# Supporting Information

## Enantioselective Construction of Spiro-Tetrahydroquinoline Scaffolds through Asymmetric Catalytic Cascade Reactions.

Jia-Lu Zhang[1], Rui Ma[1], Huan-Huan Zhao[1], and Peng-Fei Xu[1,2]*

[1]*State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China.*
[2]*State Key Laboratory of Veterinary Etiological Biology, College of Veterinary Medicine, Lanzhou University, 730000, P. R. China*

## CONTEENTS

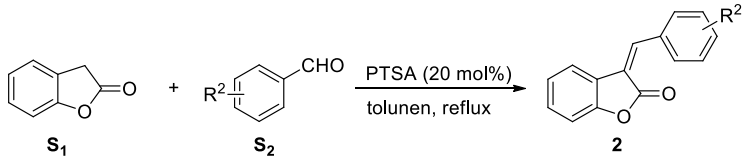
# 1. General Information

Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. tetrahydrofuran (THF), dichloromethane (DCM), 1,2-dichloroethane (DCE), toluene, acetonitrile (MeCN) were dried by passage through alumina using a Pure-Solv PS-MD-5 Solvent Purification System (Innovative Technology). Analytical thin-layer chromatography (TLC) was performed on silicycle silica gel plates with F-254 indicator and compounds were visualized by irradiation with UV light. Flash chromatography was carried out utilizing silica gel 200-300 mesh. $^{1}$H NMR, $^{13}$C NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz $^{1}$H, 100 MHz $^{13}$C). The spectra were recorded in $CDCl_3$ and DMSO as the solvent at room temperature, $^{1}$H and $^{13}$C NMR chemical shifts are reported in ppm relative to either the residual solvent peak ($^{13}$C) ($\delta$ = 77.00 ppm, $\delta$ = 39.51 ppm) or TMS ($^{1}$H) ($\delta$ = 0 ppm，$\delta$ = 2.50 ppm) as an internal standard. Data for $^{1}$H NMR are reported as follows: chemical shift ($\delta$ ppm), multiplicity (s = singlet, d = double, t = triplet, m = multiplet, dd = double doublet), integration, coupling constant (Hz) and assignment. Data for $^{13}$C NMR are reported as chemical shift. HRMS were performed on Bruker Apex II mass instrument (ESI). Enantiomeric excess values were determined by HPLC with Daicel Chirapak IA column on Agilent 1260 series with *i*-PrOH and *n*-hexane. Optical rotation was measured on the Perkin Elmer 341 polarimeter with $[\alpha]_D$ values reported in degrees. Concentration (c) is in g/100 mL. The irradiation vessels were purchased from http:// www.xinweier.com/.

# 2. General Procedure and Spectral Data of Products

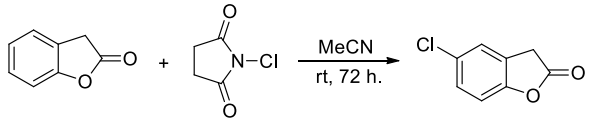
## 2.1 Preparation of Substrate 2.

**The generation of synthesis compounds 2.**

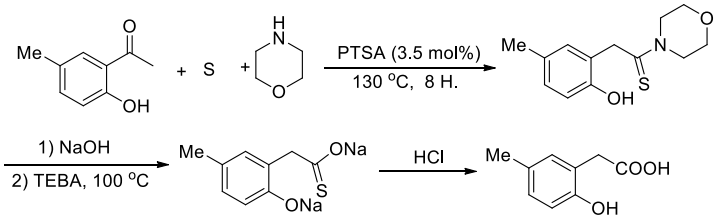



A solution of 2-coumaranone ($S_1$, 20 mmol), substituted benzaldehydes ($S_2$, 20 mmol) and P-toluenesulfonic acid (20 mol%) were added to 40 mL toluene in a 100 mL flame-dried round bottom, which was refluxed overnight. After cooling to room temperature, the solvent was evaporated under reduced vacuum, and the residues were purified by flash silica gel chromatograph to obtain the crude products, which were recrystallized from PE and EA to afford the pure compounds.

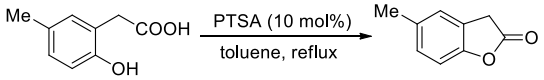
The precursors of **2q**, **2r** were synthesized after the minor modification of the reported literatures[2], which are shown as follows:




To a 100 mL round-ask, 2-benzofuranone (2-coumaranone, 1.92 g, 14.3 mmol), N-chlorosuccinimide (5.72 g, 42.6 mmol) and anhydrous $CH_3CN$ (50 ml) were added and the solution was vigorously stirred for 3 days. $CH_3CN$ was then evaporated and the residue was diluted with toluene. The organic solution was washed with one portion of $Na_2S_2O_3$ (aq) and two portions of $H_2O$, then dried over $Na_2SO_4$. After removal of the $Na_2SO_4$, the solvent was evaporated and the residue was purified by silica gel column chromatography (PE/EA/DCM = 10/1/2) to afford the desired product as a yellow solid.



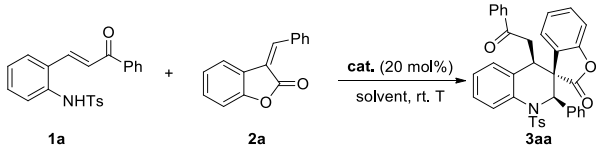

To a 100 mL round flask was added 1-(2-hydroxy-5-methylphenyl)ethanone (15 g, 100 mmol), sulfur (6.4 g, 200 mmol), morpholine (20 mL) and p-toluene sulphonic acid (0.665 g, 3.5 mmol). Then the solution was heated under constant stirring in an oil bath at 130 °C for 8 h. After completion of the reaction as monitored by TLC, the reaction mixture was allowed to cool and 20% NaOH and triethyl benzyl ammonium chloride $S_3$ (TEBA) (570 mg, 0.25 mmol) were added. The reaction mixture continued hydrolysis at 100 °C for additional 8 h. After cooling to the room temperature, 50 mL of DCM was added to the system and the residue was stirred at rt. for 0.5 h, then the system was acidified with HCl (0.3 M) to pH 6, extracted with DCM (3x50 mL), $H_2O$, brine, dried over anhydrous $Na_2SO_4$, evaporated under reduced pressure and the residue was purified by silica gel column chromatography (PE/EA/DCM = 5/1/2) to afford the desired product as a yellow solid.




A solution of 2-(2-hydroxy-5-methylphenyl)acetic acid (20 mmol), P-toluenesulfonic acid (20 mol%) were added to 40 mL toluene in a 100 mL flame-dried round bottom, which was refluxed overnight. After cooling to room temperature, the solvent was evaporated under reduced vacuum, and the residues were purified by flash silica gel chromatograph to obtain the crude products, which were recrystallized from PE and EA to afford the pure compounds.

Compound **1** can be synthesized by the reported literature[1].

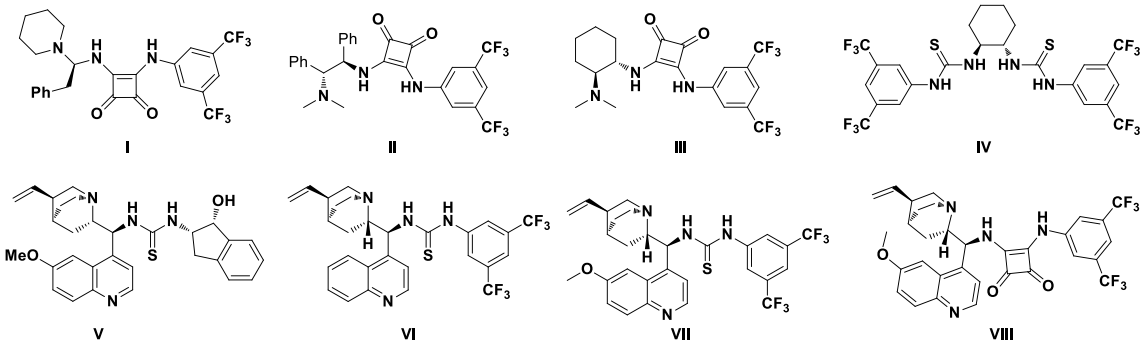
## 2.2 Optimization of *aza*-Michael addition reaction of 1a and 2a.




| entry | cat. | solvent | T (h) | yield (%)[c] | dr[d] | ee (%)[e] |
|---|---|---|---|---|---|---|

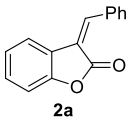
| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | **I** | DCE | 50 | 25 | >20:1 | 97 |
| 2 | **II** | DCE | 50 | 23 | >20:1 | 99 |
| 3 | **III** | DCE | 50 | 85 | >20:1 | -97 |
| 4 | **IV** | DCE | 50 | n.r. | -- | -- |
| 5 | **V** | DCE | 50 | 50 | >20:1 | 94 |
| 6 | **VI** | DCE | 50 | 65 | >20:1 | 97 |
| 7 | **VII** | DCE | 50 | 91 | >20:1 | 96 |
| 8 | **VIII** | DCE | 50 | 99 | >20:1 | 97 |
| 9 | **VIII** | Toluene | 52 | 88 | >20:1 | 97 |
| 10 | **VIII** | DCM | 50 | 99 | >20:1 | 96 |
| 11 | **VIII** | $CH_3Cl$ | 50 | 86 | >20:1 | 96 |
| 12 | **VIII** | EA | 60 | 86 | >20:1 | 97 |
| 13 | **VIII** | THF | 60 | 40 | >20:1 | 96 |
| 14 | **VIII** | MeCN | 60 | 61 | >20:1 | 96 |
| 15[a] | **VIII** | DCE | 46 | 99 | >20:1 | 97 |
| 16[b] | **VIII** | DCE | 44 | 99 | >20:1 | 97 |

Unless otherwise noted, the reactions were conducted with **1a** (0.11 mmol), **2a** (0.1 mmol), and 20 mol % of the catalyst, in solvent (1.0 mL) at rt. for 44 h. [a]0.15 mmol of **1a** was added, [b]0.2 mmol of **2a** was added. [c]Isolated yield. [d]Determined by $^1$H NMR. [e]Determined by chiral-phase HPLC analysis.



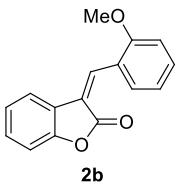

## 2.3 Spectral Data of Substrates.

**(E)-3-benzylidenebenzofuran-2(3H)-one (2a)**




Yellow solid (petroleum ether/EtOAc/$CH_2Cl_2$ = 7/1/2, 1.11g, 45% yield).$^1$H NMR （400 MHz, $CDCl_3$）δ = 7.86 (d, *J* = 3.16 Hz, 1H), 7.73 (d, *J* =7.80 Hz, 1H), 7.69-7.66 (m, 2H), 7.52-7.45 (m, 3H), 7.36-7.31 (m, 1H), 7.12 (dd, *J* = 2.52 Hz, J = 8.02 Hz, 1H), 7.03 (td, *J* = 7.70 Hz, *J* = 1.00 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 168.8, 154.3, 140.9, 133.9, 130.8, 130.4, 129.3, 128.7, 123.6, 122.7, 122.1, 121.7, 111.1.

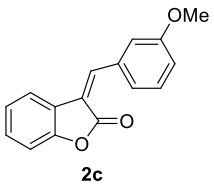
**(Z)-3-(2-methoxybenzylidene)benzofuran-2(3H)-one (2b)**




Yellow solid (petroleum ether/EtOAc/$CH_2Cl_2$ = 7/1/2, 1.35g, 48% yield).$^1$H

NMR（400 MHz, $CDCl_3$） δ = 8.03 (s, 1H), 7.72 (d, *J* = 7.24 Hz, 1H), 7.63 (d, *J* = 7.60 Hz, 1H), 7.45 (t, *J* = 7.88 Hz, 1H) , 7.31-7.25 (m, 1H), 7.09 (d, *J* = 8.14 Hz, 1H), 7.05-6.97 (m, 3H), 3.87 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 168.8, 158.0, 154.0, 137.2, 132.4, 130.3, 129.3, 123.3, 122.7, 122.5, 122.0, 121.4, 120.0, 110.9, 110.8, 55.4.

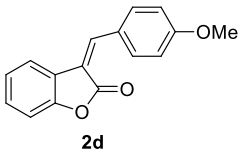
**(Z)-3-(3-methoxybenzylidene)benzofuran-2(3H)-one (2c)**



2c

Yellow solid (petroleum ether/EtOAc/$CH_2Cl_2$ = 7/1/2, 1.35g, 48% yield).$^1$H NMR（400 MHz, $CDCl_3$）δ = 7.81 (s, 1H), 7.75 (d, *J* = 7.72 Hz, 1H), 7.40 (d, *J* = 7.92 Hz, 1H), 7.35-7.31 (m, 1H), 7.25 (d, *J* = 7.56 Hz, 1H), 7.16 (s, 1H), 7.12 (d, J = 7.96 Hz, 1H), 7.05-6.99 (m, 2H), 3.84 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 168.8, 159.6, 154.4, 140.7, 135.1, 130.8, 129.8, 123.5, 122.9, 122.2, 121.6, 121.6, 116.2, 114.2, 111.1, 55.3.

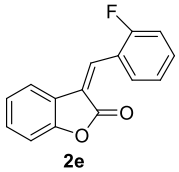
**(Z)-3-(4-methoxybenzylidene)benzofuran-2(3H)-one (2d)**



2d

Yellow solid (petroleum ether/EtOAc/$CH_2Cl_2$ = 7/1/2, 1.35g, 48% yield).$^1$H NMR（400 MHz, $CDCl_3$） δ = 8.22 (d, *J* = 8.18 Hz, 2H), 7.46-7.43 (m, 2H), 7.24 (t, *J* = 7.46 Hz, 1H), 7.11 (d, *J* = 7.30 Hz, 1H) , 7.03 (d, *J* = 7.82 Hz, 1H), 6.92 (d, *J* = 8.14 Hz, 2H), 3.82 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 166.2, 162.1, 152.3, 140.1, 134.5, 128.8, 126.2, 125.8, 123.4, 118.7, 117.5, 113.9, 110.4, 55.3.

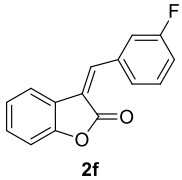
**(Z)-3-(2-fluorobenzylidene)benzofuran-2(3H)-one (2e)**



2e

Yellow solid (petroleum ether/EtOAc/$CH_2Cl_2$ = 7/1/2, 1.2g, 46% yield).$^1$H NMR（400 MHz, $CDCl_3$）δ = 7.83 (s, 1H), 7.72 (t, *J* = 7.30 Hz, 1H), 7.53 (d, *J* = 8.02 Hz 1H), 7.48 (m, 1H), 7.34 (t, *J* =7.64 Hz, 1H), 7.27 (t, *J* = 7.36 Hz, 1H), 7.19 (t, *J* = 8.08 Hz, 1H), 7.10 (d, *J* = 7.94 Hz, 1H), 7.03 (t, *J* = 7.66 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 168.2, 160.4 (*J* = 253.8 Hz), 154.5, 132.9 (J = 3.4 Hz), 132.4 (J = 8.4 Hz), 131.2, 129.8 (*J* = 2.2 Hz), 124.1 (J = 3.6 Hz), 123.9, 123.7, 122.9 (J = 1.4 Hz), 122.1 (J = 14.6 Hz), 121.5, 116.2 (*J* = 21.4), 111.1.

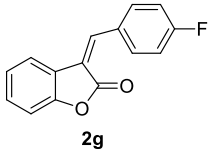
**(Z)-3-(3-fluorobenzylidene)benzofuran-2(3H)-one (2f)**



2f

Yellow solid (petroleum ether/EtOAc/$CH_2Cl_2$ = 7/1/2, 1.2g, 41% yield).$^1$H NMR（400 MHz, $CDCl_3$）δ = 7.75 (s, 1H), 7.66 (d, *J* = 7.74 Hz, 1H), 7.53-7.40 (m, 2H), 7.36-7.32 (m, 2H), 7.19-7.10 (m, 2H), 7.04 (td, *J* = 7.72 Hz, *J* = 0.90 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 168.4, 162.6 (*J* = 248.1 Hz), 154.5, 138.7 (J = 2.2 Hz), 135.9 (J = 7.9 Hz), 131.3, 130.4 (*J* = 8.5 Hz), 124.9 (J = 2.9 Hz), 123.7, 123.2, 122.8, 121.2, 119.5, 117.2 (*J* = 21.2), 115.7 (J = 22.2 Hz), 111.2.

**(Z)-3-(4-fluorobenzylidene)benzofuran-2(3H)-one (2g)**

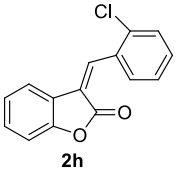


2g

Yellow solid (petroleum ether/EtOAc/$CH_2Cl_2$ = 7/1/2, 1.2g, 50% yield).$^1$H

NMR（400 MHz, $CDCl_3$）δ = 7.76 (s, 1H), 7.66 (d, *J* = 7.74 Hz, 1H), 7.50-7.42 (m, 2H), 7.34 (t, *J* =7.86 Hz, 2H), 7.18-7.14 (m, 1H), 7.11 (d, *J* = 8.22 Hz, 1H), 7.04 (t, *J* = 7.70 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 168.3, 162.6 (*J* = 248.0 Hz), 154.5, 138.7 (J = 2.3 Hz), 135.9 (J = 7.9 Hz), 131.3, 130.4 (*J* = 8.2 Hz), 124.9 (J = 2.9 Hz), 123.7, 123.2, 122.8, 122.2, 121.5, 117.2 (*J* = 21.1), 115.7 (J = 20.1 Hz), 111.2.

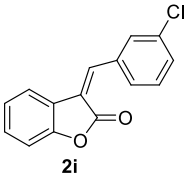
**(Z)-3-(2-chlorobenzylidene)benzofuran-2(3H)-one (2h)**



2h

Yellow solid (petroleum ether/EtOAc/$CH_2Cl_2$ = 7/1/2, 1.2g, 46% yield).$^1H$ NMR（400 MHz, $CDCl_3$）δ = 7.91 (s, 1H), 7.74 (dd, *J* =1.64 Hz, *J* = 7.42 Hz, 1H), 7.51 (d, *J* = 1.28 Hz, *J* = 7.98 Hz, 1H), 7.45-7.38 (m, 3H), 7.36-7.32 (m, 1H), 7.11 (d, *J* = 8.02 Hz, 1H), 7.00 (td, *J* = 0.70 Hz, *J* = 7.64 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 168.1, 154.4, 136.9, 134.4, 132.4, 131.4, 131.2, 130.1, 129.6, 126.6, 123.7, 123.6, 122.8, 121.2, 111.1.

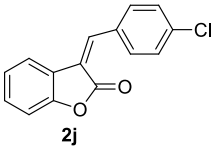
**(Z)-3-(2-chlorobenzylidene)benzofuran-2(3H)-one (2i)**



2i

Yellow solid (petroleum ether/EtOAc/$CH_2Cl_2$ = 7/1/2, 1.2g, 46% yield).$^1H$ NMR（400 MHz, $CDCl_3$）δ = 7.75 (s, 1H), 7.64 (d, *J* = 8.00 Hz, 2H), 7.54 (d, *J* = 3.88 Hz, 1H), 7.44 (d, *J* = 4.50 Hz, 1H), 7.36 (t, *J* = 7.72 Hz, 1H), 7.14 (d, J = 8.12 Hz, 1 H), 7.06 (t, *J* = 7.64 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 168.4, 154.5, 138.6, 135.6, 134.8, 131.3, 130.2, 130.1, 128.9, 127.2, 123.8, 123.3, 122.7, 121.3, 111.3.

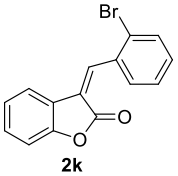
**(Z)-3-(4-chlorobenzylidene)benzofuran-2(3H)-one (2j)**



2j

Yellow solid (petroleum ether/EtOAc/$CH_2Cl_2$ = 7/1/2, 1.2g, 46% yield).$^1H$ NMR（400 MHz, $CDCl_3$）δ = 7.76 (s, 1H), 7.67-7.60 (m, 3H), 7.45 (d, *J* = 5.58 Hz, 2H), 7.34 (s, 1H), 7.13-7.04 (m, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 168.5, 154.4, 139.0, 136.3, 132.2, 131.1, 130.5, 129.0, 123.6, 122.5, 121.3, 111.2.

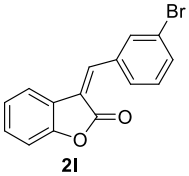
**(Z)-3-(2-bromobenzylidene)benzofuran-2(3H)-one (2k)**



2k

Yellow solid (petroleum ether/EtOAc/$CH_2Cl_2$ = 7/1/2, 1.2g, 46% yield).$^1H$ NMR（400 MHz, $CDCl_3$）δ = 7.86 (s, 1H), 7.72 (t, *J* = 6.44 Hz, 2H), 7.45-7.39 (m, 2H), 7.34 (t, *J* = 7.88 Hz, 2H), 7.12 (d, *J* = 8.00 Hz, 1H), 6.99 (t, *J* = 7.66 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 168.1, 154.4, 139.0, 134.3, 133.3, 131.5, 131.2, 129.7, 127.3, 124.3, 123.6, 123.5, 122.8, 121.3, 111.2.

**(Z)-3-(3-bromobenzylidene)benzofuran-2(3H)-one (2l)**

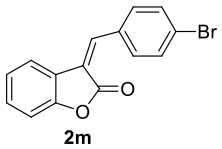


2l

Yellow solid (petroleum ether/EtOAc/$CH_2Cl_2$ = 7/1/2, 1.2g, 46% yield).$^1H$

NMR（400 MHz, $CDCl_3$）δ = 7.78 (s, 1H), 7.74 (s, 1H), 7.63 (d, *J* = 7.82 Hz, 1H), 7.58 (d, *J* = 7.86 Hz, 1H), 7.39-7.34 (m, 2H), 7.13 (d, *J* = 8.12 Hz, 1H), 7.05 (t, *J* = 7.72 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 168.3, 154.5, 138.5, 135.8, 133.1, 131.7, 131.3, 130.3, 127.6, 123.7, 123.3, 122.8, 122.6, 121.2, 111.2.

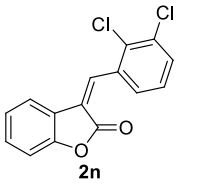
**(Z)-3-(4-bromobenzylidene)benzofuran-2(3H)-one (2m)**



2m

Yellow solid (petroleum ether/EtOAc/$CH_2Cl_2$ = 7/1/2, 1.2g, 45% yield).$^1$H NMR（400 MHz, $CDCl_3$）δ = 7.75 (s, 1H), 7.68-7.62 (m, 3H), 7.54 (d, *J* = 8.16 Hz, 2H), 7.36 (t, *J* = 7.66 Hz, 1H), 7.14 (d, *J* = 8.34Hz, 1H), 7.05 (t, *J* = 7.52 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 168.5, 154.4, 139.8, 132.7, 132.0, 131.2, 130.7, 124.7, 123.7, 122.6, 122.6, 121.4, 111.3.

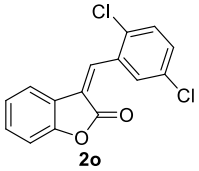
**(Z)-3-(2,3-dichlorobenzylidene)benzofuran-2(3H)-one (2n)**



2n

Yellow solid (petroleum ether/EtOAc/$CH_2Cl_2$ = 7/1/2, 1.35g, 49% yield).$^1$H NMR（400 MHz, $CDCl_3$） δ = 7.86 (s, 1H), 7.64 (d, *J* = 7.98 Hz, 1H), 7.61-7.58 (m, 1H), 7.38-7.32 (m, 3H), 7.13 (d, *J* = 7.92 Hz, 1H), 7.00 (d, *J* = 7.68 Hz, 1H). $^{13}$C NMR (100 MHz, DMSO) δ = 167.8, 154.6, 136.1, 134.6, 134.1, 132.6, 131.8, 131.6, 127.7, 127.3, 124.4, 123.7, 122.9, 121.0, 111.3.

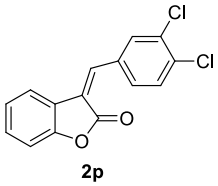
**(Z)-3-(2,5-dichlorobenzylidene)benzofuran-2(3H)-one (2o)**



2o

Yellow solid (petroleum ether/EtOAc/$CH_2Cl_2$ = 7/1/2, 1.35g, 48% yield).$^1$H NMR（400 MHz, $CDCl_3$） δ = 7.81 (s, 1H), 7.71 (d, *J* = 2.16 Hz, 1H), 7.46 (d, *J* = 8.60 Hz, 1H), 7.40-7.38 (m, 3H), 7.15 (d, *J* = 8.06 Hz, 1H), 7.05 (t, *J* = 7.66 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 167.7, 154.8, 135.0, 134.0, 132.7, 131.8, 131.3, 131.1, 129.3, 124.8, 123.9, 122.8, 121.0, 111.4.

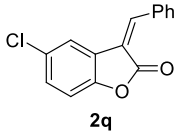
**(Z)-3-(3,4-dichlorobenzylidene)benzofuran-2(3H)-one (2p)**



2p

Yellow solid (petroleum ether/EtOAc/$CH_2Cl_2$ = 7/1/2, 1.35g, 48% yield).$^1$H NMR（400 MHz, $CDCl_3$） δ = 7.74 (d, *J* = 4.56 Hz, 1H), 7.69 (s, 1H), 7.61 (d, *J* = 7.70 Hz, 1H), 7.57 (d, *J* = 8.28 Hz, 1H), 7.50 (dd, *J* = 1.60 Hz, *J* = 8.30 Hz, 1H), 7.39-7.35 (m, 1H), 7.14 (d, *J* = 8.08 Hz, 1H), 7.07 (t, *J* = 7.72 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 168.1, 154.7, 137.2, 134.4, 133.8, 133.2, 131.6, 130.9, 130.7, 128.2, 123.8, 123.7, 122.7, 121.1, 111.4.

**(Z)-3-benzylidene-5-chlorobenzofuran-2(3H)-one (2q)**

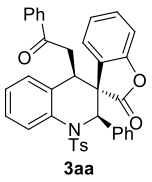


2q

Orange yellow solid (petroleum ether/EtOAc = 15/1, 1.28g, 50% yield).$^1$H NMR（400 MHz, $CDCl_3$）δ = 7.74 (s, 1H), 7.64-7.61 (m, 2H), 7.53 (d, *J* = 3.76 Hz, 1H), 7.44 (d, *J* = 4.57 Hz, 2H), 7.35 (t, *J* = 7.88 Hz, 1H), 7.13 (d, *J* = 8.04 Hz, 1H), 7.05 (d, *J* = 7.62 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 168.3, 154.5, 138.6, 135.6, 134.7, 131.3, 130.2, 130.1, 128.8, 127.1, 123.7, 123.3, 122.7, 121.2, 111.2.

## 2.4 Analytical data of compounds of 3.

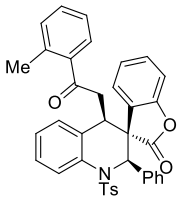
**(2'R,3R,4'R)-4'-(2-oxo-2-phenylethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3aa).**



3aa

White solid (119 mg, 99 %). PE/EA/DCM = 10/1/2, 164-166 °C. $[\alpha]_D^{24.7}$ = - 26 (*c* /.0, $CH_2Cl_2$, 97 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.86 Hz, H), 7.72 (d, *J* = 7.56 Hz, 2H), 7.60 (t, *J* = 8.00 Hz, 2H), 7.52 (t, *J* = 6.25 Hz, 2H), 7.39 (t, *J* = 7.56 Hz, 2H), 7.31 (d, *J* = 8.00 Hz, 2H), 7.19 (d, *J* = 7.50 Hz, 1H), 7.11 (d, *J* = 7.38 Hz, 2H), 7.04 (t, *J* = 7.38 Hz, 2H), 6.98 (t, *J* = 6.50 Hz, 2H), 6.79 (d, *J* = 8.04 Hz, 1H), 6.61 (d, *J* = 7.64 Hz, 1H), 6.55 (t, *J* = 7.58 Hz, 1H), 6.00 (s, 1H), 5.12 (d, *J* = 7.62 Hz, 1H), 3.03 (d, *J* = 9.98 Hz, 1H), 2.72-2.57 (m, 2H), 2.40 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.9，176.8，152.4，144.6，138.8，137.7，135.7，134.2，133.7，133.4，129.9，129.3，128.6，128.4，128.2，128.0，127.8，127.4，127.0，126.8，126.5，125.9，125.5，124.2，123.7，110.2，68.3，62.5，39.1，35.9，21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), 1mL/min; minor enantiomer $t_R$ = 36.49 min, major enantiomer $t_R$ = 17.34 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{37}H_{30}NO_5S]$:600.1839, found:600.1845.

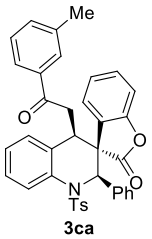
**(2'R,3R,4'R)-4'-(2-oxo-2-(o-tolyl)ethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ba).**



3ba

White solid (120 mg, 98 %). PE/EA/DCM = 10/1/2, 200-202 °C. $[\alpha]_D^{24.7}$ = - 45 (*c* /.0, $CH_2Cl_2$, 93 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.86 Hz, H), 7.59 (d, *J* = 7.86 Hz, 2H), 7.53 (t, *J* = 7.74 Hz, 1H), 7.37 (d, *J* = 7.86 Hz, 1H), 7.32 (d, *J* = 7.84 Hz, 3H), 7.23-7.20 (m, 2H), 7.18-7.15 (m, 1H), 7.11 (d, *J* = 7.62 Hz, 2H), 7.03 (t, *J* = 7.52 Hz, 2H), 6.95 (t, *J* = 8.18 Hz, 2H), 6.75 (d, *J* = 7.84 Hz, 1H), 6.60 (d, *J* = 7.64 Hz, 1H), 6.53 (t, *J* = 7.64 Hz, 1H), 6.00 (s, 1H), 5.11 (d, *J* = 7.64 Hz, 1H), 3.00 (d, *J* = 10.46 Hz, 1H), 2.64-2.48 (m, 2H), 2.42 (s, 3H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 198.0, 176.8, 152.4, 144.5, 138.8, 138.4, 137.8, 136.4, 134.1, 134.0, 132.1, 131.7, 130.0, 129.2, 128.4, 128.3, 128.1, 128.0, 127.3, 127.0, 126.8, 126.3, 125.9, 125.7, 125.4, 124.3, 123.6, 110.1, 68.3, 62.4, 39.5, 38.3, 21.6, 21.1. The enantiomeric excess was determined by HPLC with an IA column. (*n*-hexane:*i*-PrOH = 70:30), 1mL/min; minor enantiomer $t_R$ = 10.39 min, major enantiomer $t_R$ = 6.07 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{38}H_{32}NO_5S]$:614.1996, found:614.2000.

**(2'R,3R,4'R)-4'-(2-oxo-2-(m-tolyl)ethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ca).**

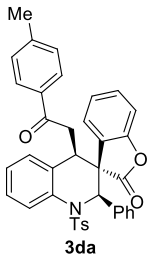


3ca

White solid (120 mg, 98 %). PE/EA/DCM = 10/1/2, m. p.:186-190 °C. $[\alpha]_D^{25.3}$ = - 27 (*c* 1.0, $CH_2Cl_2$, 97 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.80 Hz, 1H), 7.60 (d, *J* = 7.78 Hz, 2H), 7.54 (s, 1H), 7.51 (t, *J* = 5.82 Hz, 2H), 7.35-7.27 (m, 4H), 7.19 (t, *J* = 7.34 Hz, 1H), 7.12 (d, *J* = 7.22 Hz, 2H), 7.04 (t, *J* = 7.26 Hz, 2H), 7.00-6.97 (m, 2H), 6.79 (d, *J* = 7.92 Hz, 1H), 6.62 (d, *J* = 7.44 Hz, 1H), 6.55 (t, *J* = 7.50 Hz, 1H), 5.99 (s, 1H), 5.12 (d, *J* = 7.44 Hz, 1H), 3.03 (d, *J* = 9.56 Hz, 1H), 2.70-2.57 (m, 2H), 2.40 (s, 3H). 2.36 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 195.1, 176.8, 152.3, 144.5, 138.7, 138.4, 137.6, 135.7, 134.2, 134.1, 133.7, 129.9, 129.3, 128.4, 128.4, 128.2, 128.1, 128.0, 127.3, 126.9, 126.8, 126.5, 125.8, 125.5, 125.0, 124.2, 123.7, 110.1, 68.3, 62.4, 39.0, 36.0, 21.6, 21.2. The enantiomeric excess was determined by HPLC with an IC

column. (*n*-hexane:*i*-PrOH = 75:25), mL/min; minor enantiomer $t_R$ = 29.13 min, major enantiomer $t_R$ = 14.53 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{38}H_{32}NO_5S]$:614.1996, found:614.1996.

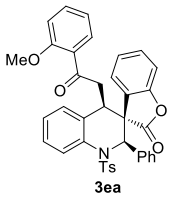
**(2'R,3R,4'R)-4'-(2-oxo-2-(p-tolyl)ethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3da).**



3da

White solid (121.6 mg, 99 %). PE/EA/DCM = 10/1/2, m. p.:220-226 °C. $[\alpha]_D^{24.6}$ = - 18 (*c* 1.0, $CH_2Cl_2$, 94 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.11 (dd, *J* = 0.96 Hz, *J* = 7.98 Hz, 1H), 7.61 (t, *J* = 8.22 Hz, 4H), 7.51 (t, *J* = 7.50 Hz, 1H), 7.31 (t, *J* = 8.08 Hz, 2H), 7.19-7.16 (m, 3H), 7.11 (d, *J* = 7.40 Hz, 2H), 7.03 (t, *J* = 7.46 Hz, 2H), 7.00-6.95 (m, 2H), 6.78 (d, *J* = 7.76 Hz, 1H), 6.62 (d, *J* = 7.76 Hz, 1H), 6.55 (td, *J* = 7.68 Hz, *J* = 0.92 Hz, 1H), 5.99 (s, 1H), 5.12 (dd, *J* = 0.8Hz, *J* = 7.68 Hz, 1H), 3.03 (d, *J* = 8.84 Hz, 1H), 2.69-2.53 (m, 2H), 2.40 (s, 3H). 2.37 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.5, 176.8, 152.4, 144.5, 144.2, 138.8, 137.7, 134.2, 133.9, 133.3, 129.9, 129.3, 129.2, 128.3, 128.2, 128.0, 127.9, 127.3, 127.0, 126.8, 126.6, 125.9, 125.5, 124.3, 123.7, 110.1, 68.3, 62.5, 39.1, 35.8, 21.5. The enantiomeric excess was determined by HPLC with an IA column. (*n*-hexane:*i*-PrOH = 90:10), mL/min; minor enantiomer $t_R$ = 14.97 min, major enantiomer $t_R$ = 18.13 min. HRMS (ESI): $[M+K]^+$ calcd for $[C_{38}H_{31}NO_5K]$:652.1555, found:652.1565.

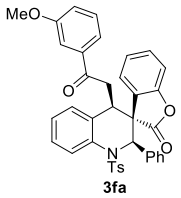
**(2'R,3R,4'R)-4'-(2-(2-methoxyphenyl)-2-oxoethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ea).**



3ea

White solid (118 mg, 94 %). PE/EA/DCM = 10/1/2, m. p.:242-244 °C. $[\alpha]_D^{25.2}$ = - 23 (*c* 1.0, $CH_2Cl_2$, 90 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 7.24 Hz, 1H), 7.63-7.59 (m, 3H), 7.51 (t, *J* = 7.66 Hz, 1H), 7.43-7.39 (m, 1H), 7.35 (d, *J* = 8.08 Hz, 2H), 7.20-7.17 (m, 1H), 7.12 (d, *J* = 7.40 Hz, 2H), 7.03 (t, J = 7.52 Hz, 2H), 6.95 (t, *J* = 7.44 Hz, 3H), 6.84 (d, *J* = 8.42 Hz, 1H), 6.67 (d, *J* = 8.00 Hz, 1H), 6.62 (d, *J* = 7.82 Hz, 1H), 6.54-6.50 (m, 1H), 6.00 (s, 1H), 5.11 (d, *J* = 7.06 Hz, 1H), 3.61 (s, 3H), 3.95 (t, *J* = 6.64 Hz, 1H), 2.67 (d, *J* = 6.64 Hz, 2H), 2.44 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 196.6, 176.9, 158.5, 152.5, 144.5, 139.1, 137.7, 134.3, 134.1, 133.9, 130.3, 130.0, 129.0, 128.2, 128.2, 128.1, 127.3, 127.1, 126.9, 126.7, 126.7, 125.9, 125.5, 124.7, 123.5, 120.7, 111.5, 109.7, 67.9, 62.6, 55.0, 41.5, 39.3, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; minor enantiomer $t_R$ = 50.89 min, major enantiomer $t_R$ = 23.96 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{38}H_{32}NO_6S]$:630.1945, found:630.1960.

**(2'R,3R,4'R)-4'-(2-(3-methoxyphenyl)-2-oxoethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3fa).**

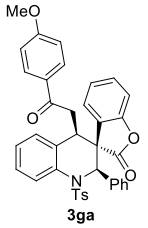


3fa

White solid (120 mg, 94 %). m. p.:106-110 °C. $[\alpha]_D^{25.3}$ = - 30 (*c* 1.0, $CH_2Cl_2$, 99% ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.00 Hz, 1H), 7.59 (d, *J* = 8.12 Hz, 2H), 7.52 (t, *J* = 7.66 Hz, 1H), 7.29 (d, *J* = 8.72 Hz, 5H), 7.20 (t, *J* = 7.42 Hz, 1H), 7.12-7.06 (m, 3H), 7.13 (t, *J* = 7.50 Hz, 2H), 7.02 (t, J = 7.46 Hz, 1H), 6.99-6.95 (m, 2H), 6.78 (d, *J* = 8.00 Hz, 1H), 6.66 (d, *J* = 7.82 Hz, 1H), 6.55 (t, *J* = 7.66 Hz, 1H), 6.00 (s, 1H), 5.11 (d, *J* = 7.80 Hz, 1H), 3.81 (s, 3H), 3.05 (dd, *J* = 3.00 Hz, *J* = 9.64 Hz, 1H), 2.69-2.57 (m, 2H), 2.38 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.9, 176.9, 159.7, 152.4, 144.5, 138.8, 137.7, 137.1, 134.3, 133.7, 129.9, 129.6, 129.3, 128.4, 128.2, 128.0, 127.4, 127.0, 126.9, 126.6, 125.9, 125.5, 124.2, 123.7, 120.4, 119.6, 112.4, 110.2, 68.3, 62.6, 55.3, 39.2, 36.2, 21.5. The enantiomeric excess was determined by HPLC

with an IC column. (*n*-hexane:*i*-PrOH = 70:30), mL/min; major enantiomer $t_R$ = 14.267 min, minor enantiomer $t_R$ = 28.490 min, HRMS (ESI): $[M+H]^+$ calcd for $[C_{38}H_{32}NO_6S]$:630.1945, found:630.1945.

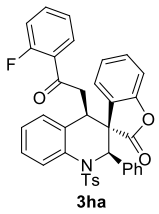
**(2'R,3R,4'R)-4'-(2-(4-methoxyphenyl)-2-oxoethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ga).**



3ga

White solid (125 mg, 99 %). PE/EA/DCM = 10/1/2, m. p.:200-203 °C. $[\alpha]_D^{25.2}$ = -20 (*c* 1.0, $CH_2Cl_2$, 93 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.04 Hz, 1H), 7.20 (d, *J* = 8.68 Hz, 2H), 7.59 (d, *J* = 8.18 Hz, 2H), 7.51 (t, *J* = 7.80 Hz, 2H), 7.29 (d, *J* = 8.18 Hz, 2H), 7.18 (t, *J* = 7.36 Hz, 1H), 7.11 (d, *J* = 7.48 Hz, 2H), 7.02 (t, J = 7.46 Hz, 1H), 6.98-6.93 (m, 2H), 6.85 (d, *J* = 8.82 Hz, 2H), 6.77 (d, *J* = 7.97 Hz, 1H), 6.67 (t, *J* = 7.76 Hz, 1H), 6.54 (t, *J* = 7.54 Hz, 1H), 6.00 (s, 1H), 5.13 (d, *J* = 7.61 Hz, 1H), 3.79 (s, 3H), 3.05 (d, *J* = 8.90 Hz, 1H), 2.66-2.52 (m, 2H), 2.38 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 193.4, 176.8, 163.6, 152.4, 144.5, 138.8, 137.6, 134.2, 133.9, 130.1, 129.8, 129.2, 128.8, 128.3, 128.0, 128.0, 127.3, 126.9, 126.8, 126.6, 125.8, 125.4, 124.2, 123.6, 113.6, 110.1, 68.3, 62.5, 55.3, 39.2, 35.6, 21.5. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; major enantiomer $t_R$ = 27.445 min, minor enantiomer $t_R$ = 54.057 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{38}H_{32}NO_6S]$: 630.1945, found: 630.1948.

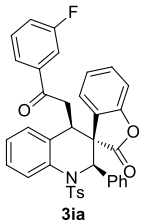
**(2'R,3R,4'R)-4'-(2-(2-fluorophenyl)-2-oxoethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ha).**



3ha

White solid (120 mg, 97 %). PE/EA/DCM = 10/1/2, m. p.:166-168 °C. $[\alpha]_D^{24.9}$ = -25 (*c* 1.0, $CH_2Cl_2$, 90 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.90 Hz, 1H), 7.72 (t, *J* = 7.00 Hz, 1H), 7.63(d, *J* = 8.10 Hz, 2H), 7.53 (t, *J* = 7.58 Hz, 1H), 7.49-7.44 (m, 1H), 7.37 (d, *J* = 8.02 Hz, 2H), 7.22-7.16 (m, 2H), 7.11 (d, *J* = 7.48 Hz, 2H), 7.03 (t, *J* = 7.60 Hz, 3H), 7.95 (t, *J* = 7.90 Hz, 2H), 6.76 (d, *J* = 8.00 Hz, 1H), 6.55-6.50 (m, 2H), 5.99 (s, 1H), 5.10 (d, *J* = 7.56 Hz, 1H), 2.99 (d, *J* = 9.05 Hz, 1H), 2.72-2.58 (m, 2H), 2.45 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 193. (*J* = 4.1 Hz), 176.8, 161.6 (*J* = 254.2 Hz), 152.4, 144.5, 138.8, 137.7, 135.0 (*J* = 9.44 Hz), 134.2, 133.7, 130.3, 130.0, 129.2, 128.3 (*J* = 5.24 Hz), 128.0, 127.3, 127.0, 126.8, 126.4, 125.8, 125.3, 124.4 (*J* = 3.4 Hz), 124.2, 123.6, 116.6 (*J* = 23.6 Hz), 110.1, 68.1, 62.3, 40.8 (*J* = 8.5 Hz), 38.9, 21.6. The enantiomeric excess was determined by HPLC with an IA column. (*n*-hexane:*i*-PrOH = 95:5), mL/min; minor enantiomer $t_R$ = 19.93 min, major enantiomer $t_R$ = 34.36 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{37}H_{29}FNO_5S]$:618.1745, found:618.1745.

**(2'R,3R,4'R)-4'-(2-(3-fluorophenyl)-2-oxoethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ia).**

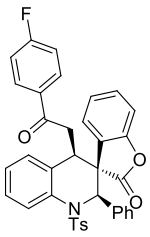


3ia

White solid (118 mg, 95 %). PE/EA/DCM = 9/1/2, m. p.:180-182 °C. $[\alpha]_D^{24.8}$ = - 19 (*c* 1.0, $CH_2Cl_2$, 77 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.86 Hz, 1H), 7.59 (d, *J* = 8.20 Hz, 2H), 7.55-7.51 (m, 1H), 7.48 (d, *J* = 7.82 Hz, 2H), 7.42 (d, *J* = 8.82 Hz, 1H), 7.38-7.34 (m, 1H), 7.30 (d, *J* = 8.20 Hz, 1H), 7.22-7.17 (m, 2H), 7.11 (d, *J* = 7.32 Hz, 1H), 7.02 (t, *J* = 7.52 Hz, 2H), 6.99-6.93 (m, 2H), 6.77 (d, *J* = 8.02 Hz, 1H), 6.58 (d, *J* = 7.63 Hz, 1H), 6.54 (t, *J* = 7.82 Hz, 1H), 6.00 (s, 1H), 5.13 (d, *J* = 7.76 Hz, 1H), 3.03 (d, *J* = 9.68 Hz, 1H), 2.70-2.53 (m, 2H), 2.40 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 193.7, 176.7, 163.8, 161.4, 152.3, 144.5, 138.7, 137.7, 137.7, 134.2, 133.5, 130.4, 130.3, 129.9, 129.4, 128.5, 128.2, 128.0, 127.3, 126.9, 126.8, 126.3, 125.8, 125.4, 124.0,

123.7, 123.6, 120.5, 120.3, 114.5, 114.3, 110.2, 68.3, 62.4, 39.0, 36.1, 21.5. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; major enantiomer $t_R$ = 16.66 min, minor enantiomer $t_R$ = 35.40 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{37}H_{29}FNO_5S]$:618.1745, found:618.1745.

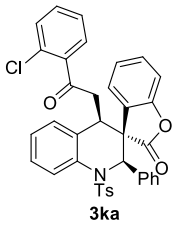
**(2'R,3R,4'R)-4'-(2-(4-fluorophenyl)-2-oxoethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ja).**



3ja

White solid (99 mg, 80 %). PE/EA/DCM = 10/1/2, m. p.:168-170 °C. $[\alpha]_D^{24.9}$ = -29 (*c* 1.0, $CH_2Cl_2$, 99 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.80 Hz, 1H), 7.77-7.74 (m, 2H), 7.59 (d, *J* = 8.10 Hz, 2H), 7.53 (t, *J* = 7.60 Hz, 1H), 7.31 (d, *J* = 7.92 Hz, 2H), 7.20 (t, *J* = 7.52 Hz, 1H), 7.12-6.97 (m, 8H), 6.79 (d, *J* = 7.94 Hz, 1H), 6.60 (d, *J* = 7.70 Hz, 1H), 6.56 (t, *J* = 7.64 Hz, 1H), 5.98 (s, 1H), 5.11 (d, *J* = 7.64 Hz, 1H), 3.01 (d, *J* = 9.98 Hz, 1H), 2.69-2.54 (m, 2H), 2.41 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 193.4, 176.8, 167.0, 164.5, 152.3, 144.6, 138.7, 137.6, 134.1, 133.6, 132.1, 132.1, 130.6, 130.5, 129.9, 129.4, 128.5, 128.3, 128.1, 127.4, 127.0, 126.9, 126.4, 125.9, 125.5, 124.1, 123.7, 115.8, 115.6, 110.2, 68.3, 62.5, 39.0, 35.9, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; major enantiomer $t_R$ = 13.70 min, minor enantiomer $t_R$ = 29.58 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{37}H_{28}FNO_5SNa]$:640.1564, found:640.1573.

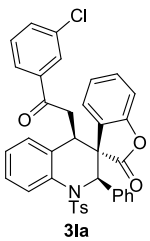
**(2'R,3R,4'R)-4'-(2-(2-chlorophenyl)-2-oxoethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ka).**



3ka

White solid (120 mg, 95 %), PE/EA/DCM = 10/1/2, m. p.:170-173 °C. $[\alpha]_D^{25}$ = -45 (*c* 1.0, $CH_2Cl_2$, 90 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.92 Hz, 1H), 7.61 (d, *J* = 8.18 Hz, 2H), 7.55 (t, *J* = 7.64 Hz, 1H), 7.37-7.32 (m, 5H), 7.28-7.22 (m, 2H), 7.10 (d, *J* = 7.44 Hz, 2H), 7.03 (t, *J* = 7.46 Hz, 2H), 6.98-6.92 (m, 2H), 6.73 (d, *J* = 8.02 Hz, 1H), 6.67 (d, *J* = 7.60 Hz, 1H), 6.51 (t, *J* = 7.58 Hz, 1H), 5.97 (s, 1H), 5.09 (d, *J* = 7.76 Hz, 1H), 2.95 (dd, *J* = 4.30 Hz, *J* = 8.30 Hz, 1H), 2.67-2.57 (m, 2H), 2.44 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 197.3, 176.7, 152.4, 144.6, 138.8, 137.9, 137.8, 134.2, 133.5, 132.1, 130.9, 130.7, 130.0, 129.3, 129.0, 128.5, 128.4, 128.1, 127.4, 127.0, 126.9, 126.8, 126.5, 125.9, 125.4, 124.1, 123.6, 110.1, 68.2, 62.4, 40.2, 39.4, 21.6. The enantiomeric excess was determined by HPLC with an IA column. (*n*-hexane:*i*-PrOH = 70:30), mL/min; minor enantiomer $t_R$ = 15.58 min, major enantiomer $t_R$ = 7.47 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{37}H_{28}ClNO_5SNa]$:656.1269, found:656.1271.

**(2'R,3R,4'R)-4'-(2-(3-chlorophenyl)-2-oxoethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3la).**

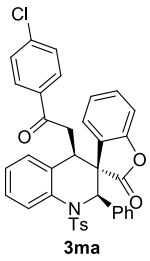


3la

White solid (123 mg, 97 %), PE/EA/DCM = 10/1/2, m. p.:190-193 °C. $[\alpha]_D^{25.1}$ = -17 (*c* 1.0, $CH_2Cl_2$, 97 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.90 Hz, 1H), 7.70 (s, 1H), 7.59 (d, *J* = 8.24 Hz, 3H), 7.56-7.50 (m, 2H), 7.36-7.30 (m, 3H), 7.20 (t, *J* = 7.40 Hz, 1H), 7.11 (d, *J* = 7.36 Hz, 2H), 7.04 (t, *J* = 7.42 Hz, 2H), 7.01-6.95 (m, 2H), 6.79 (d, *J* = 8.02 Hz, 1H), 6.59-6.54 (m, 2H), 5.98 (s, 1H), 5.12 (d, *J* = 7.58 Hz, 1H), 3.02 (d, *J* = 8.84 Hz, 1H), 2.68-2.53 (m, 2H), 2.41 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 193.8, 176.8, 152.4, 144.6, 138.7, 137.7, 137.2, 135.0, 134.2, 133.5, 134.2, 133.5, 133.4, 130.0, 129.9, 129.4, 128.5, 128.3, 128.1, 127.9, 127.4, 127.0, 126.9, 126.4, 126.0, 125.9, 125.5, 124.1, 123.8, 110.3, 68.4, 62.5, 39.0, 36.1, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 75:25),

mL/min; major enantiomer $t_R$ = 12.76 min, minor enantiomer $t_R$ = 25.37 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{37}H_{28}ClNO_5SNa]$:656.1269, found:656.1269.

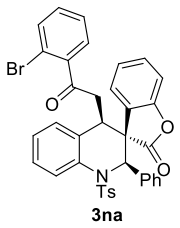
**(2'R,3R,4'R)-4'-(2-(4-chlorophenyl)-2-oxoethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ma).**



3ma

Light yellow solid (124 mg, 98%), PE/EA/DCM = 10/1/2, m. p.:186-190 °C. $[\alpha]_D^{25.1}$ = - 5 (*c* 1.0, $CH_2Cl_2$, 99% ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.94 Hz, 1H), 7.66 (d, *J* = 8.42 Hz, 2H), 7.58 (d, *J* = 7.94 Hz, 2H), 7.53 (t, *J* = 7.60 Hz, 1H), 7.35 (d, *J* = 8.42 Hz, 2H), 7.29 (d, *J* = 8.04 Hz, 2H), 7.19 (t, *J* = 7.46 Hz, 1H), 7.11 (d, *J* = 7.36 Hz, 2H), 7.03 (t, *J* = 7.36 Hz, 2H), 6.99-6.95 (m, 2H), 6.77 (d, *J* = 8.04 Hz, 1H), 6.61 (d, *J* = 7.56 Hz, 1H), 6.55 (t, *J* = 7.66 Hz, 1H), 5.99 (s, 1H), 5.12 (d, *J* = 7.56 Hz, 1H), 3.02 (d, *J* = 9.48 Hz, 1H), 2.68-2.54 (m, 2H), 2.39 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 193.8, 176.8, 152.4, 144.5, 139.8, 138.7, 137.7, 134.2, 134.0, 133.5, 129.9, 129.4, 129.2, 128.9, 128.5, 128.2, 128.0, 127.4, 127.0, 126.8, 126.4, 125.8, 125.5, 124.1, 123.7, 110.2, 68.3, 62.5, 39.1, 36.0, 21.5. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; minor enantiomer $t_R$ = 14.48 min, major enantiomer $t_R$ = 18.03 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{37}H_{28}ClNO_5SNa]$:656.1269, found:656.1273.

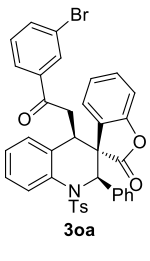
**(2'R,3R,4'R)-4'-(2-(2-bromophenyl)-2-oxoethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3na).**



3na

White solid (133 mg, 98%). PE/EA/DCM = 10/1/2, m. p.:206-209 °C. $[\alpha]_D^{24.9}$ = - 62 (*c* 1.0, $CH_2Cl_2$, 90% ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.92 Hz, 1H), 7.61 (d, *J* = 8.12 Hz, 2H), 7.55 (t, *J* = 8.20 Hz, 2H), 7.36 (d, *J* = 7.92 Hz, 2H), 7.28-7.24 (m, 4H), 7.10 (d, *J* = 7.44 Hz, 2H), 7.03 (t, *J* = 7.40 Hz, 2H), 6.95 (dd, *J* = 7.30 Hz, 17.94 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.51 (t, *J* = 7.60 Hz, 1H), 5.97 (s, 1H), 5.09 (d, *J* = 7.56 Hz, 1H), 2.91 (d, *J* = 9.72 Hz, 1H), 2.68-2.53 (m, 2H), 2.43 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 198.1, 176.7, 152.3, 144.6, 140.1, 138.7, 137.7, 134.1, 133.9, 133.5, 132.0, 132.0, 129.3, 128.5, 128.4, 128.1, 127.4, 127.4, 127.0, 126.8, 126.6, 125.8, 125.4, 124.1, 123.6, 118.7, 110.1, 68.1, 62.4, 39.7, 39.3, 21.7. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; minor enantiomer $t_R$ = 35.24 min, major enantiomer $t_R$ = 16.42 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{37}H_{28}BrNO_5SNa]$:700.0764, found:700.0766.

**(2'R,3R,4'R)-4'-(2-(3-bromophenyl)-2-oxoethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3oa).**

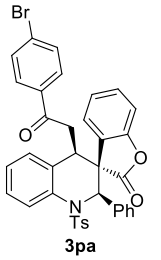


3oa

White solid (132 mg, 97 %). PE/EA/DCM = 10/1/2, m. p.:180-185 °C. $[\alpha]_D^{25.1}$ = - 16 (*c* 1.0, $CH_2Cl_2$, 99% ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.64 Hz, 1H), 7.86 (s, 1H), 7.67-7.62 (m, 2H), 7.58 (d, *J* = 8.04 Hz, 2H), 7.53 (t, *J* = 7.76 Hz, 1H), 7.31 (d, *J* = 8.30 Hz, 2H), 7.27-7.24 (m, 1H), 7.20 (t, *J* = 7.44 Hz, 1H), 7.11 (d, J = 7.44 Hz, 2H), 7.01-6.95 (m, 2H), 6.79 (t, *J* = 8.16 Hz, 1H), 6.57 (dd, *J* = 7.64 Hz, *J* = 14.00 Hz, 2H), 5.98 (s, 1H), 5.11 (d, *J* = 7.64 Hz, 1H), 3.02 (d, *J* = 8.98 Hz, 1H), 2.68-2.53 (m, 2H), 2.40 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 193.7, 176.8, 152.4, 144.6, 138.6, 137.7, 137.4, 136.3., 134.2, 133.4, 130.8, 130.2, 129.9, 129.4, 128.5, 128.3, 128.1, 127.4, 127.0, 129.6, 126.4, 126.3, 125.9, 125.5, 124.0, 123.8, 123.0, 110.2, 68.4, 62.5, 39.0, 36.1, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 75:25), mL/min; minor enantiomer $t_R$ = 30.91 min, major enantiomer $t_R$ =

15.37 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{37}H_{28}BrNO_5SNa]$:700.0764, found:700.0766.

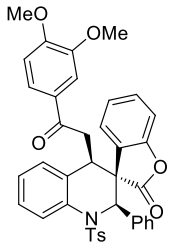
**(2'R,3R,4'R)-4'-(2-(4-bromophenyl)-2-oxoethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3pa).**



3pa

White solid (134 mg, 99%). PE/EA/DCM = 11/1/2, m. p.:187-190 °C. $[\alpha]_D^{24.6}$ = 2 (*c* 1.0, $CH_2Cl_2$, 90% ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.84 Hz, 1H), 7.58 (d, *J* = 8.22 Hz, 4H), 7.52 (d, *J* = 8.34 Hz, 3H), 7.30 (d, *J* = 7.90 Hz, 2H),7.19 (t, *J* = 7.44 Hz, 1H), 7.11 (d, J = 7.28 Hz, 2H), 7.03 (t, *J* = 7.34 Hz, 1H), 7.00-6.96 (m, 2H), 6.78 (d, *J* = 7.96 Hz, 1H), 6.59 (d, *J* = 7.72 Hz, 1H), 6.55 (t, *J* = 7.80 Hz, 1H), 5.98 (s, 1H), 5.11 (d, *J* = 7.58 Hz, 1H), 3.01 (d, *J* = 9.76 Hz, 1H), 2.67-2.53 (m, 2H), 2.40 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.0, 176.8, 152.3, 144.5, 138.6, 137.6, 134.3, 134.1, 133.5, 131.9, 129.9, 129.4, 129.3, 128.6, 128.5, 128.2, 128.0, 127.4, 126.9, 126.9, 126.3, 125.8, 125.4, 124.0, 123.7, 110.2, 68.3, 62.4, 39.0, 35.9, 21.6. The enantiomeric excess was determined by HPLC with an IA column. (*n*-hexane:*i*-PrOH = 90:10), mL/min; minor enantiomer $t_R$ = 21.70 min, major enantiomer $t_R$ = 17.59 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{37}H_{28}BrNO_5SNa]$:700.0764, found:700.0764.

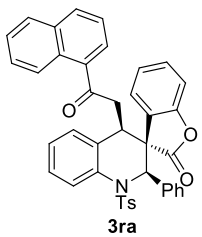
**(2'R,3R,4'R)-4'-(2-(3,4-dimethoxyphenyl)-2-oxoethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3qa).**



3qa

White solid (130 mg, 99%). PE/EA/DCM = 5/1/2, m. p.:180-186 °C. $[\alpha]_D^{23.2}$ = -10 (*c* 1.0, $CH_2Cl_2$, 99 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 7.92 Hz, 1H), 7.58 (d, *J* = 8.00 Hz, 2H), 7.53 (t, *J* = 7.58 Hz, 1H), 7.34 (s, 1H), 7.31 (d, *J* = 8.58 Hz, 1H), 7.26-7.25 (m, 2H), 7.21 (d, *J* = 7.62 Hz, 1H), 7.12 (d, *J* = 7.62 Hz, 2H), 7.04 (t, *J* = 7.62 Hz, 2H), 7.00-6.96 (m, 2H), 6.82-6.77 (m, 3H), 6.56 (d, *J* = 7.66 Hz, 1H), 6.00 (s, 1H), 5.12 (d, *J* = 7.80 Hz, 1H), 3.91 (s, 6H), 3.06 (d, *J* = 7.50 Hz, 1H), 2.66-2.55 (m, 2H), 2.34 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 193.9, 176.9, 153.4, 152.4, 148.8, 144.4, 138.7, 137.6, 134.3, 133.7, 129.7, 129.3, 128.8, 128.4, 128.0, 127.3, 126.9, 126.9, 126.7, 125.8, 125.5, 124.1, 123.7, 122.6, 110.1, 109.9, 109.8, 68.3, 62.7, 55.9, 55.9, 39.5, 35.7, 21.4. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 70:30), mL/min; minor enantiomer $t_R$ = 35.56 min, major enantiomer $t_R$ = 72.25 min. HRMS (ESI): $[M+K]^+$ calcd for $[C_{39}H_{33}NO_7SK]$:682.1870, found:682.1870.

**(2'R,3R,4'R)-4'-(2-(naphthalen-1-yl)-2-oxoethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ra).**

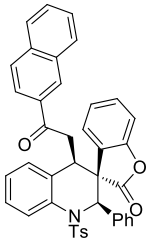


3ra

White solid (117 mg, 90 %). PE/EA/DCM = 7/1/2, m. p.:210-212 °C. $[\alpha]_D^{26.8}$ = 36 (*c* 1.0, $CH_2Cl_2$, 99% ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 8.40 Hz, 1H), 8.14 (d, *J* = 7.96 Hz, 1H), 7.96 (d, *J* = 8.04 Hz, 1H), 7.85 (d, *J* = 7.84 Hz, 1H), 7.65-7.62 (m, 3H), 7.58-7.52 (m, 3H), 7.39 (t, *J* = 7.66 Hz, 1H), 7.34 (d, *J* = 8.06 Hz, 2H), 7.18 (t, *J* = 7.66 Hz, 1H), 7.13 (d, *J* = 7.46 Hz, 1H), 7.04 (t, *J* = 7.48 Hz, 2H), 6.99-6.94 (m, 2H), 6.77 (d, *J* = 8.04 Hz, 1H), 6.72 (d, *J* = 8.02 Hz, 1H), 6.53 (t, *J* = 7.60 Hz, 1H), 6.03 (s, 1H), 5.12 (d, *J* = 7.60 Hz, 1H), 3.15-3.11 (m, 1H), 2.79-2.70 (m, 2H), 2.41 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 198.3, 176.9, 152.4, 144.6, 138.8, 137.9, 134.2, 134.0, 133.9, 133.3, 130.0, 129.3, 128.5, 128.4, 128.1, 127.6, 127.4, 127.1, 126.9, 126.5, 126.5, 125.9, 125.5, 125.4, 124.3, 124.1, 123.7, 110.2, 68.4, 62.5, 39.7, 38.7, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; minor enantiomer $t_R$ = 11.12 min, major enantiomer $t_R$ = 17.69 min. HRMS (ESI):

$[M+K]^+$ calcd for $[C_{41}H_{31}NO_5SK]$:688.1555, found:688.1554.

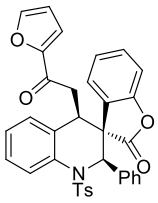
**(2'R,3R,4'R)-4'-(2-(naphthalen-2-yl)-2-oxoethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3sa).**



3sa

White solid (128 mg, 99 %). PE/EA/DCM = 10/1/2, m. p.: 206-210 °C. $[\alpha]_D^{26.9}$ = 30 (*c* 1.0, $CH_2Cl_2$, 97 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.22 (s, 1H), 8.13 (d, *J* = 7.86 Hz, 1H), 7.92 (d, *J* = 7.98 Hz, 1H), 7.83 (d, *J* = 11.12 Hz, 3H), 7.60-7.51 (m, 5H), 7.20 (d, *J* = 7.66 Hz, 1H), 7.14 (t, *J* = 7.74 Hz, 4H), 7.05 (t, *J* = 7.70 Hz, 2H), 7.01-7.69 (m, 2H), 6.82 (t, *J* = 8.00 Hz, 2H), 6.57 (t, *J* = 7.82 Hz, 1H), 6.05 (s, 1H), 5.15 (d, *J* = 7.66 Hz, 1H), 3.14 (dd, *J* = 3.10 Hz, *J* = 9.54 Hz, 1H), 2.81-2.71 (m, 2H), 2.18 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 195.2, 177.0, 152.4, 144.4, 138.7, 137.6, 135.5, 134.2, 133.7, 132.8, 132.2, 129.8, 129.7, 129.5, 129.3, 128.7, 128.5, 128.4, 128.1, 128.0, 127.6, 127.4, 126.9, 126.8, 126.7, 125.9, 125.5, 124.1, 123.7, 123.4, 110.2, 68.4, 62.7, 39.5, 36.3, 21.3002E The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; major enantiomer $t_R$ = 19.00 min, minor enantiomer $t_R$ = 43.47 min. HRMS (ESI): $[M+K]^+$ calcd for $[C_{41}H_{31}NO_5SK]$:688.1555, found:688.1555.

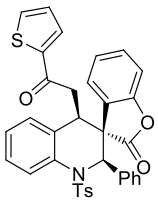
**(2'R,3R,4'R)-4'-(2-(furan-2-yl)-2-oxoethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ta).**



3ta

White solid (117 mg, 99 %). PE/EA/DCM = 7/1/2, m. p.: 150-154 °C. $[\alpha]_D^{26.4}$ = -24 (*c* 1.0, $CH_2Cl_2$, 92 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 7.86 Hz, 1H), 7.58-7.48 (m, 4H), 7.30 (d, *J* = 8.04 Hz, 2H), 7.21 (t, *J* = 7.64 Hz, 1H), 7.11 (d, *J* = 7.42 Hz, 2H), 7.06-7.01 (m, 3H), 6.99-6.95 (m, 2H), 6.76 (d, *J* = 8.10 Hz, 1H), 6.73 (d, *J* = 7.76 Hz, 1H), 6.55 (t, *J* = 7.60 Hz, 1H), 6.47 (d, *J* = 1.86 Hz, 1H), 5.97 (s, 1H), 5.12 (d, *J* = 7.60 Hz, 1H), 2.97 (d, *J* = 9.96 Hz, 1H), 2.59-2.43 (m, 2H), 2.40 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 184.2, 176.7, 152.4, 151.5, 146.4, 144.5, 138.7, 137.6, 134.2, 133.5, 129.9, 129.3, 128.5, 128.2, 128.0, 127.3, 127.0, 126.9, 126.6, 125.9, 125.4, 124.1, 123.6, 117.2, 112.3, 110.1, 68.2, 62.5, 38.8, 35.9, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; major enantiomer $t_R$ = 20.68 min, minor enantiomer $t_R$ = 40.16 min. HRMS (ESI): $[M+K]^+$ calcd for $[C_{35}H_{27}NO_6SK]$:628.1191, found:628.1190.

**(2'R,3R,4'R)-4'-(2-oxo-2-(thiophen-2-yl)ethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ua).**

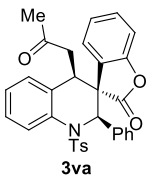


3ua

White solid (119 mg, 99 %). PE/EA/DCM = 7/1/2, m. p.: 170-174 °C. $[\alpha]_D^{26.3}$ = -23 (*c* 1.0, $CH_2Cl_2$, 96 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 7.90 Hz, 1H), 7.60 (d, *J* = 4.70 Hz, 1H), 7.57-7.52 (m, 3H), 7.47 (d, *J* = 3.30 Hz, 1H), 7.21-7.23 (m, 3H), 7.11 (d, *J* = 7.36 Hz, 2H), 7.07-7.02 (m, 3H), 6.97 (d, *J* = 7.16 Hz, 2H), 6.82 (d, *J* = 7.62 Hz, 1H), 6.77 (d, *J* = 8.00 Hz, 1H), 6.55 (t, *J* = 7.58 Hz, 1H), 5.99 (s, 1H), 5.12 (d, *J* = 7.60 Hz, 1H), 2.99 (dd, *J* = 4.80 Hz, *J* = 8.10 Hz, 1H), 2.61-2.52 (m, 2H), 2.37 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 188.1, 176.8, 152.4, 144.6, 142.9, 138.7, 137.6, 134.1, 134.1, 133.5, 132.0, 129.8, 129.4, 128.5, 128.2, 128.1, 128.1, 127.4, 127.0, 126.9, 126.6, 125.8, 125.5, 124.0, 123.7, 110.1, 68.3, 62.6, 39.3, 36.7, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; major enantiomer $t_R$ = 18.50 min, minor enantiomer $t_R$ = 40.47 min. HRMS (ESI): $[M+K]^+$ calcd for $[C_{35}H_{27}NO_5S_2K]$:644.0962, found:644.0961.

**(2'R,3R,4'R)-4'-(2-oxopropyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'**

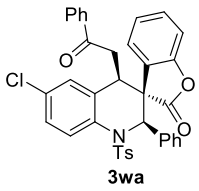
**-quinolin]-2-one (3va).**



3va

White solid (64 mg, 60 %). PE/EA/DCM = 10/1/2, m. p.: 110-116 °C. $[\alpha]_D^{26.7}$ = -30 (*c* 1.0, $CH_2Cl_2$, 82 % ee); $^1H$ NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 7.92 Hz, 1H), 7.60-7.53 (m, 3H), 7.33 (d, *J* = 8.08 Hz, 2H), 7.25 (d, *J* = 14.92 Hz, 1H), 7.08 (d, *J* = 7.24 Hz, 2H), 7.03 (t, *J* = 7.46 Hz, 2H), 6.98-6.94 (m, 2H), 6.74 (d, *J* = 8.08 Hz, 1H), 6.53 (t, *J* = 7.56 Hz, 1H), 5.95 (s, 1H), 5.07 (d, *J* = 7.46 Hz, 1H), 2.77 (t, *J* = 6.84 Hz, 1H), 2.43 (s, 3H), 2.07 (t, *J* = 2.08 Hz, 1H), 2.05 (s, 1H), 1.89 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 203.8, 176.8, 152.4, 144.5, 138.7, 137.7, 134.4, 133.5, 129.9, 129.3, 128.6, 128.4, 128.1, 127.4, 127.1, 127.0, 126.2, 125.8, 125.4, 124.0, 123.7, 68.2, 62.4, 41.3, 39.0, 29.1, 21.5. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; major enantiomer $t_R$ = 19.80 min, minor enantiomer $t_R$ = 31.25 min. HRMS (ESI): $[M+K]^+$ calcd for $[C_{32}H_{27}NO_5SK]$:576.1242, found:576.1241.

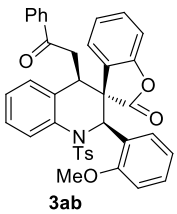
**(2'R,3R,4'R)-6'-chloro-4'-(2-oxo-2-phenylethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3wa).**



3wa

White solid (123 mg, 97 %). PE/EA/DCM = 10/1/2, m. p.:190-192 °C. $[\alpha]_D^{25.3}$ = 39 (*c* 1.0, $CH_2Cl_2$, 95 % ee); $^1H$ NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.46 Hz, 1H), 7.71 (d, *J* = 7.66 Hz, 2H), 7.63 (d, *J* = 8.06 Hz, 2H), 7.56-7.50 (m, 2H), 7.42-7.35 (m, 4H), 7.09-6.96 (m, 6H), 6.81 (d, *J* = 8.22 Hz, 1H), 6.62 (t, *J* = 7.64 Hz, 1H), 6.58 (s, 1H), 5.96 (s, 1H), 5.27 (d, *J* = 7.68 Hz, 1H), 2.96 (t, *J* = 6.28 Hz, 1H), 2.63 (d, *J* = 6.24 Hz, 2H), 2.42 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 194.5, 176.6, 152.3, 144.9, 138.3, 136.3, 135.7, 135.5, 133.8, 133.5, 132.6, 130.1, 129.5, 129.3, 128.6, 128.6, 128.1, 127.8, 127.5, 127.0, 126.7, 125.8, 125.2, 123.9, 123.8, 110.4, 68.2,. 62.2, 38.9, 35.8, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 90:10), mL/min; minor enantiomer $t_R$ = 14.40 min, major enantiomer $t_R$ = 10.43 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{37}H_{28}ClNO_5SNa]$:656.1269, found:656.1269.

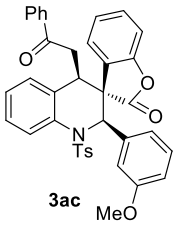
**(2'R,3R,4'R)-2'-(2-methoxyphenyl)-4'-(2-oxo-2-phenylethyl)-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ab).**



3ab

White solid (114 mg, 90 %). PE/EA/DCM = 10/1/2, m. p.:206-214 °C. $[\alpha]_D^{23.5}$ = - 24 (*c* 1.0, $CH_2Cl_2$, 99 % ee); $^1H$ NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 7.92 Hz, 1H), 7.74 (d, *J* = 8.12 Hz, 2H), 7.68 (d, *J* = 7.56 Hz, 2H), 7.57 (d, *J* = 7.54 Hz, 1H), 7.53-7.47 (m, 2H), 7.37 (t, *J* = 7.70 Hz, 2H), 7.29 (d, *J* = 8.12 Hz, 2H), 7.15 (t, *J* = 7.56 Hz, 2H), 6.99-6.92 (m, 3H), 6.78 (d, *J* = 7.54 Hz, 1H), 6.56 (d, *J* = 7.74 Hz, 1H), 6.37-6.33 (m, 3H), 5.02 (d, *J* = 7.56 Hz, 1H), 3.51 (s, 3H), 3.06 (dd, *J* = 9.74 Hz, *J* = 3.00 Hz, 1H), 2.67-2.55 (m, 2H), 2.36 (m, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 195.0, 177.2, 154.7, 152.7, 144.1, 137.4, 135.9, 135.7, 134.0, 133.2, 129.9, 128.8, 128.6, 128.5, 128.4, 128.2, 128.1, 127.7, 127.1, 126.9, 126.7, 126.1, 125.3, 125.2, 122.9, 120.2, 109.4, 108.6, 62.8, 60.8, 53.5, 39.6, 35.1, 21.5. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; minor enantiomer $t_R$ = 23.50 min, major enantiomer $t_R$ = 26.08 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{38}H_{31}NO_6SNa]$:652.1764, found:652.1770.

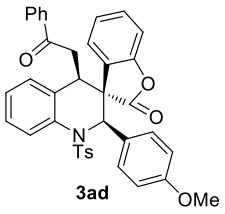
**(2'R,3R,4'R)-2'-(3-methoxyphenyl)-4'-(2-oxo-2-phenylethyl)-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ac).**




White solid (116 mg, 92 %). PE/EA/DCM = 10/1/2, m. p.:98-106 °C. $[\alpha]_D^{23.4}$ = - 23 (*c* 1.0, $CH_2Cl_2$, 91 % ee); $^1H$ NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 7.56

Hz, 1H), 7.71 (d, *J* = 7.34 Hz, 2H), 7.60 (d, *J* = 8.26 Hz, 2H), 7.54-7.49 (m, 2H), 7.38 (t, *J* = 7.72 Hz, 2H), 7.31 (d, *J* = 8.08 Hz, 2H), 7.18 (t, *J* = 7.46 Hz, 1H), 7.01-6.93 (m, 2H), 6.81 (d, *J* = 8.08 Hz, 1H), 6.61 (d, *J* = 7.72 Hz, 1H), 6.66 (s, 1H), 6.60 (d, *J* = 7.72 Hz, 1H), 6.55 (d, *J* = 7.60 Hz, 1H), 6.50 (dd, *J* = 2.04 Hz, *J* = 8.06 Hz, 1H), 5.98 (s, 3H), 5.12 (d, *J* = 7.36 Hz, 1H), 3.61 (s, 3H), 3.02 (d, *J* = 9.02 Hz, 1H), 2.71-2.56 (m, 2H), 2.40 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.9, 175.9, 152.8, 144.5, 139.1, 137.8, 135.5, 134.7, 133.5, 133.4, 132.5, 130.5, 130.0, 129.4, 128.8, 128.6, 128.5, 128.4, 127.8, 127.2, 127.0, 126.6, 126.4, 125.8, 124.2, 123.4, 121.1, 110.5, 68.1, 62.4, 54.9, 39.1, 35.9, 21.6. The enantiomeric excess was determined by HPLC with an IA column. (*n*-hexane:*i*-PrOH = 90:10), mL/min; minor enantiomer $t_R$ = 16.81 min, major enantiomer $t_R$ = 18.44 min. $[M+Na]^+$ calcd for $[C_{38}H_{31}NO_6SNa]$:652.1764, found:652.1764.

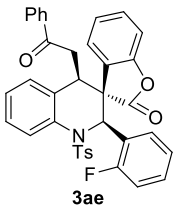
**(2'R,3R,4'R)-2'-(4-methoxyphenyl)-4'-(2-oxo-2-phenylethyl)-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ad).**



3ad

White solid (121 mg, 97 %). PE/EA/DCM = 7/1/2, m. p.:210-212 °C. $[\alpha]_D^{23.1}$ = - 36 (*c* 1.0, $CH_2Cl_2$, 99 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 7.88 Hz, 1H), 7.71 (d, *J* = 7.52 Hz, 2H), 7.58 (d, *J* = 8.32 Hz, 2H), 7.54-7.49 (m, 2H), 7.38 (t, *J* = 7.78 Hz, 2H), 7.30 (d, *J* = 8.04 Hz, 2H), 7.18 (t, *J* = 7.60 Hz, 1H), 7.04-6.97 (m, 3H), 6.79 (d, *J* = 8.04 Hz, 1H), 6.61 (d, *J* = 7.68 Hz, 1H), 6.59-6.55 (m, 3H), 5.93 (s, 1H), 5.14 (d, *J* = 7.60 Hz, 1H), 3.60 (s, 3H), 3.03 (d, *J* = 9.64 Hz, 1H), 2.71-2.55 (m, 2H), 2.39 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.9, 176.8, 158.5, 152.4, 144.5, 137.7, 135.7, 134.1, 133.8, 133.3, 130.9, 129.9, 129.3, 128.5, 128.3, 128.1, 127.7, 127.2, 127.0, 126.8, 126.5, 125.4, 124.3, 123.7, 113.4, 110.2, 68.7, 62.6, 54.9, 39.0, 36.0, 21.5. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 75:25), mL/min; minor enantiomer $t_R$ = 47.23 min, major enantiomer $t_R$ = 16.45 min. $[M+Na]^+$ calcd for $[C_{38}H_{31}NO_6SNa]$:652.1764, found:652.1767.

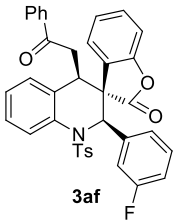
**(2'S,3R,4'R)-2'-(2-fluorophenyl)-4'-(2-oxo-2-phenylethyl)-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ae).**



3ae

White solid (114 mg, 92 %), PE/EA/DCM = 10/1/2, m. p.:230-236 °C. $[\alpha]_D^{24.5}$ = 27 (*c* 1.0, $CH_2Cl_2$, >99 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.26 Hz, 1H), 7.70 (d, *J* = 7.40 Hz, 4H), 7.53 (t, *J* = 6.80 Hz, 2H), 7.39 (t, *J* = 7.78 Hz, 3H), 7.32 (d, *J* = 8.16 Hz, 2H), 7.19 (t, *J* = 7.56 Hz, 1H), 7.04-6.91 (m, 4H), 6.68 (t, *J* = 9.10 Hz, 1H), 6.61 (d, *J* = 7.68 Hz, 1H), 6.48 (s, 1H), 6.39 (s, 1H), 5.08 (d, *J* = 6.50 Hz, 1H), 3.04 (t, *J* = 6.20 Hz, 1H), 2.69-2.59 (m, 2H), 2.39 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.8, 176.5, 152.9, 144.6, 137.3, 135.8, 134.8, 133.9, 133.4, 130.0, 129.3, 129.1, 128.6, 128.4, 128.3, 128.1, 127.8, 127.1, 126.4, 125.4, 124.3, 123.9 (J = 2.8 Hz), 123.5, 114.6 (J = 24.6 Hz), 110.3, 61.6 (J = 60.6 Hz), 39.4, 35.5, 29.6, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; minor enantiomer $t_R$ = 23.32 min, major enantiomer $t_R$ = 19.27 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{37}H_{29}FNO_5S]$:618.1745, found:618.1748.

**(2'R,3R,4'R)-2'-(3-fluorophenyl)-4'-(2-oxo-2-phenylethyl)-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3af).**

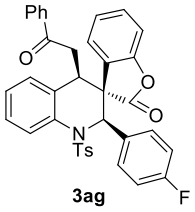


3af

White solid (112 mg, 90 %), PE/EA/DCM = 10/1/2, m. p.:228-232 °C. $[\alpha]_D^{24.8}$ = - 30 (*c* 1.0, $CH_2Cl_2$, 99 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 7.84 Hz, 1H), 7.71 (d, *J* = 7.66 Hz, 2H), 7.59 (d, *J* = 8.28 Hz, 2H), 7.53 (t, *J* = 7.50 Hz, 2H), 7.39 (t, *J* = 7.66 Hz, 2H), 7.31 (t, *J* = 7.98 Hz, 2H), 7.19 (t, *J* = 7.80 Hz,

1H), 7.04-6.99 (m, 2H), 6.90-6.81 (m, 3H), 6.66 (td, *J* = 8.24 Hz, *J* = 1.60 Hz, 1H), 6.62-6.56 (m, 2H), 5.98 (s, 1H), 5.12 (d, *J* = 7.62 Hz, 1H), 3.02 (d, *J* = 10.06 Hz, 1H), 2.72-2.55 (m, 2H), 2.41 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.8, 176.7, 162.3 (J = 247.0 Hz), 152.4, 144.8, 141.5 (J = 6.9 Hz), 137.4, 135.7, 134.0, 133.6, 133.4, 130.0, 129.7 (J = 8.3 Hz), 129.5, 128.6, 128.5 128.2, 127.8, 127.0, 126.6, 125.4, 123.9, 121.5 (J = 2.6 Hz), 114.5 (J = 21.6 Hz), 113.3 (J = 22.8 H z), 110.3, 67.7, 62.3, 39.1, 35.8, 29.5, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; major enantiomer $t_R$ = 6.66 min, minor enantiomer $t_R$ = 11.93 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{37}H_{29}FNO_5S]$:618.1745, found:618.1750.

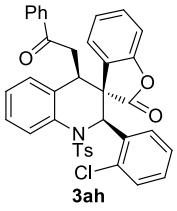
**(2'R,3R,4'R)-2'-(4-fluorophenyl)-4'-(2-oxo-2-phenylethyl)-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ag).**



3ag

White solid (118 mg, 95 %), PE/EA/DCM = 10/1/2, m. p.:190-192 °C. $[\alpha]_D^{24.1}$ = - 60 (*c* 1.0, $CH_2Cl_2$, 93 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.92 Hz, 1H), 7.72 (d, *J* = 7.60 Hz, 2H), 7.58 (d, *J* = 8.10 Hz, 2H), 7.52 (t, *J* = 6.70 Hz, 2H), 7.38 (t, *J* = 7.60 Hz, 2H), 7.32 (d, *J* = 7.90 Hz, 2H), 7.19 (t, *J* = 7.32 Hz, 1H), 7.11-7.08 (m, 2H), 7.01 (t, *J* = 7.68 Hz, 1H), 6.81 (d, *J* = 8.04 Hz, 1H), 6.73 (t, *J* = 8.52 Hz, 2H), 6.63-6.56 (m, 2H), 5.95 (s, 1H), 5.13 (d, *J* = 7.74 Hz, 1H), 3.02 (d, *J* = 10.28 Hz, 1H), 2.73-2.56 (m, 2H), 2.41 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.8, 176.7, 161.6 (J = 248.3 Hz), 152.4, 144.7, 139.4, 137.5, 135.7, 134.7 (J = 3.2 Hz), 133.9, 133.6, 133.4, 129.9, 129.5, 128.5 (J = 12.5 Hz), 128.1, 127.7 (J = 6.0 Hz), 126.9 (J = 4.26 Hz), 126.6, 125.3, 123.9 (J = 15.4 Hz), 122.4, 116.0 (J = 22.0 Hz), 115.0 (J = 21.6 Hz), 110.7 (J = 85.5 Hz), 67.8, 62.4, 39.0, 35.9, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 70:30), mL/min; minor enantiomer $t_R$ = 12.72 min, major enantiomer $t_R$ = 10.82 min. HRMS (ESI): $[M+K]^+$ calcd for $[C_{37}H_{28}FNO_5SK]$:656.1304, found:656.1309.

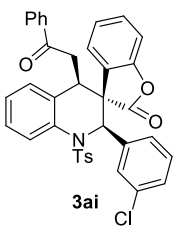
**(2'S,3R,4'R)-2'-(2-chlorophenyl)-4'-(2-oxo-2-phenylethyl)-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ah).**



3ah

White solid (124 mg, 98 %). PE/EA/DCM = 7/1/2, m. p.:238-242 °C. $[\alpha]_D^{23.0}$ = - 31 (*c* 1.0, $CH_2Cl_2$, 99 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.88 Hz, 1H), 7.71 (dd, *J* = 5.52 Hz, *J* = 7.46 Hz, 4H), 7.54 (t, *J* = 7.82 Hz, 2H), 7.39 (t, *J* = 7.76 Hz, 2H), 7.34 (d, *J* = 8.30 Hz, 2H), 7.26-7.20 (m, 2H), 7.09-7.01 (m, 2H), 6.95-9.68 (m, 3H), 6.67 (d, *J* = 7.68 Hz, 1H), 6.57 (t, *J* = 7.60 Hz, 1H), 6.52 (s, 1H), 5.30 (d, *J* = 7.56 Hz, 1H), 3.10 (d, *J* = 6.62 Hz, 1H), 2.69-2.54 (m, 2H), 2.40 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 195.0, 176.3, 152.9, 144.6, 137.9, 137.7, 135.9, 134.9, 133.6, 133.4, 131.2, 130.1, 129.9, 129.4, 129.1, 128.6, 128.6, 128.5, 127.9, 127.2, 127.0, 126.5, 126.2, 125.8, 124.3, 123.4, 110.5, 63.6, 61.1, 39.4, 35.8, 21.7. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 70:30), mL/min; minor enantiomer $t_R$ = 10.31 min, major enantiomer $t_R$ = 14.11 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{37}H_{29}ClNO_5S]$:634.1449, found:634.1453.

**(2'R,3R,4'R)-2'-(3-chlorophenyl)-4'-(2-oxo-2-phenylethyl)-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ai).**

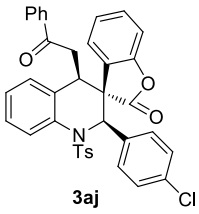


3ai

White solid (124 mg, 99 %), PE/EA/DCM = 7/1/2, m. p.:97-100 °C. $[\alpha]_D^{23.7}$ = - 14 (*c* 1.0, $CH_2Cl_2$, 99 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 7.80 Hz, 1H), 7.72 (d, *J* = 7.46 Hz, 2H), 7.58 (d, *J* = 8.22 Hz, 2H), 7.55-7.51 (m, 2H),

7.38 (t, *J* = 7.72 Hz, 2H), 7.32 (d, *J* = 8.14 Hz, 2H), 7.20 (t, *J* = 7.46 Hz, 1H), 7.10 (s, 1H), 7.04-7.93 (m, 4H), 6.83 (d, *J* = 8.06 Hz, 1H), 6.60 (d, *J* = 7.34 Hz, 2H), 5.94 (s, 1H), 5.13 (d, *J* = 7.55 Hz, 1H), 3.00 (d, *J* = 10.10 Hz, 1H), 2.73-2.55 (m, 2H), 2.41 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.7, 176.6, 152.4, 144.8, 140.9, 137.4, 135.7, 134.0, 133.6, 133.4, 130.0, 129.6, 129.4, 128.6, 128.5, 128.2, 127.7, 127.6, 127.0, 127.0, 126.6, 126.3, 125.3, 124.1, 123.9, 123.8, 110.4, 67.7, 62.3, 39.0, 35.9, 21.6. The enantiomeric excess was determined by HPLC with an IA column. (*n*-hexane:*i*-PrOH = 90:10), mL/min; minor enantiomer $t_R$ = 12.72 min, major enantiomer $t_R$ = 10.82 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{37}H_{29}ClNO_5S]$:634.1449, found:634.1449.

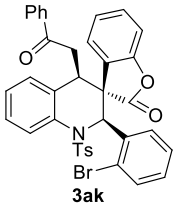
**(2'R,3R,4'R)-2'-(4-chlorophenyl)-4'-(2-oxo-2-phenylethyl)-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3aj).**



3aj

White solid (118 mg, 93 %). PE/EA/DCM = 9/1/2, m. p.:200-202 °C. $[\alpha]_D^{23.8}$ = - 29 (*c* 1.0, $CH_2Cl_2$, 99 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.82 Hz, 1H), 7.72 (d, *J* = 7.58 Hz, 2H), 7.58 (d, *J* = 8.12 Hz, 2H), 7.53-7.50 (m, 2H), 7.39 (t, *J* = 7.58 Hz, 2H), 7.32 (d, *J* = 7.94 Hz, 2H), 7.19 (t, *J* = 7.58 Hz, 1H), 7.07-7.01 (m, 5H), 6.83 (d, *J* = 8.02 Hz, 1H), 6.61-6.57 (m, 2H), 5.93 (s, 1H), 5.12 (d, *J* = 7.74 Hz, 1H), 3.01 (d, *J* = 10.34 Hz, 1H), 2.72-2.56 (m, 2H), 2.41 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.8, 176.6, 152.4, 144.8, 137.4, 135.7, 133.8, 133.6, 133.4, 133.1, 130.0, 129.6, 128.6, 128.5, 128.3, 128.1, 127.8, 127.4, 127.0, 126.6, 125.3, 123.9, 123.9, 110.4, 67.8, 62.2, 39.0, 35.9, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; major enantiomer $t_R$ = 13.84 min, minor enantiomer $t_R$ = 22.38 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{37}H_{29}ClNO_5S]$:634.1449, found:634.1454.

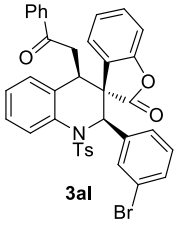
**(2'S,3R,4'R)-2'-(2-bromophenyl)-4'-(2-oxo-2-phenylethyl)-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ak).**



3ak

White solid (126 mg, 93 %). PE/EA/DCM = 10/1/2, m. p.:198-200 °C. $[\alpha]_D^{23.9}$ = - 75 (*c* 1.0, $CH_2Cl_2$, 99 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 7.84 Hz, 1H), 7.72 (t, *J* = 8.44 Hz, 4H), 7.55-7.51 (m, 2H), 7.40-7.34 (m, 4H), 7.27 (d, *J* = 7.90 Hz, 1H), 7.22(d, *J* = 7.62 Hz, 1H), 7.16 (d, *J* = 7.40 Hz, 1H), 7.03 (t, *J* = 7.74 Hz, 1H), 6.94 (t, *J* = 7.50 Hz, 1H), 6.88 (d, *J* = 8.00 Hz, 1H), 6.82 (t, *J* = 7.16 Hz, 1H), 6.69 (d, *J* = 7.74 Hz, 1H), 6.60 (t, *J* = 7.62 Hz, 1H), 6.50 (s, 1H), 5.36 (d, *J* = 7.56 Hz, 1H), 3.10 (d, *J* = 10.40 Hz, 1H), 2.71-2.64 (m, 1H), 2.55 (dd, *J* = 1.54 Hz, *J* = 17.40 Hz, 1H), 2.40 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.9, 175.9, 152.8, 144.5, 139.1, 137.8, 135.8, 134.7, 133.5, 133.4, 132.5, 130.5, 130.0, 129.4, 128.8, 128.6, 128.5, 128.4, 127.8, 127.2, 127.0, 126.6, 126.4, 125.8, 124.2, 123.4, 121.1, 110.5, 65.4, 61.1, 39.2, 35.8, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; minor enantiomer $t_R$ = 10.15 min, major enantiomer $t_R$ = 18.33 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{37}H_{29}BrNO_5S]$:678.0944, found:678.0949.

**(2'R,3R,4'R)-2'-(3-bromophenyl)-4'-(2-oxo-2-phenylethyl)-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3al).**

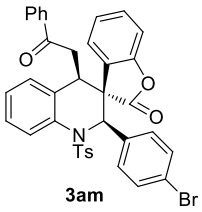


3al

White solid (134 mg, 99 %), PE/EA/DCM = 7/1/2, m. p.:110-112 °C. $[\alpha]_D^{23.8}$ = - 18 (*c* 1.0, $CH_2Cl_2$, 94 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 7.90 Hz, 1H), 7.72 (d, *J* = 7.58 Hz, 2H), 7.58 (d, *J* = 8.10 Hz, 2H), 7.53 (d, *J* = 7.00 Hz, 2H), 7.39 (t, *J* = 7.58 Hz, 2H), 7.33 (d, *J* = 7.90 Hz, 2H), 7.24 (s, 1H), 7.20 (t, *J* = 7.58 Hz, 1H), 7.10 (d, *J* = 8.00 Hz, 1H), 7.06-7.00 (m, 2H), 6.91 (t, *J* =

7.90 Hz, 1H), 6.83 (d, *J* = 8.00 Hz, 1H), 6.61 (t, *J* = 6.98 Hz, 2H), 5.92 (s, 1H), 5.13 (d, *J* = 7.58 Hz, 1H), 3.00 (d, *J* = 10.42 Hz, 1H), 2.74-2.66 (m, 1H), 2.57 (d, *J* = 16.74 Hz, 1h), 2.42 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.7, 176.6, 152.4, 144.8, 141.0, 137.3, 135.7, 133.8, 133.5, 133.4, 130.5, 130.0, 129.6, 129.2, 128.6, 128.2, 127.7, 127.0, 127.0, 126.6, 125.3, 124.6, 123.9, 123.8, 122.2, 110.4, 67.6, 62.3, 38.9, 35.9, 21.6. The enantiomeric excess was determined by HPLC with an IA column. (*n*-hexane:*i*-PrOH = 90:10), mL/min; minor enantiomer $t_R$ = 11.54 min, major enantiomer $t_R$ = 12.91 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{37}H_{29}BrNO_5S]$:678.0944, found:678.0944.

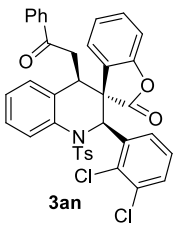
**(2'R,3R,4'R)-2'-(4-bromophenyl)-4'-(2-oxo-2-phenylethyl)-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3am).**



3am

White solid (134 mg, 99 %), PE/EA/DCM = 7/1/2, m. p.:201-203 °C. $[\alpha]_D^{25.0}$ = - 43 (*c* 1.0, $CH_2Cl_2$, >99 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.92 Hz, 1H), 7.58 (d, *J* = 8.20 Hz, 4H), 7.52 (d, *J* = 8.30 Hz, 3H), 7.30 (d, *J* = 7.80 Hz, 2H), 7.19 (t, *J* = 7.42 Hz, 1H), 7.11 (d, *J* = 7.30 Hz, 2H), 7.03 (t, *J* = 7.36 Hz, 2H), 6.97 (d, *J* = 6.42 Hz, 2H), 6.78 (d, *J* = 7.92 Hz, 1H), 6.59 (d, *J* = 7.80 Hz, 1H), 6.55 (t, *J* = 7.78 Hz, 1H), 5.98 (s, 1H), 5.11 (d, *J* = 7.56 Hz, 1H), 3.01 (d, *J* = 9.82 Hz, 1H), 2.67-2.53 (m, 2H), 2.48 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.0, 176.8, 152.3, 144.5, 138.6, 137.6, 134.3, 134.1, 133.5, 131.9, 129.9, 129.3, 128.6, 128.5, 128.2, 128.0, 127.4, 126.9, 126.3, 125.8, 125.4, 124.0, 123.7, 110.2, 68.3, 62.4, 39.0, 35.9, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; major enantiomer $t_R$ = 14.71 min, minor enantiomer $t_R$ = 28.57 min. $[M+H]^+$ calcd for $[C_{37}H_{29}BrNO_5S]$:678.0944, found:678.0947.

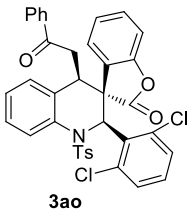
**(2'S,3R,4'R)-2'-(2,3-dichlorophenyl)-4'-(2-oxo-2-phenylethyl)-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3an).**



3an

White solid (124 mg, 93 %). PE/EA/DCM = 10/1/2, m. p.:182-186 °C. $[\alpha]_D^{24.3}$ = - 109 (*c* 1.0, $CH_2Cl_2$, 96 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.08 (dd, *J* = 0.70 Hz, *J* = 7.94 Hz, 1H), 7.72-7.68 (m, 4H), 7.56-7.51 (m, 2H), 7.40-7.34 (m, 4H), 7.23-7.19 (m, 2H), 7.10-7.03 (m, 2H), 6.39-6.87 (m, 2H), 6.67 (d, *J* = 7.86 Hz, 1H), 6.58 (td, J = 7.62 Hz, J = 0.80 Hz, 1H), 6.55 (s, 1H), 5.30 (dd, *J* = 7.66 Hz, *J* = 0.66 H, 1H), 3.10 (d, *J* = 9.80 Hz, 1H), 2.70-2.53 (m, 2H), 2.40 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.8, 176.1, 152.8, 144.7, 140.1, 137.5, 135.7, 134.6, 133.4, 133.4, 132.6, 130.1, 129.6, 129.5, 129.3, 128.6, 128.5, 128.3, 128.1, 127.7, 127.1, 126.5, 126.4, 125.5, 123.9, 123.5, 110.7, 64.0, 60.8, 39.4, 35.5, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; minor enantiomer $t_R$ = 19.24 min, major enantiomer $t_R$ = 22.50 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{37}H_{27}Cl_2NO_5SNa]$:690.0879, found:690.0880.

**(2'S,3R,4'R)-2'-(2,3-dichlorophenyl)-4'-(2-oxo-2-phenylethyl)-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ao).**

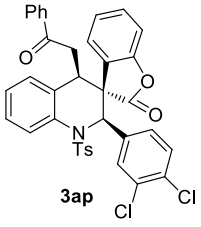


3ao

Light yellow solid (118 mg, 90 %). PE/EA/DCM = 10/1/2, m. p.:188-192 °C. $[\alpha]_D^{24.4}$ = 46 (*c* 1.0, $CH_2Cl_2$, 99 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.08 Hz, 1H), 7.70 (d, *J* = 6.70 Hz, 4H), 7.58-7.51 (m, 2H), 7.38 (dd, *J* = 7.62, *J* = 17.82 Hz, 4H), 7.24 (d, *J* = 14.94 Hz, 1H), 7.18 (d, *J* = 2.10 Hz, 1H), 7.07 (t, *J* = 7.68 Hz, 1H), 7.01 (d, *J* = 8.64 Hz, 1H), 6.92-6.87 (m, 2H), 6.66 (t, *J* = 7.78 Hz, 2H), 6.45 (s, 1H), 5.31 (d, *J* = 7.60 Hz, 1H), 3.07 (d, *J* = 10.32 Hz,

1H), 2.72-2.52 (m, 2H), 2.41 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.7, 175.9, 152.8, 144.8, 139.2, 137.4, 135.8, 134.5, 132.1, 130.2, 130.1, 129.7, 129.3, 128.7, 128.6, 128.4, 127.8, 127.2, 127.1, 126.5, 125.6, 123.9, 123.6, 110.7, 63.3, 60.9, 39.2, 35.7, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; minor enantiomer $t_R$ = 7.03 min, major enantiomer $t_R$ = 13.98 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{37}H_{27}Cl_2NO_5SNa]$:690.0879, found:690.0885.

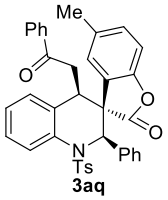
**(2'R,3R,4'R)-2'-(3,4-dichlorophenyl)-4'-(2-oxo-2-phenylethyl)-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ap).**



3ap

White solid (126 mg, 95 %). PE/EA/DCM = 10/1/2, m. p.:200-206 °C. $[\alpha]_D^{23.2}$ = - 21 (*c* 1.0, $CH_2Cl_2$, 97 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.96 Hz, 1H), 7.71 (d, *J* = 7.60 Hz, 2H), 7.58-7.52 (m, 4H), 7.39 (t, *J* = 7.70 Hz, 2H), 7.33 (d, *J* = 8.20 Hz, 2H), 7.22-7.18 (m, 2H), 7.12 (d, *J* = 8.32 Hz, 1H), 7.06 (t, *J* = 7.72 Hz, 1H), 6.96 (dd, *J* = 1.84 Hz, *J* = 8.32 Hz, 1H), 6.86 (d, *J* = 8.10 Hz, 1H), 6.65-6.59 (m, 2H), 5.88 (s, 1H), 5.13 (d, *J* = 7.66 Hz, 1H), 2.98(d, *J* = 10.12 Hz, 1H), 2.73-2.54 (m, 2H), 2.42 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.7, 176.4, 152.4, 145.0, 139.2, 137.2, 135.7, 133.6, 133.5, 133.4, 132.3, 131.5, 130.1, 130.1, 129.9, 128.6, 128.3, 128.1, 127.8, 127.1, 127.0, 126.6, 125.5, 125.2, 124.1, 123.6, 110.6, 67.3, 62.1, 39.0, 35.9, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; minor enantiomer $t_R$ = 18.29 min, major enantiomer $t_R$ = 11.26 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{37}H_{27}Cl_2NO_5SNa]$:690.0879, found:690.0879.

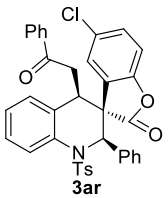
**(2'R,3R,4'R)-5-methyl-4'-(2-oxo-2-phenylethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3aq).**



3aq

White solid (120 mg, 98 %). PE/EA/DCM = 10/1/2, m. p.:198-202 °C. $[\alpha]_D^{26.6}$ = - 30 (*c* 1.0, $CH_2Cl_2$, 96 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.86 Hz, 1H), 7.73 (d, *J* = 7.48 Hz, 2H), 7.60 (d, *J* = 8.20 Hz, 2H), 7.53 (t, *J* = 7.48 Hz, 2H), 7.39 (t, *J* = 7.60 Hz, 2H), 7.31 (d, *J* = 8.06 Hz, 2H), 7.19 (t, *J* = 7.48 Hz, 2H), 7.11 (d, *J* = 7.42 Hz, 1H), 7.05 (t, *J* = 7.48 Hz, 2H), 6.98 (d, *J* = 7.14 Hz, 1H), 6.77 (d, *J* = 8.06 Hz, 1H), 6.66 (d, *J* = 8.20 Hz, 1H), 6.61 (d, *J* = 7.80 Hz, 1H), 5.98 (s, 1H), 4.83 (s, 1H), 3.00 (d, *J* = 9.36 Hz, 1H), 2.72-2.57 (m, 2H), 2.40 (m, 3H), 1.86 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 195.1, 177.2, 150.5, 144.6, 138.9, 137.9, 135.9, 134.3, 134.0, 133.4, 133.2, 130.0, 129.7, 128.6, 128.4, 128.1, 127.9, 127.4, 127.1, 126.8, 126.7, 126.1, 126.0, 124.1, 109.7, 68.4, 62.7, 39.2, 36.1, 21.7, 20.9. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 75:25), mL/min; major enantiomer $t_R$ = 12.67 min, minor enantiomer $t_R$ = 22.28 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{38}H_{31}NO_5SNa]$: 636.1815, found: 636.1814.

**(2'R,3R,4'R)-5-chloro-4'-(2-oxo-2-phenylethyl)-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-2-one (3ar).**



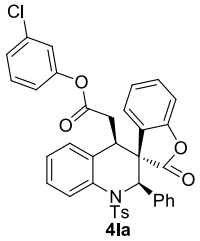
3ar

White solid (126 mg, 99 %). PE/EA/DCM = 10/1/2, m. p.:160-164 °C. $[\alpha]_D^{26.8}$ = - 13 (*c* 1.0, $CH_2Cl_2$, 87 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.86 Hz, 1H), 7.73 (d, *J* = 7.40 Hz, 2H), 7.61-7.52 (m, 4H), 7.40 (t, *J* = 7.40 Hz, 2H), 7.32 (d, *J* = 7.76 Hz, 2H), 7.21 (d, *J* = 7.60 Hz, 1H), 7.10-7.06 (m, 4H), 7.01 (d, *J* = 4.98 Hz, 1H), 6.95 (d, *J* = 8.14 Hz, 1H), 6.72 (d, *J* = 8.60 Hz, 1H), 6.62 (d, *J* = 7.50 Hz, 1H), 5.98 (s, 1H), 4.99 (s, 1H), 3.05 (d, *J* = 10.50 Hz, 1H), 2.75-2.55 (m, 2H), 2.41 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 194.6, 176.1, 150.8, 144.7, 138.4, 137.5, 135.7, 134.1,

133.5, 133.3, 130.0, 129.4, 129.0, 128.7, 128.6, 128.4, 128.3, 127.8, 127.6, 127.0, 126.5, 126.1, 125.8, 125.7, 111.3, 68.2, 62.9, 39.0, 35.8, 21.6. The enantiomeric excess was determined by HPLC with an IC column. (*n*-hexane:*i*-PrOH = 75:25), mL/min; major enantiomer $t_R$ = 10.39 min, minor enantiomer $t_R$ = 15.47 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{37}H_{28}ClNO_5SNa]$: 656.1269, found: 656.1268.

### 2.5 Analytical data of compounds of 4.

**(3-chlorophenyl2-((2'R,3R,4'R)-2-oxo-2'-phenyl-1'-tosyl-2',4'-dihydro-1'H,2H-spiro[benzofuran-3,3'-quinolin]-4'-yl)acetate (4la).**

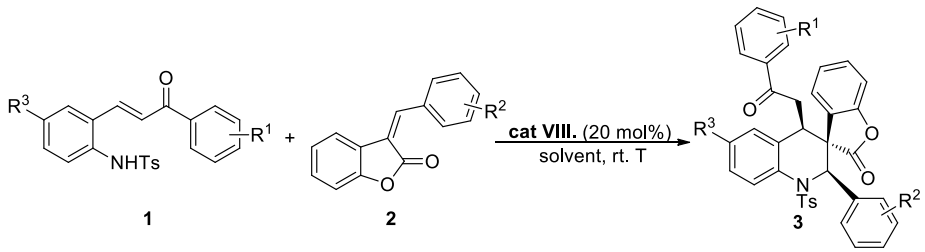


4la

White solid (124 mg, 95 %). PE/EA/DCM = 10/1/2, m. p.:182-186 °C. $[\alpha]_D^{24.3}$ = - 50 (*c* 1.0, $CH_2Cl_2$, 95 % ee); $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.98 Hz, 1H), 7.70 (s, 1H), 7.58 (d, *J* = 8.06 Hz, 3H), 7.55-7.49 (m, 2H), 7.35-7.29 (m, 3H), 7.20 (t, *J* = 7.52 Hz, 1H), 7.11 (d, *J* = 7.34 Hz, 2H), 7.03 (t, *J* = 7.42 Hz, 1H), 7.00-6.95 (m, 2H), 3.03 (d, *J* = 9.62 Hz, 1H), 2.68-2.53(m, 2H), 2.40 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 193.7, 176.8, 152.4, 144.6, 138.7, 137.7, 137.2, 134.9, 134.2, 133.5, 133.3, 130.0, 129.9, 129.4, 128.5, 128.3, 128.1, 127.8, 127.4, 127.0, 126.9, 126.3, 125.9, 125.9, 125.5, 124.1, 123.8, 110.2, 68.4, 62.5, 39.0, 36.1, 21.6. enantiomeric excess was determined by HPLC with an IA column. (*n*-hexane:*i*-PrOH = 80:20), mL/min; minor enantiomer $t_R$ = 9.25 min, major enantiomer $t_R$ = 17.73 min. HRMS (ESI): $[M+Na]^+$ calcd for $[C_{37}H_{27}Cl_2NO_5SNa]$:672.1224, found:672.1230.

## 3. General Procedure to Synthesize the Spiro-Tetrahydroquinoline Derivatives 3.

### 3.1. General procedure to construct spiro-tetrahydroquinoline derivatives.

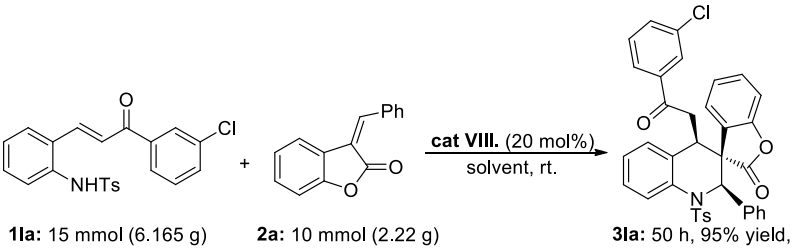


1 2 3

To a vessel were successively added **1** (0.3 mmol), **2** (0.2 mmol), **cat. VIII** (0.04 mmol) in 4 mL 1,2-dichloroethane (DCE), The reaction was stirred at rt. for quantitative time. After the reactions were completed, the solvents were evaporated, and the residue was purified by flash silica gel chromatography (PE/EA/DCM = 10/1/2) to afford the desired product. The HPLC (racemate of **3ca**, **3da**, **3ea**, **3ga**, **3ia**, **3la**, **3ab**, **3ac**, **3ad**, **3ae**, **3al**, **3am**, **3ao**, **3ap**) were mixed through the equal quality catalyzed by **III** and **VIII** and the racemate of **3qa**, **3ra**, **3sa**, **3ta**, **3ua**, **3va**, **3aq**, **3ar** were catalyzed by 20 mol% TBD as the base under standard conditions, the others

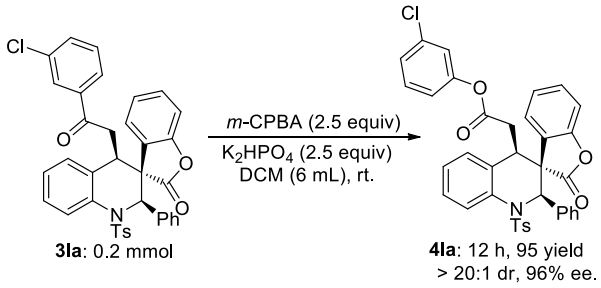
racemates of **3** were catalyzed by DABCO (50 mol%). Furthermore, chiral **3aq** was synthesized by adjusting the ration of substrates: **1a** (0.2 mmol), **2q** (0.4 mmol), **cat.** (20 mol%) in 4 mL DCE at rt. for 36h due to the pure compound of **2q** could not be successfully obtained.

### 3.2. A gram-scale synthesis of 3la.




To a round-bottomed flask were successively added **1la** (6.165g, 15 mmol), **2a** (2.22g, 10 mmol), **cat. VIII** (2 mmol, 20 mol%) in 1,2-dichloroethane (0.05M), The reaction was stirred at rt. for 50 h. After the reactions were completed, the solvents were evaporated, and the residue was purified by flash silica gel chromatography (PE/EA/DCM = 10/1/2) to afford the desired product as a white solid (95% yield, >20:1 dr, 97% ee.)

### 3.3. General procedure to synthesis 4la.

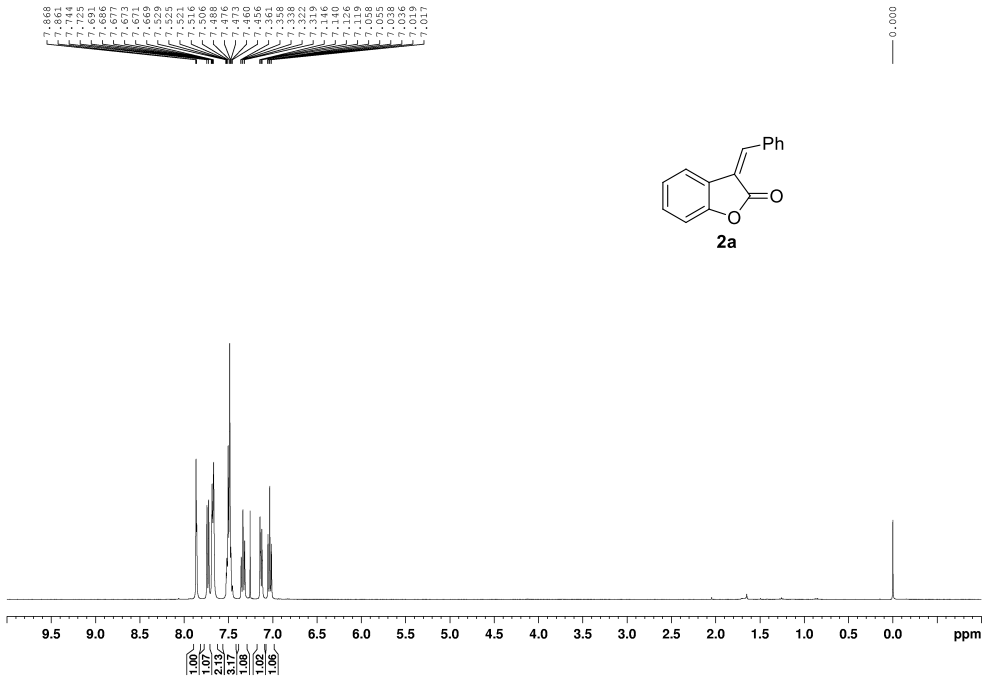



To a vessel were successively added **3la** (0.2 mmol), *m*-CPBA (0.5 mmol), $K_2HPO_4$ (0.5 mmol) in 6 mL DCM. The reaction was stirred at rt. for 12 h, after the reactions were completed, the solvents were evaporated, and the residue was purified by flash silica gel chromatography (PE/EA/DCM = 10/1/2) to afford the desired product as a white solid.

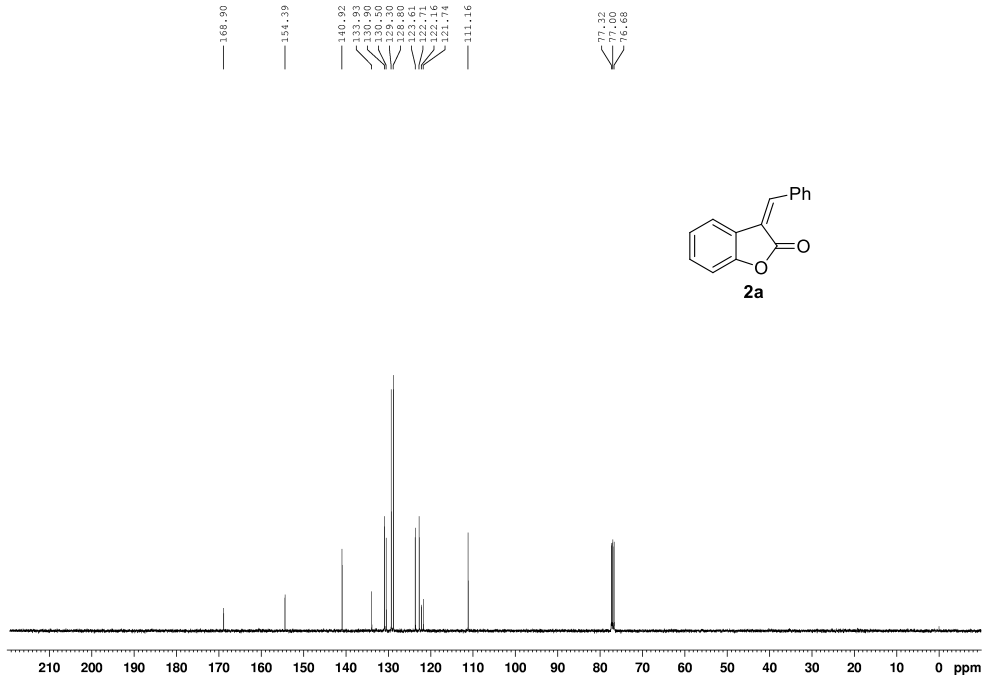
## 4. Copy of NMR Spectrogram.

### 4.1 Copy of NMR Spectrogram of 2.

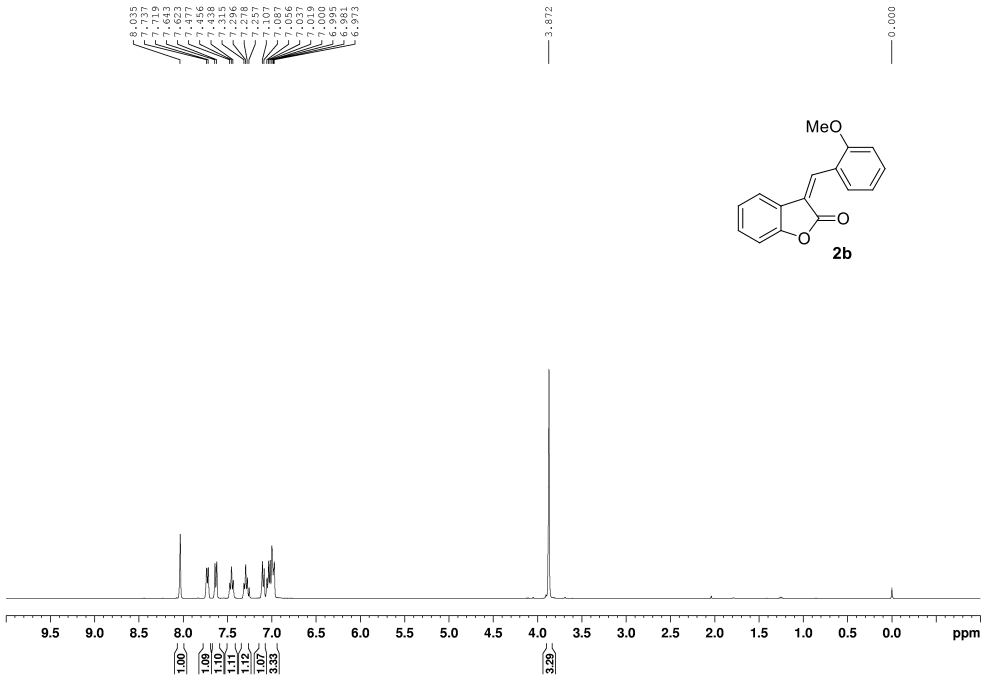
$^1$HNMR of **2a** (400M, $CDCl_3$)



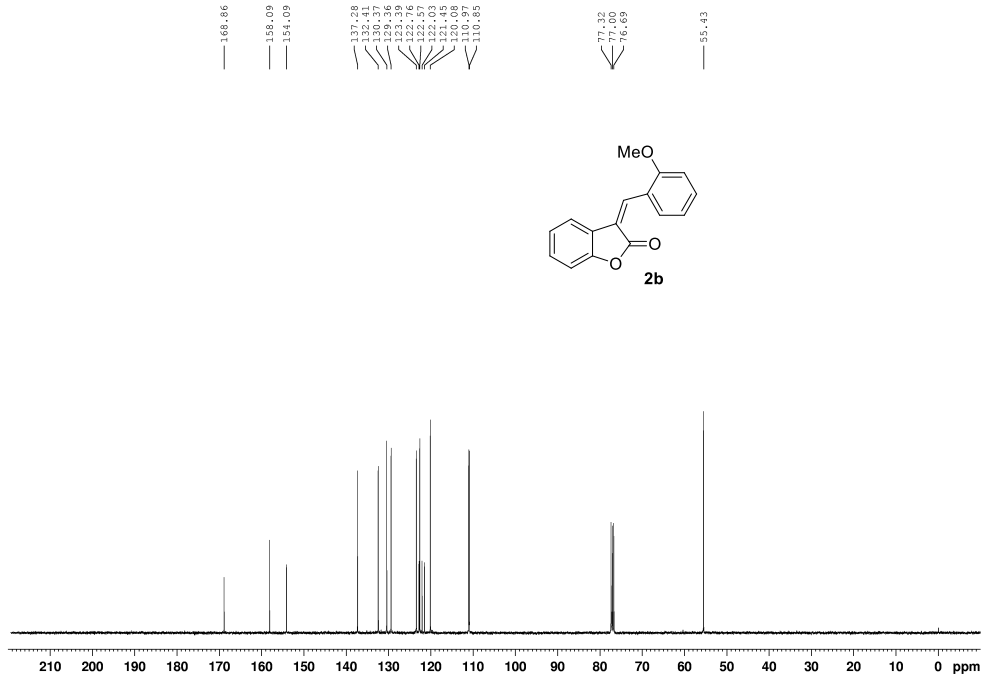

$^{13}$CNMR of **2a** (100M, $CDCl_3$)



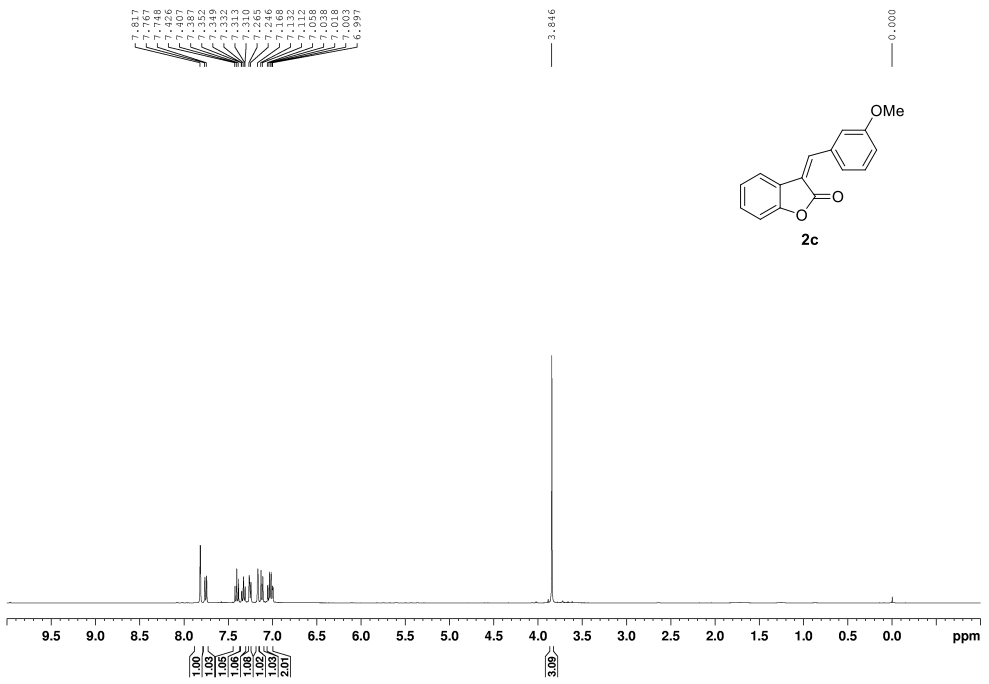

$^{1}$HNMR of **2b** (400M, $CDCl_3$)



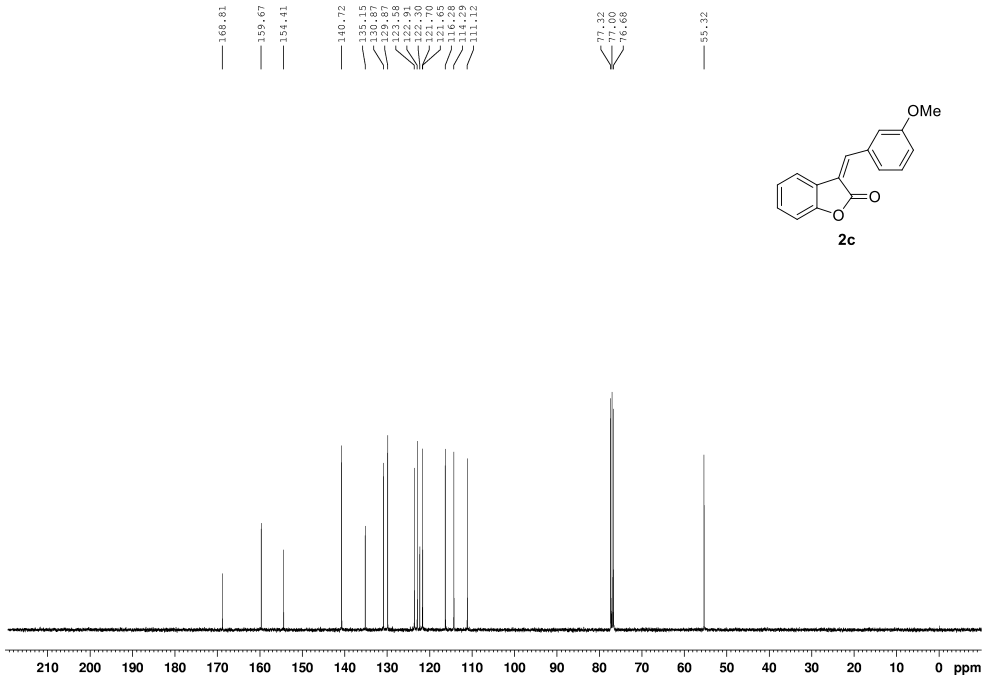

$^{13}$CNMR of **2b** (100M, $CDCl_3$)




$^{1}$HNMR of **2c** (400M, $CDCl_3$)

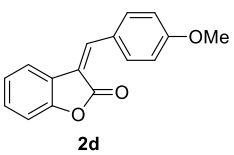


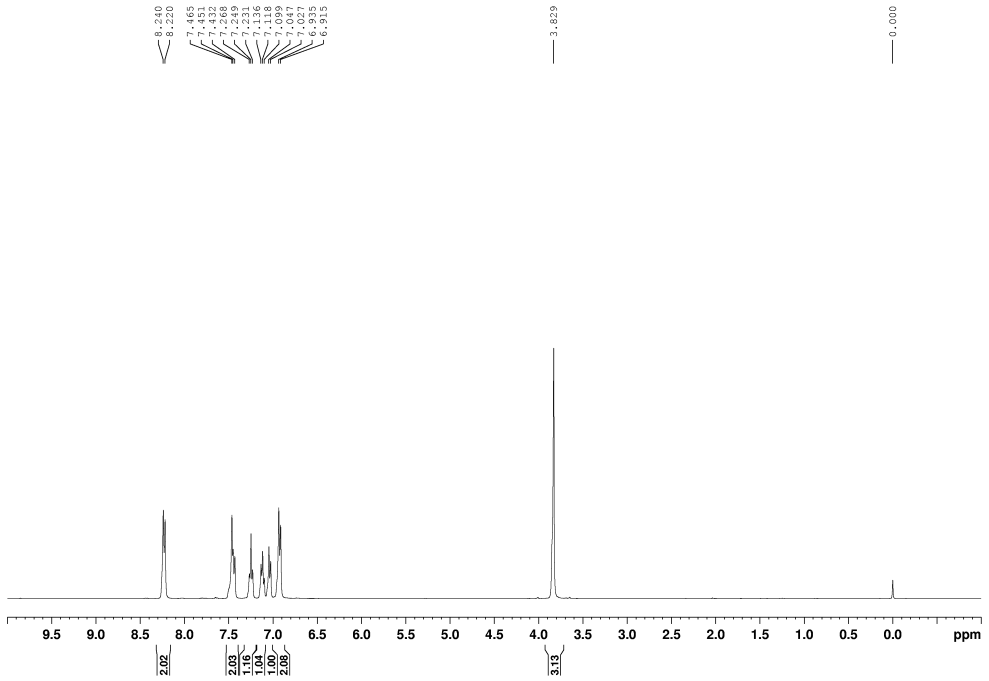

$^{13}$CNMR of **2c** (100M, $CDCl_3$)



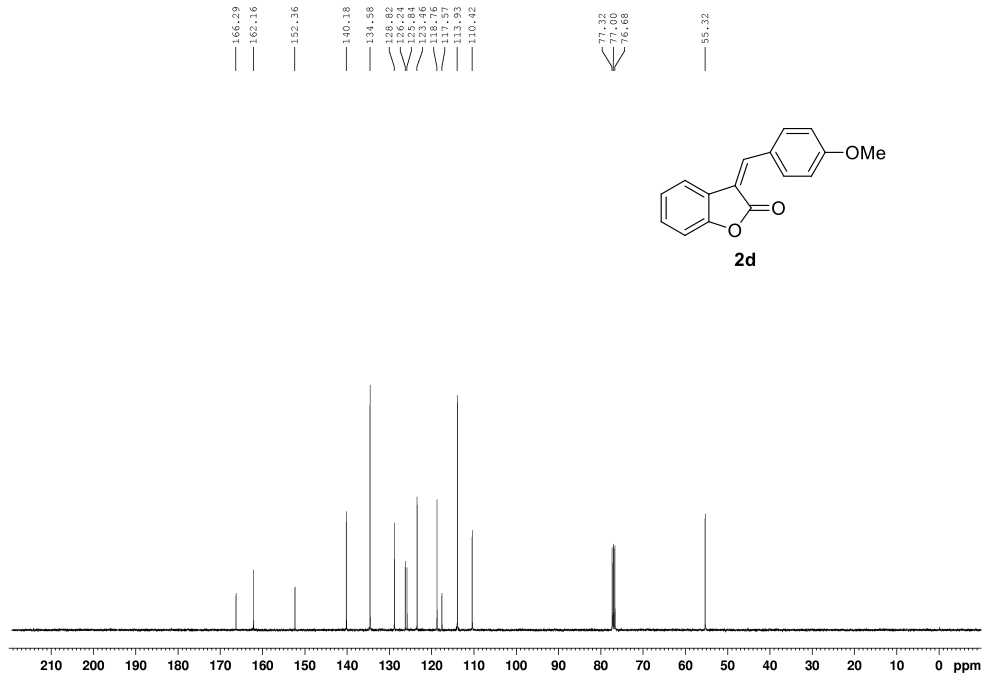

$^{1}$HNMR of **2d** (400M, $CDCl_3$)



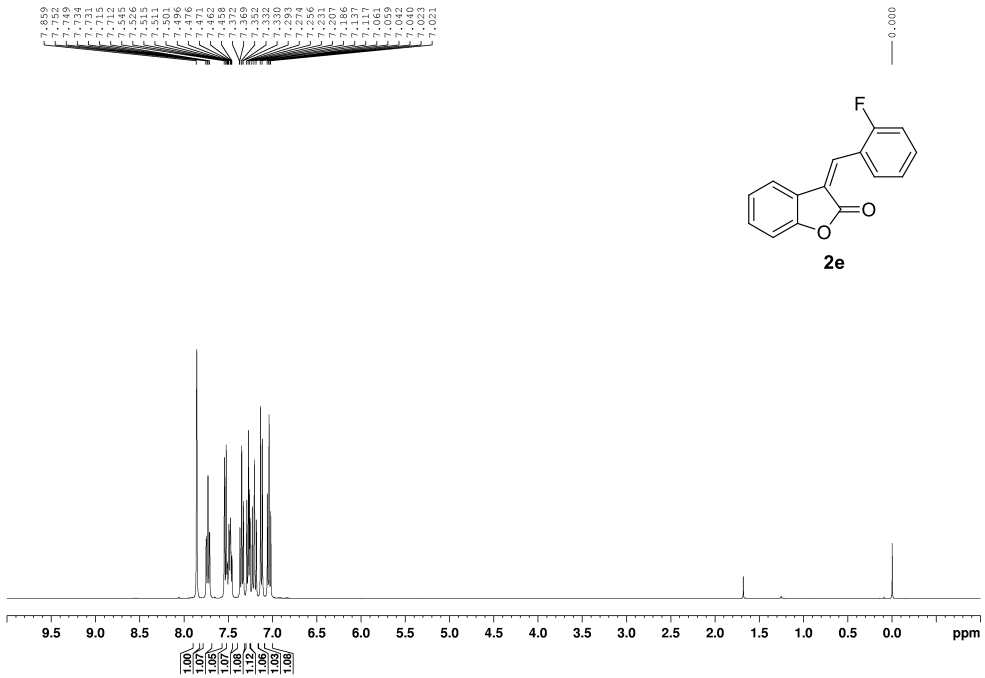




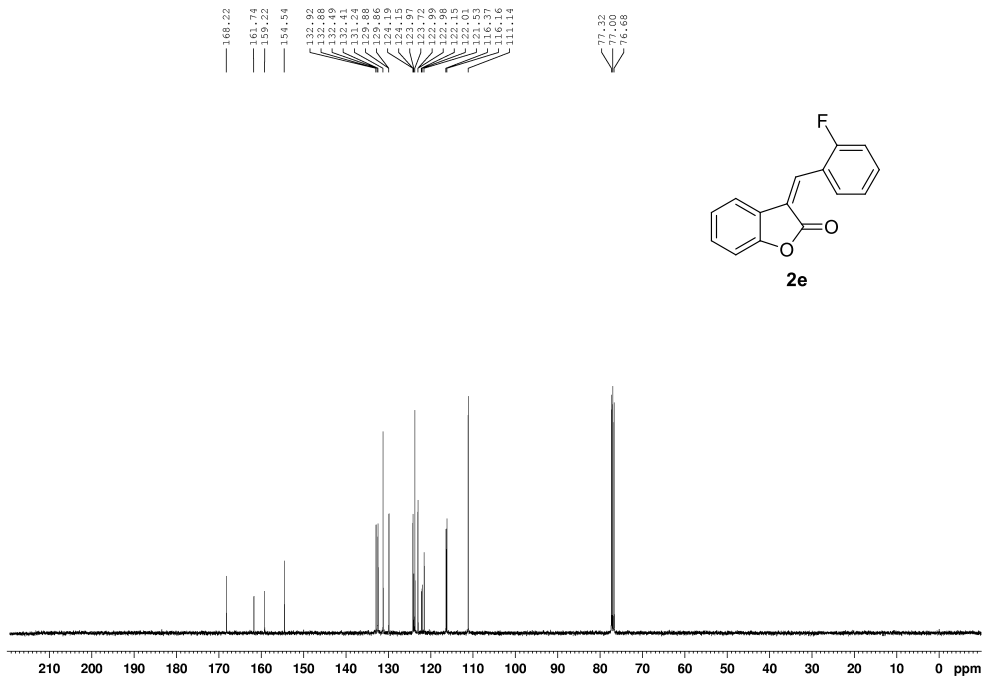

$^{13}$CNMR of **2d** (100M, $CDCl_3$)



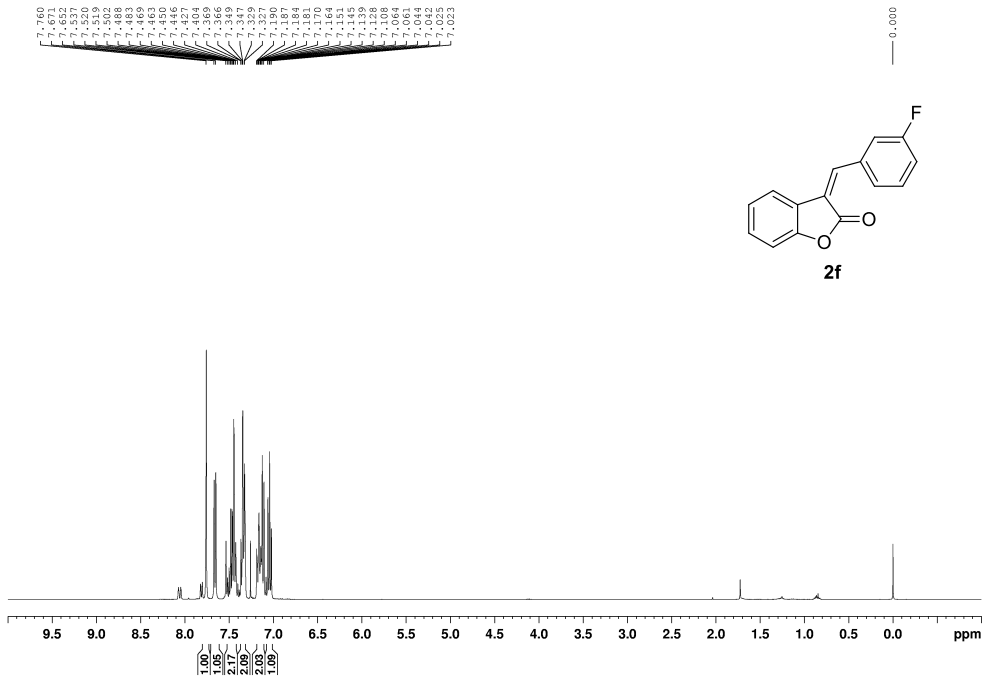

$^{1}$HNMR of **2e** (400M, $CDCl_3$)



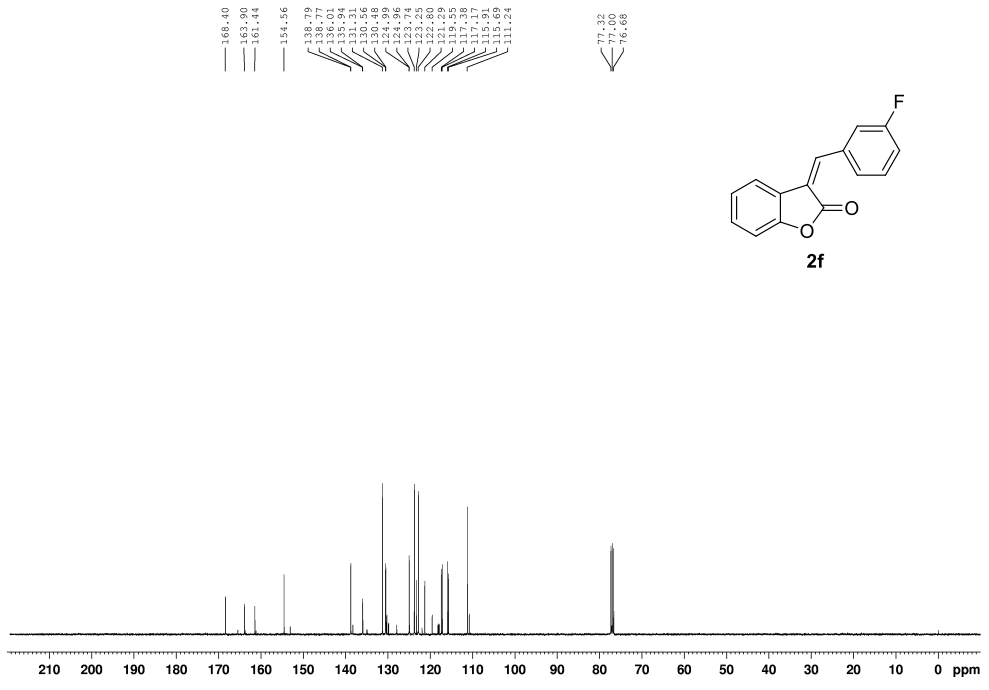

$^{13}$CNMR of **2e** (100M, $CDCl_3$)



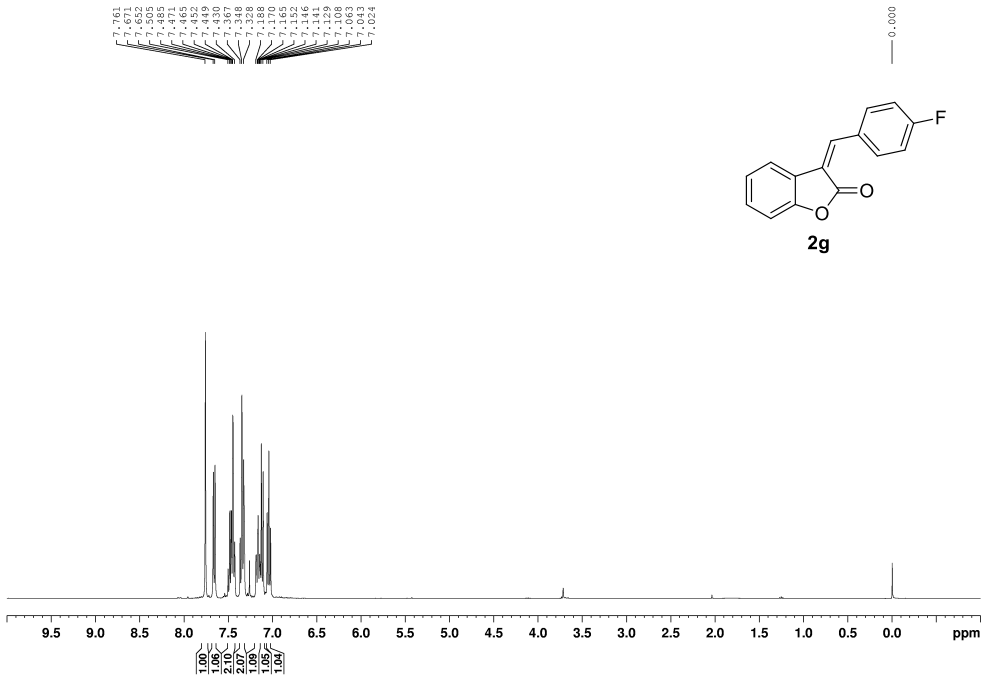

$^{1}$HNMR of **2f** (400M, $CDCl_3$)



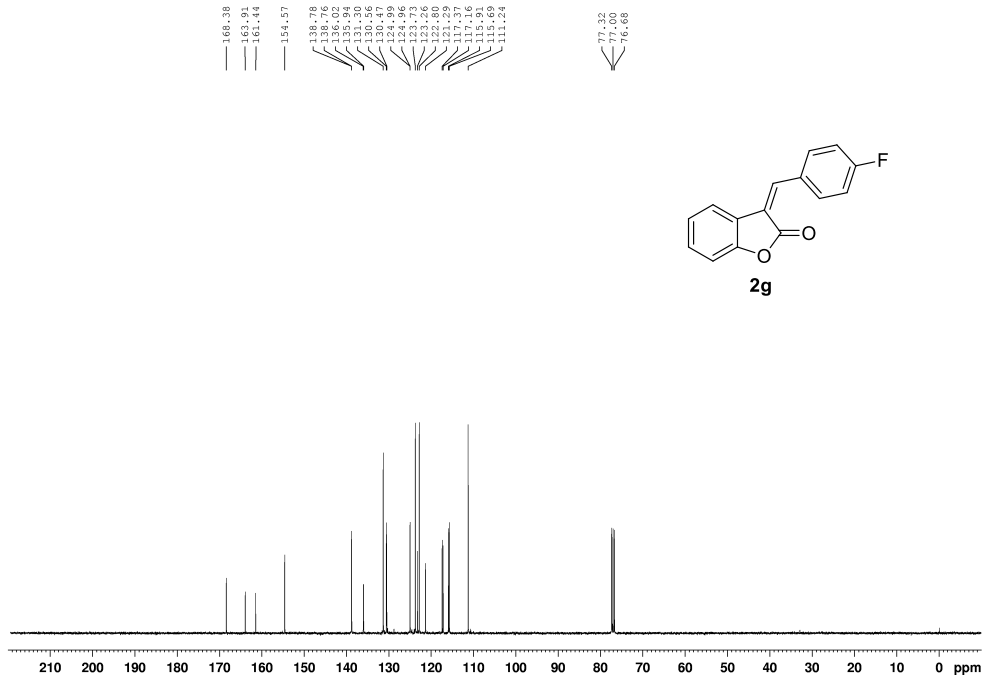

$^{13}$CNMR of **2f** (100M, $CDCl_3$)



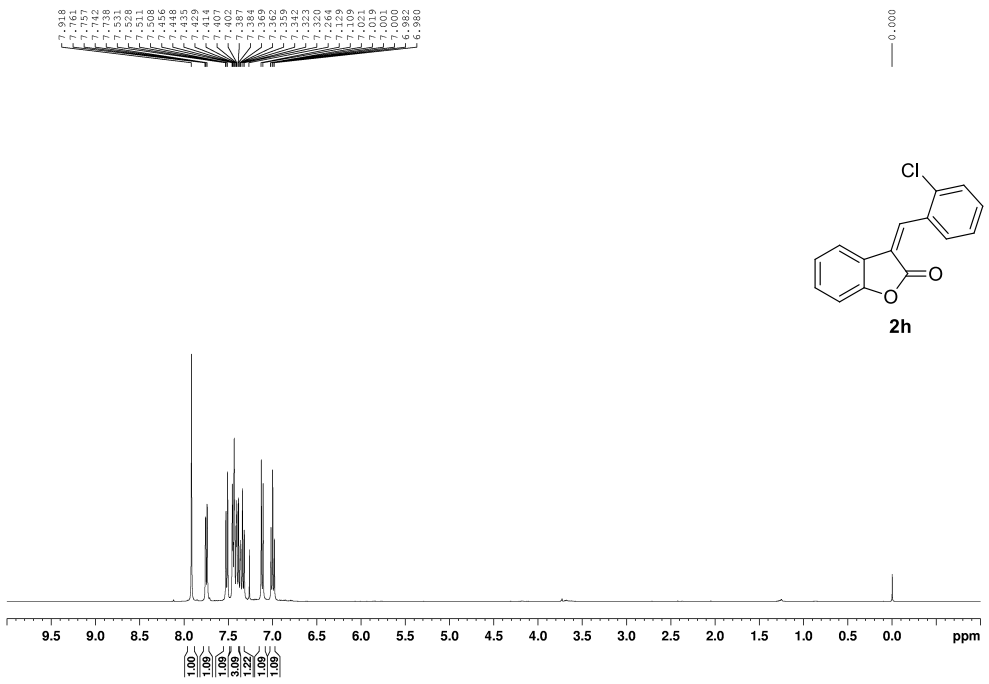

$^{1}$HNMR of **2g** (400M, $CDCl_3$)



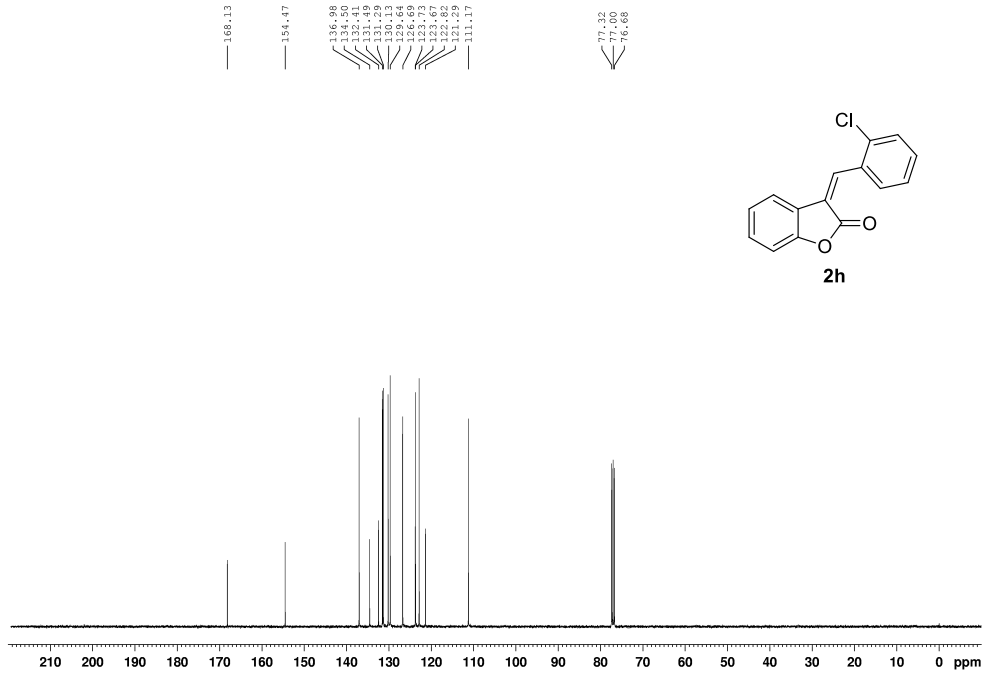

$^{13}$CNMR of **2g** (100M, $CDCl_3$)



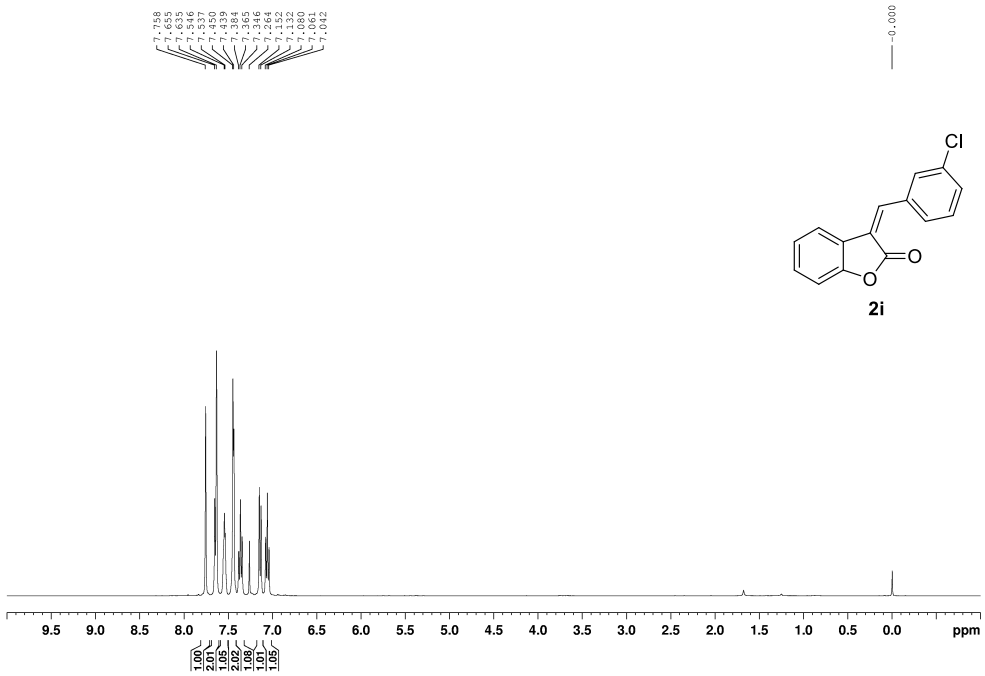

$^{1}$HNMR of **2h** (400M, $CDCl_3$)



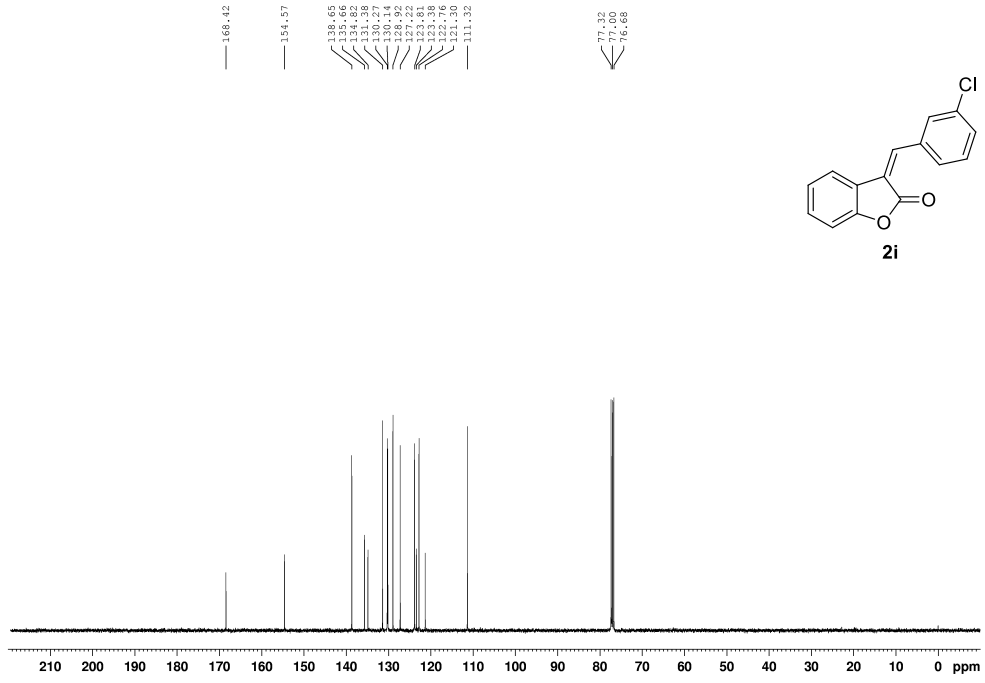

$^{13}$CNMR of **2h** (100M, $CDCl_3$)



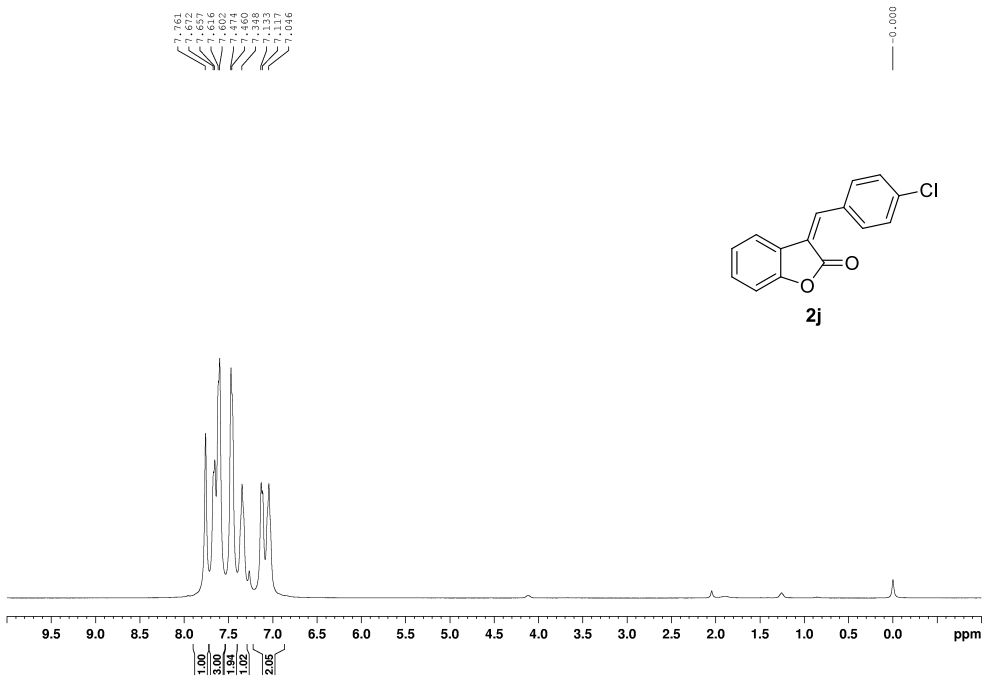

$^{1}$HNMR of **2i** (400M, $CDCl_3$)



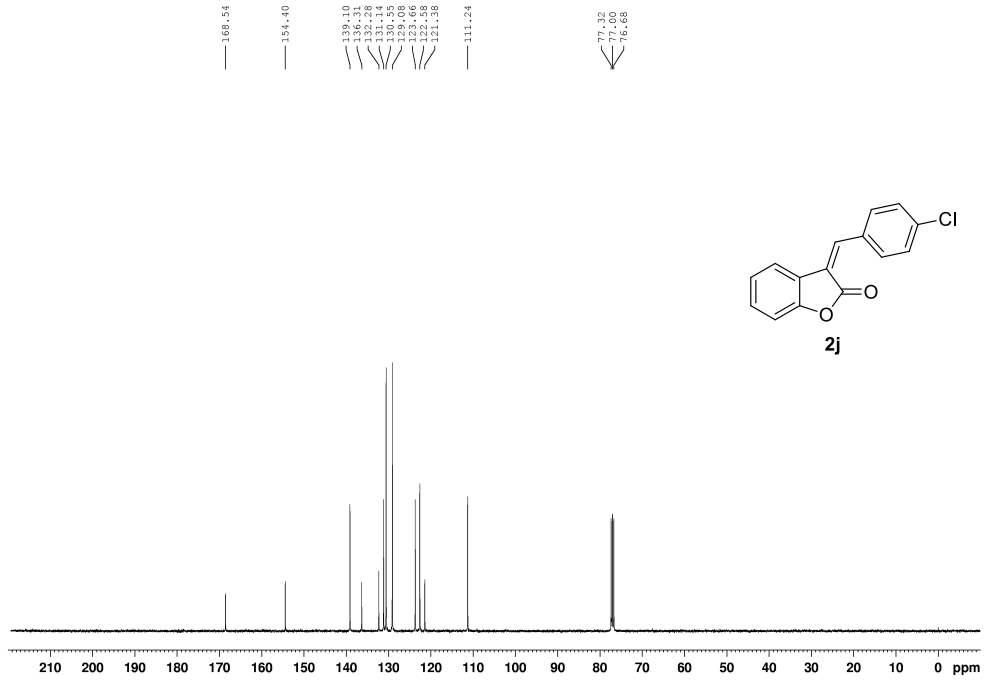

$^{13}$CNMR of **2i** (100M, $CDCl_3$)



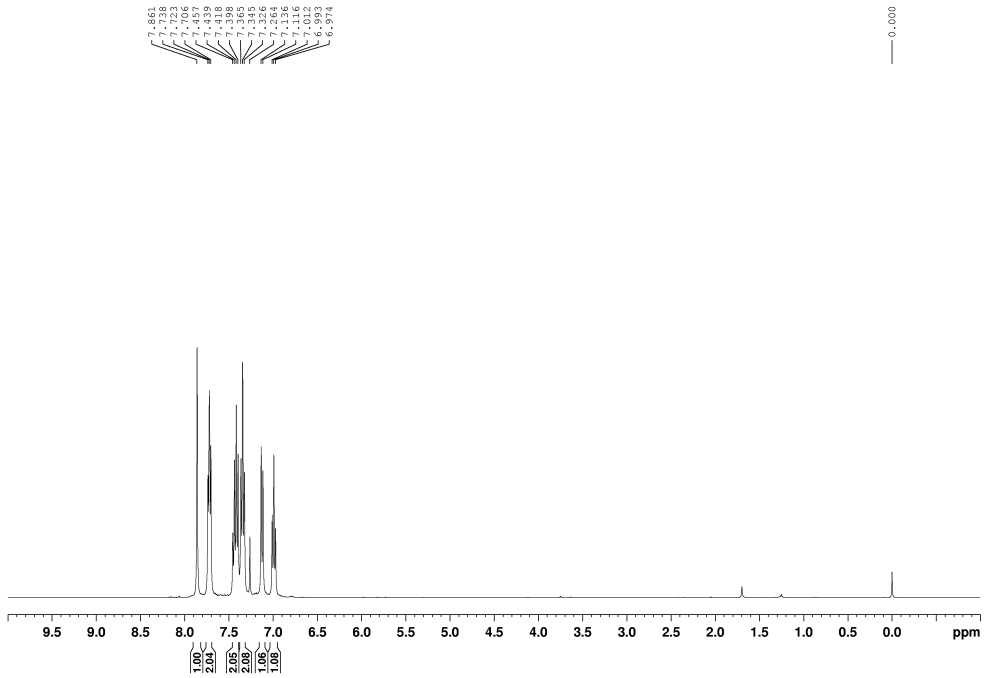

$^{1}$HNMR of **2j** (400M, $CDCl_3$)



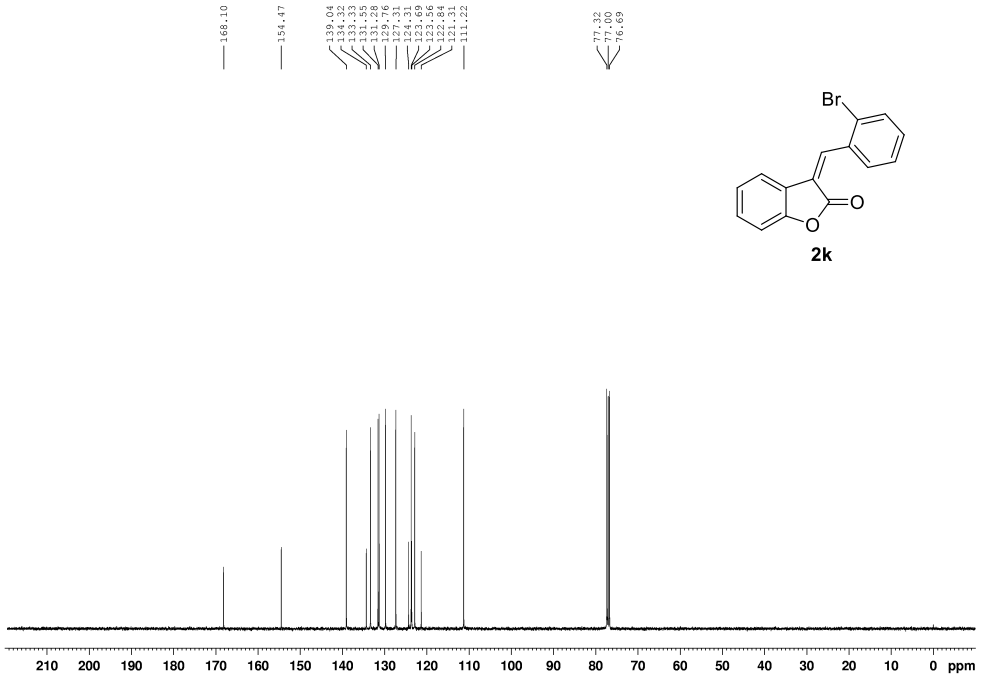

$^{13}$CNMR of **2j** (100M, $CDCl_3$)



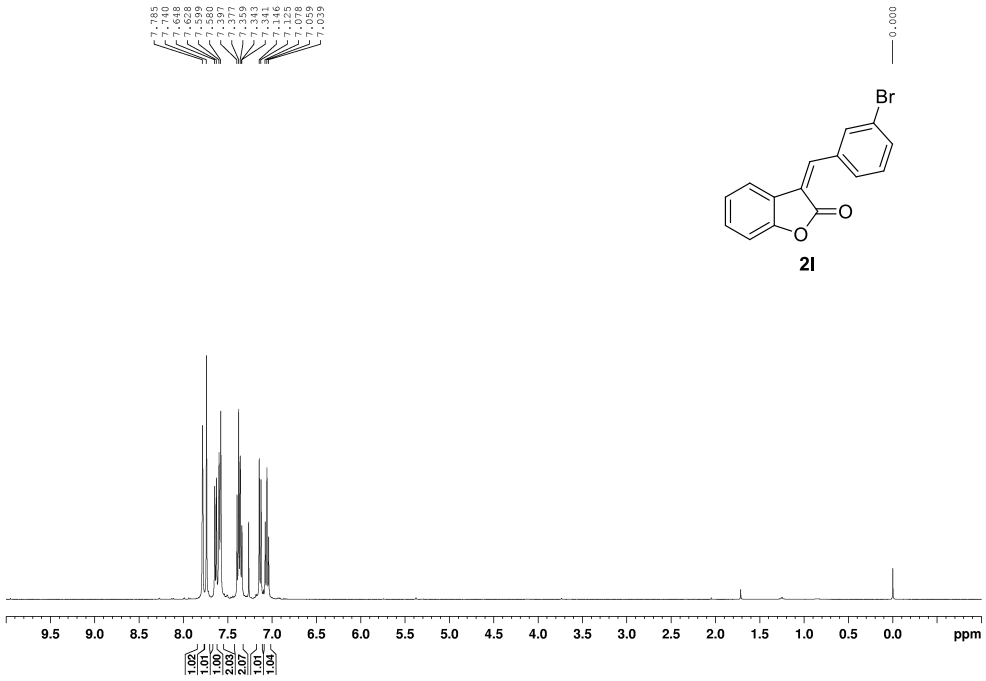

$^{1}$HNMR of **2k** (400M, $CDCl_3$)



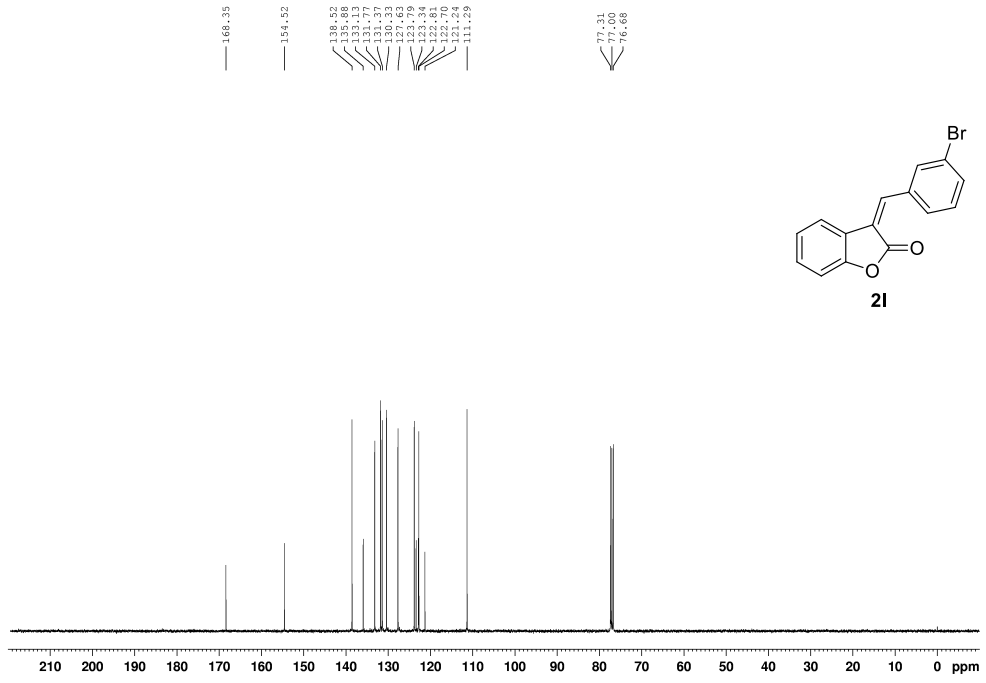

$^{13}$CNMR of **2k** (100M, $CDCl_3$)



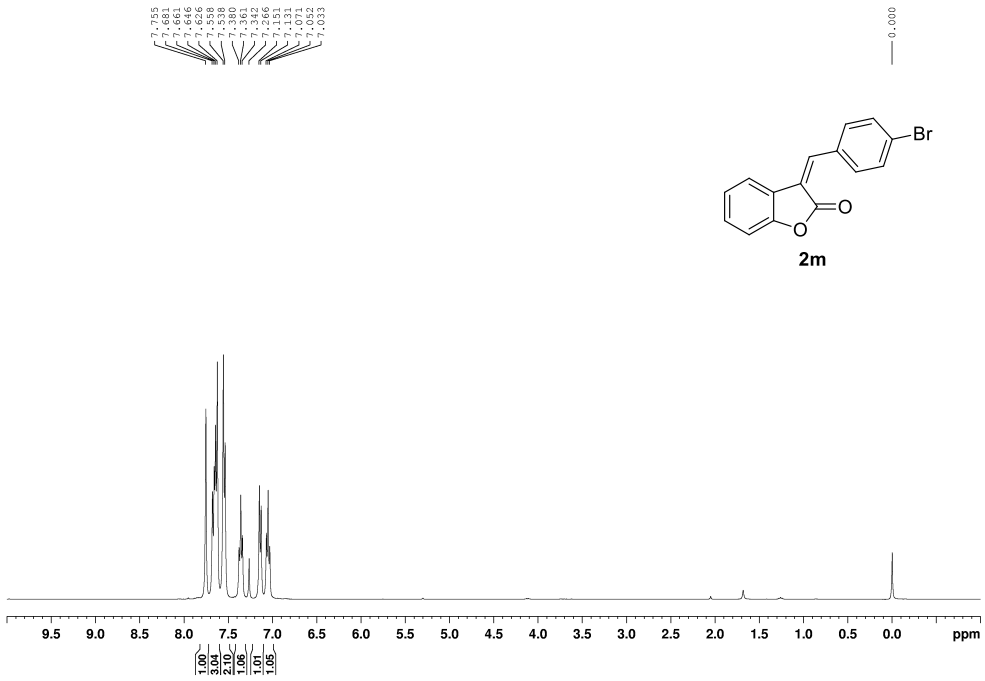

$^{1}$HNMR of **2l** (400M, $CDCl_3$)



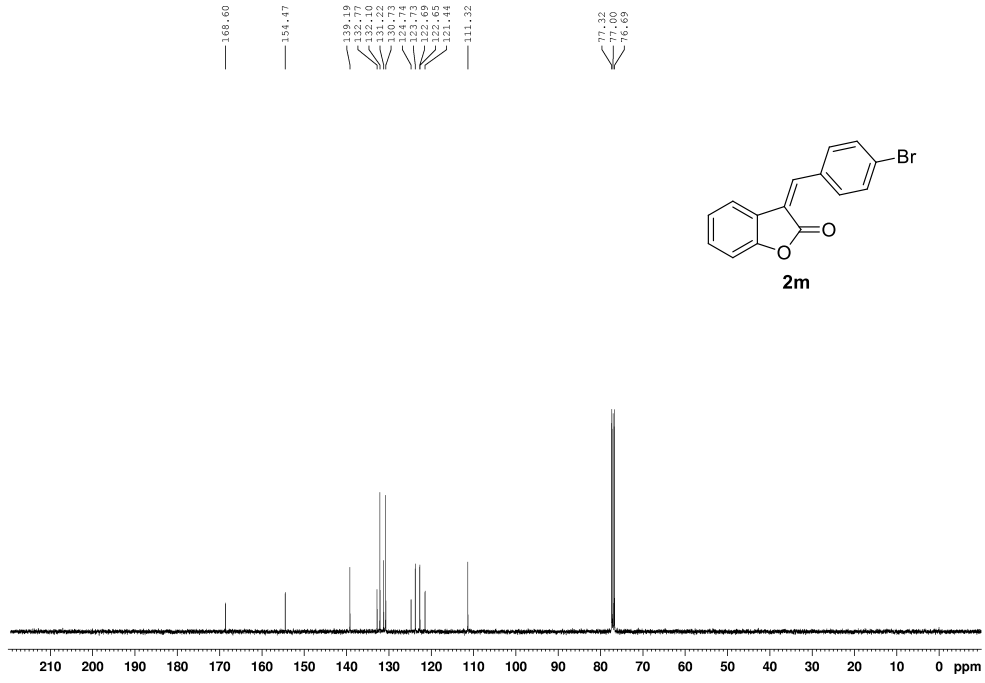

$^{13}$CNMR of **2l** (100M, $CDCl_3$)



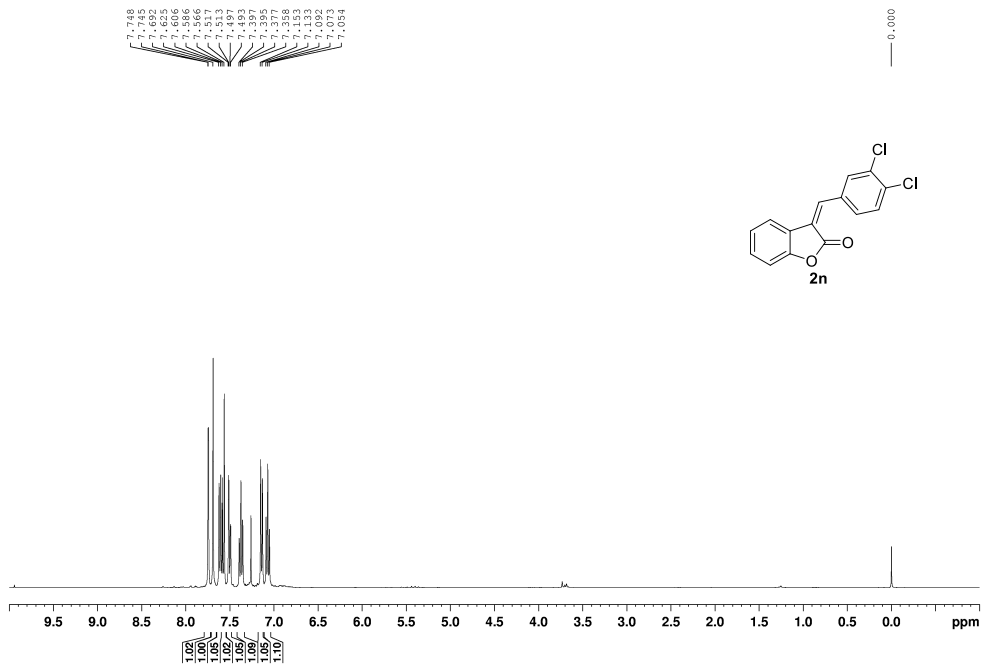

$^{1}$HNMR of **2m** (400M, $CDCl_3$)



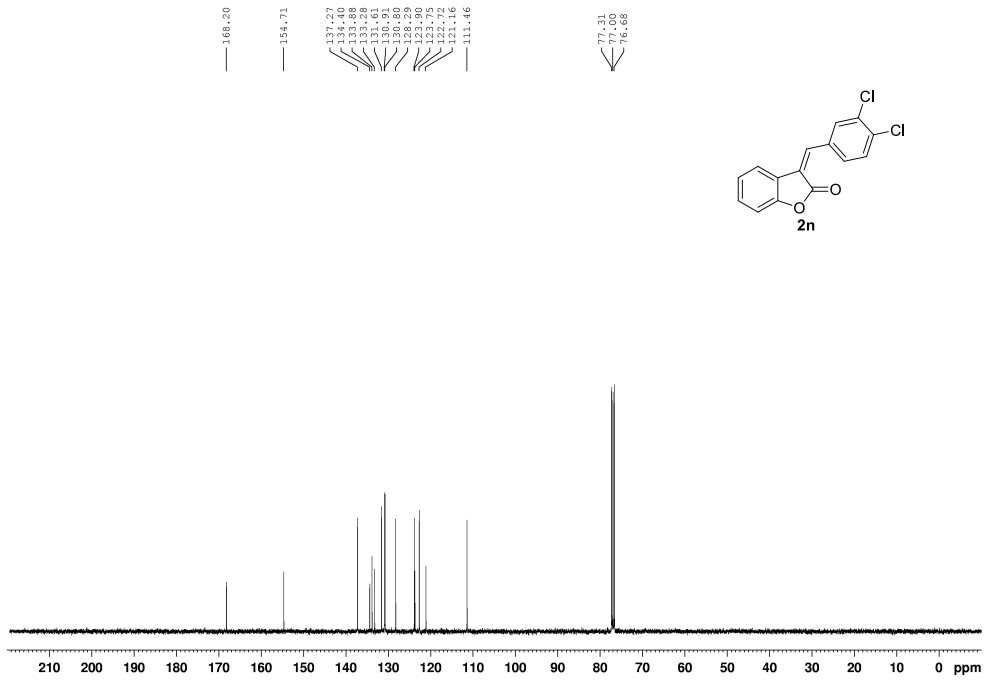

$^{13}$CNMR of **2m** (100M, $CDCl_3$)



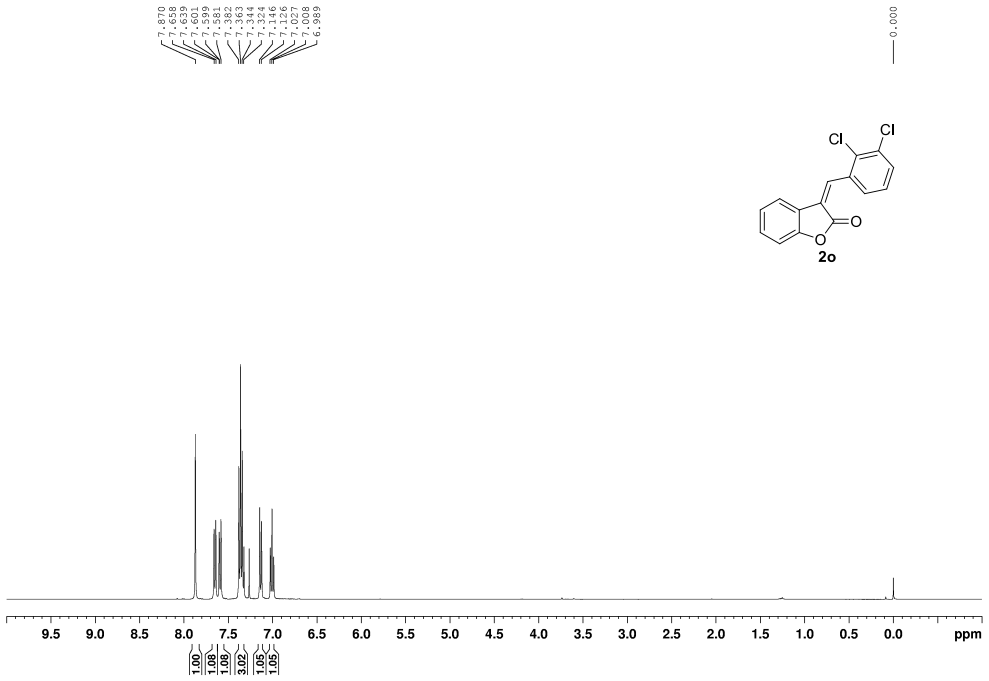

$^{1}$HNMR of **2n** (400M, $CDCl_3$)



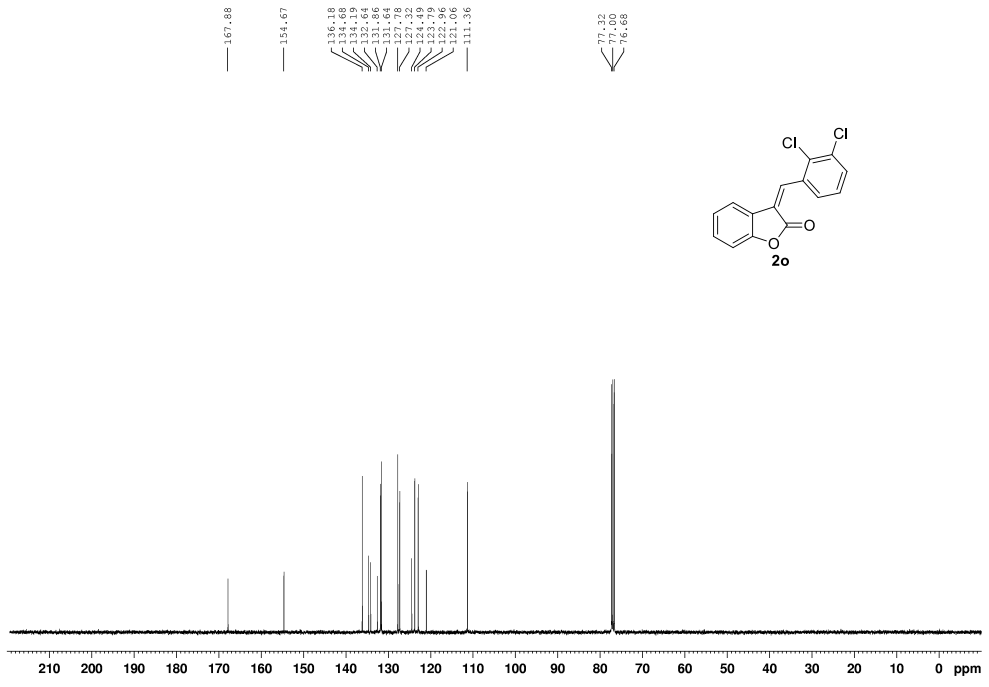

$^{13}$CNMR of **2n** (100M, $CDCl_3$)



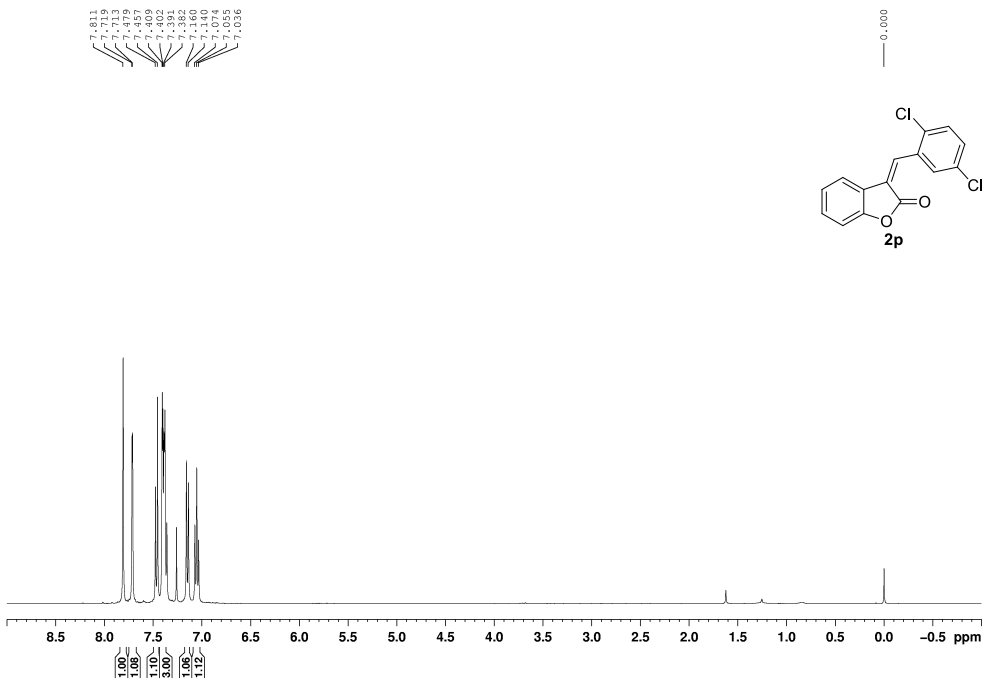

$^{1}$HNMR of **2o** (400M, $CDCl_3$)



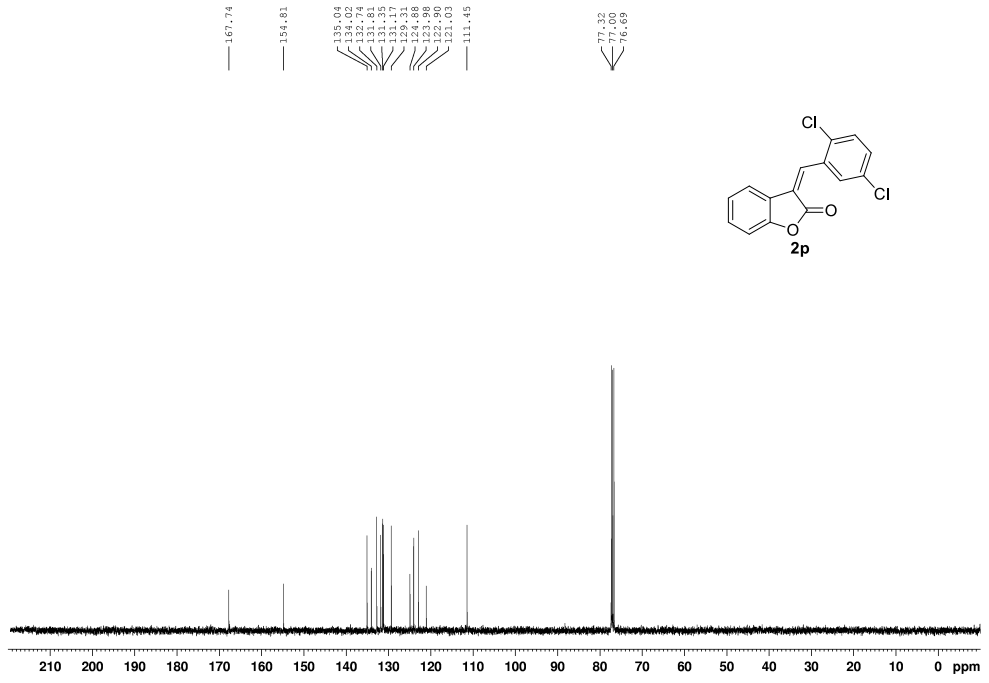

$^{13}$CNMR of **2o** (100M, $CDCl_3$)



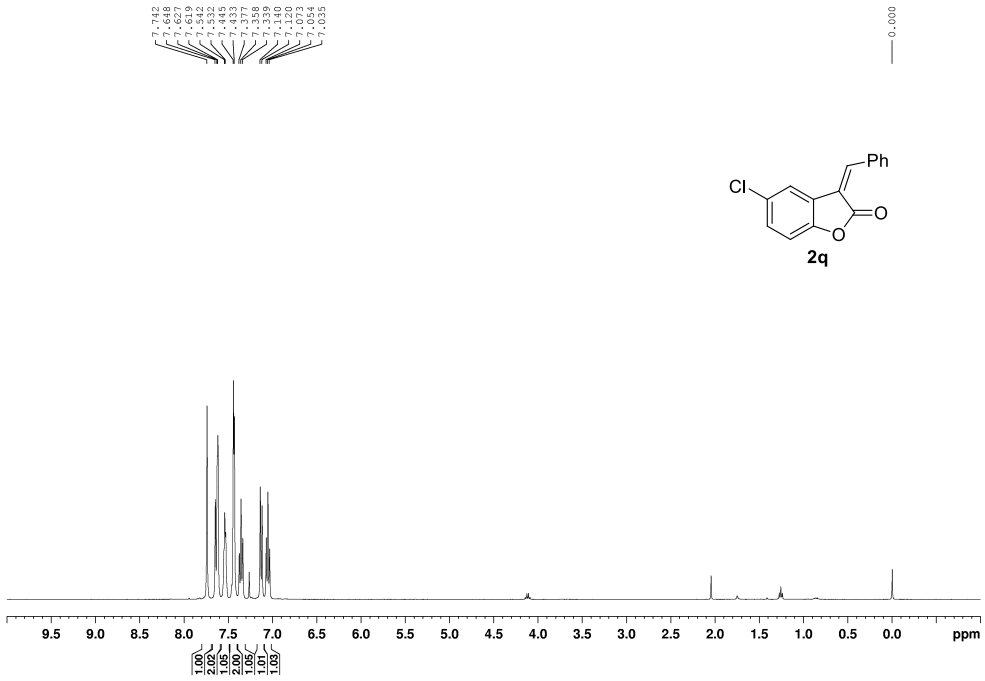

$^{1}$HNMR of **2p** (400M, $CDCl_3$)



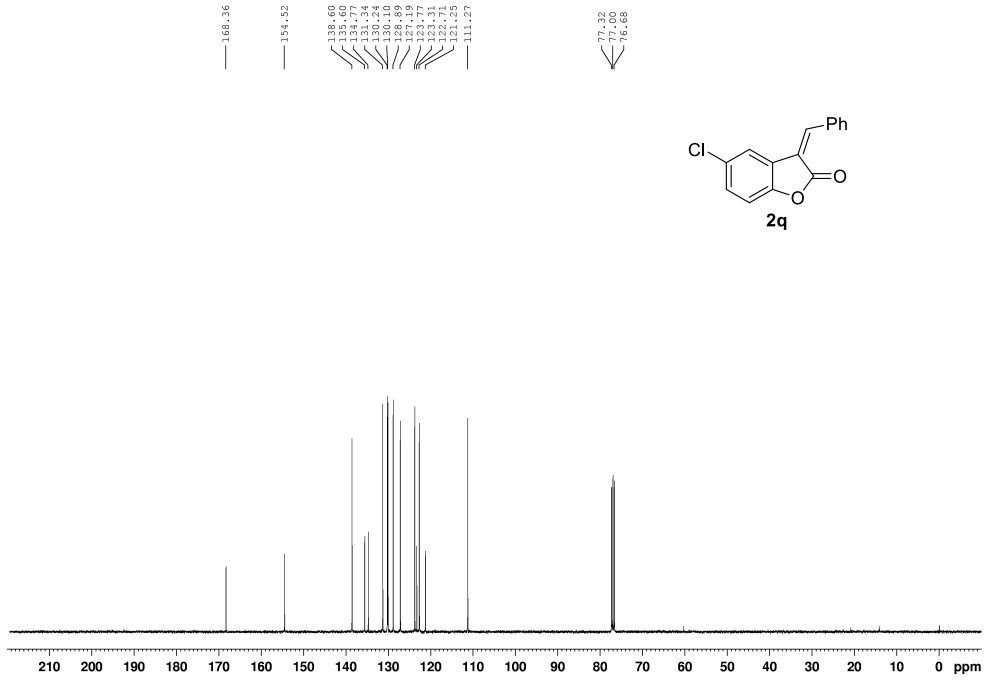

$^{13}$CNMR of **2p** (100M, $CDCl_3$)




$^{1}$HNMR of **2q** (400M, $CDCl_3$)

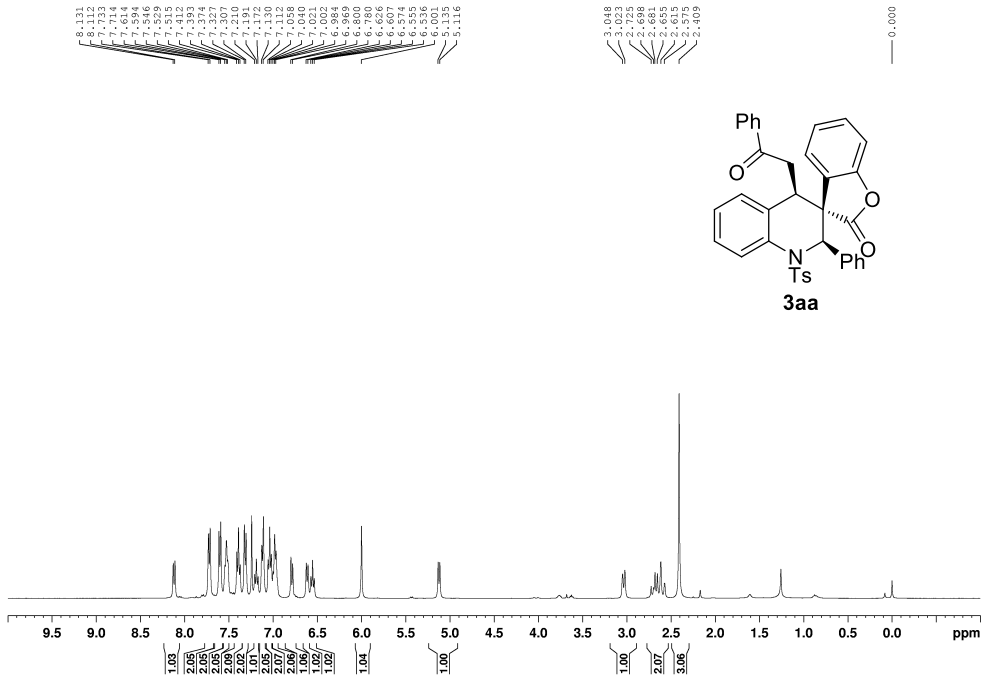



$^{13}$CNMR of **2q** (100M, $CDCl_3$)

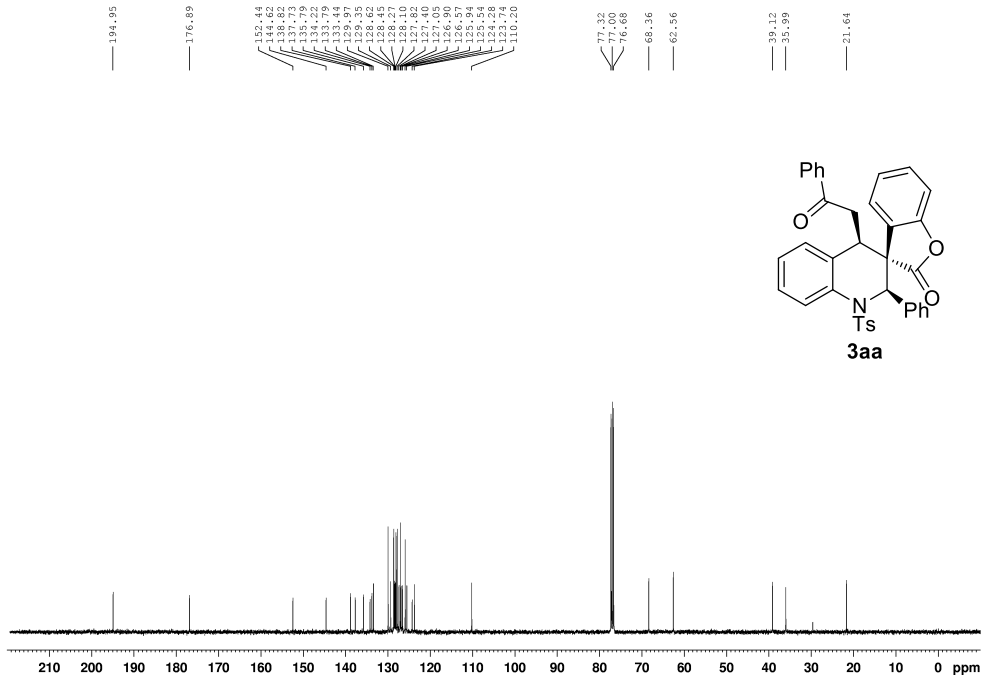



## 4.2Copy of NMR Spectrogram of 3

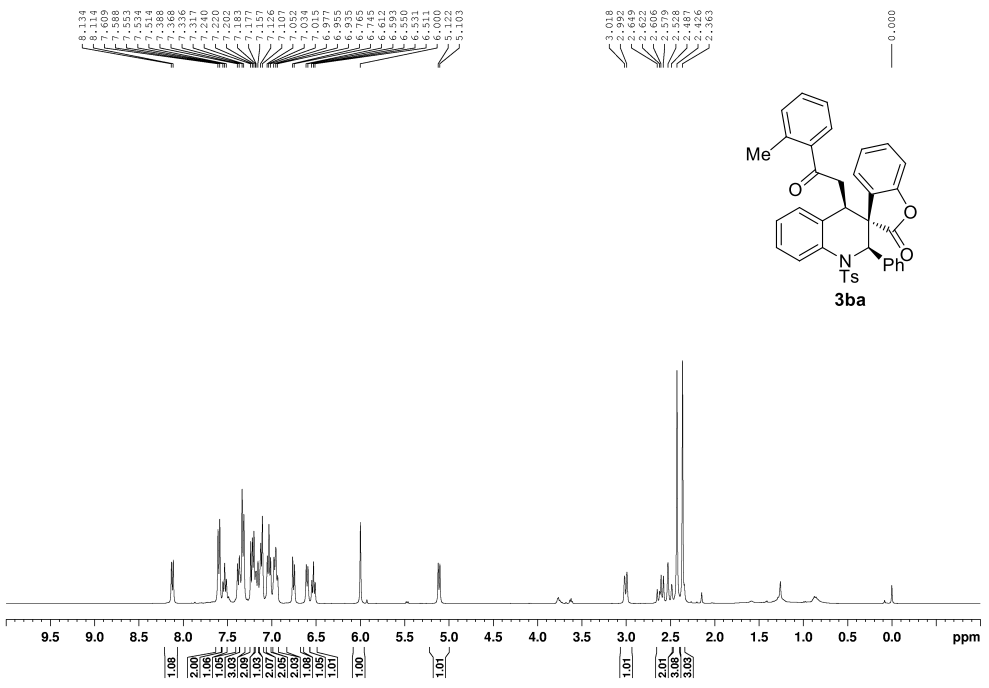
$^{1}$HNMR of **3aa** (400M, $CDCl_3$)



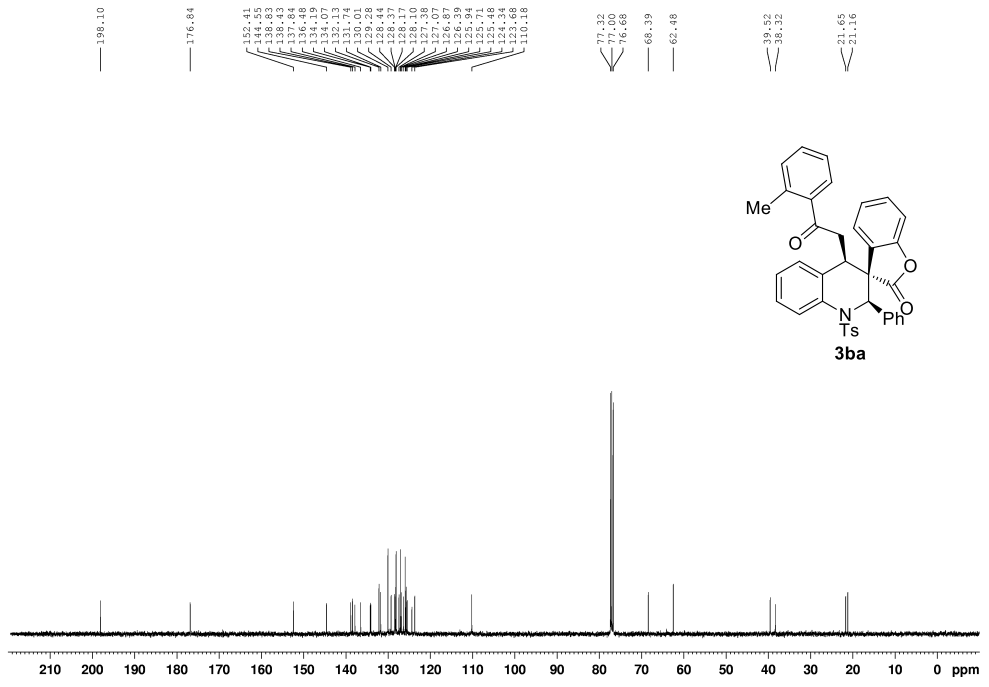

$^{13}$CNMR of **3aa** (100M, $CDCl_3$)



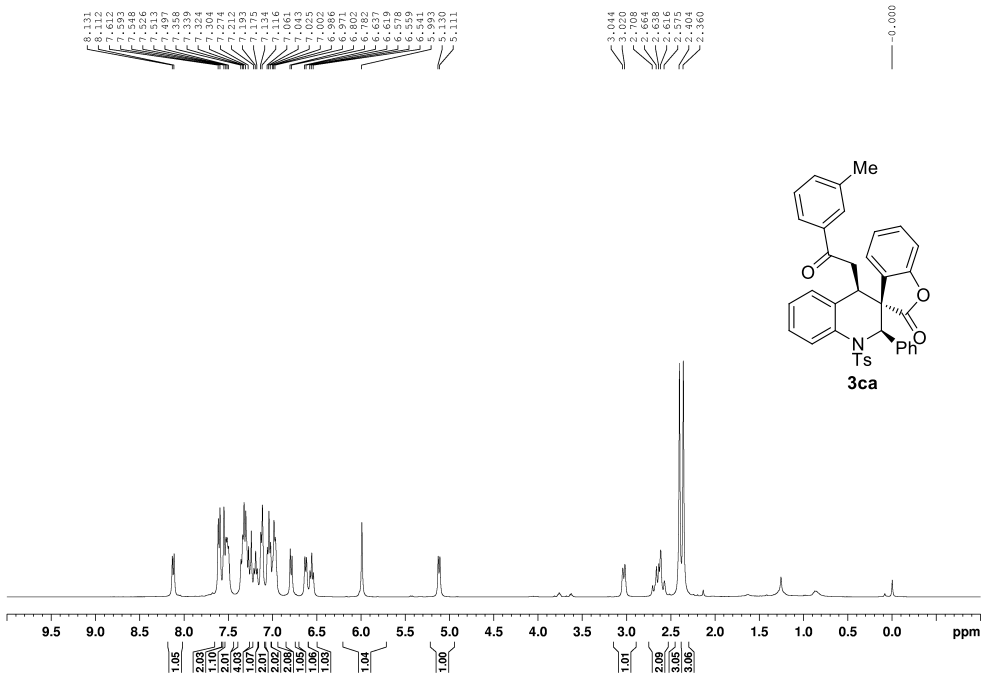

$^{1}$HNMR of **3ba** (400M, $CDCl_3$)



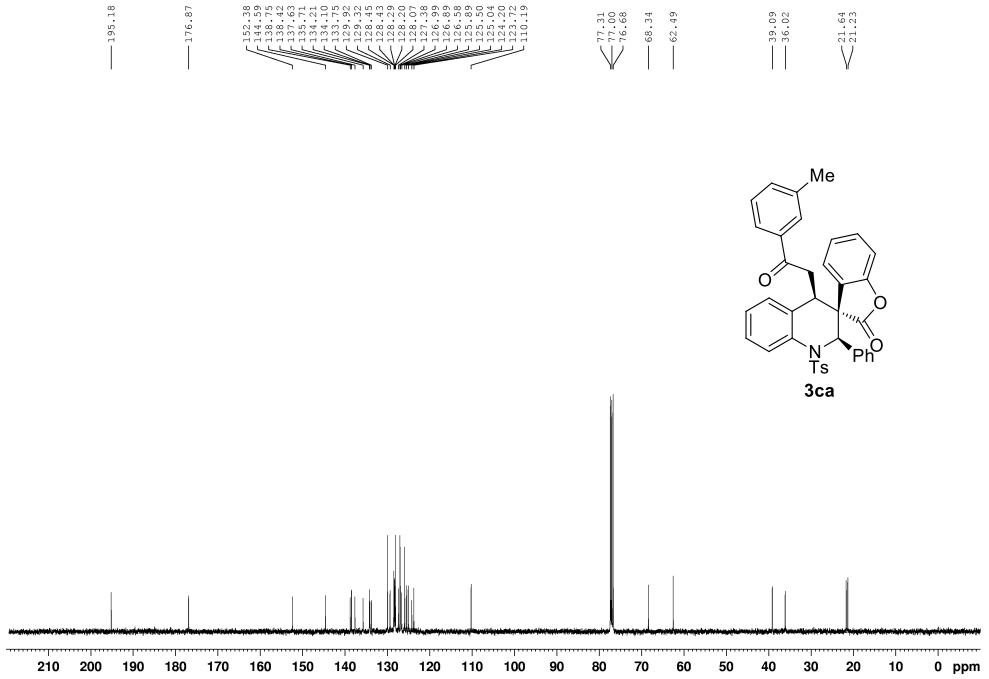

$^{13}$CNMR of **3ba** (100M, $CDCl_3$)



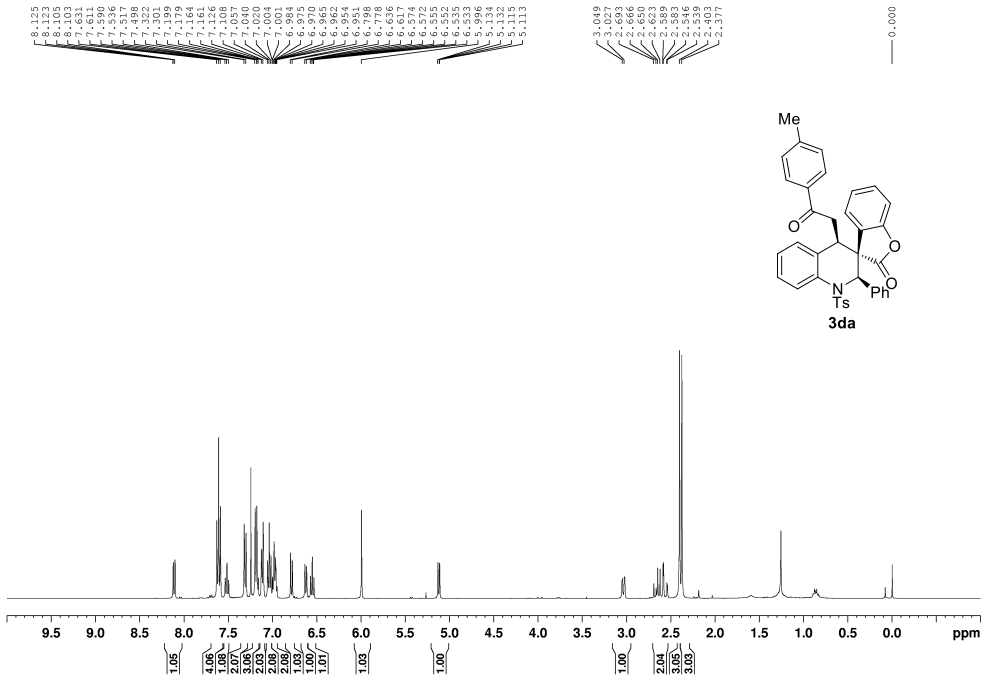

$^{1}$HNMR of **3ca** (400M, $CDCl_3$)



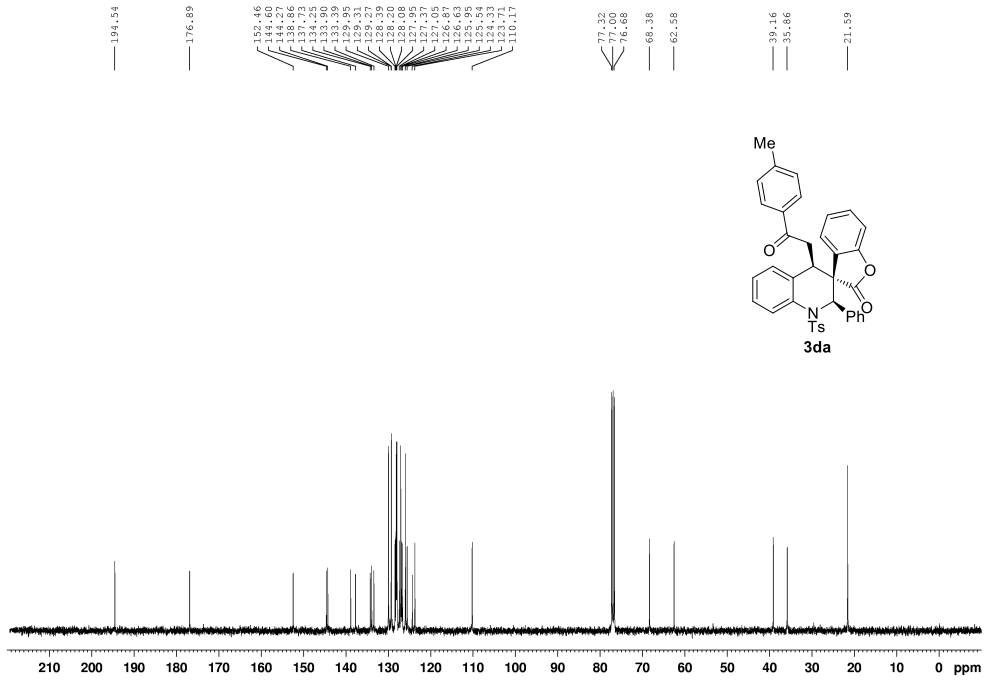

$^{13}$CNMR of **3ca** (100M, $CDCl_3$)



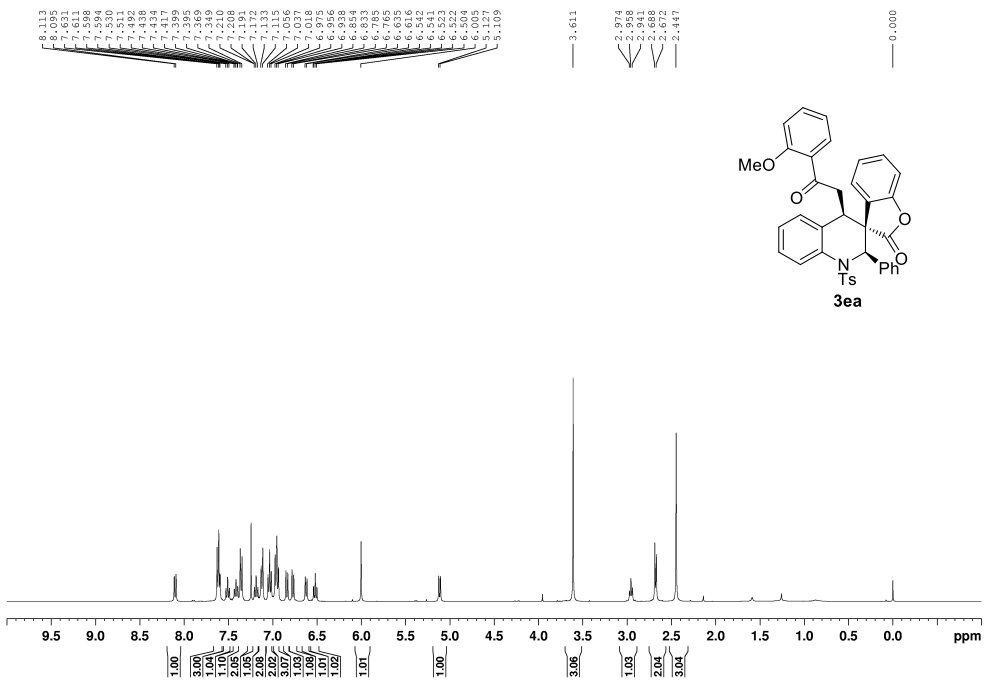

$^{1}$HNMR of **3da** (400M, $CDCl_3$)



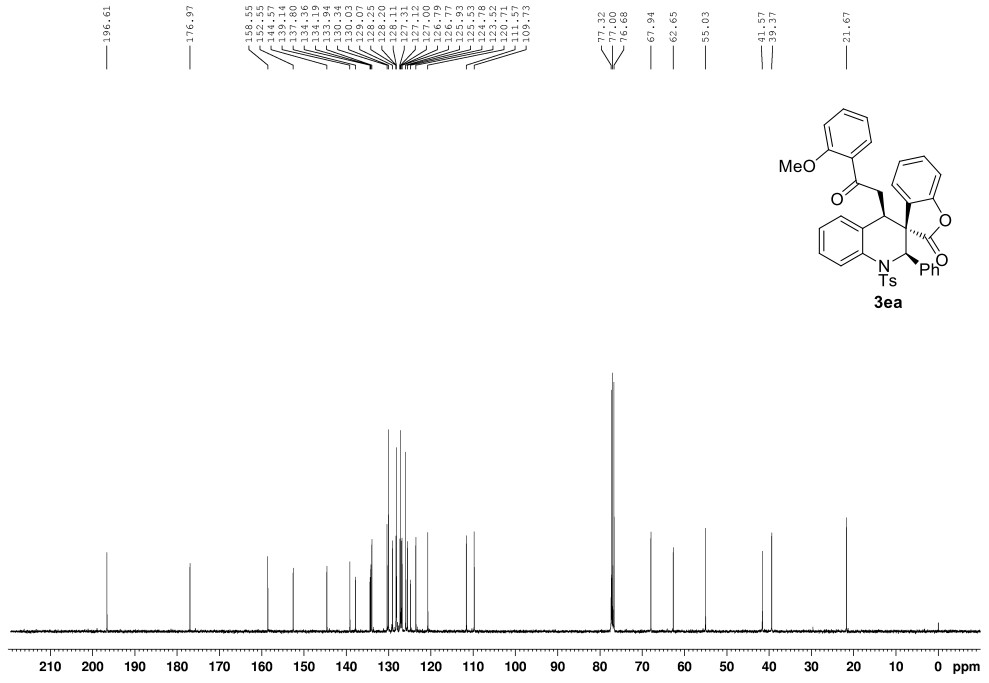

$^{13}$CNMR of **3da** (100M, $CDCl_3$)



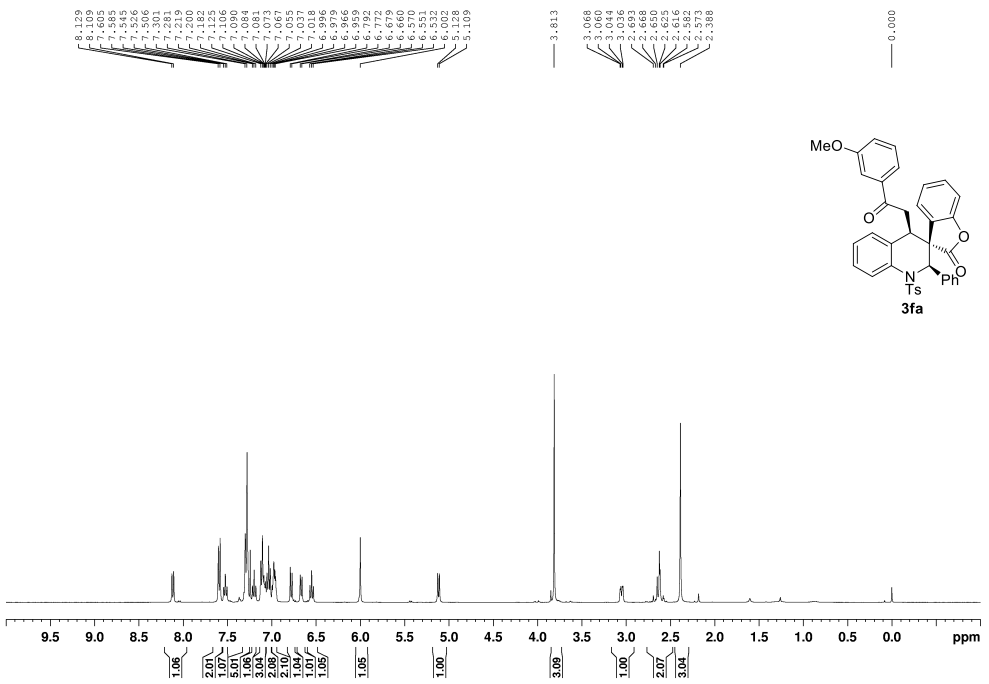

$^{1}$HNMR of **3ea** (400M, $CDCl_3$)



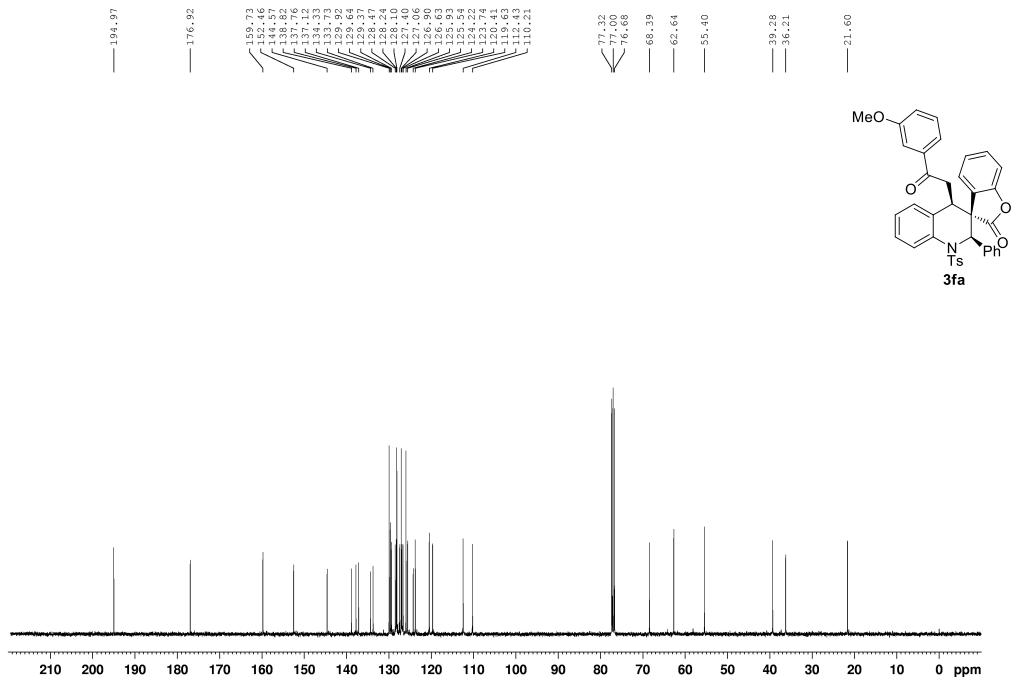

$^{13}$CNMR of **3ea** (100M, $CDCl_3$)



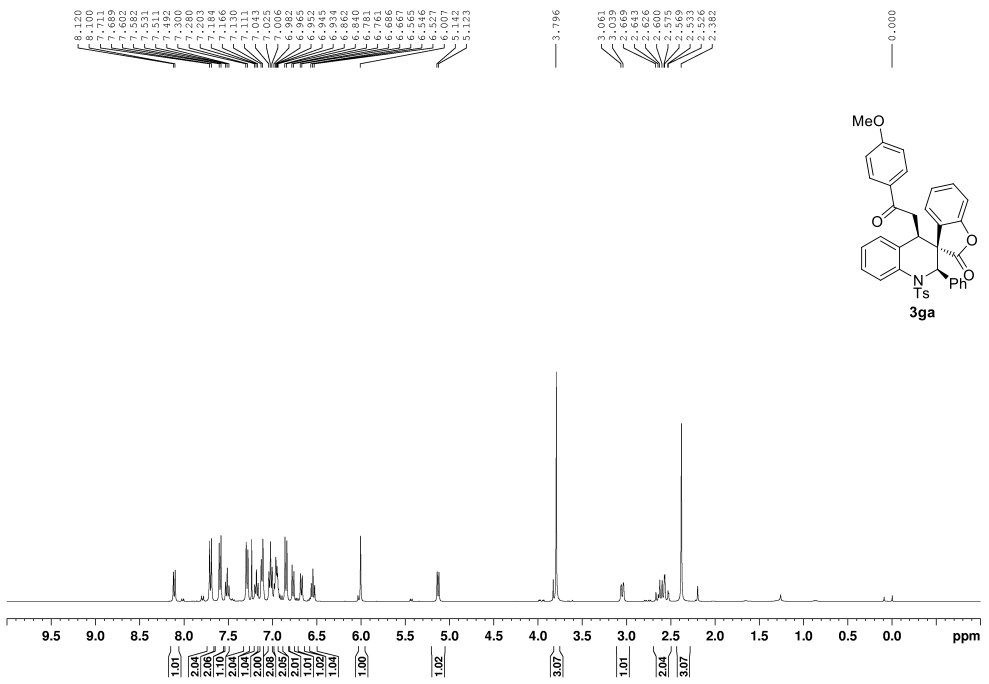

$^{1}$HNMR of **3fa** (400M, $CDCl_3$)



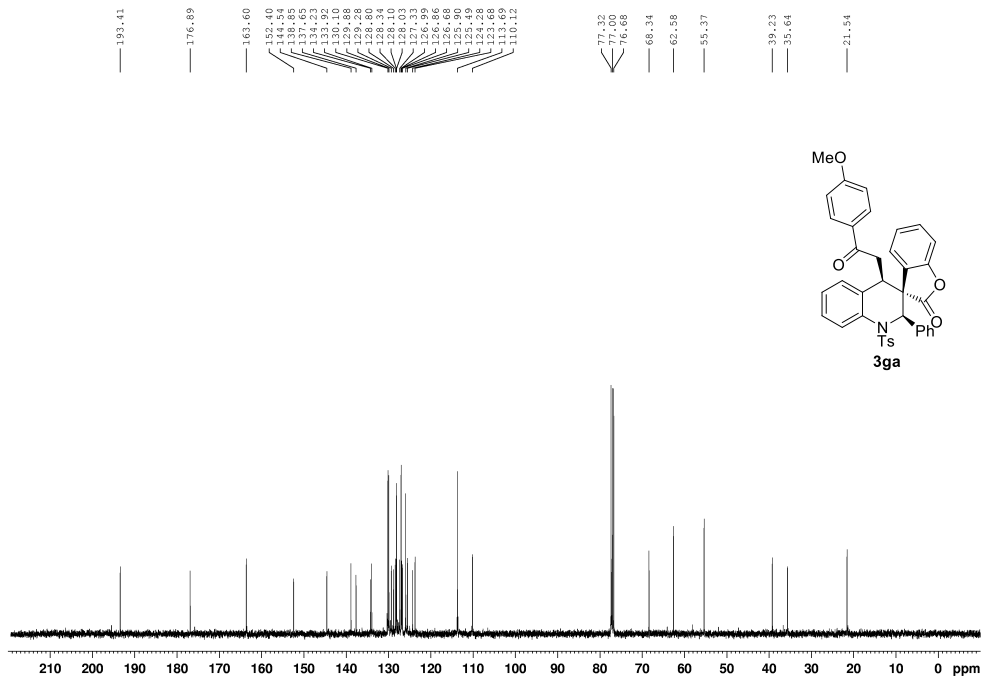

$^{13}$CNMR of **3fa** (100M, $CDCl_3$)



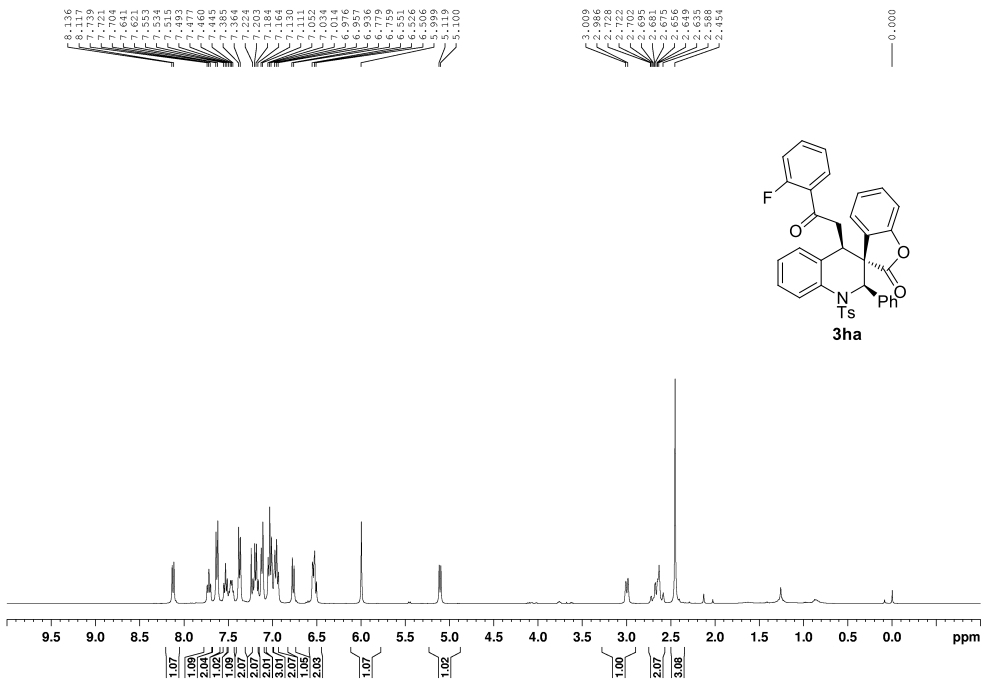

$^{1}$HNMR of **3ga** (400M, $CDCl_3$)



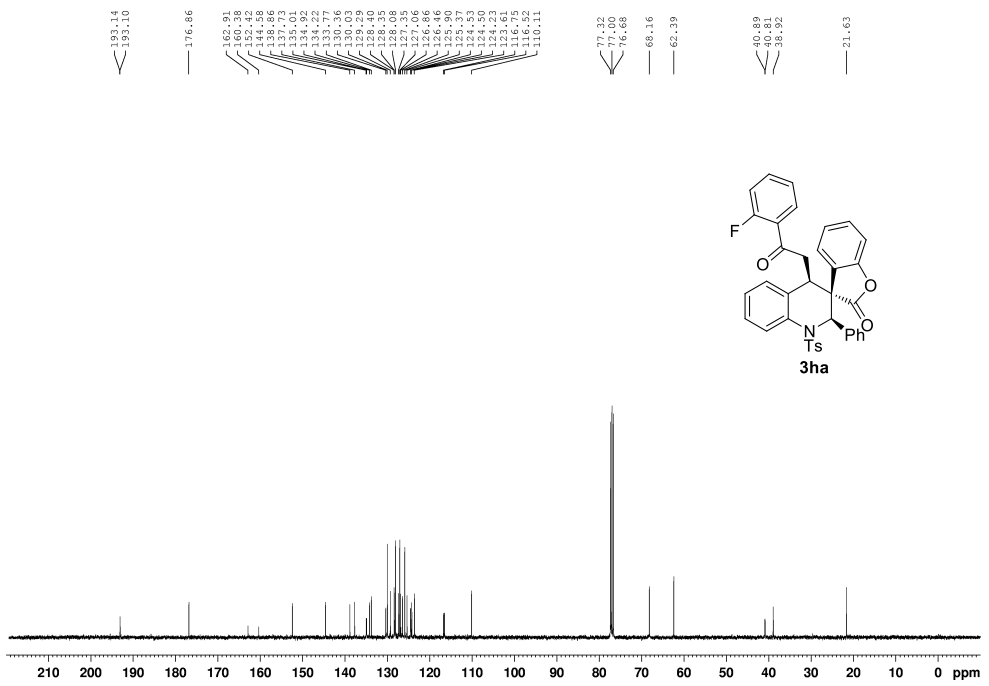

$^{13}$CNMR of **3ga** (100M, $CDCl_3$)



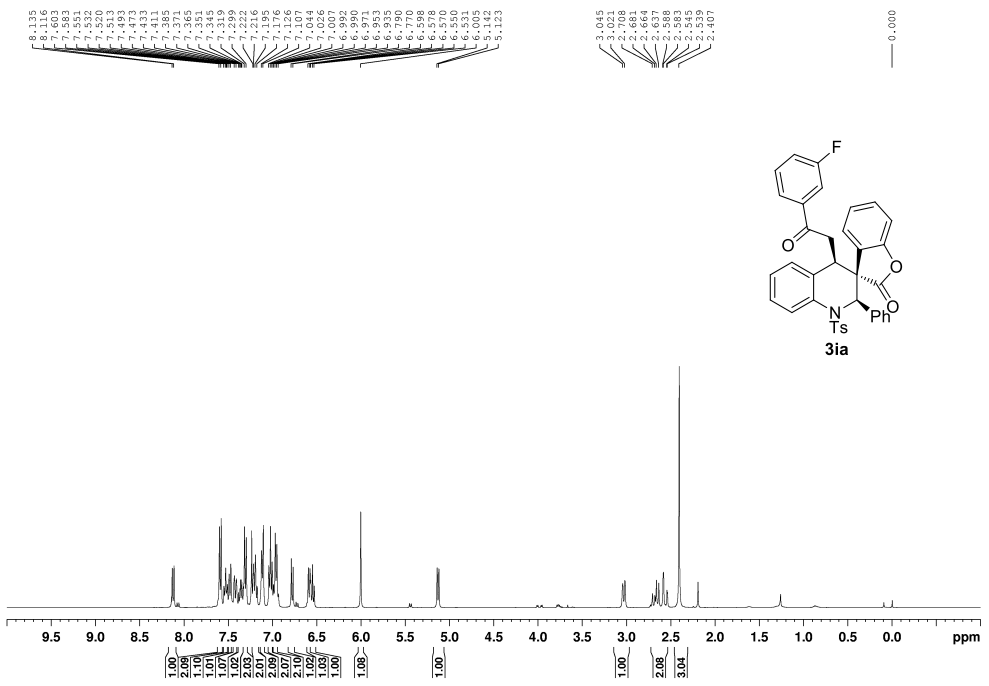

$^{1}$HNMR of **3ha** (400M, $CDCl_3$)



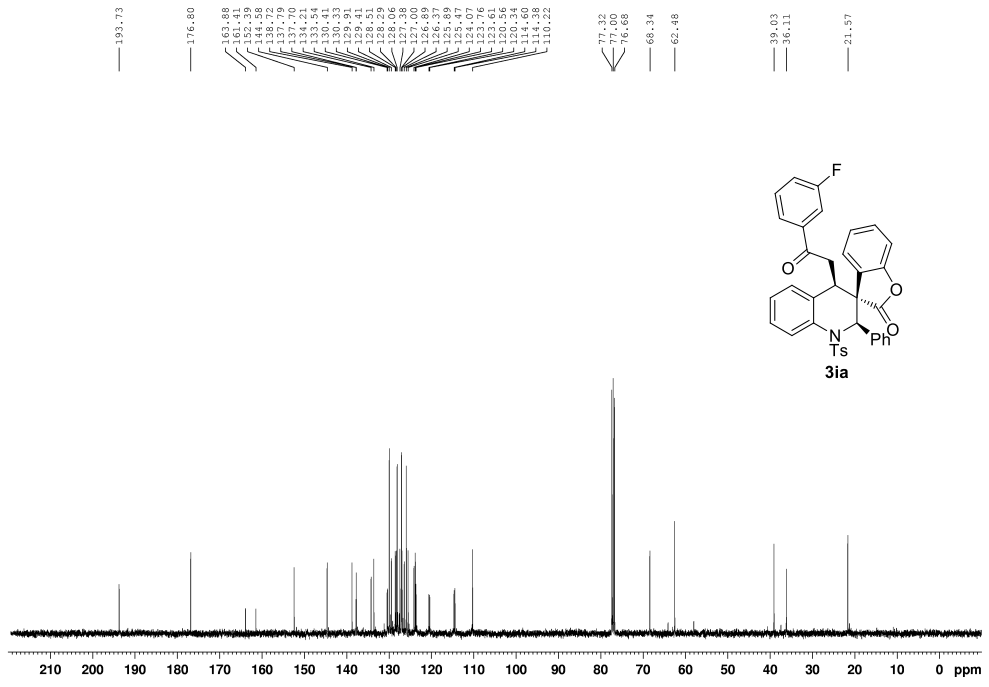

$^{13}$CNMR of **3ha** (100M, $CDCl_3$)



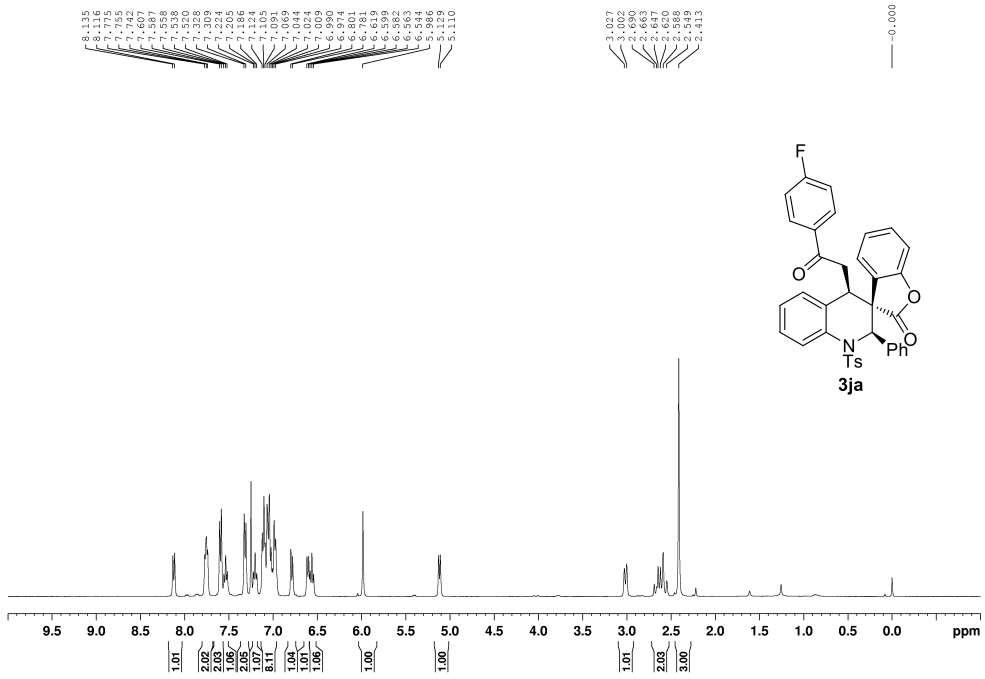

$^{1}$HNMR of **3ia** (400M, $CDCl_3$)



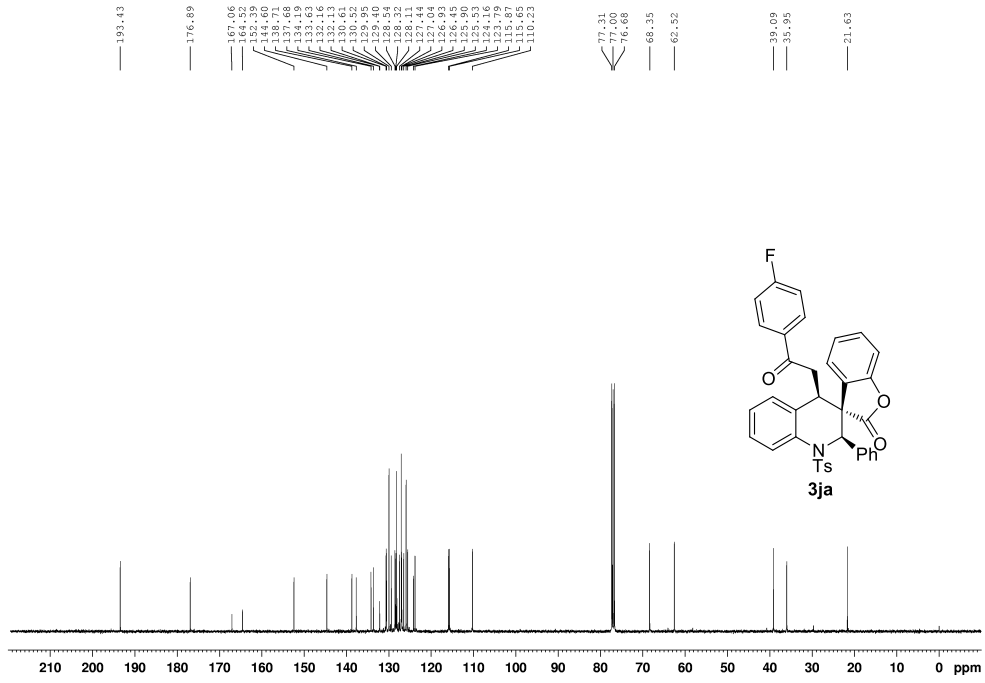

$^{13}$CNMR of **3ia** (100M, $CDCl_3$)



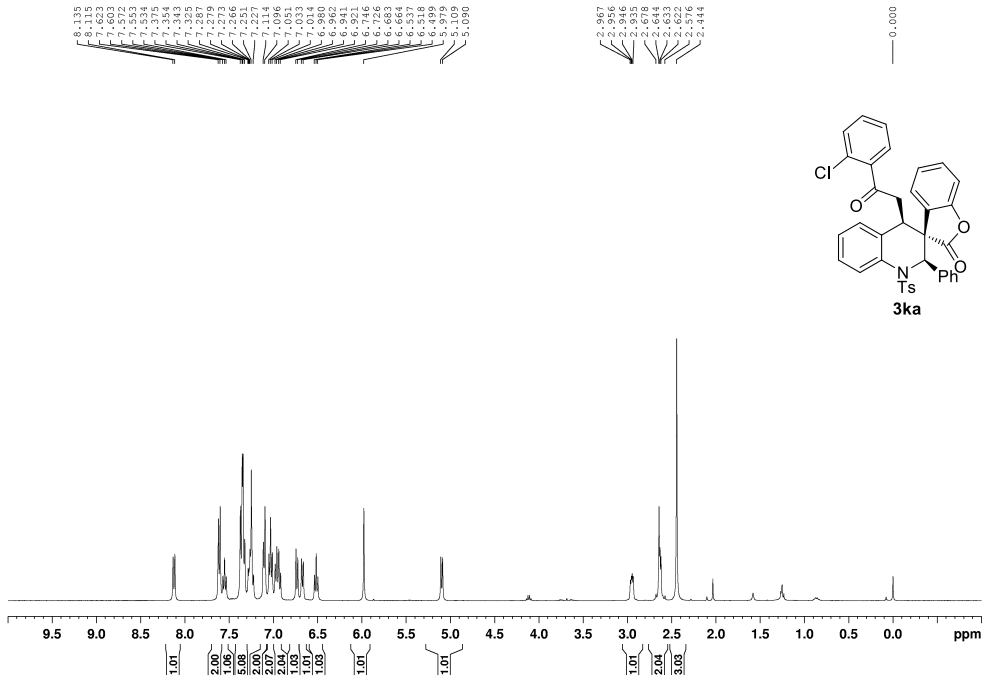

$^{1}$HNMR of **3ja** (400M, $CDCl_3$)



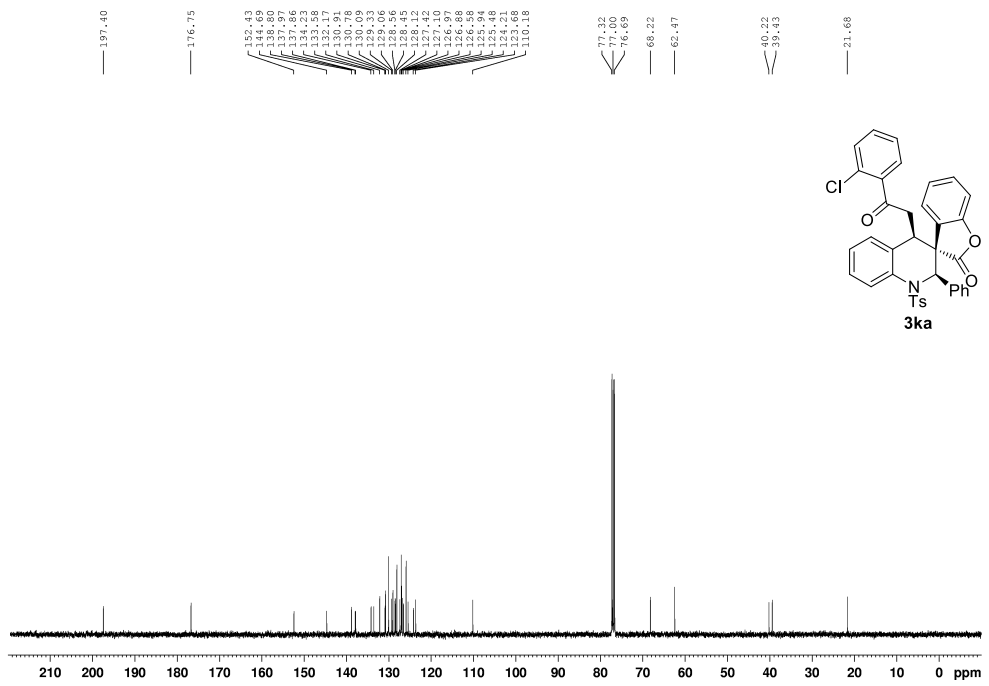

$^{13}$CNMR of **3ja** (400M, $CDCl_3$)



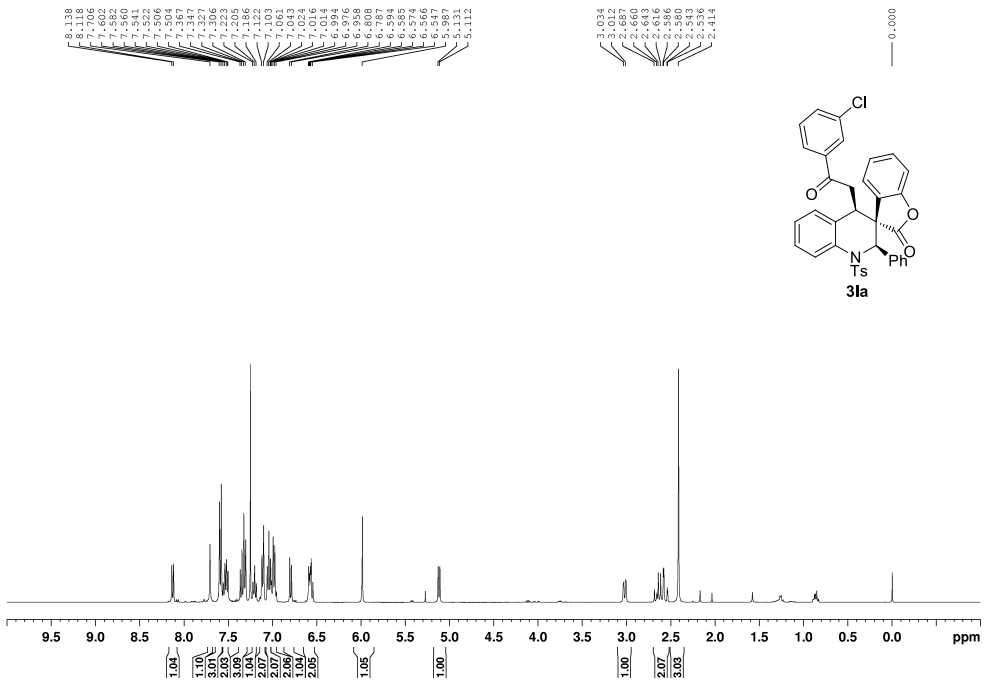

$^{1}$HNMR of **3ka** (400M, $CDCl_3$)



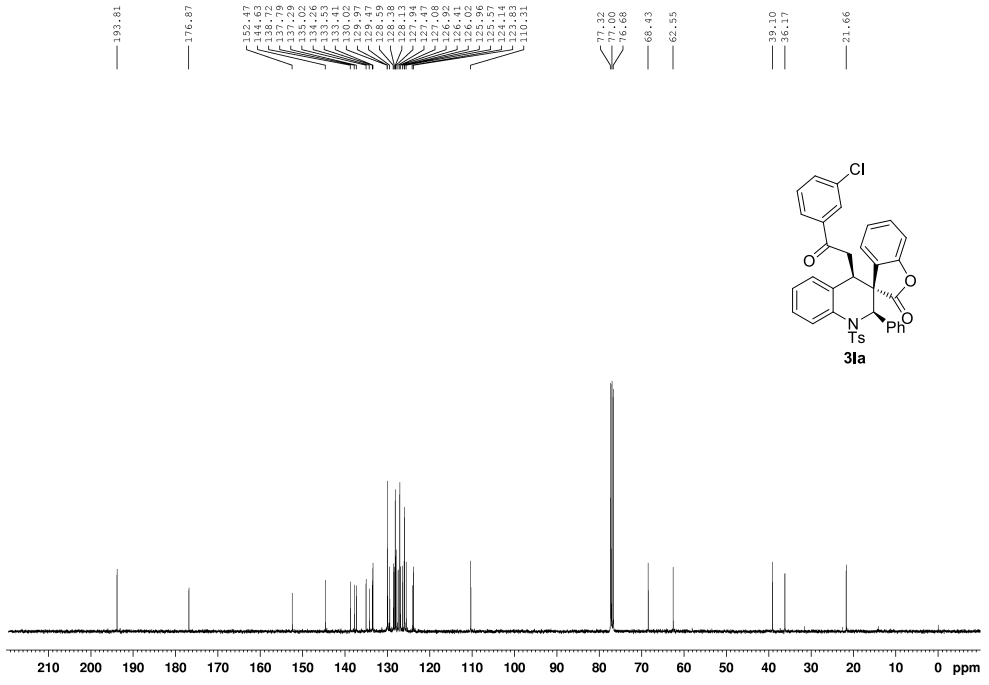

$^{13}$CNMR of **3ka** (100M, $CDCl_3$)



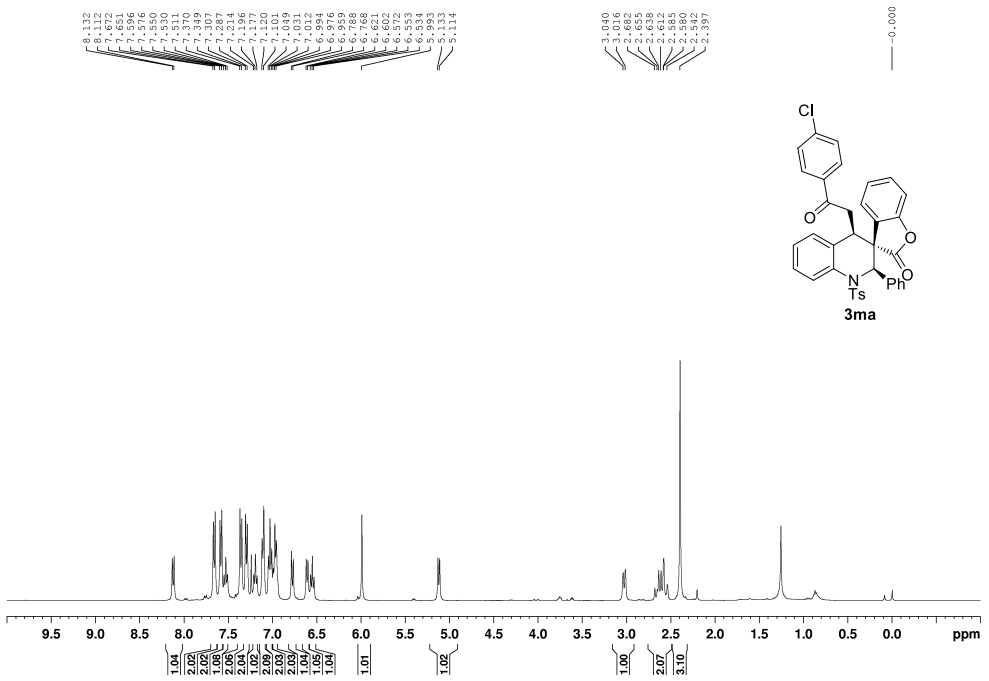

$^{1}$HNMR of **3la** (400M, $CDCl_3$)



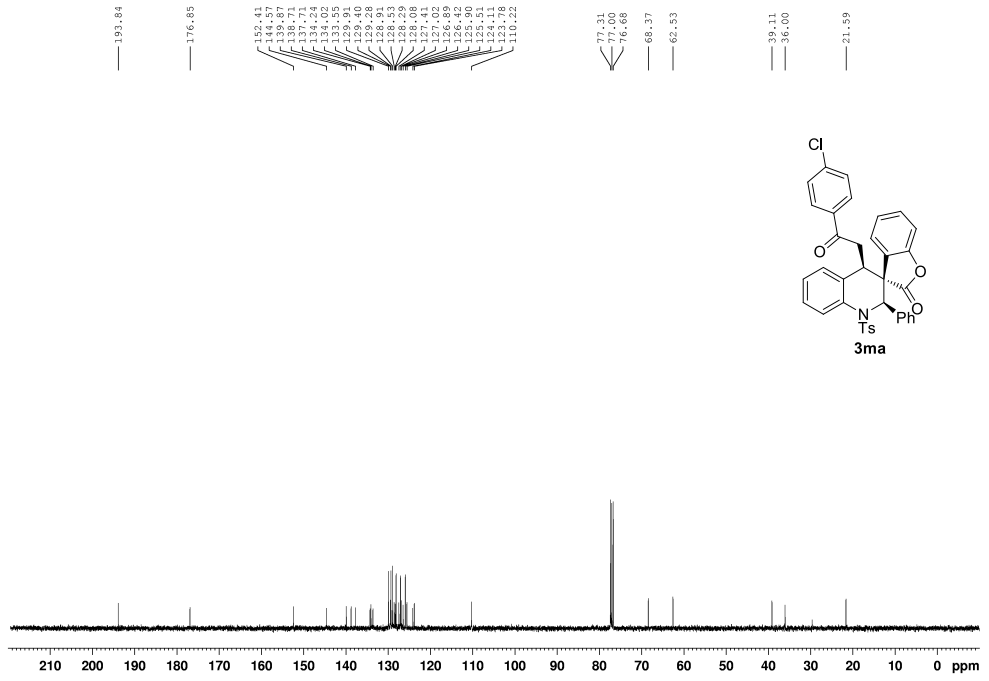

$^{13}$CNMR of **3la** (100M, $CDCl_3$)



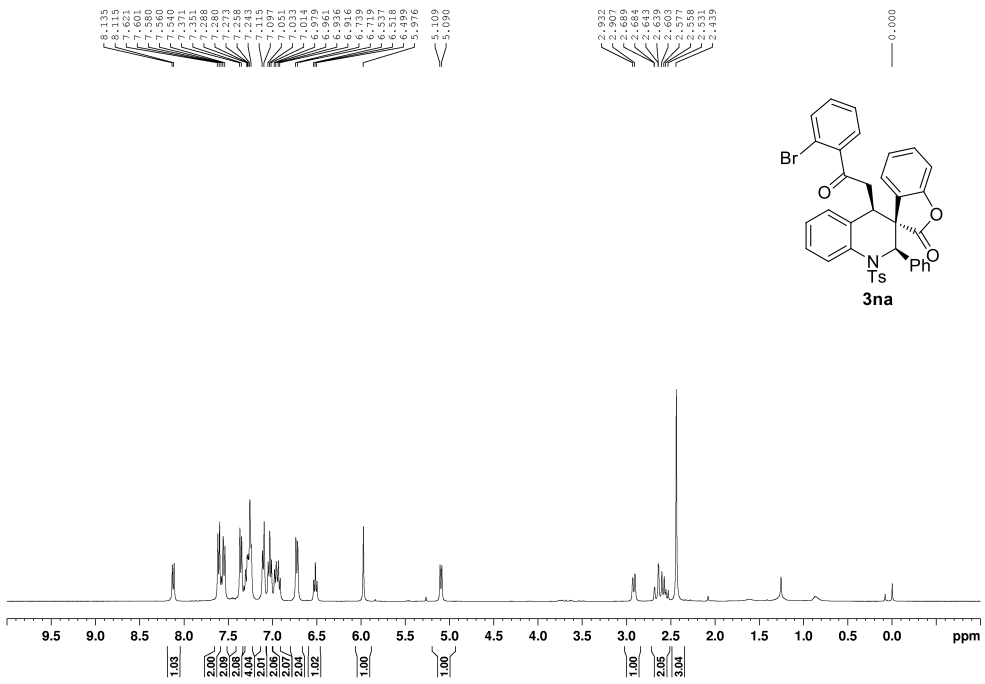

$^{1}$HNMR of **3ma** (400M, $CDCl_3$)



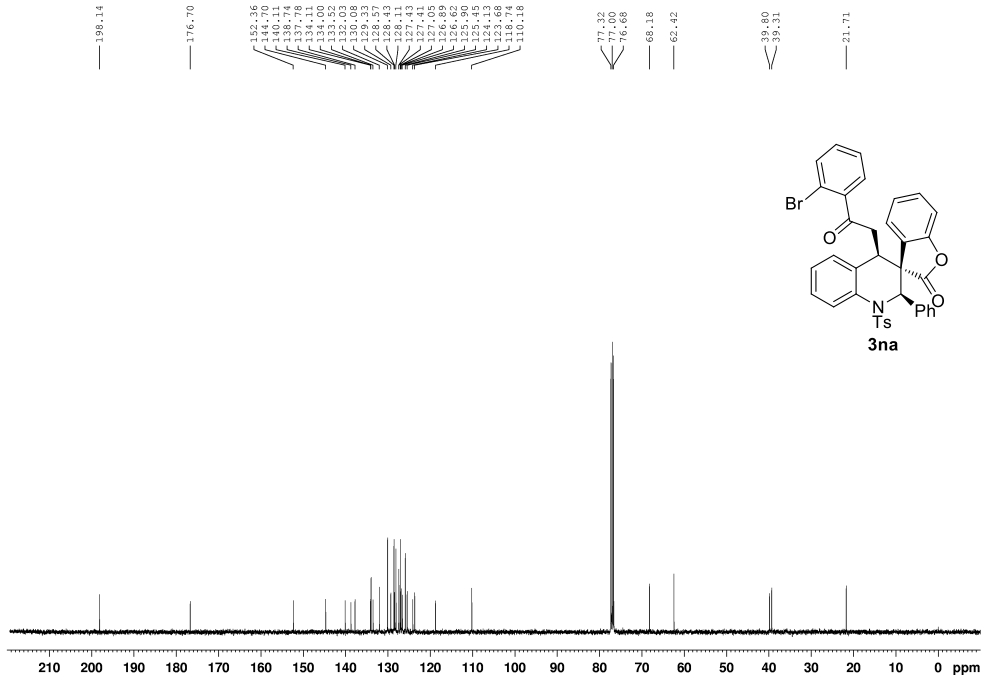

$^{13}$CNMR of **3ma** (100M, $CDCl_3$)



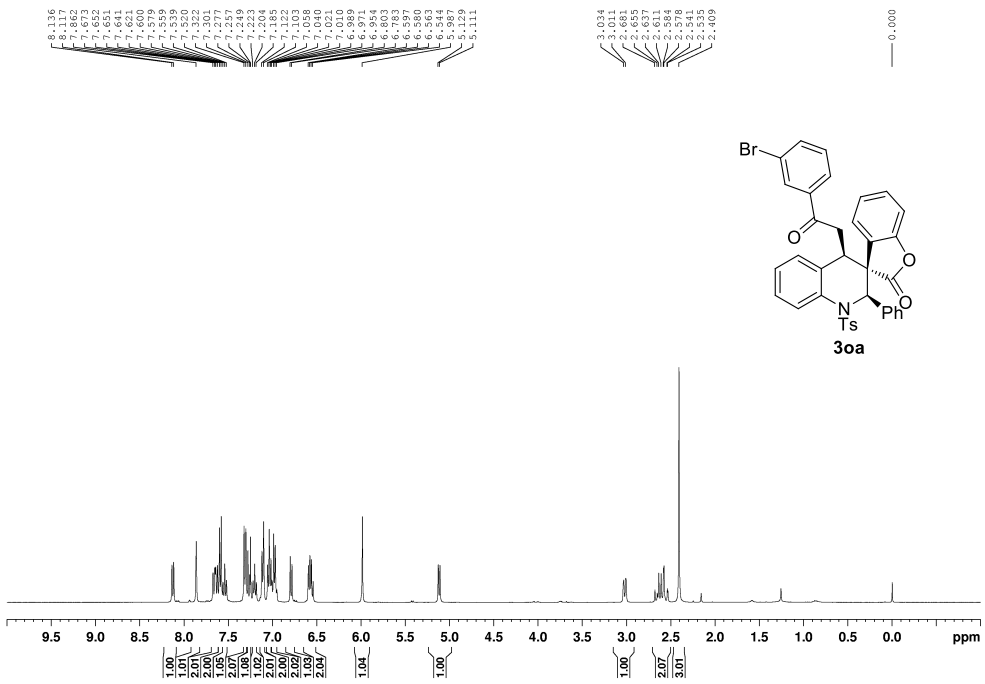

$^{1}$HNMR of **3na** (400M, $CDCl_3$)



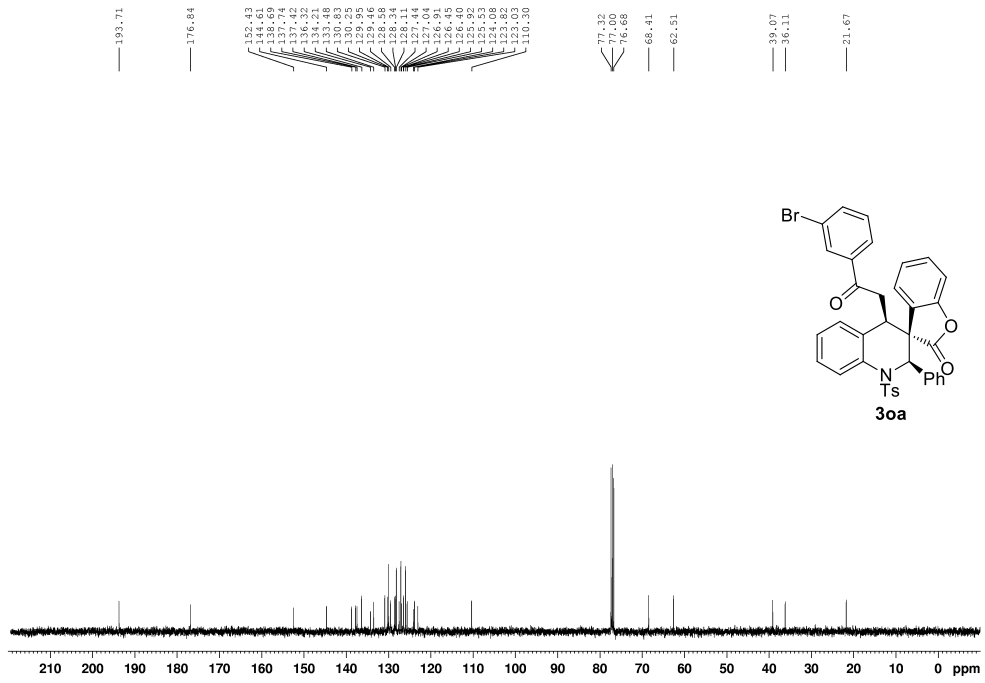

$^{13}$CNMR of **3na** (100M, $CDCl_3$)



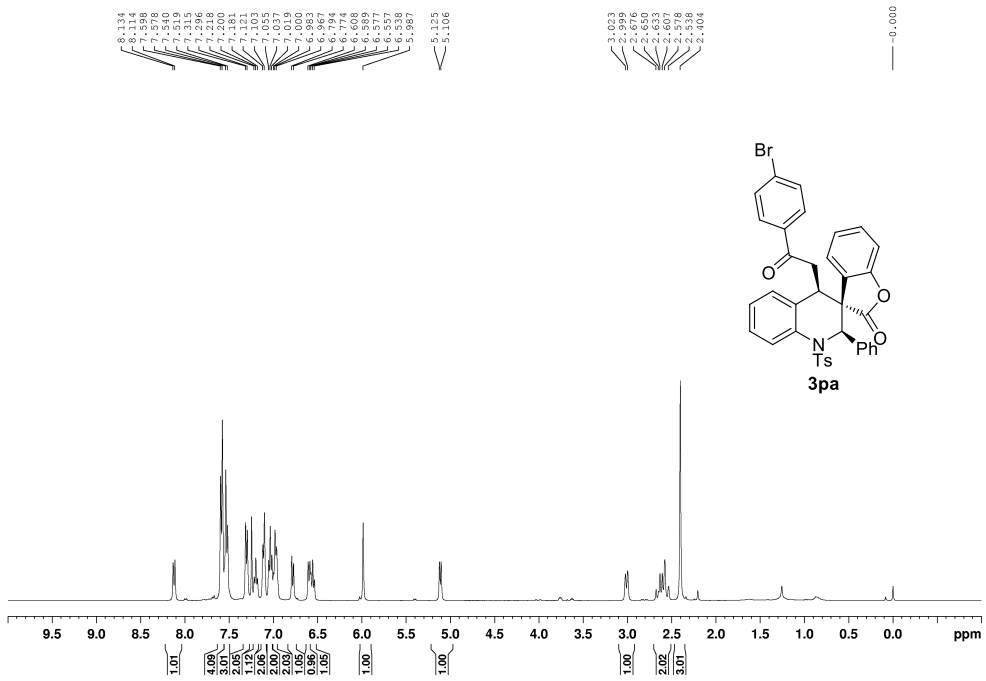

$^{1}$HNMR of **3oa** (400M, $CDCl_3$)



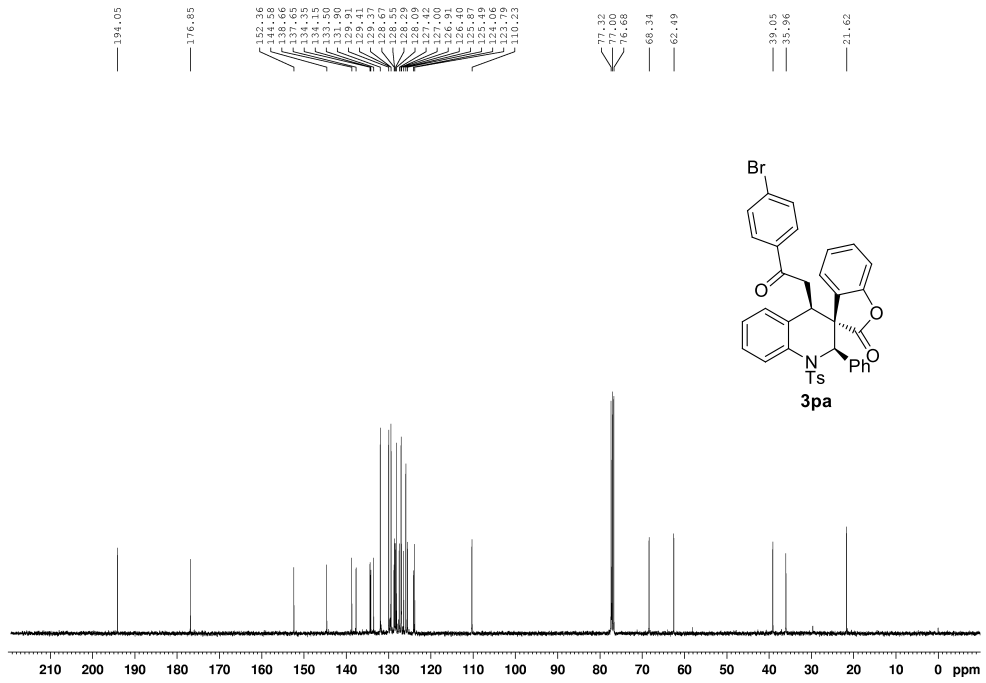

$^{13}$CNMR of **3oa** (100M, $CDCl_3$)



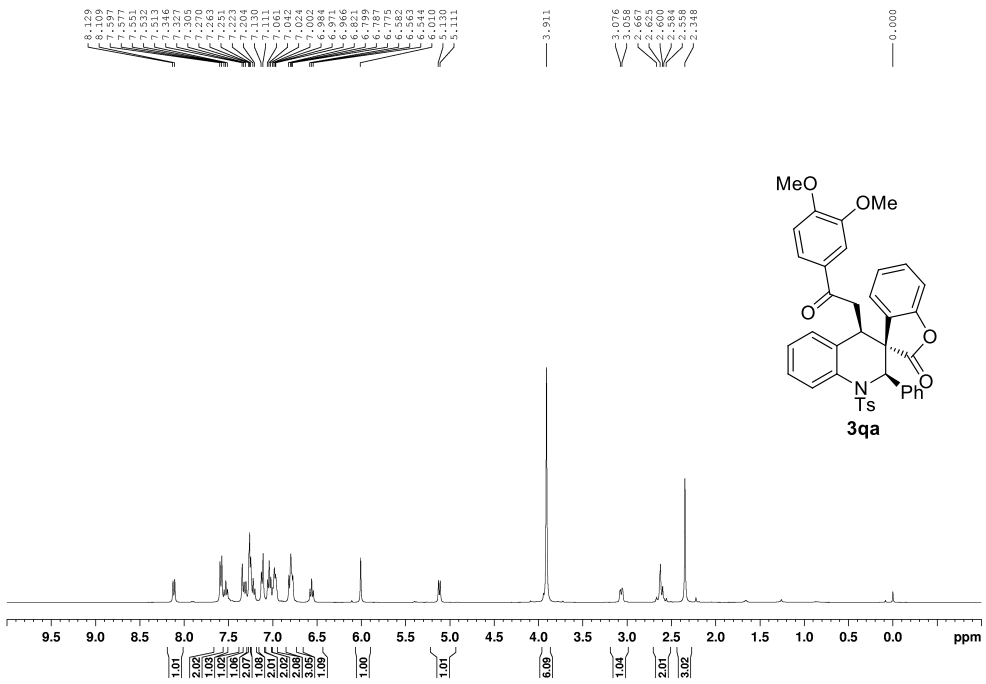

$^{1}$HNMR of **3pa** (400M, $CDCl_3$)



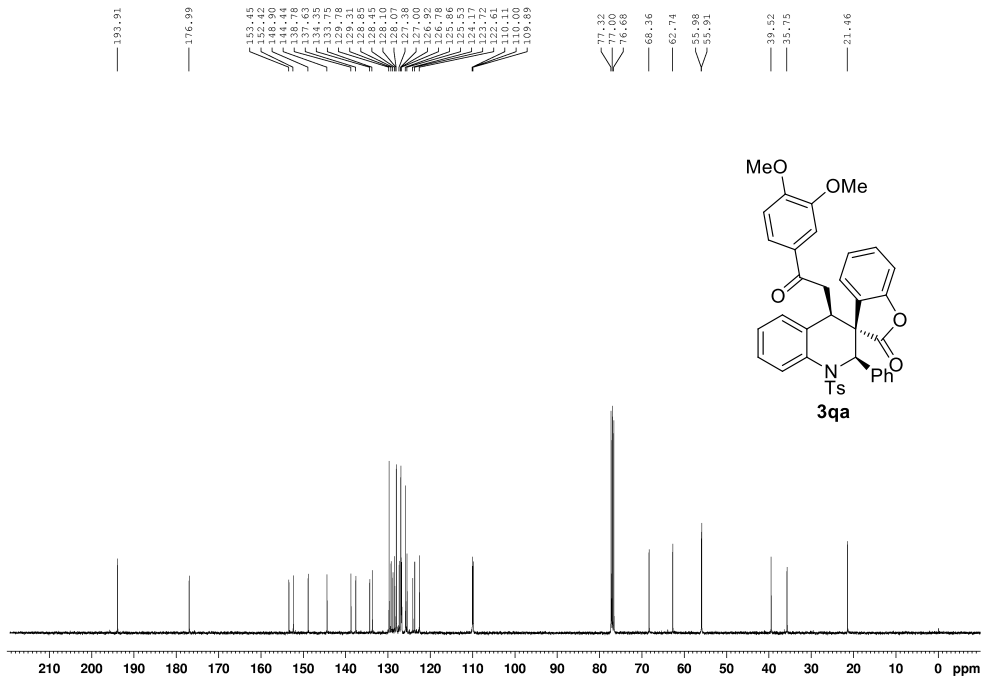

$^{13}$CNMR of **3pa** (100M, $CDCl_3$)



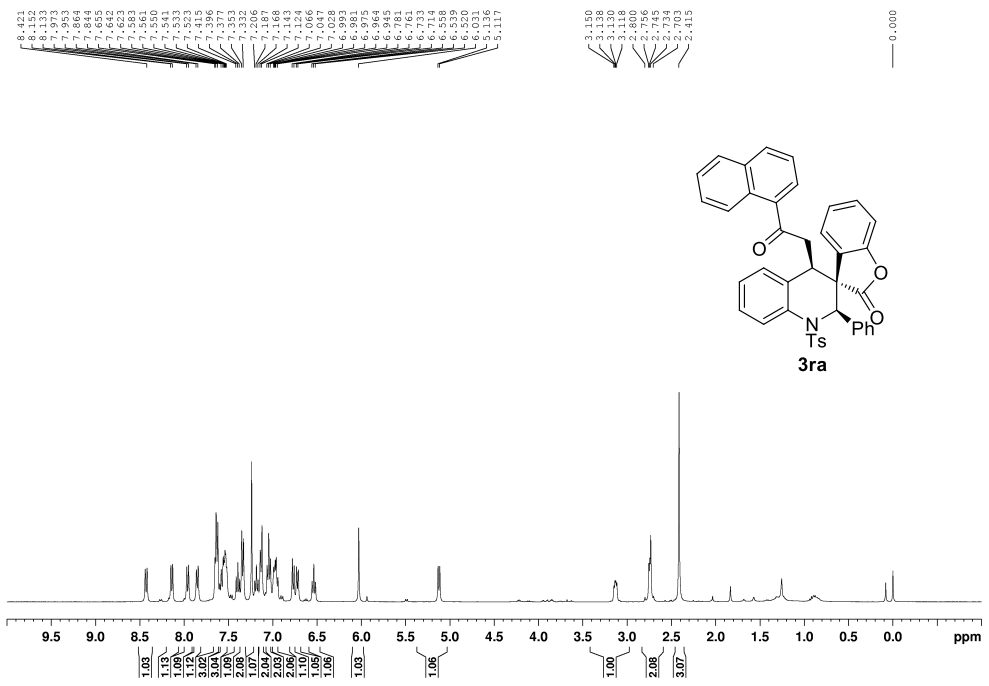

$^{1}$HNMR of **3qa** (400M, $CDCl_3$)



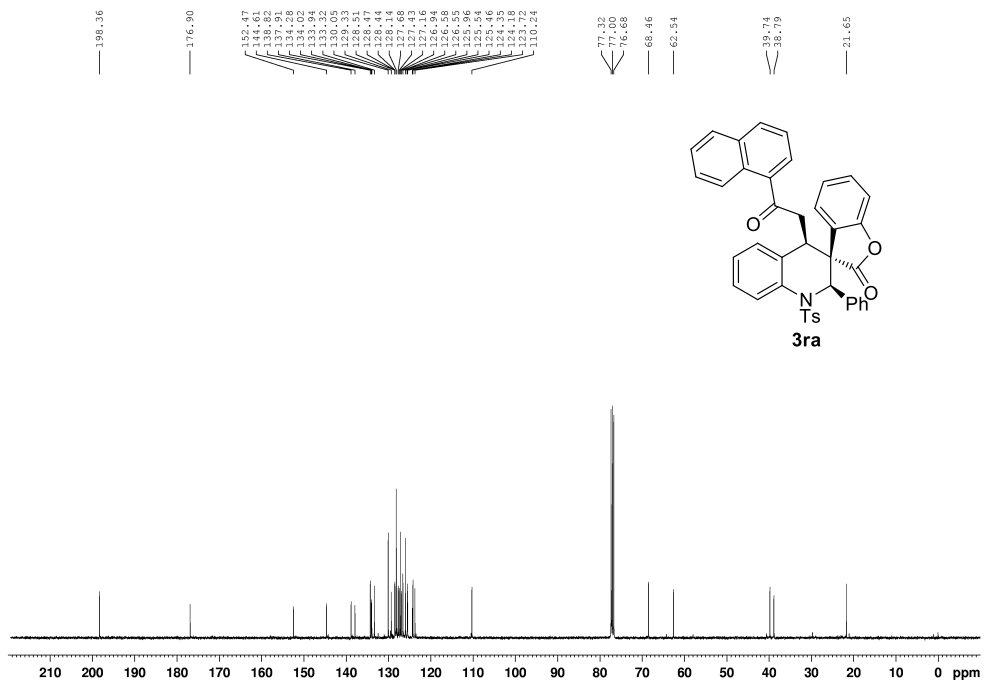

$^{13}$CNMR of **3qa** (400M, $CDCl_3$)



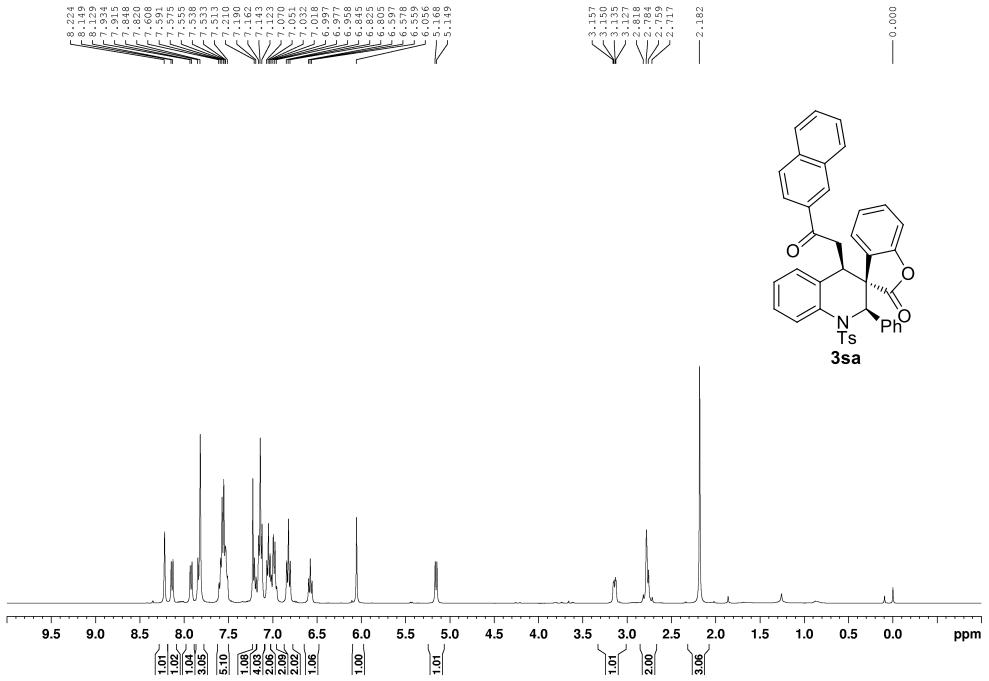

$^{1}$HNMR of **3ra** (400M, $CDCl_3$)



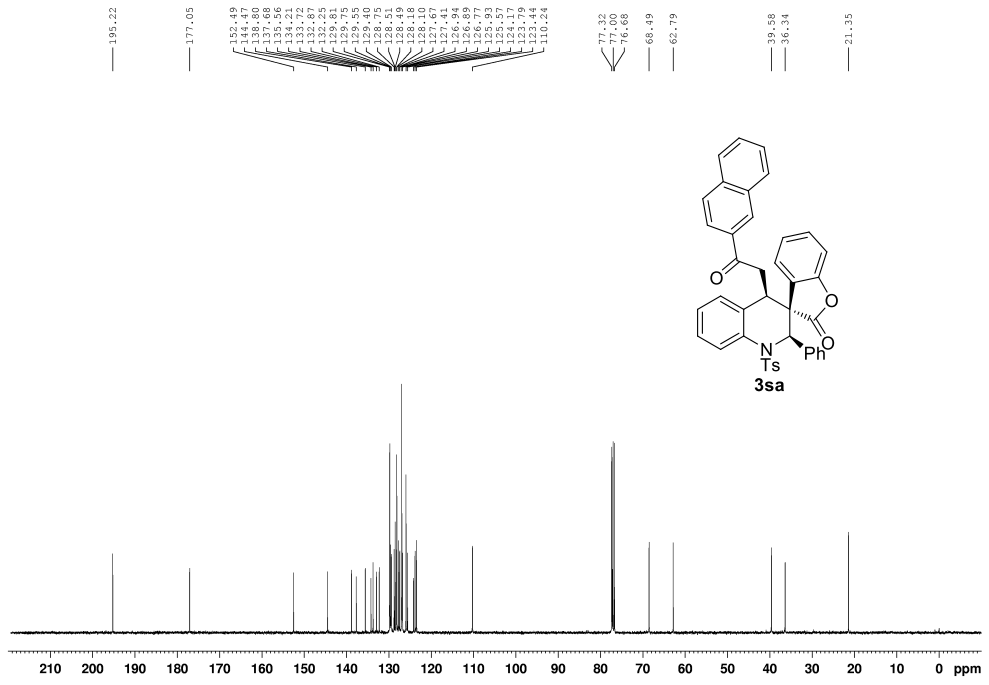

$^{13}$CNMR of **3ra** (400M, $CDCl_3$)



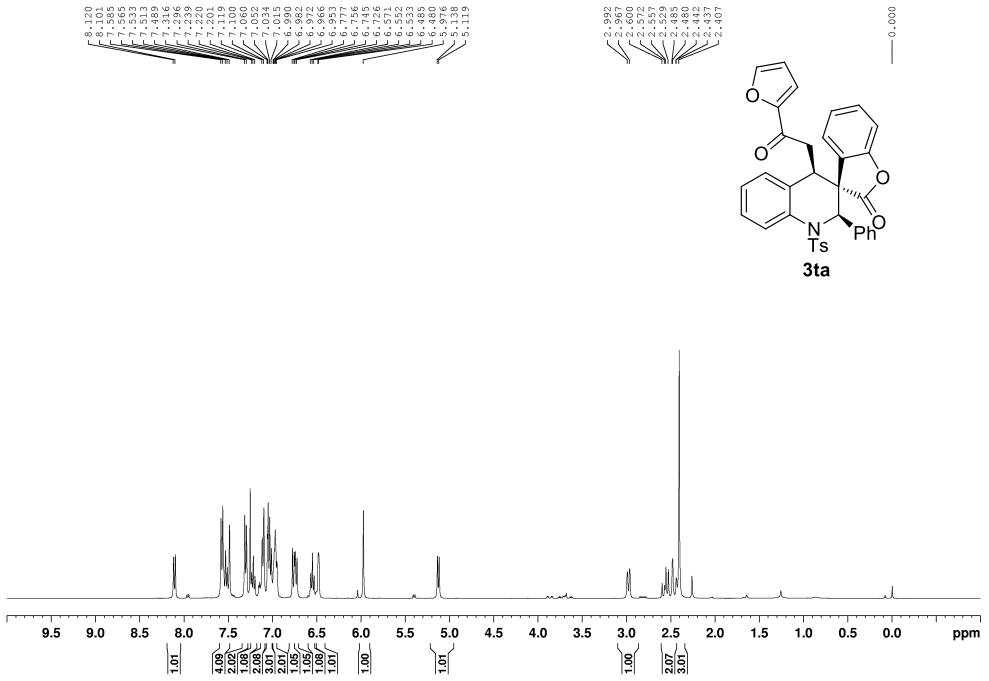

$^{1}$HNMR of **3sa** (400M, $CDCl_3$)



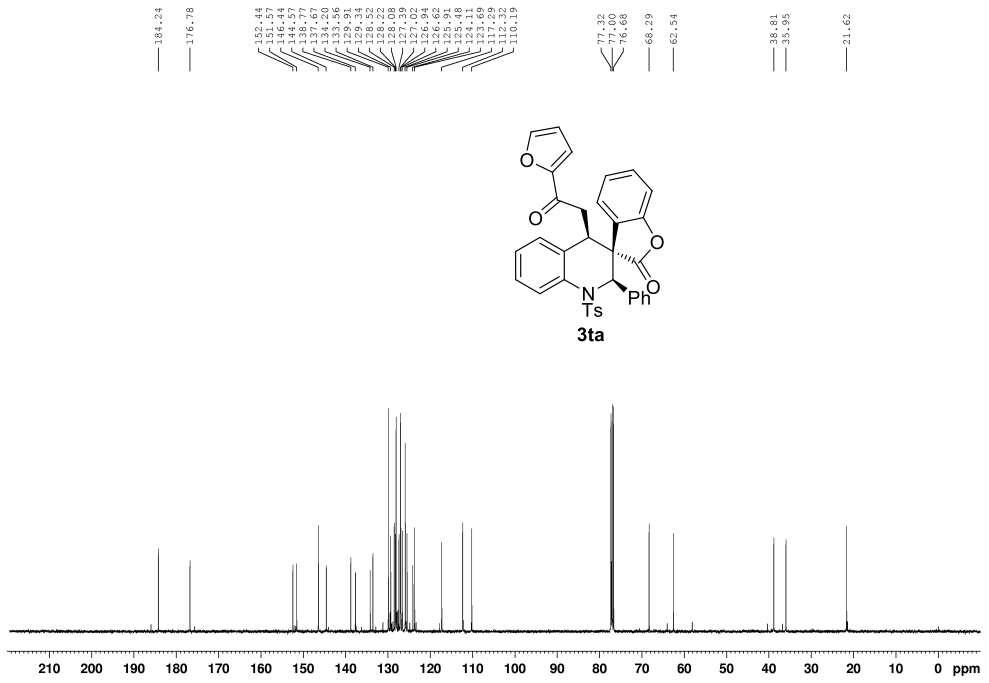

$^{13}$CNMR of **3sa** (400M, $CDCl_3$)



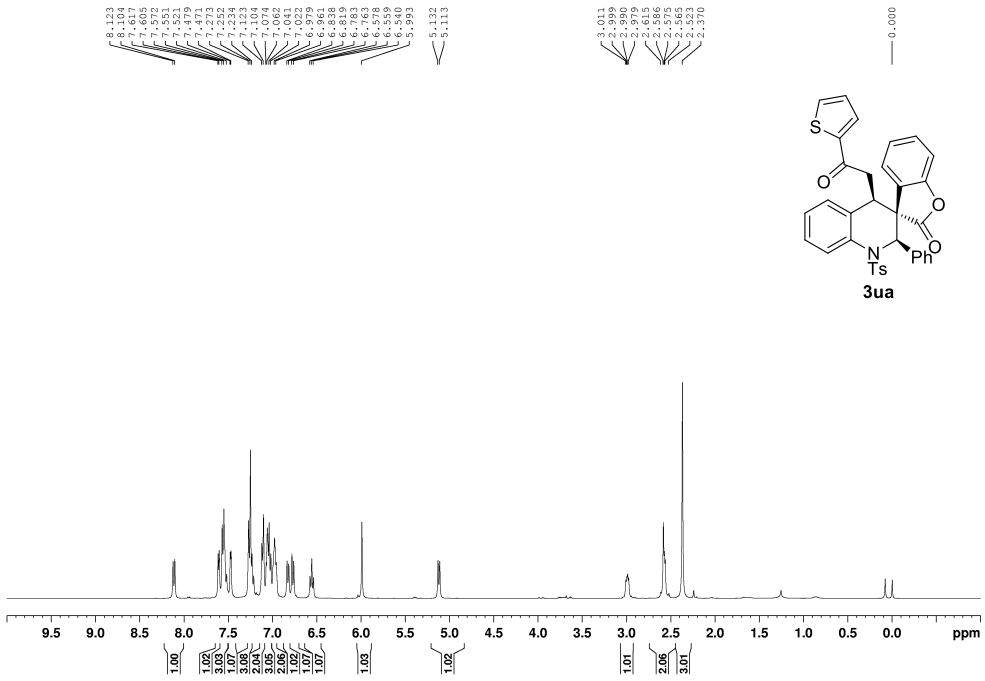

$^{1}$HNMR of **3ta** (400M, $CDCl_3$)



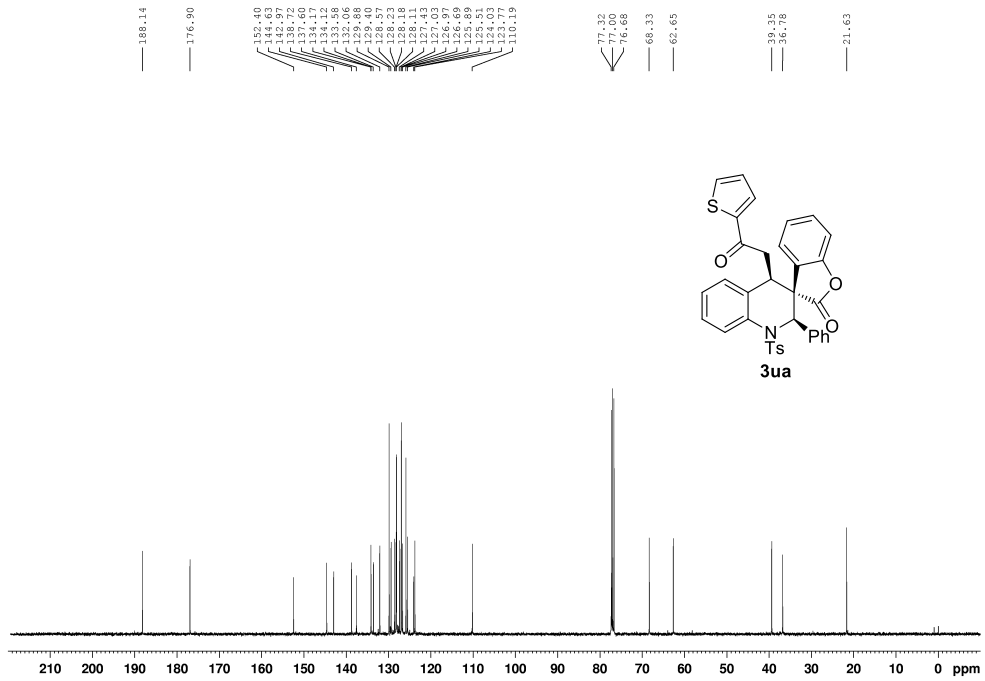

$^{13}$CNMR of **3ta** (400M, $CDCl_3$)



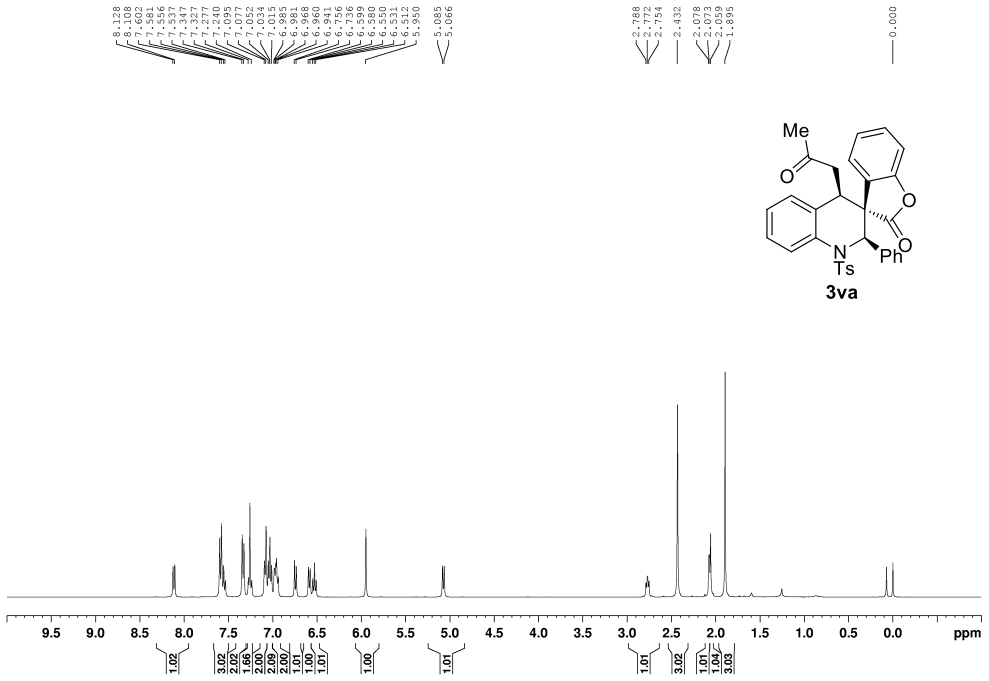

$^{1}$HNMR of **3ua** (400M, $CDCl_3$)



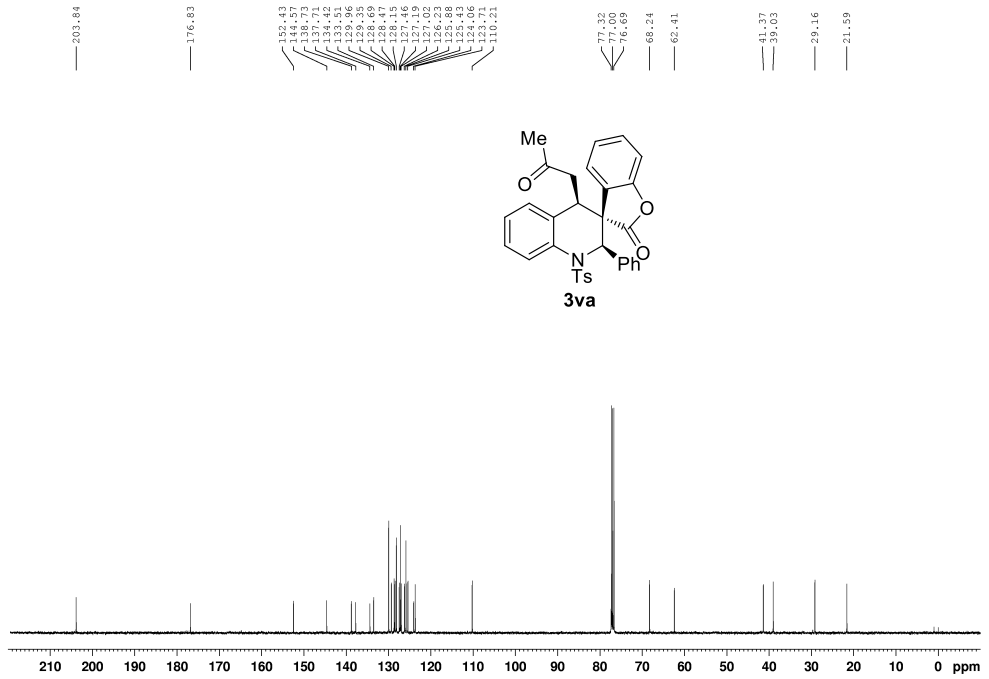

$^{13}$CNMR of **3ua** (400M, $CDCl_3$)



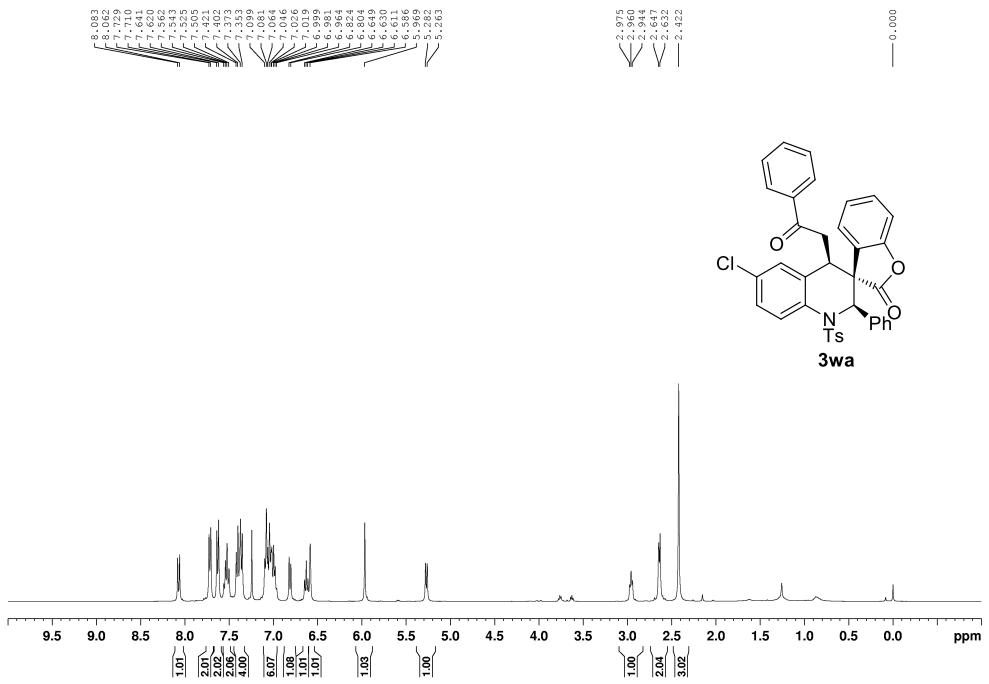

$^{1}$HNMR of **3va** (400M, $CDCl_3$)



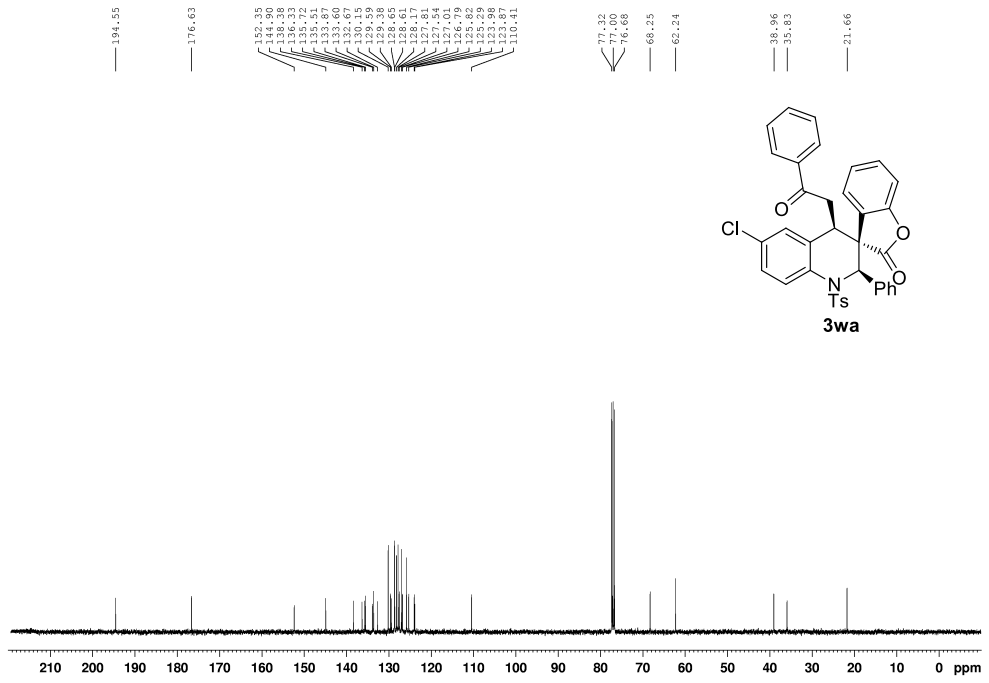

$^{13}$CNMR of **3va** (400M, $CDCl_3$)



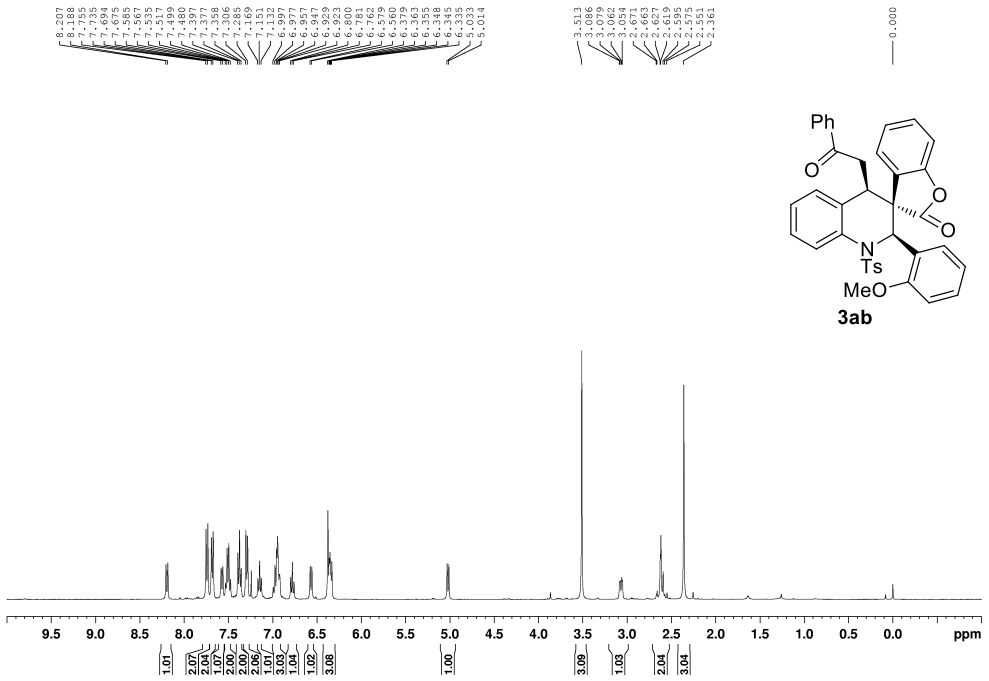

$^{1}$HNMR of **3wa** (400M, $CDCl_3$)



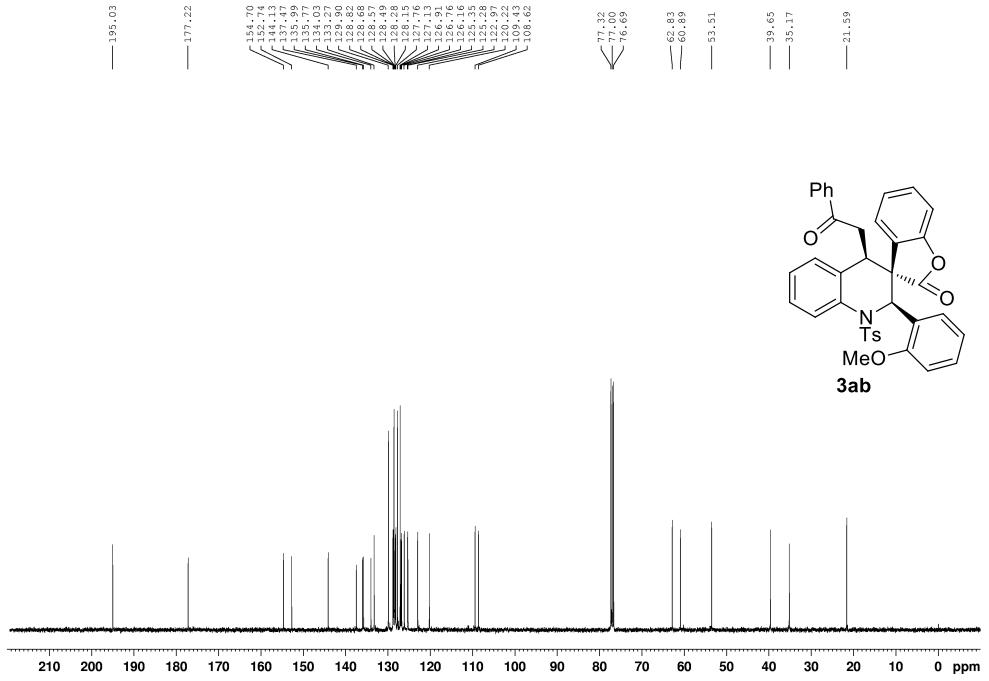

$^{13}$CNMR of **3wa** (400M, $CDCl_3$)



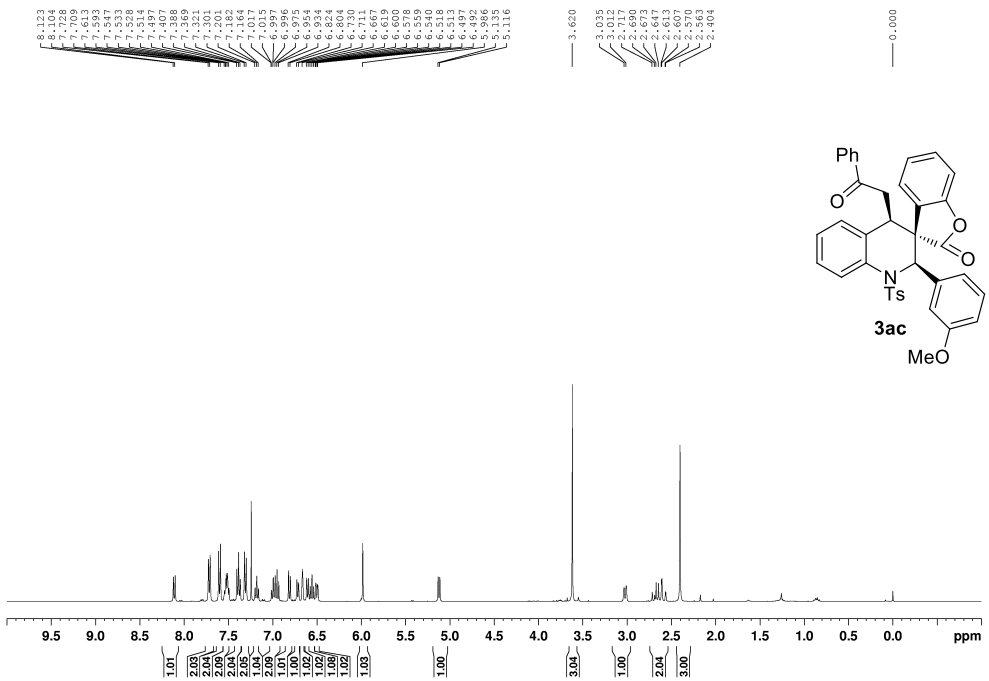

$^{1}$HNMR of **3ab** (400M, $CDCl_3$)



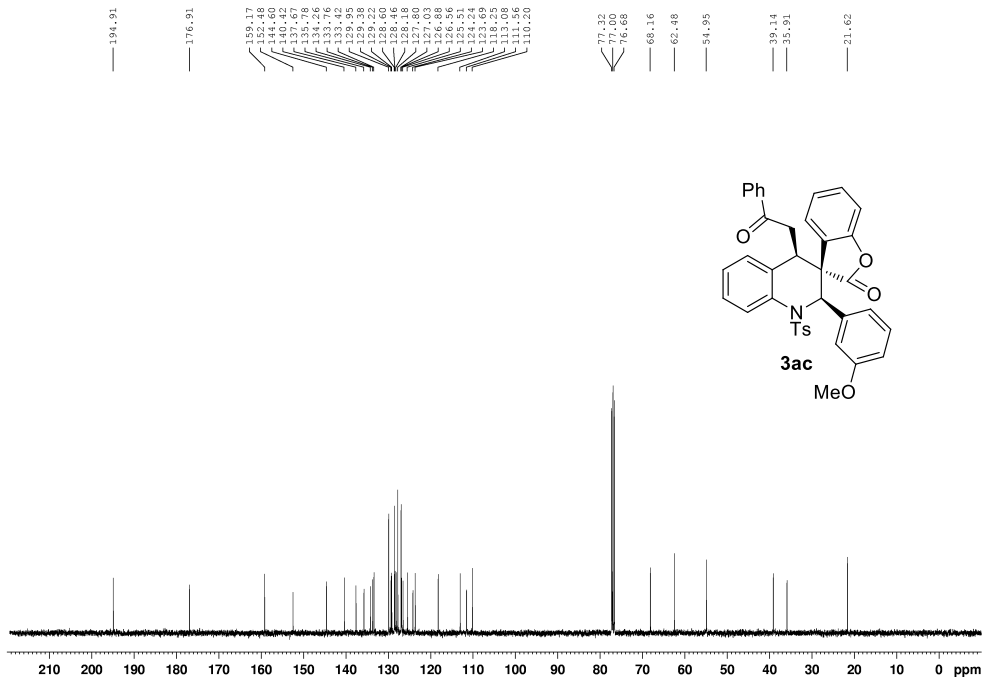

$^{13}$CNMR of **3ab** (100M, $CDCl_3$)



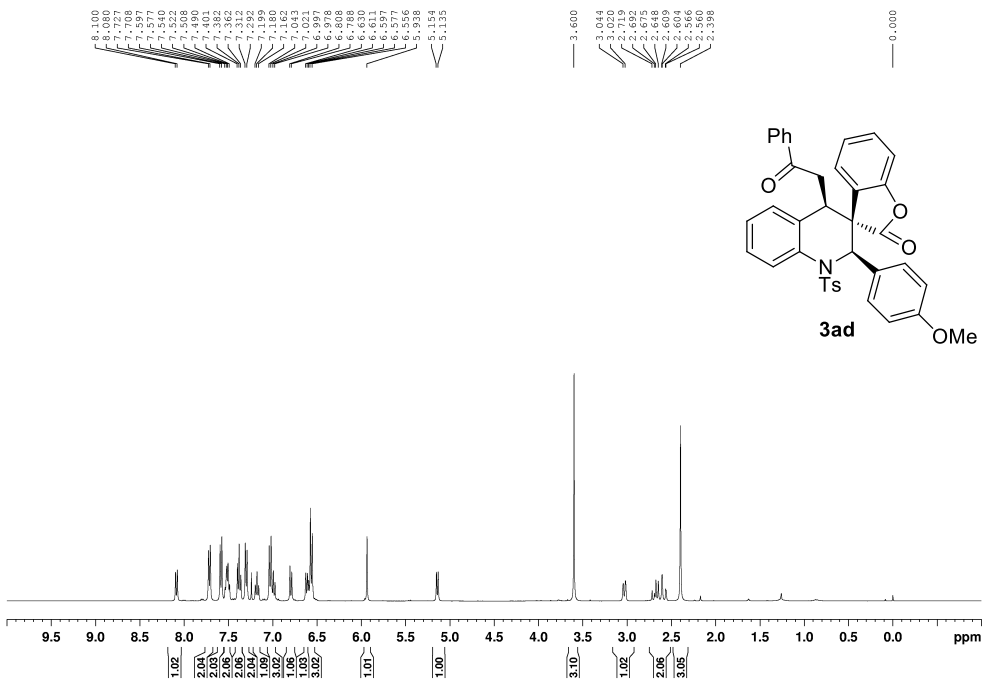

$^{1}$HNMR of **3ac** (400M, $CDCl_3$)



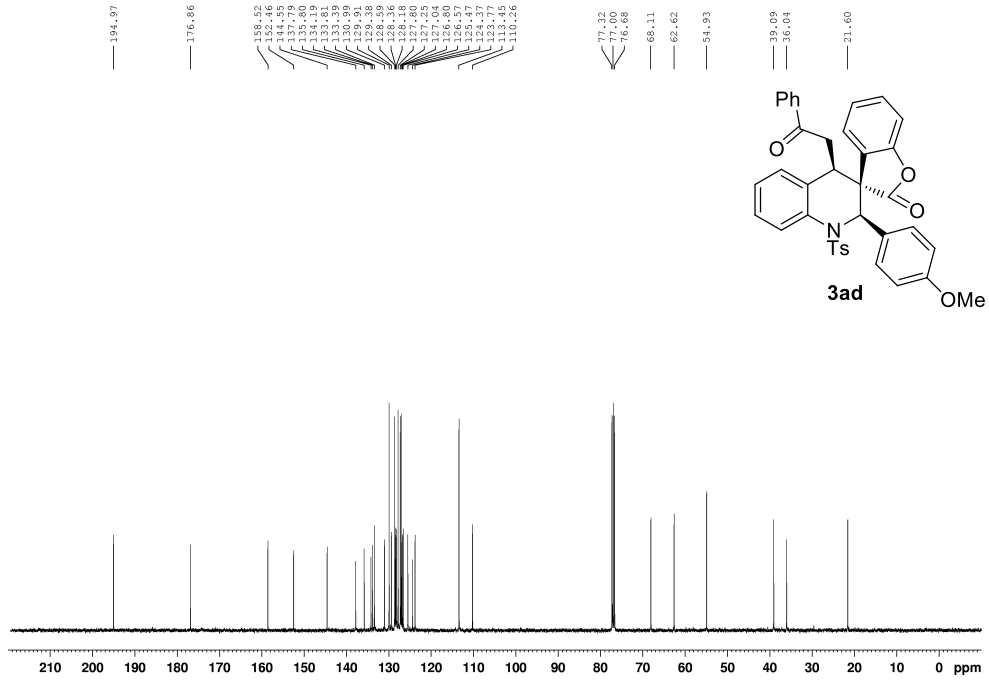

$^{13}$CNMR of **3ac** (100M, $CDCl_3$)



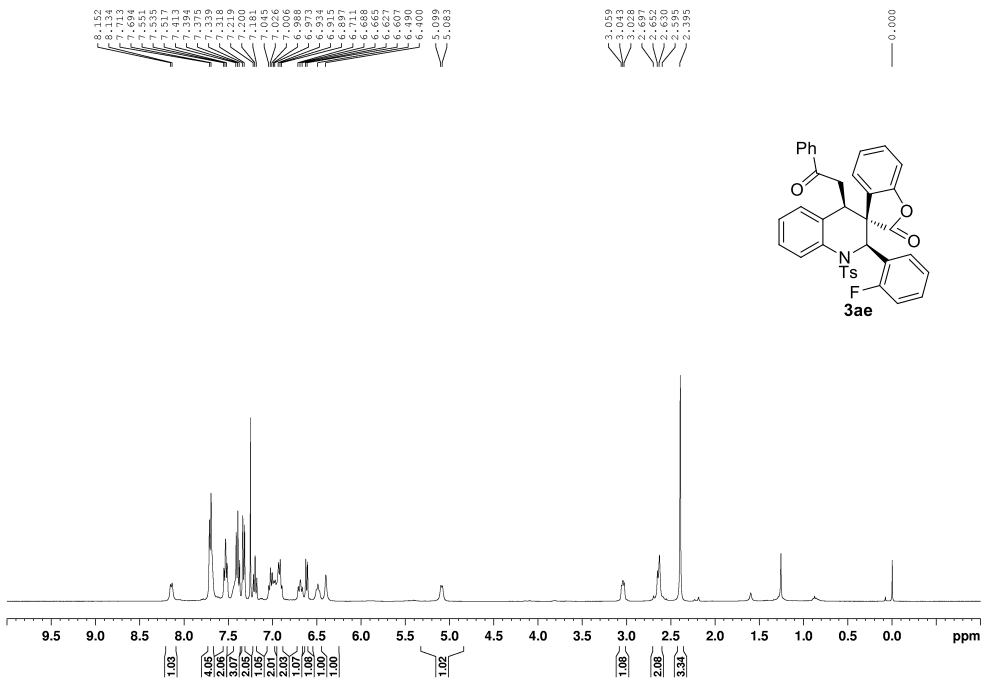

$^{1}$HNMR of **3ad** (400M, $CDCl_3$)



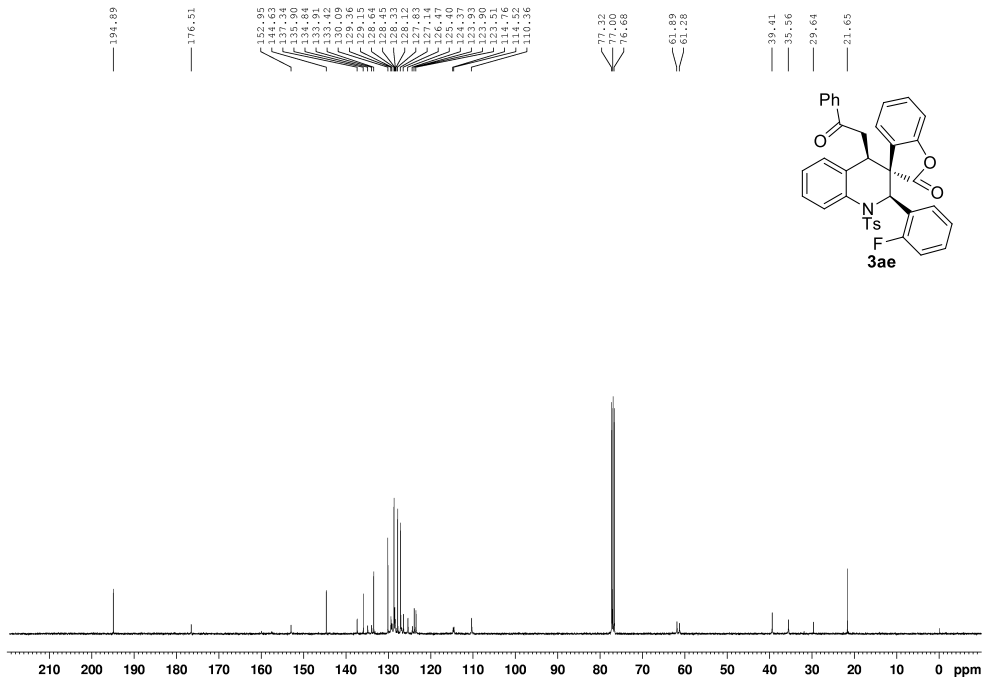

$^{13}$CNMR of **3ad** (100M, $CDCl_3$)



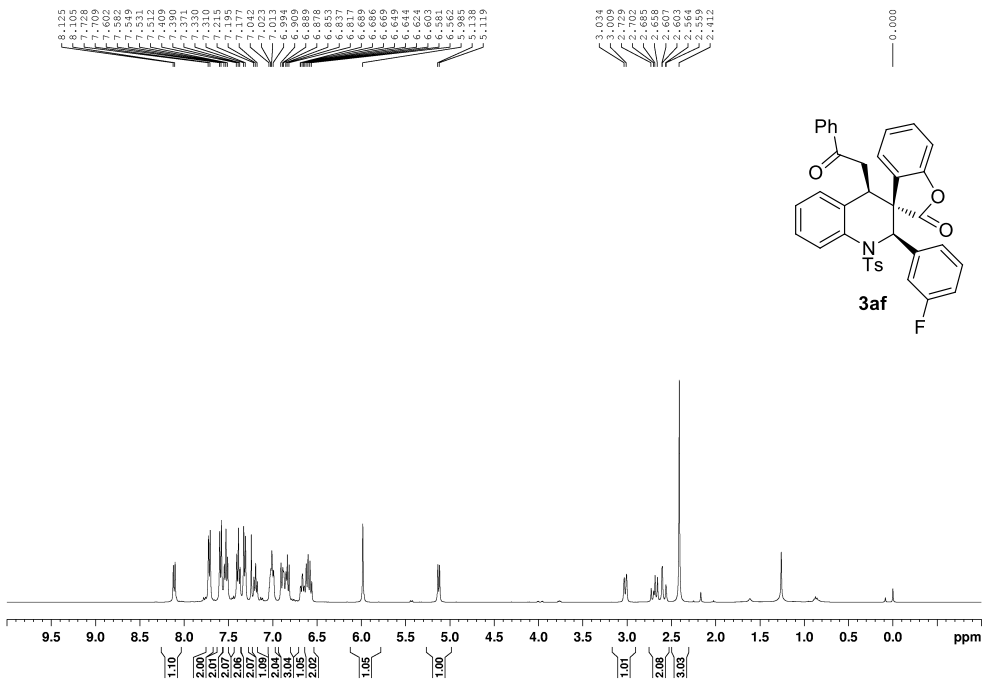

$^{1}$HNMR of **3ae** (400M, $CDCl_3$)



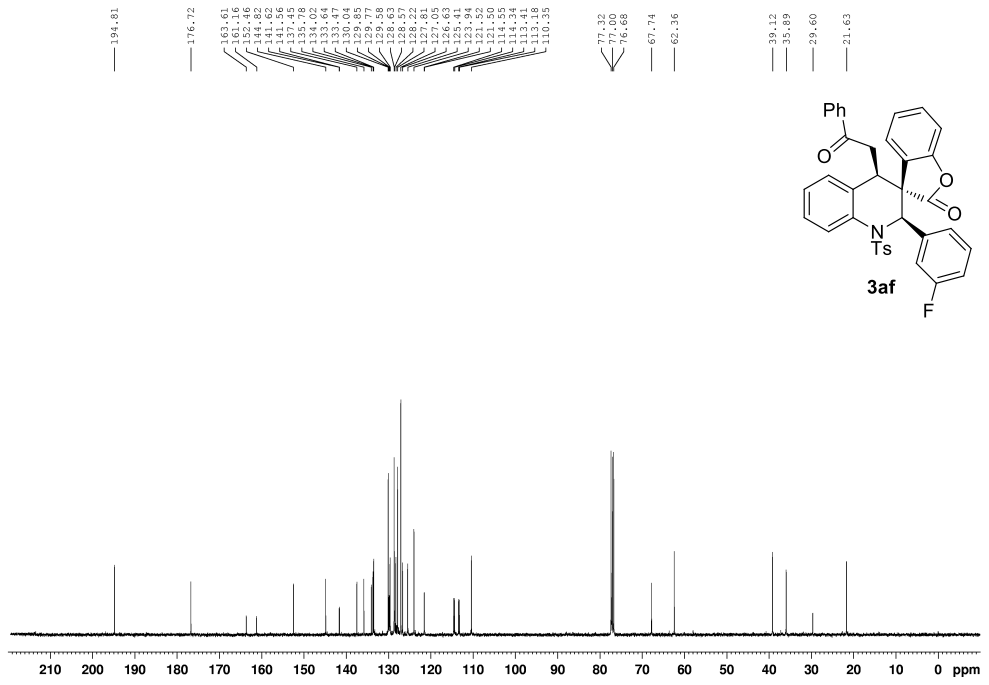

$^{13}$CNMR of **3ae** (100M, $CDCl_3$)



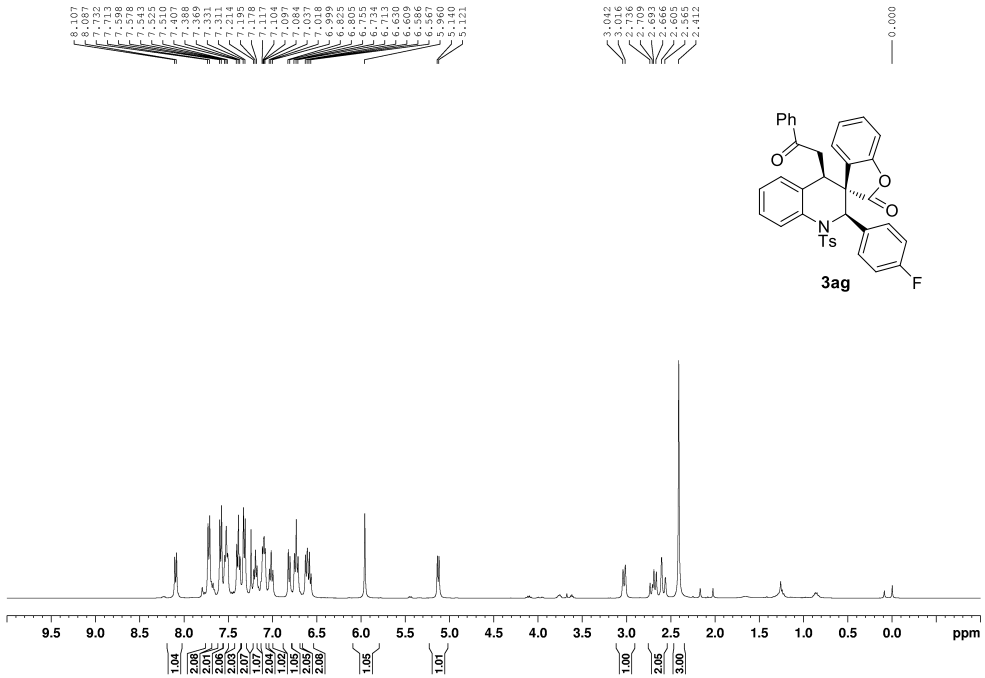

$^{1}$HNMR of **3af** (400M, $CDCl_3$)



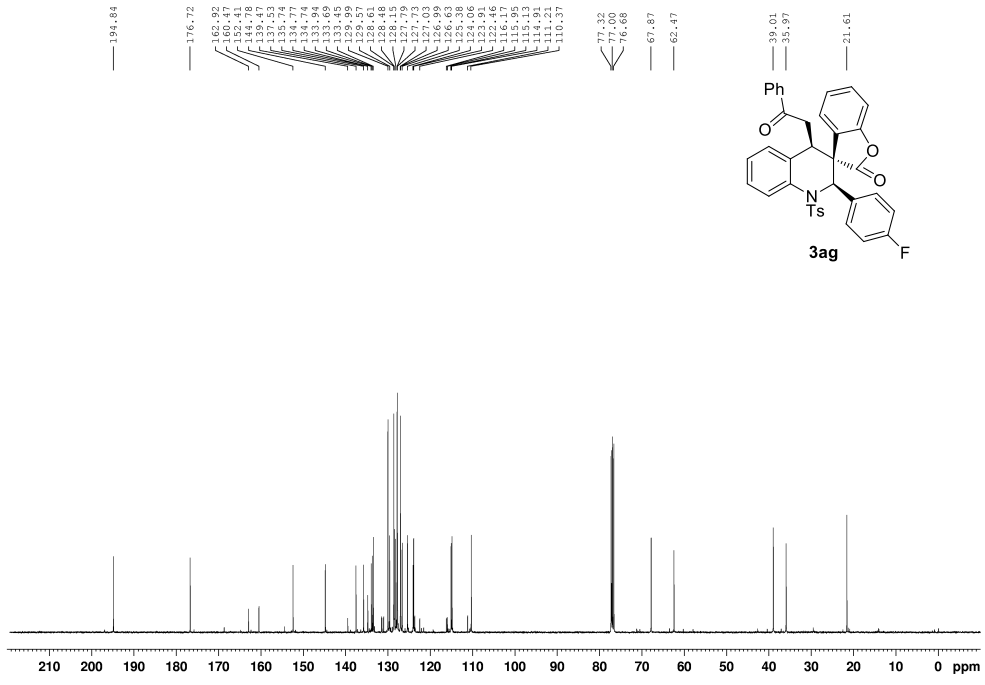

$^{13}$CNMR of **3af** (100M, $CDCl_3$)



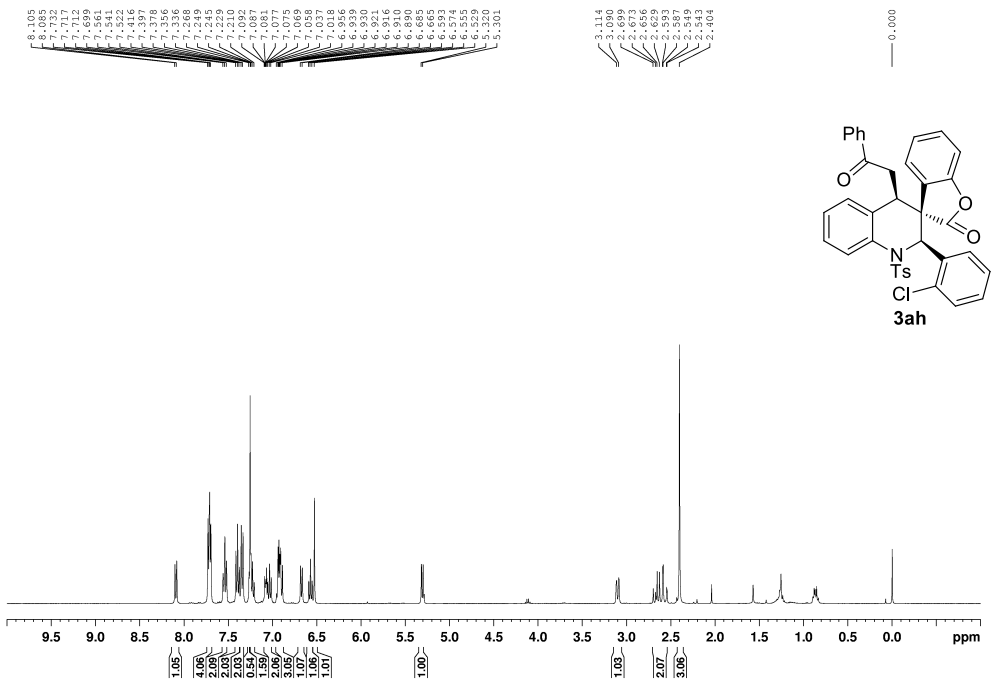

$^{1}$HNMR of **3ag** (400M, $CDCl_3$)



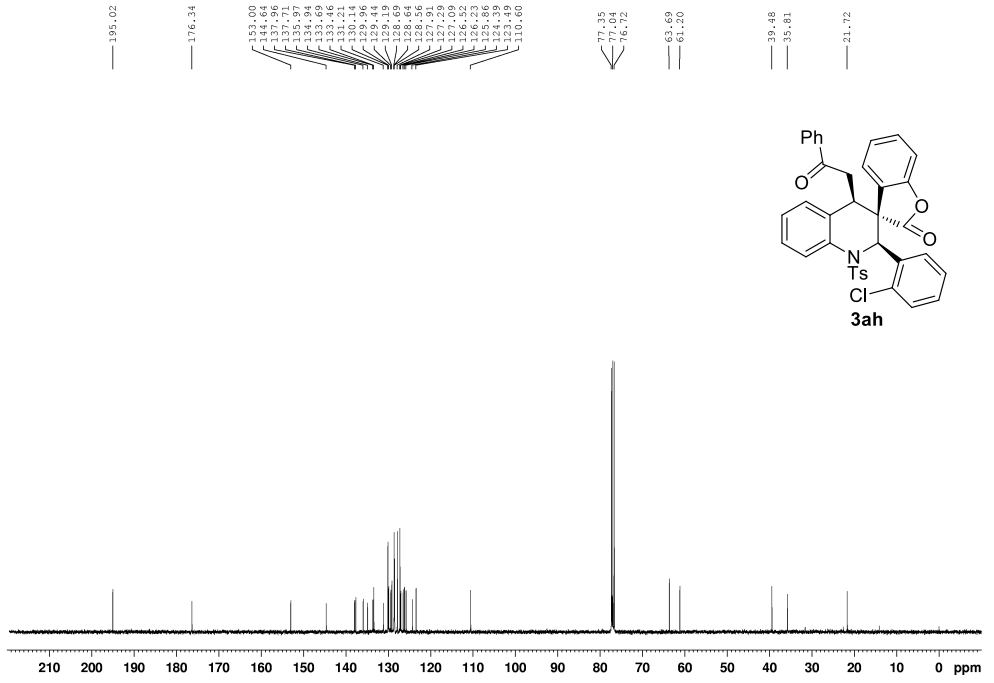

$^{13}$CNMR of **3ag** (100M, $CDCl_3$)



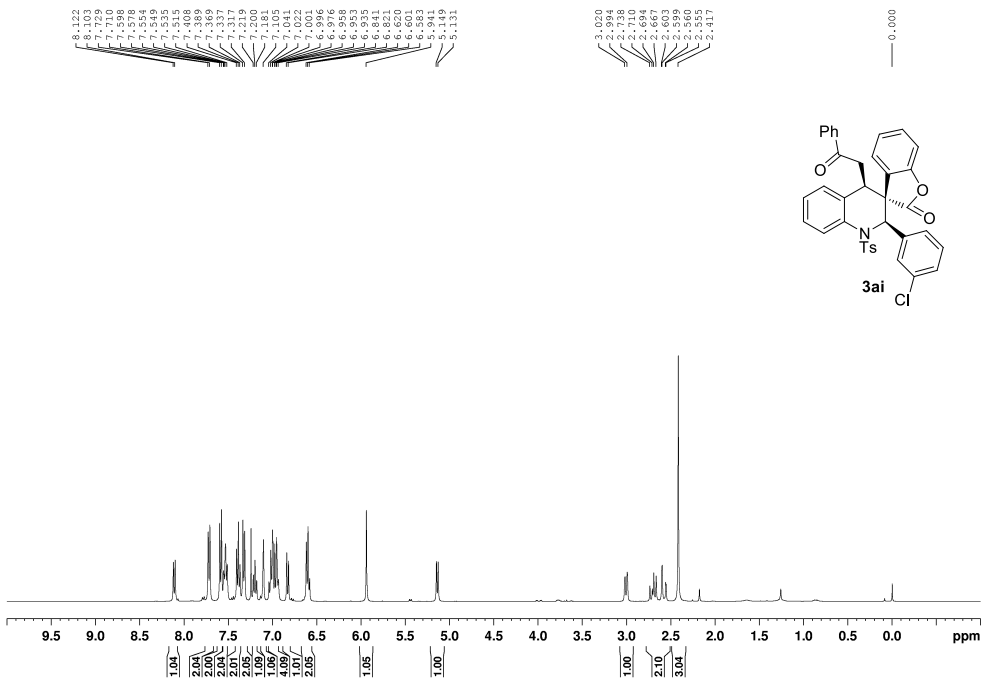

$^{1}$HNMR of **3ah** (400M, $CDCl_3$)



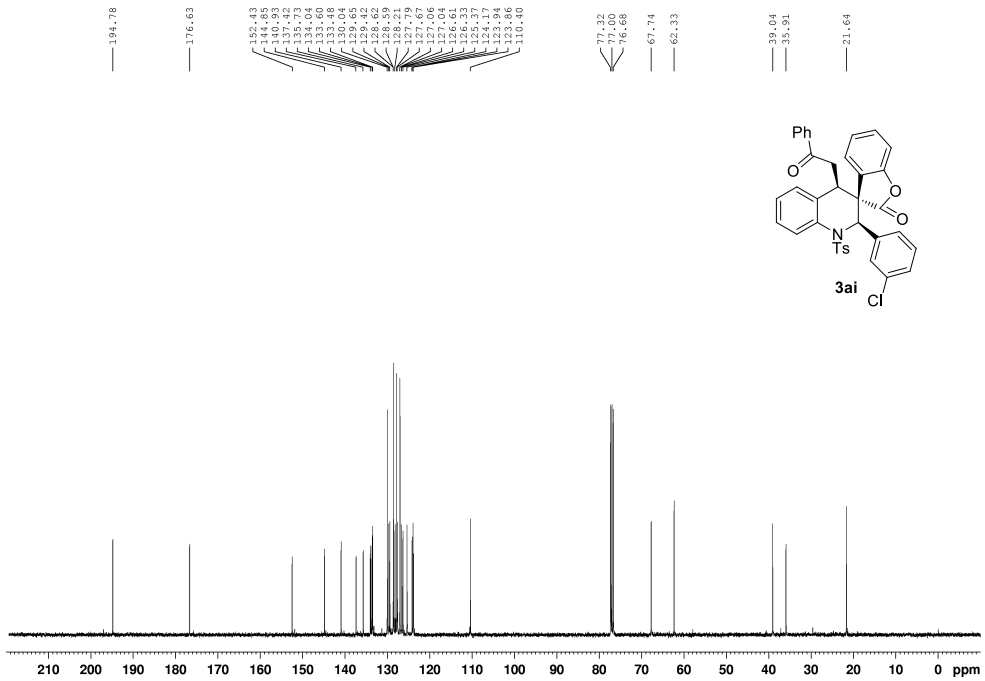

$^{13}$CNMR of **3ah** (100M, $CDCl_3$)



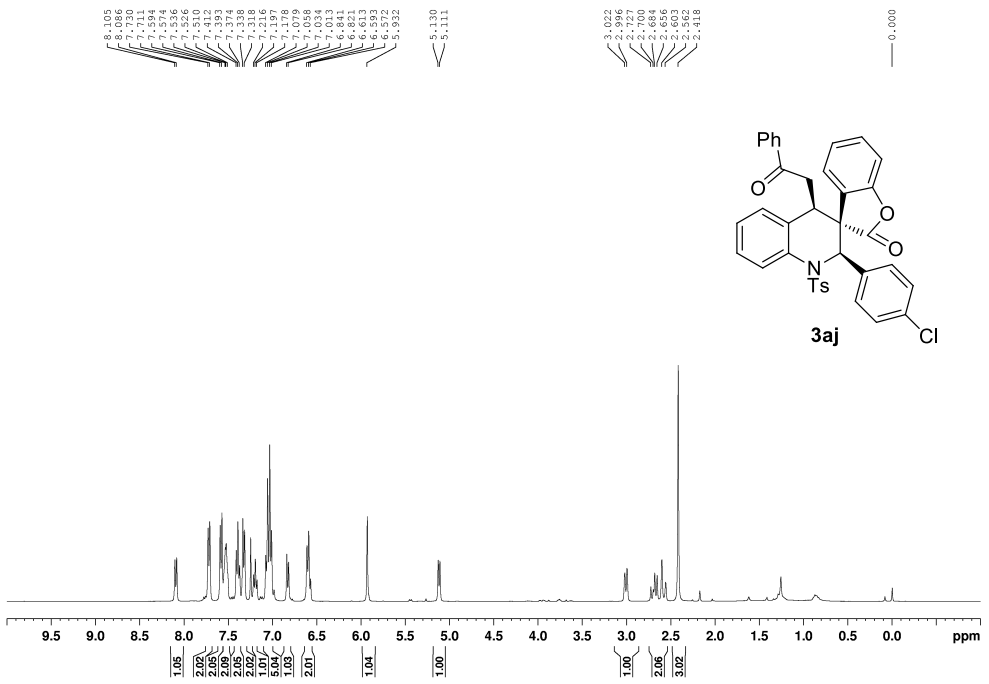

$^{1}$HNMR of **3ai** (400M, $CDCl_3$)



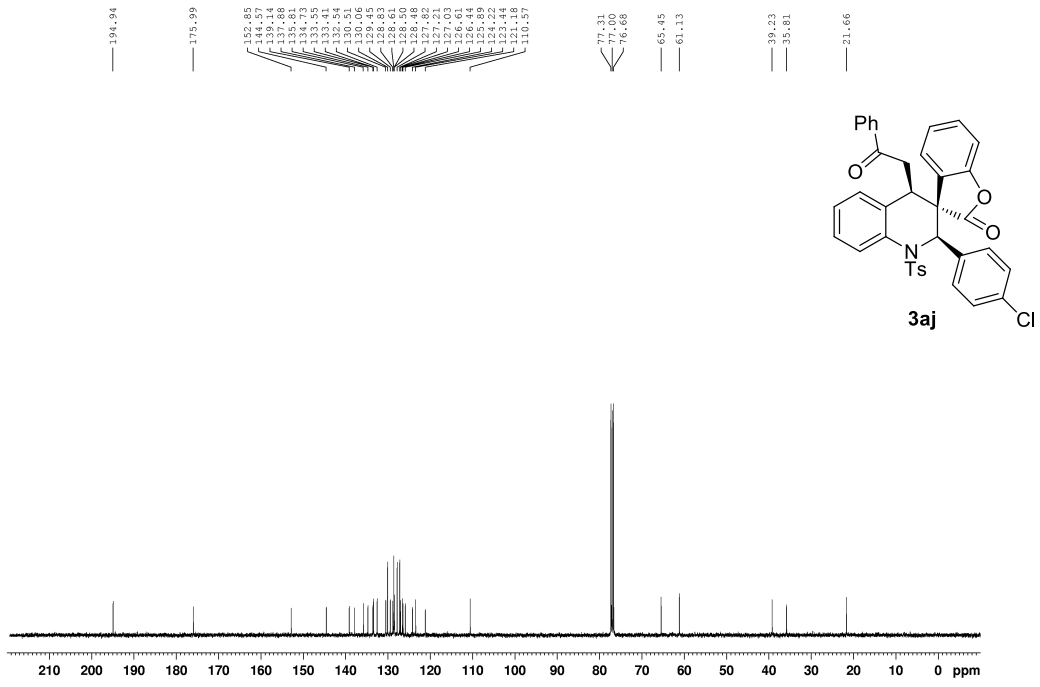

$^{13}$CNMR of **3ai** (100M, $CDCl_3$)



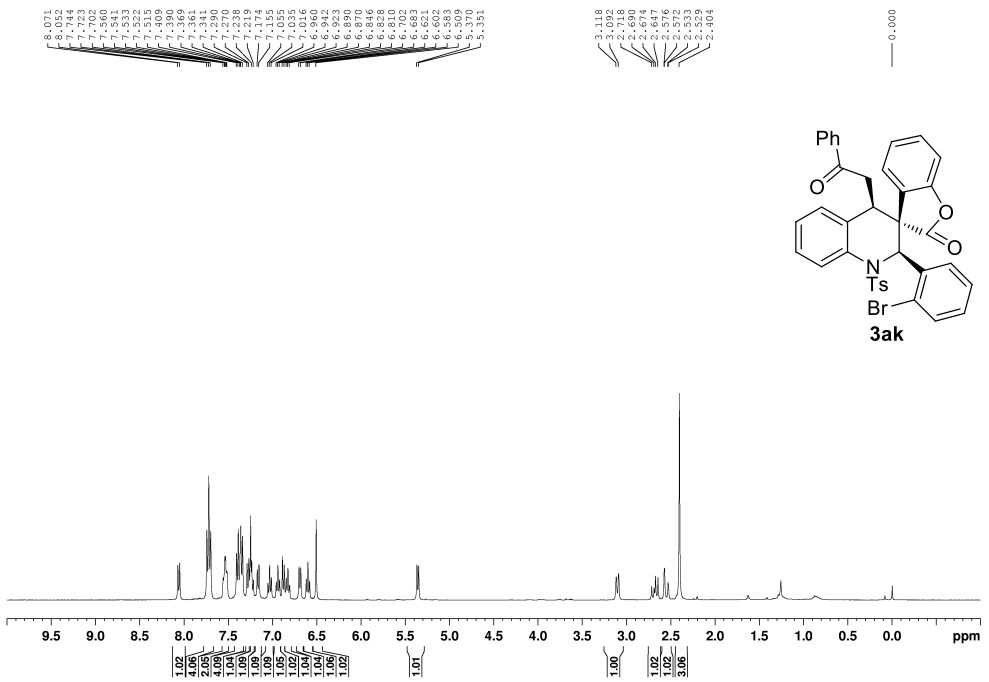

$^{1}$HNMR of **3aj** (400M, $CDCl_3$)



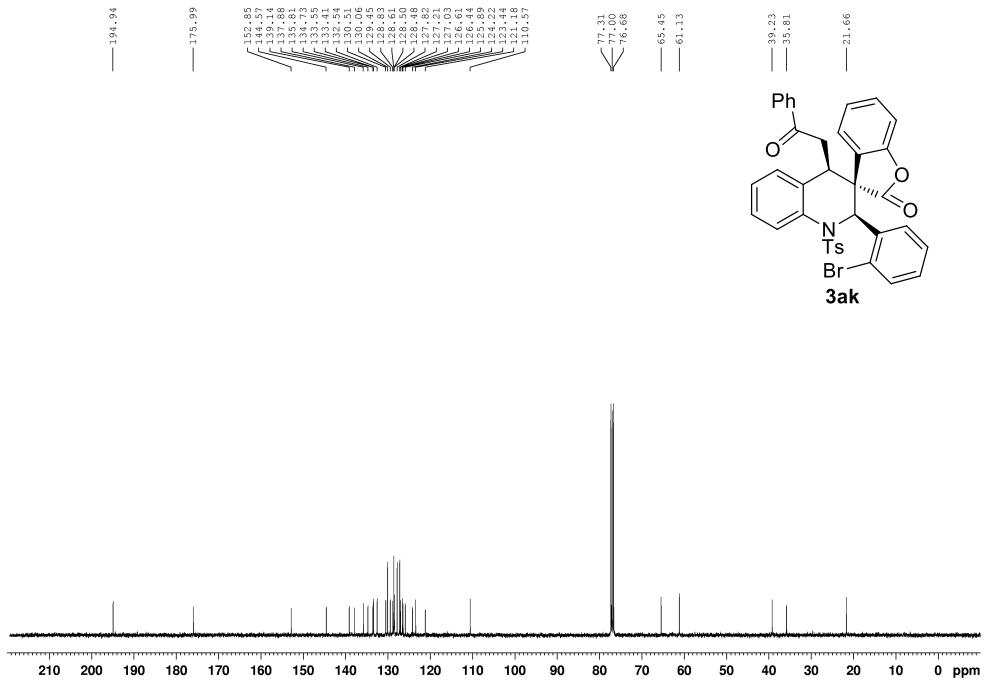

$^{13}$CNMR of **3aj** (100M, $CDCl_3$)



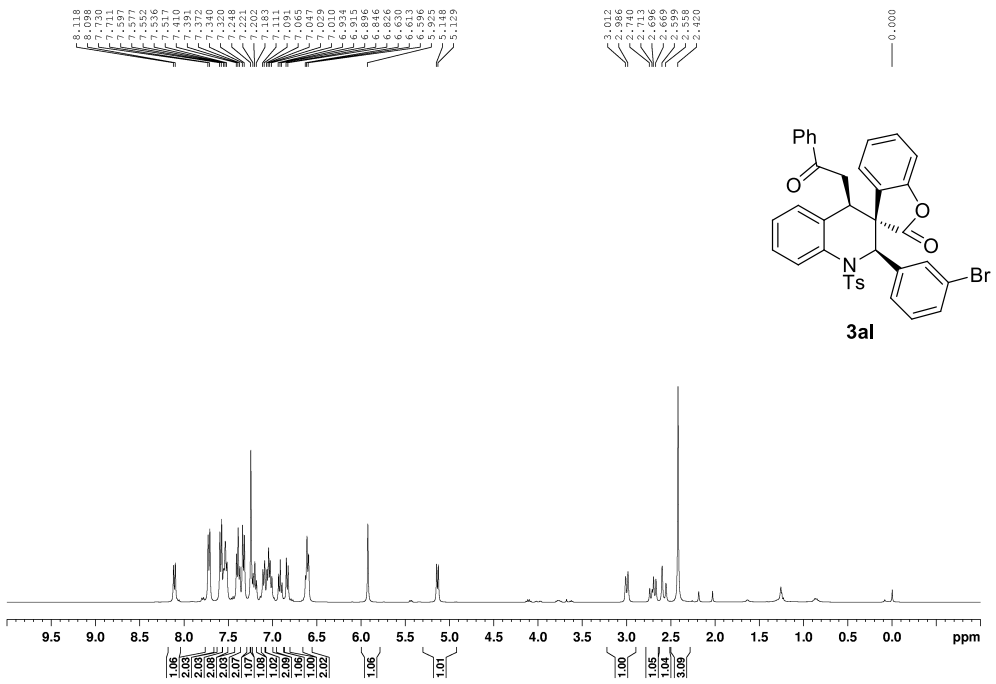

$^{1}$HNMR of **3ak** (400M, $CDCl_3$)



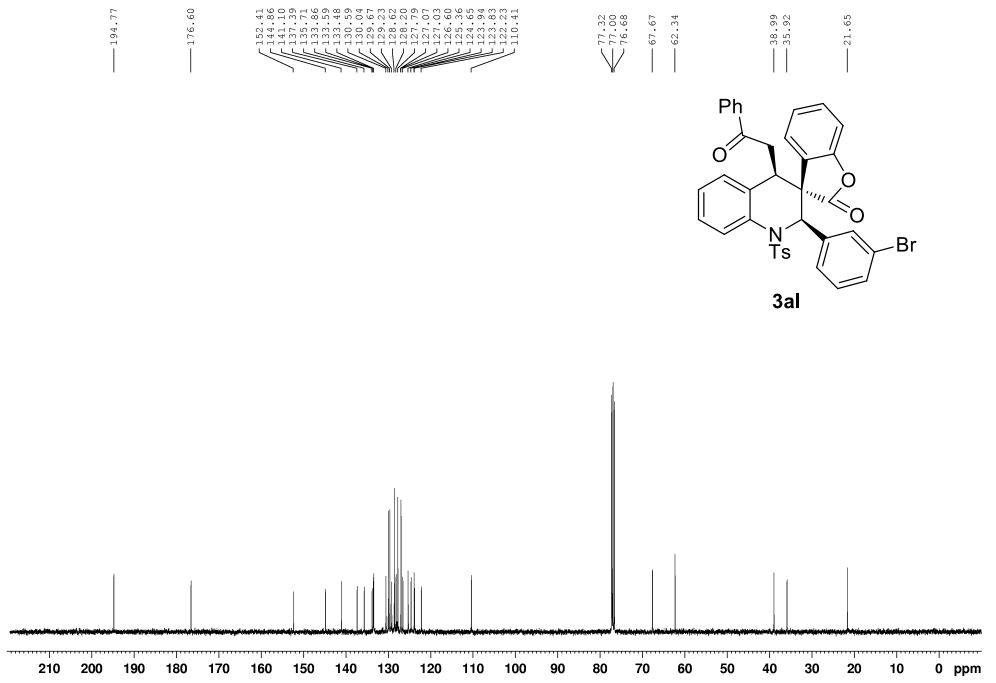

$^{13}$CNMR of **3ak** (400M, $CDCl_3$)



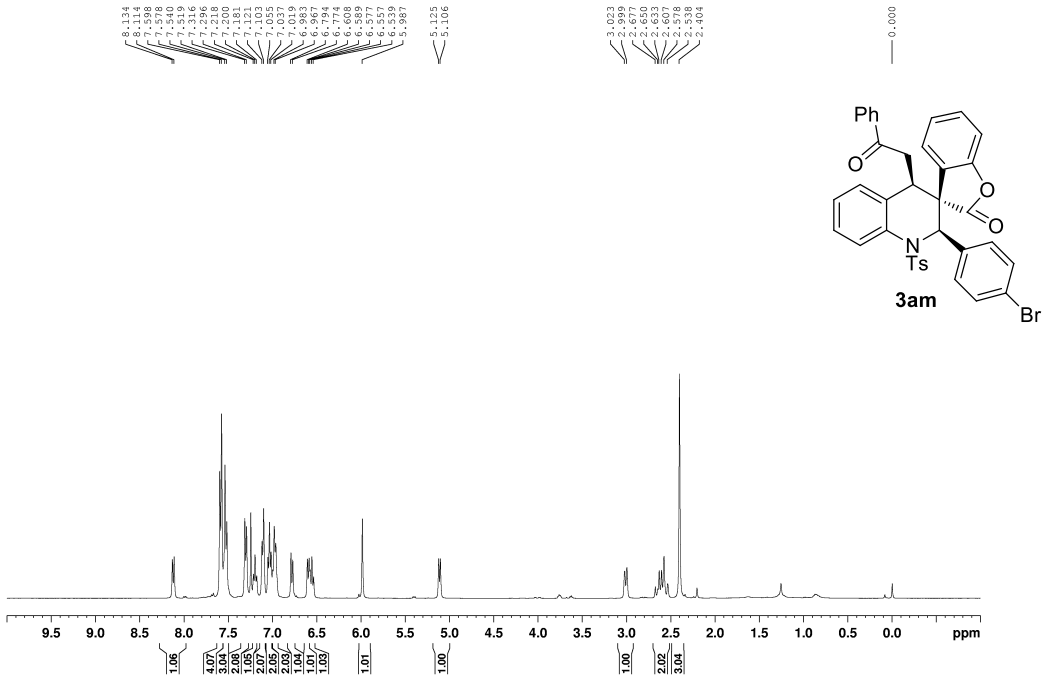

$^{1}$HNMR of **3al** (400M, $CDCl_3$)



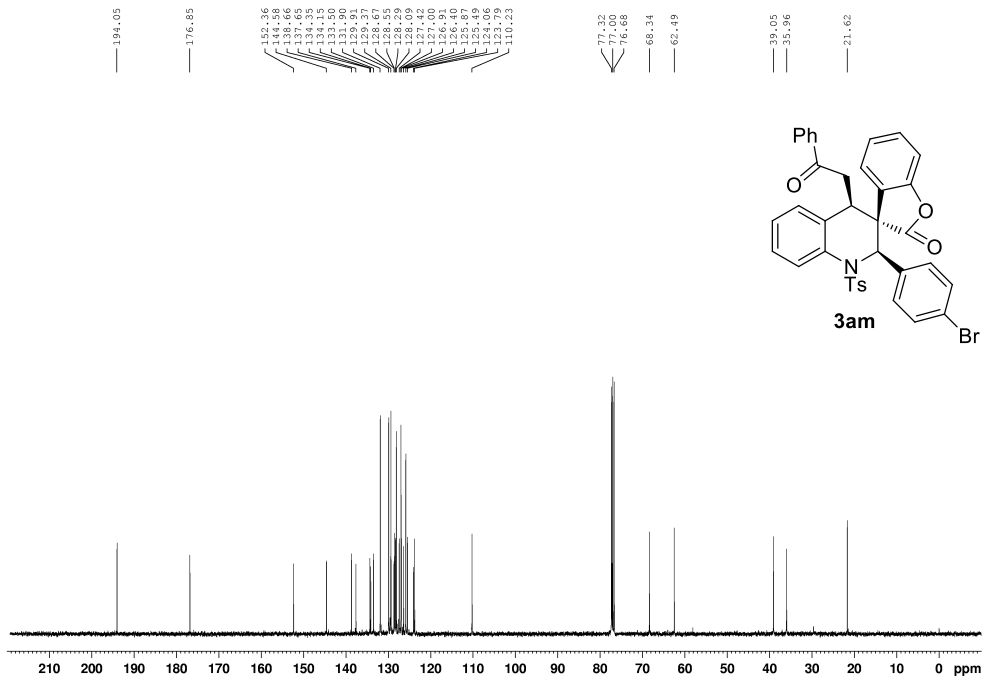

$^{13}$CNMR of **3al** (400M, $CDCl_3$)



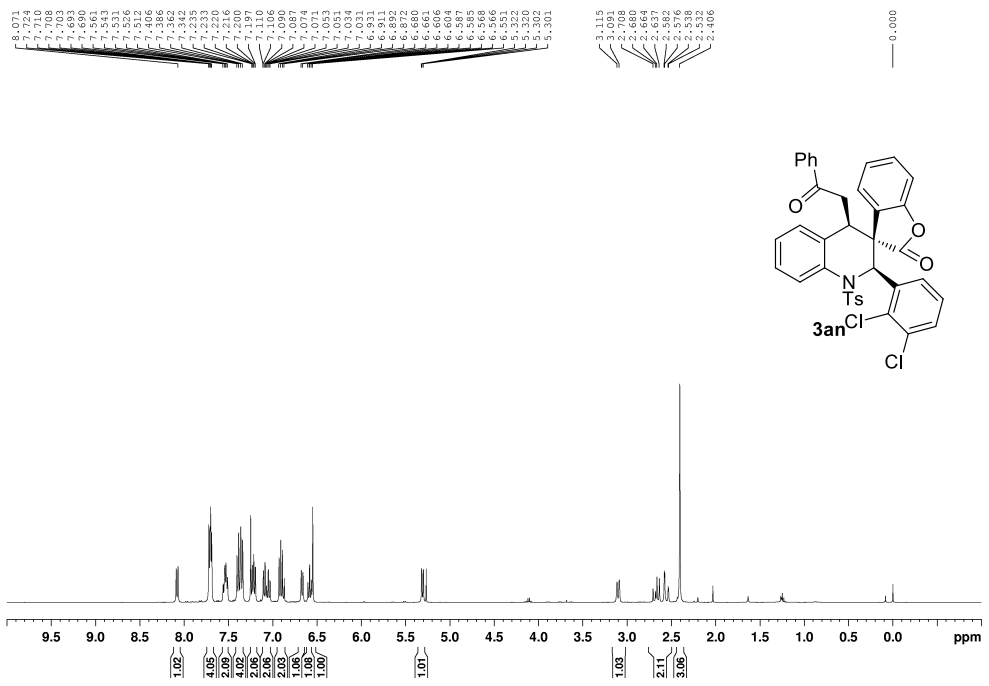

$^{1}$HNMR of **3am** (400M, $CDCl_3$)



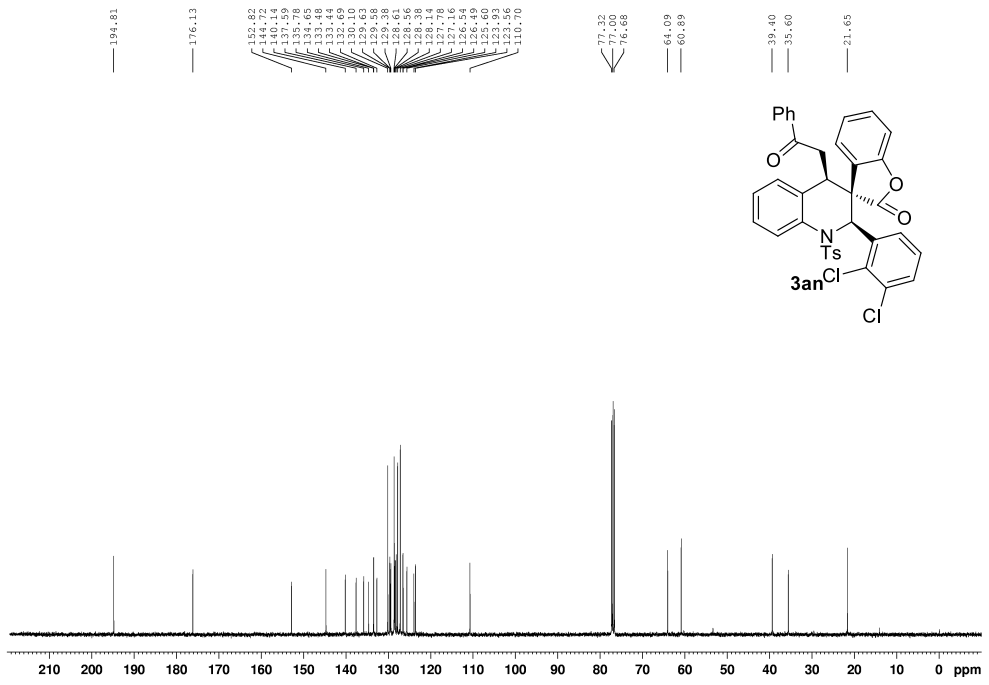

$^{13}$CNMR of **3am** (100M, $CDCl_3$)



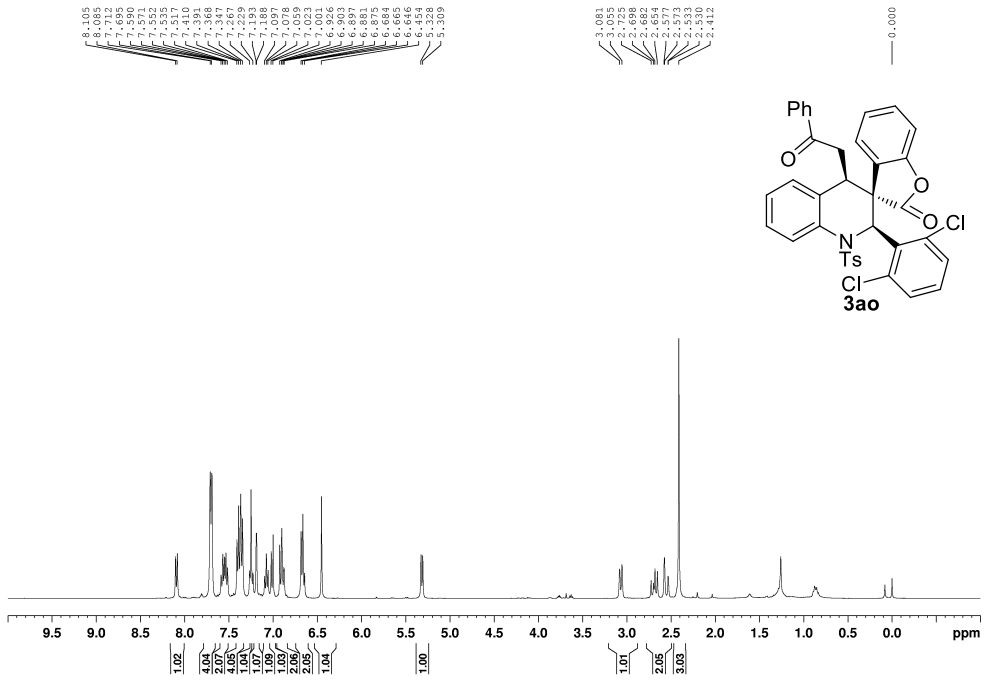

$^{1}$HNMR of **3an** (400M, $CDCl_3$)



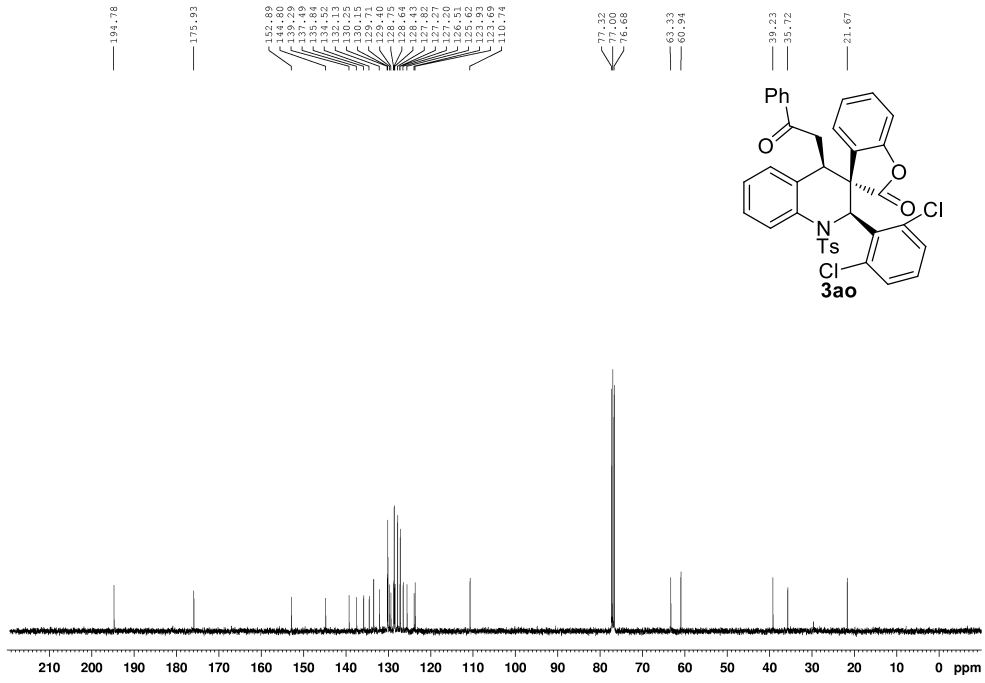

$^{13}$CNMR of **3an** (100M, $CDCl_3$)



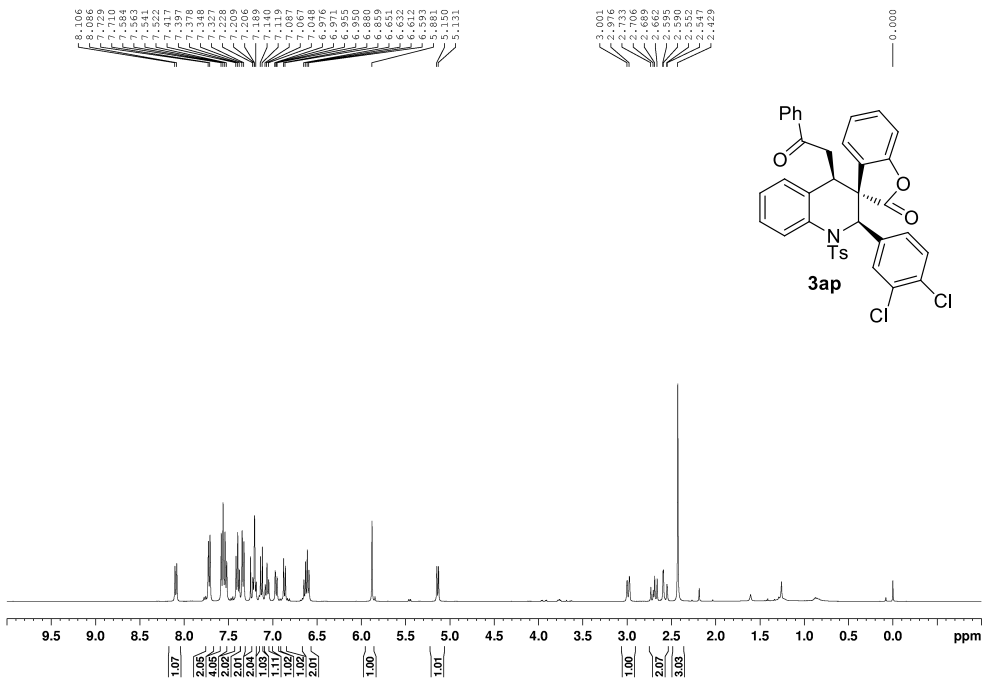

$^{1}$HNMR of **3ao** (400M, $CDCl_3$)



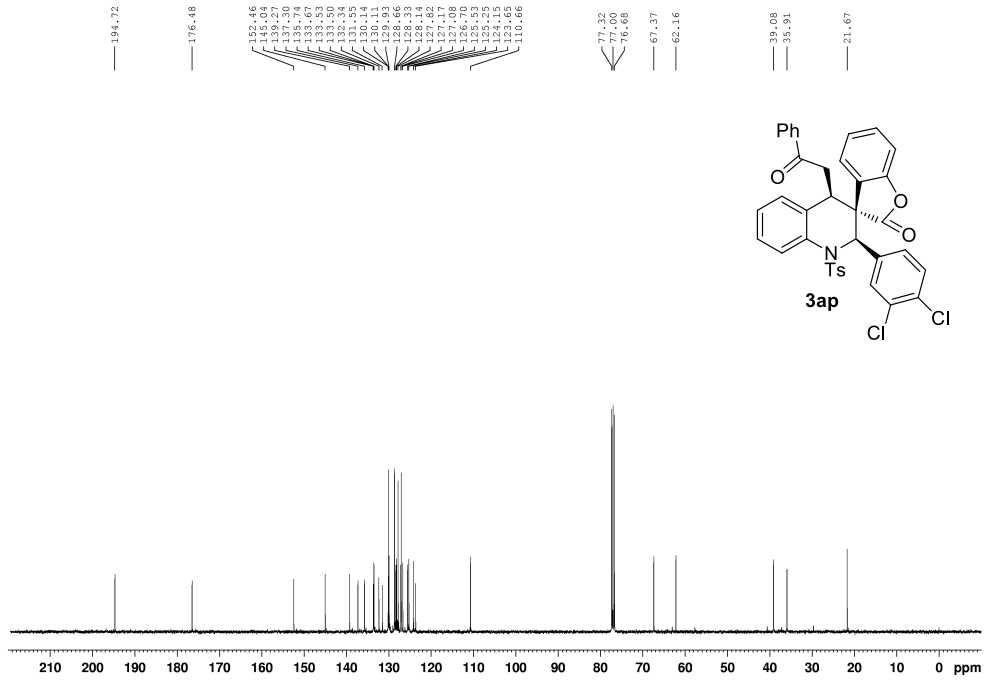

$^{13}$CNMR of **3ao** (100M, $CDCl_3$)



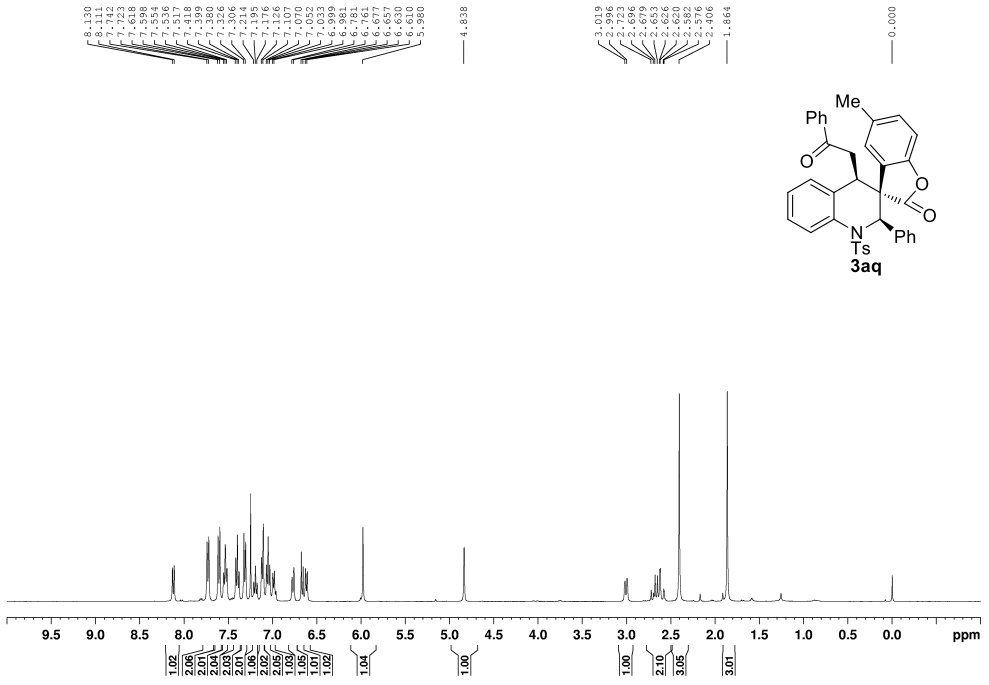

$^{1}$HNMR of **3ap** (400M, $CDCl_3$)



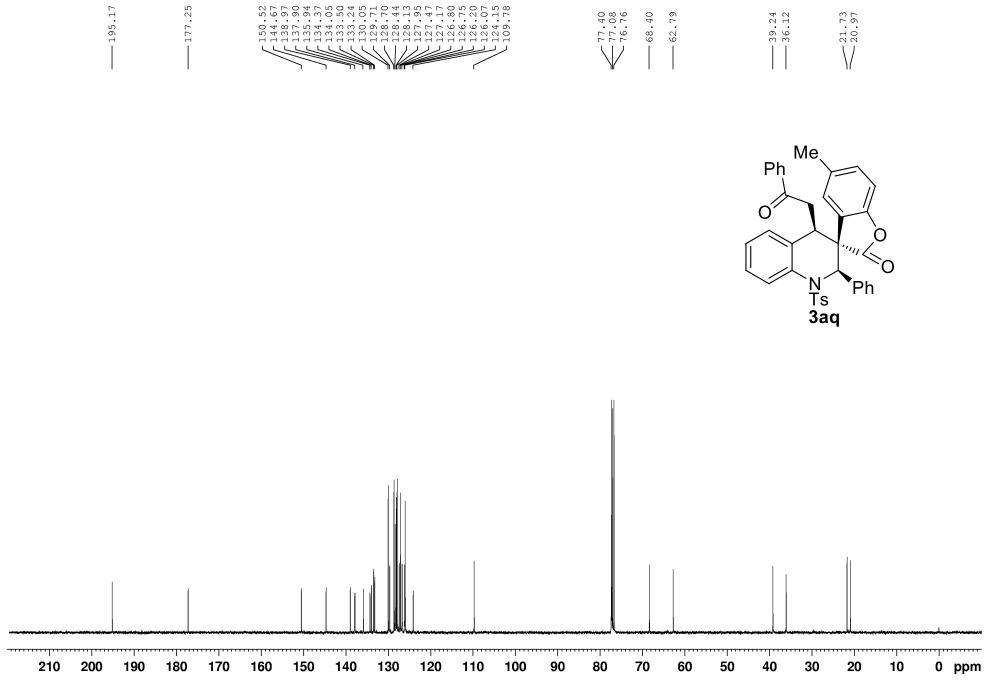

$^{13}$CNMR of **3ap** (100M, $CDCl_3$)



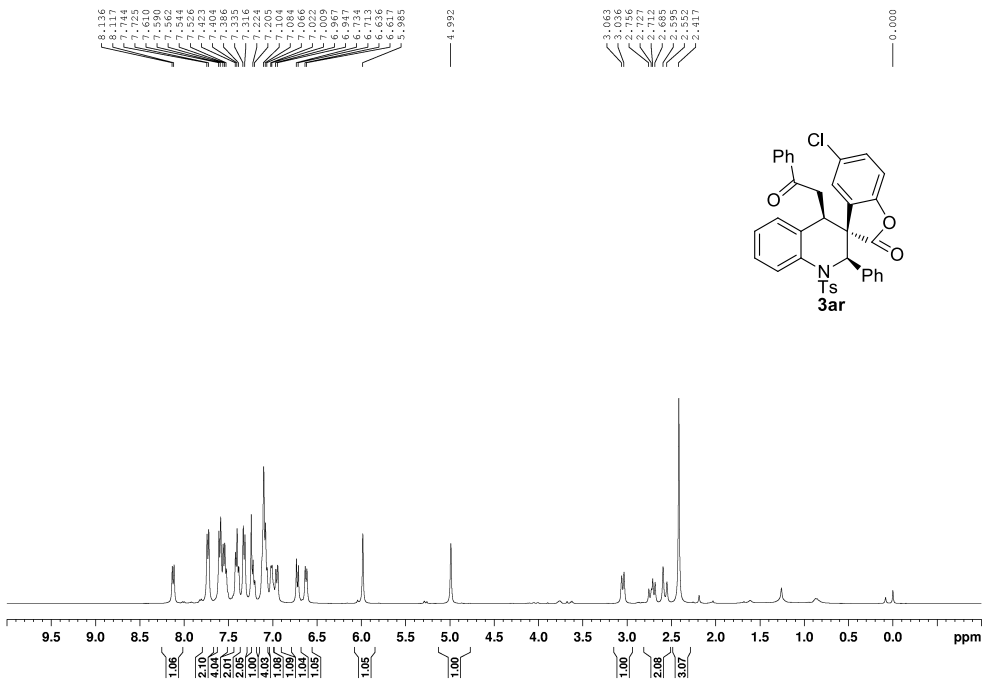

$^{1}$HNMR of **3aq** (400M, $CDCl_3$)



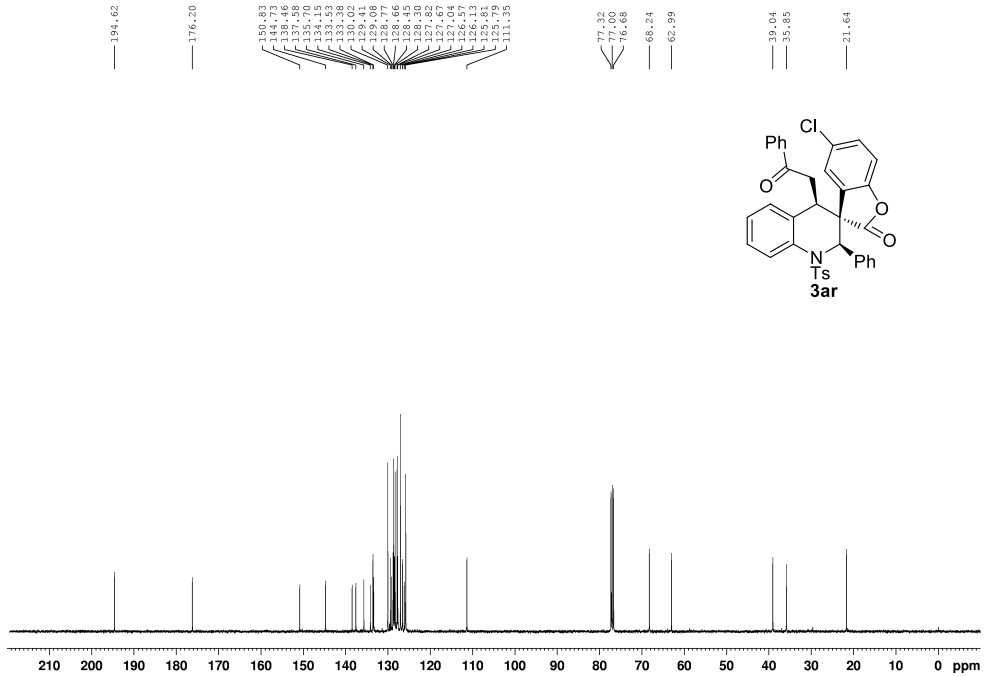

$^{13}$CNMR of **3aq** (100M, $CDCl_3$)




$^{1}$HNMR of **3ar** (400M, $CDCl_3$)

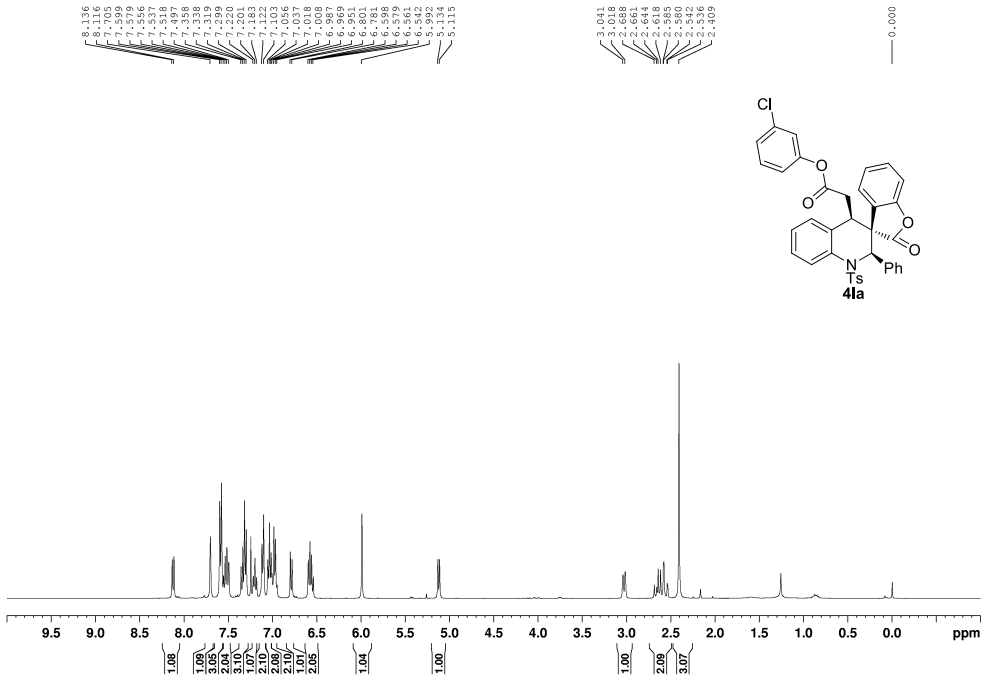



$^{13}$CNMR of **3ar** (100M, $CDCl_3$)

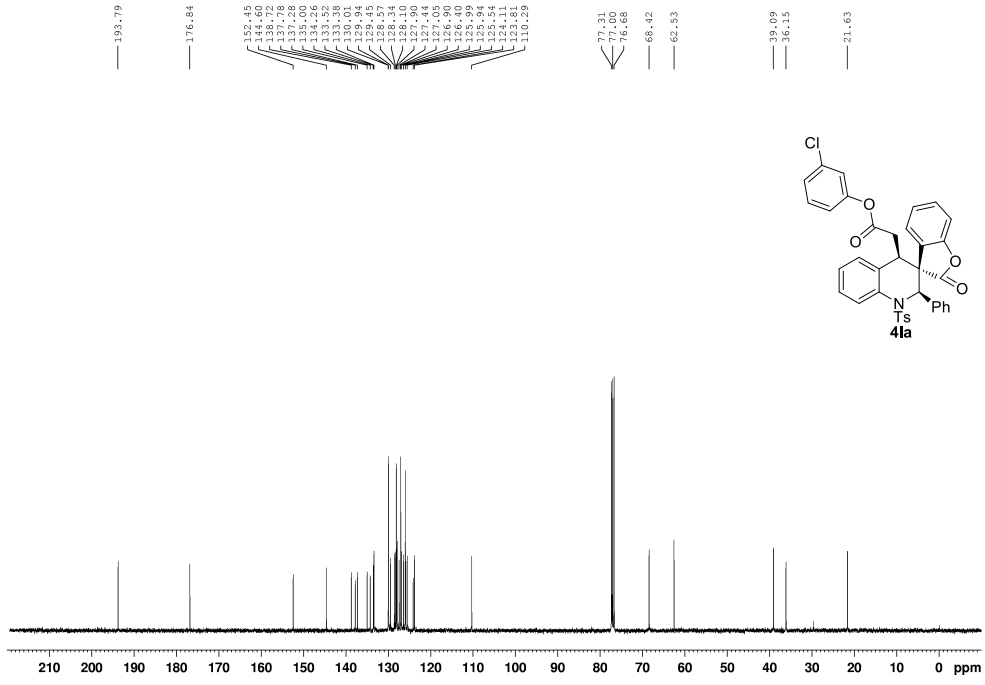



## 4.3 Copy of NMR Spectrogram of 4.

HNMR of **4la** (400M, $CDCl_3$)



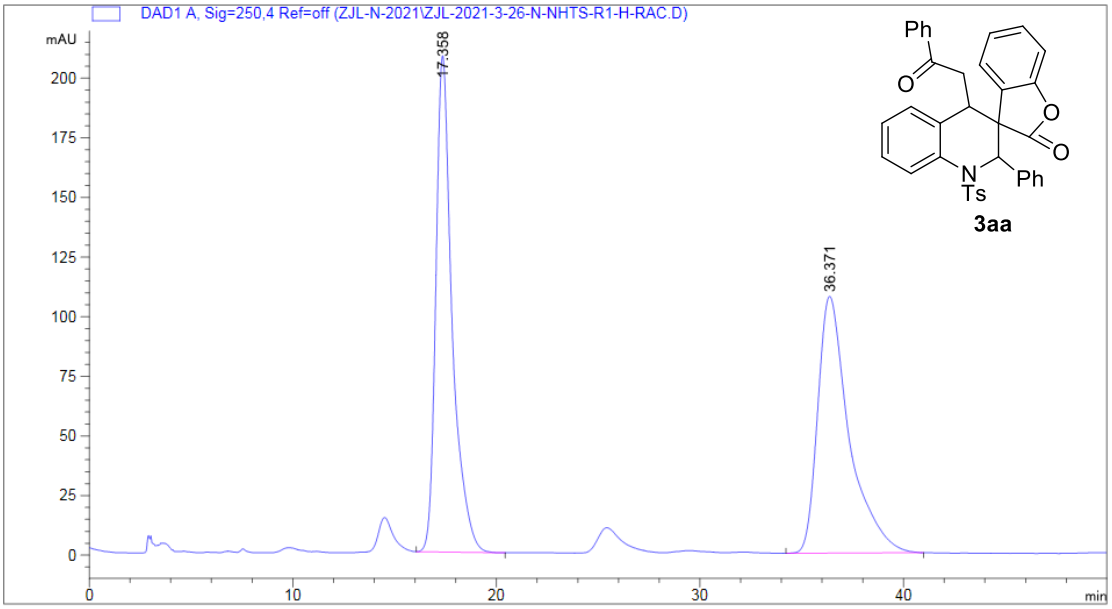

$^{13}$CNMR of **4la** (100M, $CDCl_3$)



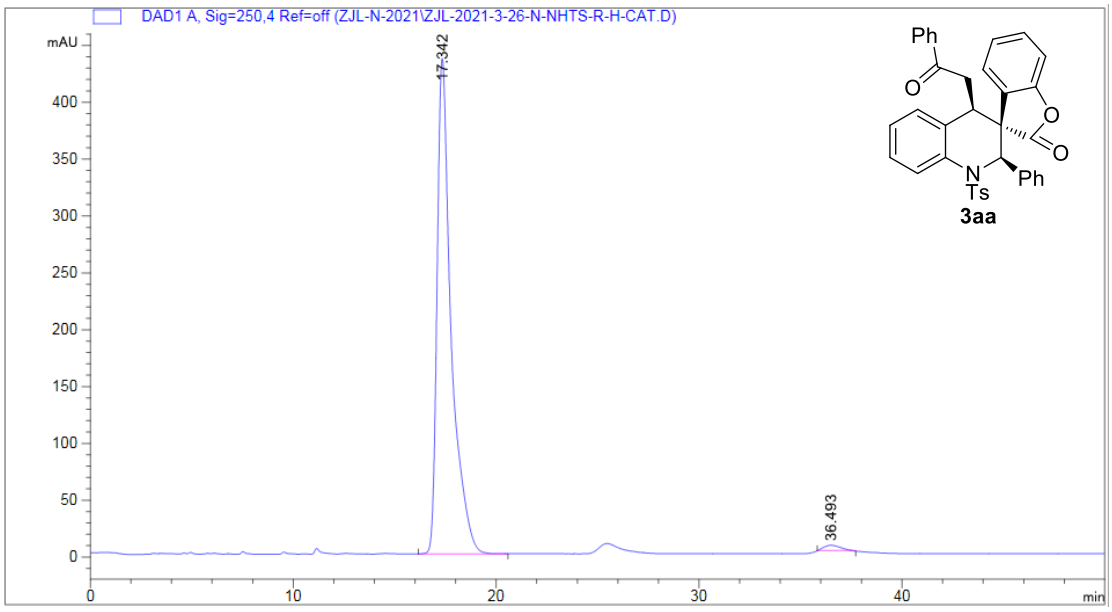
# 5. HPLC spectrogram.

## 5.1. HPLC spectrogram of compound 3.

**3aa**

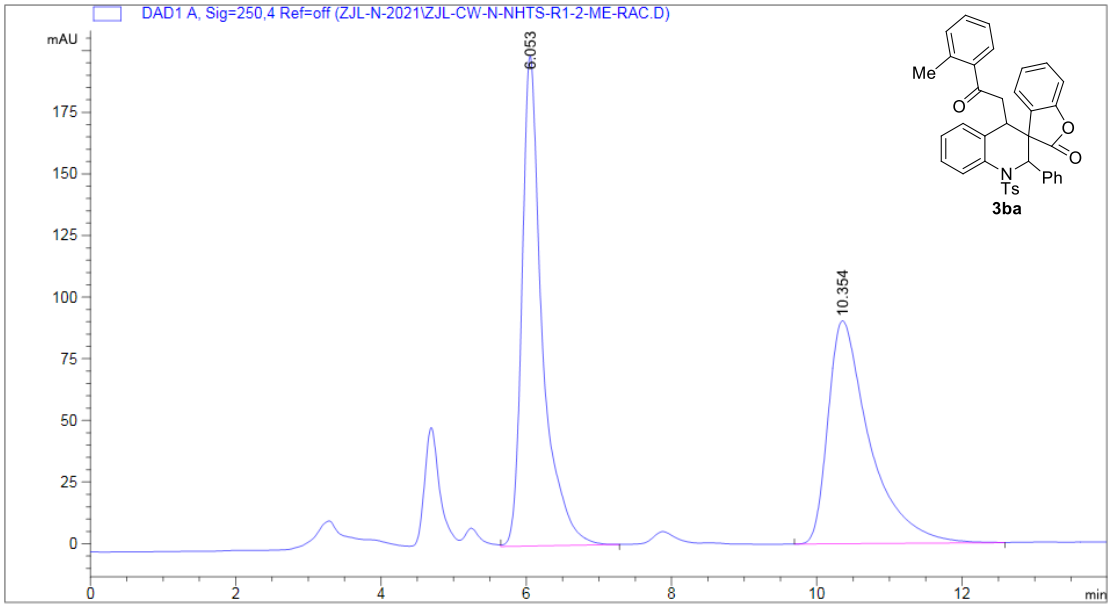



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 17.358 | 1.15828e4 | 208.11932 | 50.0524 |
| 2 | DAD 250, 4 nm | 36.371 | 1.15585e4 | 107.63284 | 49.9476 |

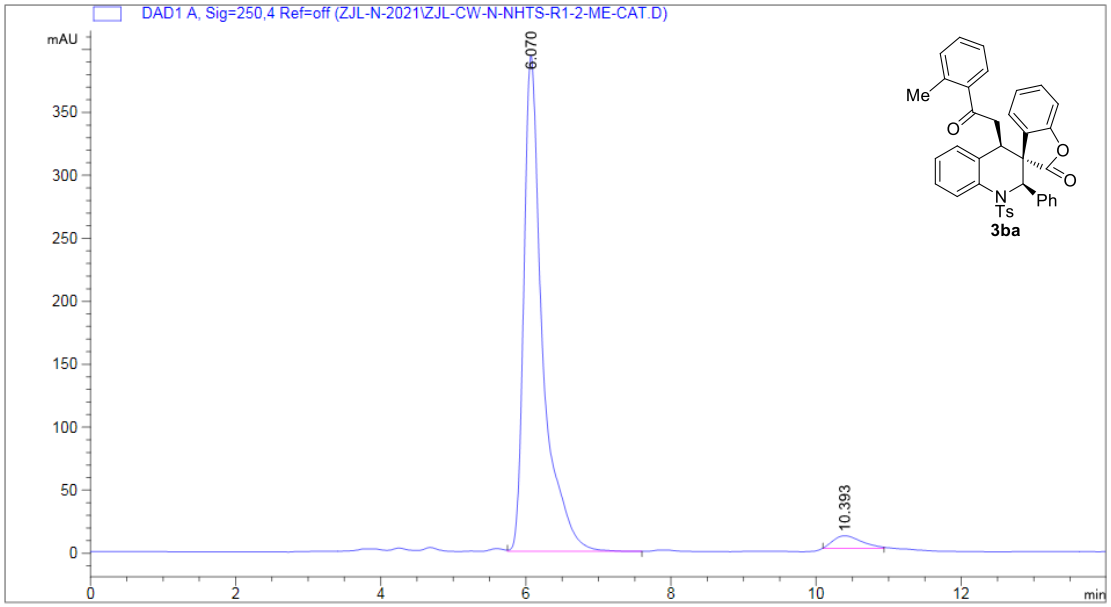


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 17.342 | 2.09784e4 | 435.78836 | 98.7841 |
| 2 | DAD 250, 4 nm | 36.493 | 258.21228 | 4.60982 | 1.2159 |

**3ba**

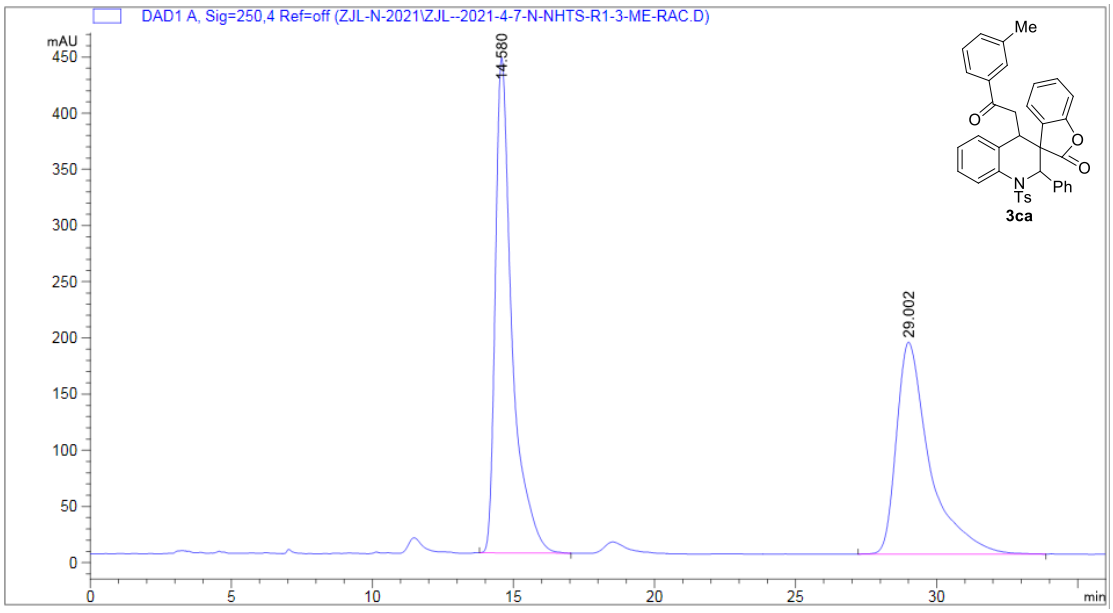



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 6.053 | 3865.71533 | 198.93677 | 51.8624 |
| 2 | DAD 250, 4 nm | 10.354 | 3588.08325 | 90.45081 | 48.1376 |

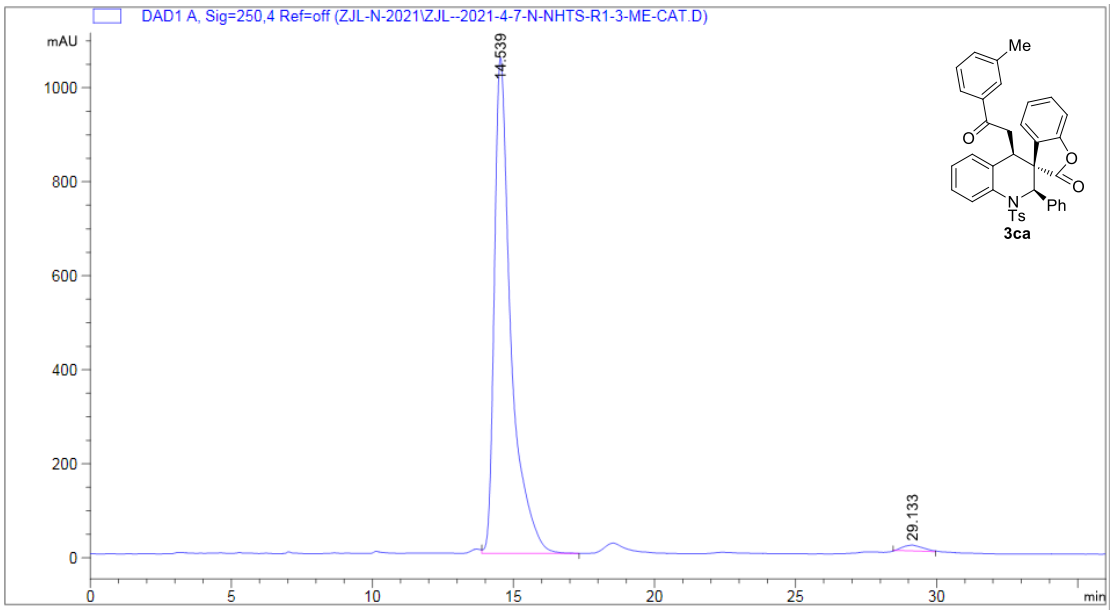


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 6.070 | 7052.77979 | 393.94077 | 96.2791 |
| 2 | DAD 250, 4 nm | 10.393 | 272.56815 | 9.98524 | 3.7209 |

**3ca**

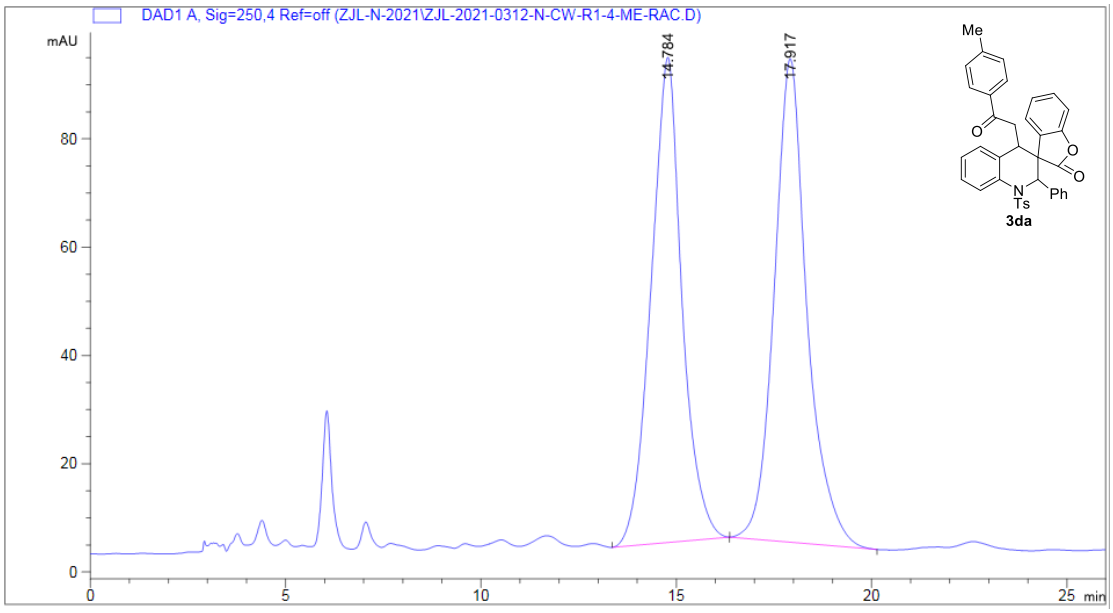



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 14.580 | 1.81340e4 | 440.57251 | 54.0773 |
| 2 | DAD 250, 4 nm | 29.002 | 1.53995e4 | 188.53185 | 45.9227 |

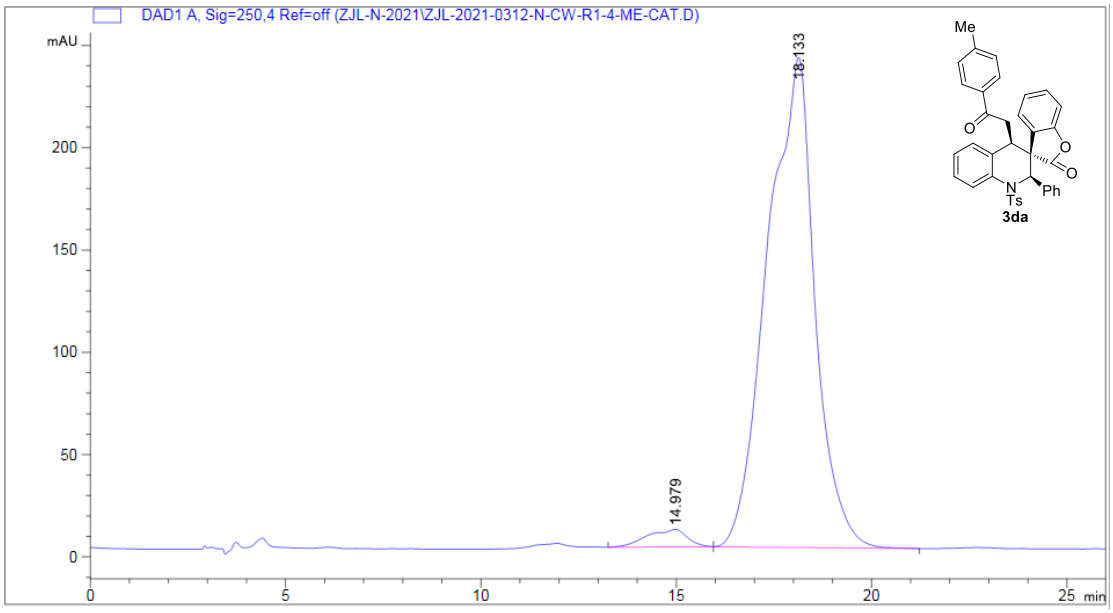


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 14.539 | 4.31380e4 | 1054.91199 | 98.6308 |
| 2 | DAD 250, 4 nm | 29.133 | 598.83057 | 12.12469 | 1.3692 |

**3da**

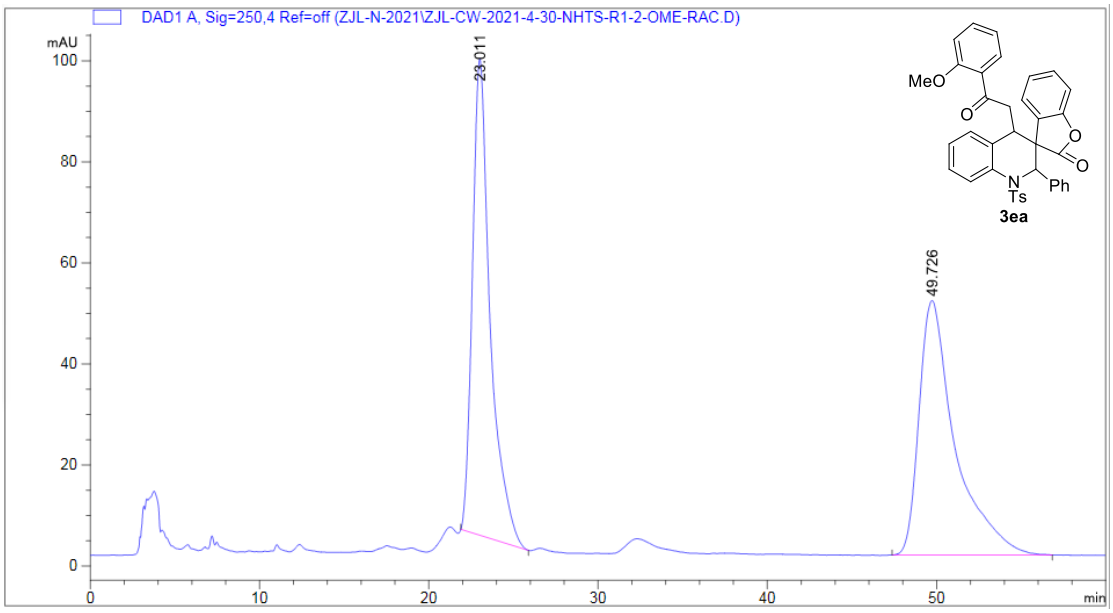



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 14.784 | 4928.29980 | 89.58771 | 48.5955 |
| 2 | DAD 250, 4 nm | 17.917 | 5213.17871 | 89.28972 | 51.4045 |

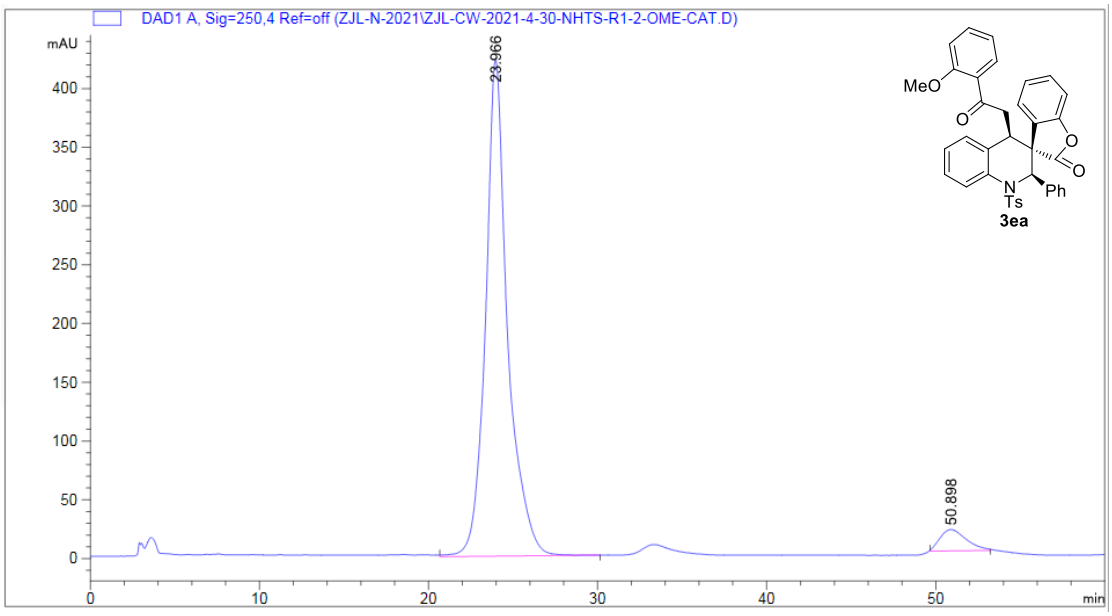


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 14.979 | 607.71344 | 8.56677 | 2.9163 |
| 2 | DAD 250, 4 nm | 18.133 | 2.02311e4 | 239.45514 | 97.0837 |

**3ea**

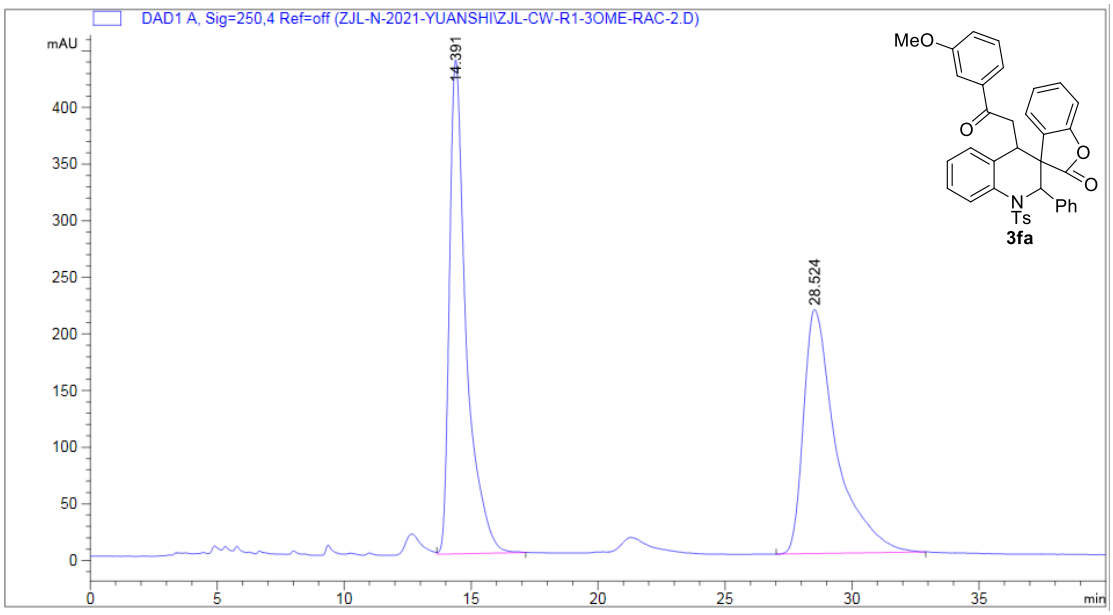



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 23.011 | 6872.66602 | 94.28802 | 48.0131 |
| 2 | DAD 250, 4 nm | 49.726 | 7441.47363 | 50.36050 | 51.9869 |

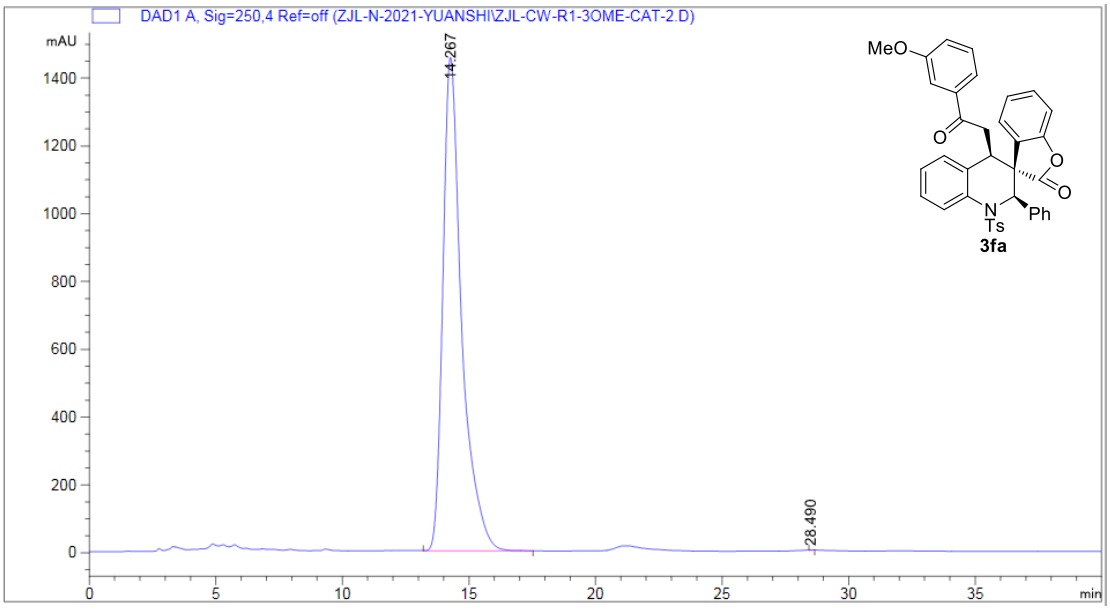


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 23.966 | 3.83354e4 | 422.24863 | 95.1559 |
| 2 | DAD 250, 4 nm | 50.898 | 1951.53491 | 18.06255 | 4.8441 |

**3fa**

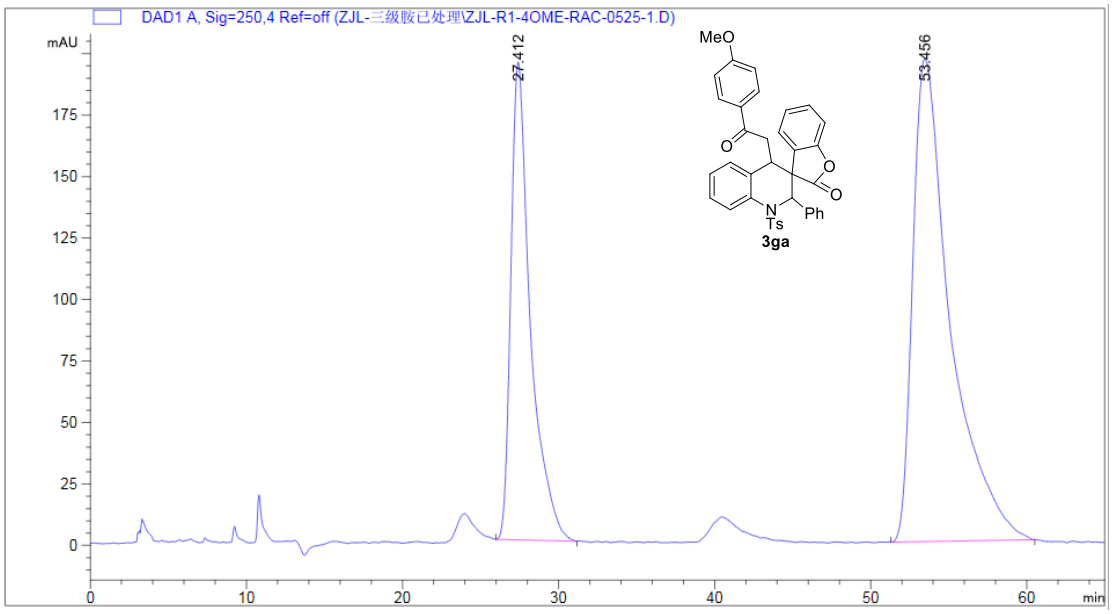



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 14.391 | 2.00347e4 | 436.27164 | 50.9378 |
| 2 | DAD 250, 4 nm | 28.524 | 1.92970e4 | 215.42924 | 49.0622 |

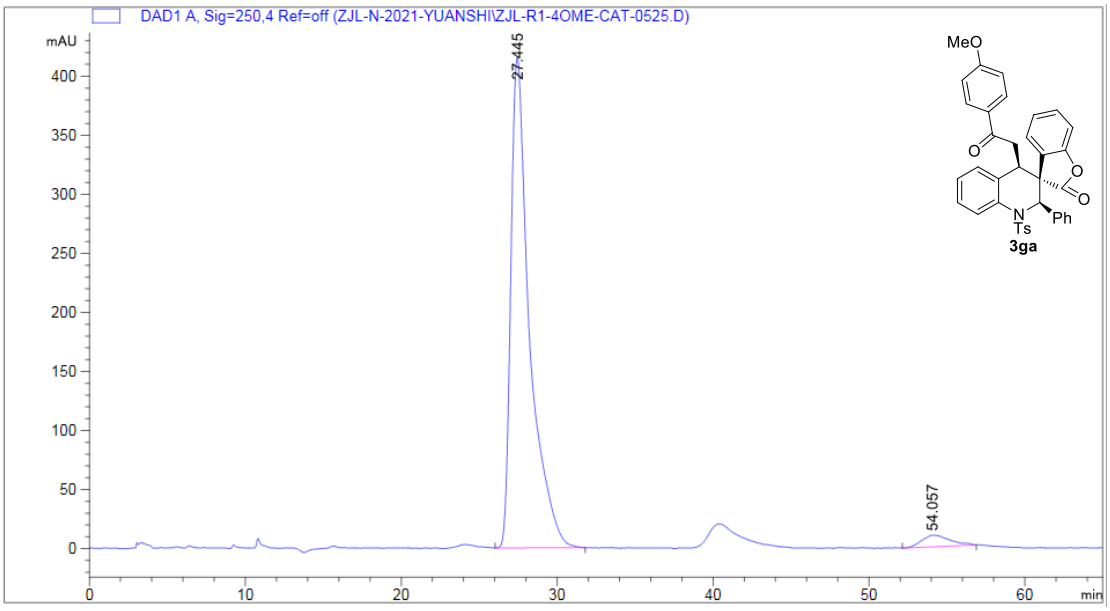


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 14.267 | 7.52313e4 | 1455.31104 | 99.9904 |
| 2 | DAD 250, 4 nm | 28.490 | 7.23830 | 1.00678 | 9.620e-3 |

**3ga**

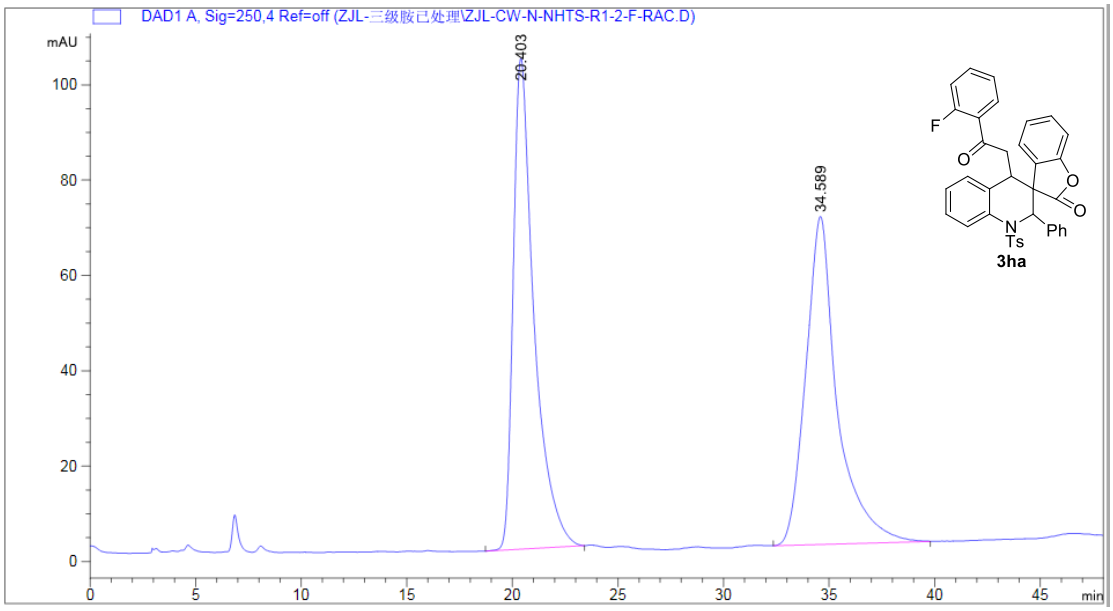



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 27.412 | 1.68873e4 | 194.29408 | 33.9812 |
| 2 | DAD 250, 4 nm | 53.456 | 3.28087e4 | 196.25618 | 66.0188 |

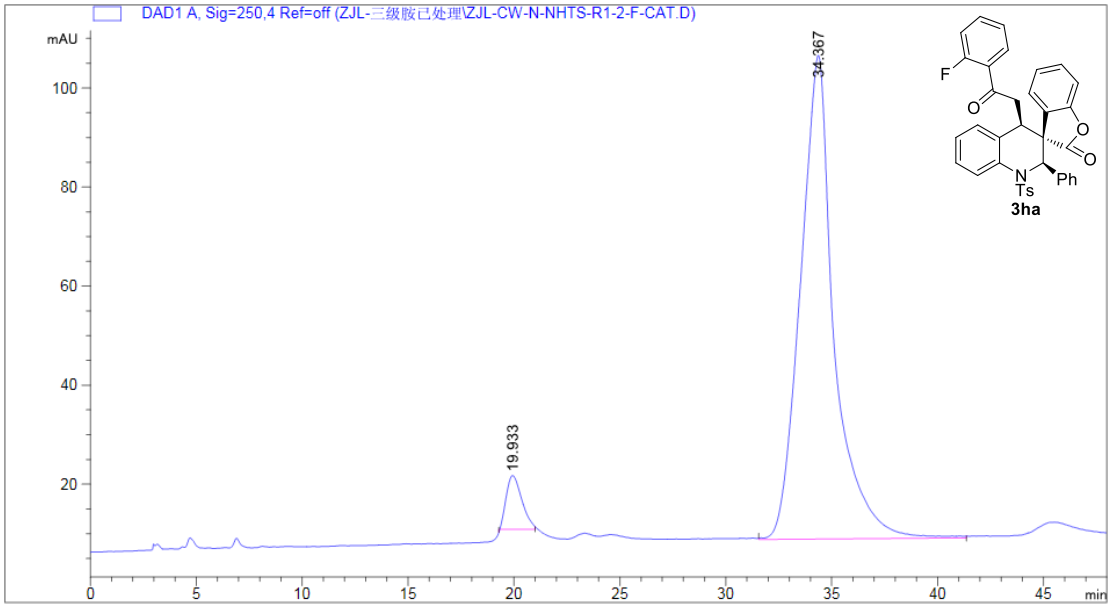


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 27.445 | 3.45381e4 | 415.24982 | 96.5282 |
| 2 | DAD 250, 4 nm | 54.057 | 1242.23608 | 9.90807 | 3.4718 |

**3ha**

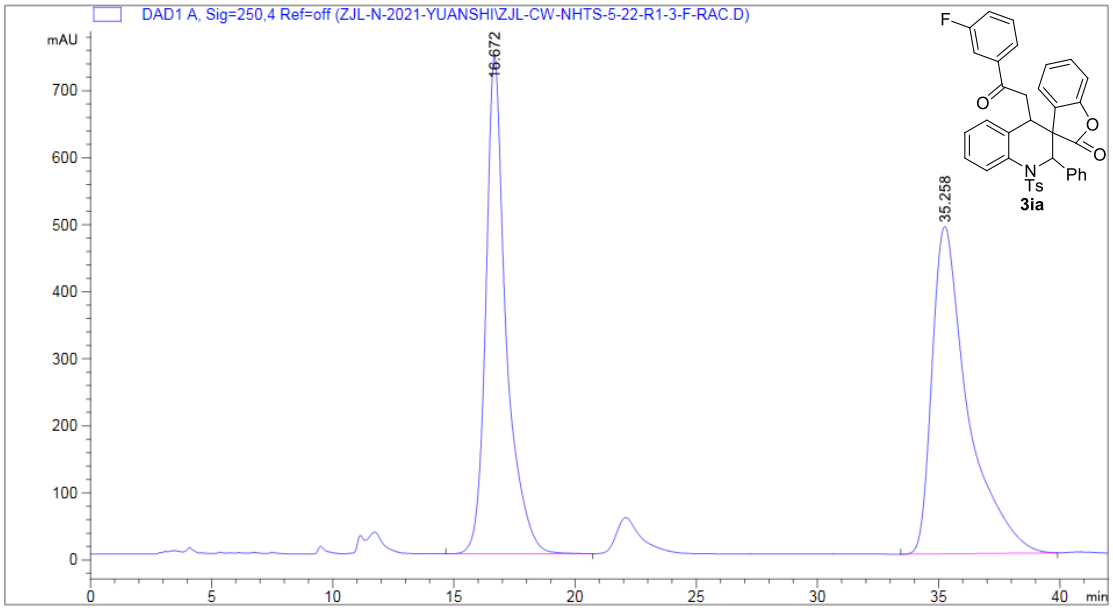



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 20.403 | 0.9934 | 7052.55811 | 49.7776 |
| 2 | DAD 250, 4 nm | 34.589 | 1.4431 | 7115.57910 | 50.2224 |

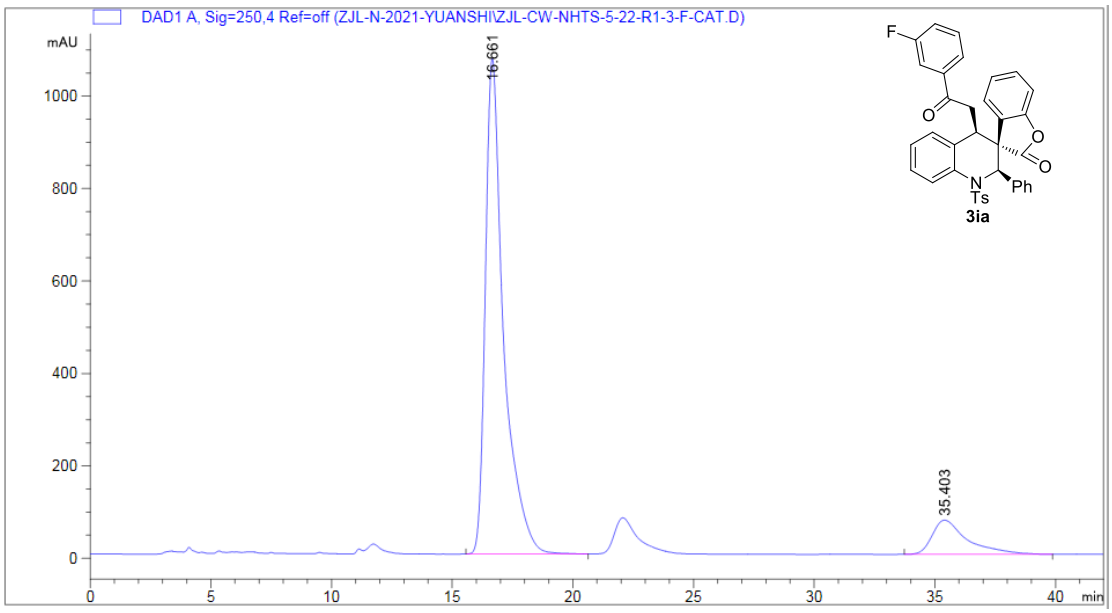


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 21.359 | 675.55219 | 11.30569 | 4.2601 |
| 2 | DAD 250, 4 nm | 39.195 | 1.51822e4 | 115.96967 | 95.7399 |

**3ia**

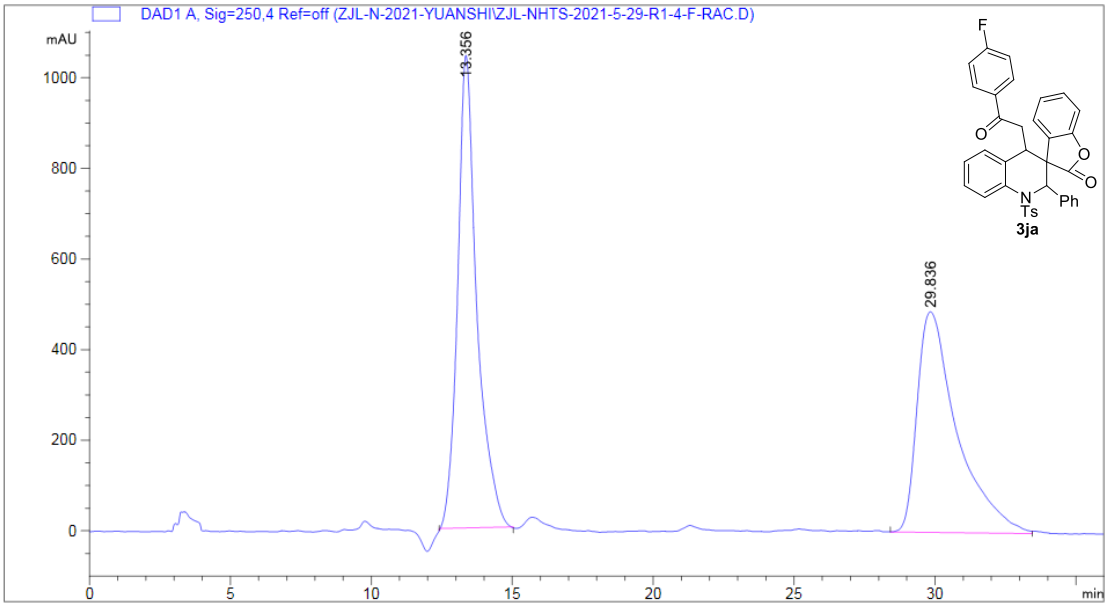



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 16.672 | 4.32177e4 | 742.42120 | 46.3847 |
| 2 | DAD 250, 4 nm | 35.258 | 4.99547e4 | 487.96448 | 53.6153 |

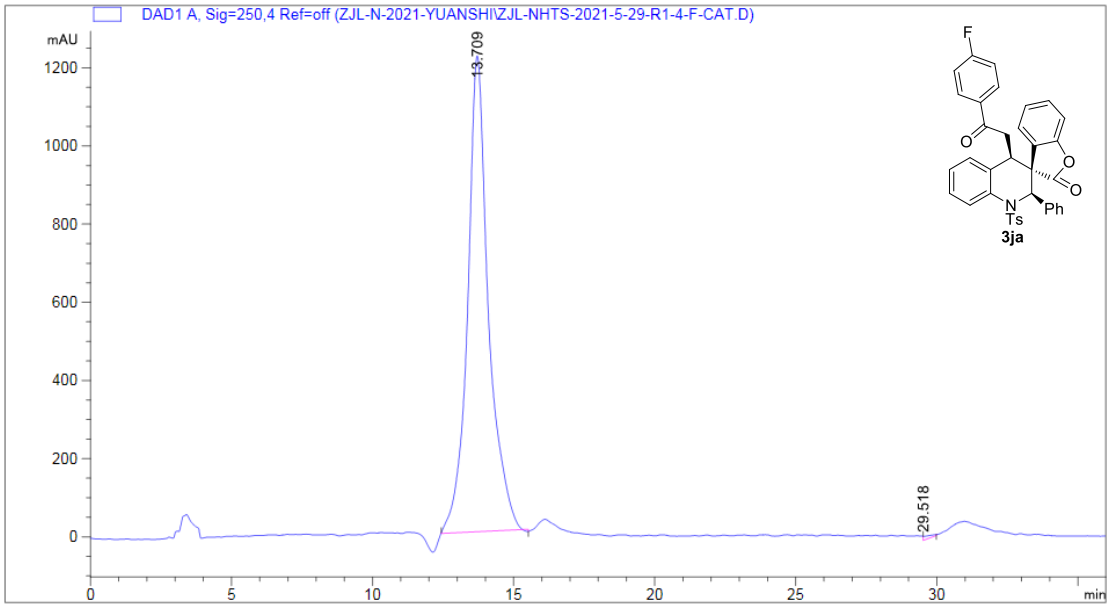


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 16.661 | 5.64118e4 | 1071.86475 | 88.3547 |
| 2 | DAD 250, 4 nm | 35.403 | 7435.19482 | 73.77364 | 11.6453 |

**3ja**

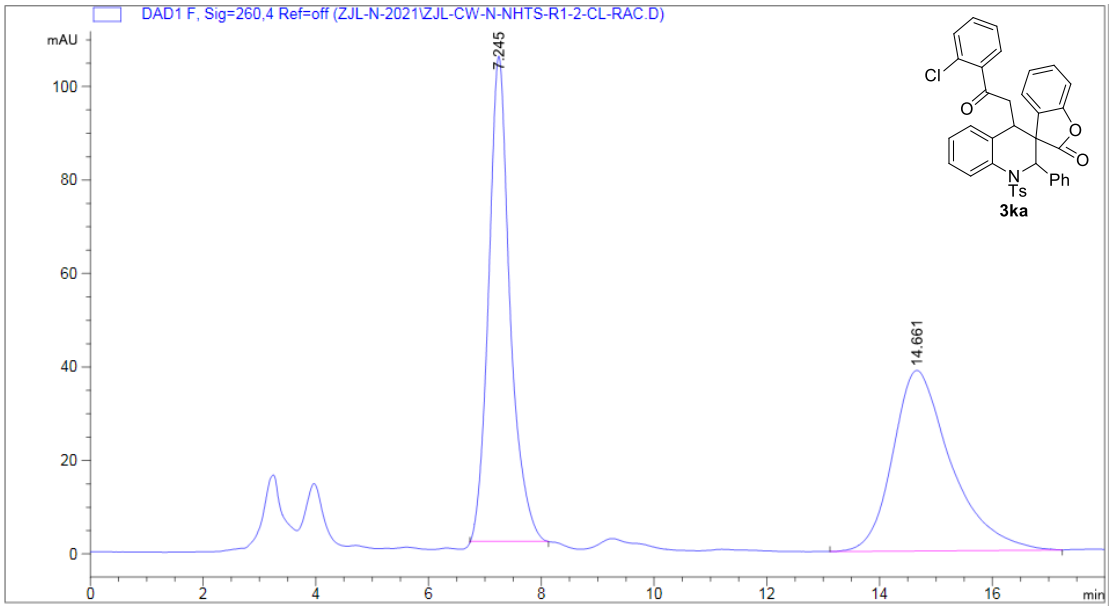



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 13.356 | 4.95393e4 | 1042.54248 | 50.8347 |
| 2 | DAD 250, 4 nm | 29.836 | 4.79125e4 | 486.72095 | 49.1653 |

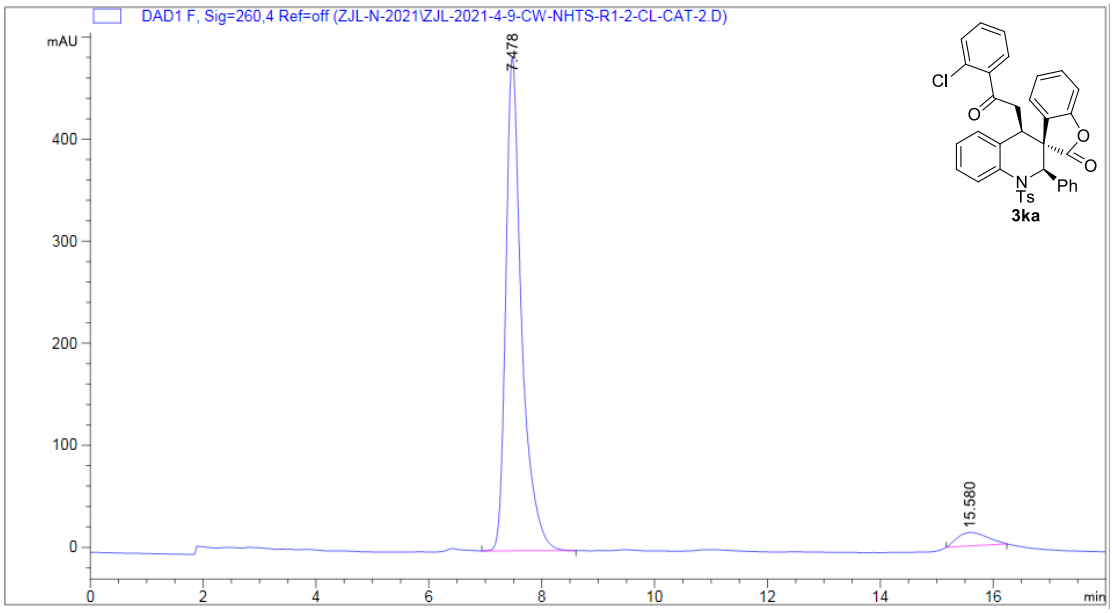


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 13.709 | 6.26077e4 | 1217.32373 | 99.7231 |
| 2 | DAD 250, 4 nm | 29.518 | 173.85800 | 10.48030 | 0.2769 |

**3ka**

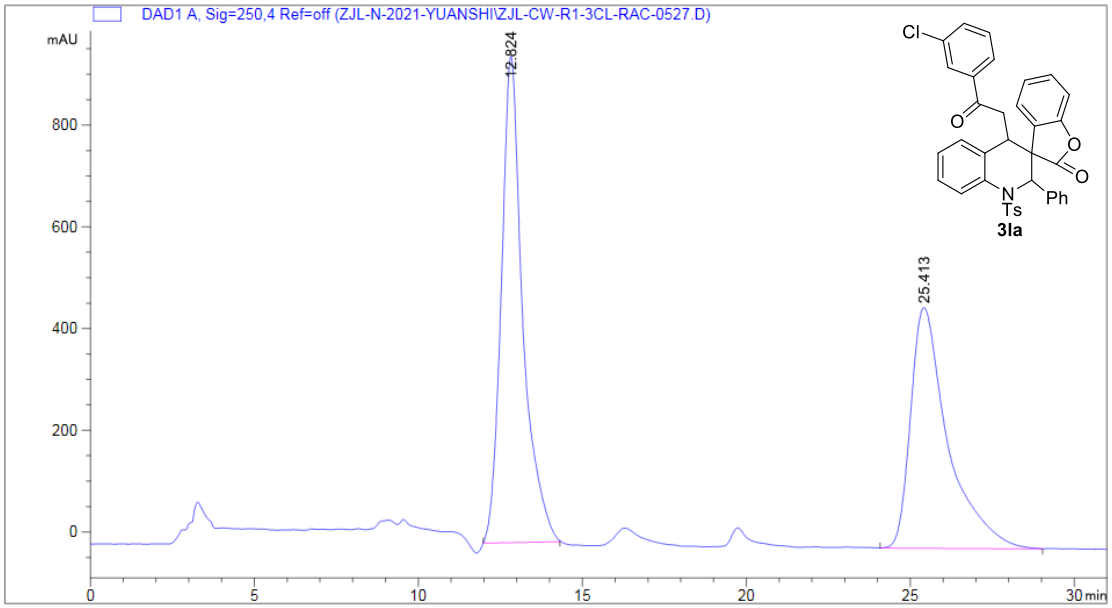



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 260, 4 nm | 7.245 | 2741.87256 | 103.82861 | 49.7848 |
| 2 | DAD 260, 4 nm | 14.661 | 2765.57788 | 38.62230 | 50.2152 |

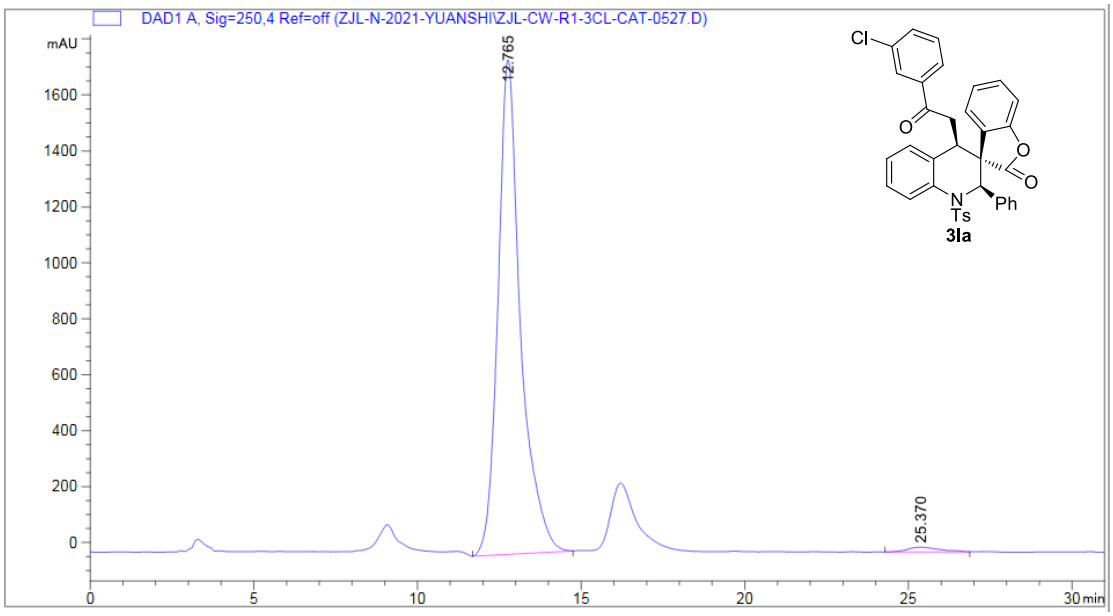


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 260, 4 nm | 7.478 | 9449.63965 | 483.37592 | 95.1811 |
| 2 | DAD 260, 4 nm | 15.580 | 478.41986 | 13.06848 | 4.8189 |

**3la**

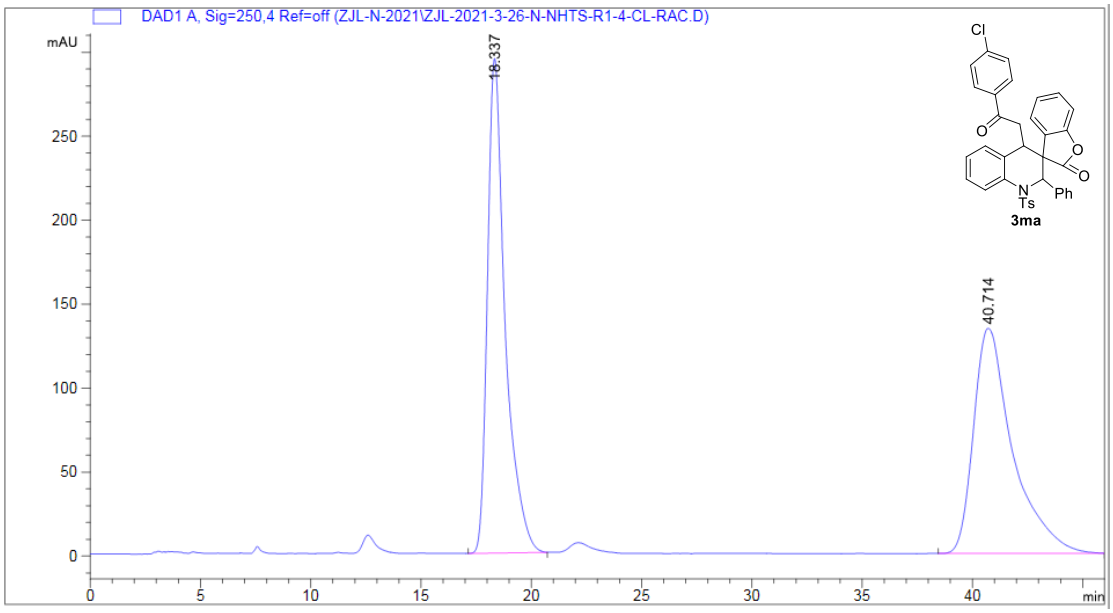



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 260, 4 nm | 12.824 | 4.35237e4 | 956.93011 | 53.8628 |
| 2 | DAD 260, 4 nm | 25.413 | 3.72811e4 | 472.90057 | 46.1372 |

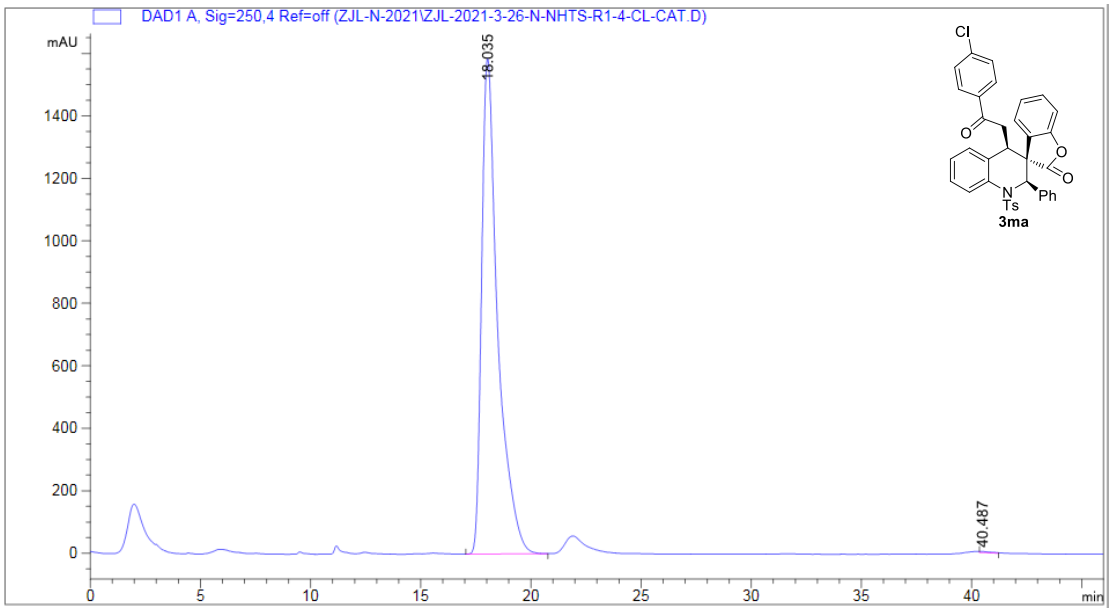


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 260, 4 nm | 12.765 | 8.45612e4 | 1766.95386 | 98.6523 |
| 2 | DAD 260, 4 nm | 25.370 | 1155.19116 | 16.69323 | 1.3477 |

**3ma**

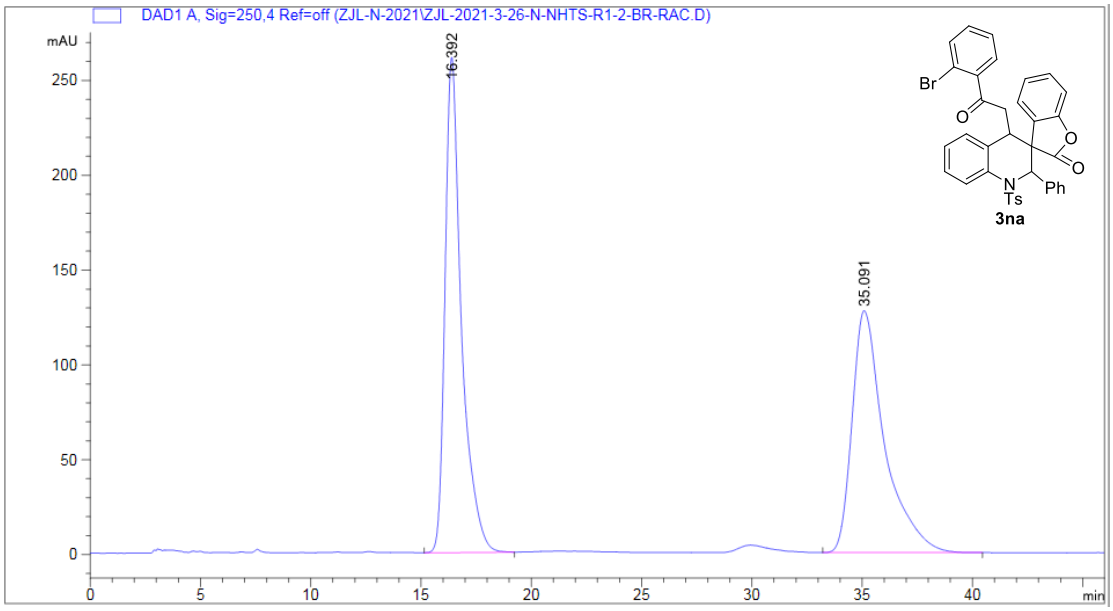



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 18.337 | 1.64716e4 | 294.52563 | 49.9713 |
| 2 | DAD 250, 4 nm | 40.714 | 1.64905e4 | 134.07349 | 50.0287 |

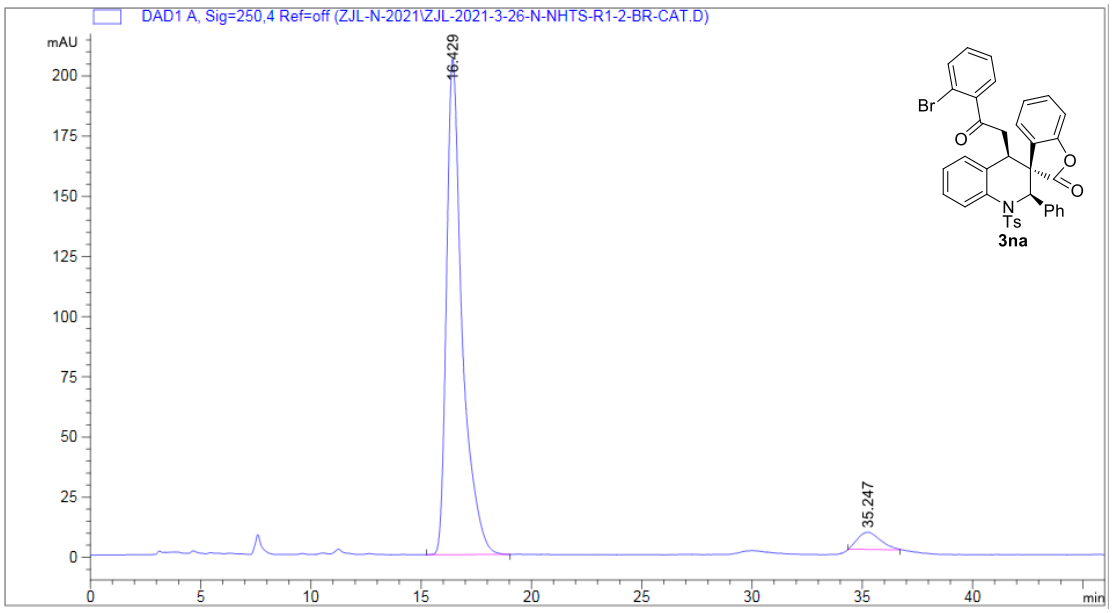


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 18.035 | 8.09576e4 | 1586.20813 | 99.8441 |
| 2 | DAD 250, 4 nm | 40.487 | 126.42647 | 3.55792 | 0.1559 |

**3na**

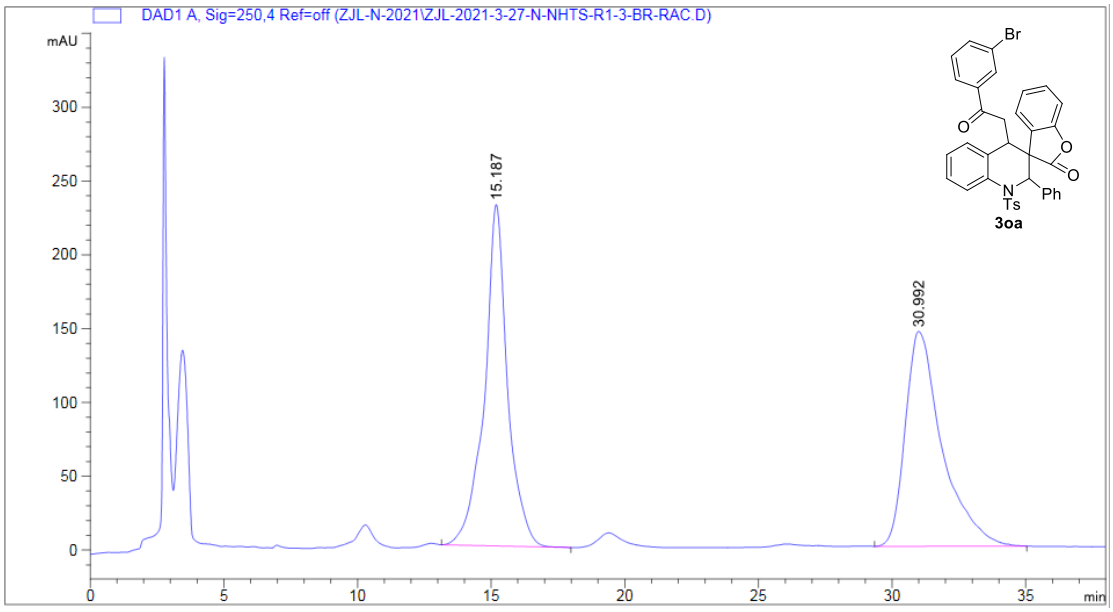



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 16.392 | 1.35207e4 | 261.14063 | 50.8641 |
| 2 | DAD 250, 4 nm | 35.091 | 1.30613e4 | 127.60278 | 49.1359 |

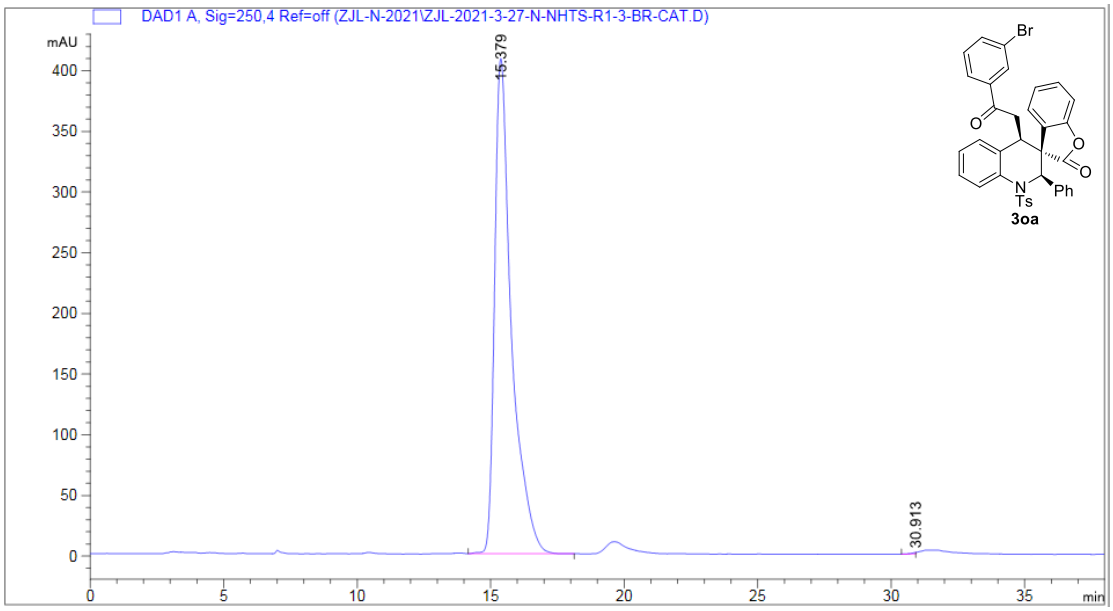


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 16.429 | 1.01928e4 | 206.11870 | 95.2244 |
| 2 | DAD 250, 4 nm | 35.247 | 511.18179 | 7.13670 | 4.7756 |

**3oa**

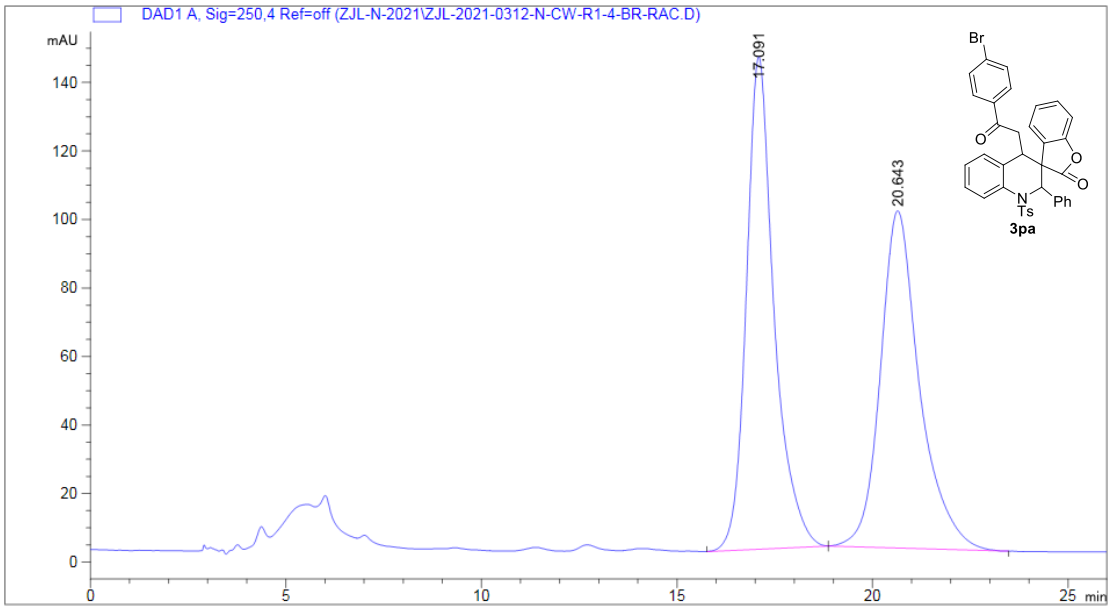



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 15.187 | 1.39068e4 | 231.35269 | 50.0133 |
| 2 | DAD 250, 4 nm | 30.992 | 1.38994e4 | 145.49487 | 49.9867 |

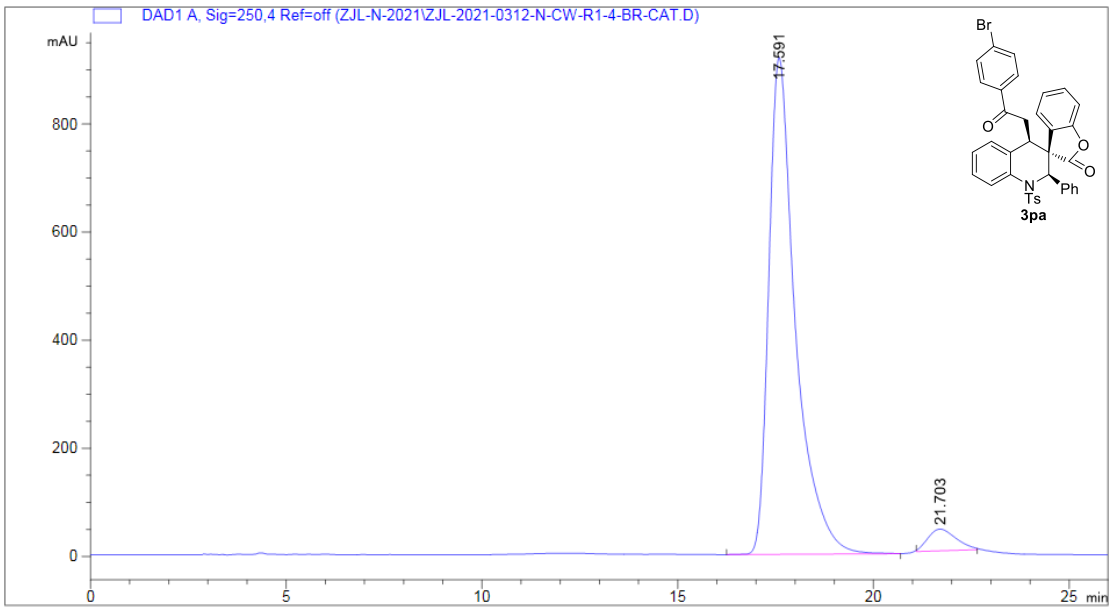


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 15.379 | 1.79240e4 | 408.03281 | 99.9246 |
| 2 | DAD 250, 4 nm | 30.913 | 13.53295 | 1.11918 | 0.0754 |

**3pa**

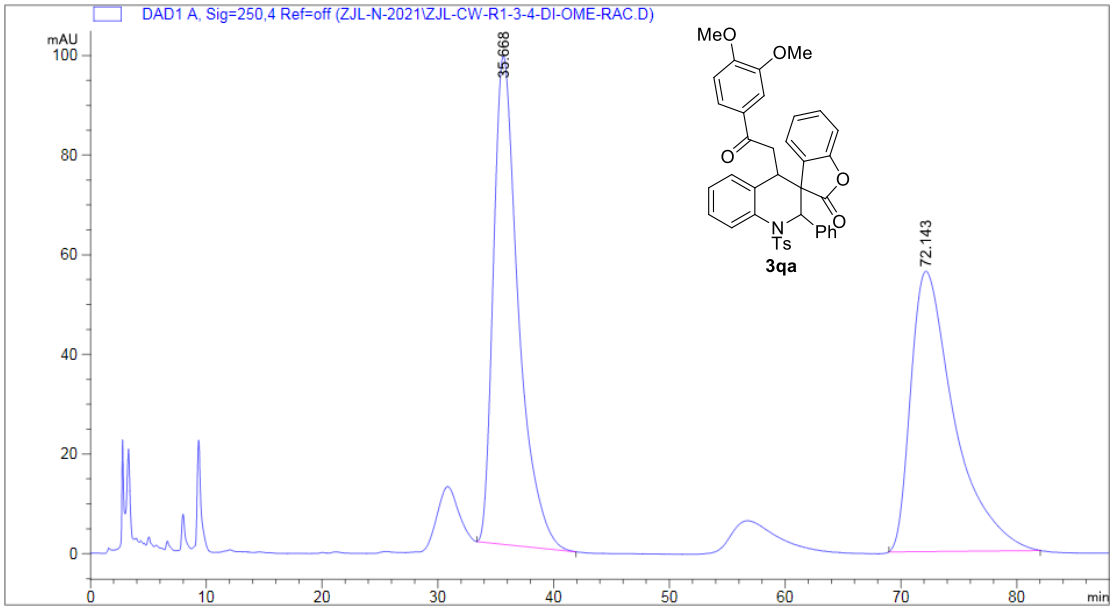



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 17.091 | 7096.58691 | 143.76282 | 50.8430 |
| 2 | DAD 250, 4 nm | 20.643 | 6861.26123 | 98.40793 | 49.1570 |

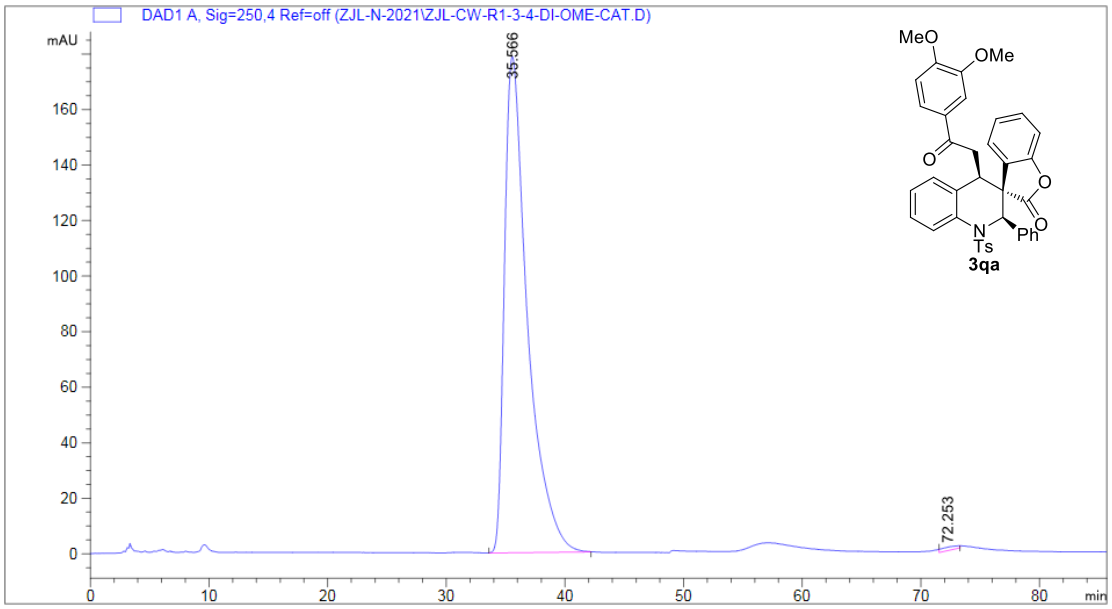


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 17.591 | 4.35885e4 | 918.84094 | 95.6189 |
| 2 | DAD 250, 4 nm | 21.703 | 1997.17004 | 40.02856 | 4.3811 |

**3qa**

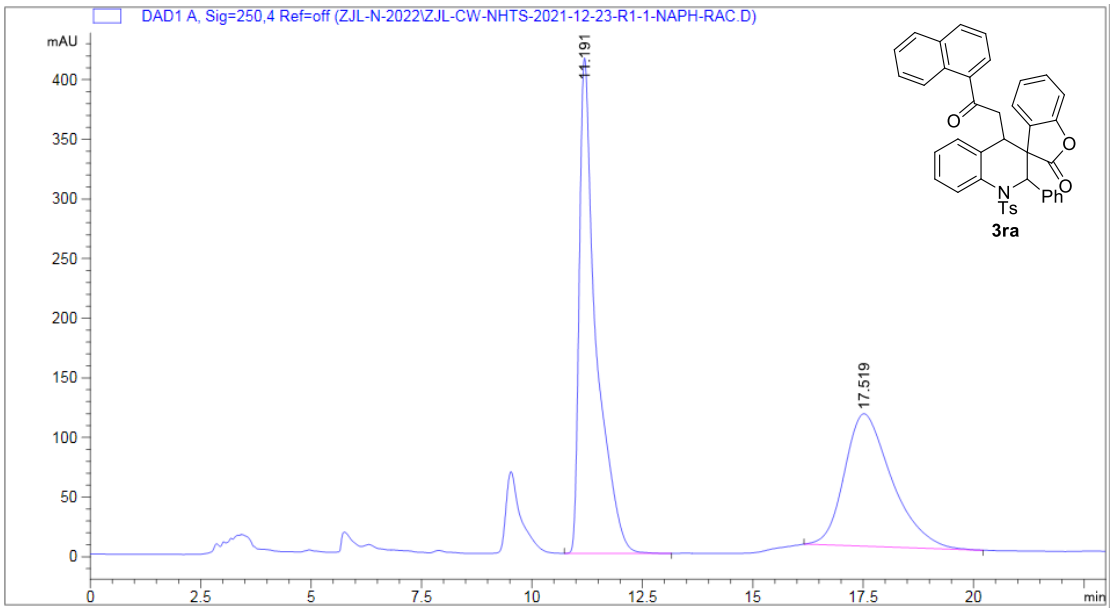



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 35.668 | 1.47099e4 | 98.03483 | 50.0432 |
| 2 | DAD 250, 4 nm | 72.143 | 1.46845e4 | 56.24397 | 49.9568 |

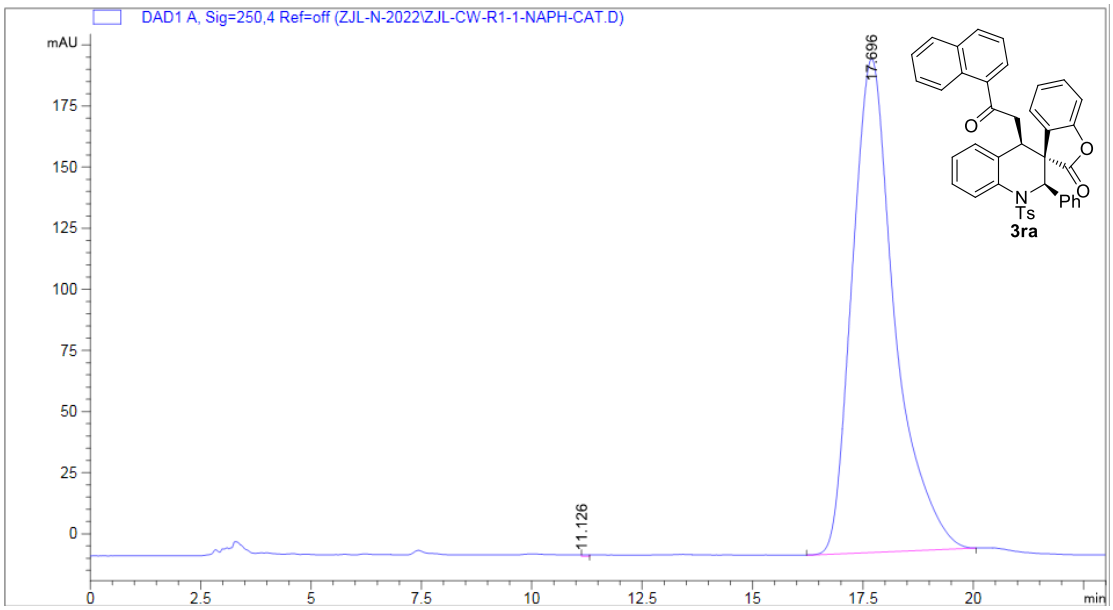


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 35.566 | 2.40554e4 | 178.58833 | 99.4946 |
| 2 | DAD 250, 4 nm | 72.253 | 122.19086 | 1.26997 | 0.5054 |

**3ra**

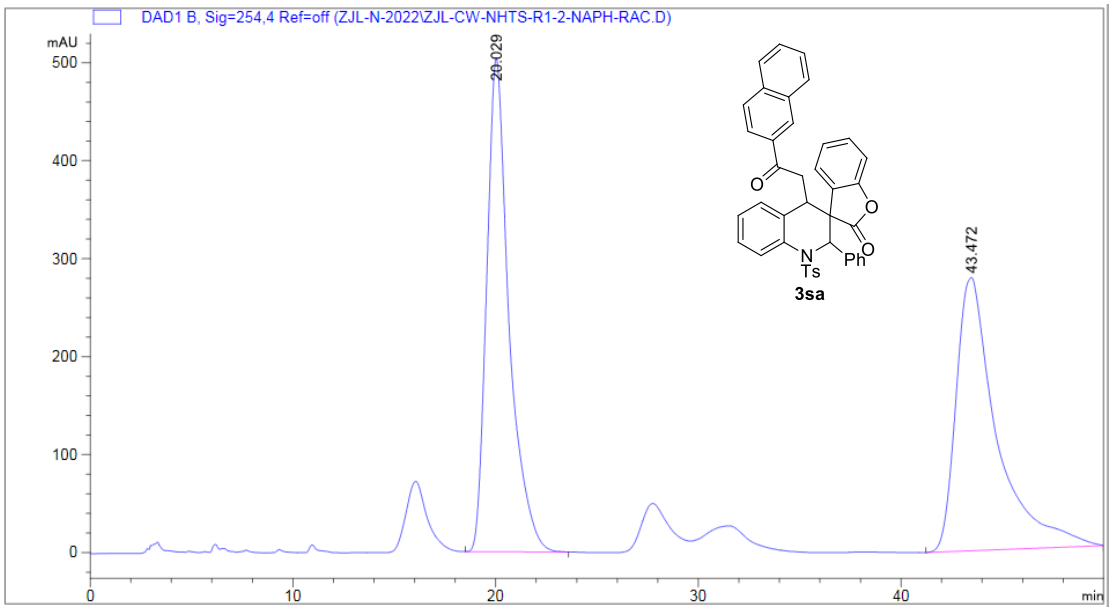



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 11.191 | 1.09992e4 | 415.67139 | 57.0671 |
| 2 | DAD 250, 4 nm | 17.519 | 8274.91797 | 111.07327 | 42.9329 |

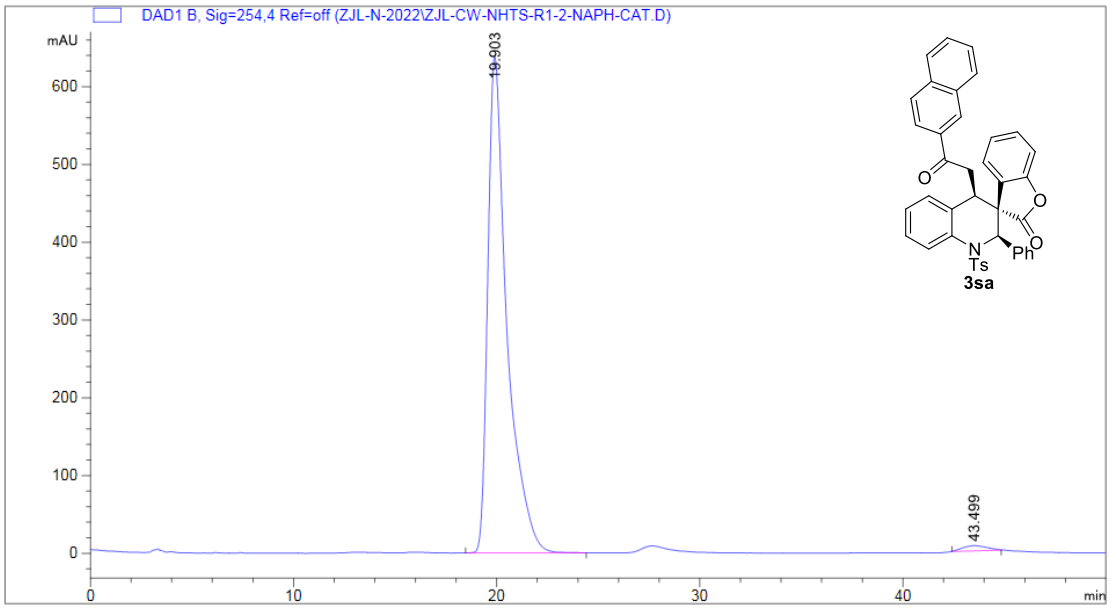


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 11.126 | 6.78193 | 6.34107e-1 | 0.0500 |
| 2 | DAD 250, 4 nm | 17.696 | 1.35674e4 | 201.95763 | 99.9500 |

**3sa**

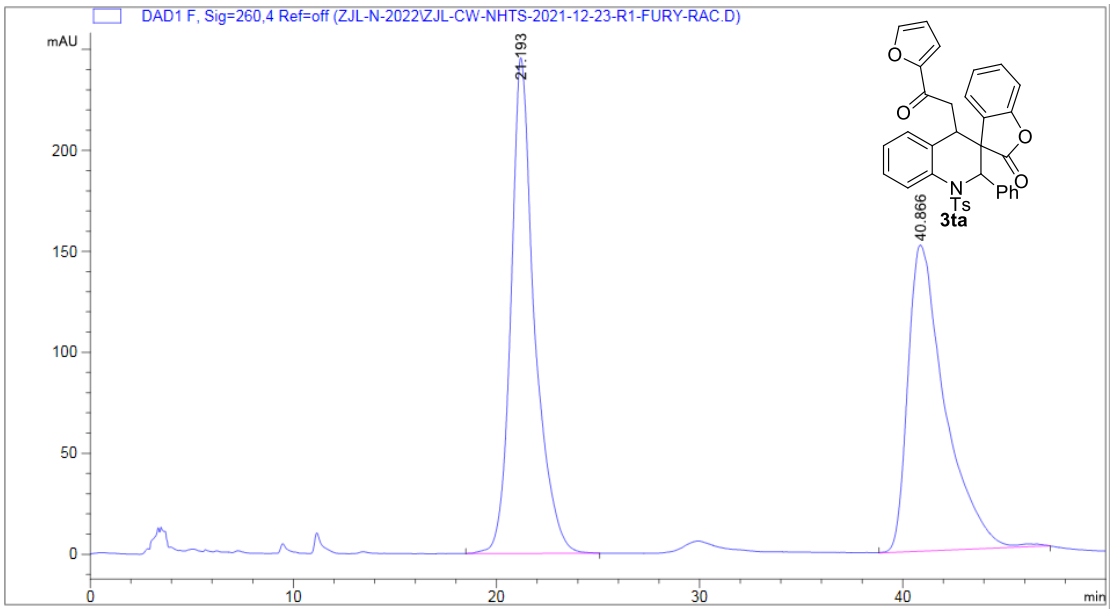



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 254, 4 nm | 20.029 | 3.85763e4 | 503.32178 | 49.9278 |
| 2 | DAD 254, 4 nm | 43.472 | 3.86879e4 | 278.80356 | 50.0722 |

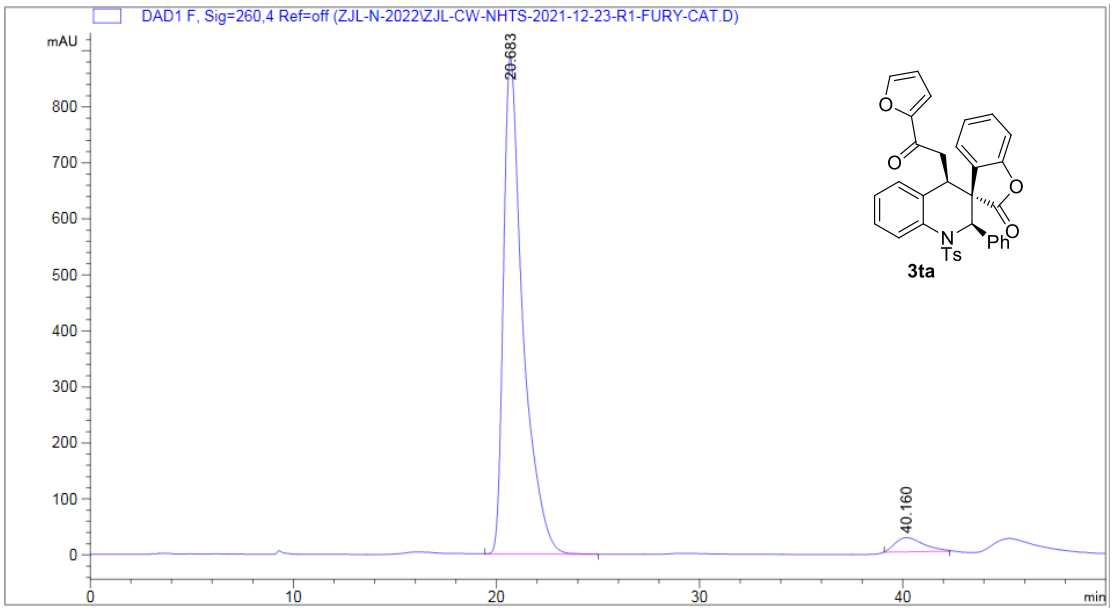


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 254, 4 nm | 19.903 | 4.19067e4 | 637.88403 | 98.7082 |
| 2 | DAD 254, 4 nm | 43.499 | 548.43799 | 6.67292 | 1.2918 |

**3ta**

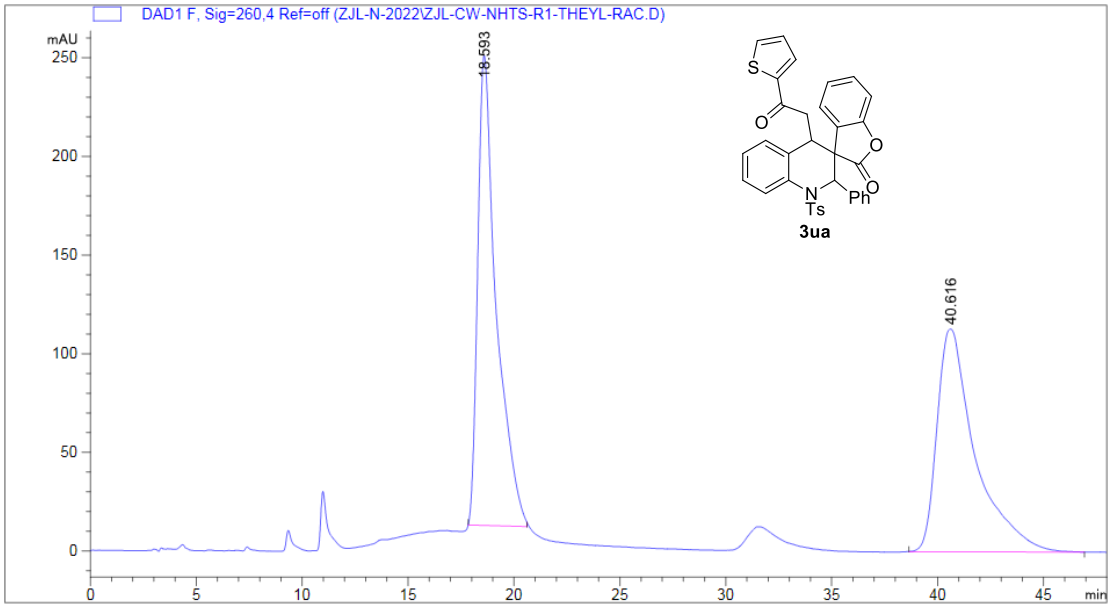



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 260, 4 nm | 21.193 | 1.97732e4 | 1.97732e4 | 50.6467 |
| 2 | DAD 260, 4 nm | 40.866 | 1.92683e4 | 40.866 | 49.3533 |

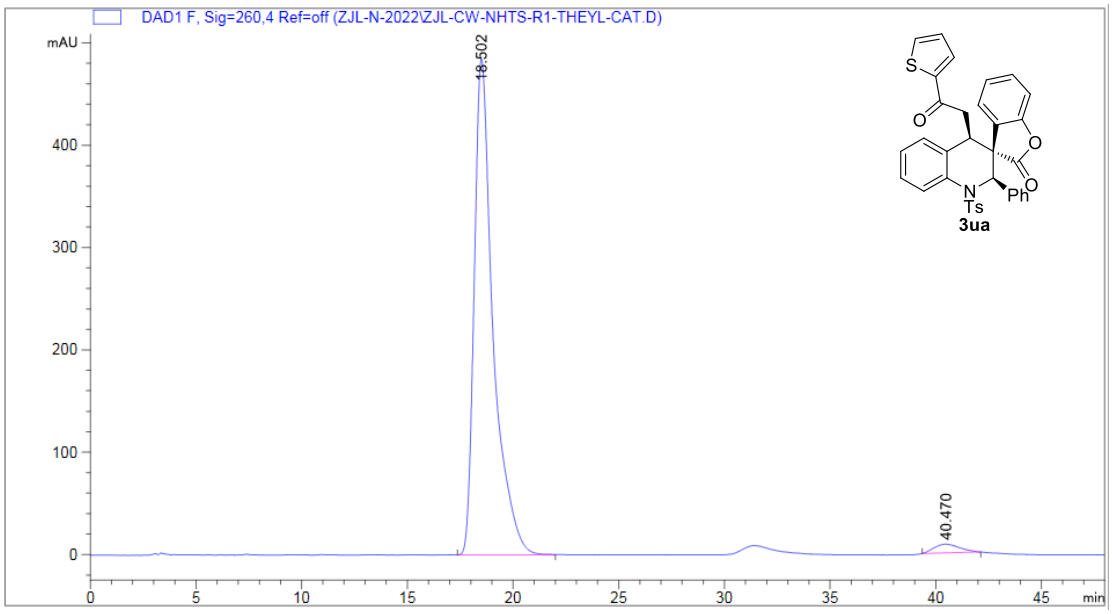


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 260, 4 nm | 20.683 | 5.90141e4 | 886.04303 | 96.0114 |
| 2 | DAD 260, 4 nm | 40.160 | 2451.61963 | 25.28139 | 3.9886 |

**3ua**

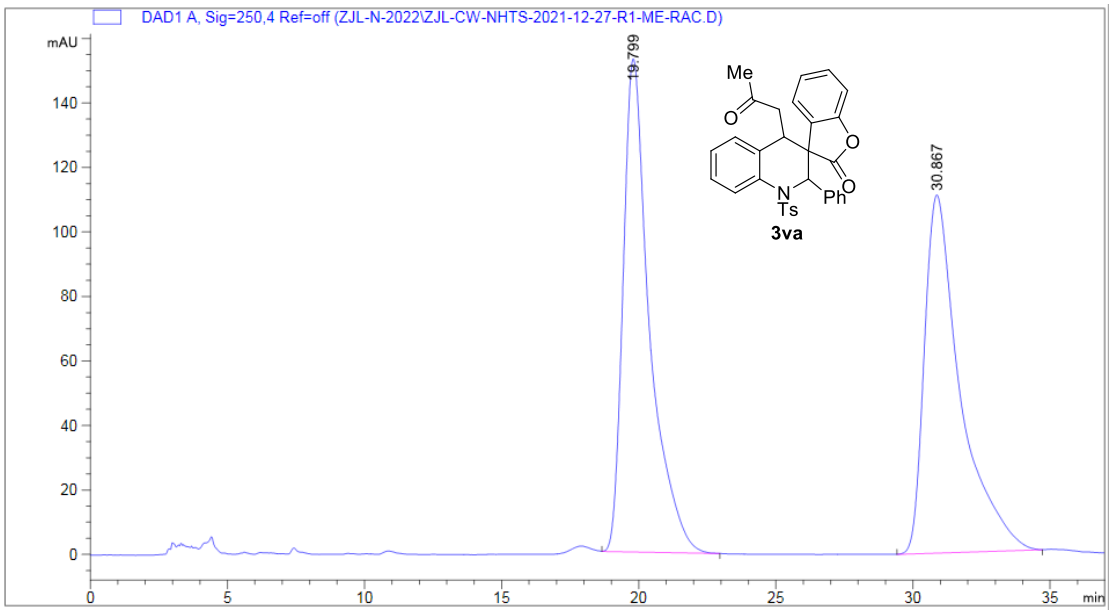



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 260, 4 nm | 18.593 | 1.45535e4 | 238.09624 | 50.8614 |
| 2 | DAD 260, 4 nm | 40.616 | 1.40605e4 | 112.84756 | 49.1386 |

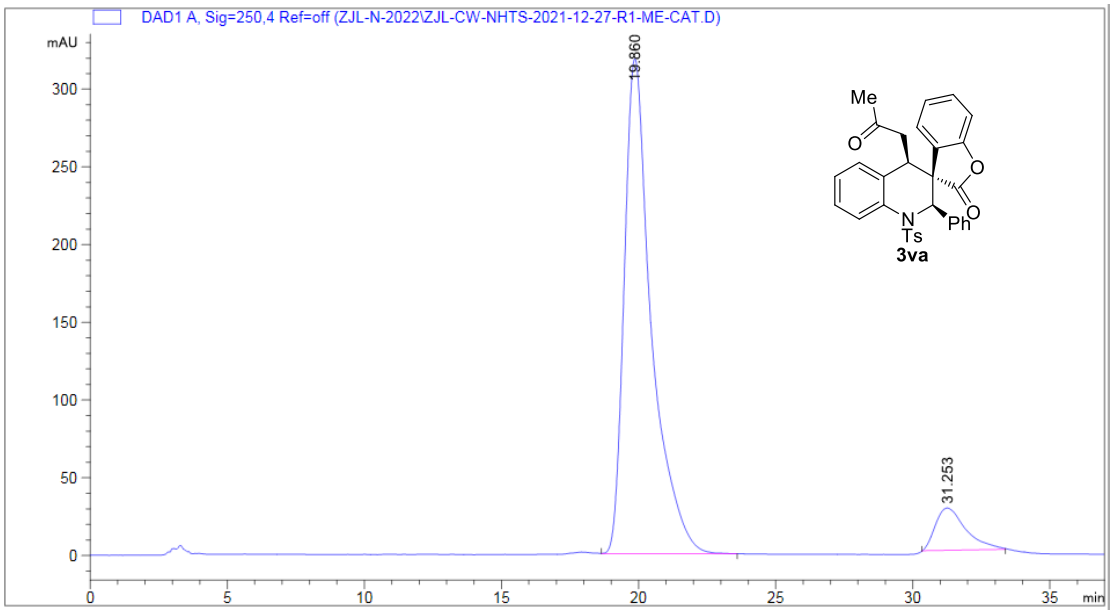


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 260, 4 nm | 18.502 | 2.99928e4 | 484.77710 | 97.7303 |
| 2 | DAD 260, 4 nm | 40.470 | 696.55865 | 8.34602 | 2.2697 |

**3va**

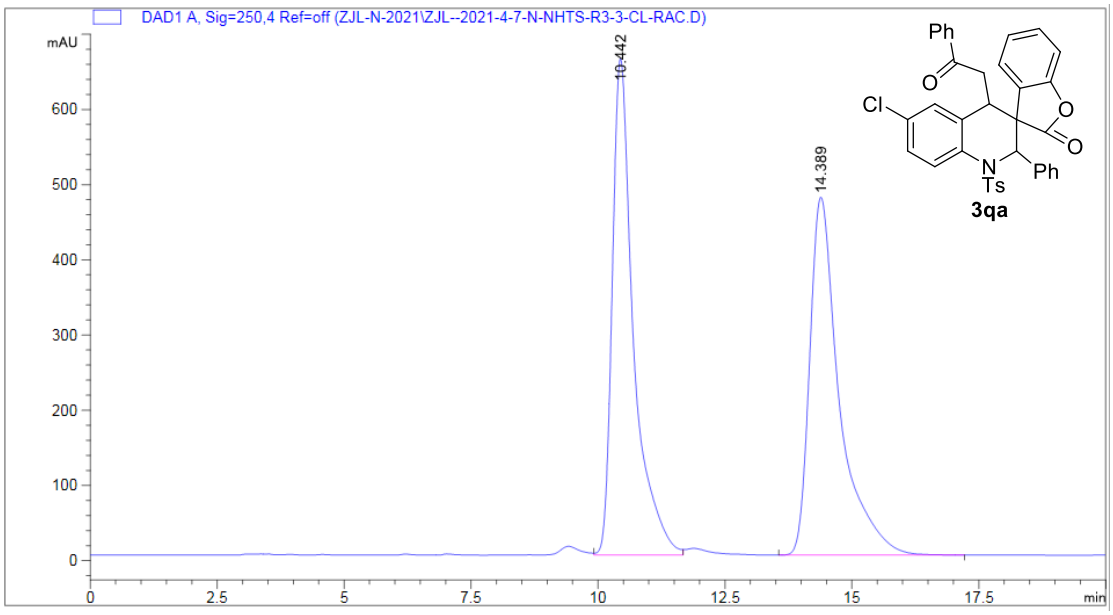



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 19.799 | 19.799 | 152.89020 | 50.3917 |
| 2 | DAD 260, 4 nm | 30.867 | 30.867 | 111.04134 | 49.6083 |

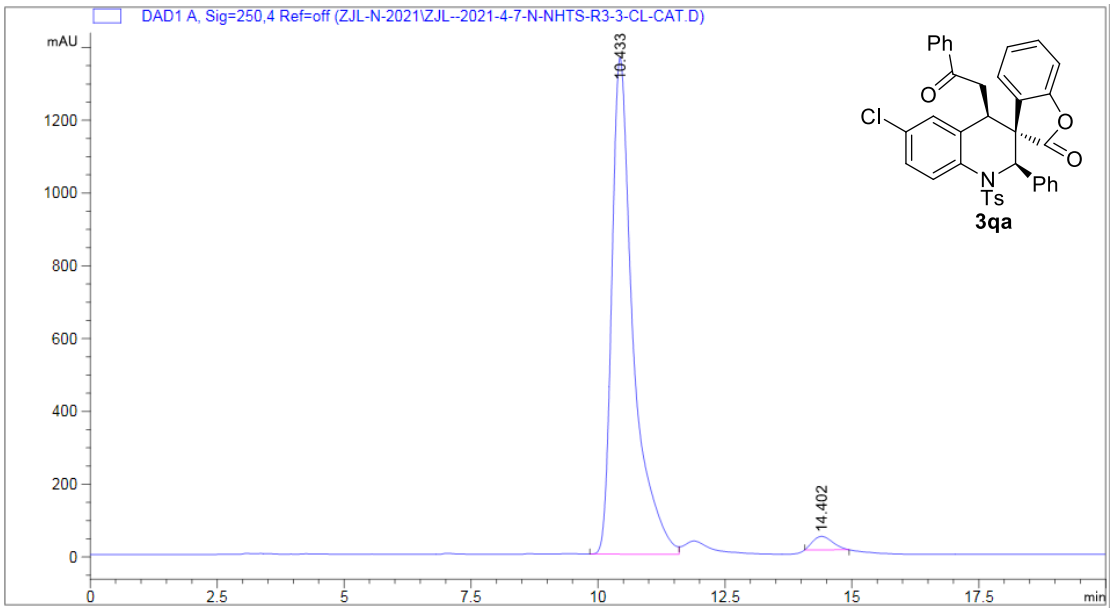


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 19.860 | 2.18952e4 | 318.32214 | 91.2515 |
| 2 | DAD 260, 4 nm | 31.253 | 2099.13135 | 27.13150 | 8.7485 |

**3qa**

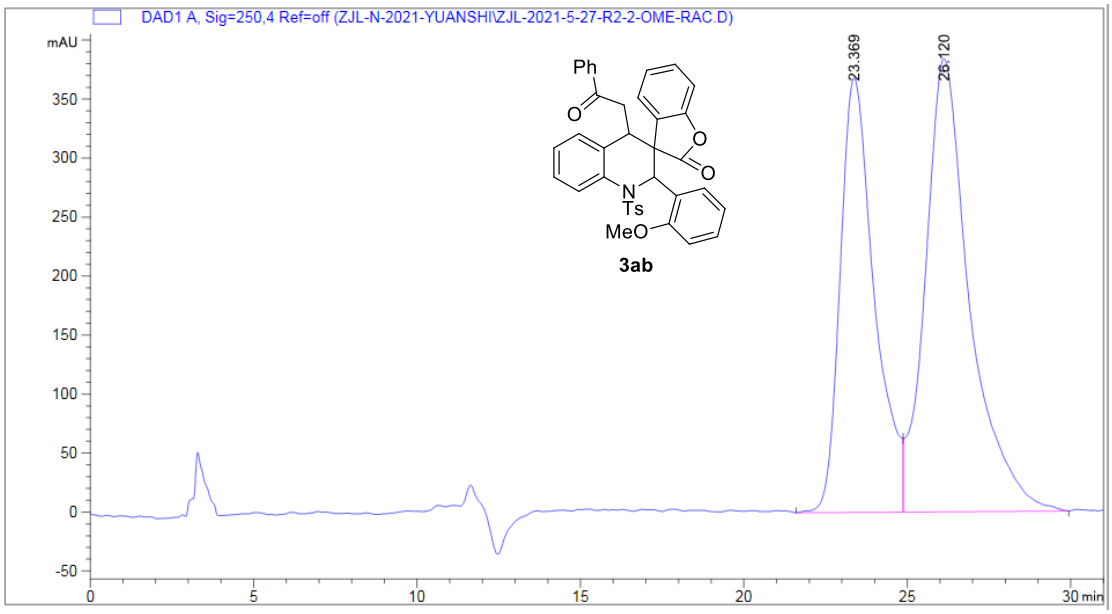



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 10.442 | 1.91928e4 | 659.83301 | 49.8602 |
| 2 | DAD 250, 4 nm | 14.389 | 1.93004e4 | 475.76855 | 50.1398 |

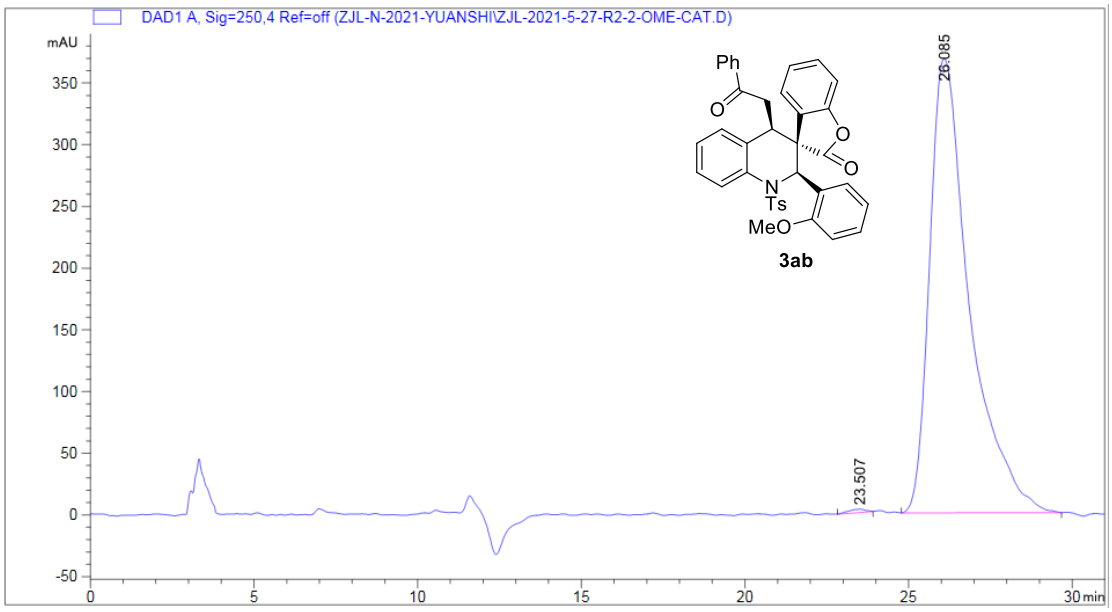


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 10.433 | 3.98394e4 | 1364.19592 | 97.5292 |
| 2 | DAD 250, 4 nm | 14.402 | 1009.30377 | 37.05903 | 2.4708 |

**3ab**

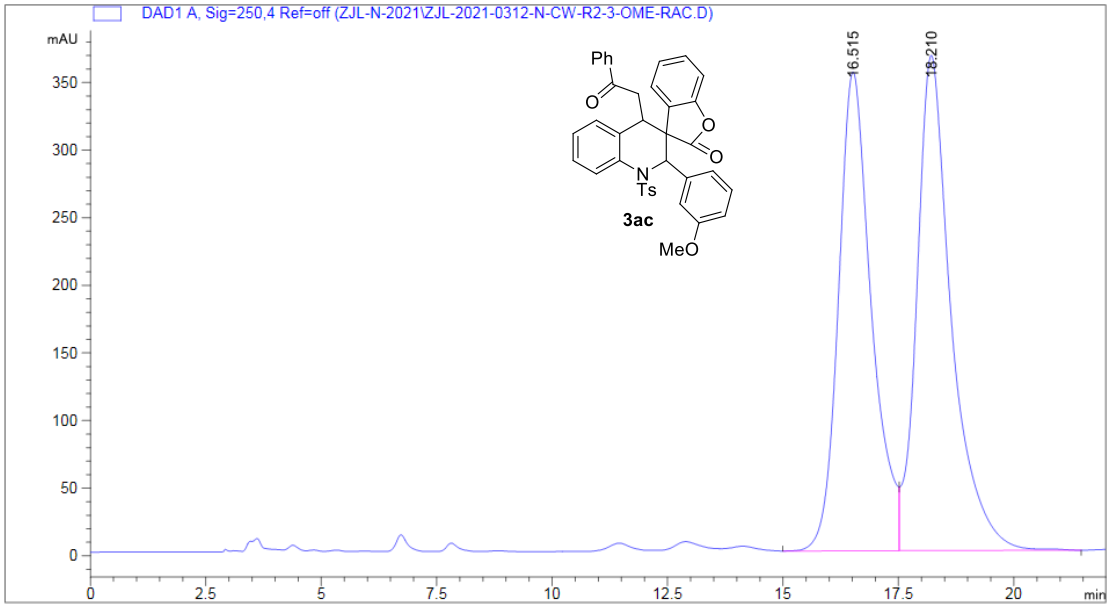



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 23.369 | 2.68786e4 | 367.89960 | 42.5137 |
| 2 | DAD 250, 4 nm | 26.120 | 3.63448e4 | 384.00610 | 57.4863 |

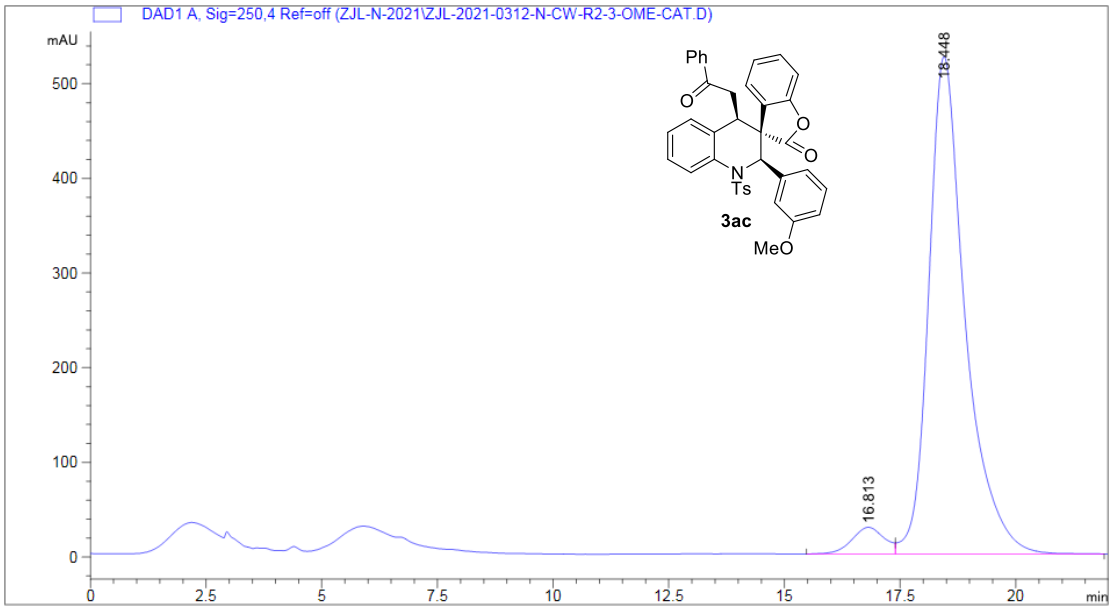


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 23.507 | 95.86879 | 2.58806 | 0.3067 |
| 2 | DAD 250, 4 nm | 26.085 | 3.11628e4 | 367.96957 | 99.6933 |

**3ac**

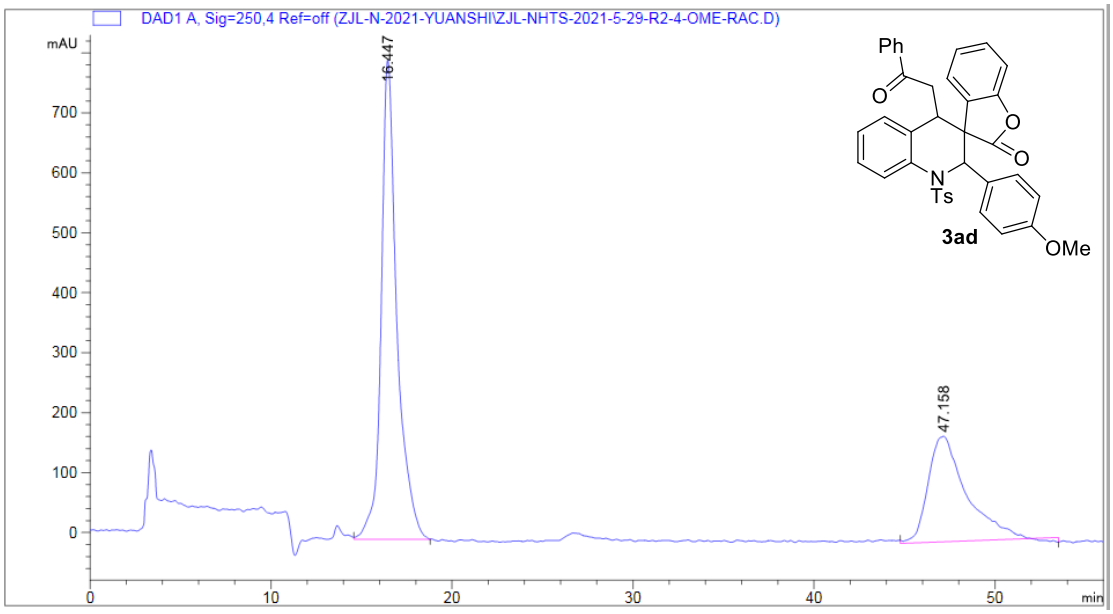



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 16.515 | 1.75938e4 | 354.12482 | 48.0240 |
| 2 | DAD 250, 4 nm | 18.210 | 1.90416e4 | 366.19574 | 51.9760 |

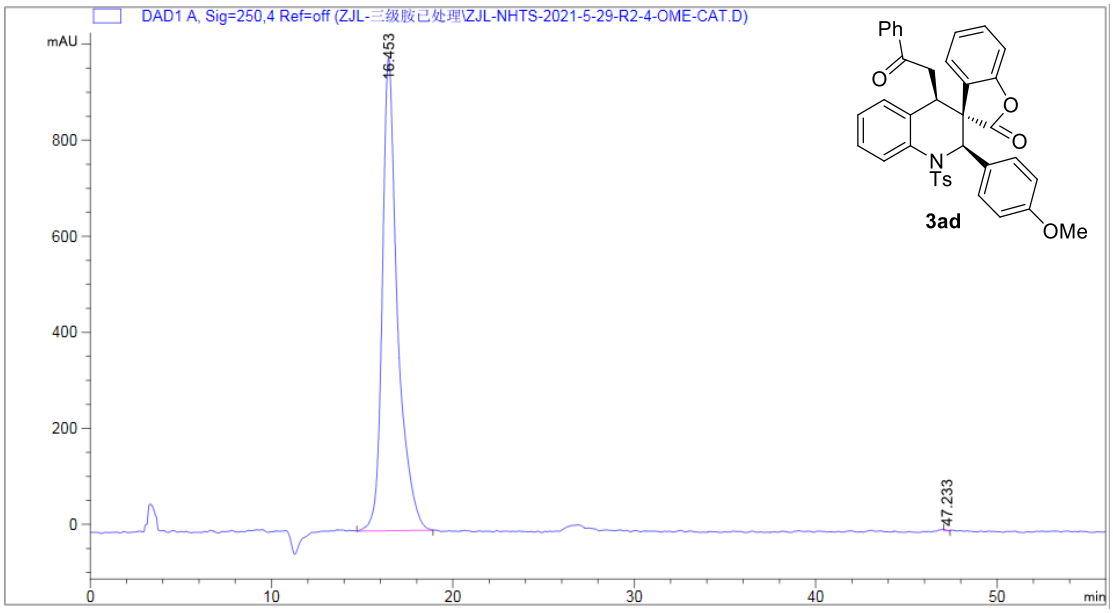


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 16.813 | 1381.38684 | 28.19214 | 4.5646 |
| 2 | DAD 250, 4 nm | 18.448 | 2.88817e4 | 525.61682 | 95.4354 |

**3ad**

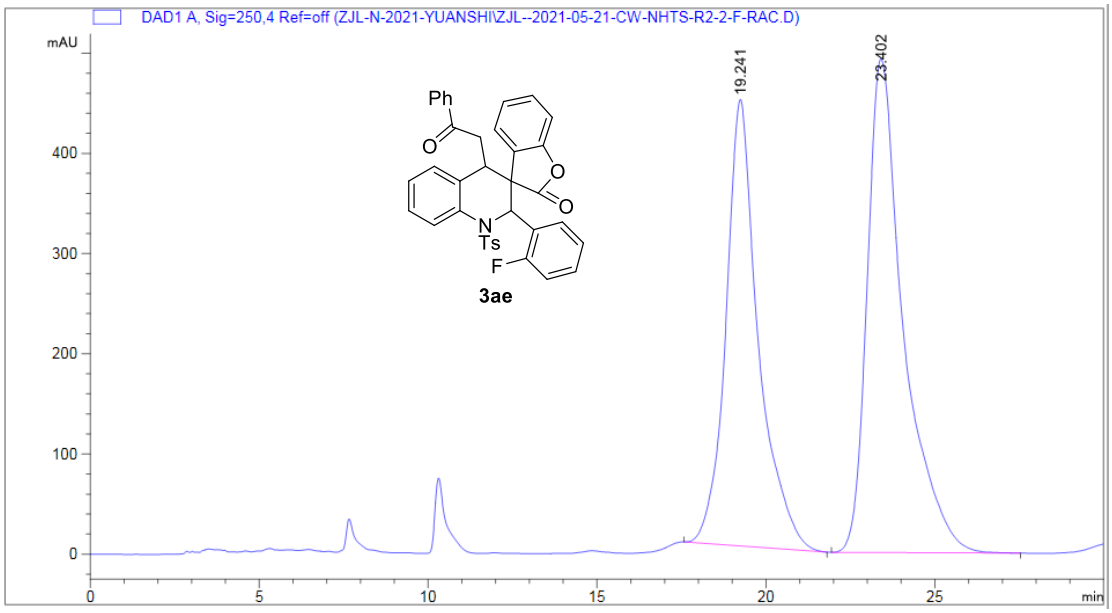



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 16.447 | 4.83617e4 | 799.42596 | 64.9939 |
| 2 | DAD 250, 4 nm | 47.158 | 2.60479e4 | 175.96487 | 35.0061 |

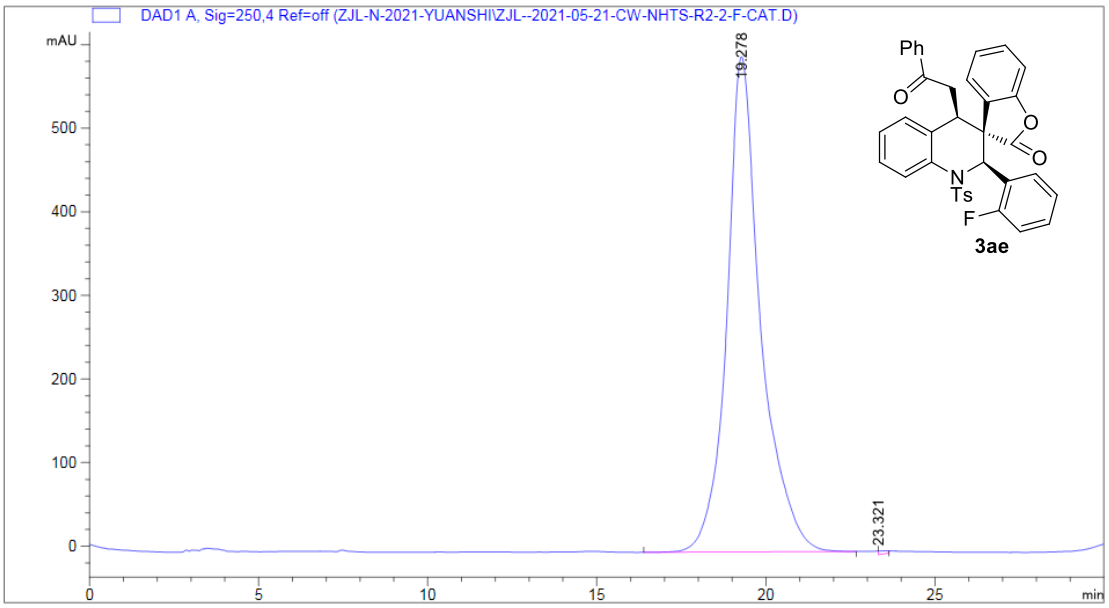


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 16.453 | 5.75612e4 | 984.93774 | 99.9357 |
| 2 | DAD 250, 4 nm | 47.233 | 37.03231 | 0.00000 | 0.0643 |

**3ae**

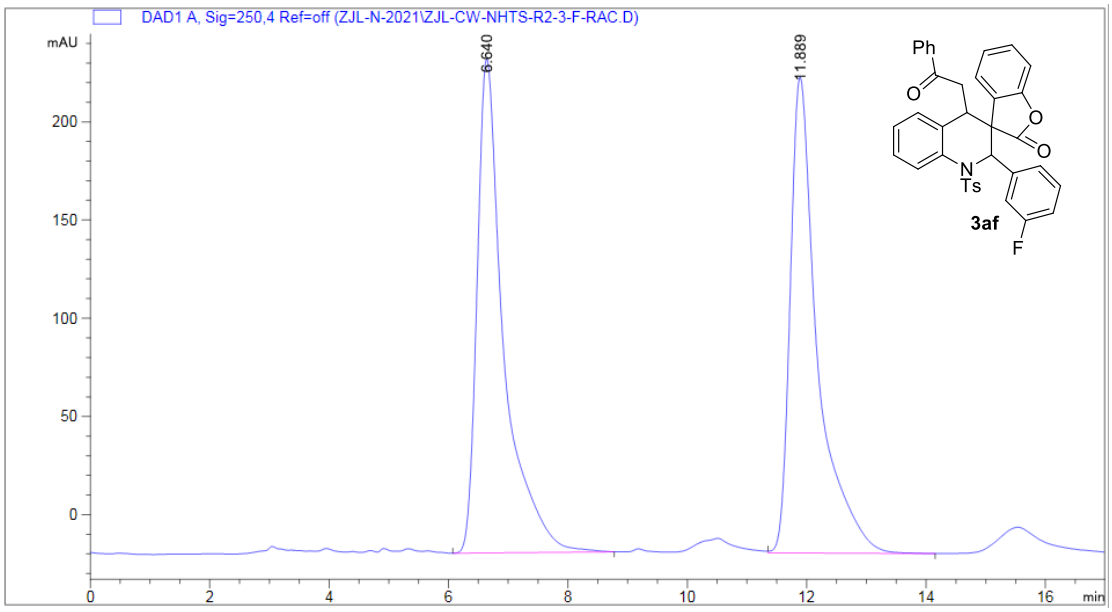



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 19.241 | 2.96940e4 | 445.60284 | 44.6913 |
| 2 | DAD 250, 4 nm | 23.402 | 3.67485e4 | 492.79968 | 55.3087 |

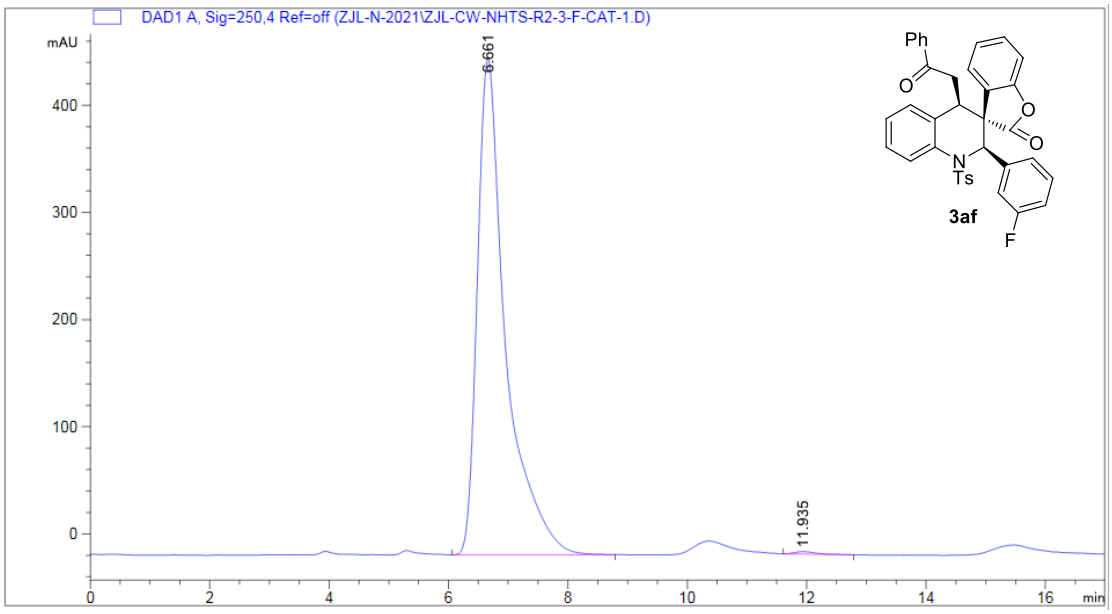


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 19.278 | 4.12637e4 | 592.18701 | 99.8402 |
| 2 | DAD 250, 4 nm | 23.321 | 66.06526 | 4.45768 | 0.1598 |

**3af**

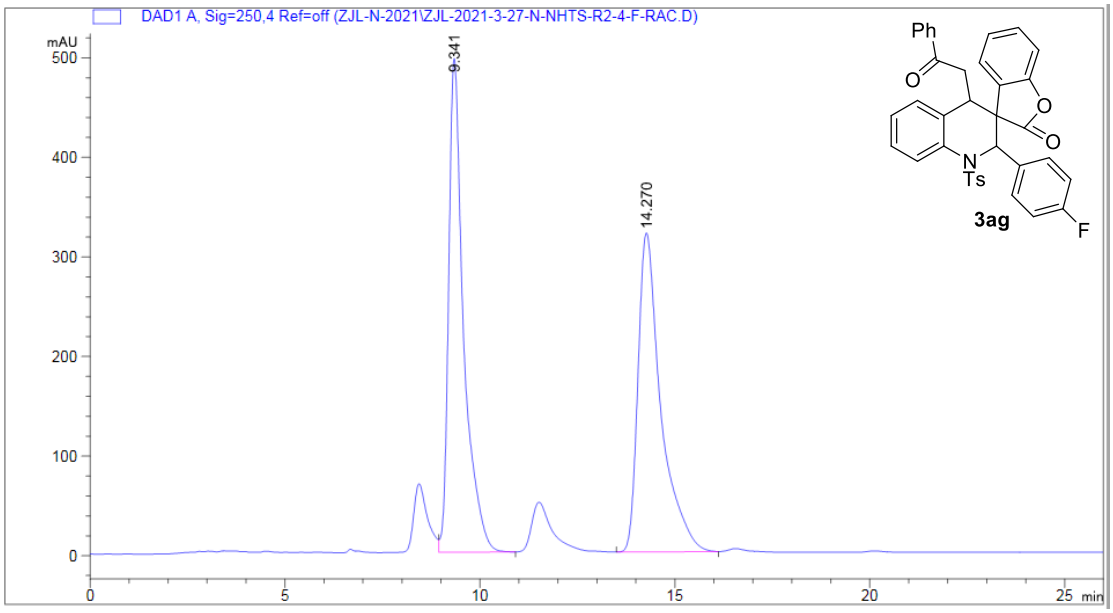



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 6.640 | 7814.92432 | 251.60643 | 50.4184 |
| 2 | DAD 250, 4 nm | 11.889 | 7685.23096 | 242.18611 | 49.5816 |

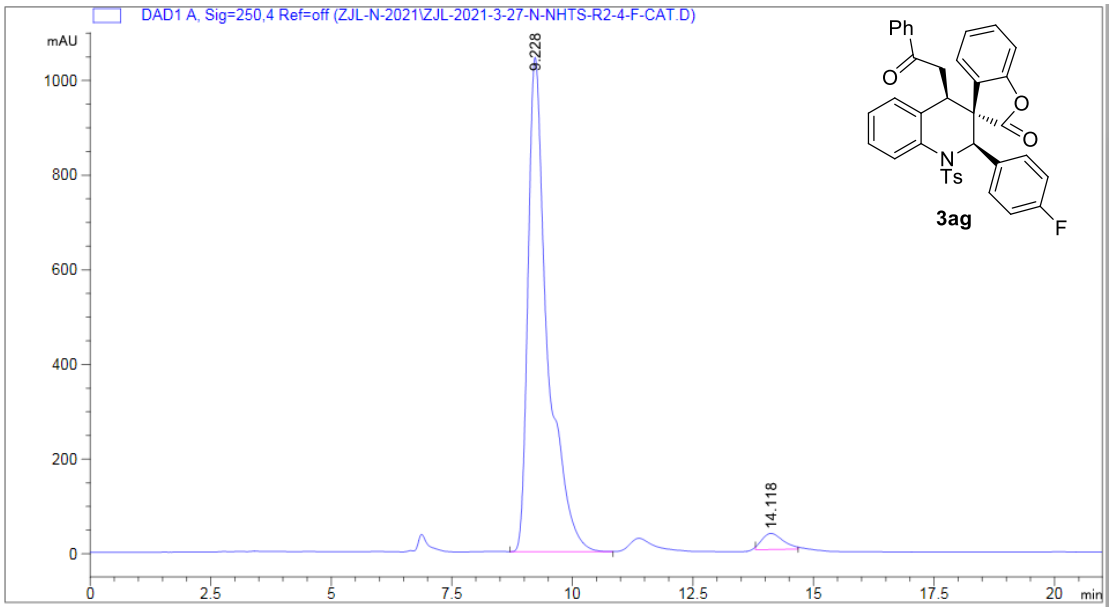


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 6.661 | 1.52919e4 | 462.95895 | 99.6399 |
| 2 | DAD 250, 4 nm | 11.935 | 55.25913 | 2.31000 | 0.3601 |

**3ag**

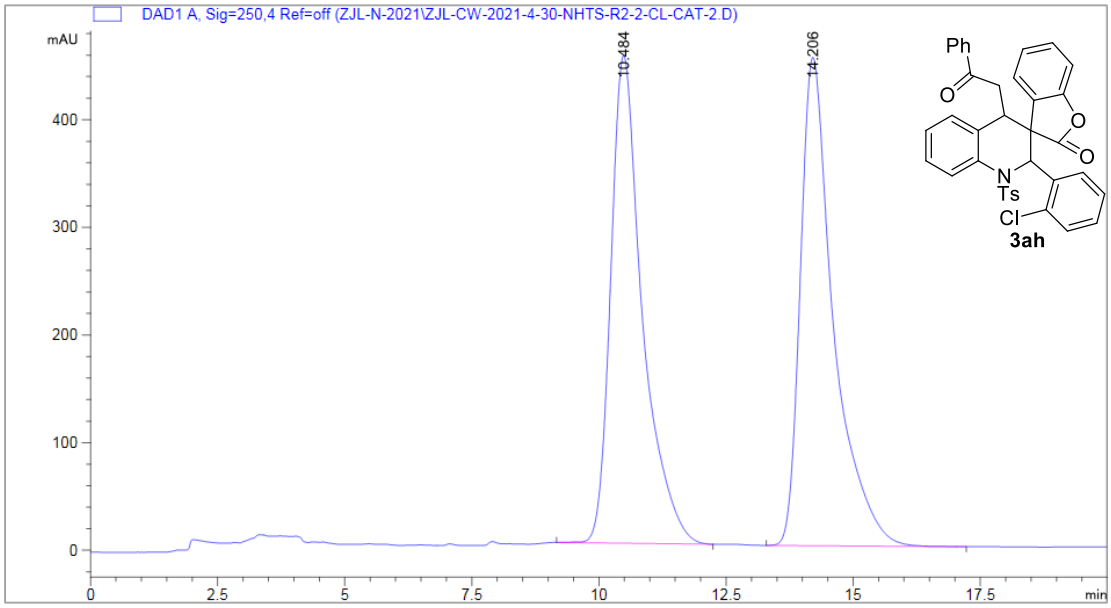



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 9.341 | 1.32303e4 | 495.82074 | 50.4281 |
| 2 | DAD 250, 4 nm | 14.270 | 1.30057e4 | 320.36255 | 49.5719 |

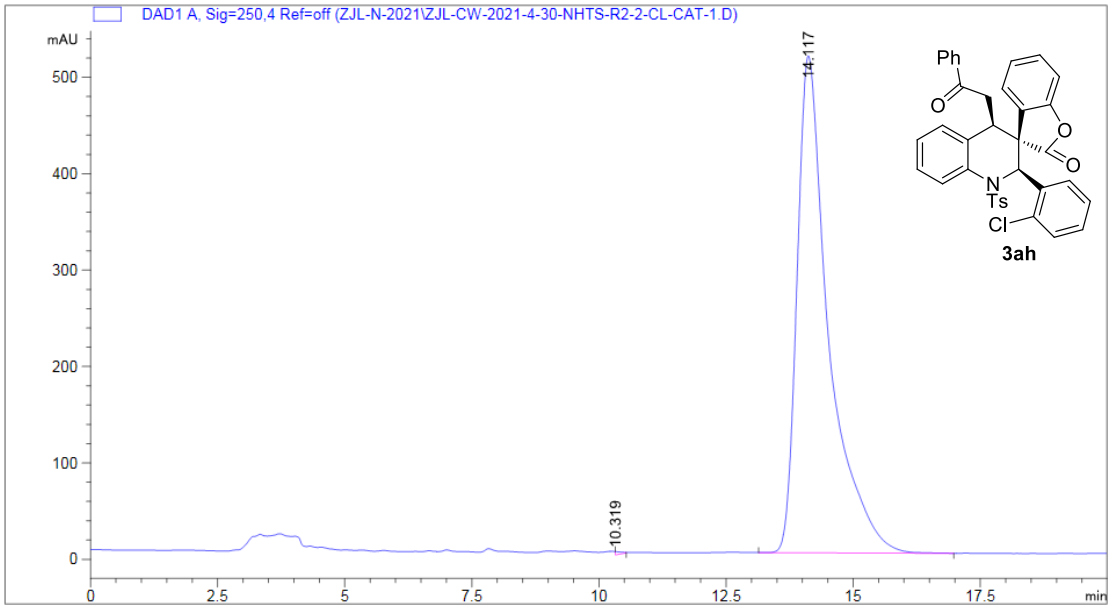


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 9.228 | 2.93502e4 | 1044.79028 | 96.5880 |
| 2 | DAD 250, 4 nm | 14.118 | 1036.80127 | 33.91952 | 3.4120 |

**3ah**

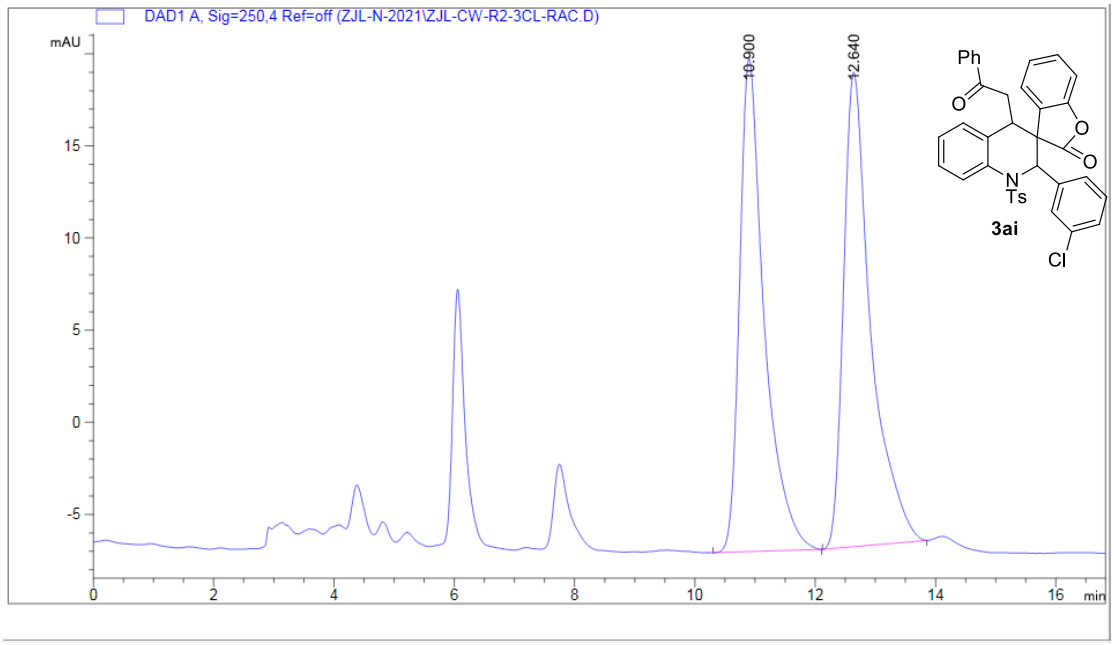



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 10.484 | 1.96023e4 | 452.89539 | 48.7679 |
| 2 | DAD 250, 4 nm | 14.206 | 2.05927e4 | 453.75775 | 51.2321 |

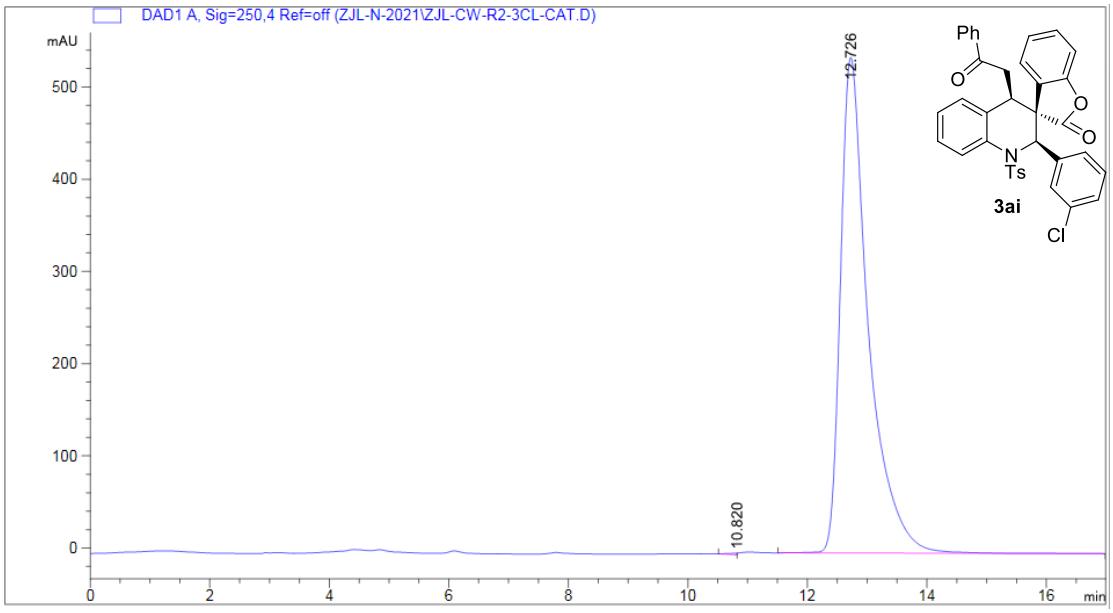


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 10.319 | 23.95238 | 3.35219 | 0.1074 |
| 2 | DAD 250, 4 nm | 14.117 | 2.22708e4 | 515.45367 | 99.8926 |

**3ai**

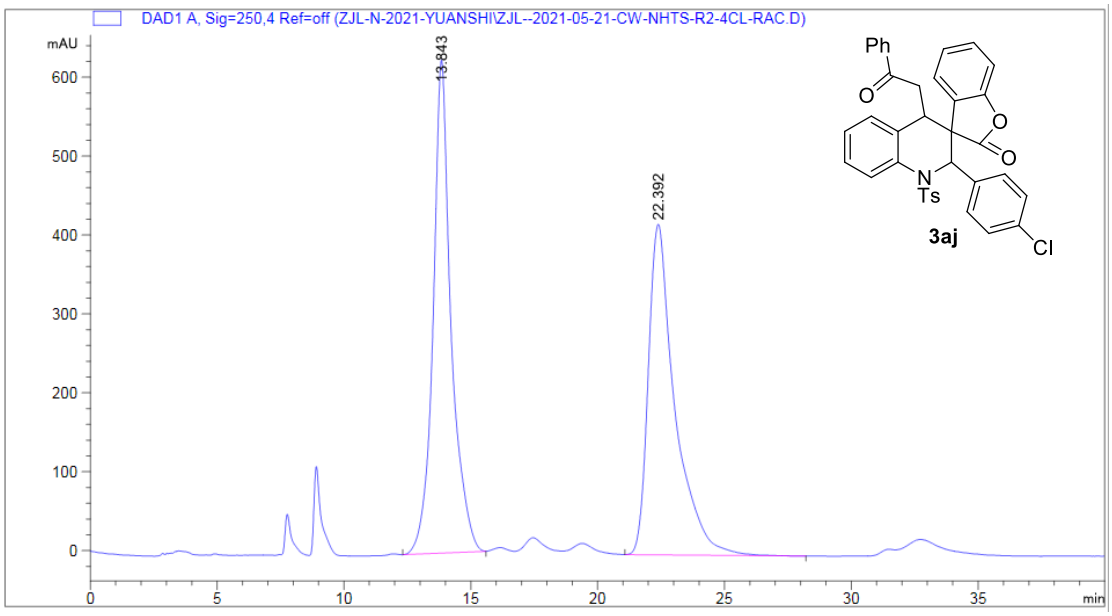



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 10.900 | 764.31610 | 26.76929 | 48.5199 |
| 2 | DAD 250, 4 nm | 12.640 | 810.94806 | 25.74880 | 51.4801 |

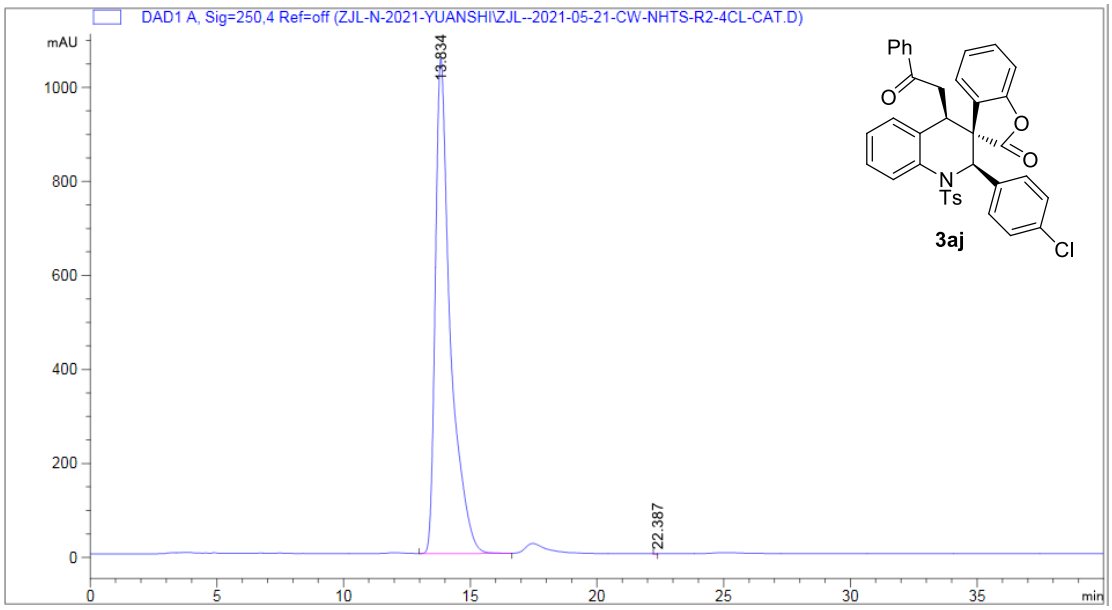


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 10.820 | 15.81770 | 2.15516 | 0.0904 |
| 2 | DAD 250, 4 nm | 12.726 | 1.74757e4 | 537.43689 | 99.9096 |

**3aj**

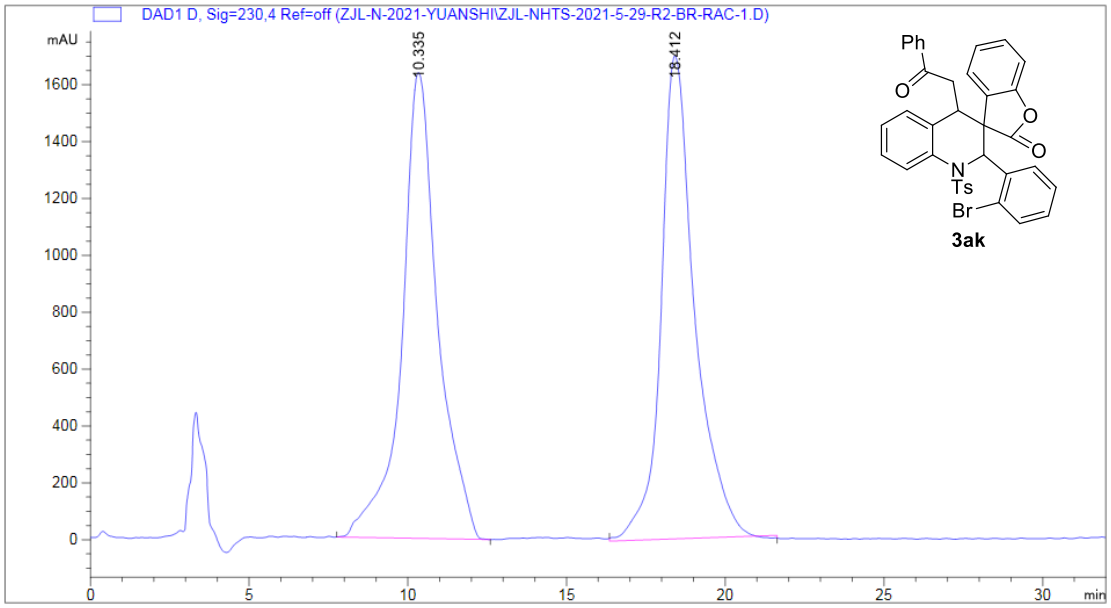



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 13.843 | 3.07664e4 | 625.15350 | 50.2371 |
| 2 | DAD 250, 4 nm | 22.392 | 3.04759e4 | 418.99353 | 49.7629 |

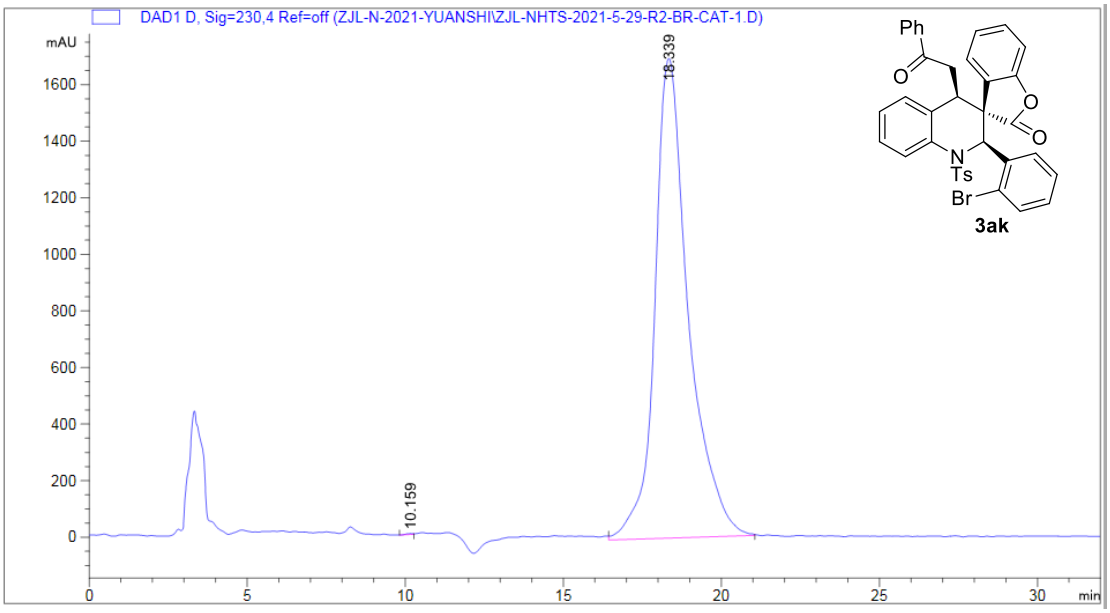


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 13.834 | 4.33991e4 | 1052.61572 | 99.9541 |
| 2 | DAD 250, 4 nm | 22.387 | 19.93125 | 1.98463 | 0.0459 |

**3ak**

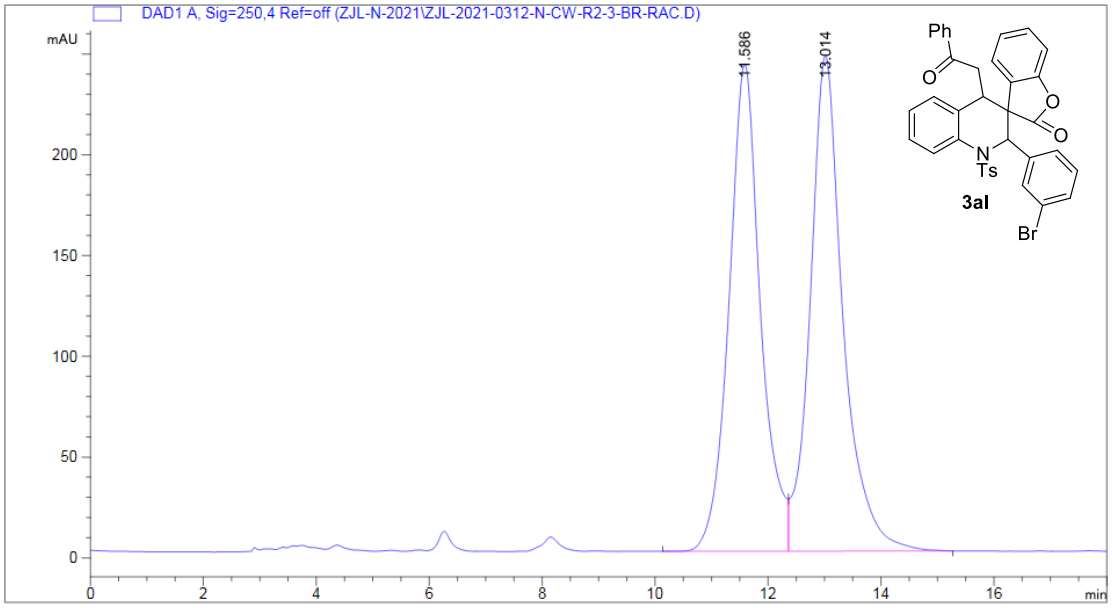



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 230, 4 nm | 10.335 | 1.28606e5 | 1637.72766 | 50.6019 |
| 2 | DAD 230, 4 nm | 18.412 | 1.25547e5 | 1697.66309 | 49.3981 |

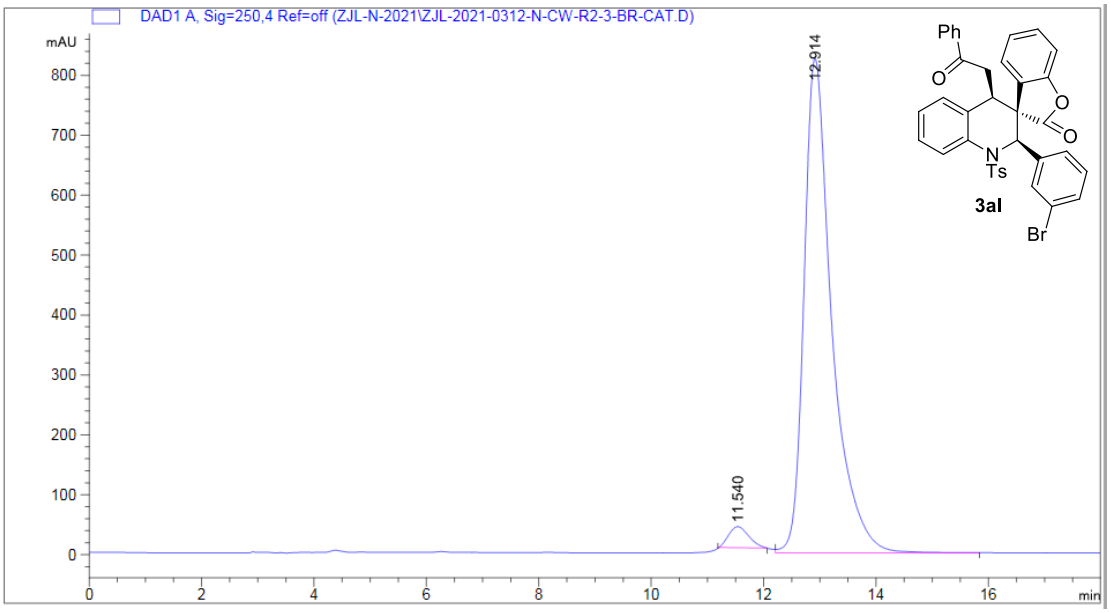


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 230, 4 nm | 10.159 | 46.23292 | 2.99066 | 0.0369 |
| 2 | DAD 230, 4 nm | 18.339 | 1.25382e5 | 1694.70581 | 99.9631 |

**3al**

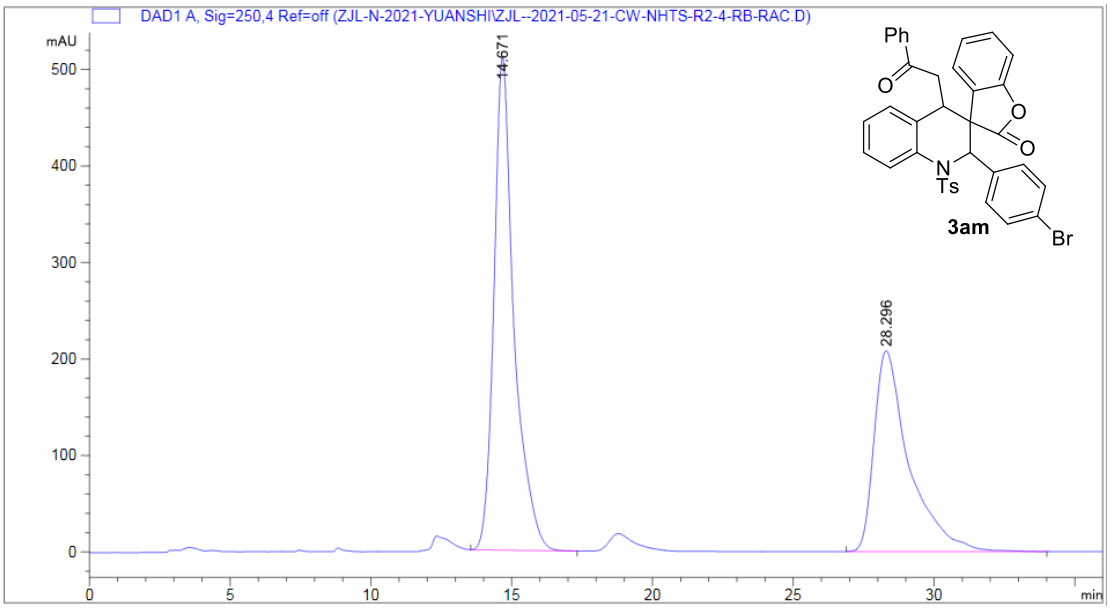



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 11.586 | 9400.35449 | 241.84549 | 48.5417 |
| 2 | DAD 250, 4 nm | 13.014 | 9965.16211 | 245.89076 | 51.4583 |

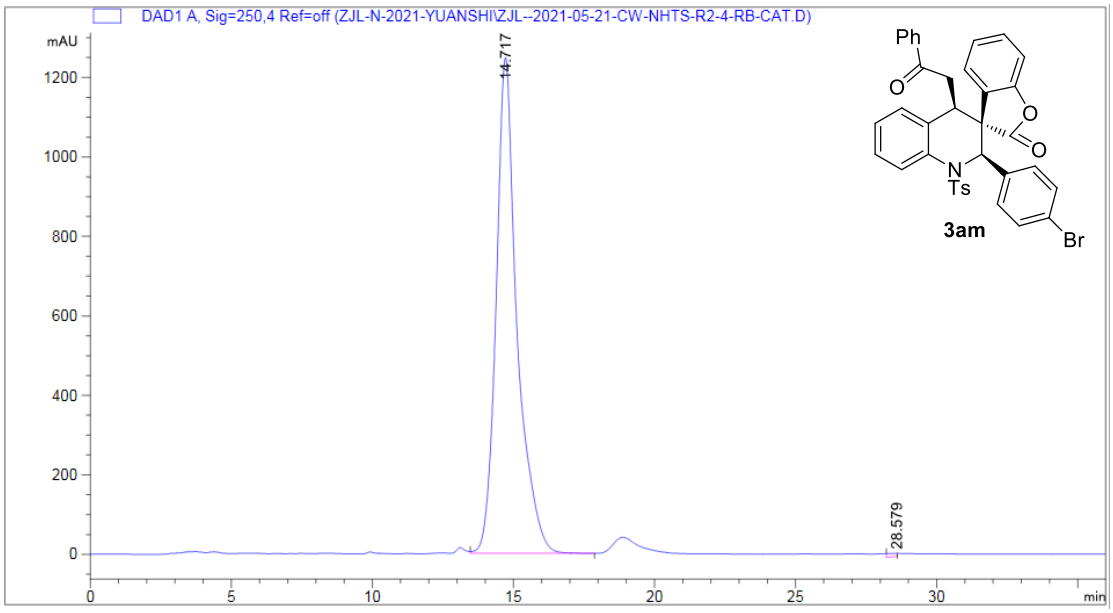


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 11.540 | 869.25537 | 35.04445 | 2.9761 |
| 2 | DAD 250, 4 nm | 12.914 | 2.83385e4 | 825.12305 | 97.0239 |

**3am**

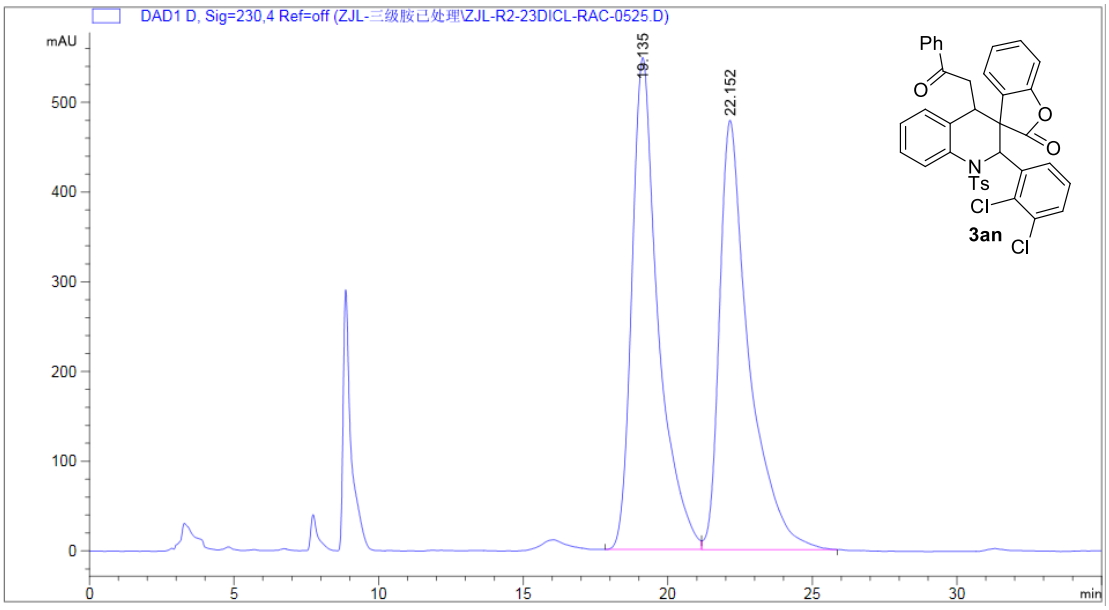



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 14.671 | 2.53226e4 | 510.63858 | 58.5561 |
| 2 | DAD 250, 4 nm | 28.296 | 1.79224e4 | 207.93053 | 41.4439 |

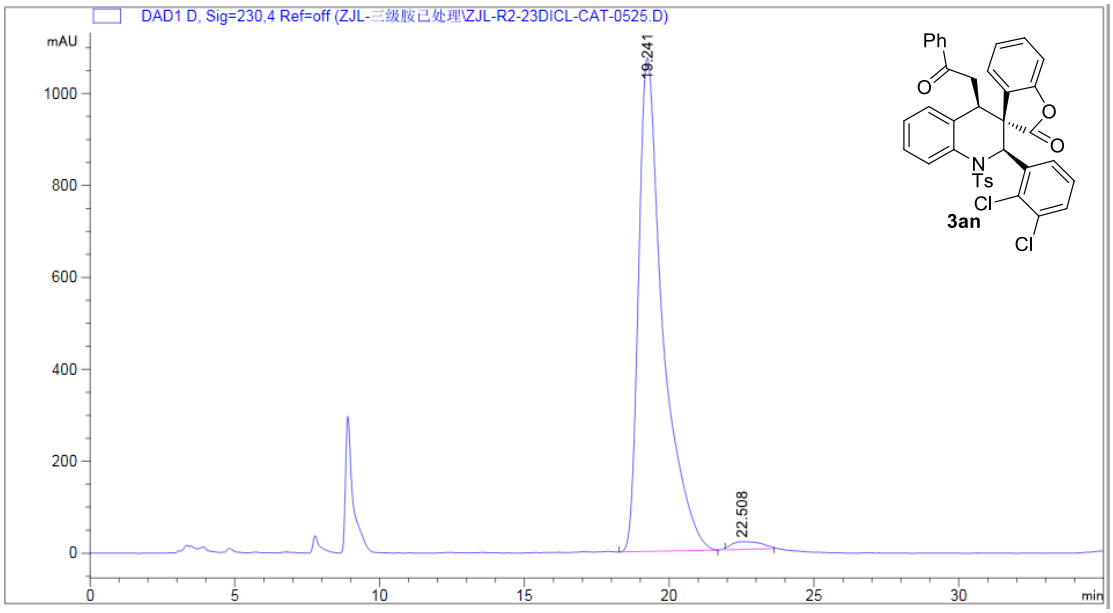


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 14.717 | 6.41367e4 | 1247.26099 | 99.7153 |
| 2 | DAD 250, 4 nm | 28.579 | 183.14842 | 6.85141 | 0.2847 |

**3an**

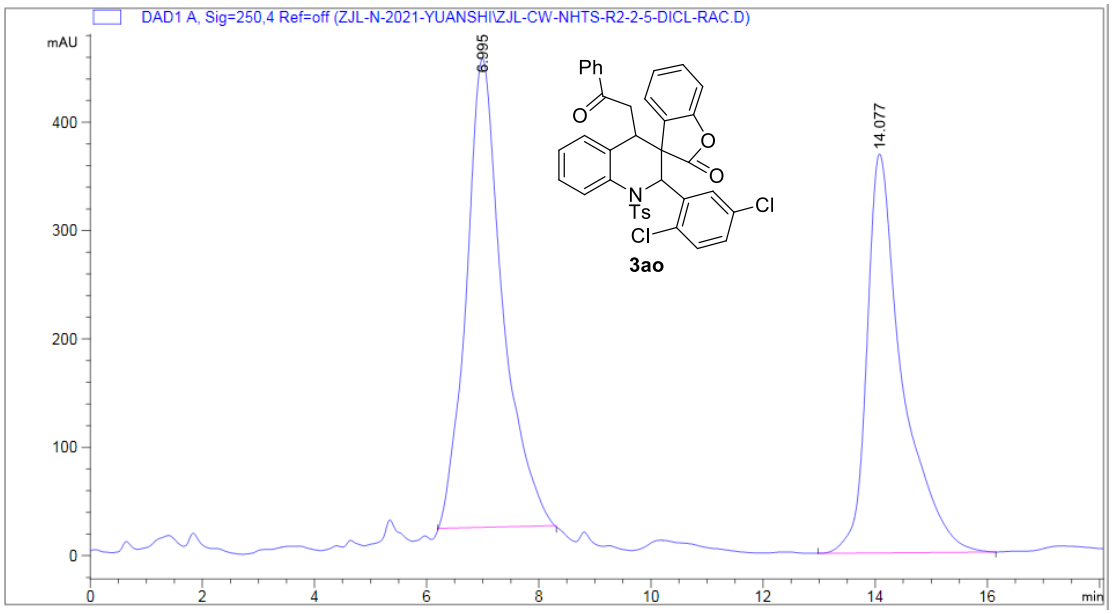



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 230, 4 nm | 19.135 | 3.47173e4 | 548.51764 | 50.6430 |
| 2 | DAD 230, 4 nm | 22.152 | 3.38357e4 | 478.56949 | 49.3570 |

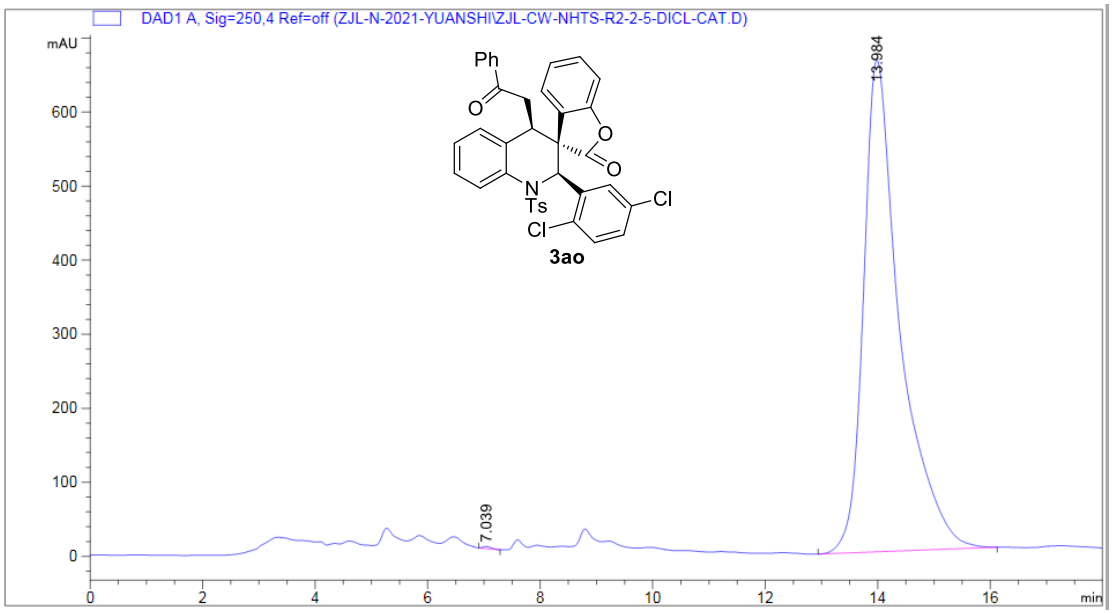


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 230, 4 nm | 19.241 | 6.25079e4 | 1074.43774 | 98.1425 |
| 2 | DAD 230, 4 nm | 22.508 | 1183.06824 | 16.35461 | 1.8575 |

**3ao**

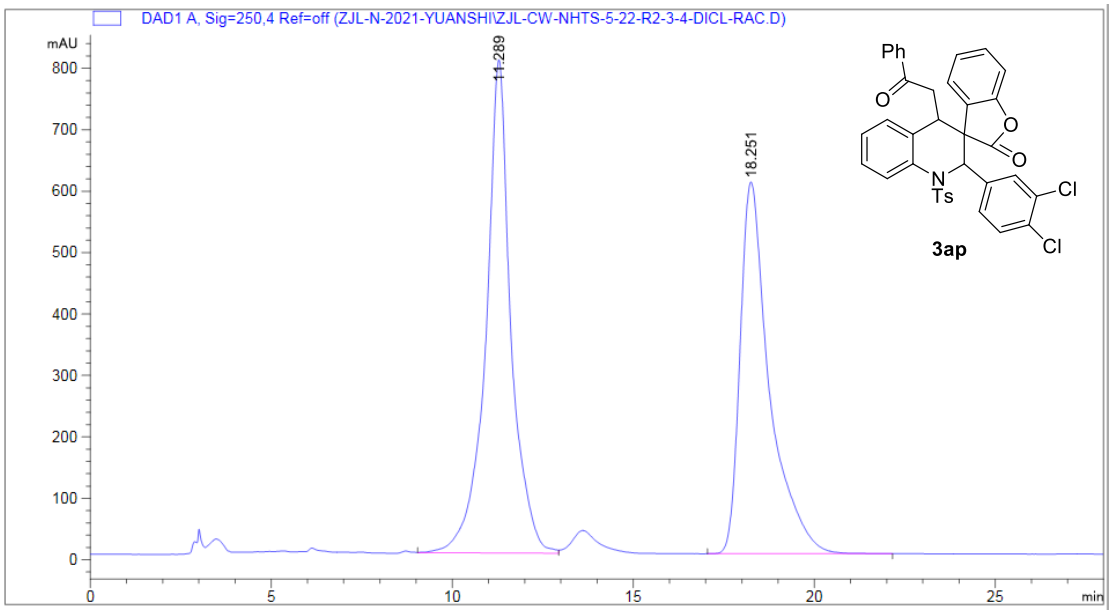



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 6.995 | 1.95291e4 | 432.42938 | 54.8084 |
| 2 | DAD 250, 4 nm | 14.077 | 1.61025e4 | 368.16867 | 45.1916 |

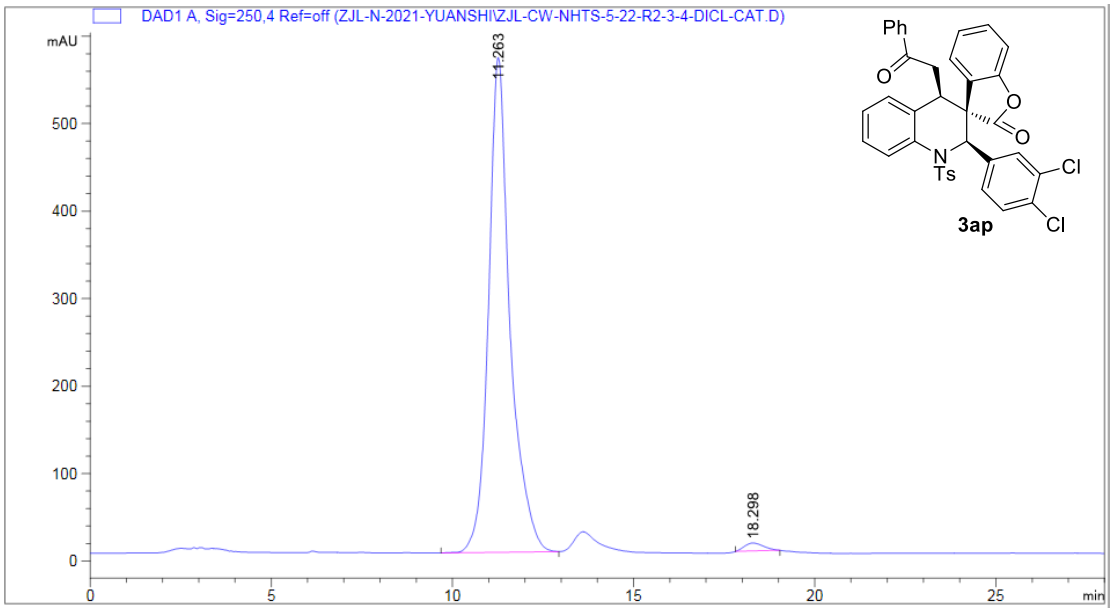


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 7.039 | 27.73716 | 2.77762 | 0.0924 |
| 2 | DAD 250, 4 nm | 13.984 | 2.99782e4 | 664.67035 | 99.9076 |

**3ap**

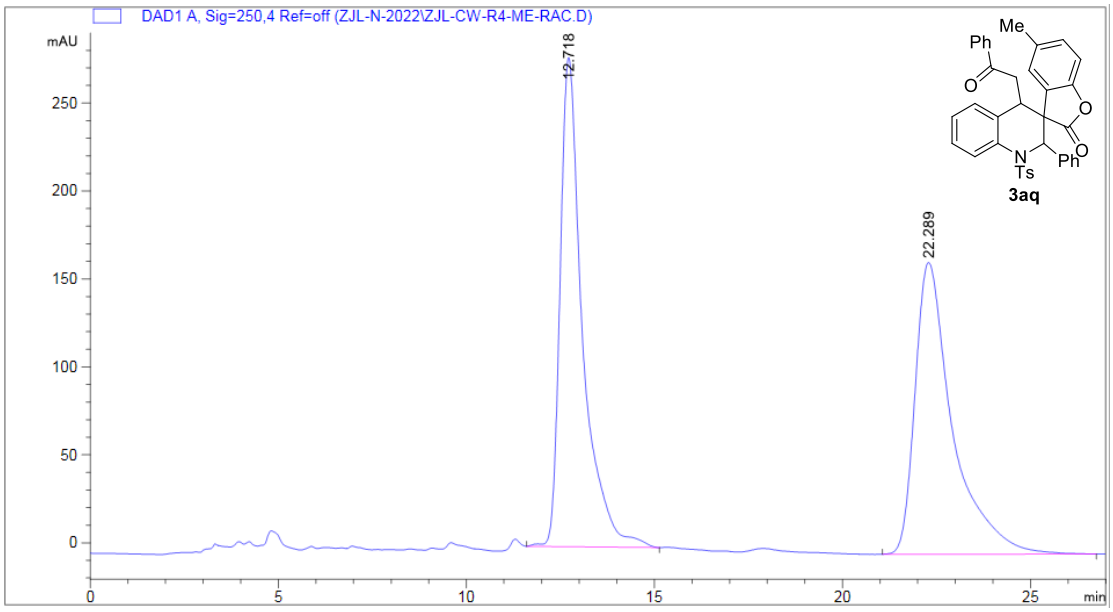



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 11.289 | 3.86402e4 | 802.77997 | 53.0966 |
| 2 | DAD 250, 4 nm | 18.251 | 3.41331e4 | 605.27765 | 46.9034 |

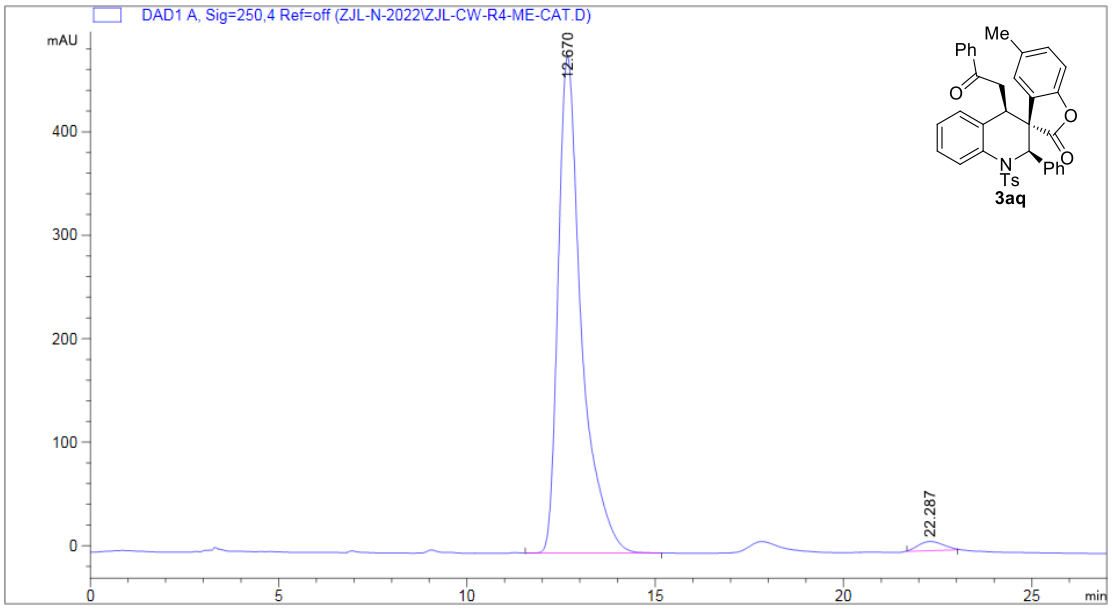


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 11.263 | 2.33624e4 | 565.45300 | 98.6482 |
| 2 | DAD 250, 4 nm | 18.298 | 320.13449 | 8.81148 | 1.3518 |

**3aq**

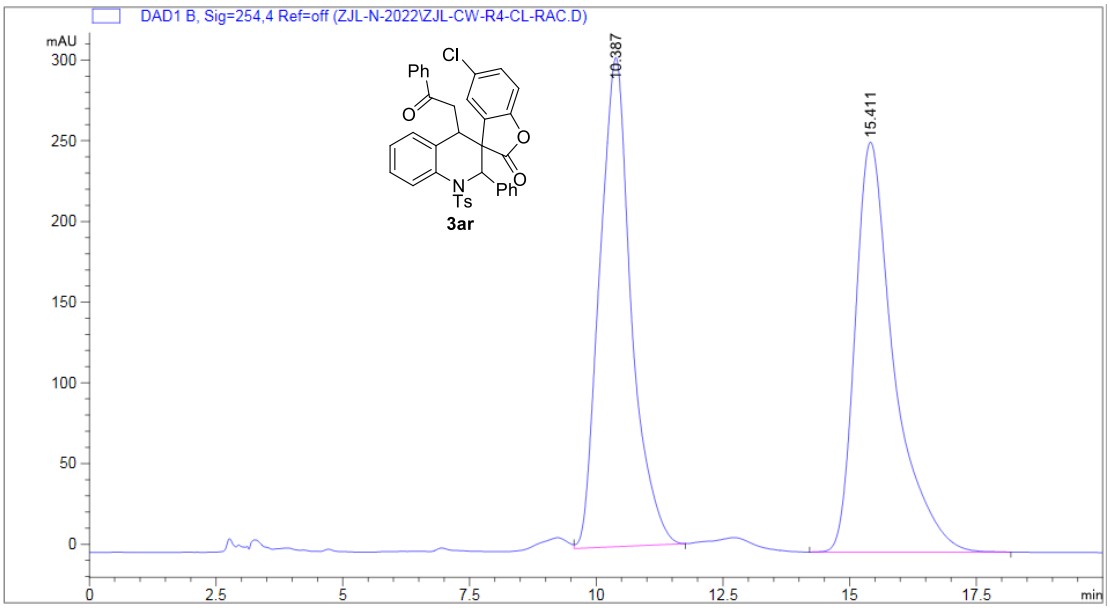



| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 12.718 | 1.15386e4 | 278.02759 | 50.1328 |
| 2 | DAD 250, 4 nm | 22.289 | 1.15386e4 | 165.82906 | 49.8672 |

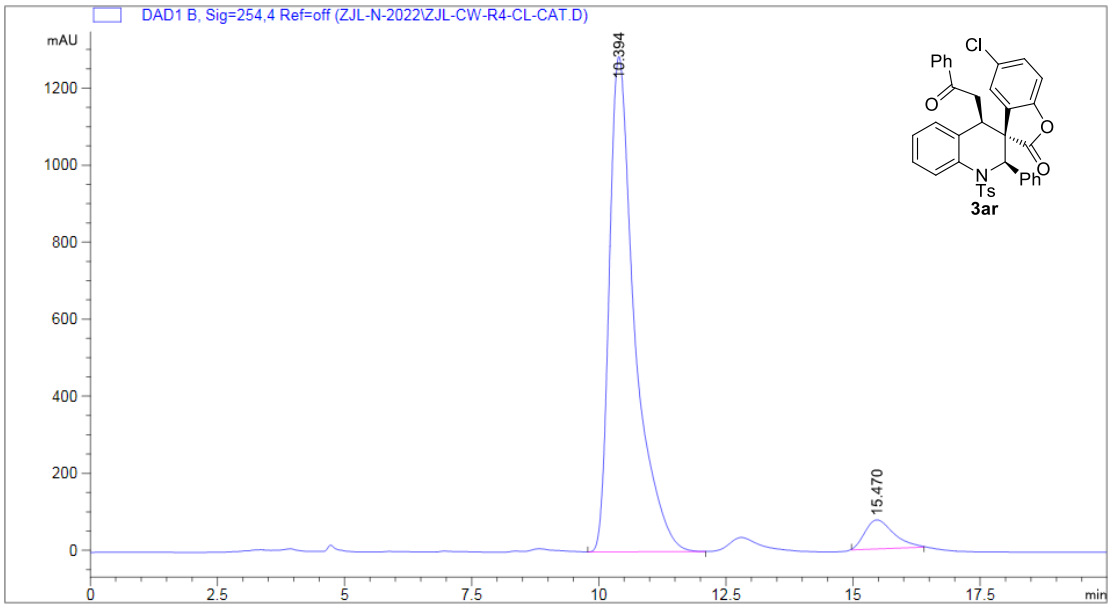


| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 12.670 | 2.06397e4 | 479.73453 | 98.0569 |
| 2 | DAD 250, 4 nm | 22.287 | 409.00366 | 8.85773 | 1.9431 |

**3ar**



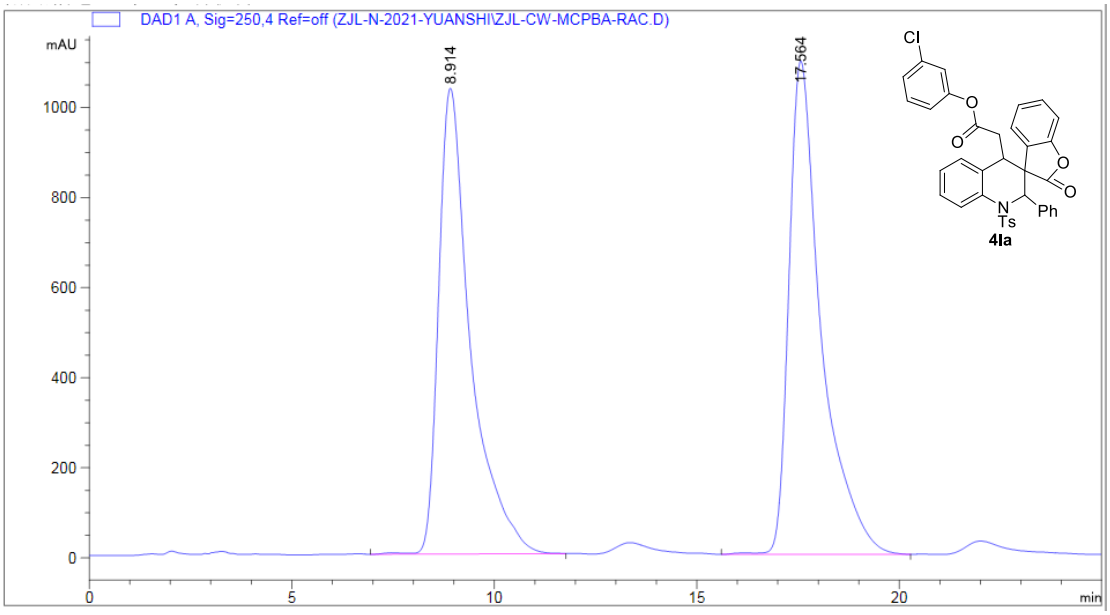

| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 254, 4 nm | 10.387 | 1.31374e4 | 303.20697 | 49.2778 |
| 2 | DAD 254, 4 nm | 15.411 | 1.35225e4 | 254.07007 | 50.7222 |




| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 254, 4 nm | 10.394 | 4.45007e4 | 1285.87891 | 93.7543 |
| 2 | DAD 254, 4 nm | 15.470 | 2964.55493 | 75.30211 | 6.2457 |

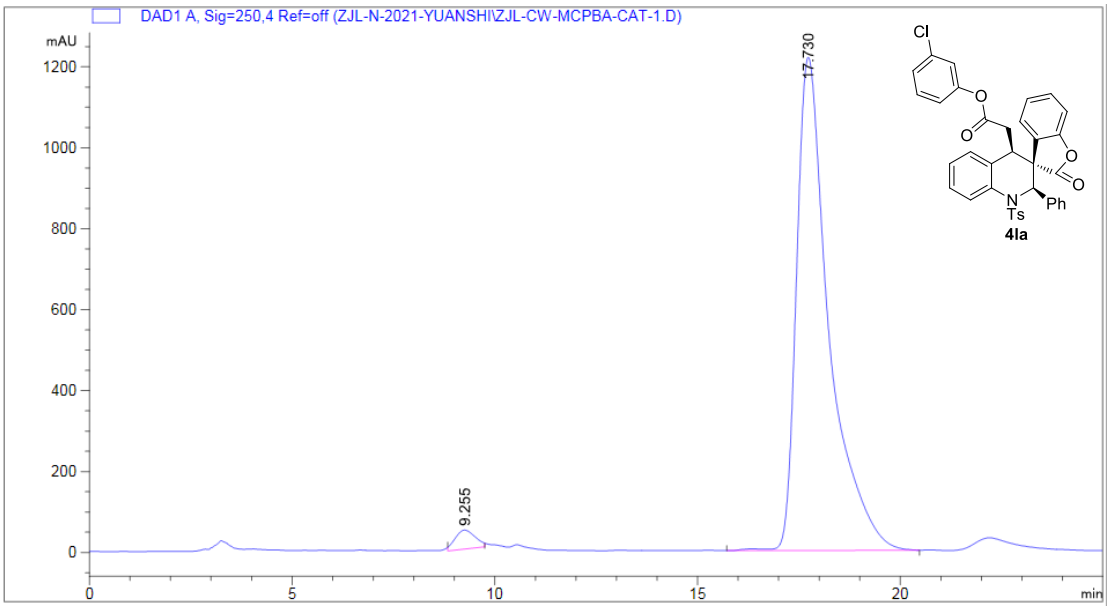
## 5.2. HPLC spectrogram of compound 4.

**4la**




| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 8.914 | 5.67747e4 | 1034.38721 | 48.2484 |
| 2 | DAD 250, 4 nm | 17.564 | 6.08971e4 | 1095.79749 | 51.7516 |




| Peak | Processed Channel | Retention Time (min) | Peak Area (mAU*s) | Peak Height (mAU) | Peak Area (%) |
|---|---|---|---|---|---|
| 1 | DAD 250, 4 nm | 9.255 | 1615.00354 | 46.72694 | 2.3261 |
| 2 | DAD 250, 4 nm | 17.730 | 6.78142e4 | 1218.31885 | 97.6739 |

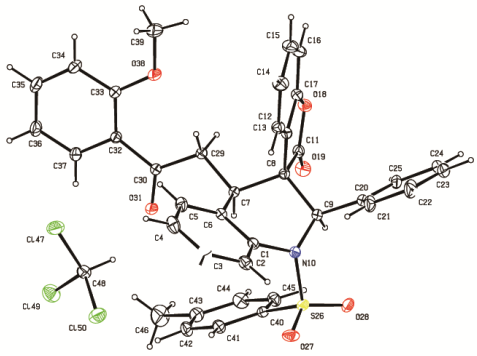
## 6. X-ray crystallographic data

### 6. 1. Preparation of the crystal.

The pure compound (123 mg) of **3la** was dissolved in $CDCl_3$ and removed in NMR tube. After the NMR experiments were finished, the tube was placed in the lab for about one week, during which the crystal was formed. The X-ray was detected after the crystal was formed. The X-ray data was detected by Smart APEX II which was purchased from Bruker.

| Name | X-Ray crystal diffractometer | Model | Smart APEX II |
|---|---|---|---|
| Serial number | 010301990904001 | Manufacturer | Bruker |
| Main Specifications | X-ray generating power: 3.0 kw, 4k 62mm CCD<br>Overall light transmittance: 70%<br>Light source yield: >170 e/Mo Photon<br>Temperature range: 100 K- 298K | | |
| Main accessories | | Mo | |

6**. 2. X-ray Crystallographic Data of Compound 3la.**



**CCDC** = 2084883

| | | | |
|---|---|---|---|
| Bond precision: | C-C = 0.0055 A | | Wavelength=1.54184 |
| Cell: | a =9.7707(1) | b = 9.8704(1) | c = 19.0616(2) |
| | alpha = 90 | beta = 98.180(1) | gamma= 90 |
| Temperature: | | 293 K | |
| | Calculated | | Reported |
| Volume | 1819.61(3) | | 1819.61(3) |
| Space group | P 21 | | P 1 21 1 |
| Hall group | P 2yb | | P 2yb |
| Moiety formula | C38 H31 N O6 S, C H Cl3 | | C38 H31 N O6 S, C H Cl3 |
| Sum formula | C39 H32 Cl3 N O6 S | | C39 H32 Cl3 N O6 S |
| Mr | 749.07 | | 749.06 |
| Dx,g cm-3 | 1.367 | | 1.367 |
| Z | 2 | | 2 |
| Mu (mm-1) | 3.211 | | 3.211 |
| F000 | 776.0 | | 776.0 |
| F000’ | 780.86 | | |
| h,k,l max | 12,12,23 | | 12,12,23 |
| Nref | 7611[ 4035] | | 6907 |
| Tmin,Tmax | 0.764,0.852 | | 0.643,1.000 |
| Tmin’ | 0.680 | | |

Correction method = # Reported T Limits: Tmin =0.643 Tmax = 1.000

| | |
|---|---|
| AbsCorr = MULTI-SCAN | |
| Data completeness = 1.71/0.91 | Theta(max) = 76.023 |
| R(reflections) = 0.0391( 6395) | wR2(reflections)= 0.1057( 6907) |
| S = 1.061 | Npar = 453 |

Displacement ellipsoids are drawn at 50% probability level

# 7. References.


1: a) Zhu, Y.-Y.; Li, B.-Y.; Wang, C.; Dong, Z.-H.; Zhong, X.-L.; Wang, K.-R.; Yan, W.-J.; Wang, R. *Org. Biomol. Chem.*, **2017**,*15*, 4544. b) Yang, W.; He, H.-X.; Gao, Y.; Du, D.-M. *Adv. Synth. Catal*. **2013**, *355*, 3670-3678.

2: a) Huang, Z.-S.; Yang, X.-Q.; Yang, F.-L.; Lu, T.; Zhou, Q.-F. *Org. Lett.* **2017**, *19*, 3524-3527. b) Chen, H.-G.; He, Y.-W.; Zhou, L. *Org. Chem. Front.*, **2018**, *5*, 3240-3244.