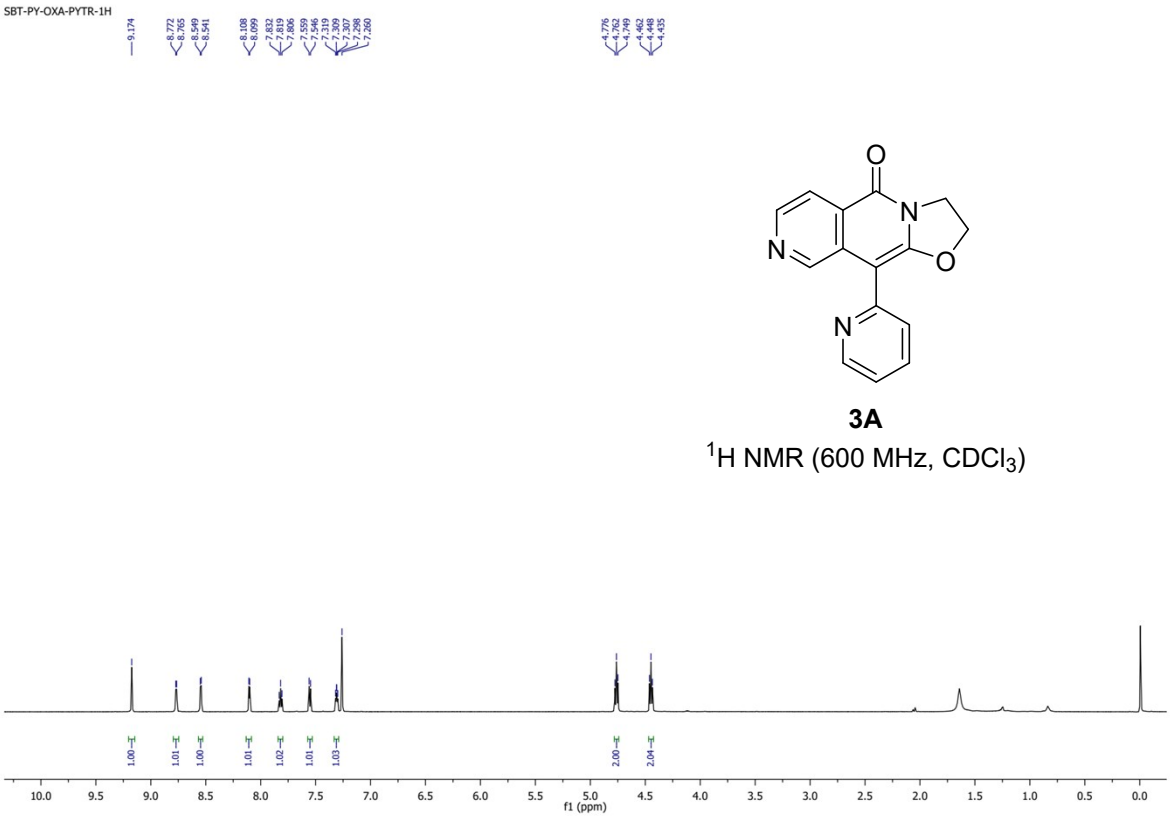
3ad

^{1}H NMR (600 MHz, $CDCl_3$)



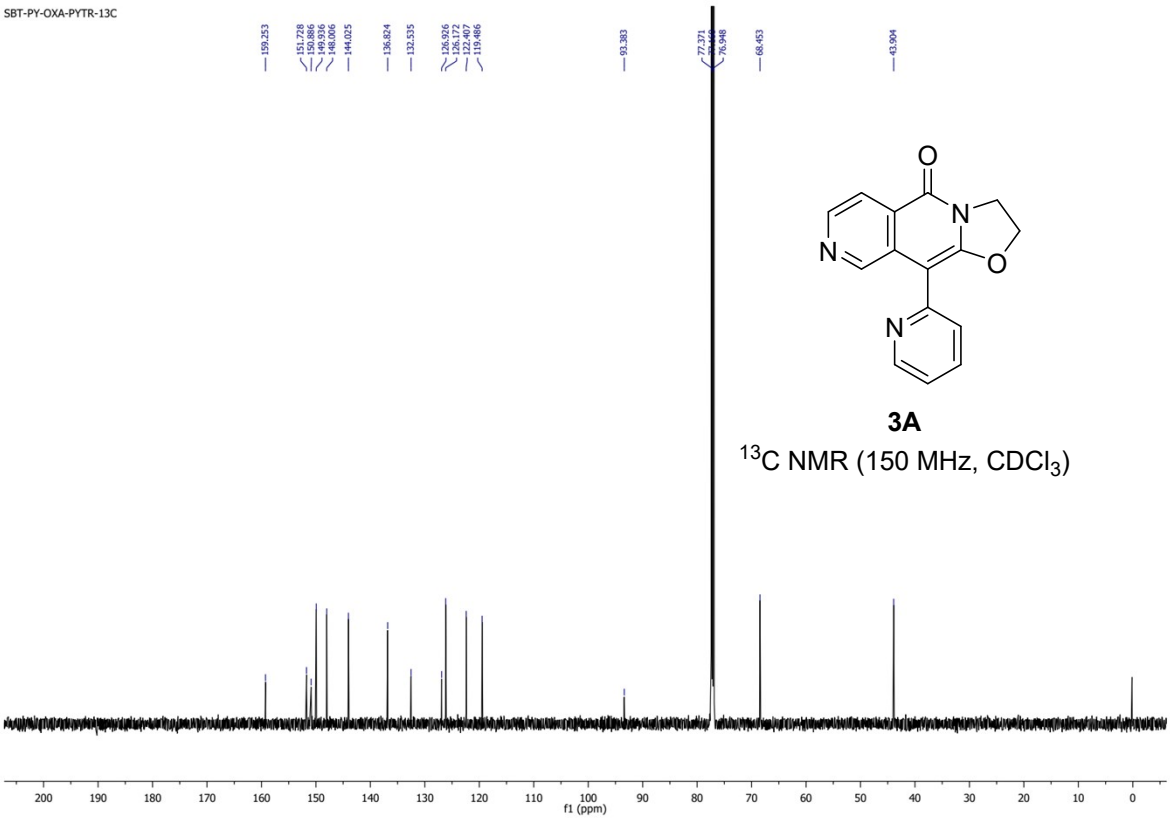
3ad

^{13}C NMR (150 MHz, $CDCl_3$)



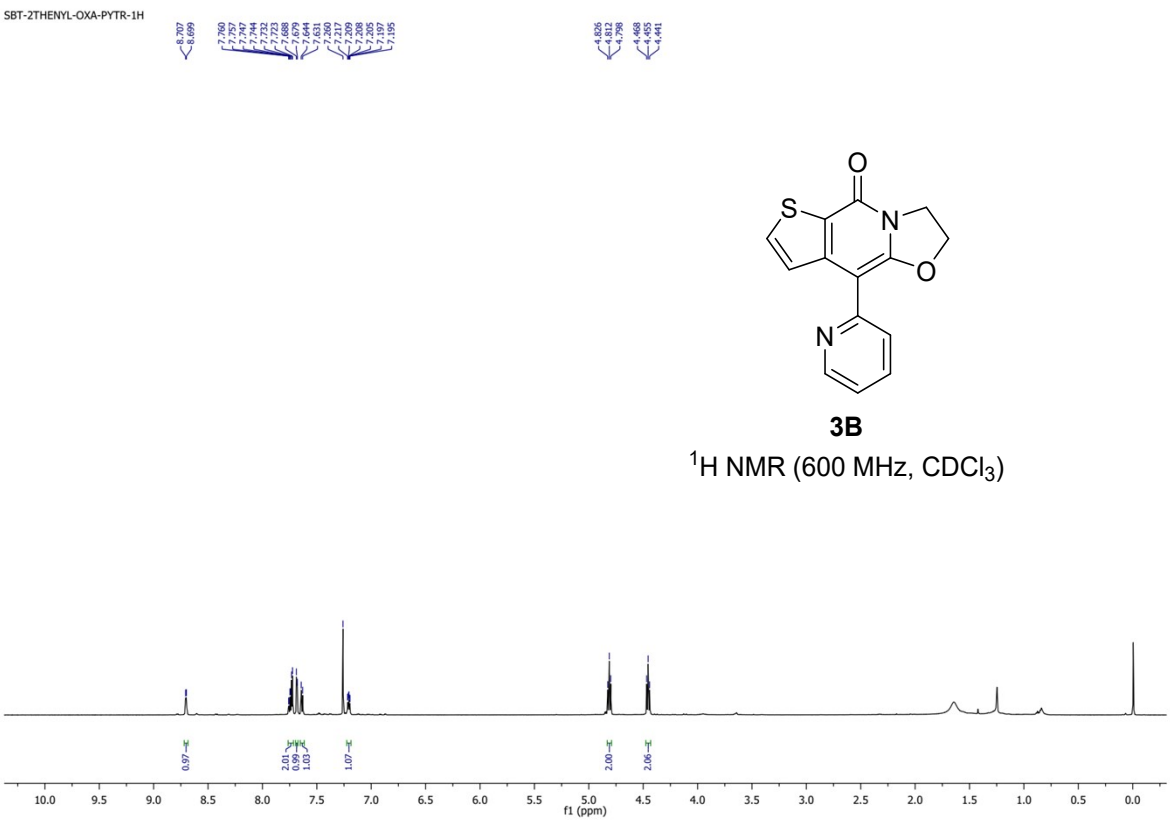
3A

^{1}H NMR (600 MHz, $CDCl_3$)



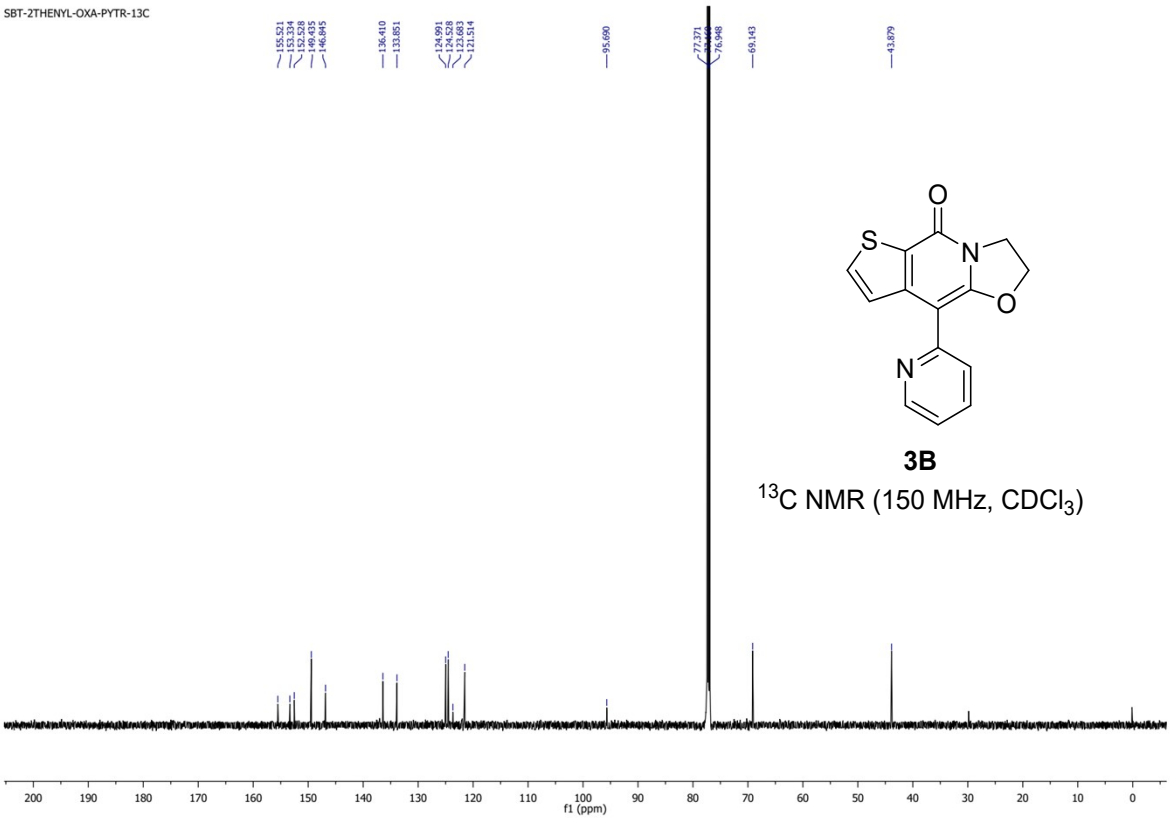
3A

^{13}C NMR (150 MHz, $CDCl_3$)



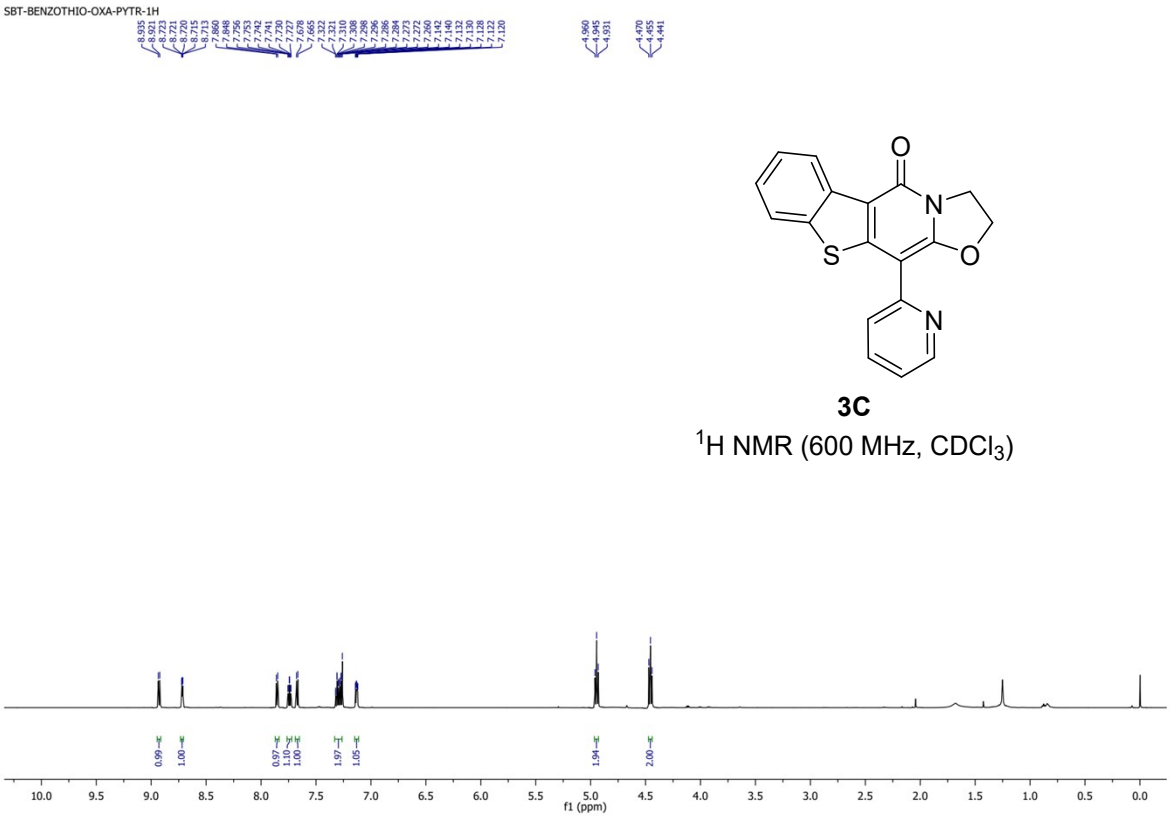
3B

^{1}H NMR (600 MHz, $CDCl_3$)



3B

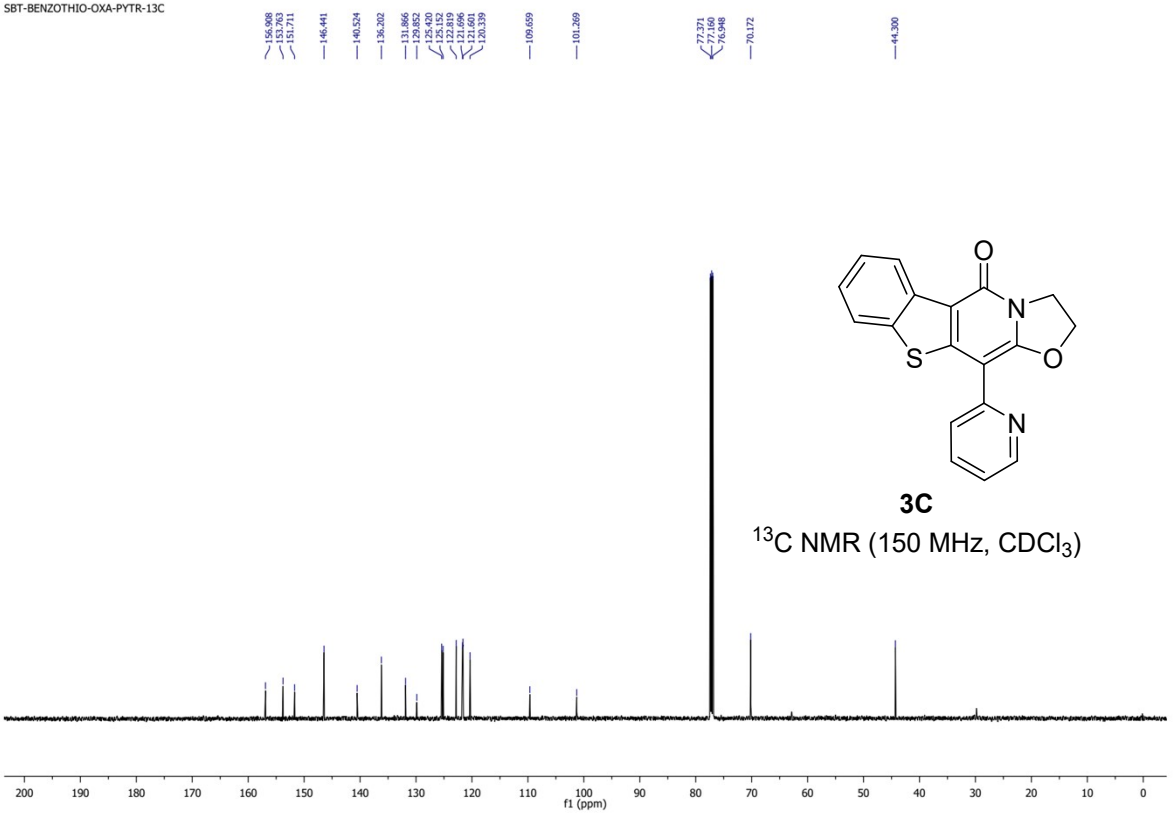
^{13}C NMR (150 MHz, $CDCl_3$)



3C

^{1}H NMR (600 MHz, $CDCl_3$)

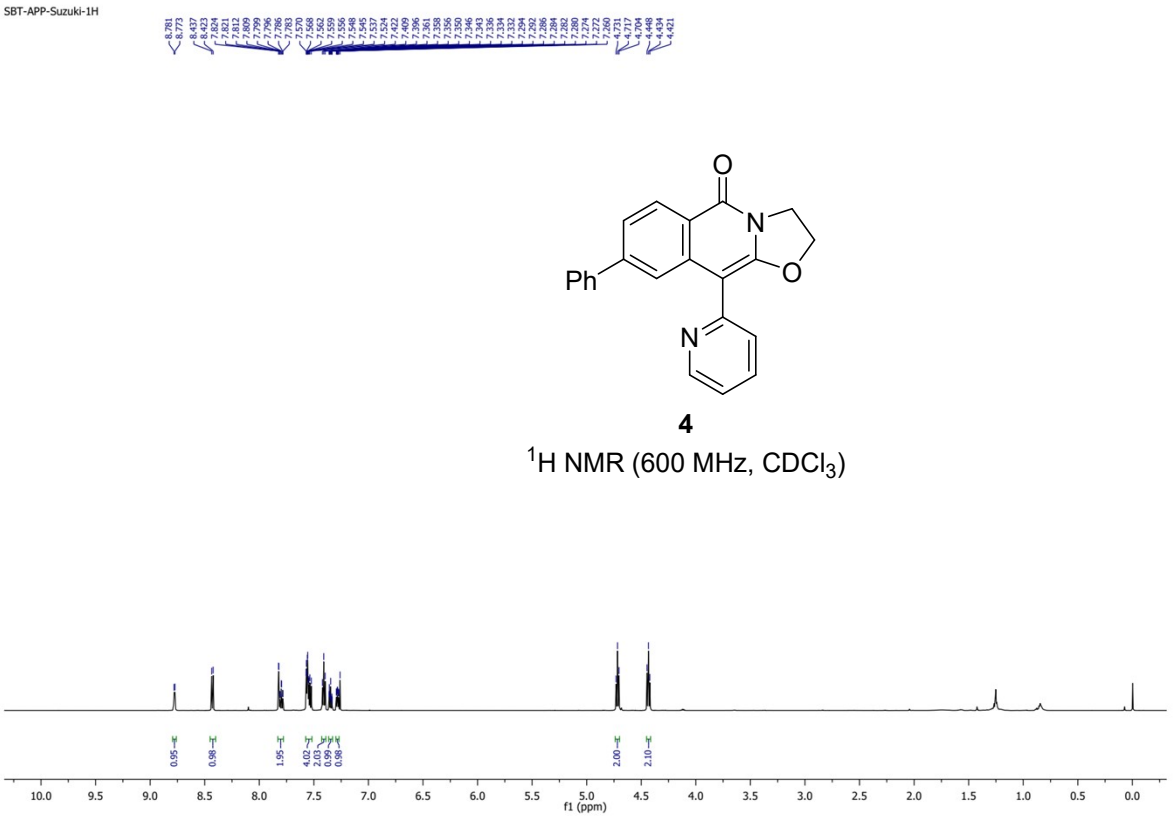
SBT-BENZOTHIO-OXA-PYTR-13C



3C

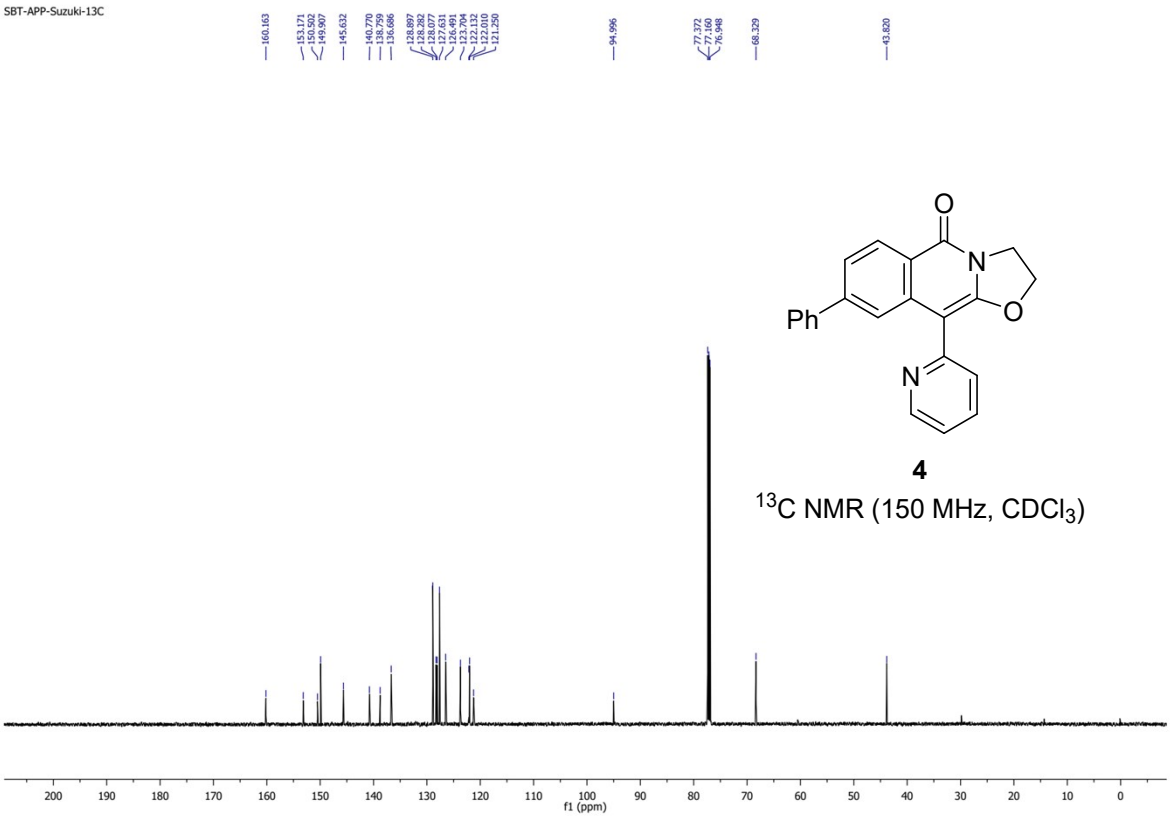
^{13}C NMR (150 MHz, $CDCl_3$)

SBT-APP-Suzuki-1H



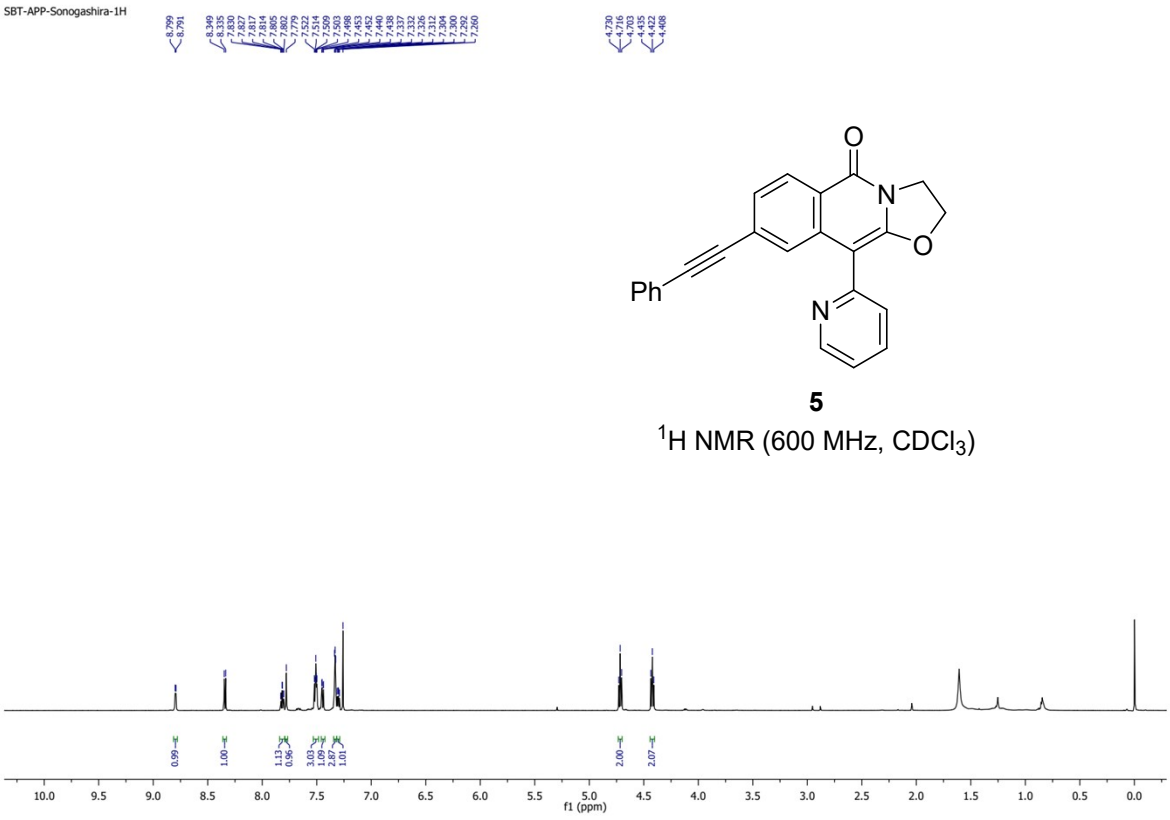
4

^{1}H NMR (600 MHz, $CDCl_3$)



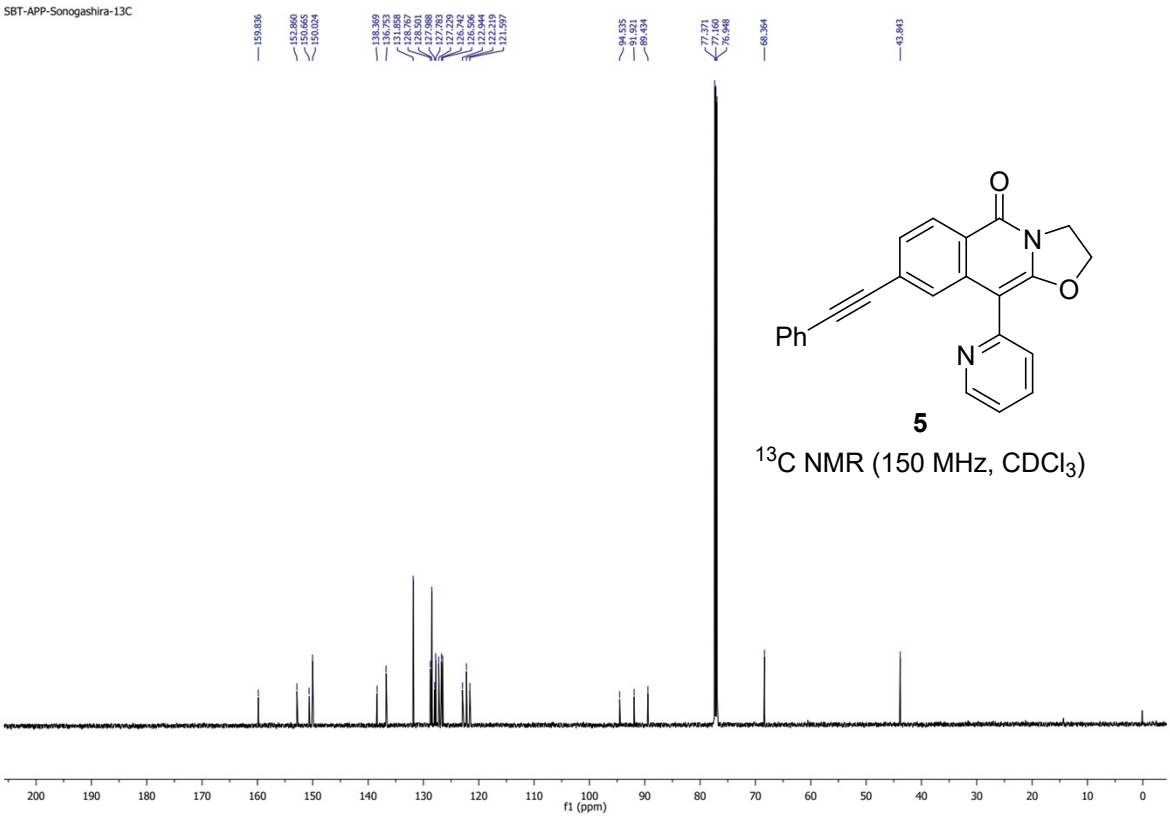
4

^{13}C NMR (150 MHz, $CDCl_3$)



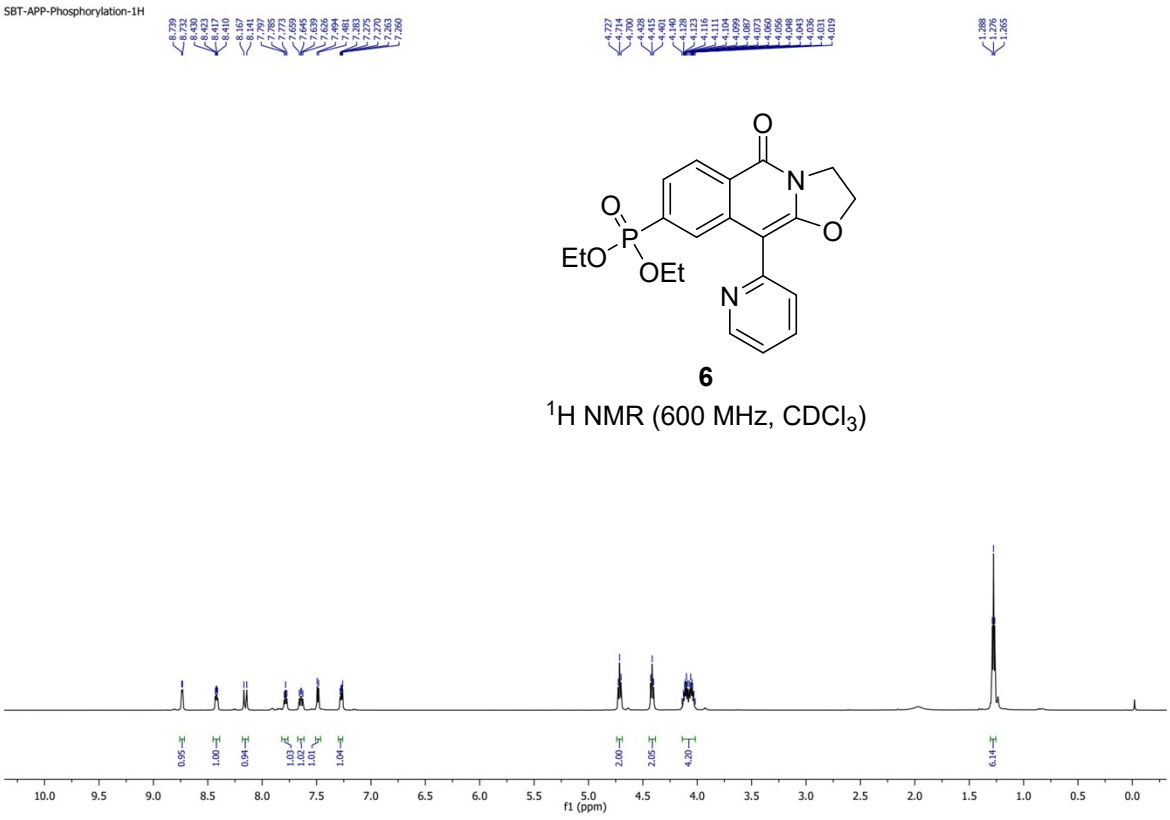
5

^{1}H NMR (600 MHz, $CDCl_3$)



5

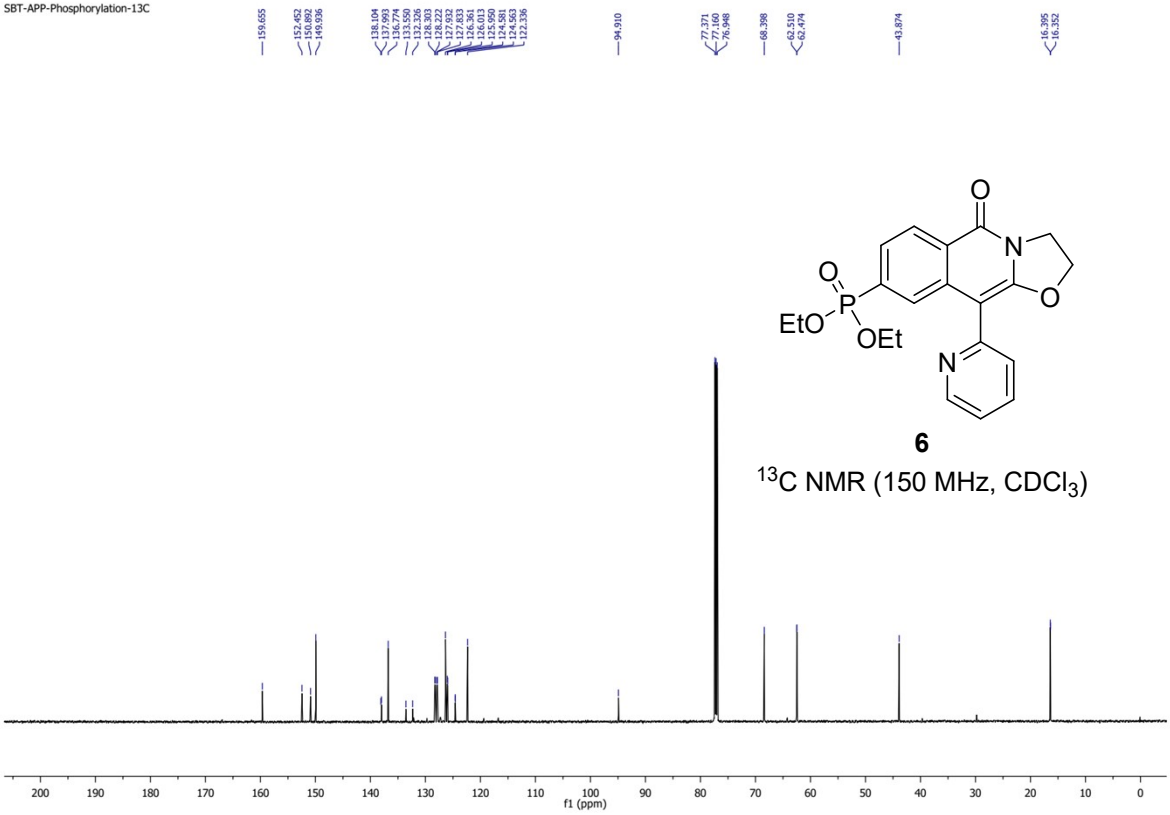
^{13}C NMR (150 MHz, $CDCl_3$)



6

^{1}H NMR (600 MHz, $CDCl_3$)

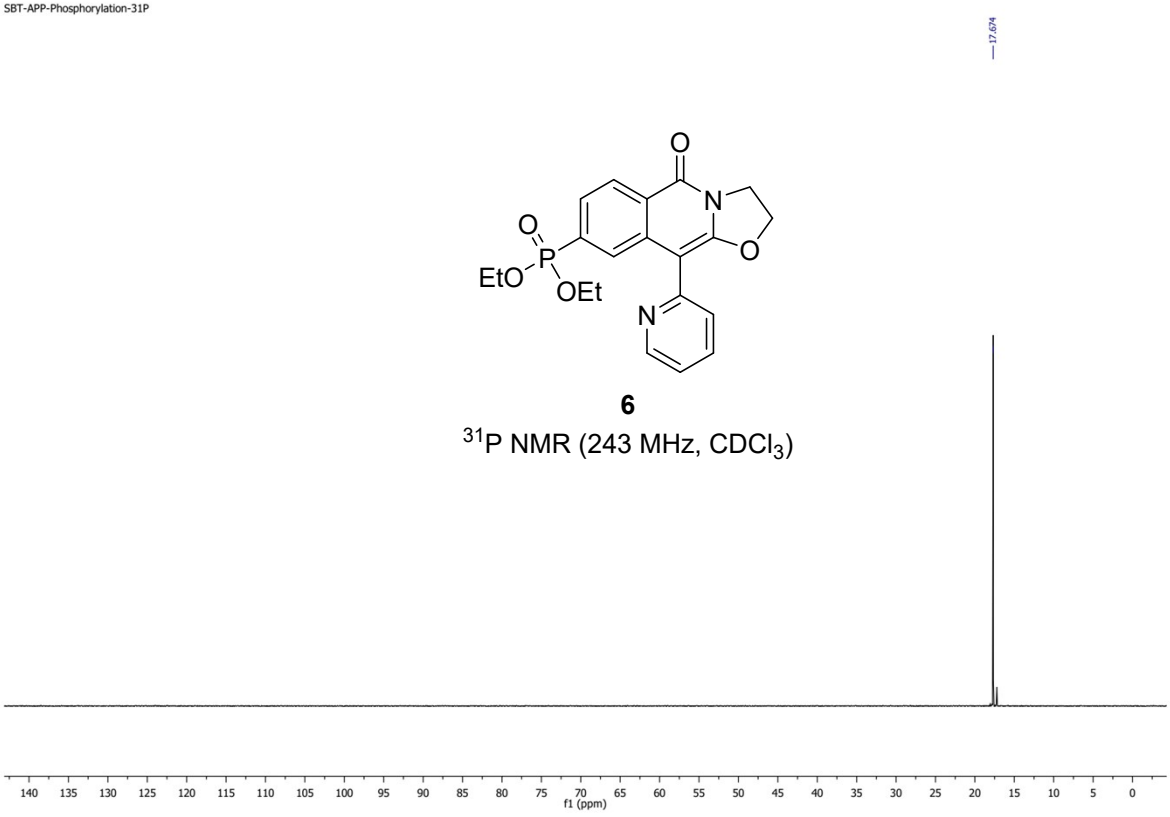
SBT-APP-Phosphorylation-13C



6

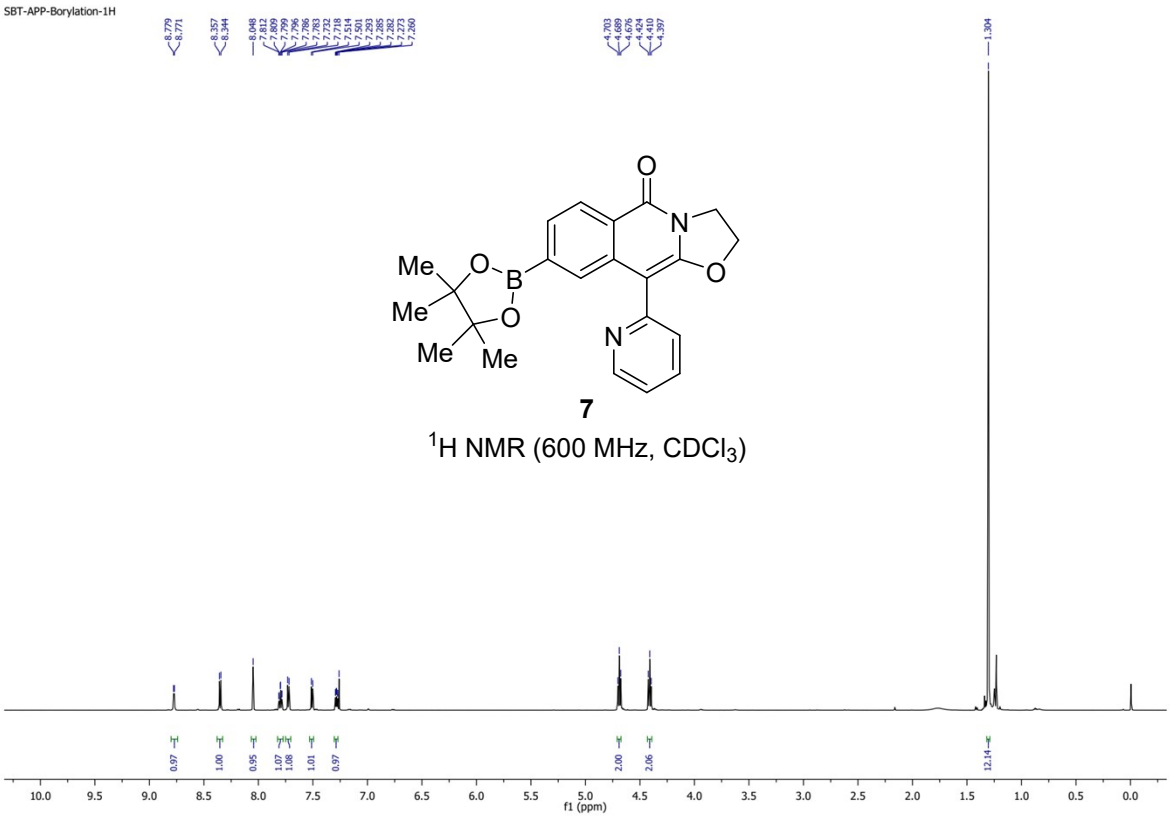
^{13}C NMR (150 MHz, $CDCl_3$)

SBT-APP-Phosphorylation-31P



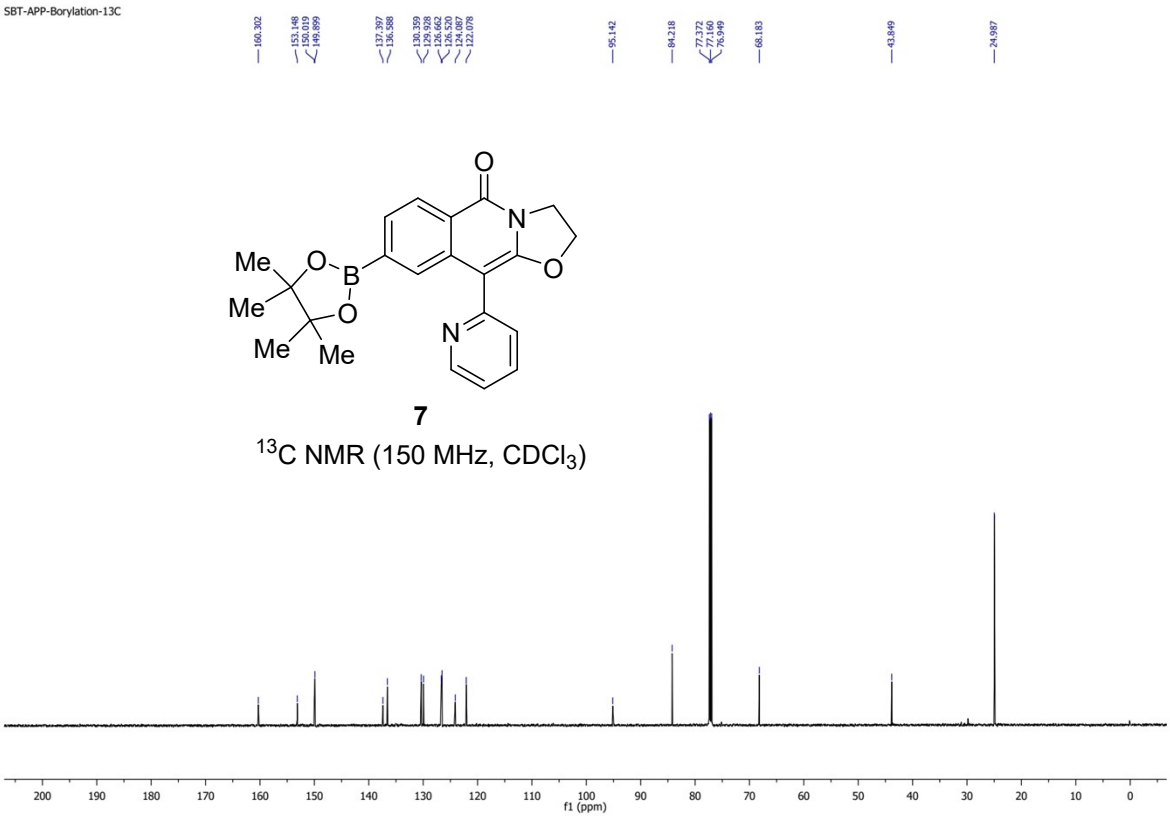
6

^{31}P NMR (243 MHz, $CDCl_3$)



7

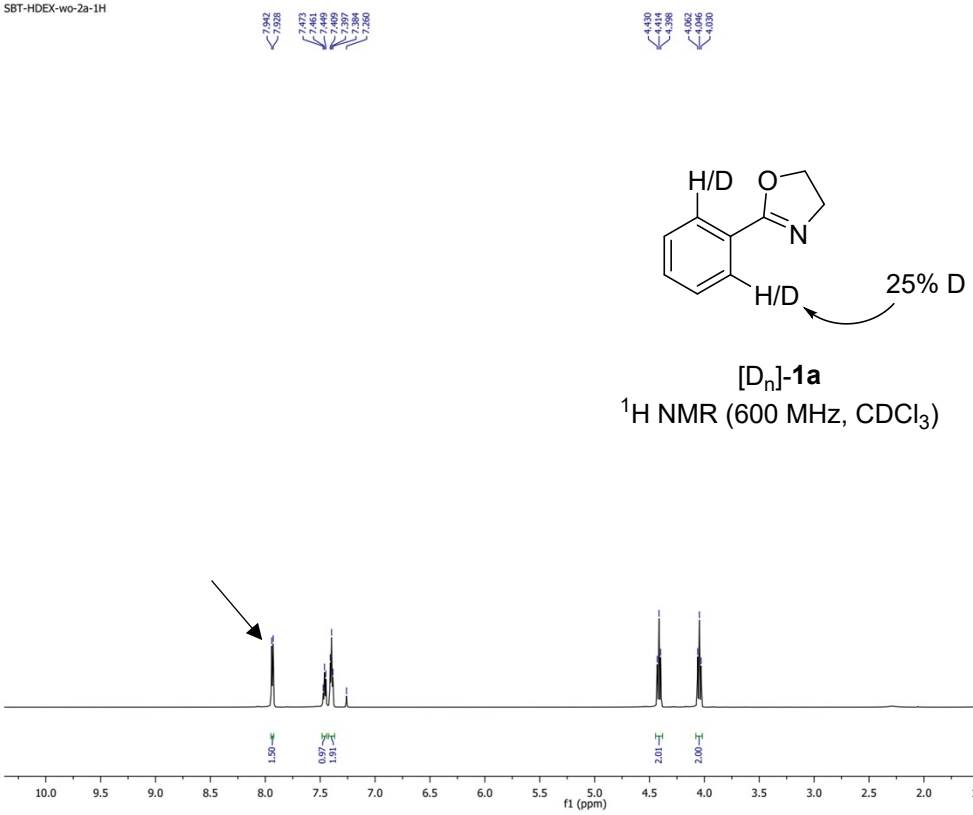
^{1}H NMR (600 MHz, $CDCl_3$)



7

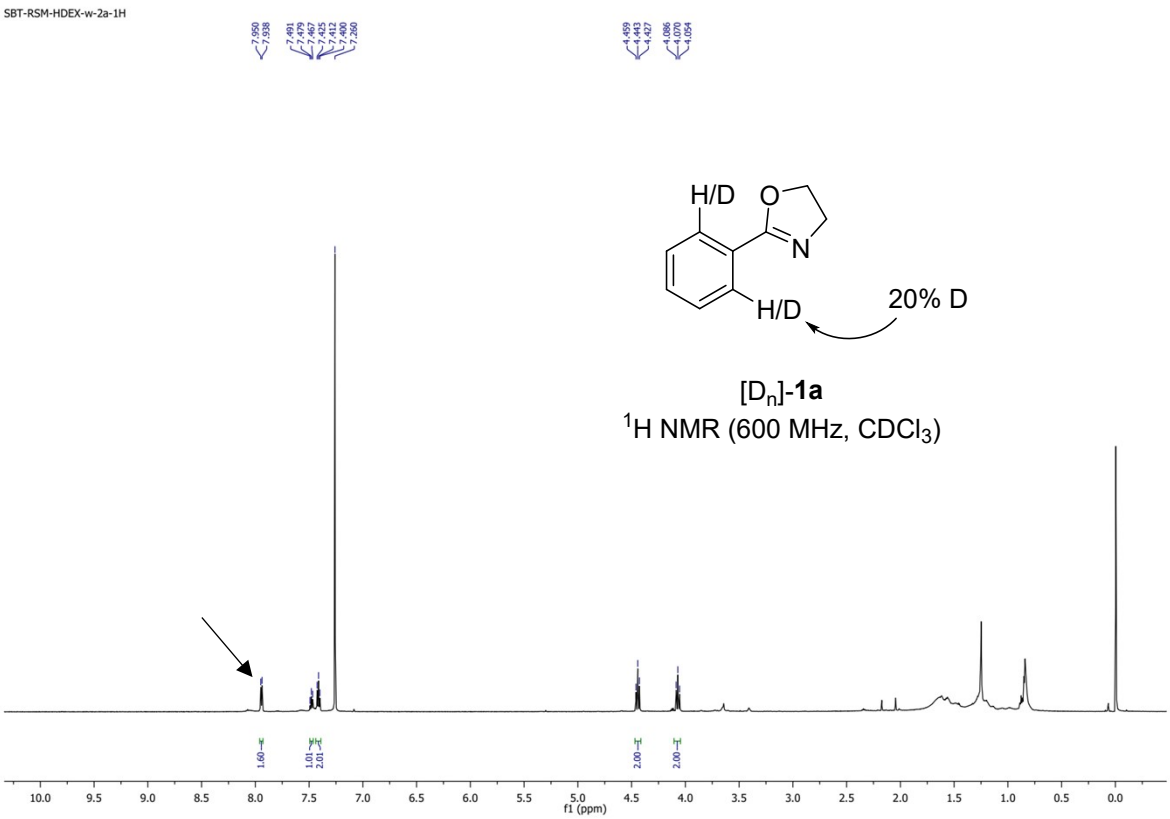
^{13}C NMR (150 MHz, $CDCl_3$)

SBT-HDEX-wo-2a-1H



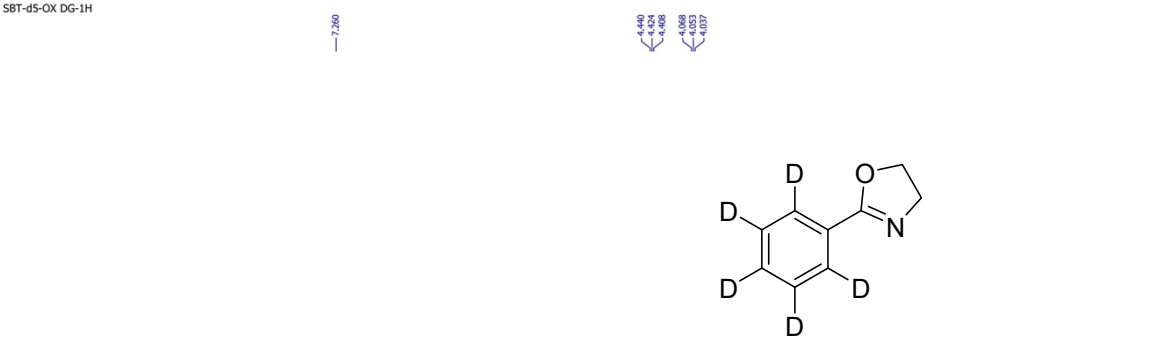
$[D_n]$-**1a**
^{1}H NMR (600 MHz, $CDCl_3$)

SBT-RSM-HDEX-w-2a-1H



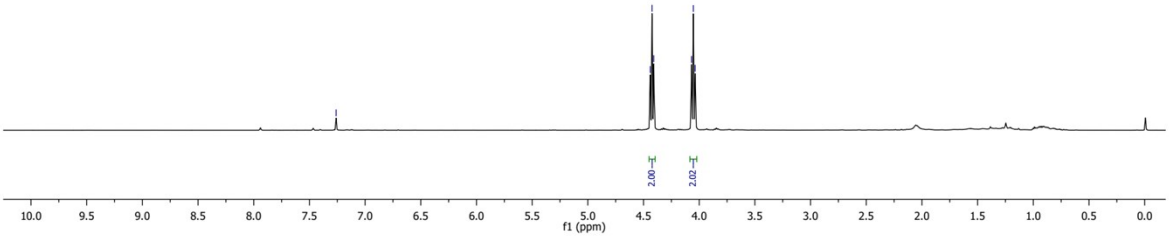
$[D_n]$-**1a**
^{1}H NMR (600 MHz, $CDCl_3$)

SBT-d5-OX DG-1H

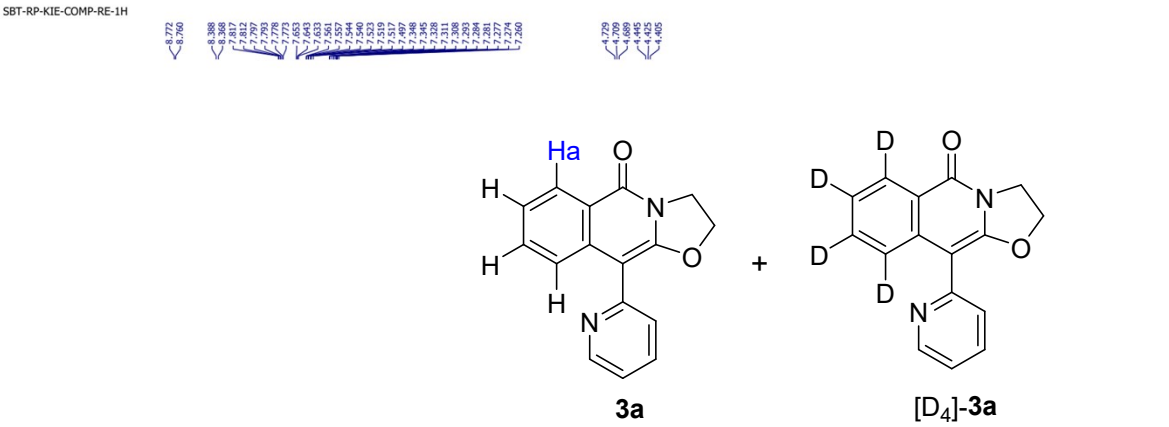


[D_5]-**1a**

^{1}H NMR (600 MHz, $CDCl_3$)



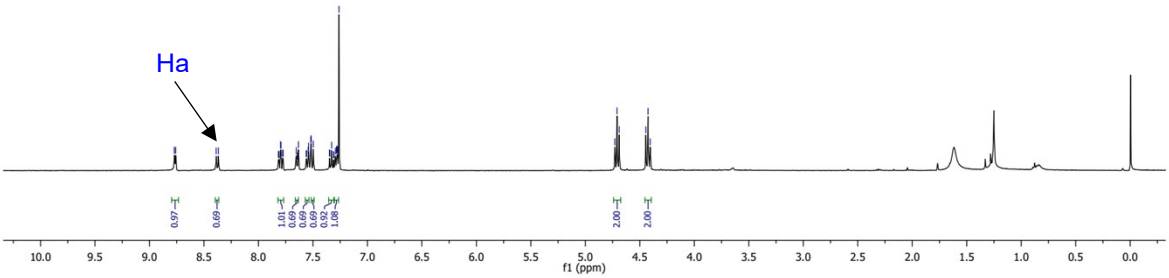
SBT-RP-KIE-COMP-RE-1H

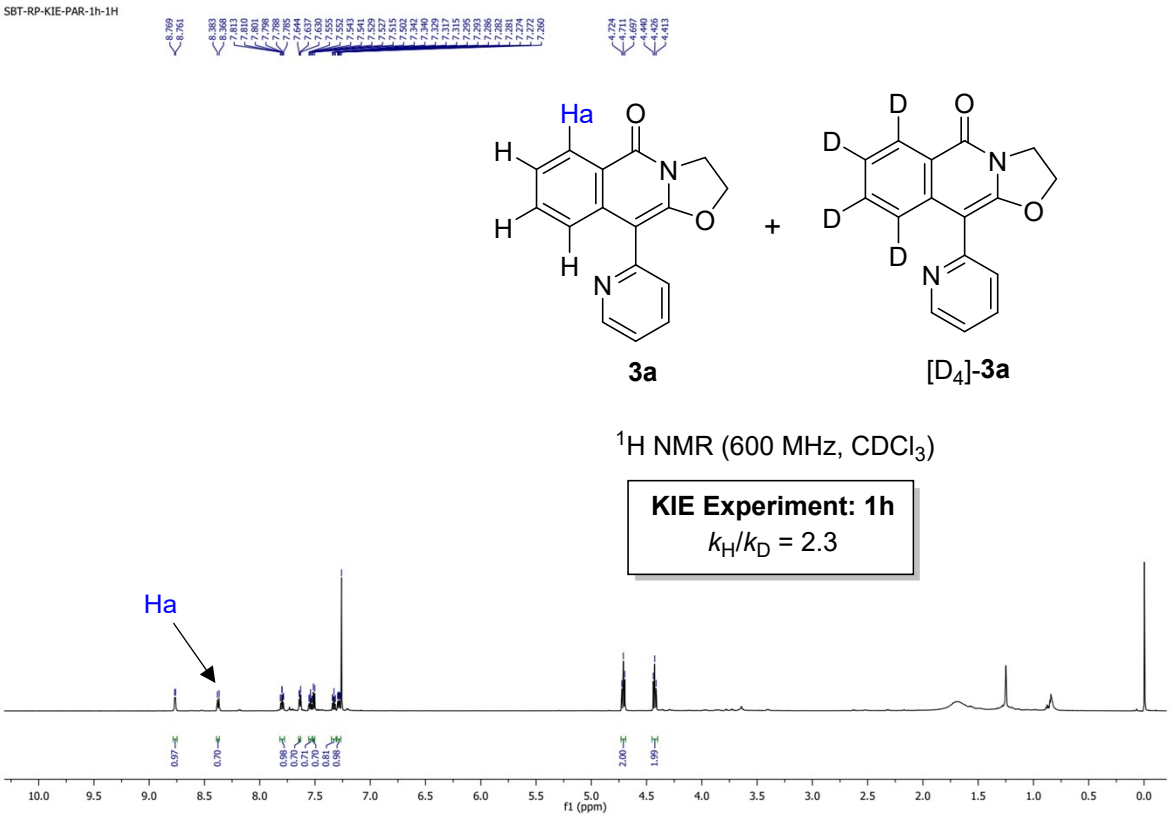


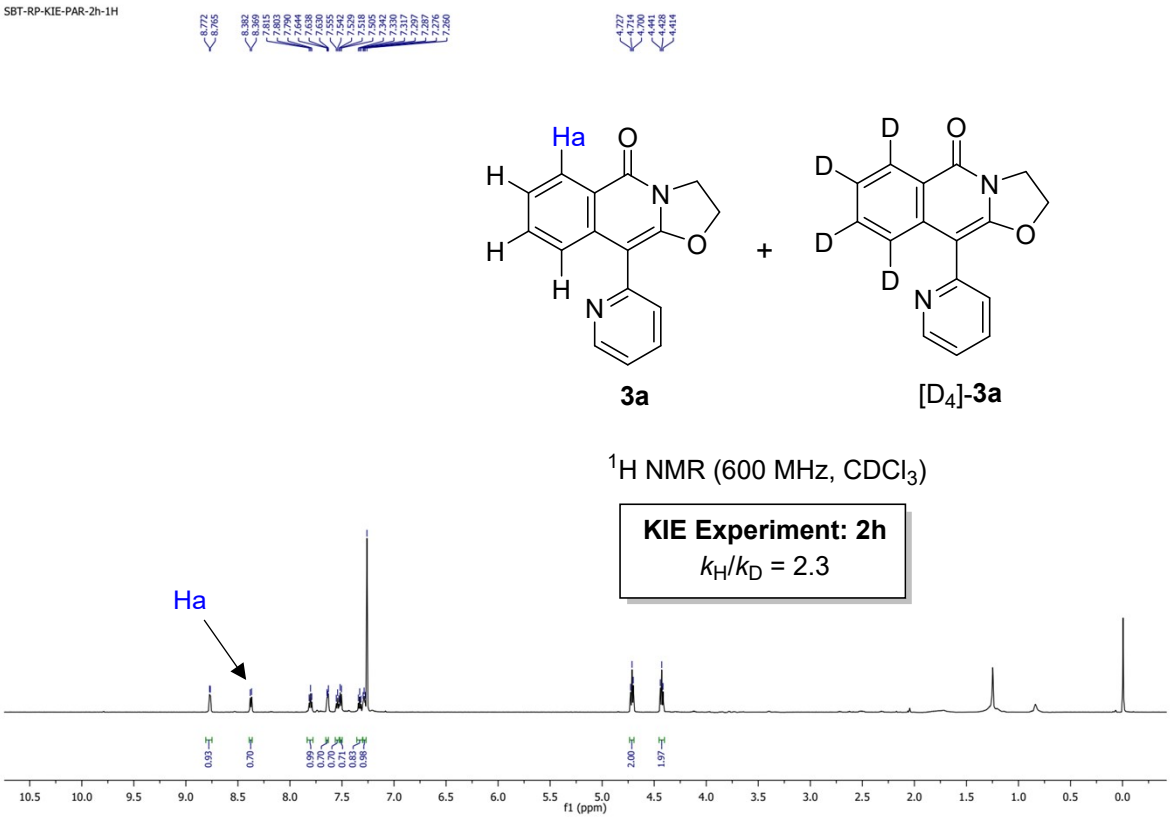
3a + [D_4]-**3a**

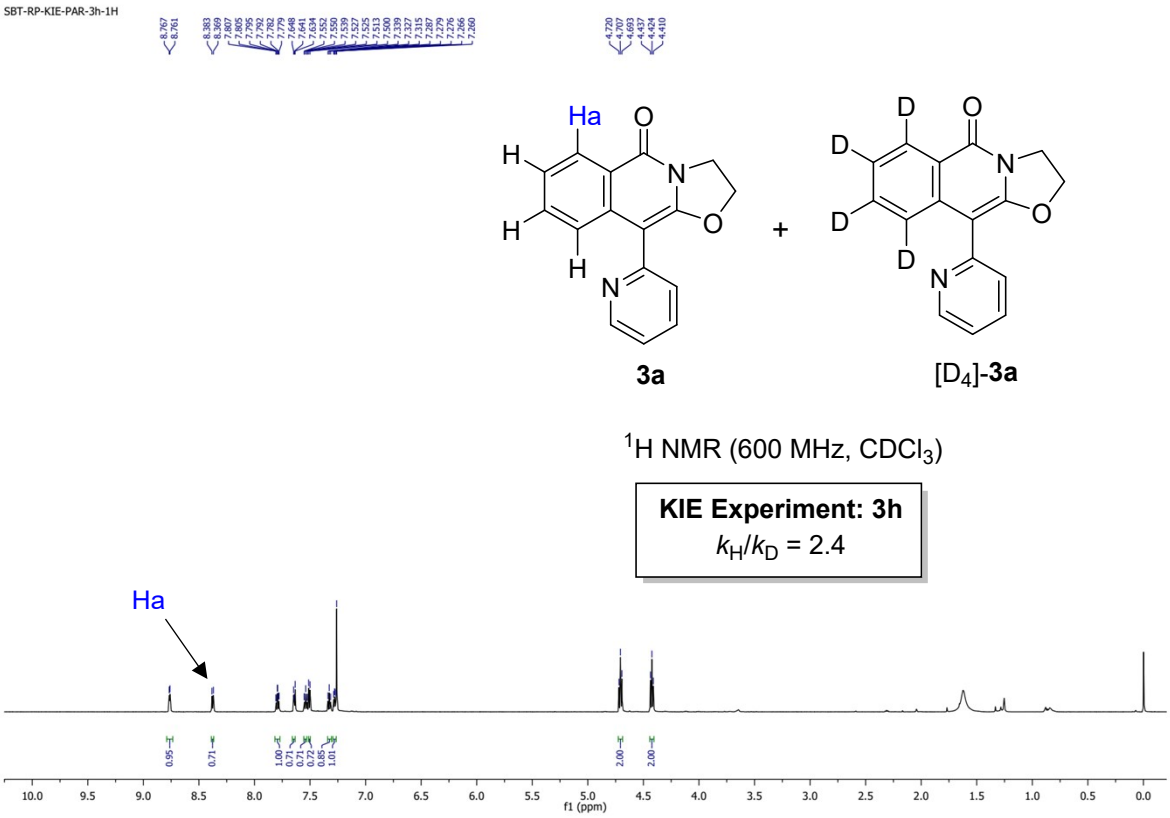
^{1}H NMR (400 MHz, $CDCl_3$)

k_H/k_D = 2.2




SBT-RP-KIE-PAR-1h-1H
Ha
H
H
H
O
N
O
N
+
D
D
D
D
O
N
O
N
3a
[D4]-3a
1H NMR (600 MHz, CDCl3)
KIE Experiment: 1h
kH/kD = 2.3
Ha
0.97
0.70
0.98
0.70
0.71
0.70
0.81
0.98
2.00
1.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


SBT-RP-KIE-PAR-2h-1H
Ha
H
H
H
O
N
O
N
+
D
D
D
D
O
N
O
N
3a
[D4]-3a
1H NMR (600 MHz, CDCl3)
KIE Experiment: 2h
kH/kD = 2.3
Ha
0.93
0.70
0.99
0.70
0.70
0.71
0.68
0.98
2.00
1.97
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


SBT-RP-KIE-PAR-3h-1H
Ha
H
H
H
O
N
O
N
+
D
D
D
D
O
N
O
N
3a
[D4]-3a
1H NMR (600 MHz, CDCl3)
KIE Experiment: 3h
kH/kD = 2.4
Ha
f1 (ppm)