Supporting Information

Synthesis of Axially Chiral Diaryl Ethers by NHCs-Catalyzed Atroposelective Esterification

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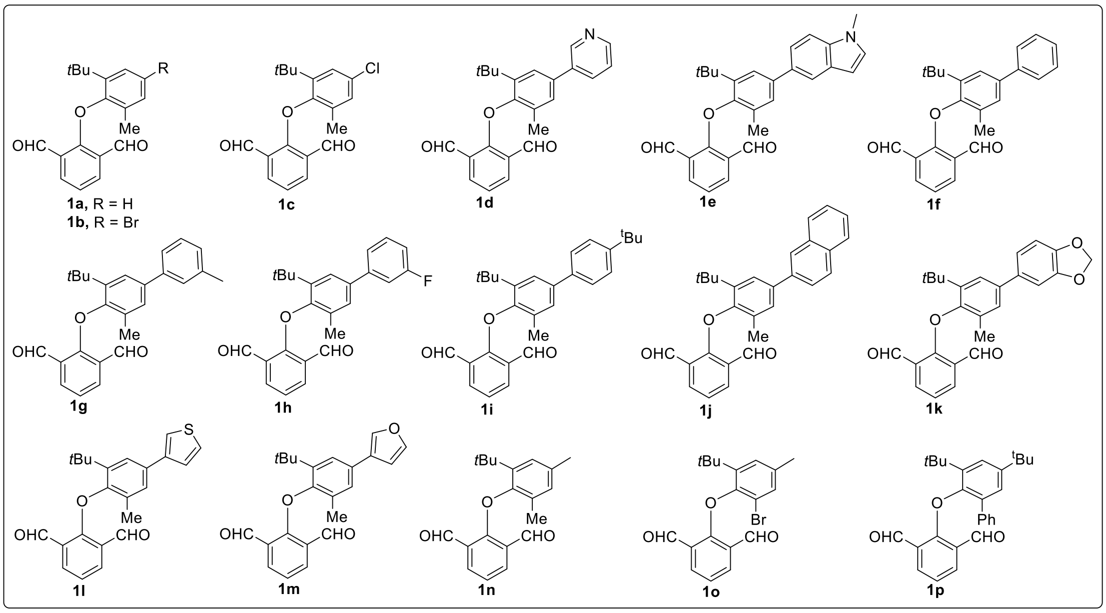
I. General Information.

All reactions were performed under nitrogen atmosphere in flame dried flasks. All reactions were monitored by thin layer chromatography (TLC) using Macherey-Nagel 0.20 mm silica gel 60 plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Taizhou, China). ^1H, ^{13}C, ^{19}F spectra were recorded with Varian 500 MHz (Inova-500) or Bruker 600 MHz (Avance-600) instrument. Chemical shifts were referenced to $\delta_{TMS} = 0.00$ ppm (^1H, ^{13}C). Chemical shifts (δ) are reported in ppm. Coupling constants (J) are reported in Hz. Dichloromethane-d_2 (δ (^1H) = 5.32 ppm, δ (^{13}C) = 53.8 ppm), chloroform-d_1 (δ (^1H) = 7.26 ppm, δ (^{13}C) = 77.0 ppm) or methanol-d_4 (δ (^1H) = 3.31 ppm, δ (^{13}C) = 49.0 ppm) were used as solvents. The following abbreviations are used to describe peak patterns as appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = triplet of doublet, td = doublet of triplet, bs = broad singlet. High-pressure liquid chromatography (HPLC) was performed on Agilent 1200 Series chromatographs using a chiral column (25 cm) as noted for each compound. High-resolution mass spectra HRMS (ESI-TOF) were recorded on Brucker microtof. Compounds were visualized by irradiation with UV light, or stained with iodine/silica gel, or potassium permanganate. Preparatory thin-layer chromatography (Prep-TLC) was performed on silica gel GF with UV 254 (20 × 20 cm, 1000 microns, from Yantai Jiang you Silica Gel Development Co., Ltd.) and visualized with UV light. Optical rotations were reported as follows: $[\alpha]_D{}^T$ = (c: g/100 mL in CH_2Cl_2).

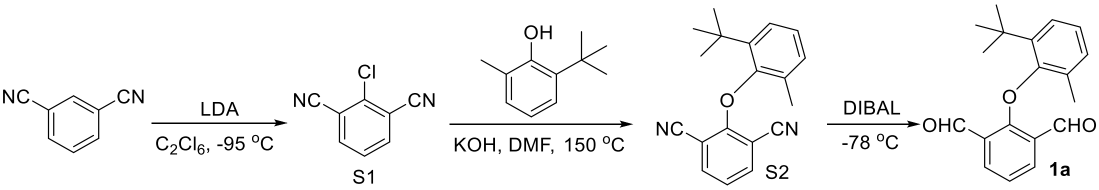
II. Experimental Section

2.1 Synthesis of Starting Materials

2.1.1 List of starting materials



2.1.2 General procedure for the synthesis of Substrates 1a-1p.[1,2] Preparation of 1a is shown as a representative example.



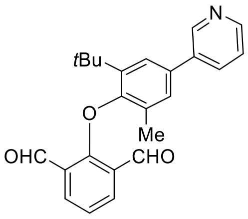
n-BuLi (2.5 M in Hexanes) (20 mL, 50 mmol) was added dropwise to a stirred solution of anhydrous diisopropylamine (7.0 mL, 50 mmol) dissolved in anhydrous THF (50 mL) in 500 mL double neck flask at 0 oC under N$_2$ and allowed to stir for 30 min at this temperature. A solution of 1,3-dicyanobenzene (5 g, 39.02 mmol, 1 equiv) in anhydrous THF (75 mL) was added dropwise to double neck flask at -95 °C and allowed to stir for 1 h. Hexachloroethane (14.8 g, 62.44 mmol, 1.6 equiv) dissolved in anhydrous THF (100 mL) was added to the reaction mixture at this temperature and the mixture allowed to stir for 1 h and slowly rise to room temperature continue to react overnight. The mixture was quenched by addition of saturated ammonium chloride solution and THF removed under reduced pressure and extract 3 times with EA. The organic phase were washed with brine, dried with anhydrous sodium sulfate and solvent removed under reduced pressure. The product was purified by flash column chromatography (10:1 = PE : EA) to yield the product **S1** as a yellow solid.

Phenol (8.46 mmol, 1 equiv), KOH (0.48 g, 8.46 mmol, 1 equiv) were stirred in toluene (25 mL) at 130 °C in eggplant bottle with water separator installed for 2-4 h. Toluene was removed under reduced pressure, **S1** (1.25 g, 7.69 mmol, 1 equiv) and anhydrous DMF (50 mL) were stirred under N$_2$ at 150 °C for 16 h. Solvent were removed under reduced pressure, and the residue was dissolved in portions of EA for 3 times and the combined organics washed with water for 3 times, dried for Na$_2$SO$_4$, and solvent removed under reduced pressure. The product was purified by flash column chromatography (10:3 = PE : EA) to yield the product **S2** as a brown oil.

DIBAL (1.5M solution in toluene) (2.5 equiv) was added slowly to a solution of **S2** (1 equiv) in anhydrous toluene (30 mL) under N_2 at -78 ºC and allowed to stir for 1 h at this temperature. After stirred 16 h at RT, cooled to 0 ºC , 5M HCl was added slowly to the mixture and allowed to stir for 2 h. The aqueous phase was extracted 3 times with EA and the combined organics washed with brine. The organics dried for Na_2SO_4, and solvent removed under reduced pressure. The product was purified by flash column chromatography (50:1 = PE : EA) to yield the product **1a** as a yellow oil (placed in the air for a period of time, it can turn into a yellow solid).

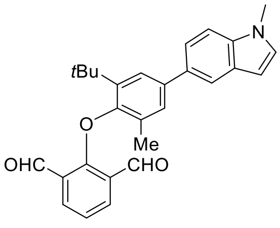
2.1.3 Characterization data of the new substrates

2-(2-(tert-butyl)-6-methyl-4-(pyridin-3-yl)phenoxy)isophthalaldehyde (1d)



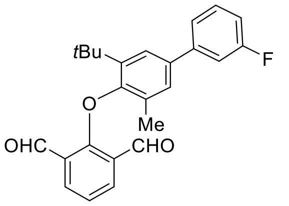
1d: light red solid; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 10.10 (s, 2H), 8.85 (s, 1H), 8.62 (s, 1H), 8.13 (d, *J* = 7.6 Hz, 2H), 7.87 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.55 (d, *J* = 2.3 Hz, 1H), 7.39 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.31 – 7.27 (m, 2H), 2.00 (s, 3H), 1.52 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.64, 160.79, 155.94, 148.57, 148.17, 141.53, 135.42, 135.36, 134.42, 130.00, 128.30, 127.12, 125.39, 123.60, 123.03, 35.55, 30.29, 18.15. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{24}H_{23}NaNO_3$, ([M + Na]$^+$), 396.1570; found 396.1540.

2-(2-(tert-butyl)-6-methyl-4-(1-methyl-1H-indol-5-yl)phenoxy)isophthalaldehyde (1e)



1e: light red solid**; ^{1}H NMR (500 MHz, Chloroform-*d*)** δ 10.10 (s, 2H), 8.11 (d, *J* = 7.7 Hz, 2H), 7.81 (d, *J* = 1.6 Hz, 1H), 7.62 (d, *J* = 2.3 Hz, 1H), 7.46 – 7.36 (m, 2H), 7.33 (d, *J* = 2.2 Hz, 1H), 7.27 – 7.20 (m, 1H), 7.09 (d, *J* = 3.0 Hz, 1H), 6.54 (d, *J* = 3.0 Hz, 1H), 3.83 (s, 3H), 2.00 (s, 3H), 1.52 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 188.02, 161.24, 154.54, 140.72, 140.31, 136.32, 135.33, 131.94, 130.04, 129.65, 128.95, 127.61, 127.17, 125.55, 122.59, 121.28, 119.44, 109.48, 101.35, 35.45, 32.99, 30.45, 18.07. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{25}H_{21}NaNO_3$, ([M + Na]$^+$), 448.1883; found 448.1886.

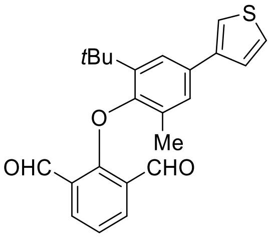
2-((3-(tert-butyl)-3'-fluoro-5-methyl-[1,1'-biphenyl]-4-yl)oxy)isophthalaldehyde (1h)



1h: light yellow solid; **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 10.09 (s, 2H), 8.12 (d, *J* = 7.7 Hz, 2H), 7.55 (d, *J* = 2.3 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.35 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.07 –

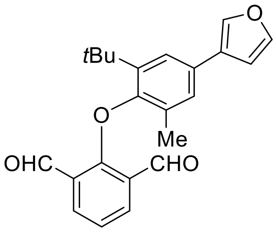
7.02 (m, 1H), 1.99 (s, 3H), 1.51 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.70, 163.96, 162.33, 160.88, 155.68, 142.58 (d, J = 7.8 Hz), 141.21, 137.47 (d, J = 2.0 Hz), 135.39, 130.30 (d, J = 8.2 Hz), 129.94, 128.01, 127.13, 125.31, 122.92, 122.76 (d, J = 2.8 Hz), 114.14 (dd, J = 36.6, 21.6 Hz), 35.50, 30.33, 18.10. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -110.15 – -115.05 (m, 1F).
HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{23}FNaO_3$, ($[M + Na]^+$), 413.1523; found 413.1553.

2-(2-(tert-butyl)-6-methyl-4-(thiophen-3-yl)phenoxy)isophthalaldehyde (1l)



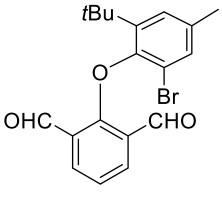
1l: yellow solid; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 10.07 (s, 2H), 8.11 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 2.3 Hz, 1H), 7.43 (dd, J = 2.9, 1.4 Hz, 1H), 7.41 (dd, J = 4.9, 3.0 Hz, 1H), 7.36 (dd, J = 5.0, 1.4 Hz, 1H), 7.29 (d, J = 1.5 Hz, 1H), 7.26 (t, J = 7.7 Hz, 1H), 1.97 (s, 3H), 1.50 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.83, 161.00, 154.96, 141.47, 141.08, 135.36, 133.54, 129.22, 127.91, 127.11, 126.45, 126.31, 124.66, 122.76, 120.54, 35.40, 30.32, 18.01. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{22}SNaO_3$, ($[M + Na]^+$), 401.1182; found 401.1185.

2-(2-(tert-butyl)-4-(furan-3-yl)-6-methylphenoxy)isophthalaldehyde (1m)



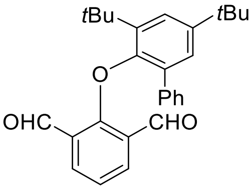
1m: yellow solid; **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 10.06 (s, 2H), 8.09 (d, J = 7.7 Hz, 2H), 7.70 (t, J = 1.2 Hz, 1H), 7.48 (t, J = 1.7 Hz, 1H), 7.44 (d, J = 2.2 Hz, 1H), 7.25 (d, J = 5.2 Hz, 1H), 7.17 (d, J = 2.2 Hz, 1H), 6.66 (d, J = 0.9 Hz, 1H), 1.94 (s, 3H), 1.48 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.83, 161.00, 154.78, 143.80, 141.15, 138.59, 135.35, 130.14, 128.64, 127.98, 127.10, 125.75, 124.03, 122.75, 108.86, 35.35, 30.29, 17.93. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{22}NaO_4$, ($[M + Na]^+$), 385.1410; found 385.1421.

2-(2-bromo-6-(tert-butyl)-4-methylphenoxy)isophthalaldehyde (1o)



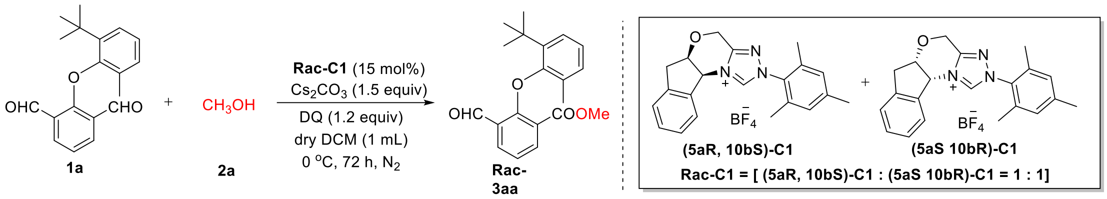
1o: yellow solid; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 10.00 (s, 2H), 8.11 (d, J = 7.6 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.24 – 7.23 (m, 1H), 2.35 (s, 3H), 1.44 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.84, 160.46, 151.58, 142.70, 136.95, 135.09, 133.47, 128.63, 127.46, 123.05, 113.81, 35.70, 30.15, 20.94. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{19}H_{19}BrNaO_2$, ($[M + Na]^+$), 397.0410; found 397.0398.

2-((3,5-di-tert-butyl-[1,1'-biphenyl]-2-yl)oxy)isophthalaldehyde (1p)



1p: yellow solid; **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.89 (s, 2H), 7.73 (d, J = 7.7 Hz, 2H), 7.53 (d, J = 2.4 Hz, 1H), 7.14 (d, J = 2.4 Hz, 1H), 7.08 – 6.99 (m, 5H), 6.90 (t, J = 7.6 Hz, 1H), 1.54 (s, 9H), 1.35 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.90, 160.83, 153.44, 148.51, 139.90, 138.05, 134.38, 131.88, 129.36, 128.18, 127.93, 127.36, 127.13, 124.72, 122.35, 35.67, 34.84, 31.51, 30.37. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{28}H_{30}NaO_3$, ([M + Na]$^+$), 437.2087; found 437.2091.

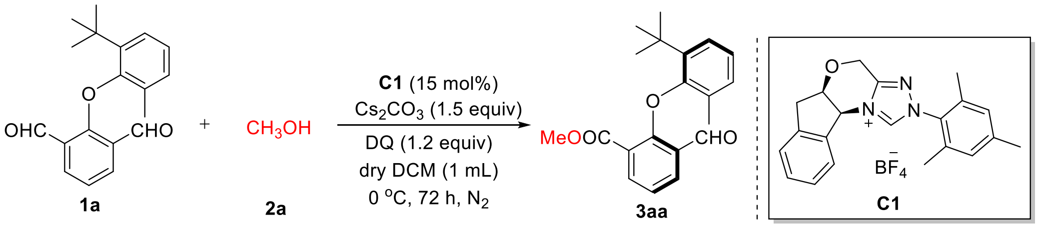
2.2 General Synthetic Procedure of 3.



Racemic Synthesis:

Preparation of **Rac-C1**: **(5aR, 10bS)-C1** (100 mg) and **(5aS, 10bR)-C1** (100 mg) are completely dissolved in dry DCM and concentrated to remove DCM.

Representative Synthesis of Product (Rac)-3aa. In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **Rac-C1** (15 mol%, 6.27 mg), Cs_2CO_3 (49.0 mg, 1.5 equiv), 2-(2-(tert-butyl)-6-methylphenoxy)isophthalaldehyde **1a** (0.1 mmol, 29.6 mg)， and anhydrous dichloromethane (1.0 mL). The mixture was stirred for 5 minutes, followed by the addition of CH_3OH **2a** (0.02 ml, 5.0 equiv) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (48 mg, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 °C for 72 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:1 (v/v) to give the racemic product **3aa**.

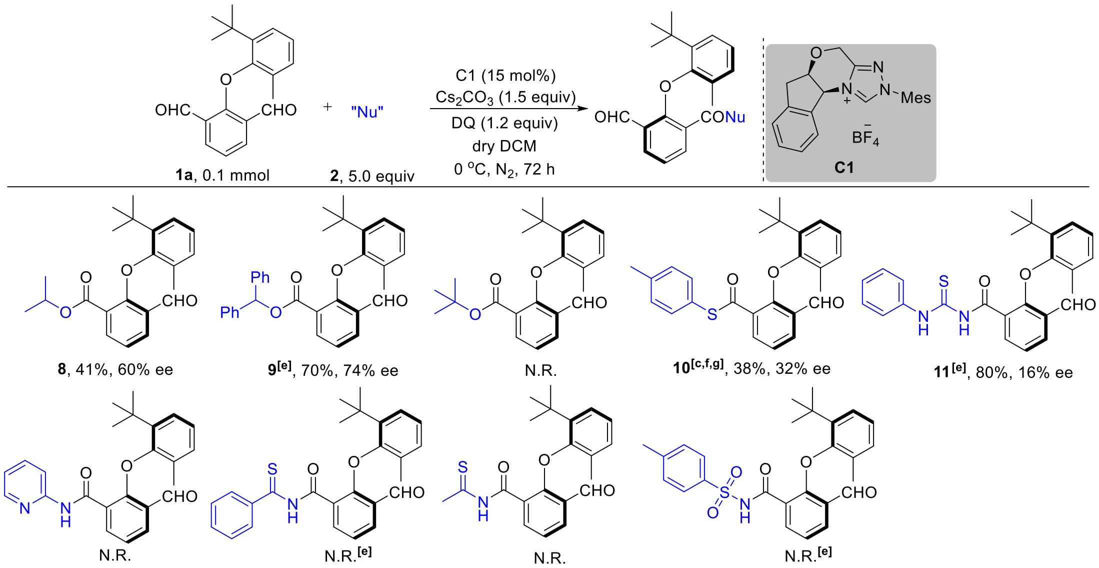


Asymmetric Synthesis:

Representative Synthesis of Product 3aa (standard conditions A): In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **C1** (15 mol%, 6.27 mg), Cs_2CO_3 (49.0 mg, 1.5 equiv), 2-(2-(tert-butyl)-6-methylphenoxy)isophthalaldehyde **1a** (0.1 mmol, 29.6 mg)， and anhydrous dichloromethane (1.0 mL). The mixture was stirred for 5 minutes, followed by the addition of CH_3OH **2a** (0.02 ml, 5.0 equiv) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (48 mg, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 °C for 72 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:1 (v/v) to give the product (S)-**3aa**.

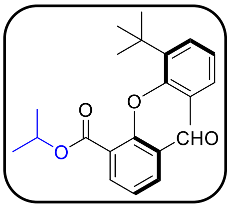
Substrate with unsatisfactory results

We have employed other nucleophiles (Nu) such as propan-2-ol, diphenylmethanol, tert-Butanol, 4-methylbenzenethiol, 1-phenylthiourea, pyridin-2-amine, benzothioamide, ethanethioamide or 4-methylbenzenesulfonamide under our optimized, or slightly modified reaction conditions, and the results were summarized in Scheme S1.



Scheme S1. Substrate scope for desymmetrizing functionalization of axially pre-chiral dialdehydes.[a,b] [a]Unless otherwise noted, all the reactions were carried out with **1** (0.1 mmol), **2** (0.5 mmol), C1 (15 mol%), DQ (1.2 equiv), Cs_2CO_3 (1.5 equiv), and dry DCM (1.0 mL) at 0 °C under N_2 atmosphere for 72 h. [b]Isolated yield, *ee* was determined by chiral-phase HPLC analysis. [c]THF was used instead of DCM. [d]PhMe was used instead of DCM. [e]Reactions were carried out with **2** (0.3 mmol). [f]Reactions were performed at 30 °C. [g]C7 was used instead of C1.

(*S*)-isopropyl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (8)

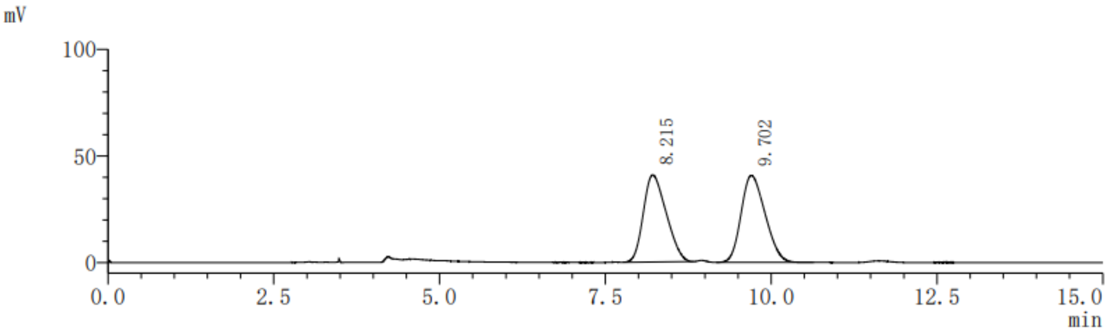


The title compound **8** was prepared under the optimized conditions and purified by preparative TLC (hexane : Et_2O = 5:1). **8** was obtained as a yellow oil (14.5 mg, 41%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.61 (s, 1H), 7.91 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.82 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.29 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.00 (dd, *J* = 7.6, 1.7 Hz, 1H), 5.13 – 5.06 (m, 1H), 1.93 (s, 3H), 1.44 (s, 9H), 1.29 (d, *J* = 6.3 Hz, 3H), 1.27 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 188.07, 165.66, 157.27, 155.42, 140.75, 136.38, 132.11, 130.99, 127.60, 126.87, 125.94, 125.11, 124.98, 122.00, 69.27, 35.28, 30.34, 21.84, 21.75, 17.53.

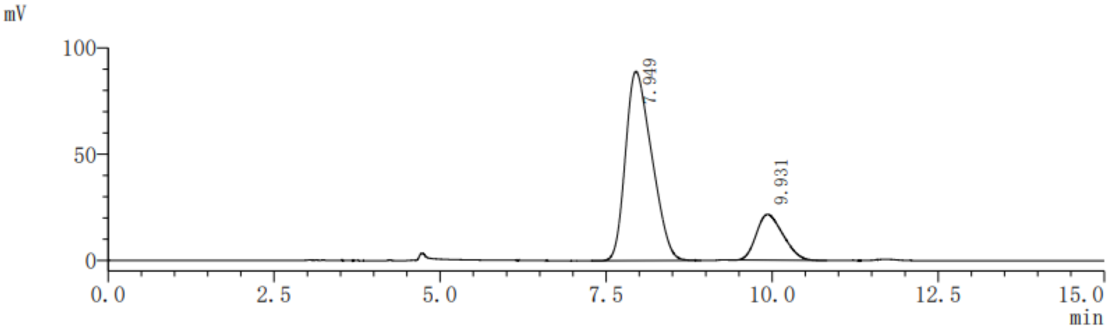
HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{26}NaO_4$, ([M + Na]$^+$), 377.1723; found 377.1725.

$[\alpha]_D^{20}$ = -24.6 (c = 0.72, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (99.5:0.5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 7.95 min, t_R (minor) = 9.93 min, 60% ee.

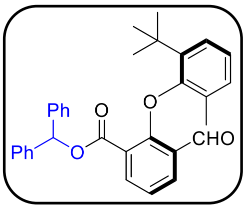


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	8.215	M	0.6644	980634	40860	48.8487
2	9.702	M	0.6821	1026857	40786	51.1513



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	7.949	M	0.7688	2453513	89078	80.2127
2	9.931	M	0.7670	605247	21555	19.7873

(*S*)-benzhydryl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (9)

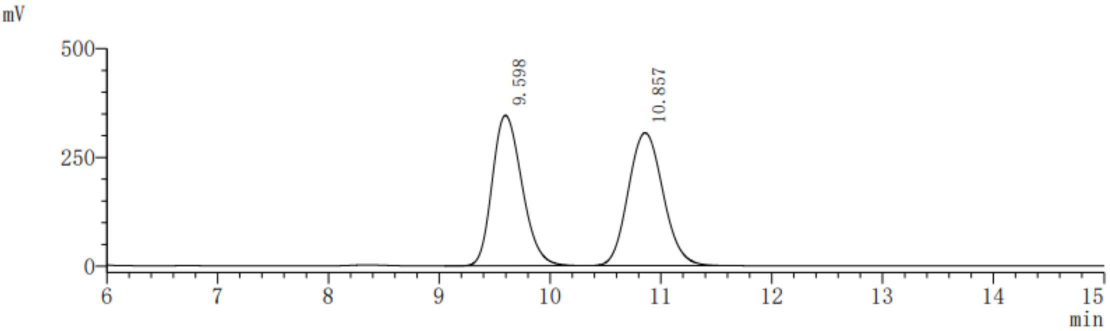


The title compound **9** was prepared under the optimized conditions and purified by preparative TLC (hexane : Et$_2$O = 5:1). **9** was obtained as a transparent oil (33.4 mg, 70%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.59 (s, 1H), 7.94 (dd, J = 7.8, 1.9 Hz, 1H), 7.90 (dd, J = 7.6, 1.9 Hz, 1H), 7.34 – 7.24 (m, 12H), 7.16 (t, J = 7.7 Hz, 1H), 7.02 (t, J = 7.7 Hz, 1H), 6.98 (s, 1H), 6.85 (dd, J = 7.6, 1.6 Hz, 1H), 1.90 (s, 3H), 1.32 (s, 9H). **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 187.94, 164.71, 157.62, 155.32, 140.68, 140.00, 139.70, 136.62, 132.63, 131.01, 128.56, 128.44, 128.03, 127.96, 127.46, 127.22, 127.00, 126.01, 125.20, 123.99, 122.02, 78.09, 35.21, 30.27, 17.64.

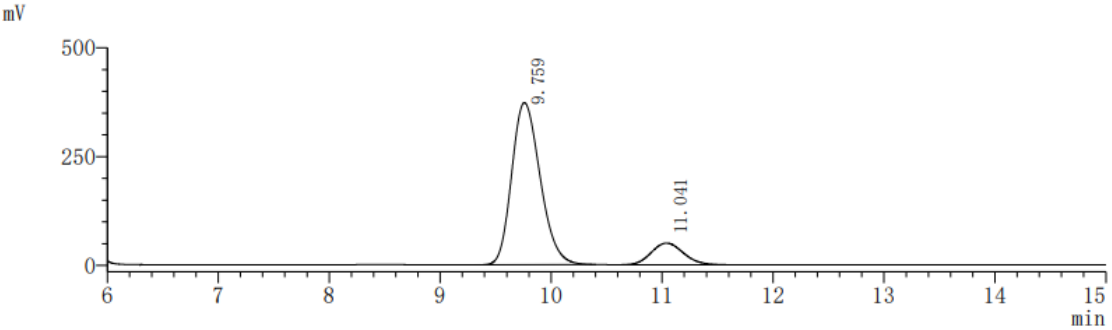
HRMS (ESI-TOF) (m/z): Calcd for $C_{32}H_{30}NaO_4$, ([M + Na]$^+$), 501.2036; found 501.2033.

$[\alpha]_D^{20}$ = -41.6 (c = 1.67, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (98:1 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 7.95 min, t_R (minor) = 9.93 min, 60% ee.

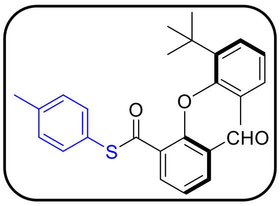


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	9.598	M	0.4867	6427124	345462	49.0707
2	10.857	M	0.5715	6670556	305330	50.9293



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	9.759	M	0.4677	6650473	372170	86.9716
2	11.041	M	0.5291	996242	49616	13.0284

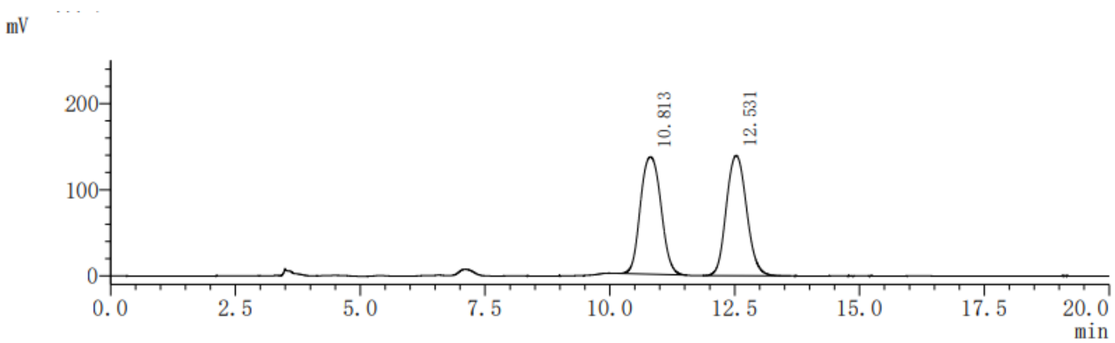
(*S*)-(p-tolyl)-2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzothioate (**10**)



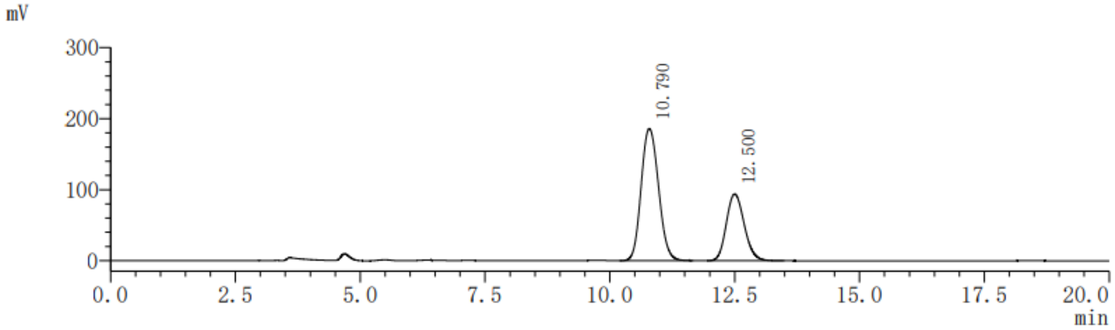
The title compound **10** was prepared under the optimized conditions and purified by preparative TLC (hexane : DCM = 1:1). **10** was obtained as a transparent oil (15.9 mg, 38%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.48 (s, 1H), 7.95 – 7.92 (m, 2H), 7.32 – 7.30 (m, 3H), 7.24 (t, *J* = 7.1 Hz, 2H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 7.04 (dd, *J* = 7.5, 1.6 Hz, 1H), 2.38 (s, 3H), 2.00 (s, 3H), 1.46 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 189.74, 187.68, 156.48, 155.38, 140.94, 140.00, 135.05, 134.63, 132.84, 131.25, 130.26, 130.13, 127.90, 126.89, 126.14, 125.54, 124.10, 122.17, 35.33, 30.49, 21.40, 17.78.

HRMS (ESI-TOF) (m/z): Calcd for $C_{26}H_{26}NaO_3S$, ([M + Na]$^+$), 441.1495; found 441.1493.

HPLC analysis: Daicel Chiralpak AD-3 column (99:1 hexane: 2-propanol, 1.0 mL/min, 25 ºC, 254 nm); t_R (major) = 10.79 min, t_R (minor) = 12.50 min, 32% ee.

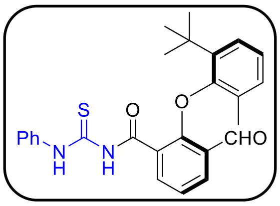


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	10.813	M	0.7269	3909752	136187	49.7166
2	12.531	M	0.7297	3954318	139548	50.2834

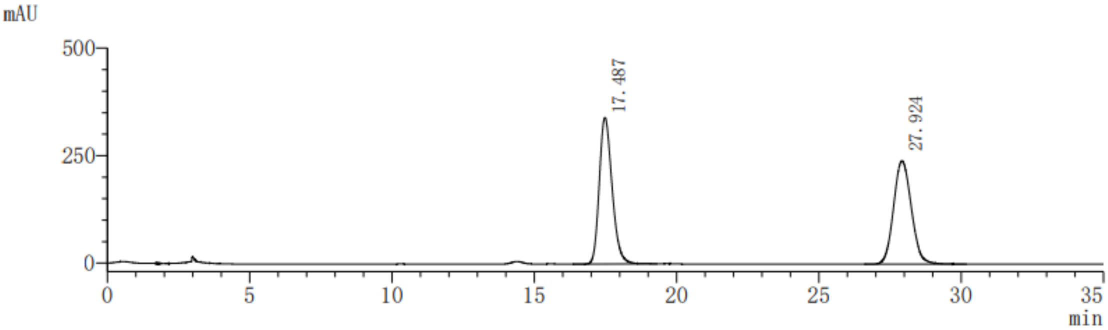


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	10.790	M	0.6305	4496346	185974	65.7702
2	12.500	M	0.6506	2340098	93877	34.2298

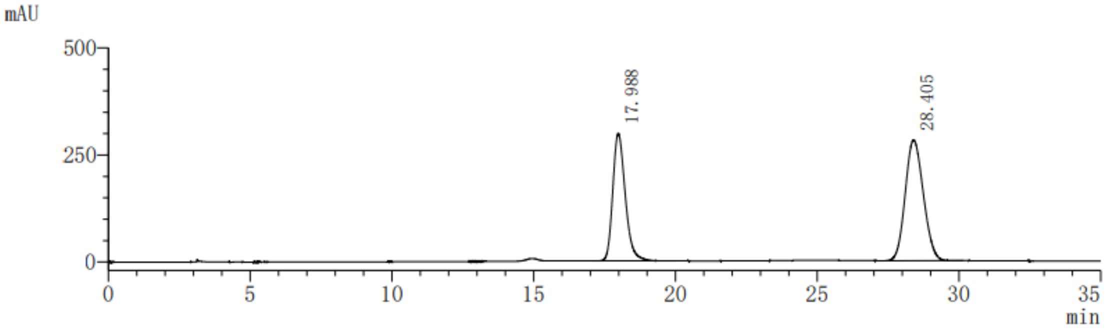
(*S*)-2-(2-(tert-butyl)-6-methylphenoxy)-3-formyl-N-(phenylcarbamothioyl)benzamide (11)



The title compound **11** was prepared under the optimized conditions and purified by preparative TLC (hexane : EA = 10:3). **11** was obtained as a yellow oil (35.7 mg, 80%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.47 (s, 1H), 10.26 (s, 1H), 9.37 (d, *J* = 0.8 Hz, 1H), 8.31 (dd, *J* = 7.7, 2.0 Hz, 1H), 7.99 (dd, *J* = 7.7, 2.0 Hz, 1H), 7.71 – 7.69 (m, 2H), 7.43 – 7.40 (m, 2H), 7.38 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.09 (dd, *J* = 7.5, 1.0 Hz, 1H), 1.99 (s, 3H), 1.50 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.17, 177.89, 164.60, 157.15, 154.63, 141.42, 137.67, 137.63, 135.30, 131.36, 128.91, 128.33, 127.38, 126.87, 126.85, 126.79, 124.05, 123.16, 122.53, 35.42, 30.94, 17.58.
HRMS (ESI-TOF) (m/z): Calcd for $C_{26}H_{26}N_2NaO_3S$, ([M + Na]$^+$), 469.1556; found 469.1556.
HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 17.99 min, t_R (major) = 28.41 min, 16% ee.

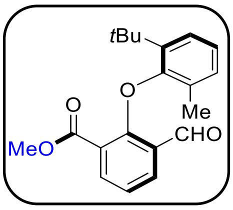


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	17.487	M	0.8156	10662893	340836	50.5434
2	27.924	M	1.1372	10433614	239903	49.4566



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	17.988	M	0.7917	9113555	297178	42.1027
2	28.405	M	1.1831	12532437	282116	57.8973

(*S*)-methyl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (**3aa**)

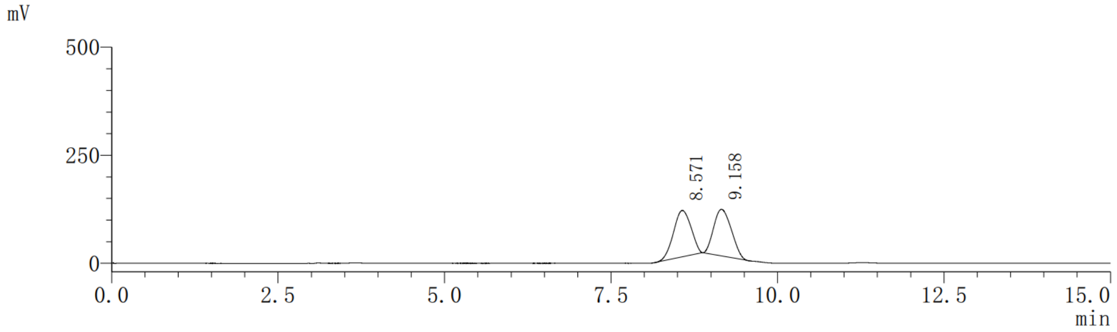


The title compound **3aa** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3aa** was obtained as a light yellow oil (28.7 mg, 88%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.87 (s, 1H), 7.96 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.82 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.30 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.18 – 7.15 (m, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.01 (dd, *J* = 7.6, 1.7 Hz, 1H), 3.63 (s, 3H), 1.89 (s, 3H), 1.45 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 188.10, 166.61, 157.21, 154.60, 140.91, 136.63, 132.24, 130.85, 127.60, 126.76, 125.80, 125.08, 123.64, 121.93, 52.32, 35.29, 30.30, 17.62.

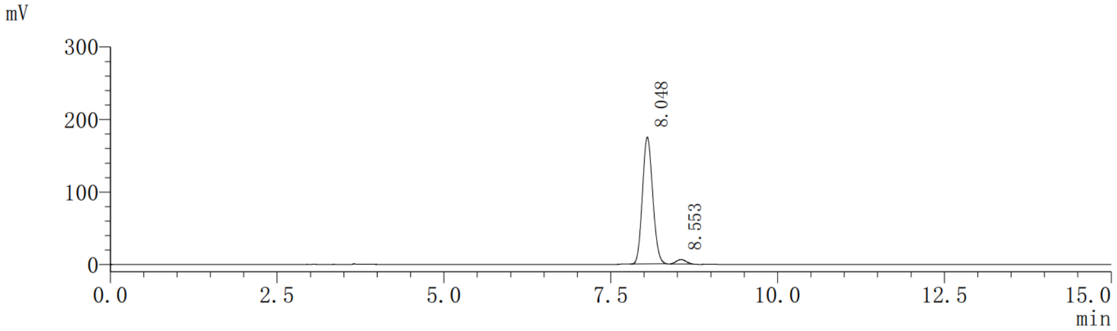
HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{22}NaO_4$, ($[M + Na]^+$), 349.1410; found 349.1404.

$[\alpha]_D^{20}$ = -28.3 (c = 1.44, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (99:1 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 8.05 min, t_R (minor) = 8.55 min, 94% ee.

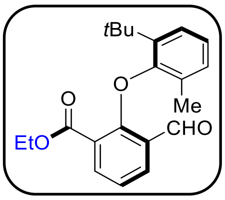


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	8.571	M	0.5025	1968180	107421	49.4968
2	9.158	M	0.5134	2008198	108008	50.5032



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	8.048	M	0.2848	1878369	174801	96.8287
2	8.553	M	0.2771	61519	6055	3.1713

(*S*)-ethyl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (**3ab**)

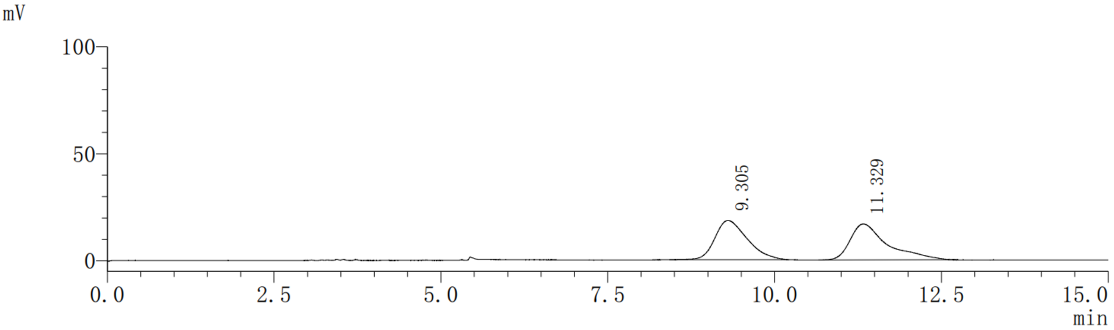


The title compound **3ab** was prepared under the optimized conditions and purified by preparative TLC (hexane : DCM = 2: 1). **3ab** was obtained as a yellow oil (26.2 mg, 77%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.77 (d, *J* = 0.9 Hz, 1H), 7.94 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.82 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.29 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.16 (td, *J* = 7.7, 0.9 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.02 – 6.99 (m, 1H), 4.21 – 4.15 (m, 1H), 4.13 – 4.06 (m, 1H), 1.92 (s, 3H), 1.44 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 188.08, 166.19, 157.16, 154.89, 140.89, 136.48, 132.10, 130.84, 127.74, 126.79, 125.81, 125.11, 124.29, 121.94, 61.57, 35.27, 30.32, 17.56, 14.10.

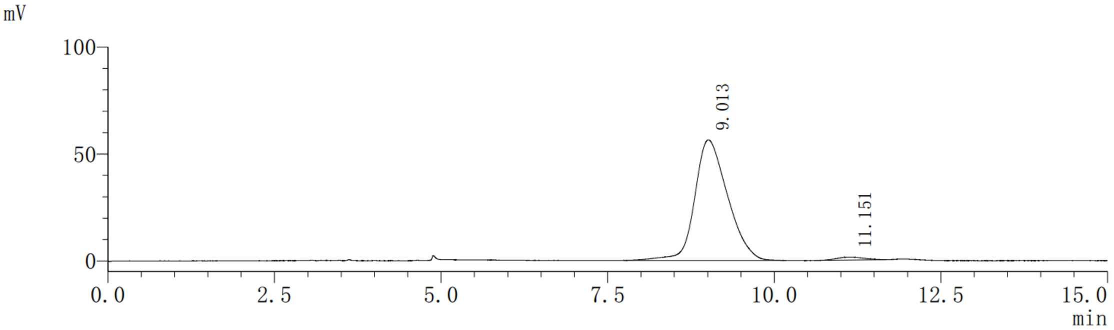
HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{24}NaO_4$, ([M + Na]$^+$), 363.1567; found 363.1566.

[α]D20 = -30.8 (c = 1.31, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (99:1 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 9.01 min, t_R (minor) = 11.15 min, 96% ee.

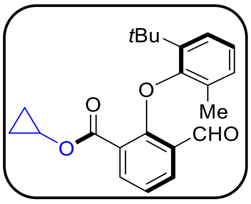


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	9.305	M	0.8906	618085	18361	48.6600
2	11.329	M	0.8936	652128	16829	51.3400



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	9.013	M	0.9014	1930709	56360	97.9905
2	11.151	M	0.7361	39593	1390	2.0095

(*S*)-cyclopropyl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3ac)

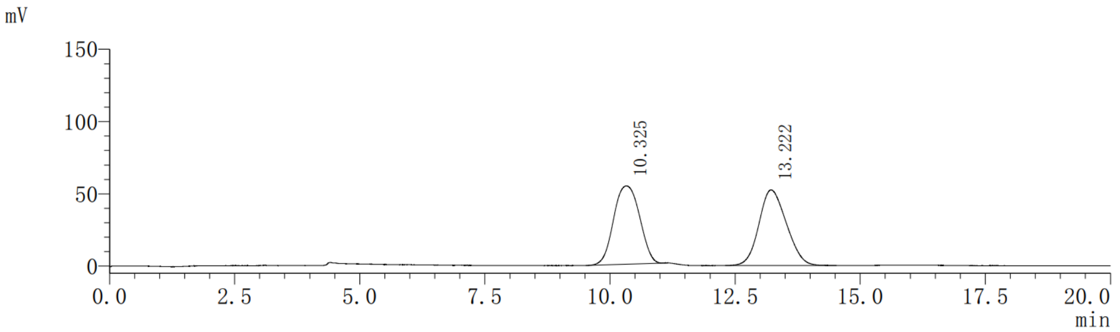


The title compound **3ac** was prepared under the optimized conditions and purified by preparative TLC (hexane : DCM = 1: 1). **3ac** was obtained as a yellow oil (26.4 mg, 75%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 9.67 (d, *J* = 0.9 Hz, 1H), 7.93 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.82 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.30 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 7.01 (dd, *J* = 7.5, 1.7 Hz, 1H), 4.13 – 4.09 (m, 1H), 1.89 (s, 3H), 1.44 (s, 9H), 0.76 – 0.69 (m, 4H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.92, 166.92, 157.32, 155.10, 140.80, 136.54, 132.47, 130.96, 127.59, 126.86, 125.92, 125.18, 123.86, 121.96, 49.92, 35.27, 30.31, 17.53, 5.21, 5.01.

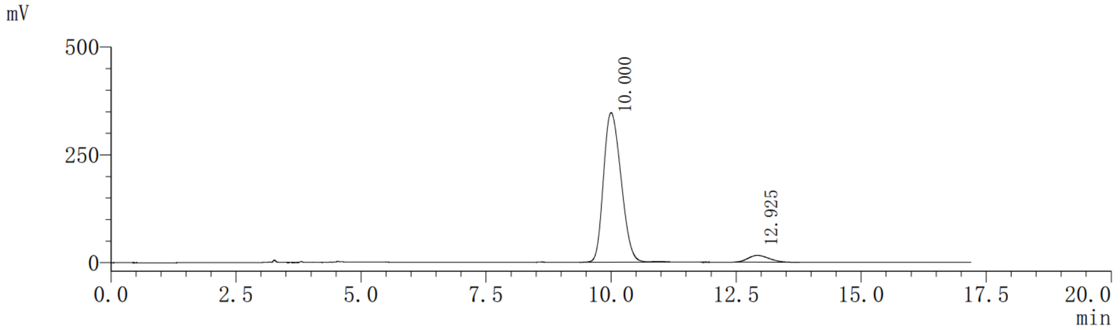
HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{24}NaO_4$, ($[M + Na]^+$), 375.1567; found 375.1535.

$[\alpha]_D^{20}$ = -25.9 (c = 1.32, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (99:1 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 10.00 min, t_R (minor) = 12.90 min, 90% ee.

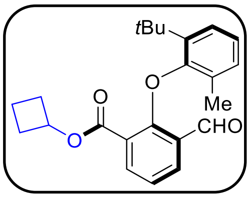


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	10.325	M	0.9344	1956627	54146	49.4918
2	13.222	M	1.0246	1996806	52311	50.5082



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	10.000	M	0.6499	8465892	346771	94.8683
2	12.925	M	0.7672	457946	15697	5.1317

(*S*)-cyclobutyl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3ad)

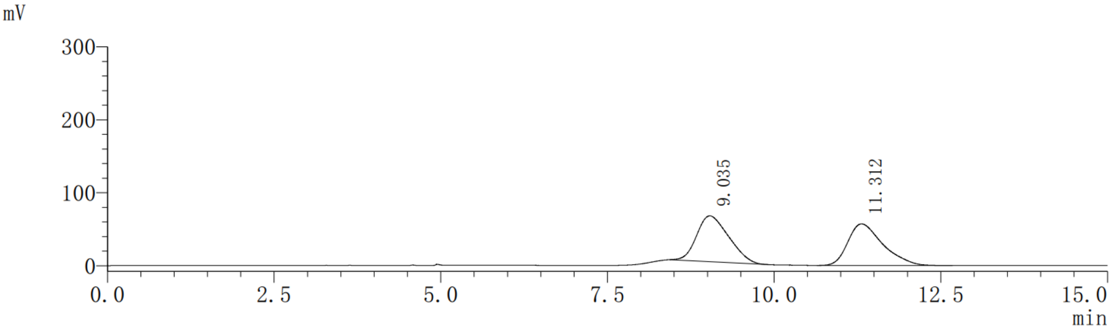


The title compound **3ad** was prepared under the optimized conditions and purified by preparative TLC (hexane : DCM = 1: 1). **3ad** was obtained as a yellow oil (25.6 mg, 70%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.70 (d, *J* = 0.9 Hz, 1H), 7.93 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.83 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.29 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.16 (td, *J* = 7.6, 0.9 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 7.01 – 7.00 (m, 1H), 4.98 – 4.92 (m, 1H), 2.39 – 2.31 (m, 2H), 2.13 – 2.03 (m, 2H), 1.92 (s, 3H), 1.82 – 1.75 (m, 1H), 1.65 – 1.59 (m, 1H), 1.44 (s, 9H). **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 188.02, 165.54, 157.21, 155.08, 140.80, 136.54, 132.18, 130.93, 127.70, 126.81, 125.83, 125.11, 124.32, 121.96, 69.99, 35.25, 30.39, 30.32, 30.20, 17.56, 13.60.

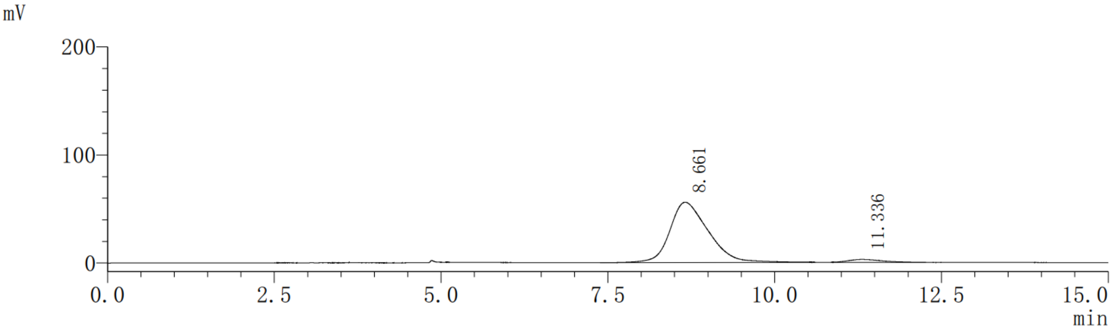
HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{26}NaO_4$, ($[M + Na]^+$), 389.1723; found 389.1731.

$[\alpha]_D^{20}$ = -30.2 (c = 1.28, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (99:1 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 8.66 min, t_R (minor) = 11.34 min, 92% ee.

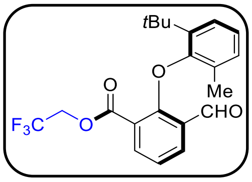


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	9.035	M	0.9314	2109417	62867	50.3558
2	11.312	M	0.9526	2079604	57016	49.6442



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	8.661	M	1.0591	2227415	55767	95.8402
2	11.336	M	0.8872	96678	2706	4.1598

(*S*)-2,2,2-trifluoroethyl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (**3ae**)

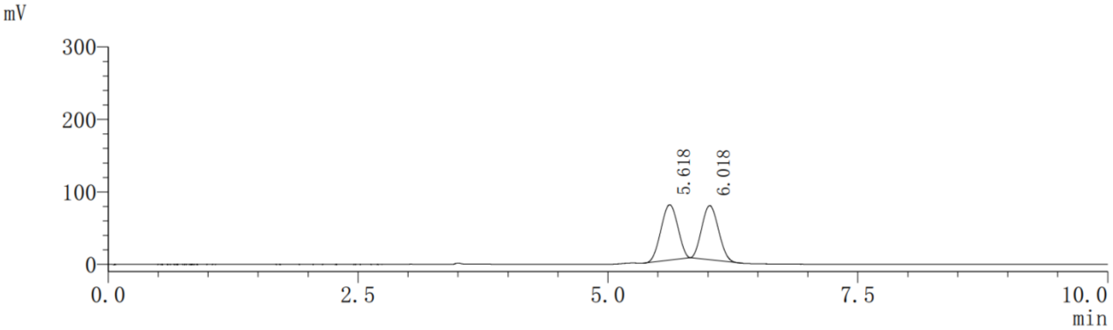


The title compound **3ae** was prepared under the optimized conditions and purified by preparative TLC (hexane : DCM = 2: 1). **3ae** was obtained as a yellow oil (28.8 mg, 73%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.70 (d, *J* = 0.9 Hz, 1H), 8.00 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.90 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.31 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.20 (td, *J* = 7.7, 0.9 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 7.02 – 7.00 (m, 1H), 4.53 – 4.42 (m, 2H), 1.91 (s, 3H), 1.43 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.68, 163.92, 157.79, 154.81, 141.08, 136.82, 133.52, 130.87, 127.72, 126.98, 126.02, 125.43, 122.84 (q, *J* = 275.1 Hz), 122.01, 121.49, 60.92 (q, *J* = 36.4 Hz), 35.27, 30.26, 17.37. ^{19}F NMR (565 MHz, $CDCl_3$) δ -73.45 – -73.47 (m, CF_3).

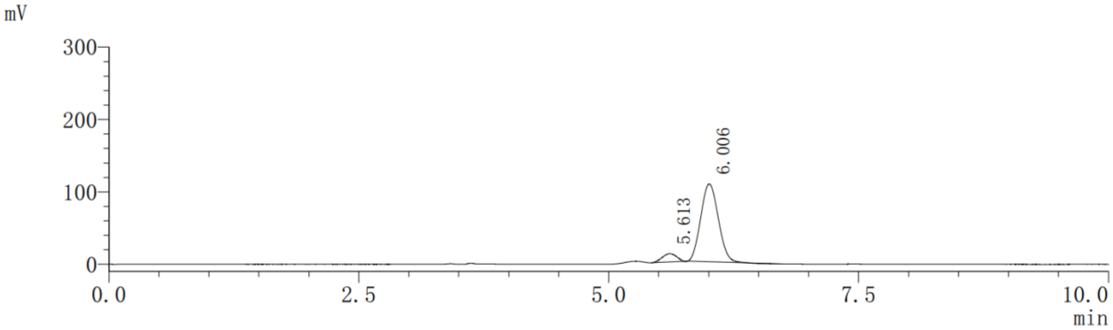
HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{21}F_3NaO_4$, ([M + Na]$^+$), 417.1284; found 417.1270.

$[\alpha]_D^{20}$ = -23.2 (c = 1.43, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (99:1 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 5.61 min, t_R (major) = 6.01 min, 84% ee.

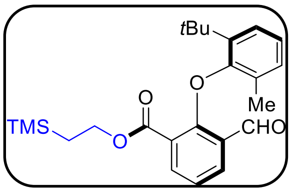


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	5.618	M	0.3196	893323	76324	50.7025
2	6.018	M	0.3156	868569	74699	49.2975

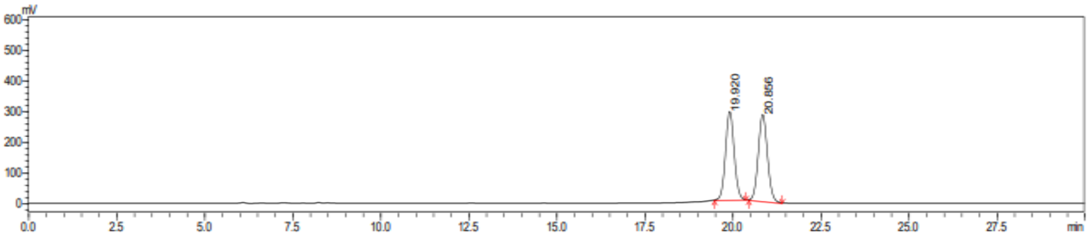


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	5.613	M	0.2738	114857	11491	8.0287
2	6.006	M	0.3286	1315729	107604	91.9713

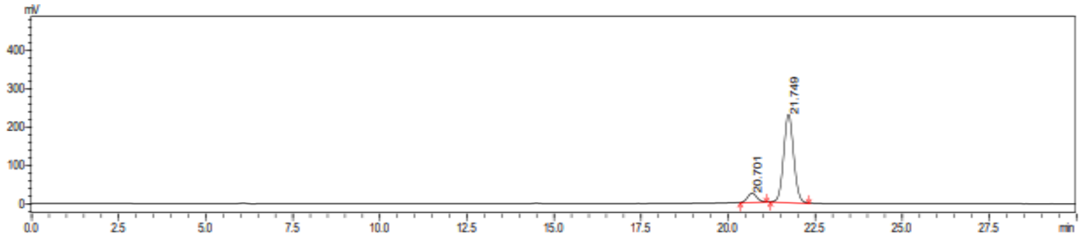
(*S*)-2-(trimethylsilyl)ethyl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3af)



The title compound **3af** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3af** was obtained as a yellow oil (35.5 mg, 86%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.81 (s, 1H), 7.93 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.79 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.29 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.00 (dd, *J* = 7.6, 1.7 Hz, 1H), 4.16 (td, *J* = 10.8, 6.8 Hz, 1H), 4.08 (td, *J* = 10.8, 6.8 Hz, 1H), 1.92 (s, 3H), 1.45 (s, 9H), 1.06 – 0.95 (m, 2H), 0.04 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 189.74, 167.90, 158.64, 156.36, 142.56, 137.91, 133.51, 132.38, 129.43, 128.31, 127.36, 126.67, 126.02, 123.49, 65.53, 36.85, 31.92, 19.15, 18.88, 0.00.
HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{32}NaO_4Si$, ([M + Na]$^+$), 435.1962; found 435.1949.
[α]$_D^{20}$ = -26.9 (c = 1.77, CH_2Cl_2).
HPLC analysis: Daicel Chiralpak OJ-3R column (20 mM Ammonium bicarbonate : Acetonitrile = 35 : 65 (v/v), 0.5 mL/min, 25 °C, 220 nm); t_R (minor) = 20.70 min, t_R (major) = 21.75 min, 83% ee.

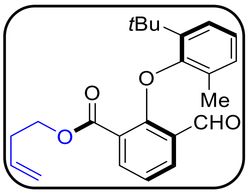


Peak	PetTime	Type	Plate number	Area	Tailing	Area%
1	19.920	M	30525	4942743	1.059	49.244
2	20.856	M	30129	5094508	1.076	50.756



Peak	PetTime	Type	Plate number	Area	Tailing	Area%
1	20.701	M	28921	422746	1.051	8.455
2	21.749	M	26866	4577176	1.060	91.545

(*S*)-but-3-en-1-yl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3ag)

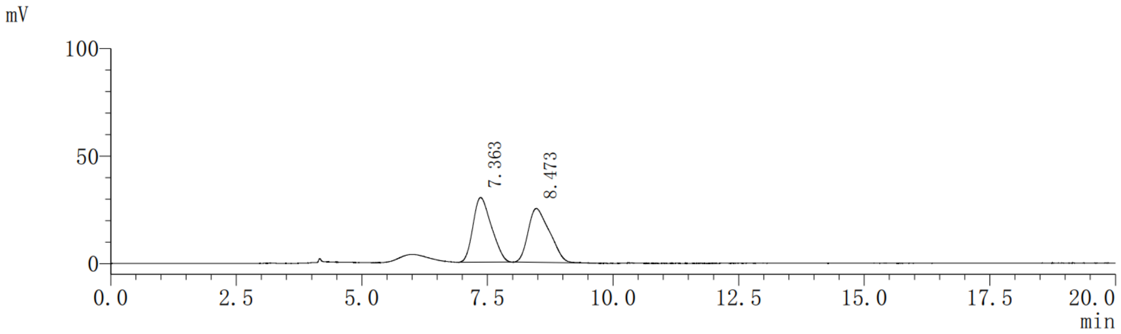


The title compound **3ag** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3ag** was obtained as a yellow oil (22.0 mg, 60%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.73 (s, 1H), 7.94 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.82 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.29 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 5.80 – 5.71 (m, 1H), 5.10 – 4.01 (m, 2H), 4.18 – 4.12 (m, 2H), 2.43 – 2.39 (m, 2H), 1.91 (s, 3H), 1.44 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 188.02, 166.00, 157.25, 154.96, 140.85, 136.53, 133.71, 132.24, 130.86, 127.65, 126.83, 125.84, 125.11, 124.05, 121.94, 117.36, 64.52, 35.27, 32.93, 30.33, 17.59.

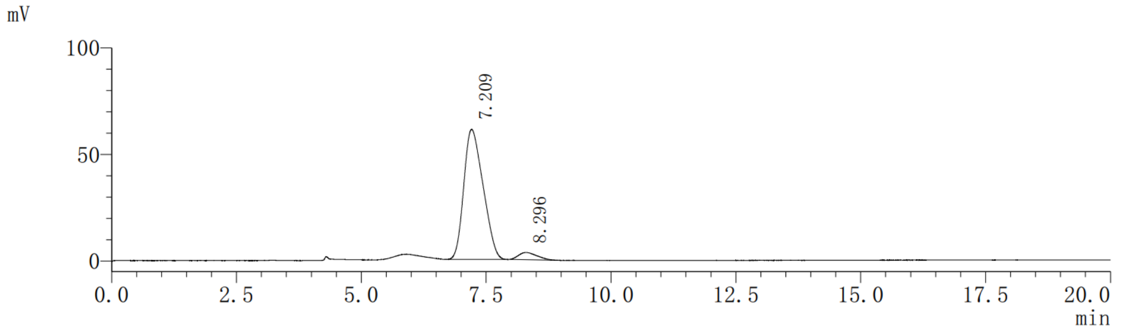
HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{26}NaO_4$, ([M + Na]$^+$), 389.1723; found 389.1715.

$[\alpha]_D^{20}$ = -38.9 (c = 1.09, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (99:1 hexane: 2-propanol, 1.0 mL/min, 25 ºC, 254 nm); t_R (major) = 7.21 min, t_R (minor) = 8.30 min, 90% ee.

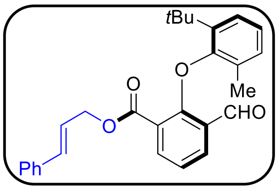


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	7.363	M	0.7106	767502	30095	50.6721
2	8.473	M	0.8798	747143	25110	49.3279



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	7.209	M	0.7576	1641250	61011	94.9902
2	8.296	M	0.7490	86559	3385	5.0098

(*S*)-cinnamyl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3ah)

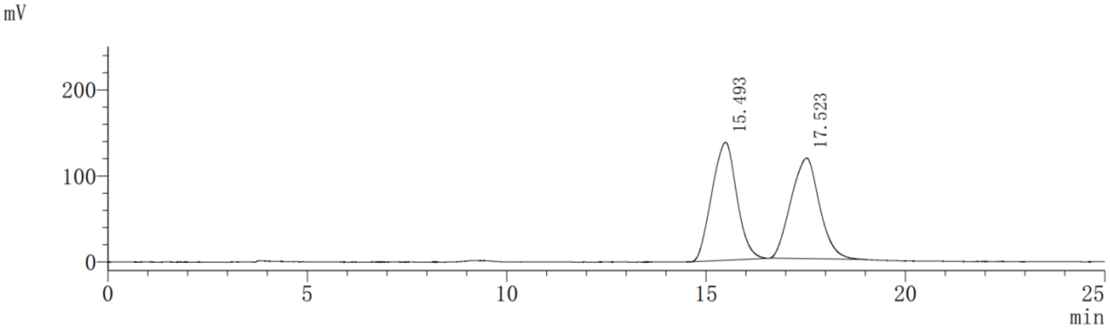


The title compound **3ah** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3ah** was obtained as a yellow oil (32.5 mg, 76%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.80 (s, 1H), 7.96 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.87 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.31 – 7.29 (m, 5H), 7.27 – 7.24 (m, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.25 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.81 – 4.76 (m, 1H), 4.69 – 4.64 (m, 1H), 1.93 (s, 3H), 1.43 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 188.05, 165.91, 157.28, 154.86, 140.93, 136.70, 136.07, 134.48, 132.36, 130.92, 128.57, 128.10, 127.71, 126.85, 126.57, 125.90, 125.14, 123.81, 122.58, 122.00, 66.08, 35.29, 30.32, 17.65.

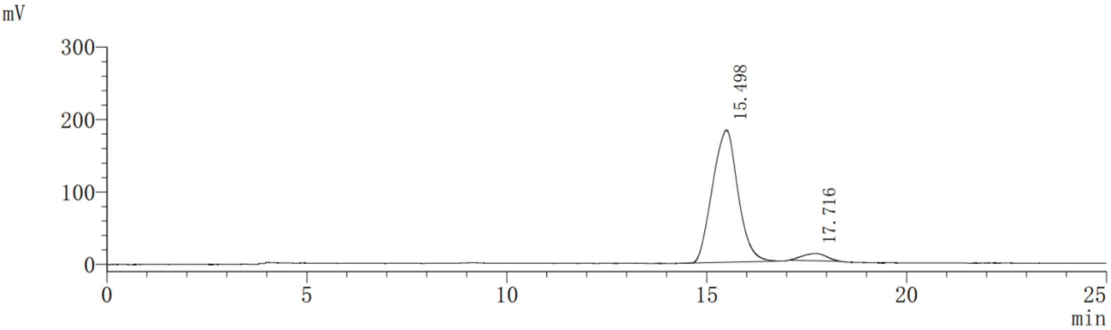
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{28}NaO_4$, ($[M + Na]^+$), 451.1880; found 451.1869.

$[\alpha]_D^{20}$ = -23.7 (c = 1.62, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (99.5:0.5 hexane: 2-propanol, 0.6 mL/min, 25 °C, 254 nm); t_R (major) = 15.50 min, t_R (minor) = 17.72 min, 90% ee.

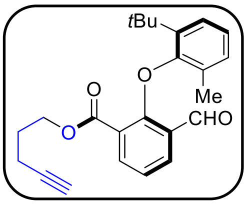


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	15.493	M	1.1806	5978251	137090	50.5737
2	17.523	M	1.3437	5842612	116955	49.4263



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	15.498	M	1.1967	8118780	182688	95.0234
2	17.716	M	1.0888	425200	10016	4.9766

(*S*)-pent-4-yn-1-yl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3ai)

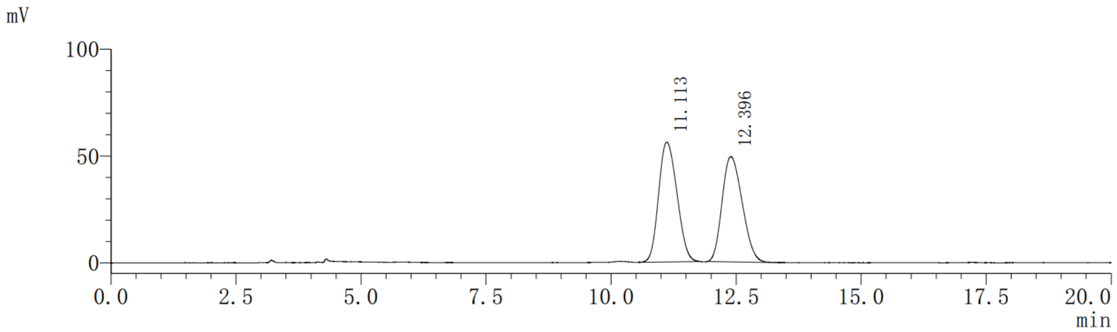


The title compound **3ai** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3ai** was obtained as a yellow oil (20.8 mg, 55%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.73 (d, *J* = 1.0 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.84 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.30 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.16 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 7.01 (dd, *J* = 7.7, 1.6 Hz, 1H), 4.26 – 4.16 (m, 2H), 2.26 (td, *J* = 7.1, 2.6 Hz, 2H), 1.92 (s, 3H), 1.92 – 1.85 (m, 2H), 1.58 (s, 1H), 1.44 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 188.02, 165.99, 157.28, 154.91, 140.87, 136.58, 132.37, 130.90, 127.59, 126.86, 125.91, 125.20, 123.89, 121.97, 82.75, 69.14, 64.05, 35.28, 30.32, 27.40, 17.56, 15.17.

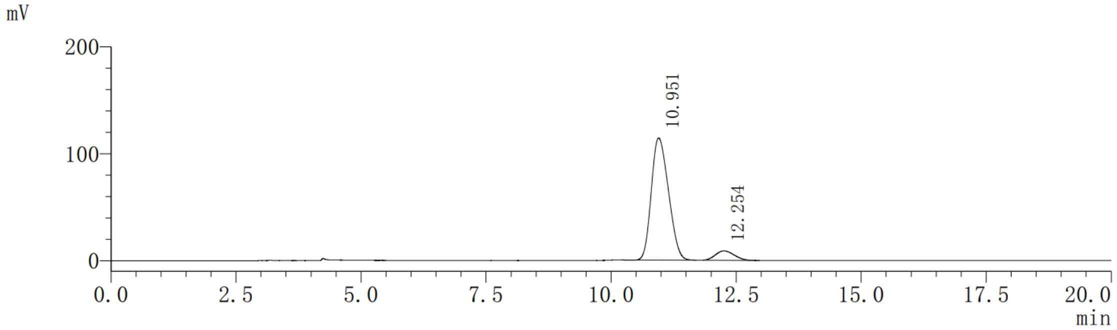
HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{26}NaO_4$, ([M + Na]$^+$), 401.1723; found 401.1719.

$[\alpha]_D^{20}$ = -23.3 (c = 1.03, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (99:1 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 10.95 min, t_R (minor) = 12.25 min, 85% ee.

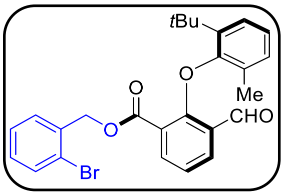


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	11.113	M	0.6864	1435806	56138	50.9760
2	12.396	M	0.7479	1380825	49327	49.0240



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	10.951	M	0.6458	2724562	114233	92.3631
2	12.254	M	0.7148	225277	8732	7.6369

(*S*)-2-bromobenzyl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3aj)

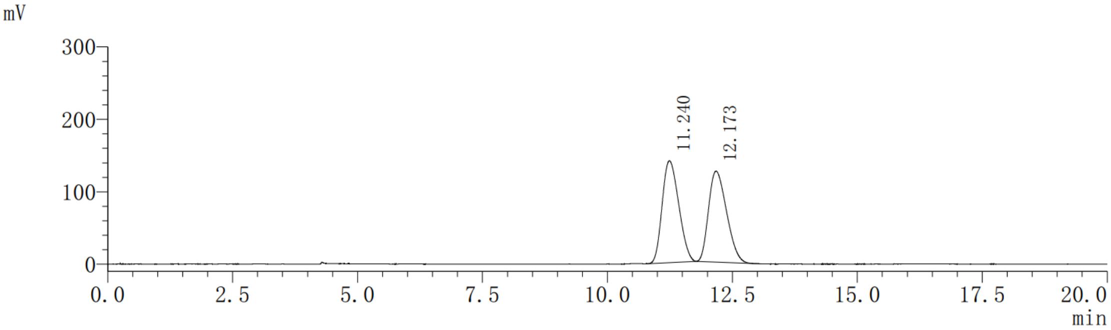


The title compound **3aj** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10:1). **3aj** was obtained as a yellow oil (30.2 mg, 63%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.74 (s, 1H), 7.95 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.90 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.57 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.40 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.29 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.20 – 7.15 (m, 2H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 7.4 Hz, 1H), 5.21 (s, 2H), 1.91 (s, 3H), 1.39 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.97, 165.47, 157.45, 154.90, 140.94, 136.73, 134.82, 132.86, 132.55, 130.86, 130.14, 129.84, 127.71, 127.43, 126.87, 125.93, 125.24, 123.57, 123.46, 121.97, 66.77, 35.26, 30.30, 17.62.

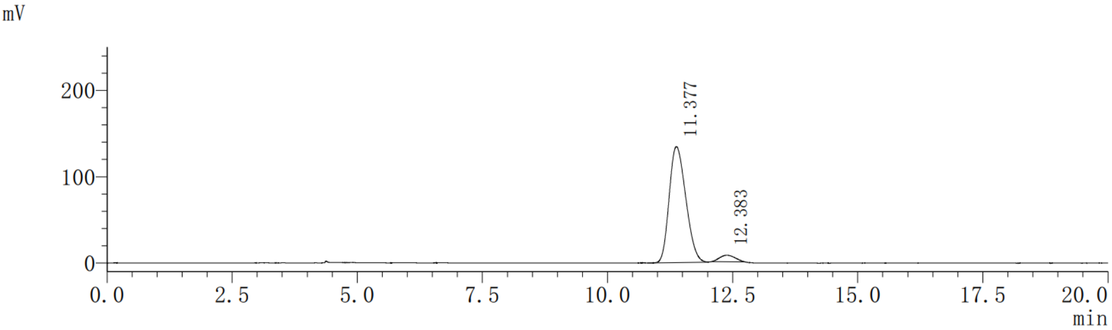
HRMS (ESI-TOF) (m/z): Calcd for $C_{26}H_{25}BrNaO_4$, ([M + Na]$^+$), 503.0828; found 503.0832.

[α]$_D^{20}$ = -33.7 (c = 1.51, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (99.5:0.5 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (major) = 11.38 min, t_R (minor) = 12.38 min, 90% ee.

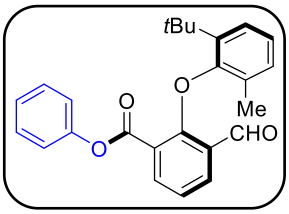


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	11.240	M	0.6221	3247359	140646	50.7194
2	12.173	M	0.6735	3155243	125602	49.2806



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	11.377	M	0.6172	3094974	134223	95.1735
2	12.383	M	0.5744	156953	7402	4.8265

(*S*)-phenyl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3ak)

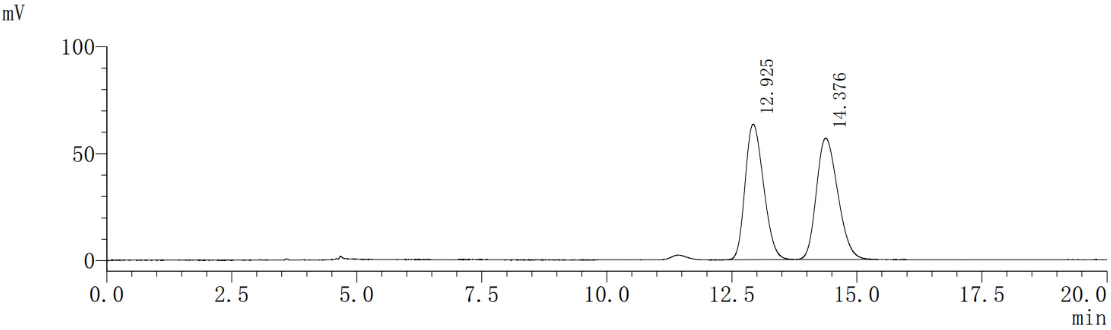


The title compound **3ak** was prepared under the optimized conditions and purified by preparative TLC (hexane : diethyl ether = 10: 1). **3ak** was obtained as a yellow oil (27.2 mg, 70%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 9.65 (d, *J* = 0.8 Hz, 1H), 8.09 (dd, *J* = 7.6, 1.9 Hz, 1H), 8.01 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.39 – 7.36 (m, 2H), 7.29 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.09 – 7.06 (m, 3H), 7.04 – 7.03 (m, 1H), 1.97 (s, 3H), 1.45 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.77, 164.36, 157.87, 155.41, 150.53, 140.78, 137.08, 133.26, 131.14, 129.42, 127.36, 127.12, 126.13, 126.02, 125.28, 123.26, 122.15, 121.47, 35.31, 30.31, 17.68.

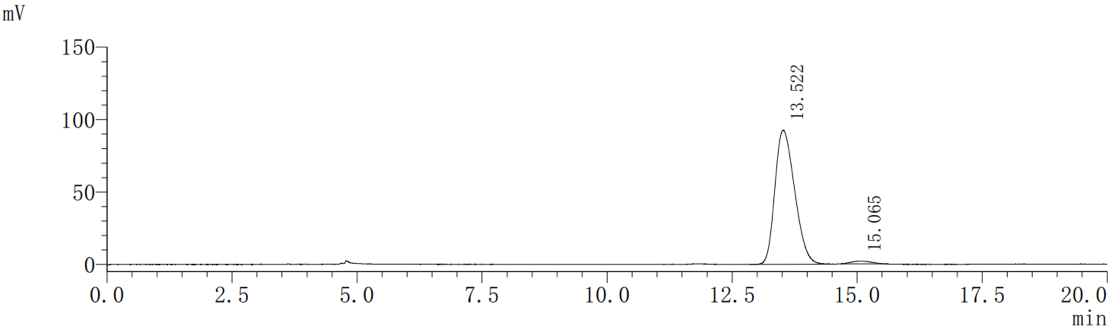
HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{24}NaO_4$, ([M + Na]$^+$), 411.1567; found 411.1571.

[α]$_D$^{20} = -25.6 (c = 1.36, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (99:1 hexane: 2-propanol, 1 mL/min, 25 °C, 254 nm); t_R (major) = 13.52 min, t_R (minor) = 15.07 min, 96% ee.

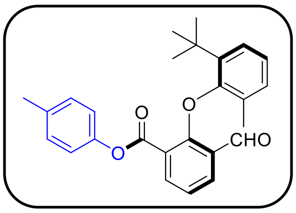


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	12.925	M	0.6830	1628833	63387	49.0626
2	14.376	M	0.7832	1691073	56768	50.9374



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	13.522	M	0.7310	2536051	92519	97.8258
2	15.065	M	0.7231	56364	2014	2.1742

(*S*)-p-tolyl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3al)

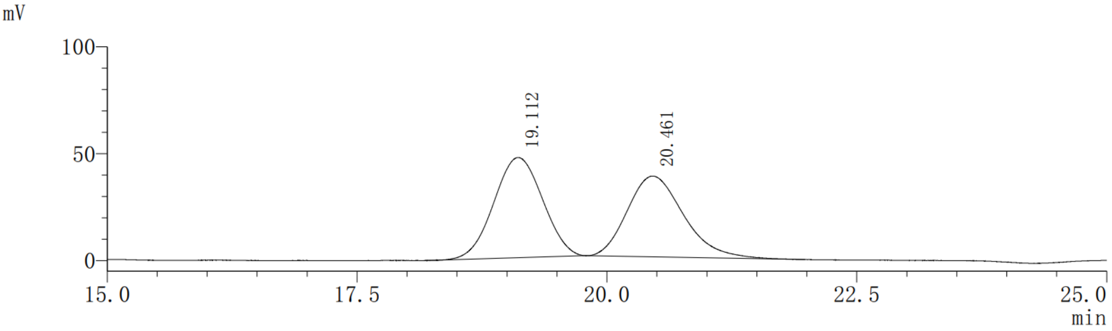


The title compound **3al** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3al** was obtained as a yellow oil (32.2 mg, 80%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.65 (s, 1H), 8.07 (dd, *J* = 7.6, 1.9 Hz, 1H), 8.00 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.29 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.03 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.95 – 6.94 (m, 2H), 2.34 (s, 3H), 1.97 (s, 3H), 1.44 (s, 9H). **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 187.81, 164.58, 157.83, 155.42, 148.32, 140.81, 137.04, 135.68, 133.14, 131.13, 129.91, 127.39, 127.12, 126.12, 125.25, 123.44, 122.13, 121.14, 35.31, 30.31, 20.85, 17.67.

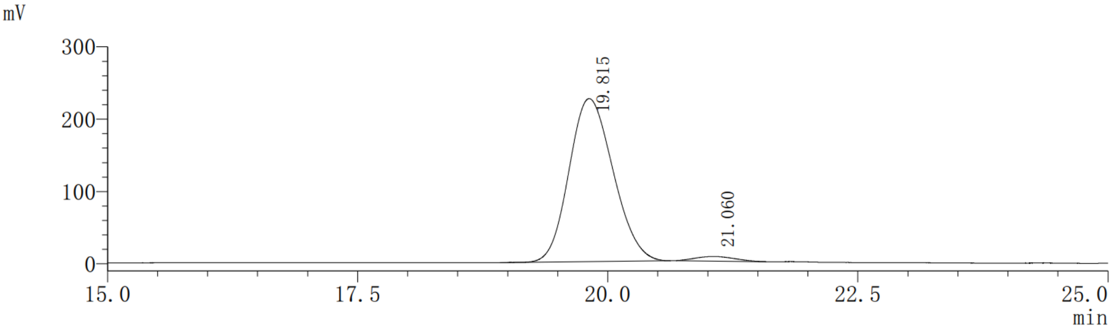
HRMS (ESI-TOF) (m/z): Calcd for $C_{26}H_{26}NaO_4$, ($[M + Na]^+$), 425.1723; found 425.1720.

$[\alpha]_D^{20}$ = -25.6 (c = 1.60, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (99:1 hexane: 2-propanol, 1 mL/min, 25 °C, 254 nm); t_R (major) = 19.82 min, t_R (minor) = 21.06 min, 95% ee.

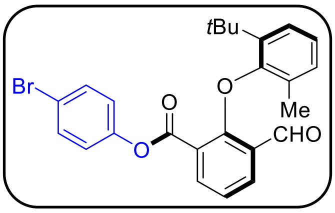


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	19.112	M	0.9092	1589406	46844	51.7649
2	20.461	M	1.0233	1481028	37781	48.2351



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	19.815	M	0.8167	6906822	225364	97.5827
2	21.060	M	0.7184	171097	6357	2.4173

(*S*)-4-bromophenyl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3am)

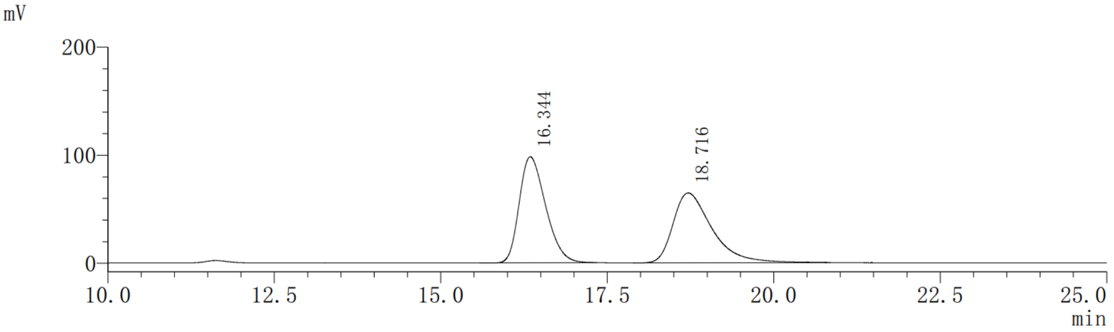


The title compound **3am** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3am** was obtained as a yellow oil (23.8 mg, 51%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 9.67 (d, *J* = 0.8 Hz, 1H), 8.06 (dd, *J* = 7.6, 1.9 Hz, 1H), 8.02 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.29 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 7.04 – 7.02 (m, 1H), 6.96 – 6.93 (m, 2H), 1.95 (s, 3H), 1.43 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.70, 163.95, 157.93, 155.27, 149.52, 140.87, 137.09, 133.53, 132.47, 131.15, 127.33, 127.22, 126.22, 125.36, 123.28, 122.72, 122.19, 119.16, 35.33, 30.33, 17.69.

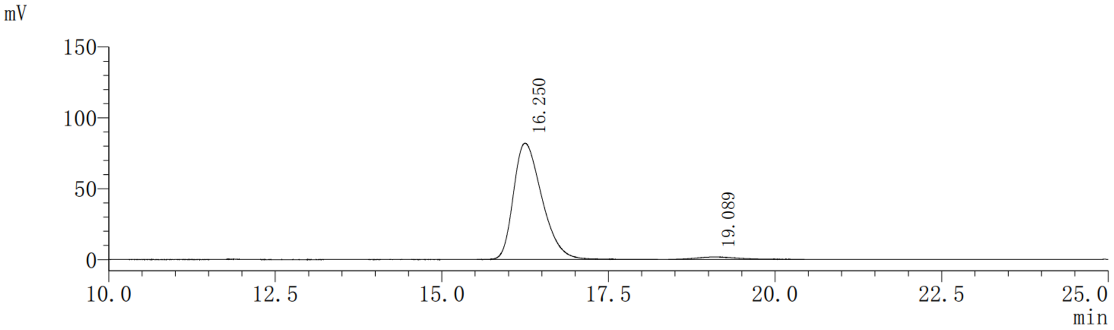
HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{23}BrNaO_4$, ($[M + Na]^+$), 489.0672; found 489.0659.

$[\alpha]_D^{20}$ = -25.9 (c = 1.19, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (99:1 hexane: 2-propanol, 1 mL/min, 25 ºC, 256 nm); t_R (major) = 16.25 min, t_R (minor) = 19.09 min, 94% ee.

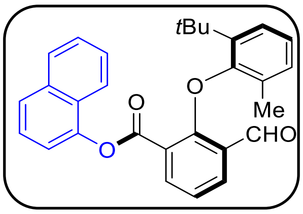


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	16.344	M	0.7291	2711091	98199	50.8174
2	18.716	M	1.0435	2623870	64667	49.1826



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	16.250	M	0.7822	2443877	82117	96.9631
2	19.089	M	1.0020	76542	1758	3.0369

(*S*)-naphthalen-1-yl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3an)

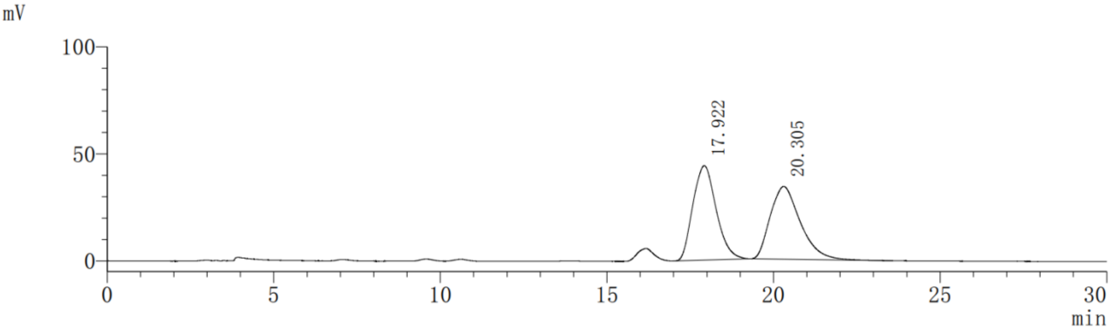


The title compound **3an** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10:1). **3an** was obtained as a yellow oil (32.9 mg, 75%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 9.57 (s, 1H), 8.26 (dd, *J* = 7.5, 1.9 Hz, 1H), 8.04 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.31 – 7.28 (m, 2H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 7.04 (dd, *J* = 7.5, 1.8 Hz, 1H), 2.03 (s, 3H), 1.44 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.66, 164.33, 158.13, 155.62, 146.50, 140.82, 137.14, 134.68, 133.60, 131.22, 128.05, 127.44, 127.33, 126.70, 126.47, 126.44, 126.21, 125.42, 125.37, 123.28, 122.26, 121.19, 118.16, 35.32, 30.35, 17.71.

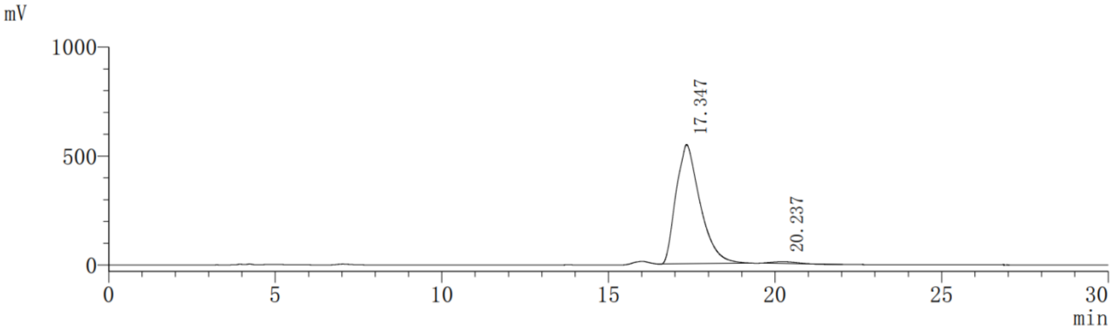
HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{26}NaO_4$, ($[M + Na]^+$), 461.1723; found 461.1731.

$[\alpha]_D^{20}$ = -25.5 (c = 1.64, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (99.5:0.5 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (major) = 17.35 min, t_R (minor) = 20.24 min, 97% ee.

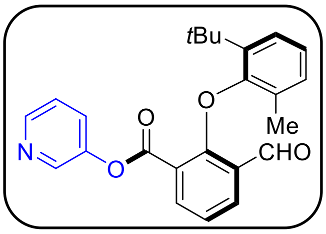


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	17.922	M	1.3199	2147777	44175	50.0937
2	20.305	M	1.6769	2139741	34052	49.9063



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	17.347	M	1.3680	27391981	546537	98.6772
2	20.237	M	1.3401	367212	8095	1.3228

(*S*)-pyridin-3-yl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3ao)

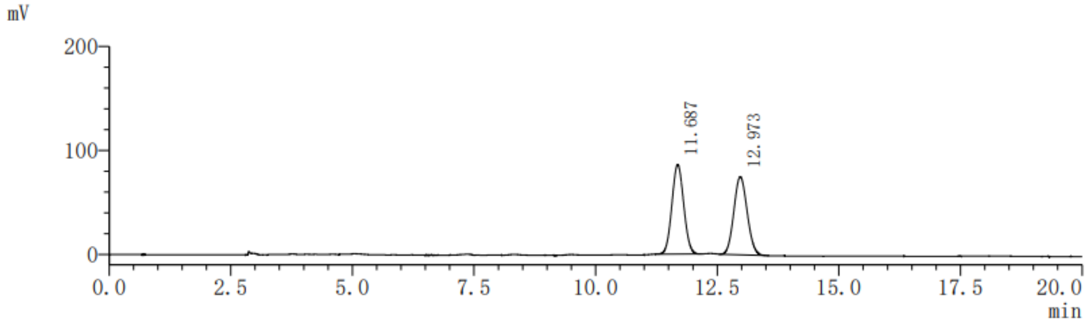


The title compound **3ao** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 2:1). **3ao** was obtained as a yellow oil (24.5 mg, 63%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.68 (s, 1H), 8.50 (s, 1H), 8.40 (s, 1H), 8.09 (dd, *J* = 7.6, 1.9 Hz, 1H), 8.03 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.42 (dt, *J* = 8.3, 2.0 Hz, 1H), 7.31 – 7.22 (m, 3H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.05 – 6.99 (m, 1H), 1.95 (s, 3H), 1.43 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.68, 163.74, 155.19, 147.15, 143.31, 137.19, 133.83, 131.18, 129.22, 127.35, 127.29, 126.28, 125.49, 123.96, 122.25, 122.19, 35.36, 30.35, 17.72.

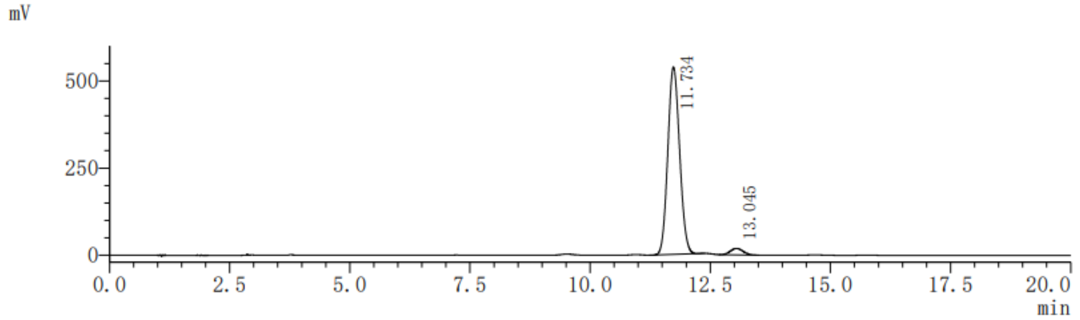
HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{23}NaNO_4$, ([M + Na]$^+$), 412.1519; found 412.1519.

[α]$_D$^{20} = -23.2 (c = 1.22, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (90:10 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (major) = 11.73 min, t_R (minor) = 13.04 min, 93% ee.

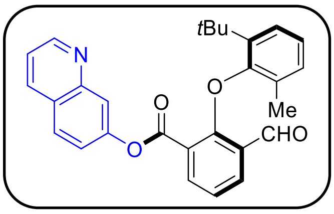


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	11.687	M	0.4497	1456769	86012	50.4340
2	12.973	M	0.5064	1431698	75185	49.5660



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	11.734	M	0.4537	9170822	536775	96.3877
2	13.045	M	0.4968	343697	18612	3.6123

(*S*)-quinolin-7-yl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3ap)

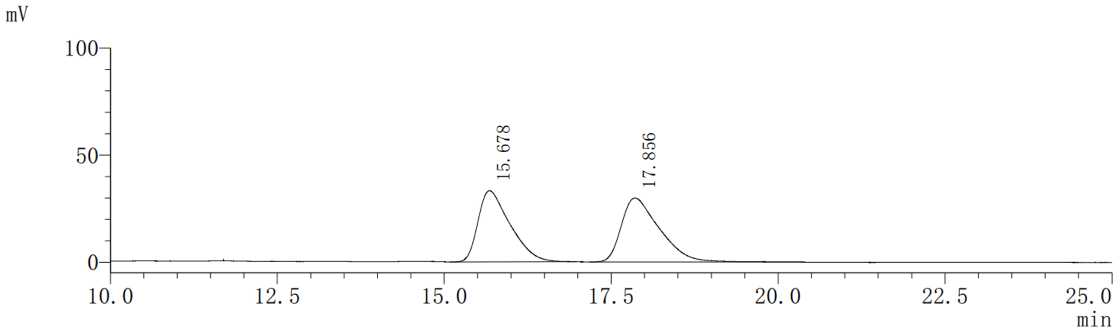


The title compound **3ap** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 2:1). **3ap** was obtained as a yellow oil (24.1 mg, 55%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.67 (s, 1H), 8.93 (s, 1H), 8.19 – 8.15 (m, 2H), 8.04 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.85 – 7.83 (m, 2H), 7.43 – 7.41 (m, 1H), 7.32 – 7.26 (m, 6H), 7.12 – 7.05 (m, 2H), 2.01 (s, 3H), 1.45 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.74, 164.14, 158.05, 155.36, 151.10, 148.69, 140.85, 137.24, 135.87, 133.57, 131.17, 128.92, 127.36, 127.21, 126.42, 126.20, 125.40, 122.81, 122.21, 122.00, 121.02, 120.40, 35.33, 30.34, 17.71.

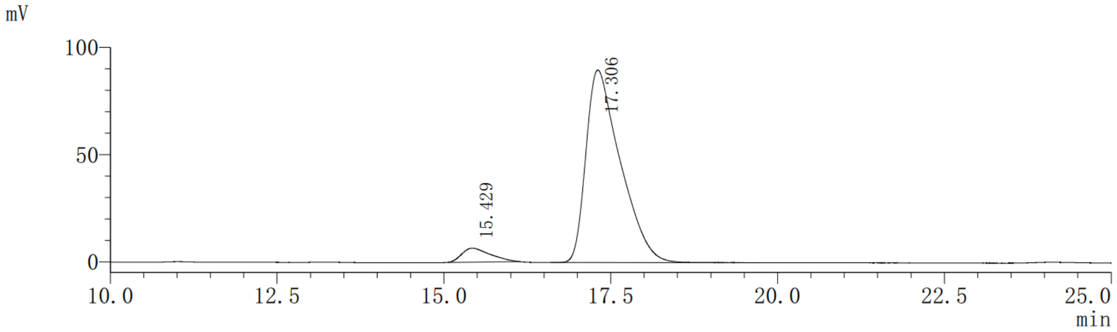
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{25}NNaO_4$, ([M + Na]$^+$), 462.1676; found 462.1678.

$[\alpha]_D^{20}$ = -28.3 (c = 1.20, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (minor) = 15.43 min, t_R (major) = 17.31 min, 89% ee.

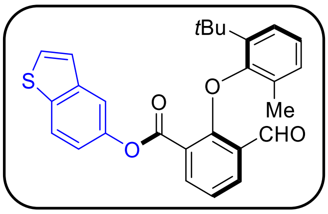


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	15.678	M	0.9244	1109233	33253	48.2886
2	17.856	M	1.0748	1187857	29908	51.7114



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	15.429	M	0.8295	193000	6502	5.6625
2	17.306	M	1.0088	3215384	89794	94.3375

(S)-benzo[b]thiophen-5-yl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3aq)

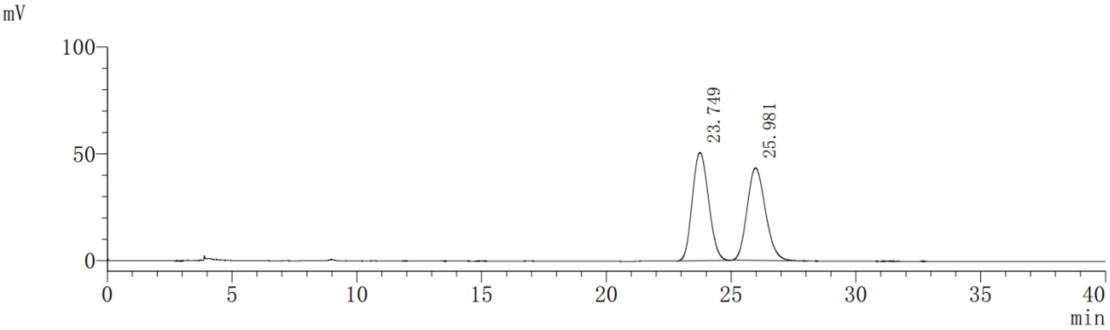


The title compound **3aq** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10:1). **3aq** was obtained as a yellow oil (35.1 mg, 79%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.68 (s, 1H), 8.12 (dd, *J* = 7.6, 1.8 Hz, 1H), 8.02 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.51 – 7.50 (m, 2H), 7.31 – 7.29 (m, 2H), 7.28 – 7.24 (m, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.05 (dd, *J* = 8.5, 2.0 Hz, 2H), 1.99 (s, 3H), 1.45 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.80, 164.68, 157.92, 155.41, 147.84, 140.91, 140.27, 137.25, 137.10, 133.31, 131.17, 128.25, 127.43, 127.22, 126.19, 125.30, 123.72, 123.29, 123.11, 122.19, 118.44, 115.87, 35.36, 30.36, 17.73.

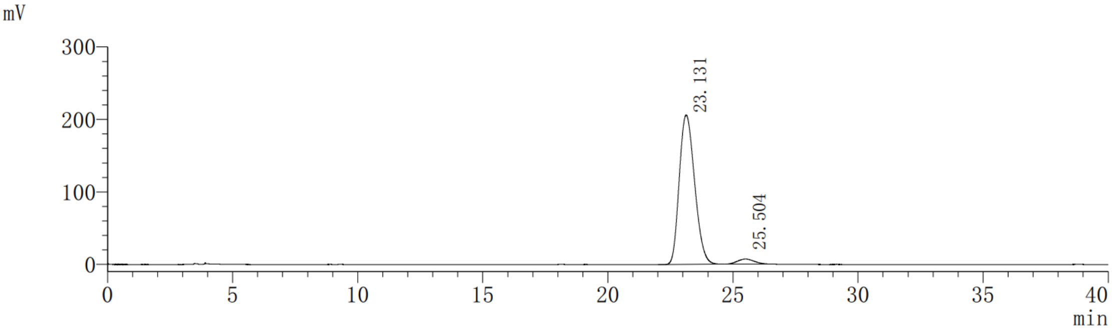
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{24}NaO_4S$, ([M + Na]$^+$), 467.1288; found 467.1287.

[α]$_D$^{20} = -27.7 (c = 1.75, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (99:1 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t$_R$ (major) = 23.13 min, t$_R$ (minor) = 25.50 min, 93% ee.

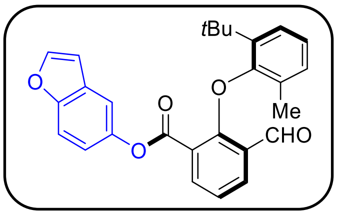


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	23.749	M	1.2084	2297139	50644	50.9408
2	25.981	M	1.3540	2212287	43296	49.0592



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	23.131	M	1.1315	8800756	206182	96.3395
2	25.504	M	1.2408	334395	7034	3.6605

(*S*)-benzofuran-5-yl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3ar)

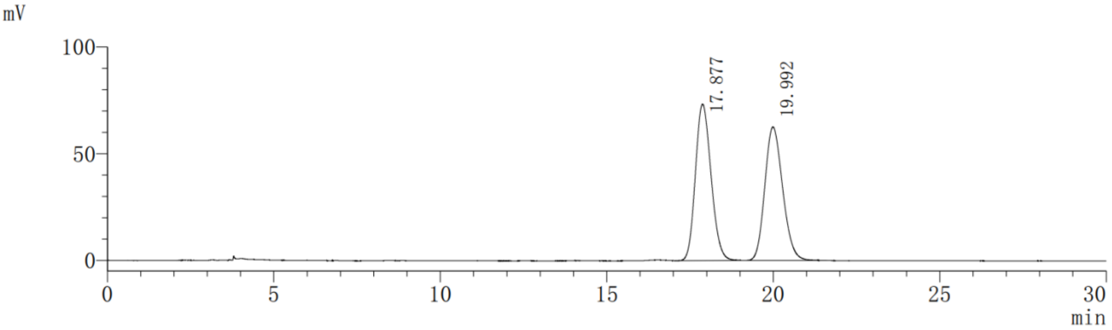


The title compound **3ar** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10:1). **3ar** was obtained as a yellow oil (33.4 mg, 78%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.66 (s, 1H), 8.11 (dd, *J* = 7.6, 1.8 Hz, 1H), 8.02 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.65 (d, *J* = 2.1 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.31 – 7.29 (m, 2H), 7.27 – 7.24 (m, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.98 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.75 (d, *J* = 1.5 Hz, 1H), 1.99 (s, 3H), 1.45 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.81, 164.89, 157.89, 155.44, 152.64, 146.32, 146.16, 140.88, 137.07, 133.25, 131.16, 128.06, 127.43, 127.20, 126.17, 125.29, 123.40, 122.17, 117.95, 113.65, 111.81, 106.84, 35.35, 30.35, 17.71.

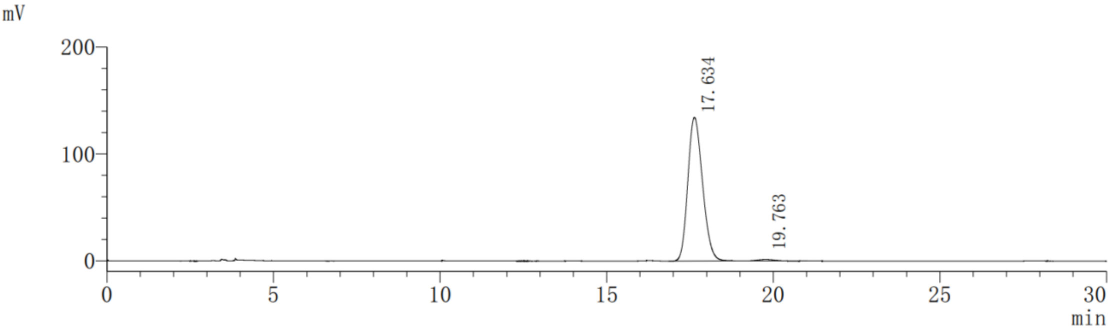
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{24}NaO_5$, ([M + Na]$^+$), 451.1516; found 451.1511.

[α]$_D$^{20} = -25.5 (c = 1.66, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (99:1 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (major) = 17.63 min, t_R (minor) = 19.76 min, 98% ee.

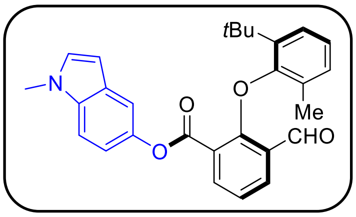


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	17.877	M	0.8619	2392561	73293	50.6224
2	19.992	M	0.9830	2333732	62572	49.3776



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	17.634	M	0.8100	4119425	134448	99.1601
2	19.763	M	0.8334	34894	1204	0.8399

(S)-1-methyl-1H-indol-5-yl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3as)

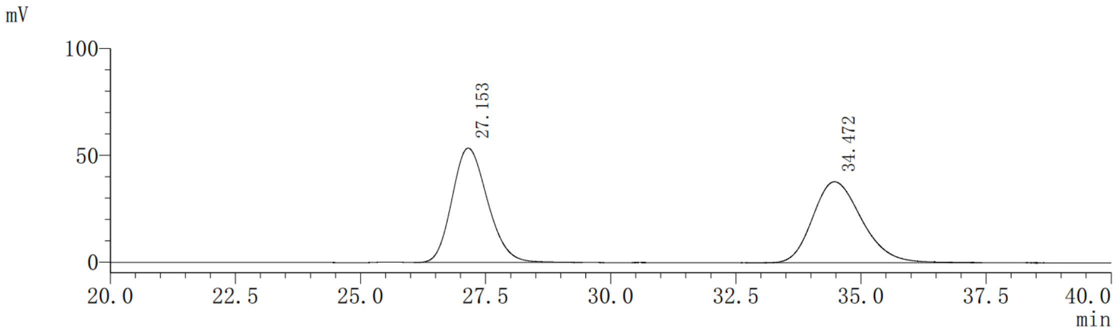


The title compound **3as** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 5:1). **3as** was obtained as a yellow oil (21.2 mg, 48%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.66 (s, 1H), 8.11 (dd, *J* = 7.6, 1.8 Hz, 1H), 8.00 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.27 – 7.23 (m, 2H), 7.10 – 7.04 (m, 3H), 6.91 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.45 (d, *J* = 3.0 Hz, 1H), 3.79 (s, 3H), 2.00 (s, 3H), 1.46 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.94, 165.32, 157.81, 155.52, 144.07, 140.86, 137.04, 134.73, 132.90, 131.14, 130.05, 128.57, 127.48, 127.12, 126.10, 125.20, 124.00, 122.13, 115.46, 112.80, 109.51, 101.21, 35.34, 33.02, 30.36, 17.73.

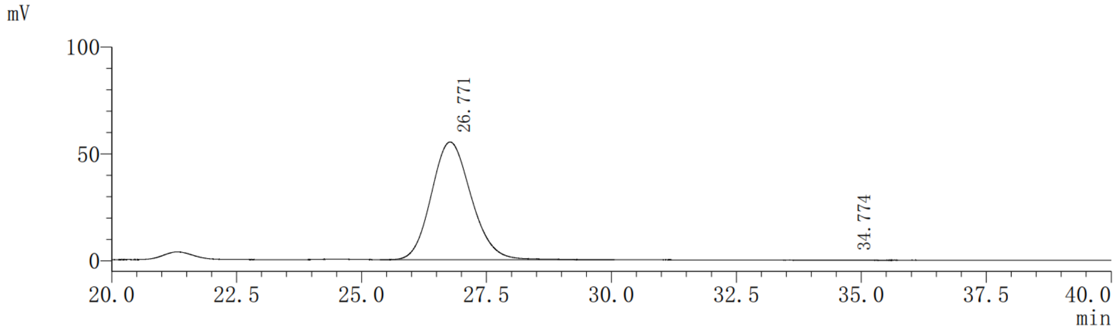
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{27}NNaO_4$, ([M + Na]$^+$), 464.1832; found 464.1828.

$[\alpha]_D^{20}$ = -24.8 (c = 1.05, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IC column (97:3 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (major) = 26.77 min, t_R (minor) = 34.77 min, 99% ee.

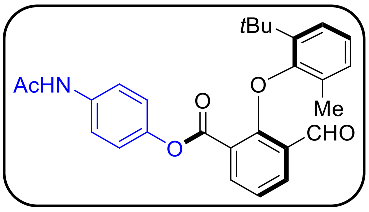


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	27.153	M	1.2929	2644181	53529	50.5420
2	34.472	M	1.7763	2587471	37937	49.4580



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	26.771	M	1.4540	3063460	55076	99.5989
2	34.774	M	1.2959	12337	143	0.4011

4-acetamidophenyl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3at)

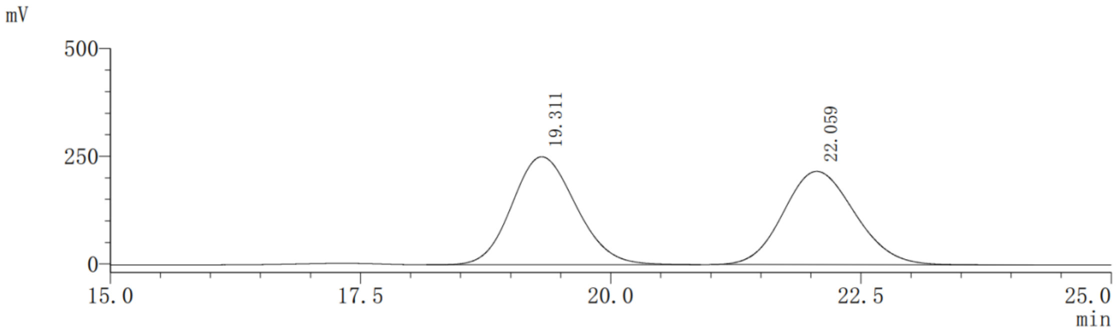


The title compound **3at** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 2:1). **3at** was obtained as a yellow oil (37.8 mg, 85%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.66 (s, 1H), 8.07 (dd, *J* = 7.6, 2.0 Hz, 1H), 8.01 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.57 (s, 1H), 7.49 – 7.46 (m, 2H), 7.29 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.03 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.00 – 6.97 (m, 2H), 2.13 (s, 3H), 1.96 (s, 3H), 1.43 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.79, 168.33, 164.51, 157.88, 155.30, 146.55, 140.79, 137.06, 135.85, 133.32, 131.12, 127.31, 127.13, 126.15, 125.31, 123.04, 122.16, 121.83, 120.75, 35.30, 30.31, 24.41, 17.67.

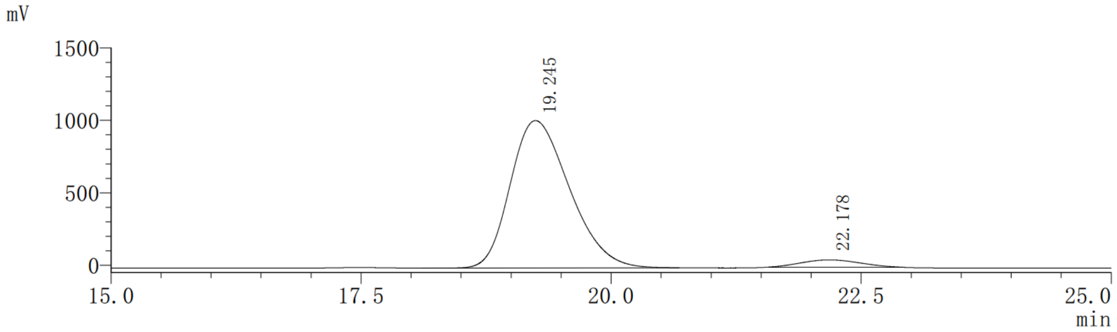
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{27}NNaO_5$, ([M + Na]$^+$), 468.1781; found 468.1780.

[α]$_D$^{20} = -22.6 (c = 1.89, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (90:10 hexane: 2-propanol, 1 mL/min, 25 °C, 254 nm); t_R (major) = 19.25 min, t_R (minor) = 22.18 min, 90% ee.

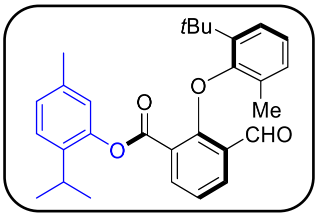


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	19.311	M	1.1721	11165655	250518	50.8251
2	22.059	M	1.3132	10803109	216595	49.1749



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	19.245	M	1.0932	41810488	1015835	95.2639
2	22.178	M	1.1280	2078627	50467	4.7361

(S)-2-isopropyl-5-methylphenyl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3au)

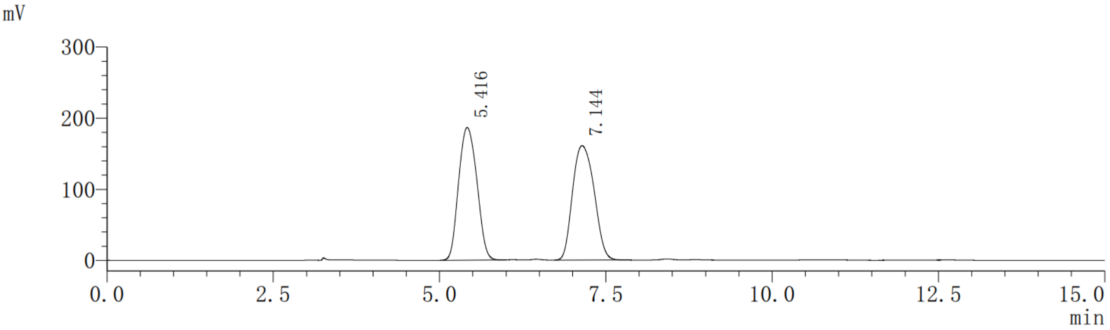


The title compound **3au** was prepared under the optimized conditions and purified by preparative TLC (hexane : DCM = 1:1). **3au** was obtained as a yellow oil (27.1 mg, 61%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 9.55 (s, 1H), 8.12 (dd, *J* = 7.6, 1.9 Hz, 1H), 8.00 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.31 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.04 (dd, *J* = 7.7, 1.7 Hz, 2H), 6.75 (d, *J* = 1.7 Hz, 1H), 3.11 – 3.03 (m, 1H), 2.30 (s, 3H), 1.97 (s, 3H), 1.45 (s, 9H), 1.17 (t, *J* = 7.5 Hz, 6H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.74, 164.49, 158.01, 155.65, 147.75, 140.77, 137.01, 136.92, 136.63, 133.32, 131.19, 127.34, 127.24, 126.41, 126.16, 125.29, 123.53, 122.69, 122.19, 35.31, 30.31, 27.05, 23.12, 23.05, 20.80, 17.64.

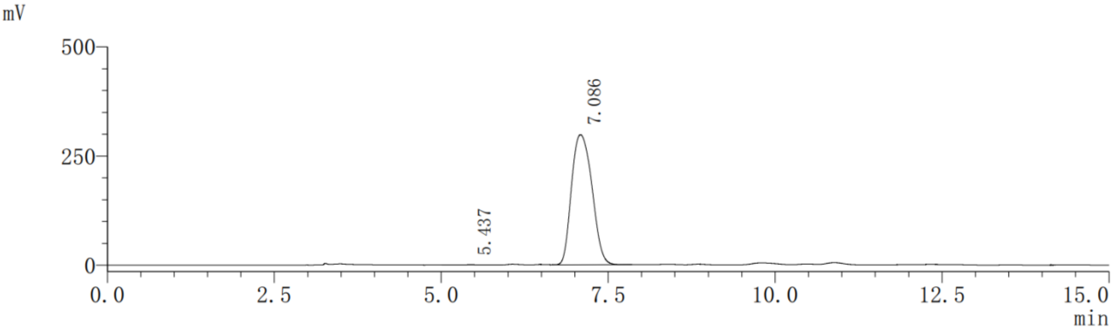
HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{32}NaO_4$, ([M + Na]$^+$), 467.2193; found 467.2184.

$[\alpha]_D^{20}$ = -24.2 (c = 1.36, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (98:2 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (minor) = 5.44 min, t_R (major) = 7.09 min, 99% ee.

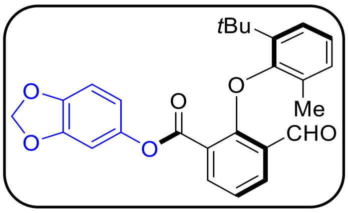


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	5.416	M	0.5094	3562017	186519	49.5181
2	7.144	M	0.5881	3631347	160817	50.4819



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	5.437	M	0.2767	13619	632	0.2140
2	7.086	M	0.5517	6349687	298044	99.7860

(S)-benzo[d][1,3]dioxol-5-yl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3av)

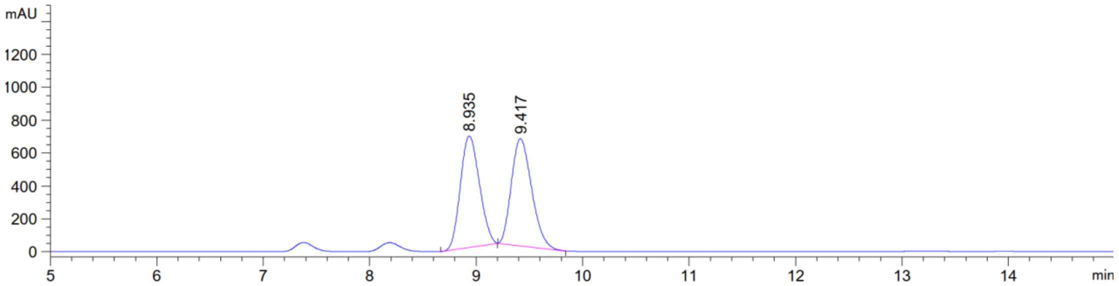


The title compound **3av** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10:1). **3av** was obtained as a yellow oil (30.2 mg, 70%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 9.67 (s, 1H), 8.05 (dd, *J* = 7.6, 1.9 Hz, 1H), 8.00 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.30 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.1 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 2.3 Hz, 1H), 6.51 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.98 (s, 2H), 1.96 (s, 3H), 1.44 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.79, 164.64, 157.83, 155.32, 147.97, 145.50, 144.79, 140.86, 137.04, 133.26, 131.12, 127.37, 127.14, 126.17, 125.30, 123.11, 122.14, 113.85, 107.93, 103.68, 101.72, 35.33, 30.33, 17.68.

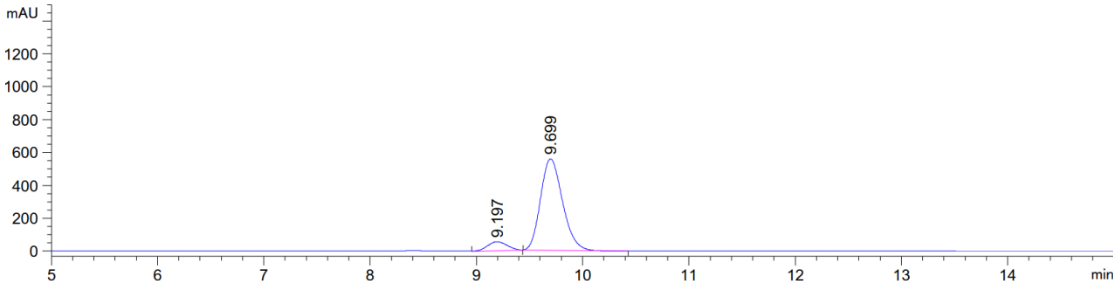
HRMS (ESI-TOF) (m/z): Calcd for $C_{26}H_{24}NaO_6$, ($[M + Na]^+$), 455.1465; found 455.1462.

$[\alpha]_D^{20}$ = -16.5 (c = 1.51, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (97:3 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (minor) = 9.20 min, t_R (major) = 9.70 min, 84% ee.

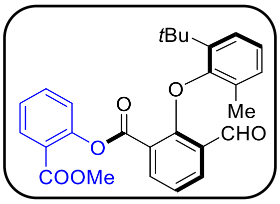


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	8.935	MM	0.2069	8422.04883	678.27191	49.3723
2	9.417	MM	0.2210	8636.18359	651.19006	50.6277

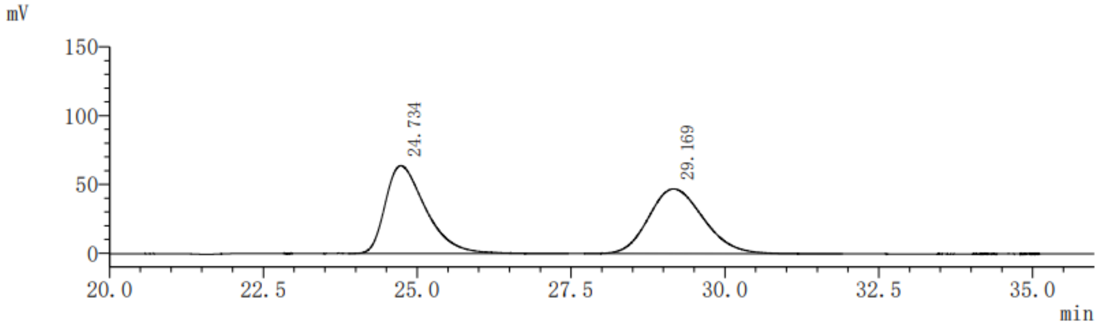


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	9.197	MM	0.2150	708.14392	54.90746	8.0816
2	9.699	MM	0.2412	8054.31982	556.65125	91.9184

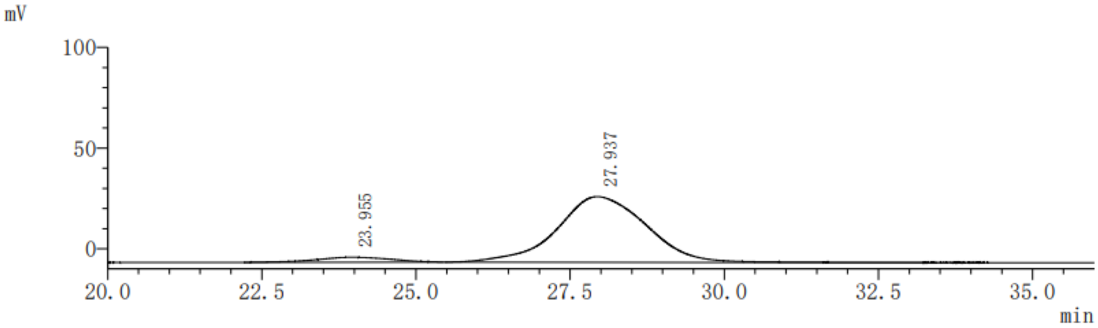
(*S*)-2-(methoxycarbonyl)phenyl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3aw)



The title compound **3aw** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10:1). **3aw** was obtained as a yellow oil (20.1 mg, 45%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.56 (s, 1H), 8.37 (dd, *J* = 7.6, 1.9 Hz, 1H), 8.04 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.00 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.55 (td, *J* = 7.8, 1.7 Hz, 1H), 7.33 (td, *J* = 7.6, 1.2 Hz, 1H), 7.28 (td, *J* = 7.2, 1.3 Hz, 2H), 7.10 – 7.01 (m, 3H), 3.82 (s, 3H), 1.97 (s, 3H), 1.45 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.78, 164.81, 163.75, 158.27, 155.85, 150.47, 140.70, 137.73, 133.87, 133.42, 131.84, 131.20, 127.37, 127.18, 126.23, 126.08, 125.19, 123.98, 123.29, 123.09, 122.29, 52.20, 35.33, 30.31, 17.66.
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{26}NaO_6$, ([M + Na]$^+$), 469.1622, found 469.1614.
[α]$_D$^{19} = -20.9 (c = 1.00, CH_2Cl_2).
HPLC analysis: Daicel Chiralpak AD-3 column (99:1 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t$_R$ (minor) = 23.96 min, t$_R$ (major) = 27.94 min, 88% ee.

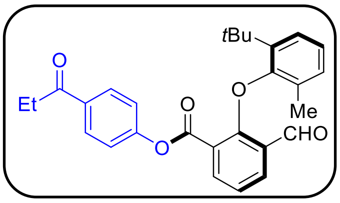


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	24.734	M	1.1855	2919821	63855	49.9176
2	29.169	M	1.6242	2929460	47089	50.0824



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	23.955	M	2.0100	205673	2469	5.8817
2	27.937	M	2.5759	3291127	32613	94.1183

(*S*)-4-propionylphenyl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3ax)

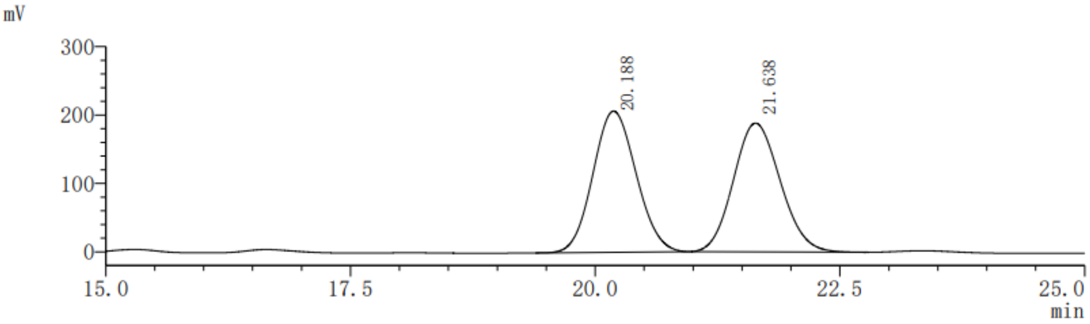


The title compound **3ax** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10:1). **3ax** was obtained as a yellow oil (27.1 mg, 61%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.67 (s, 1H), 8.09 (dd, *J* = 7.6, 1.9 Hz, 1H), 8.05 – 8.02 (m, 1H), 8.00 (d, *J* = 8.7 Hz, 2H), 7.30 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.18 – 7.14 (m, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.04 (dd, *J* = 7.5, 1.8 Hz, 1H), 3.03 – 2.96 (m, 2H), 1.97 (s, 3H), 1.44 (s, 9H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 199.50, 187.68, 163.74, 158.02, 155.30, 154.00, 140.89, 137.16, 134.73, 133.68, 131.18, 129.60, 127.35, 127.27, 126.25, 125.43, 122.60, 122.23, 121.69, 35.35, 31.80, 30.35, 17.71, 8.21.

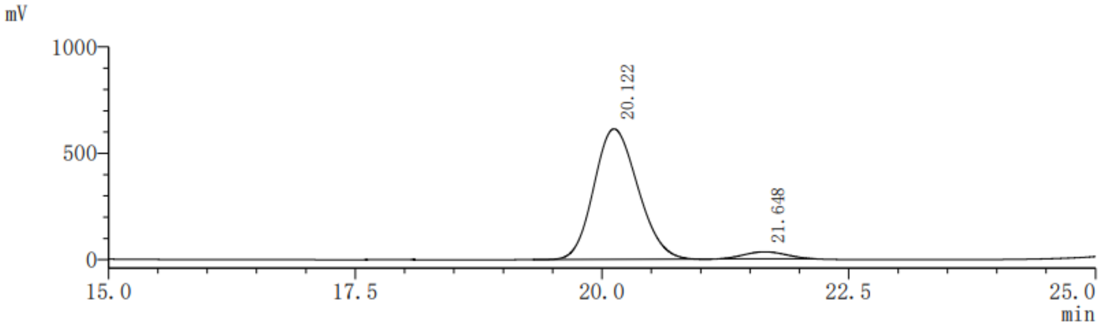
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{28}NaO_5$, ($[M + Na]^+$), 467.1829, found 467.1831.

$[\alpha]_D^{19}$ = -28.4 (c = 1.36, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (95:5 hexane: 2-propanol, 1 mL/min, 25 ºC, 256 nm); t_R (major) = 20.12 min, t_R (minor) = 21.65 min, 90% ee.

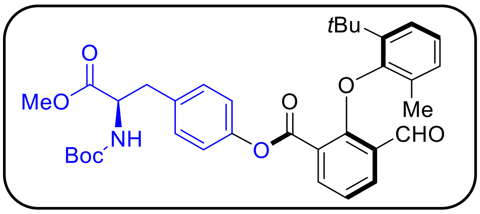


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	20.188	M	0.8165	6326184	206277	50.2419
2	21.638	M	0.8831	6265256	188224	49.7581



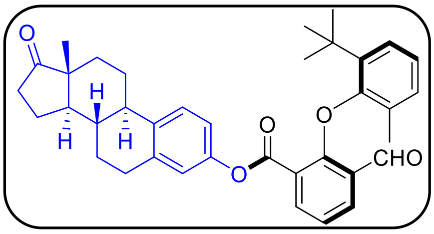
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	20.122	M	0.8248	19049935	613563	95.2188
2	21.648	M	0.8048	956543	32688	4.7812

5,7-dichloroquinolin-8-yl-6-formyl-[1,1':2',1''-terphenyl]-2-carboxylate (3ay)



The title compound **3ay** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 2:1). **3ay** was obtained as a light yellow oil (31.3 mg, 66%, dr: > 20:1). ^{1}**H NMR (500 MHz, Chloroform-*d*)** δ 9.64 (s, 1H), 8.07 (dd, *J* = 7.6, 1.9 Hz, 1H), 8.01 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.29 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.04 – 7.00 (m, 3H), 4.99 (d, *J* = 8.3 Hz, 1H), 4.60 – 4.56 (m, 1H), 3.71 (s, 3H), 3.14 – 3.02 (m, 2H), 1.96 (s, 3H), 1.44 (s, 9H), 1.42 (s, 9H). ^{13}**C NMR (150 MHz, Chloroform-*d*)** δ 187.72, 172.15, 164.24, 157.85, 155.37, 155.02, 149.57, 140.78, 137.02, 133.89, 133.28, 131.13, 130.25, 127.36, 127.14, 126.12, 125.28, 123.18, 122.14, 121.51, 79.99, 54.32, 52.24, 37.71, 35.30, 30.31, 28.27, 17.66.
HRMS (ESI-TOF) (m/z): Calcd for $C_{34}H_{39}NNaO_8$, ([M + Na]$^+$), 612.2568; found 612.2570.
[α]$_D$^{20} = -20.3 (c = 1.94, CH_2Cl_2).

(8S,9R,13R,14R)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3az)

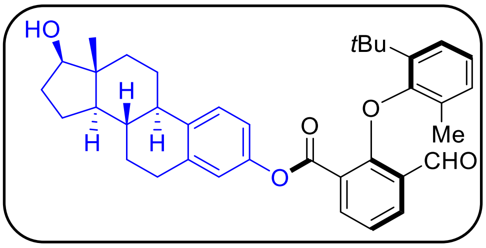


The title compound **3az** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 2:1). **3az** was obtained as a yellow oil (34.4 mg, 61%, dr > 20:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.64 (s, 1H), 8.06 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.99 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.83 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.78 (d, *J* = 2.4 Hz, 1H), 2.91 – 2.88 (m, 2H), 2.53 – 2.47 (m, 1H), 2.41 – 2.38 (m, 1H), 2.31 – 2.25 (m, 1H), 2.18 – 2.10 (m, 1H), 2.08 – 1.94 (m, 6H), 1.65 – 1.48 (m, 6H), 1.44 (s, 9H), 0.90 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 220.63, 187.77, 164.65, 157.81, 155.42, 148.42, 140.79, 138.03, 137.61, 137.03, 133.17, 131.13, 127.40, 127.13, 126.39, 126.10, 125.23, 123.39, 122.13, 121.49, 118.64, 50.41, 47.91, 44.14, 37.98, 35.82, 35.31, 31.53, 30.33, 29.37, 26.30, 25.73, 21.57, 17.69, 13.80.

HRMS (ESI-TOF) (m/z): Calcd for $C_{37}H_{40}NaO_5$, ([M + Na]$^+$), 587.2768; found 587.2768.

[α]$_D^{20}$ = +15.686 (c = 1.72, CH_2Cl_2).

(8S,9R,13R,14R,17R)-17-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3aa’)

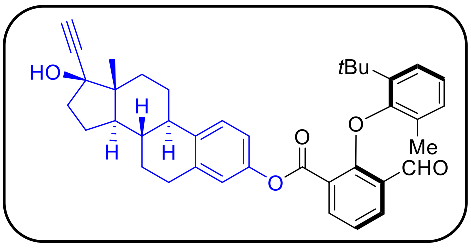


The title compound **3aa’** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 2:1). **3aa’** was obtained as a yellow oil (37.4 mg, 66%, dr > 20:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.64 (s, 1H), 8.06 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.99 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.03 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.82 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.76 (d, *J* = 2.5 Hz, 1H), 3.73 (t, *J* = 8.5 Hz, 1H), 2.86 – 2.83 (m, 2H), 2.34 – 2.29 (m, 1H), 2.24 – 2.19 (m, 1H), 2.17 – 2.08 (m, 1H), 1.96 (s, 3H), 1.90 – 1.85 (m, 1H), 1.73 – 1.67 (m, 1H), 1.59 – 1.55 (m, 1H), 1.55 – 1.47 (m, 2H), 1.44 (s, 9H), 1.41 (s, 1H), 1.38 – 1.25 (m, 4H), 1.22 – 1.16 (m, 1H), 0.77 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.87, 164.74, 157.84, 155.46, 148.29, 140.82, 138.31, 138.25, 137.08, 133.15, 131.17, 127.44, 127.14, 126.41, 126.13, 125.26, 123.51, 122.15, 121.44, 118.48, 81.87, 50.08, 44.15, 43.22, 38.47, 36.68, 35.34, 30.60, 30.35, 29.53, 27.02, 26.15, 23.13, 17.72, 11.03.

HRMS (ESI-TOF) (m/z): Calcd for $C_{37}H_{42}NaO_5$, ([M + Na]$^+$), 589.2924; found 589.2925.

[α]$_D^{20}$ = +12.3 (c = 1.86, CH_2Cl_2).

(8S,9R,13R,14R,17S)-17-ethynyl-17-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3ab’)

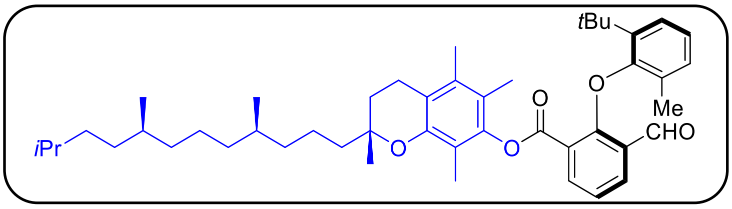


The title compound **3ab’** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 5:1). **3ab’** was obtained as a yellow oil (46.0 mg, 78%, dr > 20:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.65 (s, 1H), 8.06 (dd, J = 7.6, 1.9 Hz, 1H), 8.00 (dd, J = 7.8, 1.9 Hz, 1H), 7.30 – 7.28 (m, 2H), 7.23 (t, J = 7.7 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 7.03 (dd, J = 7.5, 1.7 Hz, 1H), 6.83 (dd, J = 8.5, 2.5 Hz, 1H), 6.76 (d, J = 2.5 Hz, 1H), 2.83 – 2.88 (m, 2H), 2.60 (s, 1H), 2.39 – 2.31 (m, 2H), 2.28 – 2.23 (m, 1H), 2.05 – 1.99 (m, 1H), 1.98 – 1.94 (m, 4H), 1.92 – 1.86 (m, 2H), 1.83 – 1.67 (m, 3H), 1.55 – 1.48 (m, 1H), 1.45 (s, 9H), 1.42 – 1.32 (m, 3H), 0.88 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.90, 164.77, 157.86, 155.48, 148.32, 140.82, 138.30, 138.16, 137.13, 133.19, 131.19, 127.44, 127.14, 126.47, 126.14, 125.28, 123.49, 122.18, 121.46, 118.53, 87.48, 79.85, 74.13, 49.49, 47.07, 43.74, 39.04, 38.97, 35.36, 32.72, 30.37, 29.56, 27.03, 26.24, 22.82, 17.75, 12.68.

HRMS (ESI-TOF) (m/z): Calcd for $C_{39}H_{42}NaO_5$, ([M + Na]$^+$), 613.2924; found 613.2932.

$[\alpha]_D^{20}$ = -15.6 (c = 1.21, CH_2Cl_2).

(R)-2,5,6,8-tetramethyl-2-((4R,8S)-4,8,11-trimethyldodecyl)chroman-7-yl 2-(2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3ac’)

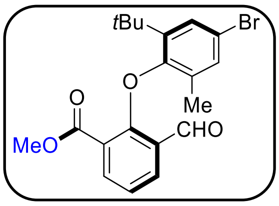


The title compound **3ac’** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10:1). **3ac’** was obtained as a yellow oil (58.6 mg, 81%, dr > 20:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.30 (s, 1H), 8.23 (dd, J = 7.6, 1.9 Hz, 1H), 7.96 (dd, J = 7.9, 1.9 Hz, 1H), 7.30 (dd, J = 7.9, 1.7 Hz, 1H), 7.24 (t, J = 7.7 Hz, 1H), 7.08 (t, J = 7.7 Hz, 1H), 7.02 (dd, J = 7.6, 1.6 Hz, 1H), 2.60 (t, J = 6.9 Hz, 3H), 2.10 (s, 6H), 2.06 (s, 3H), 1.97 (s, 3H), 1.85 – 1.73 (m, 2H), 1.58 – 1.49 (m, 3H), 1.44 (s, 9H), 1.40 – 1.35 (m, 3H), 1.32 – 1.17 (m, 12H), 1.15 – 1.03 (m, 6H), 0.87 – 0.84 (m, 12H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.60, 164.23, 158.28, 156.13, 149.59, 140.73, 140.54, 136.95, 133.45, 131.22, 127.48, 127.28, 126.70, 126.14, 125.40, 124.95, 123.96, 123.17, 122.11, 117.48, 75.10, 39.37, 37.45, 37.42, 37.29, 35.27, 32.79, 32.71, 31.09, 30.34, 27.97, 24.80, 24.44, 23.91, 22.71, 22.62, 21.03, 20.63, 19.75, 19.66, 17.53, 13.22, 12.37, 11.86.

HRMS (ESI-TOF) (m/z): Calcd for $C_{48}H_{68}NaO_5$, ([M + Na]$^+$), 747.4959; found 747.4960.

$[\alpha]_D^{20}$ = -10.886 (c = 2.87, CH_2Cl_2).

(*S*)-methyl 2-(4-bromo-2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3ba)

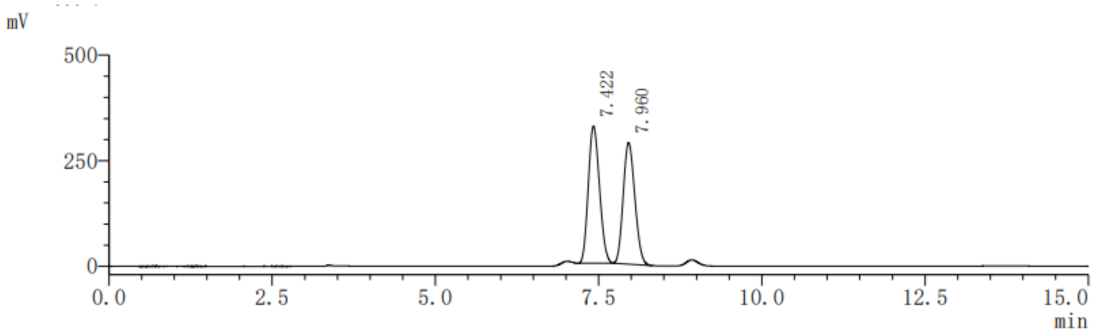


The title compound **3ba** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3ba** was obtained as a yellow oil (28.7 mg, 71%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 10.02 (s, 1H), 7.98 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.80 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 2.4 Hz, 1H), 3.63 (s, 3H), 1.86 (s, 3H), 1.43 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.81, 166.36, 156.67, 153.58, 143.24, 136.78, 133.13, 132.32, 129.77, 129.05, 126.77, 123.54, 122.42, 117.93, 52.45, 35.61, 30.16, 17.60.

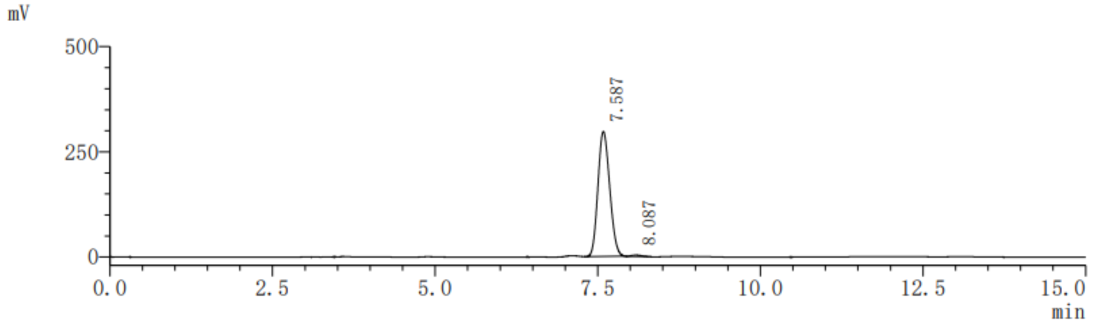
HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{21}BrNaO_4$, ($[M + Na]^+$), 427.0515; found 427.0458.

$[\alpha]_D^{20}$ = -39.4 (c = 1.43, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (99:1 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (major) = 7.59 min, t_R (minor) = 8.09 min, 98% ee.

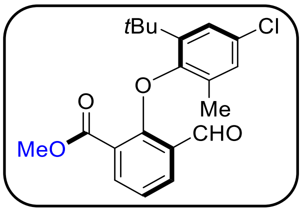


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	7.422	M	0.3197	3874764	324789	52.0222
2	7.960	M	0.3320	3573532	287233	47.9778



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	7.587	M	0.3364	3737514	296866	99.0618
2	8.087	M	0.3038	35397	3195	0.9382

(*S*)-methyl 2-(2-(tert-butyl)-4-chloro-6-methylphenoxy)-3-formylbenzoate (3ca)

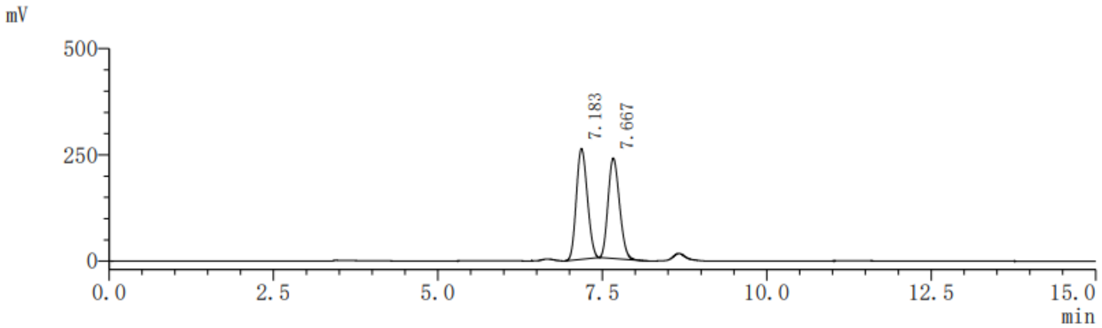


The title compound **3ca** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3ca** was obtained as a yellow oil (28.1 mg, 78%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 10.01 (s, 1H), 7.98 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.80 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.26 (s, 1H), 7.19 (td, *J* = 7.7, 0.8 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 3.63 (s, 3H), 1.87 (s, 3H), 1.43 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.83, 166.37, 156.75, 153.02, 142.92, 136.76, 132.32, 130.08, 129.97, 129.40, 126.76, 126.13, 123.53, 122.37, 52.43, 35.61, 30.14, 17.67.

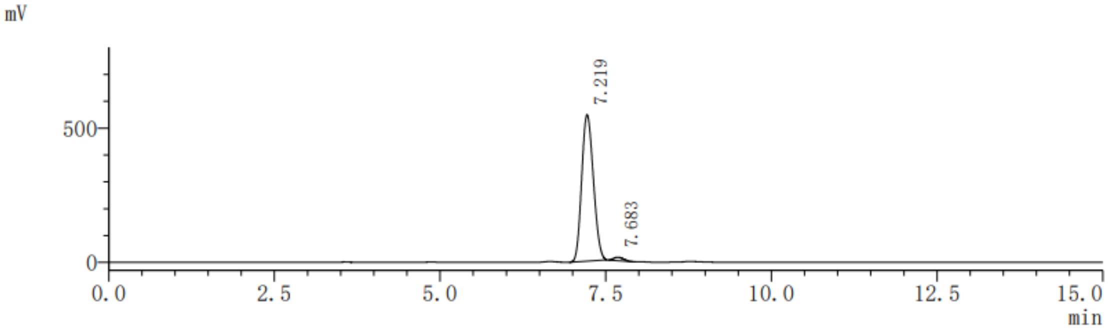
HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{21}ClNaO_4$, ([M + Na]$^+$), 383.1021; found 383.1024.

[α]$_D$^{20} = -35.6 (c = 1.40, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (99:1 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t$_R$ (major) = 7.22 min, t$_R$ (minor) = 7.68 min, 96% ee.

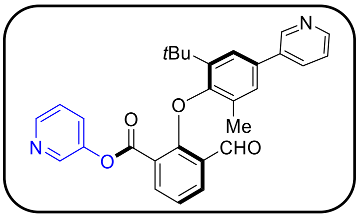


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	7.183	M	0.3127	3024705	259880	51.4389
2	7.667	M	0.3237	2855488	235517	48.5611



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	7.219	M	0.3279	6672787	544673	98.0450
2	7.683	M	0.2861	133054	12741	1.9550

(*S*)-pyridin-3-yl 2-(2-(tert-butyl)-6-methyl-4-(pyridin-3-yl)phenoxy)-3-formylbenzoate (3do)

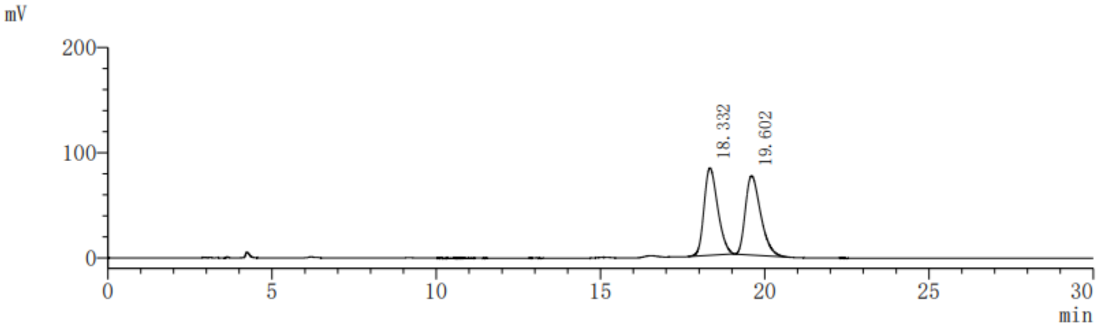


The title compound **3do** was prepared under the optimized conditions and purified by preparative TLC (ethyl acetate). **3do** was obtained as a yellow oil (28.4 mg, 61%). **^{1}H NMR (500 MHz, Chloroform-*d*)** *δ* 9.92 (s, 1H), 8.80 (s, 1H), 8.60 (d, *J* = 4.8 Hz, 1H), 8.49 (d, *J* = 4.7 Hz, 1H), 8.42 (d, *J* = 2.6 Hz, 1H), 8.15 – 8.06 (m, 2H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.48 (s, 1H), 7.44 – 7.34 (m, 2H), 7.34 – 7.27 (m, 2H), 7.25 (s, 1H), 2.04 (s, 3H), 1.50 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** *δ* 187.50, 163.53, 157.81, 155.28, 148.52, 148.20, 147.25, 147.19, 143.16, 141.67, 137.34, 136.04, 134.75, 134.36, 133.81, 129.73, 129.06, 127.97, 127.30, 125.27, 123.88, 123.57, 122.65, 122.23, 35.63, 30.32, 18.07.

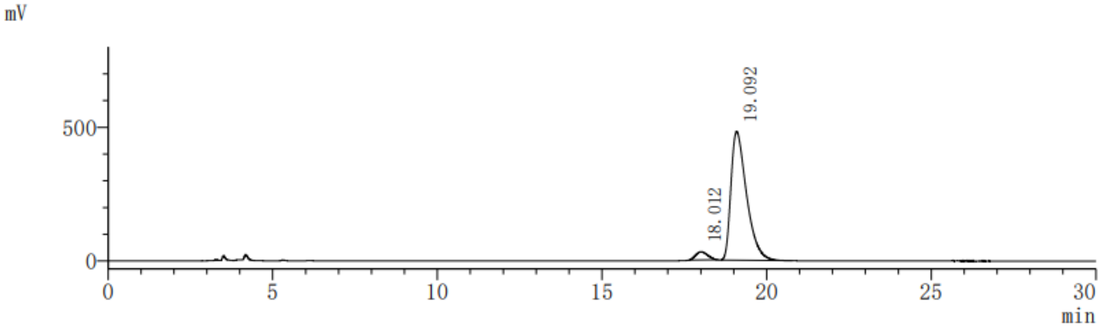
HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{26}NaN_2O_4$, ([M + Na]$^+$), 489.1785; found 489.1784.

[α]$_D$^{20} = -38.7 (c = 1.66, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (85:15 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t$_R$ (minor) = 18.01 min, t$_R$ (major) = 19.09 min, 91% ee.

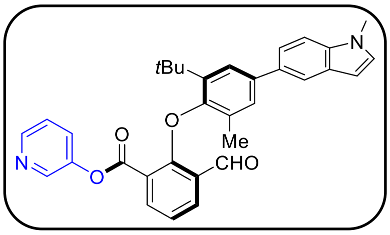


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	18.332	M	0.7696	2404530	82930	49.5557
2	19.602	M	0.8561	2447642	75457	50.4443



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	18.012	M	0.6882	757313	30186	4.5518
2	19.092	M	0.8636	15880409	480862	95.4482

(*S*)-pyridin-3-yl 2-(2-(tert-butyl)-6-methyl-4-(1-methyl-1H-indol-5-yl)phenoxy)-3-formylbenzoate (3eo)

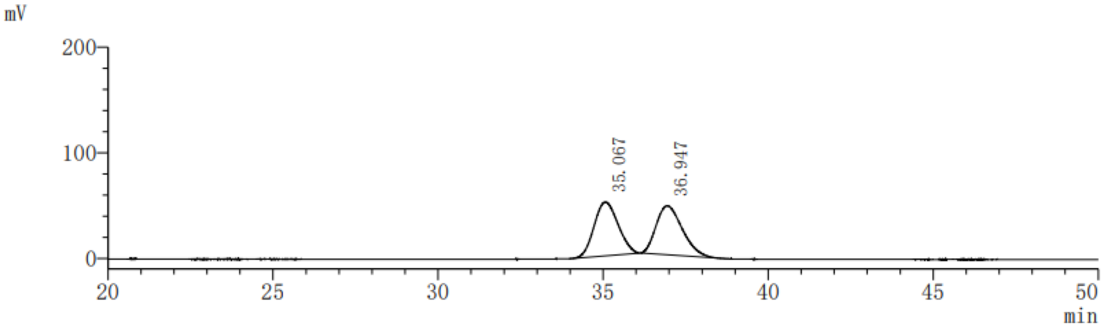


The title compound **3eo** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 2: 1). **3eo** was obtained as a yellow oil (32.7 mg, 63%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.95 (s, 1H), 8.49 – 8.41 (m, 2H), 8.13 – 8.02 (m, 2H), 7.77 (s, 1H), 7.55 (s, 1H), 7.45 – 7.32 (m, 3H), 7.30 (s, 1H), 7.29 – 7.19 (m, 2H), 7.09 (d, *J* = 3.1 Hz, 1H), 6.54 (d, *J* = 3.0 Hz, 1H), 3.83 (s, 3H), 2.05 (s, 3H), 1.50 (s, 9H). **^{13}CNMR (150 MHz, Chloroform-*d*)** δ 187.91, 163.86, 158.08, 153.78, 147.23 , 147.16, 143.11, 141.02, 139.72, 137.19, 136.27, 133.64, 132.12, 129.73, 129.60, 129.31, 128.95, 127.45, 127.30, 125.46, 123.89, 122.22, 122.20, 121.27, 119.36, 109.46, 101.31, 35.55, 32.99, 30.50, 18.01.

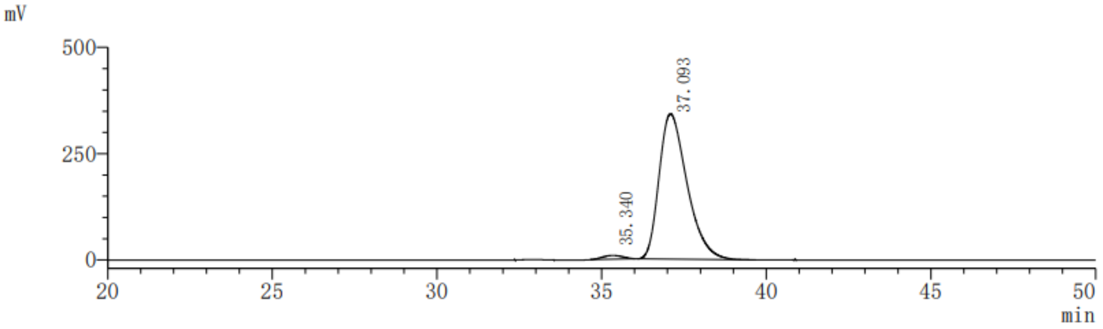
HRMS (ESI-TOF) (m/z): Calcd for $C_{33}H_{30}NaN_2O_4$, ([M + Na]$^+$), 541.2098; found 541.2101.

[α]$_D$^{20} = -43.8 (c = 1.84, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (minor) = 35.34 min, t_R (major) = 37.09 min, 96% ee.

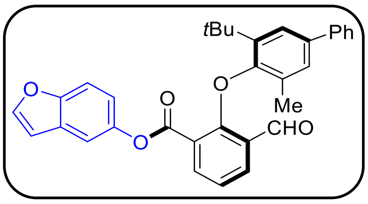


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	35.067	M	1.3593	2573704	50909	50.1042
2	36.947	M	1.4777	2563000	46308	49.8958



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	35.340	M	1.1649	383806	8936	1.8626
2	37.093	M	1.5528	20222541	341895	98.1374

(*S*)-benzofuran-5-yl 2-((3-(tert-butyl)-5-methyl-[1,1'-biphenyl]-4-yl)oxy)-3-formylbenzoate (3fr)

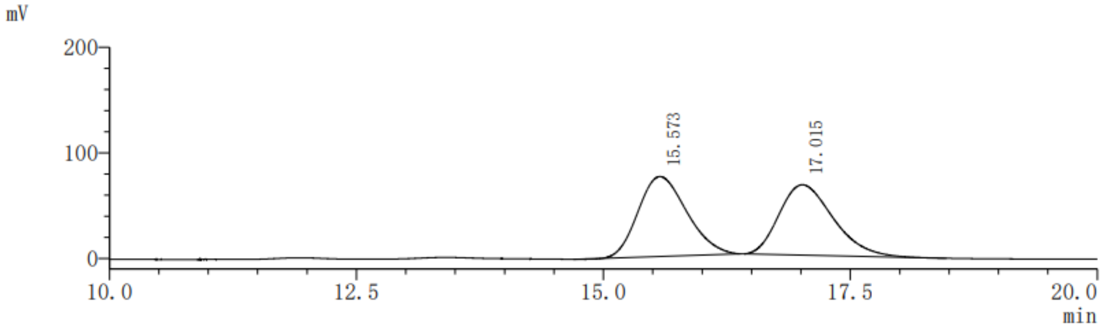


The title compound **3fr** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3fr** was obtained as a yellow oil (30.8 mg, 61%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 10.04 (s, 1H), 8.07 (dd, *J* = 7.6, 2.7 Hz, 2H), 7.61 (d, *J* = 2.1 Hz, 1H), 7.57 (s, 1H), 7.56 (s, 1H), 7.51 (d, *J* = 2.3 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.36 (d, *J* = 7.1 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 2.3 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.60 (s, 1H), 2.06 (s, 3H), 1.49 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 188.06, 164.76, 157.69, 154.45, 152.59, 146.27, 145.99, 141.37, 140.61, 137.97, 137.19, 133.00, 129.57, 128.79, 128.02, 127.67, 127.30, 127.20, 127.09, 125.22, 123.21, 122.30, 117.82, 113.68, 111.79, 106.88, 35.60, 30.47, 18.09.

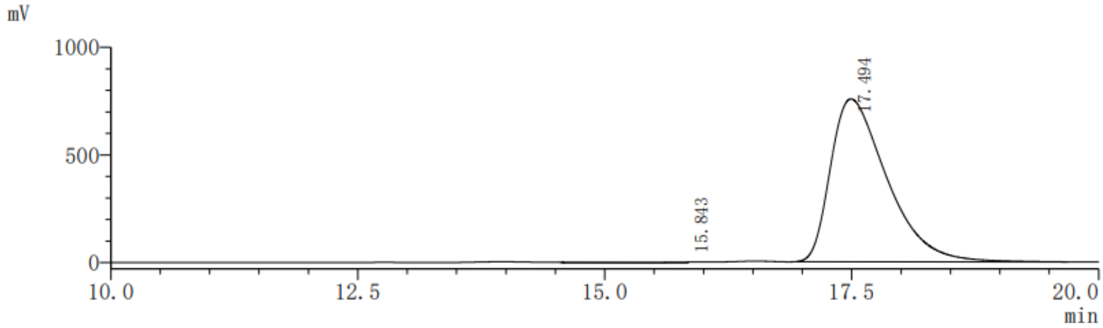
HRMS (ESI-TOF) (m/z): Calcd for $C_{33}H_{28}NaO_5$, ([M + Na]$^+$), 527.1829; found 527.1827 .

[α]$_D$^{20} = -58.7 (c = 1.54, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IC-3 column (99:1 hexane: 2-propanol, 1 mL/min, 25 °C, 254 nm); t$_R$ (minor) = 15.84 min, t$_R$ (major) = 17.49 min, 99% ee.

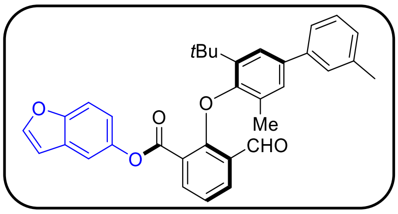


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	15.573	M	0.9163	2584603	75634	50.3946
2	17.015	M	1.0066	2544129	66670	49.6054



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	15.843	M	--	59327	3113	0.1970
2	17.494	M	1.0422	30048413	756387	99.8030

(*S*)-benzofuran-5-yl-2-((3-(tert-butyl)-3',5-dimethyl-[1,1'-biphenyl]-4-yl)oxy)-3-formylbenzoate compound with ethane (1:1) (3gr)

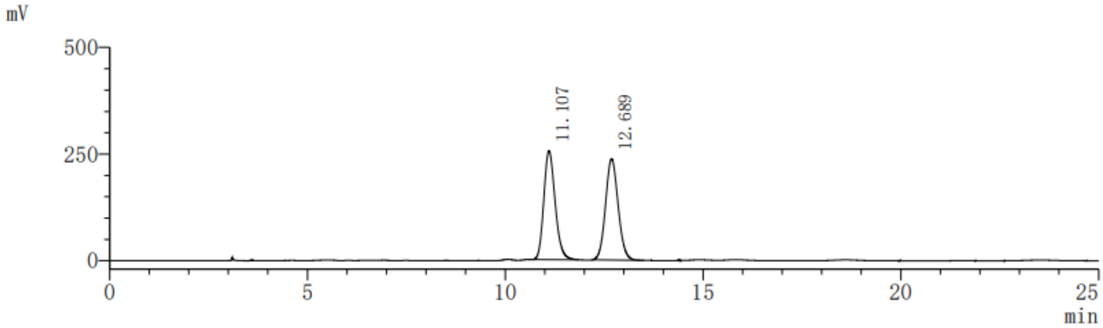


The title compound **3gr** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3gr** was obtained as a yellow oil (37.3 mg, 72%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 10.05 (s, 1H), 8.11 – 8.01 (m, 2H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.50 (d, *J* = 2.3 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.31 – 7.24 (m, 2H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.59 (d, *J* = 2.2 Hz, 1H), 2.43 (s, 3H), 2.06 (s, 3H), 1.50 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 188.10, 164.78, 157.71, 154.34, 152.59, 146.25, 145.99, 141.32, 140.64, 138.37, 138.16, 137.18, 132.98, 129.60, 128.70, 128.06, 128.02, 127.91, 127.62, 127.19, 125.24, 124.23, 123.19, 122.27, 117.82, 113.72, 111.79, 106.89, 35.60, 30.50, 21.58, 18.08.

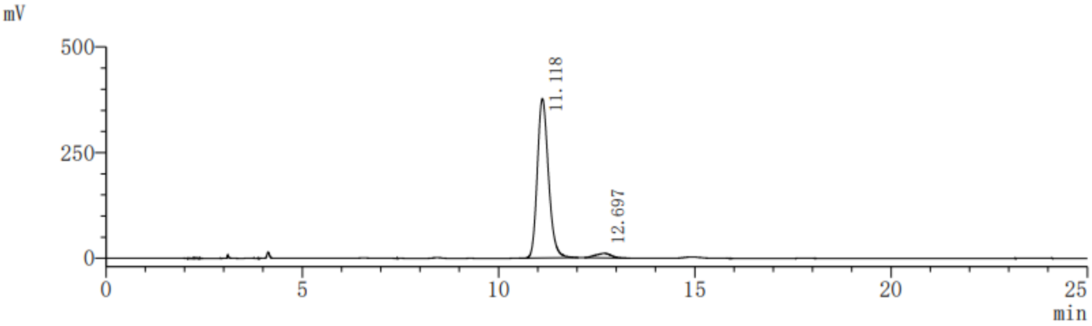
HRMS (ESI-TOF) (m/z): Calcd for $C_{34}H_{30}NaO_5$, ($[M + Na]^+$), 541.1985; found 541.1990.

$[\alpha]_D^{20}$ = -59.7 (c = 1.87, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (97:3 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (major) = 11.12 min, t_R (minor) = 12.70 min, 92% ee.

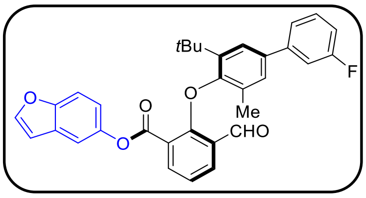


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	11.107	M	0.5194	5072701	254915	49.0552
2	12.689	M	0.5822	5268109	237580	50.9448



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	11.118	M	0.5121	7445837	377131	96.1890
2	12.697	M	0.8134	295002	10691	3.8110

(*S*)-benzofuran-5-yl-2-((3-(tert-butyl)-3'-fluoro-5-methyl-[1,1'-biphenyl]-4-yl)oxy)-3-formylbenzoate compound with ethane (1:1) (3hr)

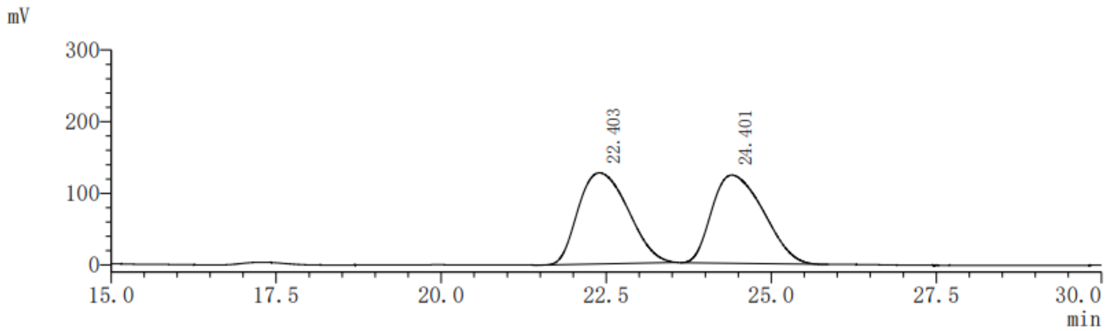


The title compound **3hr** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3hr** was obtained as a yellow oil (26.7 mg, 51%). **^{1}H NMR (500 MHz, Chloroform-*d*)** *δ* 10.03 (s, 1H), 8.07 (d, *J* = 7.7 Hz, 2H), 7.62 (d, *J* = 2.2 Hz, 1H), 7.47 (d, *J* = 2.3 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.35 – 7.28 (m, 2H), 7.26 (d, *J* = 2.5 Hz, 1H), 7.23 (t, *J* = 2.1 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 7.07 – 7.00 (m, 1H), 6.90 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.63 – 6.59 (m, 1H), 2.05 (s, 3H), 1.49 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** *δ* 187.95, 164.65, 163.97, 162.35, 157.59, 154.86, 152.59, 146.33, 145.97, 142.88 (d, *J* = 7.9 Hz), 141.55, 137.23, 136.60 (d, *J* = 2.3 Hz), 133.04, 130.25 (d, *J* = 8.5 Hz), 129.56, 128.01, 127.80, 127.19, 125.14, 123.19, 122.68 (d, *J* = 2.8 Hz), 122.44, 117.75, 113.99 (dd, *J* = 21.6, 18.7 Hz), 113.60, 111.81, 106.82, 35.62, 30.42, 18.10. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -112.94 – -112.98 (m, 1F).

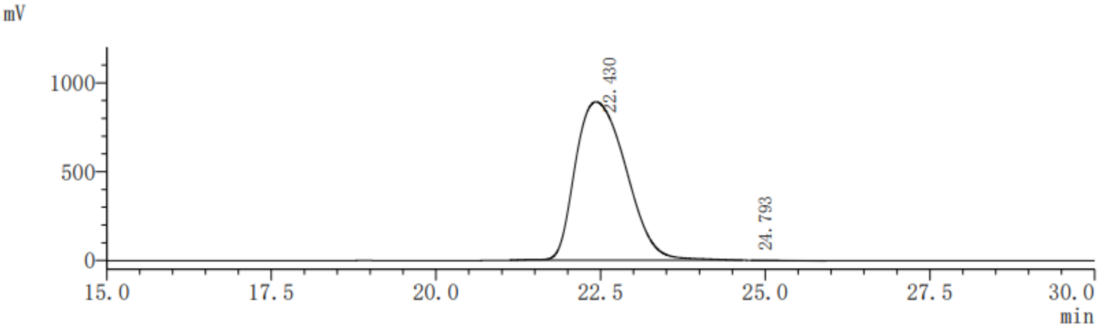
HRMS (ESI-TOF) (m/z): Calcd for $C_{33}H_{27}FNaO_5$, ([M + Na]$^+$), 545.1735; found 545.1737.

$[\alpha]_D^{20}$ = -37. 9 (c = 1.33, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (99:1 hexane: 2-propanol, 0.6 mL/min, 25 °C, 254 nm); t_R (major) = 22.43 min, t_R (minor) = 24.79 min, 99% ee.

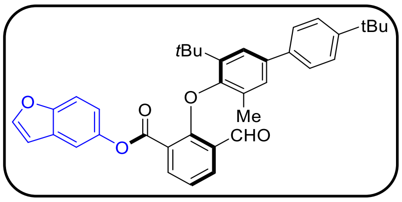


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	22.403	M	1.3875	6671878	127043	49.9507
2	24.401	M	1.4683	6685035	123057	50.0493



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	22.430	M	1.3879	47813229	891985	99.8451
2	24.793	M	--	74194	396	0.1549

(*S*)-benzofuran-5-yl-2-((3,4'-di-tert-butyl-5-methyl-[1,1'-biphenyl]-4-yl)oxy)-3-formylbenzoate (3ir)

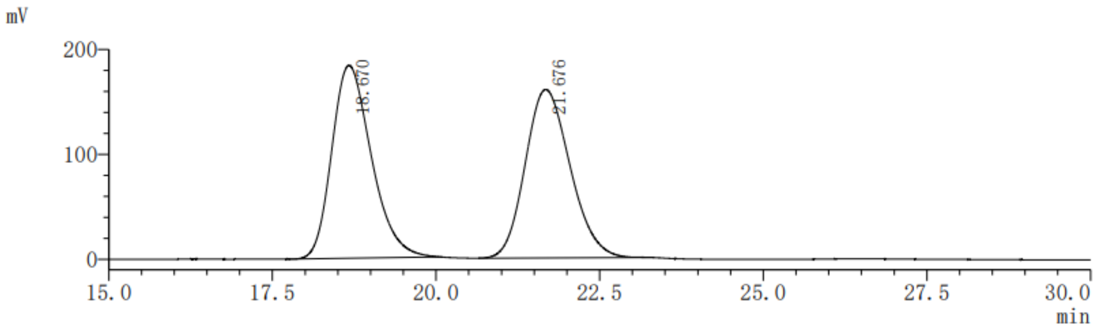


The title compound **3ir** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3ir** was obtained as a yellow oil (45.4 mg, 81%). **^{1}H NMR (500 MHz, Chloroform-*d*)** *δ* 10.01 (s, 1H), 8.07 (d, *J* = 7.7 Hz, 2H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.54 – 7.45 (m, 6H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 2.4 Hz, 1H), 6.93 (d, *J* = 2.4 Hz, 1H), 6.59 (d, *J* = 2.1 Hz, 1H), 2.06 (s, 3H), 1.50 (s, 9H), 1.38 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** *δ* 188.07, 164.80, 157.76, 154.29, 152.59, 150.35, 146.21, 146.02, 141.27, 137.88, 137.73, 137.17, 133.01, 129.41, 128.02, 127.62, 127.21, 126.75, 125.73, 125.11, 123.23, 122.25, 117.86, 113.73, 111.80, 106.90, 35.59, 34.58, 31.40, 30.49, 18.08.

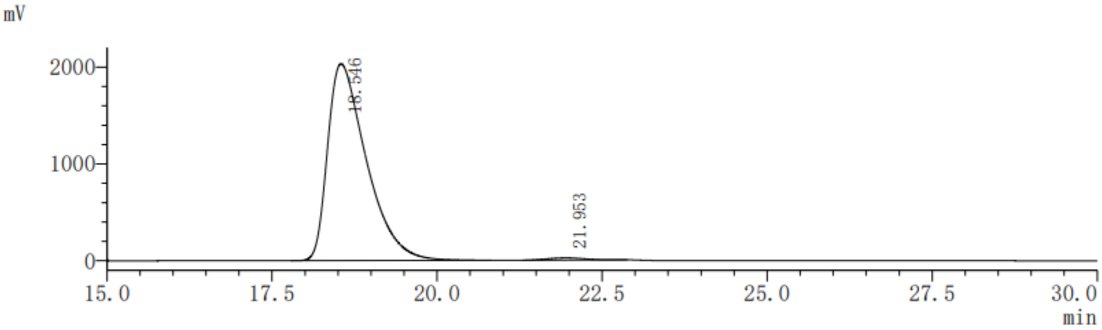
HRMS (ESI-TOF) (m/z): Calcd for $C_{37}H_{36}NaO_5$, ([M + Na]$^+$), 583.2455; found 583.2457.

$[\alpha]_D^{20}$ = -44.9 (c = 2.27, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (99:1 hexane: 2-propanol, 1 mL/min, 25 °C, 254 nm); t_R (major) = 18.55 min, t_R (minor) = 21.95 min, 98% ee.

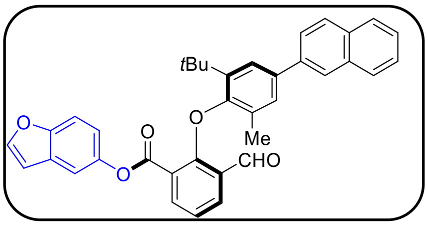


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	18.670	M	1.1009	7749472	184019	50.2653
2	21.676	M	1.2646	7667677	160638	49.7347



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	18.546	M	1.0658	82969726	2032753	98.9871
2	21.953	M	1.0308	848987	21929	1.0129

(S)-benzofuran-5-yl2-(2-(tert-butyl)-6-methyl-4-(naphthalen-2-yl)phenoxy)-3-formylbenzoate (3jr)

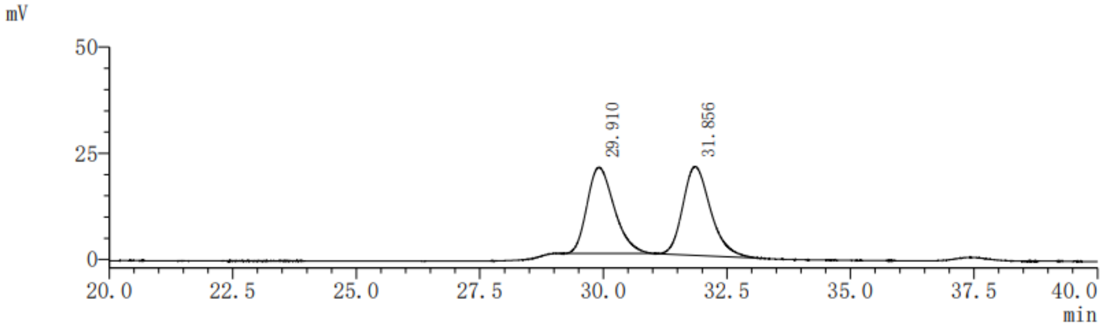


The title compound **3jr** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3jr** was obtained as a yellow oil (41.6 mg, 75%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 10.10 (s, 1H), 8.15 – 8.04 (m, 2H), 8.00 (s, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.91 – 7.86 (m, 2H), 7.72 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.64 (d, *J* = 2.3 Hz, 1H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.45 – 7.38 (m, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 2.3 Hz, 1H), 6.93 (dt, *J* = 8.9, 1.8 Hz, 1H), 6.55 (d, *J* = 2.2 Hz, 1H), 2.10 (s, 3H), 1.53 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 188.13, 164.79, 157.71, 154.54, 152.60, 146.30, 146.01, 141.54, 138.01, 137.91, 137.24, 133.67, 133.02, 132.62, 129.89, 128.50, 128.17, 128.04, 127.82, 127.71, 127.23, 126.42, 126.00, 125.71, 125.53, 125.50, 123.23, 122.36, 117.82, 113.71, 111.82, 106.90, 35.68, 30.53, 18.16.

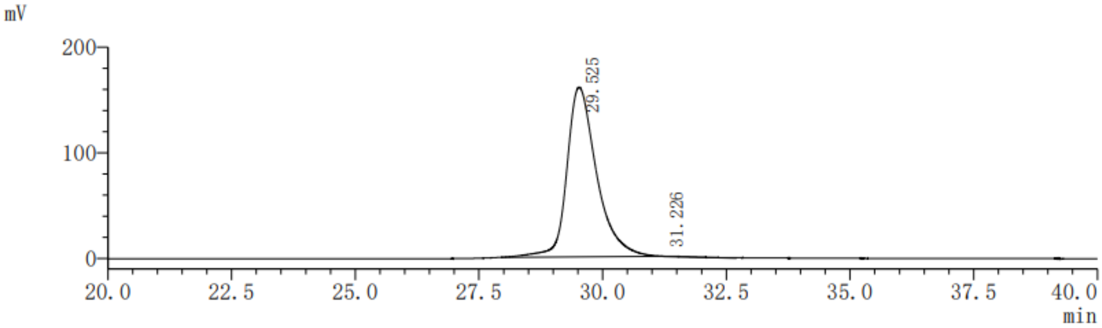
HRMS (ESI-TOF) (m/z): Calcd for $C_{37}H_{30}BrNaO_5$, ([M + Na]$^+$), 577.1985; found 577.1987.

[α]$_D$^{20} = -30.7 (c = 2.36, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IA-3 column (99:1 hexane: 2-propanol, 1 mL/min, 25 °C, 254 nm); t$_R$ (major) = 29.53 min, t$_R$ (minor) = 31.23 min, 99% ee.

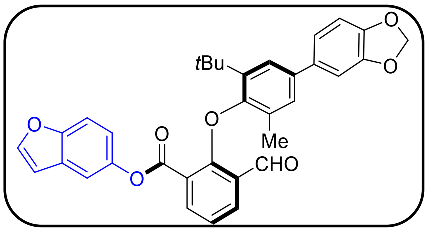


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	29.910	M	1.0131	780540	20266	48.7556
2	31.856	M	1.0132	820383	20893	51.2444



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	29.525	M	1.0329	6717287	160631	99.5723
2	31.226	M	1.2856	28852	348	0.4277

(S)-benzofuran-5-yl2-(4-(benzo[d][1,3]dioxol-5-yl)-2-(tert-butyl)-6-methylphenoxy)-3-formylbenzoate (3kr)

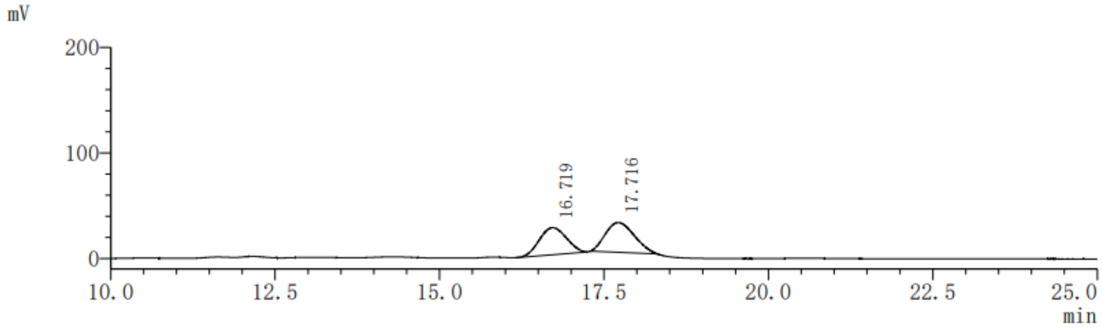


The title compound **3kr** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3kr** was obtained as a yellow oil (41.7 mg, 76%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 10.01 (s, 1H), 8.07 (d, *J* = 7.7 Hz, 2H), 7.62 (d, *J* = 2.2 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 2.3 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.04 (d, *J* = 1.7 Hz, 1H), 7.02 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.91 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.65 – 6.63 (m, 1H), 6.02 (d, *J* = 1.2 Hz, 2H), 2.04 (s, 3H), 1.48 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 188.07, 164.79, 157.72, 154.23, 152.61, 148.14, 147.09, 146.31, 146.02, 141.32, 137.72, 137.19, 135.03, 133.02, 129.28, 128.03, 127.66, 127.20, 124.94, 123.23, 122.29, 120.60, 117.84, 113.67, 111.81, 108.58, 107.63, 106.88, 101.21, 35.57, 30.45, 18.06.

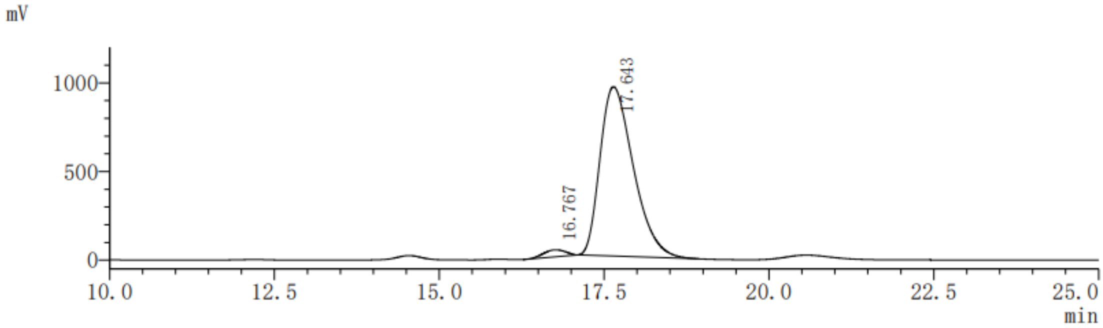
HRMS (ESI-TOF) (m/z): Calcd for $C_{34}H_{28}NaO_7$, ([M + Na]$^+$), 571.1727; found 571.1718.

$[\alpha]_D^{20}$ = -32.2 (c = 2.08, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IC-3 column (97:3 hexane: 2-propanol, 1 mL/min, 25 °C, 254 nm); t_R (minor) = 16.77 min, t_R (major) = 17.64 min, 95% ee.

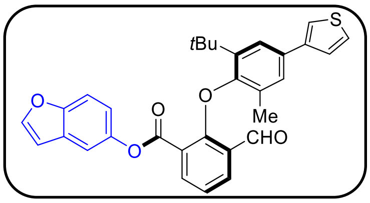


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	16.719	M	0.7767	730992	25577	45.8125
2	17.716	M	0.8437	864627	28168	54.1875



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	16.767	M	0.6396	930050	39454	2.6887
2	17.643	M	0.9263	33660728	955609	97.3113

(S)-benzofuran-5-yl 2-(2-(tert-butyl)-6-methyl-4-(thiophen-3-yl)phenoxy)-3-formylbenzoate (3lr)

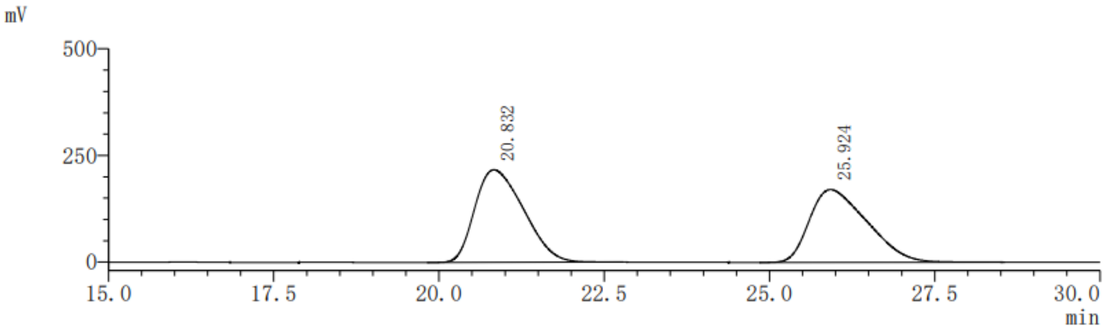


The title compound **3lr** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3lr** was obtained as a yellow oil (28.1 mg, 55%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 10.02 (d, *J* = 0.8 Hz, 1H), 8.06 (dd, *J* = 7.7, 0.8 Hz, 2H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.52 (d, *J* = 2.3 Hz, 1H), 7.43 – 7.40 (m, 3H), 7.36 (dd, *J* = 4.4, 2.0 Hz, 1H), 7.29 (d, *J* = 2.2 Hz, 1H), 7.28 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 6.92 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.57 (dd, *J* = 2.2, 1.0 Hz, 1H), 2.04 (s, 3H), 1.48 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 188.05, 164.75, 157.70, 154.20, 152.59, 146.30, 145.99, 141.78, 141.48, 137.16, 133.02, 132.77, 128.88, 128.04, 127.79, 127.18, 126.35, 124.52, 123.17, 122.29, 120.20, 117.79, 113.74, 111.78, 106.85, 35.53, 30.42, 18.00.

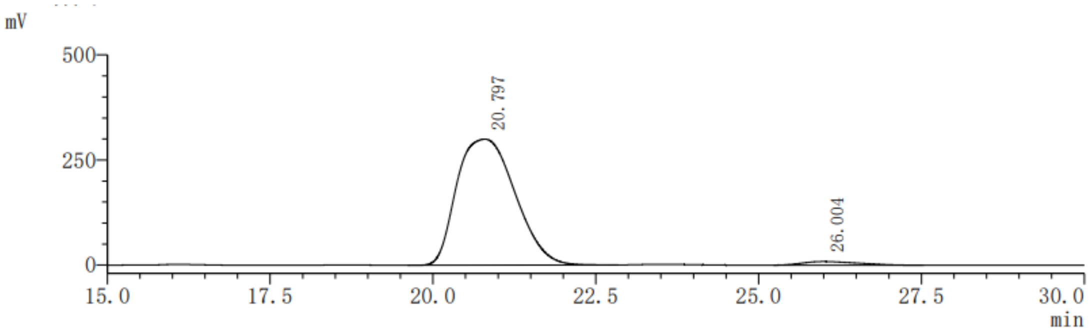
HRMS (ESI-TOF) (m/z): Calcd for $C_{31}H_{26}NaO_5S$, ([M + Na]$^+$), 533.1393; found 533.1387.

$[\alpha]_D^{20}$ = -37.1 (c = 1.40, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (97:3 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (major) = 20.80 min, t_R (minor) = 26.00 min, 95% ee.

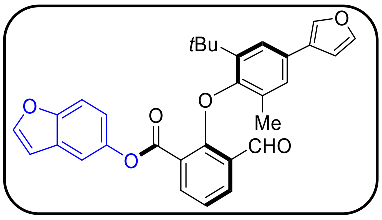


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	20.832	M	1.4030	11141021	216967	51.9316
2	25.924	M	1.7005	10312240	170642	48.0684



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	20.797	M	1.5537	18645301	299815	97.3245
2	26.004	M	1.6277	512572	8671	2.6755

(S)-benzofuran-5-yl 2-(2-(tert-butyl)-4-(furan-3-yl)-6-methylphenoxy)-3-formylbenzoate (3mr)

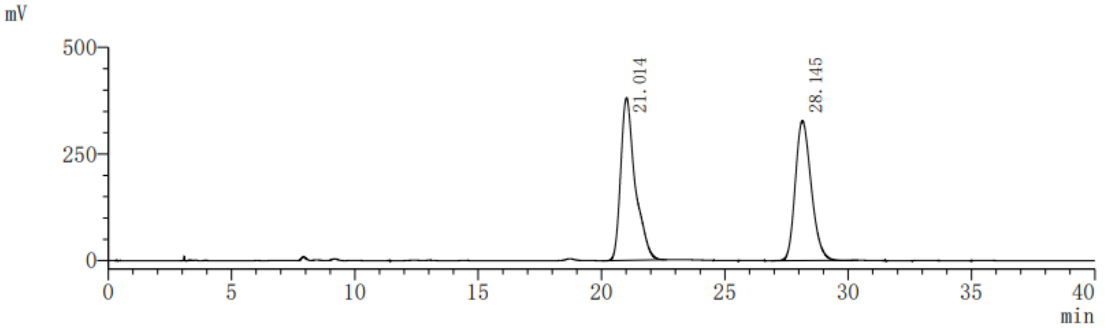


The title compound **3mr** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3mr** was obtained as a yellow oil (38.5 mg, 78%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.99 (s, 1H), 8.08 – 8.06 (m, 1H), 8.06 – 8.04 (m, 1H), 7.70 (t, *J* = 1.3 Hz, 1H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.49 (t, *J* = 1.7 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.40 (d, *J* = 2.3 Hz, 1H), 7.26 (td, *J* = 7.7, 0.9 Hz, 1H), 7.18 (d, *J* = 2.2 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 6.93 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.68 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.60 (dd, *J* = 2.2, 0.9 Hz, 1H), 2.02 (s, 3H), 1.47 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 164.75, 157.72, 154.09, 152.61, 146.32, 146.02, 143.75, 141.54, 138.44, 137.14, 133.04, 129.35, 128.32, 128.05, 127.89, 127.18, 126.00, 123.90, 123.19, 122.28, 117.80, 113.74, 111.79, 108.92, 106.84, 35.47, 30.39, 17.91.

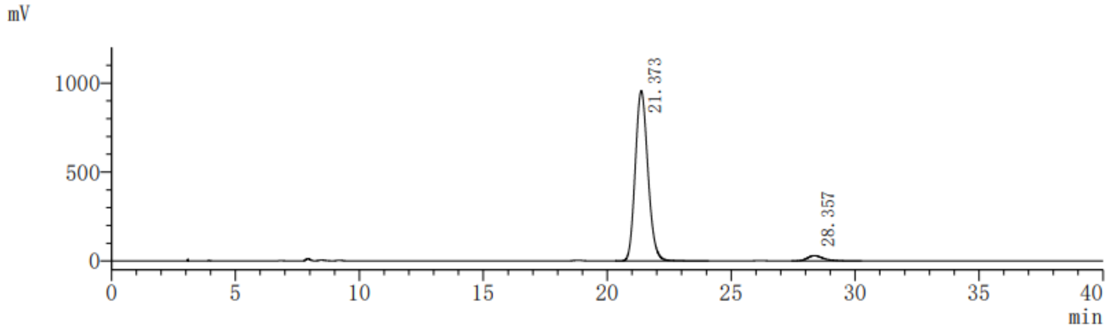
HRMS (ESI-TOF) (m/z): Calcd for $C_{31}H_{26}NaO_6$, ([M + Na]$^+$), 517.1622; found 517.1623.

$[\alpha]_D^{19}$ = -27.5 (c = 1.93, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (97:3 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (major) = 21.37 min, t_R (minor) = 28.36 min, 93% ee.

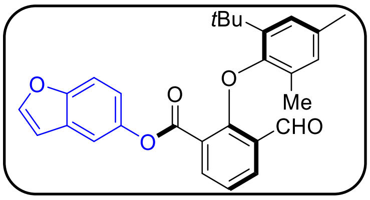


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	21.014	M	0.9792	15569946	381285	51.4491
2	28.145	M	1.1804	14692846	327637	48.5509



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	21.373	M	0.9303	33964964	956402	96.2699
2	28.357	M	1.1372	1316004	29438	3.7301

(S)-benzofuran-5-yl 2-(2-(tert-butyl)-4,6-dimethylphenoxy)-3-formylbenzoate (3nr)

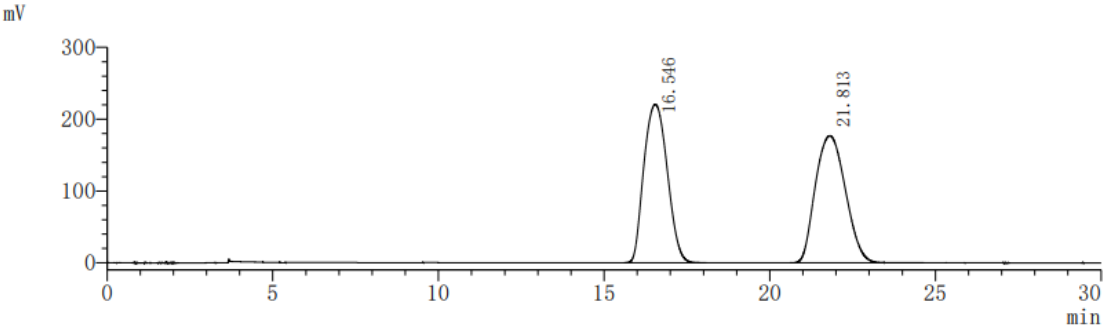


The title compound **3nr** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3nr** was obtained as a yellow oil (29.6 mg, 67%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.72 (s, 1H), 8.06 (dd, *J* = 7.6, 1.9 Hz, 1H), 8.01 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.64 (d, *J* = 2.2 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.26 (d, *J* = 2.4 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 2.2 Hz, 1H), 6.97 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.87 – 6.85 (m, 1H), 6.74 (d, *J* = 2.2 Hz, 1H), 2.31 (s, 3H), 1.95 (s, 3H), 1.43 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 188.12, 165.04, 158.04, 153.18, 152.64, 146.35, 146.17, 140.60, 137.03, 134.67, 133.16, 131.47, 128.05, 127.20, 127.12, 126.96, 123.31, 121.96, 117.96, 113.71, 111.80, 106.88, 35.23, 30.41, 21.07, 17.59.

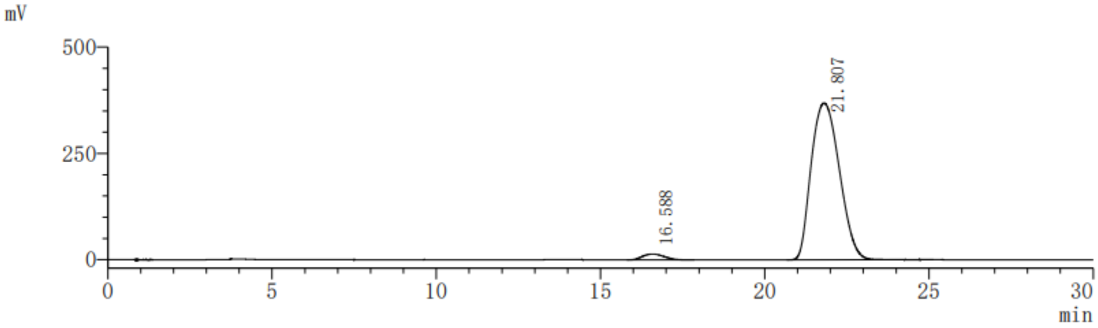
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{26}NaO_5$, ([M + Na]$^+$), 465.1672; found 465.1679.

$[\alpha]_D^{20}$ = -39.1 (c = 1.48, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (99:1 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (minor) = 16.59 min, t_R (major) = 21.81 min, 95% ee.

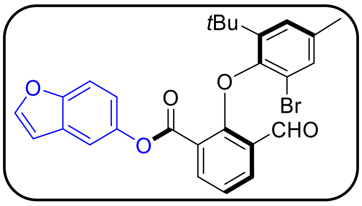


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	16.546	M	1.2894	10836195	220441	49.2268
2	21.813	M	1.6927	11176591	176885	50.7732



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	16.588	M	1.2188	625905	13698	2.7603
2	21.807	M	1.5785	22049377	368898	97.2397

(S)-benzofuran-5-yl 2-(2-bromo-6-(tert-butyl)-4-methylphenoxy)-3-formylbenzoate (3or)

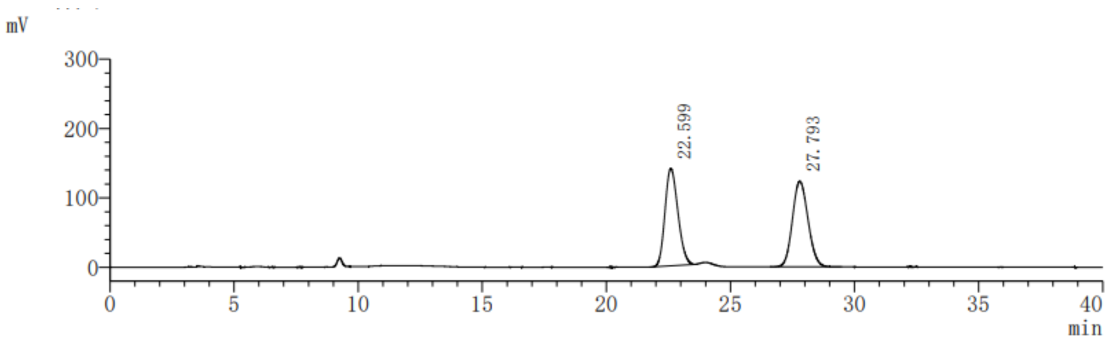


The title compound **3or** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3or** was obtained as a yellow oil (32.9 mg, 65%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.92 (s, 1H), 8.14 (dd, *J* = 7.6, 1.9 Hz, 1H), 8.07 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.64 (d, *J* = 2.2 Hz, 1H), 7.46 (dt, *J* = 8.8, 0.7 Hz, 1H), 7.28 (td, *J* = 7.7, 0.9 Hz, 1H), 7.24 (t, *J* = 2.1 Hz, 2H), 7.16 (d, *J* = 2.1 Hz, 1H), 6.95 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.73 (dd, *J* = 2.2, 0.9 Hz, 1H), 2.31 (s, 3H), 1.43 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.94, 164.34, 157.38, 152.62, 150.99, 146.32, 146.18, 142.96, 137.34, 135.88, 133.05 (d, *J* = 3.0 Hz), 128.49, 128.02, 127.50, 123.56, 122.60, 117.95, 113.66, 112.81, 111.77, 106.86, 35.83, 30.25, 20.82.

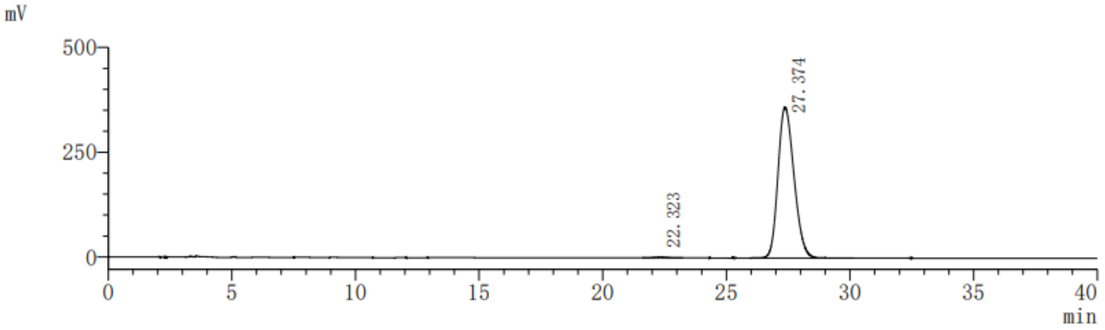
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{23}BrNaO_5$, ([M + Na]$^+$), 529.0621; found 529.0618.

[α]$_D$^{20} = -23.7 (c = 1.64, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IG column (99:1 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t$_R$ (minor) = 22.32 min, t$_R$ (major) = 27.37 min, 99% ee.

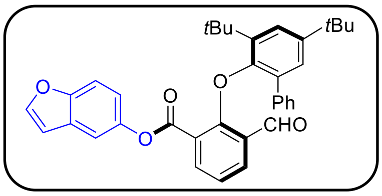


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	22.599	M	0.9638	5081254	140435	48.4866
2	27.793	M	1.1522	5398454	123435	51.5134



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	22.323	M	1.0339	78424	2071	0.4812
2	27.374	M	1.1930	16219228	359831	99.5188

(S)-benzofuran-5-yl 2-((3,5-di-tert-butyl-[1,1'-biphenyl]-2-yl)oxy)-3-formylbenzoate (3pr)

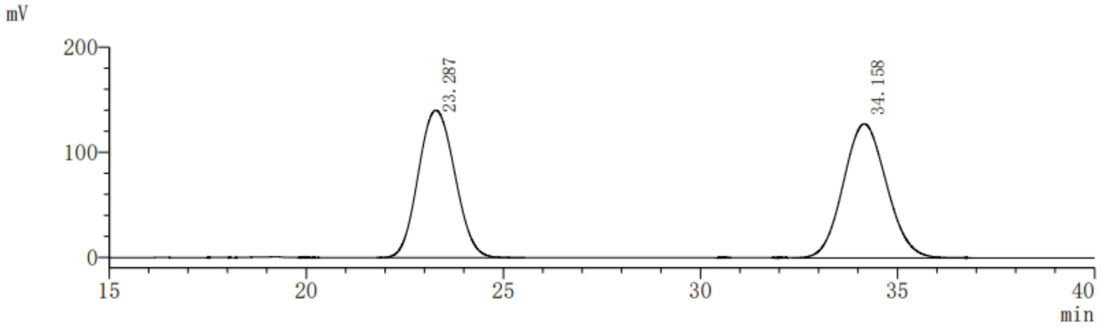


The title compound **3pr** was prepared under the optimized conditions and purified by preparative TLC (hexane : ethyl acetate = 10: 1). **3pr** was obtained as a yellow oil (24.6 mg, 45%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.81 (s, 1H), 7.79 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.70 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.67 (d, *J* = 2.2 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 2.5 Hz, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.21 (d, *J* = 6.8 Hz, 2H), 7.13 (d, *J* = 2.5 Hz, 1H), 7.10 (dd, *J* = 8.0, 6.6 Hz, 2H), 7.07 – 7.02 (m, 1H), 6.95 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.88 (td, *J* = 7.7, 0.8 Hz, 1H), 6.77 (dd, *J* = 2.2, 0.9 Hz, 1H), 1.53 (s, 9H), 1.36 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 188.04, 164.08, 158.25, 152.66, 152.57, 147.44, 146.36, 146.18, 140.32, 138.41, 137.26, 132.96, 130.97, 129.39, 128.11, 127.97, 127.71, 127.45, 127.10, 124.77, 122.77, 121.73, 118.10, 113.68, 111.88, 106.87, 35.81, 34.76, 31.58, 30.52.

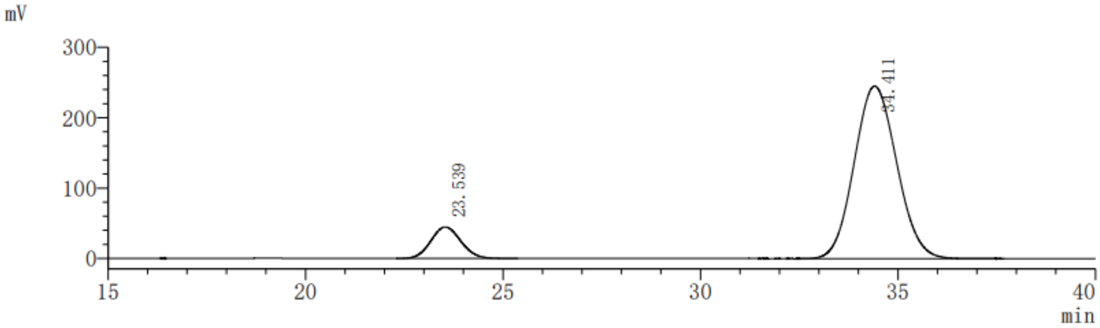
HRMS (ESI-TOF) (m/z): Calcd for $C_{33}H_{28}NaO_5$, ([M + Na]$^+$), 569.2298; found 569.2298.

[α]$_D^{20}$ = -31.8 (c = 1.22, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (97:3 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (minor) = 23.54 min, t_R (major) = 34.41 min, 77% ee.



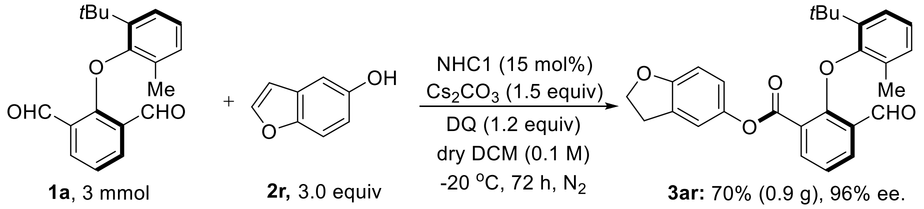
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	23.287	M	1.7055	9040823	140295	48.2107
2	34.158	M	2.0296	9711913	127558	51.7893



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	23.539	M	1.3942	2358401	44607	11.3896
2	34.411	M	1.9960	18348300	245229	88.6104

III Synthetic Applications

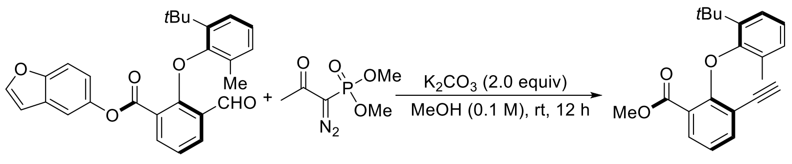
3.1 Gram-scale synthesis:



1a, 3 mmol **2r,** 3.0 equiv **3ar:** 70% (0.9 g), 96% ee.

To a flame-dried 100 mL Schlenk reaction tube equipped with a magnetic stir bar, was added the **NHC-1** (15 mol%, 0.188 g), Cs_2CO_3 (1.5 equiv, 1.466 g), 2-(2-(tert-butyl)-6-methylphenoxy)isophthalaldehyde **1a** (0.1 mmol, 0.888 g), and anhydrous dichloromethane (30 mL). The mixture was stirred for 5 minutes, followed by the addition of benzofuran-5-ol **2r** (3.0 equiv, 1.2 mg) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (1.2 equiv, 1.471 g). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at -20 ºC for 72 h. The mixture was concentrated under reduced pressure and purified by *via* column chromatography on silica gel (hexanes/EtOAc = 10:1) to afford 0.9 g product **3ar** in 70% yield with 96% ee.

3.2 Synthetic Transformation



3ar: 0.1 mmol

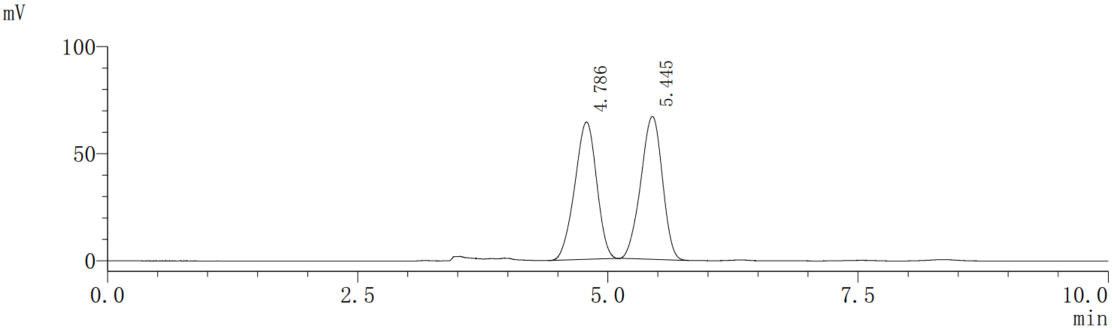
7a: 71%, 96% ee

To a solution of **3ar** (0.1 mmol, 43 mg) in 1.0 mL MeOH was added K_2CO_3 (0.2 mmol, 27.6 mg), P-(1-diazo-2-oxopropyl)-dimethylester (0.15 mmol, 22.5 µL) is slowly added. the reaction mixture was stirred at rt for 12 h, until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with water, extracted with CH_2Cl_2 (3×5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography (PE : EA = 10 : 1) to give the desired **7a** (yield: 71 %, 96% ee). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.71 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.48 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.16 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.7 Hz, 1H), 6.92 (dd, *J* = 6.3, 1.4 Hz, 1H), 3.82 (s, 3H), 2.74 (s, 1H), 1.94 (s, 3H), 1.40 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 167.12, 156.39, 153.20, 142.10, 139.01, 131.76, 130.22, 128.74, 124.46, 124.41, 123.11, 121.09, 111.53, 83.18, 77.92, 52.33, 35.11, 30.47, 17.50.

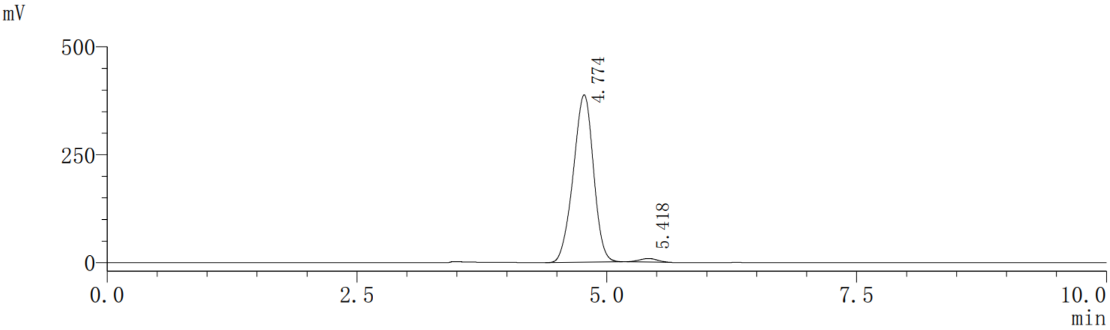
HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{22}NaO_3$, ([M + Na]$^+$), 345.1461; found 345.1462.

$[\alpha]_D^{19}$ = -29.7 (c = 1.1, CH_2Cl_2).

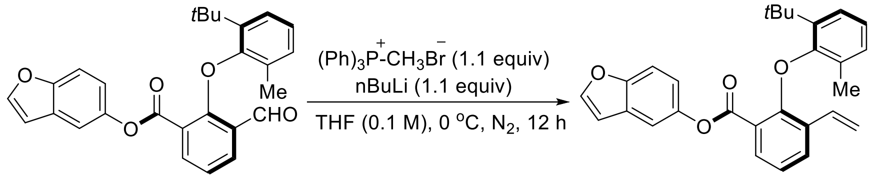
HPLC analysis: Daicel Chiralpak OD-3 column (99:1 hexane: 2-propanol, 1.0 mL/min, 25 ºC, 254 nm); t_R (major) = 4.77 min, t_R (minor) = 5.42 min, 96% ee.



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	4.786	M	0.4062	976390	64197	49.3016
2	5.445	M	0.3982	1004053	66765	50.6984



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	4.774	M	0.3708	5453620	387716	98.1175
2	5.418	M	0.3444	104633	8173	1.8825



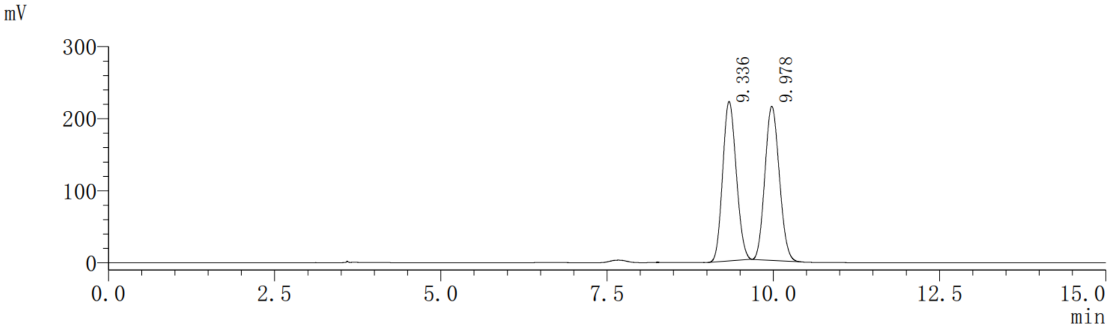
3ar: 0.1 mmol **7b**: 61%, 96% ee

In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with methyltriphenylphosphonium bromide (0.11 mmol, 39.3 mg), anhydrous tetrahydrofuran (0.5 mL) and nBuLi of 2.5 mol/L in hexane (0.11 mmol, 45 μL) was added. Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The mixture was stirred at 0 °C for 30 minutes, followed by tetrahydrofuran solution (0.5 mL) dissolved in **3ar** (0.1 mmol, 43 mg) was added dropwise and stirring at 0 °C for 12 h, until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with water, extracted with CH_2Cl_2 (3×5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography (PE : EA = 10 : 1) to give the desired **7b** (yield: 61%, 96% ee). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.76 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.62 (d, *J* = 2.2 Hz, 1H), 7.59 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 1H), 7.23 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.20 (d, *J* = 2.3 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.4 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.72 (d, *J* = 2.1 Hz, 1H), 6.53 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.47 (dd, *J* = 17.2, 1.4 Hz, 1H), 4.99 (dd, *J* = 10.9, 1.3 Hz, 1H), 1.90 (s, 3H), 1.43 (s, 9H).**^{13}C NMR (150 MHz, Chloroform-*d*)** δ 165.97, 154.24, 152.55, 152.36, 146.29, 146.16, 140.43, 131.71, 131.67, 130.79, 130.16, 129.43, 128.12, 127.95, 125.39, 123.71, 122.91, 122.22, 118.15, 115.72, 113.77, 111.67, 106.88, 35.37, 30.48, 18.08.

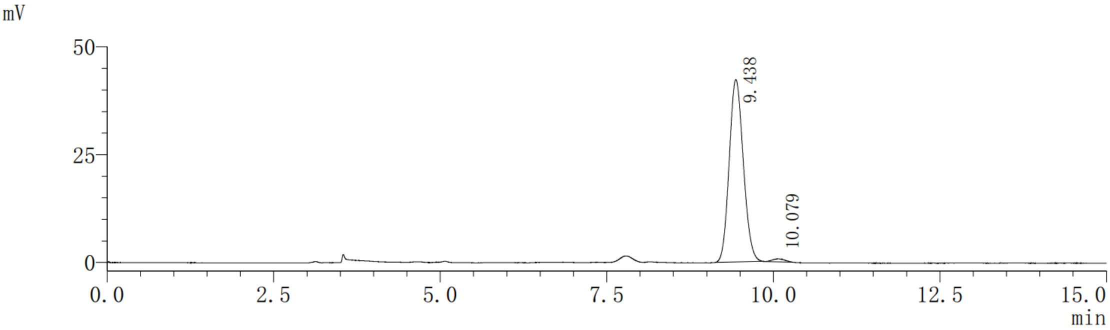
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{26}NaO_4$, ($[M + Na]^+$), 449.1723; found 449.1724.

$[\alpha]_D^{19}$ = -25.4 (c = 1.3, CH_2Cl_2).

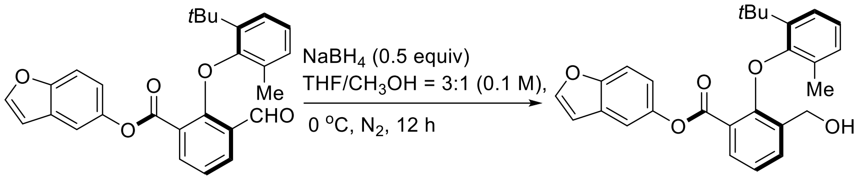
HPLC analysis: Daicel Chiralpak IG column (99:1 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 9.44 min, t_R (minor) = 10.08 min, 96% ee.



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	9.336	M	0.3796	3151900	221233	49.3579
2	9.978	M	0.4032	3233902	213762	50.6421



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	9.438	M	0.3906	623001	42288	98.6434
2	10.079	M	0.3368	8568	685	1.3566



3ar: 0.1 mmol

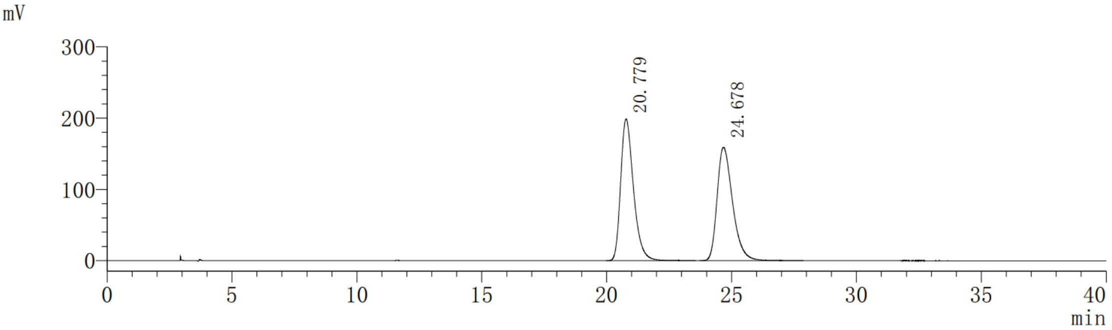
7c: 75%, 96% ee

In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **3ar** (0.1 mmol, 43 mg), NaBH$_4$ (0.05 mmol, 1.9 mg) and dry THF/CH$_3$OH = 3:1 (1.0 mL) was added. Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. Reaction mixture was stirred at 0 ºC for 12 h, until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with water, extracted with CH$_2$Cl$_2$ (3×5 mL). Drying (Na$_2$SO$_4$) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography (PE : EA = 10 : 1) to give the desired product **7c** as a colorless oil. (yield: 75%, 96% ee). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.72 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.69 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.62 (d, *J* = 2.2 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.07 – 7.01 (m, 3H), 6.76 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.71 (d, *J* = 2.1 Hz, 1H), 4.64 – 4.55 (m, 2H), 1.94 (s, 3H), 1.42 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 165.58, 153.94, 152.56, 152.53, 146.15, 146.10, 140.89, 132.63, 131.25, 130.58, 130.51, 127.87, 127.51, 125.91, 124.08, 122.34, 122.03, 118.04, 113.70, 111.58, 106.85, 60.80, 35.49, 30.56, 18.08.

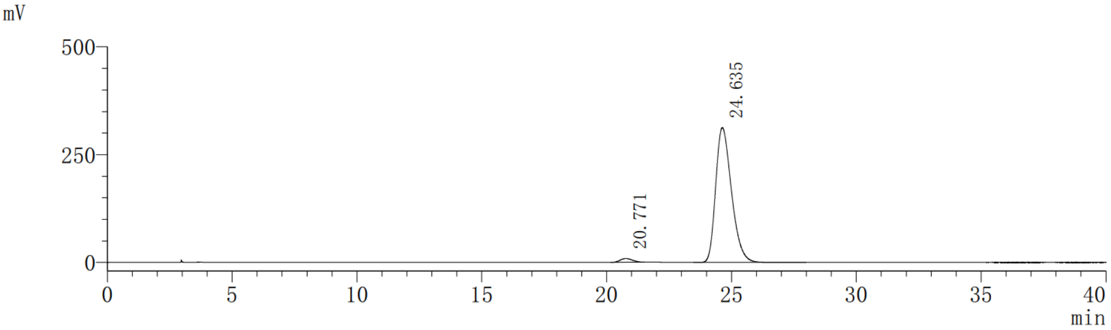
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{26}NaO_5$, ([M + Na]$^+$), 453.1672; found 453.1672.

$[\alpha]_D^{19}$ = -20.3 (c = 1.6, CH$_2$Cl$_2$).

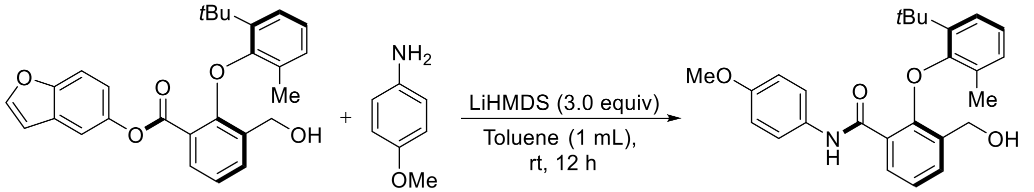
HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 ºC, 254 nm); t$_R$ (minor) = 20.77 min, t$_R$ (major) = 24.64 min, 96% ee.



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	20.779	S	0.9182	7108218	198976	50.9070
2	24.678	S	1.1092	6854928	159228	49.0930



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	20.771	M	0.9067	305307	8948	2.1643
2	24.635	M	1.1563	13801508	312948	97.8357



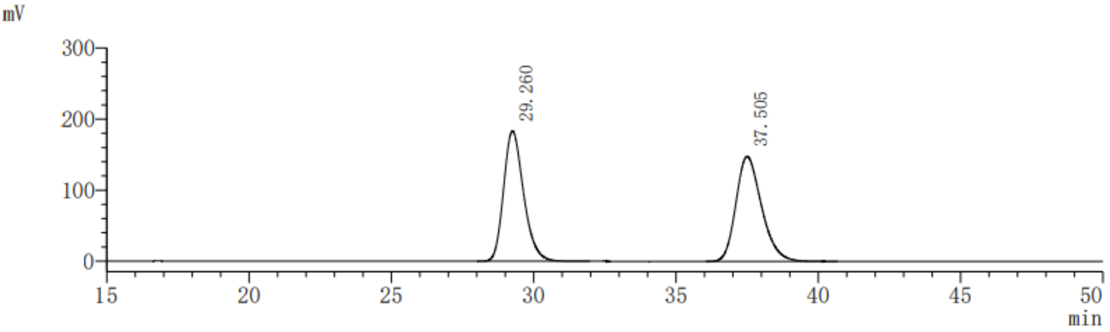
7c: 0.075 mmol 2.0 equiv **7d**: 88%, 95% ee

A flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was added **7c** (32.3 mg, 0.075 mmol, 1.0 equiv), 4-methoxyaniline (18.5 mg, 2.0 equiv), toluene (1.0 mL), lithium bis(trimethylsilyl)amide (LiHMDS) 1.0 M in THF (0.225 mL, 3.0 equiv.). The reaction was allowed to come to room temperature and was stirred for 12 hours. The reaction was quenched with saturated aqueous ammonium chloride and extracted with ethyl acetate (3 x 5 mL). The combined organic layers were washed with H_2O (4 x 2 mL), dried over magnesium sulfate and concentrated under reduced pressure. The obtained crude product was then purified by flash column chromatography on silica gel (eluting with petroleum ether/ether = 2/3) to provide the product **7d** (yield: 88 %, 95% ee) as a brown oil. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.07 (s, 1H), 8.15 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.64 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.43 – 7.40 (m, 2H), 7.32 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 7.3 Hz, 1H), 6.85 – 6.82 (m, 2H), 4.29 (dd, *J* = 13.8, 4.5 Hz, 1H), 4.10 (dd, *J* = 13.9, 4.4 Hz, 1H), 3.78 (s, 3H), 1.89 (s, 3H), 1.49 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 163.48, 156.49, 153.68, 151.80, 140.29, 133.51, 131.95, 131.02, 130.76, 130.19, 128.28, 126.23, 125.29, 125.02, 123.61, 122.18, 114.10, 59.99, 55.49, 35.53, 30.86, 18.16.

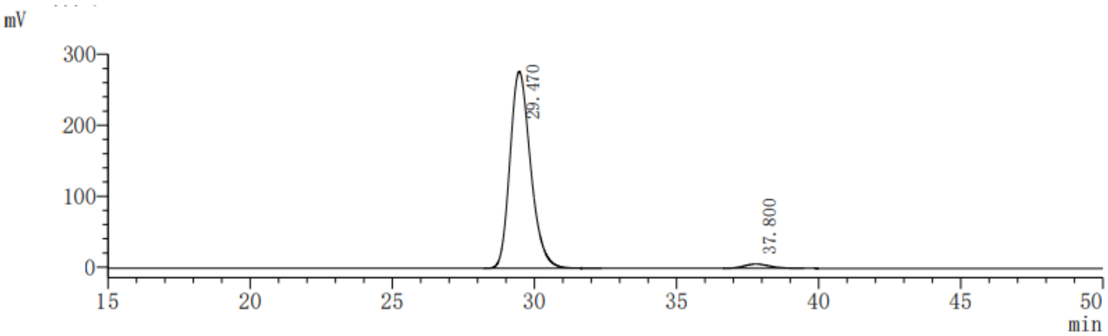
HRMS (ESI-TOF) (m/z): Calcd for $C_{26}H_{29}NNaO_4$, ([M + Na]$^+$), 442.1989; found 442.1984.

$[\alpha]_D^{19}$ = -20.5 (c = 1.3, CH_2Cl_2).

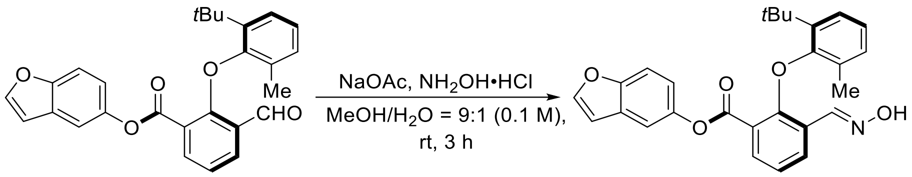
HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 ºC, 254 nm); t_R (major) = 29.47 min, t_R (minor) = 37.80 min, 95% ee.



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	29.260	M	1.2778	8982133	183426	49.2623
2	37.505	M	1.6448	9251143	147688	50.7377



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	29.470	M	1.3127	13998315	277158	97.4112
2	37.800	M	1.5613	372026	5984	2.5888



3ar: 0.1 mmol

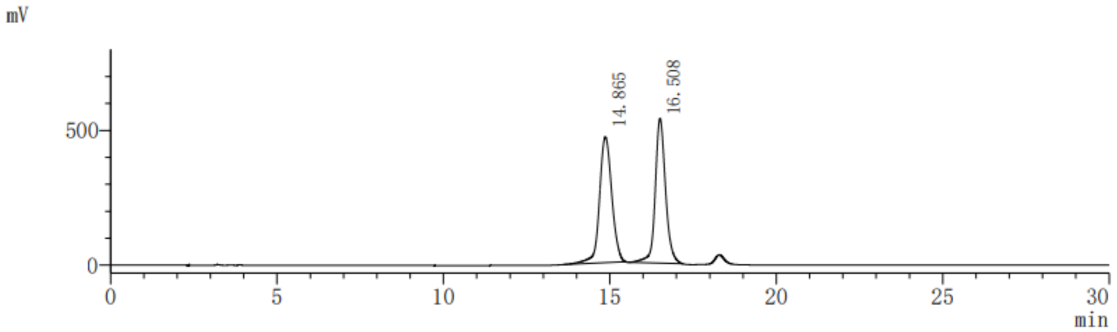
7e: 65%, 96% ee

A 10 mL screw-cap test tube with a Teflon coated magnetic stir bar was added 3ar (42.8 mg, 0.10 mmol, 1.0 equiv), NaOAc (16.4 mg, 0.20 mmol, 2.0 equiv) and $NH_2OH·HCl$ (13.9 mg, 0.2 mmol, 2.0 equiv). Then MeOH (0.9 mL) and H_2O (0.1 mL) was added to the tube via a syringe. The reaction mixture was stirred at room temperature for 3 h. After the completion of the reaction, the reaction mixture was diluted with water and extracted with EA. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (PE/EA = 15/1) to give the product **7e** (65%, 96% ee) as colorless oil. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.94–7.90 (m, 2H), 7.82 (dd, J = 7.8, 1.8 Hz, 1H), 7.78 (s, 1H), 7.63 (d, J = 2.2 Hz, 1H), 7.46 (d, J = 8.8 Hz, 1H), 7.29 (dd, J = 8.0, 1.8 Hz, 1H), 7.25 (d, J = 2.3 Hz, 1H),, 7.16 (t, J = 7.8 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 7.04–7.02 (m, 1H), 6.94 (dd, J = 8.8, 2.3 Hz, 1H), 6.73 (d, J = 2.2 Hz, 1H), 1.96 (s, 3H), 1.44 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 165.50, 153.84, 153.77, 152.63, 146.33, 146.30, 146.22, 140.90, 133.20, 132.20, 130.65, 128.15, 128.04, 125.85, 124.69, 123.03, 122.42, 122.22, 118.08, 113.76, 111.80, 106.91, 35.36, 30.42, 17.90.

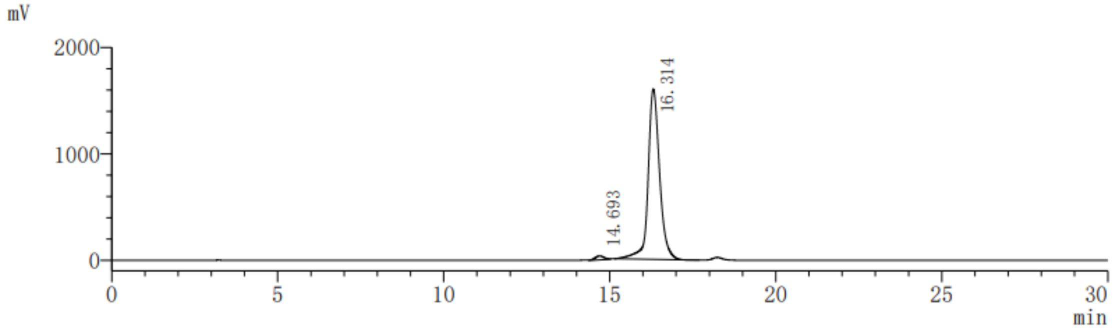
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{25}NNaO_5$, ([M + Na]$^+$), 466.1625; found 466.1623.

$[\alpha]_D^{19}$ = -14.2 (c = 1.4, $CDCl_3$).

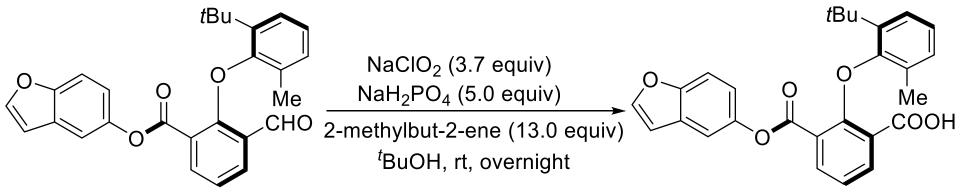
HPLC analysis: Daicel Chiralpak IA-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 ºC, 254 nm); t_R (minor) = 14.69 min, t_R (major) = 16.31 min, 96% ee.



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	14.865	M	0.6515	12064261	466974	51.0393
2	16.508	M	0.5380	11572927	535931	48.9607



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	14.693	M	0.5001	754863	38118	1.9235
2	16.314	M	0.5864	38488794	1601563	98.0765



3ar: 0.1 mmol

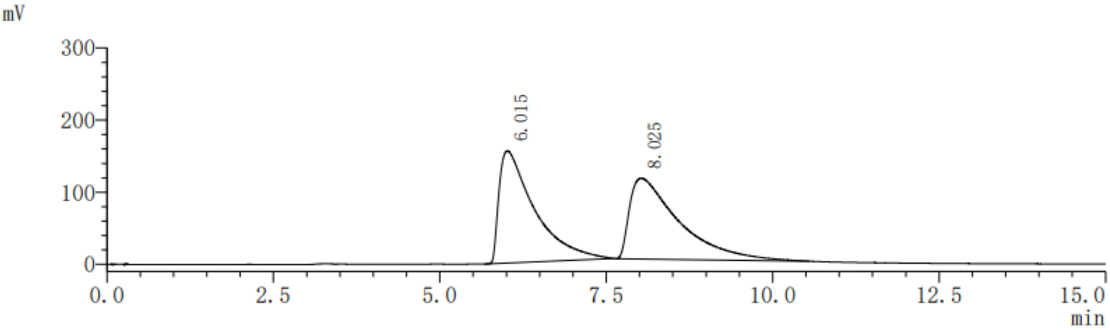
7f: 94%, 96% ee

To a stirred solution of compound **3ar** (42.8 mg, 0.1 mmol) and 2-methylbut-2-ene (138 µl, 1.3 mmol) in ^{t}BuOH (1.5 mL) were added a saturated solution of $NaClO_2$ (41.8 mg, 0.37 mmol) and NaH_2PO_4 (60.0 mg, 0.5 mmol). The mixture was stirred overnight at room temperature. The mixture was quenched with saturated NH_4Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, concentrated, and purified by silica gel column chromatography (DCM:MeOH = 10:1) to give compound **7f** (yield: 94%, 96% ee) as a white solid. **^{1}H NMR (500 MHz, Methanol-*d*$_4$)** δ 7.65 (d, J = 2.3 Hz, 1H), 7.47 (d, J = 7.0 Hz, 2H), 7.27 (d, J = 8.8 Hz, 1H), 7.09 – 7.03 (m, 2H), 6.92 – 6.87 (m, 2H), 6.75 (d, J = 2.4 Hz, 1H), 6.68 (d, J = 2.2 Hz, 1H), 6.47 (dd, J = 8.9, 2.4 Hz, 1H), 1.93 (s, 3H), 1.30 (s, 9H). **^{13}C NMR (150 MHz, Methanol-*d*$_4$)** δ 173.89, 165.81, 153.71, 152.50, 150.66, 146.40, 145.95, 141.15, 135.05, 130.56, 130.23, 129.11, 127.73, 127.52, 125.24, 123.14, 121.42, 121.34, 117.84, 113.45, 110.67, 106.34, 35.03, 29.96, 17.33.

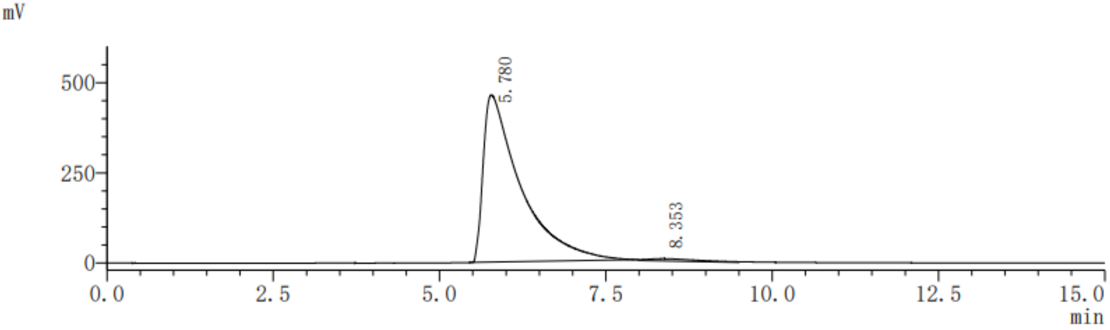
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{24}NaO_6$, ($[M + Na]^+$), 467.1465; found 467.1466.

$[\alpha]_D^{19}$ = -26.3 (c = 2.1, CD_3OD).

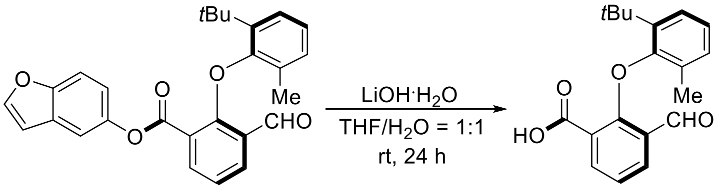
HPLC analysis: Daicel Chiralpak IC-3 column (85:15 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 5.78 min, t_R (minor) = 8.35 min, 96% ee.



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	6.015	M	0.9373	5766282	155352	49.9353
2	8.025	M	1.2995	5781229	111947	50.0647



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	5.780	M	0.9653	18143467	463259	98.0811
2	8.353	M	1.5130	354962	6496	1.9189



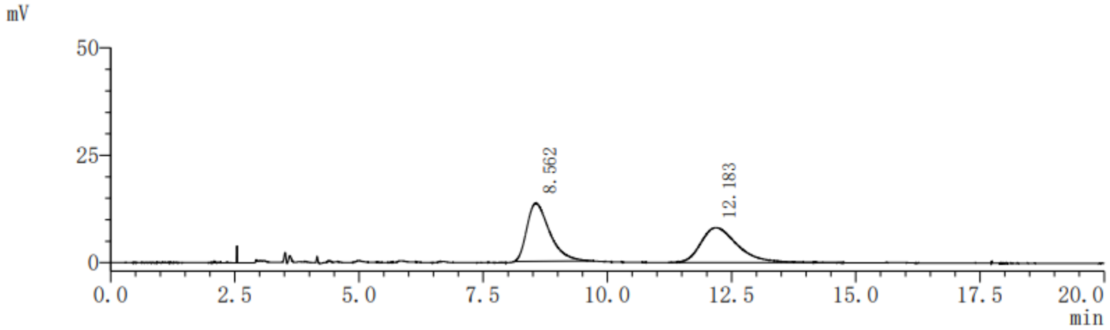
3ar: 0.1 mmol **7g**: 93%, 95% ee

To a 1.0 mL solution of LiOH•H_2O (16.8 mg, 0.4 mmol, 4.0 equiv) in THF and H_2O (v/v = 1:1), **3ar** (42.8 mg, 0.1 mmol, 1.0 equiv) was added. The reaction mixture was stirred at room temperature for 24 h, until the reaction was completed as indicated by TLC. Then quenched with 1 M HCl in ice water bath, until pH = 3. The reaction mixture was diluted with water and extracted with EA. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (DCM/MeOH = 10/1) to give the product **7g** (93% yield, 95% ee) as pink oil. **^{1}H NMR (500 MHz, Methanol-*d*$_4$)** δ 9.26 (s, 1H), 7.60 – 7.57 (m, 2H), 7.21 (dd, J = 7.8, 1.8 Hz, 1H), 7.03 (t, J = 7.6 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 7.5 Hz, 1H), 1.84 (s, 3H), 1.36 (s, 9H). **^{13}C NMR (150 MHz, Methanol-*d*$_4$)** δ 188.24, 172.48, 156.27, 155.68, 140.41, 137.26, 133.75, 130.70, 128.07, 127.76, 126.19, 125.33, 124.50, 121.88, 34.78, 29.44, 16.47.

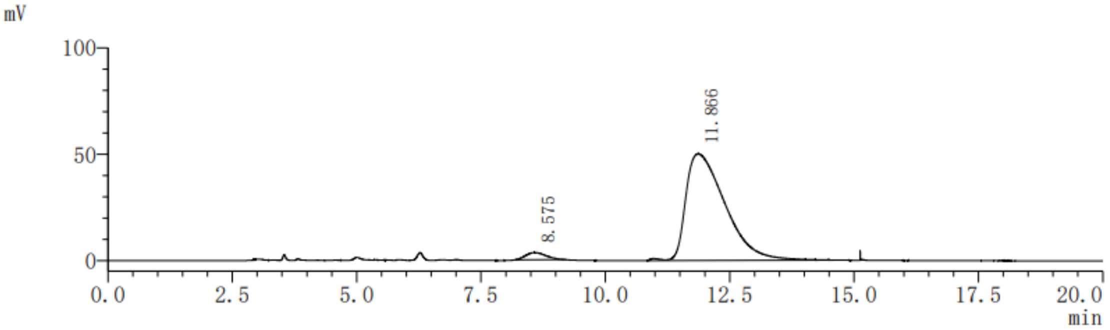
HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{20}NNaO_4$, ([M + Na]$^+$), 335.1254; found 335.1258.

$[\alpha]_D^{19}$ = +44.4 (c = 2.1, CD_3OD).

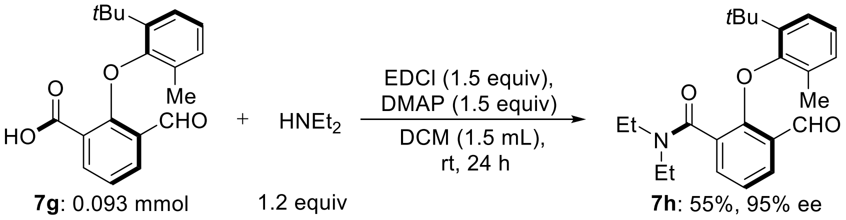
HPLC analysis: Daicel Chiralpak IG column (85:15 hexane: 2-propanol, 1.0 mL/min, 25 ºC, 254 nm); t_R (minor) = 8.58 min, t_R (major) = 11.87 min, 95% ee.



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	8.562	M	0.8038	429243	13501	50.5545
2	12.183	M	1.2547	419827	8126	49.4455



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	8.575	M	0.7647	96280	3398	2.3760
2	11.866	M	1.4112	2755643	50164	97.6240

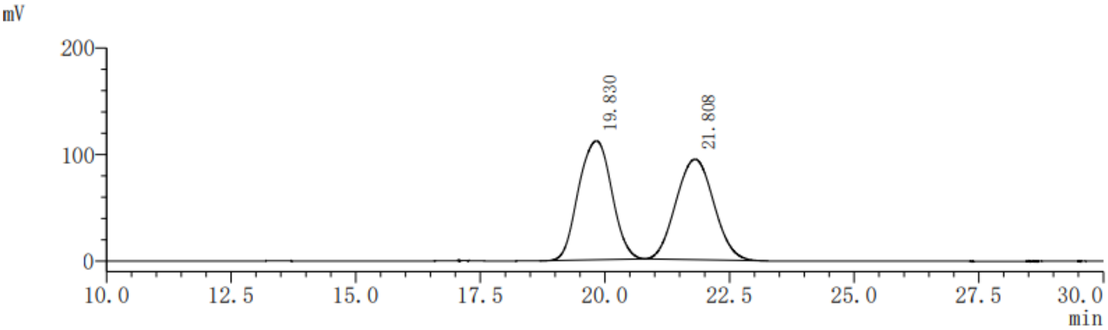


A flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was added DMAP (17.0 mg, 0.14 mmol, 1.5 equiv), followed by DCM solution (1.5 mL) containing **7g** (29.0 mg, 0.093 mmol, 1.0 equiv) and $HNEt_2$ (12 µL, 0.11 mmol, 1.2 equiv) was added. Then EDCI (26.7 mg, 0.14 mmol, 1.5 equiv) was added in ice water bath and the reaction mixture was stirred at room temperature for 24 h, until the reaction was completed as indicated by TLC. The reaction mixture was diluted with water and extracted with DCM. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (PE/EA = 2/1) to give the product **7h** (55% yield, 95% ee) as white solid. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.27 (s, 1H), 7.80 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.48 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.23 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.99 (dd, *J* = 7.6, 1.9 Hz, 1H), 3.93 – 3.86 (m, 1H), 3.42 – 3.35 (m, 1H), 3.30 – 3.21 (m, 2H), 1.97 (s, 3H), 1.41 (s, 9H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 187.69, 167.47, 156.52, 155.16, 139.49, 132.81, 131.61, 130.04, 129.62, 128.29, 126.44, 125.60, 125.08, 122.84, 42.86, 38.88, 35.14, 30.12, 17.52, 14.16, 12.87.

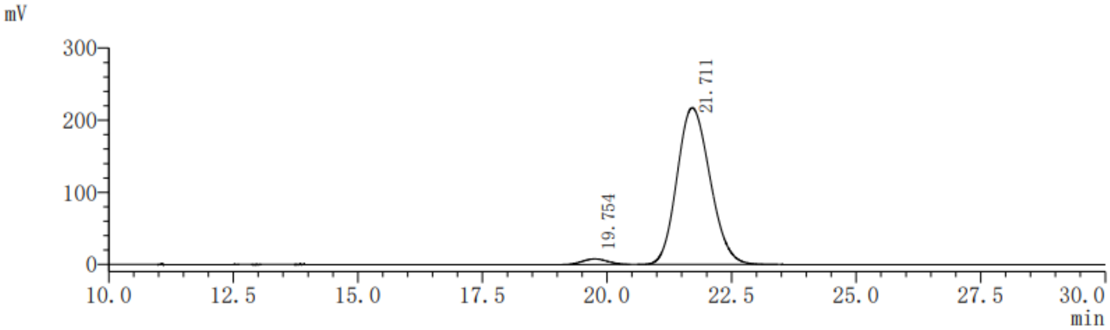
HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{29}NNaO_3$, ([M + Na]$^+$), 390.2040; found 390.2040.

$[\alpha]_D^{19}$ = +55.5 (c = 1.0, CH_2Cl_2).

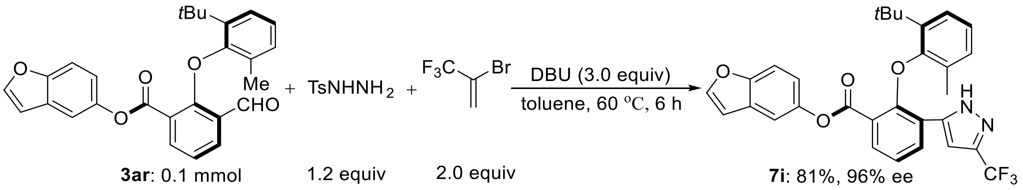
HPLC analysis: Daicel Chiralpak AD-3 column (98:2 hexane: 2-propanol, 0.7 mL/min, 25 °C, 254 nm); t_R (minor) = 19.75 min, t_R (major) = 21.71 min, 95% ee.



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	19.830	M	1.2145	5173256	111612	50.9641
2	21.808	M	1.4055	4977522	94305	49.0359



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	19.754	M	0.9204	264813	7625	2.5723
2	21.711	M	1.2198	10030188	217209	97.4277

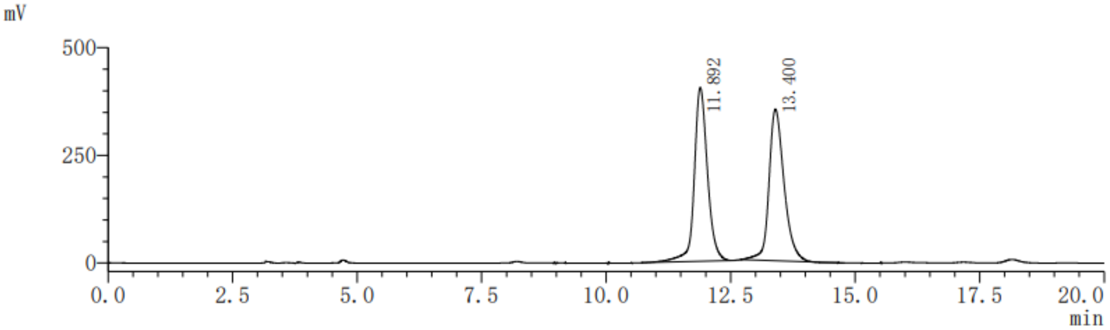


To a 10 mL round-bottom flask equipped with a magnetic stirring bar and a refluxing condenser was added aldehyde **3ar** (0.1 mmol, 42.8 mg), 4-methylbenzenesulfonohydrazide (0.12 mmol, 22.3 mg), toluene (1 mL), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.3 mmol, 45 µL), and 2-bromo-3,3,3-trifluoropropene (0.2 mmol, 21 µL). The resulting mixture was vigorously stirred at 60 °C for 6 h. Then the mixture was added water (2 mL), extracted with EtOAc (5 mL ×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The obtained crude product was then purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 2/1) to provide the product **7i** (yield: 81 %, 96% ee) as a white solid.[3] **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 11.24 (s, 1H), 7.86 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.66 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.63 (d, *J* = 2.2 Hz, 1H), 7.38 (d, *J* = 8.9 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.14 – 7.07 (m, 2H), 6.93 (s, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 6.71 (d, *J* = 2.2 Hz, 1H), 6.59 (dd, *J* = 8.8, 2.4 Hz, 1H), 1.98 (s, 3H), 1.38 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 164.45, 152.52, 152.21, 151.53, 146.30, 145.67, 142.04, 141.09, 132.20, 132.01, 130.80, 128.39, 127.77, 126.80, 125.34, 122.92, 122.79, 121.26 (q, *J* = 267.4 Hz), 119.55, 117.70, 113.49, 111.52, 106.84, 103.19, 35.60, 31.25, 18.12. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -62.22 (s, 1CF$_3$).

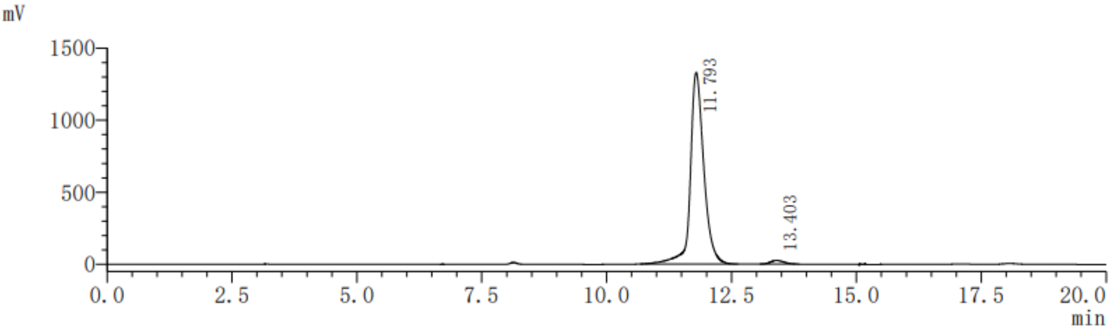
HRMS (ESI-TOF) (m/z): Calcd for $C_{30}H_{25}F_3N_2NaO_4$, ($[M + Na]^+$), 557.1659; found 557.1647.

[α]$_D$^{19} = -16.4 (c = 1.1, $CDCl_3$).

HPLC analysis: Daicel Chiralpak IA-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 11.79 min, t_R (minor) = 13.40 min, 96% ee.



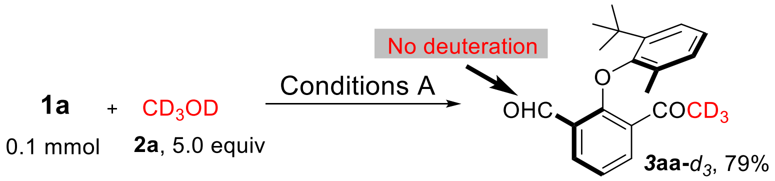
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	11.892	M	0.4545	7441338	403091	50.1204
2	13.400	M	0.5286	7405602	351726	49.8796



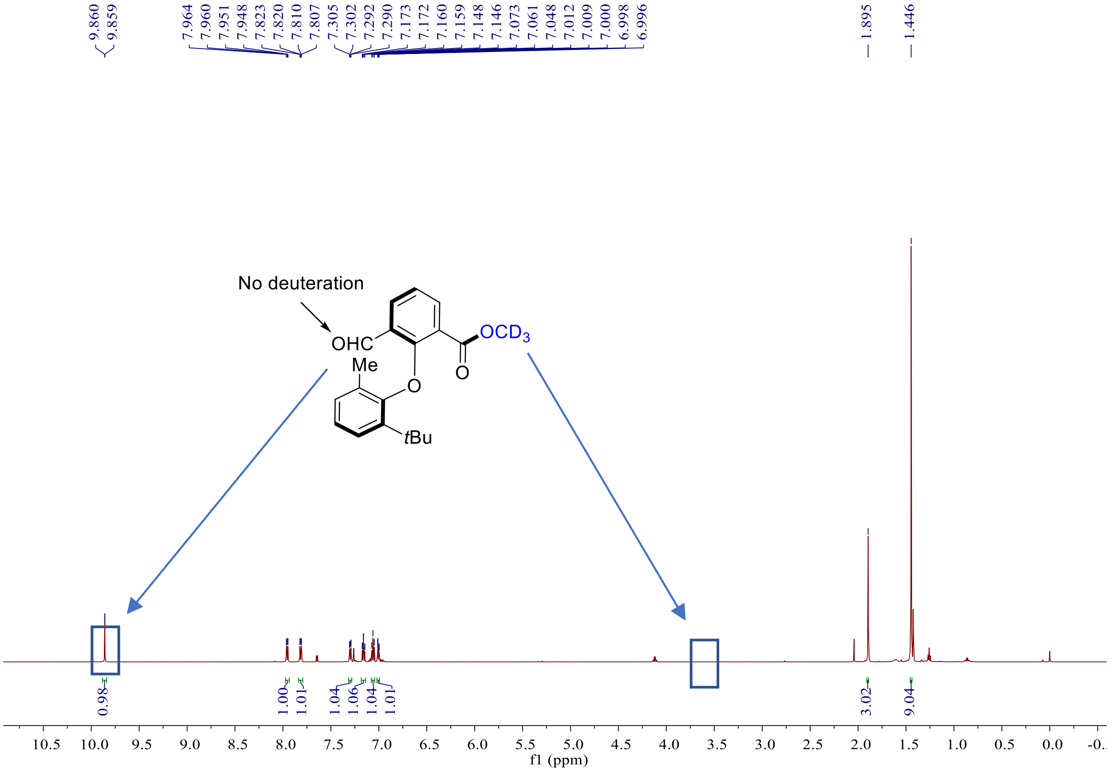
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	11.793	M	0.4537	24907171	1325505	98.1821
2	13.403	M	0.4916	461182	25084	1.8179

IV. Mechanistic Studies

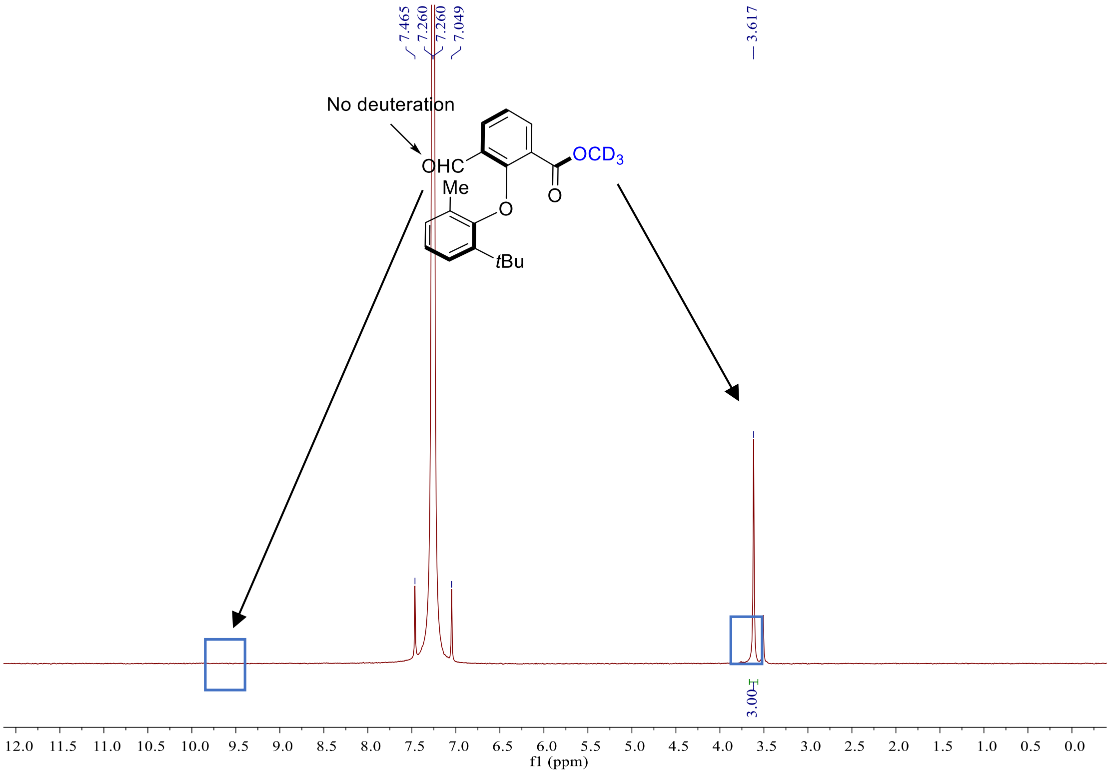
4.1 Deuterium labeling experiment



In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **NHC-1** (15 mol%, 6.27 mg), Cs_2CO_3 (49.0 mg, 1.5 equiv), and anhydrous dichloromethane (1 mL). CD_3OD **2a** (0.02 ml, 5.0 equiv) was added. The mixture was stirred for 5 minutes, followed by the addition of aldehyde 2-(naphthalen-1-yl)isophthalaldehyde **1a** (0. 1 mmol, 29.6 mg) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (48 mg, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 °C for 72 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:1 (v/v) to give the product **3aa-*d*$_3$**.



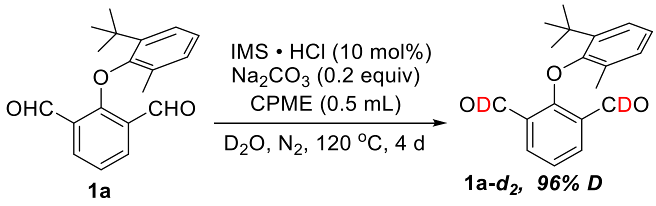
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3aa-*d*$_3$.



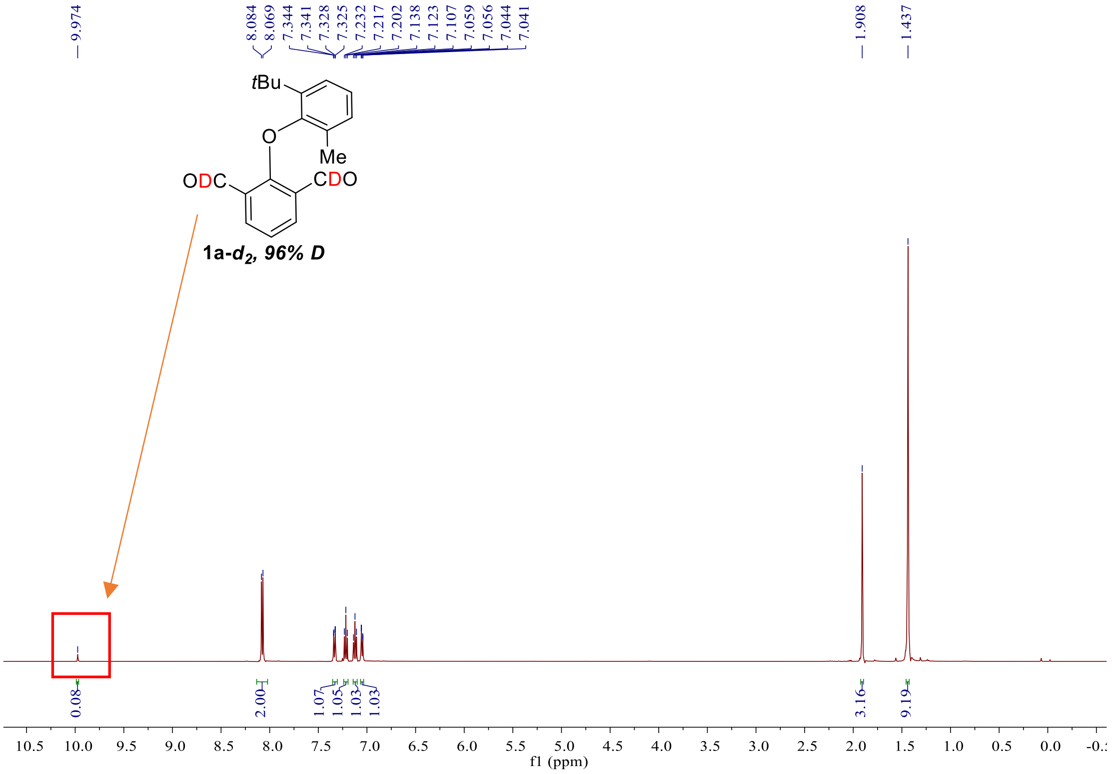
^{2}H NMR (77 MHz, CDCl$_3$) spectrum of 3aa-*d*$_3$.

4.2 Parallel Kinetic Isotope Effect Experiment

4.2.1 Procedure for synthesis of 1a-*d*$_2$[4]

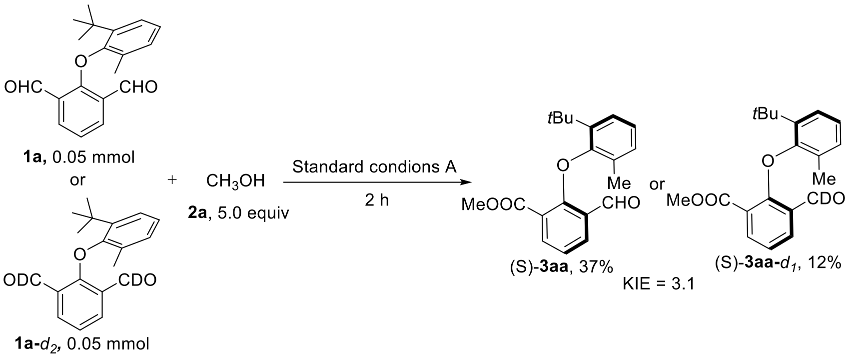


In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with aldehyde **1a** (0.5 mmol), IMes • HCl (17.0 mg, 0.05 mmol), Na_2CO_3 (11.0 mg, 0.1 mmol), CPME (0.5 mL) and D_2O (2.5 mL). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 120 °C for 4 d, and extracted with AcOEt, and the organic layers were dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography (PE : EA = 10:1), **1a-**d_2 was obtained in 88% yield, with 96% D. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.97 (s, 0.08H), 8.08 (d, *J* = 7.7 Hz, 2H), 7.33 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.05 (dd, *J* = 7.5, 1.6 Hz, 1H), 1.91 (s, 3H), 1.44 (s, 9H).

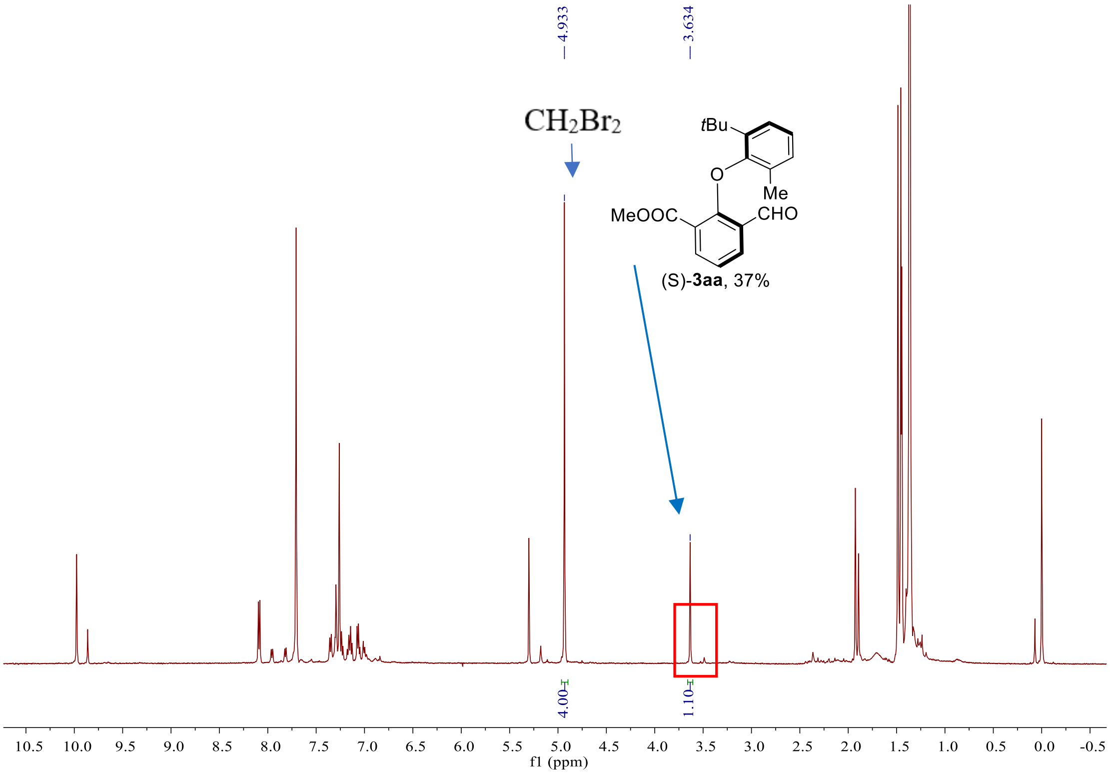


^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1a-d_2.

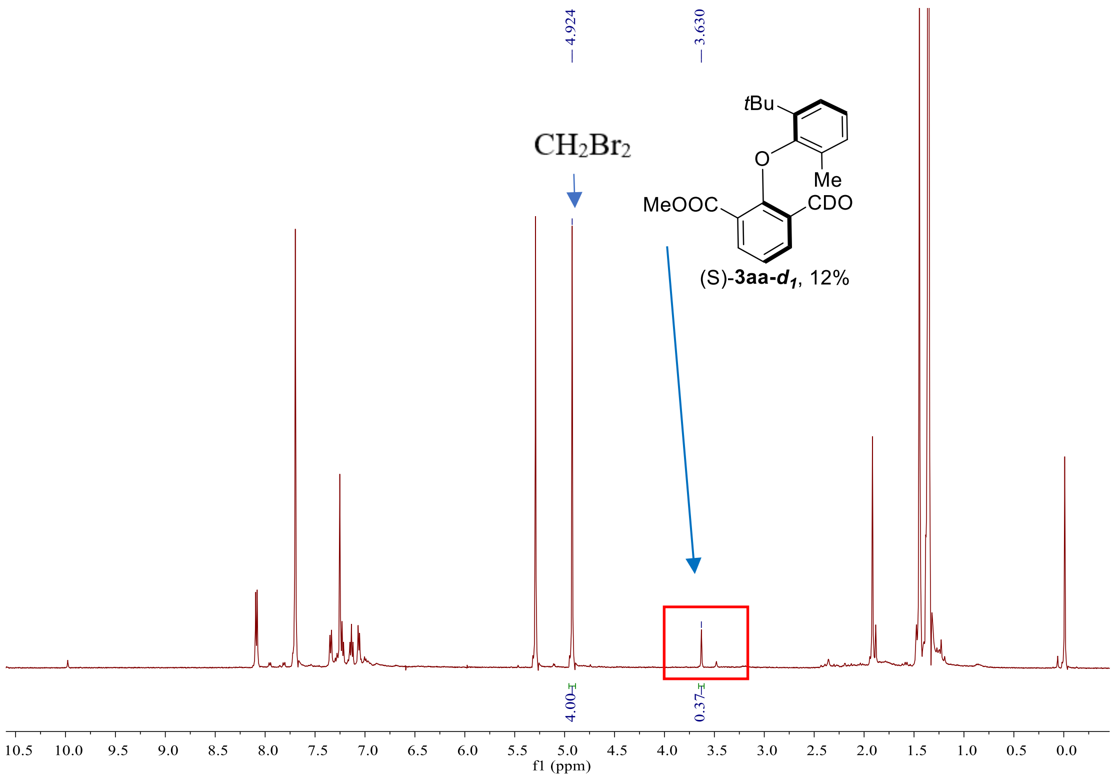
4.2.2 Experiment Procedure for the Isotope Experiments



In a nitrogen-filled glovebox, two flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged **NHC-1** (10 mol%, 3.1 mg), Cs_2CO_3 (25.0 mg, 1.5 equiv), and anhydrous dichloromethane (0.5 mL). CH_3OH **2a** (0.01 ml, 5.0 equiv) was added. The mixture was stirred for 5 minutes, followed by the addition of **1a or 1a**-*d*$_2$ (0.05 mmol, 15 mg) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (24 mg, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 °C for 2 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:1 (v/v) to give the product **S-3aa**, yield: 37%; **S-3aa-*d*$_1$**, yield: 12%. The KIE was determined by ^{1}H NMR analysis to be 3.1.



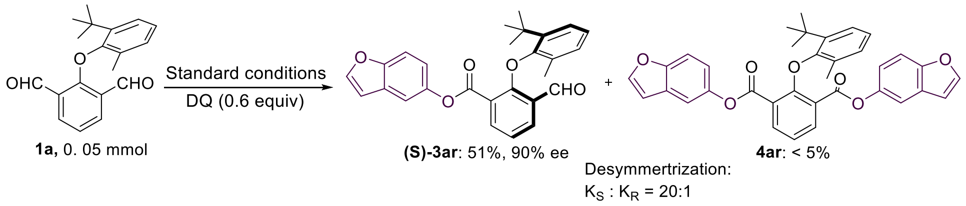
^{1}H NMR (500 MHz, $CDCl_3$) using CH_2Br_2 (0.1 mmol, 7.0 µL) as an internal standard of the reaction mixture (S-3aa)



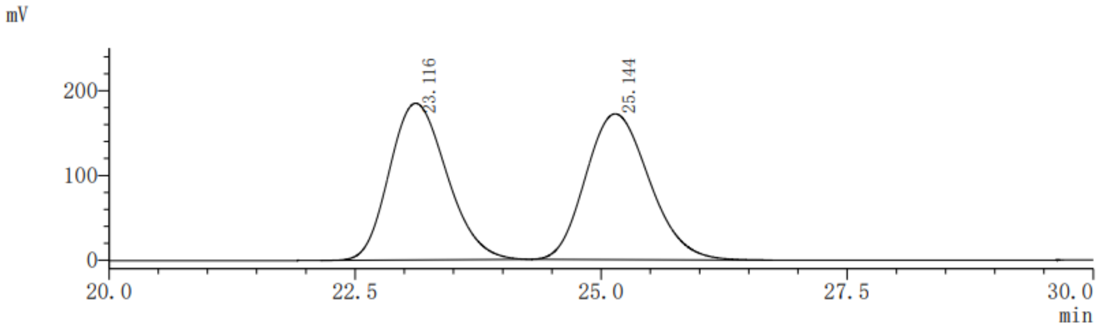
^{1}H NMR (500 MHz, $CDCl_3$) using CH_2Br_2 (0.1 mmol, 7.0 µL) as an internal standard of the reaction mixture (S-3aa-*d_1*)

4.3 Control experiment

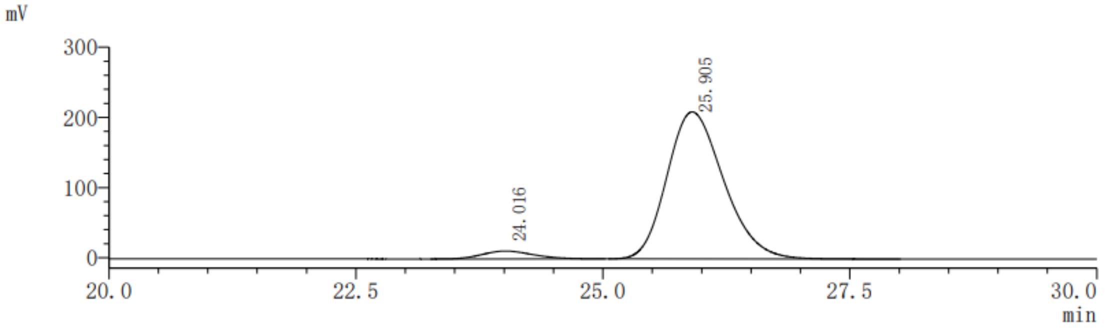
4.3.1 Procedure for NHC-catalyzed Desymmetrization of Dialdehyde1a with NHC-1.



In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged **NHC-1** (10 mol%, 3.1 mg), Cs_2CO_3 (25.0 mg, 1.5 equiv), and anhydrous dichloromethane (0.5 mL). benzofuran-5-ol **2r** (20 mg, 3.0 equiv) was added. The mixture was stirred for 5 minutes, followed by the addition of **1a** (0.05 mmol, 15 mg) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (12 mg, 0.6 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at -20 °C for 72 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:1 (v/v) to give the product (S)-**3ar** (yield: 51%; 90% ee) and **4ar** (yield: < 5%).
HPLC analysis: Daicel Chiralpak AD-3 column (99:1 hexane: 2-propanol, 1 mL/min, 25 °C, 254 nm); t_R (minor) = 24.02 min, t_R (major) = 25.91 min, 90% ee.

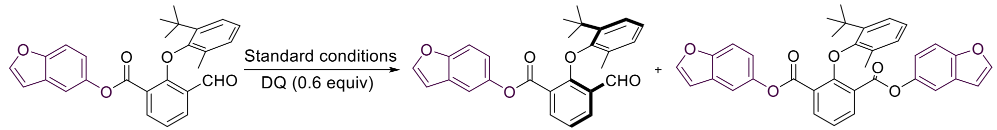


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	23.116	M	1.0757	7509740	184674	49.3069
2	25.144	M	1.1867	7720854	171810	50.6931



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	24.016	M	0.9471	405308	11229	4.6073
2	25.905	M	1.0546	8391807	209570	95.3927

4.3.2 General procedure for for NHC-catalyzed kinetic resolution (KR) of *Rac*-3aa with benzofuran-5-ol and characterization data.



(Rac)-3ar: 0.05 mmol

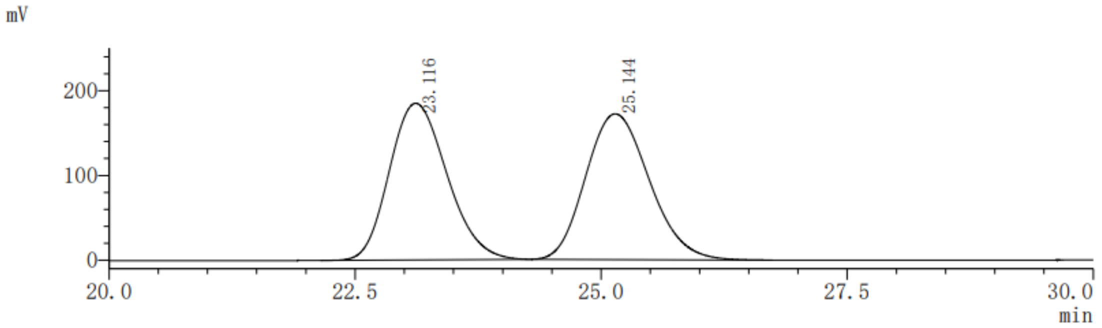
(S)-3ar: 38%, 98% ee

4ar: 56%

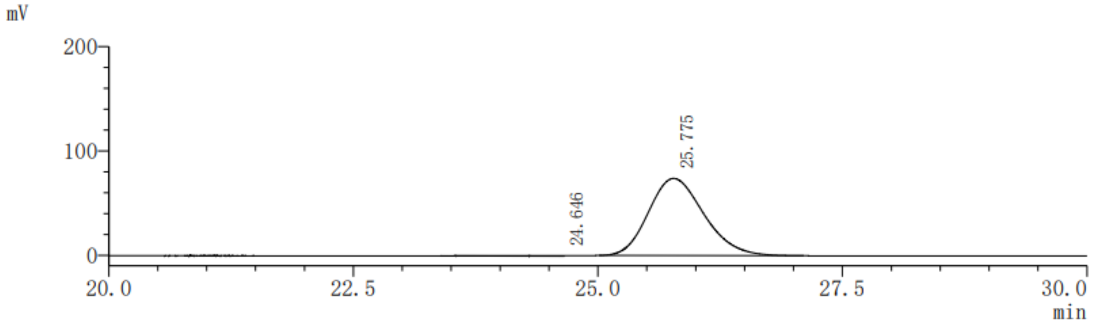
Kinetic Resolution:
$V_R : V_S = 4:1$
s factor = 34

In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged **NHC-1** (15 mol%, 3.1 mg), Cs_2CO_3 (25.0 mg, 1.5 equiv), and anhydrous dichloromethane (0.5 mL). benzofuran-5-ol **2r** (20 mg, 3.0 equiv) was added. The mixture was stirred for 5 minutes, followed by the addition of **(*Rac*)-3ar** (0.05 mmol, 21.4 mg) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (12 mg, 0.6 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at -20 ºC for 72 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:1 (v/v) to give the product (S)**-3ar** (yield: 38%; 98% ee) and **4ar** (yield: 56%).

HPLC analysis: Daicel Chiralpak AD-3 column (99:1 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (minor) = 24.65 min, t_R (major) = 25.76 min, 98% ee.

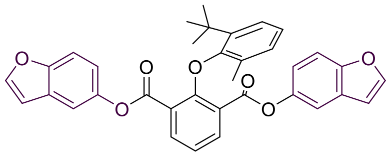


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	23.116	M	1.0757	7509740	184674	49.3069
2	25.144	M	1.1867	7720854	171810	50.6931



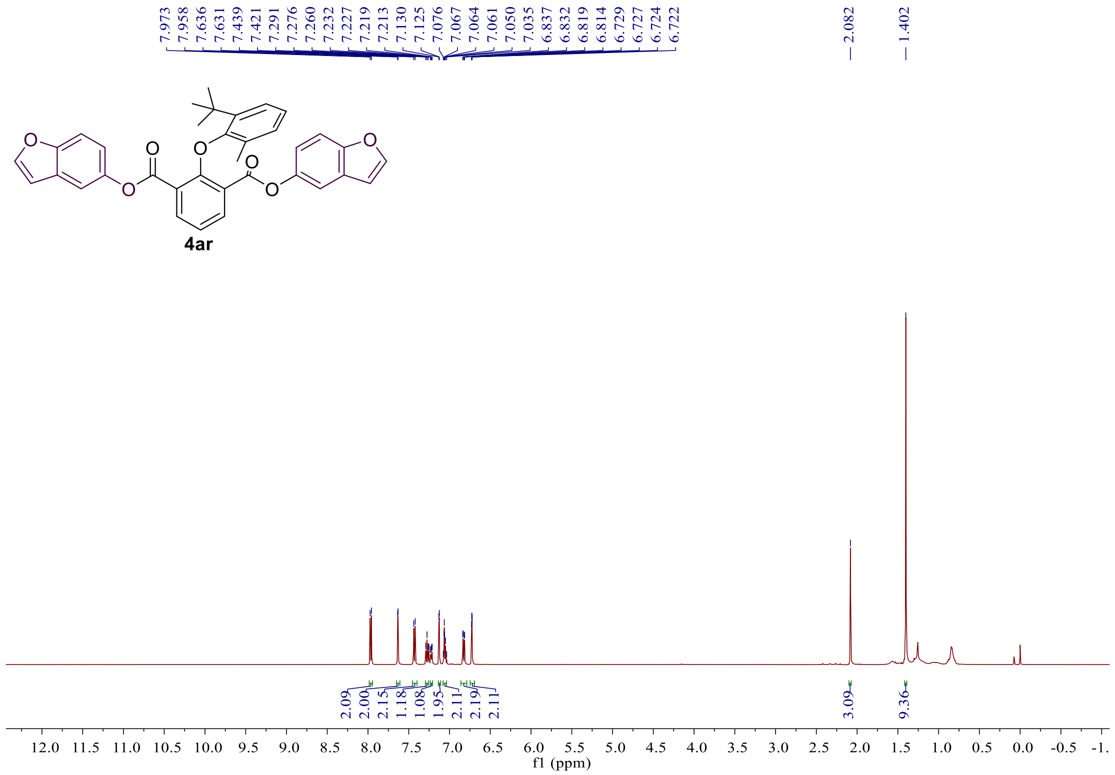
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	24.646	M	0.9037	24137	507	0.8206
2	25.775	M	1.0405	2917449	73907	99.1794

Dimethyl 2-(naphthalen-1-yl)isophthalate 4ar

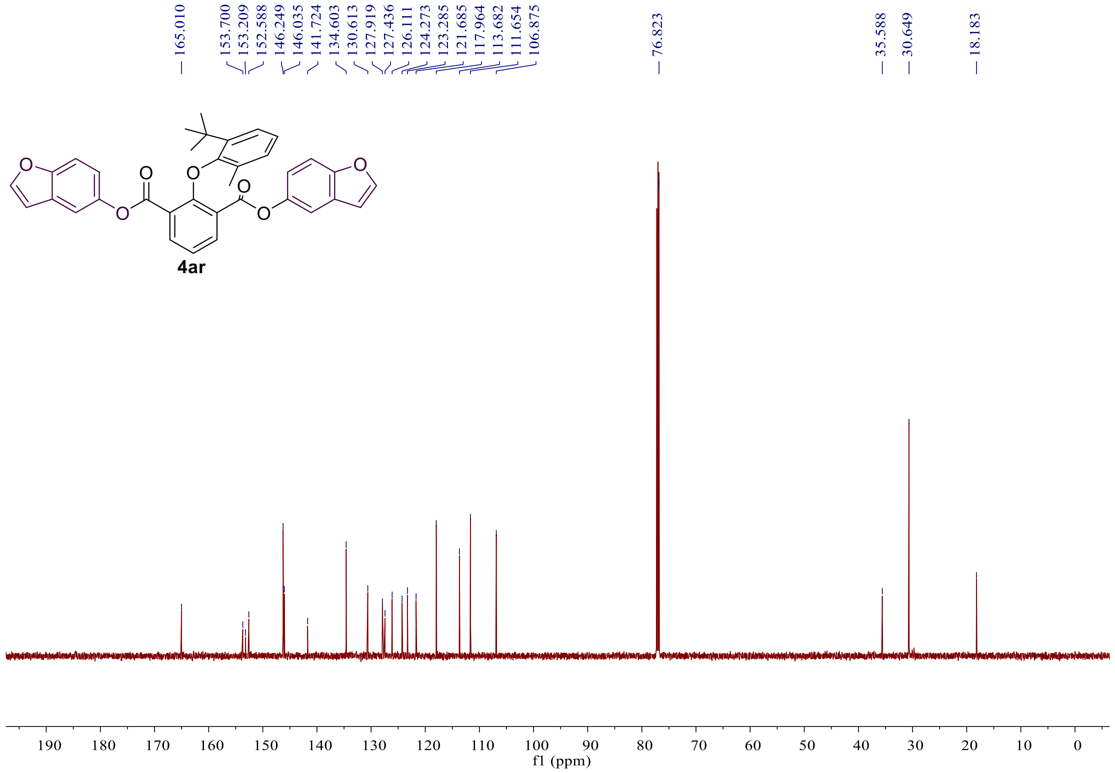


4ar

4ar: Yellow oil, 15.1 mg, 54%, 72 h; **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.63 (d, *J* = 2.2 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.22 (dd, *J* = 6.9, 2.7 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 2H), 7.09 – 7.03 (m, 2H), 6.83 (dd, *J* = 8.9, 2.4 Hz, 2H), 6.73 (dd, *J* = 2.2, 1.0 Hz, 2H), 2.08 (s, 3H), 1.40 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 165.01, 153.70, 153.21, 152.59, 146.25, 146.03, 141.72, 134.60, 130.61, 127.92, 127.44, 126.11, 124.27, 123.29, 121.69, 117.96, 113.68, 111.65, 106.88, 76.82, 35.59, 30.65, 18.18. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{35}H_{28}NaO_7$, ([M + Na]$^+$), 583.1727; found 583.1720.

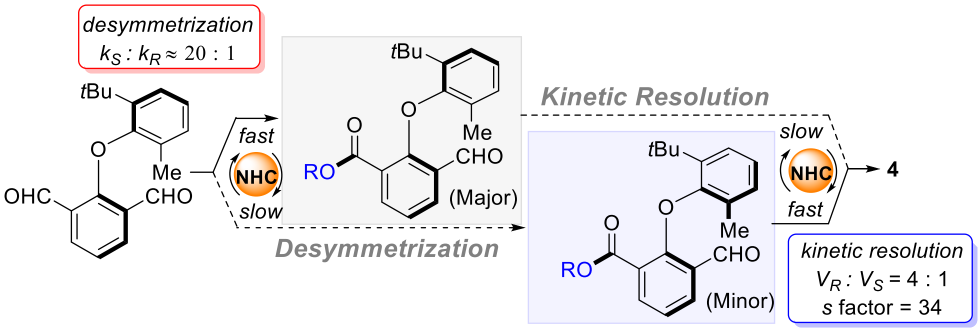


^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 4ar



^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 4ar.

4.4 NHC-catalyzed tandem desymmetrization-kinetic resolution[5,6]



4.5 Determination of Rotational Barrier and half-life for C-O Bond in 3ar.[7-9]

Following the procedure of Curran,[8] compound **3ar** was dissolved in ^{i}PrOH to make a 1 mg/mL solution in a sealed tube. The tube was kept in a pre-equilibrated metal bath maintained at 100 °C. At 1 h time intervals, the sealed tube was taken out briefly (1-2 min) from the metal bath and a 20 μL aliquot was taken out via syringe and injected onto the analytical HPLC column to determine the er. This er was plotted against time, and the barrier to rotation was calculated from the plot. In the y-axis of the graph, "m" stands for the % of the minor enantiomer, and "M" denotes the % of the major enantiomer. All the data have been recorded at 373.15 K (100 °C). The rate value can be inserted into **Equation 2** to give $\Delta G^{\ddagger}_{373.15\ \mathrm{K}}$ and into **Equation 1** to give the half-life to racemisation.

k_B = Boltzmann's constant [1.381 x 10^{-23}J K^{-1}], T = temperature in K, h = Planck's constant [6.626 x 10^{-34} J s], R = gas constant [8.3145 J mol^{-1}]. Then the simplified equation for racemization is:

$\ln [(M + m)/(M - m)] = k_{rac}t + c = 2k_{rot}t + c$

$k_{rot} = (slope/2)$

$t_{½} = \ln(2)/k_{\mathrm{rot}}$ **Equation 1**

The experimental data is shown below:

Time (h)	% of major enantiomer (M)	% of minor enantiomer (m)	M + m	M - m	(M + m) / (M - m)	ln [(M + m) / (M - m)]
0	99.1107	0.8893	100	98.2214	1.01811	0.017948
1	98.5960	1.4040	100	97.1920	1.02889	0.028481
2	98.0835	1.9165	100	96.1670	1.03986	0.039086
3	97.7254	2.2746	100	95.4508	1.04766	0.046559
4	97.3970	2.6030	100	94.7940	1.05492	0.053465
5	97.0291	2.9709	100	94.0582	1.06317	0.061255
6	96.3823	3.6177	100	92.7646	1.07800	0.075108
7	95.9050	4.0950	100	91.8100	1.08921	0.085453
8	95.4780	4.5220	100	90.9560	1.09943	0.094792
9	95.0433	4.9567	100	90.0866	1.11043	0.104747
10	94.7862	5.2138	100	89.5724	1.11642	0.110127
11	94.3094	5.6906	100	88.6188	1.12843	0.120827
12	93.7768	6.2232	100	87.5536	1.14216	0.132921
13	93.3062	6.6938	100	86.6124	1.15457	0.143728
14	92.8331	7.1669	100	85.6662	1.16732	0.154711
15	92.4885	7.5115	100	84.9770	1.17679	0.162790

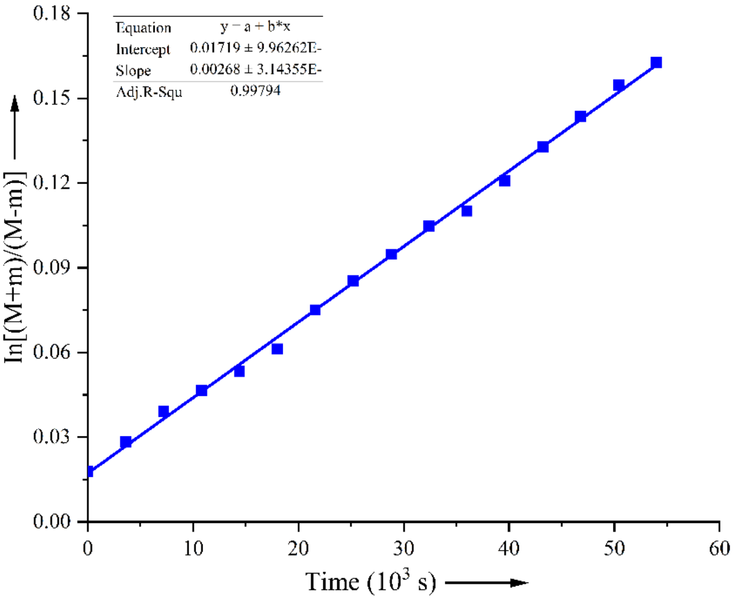


Figure 1. Plot for the Determination of Rotational Barrier and Half-Life for C-O Bond in **3ar**.

So, from plot, $k_{rot} = [(0.00268 \times 10^{-3})/2] = 1.34 \times 10^{-6}\ s^{-1}$

$k^{\ddagger}_{rot} = [\ (k_{rot} \times h)/k_B T\ ] = 0.172 \times 10^{-18}$

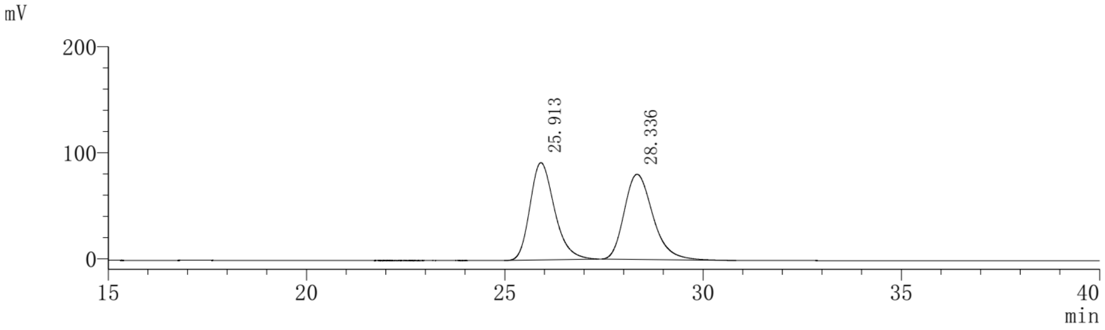
$\Delta G_{rot}^{\ddagger} = -RT\ln k^{\ddagger}_{rot}$ **Equation 2**

$= 134.046$ kJ/mol = 32.0 kcal/mol

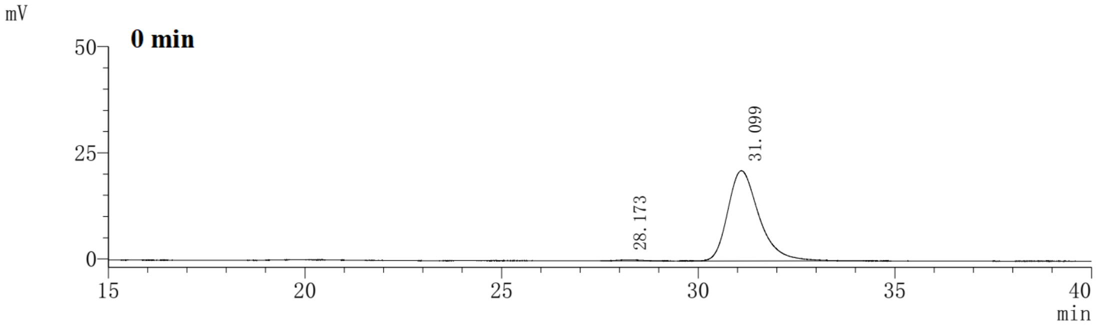
$t_{½} = \ln(2)/k_{rot} = 143.69$ h

HPLC data for the Analysis of C-O Bond Rotational Barrier:

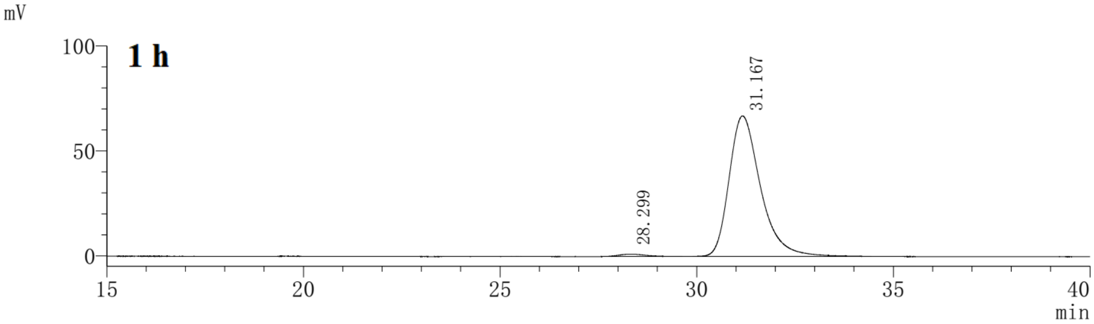
HPLC analysis: Daicel Chiralpak AD-3 column (99:1 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm)



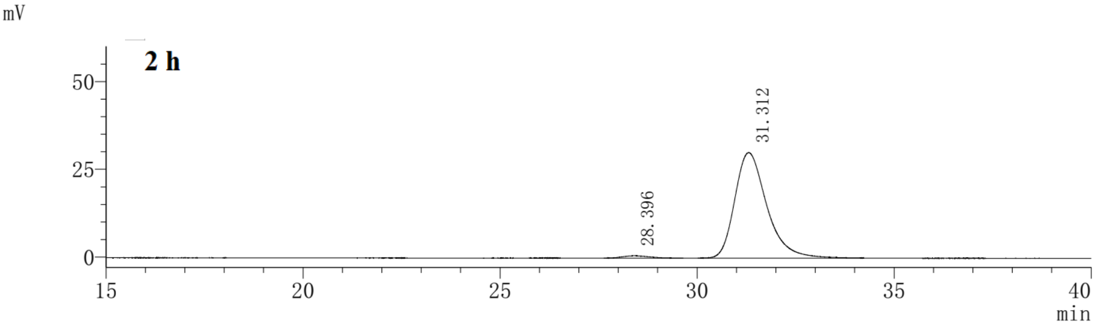
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	25.913	M	1.1182	3948832	91791	49.5170
2	28.336	M	1.2899	4025867	80285	50.4830



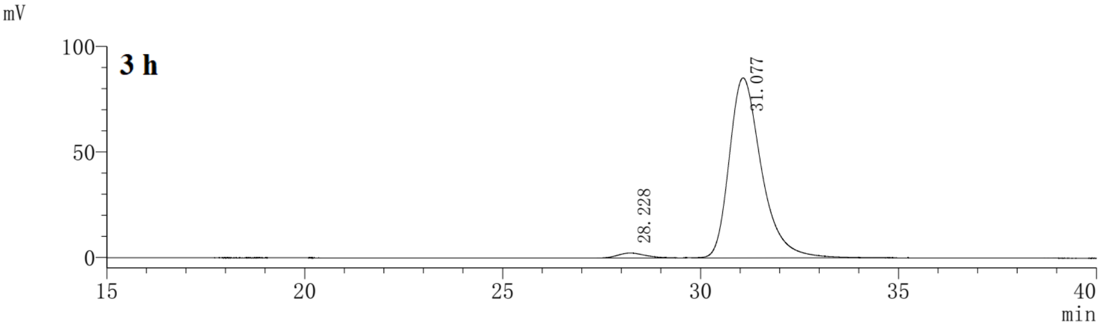
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	28.173	M	0.8605	10564	234	0.8893
2	31.099	M	1.3960	1177271	21254	99.1107



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	28.299	M	1.1567	52879	1144	1.4040
2	31.167	M	1.4099	3713538	66967	98.5960



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	28.396	M	1.1185	33219	682	1.9165
2	31.312	M	1.4452	1700076	30071	98.0835



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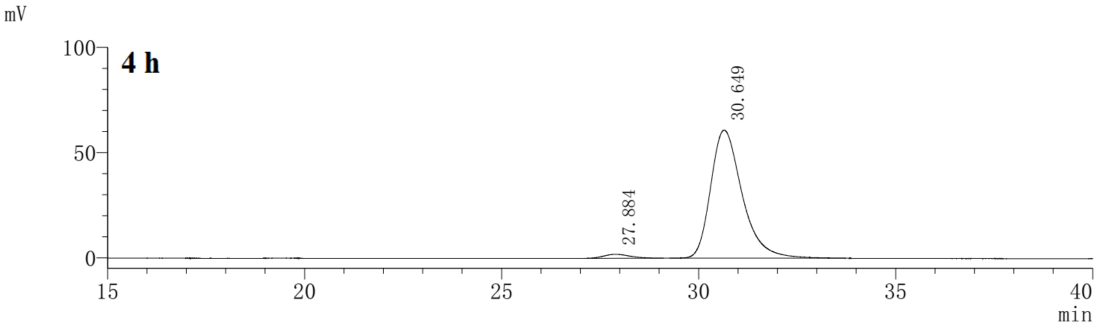

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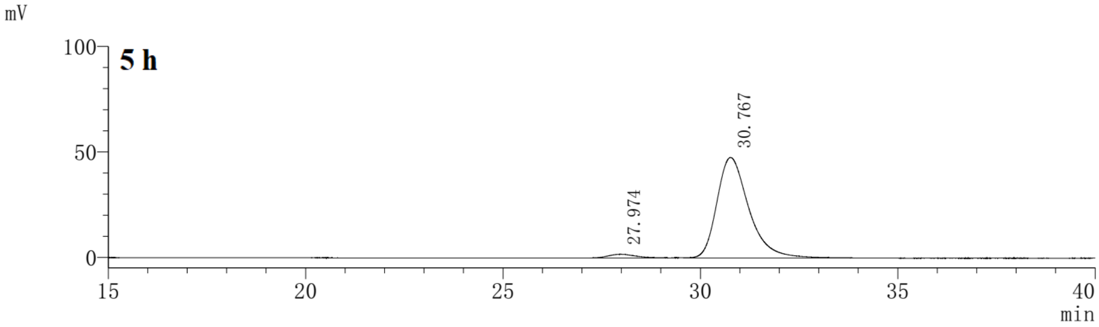
1	27.884	M	1.2039	90692	1933	2.6030
2	30.649	M	1.4191	3393365	60880	97.3970



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
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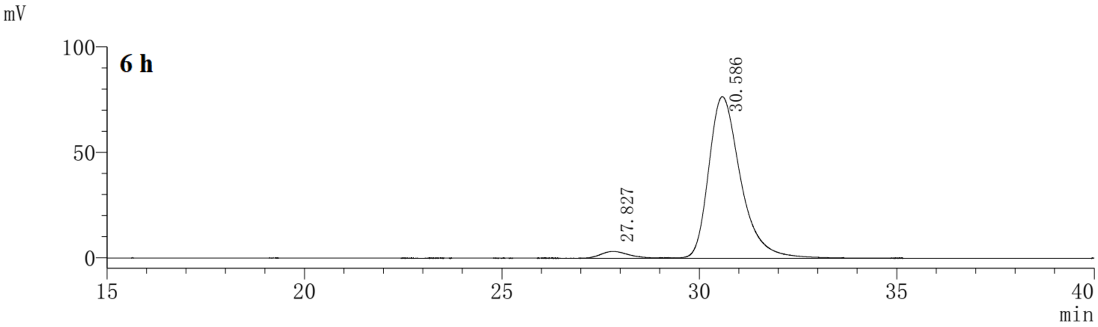

Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	27.827	M	1.2548	161650	3233	3.6177
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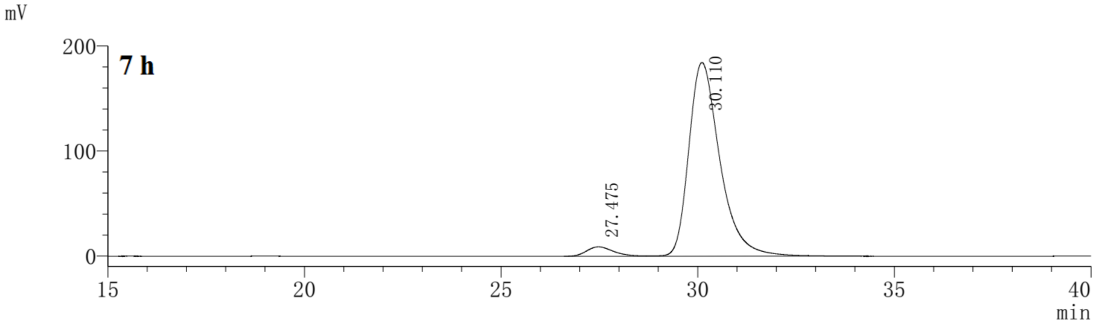
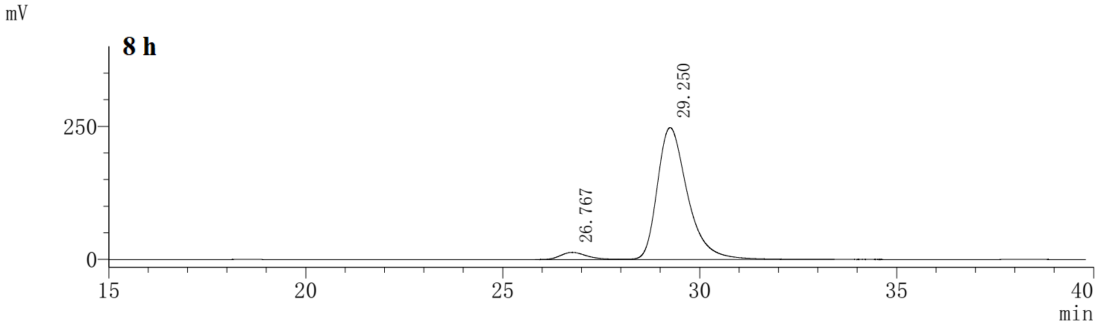


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	27.475	M	1.2216	434195	9002	4.0950

2	30.110	M	1.3948	10168957	184560	95.9050



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	26.767	M	1.1946	626510	13420	4.5220
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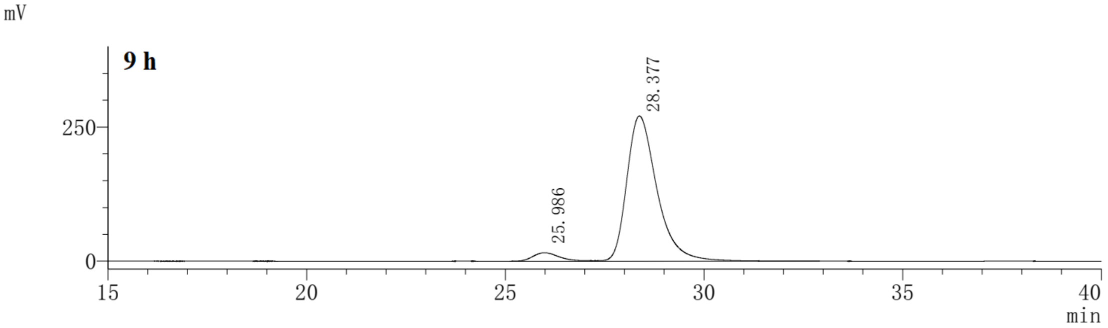

Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	25.986	M	1.1897	746370	15925	4.9567
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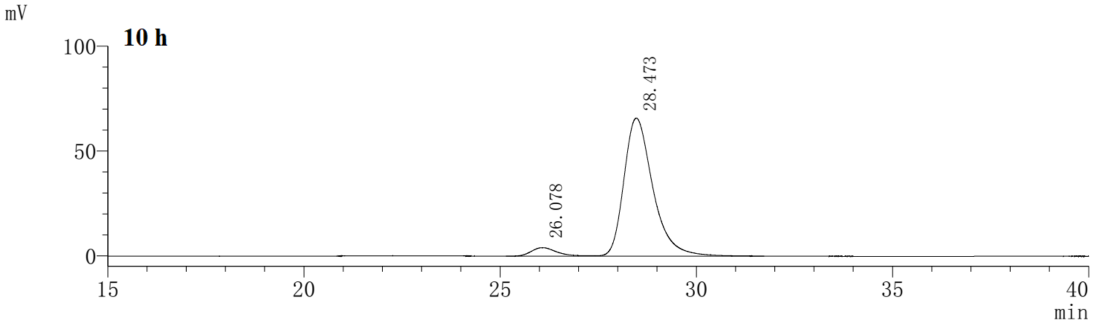
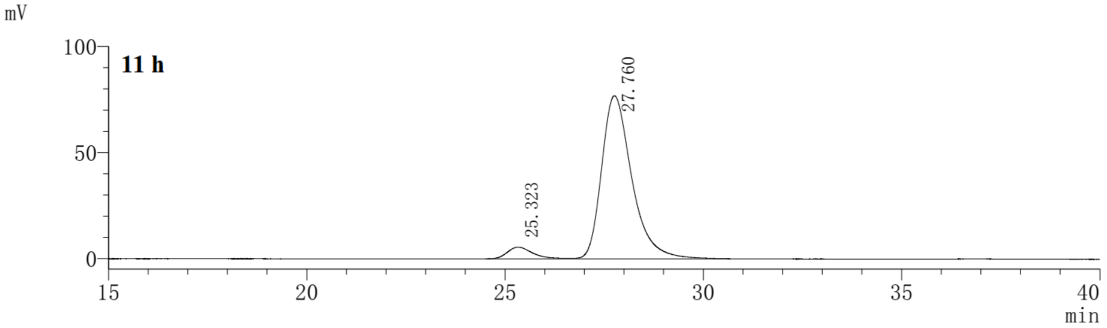
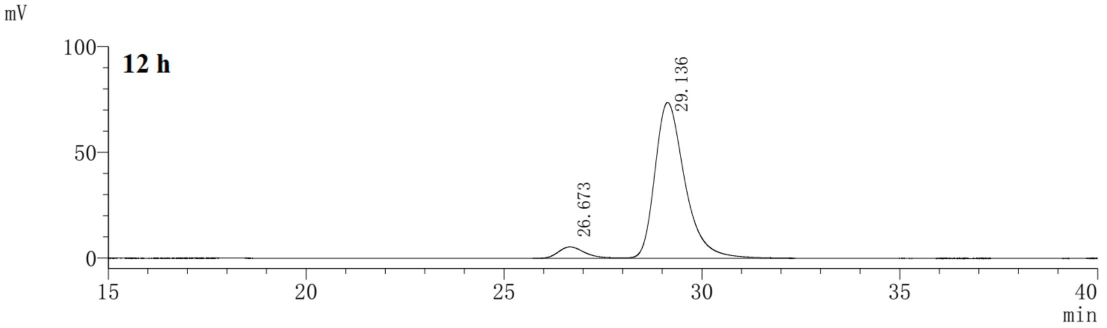


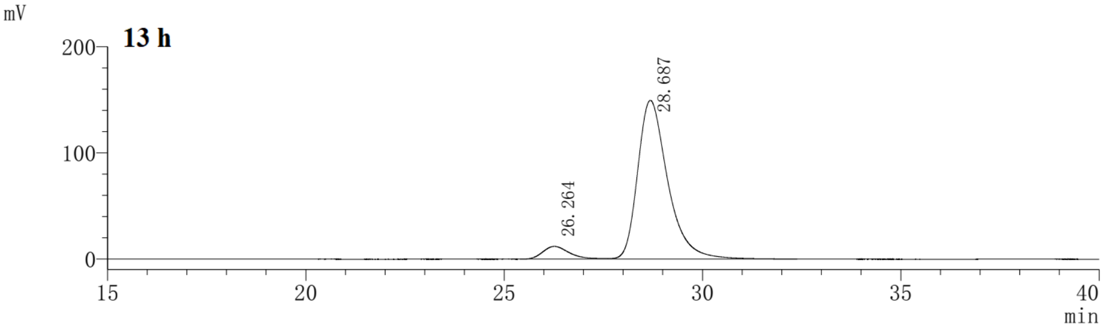
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	26.078	M	1.1403	185885	4079	5.2138
2	28.473	M	1.3059	3379354	65868	94.7862



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	25.323	M	1.1467	245553	5493	5.6906
2	27.760	M	1.3348	4069485	76883	94.3094



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	26.673	M	1.1795	257341	5442	6.2232
2	29.136	M	1.3355	3877829	73730	93.7768



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	26.264	M	1.1858	566306	12031	6.6938
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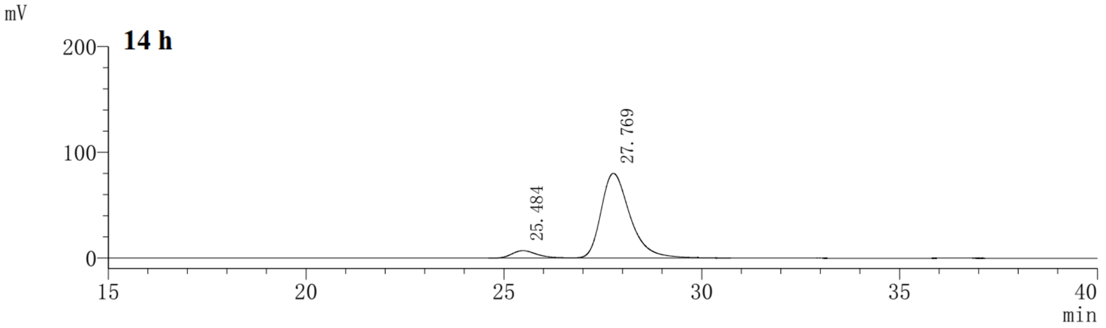
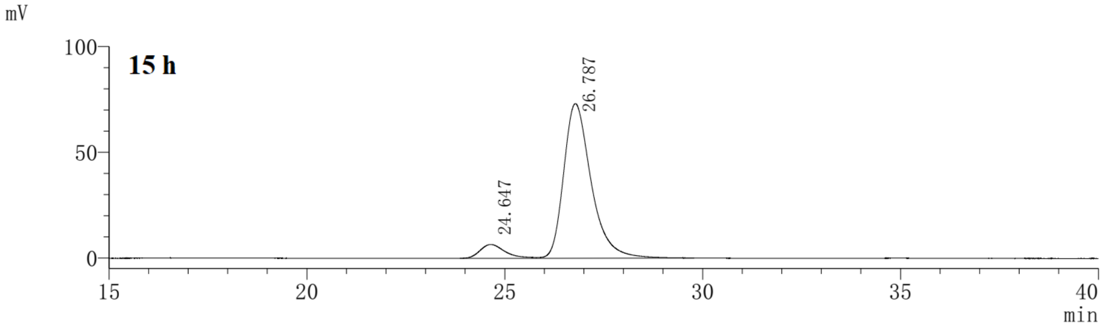


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	25.484	M	1.1269	316137	7060	7.1669
2	27.769	M	1.2987	4094922	80188	92.8331



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	24.647	M	1.0946	287083	6550	7.5115
2	26.787	M	1.2238	3534819	73139	92.4885

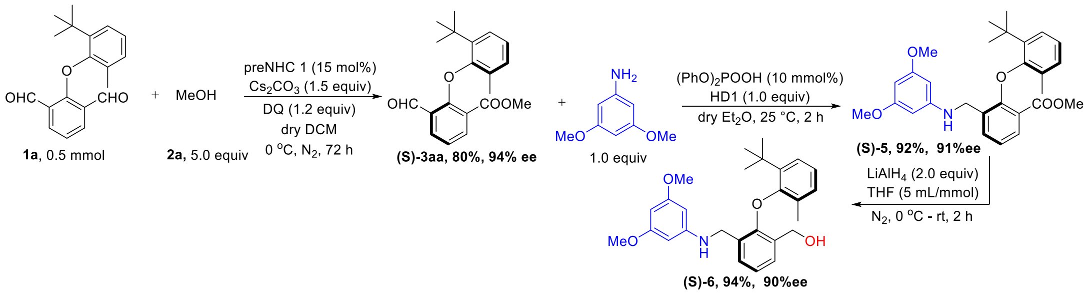
V. Determining the Absolute Configuration of 3aa[1]

The absolute stereochemistry of chiral esterification product **3aa** was determined by the HPLC compared with the known compounds (see below).

The known compound (R)- (2-(2-(tert-butyl)-6-methylphenoxy)-3-(((3,5 -dimethoxyphenyl)amino)methyl)phenyl)methanol (*R*-**6**) HPLC as follow in Zeng and Zhong's work[1] : HPLC (DAICEL Chiralpak AD, isohexane/isopropanol = 90/10, flow 1.0 mL/min, detection at 254 nm) retention time = 21.7 min (major) and 36.0 min (minor), and our experimental results show that Chiral compound **6** converted from chiral esterification product **3aa** is opposite to Zeng and Zhong's work. As follow: HPLC (DAICEL Chiralpak AD-3, isohexane/ isopropanol = 90/10, flow 1.0 mL/min, detection at 254 nm) retention time = 27.4 min (minor) and 44.2 min (major).

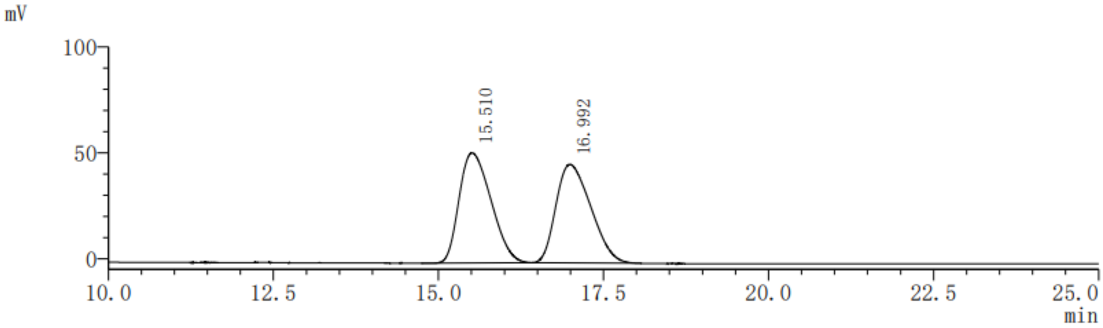
Conclusion: The results above showed that the absolute configuration of **6** we synthesized is opposite to Zeng and Zhong's work. So the absolute configuration of **3aa** is determined to be **S** type.

Synthesis method from compound **3aa** to **6**

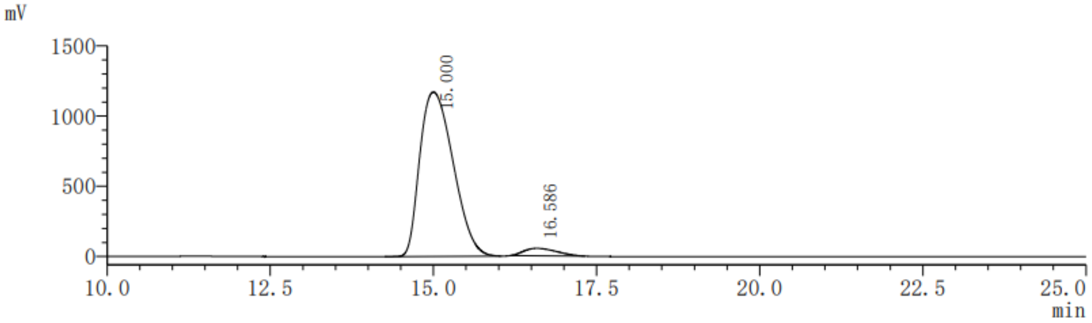


A 25 mL vial containing a magnetic stir bar, was added **(S)-3aa** (150.0 mg, 0.46 mmol, 1.0 equiv), diphenyl phosphate (11.5 mg, 0.046 mmol, 0.1 equiv), Diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (HD1) (117.0 mg, 0.046 mmol, 1.0 equiv), 3,5-dimethoxyaniline (70.0 mg, 0.46 mmol,1.0 equiv) and 30 ml dry Et_2O. After stirring at the 25 °C for 2 h, the reaction mixture concentrated in vacuo to give a residue, which was purified by flash chromatographyto afford the products **(S)-5** as Black green oil. yield: 193.9 mg (91%). R_f=0.40 (hexanes/EtOAc = 5:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.52 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.34 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.25 (d, *J* = 2.1 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 7.00 – 6.94 (m, 2H), 5.88 (t, *J* = 2.1 Hz, 1H), 5.76 (d, *J* = 2.1 Hz, 2H), 4.40 (d, *J* = 16.2 Hz, 1H), 4.29 (d, *J* = 16.2 Hz, 1H), 3.71 (s, 6H), 3.33 (s, 3H), 1.86 (s, 3H), 1.45 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 167.73, 161.73, 153.09, 151.88, 149.76, 140.95, 131.27, 130.19, 129.44, 129.25, 127.94, 125.33, 123.97, 122.06, 121.86, 91.68, 90.12, 55.13, 51.92, 43.84, 35.43, 30.66, 17.83. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{28}H_{33}NNaO_5$, ([M + Na]$^+$), 486.2251; found 486.2266.

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (major) = 15.00 min, t_R (minor) = 16.59 min, 91% ee.



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	15.510	M	0.9093	1744625	51934	50.5063
2	16.992	M	1.0058	1709649	46475	49.4937



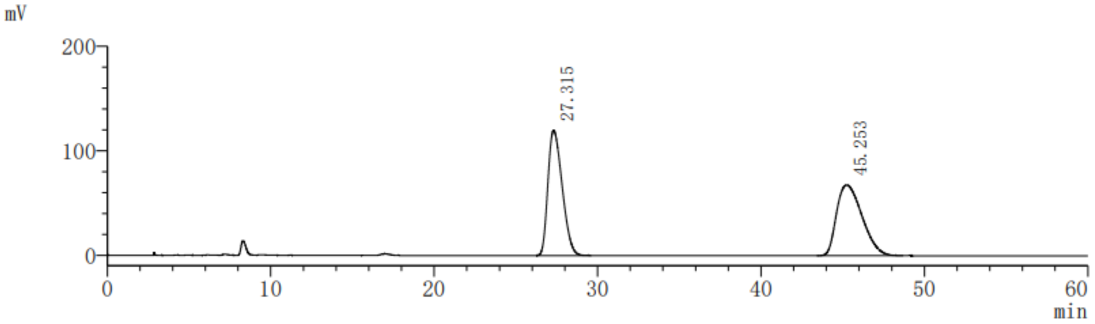
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	15.000	M	0.9380	41640097	1170374	95.7233
2	16.586	M	0.9589	1860366	53436	4.2767

1.5 equivalents of $LiAlH_4$ were added to a solution of **5** (193.0 mg, 0.41 mmol, 1.0 equiv) in THF (5 mL/mmol **5**). After 2 h of stirring at room temperature, the reaction mixture was quenched carefully with water (5 mL/mmol **5**), slightly acidified with 2N HCl, extracted with diethyl ether (3 x 5 mL/mmol **5**), and dried over $MgSO_4$. The solvent was removed in vacuo and the residue was chromatographed on silica gel (PE/EtOAc = 2:1) to give the alcohol **6** in 93% yield. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.36 (d, *J* = 7.6 Hz, 1H), 7.33 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.96 – 6.92 (m, 1H), 5.89 – 5.82 (m, 1H), 5.74 – 5.66 (m, 2H), 4.46 (d, *J* = 13.6 Hz, 1H), 4.37 (d, *J* = 13.6 Hz, 1H), 4.20 (d, *J* = 15.8 Hz, 1H), 4.03 (d, *J* = 15.8 Hz, 1H), 3.68 (s, 6H), 1.81 (s, 3H), 1.45 (s, 9H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 161.70, 154.67, 151.70, 149.98, 140.03, 130.27, 128.42, 128.40, 128.38, 128.35, 127.80, 125.69, 123.85, 123.01, 91.64, 90.02, 60.77, 55.13, 43.68, 35.45, 30.60, 17.92.

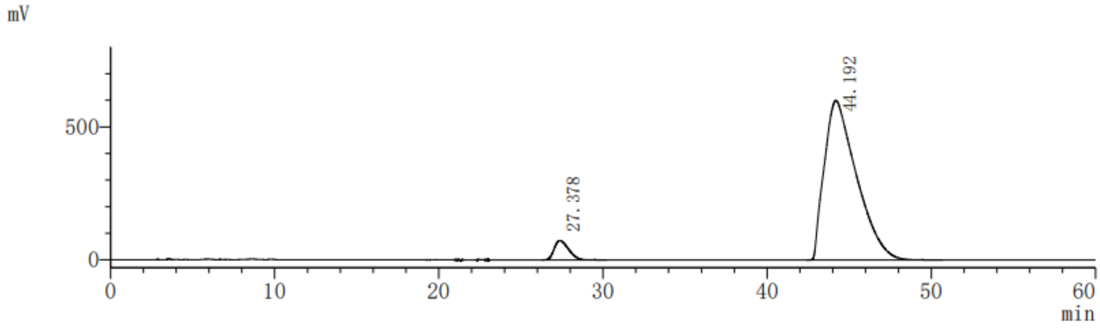
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{33}NNaO_4$, ([M + Na]$^+$), 458.2302; found 458.2302.

$[\alpha]_D^{19}$ = +26.7 (c = 0.75, CH_2Cl_2).

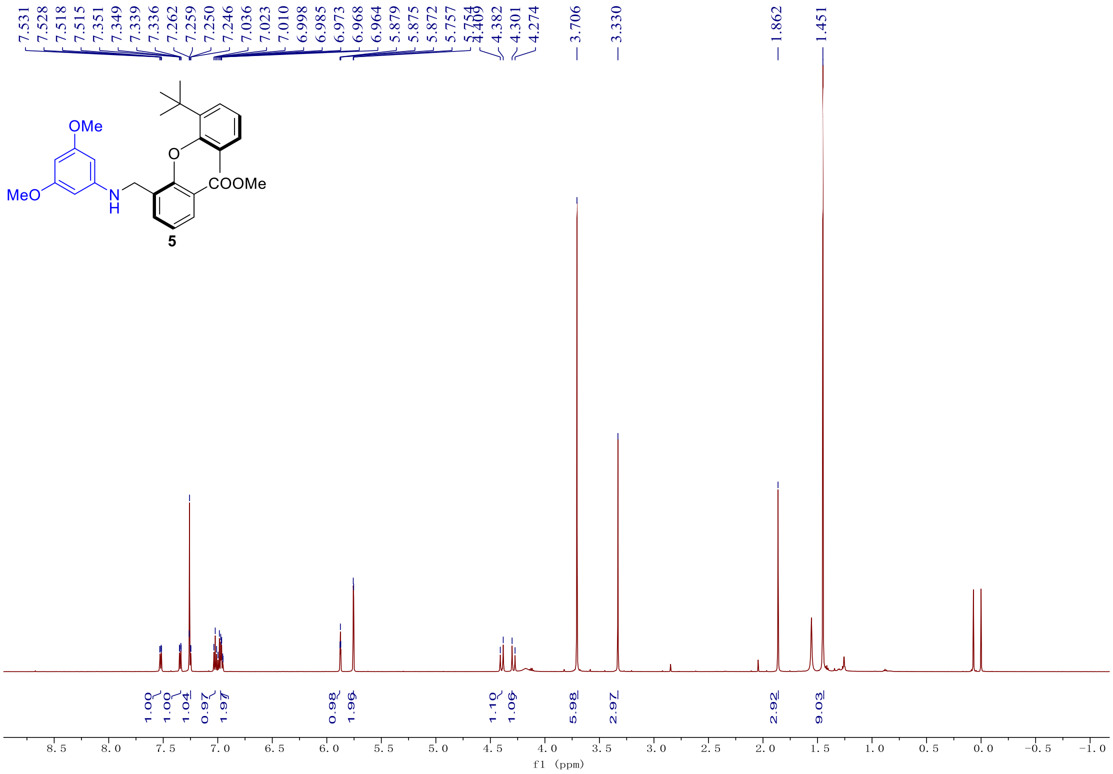
HPLC analysis: Daicel Chiralpak AD-3 column (90:10 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (minor) = 27.38 min, t_R (major) = 44.19 min, 90% ee.



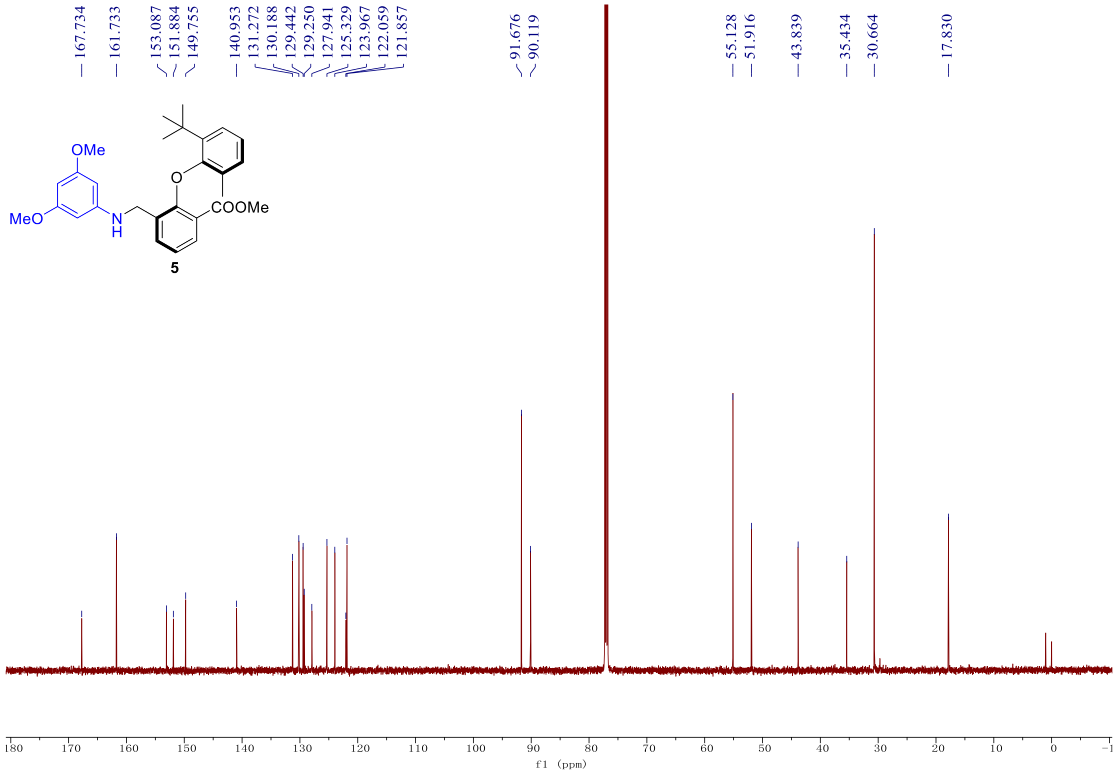
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	27.315	M	1.6247	7264173	119686	49.7964
2	45.253	M	2.8484	7323576	67671	50.2036



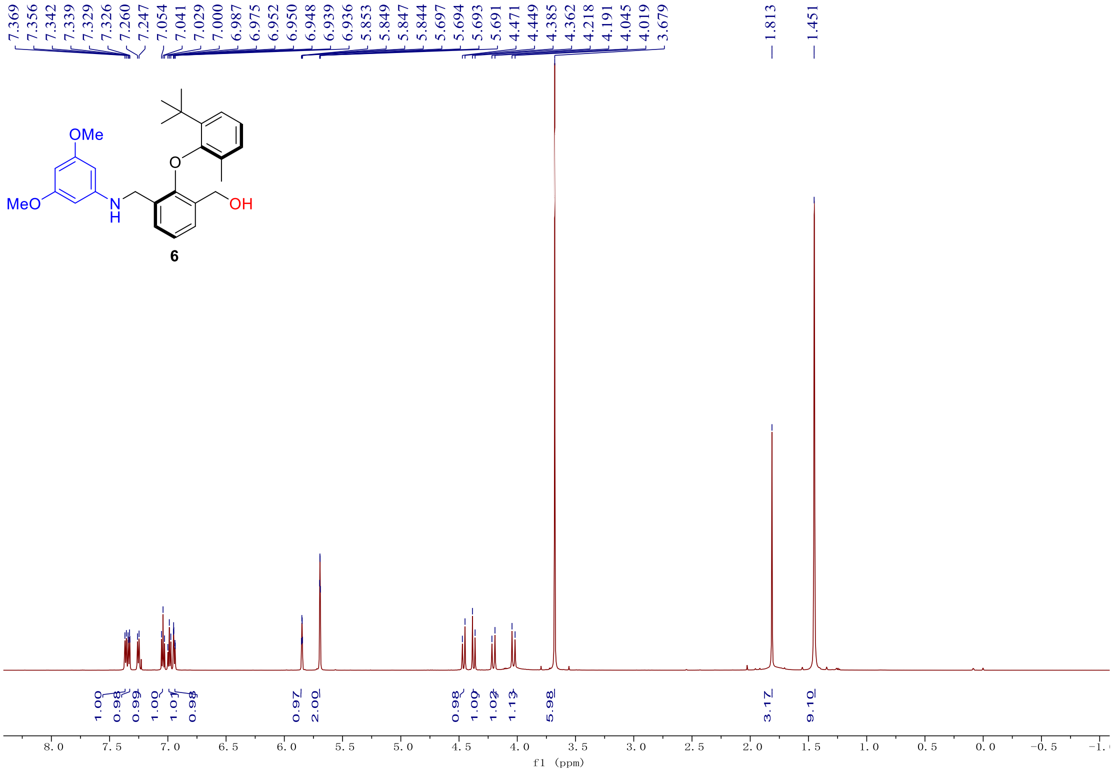
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	27.378	M	1.6367	4409646	72750	5.1149
2	44.192	M	3.9764	81801622	599504	94.8851



^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 5.



^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 5.



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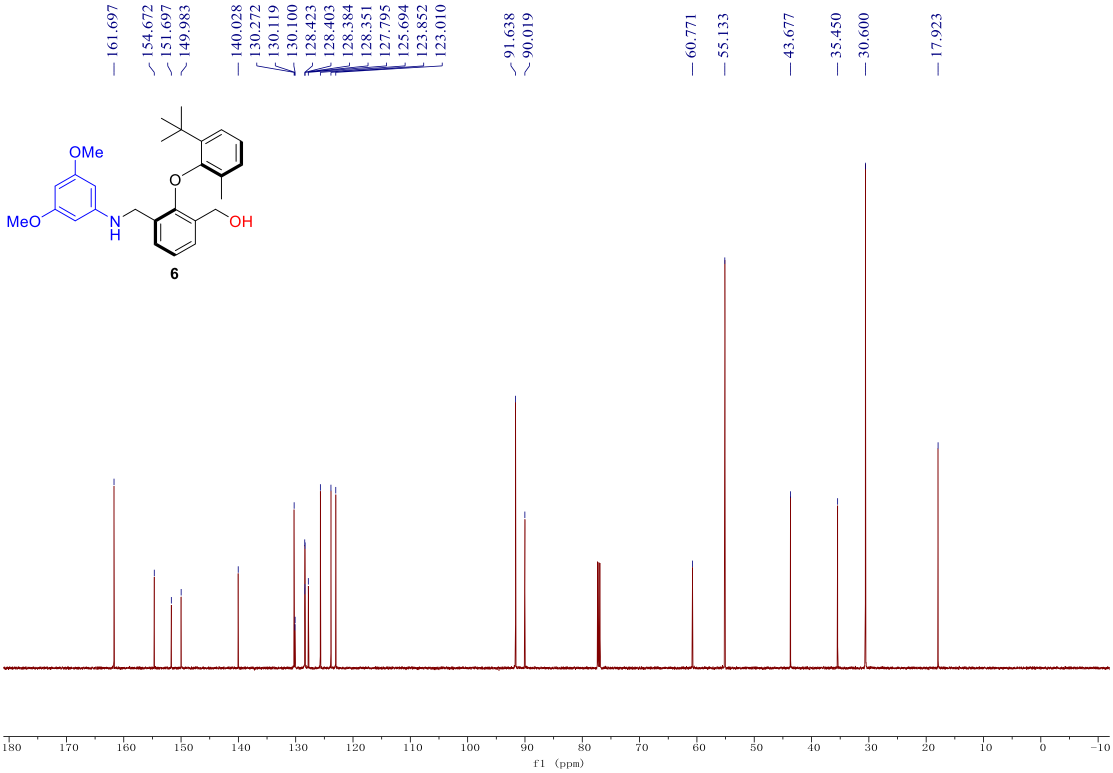

^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 6.

VI. References

[1] Dai, L.; Liu, Y.; Xu, Q.; Wang, M.; Zhu, Q.; Yu, P.; Zhong, G.; Zeng, X. A Dynamic Kinetic Resolution Approach to Axially Chiral Diaryl Ethers by Catalytic Atroposelective Transfer Hydrogenation. *Angew. Chem. Int. Ed.* **2022**, DOI： 10.1002/anie.202216534.

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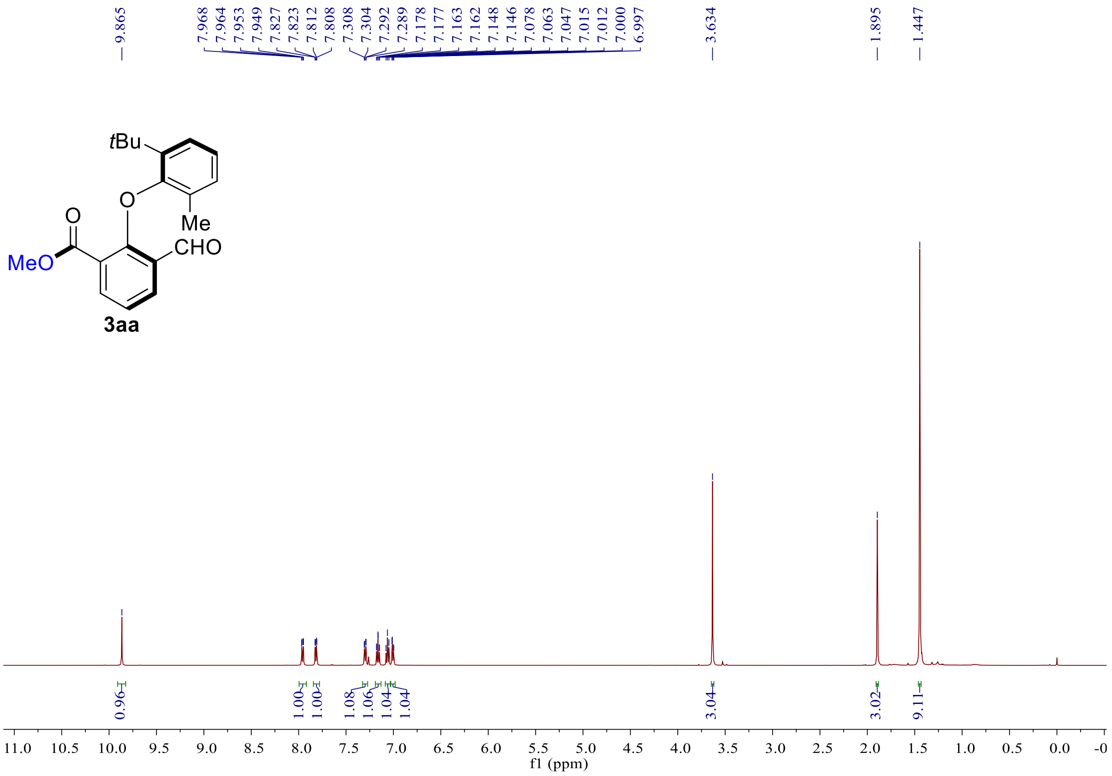
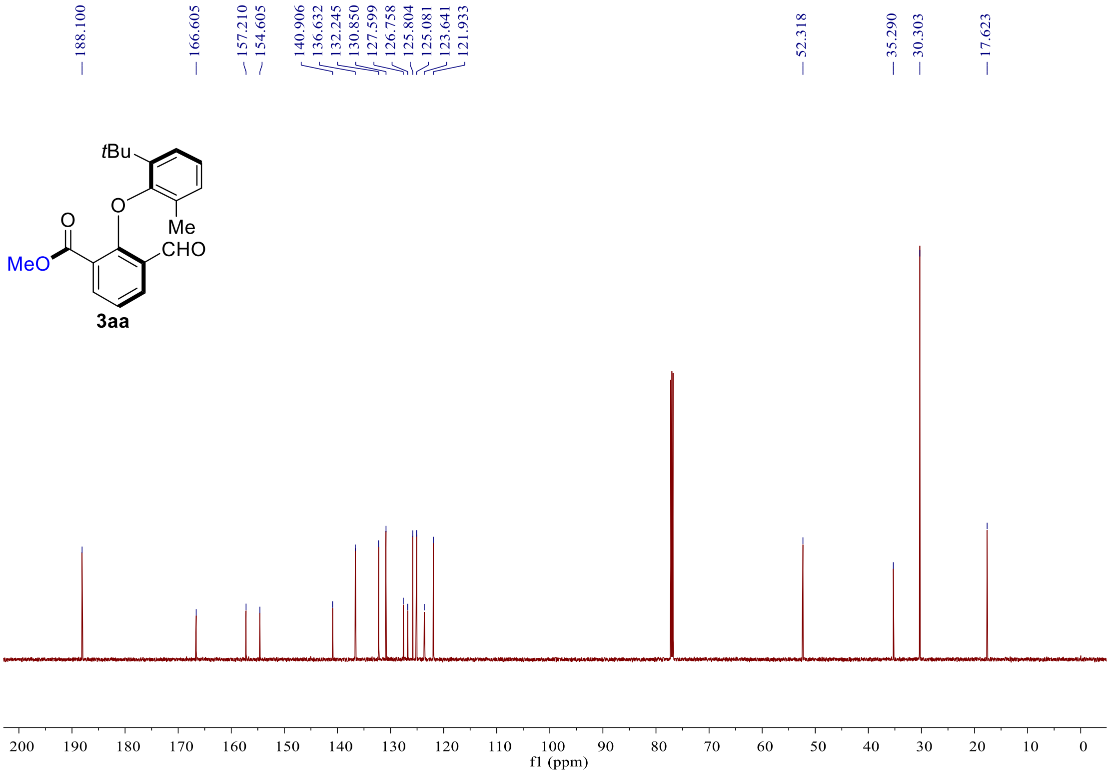
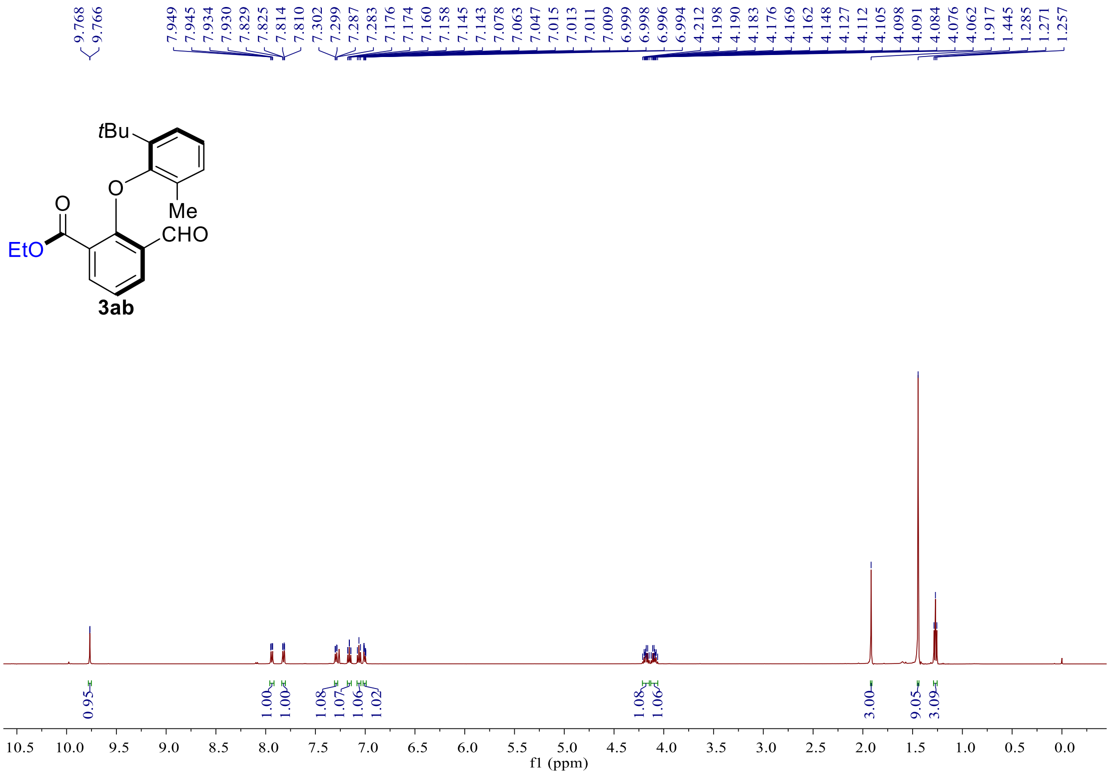
VII. ¹H, ¹³C, ¹⁹F NMR Spectra of New Compounds.



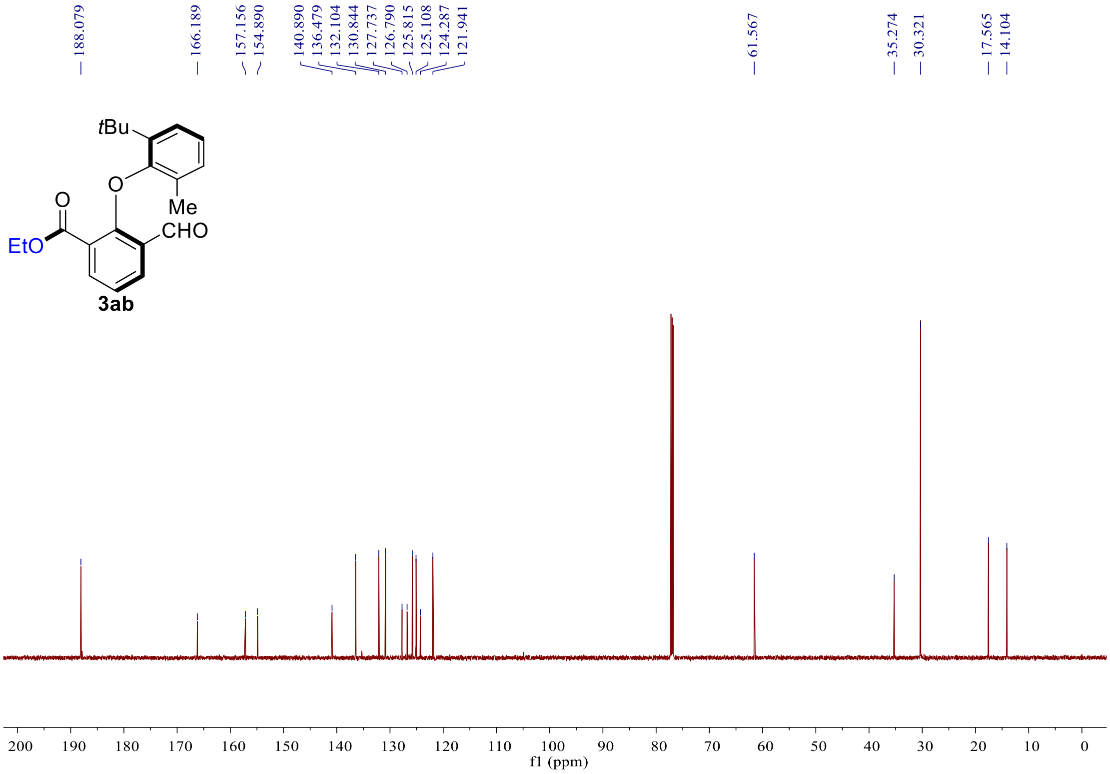
¹H NMR (500 MHz, CDCl₃) spectrum of 3aa.



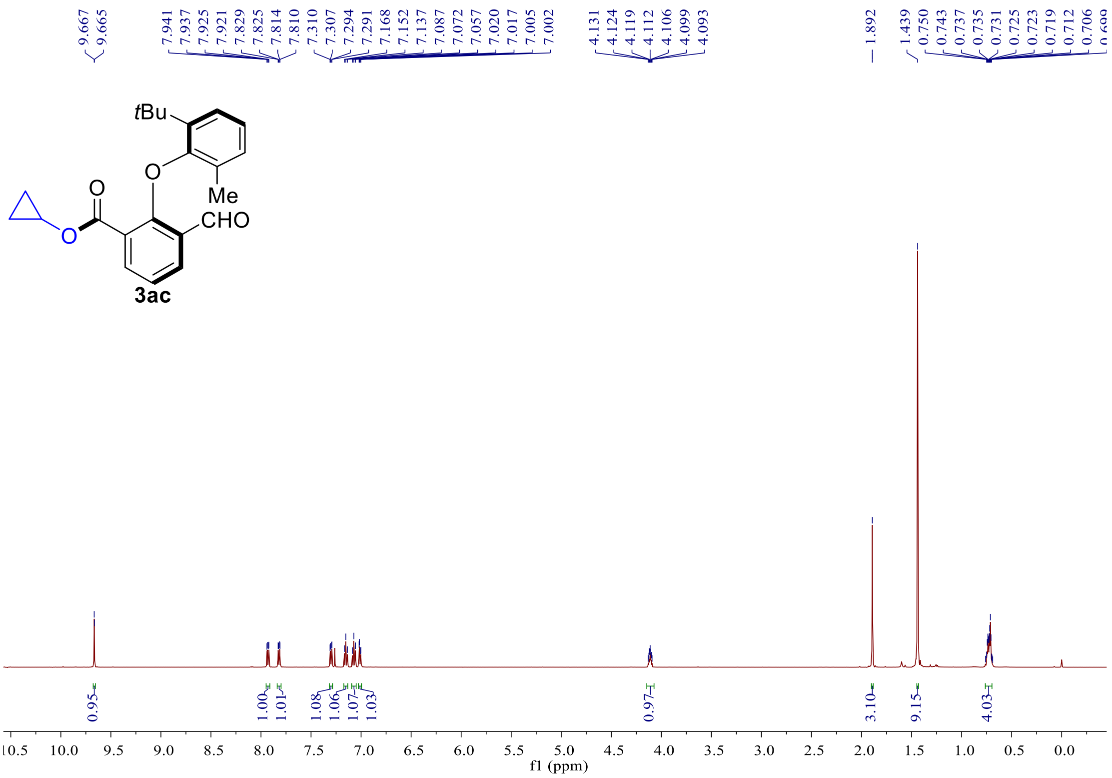
¹³C NMR (150 MHz, CDCl₃) spectrum of 3aa.



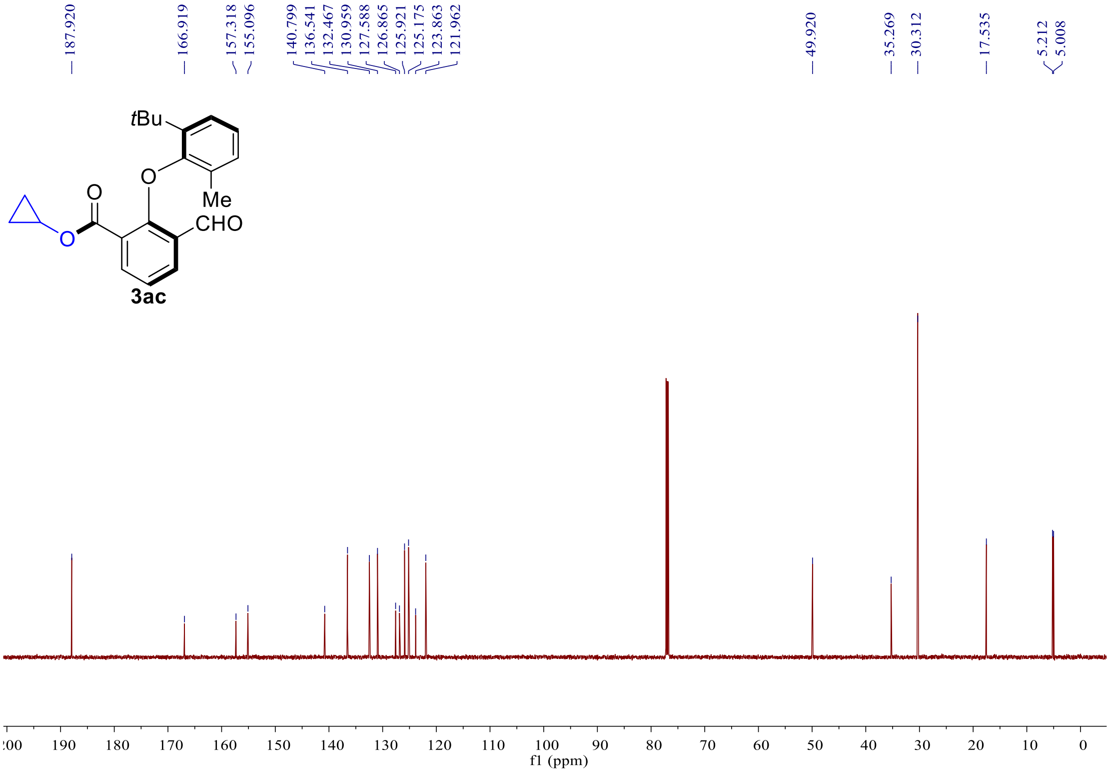
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3ab.



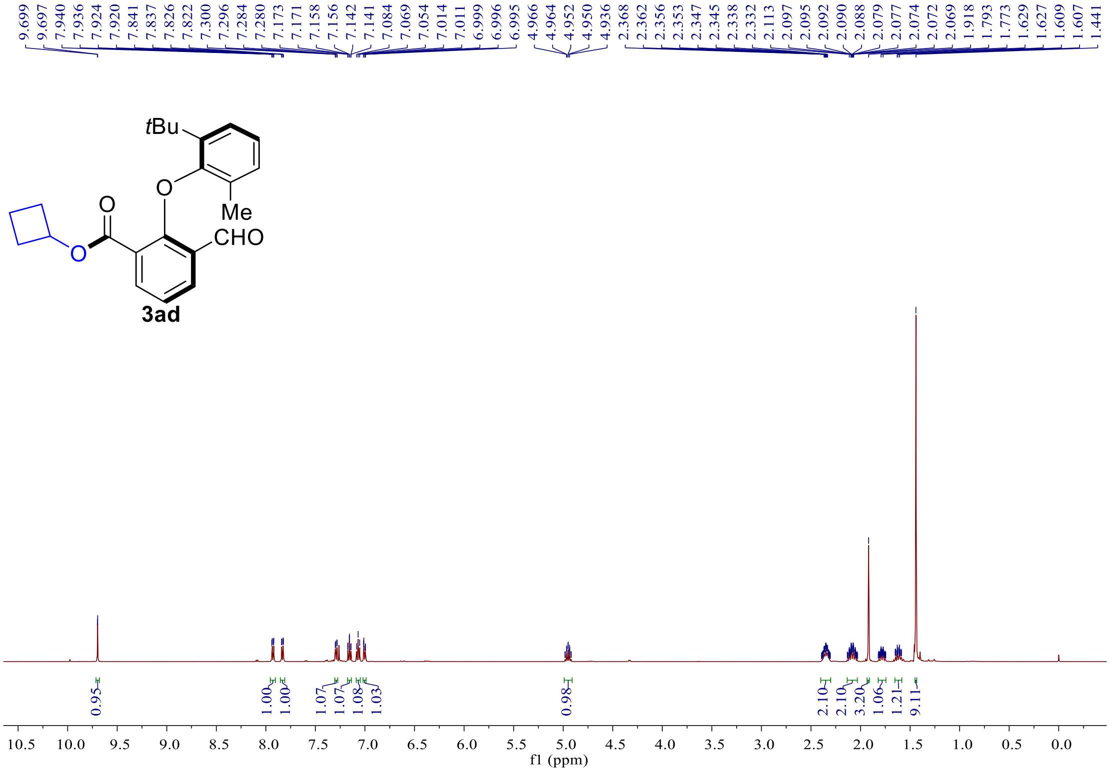
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3ab.



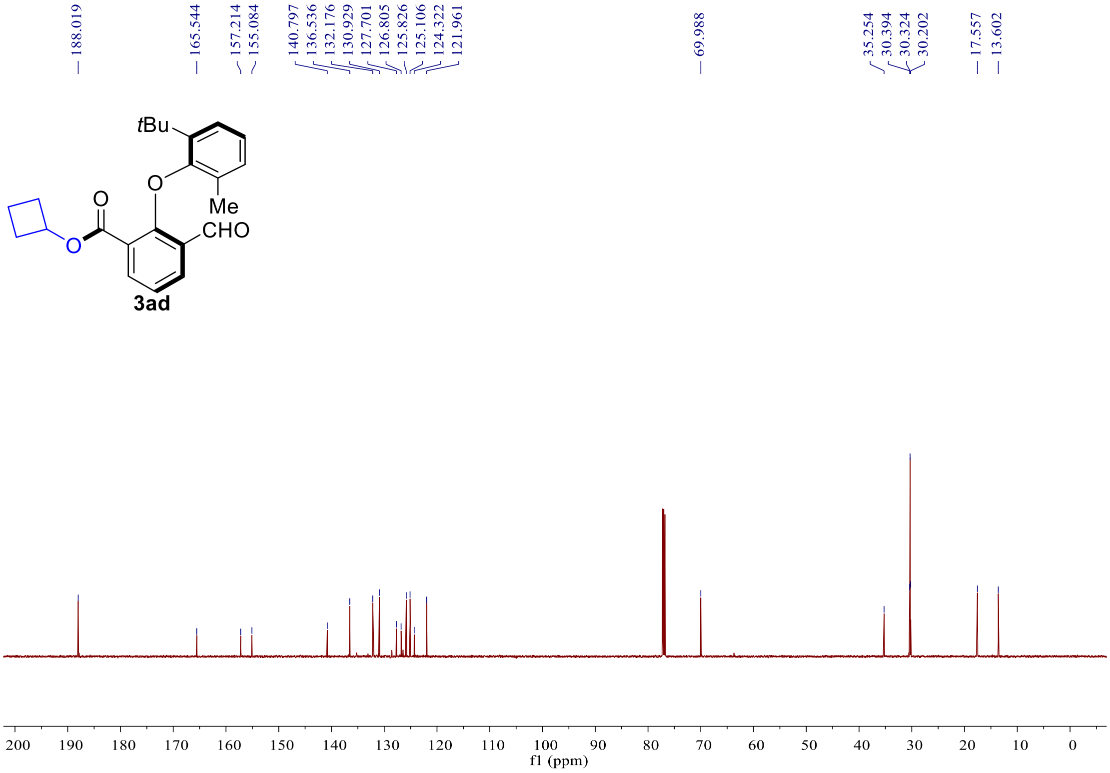
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3ac.



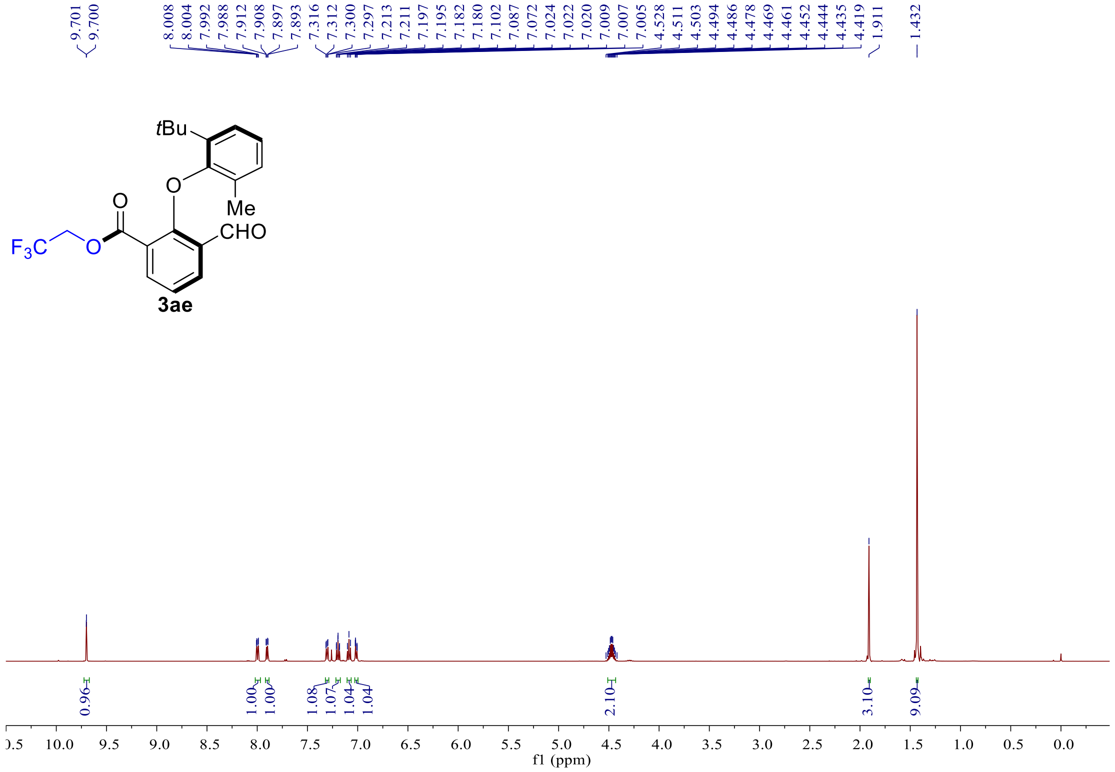
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3ac.



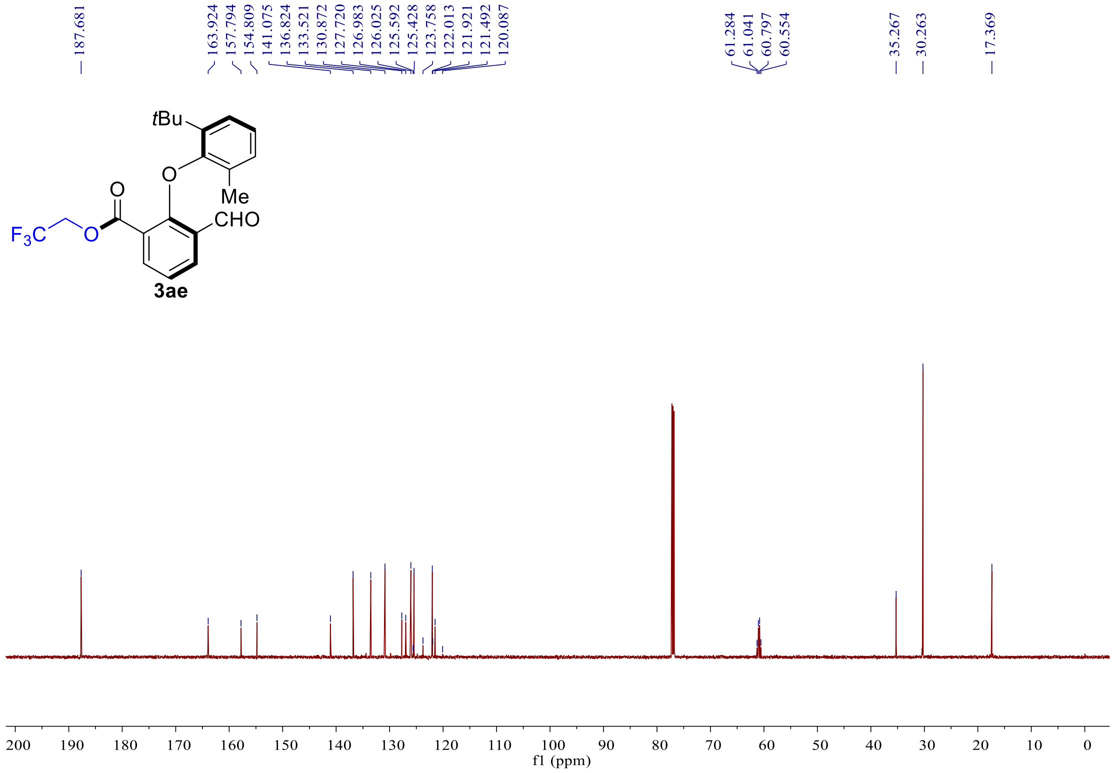
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3ad.



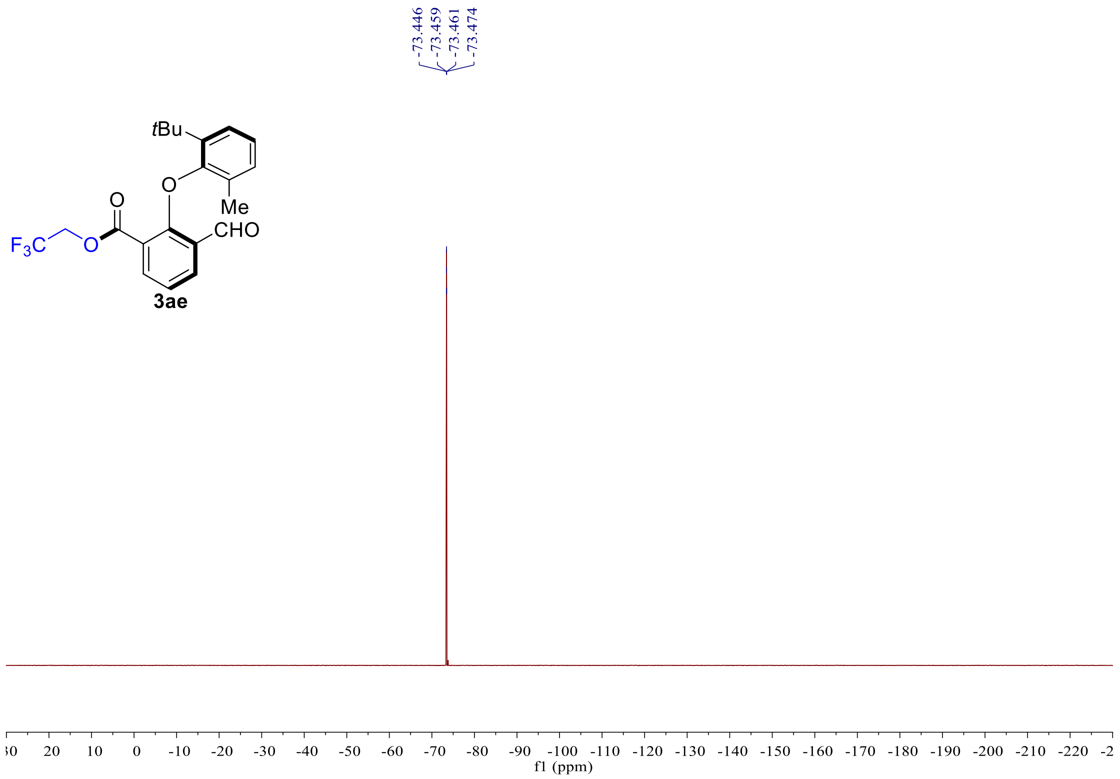
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3ad.



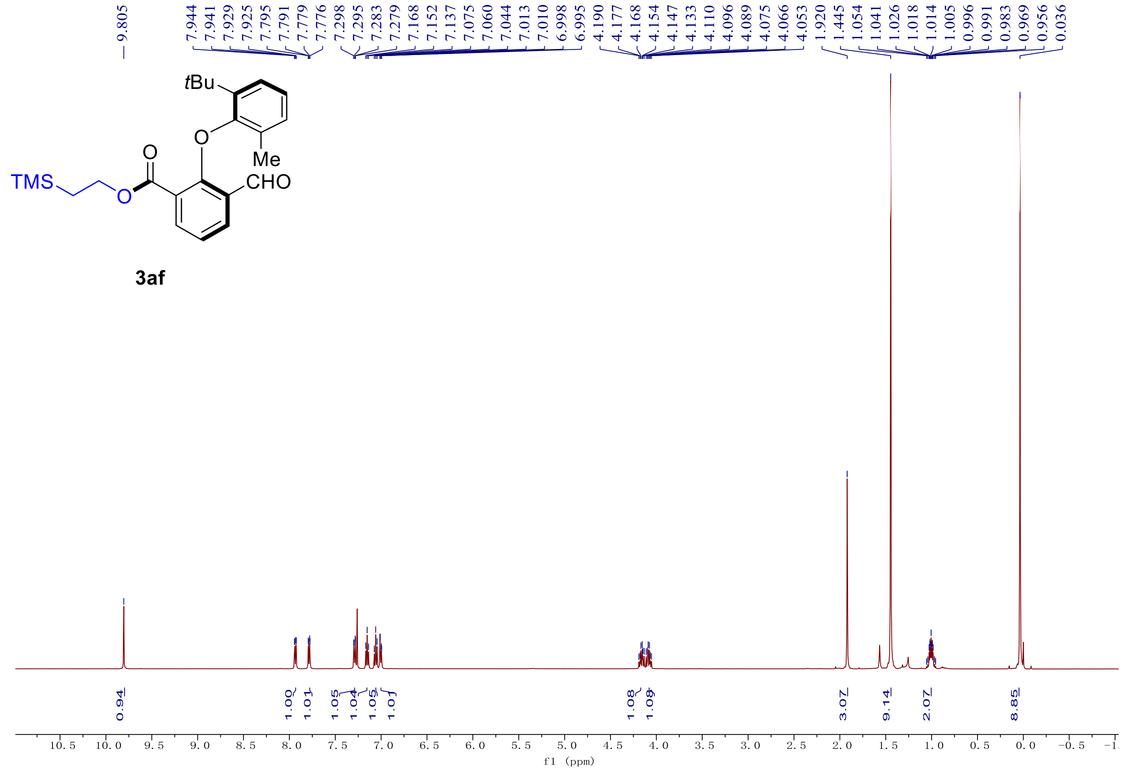
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3ae.



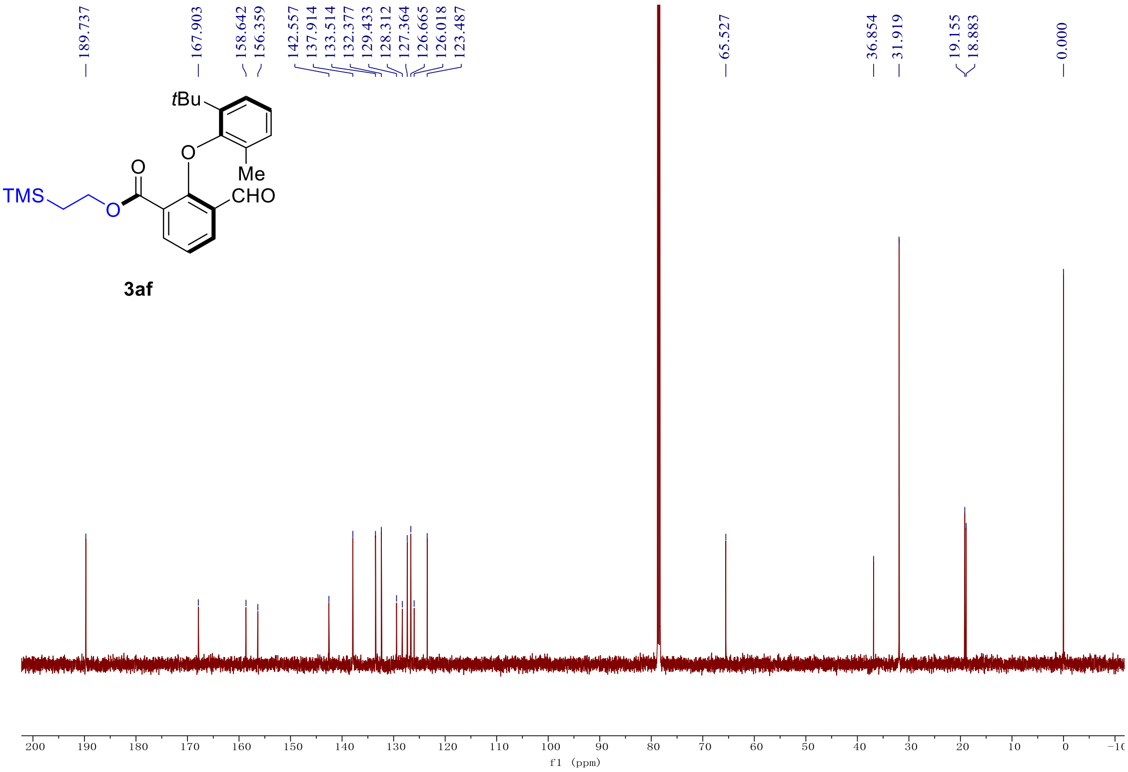
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3ae.



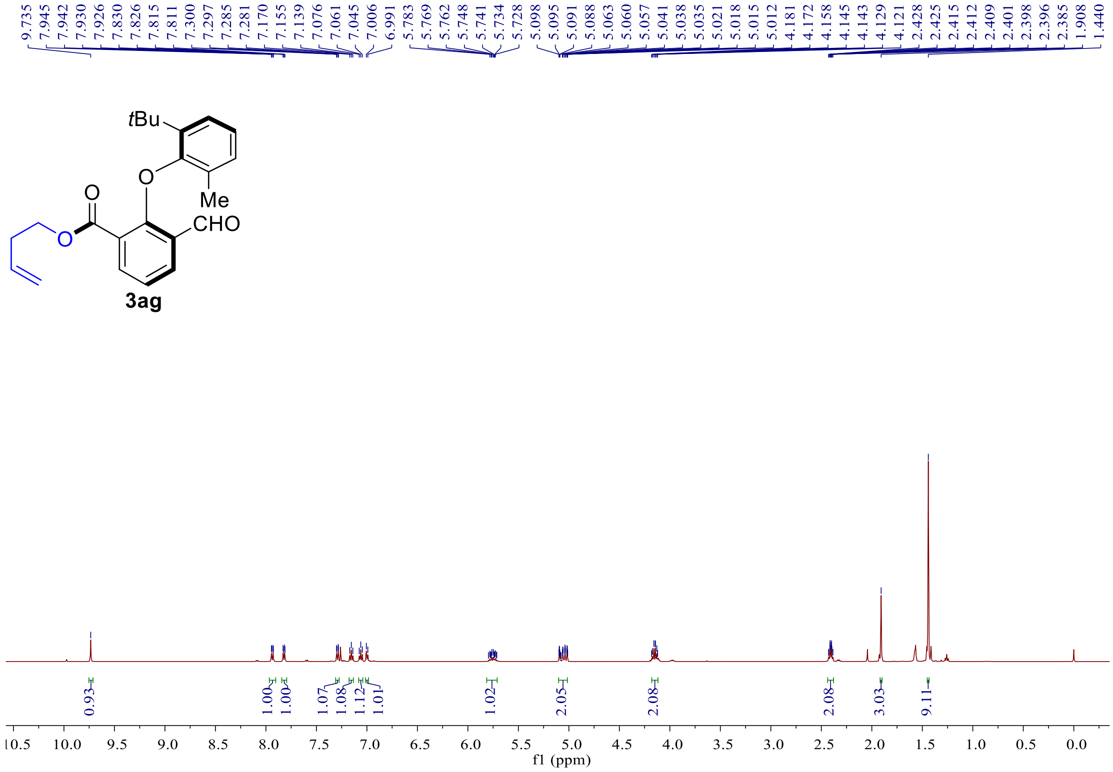
^{19}F NMR (565 MHz, CDCl$_3$) spectrum of 3ae.



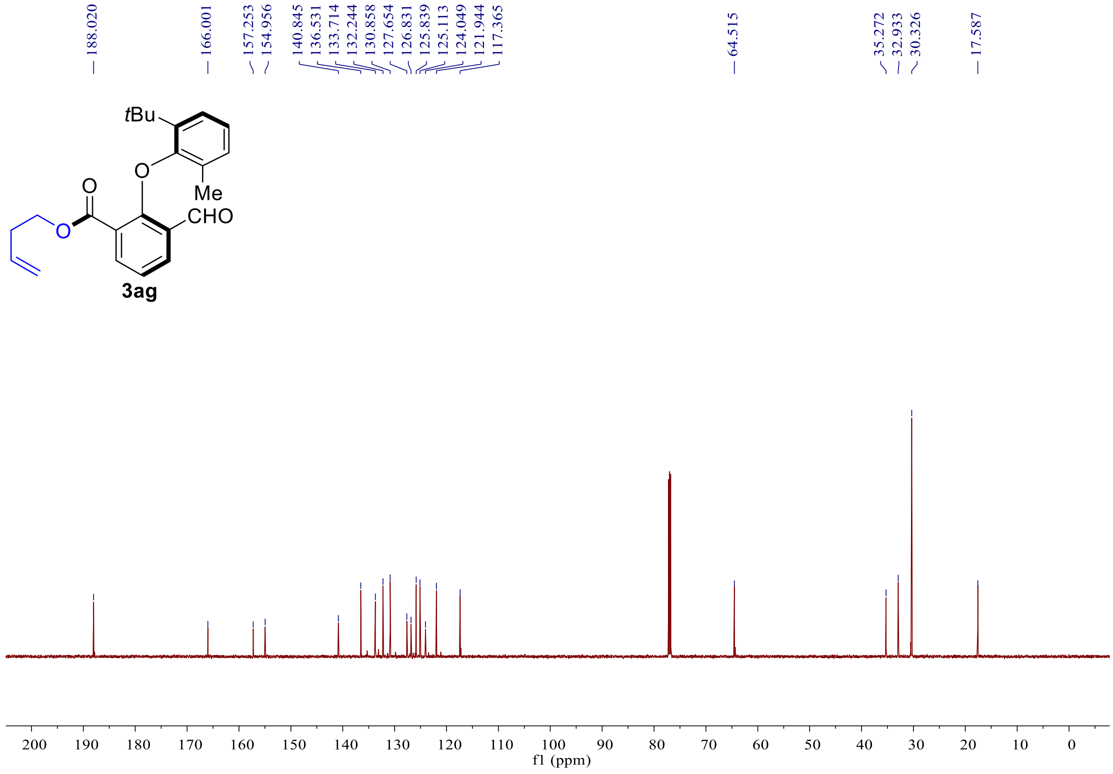
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3af.



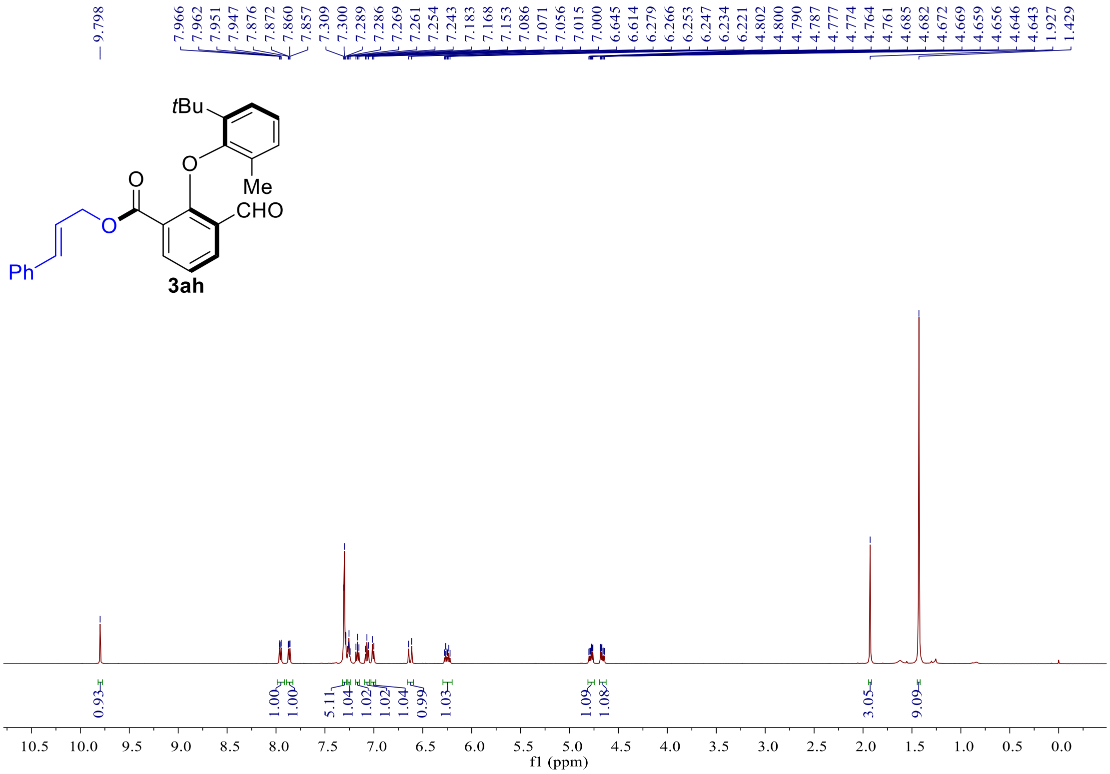
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3af.



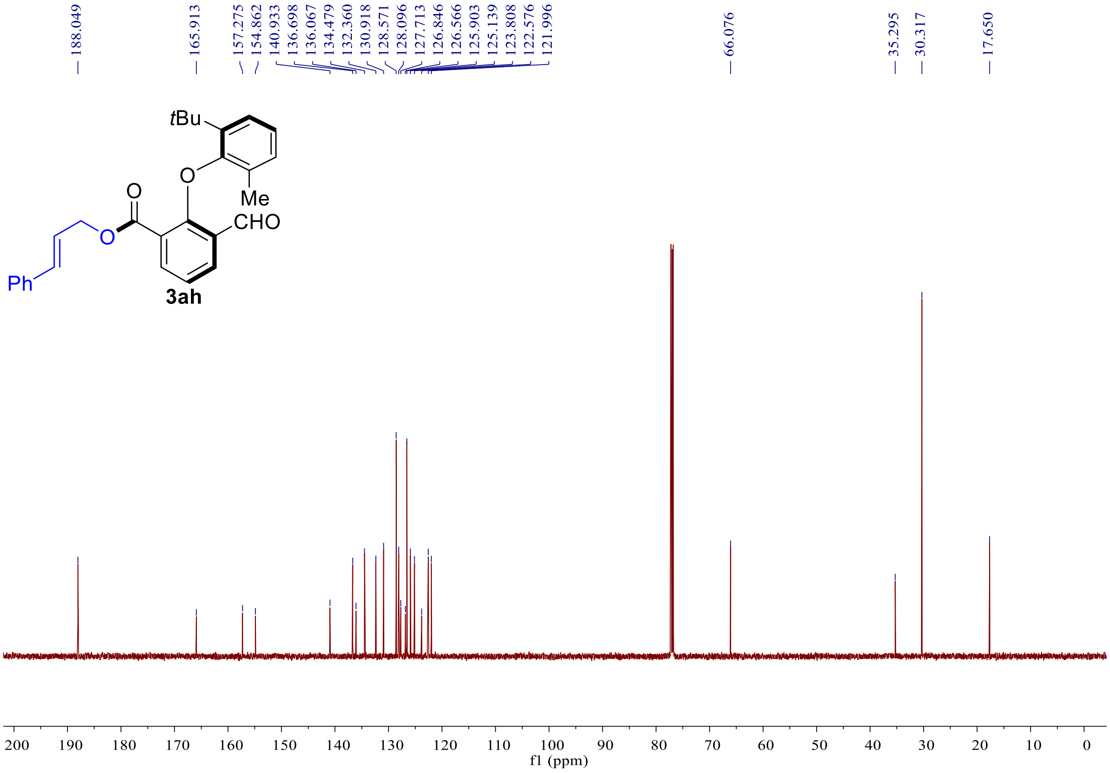
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3ag.



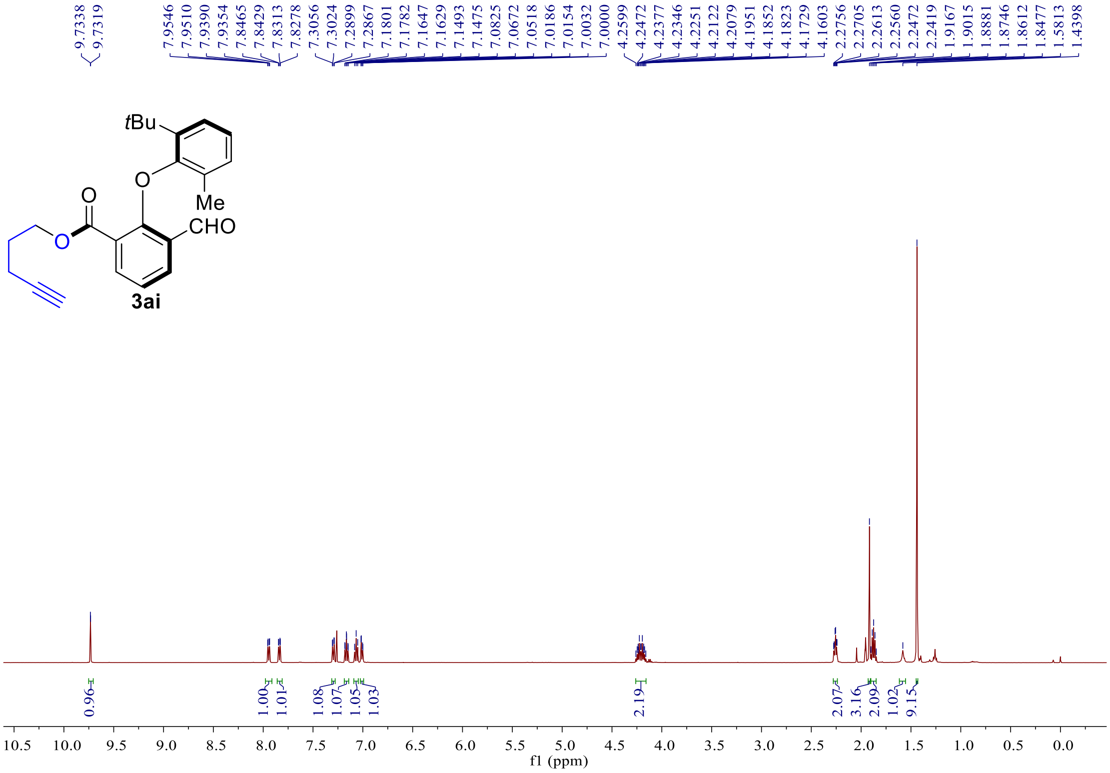
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3ag.



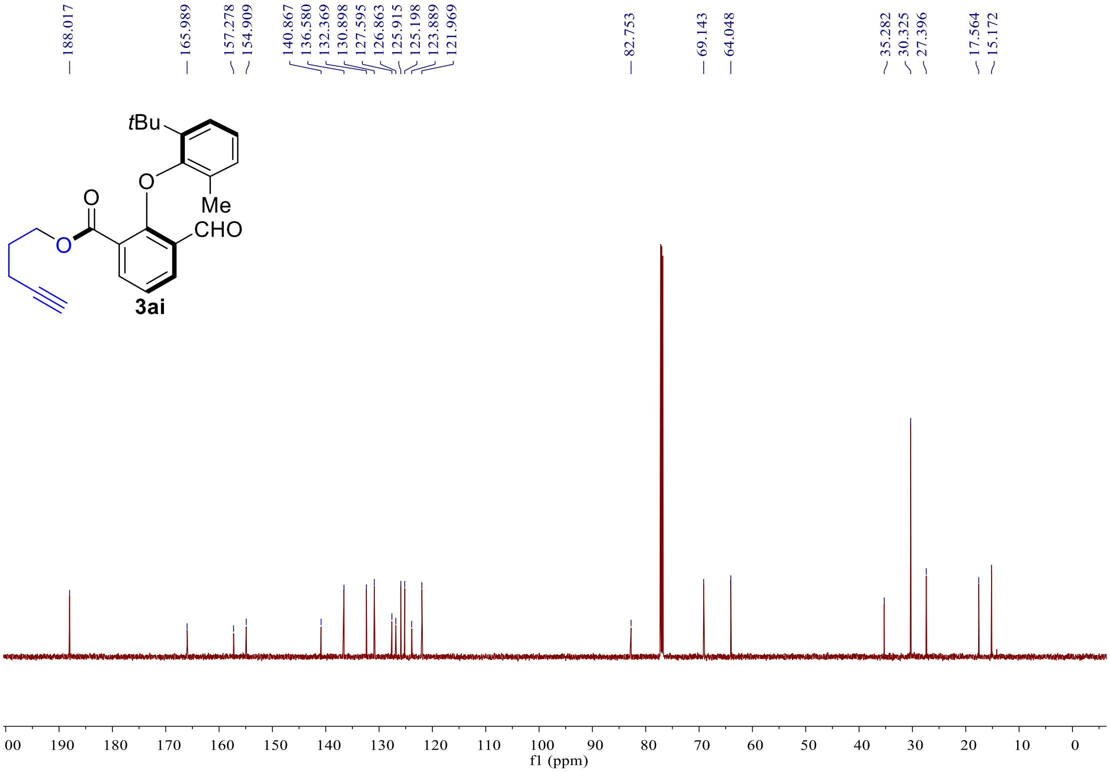
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3ah.



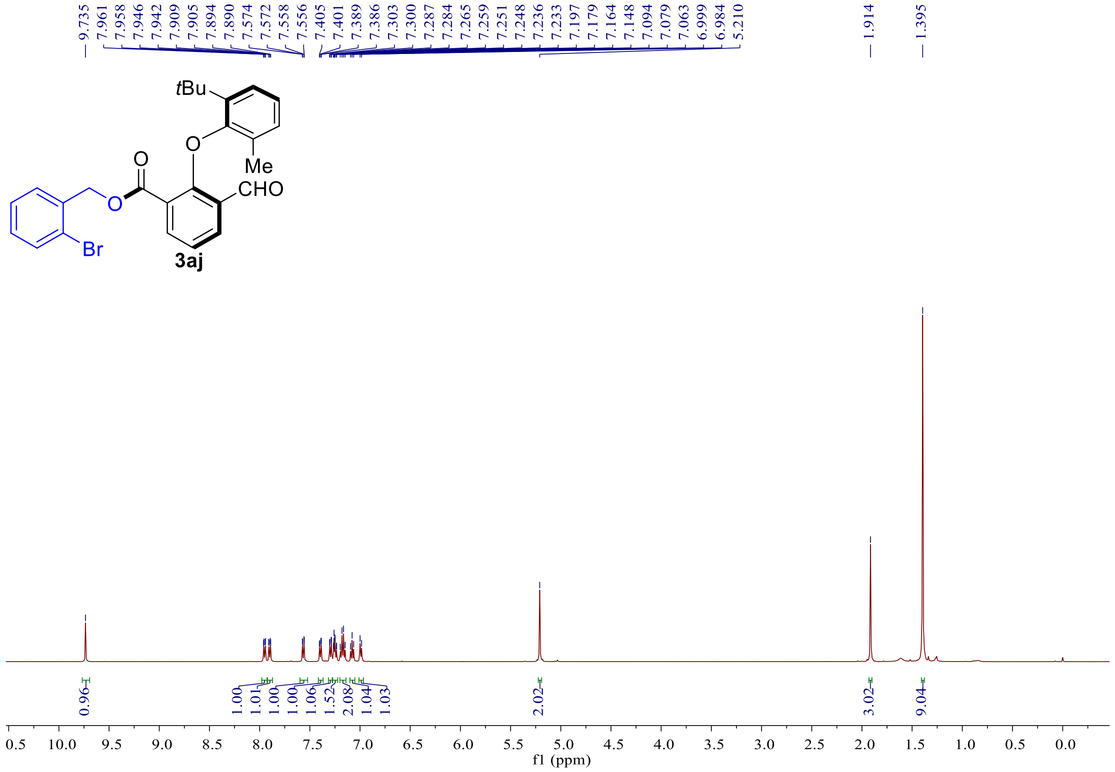
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3ah.



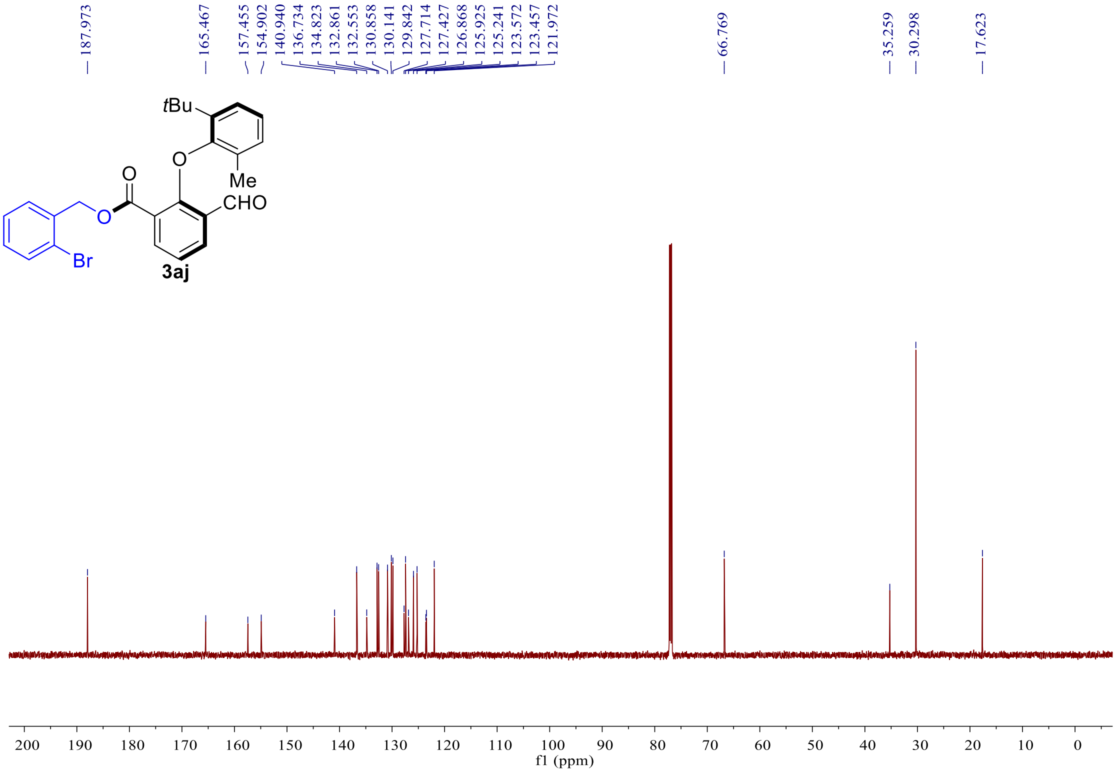
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3ai.



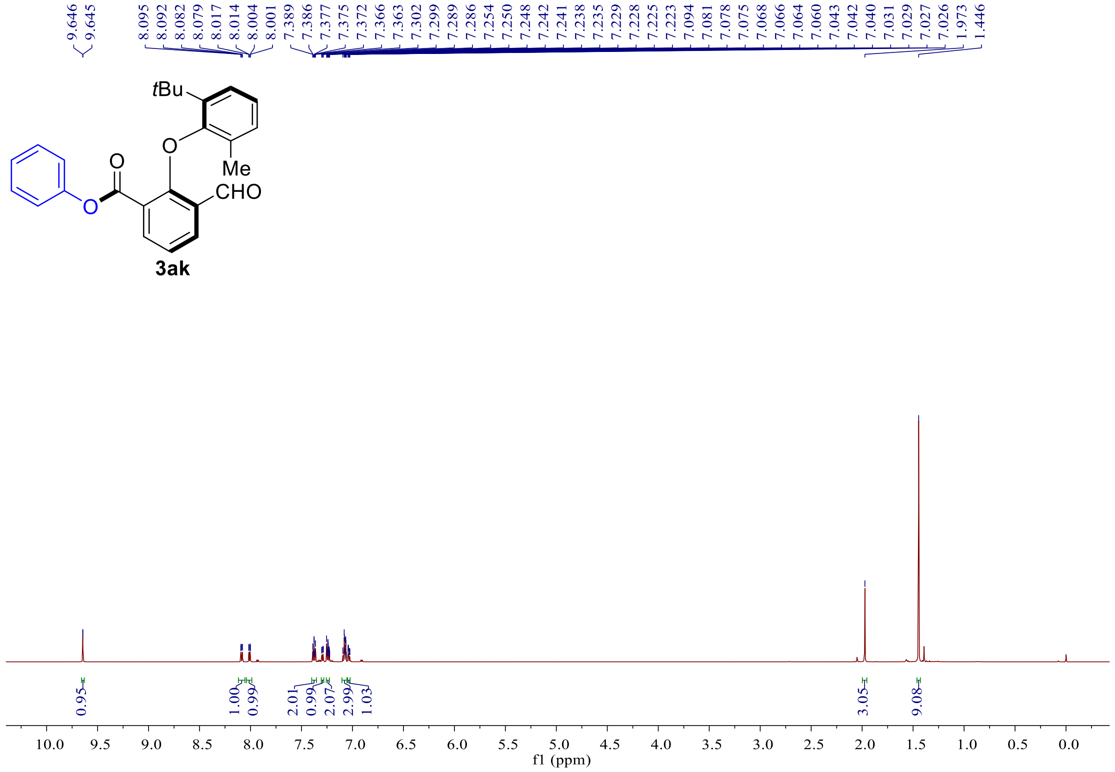
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3ai.



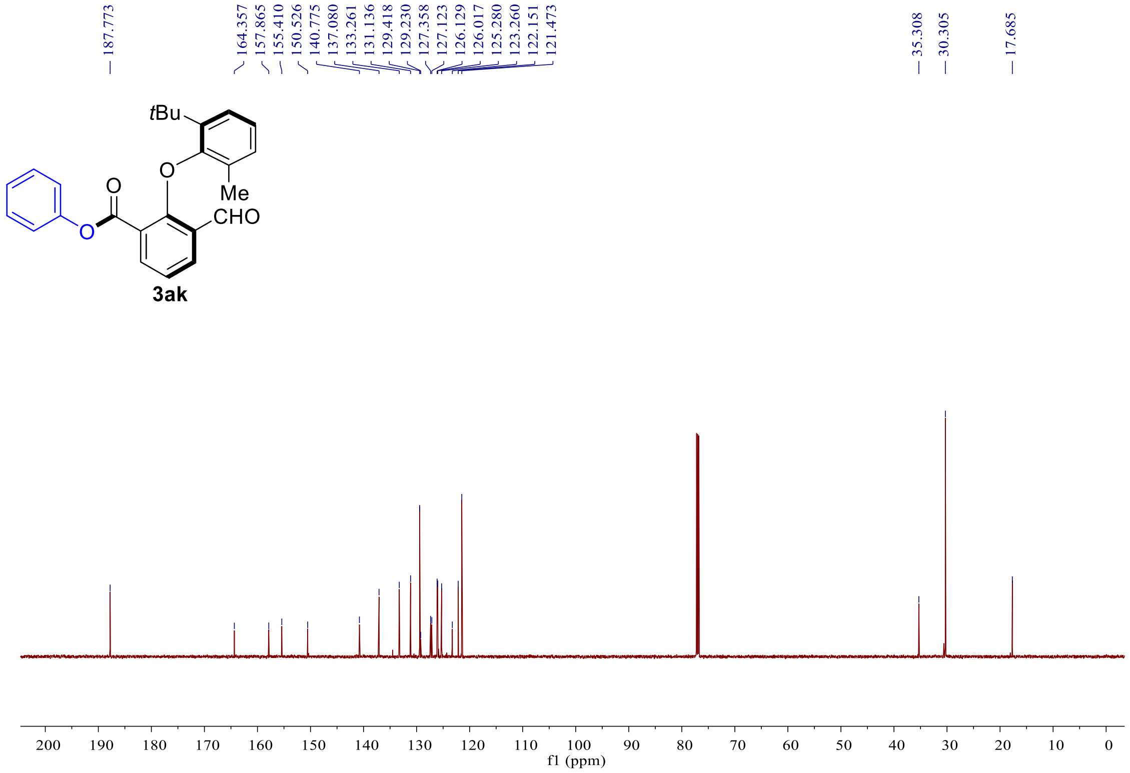
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3aj.



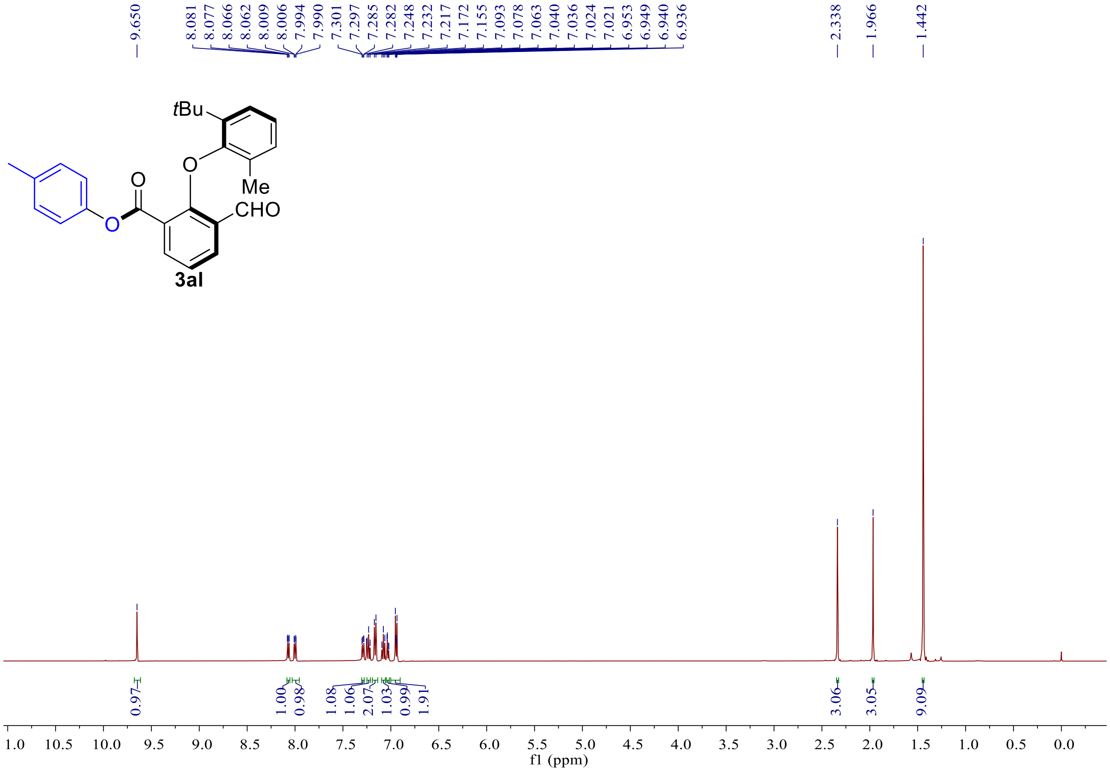
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3aj.



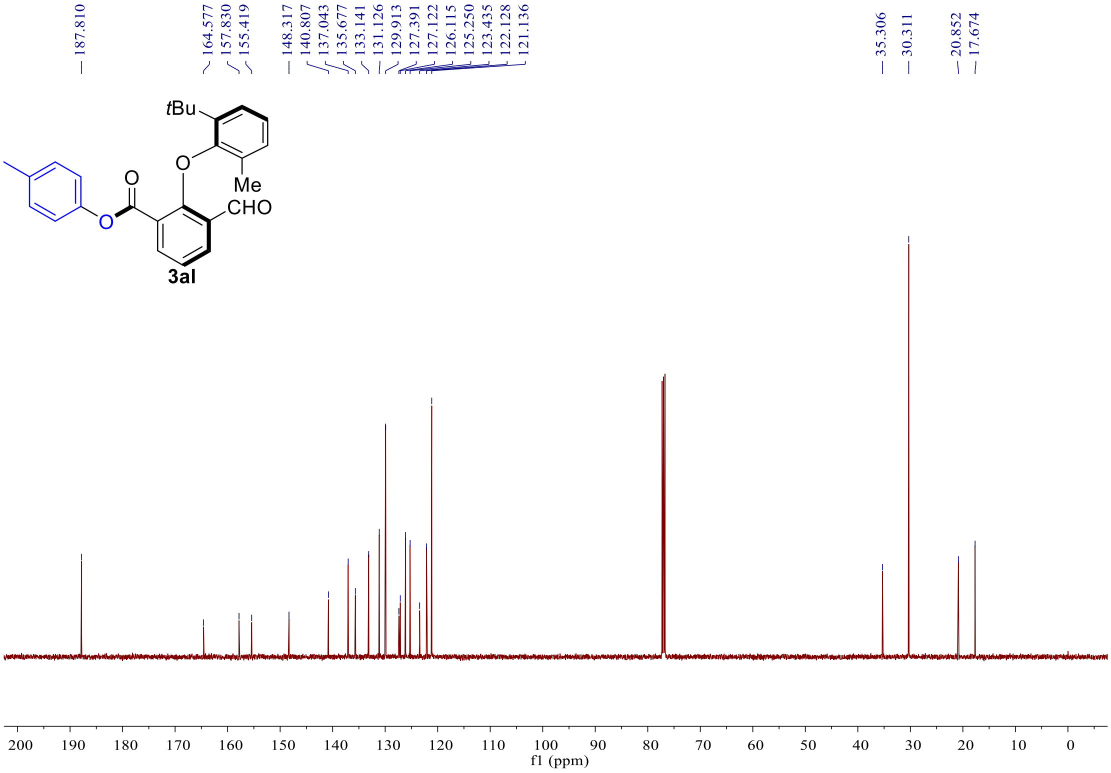
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of 3ak.



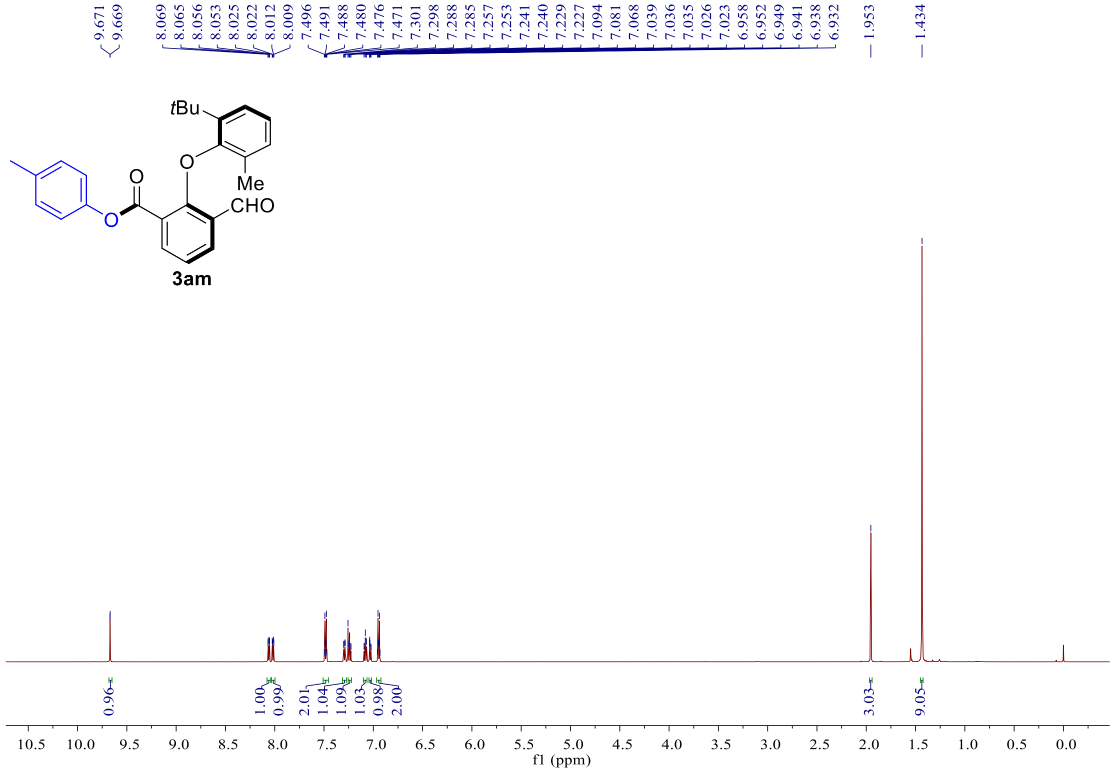
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3ak.



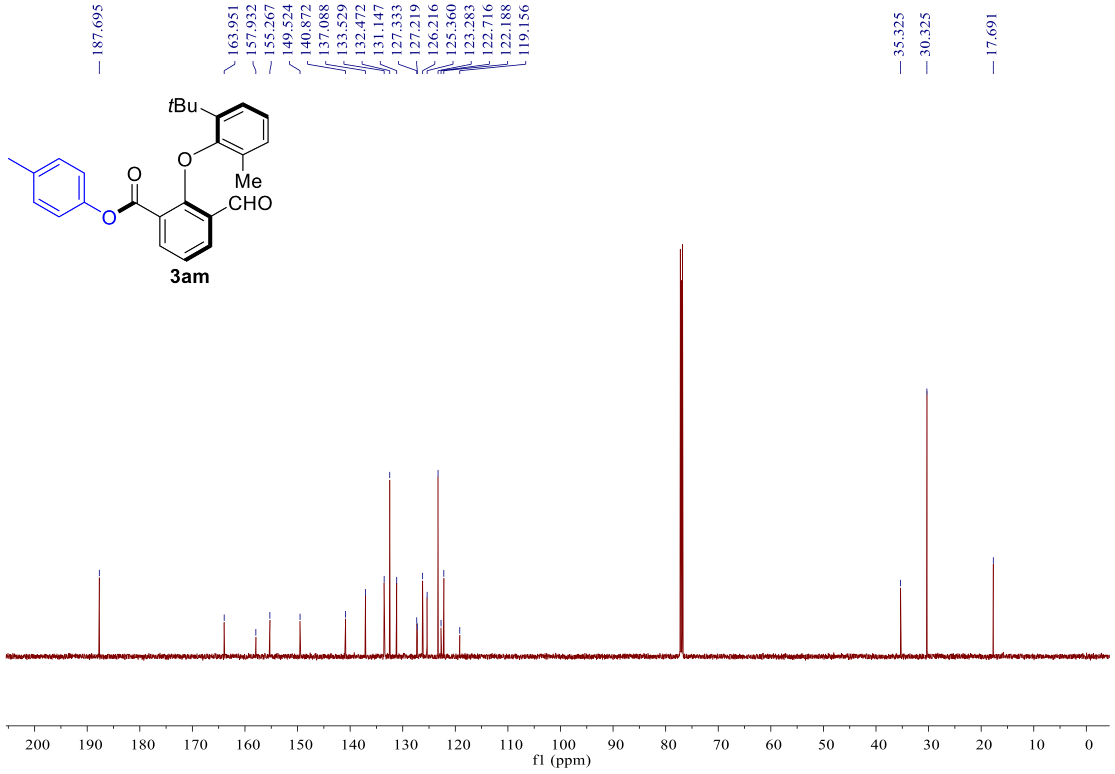
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3al.



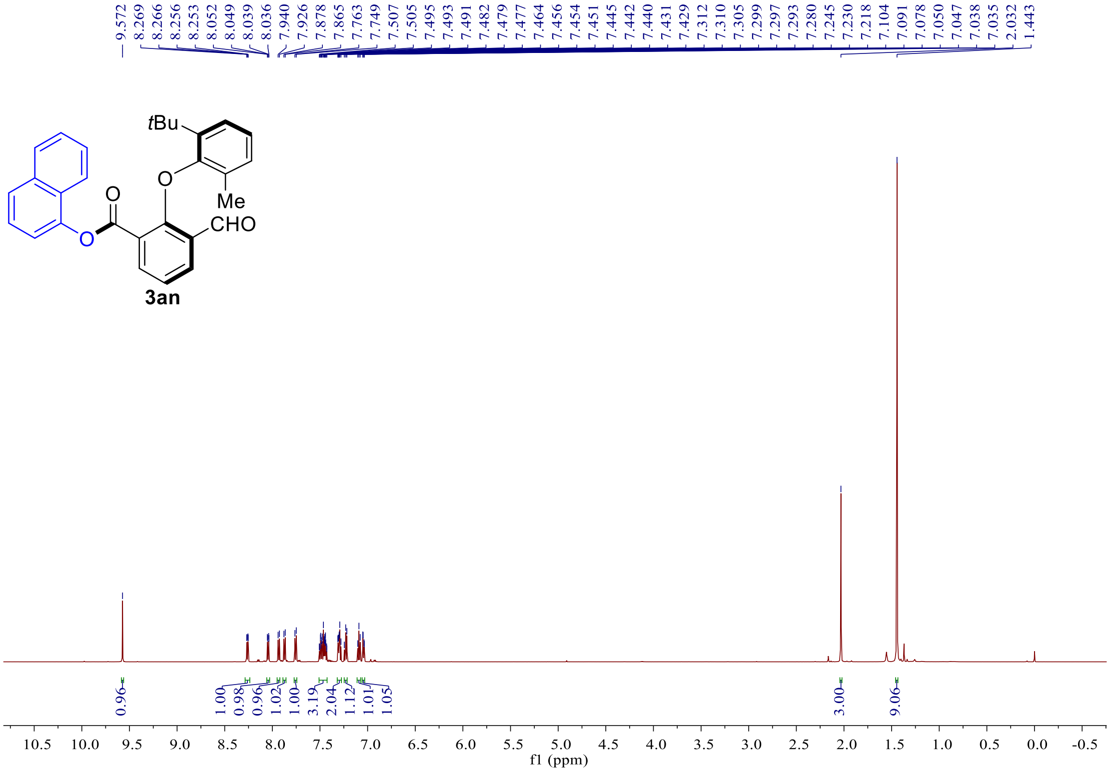
^{13}C NMR (125 MHz, CDCl$_3$) spectrum of 3al.



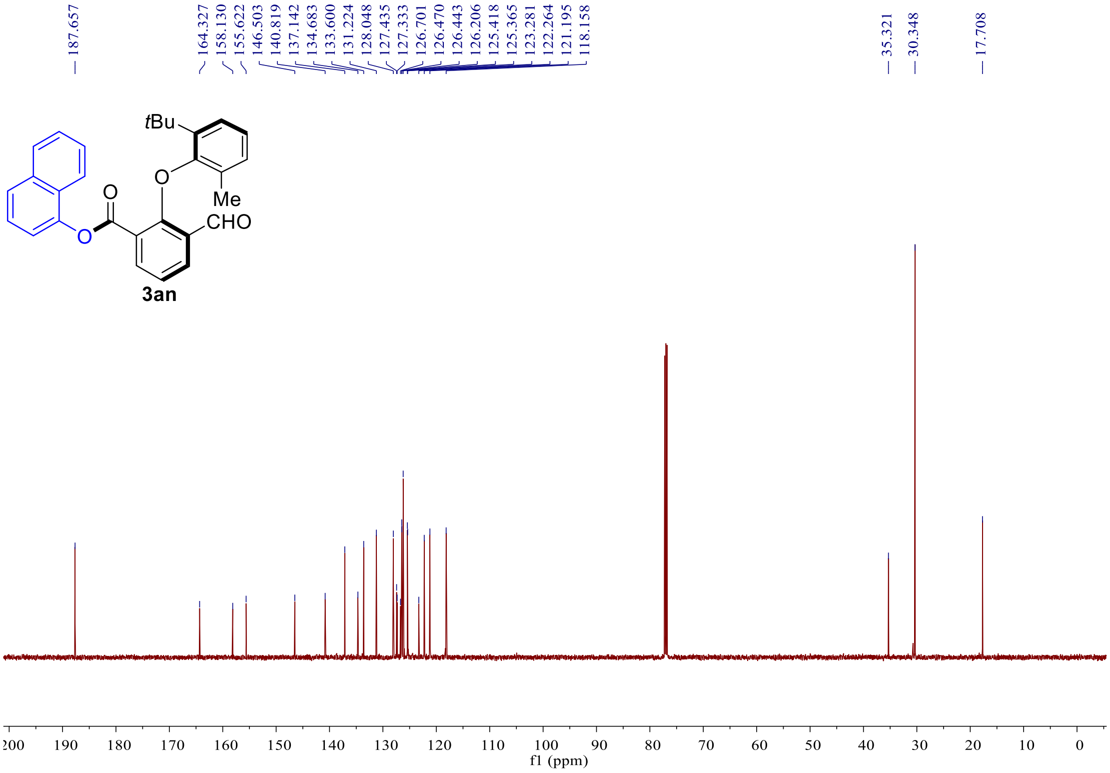
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3am.



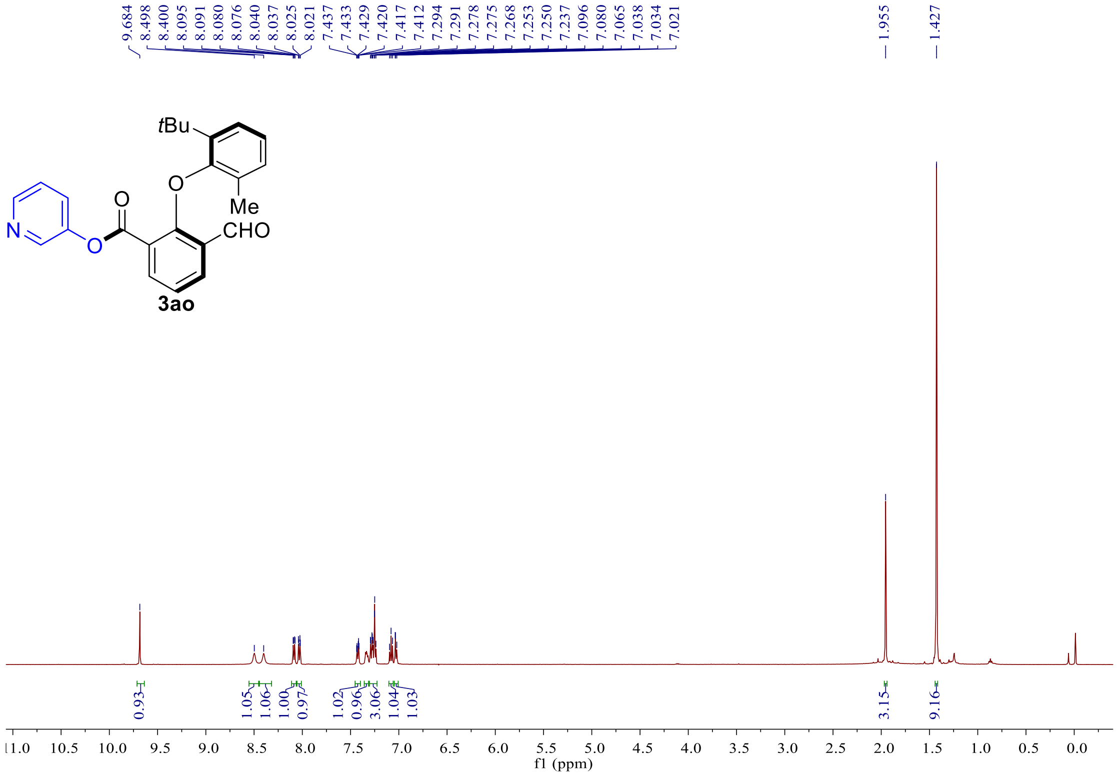
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3am.



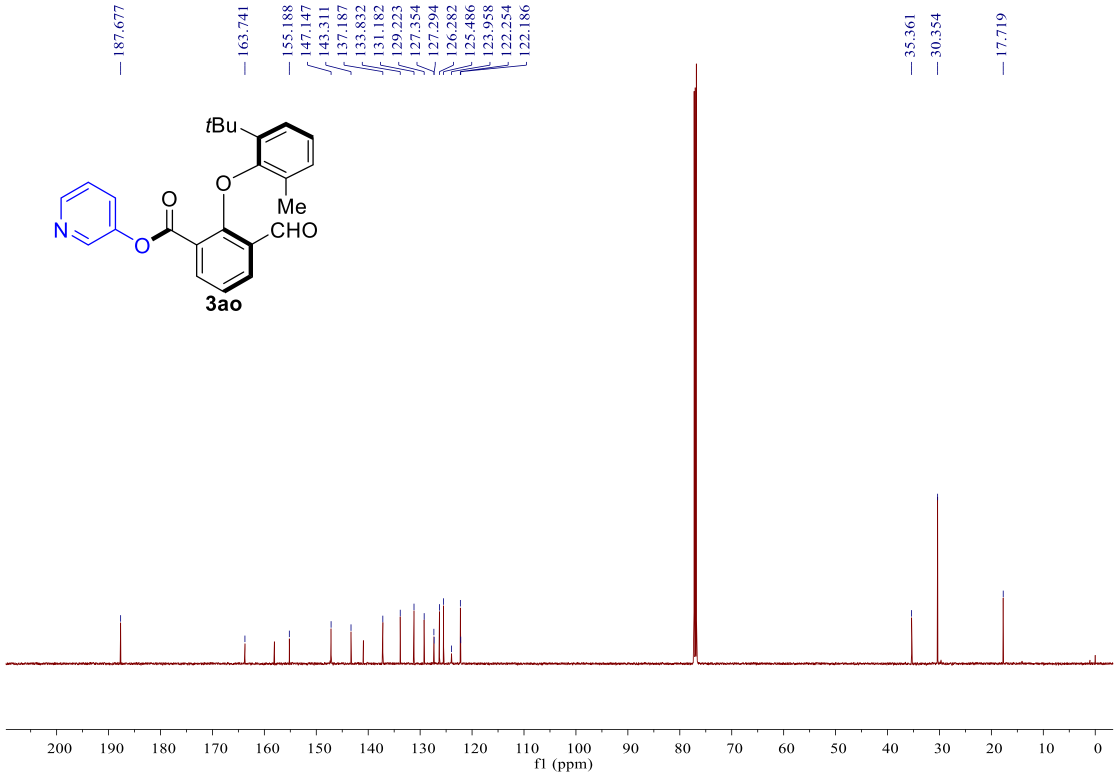
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of 3an.



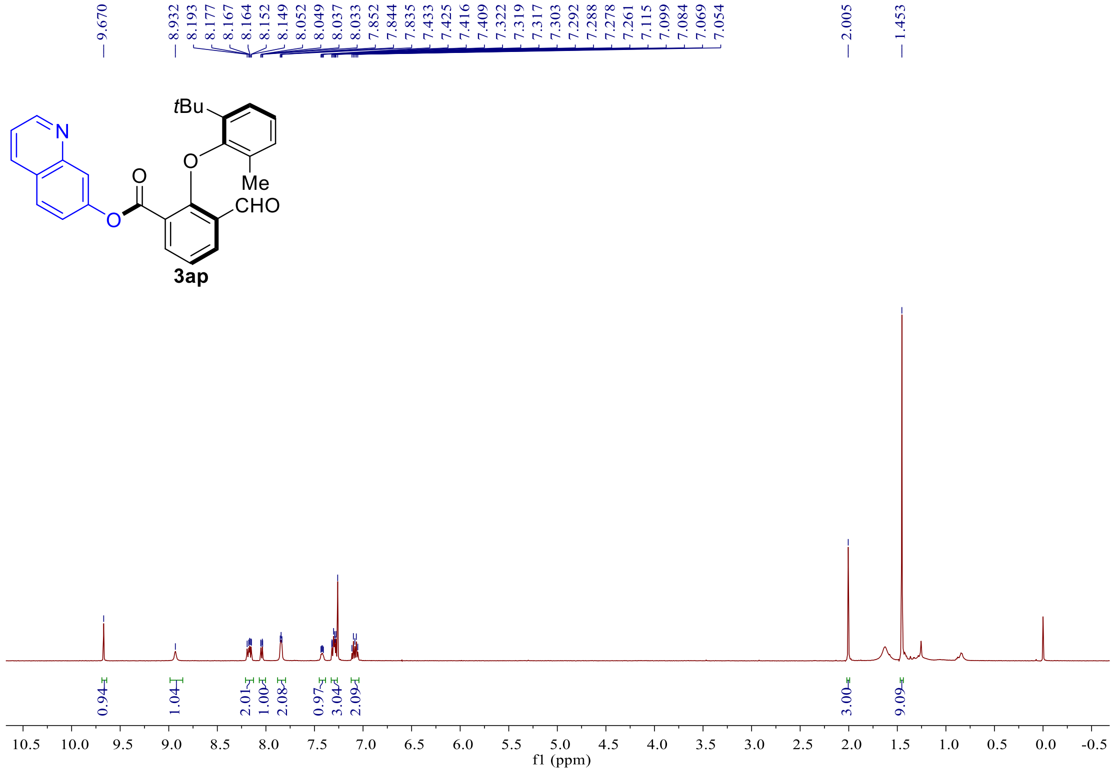
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3an.



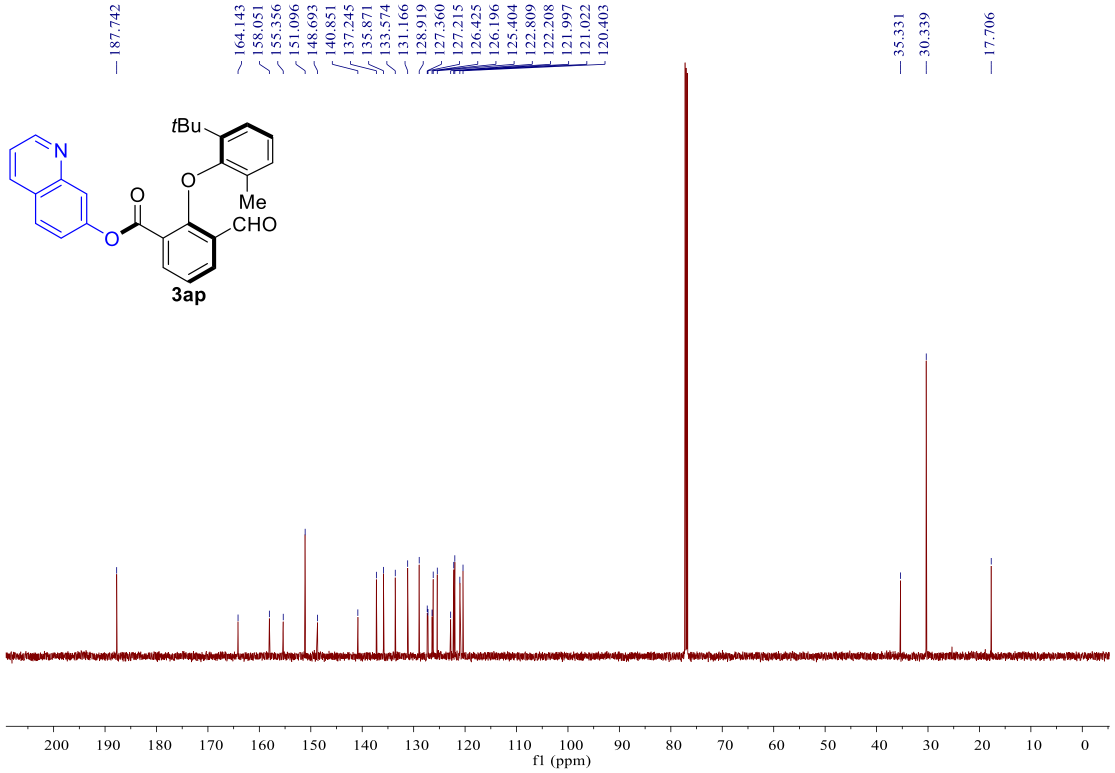
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3ao.



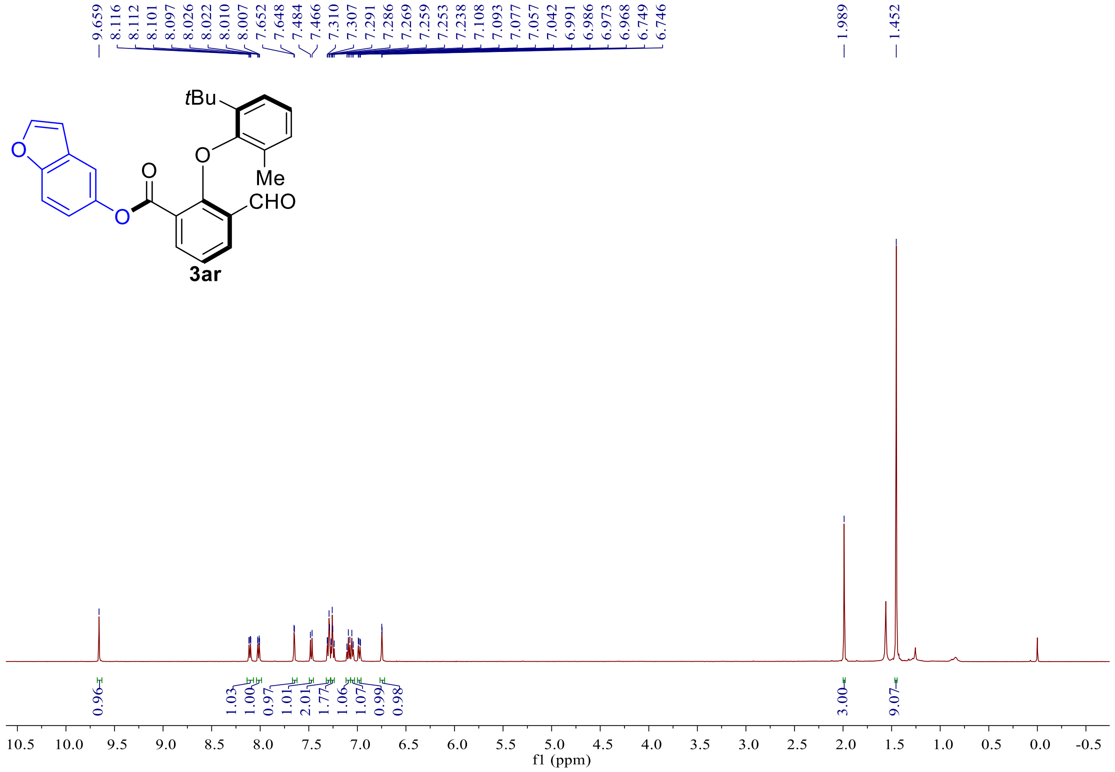
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3ao.



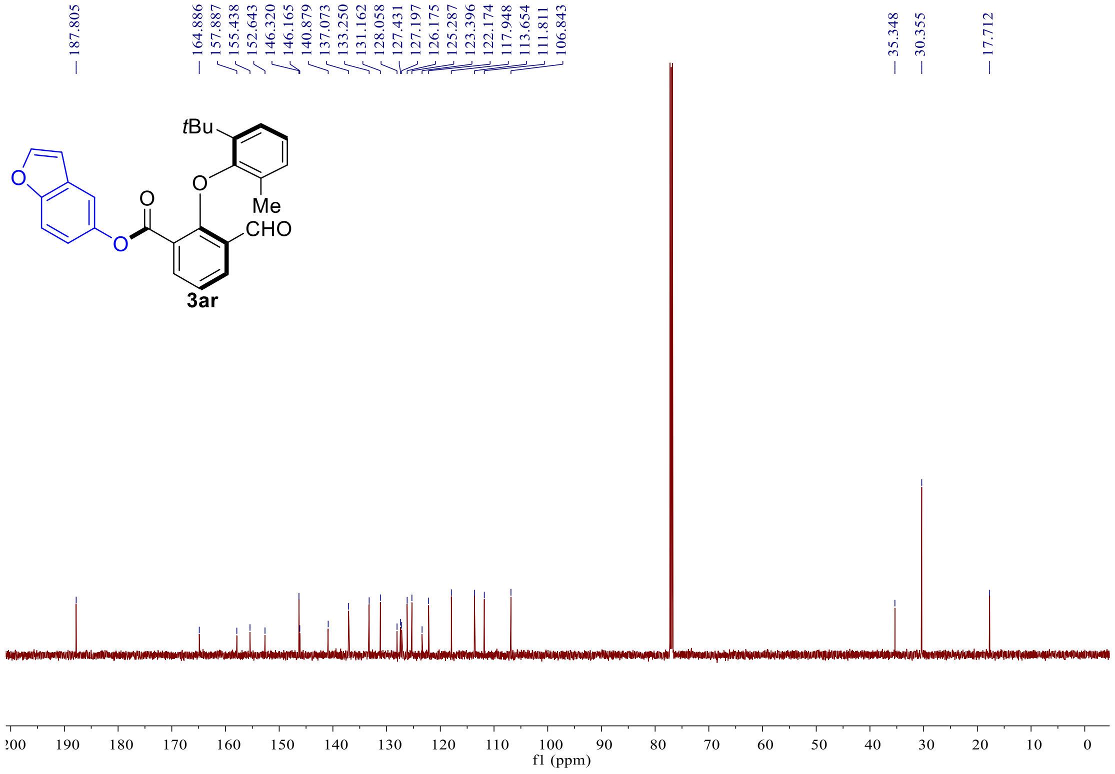
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3ap.



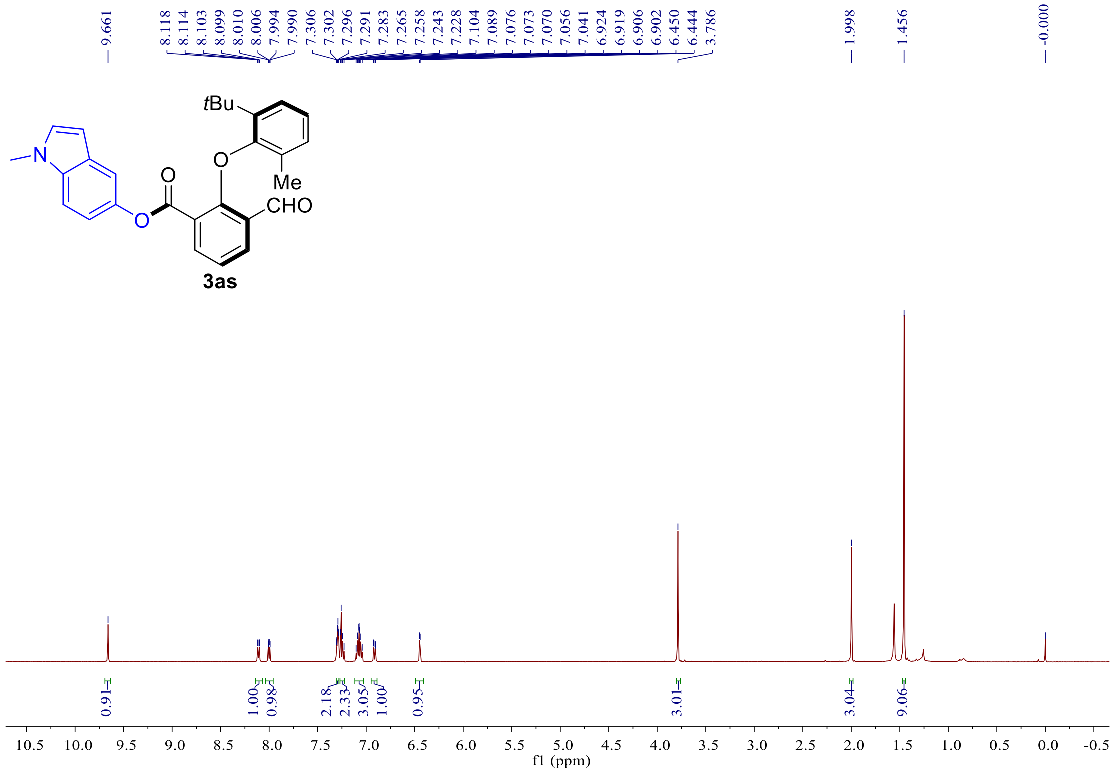
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3ap.



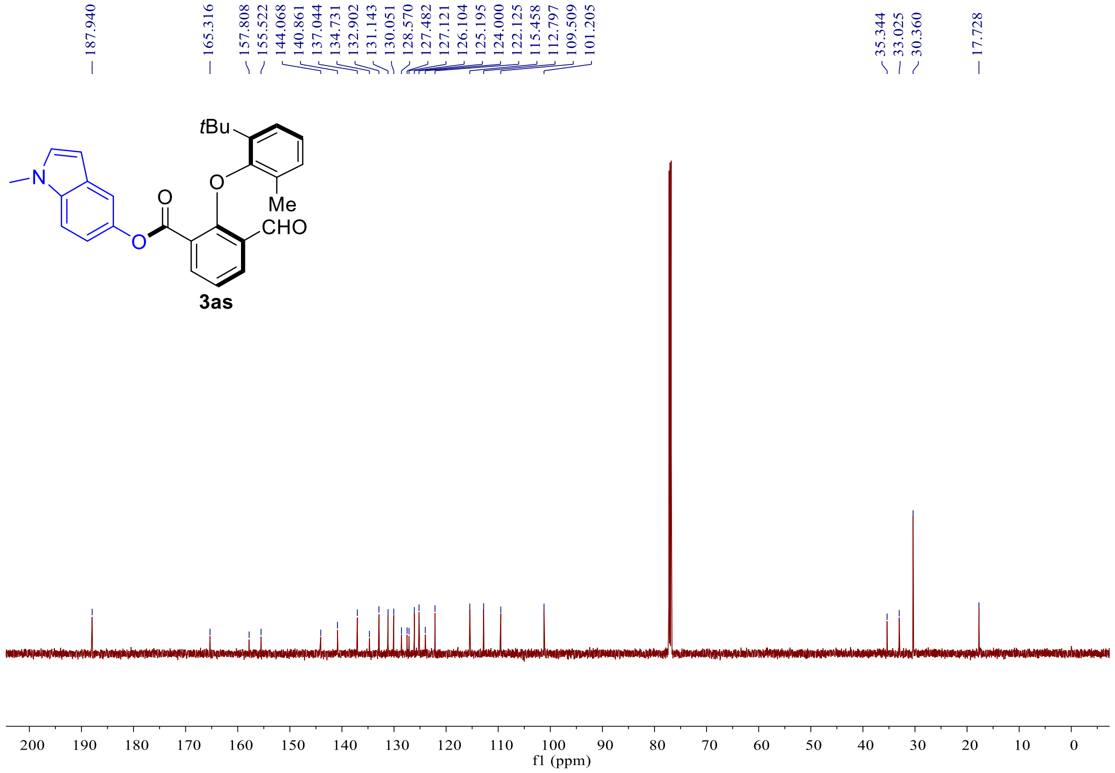
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3ar.



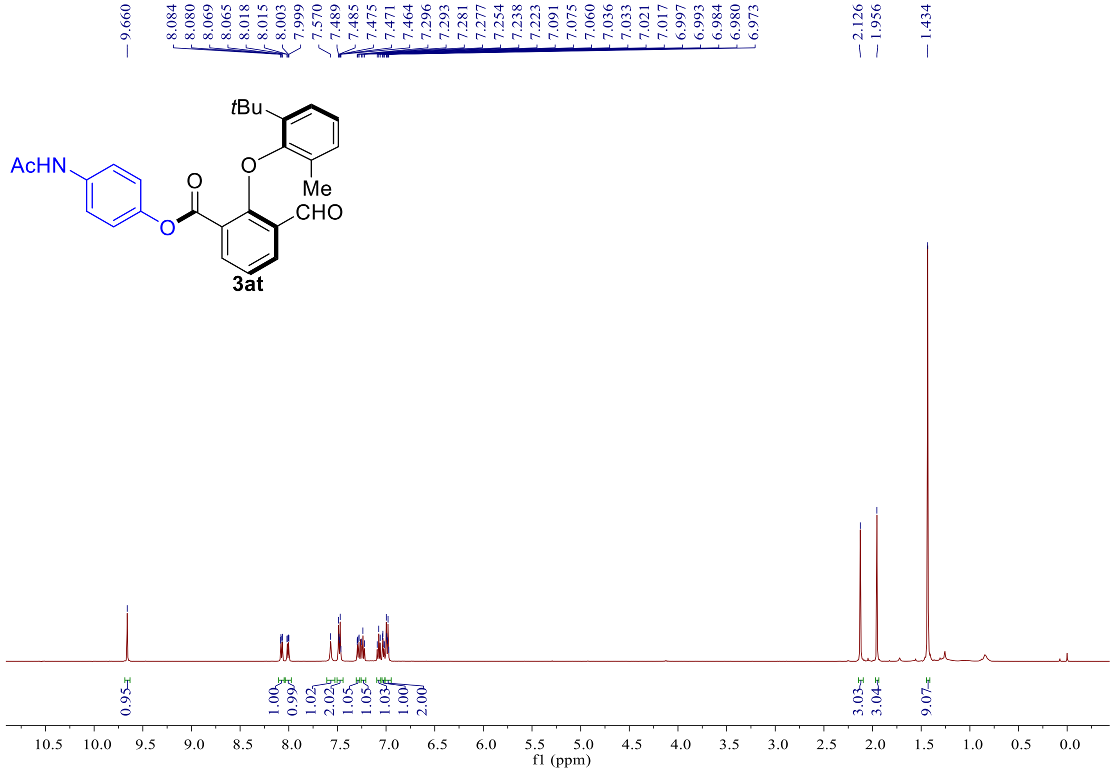
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3ar.



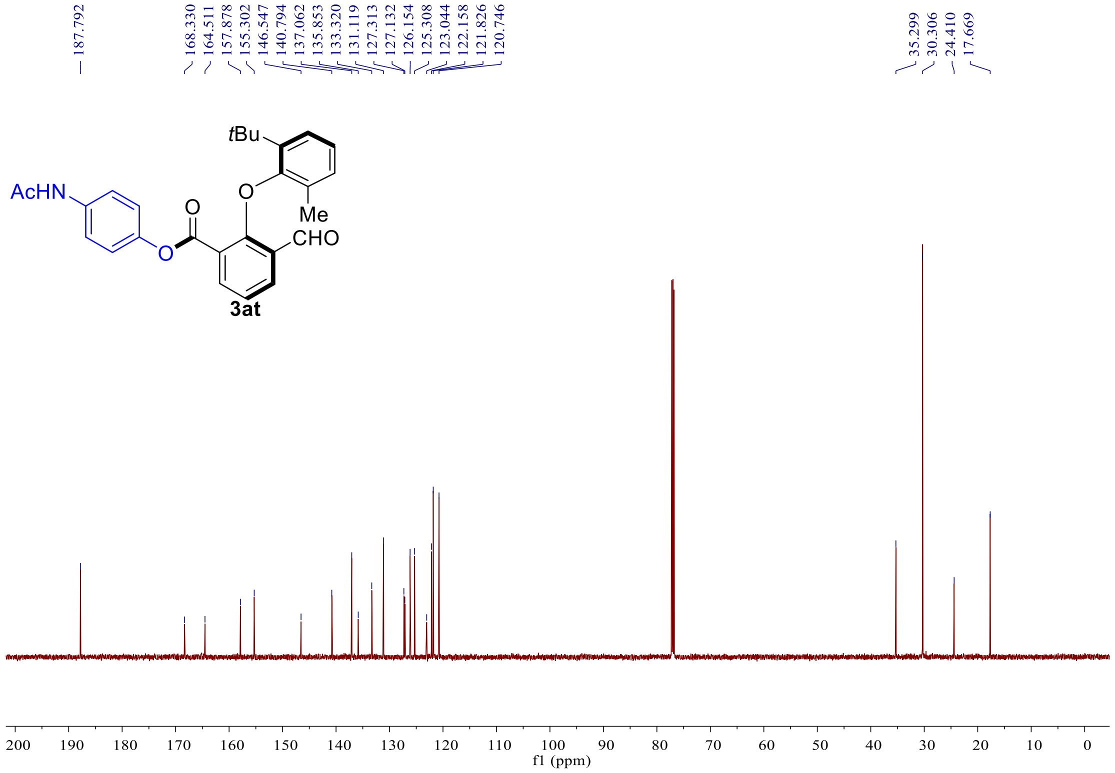
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3as.



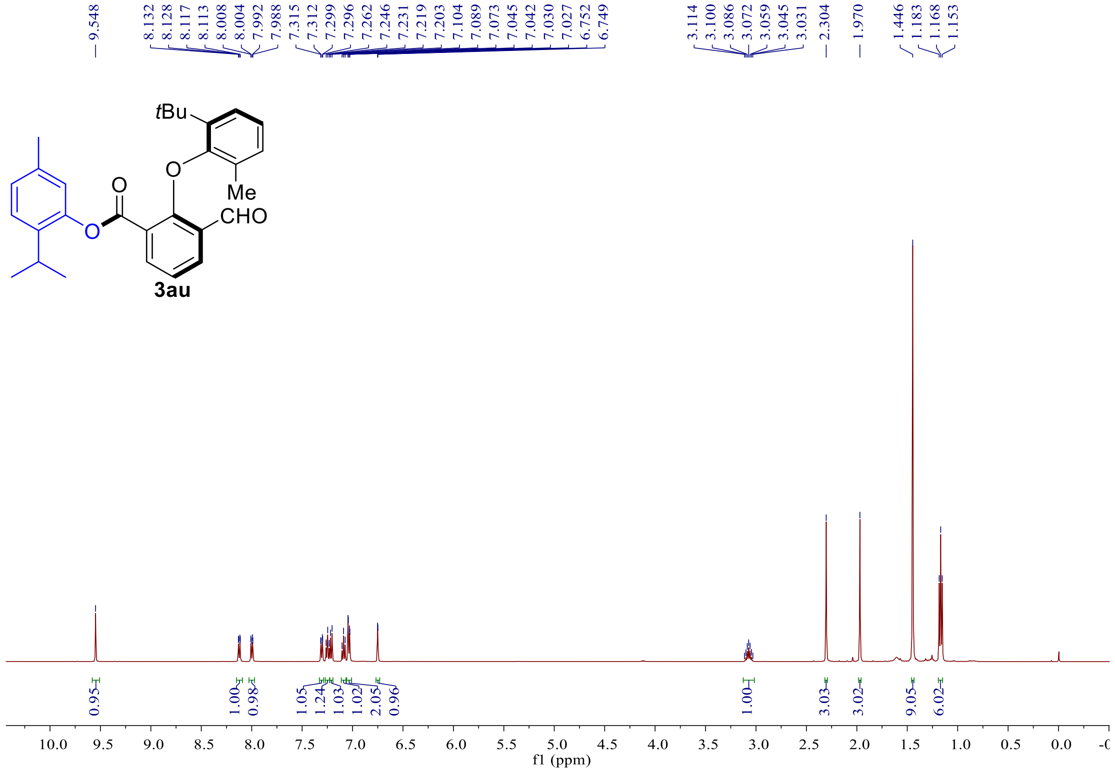
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3as.



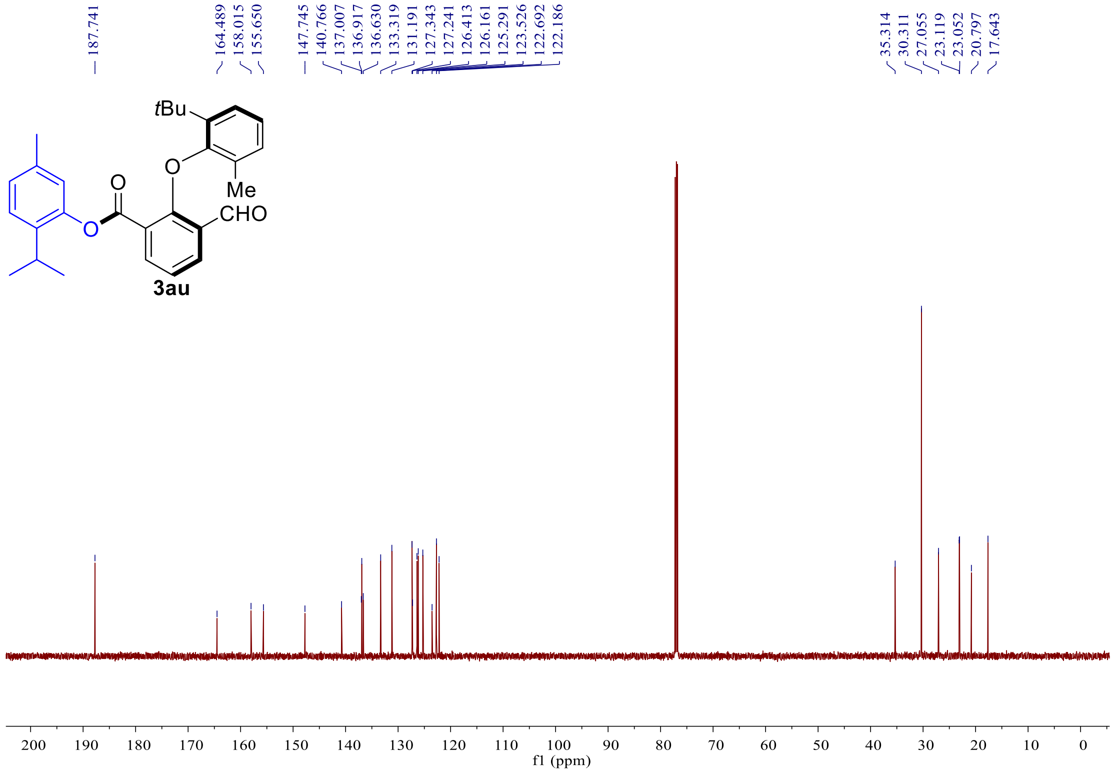
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3at.



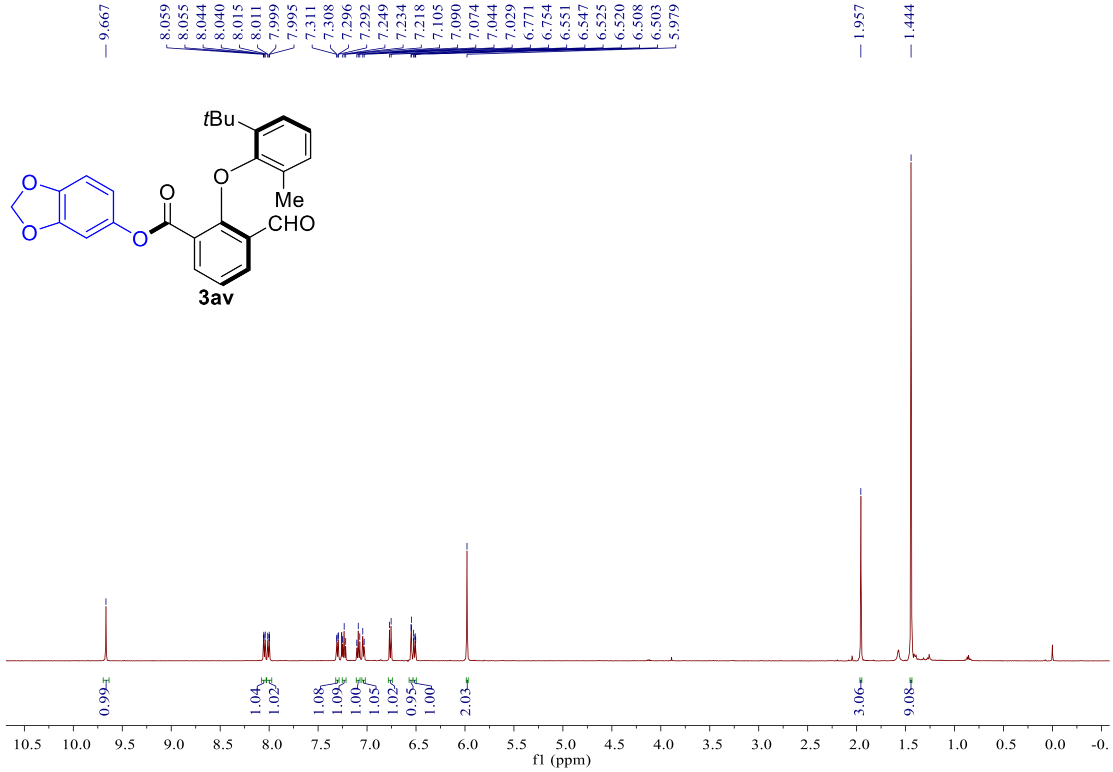
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3at.



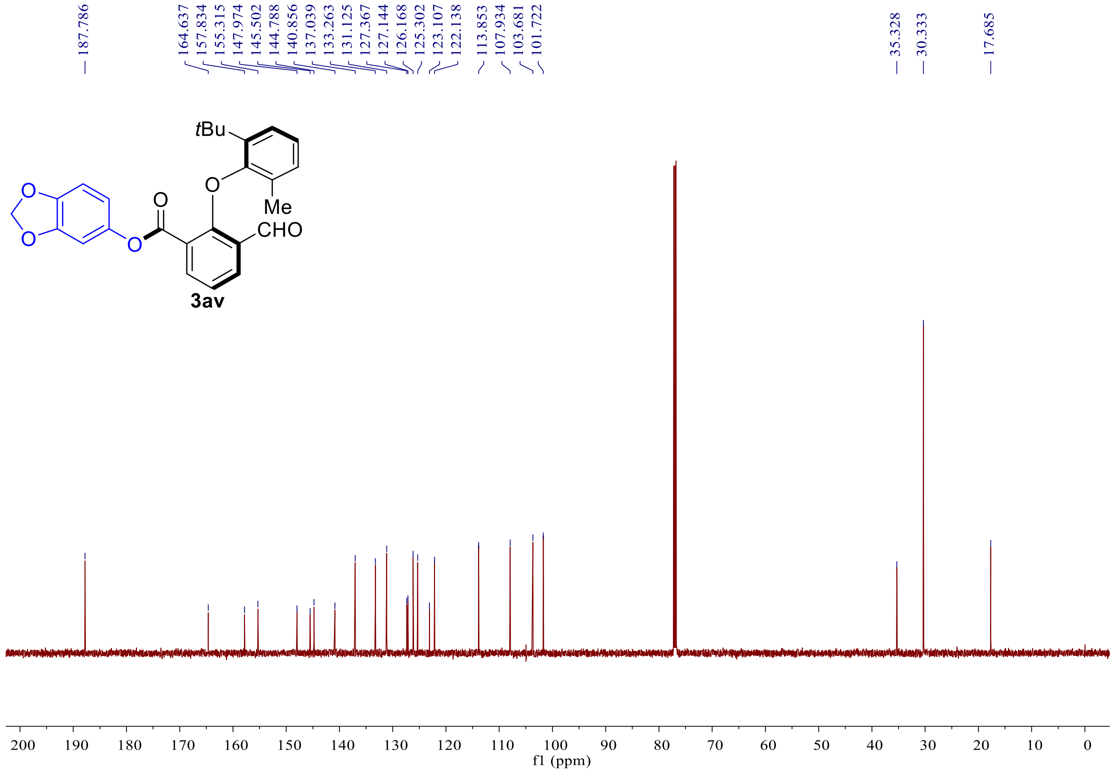
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3au.



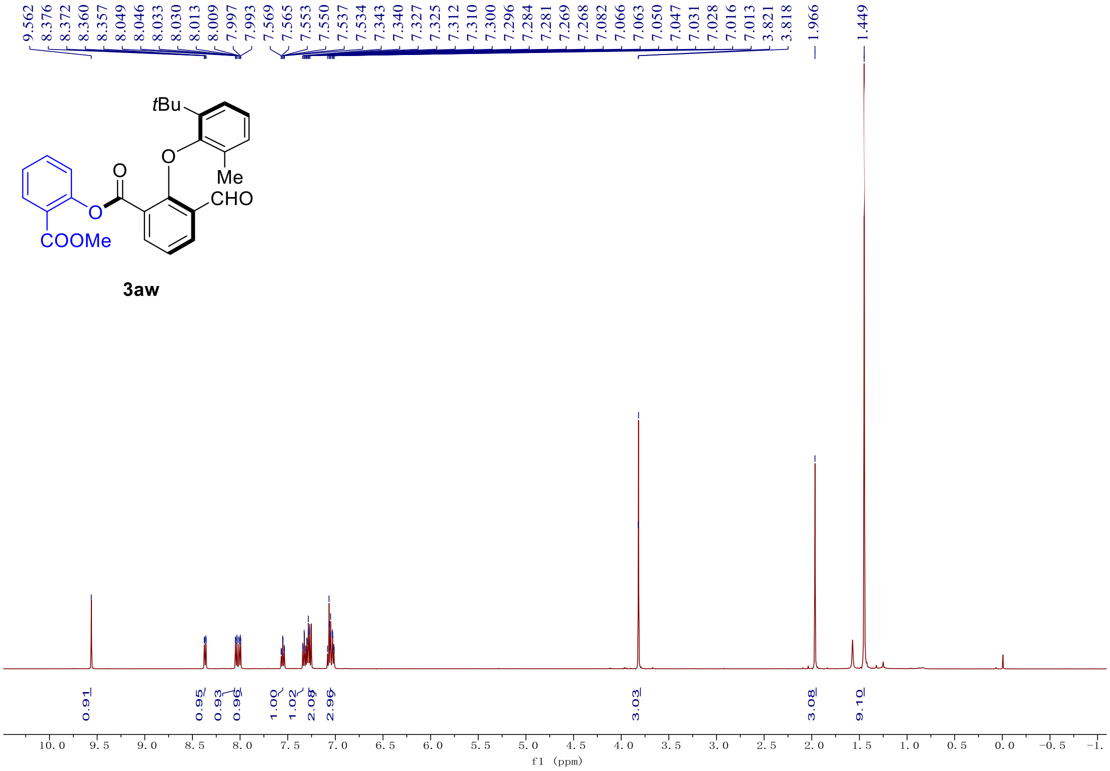
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3au.



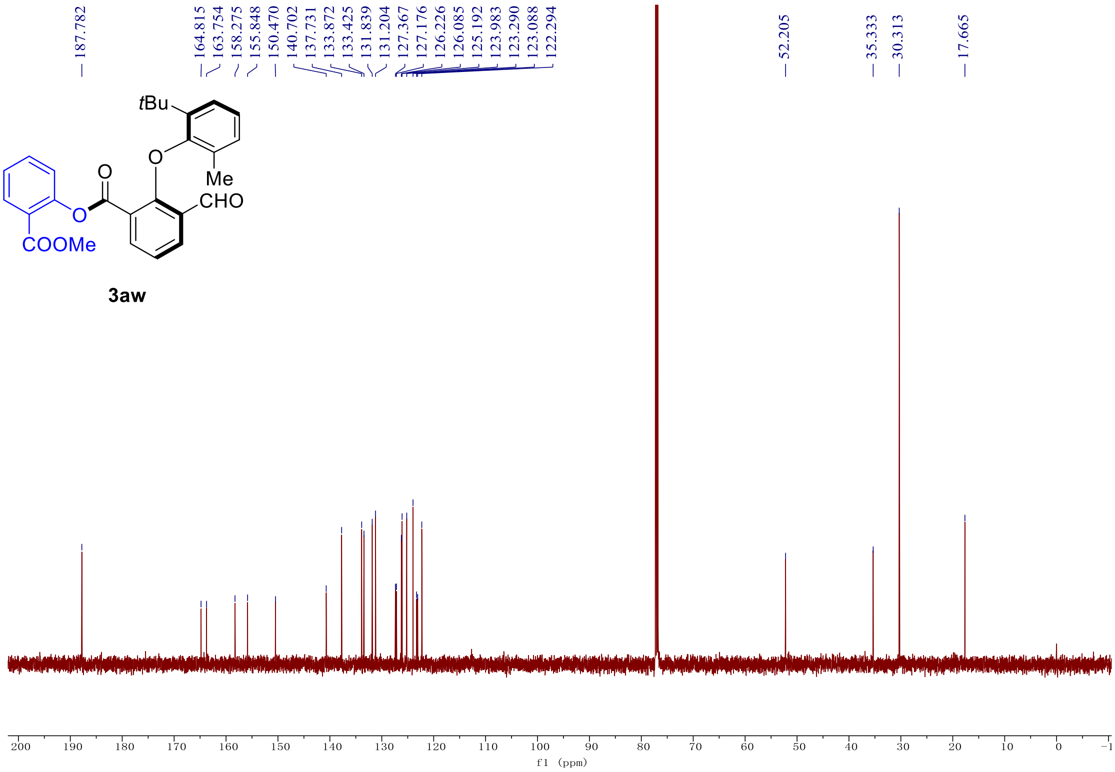
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3av.



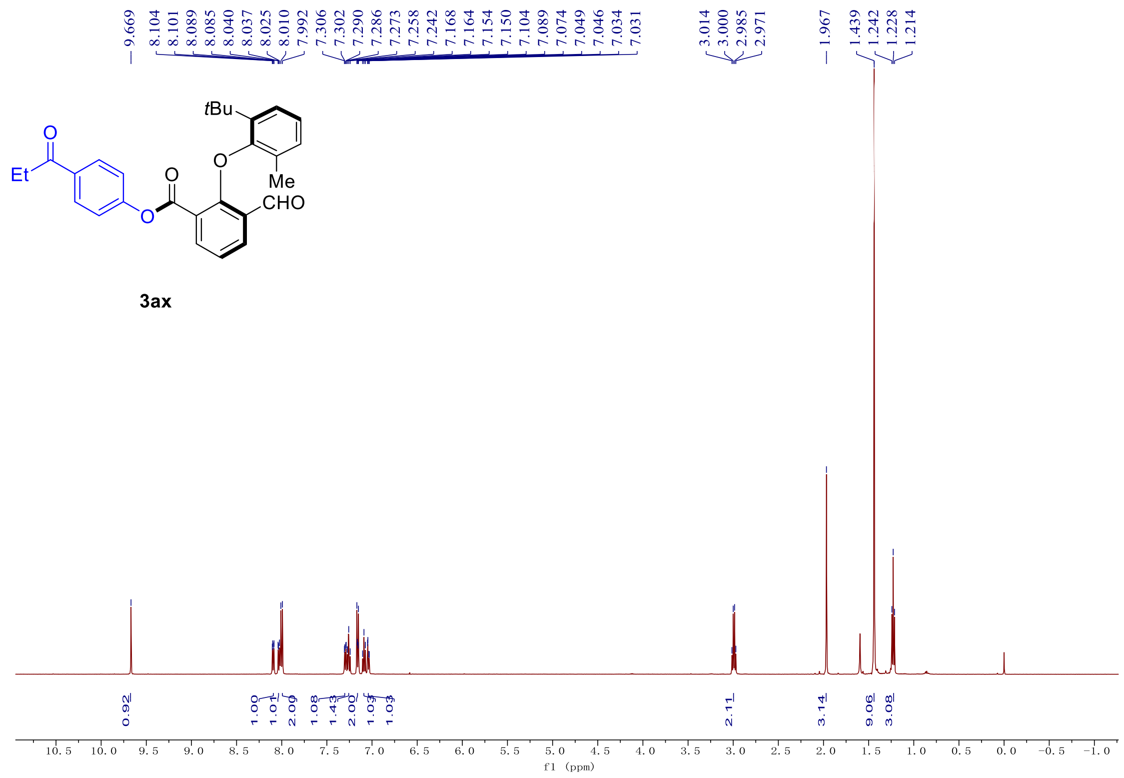
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3av.



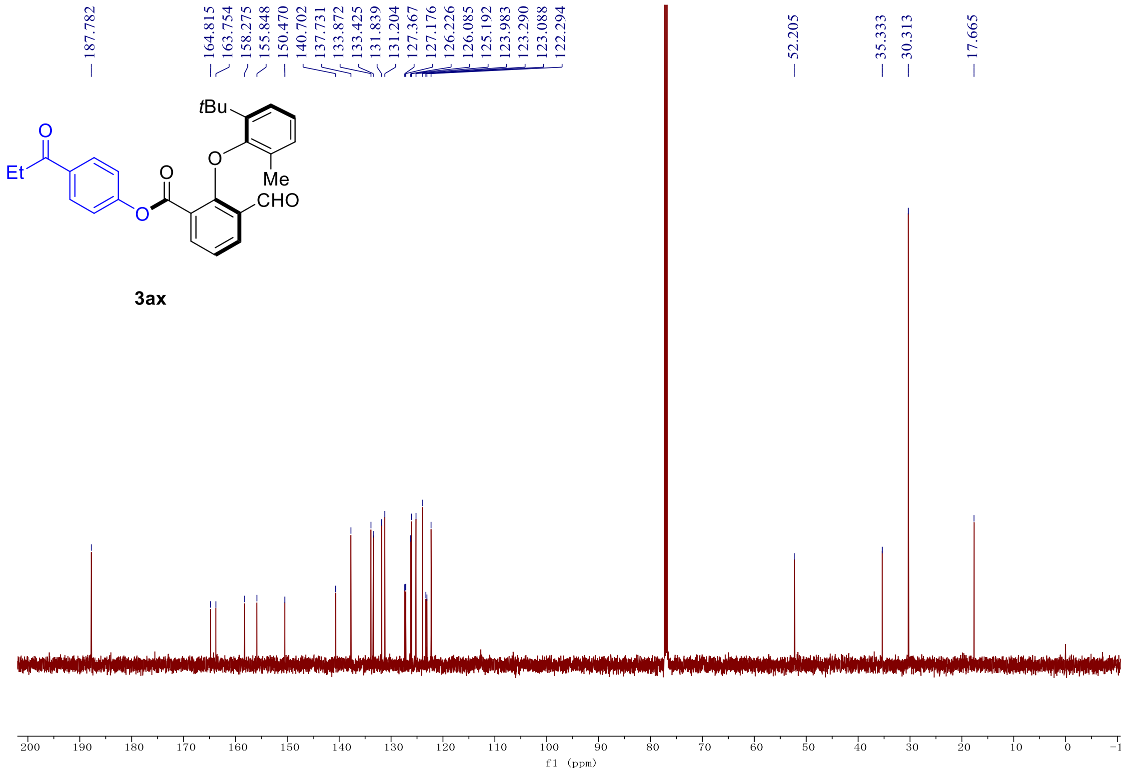
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3aw.



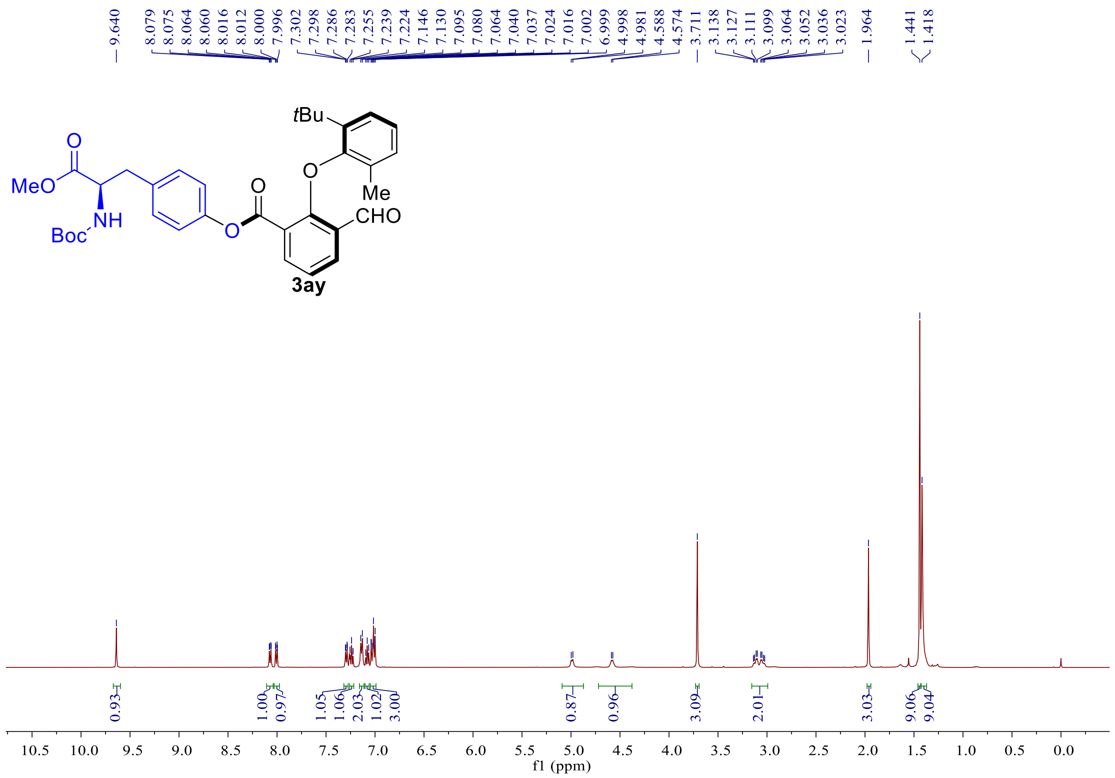
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3aw.



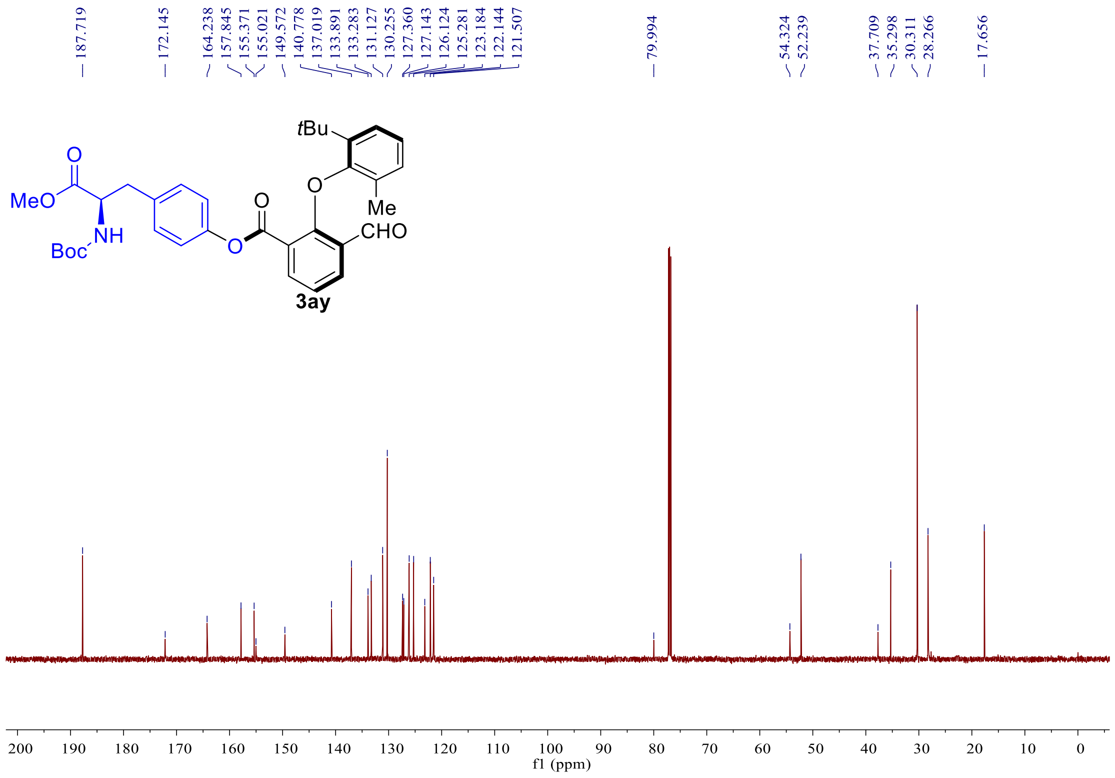
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ax.



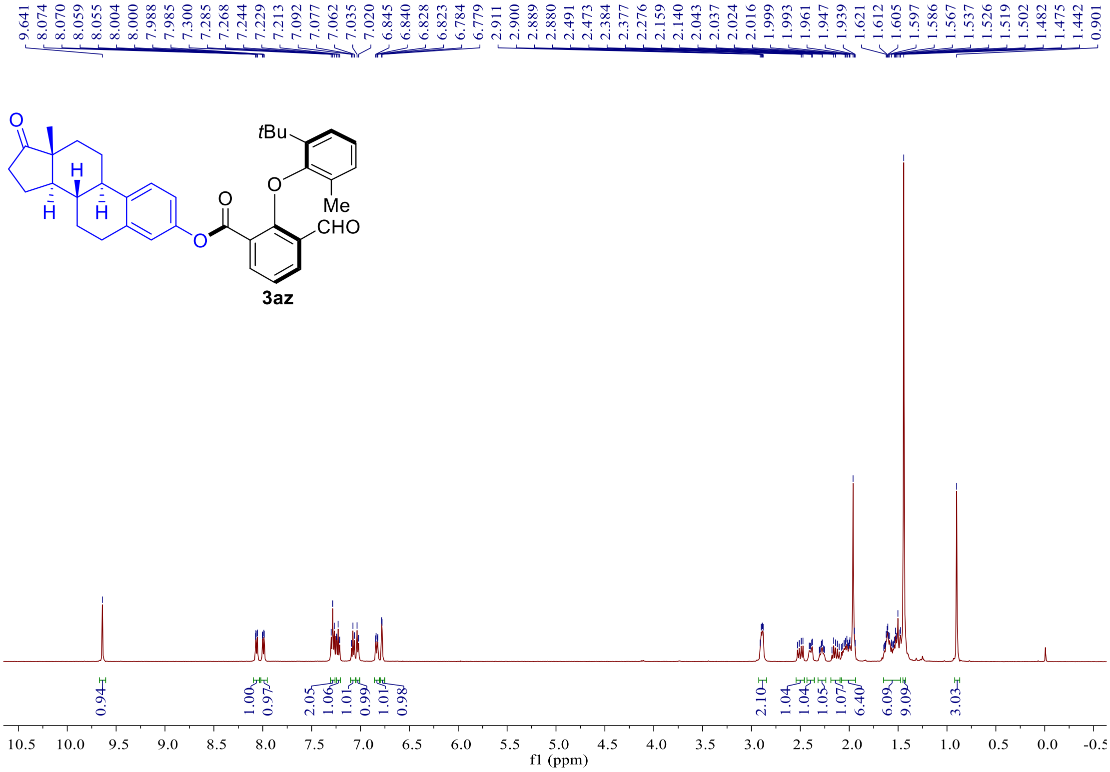
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of 3ax.



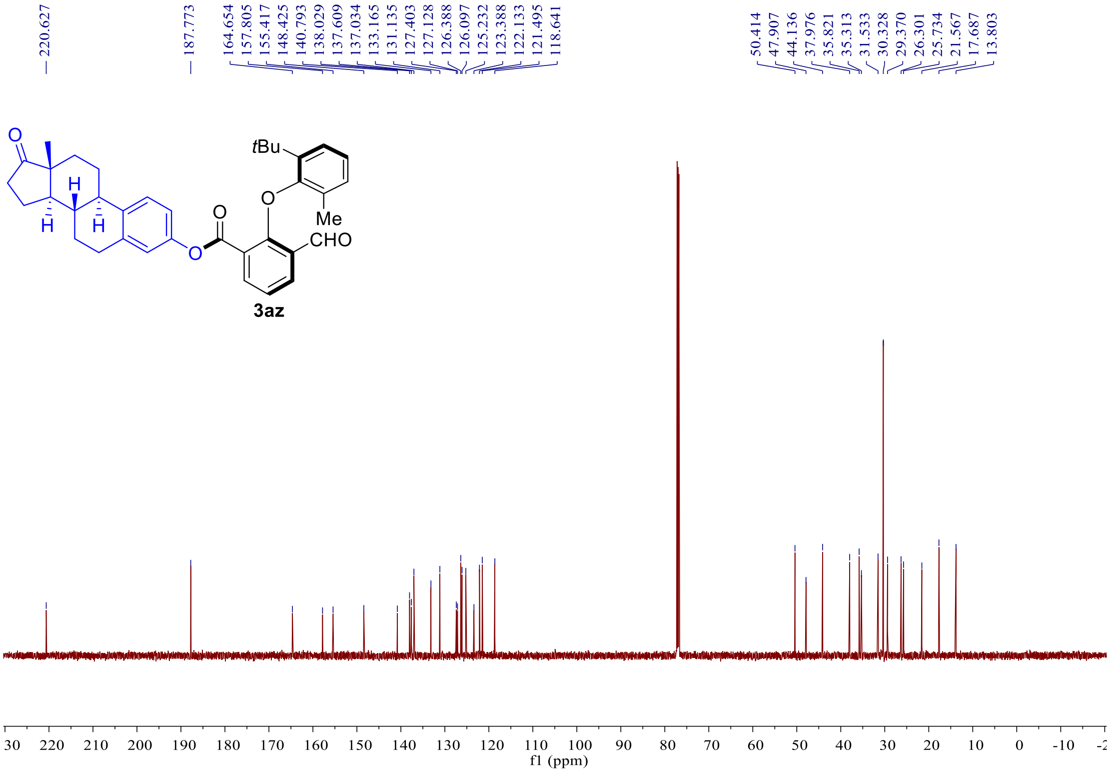
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3ay.



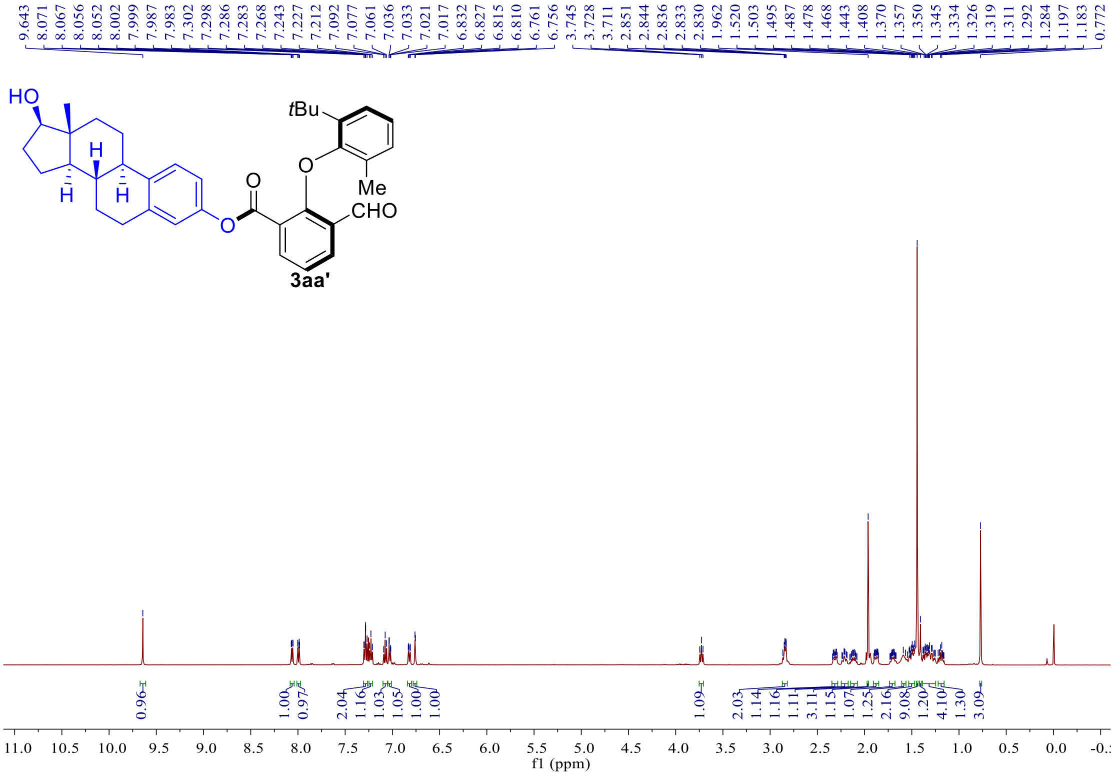
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3ay.



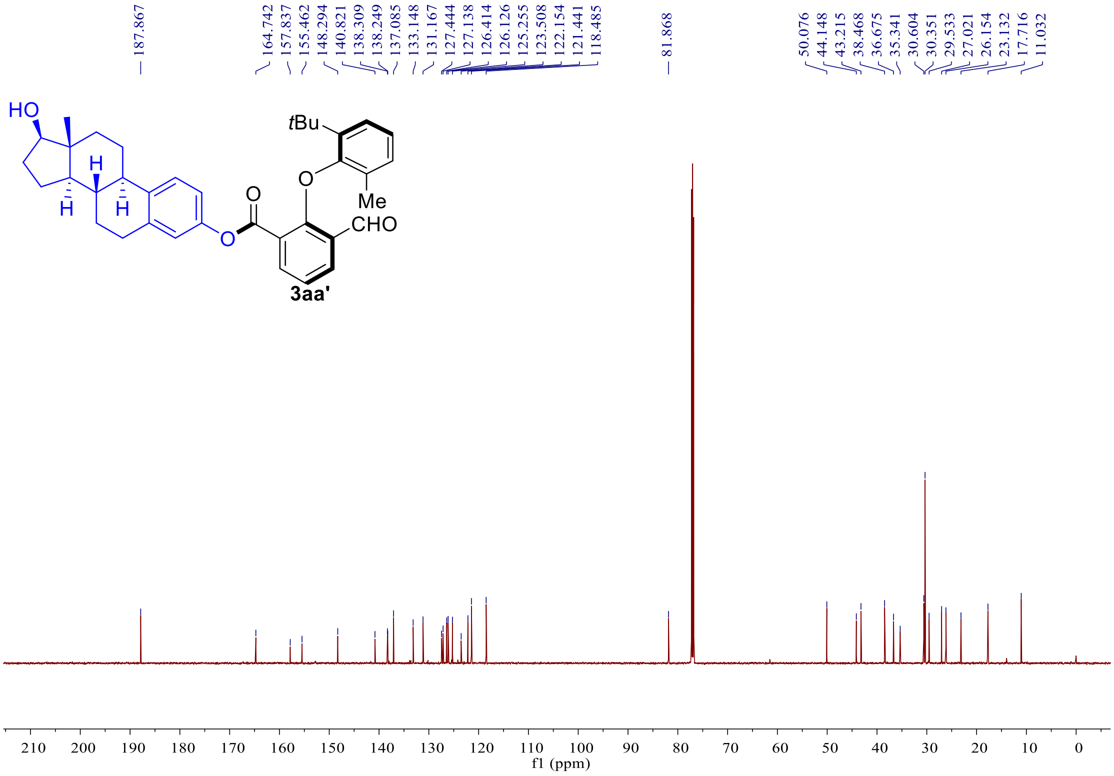
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3az.



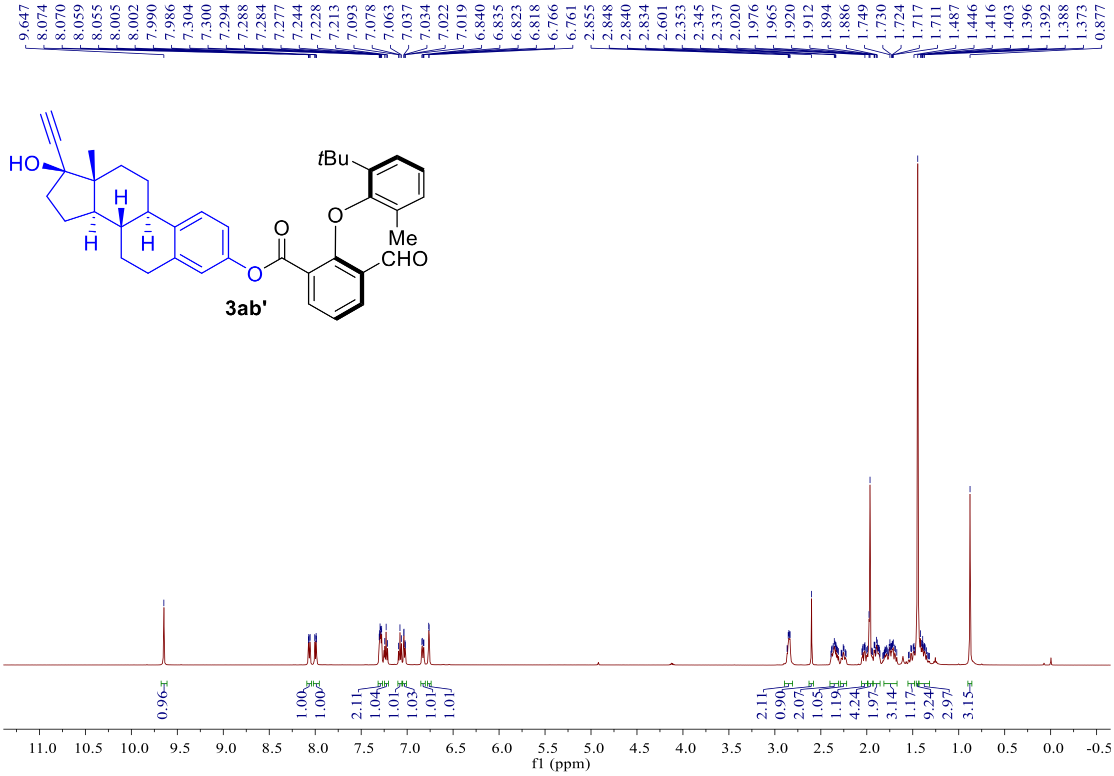
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3az.



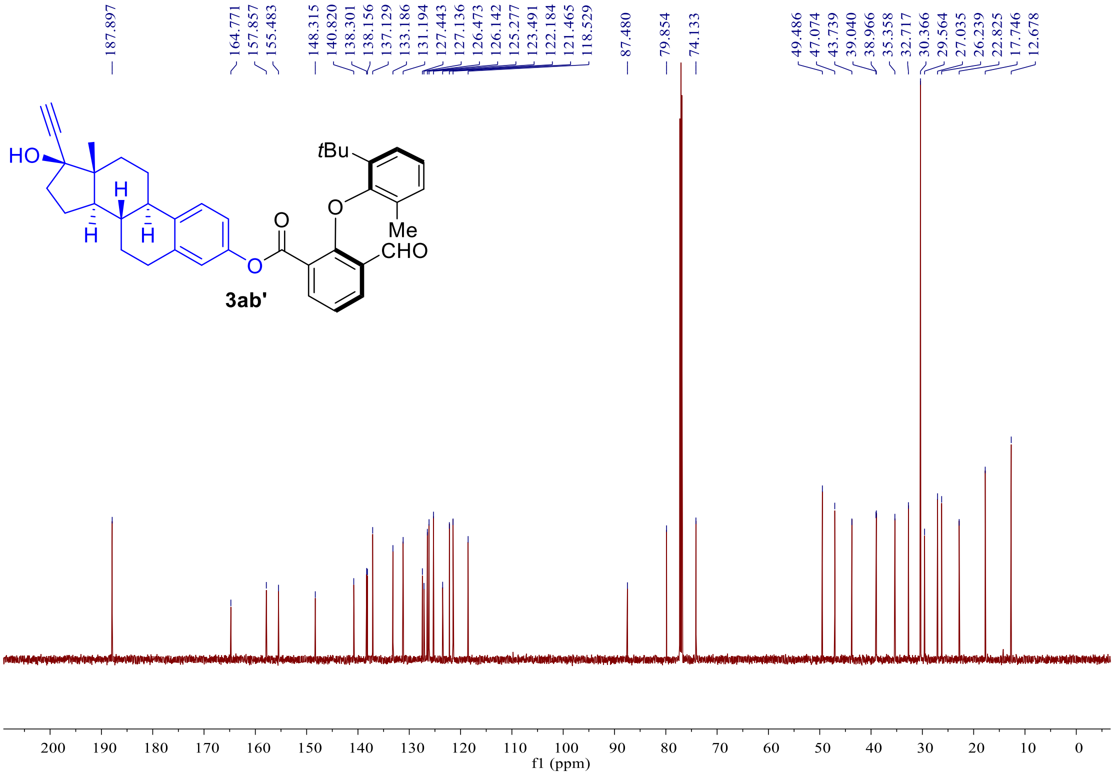
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3aa'.



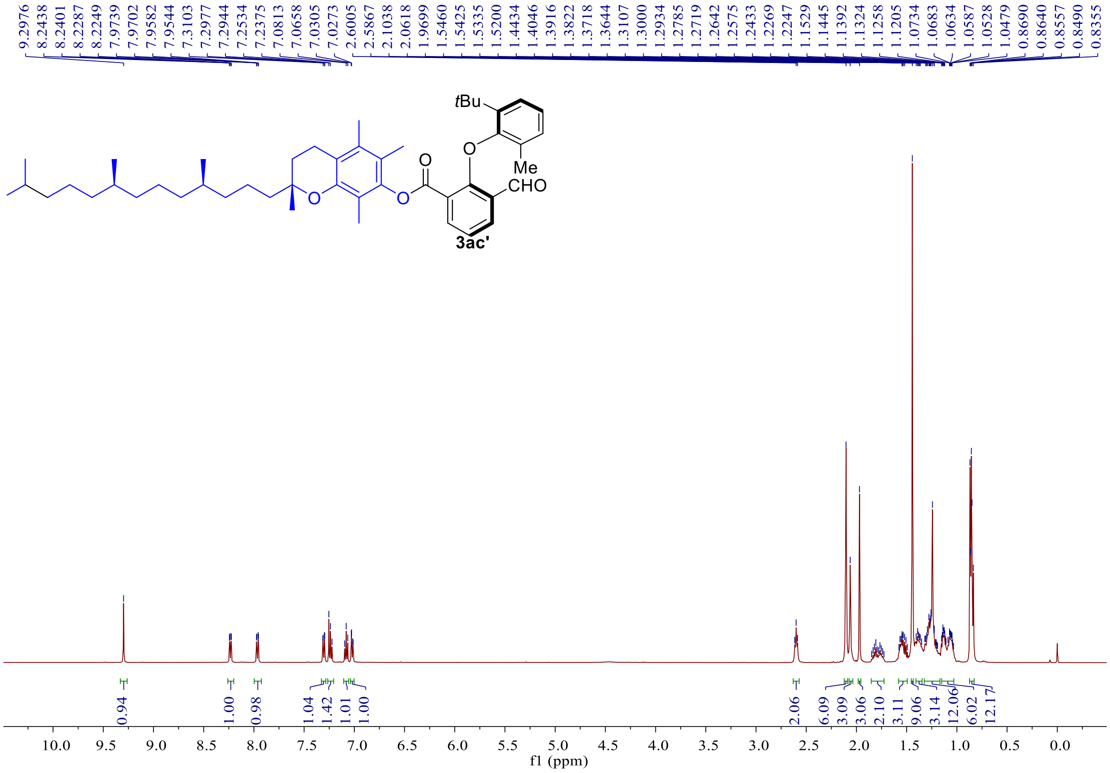
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3aa'.



^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3ab’.



^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3ab’.



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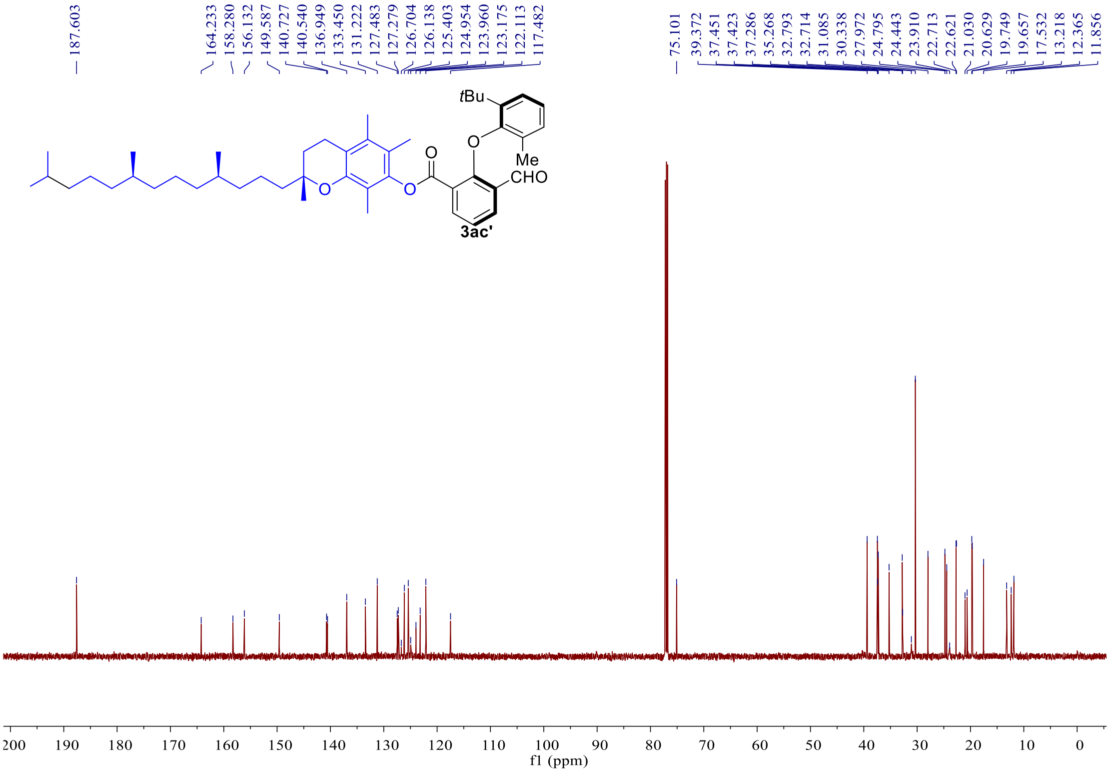
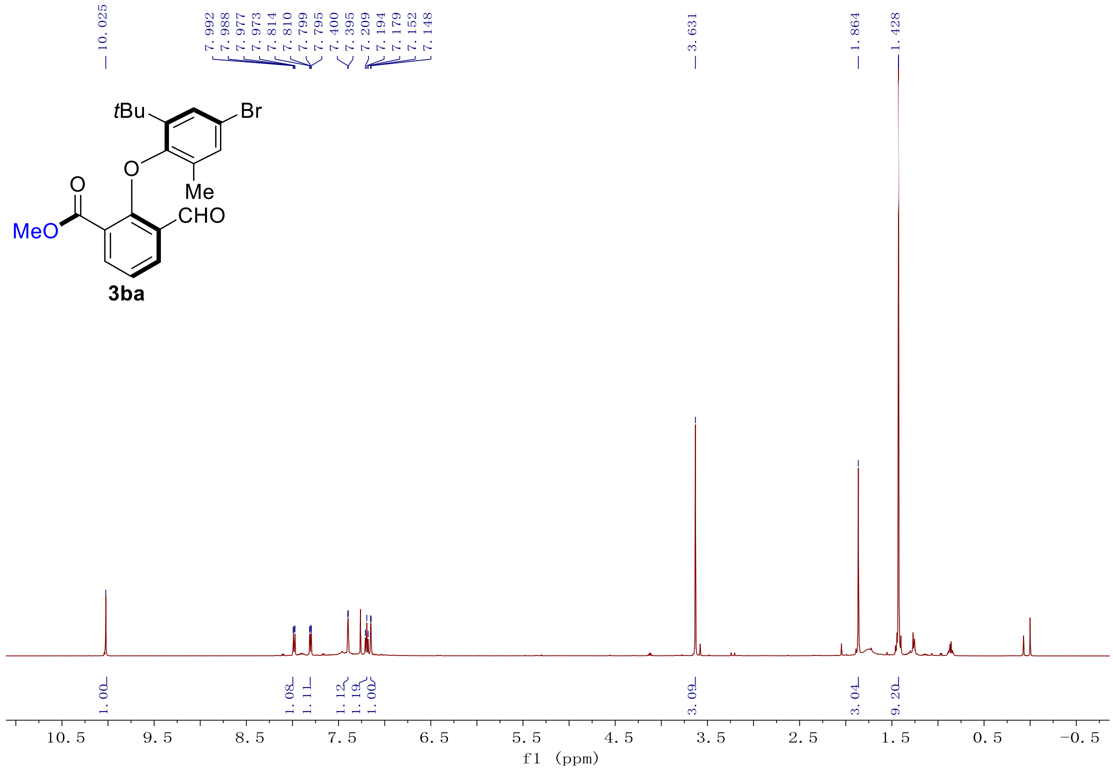
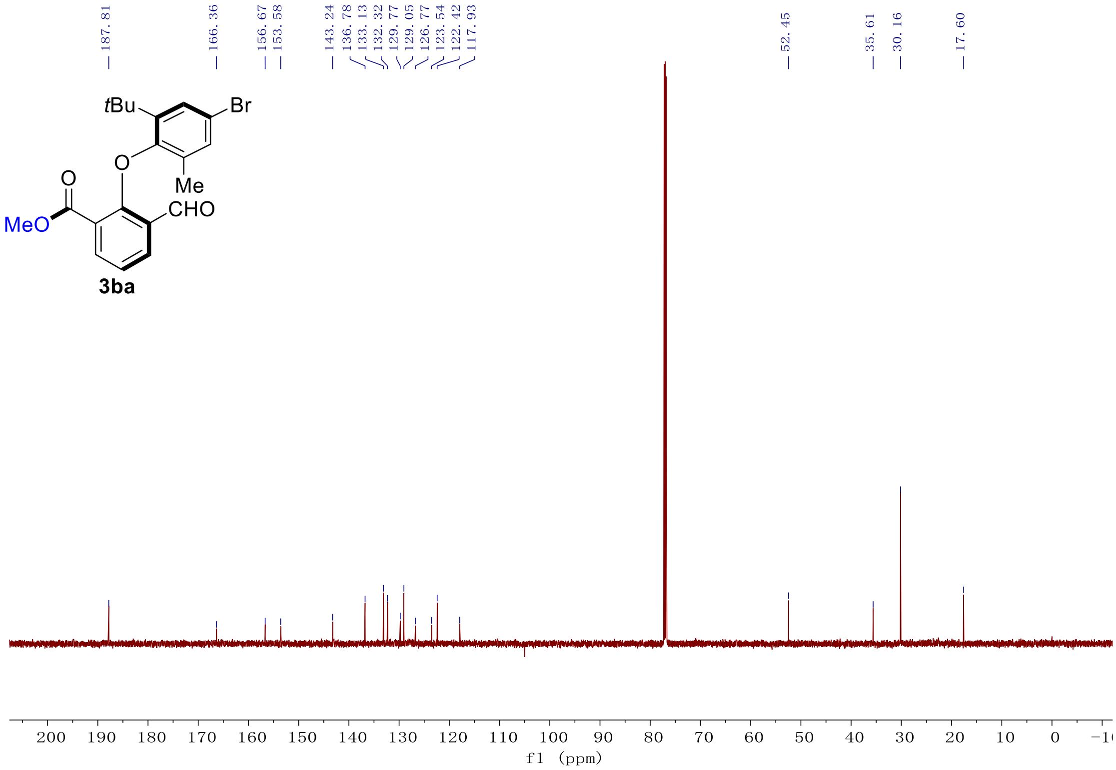


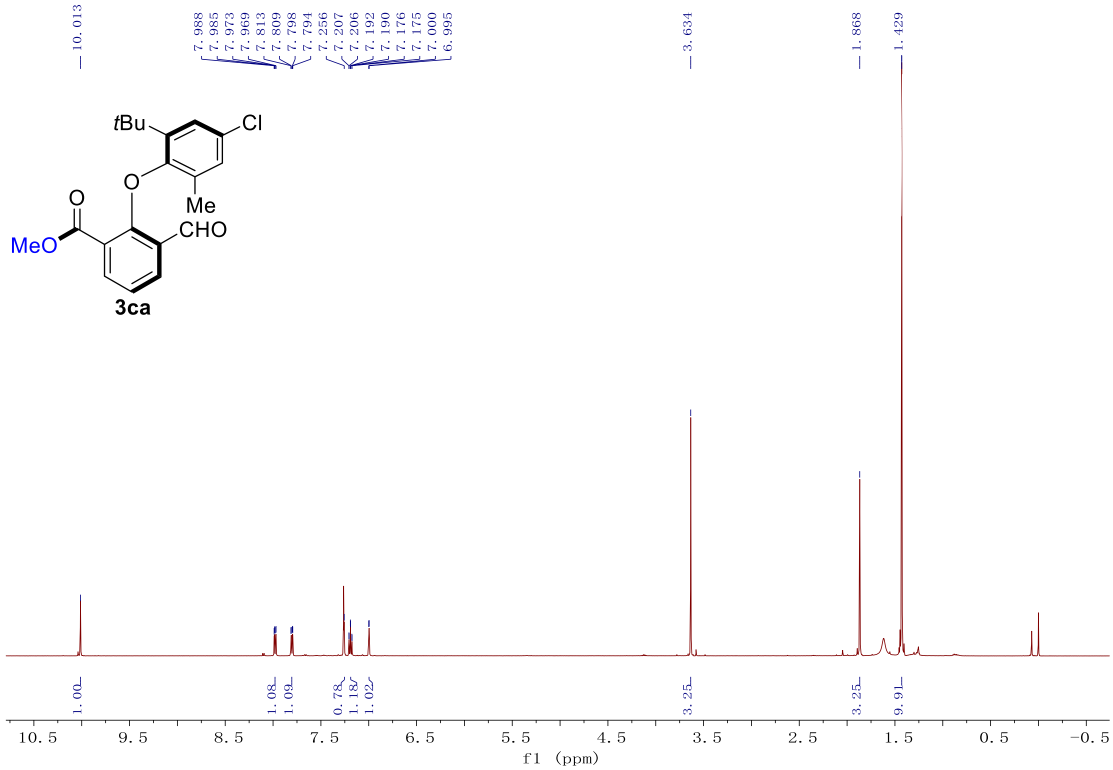
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ac'.



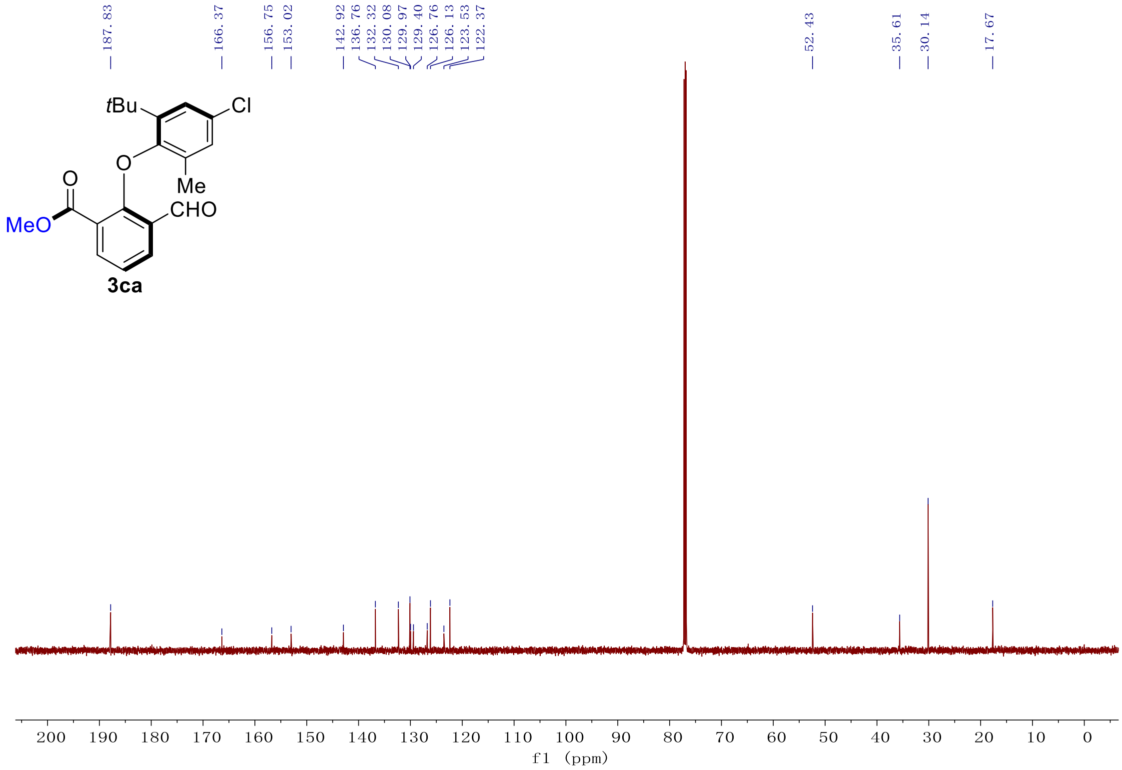
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3ba.



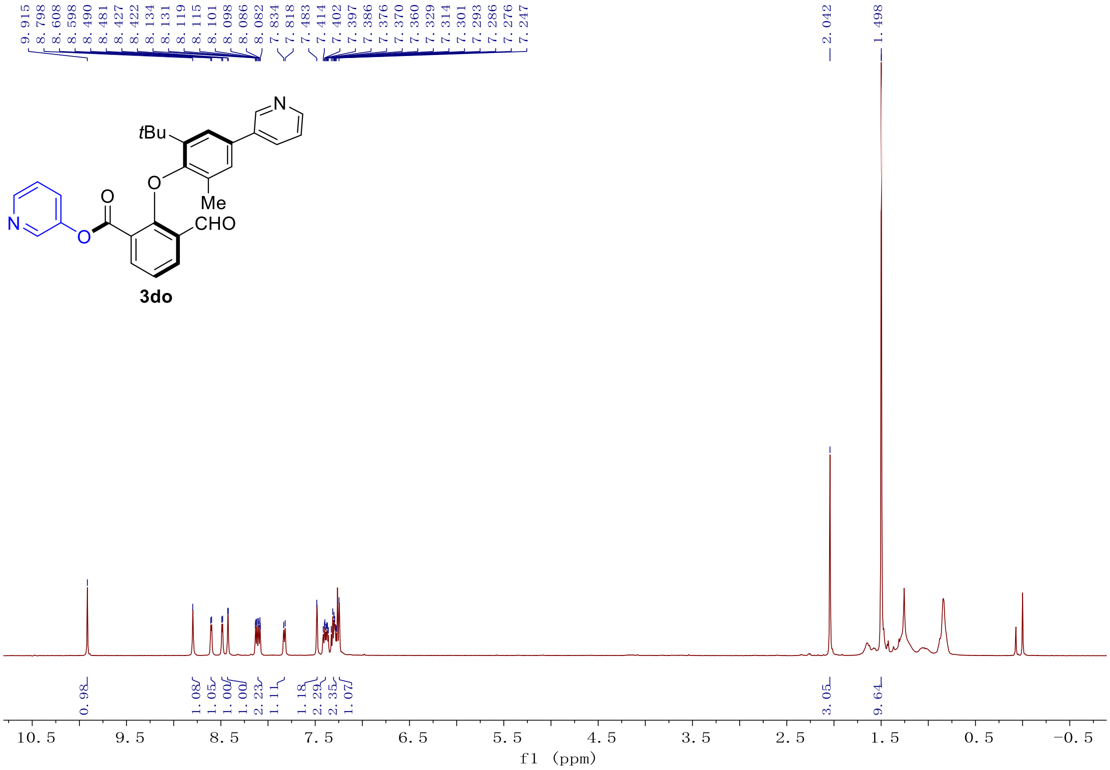
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3ba.



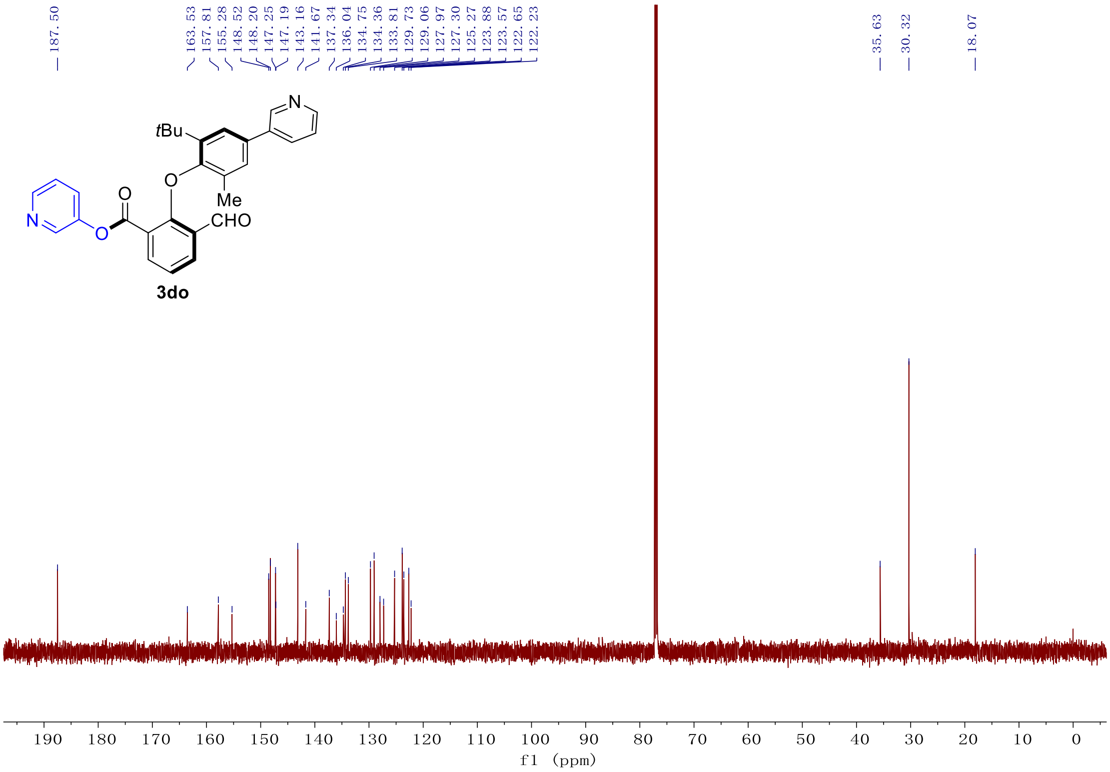
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3ca.



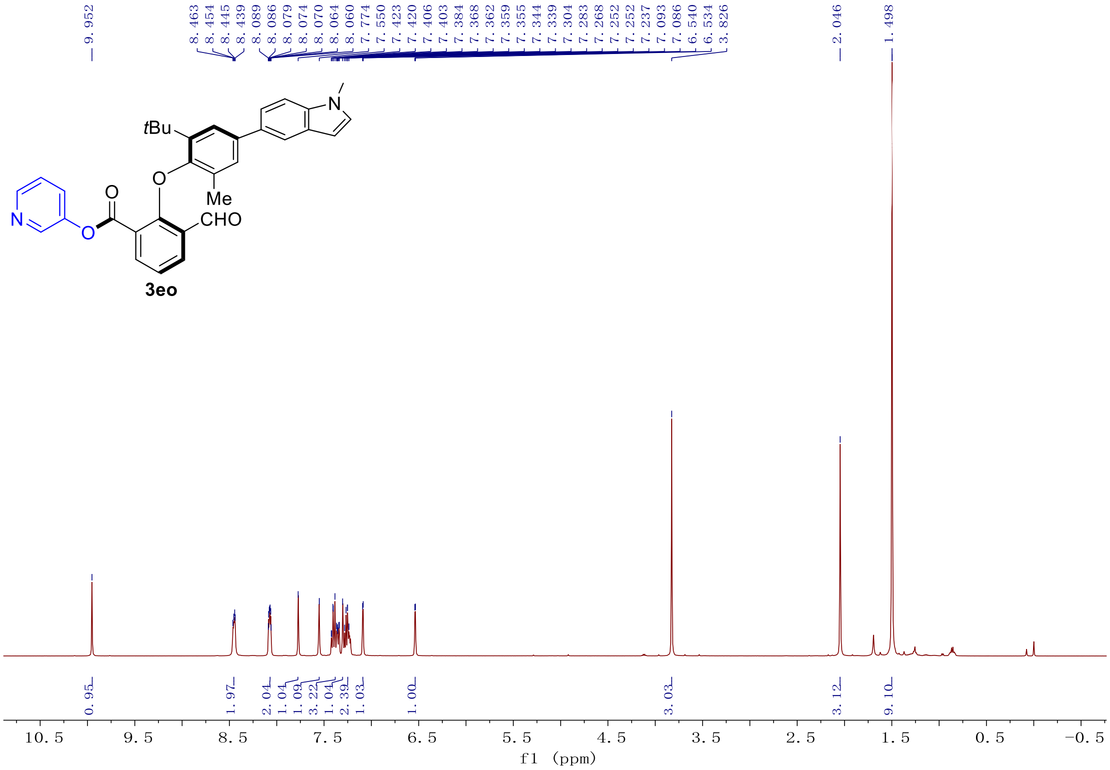
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3ca.



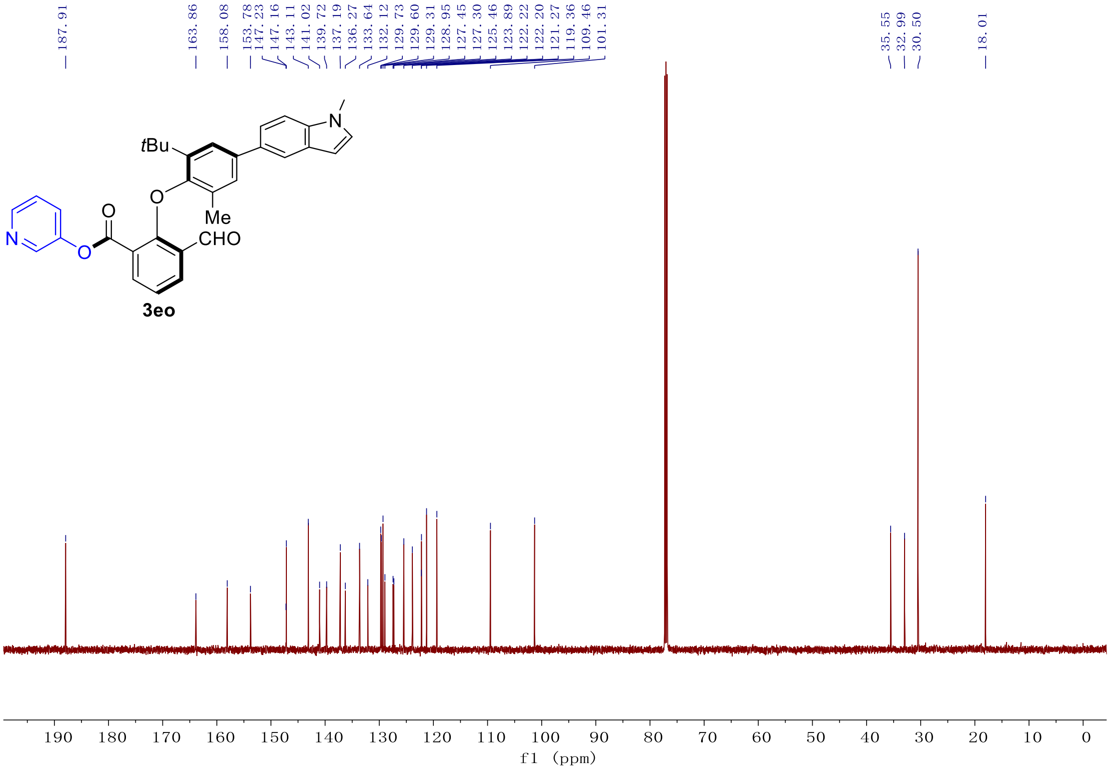
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3do.



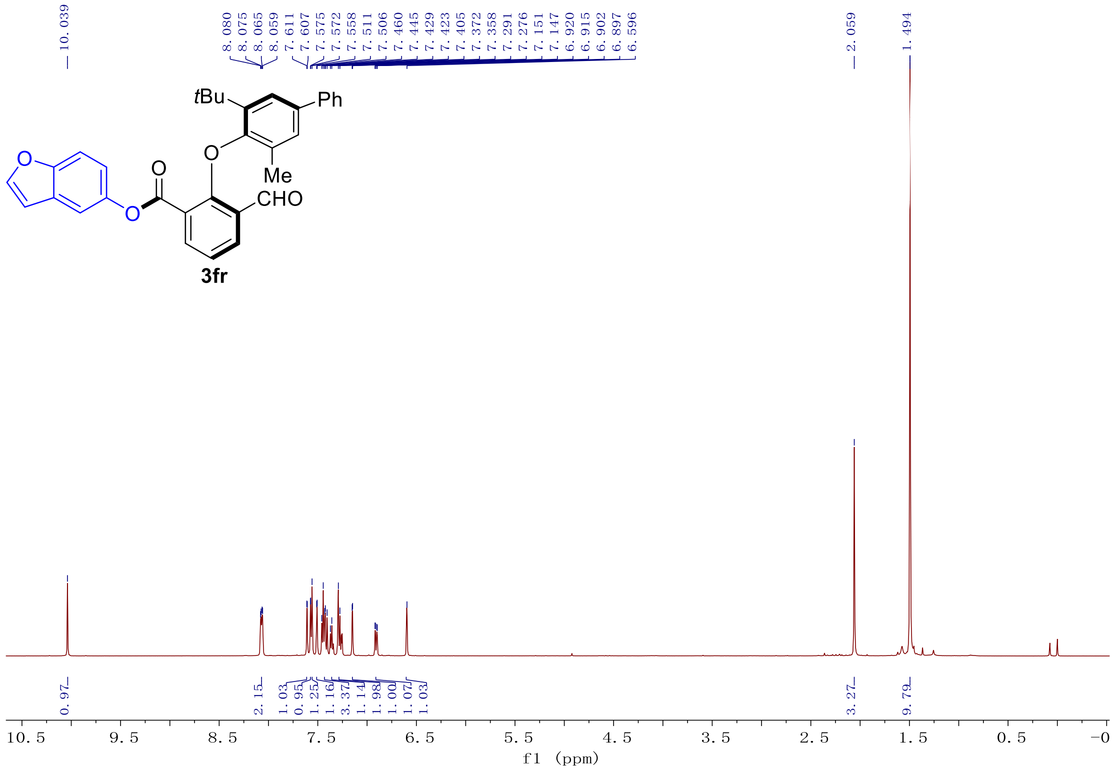
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3do.



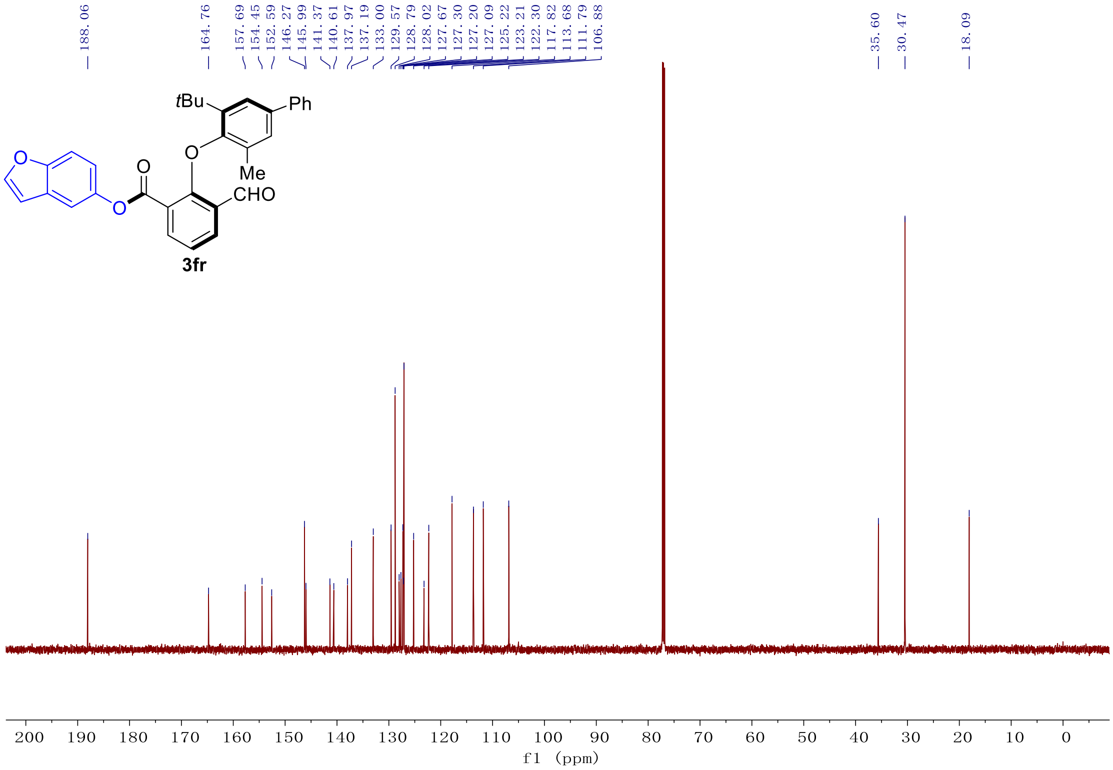
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3eo.



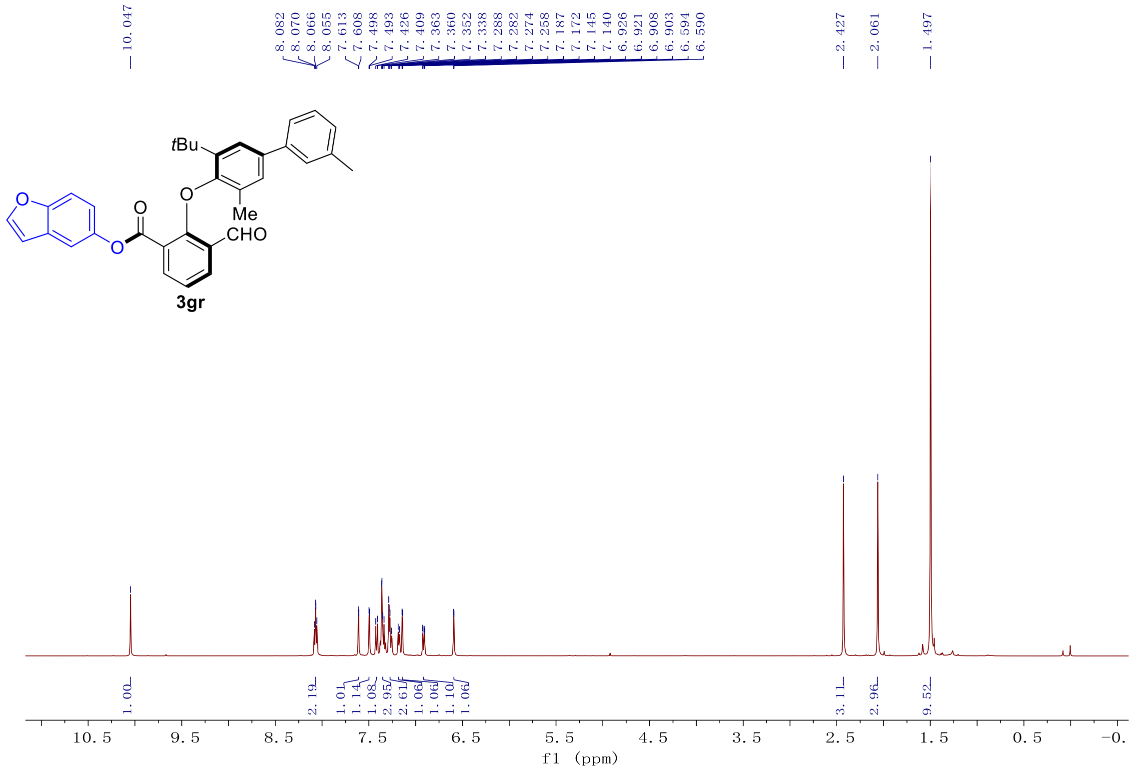
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3eo.



^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3fr.



^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3fr.



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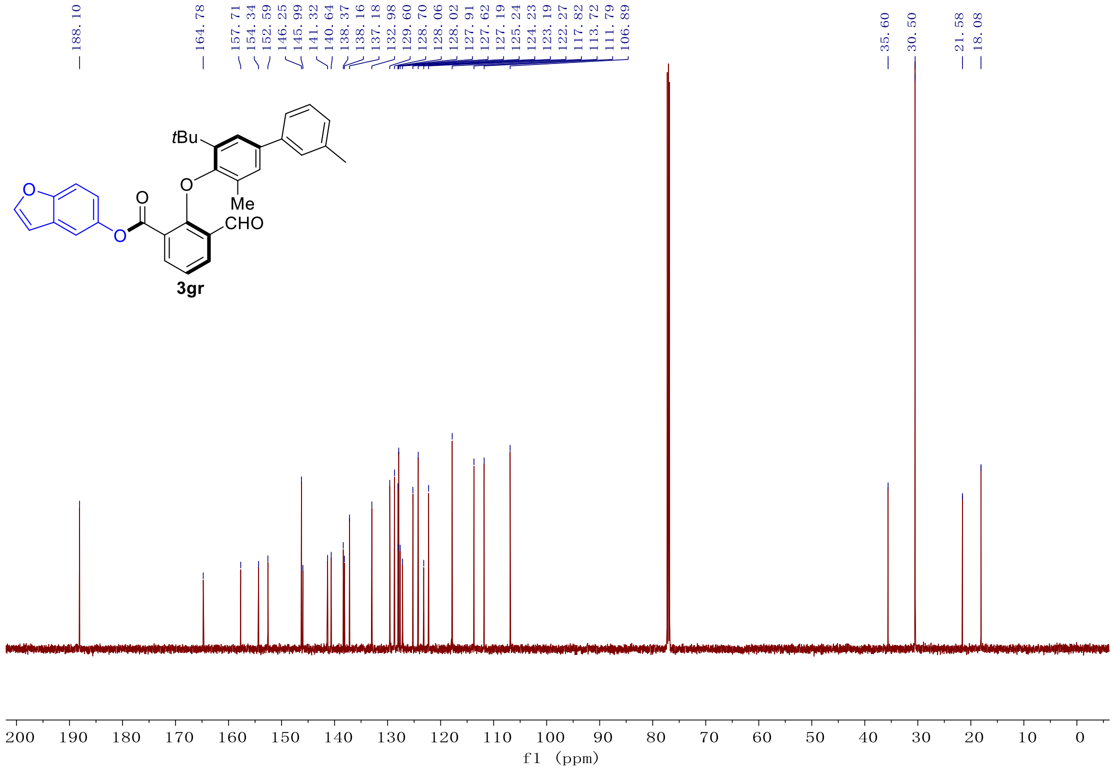
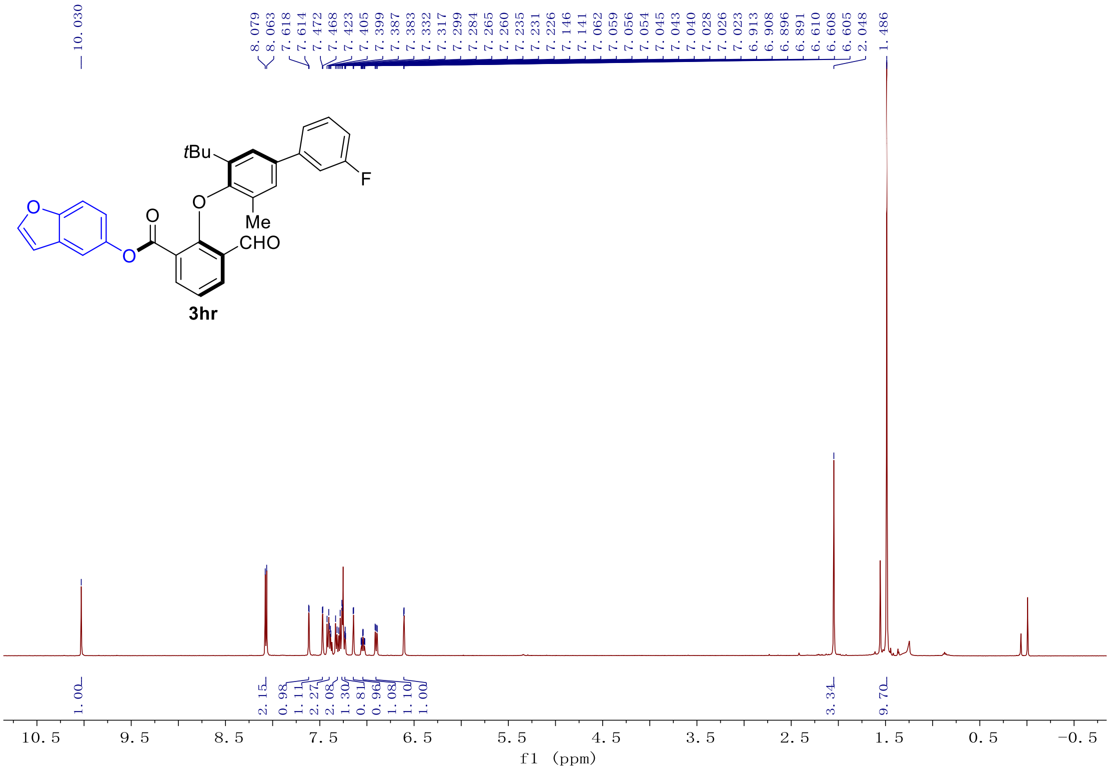
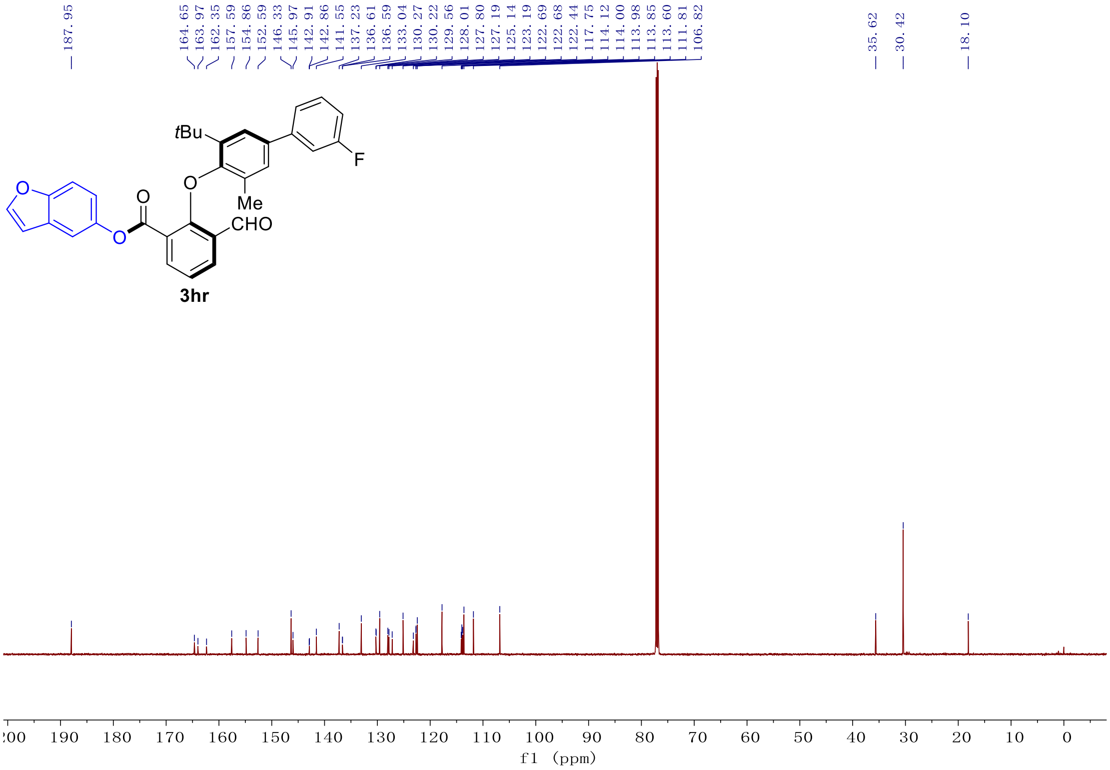


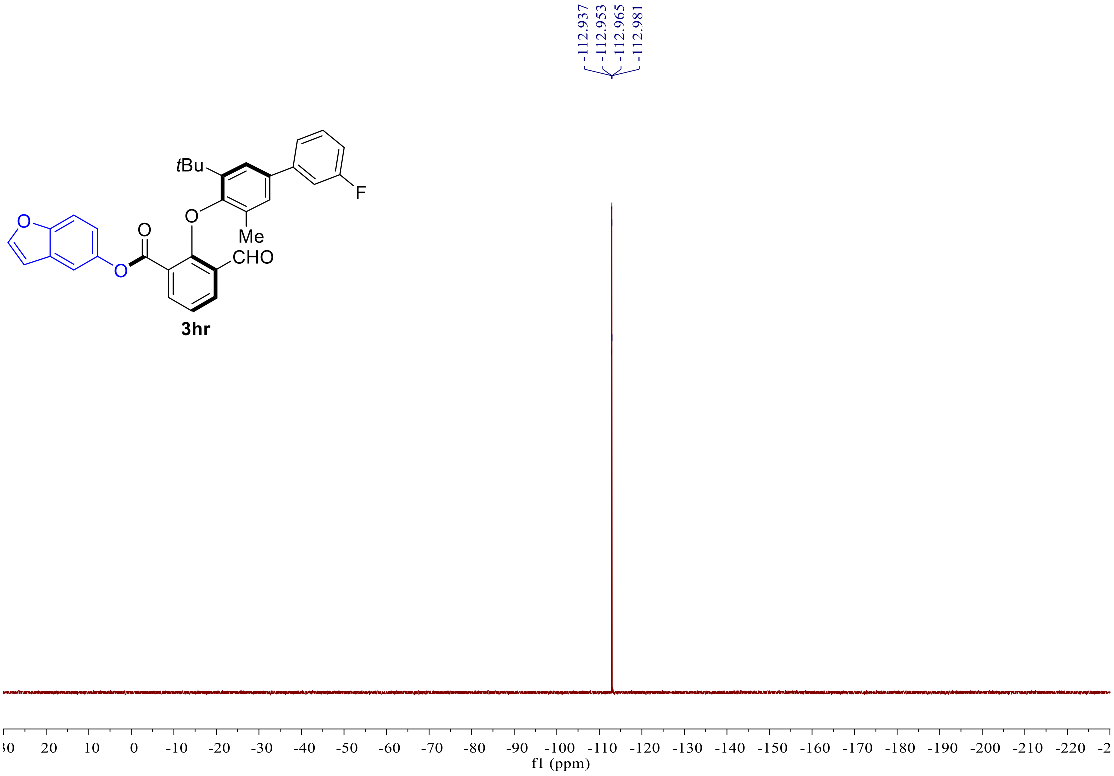
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3gr.



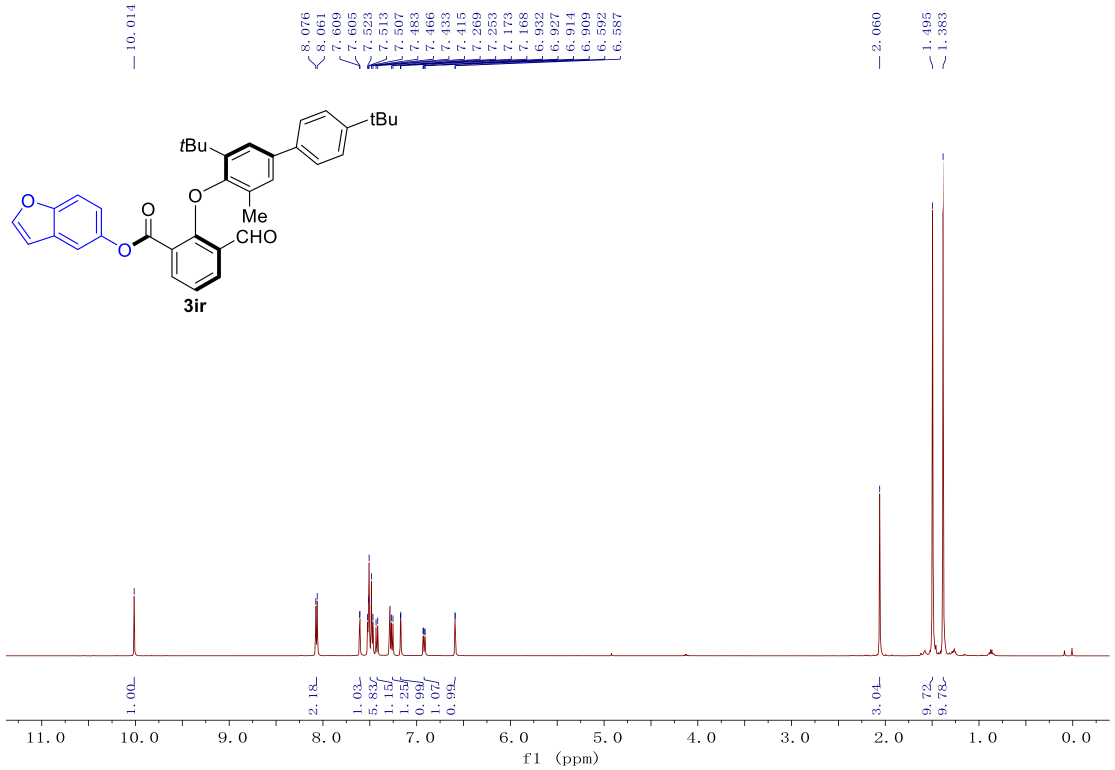
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3hr.



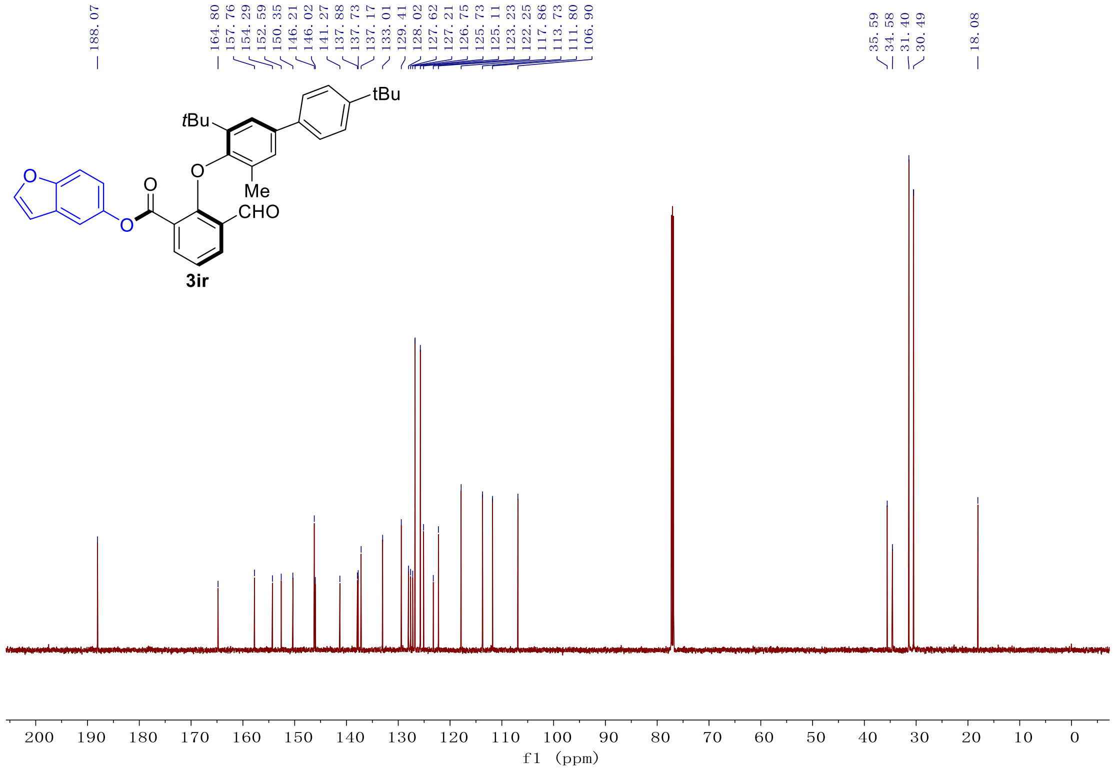
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3hr.



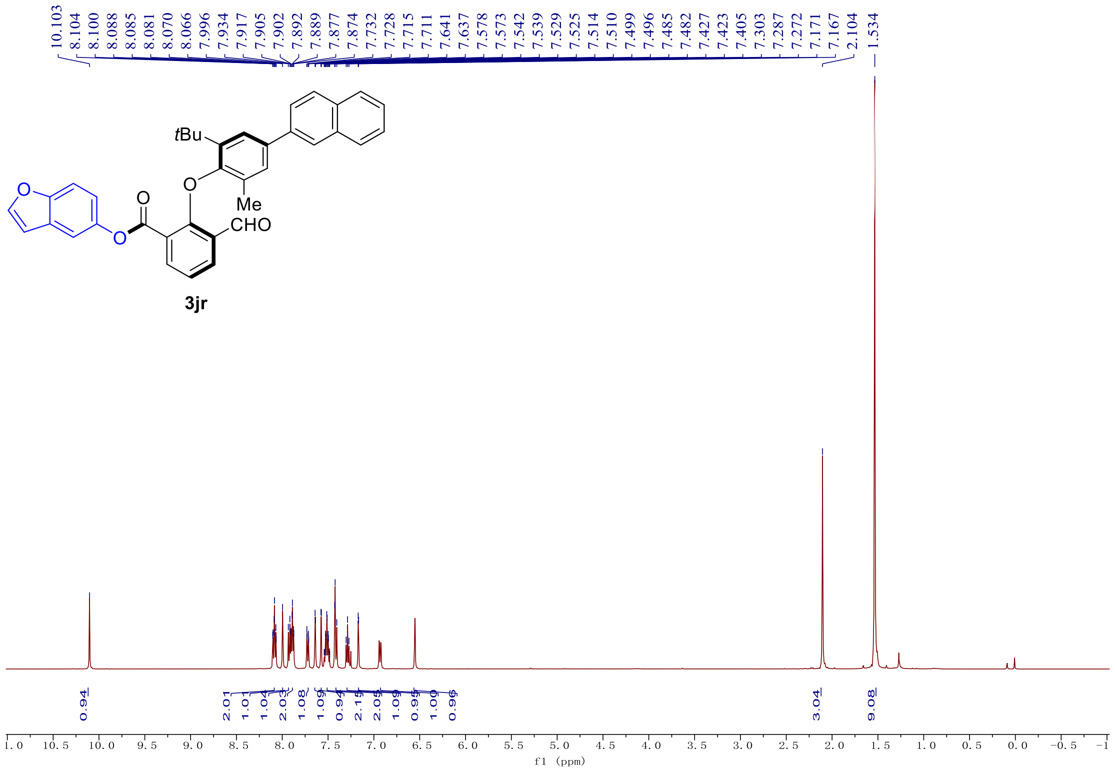
^{19}F NMR (565 MHz, CDCl$_3$) spectrum of 3hr.



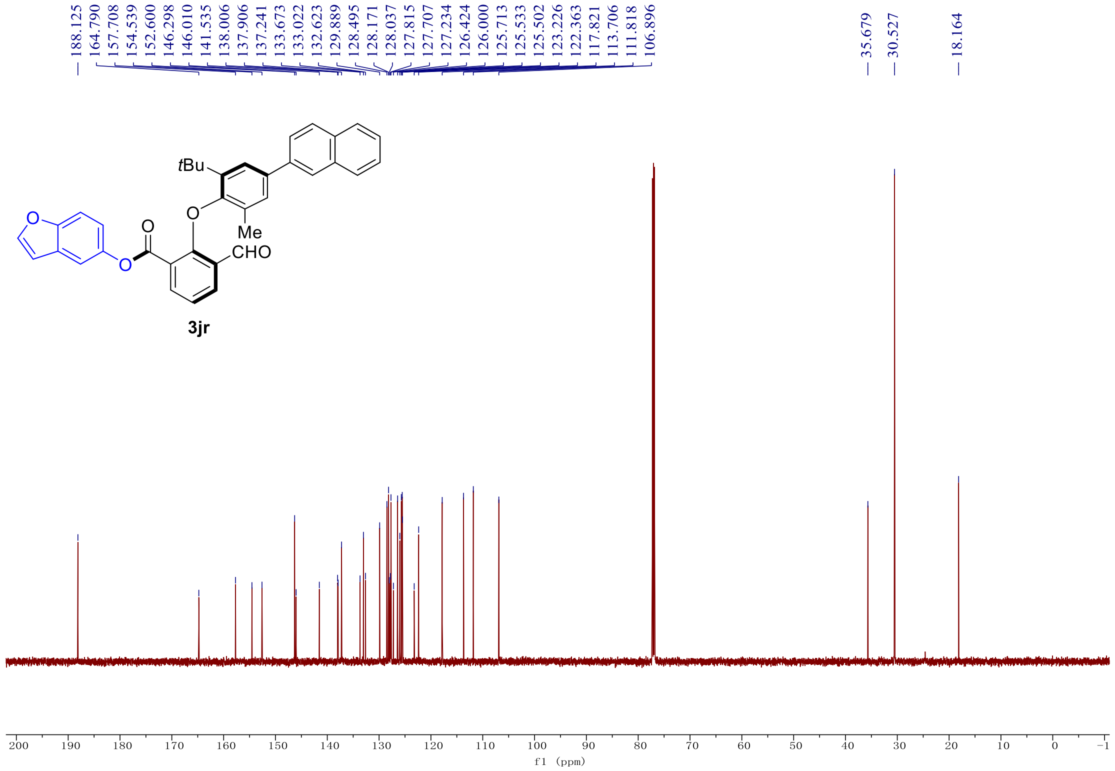
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ir.



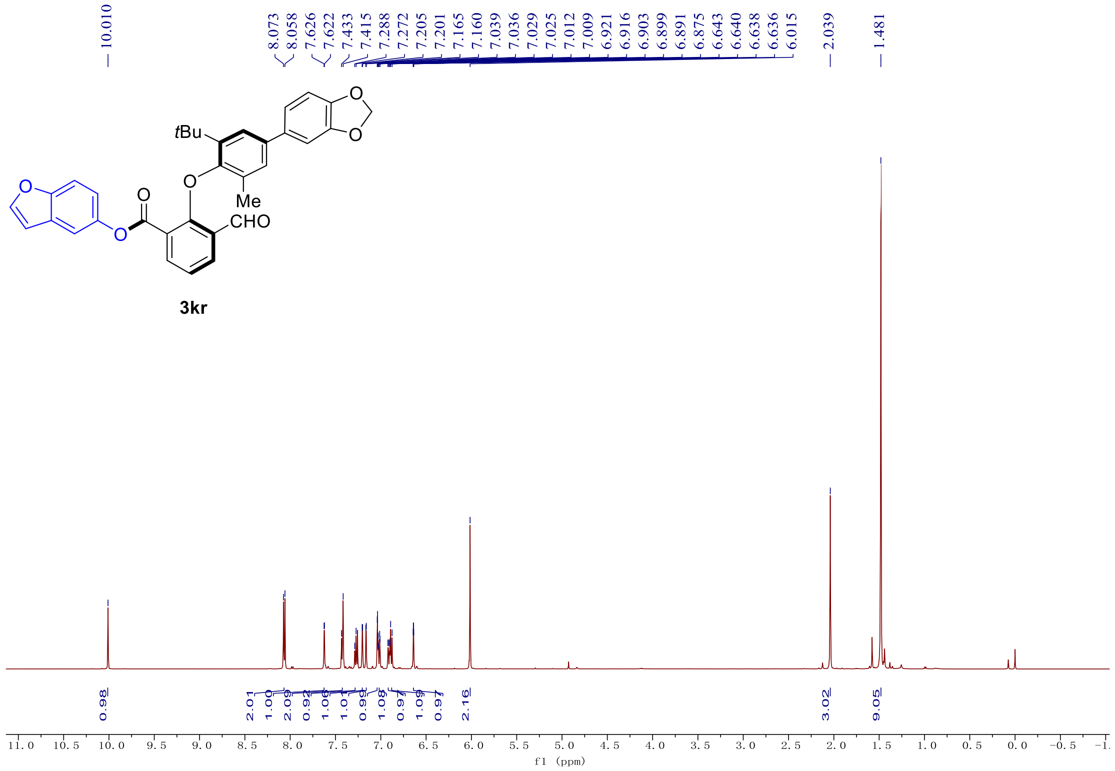
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ir.



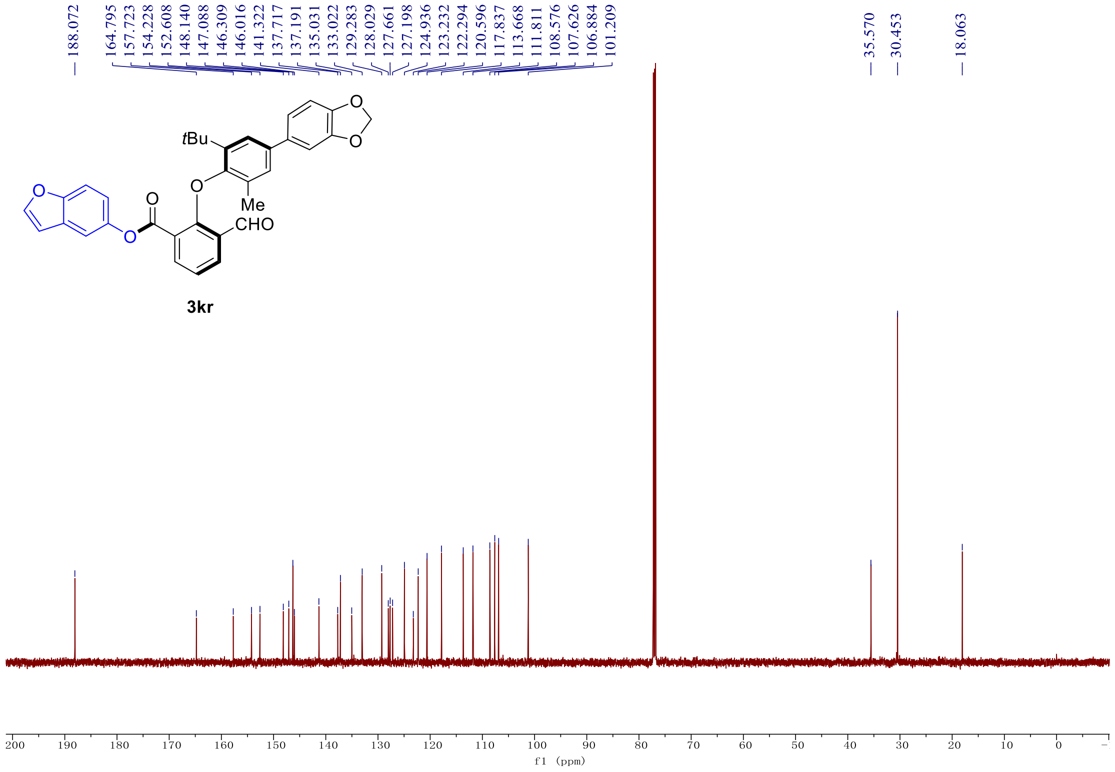
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3jr.



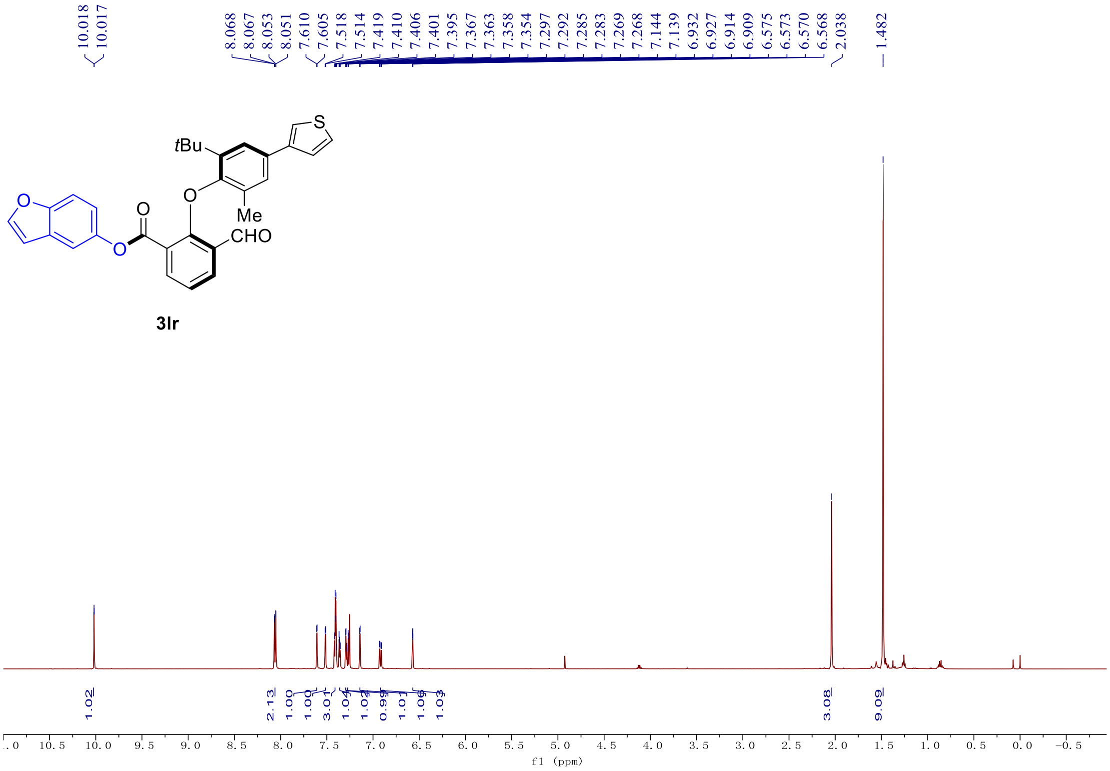
^{13}C NMR (125 MHz, CDCl$_3$) spectrum of 3kr.



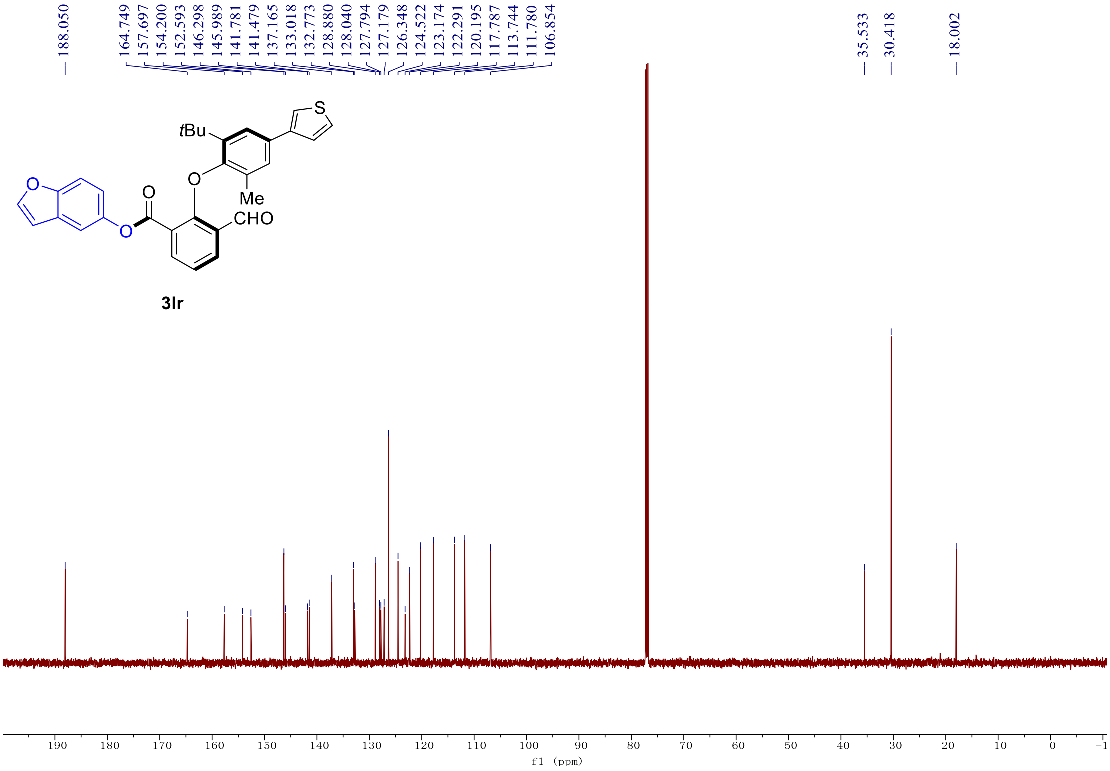
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3kr.



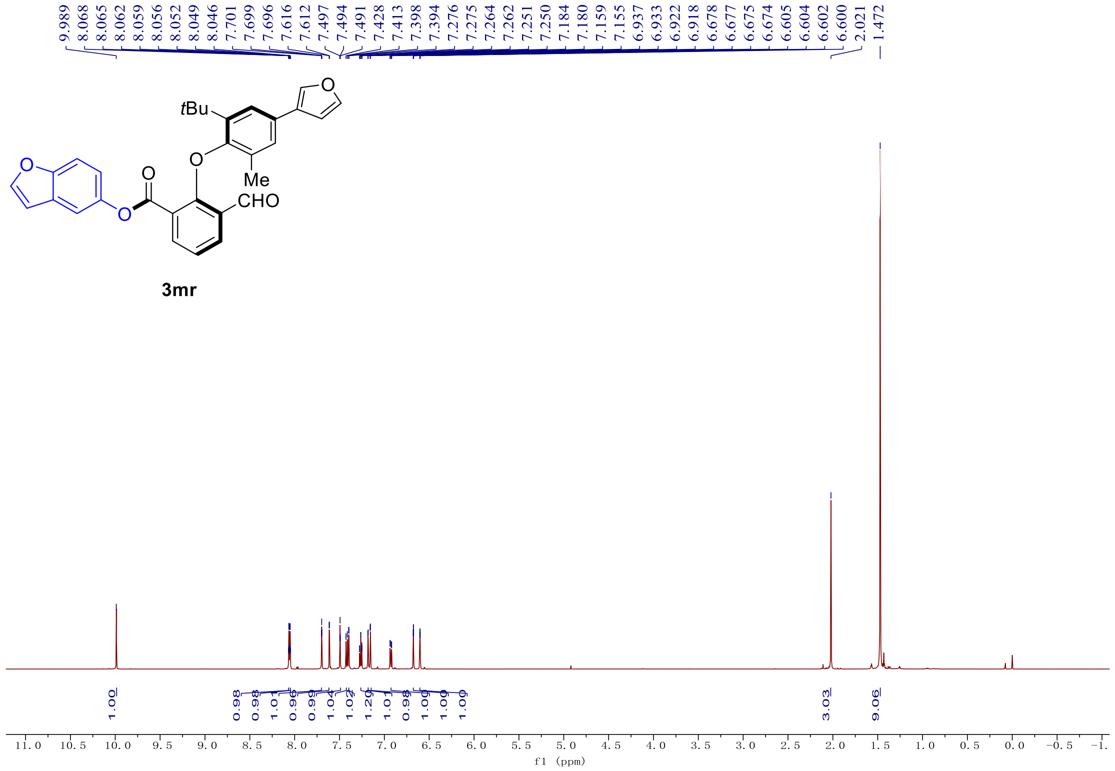
^{13}C NMR (125 MHz, CDCl$_3$) spectrum of 3kr.



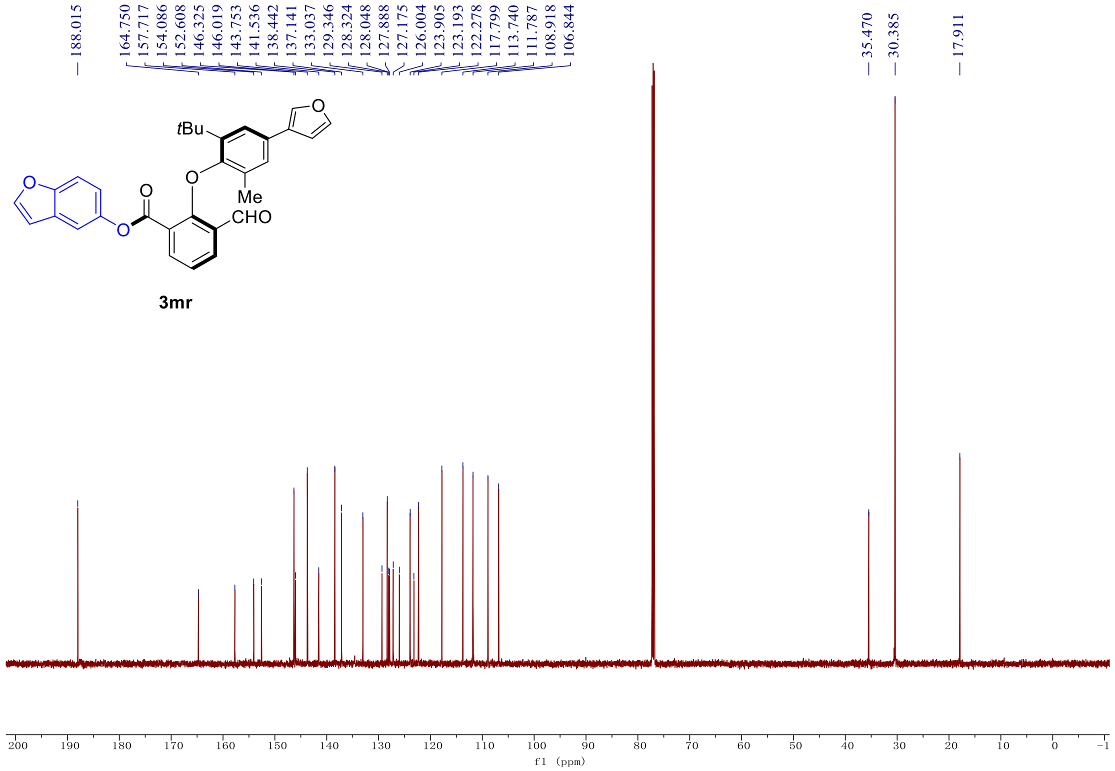
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3lr.



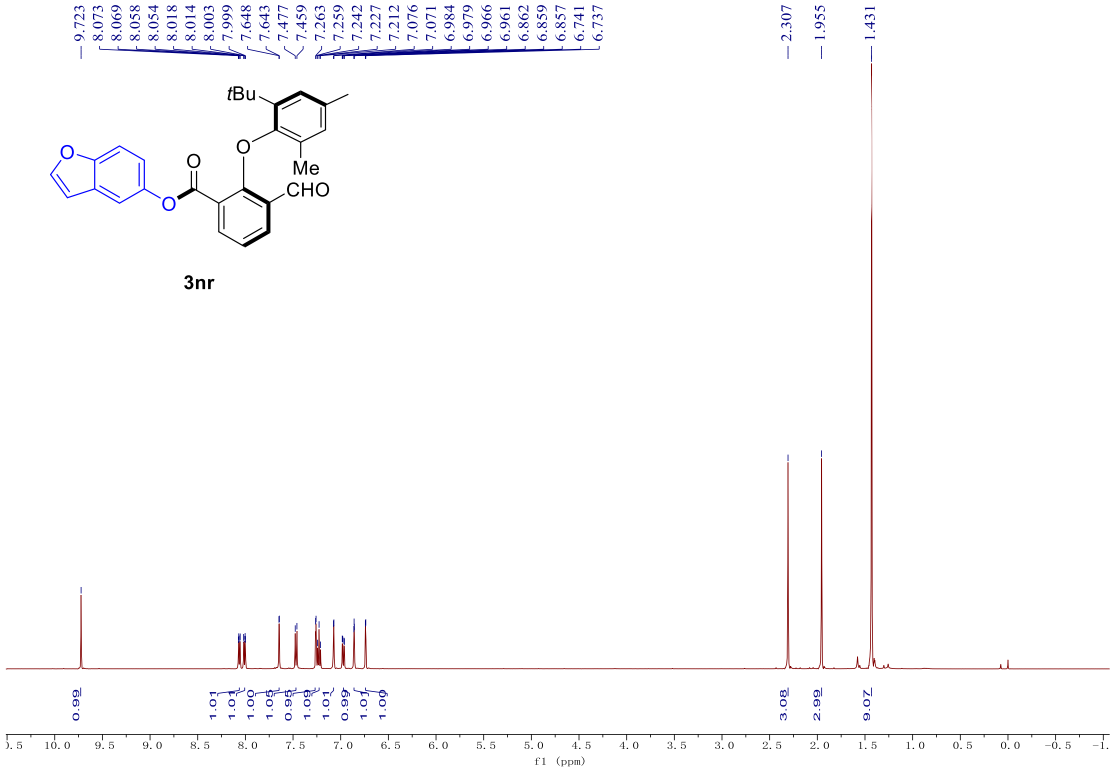
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3lr.



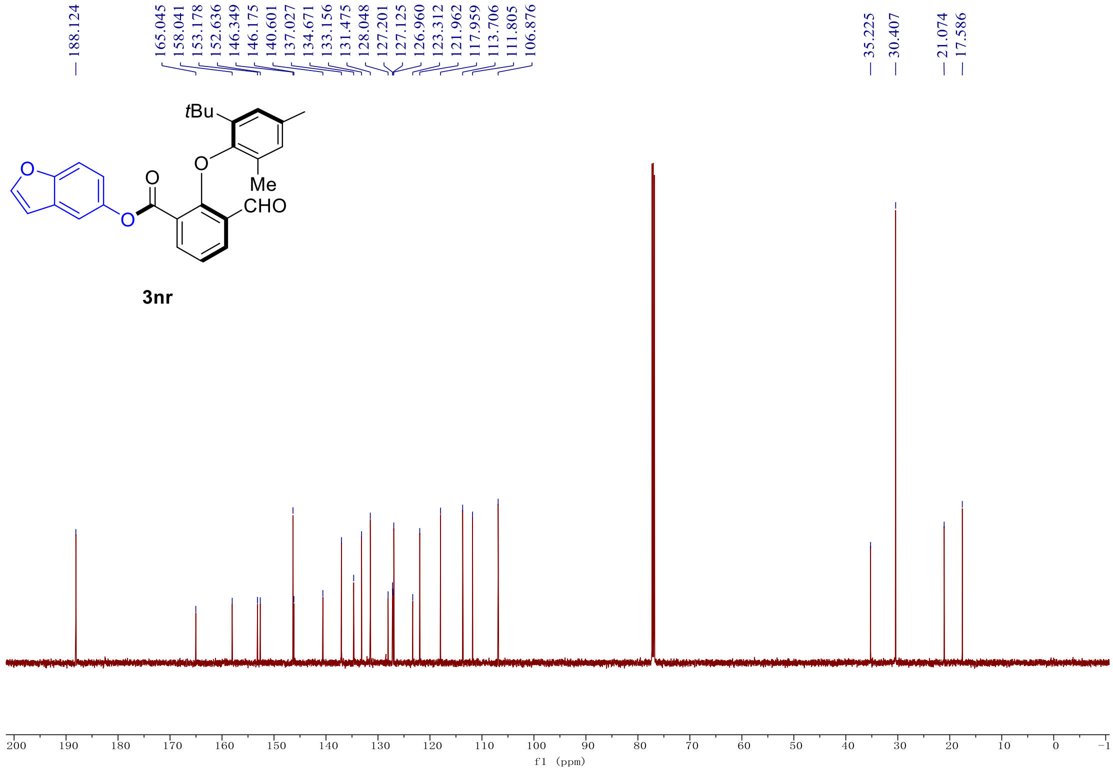
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3mr.



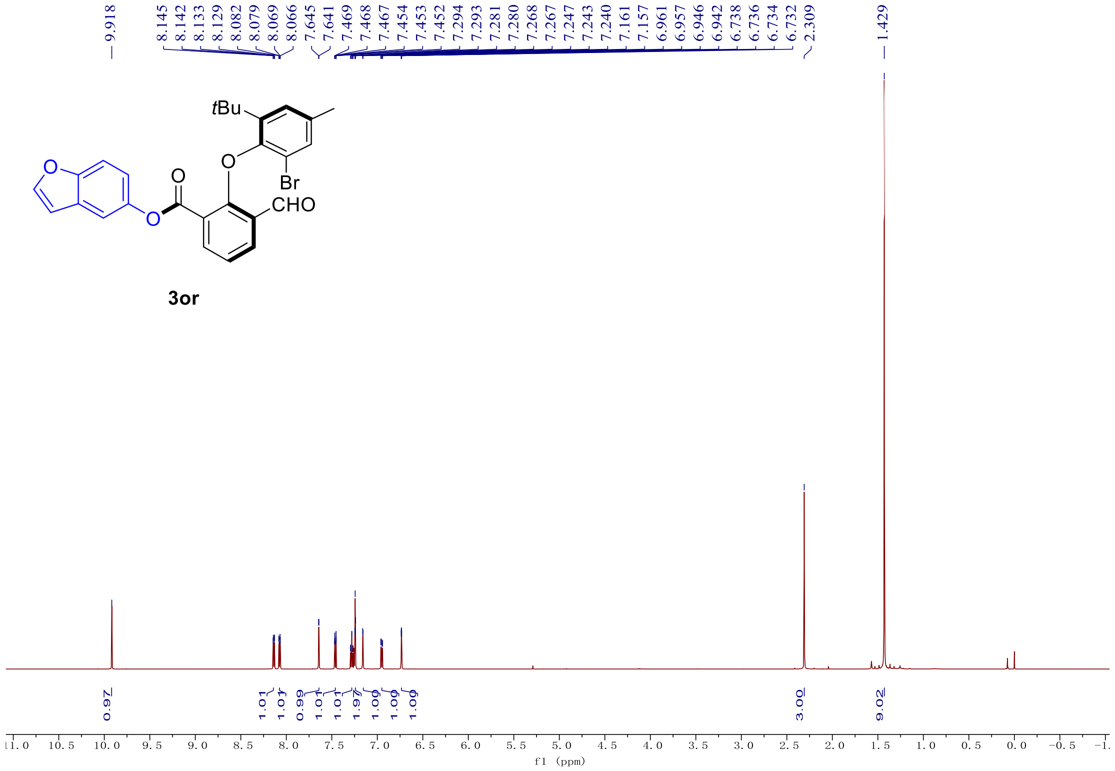
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3mr.



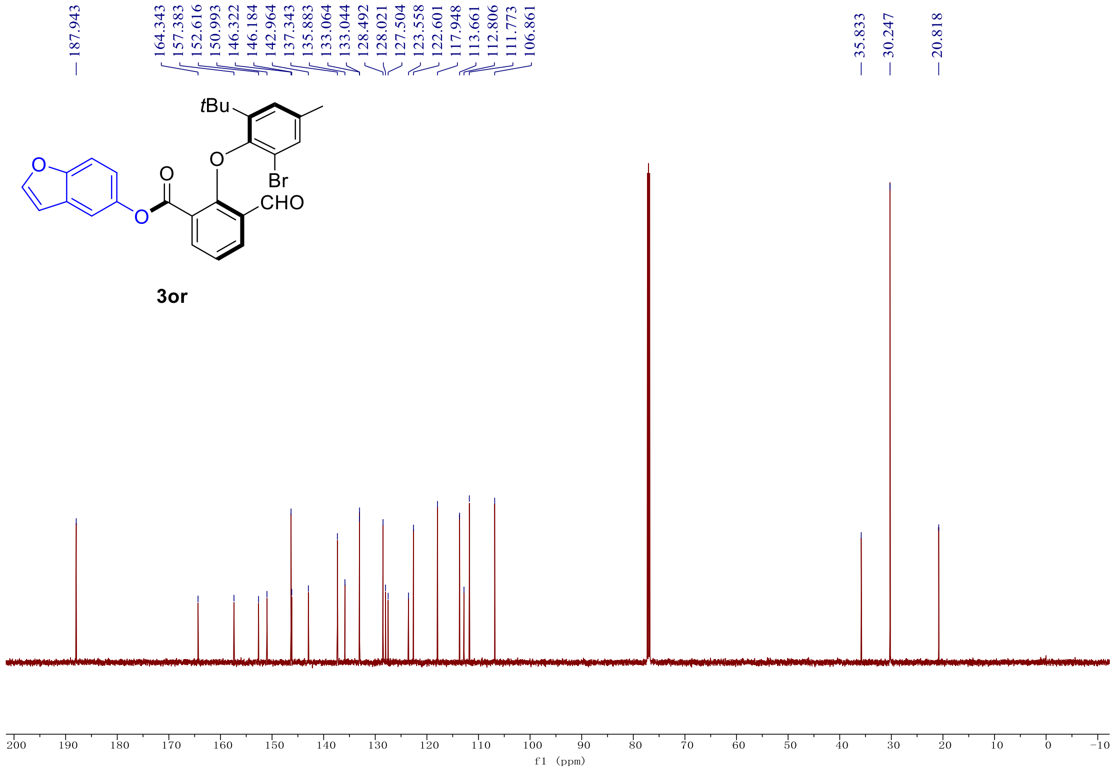
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3nr.



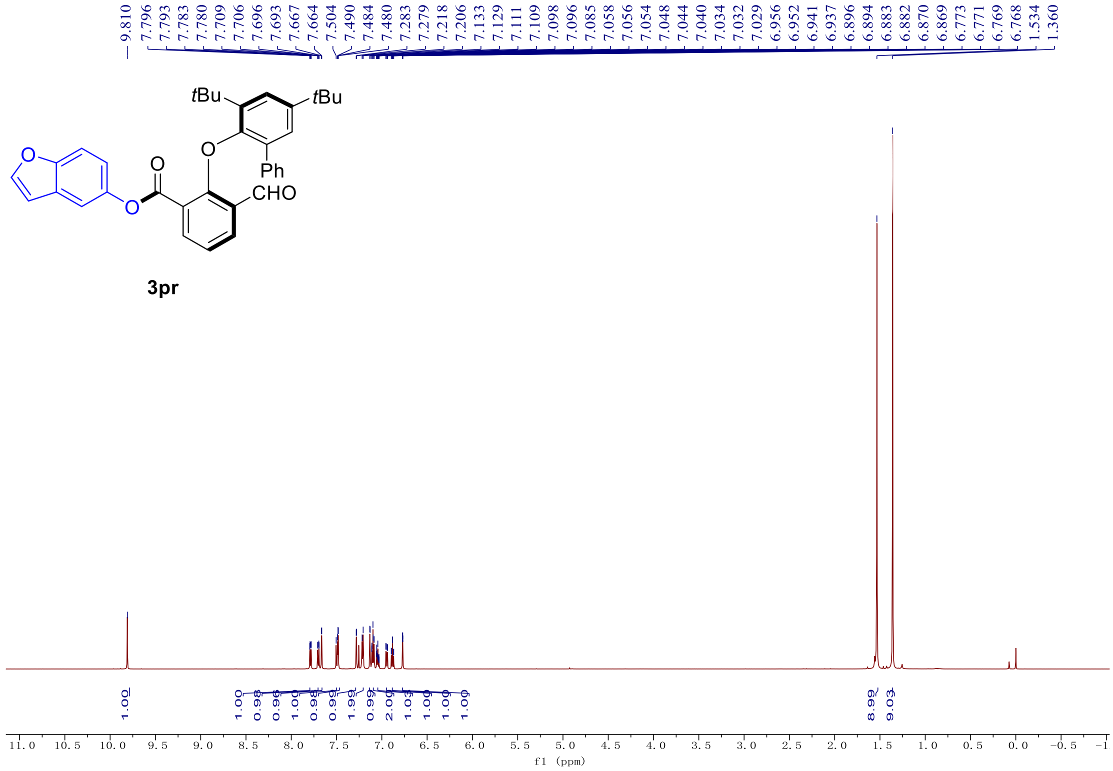
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3nr.



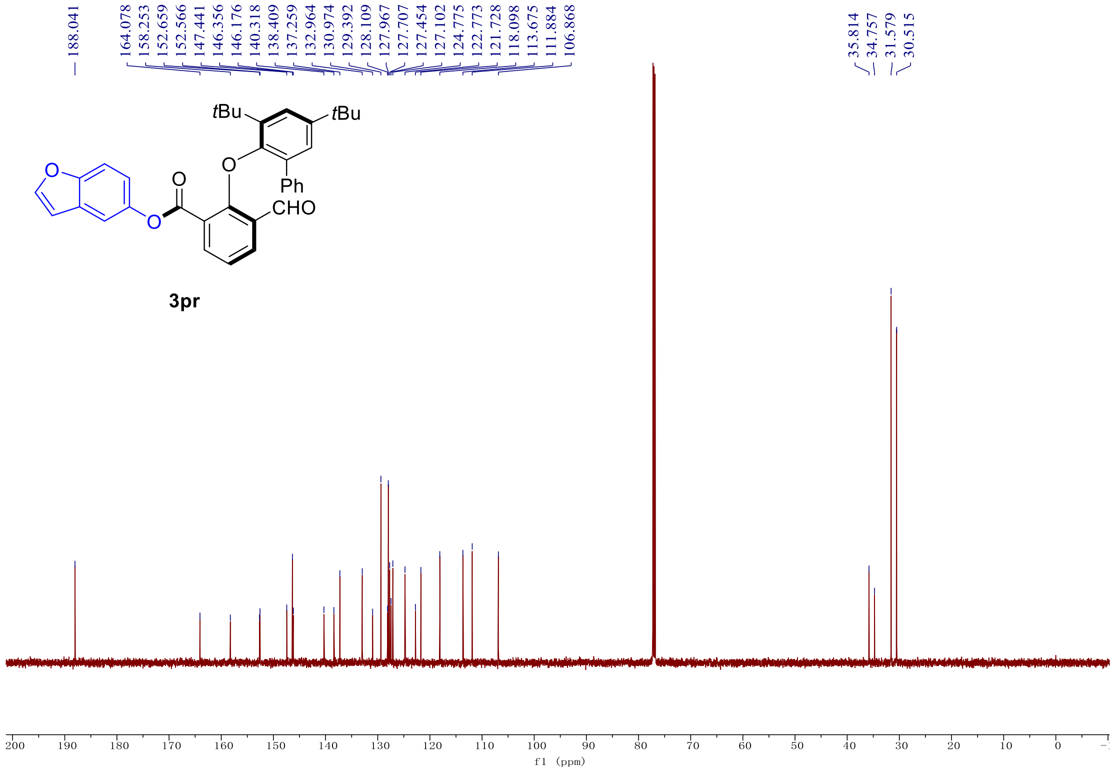
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3or.



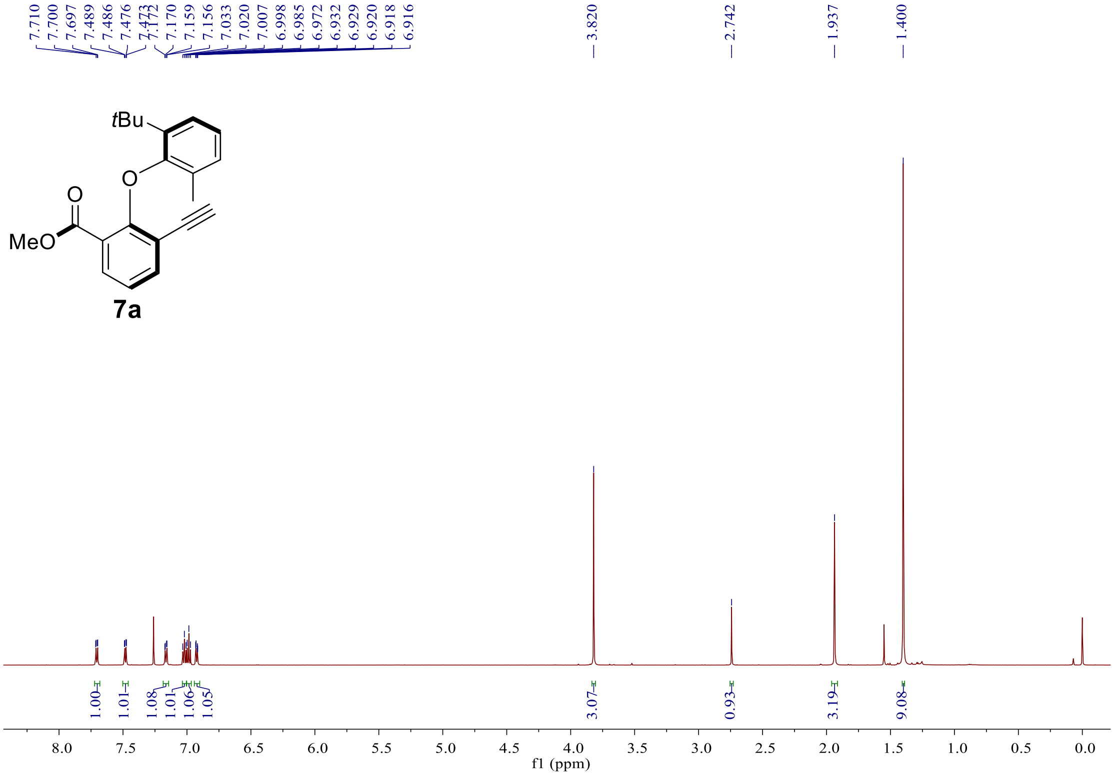
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3or.



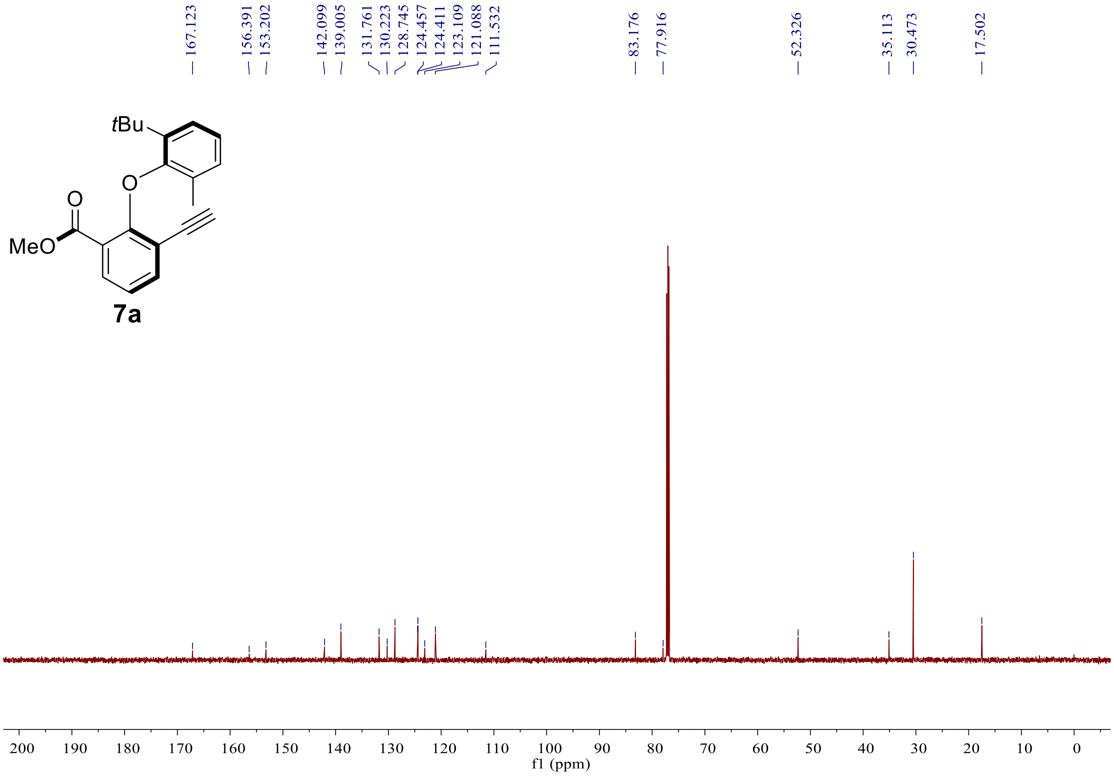
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3pr.



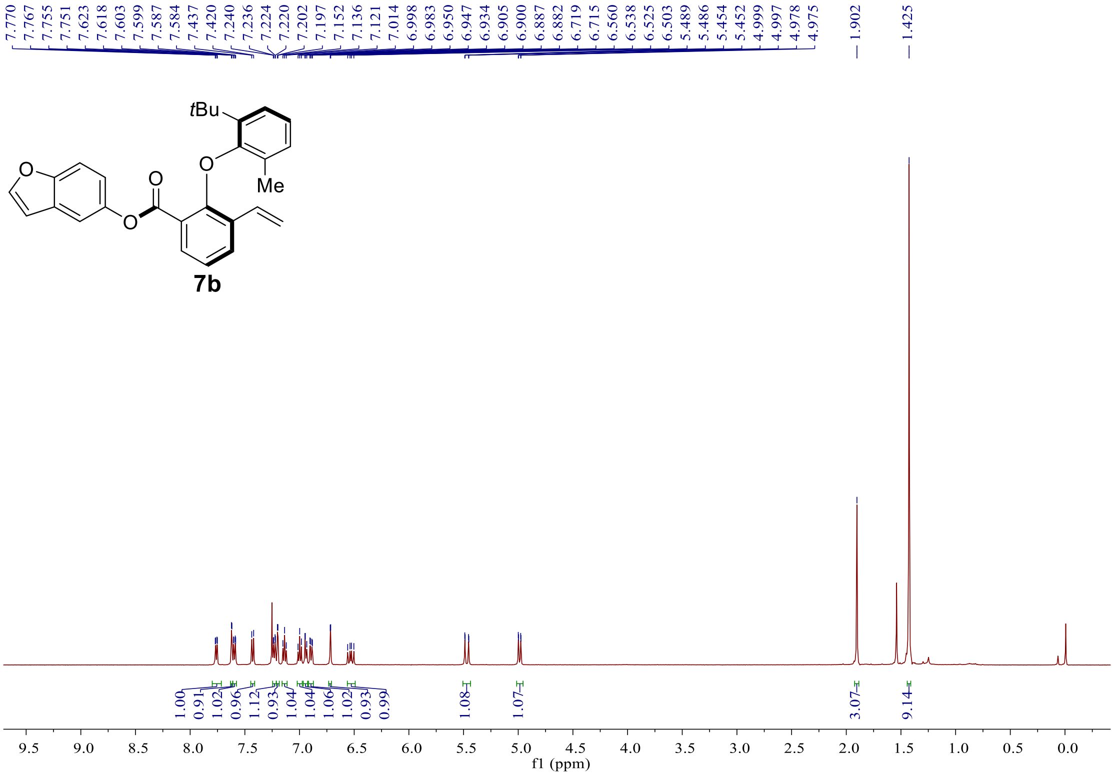
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 3pr.



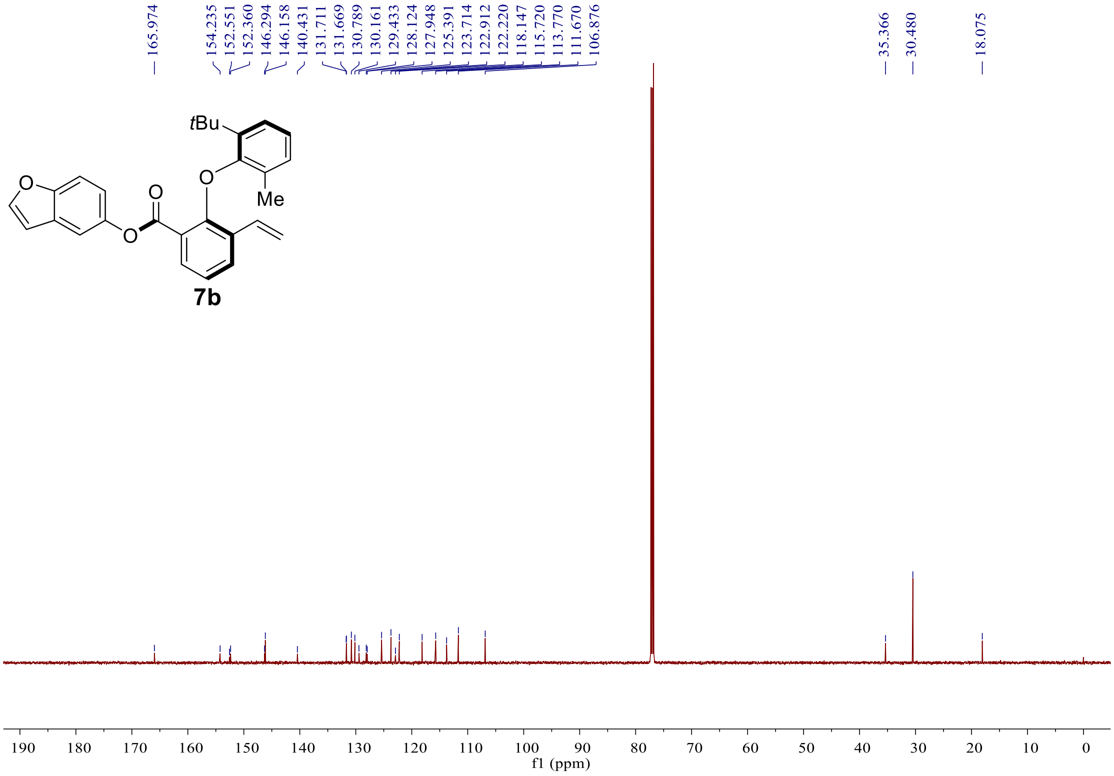
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 7a.



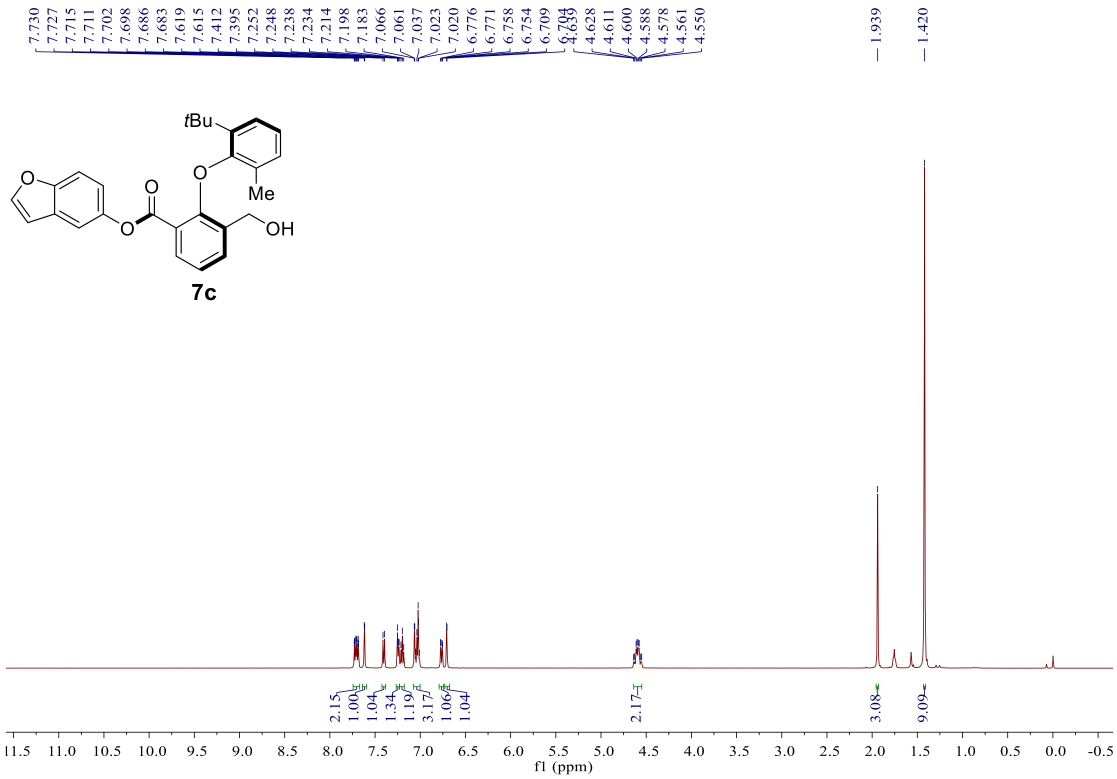
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 7a.



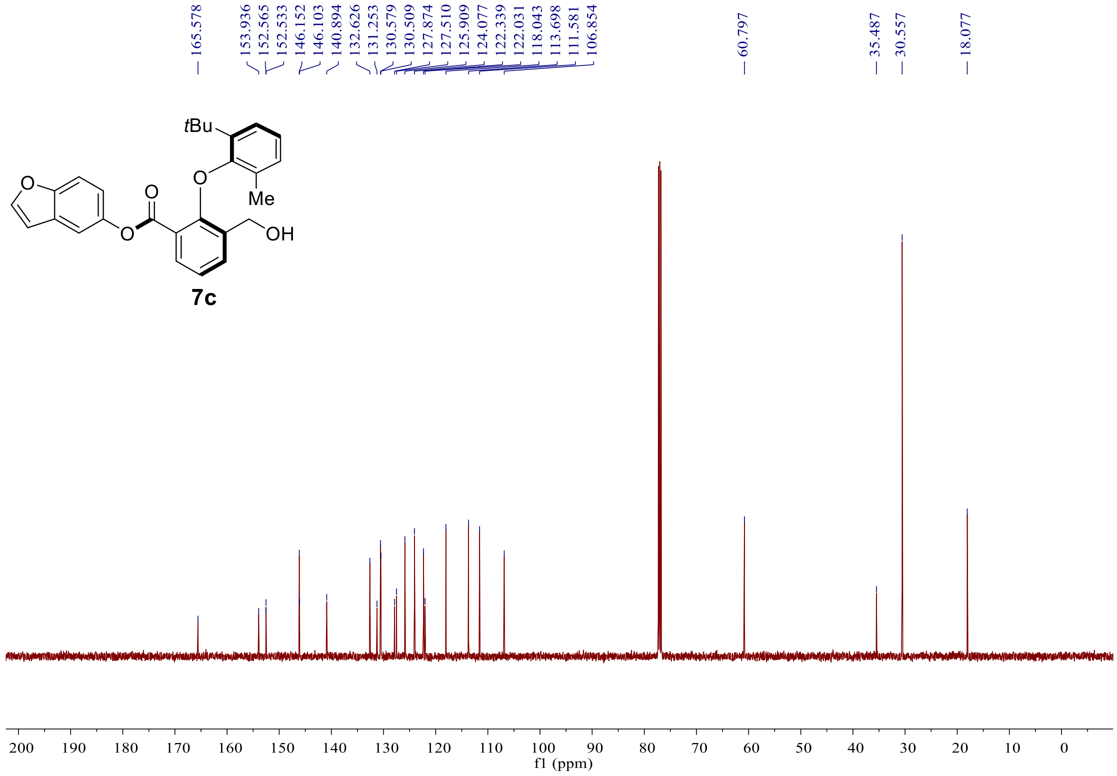
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 7b.



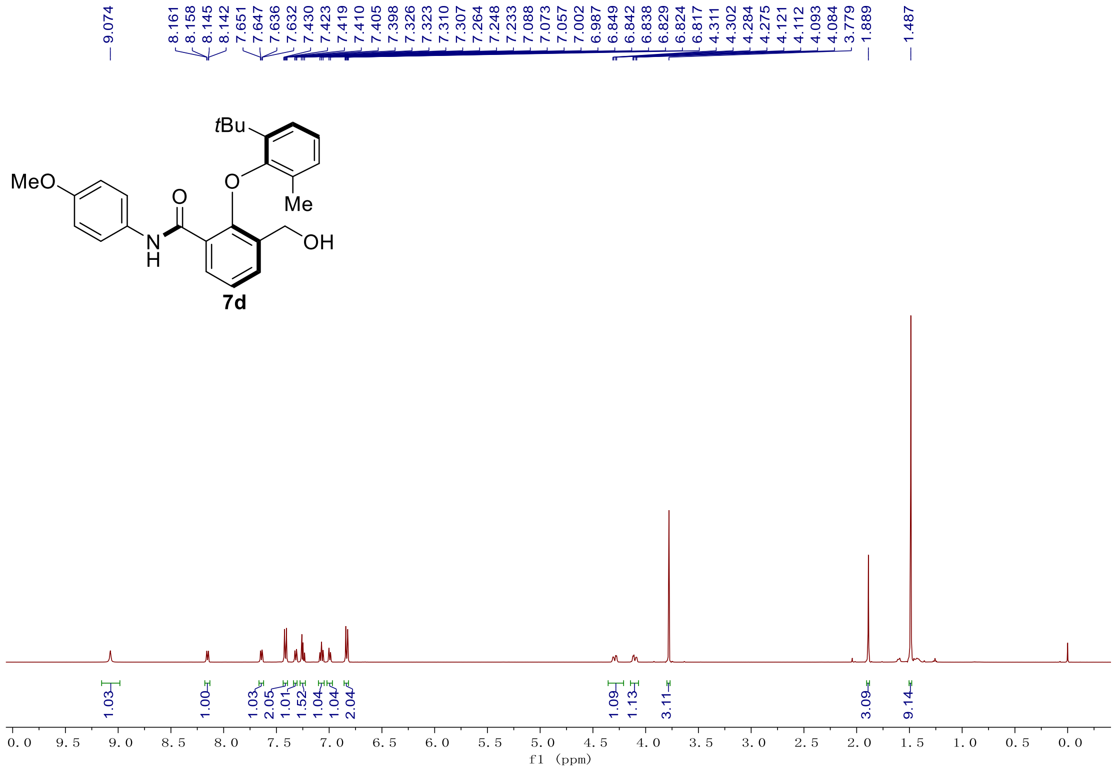
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 7b.



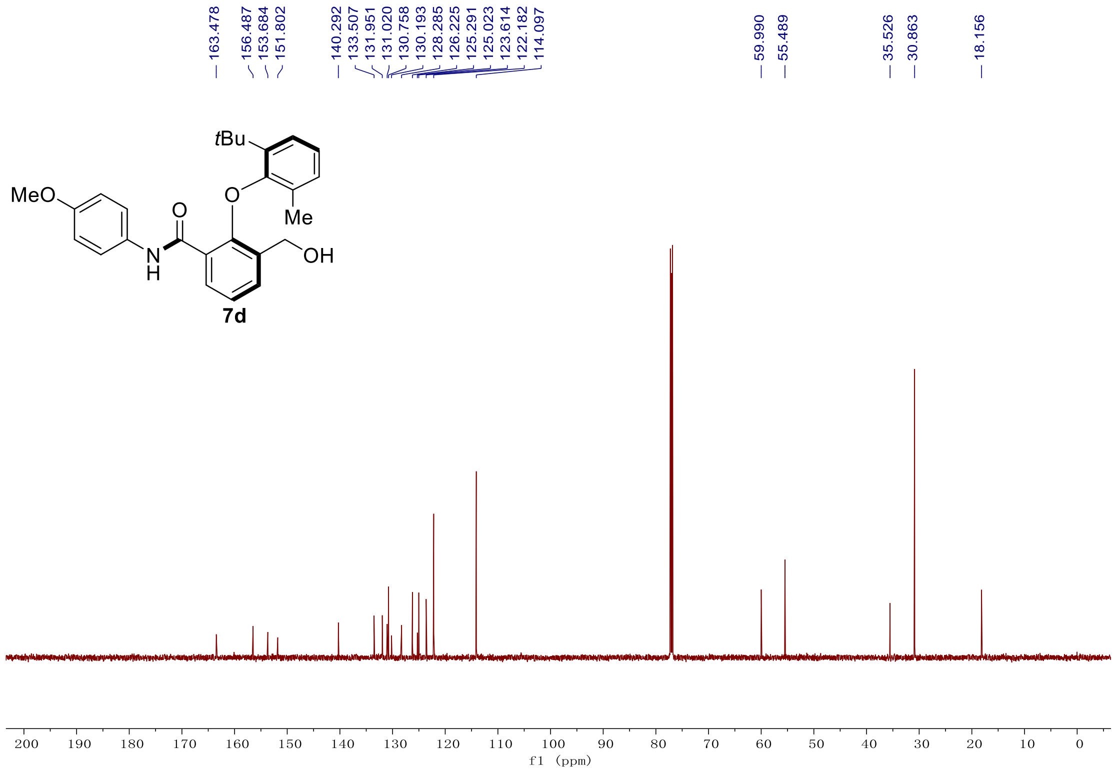
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 7c.



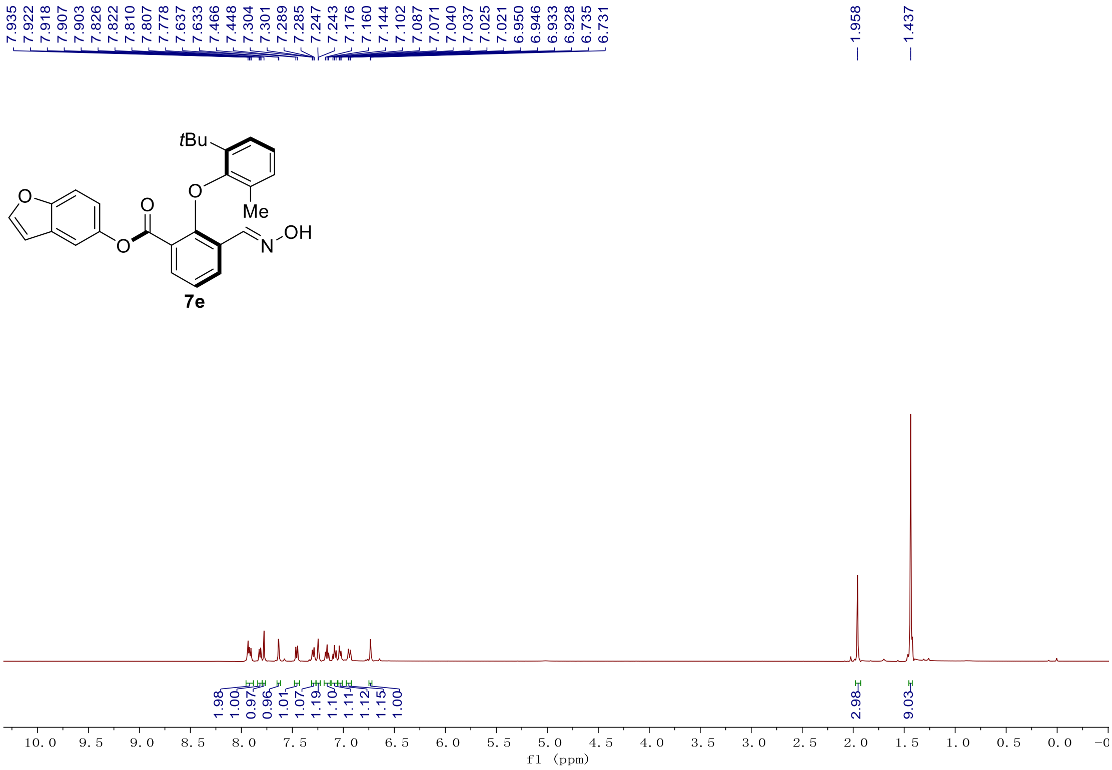
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 7c.



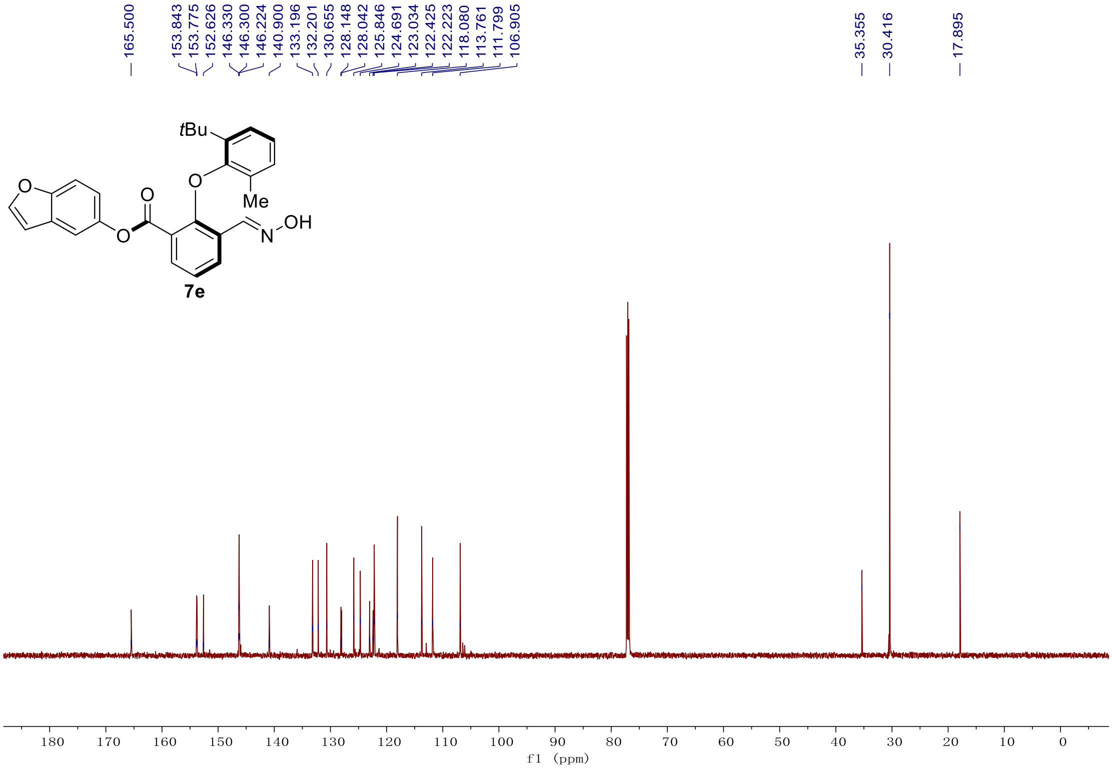
^{1}H NMR (500 MHz, CD_3OD) spectrum of 7d.



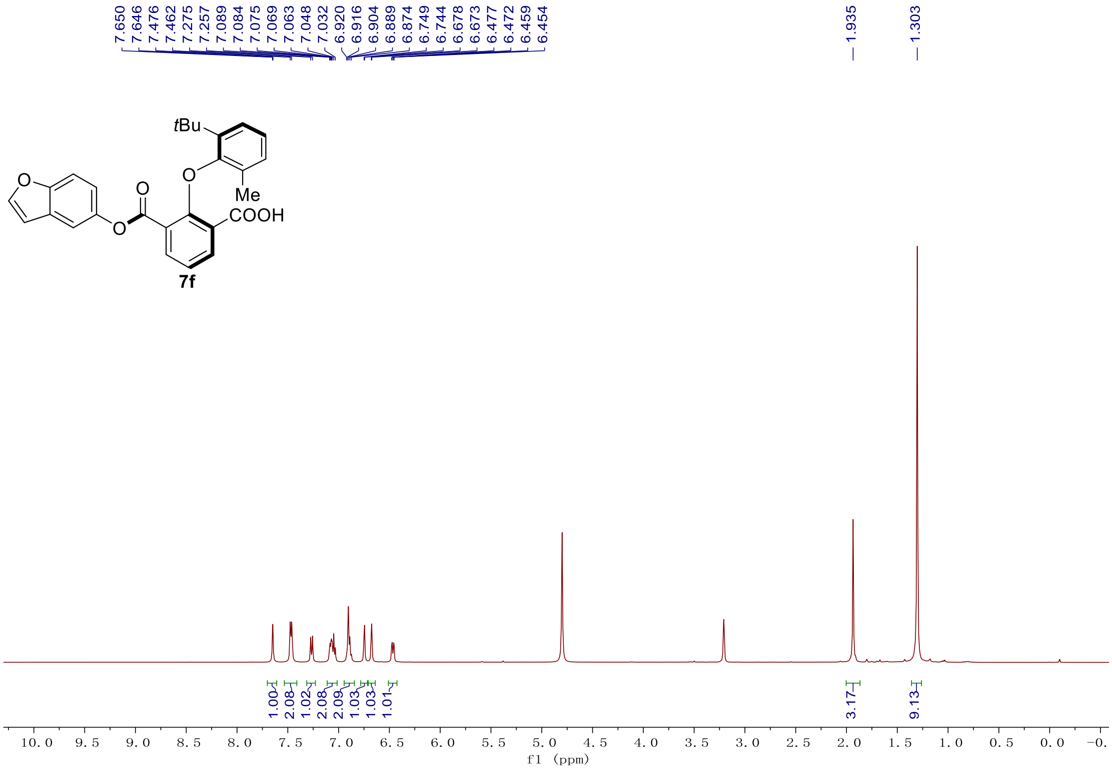
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 7d.



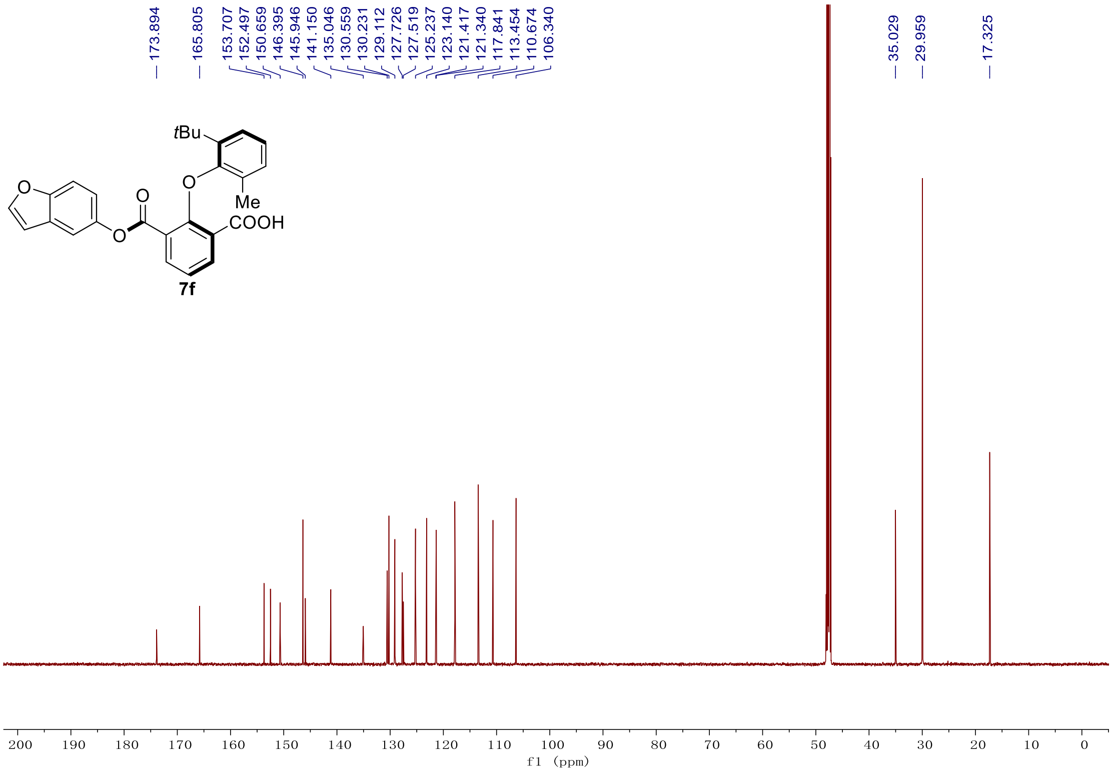
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 7e.



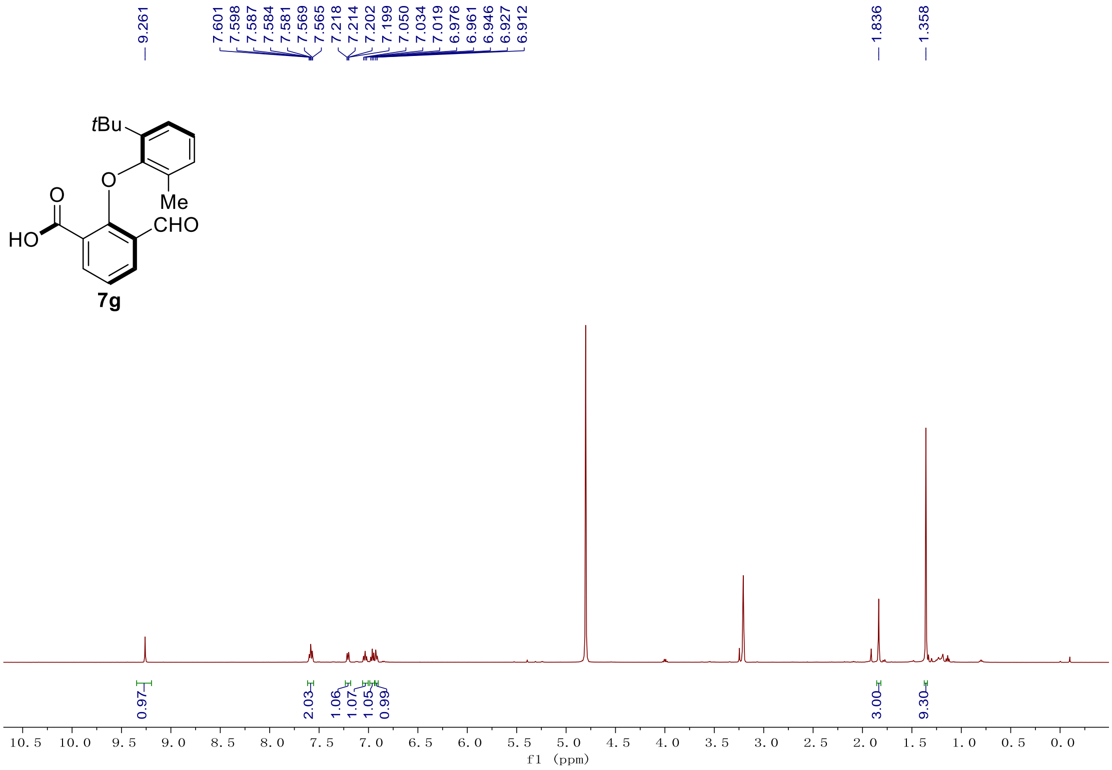
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 7e.



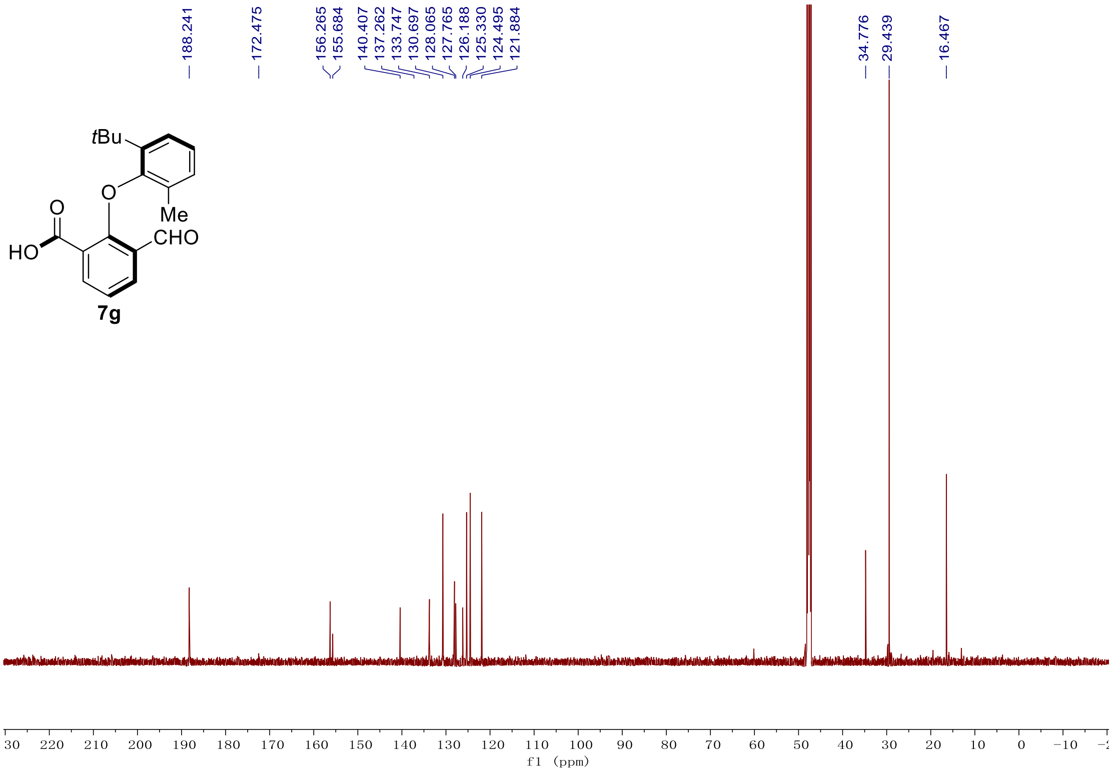
^{1}H NMR (500 MHz, CD_3OD) spectrum of 7f.



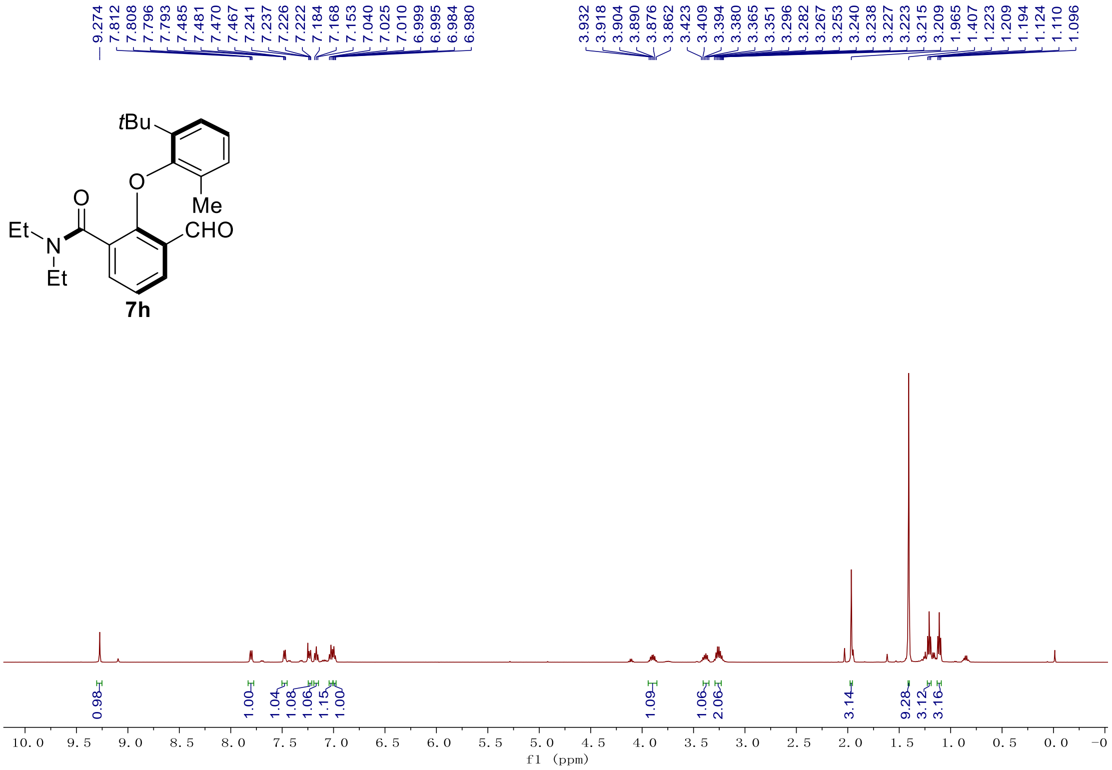
^{13}C NMR (150 MHz, CD_3OD) spectrum of 7f.



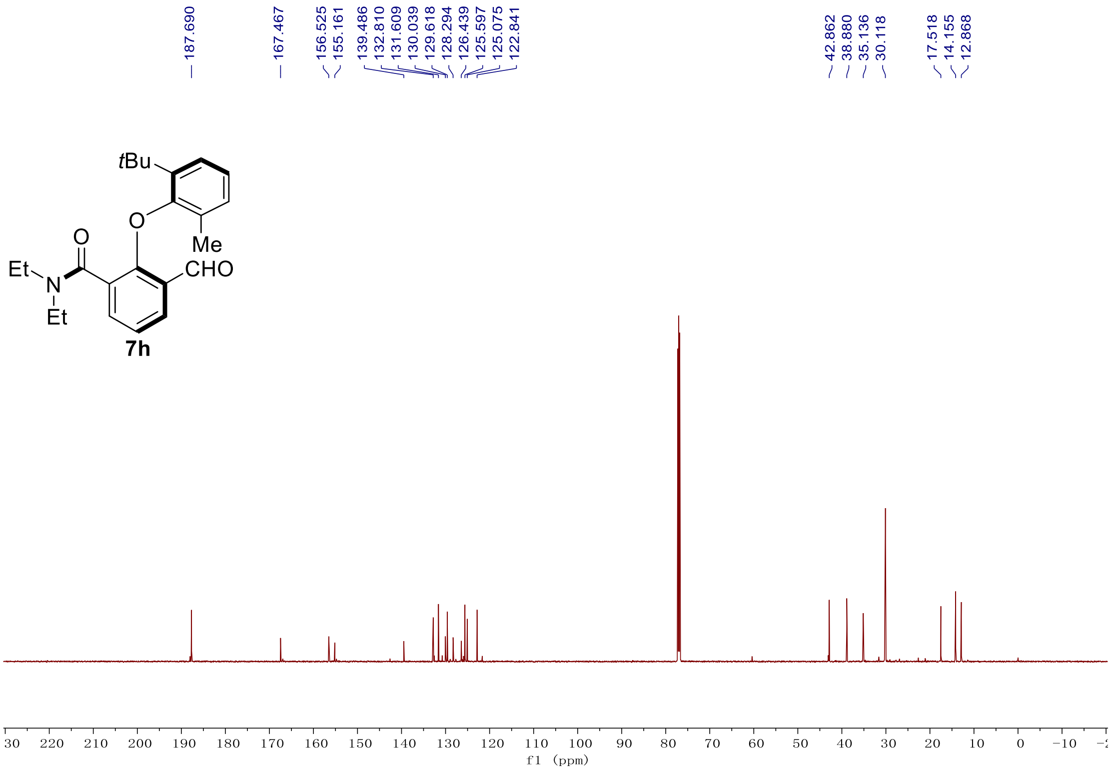
^{1}H NMR (500 MHz, CD$_3$OD) spectrum of 7g.



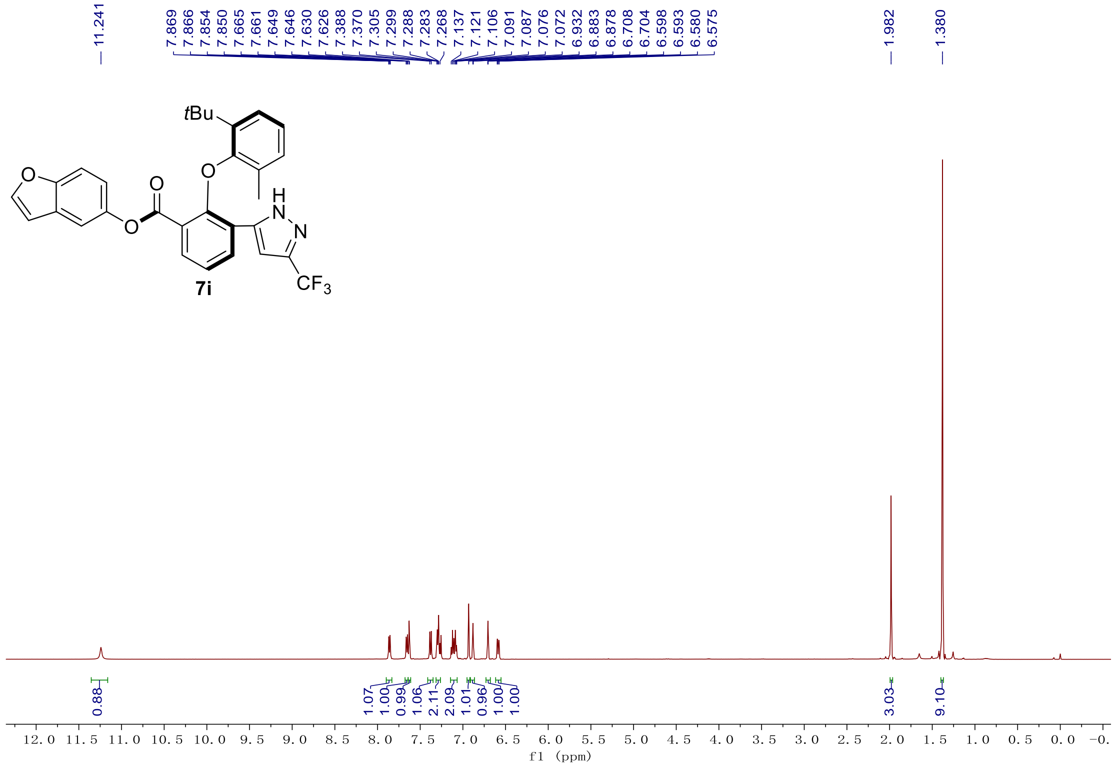
^{13}C NMR (150 MHz, CD$_3$OD) spectrum of 7g.



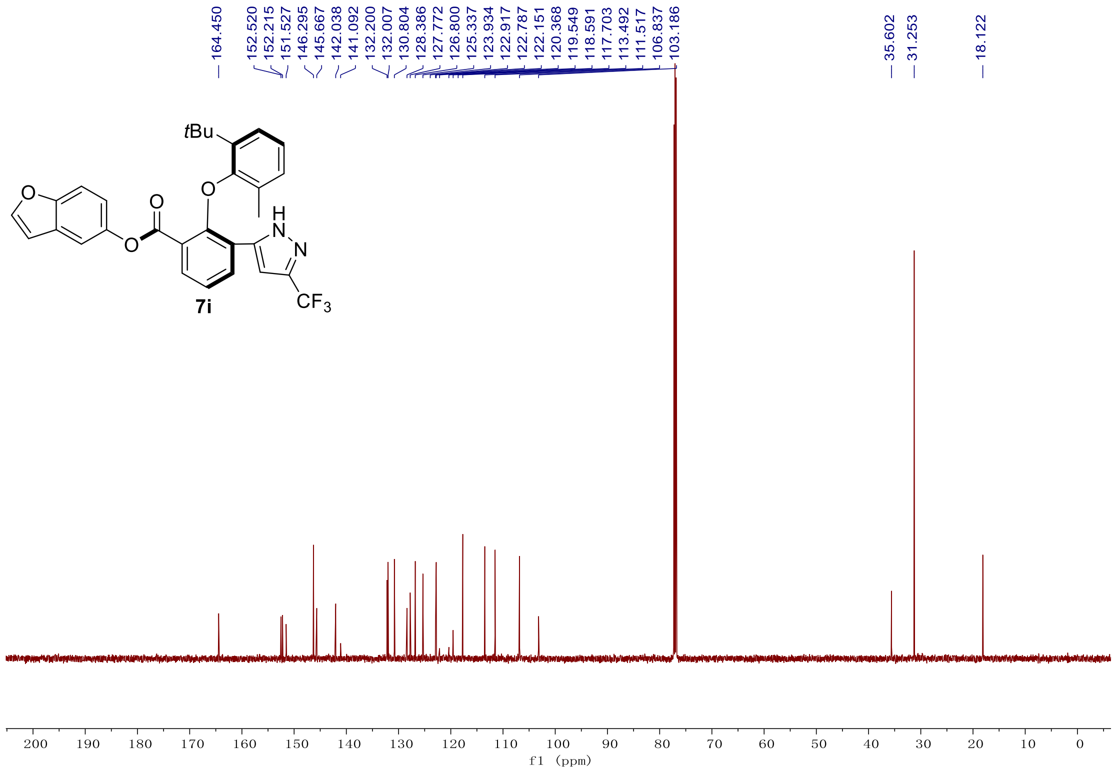
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 7h.



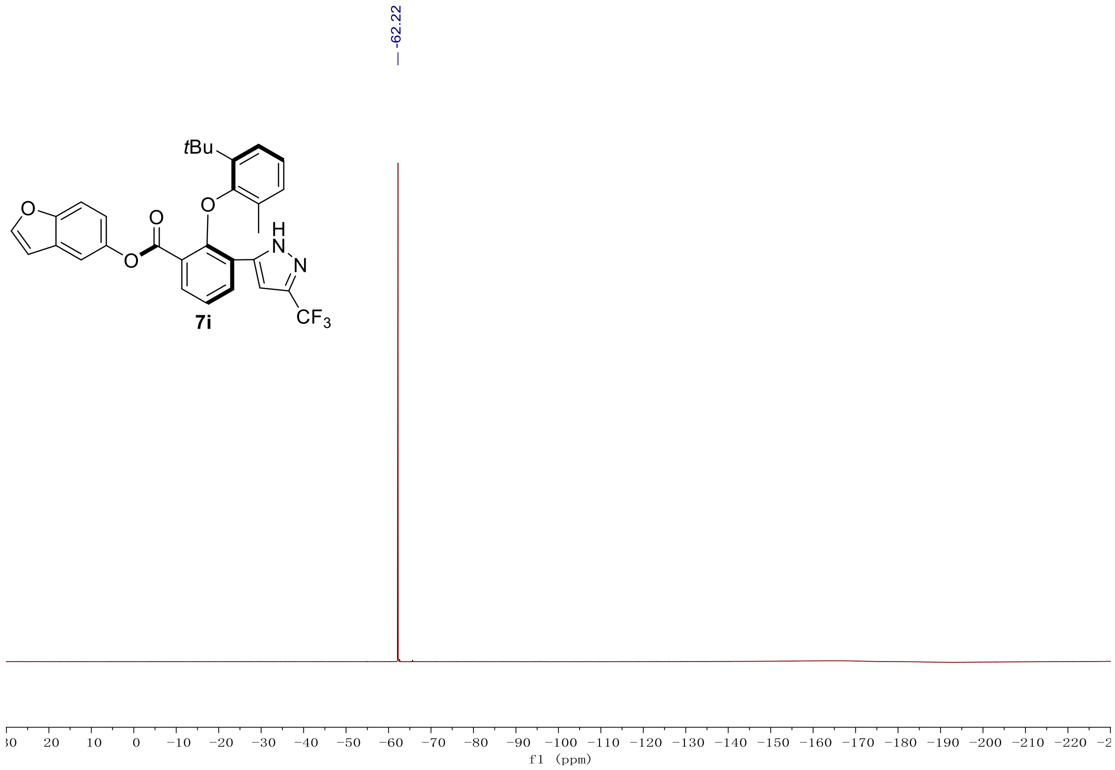
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 7h.



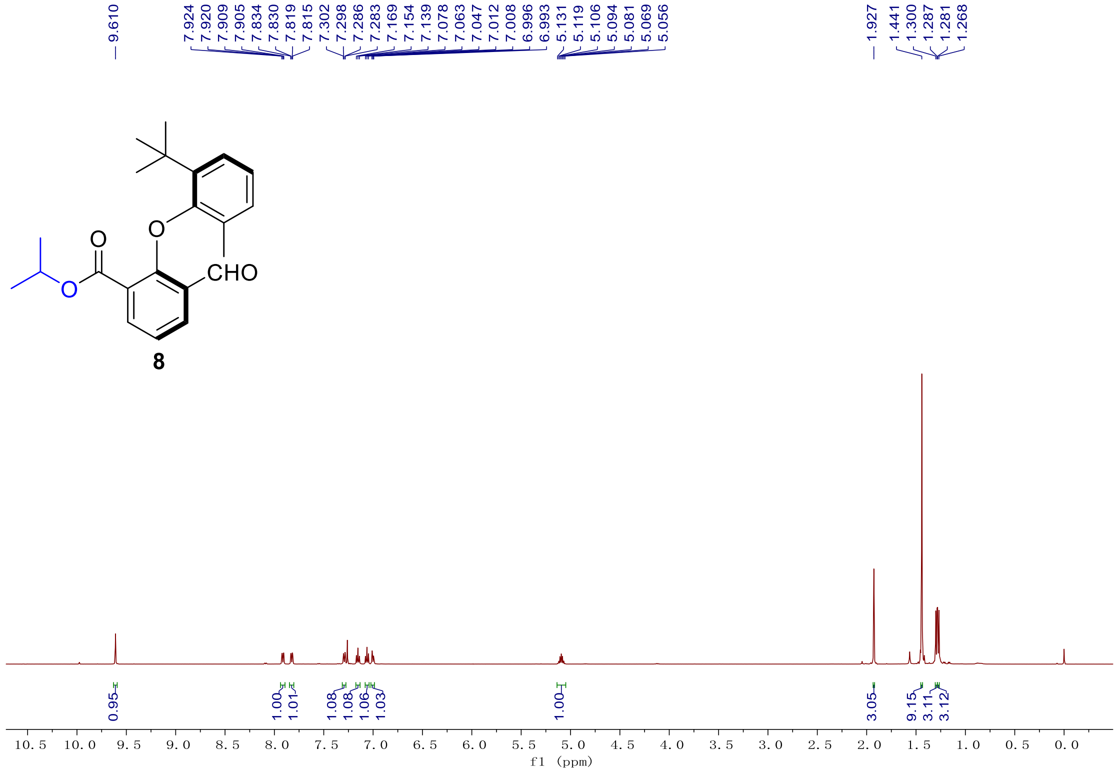
^{1}H NMR (500 MHz, CD_3OD) spectrum of 7i.



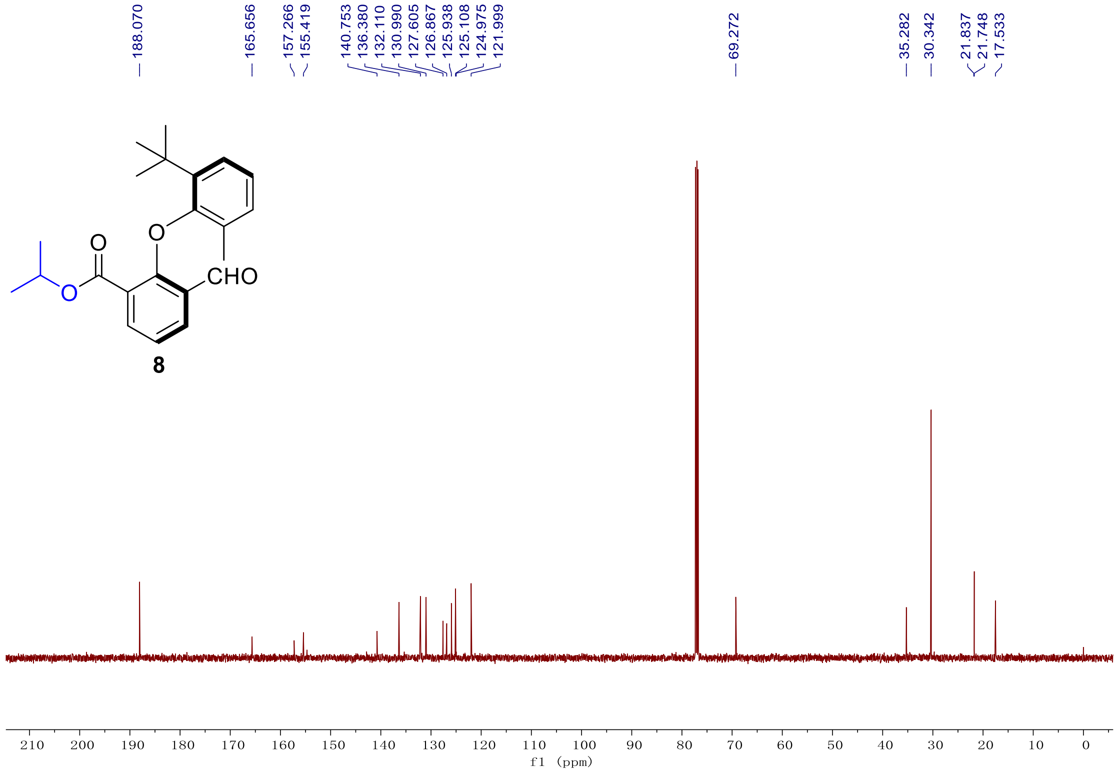
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 7i.



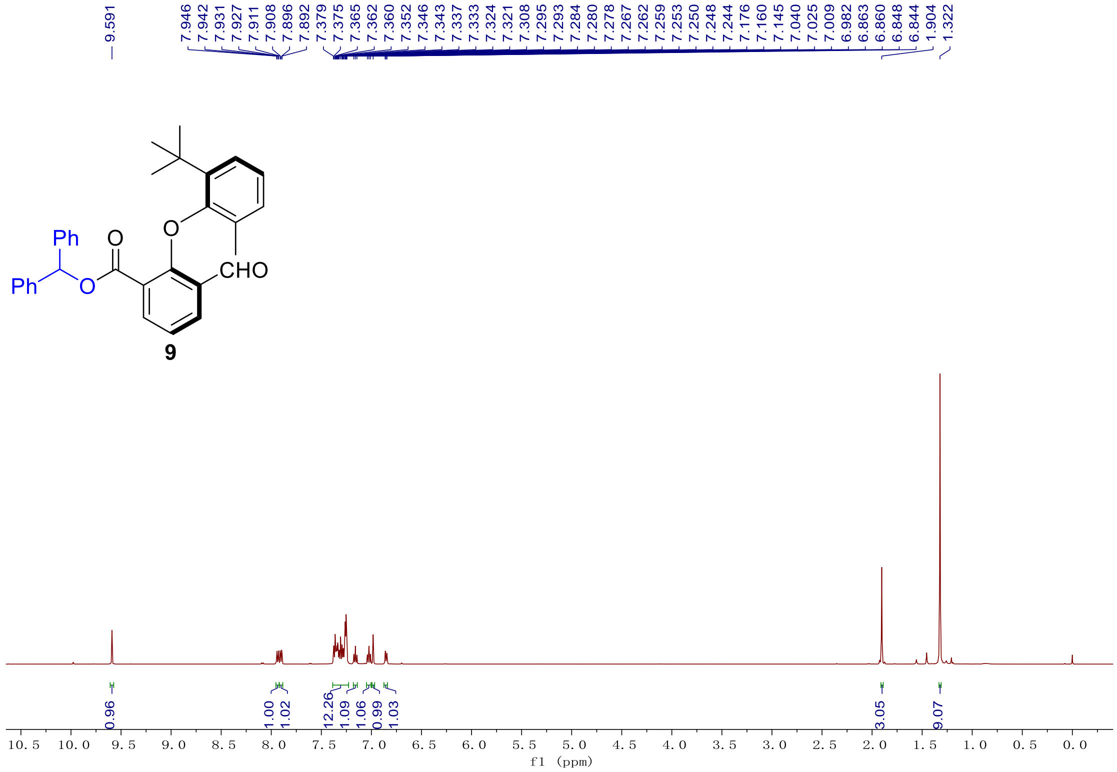
^{19}F NMR (565 MHz, CDCl$_3$) spectrum of 7i.



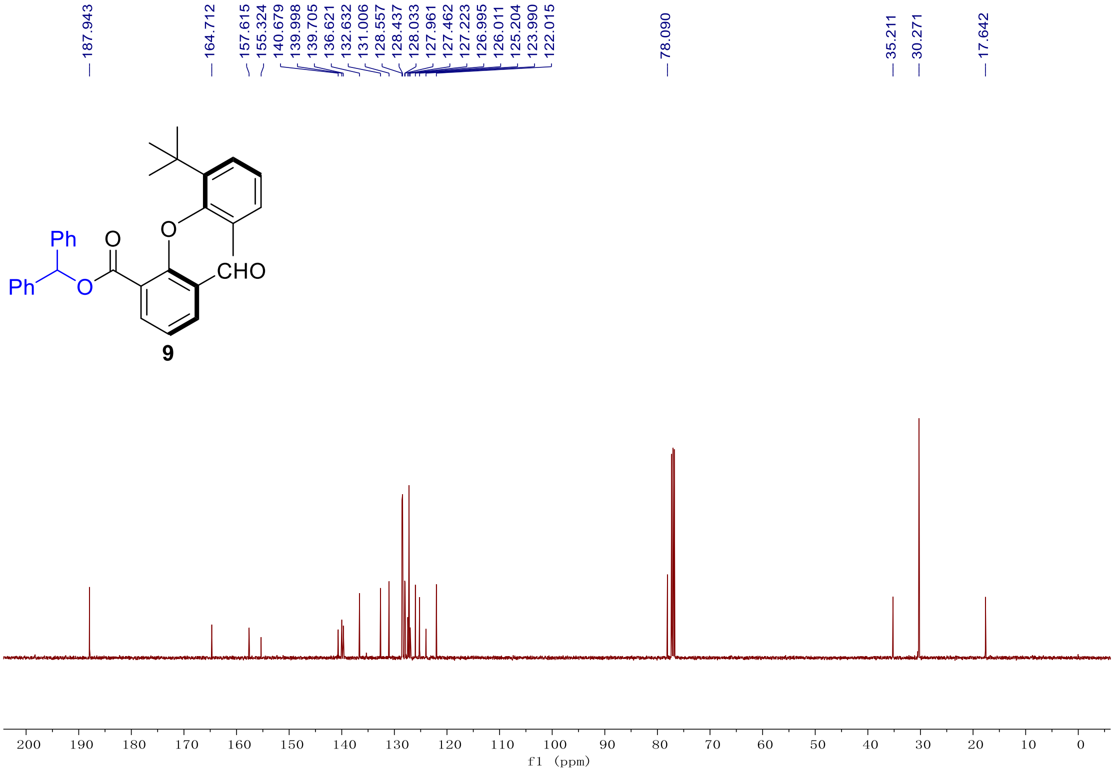
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 8.



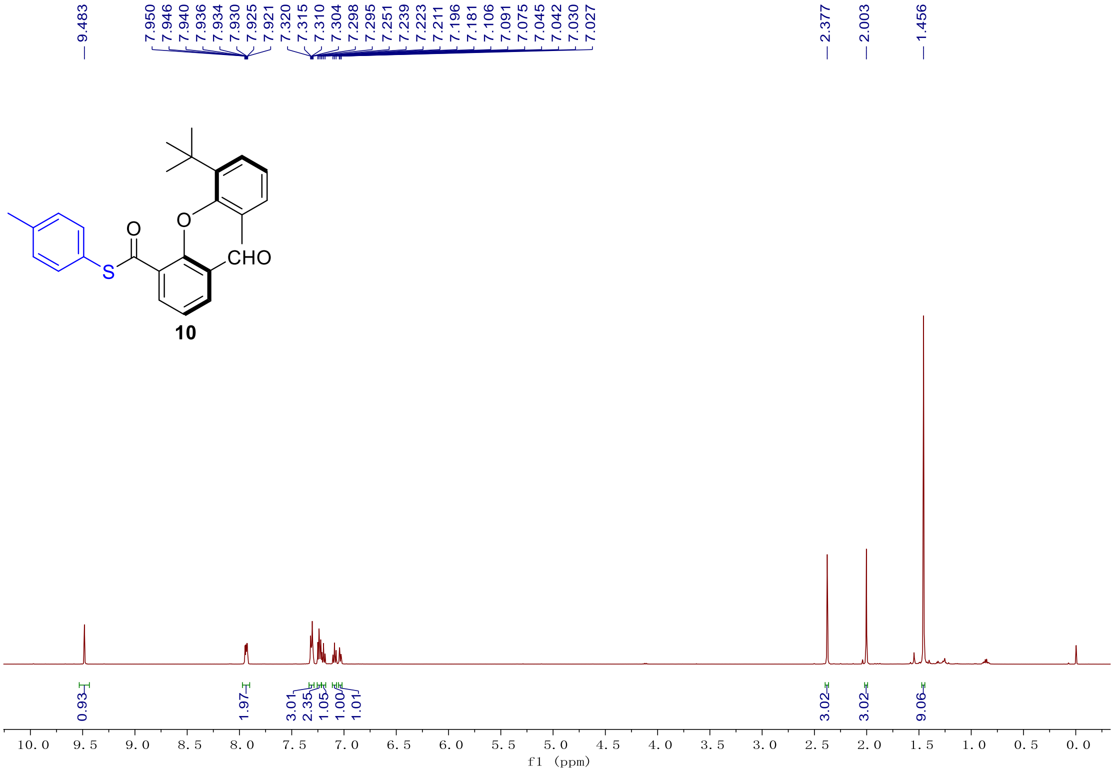
^{13}C NMR (125 MHz, CDCl$_3$) spectrum of 8.



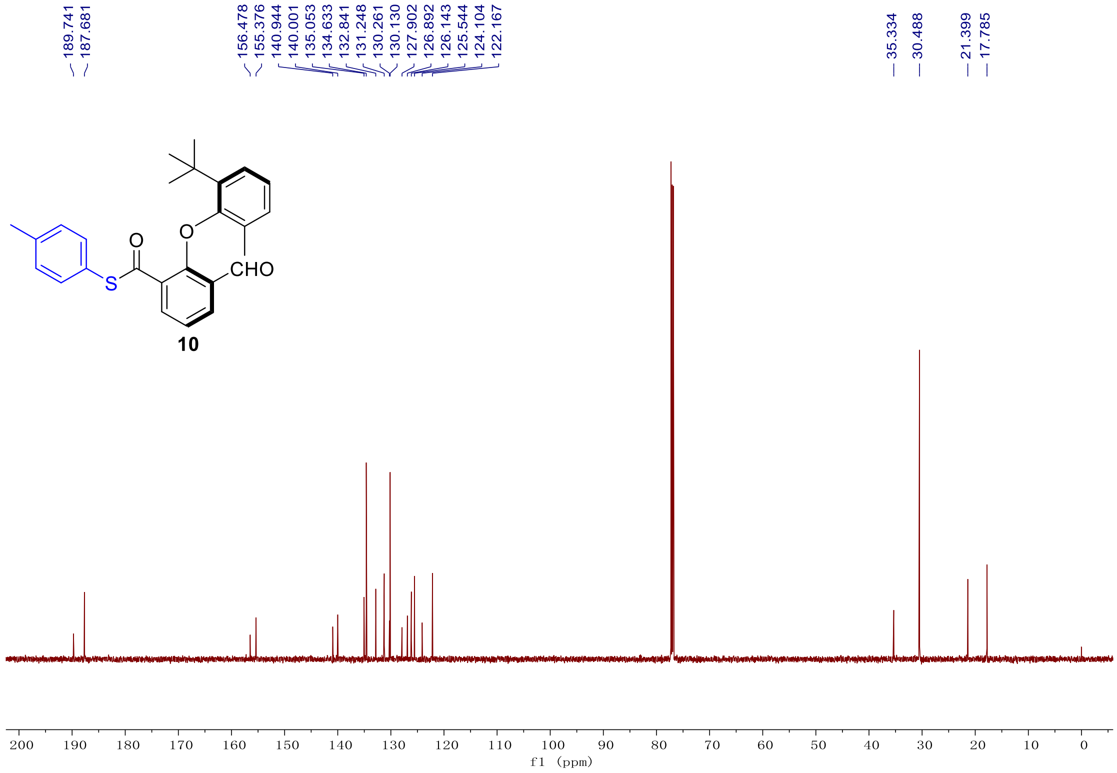
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 9.



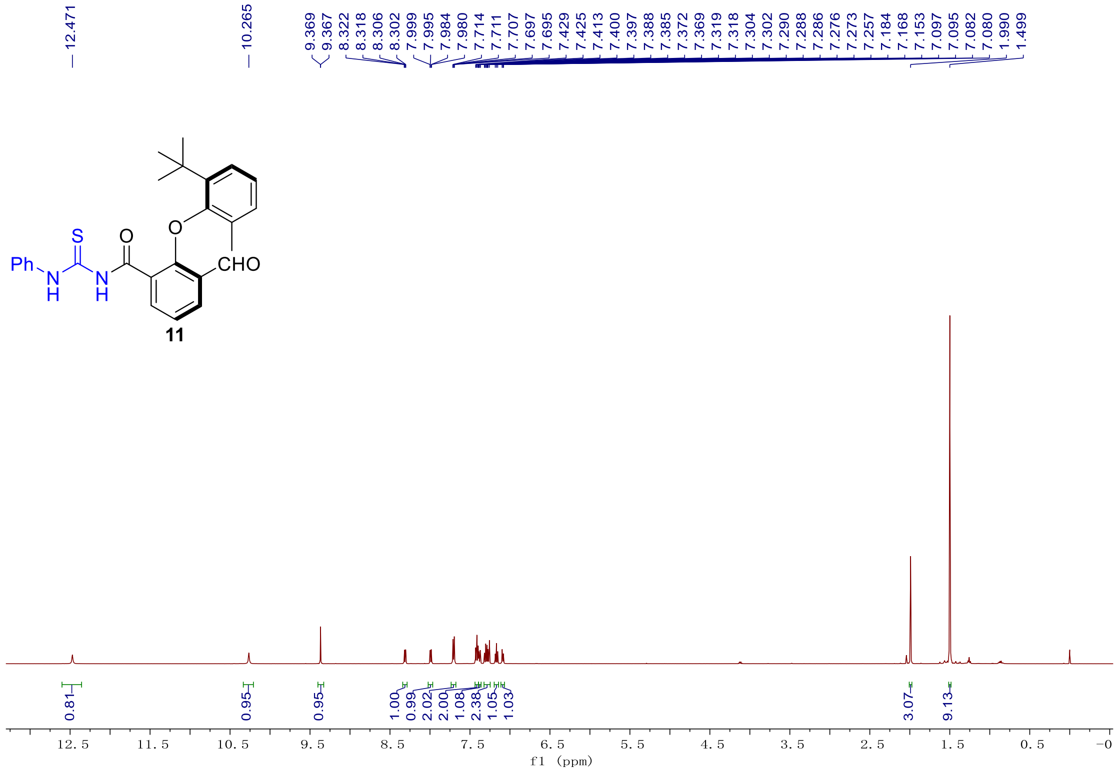
^{13}C NMR (125 MHz, CDCl$_3$) spectrum of 9.



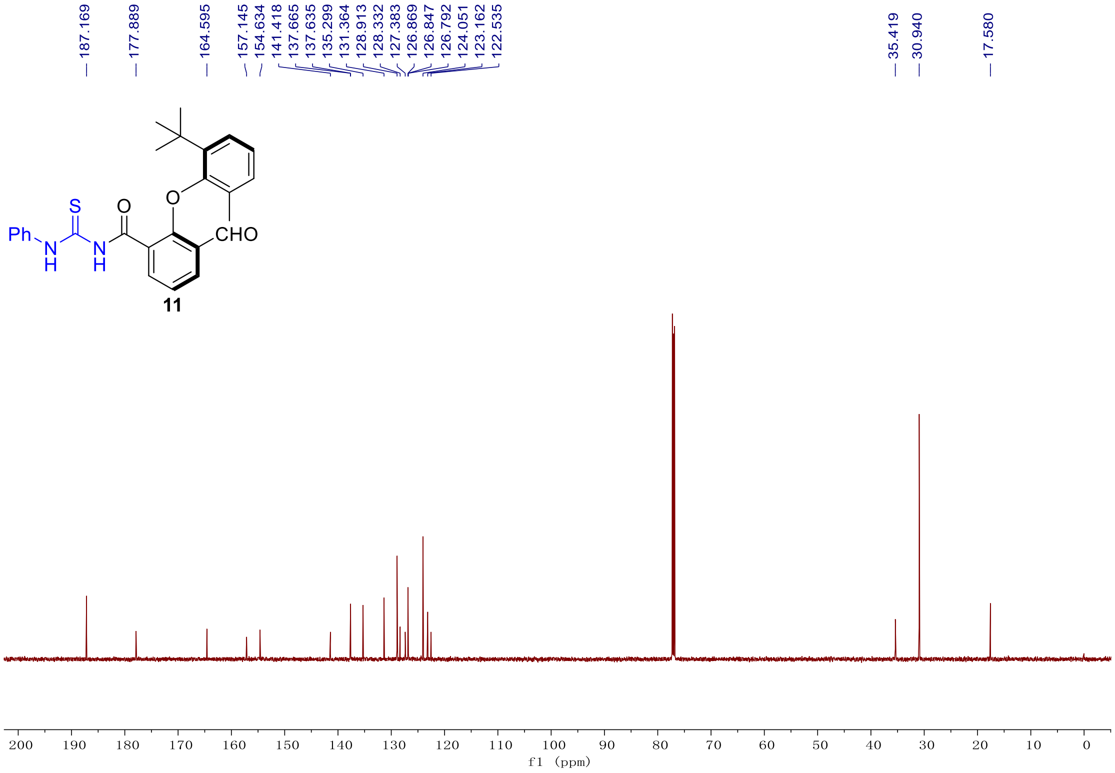
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 10.



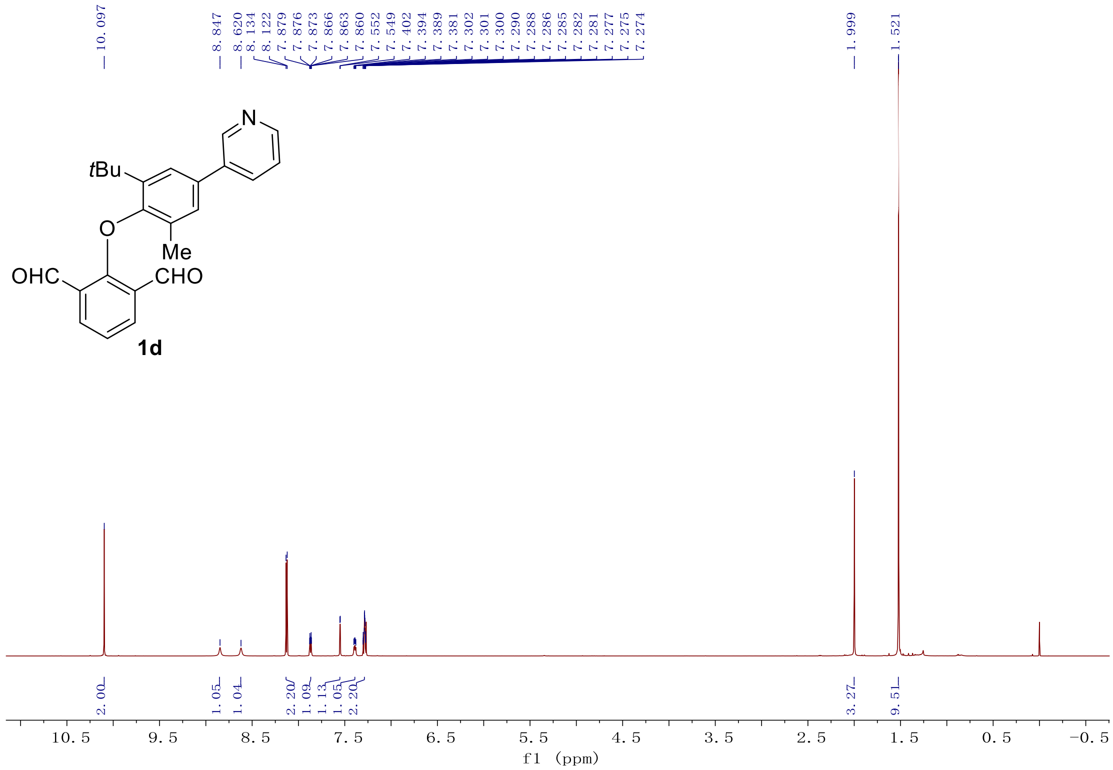
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 10.



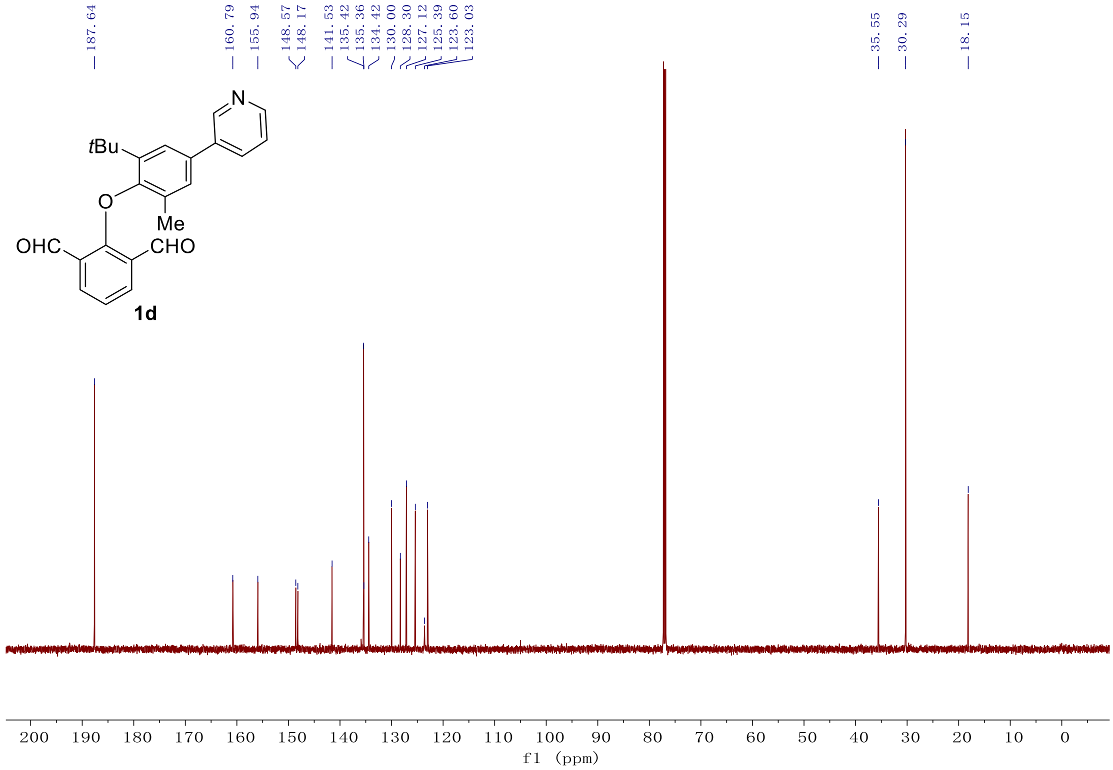
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 11.



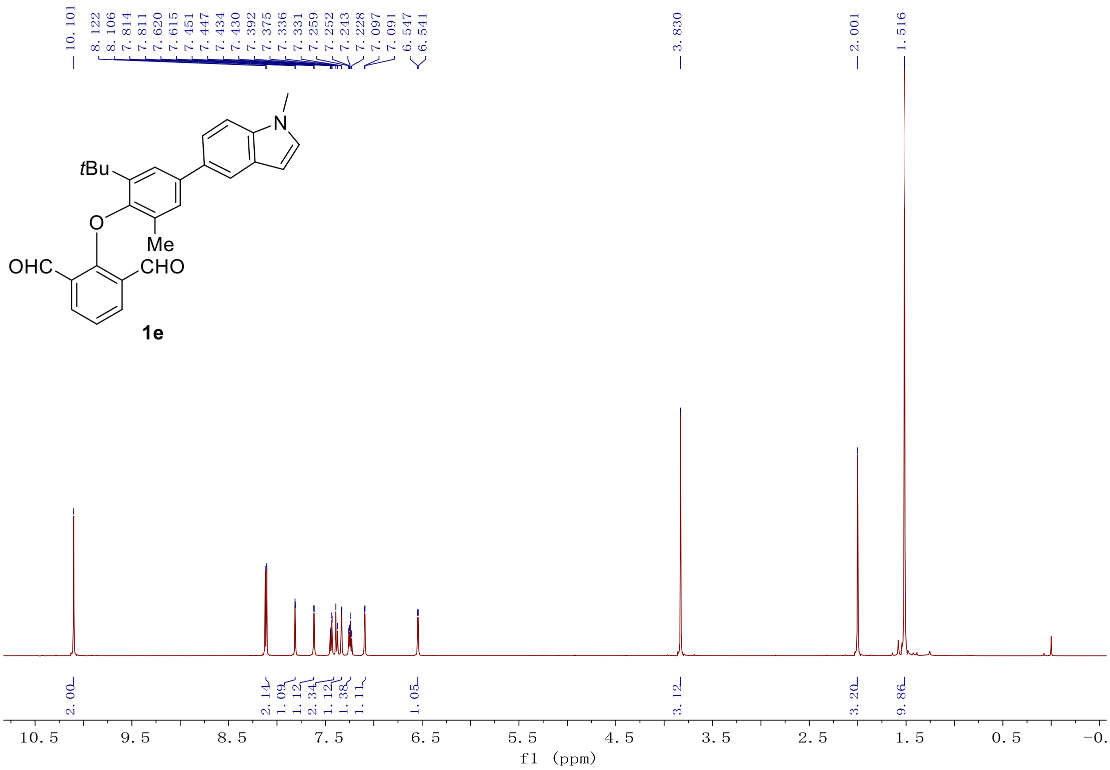
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 11.



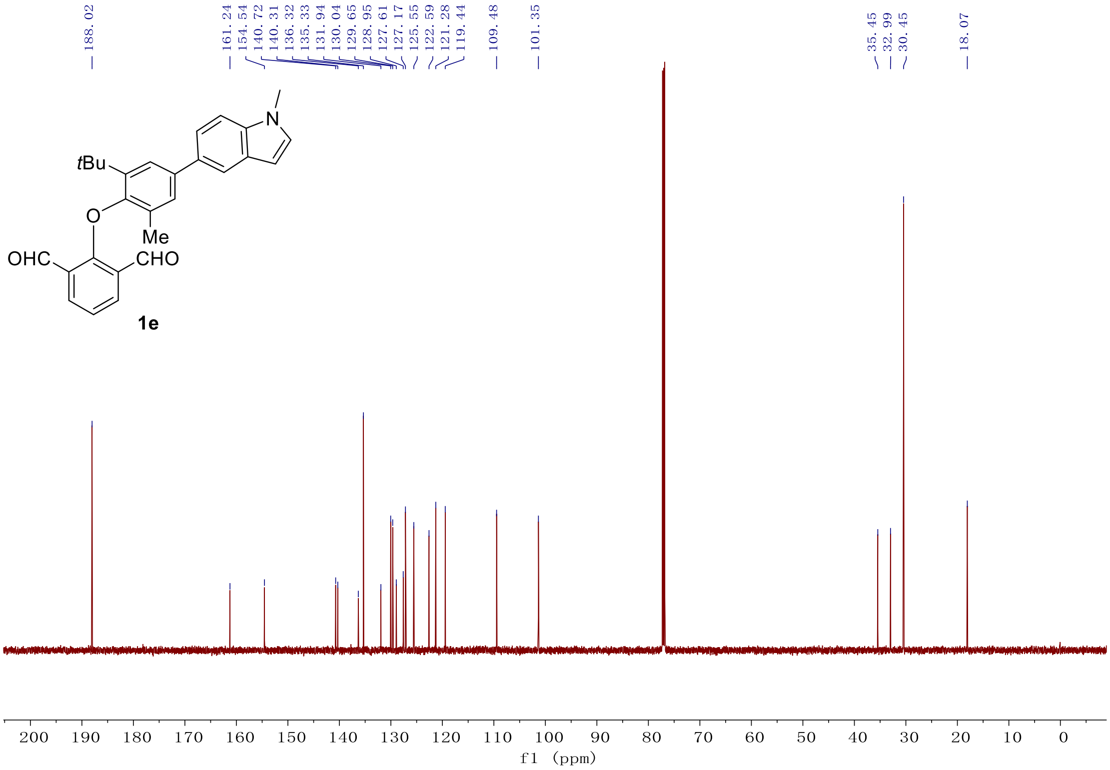
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of 1d.



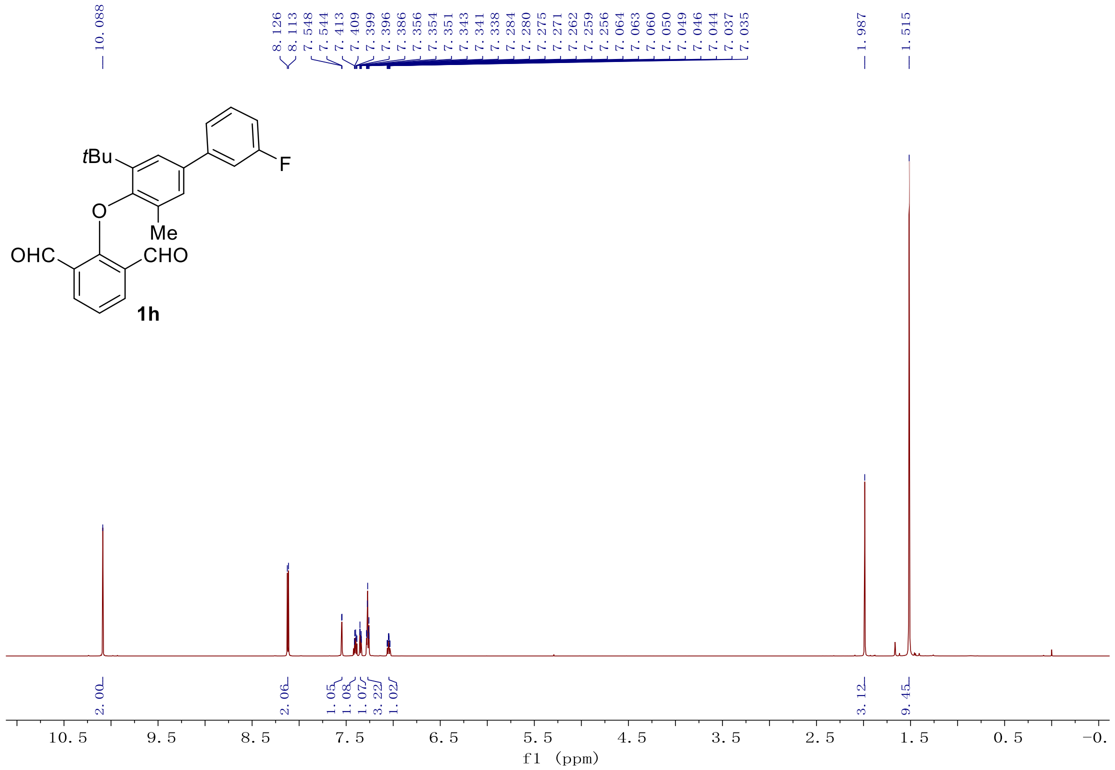
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 1d.



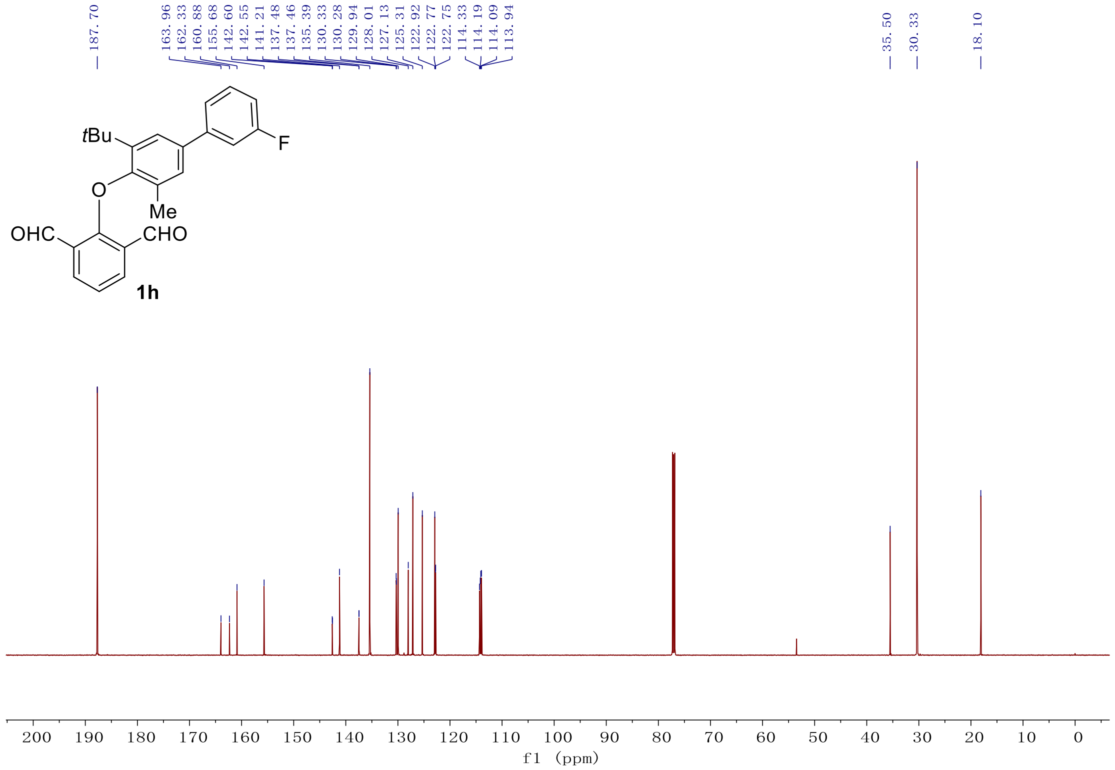
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 1e.



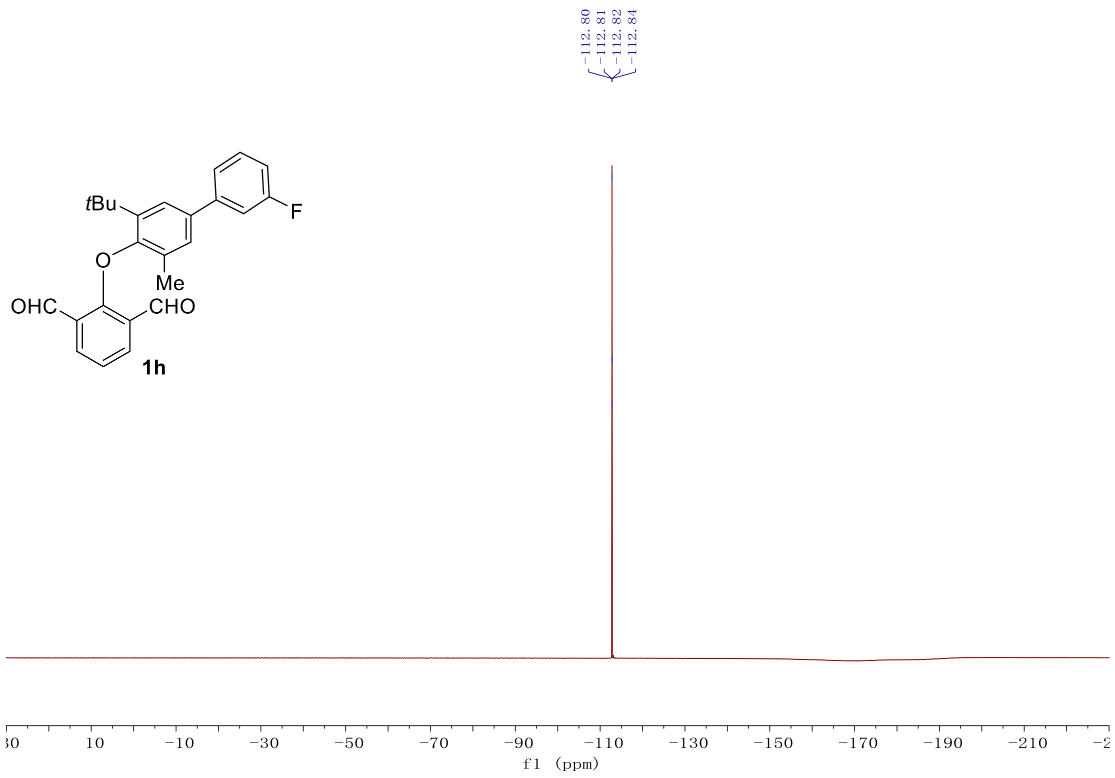
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 1e.



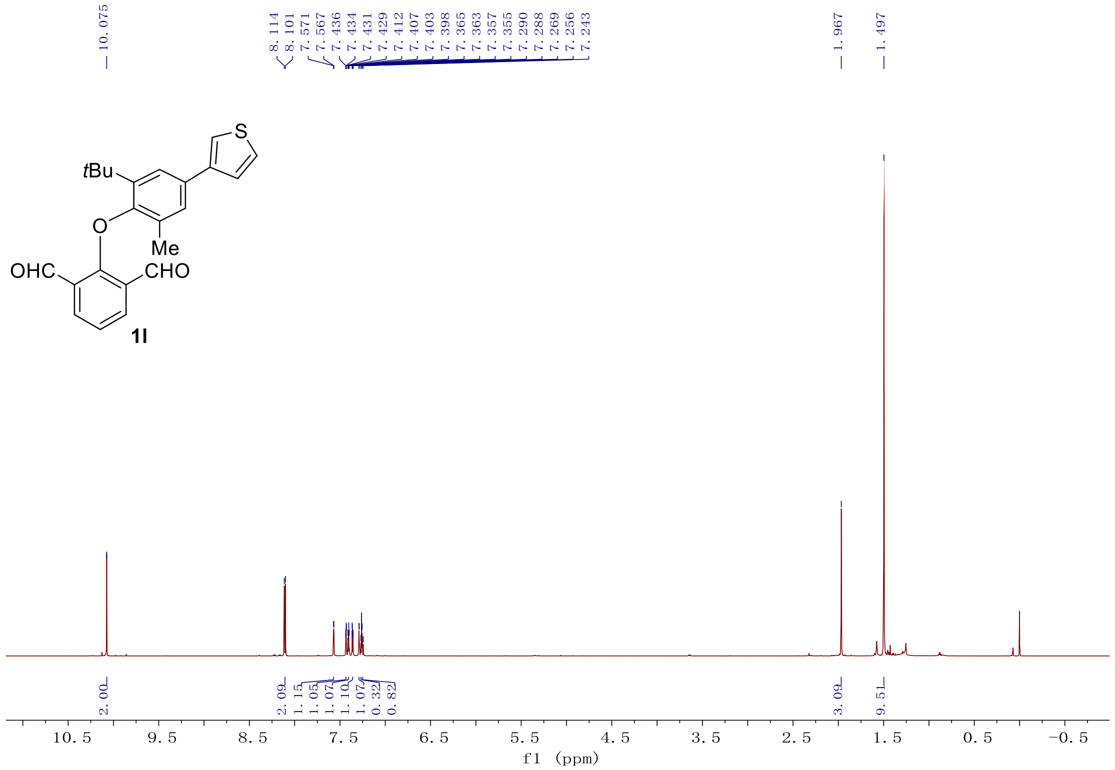
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 1h.



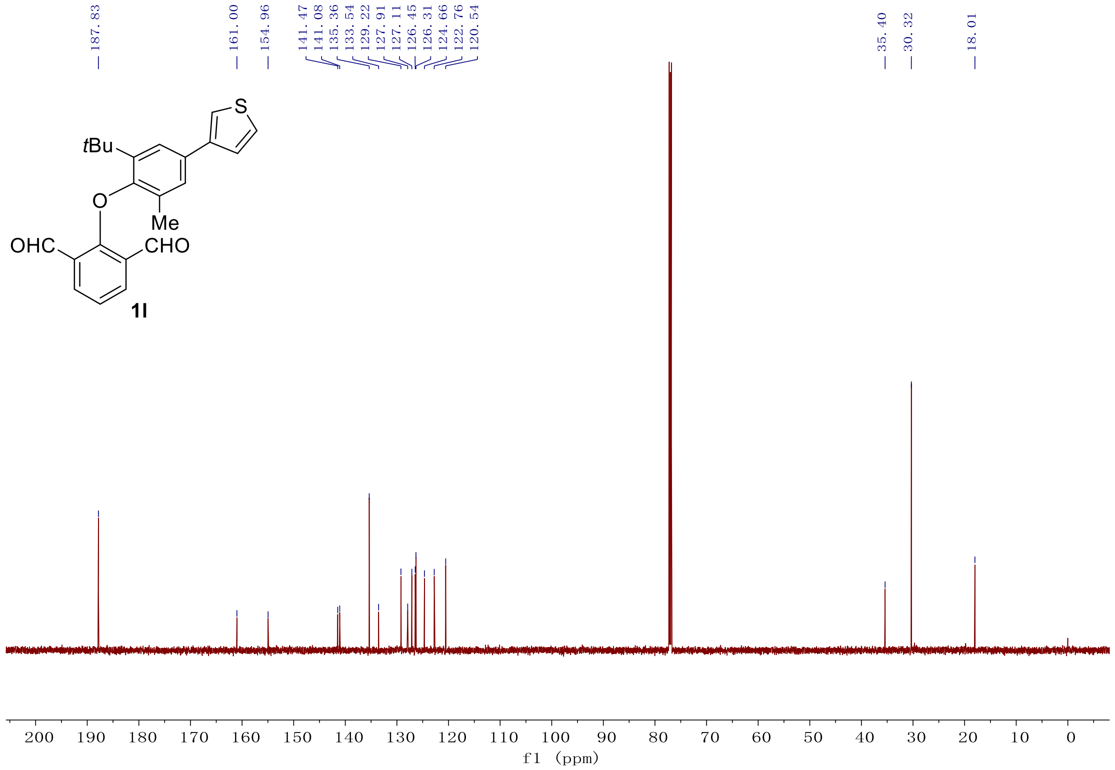
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 1h.



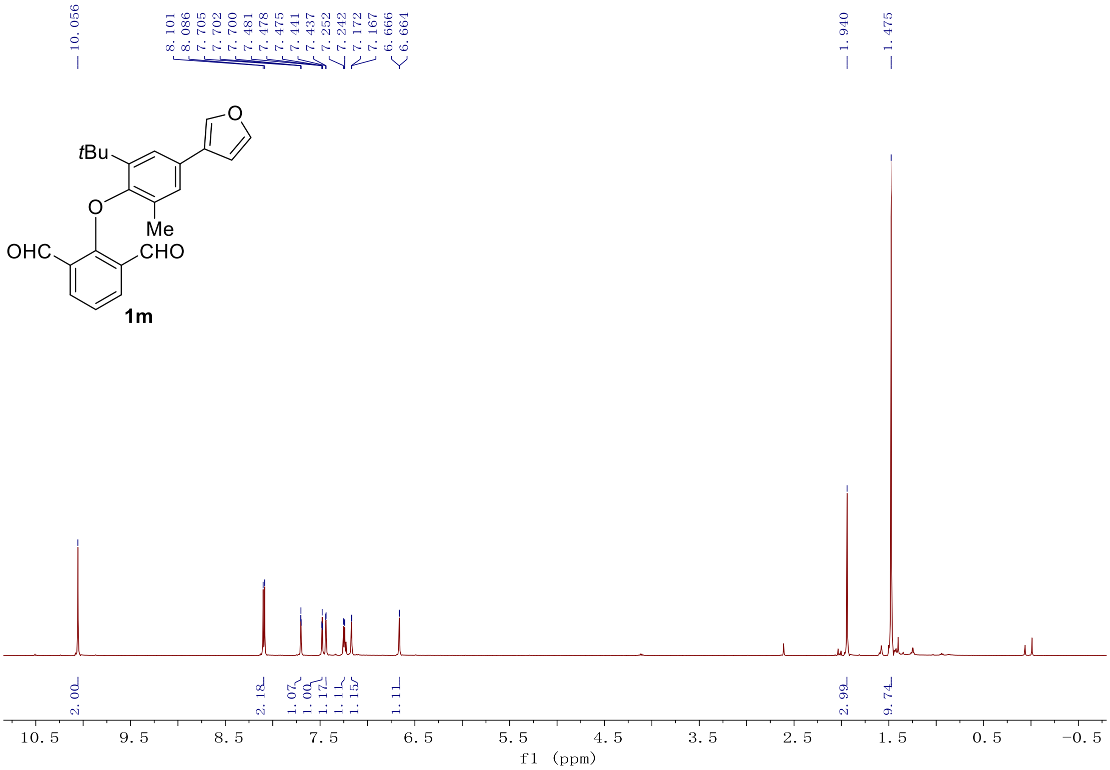
^{19}F NMR (565 MHz, CDCl$_3$) spectrum for 1h.



^{1}H NMR (600 MHz, CDCl$_3$) spectrum of 1l.



^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 1l.



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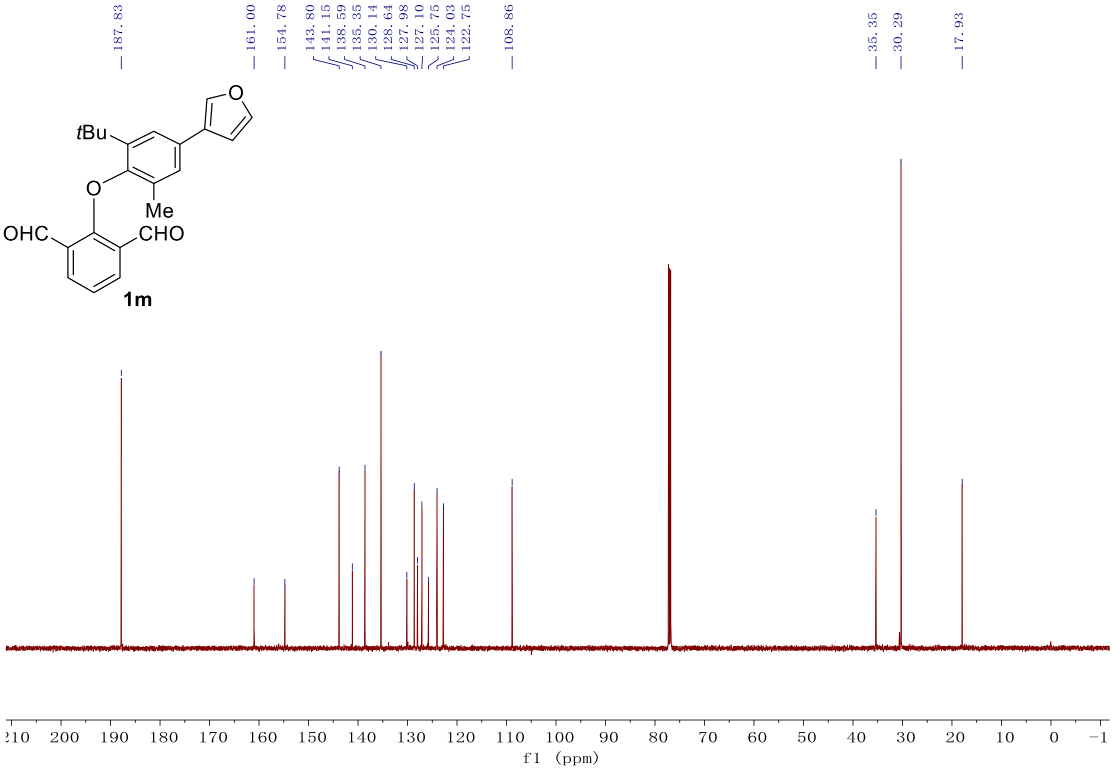
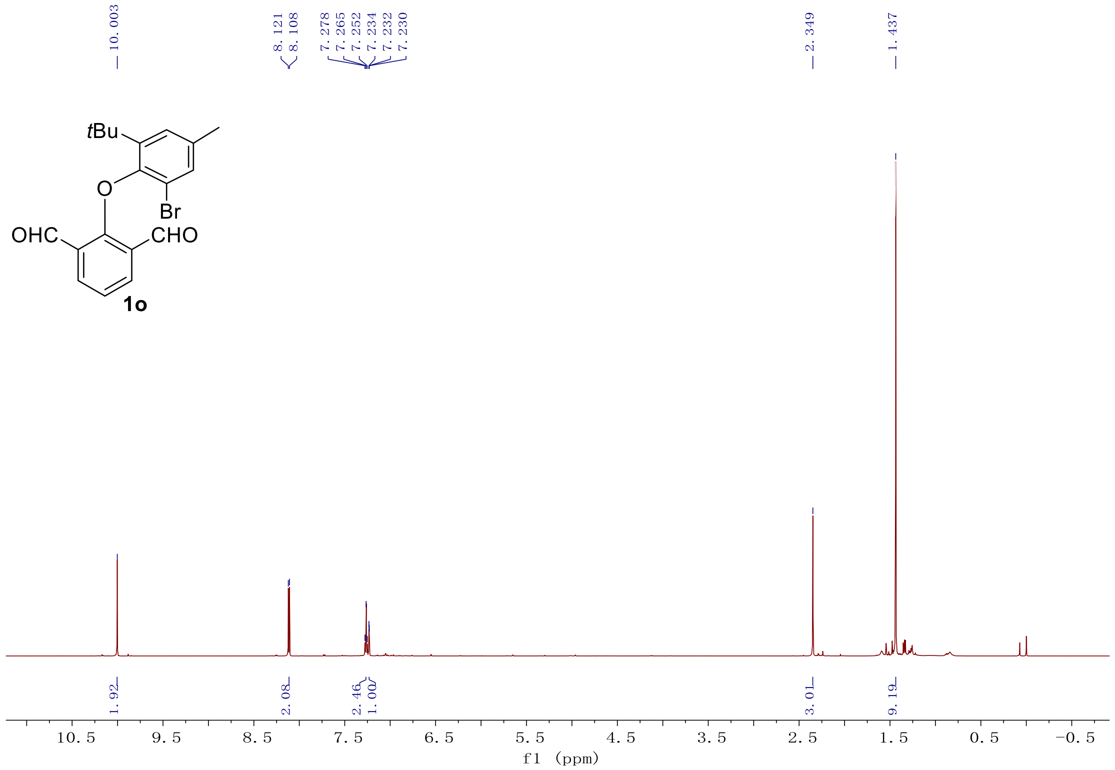
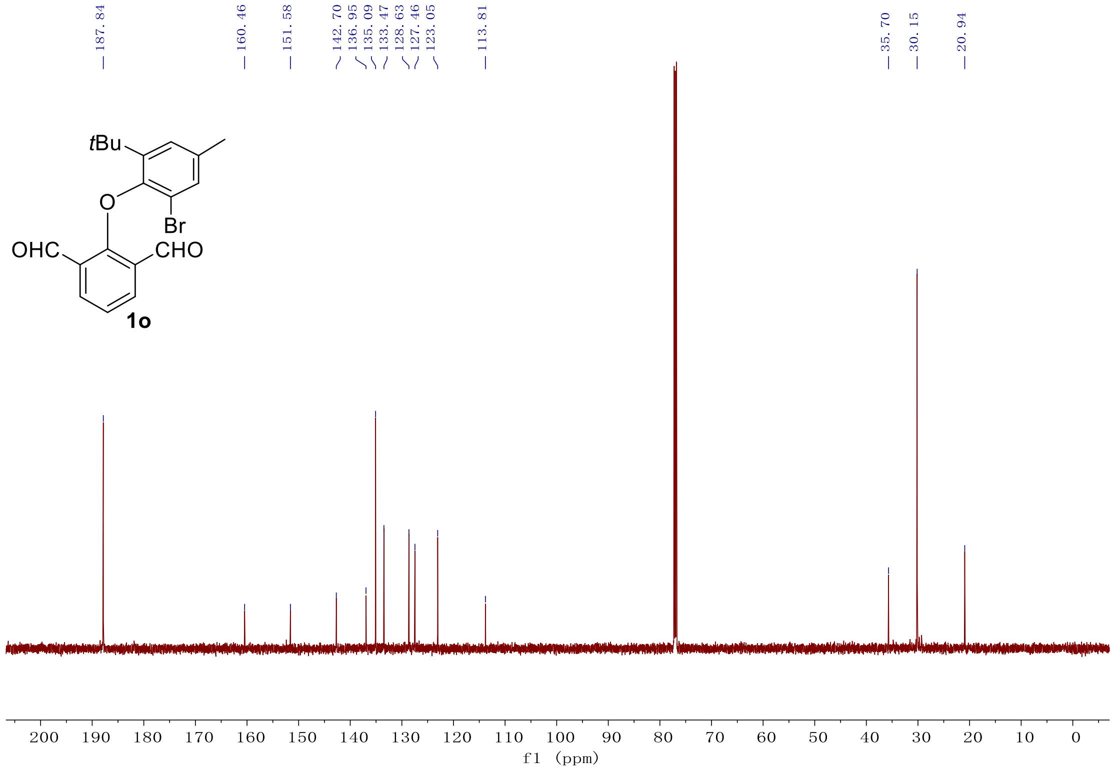


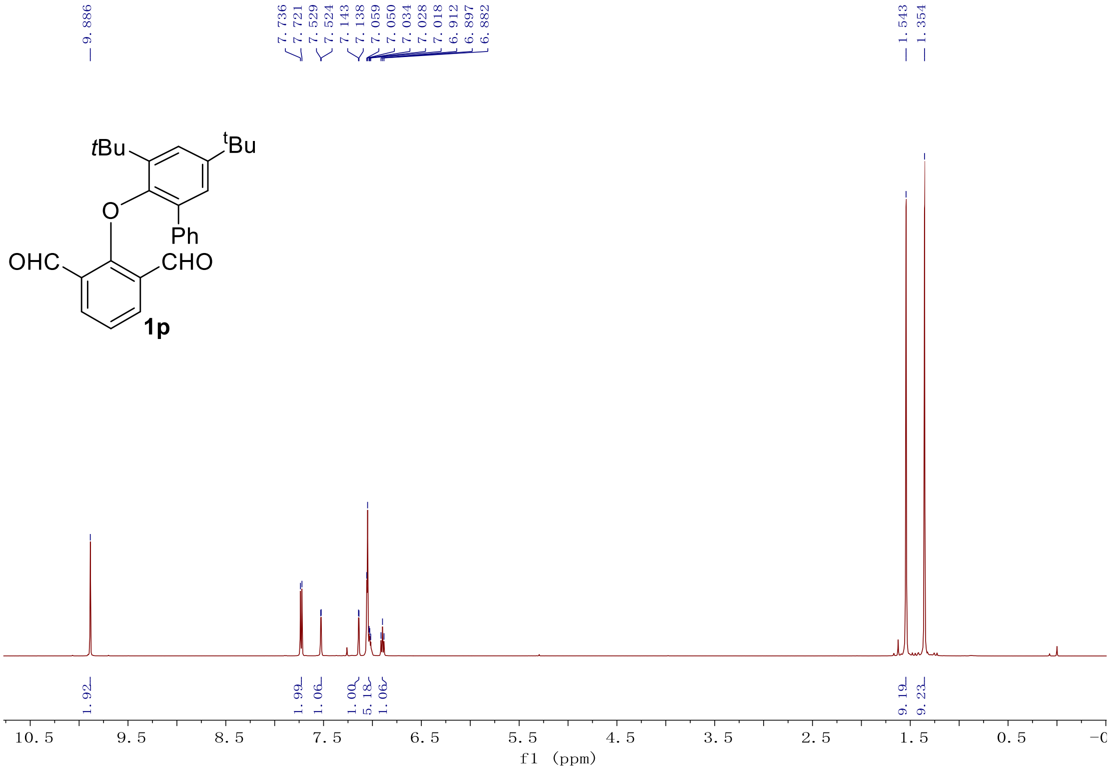
^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 1m.



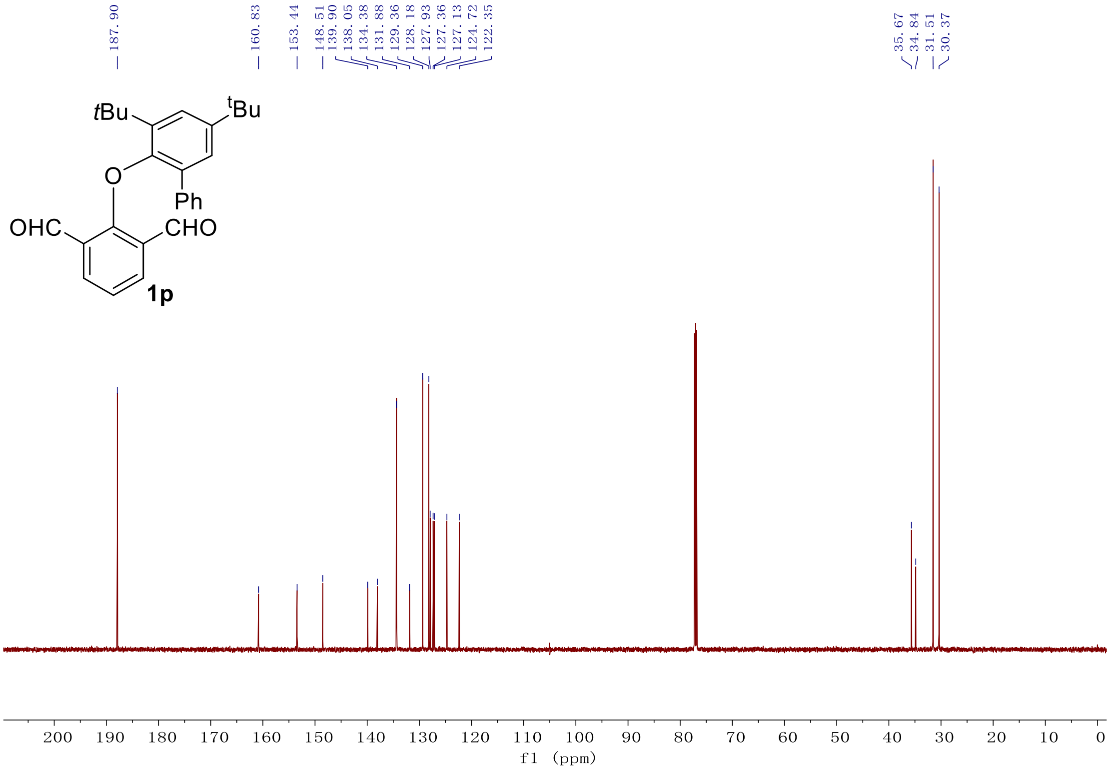
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of 1o.



^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 1o.



^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 1p.



^{13}C NMR (150 MHz, CDCl$_3$) spectrum of 1p.