Supporting Information

Palladium(II)-Catalyzed Enantioselective Desymmetrizative Ring Opening of Oxabicyclic Alkenes with Alkynylanilines: Efficient Access to Enantioenriched Functionalized Cyclohexenes

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1. General Information

(1) Analytical Methods

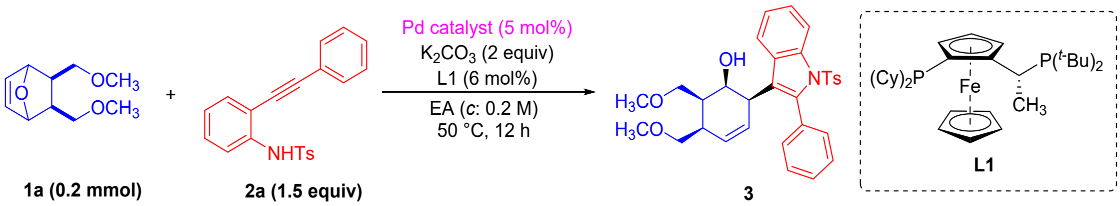
^1H and ^{13}C NMR spectra were measured on a Bruker AV-400 spectrometer instrument (400 MHz for ^1H, 101 MHz for ^{13}C NMR ,376 MHz for ^{19}F NMR spectroscopy) using Chloroform-*d* as the solvent. The following abbreviations (or combinations thereof) were used to explain chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constants (*J*) in hertz (Hz). All high-resolution mass spectra (HRMS) were obtained on a Waters Quatro Macro triple quadrupole mass spectrometer. High-pressure liquid chromatography (HPLC) was performed on Shimadzu Nexera LC-16 a chiral column as noted for each compound. Enantiomer excess was determined by HPLC analysis employing FLM Chiral INA and NY(2) column. The X-ray source used for the single crystal X-ray diffraction analysis compound **3** and **36** was Cu Kα (λ = 1.54184). The thermal ellipsoid was drawn at the 50% probability level for compound **3** and **36**.

(2) Materials

All solvents, ligands and reagents mentioned in this text were commercially available and bought from Bide pharm or Leyan and used as received without purification. Analytical thin-layer chromatography was performed on 0.20 mm silica gel plates (GF254) using UV light as a visualizing agent. Flash column chromatography was carried out using silica gel (300-400 mesh) with the indicated solvent system. All reactions were conducted in oven-dried Schlenk tubes. All the reaction temperatures reported are oil bath temperature.

2. Optimization of Reaction Conditions

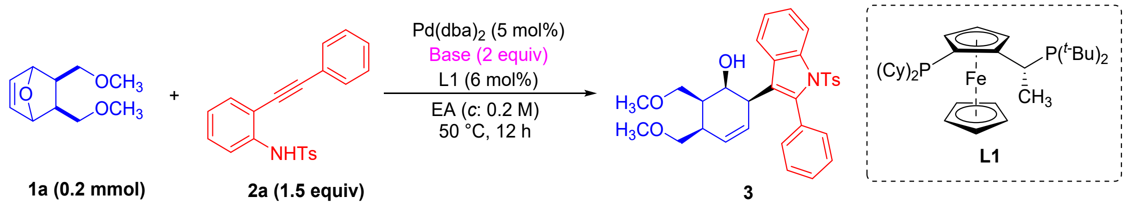
Table S1. Optimization of Pd catalyst



Entry	Pd catalyst (5 mol%)	Yield (%)	ee (%)
1[a]	$Pd_2(dba)_3$	52	93
2	$Pd(dppe)Cl_2$	48	93
3	$Pd(OAc)_2$	31	93
4	$PdCl_2(bpy)$	51	92
5	$Pd(TFA)_2$	51	93
6	$Pd(dba)_2$	62	93
7	$Pd(PhCN)_2Cl_2$	43	93
8	$Pd(acac)_2$	NR	/
9	$Pd(CH_3CN)_2Cl_2$	28	92
10	$Pd(dppf)Cl_2$	27	91
11	$PdCl_2$	34	92
12	$Pd(PPh_3)_4$	19	90
13	$PdCl_2(PPh_3)_2$	28	92
14[a]	$Pd_2(allyl)_2Cl_2$	Trace	/
15	$Pd(CF_3COCHCOCF_3)_2$	32	92
16	$Pd(^tBu_3P)_2$	32	92

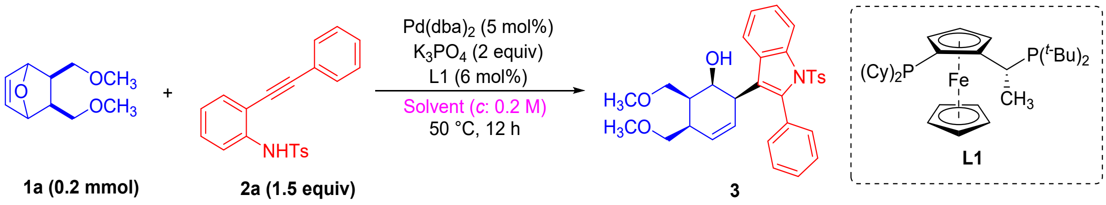
[a]Pd catalyst (2.5 mol%).

Table S2. Optimization of Base



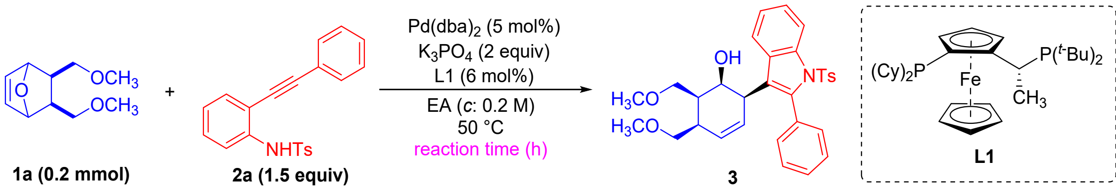
Entry	Base (2 equiv)	Yield (%)	ee (%)
1	Cs_2CO_3	67	90
2	Na_2CO_3	NR	/
3	K_2CO_3	62	93
4	Li_2CO_3	NR	/
5	KOH	38	94
6	NaOH	NR	/
7	$KHCO_3$	NR	/
8	CH_3COOK	NR	/
9	KF	trace	/
10	^{t}BuOK	trace	/
11	CsF	45	91
12	K_3PO_4	42	95
13	Na_2HPO_4	NR	/
14	NEt_3	Trace	/
15	Pyridine	NR	/
16	DBU	Trace	/
17	Imidazole	NR	/
18	TMEDA	Trace	/
19	TMG	Trace	/
20	DIPEA	NR	/
21	CH_3COONa	NR	/
22	^{t}BuONa	44	90
23	KH_2PO_4	NR	/

Table S3. Optimization of Solvent



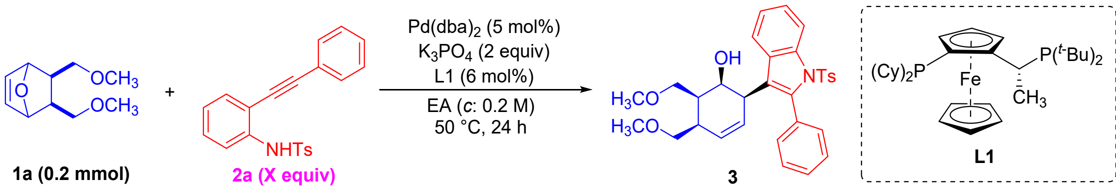
Entry	Solvent (*c*: 0.2 M)	Yield (%)	ee (%)
1	DMF	14	90
2	DMA	trace	/
3	THF	30	95
4	DMSO	NR	/
5	1,4-Dioxane	31	95
6	DME	NR	/
7	CH_3CN	12	93
8	PhMe	23	93
9	$PhCF_3$	30	94
10	PhCl	30	94
11	Acetone	36	95
12	Mesitylene	29	93
13	MeOH	NR	/
14	EtOH	Trace	/
15	DCM	31	95
16	EA	42	95
17	DCE	29	95
18	MTBE	39	93
19	Hexane	NR	/
20	Cyclohexane	17	90
21	CPME	40	94
22	$CHCl_3$	17	95
23	TFE	NR	/

Table S4. Optimization of Reaction Time



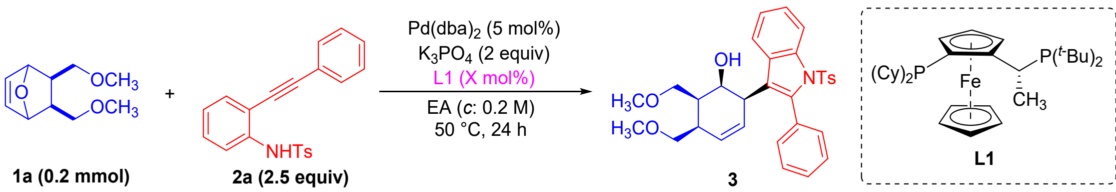
Entry	Reaction Time (h)	Yield (%)	ee (%)
1	12	42	95
2	24	65	95

Table S5 Optimization of 2a



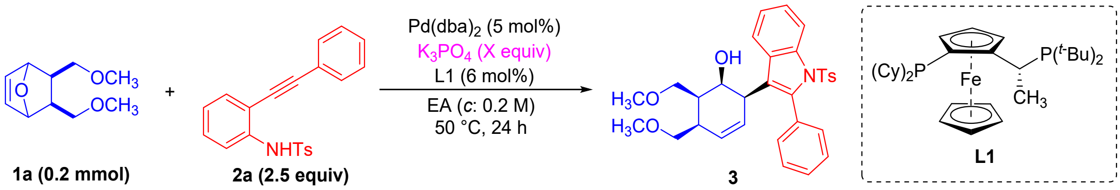
Entry	2a (X equiv)	Yield (%)	ee (%)
1	1.5	65	95
2	2.0	75	95
3	2.5	89	95
4	3.0	89	95

Table S6 Optimization of L1



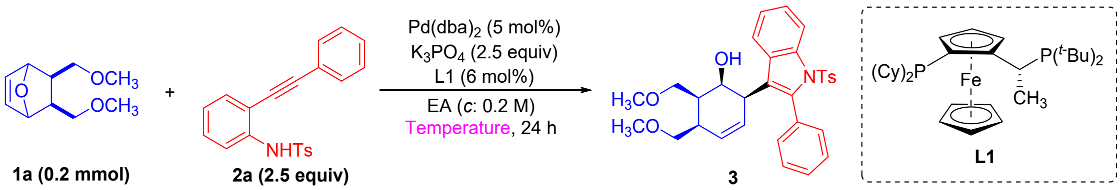
Entry	L1 (X mol%)	Yield (%)	ee (%)
1	6	89	95
2	10	80	95
3	20	76	95

Table S7 Optimization of K_3PO_4



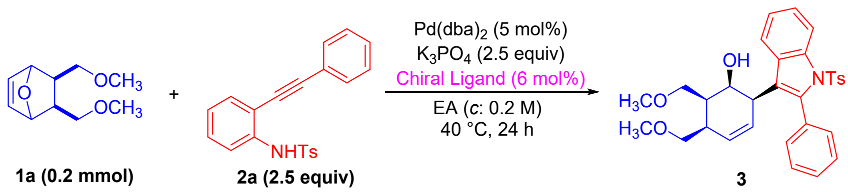
Entry	K_3PO_4 (X equiv)	Yield (%)	ee (%)
1	1.5	80	95
2	2.0	89	95
3	2.5	92	95
4	3.0	94	94

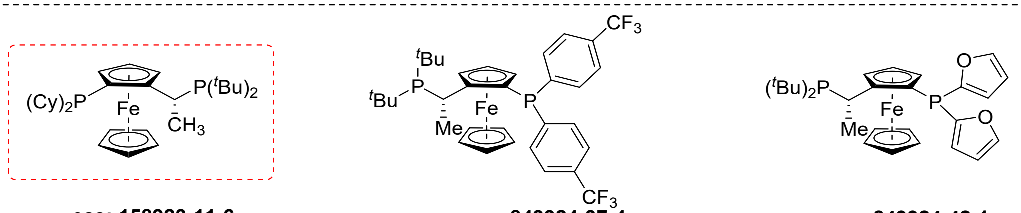
Table S8 Optimization of Temperature



Entry	Temperature	Yield (%)	ee (%)
1	40 °C	91	96
2	50 °C	92	95
3	60 °C	93	93

Table S9 Optimization of Chiral Ligands

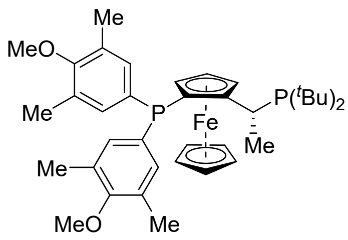




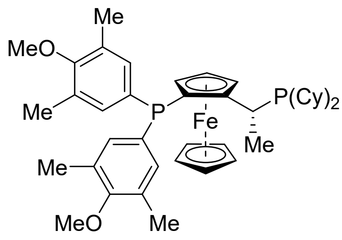
cas: 158923-11-6
L1, 91% yield, 96% ee

cas: 849924-37-4
L2, 90% yield, -87% ee

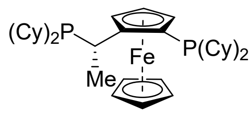
cas: 849924-42-1
L3, 90%yield, -91% ee



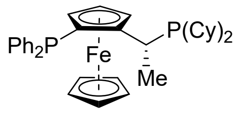
cas: 849924-74-9
L4, 95% yield, 90% ee



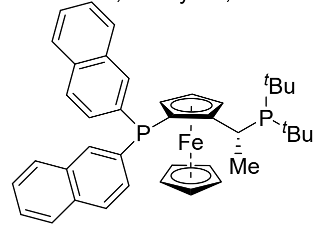
cas: 360048-63-1
L5, 50% yield, 25% ee



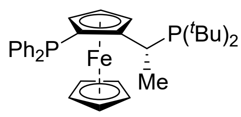
cas: 246231-77-6
L6, 22% yield, -44% ee



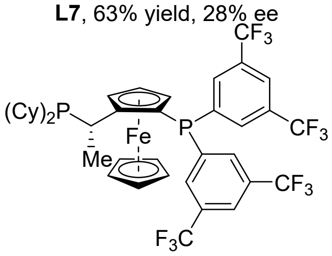
cas: 155806-35-2
L7, 63% yield, 28% ee



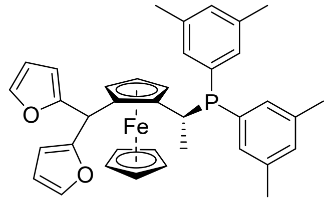
cas: 849924-44-3
L8, 82% yield, 91% ee



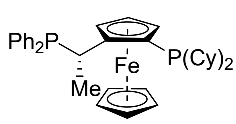
cas: 155830-69-6
L9, 91% yield, 88% ee



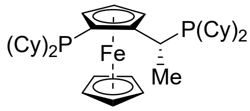
cas: 849923-15-5
L10, 60% yield, -14% ee



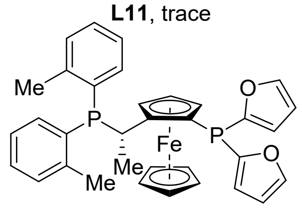
cas: 649559-65-9
L11, trace



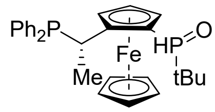
cas: 162291-01-2
L12, NR



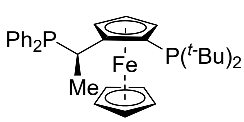
cas: 158923-07-0
L13, trace



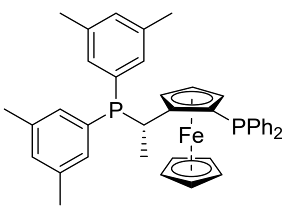
cas: 849924-74-9
L14, NR



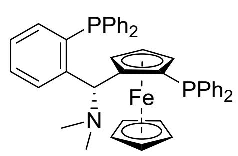
cas: 1221746-31-1
L15, NR



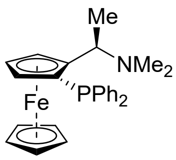
cas: 223120-71-6
L16, NR



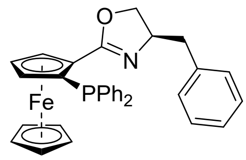
cas: 223121-07-1
L17, NR



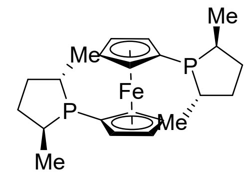
cas: 1003012-96-1
L18, NR



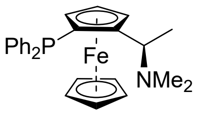
cas: 55700-44-2
L19, NR



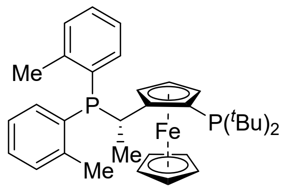
cas: 2256046-71-4
L20, NR



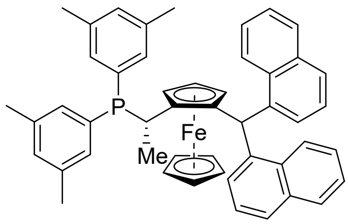
cas: 162412-87-5
L21, NR



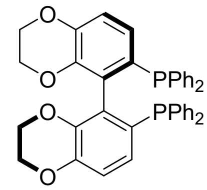
cas: 74311-54-9
L22, NR



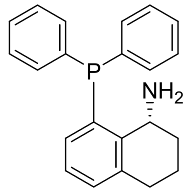
cas: 849924-77-2
L23, NR



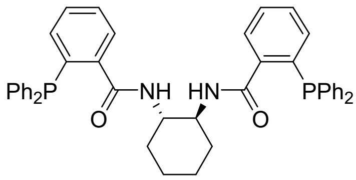
cas: 851308-41-3
L24, NR



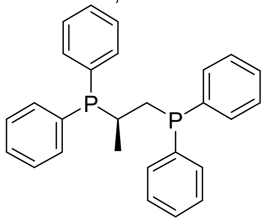
cas: 445467-61-8
L25, NR



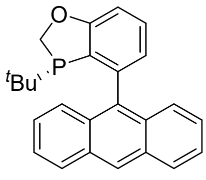
cas: 960128-64-7
L26, NR



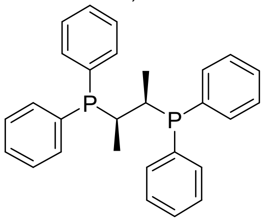
cas: 169689-05-8
L27, NR



cas: 67884-32-6
L28, NR



cas: 1807740-34-6
L29, NR



74839-84-2
L30, NR

Attention:

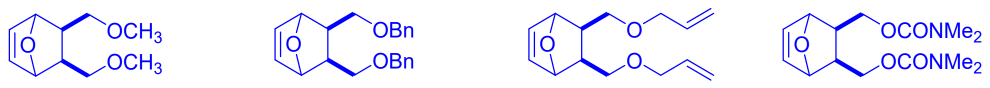
All yields are isolated yields.

All enantiomeric excesses were determined by HPLC analysis on a chiral stationary phase.

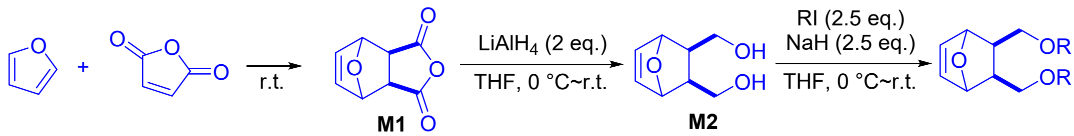
3. Preparation of Oxabicyclic Alkenes and Alkynylanilines

3.1 Preparation of Oxabicyclic Alkenes

List of Oxabicyclic Alkenes



1a-1c[1], **1d**[2] are known compounds in literature. They were prepared according to the following general procedure.



In a two-necked flask, distilled furan (70 ml, 0.93 mol) was added to maleic anhydride (18 g, 0.18 mol). The reaction mixture was vigorously stirred at room temperature overnight, Then, the reaction was filtered, and the solid residue was dry under vacuum to afford the desired product **M1** as white powder (90% yield).

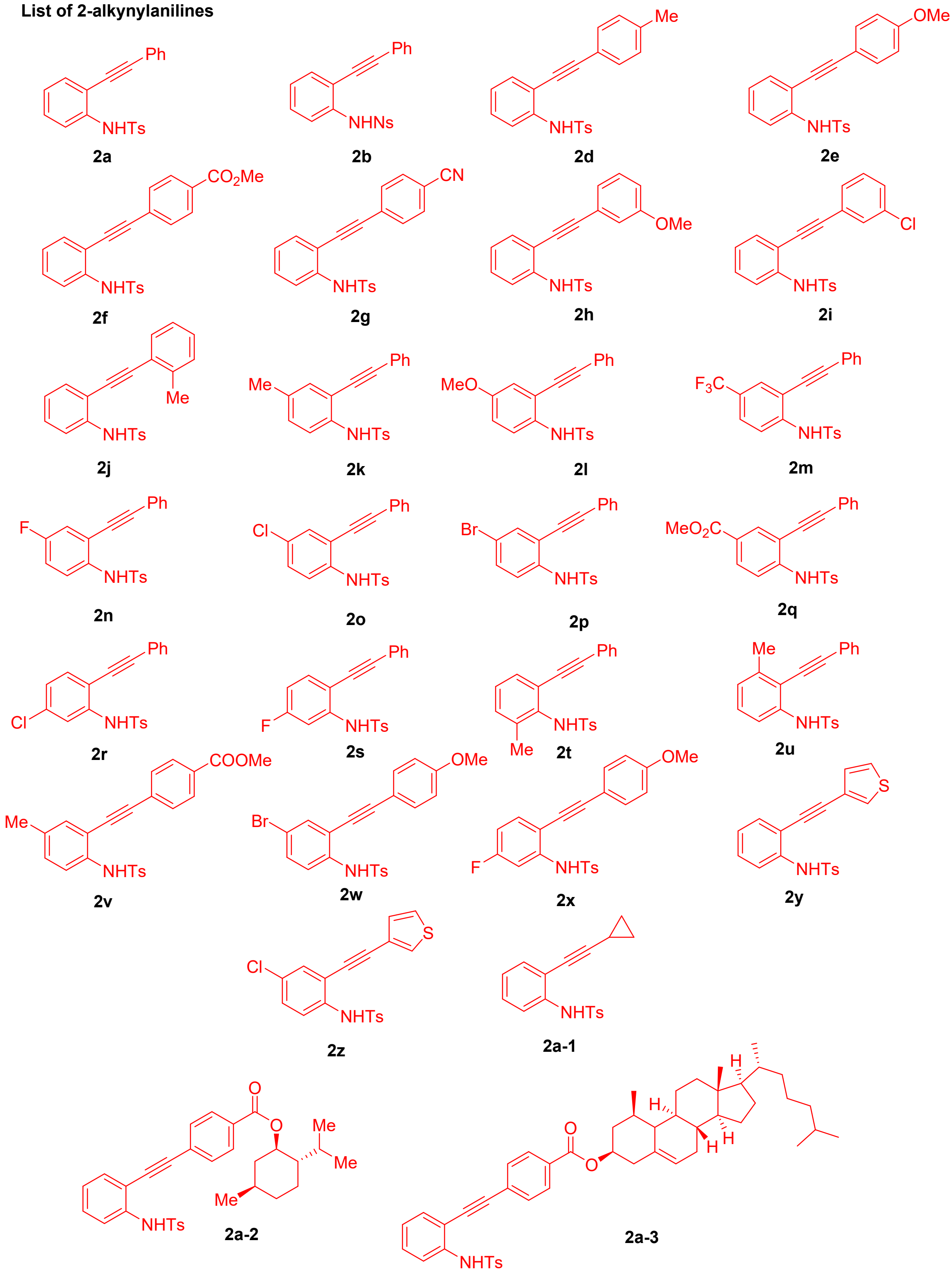
In a 250 mL two-necked flask, $LiAlH_4$ (0.759 g, 20 mmol) in powder was suspended in dry THF (20 mL) and stirred at -10 °C while a solution of **M1** (1.661 g, 10 mmol) in dry THF (50 mL) was added. The reaction mixture was allowed to warm up to room temperature and was stirred for 4 h. Then, the reaction mixture was cooled at 0°C and was quenched by successively dropwise addition of water (0.8 mL), followed by aqueous solution of NaOH (0.8 mL, 15 wt. %), and water (2.4 mL). The reaction mixture was stirred for additional 15 min at room temperature and was then filtered through Celite pad, washing with EA. The solvent was removed under vacuum to afford the desired product **M2** as a pale-yellow oil (85% yield).

To a suspension of dry sodium hydride (2.5 equiv.) in dry THF a solution of **M2** in solution in THF was added dropwise at 0 °C. The reaction mixture was stirred 30 min at r.t. after the end of gas evolution before adding iodine substitutes or dimethylcarbamoyl chloride (2.5 equiv.) followed by two hours stirring at R.T. The reaction was quenched by addition of brine 20 ml and the product was extracted with 3

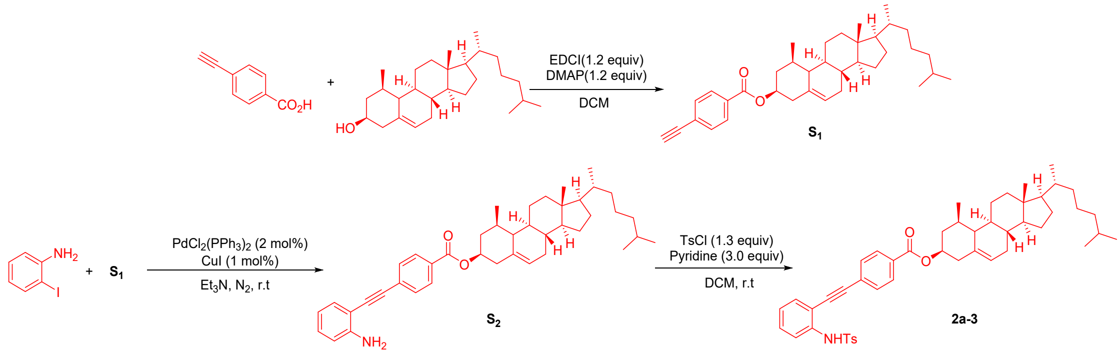
× 50 mL of EA. After drying over magnesium sulfate and evaporation of solvent under reduced pressure, the residue was purified by silica gel flash chromatography (PE/EA) to afford the oxabicyclic alkenes.

3.2 Preparation of Alkynylanilines

List of 2-alkynylanilines



2a~2a-2[3,6,7] are known compounds in literatures. **2a-3** were prepared according to the following general procedure.



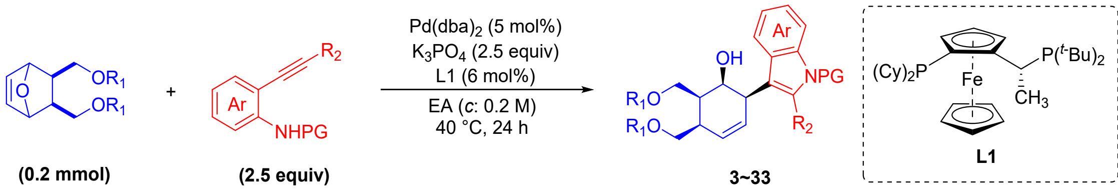
4-ethynylbenzoic acid (1.0 equiv.), cholesterol (1.2 equiv.), EDCI (1.2 equiv.) and DMAP (1.2 equiv.) were added into DCM under air atmosphere. After stirring for 12 h, the mixture was poured into water and extracted with DCM 3 times. The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel with EA/PE as an eluent to give $\mathbf{S_1}$.

A Schlenk-tube equipped with a magnetic stir bar was charged with $\mathbf{S_1}$ (1.0 equiv.), $PdCl_2(PPh_3)_2$ (2 mol%), CuI (1 mol%) and then evacuated and backfilled with N_2 for 3 times. Afterwards, Et_3N, phenylacetylene (1.3 equiv.) were added consecutively under N_2 atmosphere. After stirring for 12 h, the mixture was extracted with DCM, and the combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel with EA/PE as an eluent to give $\mathbf{S_2}$.

TsCl (1.3 equiv.) was added to a solution of $\mathbf{S_2}$ in DCM (40 mL) under R.T. and then pyridine (3.0 equiv.) was added to the solution under air atmosphere. After stirring for 12 h, the mixture was diluted with DCM, washed with HCl (6 M), saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel with EA/PE as an eluent to give the corresponding 2-alkynylaniline **2v.**

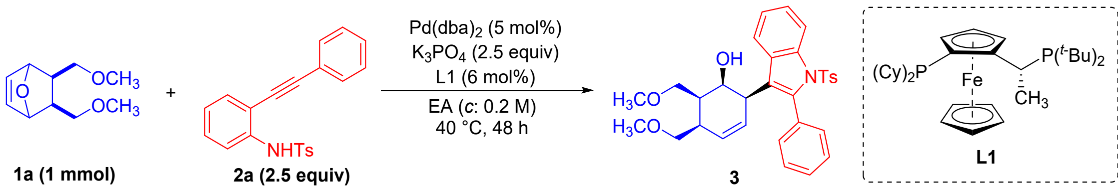
4. General Experimental Procedure for Palladium(II)-Catalyzed Enantioselective Desymmetrizative Ring Opening of Oxabicyclic Alkenes with Alkynylanilines

(1) General Experimental Procedure A



A Schlenk-tube equipped with a magnetic stir bar was charged with 2-alkynylaniline (2.5 equiv., 0.5 mmol), $Pd(dba)_2$ (5 mol%, 0.01 mmol), L1 (6 mol%, 0.012 mmol), K_3PO_4 (2.5 equiv., 0.5 mmol). Then, EA (1.0 mL) and oxabicyclic alkenes (0.2 mmol) were added consecutively under air atmosphere. The tight tube was stirred at 40 °C for 24 h. After 24 h, the resulting mixture was extracted with DCM (3 × 15 mL) and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated. The crude product was purified by column chromatography on silica gel to give the product **3~9, 11~13, 15~26, 28~32**.

(2) General Experimental Procedure for 1 mmol Synthesis of 3

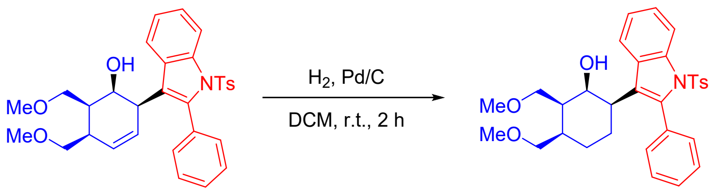


A Schlenk-tube equipped with a magnetic stir bar was charged with 2-alkynylaniline **2a**(2.5 equiv., 2.5 mmol), $Pd(dba)_2$ (5 mol%, 0.05 mmol), L1 (6 mol%, 0.06 mmol), K_3PO_4 (2.5 equiv., 2.5 mmol). Then, EA (5.0 mL) and oxabicyclic alkenes **1a**(1.0 mmol) were added consecutively under air atmosphere. The tight tube was stirred at 40 °C for 48 h. After 48 h, the resulting mixture was extracted with DCM (3 × 20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated. The crude product was purified by column chromatography on silica gel to give the product **3**(473.0 mg, 89% yield, 96% ee).

Attention:

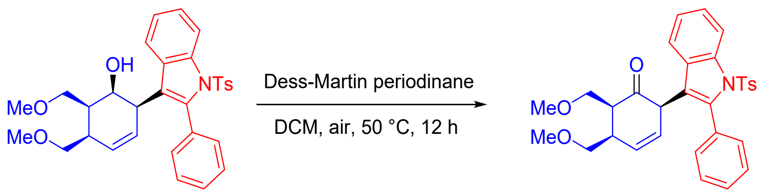
The procedure for the synthesis of compound **10, 14** and **27** is similar to **General Experimental Procedure A** at the temperature of **50 °C**, the procedure for the synthesis of compound **33** is similar to **General Experimental Procedure A** at the concentration of **0.1 M**.

5. Synthetic Applications



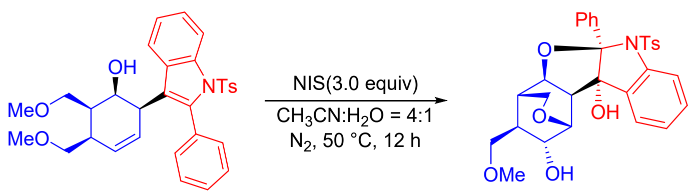
3, 96% ee **34,** 92% yield, 95% ee

According to a previous reference[4], to a stirring solution of **3** (106.3 mg, 96% ee, 0.2 mmol, 1.0 equiv.) in DCM (5.0 mL) was slowly added palladium on-activated-charcoal (10%, 40.0 mg) at room temperature. The resulting mixture was stirred at room temperature in an atmosphere of hydrogen gas for 2 hours. The mixture was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **34** (98.2 mg, 92% yield, 95% ee).



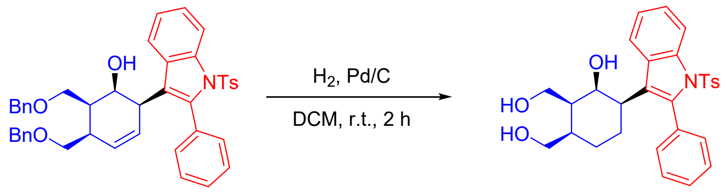
3, 96% ee **35,** 82% yield, 95% ee

To a flame-dried Schlenk tube were added **3** (106.3 mg, 96% ee, 0.2 mmol, 1.0 equiv.) and Dess-Martin periodinane (127.2 mg, 0.3 mmol, 1.5 equiv.) under air atmosphere. The resulting mixture was stirred at 50 °C under air atmosphere for 12 hours. The resulting mixture was extracted with DCM (3 × 15 mL) and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated. The crude product was purified by column chromatography on silica gel to give the product **35** (87.0 mg, 82% yield, 95% ee).



3, 96% ee **36**, 46%, 98% ee

According to a previous reference [3], to a flame-dried and N_2-purged Schlenk tube were added compound **3** (106.3 mg, 96%, 0.2 mmol, 1.0 equiv.), and NIS (135.0 mg, 0.6 mmol, 3.0 equiv.). The vial was then sealed, purged and backfilled with N_2 three times before adding MeCN (0.8 mL) and H_2O (0.2 mL) at room temperature. The resulting mixture was stirred at 50°C under N_2 atmosphere for 12 hours. The resulting mixture was extracted with DCM (3 × 15 mL) and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated. The crude product was purified by column chromatography on silica gel to give the product **36** (50.0 mg, 46% yield, 97% ee).

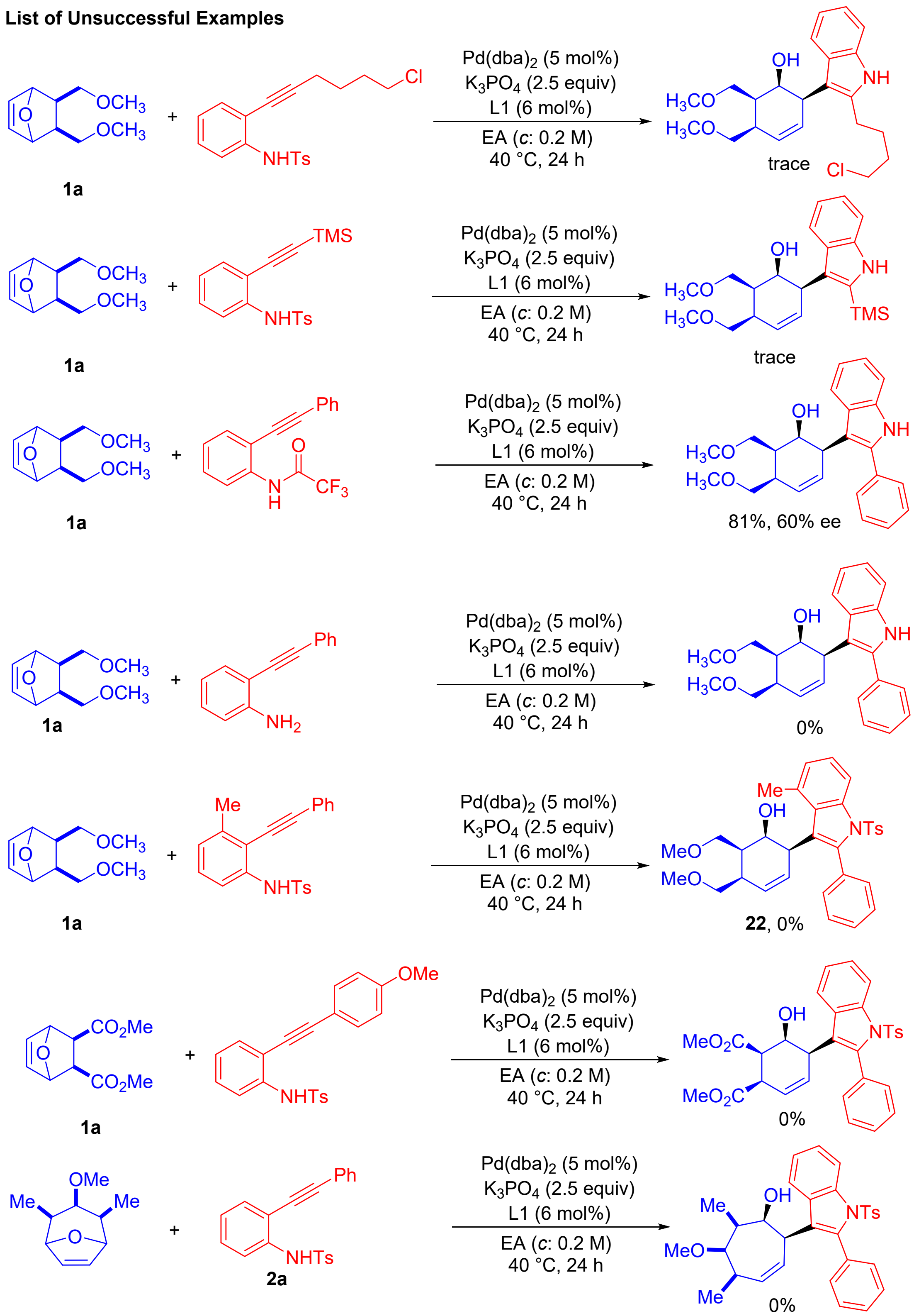


25, 96% ee　　**37,** 80% yield, 96% ee

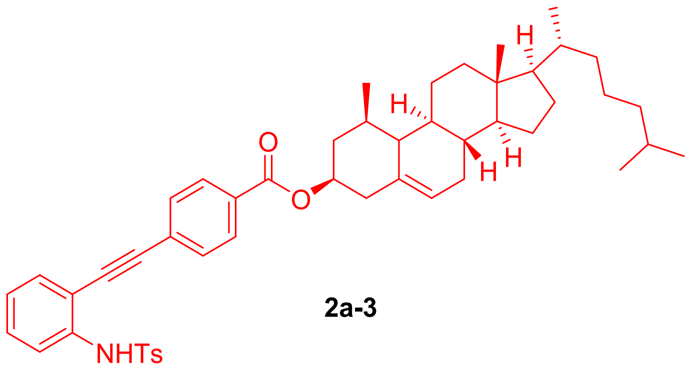
According to a previous reference[4], to a stirring solution of **3** (136.8 mg, 96% ee, 0.20 mmol, 1.0 equiv.) in DCM (5.0 mL) was slowly added palladium on-activated-charcoal (10%, 40.0 mg) at room temperature. The resulting mixture was stirred at room temperature in an atmosphere of hydrogen gas for 2 hours. The mixture was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **37** (80.9 mg, 80% yield, 96% ee).

6. List of Failed Examples

List of Unsuccessful Examples



7. Characterization Data for New Substrates



2a-3

(1*R*, 3*S*, 8*R*, 9*S*, 13*R*, 14*S*, 17*R*)-1, 13-Dimethyl-17-((*R*)-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-((2-((4-methylphenyl)sulfonamido)phenyl)ethynyl)benzoate.

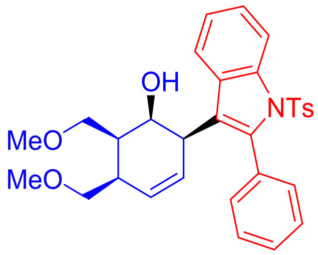
White solid, M.p: 133.0~138.0 °C, PE/EA = 10/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.71 – 7.57 (m, 3H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.38 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.32 (td, *J* = 8.0, 4.0 Hz, 1H), 7.23 – 7.12 (m, 3H), 7.08 (td, *J* = 8.0, 4.0 Hz, 1H), 5.43 (d, *J* = 4.0 Hz, 1H), 4.94 – 4.82 (m, 1H), 2.49 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H), 2.09 – 1.65 (m, 7H), 1.64 – 1.42 (m, 7H), 1.42 – 1.11 (m, 10H), 1.11 – 0.95 (m, 8H), 0.93 (d, *J* = 4.0 Hz, 3H), 0.86 (dd, *J* = 8.0, 4.0 Hz, 6H), 0.69 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.2, 144.1, 139.5, 137.7, 136.1, 132.2, 131.4, 130.9, 130.1, 129.7, 129.6 127.2, 126.4, 124.8, 122.9, 120.8, 114.3, 95.2, 86.4, 75.0, 56.7, 56.2, 50.1, 42.3, 39.8, 39.5, 38.2, 37.0, 36.7, 36.2, 35.8, 32.0, 31.9, 28.3, 28.0, 27.9, 24.3, 23.9, 22.9, 22.6, 21.6, 21.1, 19.4, 18.8, 11.9.

HRMS (ESI): m/z: [M + H]$^+$ Calcd for $C_{49}H_{62}NO_4S^+$: 760.4394; Found: 760.4 390.

8. Characterization Data for New Products



3, 91%, 96% ee

(1*S*, 2*R*, 5*R*, 6*S*)-5, 6-Bis(methoxymethyl)-2-(2-phenyl-1-tosyl-1*H*-indol-3-yl)cyclohex-3-en-1-ol.

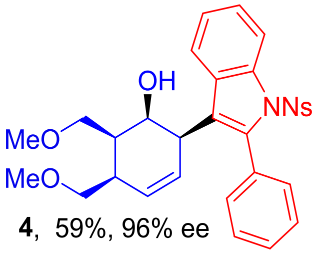
96.7 mg, 91% yield, 96% ee, white solid, M.p: 118.7~123.4 °C, PE/EA = 2/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.71 (m, 1H), 7.46 – 7.26 (m, 8H), 7.22 – 7.18 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.78 – 5.73 (m, 1H), 5.69 – 5.65 (m, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 3.69 – 3.64 (m, 1H), 3.55 – 3.45 (m, 4H), 3.34 – 3.28 (m, 4H), 2.56 – 2.52 (m, 1H), 2.30 (s, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.4, 137.0, 136.9, 135.9, 131.5, 131.1, 129.4, 128.7, 128.2, 127.4, 126.8, 124.3, 123.8, 123.1, 122.6, 115.1, 73.0, 71.4, 68.6, 58.9, 58.8, 41.1, 40.9, 35.7, 21.6.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd for $C_{31}H_{33}NNaO_5S^+$: 554.1972; Found: 554.1978.

The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 6.391 min, t_R(major) = 7.714 min.



4, 59%, 96% ee

(1*S*, 2*R*, 5*R*, 6*S*)-5, 6-Bis(methoxymethyl)-2-(1-((4-nitrophenyl)sulfonyl)-2-phenyl-1*H*-indol-3-yl)cyclohex-3-en-1-ol.

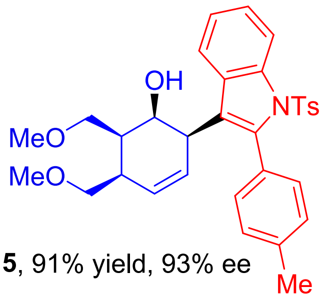
66.0 mg, 59% yield, 96% ee, yellow solid, M.p: 138.3~142.9 °C, PE/EA = 2/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 12.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 12.0 Hz, 2H), 7.48 – 7.40 (m, 3H), 7.36 – 7.27 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 1H), 5.76 – 5.74 (m, 1H), 5.62 (d, *J* = 8.0 Hz, 1H), 4.47 (d, *J* = 8.0 Hz, 1H), 3.67 (d, *J* = 8.0 Hz, 1H), 3.54 – 3.48 (m, 4H), 3.45 (s, 3H), 3.33 (s, 4H), 2.54 (s, 1H), 2.34 – 2.29 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.4, 143.6, 136.9, 136.6, 131.6, 131.0, 129.1, 128.9, 128.4, 128.1, 127.7, 125.6, 124.9, 124.0, 123.9, 123.2, 115.2, 72.9, 71.2, 68.5, 58.9, 58.9, 41.1, 40.8, 35.6.

HRMS (ESI): m/z: [M + Na]$^+$ Calcd for $C_{30}H_{30}N_2NaO_7S^+$: 585.1666; Found: 585.1673.

The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 7.653 min, t_R(major) = 9.047 min.



5, 91% yield, 93% ee

(1*S*, 2*R*, 5*R*, 6*S*)-5,6-Bis(methoxymethyl)-2-(2-(p-tolyl)-1-tosyl-1*H*-indol-3-yl)cyclohex-3-en-1-ol

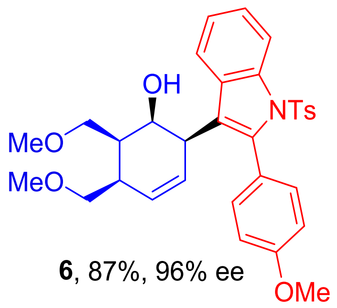
99.3 mg, 91% yield, 93% ee, white solid, M.p: 142.3~145.7 °C, PE/EA = 2/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.26 (m, 1H), 7.21 – 7.17 (m, 5H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.75 (d, *J* = 8.0 Hz, 1H), 5.66 (d, *J* = 8.0 Hz, 1H), 4.26 (d, *J* = 8.0 Hz, 1H), 3.66 (d, *J* = 8.0 Hz, 1H), 3.56 – 3.45 (m, 7H), 3.34 – 3.31 (m, 4H), 2.54 (s, 1H), 2.44 (s, 3H), 2.36 – 2.28 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.3, 138.5, 137.1, 137.0, 135.9, 131.2, 129.5, 129.4, 128.5, 128.2, 128.1, 126.8, 124.2, 123.7, 123.0, 122.6, 115.1, 73.0, 71.5, 68.7, 58.9, 58.8, 41.1, 40.9, 35.7, 21.6, 21.5.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{32}H_{36}NO_5S^+$: 546.2309; Found: 546.2296.

The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 7.145 min, t_R(major) = 9.054 min.



6, 87%, 96% ee

(1*S*, 2*R*, 5*R*, 6*S*)-5, 6-Bis(methoxymethyl)-2-(2-(4-methoxyphenyl)-1-tosyl-1*H*-indol-3-yl)cyclohex-3-en-1-ol.

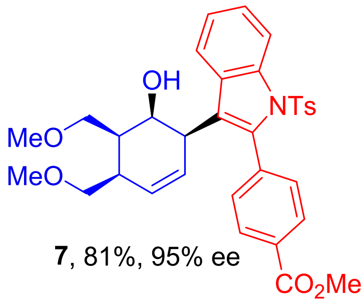
97.5 mg, 87% yield, 96% ee, yellow oil, PE/EA = 2/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 12.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 12.0, 8.0 Hz, 1H), 7.24 – 7.13 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 5.77 – 5.73 (m, 1H), 5.65 (d, *J* = 8.0 Hz, 1H), 4.30 (d, *J* = 8.0 Hz, 1H), 3.88 (s, 3H), 3.64 (d, *J* = 8.0 Hz, 1H), 3.55 – 3.48 (m, 4H), 3.44 (s, 3H), 3.33 – 3.31 (m, 4H), 2.53 (d, *J* = 4.0 Hz, 1H), 2.36 – 2.28 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.8, 144.3, 136.9, 136.8, 136.1, 131.0, 129.5, 129.4, 128.1, 126.8, 124.2, 123.6, 123.5, 123.0, 122.5, 115.1, 113.0, 73.0, 71.4, 68.6, 58.9, 58.8, 55.3, 41.1, 40.9, 35.7, 21.6.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{32}H_{36}NO_6S^+$: 562.2258; Found: 562.2248.

The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 9.231 min, t_R(major) = 10.848 min.



7, 81%, 95% ee

Methyl 4-(3-((1*R*, 4*R*, 5*S*, 6*S*)-6-hydroxy-4, 5-bis(methoxymethyl)cyclohex-2-en-1-yl)-1-tosyl-1*H*-indol-2-yl)benzoate.

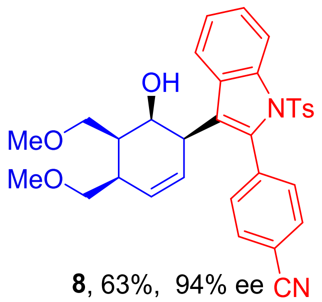
95.5 mg, 81% yield, 95% ee, pale yellow solid, M.p: 195.0~199.2 °C, PE/EA = 3/2.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.72 – 7.70 (m, 1H), 7.44 – 7.30 (m, 5H), 7.23 – 7.19 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.76 – 5.71 (m, 1H), 5.65 – 5.61 (m, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 3.96 (s, 3H), 3.67 – 3.62 (m, 1H), 3.54 – 3.43 (m, 7H), 3. 33 – 3.28 (m, 4H), 2.55 – 2.51 (m, 1H), 2.36 – 2.25 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 144.7, 137.1, 136.5, 135.6, 135.6, 131.1, 130.2, 129.5, 129.0, 128.6, 128.4, 126.7, 124.7, 123.3, 122.8, 115.2, 72.8, 71.3, 68.4, 58.9, 58.8, 52.3, 41.1, 40.8, 35.6, 21.6.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd for $C_{33}H_{36}NNaO_7S^+$: 612.2026; Found: 612.2029.

The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 20.997 min, t_R(major) = 22.955 min.



8, 63%, 94% ee

4-(3-((1*R*, 4*R*, 5*S*, 6*S*)-6-Hydroxy-4, 5-bis(methoxymethyl)cyclohex-2-en-1-yl)-1-tosyl-1*H*-indol-2-yl)benzonitrile.

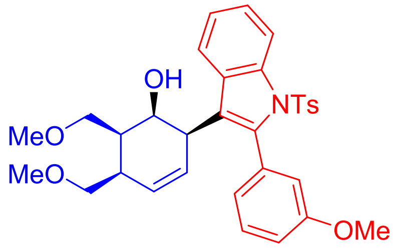
70.1 mg, 63% yield, 94% ee, white solid, M.p: 180.6~187.1 °C, PE/EA = 2/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.71 – 7.68 (m, 3H), 7.51 – 7.47 (m, 0H), 7.36 – 7.31 (m, 3H), 7.24 – 7.20 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.74 – 5.70 (m, 1H), 5.60 – 5.56 (m, 1H), 4.44 (d, *J* = 8.0 Hz, 1H), 3.67 – 3.63 (m, 1H), 3.53 – 3.41 (m, 7H), 3.35 – 3.28 (m, 4H), 2.57 – 2.52 (m, 1H), 2.35 – 2.29 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.9, 137.2, 136.7, 135.3, 134.6, 131.1, 131.0, 129.6, 128.7, 128.6, 126.6, 125.4, 125.1, 123.5, 122.7, 118.7, 115.3, 112.3, 72.7, 71.2, 68.1, 58.9, 58.9, 41.1, 40.8, 35.6, 21.6.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd for $C_{32}H_{32}N_2NaO_5S^+$: 579.1924; Found: 579.1930.

The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 11.607 min, t_R(major) = 13.319 min.



9, 85%, 93% ee

(1*S*, 2*R*, 5*R*, 6*S*)-5, 6-Bis(methoxymethyl)-2-(2-(3-methoxyphenyl)-1-tosyl-1*H*-indol-3-yl)cyclohex-3-en-1-ol

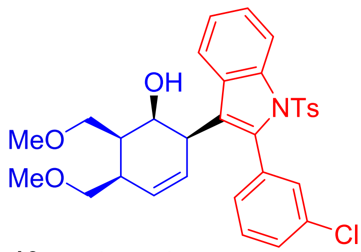
85.4 mg, 85% yield, 93% ee, colorless oil, PE/EA = 2/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.90 – 6.76 (m, 2H), 5.78 – 5.74 (m, 1H), 5.66 (d, *J* = 8.0 Hz, 1H), 4.27 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 3.69 (s, 1H), 3.52 – 3.48 (m, 4H), 3.44 (s, 3H), 3.35 – 3.29 (m, 4H), 2.54 (s, 1H), 2.32 – 2.27 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.6, 144.4, 137.0, 136.7, 136.0, 132.7, 131.0, 129.4, 128.4, 128.2, 126.9, 124.3, 123.7, 123.0, 122.7, 117.4, 116.7, 115.1, 114.7, 73.0, 71.4, 68.7, 58.9, 58.8, 55.2, 41.1, 40.9, 35.7, 21.6.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{32}H_{36}NO_6S^+$: 562.2258; Found: 562.2253.

The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 7.385 min, t_R(major) = 9.258 min.



10, 63%, 87% ee

(1*S*, 2*R*, 5*R*, 6*S*)-2-(2-(3-Chlorophenyl)-1-tosyl-1*H*-indol-3-yl)-5, 6-bis(methoxymethyl)cyclohex-3-en-1-ol

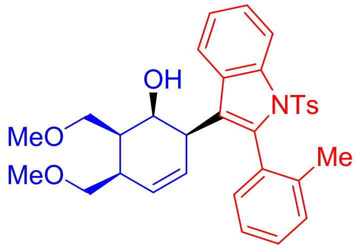
71.2 mg, 63% yield, 87% ee, white solid, M.p: 154.1~159.2 °C, PE/EA = 2/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.31 (m, 5H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.20 – 7.12 (m, 3H), 5.74 (s, 1H), 5.64 (s, 1H), 4.34 (s, 1H), 3.66 (s, 1H), 3.55 – 3.49 (m, 4H), 3.44 (s, 3H), 3.33 – 3.26 (m, 4H), 2.54 (s, 1H), 2.34 – 2.29 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.7, 137.0, 135.9, 135.1, 133.3, 133.2, 130.8, 129.5, 129.0, 128.8, 128.7, 128.4, 126.8, 124.6, 124.2, 123.2, 122.7, 122.5, 115.1, 72.9, 71.3, 68.4, 68.2, 58.9, 58.8, 41.1, 40.8, 35.7, 21.6.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{31}H_{33}ClNO_5S^+$: 556.1762; Found: 556.1764.

The product was analyzed by HPLC to determine the enantiomeric excess: 87% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 6.232 min, t_R(major) = 7.252 min.



11. 86%, 81% ee

(1*S*, 2*R*, 5*R*, 6*S*)-5, 6-Bis(methoxymethyl)-2-(2-(*o*-tolyl)-1-tosyl-1*H*-indol-3-yl)cyclohex-3-en-1-ol

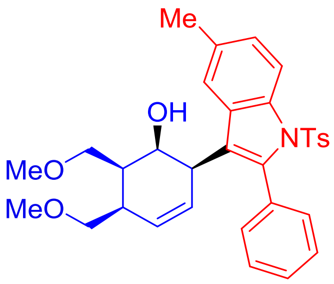
94.4 mg, 86% yield, 81% ee, white solid, M.p: 169.0~171.2 °C, PE/EA = 2/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.37 – 7.28 (m, 3H), 7.22 – 7.11 (m, 4H), 6.89 (d, *J* = 8.0 Hz, 1H), 5.80 – 5.71 (m, 2H), 4.25 (d, *J* = 12.0 Hz, 1 H), 3.53 – 3.48 (m, 4H), 3.42 – 3.35 (m, 5H), 3.29 (s, 3H), 2.52 (s, 1H), 2.3 4 (s, 3H), 2.22 – 2.18 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.4, 140.9, 136.7, 136.4, 136.1, 131.2, 131.1, 131.0, 129.7, 129.4, 129.3, 129.1, 128.3, 127.0, 124.7, 124.1, 122.8, 122.6 , 122.3, 114.8, 73.0, 71.3, 67.1, 58.8, 41.0, 40.9, 35.5, 21.6, 20.4.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{32}H_{36}NO_5S^+$: 546.2309; Found: 546.2312.

The product was analyzed by HPLC to determine the enantiomeric excess: 81% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 5.871 min, t_R(major) = 9.359 min.



12, 89%, 98% ee

(1*S*, 2*R*, 5*R*, 6*S*)-5, 6-Bis(methoxymethyl)-2-(5-methyl-2-phenyl-1-tosyl-1*H*-indol-3-yl)cyclohex-3-en-1-ol.

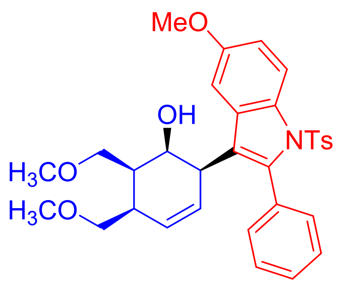
97.1 mg, 89% yield, 98% ee, white solid, M.p: 162.0~167.4 °C, PE/EA = 2/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.50 (s, 1H), 7.45 – 7.34 (m, 6H), 7.29 – 7.24 (m, 1H), 7.13 – 7.08 (m, 3H), 5.77 – 5.73 (m, 1H), 5.64 – 5.61 (m, 1H), 4.34 (d, *J* = 8.0 Hz, 1H), 3.65 (s, 1H), 3.57 – 3.48 (m, 4H), 3.46 (s, 3H), 3.33 (s, 3H), 3.30 – 3.27 (m, 1H), 2.56 – 2.50 (m, 1H), 2.39 (s, 3H), 2.31 – 2.26 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.3, 137.0, 135.9, 135.2, 132.4, 132.0, 131.3, 129.5, 129.4, 128.6, 128.0, 127.4, 126.8, 125.7, 123.7, 122.6, 114.8, 73.0, 71.3, 68.6, 58.9, 58.8, 41.1, 40.8, 35.6, 21.6.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd for $C_{32}H_{35}NNaO_5S^+$: 568.2128; Found: 568.2163.

The product was analyzed by HPLC to determine the enantiomeric excess: 98% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 6.607 min, t_R(major) = 8.399 min.



13, 96%, 93% ee

(1*S*, 2*R*, 5*R*, 6*S*)-2-(5-Methoxy-2-phenyl-1-tosyl-1*H*-indol-3-yl)-5, 6-bis(methoxy methyl)cyclohex-3-en-1-ol.

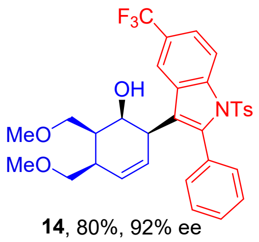
108.2 mg, 96% yield, 93% ee, white solid, M.p: 147.1~150.8 °C, PE/EA = 2/ 1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.36 – 7.31 (m, 3H), 7.30 – 7.26 (m, 1H), 7.22 (d, *J* = 4.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.91 (dd, *J* = 12.0, 4.0 Hz, 1H), 5.78 – 5.74 (m, 1 H), 5.65 (dd, *J* = 12.0, 4.0 Hz, 1H), 4.32 (d, *J* = 4.0 Hz, 1H), 3.79 (s, 3H), 3.66 (s, 1H), 3.55 – 3.46 (m, 4H), 3.42 (s, 3H), 3.33 (s, 3H), 3.29 – 3.26 (m, 1H), 2.58 – 2.50 (m, 1H), 2.35 – 2.26 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.0, 144.3, 137.8, 135.7, 132.2, 131.7, 131.5, 129.4, 129.3, 128.7, 128.2, 127.4, 126.8, 124.0, 116.0, 113.0, 105.6, 73. 0, 71.5, 68.7, 58.9, 58.8, 55.4, 41.1, 40.8, 35.6, 21.6.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd for $C_{32}H_{35}NNaO_6S^+$: 584.2077; Found: 5 84.2084.

The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 8.282 min, t_R(major) = 9.707 min.



14, 80%, 92% ee

(1*S*, 2*R*, 5*R*, 6*S*)-5, 6-Bis(methoxymethyl)-2-(2-phenyl-1-tosyl-5-(trifluoromethyl)-1*H*-indol-3-yl)cyclohex-3-en-1-ol.

128.1 mg, 80% yield, 92% ee, white solid, M.p: 158.1~162.1 °C, PE/EA = 2/1.

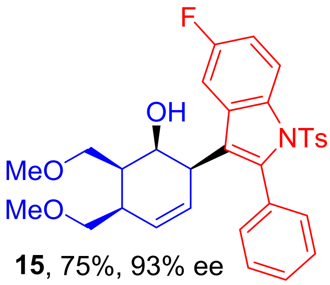
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 8.0 Hz, 1H), 8.07 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.42 – 7.38 (m, 2H), 7.36 – 7.34 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.83 – 5.79 (m, 1H), 5.66 – 5.62 (m, 1H), 4.77 (d, *J* = 8.0 Hz, 1H), 3.62 – 3.58 (m, 1H), 3.55 – 3.44 (m, 7H), 3.32 (s, 3H), 3.28 – 3.26 (m, 1H), 2.57 – 2.53 (m, 1H), 2.34 – 2.27 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.9, 138.4, 138.2, 135.8, 131.4 (d, *J* = 40.4 Hz), 130.8, 130.7, 129.6, 129.1 (d, *J* = 10.1 Hz), 128.7, 127.6, 126.9, 126.2, 125.0 (q, *J* = 30.3 Hz), 123.6, 123.5, 120.8 (q, *J* = 10.1 Hz), 120.5 (q, *J* = 10.1 Hz), 115.2, 72.8, 70.9, 68.1, 58.9, 58.8, 40.9, 40.6, 35.5, 21.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.1.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{32}H_{33}F_3NO_5S^+$: 600.2026; Found: 600.2017.

The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 5.428 min, t_R(major) = 5.955 min.



15, 75%, 93% ee

(1*S*, 2*R*, 5*R*, 6*S*)-2-(5-Fluoro-2-phenyl-1-tosyl-1*H*-indol-3-yl)-5, 6-bis(methoxymethyl)cyclohex-3-en-1-ol.

82.4 mg, 75% yield, 93% ee, white solid, M.p: 135.3~139.8 °C, PE/EA = 2/1.

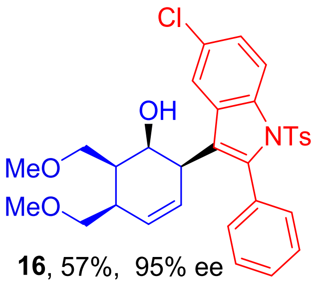
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (q, *J* = 4.0 Hz, 1H), 7.46 – 7.37 (m, 4H), 7.34 – 7.30 (m, 3H), 7.27 – 7.24 (m, 1H), 7.11 – 7.09 (m, 2H), 7.02 (td, *J* = 12.0, 4.0 Hz, 1H), 5.80 – 5.76 (m, 1H), 5.63 – 5.59 (m, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 3.64 – 3.60 (m, 1H), 3.55 – 3.45 (m, 7H), 3.32 (s, 3H), 3.27 – 3.24 (m, 1H), 2.56 – 2.51 (m, 1H), 2.33 (s, 3H), 2.31 – 2.25 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.4 (d, *J* = 232.3 Hz), 144.6, 138.5, 135.7, 133.3, 132.4 (d, *J* = 10.1 Hz), 131.1, 129.4, 129.1, 128.9, 128.6, 127.5, 126.8, 123.7 (d, *J* = 10.1 Hz), 116.1 (d, *J* = 10.1 Hz), 112.1 (d, *J* = 30.3 Hz), 108.4 (d, *J* = 30.3 Hz), 72.9, 71.1, 68.4, 58.9, 53.5, 41.0, 40.6, 35.5, 21.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.3.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{31}H_{33}FNO_5S^+$: 550.2058; Found: 550.2016.

The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min,254 nm), t_R(minor) = 6.882 min, t_R(major) = 8.913 min.



16, 57%, 95% ee

(1*S*, 2*R*, 5*R*, 6*S*)-2-(5-Chloro-2-phenyl-1-tosyl-1*H*-indol-3-yl)-5, 6-bis(methoxymethyl)cyclohex-3-en-1-ol.

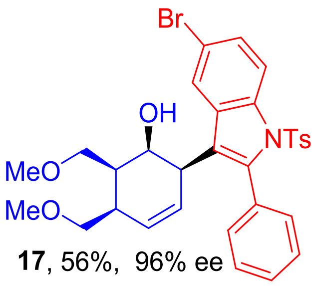
64.5 mg, 57% yield, 95% ee, white solid, M.p: 144.8~150.3 °C, PE/EA = 2/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 4.0 Hz, 1H), 7.49 – 7.35 (m, 3H), 7.36 – 7.29 (m, 3H), 7.24 (s, 2H), 7.14 – 7.07 (m, 2H), 5.83 – 5.75 (m, 1H), 5.65 – 5.57 (m, 1H), 4.62 (d, *J* = 8.0 Hz, 1H), 3.61 – 3.45 (m, 8H), 3.32 (s, 3H), 3.27 – 3.24 (m, 1H), 2.31 – 2.25 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.7, 138.1, 135.7, 135.3, 132.5, 131.0, 129.5, 129.2, 128.9, 128.6, 127.5, 126.8, 124.3, 123.2, 122.5, 116.1, 72.8, 70.9, 68.2, 59.0, 58.9, 41.0, 40.5, 35.5, 21.6.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd for $C_{31}H_{32}ClNNaO_5S^+$: 588.1582; Found: 588.1605.

The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 6.228 min, t_R(major) = 8.053 min.



17, 56%, 96% ee

(1*S*, 2*R*, 5*R*, 6*S*)-2-(5-Bromo-2-phenyl-1-tosyl-1*H*-indol-3-yl)-5, 6-bis(methoxymethyl)cyclohex-3-en-1-ol.

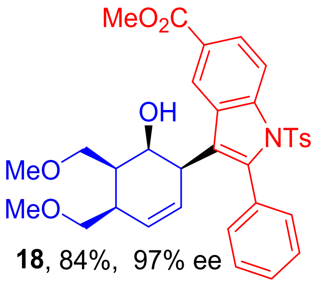
68.2 mg, 56% yield, 96% ee, white solid, M.p: 171.8~175.6 °C, PE/EA = 2/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 4.0 Hz, 1H), 7.46 – 7.36 (m, 4H), 7.33 – 7.27 (m, 3H), 7.25 – 7.20 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.81 – 5.77 (m, 1H), 5.59 (d, *J* = 8.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 3.60 – 3.44 (m, 8H), 3.32 (s, 3H), 3.26 – 3.24 (m, 1H), 2.53 (d, *J* = 4.0 Hz, 1H), 2.33 (s, 3H), 2.31 – 2.25 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.7, 137.9, 135.7, 135.7, 133.0, 130.9, 129.5, 129.2, 128.9, 128.6, 127.5, 126.9, 126.8, 125.6, 123.1, 116.5, 116.5, 72.8, 70.9, 68.1, 59.1, 58.9, 40.9, 40.5, 35.5, 21.6.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{31}H_{33}BrNO_5S^+$: 610.1257; Found: 610.1268.

The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 6.157 min, t_R(major) = 8.786 min.



18, 84%, 97% ee

Methyl 3-((1*R*, 4*R*, 5*S*, 6*S*)-6-hydroxy-4, 5-bis(methoxymethyl)cyclohex-2-en-1-yl)-2-phenyl-1-tosyl-1*H*-indole-5-carboxylate.

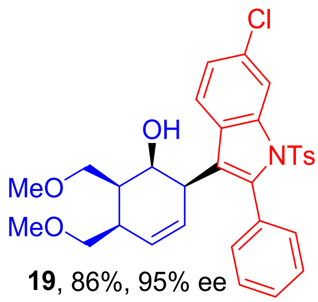
99.5 mg, 84% yield, 97% ee, pale yellow solid, M.p: 136.4~141.1 °C, PE/EA = 3/2.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 4.0 Hz, 1H), 8.32 (d, *J* = 12.0 Hz, 1H), 7.99 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.46 – 7.34 (m, 5H), 7.33 – 7.27 (m, 1H), 7.25 – 7.19 (m, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.83 – 5.78 (m, 1H), 5.65 – 5.62 (m, 1H), 4.73 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 3H), 3.65 – 3.60 (m, 1H), 3.58 – 3.45 (m, 7H), 3.32 (s, 3H), 3.30 – 3.27 (m, 1H), 2.58 – 2.51 (m, 1H), 2.32 – 2.26 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 144.8, 139.6, 137.9, 135.8, 130.9, 130.8, 129.5, 129.1, 128.9, 128.6, 127.5, 126.9, 125.4, 125.2, 125.0, 124.1, 114.6, 72.9, 70.9, 68.2, 59.1, 58.9, 51.9, 41.0, 40.7, 35.6, 21.6.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd for $C_{33}H_{35}NNaO_7S^+$: 612.2026; Found: 612.2032.

The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min,250 nm), t_R(minor) = 7.863 min, t_R(major) = 10.054 min.



19, 86%, 95% ee

(1*S*, 2*R*, 5*R*, 6*S*)-2-(6-Chloro-2-phenyl-1-tosyl-1*H*-indol-3-yl)-5, 6-bis(methoxymethyl)cyclohex-3-en-1-ol.

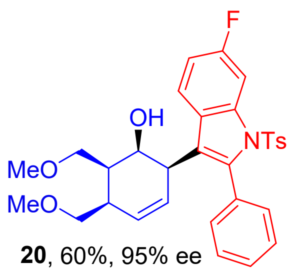
96.8 mg, 86% yield, 95% ee, pale yellow solid, M.p: 103.6~108.6 °C, PE/EA = 2/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 4.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.33 (m, 5H), 7.31 – 7.27 (m, 1H), 7.24 – 7.20 (m, 1H), 7.17 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.78 – 5.74 (m, 1 H), 5.64 – 5.60 (m, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 3.66 – 3.57 (m, 1H), 3. 53 – 3.45 (m, 4H), 3.44 (s, 3H), 3.32 (s, 3H), 3.27 – 3.22 (m, 1H), 2.57 – 2.4 9 (m, 1H), 2.34 (s, 3H), 2.30 – 2.24 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.8, 137.3, 137.3, 135.8, 130.9, 130.1, 129.5, 129.1, 128.9, 128.5, 127.5, 126.9, 123.6, 123.5, 123.4, 115.1, 72.9, 71.3, 68.4, 58.9, 58.9, 41.0, 40.7, 35.6, 21.6.

HRMS(ESI): m/z: [M + Na]$^+$ Calcd for $C_{31}H_{32}ClNNaO_5S^+$: 588.1582; Found: 5 88.1599.

The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 5.715 min, t_R(major) = 6.192 min.



20, 60%, 95% ee

(1*S*, 2*R*, 5*R*, 6*S*)-2-(6-Fluoro-2-phenyl-1-tosyl-1*H*-indol-3-yl)-5, 6-bis(methoxymethyl)cyclohex-3-en-1-ol.

66.0 mg, 60% yield, 95% ee, white solid, M.p: 160.1~162.2 °C, PE/EA = 2/1.

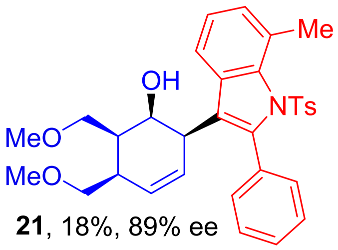
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 12.0, 4.0 Hz, 1H), 7.65 (d, *J* = 16.0 Hz, 1H), 7.46 – 7.34 (m, 5H), 7.29 (d, *J* = 4.0 Hz, 1H), 7.22 (d, *J* = 4.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.96 (dt, 1H), 5.78 – 5.74 (m, 1H), 5.66 – 5.62 (m, 1H), 4.43 (d, *J* = 8.0 Hz, 1H), 3.66 – 3.61 (m, 1H), 3.54 – 3.44 (m, 7H), 3.32 (s, 3H), 3.27 – 3.24 (m, 1H), 2.55 – 2.51 (m, 1H), 2.34 (s, 3H), 2.31 – 2.25 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.7 (d, *J* = 240.4 Hz), 144.7, 137.1 (d, *J* = 10.1 Hz), 137.0 (d, *J* = 10.1 Hz), 135.7, 131.1, 129.5, 129.3, 128.6 (d, *J* = 40.4 Hz), 127.5, 127.3 (d, *J* = 10.1 Hz), 126.9, 123.5, 123.4, 111.3 (d, *J* = 20.2 Hz), 102.3 (d, *J* = 30.3 Hz), 72.9, 71.3, 68.5, 58.9, 58.9, 41.1, 40.8, 35.6, 21.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.4.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{31}H_{33}FNO_5S^+$: 550.2058; Found: 550.2063.

The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 254 nm), t_R(minor) = 6.128 min, t_R(major) = 6.985 min.



21, 18%, 89% ee

(1*S*, 2*R*, 5*R*, 6*S*)-5, 6-Bis(methoxymethyl)-2-(7-methyl-2-phenyl-1-tosyl-1*H*-indol-3-yl)cyclohex-3-en-1-ol

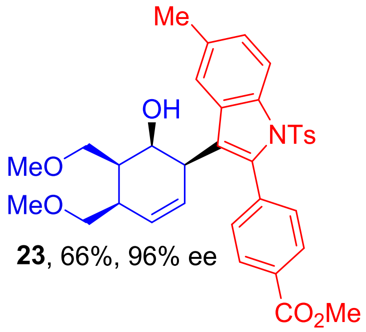
19.7 mg, 18% yield, 89% ee, white solid, M.p: 151.6~152.5 °C, PE/EA = 2/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.44 (m, 1H), 7.38 – 7.37 (m, 3H), 7.28 – 7.24 (m, 2H), 7.16 – 7.15 (m, 2H), 6.97 (dd, *J* = 32.0, 8.0 Hz, 4H), 5.74 – 5.69 (m, 1H), 5.40 (d, *J* = 8.0 Hz, 1H), 3.56 – 3.45 (m, 6H), 3.44 (s, 3H), 3.39 (s, 3H), 3.34 (d, *J* = 8.0 Hz, 1H), 2.82 (s, 3H), 2.53 (s, 1H), 2.36 – 2.27 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d* Chloroform-*d*) δ 144.2, 140.7, 140.4, 135.6, 133.6, 132.0, 130.6, 130.0, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 127.6, 127.0, 124.9, 120.9, 72.8, 72.0, 68.9, 58.9, 58.9, 41.1, 40.4, 35.7, 21.7, 21.5.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{32}H_{36}NO_5S^+$: 546.2309; Found: 546.2301.

The product was analyzed by HPLC to determine the enantiomeric excess: 89% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 10.701 min, t_R(major) = 11.577 min.



23, 66%, 96% ee

Methyl 4-(3-((1*R*, 4*R*, 5*S*, 6*S*)-6-hydroxy-4, 5-bis(methoxymethyl)cyclohex-2-en-1-yl)-5-methyl-1-tosyl-1*H*-indol-2-yl)benzoate.

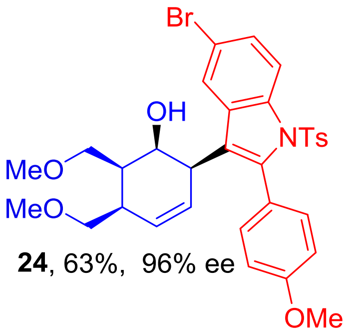
79.7 mg, 66% yield, 96% ee, white solid, M.p: 156.7~161.5 °C, PE/EA = 3/2.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 12.0 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 2H), 7.5 – 7.5 (m, 1H), 7.5 – 7.3 (m, 4H), 7.15 – 7.08 (m, 3H), 5.75 – 5.71 (m, 1H), 5.61 – 5.57 (m, 1H), 4.41 (d, *J* = 12.0 Hz, 1H), 3.96 (s, 3H), 3.65 – 3.61 (m, 1H), 3.55 – 3.45 (m, 7H), 3.32 (s, 3H), 3.29 – 3.25 (m, 1H), 2.55 – 2.51 (m, 1H), 2.39 (s, 3H), 2.31 – 2.26 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 144.5, 136.6, 135.8, 135.5, 135.4, 132.7, 131.4, 130.1, 129.5, 129.1, 128.6, 128.2, 126.7, 126.1, 124.7, 122.7, 114.9, 72.8, 71.2, 68.3, 58.9, 58.8, 52.3, 41.0, 40.8, 35.6, 21.6.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{34}H_{38}NO_7S^+$: 604.2364; Found: 604.2370.

The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 7.847 min, t_R(major) = 8.782 min.



24, 63%, 96% ee

(1*S*, 2*R*, 5*R*, 6*S*)-2-(5-Bromo-2-(4-methoxyphenyl)-1-tosyl-1*H*-indol-3-yl)-5, 6-bis(methoxymethyl)cyclohex-3-en-1-ol.

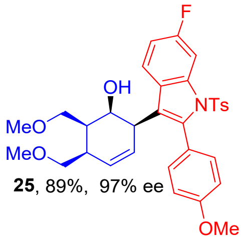
80.7 mg, 63% yield, 96% ee, yellow oil, PE/EA = 2/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 4.0 Hz, 1H), 7.36 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.31 (d, *J* = 12.0 Hz, 2H), 7.23 – 7.16 (m, 1H), 7.14 – 7.09 (m, 3H), 6.92 (d, *J* = 8.0 Hz, 2H), 5.81 – 5.77 (m, 1H), 5.61 – 5.58 (m, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 3.88 (s, 3H), 3.59 – 3.46 (m, 8H), 3.32 (s, 3H), 3.27 – 3.24 (m, 1H), 2.56 – 2.51 (m, 1H), 2.33 – 2.26 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.0, 144.6, 137.9, 135.8, 135.6, 133.0, 129.5, 129.3, 128.6, 126.8, 126.8, 125.4, 122.9, 122.9, 116.5, 116.5, 113.1, 112.9, 72.8, 70.9, 68.1, 59.1, 58.9, 55.3, 41.0, 40.6, 35.5, 21.6.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{32}H_{35}BrNO_6S^+$: 640.1363; Found: 640.1373.

The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 7.477 min, t_R(major) = 8.836 min.



25, 89%, 97% ee

(1*S*, 2*R*, 5*R*, 6*S*)-2-(6-Fluoro-2-(4-methoxyphenyl)-1-tosyl-1*H*-indol-3-yl)-5, 6-bis(methoxymethyl)cyclohex-3-en-1-ol.

102.6 mg, 89% yield, 97% ee, white solid, M.p: 97.4~101.2 °C, PE/EA = 2/1.

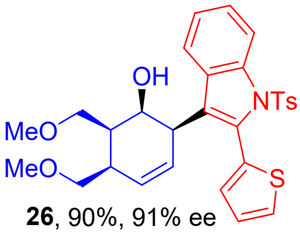
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.63 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.16 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 3H), 6.97 – 6.89 (m, 3H), 5.78 – 5.73 (m, 1H), 5.65 – 5.62 (m, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 3.87 (s, 3H), 3.65 – 3.59 (m, 1H), 3.54 – 3.46 (m, 4H), 3.44 (s, 3H), 3.32 (s, 3H), 3.28 – 3.23 (m, 1H), 2.58 – 2.50 (m, 1H), 2.33 – 2.26 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.6 (d, *J* = 242.4 Hz), 159.9, 144.6, 137.0 (d, *J* = 10.1 Hz), 137.0, 135.9, 129.5, 129.3, 128.4, 127.3 (d, *J* = 10.1 Hz), 126.9, 123.3, 123.2 (d, *J* = 20.2 Hz), 112.9 (d, *J* = 20.2 Hz), 111.2 (d, *J* = 20.2 Hz), 102.3 (d, *J* = 30.3 Hz), 72.9, 71.3, 68.5, 58.9, 58.9, 55.3, 41.1, 40.8, 35.6, 21.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.6.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{32}H_{35}FNO_6S^+$: 580.2164; Found: 580.2177.

The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 6.765 min, t_R(major) = 7.516 min.



26, 90%, 91% ee

(1*S*, 2*R*, 5*R*, 6*S*)-5, 6-Bis(methoxymethyl)-2-(2-(thiophen-2-yl)-1-tosyl-1*H*-indol-3-yl)cyclohex-3-en-1-ol.

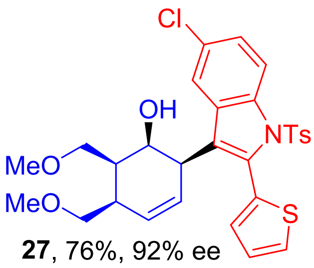
96.8 mg, 90% yield, 91% ee, white solid, M.p: 122.1~128.0 °C, PE/EA = 4/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.47 (m, 3H), 7.36 – 7.32 (m, 1H), 7.24 – 7.20 (m, 1H), 7.15 – 7.10 (m, 3H), 7.05 – 7.04 (m, 1H), 5.83 – 5.78 (m, 1H), 5.74 – 5.70 (m, 1H), 4.38 (d, *J* = 8.0 Hz, 1H), 3.76 (s, 1H), 3.59 – 3.52 (m, 4H), 3.47 (s, 3H), 3.45 – 3.42 (m, 1H), 3.36 (s, 3H), 2.61 – 2.56 (m, 1H), 2.41 – 2.35 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.5, 137.3, 135.9, 131.6, 131.2, 130.5, 129.5, 129.1, 128.7, 128.3, 126.9, 126.7, 126.4, 124.8, 123.0, 122.8, 115.0, 73.0, 71.4, 68.8, 58.9, 58.9, 41.2, 41.1, 35.7, 21.6.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{29}H_{32}NO_5S_2^+$: 538.1716; Found: 538.1716.

The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 254 nm), t_R(minor) = 8.880 min, t_R(major) = 10.610 min.



27, 76%, 92% ee

(1*S*, 2*R*, 5*R*, 6*S*)-2-(5-Chloro-2-(thiophen-2-yl)-1-tosyl-1*H*-indol-3-yl)-5,6-bis(methoxymethyl)cyclohex-3-en-1-ol.

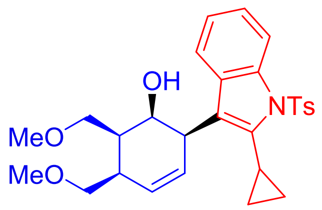
86.5 mg, 76% yield, 92% ee, white solid, M.p: 108.1~113.0 °C, PE/EA = 4/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 4.0 Hz, 1H), 7.49 – 7.47 (m, 1H), 7.42 – 7.40 (m, 2H), 7.27 – 7.24 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.10 – 7.08 (m, 1H), 7.03 – 7.01 (m, 1H), 5.84 – 5.79 (m, 1H), 5.65 – 5.61 (m, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 3.71 – 3.67 (m, 1H), 3.58 – 3.48 (m, 7H), 3.39 – 3.36 (m, 1H), 3.33 (s, 3H), 2.59 – 2.54 (m, 1H), 2.38 – 2.32 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.8, 135.7, 135.7, 131.9, 131.8, 130.5, 129.9, 129.6, 129.0, 128.7, 128.6, 128.5, 126.9, 126.5, 126.1, 124.8, 122.6, 116.0, 72.8, 70.9, 68.3, 59.0, 58.9, 41.0, 40.9, 35.5, 21.6.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{29}H_{31}ClNO_5S_2^+$: 572.1327; Found: 572.1331.

The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 7.383 min, t_R(major) = 9.143 min.



28, 83%, 81% ee

(1*S*, 2*R*, 5*R*, 6*S*)-2-(2-cyclopropyl-1-tosyl-1*H*-indol-3-yl)-5, 6-bis(methoxymethyl)cyclohex-3-en-1-ol.

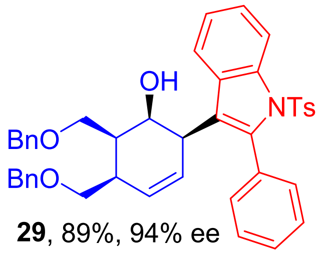
82.4 mg, 83% yield, 81% ee, yellow oil, PE/EA = 5/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.09 (m, 4H), 5.85 – 5.81 (m, 1H), 5.70 – 5.67 (m, 1H), 4.15 (d, *J* = 8.0 Hz, 1H), 4.03 (s, 1H), 3.84 (d, *J* = 8.0 Hz, 1H), 3.63 – 3.54 (m, 4H), 3.45 (s, 3H), 3.38 (s, 3H), 2.69 – 2.62 (m, 1H), 2.57 – 2.49 (m, 1H), 2.33 (s, 3H), 1.97 – 1.90 (m, 1H), 1.06 – 0.96 (m, 2H), 0.79 – 0.74 (m, 1H), 0.50 – 0.45 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.2, 138.4, 137.1, 136.9, 131.1, 129.7, 129.5, 128.2, 126.3, 124.0, 123.9, 122.7, 122.6, 114.7, 72.9, 71.7, 68.1, 59.0, 41.6, 40.7, 35.9, 21.6, 8.6, 8.5, 8.3.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{28}H_{34}NO_5S^+$: 496.2152; Found: 496.2160.

The product was analyzed by HPLC to determine the enantiomeric excess: 81% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 8.955 min, t_R(major) = 10.181 min.



29, 89%, 94% ee

(1*S*, 2*R*, 5*R*, 6*S*)-5, 6-Bis((benzyloxy)methyl)-2-(2-phenyl-1-tosyl-1*H*-indol-3-yl) cyclohex-3-en-1-ol.

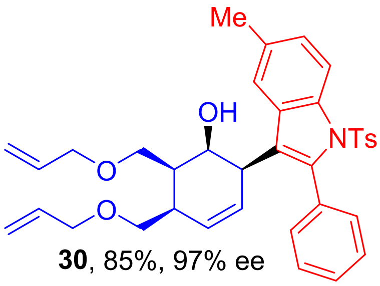
122.5 mg, 89% yield, 94% ee, white solid, M.p: 89.3~93.7 °C, PE/EA = 5/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.31 (m, 18H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.04 (t, *J* = 8. 0 Hz, 1H), 5.84 – 5.80 (m, 1H), 5.73 (d, *J* = 8.0 Hz, 1H), 4.63 – 4.35 (m, 5 H), 3.76 (d, *J* = 8.0 Hz, 1H), 3.60 (d, *J* = 4.0 Hz, 4H), 3.37 (s, 1H), 2.66 (s, 1H), 2.43 – 2.35 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.5, 138.4, 137.0, 136.9, 136.1, 131.6, 130.9, 129.5, 129.3, 128.8, 128.7, 128.4, 128.4, 128.4, 128.2, 127.9, 127.7, 127.5 , 126.9, 124.3, 123.8, 123.0, 122.8, 115.0, 73.6, 73.2, 70.6, 68.9, 68.8, 41.4, 4 0.9, 35.6, 21.6.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd for $C_{43}H_{41}NNaO_5S^+$: 706.2598; Found: 706.2 627.

The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 7.746 min, t_R(major) = 9.454 min.



30, 85%, 97% ee

(1*S*, 2*R*, 5*R*, 6*S*)-5, 6-Bis((allyloxy)methyl)-2-(5-methyl-2-phenyl-1-tosyl-1*H*-indol-3-yl)cyclohex-3-en-1-ol.

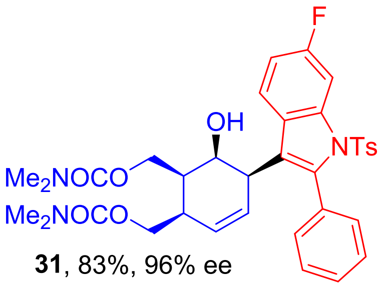
101.6 mg, 85% yield, 97% ee, white solid, M.p: 63.3~66.6 °C, PE/EA = 5/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 12.0 Hz, 1H), 7.50 (s, 1H), 7.45 – 7.35 (m, 5H), 7.34 – 7.22 (m, 2H), 7.13 – 7.08 (m, 3H), 5.97 – 5.85 (m, 2H), 5.79 – 5.75 (m, 1H), 5.68 (dd, *J* = 12.0, 4.0 Hz, 1H), 5.31 (dd, *J* = 16.0, 4.0 Hz, 1H), 5.27 – 5.21 (m, 2H), 5.16 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.36 (d, *J* = 12.0 Hz, 1H), 4.13 – 4.05 (m, 2H), 4.00 – 3.92 (m, 2H), 3.67 (d, *J* = 12.0 Hz, 1H), 3.63 – 3.53 (m, 4H), 3.28 (s, 1H), 2.63 – 2.55 (m, 1H), 2.38 (s, 3H), 2.34 – 2.29 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.3, 137.0, 136.0, 135.2, 134.8, 133.6, 132.4, 131.7, 131.2, 129.4, 129.4, 128.6, 128.2, 127.4, 126.8, 125.7, 123.7, 122.5 , 118.2, 116.8, 114.8, 72.3, 72.0, 70.5, 68.8, 68.8, 41.3, 40.9, 35.6, 21.6, 21.5.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd for $C_{36}H_{39}NNaO_5S^+$: 620.2441; Found: 620.2444.

The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 5.332 min, t_R(major) = 6.260 min.



31, 83%, 96% ee

((1*S*, 2*R*, 5*R*, 6*S*)-5-(6-Fluoro-2-phenyl-1-tosyl-1*H*-indol-3-yl)-6-hydroxycyclohex-3-ene-1,2-diyl)bis(methylene) bis(dimethylcarbamate).

118.4 mg, 83% yield, 96% ee, white solid, M.p: 191.4~195.3 °C, PE/EA = 1/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 12.0 Hz, 1H), 7.68 (q, *J* = 4.0 Hz, 1H), 7.44 – 7.34 (m, 5H), 7.15 (dd, *J* = 28.0, 8.0 Hz, 4H), 6.98 (t, *J* = 8.0 Hz, 1H), 5.89 (d, *J* = 8.0 Hz, 1H), 5.62 (d, *J* = 8.0 Hz, 1H), 4.46 – 4.42 (m, 1H), 4.36 – 4.27 (m, 2H), 4.20 – 4.16 (m, 1H), 3.81 (s, 1H), 3.33 (s, 1H), 2.90 – 2.83 (m, 12H), 2.62 (s, 1H), 2.35 (s, 3H), 2.12 (q, *J* = 8.0 Hz, 1H), 1.91 (s, 1H).

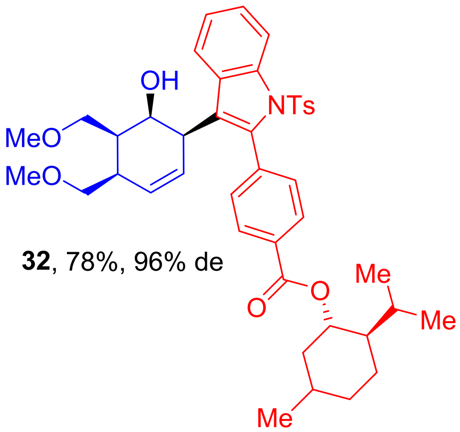
^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.1 (d, *J* = 242.4 Hz), 156.6, 156.5, 145.0, 137.7 (d, *J* = 10.1 Hz), 137.1 (d, *J* = 20.2 Hz), 135.5, 130.8, 129.5, 129.0, 127.9, 127.8, 127.0, 126.6, 123.3 (d, *J* = 10.1 Hz), 121.9, 111.8 (d, *J* = 30.3 Hz), 102.4 (d, *J* = 20.2 Hz), 69.1, 66.1, 64.7, 40.5, 40.4, 36.5, 36.4, 35.9, 35.8, 35.2, 21.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.1.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd for $C_{35}H_{38}FN_3NaO_7S^+$: 686.2307; Found: 686.2323.

The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee

(FLM NY(2) Hexane/*i*-PrOH = 85/15, flow rate: 1.0 mL/min, 254 nm), t_R(minor) = 39.522 min, t_R(major) = 54.163 min.



32, 78%, 96% de

(1*S*, 2*R*)-2-Isopropyl-5-methylcyclohexyl 4-(3-((1*R*, 4*R*, 5*S*, 6*S*)-6-hydroxy-4, 5-bis(methoxymethyl)cyclohex-2-en-1-yl)-1-tosyl-1*H*-indol-2-yl)benzoate.

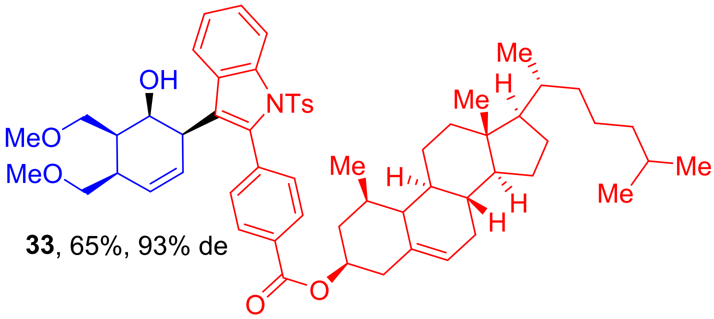
111.3 mg, 78% yield, 96% de, white solid, M.p: 105.4~112.7 °C, PE/EA = 2/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.0 Hz, 1H), 8.08 (s, 2H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.37 (m, 4H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.76 – 5.73 (m, 1H), 5.62 (d, *J* = 8.0 Hz, 1H), 4.99 (td, *J* = 12.0, 4.0 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 3.65 (d, *J* = 8.0 Hz, 1H), 3.54 – 3.46 (m, 4H), 3.43 (s, 3H), 3.33 (s, 3H), 3.30 (s, 1H), 2.53 (s, 1H), 2.37 – 2.26 (m, 4H), 2.19 (d, *J* = 12.0 Hz, 1H), 2.09 – 2.05 (m, 1H), 1.75 (d, *J* = 8.0 Hz, 2H), 1.63 – 1.57 (m, 2H), 1.21 – 1.10 (m, 2H), 0.96 (t, *J* = 8.0 Hz, 7H), 0.84 (d, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 144.7, 137.1, 136.3, 135.8, 135.5, 131.2, 130.9, 129.5, 129.0, 128.6, 128.4, 126.8, 124.9, 124.7, 123.3, 122.9, 115.2, 75.0, 72.9, 71.3, 68.4, 58.9, 58.8, 47.3, 41.1, 41.0, 40.8, 35.6, 34.3, 31.5, 26.3, 23.5, 22.1, 21.6, 20.9, 16.4.

HRMS (ESI): m/z: [M + Na]$^+$ Calcd for $C_{42}H_{51}NNaO_7S^+$: 736.3278; Found: 736.3282.

The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 13.556 min, t_R(major) = 11.151 min.



33, 65%, 93% de

(1*R*, 3*S*, 8*R*, 9*S*, 13*R*, 14*S*, 17*R*)-1, 13-Dimethyl-17-((*R*)-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-(3-((1*R*, 4*R*, 5*S*, 6*S*)-6-hydroxy-4, 5-bis(methoxymethyl)cyclohex-2-en-1-yl)-1-tosyl-1*H*-indol-2-yl)benzoate

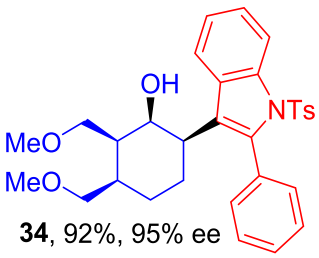
60.9 mg, 65% yield, 93% de, white solid, M.p: 201.1~207.6 °C, PE/EA = 2/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.30 (m, 5H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.76 – 5.72 (m, 1H), 5.61 (d, *J* = 12.0 Hz, 1H), 5.46 (d, *J* = 4.0 Hz, 1H), 4.95 – 4.87 (m, 1H), 4.37 (d, *J* = 12.0 Hz, 1H), 3.63 (d, *J* = 8.0 Hz, 1H), 3.54 – 3.46 (m, 4H), 3.43 (s, 3H), 3.32 (s, 3H), 3.28 (s, 1H), 2.57 – 2.47 (m, 3H), 2.32 – 2.26 (m, 4H), 2.06 – 1.93 (m, 4H), 1.88 – 1.45 (m, 9H), 1.42 – 1.19 (m, 7H), 1.17 – 1.13 (m, 3H), 1.12 – 1.08 (m, 4H), 1.07 – 0.98 (m, 4H), 0.93 (d, *J* = 4.0 Hz, 3H), 0.88 (dd, *J* = 8.0, 4.0 Hz, 6H), 0.70 (s, 3H).

^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 165.8, 144.6, 139.7, 137.1, 136.3, 135.7, 135.6, 131.1, 130.9, 129.5, 129.0, 128.6, 128.4, 126.8, 124.7, 124.7, 123.3, 122.9, 122.8, 115.2, 74.8, 72.9, 71.3, 68.4, 58.9, 58.8, 56.7, 56.2, 50.1, 42.4, 41.1, 40.8, 39.8, 39.5, 38.3, 37.1, 36.7, 36.2, 35.8, 35.6, 32.0, 31.9, 28.3, 28.0, 28.0, 24.3, 23.9, 22.9, 22.6, 21.6, 21.1, 19.4, 18.8, 11.9.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{59}H_{78}NO_7S^+$: 944.5494; Found: 944.5460.

The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 5.322 min, t_R(major) = 5.783 min.



34, 92%, 95% ee

(1*S*, 2*S*, 3*R*, 6*R*)-2, 3-Bis(methoxymethyl)-6-(2-phenyl-1-tosyl-1*H*-indol-3-yl)cyclohexan-1-ol.

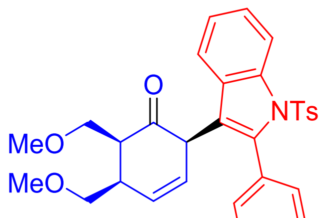
98.1 mg, 92% yield, 95% ee, white solid, M.p: 86.2~92.7 °C, PE/EA = 2/1.

^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.27 (m, 7H), 7.25 – 7.17 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.76 (s, 1H), 3.63 – 3.51 (m, 2H), 3.49 – 3.39 (m, 6H), 3.30 (s, 3H), 2.57 (dt, *J* = 12.0, 4.0 Hz, 1H), 2.33 (s, 3H), 2.30 – 2.19 (m, 1H), 2.00 – 1.80 (m, 3H), 1.44 – 1.34 (m, 1H), 1.25 – 1.20 (m, 1H).

^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 144.4, 137.0, 136.7, 136.0, 131.9, 130.3, 129.3, 128.6, 127.2, 126.9, 125.2, 124.4, 123.2, 122.1, 115.3, 73.6, 73.5, 71.2, 59.0, 58.9, 43.6, 42.5, 34.1, 29.8, 22.1, 21.6.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd for $C_{31}H_{35}NNaO_5S^+$: 556.2128; Found: 5 56.2131.

The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 7.706 min, t_R(major) = 9.152 min.



35, 82%, 96% ee

(2*R*, 5*R*, 6*S*)-5, 6-Bis(methoxymethyl)-2-(2-phenyl-1-tosyl-1*H*-indol-3-yl)cyclohe x-3-en-1-one.

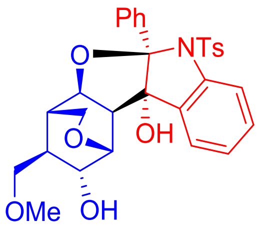
87.0 mg, 82% yield, 96% ee, pale yellow solid, M.p: 96.5~99.8 °C, PE/EA = 8/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 (d, *J* = 12.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.29 (m, 7H), 7.22 – 7.15 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.92 – 5.88 (m, 1H), 5.65 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.09 (s, 1H), 3.80 – 3.76 (m, 1H), 3.55 – 3.51 (m, 1H), 3.45 (d, *J* = 4.0 Hz, 2H), 3.32 (d, *J* = 4.0 Hz, 6H), 3.12 – 3.07 (m, 2H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 204.7, 144.5, 139.1, 137.1, 135.7, 130.8, 129.4, 129.4, 129.2, 128.9, 127.5, 126.8, 124.6, 123.3, 121.4, 119.1, 115.3, 71. 6, 68.7, 59.0, 58.6, 49.1, 48.0, 41.8, 21.6.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd for $C_{31}H_{31}NNaO_5S^+$: 552.1815; Found: 5 52.1817.

The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (FLM INA Hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, 250 nm), t_R(minor) = 6.598 min, t_R(major) = 7.705 min.



36, 46%, 98% ee

(1*R*, 2*R*, 3*R*, 4*S*, 4a*R*, 5a*S*, 10c*R*)-3-(Methoxymethyl)-5a-phenyl-6-tosyl-1, 2, 3, 4, 4a, 5a, 6, 10c-octahydro-10b*H*-1, 4-(epoxymethano)benzofuro[2, 3-*b*]indole-2, 10b-diol.

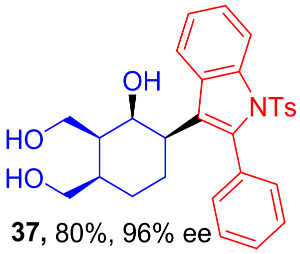
50.0 mg, 46% yield, 98% ee, white solid, M.p: 184.3~188.6 °C, PE/EA = 1/1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.27 (m, 4H), 7.25 – 7.21 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.03 (t, *J* = 8.0 Hz, 1H), 4.30 (d, *J* = 8.0 Hz, 1H), 4.12 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.06 (d, *J* = 4.0 Hz, 1H), 3.94 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.73 (d, *J* = 8.0 Hz, 1H), 3.61 (s, 1H), 3.58 – 3.55 (m, 2H), 3.39 (s, 3H), 2.63 (d, *J* = 12.0 Hz, 1H), 2.35 (s, 3H), 2.23 (s, 1H), 2.08 (s, 1H), 1.53 (q, *J* = 8.0 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 140.0, 137.4, 136.5, 132.7, 129.7, 129.2, 128.6, 128.1, 127.2, 126.1, 123.6, 123.5, 112.9, 112.5, 91.4, 76.7, 73.2, 70.5, 68.9, 59.4, 59.2, 48.9, 42.9, 32.5, 21.5.

HRMS (ESI): m/z: $[M + H]^+$ Calcd for $C_{30}H_{32}NO_7S^+$: 550.1894; Found: 550.1904.

The product was analyzed by HPLC to determine the enantiomeric excess: 98% ee (FLM INA Hexane/*i*-PrOH = 80/20, flow rate: 1.0 mL/min, 272 nm), t_R(minor) = 15.823 min, t_R(major) = 12.376 min.



37, 80%, 96% ee

((1*R*, 2*S*, 3*S*, 4*R*)-3-Hydroxy-4-(2-phenyl-1-tosyl-1*H*-indol-3-yl)cyclohexane-1, 2-diyl)dimethanol.

80.9 mg, 80% yield, 96% ee, white solid, M.p: 195.0~196.7 °C, MeOH/DCM = 1/10.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.33 (m, 6H), 7.27 – 7.25 (m, 1H), 7.24 – 7.20 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.10 – 4.06 (m, 1H), 3.99 (s, 1H), 3.86 – 3.69 (m, 3H), 2.78 (s, 3H), 2.59 (d, *J* = 16.0 Hz, 1H), 2.41 – 2.33 (m, 4H), 1.91 (s, 1H), 1.84 (d, *J* = 16.0 Hz, 1H), 1.64 (s, 1H), 1.48 – 1.41 (m, 1H), 1.33 – 1.26 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.6, 137.0, 135.9, 131.5, 129.9, 129.4, 128.8, 127.5, 126.9, 124.7, 124.1, 123.4, 122.2, 115.4, 74.4, 65.6, 65.0, 44.5, 42.5, 37.6, 30.6, 22.1, 21.6.

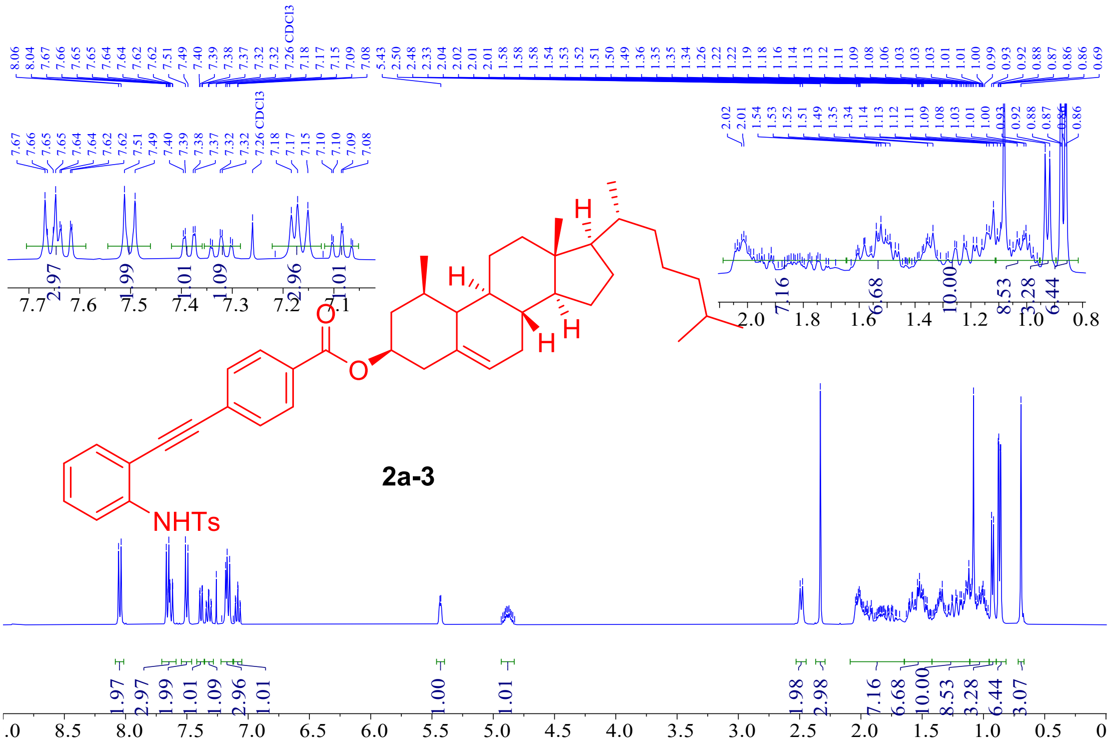
HRMS (ESI): m/z: $[M + Na]^+$ Calcd for $C_{29}H_{31}NNaO_5S^+$: 528.1815; Found: 5

28.1815.

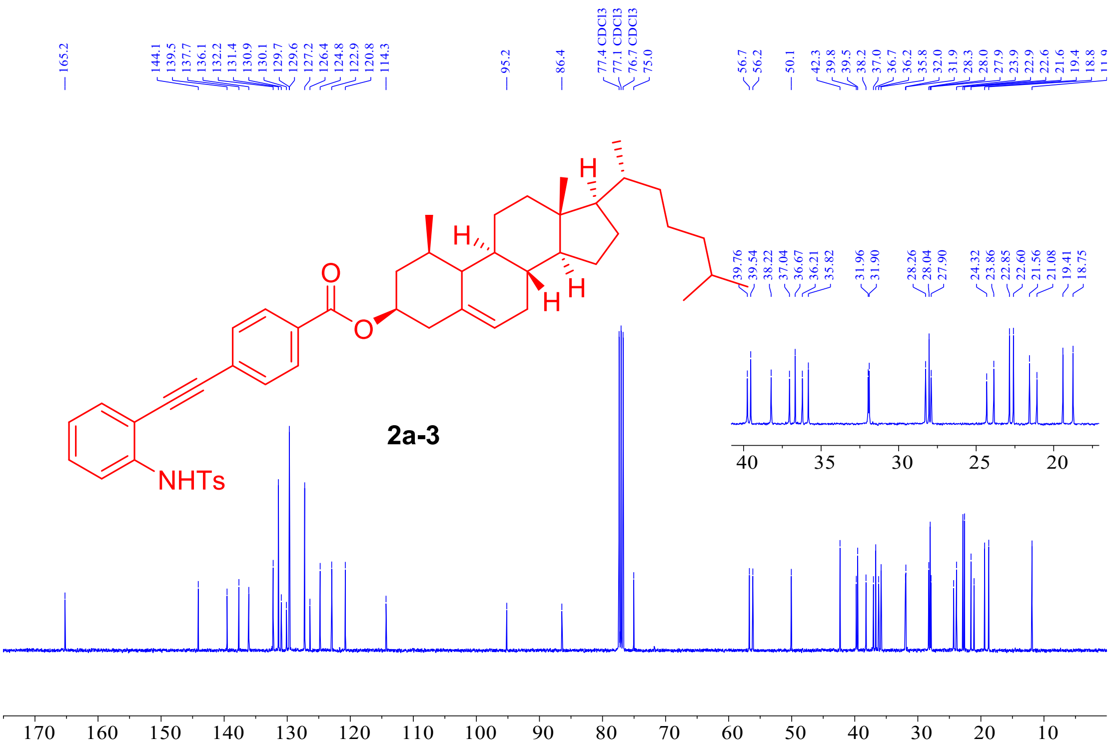
The product was analyzed by HPLC to determine the enantiomeric excess: 98% ee (FLM INA Hexane/*i*-PrOH = 80/20, flow rate: 1.0 mL/min, 272 nm), t_R(minor) = 6.815 min, t_R(major) = 7.739 min.

9. NMR Spectra of New Substrates

¹H NMR (400 MHz, Chloroform-*d*)

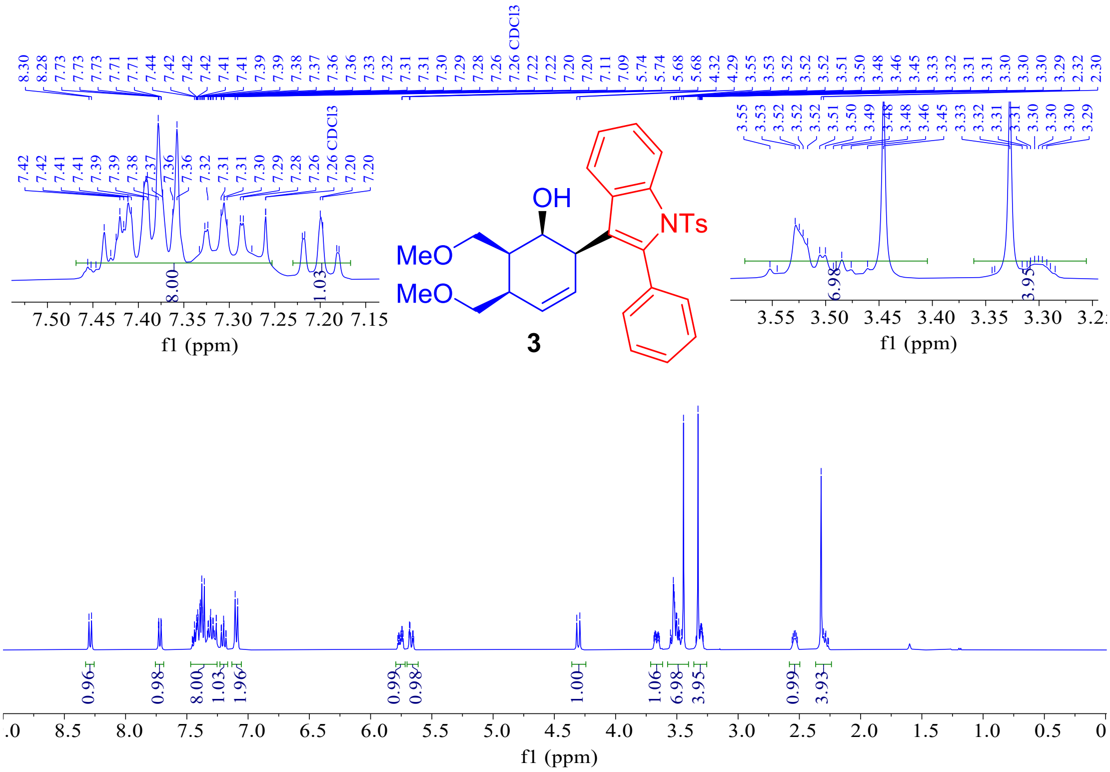


¹³C NMR (101 MHz, Chloroform-*d*)

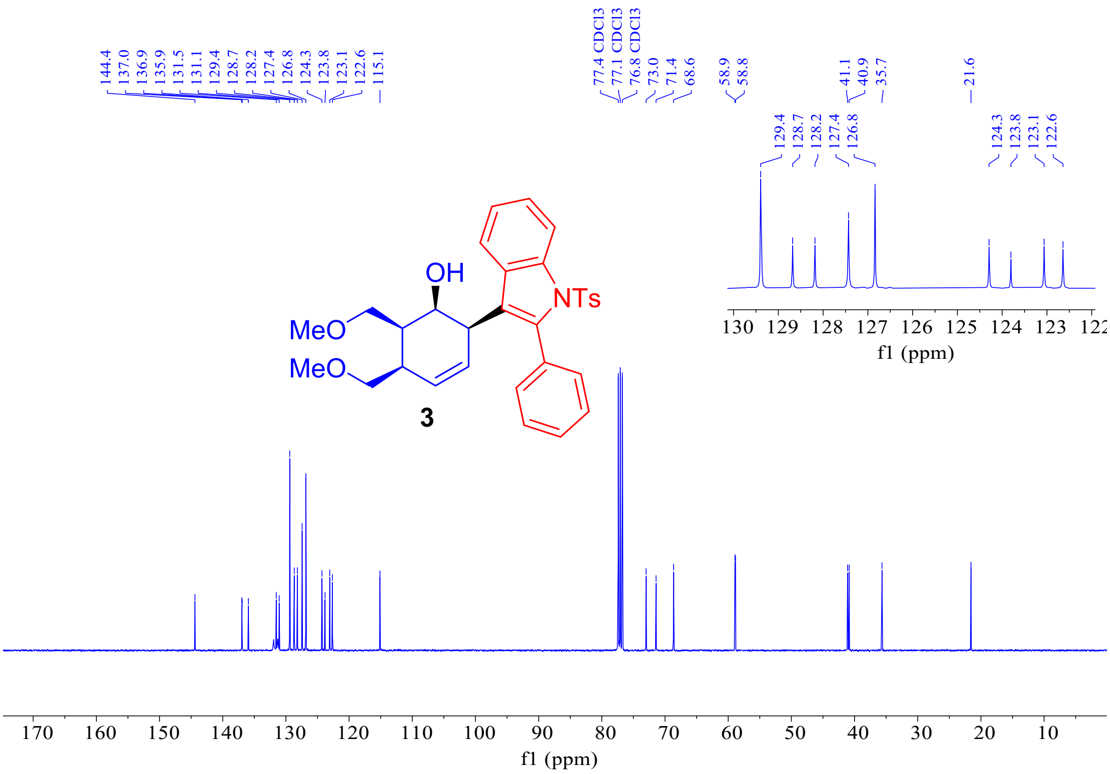


10. NMR Spectra of New Products

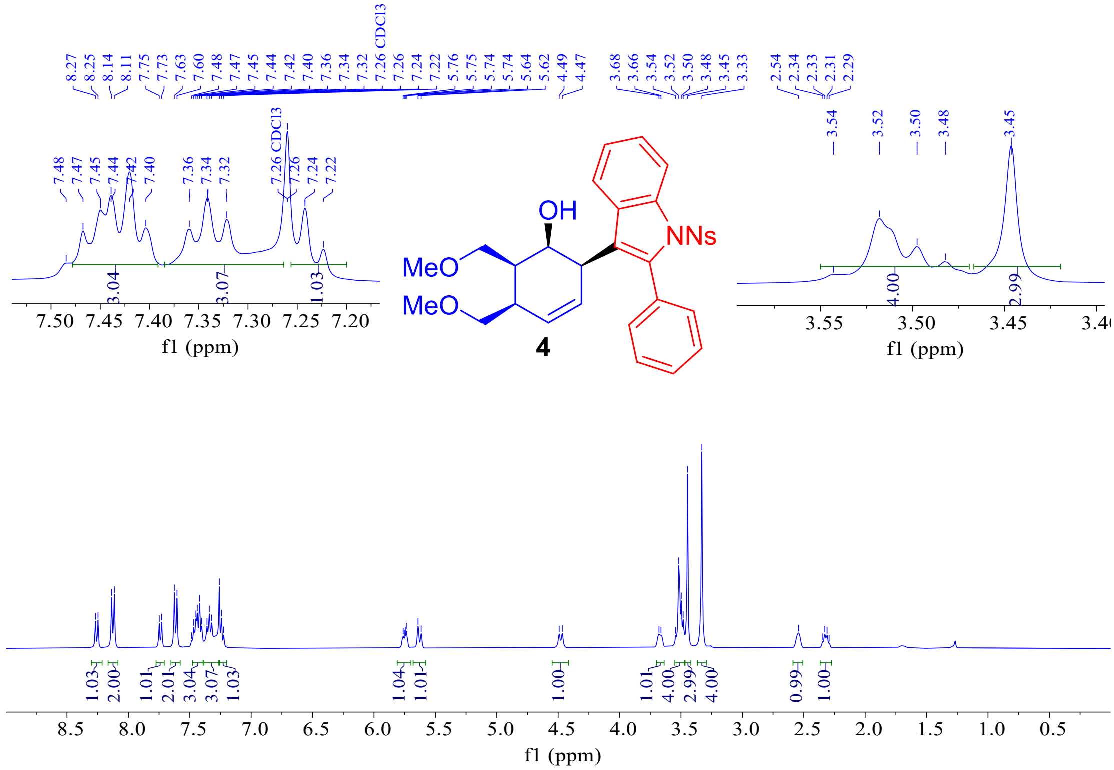
[1]H NMR (400 MHz, Chloroform-*d*)



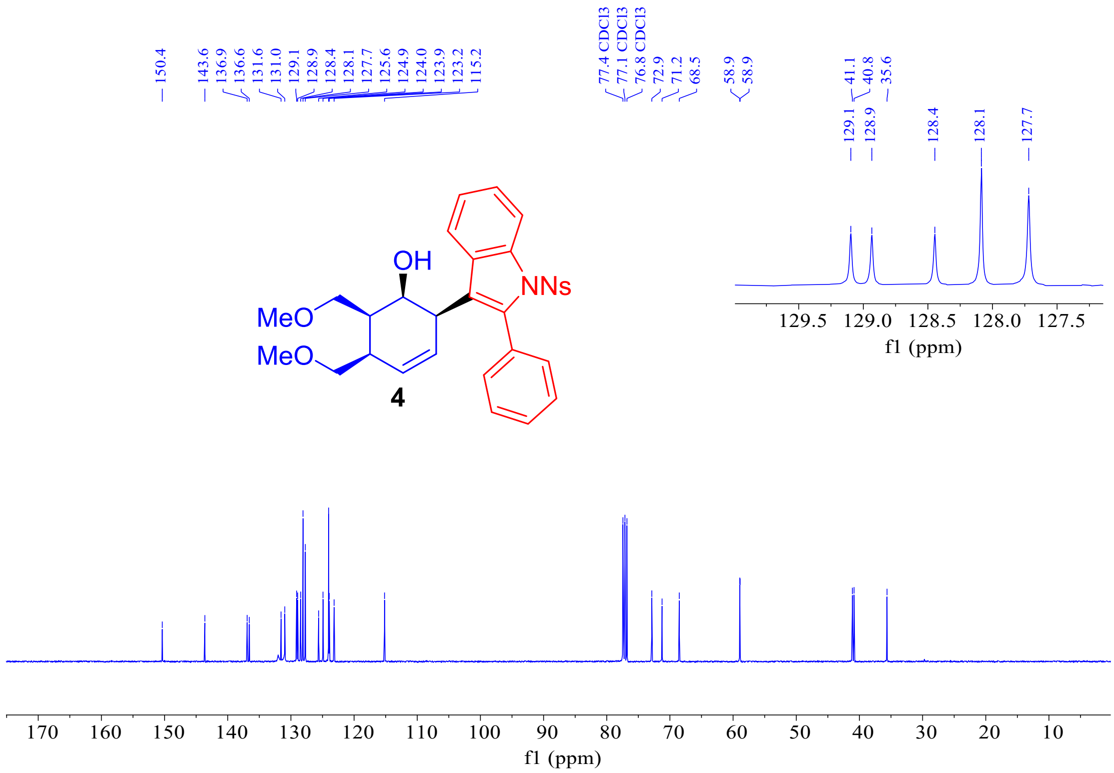
[13]C NMR (101 MHz, Chloroform-*d*)

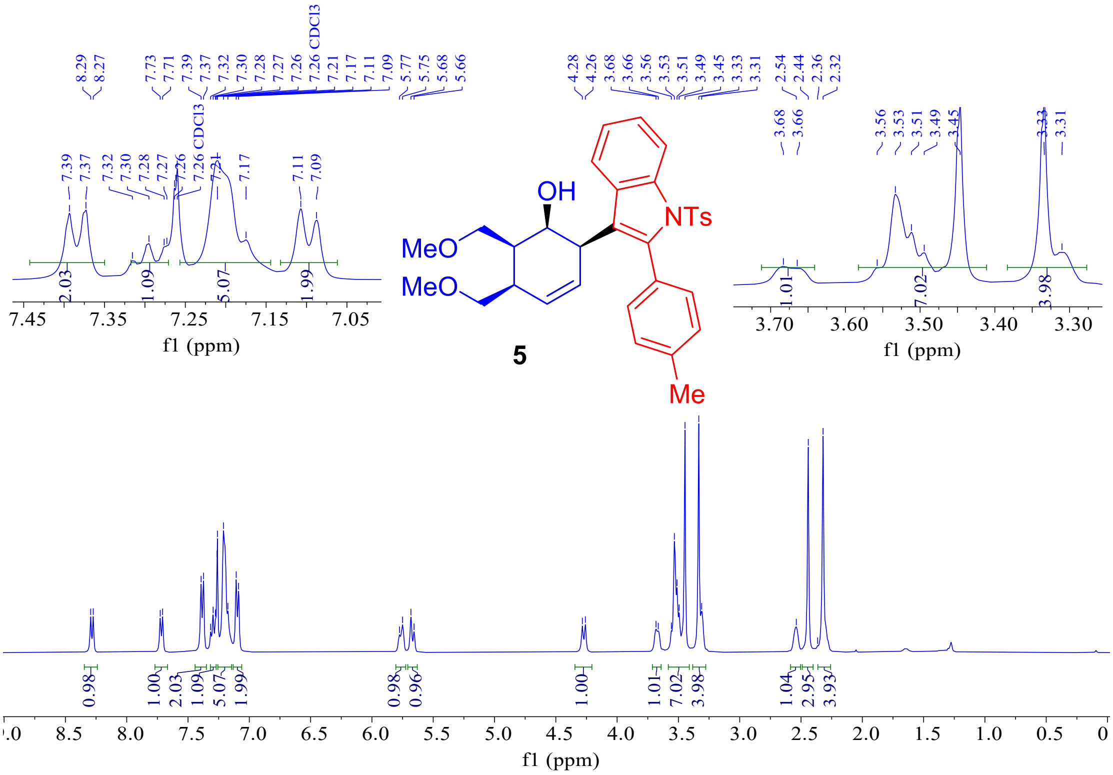


^{1}H NMR (400 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)

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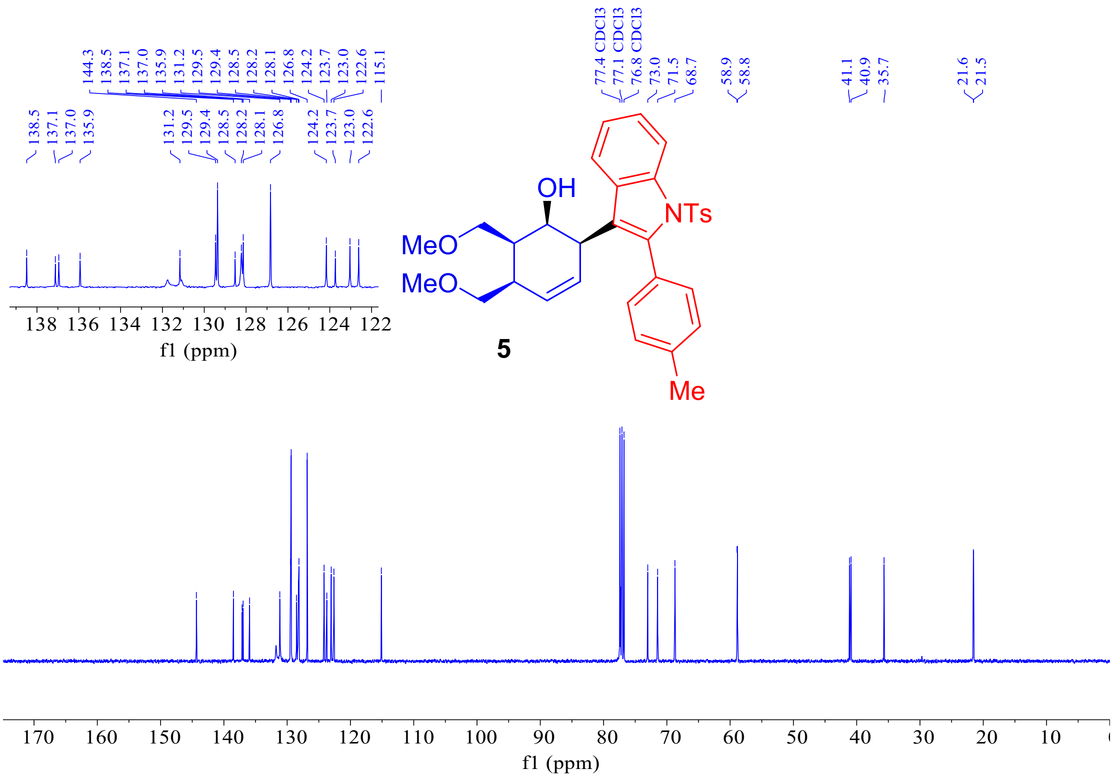
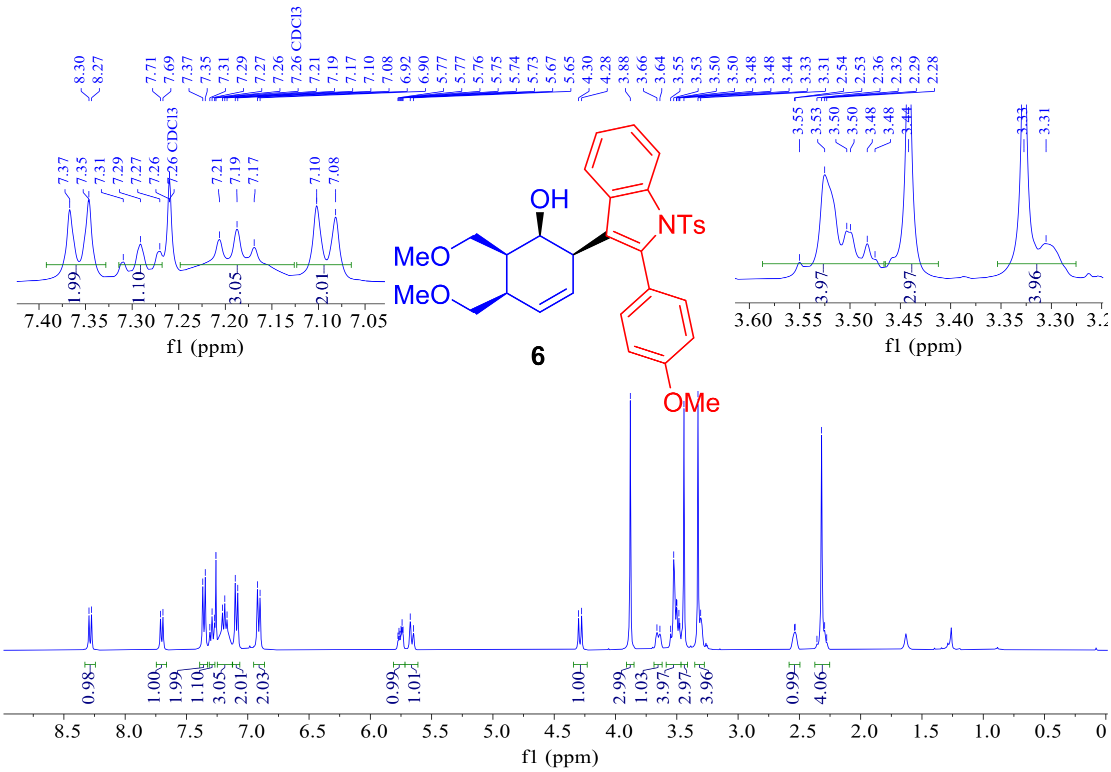
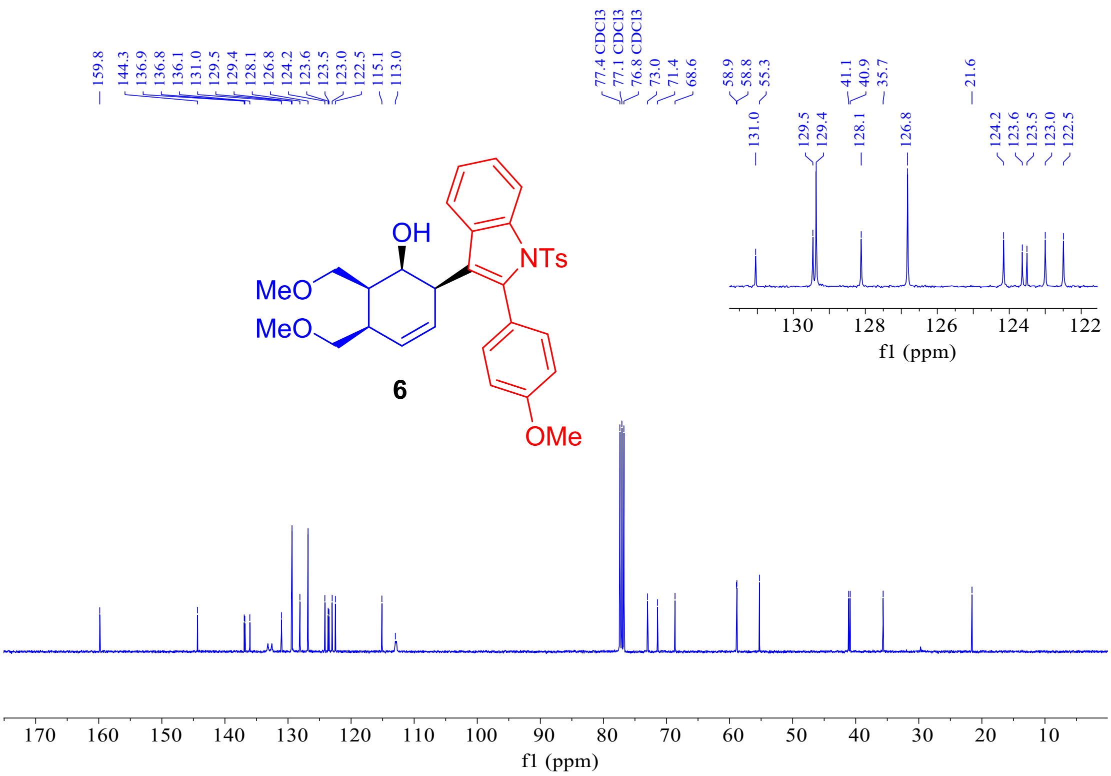
NTs
MeO
MeO
5
Me
f1 (ppm)


OH
NTs
MeO
MeO
5
Me
f1 (ppm)

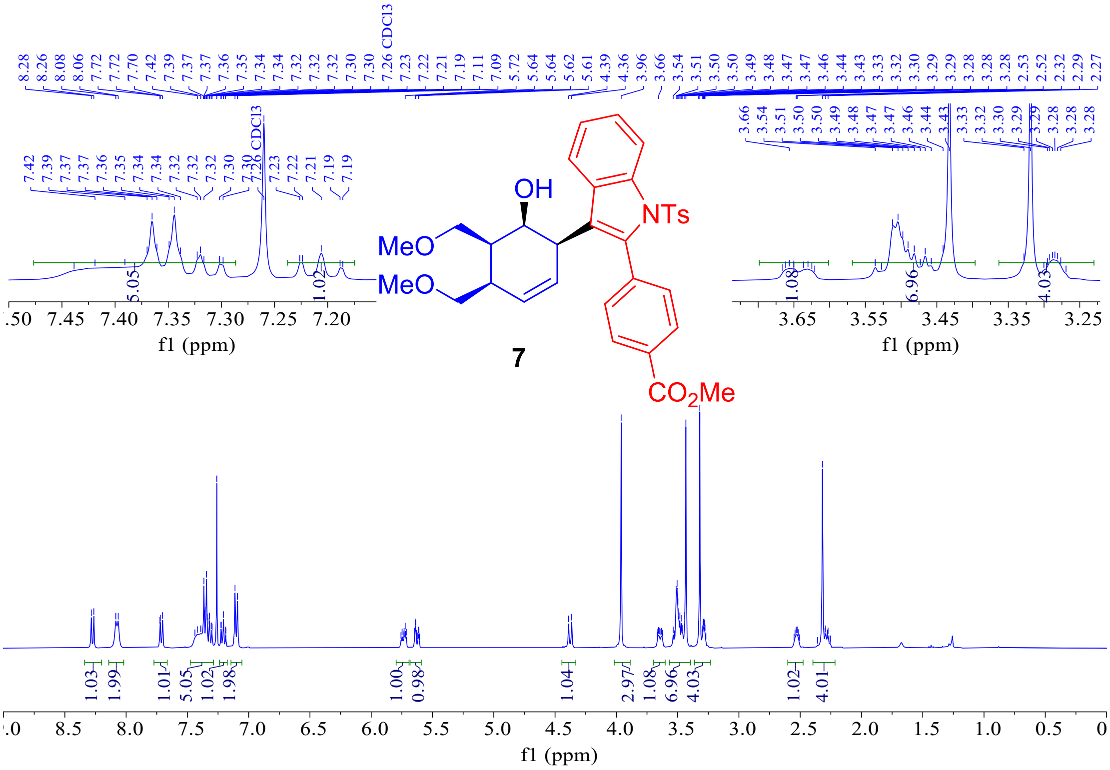
^{1}H NMR (400 MHz, Chloroform-*d*)



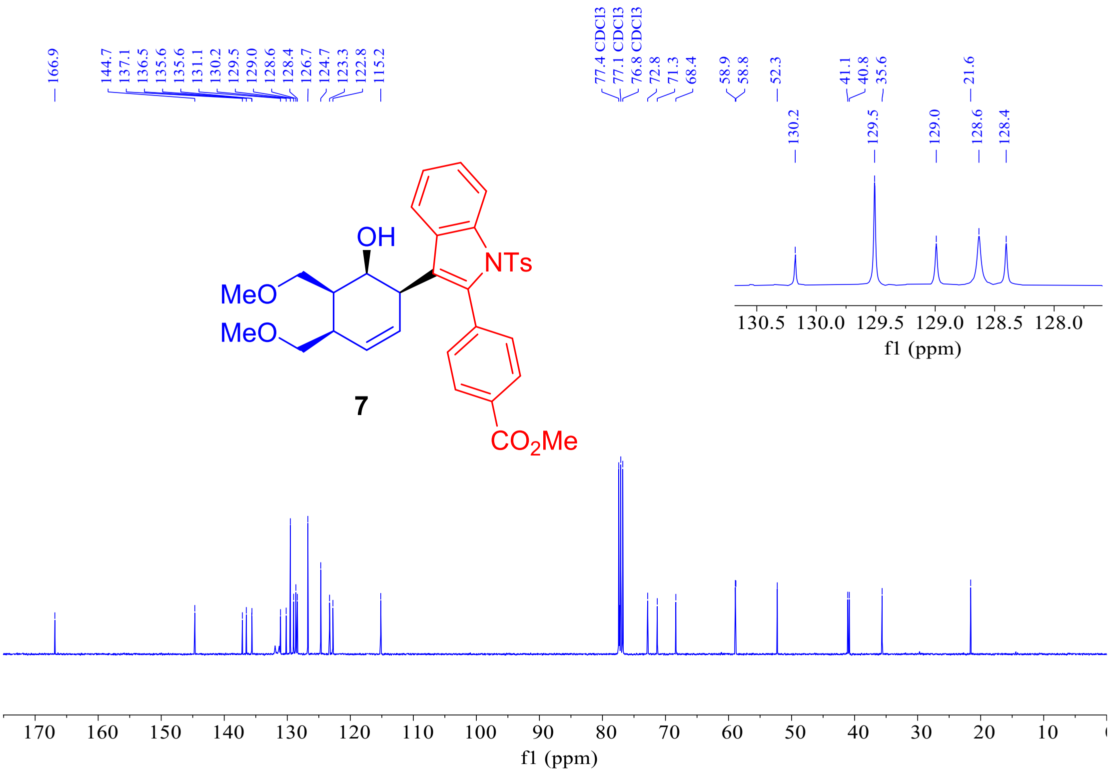
^{13}C NMR (101 MHz, Chloroform-*d*)



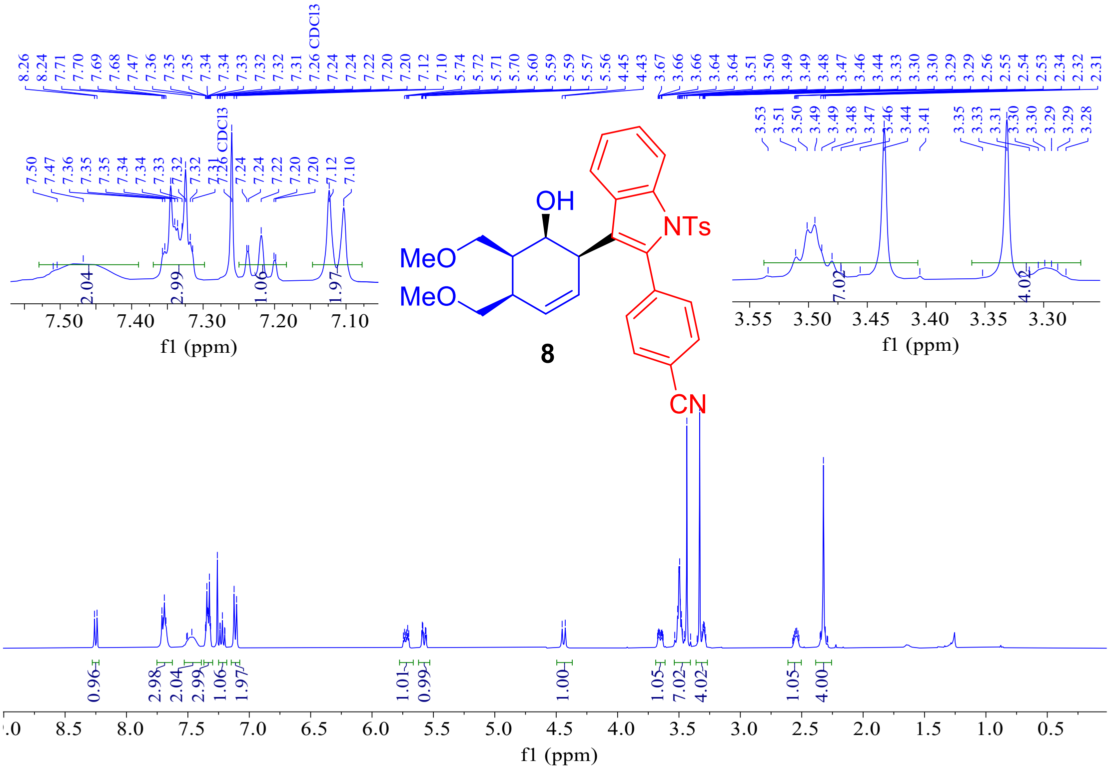
^{1}H NMR (400 MHz, Chloroform-*d*)



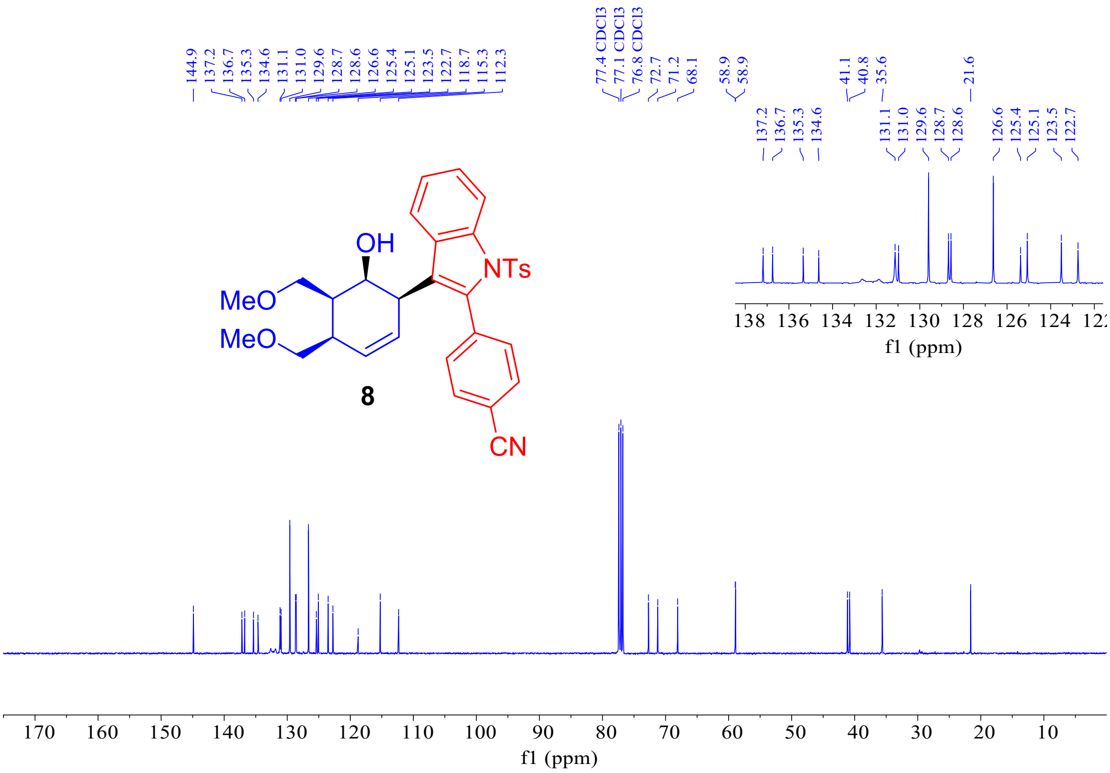
^{13}C NMR (101 MHz, Chloroform-*d*)

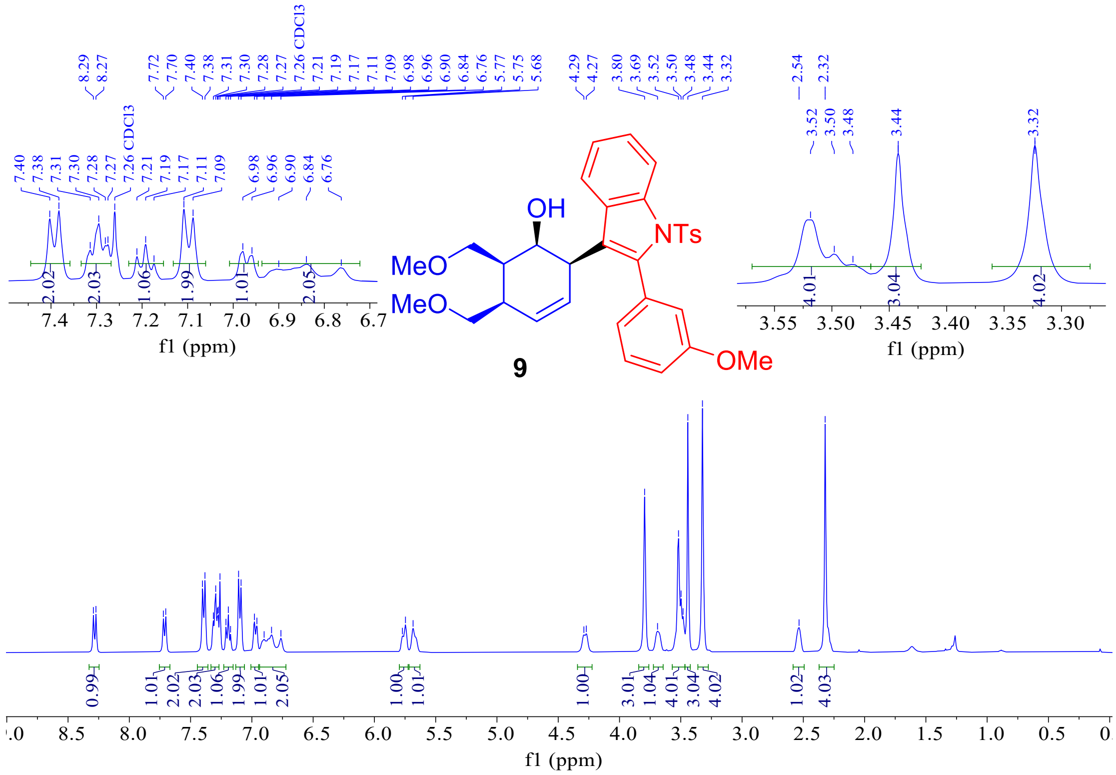


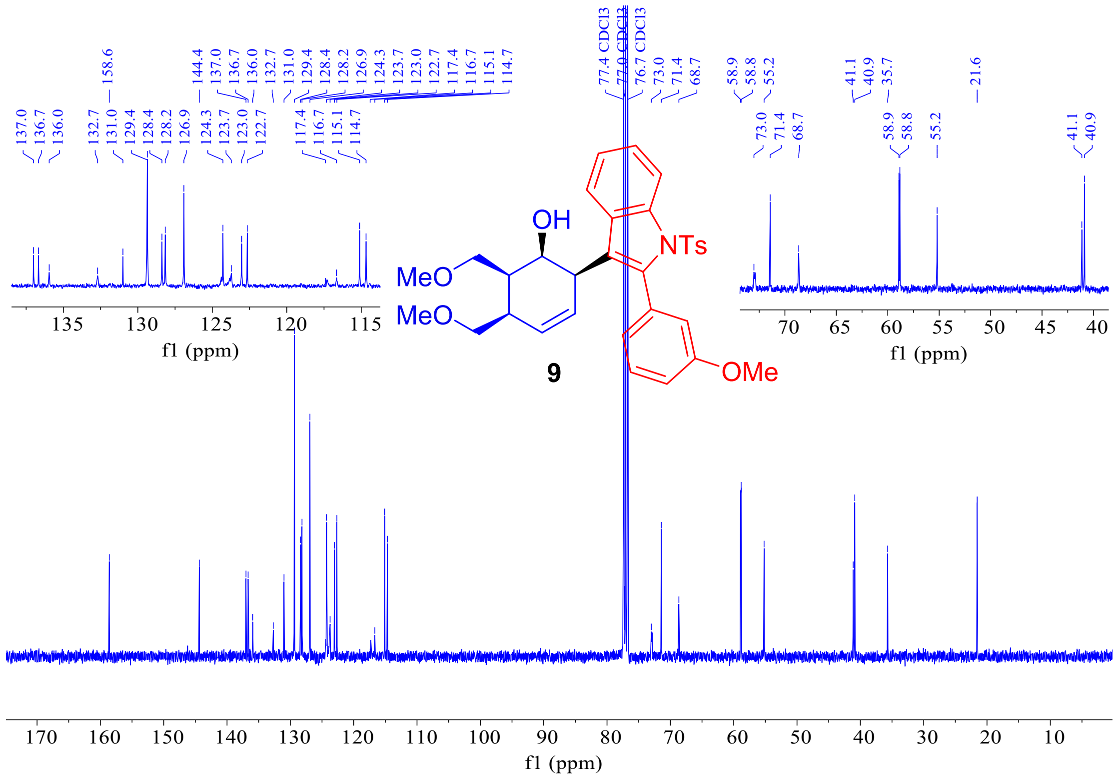
^{1}H NMR (400 MHz, Chloroform-*d*)

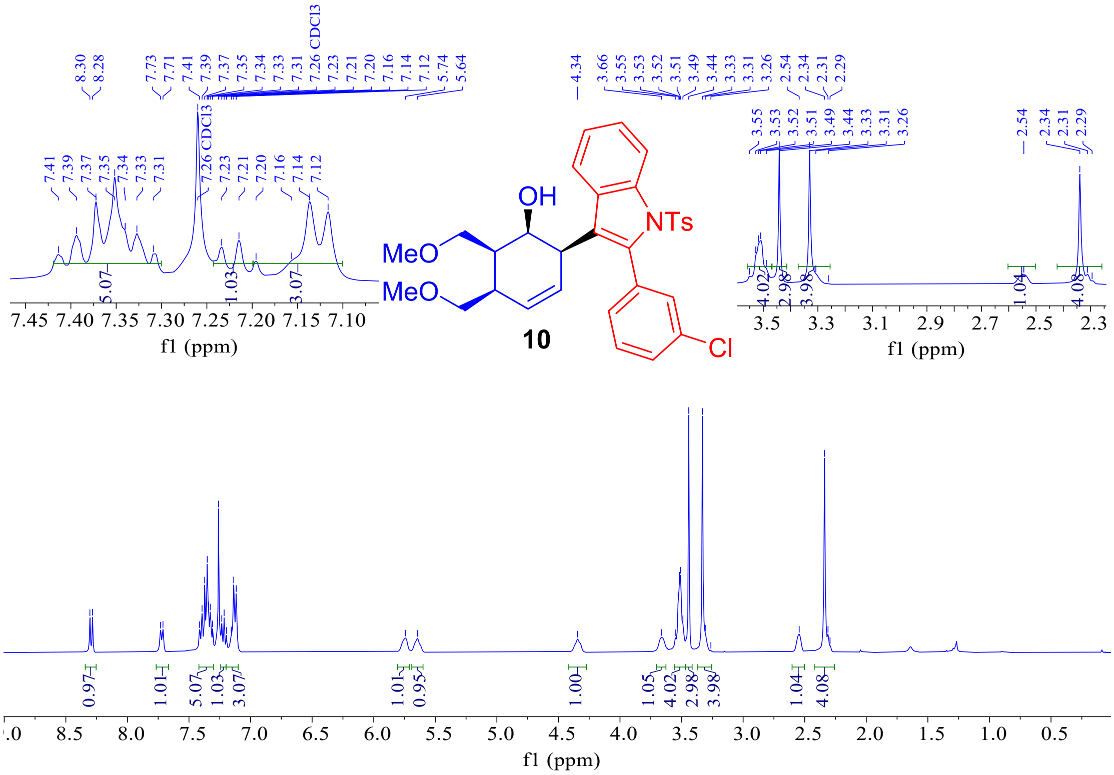


^{13}C NMR (101 MHz, Chloroform-*d*)





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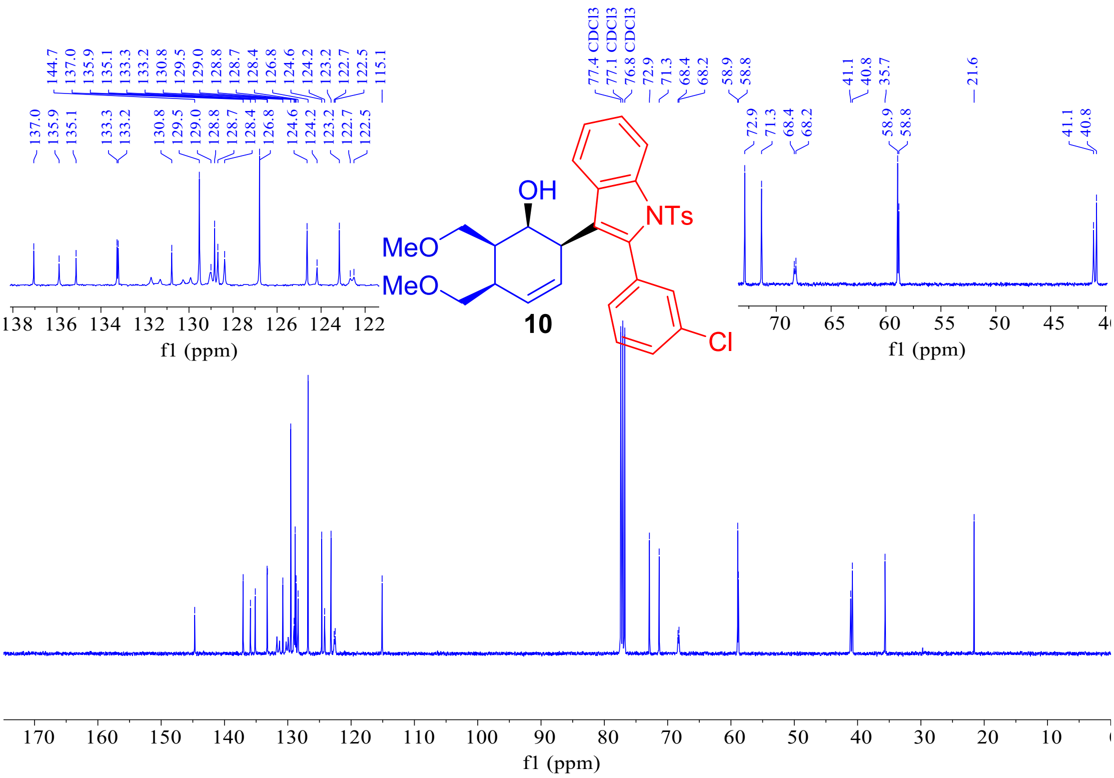
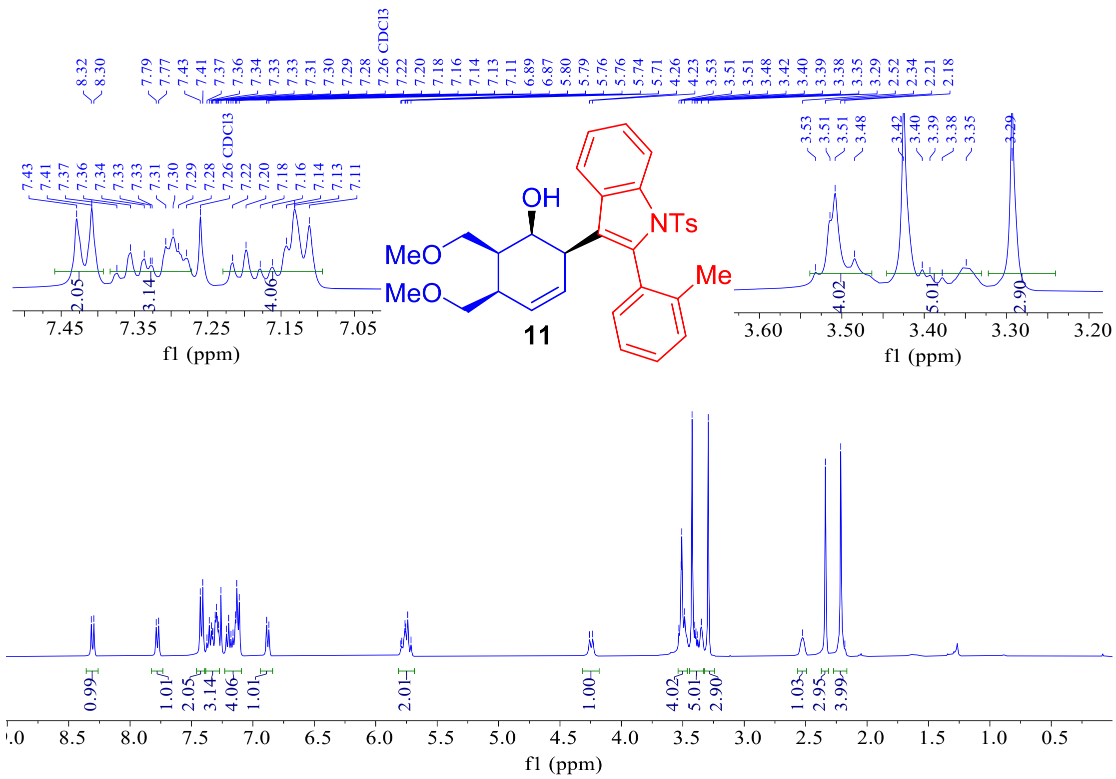
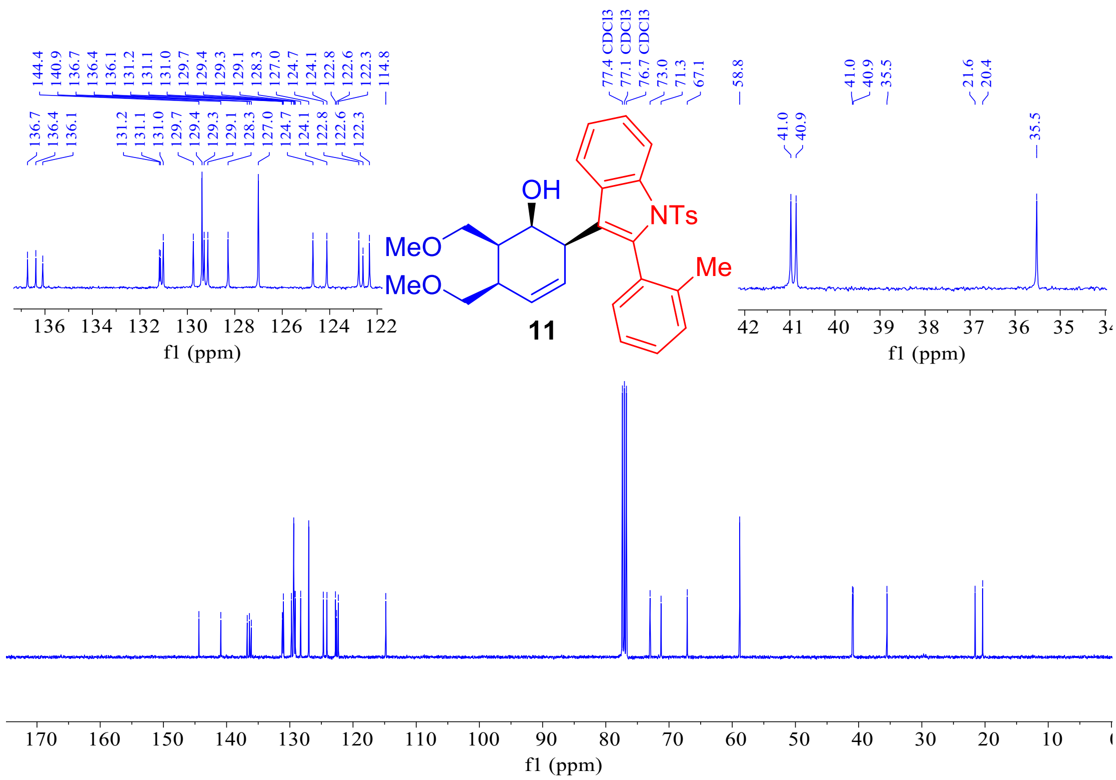
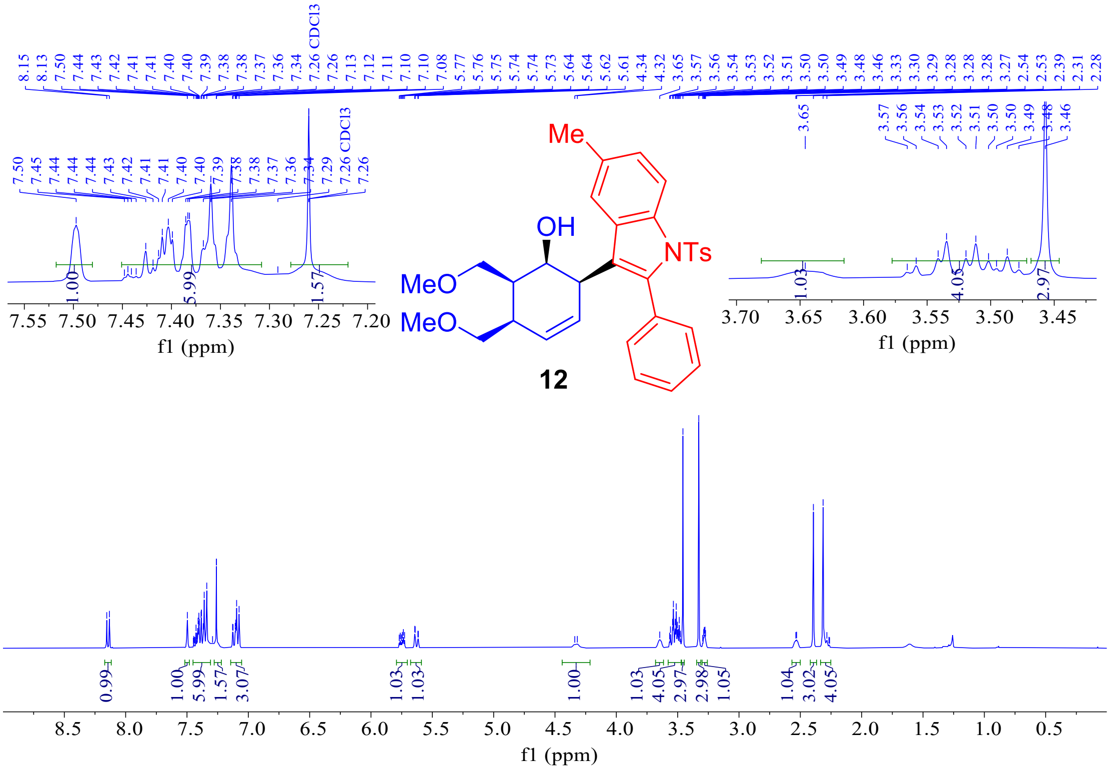
NTs
MeO
MeO
Cl
10
f1 (ppm)


OH
NTs
MeO
MeO
Cl
10
f1 (ppm)

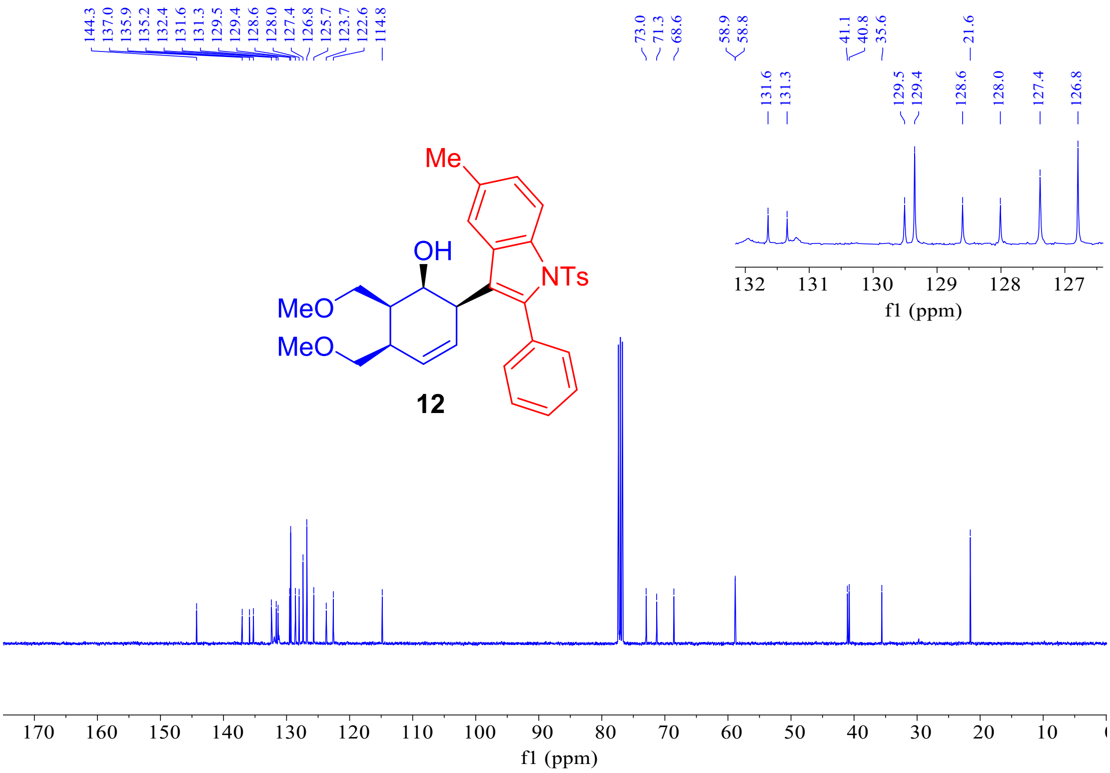




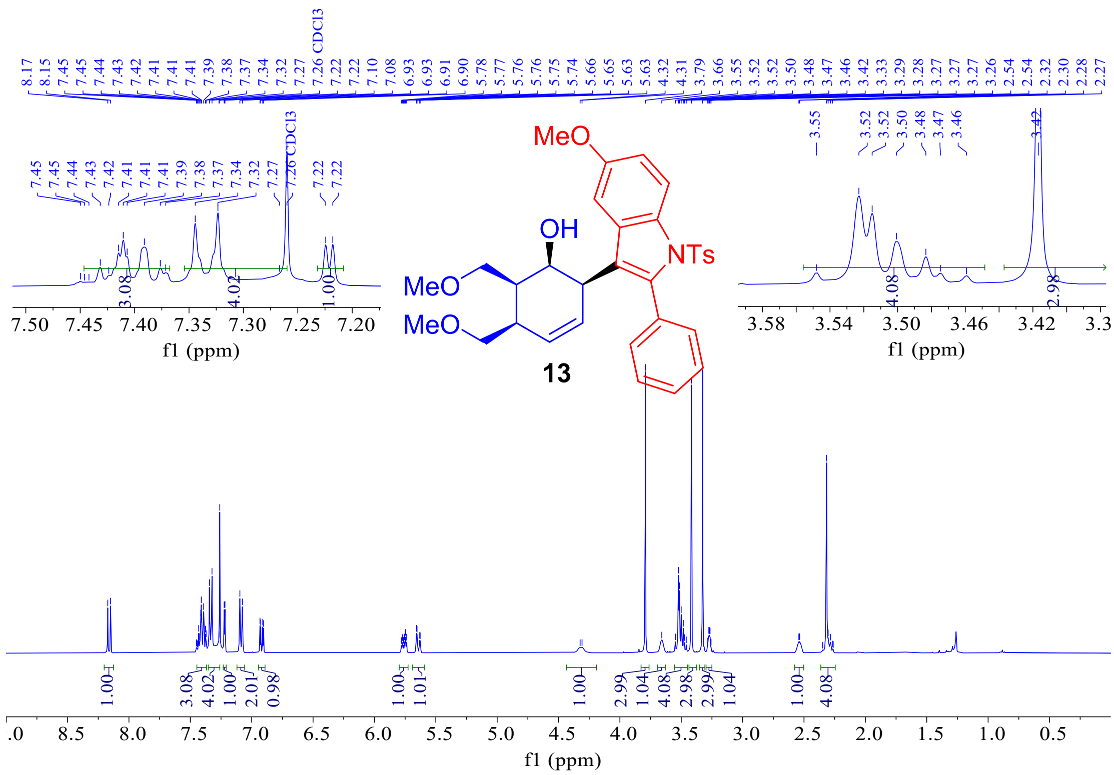
^{1}H NMR (400 MHz, Chloroform-*d*)



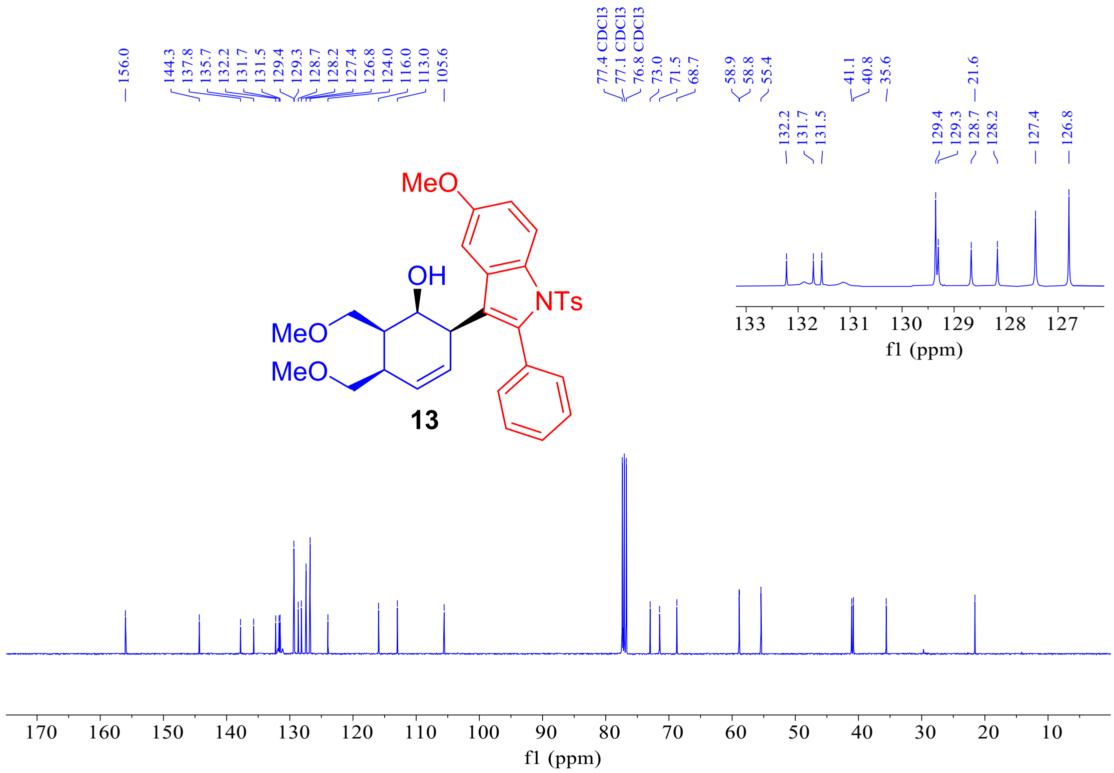
^{13}C NMR (101 MHz, Chloroform-*d*)



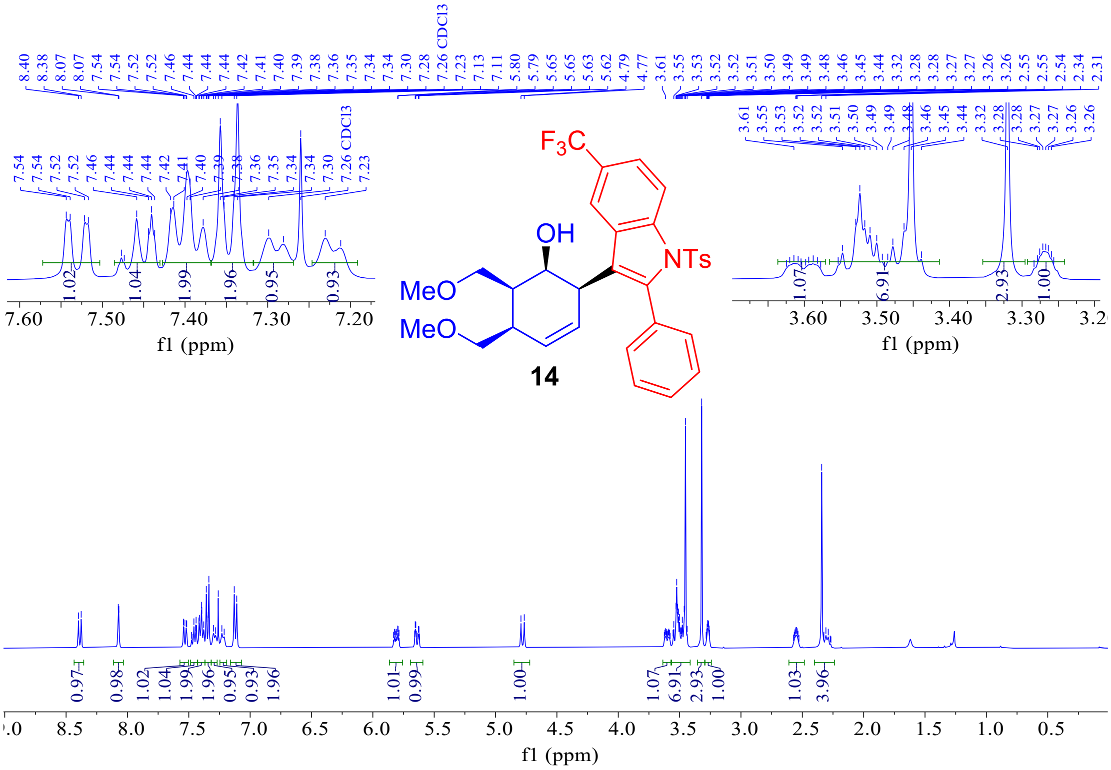
^{1}H NMR (400 MHz, Chloroform-*d*)



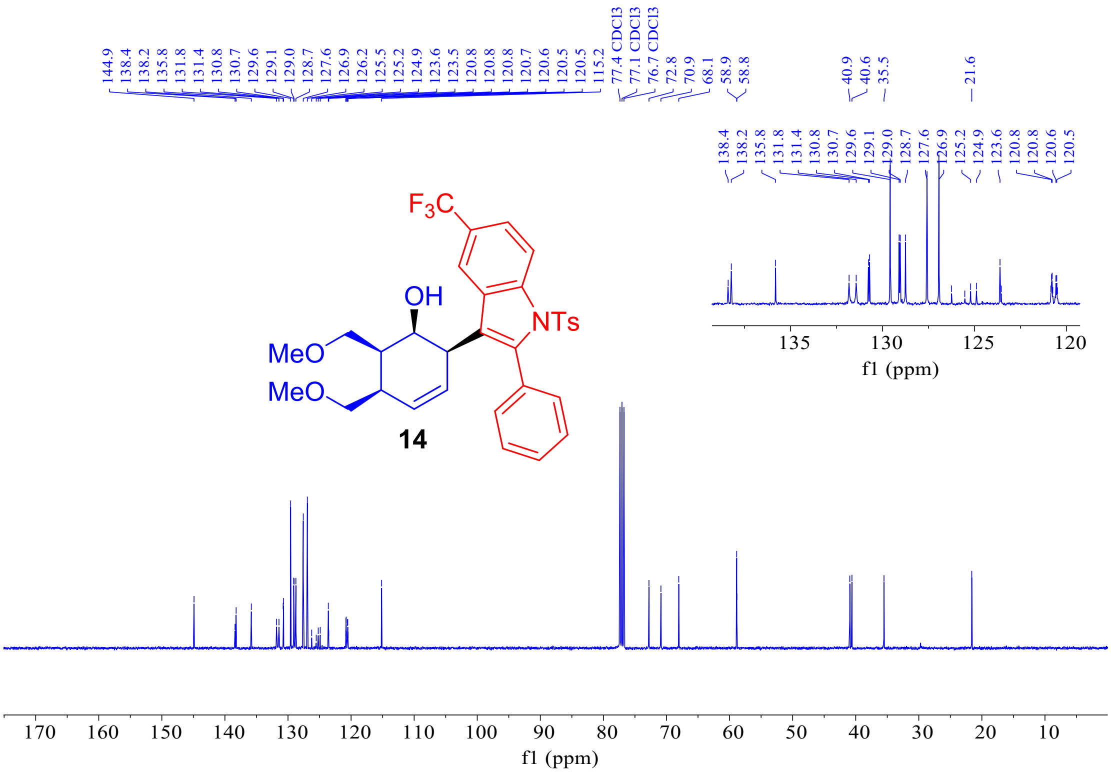
^{13}C NMR (101 MHz, Chloroform-*d*)



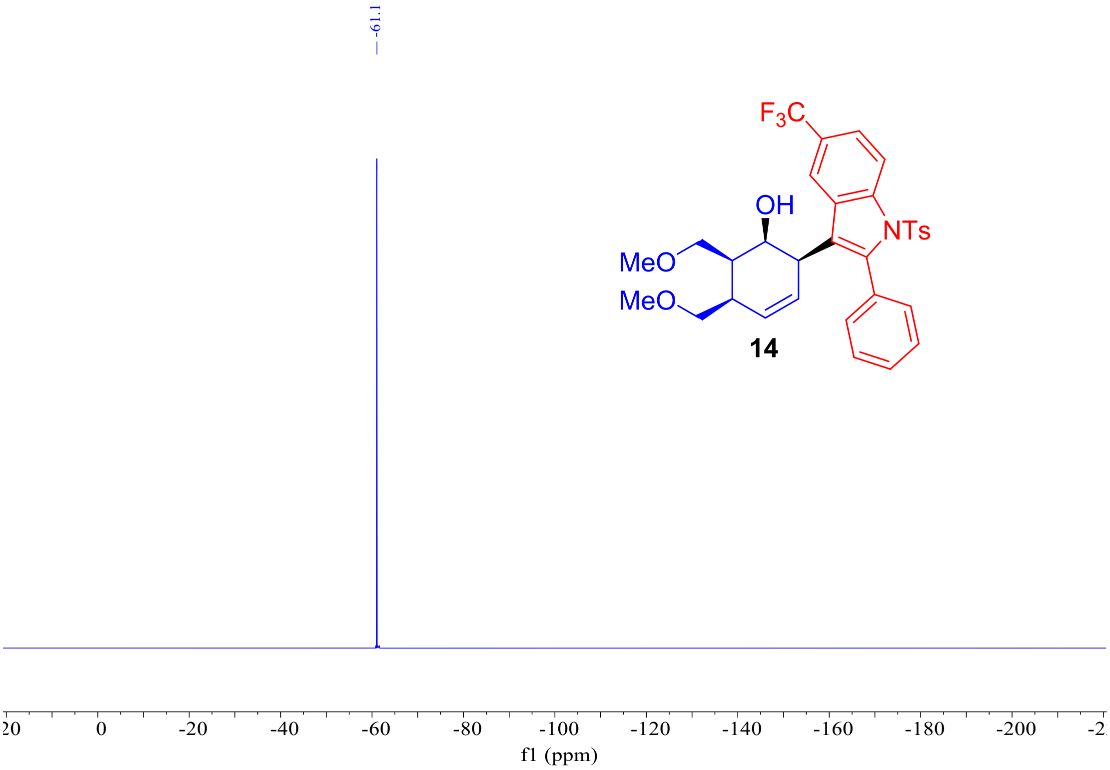
[1]H NMR (400 MHz, Chloroform-*d*)



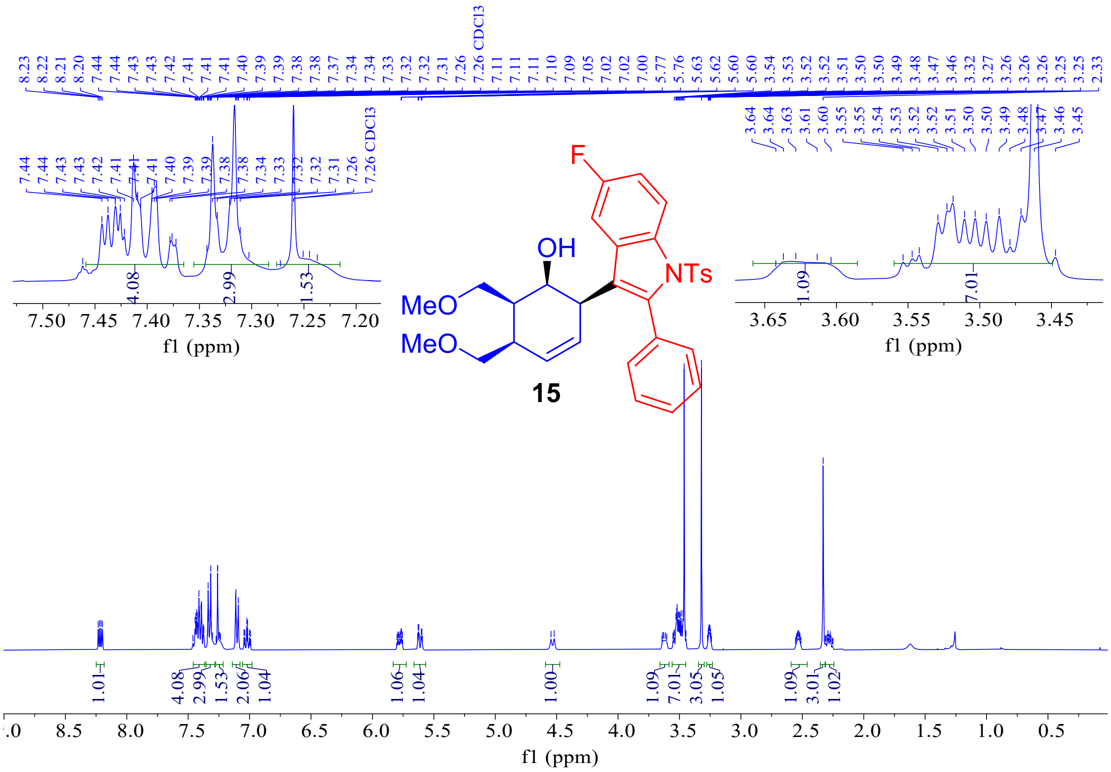
[13]C NMR (101 MHz, Chloroform-*d*)



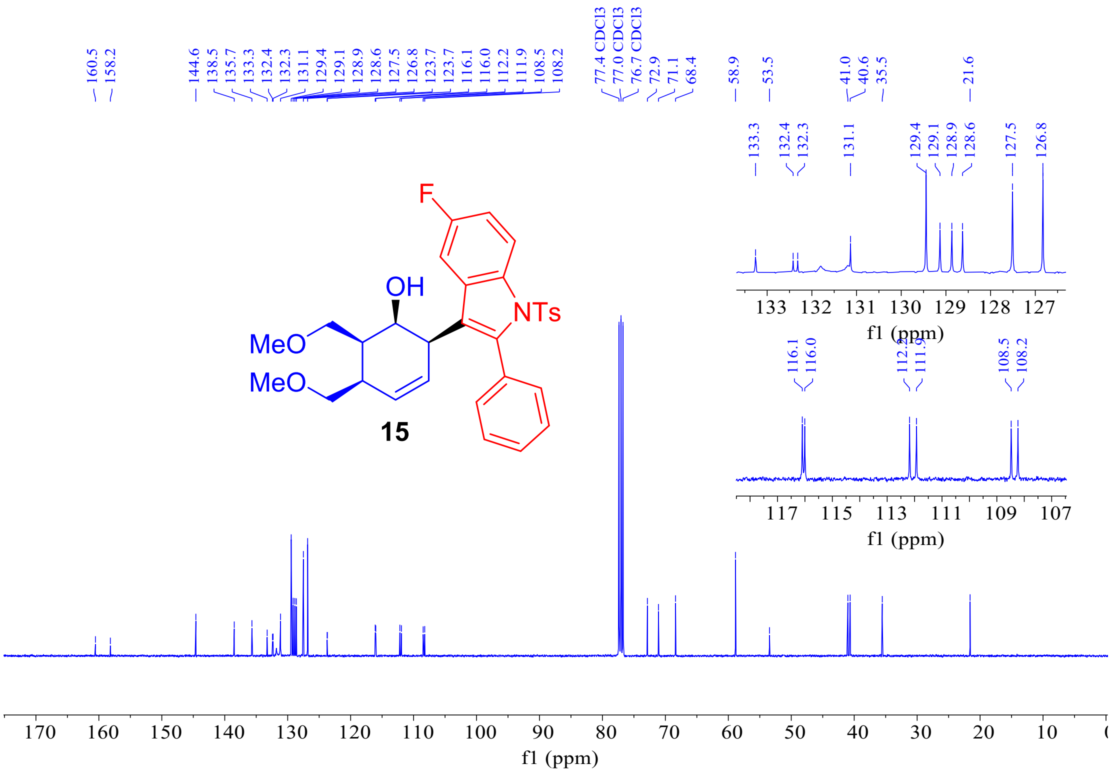
[19]F NMR (376 MHz, Chloroform-*d*)



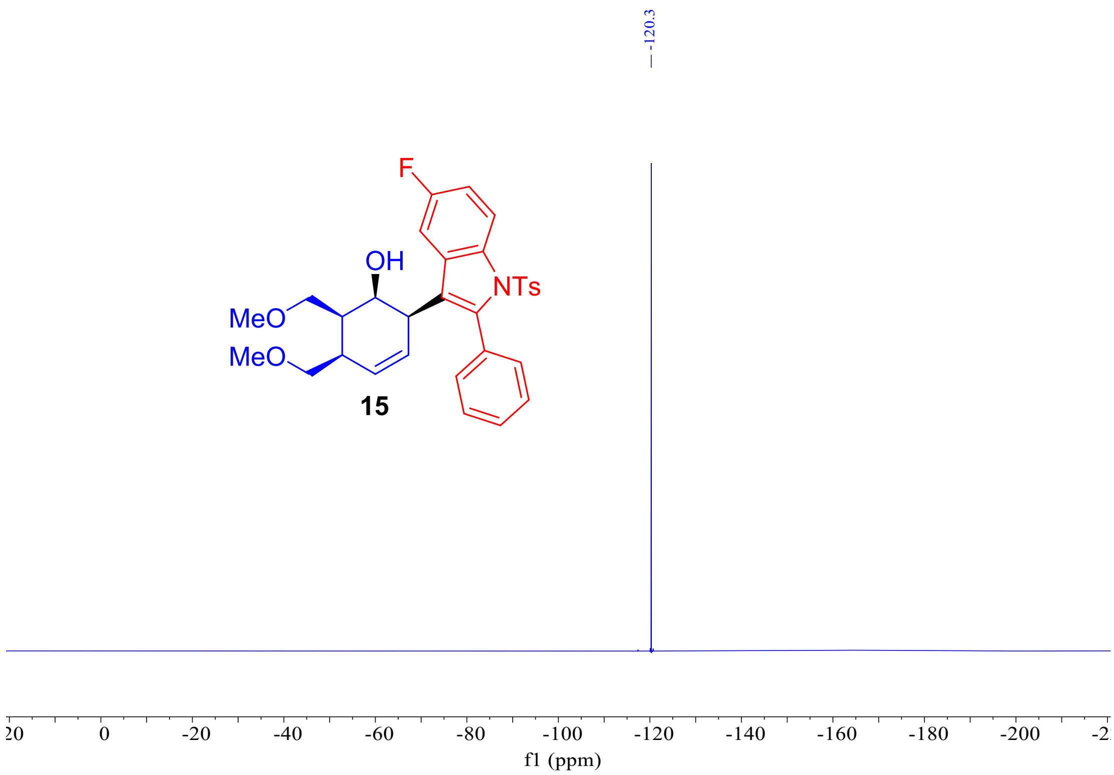
^{1}H NMR (400 MHz, Chloroform-*d*)



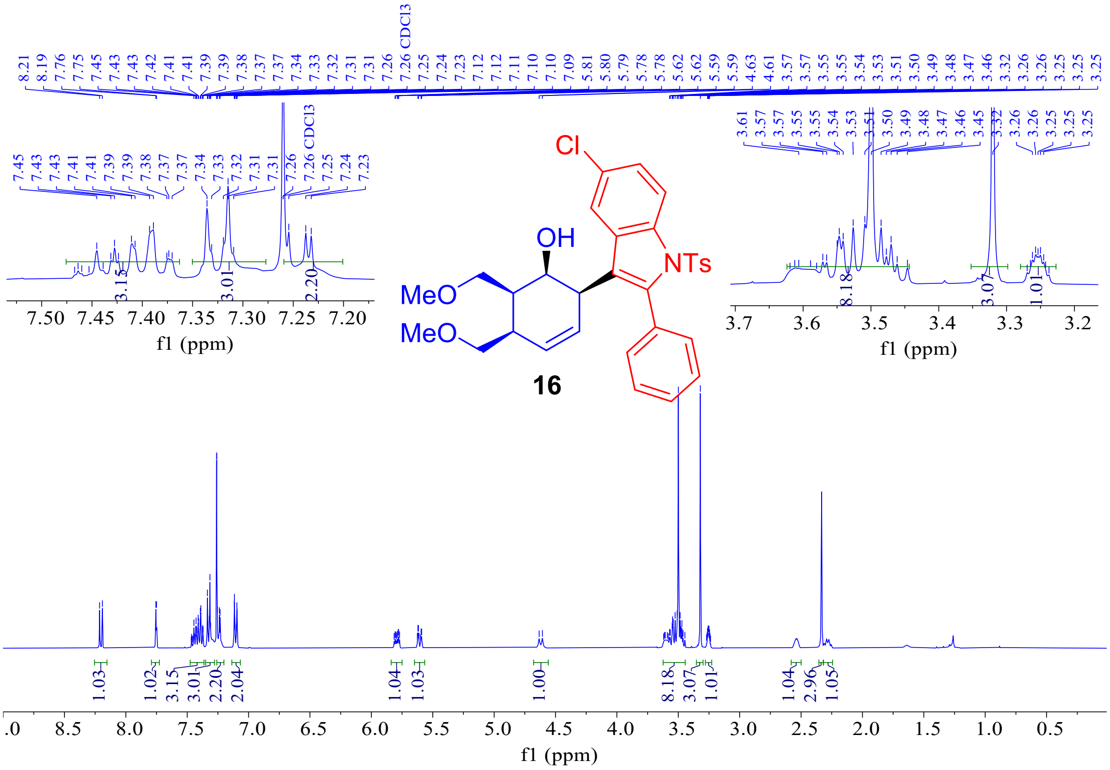
^{13}C NMR (101 MHz, Chloroform-*d*)



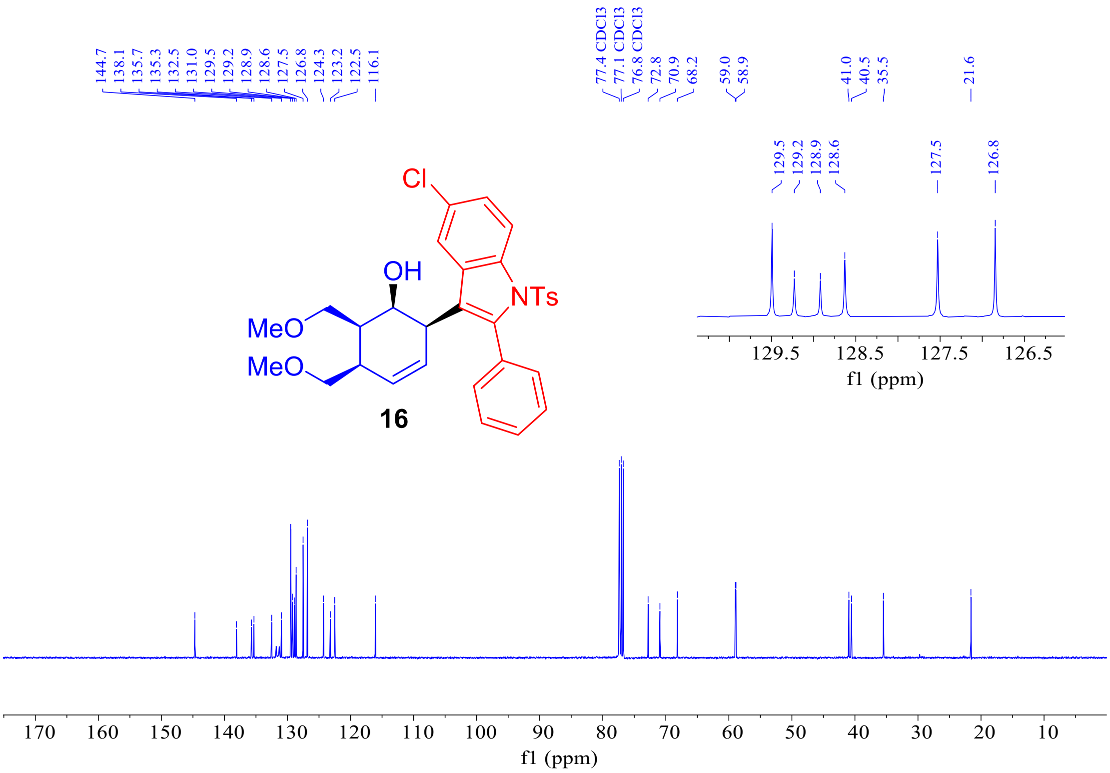
^{19}F NMR (376 MHz, Chloroform-*d*)



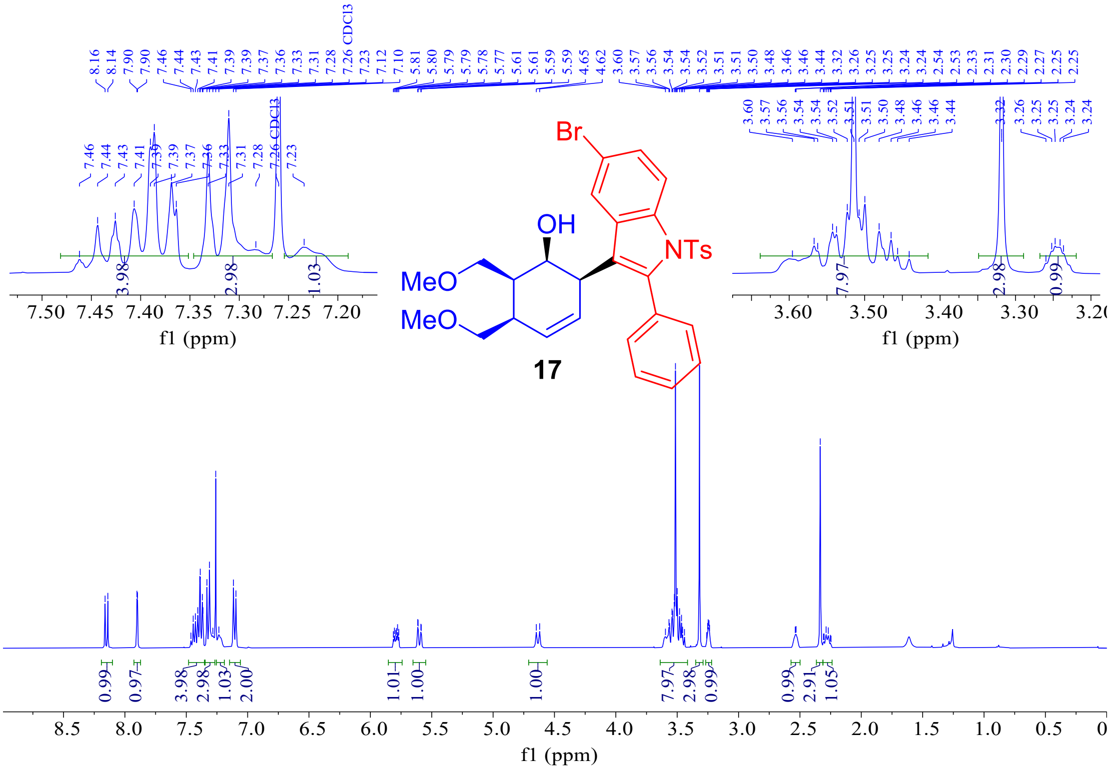
^{1}H NMR (400 MHz, Chloroform-d)



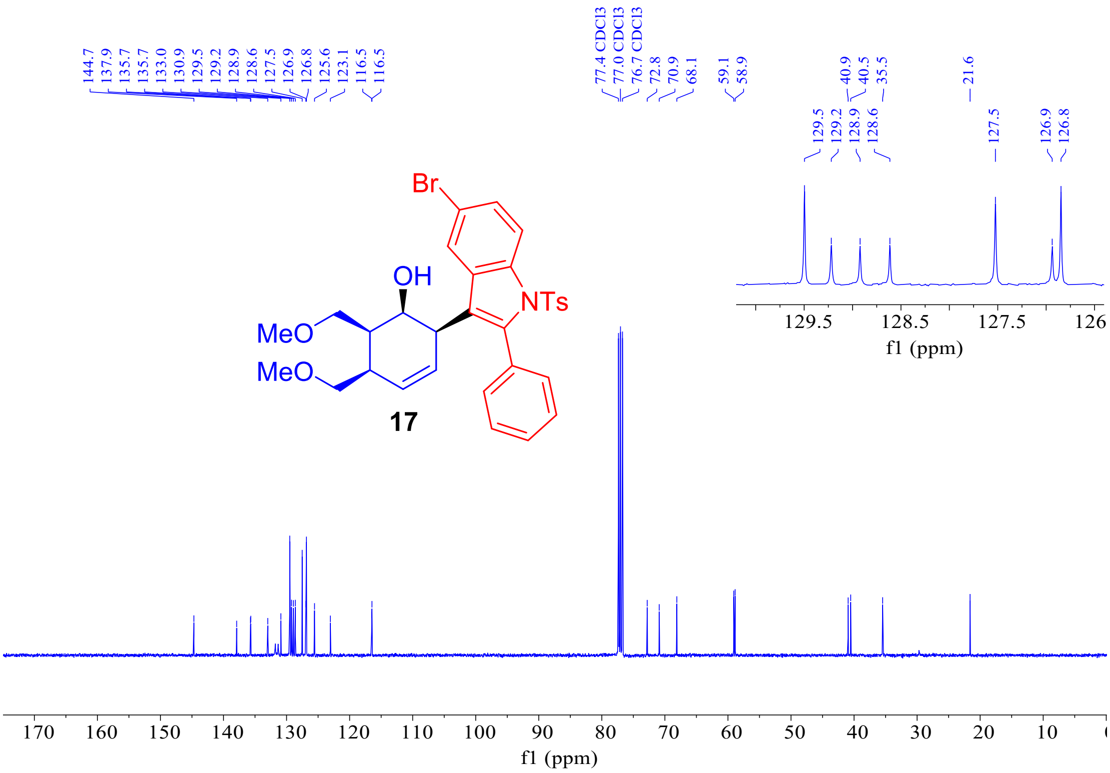
^{13}C NMR (101 MHz, Chloroform-d)



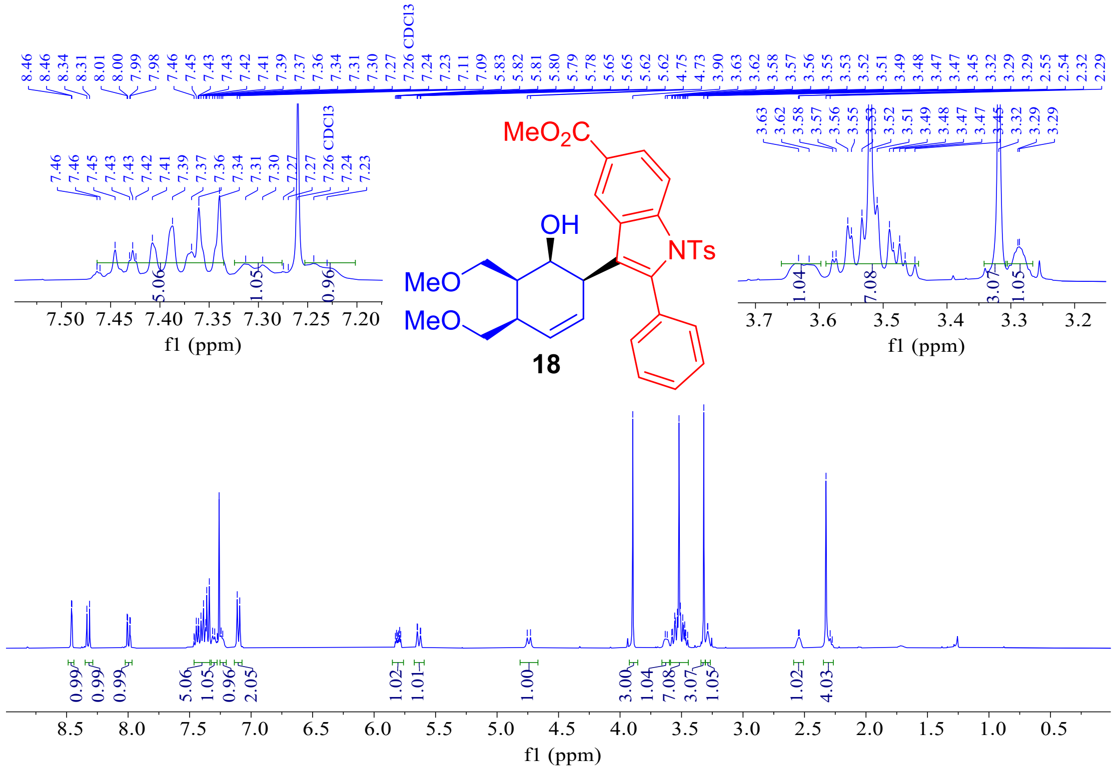
^{1}H NMR (400 MHz, Chloroform-*d*)



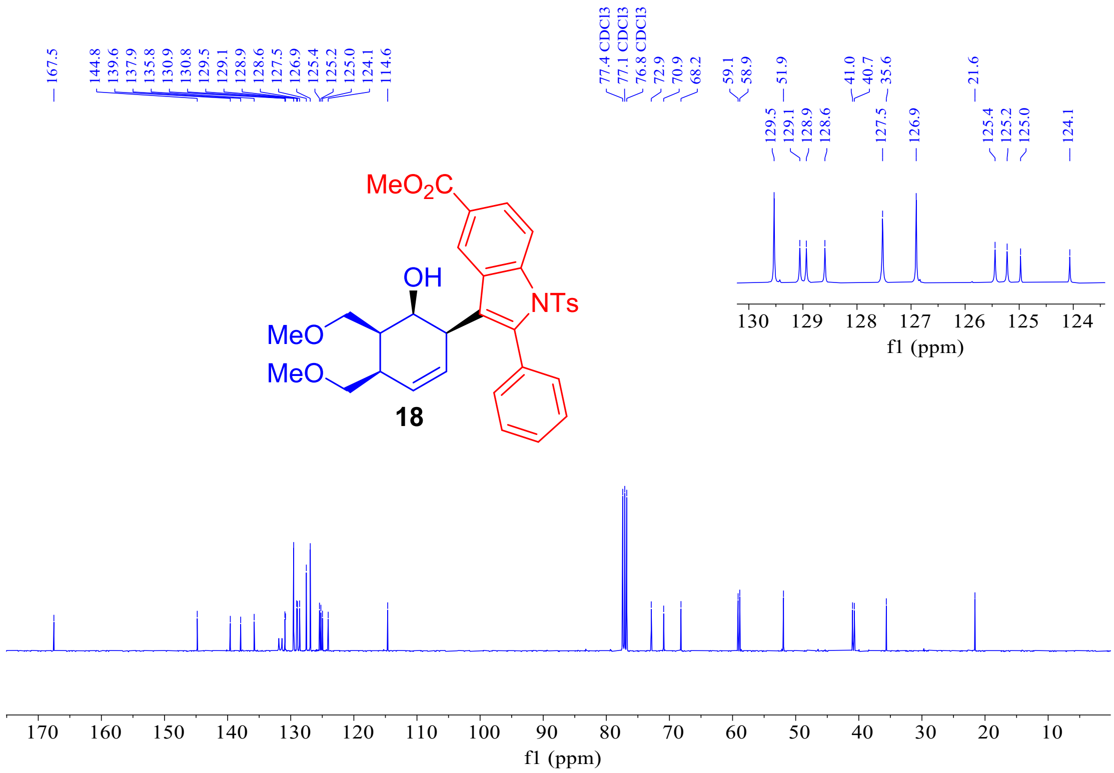
^{13}C NMR (101 MHz, Chloroform-*d*)



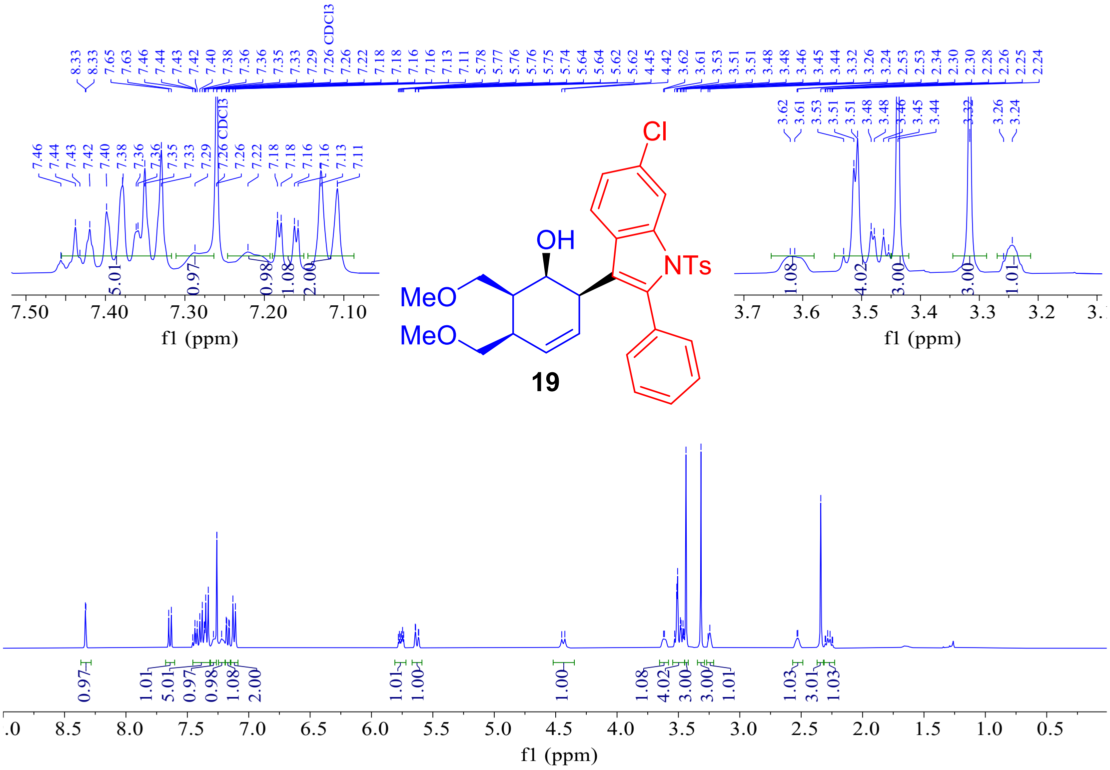
^{1}H NMR (400 MHz, Chloroform-*d*)



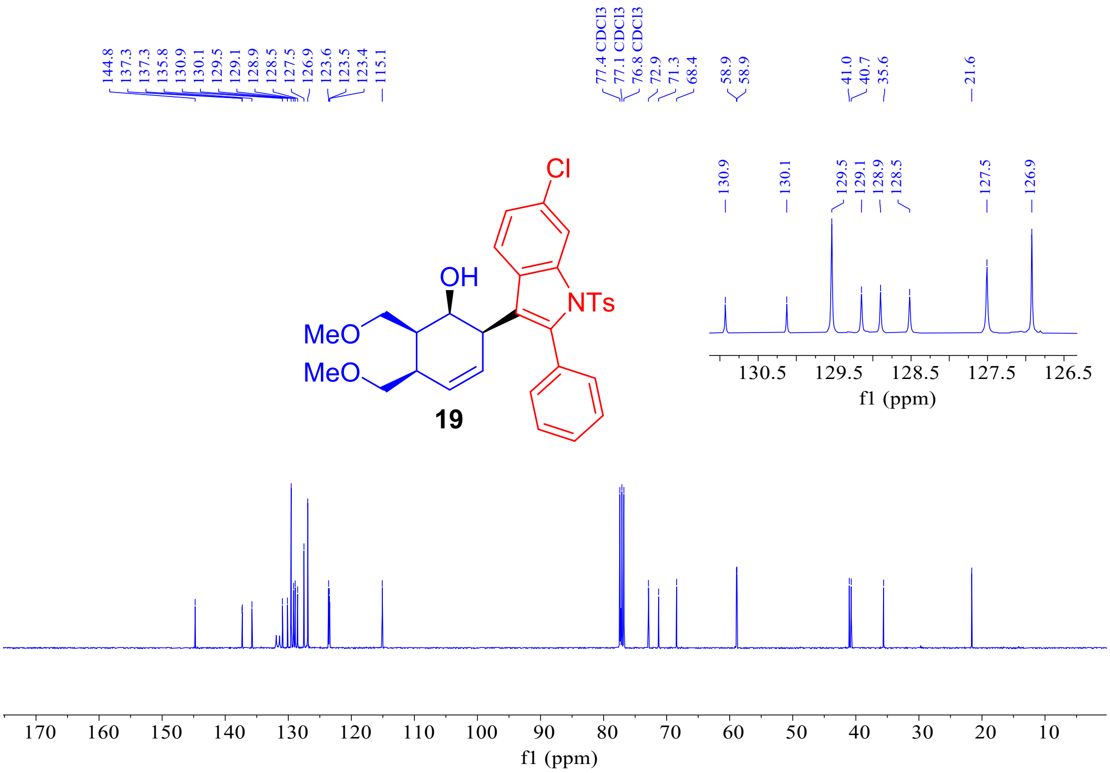
^{13}C NMR (101 MHz, Chloroform-*d*)



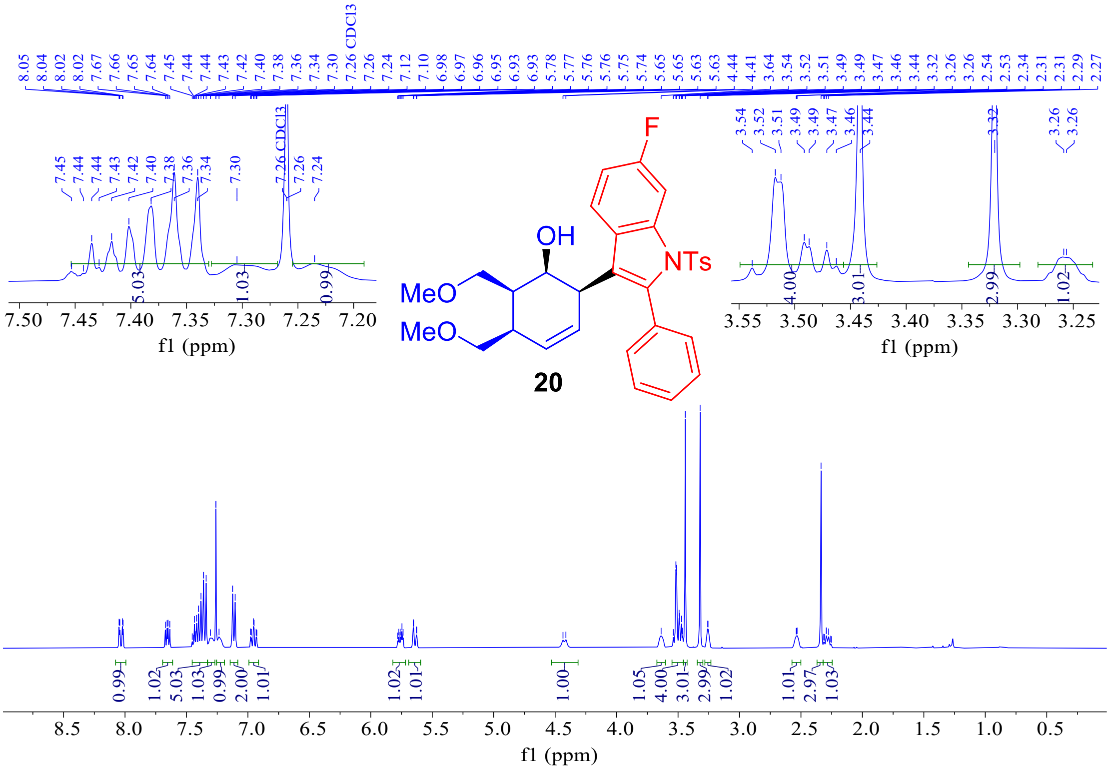
[1]H NMR (400 MHz, Chloroform-*d*)



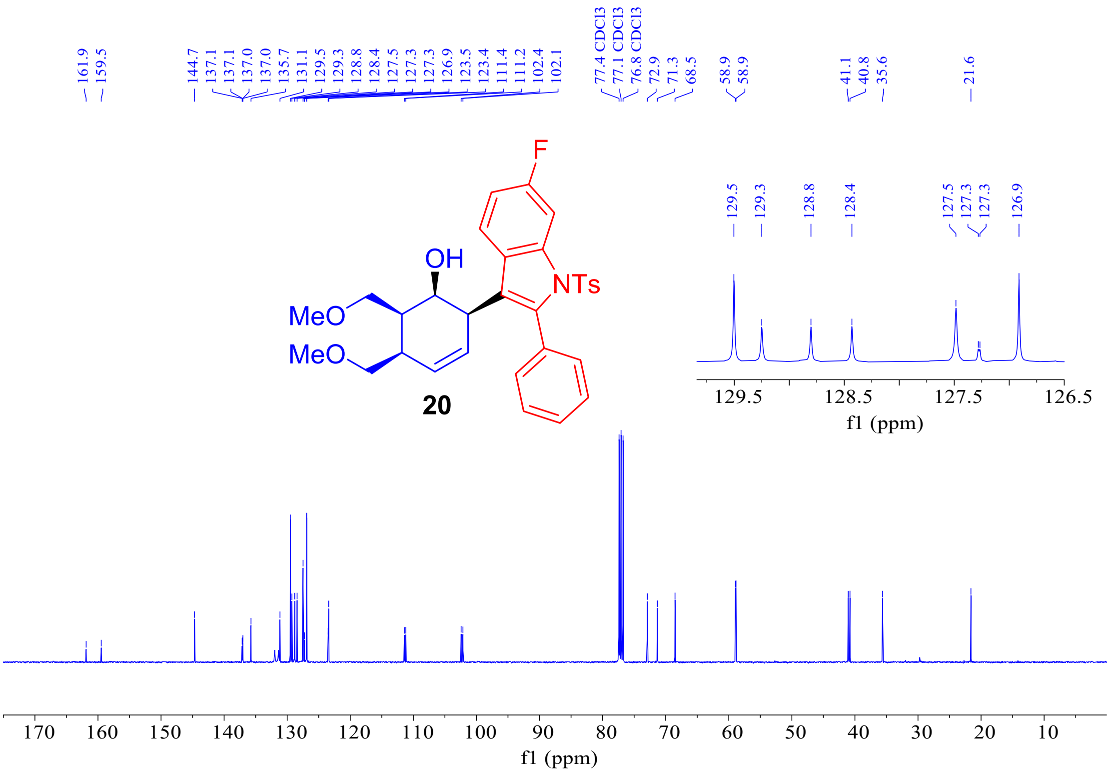
[13]C NMR (101 MHz, Chloroform-*d*)



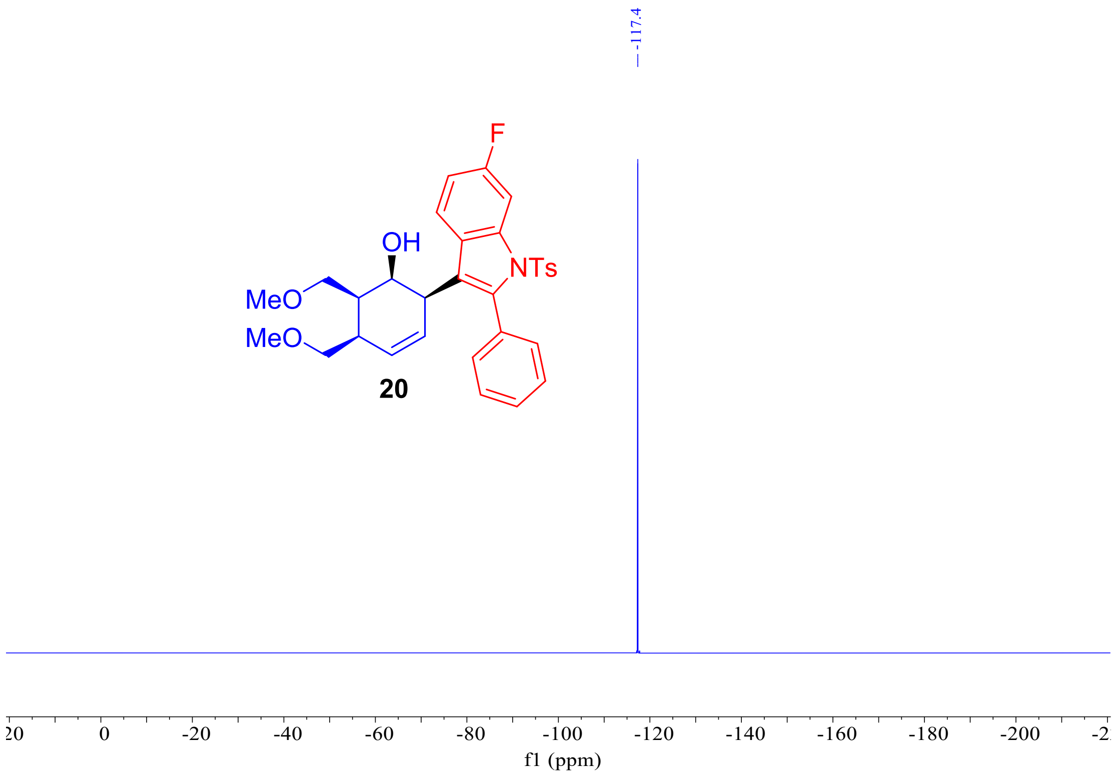
^{1}H NMR (400 MHz, Chloroform-*d*)

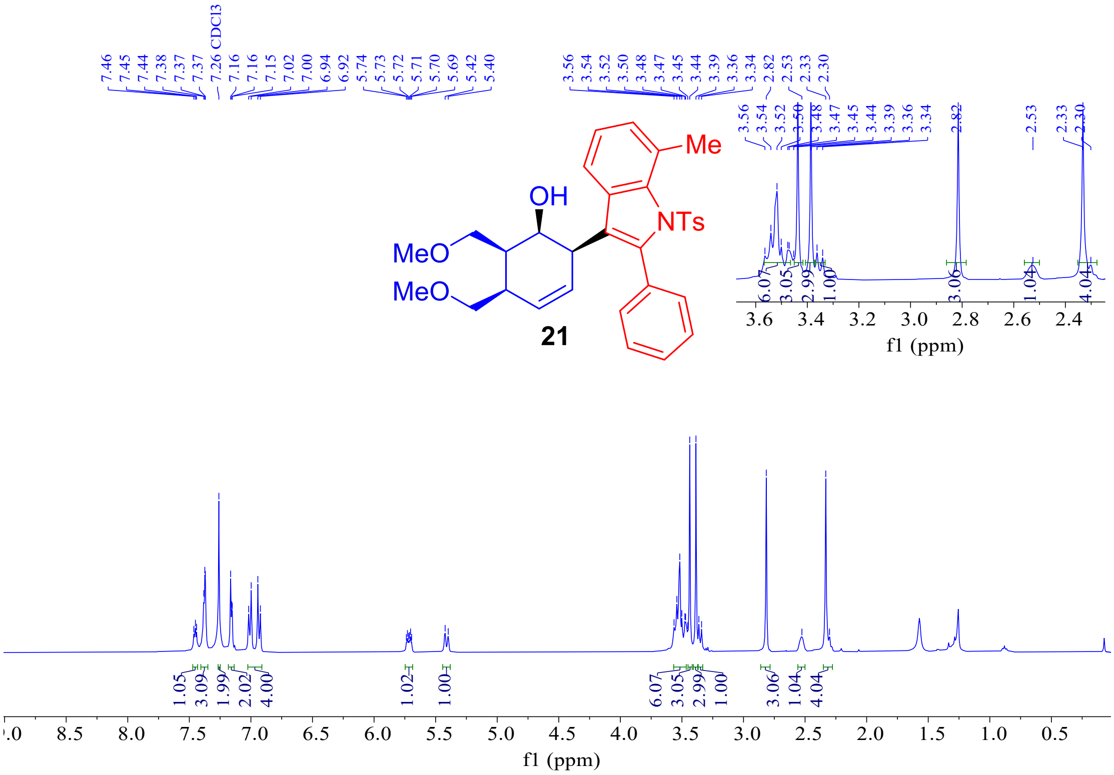


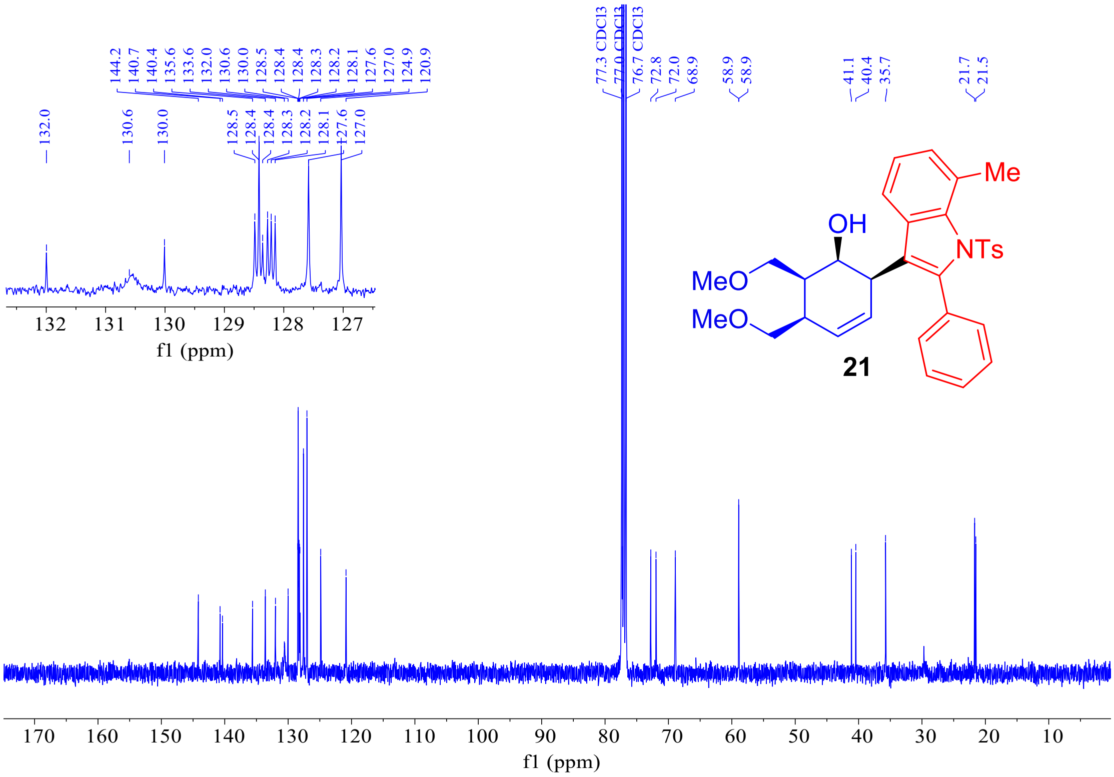
^{13}C NMR (101 MHz, Chloroform-*d*)



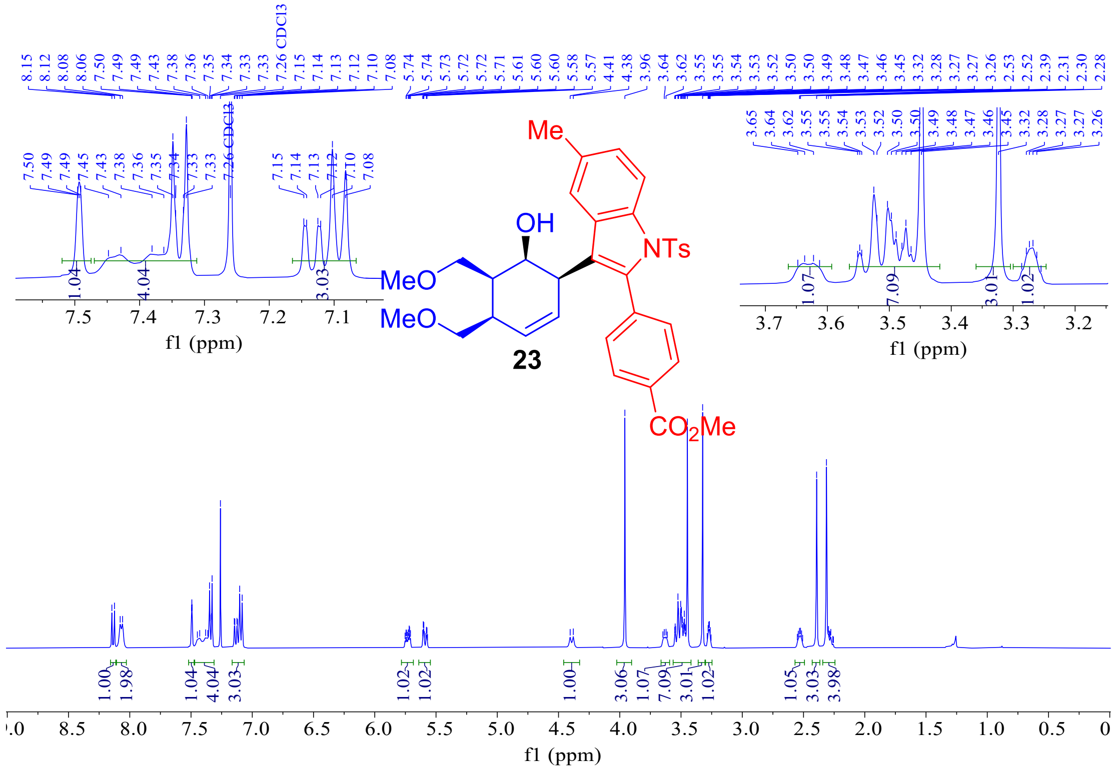
^{19}F NMR (376 MHz, Chloroform-*d*)



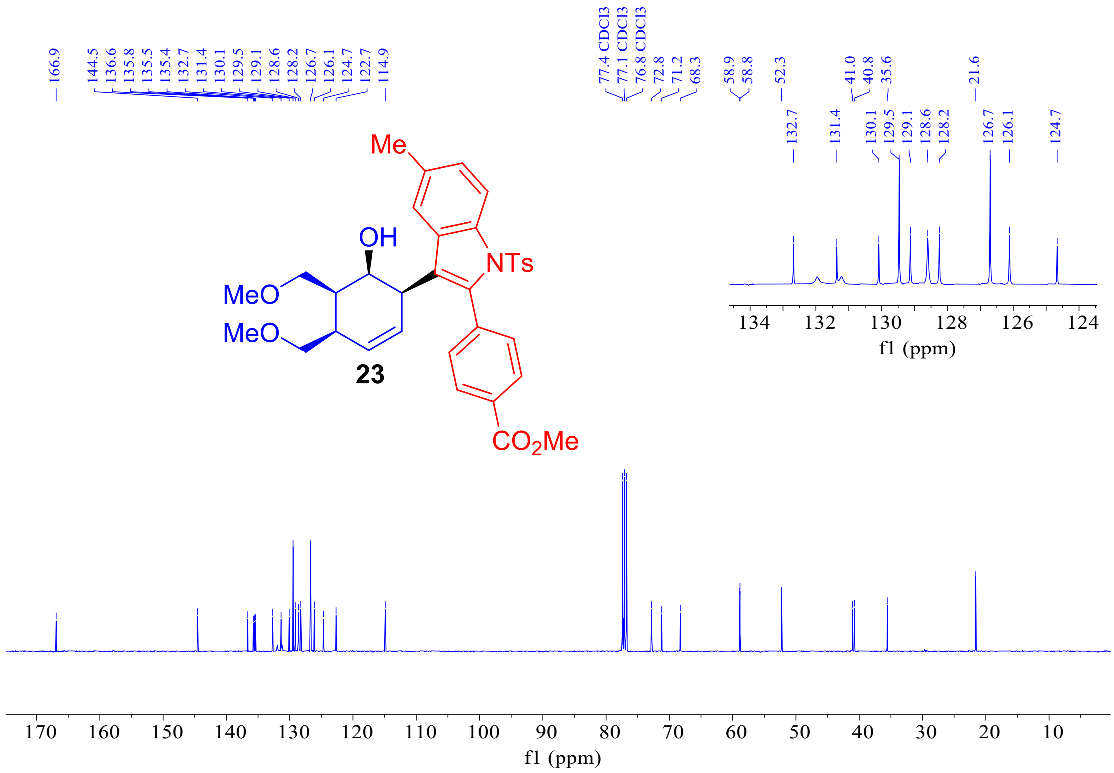

f1 (ppm)
OH
MeO
MeO
Me
NTs
21


f1 (ppm)
OH
MeO
MeO
Me
NTs
21

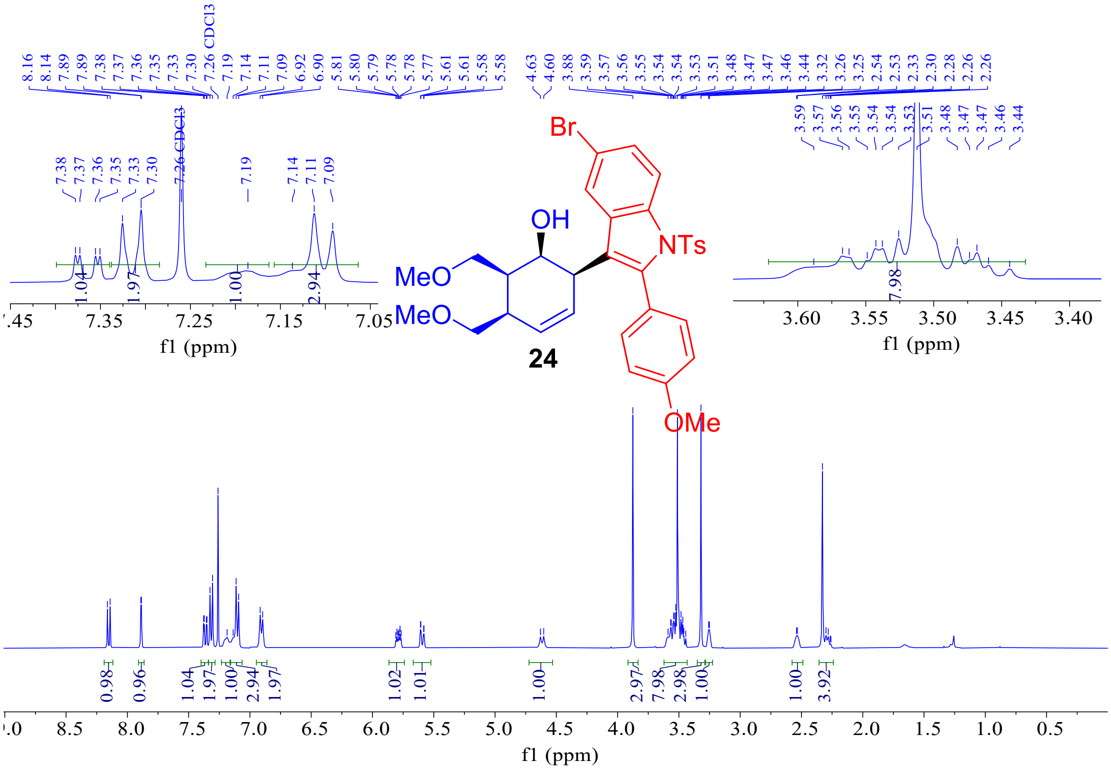
^{1}H NMR (400 MHz, Chloroform-*d*)



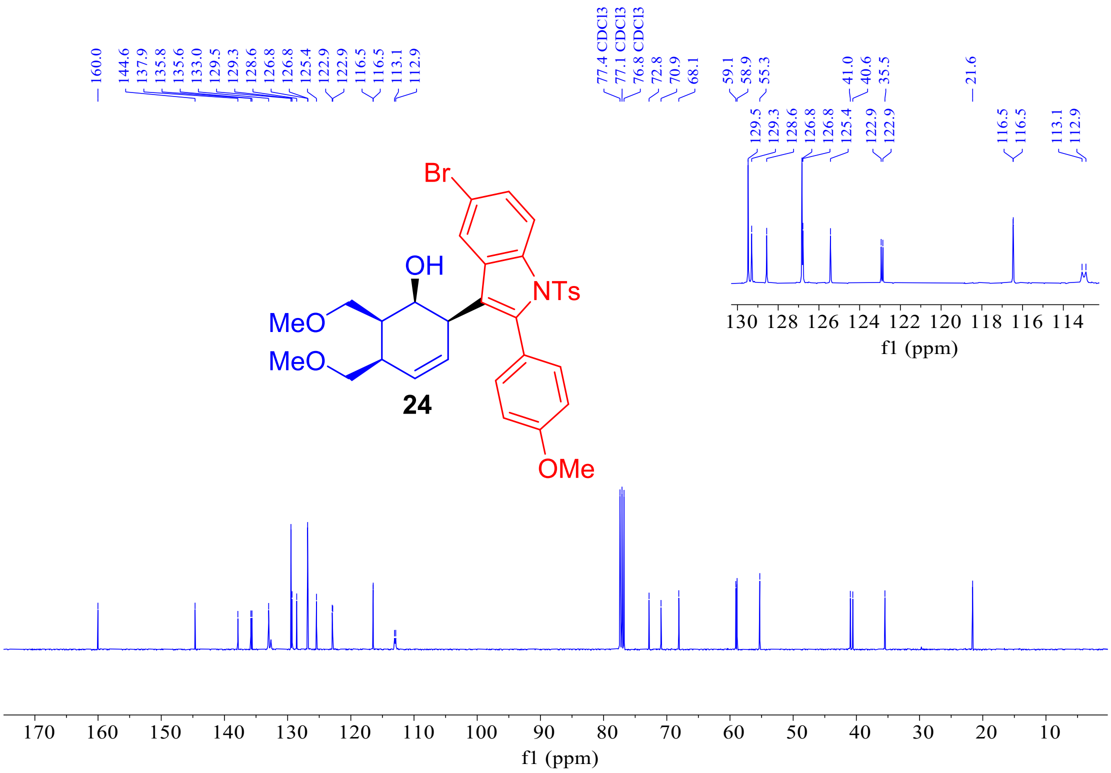
^{13}C NMR (101 MHz, Chloroform-*d*)



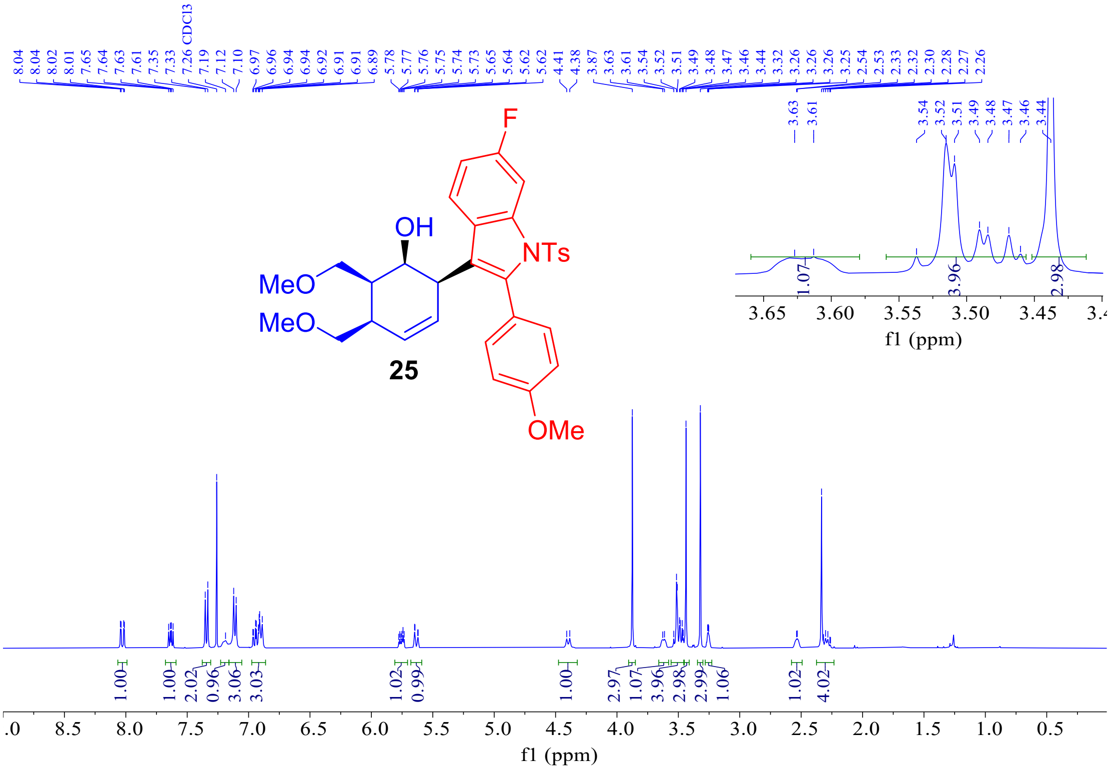
[1]H NMR (400 MHz, Chloroform-*d*)



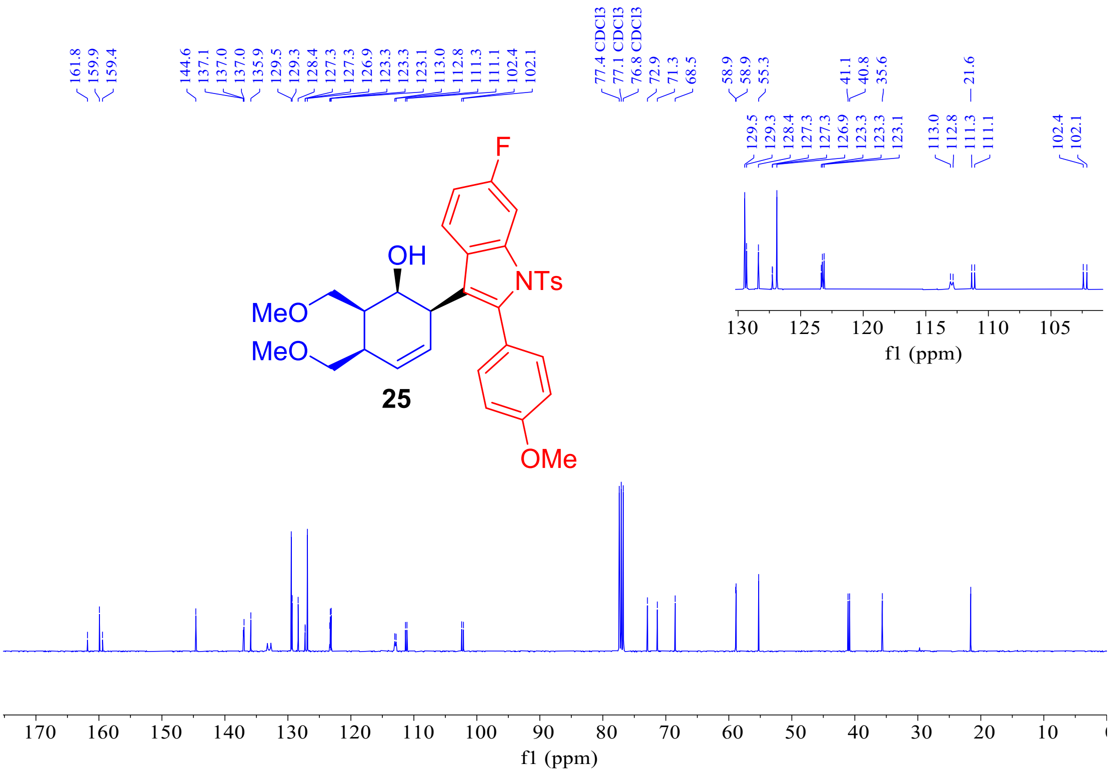
[13]C NMR (101 MHz, Chloroform-*d*)



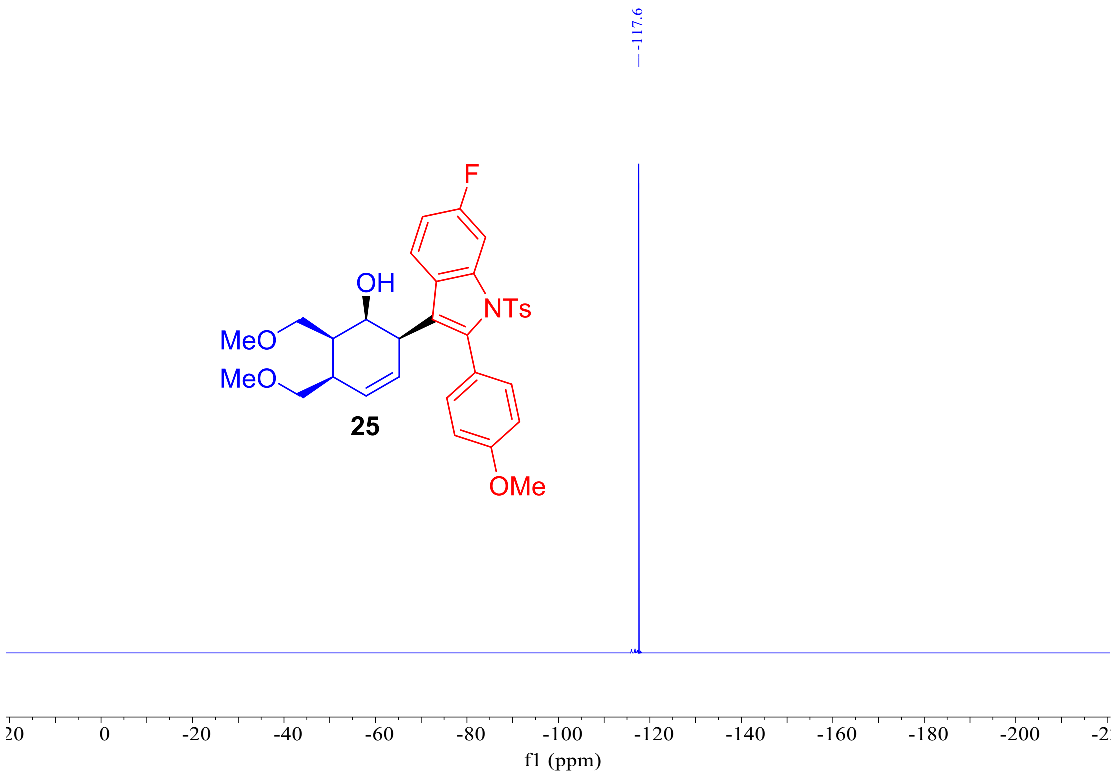
^{1}H NMR (400 MHz, Chloroform-*d*)



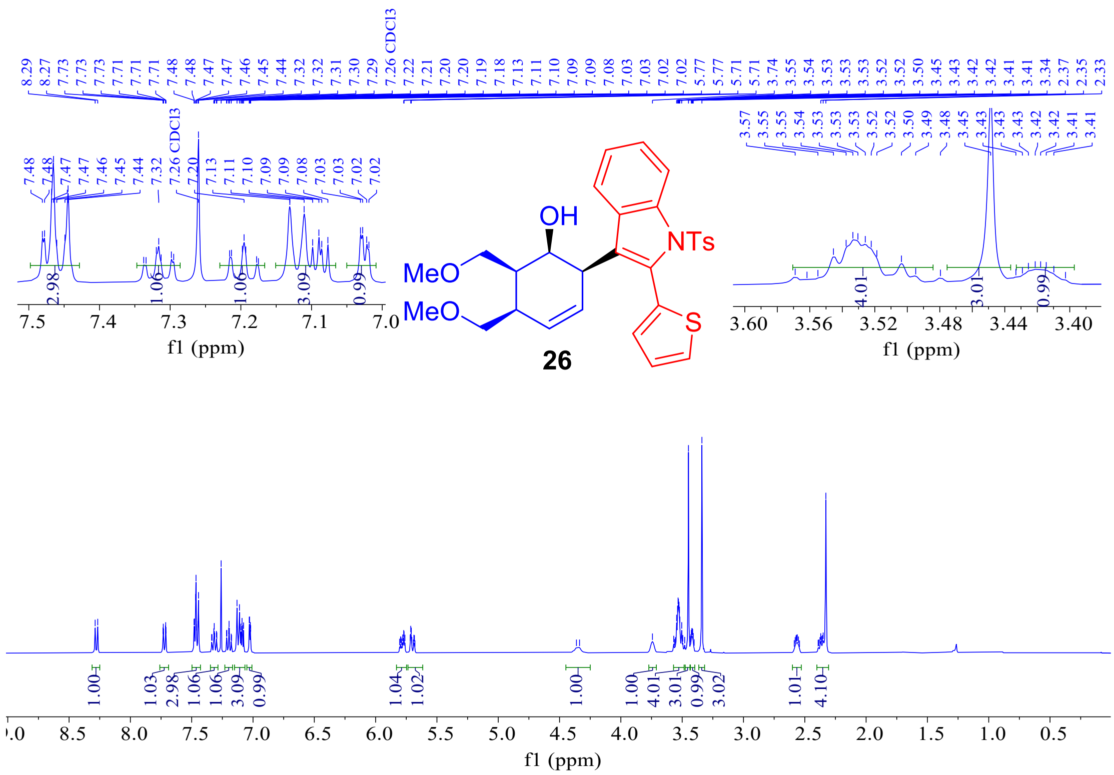
^{13}C NMR (101 MHz, Chloroform-*d*)



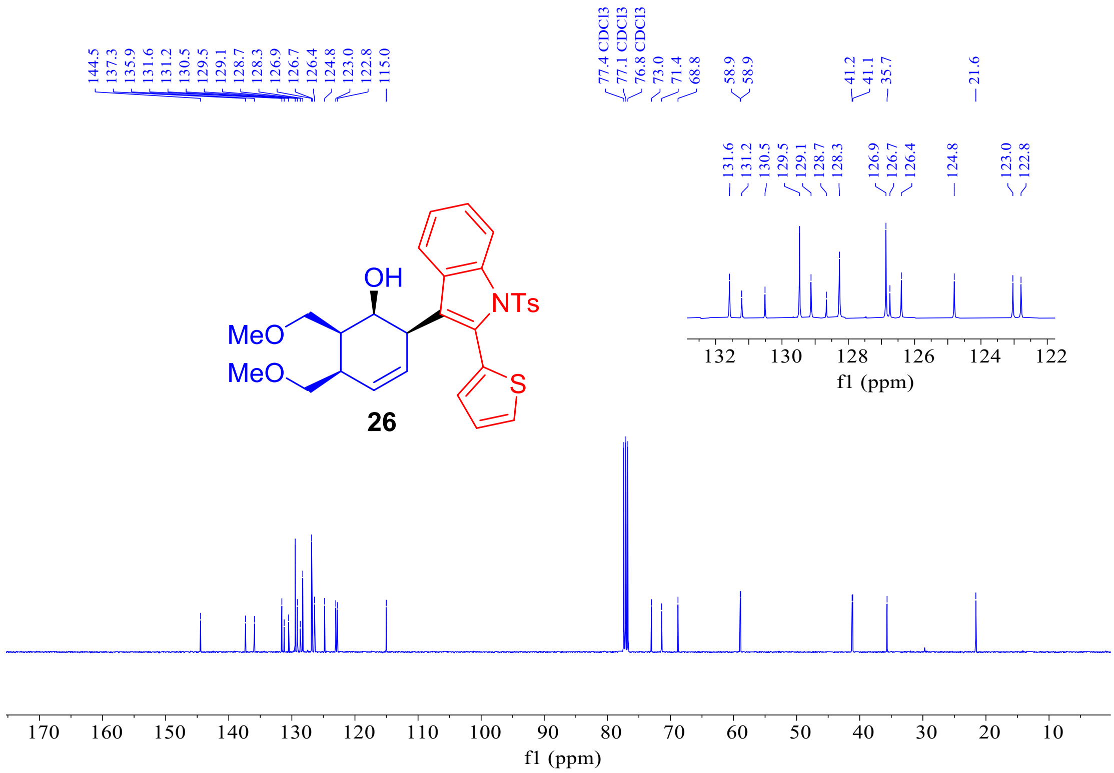
^{19}F NMR (376 MHz, Chloroform-*d*)



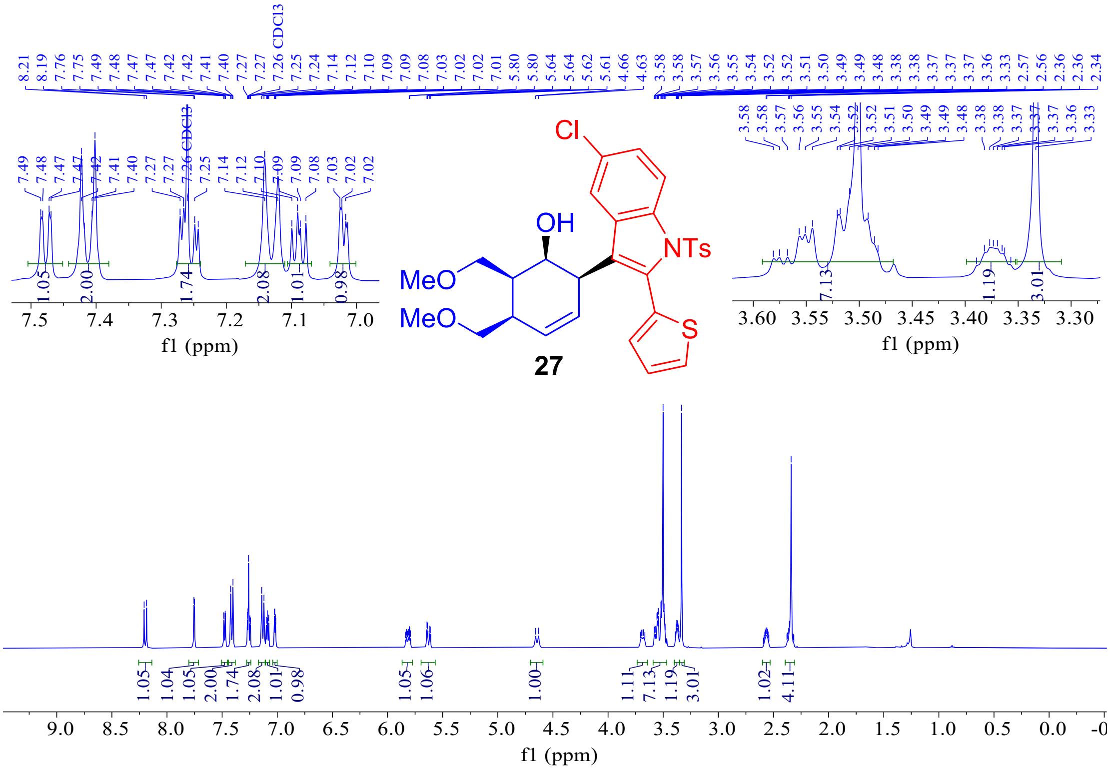
^{1}H NMR (400 MHz, Chloroform-*d*)



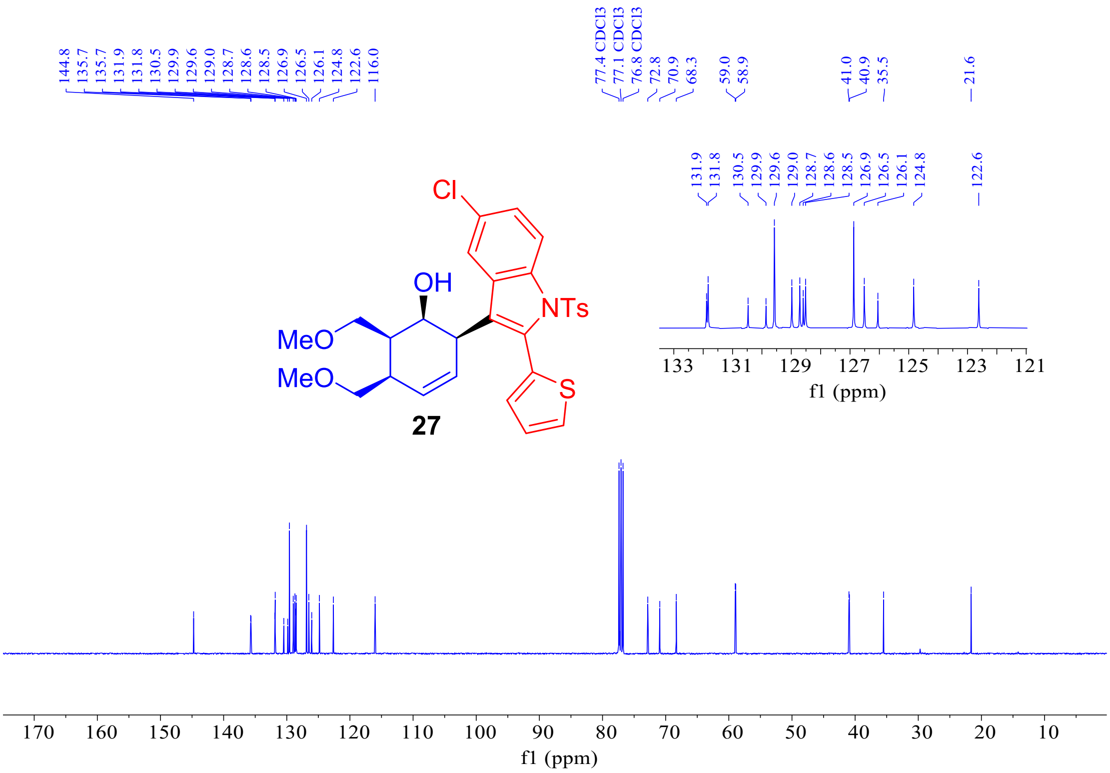
^{13}C NMR (101 MHz, Chloroform-*d*)



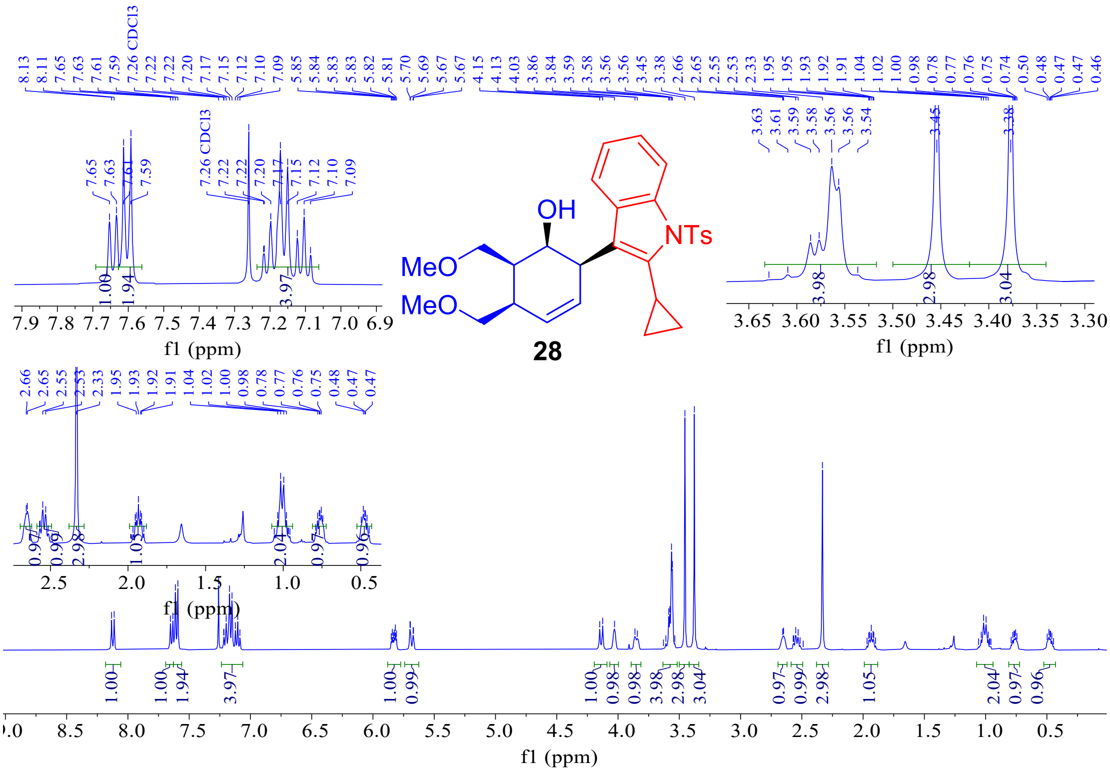
^{1}H NMR (400 MHz, Chloroform-*d*)



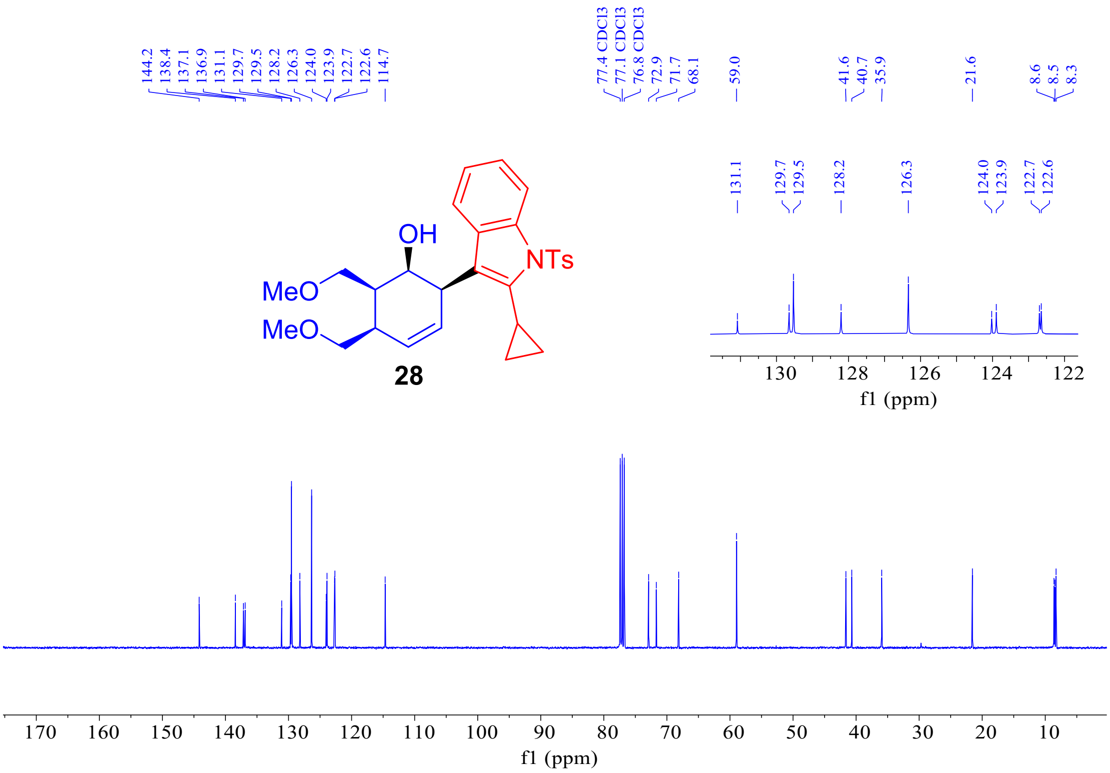
^{13}C NMR (101 MHz, Chloroform-*d*)



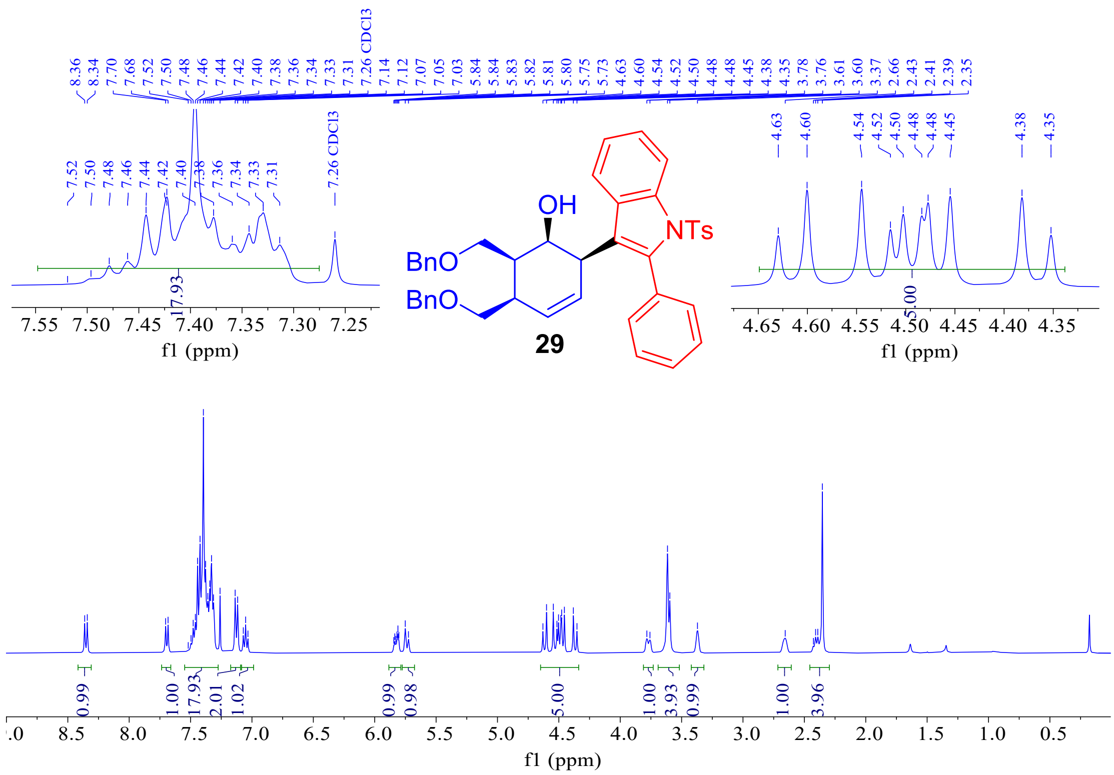
[1]H NMR (400 MHz, Chloroform-*d*)



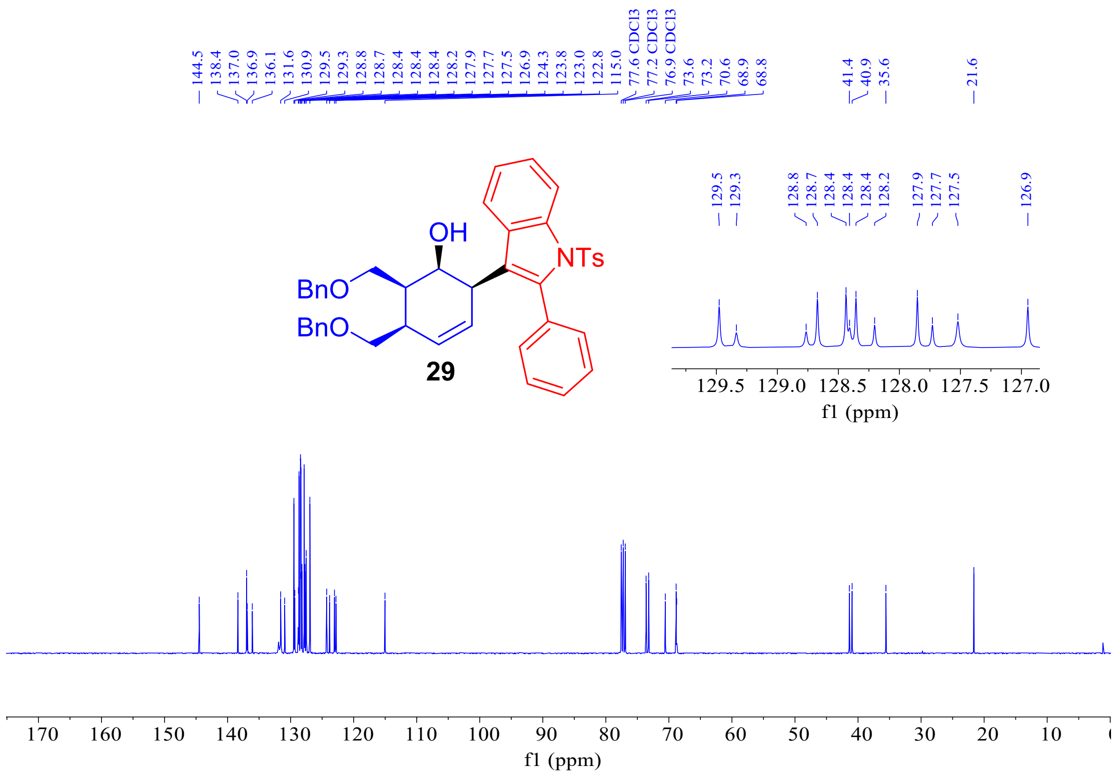
[13]C NMR (101 MHz, Chloroform-*d*)



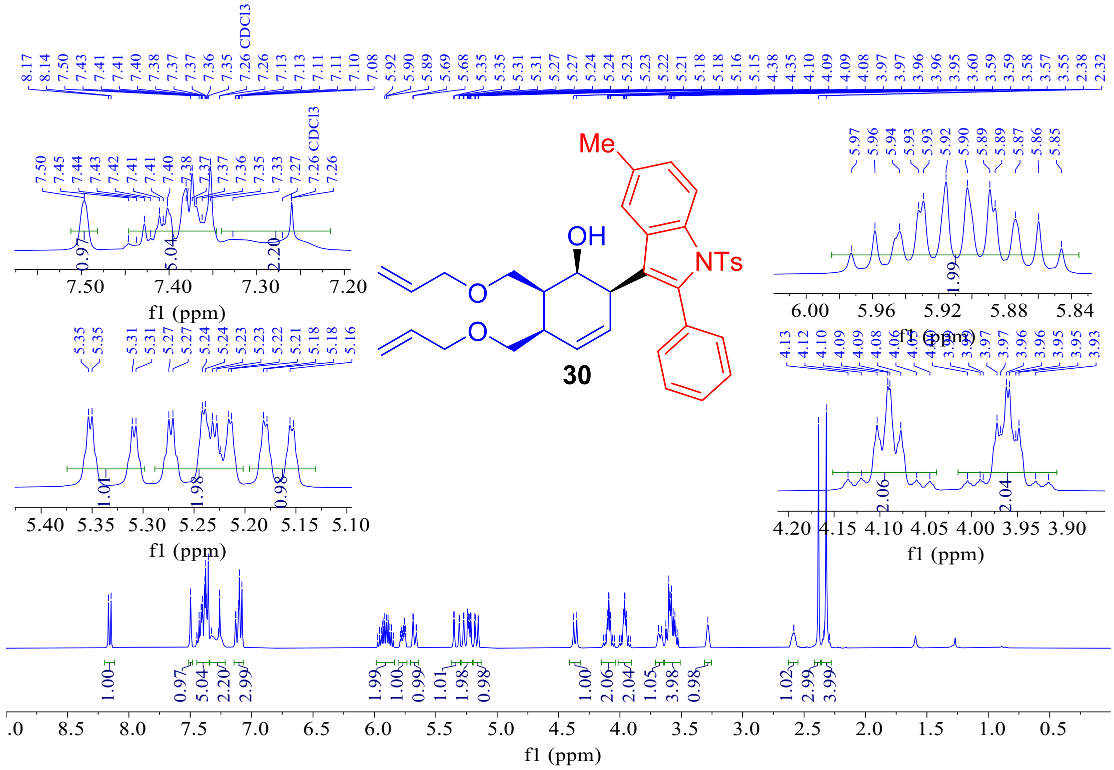
[1]H NMR (400 MHz, Chloroform-*d*)



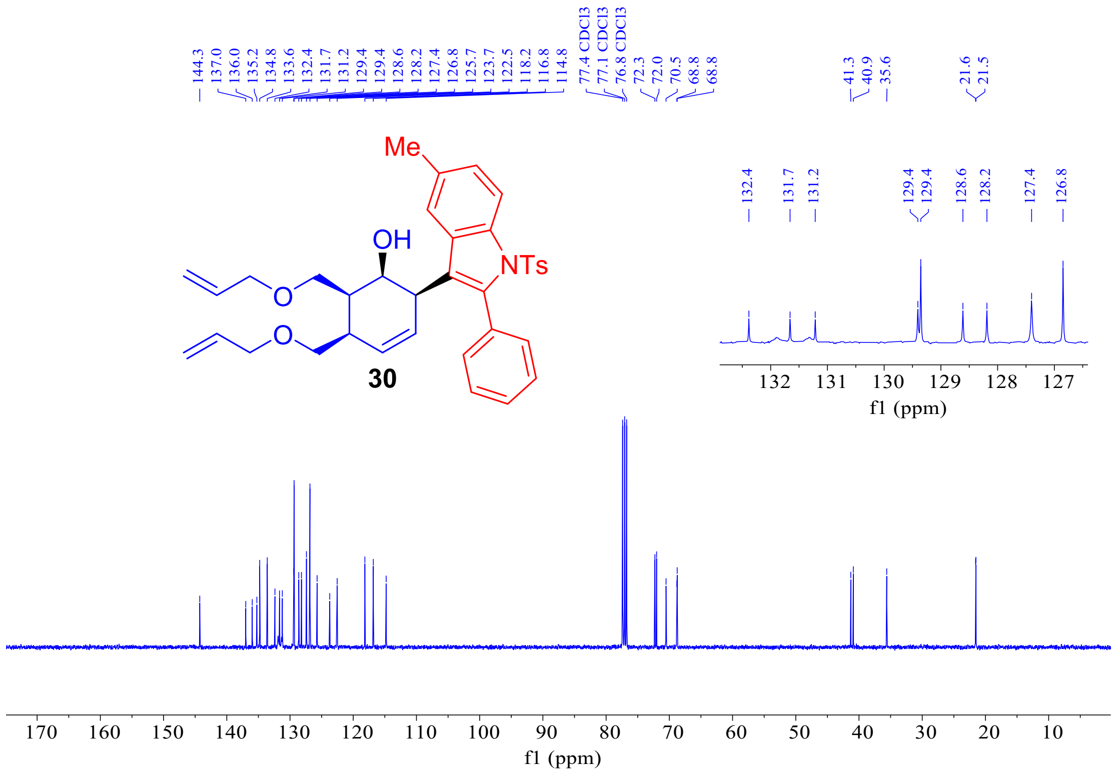
[13]C NMR (101 MHz, Chloroform-*d*)



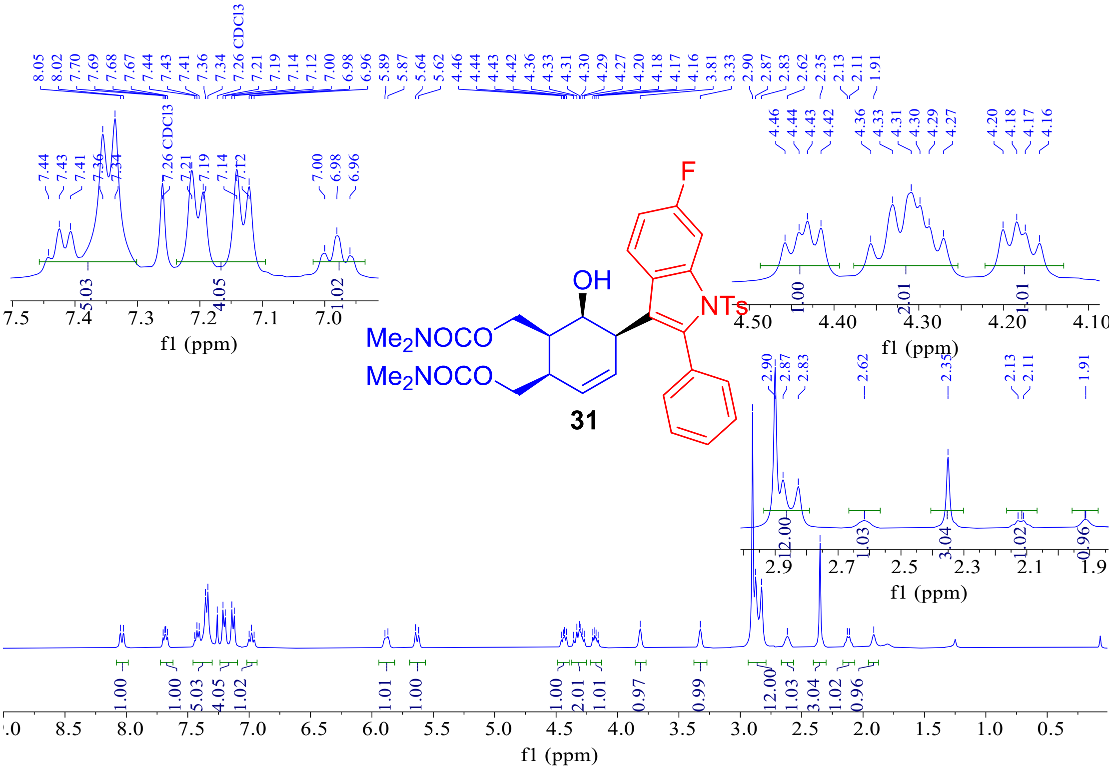
[1]H NMR (400 MHz, Chloroform-*d*)



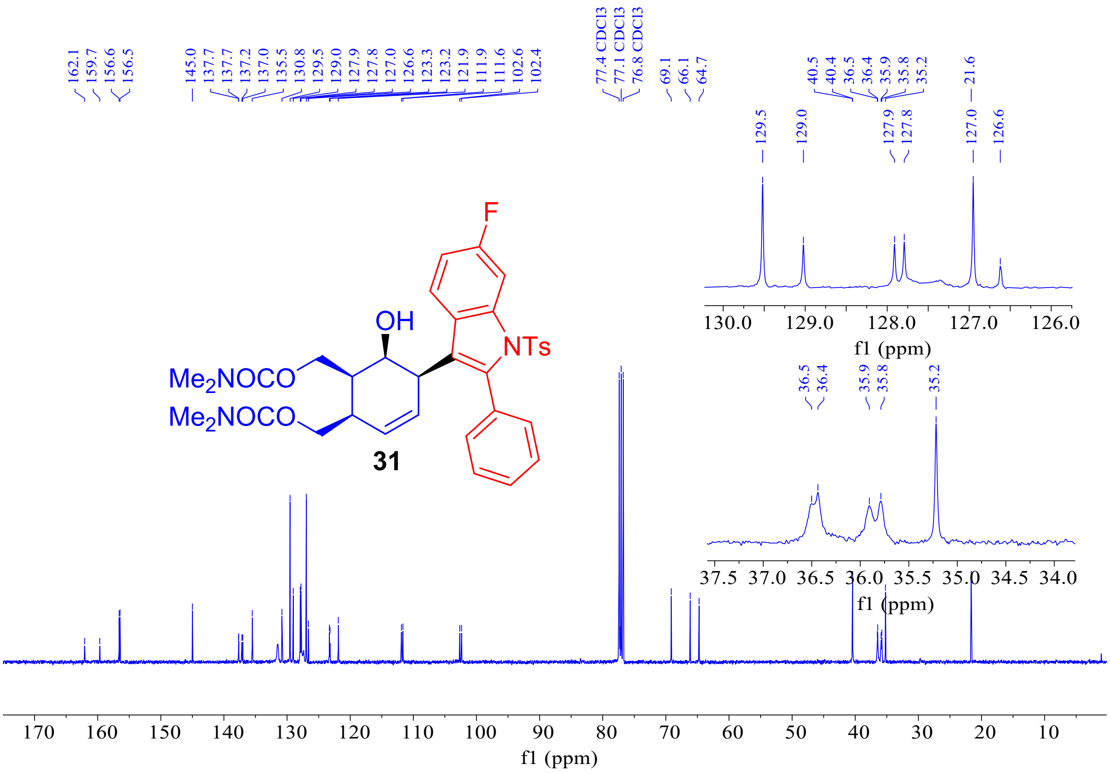
[13]C NMR (101 MHz, Chloroform-*d*)



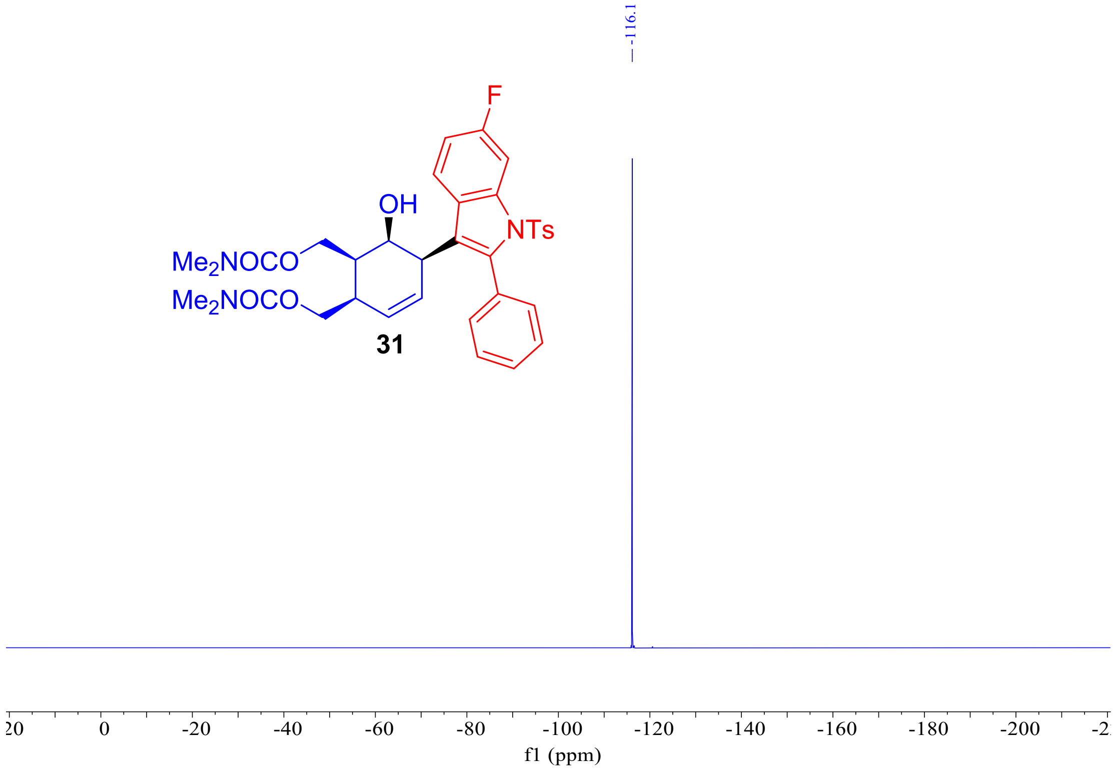
^{1}H NMR (400 MHz, Chloroform-*d*)



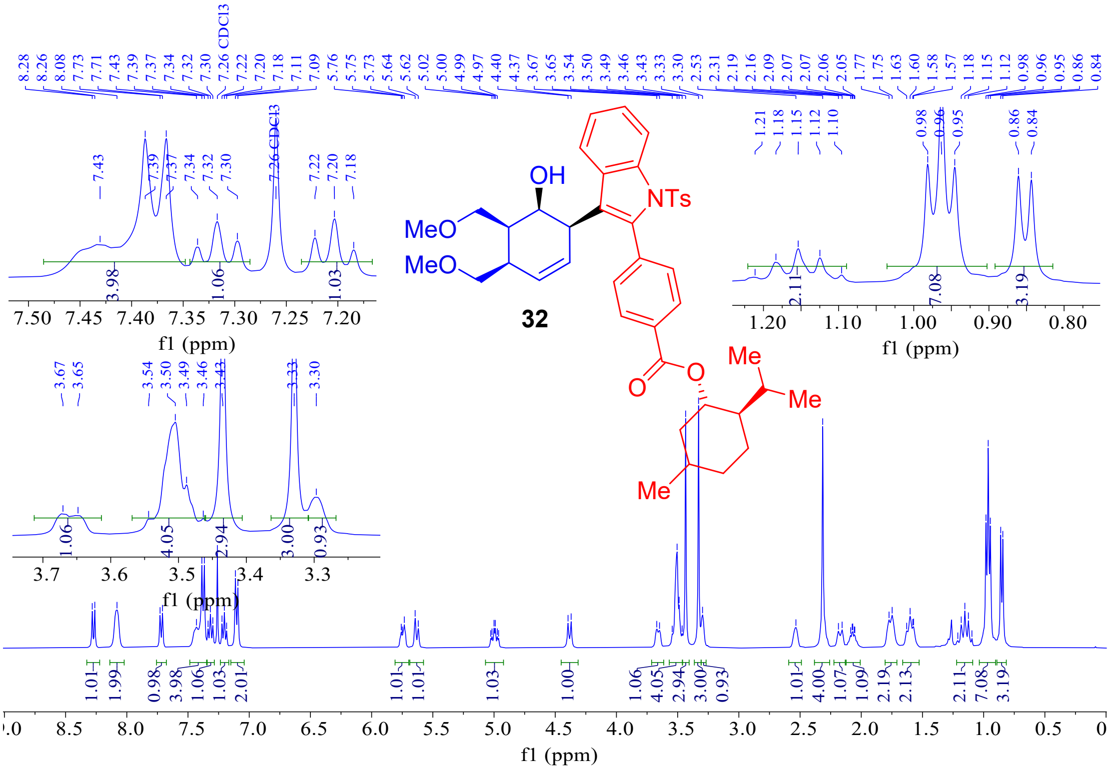
^{13}C NMR (101 MHz, Chloroform-*d*)



[19]F NMR (376 MHz, Chloroform-*d*)



^{1}H NMR (400 MHz, Chloroform-*d*)



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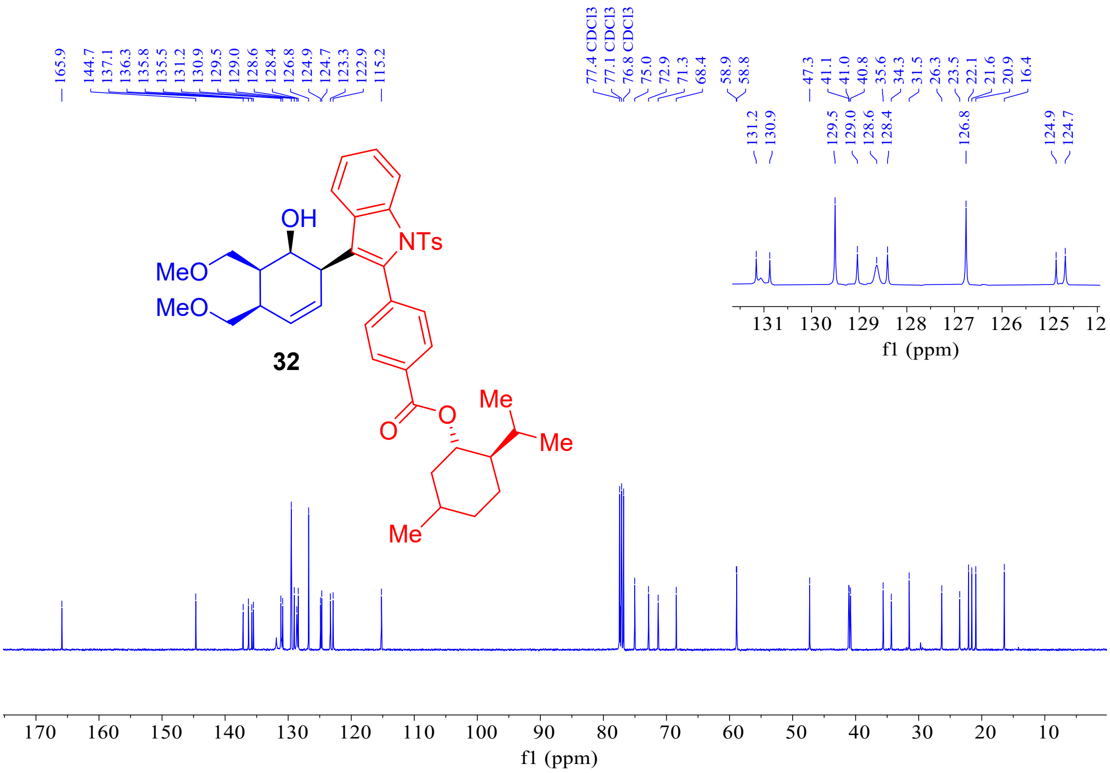

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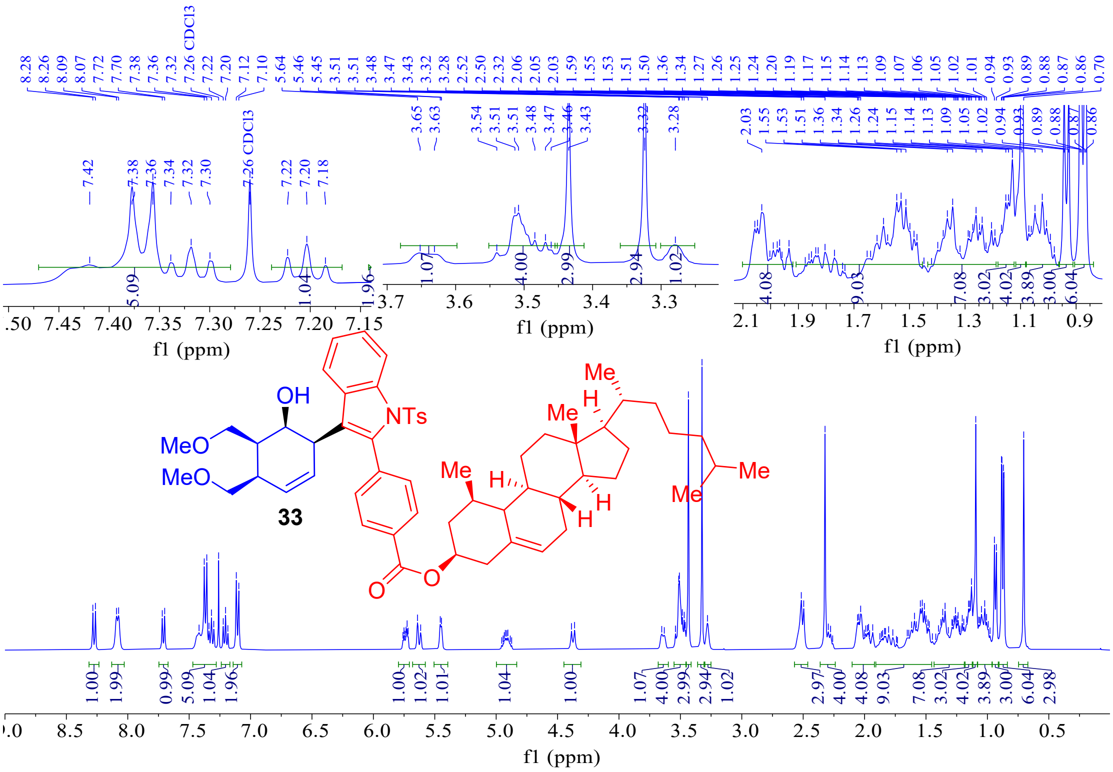
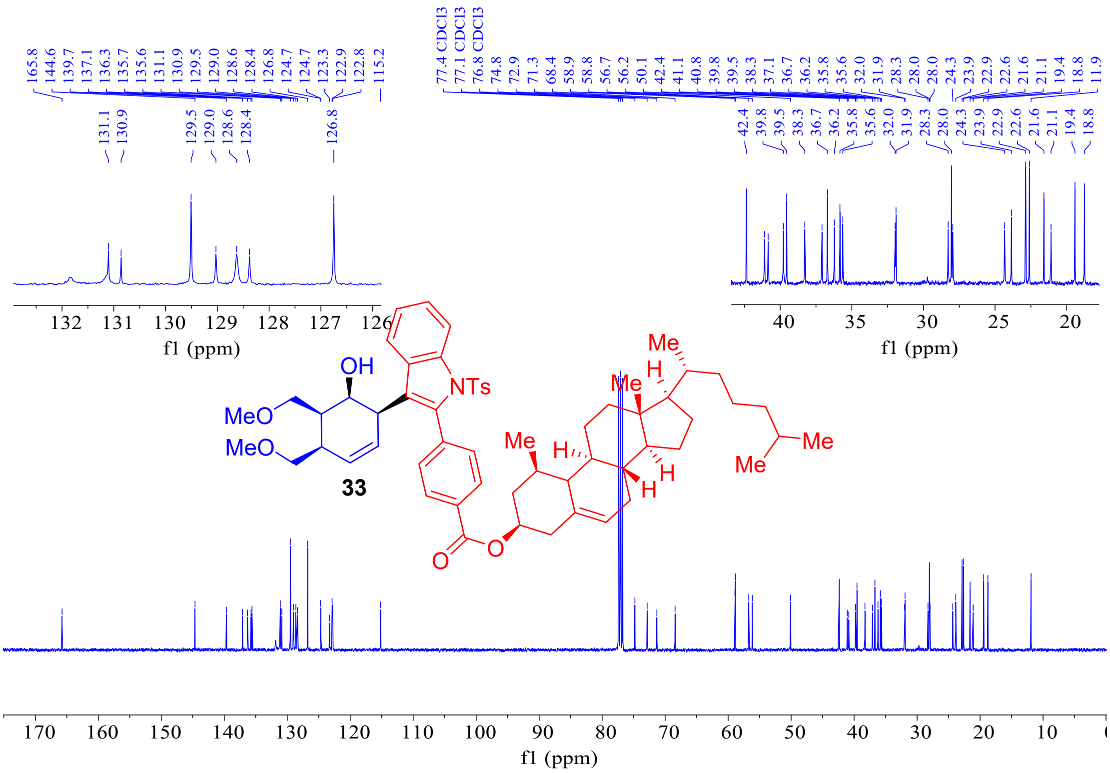
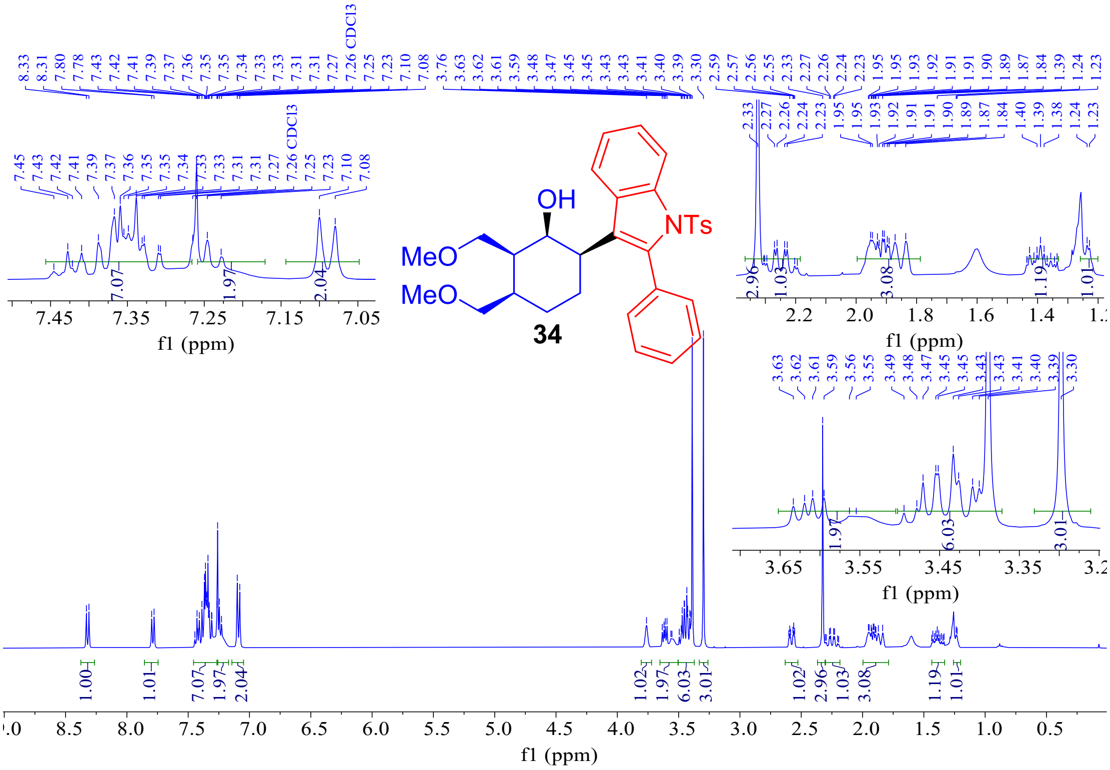


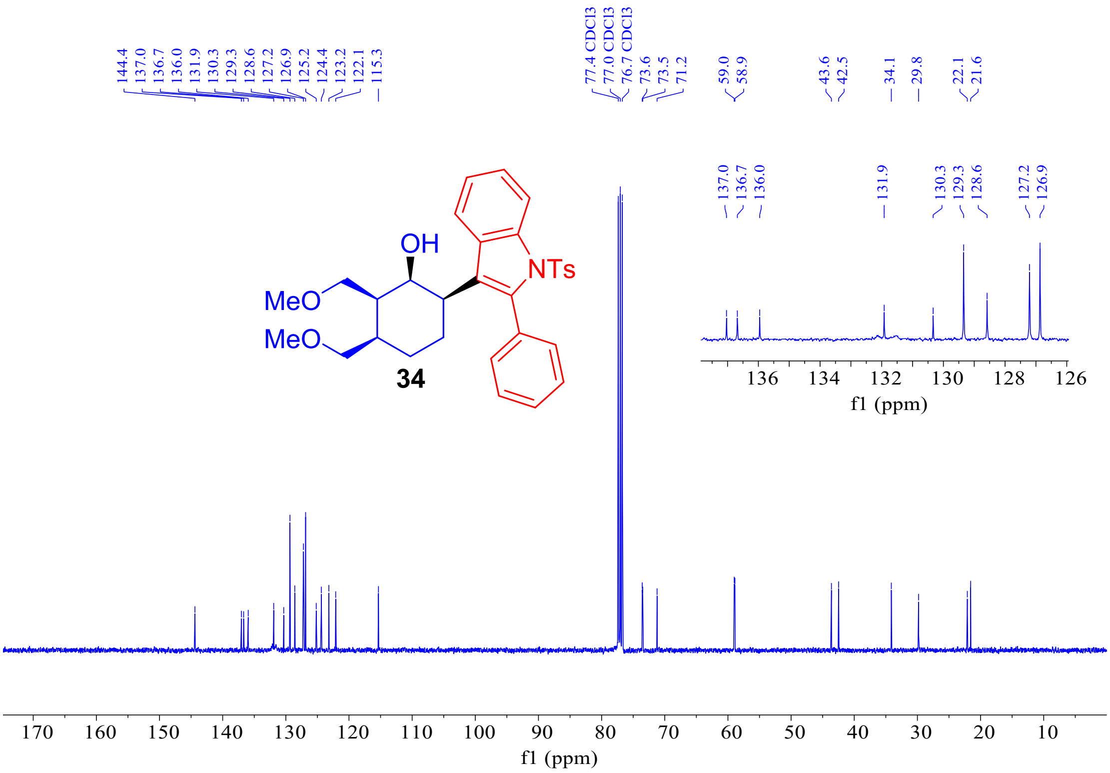
^{13}C NMR (101 MHz, Chloroform-*d*)



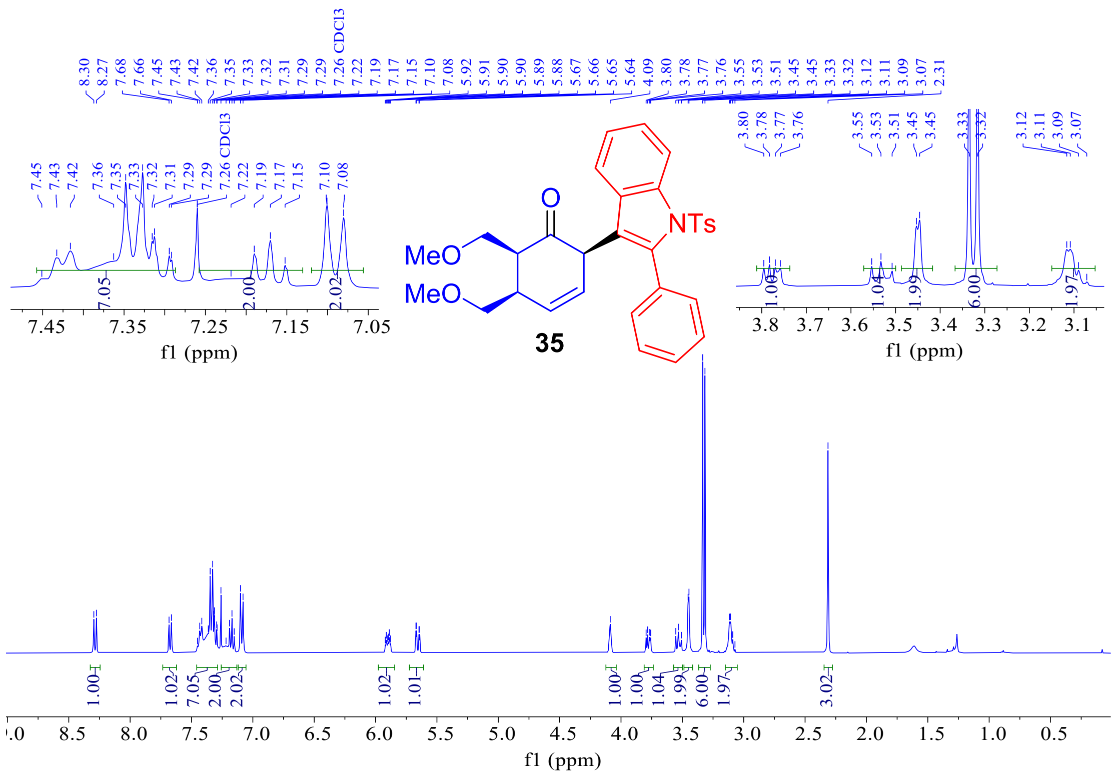
^{1}H NMR (400 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)



^{1}H NMR (400 MHz, Chloroform-*d*)



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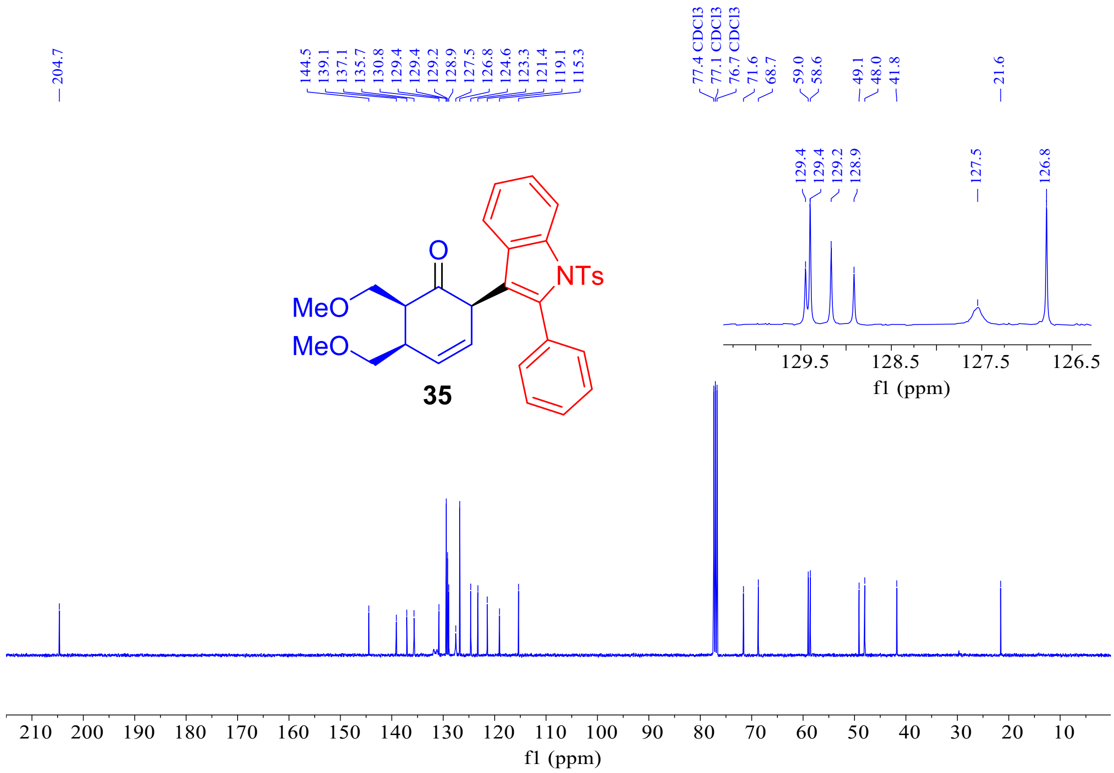
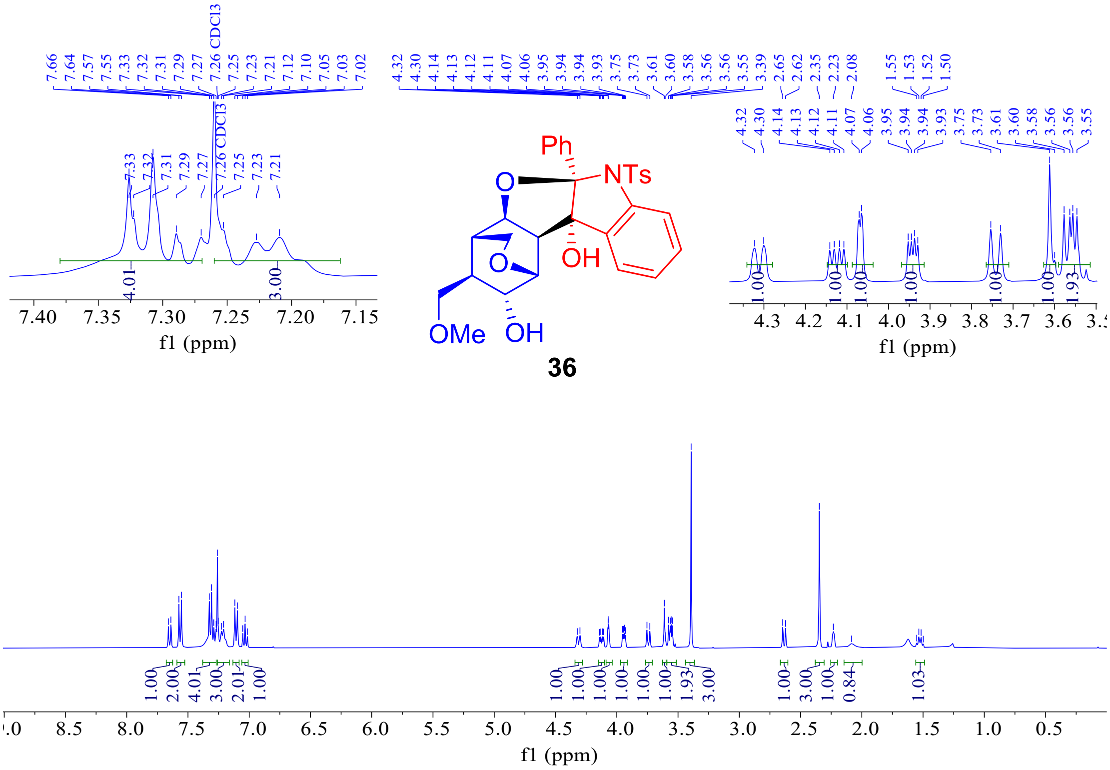
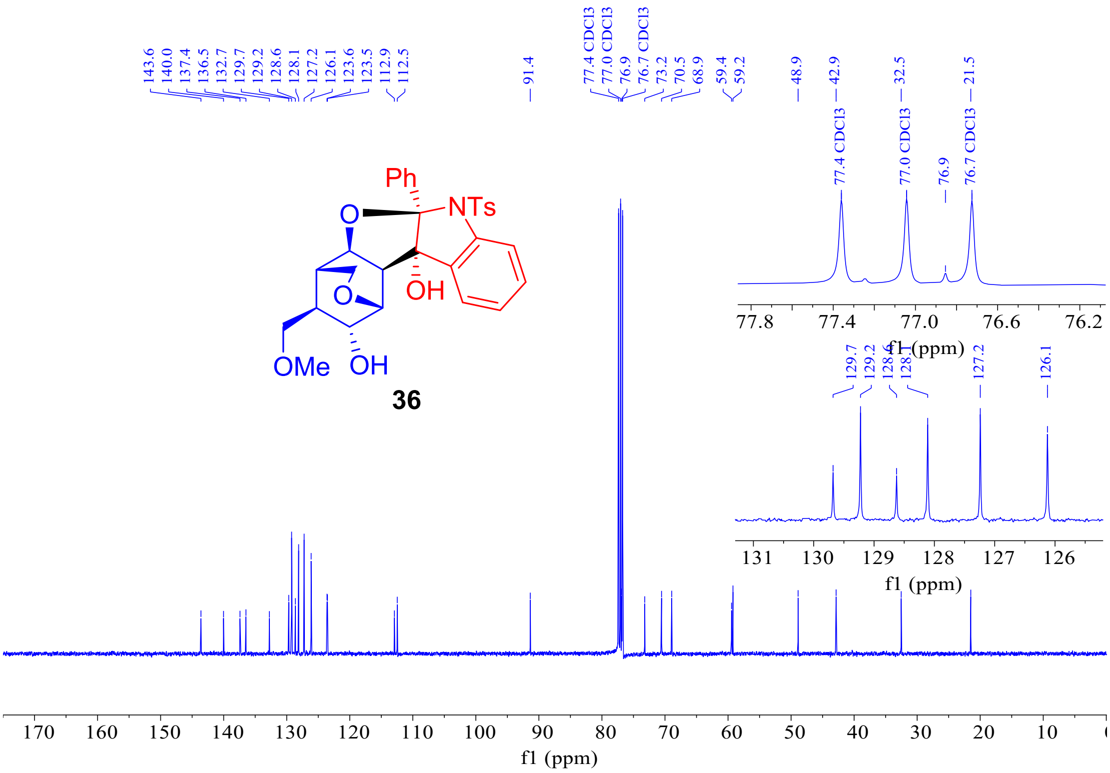


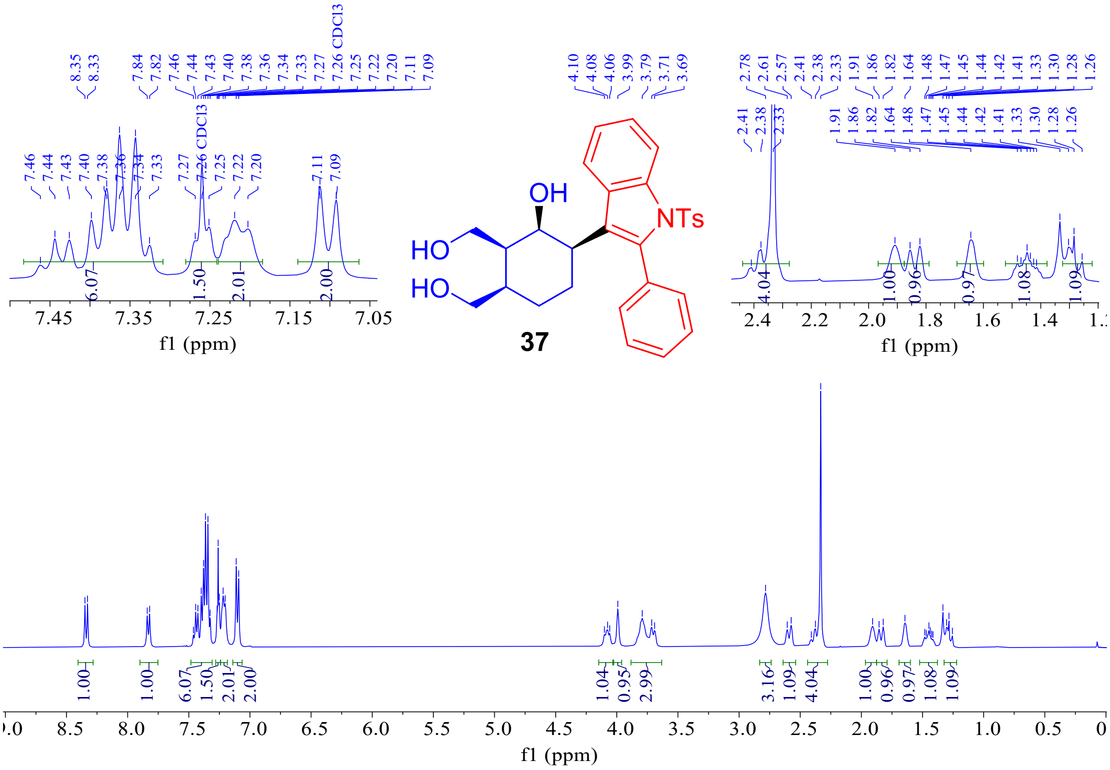
^{1}H NMR (400 MHz, Chloroform-*d*)



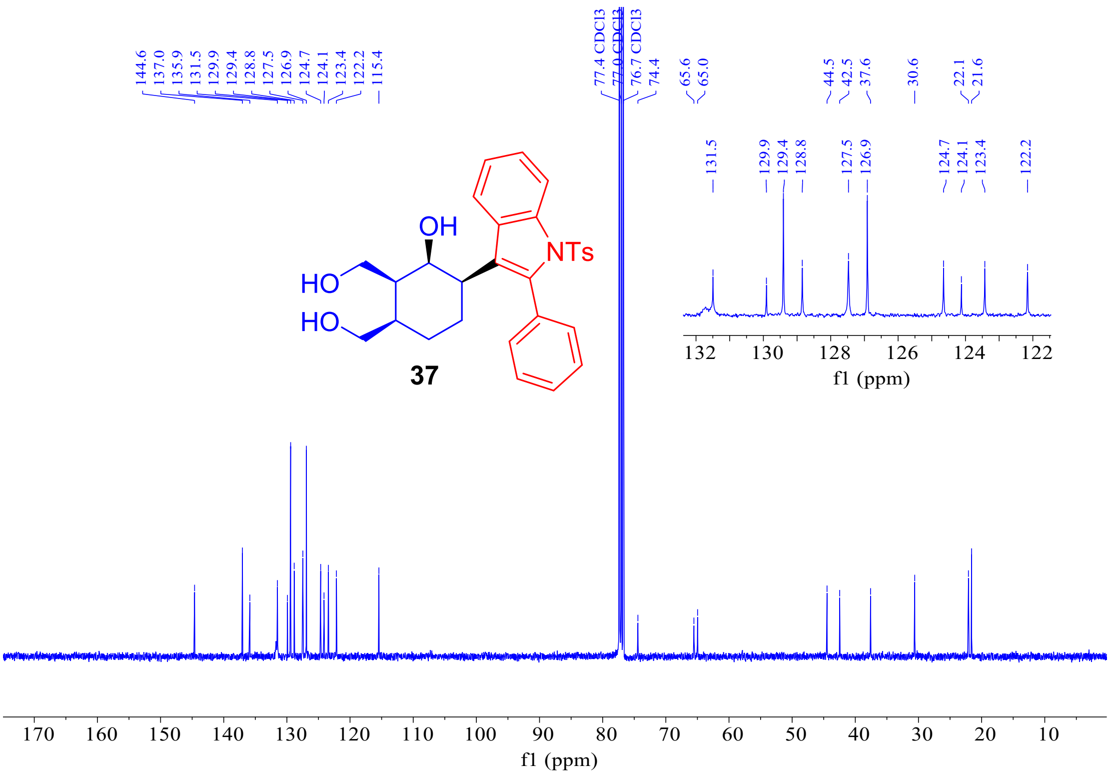
^{13}C NMR (101 MHz, Chloroform-*d*)



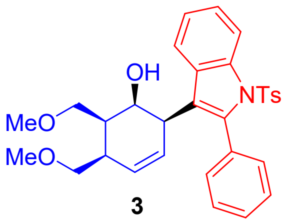
[1]H NMR (400 MHz, Chloroform-*d*)



[13]C NMR (101 MHz, Chloroform-*d*)



11. HPLC Trace



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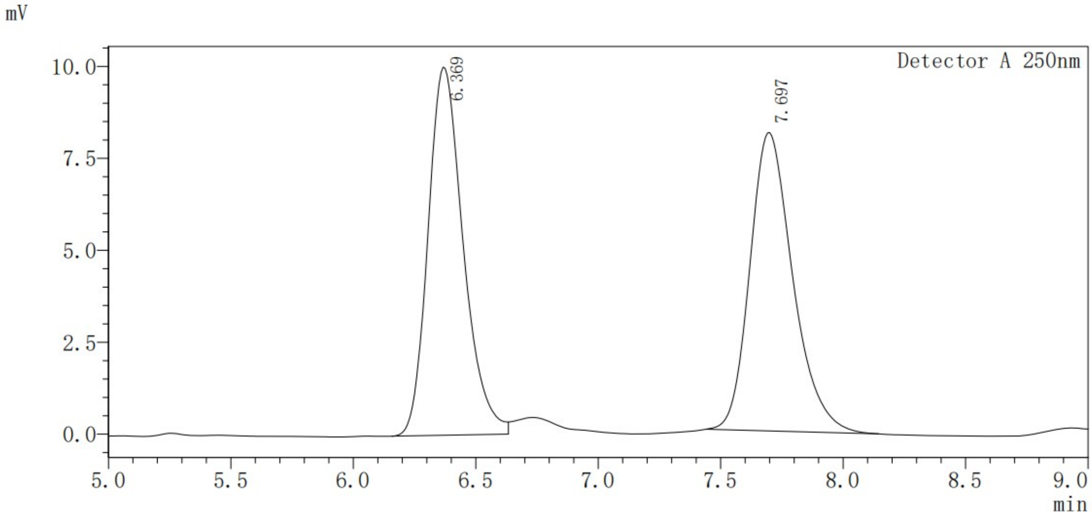
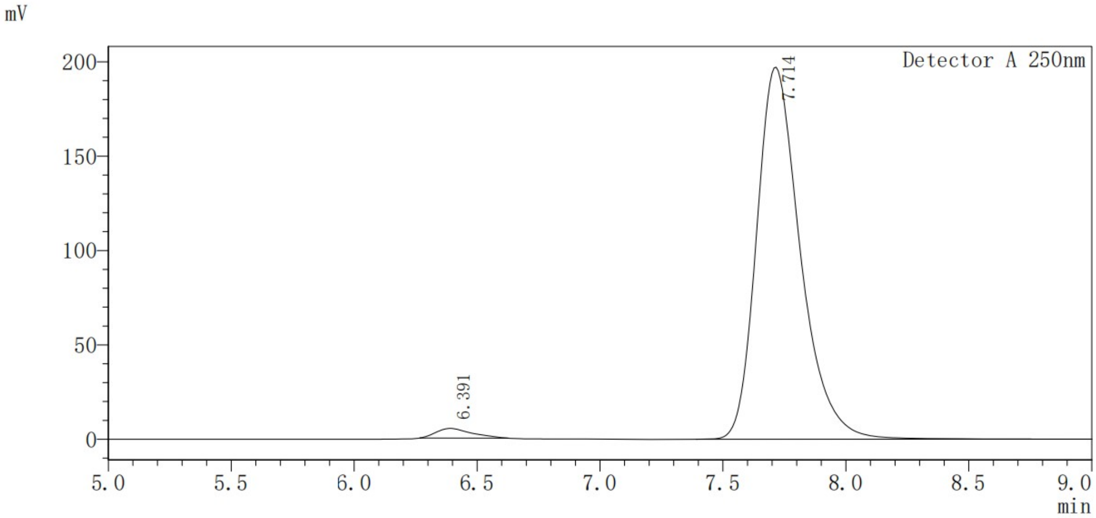
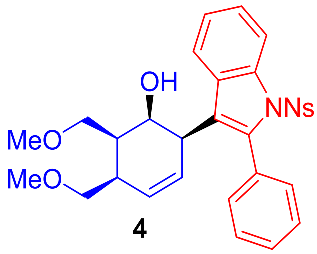


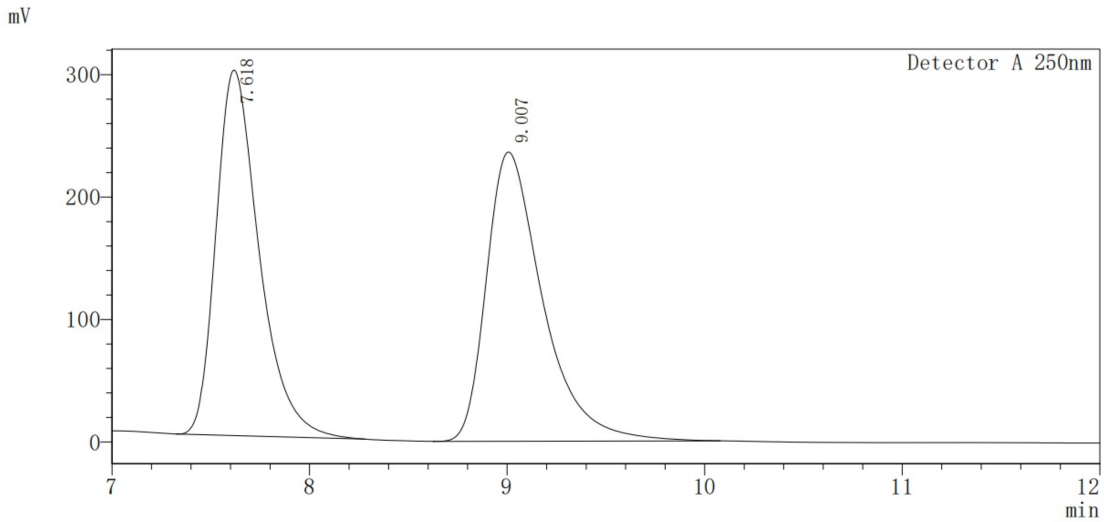
Peak#	Retention	Area	Area(%)
1	6.369	100232	50.363
2	7.697	98788	49.637



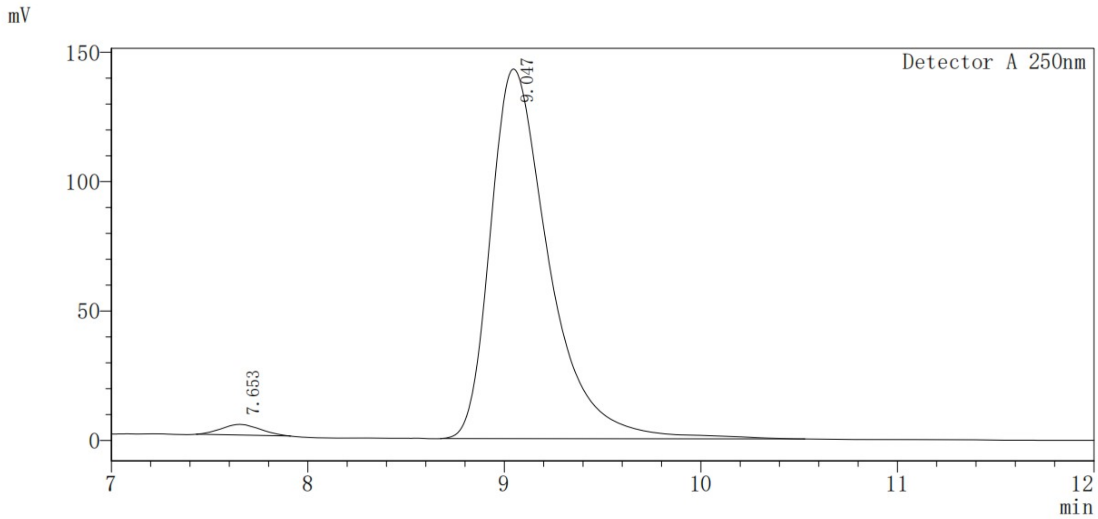
Peak#	Retention	Area	Area(%)
1	6.391	51569	2.071
2	7.714	2437898	97.929



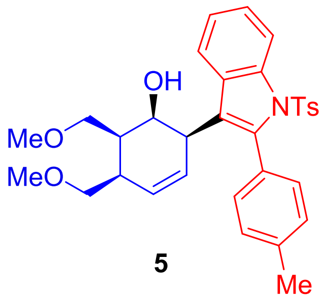
4



Peak#	Retention	Area	Area(%)
1	7.618	4534092	49.227
2	9.007	4676539	50.773



Peak#	Retention	Area	Area(%)
1	7.653	56605	1.878
2	9.047	2958010	98.122



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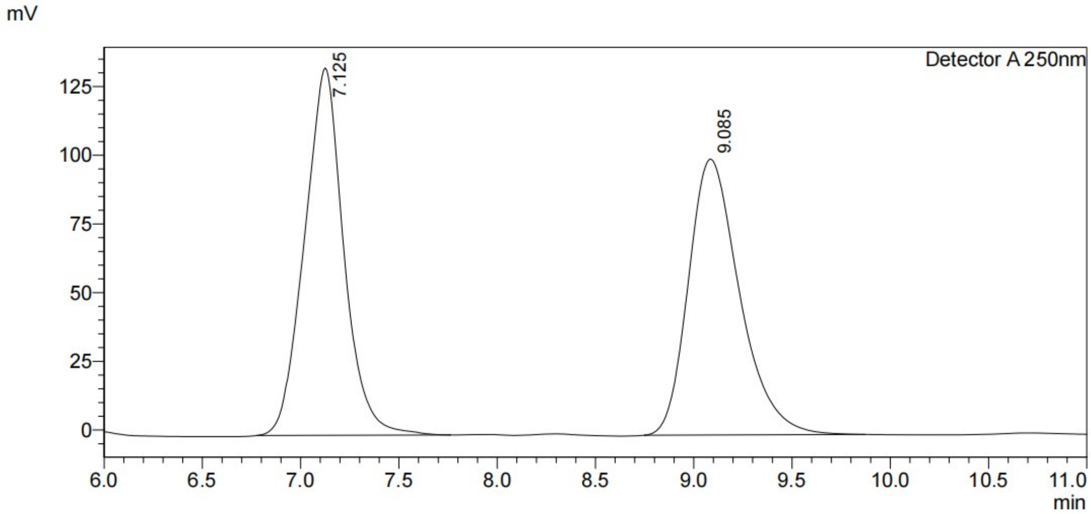
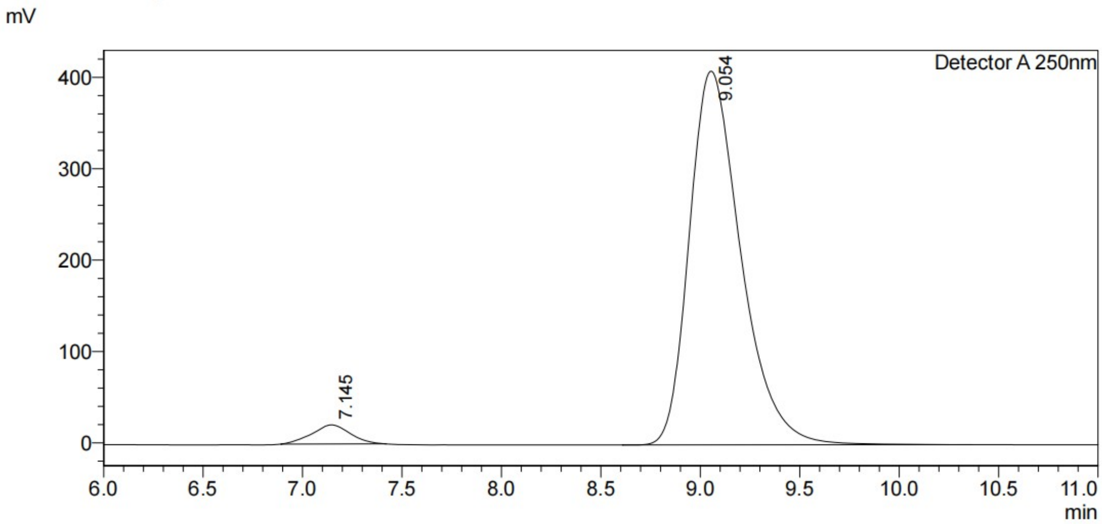
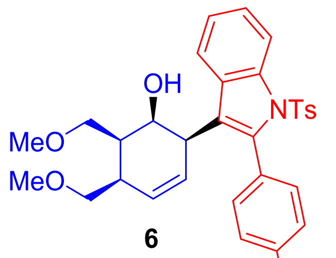


Peak#	Retention	Area	Area(%)
1	7.125	1860208	50.531
2	9.085	1821130	49.469



Peak#	Retention	Area	Area(%)
1	7.145	280651	3.661
2	9.054	7384441	96.339



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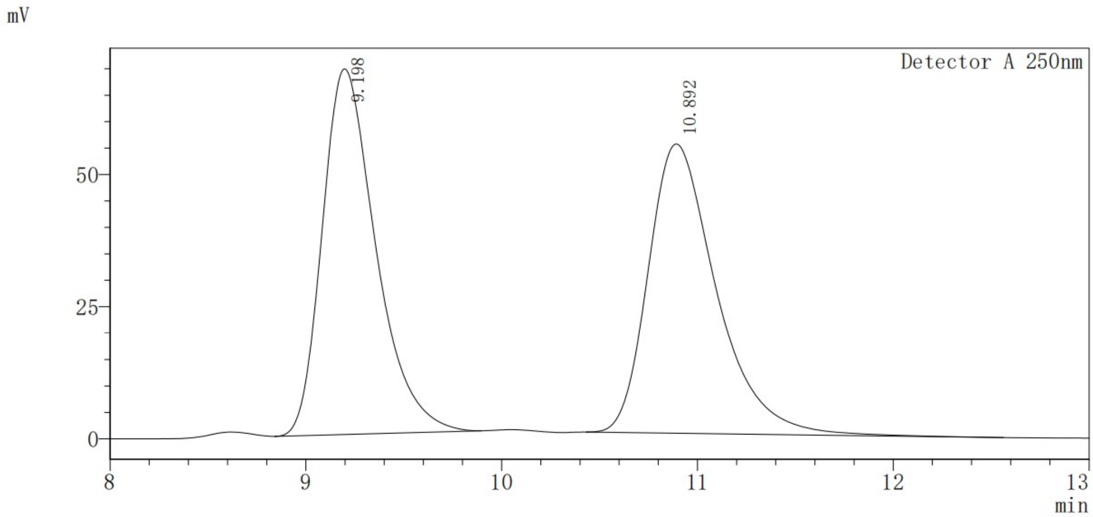
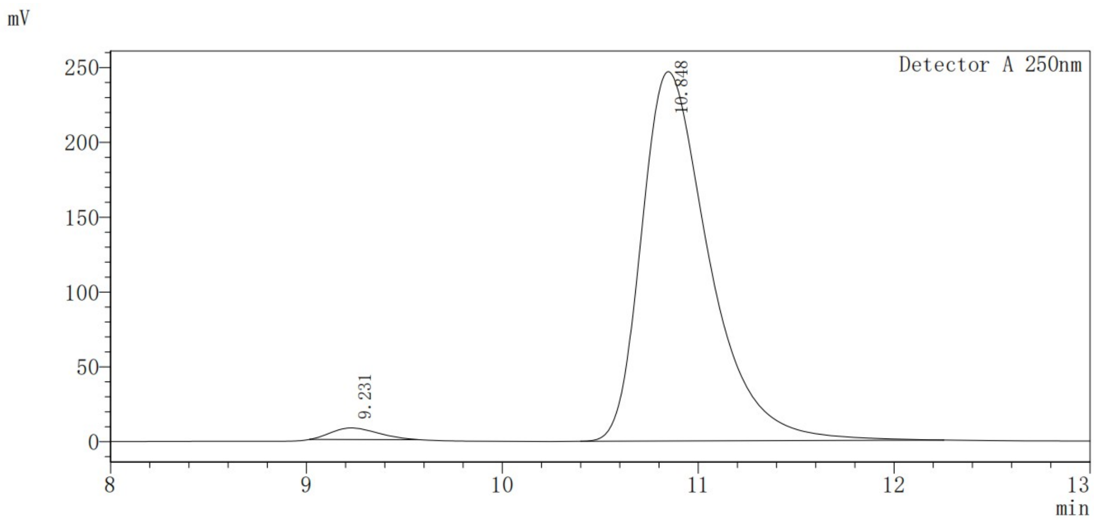
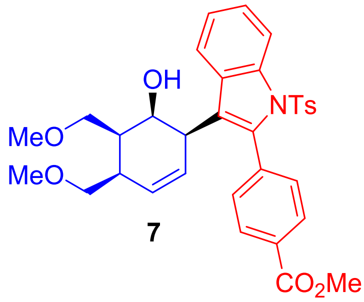


Peak#	Retention	Area	Area(%)
1	9.198	1316427	49.858
2	10.892	1323943	50.142



Peak#	Retention	Area	Area(%)
1	9.231	128173	2.120
2	10.848	5917183	97.880



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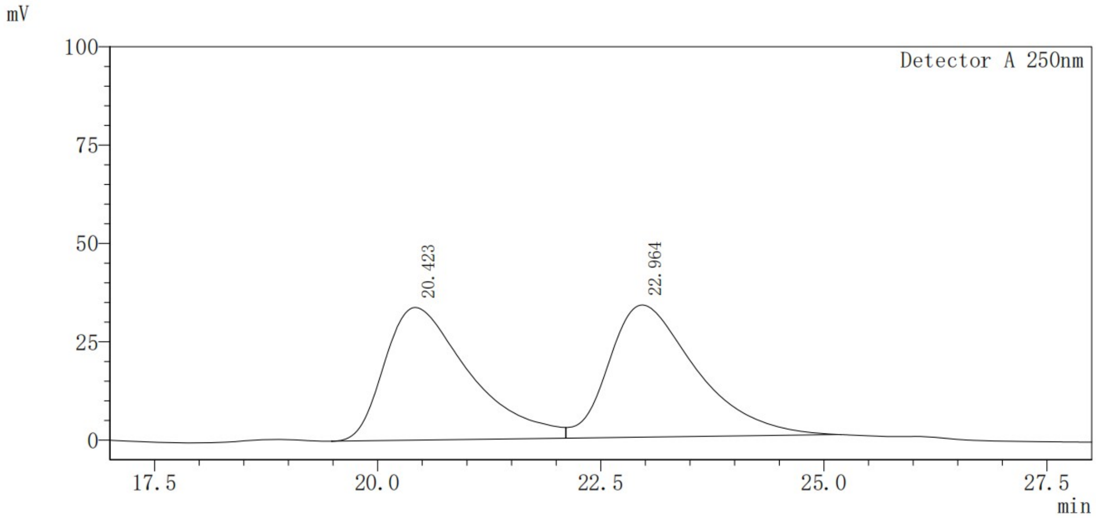
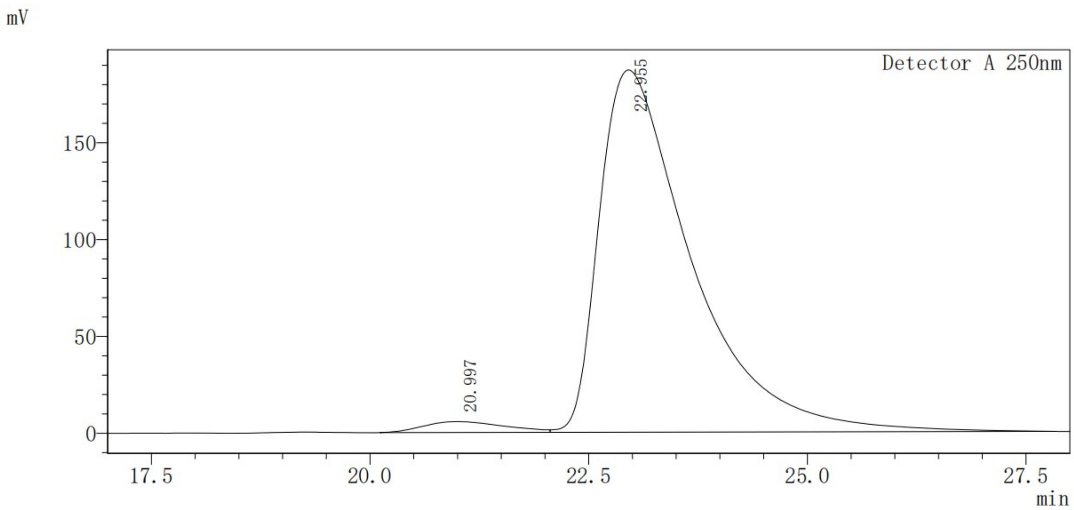
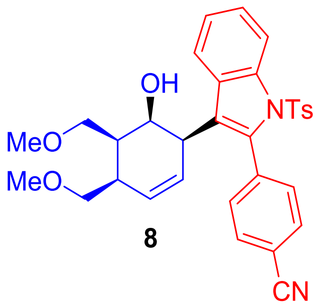


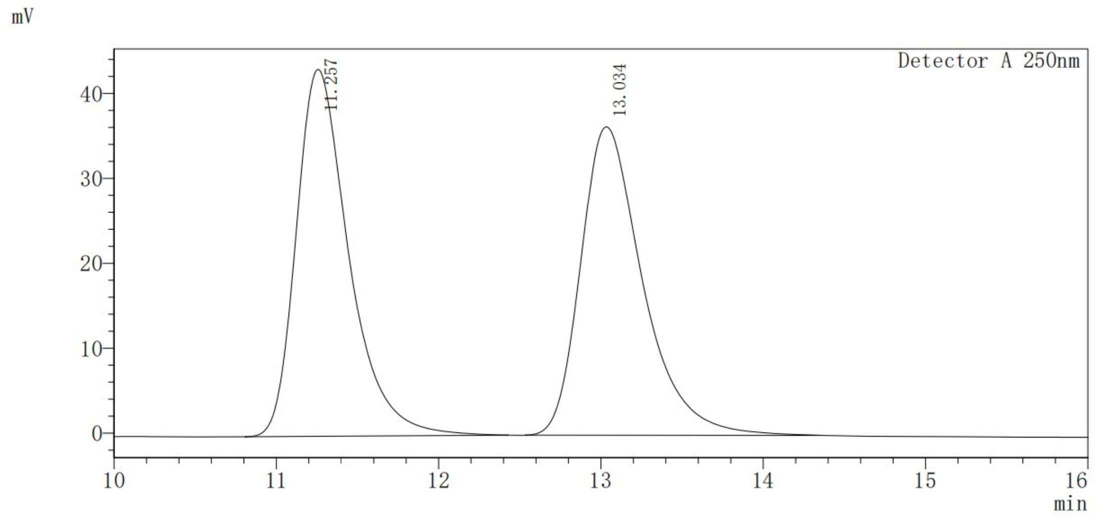
Peak#	Retention	Area	Area(%)
1	20.423	2237072	49.372
2	22.964	2294020	50.628



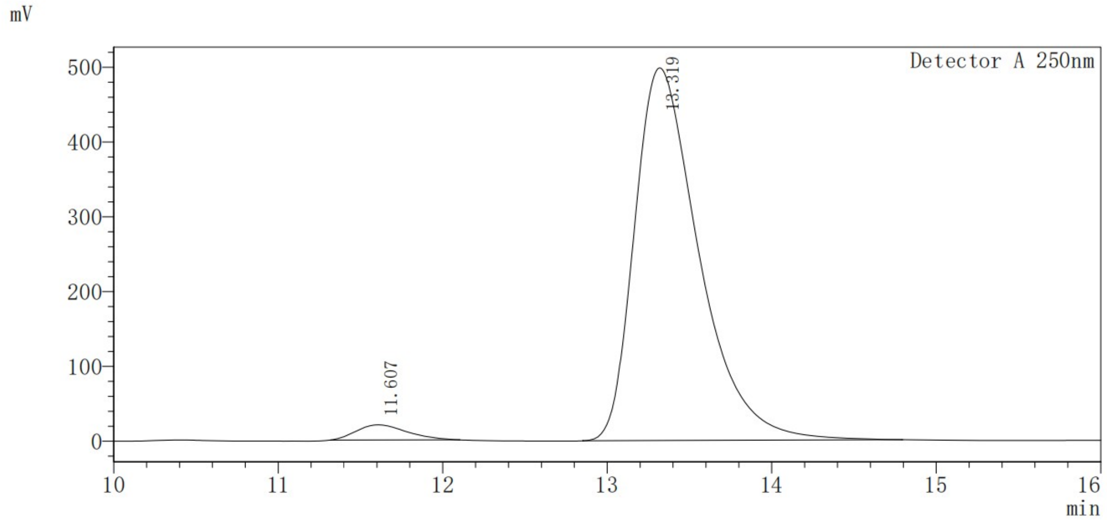
Peak#	Retention	Area	Area(%)
1	20.997	362285	2.565
2	22.955	13762730	97.435



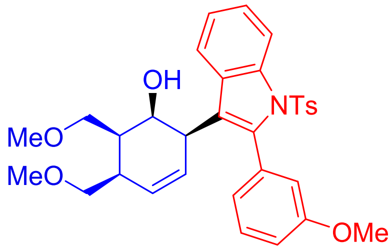
8



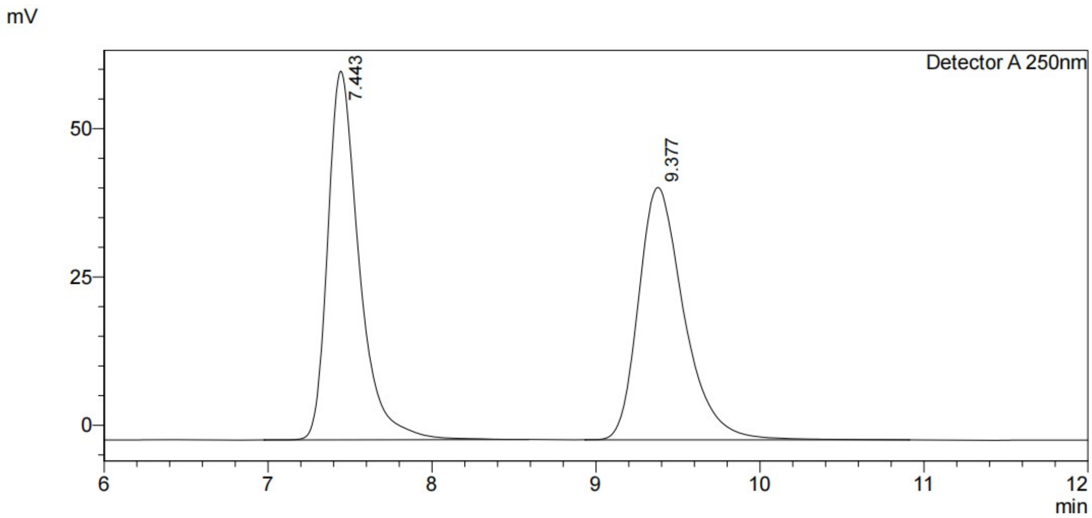
Peak#	Retention	Area	Area(%)
1	11.257	973089	50.163
2	13.034	966772	49.837



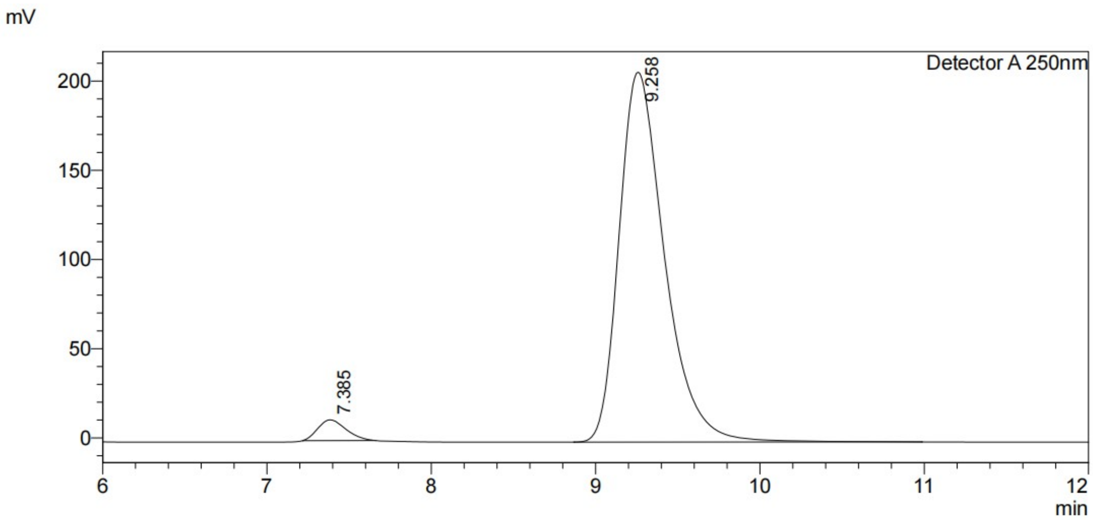
Peak#	Retention	Area	Area(%)
1	11.607	432970	3.091
2	13.319	13574261	96.909



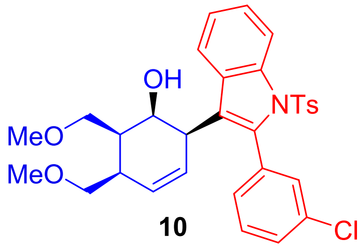
9



Peak#	Retention	Area	Area(%)
1	7.443	828705	50.201
2	9.377	822073	49.799



Peak#	Retention	Area	Area(%)
1	7.385	138352	3.358
2	9.258	3981111	96.642



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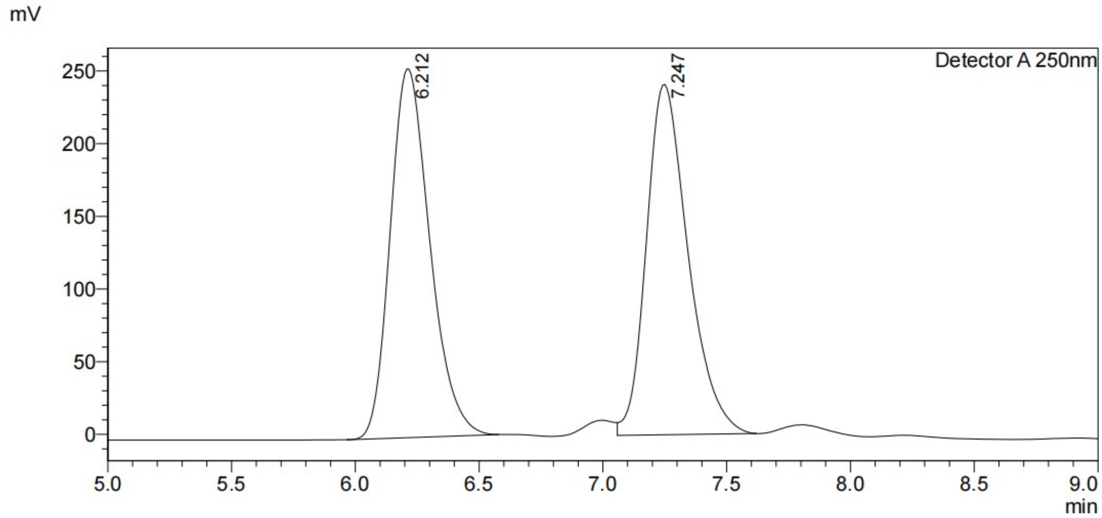
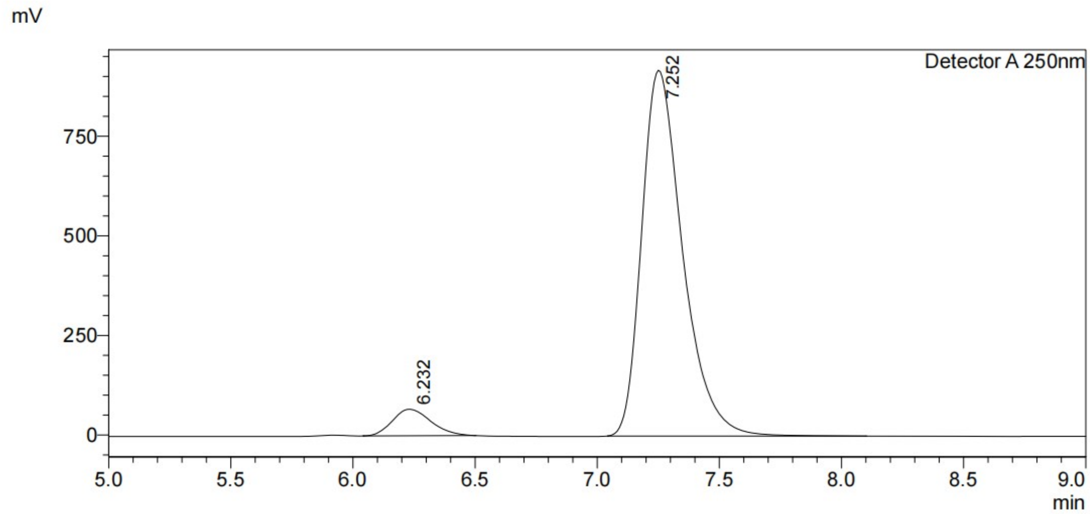
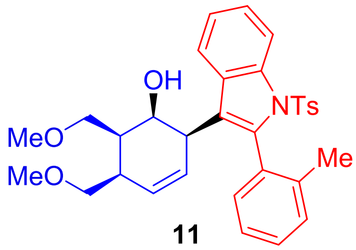


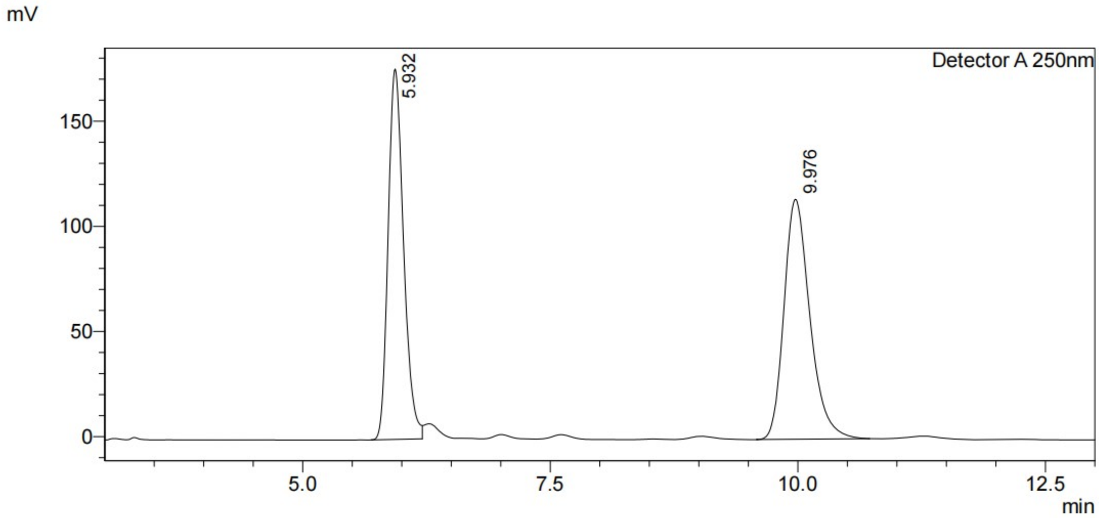
Peak#	Retention	Area	Area(%)
1	6.212	2827494	50.013
2	7.247	2826002	49.987



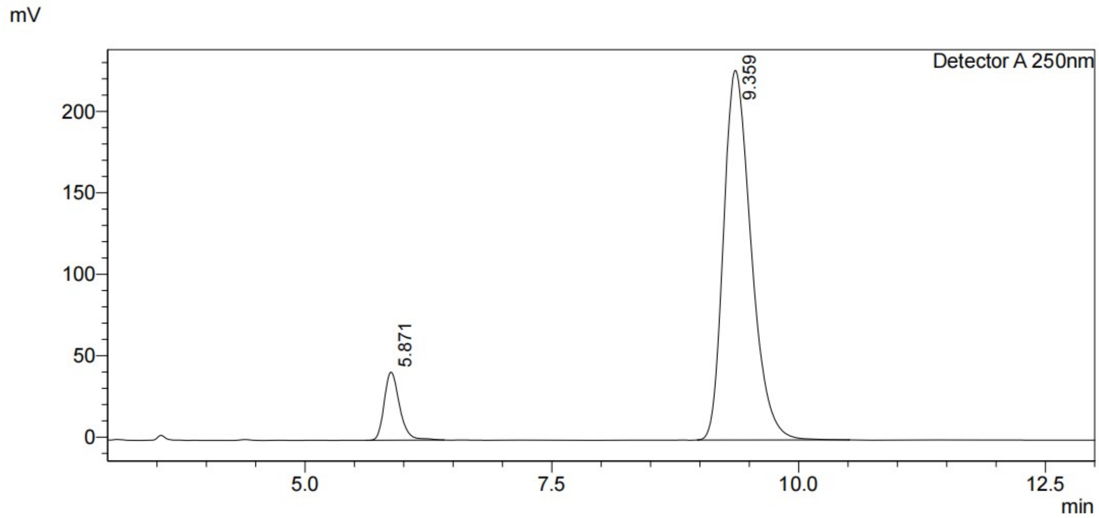
Peak#	Retention	Area	Area(%)
1	6.232	730269	6.393
2	7.252	10692162	93.607



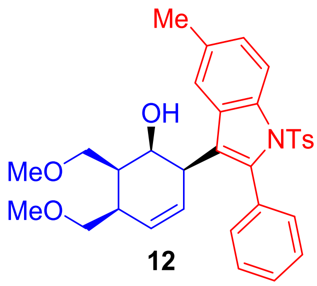
11



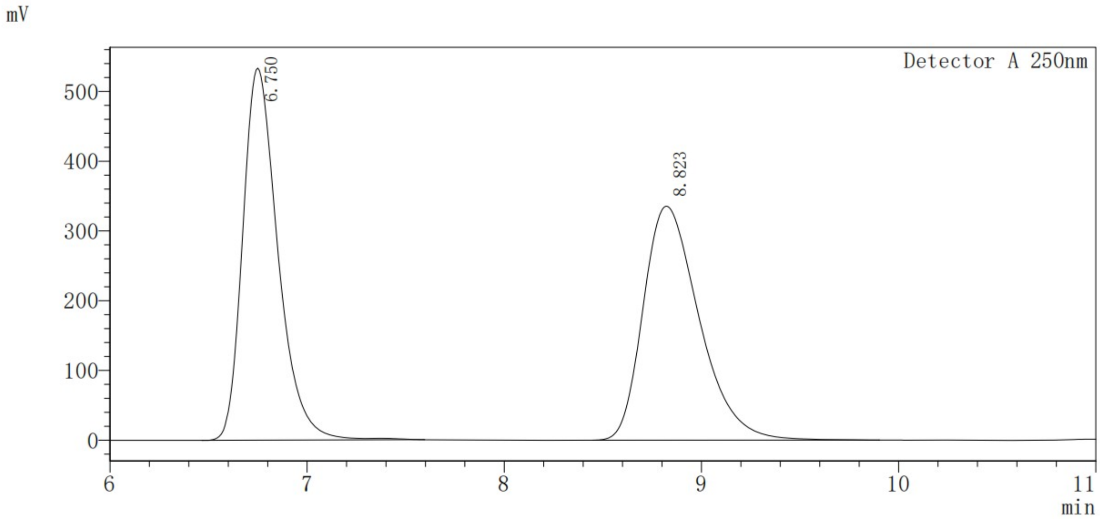
Peak#	Retention	Area	Area(%)
1	5.932	1907204	47.883
2	9.976	2075815	52.117



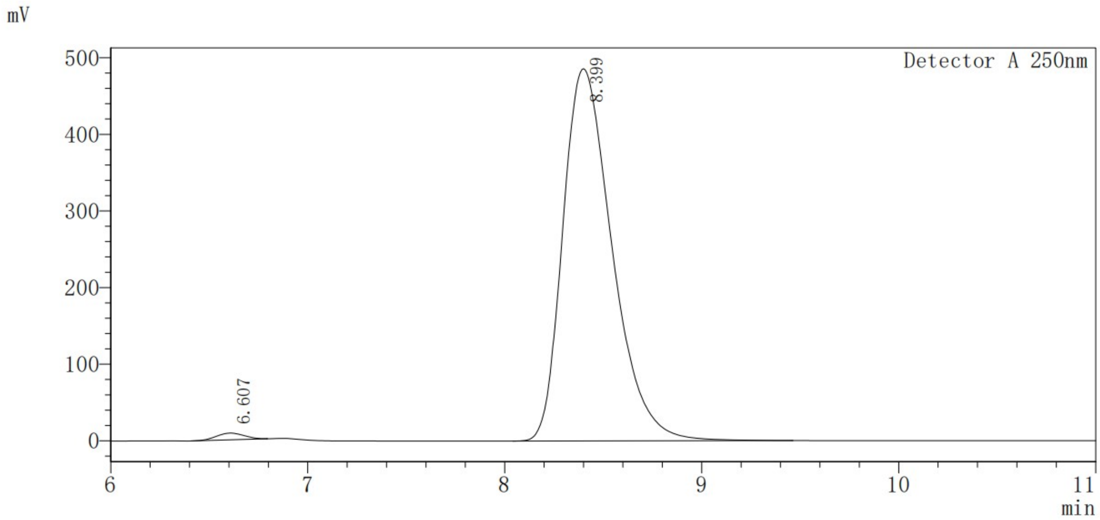
Peak#	Retention	Area	Area(%)
1	5.871	453371	9.315
2	9.359	4413600	90.685



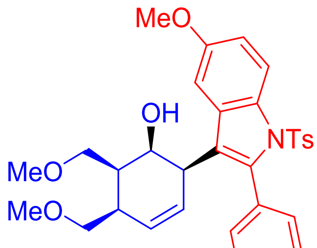
12



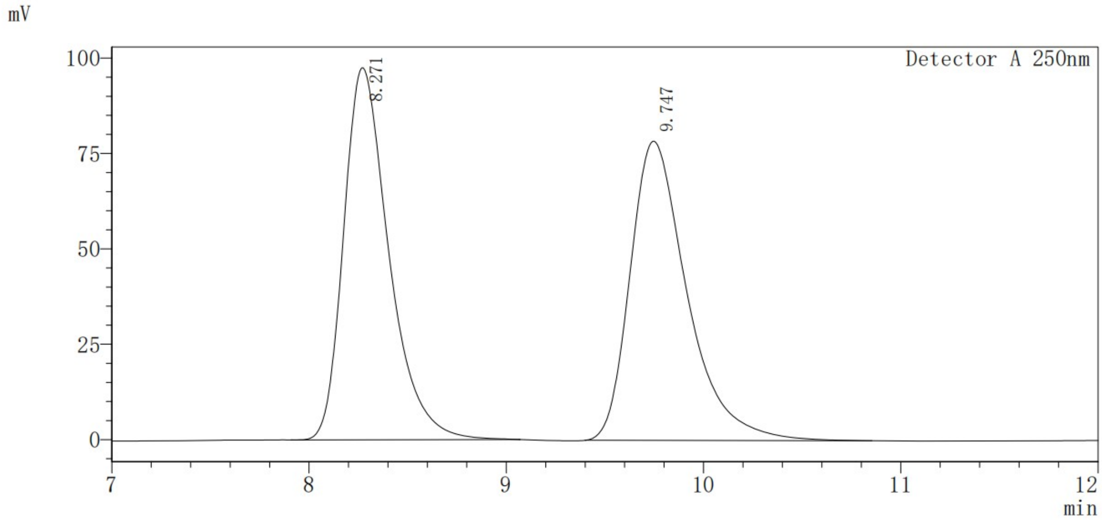
Peak#	Retention	Area	Area(%)
1	6.750	6619195	50.009
2	8.823	6616734	49.991



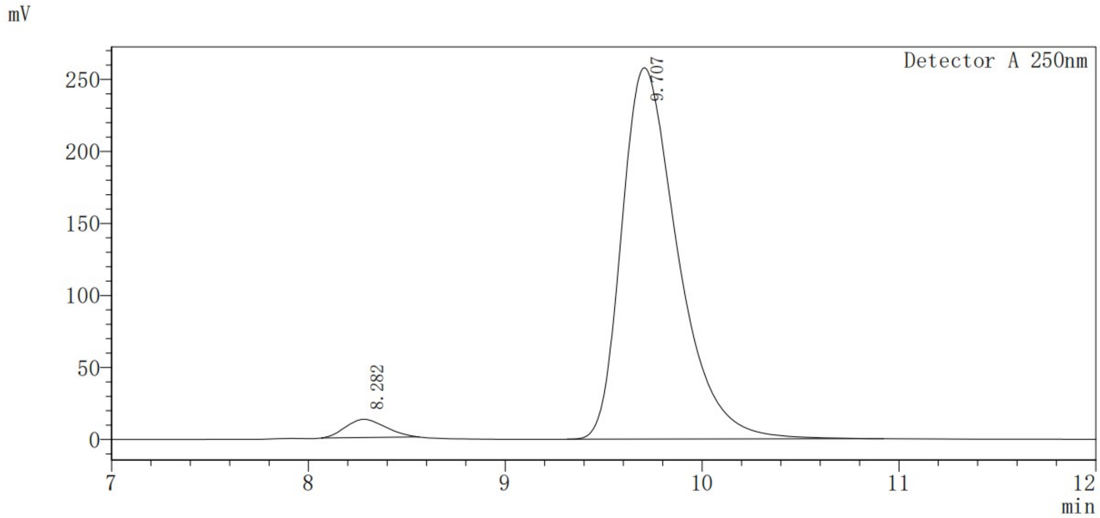
Peak#	Retention	Area	Area(%)
1	6.607	86931	1.020
2	8.399	8434969	98.980



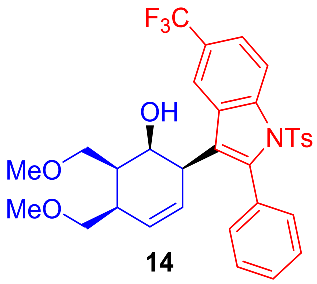
13



Peak#	Retention	Area	Area(%)
1	8.271	1553944	49.702
2	9.747	1572598	50.298



Peak#	Retention	Area	Area(%)
1	8.282	177599	3.360
2	9.707	5107912	96.640



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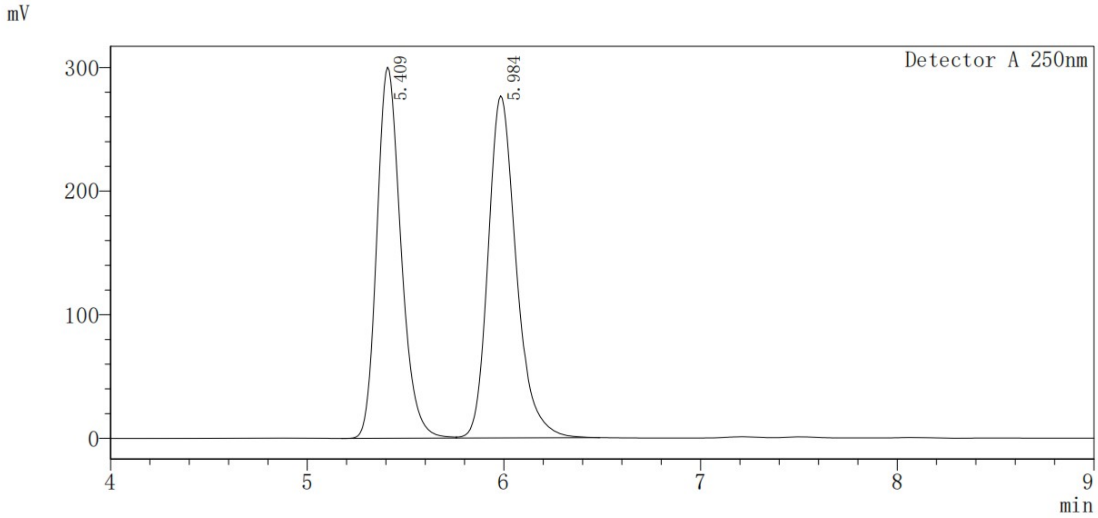
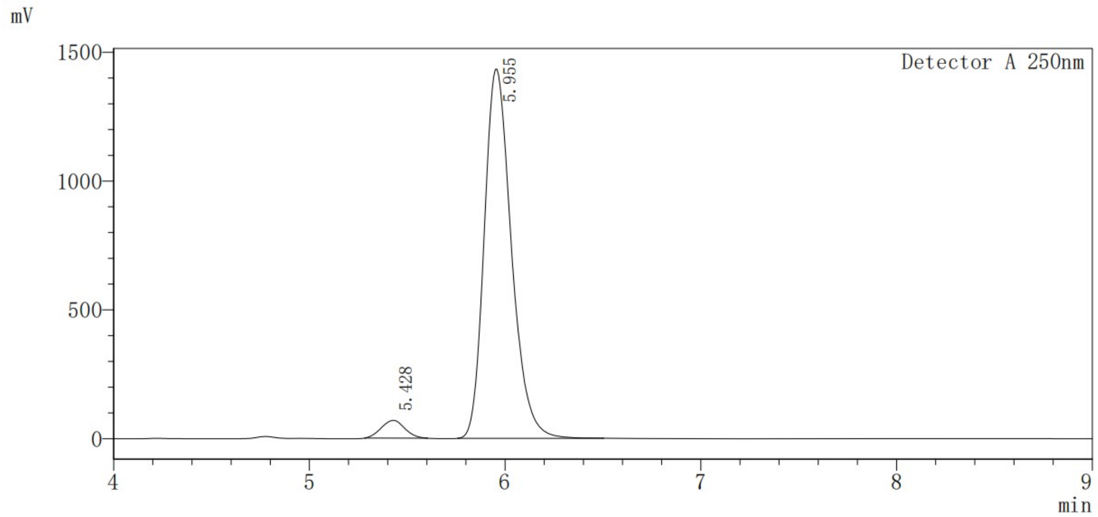
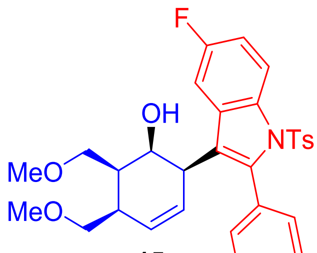


Peak#	Retention	Area	Area(%)
1	5.409	2552392	48.143
2	5.984	2749308	51.857



Peak#	Retention	Area	Area(%)
1	5.428	570520	3.962
2	5.955	13830255	96.038



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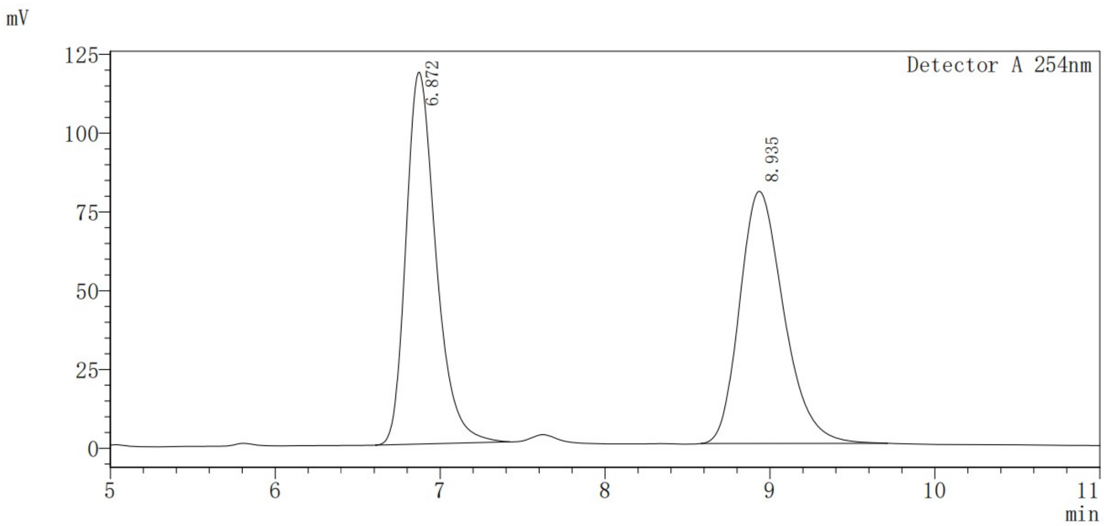
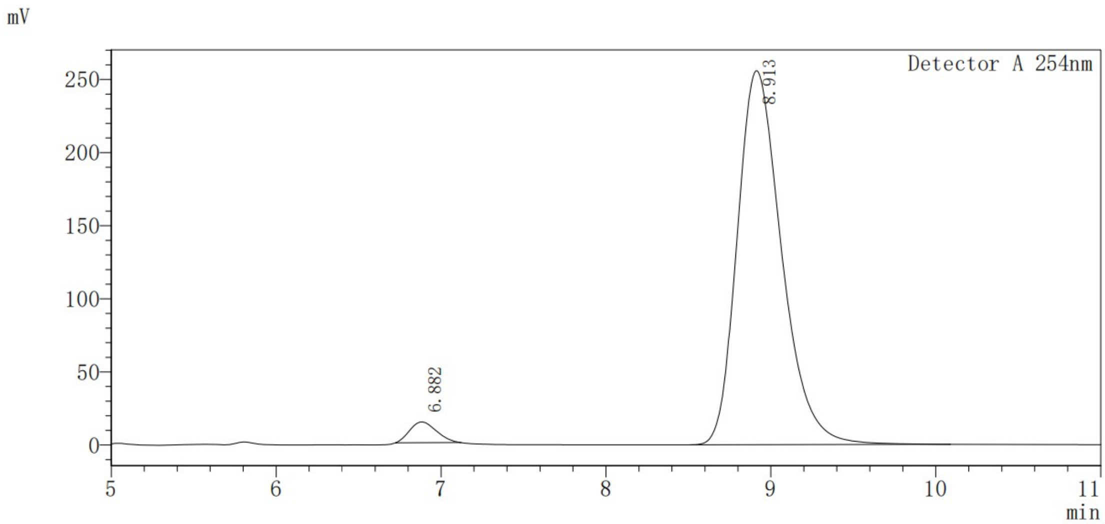
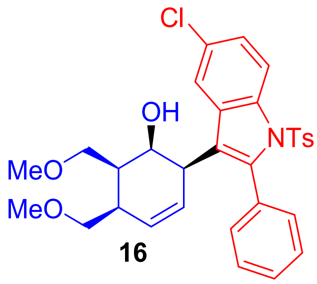


Peak#	Retention	Area	Area(%)
1	6.872	1489809	49.957
2	8.935	1492401	50.043



Peak#	Retention	Area	Area(%)
1	6.882	159575	3.229
2	8.913	4783051	96.771



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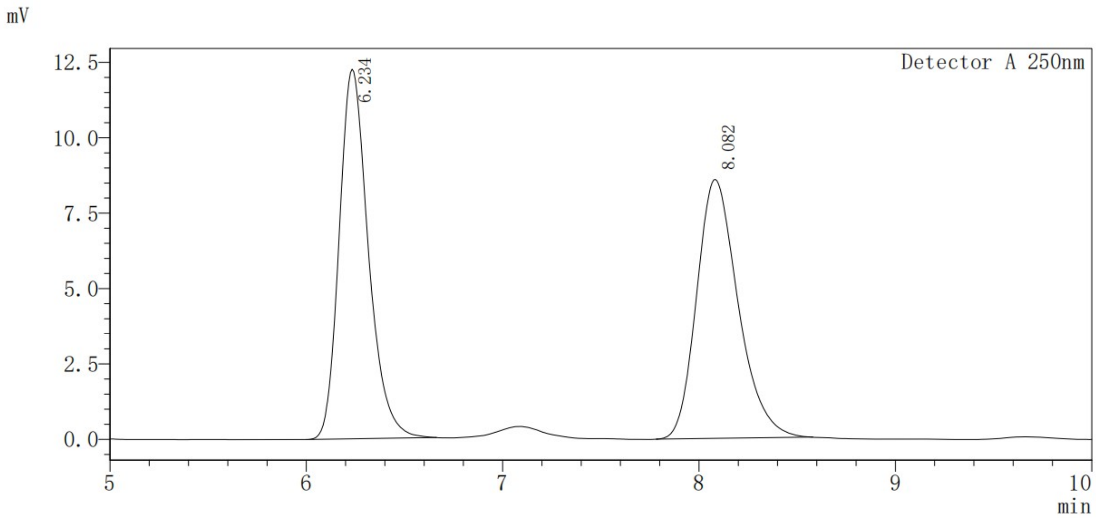
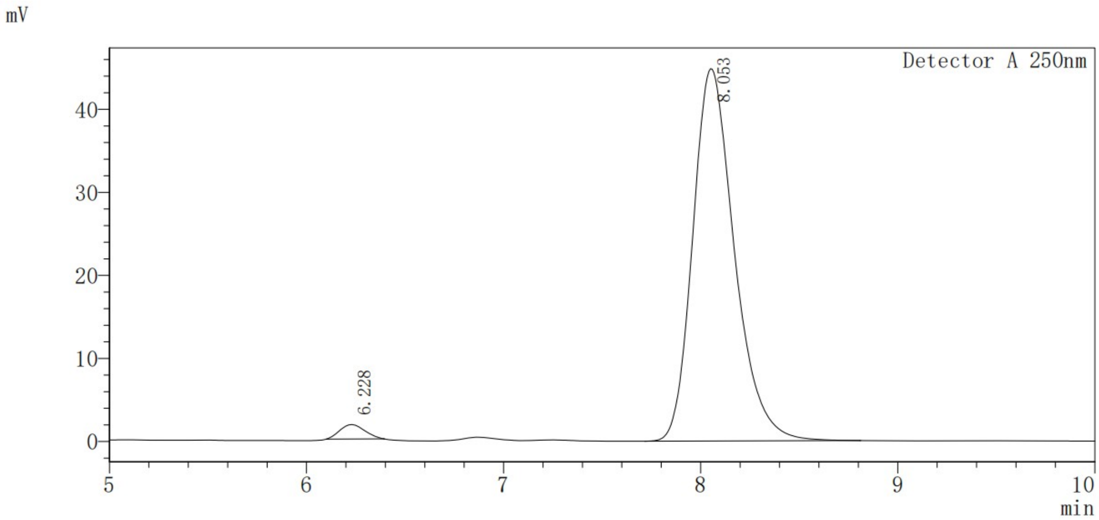
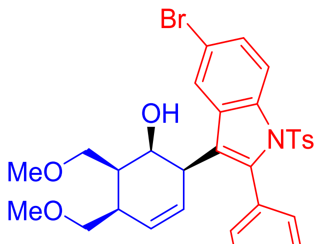


Peak#	Retention	Area	Area(%)
1	6.234	126537	50.074
2	8.082	126162	49.926



Peak#	Retention	Area	Area(%)
1	6.228	15325	2.276
2	8.053	657929	97.724



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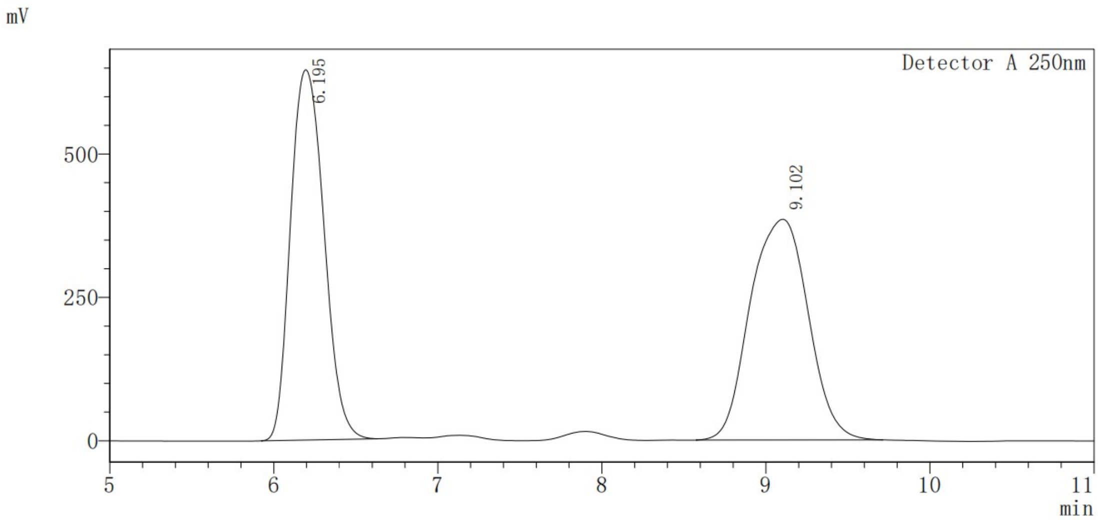
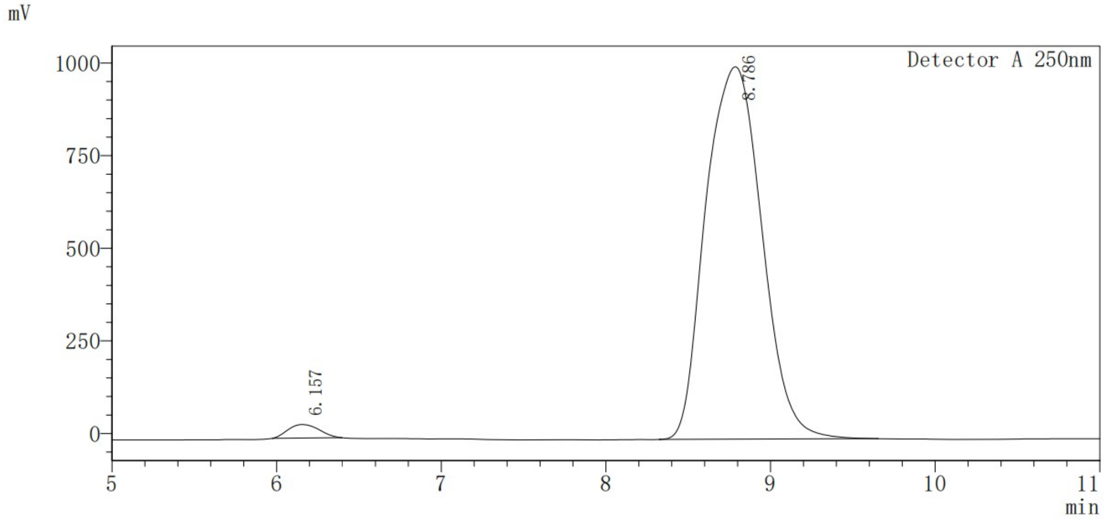
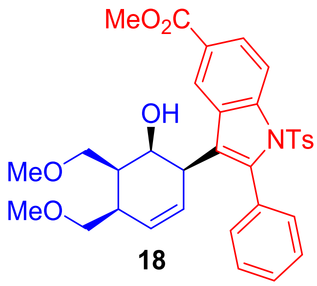


Peak#	Retention	Area	Area(%)
1	6.195	9157960	49.135
2	9.102	9480570	50.865



Peak#	Retention	Area	Area(%)
1	6.157	480205	1.974
2	8.786	23851619	98.026



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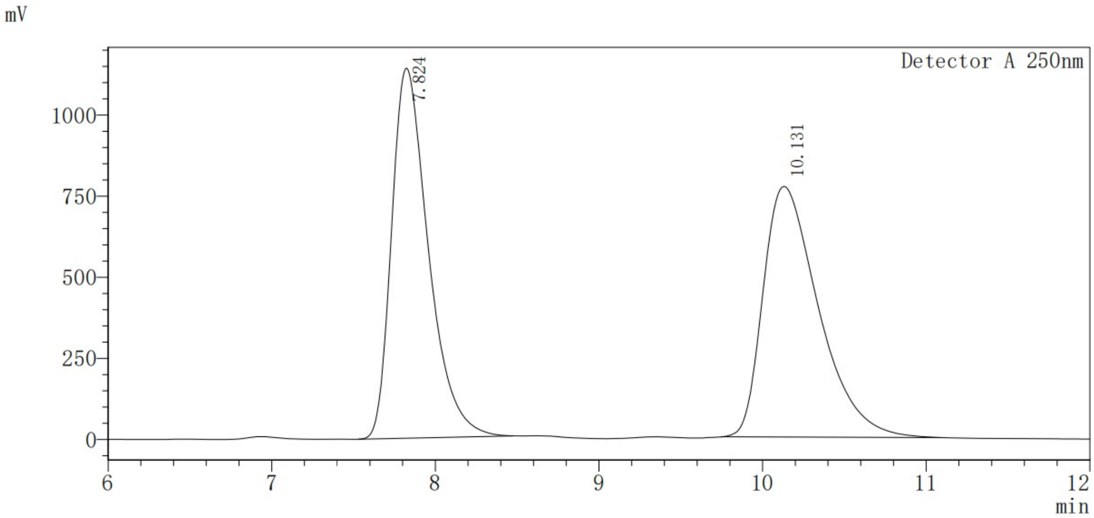
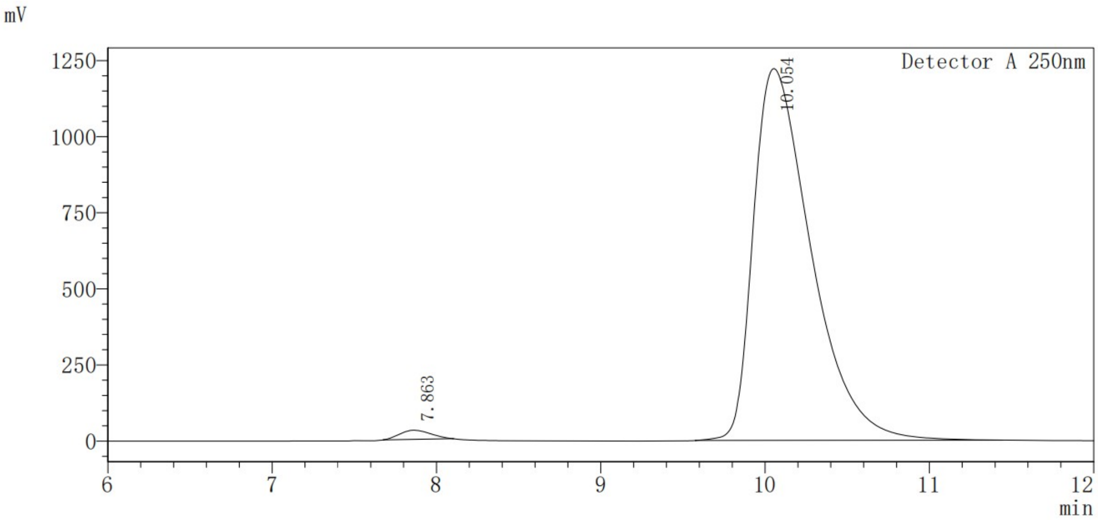
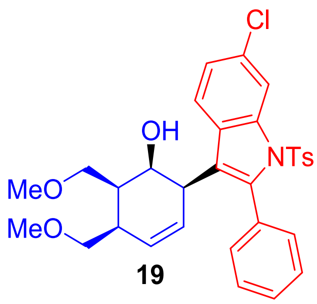


Peak#	Retention	Area	Area(%)
1	7.824	17839031	49.509
2	10.131	18193011	50.491



Peak#	Retention	Area	Area(%)
1	7.863	395365	1.309
2	10.054	29799823	98.691



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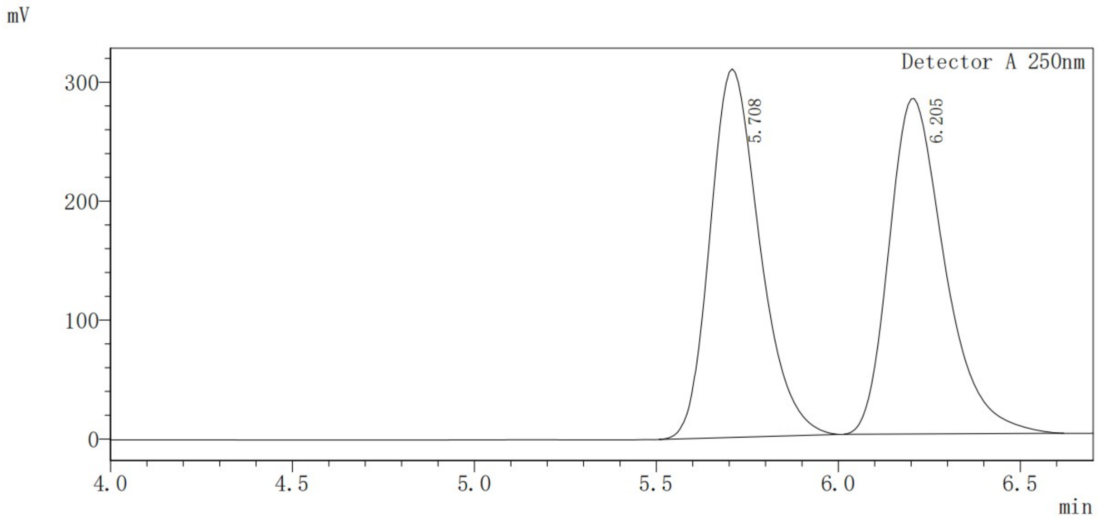
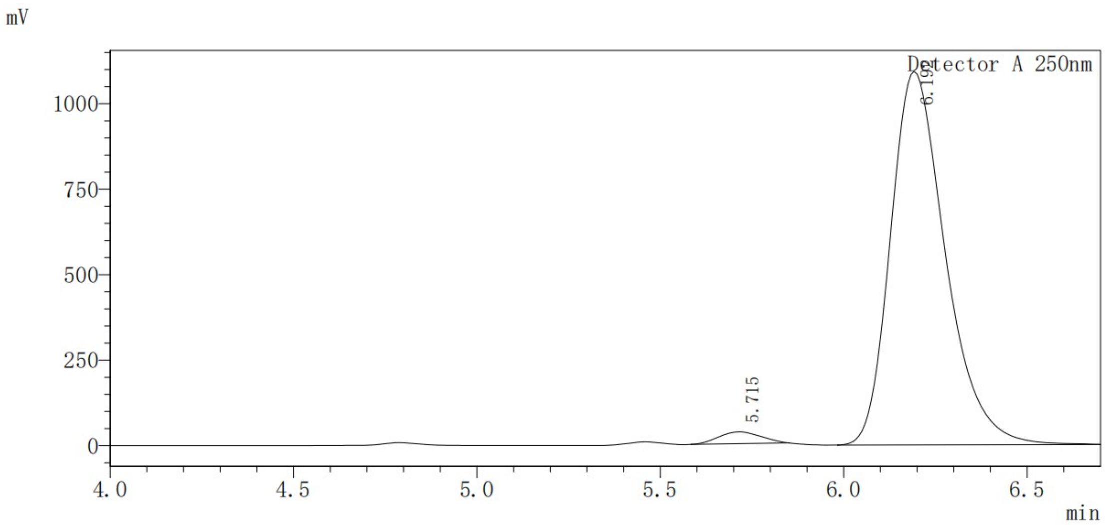
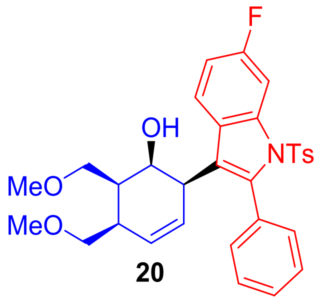


Peak#	Retention	Area	Area(%)
1	5.708	2946466	49.481
2	6.205	3008221	50.519



Peak#	Retention	Area	Area(%)
1	5.715	276878	2.378
2	6.192	11366309	97.622



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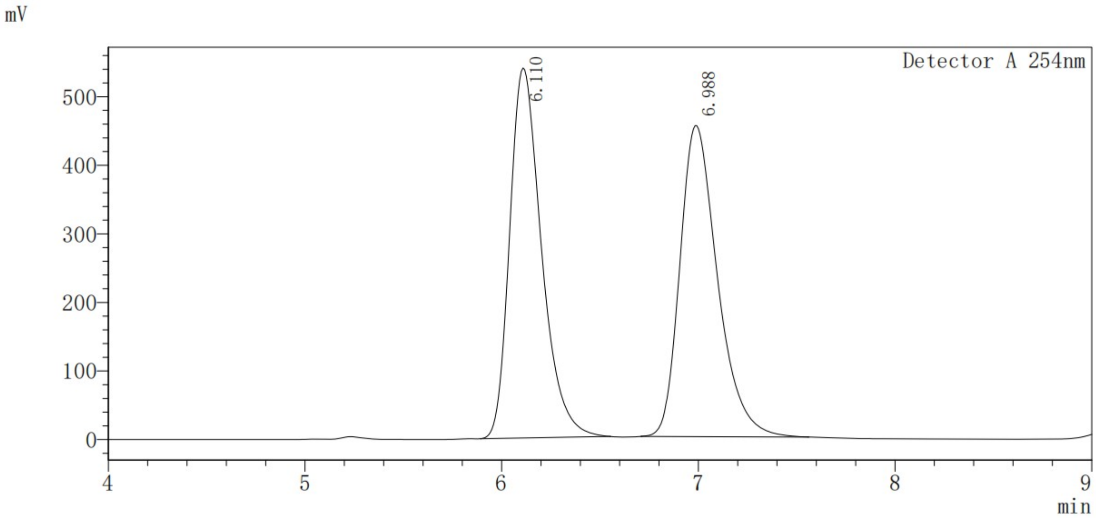
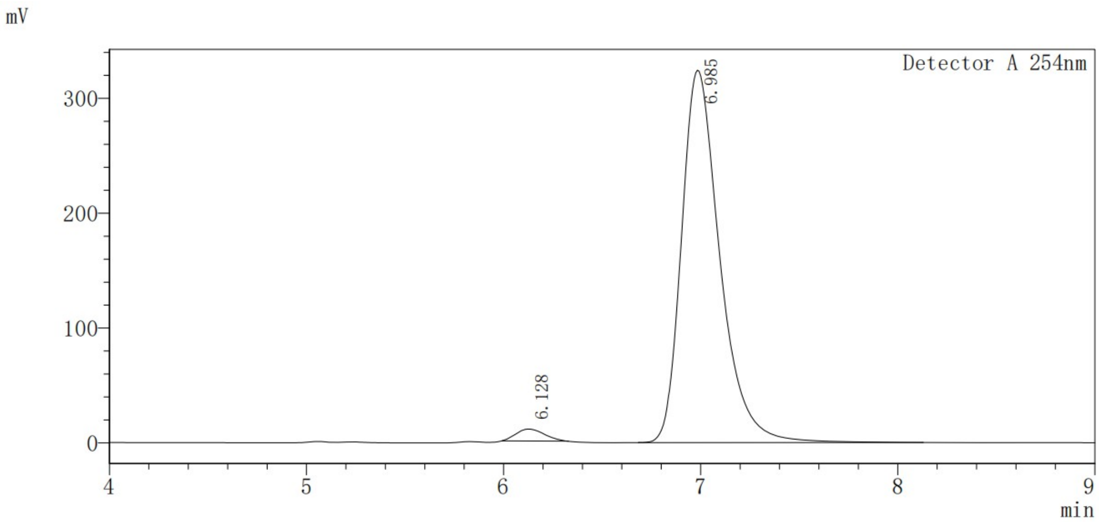
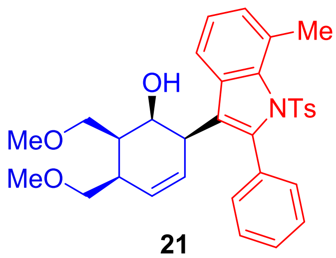


Peak#	Retention	Area	Area(%)
1	6.110	6045717	50.083
2	6.988	6025630	49.917



Peak#	Retention	Area	Area(%)
1	6.128	103323	2.303
2	6.985	4382314	97.697



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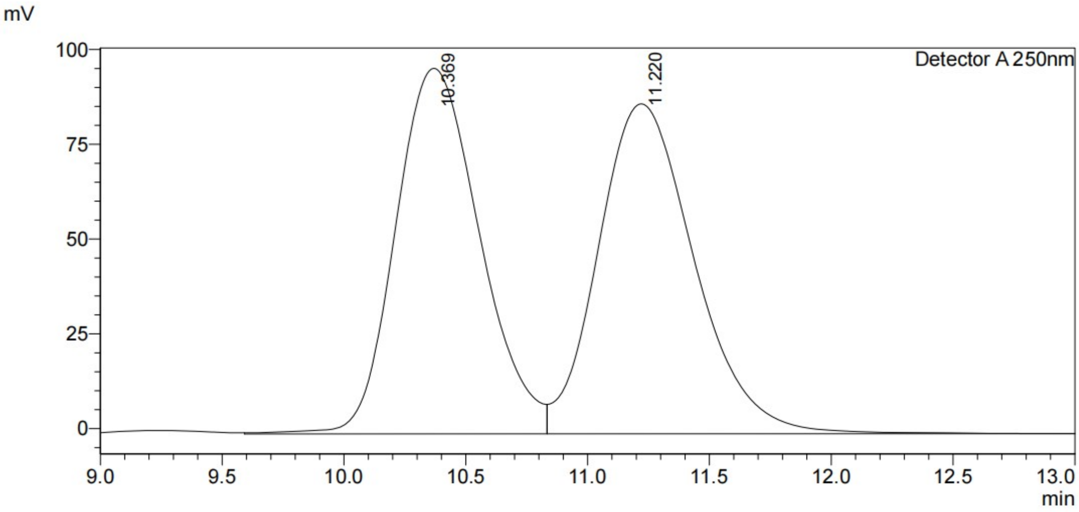
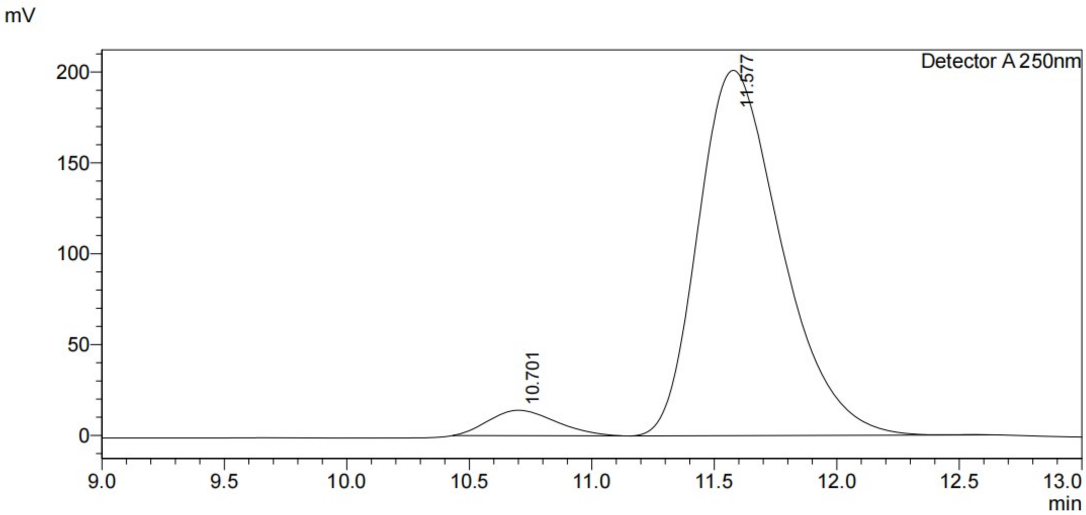
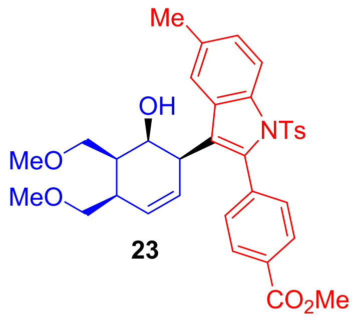


Peak#	Retention	Area	Area(%)
1	10.369	2317306	49.287
2	11.220	2384378	50.713



Peak#	Retention	Area	Area(%)
1	10.701	266524	5.309
2	11.577	4753417	94.691



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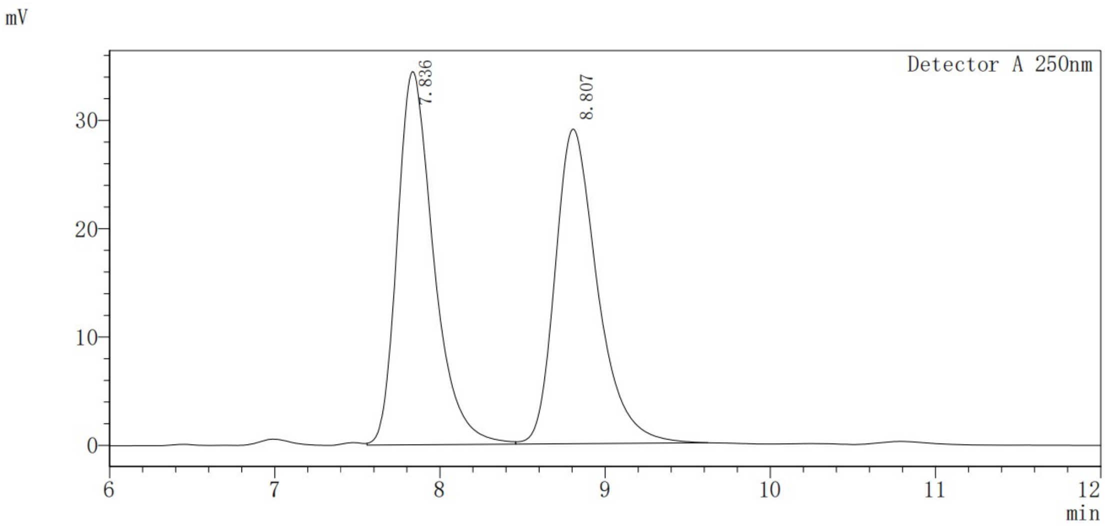
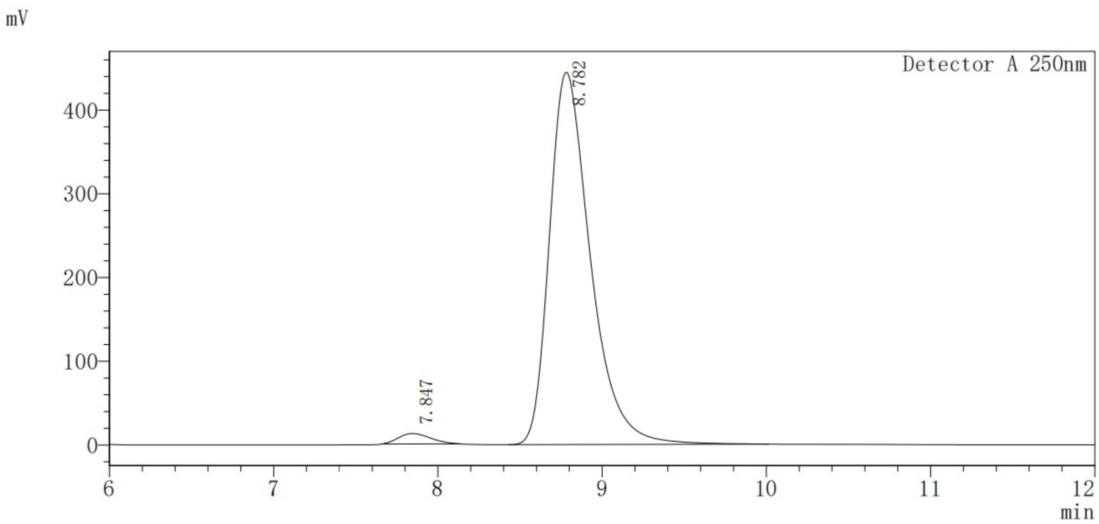
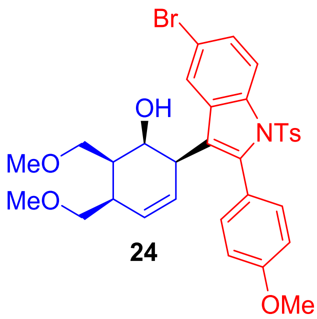


Peak#	Retention	Area	Area(%)
1	7.836	528852	50.539
2	8.807	517570	49.461



Peak#	Retention	Area	Area(%)
1	7.847	168432	2.136
2	8.782	7716715	97.864



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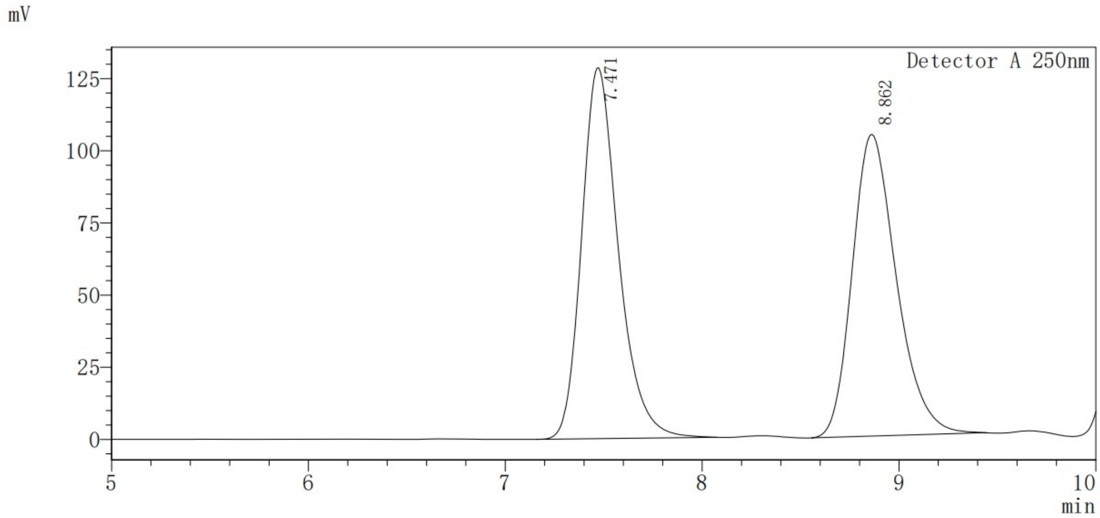
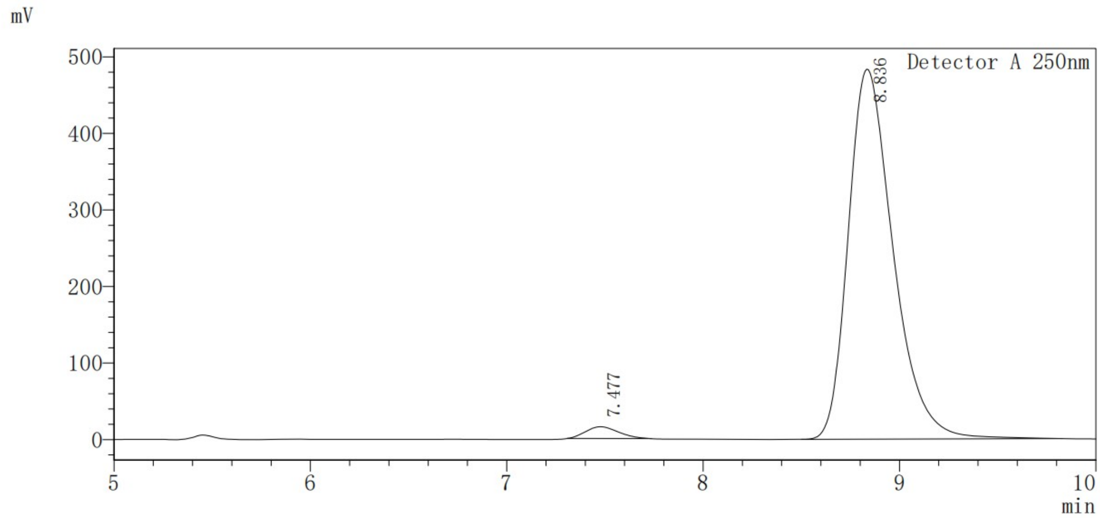
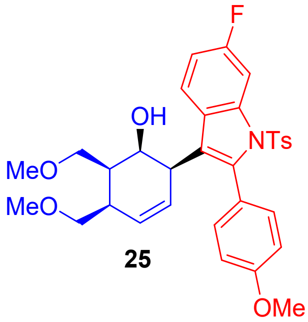


Peak#	Retention	Area	Area(%)
1	7.471	1670171	50.627
2	8.862	1628812	49.373



Peak#	Retention	Area	Area(%)
1	7.477	180711	2.298
2	8.836	7682532	97.702



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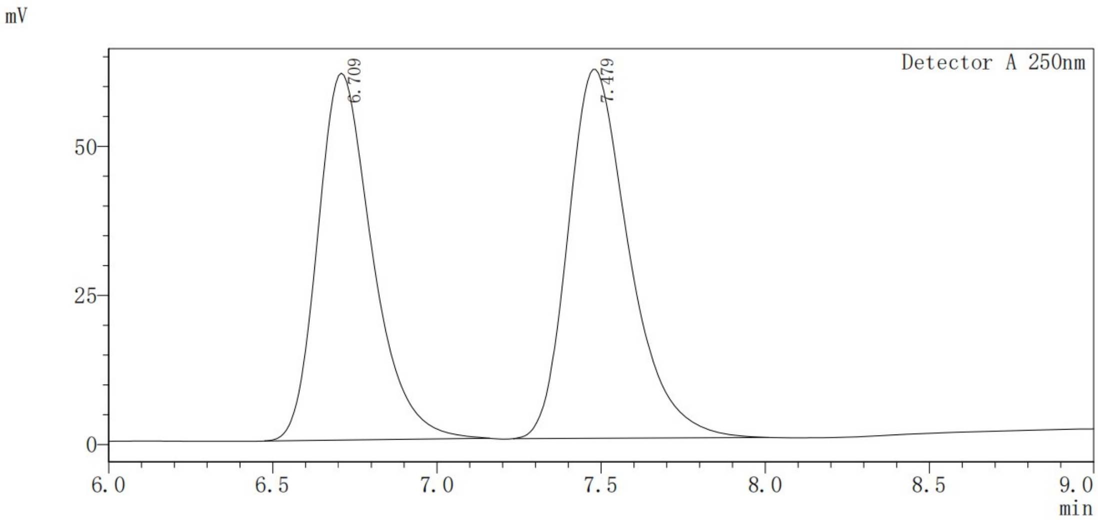
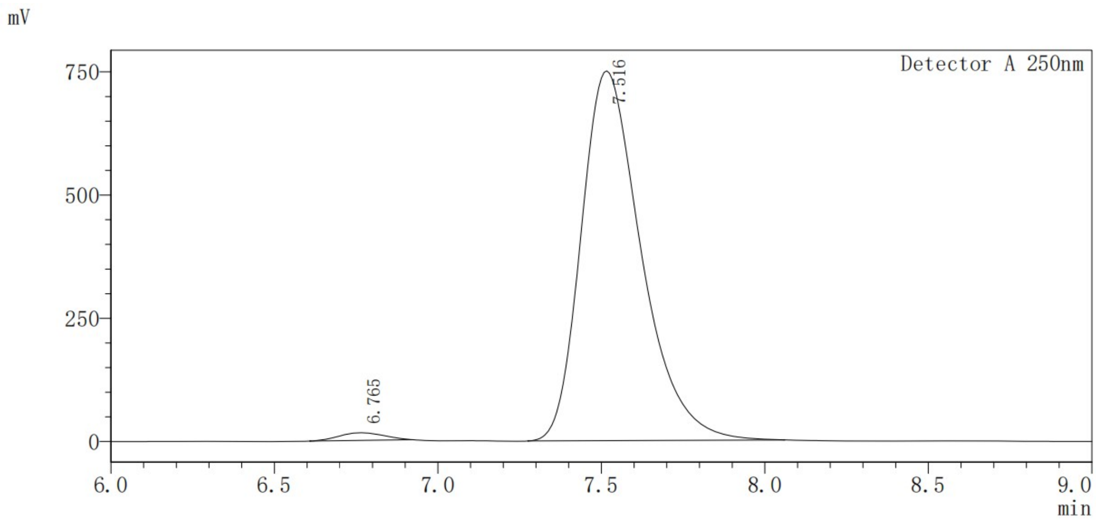
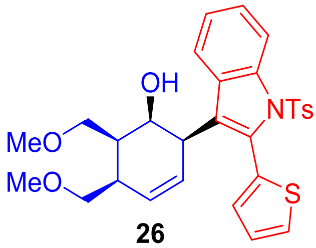


Peak#	Retention	Area	Area(%)
1	6.709	713002	47.053
2	7.479	802299	52.947



Peak#	Retention	Area	Area(%)
1	6.765	149687	1.539
2	7.516	9579711	98.461



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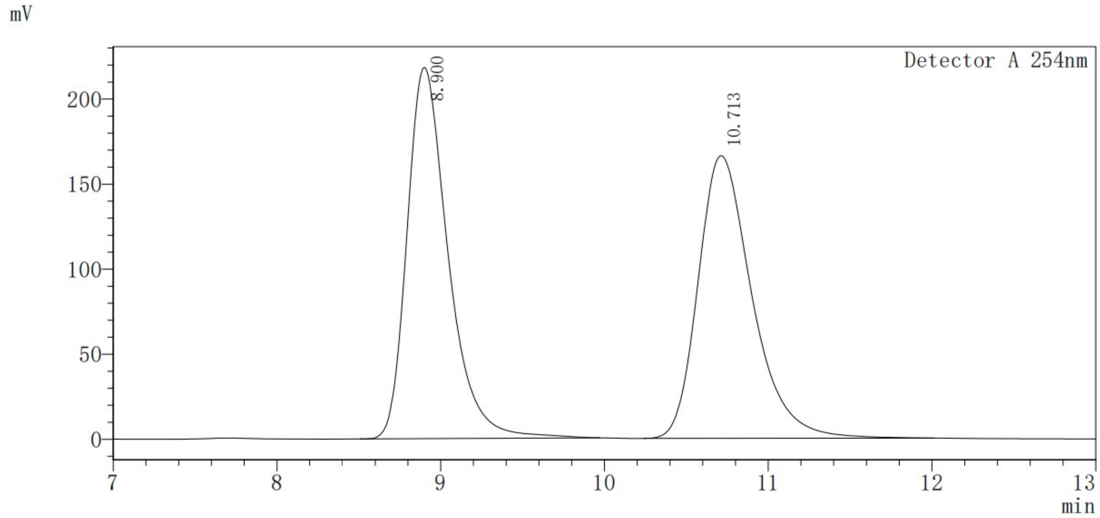
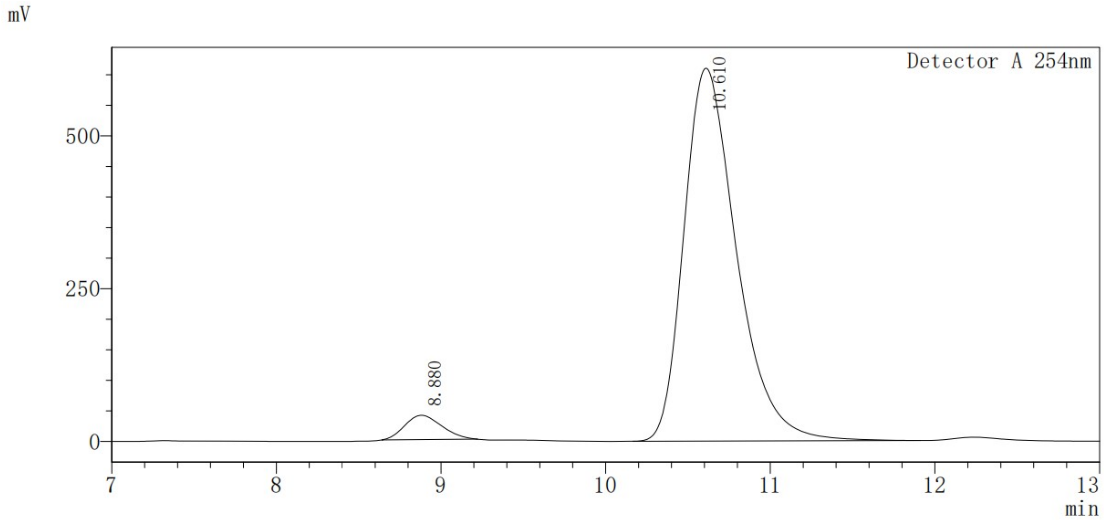
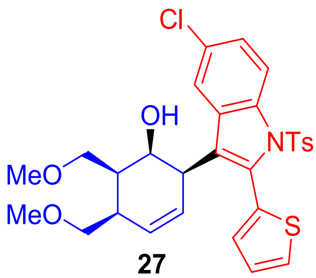


Peak#	Retention	Area	Area(%)
1	8.900	3808777	50.092
2	10.713	3794807	49.908



Peak#	Retention	Area	Area(%)
1	8.880	622324	4.386
2	10.610	13565575	95.614



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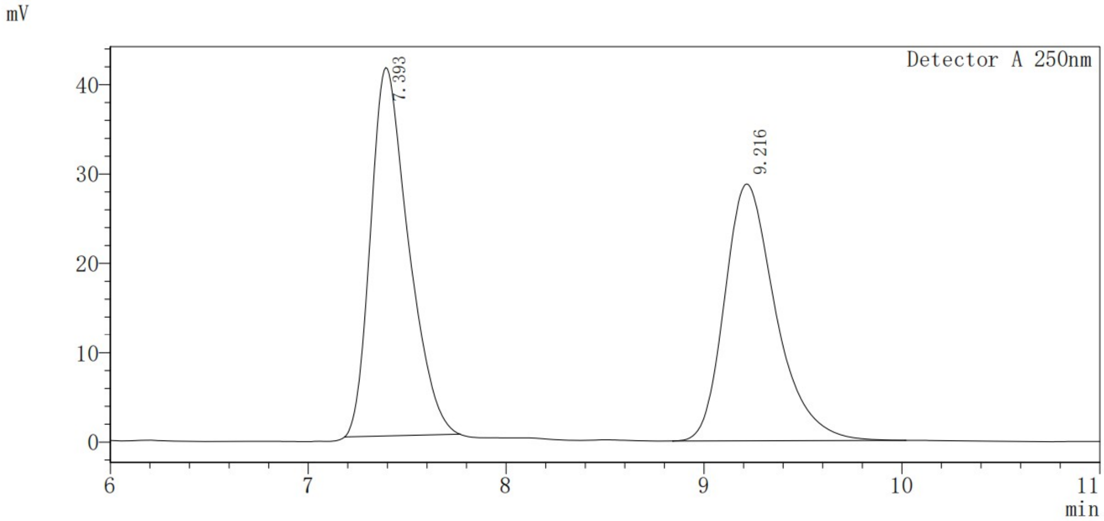
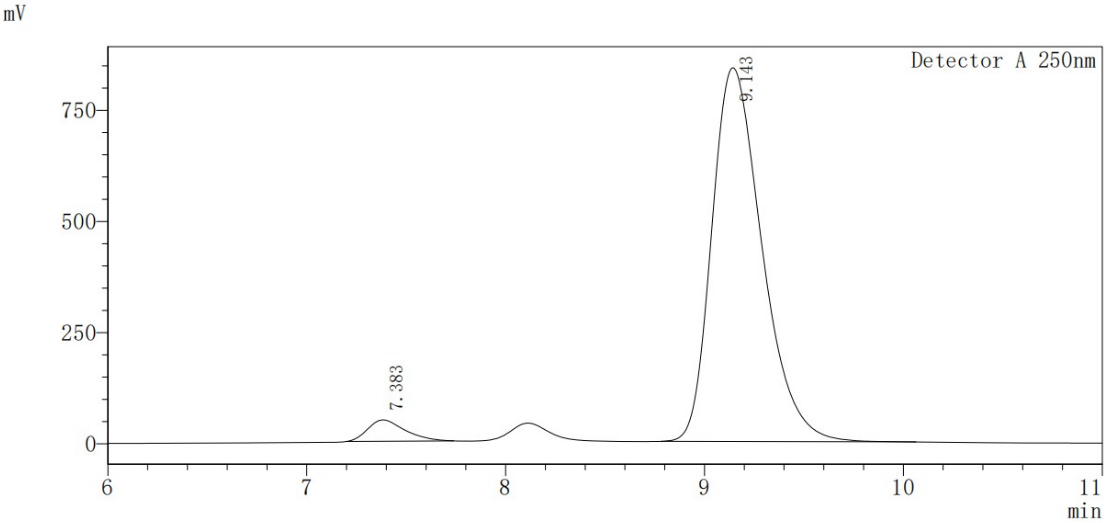
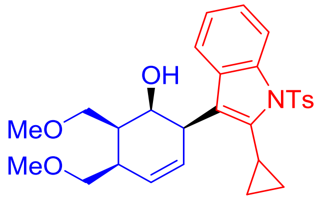


Peak#	Retention	Area	Area(%)
1	7.939	548664	51.533
2	9.126	516025	48.467



Peak#	Retention	Area	Area(%)
1	7.383	624108	4.068
2	9.143	14718946	95.932



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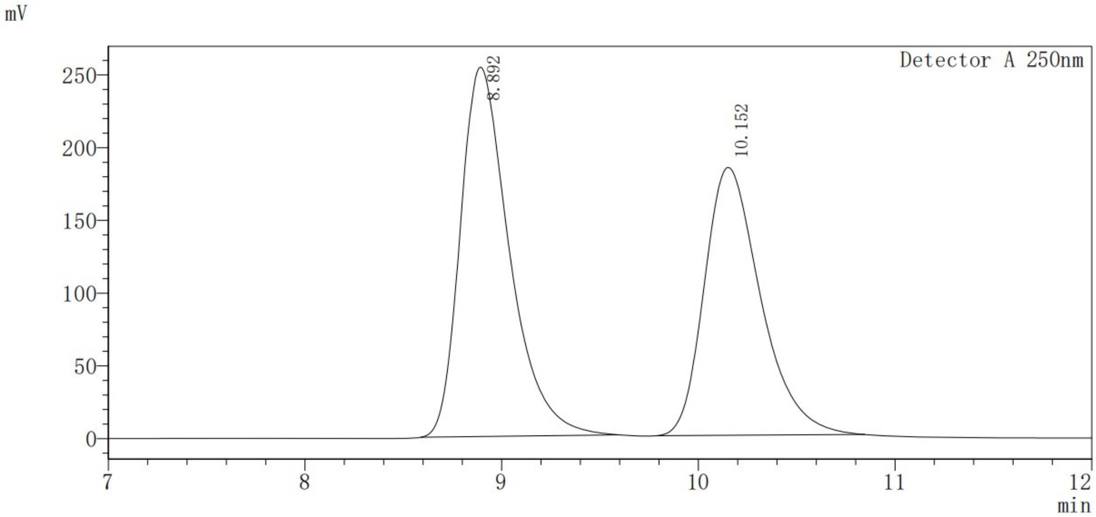
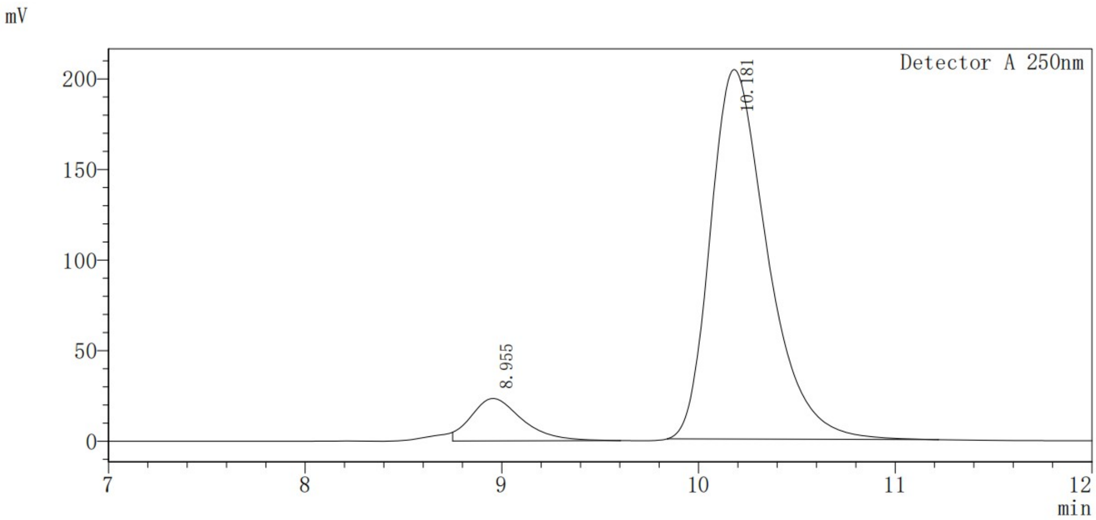
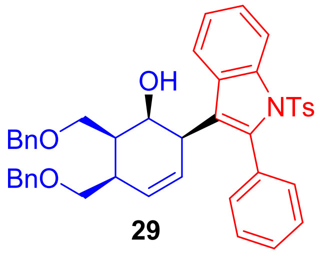


Peak#	Retention	Area	Area(%)
1	8.892	4402971	54.560
2	10.152	3667034	45.440



Peak#	Retention	Area	Area(%)
1	8.955	422476	9.318
2	10.181	4111260	90.682



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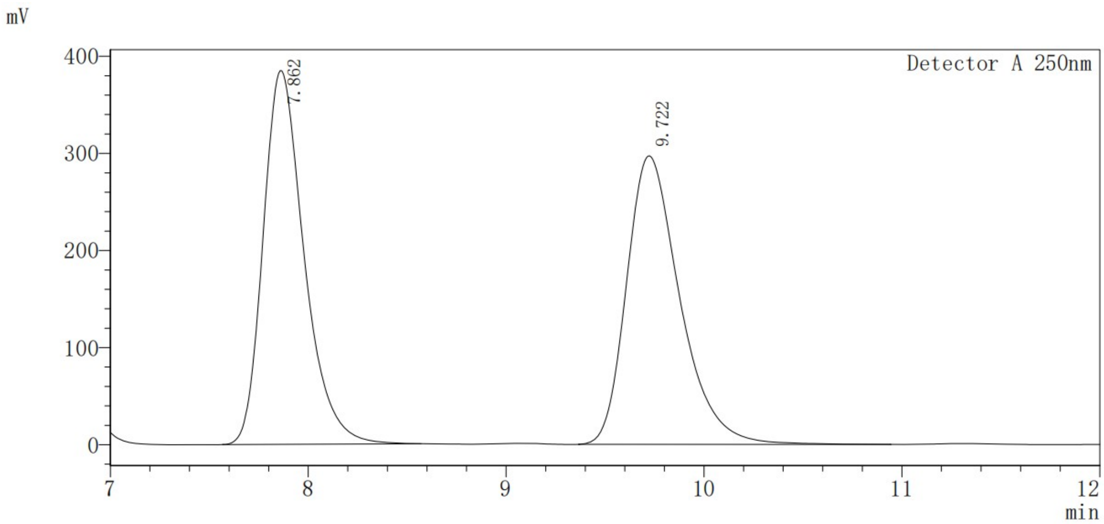
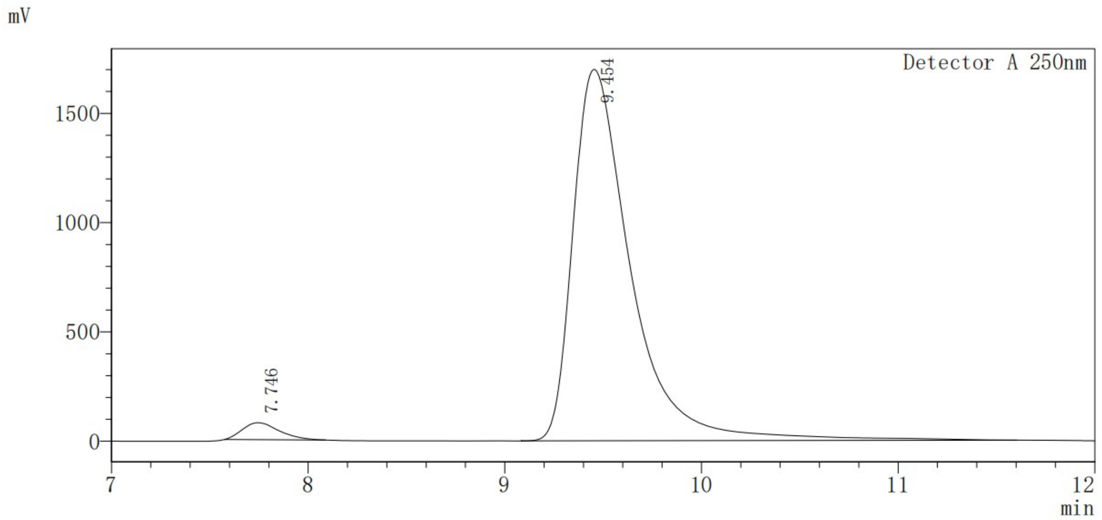
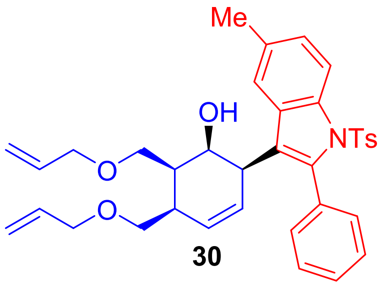


Peak#	Retention	Area	Area(%)
1	7.862	5532086	49.912
2	9.722	5551592	50.088



Peak#	Retention	Area	Area(%)
1	7.746	1008866	2.818
2	9.454	34786396	97.182



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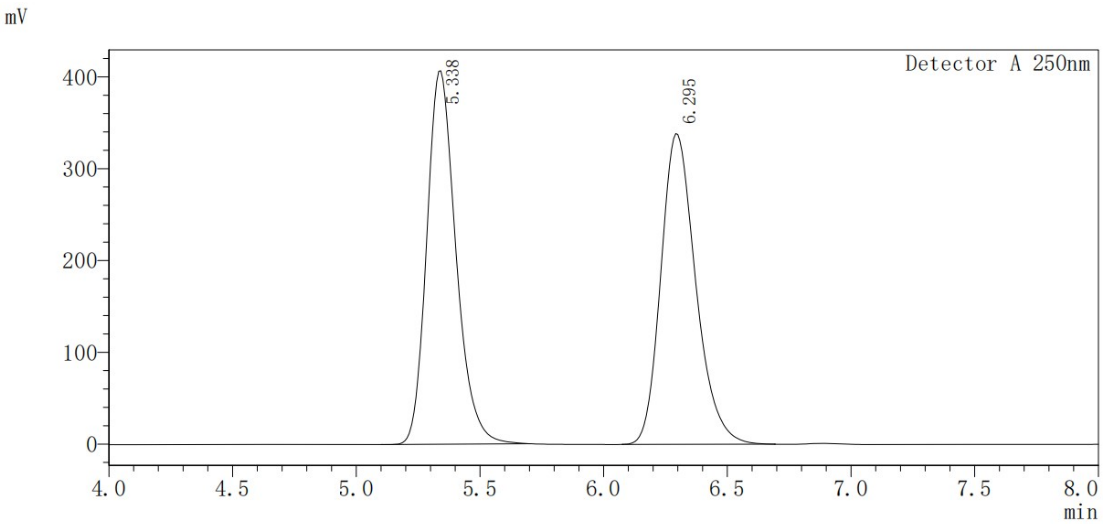
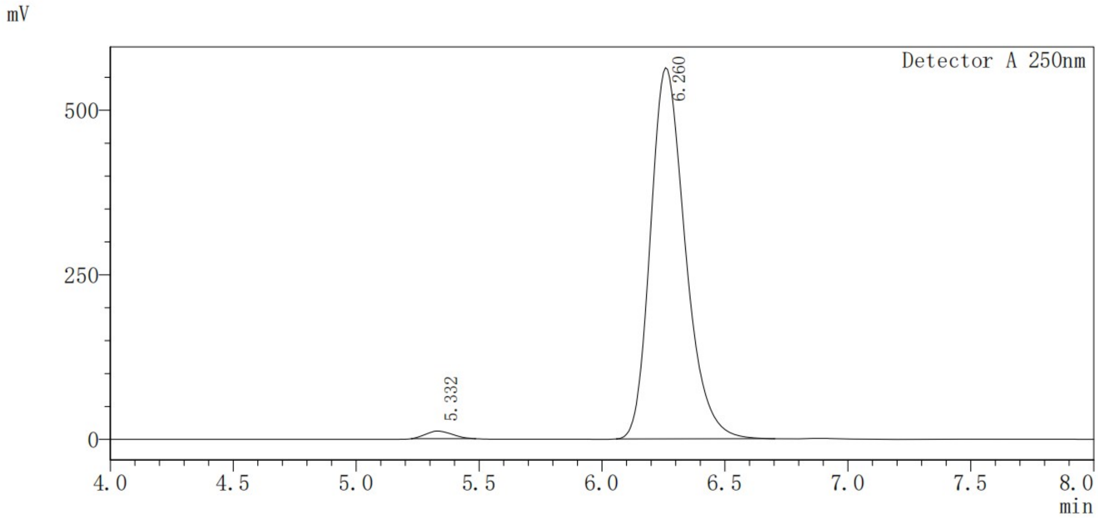
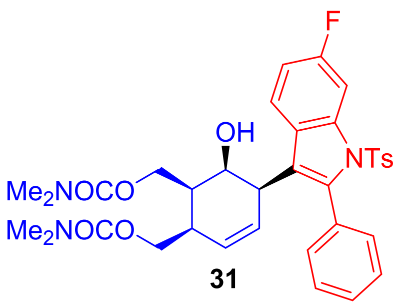


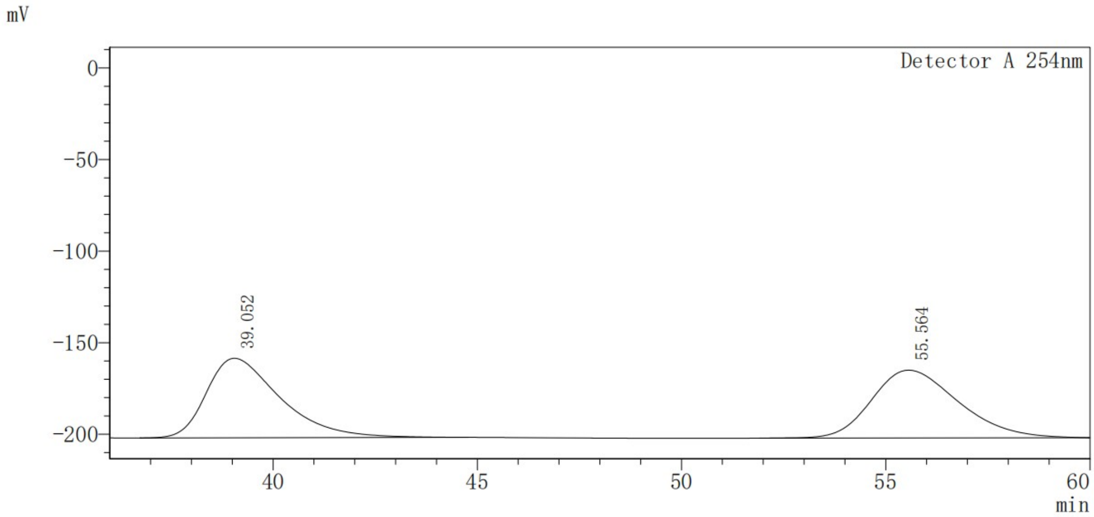
Peak#	Retention	Area	Area(%)
1	5.338	3343282	50.196
2	6.295	3317165	49.804



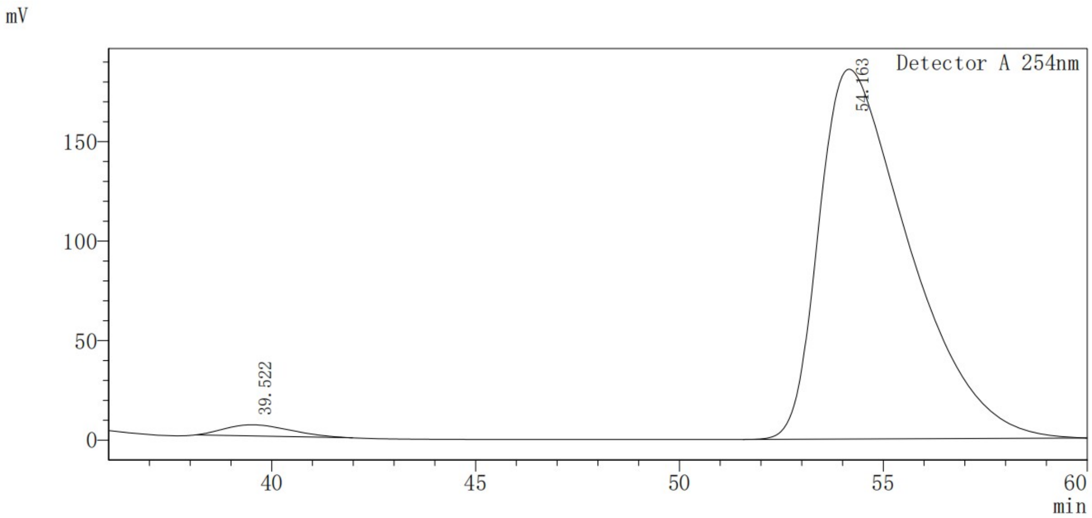
Peak#	Retention	Area	Area(%)
1	5.332	86110	1.527
2	6.260	5551810	98.473



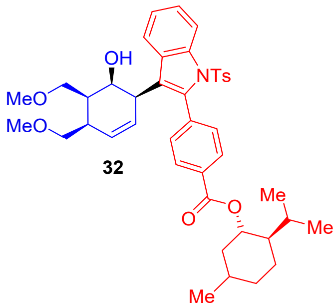
31



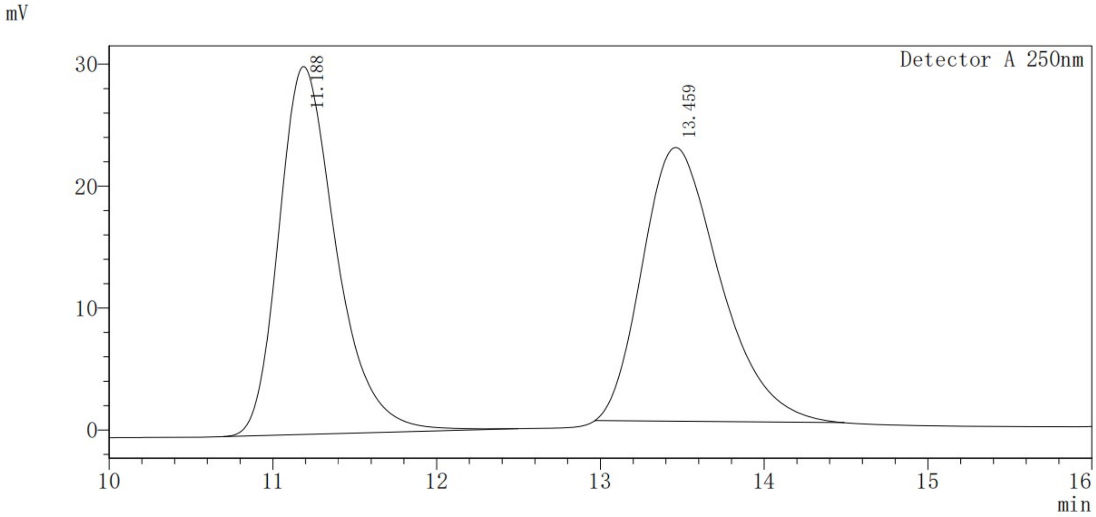
Peak#	Retention	Area	Area(%)
1	39.052	5456522	49.937
2	55.564	5470206	50.063



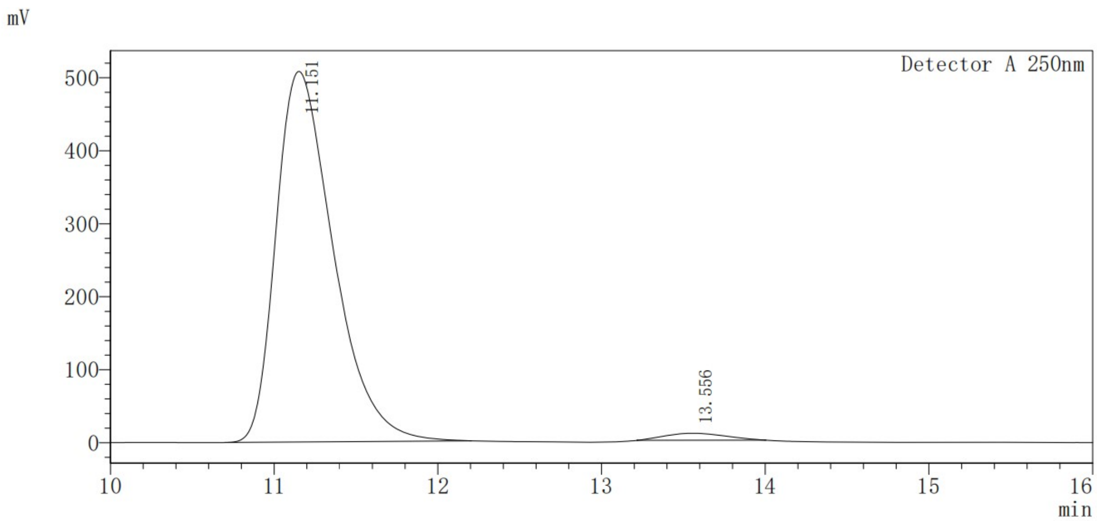
Peak#	Retention	Area	Area(%)
1	39.522	636147	2.175
2	54.163	28615719	97.825



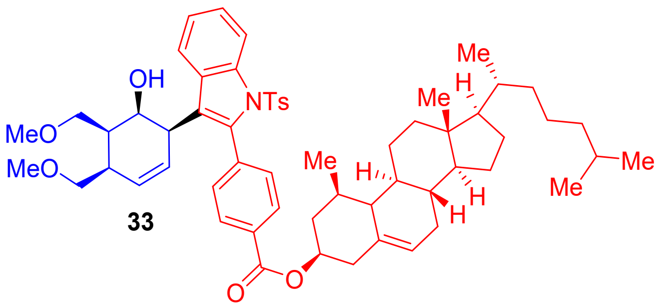
32



Peak#	Retention	Area	Area(%)
1	11.188	735264	49.842
2	13.459	739934	50.158



Peak#	Retention	Area	Area(%)
1	11.151	12341377	98.031
2	13.556	247823	1.969



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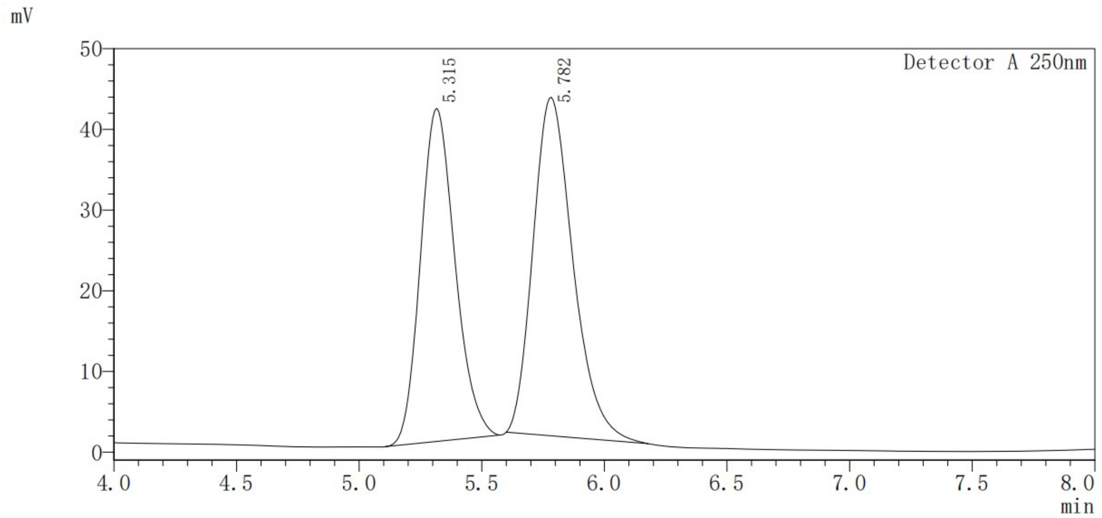
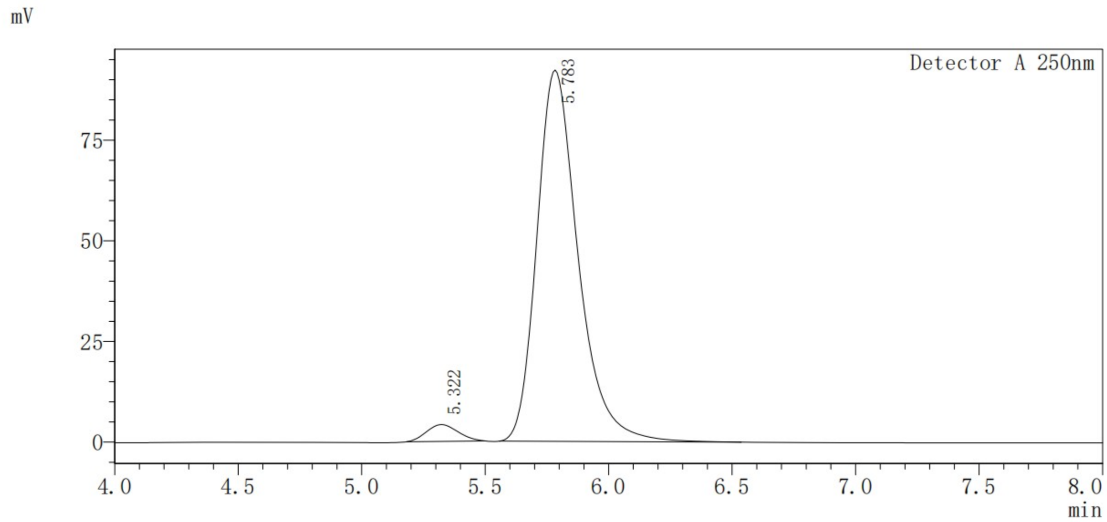
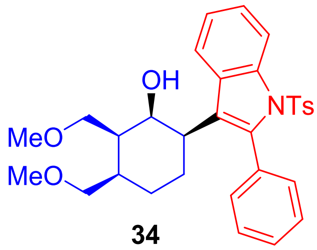


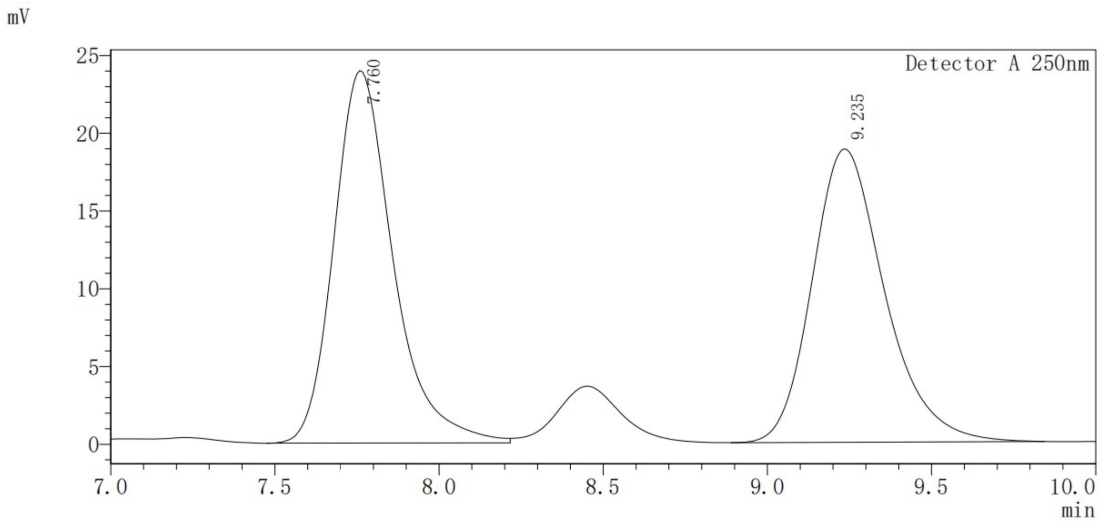
Peak#	Retention	Area	Area(%)
1	5.315	405290	46.042
2	5.782	474974	53.958



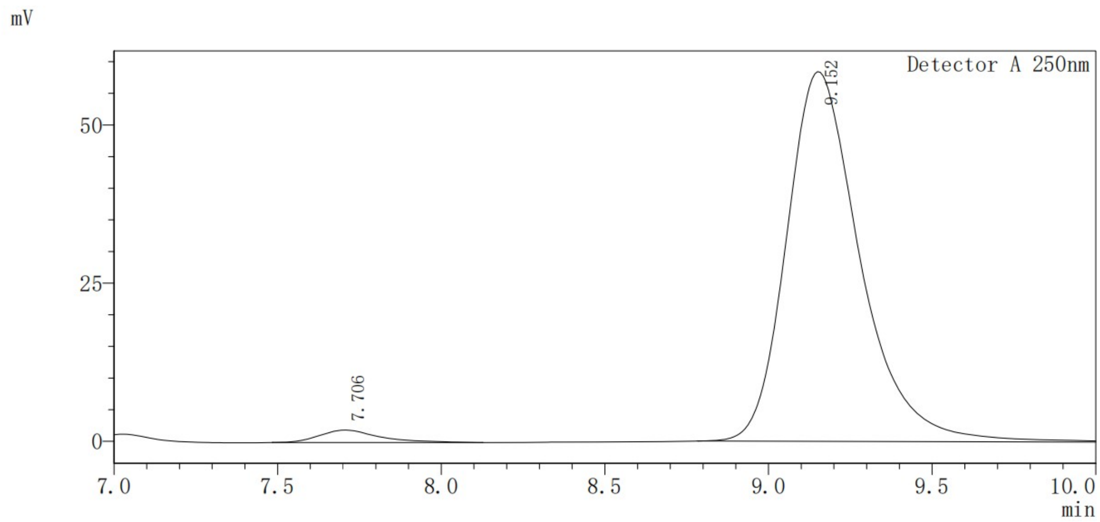
Peak#	Retention	Area	Area(%)
1	5.322	37126	3.347
2	5.783	1072256	96.653



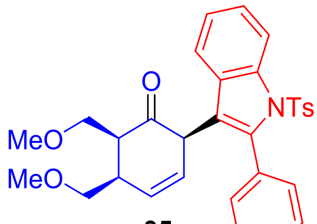
34



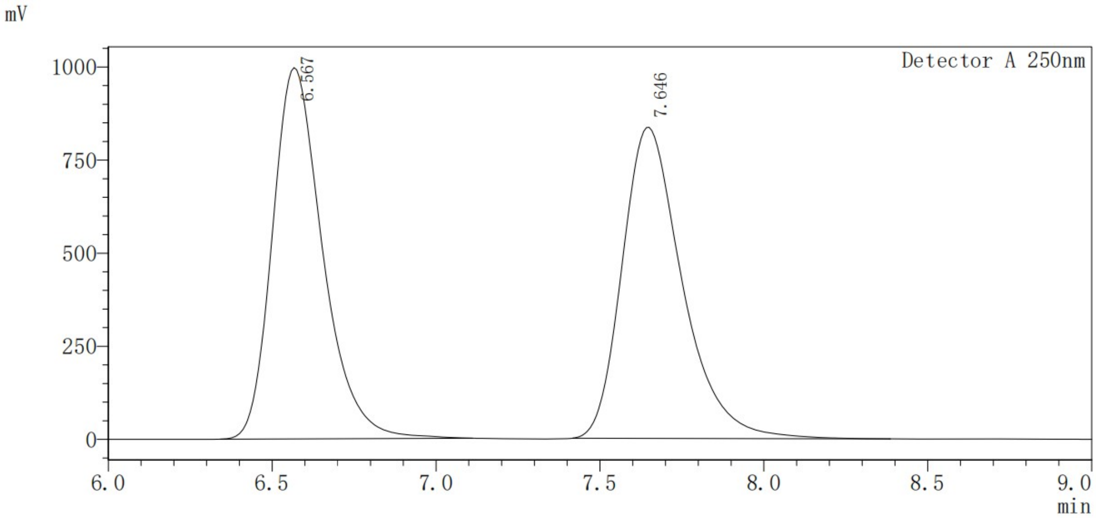
Peak#	Retention	Area	Area(%)
1	7.760	300037	50.839
2	9.235	290135	49.161



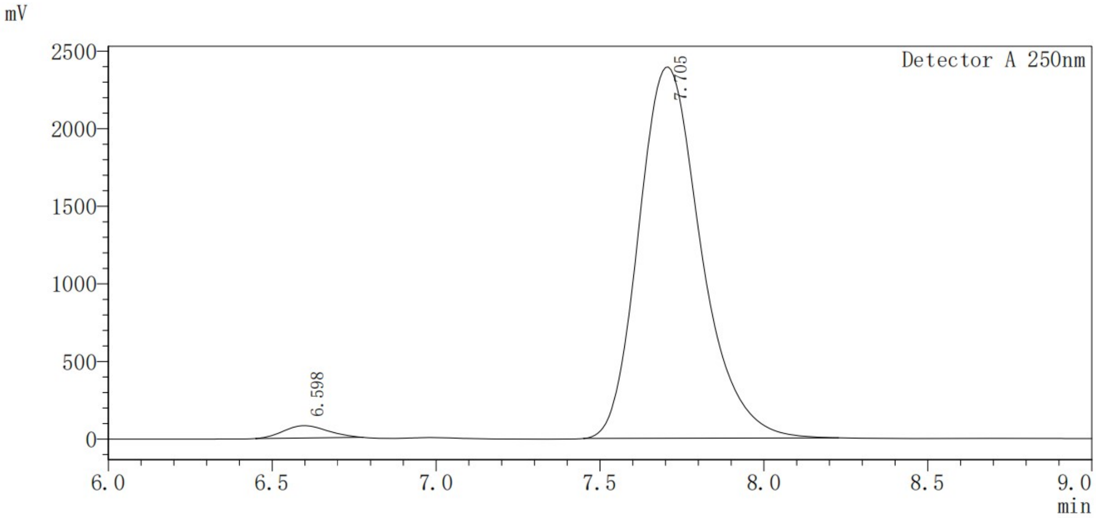
Peak#	Retention	Area	Area(%)
1	7.706	25139	2.673
2	9.152	915208	97.327



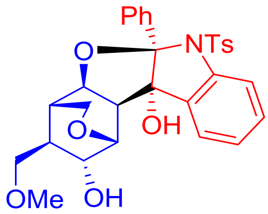
35



Peak#	Retention	Area	Area(%)
1	6.567	10624194	49.895
2	7.646	10668992	50.105



Peak#	Retention	Area	Area(%)
1	6.598	742438	2.295
2	7.705	31609796	97.705



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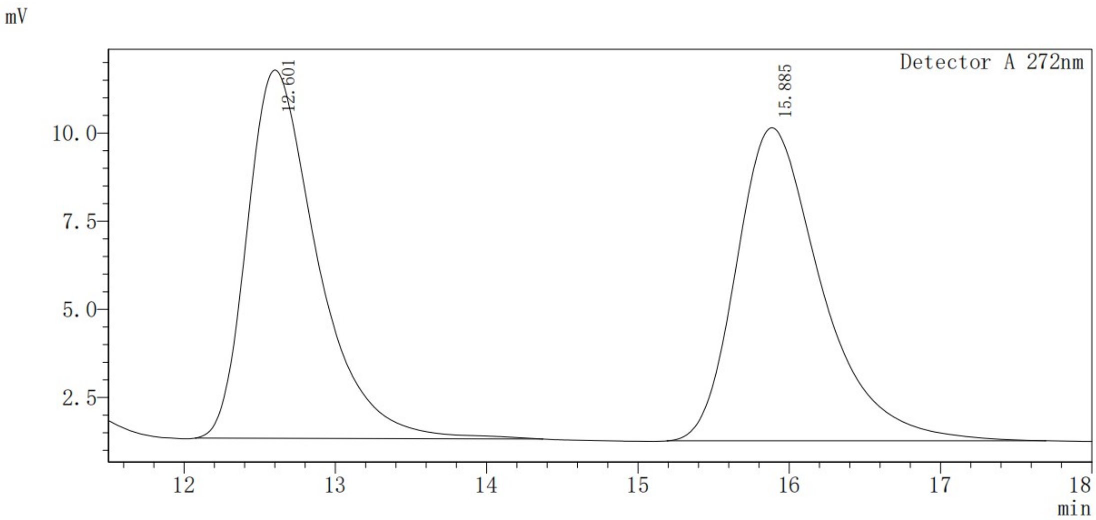
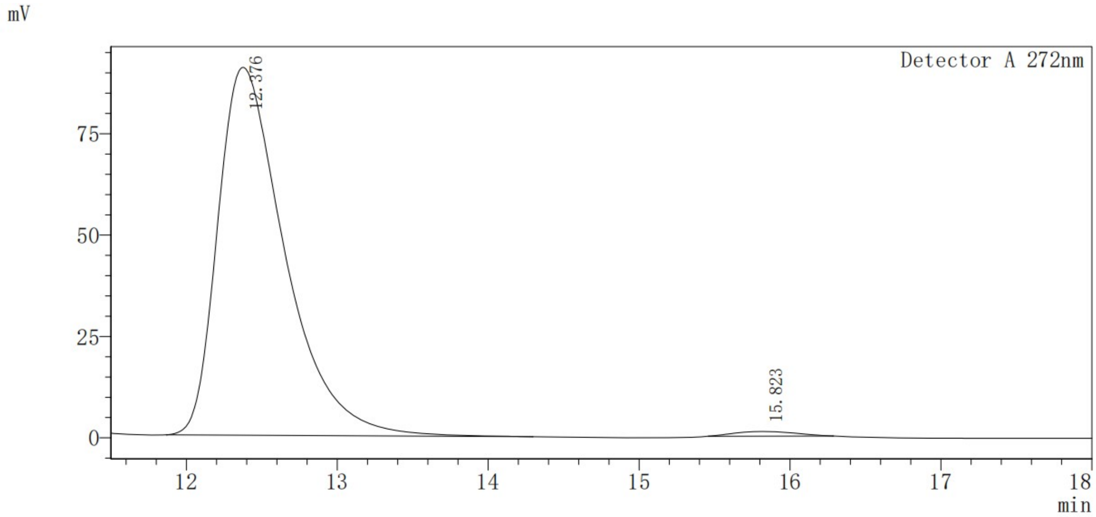
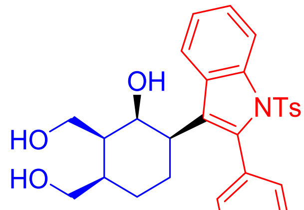


Peak#	Retention	Area	Area(%)
1	12.601	337664	49.204
2	15.885	348584	50.796



Peak#	Retention	Area	Area(%)
1	12.376	2804892	98.845
2	15.823	32779	1.155



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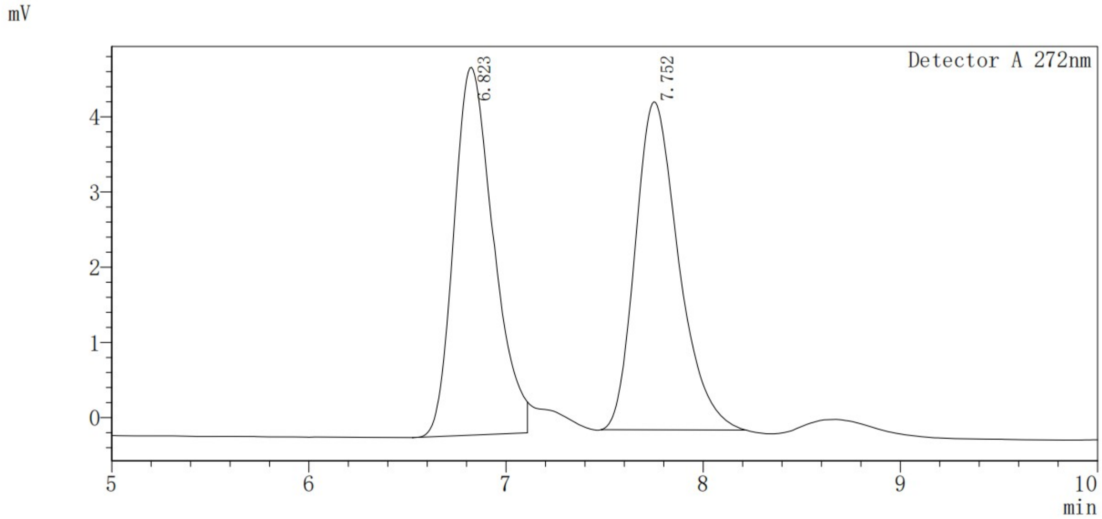
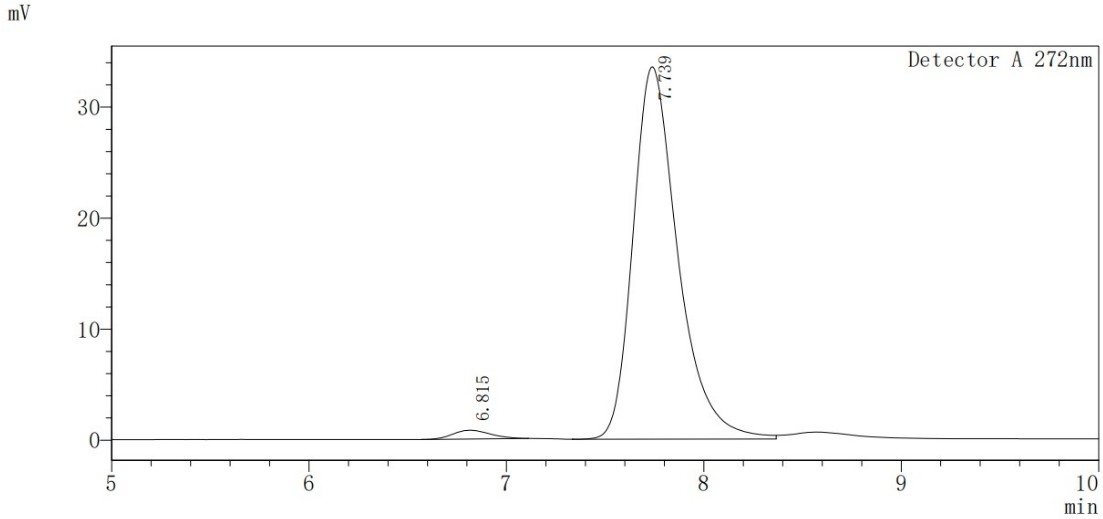


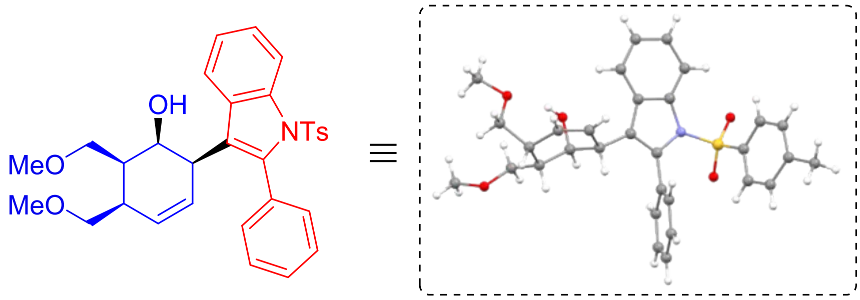
Peak#	Retention	Area	Area(%)
1	6.823	68319	50.499
2	7.752	66969	49.501



Peak#	Retention	Area	Area(%)
1	6.815	10469	1.935
2	7.739	530448	98.065

12. X-Ray Single Crystal Data for Compound 3, 36

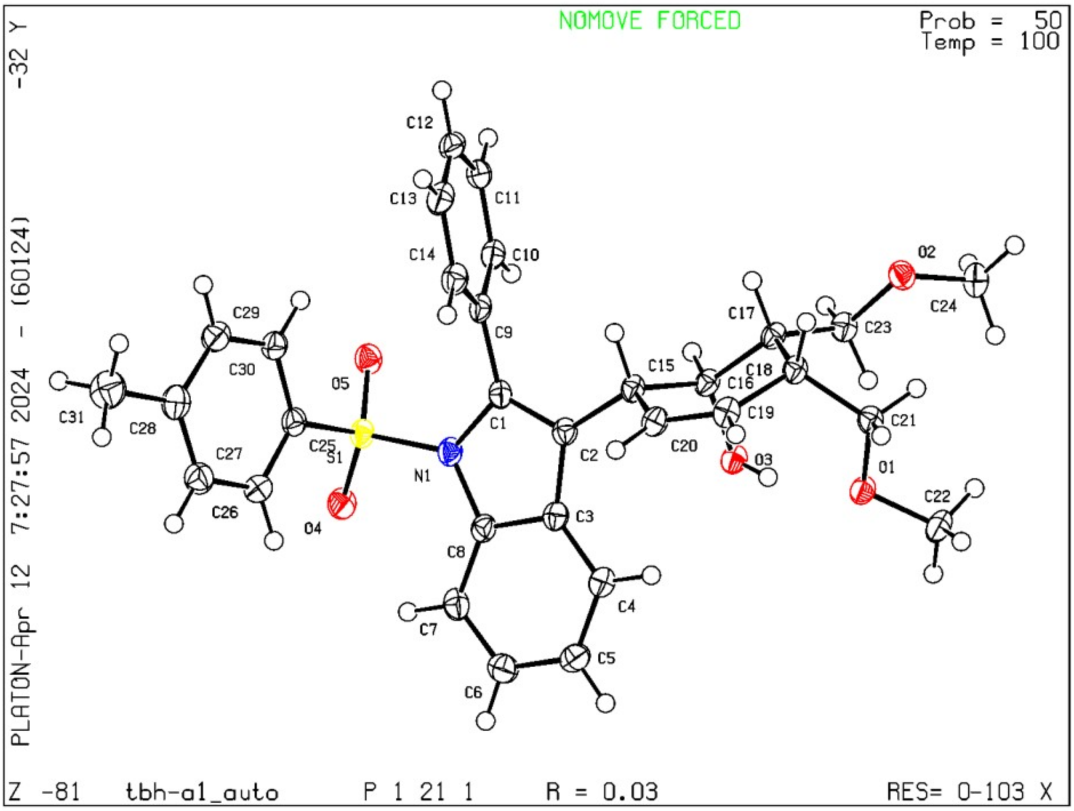
(a) X-Ray Single Crystal Data for Compound 3



X-Ray of 3

Method for single crystal cultivation: The single crystal for compound **3** were obtained by volatilization of *iso*propanol.

The thermal ellipsoid was drawn at the 50% probability level.



Identification code	**3**
Empirical formula	$C_{31}H_{33}NO_5S$
Formula weight	531.64
Temperature/K	100.00(10)

Crystal system	monoclinic
Space group	$P2_1$
a/Å	12.2559(3)
b/Å	8.42474(12)
c/Å	13.6053(3)
α/°	90
β/°	110.755(3)
γ/°	90
Volume/Å^3	1313.61(5)
Z	2
ρ_{calc}g/cm^3	1.344
μ/mm^{-1}	1.442
F(000)	564.0
Crystal size/mm^3	0.1 × 0.08 × 0.06
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.948 to 146.74
Index ranges	$-15 \leq h \leq 15$, $-10 \leq k \leq 9$, $-16 \leq l \leq 16$
Reflections collected	16806
Independent reflections	4304 [R_{int} = 0.0465, R_{sigma} = 0.0410]
Data/restraints/parameters	4304/1/347
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0331, wR_2 = 0.0854
Final R indexes [all data]	R_1 = 0.0354, wR_2 = 0.0866
Largest diff. peak/hole / e Å^{-3}	0.22/-0.30
Flack parameter	-0.013(15)

Crystal structure determination of 3

Crystal Data for $C_{31}H_{33}NO_5S$ (M =531.64 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 12.2559(3) Å, b = 8.42474(12) Å, c = 13.6053(3) Å, β = 110.755(3)°, V = 1313.61(5) Å^3, Z = 2, T = 100.00(10) K, μ(Cu Kα) = 1.442 mm^{-1}, $Dcalc$ = 1.344 g/cm^3, 16806 reflections measured (6.948° ≤ 2Θ ≤ 146.74°), 4304 unique (R_{int} = 0.0465, R_{sigma} = 0.0410) which were used in all calculations. The final R_1 was 0.0331 (I > 2σ(I)) and wR_2 was 0.0866 (all data).

Table S10 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for a1. Ueq is defined as 1/3 of the trace of the orthogonalised UIJ tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	2272.1(5)	2249.9(6)	3533.5(4)	20.44(14)
O3	3919.0(15)	5462.2(19)	8071.2(13)	21.3(4)
O1	3587.8(15)	7730.0(19)	9506.7(13)	21.8(4)
O5	3396.0(14)	2327(2)	3447.4(13)	23.6(4)
O2	6533.2(15)	8960(2)	9383.3(14)	23.6(4)
O4	1783.9(17)	757(2)	3642.1(15)	26.4(4)
N1	2322.9(18)	3330(2)	4581.6(16)	21.4(4)
C8	1668(2)	3032(3)	5238.5(19)	21.1(5)
C29	938(2)	4922(3)	951(2)	26.0(5)
C20	2449(2)	7970(3)	6536.1(19)	21.5(5)
C19	2767(2)	9012(3)	7316.3(19)	22.1(5)
C16	4300(2)	6446(3)	7395.3(19)	19.5(5)
C23	5896(2)	7570(3)	8935.0(19)	21.7(5)
C21	3952(2)	9227(3)	9228.4(19)	20.4(5)
C15	3301(2)	6813(3)	6353.0(18)	19.4(5)
C9	3611(2)	5591(3)	4330.3(18)	20.3(5)
C1	2934(2)	4782(3)	4904.3(18)	19.6(5)
C30	1713(2)	4247(3)	1857(2)	23.6(5)

C2	2739(2)	5333(3)	5763.3(19)	19.8(5)
C28	-253(2)	4575(3)	607(2)	27.6(5)
C17	4869(2)	7989(3)	7942.1(19)	18.7(5)
C4	1404(2)	4278(3)	6745.0(19)	23.3(5)
C22	3832(3)	7669(3)	10614(2)	26.2(5)
C3	1936(2)	4261(3)	5987.4(19)	20.1(5)
C7	881(2)	1821(3)	5223(2)	24.7(5)
C13	3756(3)	7764(3)	3223(2)	27.9(5)
C27	-667(2)	3606(3)	1227(2)	28.6(5)
C14	3124(2)	6919(3)	3717.0(19)	24.7(5)
C12	4881(2)	7305(3)	3339.2(19)	26.5(5)
C11	5375(2)	5999(3)	3964(2)	24.3(5)
C18	3985(2)	9178(3)	8118.7(18)	19.9(5)
C25	1282(2)	3241(3)	2439.5(19)	21.2(5)
C6	361(2)	1884(3)	5975(2)	26.8(6)
C26	95(2)	2936(3)	2148(2)	25.2(5)
C24	7316(2)	8695(3)	10425(2)	27.0(5)
C10	4750(2)	5144(3)	4456.4(19)	22.1(5)
C5	613(2)	3095(3)	6728(2)	26.0(5)
C31	-1055(3)	5218(4)	-433(2)	38.0(7)

Table S11. Anisotropic Displacement Parameters (Å^2×10^3) for 3. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	26.1(3)	17.3(2)	17.5(3)	-2.5(2)	7.2(2)	-0.7(2)
O3	29.3(9)	16.0(8)	18.9(8)	1.0(6)	9.0(7)	0.4(7)
O1	30.0(9)	18.6(8)	18.2(8)	-0.9(6)	10.2(7)	-1.4(6)
O5	23.6(8)	23.9(8)	23.2(8)	-4.4(7)	8.2(7)	0.6(7)
O2	25.9(9)	21.5(9)	21.9(9)	-1.5(7)	6.5(7)	-3.2(7)

O4	36.9(10)	17.6(8)	25.6(9)	-3.6(7)	12.2(8)	-3.3(7)
N1	27.9(11)	18.0(9)	18.1(10)	-2.7(8)	7.9(8)	-2.0(8)
C8	23.2(12)	22.2(12)	16.0(11)	2.3(9)	4.7(9)	0.1(9)
C29	32.4(14)	23.7(12)	23.4(13)	0.1(10)	11.6(11)	-0.7(10)
C20	23.4(11)	22.0(11)	18.3(11)	2.5(9)	6.2(9)	4.0(10)
C19	26.9(12)	18.8(11)	20.2(11)	0.8(9)	8.0(10)	4.1(9)
C16	26.6(12)	15.6(11)	17.8(11)	-0.2(8)	9.8(10)	1.0(9)
C23	25.4(11)	18.0(11)	21.0(11)	-0.4(9)	7.3(10)	1.5(9)
C21	26.2(12)	14.8(10)	20.3(11)	-1.8(9)	8.1(10)	-0.4(9)
C15	27.4(12)	14.5(11)	16.1(10)	-0.5(8)	7.4(9)	-0.7(8)
C9	28.7(12)	16.9(10)	14.5(10)	-3.1(8)	6.8(9)	-1.7(9)
C1	23.5(11)	16.7(11)	15.6(10)	-0.2(8)	3.3(9)	-0.7(9)
C30	27.9(13)	23.5(12)	21.0(11)	-4.0(9)	10.5(10)	-3.1(10)
C2	22.0(11)	18.8(11)	16.9(11)	2.0(9)	4.8(9)	0.9(9)
C28	30.7(13)	25.7(12)	24.9(13)	-2.0(10)	7.9(11)	4.3(10)
C17	25.7(11)	15.3(10)	17.1(11)	-0.2(8)	10.0(9)	1.6(9)
C4	25.9(12)	24.2(12)	19.3(11)	0.7(9)	7.4(10)	1.8(10)
C22	39.8(14)	23.3(12)	17.7(12)	-0.4(9)	12.6(11)	-0.1(10)
C3	22.0(11)	19.0(11)	17.5(11)	2.3(9)	4.7(9)	3.0(9)
C7	27.7(12)	22.6(12)	19.7(11)	-0.3(9)	3.1(10)	-0.9(9)
C13	43.4(15)	20.2(11)	20.6(12)	-0.6(9)	12.0(11)	-2.2(10)
C27	24.7(12)	34.3(14)	26.0(13)	-2.8(11)	8.1(11)	-0.2(11)
C14	31.5(13)	21.3(13)	21.0(11)	-2.0(9)	8.7(10)	0.7(9)
C12	39.9(13)	22.0(11)	21.9(11)	-6.6(10)	16.2(10)	-10.9(12)
C11	29.2(13)	22.3(12)	22.4(12)	-7.4(10)	10.6(10)	-5.8(10)
C18	27.0(12)	14.5(10)	18.4(11)	-1.8(9)	8.3(10)	0.6(9)
C25	25.4(12)	19.6(11)	19.4(11)	-4.9(9)	8.7(9)	-1.0(9)
C6	23.8(12)	27.7(14)	26.0(12)	5.0(10)	5.1(10)	-1.6(10)
C26	25.6(12)	28.7(12)	22.9(12)	-1.0(10)	10.7(10)	-2.2(10)

C24	29.6(13)	28.6(12)	20.4(12)	-4.6(10)	5.6(10)	1.1(11)
C10	28.0(12)	20.9(11)	16.5(11)	-1.6(9)	6.6(10)	-0.6(9)
C5	25.8(12)	30.1(13)	23.7(12)	3.4(10)	10.8(10)	1.4(10)
C31	34.9(15)	41.4(17)	33.3(16)	8.5(13)	6.7(13)	7.0(13)

Table S12. Bond Lengths for 3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O5	1.4247(17)	C21	C18	1.525(3)
S1	O4	1.4231(19)	C15	C2	1.510(3)
S1	N1	1.674(2)	C9	C1	1.490(3)
S1	C25	1.762(3)	C9	C14	1.397(3)
O3	C16	1.434(3)	C9	C10	1.396(4)
O1	C21	1.433(3)	C1	C2	1.355(3)
O1	C22	1.429(3)	C30	C25	1.387(3)
O2	C23	1.420(3)	C2	C3	1.445(3)
O2	C24	1.420(3)	C28	C27	1.392(4)
N1	C8	1.420(3)	C28	C31	1.508(4)
N1	C1	1.421(3)	C17	C18	1.556(3)
C8	C3	1.408(3)	C4	C3	1.402(3)
C8	C7	1.398(3)	C4	C5	1.384(4)
C29	C30	1.384(4)	C7	C6	1.386(4)
C29	C28	1.397(4)	C13	C14	1.388(4)
C20	C19	1.325(4)	C13	C12	1.386(4)
C20	C15	1.512(3)	C27	C26	1.389(4)
C19	C18	1.512(4)	C12	C11	1.391(4)
C16	C15	1.542(3)	C11	C10	1.385(4)
C16	C17	1.537(3)	C25	C26	1.389(4)
C23	C17	1.525(3)	C6	C5	1.401(4)

Table S13 Bond Angles for 3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O5	S1	O4	120.20(11)	C29	C30	C25	118.6(2)
O5	S1	N1	107.47(10)	C1	C2	C15	123.6(2)
O5	S1	C25	107.81(11)	C1	C2	C3	108.0(2)
O4	S1	N1	106.38(11)	C3	C2	C15	128.3(2)
O4	S1	C25	108.51(12)	C29	C28	C31	119.7(3)
N1	S1	C25	105.57(11)	C27	C28	C29	118.7(2)
C22	O1	C21	109.98(18)	C27	C28	C31	121.5(2)
C23	O2	C24	111.93(19)	C16	C17	C18	113.45(19)
C8	N1	S1	125.57(17)	C23	C17	C16	108.85(18)
C8	N1	C1	108.16(19)	C23	C17	C18	114.39(19)
C1	N1	S1	126.00(16)	C5	C4	C3	119.1(2)
C3	C8	N1	106.6(2)	C8	C3	C2	108.0(2)
C7	C8	N1	131.3(2)	C4	C3	C8	119.3(2)
C7	C8	C3	122.1(2)	C4	C3	C2	132.7(2)
C30	C29	C28	121.3(2)	C6	C7	C8	117.1(2)
C19	C20	C15	122.3(2)	C14	C13	C12	120.3(2)
C20	C19	C18	125.1(2)	C28	C27	C26	120.8(2)
O3	C16	C15	111.9(2)	C13	C14	C9	120.4(2)
O3	C16	C17	111.94(18)	C11	C12	C13	119.4(2)
C17	C16	C15	110.60(19)	C10	C11	C12	120.8(2)
O2	C23	C17	110.20(18)	C19	C18	C21	110.6(2)
O1	C21	C18	110.98(18)	C19	C18	C17	113.11(19)
C20	C15	C16	110.35(19)	C21	C18	C17	115.74(19)
C2	C15	C20	114.1(2)	C30	C25	S1	118.95(19)
C2	C15	C16	112.79(18)	C30	C25	C26	121.5(2)
C14	C9	C1	118.6(2)	C26	C25	S1	119.46(19)
C10	C9	C1	122.0(2)	C7	C6	C5	121.9(2)

C10	C9	C14	119.1(2)	C25	C26	C27	118.9(2)
N1	C1	C9	124.2(2)	C11	C10	C9	120.0(2)
C2	C1	N1	109.1(2)	C4	C5	C6	120.5(2)
C2	C1	C9	126.6(2)				

Table S14. Torsion Angles for 3.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	N1	C8	C3	-177.32(17)	C23	C17	C18	C19	-153.4(2)
S1	N1	C8	C7	2.2(4)	C23	C17	C18	C21	-24.4(3)
S1	N1	C1	C9	1.5(3)	C15	C20	C19	C18	-0.7(4)
S1	N1	C1	C2	177.88(18)	C15	C16	C17	C23	-176.8(2)
S1	C25	C26	C27	-173.9(2)	C15	C16	C17	C18	54.6(2)
O3	C16	C15	C20	72.3(2)	C15	C2	C3	C8	-178.7(2)
O3	C16	C15	C2	-56.5(3)	C15	C2	C3	C4	3.4(4)
O3	C16	C17	C23	57.8(2)	C9	C1	C2	C15	-6.9(4)
O3	C16	C17	C18	-70.8(2)	C9	C1	C2	C3	173.6(2)
O1	C21	C18	C19	67.3(2)	C1	N1	C8	C3	-3.0(2)
O1	C21	C18	C17	-63.0(3)	C1	N1	C8	C7	176.4(3)
O5	S1	N1	C8	-148.9(2)	C1	C9	C14	C13	176.0(2)
O5	S1	N1	C1	37.8(2)	C1	C9	C10	C11	-175.5(2)
O5	S1	C25	C30	-16.6(2)	C1	C2	C3	C8	0.8(3)
O5	S1	C25	C26	160.1(2)	C1	C2	C3	C4	-177.1(3)
O2	C23	C17	C16	172.31(18)	C30	C29	C28	C27	4.0(4)
O2	C23	C17	C18	-59.6(3)	C30	C29	C28	C31	-174.6(3)
O4	S1	N1	C8	-18.9(2)	C30	C25	C26	C27	2.7(4)
O4	S1	N1	C1	167.80(19)	C28	C29	C30	C25	-1.7(4)
O4	S1	C25	C30	-148.21(19)	C28	C27	C26	C25	-0.3(4)
O4	S1	C25	C26	28.4(2)	C17	C16	C15	C20	-53.2(3)
N1	S1	C25	C30	98.1(2)	C17	C16	C15	C2	177.94(19)

N1	S1	C25	C26	-85.3(2)	C22	O1	C21	C18	165.9(2)
N1	C8	C3	C2	1.4(3)	C3	C8	C7	C6	0.6(4)
N1	C8	C3	C4	179.7(2)	C3	C4	C5	C6	0.9(4)
N1	C8	C7	C6	-178.8(2)	C7	C8	C3	C2	-178.1(2)
N1	C1	C2	C15	176.8(2)	C7	C8	C3	C4	0.1(4)
N1	C1	C2	C3	-2.7(3)	C7	C6	C5	C4	-0.2(4)
C8	N1	C1	C9	-172.8(2)	C13	C12	C11	C10	1.0(4)
C8	N1	C1	C2	3.6(3)	C14	C9	C1	N1	103.5(3)
C8	C7	C6	C5	-0.6(4)	C14	C9	C1	C2	-72.3(3)
C29	C30	C25	S1	174.88(19)	C14	C9	C10	C11	-1.0(4)
C29	C30	C25	C26	-1.7(4)	C14	C13	C12	C11	-0.7(4)
C29	C28	C27	C26	-2.9(4)	C12	C13	C14	C9	-0.5(4)
C20	C19	C18	C21	-131.3(3)	C12	C11	C10	C9	-0.1(4)
C20	C19	C18	C17	0.4(3)	C25	S1	N1	C8	96.2(2)
C20	C15	C2	C1	129.2(3)	C25	S1	N1	C1	-77.0(2)
C20	C15	C2	C3	-51.4(3)	C24	O2	C23	C17	166.05(19)
C19	C20	C15	C16	27.6(3)	C10	C9	C1	N1	-82.0(3)
C19	C20	C15	C2	155.8(2)	C10	C9	C1	C2	102.2(3)
C16	C15	C2	C1	-103.9(3)	C10	C9	C14	C13	1.3(4)
C16	C15	C2	C3	75.5(3)	C5	C4	C3	C8	-0.9(4)
C16	C17	C18	C19	-27.7(3)	C5	C4	C3	C2	176.8(2)
C16	C17	C18	C21	101.3(2)	C31	C28	C27	C26	175.6(3)

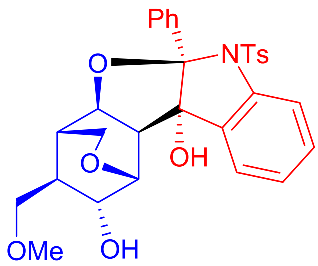
Table S15. Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for 3.

Atom	*x*	*y*	*z*	U(eq)
H3	3701.57	6037.25	8471.7	32
H29	1221.17	5634.77	556.08	31
H20	1657.75	7949.22	6075.41	26

H19	2183.59	9707.8	7376.13	26
H16	4908.7	5839.73	7219.3	23
H23A	5603.88	7060.47	9449.67	26
H23B	6414.21	6807.79	8760.58	26
H21A	4737.46	9492.37	9733.4	25
H21B	3405.36	10066.49	9270.99	25
H15	3663.95	7374.47	5898.23	23
H30	2524.6	4467.98	2075.07	28
H17	5206.06	8523.8	7457.79	22
H4	1582.67	5090.04	7262.58	28
H22A	3592.02	6636.11	10799.15	39
H22B	3401.73	8514.08	10813.14	39
H22C	4671.18	7815.27	10988.45	39
H7	711.53	990.35	4718.1	30
H13	3415.83	8661.57	2803.6	33
H27	-1479.77	3401.63	1018.47	34
H14	2355.3	7246.23	3637.59	30
H12	5310.61	7876.52	2995.3	32
H11	6150.1	5690.44	4054.24	29
H18	4256.88	10254.71	7997.19	24
H6	-182.85	1082.96	5979.84	32
H26	-191.35	2279.77	2570.56	30
H24A	7892.41	7893.23	10418.34	41
H24B	6879.31	8320.15	10860.06	41
H24C	7715.92	9688.64	10716.21	41
H10	5096.21	4253.08	4880.13	27
H5	239.06	3104.49	7232.04	31
H31A	-788.62	6274.66	-548.04	57
H31B	-1850.27	5290.06	-426.39	57

H31C	-1046.33	4505.68	-999.86	57

(b) X-Ray Single Crystal Data for Compound 36



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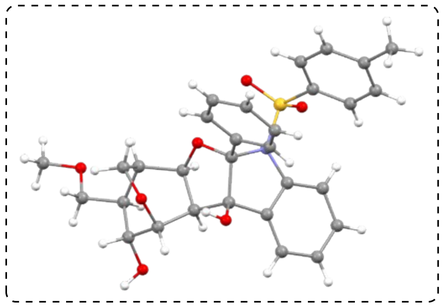
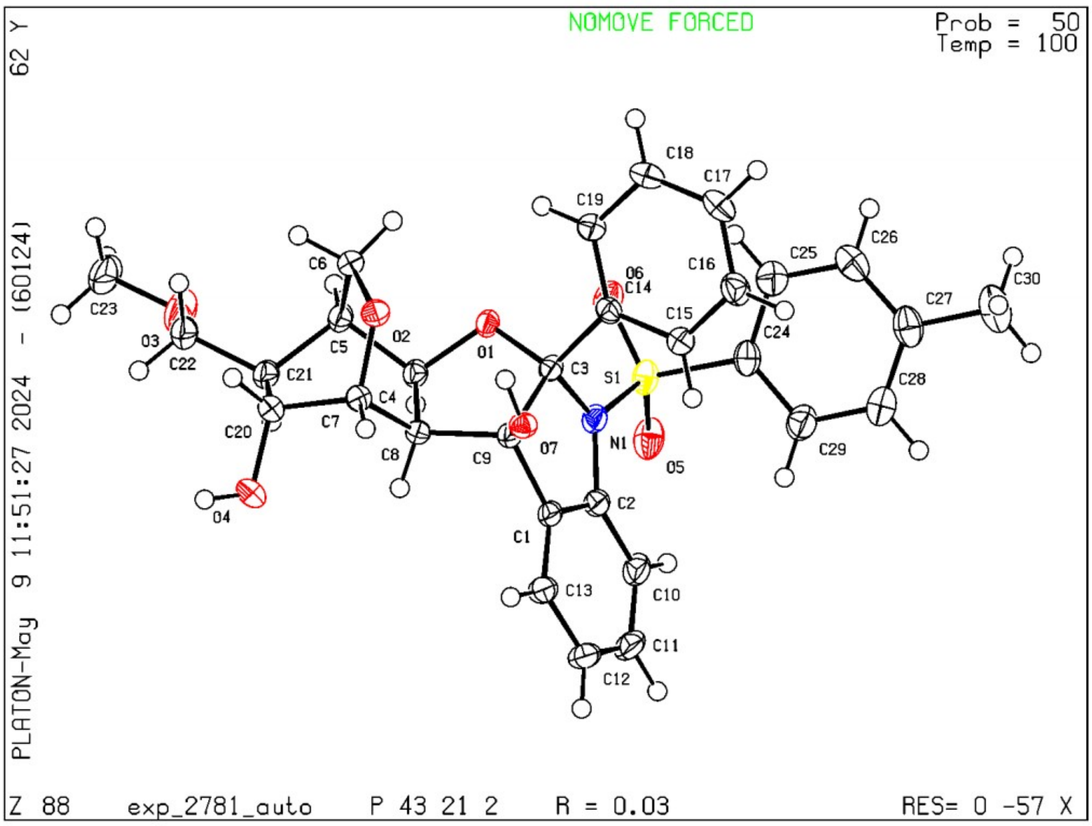


X-Ray of 36

Method for single crystal cultivation: The single crystal for compound **36** were obtained by volatilization of *iso*propanol.

The thermal ellipsoid was drawn at the 50% probability level.



Identification code	**36**
Empirical formula	$C_{30}H_{31}NO_7S$
Formula weight	549.62
Temperature/K	99.98(11)

Crystal system	tetragonal
Space group	$P4_32_12$
a/Å	9.61046(4)
b/Å	9.61046(4)
c/Å	59.2426(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5471.71(6)
Z	8
ρ_{calc}g/cm^3	1.334
μ/mm^{-1}	1.460
F(000)	2320.0
Crystal size/mm^3	0.1 × 0.08 × 0.06
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.968 to 146.89
Index ranges	$-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-73 \leq l \leq 73$
Reflections collected	86280
Independent reflections	5466 [R_{int} = 0.0588, R_{sigma} = 0.0199]
Data/restraints/parameters	5466/0/357
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0348, wR_2 = 0.0985
Final R indexes [all data]	R_1 = 0.0359, wR_2 = 0.0995
Largest diff. peak/hole / e Å^{-3}	1.17/-0.27
Flack parameter	-0.033(9)

Crystal structure determination of 36

Crystal Data for $C_{30}H_{31}NO_7S$ (M =549.62 g/mol): tetragonal, space group P43212 (no. 96), a = 9.61046(4) Å, c = 59.2426(5) Å, V = 5471.71(6) Å3, Z = 8, T = 99.98(11) K, μ(Cu Kα) = 1.460 mm^{-1}, $Dcalc$ = 1.334 g/cm^3, 86280 reflections measured (5.968 ≤ 2Θ ≤ 146.89), 5466 unique (R_{int} = 0.0588, R_{sigma} = 0.0199) which were used in all calculations. The final R_1 was 0.0348 (I > 2σ(I)) and wR_2 was 0.0995 (all data).

Table S16. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for c2. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	-178.9(6)	4924.1(6)	6686.9(2)	24.63(15)
O1	900.4(15)	4947.2(16)	7198.5(2)	19.3(3)
O7	4378.4(16)	5113.2(16)	7112.5(3)	19.7(3)
O2	2925.6(16)	5062.0(16)	7576.4(3)	21.3(3)
O6	-1037.6(18)	5511(2)	6859.7(3)	30.5(4)
O5	-639(2)	3742(2)	6560.4(3)	33.2(4)
O4	3678(3)	1358(2)	7621.0(3)	42.2(5)
O3	-642(2)	1837(2)	7878.4(3)	42.7(5)
N1	1275(2)	4452(2)	6809.5(3)	21.0(4)
C2	2299(3)	3539(2)	6717.7(4)	22.3(5)
C8	2736(2)	3373(2)	7276.7(4)	19.6(4)
C1	3428(2)	3462(2)	6864.1(4)	19.7(4)
C4	1164(2)	3622(2)	7303.7(4)	20.3(4)
C14	2034(2)	6703(2)	6982.8(4)	19.0(4)
C5	782(2)	3732(2)	7553.3(4)	21.5(5)
C6	1482(2)	5029(2)	7647.8(4)	21.0(4)
C3	1818(2)	5159(2)	7018.9(3)	18.2(4)
C13	4585(3)	2657(2)	6813.2(4)	25.2(5)
C18	1679(3)	9098(2)	7089.9(4)	26.6(5)

C9	3187(2)	4304(2)	7074.4(4)	17.8(4)
C19	1485(2)	7680(2)	7131.0(4)	22.6(5)
C7	3405(2)	3723(2)	7502.8(4)	21.1(4)
C21	1398(3)	2436(2)	7669.0(4)	26.3(5)
C15	2815(3)	7154(2)	6798.6(4)	23.8(5)
C17	2426(3)	9542(2)	6904.4(4)	27.8(5)
C20	2990(3)	2620(2)	7676.4(4)	26.9(5)
C10	2291(3)	2776(3)	6516.7(4)	29.2(5)
C12	4597(3)	1928(3)	6609.8(4)	30.6(6)
C24	182(3)	6271(3)	6491.5(4)	26.0(5)
C22	789(3)	2151(3)	7901.7(4)	31.2(6)
C27	677(3)	8388(3)	6180.8(5)	32.2(6)
C29	846(3)	5967(3)	6289.9(4)	32.0(6)
C28	1088(3)	7026(3)	6137.0(5)	35.1(6)
C16	3010(3)	8568(3)	6759.9(4)	27.9(5)
C11	3465(3)	1988(3)	6466.3(4)	33.2(6)
C26	17(3)	8662(3)	6384.2(5)	39.5(6)
C25	-231(3)	7614(3)	6539.8(5)	37.8(6)
C30	944(3)	9543(3)	6013.8(5)	42.7(7)
C23	-1272(4)	1523(3)	8087.9(5)	46.6(8)

Table S17. Anisotropic Displacement Parameters (Å2×103) for 36. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	25.7(3)	30.2(3)	18.1(3)	3.1(2)	-3.9(2)	-4.6(2)
O1	19.6(7)	22.2(8)	16.1(7)	3.2(6)	2.4(5)	0.9(6)
O7	20.5(7)	17.9(7)	20.7(7)	-2.0(6)	0.8(6)	-0.7(6)
O2	23.3(8)	20.3(8)	20.4(7)	-2.2(6)	-0.4(6)	-0.2(6)

O6	22.9(8)	46.7(11)	22.0(8)	4.5(7)	-0.6(6)	2.4(7)
O5	39.6(10)	36.9(10)	23.1(8)	1.5(7)	-8.7(7)	-13.3(8)
O4	65.7(14)	29.9(10)	31.0(9)	8.2(8)	7.0(9)	25.1(10)
O3	48.4(12)	48.4(12)	31.2(10)	6.4(9)	12.6(9)	-13.2(10)
N1	26.5(10)	21.3(9)	15.2(8)	-0.3(7)	-1.2(7)	-1.3(8)
C2	30.5(12)	16.6(10)	19.7(10)	0.0(8)	4.3(9)	-2.5(9)
C8	26.4(11)	14.9(10)	17.5(10)	-0.4(8)	2.3(8)	1.0(8)
C1	26.5(11)	15.2(10)	17.5(9)	0.4(8)	4.4(9)	-2.3(8)
C4	26.2(11)	17.8(10)	16.9(10)	0.8(8)	1.5(8)	-3.2(8)
C14	18.5(10)	18.7(10)	19.7(10)	1.3(8)	-2.2(8)	1.8(8)
C5	24.1(11)	23.2(11)	17.2(10)	2.0(8)	2.8(8)	-1.1(9)
C6	24.0(10)	20.1(10)	18.8(10)	-0.2(8)	3.0(8)	2.5(9)
C3	20.3(10)	19.5(10)	14.7(9)	-0.4(8)	1.0(8)	-1.2(8)
C13	30.2(12)	20.6(11)	24.8(11)	-1.4(9)	7.6(9)	-0.4(9)
C18	27.0(12)	18.6(11)	34.2(13)	-4.0(10)	-1.7(10)	4.2(9)
C9	20.1(10)	16.6(9)	16.8(10)	0.2(8)	1.4(8)	-0.7(8)
C19	22.8(11)	22.4(11)	22.7(11)	0.0(9)	0.5(9)	2.7(9)
C7	22.8(11)	22.0(11)	18.5(10)	1.1(9)	-0.6(9)	4.3(9)
C21	39.9(14)	18.7(10)	20.1(11)	0.8(9)	7.1(10)	-1.4(10)
C15	26.5(11)	22.3(11)	22.6(11)	1.5(9)	3.6(9)	2.4(9)
C17	29.0(12)	17.2(11)	37.3(13)	3.5(9)	-5.1(10)	0.8(9)
C20	36.8(13)	22.2(11)	21.7(11)	3.4(9)	2.8(10)	9.2(10)
C10	45.3(15)	23.8(12)	18.4(11)	-1.3(9)	0.9(10)	-4.4(10)
C12	40.6(14)	23.0(12)	28.3(12)	-4.2(9)	13.0(11)	2.4(10)
C24	25.9(12)	31.3(12)	20.9(10)	4.6(9)	-5.7(9)	-2.1(10)
C22	44.4(15)	25.6(12)	23.6(12)	4.5(10)	6.2(11)	-0.1(11)
C27	25.2(12)	38.1(14)	33.3(13)	11.1(11)	-8.0(10)	-2.9(11)
C29	39.1(14)	33.6(14)	23.4(11)	0.6(10)	0.3(10)	-3.0(11)
C28	39.2(14)	40.6(15)	25.6(12)	5.7(11)	2.3(11)	-3.0(12)

C16	29.2(12)	23.1(12)	31.4(12)	6.2(10)	2.9(10)	-1.8(9)
C11	54.9(17)	23.9(12)	20.7(11)	-5.4(9)	11.6(11)	-3.8(11)
C26	44.6(16)	32.9(14)	41.1(15)	8.9(12)	-2.4(13)	11.1(12)
C25	44.5(16)	39.0(15)	30.0(13)	5.2(11)	3.2(12)	9.7(12)
C30	36.3(15)	44.7(17)	47.1(17)	20.3(14)	-4.8(13)	-5.7(12)
C23	65(2)	39.2(16)	35.8(15)	5.5(13)	23.9(15)	-6.1(15)

Table S18. Bond Lengths for 36.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O6	1.4308(18)	C14	C19	1.389(3)
S1	O5	1.4309(19)	C14	C15	1.394(3)
S1	N1	1.639(2)	C5	C6	1.523(3)
S1	C24	1.771(3)	C5	C21	1.539(3)
O1	C4	1.440(3)	C3	C9	1.585(3)
O1	C3	1.397(2)	C13	C12	1.393(3)
O7	C9	1.403(3)	C18	C19	1.397(3)
O2	C6	1.450(3)	C18	C17	1.380(4)
O2	C7	1.434(3)	C7	C20	1.530(3)
O4	C20	1.420(3)	C21	C20	1.541(4)
O3	C22	1.414(4)	C21	C22	1.522(3)
O3	C23	1.414(3)	C15	C16	1.391(3)
N1	C2	1.426(3)	C17	C16	1.387(4)
N1	C3	1.508(3)	C10	C11	1.391(4)
C2	C1	1.392(3)	C12	C11	1.382(4)
C2	C10	1.398(3)	C24	C29	1.385(4)
C8	C4	1.537(3)	C24	C25	1.381(4)
C8	C9	1.557(3)	C27	C28	1.391(4)
C8	C7	1.523(3)	C27	C26	1.387(4)
C1	C13	1.388(3)	C27	C30	1.509(4)

C1	C9	1.504(3)	C29	C28	1.382(4)
C4	C5	1.527(3)	C26	C25	1.386(4)
C14	C3	1.513(3)			

Table S19. Bond Angles for 36.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O6	S1	O5	120.62(12)	C14	C3	C9	115.09(18)
O6	S1	N1	106.48(10)	C1	C13	C12	118.4(2)
O6	S1	C24	107.01(12)	C17	C18	C19	120.7(2)
O5	S1	N1	106.01(11)	O7	C9	C8	114.96(17)
O5	S1	C24	107.39(11)	O7	C9	C1	107.78(17)
N1	S1	C24	108.96(11)	O7	C9	C3	115.06(17)
C3	O1	C4	110.34(16)	C8	C9	C3	103.10(17)
C7	O2	C6	112.10(17)	C1	C9	C8	111.79(17)
C23	O3	C22	112.1(2)	C1	C9	C3	103.63(17)
C2	N1	S1	126.11(16)	C14	C19	C18	119.9(2)
C2	N1	C3	110.65(18)	O2	C7	C8	109.24(17)
C3	N1	S1	122.35(15)	O2	C7	C20	109.46(18)
C1	C2	N1	109.45(19)	C8	C7	C20	109.1(2)
C1	C2	C10	120.5(2)	C5	C21	C20	107.52(19)
C10	C2	N1	130.1(2)	C22	C21	C5	113.6(2)
C4	C8	C9	105.30(17)	C22	C21	C20	112.1(2)
C7	C8	C4	106.81(18)	C16	C15	C14	120.4(2)
C7	C8	C9	115.59(19)	C18	C17	C16	119.5(2)
C2	C1	C9	111.54(19)	O4	C20	C7	108.39(19)
C13	C1	C2	121.2(2)	O4	C20	C21	110.9(2)
C13	C1	C9	127.2(2)	C7	C20	C21	108.64(19)
O1	C4	C8	105.41(17)	C11	C10	C2	117.6(2)
O1	C4	C5	108.44(17)	C11	C12	C13	120.3(2)

C5	C4	C8	110.32(18)	C29	C24	S1	120.0(2)
C19	C14	C3	121.4(2)	C25	C24	S1	119.45(19)
C19	C14	C15	119.3(2)	C25	C24	C29	120.5(2)
C15	C14	C3	119.31(19)	O3	C22	C21	108.9(2)
C4	C5	C21	106.46(18)	C28	C27	C30	121.4(3)
C6	C5	C4	107.82(18)	C26	C27	C28	118.1(2)
C6	C5	C21	109.20(19)	C26	C27	C30	120.5(3)
O2	C6	C5	109.46(18)	C28	C29	C24	119.2(3)
O1	C3	N1	110.03(17)	C29	C28	C27	121.5(3)
O1	C3	C14	109.71(17)	C17	C16	C15	120.2(2)
O1	C3	C9	106.88(16)	C12	C11	C10	122.0(2)
N1	C3	C14	111.88(17)	C25	C26	C27	121.2(3)
N1	C3	C9	102.94(16)	C24	C25	C26	119.5(3)

Table S20. Torsion Angles for 36.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	N1	C2	C1	175.98(16)	C14	C15	C16	C17	0.0(4)
S1	N1	C2	C10	-4.5(4)	C5	C21	C20	O4	-137.78(19)
S1	N1	C3	O1	64.3(2)	C5	C21	C20	C7	-18.7(3)
S1	N1	C3	C14	-57.9(2)	C5	C21	C22	O3	64.5(3)
S1	N1	C3	C9	177.97(14)	C6	O2	C7	C8	71.6(2)
S1	C24	C29	C28	178.4(2)	C6	O2	C7	C20	-47.9(2)
S1	C24	C25	C26	-178.2(2)	C6	C5	C21	C20	-44.5(2)
O1	C4	C5	C6	-49.8(2)	C6	C5	C21	C22	80.2(3)
O1	C4	C5	C21	-166.82(18)	C3	O1	C4	C8	31.7(2)
O1	C3	C9	O7	-113.89(19)	C3	O1	C4	C5	149.84(18)
O1	C3	C9	C8	12.1(2)	C3	N1	C2	C1	6.7(2)
O1	C3	C9	C1	128.71(17)	C3	N1	C2	C10	-173.8(2)
O2	C7	C20	O4	-169.9(2)	C3	C14	C19	C18	-178.7(2)

O2	C7	C20	C21	69.4(2)	C3	C14	C15	C16	179.0(2)
O6	S1	N1	C2	164.40(19)	C13	C1	C9	O7	49.3(3)
O6	S1	N1	C3	-27.5(2)	C13	C1	C9	C8	-77.9(3)
O6	S1	C24	C29	-171.6(2)	C13	C1	C9	C3	171.7(2)
O6	S1	C24	C25	6.9(3)	C13	C12	C11	C10	0.6(4)
O5	S1	N1	C2	34.8(2)	C18	C17	C16	C15	1.6(4)
O5	S1	N1	C3	-157.08(17)	C9	C8	C4	O1	-22.0(2)
O5	S1	C24	C29	-40.8(2)	C9	C8	C4	C5	-138.84(18)
O5	S1	C24	C25	137.7(2)	C9	C8	C7	O2	66.9(2)
N1	S1	C24	C29	73.6(2)	C9	C8	C7	C20	-173.48(18)
N1	S1	C24	C25	-107.9(2)	C9	C1	C13	C12	178.7(2)
N1	C2	C1	C13	-179.0(2)	C19	C14	C3	O1	6.7(3)
N1	C2	C1	C9	2.5(2)	C19	C14	C3	N1	129.1(2)
N1	C2	C10	C11	178.3(2)	C19	C14	C3	C9	-113.9(2)
N1	C3	C9	O7	130.20(17)	C19	C14	C15	C16	-1.9(4)
N1	C3	C9	C8	-103.86(18)	C19	C18	C17	C16	-1.2(4)
N1	C3	C9	C1	12.8(2)	C7	O2	C6	C5	-18.4(2)
C2	N1	C3	O1	-125.90(19)	C7	C8	C4	O1	101.42(19)
C2	N1	C3	C14	111.9(2)	C7	C8	C4	C5	-15.4(2)
C2	N1	C3	C9	-12.3(2)	C7	C8	C9	O7	14.6(3)
C2	C1	C13	C12	0.4(3)	C7	C8	C9	C1	137.9(2)
C2	C1	C9	O7	-132.26(19)	C7	C8	C9	C3	-111.4(2)
C2	C1	C9	C8	100.5(2)	C21	C5	C6	O2	68.3(2)
C2	C1	C9	C3	-9.9(2)	C15	C14	C3	O1	-174.25(19)
C2	C10	C11	C12	1.3(4)	C15	C14	C3	N1	-51.8(3)
C8	C4	C5	C6	65.2(2)	C15	C14	C3	C9	65.2(3)
C8	C4	C5	C21	-51.9(2)	C15	C14	C19	C18	2.2(3)
C8	C7	C20	O4	70.6(2)	C17	C18	C19	C14	-0.7(4)
C8	C7	C20	C21	-50.1(2)	C20	C21	C22	O3	-173.4(2)

C1	C2	C10	C11	-2.3(3)	C10	C2	C1	C13	1.5(3)
C1	C13	C12	C11	-1.5(4)	C10	C2	C1	C9	-177.1(2)
C4	O1	C3	N1	83.5(2)	C24	S1	N1	C2	-80.5(2)
C4	O1	C3	C14	-153.04(17)	C24	S1	N1	C3	87.62(19)
C4	O1	C3	C9	-27.6(2)	C24	C29	C28	C27	-0.2(4)
C4	C8	C9	O7	132.23(18)	C22	C21	C20	O4	96.6(2)
C4	C8	C9	C1	-104.5(2)	C22	C21	C20	C7	-144.3(2)
C4	C8	C9	C3	6.2(2)	C27	C26	C25	C24	-0.2(5)
C4	C8	C7	O2	-49.9(2)	C29	C24	C25	C26	0.3(4)
C4	C8	C7	C20	69.8(2)	C28	C27	C26	C25	-0.1(4)
C4	C5	C6	O2	-47.0(2)	C26	C27	C28	C29	0.3(4)
C4	C5	C21	C20	71.6(2)	C25	C24	C29	C28	-0.1(4)
C4	C5	C21	C22	-163.7(2)	C30	C27	C28	C29	179.9(3)
C14	C3	C9	O7	8.2(3)	C30	C27	C26	C25	-179.7(3)
C14	C3	C9	C8	134.14(19)	C23	O3	C22	C21	178.4(2)
C14	C3	C9	C1	-109.20(19)					

Table S21. Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for 36.

Atom	*x*	*y*	*z*	U(eq)
H7	4236.23	5653.26	7221.55	30
H4	4027.9	1012.97	7738.25	63
H8	2908.64	2373.06	7239.48	24
H4A	618.45	2867.74	7228.42	24
H5	-249.34	3774.08	7574	26
H6A	994.73	5870.07	7592.73	25
H6B	1431.89	5019.82	7814.71	25
H13	5349.89	2603.61	6914.38	30
H18	1293.98	9762.86	7190.72	32

H19	977.79	7383.48	7260	27
H7A	4440.62	3738.95	7486.04	25
H21	1190.03	1613.21	7571.32	32
H15	3217.32	6492.18	6699	29
H17	2539.06	10508.15	6875.94	33
H20	3278.95	2929.71	7830.56	32
H10	1511.69	2794.09	6418.15	35
H12	5386.74	1386.7	6569.74	37
H22A	1280.08	1359.12	7972.87	37
H22B	907.76	2978.99	7999.37	37
H29	1131.22	5042.5	6257.04	38
H28	1545.53	6819.79	5998.9	42
H16	3544.12	8868.13	6634.08	33
H11	3489.49	1476.72	6329.14	40
H26	-270.6	9585.82	6417.43	47
H25	-682.45	7818.73	6678.56	45
H30A	1815.03	10016.21	6052.44	64
H30B	174.22	10211.41	6018.98	64
H30C	1015.21	9151.72	5861.47	64
H23A	-2274.83	1395.61	8066.27	70
H23B	-1110.59	2290.05	8193.74	70
H23C	-867.39	666.02	8148.94	70

13. References

[1] A. Lepronier, T. Achard, L. Giordano, A. Tenaglia, G. Buono and H. Clavier, *Adv. Synth. Catal.,* **2016**, *358*, 631–642.

[2] D. Morton, S. Leach, C. Cordier, S. Warriner, and A. Nelson, *Angew. Chem., Int. Ed.*, **2009**, *48*, 104-109.

[3] J. Meng, H. He, Q. Liu, H. Xu, H. Huang, S.-F. Ni and Z. Li, *Angew. Chem., Int. Ed.,* **2024**, *63*, e202315092.

[4] S. Bar, *Can. J. Chem.,* **2010**, *88*, 605-612.

[5] Y.-H. Wen, F. Yang, S. Li, X. Yao, J. Song, L.-Z. Gong, *J. Am. Chem. Soc.,* **2023**, *145*, 4199-4207.

[6]I. Kiyofumi, A. Narumi, N. Yuka, Y. Misato and K. Yoshinori, *Org. Lett*. **2012** *14*, 2622-2625.

[7] J. Zhang, M. Guo, Y. Chen, S. Zhang, X. Wang, and J. Chang, *Org. Lett*. **2019** *21*, 1331-1336.