Supplementary Information

A Modular Approach to Catalytic Stereoselective Synthesis of Chiral 1,2-Diols and 1,3-Diols

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Contents

1. General Information

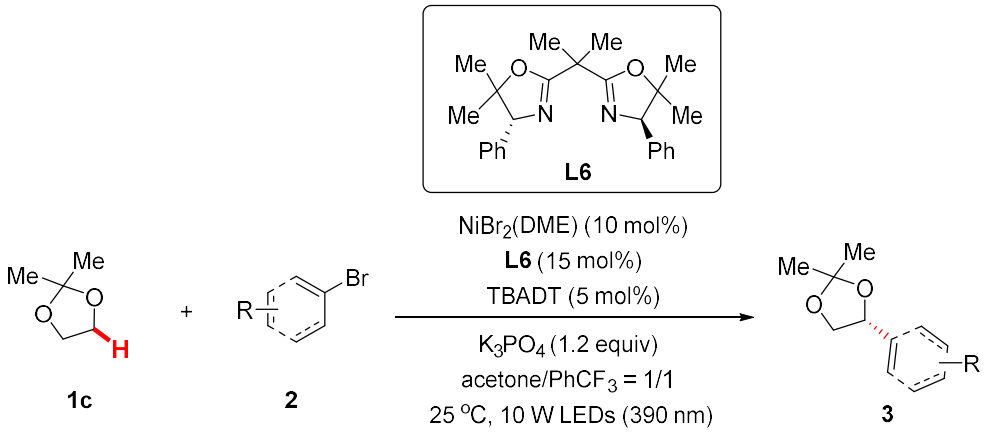
^{1}H NMR, ^{13}C NMR and ^{19}F NMR data were recorded with Bruker ADVANCE III (600 MHz) or JNM-ECZ400S/L1 (400 MHz) spectrometers. Chemical shifts are given in ppm. The spectra are calibrated to the residual ^{1}H and ^{13}C signals of the solvents. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), septet (sept), multiplet (m), and broad (b). ^{19}F NMR spectra were recorded using $CFCl_3$ as internal standard. Gas chromatography were determined with a SHIMADZU Nexis GC 2030 gas chromatography instrument with a FID detector. High-resolution mass spectra (HRMS) were recorded on Thermo Fisher Orbitrap Elite mass spectrometer. The photoreaction instrument (WPTEC-1020LC) was purchased from WATTCAS, China.

Unless otherwise stated, starting materials were purchased from commercial suppliers (Stream, Leyan.com, Energy Chemical and so on). All reactions dealing with air- or moisture-sensitive compounds were performed in the argon-filled glove box or by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere. Solvents were purchased in HPLC quality, degassed by purging thoroughly with argon and dried over activated molecular sieves of appropriate size. More sensitive compounds were stored in a desiccator or in a glove-box if required. Reactions were monitored by thin layer chromatography (TLC) using glass 0.25 mm silica gel plates. Compounds were visualized by UV-light at 254 nm and by dipping the plates in an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (200-400 mesh).

Supplementary Figure 1. The photoreaction instrument: WATTCAS_WP-TEC-1020LC

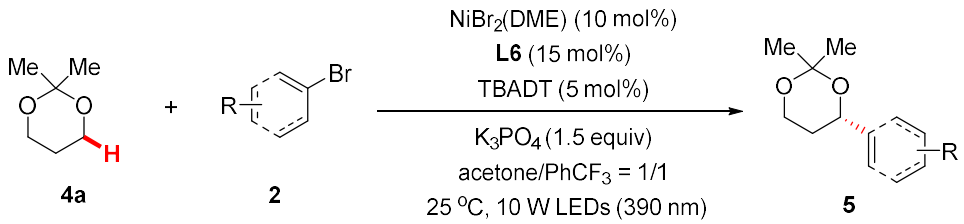
2. General Procedures

2.1 General procedure for the synthesis of 1-aryl-1,2-diols



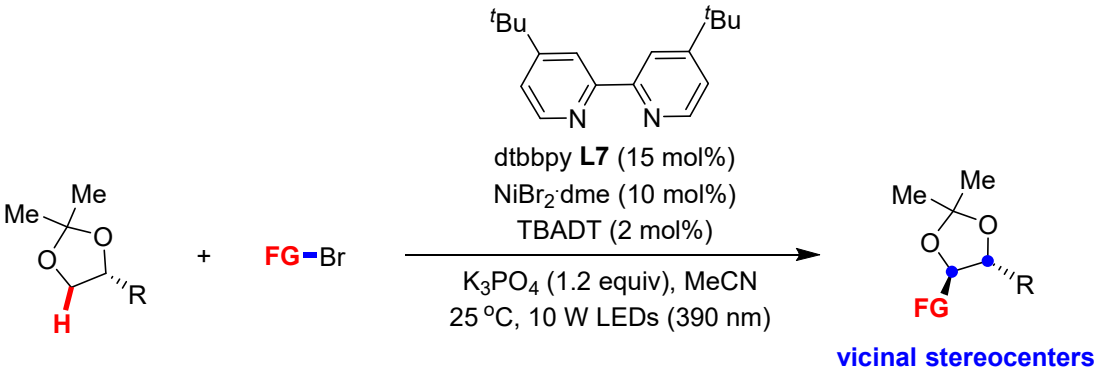
An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with $NiBr_2$(dme) (6.1 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%) and anhydrous acetone (0.5 mL). This reaction mixture was stirred at room temperature for 1 hour in an argon-filled glovebox. TBADT (33.5 mg, 0.02 mmol, 5 mol%), aryl or alkenyl bromide **2** (0.2 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane **1c** (102.1 mg, 1.0 mmol, 5 equiv), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv) and $PhCF_3$ (0.5 mL) was then added. The reaction mixture was stirred and irradiated with a 10 W 390 nm LED lamp at 25 ℃ for 60 hours. The resulting mixture was removed from light, diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. The combined solvent was then evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with hexane/EA (20/1~1/1) to afford the corresponding products **3**.

2.2 General procedure for the synthesis of 1-aryl-1,3-diols



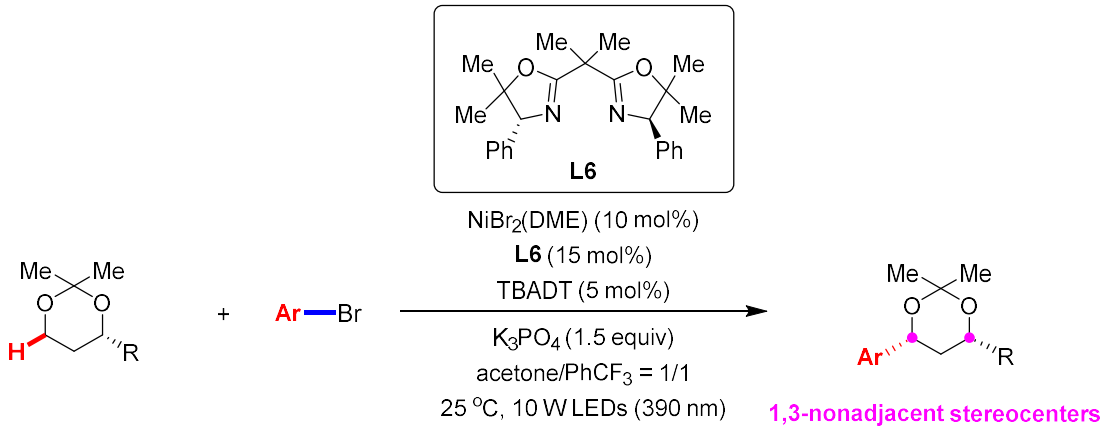
An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with $NiBr_2$(dme) (6.1 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%) and anhydrous acetone (0.5 mL). This reaction mixture was stirred at room temperature for 1 hour in an argon-filled glovebox. TBADT (33.5 mg, 0.02 mmol, 5 mol%), aryl or alkenyl bromide **2** (0.2 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxane **4a** (232.0 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) was then added. The reaction mixture was stirred and irradiated with a 10 W 390 nm LED lamp at 25 ℃ for 60 hours. The resulting mixture was removed from light, diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. The combined solvent was then evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with hexane/EA (20/1~1/1) to afford the corresponding products **5**.

2.3 General procedure for the synthesis of 1,2-syn-diols bearing vicinal stereocenters



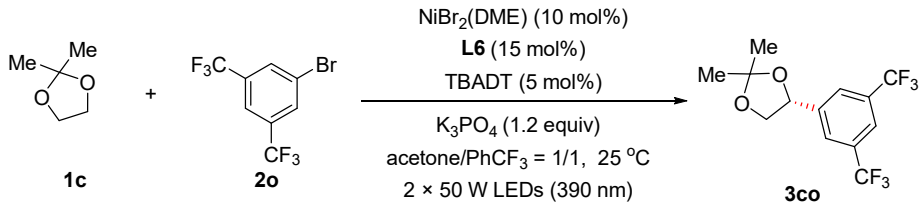
An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with $NiBr_2$(dme) (6.2 mg, 0.02 mmol, 10 mol%), dtbbpy (8.1 mg, 0.03 mmol, 15 mol%), TBADT (13.4 mg, 0.004 mmol, 2 mol%), electrophilic reagent (aryl bromide, alkenyl bromide, *gem*-difluoroalkene, or alkynyl bromide) (0.2 mmol, 1 equiv), acetonide-protected 1,2-diol (1.0 mmol, 5 equiv), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv) and anhydrous MeCN (2 mL). The reaction mixture was stirred and irradiated with a 10 W 390 nm LED lamp at 25 ℃ for 60 hours. The resulting mixture was removed from light, diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. The combined solvent was then evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with hexane/EA (20/1~1/1) to afford the corresponding products.

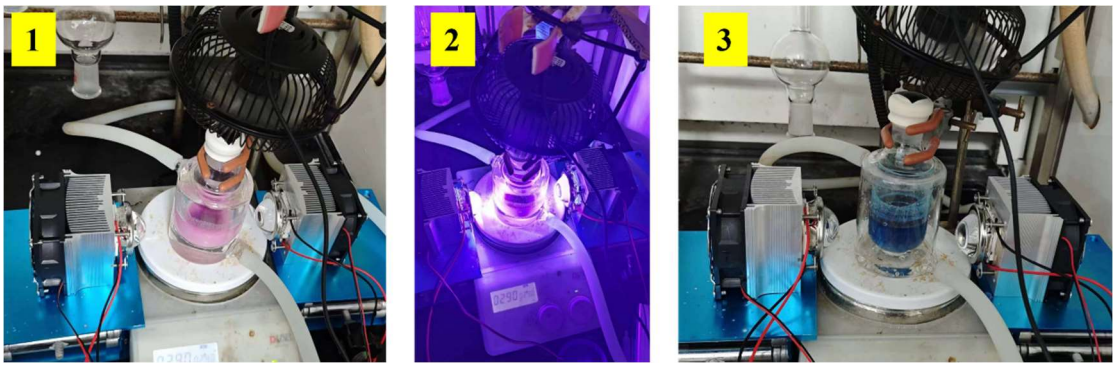
2.4 General procedure for the synthesis of 1,3-*syn*-diols bearing 1,3-nonadjacent stereocenters



An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with $NiBr_2$(dme) (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), TBADT (33.5 mg, 0.02 mmol, 5 mol%), aryl bromides (0.2 mmol, 1 equiv), acetonide-protected 1,3-diol (0.6 mmol, 3 equiv), K_3PO_4 (42.4 mg, 0.2 mmol, 1.0 equiv) and anhydrous MeCN (1 mL) and anhydrous acetone (1 mL). The reaction mixture was stirred and irradiated with a 10 W 390 nm LED lamp at 25 ℃ for 60 hours. The resulting mixture was removed from light, diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. The combined solvent was then evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with hexane/EA (20/1~1/1) to afford the corresponding products.

2.5 General procedure for the gram-scale batch synthesis of product 3co.

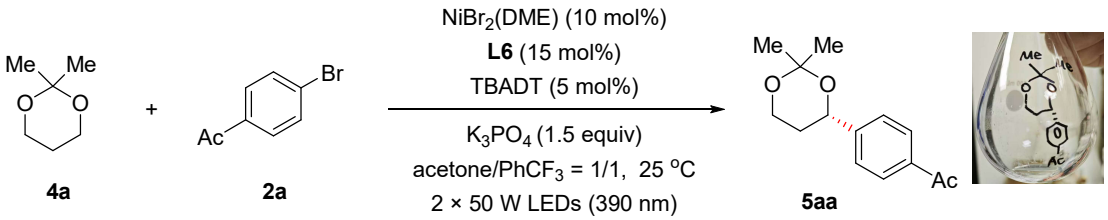




Supplementary Figure 2. Reaction process diagram

An oven-dried 100-mL vial equipped with a PTFE-coated stir bar was charged with $NiBr_2$(dme) (184.8 mg, 0.6 mmol, 10 mol%), **L6** (350.1 mg, 0.9 mmol, 15 mol%) and anhydrous acetone (15 mL). This reaction mixture was stirred at room temperature for 1 hour in an argon-filled glovebox. TBADT (777.6 mg, 0.3 mmol, 5 mol%), 1-bromo-3,5-bis(trifluoromethyl)benzene **2o** (1.75 g, 6.0 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane **1c** (3.06 g, 30.0 mmol, 5 equiv), K_3PO_4 (1.52 g, 7.2 mmol, 1.2 equiv) and $PhCF_3$ (15 mL) was then added. The reaction mixture was stirred and irradiated with a 2×50 W 390 nm LED lamp at 25 ℃. The resulting mixture was removed from light, diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. The combined solvent was then evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with hexane/EA (100/1~50/1) to afford the corresponding products **3co** (1.18 g, 63% yield, 90% ee).

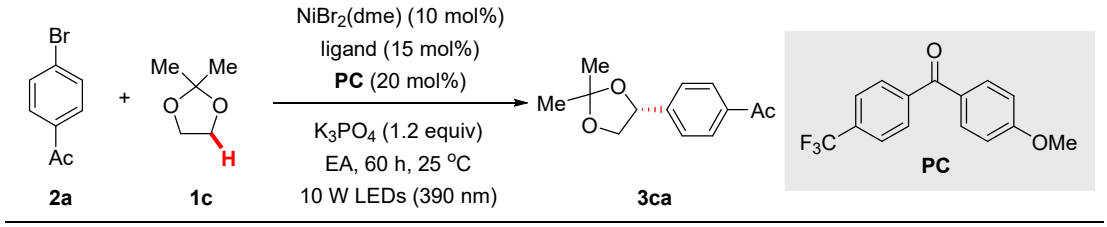
2.6 General procedure for the gram-scale batch synthesis of product 5aa

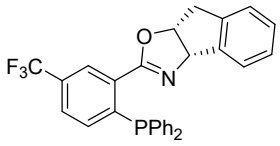


An oven-dried 100-mL vial equipped with a PTFE-coated stir bar was charged with $NiBr_2$(dme) (307.9 mg, 1.0 mmol, 10 mol%), **L6** (583.5 mg, 1.5 mmol, 15 mol%) and anhydrous acetone (25 mL). This reaction mixture was stirred at room temperature for 1 hour in an argon-filled glovebox. TBADT (1.29 g, 0.5 mmol, 5 mol%), 1-(4-bromophenyl)ethan-1-one **2a** (1.98 g, 10.0 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxane **4a** (5.81 g, 50.0 mmol, 5 equiv), K_3PO_4 (3.18 g, 15.0 mmol, 1.5 equiv) and $PhCF_3$ (25 mL) was then added. The reaction mixture was stirred and irradiated with a 2×50 W 390 nm LED lamp at 25 ℃. The resulting mixture was removed from light, diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. The combined solvent was then evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with hexane/EA (20/1~3/1) to afford the corresponding products **5aa** (1.49 g, 64% yield, 91% ee).

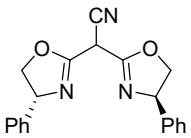
3. Optimization of Reaction Conditions

Table S1: Screening of chiral ligands

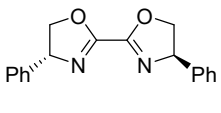




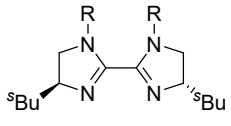
L1
45% yield, -60% ee



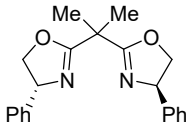
L2
24% yield, 45% ee



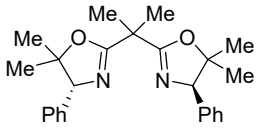
L3
10% yield, 36% ee



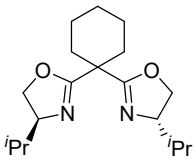
L4, R = 4-^{t}Bu-C$_6$H$_4$
42% yield, -30% ee



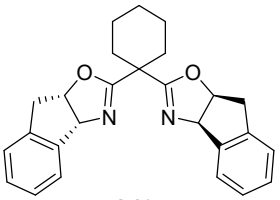
L5
11% yield, 35% ee



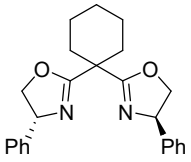
L6
43% yield, 80% ee



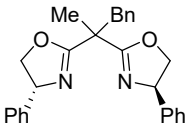
L9
23% yield, -43% ee



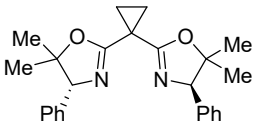
L10
17% yield, 57% ee



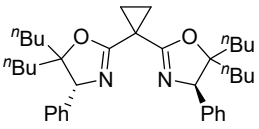
L11
10% yield, 57% ee



L12
18% yield, 58% ee



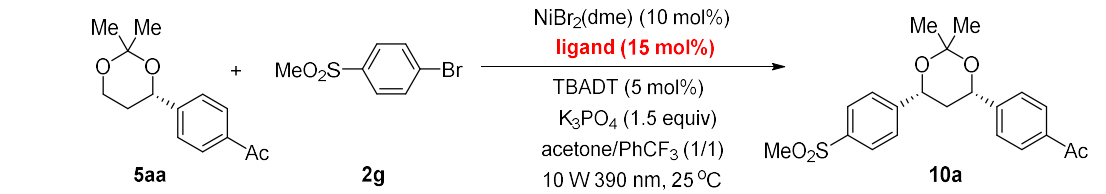
L13
80% yield, 65% ee

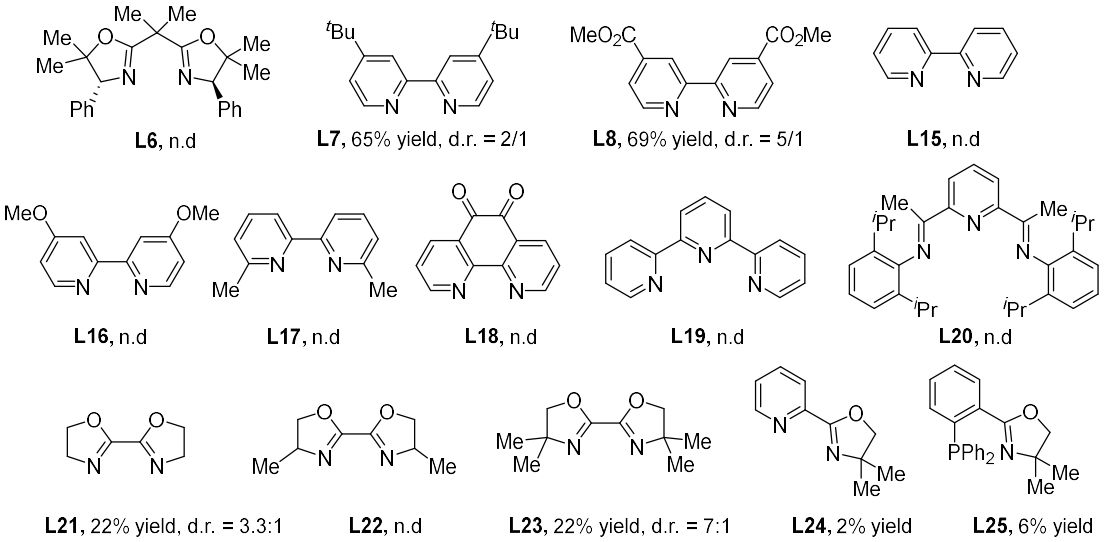


L14
25% yield, 80% ee

Reaction conditions: **2a** (0.20 mmol, 1 equiv), **1c** (1.0 mmol, 5 equiv), $NiBr_2$(dme) (10 mol%), ligand (15 mol%), **PC** (20 mol%), K_3PO_4 (1.2 equiv) in EA (1 mL) at 25 ℃ under irradiation of LEDs (10 W, 390 nm) for 60 h.

Table S2: Optimization of reaction conditions for the diastereoselective C(sp^3)-H arylation for the synthesis of 1,3-diaryl-1,3-*syn*-diols

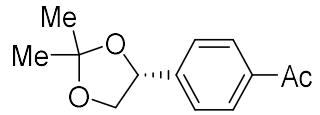




Reaction conditions: **5aa** (2 mmol, 10 equiv), **2g** (0.2 mmol, 1 equiv), $NiBr_2$(dme) (10 mol%), ligand (15 mol%), TBADT (5 mol%), K_3PO_4 (1.5 equiv) in acetone/$PhCF_3$ (0.5/0.5 mL) at 25 ℃ under irradiation of LEDs (10 W, 390 nm) for 60 h.

4. Characterization data of products

(*R*)-1-(4-(2,2-dimethyl-1,3-dioxolan-4-yl)phenyl)ethan-1-one (3ca)



Chemical Formula: $C_{13}H_{16}O_3$
Exact Mass: 220.1099

3ca was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 1-(4-bromophenyl)ethan-1-one (40.0 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 10/1) to obtain **3ca** as colorless oil (34.8 mg, 71% yield, 90% ee). R_f = 0.4 (PE/EA = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 – 7.89 (m, 2H), 7.63 – 7.36 (m, 2H), 5.14 (t, *J* = 7.1 Hz, 1H), 4.35 (dd, *J* = 8.2, 6.4 Hz, 1H), 3.69 (t, *J* = 8.0 Hz, 1H), 2.60 (s, 3H), 1.56 (s, 3H), 1.50 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.7, 144.8, 136.8, 128.6, 126.2, 110.2, 77.4, 71.4, 26.6, 26.5, 25.9;

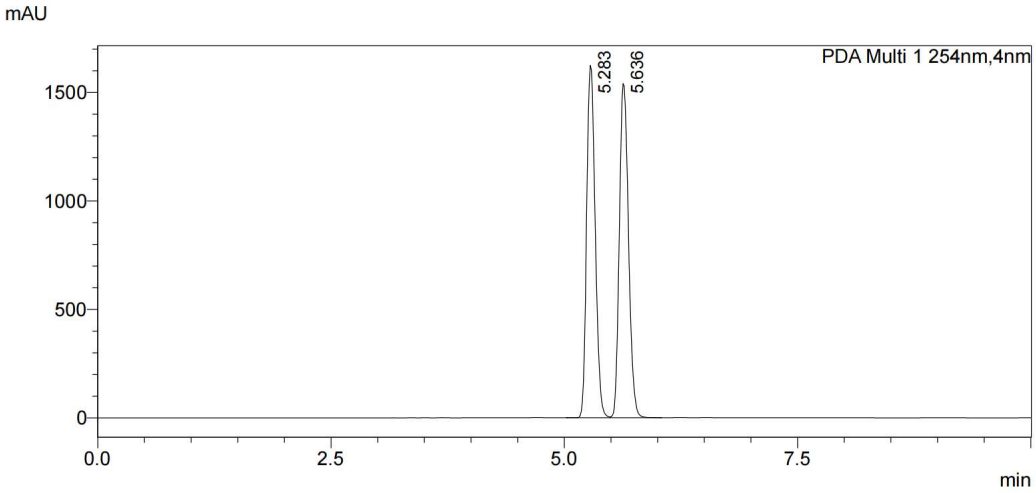
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 80/20 as eluent, 224 nm, 1 mL/min. tR = 5.5 min (major), 5.2 min (minor).

HRMS: (APCI) calcd for $C_{13}H_{17}O_3^+$[M+H]$^+$ 221.1172; found 221.1168.

Optical Rotation: $[\alpha]_D^{21}$ -77.0 (c 0.2, ^{i}PrOH) for 90% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



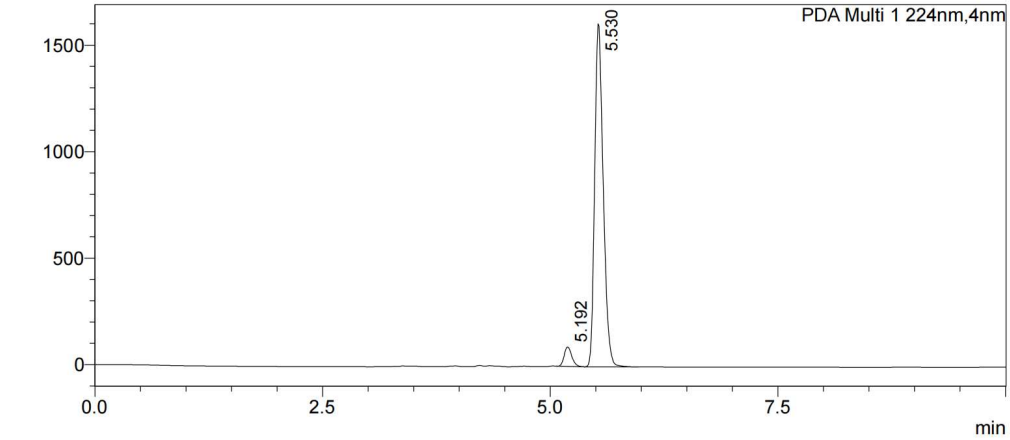
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.283	10347060	1623451	0.000		M	
2	5.636	10516954	1539909	0.000		V M	
Total		20864014	3163360				

Supplementary Figure 3. HPLC spectrum of racemic-**3ca**

<Chromatogram>



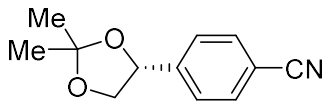
<Peak Table>

PDA Ch1 224nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.192	531445	91556	4.817		M	
2	5.530	10502285	1609999	95.183		M	
Total		11033730	1701555				

Supplementary Figure 4. HPLC spectrum of (*R*)-**3ca**

(*R*)-4-(2,2-dimethyl-1,3-dioxolan-4-yl)benzonitrile (3cb)



Chemical Formula: $C_{12}H_{13}NO_2$
Exact Mass: 203.0946

3cb was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 4-bromobenzonitrile (36.4 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 10/1) to obtain **3cb** as colorless oil (25.2 mg, 62% yield, 93% ee). R_f = 0.5 (PE/EA = 10/1).

The NMR data matched those reported in the literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 2H), 7.51 – 7.43 (m, 2H), 5.11 (t, *J* = 7.0 Hz, 1H), 4.35 (dd, *J* = 8.3, 6.4 Hz, 1H), 3.66 (t, *J* = 7.9 Hz, 1H), 1.54 (s, 3H), 1.48 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 132.5, 126.8, 118.8, 111.9, 110.5, 71.4, 26.5, 25.8;

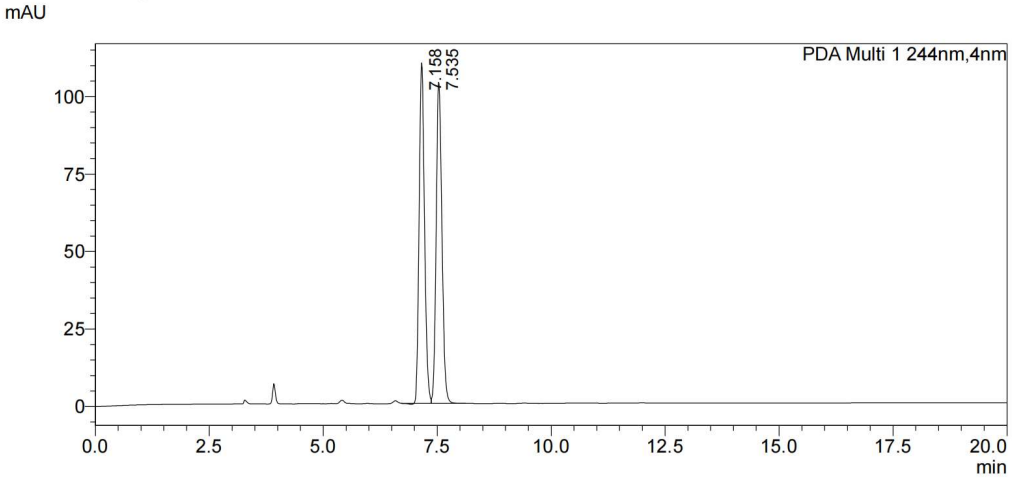
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 95/5 as eluent, 204 nm, 1 mL/min. tR = 7.5 min (major), 7.1 min (minor).

HRMS: (APCI) calcd for $C_{12}H_{14}NO_2^+$[M+H]$^+$ 204.1019; found 204.1014.

Optical Rotation: $[\alpha]_D^{21}$ -69.6 (c 0.1, ^{i}PrOH) for 93% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



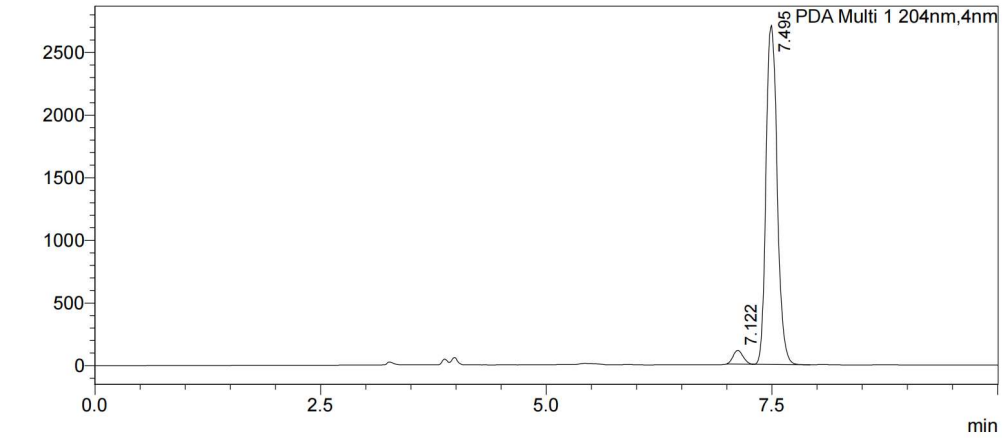
<Peak Table>

PDA Ch1 244nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.158	903717	109829	0.000		M	
2	7.535	912413	103609	0.000		V M	
Total		1816130	213438				

Supplementary Figure 5. HPLC spectrum of racemic-**3cb**

<Chromatogram>



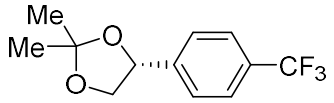
<Peak Table>

PDA Ch1 204nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.122	842626	109790	0.000		M	
2	7.495	23266140	2707824	0.000		M	
Total		24108767	2817614				

Supplementary Figure 6. HPLC spectrum of (*R*)-**3cb**

(*R*)-2,2-dimethyl-4-(4-(trifluoromethyl)phenyl)-1,3-dioxolane (3cc)



Chemical Formula: $C_{12}H_{13}F_3O_2$
Exact Mass: 246.0868

3cc was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 1-bromo-4-(trifluoromethyl)benzene (45.0 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 50/1) to obtain **3cb** as colorless oil (29.5 mg, 60% yield, 90% ee). R_f = 0.5 (PE/EA = 50/1). The NMR data matched those reported in the literature.[2]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 5.13 (t, *J* = 7.0 Hz, 1H), 4.36 (dd, *J* = 8.3, 6.3 Hz, 1H), 3.69 (t, *J* = 8.0 Hz, 1H), 1.56 (s, 3H), 1.50 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.5, 130.2 (q, *J* = 32.5 Hz), 126.3, 125.5 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.0 Hz), 110.2, 77.2, 71.5, 26.5, 25.8;

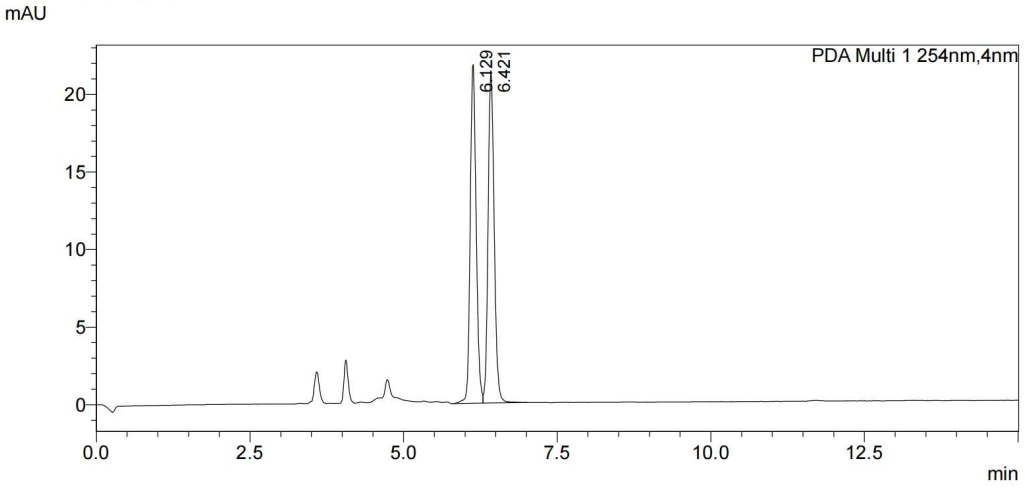
^{19}F NMR (565 MHz, $CDCl_3$) δ -62.55.

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 97/3 as eluent, 254 nm, 1 mL/min. tR = 6.4 min (major), 6.1 min (minor).

Optical Rotation: $[\alpha]_D^{22}$ -13.8 (c 0.2, ^{i}PrOH) for 90% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



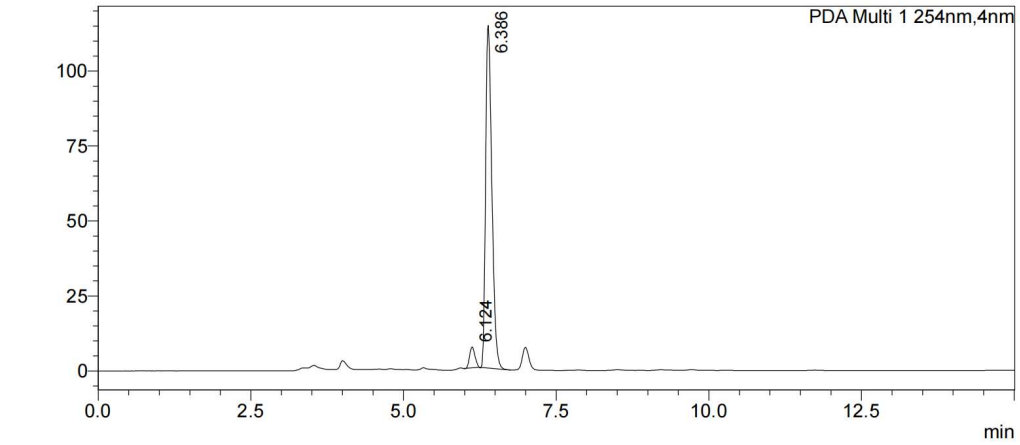
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.129	148004	21832	50.063		M	
2	6.421	147629	21404	49.937		V M	
Total		295633	43236				

Supplementary Figure 7. HPLC spectrum of racemic-**3cc**

<Chromatogram>



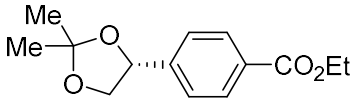
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.124	42694	6987	4.986		M	
2	6.386	813608	114233	95.014		M	
Total		856302	121220				

Supplementary Figure 8. HPLC spectrum of (*R*)-**3cc**

ethyl (*R*)-4-(2,2-dimethyl-1,3-dioxolan-4-yl)benzoate (3cd)



Chemical Formula: $C_{14}H_{18}O_4$
Exact Mass: 250.1205

3cd was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), ethyl 4-bromobenzoate (45.8 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 20/1) to obtain **3cd** as colorless oil (33.1 mg, 66% yield, 91% ee). R_f = 0.5 (PE/EA = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 2H), 7.45 – 7.41 (m, 2H), 5.13 (dd, *J* = 7.8, 6.3 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.39 – 4.32 (m, 1H), 3.69 (t, *J* = 8.0 Hz, 1H), 1.56 (s, 3H), 1.50 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.4, 144.4, 129.8, 125.9, 110.1, 77.4, 71.5, 61.0, 26.5, 25.9, 14.3;

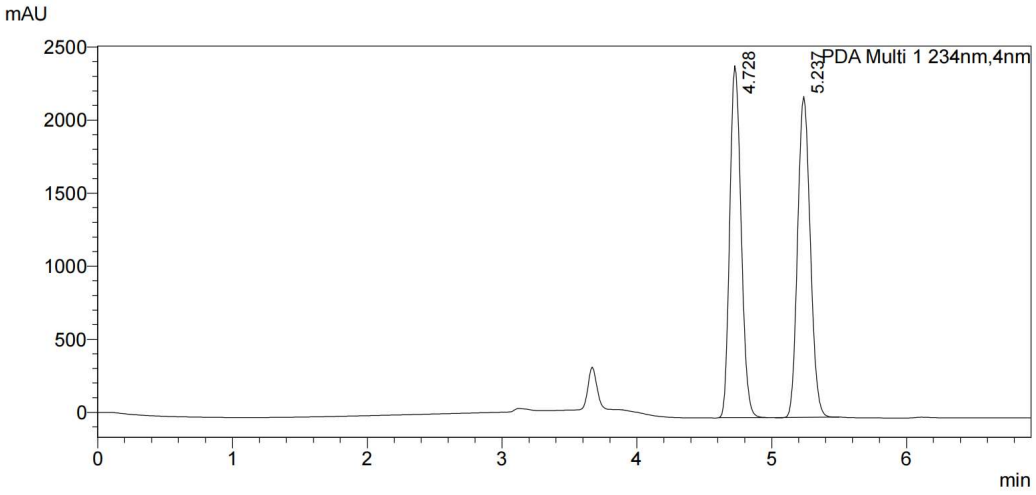
HRMS: (APCI) calcd for $C_{14}H_{19}O_4^+$[M+H]$^+$ 251.1278; found 251.1284.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 85/15 as eluent, 218 nm, 1 mL/min. tR = 5.2 min (major), 4.7 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -85.3 (c 0.2, ^{i}PrOH) for 91% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



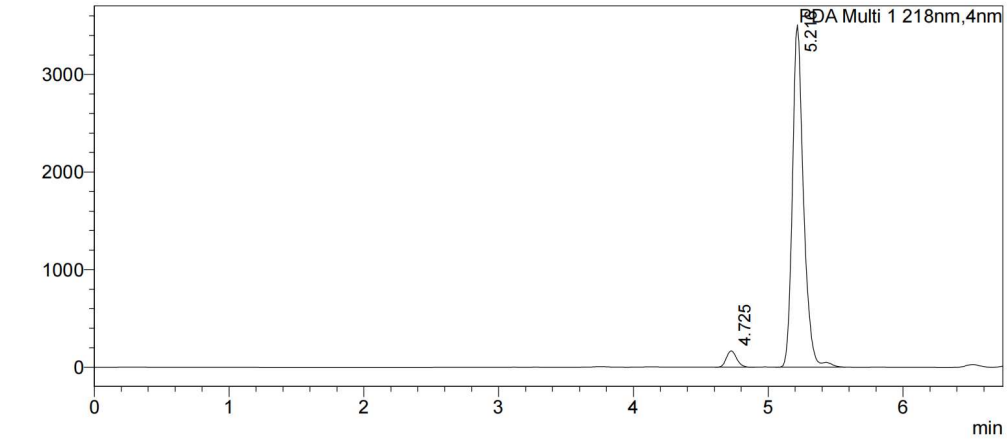
<Peak Table>

PDA Ch1 234nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.728	14113093	2408052	0.000		M	
2	5.237	14315249	2196427	0.000		M	
Total		28428342	4604479				

Supplementary Figure 9. HPLC spectrum of racemic-**3cd**

<Chromatogram>



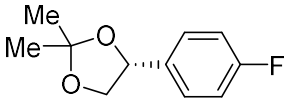
<Peak Table>

PDA Ch1 218nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.725	890254	168493	4.236		M	
2	5.216	20126213	3506257	95.764		M	
Total		21016467	3674750				

Supplementary Figure 10. HPLC spectrum of (*R*)-**3cd**

(*R*)-4-(4-fluorophenyl)-2,2-dimethyl-1,3-dioxolane (3ce)



Chemical Formula: $C_{11}H_{13}FO_2$
Exact Mass: 196.0900

3ce was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 1-bromo-4-fluorobenzene (35.0 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 50/1) to obtain **3ce** as colorless oil (17.9 mg, 47% yield, 84% ee). R_f = 0.6 (PE/EA = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.08 – 6.99 (m, 2H), 5.05 (dd, *J* = 8.0, 6.2 Hz, 1H), 4.29 (dd, *J* = 8.2, 6.2 Hz, 1H), 3.67 (t, *J* = 8.1 Hz, 1H), 1.55 (s, 3H), 1.48 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.6 (d, *J* = 246.2 Hz), 134.8 (d, *J* = 3.2 Hz), 128.0 (d, *J* = 8.2 Hz), 115.5 (d, *J* = 21.5 Hz), 109.8, 77.4, 71.7, 26.6, 25.9;

^{19}F NMR (565 MHz, $CDCl_3$) δ -114.3.

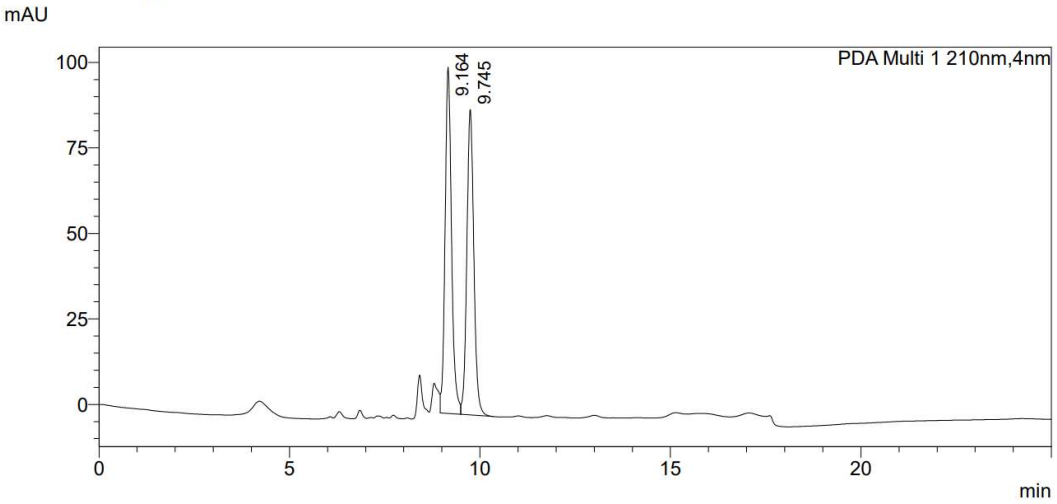
HRMS: (ESI) calcd for $C_{11}H_{13}FO_2Na^+$[M+Na]$^+$ 219.0792; found 219.0790.

The enantiomeric purity was established by HPLC analysis using a chiral column: IA-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 99/1 as eluent, 264 nm, 0.5 mL/min. tR = 9.6 min (major), 9.1 min (minor).

Optical Rotation: $[\alpha]_D^{26}$ 3.1 (c 0.1, ^{i}PrOH) for 84% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



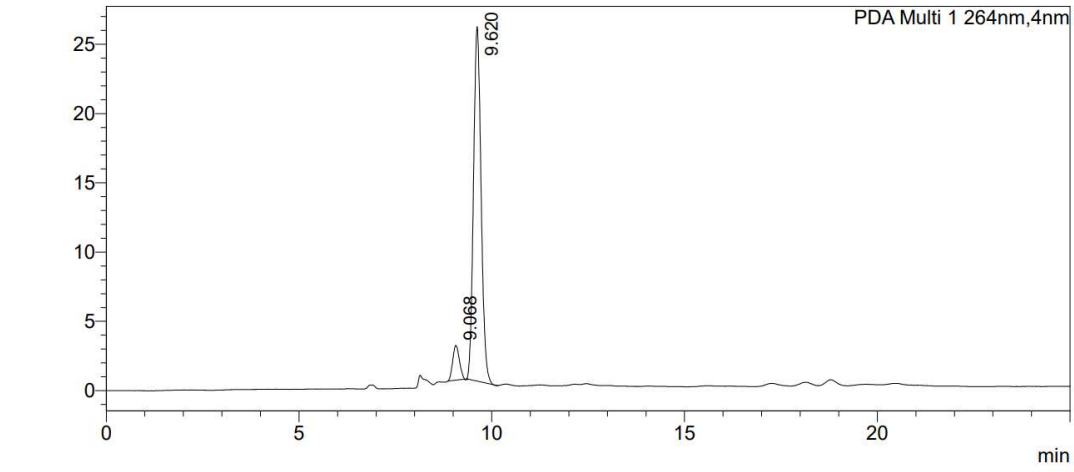
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.164	1186724	101221	0.000		M	
2	9.745	1138413	89266	0.000		V M	
Total		2325137	190486				

Supplementary Figure 11. HPLC spectrum of racemic-**3ce**

<Chromatogram>



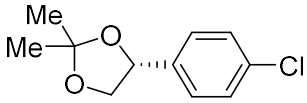
<Peak Table>

PDA Ch1 264nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.068	30009	2512	7.891		M	
2	9.620	350268	25584	92.109		M	
Total		380277	28096				

Supplementary Figure 12. HPLC spectrum of (*R*)-**3ce**

(*R*)-4-(4-chlorophenyl)-2,2-dimethyl-1,3-dioxolane (**3cf**)



Chemical Formula: $C_{11}H_{13}ClO_2$
Exact Mass: 212.0604

3cf was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 1-bromo-4-chlorobenzene (38.2 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 50/1) to obtain **3cf** as colorless oil (27.5 mg, 65% yield, 91% ee). R_f = 0.6 (PE/EA = 50/1).

The NMR data matched those reported in the literature.[3]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 4H), 5.05 (dd, *J* = 7.9, 6.2 Hz, 1H), 4.30 (dd, *J* = 8.2, 6.2 Hz, 1H), 3.66 (t, *J* = 8.1 Hz, 1H), 1.56 (s, 3H), 1.48 (s, 3H);

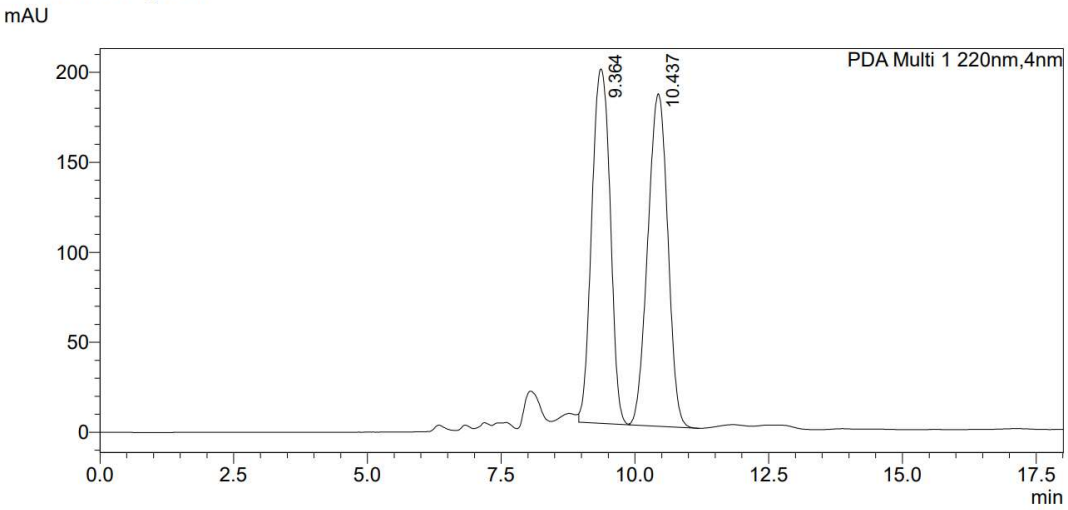
^{13}C NMR (151 MHz, $CDCl_3$) δ 137.8, 133.8, 128.7, 127.5, 109.9, 77.3, 71.6, 26.6, 25.9;

The enantiomeric purity was established by HPLC analysis using a chiral column: IA-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 99/1 as eluent, 202 nm, 0.5 mL/min. tR = 10.9 min (major), 9.8 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -42.6 (c 0.2, ^{i}PrOH) for 91% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



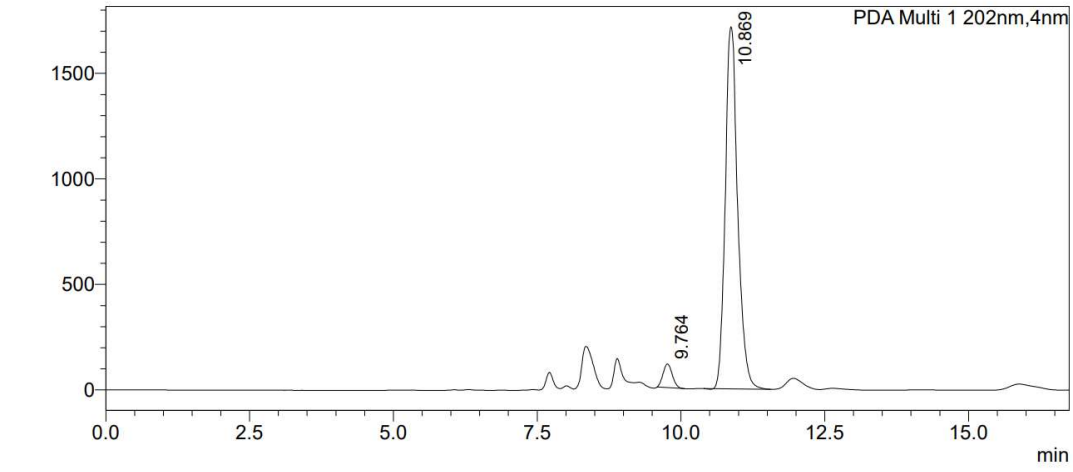
<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.364	4720241	196939	0.000		M	
2	10.437	4807814	184770	0.000		V M	
Total		9528054	381710				

Supplementary Figure 13. HPLC spectrum of racemic-**3cf**

<Chromatogram>



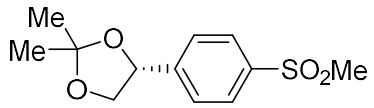
<Peak Table>

PDA Ch1 202nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.764	1246022	111660	4.613		M	
2	10.869	25764463	1715899	95.387		M	
Total		27010485	1827560				

Supplementary Figure 14. HPLC spectrum of (*R*)-**3cf**

(*R*)-2,2-dimethyl-4-(4-(methylsulfonyl)phenyl)-1,3-dioxolane (3cg)



Chemical Formula: $C_{12}H_{16}O_4S$
Exact Mass: 256.0769

3cg was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 1-bromo-4-(methylsulfonyl)benzene (47.2 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 4/1) to obtain **3cg** as white soild (35.8 mg, 70% yield, 93% ee). R_f = 0.3 (PE/EA = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 2H), 7.59 – 7.55 (m, 2H), 5.16 (t, *J* = 7.0 Hz, 1H), 4.39 (dd, *J* = 8.3, 6.4 Hz, 1H), 3.70 (t, *J* = 7.9 Hz, 1H), 3.05 (s, 3H), 1.56 (s, 3H), 1.50 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.1, 140.1, 127.7, 126.9, 110.5, 77.0, 71.4, 44.6, 26.5, 25.8;

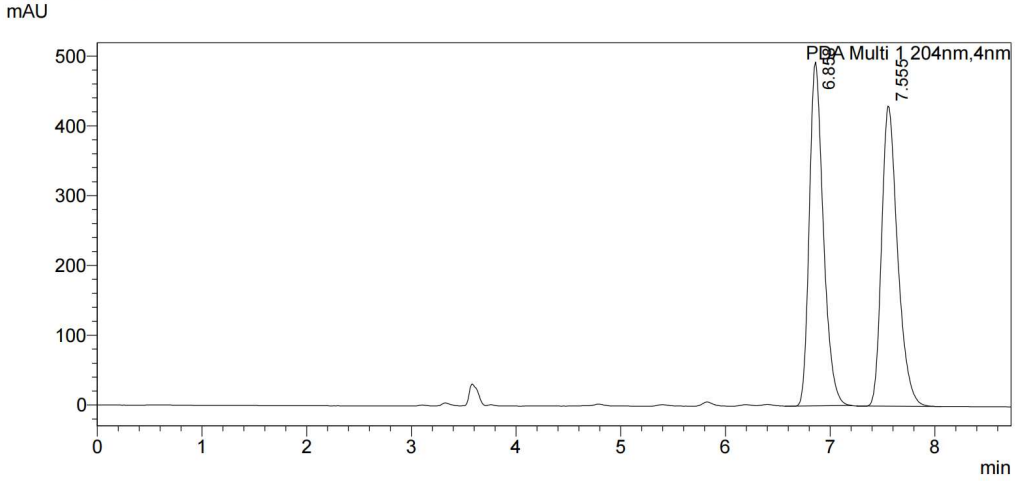
HRMS: (APCI) calcd for $C_{12}H_{17}O_4S^+$[M+H]$^+$ 257.0842; found 257.0849.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 70/30 as eluent, 204 nm, 1 mL/min. tR = 6.8 min (major), 7.5 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -23.0 (c 0.2, ^{i}PrOH) for 93% ee.

Absolute stereochemistry was determined by X-ray crystallography analysis.

<Chromatogram>



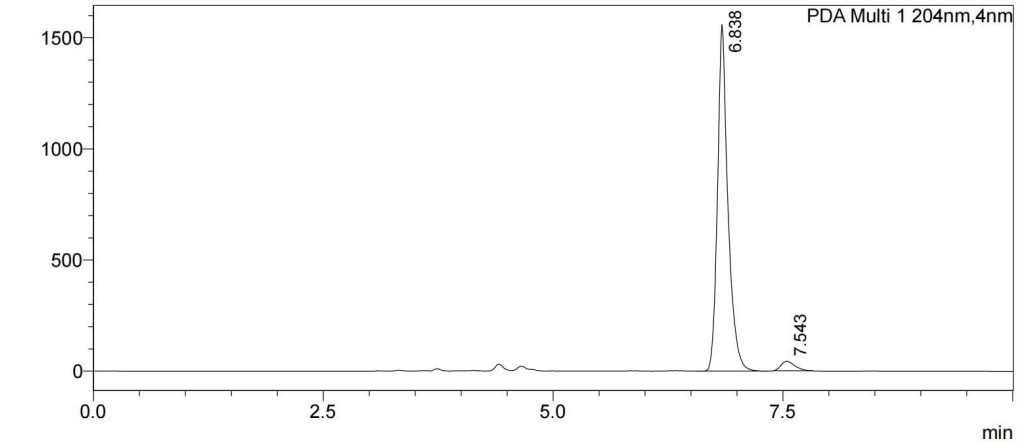
<Peak Table>

PDA Ch1 204nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.858	4581672	492564	0.000		M	
2	7.555	4579468	430296	0.000		M	
Total		9161140	922860				

Supplementary Figure 15. HPLC spectrum of racemic-**3cg**

<Chromatogram>



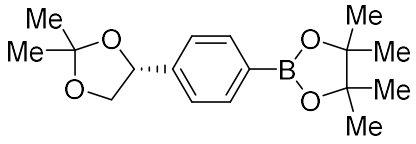
<Peak Table>

PDA Ch1 204nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.838	12316719	1558353	0.000		M	
2	7.543	442298	42609	0.000		M	
Total		12759016	1600962				

Supplementary Figure 16. HPLC spectrum of (*R*)-**3cg**

(*R*)-2-(4-(2,2-dimethyl-1,3-dioxolan-4-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ch)



Chemical Formula: $C_{17}H_{25}BO_4$
Exact Mass: 304.1846

3ch was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (56.6 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 10/1) to obtain **3ch** as colorless oil (34.0 mg, 58% yield, 88% ee). R_f = 0.6 (PE/EA = 10/1).

The NMR data matched those reported in the patent.[4]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 2H), 7.39 – 7.34 (m, 2H), 5.09 (dd, *J* = 8.0, 6.3 Hz, 1H), 4.31 (dd, *J* = 8.2, 6.3 Hz, 1H), 3.68 (t, *J* = 8.1 Hz, 1H), 1.55 (s, 3H), 1.49 (s, 3H), 1.34 (s, 12H);

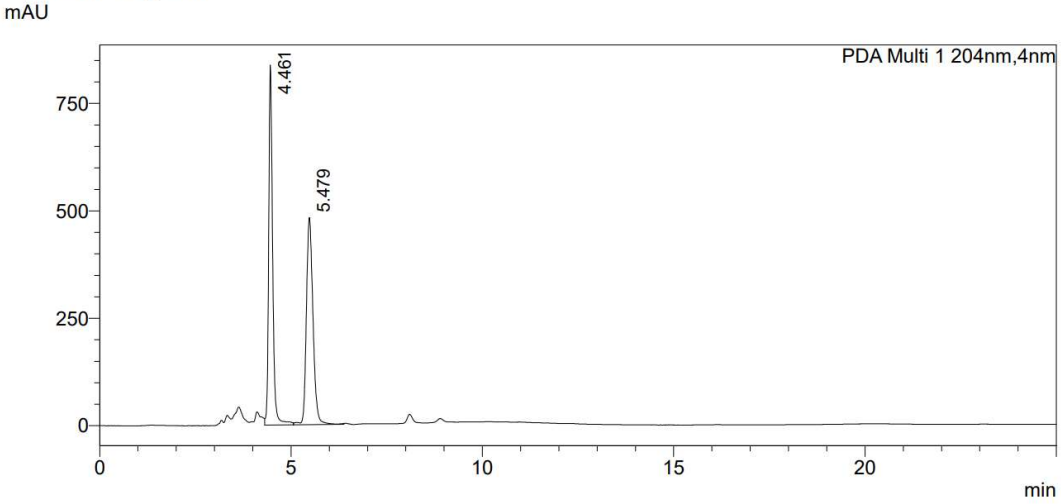
^{13}C NMR (151 MHz, $CDCl_3$) δ 142.3, 135.0, 125.4, 109.9, 83.8, 77.9, 71.6, 26.6, 26.0, 24.89, 24.87;

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 90/10 as eluent, 201 nm, 1 mL/min. tR = 5.5 min (major), tR = 4.5 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -74.6 (c 0.1, ^{i}PrOH) for 88% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



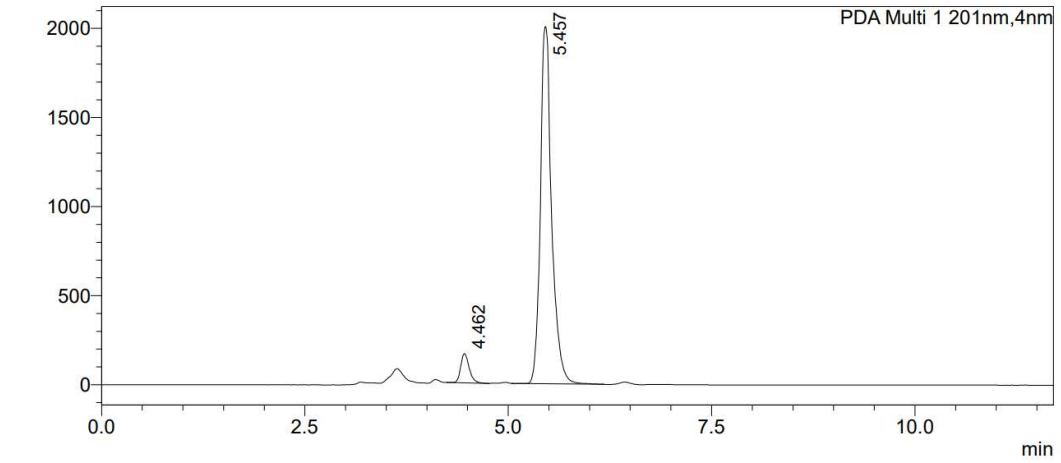
<Peak Table>

PDA Ch1 204nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.461	5992477	837671	0.000		M	
2	5.479	5768843	481910	0.000		V M	
Total		11761320	1319580				

Supplementary Figure 17. HPLC spectrum of racemic-**3ch**

<Chromatogram>



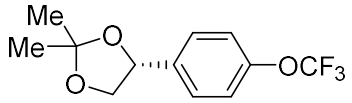
<Peak Table>

PDA Ch1 201nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.462	1186247	163986	0.000		M	
2	5.457	19348925	2005110	0.000		M	
Total		20535172	2169096				

Supplementary Figure 18. HPLC spectrum of (*R*)-**3ch**

(*R*)-2,2-dimethyl-4-(4-(trifluoromethoxy)phenyl)-1,3-dioxolane (3ci)



Chemical Formula: $C_{12}H_{13}F_3O_3$
Exact Mass: 262.0817

3ci was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 1-bromo-4-(trifluoromethoxy)benzene (48.2 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 50/1) to obtain **3ci** as colorless oil (28.8 mg, 55% yield, 88% ee). R_f = 0.6 (PE/EA = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.23 – 7.18 (m, 2H), 5.07 (dd, *J* = 7.8, 6.2 Hz, 1H), 4.31 (dd, *J* = 8.3, 6.3 Hz, 1H), 3.69 (t, *J* = 8.1 Hz, 1H), 1.55 (s, 3H), 1.48 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.9 (q, *J* = 2.1 Hz), 138.0, 127.6, 121.1, 120.5 (q, *J* = 257.1 Hz), 110.0, 77.2, 71.6, 26.6, 25.8;

^{19}F NMR (565 MHz, $CDCl_3$) δ -57.92.

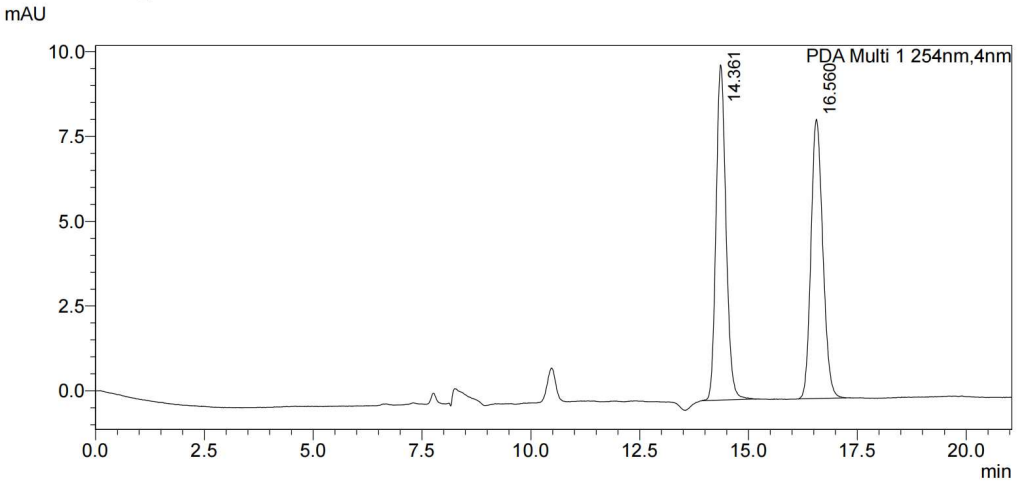
HRMS: (ESI) calcd for $C_{12}H_{13}F_3O_3Na^+$[M+Na]$^+$ 285.0709; found 285.0703.

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 99/1 as eluent, 204 nm, 0.5 mL/min. tR = 16.9 min (major), 14.4 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -66.5 (c 0.1, ^{i}PrOH) for 88% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



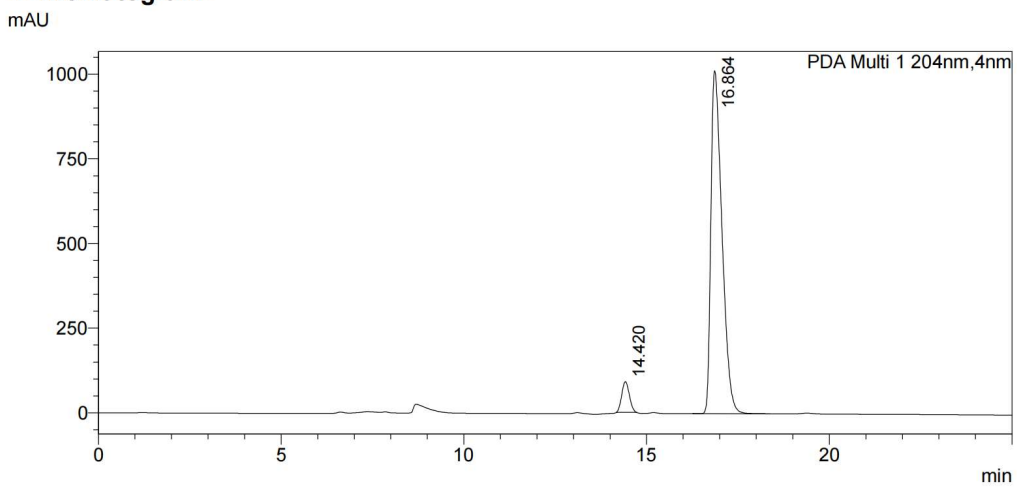
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.361	156999	9884	0.000		M	
2	16.560	155577	8229	0.000			
Total		312577	18112				

Supplementary Figure 19. HPLC spectrum of racemic-**3ci**

<Chromatogram>



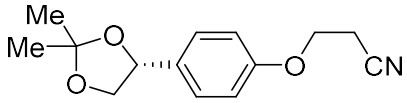
<Peak Table>

PDA Ch1 204nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.420	1310220	90681	0.000		M	
2	16.864	21358591	1013041	0.000		M	
Total		22668811	1103722				

Supplementary Figure 20. HPLC spectrum of (*R*)-**3ci**

(*R*)-3-(4-(2,2-dimethyl-1,3-dioxolan-4-yl)phenoxy)propanenitrile (3cj)



Chemical Formula: $C_{14}H_{17}NO_3$
Exact Mass: 247.1208

3cj was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 3-(4-bromophenoxy)propanenitrile (45.2 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 5/1) to obtain **3cj** as colorless oil (28.2 mg, 57% yield, 88% ee). R_f = 0.5 (PE/EA = 4/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 6.92 – 6.87 (m, 2H), 5.02 (dd, *J* = 8.1, 6.1 Hz, 1H), 4.26 (dd, *J* = 8.2, 6.1 Hz, 1H), 4.19 (t, *J* = 6.4 Hz, 2H), 3.68 (t, *J* = 8.2 Hz, 1H), 2.82 (t, *J* = 6.4 Hz, 2H), 1.54 (s, 3H), 1.47 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.6, 132.3, 127.8, 117.1, 114.8, 109.6, 77.6, 71.7, 62.7, 26.7, 26.0, 18.6;

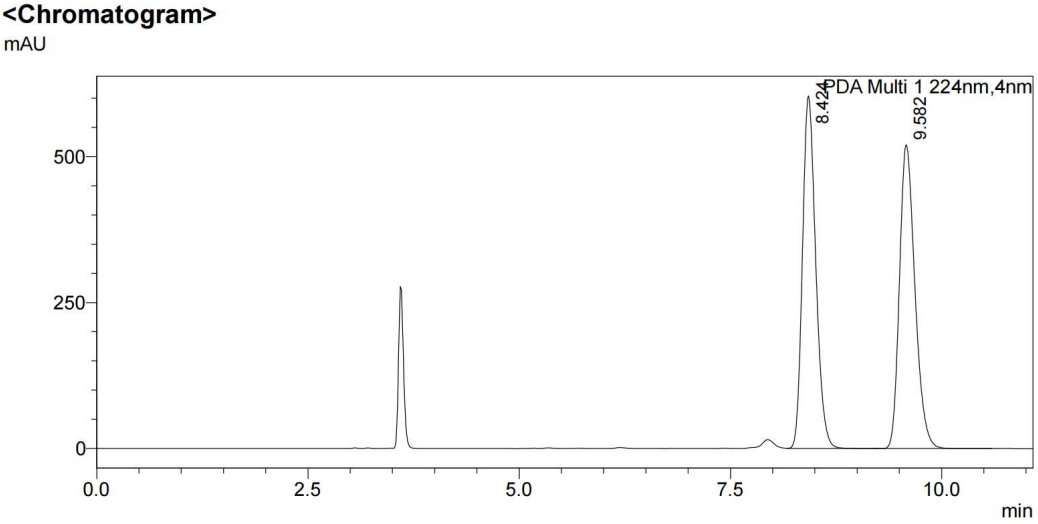
HRMS: (ESI) calcd for $C_{14}H_{17}O_3Na^+$[M+Na]$^+$ 270.1101; found 270.1102.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 85/15 as eluent, 194 nm, 1 mL/min. tR = 9.6 min (major), 8.4 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -34.2 (c 0.1, ^{i}PrOH) for 88% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



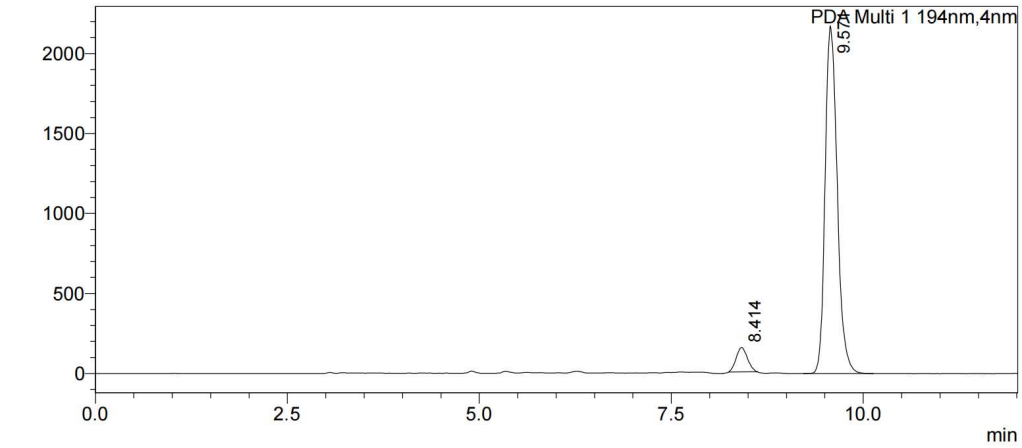
<Peak Table>

PDA Ch1 224nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.424	6632110	604114	0.000			
2	9.582	6646896	520481	0.000		V	
Total		13279007	1124595				

Supplementary Figure 21. HPLC spectrum of racemic-**3cj**

<Chromatogram>



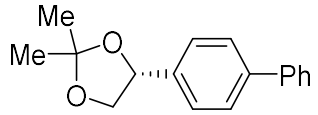
<Peak Table>

PDA Ch1 194nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.414	1556851	152582	6.133		M	
2	9.571	23829928	2173228	93.867		M	
Total		25386779	2325810				

Supplementary Figure 22. HPLC spectrum of (*R*)-**3cj**

(*R*)-4-([1,1'-biphenyl]-4-yl)-2,2-dimethyl-1,3-dioxolane (3ck)



Chemical Formula: $C_{17}H_{18}O_2$
Exact Mass: 254.1307

3ck was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 4-bromo-1,1'-biphenyl (46.6 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 50/1) to obtain **3ck** as colorless oil (25.9 mg, 51% yield, 87% ee). R_f = 0.6 (PE/EA = 50/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.54 (m, 4H), 7.44 (dd, *J* = 7.9, 5.8 Hz, 4H), 7.39 – 7.32 (m, 1H), 5.13 (dd, *J* = 8.1, 6.2 Hz, 1H), 4.34 (dd, *J* = 8.2, 6.2 Hz, 1H), 3.77 (t, *J* = 8.1 Hz, 1H), 1.58 (s, 3H), 1.51 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 140.8, 138.0, 128.8, 127.34, 127.30, 127.1, 126.7, 109.8, 77.7, 71.6, 26.6, 26.0;

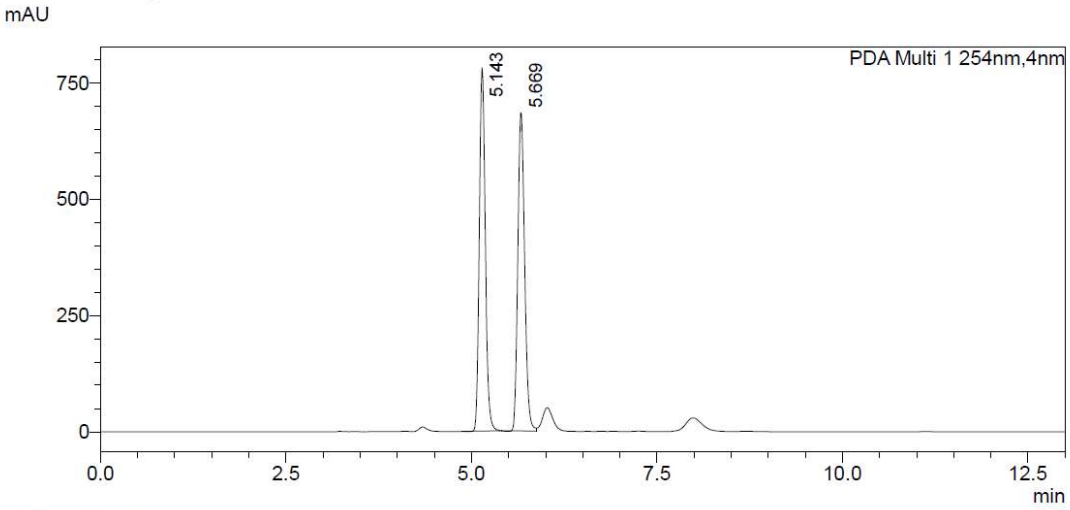
HRMS: (ESI) calcd for $C_{17}H_{18}O_2Na^+$[M+Na]$^+$ 277.1199; found 277.1201.

The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 95/5 as eluent, 224 nm, 1 mL/min. tR = 5.7 min (major), 5.1 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -9.3 (c 0.1, ^{i}PrOH) for 87% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



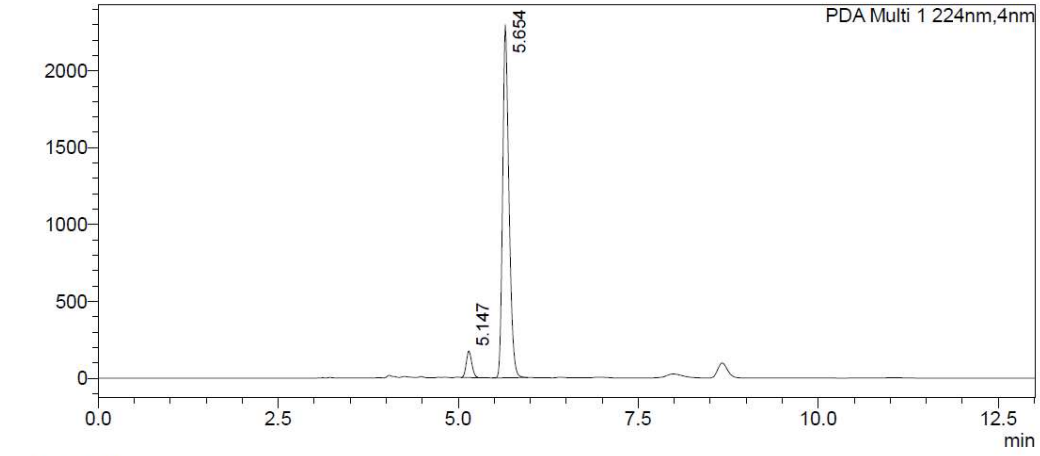
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.143	4421879	781757	0.000		M	
2	5.669	4336987	684667	0.000		M	
Total		8758866	1466423				

Supplementary Figure 23. HPLC spectrum of racemic-**3ck**

<Chromatogram>



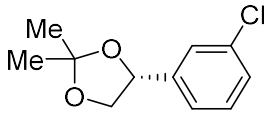
<Peak Table>

PDA Ch1 224nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.147	943643	171998	0.000		M	
2	5.654	13839170	2296924	0.000		M	
Total		14782813	2468921				

Supplementary Figure 24. HPLC spectrum of (*R*)-**3ck**

(*R*)-4-(3-chlorophenyl)-2,2-dimethyl-1,3-dioxolane (3cl)



Chemical Formula: $C_{11}H_{13}ClO_2$
Exact Mass: 212.0604

3cl was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 1-bromo-3-chlorobenzene (38.2 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 50/1) to obtain **3cl** as colorless oil (27.1 mg, 64% yield, 89% ee). R_f = 0.6 (PE/EA = 50/1).

The NMR data matched those reported in the patent.[5]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 2.1 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.25 – 7.21 (m, 1H), 5.04 (dd, *J* = 7.8, 6.3 Hz, 1H), 4.31 (dd, *J* = 8.3, 6.3 Hz, 1H), 3.68 (t, *J* = 8.0 Hz, 1H), 1.55 (s, 3H), 1.48 (s, 3H);

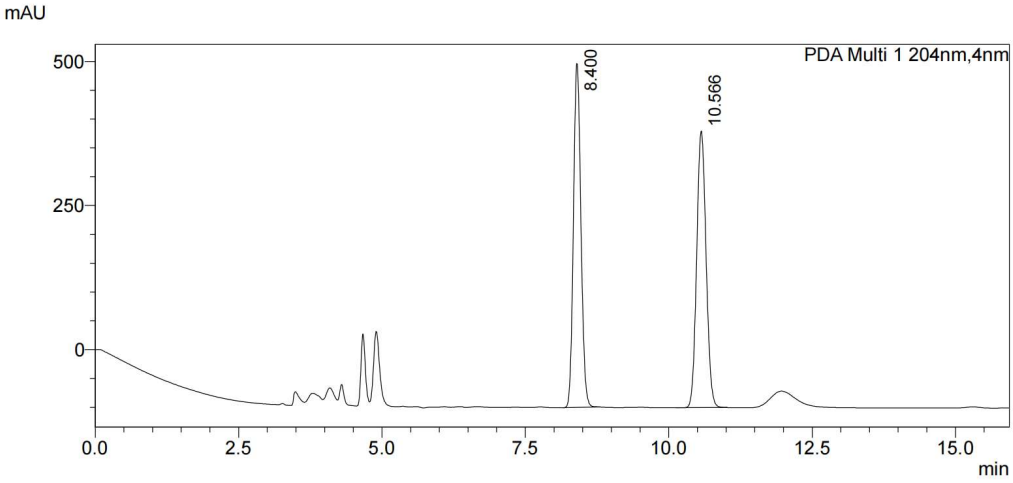
^{13}C NMR (151 MHz, $CDCl_3$) δ 141.4, 134.5, 129.8, 128.2, 126.3, 124.3, 110.1, 77.2, 71.5, 26.5, 25.9;

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 97/3 as eluent, 204 nm, 1 mL/min. tR = 8.3 min (major), 10.5 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -87.3 (c 0.1, ^{i}PrOH) for 89% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



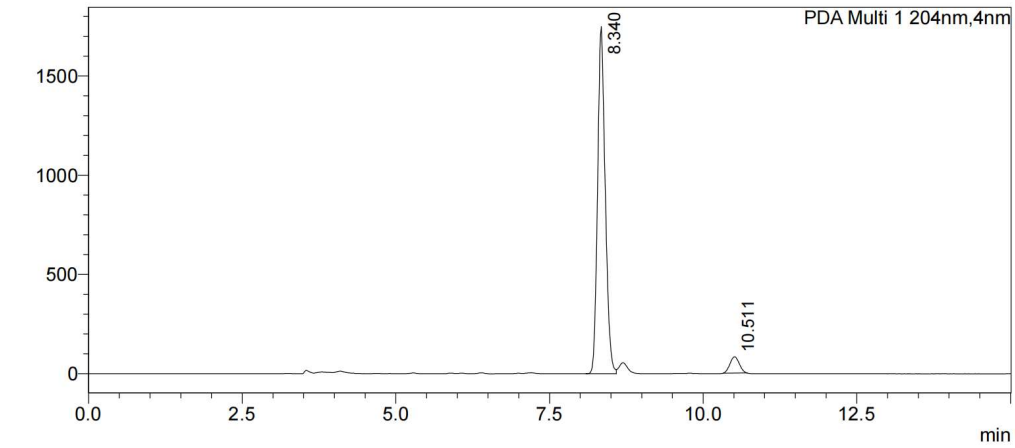
<Peak Table>

PDA Ch1 204nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.400	5411880	596292	0.000		M	
2	10.566	5464186	479835	0.000		M	
Total		10876066	1076127				

Supplementary Figure 25. HPLC spectrum of racemic-**3cl**

<Chromatogram>



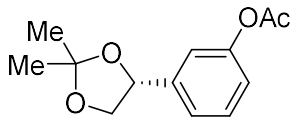
<Peak Table>

PDA Ch1 204nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.340	15108454	1747968	94.614		M	
2	10.511	860128	81625	5.386		M	
Total		15968582	1829592				

Supplementary Figure 26. HPLC spectrum of (*R*)-**3cl**

(*R*)-3-(2,2-dimethyl-1,3-dioxolan-4-yl)phenyl acetate (3cm)



Chemical Formula: $C_{13}H_{16}O_4$
Exact Mass: 236.1049

3cm was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 3-bromophenyl acetate (43.0 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 10/1) to obtain **3cm** as colorless oil (24.5 mg, 52% yield, 85% ee). R_f = 0.5 (PE/EA = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.9 Hz, 1H), 7.22 (ddt, *J* = 7.7, 1.6, 0.8 Hz, 1H), 7.11 (t, *J* = 2.0 Hz, 1H), 7.03 (ddd, *J* = 8.1, 2.4, 1.0 Hz, 1H), 5.07 (dd, *J* = 7.9, 6.2 Hz, 1H), 4.31 (dd, *J* = 8.2, 6.2 Hz, 1H), 3.71 (t, *J* = 8.1 Hz, 1H), 2.30 (s, 3H), 1.54 (s, 3H), 1.48 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 150.9, 141.1, 129.6, 123.5, 121.2, 119.3, 109.9, 77.3, 71.5, 26.5, 25.9, 21.1;

HRMS: (ESI) calcd for $C_{13}H_{17}O_4^+$[M+H]$^+$ 237.1121; found 237.1126.

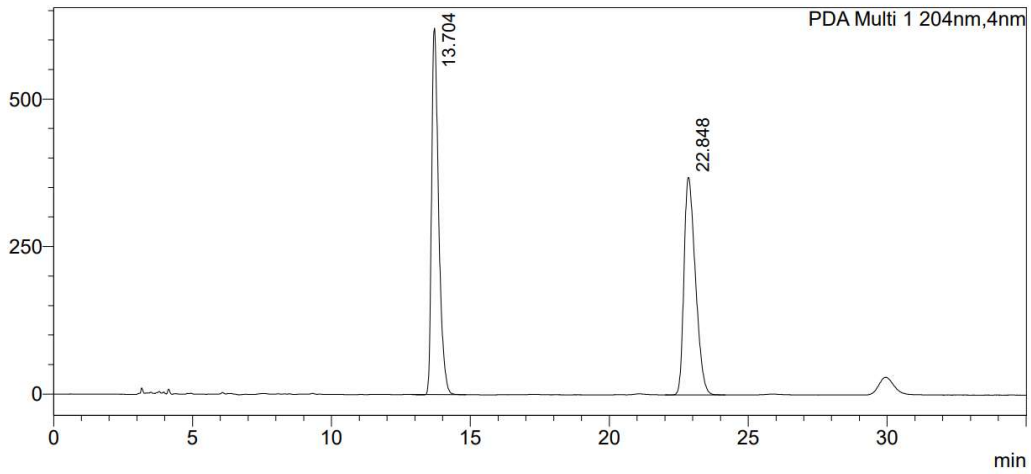
The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 90/10 as eluent, 204 nm, 1 mL/min. tR = 22.9 min (major), 13.8 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -39.1 (c 0.1, ^{i}PrOH) for 85% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>

mAU



<Peak Table>

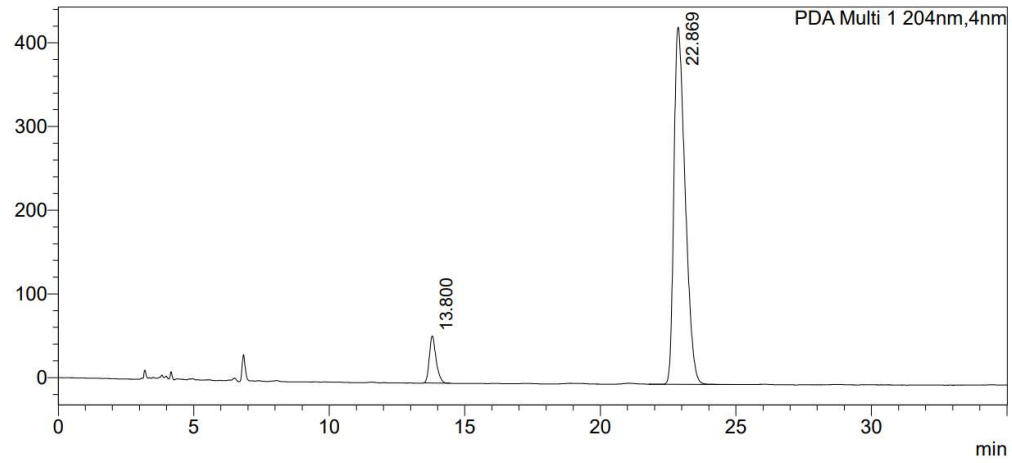
PDA Ch1 204nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.704	10944673	620832	0.000		M	
2	22.848	10555364	368577	0.000		M	
Total		21500037	989409				

Supplementary Figure 27. HPLC spectrum of racemic-**3cm**

<Chromatogram>

mAU



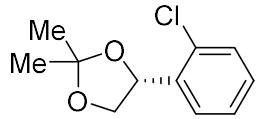
<Peak Table>

PDA Ch1 204nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.800	973178	56228	0.000		M	
2	22.869	12332642	426823	0.000		M	
Total		13305819	483051				

Supplementary Figure 28. HPLC spectrum of (*R*)-**3cm**

(*R*)-4-(2-chlorophenyl)-2,2-dimethyl-1,3-dioxolane (3cn)



Chemical Formula: $C_{11}H_{13}ClO_2$
Exact Mass: 212.0604

3cn was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 1-bromo-2-chlorobenzene (38.2 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 50/1) to obtain **3cn** as colorless oil (25.9 mg, 61% yield, 85% ee). R_f = 0.6 (PE/EA = 50/1).

The NMR data matched those reported in the patent.[6]

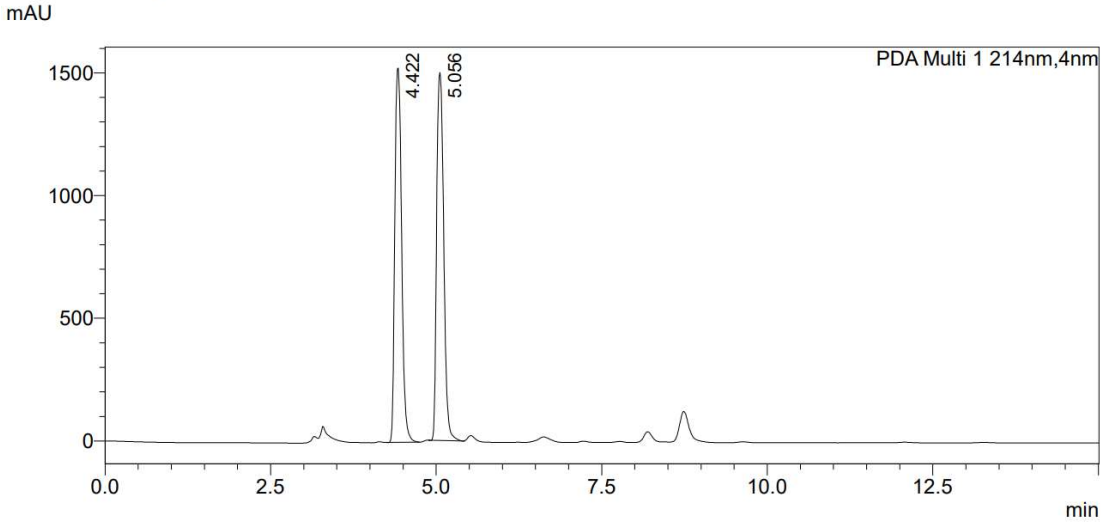
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.33 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.29 (td, *J* = 7.5, 1.3 Hz, 1H), 7.22 (td, *J* = 7.6, 1.8 Hz, 1H), 5.42 (t, *J* = 6.9 Hz, 1H), 4.54 (dd, *J* = 8.3, 6.6 Hz, 1H), 3.64 (dd, *J* = 8.3, 7.3 Hz, 1H), 1.57 (s, 3H), 1.51 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.0, 131.7, 129.2, 128.7, 127.0, 126.7, 109.7, 74.9, 70.4, 26.4, 25.7;

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 97/3 as eluent, 254 nm, 1 mL/min. tR = 4.4 min (major), 5.0 min (minor).

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



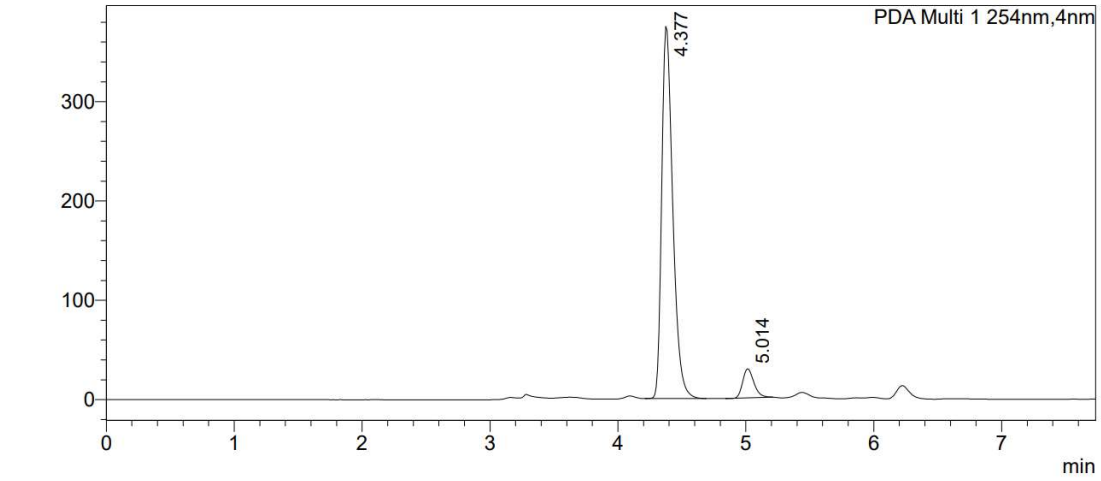
<Peak Table>

PDA Ch1 214nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.422	10913055	1525021	49.639		M	
2	5.056	11071977	1500461	50.361		M	
Total		21985033	3025483				

Supplementary Figure 29. HPLC spectrum of racemic-**3cn**

<Chromatogram>



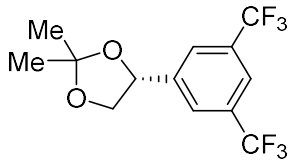
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.377	2252584	374552	92.747		M	
2	5.014	176152	29223	7.253		M	
Total		2428736	403775				

Supplementary Figure 30. HPLC spectrum of (*R*)-**3cn**

(*R*)-4-(3,5-bis(trifluoromethyl)phenyl)-2,2-dimethyl-1,3-dioxolane (3co)



Chemical Formula: $C_{13}H_{12}F_6O_2$
Exact Mass: 314.0741

3co was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 1-bromo-3,5-bis(trifluoromethyl)benzene (58.6 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 50/1) to obtain **3co** as colorless oil (41.4 mg, 66% yield, 91% ee). R_f = 0.6 (PE/EA = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 – 7.76 (m, 3H), 5.18 (t, *J* = 6.9 Hz, 1H), 4.41 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.72 (dd, *J* = 8.3, 7.4 Hz, 1H), 1.57 (s, 3H), 1.50 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.5, 131.9 (q, *J* = 33.3 Hz), 126.2 (q, *J* = 3.9 Hz), 123.2 (q, *J* = 272.7 Hz), 121.9 (p, *J* = 3.9 Hz), 110.7, 76.5, 71.3, 26.4, 25.7;

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.93.

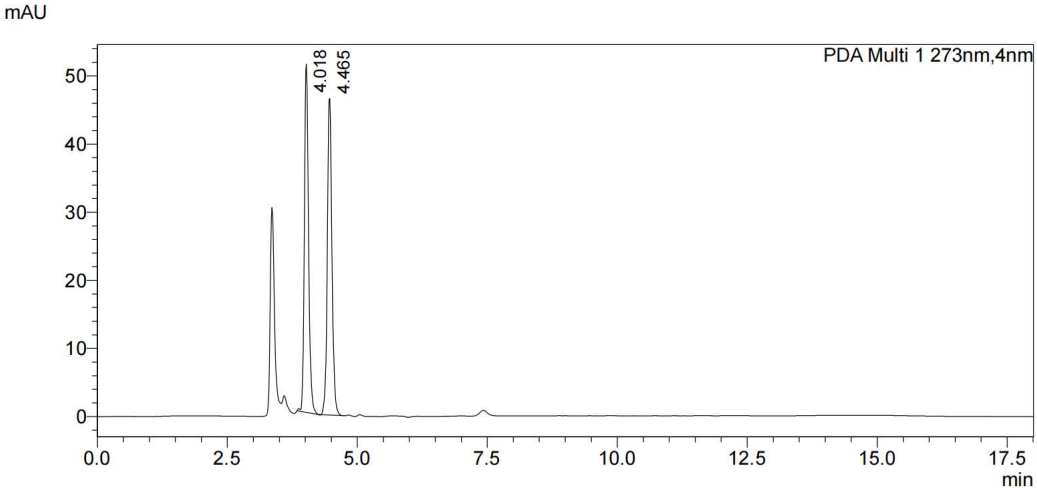
HRMS: (APCI) calcd for $C_{13}H_{13}F_6O_2^+$[M+H]$^+$ 315.0814; found 315.0811.

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 97/3 as eluent, 196 nm, 1 mL/min. tR = 4.4 min (major), 3.9 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -12.0 (c 0.4, ^{i}PrOH) for 91% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



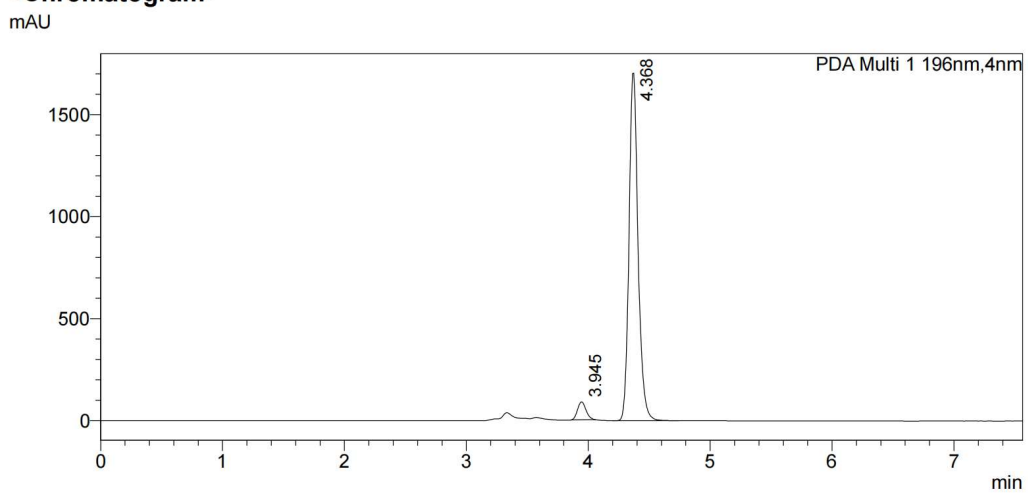
<Peak Table>

PDA Ch1 273nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.018	285000	51093	0.000		M	
2	4.465	287260	46499	0.000		M	
Total		572260	97592				

Supplementary Figure 31. HPLC spectrum of racemic-**3co**

<Chromatogram>



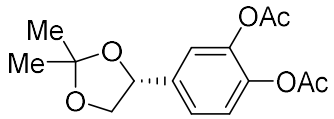
<Peak Table>

PDA Ch1 196nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.945	419784	88289	4.528		M	
2	4.368	8850321	1701576	95.472		M	
Total		9270105	1789866				

Supplementary Figure 32. HPLC spectrum of (*R*)-**3co**

(*R*)-4-(2,2-dimethyl-1,3-dioxolan-4-yl)-1,2-phenylene diacetate (3cp)



Chemical Formula: $C_{15}H_{18}O_6$
Exact Mass: 294.1103

3cp was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 4-bromo-1,2-phenylene diacetate (54.6 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 5/1) to obtain **3cp** as colorless oil (28.2 mg, 48% yield, 88% ee). R_f = 0.4 (PE/EA = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (ddd, *J* = 8.3, 2.1, 0.6 Hz, 1H), 7.21 (d, *J* = 2.0 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 5.05 (dd, *J* = 7.8, 6.2 Hz, 1H), 4.30 (dd, *J* = 8.3, 6.2 Hz, 1H), 3.71 (t, *J* = 8.0 Hz, 1H), 2.29 (s, 3H), 2.28 (s, 3H), 1.53 (s, 3H), 1.47 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 168.2, 142.1, 141.6, 138.3, 124.2, 123.5, 121.2, 110.0, 77.0, 71.4, 26.6, 25.9, 20.67, 20.66;

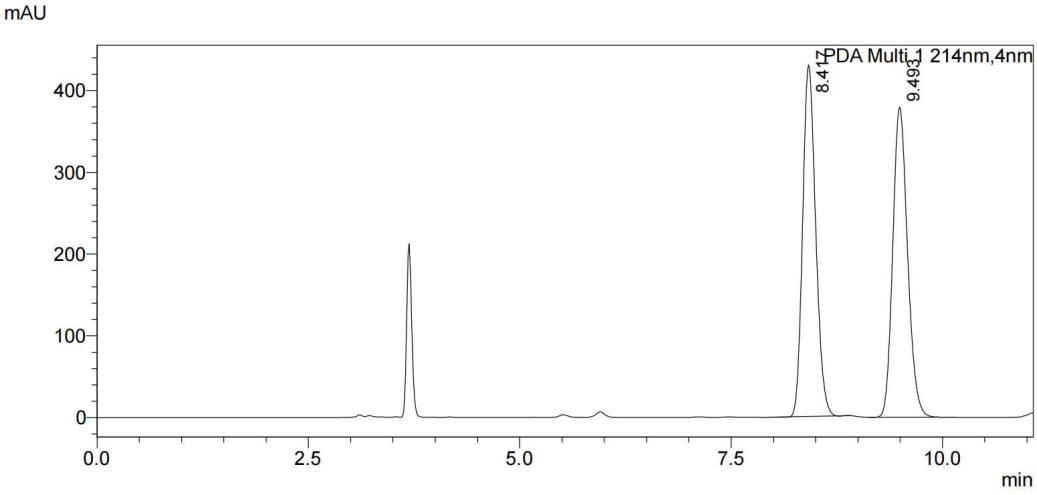
HRMS: (ESI) calcd for $C_{15}H_{18}O_6Na^+$[M+Na]$^+$ 317.0996; found 317.0988.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 90/10 as eluent, 194 nm, 1 mL/min. tR = 9.5 min (major), 8.4 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -18.3 (c 0.1, ^{i}PrOH) for 88% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



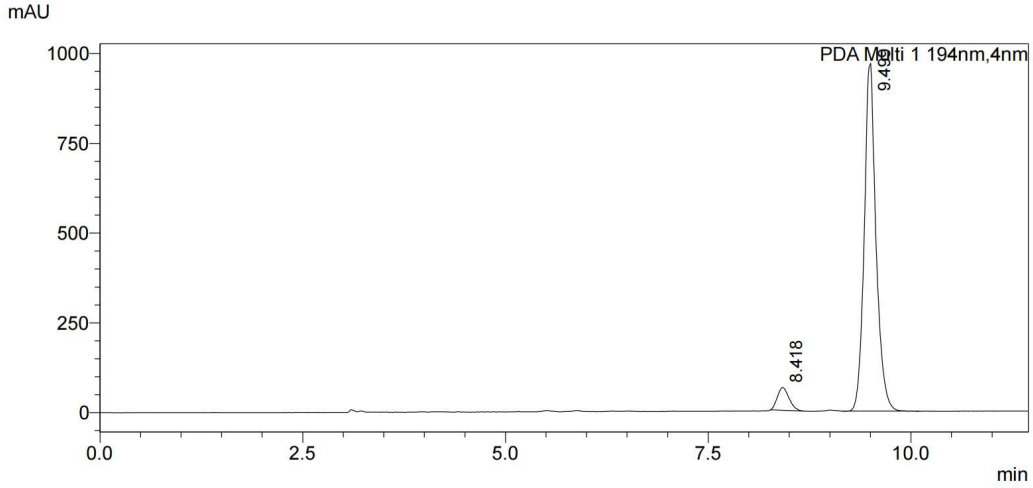
<Peak Table>

PDA Ch1 214nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.417	4604975	430001	0.000		M	
2	9.493	4629495	379569	0.000		M	
Total		9234470	809571				

Supplementary Figure 33. HPLC spectrum of racemic-**3cp**

<Chromatogram>



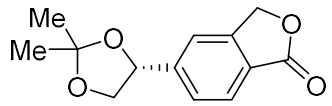
<Peak Table>

PDA Ch1 194nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.418	632316	63073	0.000		M	
2	9.499	9779679	968122	0.000		M	
Total		10411994	1031196				

Supplementary Figure 34. HPLC spectrum of (*R*)-**3cp**

(*R*)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)isobenzofuran-1(3*H*)-one (3cq)



Chemical Formula: $C_{13}H_{14}O_4$
Exact Mass: 234.0892

3cq was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 5-bromoisobenzofuran-1(3*H*)-one (42.6 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 3/1) to obtain **3cq** as colorless oil (25.3 mg, 54% yield, 93% ee). R_f = 0.4 (PE/EA = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.50 (dd, *J* = 7.8, 1.3 Hz, 1H), 5.33 (d, *J* = 2.0 Hz, 2H), 5.23 – 5.18 (m, 1H), 4.40 (dd, *J* = 8.3, 6.4 Hz, 1H), 3.70 (dd, *J* = 8.3, 7.6 Hz, 1H), 1.58 (s, 3H), 1.51 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.8, 147.2, 146.6, 127.0, 126.0, 125.5, 119.4, 110.4, 77.3, 71.5, 69.6, 26.5, 25.8;

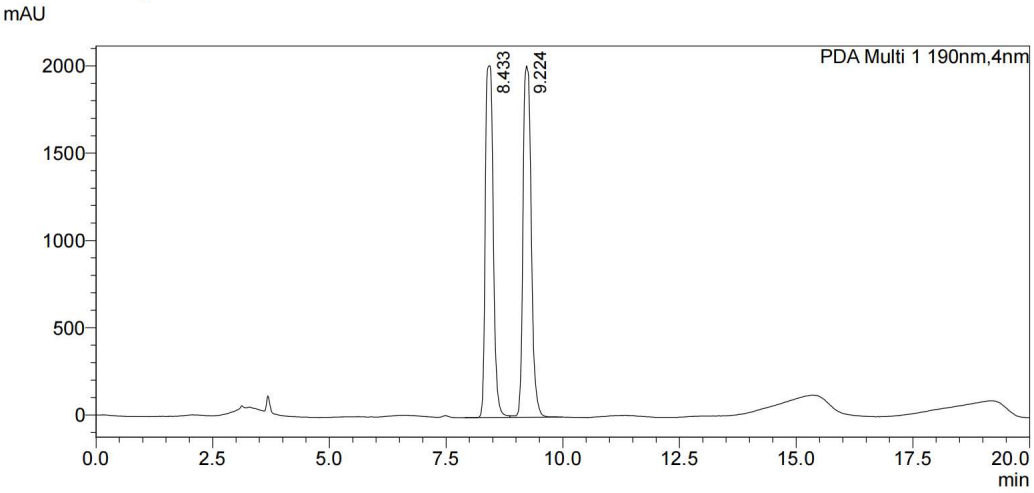
HRMS: (ESI) calcd for $C_{13}H_{15}O_4^+$[M+H]$^+$ 235.0965; found 235.0966.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 85/15 as eluent, 234 nm, 1 mL/min. tR = 9.2 min (major), 8.4 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -22.8 (c 0.1, ^{i}PrOH) for 93% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



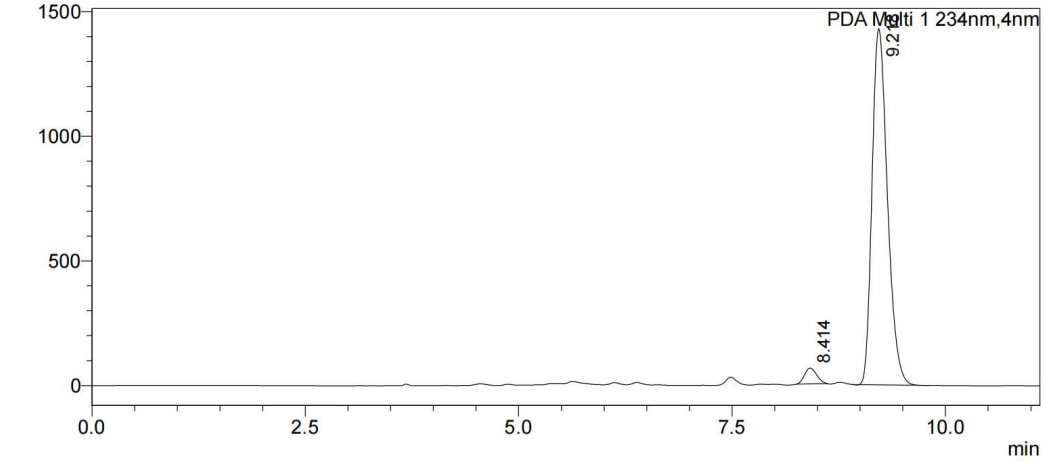
<Peak Table>

PDA Ch1 190nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.433	23803164	2015849	0.000		M	
2	9.224	24654673	2012991	0.000		V M	
Total		48457838	4028840				

Supplementary Figure 35. HPLC spectrum of racemic-**3cq**

<Chromatogram>



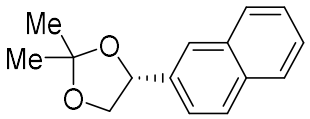
<Peak Table>

PDA Ch1 234nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.414	621650	63559	0.000		M	
2	9.218	17921306	1429602	0.000		M	
Total		18542956	1493161				

Supplementary Figure 36. HPLC spectrum of (*R*)-**3cq**

(*R*)-2,2-dimethyl-4-(naphthalen-2-yl)-1,3-dioxolane (3cr)



Chemical Formula: $C_{15}H_{16}O_2$
Exact Mass: 228.1150

3cr was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 2-bromonaphthalene (41.4 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 50/1) to obtain **3cr** as colorless oil (20.5 mg, 45% yield, 86% ee). R_f = 0.5 (PE/EA = 50/1).

The NMR data matched those reported in the literature.[7]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 4H), 7.52 – 7.46 (m, 3H), 5.26 (dd, *J* = 8.0, 6.3 Hz, 1H), 4.39 (dd, *J* = 8.2, 6.3 Hz, 1H), 3.81 (t, *J* = 8.1 Hz, 1H), 1.63 (s, 3H), 1.55 (s, 3H);

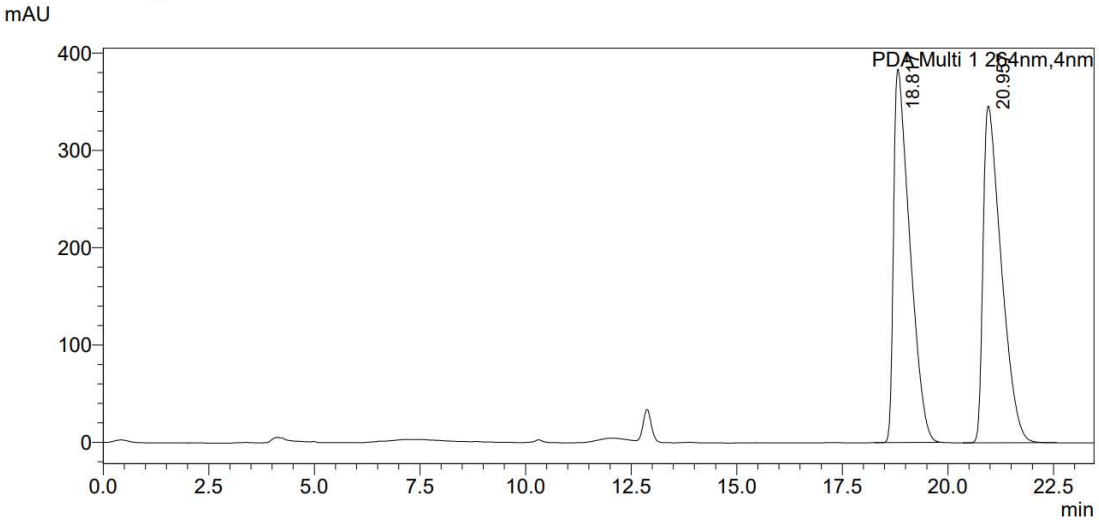
^{13}C NMR (151 MHz, $CDCl_3$) δ 136.5, 133.24, 133.23, 128.5, 128.0, 127.8, 126.3, 126.1, 125.3, 123.9, 109.9, 78.1, 71.6, 26.7, 26.0;

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 99/1 as eluent, 254 nm, 0.5 mL/min. tR = 18.9 min (major), 21.4 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -45.1 (c 0.1, ^{i}PrOH) for 86% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



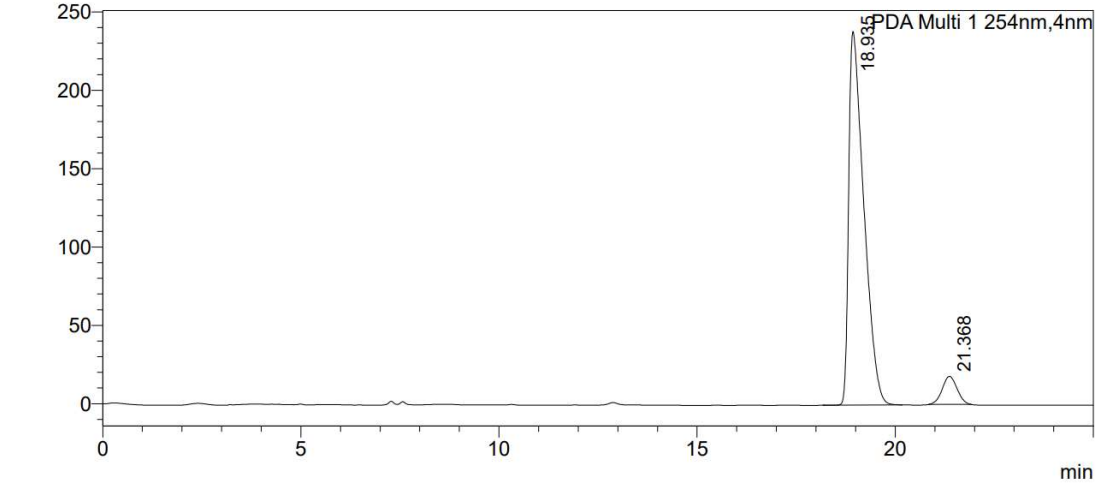
<Peak Table>

PDA Ch1 264nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.817	10289767	383793	0.000		M	
2	20.957	10393042	346126	0.000		M	
Total		20682809	729919				

Supplementary Figure 37. HPLC spectrum of racemic-**3cr**

<Chromatogram>



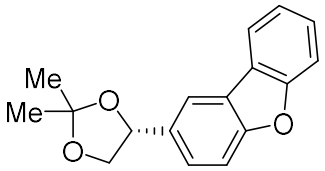
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.935	6317375	238377	0.000		M	
2	21.368	465876	17904	0.000		M	
Total		6783251	256281				

Supplementary Figure 38. HPLC spectrum of (*R*)-**3cr**

(*R*)-2-(2,2-dimethyl-1,3-dioxolan-4-yl)dibenzo[*b*,*d*]furan (3cs)



Chemical Formula: $C_{17}H_{16}O_3$
Exact Mass: 268.1099

3cs was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 2-bromodibenzo[*b*,*d*]furan (49.4 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 50/1) to obtain **3cs** as colorless oil (27.3 mg, 51% yield, 88% ee). R_f = 0.5 (PE/EA = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.60 – 7.53 (m, 2H), 7.48 – 7.44 (m, 2H), 7.37 – 7.33 (m, 1H), 5.25 (dd, *J* = 8.1, 6.2 Hz, 1H), 4.38 (dd, *J* = 8.3, 6.2 Hz, 1H), 3.80 (t, *J* = 8.2 Hz, 1H), 1.63 (s, 3H), 1.54 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.6, 156.0, 133.6, 127.3, 125.5, 124.5, 124.0, 122.8, 120.7, 118.5, 111.8, 111.7, 109.8, 78.1, 72.0, 26.8, 26.0;

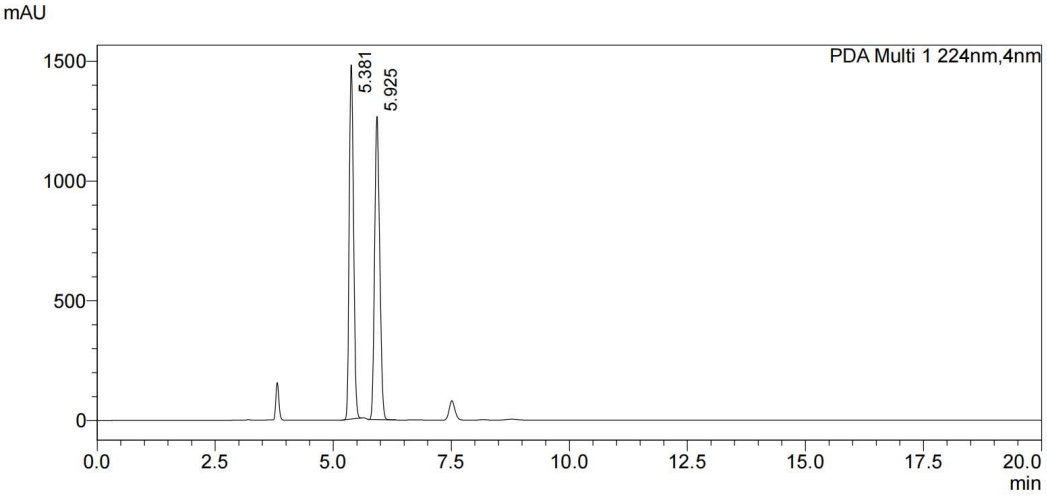
HRMS: (ESI) calcd for $C_{17}H_{16}O_3Na^+$[M+Na]$^+$ 291.0992; found 291.0988.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 95/5 as eluent, 240 nm, 1 mL/min. tR = 5.9 min (major), 5.4 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -44.1 (c 0.1, ^{i}PrOH) for 88% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



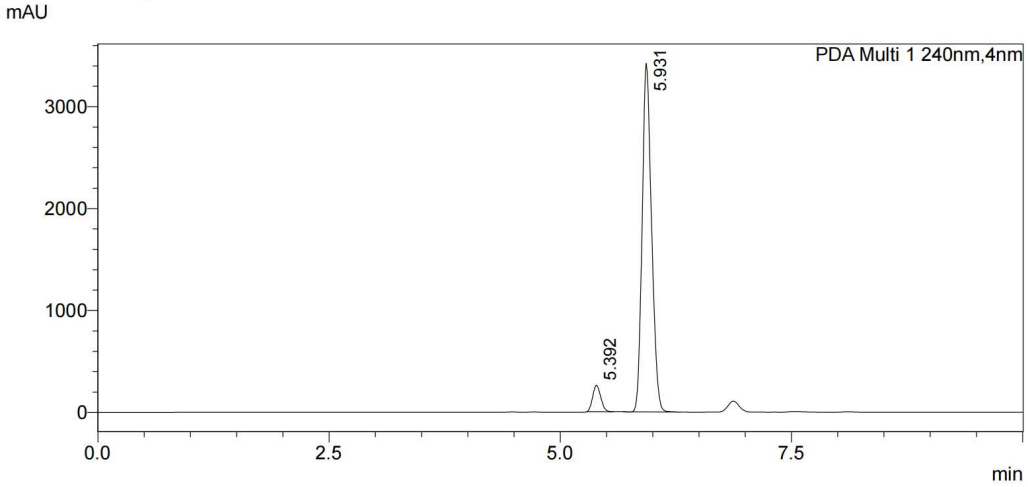
<Peak Table>

PDA Ch1 224nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.381	9342078	1478076	0.000		M	
2	5.925	9537838	1264020	0.000		M	
Total		18879916	2742096				

Supplementary Figure 39. HPLC spectrum of racemic-**3cs**

<Chromatogram>



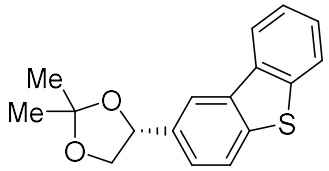
<Peak Table>

PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.392	1561546	258463	0.000		M	
2	5.931	24222893	3417066	0.000		M	
Total		25784439	3675529				

Supplementary Figure 40. HPLC spectrum of (*R*)-**3cs**

(*R*)-4-(dibenzo[b,d]thiophen-2-yl)-2,2-dimethyl-1,3-dioxolane (3ct)



Chemical Formula: $C_{17}H_{16}O_2S$
Exact Mass: 284.0871

3ct was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 2-bromodibenzo[*b*,*d*]thiophene (52.6 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 50/1) to obtain **3ct** as colorless oil (31.8 mg, 56% yield, 90% ee). R_f = 0.5 (PE/EA = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 – 8.15 (m, 2H), 7.89 – 7.82 (m, 2H), 7.49 – 7.44 (m, 3H), 5.27 (dd, *J* = 8.0, 6.2 Hz, 1H), 4.40 (dd, *J* = 8.3, 6.3 Hz, 1H), 3.81 (t, *J* = 8.2 Hz, 1H), 1.64 (s, 3H), 1.56 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.9, 139.2, 135.7, 135.6, 135.3, 126.9, 124.9, 124.4, 123.0, 122.9, 121.7, 119.3, 109.9, 78.1, 71.9, 26.7, 26.0;

HRMS: (ESI) calcd for $C_{17}H_{16}O_2SNa^+$[M+Na]$^+$ 307.0763; found 307.0763.

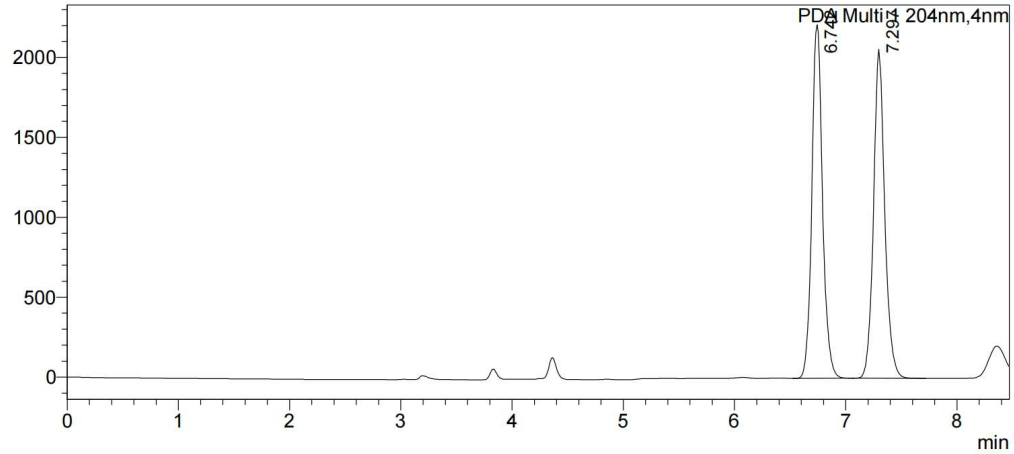
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 95/5 as eluent, 264 nm, 1 mL/min. tR = 7.3 min (major), 6.7 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -90.4 (c 0.1, ^{i}PrOH) for 90% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>

mAU



<Peak Table>

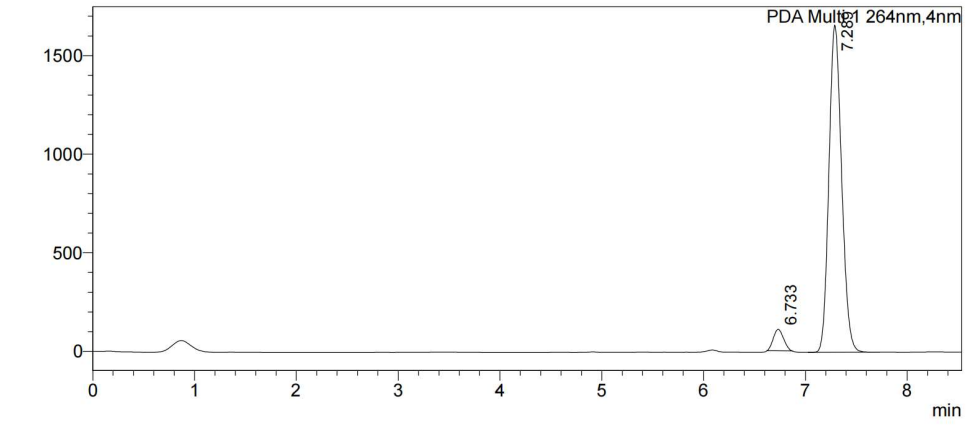
PDA Ch1 204nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.742	14770591	2211955	0.000		M	
2	7.297	14425664	2058569	0.000		M	
Total		29196255	4270524				

Supplementary Figure 41. HPLC spectrum of racemic-**3ct**

<Chromatogram>

mAU



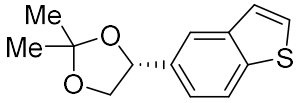
<Peak Table>

PDA Ch1 264nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.733	766878	109228	0.000		M	
2	7.289	14404275	1659312	0.000		M	
Total		15171153	1768540				

Supplementary Figure 42. HPLC spectrum of (*R*)-**3ct**

(*R*)-4-(benzo[b]thiophen-5-yl)-2,2-dimethyl-1,3-dioxolane (3cu)



Chemical Formula: $C_{13}H_{14}O_2S$
Exact Mass: 234.0715

3cu was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 5-bromobenzo[*b*]thiophene (42.6 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 50/1) to obtain **3cu** as colorless oil (24.8 mg, 53% yield, 89% ee). R_f = 0.5 (PE/EA = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 1.6 Hz, 1H), 7.46 (d, *J* = 5.4 Hz, 1H), 7.37 – 7.31 (m, 2H), 5.21 (dd, *J* = 8.0, 6.2 Hz, 1H), 4.35 (dd, *J* = 8.2, 6.2 Hz, 1H), 3.76 (t, *J* = 8.1 Hz, 1H), 1.59 (s, 3H), 1.57 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.8, 139.4, 135.3, 127.1, 123.8, 122.7, 122.5, 121.3, 109.8, 78.1, 71.9, 26.7, 26.0;

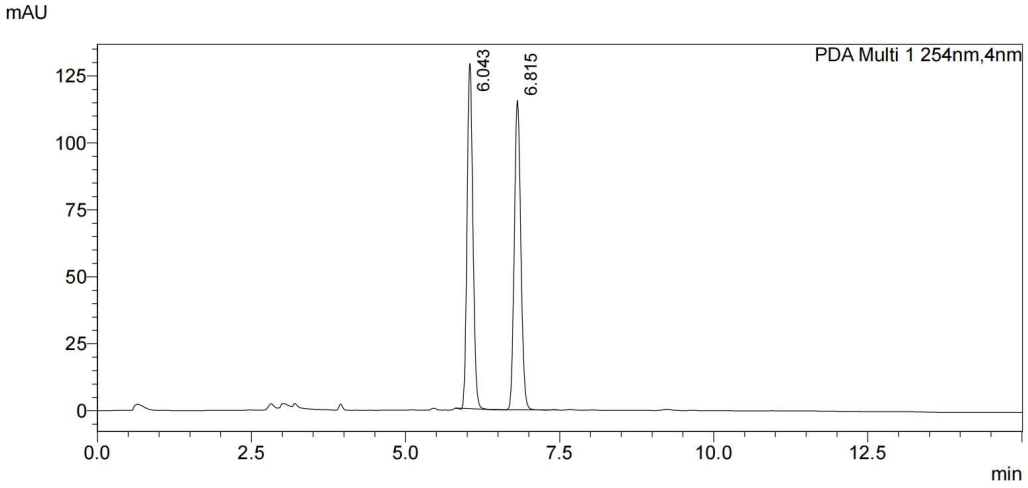
HRMS: (ESI) calcd for $C_{13}H_{14}O_2SNa^+$[M+Na]$^+$ 257.0607; found 257.0609.

The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 95/5 as eluent, 210 nm, 1 mL/min. tR = 6.6 min (major), 5.8 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -31.2 (c 0.1, ^{i}PrOH) for 89% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



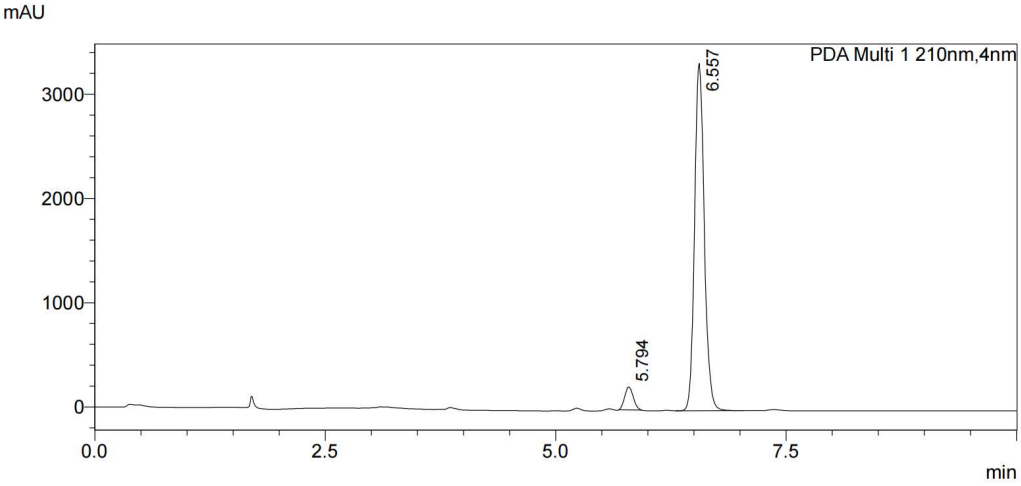
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.043	846890	128798	0.000		M	
2	6.815	850219	115523	0.000		M	
Total		1697108	244320				

Supplementary Figure 43. HPLC spectrum of racemic-**3cu**

<Chromatogram>



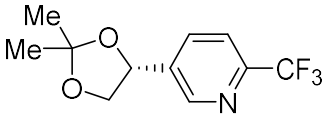
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.794	1434693	221567	5.542		M	
2	6.557	24454942	3331979	94.458		M	
Total		25889635	3553546				

Supplementary Figure 44. HPLC spectrum of (*R*)-**3cu**

(*R*)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-(trifluoromethyl)pyridine (3cv)



Chemical Formula: $C_{11}H_{12}F_3NO_2$
Exact Mass: 247.0820

3cv was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 5-bromo-2-(trifluoromethyl)pyridine (45.2 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 5/1) to obtain **3cv** as colorless oil (30.1 mg, 61% yield, 91% ee). R_f = 0.6 (PE/EA = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, *J* = 2.1 Hz, 1H), 7.90 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 5.19 (t, *J* = 6.8 Hz, 1H), 4.42 (dd, *J* = 8.4, 6.5 Hz, 1H), 3.77 – 3.71 (m, 1H), 1.56 (s, 3H), 1.50 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.1, 147.9 (q, *J* = 34.7 Hz), 138.7, 135.0, 121.5 (q, *J* = 274.8 Hz), 120.4 (q, *J* = 3.0 Hz), 110.7, 75.0, 71.2, 26.4, 25.6;

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.88.

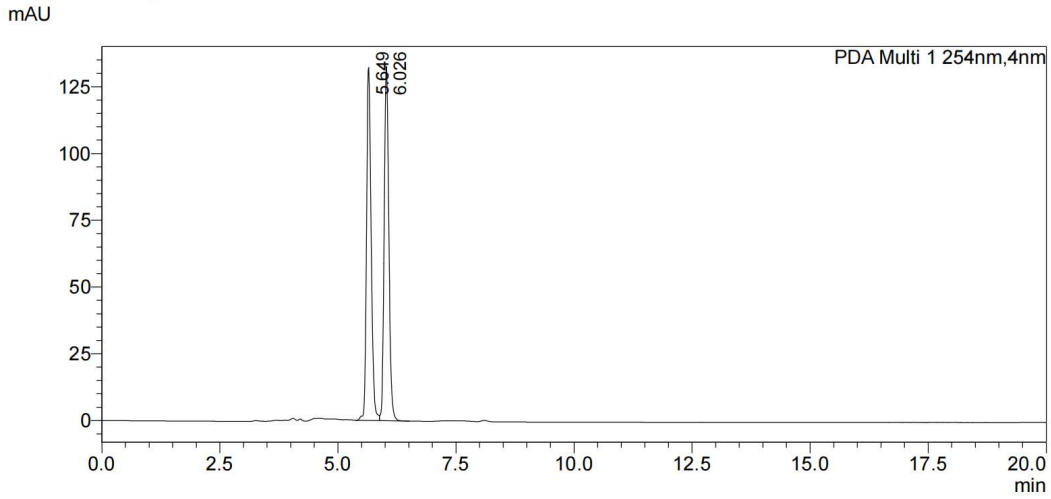
HRMS: (APCI) calcd for $C_{11}H_{13}F_3NO_2^+$[M+H]$^+$ 248.0893; found 248.0887.

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 85/15 as eluent, 244 nm, 1 mL/min. tR = 5.6 min (major), 6.0 min (minor).

Optical Rotation: $[\alpha]_D^{22}$ -46.0 (c 0.1, ^{i}PrOH) for 91% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



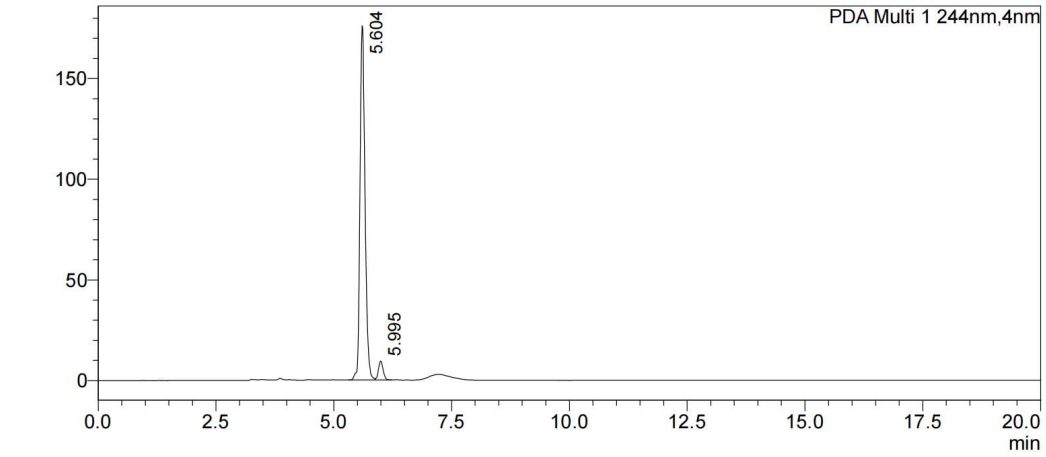
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.649	908522	132154	0.000		M	
2	6.026	902400	132669	0.000		V M	
Total		1810922	264823				

Supplementary Figure 45. HPLC spectrum of racemic-**3cv**

<Chromatogram>



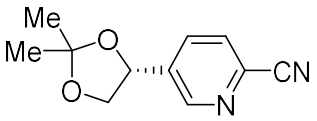
<Peak Table>

PDA Ch1 244nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.604	1315765	175897	0.000		M	
2	5.995	63849	9384	0.000		V M	
Total		1379614	185281				

Supplementary Figure 46. HPLC spectrum of (*R*)-**3cv**

(*R*)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)picolinonitrile (3cw)



Chemical Formula: $C_{11}H_{12}N_2O_2$
Exact Mass: 204.0899

3cw was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 5-bromopicolinonitrile (36.6 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 3/1) to obtain **3cw** as colorless oil (30.6 mg, 75% yield, 90% ee). R_f = 0.6 (PE/EA = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (d, *J* = 2.2 Hz, 1H), 7.85 (dd, *J* = 8.0, 2.2 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 5.16 (t, *J* = 6.8 Hz, 1H), 4.40 (dd, *J* = 8.4, 6.5 Hz, 1H), 3.71 (dd, *J* = 8.5, 7.1 Hz, 1H), 1.54 (s, 3H), 1.48 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.2, 139.5, 134.6, 133.3, 128.3, 117.1, 110.8, 75.0, 71.0, 26.4, 25.6;

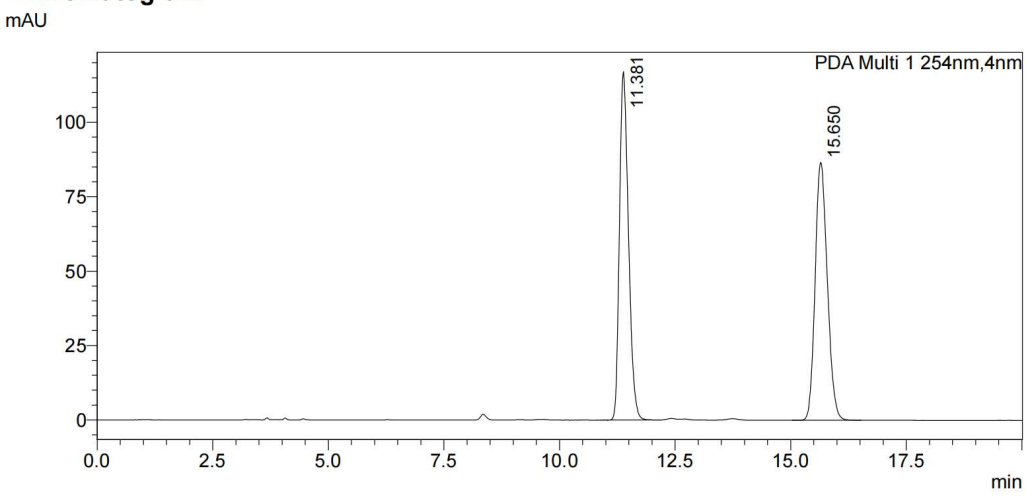
HRMS: (APCI) calcd for $C_{11}H_{13}N_2O_2^+$[M+H]$^+$ 205.0972; found 205.0967.

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 80/20 as eluent, 198 nm, 1 mL/min. tR = 11.3 min (major), 15.7 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -71.7 (c 0.2, ^{i}PrOH) for 90% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



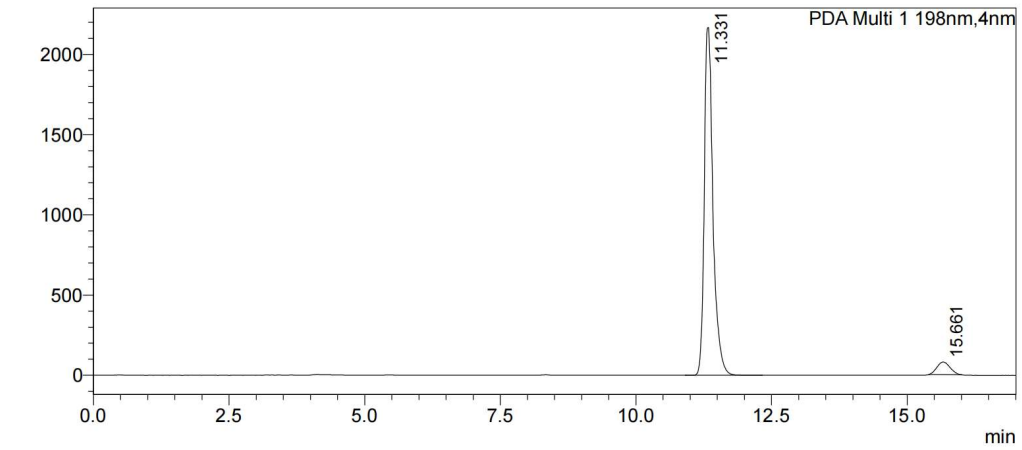
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.381	1586685	117038	0.000		M	
2	15.650	1587833	86625	0.000		M	
Total		3174518	203662				

Supplementary Figure 47. HPLC spectrum of racemic-**3cw**

<Chromatogram>



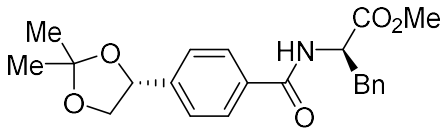
<Peak Table>

PDA Ch1 198nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.331	24154819	2167966	94.848		M	
2	15.661	1312094	78503	5.152		M	
Total		25466913	2246469				

Supplementary Figure 48. HPLC spectrum of (*R*)-**3cw**

methyl (4-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)benzoyl)-*D*-phenylalaninate (3cx)



Chemical Formula: $C_{22}H_{25}NO_5$
Exact Mass: 383.1733

3cx was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), methyl (4-bromobenzoyl)-*D*-phenylalaninate (72.4 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 3/1) to obtain **3cx** as colorless oil (55.2 mg, 72% yield, d.r. > 19/1). R_f = 0.4 (PE/EA = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.42 – 7.38 (m, 2H), 7.30 – 7.26 (m, 2H), 7.26 – 7.22 (m, 1H), 7.14 – 7.10 (m, 2H), 6.62 (d, *J* = 7.5 Hz, 1H), 5.12 – 5.05 (m, 2H), 4.32 (dd, *J* = 8.2, 6.3 Hz, 1H), 3.76 (s, 3H), 3.67 (t, *J* = 8.0 Hz, 1H), 3.28 (dd, *J* = 13.9, 5.8 Hz, 1H), 3.21 (dd, *J* = 13.9, 5.5 Hz, 1H), 1.54 (s, 3H), 1.48 (s, 3H);

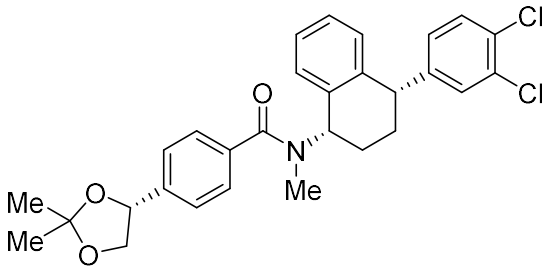
^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 166.5, 143.4, 135.8, 133.5, 129.3, 128.7, 127.3, 127.2, 126.3, 110.1, 77.3, 71.5, 53.5, 52.5, 37.9, 26.5, 25.9;

HRMS: (APCI) calcd for $C_{22}H_{26}NO_5^+$[M+H]$^+$ 384.1804; found 384.1800.

Optical Rotation: $[\alpha]_D^{21}$ 50.1 (c 0.2, ^{i}PrOH).

Absolute stereochemistry was determined through analogy with **3cg**.

***N*-((1*S*,4*S*)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-4-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-*N*-methylbenzamide (3cy)**



Chemical Formula: $C_{29}H_{29}Cl_2NO_3$
Exact Mass: 509.1524

3cy was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 4-bromo-*N*-((1*S*,4*S*)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-*N*-methylbenzamide (97.8 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 3/1) to obtain **3cy** as colorless oil (55.0 mg, 54% yield, d.r. > 19/1). R_f = 0.5 (PE/EA = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.47 – 7.39 (m, 2H), 7.36 – 7.27 (m, 3H), 7.25 – 7.05 (m, 2H), 7.01 – 6.94 (m, 1H), 6.89 – 6.74 (m, 1H), 6.08 – 5.10 (m, 1H), 5.09 – 4.91 (m, 1H), 4.37 – 4.28 (m, 1H), 4.26 – 4.09 (m, 1H), 3.73 – 3.64 (m, 1H), 2.92 – 2.64 (m, 3H), 2.41 – 1.77 (m, 4H), 1.58 – 1.45 (m, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.5, 172.2, 147.0, 146.7, 141.98, 140.8, 138.4, 137.9, 136.3, 135.7, 135.6, 132.5, 132.3, 131.1, 131.0, 130.7, 130.6, 130.3, 130.2, 130.1, 128.12, 128.07, 127.94, 127.93, 127.8, 127.6, 127.5, 127.3, 127.27, 127.25, 126.7, 126.51, 126.49, 126.3, 110.03, 110.00, 77.5, 71.61, 71.56, 58.6, 52.8, 43.1, 42.7, 33.1, 30.1, 20.0, 28.9, 26.6, 25.92, 25.86, 22.6, 21.2;

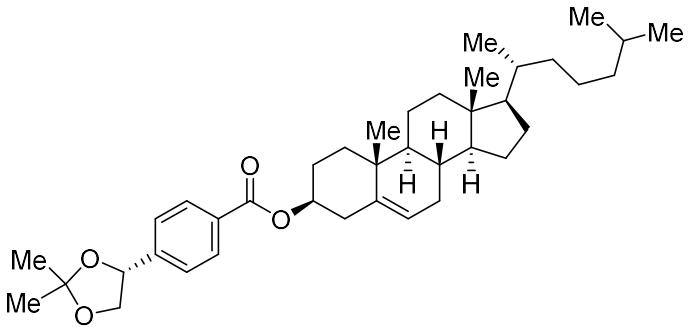
HRMS: (ESI) calcd for $C_{29}H_{30}Cl_2NO_3^+[M+H]^+$ 510.1597; found 510.1591.

Optical Rotation: $[\alpha]_D^{21}$ -79.8 (c 0.1, ^{i}PrOH).

Absolute stereochemistry was determined through analogy with **3cg**.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-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-

((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)benzoate (3cz)



Chemical Formula: $C_{39}H_{58}O_4$
Exact Mass: 590.4335

3cz was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-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-bromobenzoate (114.1 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 10/1) to obtain **3cz** as colorless oil (68.4 mg, 58% yield, d.r. > 19/1). R_f = 0.6 (PE/EA = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 2H), 7.45 – 7.38 (m, 2H), 5.43 – 5.39 (m, 1H), 5.12 (dd, *J* = 7.8, 6.3 Hz, 1H), 4.89 – 4.81 (m, 1H), 4.33 (dd, *J* = 8.2, 6.3 Hz, 1H), 3.67 (t, *J* = 8.1 Hz, 1H), 2.46 (d, *J* = 7.7 Hz, 2H), 2.05 – 1.96 (m, 3H), 1.94 – 1.89 (m, 1H), 1.87 – 1.80 (m, 1H), 1.77 – 1.70 (m, 1H), 1.61 – 1.43 (m, 12H), 1.41 – 1.30 (m, 3H), 1.29 – 1.08 (m, 8H), 1.06 (s, 3H), 1.04 – 0.95 (m, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 2.7 Hz, 3H), 0.86 (d, *J* = 2.7 Hz, 3H), 0.69 (s, 3H);

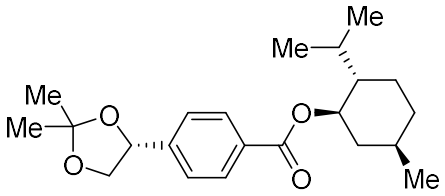
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7, 144.3, 139.6, 130.5, 129.8, 125.9, 122.8, 110.1, 77.5, 74.7, 71.5, 56.7, 56.2, 50.1, 42.3, 39.8, 39.5, 38.2, 37.0, 36.7, 36.2, 35.8, 32.0, 31.9, 28.3, 28.0, 27.9, 26.5, 25.9, 24.3, 23.9, 22.9, 22.6, 21.1, 19.4, 18.7, 11.9.

HRMS: (APCI) calcd for $C_{39}H_{59}O_4^+$[M+H]$^+$ 591.4408; found 591.4390.

Optical Rotation: $[\alpha]_D^{21}$ -93.0 (c 0.1, ^{i}PrOH).

Absolute stereochemistry was determined through analogy with **3cg**.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl) benzoate (3caa)



Chemical Formula: $C_{22}H_{32}O_4$
Exact Mass: 360.2301

3caa was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-bromobenzoate (67.8 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 10/1) to obtain **3caa** as colorless oil (48.2 mg, 67% yield, d.r. > 19/1). R_f = 0.6 (PE/EA = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 – 8.01 (m, 2H), 7.45 – 7.39 (m, 2H), 5.12 (dd, *J* = 7.8, 6.3 Hz, 1H), 4.95 – 4.89 (m, 1H), 4.33 (dd, *J* = 8.3, 6.3 Hz, 1H), 3.67 (t, *J* = 8.0 Hz, 1H), 2.14 – 2.09 (m, 1H), 1.98 – 1.90 (m, 1H), 1.75 – 1.68 (m, 2H), 1.54 (s, 5H), 1.49 (s, 3H), 1.17 – 1.06 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 7H), 0.78 (d, *J* = 6.9 Hz, 3H);

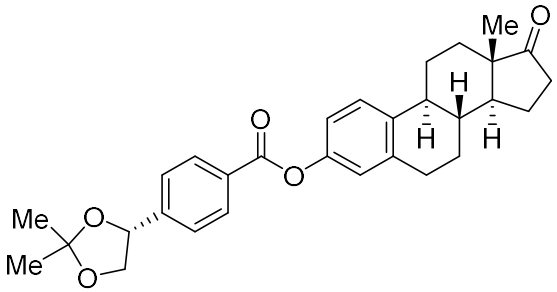
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 144.4, 130.5, 129.9, 125.9, 110.1, 77.4, 74.9, 71.5, 47.3, 41.0, 34.3, 31.5, 26.53, 26.49, 25.9, 23.7, 22.1, 20.8, 16.5;

HRMS: (ESI) calcd for $C_{22}H_{33}O_4^+$[M+H]$^+$ 361.2373; found 361.2365.

Optical Rotation: $[\alpha]_D^{21}$ -218.2 (c 0.2, ^{i}PrOH).

Absolute stereochemistry was determined through analogy with **3cg**.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 4-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)benzoate (3cab)



Chemical Formula: $C_{30}H_{34}O_5$
Exact Mass: 474.2406

3cab was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), (8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 4-bromobenzoate (90.6 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 3/1) to obtain **3cab** as colorless oil (61.6 mg, 65% yield, d.r. > 19/1). R_f = 0.4 (PE/EA = 4/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 – 8.15 (m, 2H), 7.53 – 7.48 (m, 2H), 7.33 (dd, *J* = 8.6, 1.1 Hz, 1H), 6.98 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.94 (d, *J* = 2.5 Hz, 1H), 5.17 (dd, *J* = 7.7, 6.4 Hz, 1H), 4.37 (dd, *J* = 8.2, 6.4 Hz, 1H), 3.71 (t, *J* = 8.0 Hz, 1H), 2.96 – 2.90 (m, 2H), 2.54 – 2.48 (m, 1H), 2.45 – 2.40 (m, 1H), 2.35 – 2.28 (m, 1H), 2.18 – 2.11 (m, 1H), 2.09 – 2.00 (m, 2H), 2.00 – 1.95 (m, 1H), 1.66 – 1.60 (m, 2H), 1.59 – 1.43 (m, 10H), 0.92 (s, 3H);

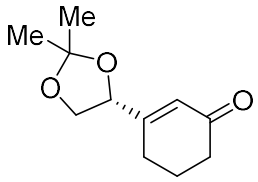
^{13}C NMR (151 MHz, $CDCl_3$) δ 220.9, 165.2, 148.8, 145.3, 138.1, 137.5, 130.5, 129.3, 126.5, 126.1, 121.7, 118.9, 110.2, 77.4, 71.5, 50.5, 48.0, 44.2, 38.0, 35.9, 31.6, 29.5, 26.5, 26.4, 25.9, 25.8, 21.6, 13.9;

HRMS: (ESI) calcd for $C_{30}H_{35}O_5^+$[M+H]$^+$ 475.2479; found 475.2473.

Optical Rotation: $[\alpha]_D^{21}$ 103.8 (c 0.2, ^{i}PrOH).

Absolute stereochemistry was determined through analogy with **3cg**.

(*R*)-3-(2,2-dimethyl-1,3-dioxolan-4-yl)cyclohex-2-en-1-one (3cac)



Chemical Formula: $C_{11}H_{16}O_3$
Exact Mass: 196.1099

3cac was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.6 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), 3-bromocyclohex-2-en-1-one (35.0 mg, 0.20 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane (102.1 mg, 1.0 mmol, 5 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), K_3PO_4 (51.2 mg, 0.24 mmol, 1.2 equiv) and anhydrous acetone/$PhCF_3$ (0.5 mL/0.5 mL) and was purified by silica gel column chromatography (PE/EA = 4/1) to obtain **3cac** as colorless oil (16.5 mg, 42% yield, 95% ee). R_f = 0.5 (PE/EA = 4/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.13 (q, *J* = 1.5 Hz, 1H), 4.63 (t, *J* = 7.0 Hz, 1H), 4.23 (dd, *J* = 8.3, 6.9 Hz, 1H), 3.72 – 3.68 (m, 1H), 2.41 (td, *J* = 6.2, 1.1 Hz, 2H), 2.29 (qd, *J* = 6.1, 1.6 Hz, 2H), 2.06 – 2.00 (m, 2H), 1.46 (s, 3H), 1.42 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 199.5, 161.7, 124.9, 110.4, 77.7, 68.5, 37.8, 26.1, 25.5, 25.4, 22.6;

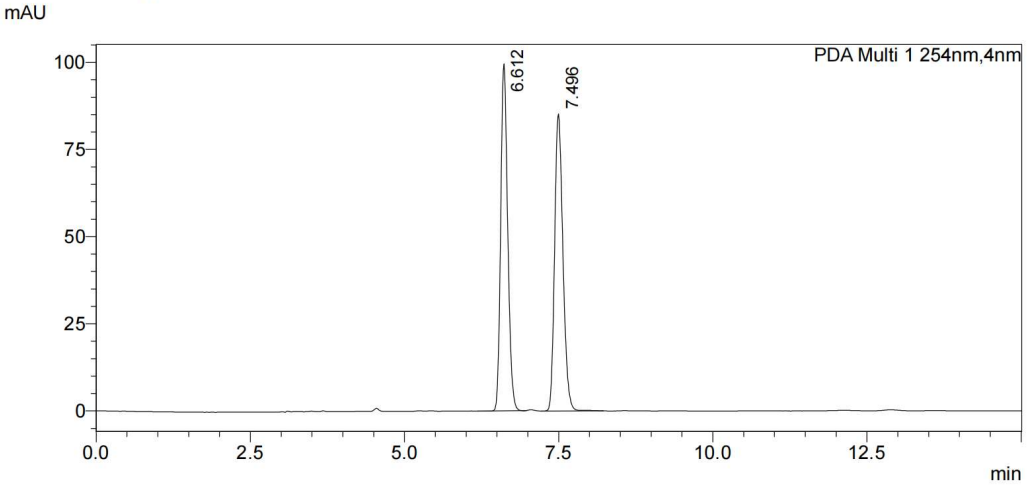
HRMS: (APCI) calcd for $C_{11}H_{17}O_3^+$[M+H]$^+$ 197.1172; found 197.1170.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 90/10 as eluent, 204 nm, 1 mL/min. tR = 6.7 min (major), 7.6 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -14.5 (c 0.1, ^{i}PrOH) for 95% ee.

Absolute stereochemistry was determined through analogy with **3cg**.

<Chromatogram>



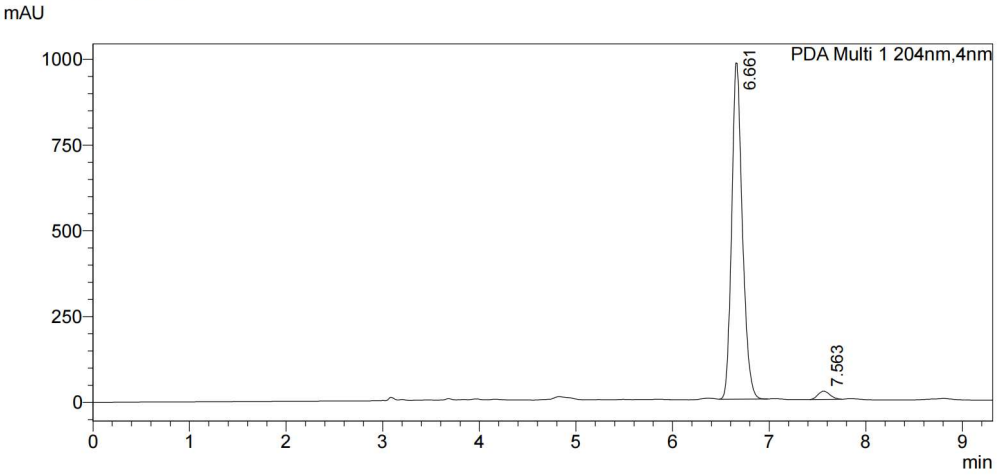
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.612	785869	99509	0.000		M	
2	7.496	797401	85242	0.000		M	
Total		1583269	184750				

Supplementary Figure 49. HPLC spectrum of racemic-**3cac**

<Chromatogram>



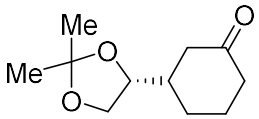
<Peak Table>

PDA Ch1 204nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.661	7538653	980038	0.000		M	
2	7.563	198822	23528	0.000		M	
Total		7737475	1003566				

Supplementary Figure 50. HPLC spectrum of (*R*)-**3cac**

(*R*)-3-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)cyclohexan-1-one (3cad)



Chemical Formula: $C_{11}H_{18}O_3$
Exact Mass: 198.1256

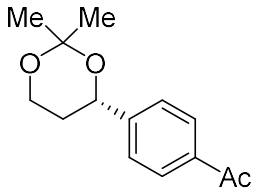
An oven-dried 10-mL Schlenk equipped with a PTFE-coated stir bar was charged with 5% Pd/C (36.6 mg, 0.018 mmol, 15 mol%) and **3cac** (19.6 mg, 0.10 mmol, 1 equiv) in toluene (1 mL) and CH_2Cl_2 (1 mL). The reaction mixture was stirred under H_2 atmosphere (10 bar) at 25 °C for 24 hours. The mixture was filtered through Celite and the filtrate was condensed. The residue was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **3cad** as colorless oil (17.4 mg, 88%, d.r. > 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.05 – 3.98 (m, 1H), 3.92 (q, *J* = 6.8 Hz, 1H), 3.67 – 3.60 (m, 1H), 2.39 (ddd, *J* = 13.9, 5.6, 2.9 Hz, 1H), 2.33 – 2.24 (m, 2H), 2.11 (dtd, *J* = 20.4, 13.6, 2.6 Hz, 3H), 1.92 (dtd, *J* = 14.9, 7.1, 3.5 Hz, 1H), 1.72 – 1.60 (m, 1H), 1.53 – 1.43 (m, 1H), 1.40 (s, 3H), 1.35 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 210.5, 109.1, 78.8, 67.3, 44.1, 42.4, 41.4, 27.2, 26.5, 25.4, 24.9;

HRMS: (ESI) calcd for $C_{11}H_{19}O_3^+$[M+H]$^+$ 199.1329; found 199.1328.

(*S*)-1-(4-(2,2-dimethyl-1,3-dioxan-4-yl)phenyl)ethan-1-one (5aa)



Chemical Formula: $C_{14}H_{18}O_3$
Exact Mass: 234.1256

5aa was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 1-(4-bromophenyl)ethan-1-one (39.8 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 10/1) to obtain **5aa** as colorless oil (29.0 mg, 62% yield, 91% ee).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 – 7.94 (m, 2H), 7.49 – 7.46 (m, 2H), 5.00 (dd, *J* = 11.7, 2.8 Hz, 1H), 4.15 (td, *J* = 12.2, 2.7 Hz, 1H), 3.94 (ddd, *J* = 11.8, 5.3, 1.6 Hz, 1H), 2.60 (s, 3H), 1.90 – 1.81 (m, 1H), 1.75 – 1.67 (m, 1H), 1.58 (s, 3H), 1.51 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.8, 147.7, 136.4, 128.6, 125.9, 98.9, 70.9, 60.0, 33.4, 30.0, 26.6, 19.2;

HRMS: (APCI) calcd for $C_{14}H_{19}O_3^+$[M+H]$^+$ 235.1329; found 235.1320.

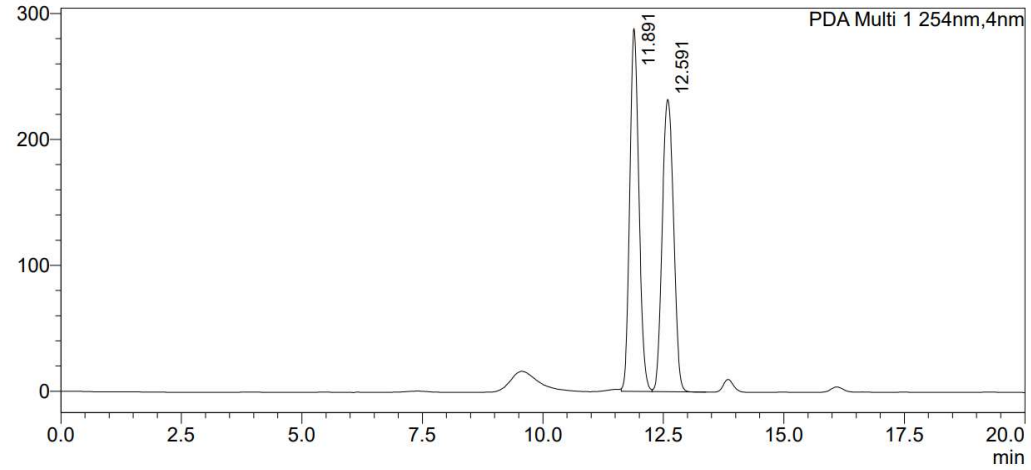
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 90/10 as eluent, 246 nm, 1 mL/min. tR = 12.6 min (major), 11.9 min (minor).

Optical Rotation: $[\alpha]_D^{24}$ -7.5 (c 0.2, ^{i}PrOH) for 91% ee.

Absolute stereochemistry was determined through analogy with **5ag**.

<Chromatogram>

mAU



<Peak Table>

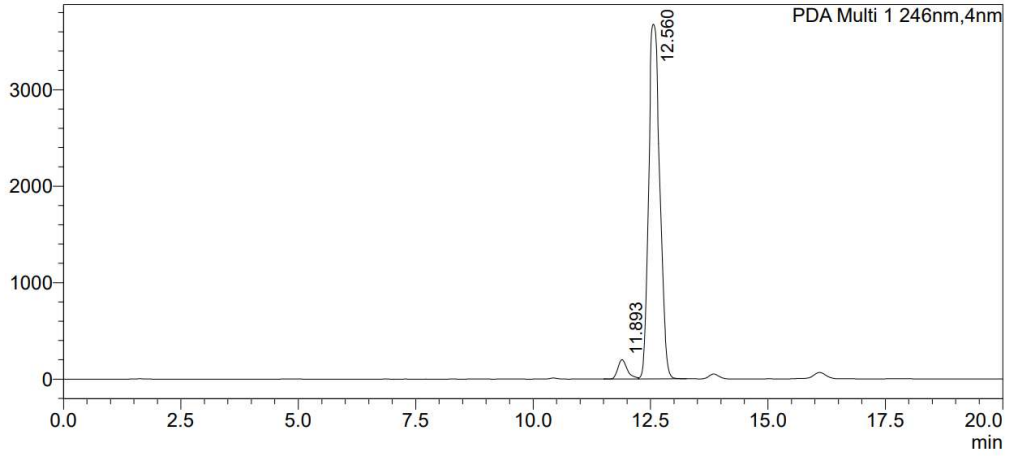
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.891	3811874	288191	0.000		M	
2	12.591	3806980	232106	0.000		V M	
Total		7618853	520297				

Supplementary Figure 51. HPLC spectrum of racemic-**5aa**

<Chromatogram>

mAU



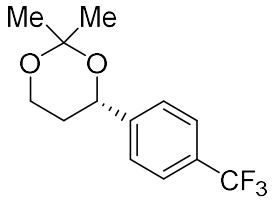
<Peak Table>

PDA Ch1 246nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.893	2822812	201075	4.432		M	
2	12.560	60875398	3673934	95.568		V M	
Total		63698210	3875009				

Supplementary Figure 52. HPLC spectrum of (*S*)-**5aa**

(*S*)-2,2-dimethyl-4-(4-(trifluoromethyl)phenyl)-1,3-dioxane (5ac)



Chemical Formula: $C_{13}H_{15}F_3O_2$
Exact Mass: 260.1024

5ac was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 1-bromo-4-(trifluoromethyl)benzene (45.0 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 50/1) to obtain **5ac** as colorless oil (21.8 mg, 42% yield, 95% ee).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 4.92 (dd, *J* = 11.8, 2.7 Hz, 1H), 4.07 (td, *J* = 12.2, 2.6 Hz, 1H), 3.87 (dd, *J* = 11.9, 5.2 Hz, 1H), 1.78 (qd, *J* = 12.5, 5.2 Hz, 1H), 1.65 – 1.60 (m, 1H), 1.51 (s, 3H), 1.44 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.4, 129.8 (q, *J* = 32.3 Hz), 126.2, 125.4 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 271.9 Hz), 98.9, 70.8, 60.0, 33.4, 30.0, 19.2;

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.50.

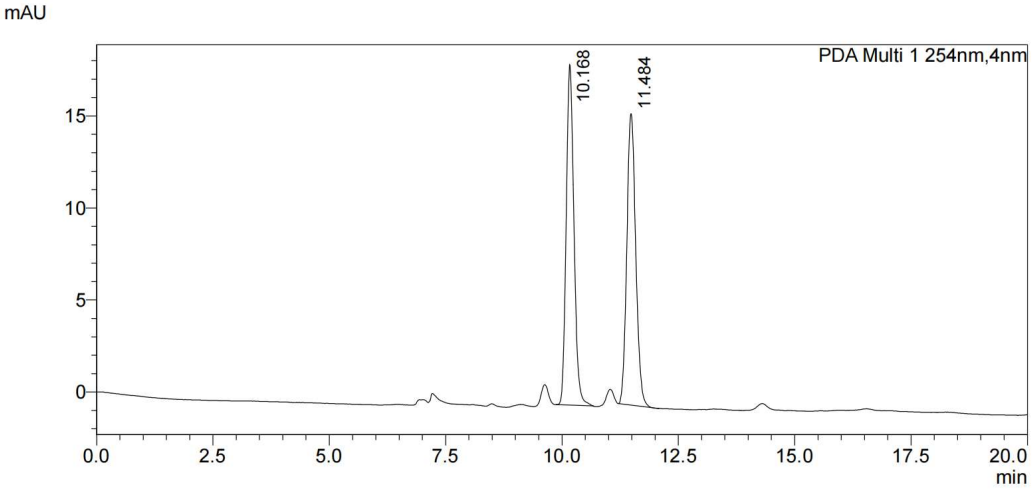
HRMS: (ESI) calcd for $C_{13}H_{16}F_3O_2^+$[M+H]$^+$ 261.1097; found 261.1102.

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 98/2 as eluent, 190 nm, 0.5 mL/min. tR = 11.5 min (major), 10.2 min (minor).

Optical Rotation: $[\alpha]_D^{24}$ -18.8 (c 0.1, ^{i}PrOH) for 95% ee.

Absolute stereochemistry was determined through analogy with **5ag**.

<Chromatogram>



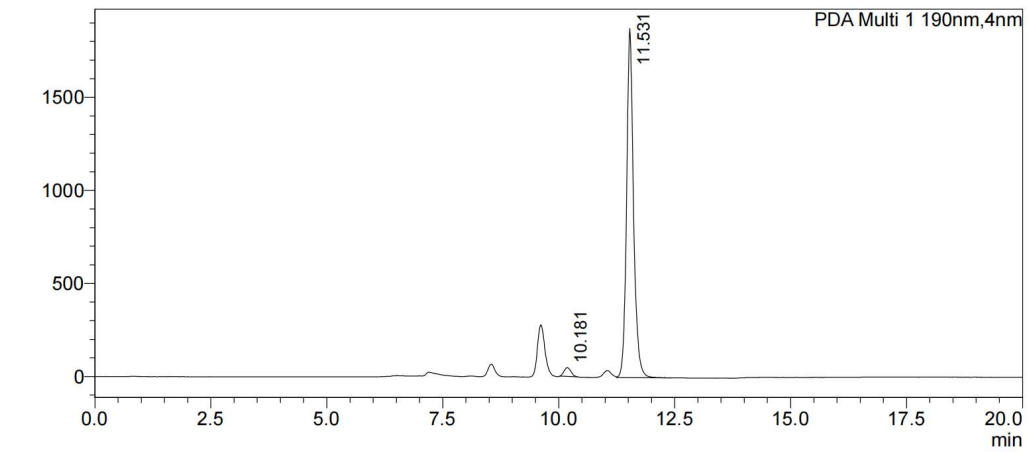
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.168	214332	18516	0.000		M	
2	11.484	211341	15843	0.000		M	
Total		425674	34359				

Supplementary Figure 53. HPLC spectrum of racemic-**5ac**

<Chromatogram>



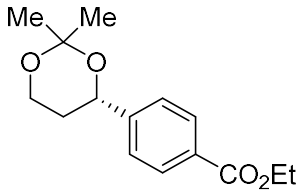
<Peak Table>

PDA Ch1 190nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.181	489420	47266	0.000		M	
2	11.531	19508985	1874902	0.000		M	
Total		19998405	1922169				

Supplementary Figure 54. HPLC spectrum of (*S*)-**5ac**

ethyl (*S*)-4-(2,2-dimethyl-1,3-dioxan-4-yl)benzoate (5ad)



Chemical Formula: $C_{15}H_{20}O_4$
Exact Mass: 264.1362

5ad was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), ethyl 4-bromobenzoate (45.8 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 15/1) to obtain **5ad** as colorless oil (21.1 mg, 40% yield, 91% ee).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.92 (dd, *J* = 11.6, 2.7 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.07 (td, *J* = 12.2, 2.5 Hz, 1H), 3.86 (dd, *J* = 11.9, 5.1 Hz, 1H), 1.78 (qd, *J* = 12.5, 5.2 Hz, 1H), 1.62 – 1.57 (m, 1H), 1.55 (s, 3H), 1.44 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 147.4, 129.8 129.7 125.7 98.9 71.0, 61.0, 60.0, 33.4, 30.0, 19.2, 14.3;

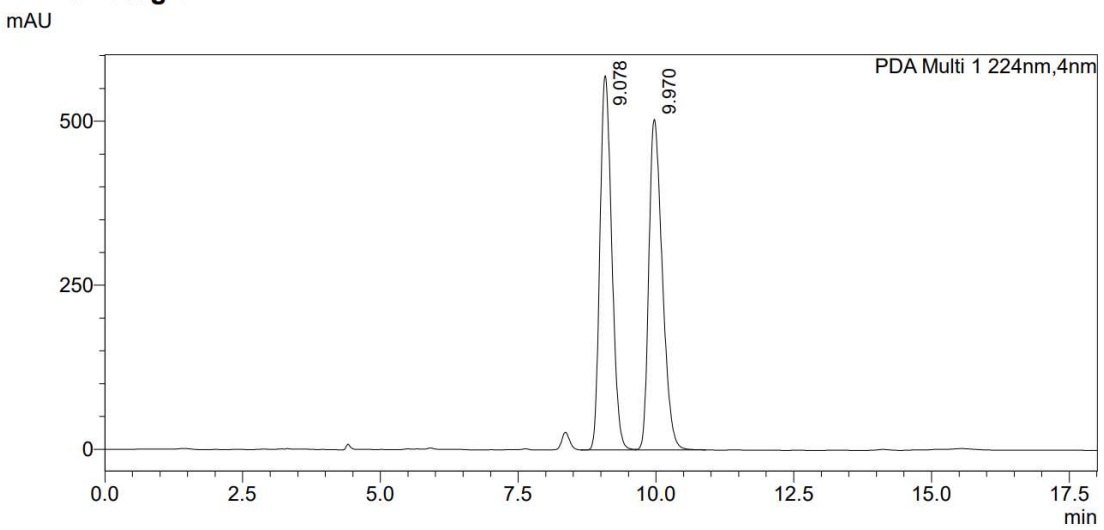
HRMS: (APCI) calcd for $C_{15}H_{21}O_4^+$[M+H]$^+$ 265.1434; found 265.1434.

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 95/5 as eluent, 224 nm, 1 mL/min. tR = 9.0 min (major), 9.9 min (minor).

Optical Rotation: $[\alpha]_D^{24}$ -41.6 (c 0.1, ^{i}PrOH) for 91% ee.

Absolute stereochemistry was determined through analogy with **5ag**.

<Chromatogram>



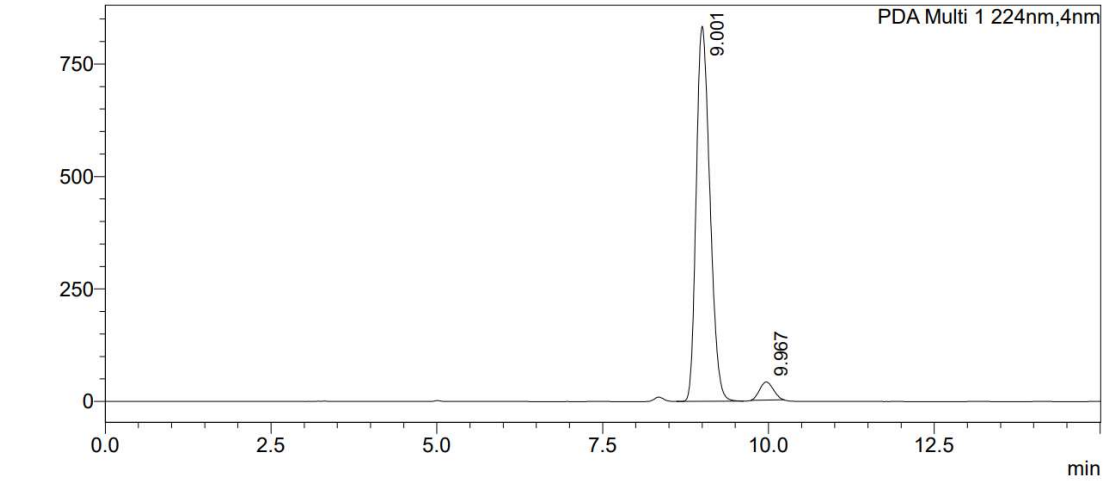
<Peak Table>

PDA Ch1 224nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.078	8492705	570304	0.000		M	
2	9.970	8549454	503686	0.000		V M	
Total		17042158	1073990				

Supplementary Figure 55. HPLC spectrum of racemic-**5ad**

<Chromatogram>



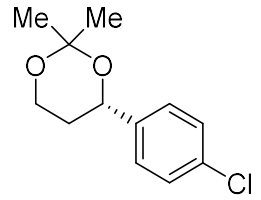
<Peak Table>

PDA Ch1 224nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.001	11959963	833786	0.000		M	
2	9.967	575323	40062	0.000		M	
Total		12535286	873848				

Supplementary Figure 56. HPLC spectrum of (*S*)-**5ad**

(*S*)-4-(4-chlorophenyl)-2,2-dimethyl-1,3-dioxane (5af)



Chemical Formula: $C_{12}H_{15}ClO_2$
Exact Mass: 226.0761

5af was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 1-bromo-4-chlorobenzene (38.2 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 50/1) to obtain **5af** as colorless oil (28.5 mg, 63% yield, 84% ee).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 1.7 Hz, 4H), 4.83 (dt, *J* = 11.9, 2.2 Hz, 1H), 4.08 – 4.01 (m, 1H), 3.88 – 3.82 (m, 1H), 1.82 – 1.72 (m, 1H), 1.62 – 1.55 (m, 1H), 1.50 (s, 3H), 1.42 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.0, 133.2, 128.6, 127.3, 98.9, 70.8, 60.0, 33.5, 30.1, 19.2;

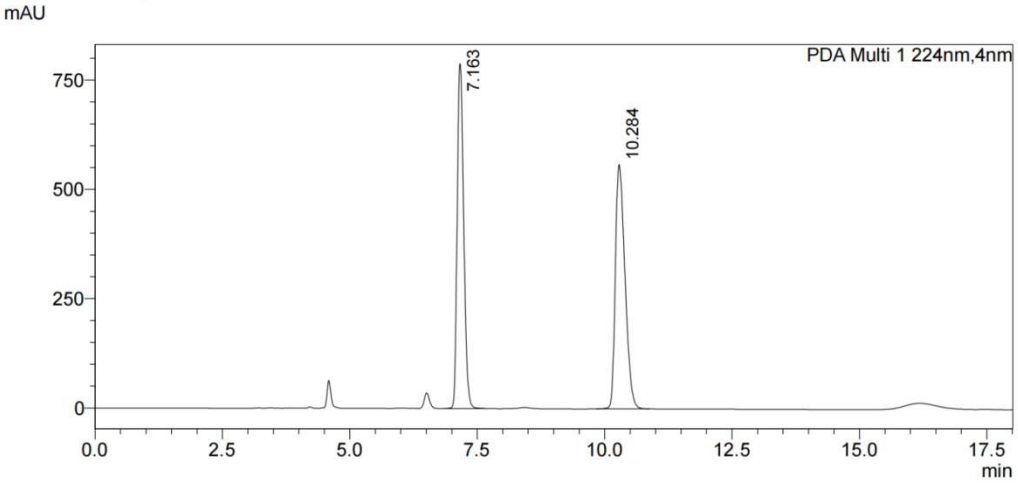
HRMS: (APCI) calcd for $C_{12}H_{16}ClO_2^+$[M+H]$^+$ 227.0833; found 227.0827.

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 97/3 as eluent, 224 nm, 1 mL/min. tR = 10.2 min (major), 7.1 min (minor).

Optical Rotation: $[\alpha]_D^{26}$ -5.7 (c 0.1, ^{i}PrOH) for 84% ee.

Absolute stereochemistry was determined through analogy with **5ag**.

<Chromatogram>



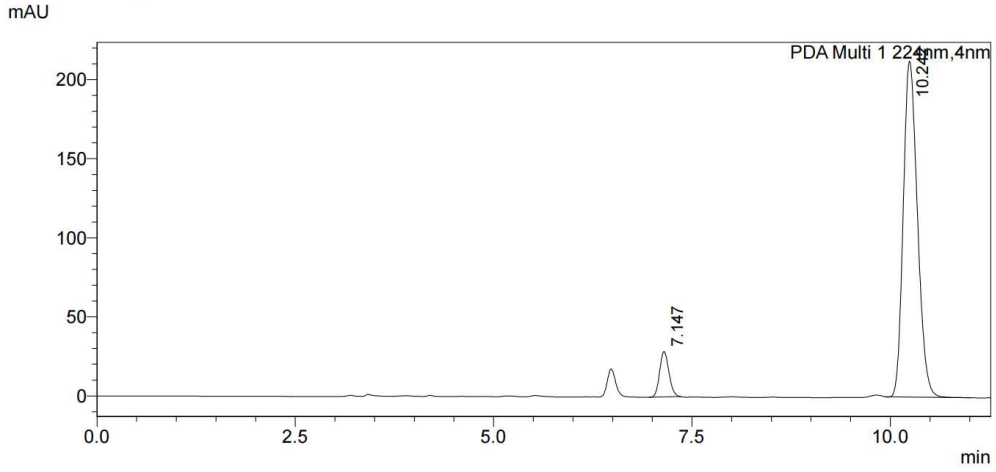
<Peak Table>

PDA Ch1 224nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.163	7007918	788473	0.000		M	
2	10.284	7362535	558830	0.000		M	
Total		14370453	1347303				

Supplementary Figure 57. HPLC spectrum of racemic-**5af**

<Chromatogram>



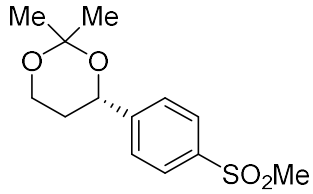
<Peak Table>

PDA Ch1 224nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.147	234080	28857	0.000		M	
2	10.242	2641777	212348	0.000		M	
Total		2875857	241205				

Supplementary Figure 58. HPLC spectrum of (*S*)-**5af**

(*S*)-2,2-dimethyl-4-(4-(methylsulfonyl)phenyl)-1,3-dioxane (5ag)



Chemical Formula: $C_{13}H_{18}O_4S$
Exact Mass: 270.0926

5ag was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 1-bromo-4-(methylsulfonyl)benzene (47.0 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 2/1) to obtain **5ag** as white solid (36.7 mg, 68% yield, 92% ee).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.91 (m, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 5.03 (dd, *J* = 11.7, 2.8 Hz, 1H), 4.15 (td, *J* = 12.2, 2.8 Hz, 1H), 3.95 (ddd, *J* = 11.8, 5.2, 1.6 Hz, 1H), 3.03 (s, 3H), 1.88 – 1.80 (m, 1H), 1.75 – 1.70 (m, 1H), 1.58 (s, 3H), 1.51 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.7, 139.6, 127.6, 126.8, 99.0, 70.7, 59.9, 44.6, 33.4, 30.0, 19.2;

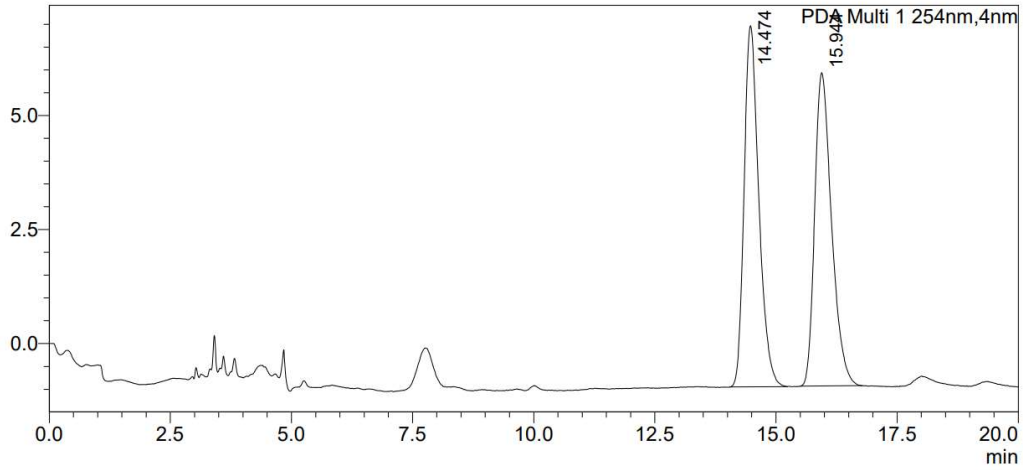
HRMS: (APCI) calcd for $C_{13}H_{19}O_4S^+[M+H]^+$ 271.0999; found 271.1002.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 90/10 as eluent, 254 nm, 1 mL/min. tR = 14.5 min (major), 15.9 min (minor).

Optical Rotation: $[\alpha]_D^{22}$ -38.5 (c 0.2, MeCN) for 92% ee.

<Chromatogram>

mAU



<Peak Table>

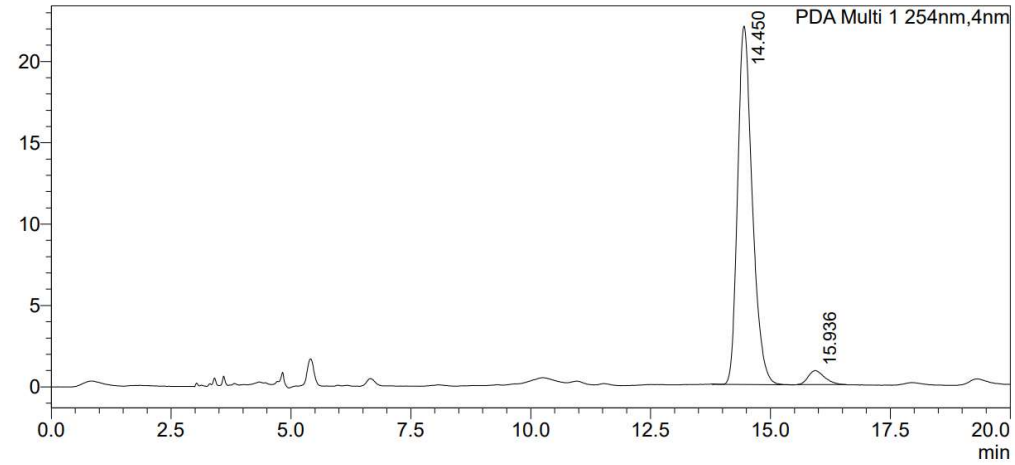
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.474	167364	7916	50.177			
2	15.944	166185	6869	49.823			
Total		333549	14785				

Supplementary Figure 59. HPLC spectrum of racemic-**5ag**

<Chromatogram>

mAU



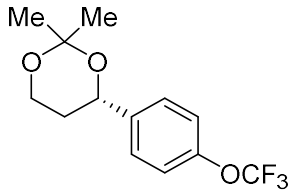
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.450	468617	22024	0.000		M	
2	15.936	20145	857	0.000		M	
Total		488762	22881				

Supplementary Figure 60. HPLC spectrum of (*S*)-**5ag**

(*S*)-2,2-dimethyl-4-(4-(trifluoromethoxy)phenyl)-1,3-dioxane (5ai)



Chemical Formula: $C_{13}H_{15}F_3O_3$
Exact Mass: 276.0973

5ai was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 1-bromo-4-(trifluoromethoxy)benzene (48.2 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain **5ai** as colorless oil (21.5 mg, 39% yield, 89% ee).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 4.94 (dd, *J* = 11.7, 2.7 Hz, 1H), 4.13 (td, *J* = 12.2, 2.7 Hz, 1H), 3.93 (ddd, *J* = 11.9, 5.4, 1.6 Hz, 1H), 1.87 (qd, *J* = 12.5, 5.3 Hz, 1H), 1.67 (dq, *J* = 13.2, 2.3 Hz, 1H), 1.58 (s, 3H), 1.50 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.5 (q, *J* = 1.5 Hz), 141.2, 127.4, 121.1, 120.5 (q, *J* = 256.9 Hz), 98.9, 70.8, 60.0, 33.5, 30.1, 19.2;

^{19}F NMR (565 MHz, $CDCl_3$) δ -57.89

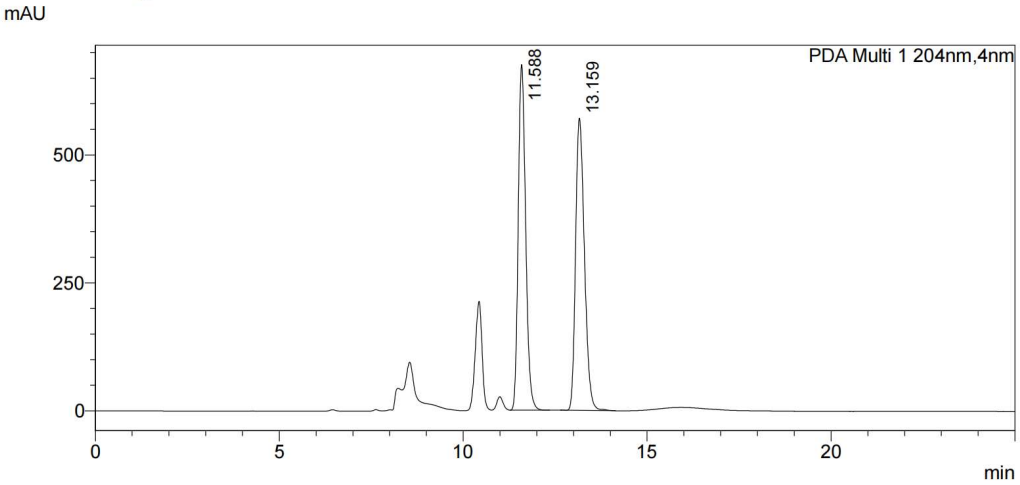
HRMS: (APCI) calcd for $C_{13}H_{16}F_3O_3^+$[M+H]$^+$ 277.1046; found 277.1048.

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 99/1 as eluent, 191 nm, 0.5 mL/min. tR = 13.0 min (major), 11.5 min (minor).

Optical Rotation: $[\alpha]_D^{23}$ -28.4 (c 0.1, ^{i}PrOH) for 89% ee.

Absolute stereochemistry was determined through analogy with **5ag**.

<Chromatogram>



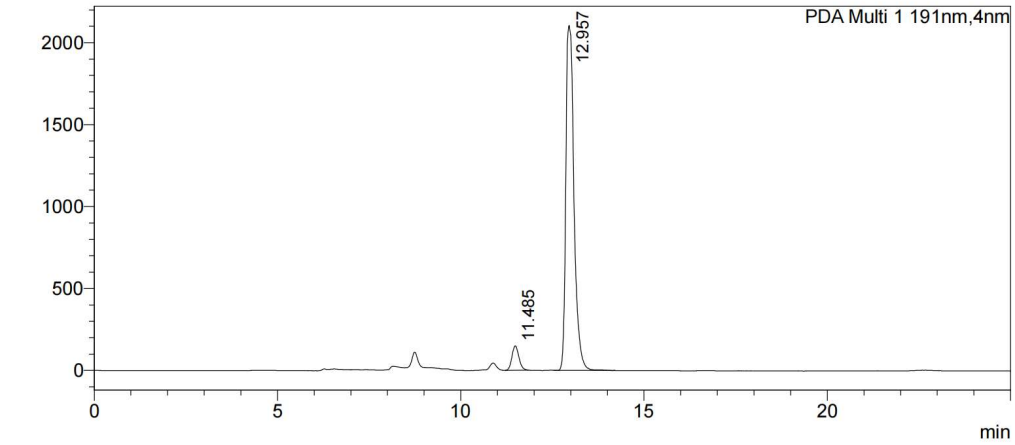
<Peak Table>

PDA Ch1 204nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.588	9451550	675058	0.000		M	
2	13.159	9526754	570771	0.000		M	
Total		18978304	1245828				

Supplementary Figure 61. HPLC spectrum of racemic-**5ai**

<Chromatogram>



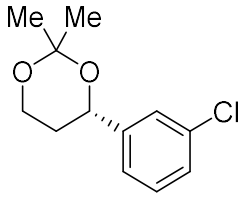
<Peak Table>

PDA Ch1 191nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.485	1951388	149173	5.660		M	
2	12.957	32522567	2103878	94.340		M	
Total		34473955	2253051				

Supplementary Figure 62. HPLC spectrum of (*S*)-**5ai**

(*S*)-4-(3-chlorophenyl)-2,2-dimethyl-1,3-dioxane (5al)



Chemical Formula: $C_{12}H_{15}ClO_2$
Exact Mass: 226.0761

5al was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 1-bromo-3-chlorobenzene (38.2 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 50/1) to obtain **5al** as colorless oil (28.0 mg, 62% yield, 88% ee).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (t, *J* = 1.9 Hz, 1H), 7.27 – 7.22 (m, 3H), 4.91 (dd, *J* = 11.7, 2.8 Hz, 1H), 4.12 (td, *J* = 12.2, 2.7 Hz, 1H), 3.93 (ddd, *J* = 11.8, 5.3, 1.6 Hz, 1H), 1.90 – 1.81 (m, 1H), 1.67 (dtd, *J* = 13.2, 2.7, 1.6 Hz, 1H), 1.57 (s, 3H), 1.50 (s, 3H);

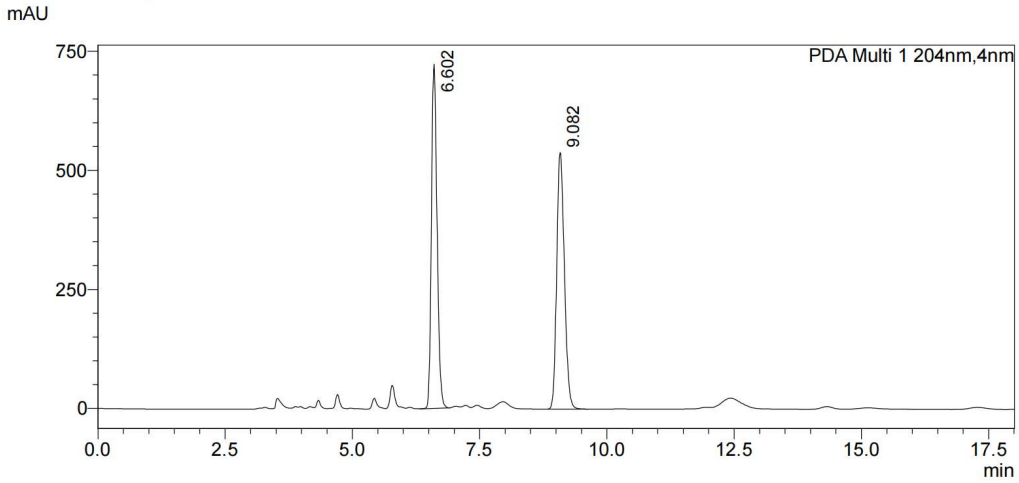
^{13}C NMR (151 MHz, $CDCl_3$) δ 144.5, 134.4, 129.7, 127.7, 126.2, 124.0, 98.9, 70.8, 60.0, 33.4, 30.0, 19.2;

HRMS: (APCI) calcd for $C_{12}H_{16}ClO_2^+$[M+H]$^+$ 227.0833; found 227.0827.

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 97/3 as eluent, 200 nm, 1 mL/min. tR = 6.5 min (major), 9.0 min (minor).

Absolute stereochemistry was determined through analogy with **5ag**.

<Chromatogram>



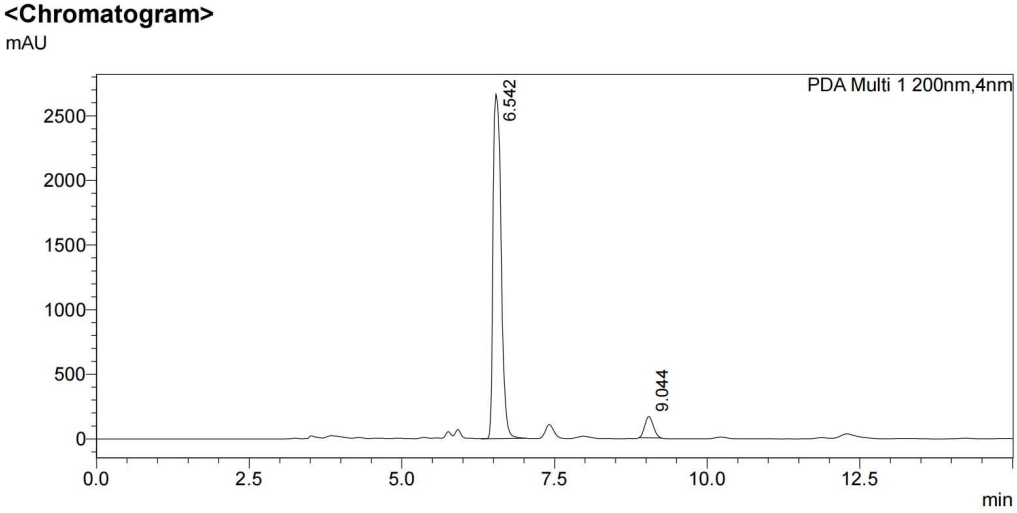
<Peak Table>

PDA Ch1 204nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.602	5567262	722126	0.000		M	
2	9.082	5655278	538406	0.000		M	
Total		11222540	1260532				

Supplementary Figure 63. HPLC spectrum of racemic-**5al**

<Chromatogram>



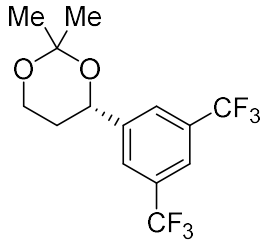
<Peak Table>

PDA Ch1 200nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.542	24402983	2667852	0.000		M	
2	9.044	1595680	164710	0.000		M	
Total		25998663	2832562				

Supplementary Figure 64. HPLC spectrum of (*S*)-**5al**

(*S*)-4-(3,5-bis(trifluoromethyl)phenyl)-2,2-dimethyl-1,3-dioxane (5ao)



Chemical Formula: $C_{14}H_{14}F_6O_2$
Exact Mass: 328.0898

5ao was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 1-bromo-3,5-bis(trifluoromethyl)benzene (58.6 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 50/1) to obtain **5ao** as colorless oil (38.0 mg, 58% yield, 93% ee).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 1.6 Hz, 2H), 7.79 (s, 1H), 5.06 (dd, *J* = 11.6, 3.0 Hz, 1H), 4.15 (td, *J* = 12.1, 2.9 Hz, 1H), 3.96 (ddd, *J* = 11.9, 5.2, 1.7 Hz, 1H), 1.84 (dtd, *J* = 13.1, 11.9, 5.2 Hz, 1H), 1.76 (dtd, *J* = 13.2, 2.9, 1.7 Hz, 1H), 1.58 (s, 3H), 1.53 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.0, 131.7 (q, *J* = 33.2 Hz), 126.1 (q, *J* = 4.9, 4.1 Hz), 123.3 (q, *J* = 272.5 Hz), 121.5 (p, *J* = 3.9 Hz), 99.2, 70.2, 59.8, 33.3, 29.9, 19.1;

^{19}F NMR (575 MHz, $CDCl_3$) δ -62.82.

HRMS: (APCI) calcd for $C_{14}H_{15}F_6O_2^+$[M+H]$^+$ 329.0971; found 329.0962.

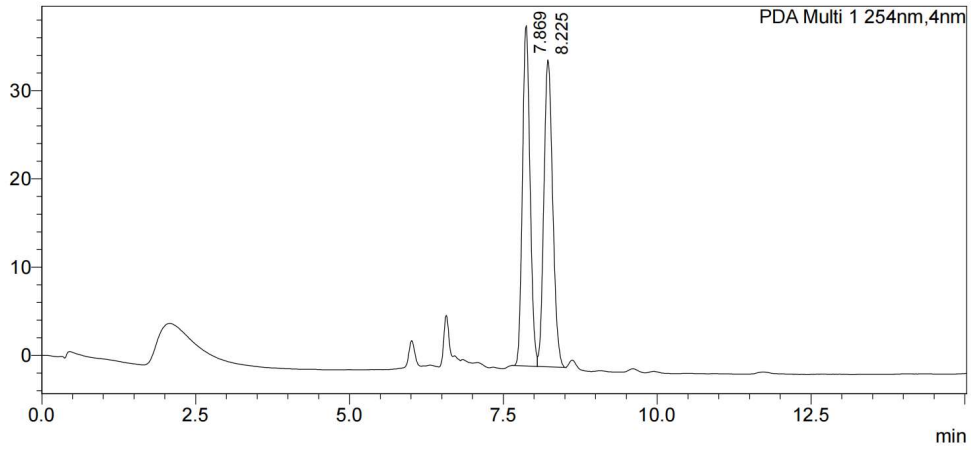
The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 99/1 as eluent, 254 nm, 0.5 mL/min. tR = 8.5 min (major), 8.0 min (minor).

Optical Rotation: $[\alpha]_D^{25}$ -121.6 (c 0.1, ^{i}PrOH) for 93% ee.

Absolute stereochemistry was determined through analogy with **5ag**.

<Chromatogram>

mAU



<Peak Table>

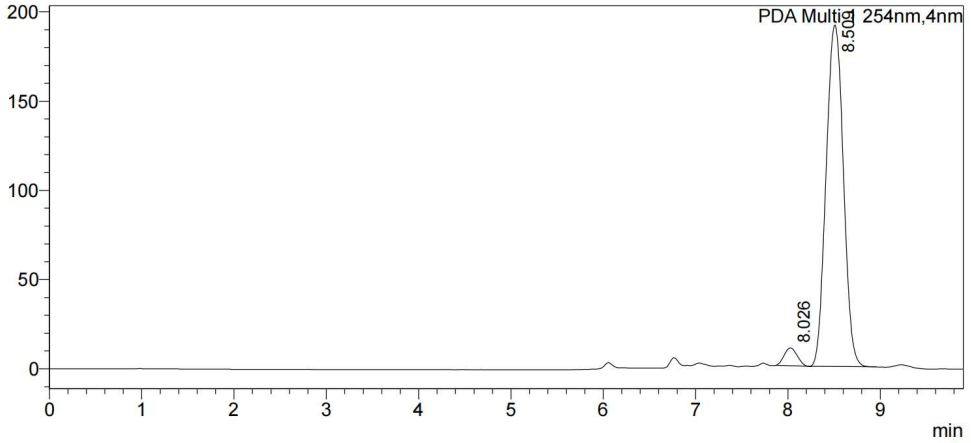
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.869	331433	38530	0.000		M	
2	8.225	347239	34744	0.000		V M	
Total		678672	73274				

Supplementary Figure 65. HPLC spectrum of racemic-**5ao**

<Chromatogram>

mAU



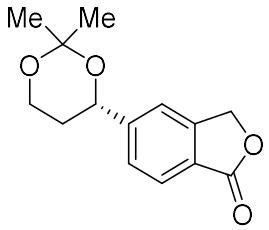
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.026	97120	9985	0.000		M	
2	8.509	2494123	191390	0.000		M	
Total		2591243	201375				

Supplementary Figure 66. HPLC spectrum of (*S*)-**5ao**

(*S*)-5-(2,2-dimethyl-1,3-dioxan-4-yl)isobenzofuran-1(3H)-one (5aq)



Chemical Formula: $C_{14}H_{16}O_4$
Exact Mass: 248.1049

5aq was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 5-bromoisobenzofuran-1(3H)-one (42.6 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **5aq** as colorless oil (21.3 mg, 43% yield, 95% ee).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.9 Hz, 1H), 7.50 (s, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 5.25 (s, 2H), 5.02 – 4.98 (m, 1H), 4.09 (tt, *J* = 12.2, 2.0 Hz, 1H), 3.88 (dd, *J* = 11.9, 5.2 Hz, 1H), 1.77 (qd, *J* = 12.3, 5.1 Hz, 1H), 1.67 (d, *J* = 3.3 Hz, 1H), 1.52 (s, 3H), 1.45 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 149.4, 147.2, 126.9, 125.8, 125.0, 119.3, 99.0, 71.0, 69.7, 59.9, 33.6, 30.0, 19.2;

HRMS: (ESI) calcd for $C_{14}H_{17}O_4^+$[M+H]$^+$ 249.1121; found 249.1123.

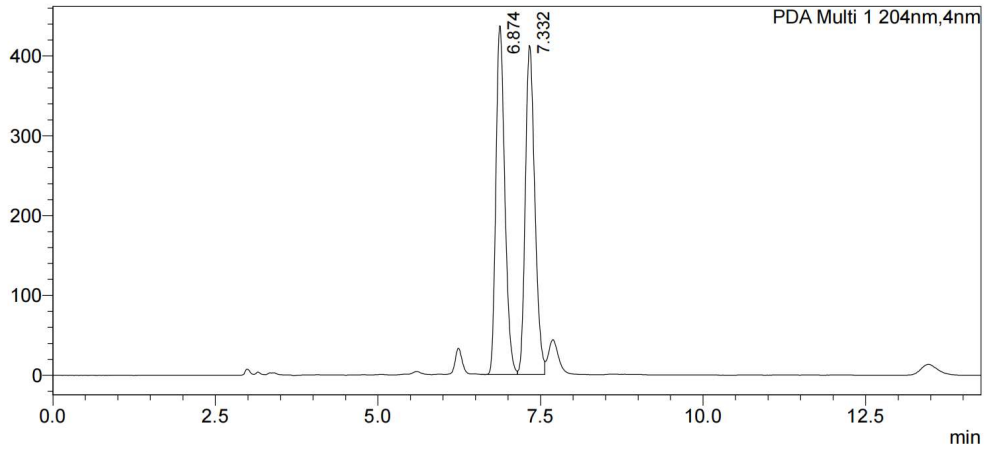
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 80/20 as eluent, 204 nm, 1 mL/min. tR = 7.3 min (major), 6.9 min (minor).

Optical Rotation: $[\alpha]_D^{23}$ -4.5 (c 0.1, ^{i}PrOH) for 95% ee.

Absolute stereochemistry was determined through analogy with **5ag**.

<Chromatogram>

mAU



<Peak Table>

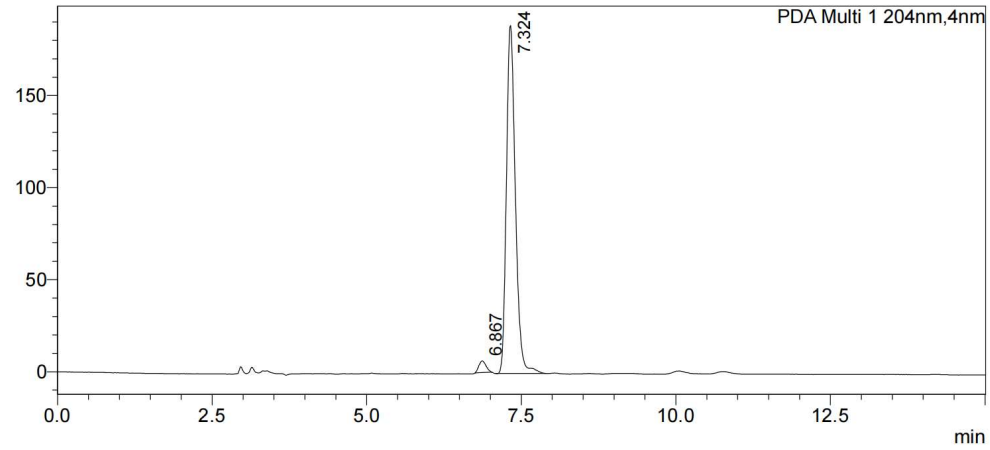
PDA Ch1 204nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.874	4162748	436518	0.000		M	
2	7.332	4191976	412056	0.000		V M	
Total		8354724	848574				

Supplementary Figure 67. HPLC spectrum of racemic-**5aq**

<Chromatogram>

mAU



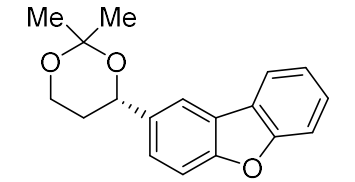
<Peak Table>

PDA Ch1 204nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.867	50969	6335	0.000		M	
2	7.324	1905729	188916	0.000		M	
Total		1956698	195251				

Supplementary Figure 68. HPLC spectrum of (*S*)-**5aq**

(*S*)-2-(2,2-dimethyl-1,3-dioxan-4-yl)dibenzo[b,d]furan (5as)



Chemical Formula: $C_{18}H_{18}O_3$
Exact Mass: 282.1256

5as was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 2-bromodibenzo[b,d]furan (49.4 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain **5as** as colorless oil (26.0 mg, 46% yield, 82% ee).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 1.8 Hz, 1H), 7.98 – 7.95 (m, 1H), 7.55 (dd, *J* = 12.2, 8.3 Hz, 2H), 7.48 – 7.44 (m, 2H), 7.34 (td, *J* = 7.5, 1.0 Hz, 1H), 5.10 (dd, *J* = 11.7, 2.8 Hz, 1H), 4.19 (td, *J* = 12.2, 2.6 Hz, 1H), 3.98 (ddd, *J* = 11.8, 5.3, 1.5 Hz, 1H), 2.04 – 1.97 (m, 1H), 1.76 (dtd, *J* = 13.3, 2.7, 1.5 Hz, 1H), 1.63 (s, 3H), 1.55 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.6, 155.7, 137.2, 127.2, 127.1, 125.4, 124.3, 124.2, 122.7, 120.8, 118.2, 111.7, 111.5, 99.0, 71.6, 60.3, 34.0, 30.2, 19.3;

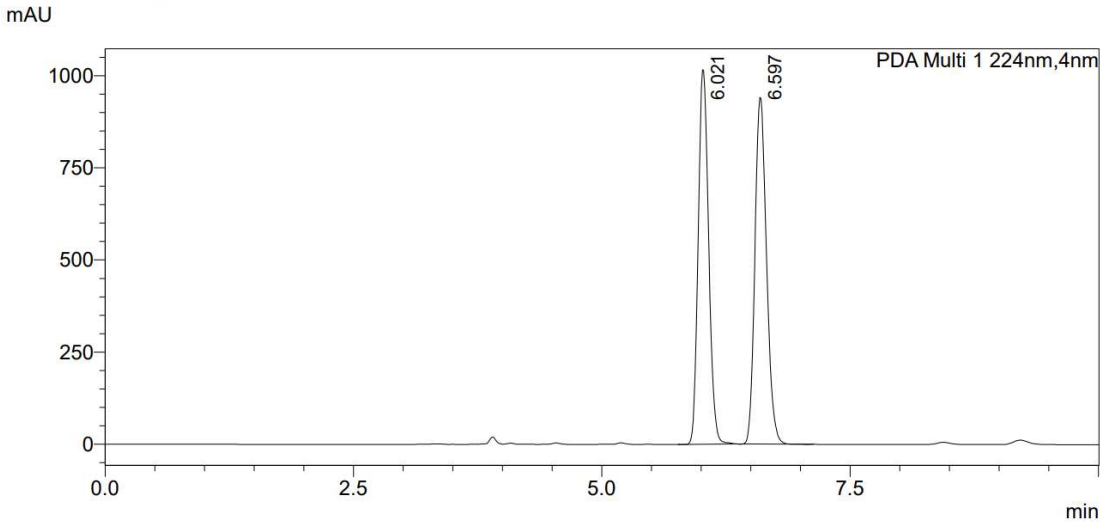
HRMS: (APCI) calcd for $C_{18}H_{19}O_3^+$[M+H]$^+$ 283.1329; found 283.1321.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 97/3 as eluent, 224 nm, 1 mL/min. tR = 5.9 min (major), 6.6 min (minor).

Optical Rotation: $[\alpha]_D^{21}$ -6.0 (c 0.1, ^{i}PrOH) for 82% ee.

Absolute stereochemistry was determined through analogy with **5ag**.

<Chromatogram>



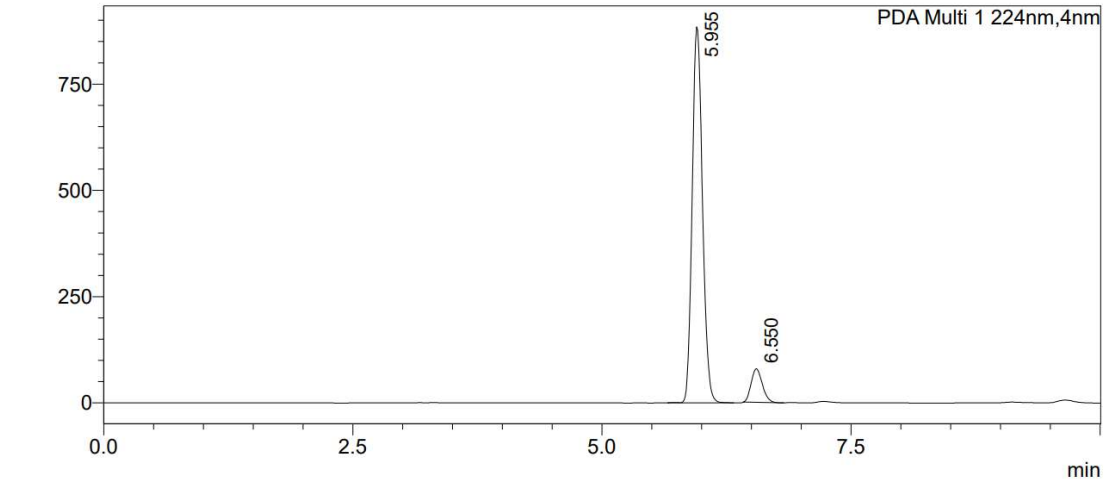
<Peak Table>

PDA Ch1 224nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.021	7401953	1015779	0.000		M	
2	6.597	7644467	940212	0.000		M	
Total		15046420	1955991				

Supplementary Figure 69. HPLC spectrum of racemic-**5as**

<Chromatogram>



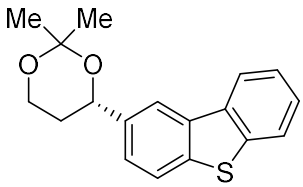
<Peak Table>

PDA Ch1 224nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.955	6350160	884044	0.000		M	
2	6.550	617246	79281	0.000		M	
Total		6967406	963325				

Supplementary Figure 70. HPLC spectrum of (*S*)-**5as**

(*S*)-4-(dibenzo[b,d]thiophen-2-yl)-2,2-dimethyl-1,3-dioxane (5at)



Chemical Formula: $C_{18}H_{18}O_2S$
Exact Mass: 298.1028

5at was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 2-bromodibenzo[b,d]thiophene (52.6 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain **5at** as colorless oil (27.4 mg, 46% yield, 91% ee).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 3.0 Hz, 2H), 7.86 – 7.79 (m, 2H), 7.46 (ddd, *J* = 12.5, 6.4, 1.6 Hz, 3H), 5.11 (dd, *J* = 11.7, 2.8 Hz, 1H), 4.18 (td, *J* = 12.1, 2.6 Hz, 1H), 3.99 – 3.94 (m, 1H), 2.00 (qd, *J* = 12.5, 3.3 Hz, 1H), 1.75 (dq, *J* = 13.2, 2.3 Hz, 1H), 1.63 (s, 3H), 1.56 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.8, 139.0, 138.7, 135.7, 135.5, 126.8, 125.0, 124.4, 122.9, 122.8, 121.7, 119.0, 99.0, 71.6, 60.2, 33.9, 30.2, 19.3;

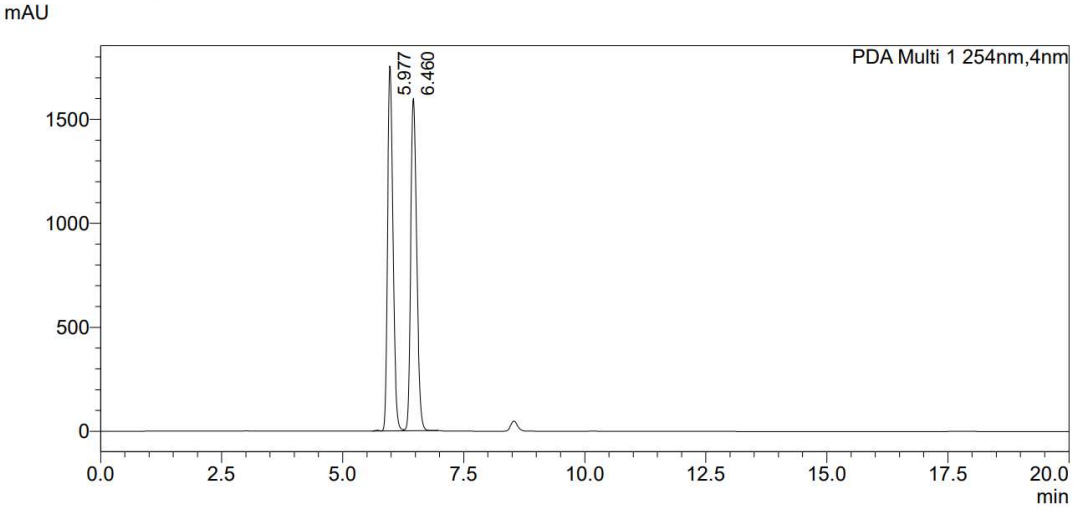
HRMS: (APCI) calcd for $C_{18}H_{19}O_2S^+[M+H]^+$ 299.1100; found 299.1092.

The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 90/10 as eluent, 254 nm, 1 mL/min. tR = 6.0 min (major), 6.5 min (minor).

Optical Rotation: $[\alpha]_D^{23}$ -29.6 (c 0.1, ^{i}PrOH) for 91% ee.

Absolute stereochemistry was determined through analogy with **5ag**.

<Chromatogram>



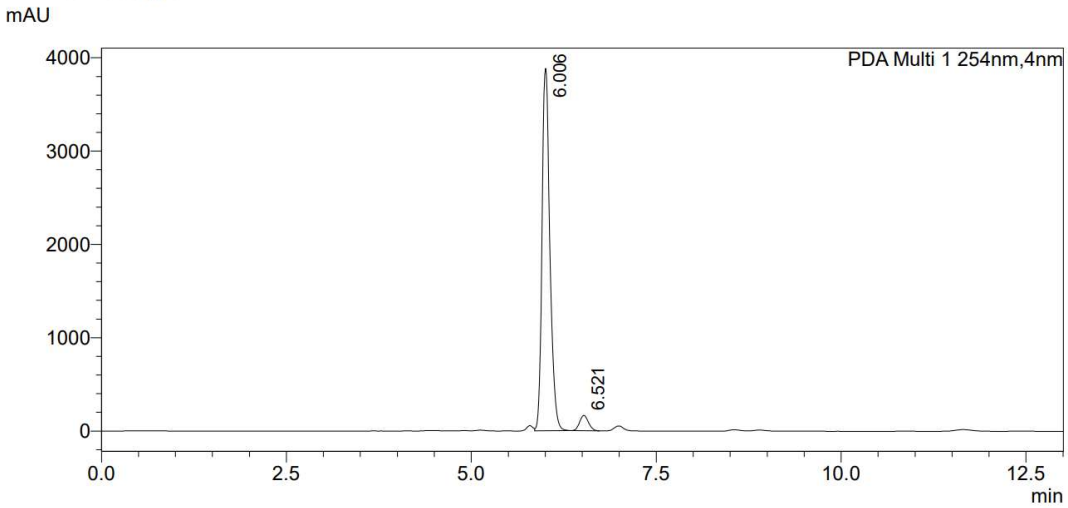
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.977	13666505	1753924	0.000		M	
2	6.460	13736060	1596837	0.000		V M	
Total		27402565	3350761				

Supplementary Figure 71. HPLC spectrum of racemic-**5at**

<Chromatogram>



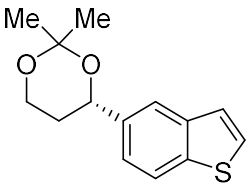
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.006	28678842	3882770	0.000		M	
2	6.521	1349813	164109	0.000		M	
Total		30028654	4046878				

Supplementary Figure 72. HPLC spectrum of (*S*)-**5at**

(*S*)-4-(benzo[b]thiophen-5-yl)-2,2-dimethyl-1,3-dioxane (5au)



Chemical Formula: $C_{14}H_{16}O_2S$
Exact Mass: 248.0871

5au was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 5-bromobenzo[b]thiophene (42.6 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 20/1) to obtain **5au** as colorless oil (22.8 mg, 46% yield, 89% ee).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 – 7.84 (m, 2H), 7.44 (d, *J* = 5.4 Hz, 1H), 7.37 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.33 (d, *J* = 5.4 Hz, 1H), 5.06 (dd, *J* = 11.7, 2.7 Hz, 1H), 4.17 (td, *J* = 12.2, 2.7 Hz, 1H), 3.96 (ddd, *J* = 11.8, 5.3, 1.6 Hz, 1H), 2.02 – 1.93 (m, 1H), 1.73 (dtd, *J* = 13.3, 2.7, 1.5 Hz, 1H), 1.53 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.8, 139.0, 138.7, 126.8, 123.9, 122.6, 122.5, 120.9, 98.9, 71.6, 60.2, 33.8, 30.2, 19.3;

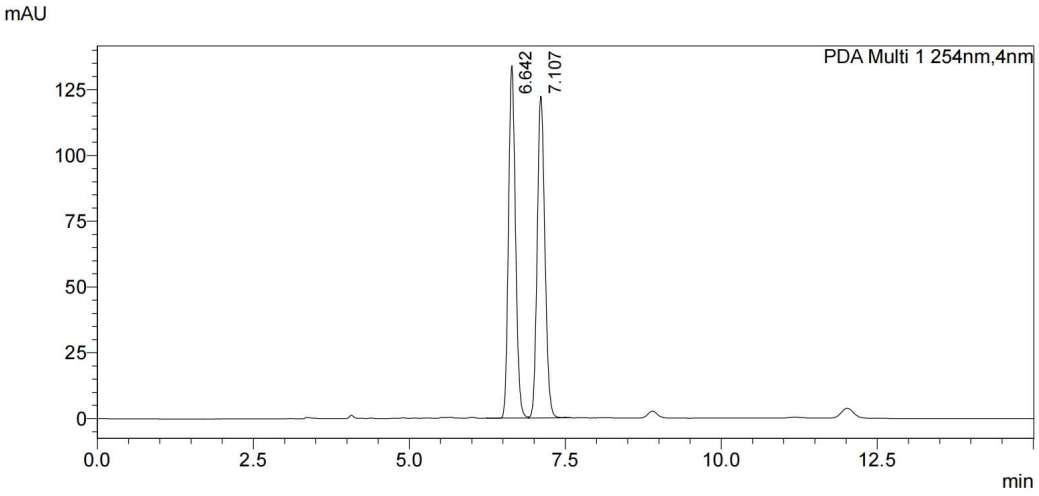
HRMS: (APCI) calcd for $C_{14}H_{17}O_2S^+[M+H]^+$ 249.0944; found 249.0940.

The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 98/2 as eluent, 214 nm, 1 mL/min. tR = 6.7 min (major), 7.2 min (minor).

Optical Rotation: $[\alpha]_D^{25}$ -2.6 (c 0.1, ^{i}PrOH) for 89% ee.

Absolute stereochemistry was determined through analogy with **5ag**.

<Chromatogram>



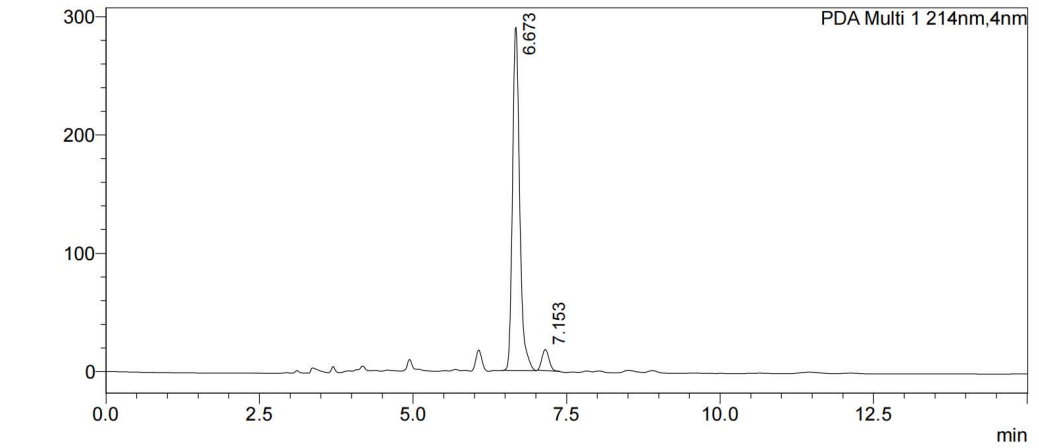
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.642	1044580	133912	0.000		M	
2	7.107	1048090	122271	0.000		V M	
Total		2092670	256183				

Supplementary Figure 73. HPLC spectrum of racemic-**5au**

<Chromatogram>



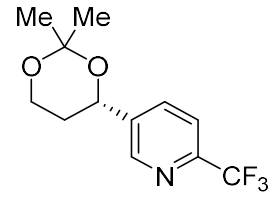
<Peak Table>

PDA Ch1 214nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.673	2362741	290245	94.341		M	
2	7.153	141736	17831	5.659		M	
Total		2504478	308075				

Supplementary Figure 74. HPLC spectrum of (*S*)-**5au**

(*S*)-5-(2,2-dimethyl-1,3-dioxan-4-yl)-2-(trifluoromethyl)pyridine (5av)



Chemical Formula: $C_{12}H_{14}F_3NO_2$
Exact Mass: 261.0977

5av was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 5-bromo-2-(trifluoromethyl)pyridine (45.2 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **5av** as colorless oil (24.5 mg, 47% yield, 91% ee).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (d, *J* = 2.1 Hz, 1H), 7.93 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 5.08 (dd, *J* = 11.8, 2.9 Hz, 1H), 4.16 (td, *J* = 12.2, 2.8 Hz, 1H), 3.96 (ddd, *J* = 12.0, 5.3, 1.6 Hz, 1H), 1.86 (qd, *J* = 12.4, 5.3 Hz, 1H), 1.75 (dq, *J* = 13.2, 2.4 Hz, 1H), 1.59 (s, 3H), 1.51 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.9, 147.4 (q, *J* = 34.7 Hz), 141.1, 134.9, 121.5 (q, *J* = 273.8 Hz), 120.3 (q, *J* = 2.5 Hz), 99.1, 68.8, 59.7, 33.2, 29.9, 19.1;

^{19}F NMR (377 MHz, $CDCl_3$) δ -67.71.

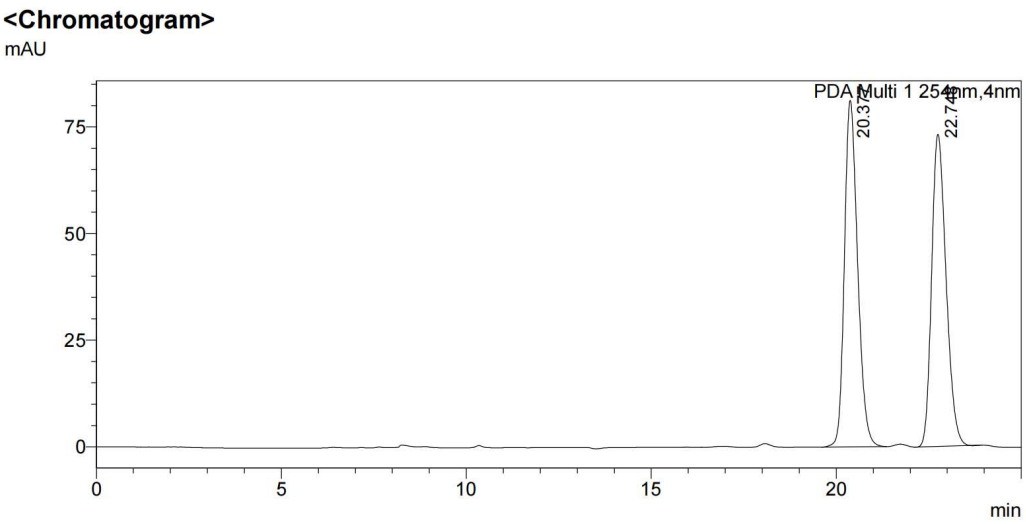
HRMS: (APCI) calcd for $C_{12}H_{15}F_3NO_2^+$[M+H]$^+$ 262.1049; found 262.1042.

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 99/1 as eluent, 254 nm, 0.5 mL/min. tR = 22.9 min (major), 20.5 min (minor).

Optical Rotation: $[\alpha]_D^{24}$ -51.0 (c 0.1, ^{i}PrOH) for 91% ee.

Absolute stereochemistry was determined through analogy with **5ag**.

<Chromatogram>



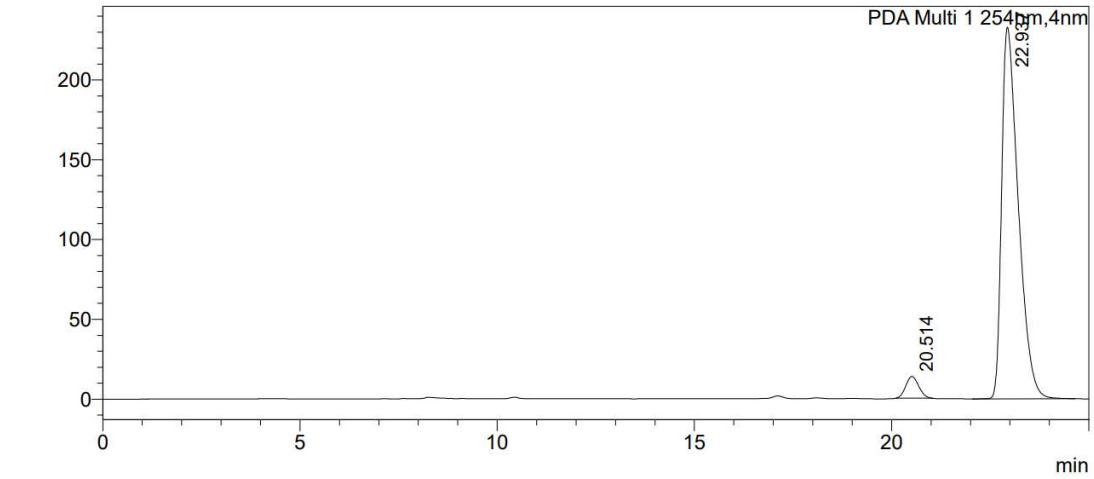
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.377	2013020	81223	0.000		M	
2	22.748	1981980	73179	0.000		M	
Total		3994999	154403				

Supplementary Figure 75. HPLC spectrum of racemic-**5av**

<Chromatogram>



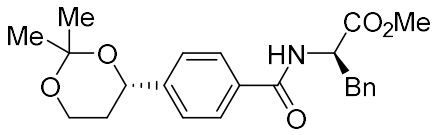
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.514	309606	13587	0.000		M	
2	22.937	6832496	232928	0.000		M	
Total		7142102	246515				

Supplementary Figure 76. HPLC spectrum of (*S*)-**5av**

methyl (4-((*S*)-2,2-dimethyl-1,3-dioxan-4-yl)benzoyl)-*D*-phenylalaninate (5ax)



Chemical Formula: $C_{23}H_{27}NO_5$
Exact Mass: 397.1889

5ax was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), methyl (4-bromobenzoyl)-*D*-phenylalaninate (72.2 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 3/1) to obtain **5ax** as colorless oil (57.9 mg, 73% yield, d.r. > 20/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.22 (m, 3H), 7.14 – 7.09 (m, 2H), 6.59 (d, *J* = 7.6 Hz, 1H), 5.11 – 5.05 (m, 1H), 4.97 (dd, *J* = 11.7, 2.8 Hz, 1H), 4.16 – 4.10 (m, 1H), 3.95 – 3.90 (m, 1H), 3.76 (s, 3H), 3.29 (dd, *J* = 13.9, 5.8 Hz, 1H), 3.21 (dd, *J* = 13.9, 5.4 Hz, 1H), 1.89 – 1.80 (m, 1H), 1.71 – 1.65 (m, 1H), 1.57 (s, 3H), 1.50 (s, 3H);

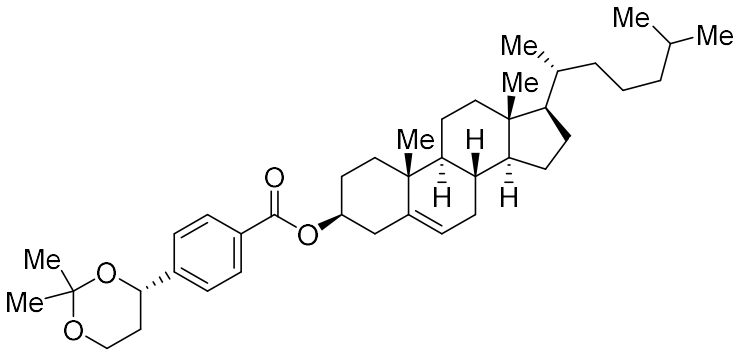
^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 166.6, 146.4, 135.9, 133.1, 129.3, 128.6, 127.2, 126.0, 98.9, 70.9, 60.0, 53.5, 52.4, 37.9, 33.4, 30.0, 19.2;

HRMS: (ESI) calcd for $C_{23}H_{28}NO_5^+[M+H]^+$ 398.1962; found 398.1961.

Optical Rotation: $[\alpha]_D^{24}$ 71.8 (c 0.2, ^{i}PrOH).

Absolute stereochemistry was determined through analogy with **5ag**.

3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-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-((*S*)-2,2-dimethyl-1,3-dioxan-4-yl)benzoate (5az)



Chemical Formula: $C_{40}H_{60}O_4$
Exact Mass: 604.4492

5az was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-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-bromobenzoate (113.9 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 40/1) to obtain **5az** as colorless oil (67.7 mg, 56% yield, d.r. > 20/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 2H), 7.45 – 7.42 (m, 2H), 5.42 (dd, *J* = 5.0, 2.1 Hz, 1H), 4.99 (dd, *J* = 11.7, 2.8 Hz, 1H), 4.85 (dtd, *J* = 16.3, 8.4, 4.5 Hz, 1H), 4.14 (td, *J* = 12.2, 2.7 Hz, 1H), 3.93 (ddd, *J* = 11.8, 5.3, 1.6 Hz, 1H), 2.47 – 2.44 (m, 2H), 2.04 – 1.96 (m, 3H), 1.91 (dt, *J* = 13.4, 3.6 Hz, 1H), 1.84 (tdd, *J* = 12.8, 10.3, 5.4 Hz, 2H), 1.75 – 1.71 (m, 1H), 1.71 – 1.67 (m, 1H), 1.59 – 1.45 (m, 12H), 1.40 – 1.31 (m, 3H), 1.28 – 1.09 (m, 8H), 1.07 (s, 3H), 1.03 – 0.96 (m, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 2.8 Hz, 3H), 0.86 (d, *J* = 2.8 Hz, 3H), 0.69 (s, 3H);

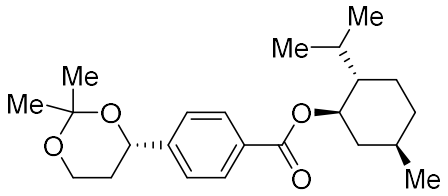
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 147.4, 139.7, 130.0, 129.8, 125.6, 122.8, 98.9, 74.6, 71.0, 60.0, 56.7, 56.2, 50.1, 42.3, 39.8, 39.5, 38.2, 37.0, 36.7, 36.2, 35.8, 33.5, 32.0, 31.9, 30.0, 28.3, 28.0, 27.9, 24.3, 23.8, 22.9, 22.6, 21.1, 19.4, 19.2, 18.7, 11.9;

HRMS: (APCI) calcd for $C_{40}H_{61}O_4^+$[M+H]$^+$ 605.4564; found 605.4558.

Optical Rotation: $[\alpha]_D^{22}$ -6.2 (c 0.1, ^{i}PrOH).

Absolute stereochemistry was determined through analogy with **5ag**.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-((*S*)-2,2-dimethyl-1,3-dioxan-4-yl)benzoate (5aaa)



Chemical Formula: $C_{23}H_{34}O_4$
Exact Mass: 374.2457

5aaa was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-bromobenzoate (67.6 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 3/1) to obtain **5aaa** as colorless oil (46.4 mg, 62% yield, d.r. > 20/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 2H), 7.46 – 7.42 (m, 2H), 4.98 (dd, *J* = 11.7, 2.8 Hz, 1H), 4.94 – 4.89 (m, 1H), 4.16 – 4.10 (m, 1H), 3.95 – 3.90 (m, 1H), 2.15 – 2.08 (m, 1H), 1.97 – 1.90 (m, 1H), 1.89 – 1.80 (m, 1H), 1.75 – 1.66 (m, 3H), 1.60 – 1.52 (m, 5H), 1.50 (s, 3H), 1.16 – 1.05 (m, 2H), 0.91 (dd, *J* = 9.9, 6.8 Hz, 7H), 0.78 (d, *J* = 6.9 Hz, 3H);

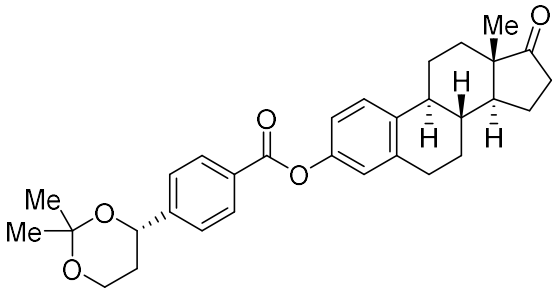
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 147.3, 130.1, 129.8, 125.7, 98.9, 74.8, 70.9, 60.0, 47.3, 41.0, 34.3, 33.4, 31.5, 30.0, 26.6, 23.7, 22.1, 20.8, 19.2, 16.6;

HRMS: (APCI) calcd for $C_{23}H_{35}O_4^+$[M+H]$^+$ 375.2529; found 375.2522.

Optical Rotation: $[\alpha]_D^{24}$ 71.8 (c 0.2, ^{i}PrOH).

Absolute stereochemistry was determined through analogy with **5ag**.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 4-((*S*)-2,2-dimethyl-1,3-dioxan-4-yl)benzoate (5aab)



Chemical Formula: $C_{31}H_{36}O_5$
Exact Mass: 488.2563

5aab was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), (8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 4-bromobenzoate (90.7 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 4/1) to obtain **5aab** as yellow solid (45.9 mg, 47% yield, d.r. > 20/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 1H), 6.98 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.94 (d, *J* = 2.5 Hz, 1H), 5.03 (dd, *J* = 11.8, 2.8 Hz, 1H), 4.16 (td, *J* = 12.1, 2.6 Hz, 1H), 3.97 – 3.93 (m, 1H), 2.97 – 2.92 (m, 2H), 2.52 (dd, *J* = 19.1, 8.8 Hz, 1H), 2.46 – 2.41 (m, 1H), 2.32 (td, *J* = 11.0, 4.2 Hz, 1H), 2.16 (dt, *J* = 18.6, 8.8 Hz, 2H), 2.10 – 2.00 (m, 3H), 1.98 (dt, *J* = 12.9, 3.1 Hz, 1H), 1.87 (qd, *J* = 12.5, 5.2 Hz, 1H), 1.75 – 1.71 (m, 1H), 1.62 – 1.51 (m, 10H), 0.93 (s, 3H);

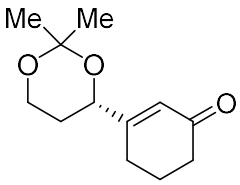
^{13}C NMR (151 MHz, $CDCl_3$) δ 220.8, 165.3, 148.8, 148.3, 138.1, 137.4, 130.4, 128.8, 126.5, 125.9, 121.7, 118.9, 99.0, 70.9, 60.0, 50.5, 48.0, 44.2, 38.0, 35.9, 33.5, 31.6, 30.0, 29.4, 26.4, 25.8, 21.6, 19.2, 13.9;

HRMS: (APCI) calcd for $C_{31}H_{37}O_5^+[M+H]^+$ 489.2636; found 489.2631.

Optical Rotation: $[\alpha]_D^{22}$ 86.9 (c 0.1, ^{i}PrOH).

Absolute stereochemistry was determined through analogy with **5ag**.

(*S*)-3-(2,2-dimethyl-1,3-dioxan-4-yl)cyclohex-2-en-1-one (5aac)



Chemical Formula: $C_{12}H_{18}O_3$
Exact Mass: 210.1256

5aac was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 3-bromocyclohex-2-en-1-one (35.0 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxane **4a** (232.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **5aac** as colorless oil (21.4 mg, 51% yield, 97% ee).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.11 (s, 1H), 4.45 (dt, *J* = 12.0, 2.0 Hz, 1H), 4.04 (td, *J* = 12.1, 2.8 Hz, 1H), 3.90 (ddd, *J* = 11.9, 5.4, 1.7 Hz, 1H), 2.40 (t, *J* = 6.7 Hz, 2H), 2.35 (dtd, *J* = 12.5, 6.2, 1.6 Hz, 1H), 2.32 – 2.26 (m, 1H), 2.01 (q, *J* = 6.4 Hz, 2H), 1.72 (dd, *J* = 12.3, 5.3 Hz, 1H), 1.60 (dq, *J* = 13.1, 2.4 Hz, 1H), 1.49 (s, 3H), 1.43 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 199.9, 163.9, 124.1, 98.7, 71.0, 59.7, 37.8, 29.8, 29.7, 25.6, 22.6, 19.1;

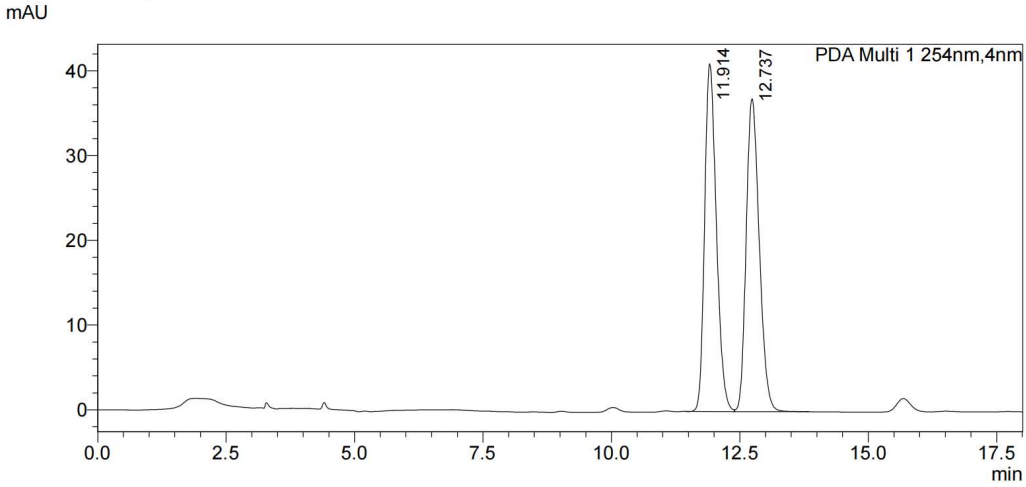
HRMS: (APCI) calcd for $C_{12}H_{19}O_2^+$[M+H]$^+$ 211.1329; found 211.1328.

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 95/5 as eluent, 254 nm, 1 mL/min. tR = 12.8 min (major), 12.0 min (minor).

Optical Rotation: $[\alpha]_D^{22}$ -13.6 (c 0.1, ^{i}PrOH) for 97% ee.

Absolute stereochemistry was determined through analogy with **5ag**.

<Chromatogram>



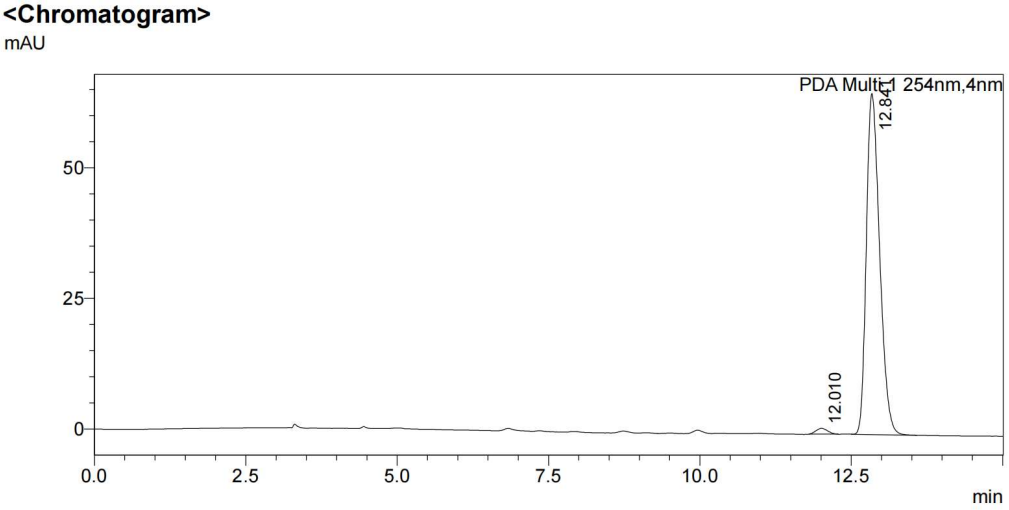
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.914	651921	41030	0.000		M	
2	12.737	654193	36914	0.000		V M	
Total		1306114	77944				

Supplementary Figure 77. HPLC spectrum of racemic-**5aac**

<Chromatogram>



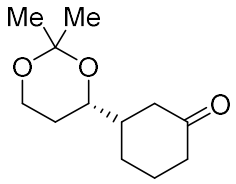
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.010	14478	1092	0.000		M	
2	12.841	996508	65276	0.000		M	
Total		1010986	66367				

Supplementary Figure 78. HPLC spectrum of (*S*)-**5aac**

(*R*)-3-((*S*)-2,2-dimethyl-1,3-dioxan-4-yl)cyclohexan-1-one (5aad)



Chemical Formula: $C_{12}H_{20}O_3$
Exact Mass: 212.1412

An oven-dried 10-mL Schlenk equipped with a PTFE-coated stir bar was charged with 5% Pd/C (36.6 mg, 0.018 mmol, 15 mol%) and **5aac** (21.0 mg, 0.10 mmol, 1 equiv) in toluene (1 mL) and CH_2Cl_2 (1 mL). The reaction mixture was stirred under H_2 atmosphere (10 bar) at 25 °C for 24 hours. The mixture was filtered through Celite and the filtrate was condensed. The residue was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **5aad** as colorless oil (16.1 mg, 76%, d.r. > 20/1).

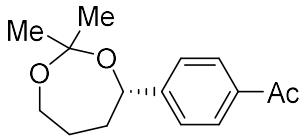
^{1}H NMR (600 MHz, $CDCl_3$) δ 3.94 (t, *J* = 12.0 Hz, 1H), 3.85 (dd, *J* = 11.6, 5.2 Hz, 1H), 3.74 – 3.65 (m, 1H), 2.36 (t, *J* = 11.1 Hz, 2H), 2.27 (td, *J* = 14.0, 13.3, 5.9 Hz, 1H), 2.16 (t, *J* = 13.0 Hz, 1H), 2.05 (t, *J* = 14.1 Hz, 2H), 1.84 (dt, *J* = 16.3, 8.3 Hz, 1H), 1.63 (tt, *J* = 12.2, 6.0 Hz, 3H), 1.54 – 1.45 (m, 1H), 1.42 (s, 3H), 1.37 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.7, 98.4, 71.6, 59.8, 43.7, 43.1, 41.5, 29.8, 28.2, 26.1, 24.8, 19.1;

HRMS: (ESI) calcd for $C_{12}H_{21}O_3^+[M+H]^+$ 213.1485; found 213.1480.

Optical Rotation: $[\alpha]_D^{21}$ -0.4 (c 0.1, ^{i}PrOH).

(*S*)-1-(4-(2,2-dimethyl-1,3-dioxepan-4-yl)phenyl)ethan-1-one (7aa)



Chemical Formula: $C_{15}H_{20}O_3$
Exact Mass: 248.1412

7aa was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 1-(4-bromophenyl)ethan-1-one (39.8 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxepane **6a** (130.2 mg, 1.0 mmol, 5 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **7aa** as colorless oil (2 mg, 4% yield, 33% ee).

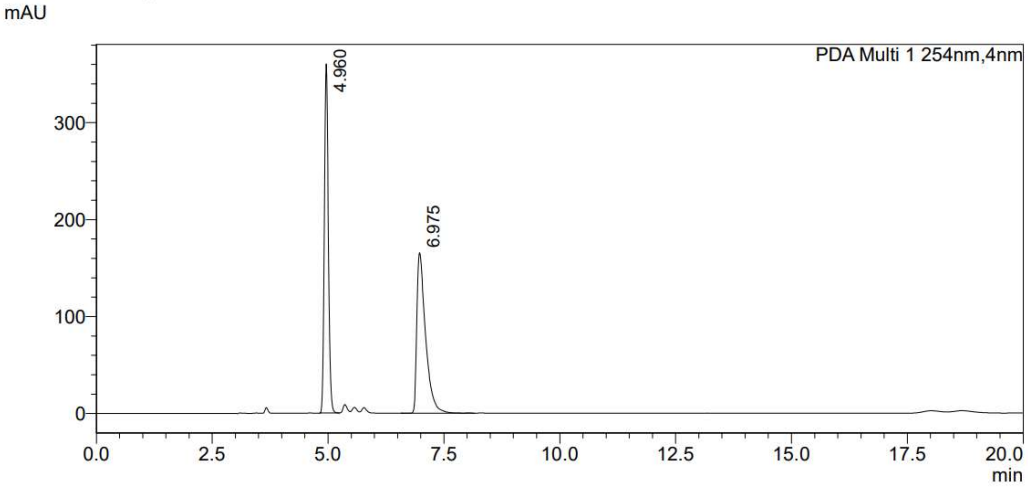
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 2H), 7.46 – 7.43 (m, 2H), 4.87 (d, *J* = 10.7 Hz, 1H), 3.91 – 3.87 (m, 1H), 3.75 – 3.71 (m, 1H), 2.60 (s, 3H), 1.97 – 1.92 (m, 1H), 1.75 (dt, *J* = 5.3, 3.0 Hz, 1H), 1.65 (dddd, *J* = 13.8, 12.4, 10.7, 5.4 Hz, 2H), 1.43 (s, 3H), 1.38 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.8, 150.1, 136.3, 128.6, 125.9, 73.8, 62.9, 36.4, 31.0, 29.7, 28.9, 26.7;

HRMS: (APCI) calcd for $C_{15}H_{21}O_3^+$[M+H]$^+$ 249.1485; found 249.1484.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 90/10 as eluent, 254 nm, 1 mL/min. tR = 5.0 min (minor), 6.9 min (major).

<Chromatogram>



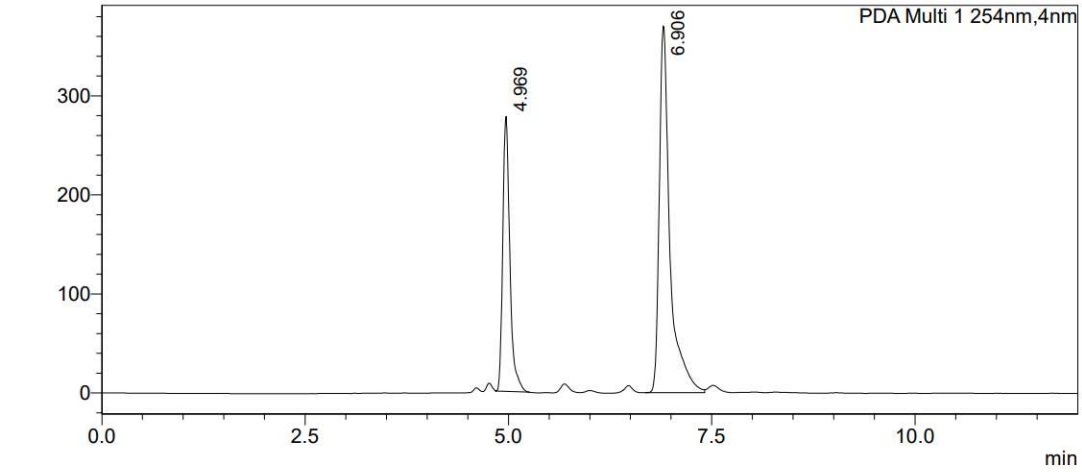
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.960	2139871	359951	0.000		M	
2	6.975	2162050	165615	0.000		M	
Total		4301921	525566				

Supplementary Figure 79. HPLC spectrum of racemic-**7aa**

<Chromatogram>



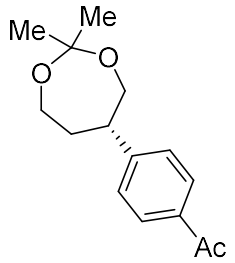
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.969	1684293	277503	33.314		M	
2	6.906	3371496	370302	66.686		M	
Total		5055789	647805				

Supplementary Figure 80. HPLC spectrum of (*S*)-**7aa**

(*S*)-1-(4-(2,2-dimethyl-1,3-dioxepan-5-yl)phenyl)ethan-1-one (7aa')



Chemical Formula: $C_{15}H_{20}O_3$
Exact Mass: 248.1412

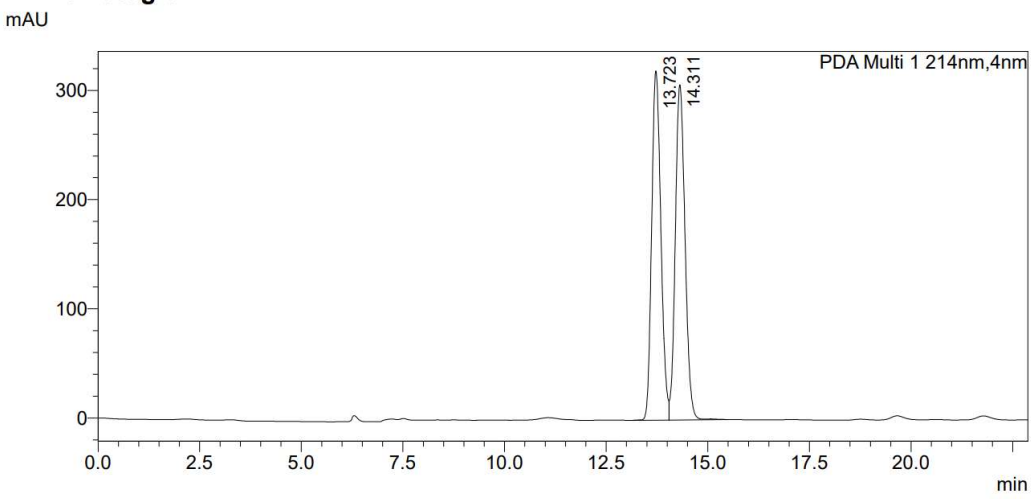
7aa' was prepared according to general procedure **2.1** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 1-(4-bromophenyl)ethan-1-one (39.8 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), 2,2-dimethyl-1,3-dioxepane **6a** (130.2 mg, 1.0 mmol, 5 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **7aa'** as colorless oil (3.2 mg, 6% yield, 18% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 2H), 7.33 – 7.28 (m, 2H), 3.96 – 3.85 (m, 2H), 3.74 (dt, *J* = 12.3, 3.4 Hz, 1H), 3.61 (ddd, *J* = 11.9, 3.2, 1.4 Hz, 1H), 2.95 (tdd, *J* = 10.4, 6.0, 3.2 Hz, 1H), 2.58 (s, 3H), 1.92 – 1.85 (m, 2H), 1.39 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.7, 148.0, 135.7, 128.7, 127.7, 101.5, 66.6, 60.9, 47.0, 37.1, 26.6, 25.0, 24.9.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, ^{n}Hexane/^{i}Propanol = 95/5 as eluent, 250 nm, 0.5 mL/min. tR = 14.3 min (minor), 13.7 min (major).

<Chromatogram>



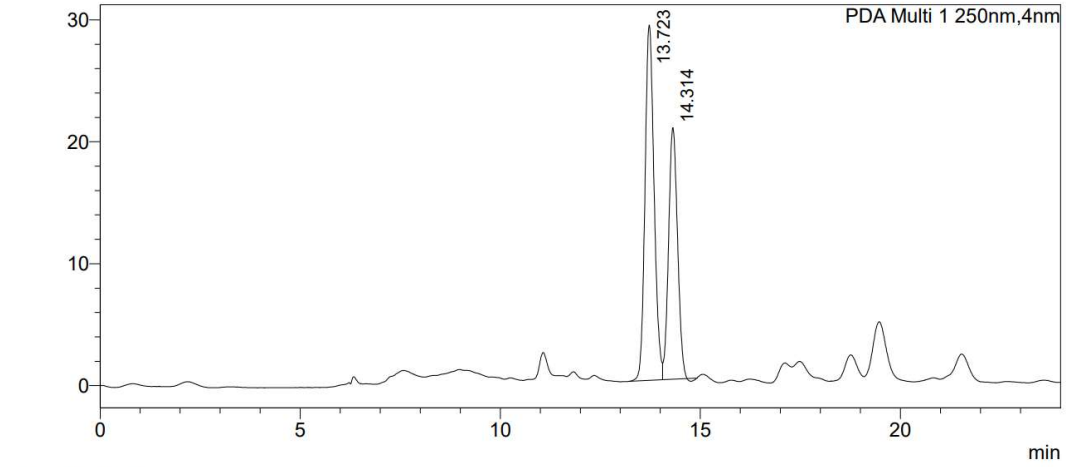
<Peak Table>

PDA Ch1 214nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.723	5042775	319587	0.000		M	
2	14.311	5089008	306805	0.000		V M	
Total		10131783	626392				

Supplementary Figure 81. HPLC spectrum of racemic-**7aa'**

<Chromatogram>



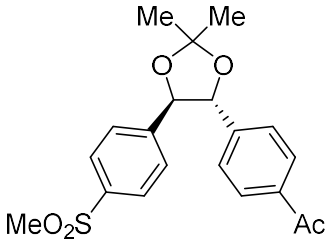
<Peak Table>

PDA Ch1 250nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.723	460559	29136	0.000		M	
2	14.314	320015	20642	0.000		V M	
Total		780574	49778				

Supplementary Figure 82. HPLC spectrum of (*S*)-**7aa'**

1-(4-((4*R*,5*R*)-2,2-dimethyl-5-(4-(methylsulfonyl)phenyl)-1,3-dioxolan-4-yl)phenyl)ethan-1-one (9a)



Chemical Formula: $C_{20}H_{22}O_5S$
Exact Mass: 374.1188

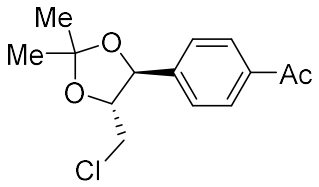
9a was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 1-bromo-4-(methylsulfonyl)benzene (47.0 mg, 0.20 mmol, 1.0 equiv), **3ca** (66.0 mg, 0.6 mmol, 3.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 2/1) to obtain **9a** as colorless oil (62.1 mg, 83% yield, d.r. > 20/1). R_f = 0.3 (PE/EA = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.91 (m, 2H), 7.91 – 7.87 (m, 2H), 7.40 – 7.36 (m, 2H), 7.32 – 7.27 (m, 2H), 4.78 (d, *J* = 8.4 Hz, 1H), 4.72 (d, *J* = 8.4 Hz, 1H), 3.05 (s, 3H), 2.59 (s, 3H), 1.69 (s, 3H), 1.68 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.6, 142.9, 141.2, 140.6, 137.4, 128.7, 127.7, 127.5, 126.9, 110.5, 84.9, 84.6, 44.5, 27.1, 27.0, 26.7;

HRMS: (APCI) calcd for $C_{20}H_{23}O_5S^+$[M+H]$^+$ 375.1261; found 375.1252.

1-(4-((4*S*,5*R*)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)phenyl)ethan-1-one (9b)



Chemical Formula: $C_{14}H_{17}ClO_3$
Exact Mass: 268.0866

9b was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 1-(4-bromophenyl)ethan-1-one (40.0 mg, 0.20 mmol,

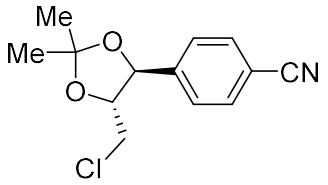
1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 10/1) to obtain **9b** as colorless oil (47.2 mg, 88% yield, d.r. > 20/1). R_f = 0.4 (PE/EA = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.52 – 7.47 (m, 2H), 4.97 (d, *J* = 8.1 Hz, 1H), 4.01 (dt, *J* = 8.3, 4.3 Hz, 1H), 3.75 (dd, *J* = 12.1, 4.1 Hz, 1H), 3.62 (dd, *J* = 12.1, 4.5 Hz, 1H), 2.60 (s, 3H), 1.58 (s, 3H), 1.55 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.5, 142.6, 137.2, 128.7, 126.6, 110.2, 82.1, 79.9, 42.8, 27.1, 26.9, 26.6;

HRMS: (ESI) calcd for $C_{14}H_{18}ClO_3^+$[M+H]$^+$ 269.0939; found 269.0939.

4-((4*S*,5*R*)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)benzonitrile (9c)



Chemical Formula: $C_{13}H_{14}ClNO_2$
Exact Mass: 251.0713

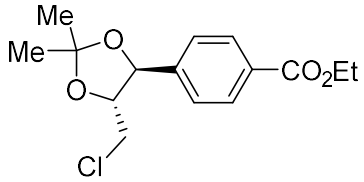
9c was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 4-bromobenzonitrile (36.4 mg, 0.20 mmol, 1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 10/1) to obtain **9c** as colorless oil (41.7 mg, 83% yield, d.r. > 20/1). R_f = 0.5 (PE/EA = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 2H), 7.54 – 7.51 (m, 2H), 4.97 (d, *J* = 7.9 Hz, 1H), 3.99 (dt, *J* = 7.9, 4.3 Hz, 1H), 3.75 (dd, *J* = 12.1, 4.4 Hz, 1H), 3.63 (dd, *J* = 12.1, 4.3 Hz, 1H), 1.57 (s, 3H), 1.54 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.9, 132.5, 127.2, 118.4, 112.3, 110.5, 82.0, 79.7, 42.6, 27.0, 26.9;

HRMS: (ESI) calcd for $C_{13}H_{15}ClNO_2^+$[M+H]$^+$ 252.0785; found 252.0783.

ethyl 4-((4*S*,5*R*)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)benzoate (9d)



Chemical Formula: $C_{15}H_{19}ClO_4$
Exact Mass: 298.0972

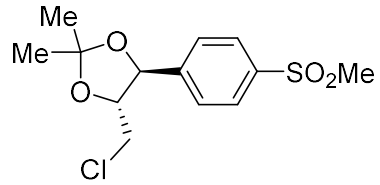
9d was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), ethyl 4-bromobenzoate (46.0 mg, 0.20 mmol, 1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 10/1) to obtain **9d** as colorless oil (47.7 mg, 80% yield, d.r. > 20/1). R_f = 0.5 (PE/EA = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.50 – 7.44 (m, 2H), 4.97 (d, *J* = 8.1 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.01 (dt, *J* = 8.2, 4.2 Hz, 1H), 3.75 (dd, *J* = 12.1, 4.0 Hz, 1H), 3.62 (dd, *J* = 12.1, 4.5 Hz, 1H), 1.59 (s, 3H), 1.55 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 142.3, 130.7, 129.9, 126.4, 110.2, 82.2, 80.0, 61.1, 42.8, 27.1, 26.9, 14.3;

HRMS: (ESI) calcd for $C_{15}H_{20}ClO_4^+$[M+H]$^+$ 299.1044; found 299.1041.

(4*R*,5*S*)-4-(chloromethyl)-2,2-dimethyl-5-(4-(methylsulfonyl)phenyl)-1,3-dioxolane (9e)



Chemical Formula: $C_{13}H_{17}ClO_4S$
Exact Mass: 304.0536

9e was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 1-bromo-4-(methylsulfonyl)benzene (47.0 mg, 0.20 mmol, 1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 5/1) to obtain **9e** as colorless oil (48.6 mg, 80% yield, d.r. > 20/1). R_f = 0.3 (PE/EA

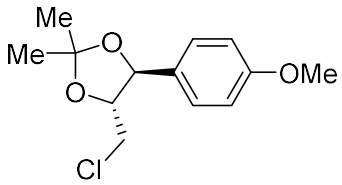
= 5/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.63 – 7.58 (m, 2H), 5.00 (d, *J* = 7.9 Hz, 1H), 4.01 (dt, *J* = 8.0, 4.3 Hz, 1H), 3.76 (dd, *J* = 12.1, 4.4 Hz, 1H), 3.64 (dd, *J* = 12.1, 4.3 Hz, 1H), 3.05 (s, 3H), 1.57 (s, 3H), 1.54 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.9, 140.6, 127.8, 127.4, 110.5, 82.1, 79.6, 44.4, 42.7, 27.0, 26.9;

HRMS: (ESI) calcd for $C_{13}H_{18}ClO_4S^+[M+H]^+$ 305.0608; found 305.0604.

(4*R*,5*S*)-4-(chloromethyl)-5-(4-methoxyphenyl)-2,2-dimethyl-1,3-dioxolane (9f)



Chemical Formula: $C_{13}H_{17}ClO_3$
Exact Mass: 256.0866

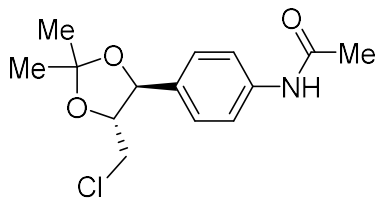
9f was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 1-bromo-4-methoxybenzene (37.4 mg, 0.20 mmol, 1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 30/1) to obtain **9f** as colorless oil (35.8 mg, 70% yield, d.r. > 20/1). R_f = 0.5 (PE/EA = 30/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 6.94 – 6.89 (m, 2H), 4.83 (d, *J* = 8.3 Hz, 1H), 4.03 – 3.98 (m, 1H), 3.81 (s, 3H), 3.71 (dd, *J* = 12.0, 3.6 Hz, 1H), 3.59 (dd, *J* = 12.0, 4.9 Hz, 1H), 1.58 (s, 3H), 1.54 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.9, 128.8, 128.0, 114.1, 109.6, 82.2, 80.2, 55.3, 43.0, 27.2, 26.9;

HRMS: (ESI) calcd for $C_{13}H_{18}ClO_3^+[M+H]^+$ 257.0944; found 257.0948.

***N*-(4-((4*S*,5*R*)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)phenyl)acetamide (9g)**



Chemical Formula: $C_{14}H_{18}ClNO_3$
Exact Mass: 283.0975

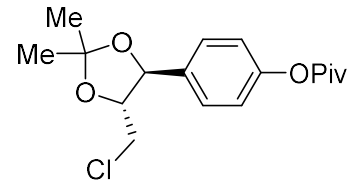
9g was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), *N*-(4-bromophenyl)acetamide (42.8 mg, 0.20 mmol, 1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 1/1) to obtain **9g** as colorless oil (35.7 mg, 63% yield, d.r. > 20/1). R_f = 0.4 (PE/EA = 2/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 4.85 (d, *J* = 8.2 Hz, 1H), 4.02 – 3.97 (m, 1H), 3.72 (dd, *J* = 12.0, 3.7 Hz, 1H), 3.59 (dd, *J* = 12.1, 4.8 Hz, 1H), 2.17 (s, 3H), 1.58 (s, 3H), 1.54 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.6, 138.2, 132.8, 127.4, 120.1, 109.8, 82.3, 80.1, 42.9, 27.2, 27.0, 24.6;

HRMS: (ESI) calcd for $C_{14}H_{19}ClNO_3^+$[M+H]$^+$ 284.1048; found 284.1045.

4-((4*S*,5*R*)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)phenyl pivalate (9h)



Chemical Formula: $C_{17}H_{23}ClO_4$
Exact Mass: 326.1285

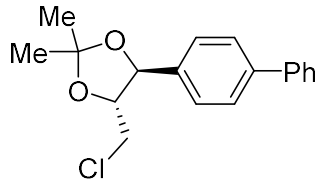
9h was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 4-bromophenyl pivalate (51.4 mg, 0.20 mmol, 1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 20/1) to obtain **9h** as colorless oil (43.0 mg, 66% yield, d.r. > 20/1). R_f = 0.6 (PE/EA = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.09 – 7.05 (m, 2H), 4.91 (d, *J* = 8.2 Hz, 1H), 4.02 – 3.98 (m, 1H), 3.74 (dd, *J* = 12.1, 3.6 Hz, 1H), 3.60 (dd, *J* = 12.1, 4.6 Hz, 1H), 1.58 (s, 3H), 1.54 (s, 3H), 1.36 (s, 9H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 177.0, 151.3, 134.5, 127.6, 121.9, 109.9, 82.3, 79.9, 42.8, 39.1, 27.2, 27.1, 27.0;

HRMS: (ESI) calcd for $C_{17}H_{24}ClO_4^+$[M+H]$^+$ 327.1357; found 327.1356.

(4*S*,5*R*)-4-([1,1'-biphenyl]-4-yl)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (9i)



Chemical Formula: $C_{18}H_{19}ClO_2$
Exact Mass: 302.1074

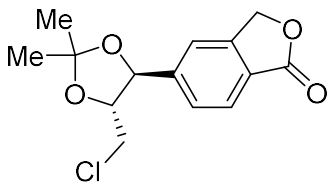
9i was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 4-bromo-1,1'-biphenyl (46.6 mg, 0.20 mmol, 1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EtOAc = 50/1) to obtain **9i** as colorless solid (39.8 mg, 66% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 4H), 7.50 – 7.43 (m, 4H), 7.39 – 7.35 (m, 1H), 4.95 (d, *J* = 8.2 Hz, 1H), 4.12 – 4.07 (m, 1H), 3.79 (dd, *J* = 12.0, 3.6 Hz, 1H), 3.66 (dd, *J* = 12.1, 4.8 Hz, 1H), 1.63 (s, 3H), 1.58 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.6, 140.6, 136.1, 128.8, 127.5, 127.09, 127.05, 109.9, 82.3, 80.2, 43.0, 27.2, 27.0;

HRMS: (ESI) calcd for $C_{18}H_{20}ClO_2^+$[M+H]$^+$ 303.1152; found 303.1154.

5-((4*S*,5*R*)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)isobenzofuran-1(3*H*)-one (9j)



Chemical Formula: $C_{14}H_{15}ClO_4$
Exact Mass: 282.0659

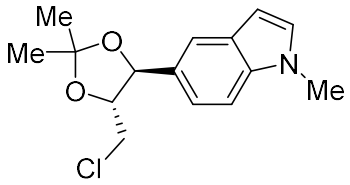
9j was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 5-bromoisobenzofuran-1(3*H*)-one (42.6 mg, 0.20 mmol, 1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 3/1) to obtain **9j** as colorless oil (43.4 mg, 77% yield, d.r. > 20/1). R_f = 0.3 (PE/EA = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.54 (m, 2H), 5.33 (s, 2H), 5.05 (d, *J* = 8.0 Hz, 1H), 4.02 (dt, *J* = 8.2, 4.2 Hz, 1H), 3.78 (dd, *J* = 12.1, 4.3 Hz, 1H), 3.65 (dd, *J* = 12.1, 4.2 Hz, 1H), 1.59 (s, 3H), 1.55 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 147.2, 144.5, 127.5, 126.1, 126.0, 120.1, 110.4, 82.2, 80.0, 69.5, 42.6, 27.1, 26.9;

HRMS: (ESI) calcd for $C_{14}H_{16}ClO_4^+$[M+H]$^+$ 283.0732; found 283.0733.

5-((4*S*,5*R*)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-1-methyl-1*H*-indole (9k)



Chemical Formula: $C_{15}H_{18}ClNO_2$
Exact Mass: 279.1026

9k was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 5-bromo-1-methyl-1*H*-indole (42.0 mg, 0.20 mmol, 1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA

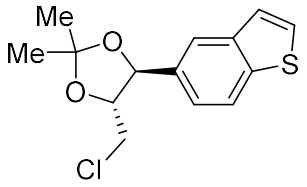
= 15/1) to obtain **9k** as yellow oil (29.6 mg, 53% yield, d.r. > 20/1). R_f = 0.7 (PE/EA = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 1.6 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.07 (d, *J* = 3.1 Hz, 1H), 6.48 (dd, *J* = 3.1, 0.9 Hz, 1H), 4.98 (d, *J* = 8.4 Hz, 1H), 4.12 – 4.06 (m, 1H), 3.79 (s, 3H), 3.74 (dd, *J* = 12.0, 3.2 Hz, 1H), 3.60 (dd, *J* = 12.0, 5.0 Hz, 1H), 1.64 (s, 3H), 1.57 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 136.9, 129.6, 128.5, 127.5, 120.1, 119.5, 109.6, 109.5, 101.1, 82.7, 81.2, 43.2, 33.0, 27.4, 27.1;

HRMS: (ESI) calcd for $C_{15}H_{19}ClNO_2^+$[M+H]$^+$ 280.1098; found 280.1095.

(4*S*,5*R*)-4-(benzo[b]thiophen-5-yl)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (9l)



Chemical Formula: $C_{14}H_{15}ClO_2S$
Exact Mass: 282.0481

9l was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 5-bromobenzo[*b*]thiophene (42.6 mg, 0.20 mmol, 1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 50/1) to obtain **9l** as yellow oil (32.1 mg, 57% yield, d.r. > 20/1). R_f = 0.5 (PE/EA = 50/1).

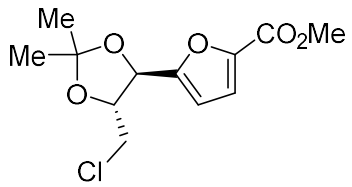
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 1.6 Hz, 1H), 7.49 (d, *J* = 5.4 Hz, 1H), 7.39 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.35 (dd, *J* = 5.4, 0.8 Hz, 1H), 5.03 (d, *J* = 8.2 Hz, 1H), 4.11 – 4.07 (m, 1H), 3.77 (dd, *J* = 12.1, 3.6 Hz, 1H), 3.64 (dd, *J* = 12.1, 4.7 Hz, 1H), 1.64 (s, 3H), 1.58 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.0, 139.8, 133.3, 127.4, 123.8, 122.9, 122.6, 121.8, 109.9, 82.5, 80.5, 42.9, 27.3, 27.0;

HRMS: (ESI) calcd for $C_{14}H_{16}ClO_2S^+$[M+H]$^+$ 283.0560; found 283.0561.

methyl 5-((4*R*,5*R*)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)furan-2-carboxylate

(9m)



Chemical Formula: $C_{12}H_{15}ClO_5$
Exact Mass: 274.0608

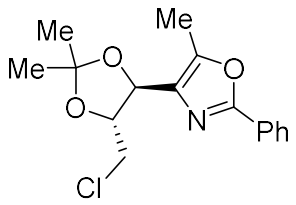
9m was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), methyl 5-bromofuran-2-carboxylate (41.0 mg, 0.20 mmol, 1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 10/1) to obtain **9m** as colorless oil (33.4 mg, 61% yield, d.r. > 20/1). R_f = 0.6 (PE/EA = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (d, *J* = 3.5 Hz, 1H), 6.51 (d, *J* = 3.5 Hz, 1H), 4.94 (d, *J* = 7.7 Hz, 1H), 4.51 – 4.46 (m, 1H), 3.88 (s, 3H), 3.75 (dd, *J* = 11.9, 4.7 Hz, 1H), 3.68 (dd, *J* = 11.9, 4.8 Hz, 1H), 1.51 (d, *J* = 5.7 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 155.0, 144.9, 118.7, 111.2, 110.7, 79.0, 74.2, 52.0, 43.3, 27.0, 26.7;

HRMS: (ESI) calcd for $C_{12}H_{16}O_5Cl^+[M+H]^+$ 275.0681; found 275.0673.

4-((4*S*,5*R*)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-5-methyl-2-phenyloxazole (9n)



Chemical Formula: $C_{16}H_{18}ClNO_3$
Exact Mass: 307.0975

9n was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 4-bromo-5-methyl-2-phenyloxazole (47.6 mg, 0.20

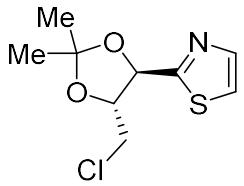
mmol, 1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 10/1) to obtain **9n** as yellow oil (31.3 mg, 51% yield, d.r. > 20/1). R_f = 0.6 (PE/EA = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 7.46 – 7.38 (m, 3H), 4.90 (d, *J* = 8.0 Hz, 1H), 4.62 – 4.58 (m, 1H), 3.82 (dd, *J* = 11.9, 4.1 Hz, 1H), 3.69 (dd, *J* = 11.9, 4.8 Hz, 1H), 2.44 (s, 3H), 1.61 (s, 3H), 1.55 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.2, 147.1, 132.1, 130.1, 128.7, 127.5, 126.2, 110.3, 79.1, 73.2, 43.6, 27.01, 26.95, 10.5;

HRMS: (ESI) calcd for $C_{16}H_{19}ClNO_3^+$[M+H]$^+$ 308.1048; found 308.1039.

2-((4*R*,5*R*)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)thiazole (9o)



Chemical Formula: $C_9H_{12}ClNO_2S$
Exact Mass: 233.0277

9o was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 2-bromothiazole (32.8 mg, 0.20 mmol, 1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 20/1) to obtain **9o** as colorless oil (20.0 mg, 43% yield, d.r. > 20/1). R_f = 0.6 (PE/EA = 20/1).

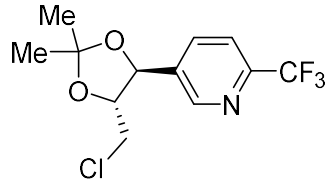
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 3.2 Hz, 1H), 7.34 (d, *J* = 3.2 Hz, 1H), 5.18 (d, *J* = 7.7 Hz, 1H), 4.37 – 4.33 (m, 1H), 3.95 (dd, *J* = 12.0, 3.4 Hz, 1H), 3.82 (dd, *J* = 12.0, 5.3 Hz, 1H), 1.57 (s, 3H), 1.53 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 143.1, 119.4, 111.4, 81.2, 77.7, 43.3, 27.0, 26.8;

HRMS: (ESI) calcd for $C_9H_{13}ClNO_2S^+$[M+H]$^+$ 234.0350; found 234.0344.

5-((4*S*,5*R*)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-2-(trifluoromethyl)pyridine

(9p)



Chemical Formula: $C_{12}H_{13}ClF_3NO_2$
Exact Mass: 295.0587

9p was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 5-bromo-2-(trifluoromethyl)pyridine (45.2 mg, 0.20 mmol, 1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 10/1) to obtain **9p** as colorless oil (50.1 mg, 85% yield, d.r. > 20/1). R_f = 0.5 (PE/EA = 5/1).

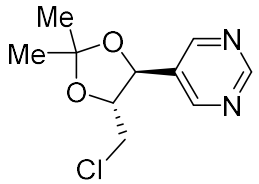
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (d, *J* = 2.1 Hz, 1H), 7.93 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 5.04 (d, *J* = 7.8 Hz, 1H), 4.08 – 4.02 (m, 1H), 3.76 (dd, *J* = 12.0, 5.1 Hz, 1H), 3.68 (dd, *J* = 12.0, 4.2 Hz, 1H), 1.57 (s, 3H), 1.55 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.6, 148.3 (q, *J* = 35.0 Hz), 136.8, 135. 7, 121.4 (q, *J* = 274.1 Hz), 120.4 (q, *J* = 2.7 Hz), 110.9, 82.0, 78.3, 42.6, 27.0, 26.9;

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.93.

HRMS: (ESI) calcd for $C_{12}H_{14}ClF_3NO_2^+$[M+H]$^+$ 296.0659; found 296.0650.

5-((4*S*,5*R*)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)pyrimidine (9q)



Chemical Formula: $C_{10}H_{13}ClN_2O_2$
Exact Mass: 228.0666

9q was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 5-bromopyrimidine (31.8 mg, 0.20 mmol, 1.0 equiv),

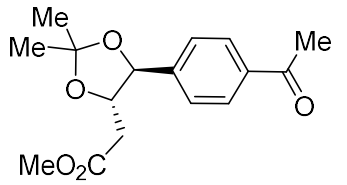
(*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 3/1) to obtain **9q** as colorless oil (35.6 mg, 78% yield, d.r. > 20/1). R_f = 0.7 (PE/EA = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.79 (s, 2H), 4.96 (d, *J* = 7.8 Hz, 1H), 4.12 – 4.07 (m, 1H), 3.74 (dd, *J* = 11.9, 5.6 Hz, 1H), 3.69 (dd, *J* = 11.9, 4.2 Hz, 1H), 1.57 (s, 3H), 1.54 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 155.7, 131.4, 110.9, 81.8, 77.28, 42.7, 27.1, 26.8;

HRMS: (ESI) calcd for $C_{10}H_{14}ClN_2O_2^+$[M+H]$^+$ 229.0738; found 229.0730.

methyl 2-((4*S*,5*S*)-5-(4-acetylphenyl)-2,2-dimethyl-1,3-dioxolan-4-yl)acetate (9r)



Chemical Formula: $C_{16}H_{20}O_5$
Exact Mass: 292.1311

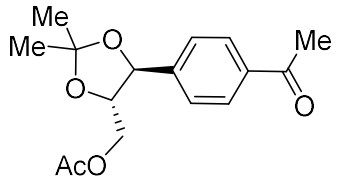
9r was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 1-(4-bromophenyl)ethan-1-one (40.0 mg, 0.20 mmol, 1.0 equiv), methyl (*S*)-2-(2,2-dimethyl-1,3-dioxolan-4-yl)acetate (174 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 5/1) to obtain **9r** as colorless oil (52.6 mg, 90% yield, d.r. > 20/1). R_f = 0.4 (PE/EA = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.49 – 7.45 (m, 2H), 4.72 (d, *J* = 8.5 Hz, 1H), 4.18 – 4.13 (m, 1H), 3.60 (s, 3H), 2.66 – 2.57 (m, 2H), 2.58 (s, 3H), 1.57 (s, 3H), 1.50 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.6, 170.5, 142.4, 137.3, 128.7, 126.9, 109.8, 81.9, 79.3, 51.9, 36.4, 27.2, 27.0, 26.7;

HRMS: (ESI) calcd for $C_{16}H_{21}O_5^+$[M+H]$^+$ 293.1389; found 293.1393.

((4*S*,5*S*)-5-(4-acetylphenyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl acetate (9s)



Chemical Formula: $C_{16}H_{20}O_5$
Exact Mass: 292.1311

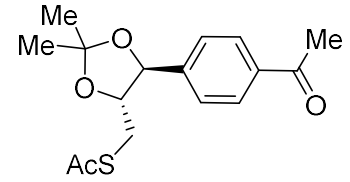
9s was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 1-(4-bromophenyl)ethan-1-one (40.0 mg, 0.20 mmol, 1.0 equiv), (*R*)-(2,2-dimethyl-1,3-dioxolan-4-yl)methyl acetate (174 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 5/1) to obtain **9s** as colorless oil (45.0 mg, 77% yield, d.r. > 20/1). R_f = 0.4 (PE/EA = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.52 – 7.46 (m, 2H), 4.83 (d, *J* = 8.5 Hz, 1H), 4.36 (dd, *J* = 12.0, 3.4 Hz, 1H), 4.17 (dd, *J* = 12.1, 5.6 Hz, 1H), 4.01 – 3.97 (m, 1H), 2.60 (s, 3H), 2.06 (s, 3H), 1.59 (s, 3H), 1.53 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.6, 170.7, 142.8, 137.2, 128.8, 126.6, 110.3, 80.9, 79.3, 62.8, 27.0, 26.9, 26.7, 20.8;

HRMS: (ESI) calcd for $C_{16}H_{21}O_5^+$[M+H]$^+$ 293.1389; found 293.1384.

_S_-(((4_R_,5_S_)-5-(4-acetylphenyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl) ethanethioate (9t)



Chemical Formula: $C_{16}H_{20}O_4S$
Exact Mass: 308.1082

9t was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 1-(4-bromophenyl)ethan-1-one (40.0 mg, 0.20 mmol, 1.0 equiv), (*R*)-*S*-((2,2-dimethyl-1,3-dioxolan-4-yl)methyl) ethanethioate (190 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 5/1) to obtain **9t** as yellow oil (43.7 mg, 71% yield, d.r. > 20/1). R_f = 0.5 (PE/EA =

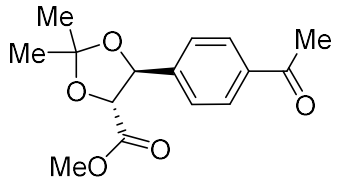
5/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.52 – 7.46 (m, 2H), 4.70 (d, *J* = 8.2 Hz, 1H), 4.00 – 3.92 (m, 1H), 3.27 (dd, *J* = 14.2, 4.1 Hz, 1H), 3.18 (dd, *J* = 14.2, 5.6 Hz, 1H), 2.59 (s, 4H), 2.33 (s, 4H), 1.53 (s, 3H), 1.51 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.7, 195.0, 142.8, 137.1, 128.7, 126.7, 109.9, 81.3, 81.2, 30.5, 29.8, 27.1, 27.0, 26.7;

HRMS: (ESI) calcd for $C_{16}H_{21}O_4S^+[M+H]^+$ 309.1155; found 309.1154.

methyl (4*R*,5*S*)-5-(4-acetylphenyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate (9u)



Chemical Formula: $C_{15}H_{18}O_5$
Exact Mass: 278.1154

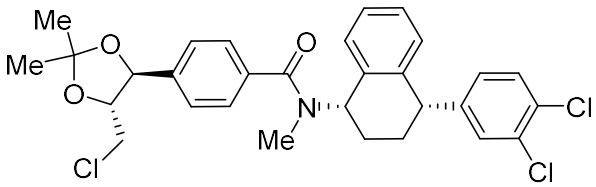
9u was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 1-(4-bromophenyl)ethan-1-one (40.0 mg, 0.20 mmol, 1.0 equiv), methyl (*R*)-2,2-dimethyl-1,3-dioxolane-4-carboxylate (160 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 5/1) to obtain **9u** as yellow oil (47.3 mg, 85% yield, d.r. > 20/1). R_f = 0.5 (PE/EA = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.55 – 7.50 (m, 2H), 5.21 (d, *J* = 7.6 Hz, 1H), 4.32 (d, *J* = 7.6 Hz, 1H), 3.79 (s, 3H), 2.59 (s, 3H), 1.60 (s, 3H), 1.55 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.7, 170.5, 143.1, 137.2, 128.7, 126.6, 112.1, 81.1, 80.1, 52.6, 26.8, 26.7, 25.8;

HRMS: (ESI) calcd for $C_{15}H_{19}O_5^+[M+H]^+$ 279.1227; found 279.1225.

4-((4*S*,5*R*)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-N-((1*S*,4*S*)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-N-methylbenzamide (9v)



Chemical Formula: $C_{30}H_{30}Cl_3NO_3$
Exact Mass: 557.1291

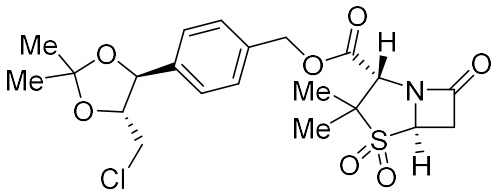
9v was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 4-bromo-*N*-((1*S*,4*S*)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-*N*-methylbenzamide (97.8 mg, 0.20 mmol, 1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 3/1) to obtain **9v** as colorless oil (85.8 mg, 77% yield, d.r. > 20/1). R_f = 0.4 (PE/EA = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.42 (m, 4H), 7.36 – 7.28 (m, 3H), 7.24 – 7.19 (m, 1H), 7.10 – 7.06 (m, 1H), 7.00 – 6.94 (m, 1H), 6.87 – 6.74 (m, 1H), 6.08 – 4.89 (m, 2H), 4.25 – 4.12 (m, 1H), 4.06 – 3.97 (m, 1H), 3.78 – 3.72 (m, 1H), 3.65 – 3.57 (m, 1H), 2.90 – 2.69 (m, 3H), 2.11 – 2.04 (m, 1H), 2.00 – 1.65 (m, 3H), 1.62 – 1.51 (m, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.3, 172.0, 147.0, 146.7, 139.0, 138.8, 138.4, 138.0, 136.9, 135.7, 135.6, 132.5, 132.3, 131.2, 131.0, 130. 7, 130.6, 130.3, 130.2, 130.1, 128.1, 127.97, 127.96, 127.8, 127.6, 127.5, 127.4, 127.2, 127.1, 126.8, 126.7, 126.5, 110.13, 110.10, 82.3, 82.2, 80.1, 80.0, 58.6, 52.8, 43.1, 42.8, 42.8, 42.9, 33.1, 30.1, 30.0, 29.0, 27.2, 27.0, 27.0, 22.6, 21.2;

HRMS: (ESI) calcd for $C_{30}H_{31}Cl_3NO_3^+$[M+H]$^+$ 558.1364; found 558.1367.

4-((4*S*,5*R*)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)benzyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (9w)



Chemical Formula: $C_{21}H_{26}ClNO_7S$
Exact Mass: 471.1119

9w was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10

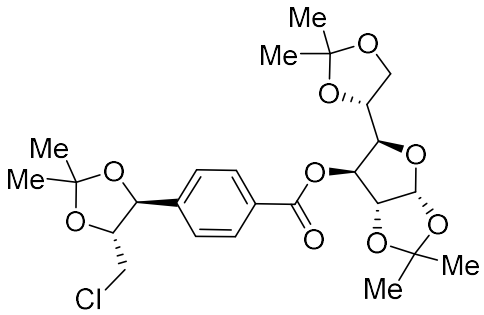
mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 4-bromobenzyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (80.4 mg, 0.20 mmol, 1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 3/1) to obtain **9w** as colorless oil (50.8 mg, 54% yield, d.r. > 20/1). R_f = 0.2 (PE/EA = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 5.27 (d, *J* = 12.1 Hz, 1H), 5.18 (d, *J* = 12.1 Hz, 1H), 4.91 (d, *J* = 8.1 Hz, 1H), 4.59 (dd, *J* = 4.4, 2.1 Hz, 1H), 4.40 (s, 1H), 4.03 – 3.99 (m, 1H), 3.74 (dd, *J* = 12.1, 4.0 Hz, 1H), 3.61 (dd, *J* = 12.1, 4.6 Hz, 1H), 3.48 (dd, *J* = 16.2, 4.3 Hz, 1H), 3.43 (dd, *J* = 16.2, 2.1 Hz, 1H), 1.58 (s, 3H), 1.55 (s, 3H), 1.54 (s, 3H), 1.29 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.8, 166.8, 138.3, 134.7, 129.2, 127.1, 110.1, 82.3, 80.1, 67.7, 63.2, 62.7, 61.1, 42.9, 38.3, 27.2, 27.0, 20.2, 18.6;

HRMS: (ESI) calcd for $C_{21}H_{27}ClNO_7S^+[M+H]^+$ 472.1191; found 472.1192.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 4-((4*S*,5*R*)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)benzoate (9x)



Chemical Formula: $C_{25}H_{33}ClO_9$
Exact Mass: 512.1813

9x was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), (3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4-bromobenzoate (88.6 mg, 0.20 mmol, 1.0 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (150 mg, 1.0 mmol, 5.0 equiv)

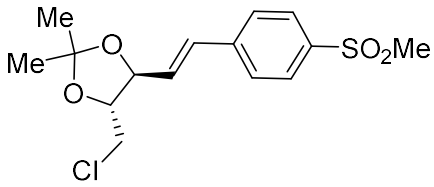
and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 5/1) to obtain **9x** as colorless oil (63.5 mg, 62% yield, d.r. > 20/1). R_f = 0.4 (PE/EA = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 5.94 (d, *J* = 3.6 Hz, 1H), 5.49 (d, *J* = 2.7 Hz, 1H), 4.97 (d, *J* = 8.0 Hz, 1H), 4.62 (d, *J* = 3.7 Hz, 1H), 4.37 – 4.30 (m, 2H), 4.12 – 4.05 (m, 2H), 4.03 – 3.98 (m, 1H), 3.75 (dd, *J* = 12.1, 4.1 Hz, 1H), 3.62 (dd, *J* = 12.1, 4.4 Hz, 1H), 1.58 (s, 3H), 1.55 (s, 6H), 1.40 (s, 3H), 1.31 (s, 3H), 1.26 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.8, 143.3, 130.2, 129.7, 126.7, 112.4, 110.4, 109.4, 105.1, 83.4, 82.2, 80.00, 79.95, 76.8, 72.6, 67.3, 42.8, 27.1, 27.0, 26.9, 26.7, 26.2, 25.2;

HRMS: (ESI) calcd for $C_{25}H_{33}ClO_9Na^+$[M+Na]$^+$ 535.1705; found 535.1707.

(4*R*,5*S*)-4-(chloromethyl)-2,2-dimethyl-5-((*E*)-4-(methylsulfonyl)styryl)-1,3-dioxolane (9y)



Chemical Formula: $C_{15}H_{19}ClO_4S$
Exact Mass: 330.0693

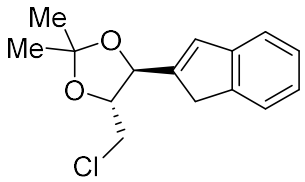
9y was prepared according to general procedure **2.3** using $NiBr_2$•dme (3.3 mg, 0.01 mmol, 10 mol%), dtbbpy (4.2 mg, 0.015 mmol, 15 mol%), (*E*)-1-(2-bromovinyl)-4-(methylsulfonyl) benzene (26.2 mg, 0.10 mmol, 1 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (75.2 mg, 0.5 mmol, 5 equiv), TBADT (6.8 mg, 0.002 mmol, 2 mol%), (*E*)-1,2-diphenylethene (18.0 mg, 0.1 mmol, 1 equiv), K_3PO_4 (25.3 mg, 0.12 mmol, 1.2 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 3/1) to obtain **9y** as colorless oil (14.2 mg, 43% yield, d.r. > 20/1, *E*/*Z* = 16/1). R_f = 0.3 (PE/EA = 4/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 15.9 Hz, 1H), 6.37 (dd, *J* = 15.9, 7.0 Hz, 1H), 4.56 – 4.52 (m, 1H), 4.06 (dt, *J* = 7.9, 4.9 Hz, 1H), 3.74 – 3.66 (m, 2H), 3.05 (s, 3H), 1.50 (s, 3H), 1.49 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.4, 139.6, 131.9, 129.9, 127.8, 127.4, 110.3, 80.0, 79.8, 44.5, 43.3, 27.1, 26.9;

HRMS: (ESI) calcd for $C_{15}H_{20}ClO_4S^+$[M+H]$^+$ 331.0765; found 331.0761.

(4R,5S)-4-(chloromethyl)-5-(1H-inden-2-yl)-2,2-dimethyl-1,3-dioxolane (9z)



Chemical Formula: $C_{15}H_{17}ClO_2$
Exact Mass: 264.0917

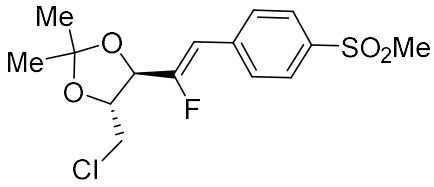
9z was prepared according to general procedure **2.3** using $NiBr_2$•dme (3.3 mg, 0.01 mmol, 10 mol%), dtbbpy (4.2 mg, 0.015 mmol, 15 mol%), 2-bromo-1*H*-indene (19.4 mg, 0.10 mmol, 1 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (75.2 mg, 0.5 mmol, 5 equiv), TBADT (6.8 mg, 0.002 mmol, 2 mol%), K_3PO_4 (25.3 mg, 0.12 mmol, 1.2 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 50/1) to obtain **9z** as colorless oil (11.1 mg, 42% yield, d.r. > 20/1). R_f = 0.5 (PE/EA = 50/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 1H), 7.38 – 7.32 (m, 1H), 7.30 – 7.26 (m, 1H), 7.20 (td, *J* = 7.4, 1.2 Hz, 1H), 6.91 – 6.85 (m, 1H), 4.88 (dd, *J* = 8.0, 0.9 Hz, 1H), 4.18 (ddd, *J* = 8.0, 5.1, 4.3 Hz, 1H), 3.74 (dd, *J* = 11.9, 4.3 Hz, 1H), 3.66 (dd, *J* = 11.8, 5.0 Hz, 1H), 3.56 (ddd, *J* = 22.6, 1.7, 0.8 Hz, 1H), 3.43 (ddd, *J* = 22.6, 1.7, 0.8 Hz, 1H), 1.52 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.6, 143.9, 143.2, 130.4, 126.6, 125.1, 123.9, 121.2, 110.0, 80.0, 77.9, 43.6, 37.8, 27.2, 27.0;

HRMS: (ESI) calcd for $C_{15}H_{18}ClO_2^+$[M+H]$^+$ 265.0995; found 265.0992.

(4*R*,5*R*)-4-(chloromethyl)-5-((*Z*)-1-fluoro-2-(4-(methylsulfonyl)phenyl)vinyl)-2,2-dimethyl-1,3-dioxolane (9aa)



Chemical Formula: $C_{15}H_{18}ClFO_4S$
Exact Mass: 348.0598

9aa was prepared according to general procedure **2.3** using $NiBr_2$•dme (3.3 mg, 0.01 mmol, 10 mol%), dtbbpy (4.2 mg, 0.015 mmol, 15 mol%), 1-(2,2-difluorovinyl)-4-(methylsulfonyl)benzene (21.8 mg, 0.10 mmol, 1 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-

1,3-dioxolane (75.2 mg, 0.5 mmol, 5 equiv), TBADT (6.8 mg, 0.002 mmol, 2 mol%), (*E*)-1,2-diphenylethene (18.0 mg, 0.1 mmol, 1 equiv), K_3PO_4 (25.3 mg, 0.12 mmol, 1.2 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 3/1) to obtain **9aa** as colorless oil (16.3 mg, 47% yield, d.r. > 20/1, *E/Z* = 20/1). R_f = 0.4 (PE/EA = 3/1).

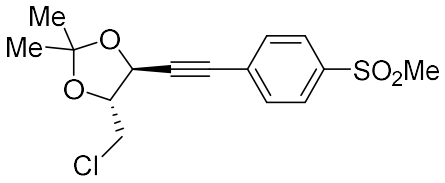
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 2H), 7.72 – 7.67 (m, 2H), 6.00 (d, *J* = 37.5 Hz, 1H), 4.52 (dd, *J* = 15.7, 7.6 Hz, 1H), 4.44 (dt, *J* = 7.6, 4.6 Hz, 1H), 3.80 (dd, *J* = 11.9, 4.6 Hz, 1H), 3.73 (dd, *J* = 11.9, 4.5 Hz, 1H), 3.06 (s, 3H), 1.53 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 156.8, 139.3, 137.7, 129.5 (d, *J* = 7.5 Hz), 127.7, 111.5, 107.9, 107.8, 44.5, 43.6, 27.1, 26.5;

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.9 (dd, *J* = 37.6, 15.8 Hz).

HRMS: (ESI) calcd for $C_{15}H_{19}ClFO_4S^+$[M+H]$^+$ 349.0677; found 349.0672.

(4R,5S)-4-(chloromethyl)-2,2-dimethyl-5-((4-(methylsulfonyl)phenyl)ethynyl)-1,3-dioxolane (9ab)



Chemical Formula: $C_{15}H_{17}ClO_4S$
Exact Mass: 328.0536

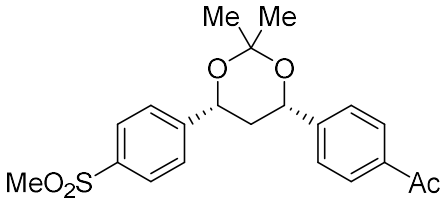
9ab was prepared according to general procedure **2.3** using $NiBr_2$•dme (3.3 mg, 0.01 mmol, 10 mol%), dtbbpy (4.2 mg, 0.015 mmol, 15 mol%), 1-(bromoethynyl)-4-(methylsulfonyl)benzene (26.0 mg, 0.1 mmol, 1 equiv), (*R*)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (75.2 mg, 0.5 mmol, 5 equiv), TBADT (6.8 mg, 0.002 mmol, 2 mol%), K_3PO_4 (25.3 mg, 0.12 mmol, 1.2 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 3/1) to obtain **9ab** as colorless oil (15.7 mg, 48% yield, d.r. > 20/1). R_f = 0.4 (PE/EA = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.80 (m, 2H), 7.74 – 7.54 (m, 2H), 4.85 (d, *J* = 6.4 Hz, 1H), 4.43 (dt, *J* = 6.4, 5.1 Hz, 1H), 3.71 (d, *J* = 5.1 Hz, 2H), 3.06 (s, 3H), 1.57 (s, 3H), 1.49 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.4, 132.6, 127.8, 127.4, 111.8, 89.5, 85.0, 81.0, 44.5, 43.3, 27.1, 26.5;

HRMS: (ESI) calcd for $C_{15}H_{18}ClO_4S^+[M+H]^+$ 329.0614; found 329.0615.

1-(4-((4*S*,6*R*)-2,2-dimethyl-6-(4-(methylsulfonyl)phenyl)-1,3-dioxan-4-yl)phenyl)ethan-1-one (10a)



Chemical Formula: $C_{21}H_{24}O_5S$
Exact Mass: 388.1344

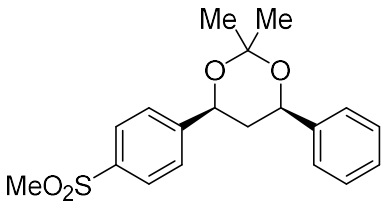
10a was prepared according to general procedure **2.4** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L4** (15.4 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 1-bromo-4-(methylsulfonyl)benzene (47.0 mg, 0.20 mmol, 1.0 equiv), (*S*)-1-(4-(2,2-dimethyl-1,3-dioxan-4-yl)phenyl)ethan-1-one (468.6 mg, 2.0 mmol, 10.0 equiv), TBADT (33.5 mg, 0.2 mmol, 5 mol%), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 3/1) to obtain **10a** as colorless oil (51.9 mg, 67% yield, d.r. = 15/1). R_f = 0.2 (PE/EA = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (t, *J* = 8.9 Hz, 4H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 2H), 5.23 – 5.11 (m, 2H), 3.02 (s, 3H), 2.59 (s, 3H), 2.04 (d, *J* = 13.1 Hz, 1H), 1.69 (s, 3H), 1.64 (s, 3H), 1.60 (d, *J* = 19.9 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.7, 148.0, 146.8, 139.7, 136.5, 128.6, 127.6, 126.7, 125.9, 99.9, 70.9, 70.8, 44.5, 40.9, 30.1, 26.6, 19.7;

HRMS: (APCI) calcd for $C_{21}H_{25}O_5S^+[M+H]^+$ 389.1417; found 389.1408.

(4*S*,6*R*)-2,2-dimethyl-4-(4-(methylsulfonyl)phenyl)-6-phenyl-1,3-dioxane (10b)



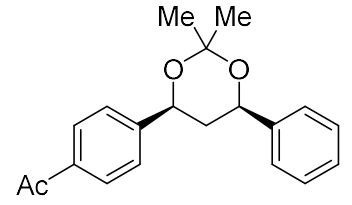
Chemical Formula: $C_{19}H_{22}O_4S$
Exact Mass: 346.1239

10b was prepared according to general procedure **2.4** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 1-bromo-4-(methylsulfonyl)benzene (47.0 mg, 0.20 mmol, 1.0 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), (*R*)-2,2-dimethyl-4-phenyl-1,3-dioxane (384.2 mg, 2.0 mmol, 10.0 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 3/1) to obtain **10b** as colorless oil (38.1 mg, 55% yield, d.r. > 20/1). R_f = 0.3 (PE/EA = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 6.9 Hz, 1H), 5.17 (d, *J* = 11.6 Hz, 1H), 5.09 (d, *J* = 11.5 Hz, 1H), 3.02 (d, *J* = 2.4 Hz, 3H), 2.05 – 1.99 (m, 1H), 1.72 (d, *J* = 12.7 Hz, 1H), 1.69 (s, 3H), 1.63 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.4, 141.5, 139.6, 128.5, 127.9, 127.6, 126.7, 125.9, 99.8, 71.4, 70.9, 44.6, 41.1, 30.2, 19.8;

HRMS: (ESI) calcd for $C_{19}H_{22}O_4SNa^+$[M+Na]$^+$ 369.1058; found 369.1054.

1-(4-((4*S*,6*R*)-2,2-dimethyl-6-phenyl-1,3-dioxan-4-yl)phenyl)ethan-1-one (10c)



Chemical Formula: $C_{20}H_{22}O_3$
Exact Mass: 310.1569

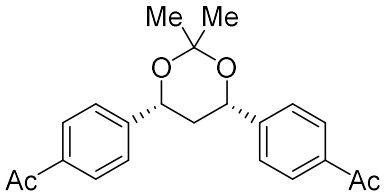
10c was prepared according to general procedure **2.4** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 1-(4-bromophenyl)ethan-1-one (40.0 mg, 0.20 mmol, 1.0 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), (*R*)-2,2-dimethyl-4-phenyl-1,3-dioxane (384.2 mg, 2.0 mmol, 10.0 equiv), K_3PO_4 (63.6

mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **10c** as colorless oil (37.8 mg, 61% yield, d.r. > 20/1). R_f = 0.4 (PE/EA = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 1H), 5.14 (dd, *J* = 11.7, 2.5 Hz, 1H), 5.09 (dd, *J* = 11.7, 2.5 Hz, 1H), 2.59 (s, 3H), 2.01 (dt, *J* = 13.2, 2.5 Hz, 1H), 1.77 – 1.71 (m, 1H), 1.69 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.8, 147.4, 141.8, 136.4, 128.6, 128.5, 127.8, 125.91, 125.88, 99.7, 71.5, 71.2, 41.1, 30.3, 26.6, 19.8.

HRMS: (APCI) calcd for $C_{20}H_{23}O_3^+$[M+H]$^+$ 311.1642; found 311.1639.

1,1'-(((4*S*,6*R*)-2,2-dimethyl-1,3-dioxane-4,6-diyl)bis(4,1-phenylene))bis(ethan-1-one) (10d)



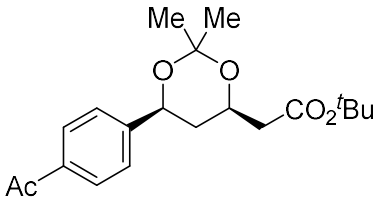
Chemical Formula: $C_{22}H_{24}O_4$
Exact Mass: 352.1675

10d was prepared according to general procedure **2.4** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L4** (15.4 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 1-(4-bromophenyl)ethan-1-one (40.0 mg, 0.20 mmol, 1.0 equiv), (*S*)-1-(4-(2,2-dimethyl-1,3-dioxan-4-yl)phenyl)ethan-1-one (468.6 mg, 2.0 mmol, 10.0 equiv), TBADT (33.5 mg, 0.2 mmol, 5 mol%), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 3/1) to obtain **10d** as colorless oil (51.4 mg, 73% yield, d.r. = 15/1). R_f = 0.4 (PE/EA = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.3 Hz, 4H), 7.49 (d, *J* = 7.4 Hz, 4H), 5.15 (d, *J* = 11.4 Hz, 2H), 2.59 (s, 6H), 2.03 (d, *J* = 13.4 Hz, 1H), 1.69 (s, 3H), 1.68 (s, 1H), 1.65 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.8, 147.1, 136.5, 128.6, 125.9, 99.8, 71.0, 40.9, 30.2, 26.6, 19.7;

HRMS: (ESI) calcd for $C_{22}H_{25}O_4^+$[M+H]$^+$ 353.1747; found 353.1737.

***tert*-butyl 2-((4*R*,6*S*)-6-(4-acetylphenyl)-2,2-dimethyl-1,3-dioxan-4-yl)acetate (10e)**



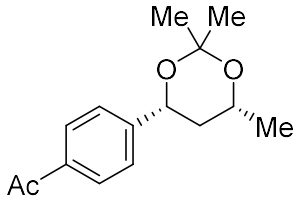
Chemical Formula: $C_{20}H_{28}O_5$
Exact Mass: 348.1937

10e was prepared according to general procedure **2.4** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 1-(4-bromophenyl)ethan-1-one (40.0 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), *tert*-butyl (*R*)-2-(2,2-dimethyl-1,3-dioxan-4-yl)acetate (460.6 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **10e** as colorless oil (36.2 mg, 52% yield, d.r. > 20:1). R_f = 0.6 (PE/EA = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.48 – 7.43 (m, 2H), 4.99 (dd, *J* = 11.7, 2.7 Hz, 1H), 4.43 (dtd, *J* = 11.6, 6.6, 2.4 Hz, 1H), 2.59 (s, 3H), 2.48 (dd, *J* = 15.3, 7.0 Hz, 1H), 2.33 (dd, *J* = 15.3, 6.2 Hz, 1H), 1.84 (dt, *J* = 12.9, 2.5 Hz, 1H), 1.57 (s, 3H), 1.49 (s, 3H), 1.45 (s, 10H), 1.39 – 1.27 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.8, 170.1, 147.5, 136.4, 128.6, 126.0, 99.3, 80.8, 71.0, 66.3, 42.5, 38.6, 30.1, 28.1, 26.7, 19.7.

HRMS: (ESI) calcd for $C_{20}H_{28}O_5Na^+$[M+Na]$^+$ 372.1863; found 372.1855.

1-(4-((4*R*,6*R*)-2,2,6-trimethyl-1,3-dioxan-4-yl)phenyl)ethan-1-one (10f)



Chemical Formula: $C_{15}H_{20}O_3$
Exact Mass: 248.1412

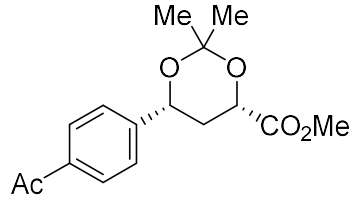
10f was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L4** (15.4 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 1-(4-bromophenyl)ethan-1-one (40.0 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), (*R*)-2,2,4-trimethyl-1,3-dioxane (260.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3

mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 10/1) to obtain **10f** as colorless oil (34.7 mg, 70% yield, d.r. = 15/1). R_f = 0.4 (PE/EA = 10/1).

^1H NMR (600 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.48 – 7.43 (m, 2H), 4.96 (dd, *J* = 11.8, 2.7 Hz, 1H), 4.15 (dqd, *J* = 12.2, 6.1, 2.3 Hz, 1H), 2.58 (s, 3H), 1.75 (dt, *J* = 13.1, 2.6 Hz, 1H), 1.56 (s, 3H), 1.52 (s, 3H), 1.39 (dt, *J* = 13.1, 11.6 Hz, 1H), 1.21 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.9, 147.8, 136.3, 128.6, 125.9, 99.1, 71.1, 65.2, 40.8, 30.3, 26.7, 22.1, 19.8.

HRMS: (ACPI) calcd for $C_{15}H_{21}O_3^+[M+H]^+$ 249.1485; found 249.1479.

methyl (4*S*,6*R*)-6-(4-acetylphenyl)-2,2-dimethyl-1,3-dioxane-4-carboxylate (10g)



Chemical Formula: $C_{16}H_{20}O_5$
Exact Mass: 292.1311

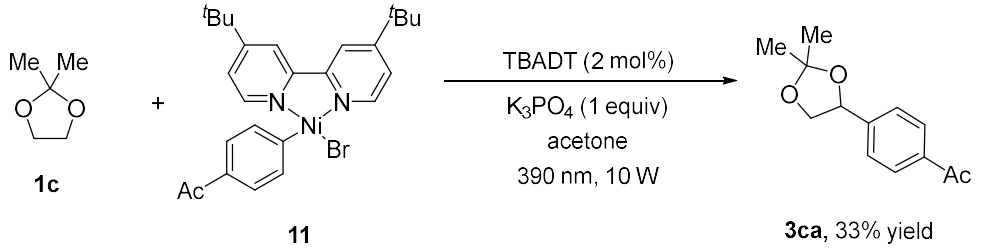
10g was prepared according to general procedure **2.2** using $NiBr_2$•dme (6.2 mg, 0.02 mmol, 10 mol%), **L4** (15.4 mg, 0.03 mmol, 15 mol%), anhydrous acetone (0.5 mL), 1-(4-bromophenyl)ethan-1-one (40.0 mg, 0.20 mmol, 1 equiv), TBADT (33.5 mg, 0.02 mmol, 5 mol%), methyl (*S*)-2,2-dimethyl-1,3-dioxane-4-carboxylate (348.4 mg, 2.0 mmol, 10 equiv), K_3PO_4 (63.6 mg, 0.3 mmol, 1.5 equiv) and $PhCF_3$ (0.5 mL) and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **10g** as colorless oil (37.4 mg, 64% yield, d.r. = 12/1). R_f = 0.3 (PE/EA = 5/1).

^1H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.80 (m, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 5.03 (dd, *J* = 11.7, 2.7 Hz, 1H), 4.68 (dd, *J* = 12.2, 2.7 Hz, 1H), 3.76 (s, 3H), 2.58 (s, 3H), 2.11 (dt, *J* = 13.1, 2.7 Hz, 1H), 1.74 (q, *J* = 12.1 Hz, 1H), 1.61 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.8, 170.9, 146.6, 136.6, 128.6, 126.0, 100.0, 70.7, 68.9, 52.4, 35.5, 29.9, 26.7, 19.4.

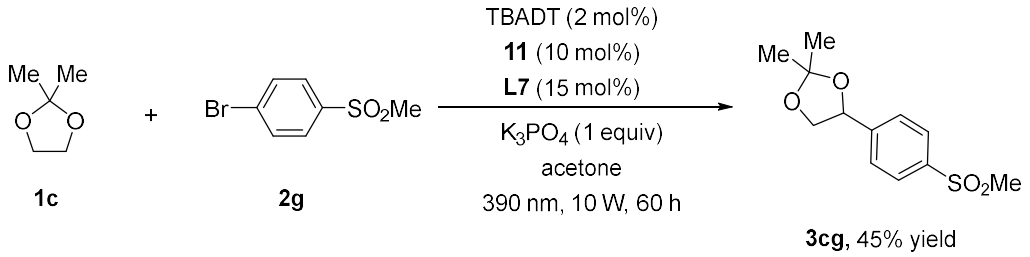
HRMS: (APCI) calcd for $C_{16}H_{21}O_5^+[M+H]^+$ 293.1383; found 293.1376.

5. Mechanistic studies

5.1 Reaction of aryl-Ni(II) complex 11

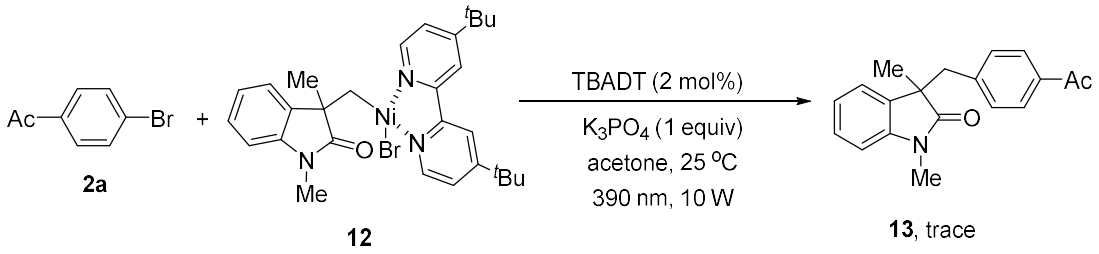


An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with complex **11** (26.3 mg, 0.05 mmol, 1 equiv), 2,2-dimethyl-1,3-dioxolane **1c** (25.5 mg, 0.25 mmol, 5 equiv), TBADT (3.4 mg, 0.001 mmol, 2 mol%), K_3PO_4 (10.6 mg, 0.05 mmol, 1 equiv) and anhydrous acetone (0.5 mL). The sealed tube was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp at 25 °C. The resulting mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel, eluting with PE/EA (10/1) to afford the corresponding product **3ca** (3.6 mg, 33% yield).

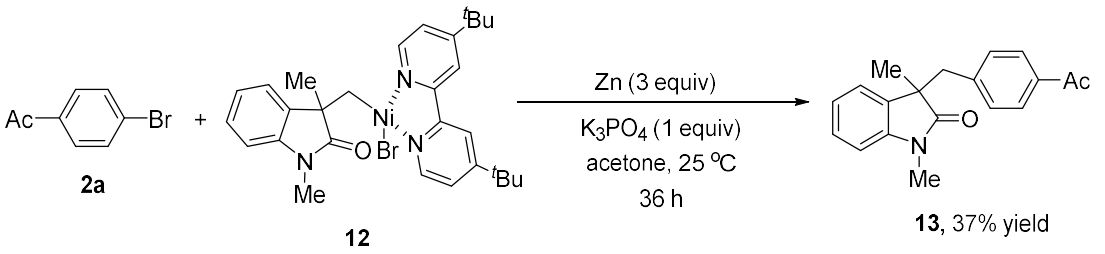


An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with complex **11** (5.6 mg, 0.01 mmol, 10 mol%), **L7** (4.0 mg, 0.015 mmol, 15 mol%), TBADT (6.8 mg, 0.002 mmol, 2 mol%), 2,2-dimethyl-1,3-dioxolane **1c** (51.0 mg, 0.50 mmol, 5 equiv), 1-bromo-4-(methylsulfonyl)benzene **2g** (23.5 mg, 0.10 mmol, 1.0 equiv), K_3PO_4 (21.2 mg, 0.10 mmol, 1 equiv) and anhydrous acetone (1.0 mL). The sealed tube was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp at 25 °C. The resulting mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel, eluting with PE/EA (5/1) to afford the corresponding product **3cg** (11.5 mg, 45% yield).

5.2 Reaction of *σ*-alkyl-Ni(II) complex 12



An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with complex **12** (29.1 mg, 0.05 mmol, 1 equiv), 1-(4-bromophenyl)ethan-1-one **2a** (10.0 mg, 0.05 mmol, 1 equiv), TBADT (3.4 mg, 0.001 mmol, 2 mol%), K_3PO_4 (10.6 mg, 0.05 mmol, 1 equiv) and anhydrous acetone (0.5 mL). The sealed tube was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp at 25 °C. The resulting mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel, eluting with PE/EA (4/1) to afford trace product **13**.

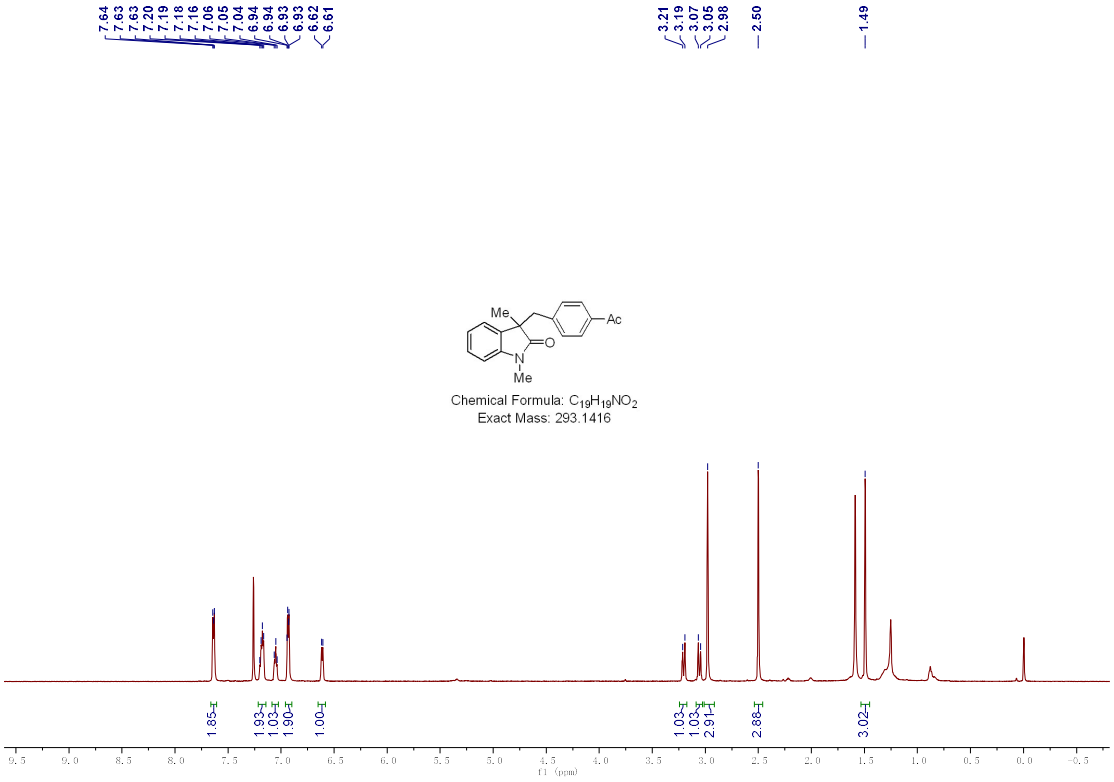


An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with complex **12** (29.1 mg, 0.05 mmol, 1 equiv), 1-(4-bromophenyl)ethan-1-one **2a** (10.0 mg, 0.05 mmol, 1 equiv), Zn (9.8 mg, 0.15 mmol, 3 equiv) K_3PO_4 (10.6 mg, 0.05 mmol, 1 equiv) and anhydrous acetone (0.5 mL). The sealed tube was sealed and removed from the glovebox. Then the reaction was stirred at 25 °C in an aluminium bead bath for 12 hours. The resulting mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel, eluting with PE/EA (4/1) to afford the corresponding product **13** (5.4 mg, 37% yield).

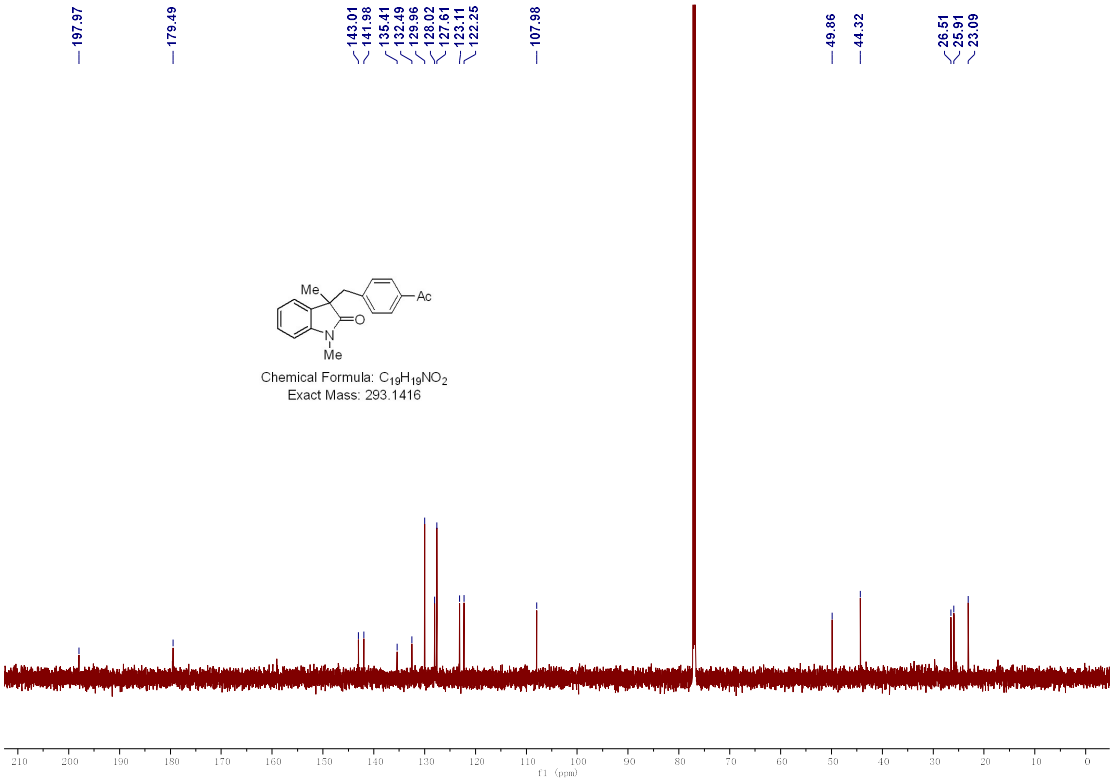
The NMR data matched those reported in the literature.[8]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.18 (q, J = 7.4, 6.9 Hz, 2H), 7.05 (t, J = 7.6 Hz, 1H), 6.93 (dd, J = 8.4, 2.9 Hz, 2H), 6.61 (d, J = 7.7 Hz, 1H), 3.20 (d, J = 12.9 Hz, 1H), 3.06 (d, J = 12.9 Hz, 1H), 2.98 (s, 3H), 2.50 (s, 3H), 1.49 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.0, 179.5, 143.0, 142.0, 135.4, 132.5, 130.0, 128.0, 127.6, 123.1, 122.3, 108.0, 49.9, 44.3, 26.5, 25.9, 23.1.

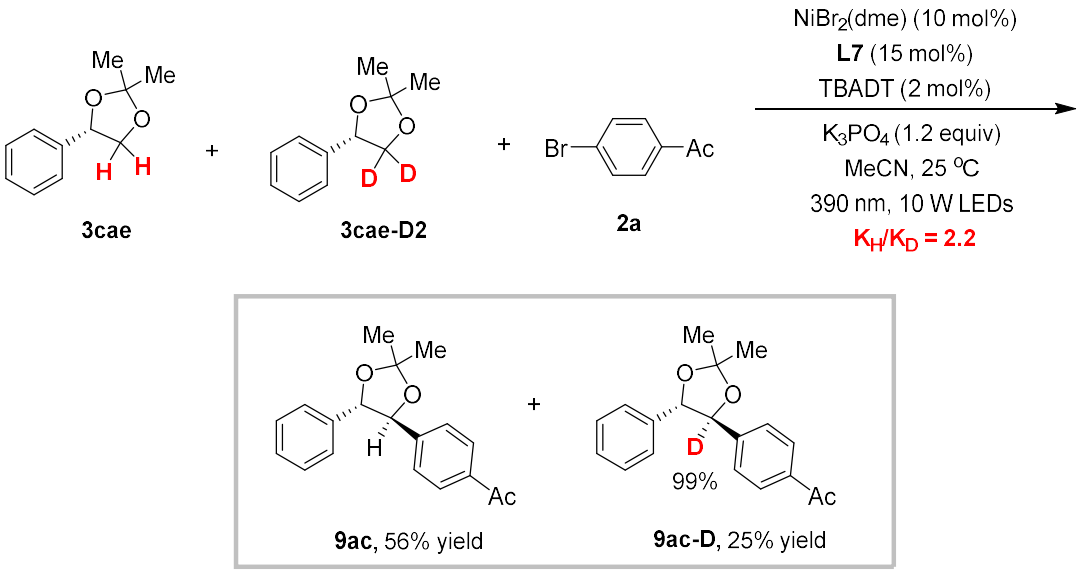


Supplementary Figure 83. ^{1}H NMR Spectrum of **13**

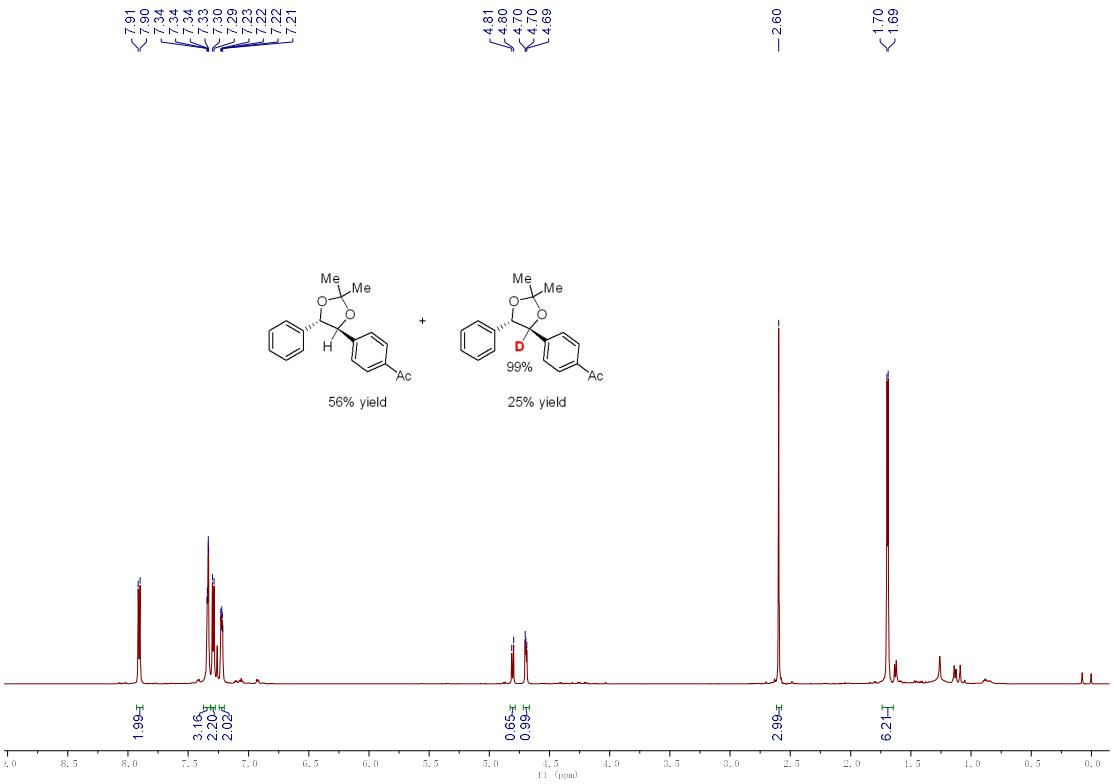


Supplementary Figure 84. ^{13}C NMR Spectrum of **13**

5.3 Kinetic isotope effect (KIE) from an intermolecular competition experiment

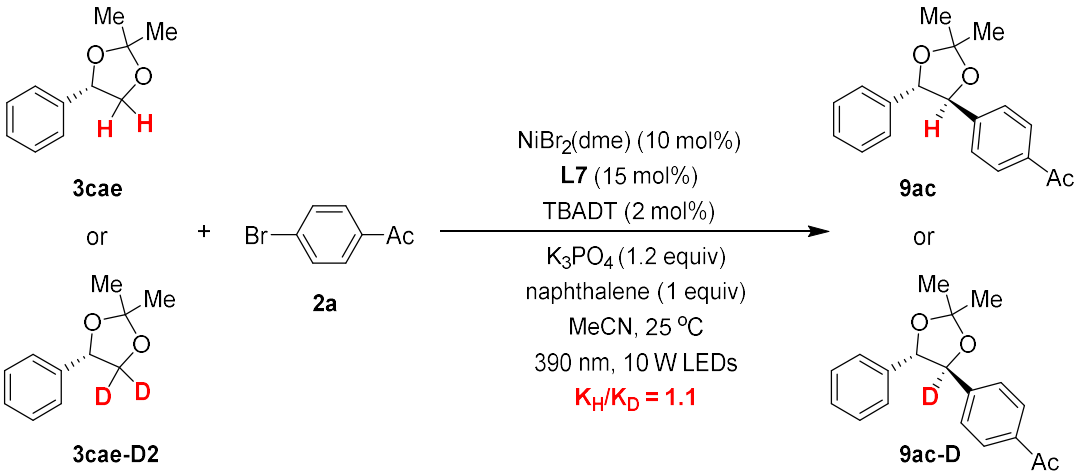


An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with $NiBr_2$(dme) (3.1 mg, 0.01 mmol, 10 mol%), **L7** (4.0 mg, 0.015 mmol, 15 mol%), TBADT (6.8 mg, 0.002 mmol, 2 mol%), **2a** (19.9 mg, 0.10 mmol, 1.0 equiv), **3cae** (89.0 mg, 0.50 mmol, 5.0 equiv), **3cae-D2** (90.0 mg, 0.50 mmol, 5.0 equiv), K_3PO_4 (25.2 mg, 0.12 mmol, 1.2 equiv) and anhydrous MeCN (1 mL). The reaction mixture was stirred and irradiated with a 10 W 390 nm LED lamp at 25 ℃. The resulting mixture was removed from light, diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. The combined solvent was then evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with PE/EA (5/1) to afford **9ac** (56% yield) and **9ac-D** (25% yield).

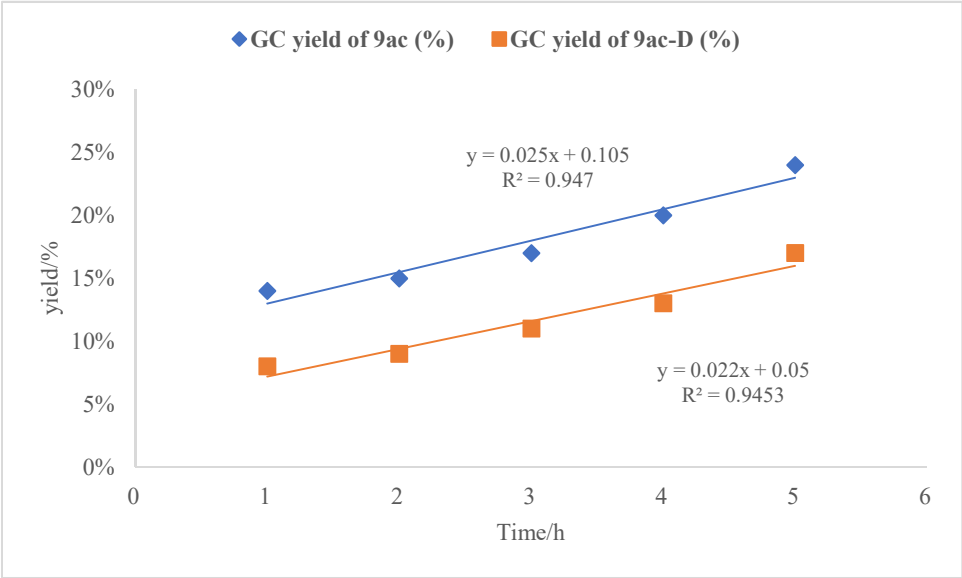


Supplementary Figure 85. ^{1}H NMR Spectrum of **9ac** and **9ac-D**

5.4 Kinetic isotope effect (KIE) from two parallel reactions

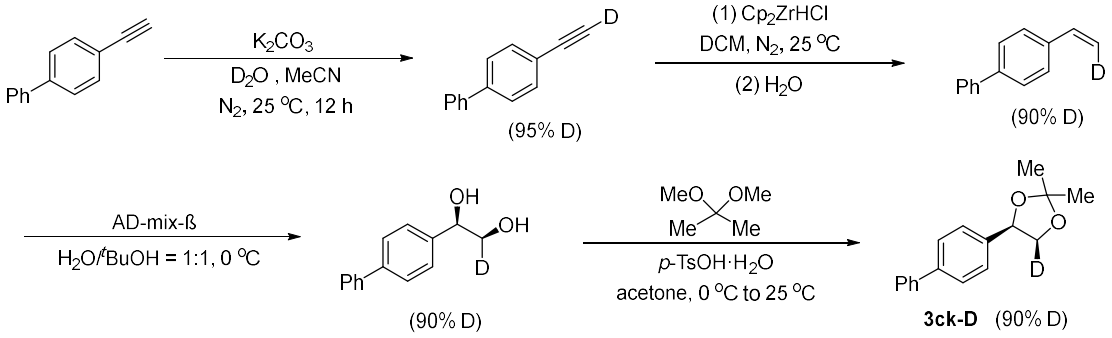


Two oven-dried 10-mL vials equipped with a PTFE-coated stir bar was charged with $NiBr_2$(dme) (3.1 mg, 0.01 mmol, 10 mol%), **L7** (4.0 mg, 0.015 mmol, 15 mol%), TBADT (6.8 mg, 0.002 mmol, 2 mol%), **3cae** or **3cae-D2** (90.0 mg, 0.50 mmol, 5.0 equiv), **2a** (19.9 mg, 0.10 mmol, 1.0 equiv), anhydrous K_3PO_4 (25.2 mg, 0.12 mmol, 1.2 equiv) and dry MeCN (1.0 mL) in an argon-filled glovebox. The vial was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp at 25 °C. The reactions were stirred under irradiation for the time stated for each experiment. The kinetic isotope effect (KIE) was determined to be 1.1. The reaction uses naphthalene as an internal standard.



Supplementary Figure 86. Curve of Kinetic isotope effect from two parallel reactions

5.5 Intramolecular competition experiment of 3ck-D



An oven-dried 100 mL Schlenk flask was charged with 4-ethynyl-1,1'-biphenyl (1.78 g, 10 mmol), K_3PO_4 (2.0 g, 1.5 equiv) and anhydrous MeCN (10 mL). The reaction mixture was stirred under N_2 atmosphere for 30 minutes. D_2O (10.0 mL, 50 equiv) was then added and the resulting mixture was stirring at 25 °C for overnight. The reaction mixture was diluted with DCM. The organic layer was dried over Na_2SO_4, filtered and solvent was removed under reduced pressure to afford the 4-(ethynyl-*d*)-1,1'-biphenyl (1.77 g, 99% yield, 95% D).

An oven-dried 100 mL Schlenk flask was charged with 4-(ethynyl-*d*)-1,1'-biphenyl (0.896 g, 5 mmol), Cp_2ZrHCl (Schwartz' reagent) (1.42 g, 5.5 mmol, 1.1 equiv) and anhydrous DCM (10 mL). After stirring at room temperature in the dark for 2 h, water (0.71 mL, 40 mmol, 8 equiv) was added and the reaction was stirred for overnight. The reaction was diluted with DCM and the organic layer was washed with brine, dried over Na_2SO_4, filtered, and solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (PE) to afford (*Z*)-4-(vinyl-2-*d*)-1,1'-biphenyl (815.6 mg, 90% yield, 90% D).

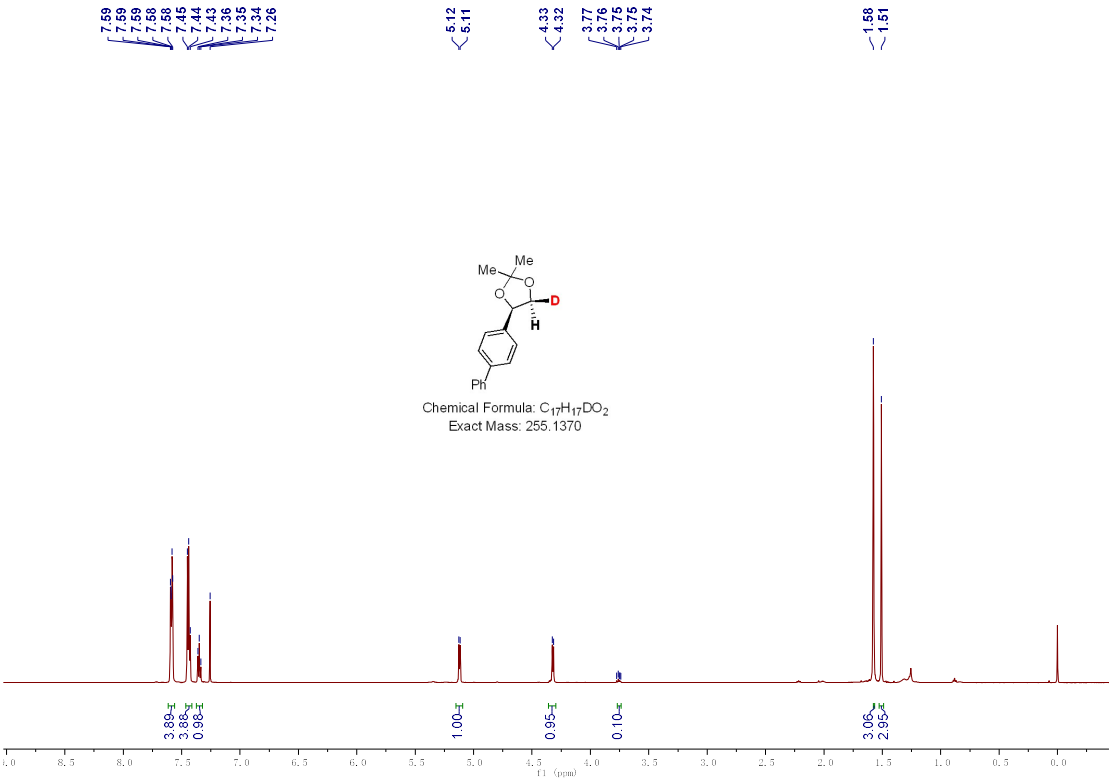
A round-bottomed flask was charged with tert-butyl alcohol (20 mL), H_2O (20 mL) and AD-mix-β (5.6 g). The mixture was stirred at room temperature until the aqueous phase appears bright yellow. The mixture was cooled to 0 ℃ whereupon some of the dissolved salts precipitated, (*Z*)-4-(vinyl-2-*d*)-1,1'-biphenyl (815.6 mg, 4.5 mmol) was added once, and the heterogenous slurry was stirred vigorously at 0 ℃ for 24 h. While the mixture was stirred at 0 ℃, anhydrous sodium sulfite was added and the mixture was allowed to warm to 25 °C and further stirred for 30 minutes. The reaction mixture was extracted with EA. The organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was

purified by flash chromatography on silica gel (PE/EA) to afford (1*R*,2*S*)-1-([1,1'-biphenyl]-4-yl)ethane-2-*d*-1,2-diol (238.8 mg, 40% yield, 90% D).

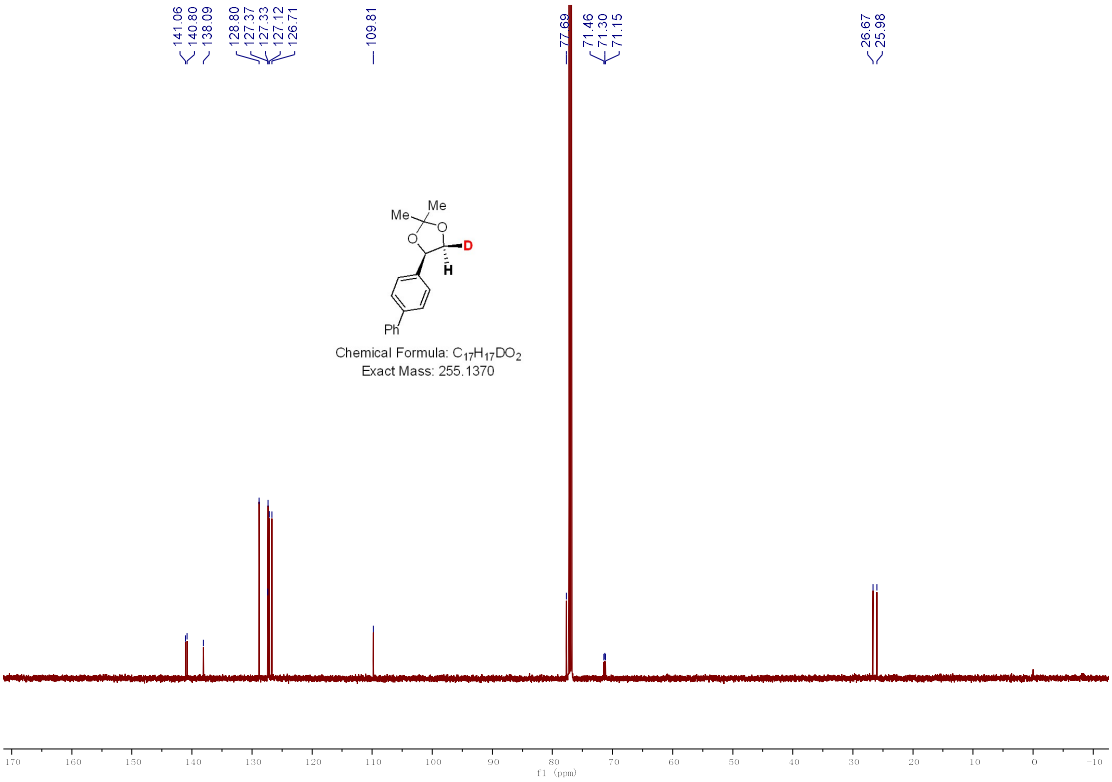
To a solution of (1*R*,2*S*)-1-([1,1'-biphenyl]-4-yl)ethane-2-*d*-1,2-diol (89.7 mg, 0.42 mmol) in acetone (5 mL) was added PTSA·H_2O (8.0 mg, 0.042 mmol, 10 mol%). The reaction mixture was cooled to 0 ℃ and added 2,2-dimethoxypropane (0.14 mL, 1.05 equiv, 0.44 mmol). The reaction mixture was stirred at room temperature for 16 h. The reaction was quenched by adding saturated $NaHCO_3$ solution (2 mL). The reaction mixture was extracted with DCM. The organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel (PE/EA) to afford **3ck-D** (86.2 mg, 81% yield, 90% D).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 4H), 7.44 (t, *J* = 7.4 Hz, 4H), 7.35 (t, *J* = 7.4 Hz, 1H), 5.12 (d, *J* = 6.2 Hz, 1H), 4.32 (d, *J* = 6.2 Hz, 1H), 1.58 (s, 3H), 1.51 (s, 3H).

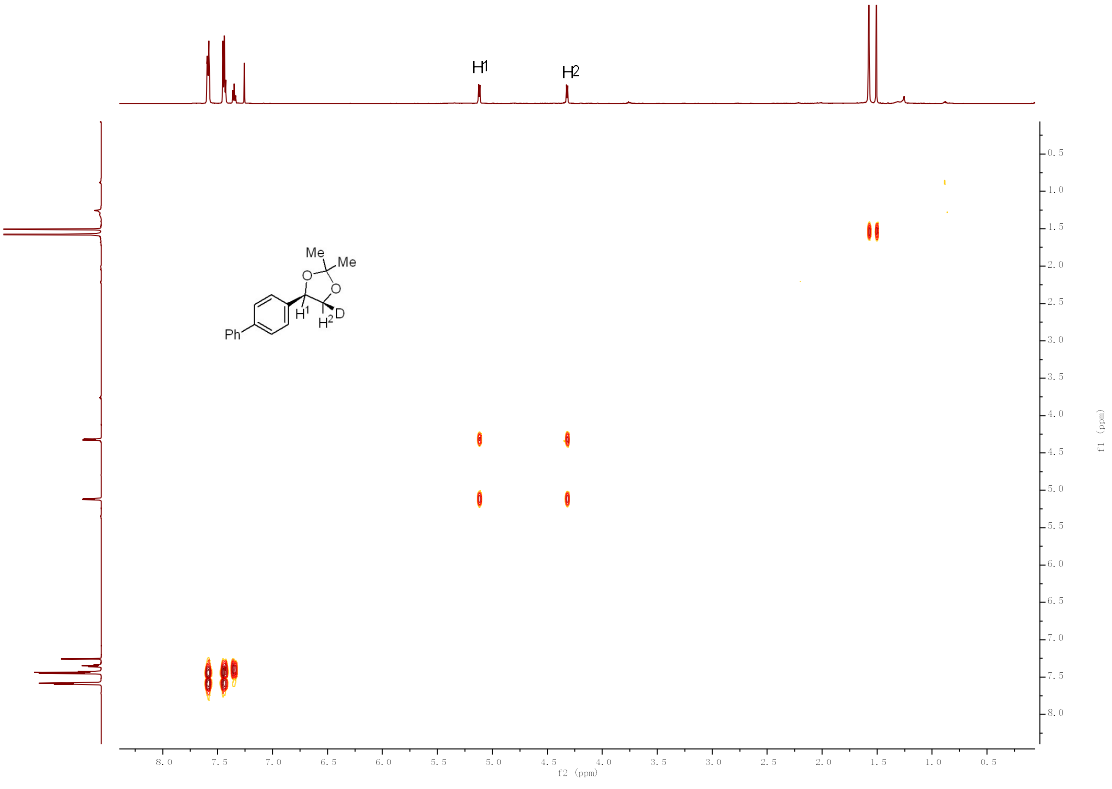
^{13}C NMR (151 MHz, $CDCl_3$) δ 141.1, 140.8, 138.1, 128.8, 127.4, 127.3, 127.1, 126.7, 109.8, 77.7, 71.3 (t, *J* = 24.2 Hz), 26.7, 26.0.



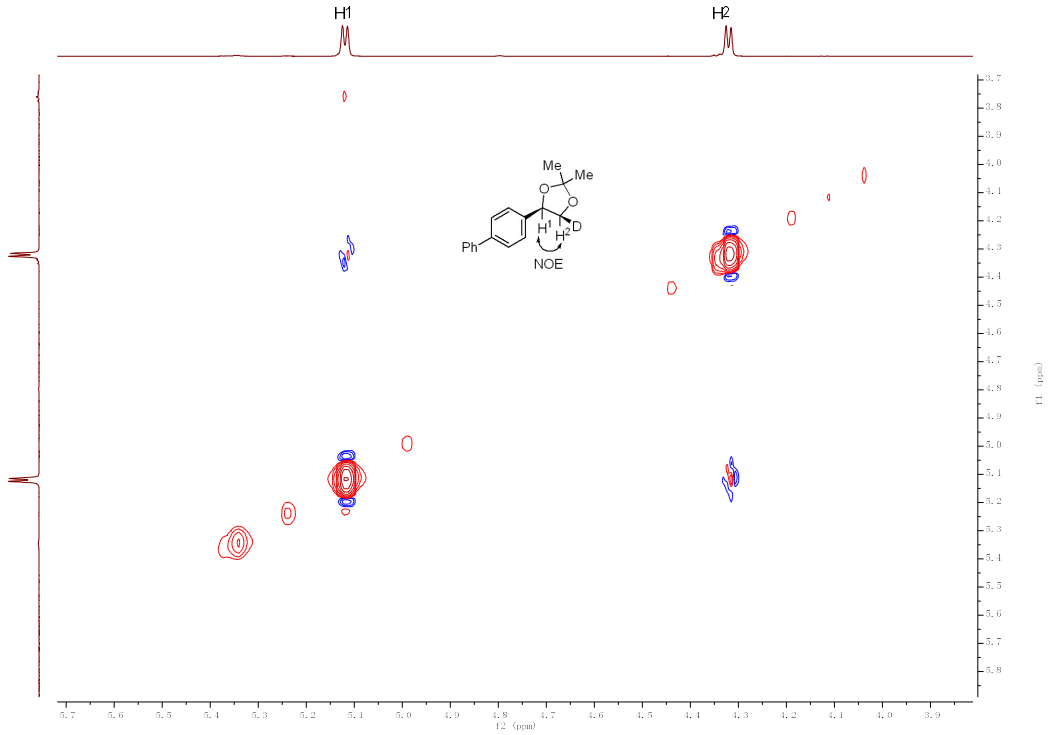
Supplementary Figure 87. ^{1}H NMR Spectrum of **3ck-D**



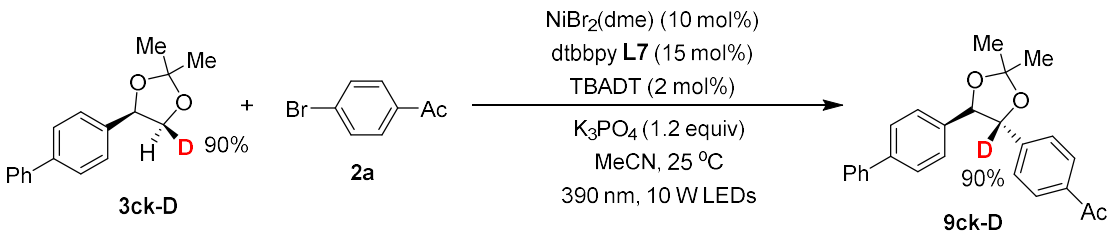
Supplementary Figure 88. ^{13}C NMR Spectrum of **3ck-D**



Supplementary Figure 89. H-H COSY Spectrum of **3ck-D**



Supplementary Figure 90. H-H NOESY Spectrum of **3ck-D**



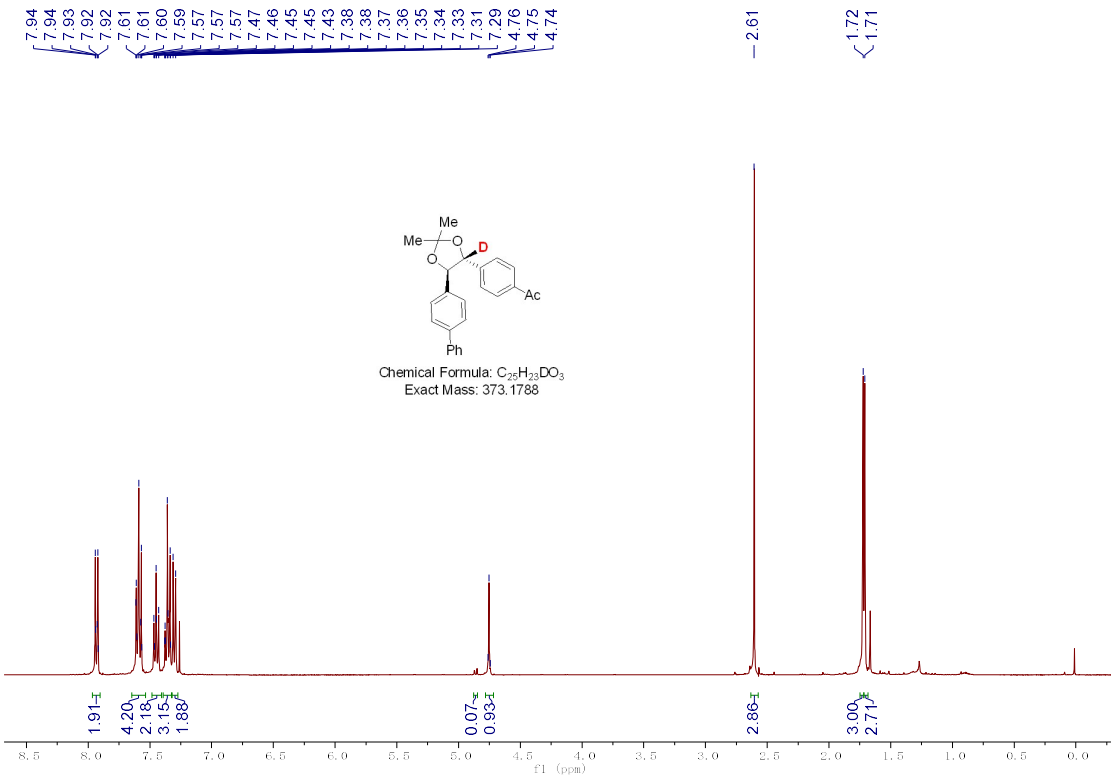
An oven-dried 10-mL vial equipped with a PTFE-coated stir bar was charged with $NiBr_2$(dme) (1.6 mg, 0.005 mmol, 10 mol%), **L7** (2.0 mg, 0.0075 mmol, 15 mol%), TBADT (3.4 mg, 0.001 mmol, 2 mol%), **2a** (10.0 mg, 0.05 mmol, 1.0 equiv), **3ck-D** (63.7 mg, 0.25 mmol, 5.0 equiv), K_3PO_4 (12.7 mg, 0.06 mmol, 1.2 equiv) and anhydrous MeCN (0.5 mL). The reaction mixture was stirred and irradiated with a 10 W 390 nm LED lamp at 25 ℃. The resulting mixture was removed from light, diluted with ethyl acetate and passed through a pad of celite. The celite plug was further washed with ethyl acetate. The combined solvent was then evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with PE/EA (5/1) to afford **9ck-D** (12.1 mg, 65% yield, > 20:1 d.r.).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 2H), 7.65 – 7.54 (m, 4H), 7.48 – 7.41 (m, 2H), 7.39 – 7.32 (m, 3H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.76 (d, *J* = 3.5 Hz, 1H), 2.61 (s, 3H), 1.72 (s, 3H), 1.71 (s, 3H).

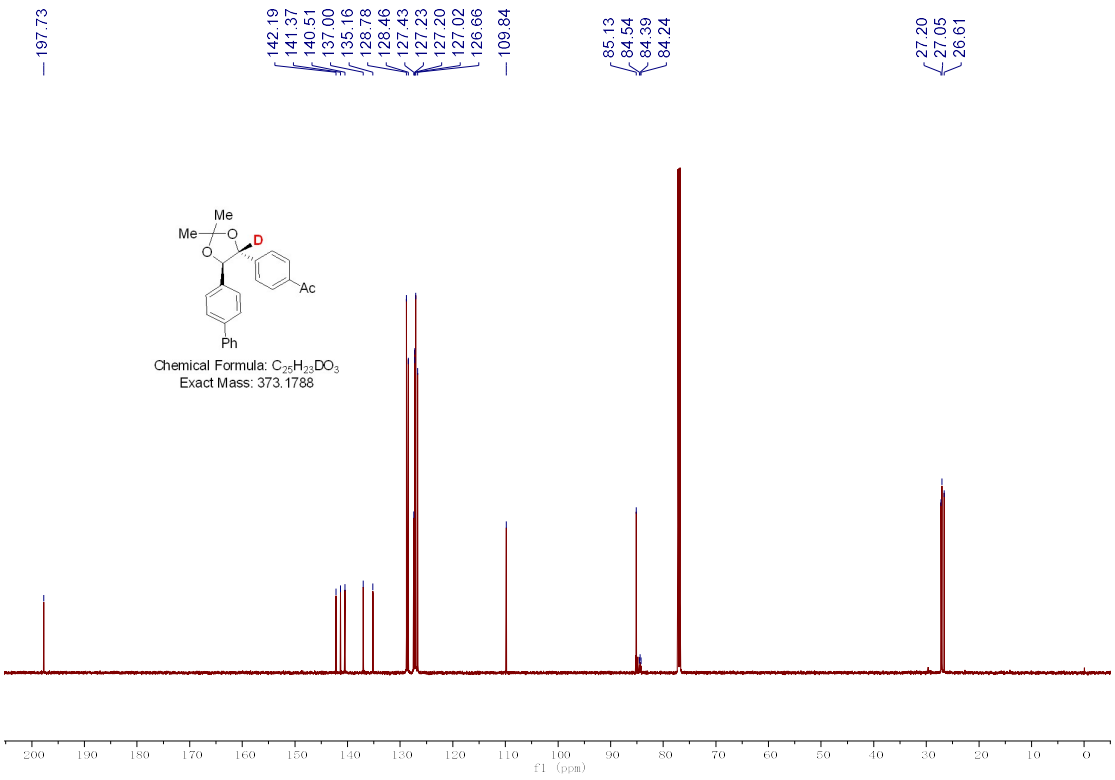
^{13}C NMR (151 MHz, $CDCl_3$) δ 197.7, 142.2, 141.4, 140.5, 137.0, 135.2, 128.8, 128.5, 127.4, 127.23, 127.2, 127.0, 126.7, 109.8, 85.1, 84.6 – 84.0 (m), 27.2, 27.0, 26.6.

^{2}H NMR (92 MHz, $CDCl_3$) δ 4.79 (s, 1H).

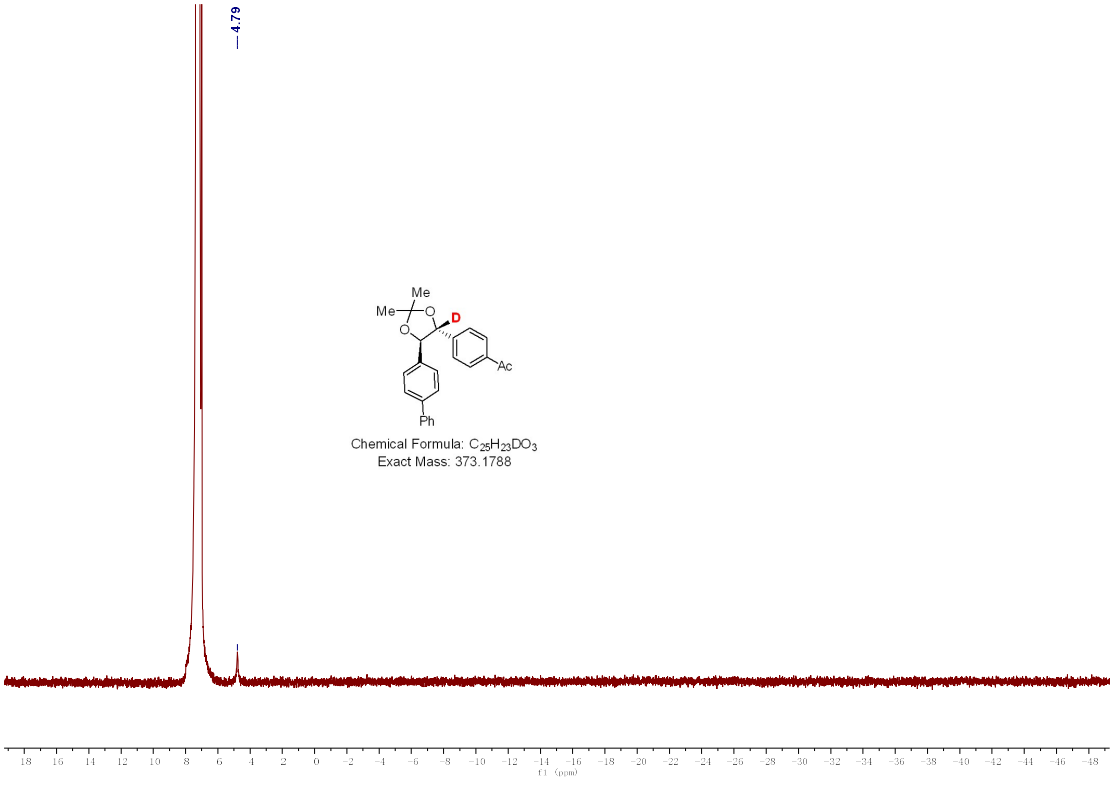
HRMS: (APCI) calcd for $C_{25}H_{24}DO_3^+$[M+H]$^+$ 374.1861; found 374.1858.



Supplementary Figure 91. ^{1}H NMR Spectrum of **9ck-D**



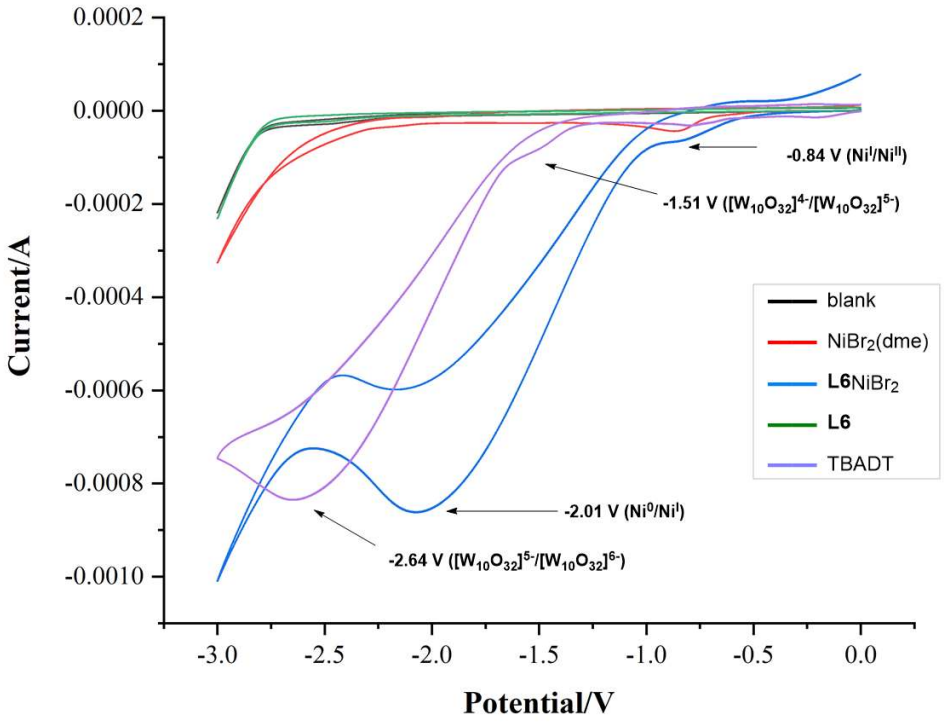
Supplementary Figure 92. ^{13}C NMR Spectrum of **9ck-D**



Supplementary Figure 93. ^{2}H NMR Spectrum of **9ck-D**

5.6 Cyclic voltammetry experiments

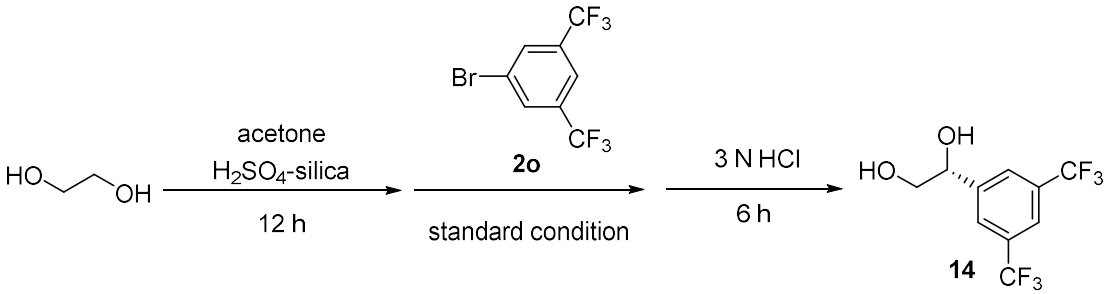
General information: Cyclic voltammetry (CV) experiments were conducted in a 20 mL two-necked cell set-up fitted with a glassy carbon working electrode (3 mm in diameter), an Ag/AgCl reference electrode, and a platinum wire counter electrode. All measurements were carried out in anhydrous MeCN, using a scan rate of 100 mV/s. Blank line: $^{n}Bu_4NBF_4$ (0.10 mmol) in 6.0 mL MeCN. Red line: $NiBr_2$(dme) (0.01 mmol), $^{n}Bu_4NBF_4$ (0.10 mmol) in 6.0 mL MeCN. Blue line: **L6**$NiBr_2$ (0.01 mmol), $^{n}Bu_4NBF_4$ (0.10 mmol) in 6.0 mL MeCN. Green line: **L6** (0.01 mmol), $^{n}Bu_4NBF_4$ (0.10 mmol) in 6.0 mL MeCN. Purple line: TBADT (0.01 mmol), $^{n}Bu_4NBF_4$ (0.10 mmol) in 6.0 mL MeCN. As shown in cyclic voltammetry studies, two reductive peaks of **L6**$NiBr_2$ were observed at Ni^{II}/Ni^{I} = - 0.84 V (*vs* Ag/Ag^{+}) and Ni^{I}/Ni^{0} = - 2.01 V (*vs* Ag/Ag^{+}). Two reductive peaks of TBADT were observed at $[W_{10}O_{32}]^{4}/[W_{10}O_{32}]^{5-}$ = - 1.51 V (*vs* Ag/Ag^{+}) and $[W_{10}O_{32}]^{5-}/[W_{10}O_{32}]^{6-}$ = - 2.64 V (*vs* Ag/Ag^{+}).



Supplementary Figure 94. Cyclic voltammetry experiments

6. Synthetic Applications

6.1 Synthesis of the (*R*)-1-(3,5-bis(trifluoromethyl)phenyl)ethane-1,2-diol (14)



An oven-dried 10 mL tube equipped with a PTFE-coated stir bar was charged with ethane-1,2-diol (62.0 mg, 1.0 mmol, 5.0 equiv), anhydrous acetone (0.5 mL) was stirred in the presence of H_2SO_4-silica[9] at room temperature in an argon-filled glovebox. The tube was sealed and stirred at room temperature for 12 hours. The reaction then proceeds with the addition of powdered $CaCl_2$ (22.0 mg, 0.2 mmol, 1.0 equiv). Subsequently, the tube was charged with $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), TBADT (24.6 mg, 0.01 mmol, 5 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), 1-bromo-3,5-bis(trifluoromethyl)benzene **2o** (58.6 mg, 0.20 mmol, 1.0 equiv), anhydrous acetone (1 mL) and $PhCF_3$ (1 mL). The tube was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp for 48 hours. The light was removed and 3 N HCl (6 mL) was added to the resulting reaction mixture. After string at room temperature for another 6 hours, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (EA) to afford **14** as colorless oil (35.6 mg, 65% yield, 90% ee).

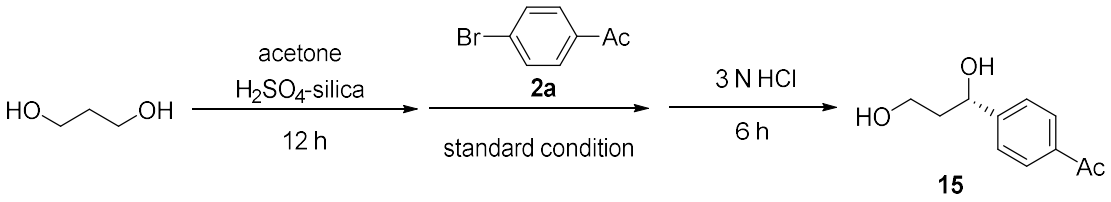
The NMR data matched those reported in the literature.[10]

^{1}H NMR (600 MHz, Methanol-d_4) δ 7.99 (s, 2H), 7.85 (s, 1H), 4.86 – 4.82 (m, 1H), 3.67 (d, J = 5.6 Hz, 2H);

^{13}C NMR (151 MHz, Methanol-d_4) δ 146.1, 131.0 (q, J = 33.1 Hz), 126.7 (q, J = 4.1 Hz), 123.6 (q, J = 271.8 Hz), 120.6 (p, J = 3.9 Hz), 72.9, 66.7;

^{19}F NMR (565 MHz, Methanol-d_4) δ -64.32.

6.2 Synthesis of the (*S*)-1-(4-(1,3-dihydroxypropyl)phenyl)ethan-1-one (15)

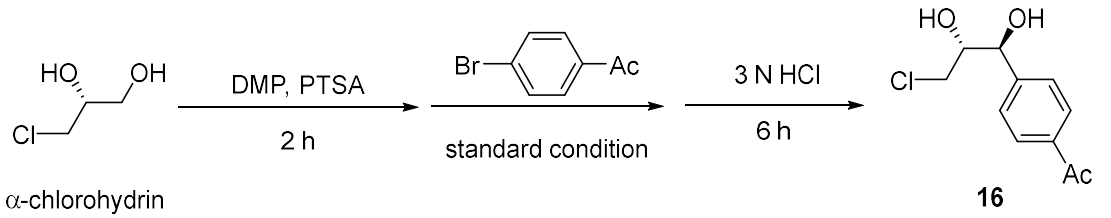


An oven-dried 10 mL tube equipped with a PTFE-coated stir bar was charged with propane-1,3-diol (76.0 mg, 1.0 mmol, 5.0 equiv), anhydrous acetone (0.5 mL) was stirred in the presence of H_2SO_4-silica at room temperature in an argon-filled glovebox. The tube was sealed and stirred at room temperature for 12 hours. The reaction then proceeds with the addition of powdered $CaCl_2$ (22.0 mg, 0.2 mmol, 1.0 equiv). Subsequently, the tube was charged with $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), **L6** (11.7 mg, 0.03 mmol, 15 mol%), TBADT (24.6 mg, 0.01 mmol, 5 mol%), K_3PO_4 (106.0 mg, 0.50 mmol, 2.5 equiv), 1-(4-bromophenyl)ethan-1-one **2a** (40.0 mg, 0.20 mmol, 1.0 equiv), anhydrous acetone (1 mL) and $PhCF_3$ (1 mL). The tube was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp for 48 hours. The light was removed and 3 N HCl (6 mL) was added to the resulting reaction mixture. After string at room temperature for another 6 hours, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (EA) to afford **15** as colorless oil (24.0 mg, 62% yield, 90% ee). The NMR data matched those reported in the literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 2H), 7.44 (d, J = 8.2 Hz, 2H), 5.02 (dd, J = 7.2, 5.1 Hz, 1H), 3.86 (t, J = 5.5 Hz, 2H), 2.82 (s, 2H), 2.58 (s, 3H), 1.99 – 1.91 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.1, 149.8, 136.2, 128.6, 125.7, 73.7, 61.2, 40.2, 26.6.

6.3 Synthesis of the 1-(4-((1*S*,2*R*)-3-chloro-1,2-dihydroxypropyl)phenyl)ethan-1-one (16)



An oven-dried 10 mL tube equipped with a PTFE-coated stir bar was charged with α-chlorohydrin (110 mg, 1.0 mmol, 5.0 equiv), PTSA·H_2O (19.0 mg, 0.1 mmol, 10 mol%) and

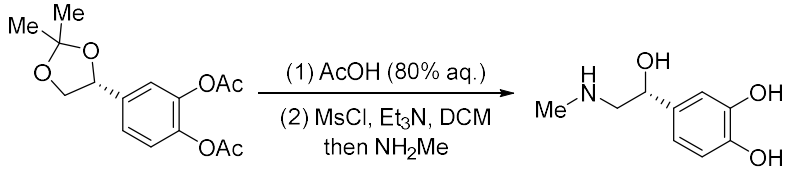
2,2-dimethoxypropane (124.8 mg, 1.2 mmol, 6.0 equiv) in an argon-filled glovebox. The tube was sealed and stirred at room temperature for 2 hours. Subsequently, the tube was charged with $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (93.3 mg, 0.44 mmol, 2.2 equiv), 1-(4-bromophenyl)ethan-1-one (40.0 mg, 0.20 mmol, 1.0 equiv) and anhydrous MeCN (1 mL). The tube was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp for 48 hours. The light was removed and 3 N HCl (6 mL) was added to the resulting reaction mixture. After string at room temperature for another 6 hours, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (EA) to afford **16** as colorless oil (34.2 mg, 75% yield, d.r. > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.79 (m, 2H), 7.63 – 7.45 (m, 2H), 4.83 (d, *J* = 6.0 Hz, 1H), 3.89 (q, *J* = 5.5 Hz, 1H), 3.60 (dd, *J* = 11.5, 4.4 Hz, 1H), 3.41 (dd, *J* = 11.5, 5.6 Hz, 1H), 3.13 (s, 1H), 2.97 (s, 1H), 2.58 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 145.4, 137.1, 128.8, 126.9, 75.3, 74.0, 45.9, 26.8;

HRMS: (ESI) calcd for $C_{11}H_{14}ClO_3^+[M+H]^+$ 229.0626; found 229.0629.

6.4 Synthesis of (*R*)-4-(1-hydroxy-2-((methylsulfonyl)oxy)ethyl)-1,2-phenylene diacetate ((-)-Epinephrine)



3cp **(-)-Epinephrine**

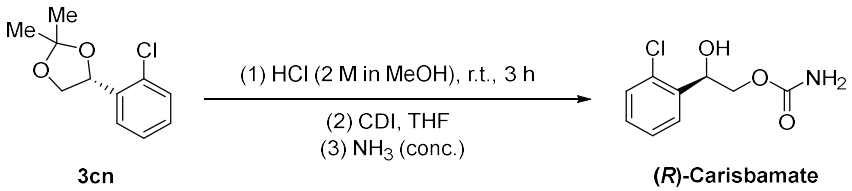
To a 50 mL flask equipped with a PTFE-coated stir bar was added **3cp** (147.3 mg, 0.5 mmol, 1 equiv) and AcOH (4 mL, 80% aq.). The reaction mixture was stirred at room temperature for 4 hours. The solvent was evaporated under reduced pressure and the residue was added DCM (5 mL), Et_3N (151.8 mg, 1.5 mmol, 3 equiv) and MsCl (85.9 mg, 0.75 mmol, 1.5 equiv) at 0 ℃. The reaction was stirred at 0 ℃ for an hour, then NH_2Me (155.3 mg, 5 mmol, 10 equiv, 33% in EtOH) was added. After stirring at room temperature overnight, the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (DCM/MeOH/Et_3N) to afford **(-)-Epinephrine** as brown solid (58.6 mg, 64% yield).

The NMR data matched those reported in the literature.[12]

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.68 (d, J = 2.0 Hz, 1H), 6.61 (d, J = 8.1 Hz, 1H), 6.51 (dd, J = 8.0, 2.0 Hz, 1H), 4.41 (dd, J = 8.2, 4.5 Hz, 1H), 2.56 – 2.47 (m, 2H), 2.26 (s, 3H);

^{13}C NMR (151 MHz, DMSO-d_6) δ 145.4, 144.6, 135.8, 117.2, 115.5, 113.9, 71.1, 60.0, 36.2.

6.5 Synthesis of (*R*)-2-(2-chlorophenyl)-2-hydroxyethyl carbamate ((*R*)-Carisbamate)



3cn **(*R*)-Carisbamate**

To a 50 mL flask equipped with a PTFE-coated stir bar was added **3cn** (82.5 mg, 0.388 mmol, 1 equiv) and HCl (6 mL) (2 M in MeOH). The reaction mixture was stirred at room temperature for 3 hours. The solvent was evaporated under reduced pressure and the residue was used in the next step without further purification.

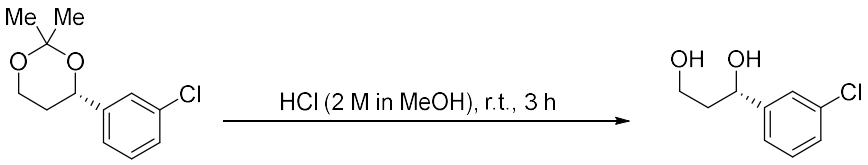
To a solution of the obtained crude product in THF (2 mL) was added CDI (67.0 mg, 0.41 mmol). The resulting mixture was stirred at room temperature for overnight, then ammonia solution (0.11 mL) was added. After stirring for another 12 hours, the reaction was quenched with 1 M HCl solution and extracted with EA. The organic phase was washed with saturated $NaHCO_3$ (aq.) and brine, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (EA) to afford **(*R*)-Carisbamate** (18.4 mg, 22% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (dd, J = 7.8, 1.7 Hz, 1H), 7.35 (dd, J = 7.9, 1.3 Hz, 1H), 7.32 (td, J = 7.6, 1.3 Hz, 1H), 7.24 (dd, J = 7.6, 1.7 Hz, 1H), 5.37 (dd, J = 7.8, 2.6 Hz, 1H), 4.82 (s, 2H), 4.34 (dd, J = 11.9, 2.7 Hz, 1H), 4.22 (dd, J = 11.9, 7.7 Hz, 1H), 3.38 (s, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.4, 137.2, 132.0, 129.5, 129.2, 127.9, 127.2, 70.0, 68.8;

Optical Rotation: $[\alpha]_D^{22}$ -20.4 (c 0.1, ^{i}PrOH) for 82% ee.

6.6 Synthesis of (*S*)-1-(3-chlorophenyl)propane-1,3-diol (17)



5al **17**

To a 50-mL flask equipped with a PTFE-coated stir bar was added **5al** (28.1 mg, 0.124 mmol, 1 equiv) and HCl (2 mL) (2 M in MeOH). The reaction mixture was stirred at room temperature for 3 hours. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (EA) to afford **17** (20.8 mg, 90% yield).

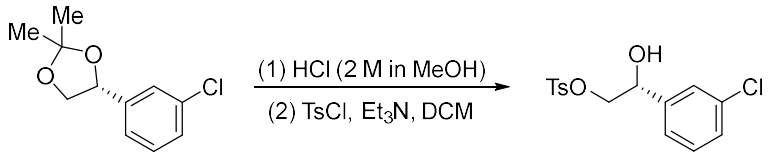
The NMR data matched those reported in the literature.[13]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.31 – 7.19 (m, 4H), 5.00 – 4.91 (m, 1H), 3.88 (t, *J* = 5.2 Hz, 2H), 2.58 (s, 3H), 2.05 – 1.90 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.4, 134.4, 129.8, 127.6, 125.9, 123.8, 73.7, 61.4, 40.4;

Optical Rotation: $[\alpha]_D^{23}$ -20.5 (c 0.2, ^{i}PrOH) for 88% ee.

6.7 Synthesis of (*R*)-2-(3-chlorophenyl)-2-hydroxyethyl 4-methylbenzenesulfonate (18)



3cl **18**

To a 50 mL flask equipped with a PTFE-coated stir bar was added **3cl** (118.1 mg, 0.555 mmol, 1 equiv) and HCl (6 mL) (2 M in MeOH). The reaction mixture was stirred at room temperature for 3 hours. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (EA) to afford the crude diol (85.6 mg, 89% yield).

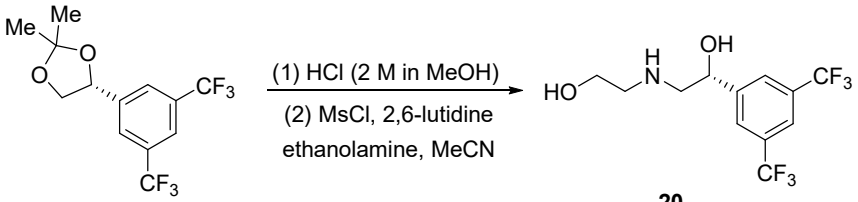
To a solution of the obtained crude diol in DCM (2 mL) and Et_3N (0.1 mL, 0.735 mmol, 1.5 equiv) was added TsCl (103.0 mg, 0.54 mmol, 1.1 equiv) at 0 ℃. The reaction was stirred at rt for 24 hours. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (PE/EA) to afford **18** (100.8 mg, 62% yield).

The NMR data matched those reported in the literature.[14]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 – 7.74 (m, 2H), 7.35 – 7.32 (m, 2H), 7.30 (d, *J* = 4.2 Hz, 1H), 7.28 – 7.26 (m, 2H), 7.21 – 7.18 (m, 1H), 4.96 (dt, *J* = 8.3, 2.7 Hz, 1H), 4.14 (dd, *J* = 10.5, 3.3 Hz, 1H), 4.02 (dd, *J* = 10.5, 8.3 Hz, 1H), 2.66 (d, *J* = 3.1 Hz, 1H), 2.45 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.3, 140.3, 134.7, 132.5, 130.02, 129.95, 128.7, 128.0, 126.4, 124.4, 74.0, 71.4, 21.7.

6.8 Synthesis of the (*R*)-1-(3,5-bis(trifluoromethyl)phenyl)-2-((2-hydroxyethyl)amino)ethan-1-ol (20)



3co **20**

To a solution of **14** (274.1 mg, 1 mmol, 1 equiv) in MeCN (5 mL) and 2,6-lutidine (535.5 mg, 5 mmol, 5 equiv) was added MsCl (137.5 mg, 1.2 mmol, 1.2 equiv) at 0 ℃. The reaction was stirred at 0 ℃ for an hour followed by addition of ethanolamine (305.4 mg, 5 mmol, 5 equiv). After stirring at room temperature overnight, the reaction mixture was partitioned between aqueous $NaHCO_3$ and EA and the organic layer was washed with brane. After drying with Na_2SO_4, the organic layer was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (DCM/MeOH/Et_3N) to afford **20** as white solid (237.6 mg, 74% yield).

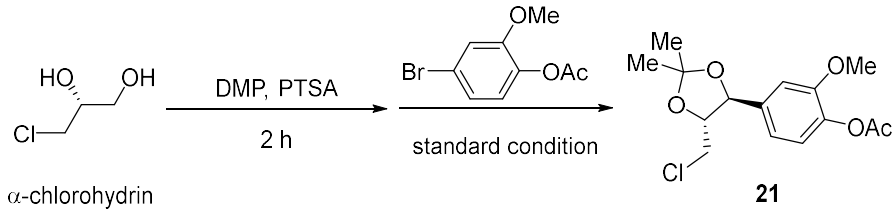
The NMR data matched those reported in the literature.[10]

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.98 (s, 2H), 7.84 (s, 1H), 4.94 (dd, *J* = 8.9, 3.8 Hz, 1H), 3.71 – 3.61 (m, 2H), 2.86 (dd, *J* = 12.4, 3.7 Hz, 1H), 2.83 – 2.72 (m, 3H);

^{13}C NMR (151 MHz, Methanol-d_4) δ 147.0, 131.3 (q, *J* = 33.1 Hz), 126.2 (q, *J* = 4.2 Hz), 123.8 (q, *J* = 272.3 Hz), 120.7 (m), 70.5, 60.0, 56.1, 50.6.

^{19}F NMR (565 MHz, Methanol-d_4) δ -64.33.

6.9 Synthesis of 4-((4*S*,5*R*)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-2-methoxyphenyl acetate (21)



α-chlorohydrin

21

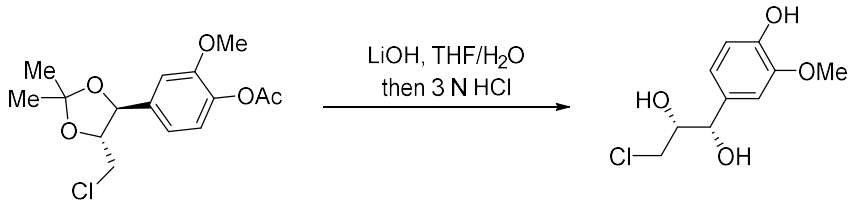
An oven-dried 10 mL tube equipped with a PTFE-coated stir bar was charged with α-chlorohydrin (110 mg, 1.0 mmol, 5.0 equiv), PTSA·H_2O (19.0 mg, 0.1 mmol, 10 mol%) and 2,2-dimethoxypropane (124.8 mg, 1.2 mmol, 1.2 equiv) in an argon-filled glovebox. The tube was sealed and stirred at room temperature for 2 hours. Subsequently, the tube was charged with $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (93.3 mg, 0.44 mmol, 2.2 equiv), 4-bromo-2-methoxyphenyl acetate (49.2 mg, 0.2 mmol, 1.0 equiv) and anhydrous MeCN (1 mL). The tube was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp for 48 hours. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EA = 10/1) to afford **21** as colorless oil (47.9 mg, 70% yield, d.r. > 20/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 – 7.01 (m, 2H), 6.95 (dd, *J* = 8.1, 1.9 Hz, 1H), 4.89 (d, *J* = 8.1 Hz, 1H), 4.03 (ddd, *J* = 8.1, 4.6, 3.6 Hz, 1H), 3.85 (s, 3H), 3.76 (dd, *J* = 12.1, 3.5 Hz, 1H), 3.63 (dd, *J* = 12.1, 4.6 Hz, 1H), 2.31 (s, 3H), 1.58 (s, 3H), 1.55 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 151.4, 139.8, 136.1, 123.0, 118.8, 110.3, 109.9, 82.1, 79.9, 55.9, 42.9, 27.2, 27.0, 20.7;

HRMS: (ESI) calcd for $C_{15}H_{20}ClO_5^+$[M+H]$^+$ 315.0999; found 315.0997.

6.10 Synthesis of (1*S*,2*R*)-3-chloro-1-(4-hydroxy-3-methoxyphenyl)propane-1,2-diol (22)



22

To a 50 mL flask equipped with a PTFE-coated stir bar was added **15** (47.9 mg, 0.14 mmol, 1 equiv), LiOH (33.6, 1.4 mmol, 10.0 equiv), THF (1 mL) and H_2O (1.5 mL). The reaction mixture was stirred at room temperature for 2 hours, then 3 N HCl (6 mL) was added. After

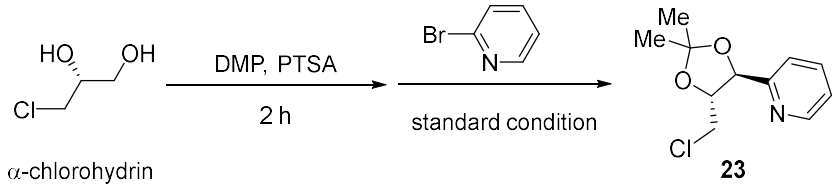
stirring at room temperature for another 6 hours, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (DCM/MeOH = 30/1) to afford **22** as yellow oil (19.5 mg, 60% yield, d.r. > 20/1).

The NMR data consistent with reported literature.[15]

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.92 (d, *J* = 1.9 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.86 (dd, *J* = 8.1, 1.9 Hz, 1H), 5.66 (s, 1H), 4.66 (d, *J* = 7.0 Hz, 1H), 3.91 (s, 3H), 3.87 (ddd, *J* = 7.0, 5.8, 3.7 Hz, 1H), 3.57 (dd, *J* = 11.5, 3.7 Hz, 1H), 3.40 (dd, *J* = 11.5, 5.7 Hz, 1H), 2.89 – 2.59 (m, 2H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.8, 145.8, 131.6, 119.8, 114.5, 108.9, 75.6, 74.8, 56.0, 46.3.

6.11 Synthesis of 2-((4*S*,5*R*)-5-(chloromethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)pyridine (23)



α-chlorohydrin **23**

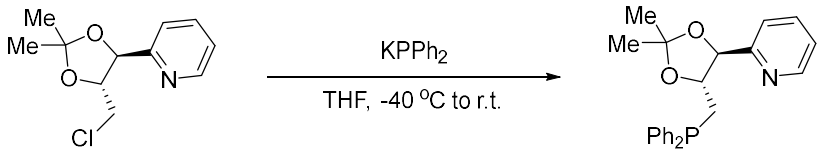
An oven-dried 10-mL tube equipped with a PTFE-coated stir bar was charged with α-chlorohydrin (110 mg, 1.0 mmol, 5.0 equiv), PTSA·H_2O (19.0 mg, 0.1 mmol, 10 mol%) and 2,2-dimethoxypropane (124.8 mg, 1.2 mmol, 1.2 equiv) in an argon-filled glovebox. The tube was sealed and stirred at room temperature for 2 hours. Subsequently, the tube was charged with $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (93.3 mg, 0.44 mmol, 2.2 equiv), 2-bromopyridine (31.4 mg, 0.2 mmol, 1.0 equiv) and anhydrous MeCN (1 mL). The tube was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp for 48 hours. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EA = 10/1) to afford **23** as yellow oil (30.8 mg, 68% yield, d.r. > 20/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 – 8.40 (m, 1H), 7.79 – 7.59 (m, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.24 – 7.20 (m, 1H), 4.94 (d, *J* = 8.0 Hz, 1H), 4.24 (ddd, *J* = 8.0, 5.9, 3.0 Hz, 1H), 4.02 (dd, *J* = 11.9, 3.0 Hz, 1H), 3.84 (dd, *J* = 11.9, 5.9 Hz, 1H), 1.58 (s, 3H), 1.53 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 149.2, 136.9, 122.9, 120.2, 110.5, 81.5, 80.2, 44.4, 27.1, 27.0;

HRMS: (ESI) calcd for $C_{11}H_{15}ClNO_2^+[M+H]^+$ 228.0791; found 228.0793.

6.12 Synthesis of 2-((4*S*,5*R*)-5-((diphenylphosphaneyl)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)pyridine (24)



23 **24**

An oven-dried 10-mL tube equipped with a PTFE-coated stir bar was charged with **23** (30.8 mg, 0.14 mmol, 1 equiv) and anhydrous THF (1 mL) under Ar atmosphere. $KPPh_2$ (420 μL, 0.2 mmol, 1.5 equiv, 0.5 M in THF) was added to the mixture at -40 ℃ and the reaction mixture was warmed to room temperature. After the reaction was complete, the reaction mixture was quenched with NH_4Cl (aq.). The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EA = 15/1) to afford **24** as yellow oil (39.8 mg, 78% yield, d.r. > 20/1).

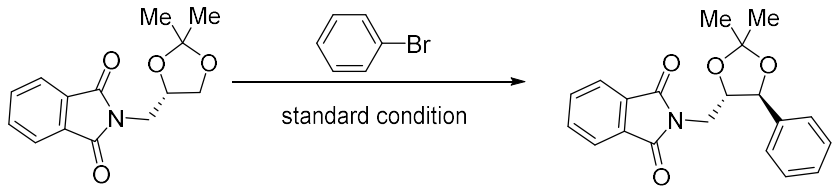
The NMR data consistent with reported literature.[16]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 – 8.46 (m, 1H), 7.69 – 7.59 (m, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.40 – 7.34 (m, 4H), 7.30 – 7.22 (m, 6H), 7.21 – 7.16 (m, 1H), 4.88 (d, *J* = 8.1 Hz, 1H), 4.05 (qd, *J* = 8.3, 3.5 Hz, 1H), 2.78 (ddd, *J* = 14.1, 3.5, 2.5 Hz, 1H), 2.48 (ddd, *J* = 14.2, 8.7, 3.1 Hz, 1H), 1.53 (s, 3H), 1.47 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.3, 149.0, 139.1, 139.0, 138.0, 137.9, 136.8, 133.2, 133.1, 132.6, 132.5, 128.7, 128.37, 128.35, 128.32, 128.29, 128.2, 122.9, 120.7, 109.8, 84.2, 84.1, 80.0, 79.9, 31.7, 31.6, 27.4, 26.8;

^{31}P NMR (243 MHz, $CDCl_3$) δ -22.39.

6.13 Synthesis of 2-(((4*S*,5*S*)-2,2-dimethyl-5-phenyl-1,3-dioxolan-4-yl)methyl)isoindoline-1,3-dione (25)



25

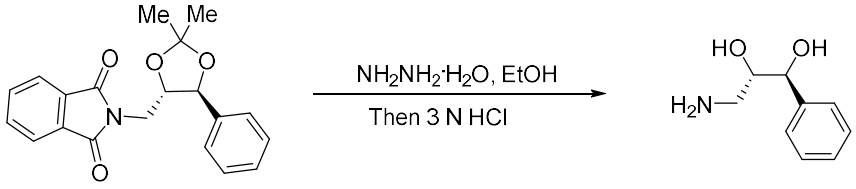
The tube was charged with $NiBr_2$•dme (3.1 mg, 0.01 mmol, 10 mol%), dtbbpy (4.2 mg, 0.015 mmol, 15 mol%), TBADT (6.8 mg, 0.002 mmol, 2 mol%), (*S*)-2-((2,2-dimethyl-1,3-dioxolan-4-yl)methyl)isoindoline-1,3-dione (130.5 mg, 0.5 mmol, 5 equiv), K_3PO_4 (46.0 mg, 0.22 mmol, 2.2 equiv), bromobenzene (15.7 mg, 0.1 mmol, 1.0 equiv) and anhydrous MeCN (1 mL). The tube was sealed and removed from the glovebox. The reaction mixture was stirred and irradiated using a 10 W 390 nm LED lamp for 48 hours. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EA = 10/1) to afford **25** as yellow oil (29.6 mg, 88% yield, d.r. > 20/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.69 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.43 – 7.40 (m, 2H), 7.26 – 7.23 (m, 2H), 7.20 – 7.17 (m, 1H), 4.76 (d, *J* = 8.5 Hz, 1H), 4.26 (dt, *J* = 8.5, 5.5 Hz, 1H), 3.98 (d, *J* = 5.5 Hz, 2H), 1.54 (s, 3H), 1.44 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.2, 136.9, 134.0, 131.8, 128.5, 128.4, 127.0, 123.3, 109.7, 81.4, 79.8, 38.4, 27.1, 27.0.

HRMS: (ESI) calcd for $C_{20}H_{19}NO_4Na^+$[M+Na]$^+$ 360.1206; found 360.1194.

6.14 Synthesis of (1*S*,2*S*)-3-amino-1-phenylpropane-1,2-diol (26)



25 **26**

To a solution of **25** (51.2 mg, 0.15 mmol) in EtOH (1 mL) was added hydrazine hydrate (20 μL, > 85%). The rsulting mixture was reflux for 6 hours. The reaction solution was filtered through celite, and the organic layer was concentrated in vacuo to afford the crude amine.

To a solution of the crude amine in THF (1 mL) was added 3 N HCl (1 mL). The resulting mixture was strred at rt for 1 hour, and than 1 N NaOH (1 mL) was added. The solvent was removed under reduced pressure and the residue was purified by column chromatography on

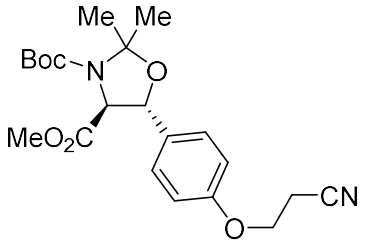
silica gel (EA) to afford **26** as colorless oil (18.0 mg, 90% yield, d.r. > 20/1).

The NMR data matched those reported in the literature.[17]

^{1}H NMR (600 MHz, Methanol-d_4) δ 7.40 – 7.36 (m, 2H), 7.36 – 7.32 (m, 2H), 7.29 – 7.25 (m, 1H), 4.50 (d, J = 6.1 Hz, 1H), 3.65 (q, J = 6.1 Hz, 1H), 2.52 (d, J = 6.0 Hz, 2H);

^{13}C NMR (151 MHz, Methanol-d_4) δ 143.0, 129.1, 128.5, 127.8, 77.4, 76.9, 44.6.

6.15 Synthesis of 3-(*tert*-butyl) 4-methyl (4*S*,5*R*)-5-(4-(2-cyanoethoxy)phenyl)-2,2-dimethyloxazolidine-3,4-dicarboxylate (28)



Chemical Formula: $C_{21}H_{28}N_2O_6$
Exact Mass: 404.1947

28 was prepared according to general procedure **2.3** using $NiBr_2$•dme (6.4 mg, 0.02 mmol, 10 mol%), dtbbpy (8.0 mg, 0.03 mmol, 15 mol%), TBADT (13.3 mg, 0.004 mmol, 2 mol%), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv), 3-(4-bromophenoxy)propanenitrile (45.0 mg, 0.20 mmol, 1.0 equiv), 3-(*tert*-butyl) 4-methyl (*S*)-2,2-dimethyloxazolidine-3,4-dicarboxylate **27** (259 mg, 1.0 mmol, 5.0 equiv) and anhydrous MeCN (1 mL) and was purified by silica gel column chromatography (PE/EA = 5/1) to obtain **28** as colorless oil (59.1 mg, 73% yield, d.r. > 20/1).

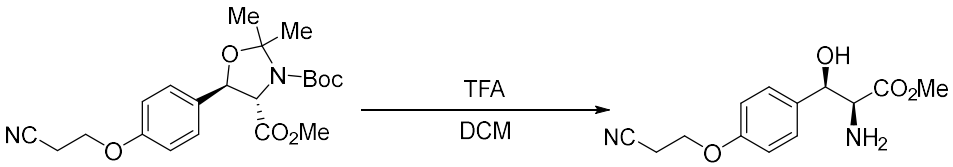
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 6.95 – 6.72 (m, 2H), 5.07 – 4.82 (m, 1H), 4.29 – 4.07 (m, 3H), 3.73 (s, 3H), 2.81 (t, J = 6.3 Hz, 2H), 1.81 – 1.63 (m, 6H), 1.48 (s, 3H), 1.38 (s, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 158.1, 151.8, 150.9, 130.7, 130.6, 128.1, 128.0, 117.1, 114.8, 95.6, 94.9, 81.1, 80.6, 79.2, 78.9, 66.8, 66.6, 62.71, 62.69, 52.5, 52.3, 28.4, 28.2, 27.6, 26.4, 25.0, 24.1, 18.6 (rotamer);

HRMS: (ESI) calcd for $C_{21}H_{29}N_2O_6^+$[M+H]$^+$ 405.2020; found 405.2006.

6.16 Synthesis of methyl (2*S*,3*R*)-2-amino-3-(4-(2-cyanoethoxy)phenyl)-3-hydroxy

propanoate (29)



28 **29**

To a solution of **28** (59.1 mg, 0.15 mmol) in DCM (5 mL) was added TFA (0.5 mL). After stirring at room temperture for 6 hours, the solvent was concentrated in vacuo and the residue was purified by flash chromatography on silica gel (PE/EA = 1/1) to afford **29** as yellow oil (29.3 mg, 76% yield).

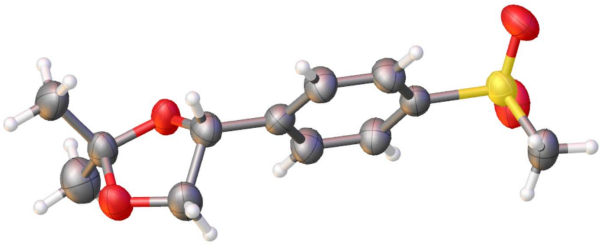
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 2H), 7.11 – 6.79 (m, 2H), 6.06 (s, 1H), 5.60 (d, *J* = 5.1 Hz, 1H), 4.27 (d, *J* = 5.1 Hz, 1H), 4.21 (t, *J* = 6.3 Hz, 2H), 3.86 (s, 3H), 2.85 (t, *J* = 6.3 Hz, 2H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.0, 158.4, 157.9, 131.2, 127.2, 117.1, 115.1, 79.2, 62.8, 61.3, 53.3, 18.6;

HRMS: (ESI) calcd for $C_{13}H_{14}N_2O_3^+$[M-H_2O+H]$^+$ 247.1077; found 247.1076.

7. X-Ray Crystallographic Data

7.1 X-Ray Crystallographic Analysis of 3cg



CCDC: 2335066

Supplementary Figure 95. Structure of compound **3cg**

Table S4: Crystal data and structure refinement for 3cg.

Empirical formula	$C_{12}H_{16}O_4S$
Formula weight	256.31
Temperature/K	299.58(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.6714(2)
b/Å	14.3623(7)
c/Å	7.9791(4)
α/°	90
β/°	101.543(4)
γ/°	90
Volume/Å^3	636.78(5)
Z	2
ρ_{calc}g/cm^3	1.337
μ/mm^{-1}	2.285
F(000)	272.0
Crystal size/mm^3	0.12 × 0.09 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	11.318 to 133.062
Index ranges	-6 ≤ h ≤ 4, -17 ≤ k ≤ 16, -9 ≤ l ≤ 9

Reflections collected	4349
Independent reflections	1930 [R_{int} = 0.0155, R_{sigma} = 0.0209]
Data/restraints/parameters	1930/1/157
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0288, wR_2 = 0.0751
Final R indexes [all data]	R_1 = 0.0296, wR_2 = 0.0758
Largest diff. peak/hole / e $Å^{-3}$	0.11/-0.20
Flack parameter	-0.001(11)

Table S5: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for 3cg. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S14	174.4(11)	6500.6(5)	6718.5(8)	47.5(2)
O15	-174(4)	6929(2)	8272(3)	69.6(7)
O16	2574(3)	6274.3(19)	6536(3)	67.8(7)
O11	-2432(3)	9562.1(15)	315(3)	54.8(5)
C5	-41(5)	7310(2)	3587(4)	49.5(7)
O9	-5310(3)	9227.7(17)	-2035(3)	56.8(6)
C1	-3115(5)	8393.8(19)	2324(4)	44.9(6)
C10	-3434(5)	9877(2)	-1368(4)	49.8(7)
C17	-1569(5)	5483(2)	6404(4)	58.3(8)
C7	-4239(5)	9025(2)	873(4)	51.1(7)
C2	-4164(5)	8299(2)	3732(4)	52.6(7)
C6	-1062(5)	7889(2)	2247(4)	53.3(7)
C3	-3194(5)	7717(2)	5072(4)	52.5(7)
C4	-1112(5)	7235.0(19)	4999(3)	42.0(6)
C8	-5389(6)	8543(3)	-776(4)	60.0(8)
C13	-4508(7)	10834(3)	-1329(5)	68.9(9)
C12	-1506(6)	9826(3)	-2409(5)	74.8(10)

Table S6: Anisotropic Displacement Parameters ($Å^2×10^3$) for 3cg. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S14	43.4(3)	53.4(4)	43.1(3)	6.0(3)	2.7(2)	-2.4(3)
O15	85.4(16)	81.9(17)	37.9(12)	-3.7(11)	3.9(10)	2.6(13)
O16	40.2(9)	82.7(19)	77.7(15)	24.9(13)	5.3(9)	3.3(11)
O11	61.5(11)	47.2(12)	47.3(11)	10.3(9)	-9.7(8)	-13.4(10)
C5	47.0(15)	50.2(18)	54.0(16)	6.7(14)	16.5(12)	6.5(12)
O9	57.0(12)	62.6(14)	45.4(10)	3.4(10)	-2.4(8)	-16.3(10)
C1	50.8(14)	39.5(15)	44.2(14)	-0.2(12)	9.6(11)	0.1(12)
C10	46.8(15)	52.3(18)	45.4(16)	8.2(13)	-2.5(11)	-6.3(12)
C17	56.6(16)	52.7(17)	63(2)	15.1(15)	5.8(14)	-3.6(14)
C7	53.2(16)	51.1(17)	48.7(16)	4.3(13)	9.5(13)	8.1(13)
C2	52.2(16)	54.2(18)	53.0(17)	4.4(14)	13.9(13)	11.9(14)
C6	58.8(16)	55.2(18)	50.0(16)	5.1(14)	20.6(12)	3.0(14)
C3	57.7(15)	58.3(18)	45.3(15)	1.7(14)	19.5(12)	6.4(14)
C4	42.8(13)	40.8(14)	41.3(13)	0.2(11)	6.0(10)	-2.7(11)
C8	57.3(17)	61(2)	56.4(18)	7.1(16)	-0.4(13)	-14.3(15)
C13	80(2)	53.0(19)	65(2)	7.6(16)	-6.3(16)	5.4(17)
C12	65(2)	88(3)	74(2)	12(2)	18.6(16)	-6.6(19)

Table S7: Bond Lengths for 3cg.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S14	O15	1.433(2)	O9	C8	1.413(4)
S14	O16	1.434(2)	C1	C7	1.508(4)
S14	C17	1.754(3)	C1	C2	1.379(4)
S14	C4	1.768(3)	C1	C6	1.384(4)
O11	C10	1.423(3)	C10	C13	1.507(5)
O11	C7	1.424(4)	C10	C12	1.501(5)
C5	C6	1.387(4)	C7	C8	1.514(4)
C5	C4	1.386(4)	C2	C3	1.382(4)
O9	C10	1.434(4)	C3	C4	1.380(4)

Table S8: Bond Angles for 3cg.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O15	S14	O16	118.87(15)	O11	C10	C12	108.0(3)
O15	S14	C17	108.10(17)	O9	C10	C13	109.1(2)
O15	S14	C4	107.96(15)	O9	C10	C12	109.4(3)
O16	S14	C17	108.40(16)	C12	C10	C13	113.4(3)
O16	S14	C4	107.99(14)	O11	C7	C1	110.2(2)
C17	S14	C4	104.64(13)	O11	C7	C8	100.8(2)
C10	O11	C7	106.9(2)	C1	C7	C8	115.8(3)
C4	C5	C6	119.3(3)	C1	C2	C3	121.3(3)
C8	O9	C10	108.4(2)	C1	C6	C5	120.3(3)
C2	C1	C7	120.0(3)	C4	C3	C2	118.8(3)
C2	C1	C6	119.2(3)	C5	C4	S14	119.8(2)
C6	C1	C7	120.7(3)	C3	C4	S14	119.3(2)
O11	C10	O9	105.7(2)	C3	C4	C5	120.9(3)
O11	C10	C13	110.9(3)	O9	C8	C7	103.3(3)

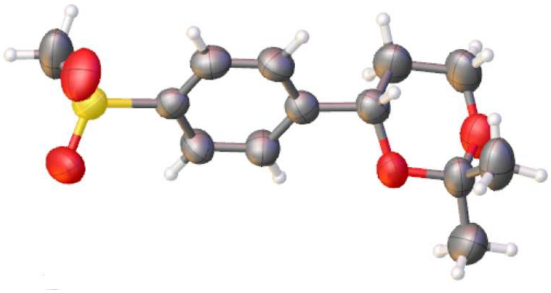
Table S9: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3cg.

Atom	*x*	*y*	*z*	U(eq)
H5	1348.38	6975.09	3540.24	59
H17A	-933.41	5037.2	7273.35	87
H17B	-1525.66	5227.4	5298.91	87
H17C	-3200.79	5628.51	6467.08	87
H7	-5410.23	9438.41	1244.63	61
H2	-5552.57	8633.52	3780.73	63
H6	-362.9	7937.56	1290.59	64
H3	-3931.05	7650.59	6006.61	63
H8A	-4483.82	7993.72	-968.47	72
H8B	-7034.24	8363.5	-762.52	72
H13A	-5699.31	10824.48	-627.24	103
H13B	-5246.03	11018.52	-2470.27	103
H13C	-3263.75	11269.51	-865.32	103
H12A	-268.26	10270.98	-1981.63	112
H12B	-2189.56	9963.74	-3583.07	112
H12C	-827.94	9211.44	-2327.66	112

Crystal structure determination of [3cg]

Crystal Data for $C_{12}H_{16}O_4S$ (M =256.31 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 5.6714(2) Å, b = 14.3623(7) Å, c = 7.9791(4) Å, β = 101.543(4)°, V = 636.78(5) Å^3, Z = 2, T = 299.58(10) K, μ(Cu Kα) = 2.285 mm^{-1}, *Dcalc* = 1.337 g/cm^3, 4349 reflections measured (11.318° ≤ 2Θ ≤ 133.062°), 1930 unique (R_{int} = 0.0155, R_{sigma} = 0.0209) which were used in all calculations. The final R_1 was 0.0288 (I > 2σ(I)) and wR_2 was 0.0758 (all data).

7.2 X-Ray Crystallographic Analysis of 5ag



CCDC: 2335067

Supplementary Figure 96. Structure of compound **5ag**

Table S10: Crystal data and structure refinement for 5ag.

Empirical formula	$C_{26}H_{36}O_8S_2$
Formula weight	540.67
Temperature/K	296.54(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	12.4193(10)
b/Å	10.1926(5)
c/Å	12.5200(9)
α/°	90
β/°	118.653(10)
γ/°	90
Volume/Å^3	1390.8(2)
Z	2
ρ_{calc}g/cm^3	1.291
μ/mm^{-1}	2.119
F(000)	576.0
Crystal size/mm^3	0.12 × 0.08 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.048 to 133.198
Index ranges	-14 ⩽ h ⩽ 14, -11 ⩽ k ⩽ 12, -14 ⩽ l ⩽ 14
Reflections collected	8306

Independent reflections	4002 [R_{int} = 0.0257, R_{sigma} = 0.0361]
Data/restraints/parameters	4002/1/331
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0370, wR_2 = 0.0951
Final R indexes [all data]	R_1 = 0.0463, wR_2 = 0.0996
Largest diff. peak/hole / e $Å^{-3}$	0.15/-0.17
Flack parameter	0.080(16)

Table S11: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 5ag. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S13	1015.6(8)	7631.0(10)	3439.1(7)	58.2(2)
S31	4053.1(8)	2653.9(9)	5460.1(8)	62.5(2)
O6	1264(2)	8142(3)	-1729(2)	61.8(6)
O4	1875(3)	6988(3)	-2951(3)	71.0(7)
O14	1338(3)	8962(3)	3813(3)	79.2(8)
O20	3629(3)	3005(3)	10553(2)	67.6(7)
O15	-99(2)	7135(4)	3345(2)	84.0(10)
O22	3466(3)	1675(3)	11996(3)	83.0(9)
O32	5244(3)	2977(4)	5647(3)	100.1(11)
O33	3079(3)	3539(3)	4759(3)	102.7(12)
C25	4346(3)	2290(3)	9204(3)	55.5(8)
C28	4147(3)	2469(3)	6907(3)	53.3(8)
C8	1525(3)	8144(4)	531(3)	59.3(9)
C9	1601(3)	8266(4)	1669(3)	57.7(9)
C10	956(3)	7433(4)	2007(3)	53.9(8)
C26	3220(3)	2530(5)	8197(3)	63.5(9)
C7	799(3)	7195(4)	-269(3)	58.9(9)
C27	3120(3)	2618(5)	7050(3)	63.6(9)
C1	700(4)	7032(4)	-1517(3)	66.5(10)
C29	5271(3)	2219(4)	7896(4)	66.4(10)
C19	4499(4)	2160(4)	10470(3)	62.0(9)
C23	4304(5)	748(5)	11976(4)	89.8(15)
C5	1268(4)	8142(4)	-2879(3)	65.4(10)
C24	4279(5)	765(4)	10750(4)	83.4(13)
C18	2077(5)	9273(5)	-2809(4)	87.8(14)
C16	2222(4)	6638(5)	4435(4)	75.5(11)
C2	1292(5)	5785(4)	-1647(4)	78.9(12)
C30	5370(3)	2138(4)	9045(3)	67.3(10)
C17	-14(4)	8269(7)	-3935(4)	103.5(19)

Atom	*x*	*y*	*z*	U(eq)
C35	4845(5)	3537(5)	12700(4)	97.4(16)
C21	3643(4)	2978(4)	11705(3)	73.7(12)
C11	222(5)	6465(5)	1222(4)	84.1(14)
C3	1333(5)	5800(4)	-2846(4)	89.4(15)
C34	3624(6)	1119(5)	4767(4)	101.8(18)
C12	149(5)	6363(5)	85(4)	94.2(16)
C36	2554(5)	3758(6)	11538(5)	110.1(19)

Table S12: Anisotropic Displacement Parameters ($Å^2×10^3$) for 5ag. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S13	59.6(5)	67.2(5)	53.1(4)	-1.6(5)	31.2(4)	2.3(5)
S31	76.5(5)	53.1(4)	69.1(5)	7.0(5)	43.9(5)	4.7(5)
O6	77.4(16)	62.1(14)	52.5(13)	-2.1(11)	36.4(12)	1.6(13)
O4	86.7(19)	64.2(16)	79.1(17)	-6.9(14)	53.2(16)	5.4(15)
O14	111(2)	66.5(17)	72.3(18)	-7.8(14)	53.2(17)	6.4(16)
O20	90.7(17)	59.9(16)	52.0(13)	6.4(11)	34.0(13)	7.8(14)
O15	66.1(15)	128(3)	69.1(16)	-15.2(16)	41.5(14)	-16.8(17)
O22	115(3)	67.4(18)	74.2(18)	5.7(15)	51.4(18)	-13.1(18)
O32	91.6(19)	139(3)	92(2)	-9(2)	61.9(17)	-22(2)
O33	136(3)	103(3)	92(2)	45(2)	73(2)	52(2)
C25	61(2)	44.6(18)	56.9(19)	-0.6(15)	25.0(17)	-4.9(16)
C28	60.7(19)	42.0(18)	61.1(18)	1.9(16)	32.5(16)	0.8(16)
C8	61(2)	63(2)	56(2)	-2.9(18)	30.1(17)	-7.5(18)
C9	58(2)	61(2)	54(2)	-7.7(17)	26.6(17)	-5.7(18)
C10	57.2(18)	55(2)	52.2(17)	1.1(16)	28.5(15)	1.3(17)
C26	54.6(18)	75(2)	60.0(19)	0(2)	27.0(16)	1(2)
C7	56.9(19)	68(2)	51.8(18)	-6.1(17)	26.4(16)	-8.0(18)
C27	53.7(18)	78(2)	54.5(18)	9(2)	22.2(15)	8(2)
C1	69(2)	78(3)	51(2)	-8.0(19)	28.0(18)	-14(2)
C29	57(2)	63(2)	81(3)	-0.8(19)	35(2)	1.2(18)
C19	67(2)	56(2)	57(2)	1.5(17)	25.3(18)	0.2(19)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C23	137(4)	62(2)	72(3)	13(2)	51(3)	0(3)
C5	73(2)	78(3)	53(2)	2.0(19)	36.8(19)	8(2)
C24	124(4)	52(2)	80(3)	6(2)	54(3)	5(2)
C18	131(4)	67(3)	96(3)	4(2)	79(3)	6(3)
C16	77(3)	91(3)	59(2)	15(2)	33(2)	10(2)
C2	111(4)	63(2)	72(3)	-16(2)	51(3)	-19(2)
C30	56(2)	72(2)	63(2)	5.1(19)	20.1(18)	9.1(19)
C17	86(3)	172(6)	55(2)	13(3)	35(2)	19(4)
C35	145(5)	80(3)	68(3)	-14(2)	52(3)	-29(3)
C21	104(3)	66(3)	54(2)	2.4(19)	39(2)	0(2)
C11	109(3)	87(3)	73(3)	-16(2)	57(3)	-37(3)
C3	136(4)	67(2)	84(3)	-20(2)	68(3)	-20(3)
C34	167(5)	72(3)	67(3)	-5(2)	57(3)	-12(3)
C12	115(4)	107(4)	71(3)	-31(3)	53(3)	-54(3)
C36	143(5)	114(4)	94(4)	18(3)	74(4)	38(4)

Table S13: Bond Lengths for 5ag.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S13	O14	1.429(3)	C28	C27	1.379(5)
S13	O15	1.425(3)	C28	C29	1.374(5)
S13	C10	1.770(3)	C8	C9	1.387(5)
S13	C16	1.741(4)	C8	C7	1.373(5)
S31	O32	1.421(3)	C9	C10	1.366(5)
S31	O33	1.425(3)	C10	C11	1.383(5)
S31	C28	1.769(3)	C26	C27	1.384(5)
S31	C34	1.744(5)	C7	C1	1.516(5)
O6	C1	1.421(5)	C7	C12	1.383(6)
O6	C5	1.442(4)	C1	C2	1.516(6)
O4	C5	1.423(5)	C29	C30	1.386(5)
O4	C3	1.422(5)	C19	C24	1.520(6)
O20	C19	1.425(4)	C23	C24	1.521(6)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O20	C21	1.434(4)	C5	C18	1.503(6)
O22	C23	1.414(6)	C5	C17	1.510(6)
O22	C21	1.422(5)	C2	C3	1.527(6)
C25	C26	1.383(5)	C35	C21	1.524(6)
C25	C19	1.509(5)	C21	C36	1.495(7)
C25	C30	1.388(5)	C11	C12	1.386(6)

Table S14: Bond Angles for 5ag.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O14	S13	C10	108.00(17)	C8	C7	C12	118.5(3)
O14	S13	C16	107.9(2)	C12	C7	C1	119.5(3)
O15	S13	O14	118.2(2)	C28	C27	C26	119.9(3)
O15	S13	C10	107.99(16)	O6	C1	C7	107.6(3)
O15	S13	C16	108.7(2)	O6	C1	C2	109.9(3)
C16	S13	C10	105.24(18)	C2	C1	C7	113.4(3)
O32	S31	O33	117.6(2)	C28	C29	C30	119.5(3)
O32	S31	C28	107.68(17)	O20	C19	C25	107.8(3)
O32	S31	C34	109.6(3)	O20	C19	C24	108.8(3)
O33	S31	C28	108.56(17)	C25	C19	C24	112.3(3)
O33	S31	C34	107.2(2)	O22	C23	C24	110.6(4)
C34	S31	C28	105.59(19)	O6	C5	C18	105.3(3)
C1	O6	C5	115.2(3)	O6	C5	C17	111.5(3)
C3	O4	C5	114.2(3)	O4	C5	O6	108.6(3)
C19	O20	C21	114.7(3)	O4	C5	C18	106.1(3)
C23	O22	C21	114.5(3)	O4	C5	C17	112.5(4)
C26	C25	C19	122.4(3)	C18	C5	C17	112.4(4)
C26	C25	C30	119.0(3)	C19	C24	C23	109.0(3)
C30	C25	C19	118.6(3)	C1	C2	C3	110.1(4)
C27	C28	S31	120.7(3)	C29	C30	C25	120.7(3)
C29	C28	S31	118.8(3)	O20	C21	C35	110.4(4)
C29	C28	C27	120.5(3)	O20	C21	C36	106.0(3)
C7	C8	C9	120.7(3)	O22	C21	O20	110.3(3)
C10	C9	C8	120.1(3)	O22	C21	C35	110.5(4)
C9	C10	S13	119.9(3)	O22	C21	C36	107.0(4)
C9	C10	C11	120.5(3)	C36	C21	C35	112.4(4)
C11	C10	S13	119.6(3)	C10	C11	C12	118.7(4)
C25	C26	C27	120.4(3)	O4	C3	C2	109.9(3)
C8	C7	C1	122.0(3)	C7	C12	C11	121.5(4)

Table S15: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 5ag.

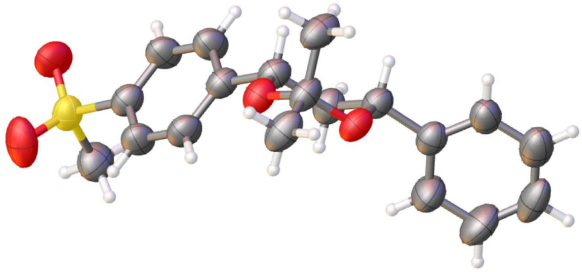
Atom	*x*	*y*	*z*	U(eq)
H8	1968.73	8711.51	307.69	71
H9	2092.46	8915.03	2201.86	69
H26	2526.52	2632.36	8291.64	76
H27	2360.53	2776.98	6376	76
H1	-170.35	7023.76	-2127.68	80
H29	5959.84	2105.5	7794.52	80
H19	5330.13	2433.51	11065.37	74
H23A	4091.02	-121.13	12129.44	108
H23B	5125.23	951.7	12615.26	108
H24A	4911.03	188.71	10772.14	100
H24B	3490.14	455.29	10120.53	100
H18A	1737.71	10074.8	-2697.7	132
H18B	2126.08	9320.81	-3550.64	132
H18C	2883.27	9144.86	-2135.56	132
H16A	2970.97	6928.07	4464.45	113
H16B	2062.12	5745.73	4156.37	113
H16C	2297.65	6692.15	5233.88	113
H2A	826.39	5030.51	-1625.78	95
H2B	2118.44	5712.25	-972.39	95
H30	6131.55	1978.9	9716.29	81
H17A	-484.29	7507.29	-3967.87	155
H17B	25.35	8340.63	-4679.81	155
H17C	-398.16	9037.74	-3827.74	155
H35A	5504.54	2947.16	12844.97	146
H35B	4791.29	3642.07	13434.31	146
H35C	4998.16	4373.61	12446.1	146
H11	-213.9	5894	1451.72	101
H3A	1808.3	5058.45	-2874.92	107
H3B	507.96	5723.41	-3521.55	107
H34A	3488.07	1175.66	3946.18	153

Atom	*x*	*y*	*z*	U(eq)
H34B	2883.12	838.97	4760.9	153
H34C	4265.37	496.36	5212.66	153
H12	-349.78	5720.3	-452.37	113
H36A	2666.6	4661.29	11397.04	165
H36B	2466.26	3691.46	12257.8	165
H36C	1829.02	3423.65	10853.52	165

Crystal structure determination of 5ag

Crystal Data for $C_{26}H_{36}O_8S_2$ (M =540.67 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 12.4193(10) Å, b = 10.1926(5) Å, c = 12.5200(9) Å, β = 118.653(10)°, V = 1390.8(2) Å^3, Z = 2, T = 296.54(10) K, μ(Cu Kα) = 2.119 mm^{-1}, *Dcalc* = 1.291 g/cm^3, 8306 reflections measured (8.048° ⩽ 2Θ ⩽ 133.198°), 4002 unique (R_{int} = 0.0257, R_{sigma} = 0.0361) which were used in all calculations. The final R_1 was 0.0370 (I > 2σ(I)) and wR_2 was 0.0996 (all data).

7.3 X-Ray Crystallographic Analysis of 10b



CCDC:2353650

Supplementary Figure 97. Structure of compound **10b**

Table S16: Crystal data and structure refinement for 10b.

Empirical formula	$C_{19}H_{22}O_4S$
Formula weight	346.42
Temperature/K	298.58(10)
Crystal system	monoclinic
Space group	C2
a/Å	17.440(2)
b/Å	8.8300(4)
c/Å	15.9598(19)
α/°	90
β/°	131.37(2)
γ/°	90
Volume/Å^3	1844.5(5)
Z	4
ρ_{calc}g/cm^3	1.247
μ/mm^{-1}	1.715
F(000)	736.0
Crystal size/mm^3	0.15 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.38 to 133.148
Index ranges	-20 ⩽ h ⩽ 16, -10 ⩽ k ⩽ 10, -18 ⩽ l ⩽ 18
Reflections collected	10747
Independent reflections	3197 [R_{int} = 0.0574, R_{sigma} = 0.0474]
Data/restraints/parameters	3197/1/220
Goodness-of-fit on F^2	1.034

Final R indexes [I>=2σ (I)]	R_1 = 0.0489, wR_2 = 0.1314
Final R indexes [all data]	R_1 = 0.0609, wR_2 = 0.1409
Largest diff. peak/hole / e Å^{-3}	0.46/-0.22
Flack parameter	0.04(2)

Table S17: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 10b. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S13	5478.5(9)	6721.1(13)	1678.7(9)	60.0(3)
O4	6978(2)	5964(4)	7939(3)	59.3(8)
O2	7201(2)	7198(4)	6815(3)	62.1(8)
O14	6188(3)	6220(5)	1571(3)	80.5(12)
O15	5100(4)	8243(4)	1348(4)	95.0(14)
C5	7081(4)	4478(5)	7636(4)	57.6(11)
C3	7518(4)	7130(6)	7895(4)	62.3(13)
C10	6033(3)	6471(5)	3077(4)	56.6(11)
C11	6826(4)	5471(6)	3761(4)	66.3(12)
C7	6855(4)	6073(5)	5258(4)	55.8(10)
C6	6722(4)	4558(6)	6492(4)	62.2(11)
C9	5647(4)	7271(6)	3478(4)	62.6(11)
C17	6510(4)	3408(5)	7789(4)	60.3(11)
C8	6047(4)	7076(6)	4544(4)	62.5(12)
C12	7234(4)	5279(6)	4842(4)	66.6(13)
C1	7293(4)	5813(6)	6432(4)	58.8(11)
C24	8673(4)	6950(9)	8798(4)	77.9(17)
C22	7032(4)	2628(7)	8767(5)	71.0(13)
C23	7148(5)	8596(6)	8012(6)	78.5(16)
C21	6541(5)	1639(9)	8944(6)	88.4(17)
C18	5460(4)	3222(7)	6975(5)	81.3(15)
C20	5520(6)	1422(6)	8138(7)	87.8(19)
C16	4446(4)	5489(8)	936(5)	80.9(15)
C19	4966(5)	2231(8)	7153(6)	95(2)

Table S18: Anisotropic Displacement Parameters ($Å^2×10^3$) for 10b. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S13	78.3(7)	57.4(5)	64.4(6)	1.7(5)	55.7(6)	5.0(6)
O4	65.4(18)	63.5(17)	67.8(19)	-10.9(14)	52.0(17)	-12.5(14)
O2	74.0(19)	63.1(19)	64.4(19)	-10.6(14)	52.2(17)	-13.2(14)
O14	86(2)	110(3)	75(2)	5.1(19)	66(2)	13(2)
O15	161(4)	55(2)	103(3)	15.9(19)	102(3)	24(2)
C5	60(3)	62(2)	65(3)	-1(2)	47(2)	-2(2)
C3	69(3)	70(3)	64(3)	-11(2)	52(3)	-17(2)
C10	65(2)	57(3)	65(3)	-7(2)	50(2)	-3(2)
C11	70(3)	79(3)	66(3)	1(2)	52(3)	16(3)
C7	58(2)	62(2)	60(3)	-6(2)	44(2)	-7(2)
C6	76(3)	60(2)	65(3)	-7(2)	52(3)	-6(2)
C9	69(3)	69(3)	67(3)	4(2)	52(3)	14(2)
C17	72(3)	57(2)	70(3)	-2(2)	55(3)	0(2)
C8	70(3)	69(3)	71(3)	-6(2)	56(3)	3(2)
C12	69(3)	79(3)	63(3)	5(2)	49(3)	17(2)
C1	59(3)	64(3)	63(3)	-6(2)	45(2)	-3(2)
C24	67(3)	115(5)	61(3)	-19(3)	46(2)	-27(3)
C22	82(3)	72(3)	79(3)	15(3)	62(3)	15(3)
C23	102(4)	69(3)	100(4)	-25(3)	82(4)	-26(3)
C21	116(5)	76(3)	118(5)	21(4)	96(4)	21(4)
C18	75(3)	86(4)	82(4)	7(3)	51(3)	-12(3)
C20	133(6)	55(3)	139(6)	-1(3)	117(5)	-9(3)
C16	82(4)	95(4)	61(3)	-2(3)	45(3)	-6(3)
C19	97(4)	98(5)	113(5)	-15(4)	79(4)	-34(4)

Table S19: Bond Lengths for 10b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S13	O14	1.426(3)	C10	C9	1.389(6)
S13	O15	1.435(4)	C11	C12	1.375(7)
S13	C10	1.765(5)	C7	C8	1.395(7)
S13	C16	1.735(6)	C7	C12	1.396(6)
O4	C5	1.450(6)	C7	C1	1.501(7)
O4	C3	1.428(5)	C6	C1	1.535(7)
O2	C3	1.421(5)	C9	C8	1.357(7)
O2	C1	1.424(6)	C17	C22	1.364(7)
C5	C6	1.490(7)	C17	C18	1.387(8)
C5	C17	1.506(6)	C22	C21	1.378(9)
C3	C24	1.524(7)	C21	C20	1.354(9)
C3	C23	1.512(7)	C18	C19	1.384(8)
C10	C11	1.374(7)	C20	C19	1.381(10)

Table S20: Bond Angles for 10b.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O14	S13	O15	118.1(3)	C10	C11	C12	119.3(4)
O14	S13	C10	108.6(2)	C8	C7	C12	118.1(4)
O14	S13	C16	108.3(3)	C8	C7	C1	121.5(4)
O15	S13	C10	108.5(2)	C12	C7	C1	120.4(4)
O15	S13	C16	108.6(3)	C5	C6	C1	110.3(4)
C16	S13	C10	103.8(2)	C8	C9	C10	120.6(4)
C3	O4	C5	113.9(3)	C22	C17	C5	119.3(5)
C3	O2	C1	114.9(4)	C22	C17	C18	118.9(5)
O4	C5	C6	108.8(4)	C18	C17	C5	121.8(5)
O4	C5	C17	105.8(3)	C9	C8	C7	120.6(4)
C6	C5	C17	116.2(4)	C11	C12	C7	121.3(5)
O4	C3	C24	112.4(4)	O2	C1	C7	107.3(4)
O4	C3	C23	105.2(4)	O2	C1	C6	109.4(3)
O2	C3	O4	110.5(3)	C7	C1	C6	111.8(4)
O2	C3	C24	111.3(3)	C17	C22	C21	121.3(6)
O2	C3	C23	104.9(4)	C20	C21	C22	120.0(6)
C23	C3	C24	112.2(5)	C19	C18	C17	119.9(6)
C11	C10	S13	120.5(3)	C21	C20	C19	120.0(5)
C11	C10	C9	120.1(4)	C20	C19	C18	119.9(6)
C9	C10	S13	119.4(4)				

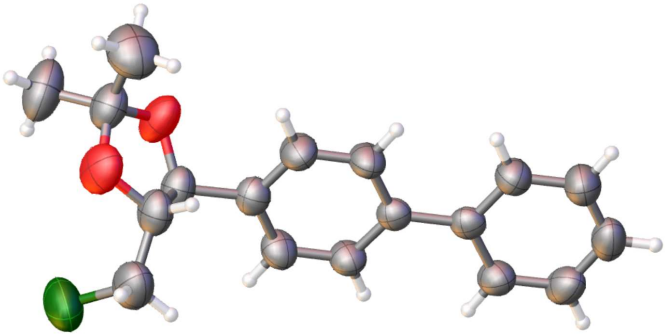
Table S21: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 10b.

Atom	*x*	*y*	*z*	U(eq)
H5	7805.46	4195.84	8160.48	69
H11	7084.52	4929.35	3494.68	80
H6A	5994.2	4760.91	5954.99	75
H6B	6840.7	3592.92	6303.24	75
H9	5110.59	7945.88	3011.84	75
H8	5780.1	7617.06	4800.84	75
H12	7773.43	4606.39	5306.26	80
H1	8016.26	5541.73	6904.5	71
H24A	8869.76	6976.31	9519.37	117
H24B	9003.12	7761.09	8741.4	117
H24C	8873.34	5998.88	8701.96	117
H22	7734.01	2766.8	9325.3	85
H23A	6424.15	8688.05	7407.78	118
H23B	7488.58	9433.31	7995.32	118
H23C	7296.86	8596.74	8708.87	118
H21	6910.08	1119.68	9617.5	106
H18	5088.63	3763.25	6310.25	98
H20	5192.55	728.73	8248.05	105
H16A	4083.04	5574.3	153.65	121
H16B	3997.2	5740.81	1067.06	121
H16C	4686.44	4468.74	1177.47	121
H19	4261.1	2109.19	6610.92	114

Crystal structure determination of 10b

Crystal Data for $C_{19}H_{22}O_4S$ (*M* =346.42 g/mol): monoclinic, space group C2 (no. 5), *a* = 17.440(2) Å, *b* = 8.8300(4) Å, *c* = 15.9598(19) Å, *β* = 131.37(2)°, *V* = 1844.5(5) Å^3, *Z* = 4, *T* = 298.58(10) K, μ(Cu Kα) = 1.715 mm^{-1}, *Dcalc* = 1.247 g/cm^3, 10747 reflections measured (7.38° ⩽ 2Θ ⩽ 133.148°), 3197 unique (R_{int} = 0.0574, R_{sigma} = 0.0474) which were used in all calculations. The final R_1 was 0.0489 (I > 2σ(I)) and wR_2 was 0.1409 (all data).

7.4 X-Ray Crystallographic Analysis of 9i



CCDC: 2236741

Supplementary Figure 98. Structure of compound **9i**

Table S22: Crystal data and structure refinement for 9i.

Empirical formula	$C_{18}H_{19}ClO_2$
Formula weight	302.78
Temperature/K	300.62(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.9444(4)
b/Å	7.6111(6)
c/Å	17.7601(11)
α/°	90
β/°	98.633(6)
γ/°	90
Volume/Å^3	794.43(10)
Z	2
ρ_{calc}g/cm^3	1.266
μ/mm^{-1}	2.135
F(000)	320.0
Crystal size/mm^3	0.2 × 0.1 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.032 to 152.182
Index ranges	$-7 \leqslant h \leqslant 6$, $-9 \leqslant k \leqslant 8$, $-21 \leqslant l \leqslant 22$
Reflections collected	6998
Independent reflections	2859 [R_{int} = 0.0286, R_{sigma} = 0.0321]

Data/restraints/parameters	2859/1/192
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0410, wR_2 = 0.1107
Final R indexes [all data]	R_1 = 0.0548, wR_2 = 0.1187
Largest diff. peak/hole / e $Å^{-3}$	0.14/-0.28
Flack parameter	0.026(11)

Table S23: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for 9i. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl13	8829(2)	7628(2)	8762.7(7)	128.4(6)
O11	5523(5)	2913(4)	8166.7(13)	86.1(8)
O9	4937(5)	5136(4)	8972.9(14)	93.2(9)
C4	3044(5)	4455(4)	5413.2(16)	48.2(6)
C16	1969(5)	4465(4)	4604.3(17)	49.2(6)
C5	5141(5)	5212(5)	5659.9(17)	58.9(8)
C6	6097(5)	5211(5)	6417.3(18)	62.0(8)
C1	4992(5)	4436(4)	6969.0(17)	56.4(7)
C21	2985(6)	5302(5)	4032.9(18)	63.5(8)
C3	1964(5)	3668(5)	5969.3(19)	66.2(9)
C17	-108(5)	3637(5)	4365.1(19)	64.9(8)
C7	5974(5)	4498(5)	7801.4(17)	64.6(8)
C19	-95(6)	4487(5)	3072(2)	73.7(10)
C20	1958(7)	5306(5)	3286.0(19)	74.1(10)
C2	2914(6)	3658(5)	6725(2)	69.4(9)
C8	4856(7)	5884(5)	8244.5(19)	72.4(10)
C10	5035(6)	3259(6)	8913.4(19)	76.9(11)
C18	-1116(6)	3646(6)	3612(2)	77.9(10)
C12	5954(8)	7673(7)	8305(2)	97.3(13)
C15	6902(8)	2617(9)	9501(2)	114.6(17)
C14	2775(8)	2476(9)	8992(3)	122.7(18)

Table S24: Anisotropic Displacement Parameters ($Å^2×10^3$) for 9i. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl13	141.3(10)	158.9(13)	76.6(7)	-10.8(8)	-10.7(6)	-54.0(10)
O11	131(2)	79.2(18)	50.3(12)	4.9(12)	19.6(12)	21.0(16)
O9	128(2)	101(2)	54.9(14)	-12.3(14)	28.3(14)	6.6(18)
C4	55.0(16)	42.7(14)	48.5(15)	-3.9(13)	12.9(12)	0.7(13)
C16	56.7(16)	40.2(14)	52.3(16)	-4.5(13)	13.2(12)	1.8(14)
C5	57.6(18)	67.0(19)	54.5(17)	-1.0(16)	15.6(13)	-12.2(16)
C6	51.3(17)	77(2)	58.3(18)	-6.9(18)	11.0(13)	-8.2(17)
C1	59.7(17)	60.1(18)	50.4(16)	-5.2(15)	11.7(13)	6.3(16)
C21	73(2)	62(2)	57.3(18)	-1.1(17)	14.9(15)	-11.7(18)
C3	66.3(19)	76(2)	56(2)	-0.2(17)	10.3(15)	-25.3(18)
C17	63.9(19)	71(2)	59(2)	1.5(16)	7.1(15)	-11.4(18)
C7	68.2(19)	78(2)	47.9(16)	-2.0(16)	9.6(14)	10.1(18)
C19	93(2)	69(2)	54.4(19)	-5.6(18)	-5.3(17)	5(2)
C20	105(3)	64(2)	54.8(19)	-0.3(19)	19.1(18)	-6(2)
C2	76(2)	83(2)	51.9(18)	3.7(17)	17.0(15)	-21(2)
C8	85(2)	84(3)	48.9(18)	-9.9(17)	10.6(15)	6(2)
C10	85(2)	95(3)	51.8(19)	4.5(18)	14.0(16)	7(2)
C18	81(2)	86(3)	63(2)	0.2(19)	-0.5(17)	-15(2)
C12	132(3)	88(3)	69(2)	-12(2)	5(2)	-2(3)
C15	103(3)	173(5)	67(2)	19(3)	6(2)	23(4)
C14	100(3)	154(5)	118(4)	-8(4)	29(3)	-25(4)

Table S25: ond Lengths for 9i.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl13	C12	1.779(5)	C1	C7	1.506(4)
O11	C7	1.414(5)	C1	C2	1.380(5)
O11	C10	1.424(4)	C21	C20	1.375(5)
O9	C8	1.408(4)	C3	C2	1.376(5)
O9	C10	1.434(5)	C17	C18	1.381(5)
C4	C16	1.482(4)	C7	C8	1.527(5)
C4	C5	1.383(4)	C19	C20	1.372(5)
C4	C3	1.392(4)	C19	C18	1.369(5)
C16	C21	1.409(4)	C8	C12	1.507(6)
C16	C17	1.394(5)	C10	C15	1.487(6)
C5	C6	1.379(4)	C10	C14	1.495(6)
C6	C1	1.390(4)			

Table S26: Bond Angles for 9i.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	O11	C10	110.4(3)	O11	C7	C8	103.1(2)
C8	O9	C10	109.3(3)	C1	C7	C8	113.1(3)
C5	C4	C16	122.8(2)	C18	C19	C20	119.1(3)
C5	C4	C3	116.4(3)	C19	C20	C21	121.0(3)
C3	C4	C16	120.8(3)	C3	C2	C1	121.4(3)
C21	C16	C4	122.1(3)	O9	C8	C7	103.7(3)
C17	C16	C4	121.8(3)	O9	C8	C12	110.2(3)
C17	C16	C21	116.1(3)	C12	C8	C7	116.3(3)
C6	C5	C4	121.9(3)	O11	C10	O9	105.6(3)
C5	C6	C1	121.2(3)	O11	C10	C15	111.0(3)
C6	C1	C7	121.6(3)	O11	C10	C14	108.9(4)
C2	C1	C6	117.1(3)	O9	C10	C15	108.1(4)
C2	C1	C7	121.2(3)	O9	C10	C14	110.0(4)
C20	C21	C16	121.3(3)	C15	C10	C14	113.0(4)
C2	C3	C4	122.0(3)	C19	C18	C17	120.5(3)
C18	C17	C16	121.9(3)	C8	C12	Cl13	113.0(3)
O11	C7	C1	110.6(3)				

Table S27: Torsion Angles for 9i.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O11	C7	C8	O9	27.8(4)	C21	C16	C17	C18	-0.4(5)
O11	C7	C8	C12	148.9(3)	C3	C4	C16	C21	177.8(4)
O9	C8	C12	Cl13	57.7(4)	C3	C4	C16	C17	-2.4(4)
C4	C16	C21	C20	-179.7(3)	C3	C4	C5	C6	-0.9(5)
C4	C16	C17	C18	179.9(3)	C17	C16	C21	C20	0.6(5)
C4	C5	C6	C1	0.3(5)	C7	O11	C10	O9	6.5(4)
C4	C3	C2	C1	0.1(6)	C7	O11	C10	C15	-110.4(4)
C16	C4	C5	C6	179.0(3)	C7	O11	C10	C14	124.7(4)
C16	C4	C3	C2	-179.2(3)	C7	C1	C2	C3	177.1(3)
C16	C21	C20	C19	-0.2(6)	C7	C8	C12	Cl13	-59.9(4)
C16	C17	C18	C19	-0.3(6)	C20	C19	C18	C17	0.7(6)
C5	C4	C16	C21	-2.2(4)	C2	C1	C7	O11	38.5(4)
C5	C4	C16	C17	177.6(4)	C2	C1	C7	C8	-76.5(4)
C5	C4	C3	C2	0.7(5)	C8	O9	C10	O11	12.7(4)
C5	C6	C1	C7	-177.3(3)	C8	O9	C10	C15	131.5(3)
C5	C6	C1	C2	0.5(5)	C8	O9	C10	C14	-104.8(4)
C6	C1	C7	O11	-143.8(3)	C10	O11	C7	C1	-142.3(3)
C6	C1	C7	C8	101.2(4)	C10	O11	C7	C8	-21.1(4)
C6	C1	C2	C3	-0.8(6)	C10	O9	C8	C7	-25.1(4)
C1	C7	C8	O9	147.2(3)	C10	O9	C8	C12	-150.2(4)
C1	C7	C8	C12	-91.6(4)	C18	C19	C20	C21	-0.5(6)

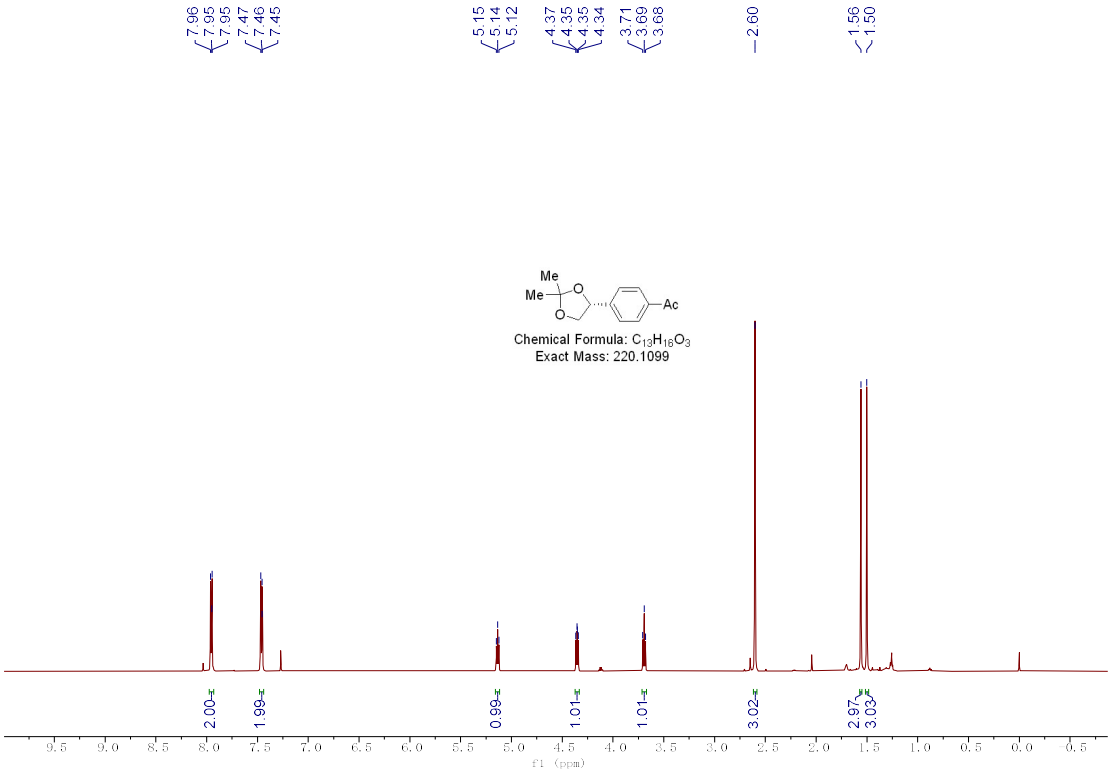
Table S28: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 9i.

Atom	*x*	*y*	*z*	U(eq)
H5	5928.62	5735.98	5304.91	71
H6	7506.9	5738.54	6561.44	74
H21	4378.27	5863.96	4163.69	76
H3	559.13	3132.53	5825.83	79
H17	-835.06	3061.8	4722.98	78
H7	7618.31	4701.39	7859.31	78
H19	-784.24	4502.86	2565.55	88
H20	2664.28	5872.09	2920.61	89
H2	2138.64	3115.81	7078.91	83
H8	3259.97	6011.37	8013.74	87
H18	-2498.79	3076.79	3471.14	94
H12A	5084.33	8444.93	8586.53	117
H12B	5904.46	8157.17	7797.16	117
H15A	7181.28	1396.97	9413.04	172
H15B	6470.84	2757.61	9996.92	172
H15C	8258.98	3281.06	9471.38	172
H14A	1621.95	2987.46	8619.55	184
H14B	2428.92	2708.81	9492.91	184
H14C	2823.03	1230.1	8912.25	184

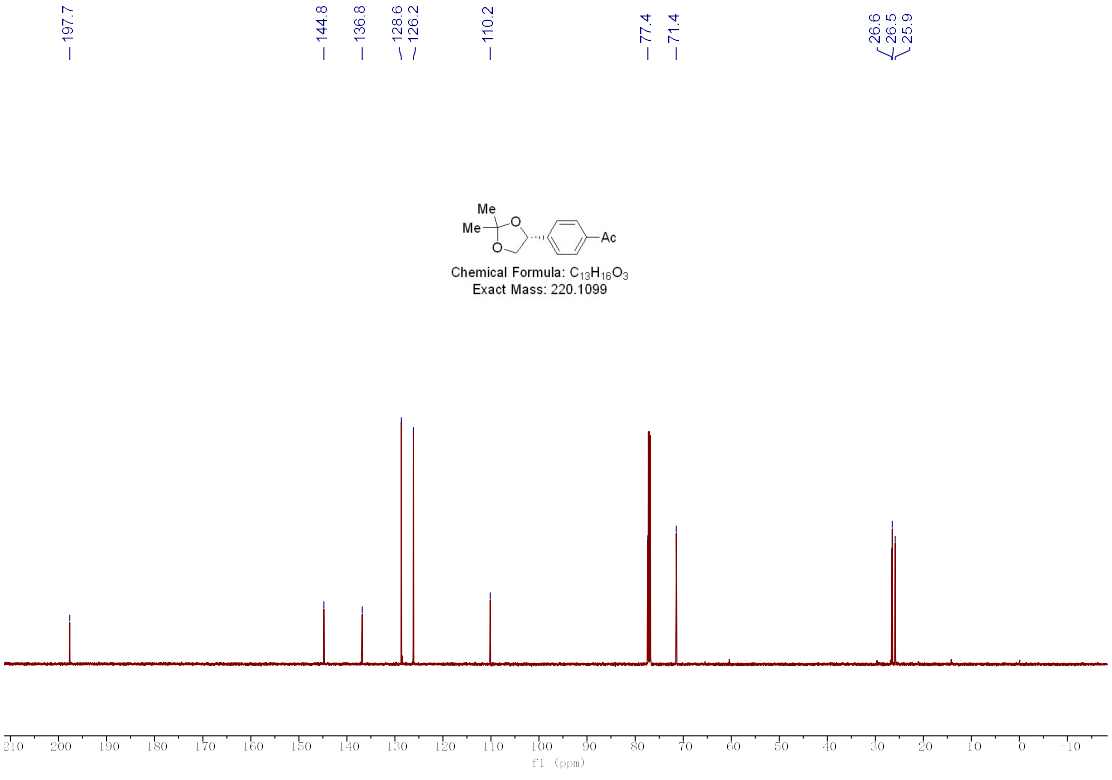
Crystal structure determination of 9i

Crystal Data for $C_{18}H_{19}ClO_2$ (*M* =302.78 g/mol): monoclinic, space group $P2_1$ (no. 4), *a* = 5.9444(4) Å, *b* = 7.6111(6) Å, *c* = 17.7601(11) Å, *β* = 98.633(6)°, *V* = 794.43(10) Å^3, *Z* = 2, *T* = 300.62(10) K, μ(Cu Kα) = 2.135 mm^{-1}, *Dcalc* = 1.266 g/cm^3, 6998 reflections measured (5.032° ⩽ 2Θ ⩽ 152.182°), 2859 unique (R_{int} = 0.0286, R_{sigma} = 0.0321) which were used in all calculations. The final R_1 was 0.0410 (I > 2σ(I)) and wR_2 was 0.1187 (all data).

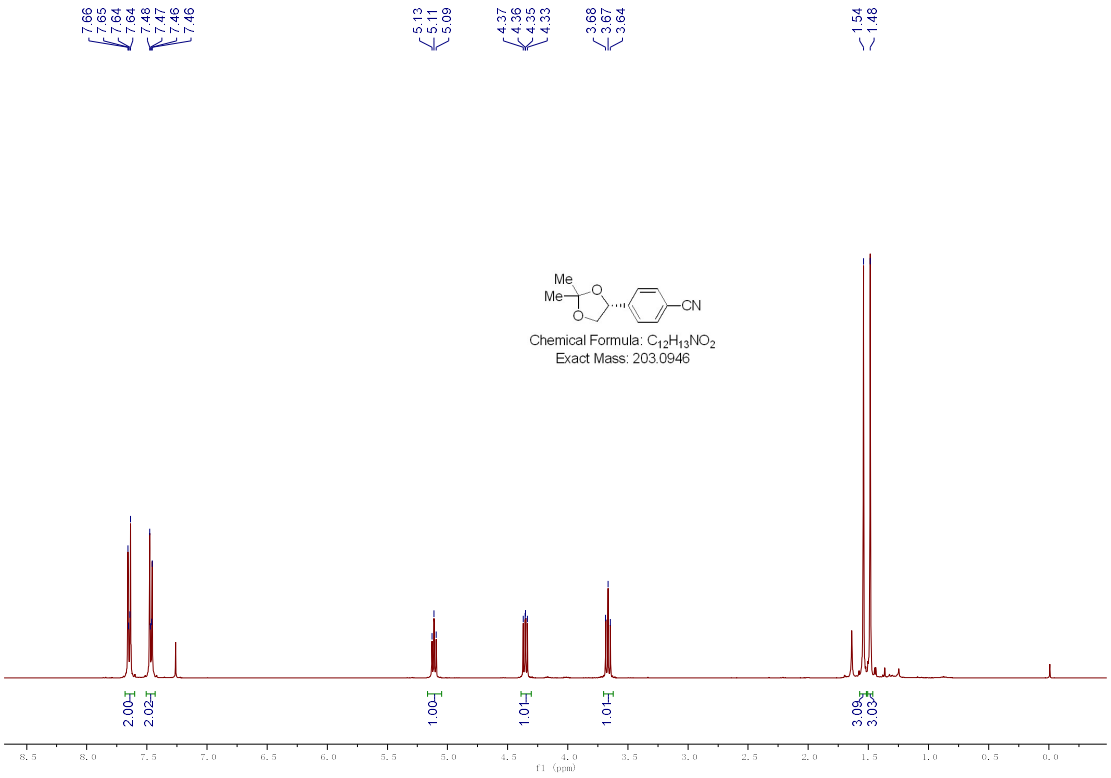
8. NMR Spectra



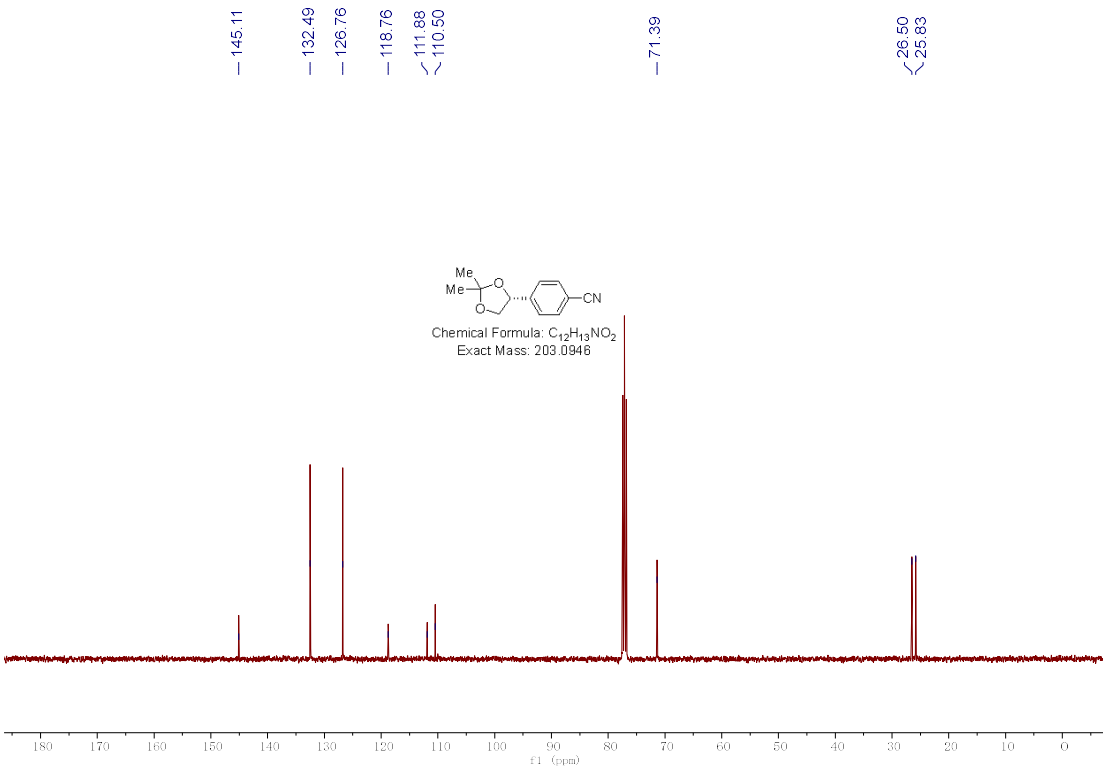
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3ca



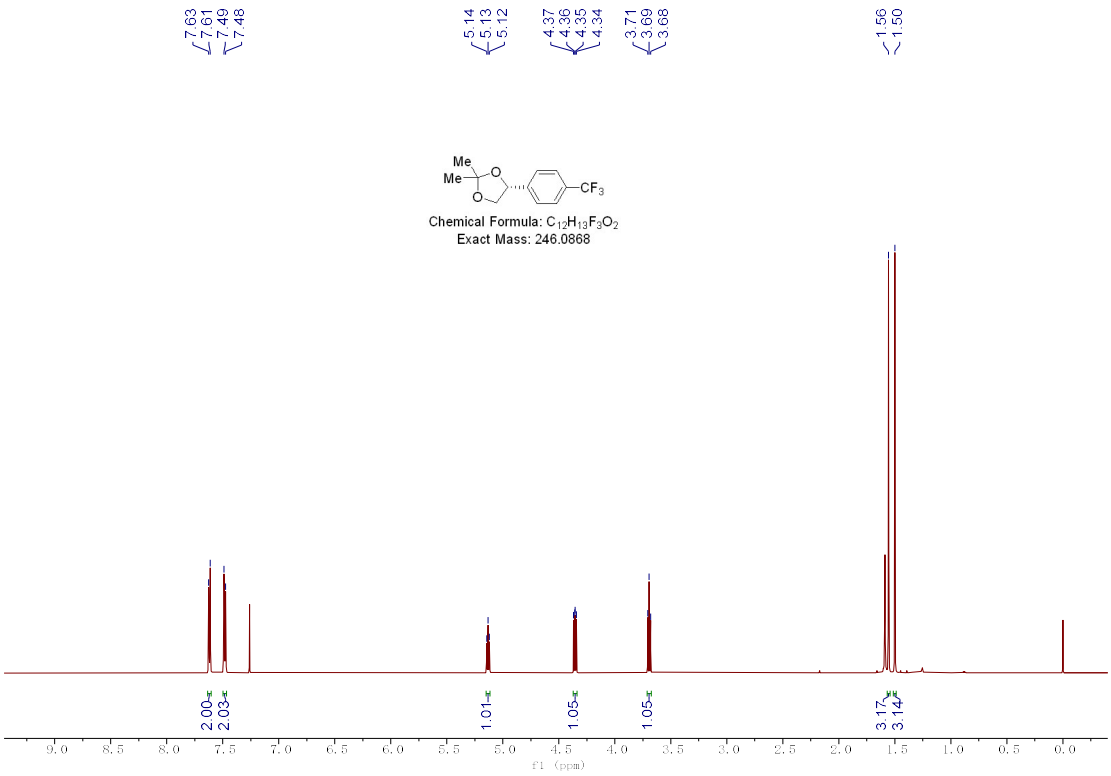
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3ca



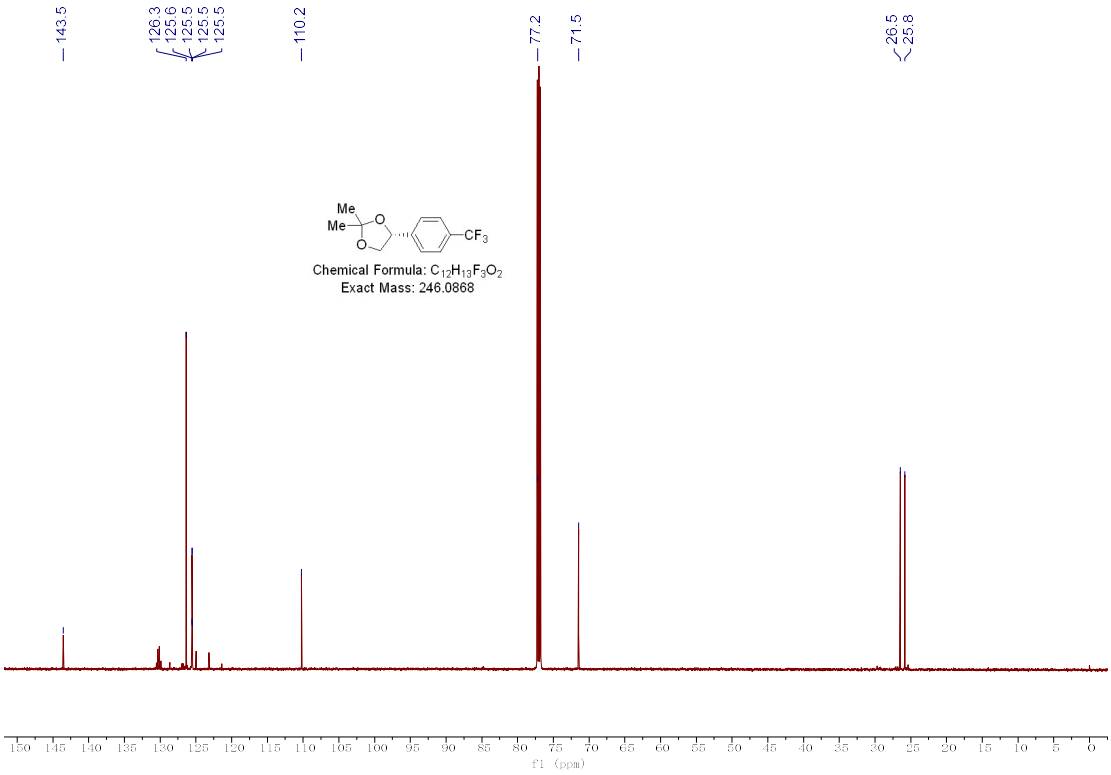
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3cb



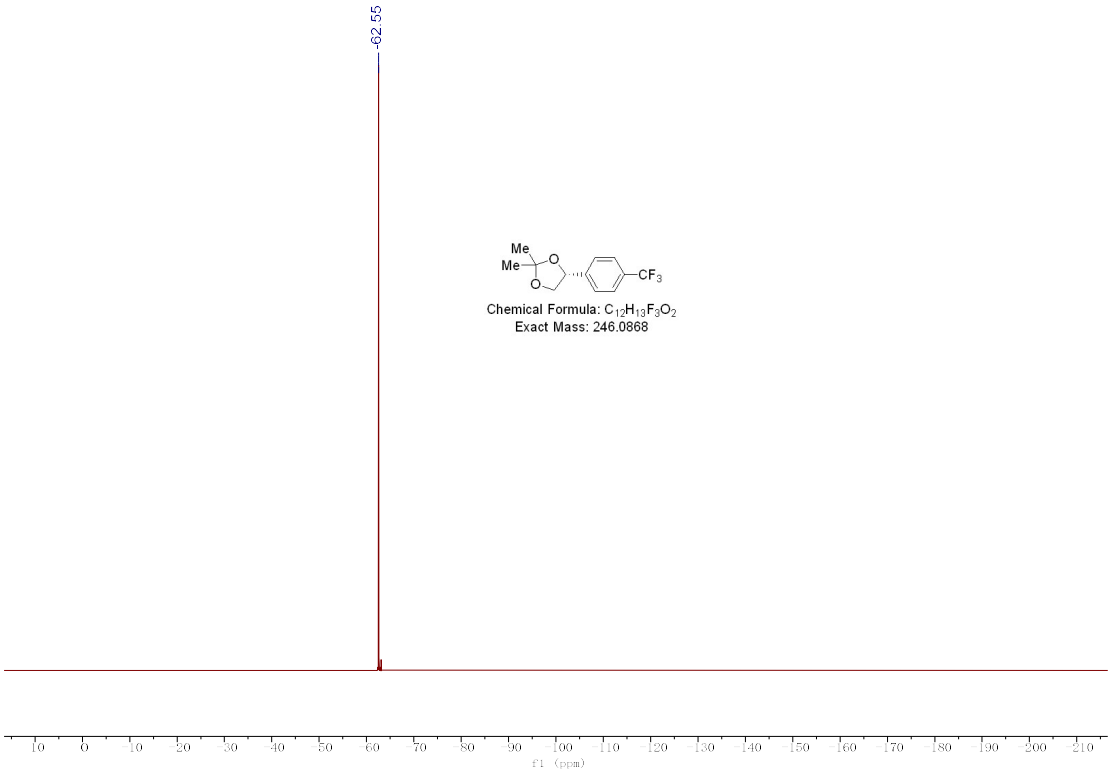
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3cb



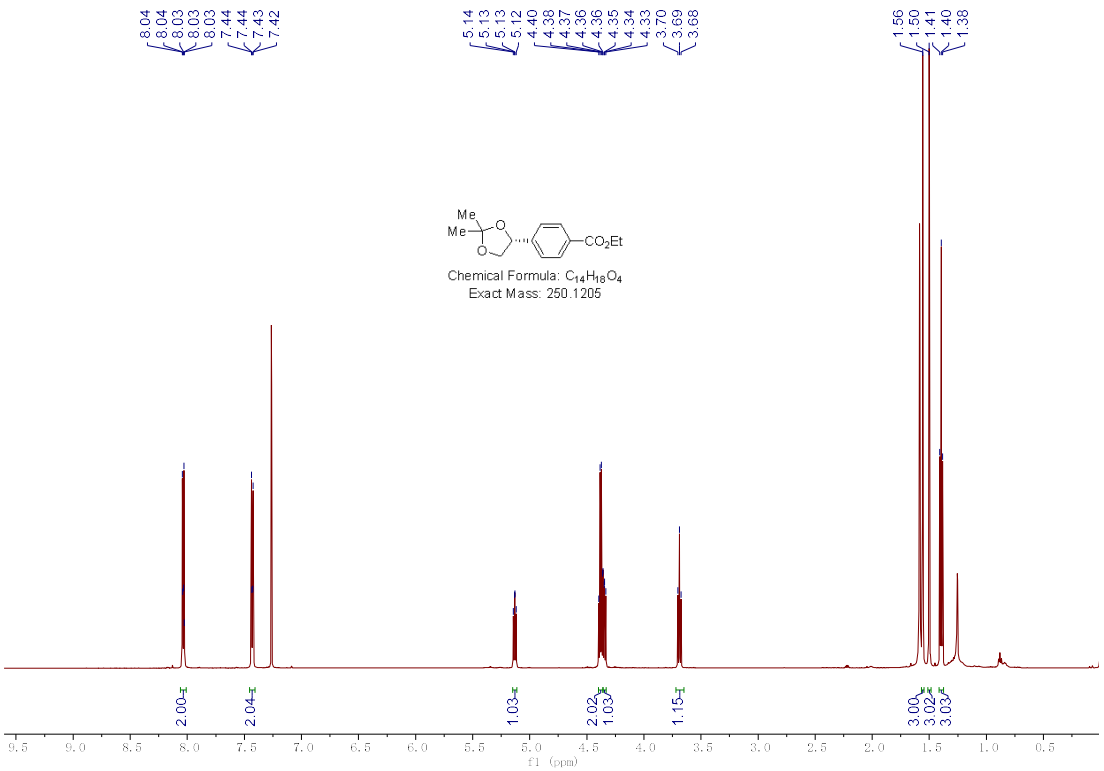
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cc



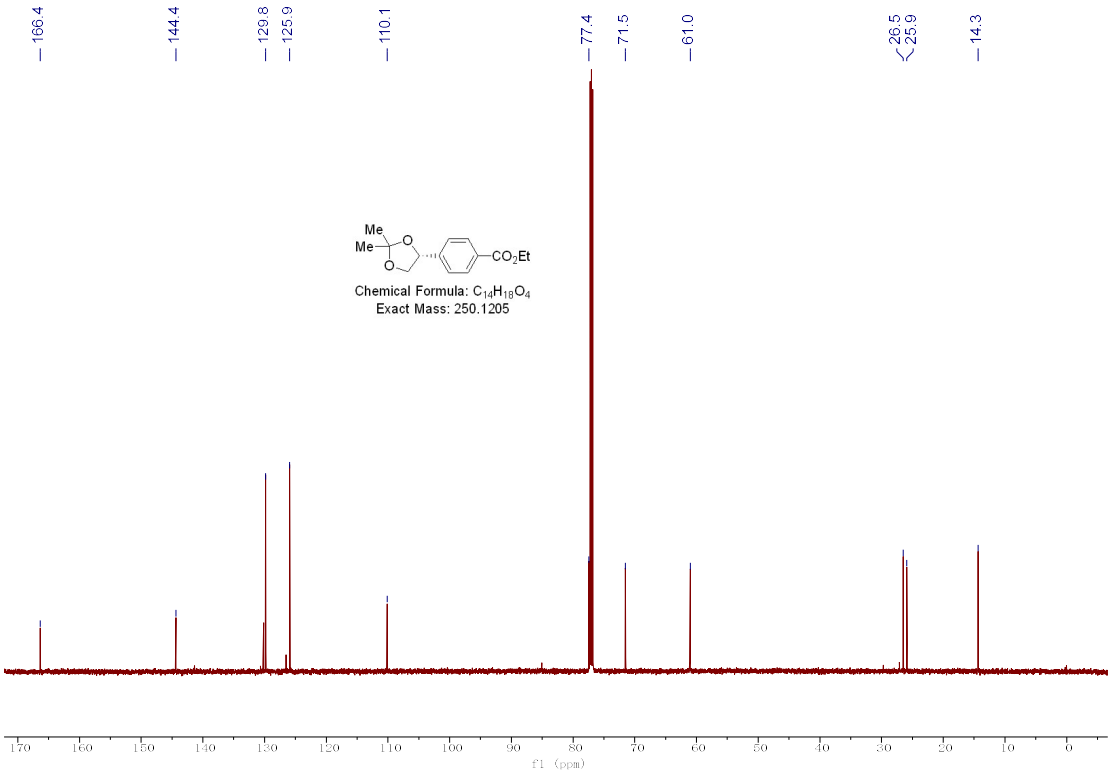
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cc



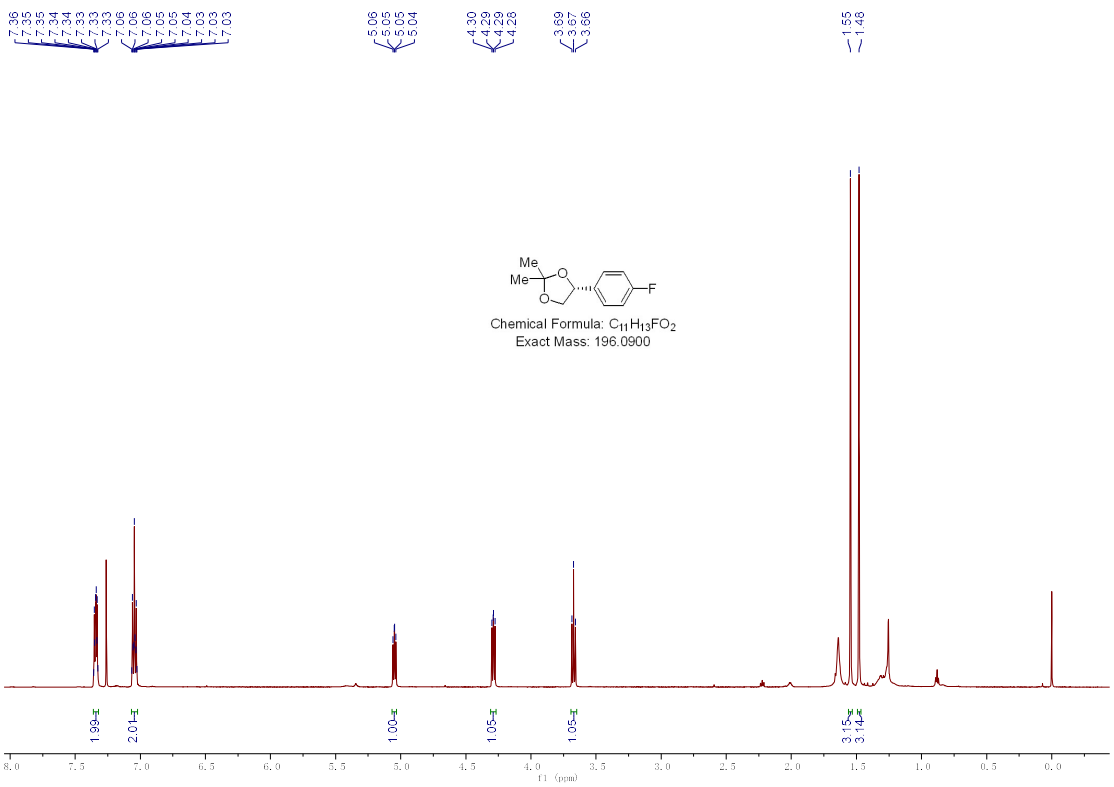
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of 3cc



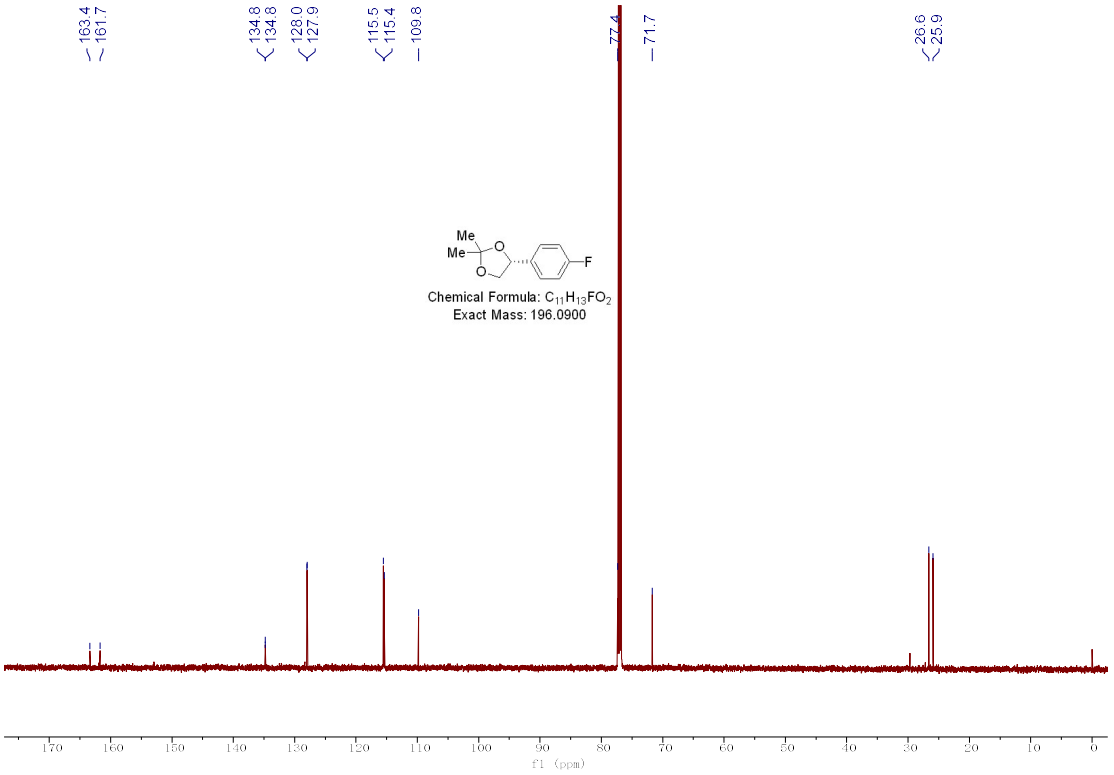
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cd



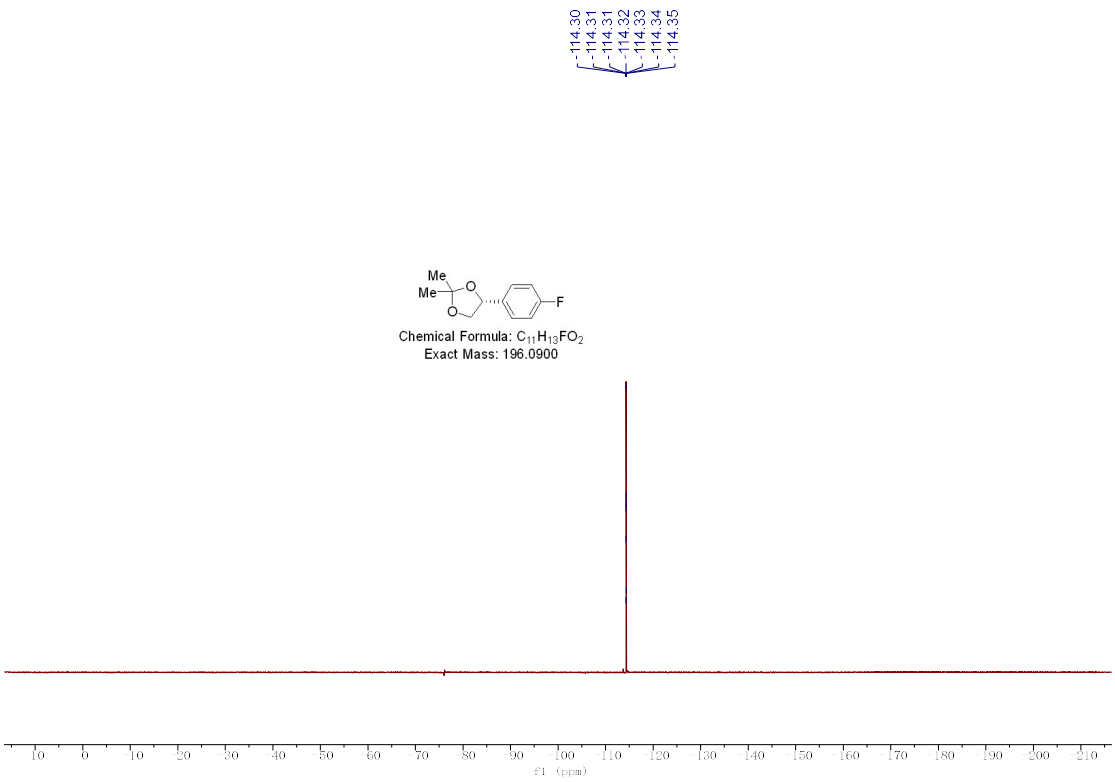
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cd



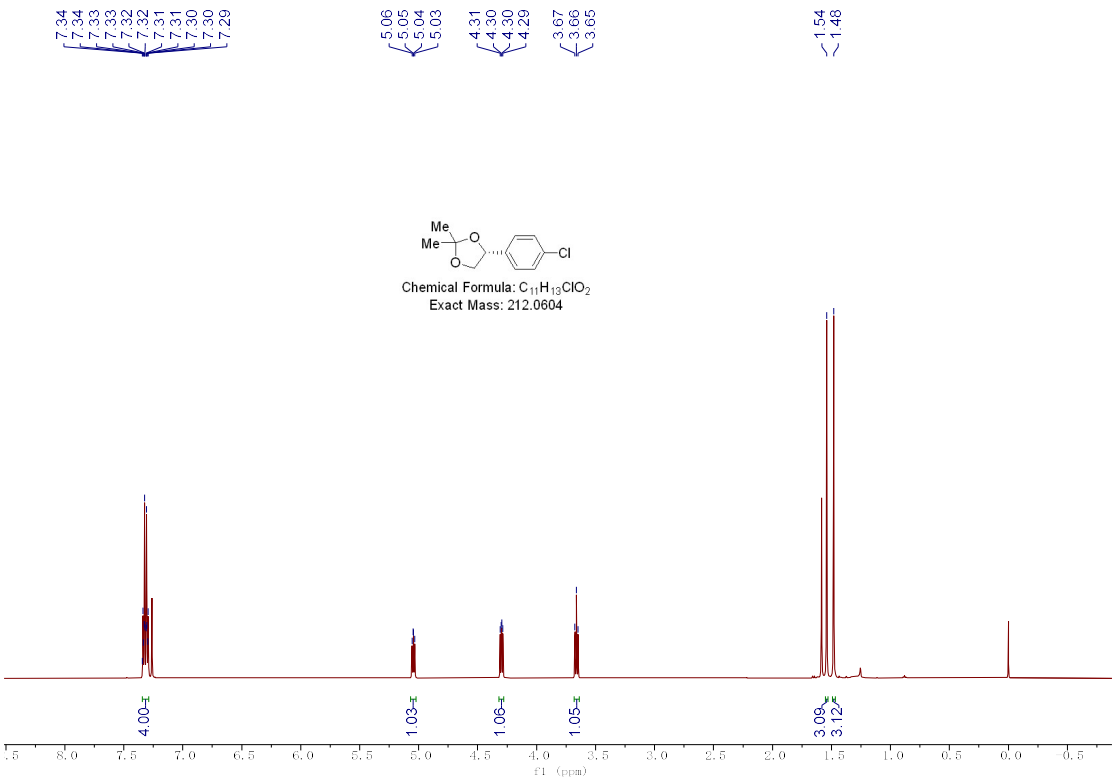
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3ce



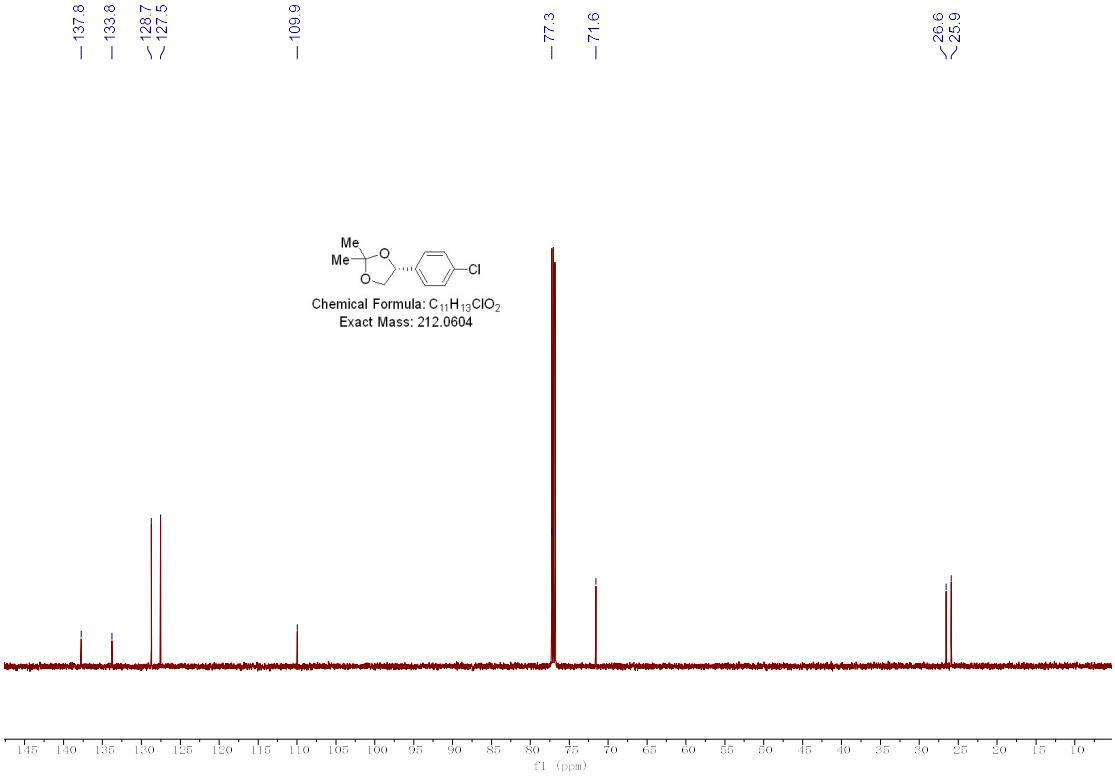
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3ce



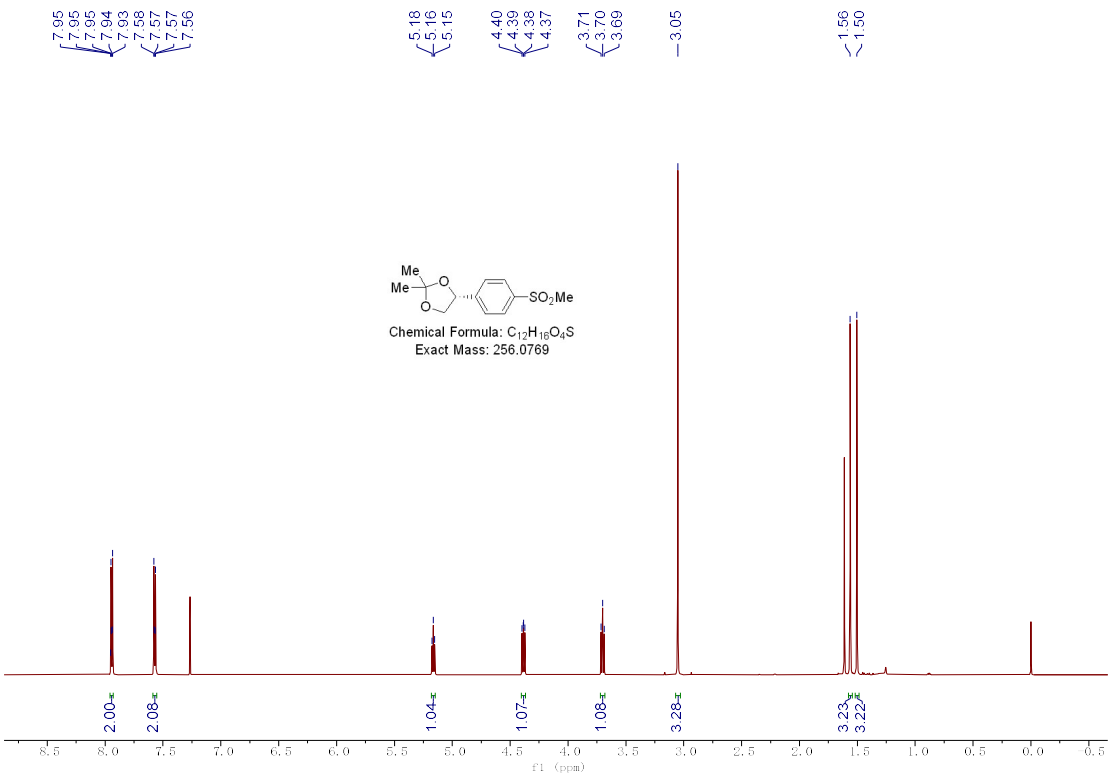
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of 3ce



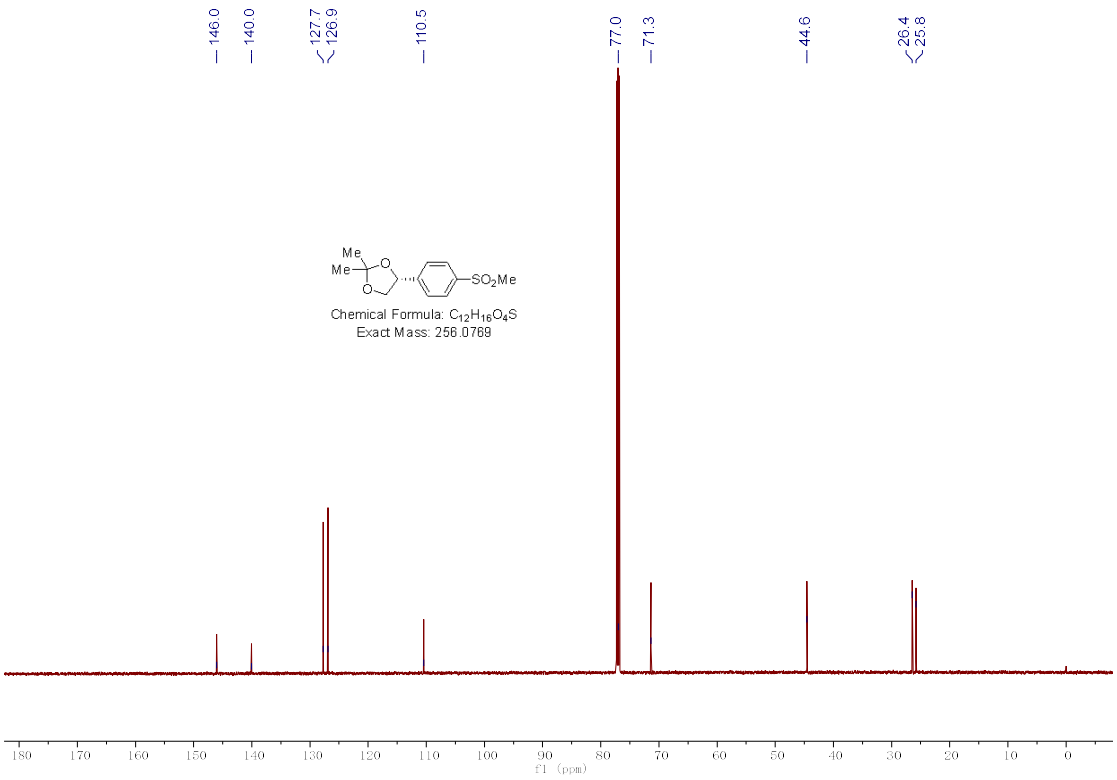
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cf



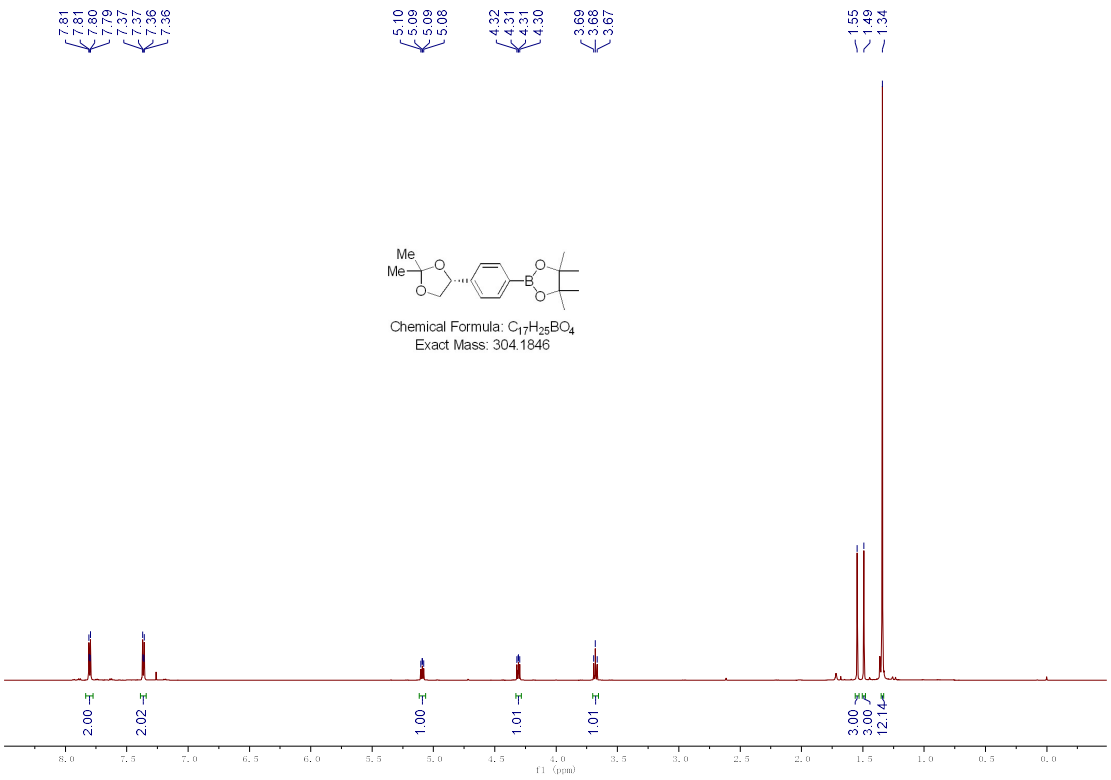
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cf



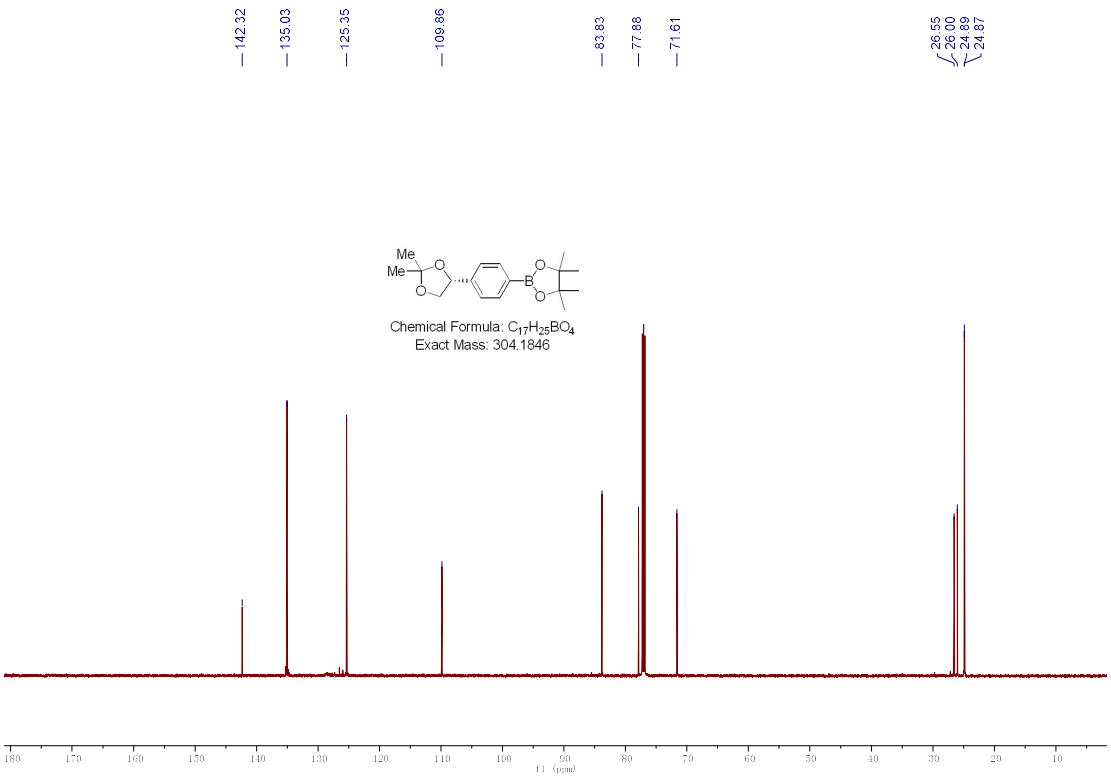
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cg



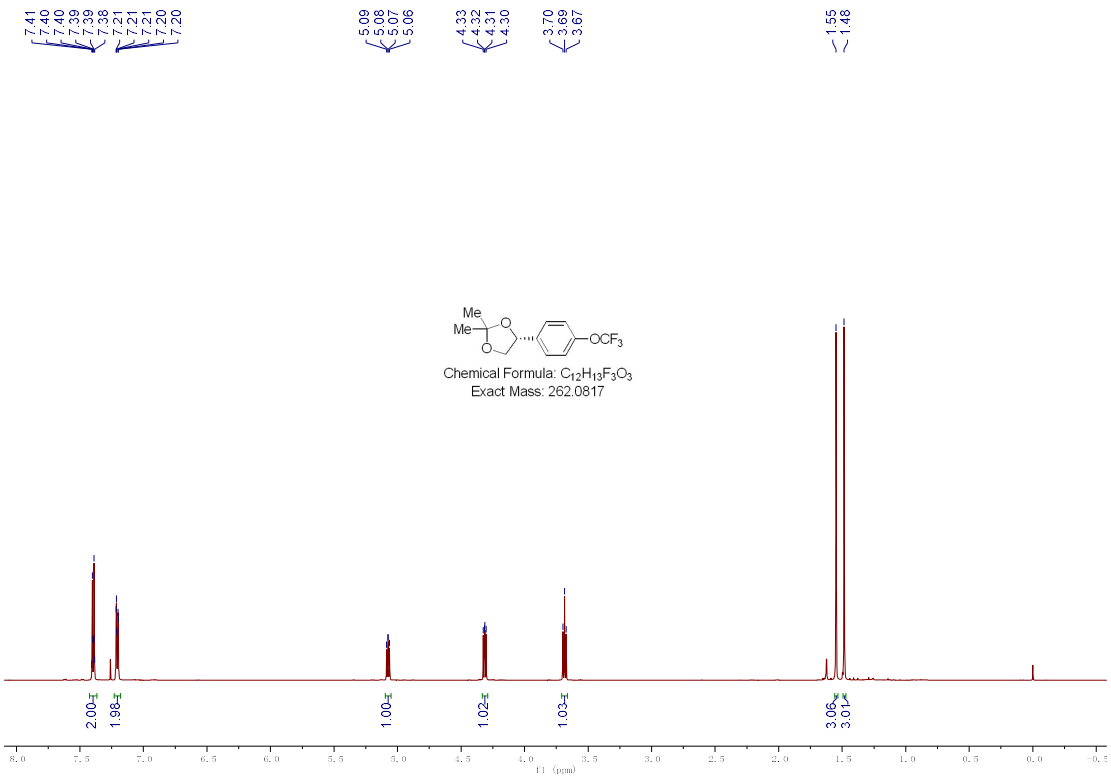
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cg



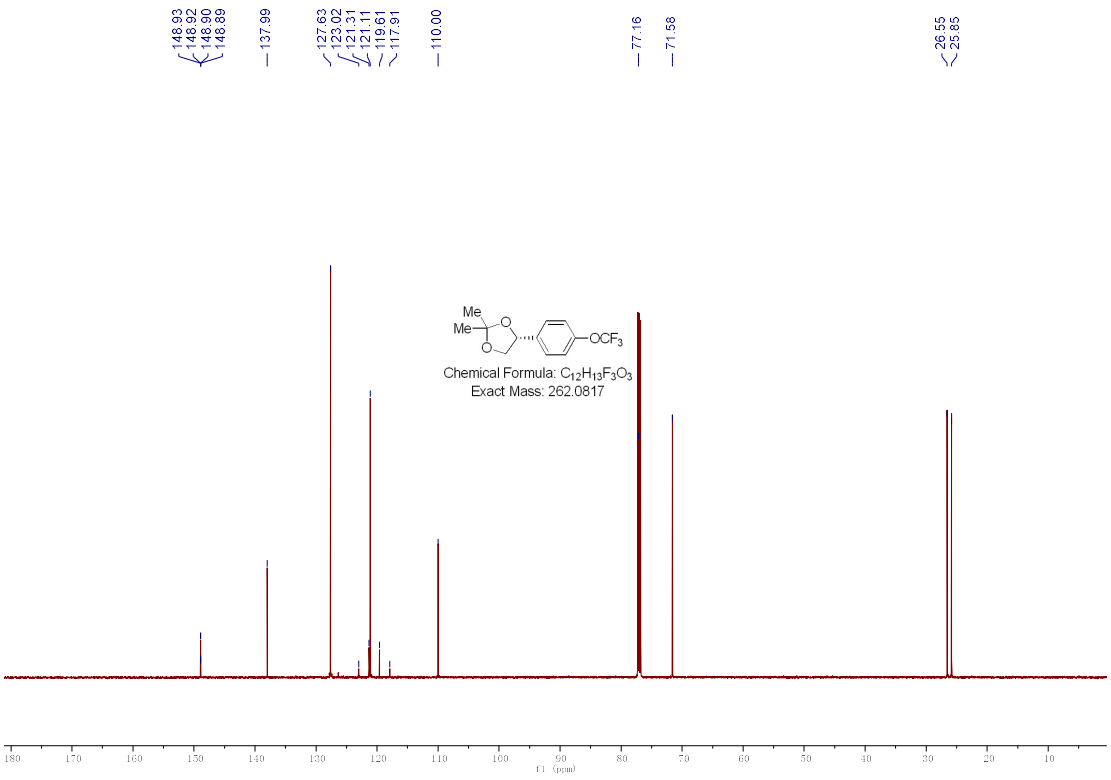
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3ch



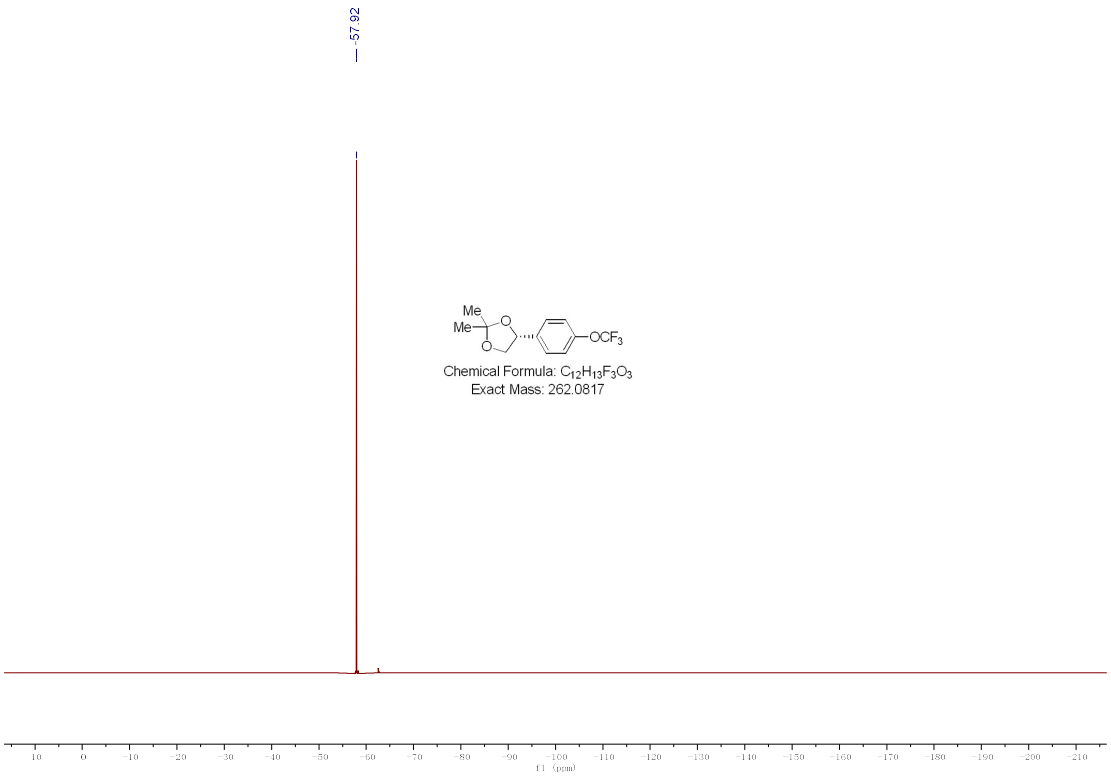
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3ch



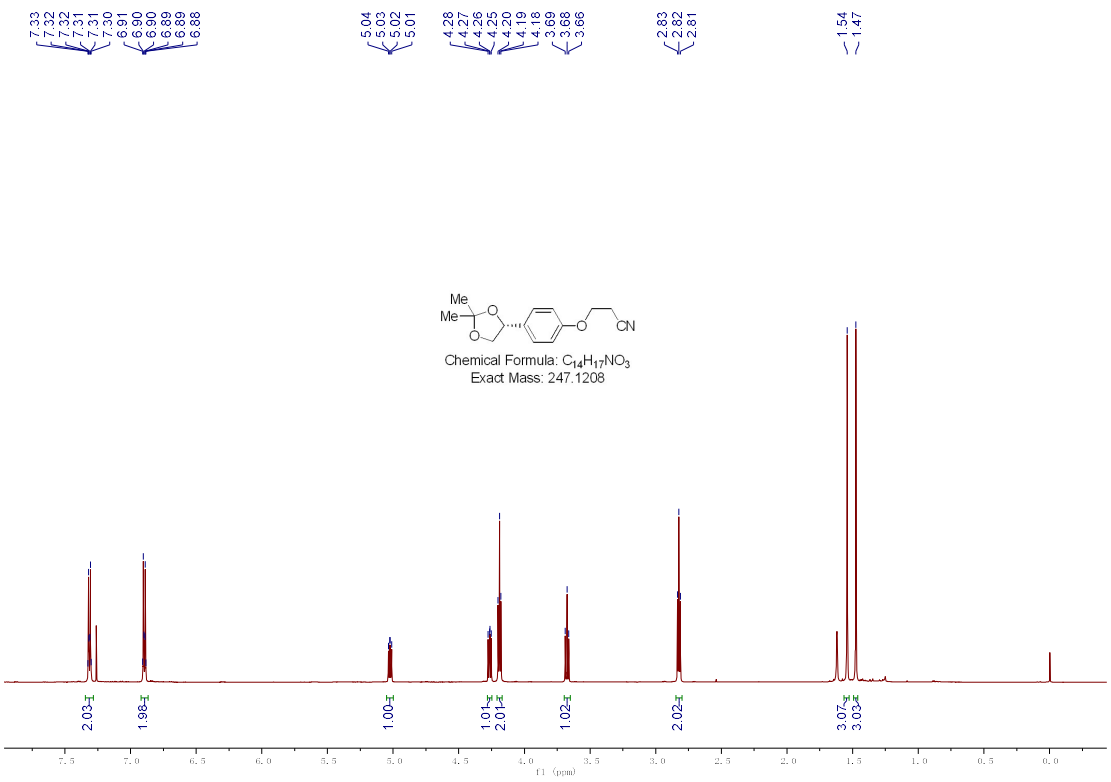
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3ci



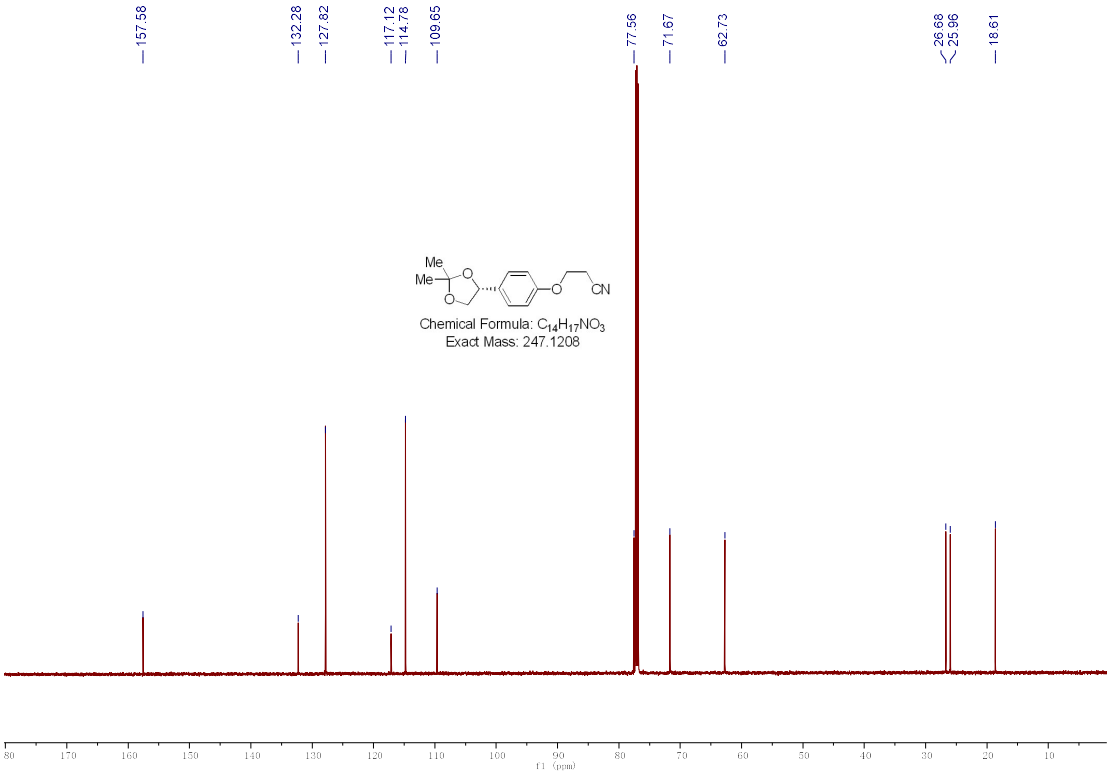
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3ci



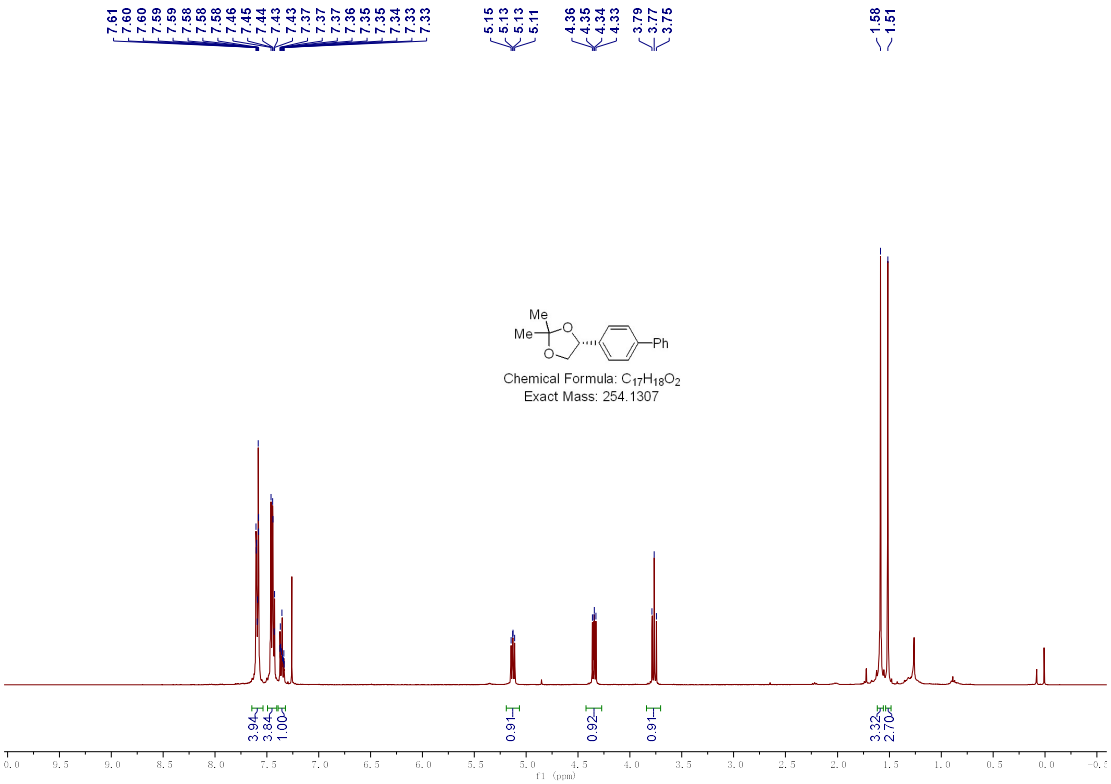
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of 3ci



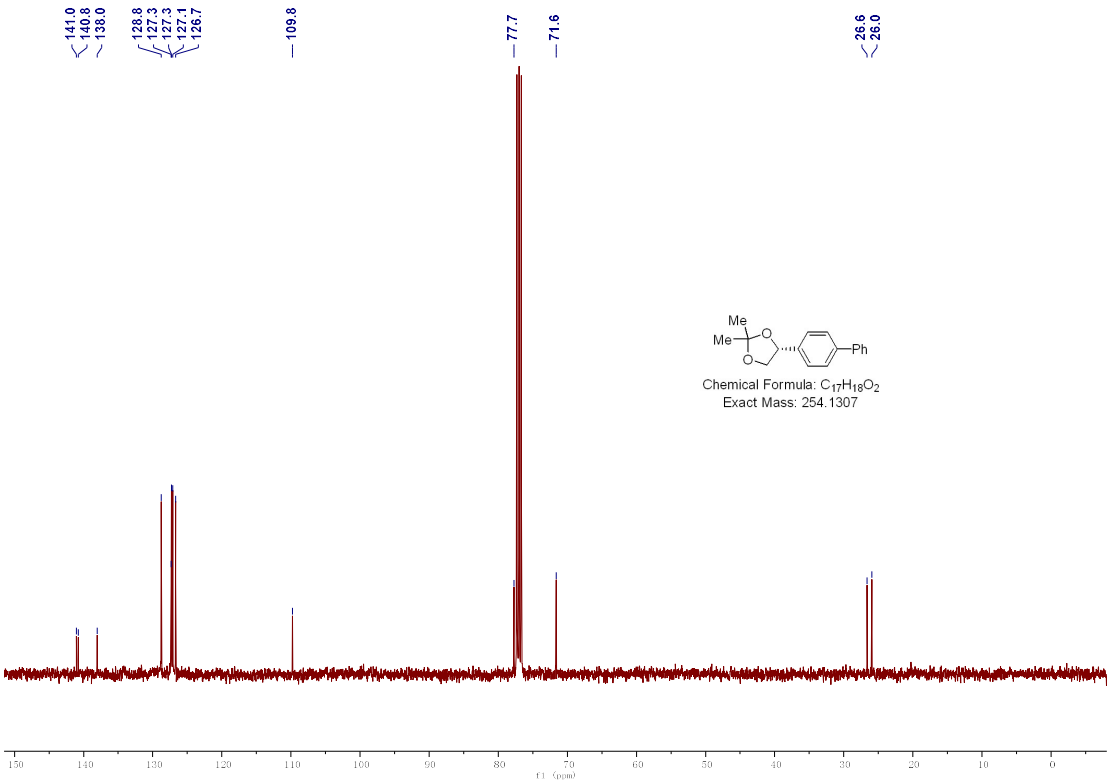
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cj



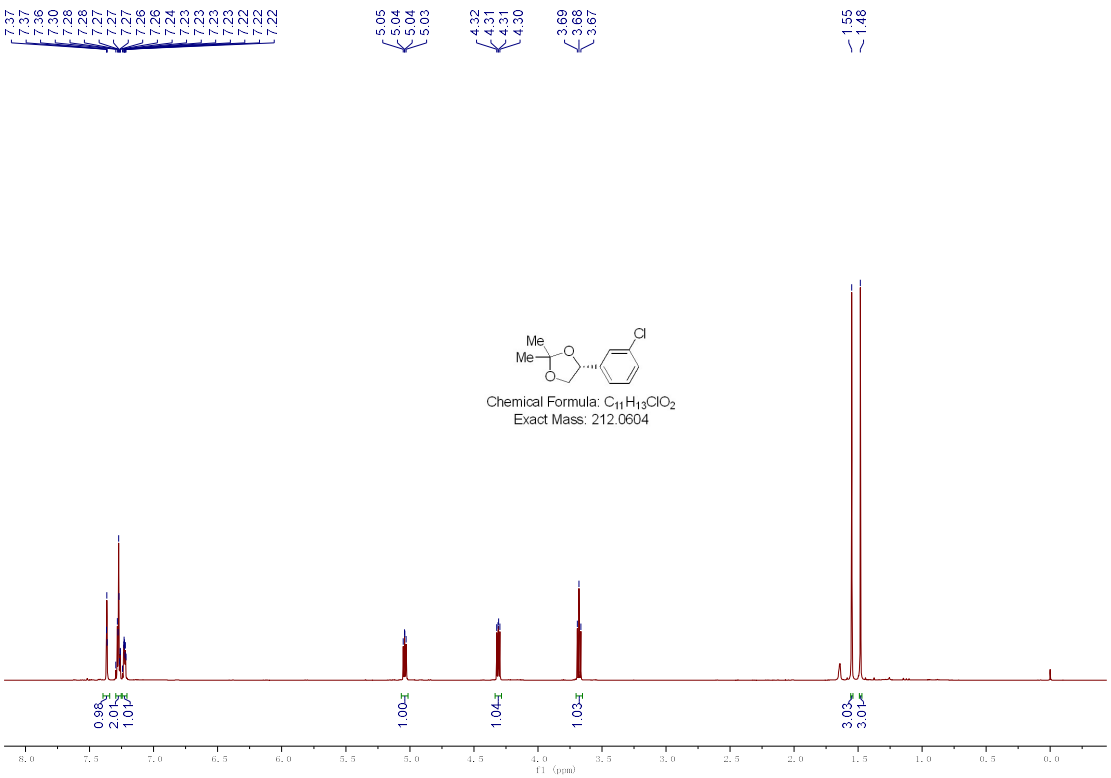
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cj



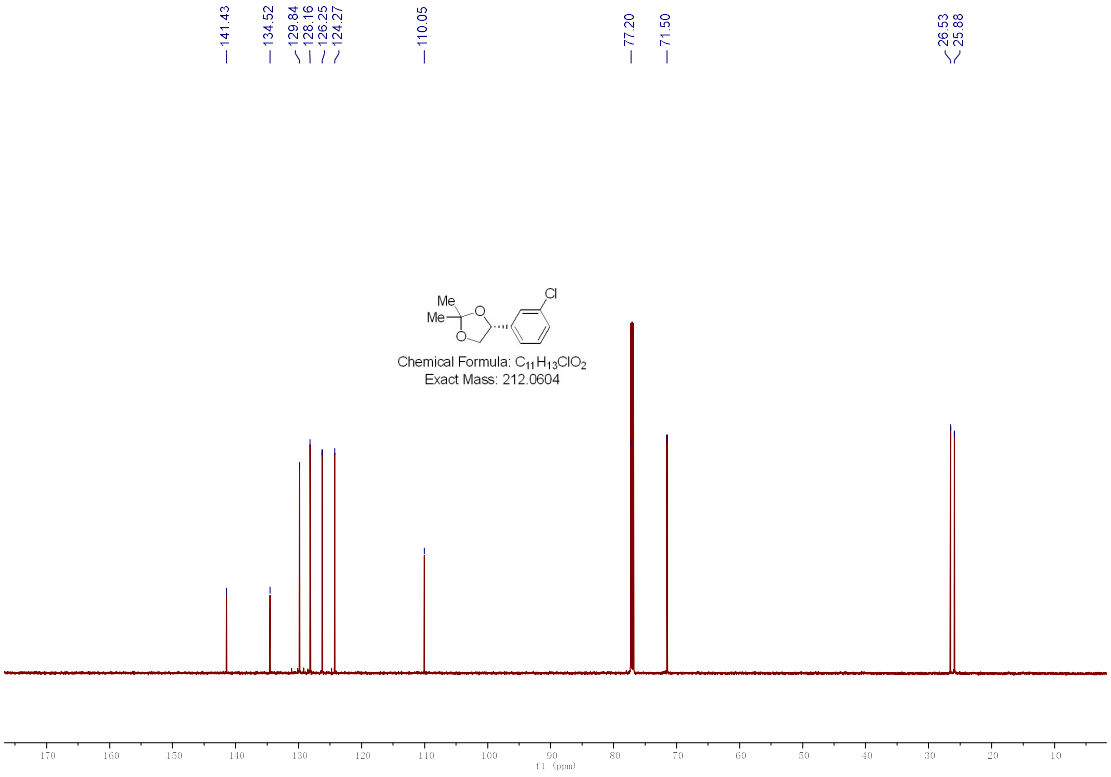
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ck



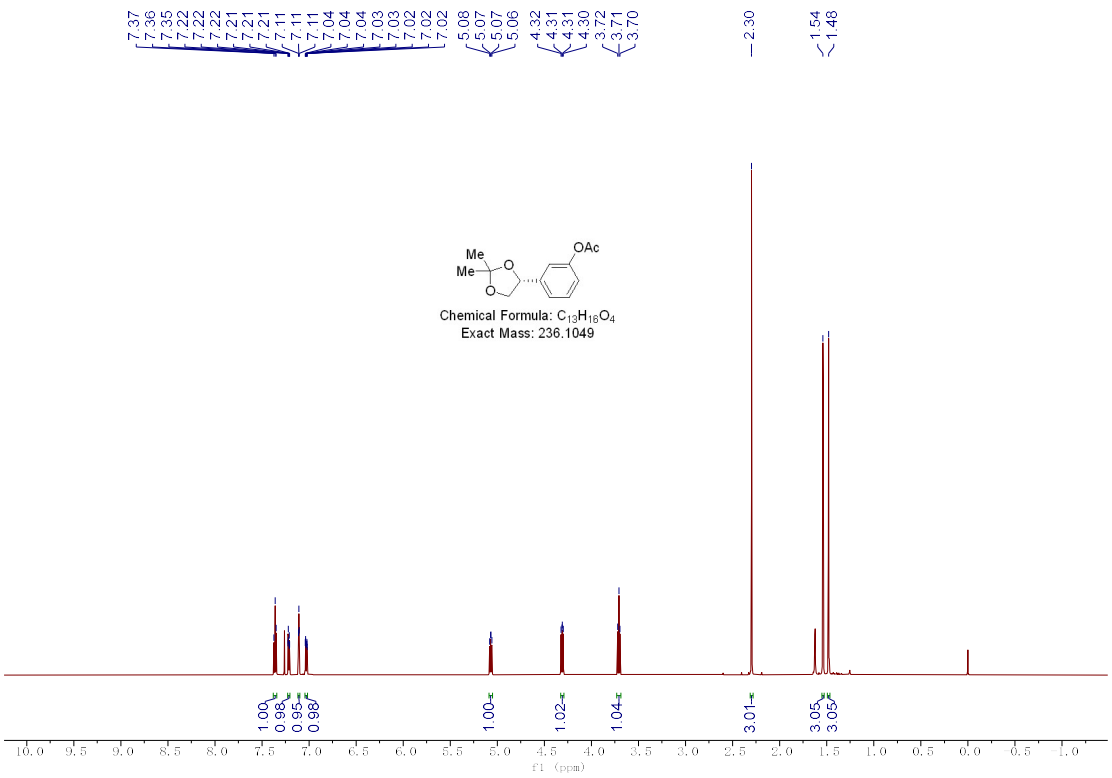
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 3ck



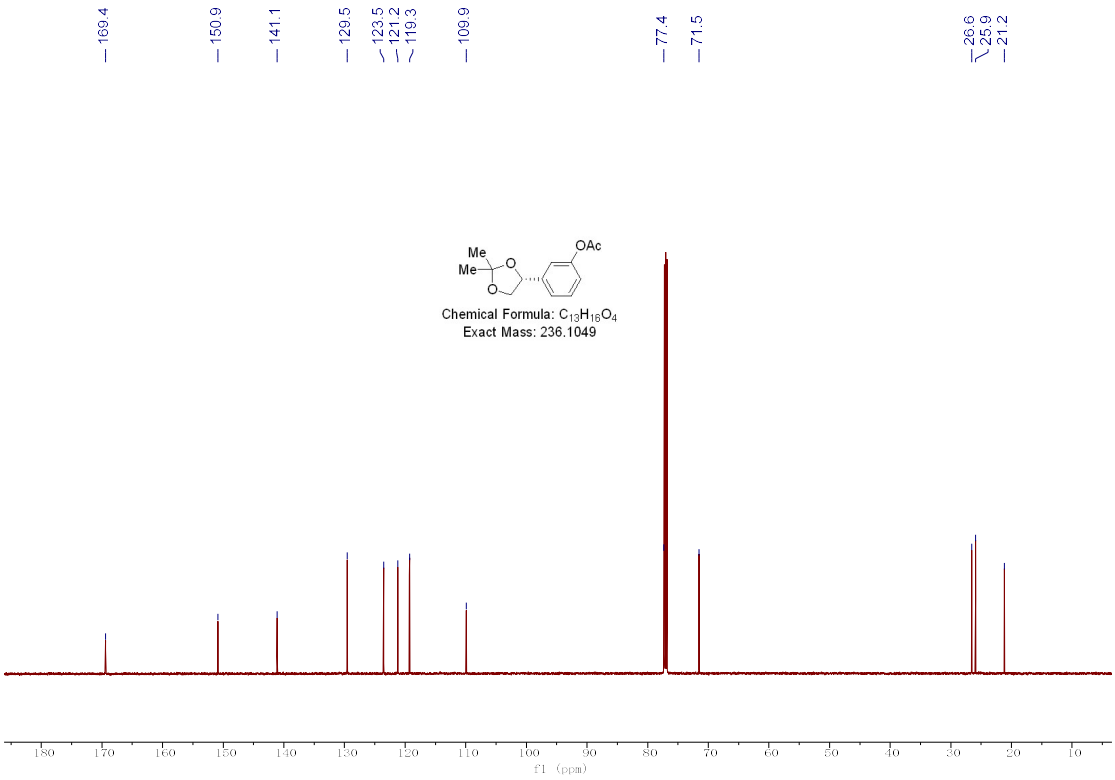
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cl



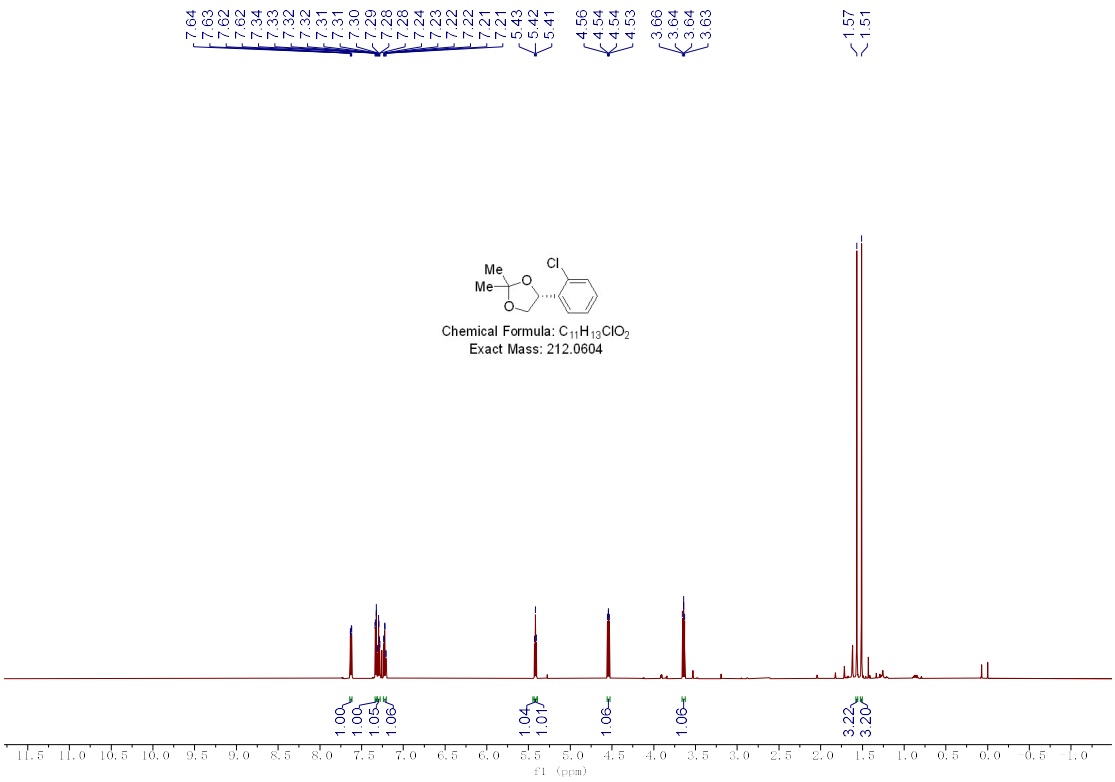
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cl



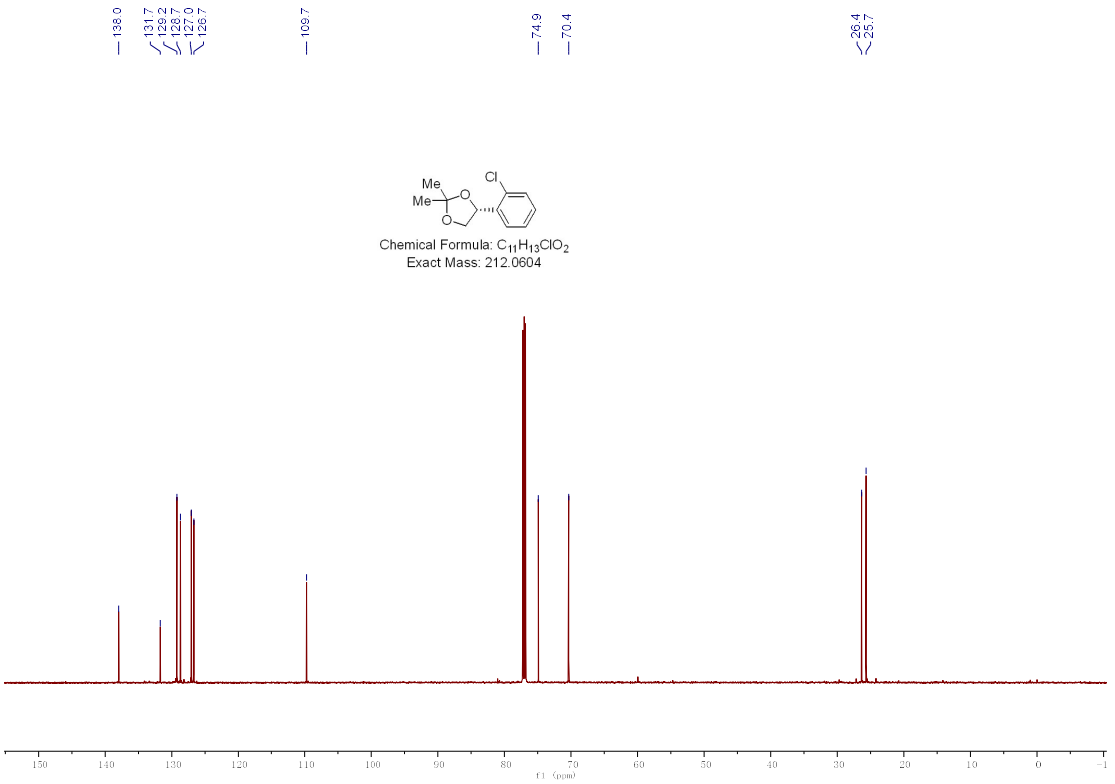
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cm



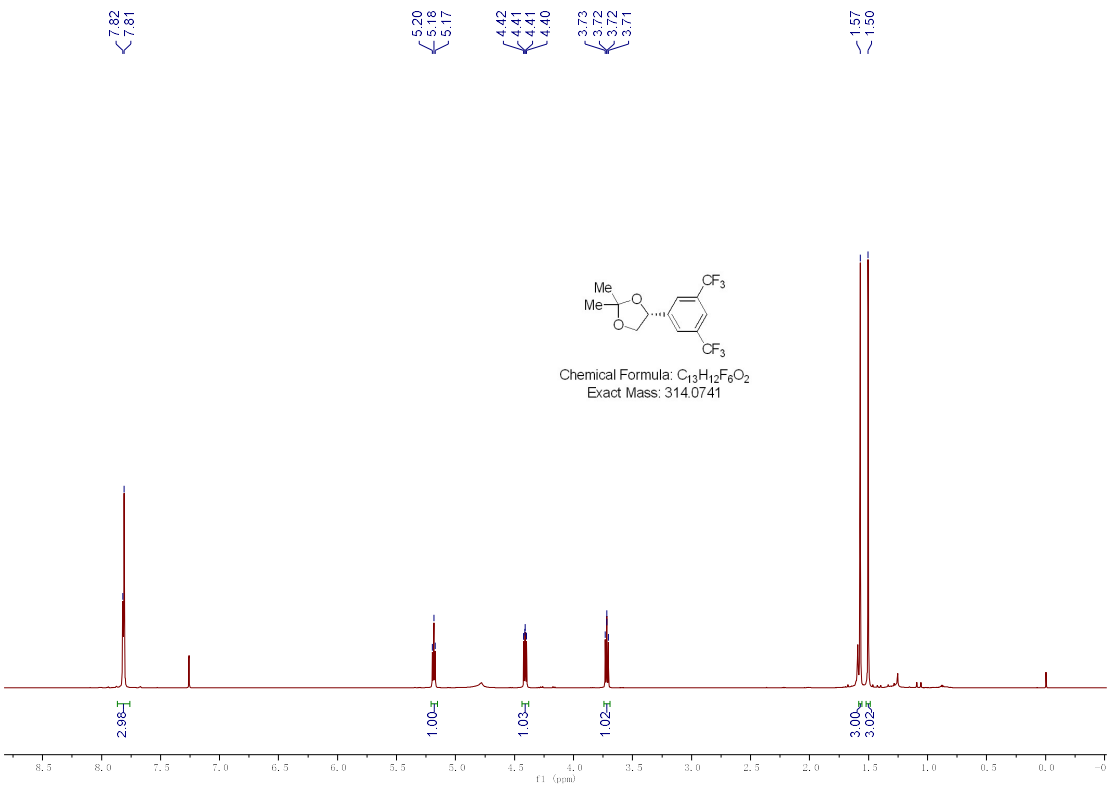
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cm



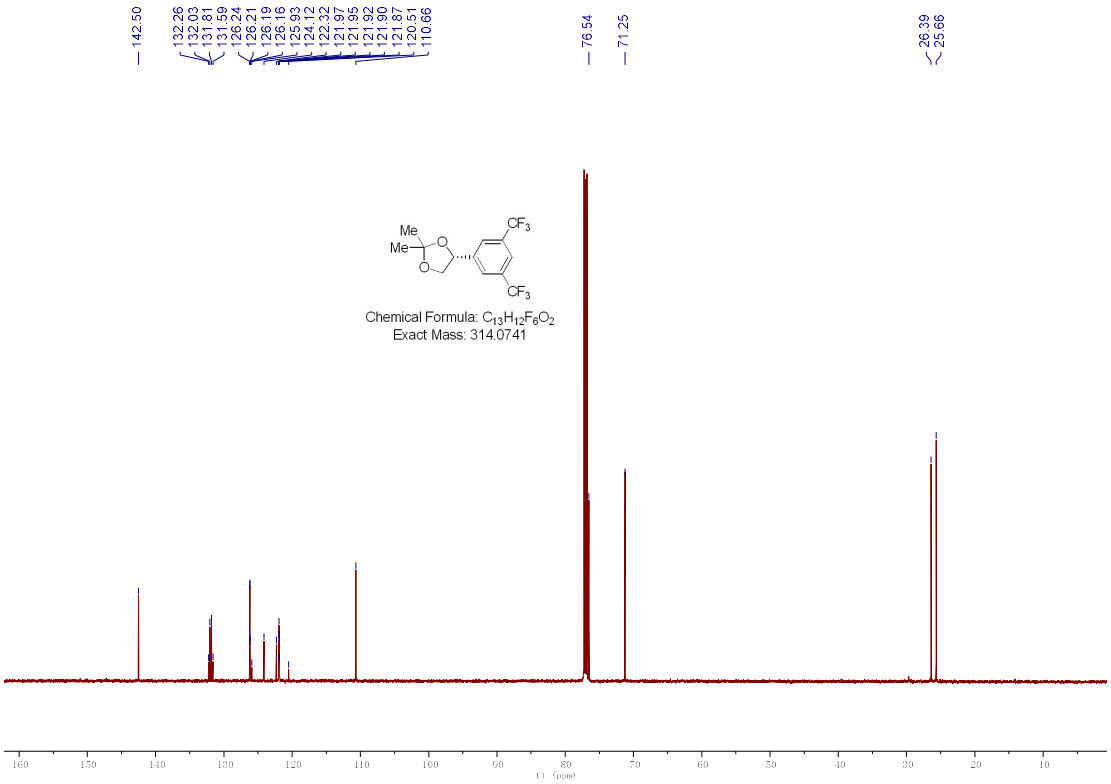
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cn



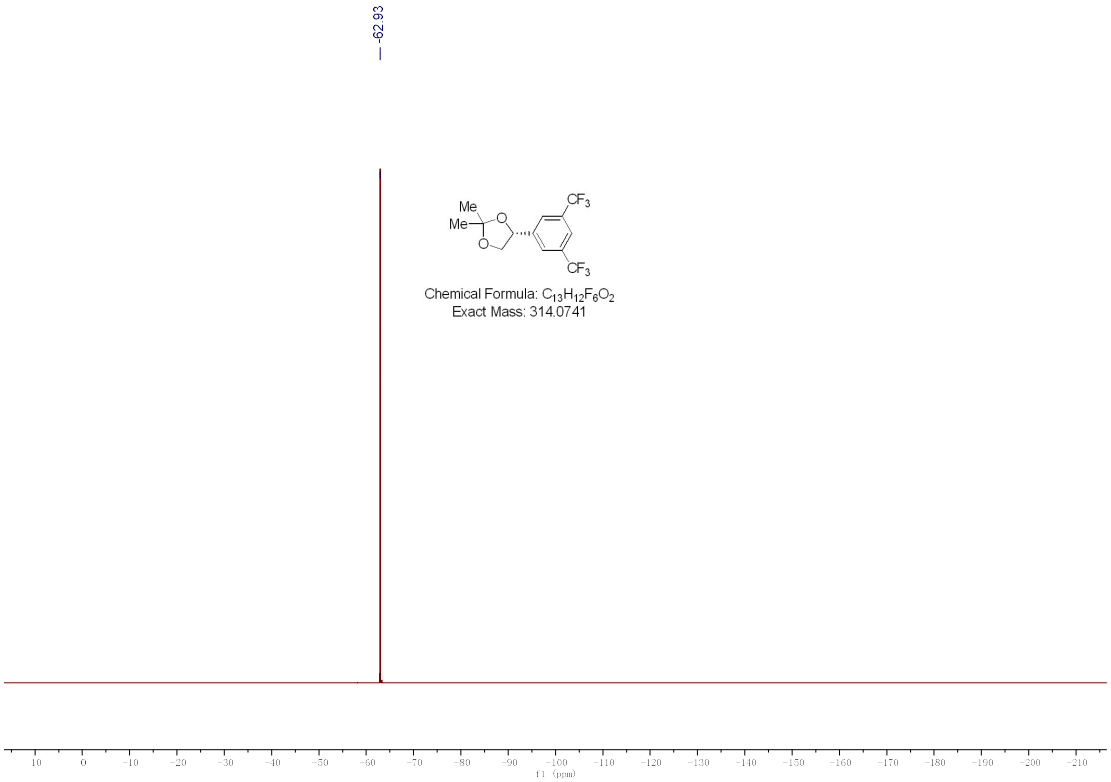
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cn



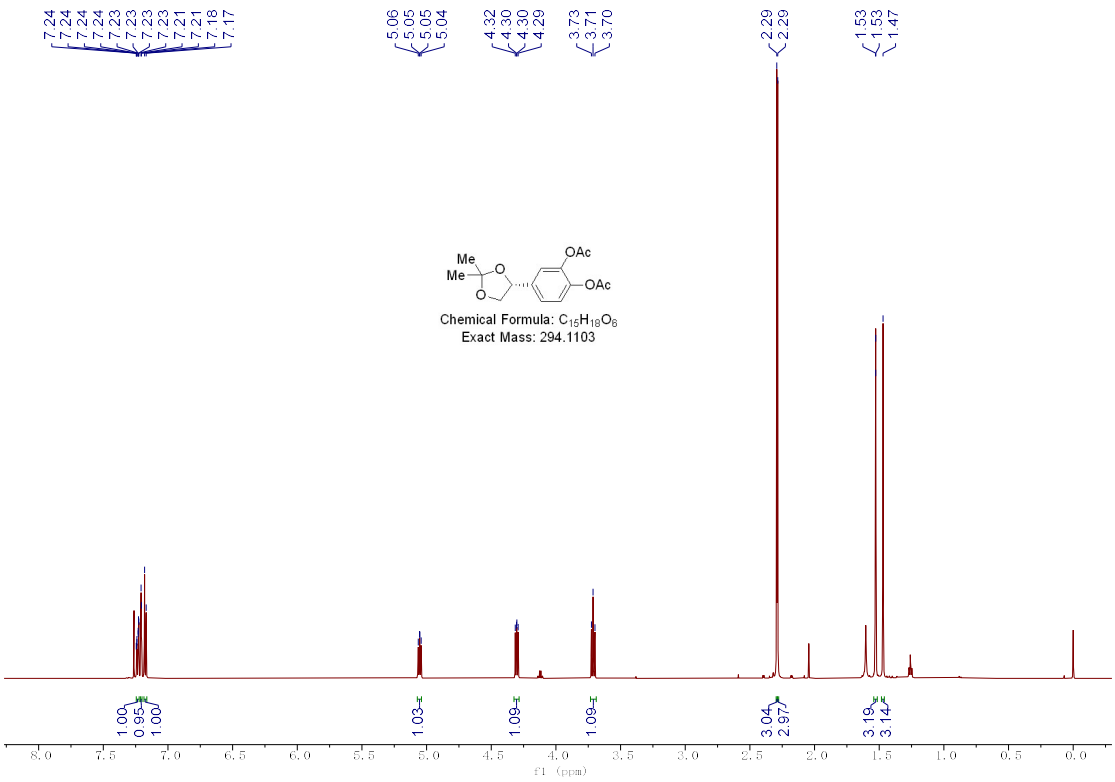
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3co



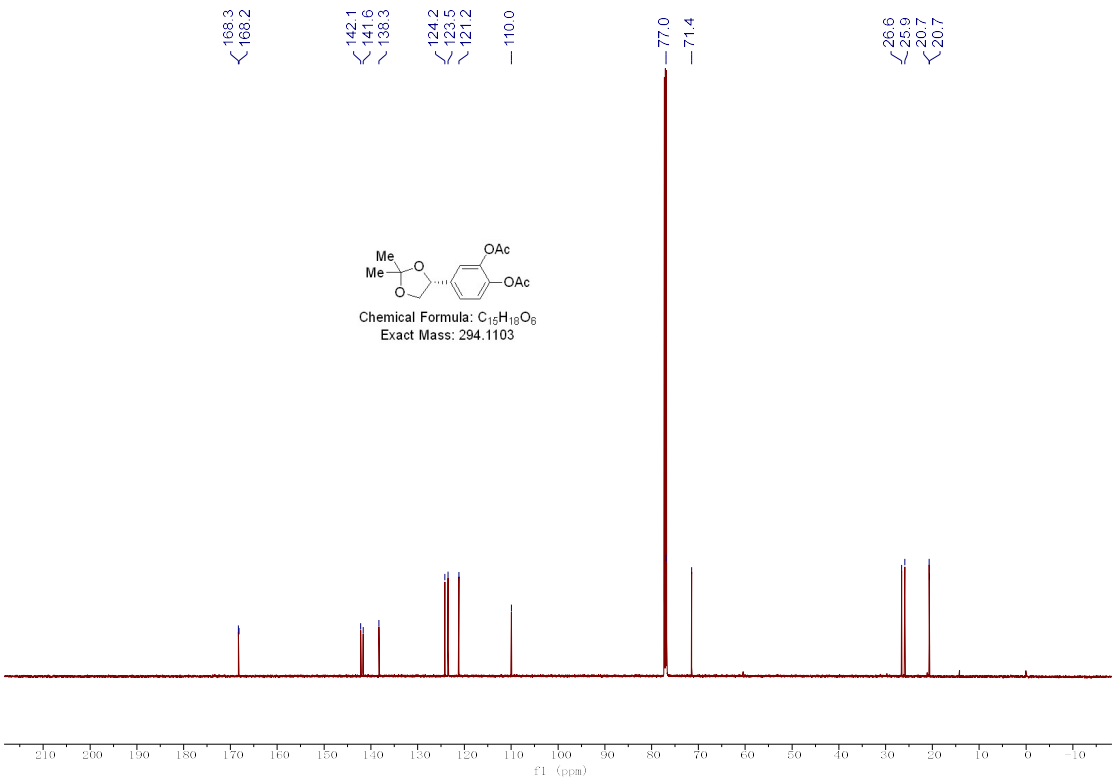
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3co



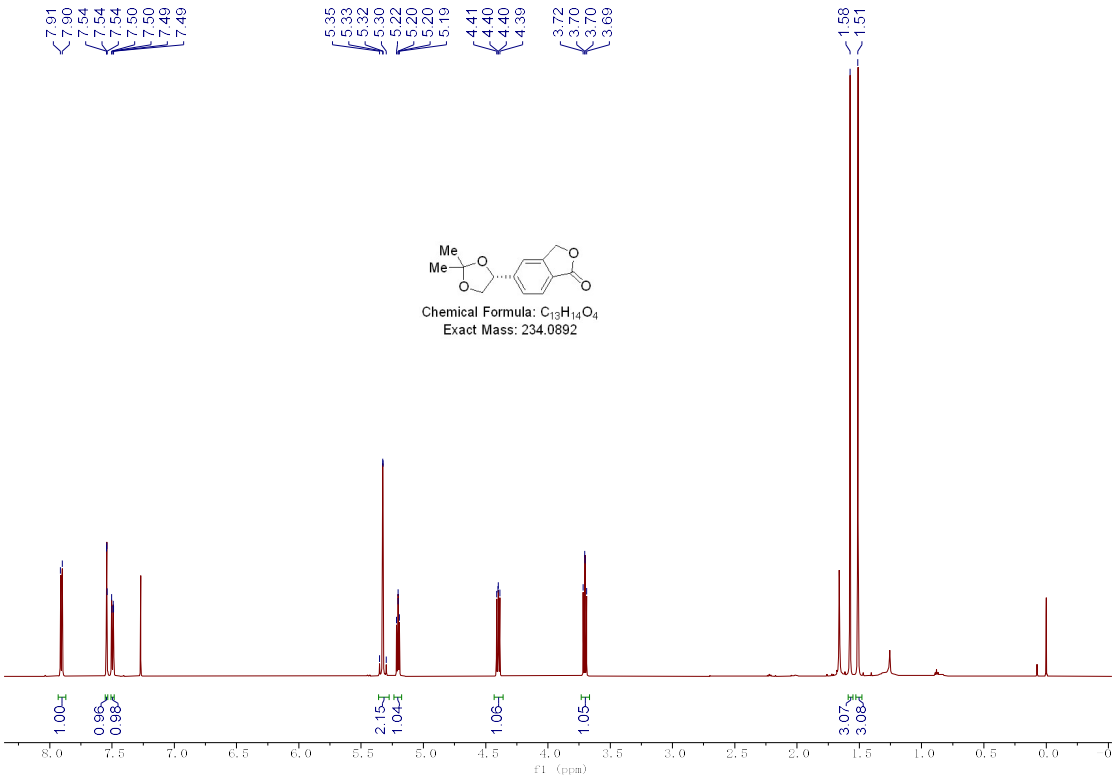
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of 3co



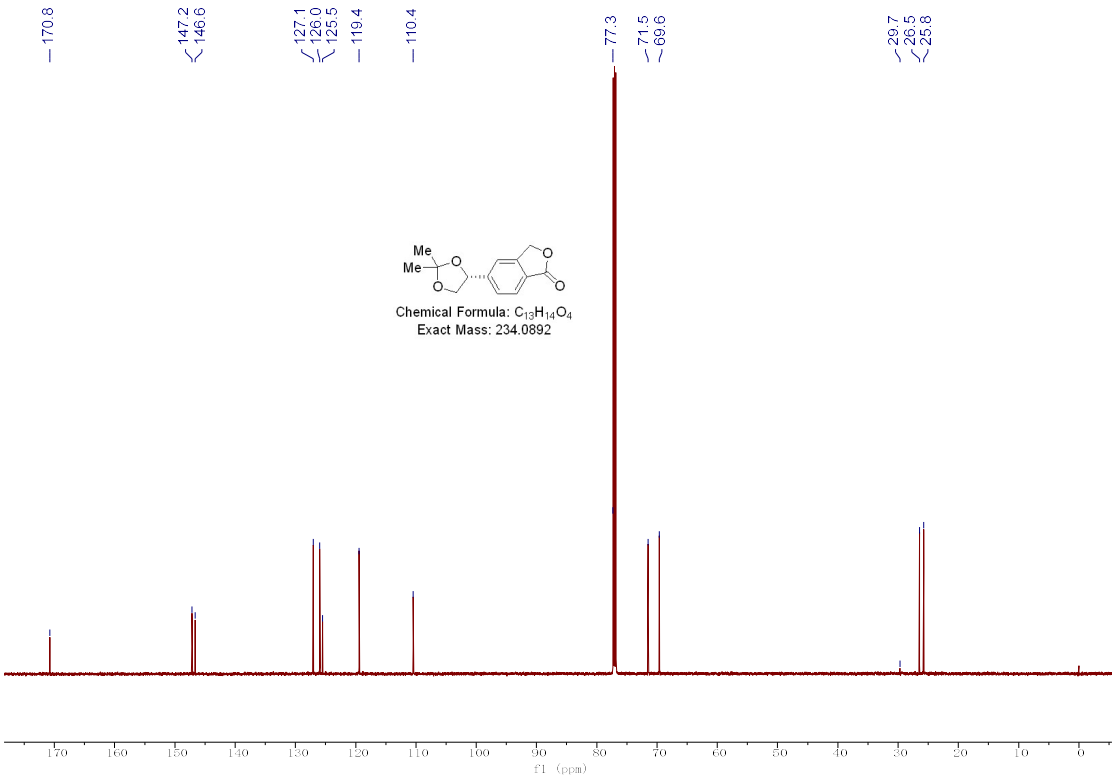
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cp



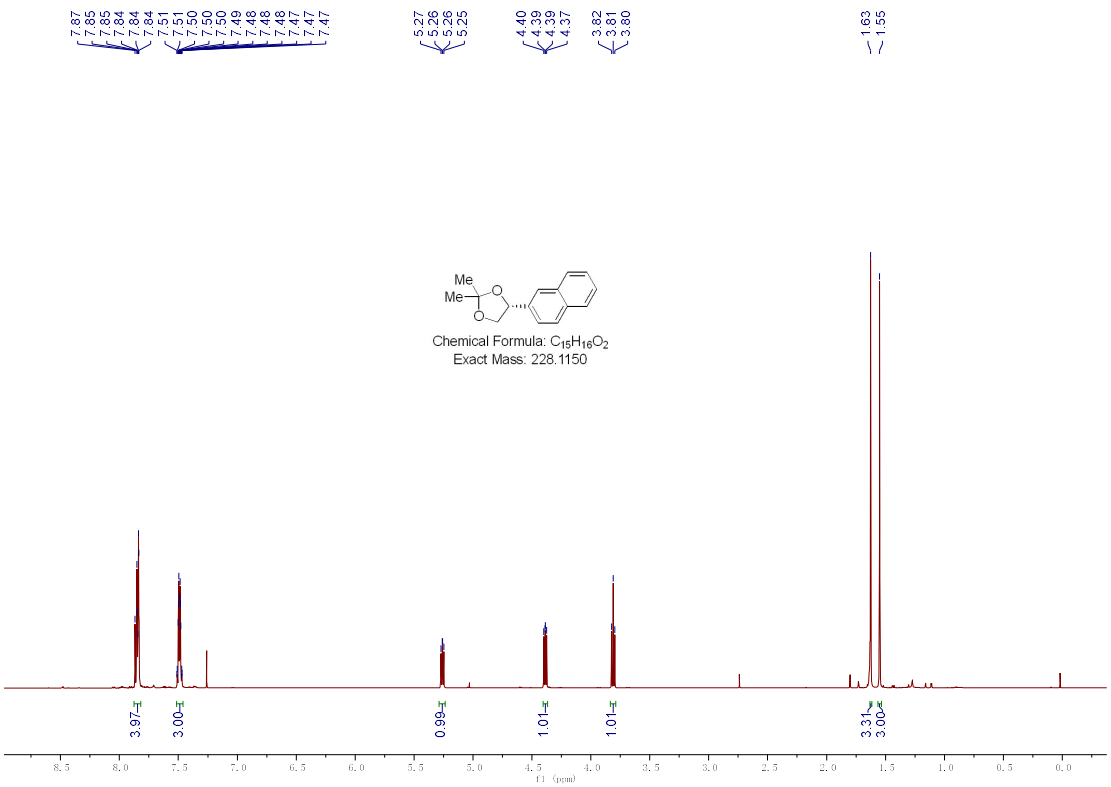
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cp



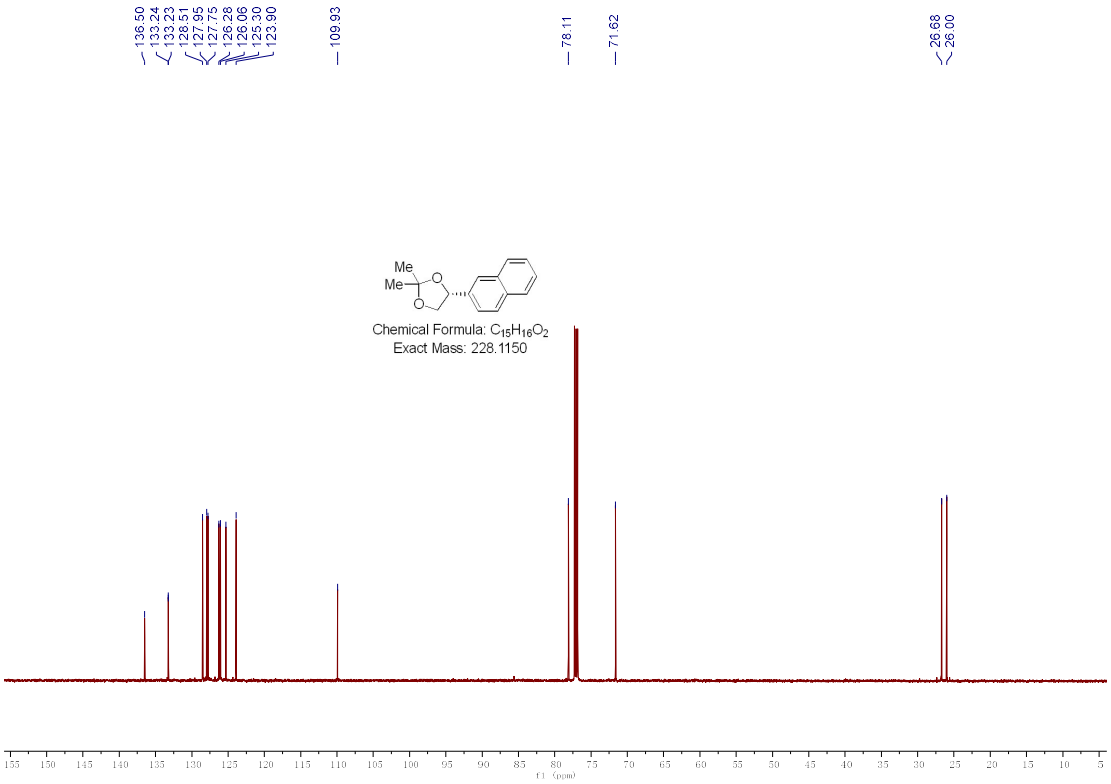
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cq



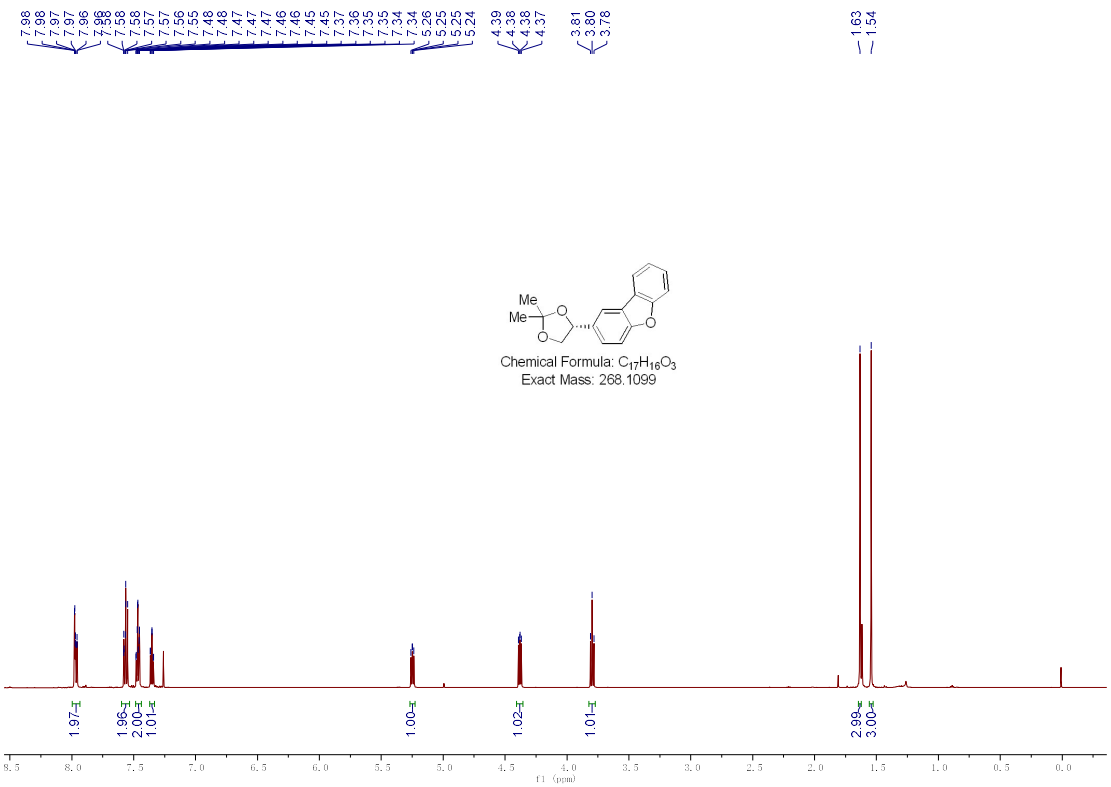
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cq



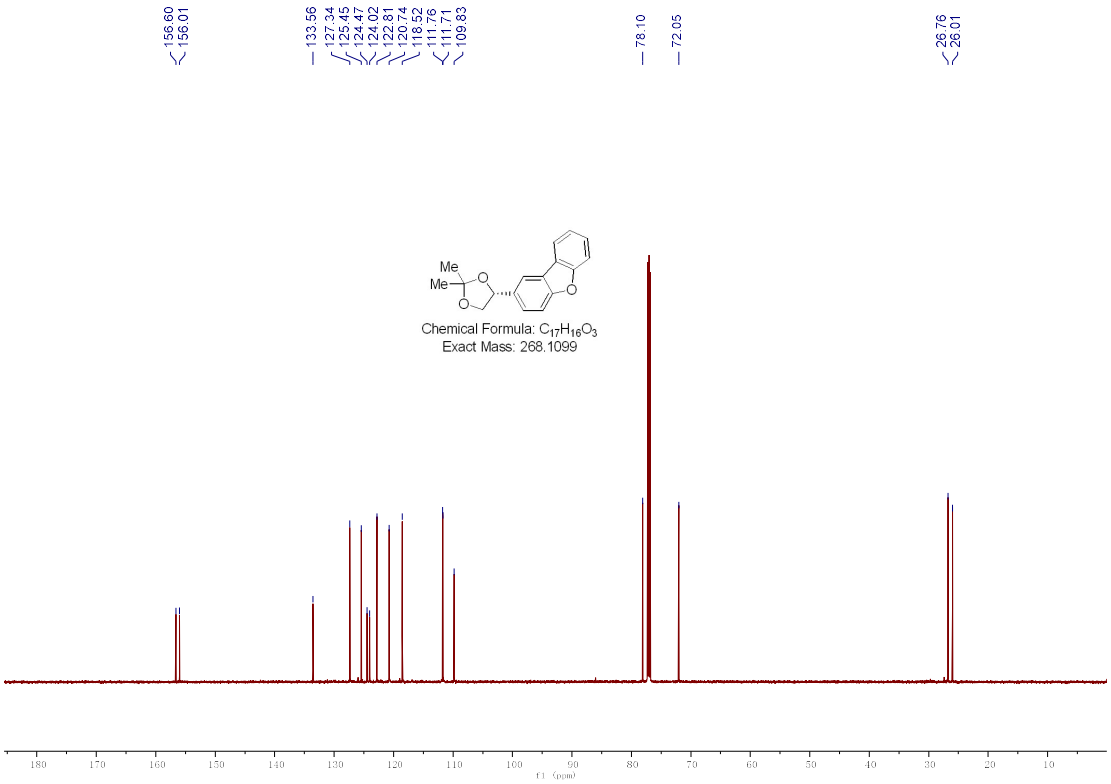
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cr



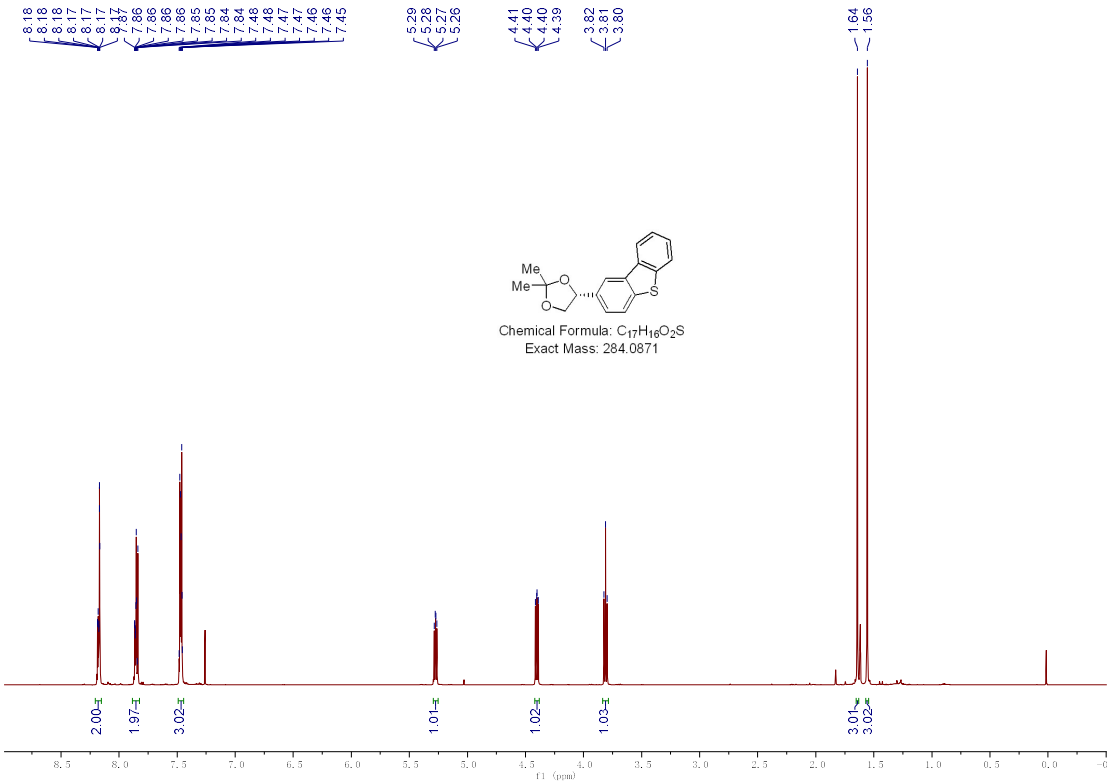
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cr



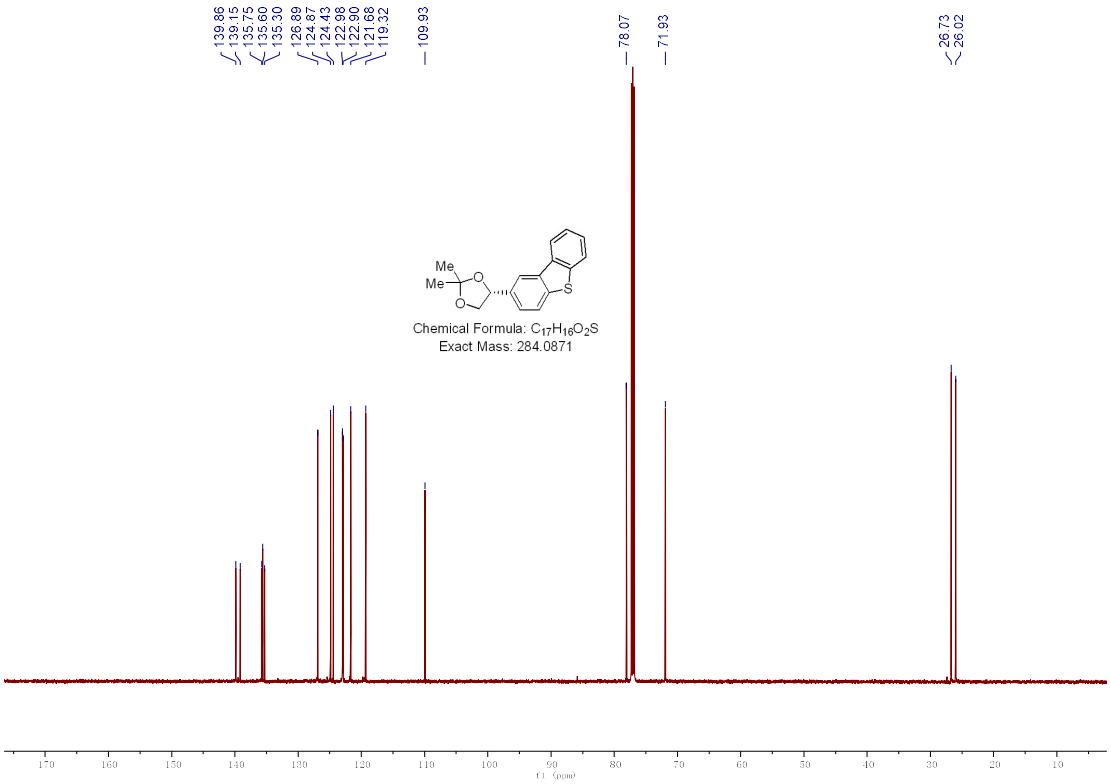
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cs



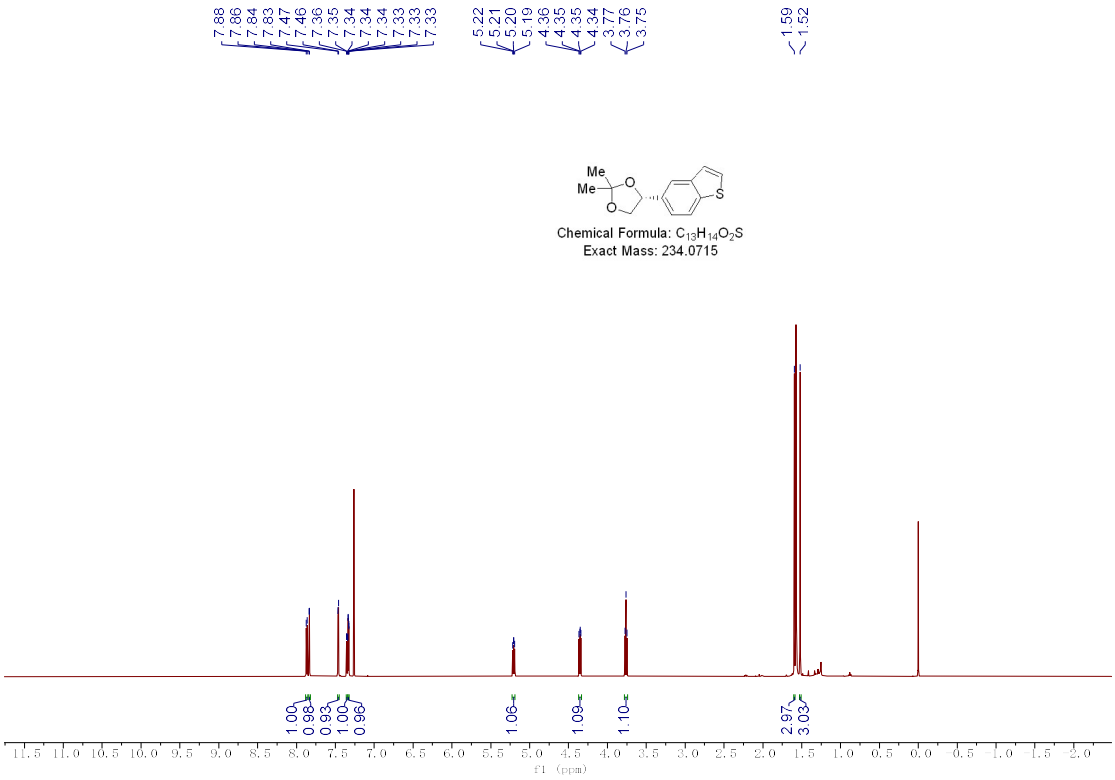
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cs



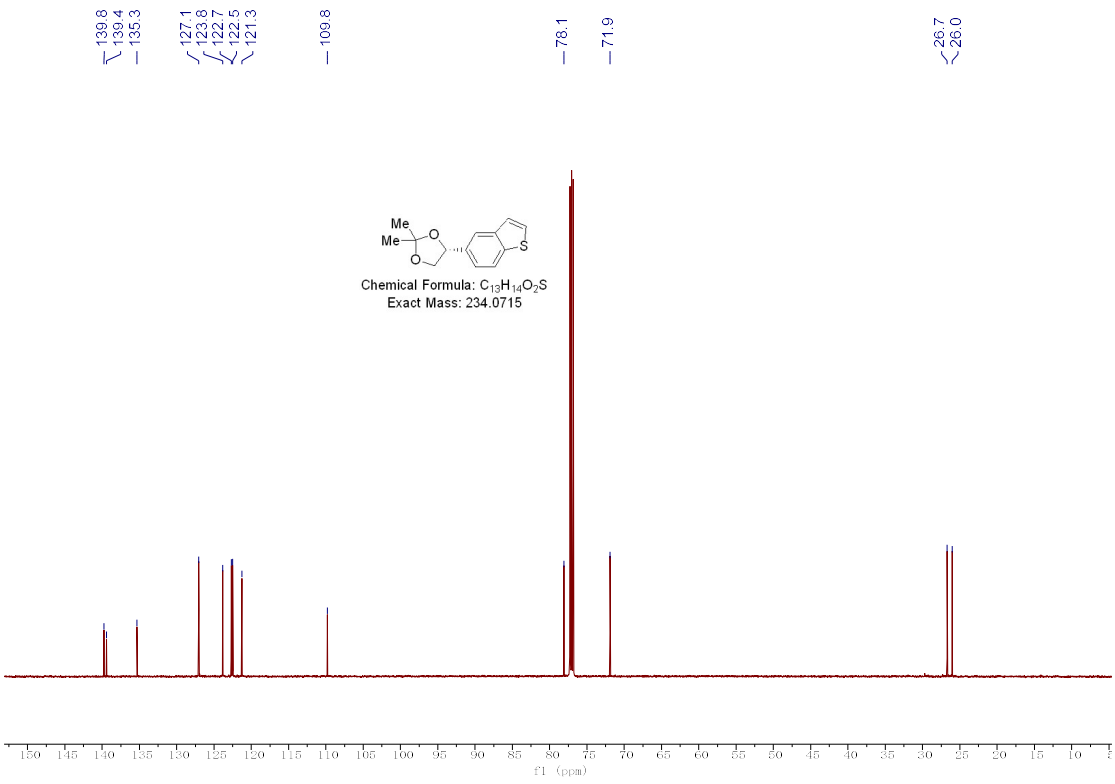
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3ct



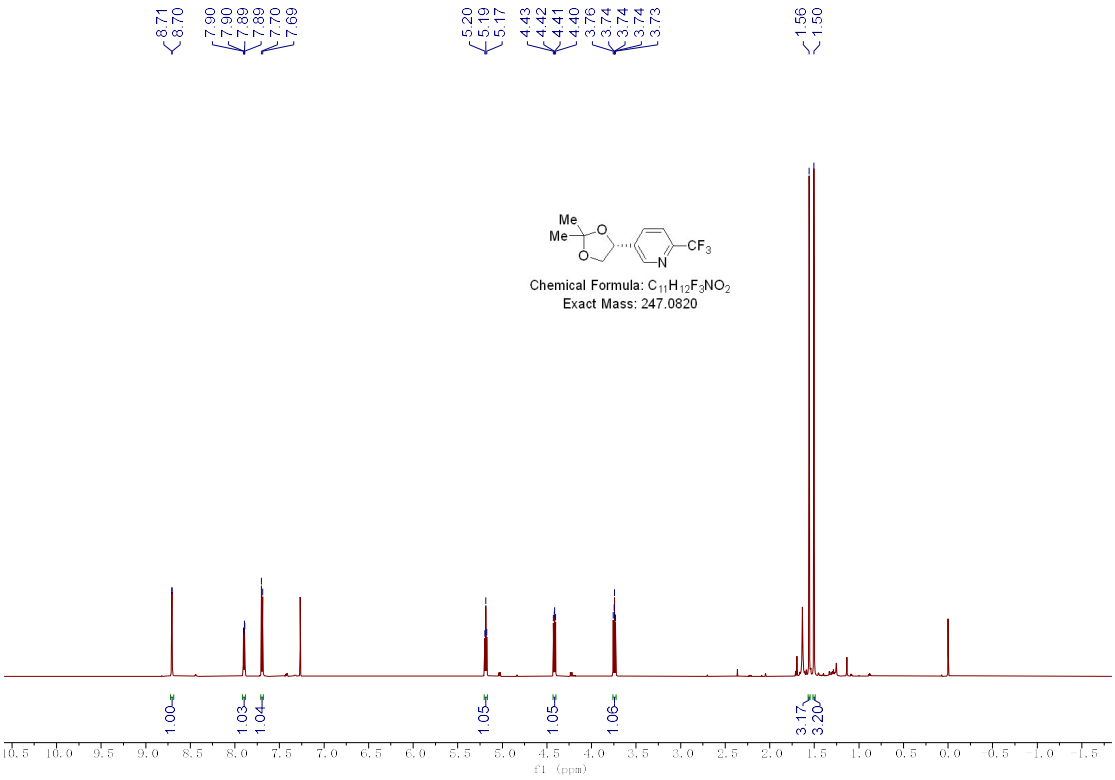
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cT



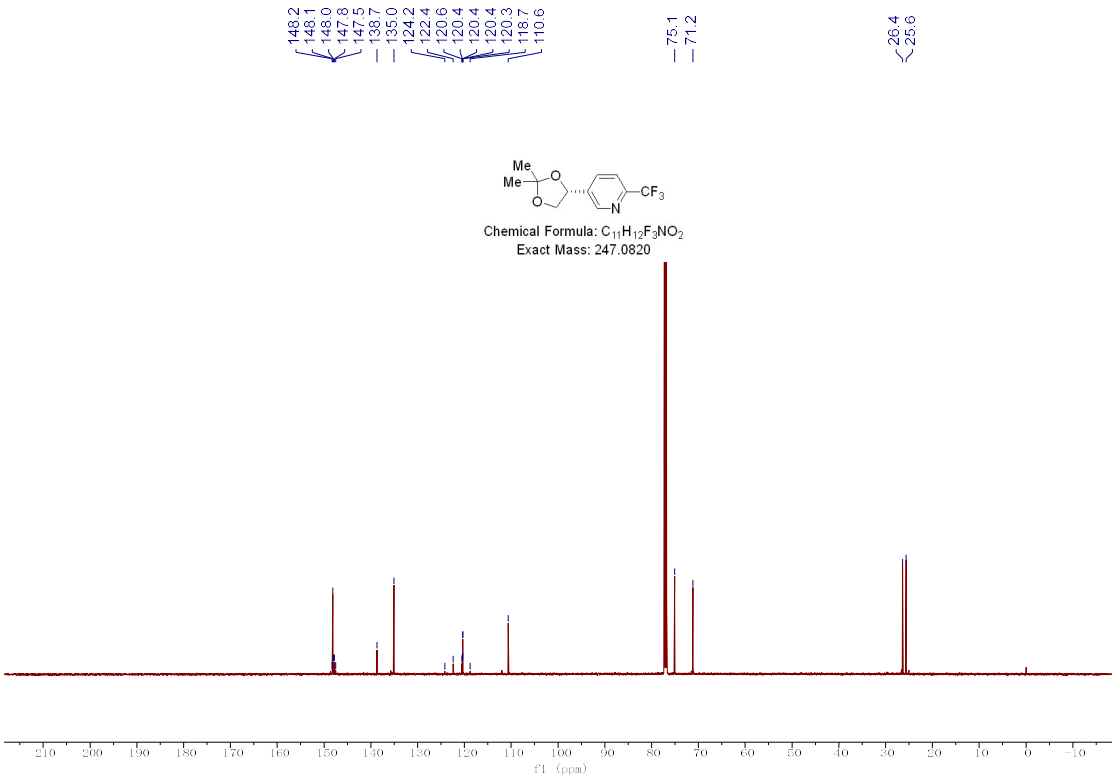
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cu



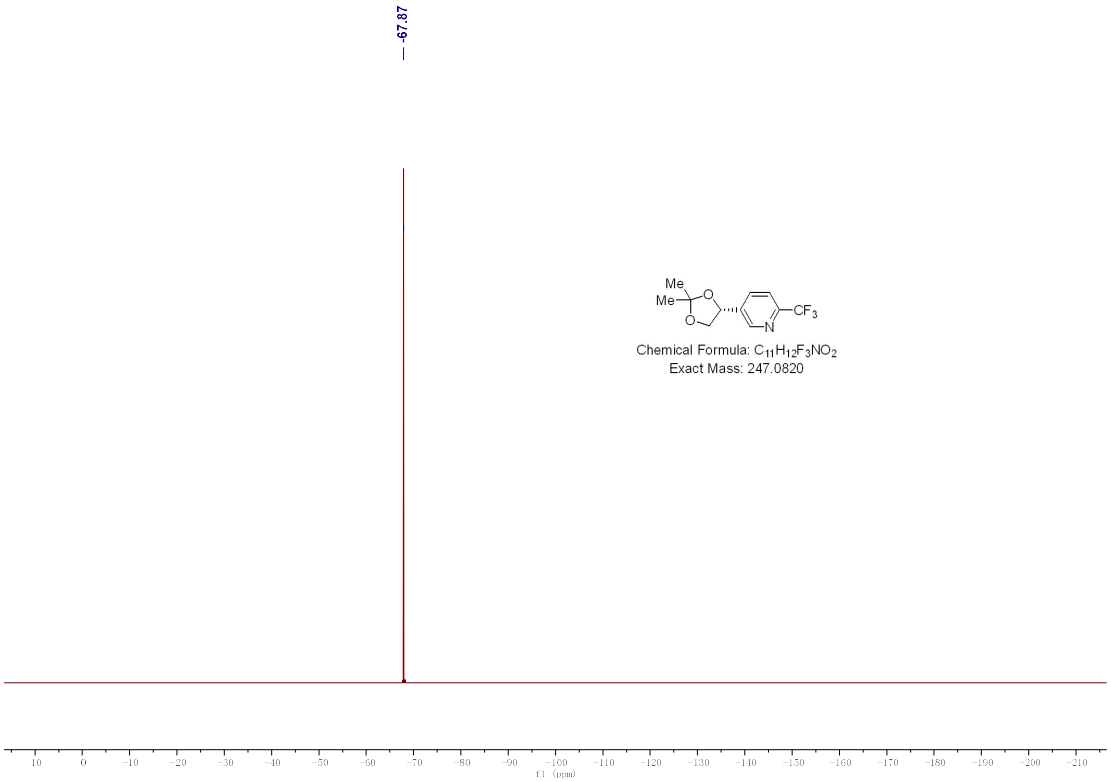
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cu



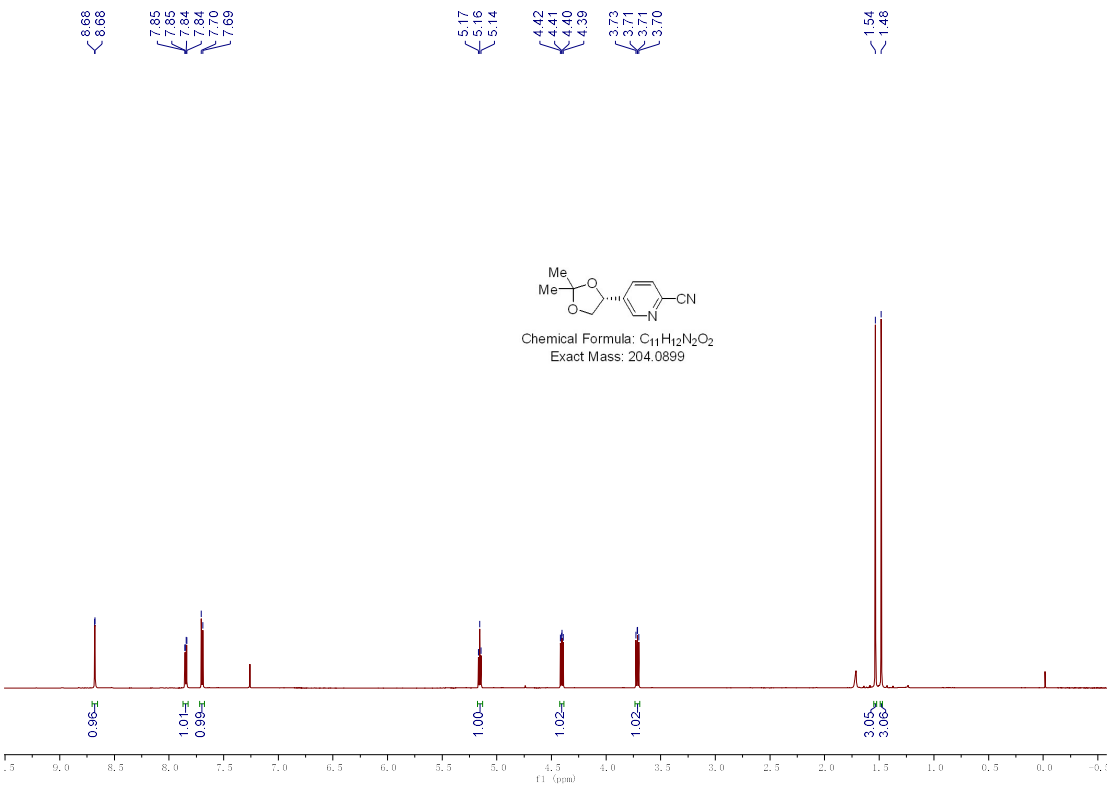
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cv



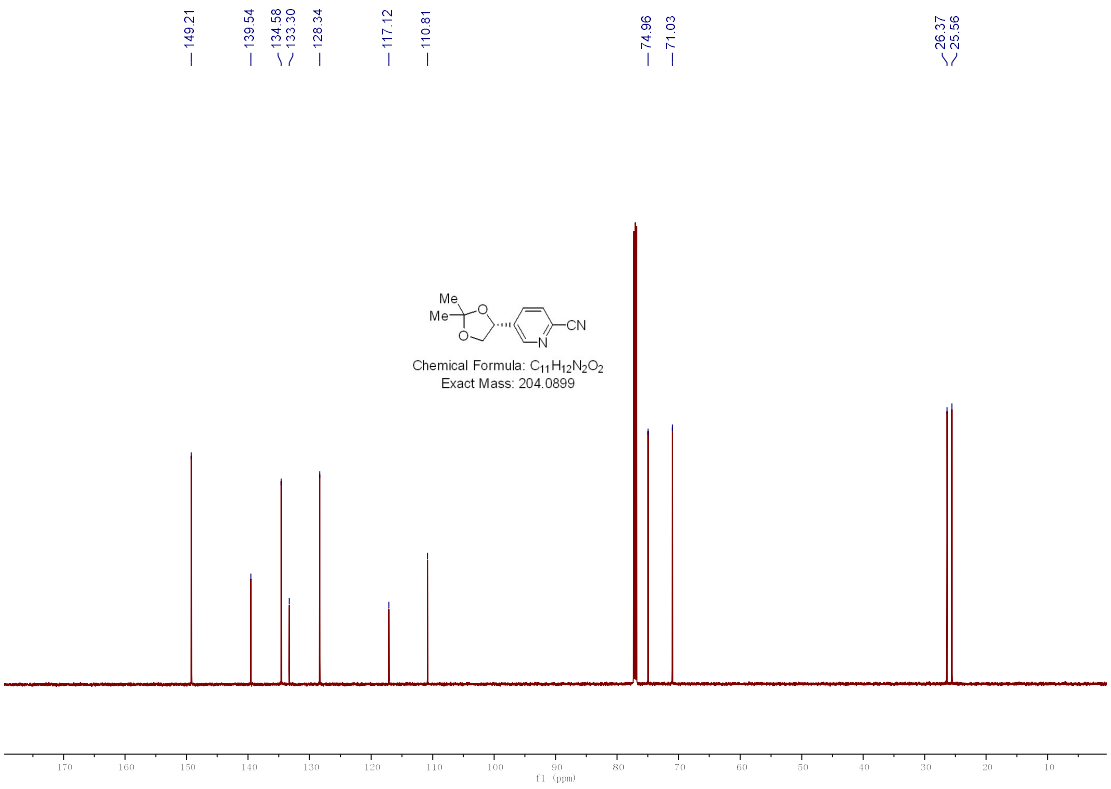
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cv



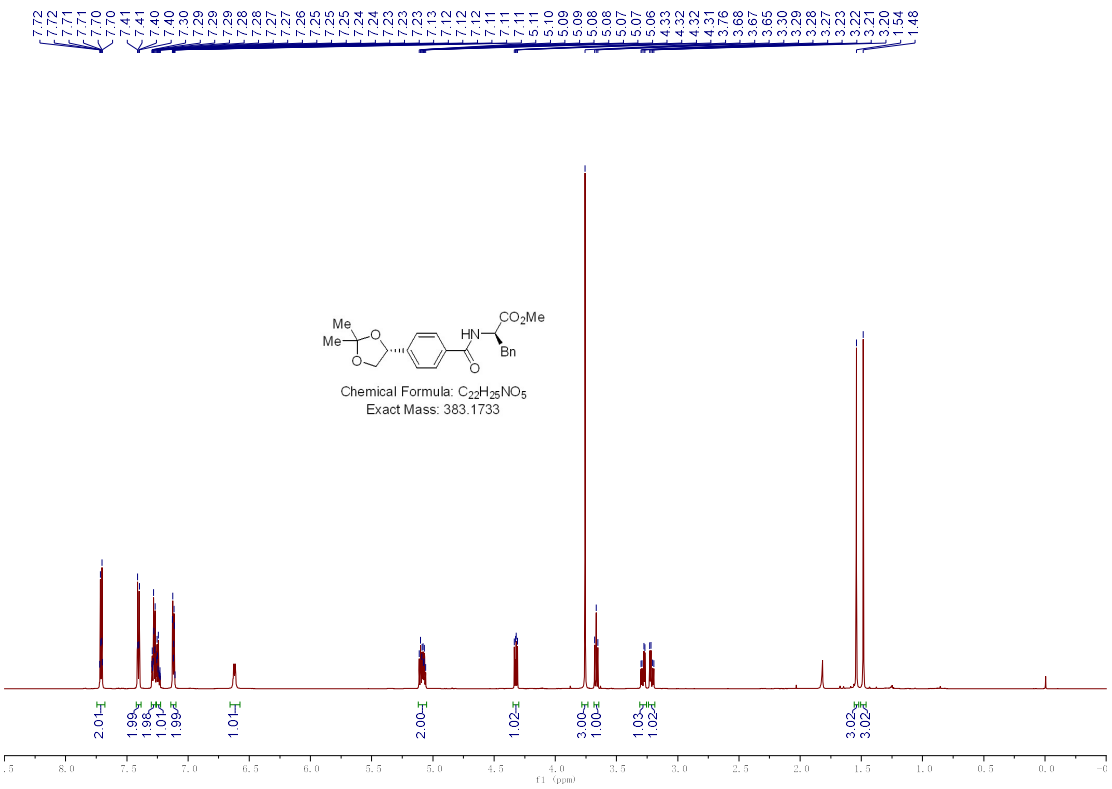
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of 3cv



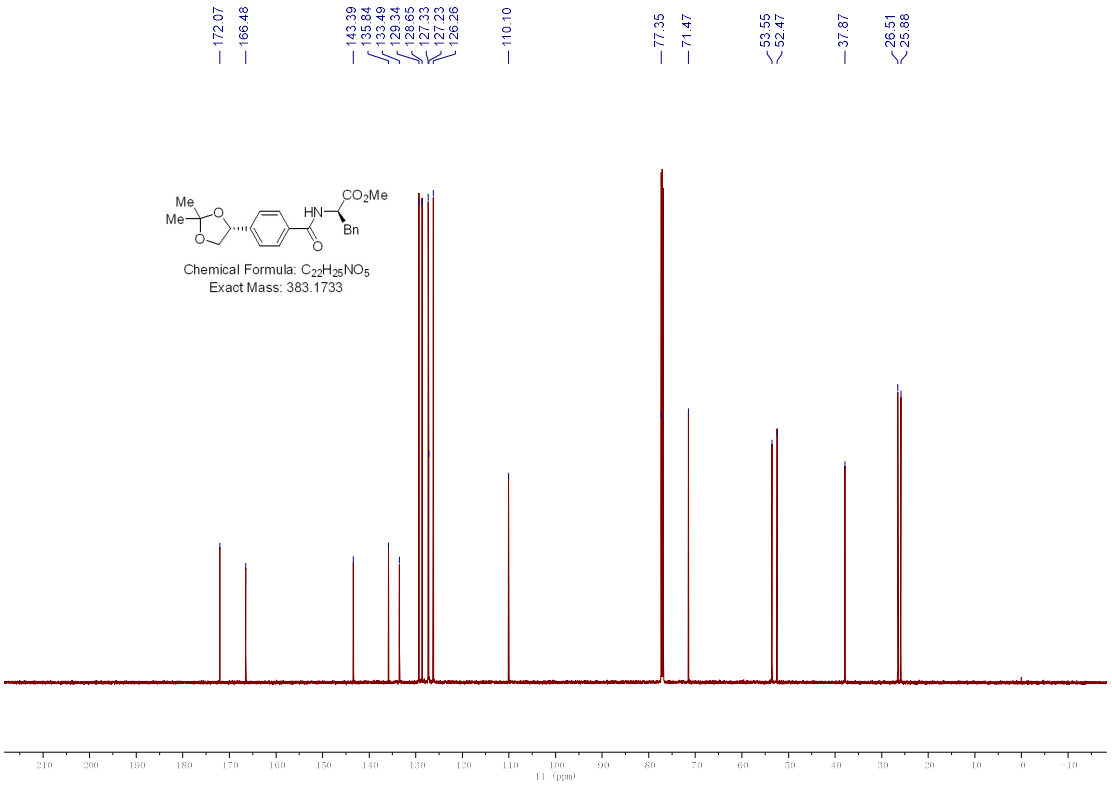
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cw



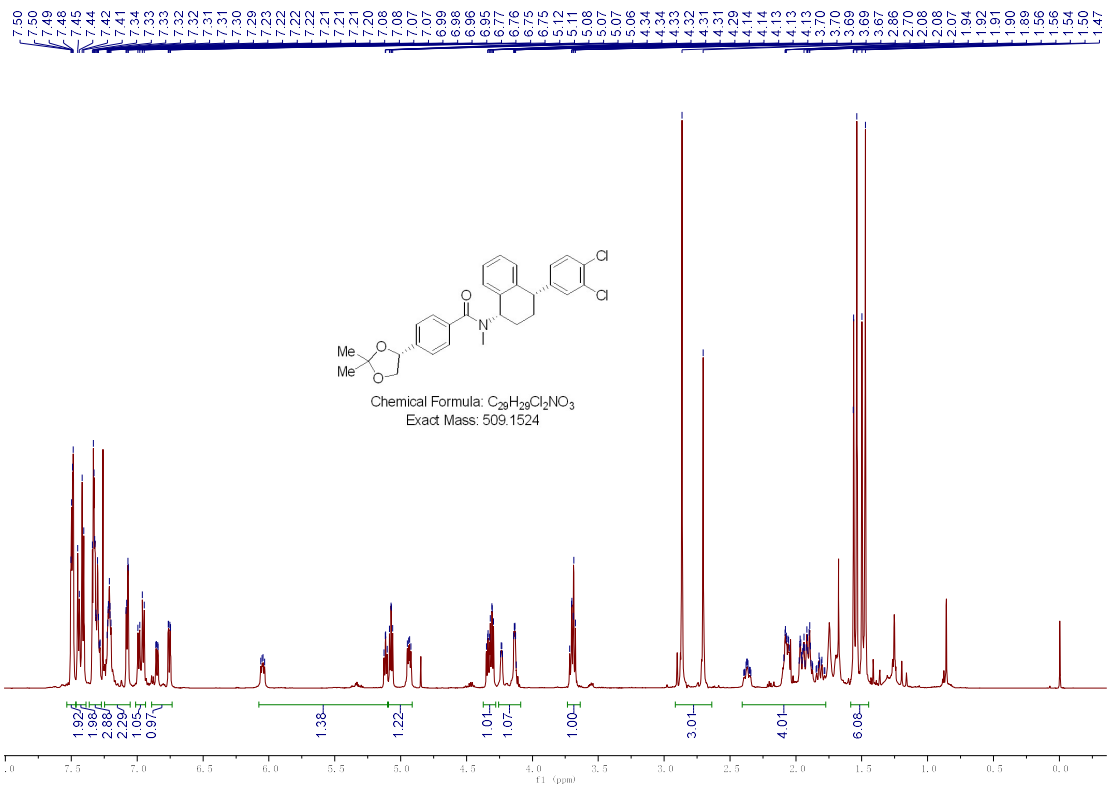
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cw



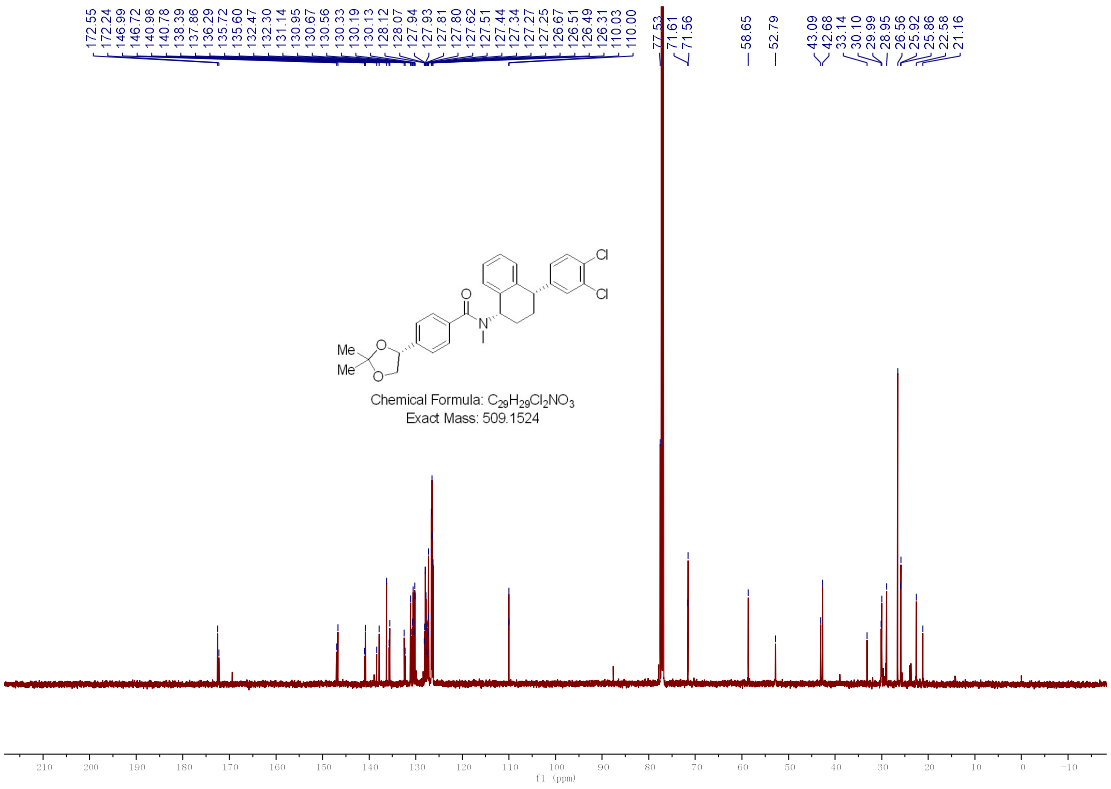
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cx



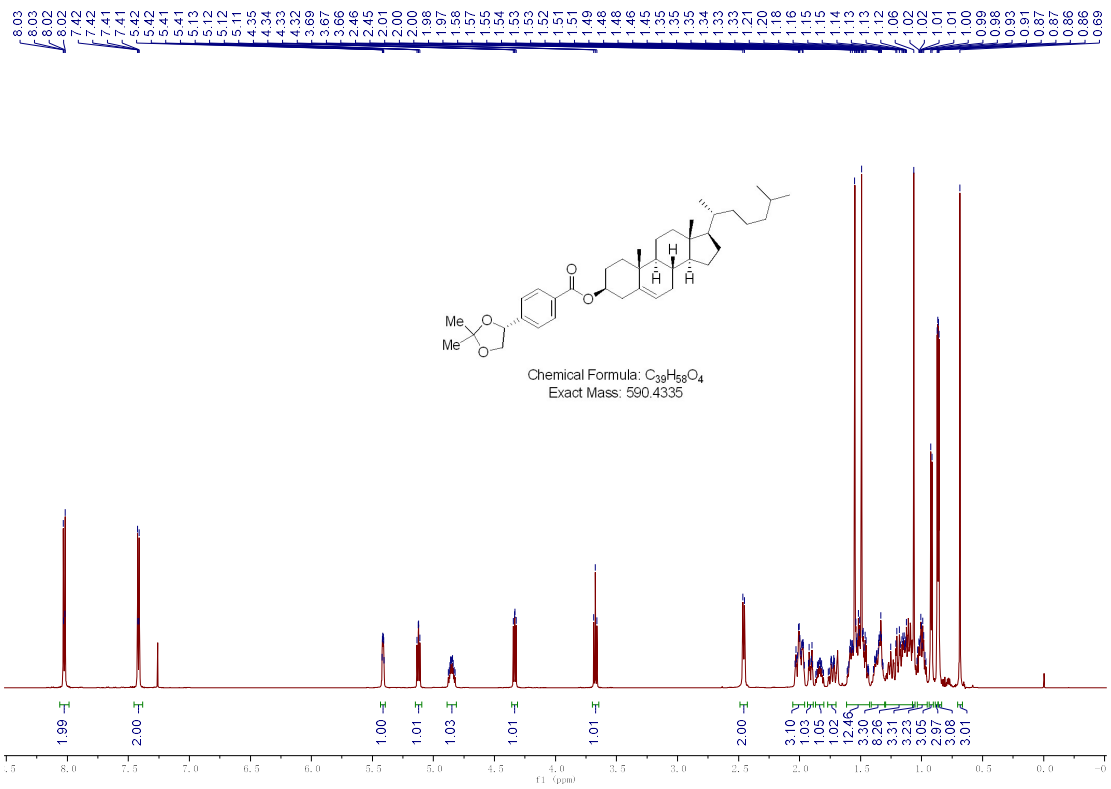
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cx



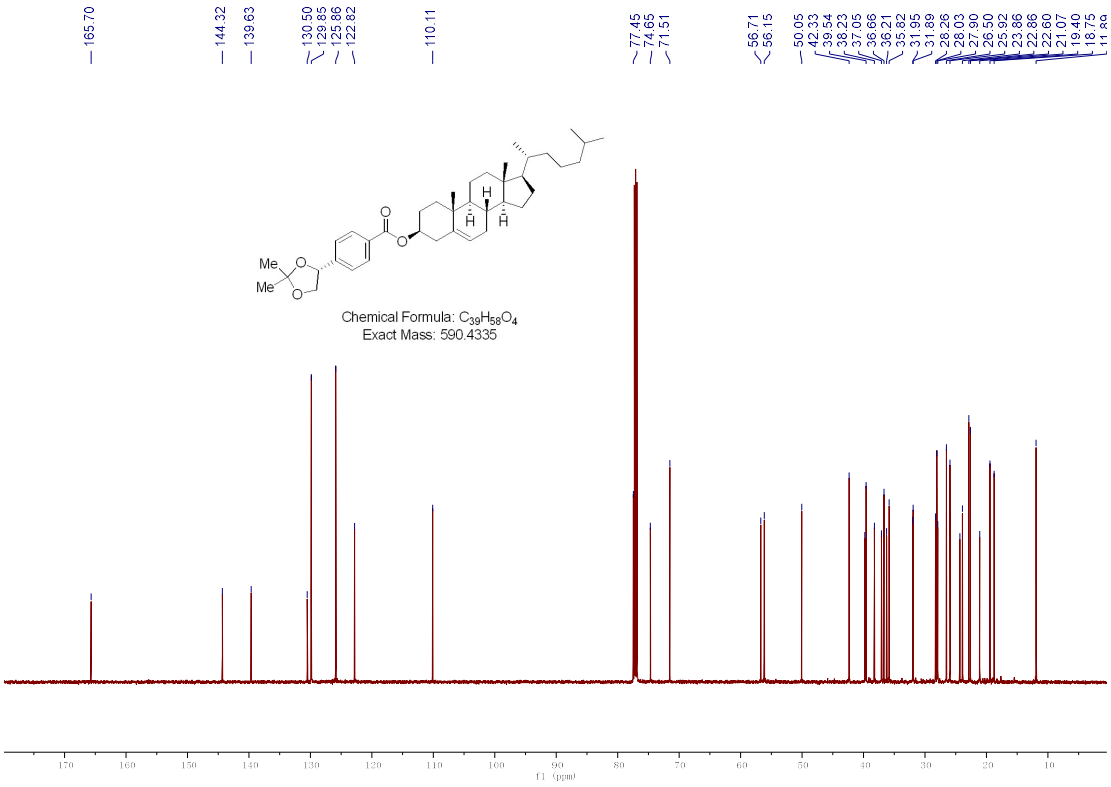
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cy



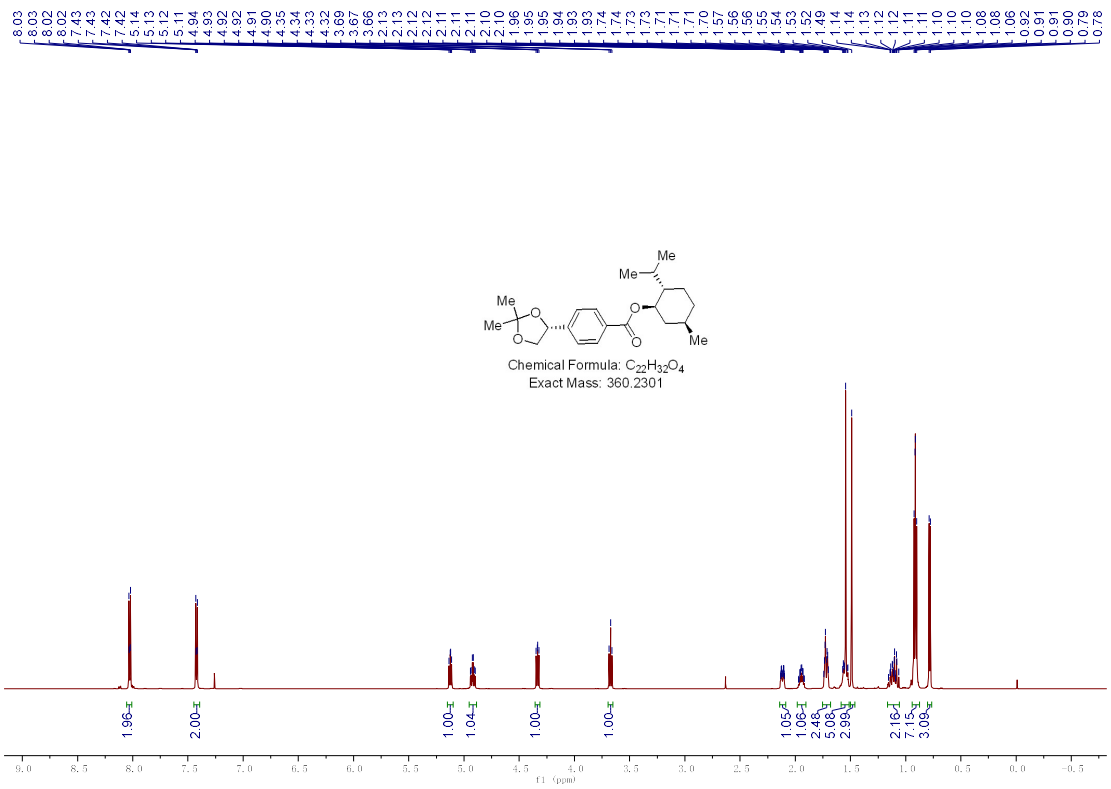
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cy



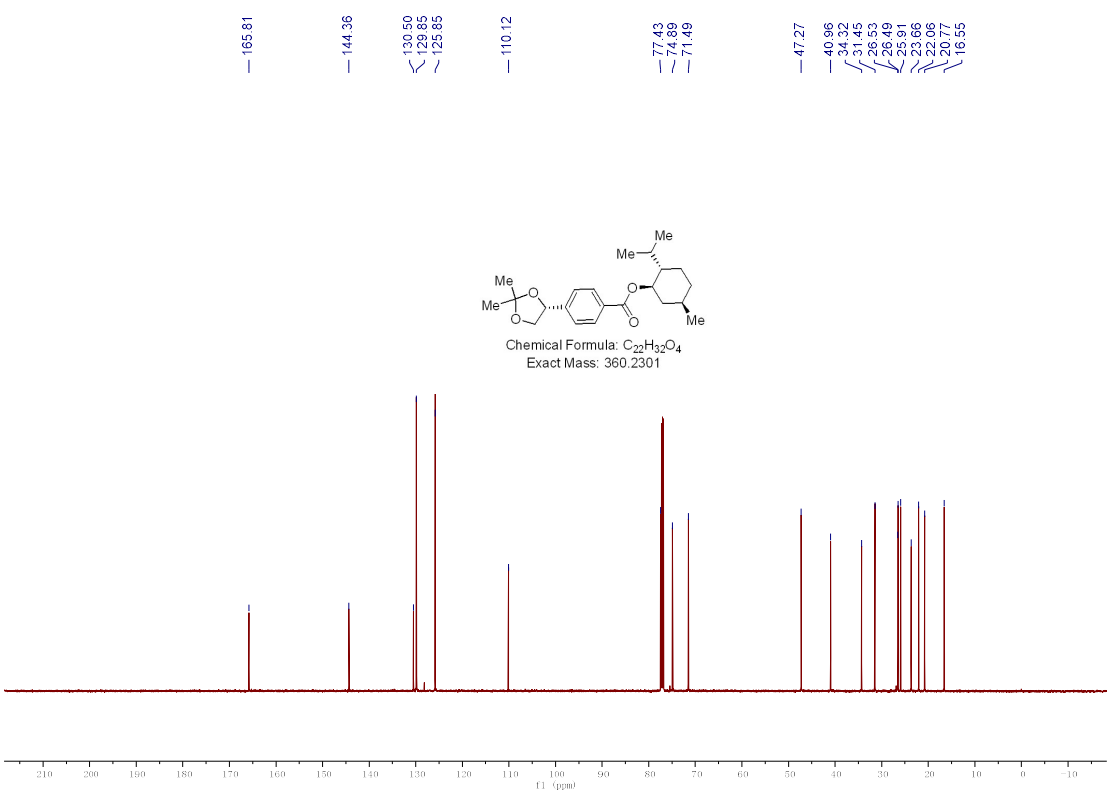
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cz



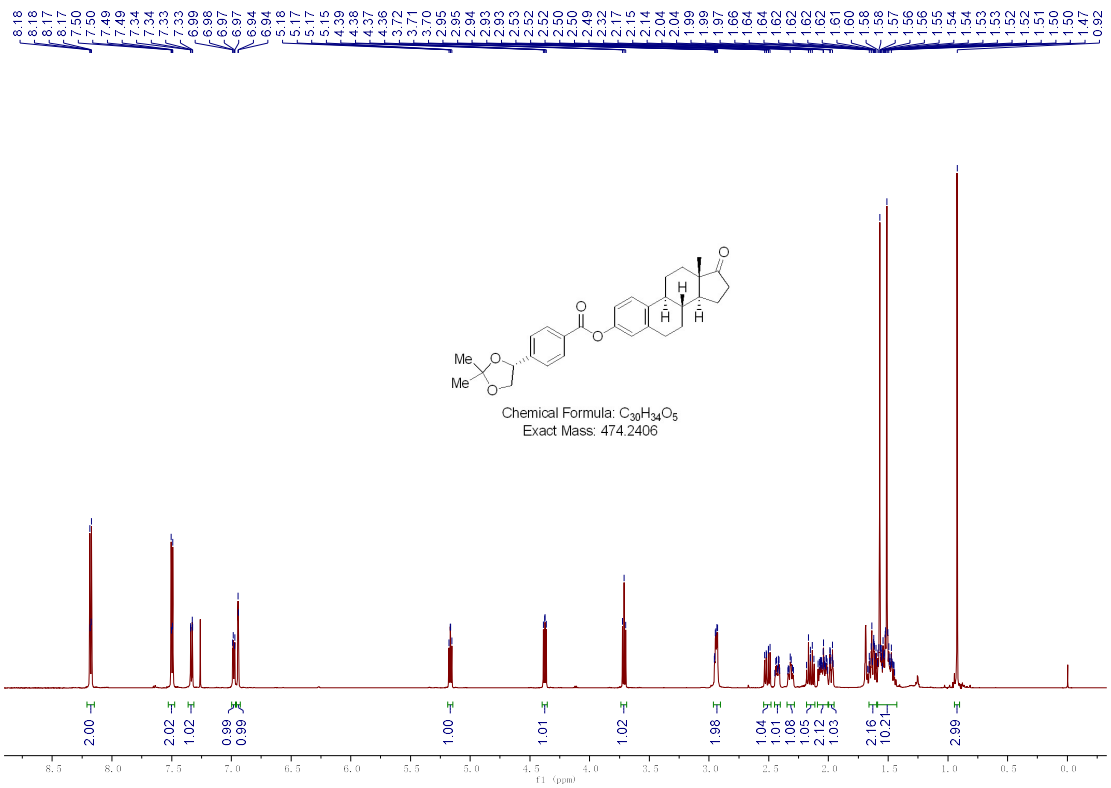
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cz



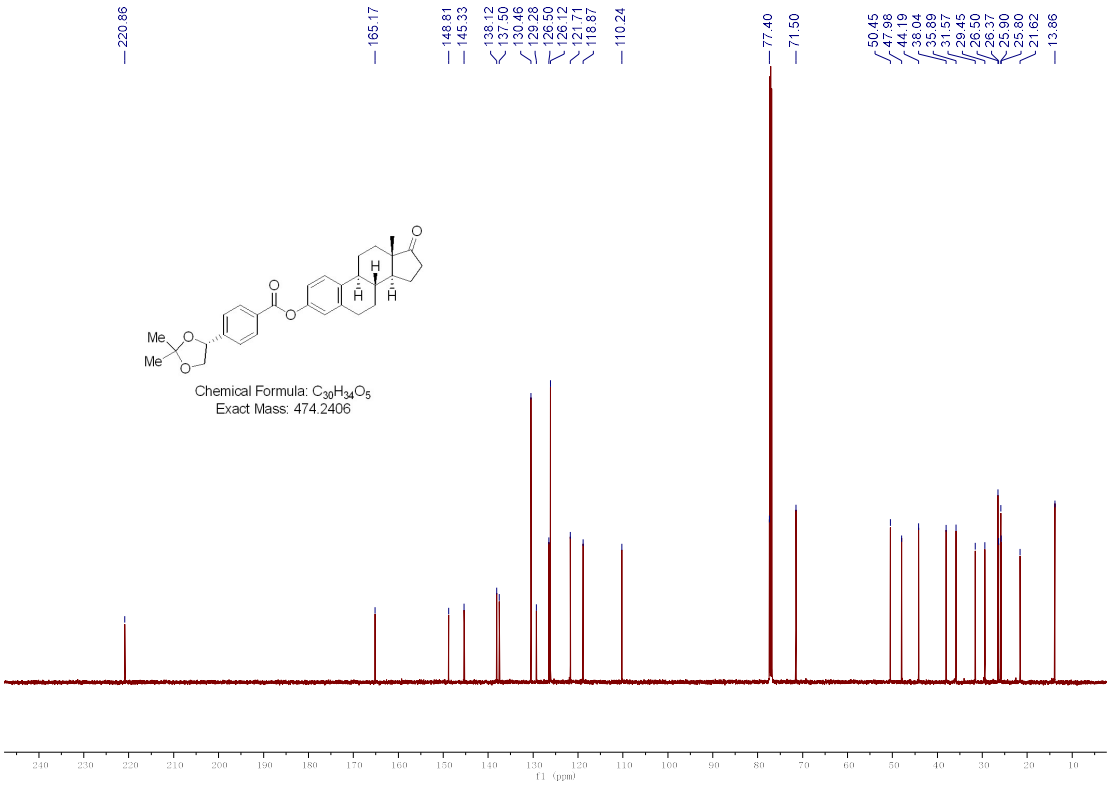
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3caa



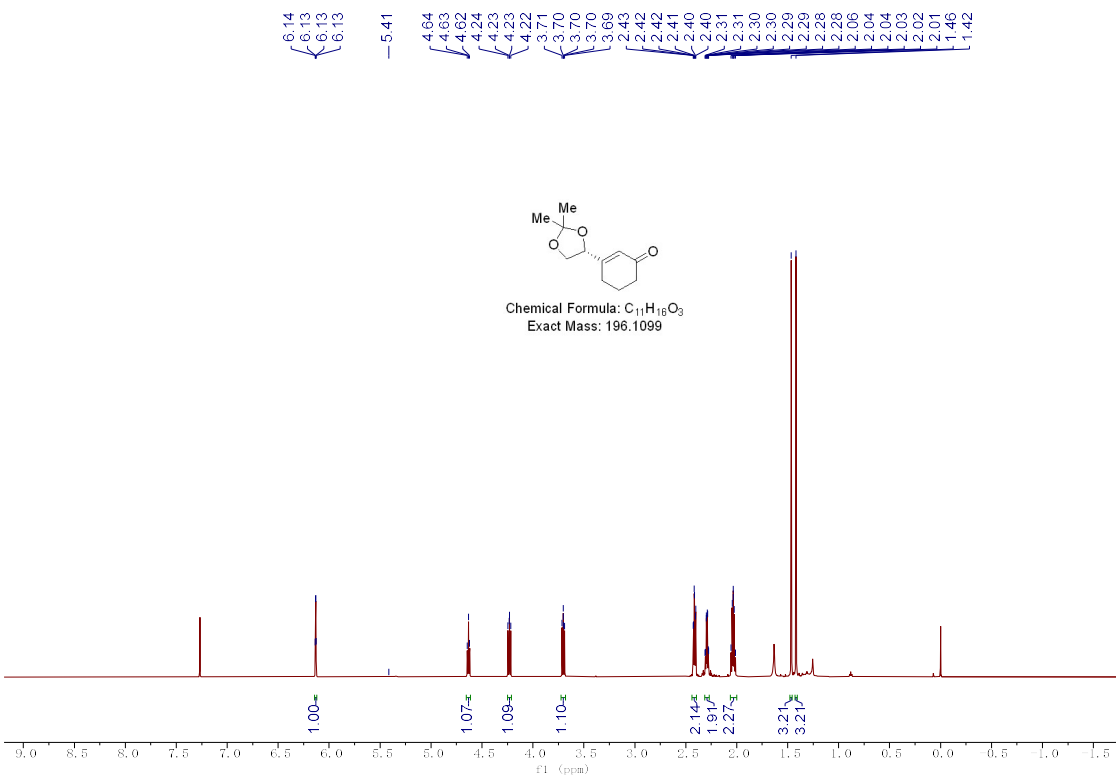
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3caa



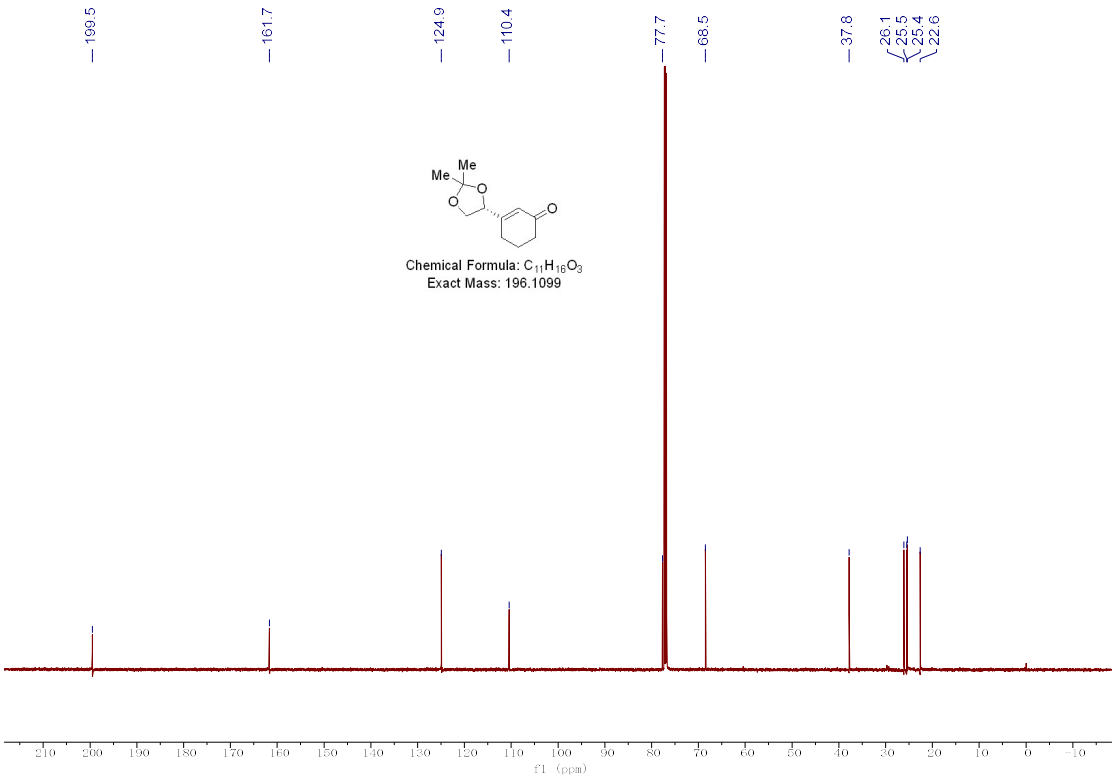
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cb



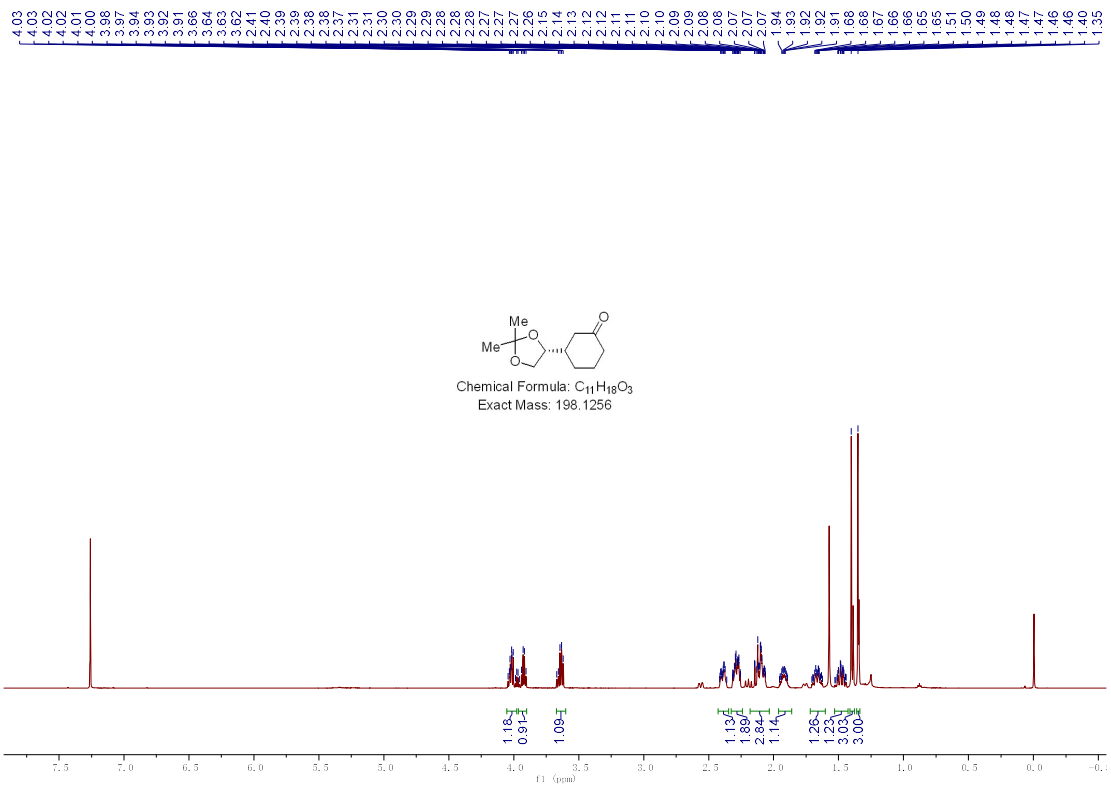
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cab



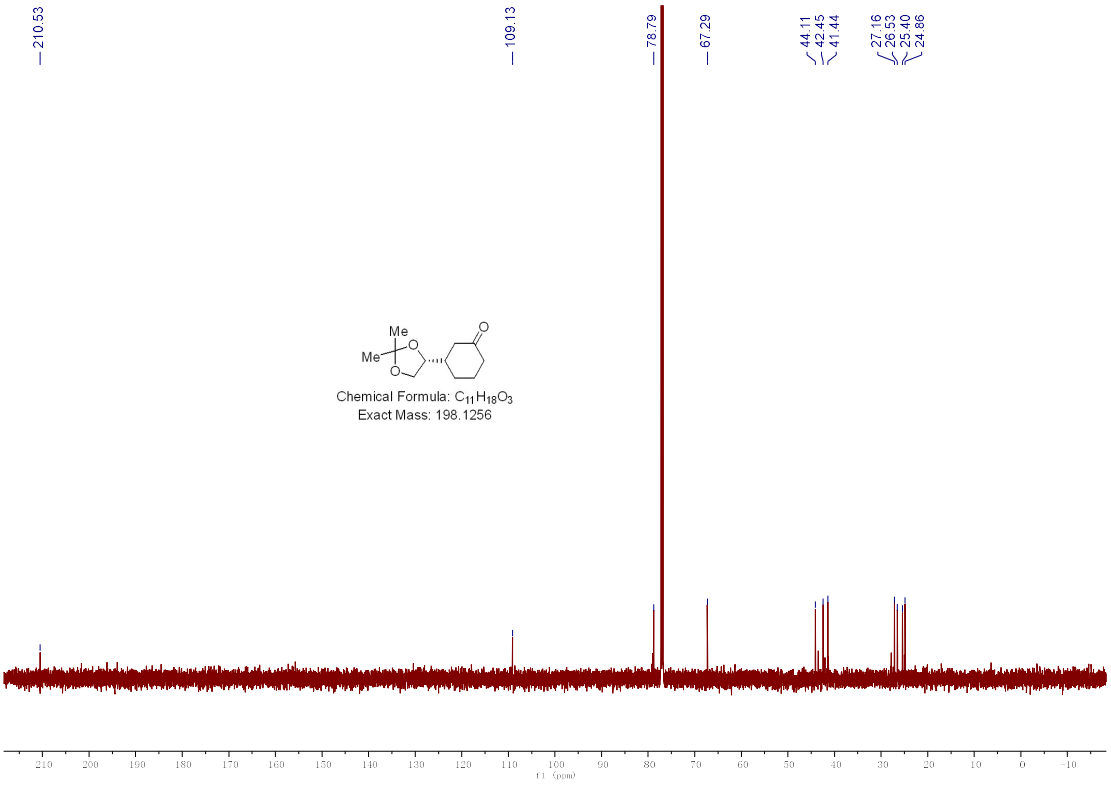
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cac



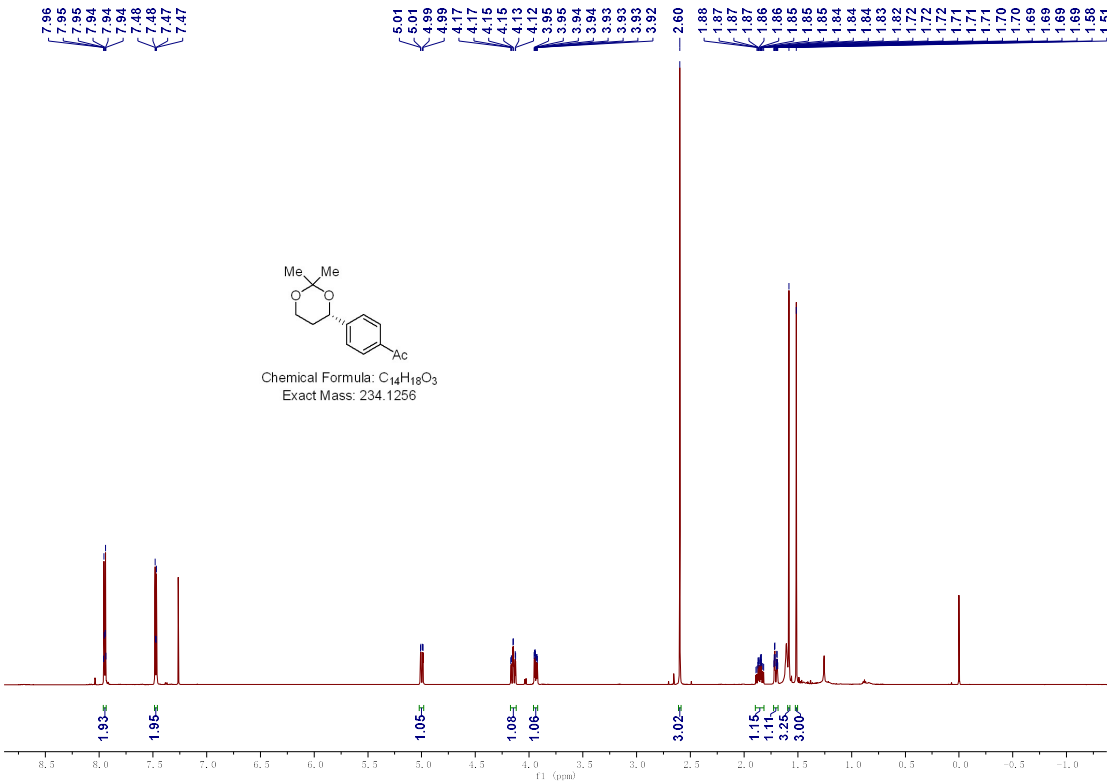
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cac



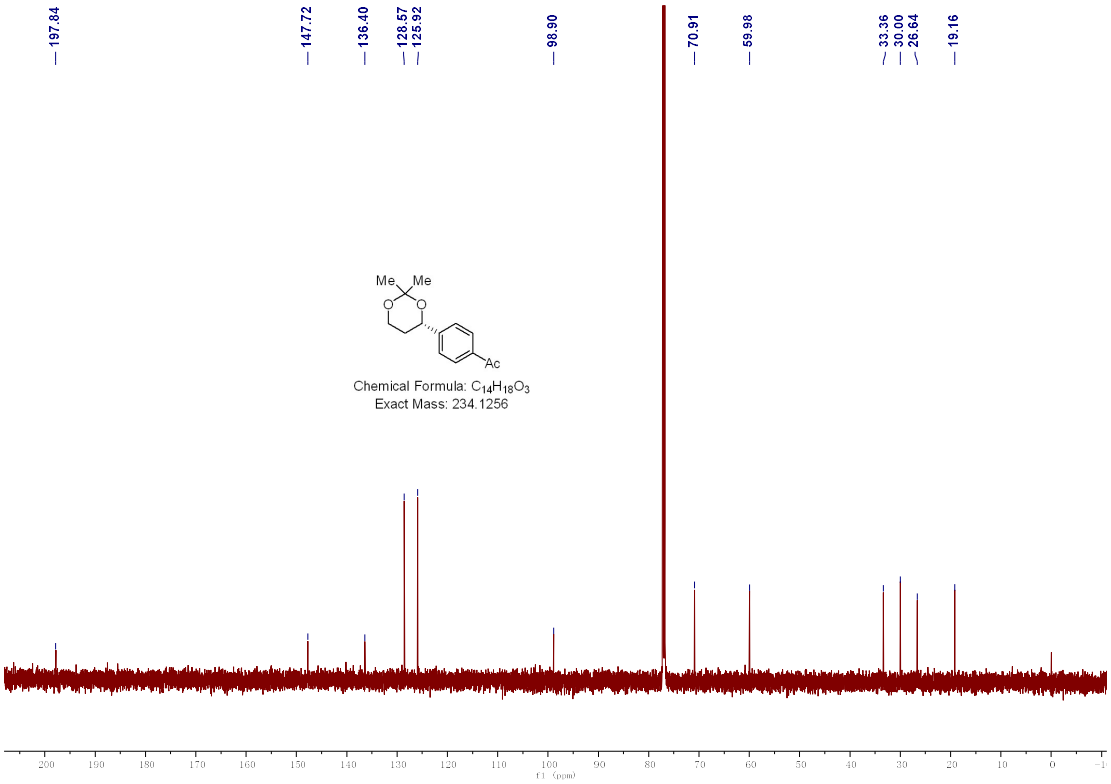
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 3cad



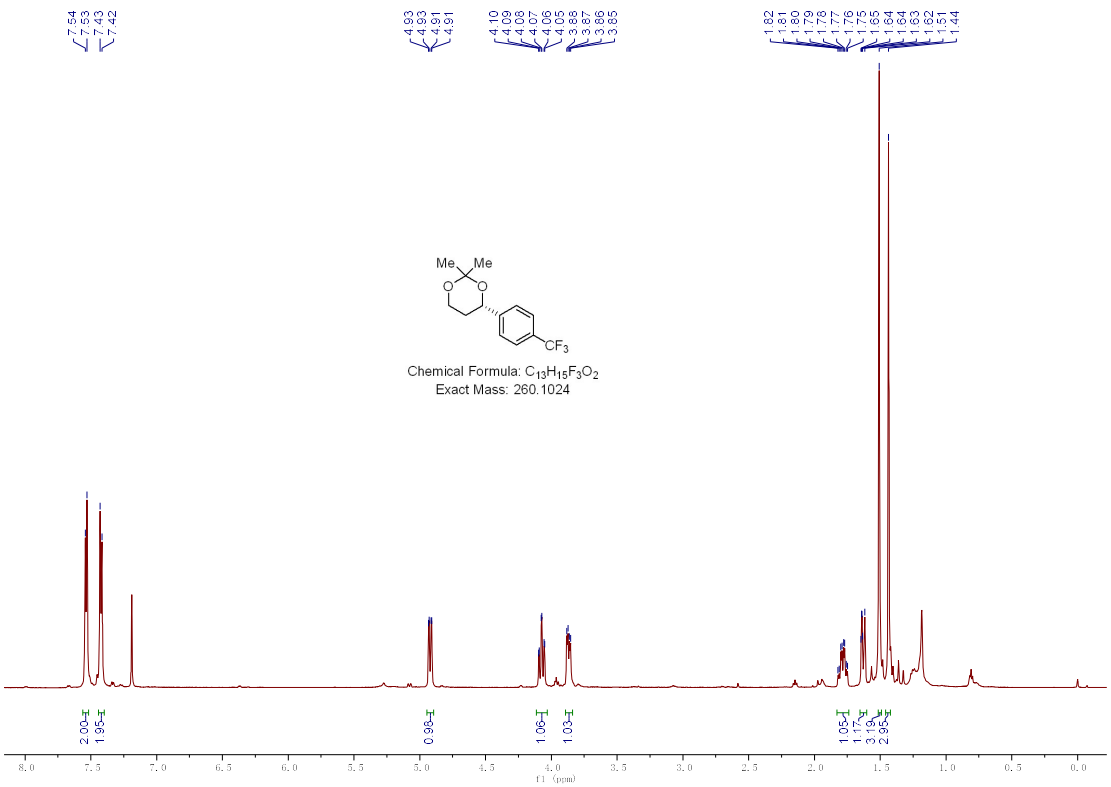
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 3cad



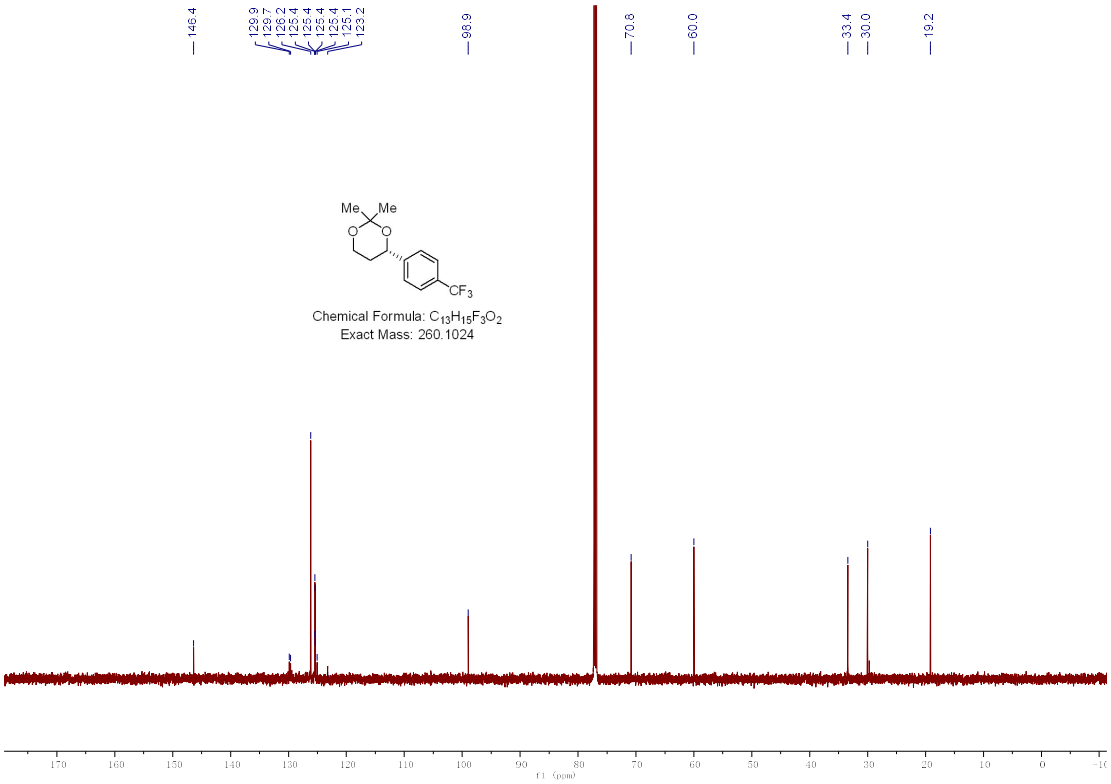
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5aa



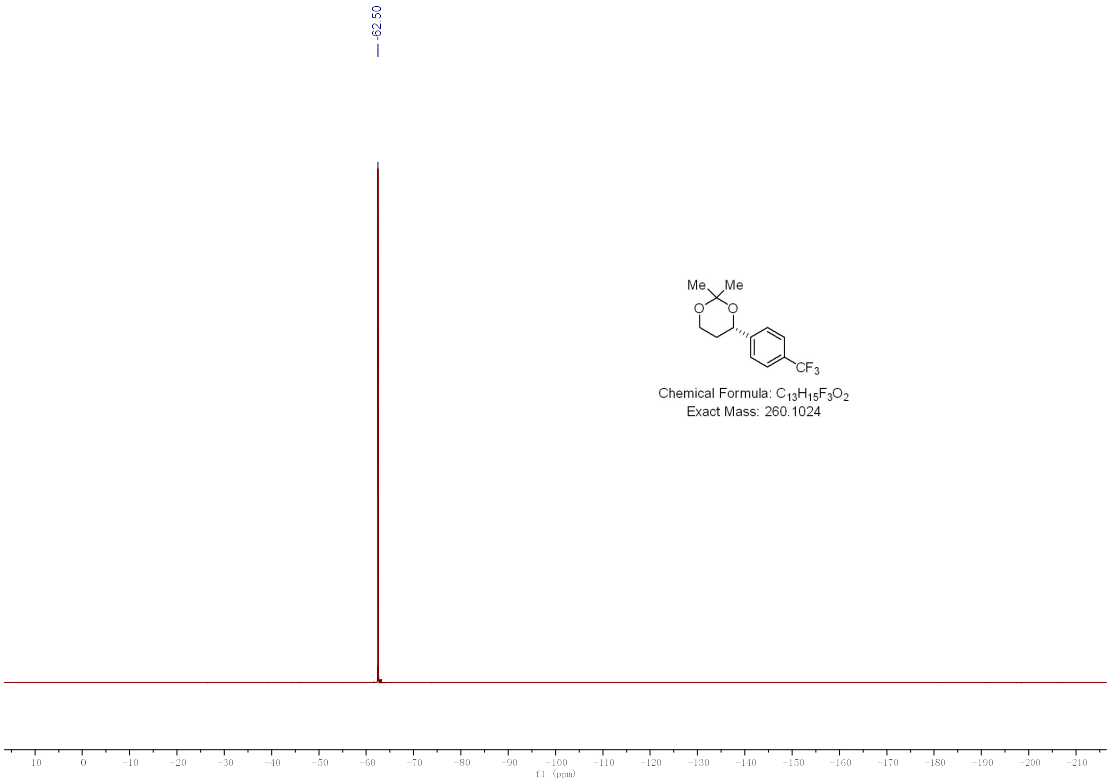
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5aa



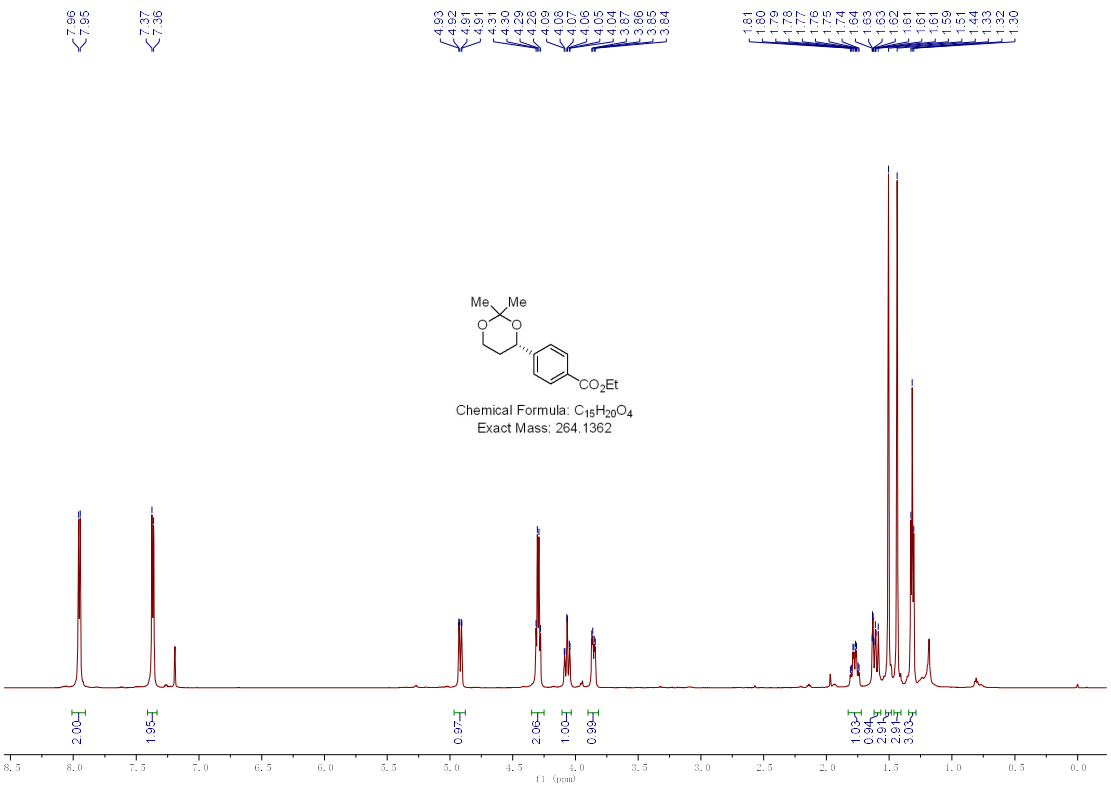
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5ac



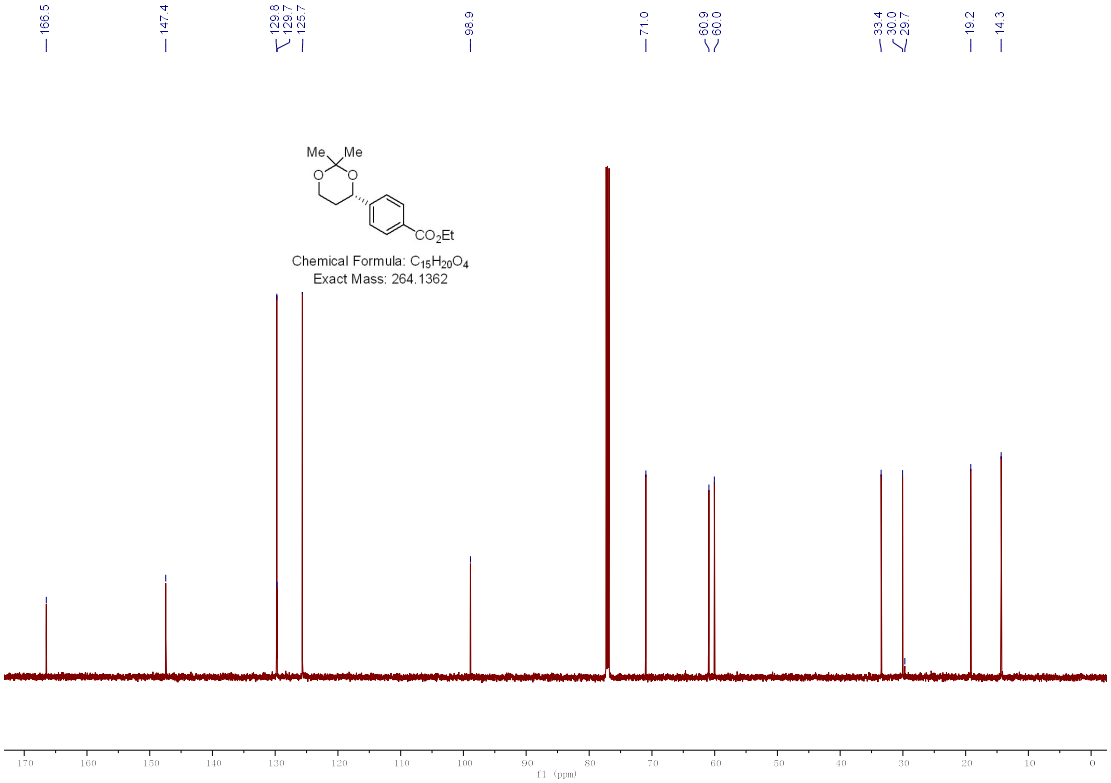
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5ac



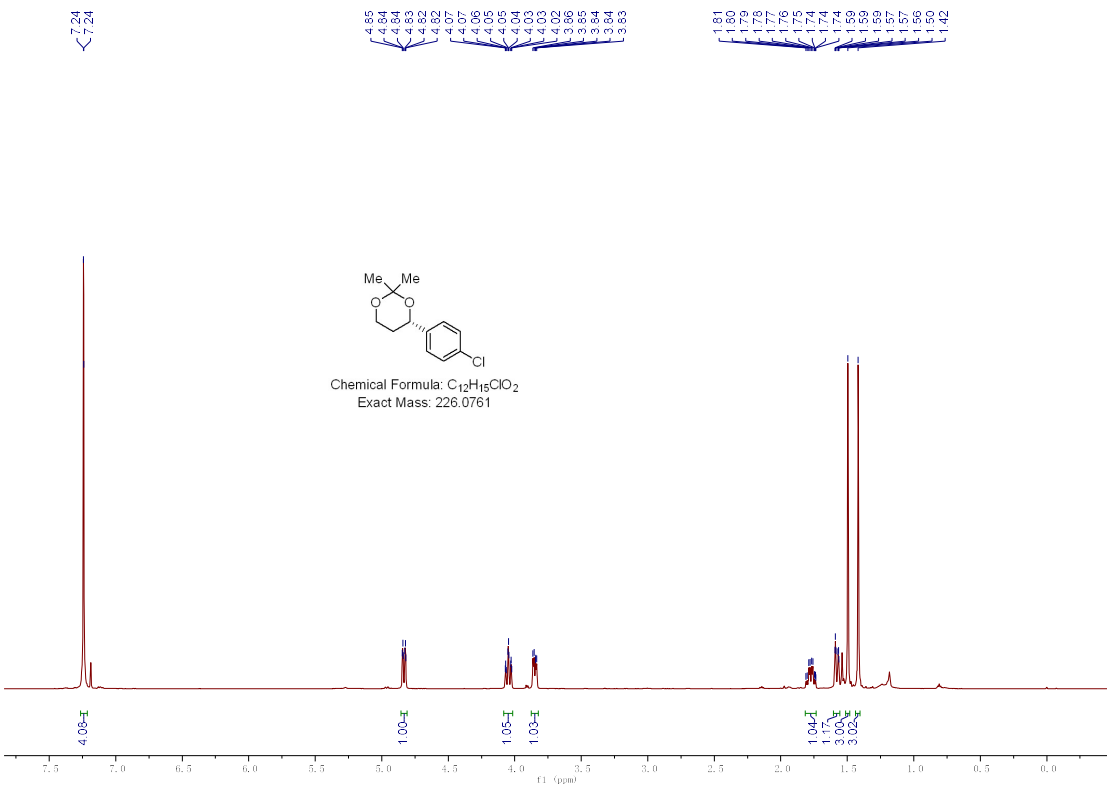
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of 5ac



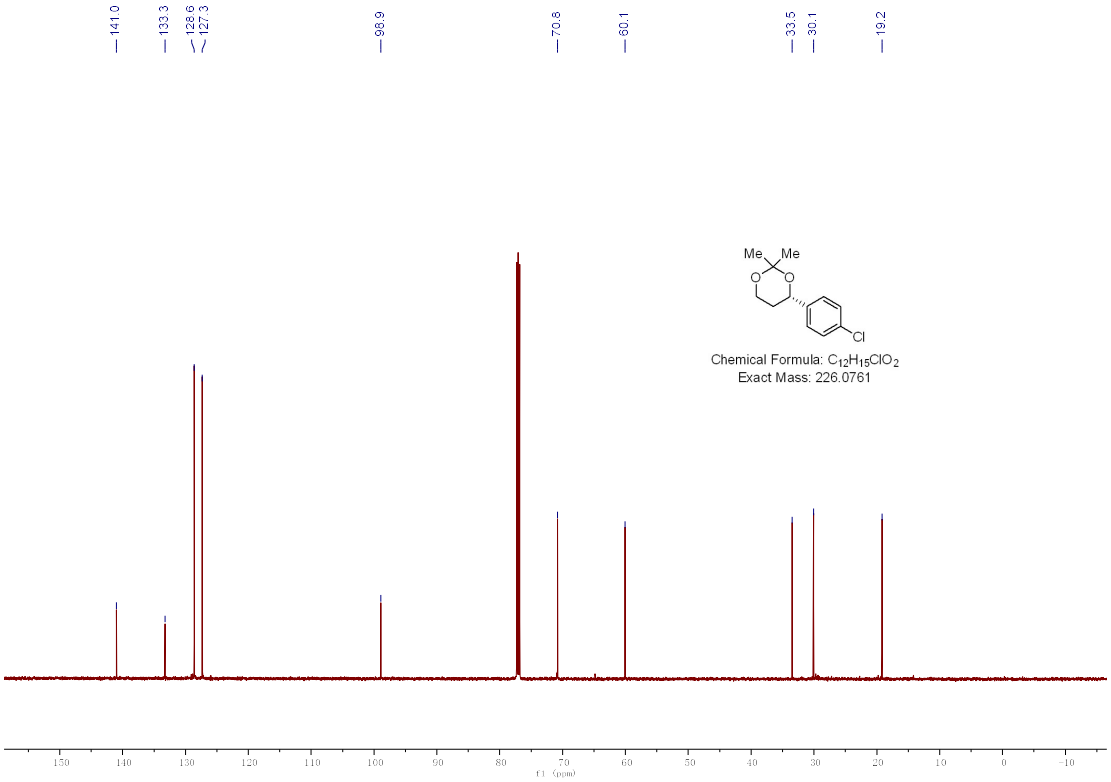
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5ad



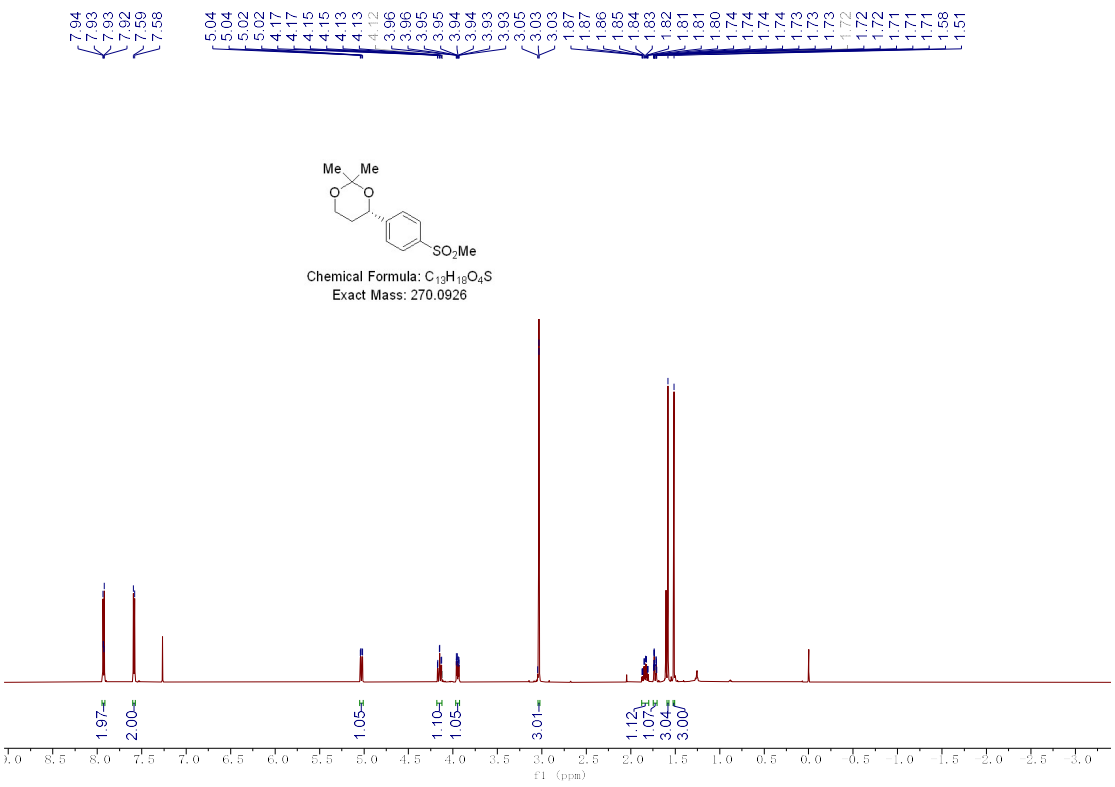
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5ad



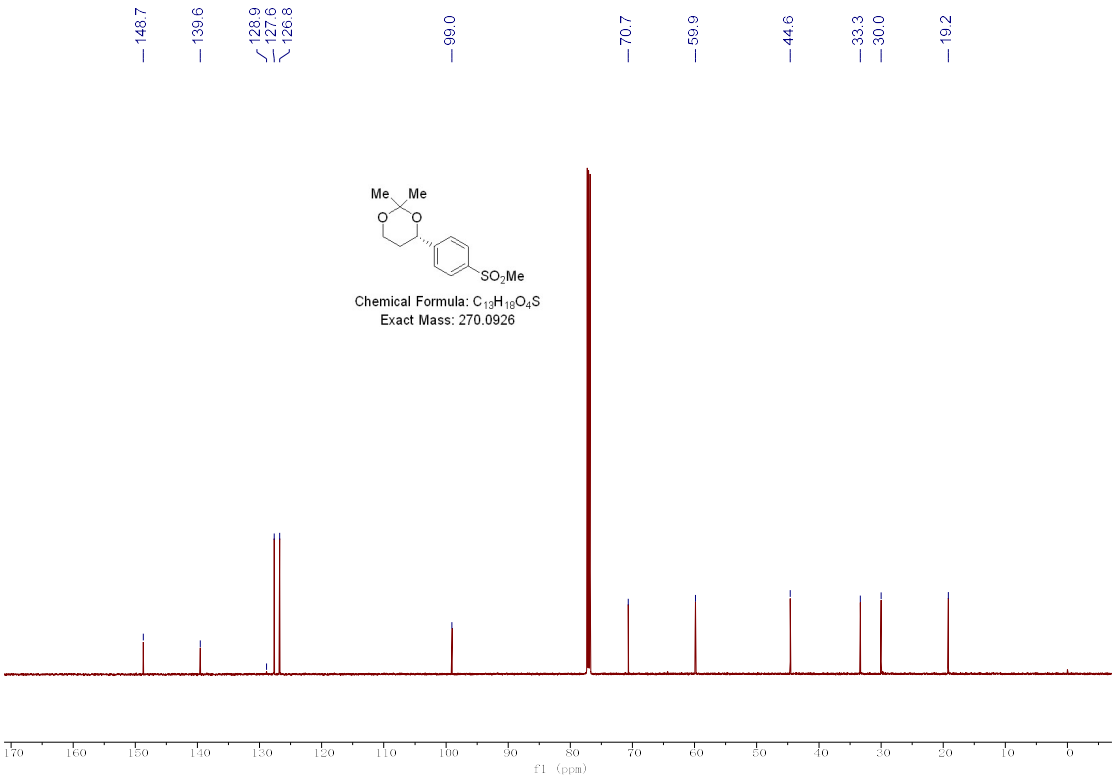
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5af



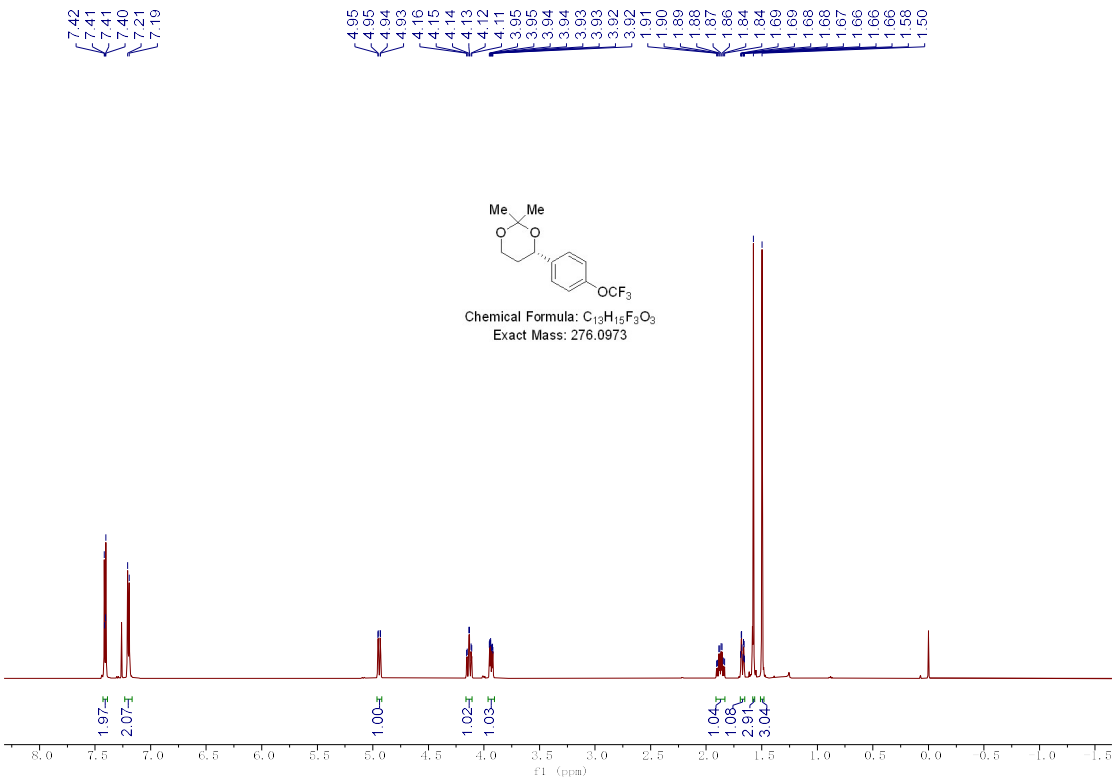
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5af



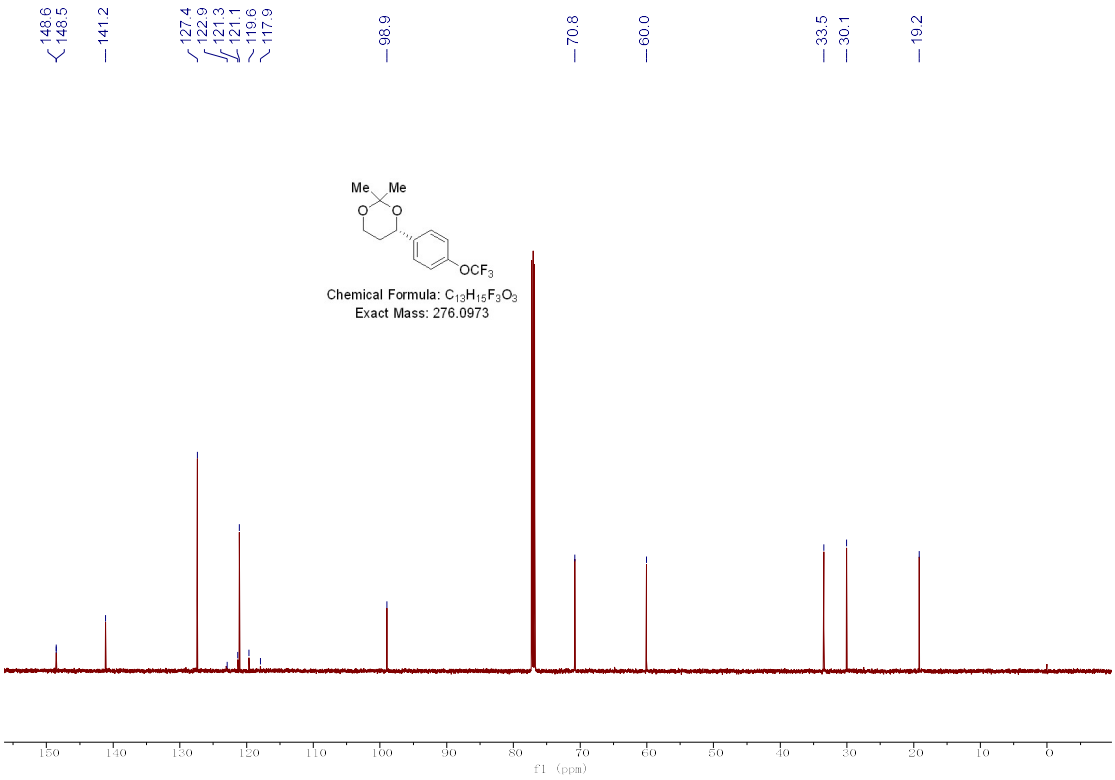
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5ag



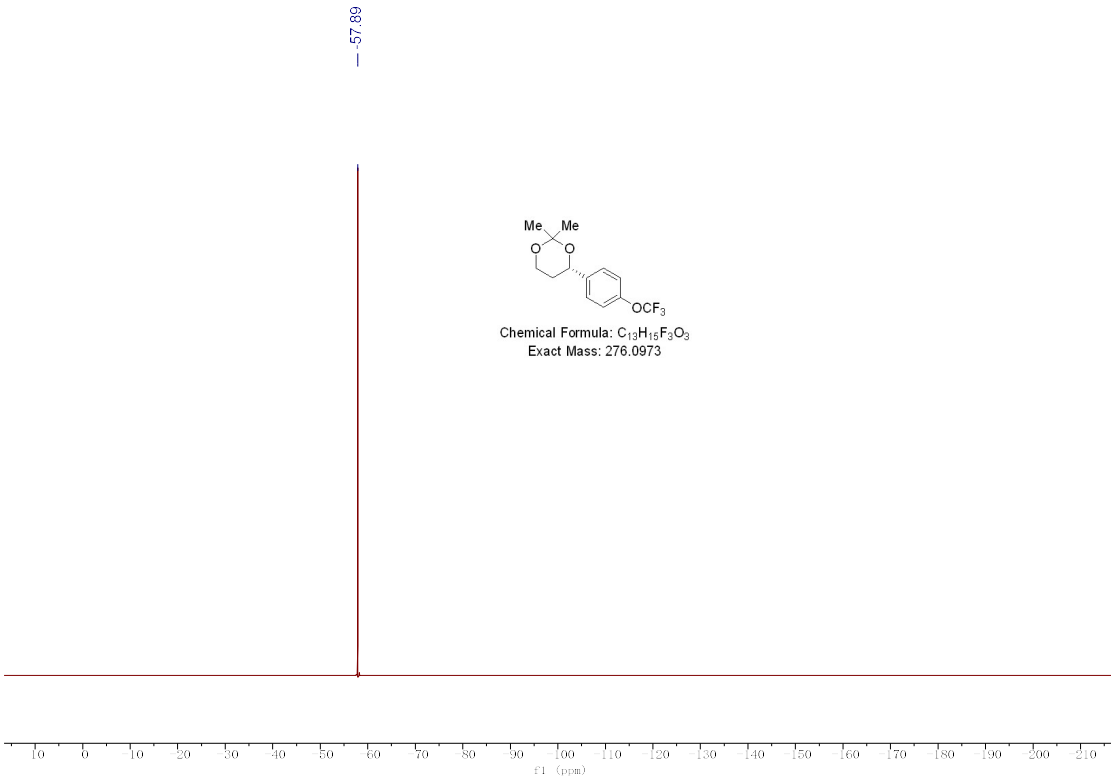
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5ag



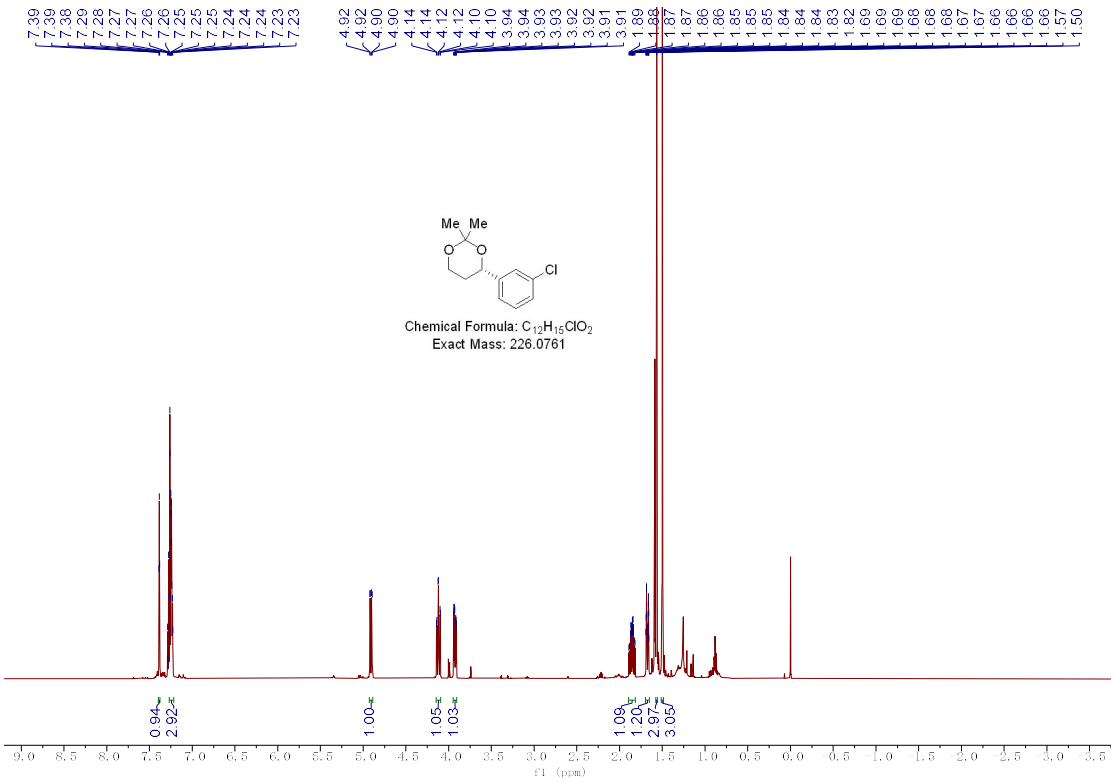
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5ai



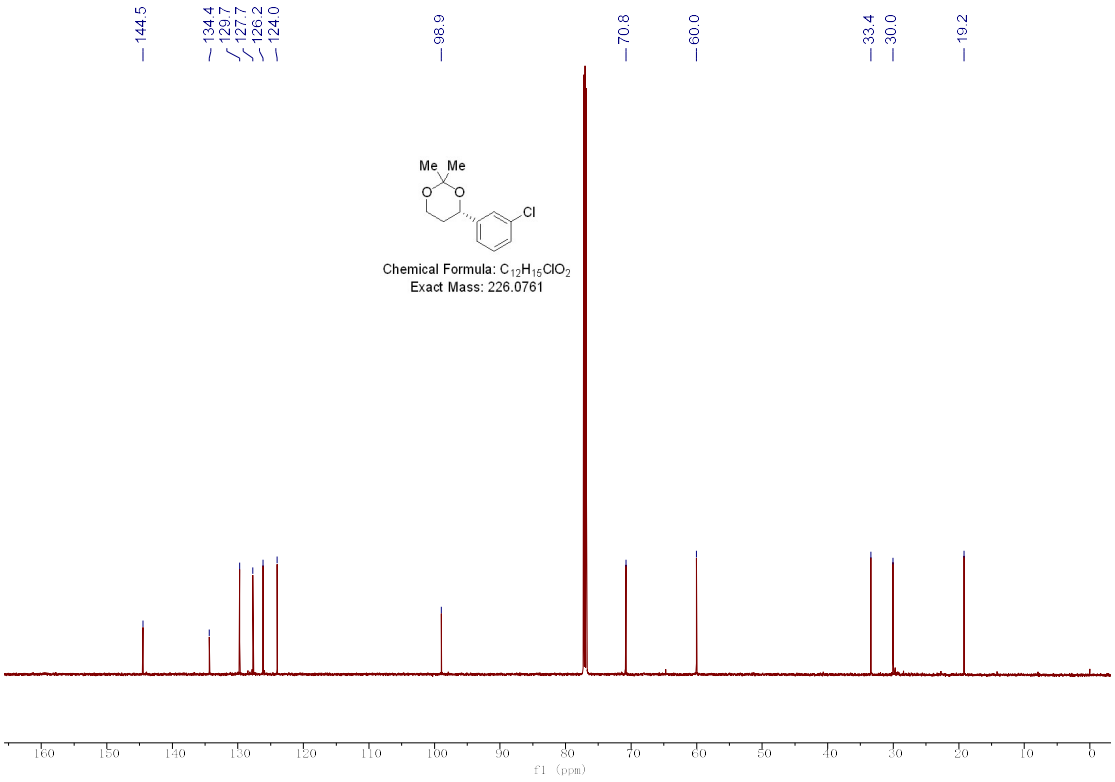
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5ai



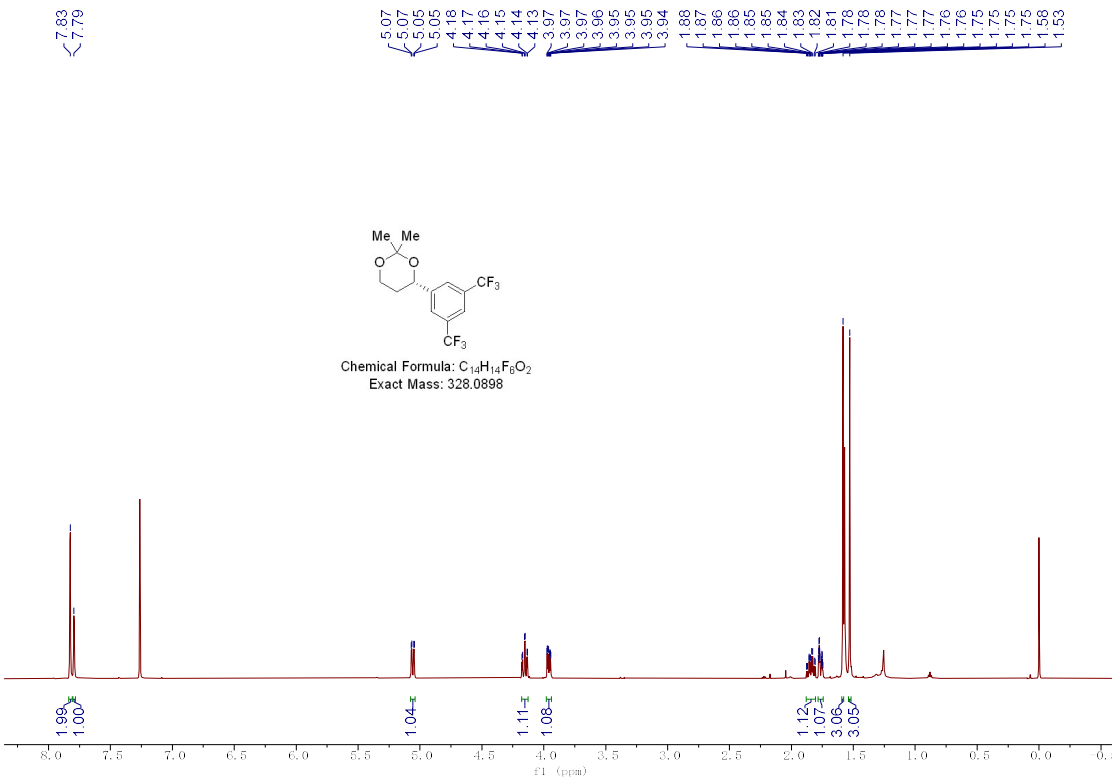
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of 5ai



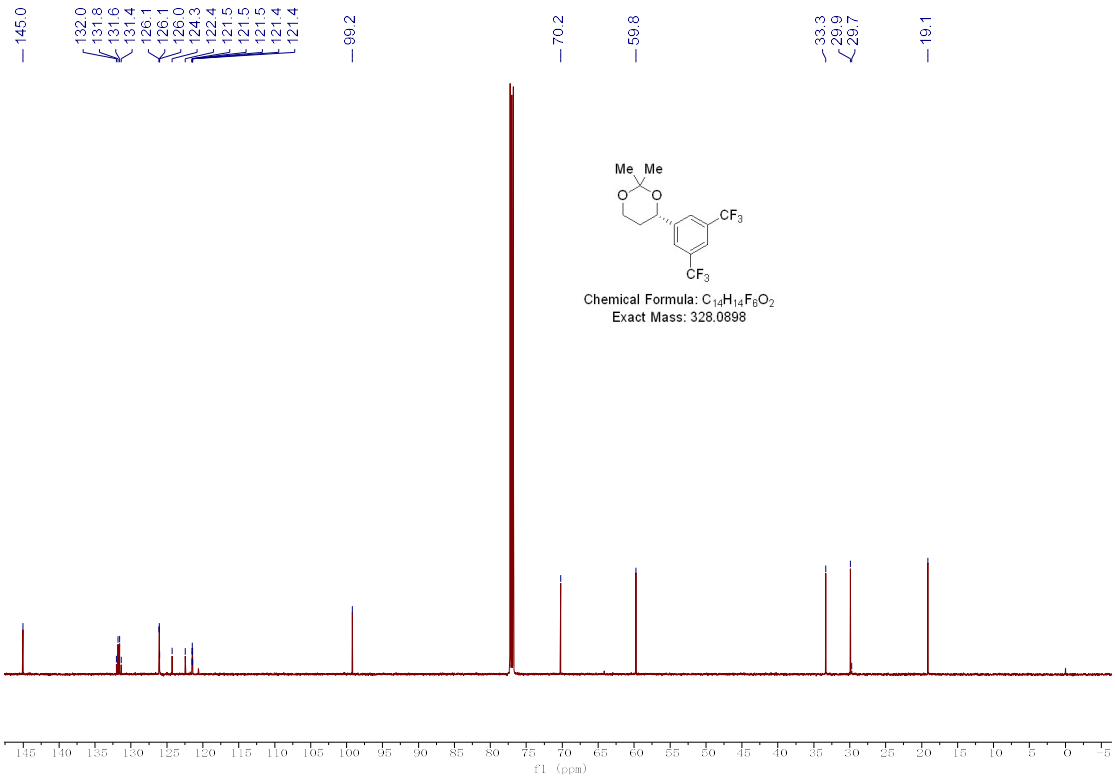
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5al



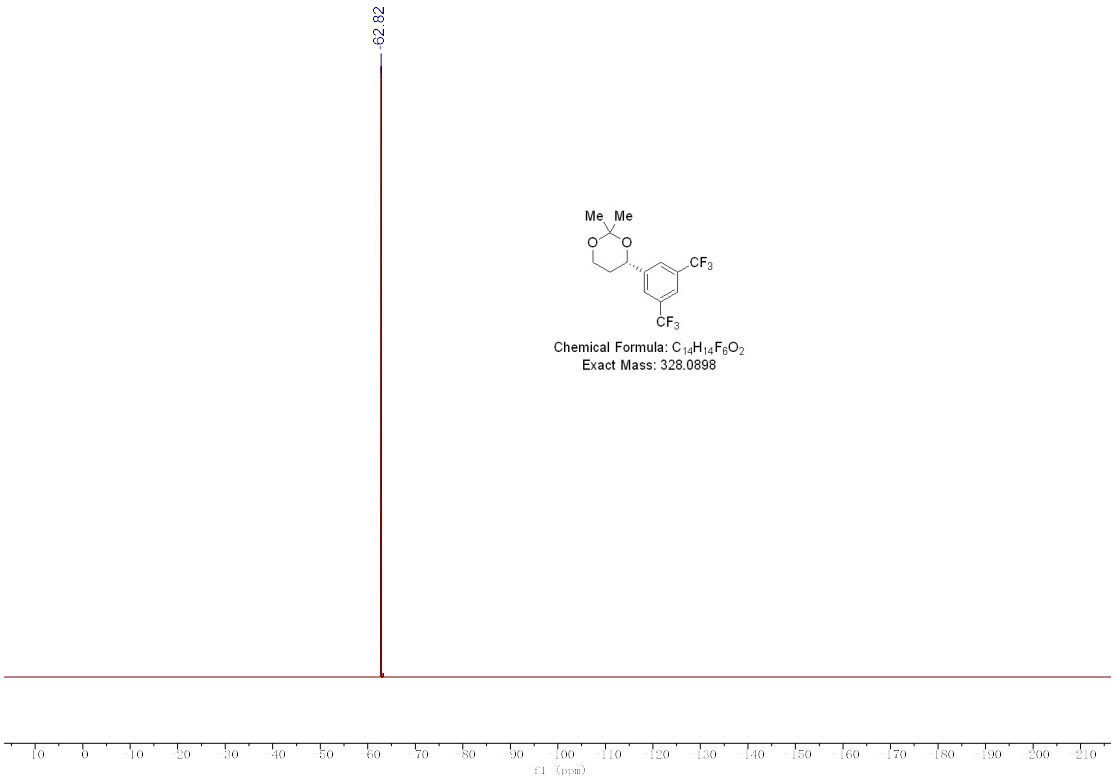
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5al



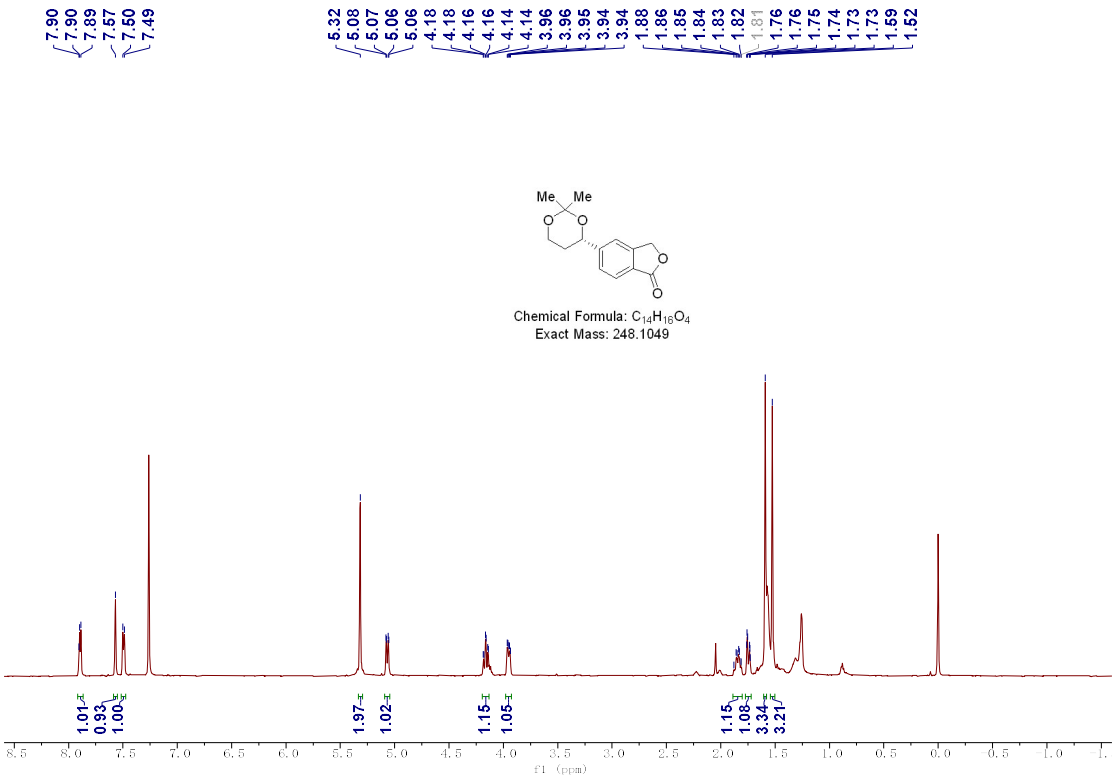
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5ao



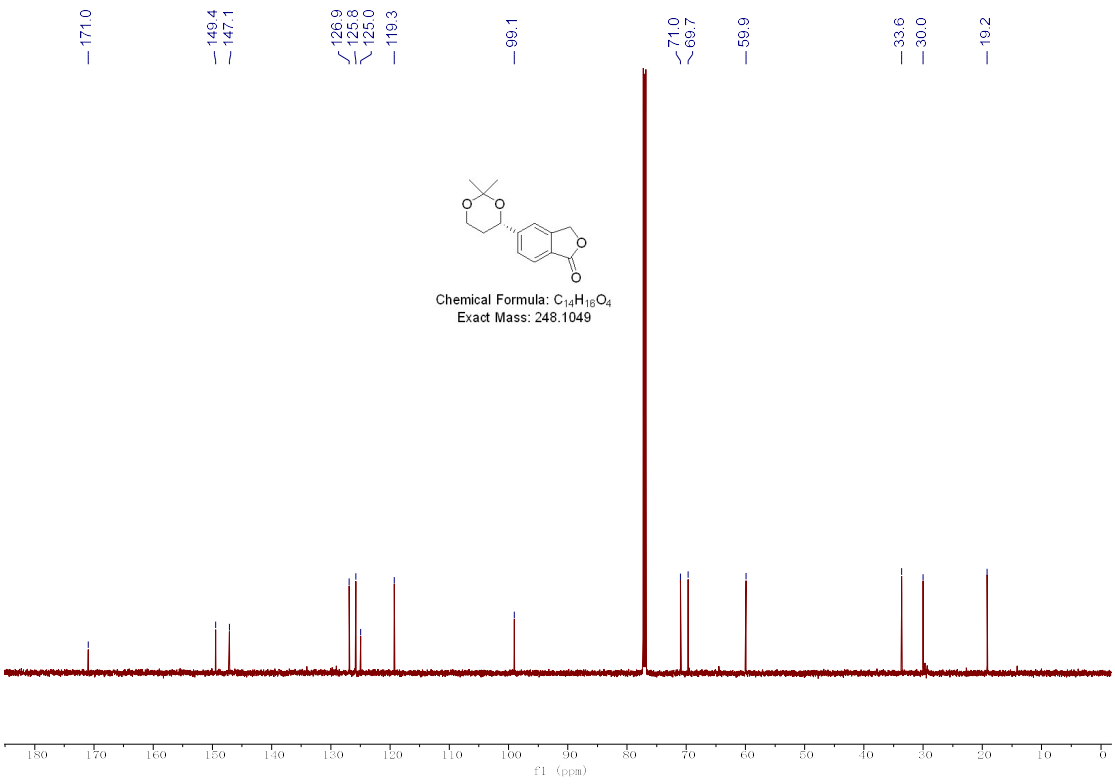
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5ao



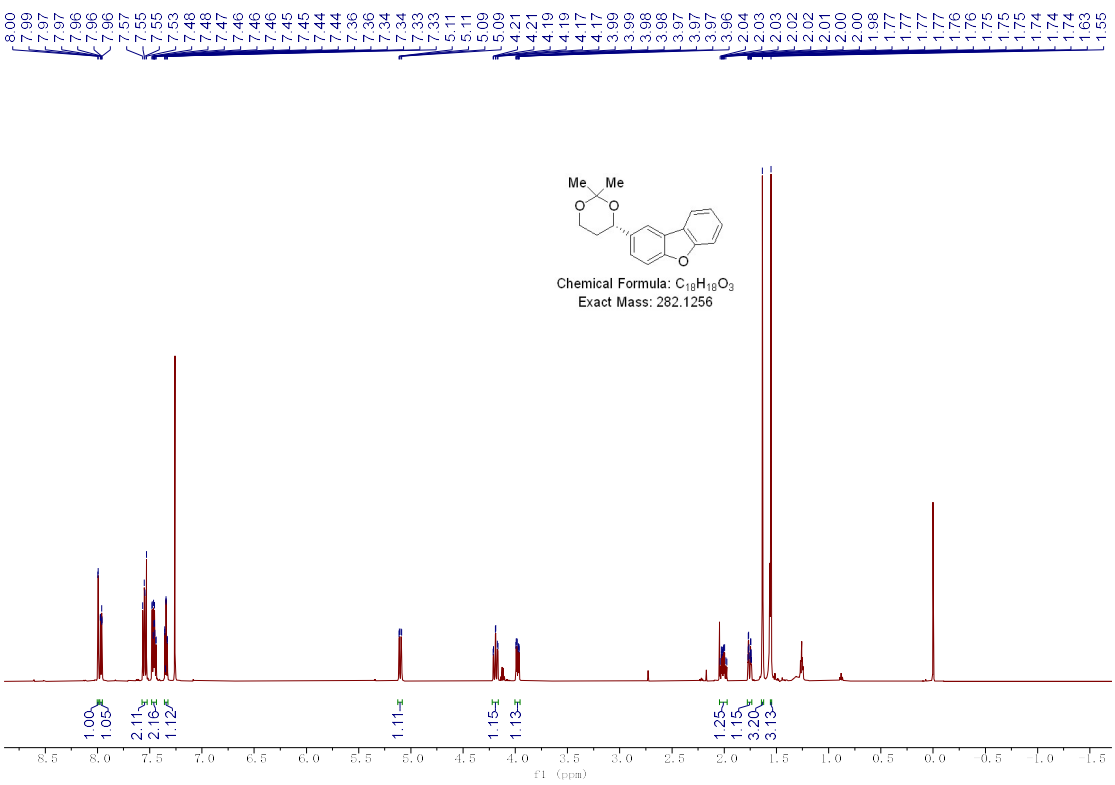
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of 5ao



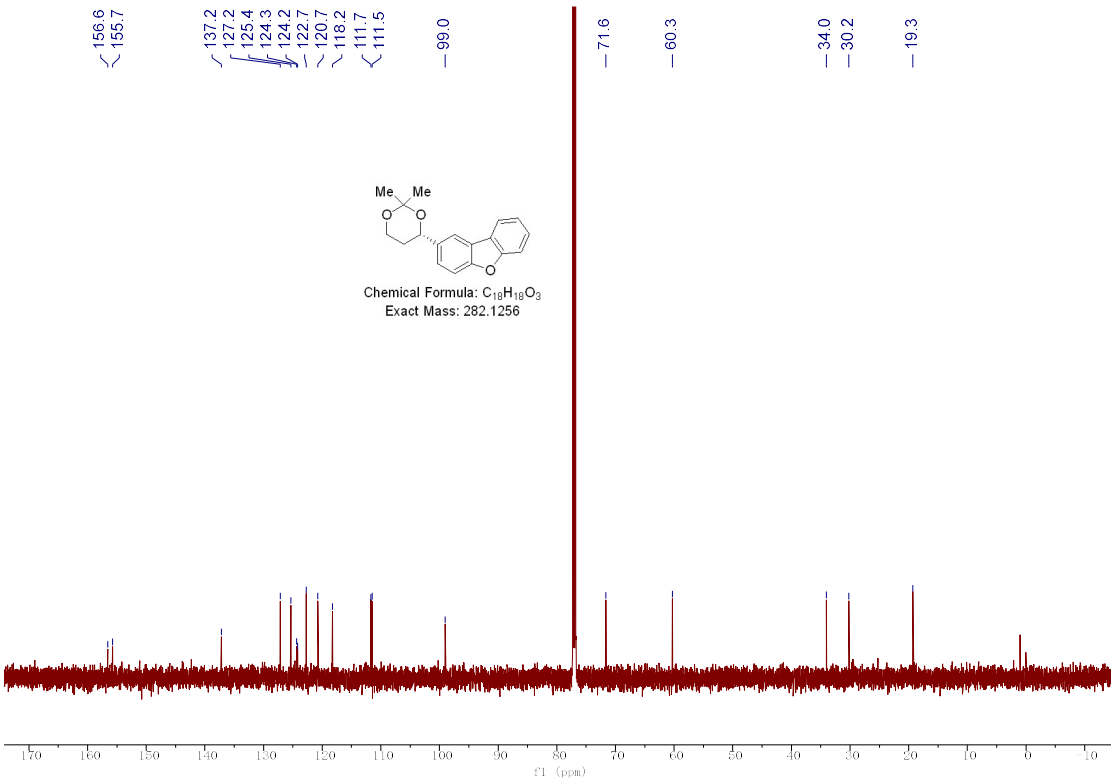
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5aq



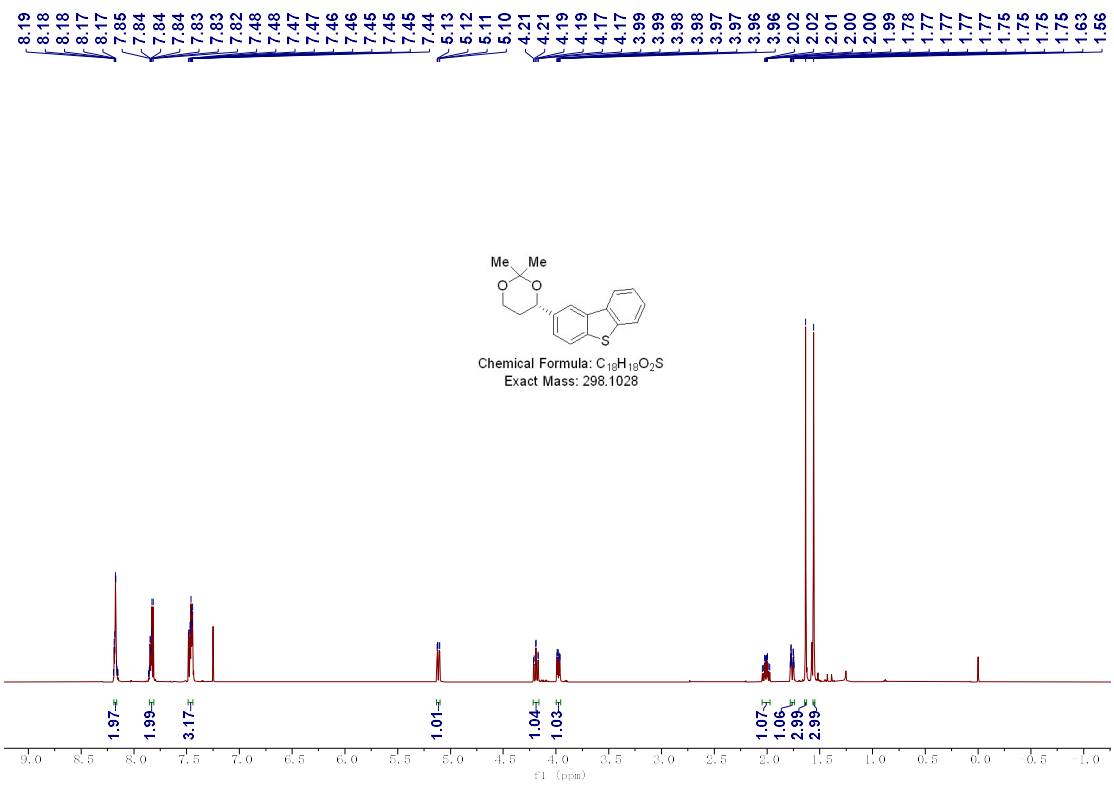
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5aq



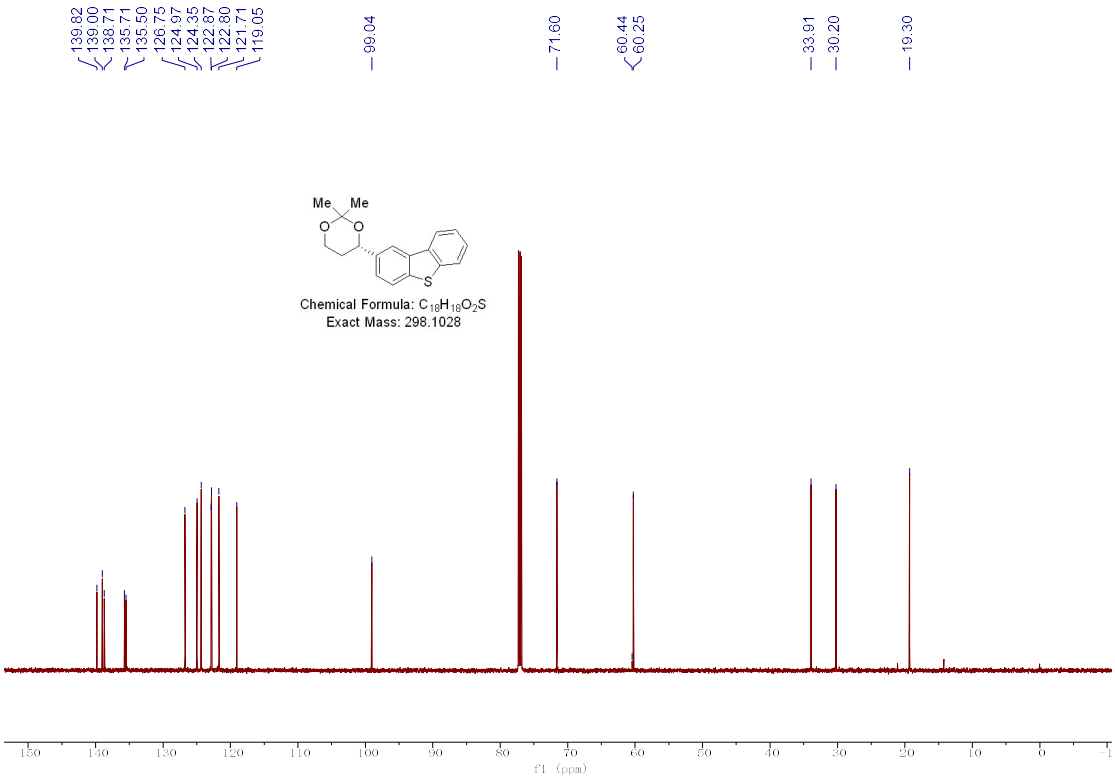
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5as



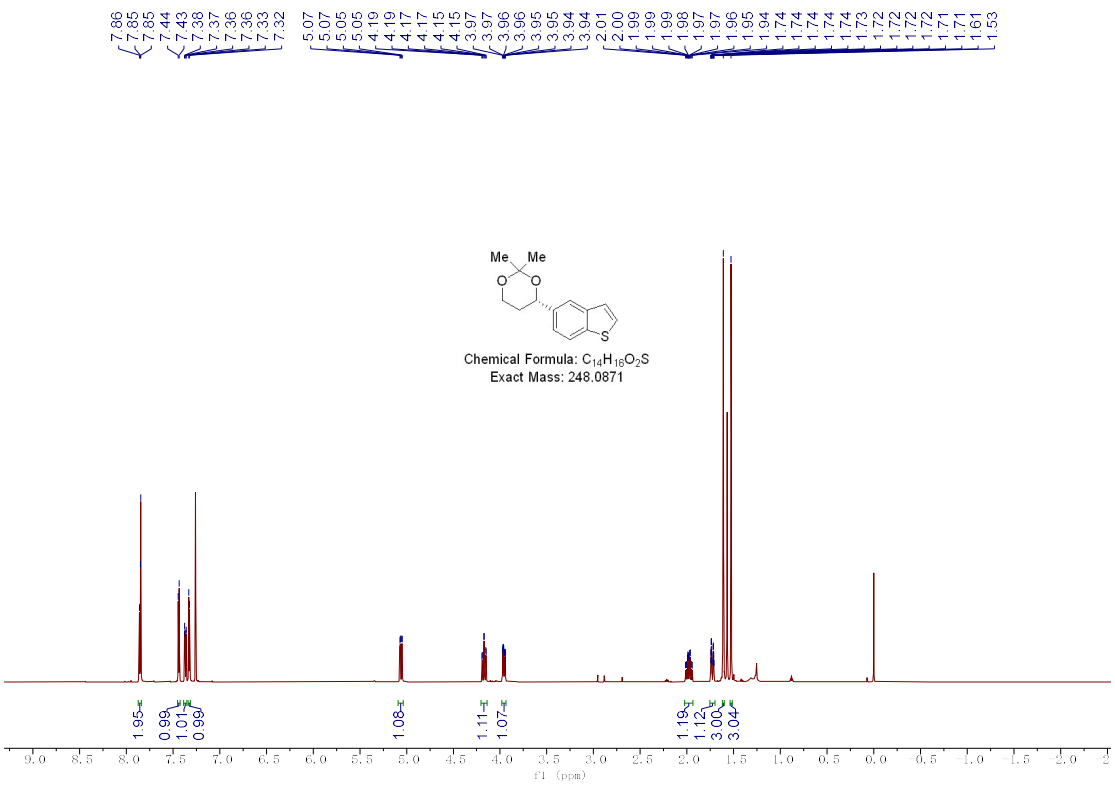
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5as



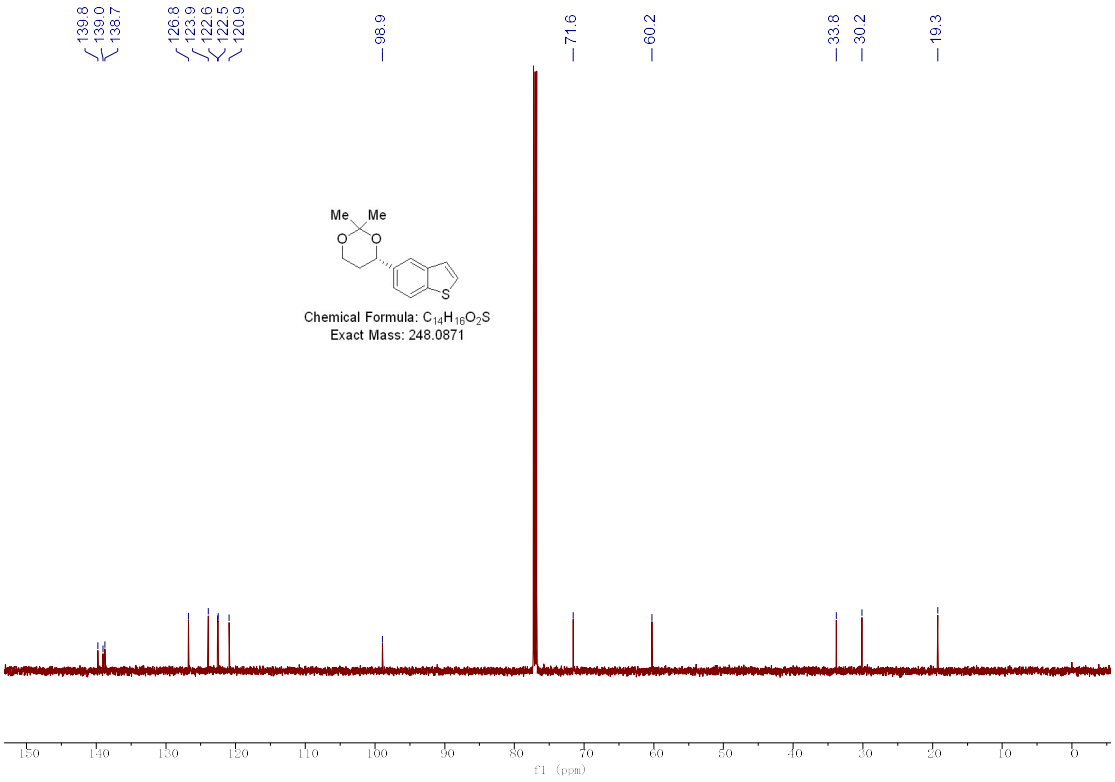
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5at



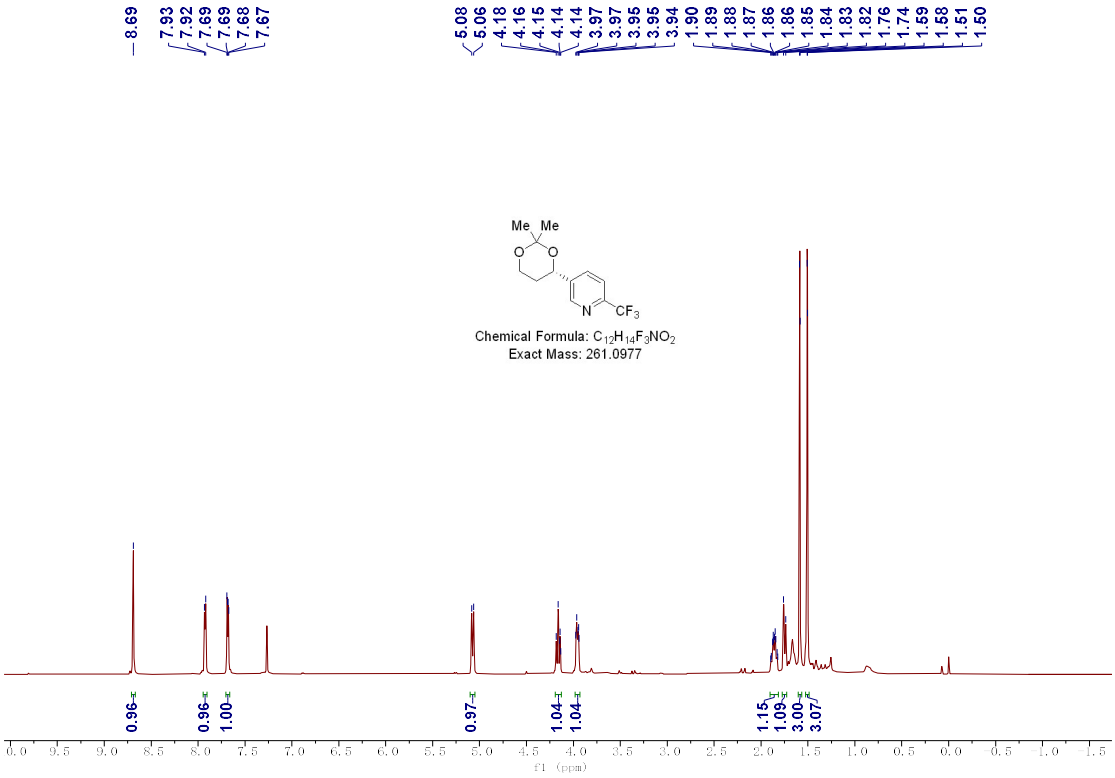
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5at



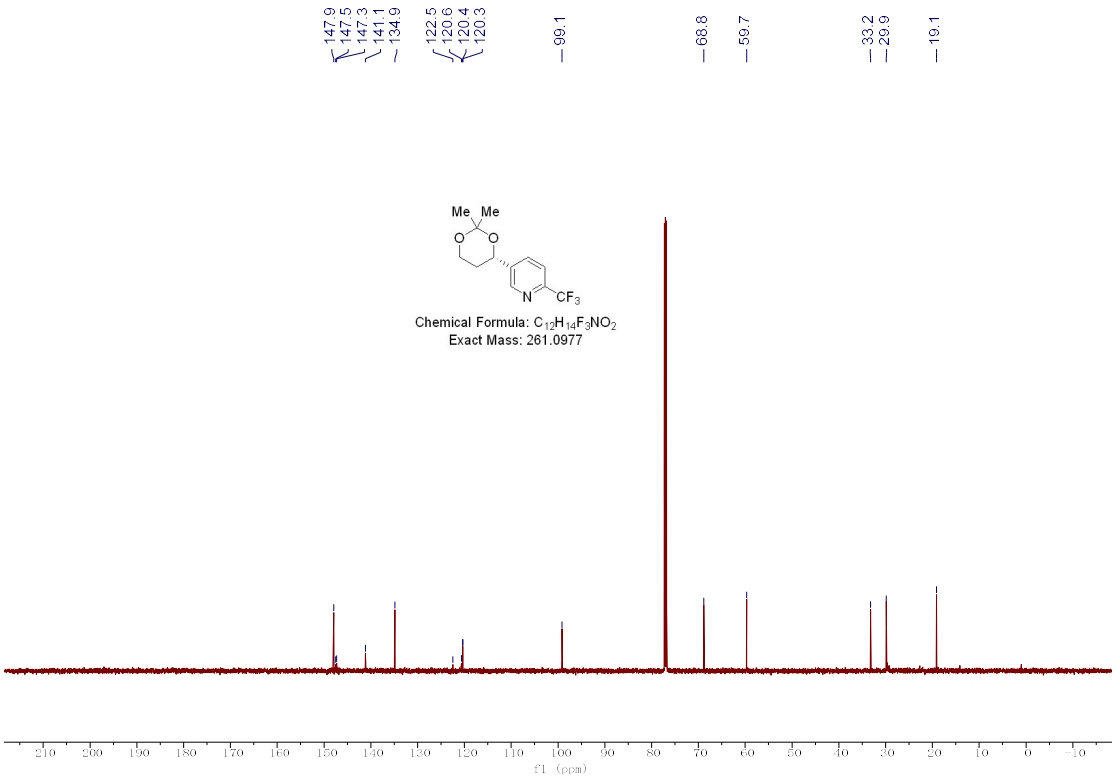
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5au



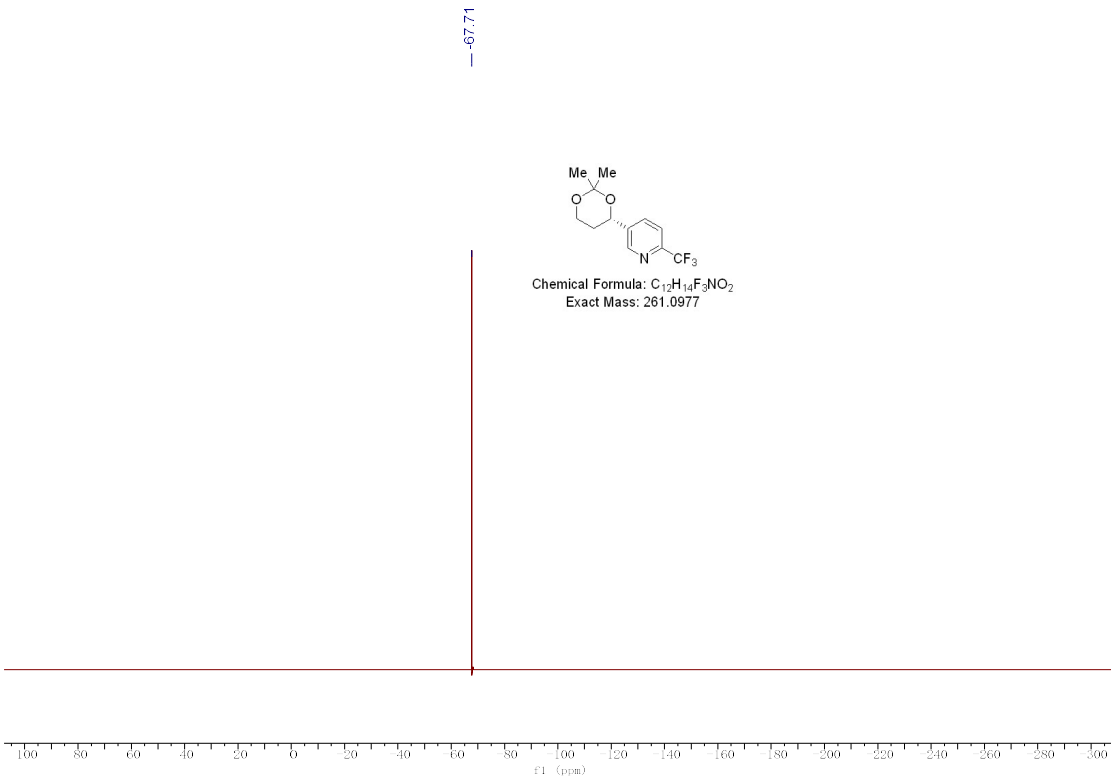
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5au



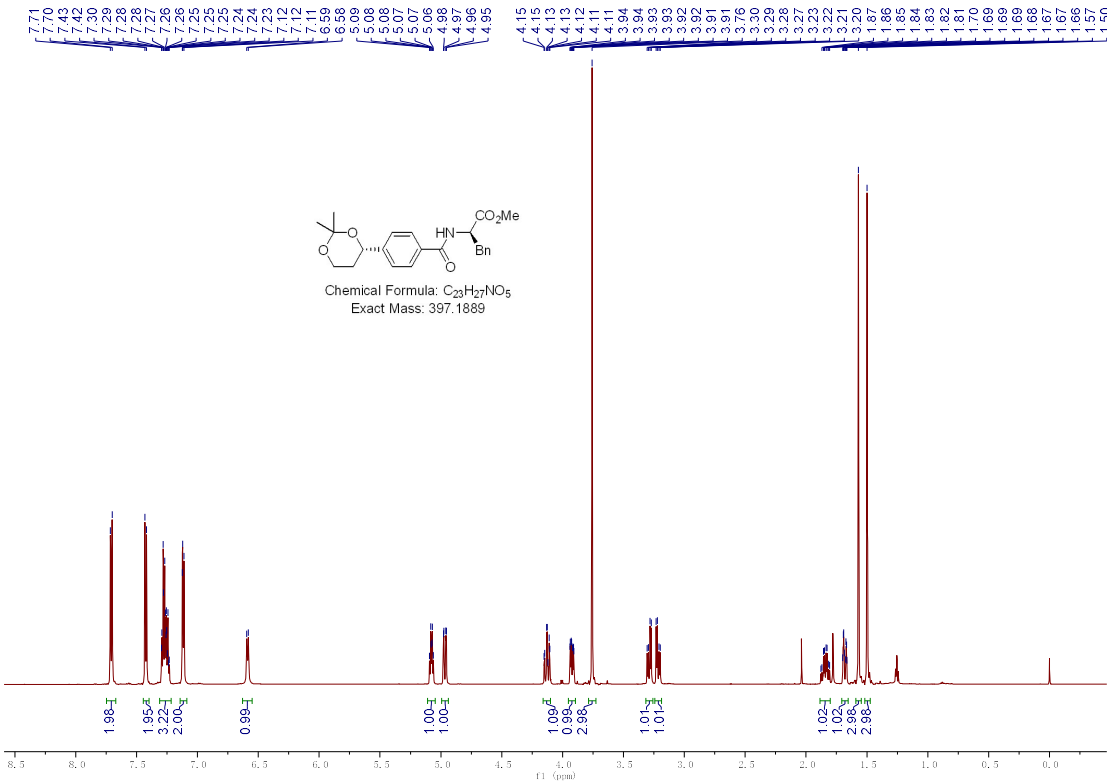
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5av



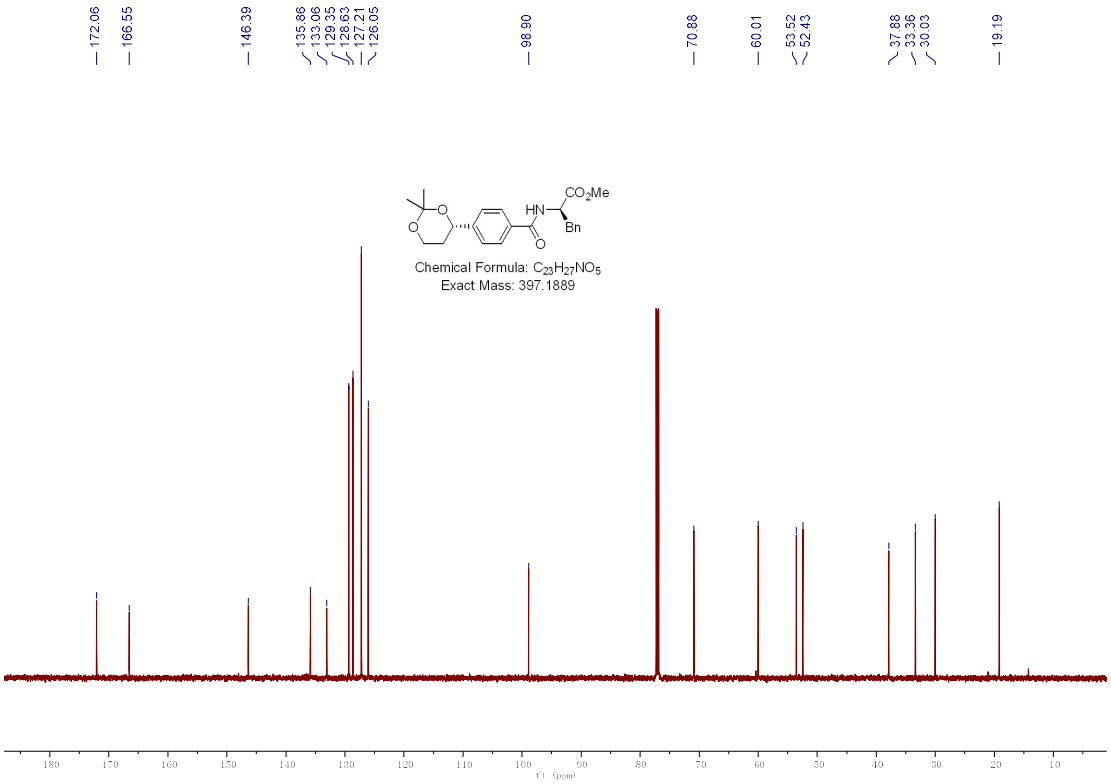
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5av



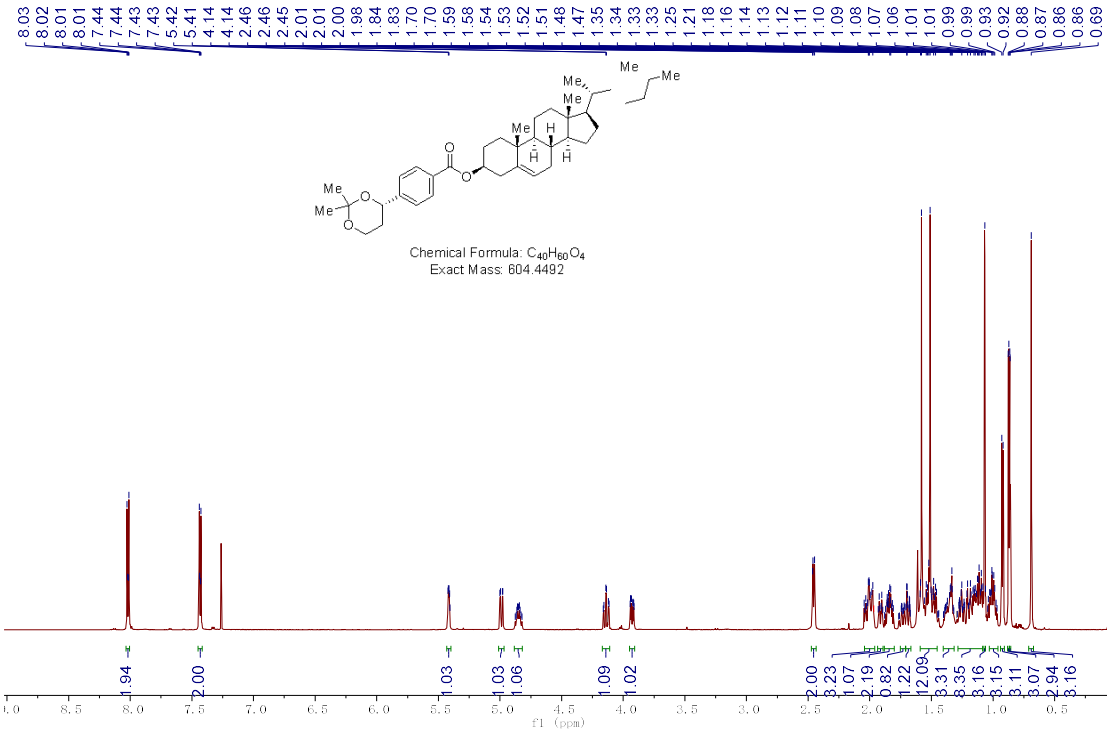
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of 5av



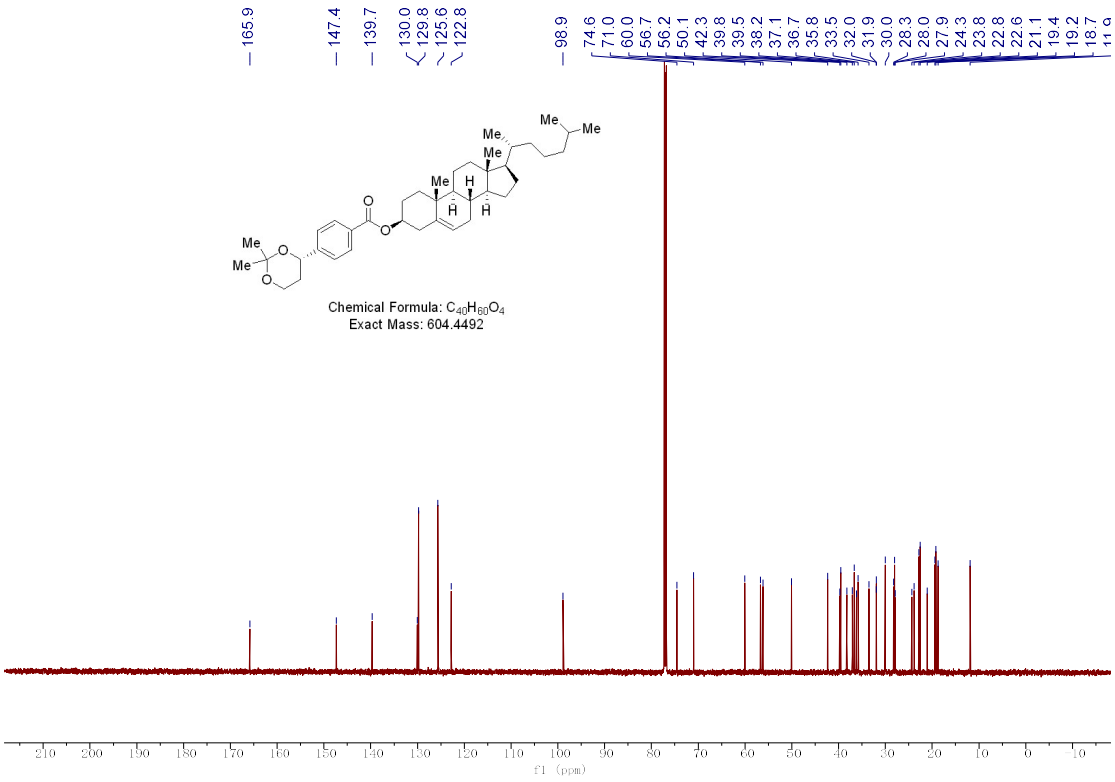
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5ax



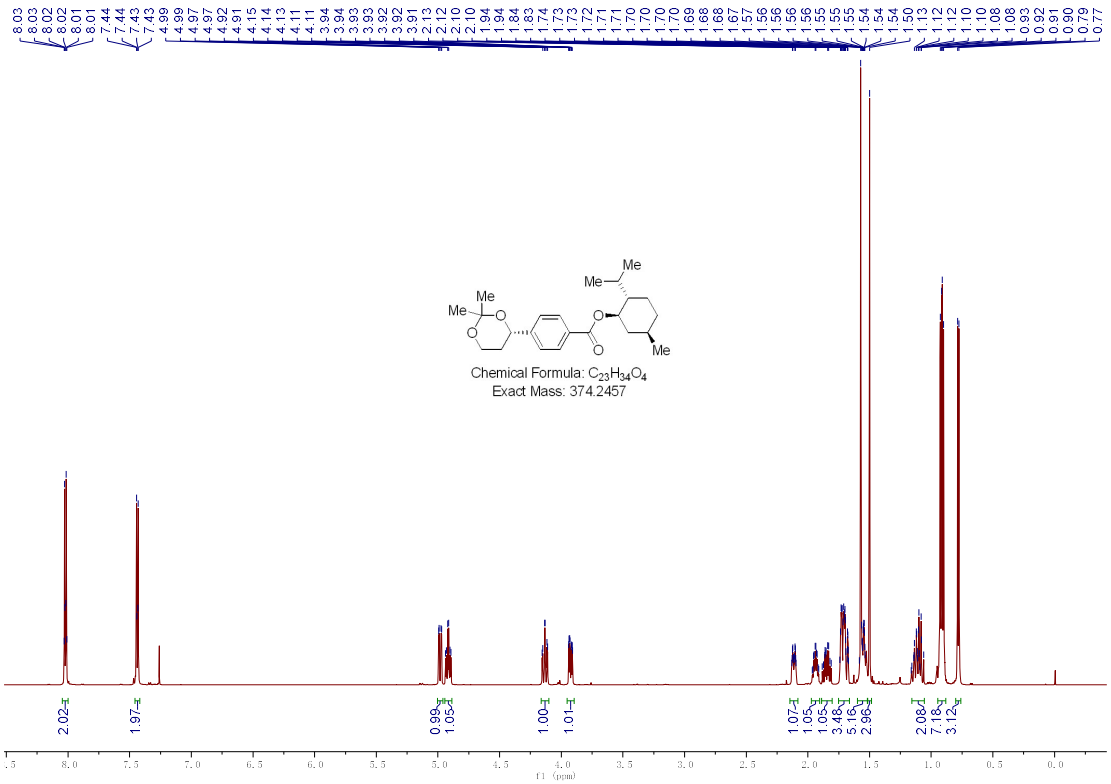
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5ax



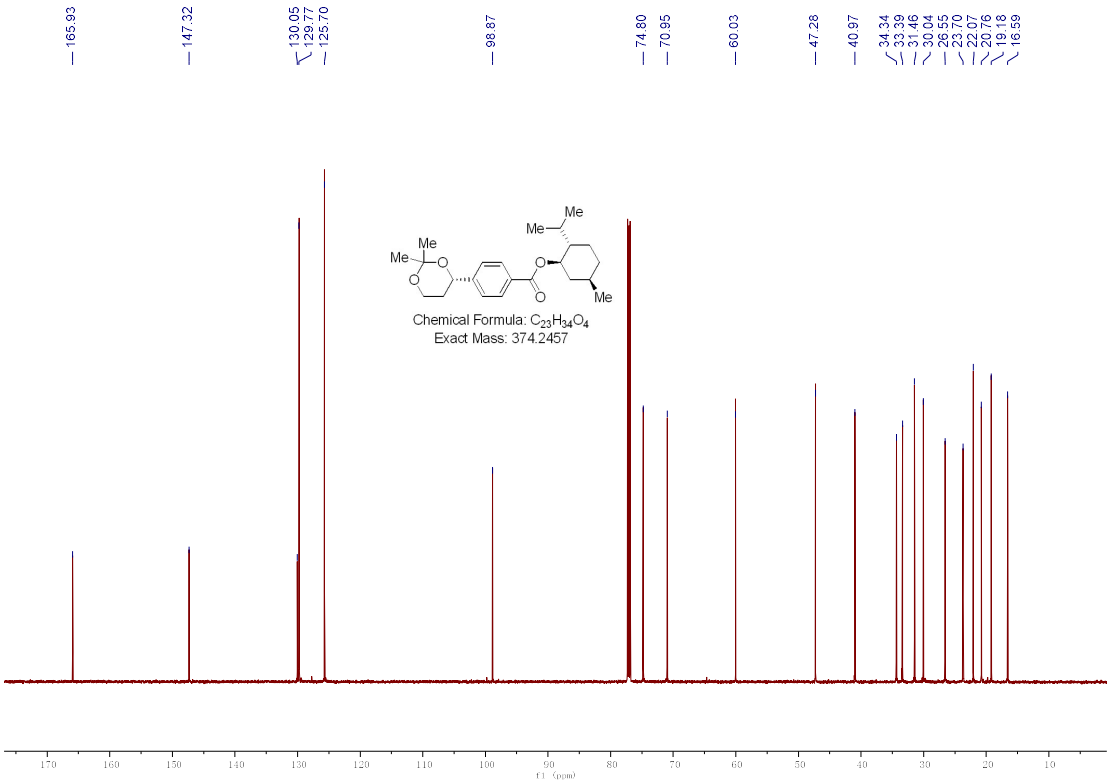
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5az



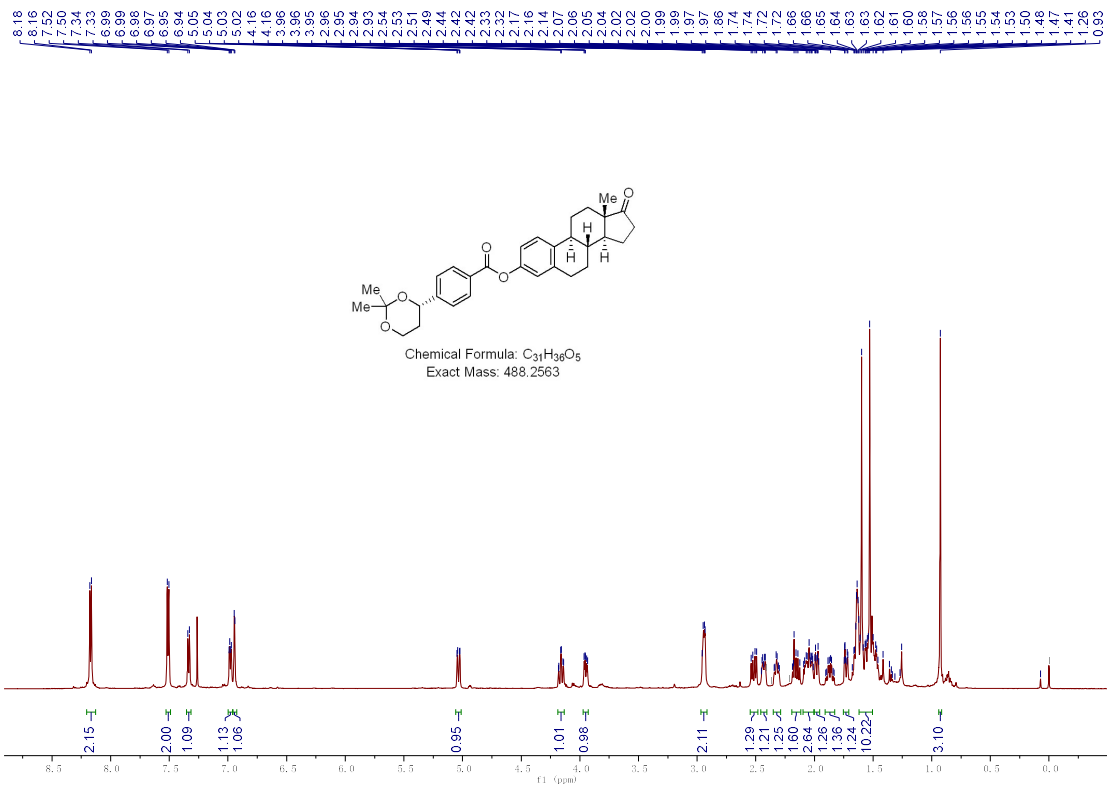
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5az



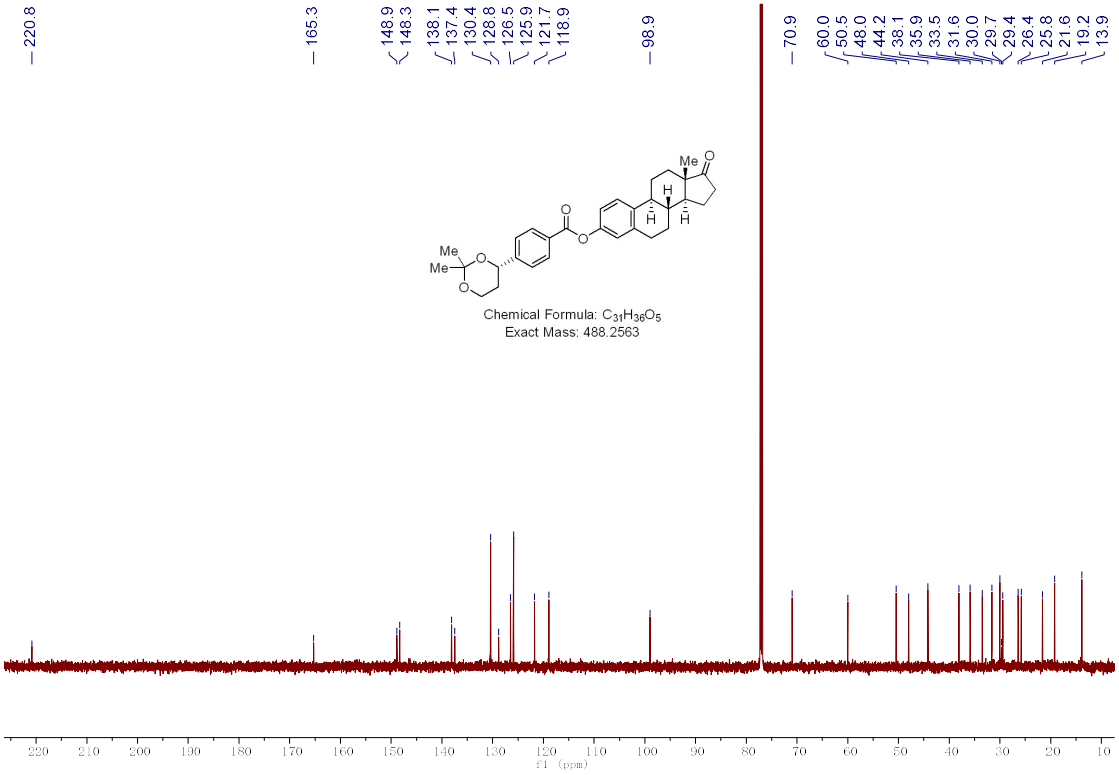
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5aaa



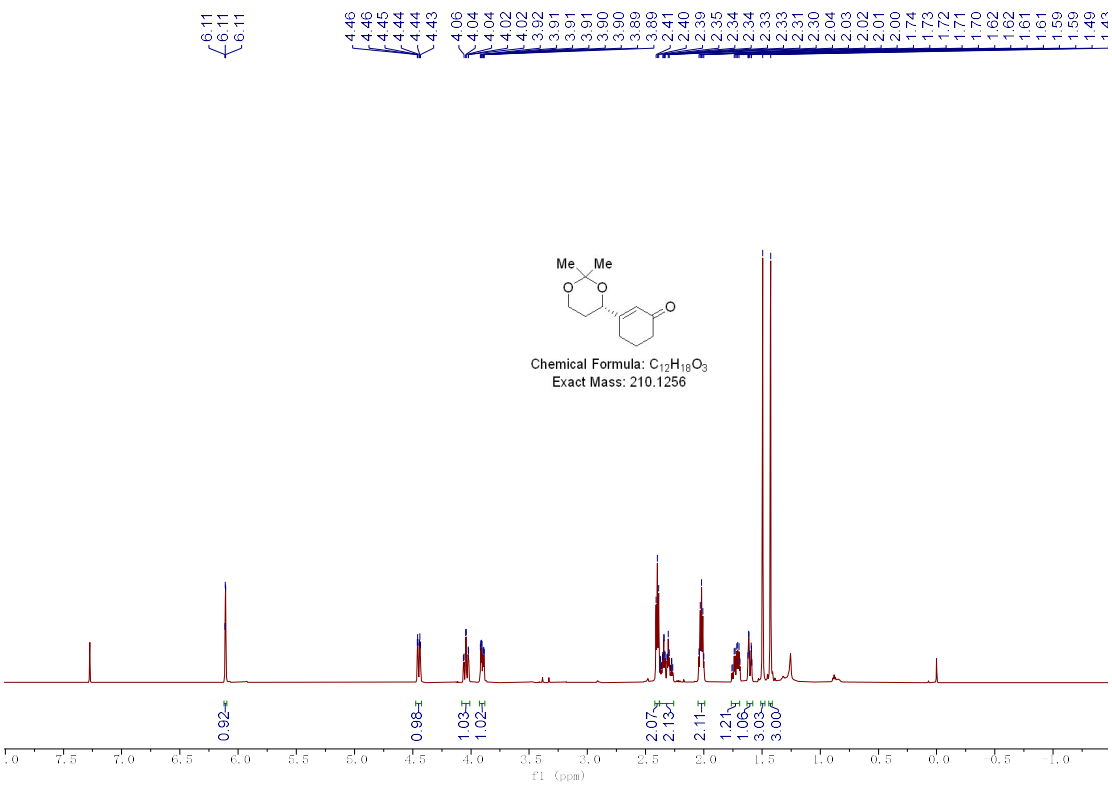
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5aaa



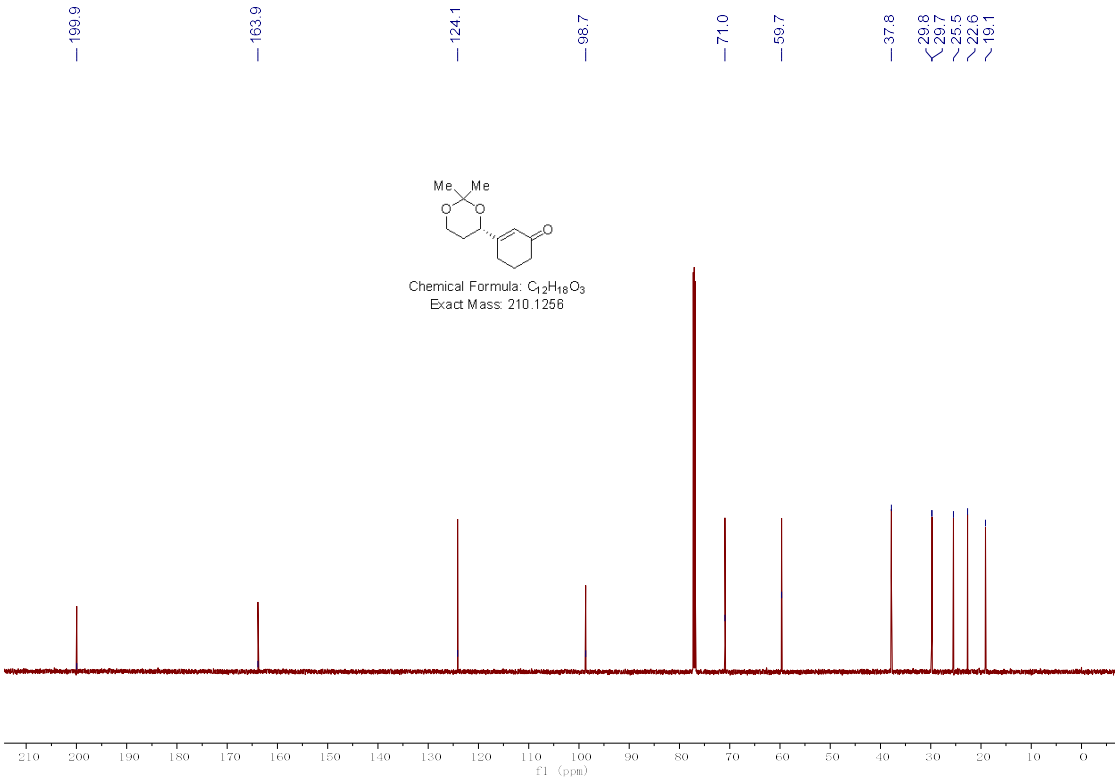
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5aab



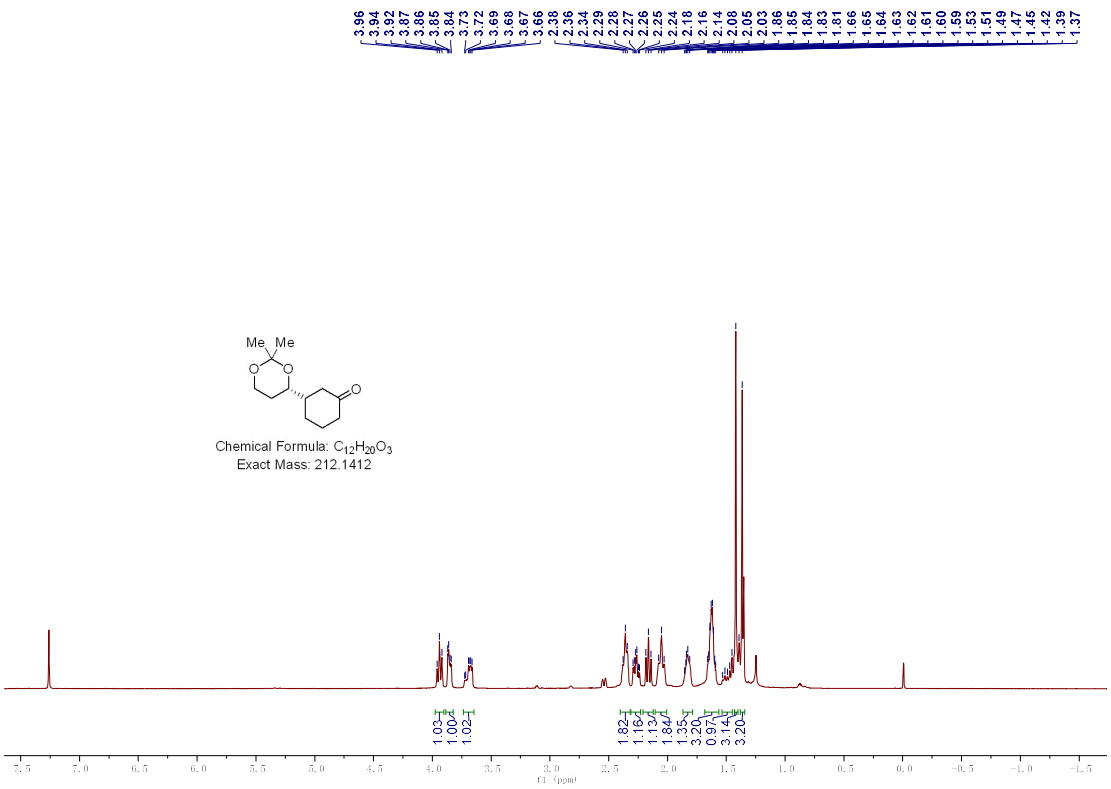
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5aab



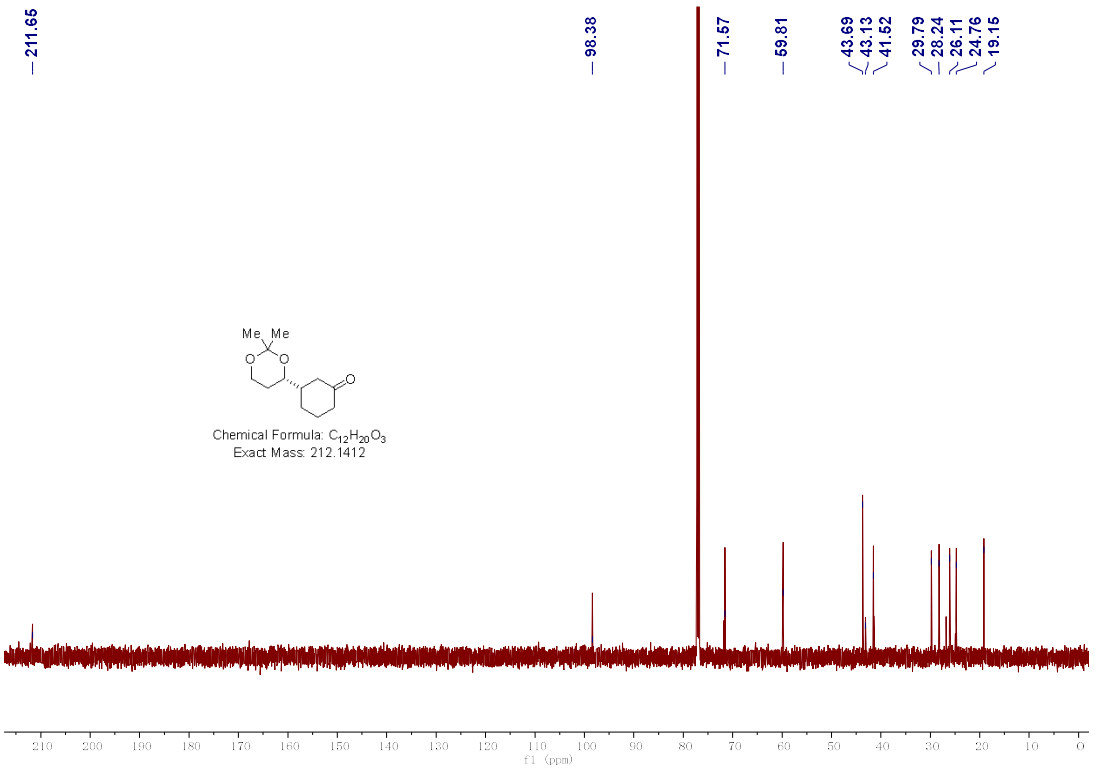
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5aac



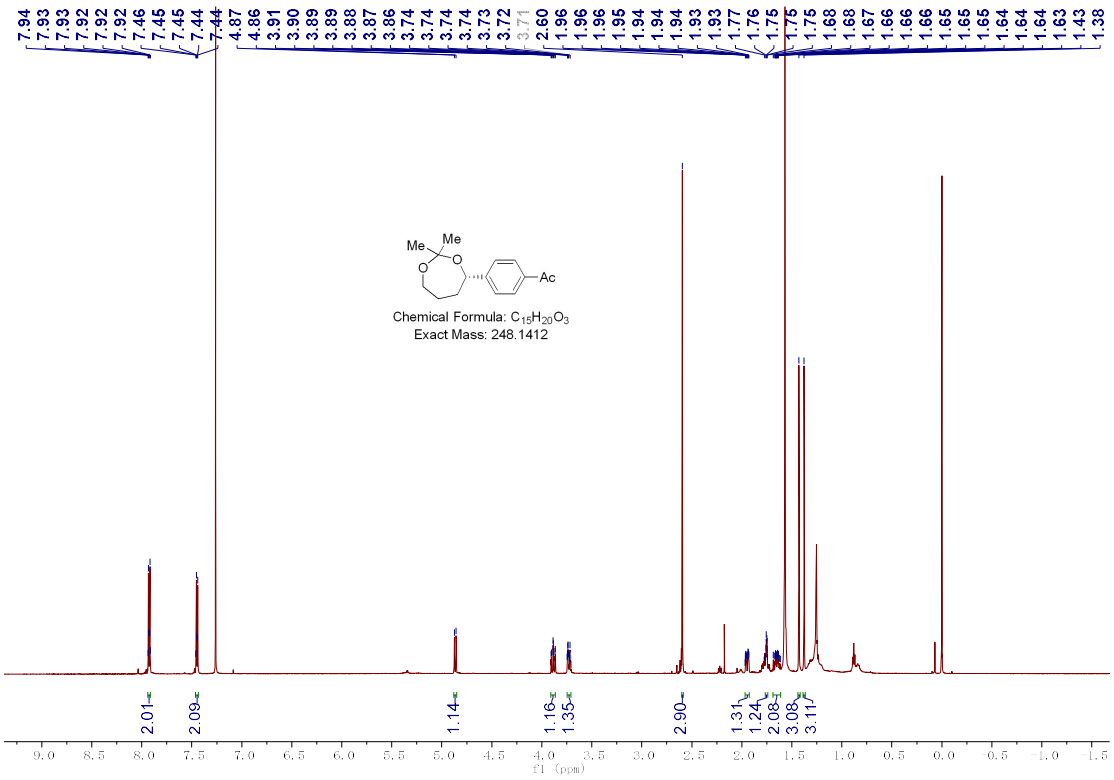
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5aac



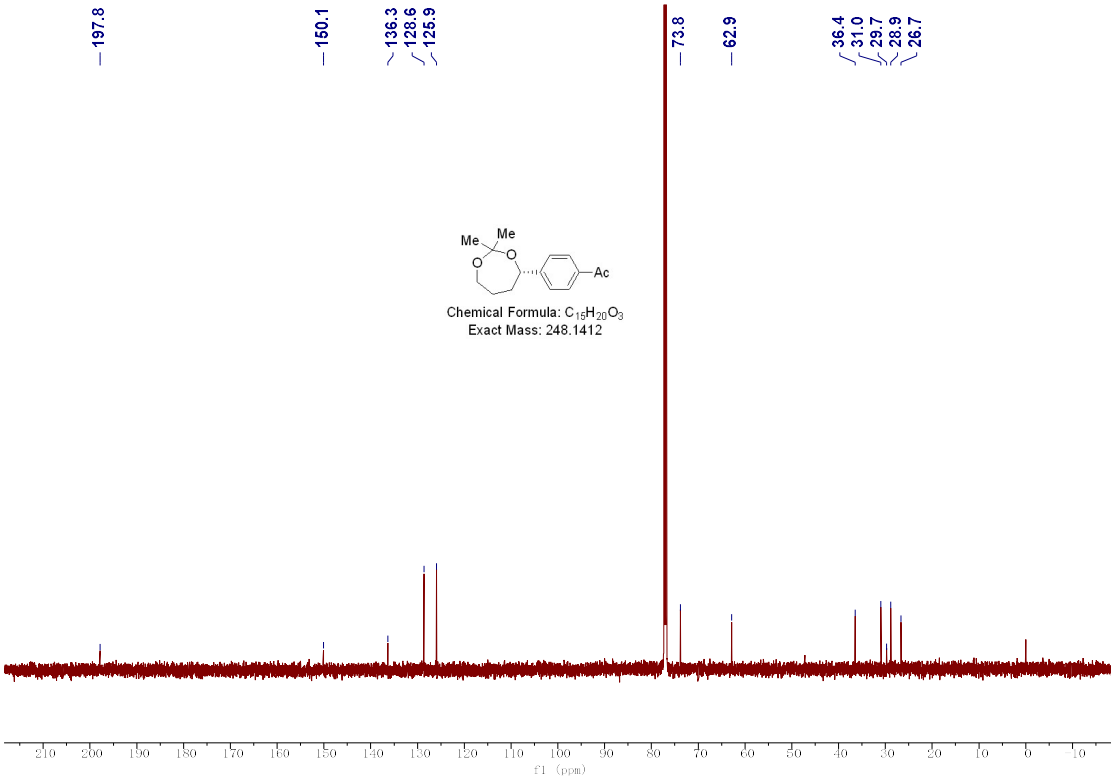
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 5aad



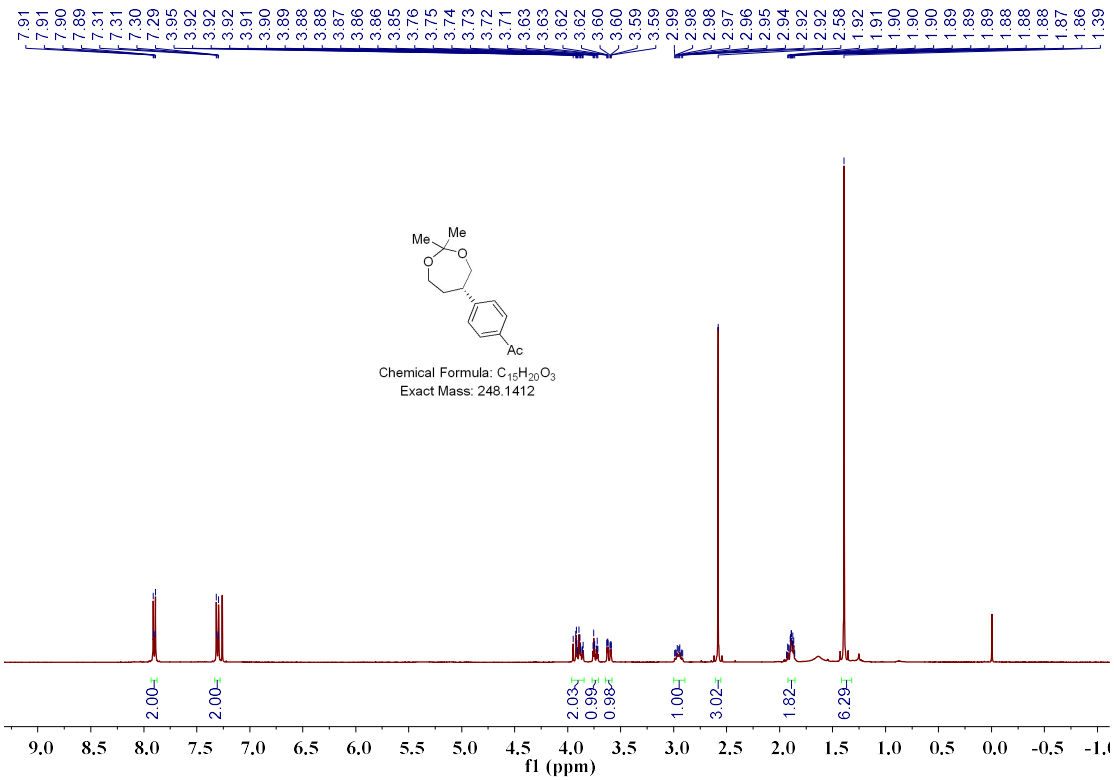
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 5aad



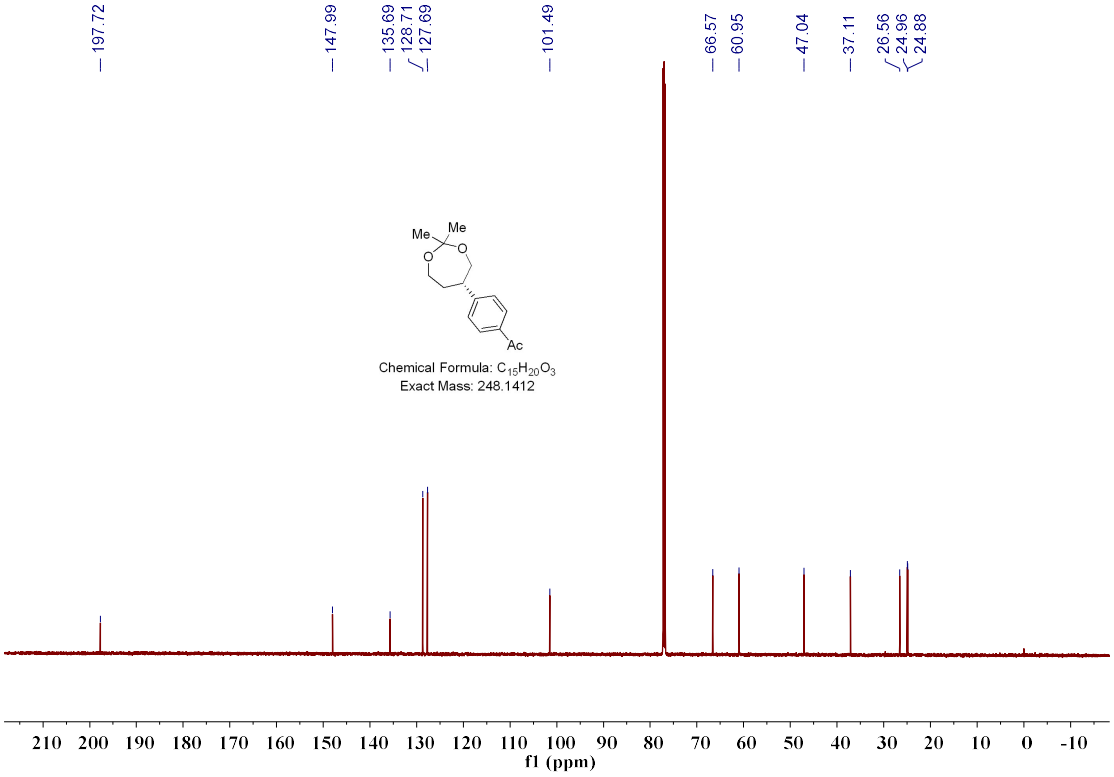
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 7aa



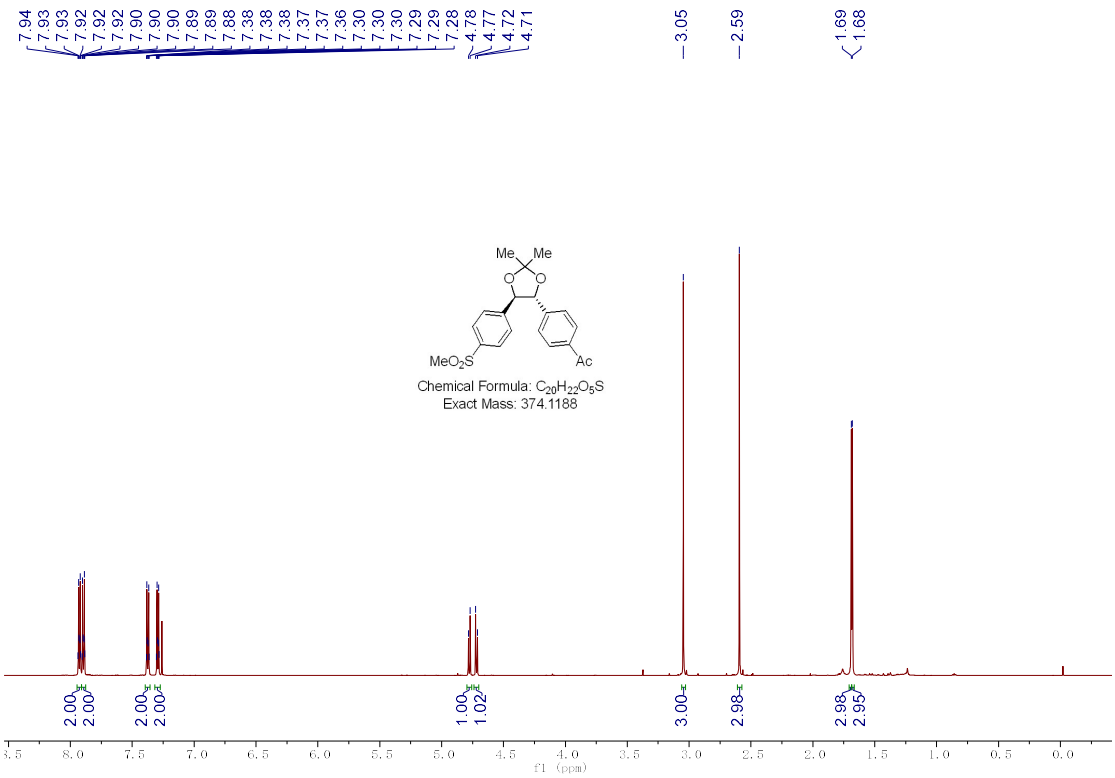
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 7aa



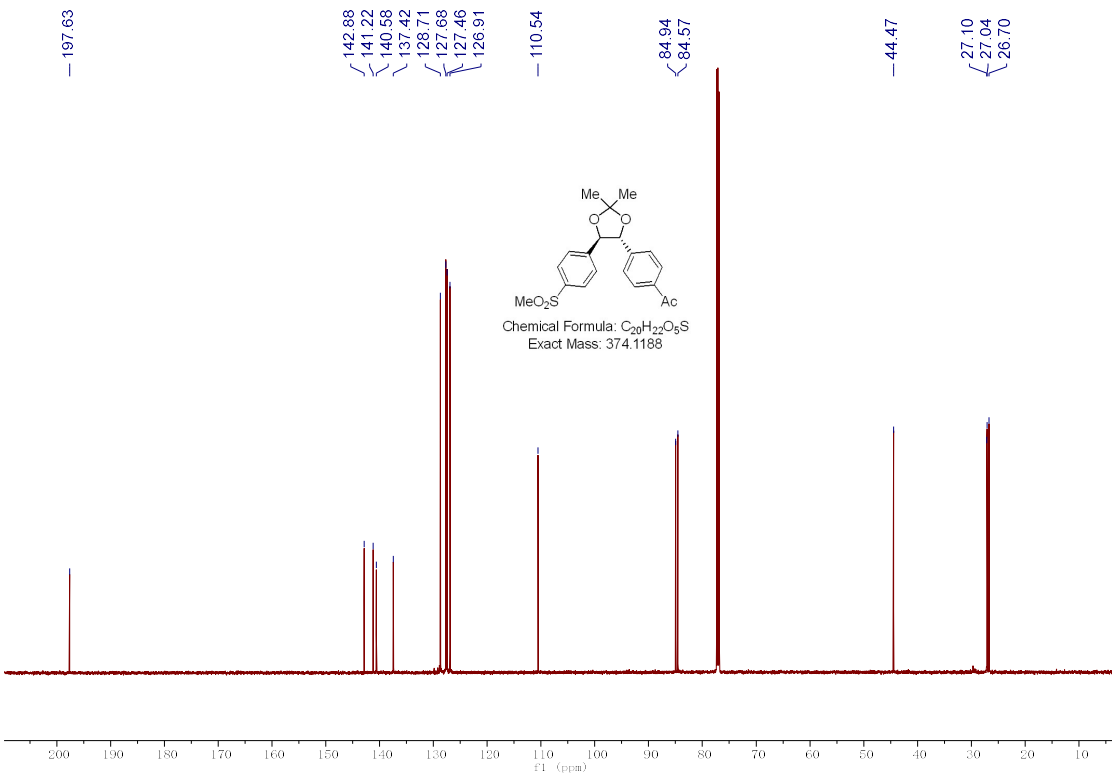
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 7aa'



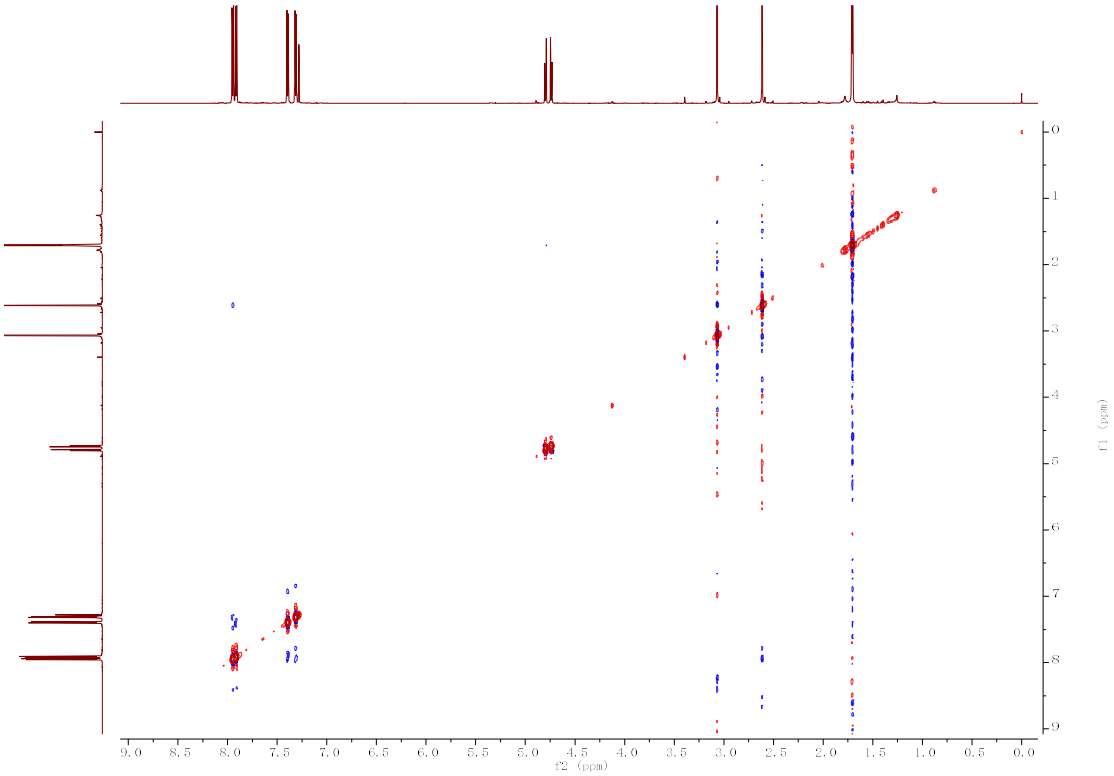
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 7aa'



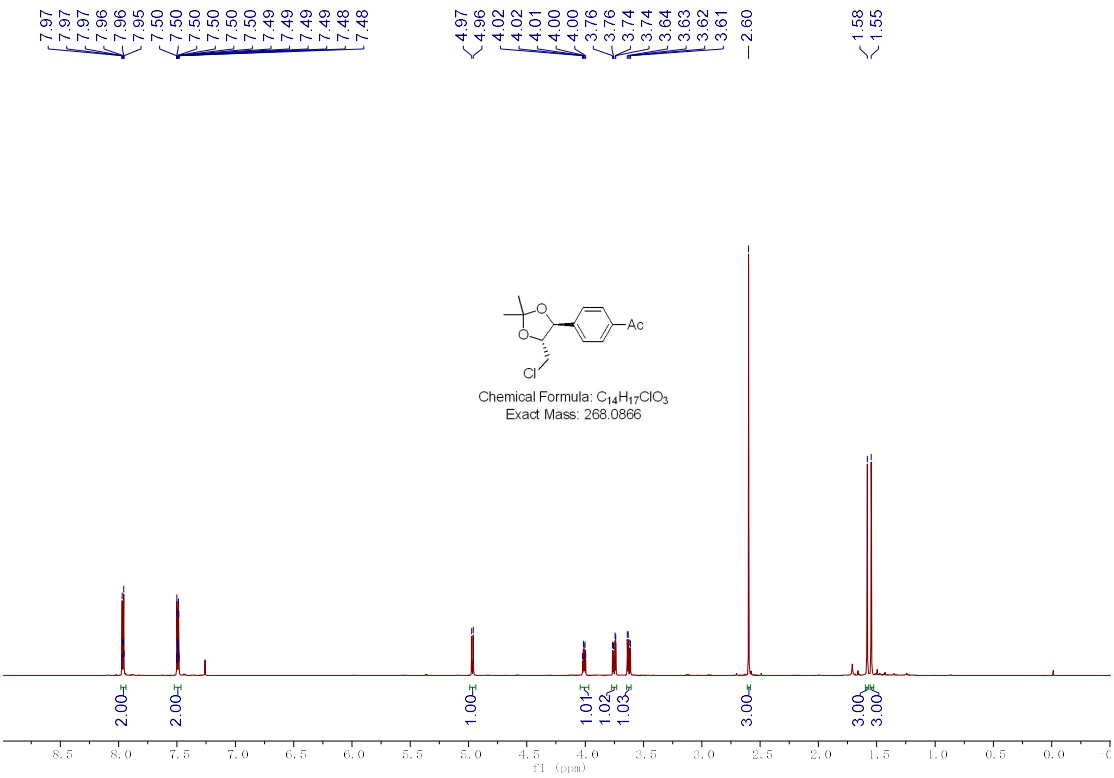
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9a



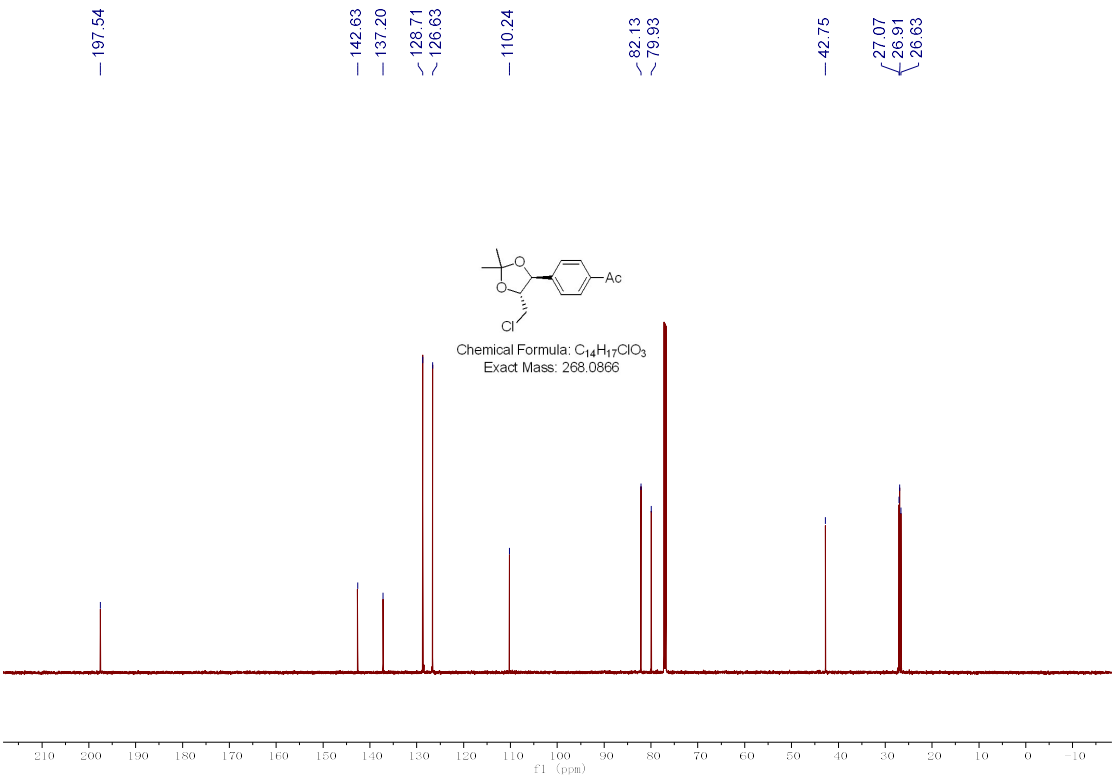
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9a



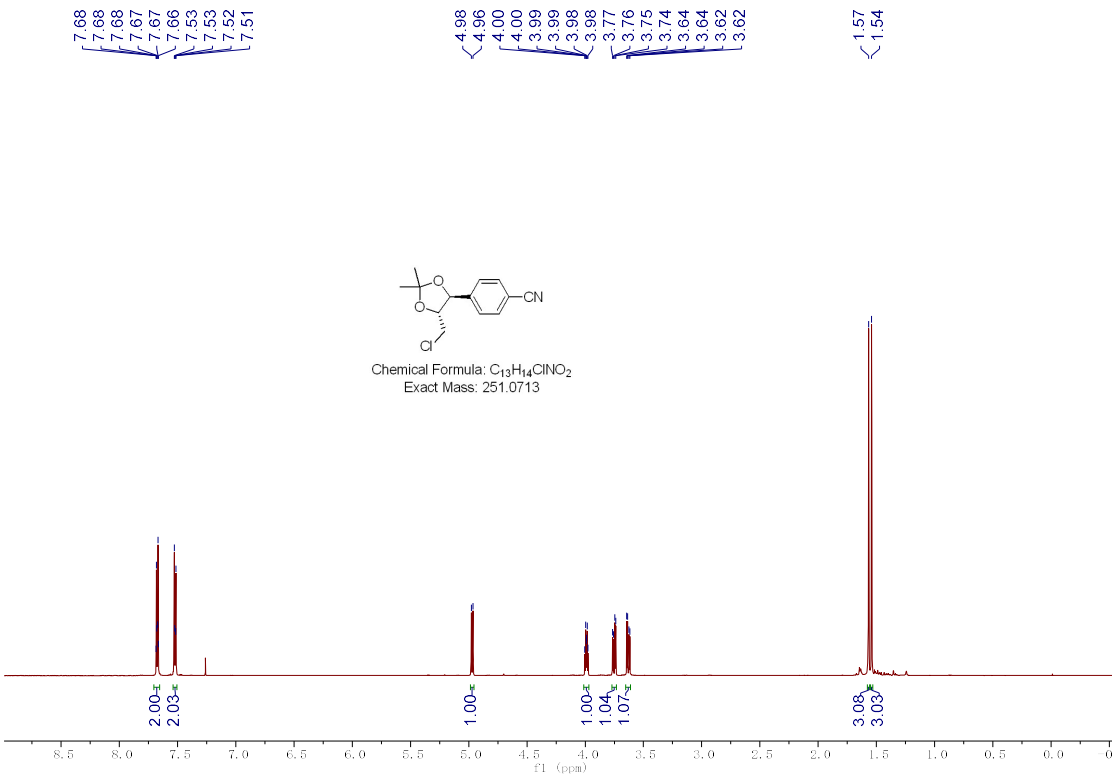
NOE Spectrum of 9a



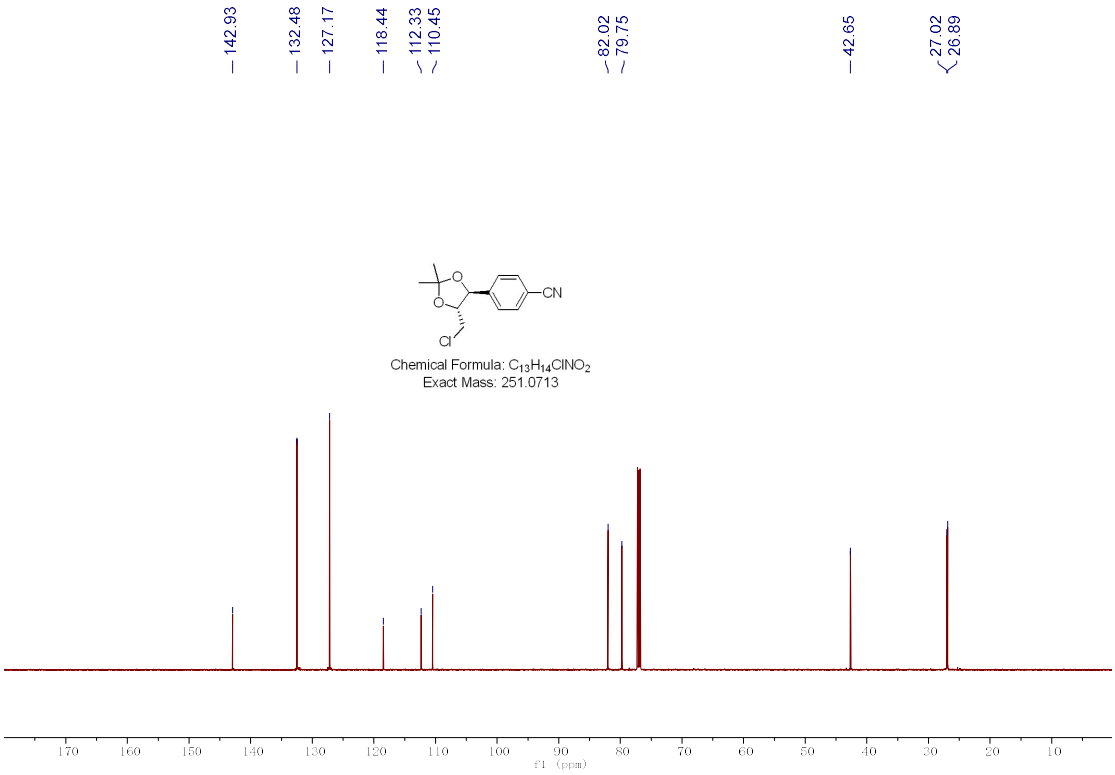
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9b



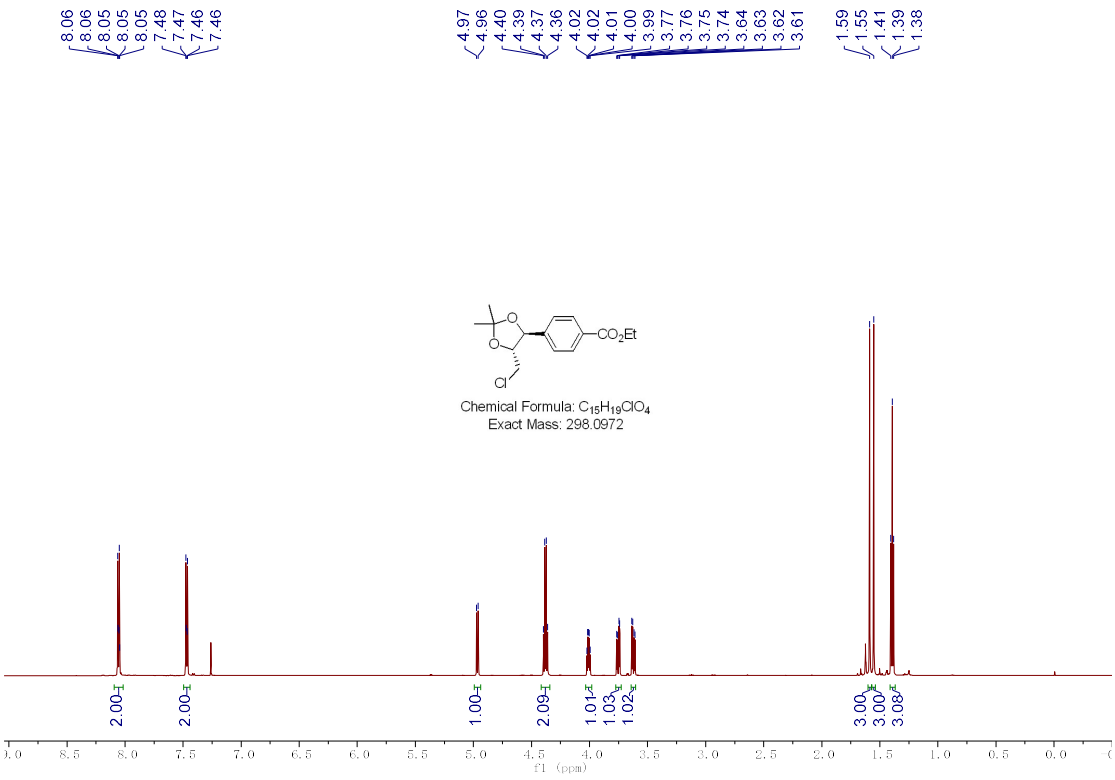
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9b



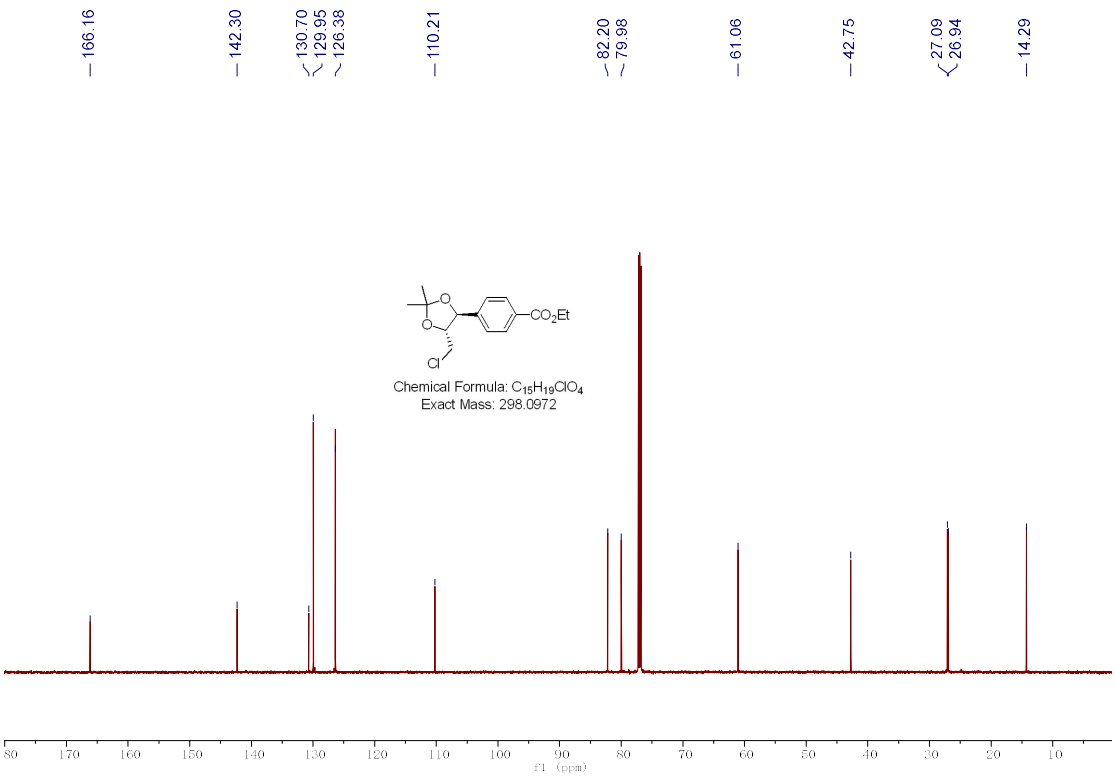
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9c



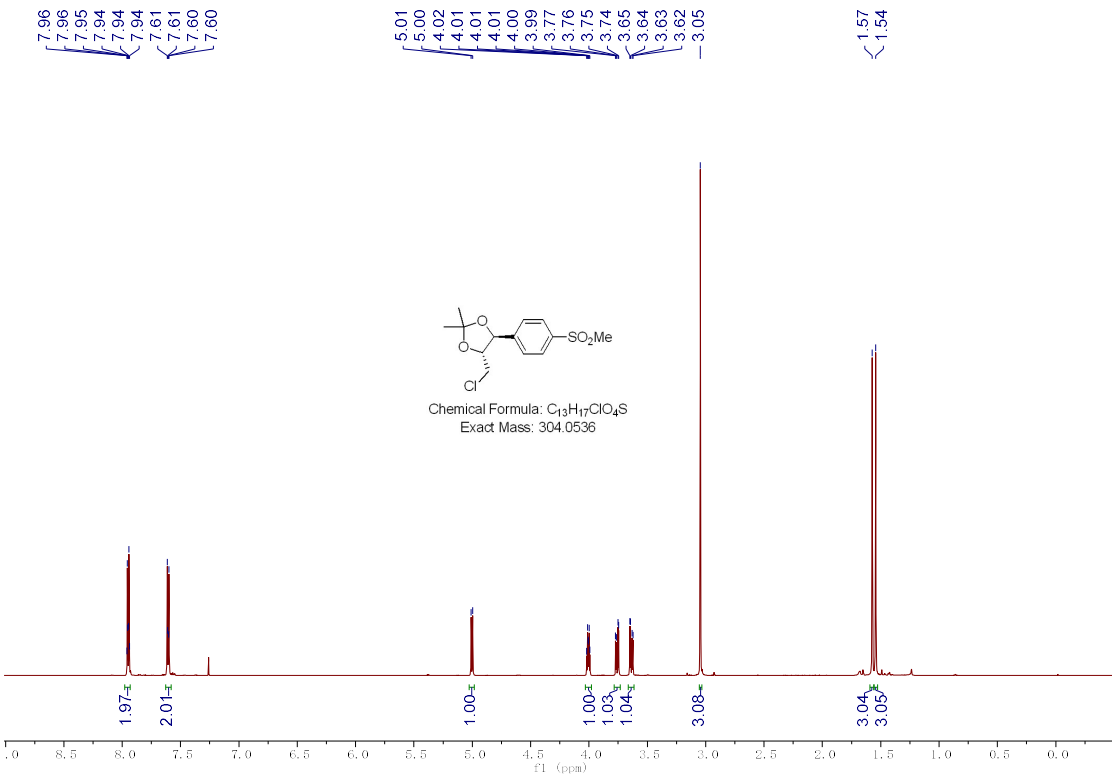
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9c



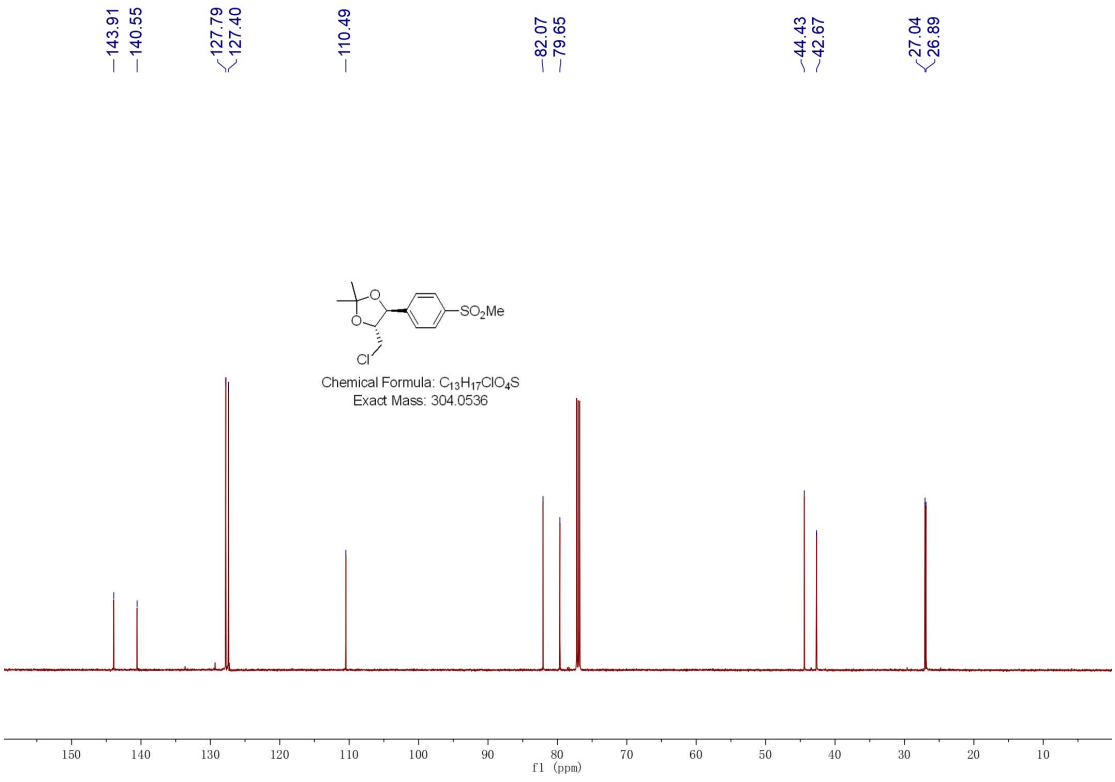
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9d



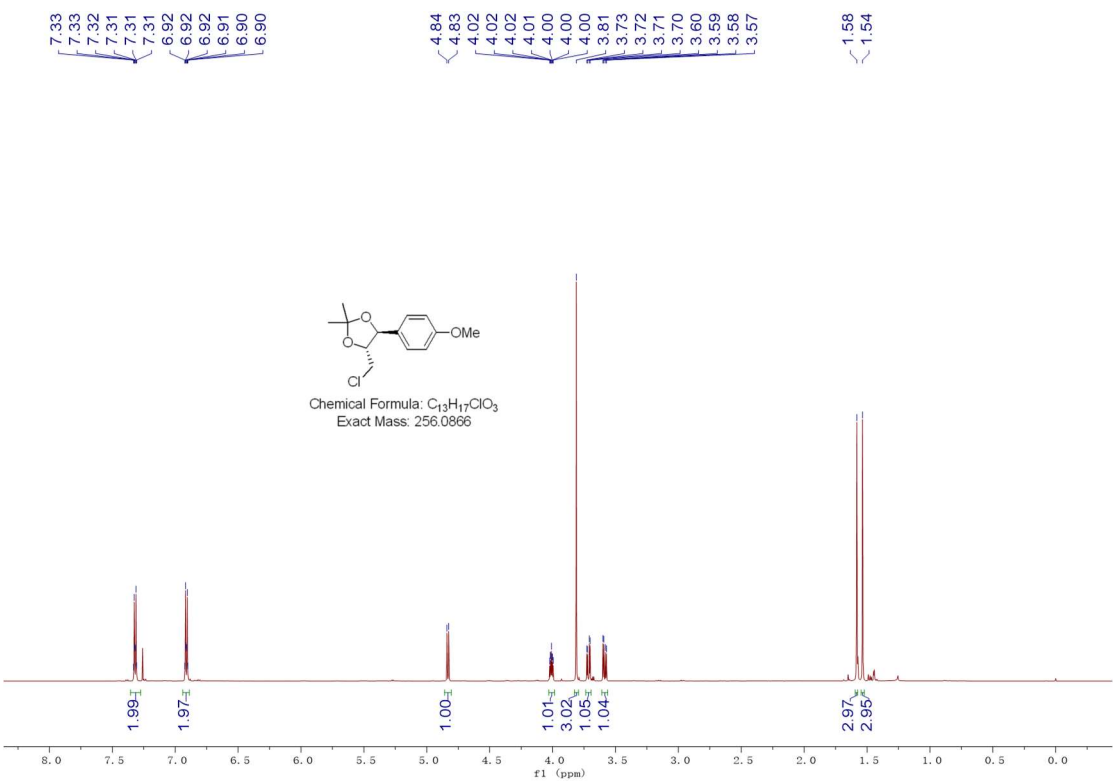
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9d



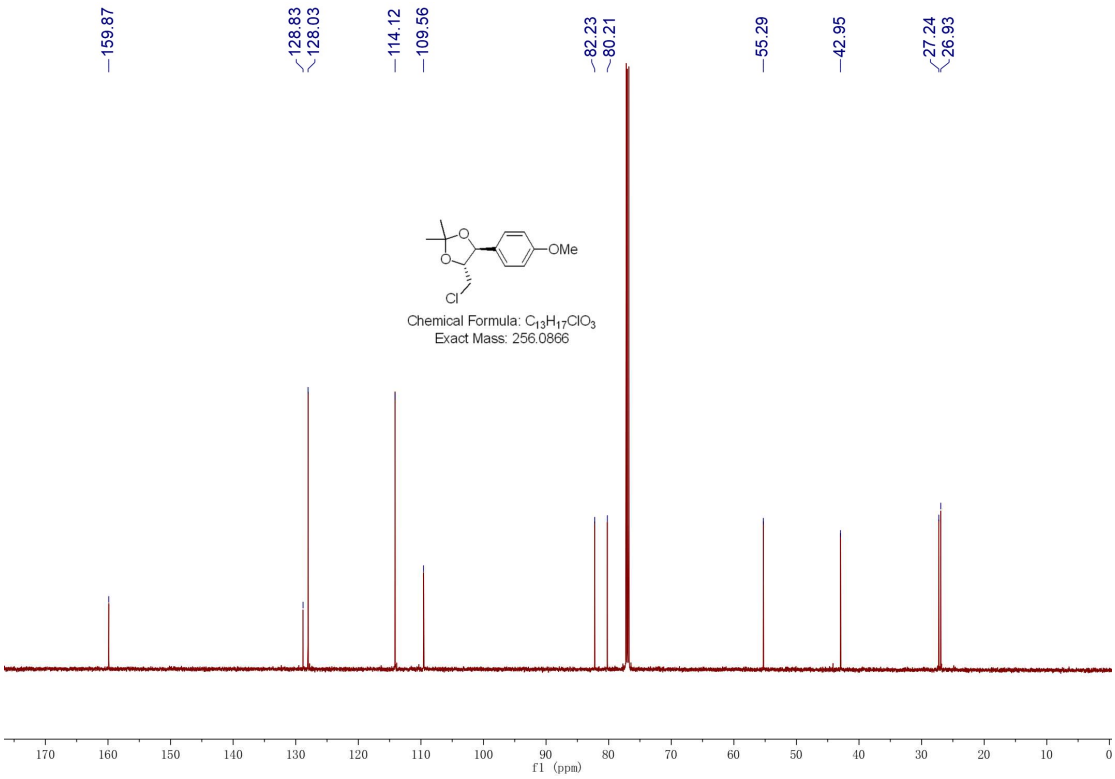
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9e



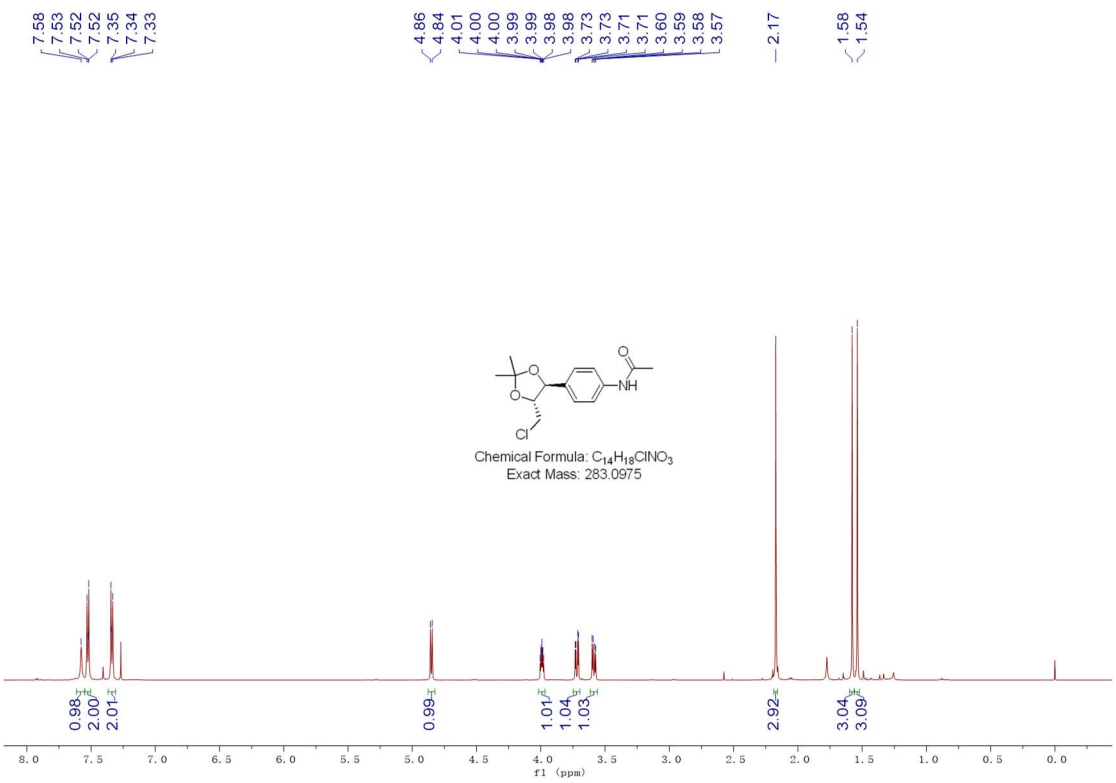
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9e



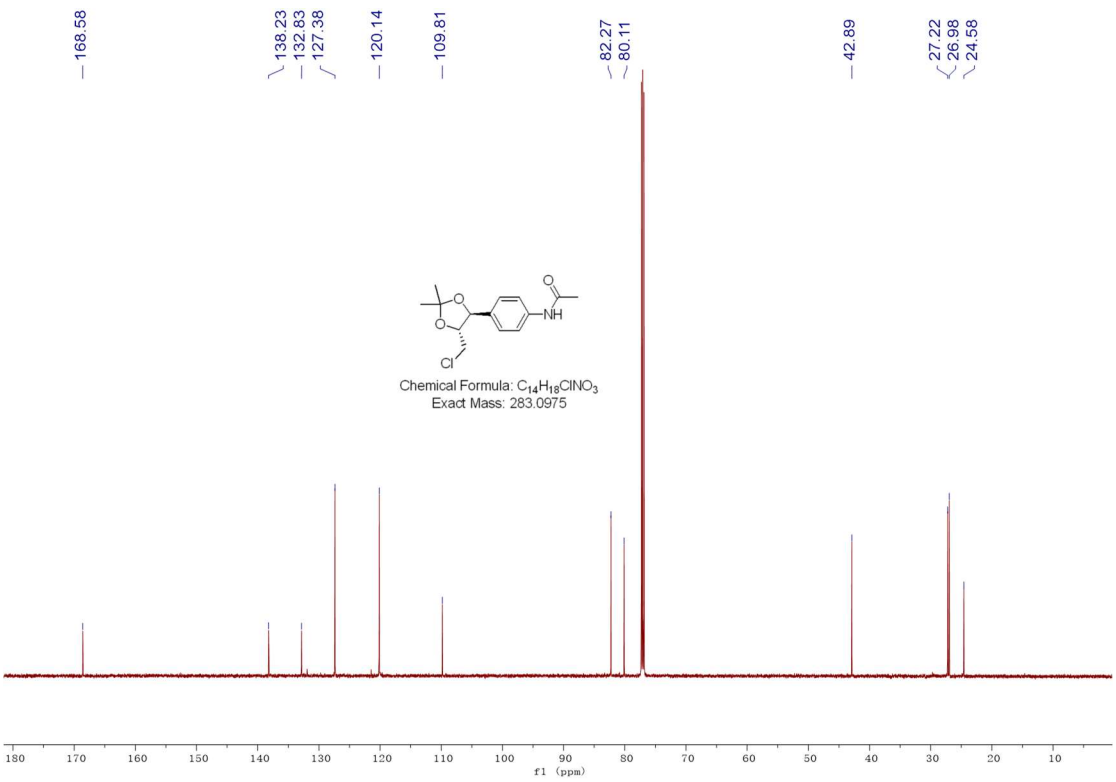
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9f



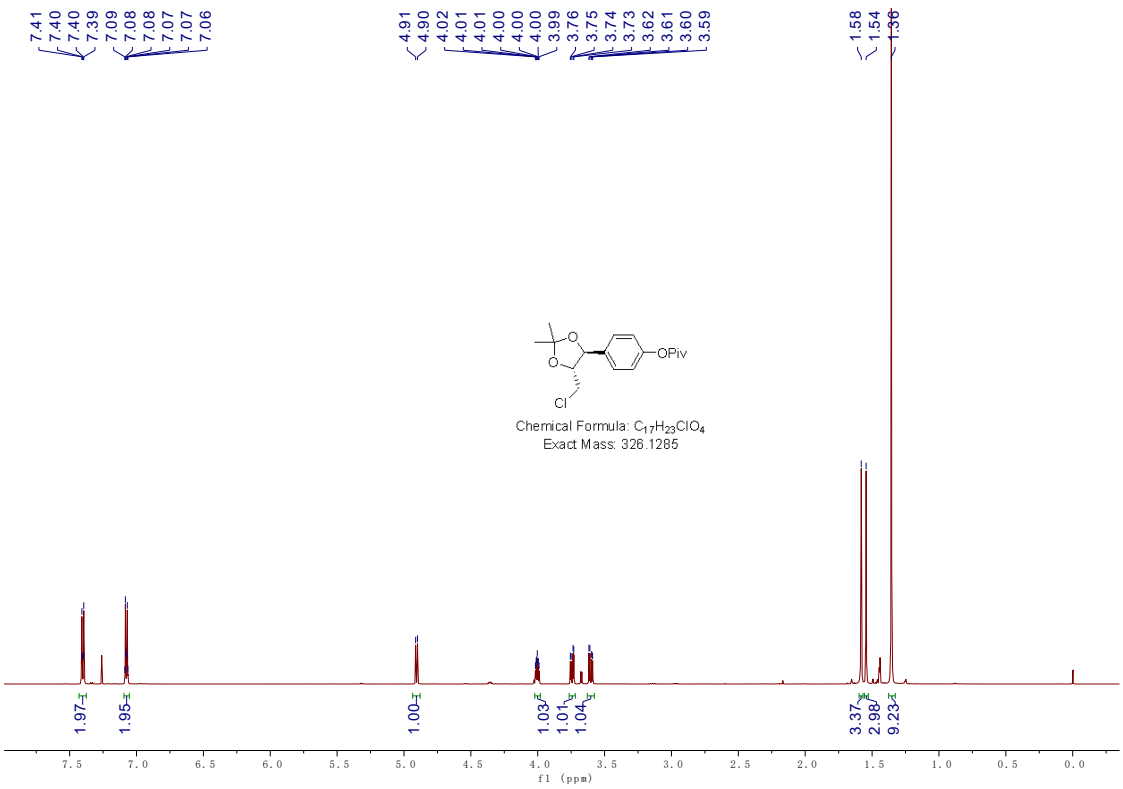
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9f



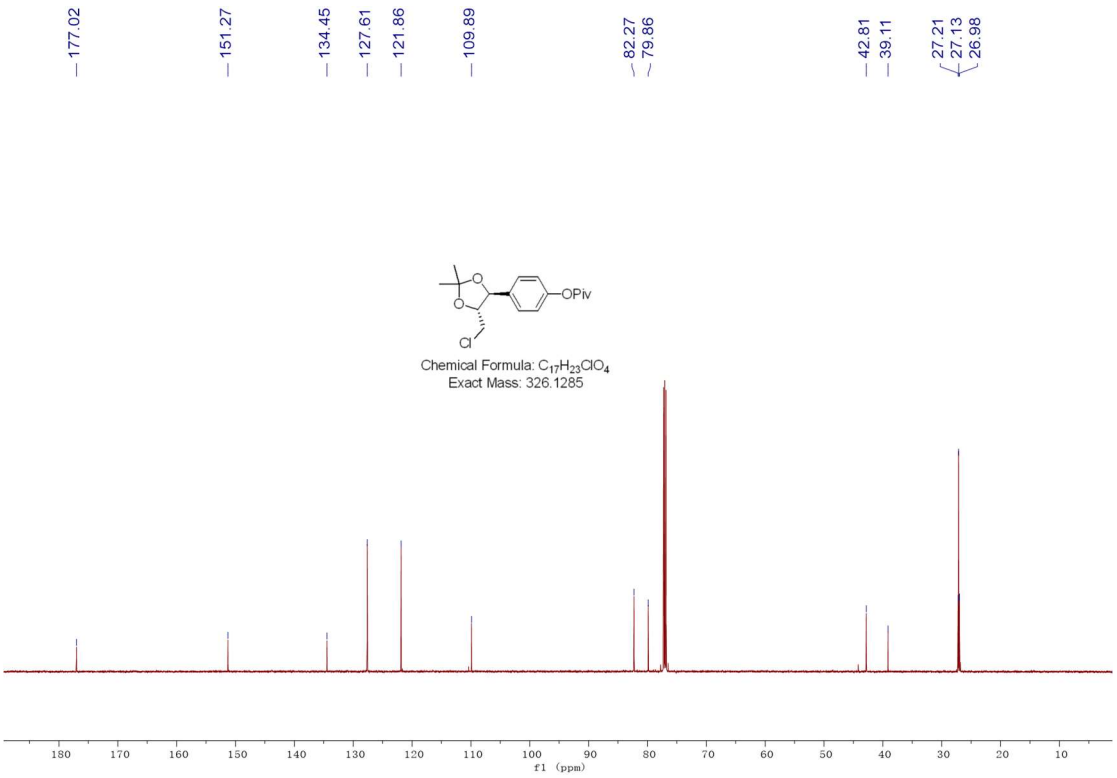
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9g



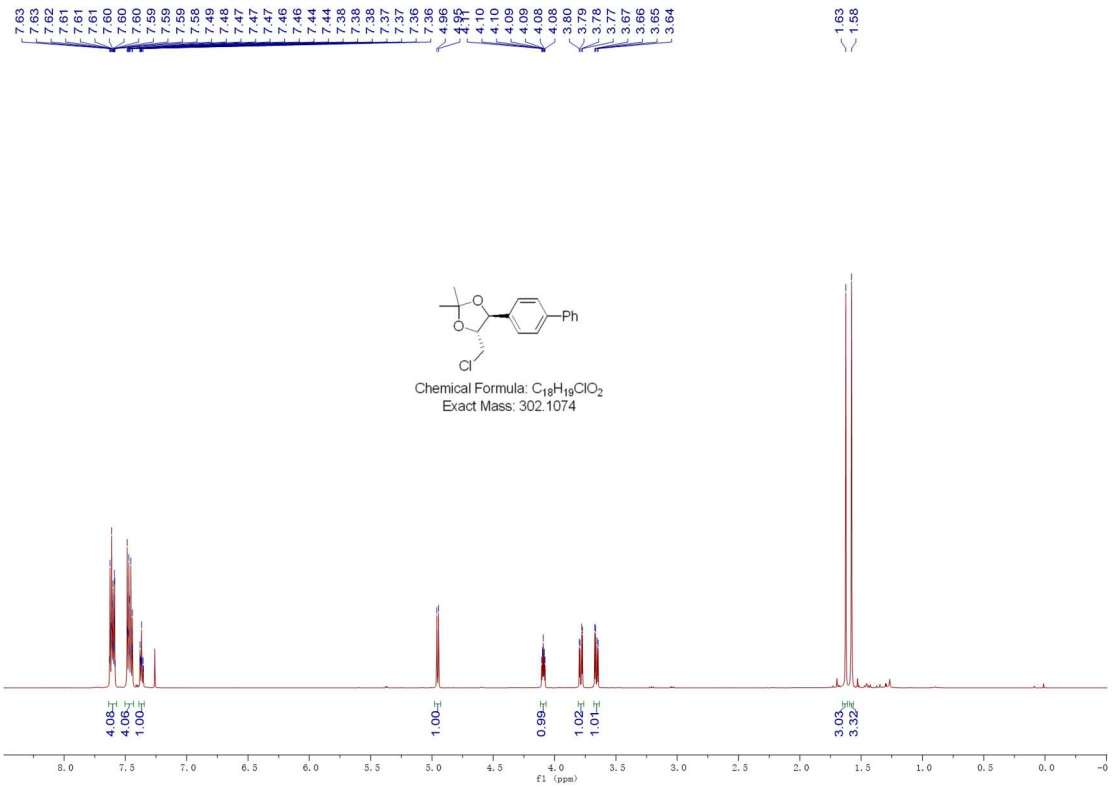
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9g



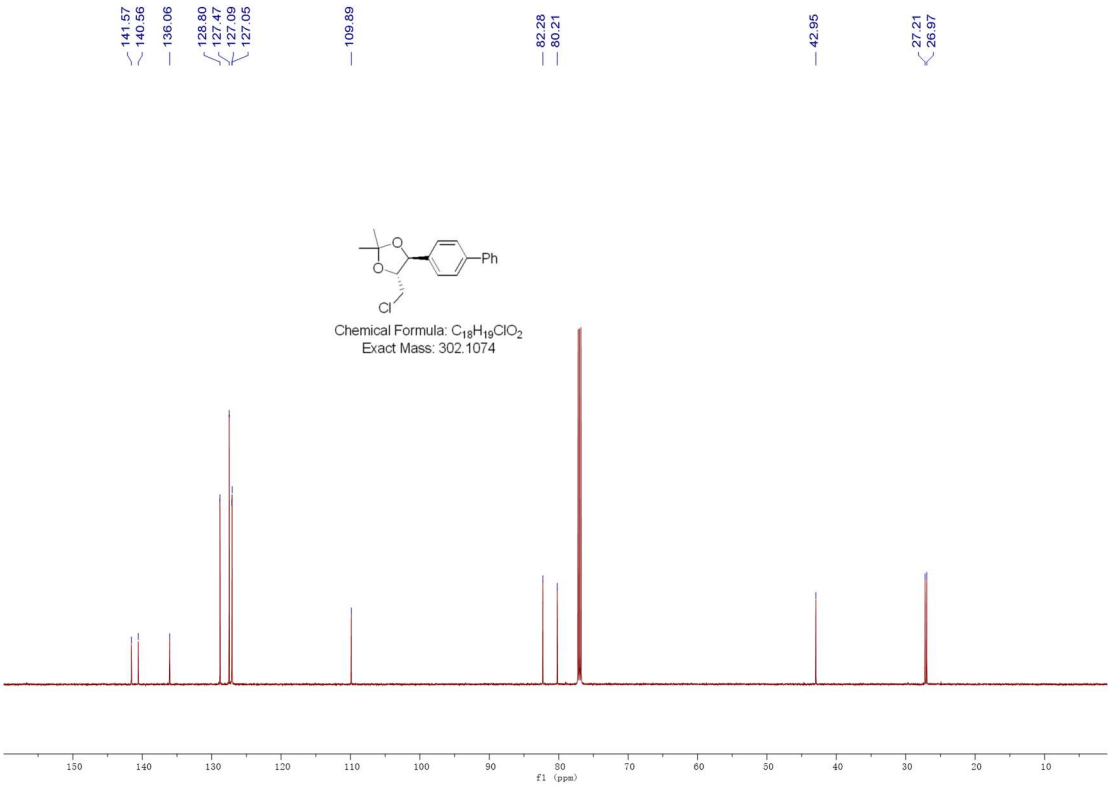
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9h



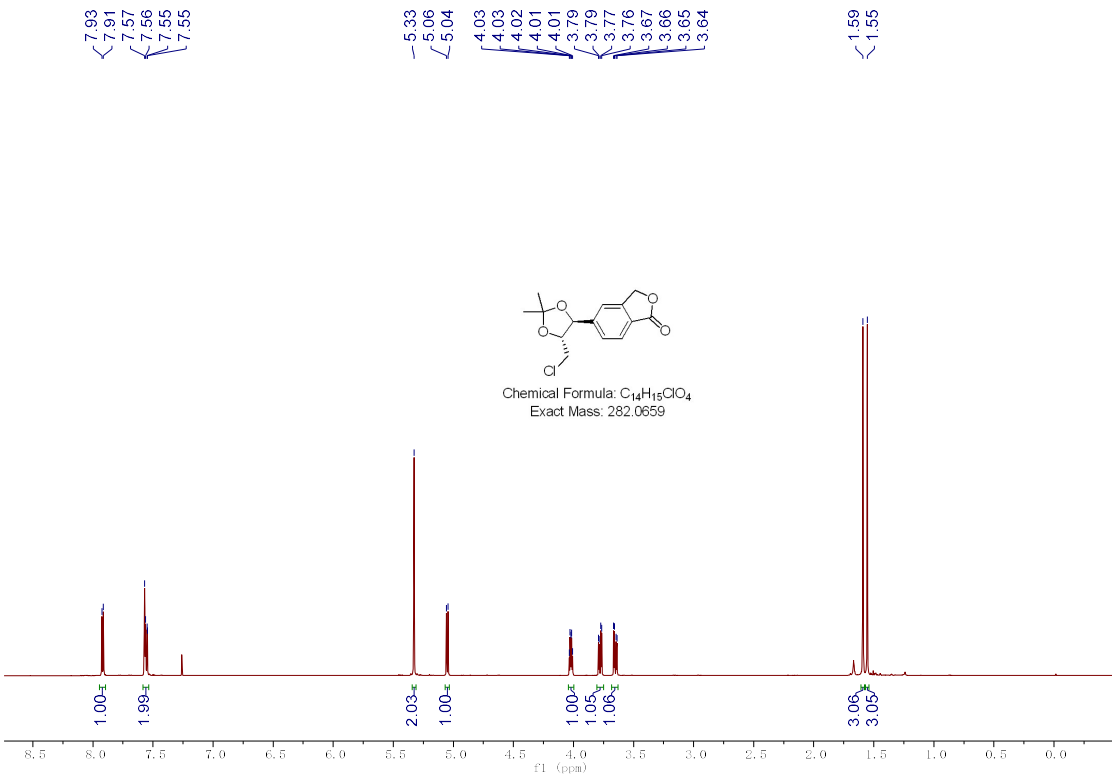
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9h



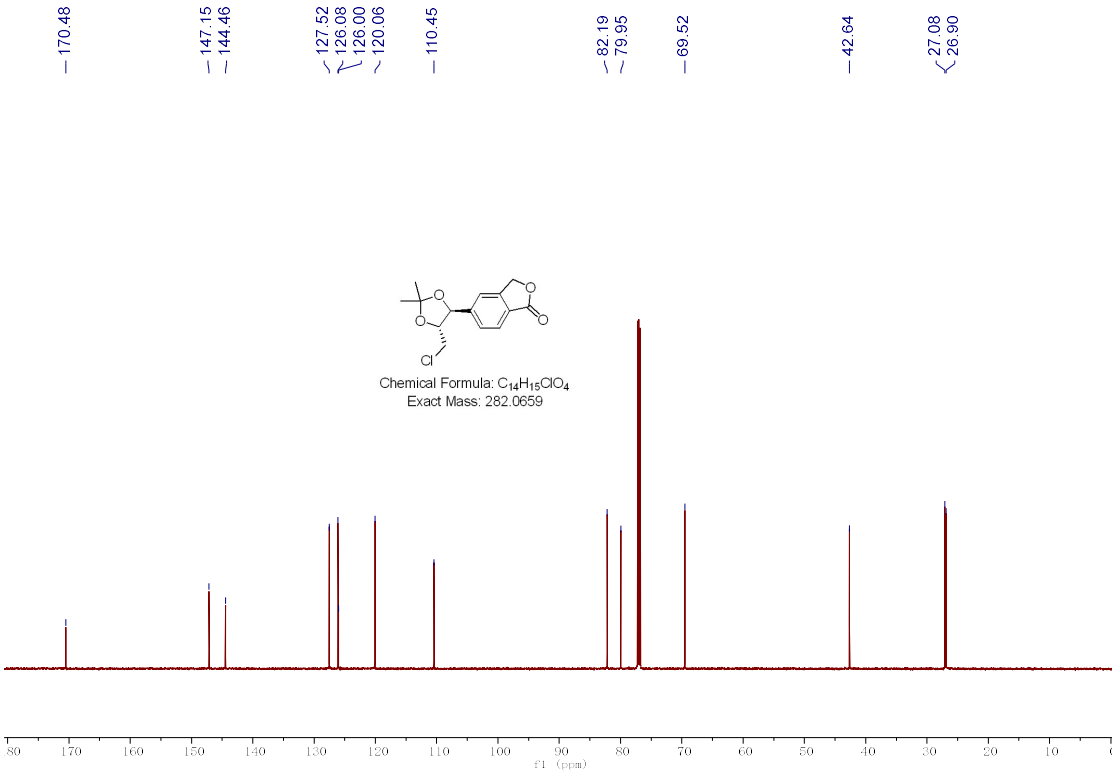
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9i



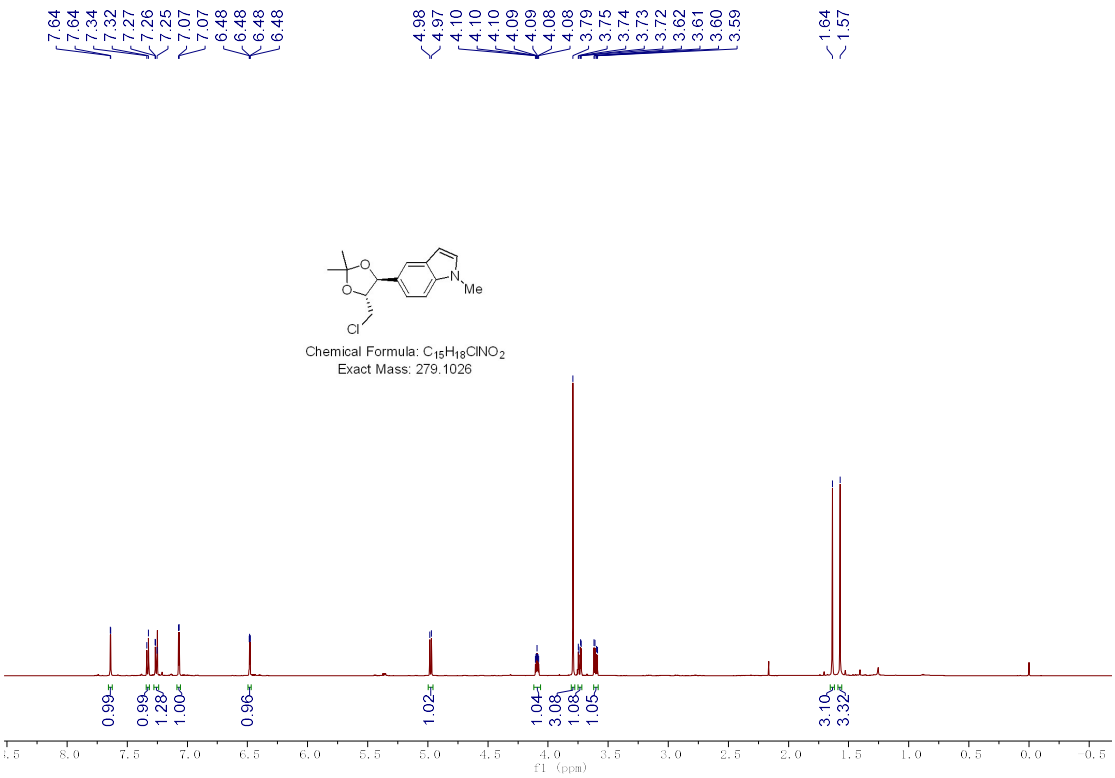
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9i



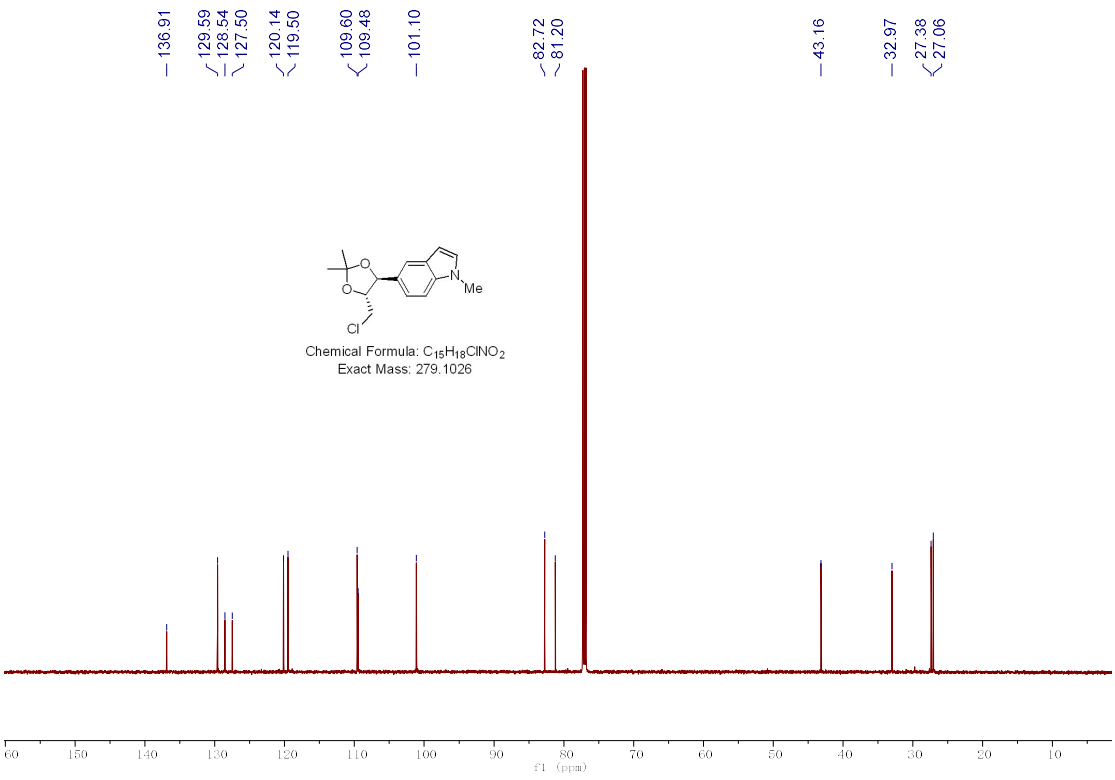
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9j



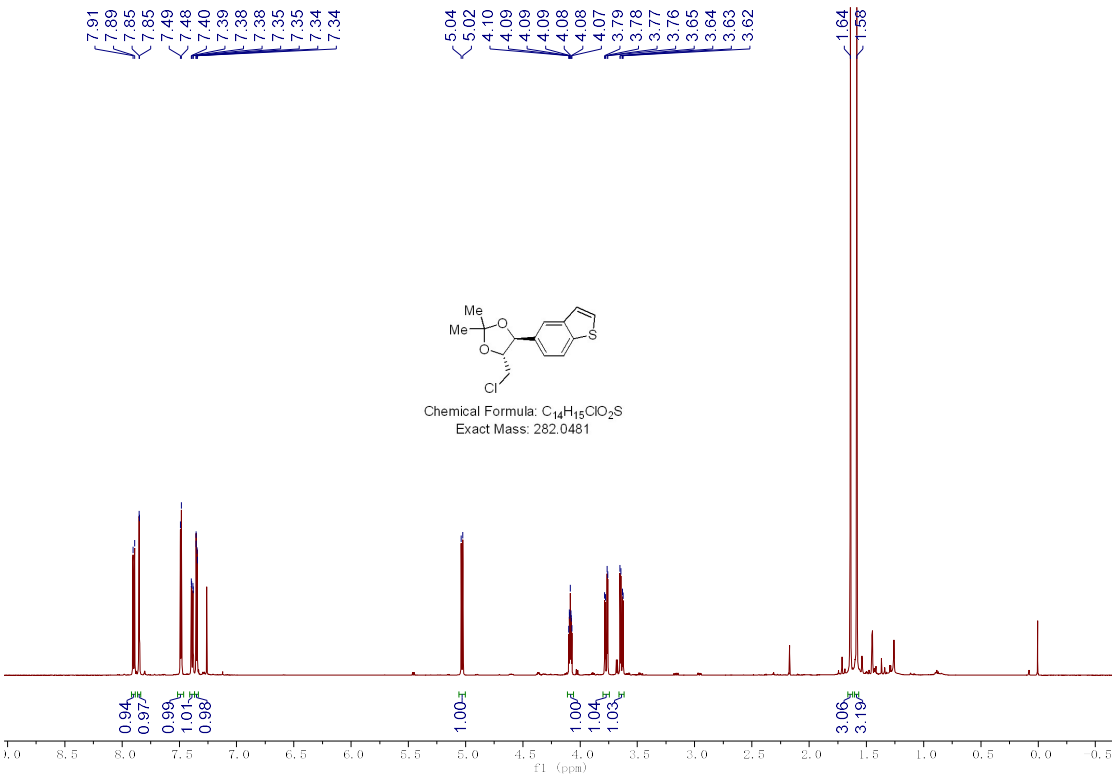
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9j



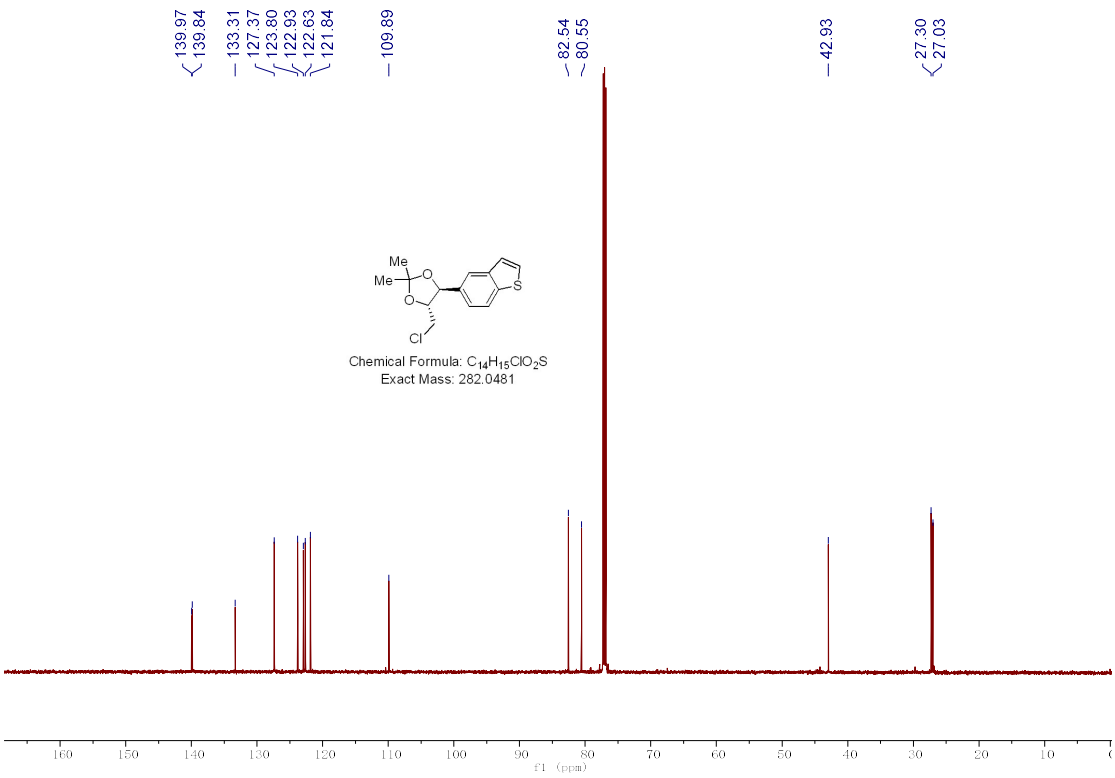
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9k



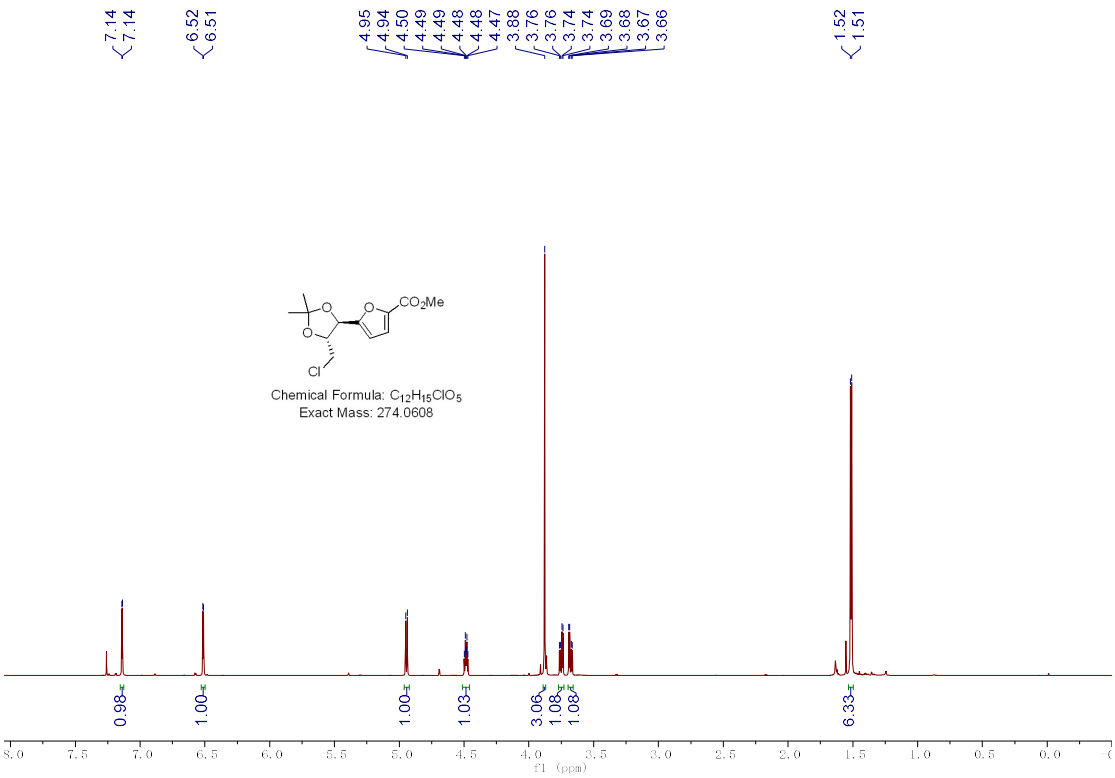
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9k



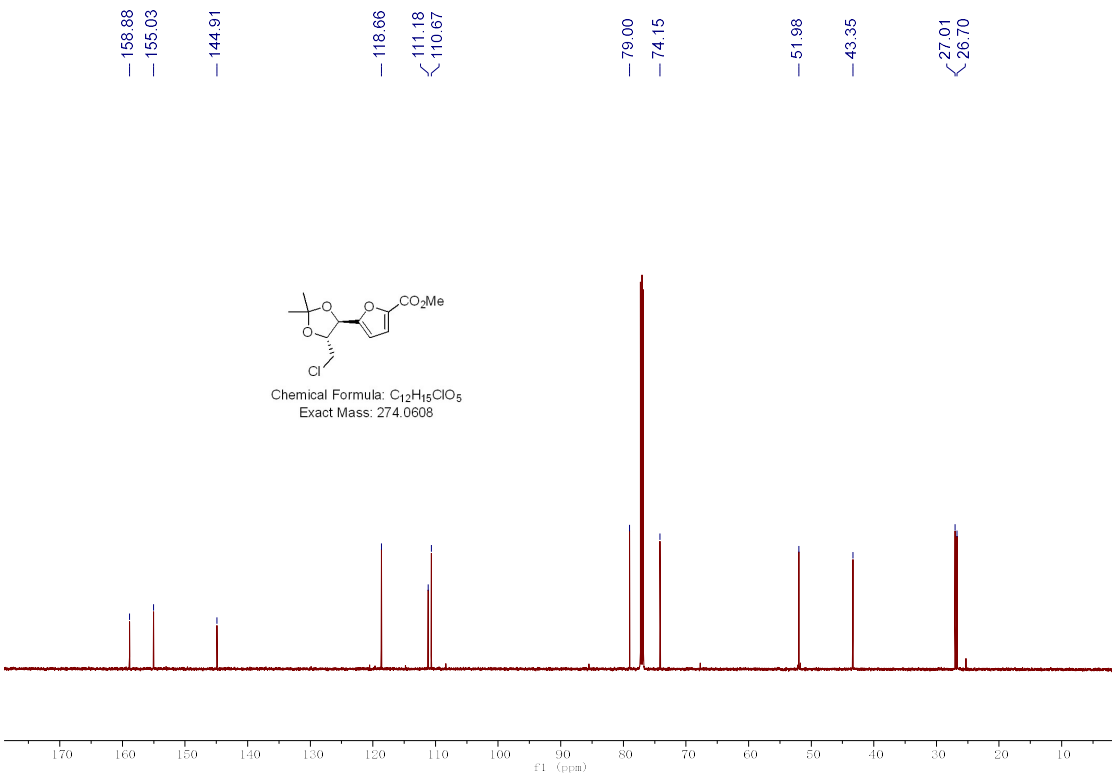
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9l



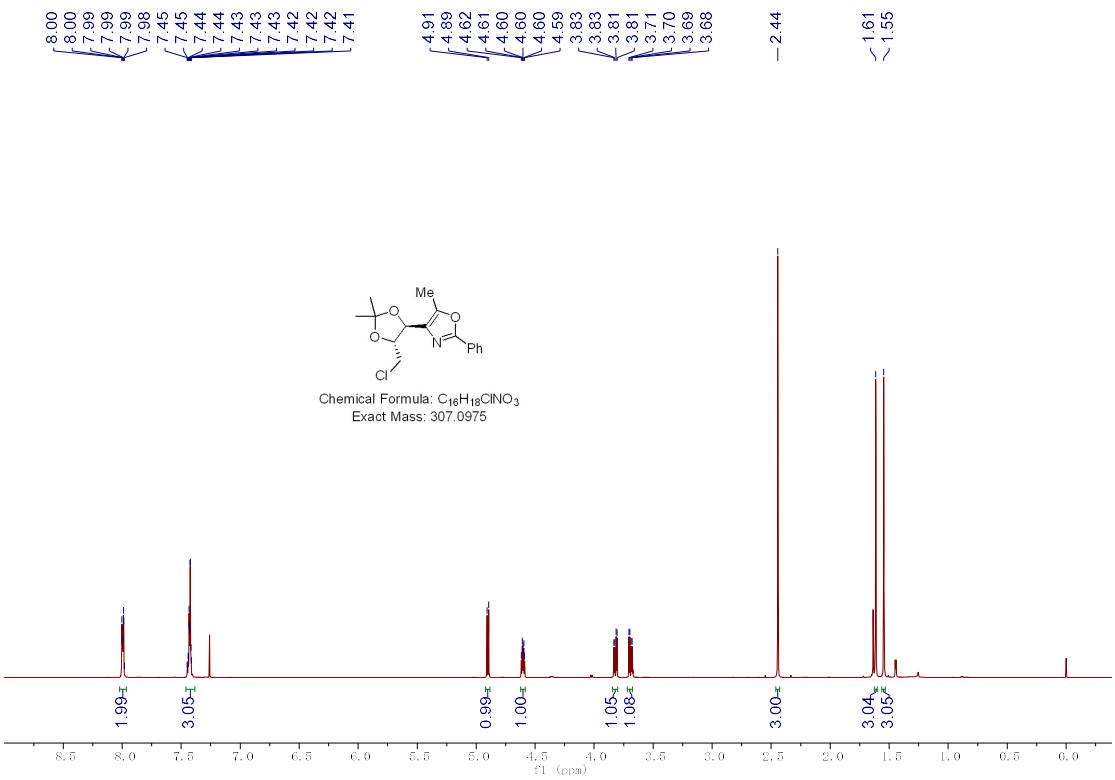
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9l



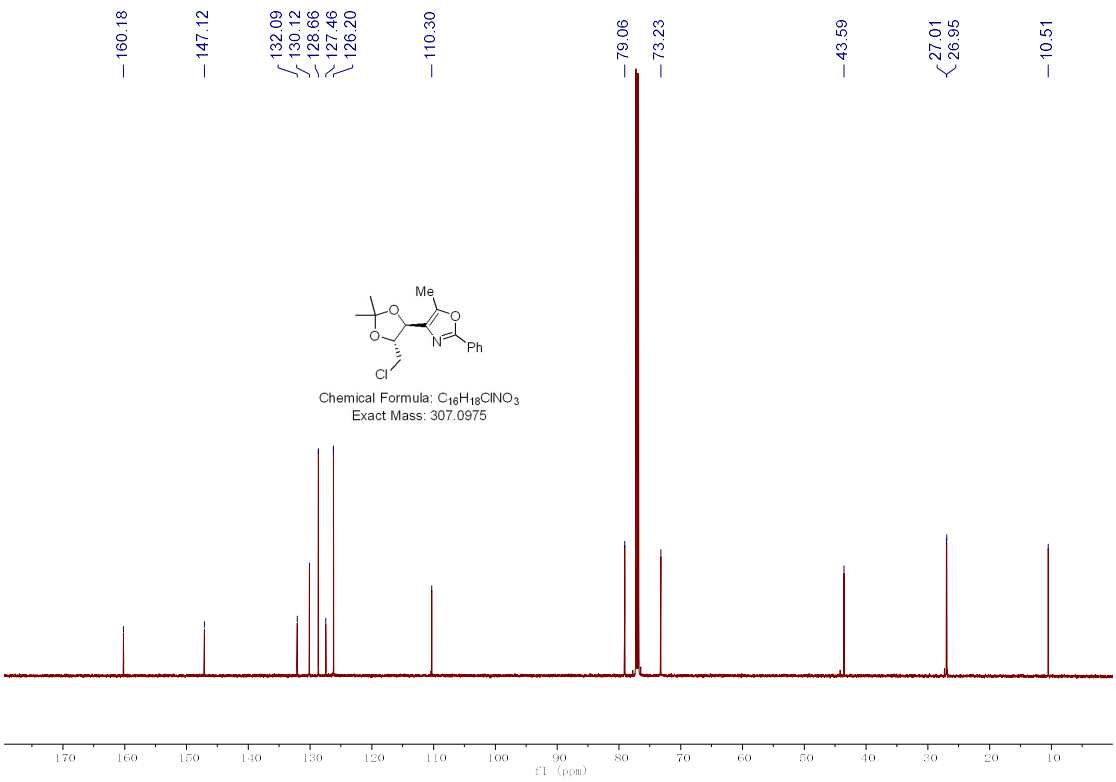
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9m



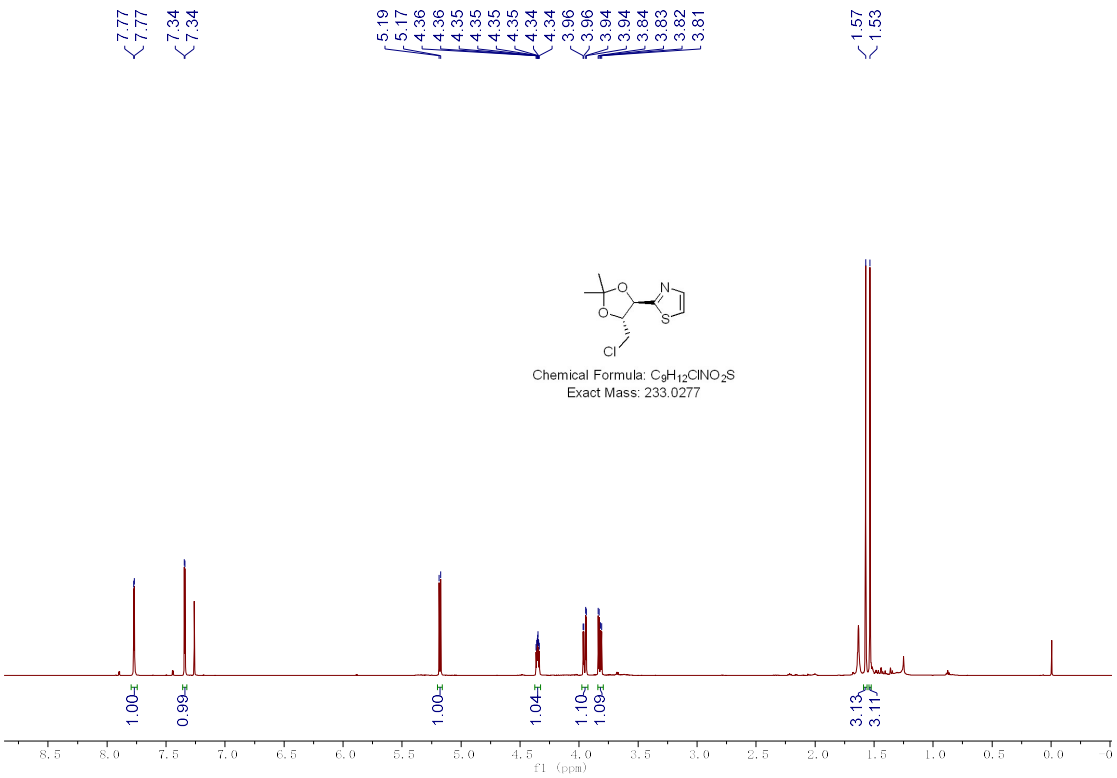
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9m



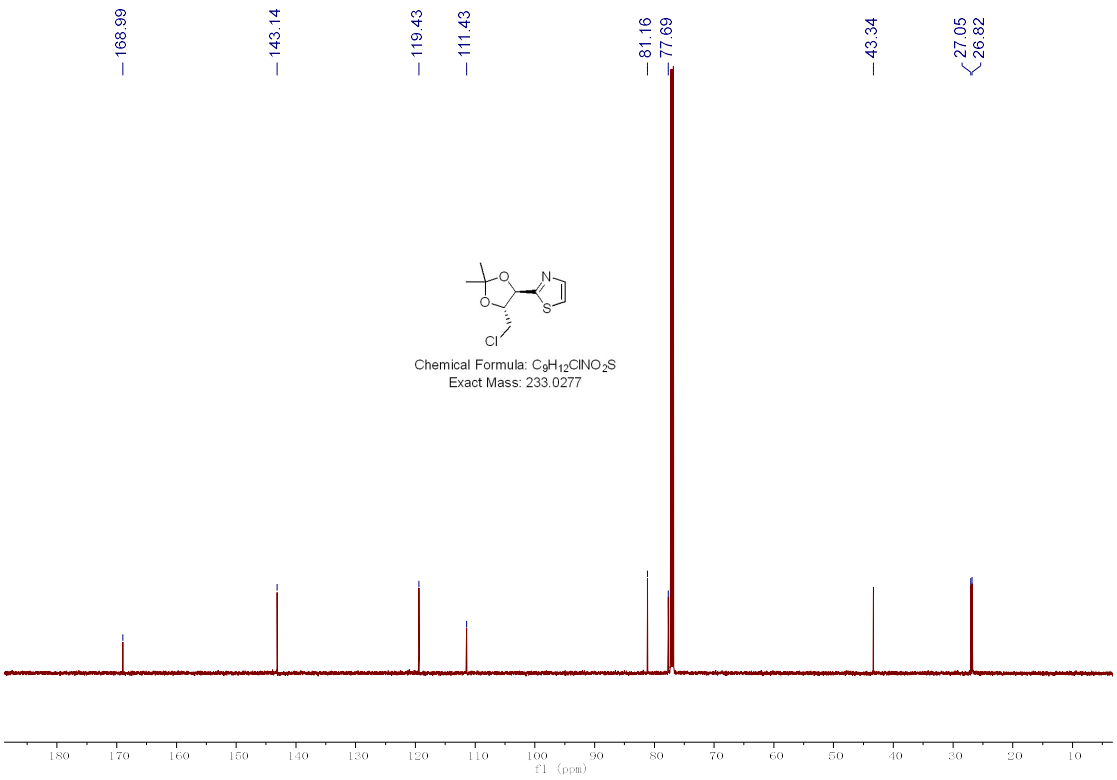
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9n



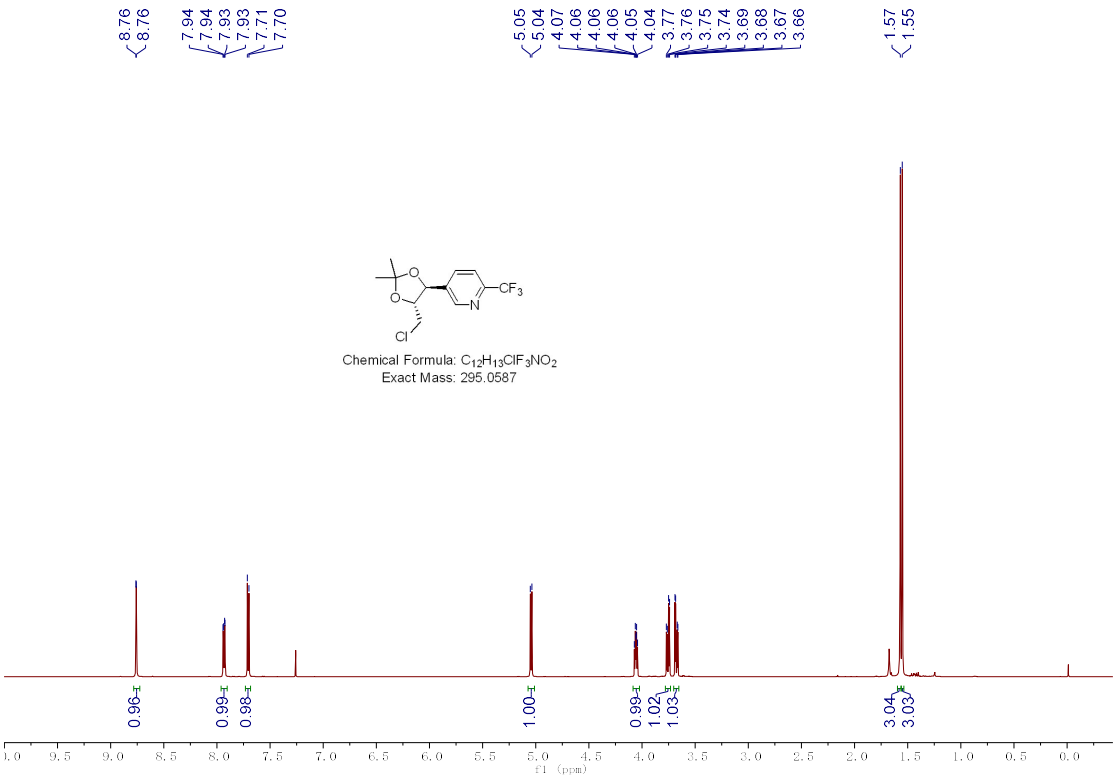
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9n



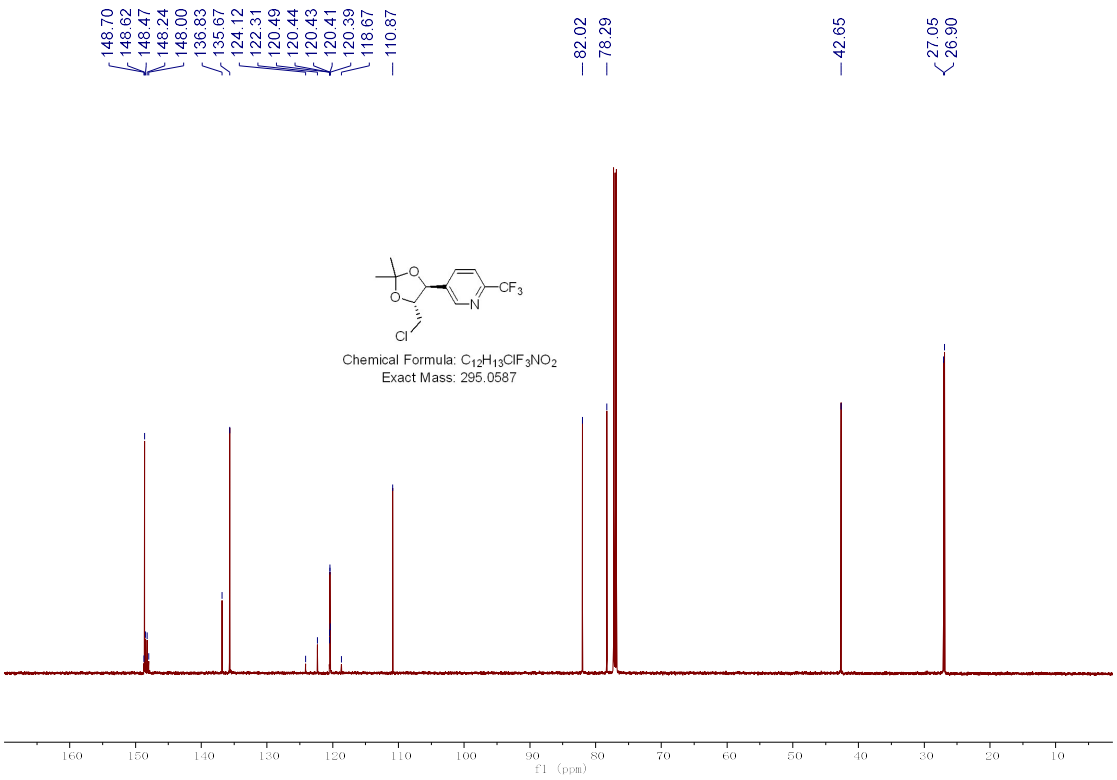
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9o



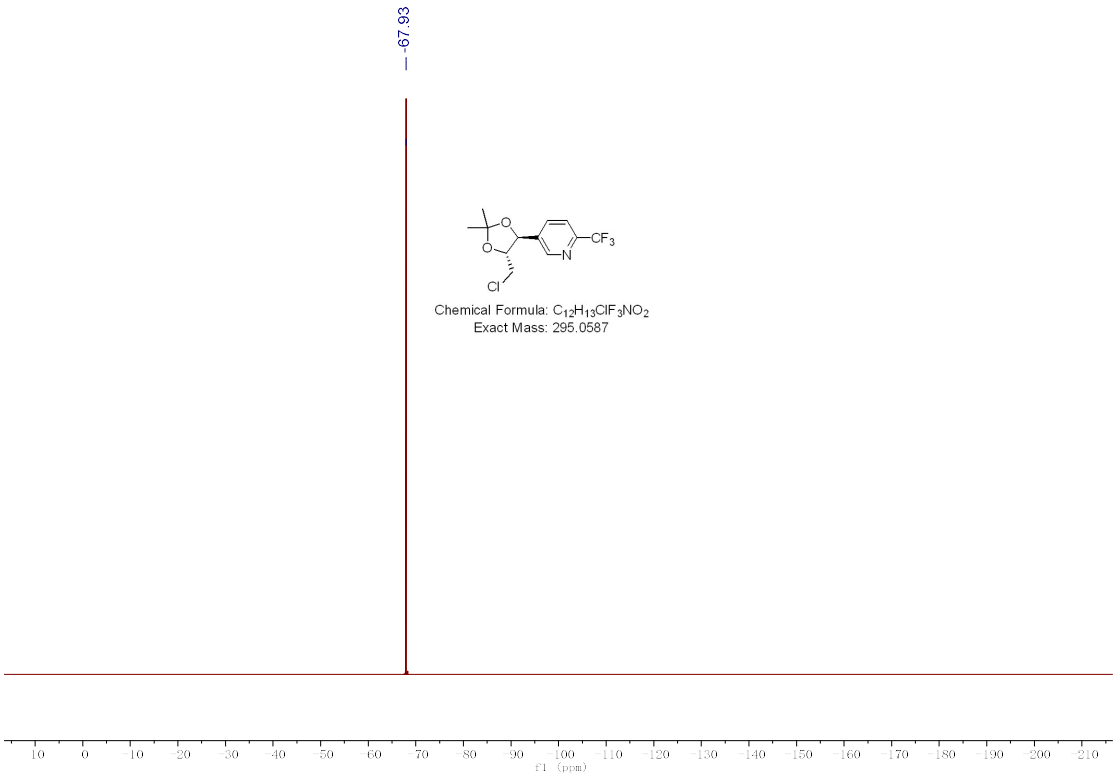
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9o



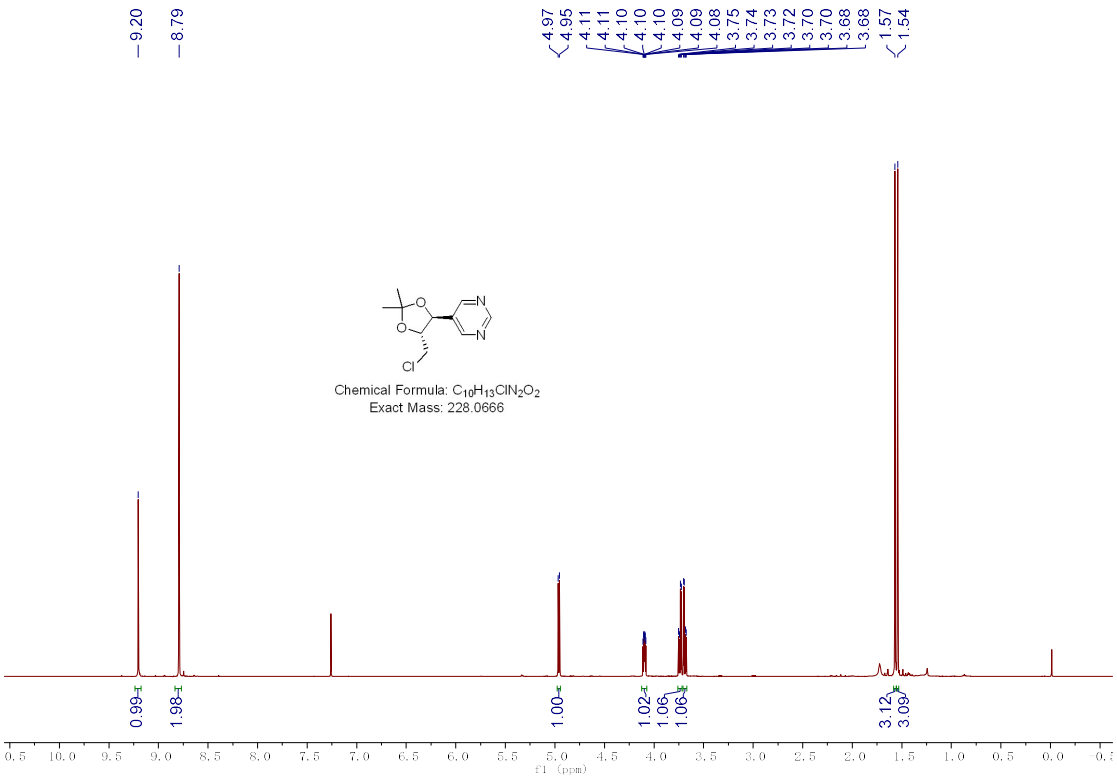
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9p



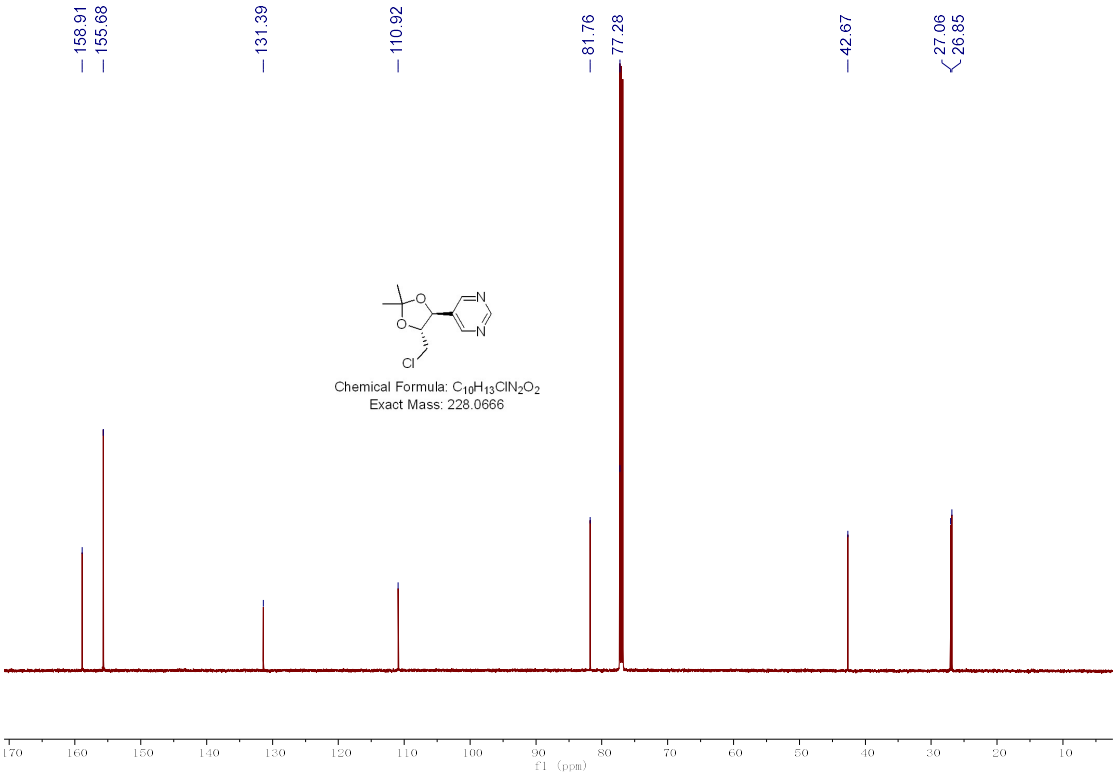
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9p



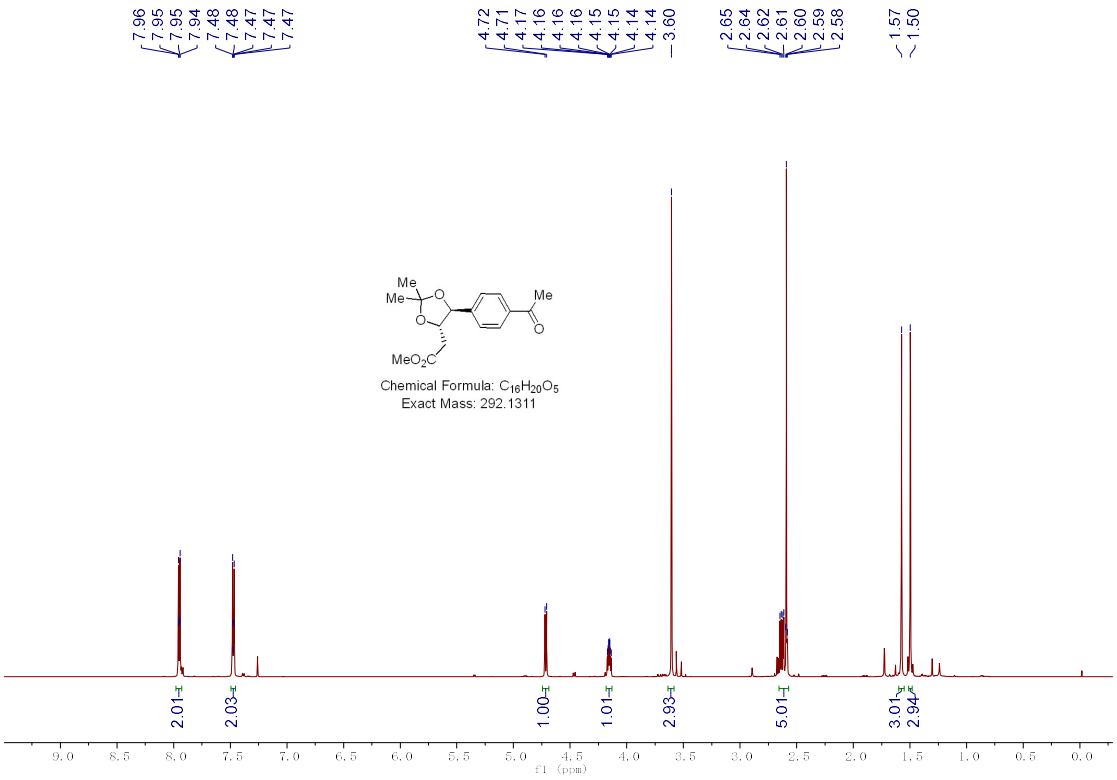
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of 9p



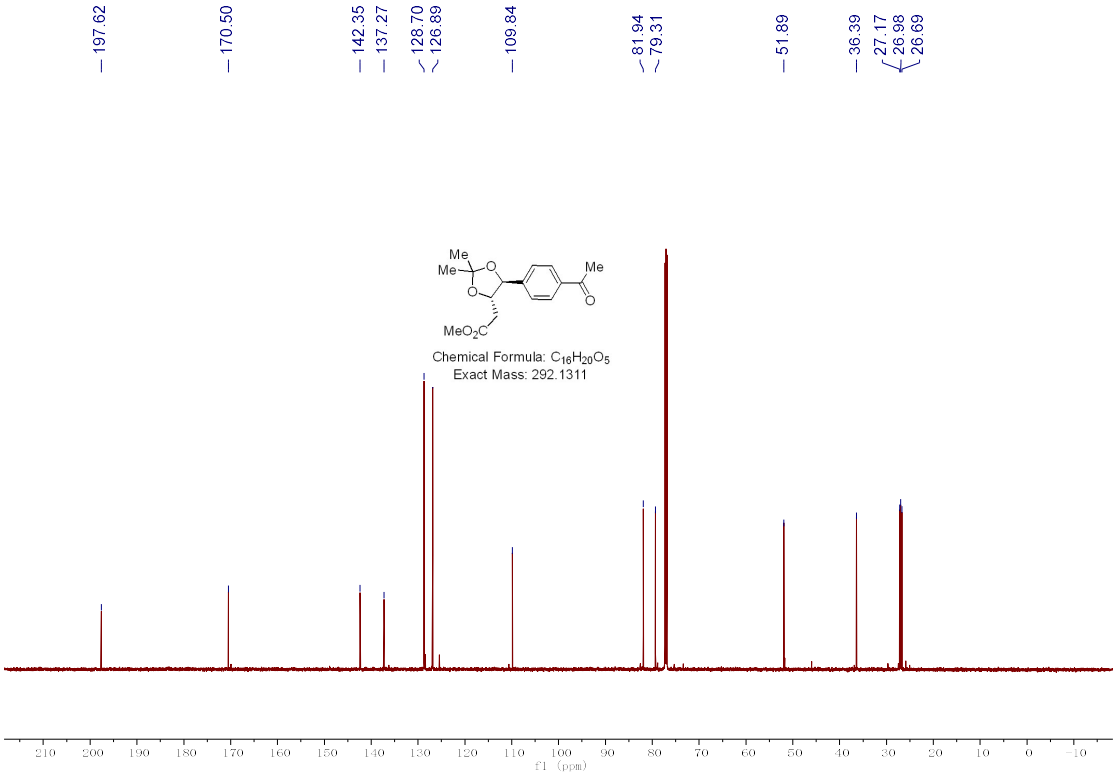
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9q



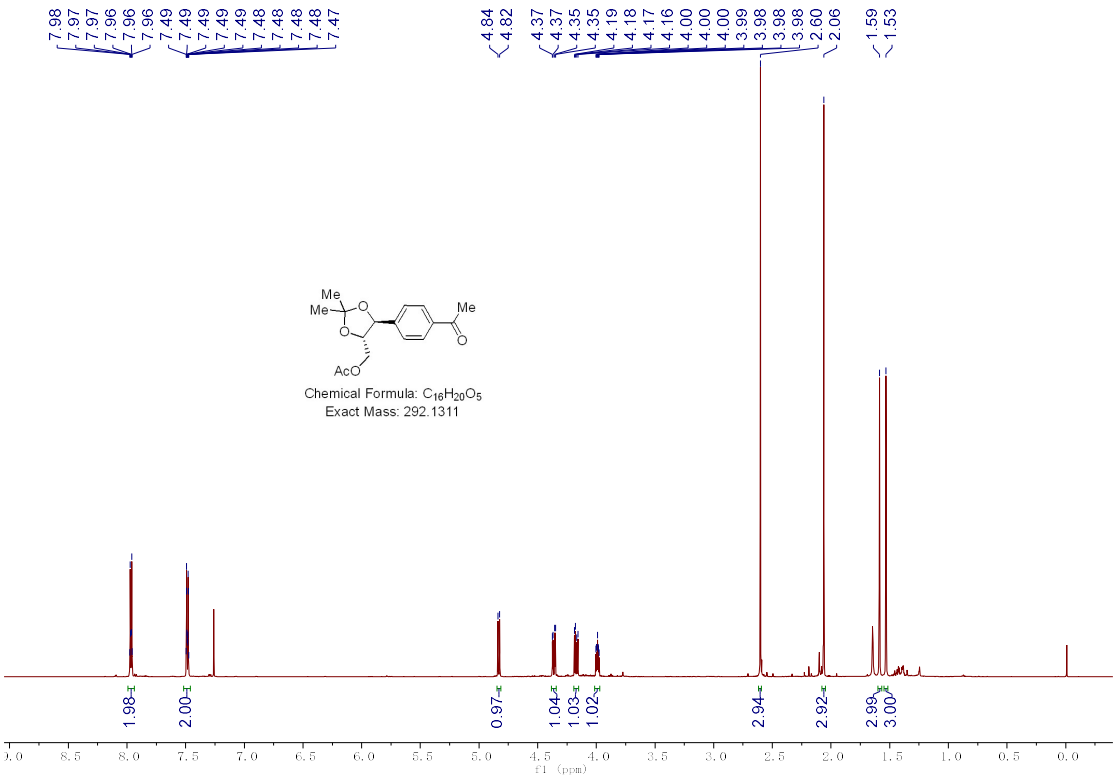
^{13}C NMR (565 MHz, $CDCl_3$) Spectrum of 9q



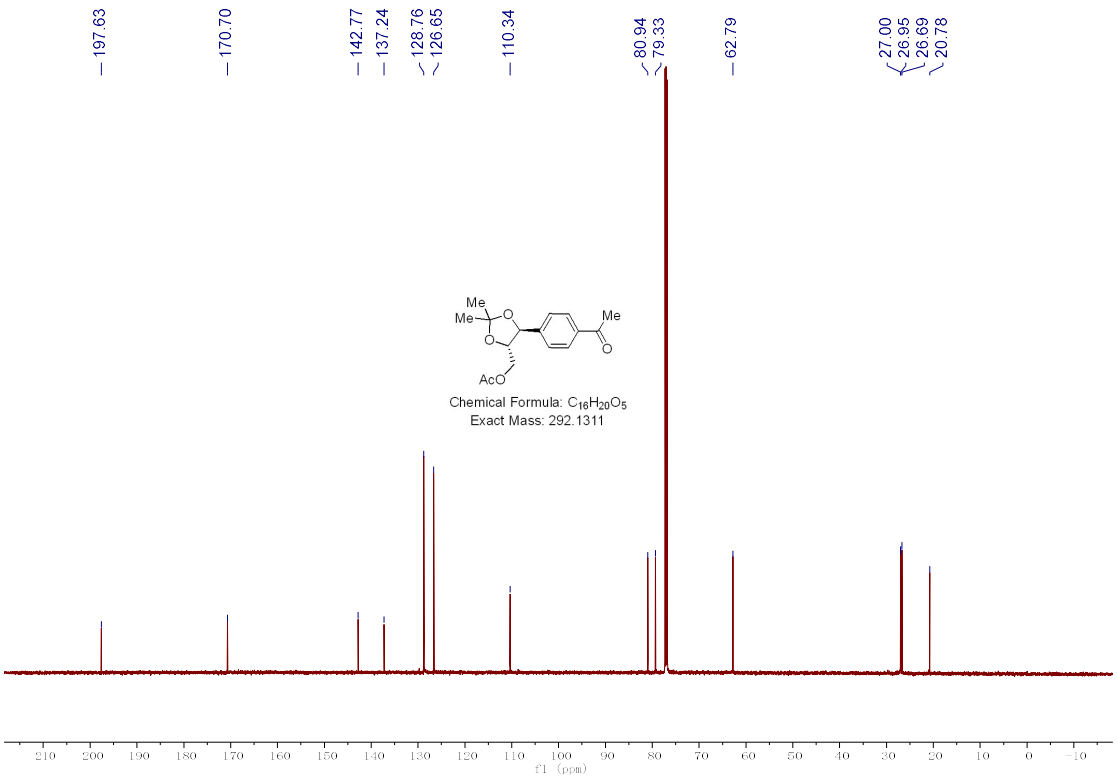
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9r



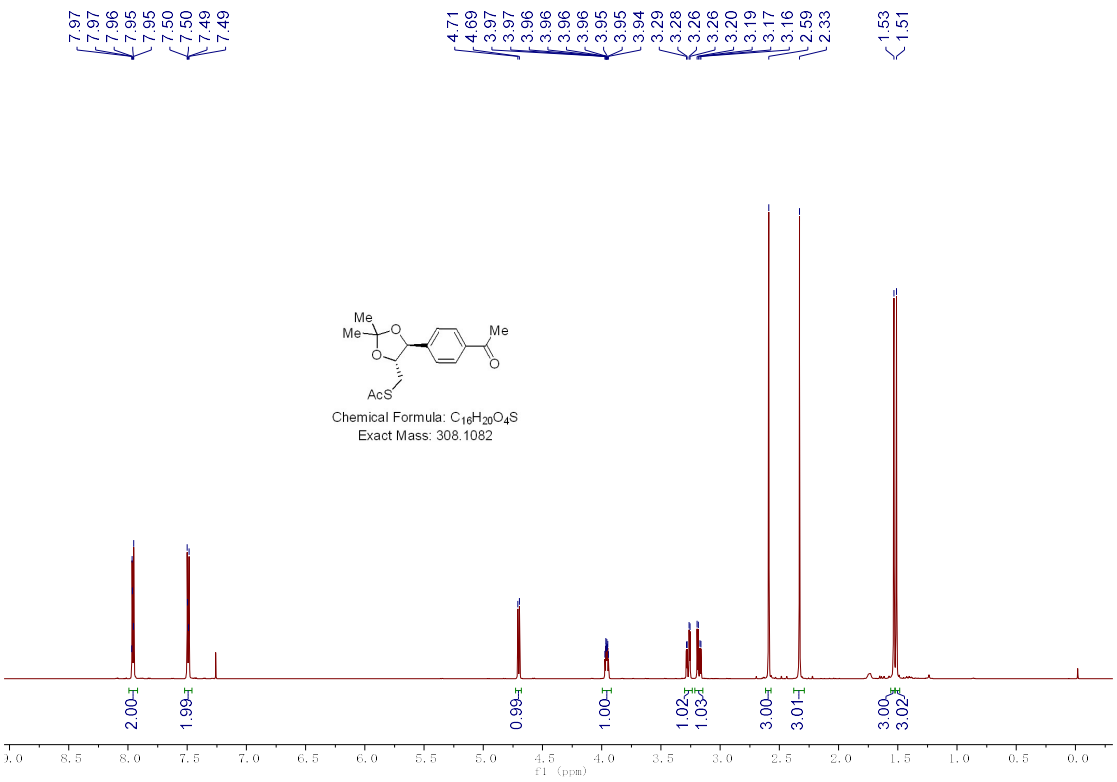
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9r



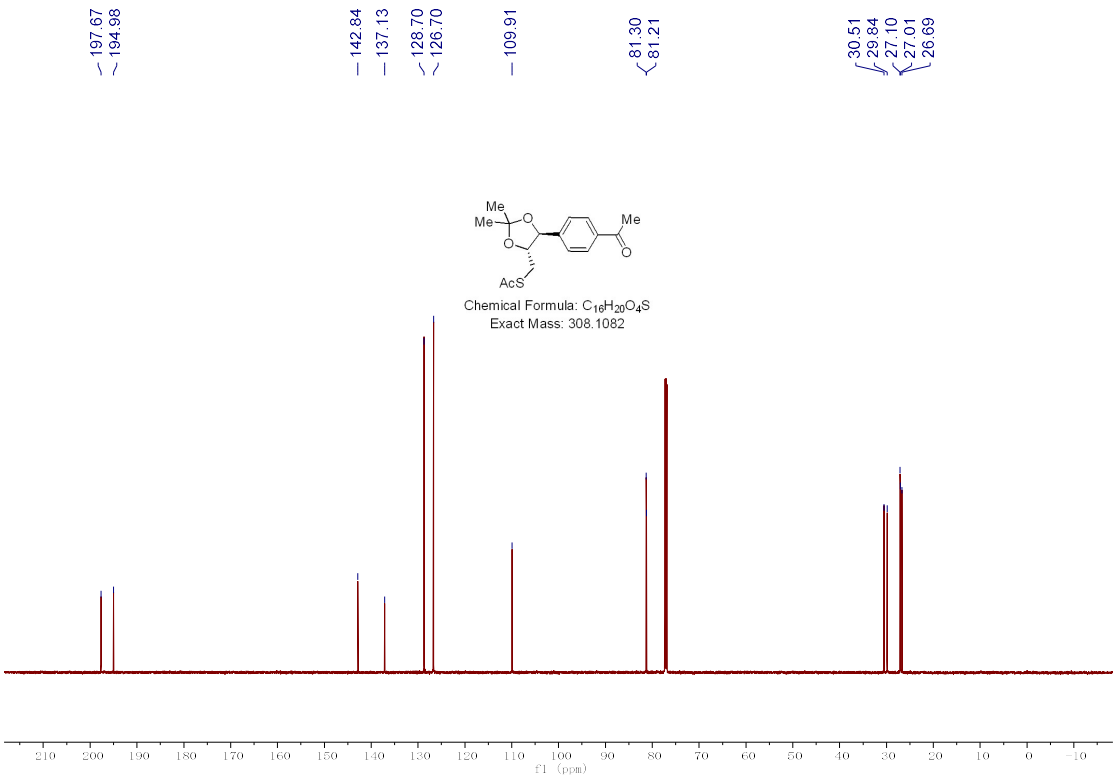
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9s



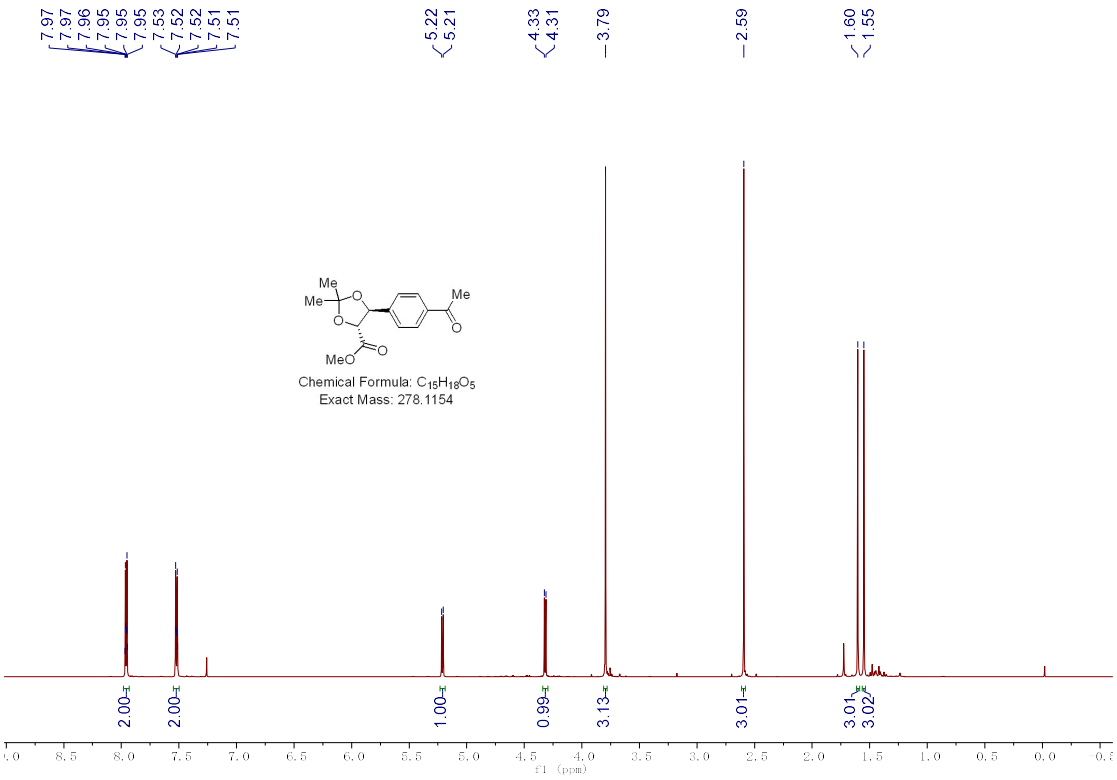
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9s



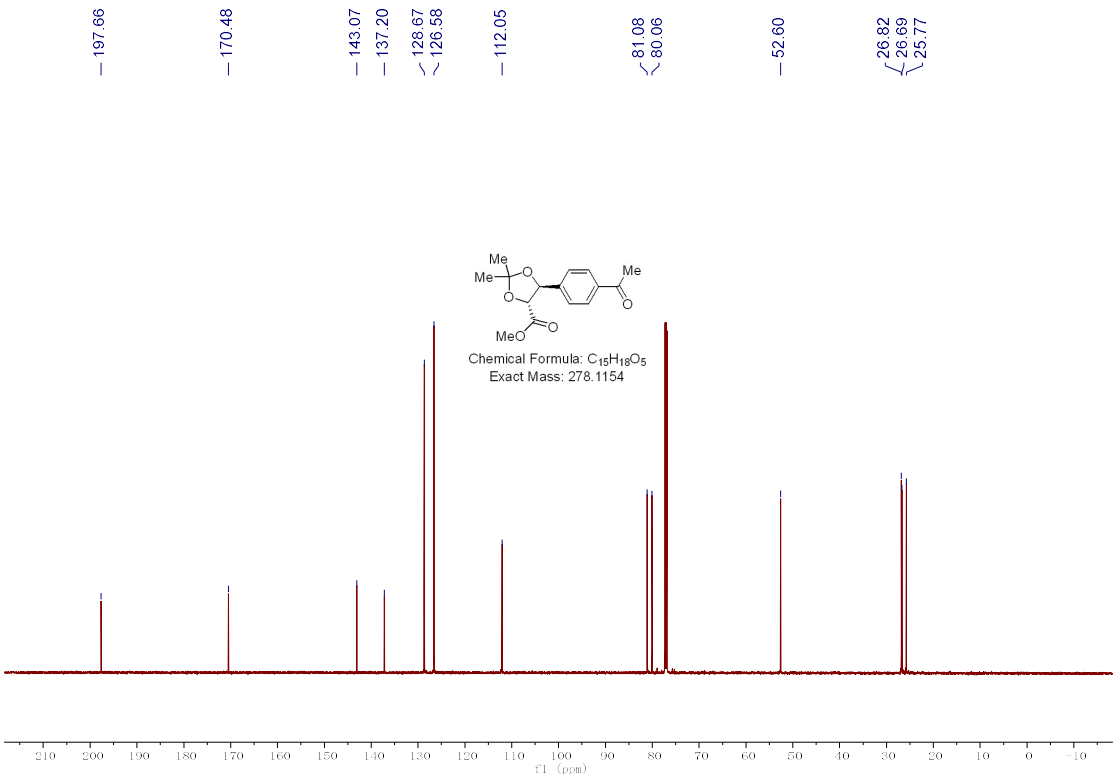
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9t



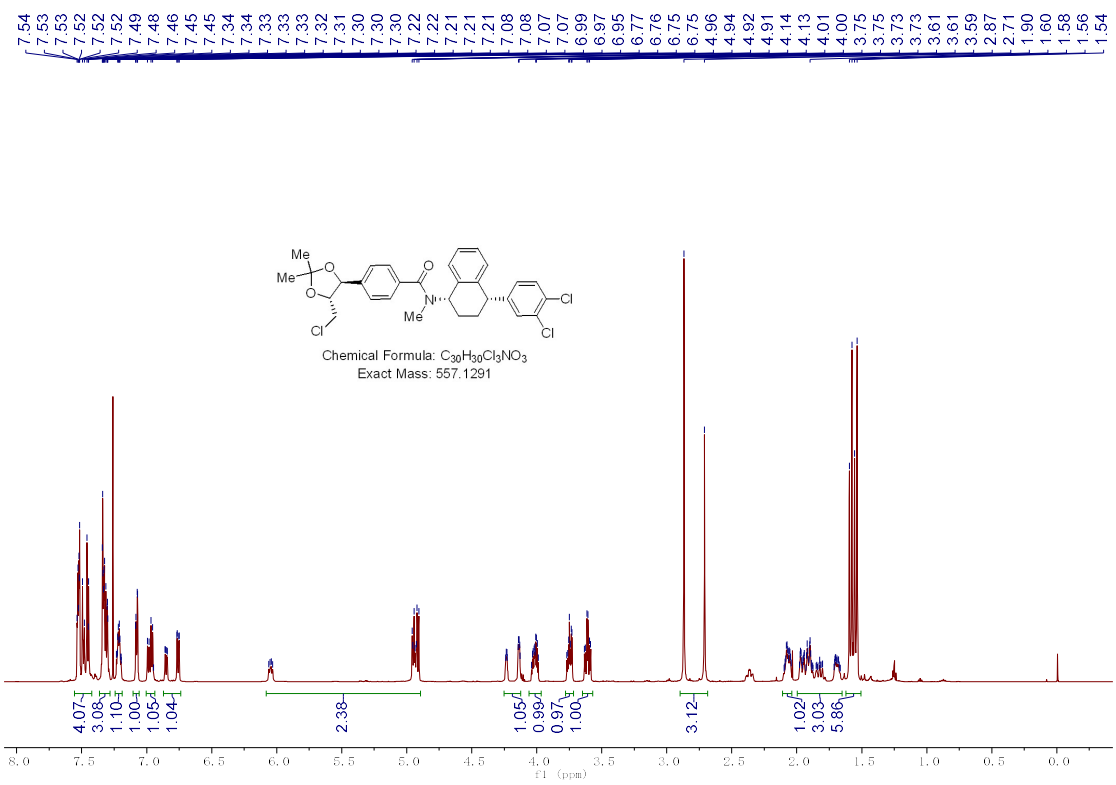
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9t



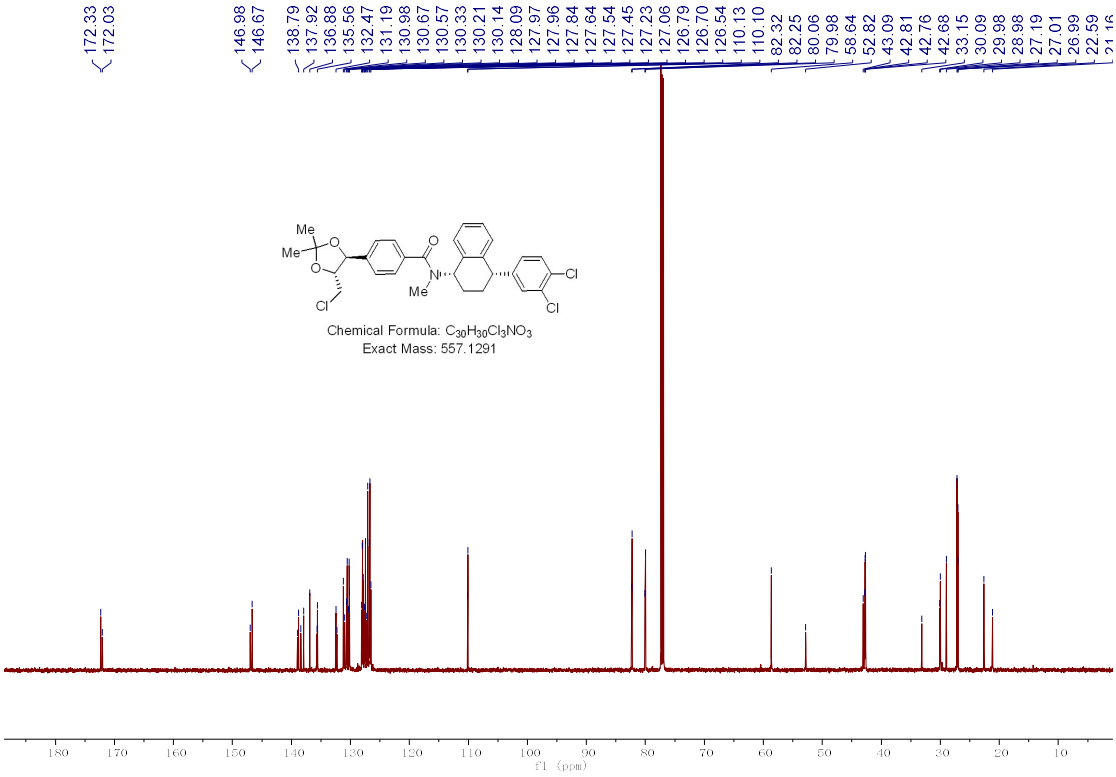
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9u



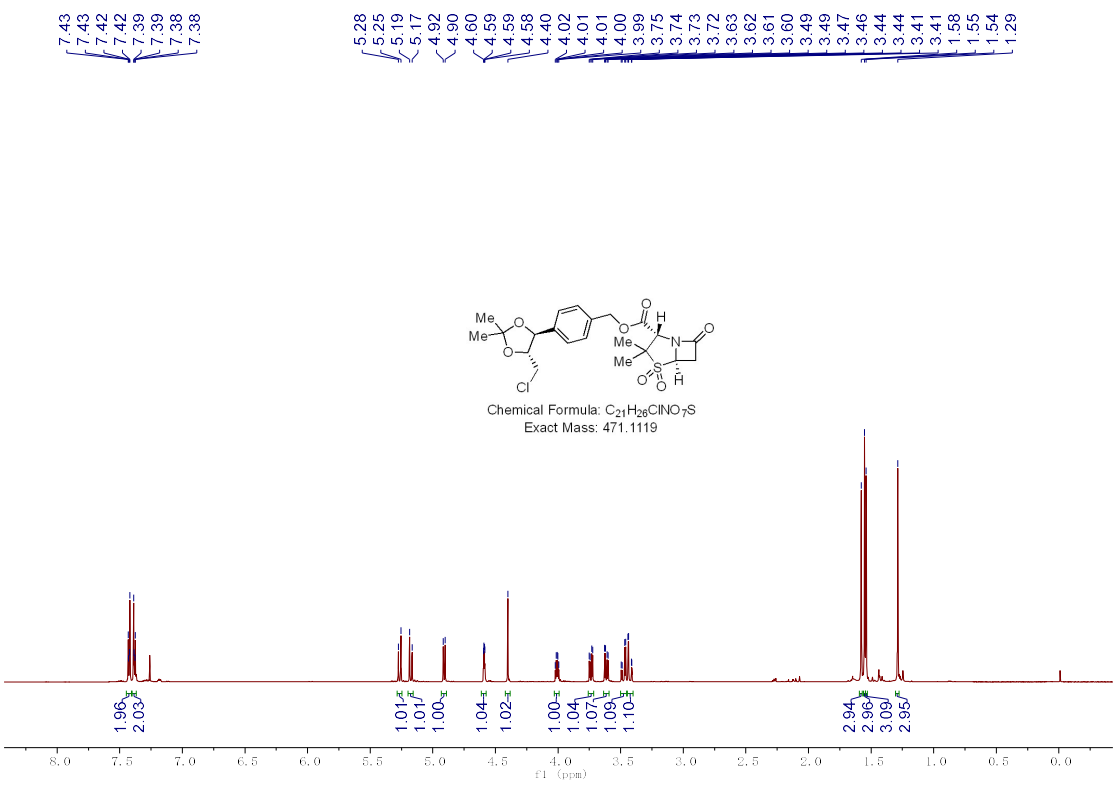
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9u



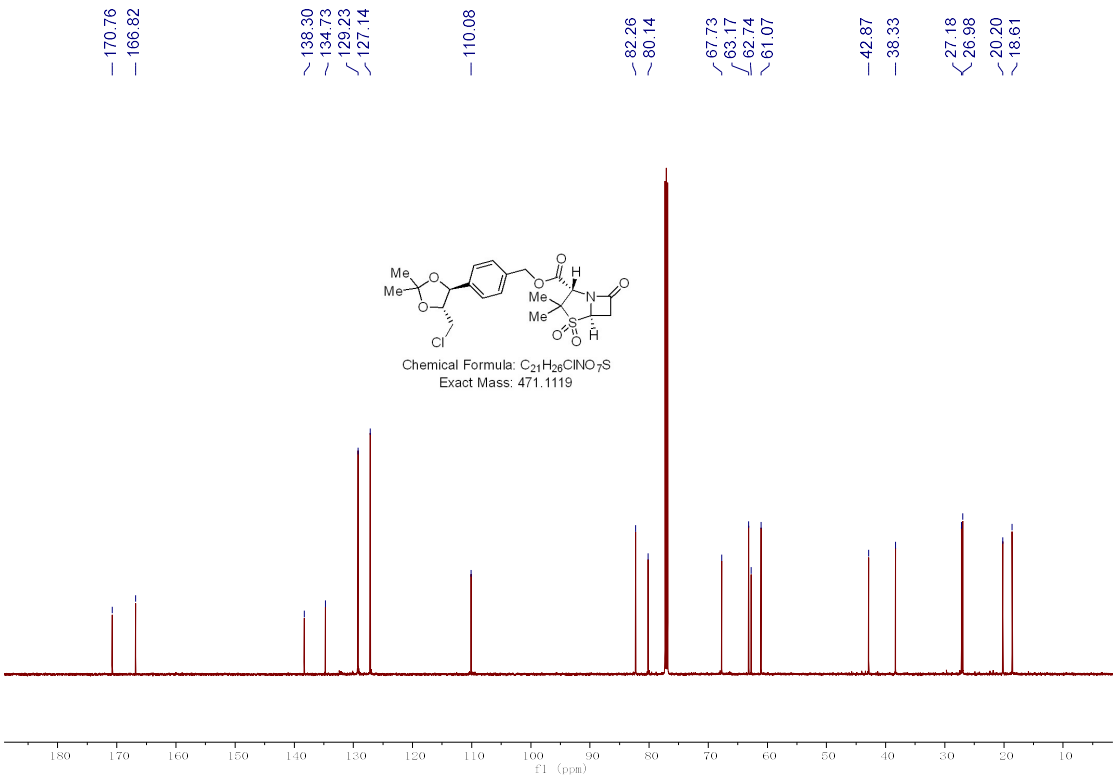
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9v



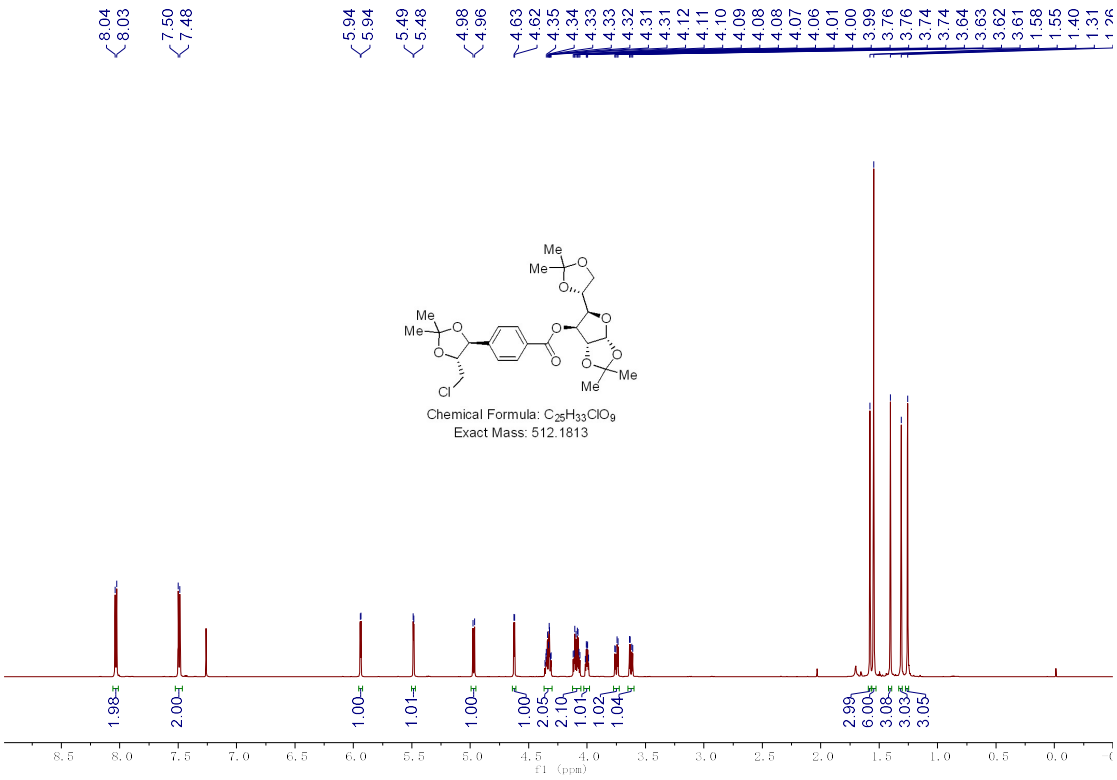
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9v



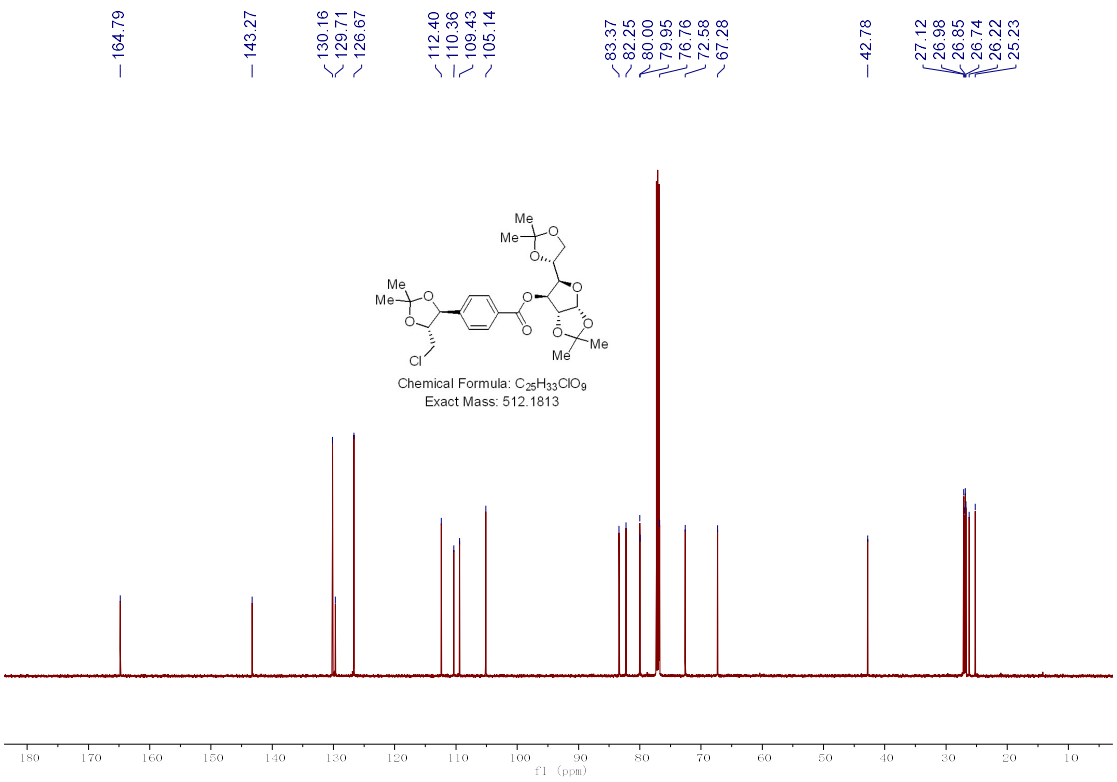
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9w



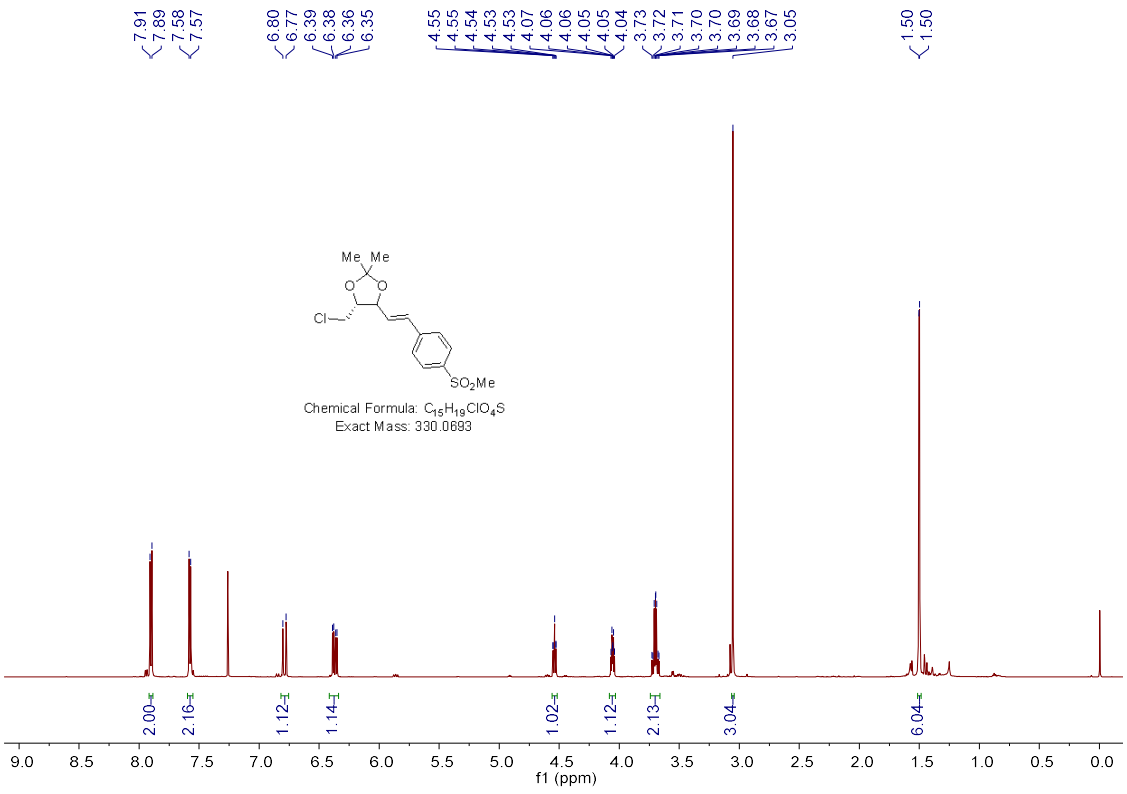
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9w



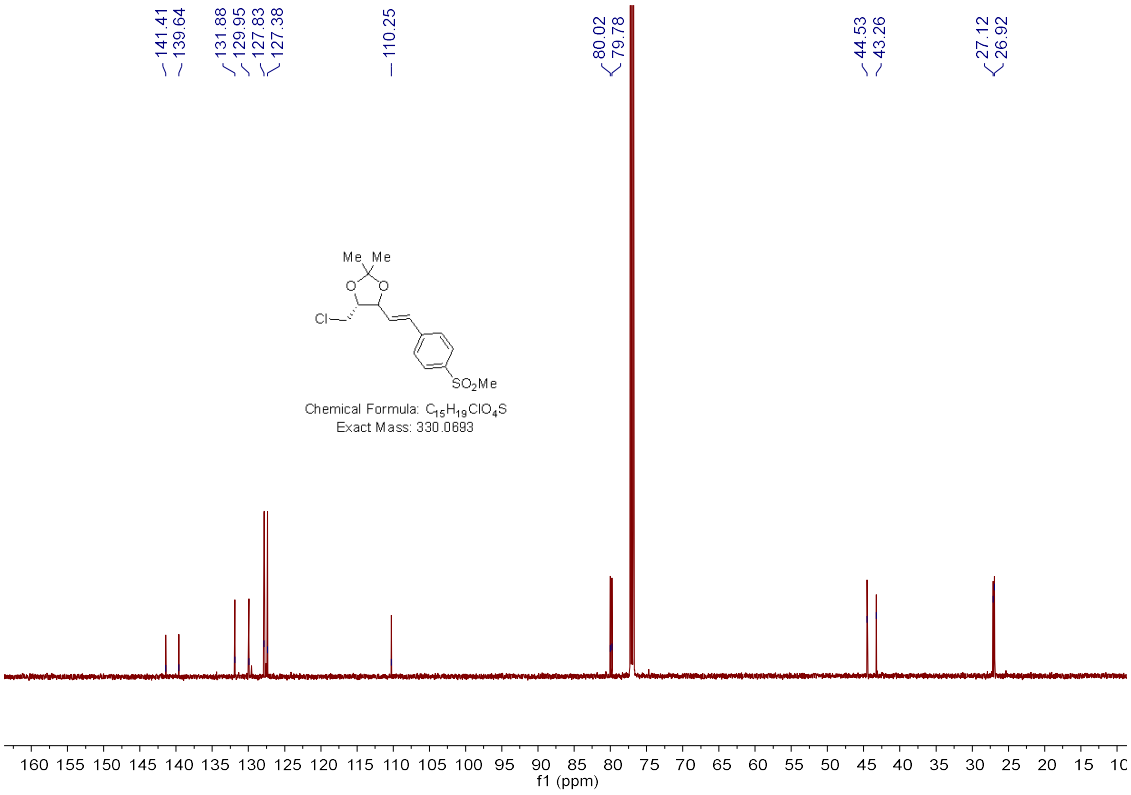
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9x



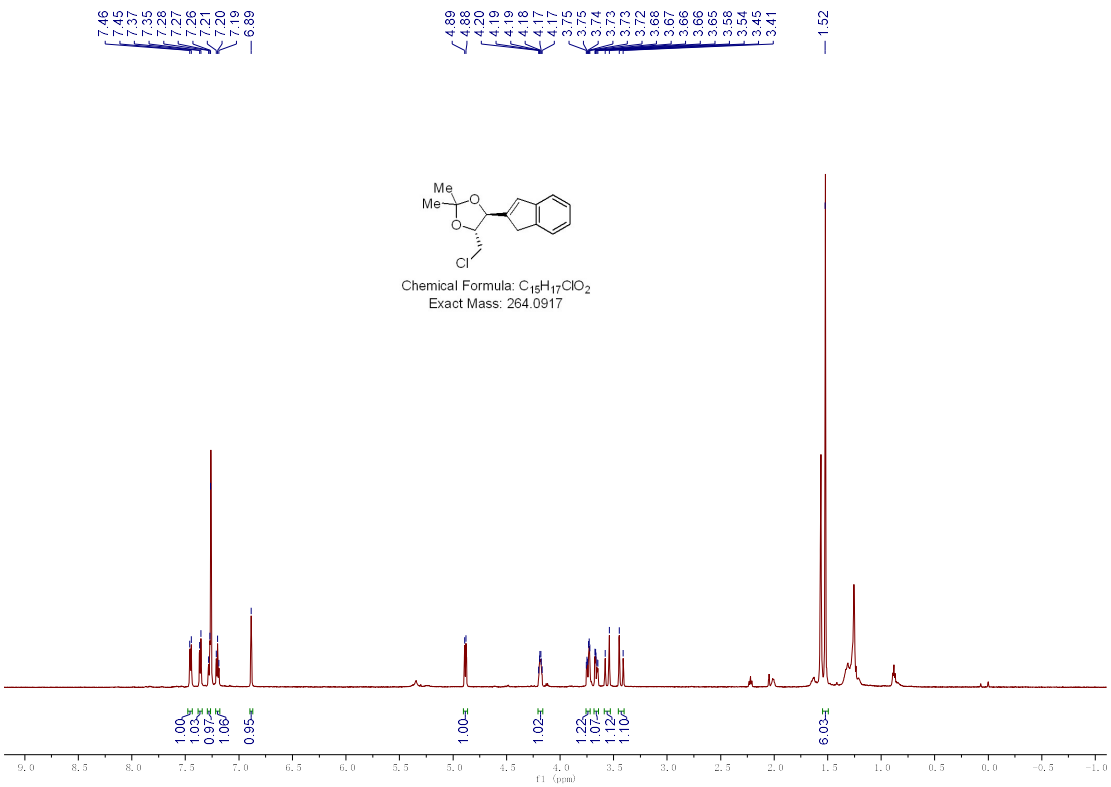
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9x



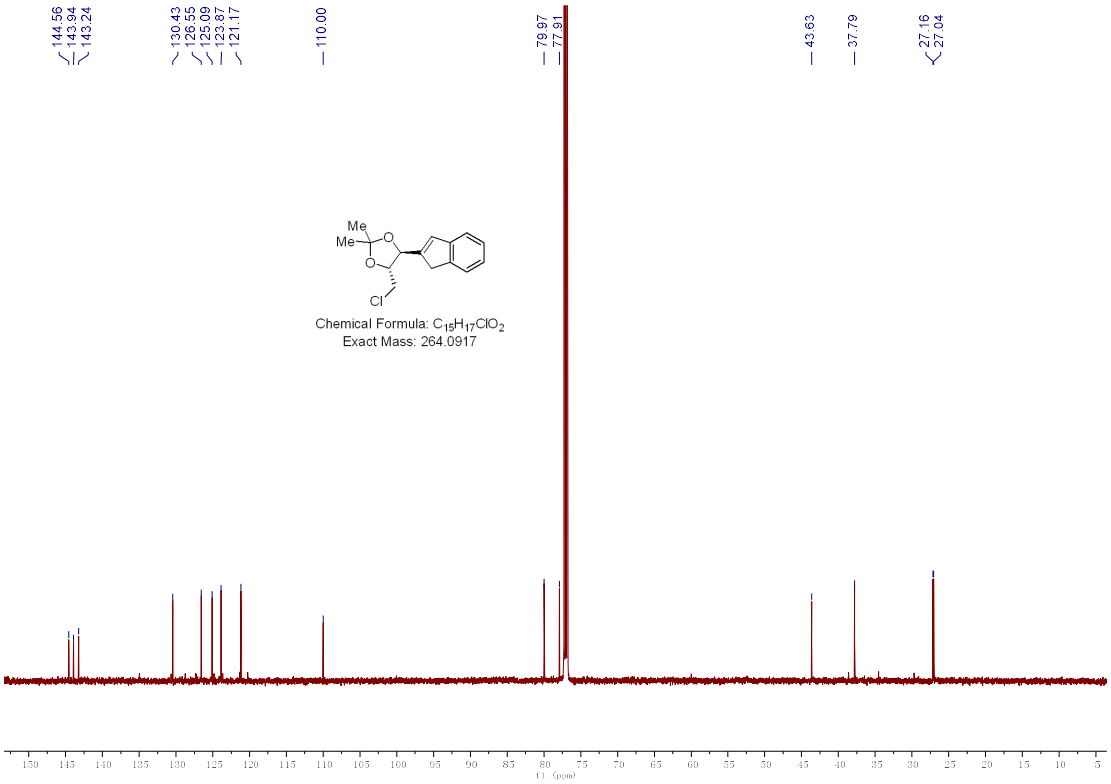
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9y



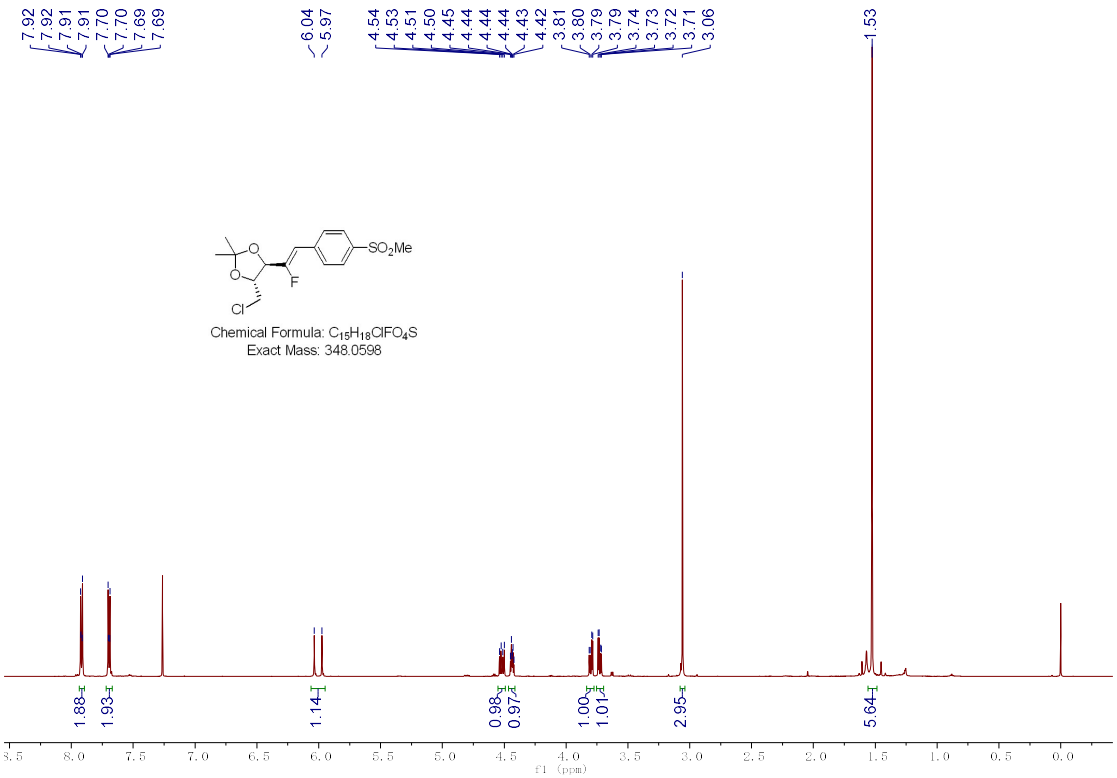
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9y



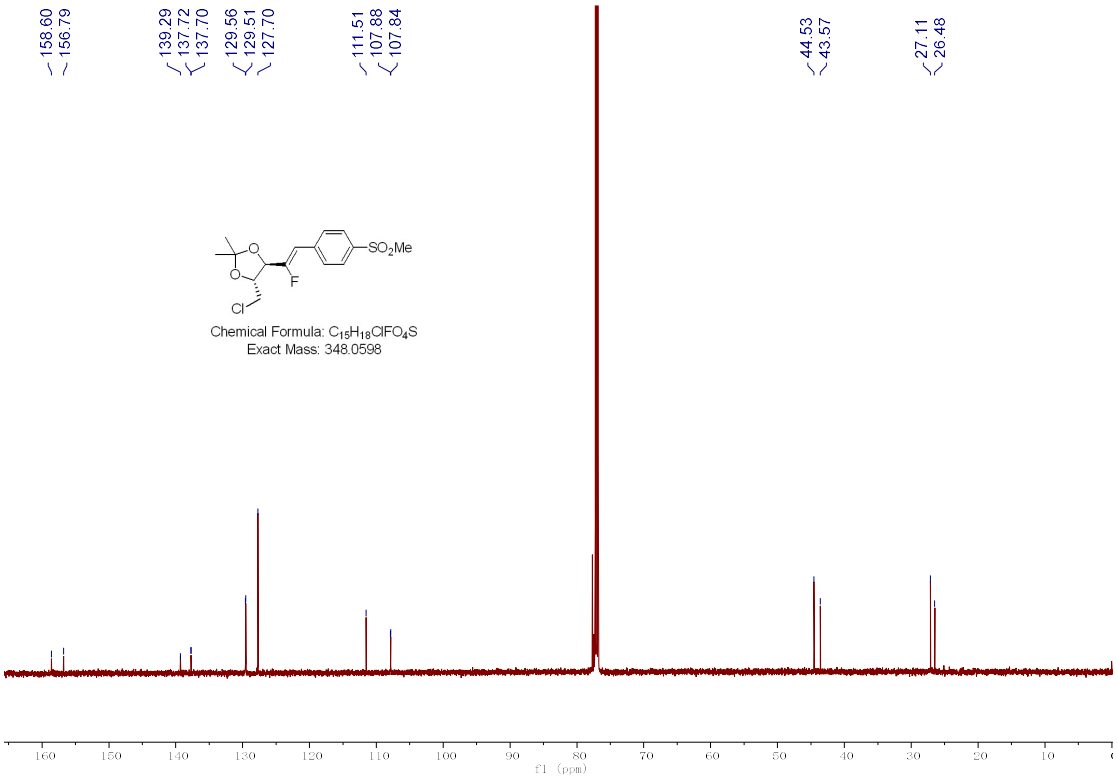
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9z



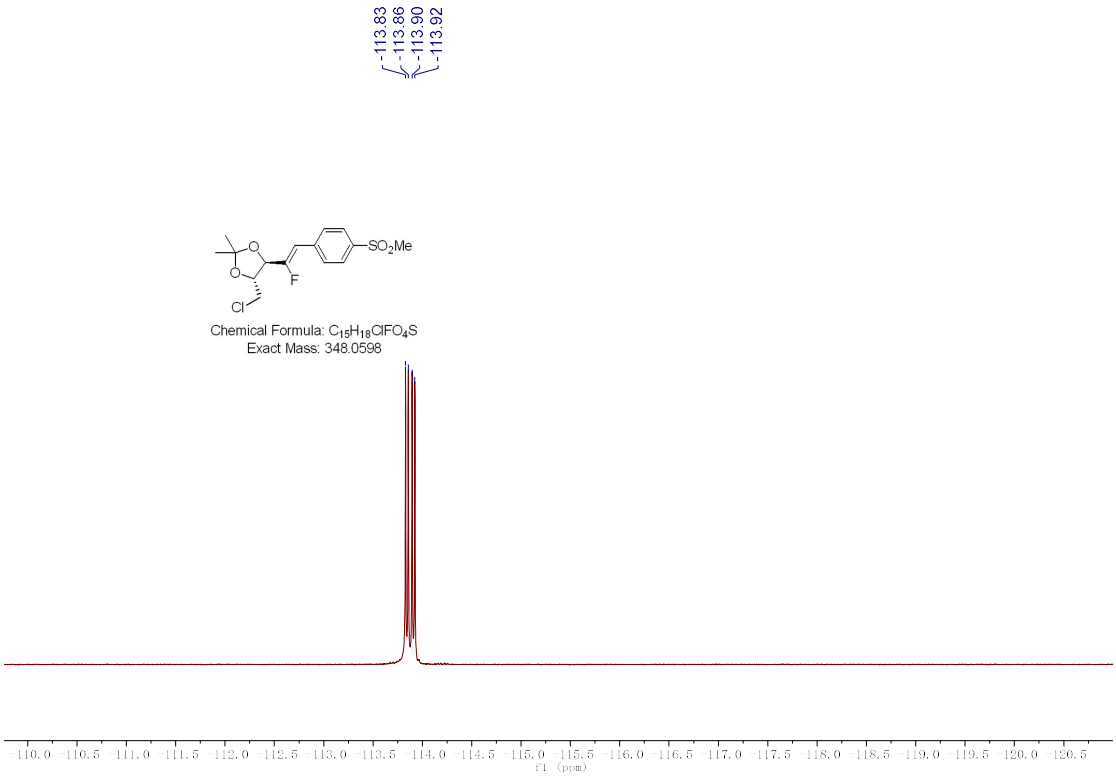
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9z



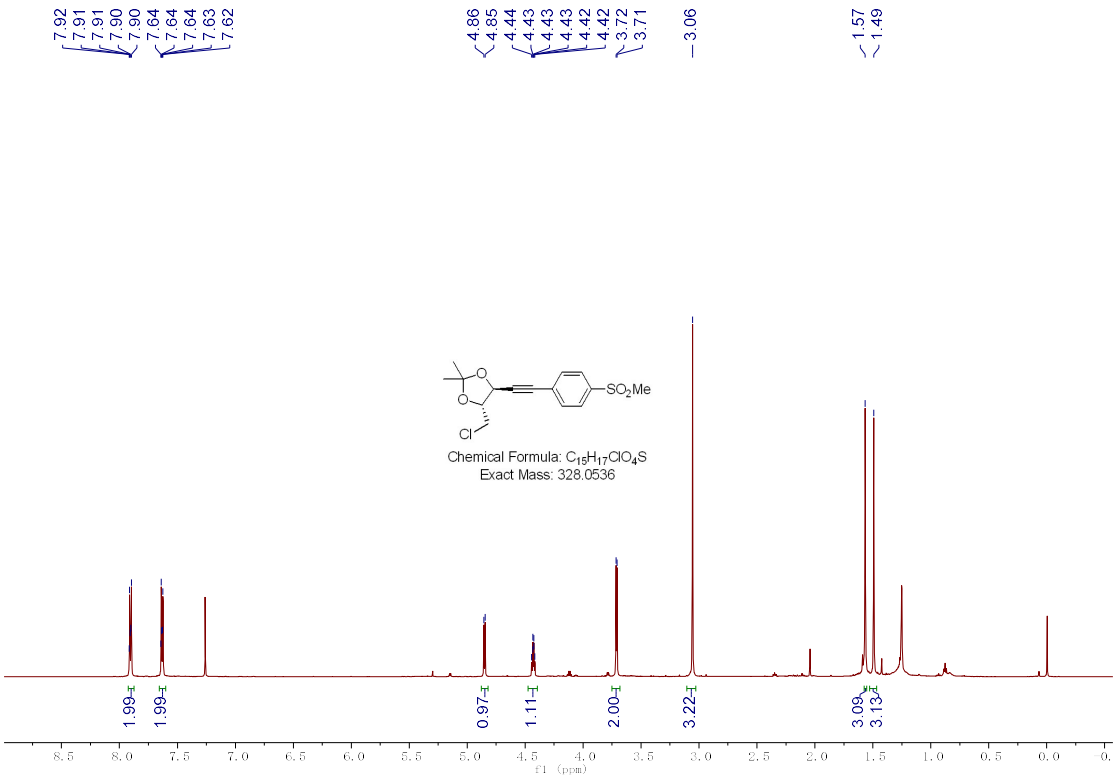
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9aa



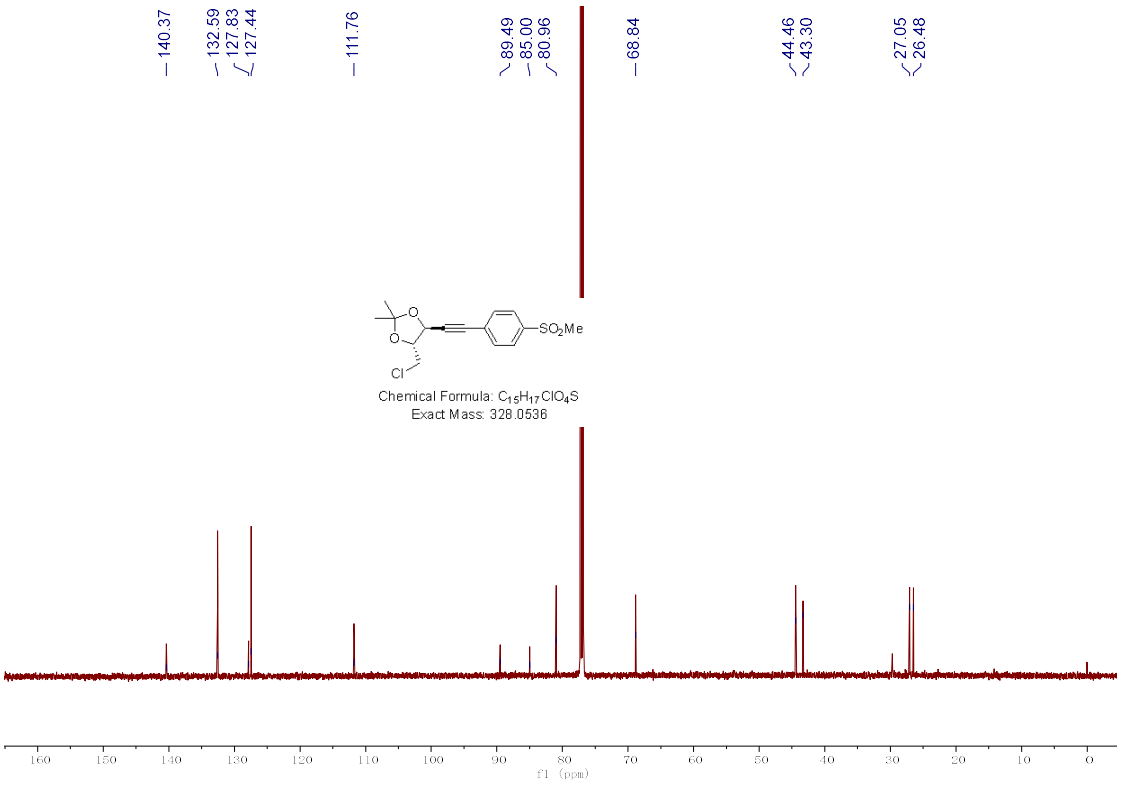
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9aa



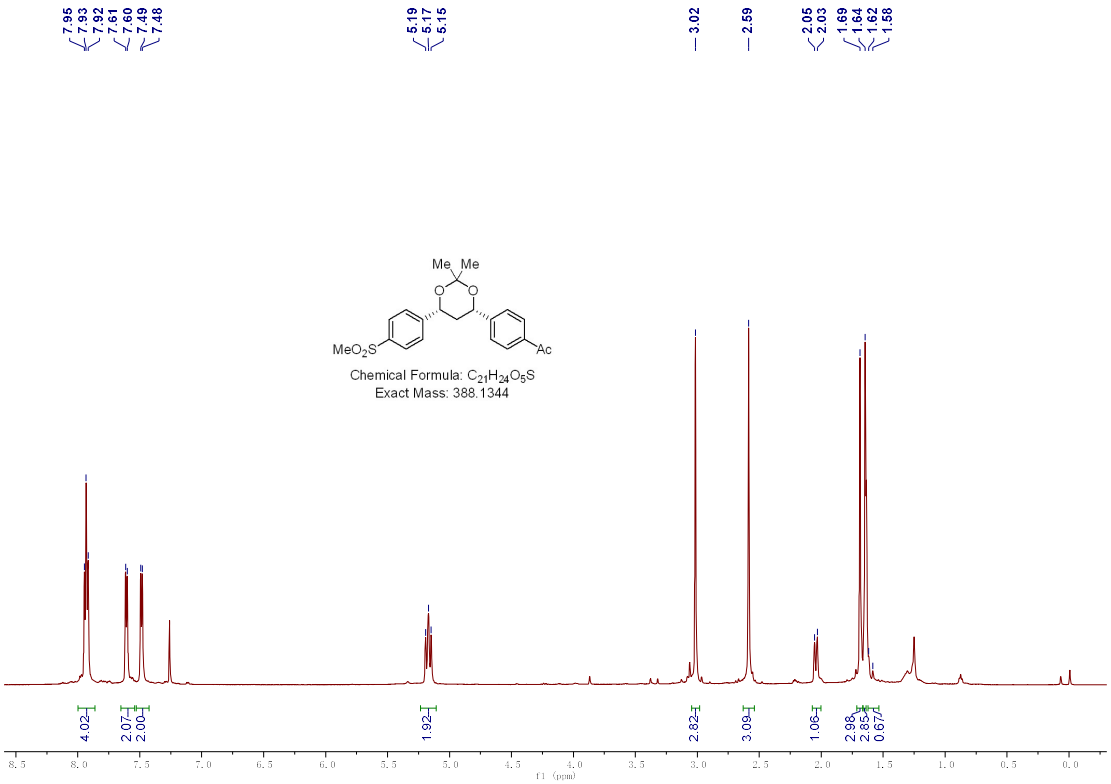
^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of 9aa



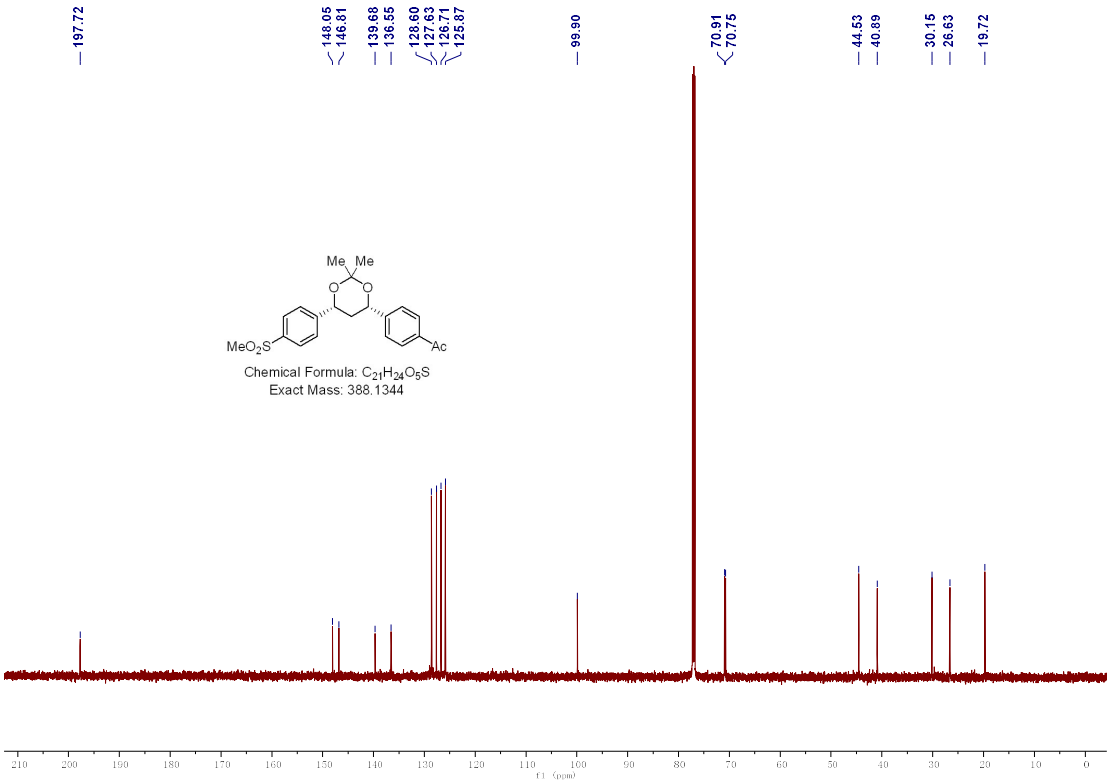
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 9ab



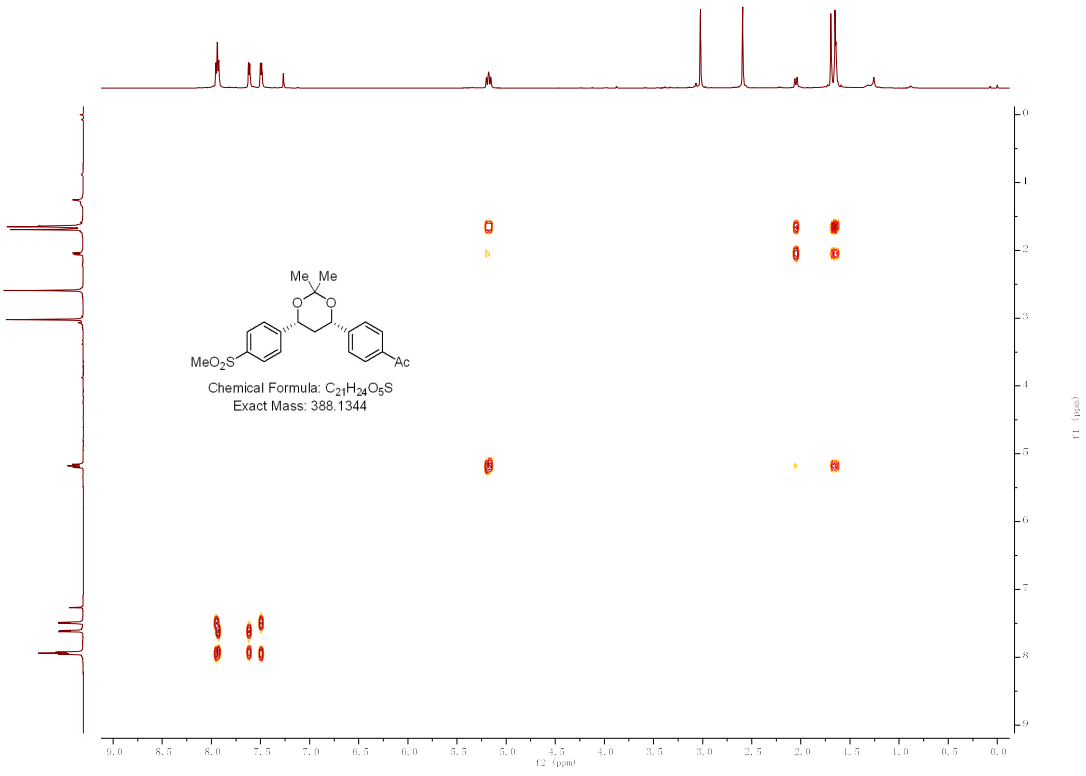
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 9ab



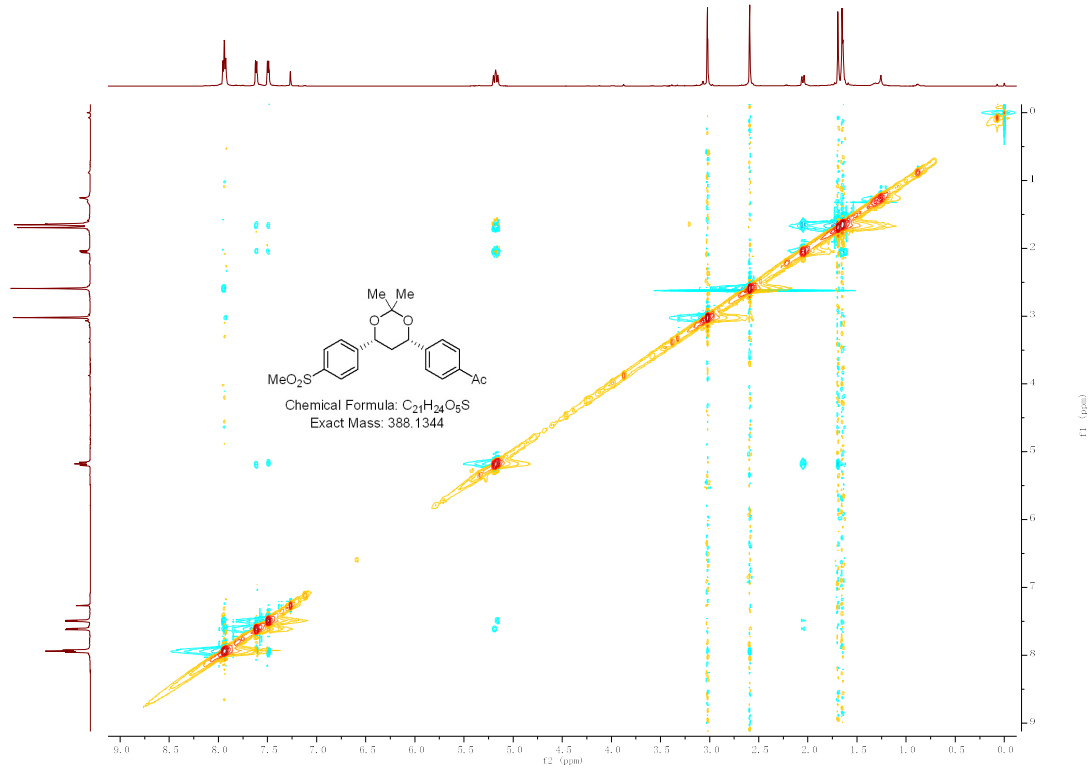
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 10a



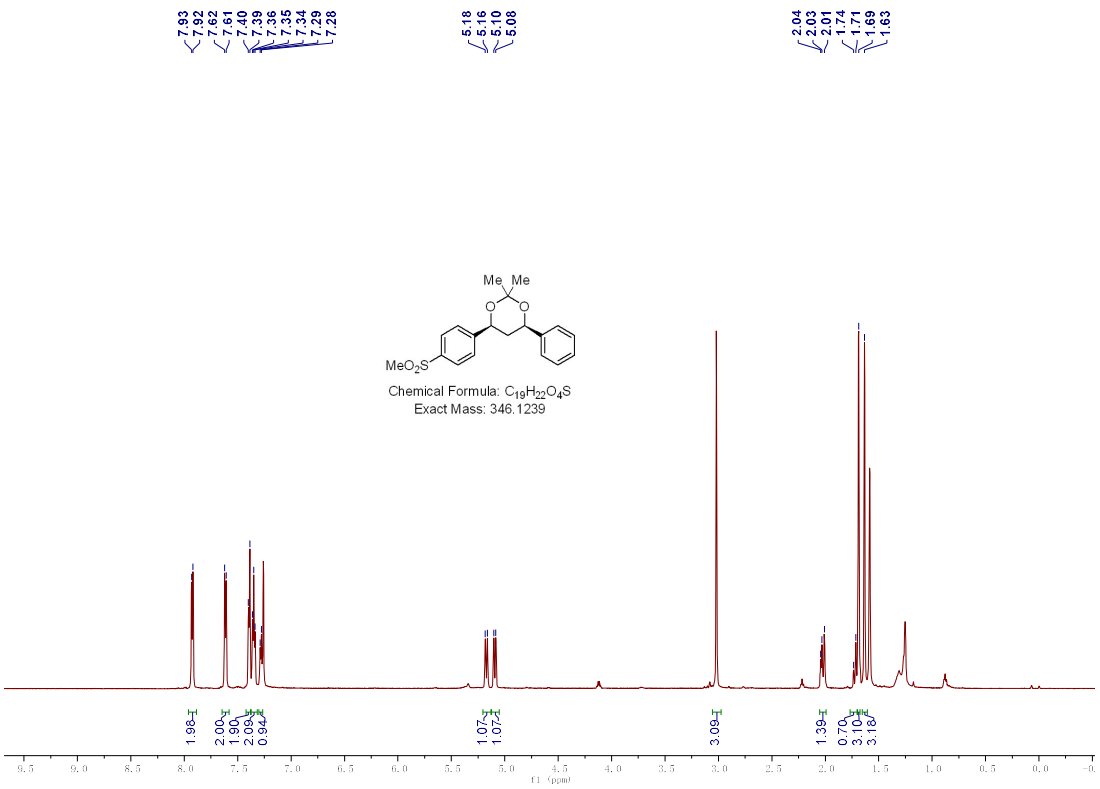
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 10a



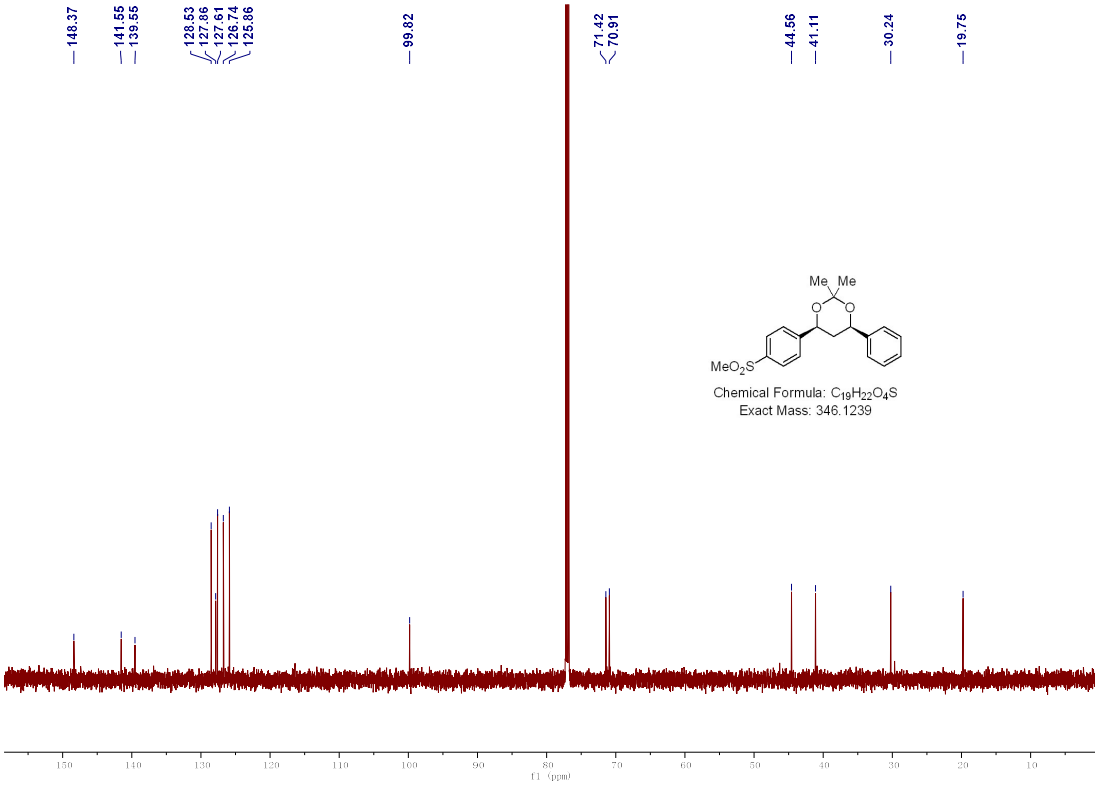
COSY Spectrum of 10a



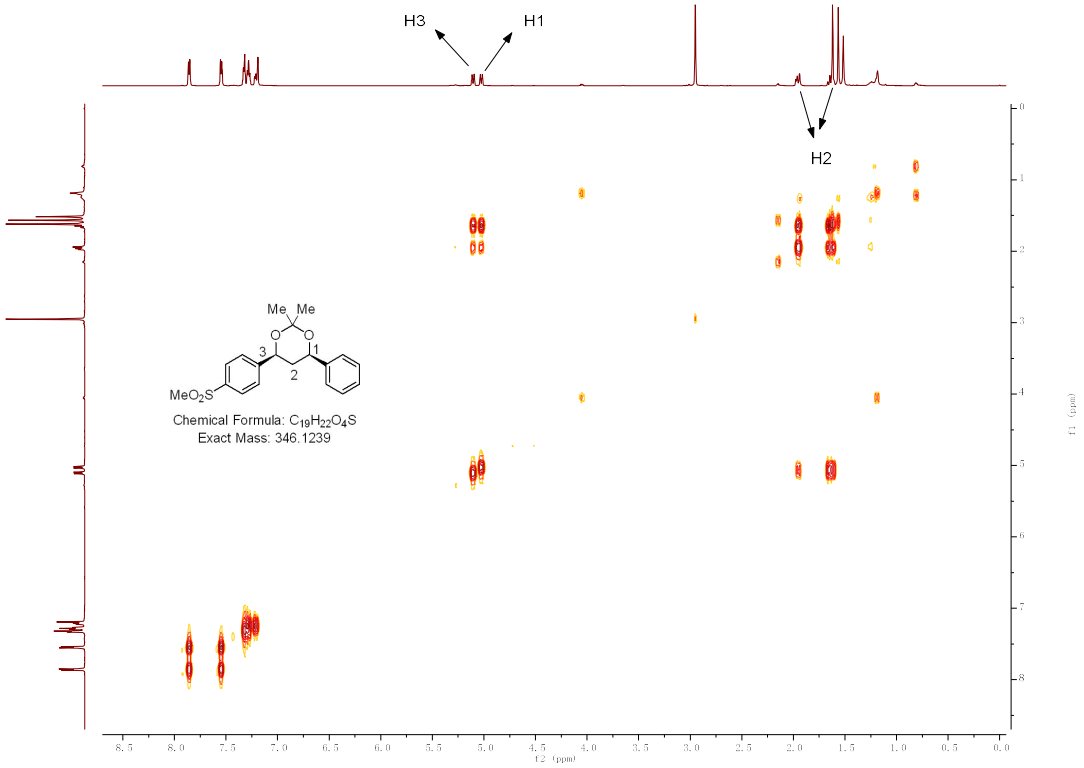
NOE Spectrum of 10a



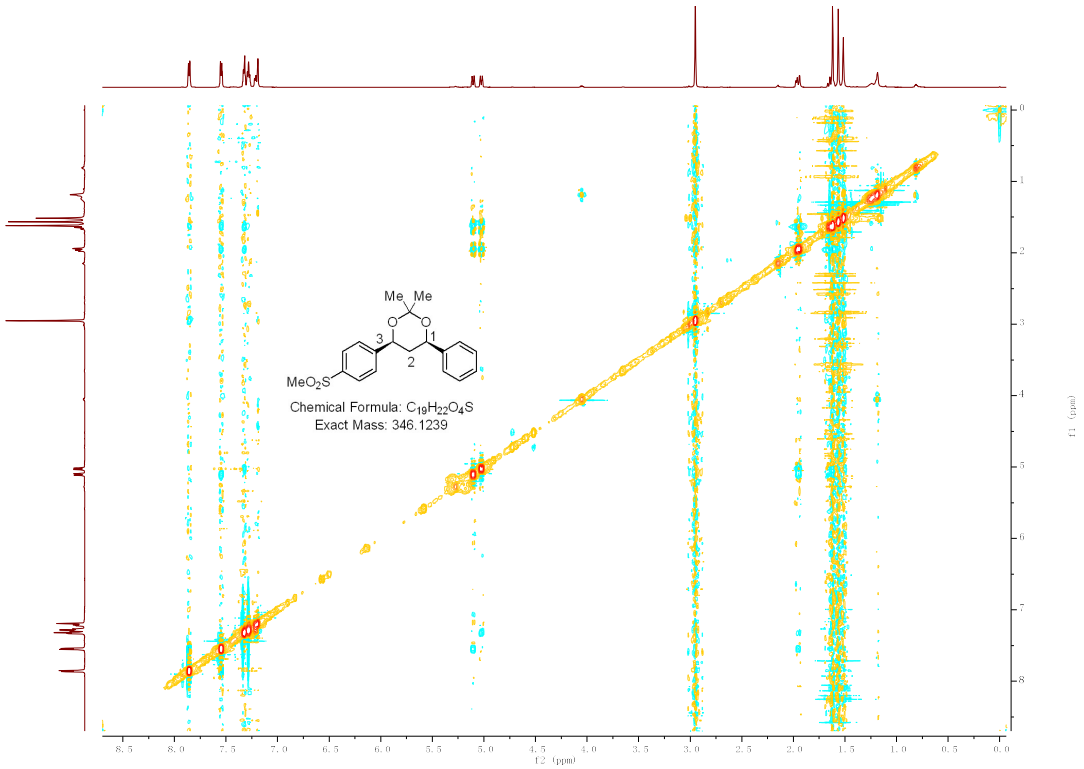
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 10b



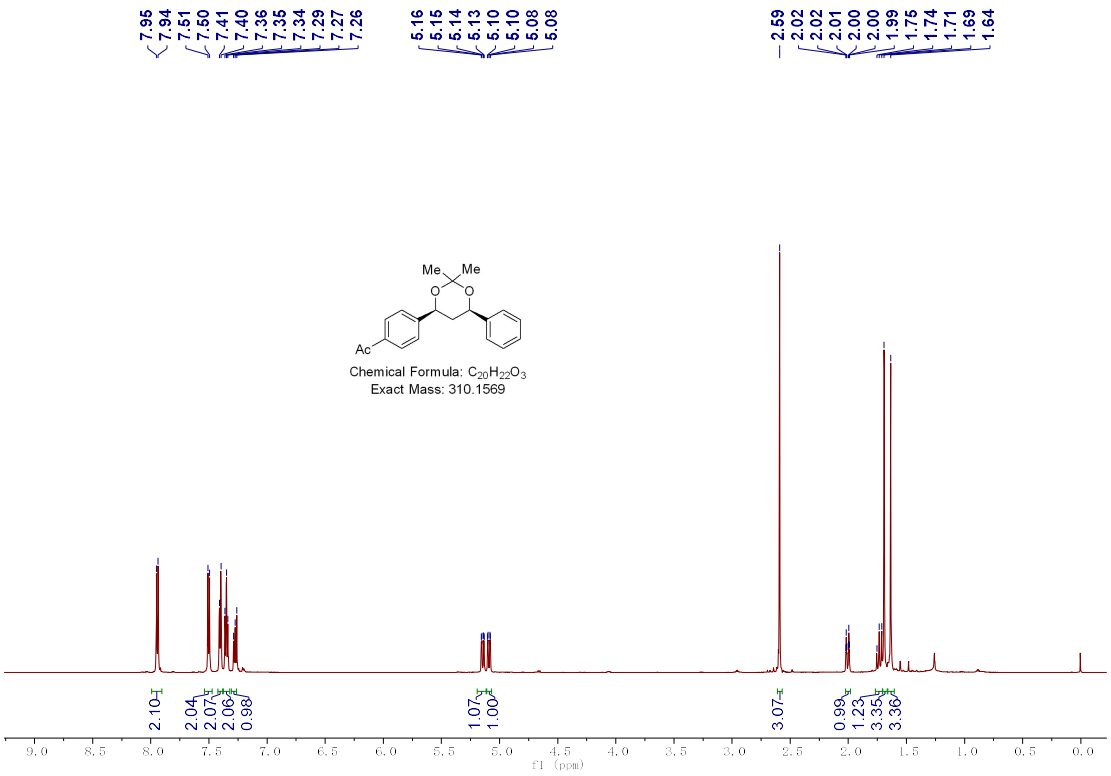
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 10b



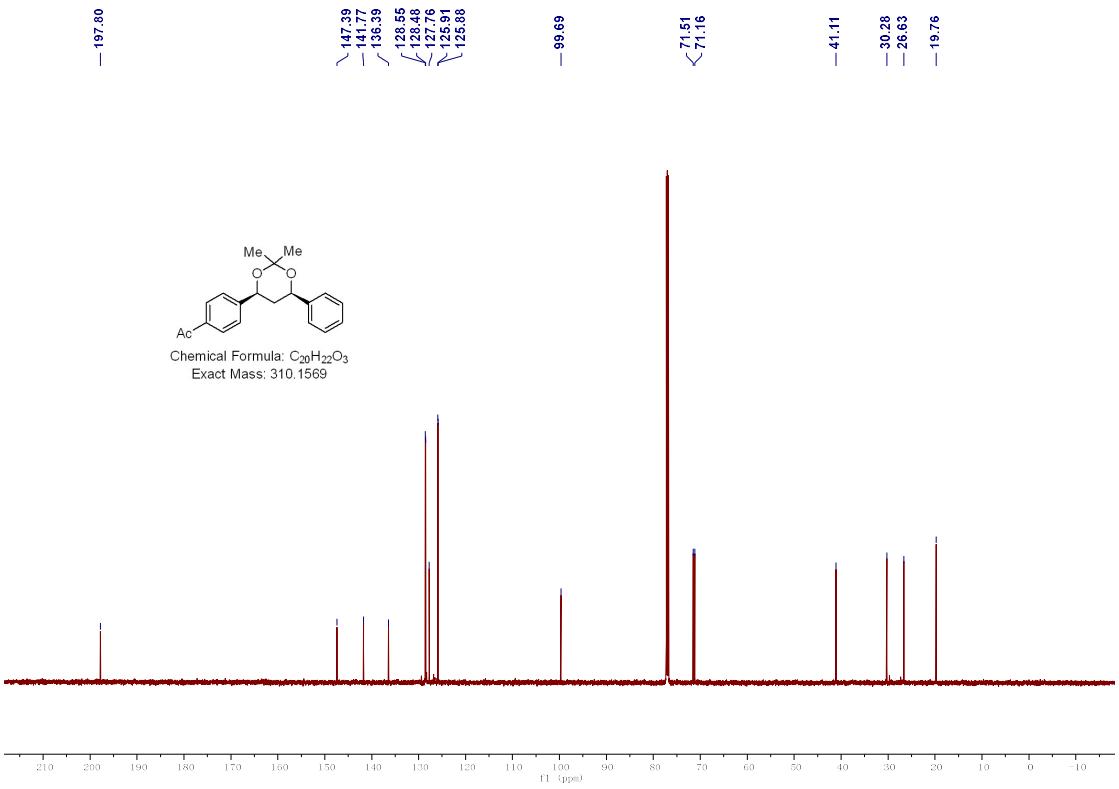
COSY Spectrum of 10b



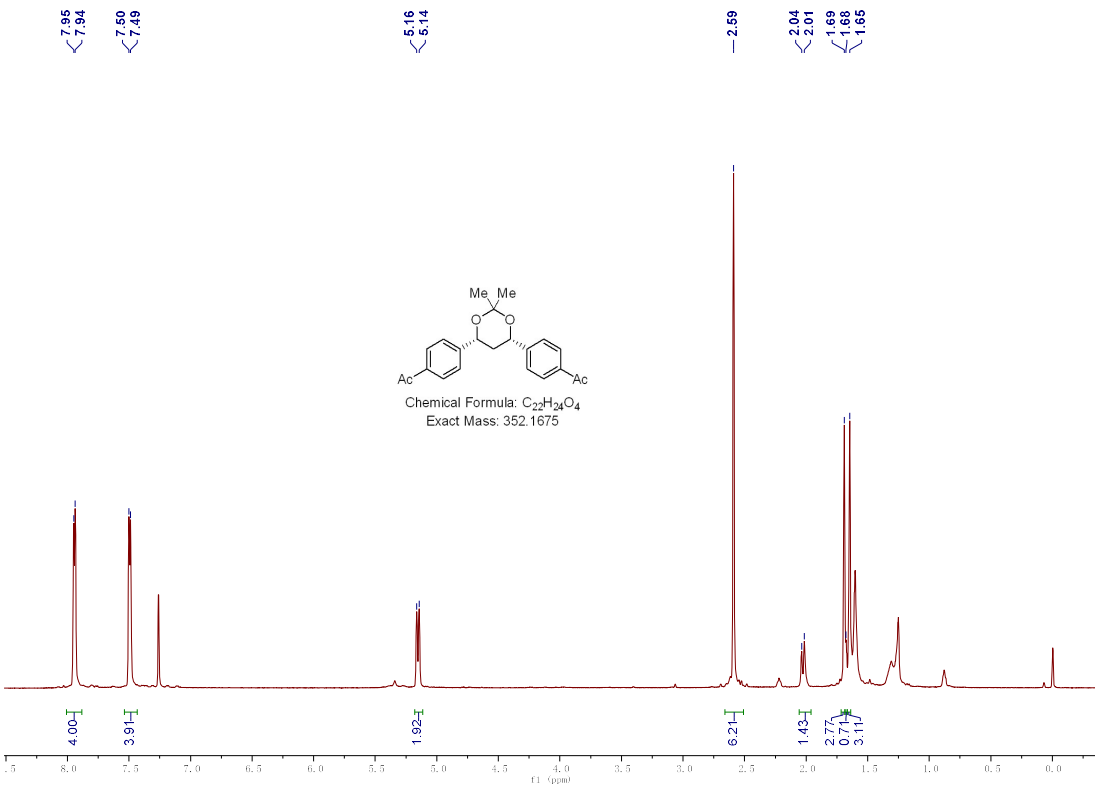
NOE Spectrum of 10b



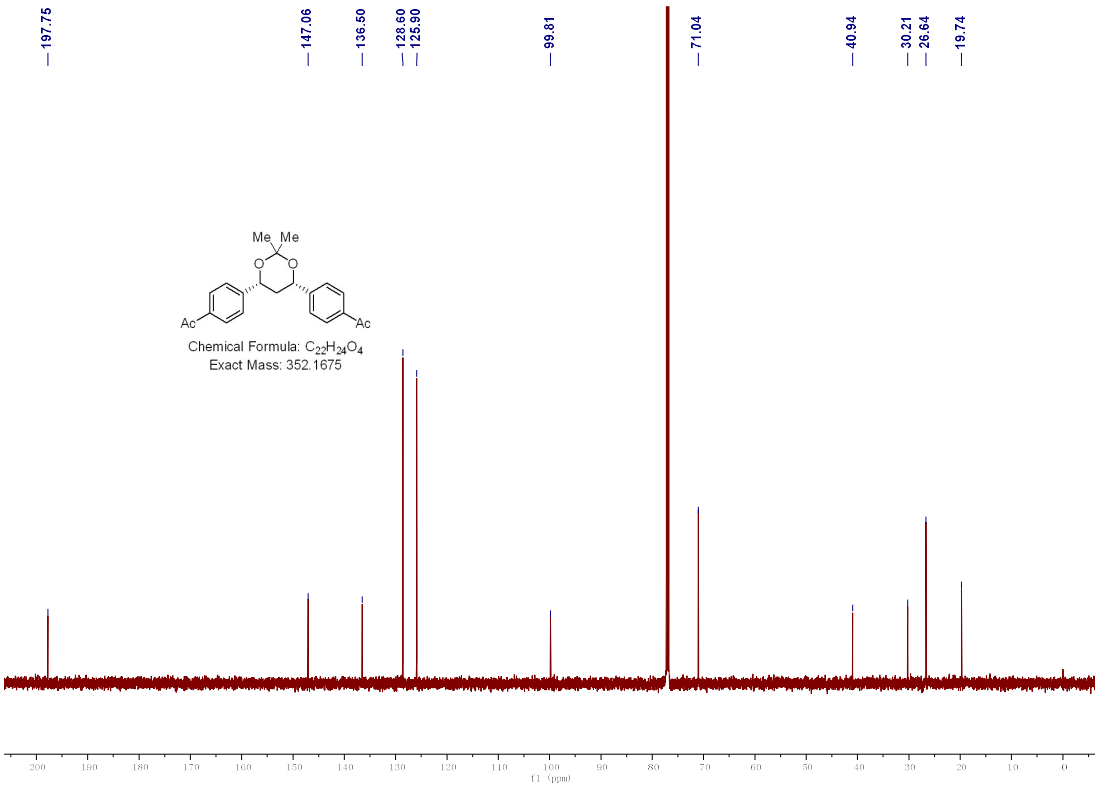
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 10c



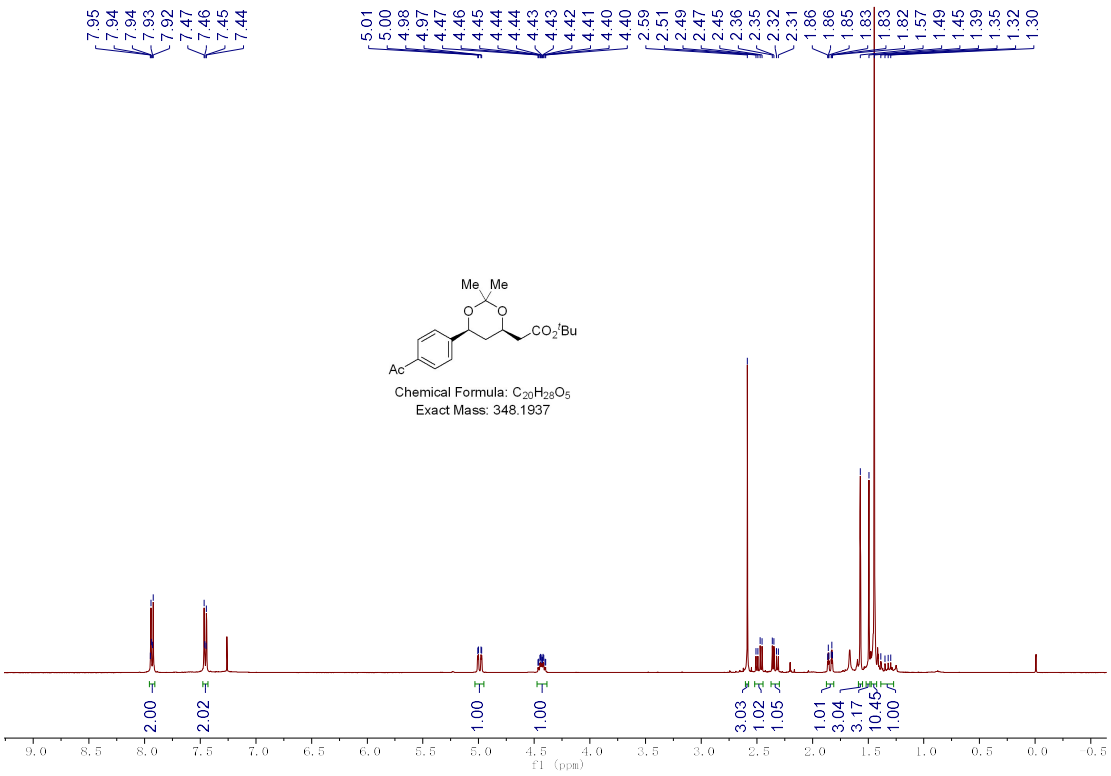
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 10c



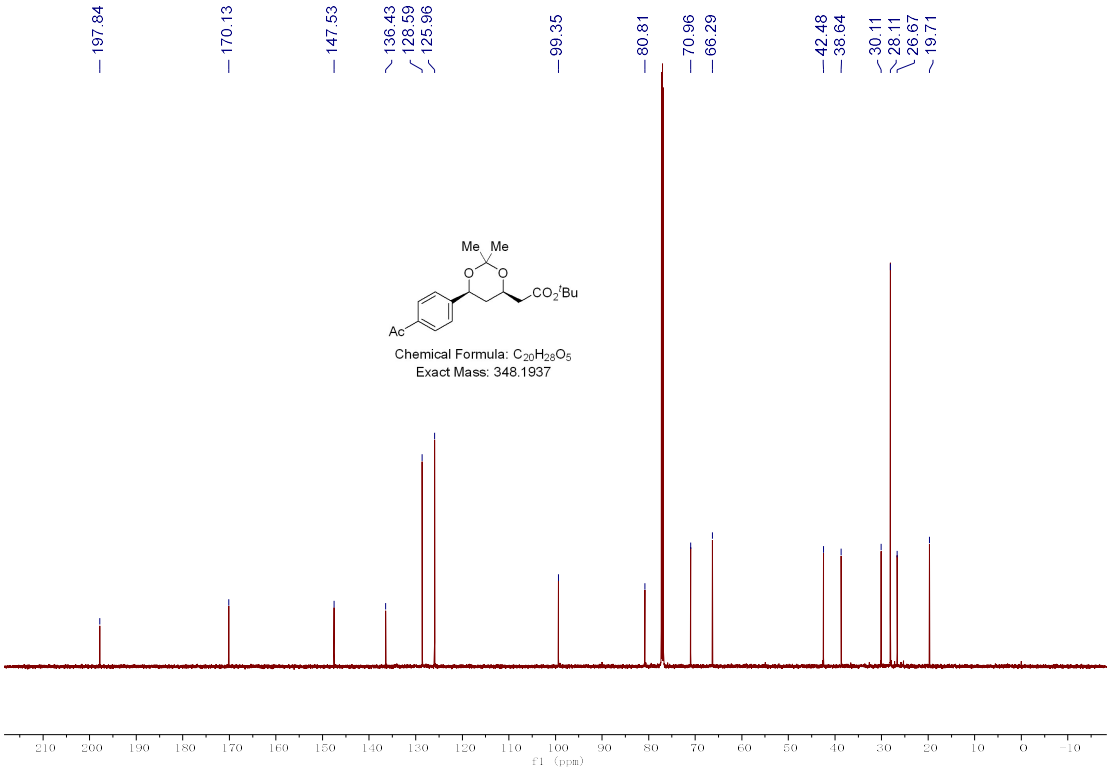
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 10d



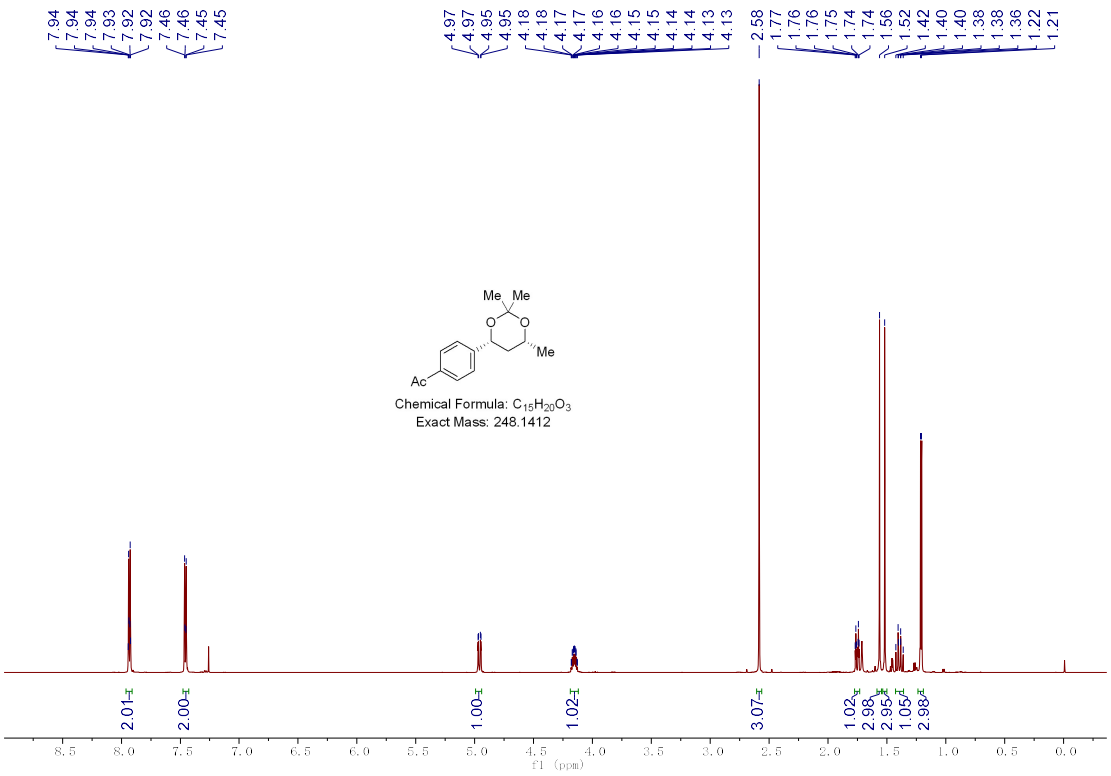
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 10d



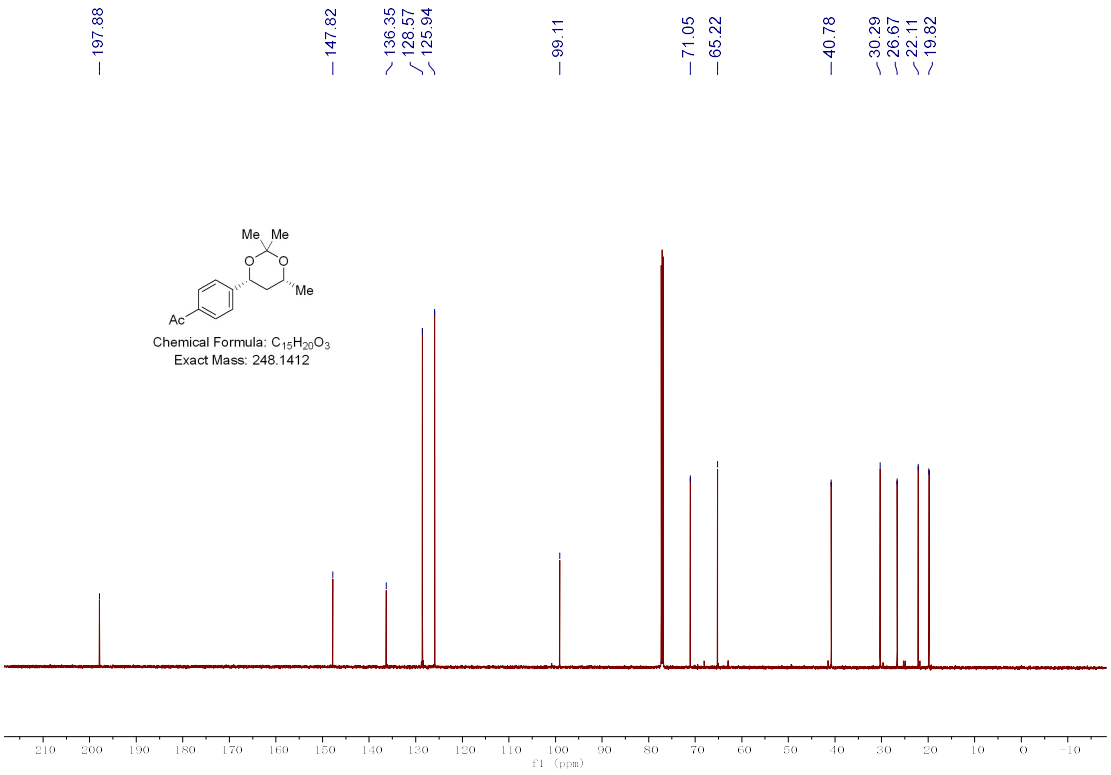
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 10e



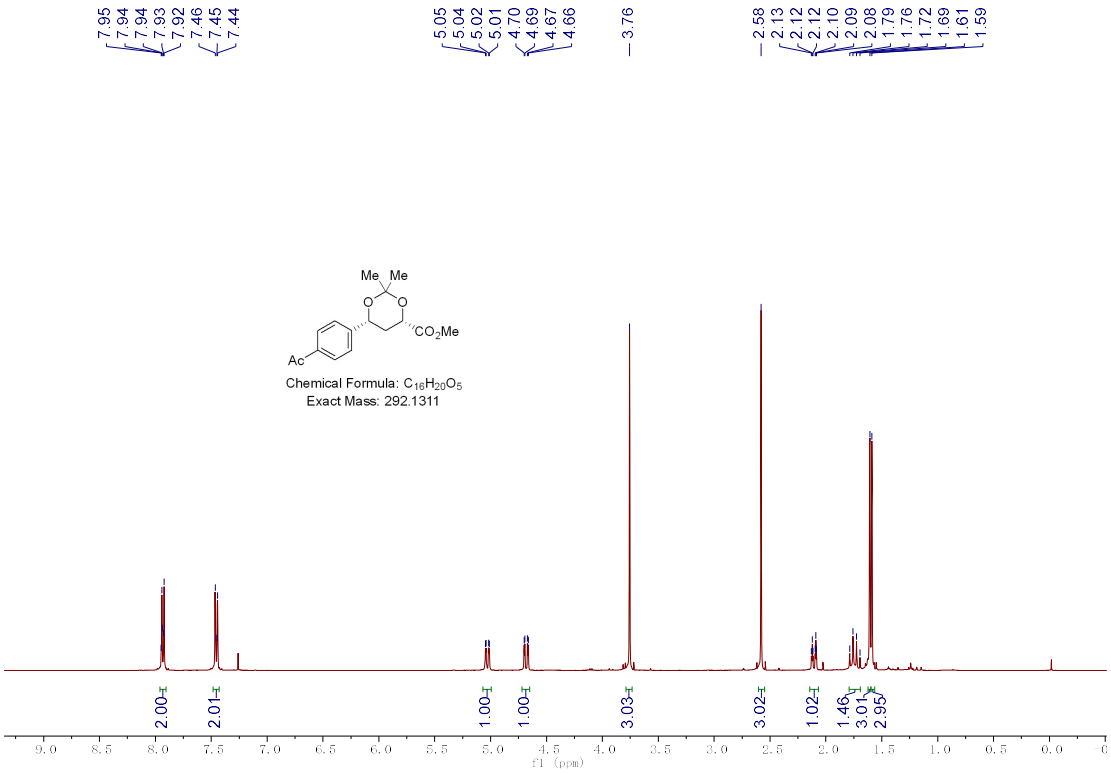
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 10e



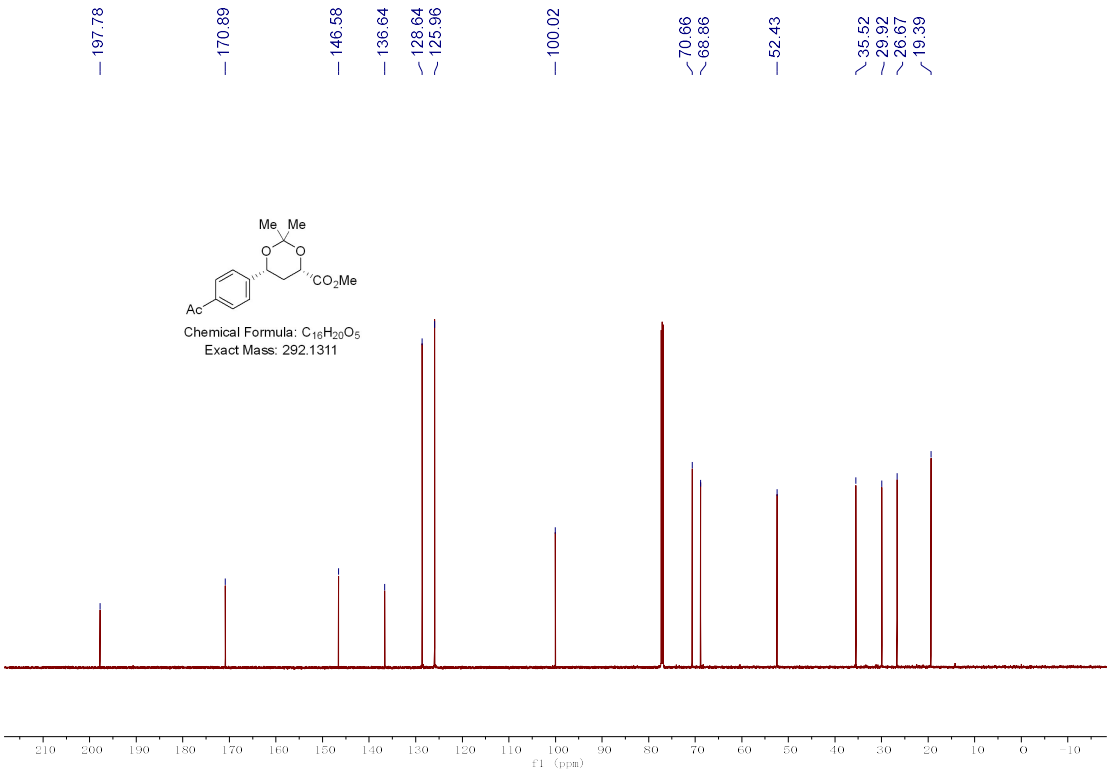
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 10f



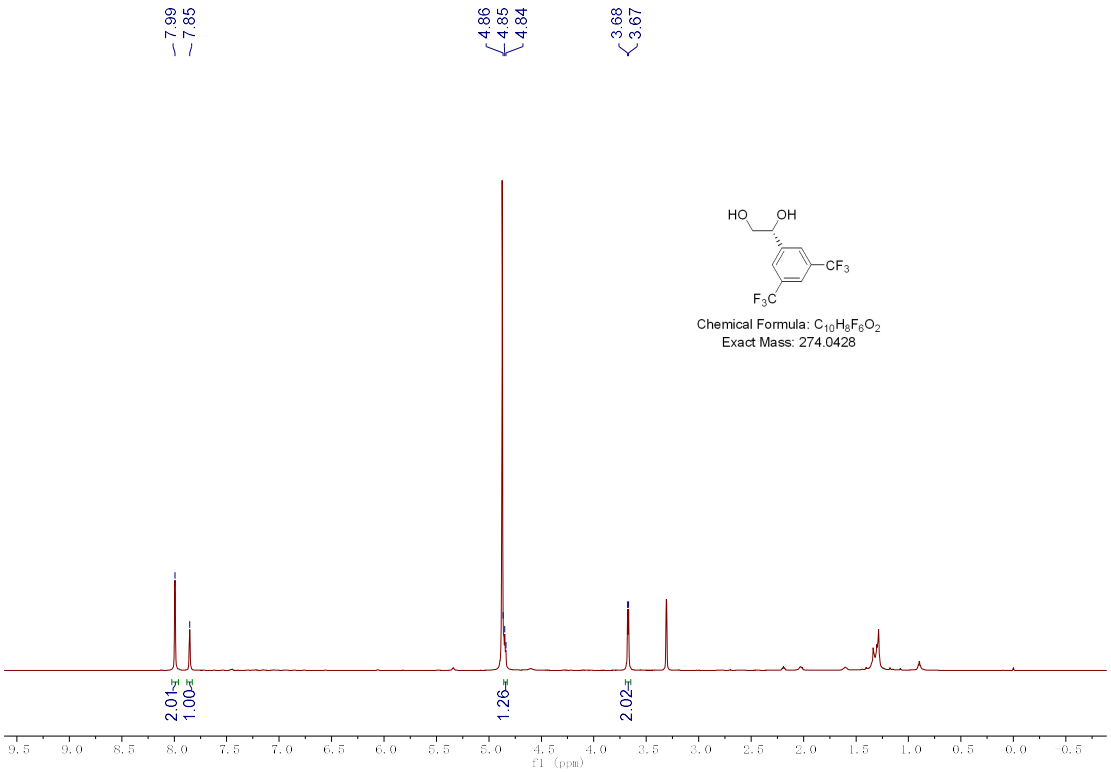
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 10f



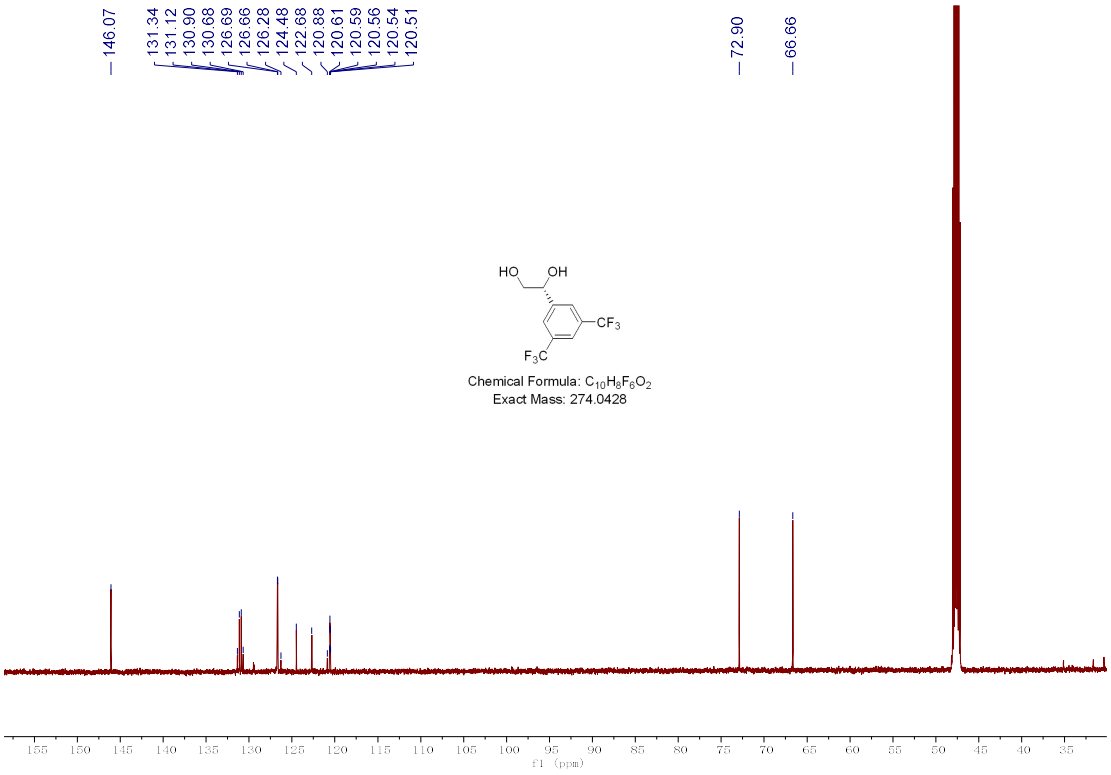
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 10g



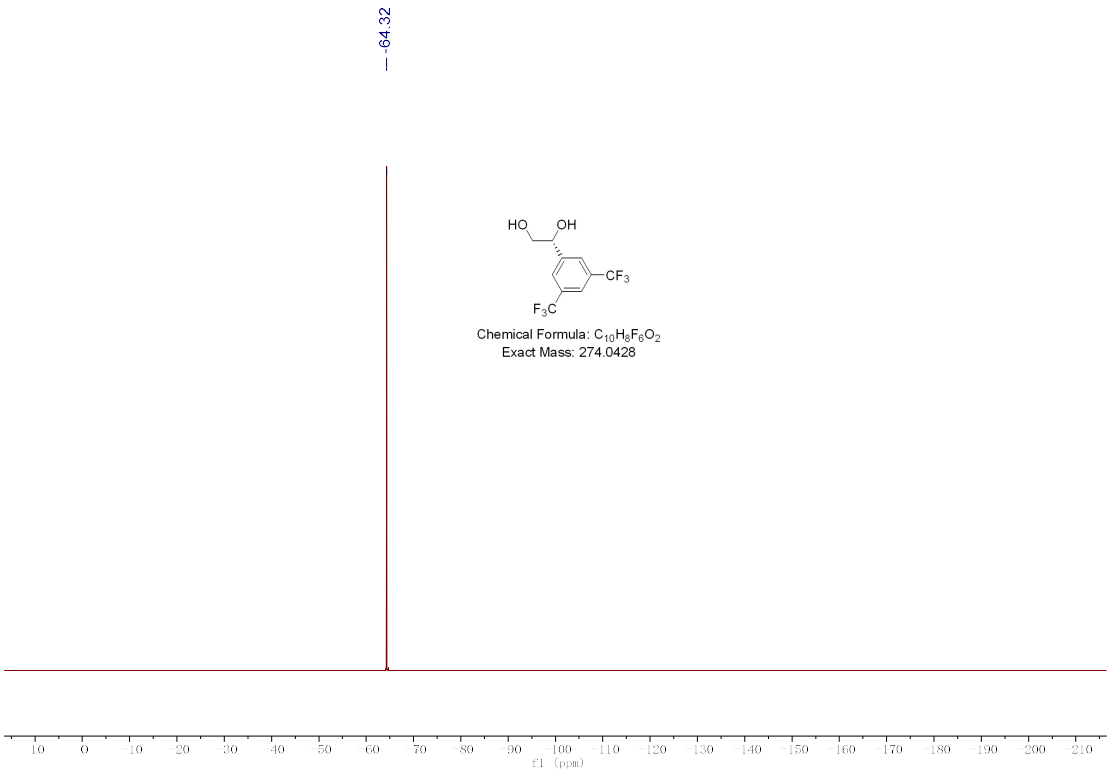
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 10g



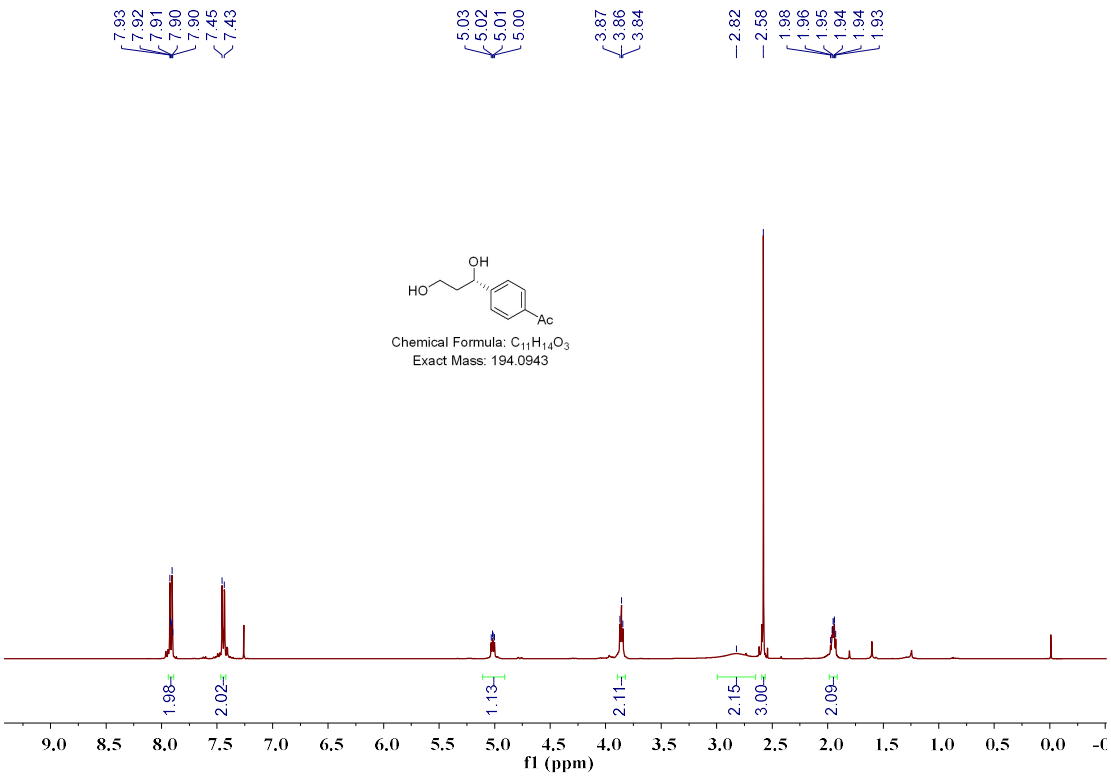
^{1}H NMR (600 MHz, CD_3OD) Spectrum of 14



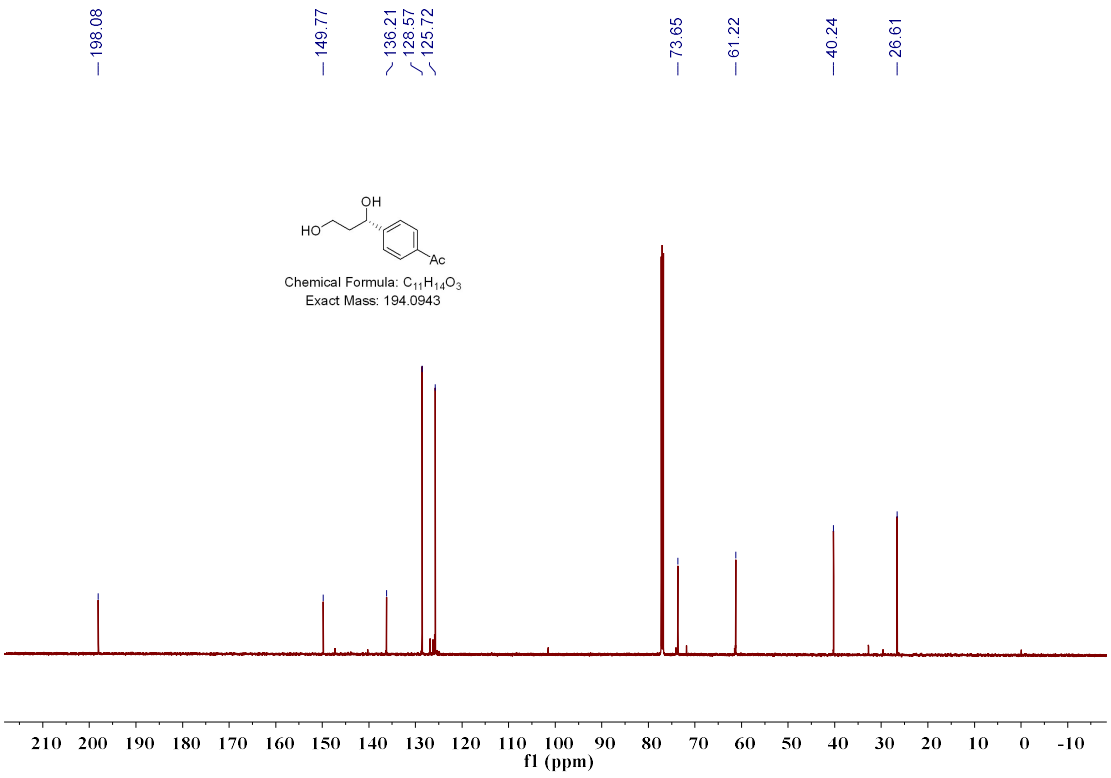
^{13}C NMR (151 MHz, CD_3OD) Spectrum of 14



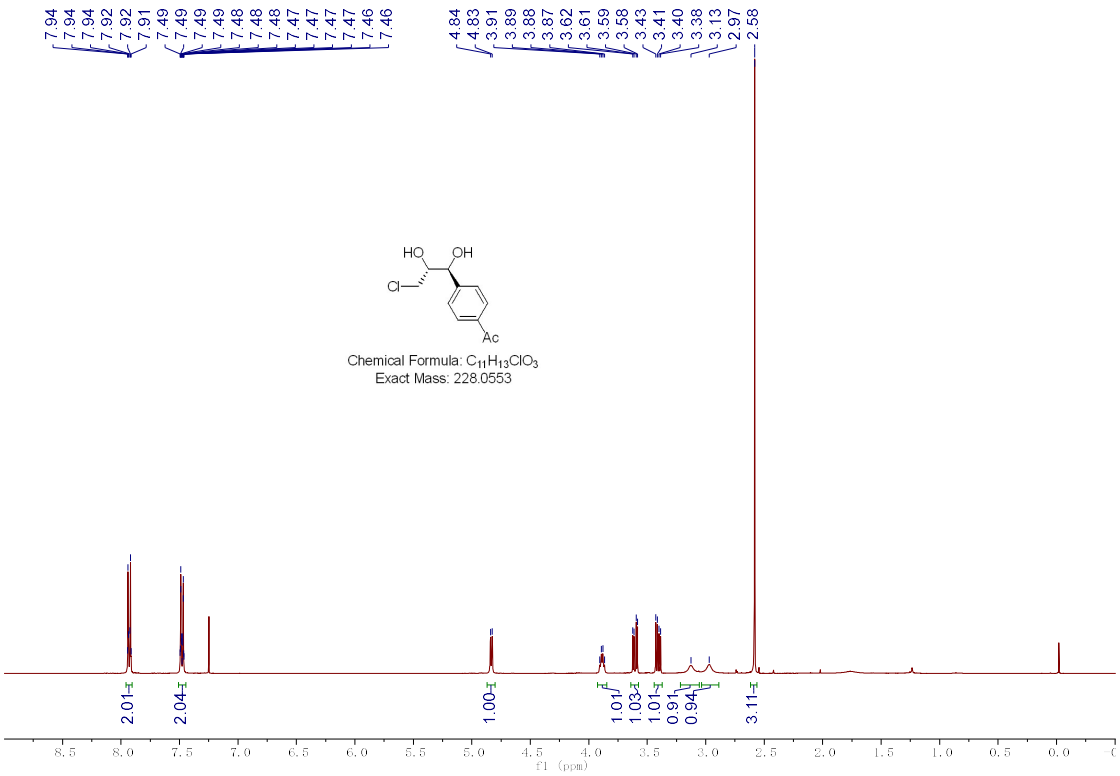
^{19}F NMR (565 MHz, CD_3OD) Spectrum of 14



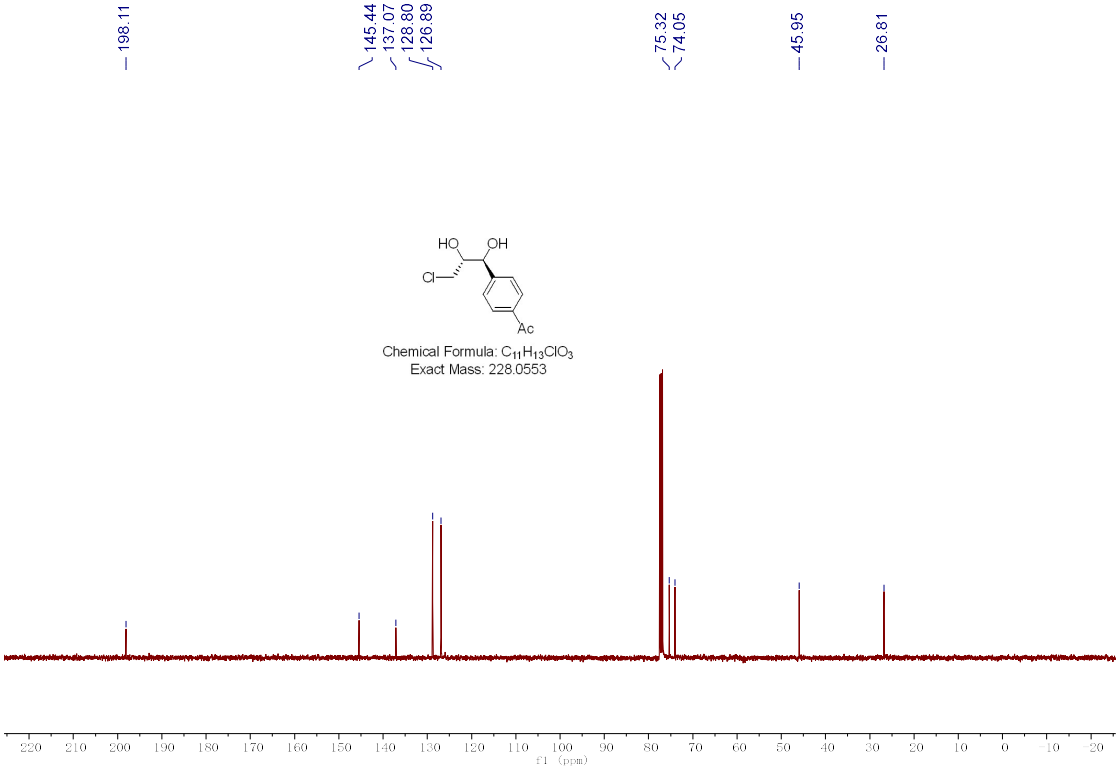
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 15



^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 15

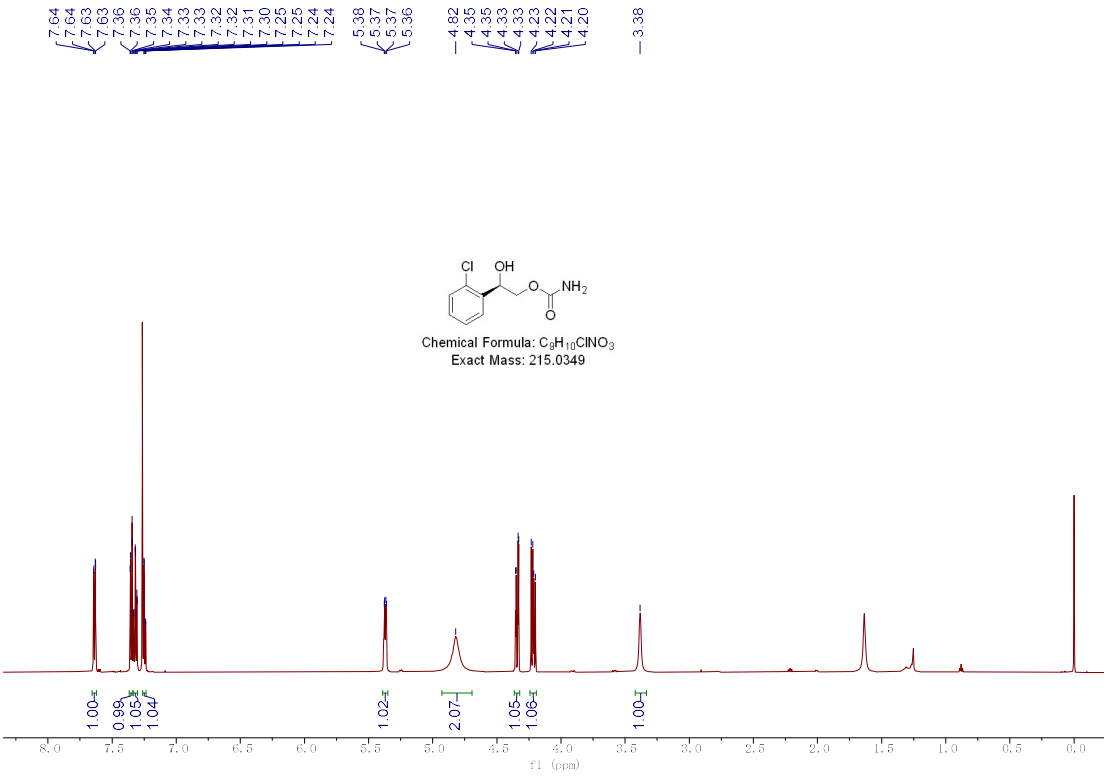


^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 16

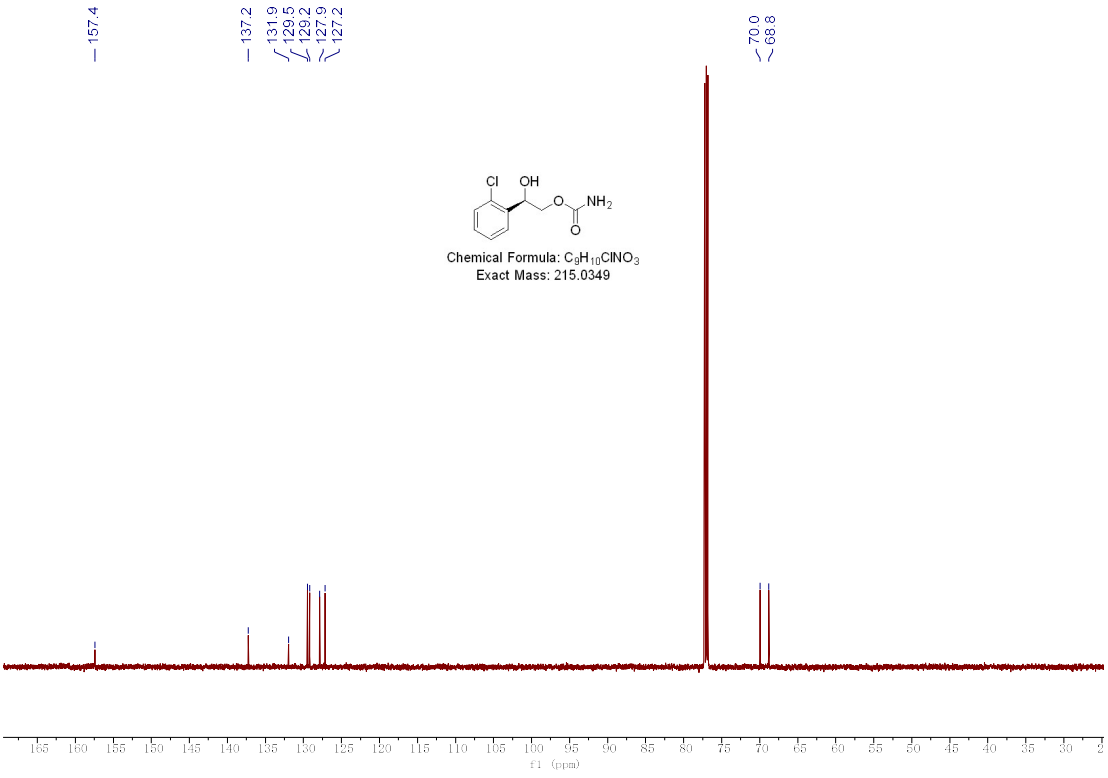


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of 16

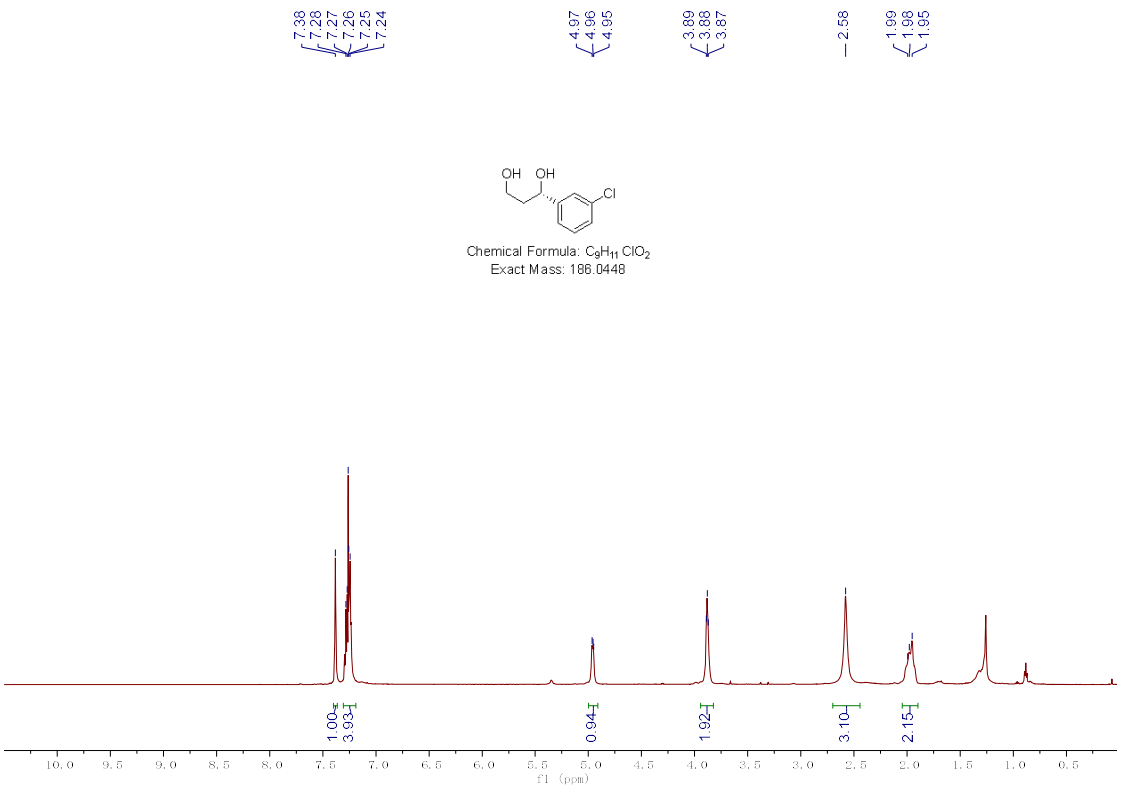
(*R*)-Carisbamate



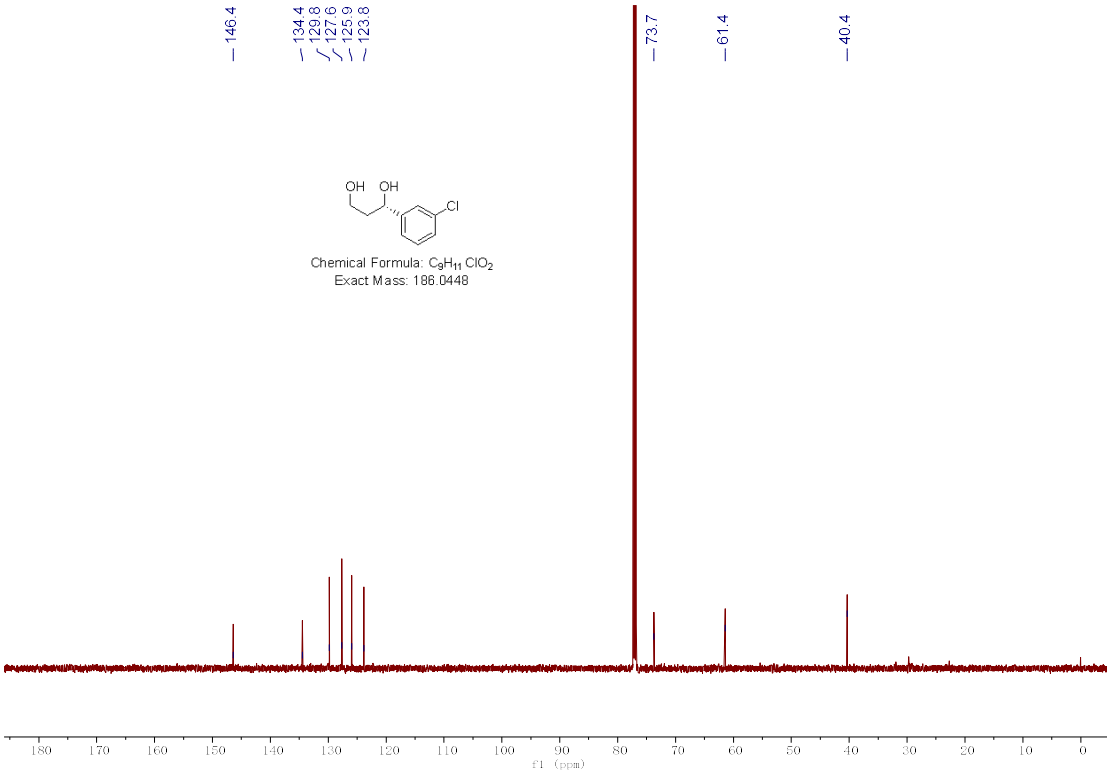
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of (*R*)-Carisbamate



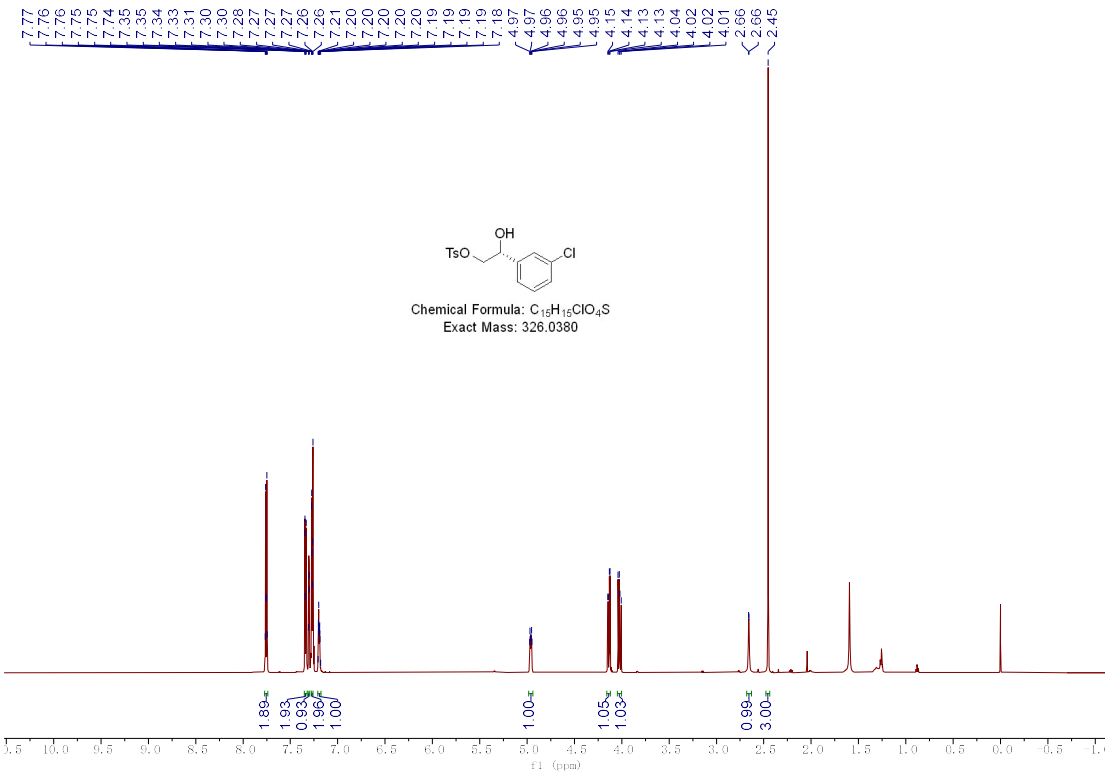
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of (*R*)-Carisbamate



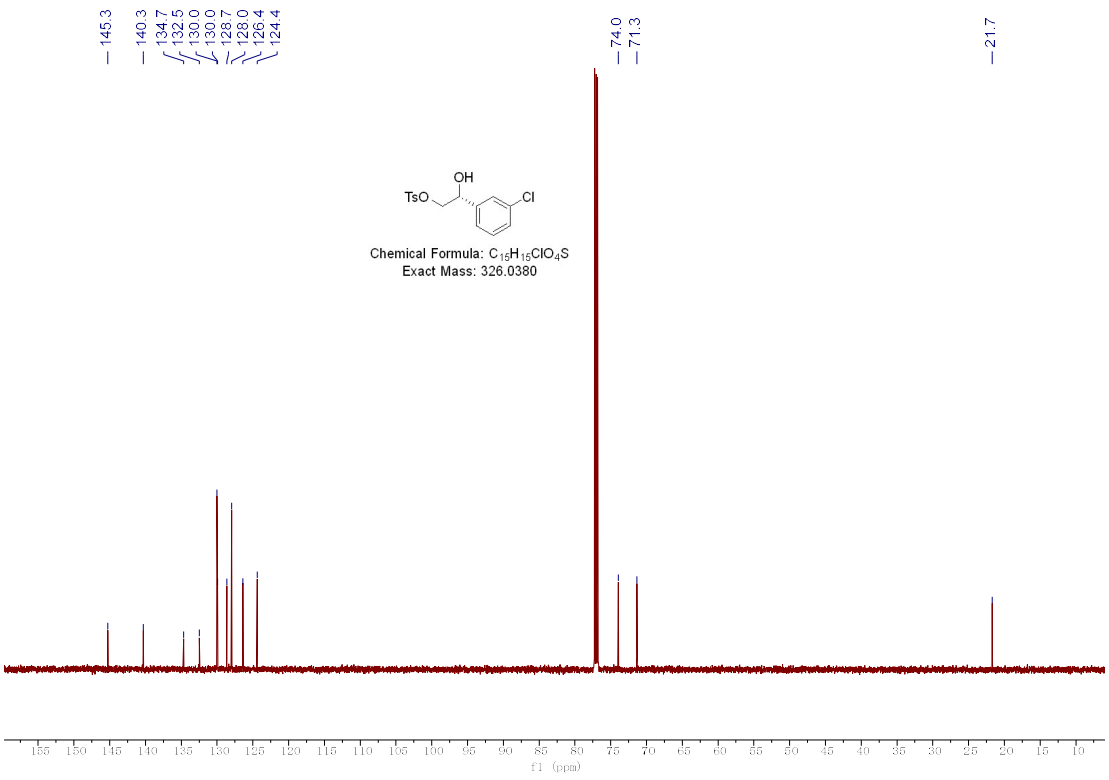
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 17



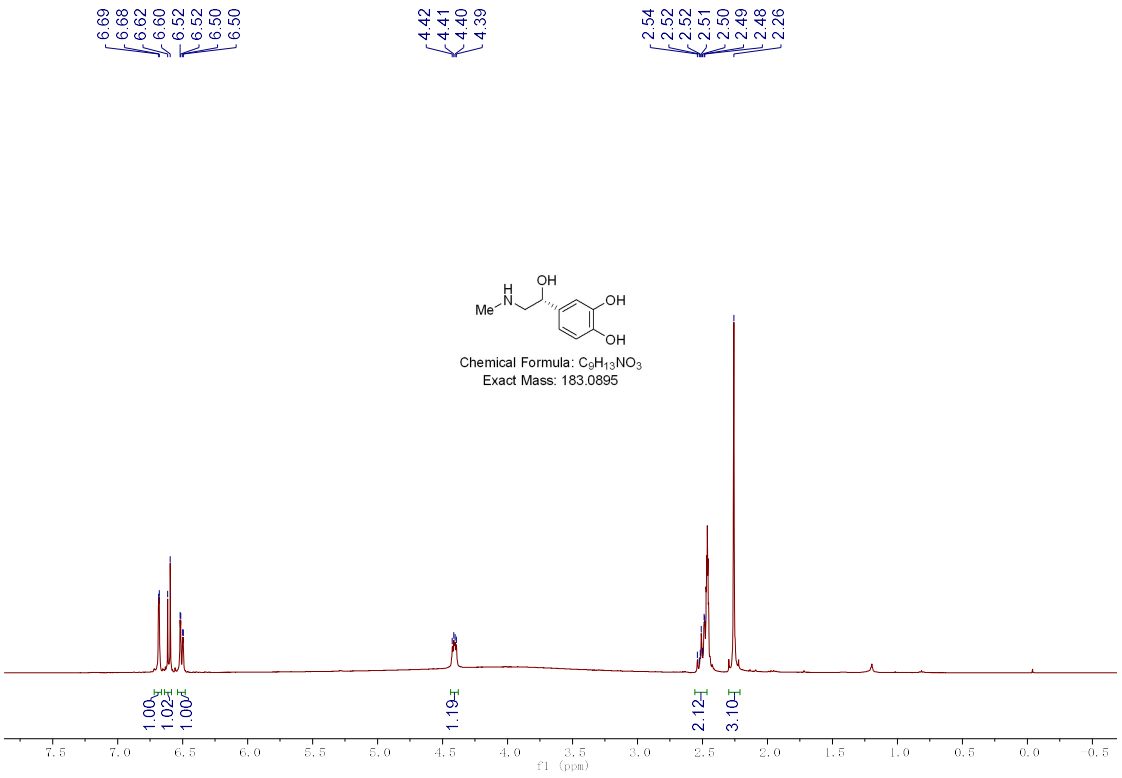
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 17



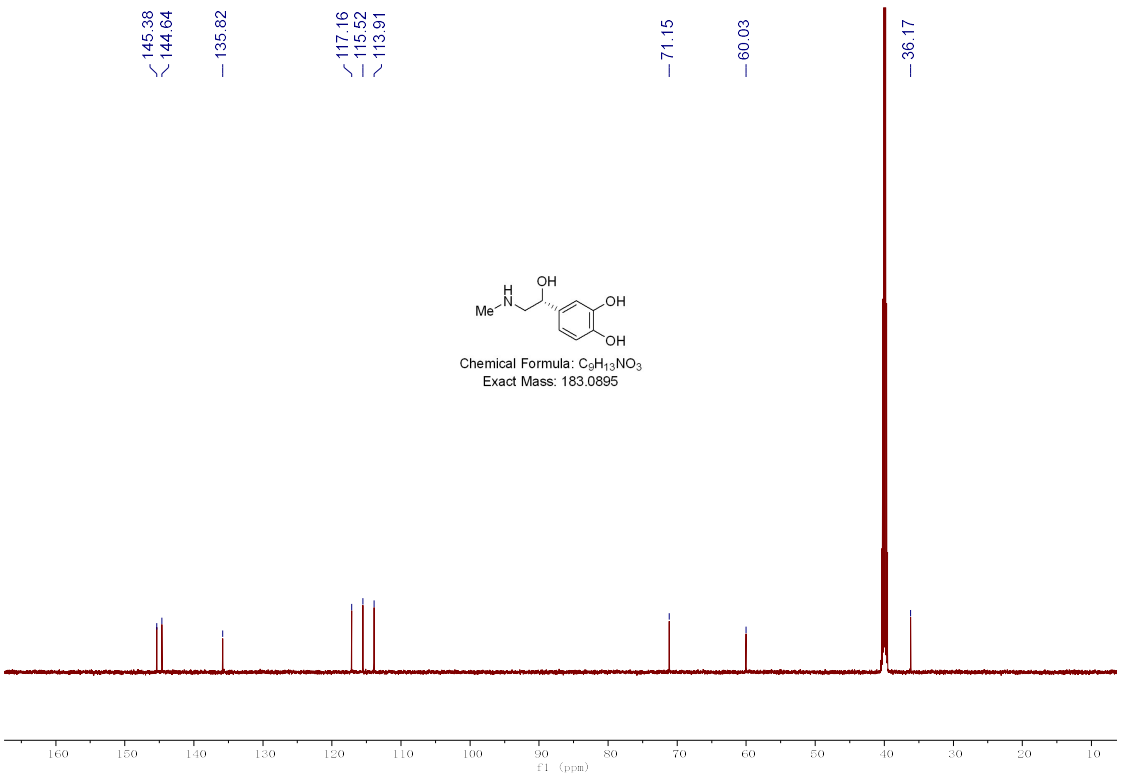
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 18



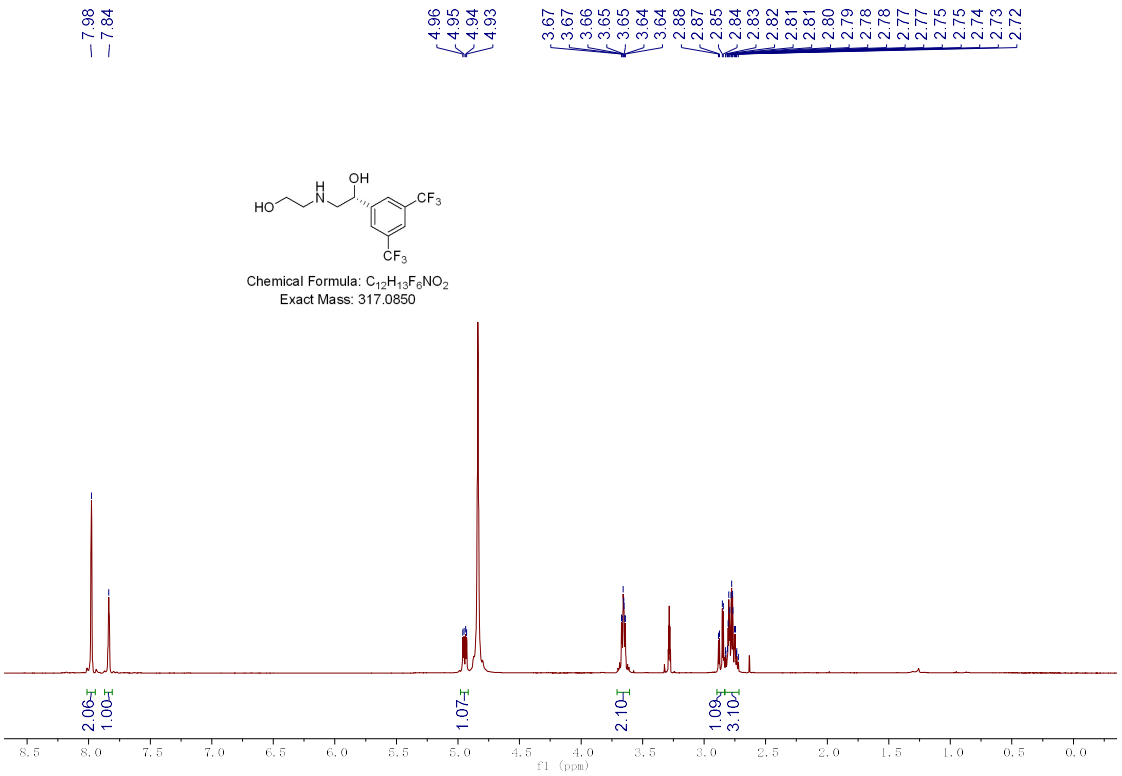
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 18



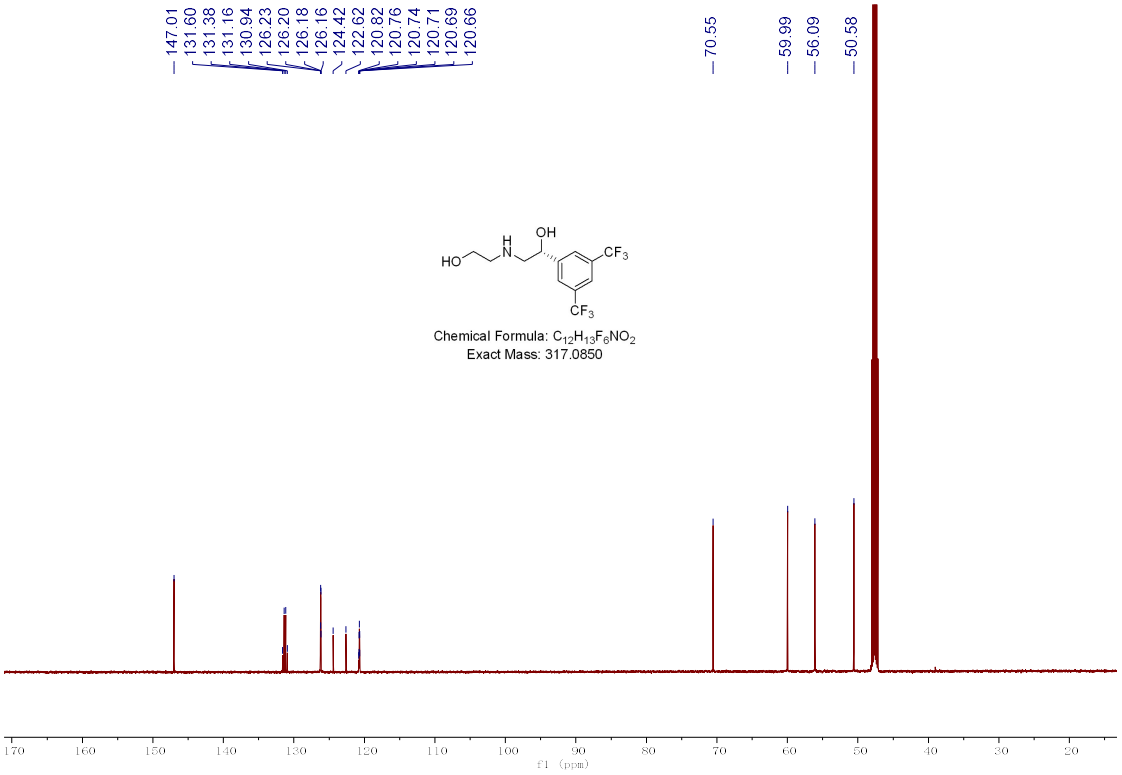
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of (-)-Epinephrine



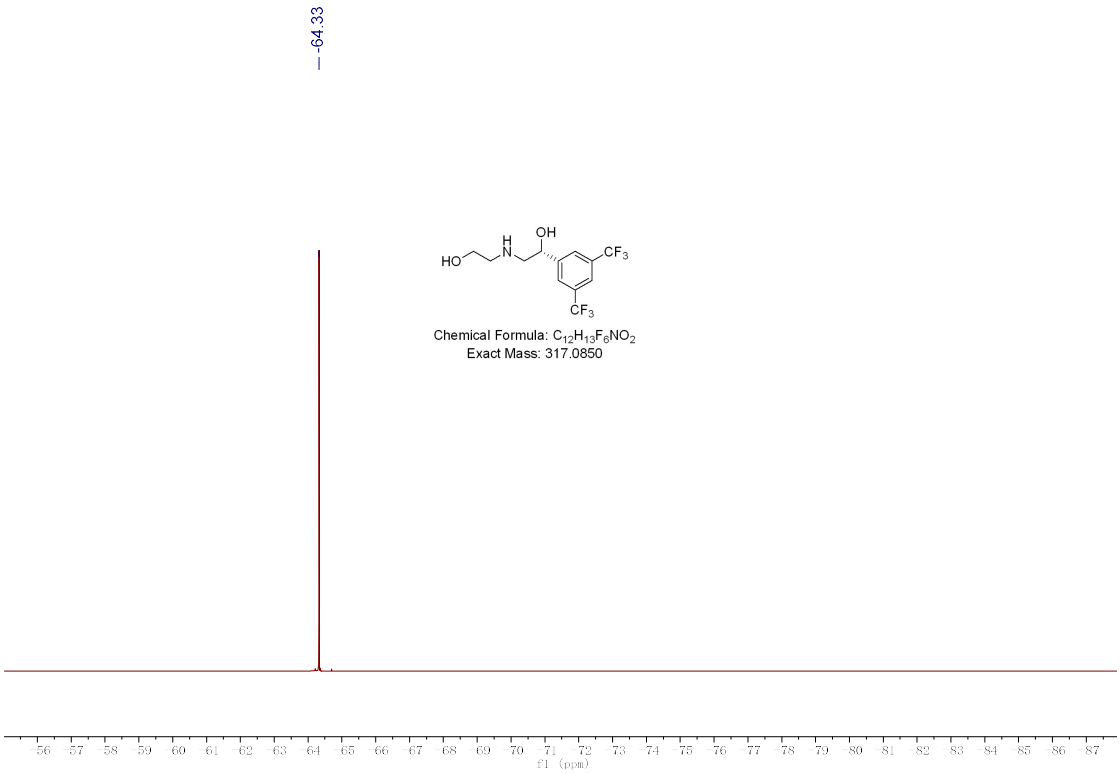
^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of (-)-Epinephrine



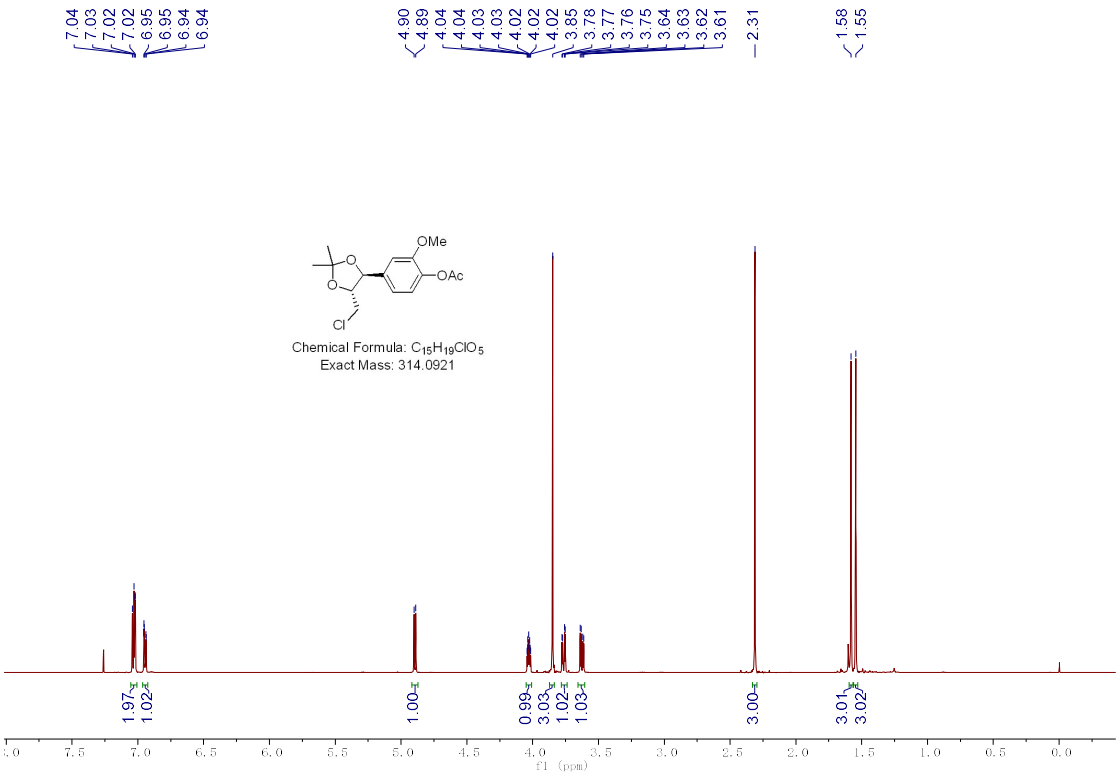
^{1}H NMR (400 MHz, Methanol-d_4) Spectrum of 20



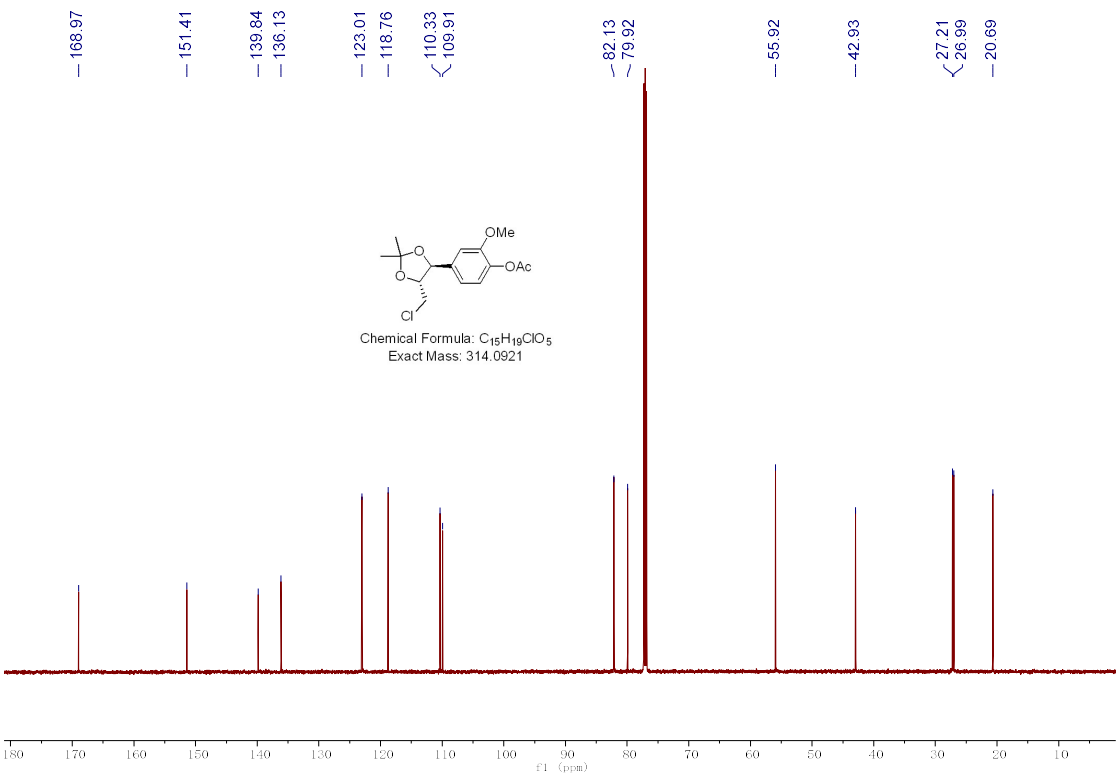
^{13}C NMR (151 MHz, Methanol-d_4) Spectrum of 20



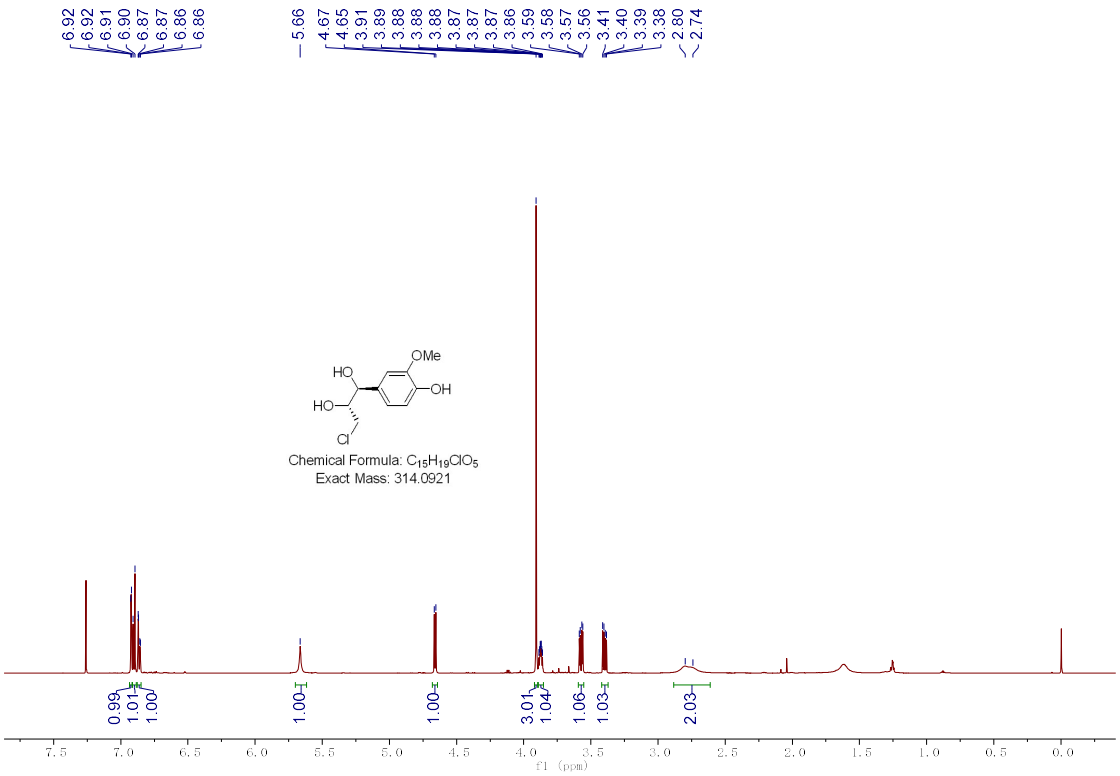
^{19}F NMR (565 MHz, Methanol-d_4) Spectrum of 20



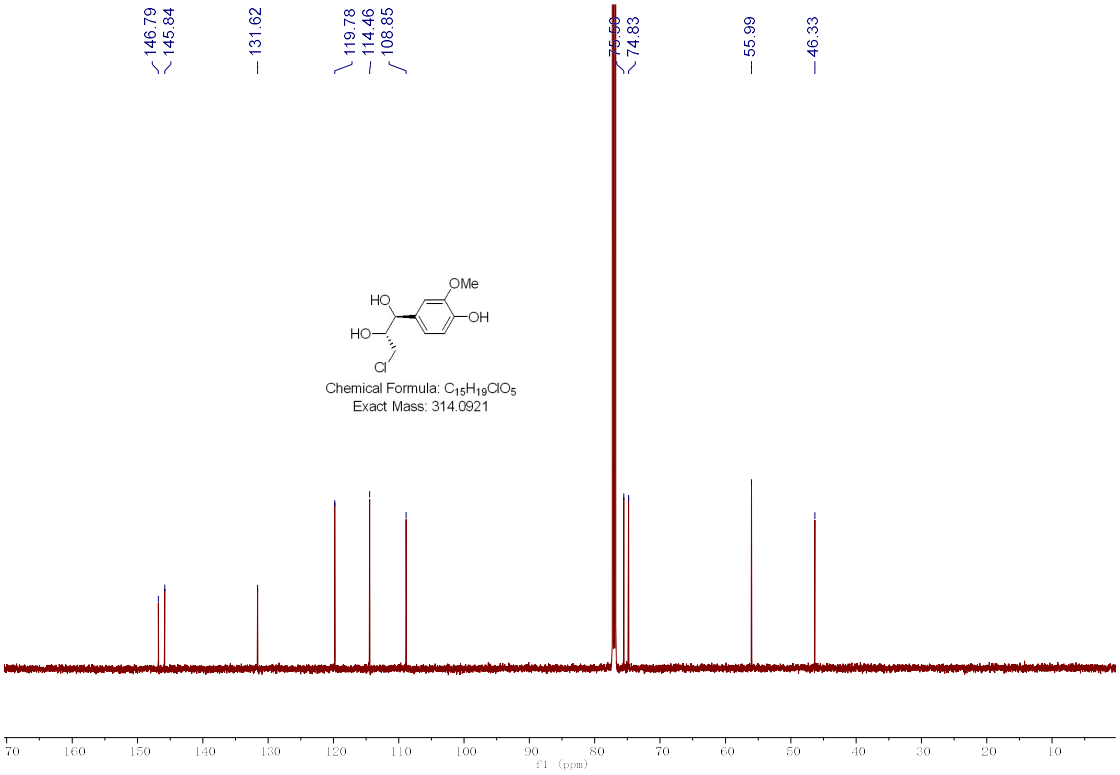
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 21



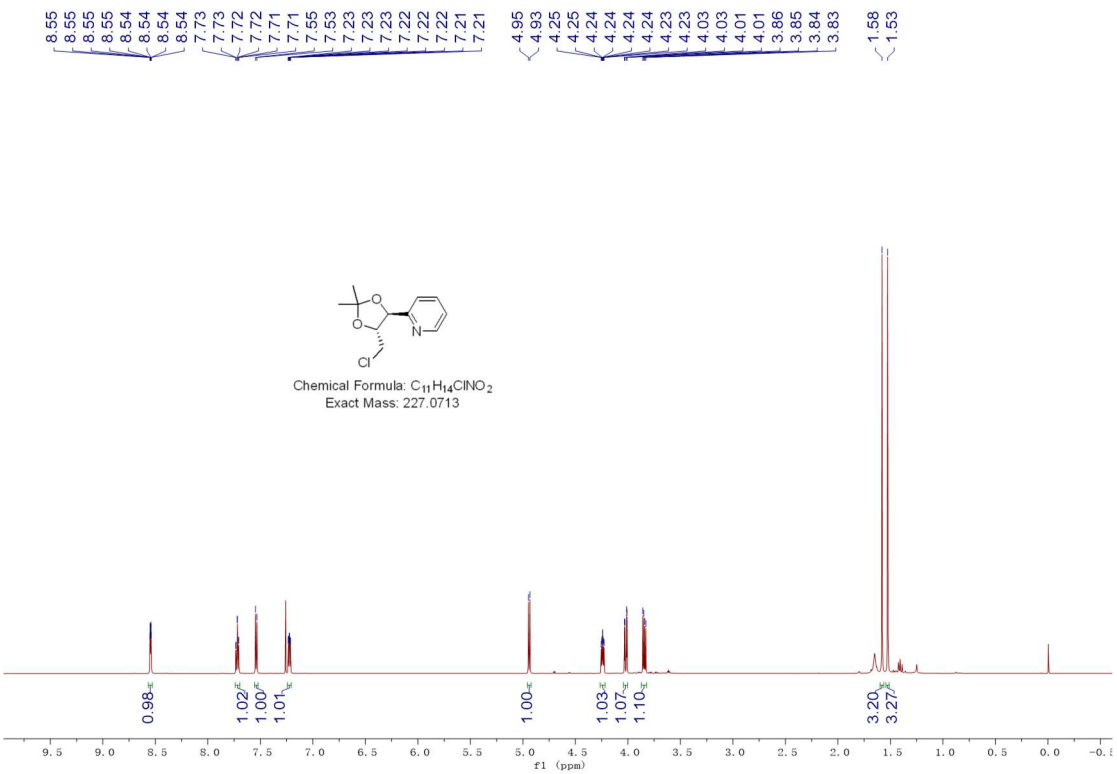
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 21



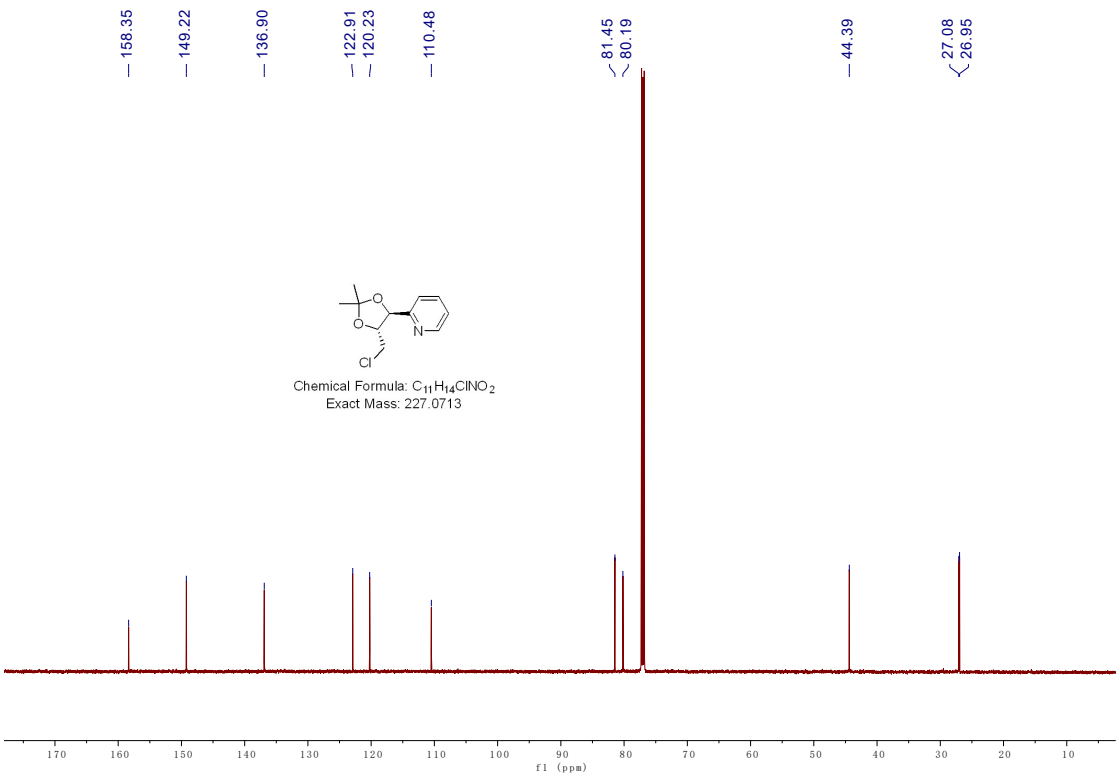
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 22



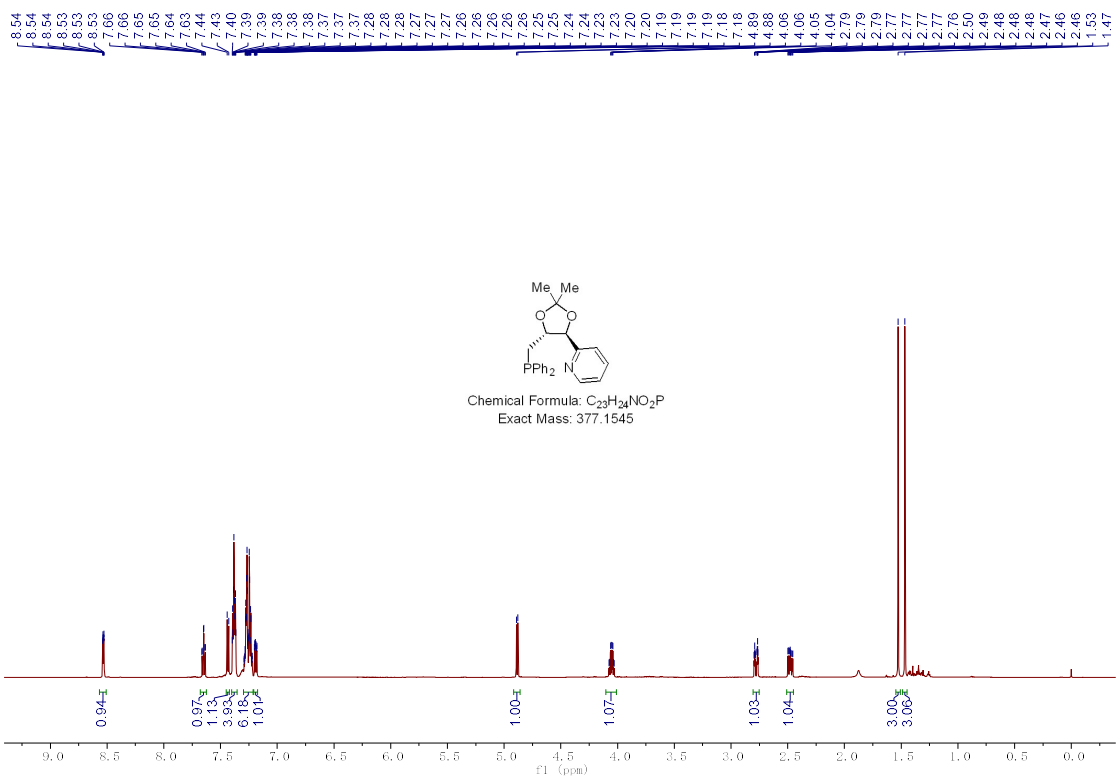
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 22



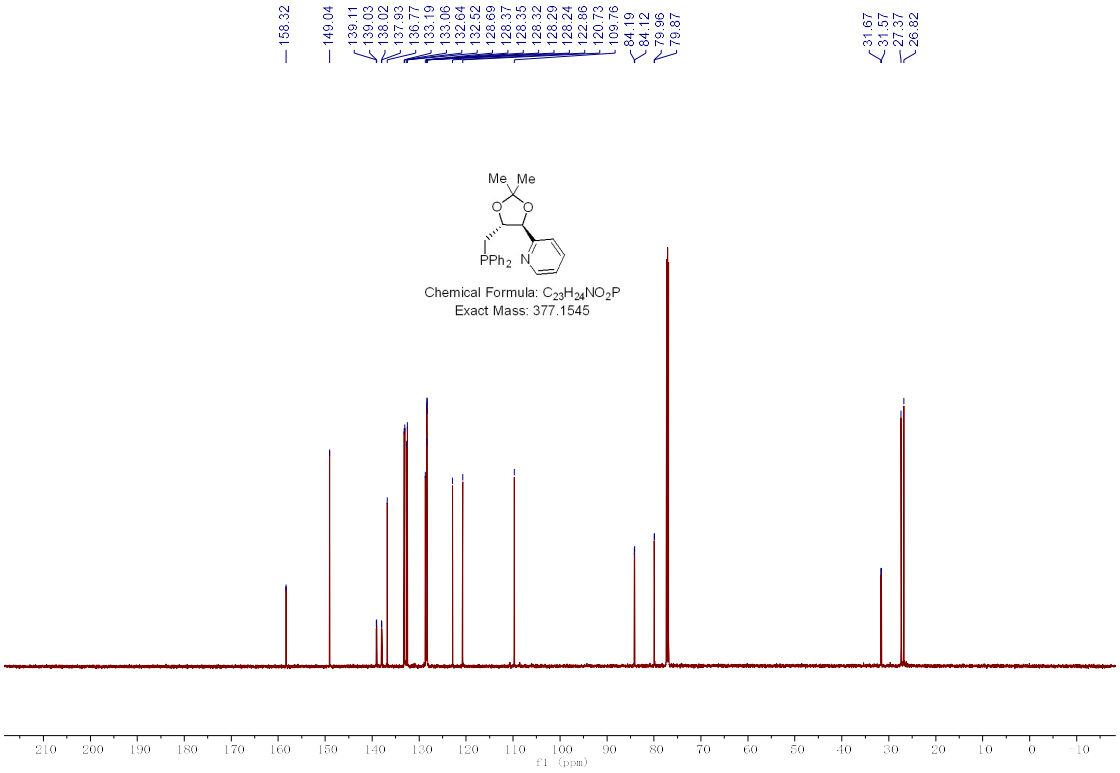
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 23



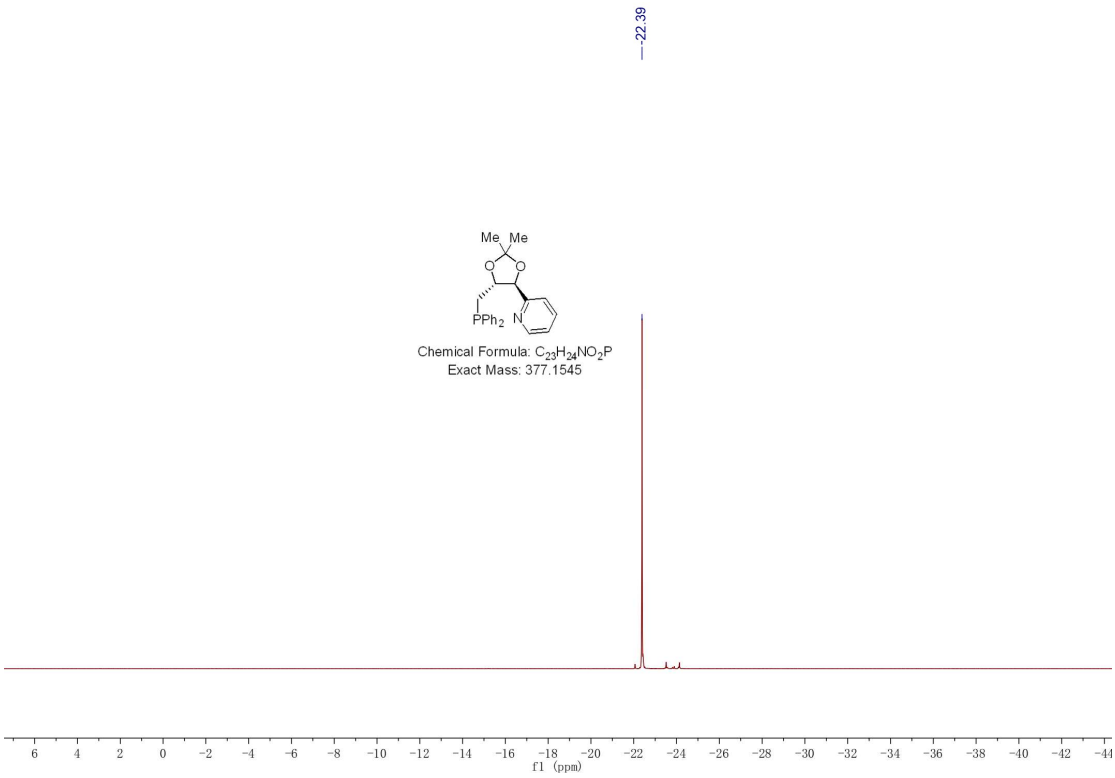
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 23



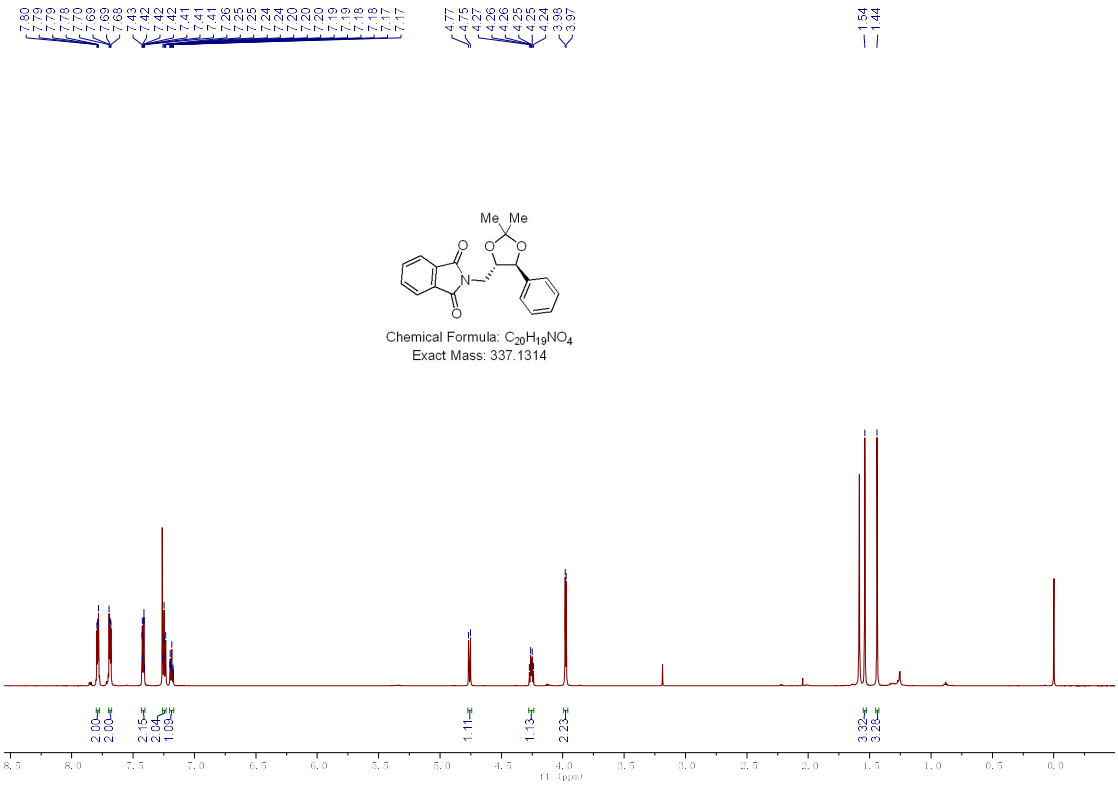
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 24



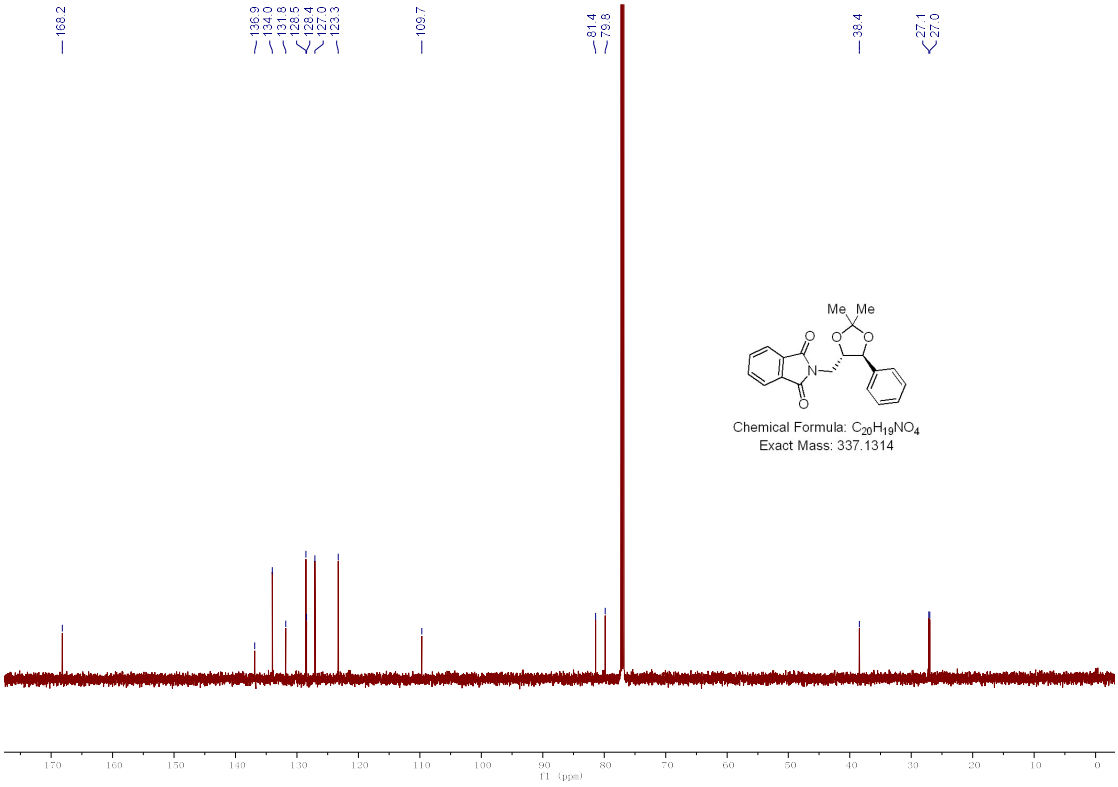
^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 24



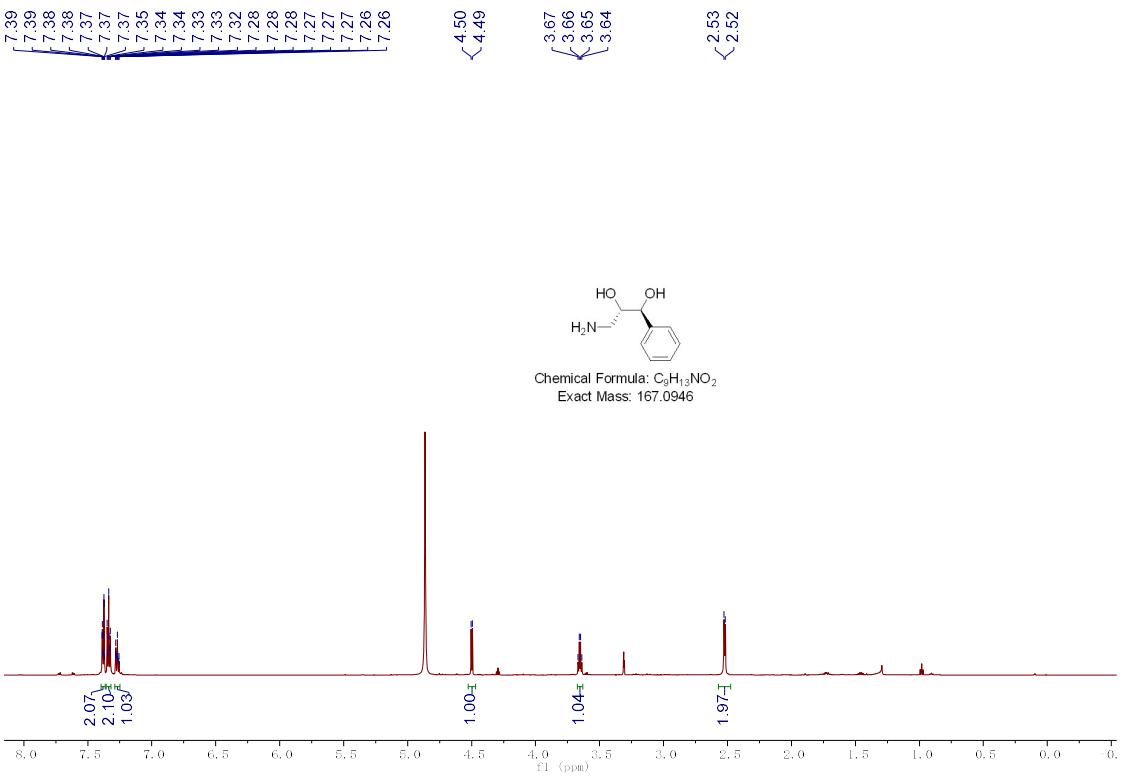
^{13}P NMR (243 MHz, $CDCl_3$) Spectrum of 20



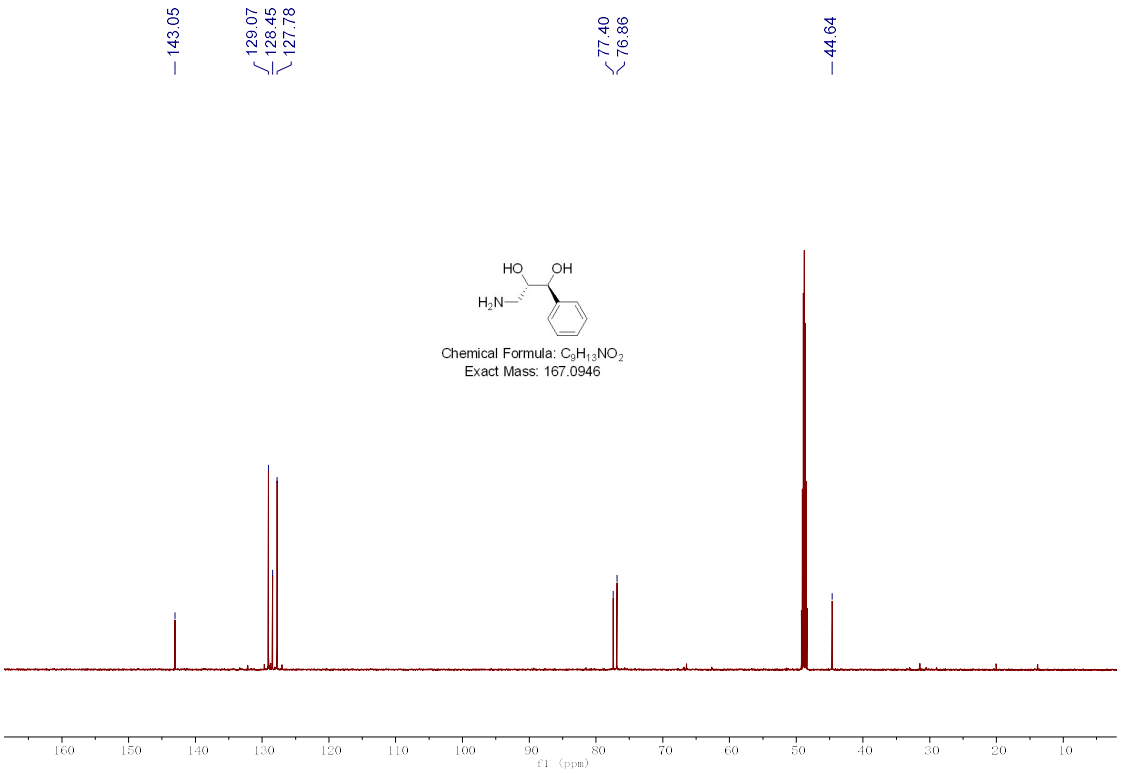
^{1}H NMR (600 MHz, Methanol-d_4) Spectrum of 25



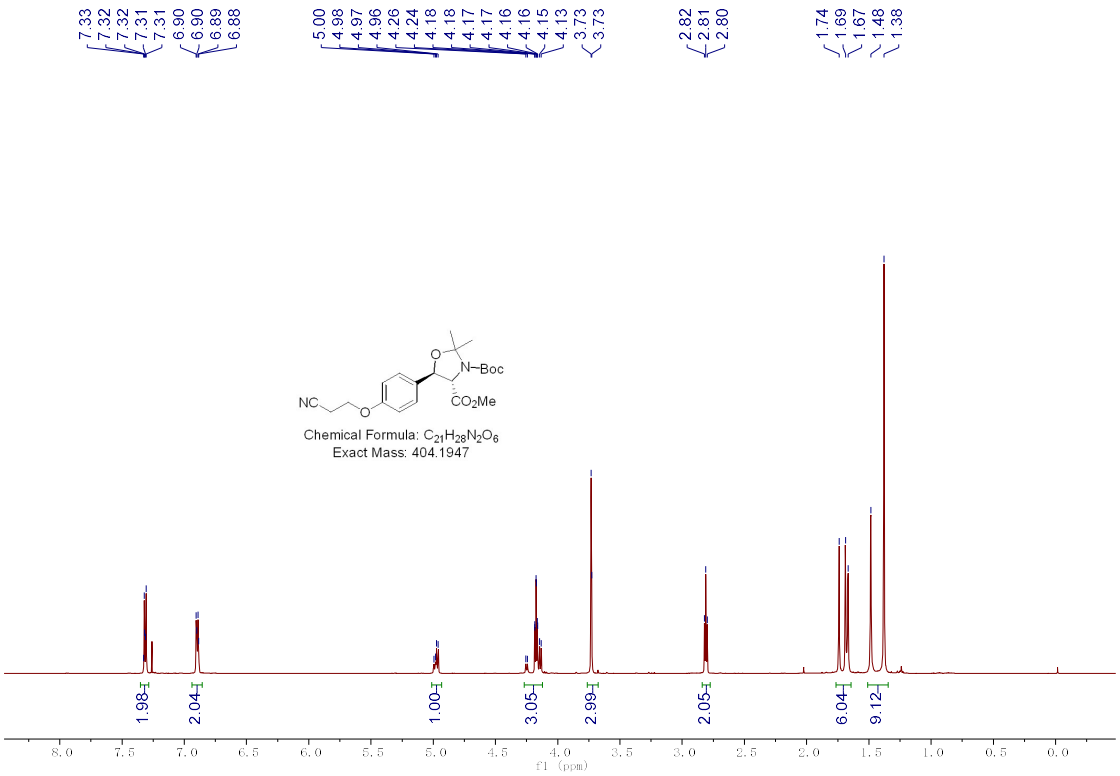
^{13}C NMR (151 MHz, Methanol-d_4) Spectrum of 25



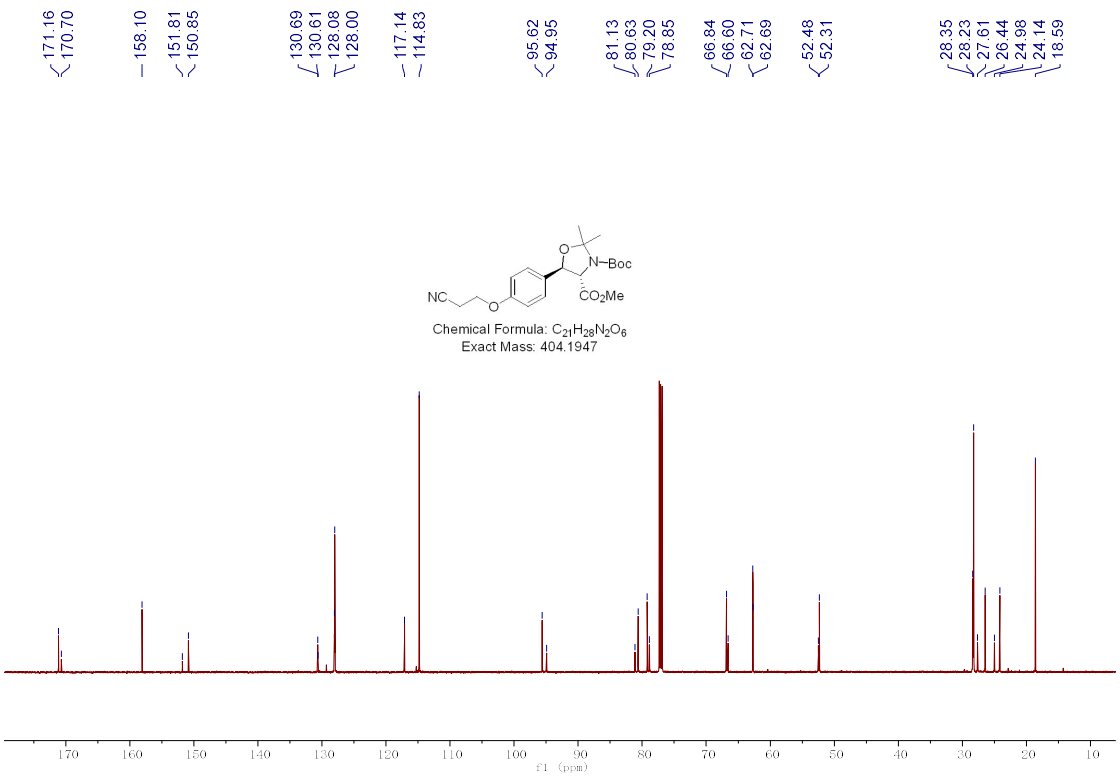
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 26



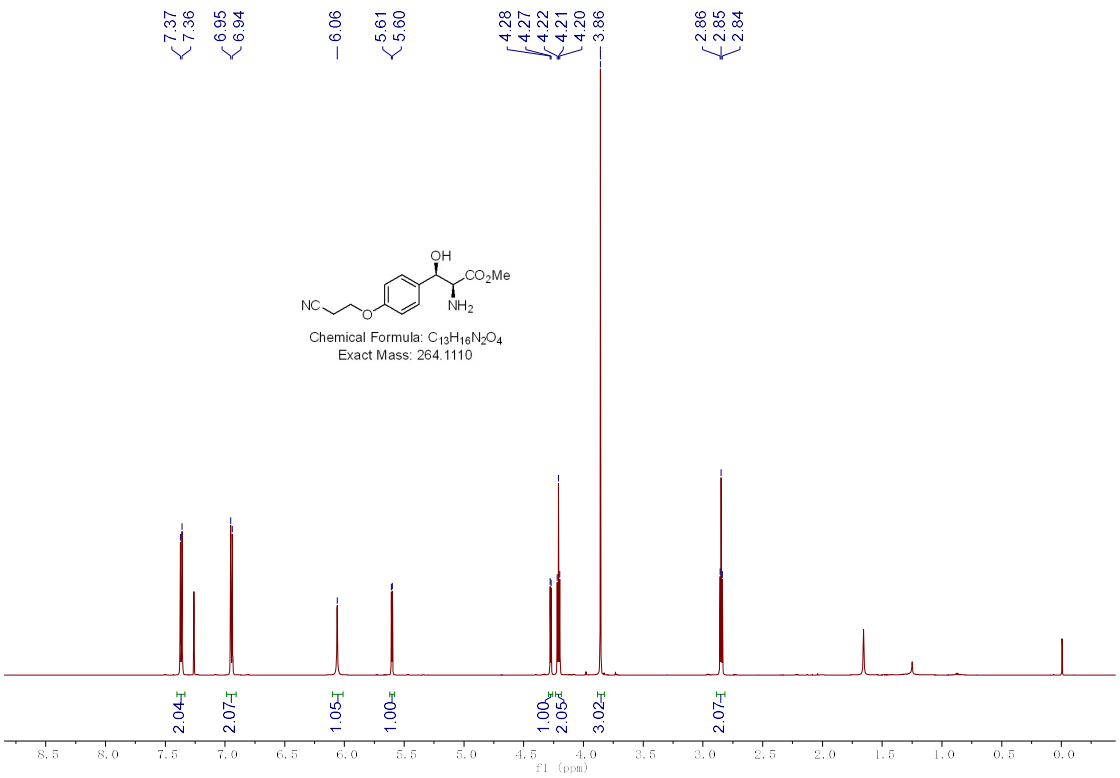
^{13}C NMR (151MHz, $CDCl_3$) Spectrum of 26



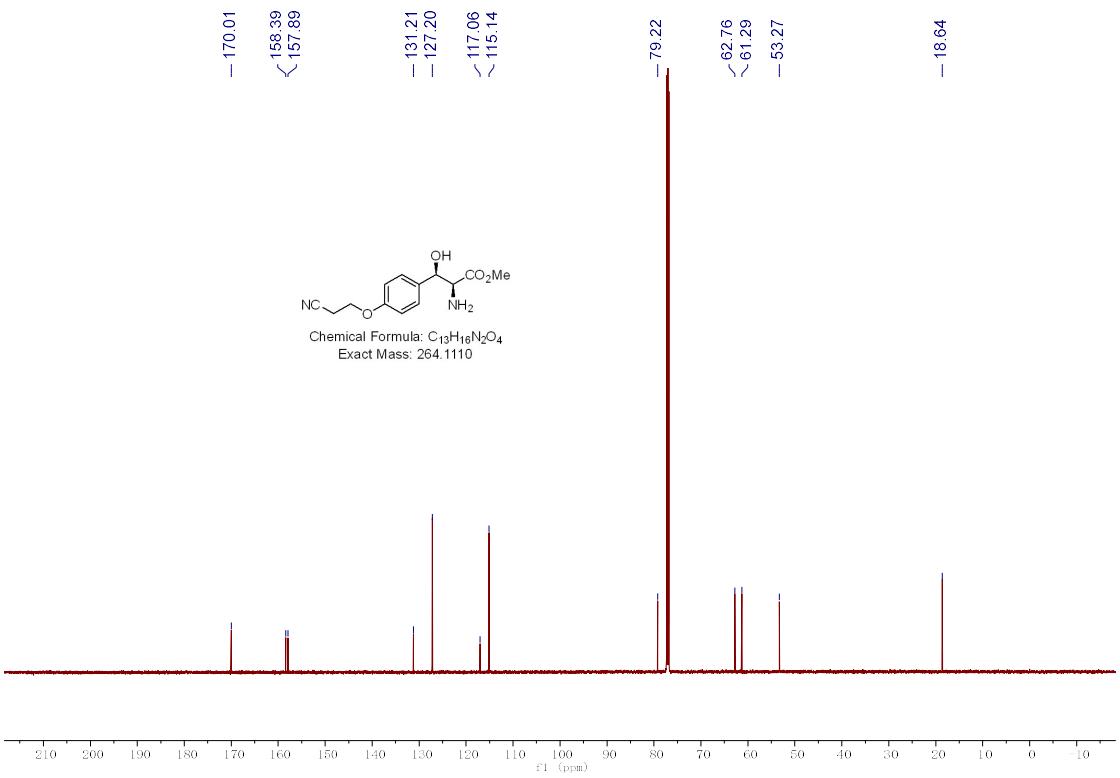
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 28



^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 28



^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of 29



^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of 29

9. Supplementary References

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