Supporting Information

Palladium-Catalyzed Asymmetric [4+3] Cycloaddition of Methylene-Trimethylenemethane: Access to Seven-Membered Exocyclic Axially Chiral Allenes

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General Information

All reactions were performed under Ar atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel-precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). NMR spectra were recorded on a Bruker spectrometer at 800 MHz (^{1}H NMR), 201 MHz (^{13}C NMR). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Optical rotation was obtained on a Rudolph Autopol VI automatic polarimeter. Melting points were determined by an X-4 digital micro melting point apparatus. Accurate mass measurements were performed using a Bruker micrOTOF-QII instrument with the ESI-MS technique. HPLC analysis was performed on DIONEX UltiMate 3000, UV detection monitored at 210 nm or 254 nm, using a Chiralcel AD-H column, Chiralcel OX-H column, Chiralcel AS-H column, Chiralpak IA column, Chiralpak IB column and Chiralpak IC column with *n*-hexane and *i*-PrOH as the eluent. X-ray crystallographic data were collected using a Bruker D8 Venture.

Starting materials and reagents were purchased directly from commercial suppliers and used without further purifications. All solvents used as reaction medium were distilled before the use. The allene TMM donors **1**[1] and benzofuran-derived azadienes **2**[2] were synthesized using known literature procedures.

The stereochemistry analysis and the proposed transition state TS-1

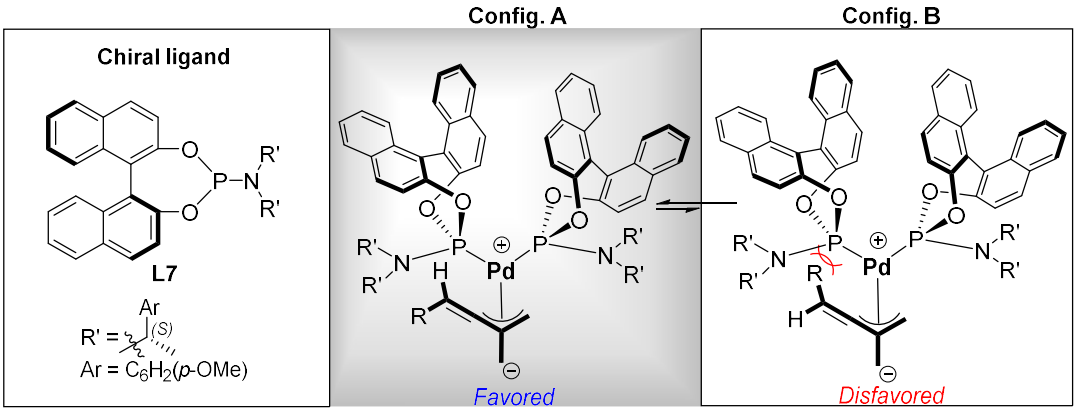


Figure A. The stereochemistry analysis.

We propose two possible configurations separately (Config. A and B) for key intermediate to explain the opposite diastereoselectivity when using chiral ligand **L7**. Due to steric hindrance, the bulky palladium complex and the R-substituent of the allene will be placed on opposing faces, resulting in the competition of two configurations, and the configuration A is favorable (Fig. A). The sterically crowded chiral ligand dominates so that the carbanion of the intermediate **A** attacks at the *Si* face of the olefinic bond in the benzofuran-derived azadiene **2** in the transition state **TS-1** (Fig. B). It could be observed from bottom to top in **TS-1** in the Fischer projection.

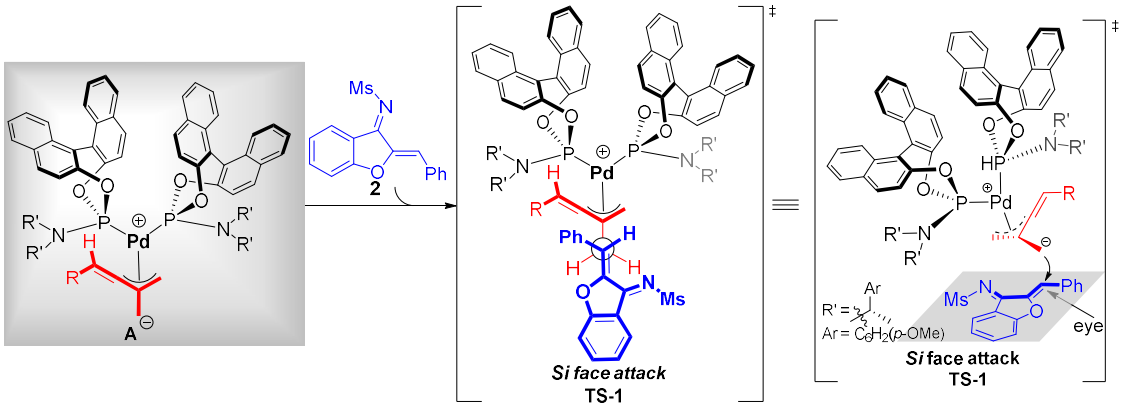


Figure B. The proposed transition state **TS-1**.

Further optimizations

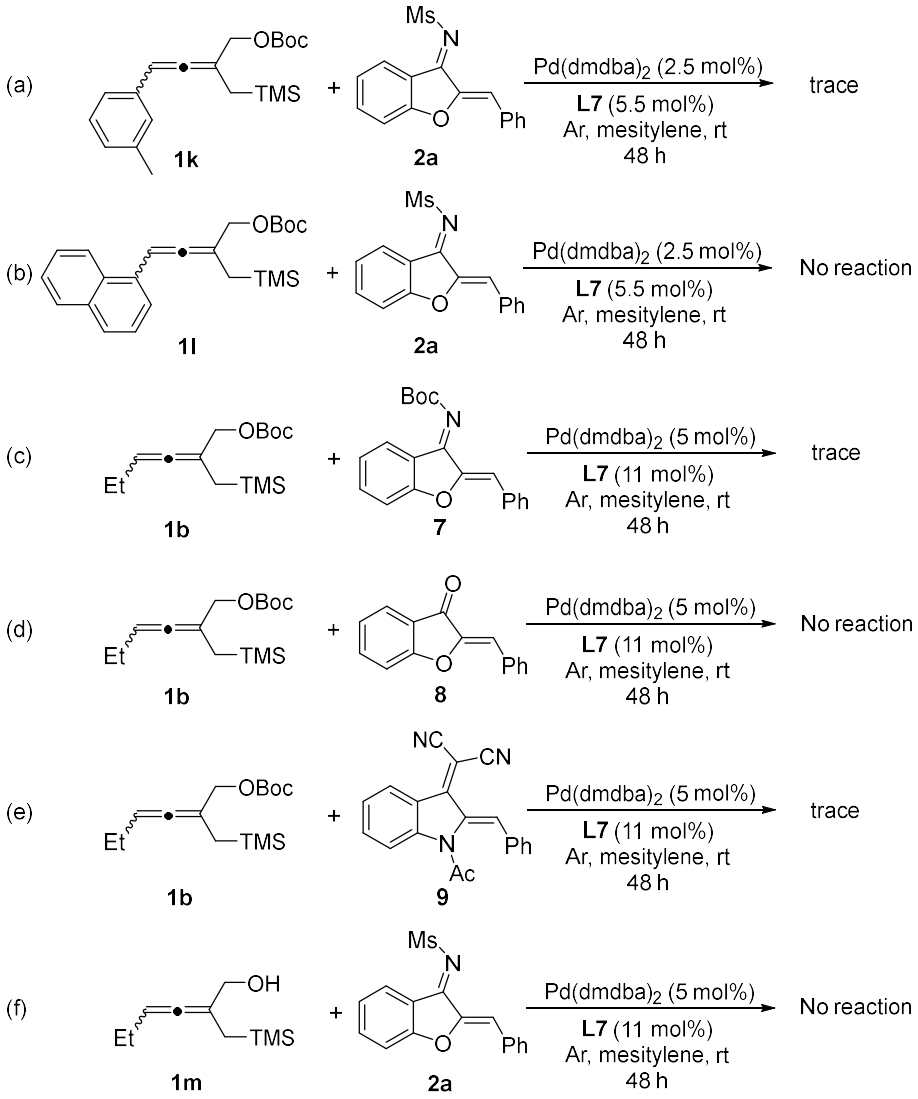
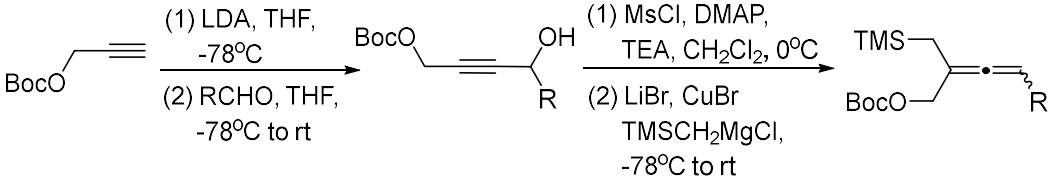


Figure C. Other azadiene, unsaturated ketone, diene and allenes tested in the reaction.

Synthesis of Substrates 1 and 2

A: The substrates **1** were synthesized according to previous reported protocols.[1]



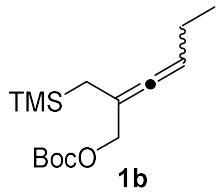
A solution of LDA (1.2 equiv, 2 M in THF) was dropwise to a solution of tert-butyl prop-2-yn-1-yl carbonate (1.0 equiv) in THF (0.2 M) at -78 °C under argon atmosphere and the reaction mixture was stirred for 1 h. The corresponding aldehyde (1.2 equiv) was then added and the solution was stirred at room temperature for 2 h. The reaction was quenched by addition of saturated aqueous NH_4Cl solution, the organic phase was separated, and the aqueous phase was extracted with ethyl acetate. The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude solid was purified by silica gelchromatography (10% EtOAc/PE) to yield a yellow oil.

To a solution of the corresponding alcohol (1.0 equiv), triethylamine (1.2 equiv), and DMAP (0.2 equiv) in CH_2Cl_2 (0.2 M) at 0 °C was added methanesulfonyl chloride (1.1 equiv). The solution was warmed to room temperature and stirred for 30 min while being monitored by TLC. The reaction mixture washed twice with water, dried over $MgSO_4$. and concentrated by rotary evaporation. The crude oil was used immediately in the next reaction without further purification or characterization. A solution of LiBr (1.0 equiv) and CuBr (1.0 equiv) in THF (0.4 M) was stirred for 15 min at room temperature. The reaction mixture was then cooled to -78 °C and a solution of ((trimethylsilyl)methyl) magnesium chloride (1.0 M in THF, 1.0 equiv) was added. The solution stirred at this temperature for 15 min, then the crude mesylate (1.0 equiv) in THF was added followed by dry HMPA. The reaction was warmed to room temperature, stirred 30 min, then quenched with saturated aqueous NH_4Cl. The organic phase was separated, and the aqueous phase was extracted three times with petroleum ether. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude oil was purified by column chromatography on silica gel (1-5%Et_2O/PE) to give a yellow oil.

B: The substrates **2** (benzofuran-derived azadiene) : All benzofuran-derived azadienes (**2**) were prepared by the reported procedure.[2]

Characterization Data of the Allene Donors 1b, 1c, 1e, 1f, 1g, 1j

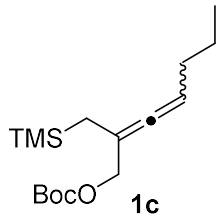
***tert*-butyl (2-((trimethylsilyl)methyl)hexa-2,3-dien-1-yl) carbonate (1b)**



1b

1b was prepared according to the general procedure as described above and purified by column chromatography on silica gel (0-5% Et_2O/PE) to give a yellow oil. ^1H NMR (800 MHz, $CDCl_3$) δ 5.17 (ddd, *J* = 6.4, 3.9, 2.3 Hz, 1H), 4.43 – 4.36 (m, 3H), 1.95 (ddd, *J* = 7.9, 6.4, 2.0 Hz, 2H), 1.43 (s, 11H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.00 (s, 9H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 202.9, 154.8, 99.0, 95.9, 95.9, 83.1, 70.3, 29.1, 23.8, 19.6, 14.8, 0.0. HRMS (ESI) calcd for $C_{15}H_{29}O_3Si^+$ $[M+H]^+$ 285.1880, found 285.1890.

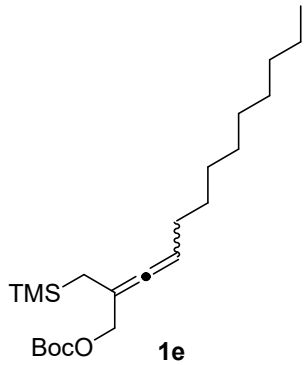
***tert*-butyl (2-((trimethylsilyl)methyl)hepta-2,3-dien-1-yl) carbonate (1c)**



1c

1c was prepared according to the general procedure as described above and purified by column chromatography on silica gel (0-5% Et_2O/PE) to give a yellow oil. ^1H NMR (800 MHz, $CDCl_3$) δ 5.12 (tt, *J* = 4.4, 2.3 Hz, 1H), 4.42 – 4.33 (m, 2H), 1.92 (q, *J* = 7.2 Hz, 2H), 1.53 – 1.27 (m, 13H), 0.87 (t, *J* = 7.4 Hz, 3H), 0.00 (s, 9H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 203.5, 154.8, 98.3, 93.9, 83.1, 70.4, 32.7, 32.7, 29.1, 23.7, 19.6, 14.9, 0.0. HRMS (ESI) calcd for $C_{16}H_{31}O_3Si^+$ $[M+H]^+$ 299.2037, found 299.2037.

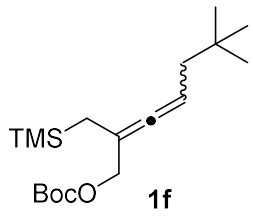
***tert*-butyl (2-((trimethylsilyl)methyl)trideca-2,3-dien-1-yl) carbonate (1e)**



1e

1e was prepared according to the general procedure as described above and purified by column chromatography on silica gel (0-5% Et_2O/PE) to give a yellow oil. ^1H NMR (800 MHz, $CDCl_3$) δ 5.19 – 5.07 (m, 1H), 4.39 (dd, *J* = 4.3, 2.4 Hz, 2H), 1.97 – 1.86 (m, 2H), 1.44 (s, 9H), 1.37 – 1.14 (m, 16H), 0.83 (t, *J* = 7.1 Hz, 3H), 0.00 (s, 9H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 203.5, 154.8, 98.3, 94.1, 83.1, 70.4, 33.2, 30.9, 30.8, 30.6, 30.5, 30.4, 29.1, 23.9, 19.5, 15.4, 0.0. HRMS (ESI) calcd for $C_{22}H_{43}O_3Si^+$ $[M+H]^+$ 383.2976, found 383.2968.

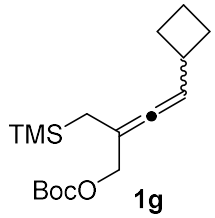
***tert*-butyl (6,6-dimethyl-2-((trimethylsilyl)methyl)hepta-2,3-dien-1-yl) carbonate (1f)**



1f

1f was prepared according to the general procedure as described above and purified by column chromatography on silica gel (0-5% Et_2O/PE) to give a yellow oil. ^{1}H NMR (800 MHz, $CDCl_3$) δ 5.10 (ddt, *J* = 10.3, 4.8, 2.3 Hz, 1H), 4.48 – 4.32 (m, 2H), 1.87 – 1.78 (m, 2H), 1.51 – 1.22 (m, 11H), 0.86 (s, 9H), 0.00 (s, 9H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 204.8, 154.8, 97.1, 90.7, 83.1, 70.4, 45.3, 32.3, 30.3, 29.1, 19.5, 0.0. HRMS (ESI) calcd for $C_{18}H_{34}O_3Si^+$ $[M+H]^+$ 327.2350, found 327.2357.

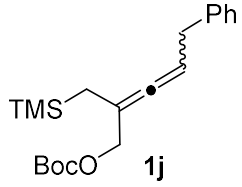
***tert*-butyl (4-cyclobutyl-2-((trimethylsilyl)methyl)buta-2,3-dien-1-yl) carbonate (1g)**



1g

1g was prepared according to the general procedure as described above and purified by column chromatography on silica gel (0-5% Et_2O/PE) to give a yellow oil. ^{1}H NMR (800 MHz, $CDCl_3$) δ 5.25 (dt, *J* = 6.7, 2.4 Hz, 1H), 4.41 (d, *J* = 2.5 Hz, 2H), 2.86 – 2.76 (m, 1H), 2.14 – 1.98 (m, 2H), 1.89 – 1.68 (m, 4H), 1.44 (s, 9H), 1.31 (dd, *J* = 5.7, 2.5 Hz, 2H), 0.00 (s, 9H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 202.2, 154.7, 99.5, 99.4, 83.1, 70.3, 36.3, 30.3, 29.8, 29.1, 19.7, 19.6, 0.0. HRMS (ESI) calcd for $C_{17}H_{31}O_3Si^+$ $[M+H]^+$ 311.2037, found 311.2028.

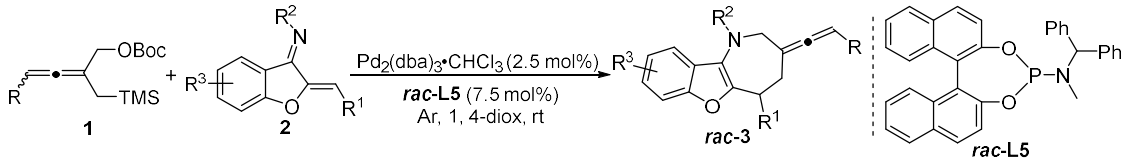
***tert*-butyl (5-phenyl-2-((trimethylsilyl)methyl)penta-2,3-dien-1-yl) carbonate (1j)**



1j

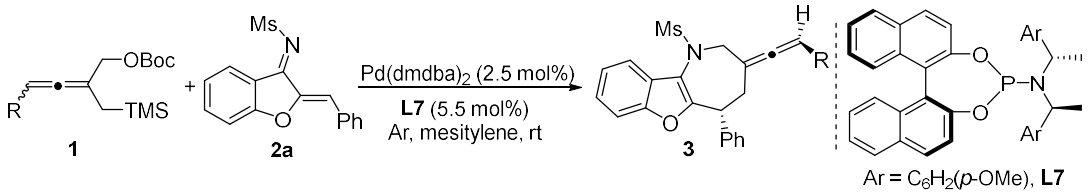
1j was prepared according to the general procedure as described above and purified by column chromatography on silica gel (0-5% Et_2O/PE) to give a yellow oil. ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.28 – 7.06 (m, 5H), 5.29 (ddd, *J* = 7.3, 4.9, 2.4 Hz, 1H), 4.41 (t, *J* = 2.5 Hz, 2H), 3.30 (dd, *J* = 7.3, 2.1 Hz, 2H), 1.43 (s, 9H), 1.32 (dd, *J* = 6.0, 2.4 Hz, 2H), 0.00 (s, 9H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 203.7, 154.7, 141.6, 129.8, 129.7, 129.6, 127.4, 99.2, 93.5, 83.2, 69.9, 37.4, 29.1, 19.5, 0.0. HRMS (ESI) calcd for $C_{20}H_{31}O_3Si^+$ $[M+H]^+$ 347.2037, found 347.2044.

General Procedure for Preparation of Racemic [4+3] Products

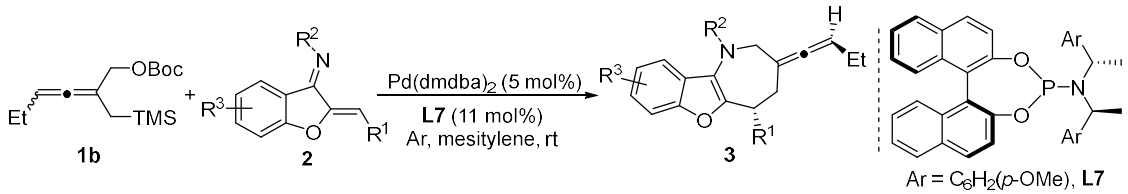


Under argon atmosphere, to a mixture of TMM donor **1** (0.20 mmol), benzofuran-derived azadiene **2** (0.10 mmol) and catalyst $Pd_2(dba)_3 \cdot CHCl_3$ (2.5 mol%, 0.0025mmol) / ***rac*-L5** (7.5 mol%, 0.0075 mmol) in a Schlenk tube, 1 mL of 1, 4-dioxane were added at room temperature. The resulting mixture was stirred until the starting material were completely consumed (monitored by TLC) and then was concentrated to dryness. The residue was purified through flash column chromatography (EtOAc/PE= 1:25) to afford the corresponding racemic cycloaddition product ***rac*-3**.

General Procedure for Preparation of Chiral [4+3] Products



Under argon atmosphere, to a mixture of TMM donor **1** (0.20 mmol), benzofuran-derived azadiene **2a** (0.10 mmol) and catalyst $Pd(dmdba)_2$ (2.5 mol%, 0.0025mmol) / **L7** (5.5 mol%, 0.0055 mmol) in a Schlenk tube, 1 mL of mesitylene were added at room temperature. The resulting mixture was stirred until the starting material were completely consumed (monitored by TLC) and then was concentrated to dryness. The residue was purified through flash column chromatography (EtOAc/PE= 1:25) to afford the corresponding chiral cycloaddition product **3**.

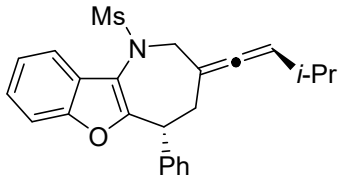


Under argon atmosphere, to a mixture of TMM donor **1b** (0.20 mmol), benzofuran-derived azadiene **2** (0.10 mmol) and catalyst $Pd(dmdba)_2$ (5 mol%, 0.005mmol) / **L7** (11 mol%, 0.011 mmol) in a Schlenk tube, 1 mL of mesitylene were added at room temperature. The resulting mixture was stirred until the starting material were completely consumed

(monitored by TLC) and then was concentrated to dryness. The residue was purified through flash column chromatography (EtOAc/PE= 1:25) to afford the corresponding chiral cycloaddition product **3**.

Characterization Data of the Products 3

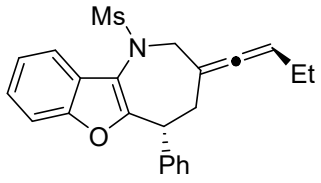
(*R*)-3-((*S*)-3-methylbut-1-en-1-ylidene)-1-(methylsulfonyl)-5-phenyl-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3aa)



3aa

Prepared according to the general procedure as described above in 92% yield (37.4 mg), 6:1 dr and 98% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp =48 – 50°C; $[\alpha]^{25}_{D}$= -53.1 (*c* 1.33, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.1 Hz, 1H), 7.47 – 7.09 (m, 8H), 5.26 – 5.12 (m, 1H), 4.66 (d, *J* = 15.4 Hz, 1H), 4.52 – 4.40 (m, 1H), 4.28 – 4.05 (m, 1H), 3.07 – 2.72 (m, 5H), 2.36 – 2.16 (m, 1H), 0.97 (dd, *J* = 10.6, 6.8 Hz, 6H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 201.7, 153.3, 140.7, 128.7, 128.6, 127.8, 127.7, 127.3, 127.2, 126.6, 124.6, 123.2, 120.4, 111.41, 111.39, 100.2, 98.5, 54.2, 45.3, 40.5, 34.5, 28.1, 22.5, 22.4. HRMS (ESI) calcd for $C_{24}H_{26}NO_3S^+$ $[M+H]^+$ 408.1628, found 408.1628. HPLC analysis: **3aa**, 98% ee (IA, 5% isopropanol/hexane, 1.0 mL/min, UV: 210 nm), t_R= 12.363 min (minor), 19.780 min (major).

(*R*)-3-((*S*)-but-1-en-1-ylidene)-1-(methylsulfonyl)-5-phenyl-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3ba)

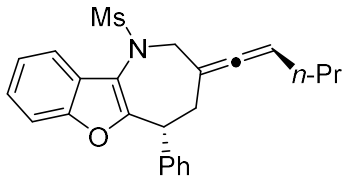


3ba

Prepared according to the general procedure as described above in 95% yield (37.3 mg), 19:1 dr and 96% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp =140 – 142°C; $[\alpha]^{25}_{D}$= -74.3 (*c* 1.60, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.76 – 7.58 (m, 1H), 7.39 – 7.04 (m, 8H), 5.16 (ddq, *J* = 6.2, 4.1, 2.2 Hz, 1H), 4.57 (d, *J* = 14.5 Hz, 1H), 4.39 (dd, *J* = 8.6, 5.1 Hz, 1H), 4.18 – 3.93 (m, 1H), 2.95 (dd, *J* = 14.1, 8.6 Hz, 1H), 2.72 (d, *J* = 11.7 Hz, 4H), 2.00 – 1.84 (m, 2H), 0.88 (td, *J* = 7.4, 1.3 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 202.9, 154.4, 153.2, 140.6, 128.7, 128.6, 127.8, 127.2, 126.7, 124.6, 123.2, 120.5, 119.5, 111.4, 97.9, 94.4, 54.1, 45.2, 40.5, 34.5, 21.8, 13.3. HRMS (ESI) calcd for $C_{23}H_{24}NO_3S^+$ $[M+H]^+$

394.1471, found 394.1465. HPLC analysis: **3ba**, 96% ee (IA, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 12.143 min (minor), 23.803 min (major).

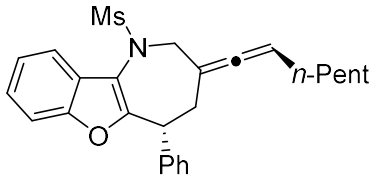
(*R*)-1-(methylsulfonyl)-3-((*S*)-pent-1-en-1-ylidene)-5-phenyl-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3ca)



3ca

Prepared according to the general procedure as described above in 50% yield (20.4 mg), 19:1 dr and 98% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a viscous liquid; $[\alpha]^{25}_D$= -52.4 (*c* 0.94, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 1H), 7.41 – 7.02 (m, 8H), 5.08 (tt, *J* = 6.8, 2.1 Hz, 1H), 4.64 – 4.50 (m, 1H), 4.39 (dd, *J* = 8.4, 5.0 Hz, 1H), 4.06 (d, *J* = 14.3 Hz, 1H), 3.02 – 2.65 (m, 5H), 1.91 (hept, *J* = 7.7 Hz, 2H), 1.31 (dtt, *J* = 28.3, 14.1, 7.1 Hz, 2H), 0.82 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 203.4, 154.4, 153.2, 140.6, 128.7, 128.6, 127.8, 127.7, 127.2, 127.1, 126.7, 124.6, 123.2, 120.5, 119.5, 111.4, 97.1, 92.4, 54.1, 45.2, 40.5, 34.6, 30.7, 22.1, 13.6. HRMS (ESI) calcd for $C_{24}H_{26}NO_3S^+$ $[M+H]^+$ 408.1628, found 408.1625. HPLC analysis: **3ca**, 98% ee (IC, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 27.453 min (major), 32.047 min (minor).

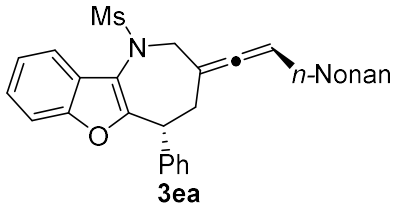
(*R*)-3-((*S*)-hept-1-en-1-ylidene)-1-(methylsulfonyl)-5-phenyl-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3da)



3da

Prepared according to the general procedure as described above in 80% yield (34.8 mg), >20:1 dr and 96% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a viscous liquid; $[\alpha]^{25}_D$= -40.8 (*c* 0.80, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.75 – 7.64 (m, 1H), 7.43 – 7.15 (m, 8H), 5.17 (tt, *J* = 6.7, 2.2 Hz, 1H), 4.65 (d, *J* = 15.8 Hz, 1H), 4.46 (dd, *J* = 8.6, 5.1 Hz, 1H), 4.23 – 4.01 (m, 1H), 3.08 – 2.67 (m, 5H), 2.12 – 1.94 (m, 2H), 1.41 – 1.15 (m, 6H), 0.83 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 203.2, 154.4, 153.3, 140.6, 128.69, 128.67, 127.8, 127.2, 126.7, 124.6, 123.2, 120.4, 119.4, 111.4, 97.2, 92.7, 54.1, 45.3, 40.5, 34.5, 31.2, 28.6, 28.5, 22.4, 14.0. HRMS (ESI) calcd for $C_{26}H_{30}NO_3S^+$ $[M+H]^+$ 436.1941, found 436.1943. HPLC analysis: **3da**, 96% ee (IA, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 11.44 min (minor), 20.557 min (major).

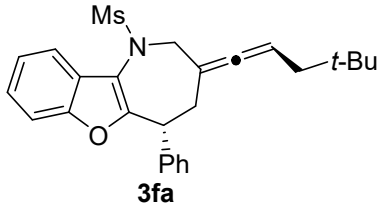
(*R*)-1-(methylsulfonyl)-5-phenyl-3-((*S*)-undec-1-en-1-ylidene)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3ea)



3ea

Prepared according to the general procedure as described above in 89% yield (43.8 mg), >20:1 dr and 96% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a viscous liquid; $[\alpha]^{25}_{D}$= -59.4 (*c* 2.20, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.70 (ddt, *J* = 7.7, 5.2, 3.0 Hz, 1H), 7.47 – 7.17 (m, 8H), 5.17 (td, *J* = 6.9, 6.4, 3.4 Hz, 1H), 4.71 – 4.59 (m, 1H), 4.45 (dd, *J* = 8.6, 5.1 Hz, 1H), 4.20 – 4.07 (m, 1H), 3.06 – 2.74 (m, 5H), 1.47 – 1.18 (m, 14), 0.88 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 203.2, 154.4, 153.3, 140.7, 128.7, 128.6, 127.8, 127.2, 126.7, 124.6, 123.2, 120.4, 119.4, 111.4, 97.3, 92.7, 54.1, 45.4, 40.5, 34.5, 31.9, 29.6, 29.4, 29.3, 29.11, 28.9, 28.6, 22.7, 14.2. HRMS (ESI) calcd for $C_{30}H_{38}NO_3S^+$ $[M+H]^+$ 492.2567, found 492.2554. HPLC analysis: **3ea**, 96% ee (IA, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 10.123 min (minor), 18.617 min (major).

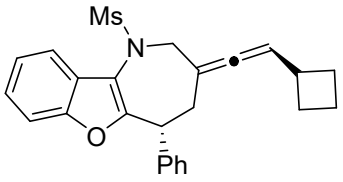
(*R*)-3-((*S*)-4,4-dimethylpent-1-en-1-ylidene)-1-(methylsulfonyl)-5-phenyl-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3fa)



3fa

Prepared according to the general procedure as described above in 70% yield (30.4 mg), 9:1 dr and 97% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp =52 – 54°C; $[\alpha]^{25}_{D}$= -47.7 (*c* 1.00, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 1H), 7.37 – 7.12 (m, 8H), 5.04 (tt, *J* = 8.3, 2.1 Hz, 1H), 4.56 (s, 1H), 4.40 (dd, *J* = 8.3, 4.8 Hz, 1H), 4.07 (s, 1H), 2.98 (dd, *J* = 14.2, 8.3 Hz, 1H), 2.69 (d, *J* = 17.5 Hz, 4H), 1.82 (d, *J* = 8.2 Hz, 2H), 0.83 (d, *J* = 18.3 Hz, 9H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 204.4, 153.2, 140.6, 128.7, 128.6, 127.8, 127.7, 127.2, 126.7, 124.6, 123.2, 120.5, 119.6, 111.4, 95.7, 89.2, 53.9, 45.1, 43.6, 40.5, 34.7, 31.1, 29.1, 29.0. HRMS (ESI) calcd for $C_{26}H_{30}NO_3S^+$ $[M+H]^+$ 436.1941, found 436.1933. HPLC analysis: **3fa**, 97% ee (IA, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 9.67 min (minor), 16.79 min (major).

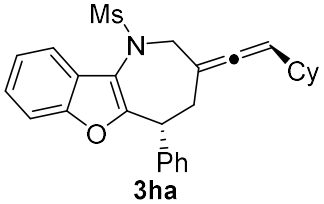
(*R*)-3-((*S*)-2-cyclobutylvinylidene)-1-(methylsulfonyl)-5-phenyl-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3ga)



3ga

Prepared according to the general procedure as described above in 96% yield (40.2 mg), 9:1 dr and 85% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp =62 – 64°C; $[\alpha]^{25}_{D}$= -51.8 (*c* 1.95, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.69 – 7.55 (m, 1H), 7.38 – 7.06 (m, 8H), 5.27 – 5.18 (m, 1H), 4.58 (d, *J* = 15.3 Hz, 1H), 4.38 (dd, *J* = 8.6, 5.1 Hz, 1H), 4.07 (d, *J* = 15.3 Hz, 1H), 3.04 – 2.62 (m, 6H), 2.03 (p, *J* = 8.0 Hz, 2H), 1.88 – 1.60 (m, 4H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 202.1, 154.4, 153.3, 140.6, 128.7, 128.6, 127.82, 127.80, 127.2, 126.7, 124.6, 123.2, 120.4, 119.5, 111.4, 98.4, 97.8, 54.1, 45.4, 40.5, 34.6, 34.3, 28.9, 28.8, 18.5. HRMS (ESI) calcd for $C_{25}H_{26}NO_3S^+$ $[M+H]^+$ 420.1628, found 420.1626. HPLC analysis: **3ga**, 85% ee (AD-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 16.073 min (minor), 28.217 min (major).

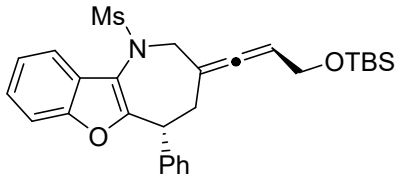
(*R*)-3-((*S*)-2-cyclohexylvinylidene)-1-(methylsulfonyl)-5-phenyl-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3ha)



3ha

Prepared according to the general procedure as described above in 89% yield (39.8 mg), 5.7:1 dr and 95% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp = 61 – 64°C; $[\alpha]^{25}_{D}$= -67.2 (*c* 1.79, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 1H), 7.40 – 7.10 (m, 8), 5.08 (dt, *J* = 5.7, 2.5 Hz, 1H), 4.58 (d, *J* = 15.1 Hz, 1H), 4.38 (dd, *J* = 8.6, 5.3 Hz, 1H), 4.12 – 3.98 (m, 1H), 3.02 – 2.65 (m, 5H), 1.91 (ddd, *J* = 10.9, 7.7, 4.1 Hz, 1H), 1.70 – 1.45 (m, 5H), 1.26 – 0.87 (m, 5H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 202.2, 154.4, 153.3, 140.7, 128.7, 128.6, 127.9, 127.8, 127.2, 127.1, 126.7, 124.6, 123.23, 123.21, 120.4, 119.5, 111.4, 111.3, 98.7, 98.1, 54.3, 45.2, 40.5, 37.1, 34.5, 33.0, 32.9, 26.1, 25.93, 25.90. HRMS (ESI) calcd for $C_{27}H_{30}NO_3S^+$ $[M+H]^+$ 448.1941, found 448.1949. HPLC analysis: **3ha**, 95% ee (AD-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R= 19.553 min (minor), 21.077 min (major).

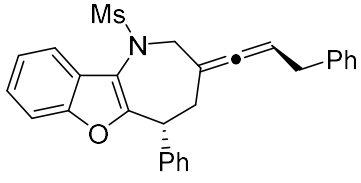
(*R*)-3-((*S*)-3-((tert-butyldimethylsilyl)oxy)prop-1-en-1-ylidene)-1-(methylsulfonyl)-5-phenyl-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3ia)



3ia

Prepared according to the general procedure as described above in 73% yield (37.2 mg), >20:1 dr and 99% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a viscous liquid; $[\alpha]^{25}_D$= -58.5 (*c* 1.50, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 1H), 7.37 – 7.18 (m, 8), 5.27 – 5.18 (m, 1H), 4.69 – 4.55 (m, 1), 4.41 (dd, *J* = 8.6, 4.9 Hz, 1H), 4.12 (d, *J* = 5.9 Hz, 3H), 3.04 – 2.99 (m, 1H), 2.75 (s, 4), 0.81 (s, 9), -0.01 (d, *J* = 14.1 Hz, 6). ^{13}C NMR (201 MHz, $CDCl_3$) δ 202.2, 154.3, 153.3, 140.5, 128.7, 127.8, 127.3, 126.6, 124.7, 123.3, 120.3, 119.5, 111.4, 99.1, 93.5, 61.1, 53.5, 45.2, 40.6, 34.3, 25.9, 25.8, 18.3, -5.09, -5.12. HRMS (ESI) calcd for $C_{28}H_{36}NO_4SSi^+$ $[M+H]^+$ 510.2129, found 510.2132. HPLC analysis: **3ia**, 99% ee (IA, 2% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 15.677 min (minor), 28.797 min (major).

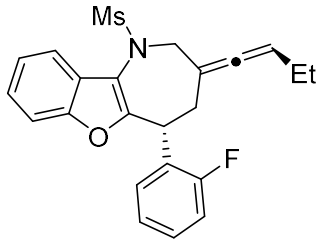
(*R*)-1-(methylsulfonyl)-5-phenyl-3-((*S*)-3-phenylprop-1-en-1-ylidene)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3ja)



3ja

Prepared according to the general procedure as described above in 77% yield (35.0 mg), 9:1 dr and 95% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp =68 – 70°C; $[\alpha]^{25}_D$= -80.3 (*c* 1.08, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 1H), 7.40 – 7.04 (m, 13H), 5.42 (tdd, *J* = 6.5, 4.6, 2.9 Hz, 1H), 4.63 (s, 1H), 4.17 – 3.98 (m, 2H), 3.36 – 3.23 (m, 2H), 2.96 – 2.88 (m, 1H), 2.82 (s, 3H), 2.68 (dd, *J* = 13.9, 5.0 Hz, 1H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 203.5, 154.3, 153.3, 140.7, 139.4, 128.8, 128.7, 128.6, 128.4, 128.3, 127.8, 127.7, 127.3, 127.2, 126.6, 126.5, 124.6, 123.3, 123.2, 120.1, 111.5, 111.4, 98.8, 93.1, 53.4, 45.7, 40.6, 35.1, 34.7. HRMS (ESI) calcd for $C_{28}H_{26}NO_3S^+$ $[M+H]^+$ 456.1628,found 456.1620. HPLC analysis: **3ja**, 95% ee (OX-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 29.707 min (minor), 55.623 min (major).

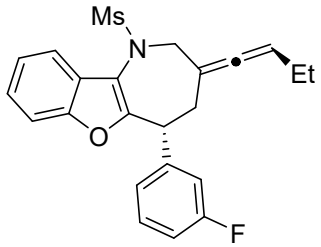
(*R*)-3-((*S*)-but-1-en-1-ylidene)-5-(2-fluorophenyl)-1-(methylsulfonyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bb)



3bb

Prepared according to the general procedure as described above in 76% yield (31.2 mg), >20:1 dr and 95% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a viscous liquid; $[\alpha]^{25}_{D}$= -69.3 (*c* 1.23, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.36 – 7.03 (m, 7H), 5.29 – 5.19 (m, 1H), 4.68 (dd, *J* = 10.1, 5.5 Hz, 1H), 4.46 (d, *J* = 113.6 Hz, 2H), 3.16 (s, 3H), 2.98 – 2.81 (m, 2H), 2.09 – 1.91 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 201.9, 160.5 (d, *J* = 246.2 Hz), 153.4, 152.9, 129.6 (d, *J* = 4.1 Hz), 128.9 (d, *J* = 8.2 Hz), 127.6 (d, *J* = 13.8 Hz), 126.4, 124.7, 124.5 (d, *J* = 3.4 Hz), 123.2, 120.0, 119.9, 115.6= (d, *J* = 22.1 Hz), 111.5, 98.2, 95.0, 54.0, 40.8, 40.1, 34.2, 21.9, 13.3. HRMS (ESI) calcd for $C_{23}H_{23}FNO_3S^+$ $[M+H]^+$ 412.1377, found 412.1385. HPLC analysis: **3bb**, 95% ee (IA, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 9.917 min (minor), 14.07 min (major).

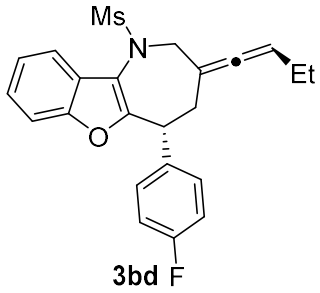
(*R*)-3-((*S*)-but-1-en-1-ylidene)-5-(3-fluorophenyl)-1-(methylsulfonyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bc)



3bc

Prepared according to the general procedure as described above in 70% yield (28.8 mg), 15.5:1 dr and 96% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a viscous liquid; $[\alpha]^{25}_{D}$= -51.0 (*c* 0.98, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 6.0, 3.1 Hz, 1H), 7.34 – 7.15 (m, 4H), 7.02 – 6.84 (m, 3H), 5.18 (tt, *J* = 6.5, 2.2 Hz, 1H), 4.58 (d, *J* = 15.5 Hz, 1H), 4.37 (dd, *J* = 8.6, 5.1 Hz, 1H), 4.08 (d, *J* = 15.2 Hz, 1H), 3.00 – 2.69 (m, 5H), 2.03 – 1.84 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 202.8, 162.9 (d, *J* = 246.6 Hz), 153.66, 153.3, 143.1 (d, *J* = 6.9 Hz), 130.2 (d, *J* = 8.2 Hz), 126.5, 124.8, 123.6 (d, *J* = 2.9 Hz), 123.3, 120.4, 119.6, 114.9 (d, *J* = 22.1 Hz), 114.1 (d, *J* = 20.8 Hz), 111.5, 97.8, 94.7, 54.0, 45.1, 40.7, 34.5, 21.9, 21.8, 13.2. HRMS (ESI) calcd for $C_{23}H_{23}FNO_3S^+$ $[M+H]^+$ 412.1377, found 412.1368. HPLC analysis: **3bc**, 96% ee (IA, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 12.157 min (minor), 20.637 min (major).

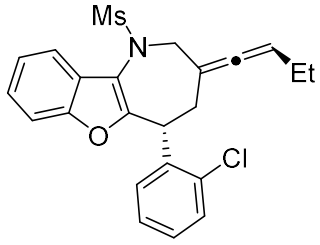
(*R*)-3-((*S*)-but-1-en-1-ylidene)-5-(4-fluorophenyl)-1-(methylsulfonyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bd)



3bd

Prepared according to the general procedure as described above in 88% yield (36.1 mg), 11.5:1 dr and 95% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a viscous liquid; $[\alpha]^{25}_{D}$= -53.8 (*c* 1.90, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.71 – 7.60 (m, 1H), 7.40 – 7.21 (m, 5H), 7.11 – 6.92 (m, 2H), 5.34 – 5.18 (m, 1H), 4.75 – 4.51 (m, 1H), 4.41 (dd, *J* = 8.9, 5.2 Hz, 1H), 4.25 – 4.10 (m, 1H), 3.02 – 2.72 (m, 5H), 2.01 (qd, *J* = 7.4, 6.0 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 202.7, 161.9 (d, *J* = 245.9 Hz), 154.2, 153.3, 136.4 (d, *J* = 3.1 Hz), 129.5, 129.4 (d, *J* = 7.7 Hz), 126.5, 124.7, 123.3, 120.2, 119.4, 115.5 (d, *J* = 21.4 Hz), 111.5, 97.9, 94.7, 54.0, 53.9, 44.9, 40.8, 34.8, 21.9, 21.8, 13.5, 13.2. HRMS (ESI) calcd for $C_{23}H_{23}FNO_3S^+$ $[M+H]^+$ 412.1377, found 412.1372. HPLC analysis: **3bd**, 95% ee (AD-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 16.15 min (minor), 31.17 min (major).

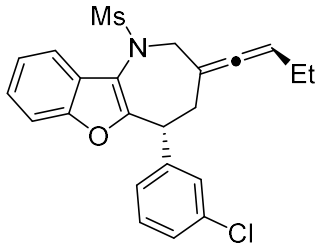
(*R*)-3-((*S*)-but-1-en-1-ylidene)-5-(2-chlorophenyl)-1-(methylsulfonyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3be)



3be

Prepared according to the general procedure as described above in 91% yield (38.8 mg), >20:1 dr and 98% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp = 62 – 64°C; $[\alpha]^{25}_{D}$= -81.0 (*c* 1.44, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.49 – 7.37 (m, 1H), 7.35 – 7.11 (m, 6H), 5.26 (s, 1H), 4.85 (dd, *J* = 11.0, 5.0 Hz, 1H), 4.49 (d, *J* = 122.0 Hz, 2H), 3.21 (s, 3H), 3.00 – 2.66 (m, 2H), 2.04 – 1.87 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 201.7, 153.6, 153.5, 138.2, 133.3, 129.8, 129.7, 129.5, 128.6, 128.5, 127.4, 126.3, 124.7, 123.3, 120.0, 119.7, 111.6, 111.5, 98.3, 95.3, 53.8, 43.7, 41.1, 33.7, 21.9, 13.3. HRMS (ESI) calcd for $C_{23}H_{23}ClNO_3S^+$ [M+H]+ 428.1082, found 428.1081. HPLC analysis: **3be**, 98% ee (IA, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 10.177 min (minor), 12.233 min (major).

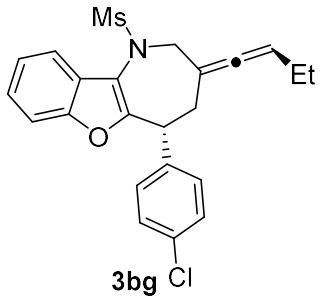
(*R*)-3-((*S*)-but-1-en-1-ylidene)-5-(3-chlorophenyl)-1-(methylsulfonyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bf)



3bf

Prepared according to the general procedure as described above in 76% yield (32.5 mg), 11:1 dr and 95% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp =118 – 120°C; $[\alpha]^{25}_{D}$= -67.2 (*c* 1.25, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.67 – 7.52 (m, 1H), 7.38 – 7.04 (m, 7H), 5.19 (qd, *J* = 6.1, 5.0, 2.1 Hz, 1H), 4.67 – 4.45 (m, 1H), 4.34 (dd, *J* = 8.7, 5.1 Hz, 1H), 4.16 – 3.97 (m, 1H), 2.99 – 2.65 (m, 5H), 2.00 – 1.84 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 202.8, 153.6, 153.3, 142.6, 134.5, 130.0, 129.9, 128.0, 127.9, 127.4, 127.3, 126.48, 126.47, 126.2, 124.8, 123.3, 120.3, 119.6, 111.5, 97.7, 94.8, 54.0, 45.2, 40.74, 40.72, 34.5, 21.8, 13.3. HRMS (ESI) calcd for $C_{23}H_{23}ClNO_3S^+$ $[M+H]^+$ 428.1082, found 428.1084. HPLC analysis: **3bf**, 95% ee (AD-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 13.467 min (minor), 22.813 min (major).

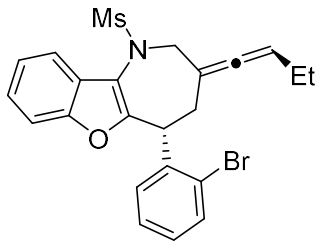
(*R*)-3-((*S*)-but-1-en-1-ylidene)-5-(4-chlorophenyl)-1-(methylsulfonyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bg)



3bg

Prepared according to the general procedure as described above in 76% yield (32.5 mg), 11.5:1 dr and 95% ee.. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp = 59 – 62°C; $[\alpha]^{25}_{D}$= -78.5 (*c* 1.34, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 6.3, 2.9 Hz, 1H), 7.46 – 7.14 (m, 8H), 5.25 (tt, *J* = 6.1, 2.6 Hz, 1H), 4.64 (d, *J* = 14.5 Hz, 1H), 4.40 (dd, *J* = 9.0, 5.1 Hz, 1H), 4.17 (d, *J* = 14.3 Hz, 1H), 3.07 – 2.67 (m, 5H), 2.05 – 1.91 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 202.6, 153.9, 153.3, 139.2, 133.0, 130.9, 129.3, 129.2, 128.9, 128.8, 126.5, 124.8, 123.3, 120.2, 119.5, 111.5, 97.9, 94.8, 94.7, 53.9, 45.1, 40.8, 34.7, 21.8, 13.2. HRMS (ESI) calcd for $C_{23}H_{23}ClNO_3S^+$ $[M+H]^+$ 428.1082, found 428.1073. HPLC analysis: **3bg**, 95% ee (AD-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 19.493 min (minor), 33.68 min (major).

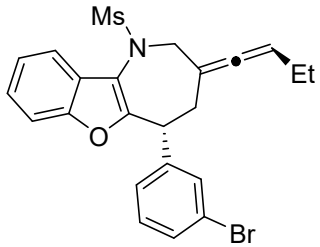
(*R*)-5-(2-bromophenyl)-3-((*S*)-but-1-en-1-ylidene)-1-(methylsulfonyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bh)



3bh

Prepared according to the general procedure as described above in 90% yield (42.3 mg), >20:1 dr and 98% ee.. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp = 66 – 68°C; $[\alpha]^{25}_{D}$= -71.6 (*c* 1.76, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.73 – 7.55 (m, 2H), 7.40 – 7.10 (m, 6H), 5.27 (s, 1H), 4.83 (dd, *J* = 11.1, 5.0 Hz, 1H), 4.49 (d, *J* = 126.1 Hz, 2H), 3.22 (s, 3H), 2.93 (ddd, *J* = 13.7, 5.0, 1.1 Hz, 1H), 2.74 (ddd, *J* = 13.5, 11.0, 2.2 Hz, 1H), 1.98 (qd, *J* = 7.4, 6.1 Hz, 2H), 1.02 – 0.87 (m, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 201.3, 153.3, 153.1, 139.5, 132.7, 132.6, 129.2, 128.5, 127.7, 125.9, 124.4, 123.6, 122.9, 119.6, 119.2, 111.3, 97.9, 94.9, 53.4, 46.0, 40.8, 33.6, 21.5, 12.9. HRMS (ESI) calcd for $C_{23}H_{23}BrNO_3S^+$ $[M+H]^+$ 472.0577, found 472.0565. HPLC analysis: **3bh**, 98% ee (AD-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 12.39 min (major), 13.243 min (minor).

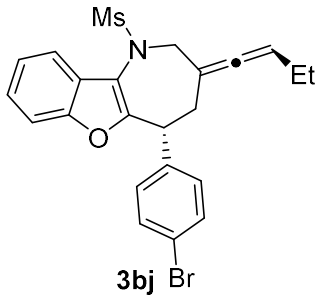
(*R*)-5-(3-bromophenyl)-3-((*S*)-but-1-en-1-ylidene)-1-(methylsulfonyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bi)



3bi

Prepared according to the general procedure as described above in 78% yield (36.7 mg), 9:1 dr and 95% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp = 107 – 110°C; $[\alpha]^{25}_{D}$= -57.5 (*c* 1.06, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.74 – 7.63 (m, 1H), 7.55 – 7.02 (m, 7H), 5.28 (ddq, *J* = 6.5, 4.4, 2.1 Hz, 1H), 4.66 (d, *J* = 14.7 Hz, 1H), 4.49 – 4.36 (m, 1H), 4.15 (d, *J* = 14.9 Hz, 1H), 3.11 – 2.73 (m, 5H), 2.09 – 1.91 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 202.8, 153.6, 153.3, 142.9, 130.9, 130.4, 130.33, 130.31, 130.3, 126.7, 126.6, 126.5, 124.8, 123.3, 122.7, 120.3, 119.6, 111.5, 97.7, 94.8, 54.0, 45.2, 40.7, 34.5, 21.8, 13.3. HRMS (ESI) calcd for $C_{23}H_{23}BrNO_3S^+$ $[M+H]^+$ 472.0577, found 472.0577. HPLC analysis: **3bi**, 95% ee (AD-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 13.92 min (minor), 21.70 min (major).

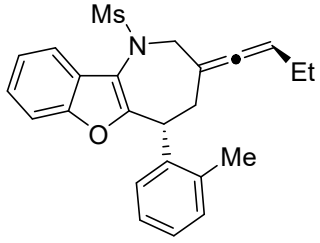
(*R*)-5-(4-bromophenyl)-3-((*S*)-but-1-en-1-ylidene)-1-(methylsulfonyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bj)



3bj

Prepared according to the general procedure as described above in 78% yield (36.7 mg), 11.5:1 dr and 95% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a viscous liquid; $[\alpha]^{25}_{D}$= -74.4 (*c* 1.41, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.72 – 7.63 (m, 1H), 7.49 – 7.11 (m, 8H), 5.25 (dt, *J* = 6.7, 4.0 Hz, 1H), 4.63 (d, *J* = 15.4 Hz, 1H), 4.38 (dd, *J* = 9.0, 5.2 Hz, 1H), 4.17 (d, *J* = 12.3 Hz, 1H), 3.03 – 2.71 (m, 6H), 2.08 – 1.90 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 202.6, 153.3, 139.7, 131.8, 131.7, 129.63, 129.60, 126.5, 124.8, 123.3, 121.1, 120.2, 119.6, 111.5, 97.9, 94.8, 53.9, 45.2, 40.9, 34.6, 21.8, 13.2. HRMS (ESI) calcd for $C_{23}H_{23}BrNO_3S^+$ $[M+H]^+$ 472.0577, found 472.0567. HPLC analysis: **3bj**, 95% ee (AD-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 21.52 min (minor), 35.09 min (major).

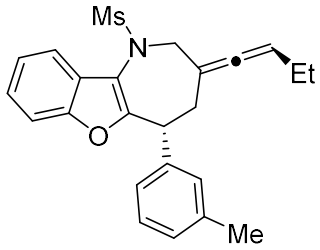
(*R*)-3-((*S*)-but-1-en-1-ylidene)-1-(methylsulfonyl)-5-(o-tolyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bk)



3bk

Prepared according to the general procedure as described above in 93% yield (37.9 mg), >20:1 dr and 98% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp = 66 – 70°C; $[\alpha]^{25}_{D}$= -74.9 (*c* 1.50, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.38 – 7.03 (m, 7H), 5.39 – 5.19 (m, 1H), 4.66 – 4.30 (m, 3H), 3.20 (s, 3H), 2.87 – 2.75 (m, 2H), 2.44 (s, 3H), 2.05 – 1.92 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 201.5, 154.6, 153.4, 139.0, 135.3, 130.7, 127.8, 127.2, 126.6, 126.4, 124.5, 123.2, 119.7, 119.6, 111.6, 98.9, 95.2, 53.8, 43.6, 40.9, 34.5, 21.9, 19.4, 13.4. HRMS (ESI) calcd for $C_{24}H_{26}NO_3S^+$ $[M+H]^+$ 408.1628, found 408.1634. HPLC analysis: **3bk**, 98% ee (IA, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 9.607 min (minor), 15.77 min (major).

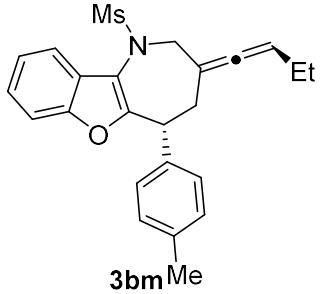
(*R*)-3-((*S*)-but-1-en-1-ylidene)-1-(methylsulfonyl)-5-(m-tolyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bl)



3bl

Prepared according to the general procedure as described above in 88% yield (35.8 mg), 12:1 dr and 93% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp = 56 – 58°C; $[\alpha]^{25}_{D}$= -67.5 (*c* 1.22, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 1H), 7.37 – 6.93 (m, 7H), 5.16 (tt, *J* = 6.4, 2.1 Hz, 1H), 4.57 (d, *J* = 14.1 Hz, 1H), 4.34 (dd, *J* = 8.7, 5.1 Hz, 1H), 4.14 – 3.98 (m, 1H), 3.01 – 2.64 (m, 5H), 2.24 (s, 3H), 2.05 – 1.85 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 202.8, 154.5, 153.3, 140.5, 138.3, 128.6, 128.5, 127.9, 126.7, 124.8, 124.6, 123.2, 120.4, 119.4, 111.4, 98.1, 94.4, 54.1, 45.3, 40.4, 34.6, 21.8, 21.6, 13.3. HRMS (ESI) calcd for $C_{24}H_{26}NO_3S^+$ $[M+H]^+$ 408.1628, found 408.1623. HPLC analysis: **3bl**, 93% ee (AD-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 11.117 min (minor), 17.733 min (major).

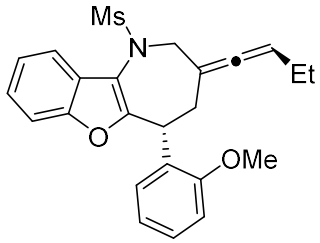
(*R*)-3-((*S*)-but-1-en-1-ylidene)-1-(methylsulfonyl)-5-(p-tolyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bm)



3bm

Prepared according to the general procedure as described above in 73% yield (29.7 mg), 13:1 dr and 95% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a viscous liquid; $[\alpha]^{25}_{D}$= -61.4 (*c* 0.70, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.77 – 7.64 (m, 1H), 7.48 – 7.03 (m, 7H), 5.24 (tt, *J* = 6.2, 2.1 Hz, 1H), 4.64 (d, *J* = 15.2 Hz, 1H), 4.42 (dd, *J* = 8.7, 5.0 Hz, 1H), 4.14 (d, *J* = 15.0 Hz, 1H), 3.12 – 2.70 (m, 5H), 2.32 (s, 3H), 2.02 (qd, *J* = 7.3, 5.8 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 202.1, 153.8, 152.4, 136.8, 136.0, 128.6, 128.5, 126.9, 126.8, 125.9, 123.8, 122.4, 119.6, 118.5, 110.6, 97.3, 93.5, 53.3, 44.2, 39.6, 33.9, 21.0, 20.3, 12.5. HRMS (ESI) calcd for $C_{24}H_{26}NO_3S^+$ $[M+H]^+$ 408.1628, found 408.1616. HPLC analysis: **3bm**, 95% ee (IA, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 13.203 min (minor), 27.423 min (major).

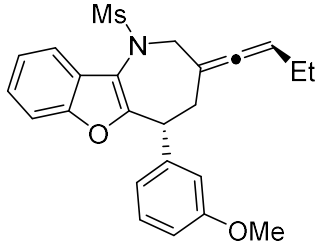
(*R*)-3-((*S*)-but-1-en-1-ylidene)-5-(2-methoxyphenyl)-1-(methylsulfonyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bn)



3bn

Prepared according to the general procedure as described above in 60% yield (25.4 mg), >20:1 dr and 95% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp = 60 – 62°C; $[\alpha]^{25}_{D}$= -74.9 (*c* 0.90, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.76 – 7.56 (m, 1H), 7.34 – 6.84 (m, 7H), 5.27 – 5.15 (m, 1H), 4.77 (dd, *J* = 10.5, 4.9 Hz, 1H), 4.46 (d, *J* = 56.0 Hz, 2H), 3.84 (s, 3H), 3.16 (s, 3H), 2.94 – 2.72 (m, 2H), 2.03 – 1.92 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 201.8, 156.8, 154.3, 153.3, 132.3, 130.9, 128.9, 128.7, 128.4, 128.4, 126.6, 124.4, 123.1, 120.8, 120.0, 119.7, 111.4, 110.8, 110.7, 98.7, 94.6, 65.6, 55.6, 54.1, 40.5, 33.9, 21.9, 19.2, 13.8, 13.4. HRMS (ESI) calcd for $C_{24}H_{26}NO_4S^+$ $[M+H]^+$ 424.1577, found 424.1575. HPLC analysis: **3bn**, 95% ee (AD-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 15.70 min (minor), 21.12 min (major).

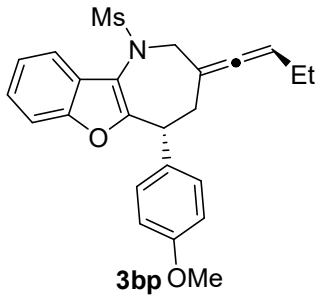
(*R*)-3-((*S*)-but-1-en-1-ylidene)-5-(3-methoxyphenyl)-1-(methylsulfonyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bo)



3bo

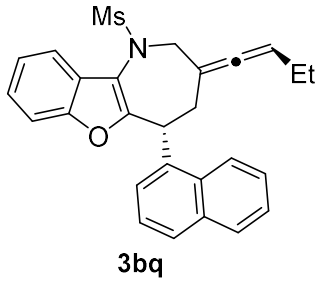
Prepared according to the general procedure as described above in 99% yield (41.7 mg), 15.5:1 dr and 95% ee.. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp = 44 – 46°C; $[\alpha]^{25}_{D}$= -67.4 (*c* 1.91, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.67 – 7.53 (m, 1H), 7.39 – 7.10 (m, 4H), 6.87 – 6.66 (m, 3H), 5.18 (tdt, *J* = 6.3, 4.7, 2.3 Hz, 1H), 4.68 – 4.49 (m, 1H), 4.32 (dd, *J* = 8.9, 5.2 Hz, 1H), 4.13 – 3.95 (m, 1H), 3.67 (s, 3H), 3.01 – 2.66 (m, 5H), 1.93 (qdd, *J* = 7.3, 6.0, 1.2 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 202.8, 159.9, 154.4, 153.3, 142.2, 129.7, 126.6, 124.6, 123.2, 120.2, 120.1, 119.3, 113.5, 112.7, 111.5, 98.1, 94.5, 55.3, 55.2, 54.1, 45.5, 40.7, 34.6, 21.8, 13.2. HRMS (ESI) calcd for $C_{24}H_{26}NO_4S^+$ $[M+H]^+$ 424.1577, found 424.1580. HPLC analysis: **3bo**, 95% ee (AD-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 18.717min (minor), 30.483min (major).

(*R*)-3-((*S*)-but-1-en-1-ylidene)-5-(4-methoxyphenyl)-1-(methylsulfonyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bp)



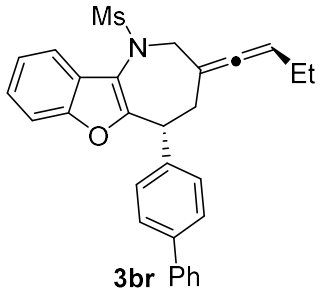
Prepared according to the general procedure as described above in 71% yield (30.0 mg), >20:1 dr and 98% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp = 52 – 54°C; $[\alpha]^{25}_{D}$= -77.9 (*c* 1.18, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.75 – 7.64 (m, 1H), 7.41 – 7.13 (m, 5H), 6.92 – 6.76 (m, 2H), 5.24 (tt, *J* = 6.3, 2.0 Hz, 1H), 4.64 (d, *J* = 14.6 Hz, 1H), 4.41 (dd, *J* = 8.5, 5.0 Hz, 1H), 4.13 (d, *J* = 14.8 Hz, 1H), 3.78 (s, 3H), 3.04 – 2.71 (m, 5H), 2.02 (qd, *J* = 7.4, 6.0 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 202.8, 158.6, 154.8, 153.2, 132.7, 128.8, 126.7, 124.6, 123.2, 120.4, 119.2, 114.0, 113.9, 111.4, 98.0, 94.3, 55.3, 54.1, 44.5, 40.5, 34.7, 21.8, 13.3. HRMS (ESI) calcd for $C_{24}H_{26}NO_4S^+$ $[M+H]^+$ 424.1577, found 424.1589. HPLC analysis: **3bp**, 98% ee (AS-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 31.56 min (major), 69.513 min (minor).

(*R*)-3-((*S*)-but-1-en-1-ylidene)-1-(methylsulfonyl)-5-(naphthalen-1-yl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bq)



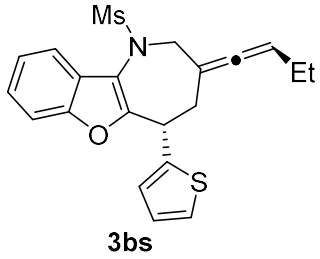
Prepared according to the general procedure as described above in 84% yield (37.2 mg), >20:1 dr and 97% ee.. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp = 62 – 64°C; $[\alpha]^{25}_{D}$= -141.0 (*c* 2.50, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 1H), 7.97 – 7.86 (m, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.69 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.59 – 7.18 (m, 7H), 5.27 (s, 1H), 5.17 (dd, *J* = 11.0, 5.2 Hz, 1H), 4.73 – 4.36 (m, 2H), 3.23 (s, 3H), 3.11 – 2.87 (m, 2H), 2.09 – 1.93 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 201.6, 154.4, 153.5, 136.7, 134.1, 131.0, 129.2, 129.2, 127.9, 126.6, 126.5, 125.74, 125.72, 125.6, 125.6, 124.6, 123.2, 122.5, 120.1, 119.7, 111.6, 111.5, 98.8, 95.3, 53.9, 43.1, 41.0, 34.8, 21.9, 13.4. HRMS (ESI) calcd for $C_{27}H_{26}NO_3S^+$ $[M+H]^+$ 444.1628, found 444.1630. HPLC analysis: **3bq**, 97% ee (IC, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 24.153 min (major), 34.833 min (minor).

(*R*)-5-([1,1'-biphenyl]-4-yl)-3-((*S*)-but-1-en-1-ylidene)-1-(methylsulfonyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3br)



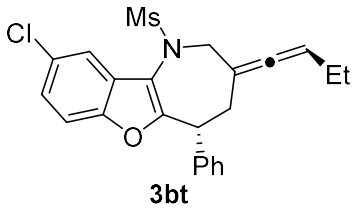
Prepared according to the general procedure as described above in 97% yield (45.4 mg), 15.5:1 dr and 96% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp = 80 – 82°C; $[\alpha]^{25}_{D}$= -112.8 (*c* 1.30, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 1H), 7.59 – 7.17 (m, 11H), 5.25 (tt, *J* = 6.5, 2.1 Hz, 1H), 4.77 – 4.61 (m, 1H), 4.50 (dd, *J* = 8.7, 5.1 Hz, 1H), 4.29 – 4.06 (m, 1H), 3.13 – 2.75 (m, 5H), 2.13 – 1.90 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 201.5, 152.9, 151.9, 139.2, 138.7, 138.3, 127.5, 126.9, 126.1, 125.9, 125.7, 125.68, 125.66, 125.3, 123.3, 121.9, 119.1, 118.2, 110.1, 96.6, 93.2, 52.8, 43.8, 39.2, 33.3, 20.5, 11.9. HRMS (ESI) calcd for $C_{29}H_{28}NO_3S^+$ $[M+H]^+$ 470.1784, found 470.1780. HPLC analysis: **3br**, 96% ee (AD-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 29.163 min (minor), 51.993 min (major).

(*S*)-3-((*S*)-but-1-en-1-ylidene)-1-(methylsulfonyl)-5-(thiophen-2-yl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bs)



Prepared according to the general procedure as described above in 92% yield (36.7 mg), 13:1 dr and 94% ee.. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp = 70 – 72°C; $[\alpha]^{25}_{D}$= -38.7 (*c* 1.48, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.75 – 7.58 (m, 1H), 7.38 – 7.31 (m, 1H), 7.28 – 7.07 (m, 3H), 6.92 – 6.68 (m, 2H), 5.27 – 5.15 (m, 1H), 4.74 – 4.53 (m, 2H), 3.91 (d, *J* = 15.2 Hz, 1H), 3.08 – 2.72 (m, 2H), 2.55 (s, 3H), 1.98 (qd, *J* = 7.4, 6.0 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 204.1, 153.2, 152.9, 143.9, 126.8, 126.7, 125.5, 124.9, 124.6, 123.3, 121.3, 119.4, 111.3, 111.2, 97.2, 93.9, 54.5, 40.2, 39.8, 34.9, 21.7, 13.3. HRMS (ESI) calcd for $C_{21}H_{22}NO_3S_2^+$ $[M+H]^+$ 400.1036, found 400.1031. HPLC analysis: **3bs**, 94% ee (AD-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 18.653 min (minor), 33.143 min (major).

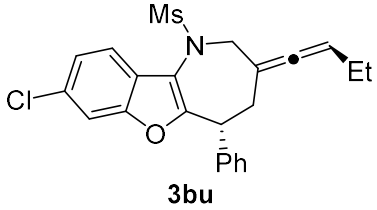
(*R*)-3-((*S*)-but-1-en-1-ylidene)-9-chloro-1-(methylsulfonyl)-5-phenyl-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bt)



3bt

Prepared according to the general procedure as described above in 62% yield (26.5 mg), 19:1 dr and 92% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a viscous liquid; $[\alpha]^{25}_D$= -84.1 (*c* 0.70, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.67 (d, *J* = 2.2 Hz, 1H), 7.44 – 7.15 (m, 7H), 5.25 (ddq, *J* = 6.5, 4.4, 2.1 Hz, 1H), 4.62 (d, *J* = 15.4 Hz, 1H), 4.45 (dd, *J* = 8.5, 5.1 Hz, 1H), 4.24 – 4.05 (m, 1H), 3.01 (dd, *J* = 14.2, 8.5 Hz, 1H), 2.78 (s, 4H), 2.02 (p, *J* = 7.1 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 203.0, 155.9, 151.6, 140.2, 129.1, 128.8, 128.7, 128.1, 127.7, 127.3, 124.9, 120.2, 119.1, 112.4, 97.7, 94.5, 54.1, 45.2, 40.5, 34.4, 21.8, 13.2. HRMS (ESI) calcd for **$C_{23}H_{23}ClNO_3S^+$** $[M+H]^+$ 428.1082, found 428.1081. HPLC analysis: **3bt**, 92% ee (AD-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 13.183 min (minor), 24.98 min (major).

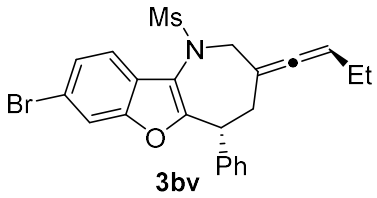
(*R*)-3-((*S*)-but-1-en-1-ylidene)-8-chloro-1-(methylsulfonyl)-5-phenyl-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bu)



3bu

Prepared according to the general procedure as described above in 77% yield (32.9 mg), 13:1 dr and 93% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp = 48 – 50°C; $[\alpha]^{25}_D$= -16.7 (*c* 0.70, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.5 Hz, 1H), 7.43 – 7.11 (m, 7H), 5.24 (tt, *J* = 6.2, 2.0 Hz, 1H), 4.62 (d, *J* = 15.4 Hz, 1H), 4.46 (dd, *J* = 8.2, 5.0 Hz, 1H), 4.23 – 4.05 (m, 1H), 3.01 (dd, *J* = 14.2, 8.3 Hz, 1H), 2.86 – 2.69 (m, 4H), 2.11 – 1.92 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 203.1, 154.2, 153.2, 140.2, 130.5, 128.74, 128.71, 127.7, 127.6, 127.3, 125.4, 124.0, 121.4, 119.6, 111.8, 97.6, 94.4, 54.2, 54.1, 44.9, 40.3, 34.4, 21.8, 13.2. HRMS (ESI) calcd for $C_{23}H_{23}ClNO_3S^+$ $[M+H]^+$ 428.1082, found 428.1096. HPLC analysis: **3bu**, 93% ee (IA, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 13.073 min (minor), 34.76 min (major).

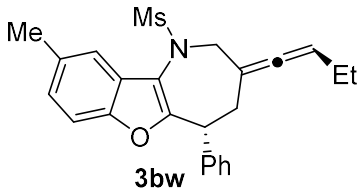
(*R*)-8-bromo-3-((*S*)-but-1-en-1-ylidene)-1-(methylsulfonyl)-5-phenyl-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bv)



3bv

Prepared according to the general procedure as described above in 66% yield (31.1 mg), 13:1 dr and 92% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a viscous liquid; $[\alpha]^{25}_{D}$= -19.7 (*c* 1.18, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.60 – 7.38 (m, 2H), 7.35 – 7.08 (m, 6H), 5.17 (tt, *J* = 6.2, 2.1 Hz, 1H), 4.59 – 4.48 (m, 1H), 4.38 (dd, *J* = 8.2, 5.0 Hz, 1H), 4.13 – 3.96 (m, 1H), 3.03 – 2.56 (m, 5H), 1.95 (qdd, *J* = 7.3, 6.1, 0.9 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 203.1, 154.8, 153.4, 140.2, 128.74, 128.71, 127.7, 127.6, 127.3, 126.7, 125.9, 121.8, 119.6, 117.9, 114.7, 97.6, 94.4, 54.2, 44.9, 40.3, 34.4, 21.8, 13.2. HRMS (ESI) calcd for $C_{23}H_{23}BrNO_3S^+$ $[M+H]^+$ 472.0577, found 472.0570. HPLC analysis: **3bv**, 92% ee (AD-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 14.937 min (minor), 63.11 min (major).

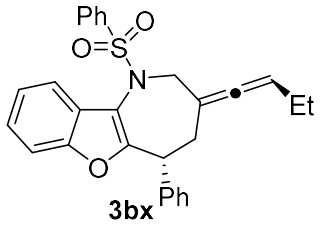
(*R*)-3-((*S*)-but-1-en-1-ylidene)-9-methyl-1-(methylsulfonyl)-5-phenyl-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bw)



3bw

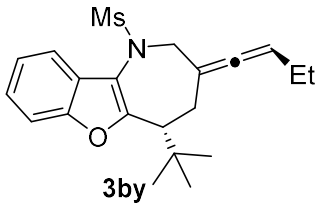
Prepared according to the general procedure as described above in 95% yield (38.6 mg), >20:1 dr and 96% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a viscous liquid; $[\alpha]^{25}_{D}$= -73.8 (*c* 1.19, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.48 (d, *J* = 1.8 Hz, 1H), 7.36 – 7.18 (m, 6H), 7.08 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.23 (ddq, *J* = 6.3, 4.2, 2.0 Hz, 1H), 4.63 (s, 1H), 4.45 (dd, *J* = 8.4, 5.1 Hz, 1H), 4.11 (d, *J* = 14.7 Hz, 1H), 3.02 (dd, *J* = 14.2, 8.4 Hz, 1H), 2.77 (d, *J* = 16.4 Hz, 4H), 2.45 (s, 3H), 2.12 – 1.92 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 202.9, 154.5, 151.7, 140.7, 132.8, 128.7, 128.6, 127.8, 127.1, 126.7, 125.9, 120.1, 119.2, 110.9, 97.9, 94.3, 54.1, 45.2, 40.4, 34.5, 21.8, 21.5, 13.3. HRMS (ESI) calcd for $C_{24}H_{26}NO_3S^+$ $[M+H]^+$ 408.1628, found 408.1619. HPLC analysis: **3bw**, 96% ee (AD-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 11.41 min (minor), 23.727 min (major).

(*R*)-3-((*S*)-but-1-en-1-ylidene)-5-phenyl-1-(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3bx)



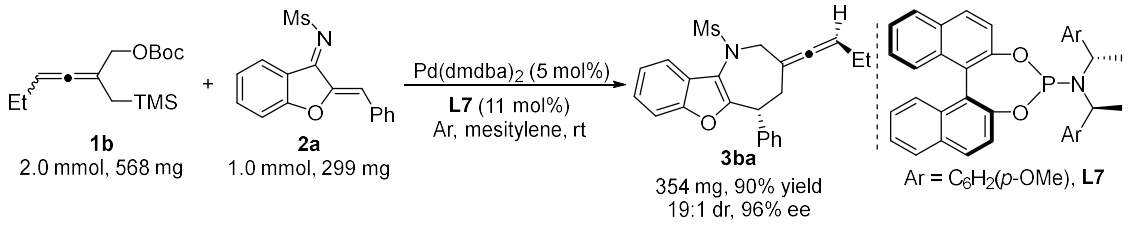
Prepared according to the general procedure as described above in 99% yield (45.1 mg), 9:1 dr and 95% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a white solid. mp =50 – 52°C; $[\alpha]^{25}_{D}$= -346.8 (*c* 0.95, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.9 Hz, 2H), 7.59 – 7.31 (m, 4H), 7.27 – 7.10 (m, 6H), 6.91 (d, *J* = 7.7 Hz, 2H), 5.21 – 4.97 (m, 1H), 4.69 (s, 1H), 4.41 – 4.16 (m, 1H), 4.05 – 3.87 (m, 1H), 2.41 – 2.18 (m, 1H), 2.04 (t, *J* = 12.6 Hz, 1H), 1.93 – 1.59 (m, 2H), 0.93 – 0.66 (m, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 201.3, 167.8, 153.9, 153.7, 153.6, 141.1, 139.4, 133.1, 133.0, 132.4, 130.9, 129.3, 129.1, 129.0, 128.9, 128.6, 128.0, 127.9, 127.8, 127.7, 127.13, 127.10, 126.7, 126.6, 124.54, 124.51, 123.1, 123.0, 121.0, 119.5, 111.3, 98.4, 95.0, 65.6, 54.5, 54.4, 46.6, 34.8, 30.6, 21.8, 19.2, 13.8, 13.3. HRMS (ESI) calcd for $C_{28}H_{26}NO_3S^+$ $[M+H]^+$ 456.1628, found 456.1637. HPLC analysis: **3bx**, 95% ee (AD-H, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 10.57 min (minor), 33.583 min (major).

(*R*)-3-((*S*)-but-1-en-1-ylidene)-5-(tert-butyl)-1-(methylsulfonyl)-2,3,4,5-tetrahydro-1*H*-benzofuro[3,2-*b*]azepine (3by)



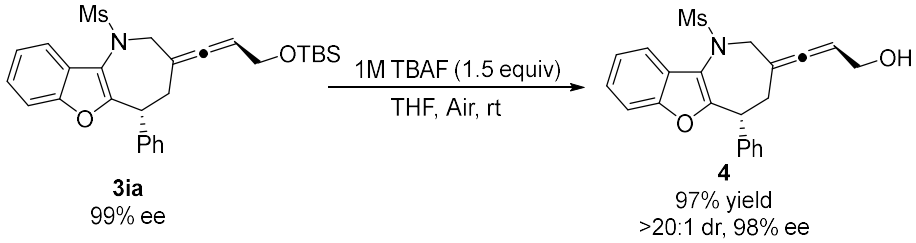
Prepared according to the general procedure as described above in 86% yield (32.1 mg), 6:1 dr and 92% ee. It was purified by flash chromatography 4% EtOAc/PE) to afford a viscous liquid. $[\alpha]^{25}_{D}$= 36.5 (*c* 1.54, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 1H), 7.43 – 7.36 (m, 1H), 7.25 (m, 2H), 5.32 – 5.14 (m, 1H), 4.51 (s, 1H), 4.01 (s, 1H), 3.19 (s, 3H), 2.85 (dd, J = 11.3, 6.9 Hz, 1H), 2.63 (dt, J = 9.4, 4.8 Hz, 1H), 2.46 (t, J = 12.2 Hz, 1H), 1.84 (dq, J = 14.5, 7.7 Hz, 2H), 1.11 (s, 9H), 0.63 (s, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 201.9, 155.9, 153.3, 126.4, 124.1, 124.0, 122.9, 122.9, 119.1, 118.2, 111.3, 111.2, 99.0, 95.1, 53.8, 53.5, 51.4, 41.0, 35.3, 28.5, 28.4, 21.9, 21.4, 13.3, 12.4. HRMS (ESI) calcd for $C_{21}H_{28}NO_3S^+$ $[M+H]^+$ 374.1790, found 374.1786. HPLC analysis: **3by**, 95% ee (IA, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 10.273 min (major), 11.033 min (minor).

Scaled-up Synthesis of the Product 3ba



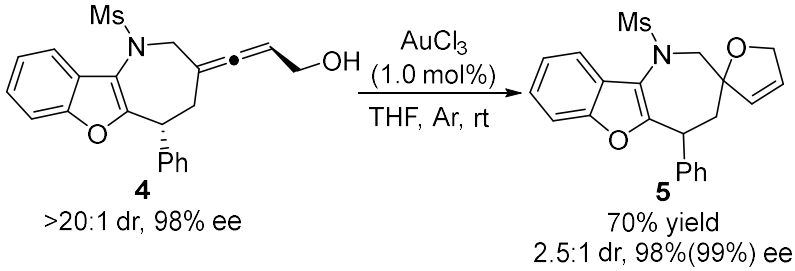
Under argon atmosphere, to a mixture of TMM donor **1b** (2.0 mmol), benzofuran-derived azadiene **2a** (1.0 mmol) and catalyst $Pd(dmdba)_2$ (5 mol%, 0.5mmol) / **L7** (11 mol%, 0. 11 mmol) in a Schlenk tube, 10 mL of mesitylene were added at room temperature. The resulting mixture was stirred until the starting material were completely consumed (monitored by TLC) and then was concentrated to dryness. The residue was purified through flash column chromatography (EtOAc/PE= 1:25) to afford the corresponding chiral cycloaddition product **3ba** with 90% yield (354 mg) and 96% ee, 19:1 dr.

Transformations of the Product 3ia and 3ba

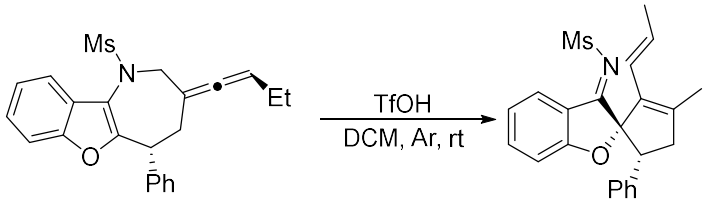


To a solution of **3ia** (50 mg, 0.10 mmol, 1.0 equiv) in THF (1M, 3.5 mL) at room temperature was added 1M TBAF solution in THF (0.15 mL), stirred for 30 min while being monitored by TLC. The solution was diluted with H_2O and extracted with diethyl ether. The extracts were washed with brine and dried over $MgSO_4$ and the solvent was removed in vacuo. The product was purified by column chromatography on silica gel (25% EtOAc/PE) to give a viscous liquid **4** (38.4 mg, 97% yield with 98% ee, >20:1 dr). **4: (*S*)-3-((*R*)-1-(methylsulfonyl)-5-phenyl-1,2,4,5-tetrahydro-3*H*-benzofuro[3,2-b]azepin-3-ylidene)prop-2-en-1-ol** $[\alpha]^{25}_D$= -56.1 (*c* 1.10, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.75 – 7.61 (m, 1H), 7.43 – 7.14 (m, 9H), 5.38 (tt, *J* = 5.4, 2.3 Hz, 1H), 4.60 – 4.25 (m, 2H), 4.19 – 4.09 (m, 2H), 3.12 – 2.73 (m, 5H), 1.84 (s, 1H). ^{13}C NMR (201 MHz, $CDCl_3$) δ

202.2, 154.4, 153.2, 140.1, 128.8, 128.7, 127.9, 127.8, 127.3, 126.4, 124.7, 123.4, 120.2, 119.6, 111.5, 100.5, 93.3, 60.1, 53.9, 45.11, 40.5, 34.9. HRMS (ESI) calcd for $C_{22}H_{22}NO_4S^+$[M+H]$^+$ 396.1264, found 396.1266. HPLC analysis: **4**, 98% ee (IA, 15% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 13.197 min (minor), 27.903 min (major).



A solution of **4** (79.0 mg, 0.20 mmol, 1.0 equiv) and $AuCl_3$ (0.6 mg, 1.0 mol %) in THF (0.20 mL) was stirred at room temperature for 5 h. The reaction mixture was concentrated to a crude oil and purified by column chromatography on silica gel (10% EtOAc/PE) to give a viscous liquid **5** (55.3 mg, 70% yield with 98% (99%) ee, 2.5:1 dr). **5: 1-(methylsulfonyl)-5-phenyl-1,2,4,5-tetrahydro-5'*H*-spiro[benzofuro[3,2-*b*]azepine-3,2'-furan]** $[\alpha]^{25}_D$= 4.3 (*c* 2.00, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 8.06 – 7.05 (m, 9H), 6.12 – 5.48 (m, 2H), 4.91 – 4.57 (m, 2H), 4.35 – 4.14 (m, 1H), 4.03 – 3.89 (m, 1H), 3.29 (d, *J* = 9.0 Hz, 3H), 2.38 – 1.71 (m, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 154.7, 153.4, 152.9, 141.8, 131.7, 129.8, 129.4, 128.8, 128.7, 128.68, 128.66, 127.9, 127.6, 127.4, 127.2, 126.2, 125.8, 124.7, 124.2, 123.2, 123.1, 121.8, 120.9, 111.4, 111.2, 107.7, 106.4, 92.6, 91.2, 74.6, 74.4, 67.7, 67.5, 60.4, 56.5, 43.1, 41.9, 41.7, 40.2, 39.9, 29.6, 29.5, 23.9, 23.8. HRMS (ESI) calcd for $C_{22}H_{22}NO_4S^+$ [M+H]$^+$ 396.1264, found 396.1274. HPLC analysis: **5**, 98% (99%) ee (IB, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), the major diastereomer t_R= 12.113 min (minor), 12.74 min (major), the minor diastereomer t_R= 13.913 min (trans-major).



3ba
19:1 dr, 96% ee

6
50% yield
11.5:1 dr, 87% ee

To a solution of **3ba** (40 mg, 0.10 mmol) in dichloromethane (1 mL), TfOH (18 μL, 0.2 mmol) was added. The reaction mixture was stirred at room temperature for 12 hours under argon atmosphere. Then, saturated aqueous $NaHCO_3$ solution was added and the mixture was extracted with dichloromethane three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated. The product was purified by column chromatography on silica gel (5% EtOAc/PE) to give a white solid **6** (19.6 mg, 50% yield with 87% ee, 11.5:1 dr). **6: *N*-((2*S*,5'*R*,*E*)-3'-methyl-5'-phenyl-2'-((*E*)-prop-1-en-1-yl)-3*H*-spiro[benzofuran-2,1'-cyclopentan]-2'-en-3-ylidene)methanesulfonamide** mp =70 – 73°C; $[\alpha]^{25}_D$= 210.8 (*c* 0.60, CH_2Cl_2); ^{1}H NMR (800 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.1 Hz, 1H), 7.36 (ddd, *J* = 8.5, 7.1, 1.4 Hz, 1H), 7.18 – 6.97 (m, 5H), 6.95 – 6.85 (m, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 6.13 – 5.99 (m, 1H), 5.07 (dq, *J* = 16.0, 6.6 Hz, 1H), 3.86 (t, *J* = 8.5 Hz, 1H), 3.28 (s, 3H), 3.13 (dd, *J* = 17.3, 8.8 Hz, 1H), 2.83 (dd, *J* = 17.2, 7.9 Hz, 1H), 2.02 (s, 3H), 1.72 – 1.59 (m, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 183.7, 169.0, 145.5, 138.7, 135.3, 131.7, 130.2, 129.0, 127.7, 127.2, 126.7, 121.7, 121.5, 118.9, 112.3, 103.7, 57.6, 43.0, 42.4, 19.1, 15.2. HRMS (ESI) calcd for $C_{23}H_{24}NO_3S^+$ $[M+H]^+$ 394,1471, found 394.1473. HPLC analysis: **6**, 87% ee (IA, 5% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), t_R = 9.443 min (major), 9.927 min (minor).

References

[1] B. M. Trost, Z. Daniel, M. Guillaume, H. Christoph, Autumn, M. Enantio- and Diastereoselective Synthesis of Chiral Allenes by Palladium-Catalyzed Asymmetric [3+2] Cycloaddition Reactions. *Angew. Chem. Int. Ed.* **2018**, *57*, 12916–12920.

[2] H. Xie, L. Sun, B. Wu, Y. Zhou, Copper-Catalyzed Alkynylation/ Cyclization/ Isomerization Cascade for Synthesis of 1,2-Dihydrobenzofuro[3,2-*b*]pyridines andBenzofuro[3,2-*b*]pyridines. *J. Org. Chem.* **2019**, *84*, 15498–15507.

^{1}H and ^{13}C NMR Spectra of All Products

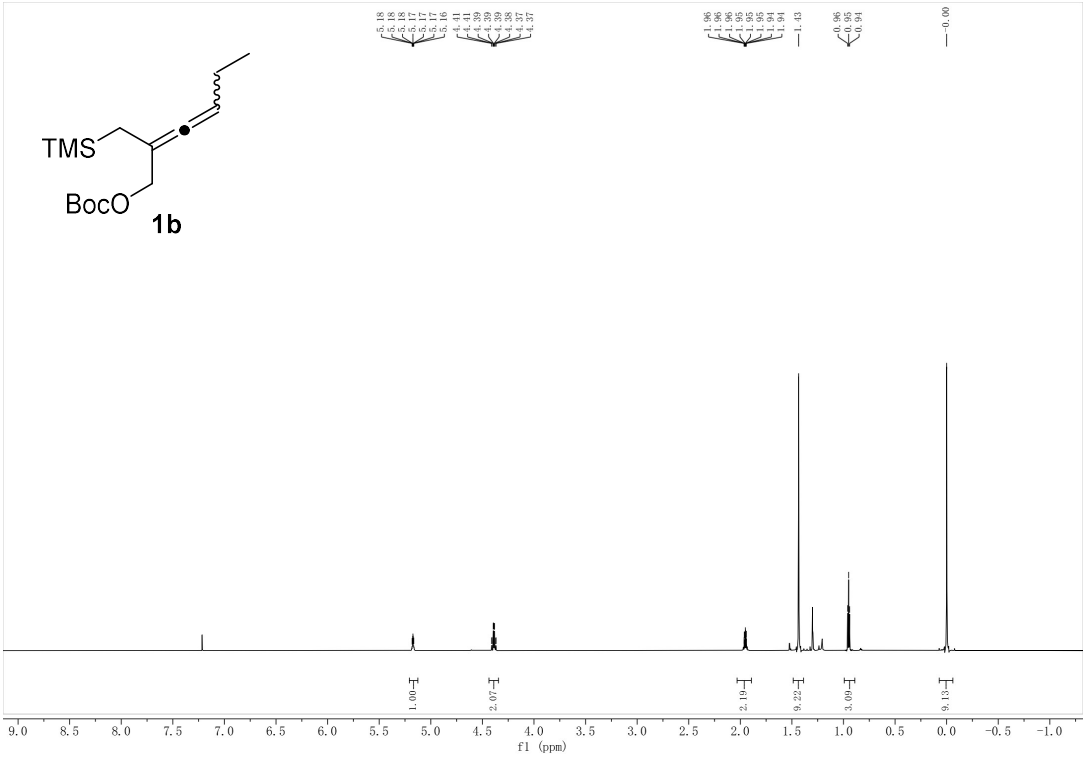


Figure S1. ^{1}H NMR spectrum of compound **1b** in $CDCl_3$ at 800 MHz.

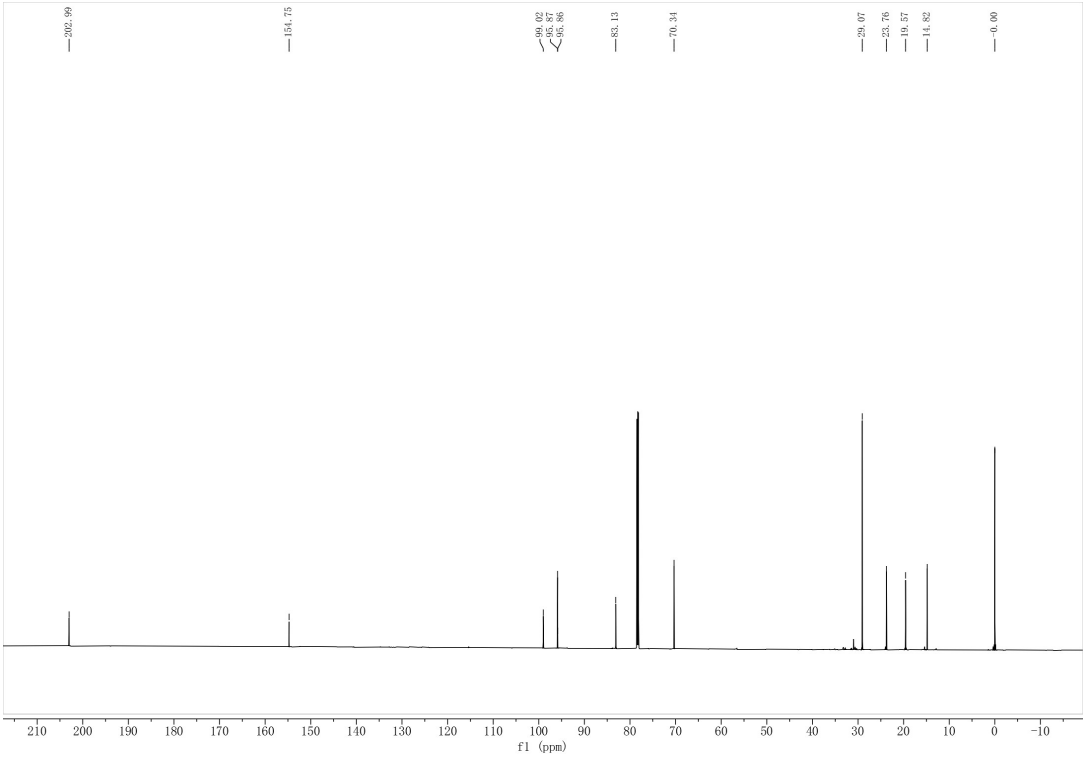


Figure S2. ^{13}C NMR spectrum of compound **1b** in $CDCl_3$ at 201 MHz.

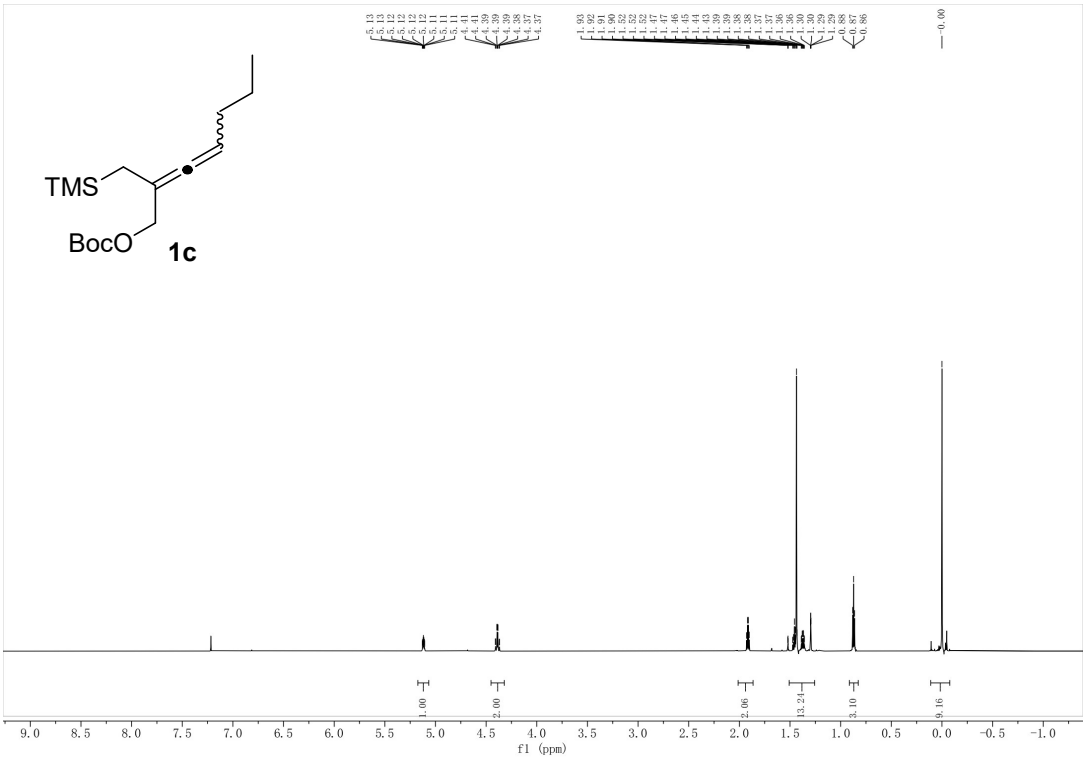


Figure S3. ^{1}H NMR spectrum of compound **1c** in $CDCl_3$ at 800 MHz.

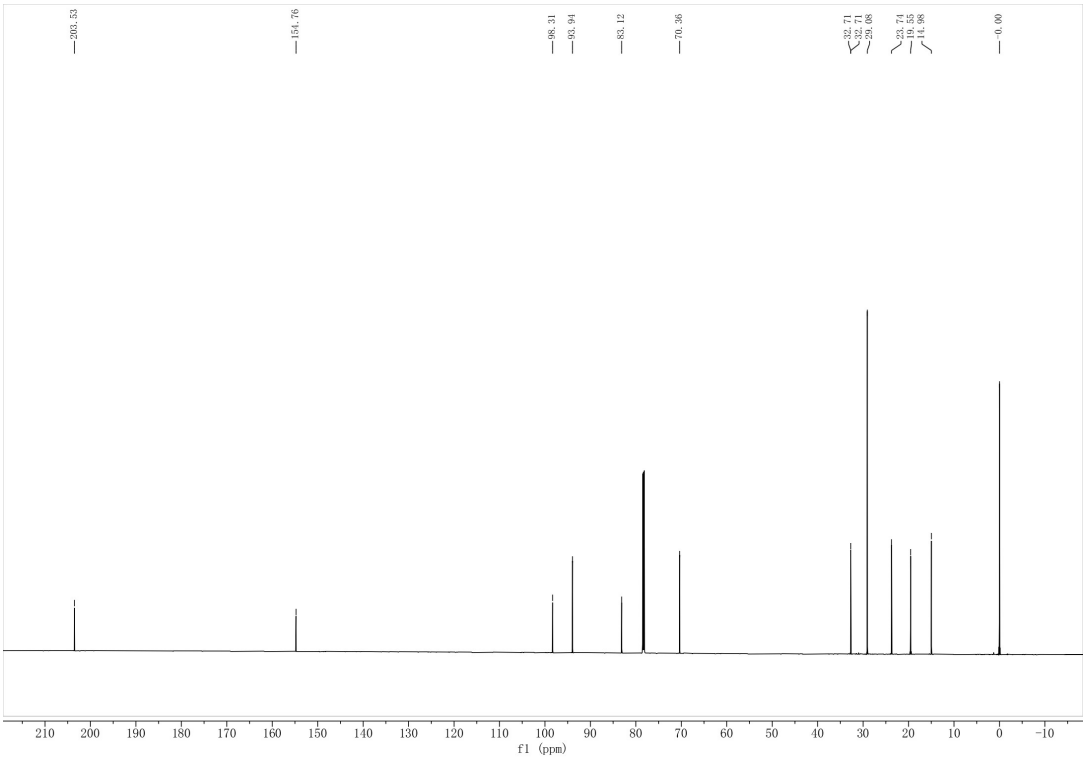


Figure S4. ^{13}C NMR spectrum of compound **1c** in $CDCl_3$ at 201 MHz.

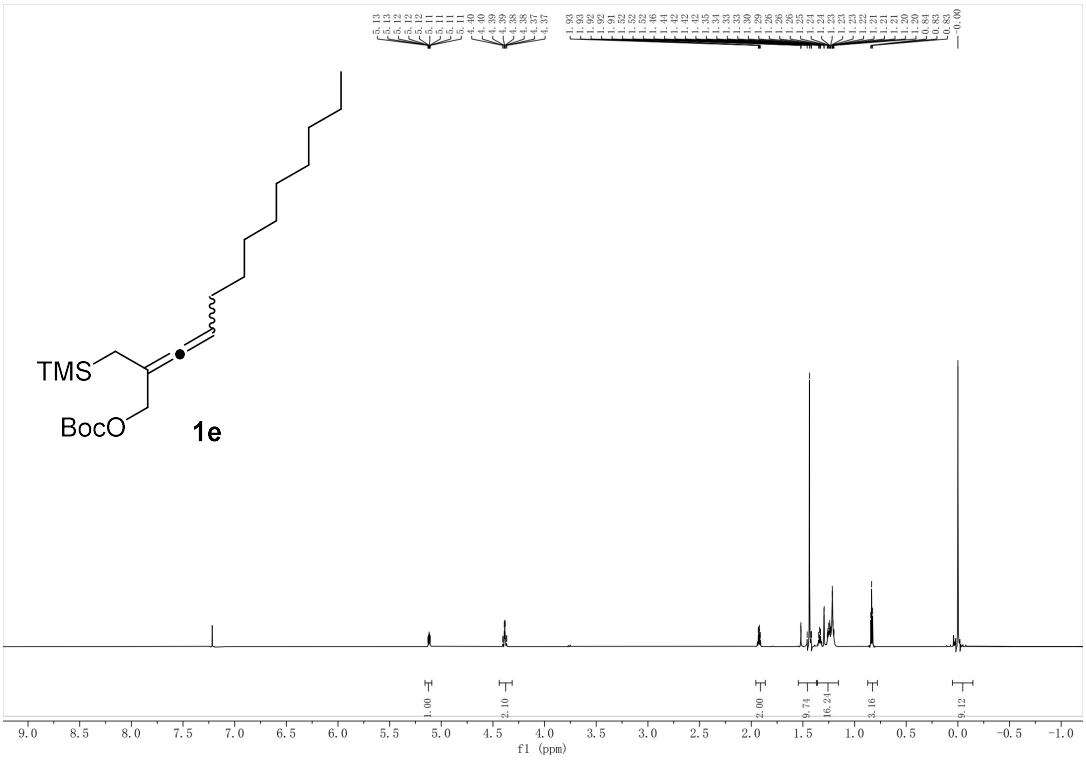


Figure S5. ^{1}H NMR spectrum of compound **1e** in $CDCl_3$ at 800 MHz.

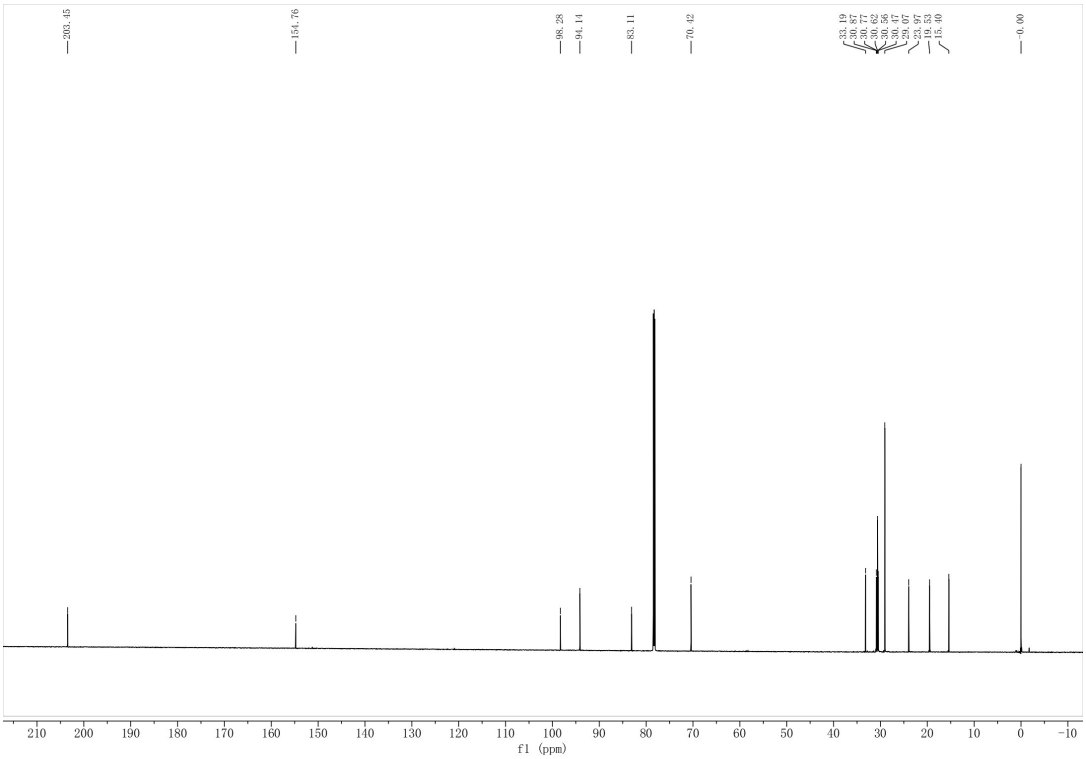


Figure S6. ^{13}C NMR spectrum of compound **1e** in $CDCl_3$ at 201 MHz.

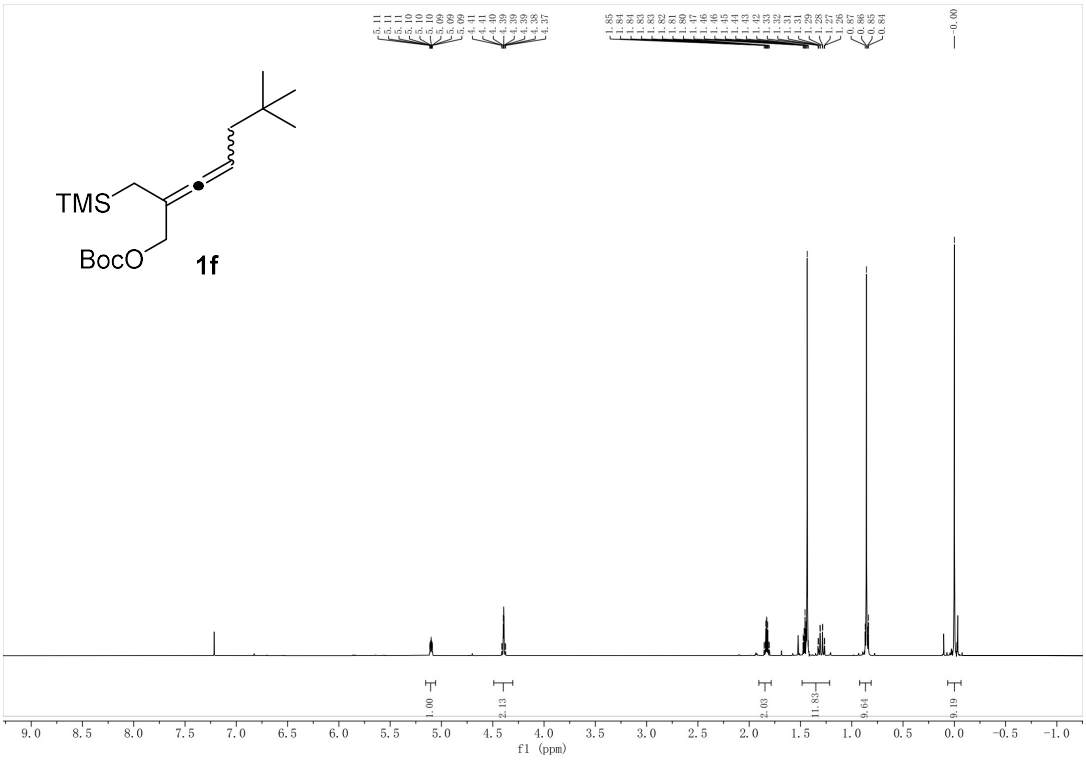


Figure S7. ^{1}H NMR spectrum of compound **1f** in $CDCl_3$ at 800 MHz.

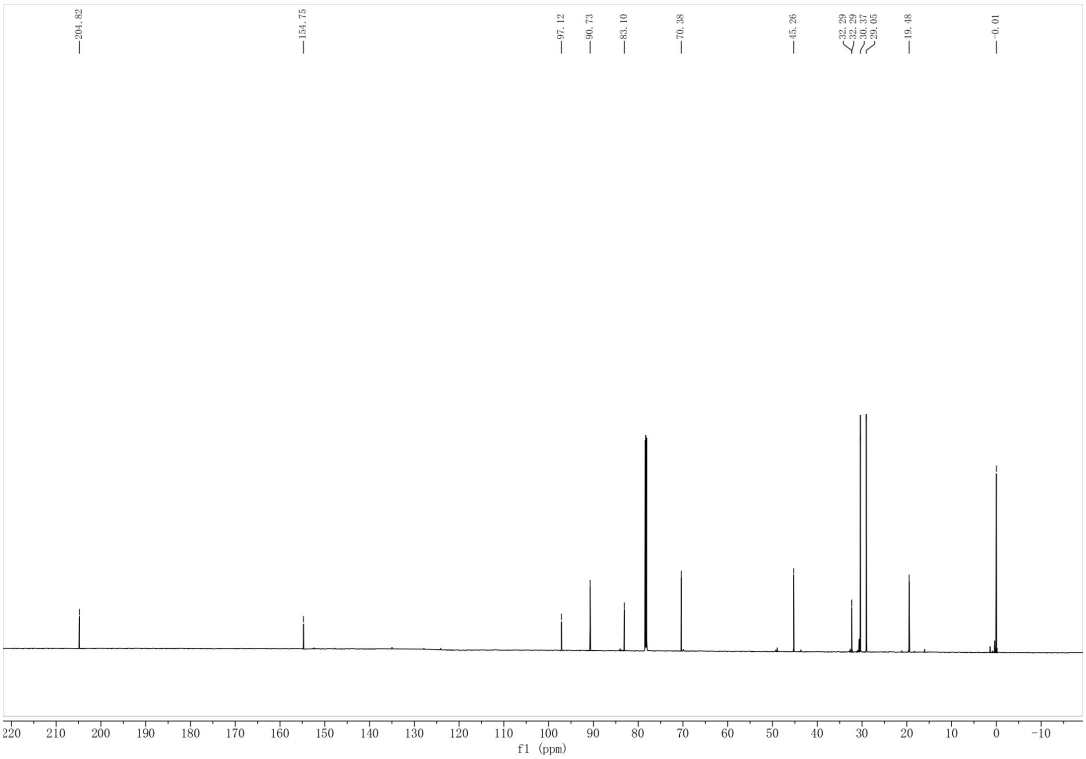


Figure S8. ^{13}C NMR spectrum of compound **1f** in $CDCl_3$ at 201 MHz.

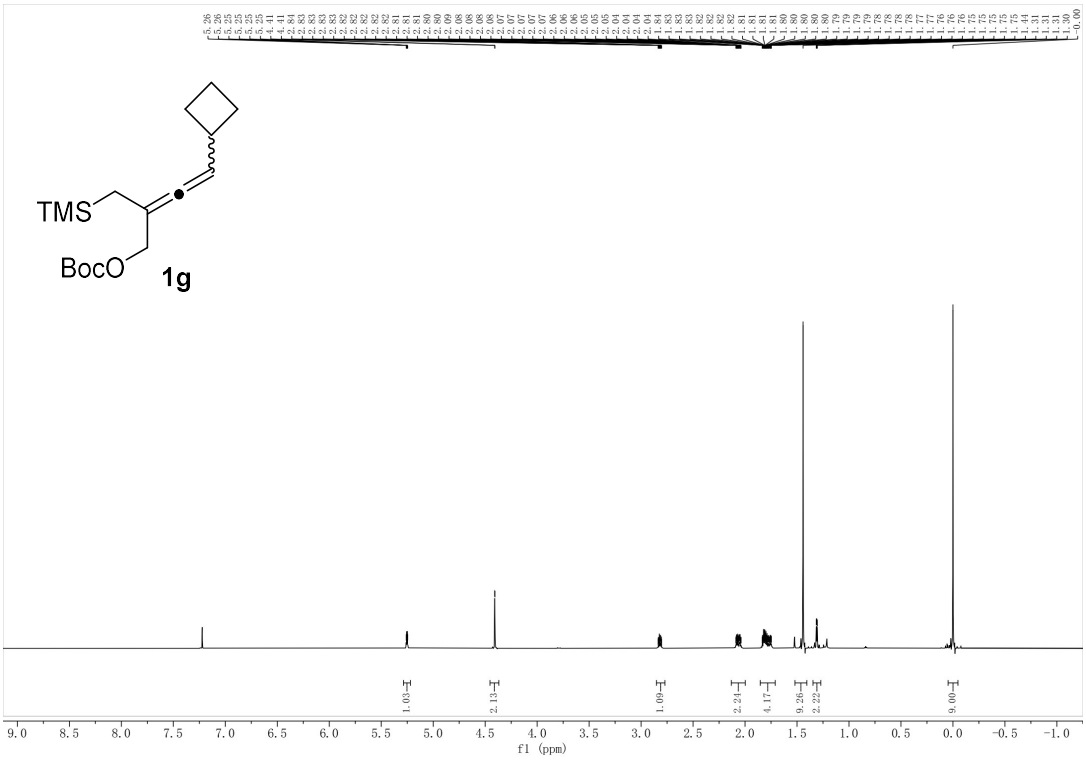


Figure S9. ^{1}H NMR spectrum of compound **1g** in $CDCl_3$ at 800 MHz.

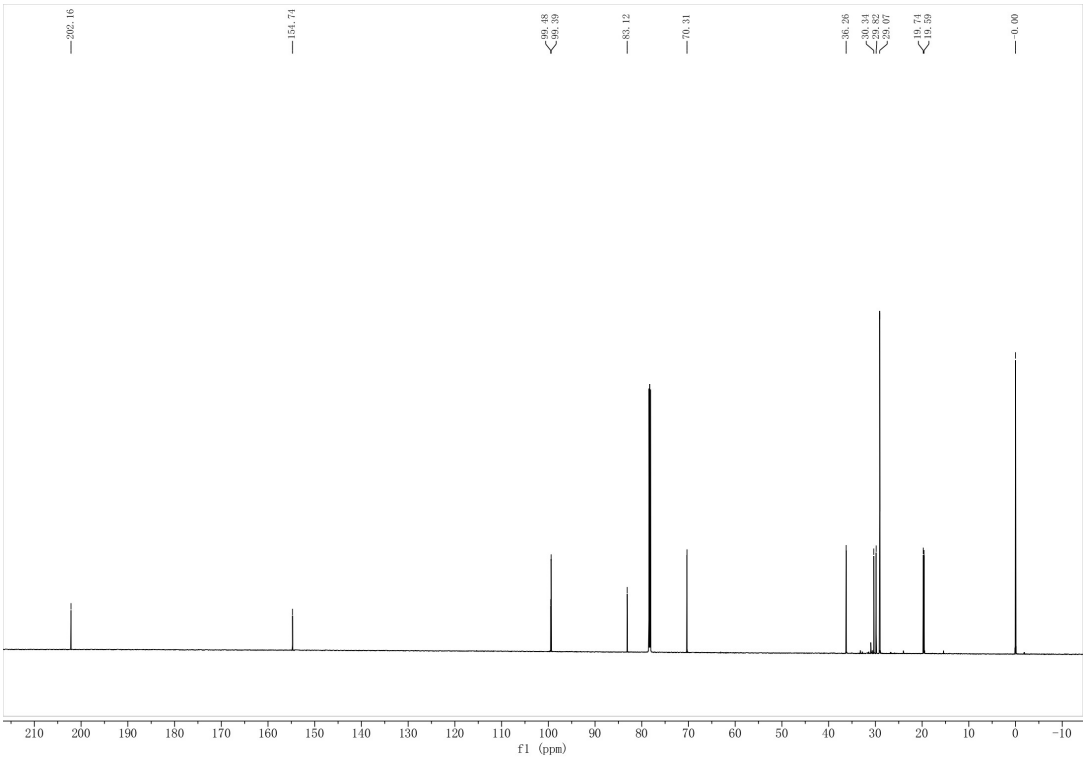


Figure S10. ^{13}C NMR spectrum of compound **1g** in $CDCl_3$ at 201 MHz.

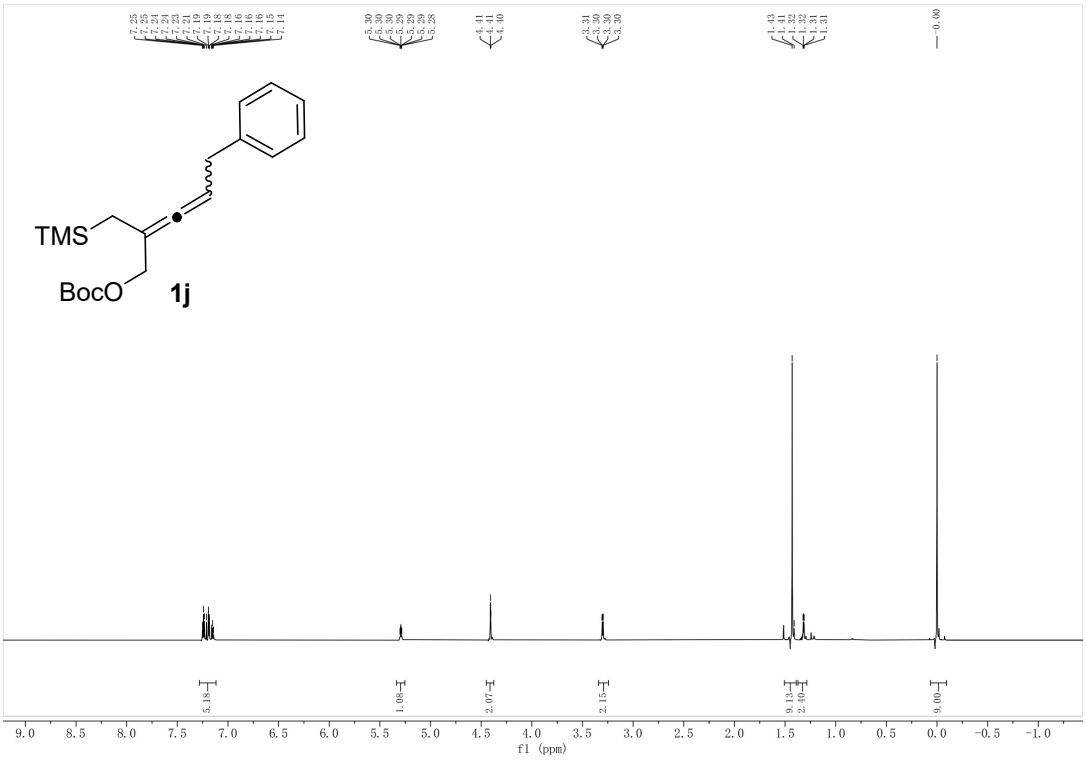


Figure S11. ^{1}H NMR spectrum of compound **1j** in $CDCl_3$ at 800 MHz.

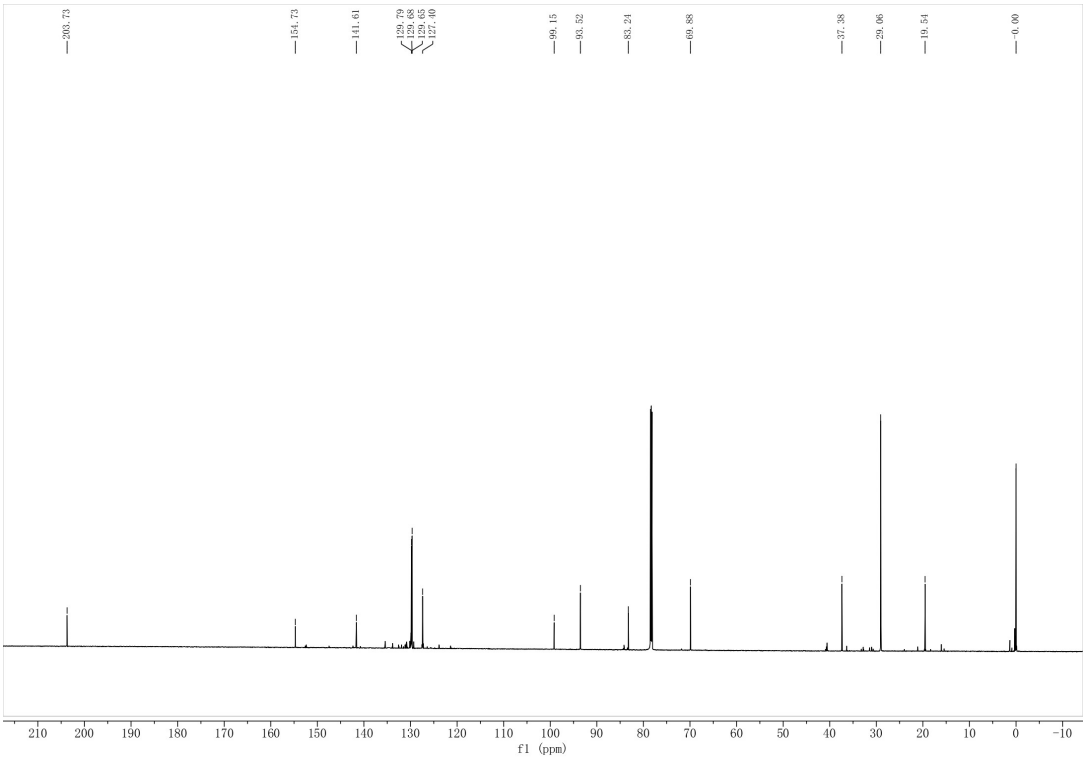


Figure S12. ^{13}C NMR spectrum of compound **1j** in $CDCl_3$ at 201 MHz.

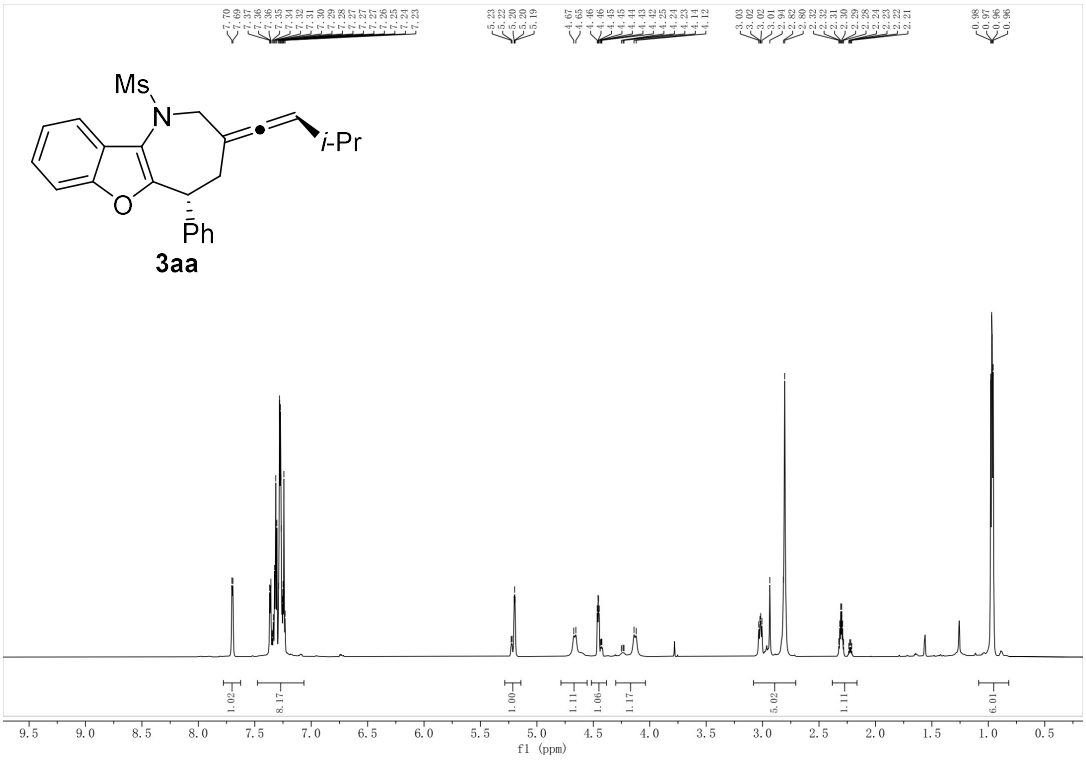


Figure S13. ^{1}H NMR spectrum of compound **3aa** in $CDCl_3$ at 800 MHz.

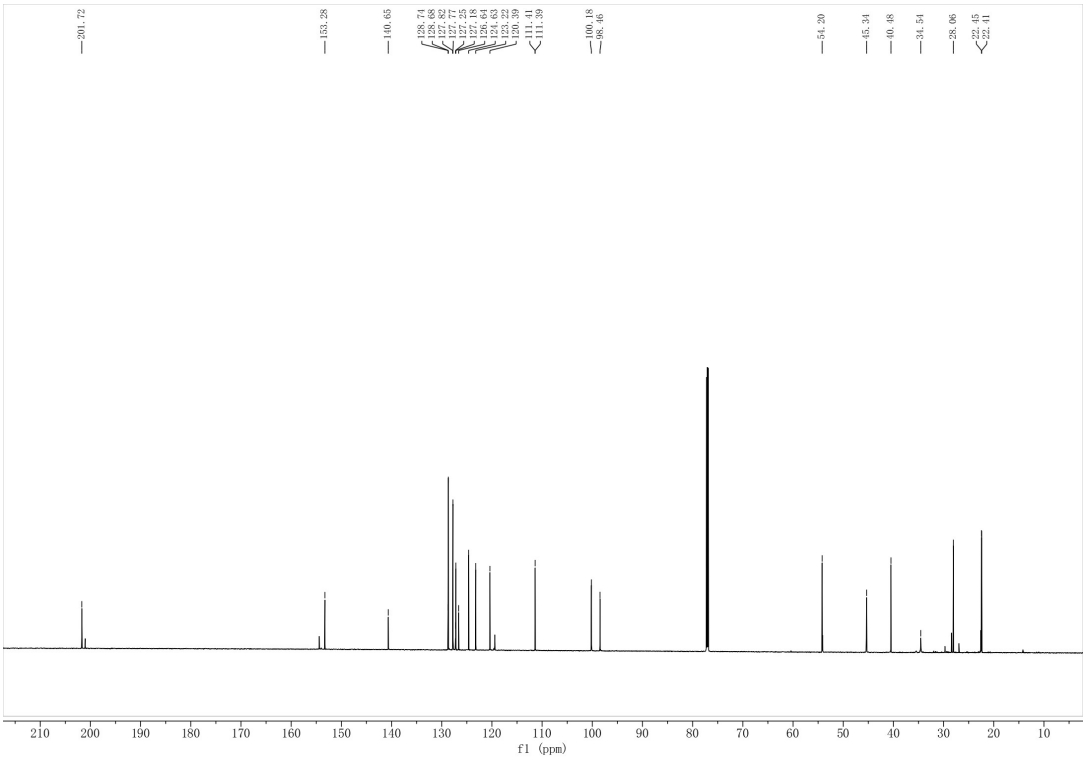


Figure S14. ^{13}C NMR spectrum of compound **3aa** in $CDCl_3$ at 201 MHz.

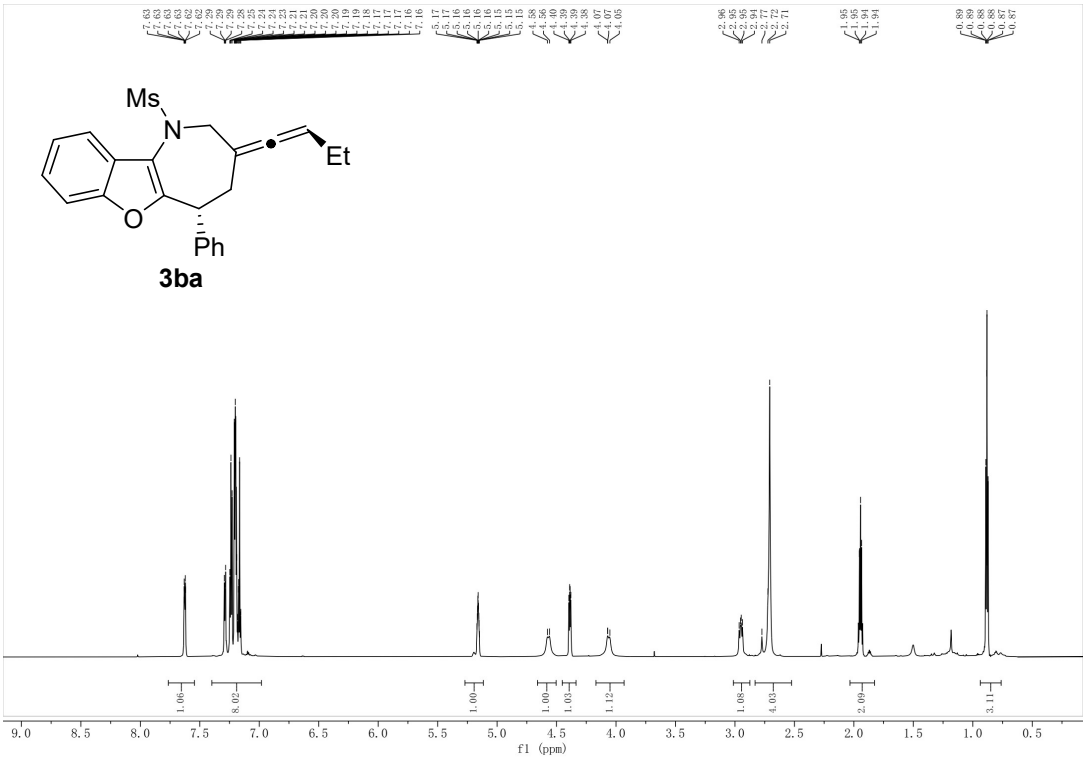


Figure S15. ^{1}H NMR spectrum of compound **3ba** in $CDCl_3$ at 800 MHz.

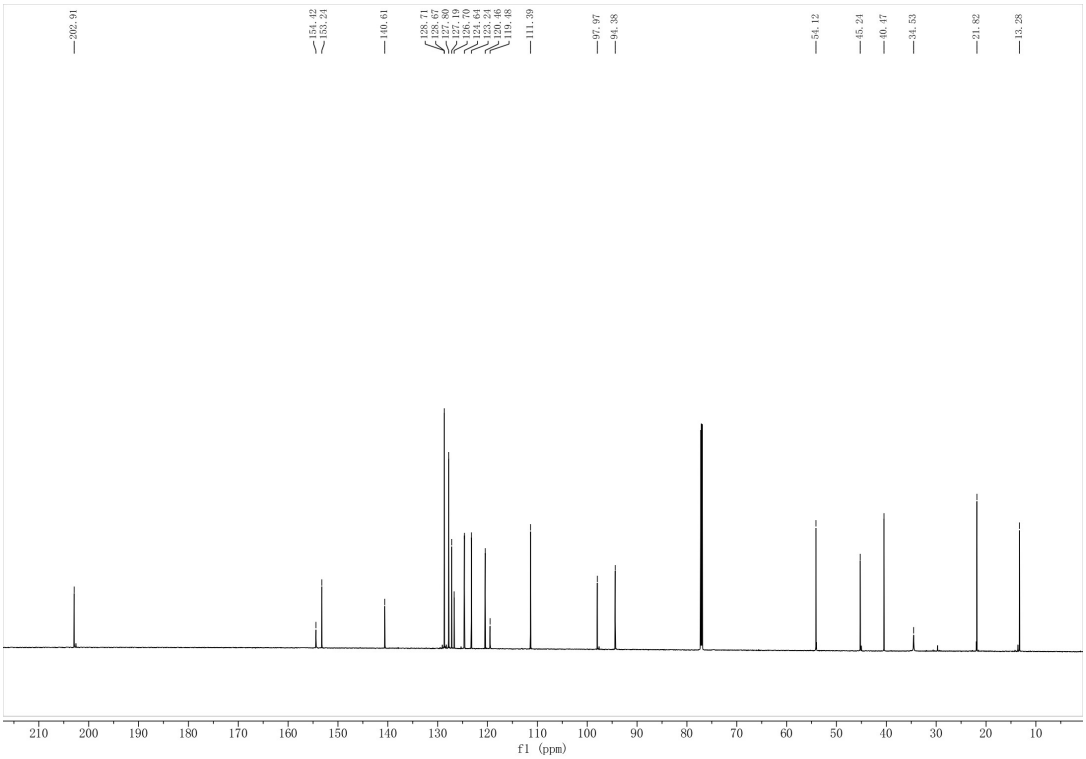


Figure S16. ^{13}C NMR spectrum of compound **3ba** in $CDCl_3$ at 201 MHz.

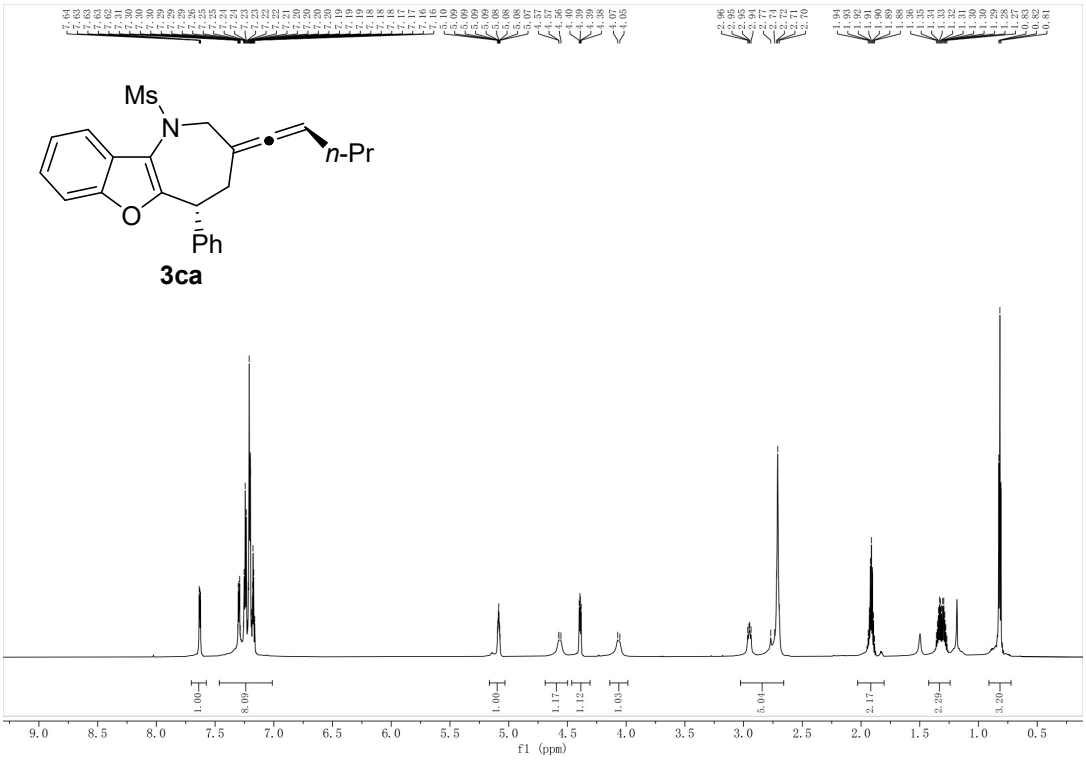


Figure S17. ^{1}H NMR spectrum of compound **3ca** in $CDCl_3$ at 800 MHz.

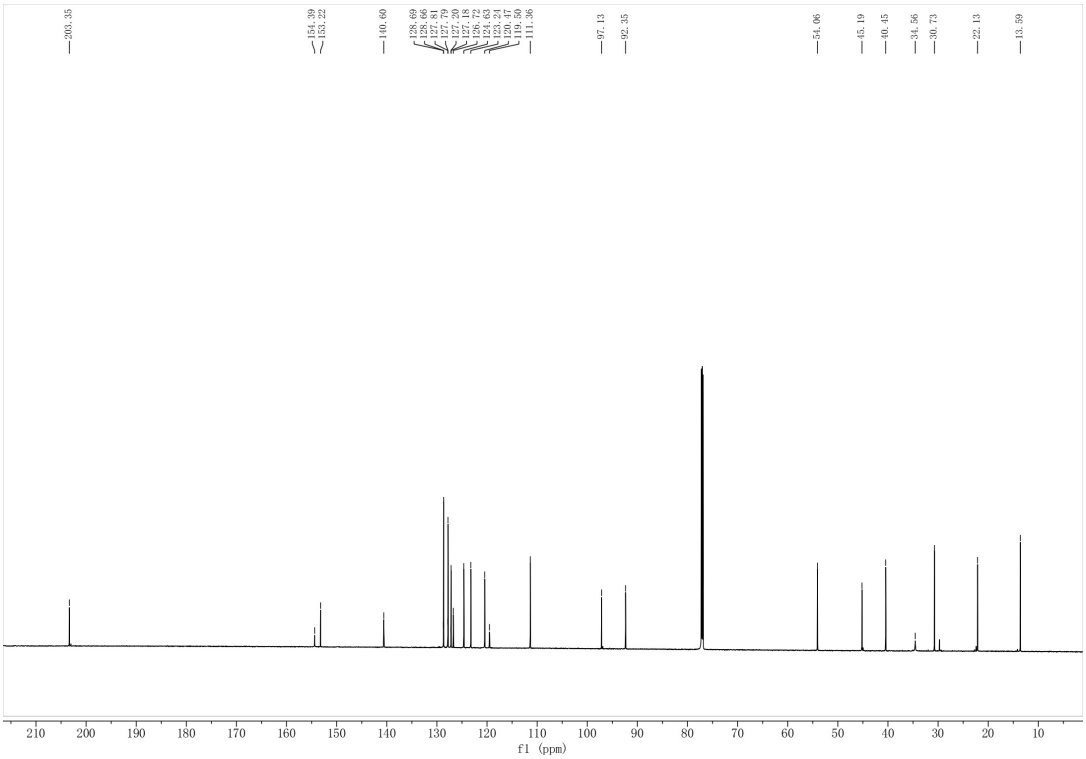


Figure S18. ^{13}C NMR spectrum of compound **3ca** in $CDCl_3$ at 201 MHz.

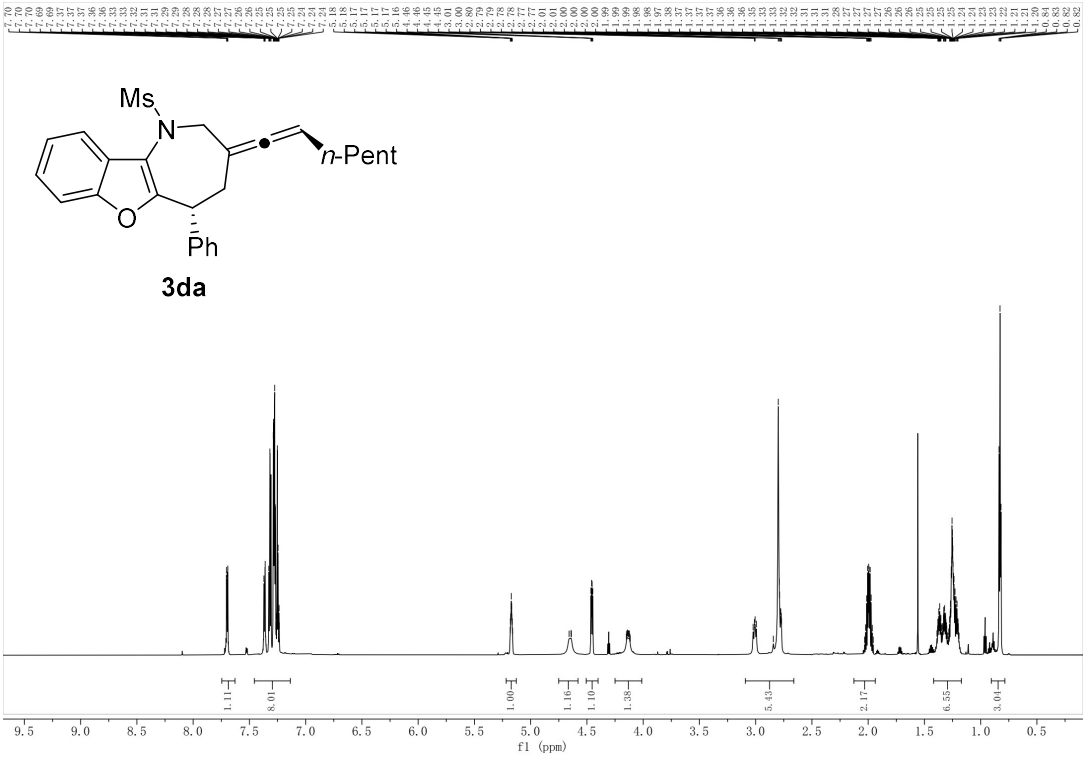


Figure S19. ^{1}H NMR spectrum of compound **3da** in $CDCl_3$ at 800 MHz.

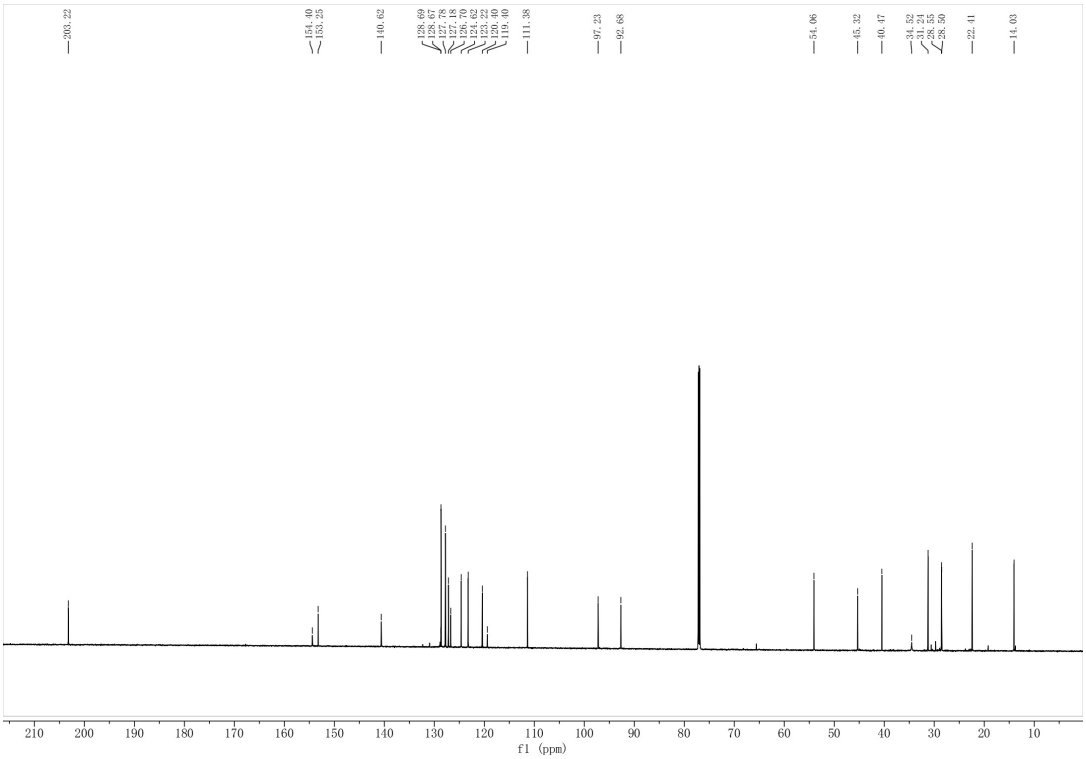


Figure S20. ^{13}C NMR spectrum of compound **3da** in $CDCl_3$ at 201 MHz.

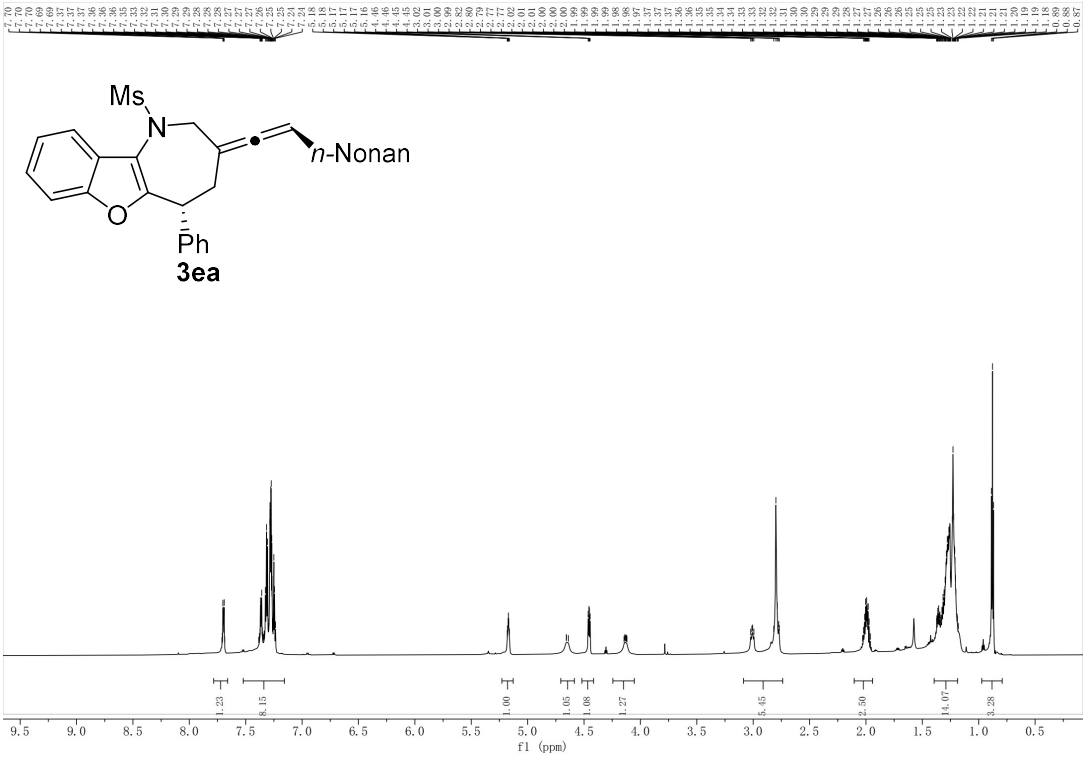


Figure S21. ^{1}H NMR spectrum of compound **3ea** in $CDCl_3$ at 800 MHz.

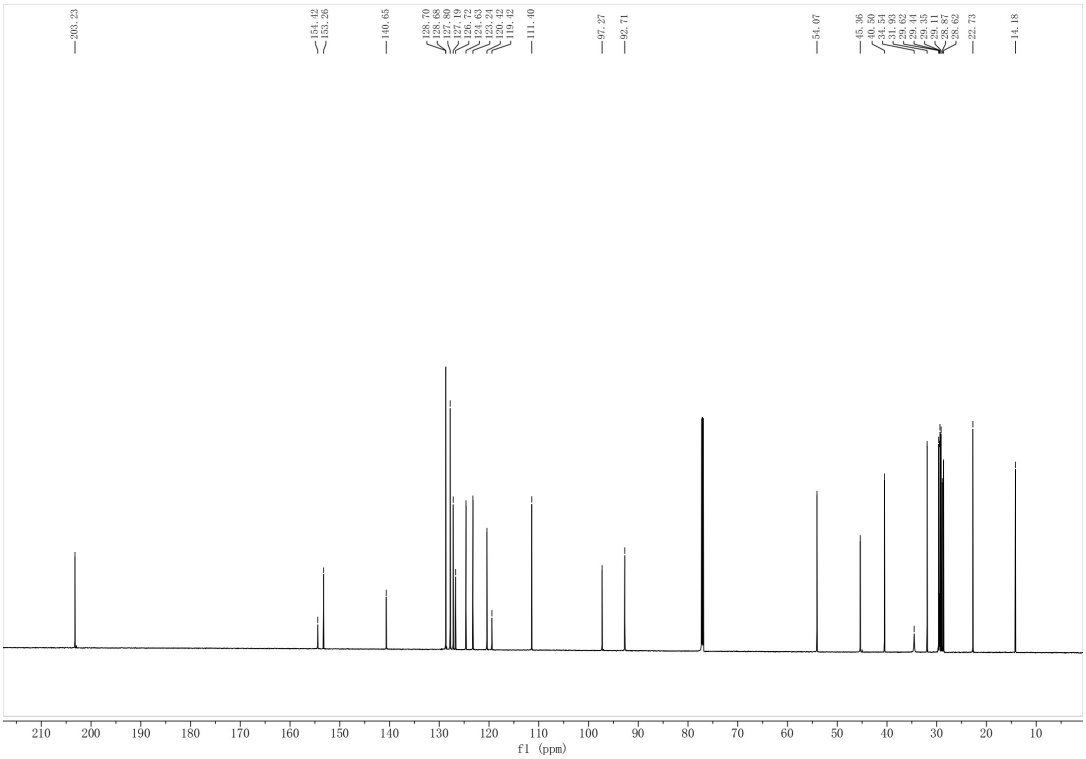


Figure S22. ^{13}C NMR spectrum of compound **3ea** in $CDCl_3$ at 201 MHz.

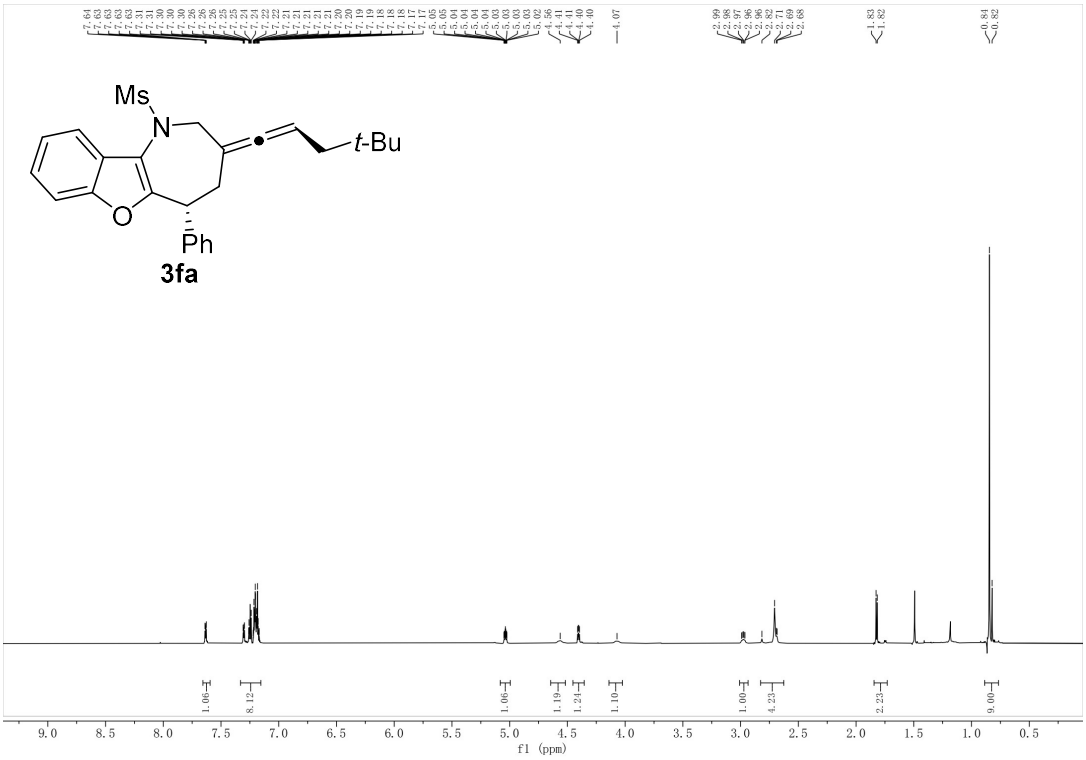


Figure S23. ^{1}H NMR spectrum of compound **3fa** in $CDCl_3$ at 800 MHz.

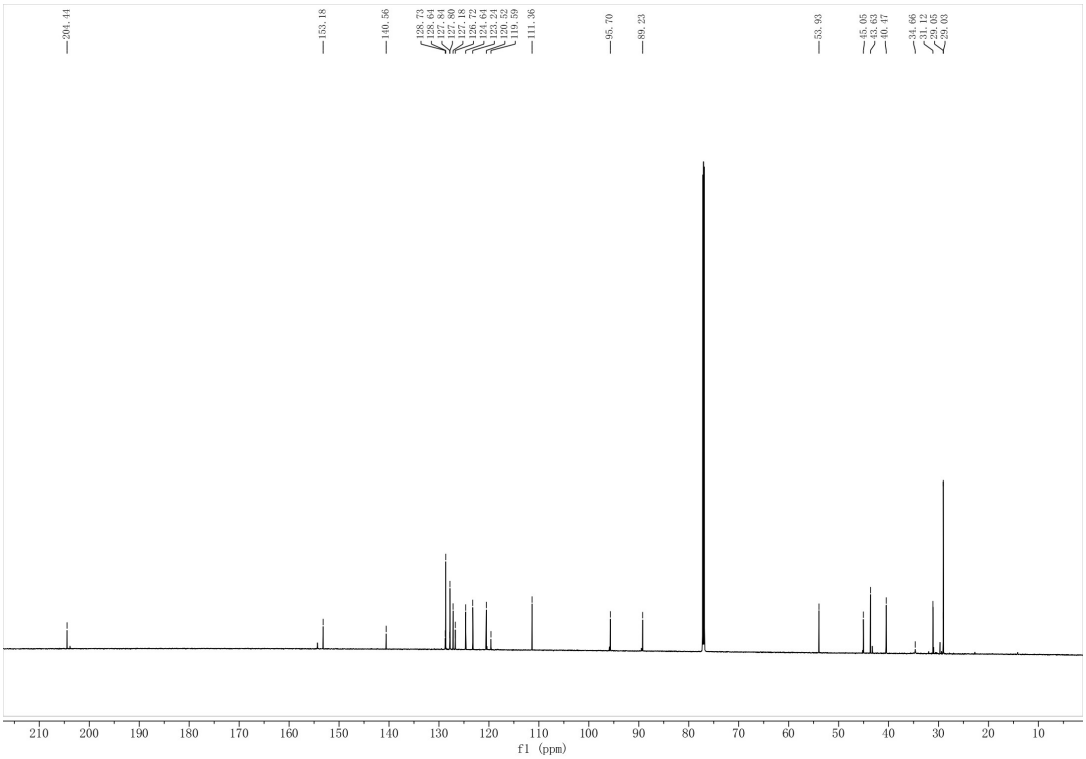


Figure S24. ^{13}C NMR spectrum of compound **3fa** in $CDCl_3$ at 201 MHz.

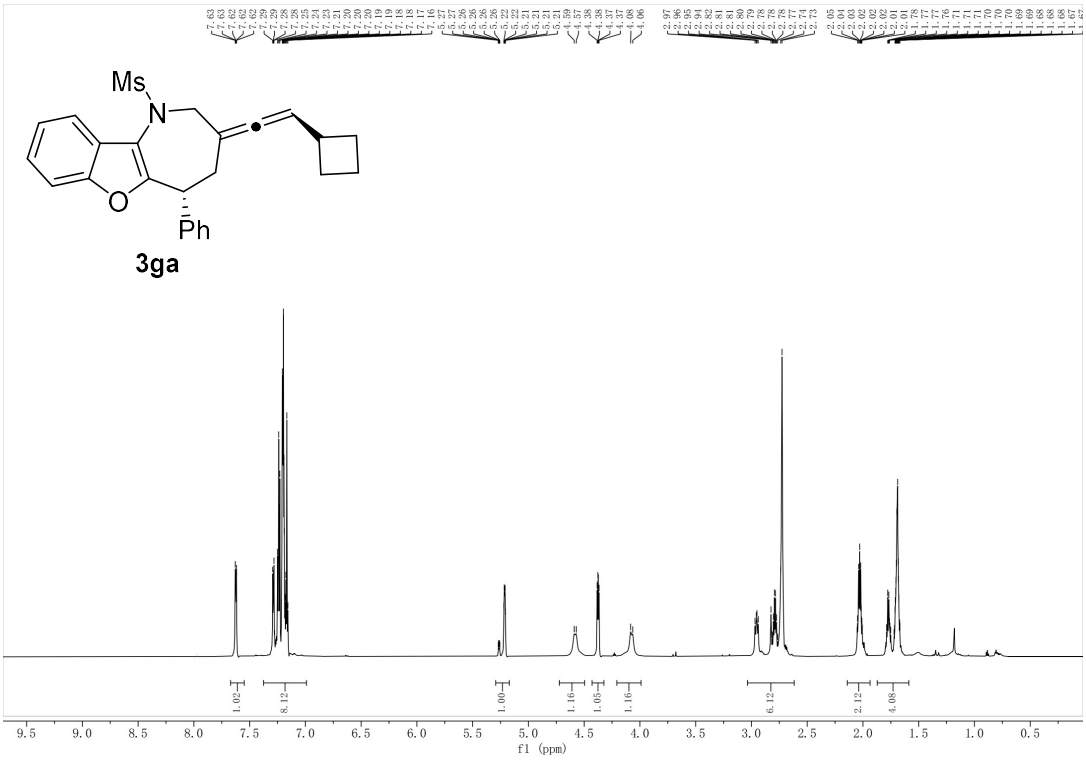


Figure S25. ^{1}H NMR spectrum of compound **3ga** in $CDCl_3$ at 800 MHz.

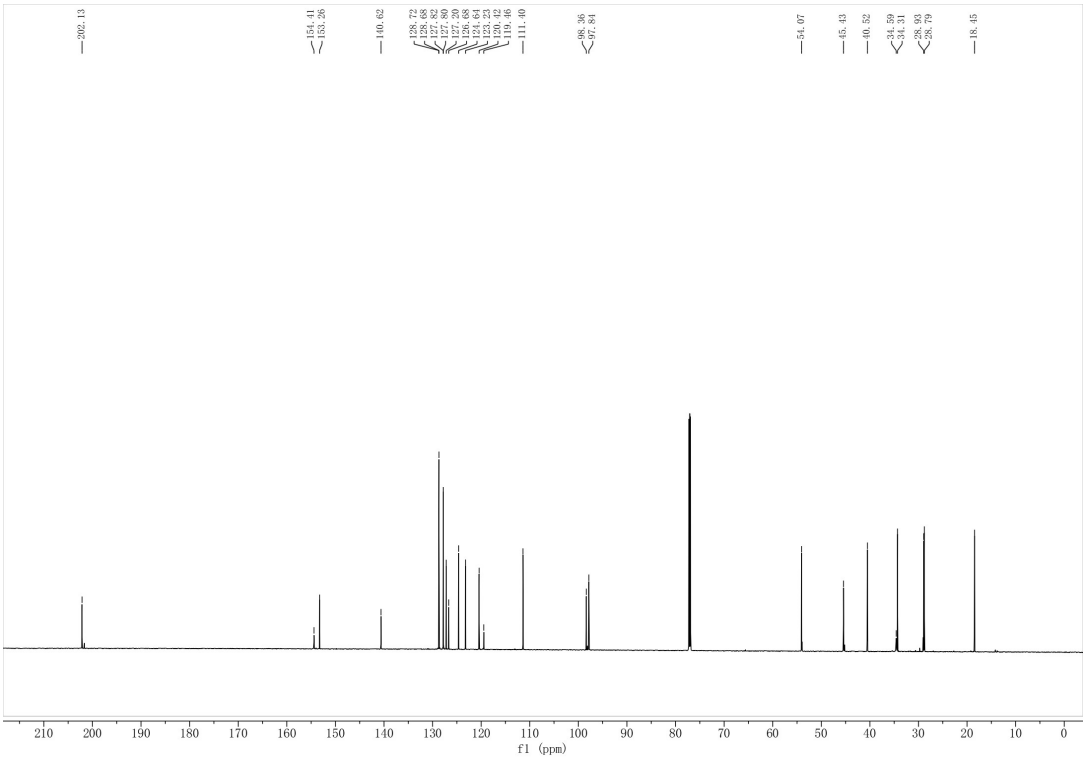


Figure S26. ^{13}C NMR spectrum of compound **3ga** in $CDCl_3$ at 201 MHz.

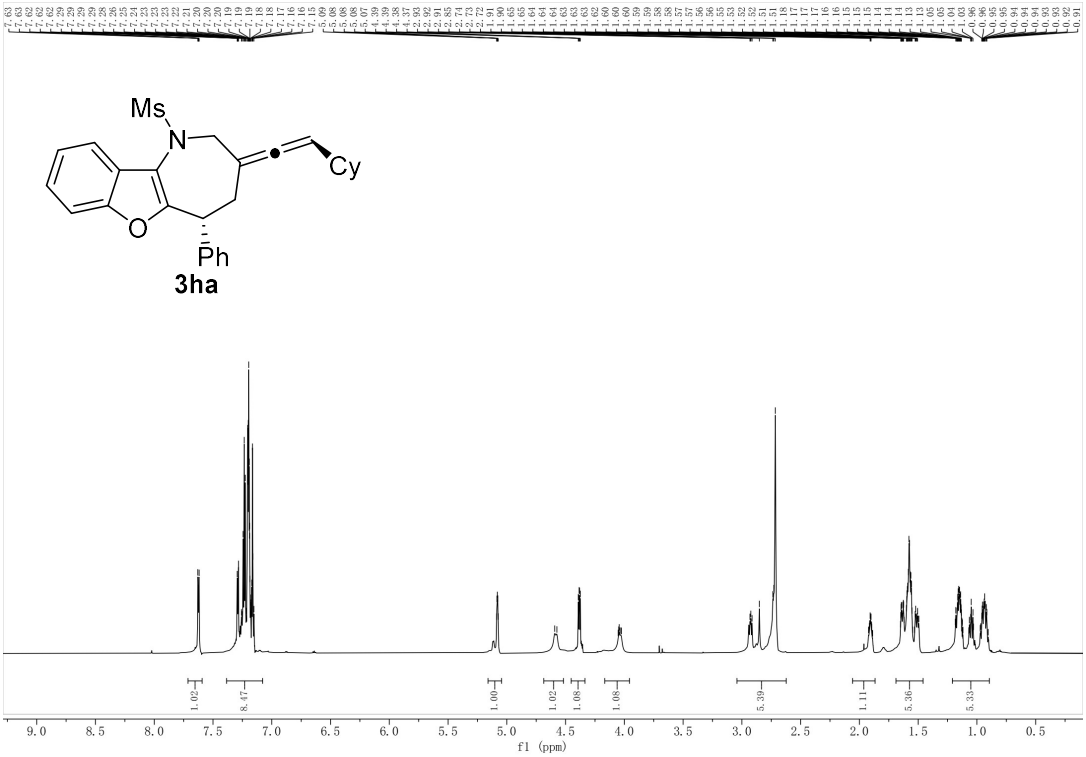


Figure S27. ^{1}H NMR spectrum of compound **3ha** in $CDCl_3$ at 800 MHz.

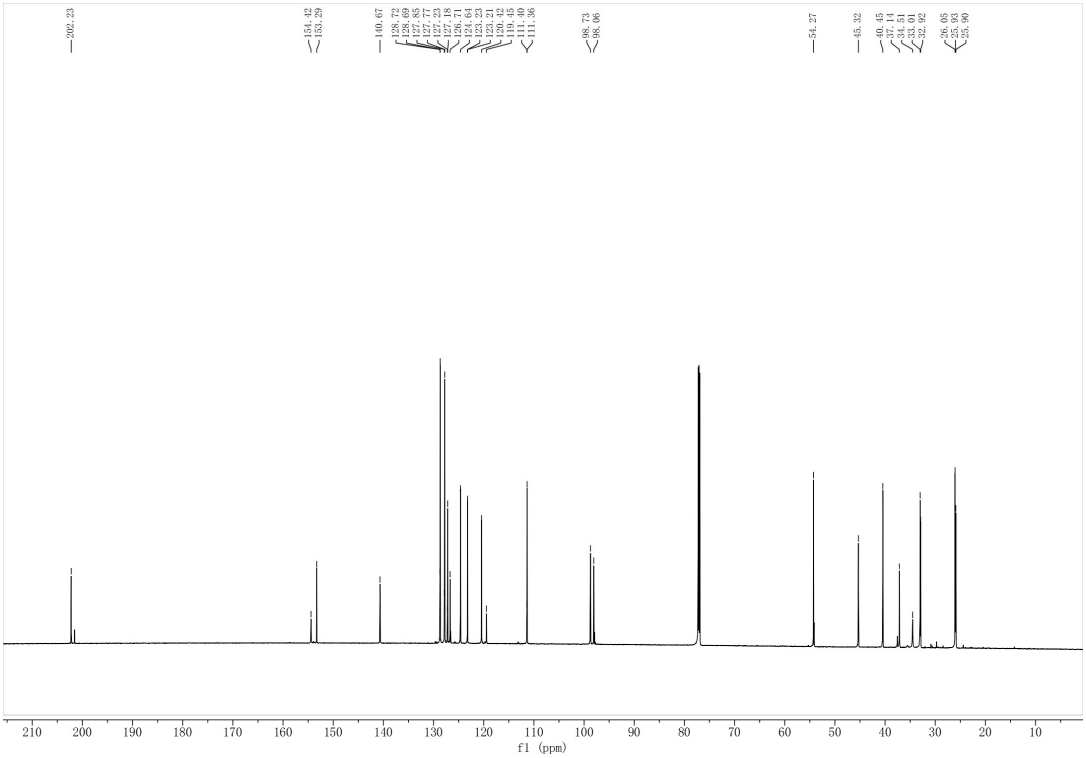


Figure S28. ^{13}C NMR spectrum of compound **3ha** in $CDCl_3$ at 201 MHz.

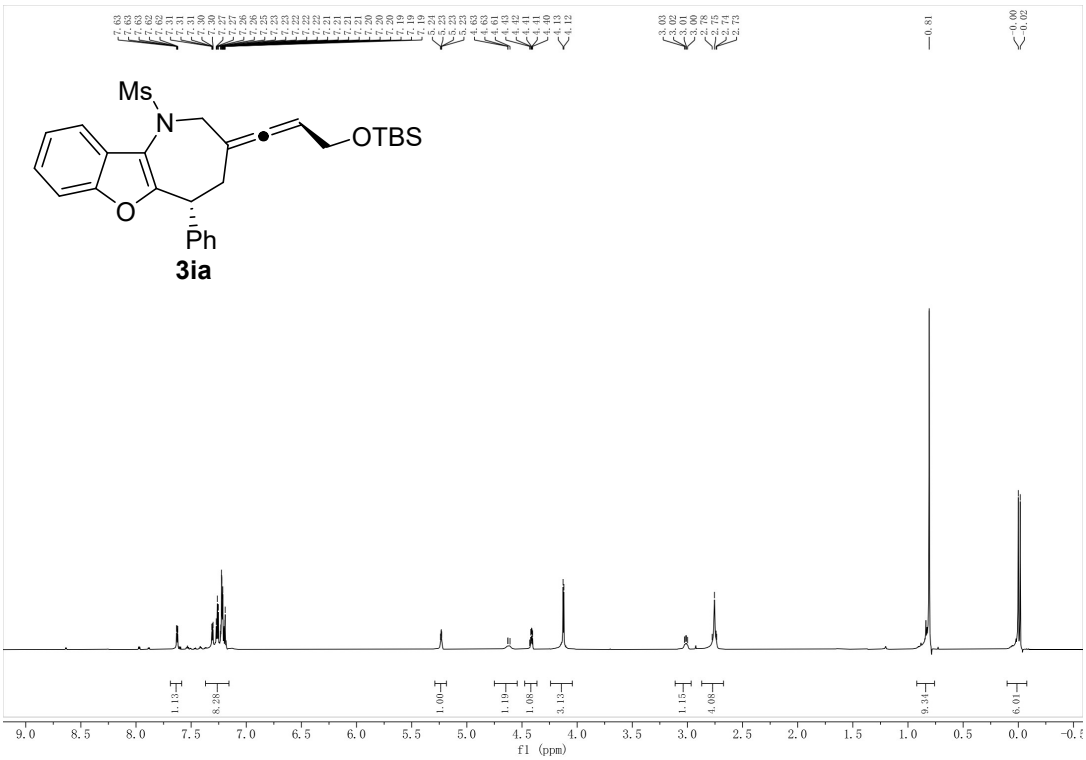


Figure S29. ^{1}H NMR spectrum of compound **3ia** in $CDCl_3$ at 800 MHz.

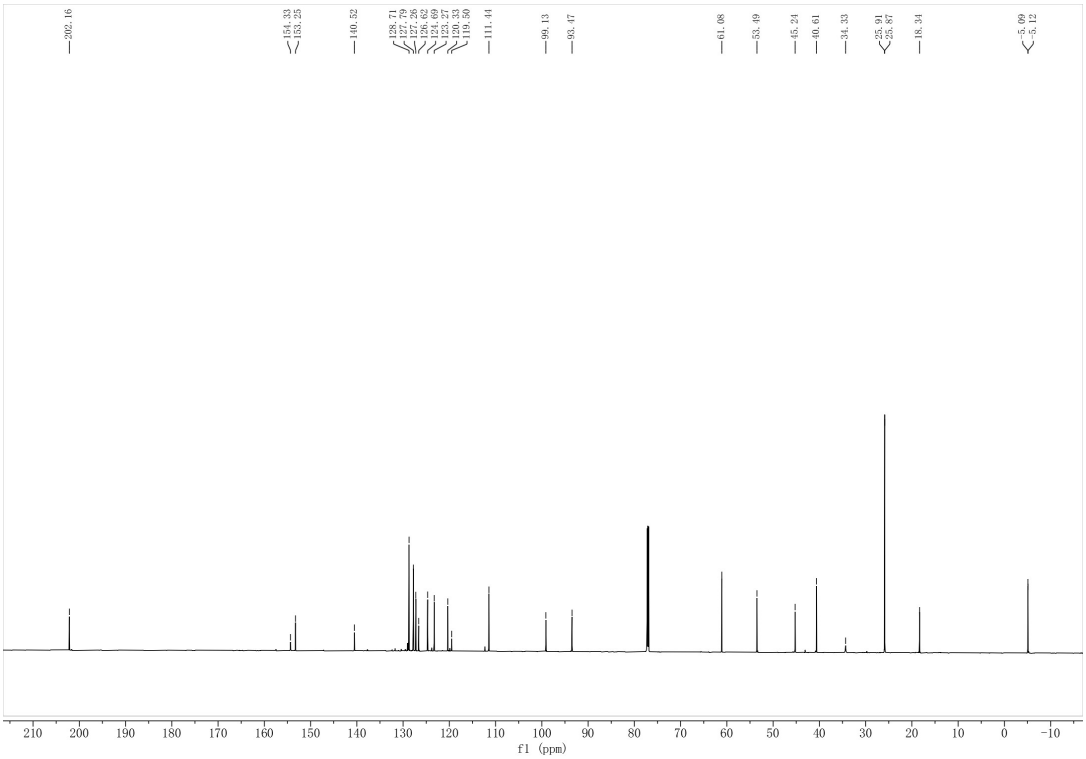


Figure S30. ^{13}C NMR spectrum of compound **3ia** in $CDCl_3$ at 201 MHz.

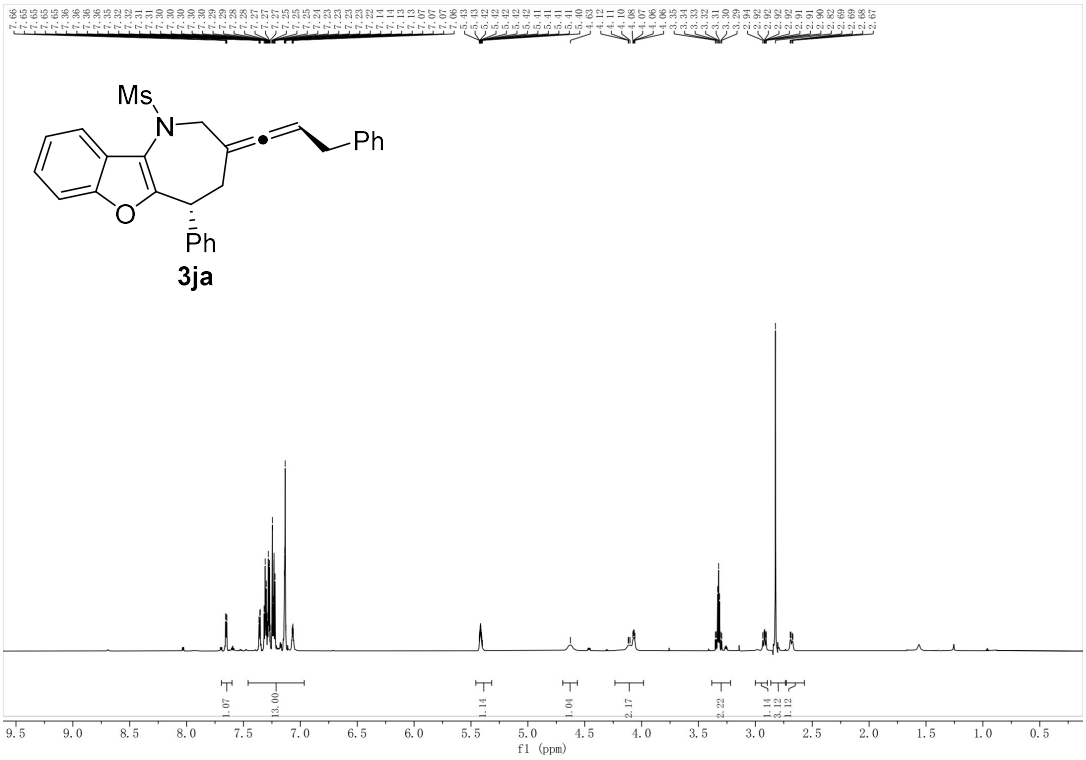


Figure S31. ^{1}H NMR spectrum of compound **3ja** in $CDCl_3$ at 800 MHz.

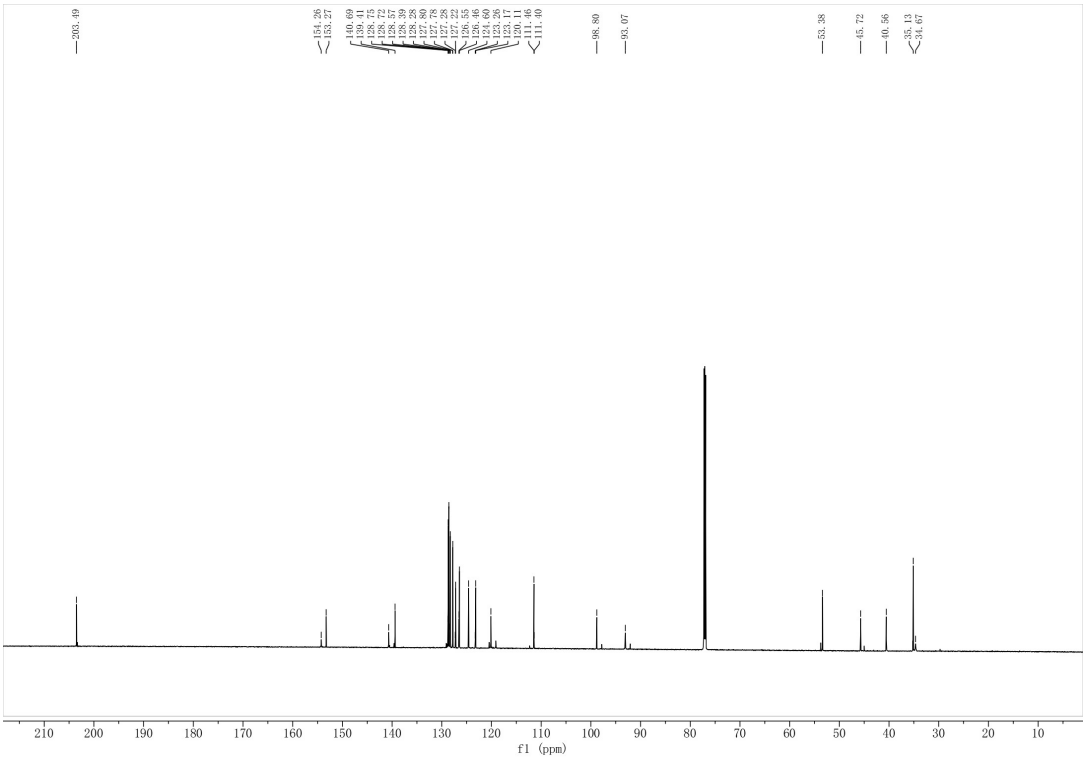


Figure S32. ^{13}C NMR spectrum of compound **3ja** in $CDCl_3$ at 201 MHz.

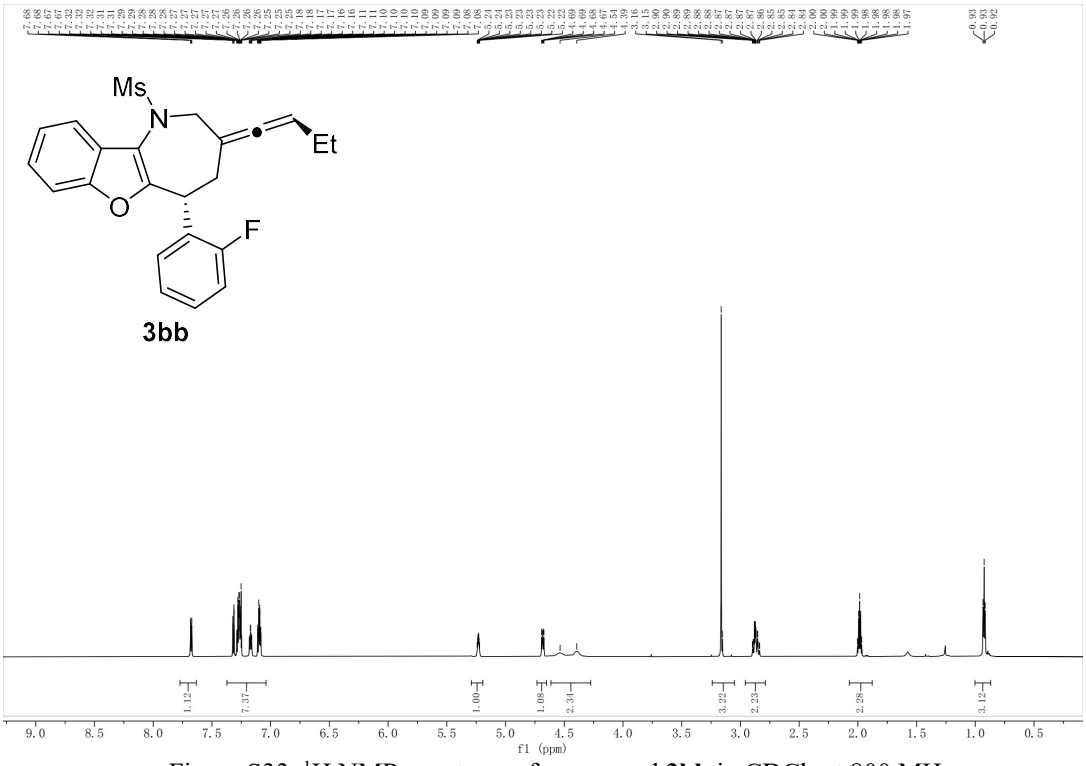


Figure S33. ^{1}H NMR spectrum of compound **3bb** in $CDCl_3$ at 800 MHz.

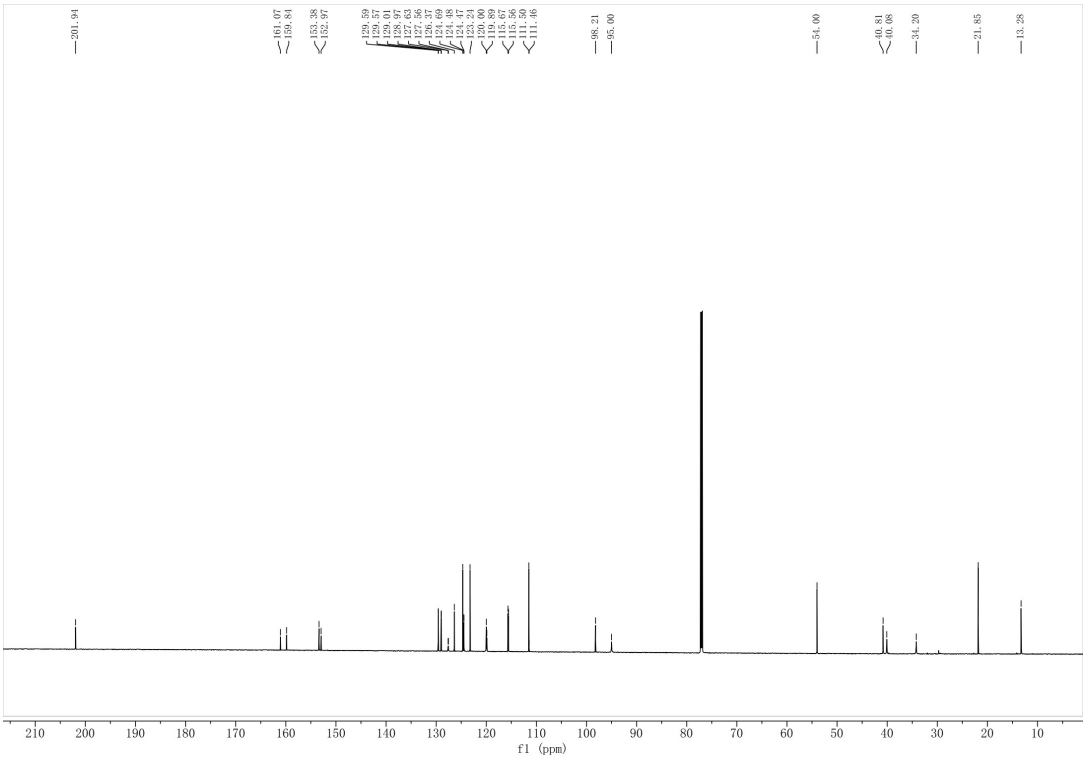


Figure S34. ^{13}C NMR spectrum of compound **3bb** in $CDCl_3$ at 201 MHz.

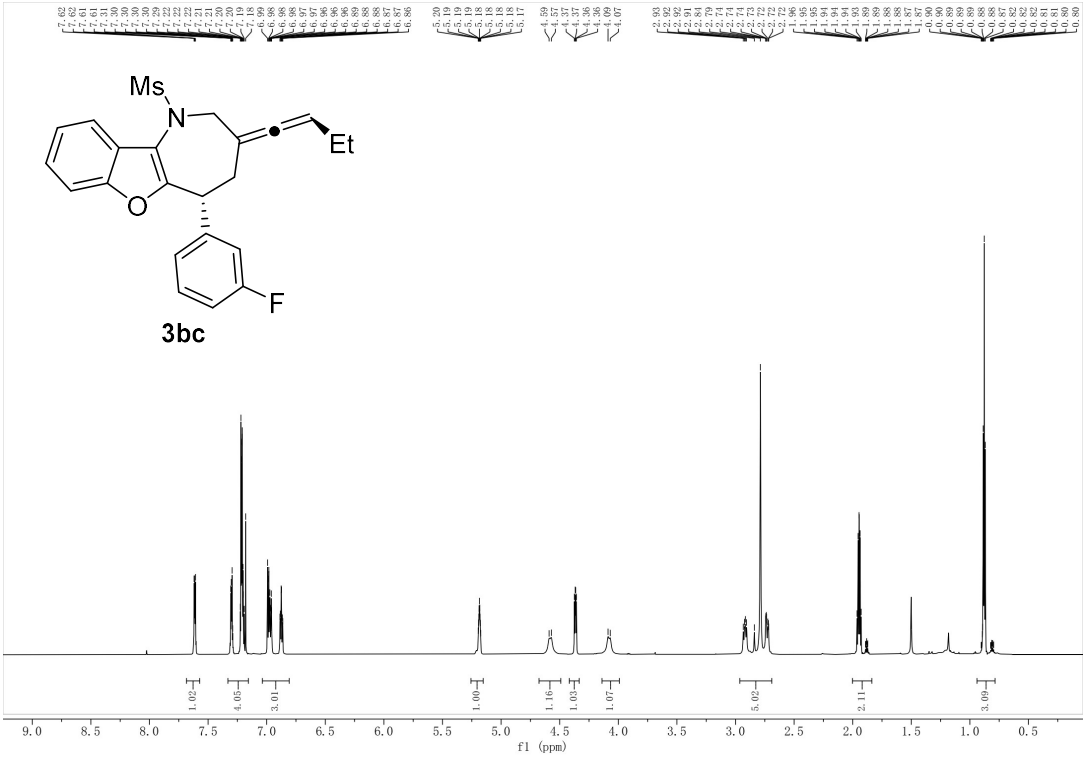


Figure S35. ^{1}H NMR spectrum of compound **3bc** in $CDCl_3$ at 800 MHz.

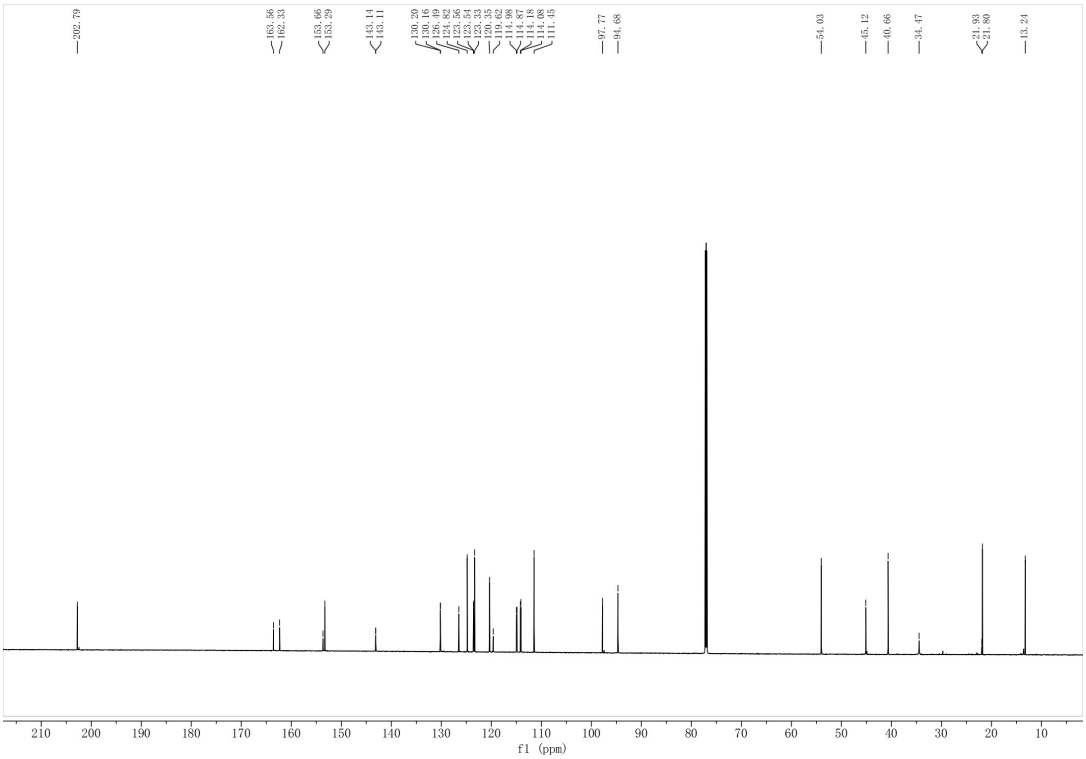


Figure S36. ^{13}C NMR spectrum of compound **3bc** in $CDCl_3$ at 201 MHz.

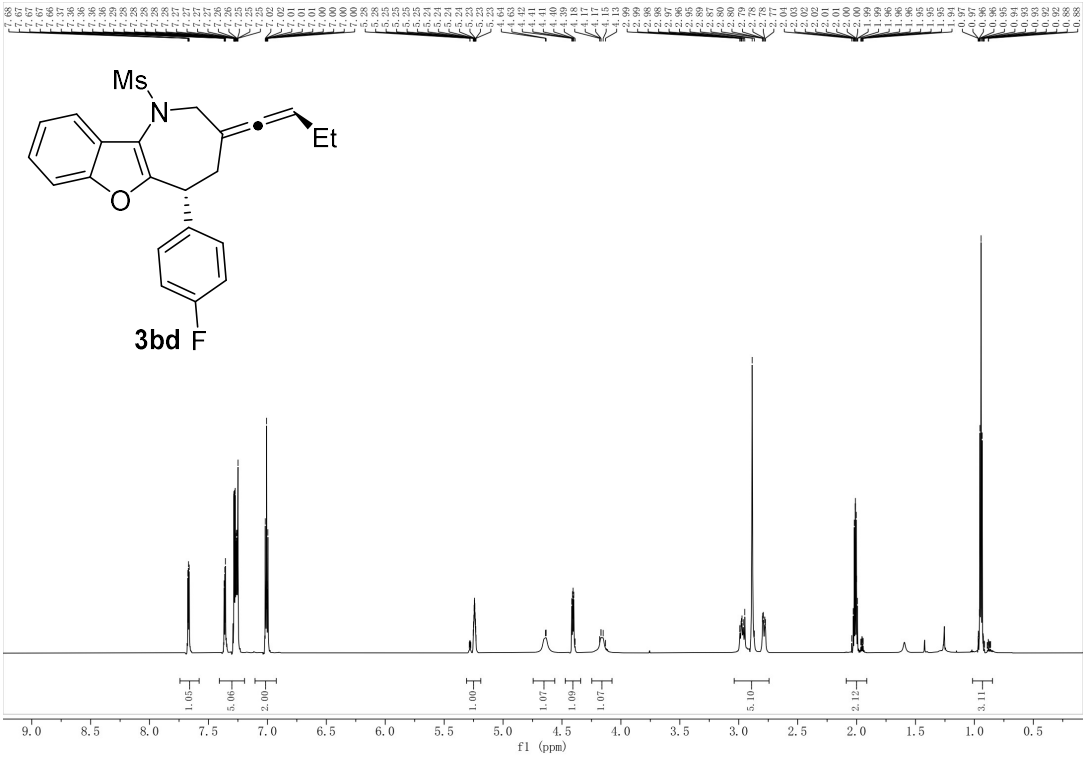


Figure S37. ^{1}H NMR spectrum of compound **3bd** in $CDCl_3$ at 800 MHz.

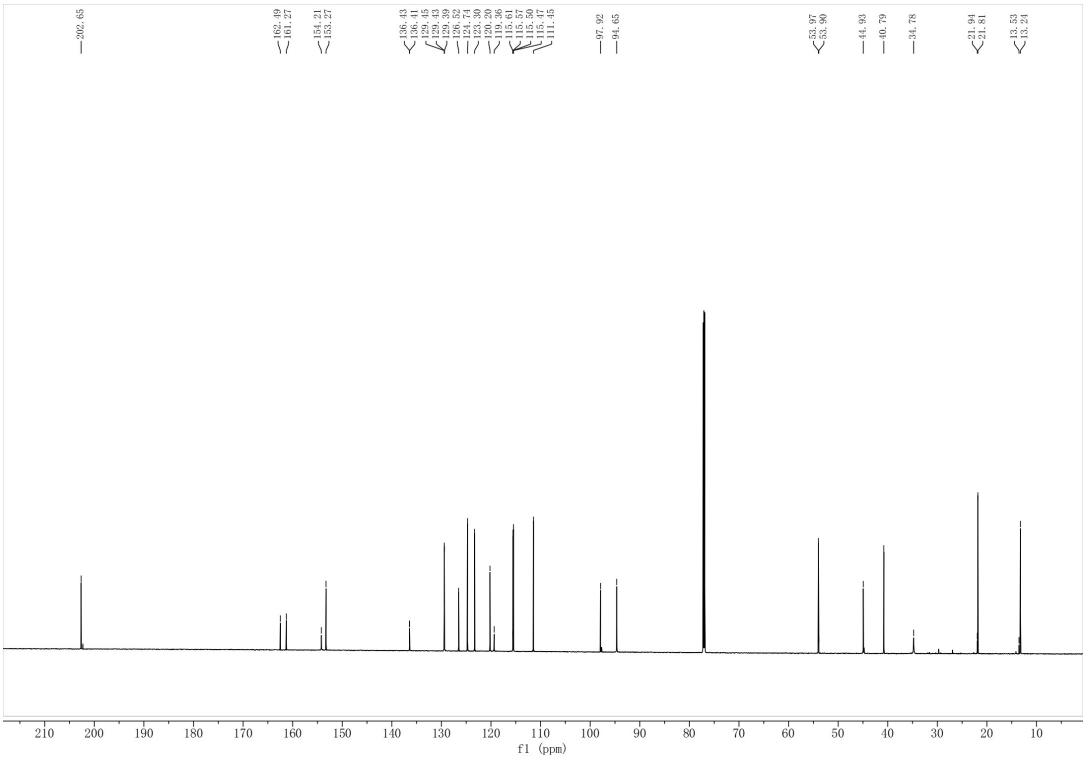


Figure S38. ^{13}C NMR spectrum of compound **3bd** in $CDCl_3$ at 201 MHz.

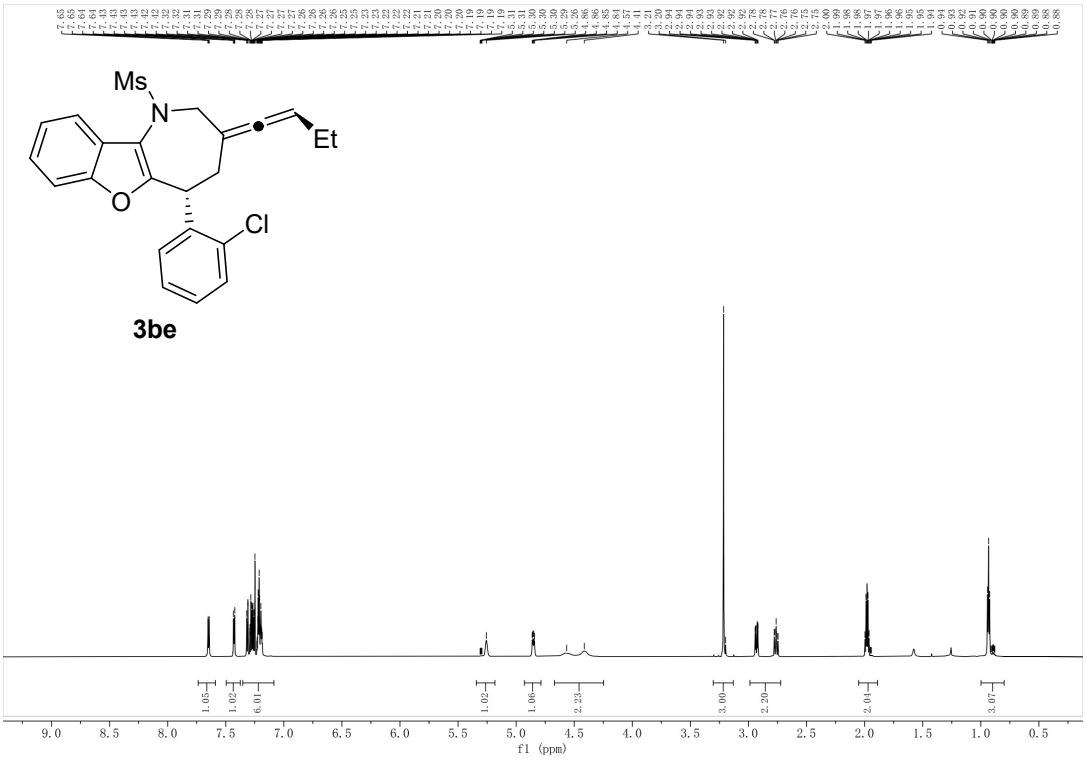


Figure S39. ^{1}H NMR spectrum of compound **3be** in $CDCl_3$ at 800 MHz.

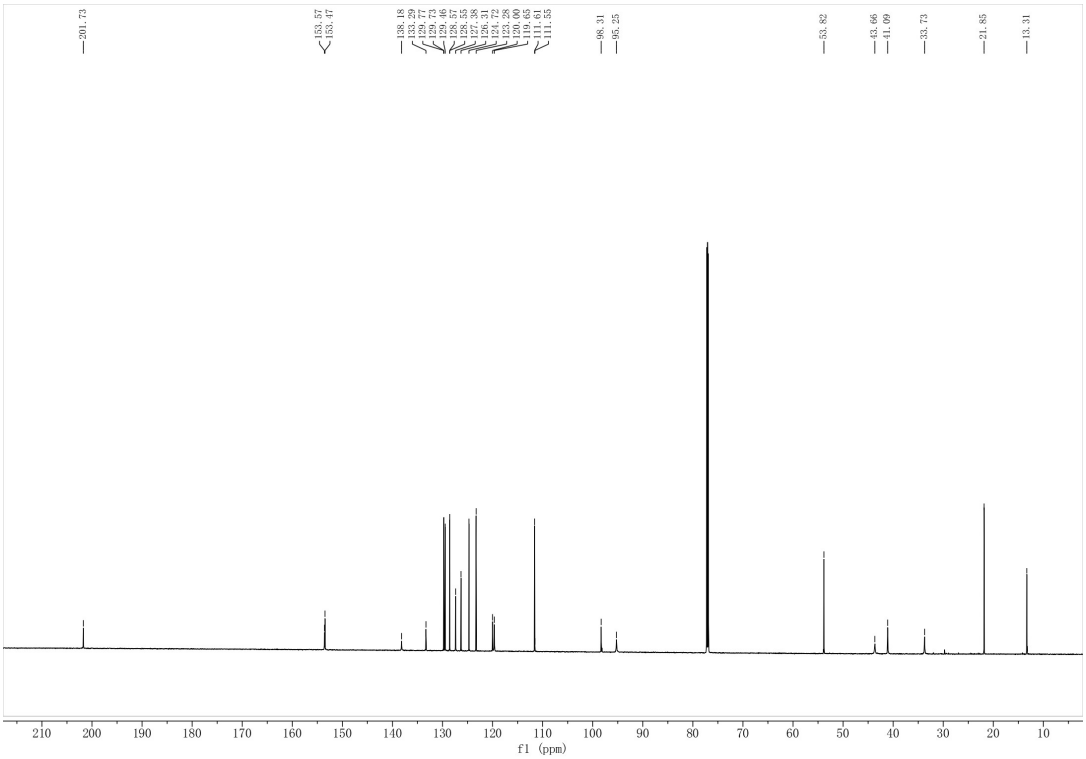


Figure S40. ^{13}C NMR spectrum of compound **3be** in $CDCl_3$ at 201 MHz.

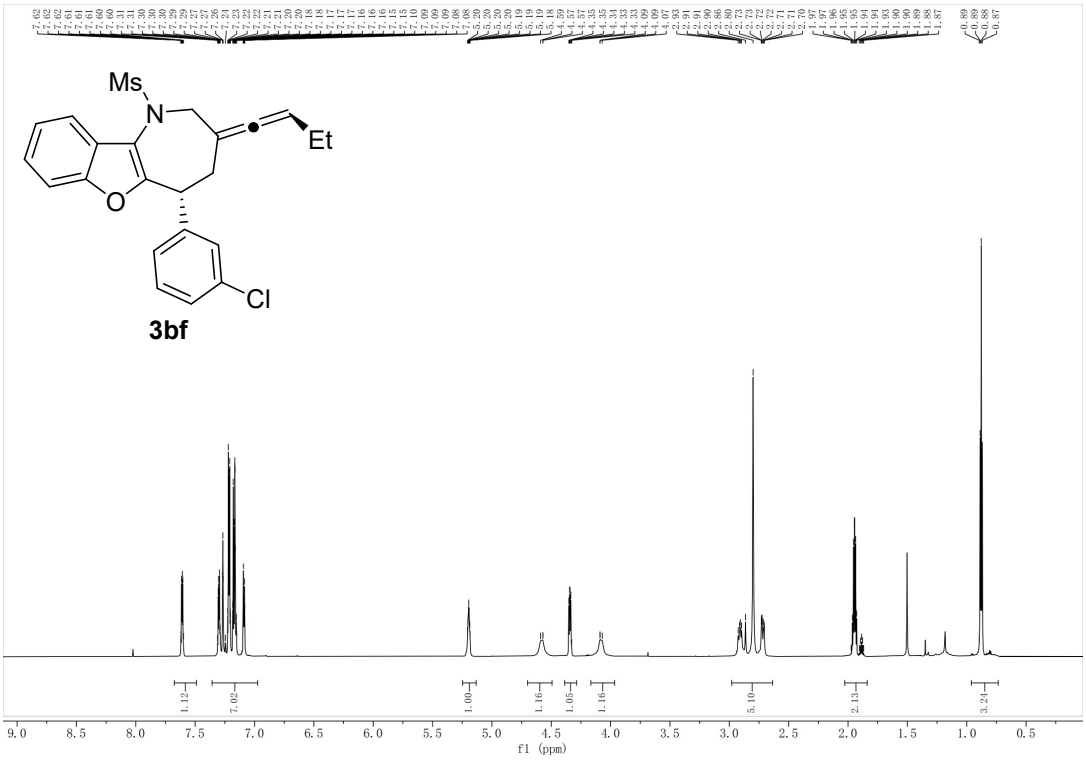


Figure S41. ^{1}H NMR spectrum of compound **3bf** in $CDCl_3$ at 800 MHz.

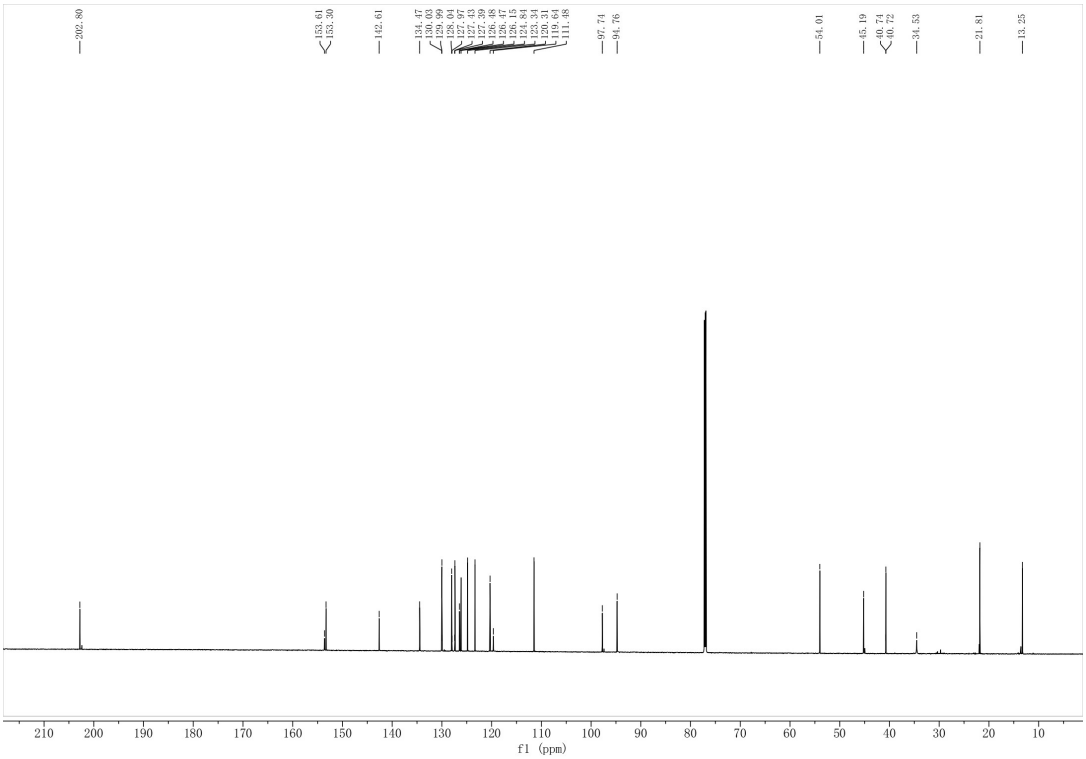


Figure S42. ^{13}C NMR spectrum of compound **3bf** in $CDCl_3$ at 201 MHz.

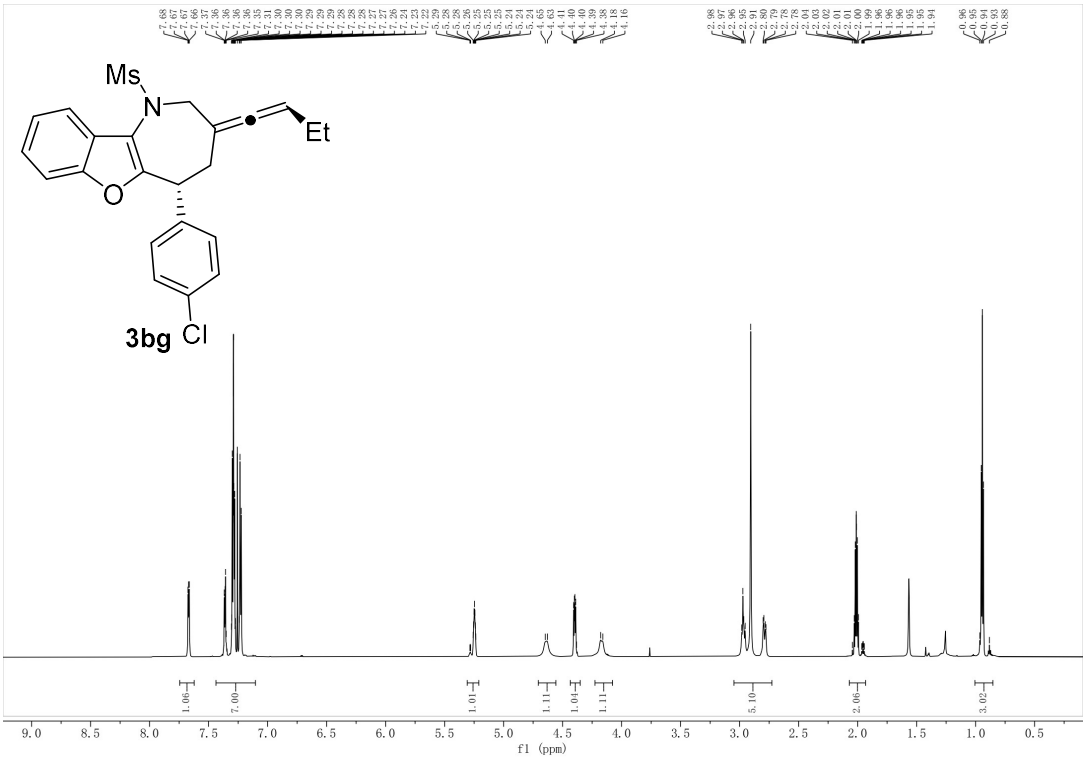


Figure S43. ^{1}H NMR spectrum of compound **3bg** in $CDCl_3$ at 800 MHz.

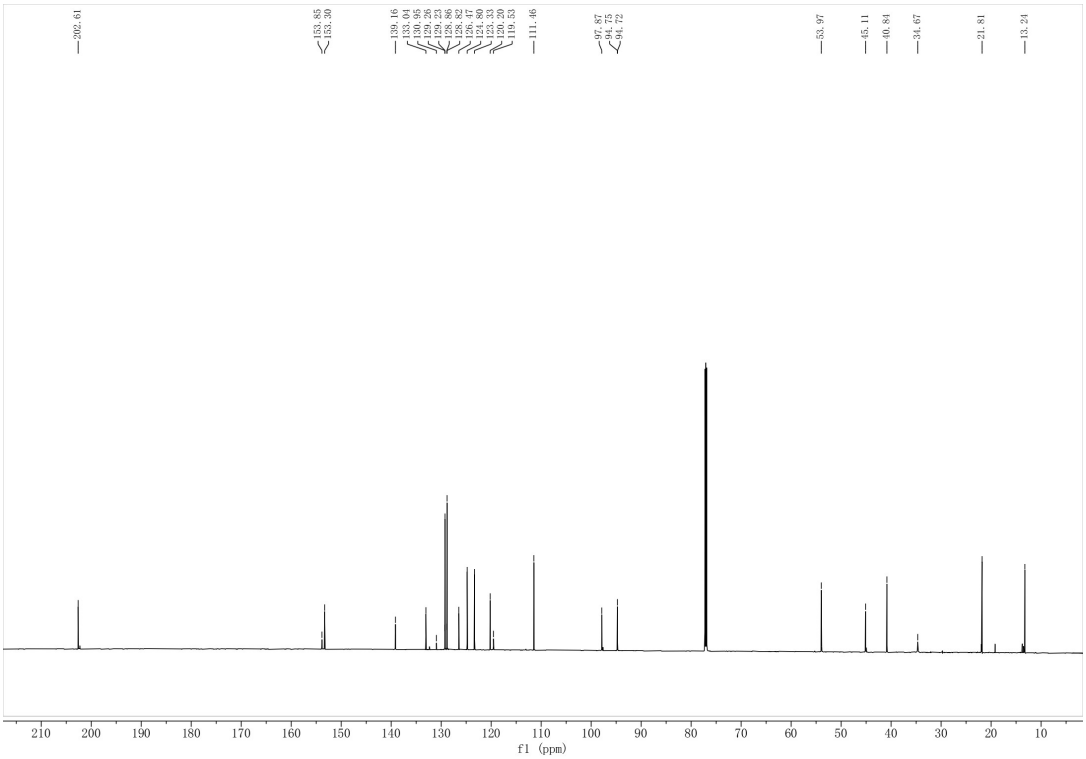


Figure S44. ^{13}C NMR spectrum of compound **3bg** in $CDCl_3$ at 201 MHz.

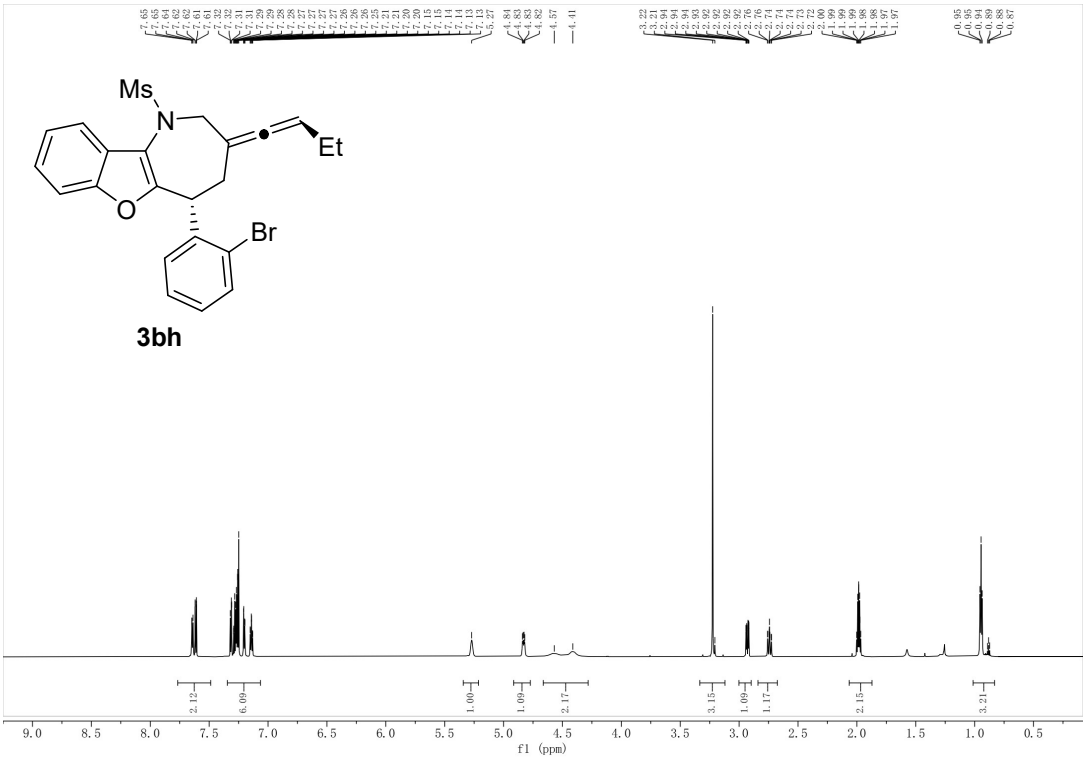


Figure S45. ^{1}H NMR spectrum of compound **3bh** in $CDCl_3$ at 800 MHz.

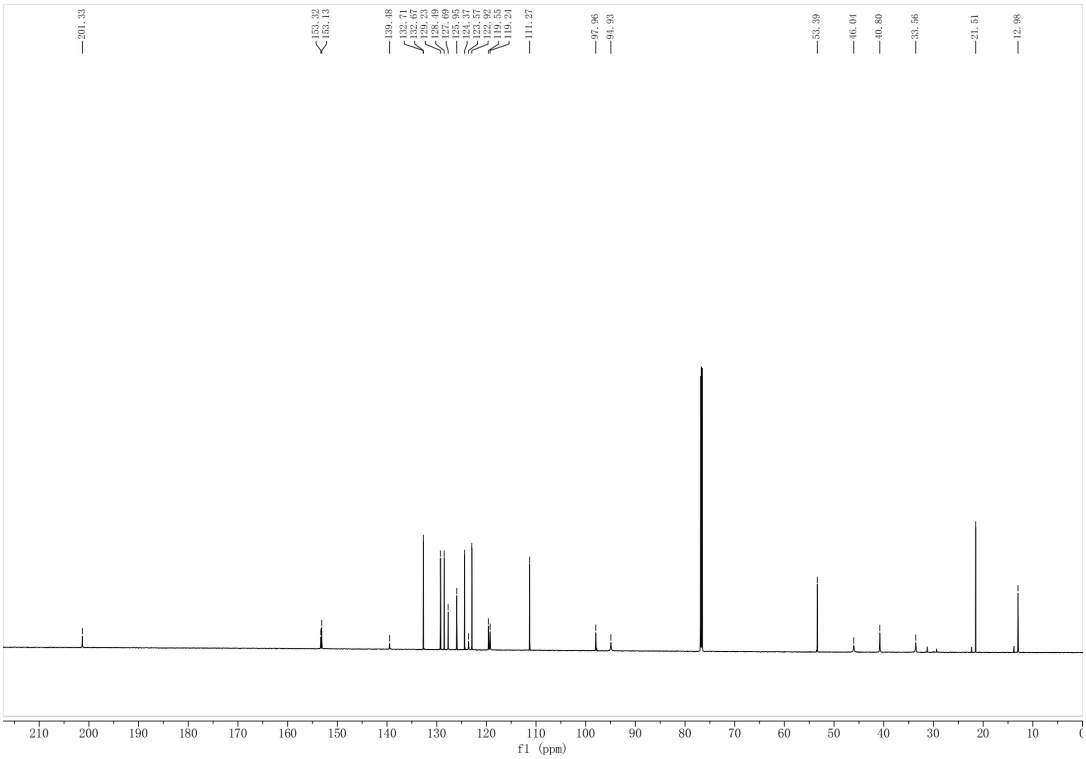


Figure S46. ^{13}C NMR spectrum of compound **3bh** in $CDCl_3$ at 201 MHz.

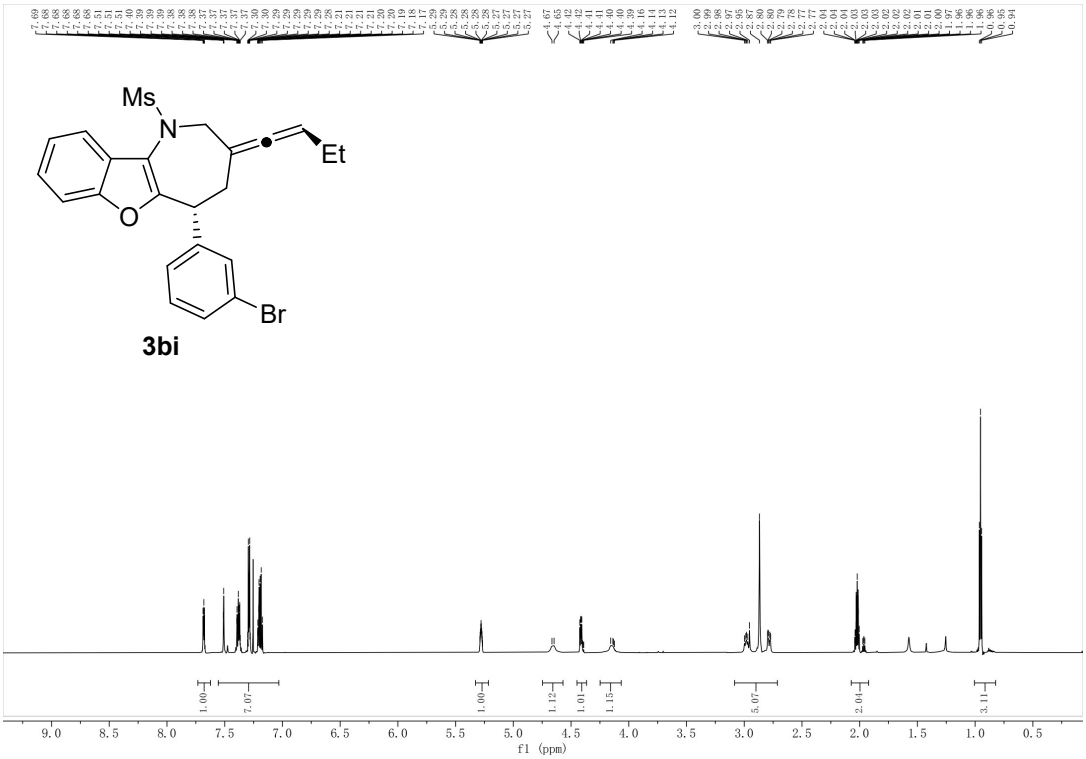


Figure S47. ^{1}H NMR spectrum of compound **3bi** in $CDCl_3$ at 800 MHz.

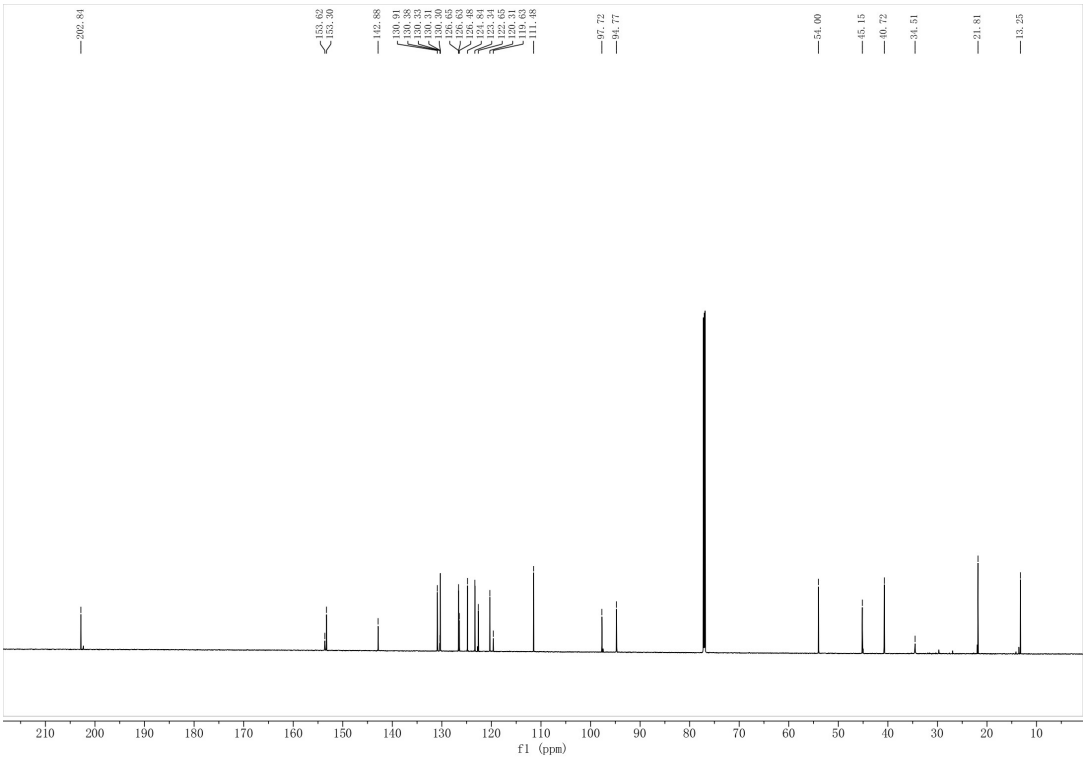


Figure S48. ^{13}C NMR spectrum of compound **3bi** in $CDCl_3$ at 201 MHz.

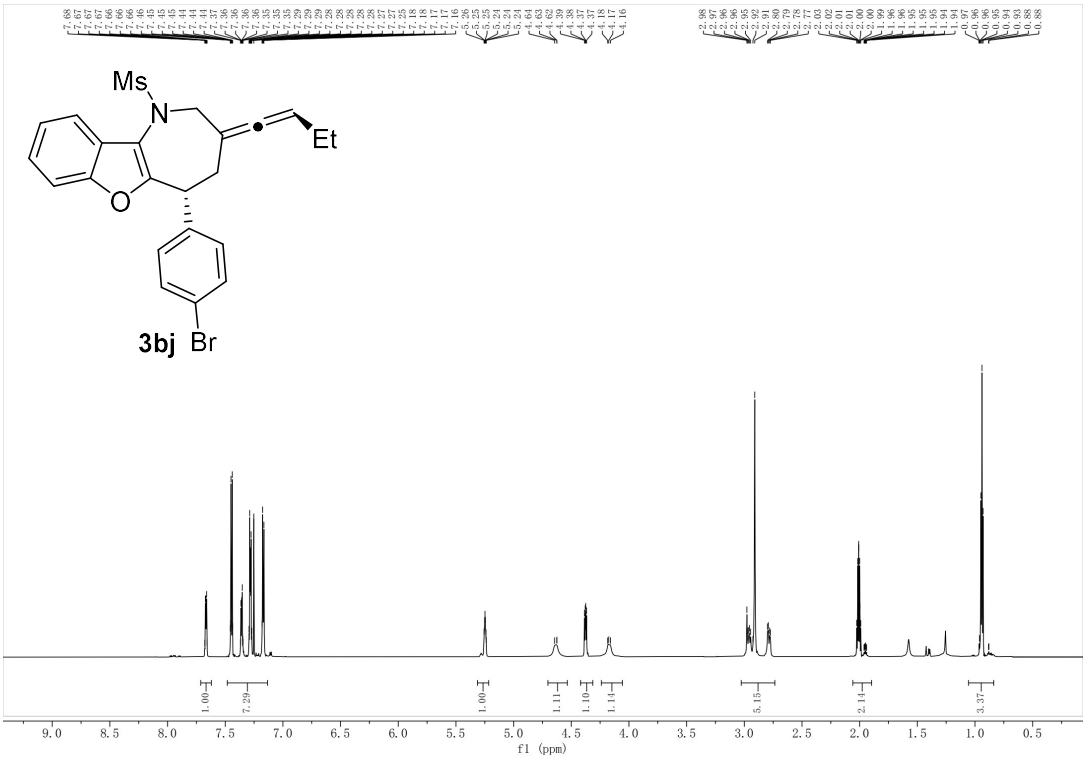


Figure S49. ^{1}H NMR spectrum of compound **3bj** in $CDCl_3$ at 800 MHz.

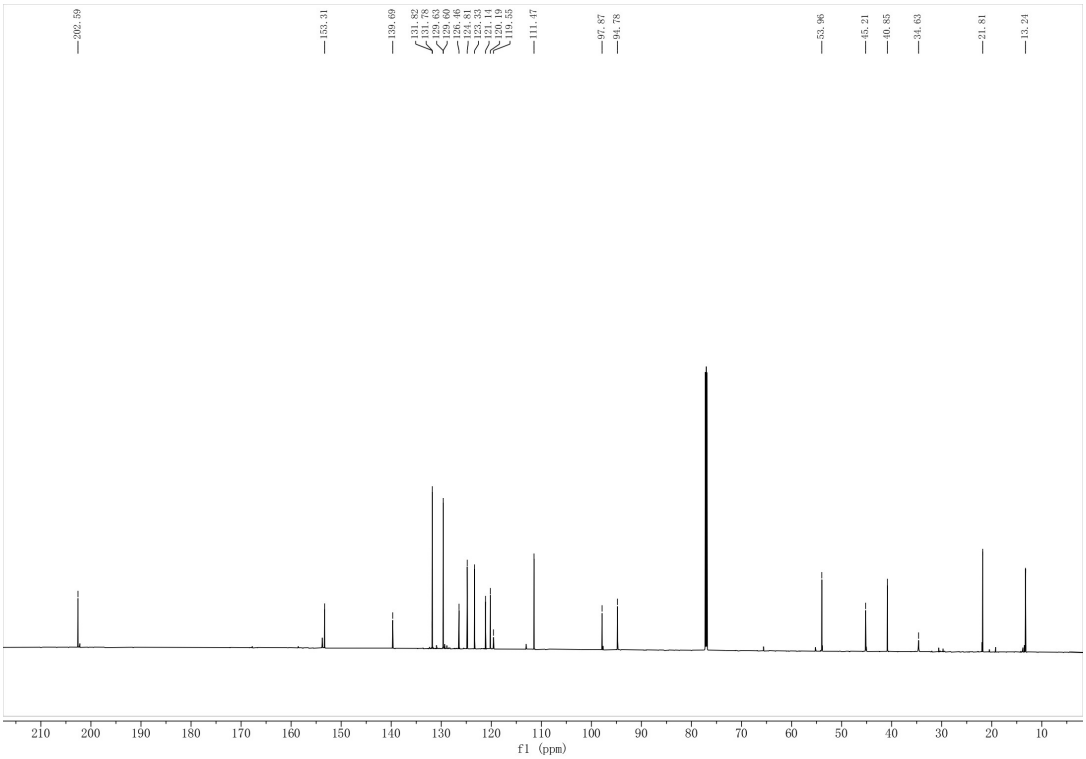


Figure S50. ^{13}C NMR spectrum of compound **3bj** in $CDCl_3$ at 201 MHz.

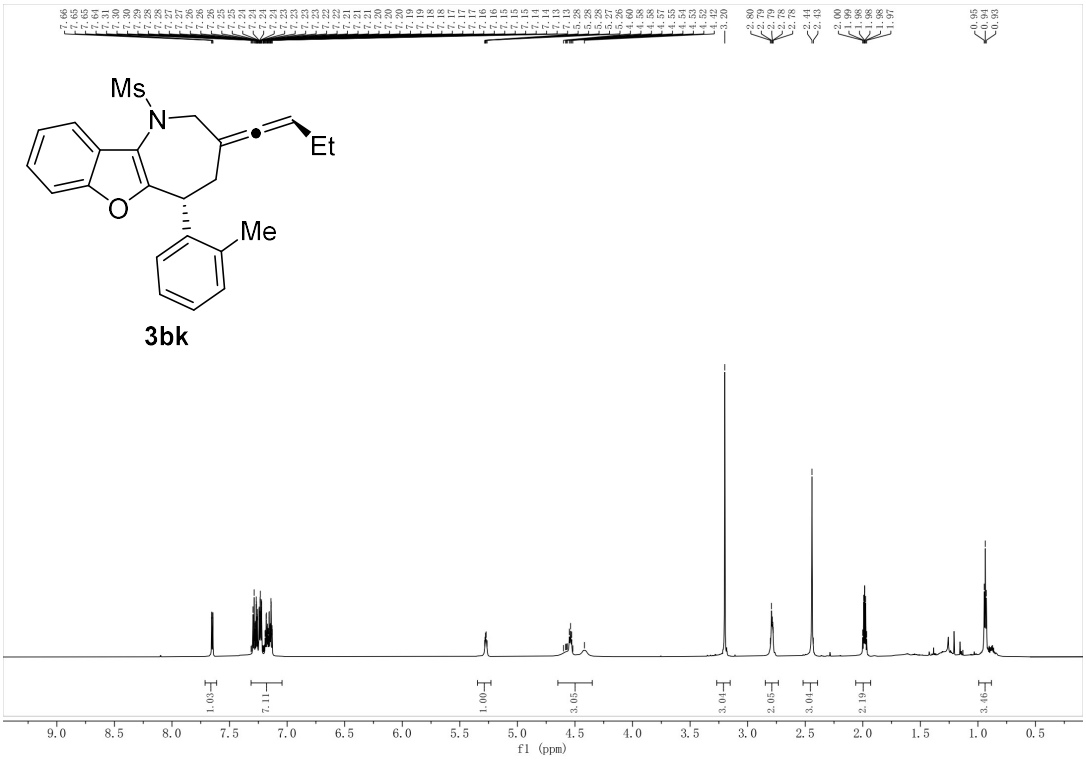


Figure S51. ^{1}H NMR spectrum of compound **3bk** in $CDCl_3$ at 800 MHz.

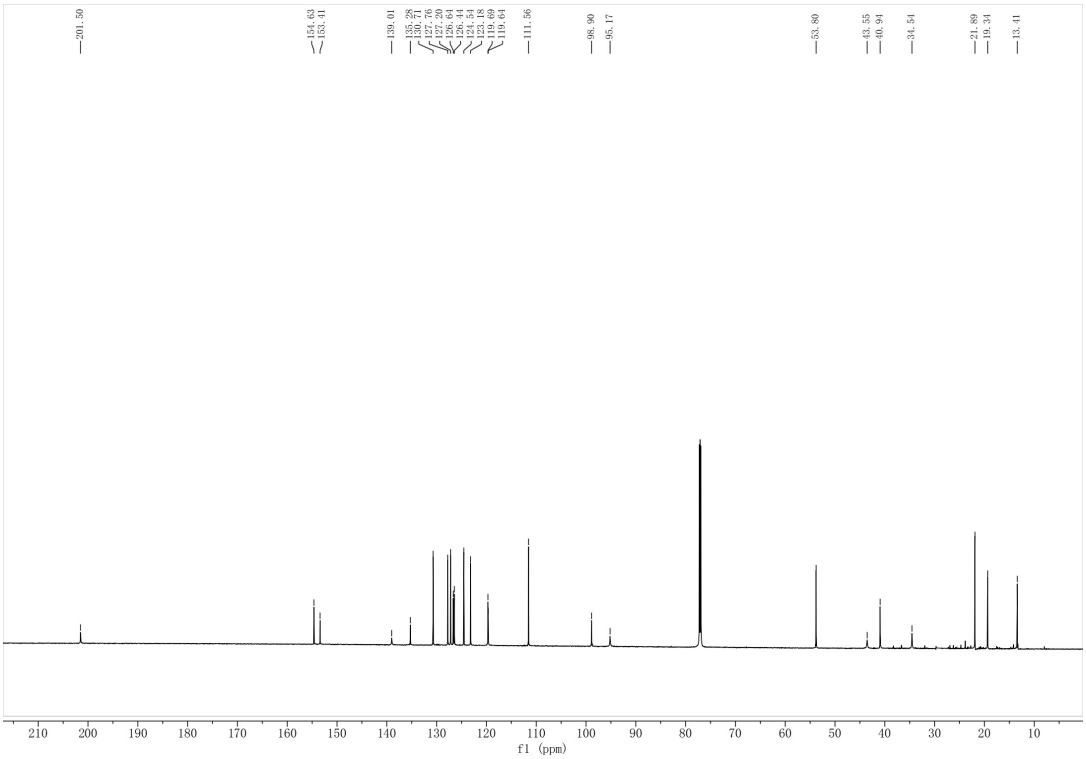


Figure S52. ^{13}C NMR spectrum of compound **3bk** in $CDCl_3$ at 201 MHz.

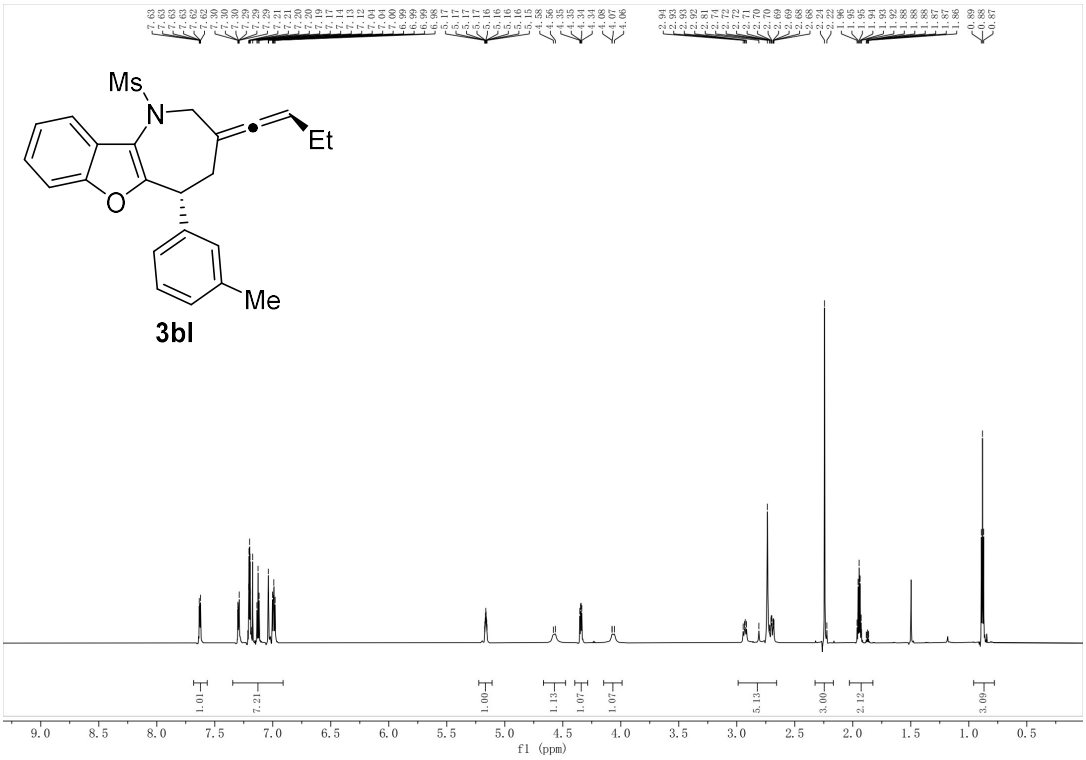


Figure S53. ^{1}H NMR spectrum of compound **3bl** in $CDCl_3$ at 800 MHz.

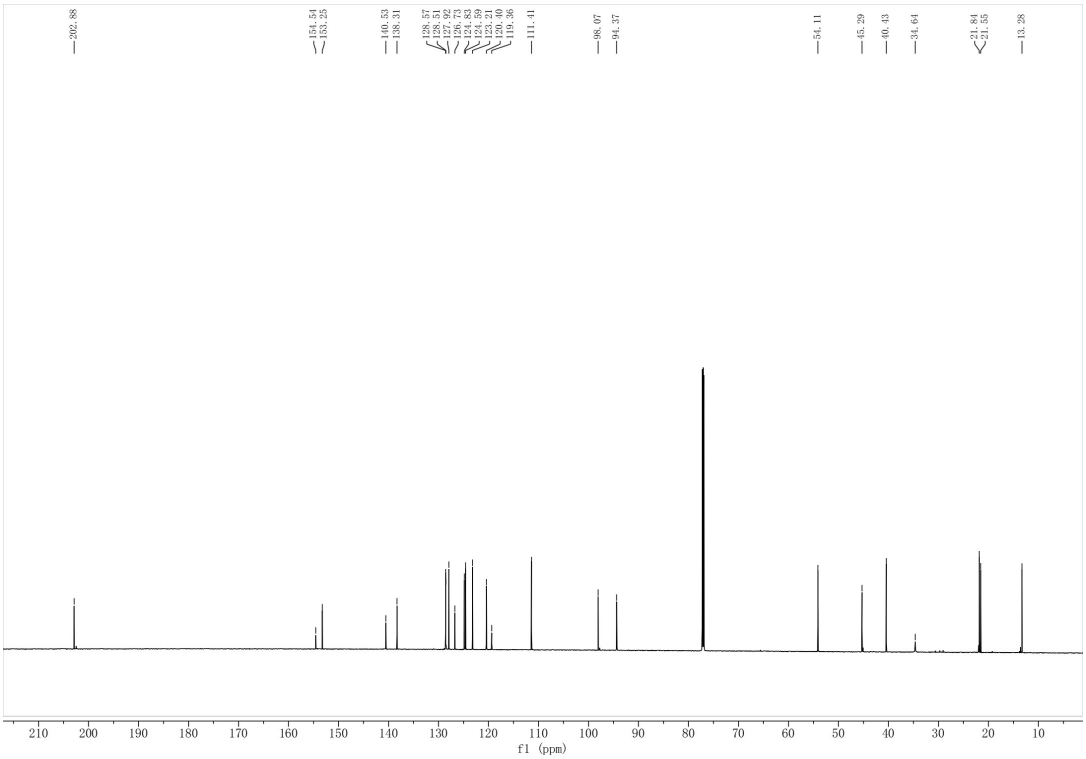


Figure S54. ^{13}C NMR spectrum of compound **3bl** in $CDCl_3$ at 201 MHz.

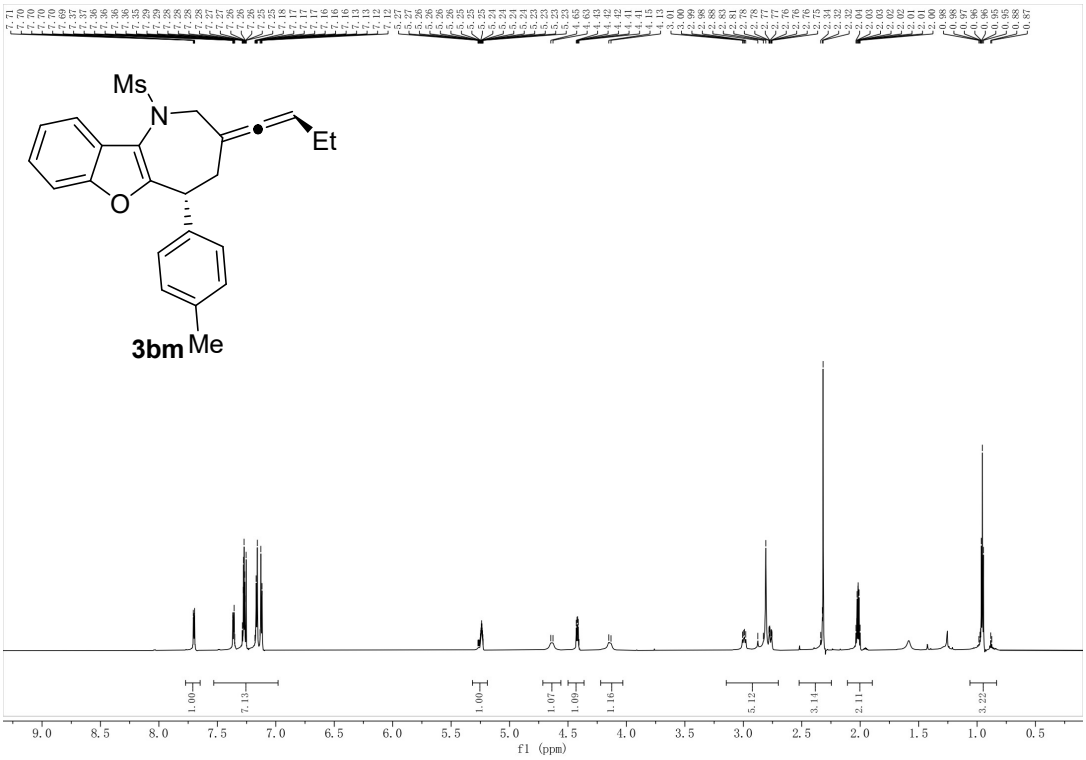


Figure S55. ^{1}H NMR spectrum of compound **3bm** in $CDCl_3$ at 800 MHz.

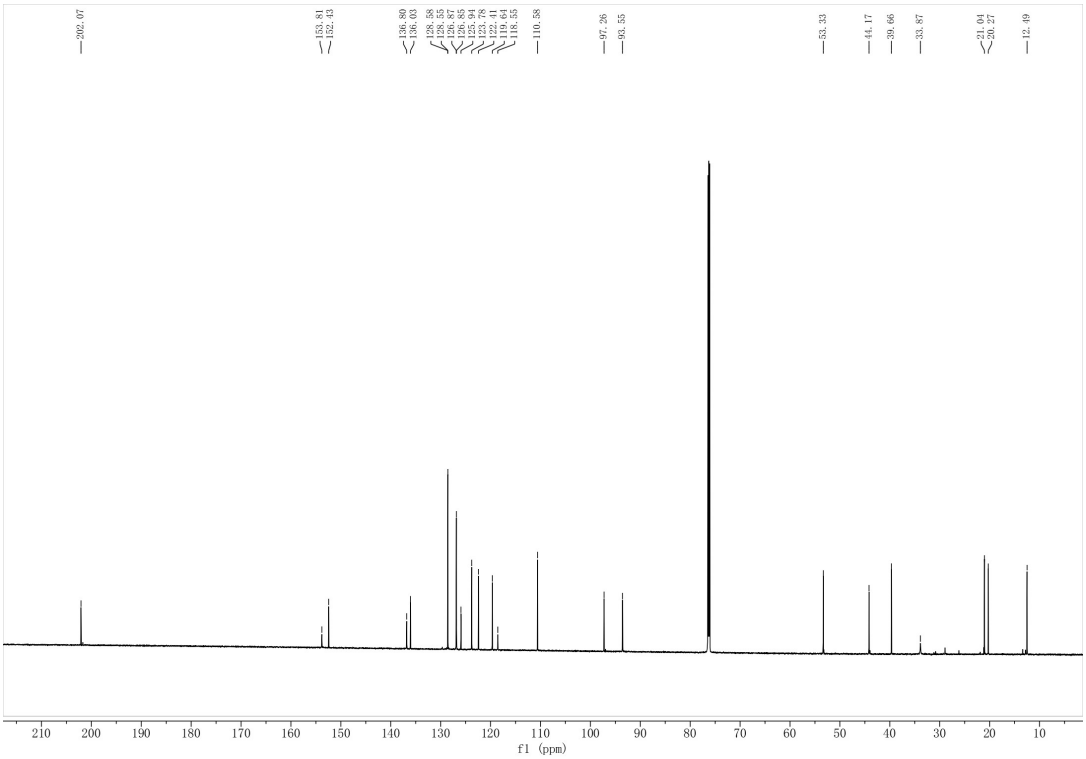


Figure S56. ^{13}C NMR spectrum of compound **3bm** in $CDCl_3$ at 201 MHz.

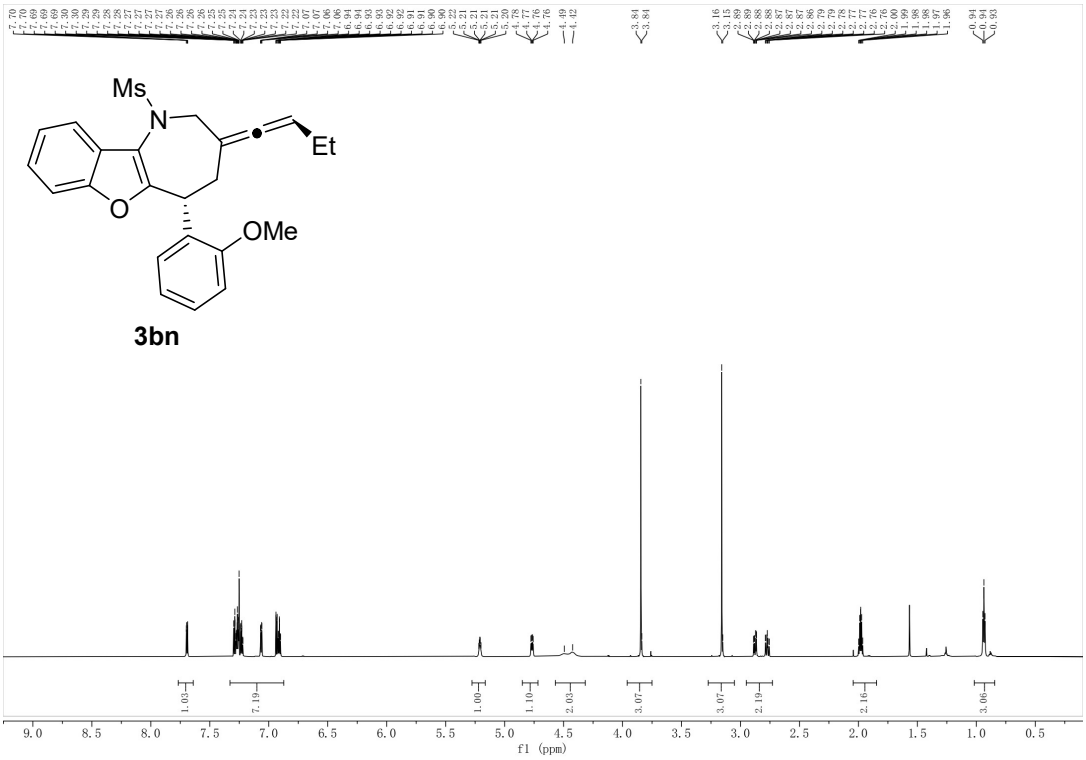


Figure S57. ^{1}H NMR spectrum of compound **3bn** in $CDCl_3$ at 800 MHz.

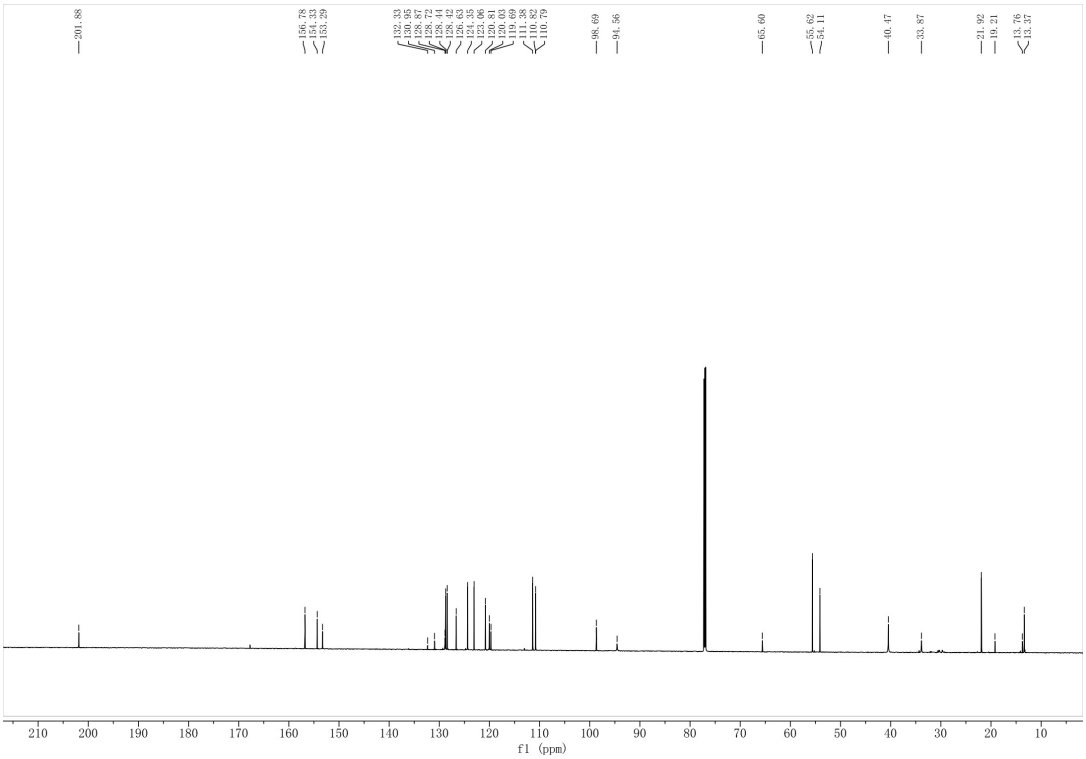


Figure S58. ^{13}C NMR spectrum of compound **3bn** in $CDCl_3$ at 201 MHz.

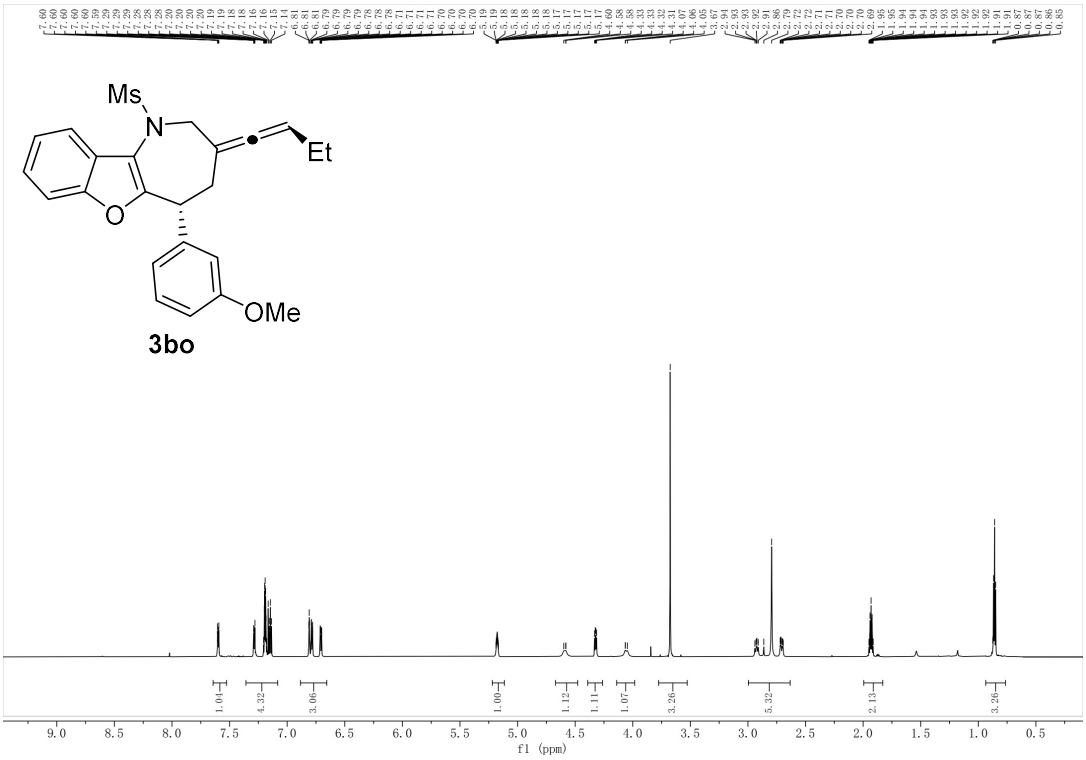


Figure S59. ^{1}H NMR spectrum of compound **3bo** in $CDCl_3$ at 800 MHz.

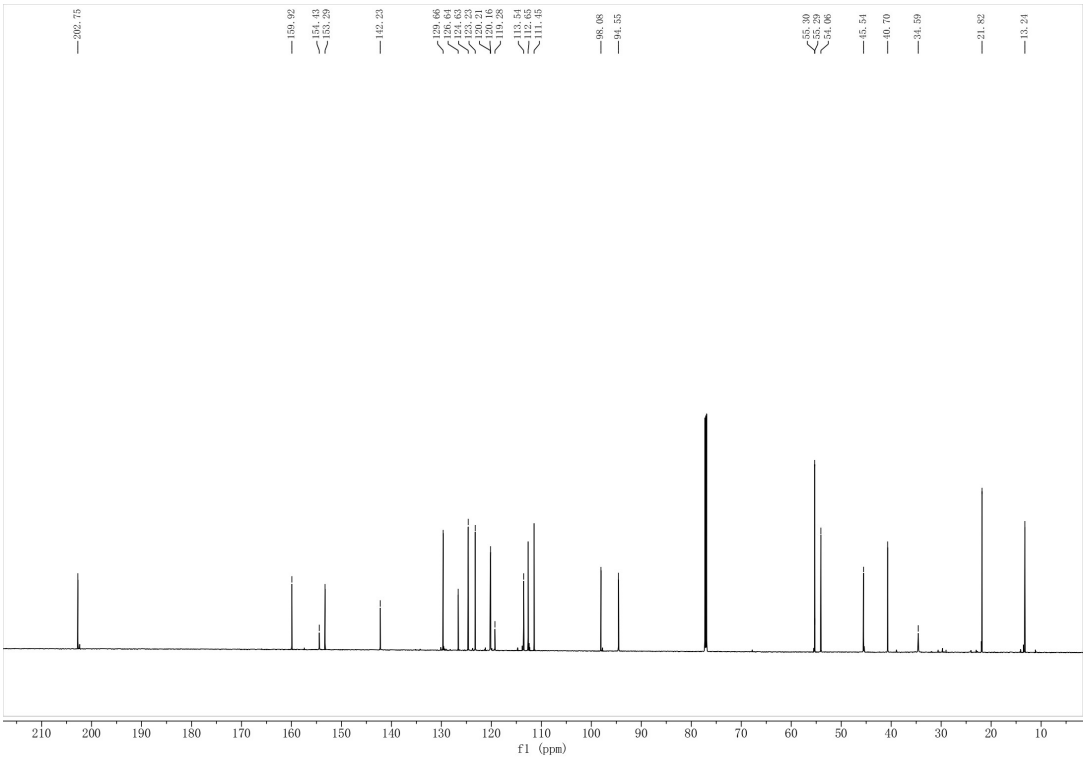


Figure S60. ^{13}C NMR spectrum of compound **3bo** in $CDCl_3$ at 201 MHz.

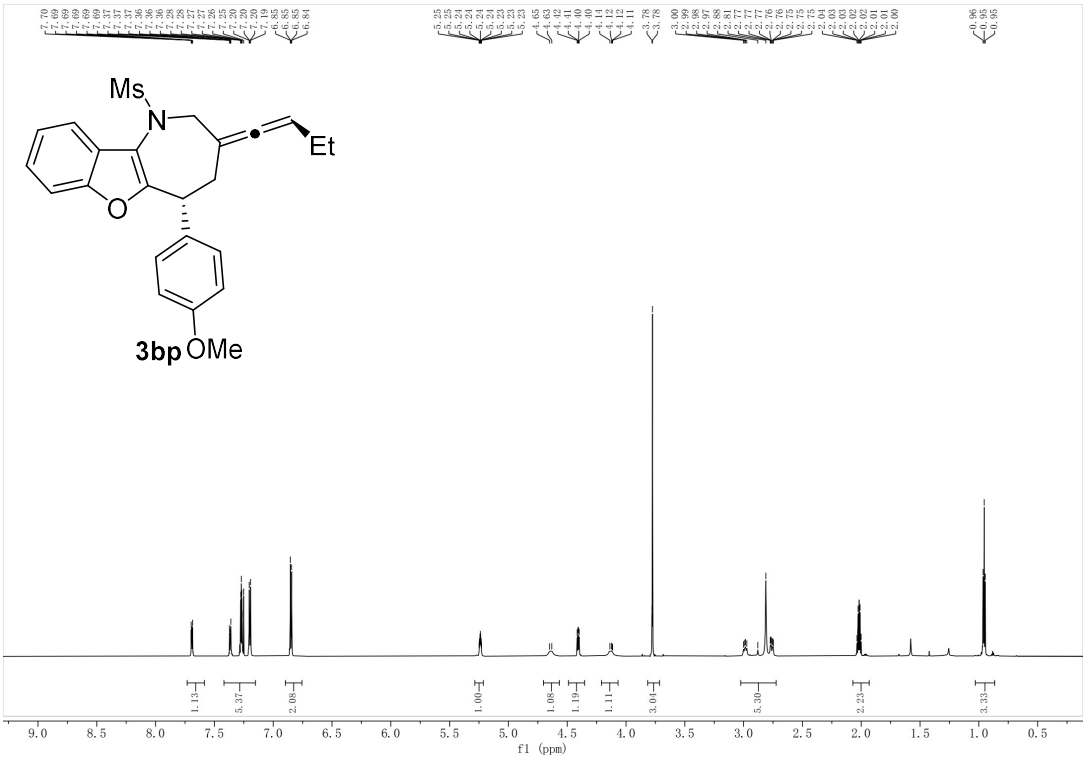


Figure S61. ^{1}H NMR spectrum of compound **3bp** in $CDCl_3$ at 800 MHz.

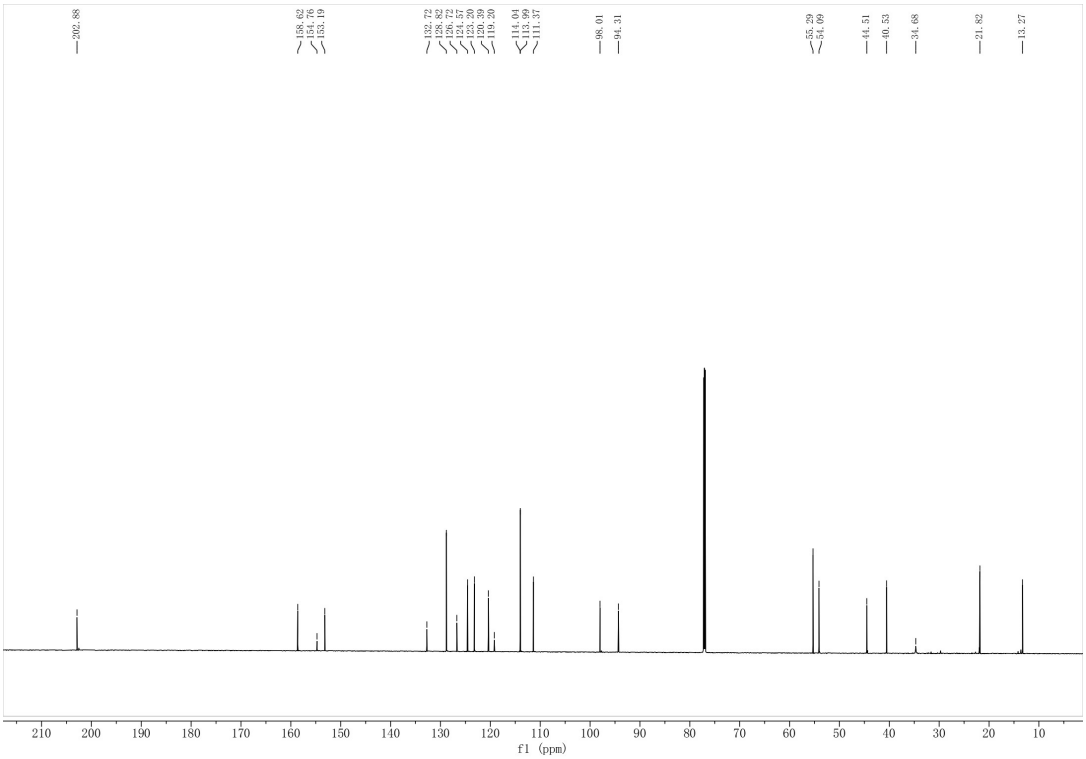


Figure S62. ^{13}C NMR spectrum of compound **3bp** in $CDCl_3$ at 201 MHz.

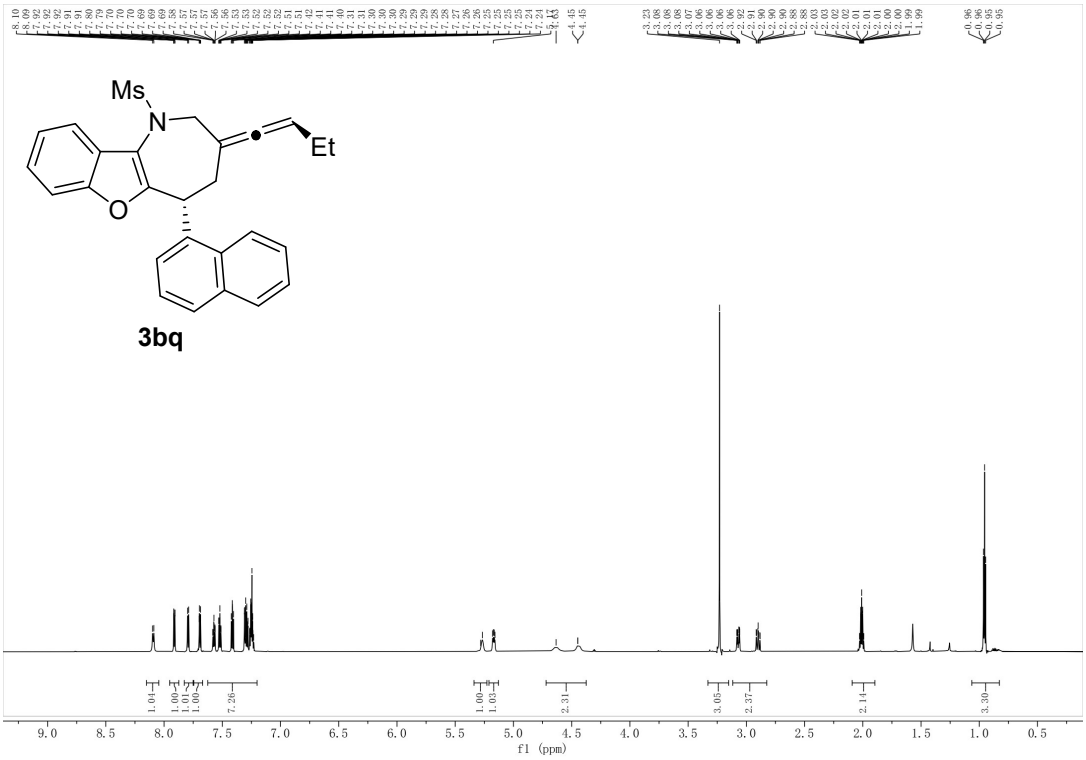


Figure S63. ^{1}H NMR spectrum of compound **3bq** in $CDCl_3$ at 800 MHz.

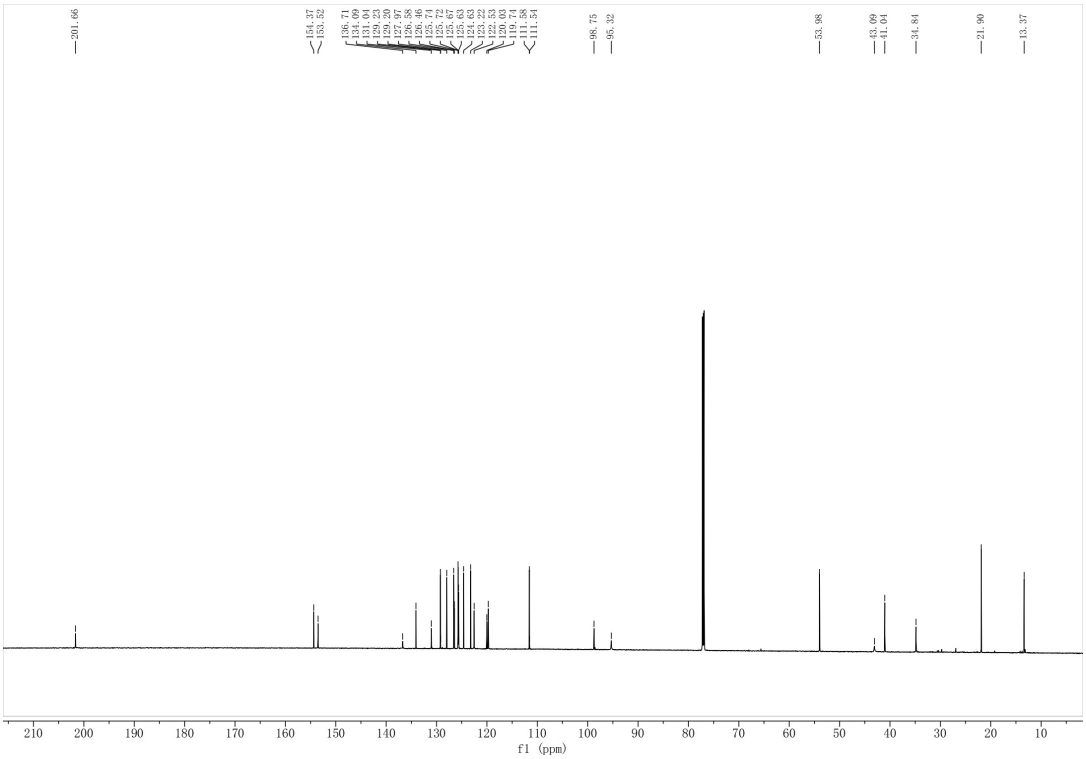


Figure S64. ^{13}C NMR spectrum of compound **3bq** in $CDCl_3$ at 201 MHz.

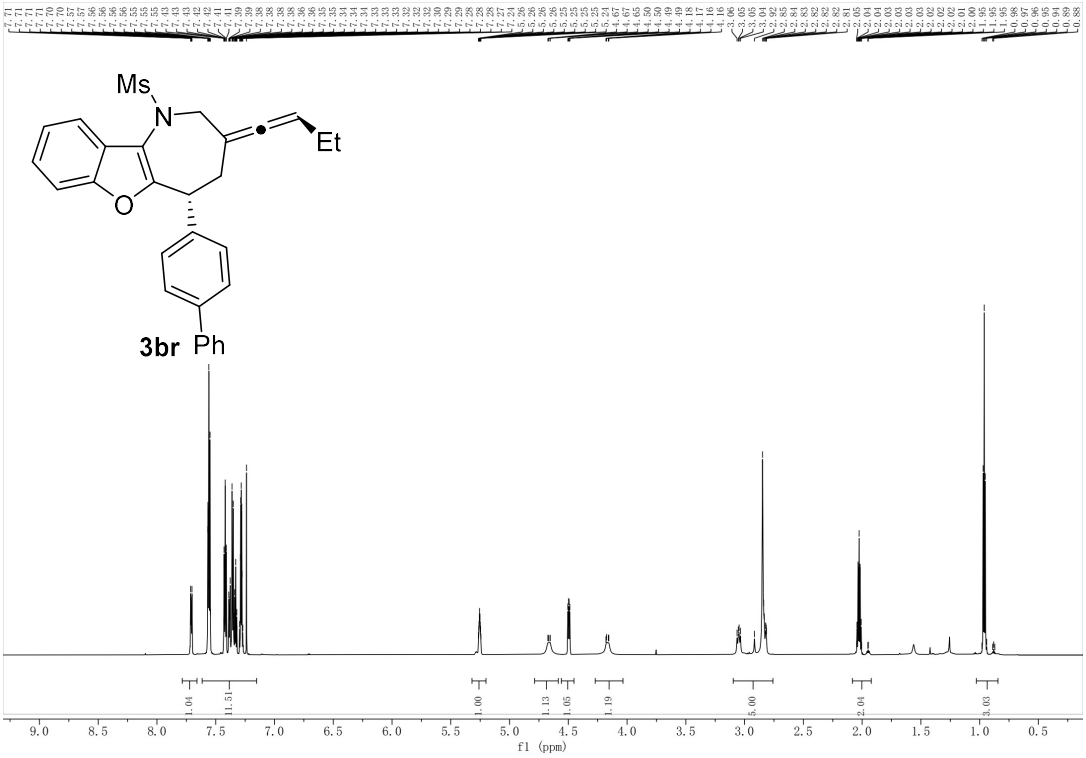


Figure S65. ^{1}H NMR spectrum of compound **3br** in $CDCl_3$ at 800 MHz.

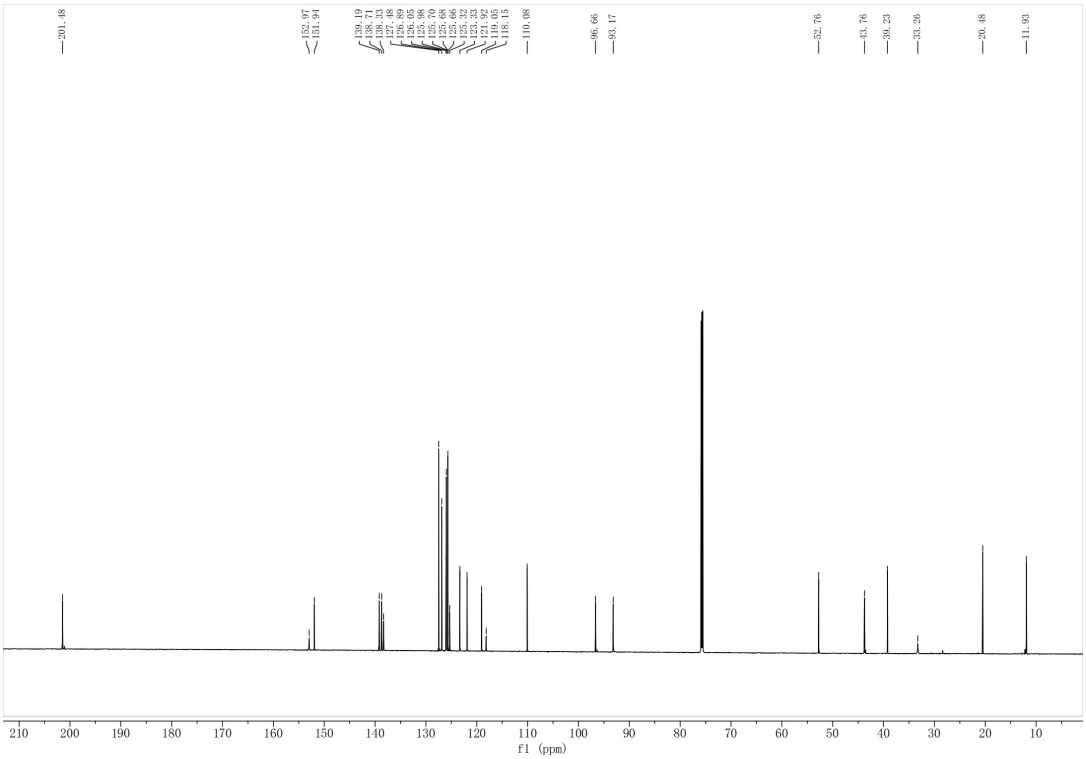


Figure S66. ^{13}C NMR spectrum of compound **3br** in $CDCl_3$ at 201 MHz.

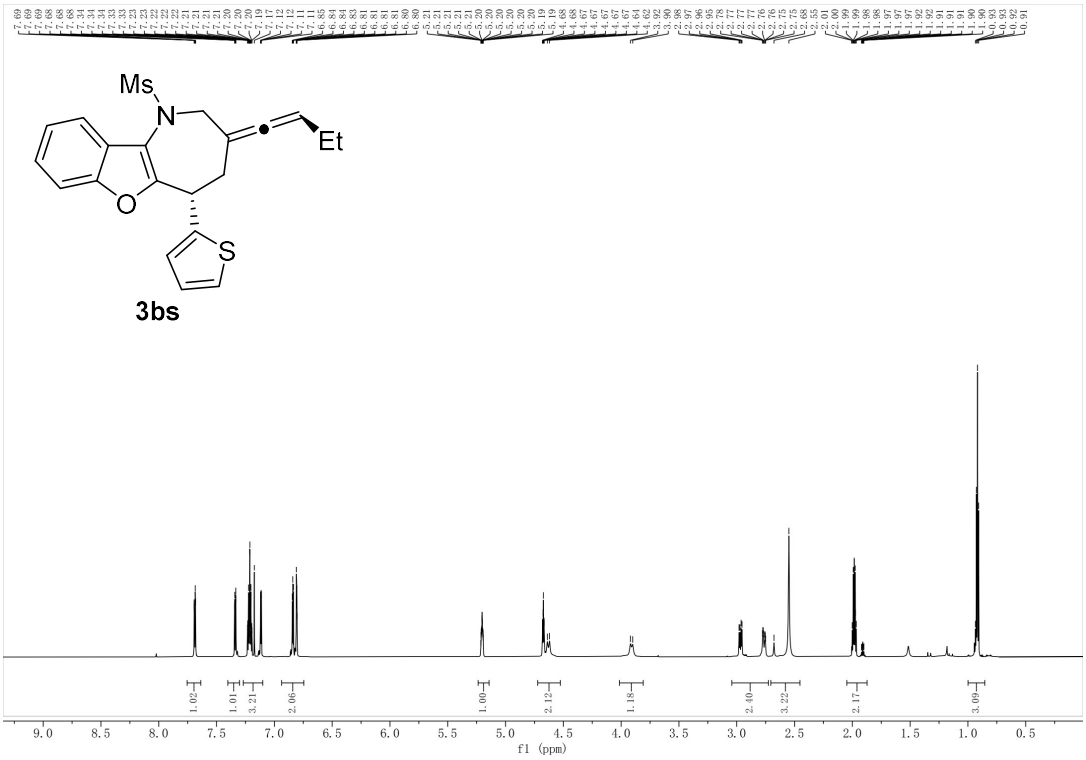


Figure S67. ^{1}H NMR spectrum of compound **3bs** in $CDCl_3$ at 800 MHz.

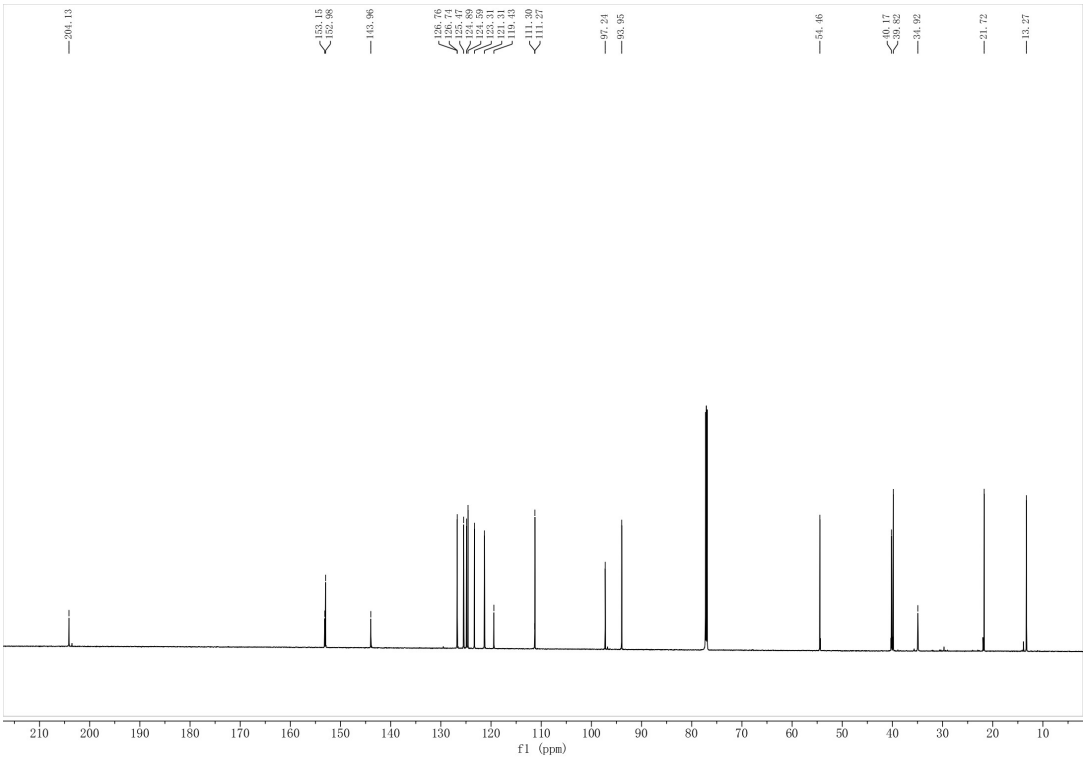


Figure S68. ^{13}C NMR spectrum of compound **3bs** in $CDCl_3$ at 201 MHz.

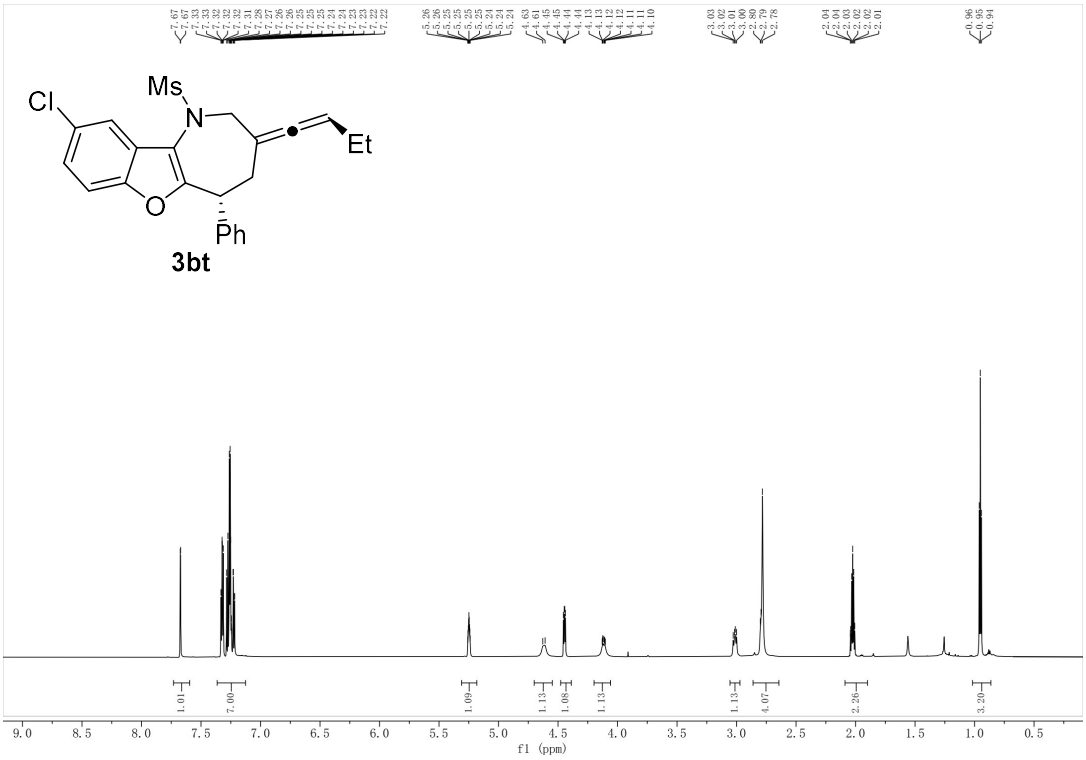


Figure S69. ^{1}H NMR spectrum of compound **3bt** in $CDCl_3$ at 800 MHz.

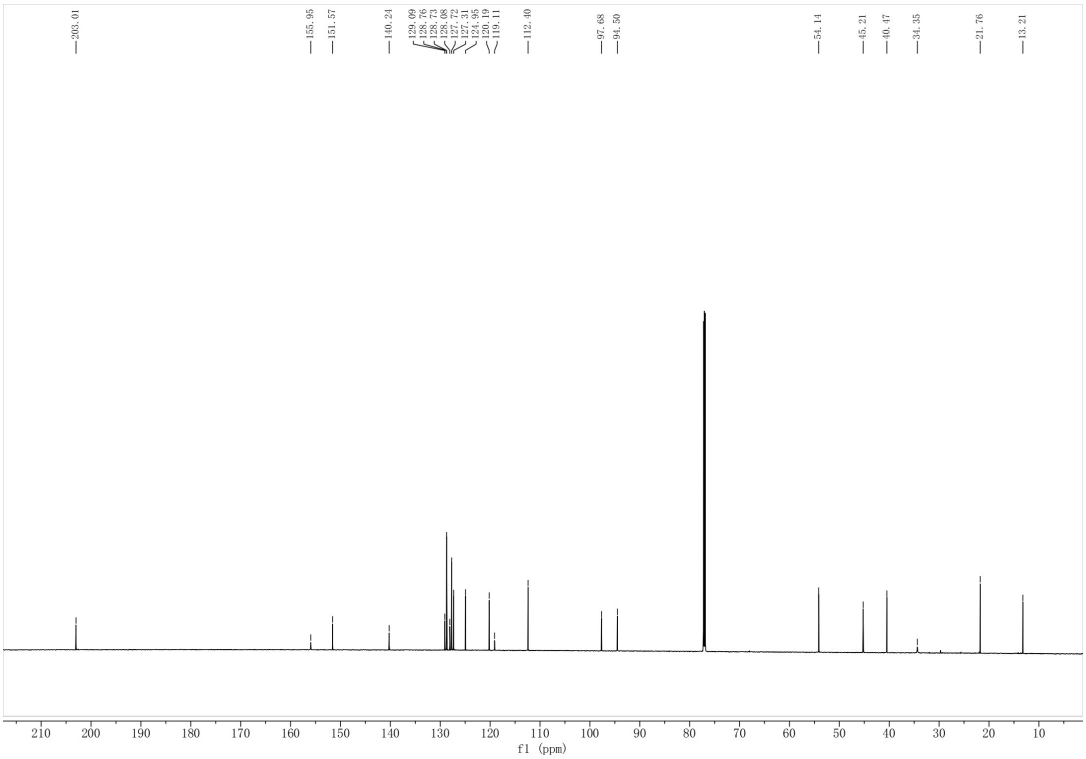


Figure S70. ^{13}C NMR spectrum of compound **3bt** in $CDCl_3$ at 201 MHz.

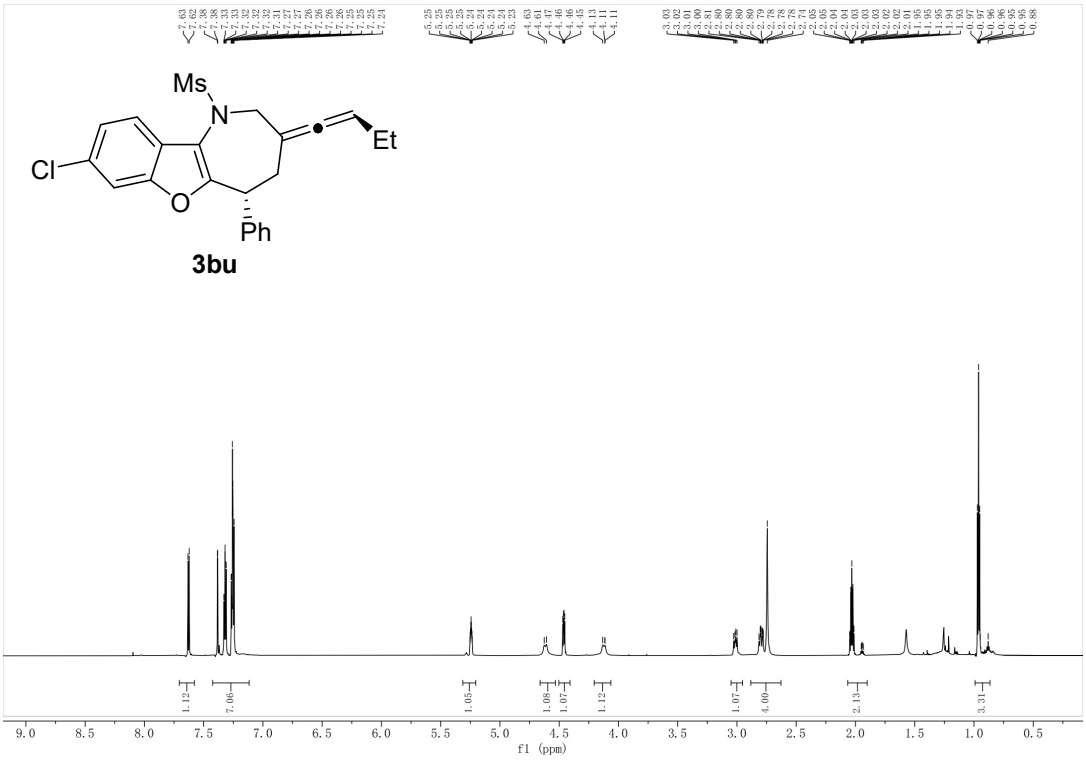


Figure S71. ^{1}H NMR spectrum of compound **3bu** in $CDCl_3$ at 800 MHz.

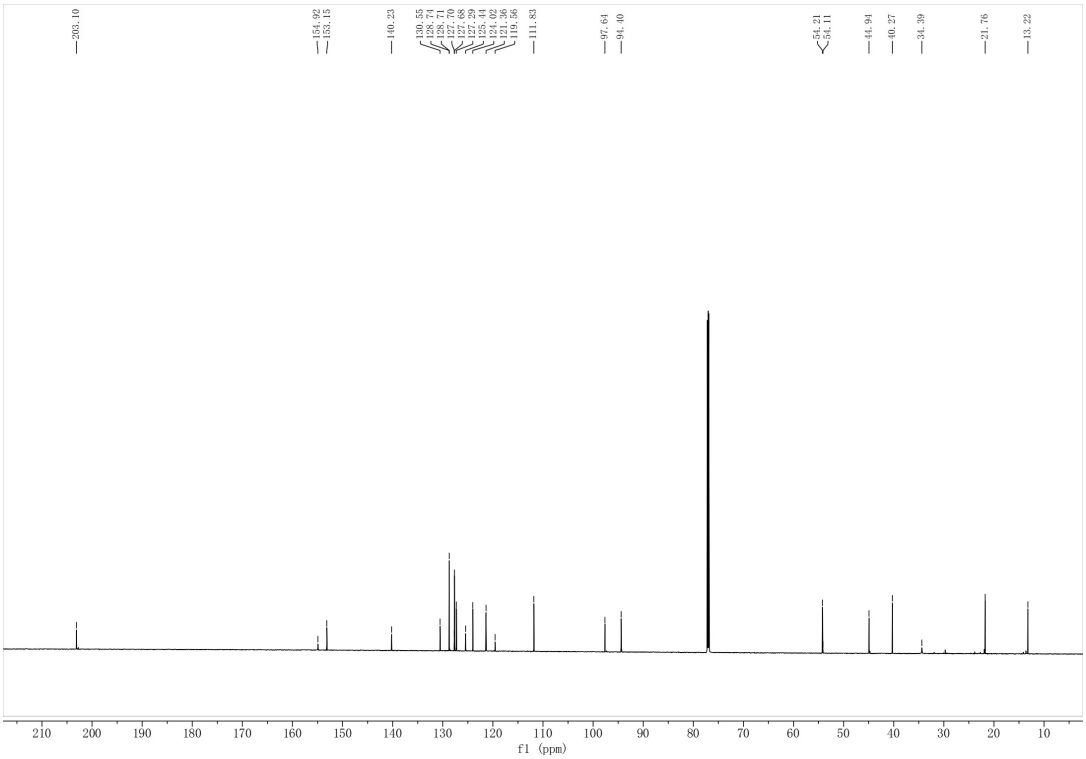


Figure S72. ^{13}C NMR spectrum of compound **3bu** in $CDCl_3$ at 201 MHz.

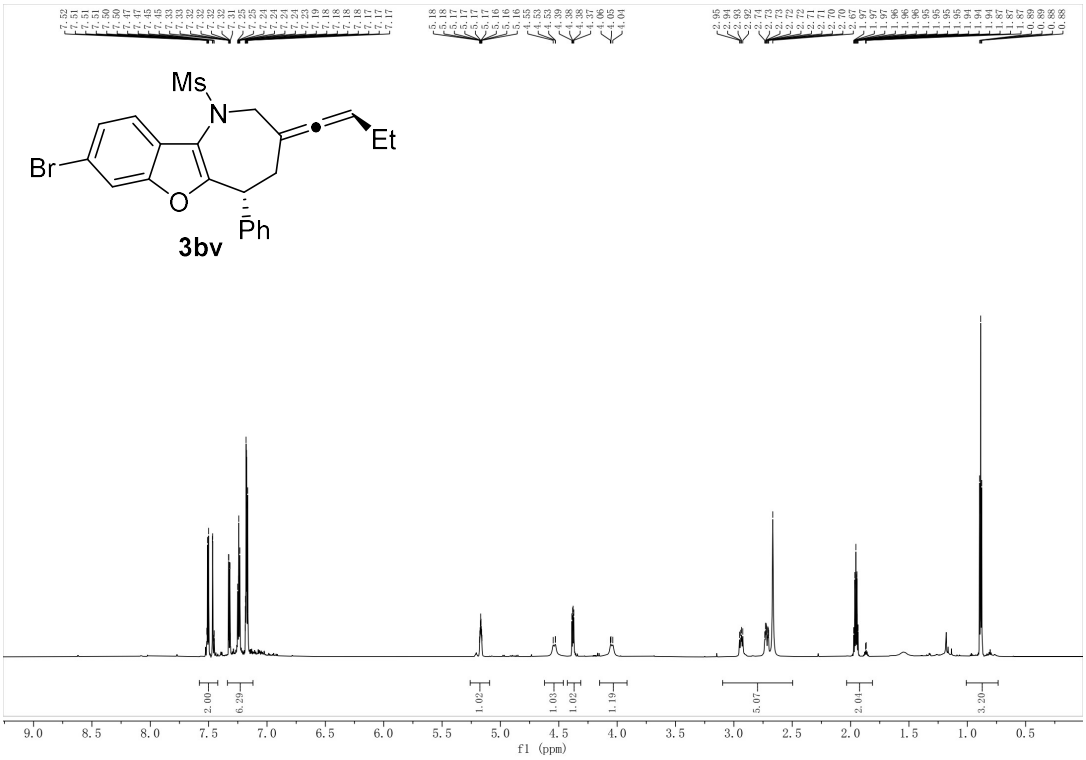


Figure S73. ^{1}H NMR spectrum of compound **3bv** in $CDCl_3$ at 800 MHz.

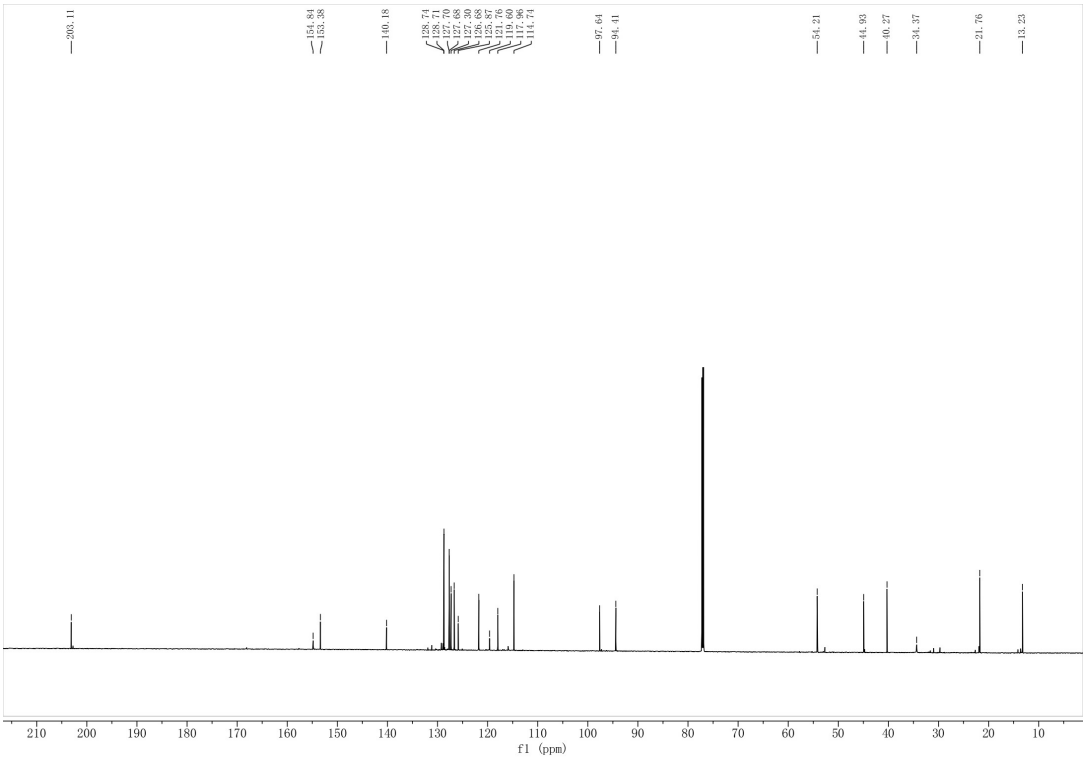


Figure S74. ^{13}C NMR spectrum of compound **3bv** in $CDCl_3$ at 201 MHz.

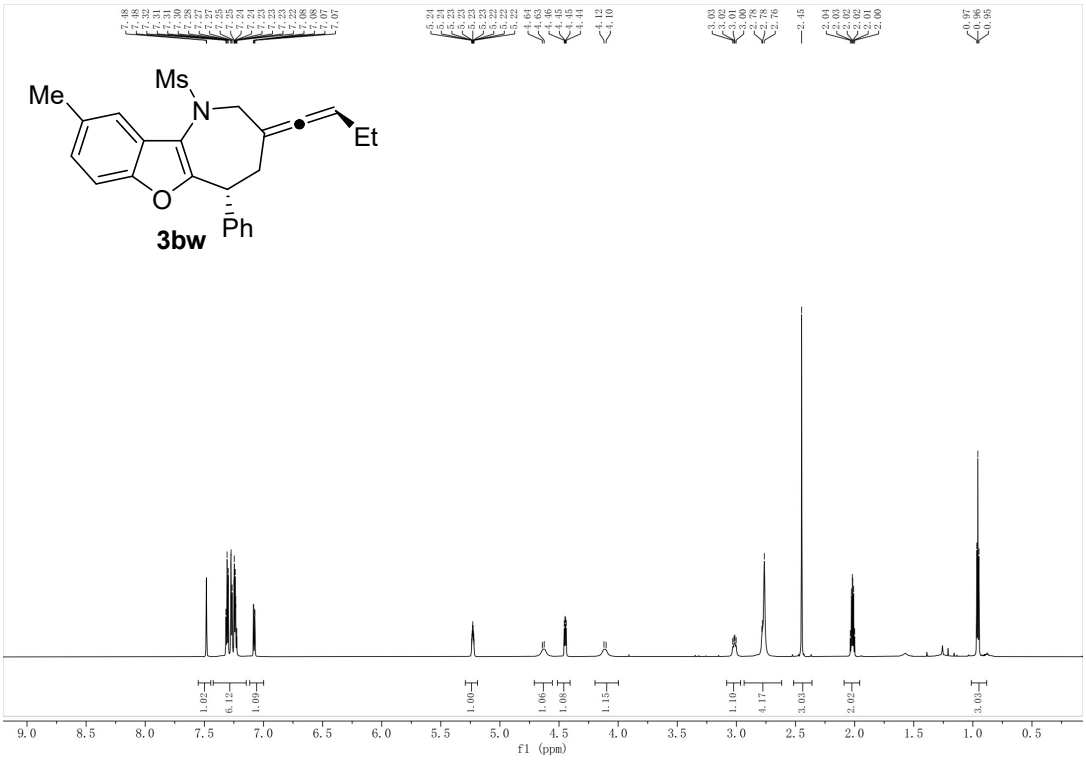


Figure S75. ^{1}H NMR spectrum of compound **3bw** in $CDCl_3$ at 800 MHz.

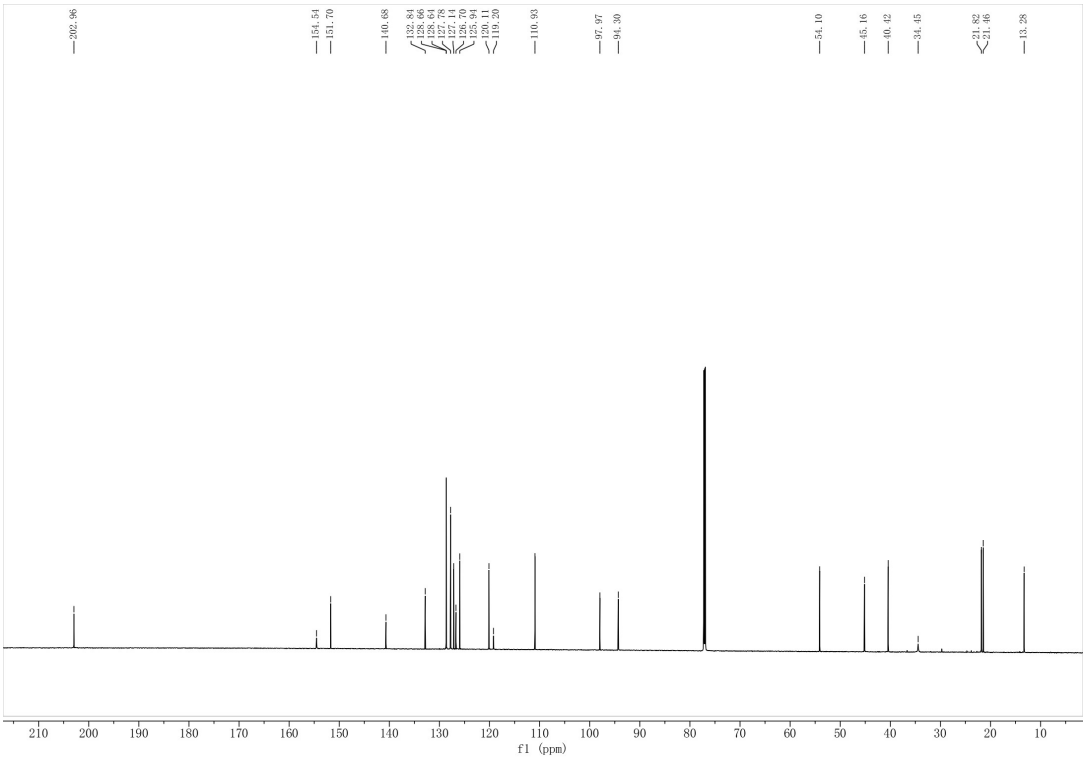


Figure S76. ^{13}C NMR spectrum of compound **3bw** in $CDCl_3$ at 201 MHz.

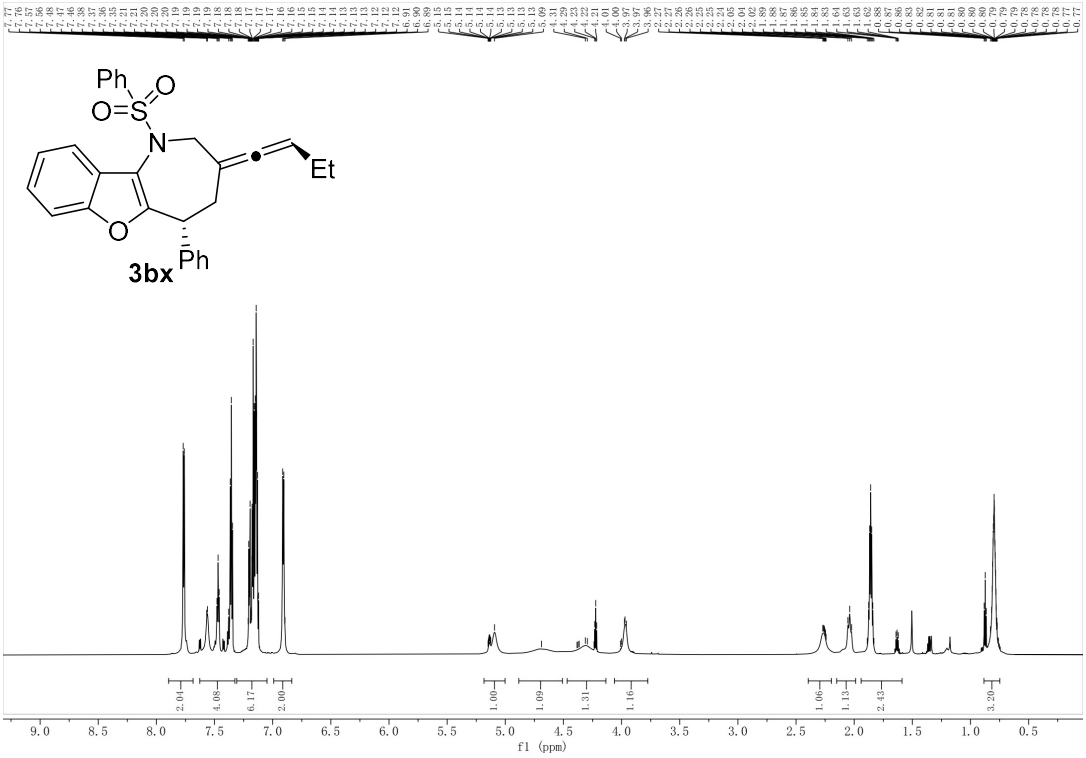


Figure S77. ^{1}H NMR spectrum of compound **3bx** in $CDCl_3$ at 800 MHz.

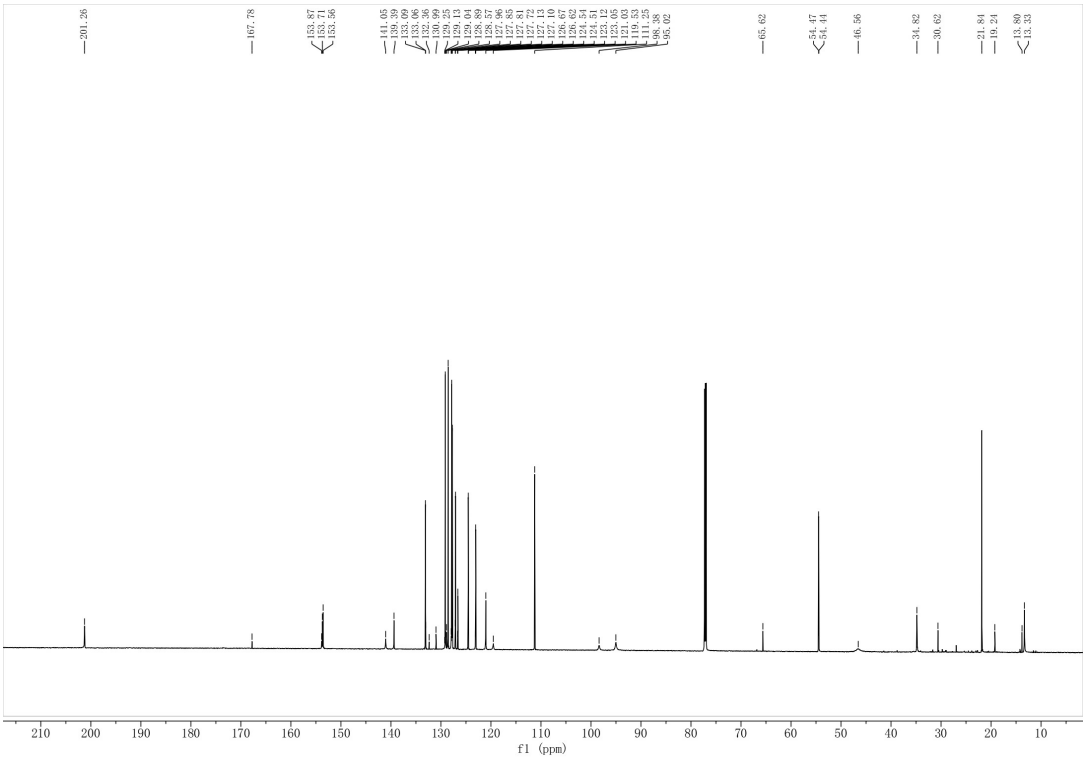


Figure S78. ^{13}C NMR spectrum of compound **3bx** in $CDCl_3$ at 201 MHz.

Figure S79. ^{1}H NMR spectrum of compound **3by** in $CDCl_3$ at 800 MHz.

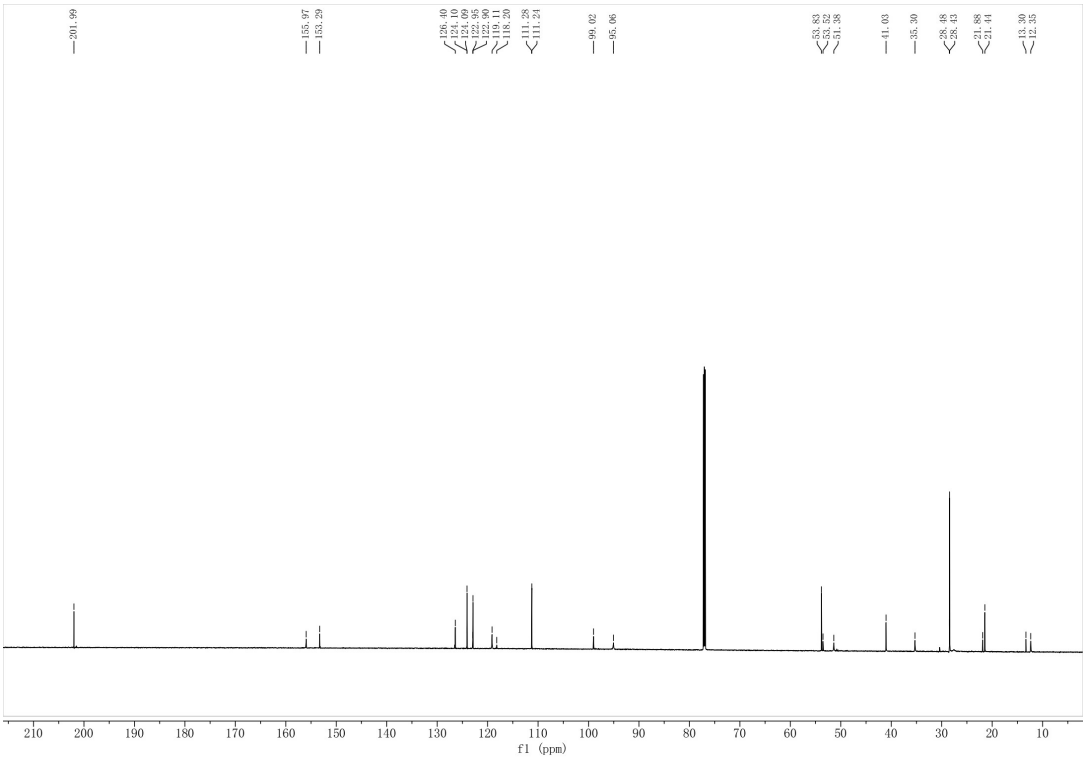


Figure S80. ^{13}C NMR spectrum of compound **3by** in $CDCl_3$ at 201 MHz.

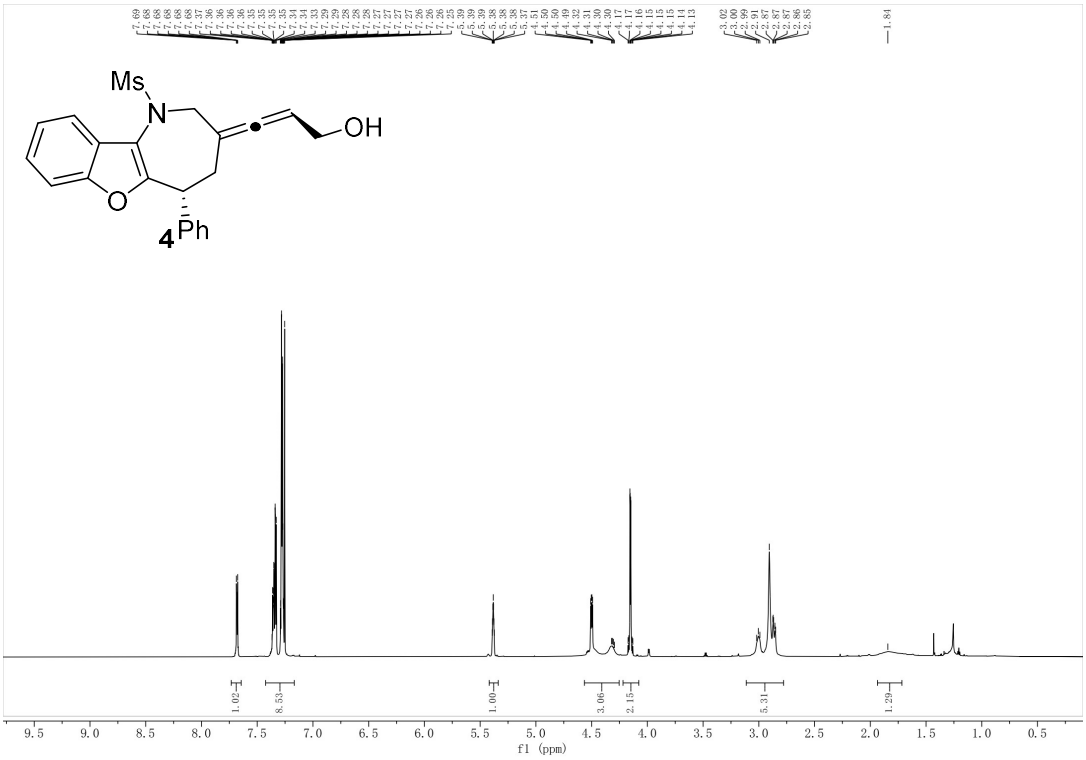


Figure S81. ^{1}H NMR spectrum of compound **4** in $CDCl_3$ at 800 MHz.

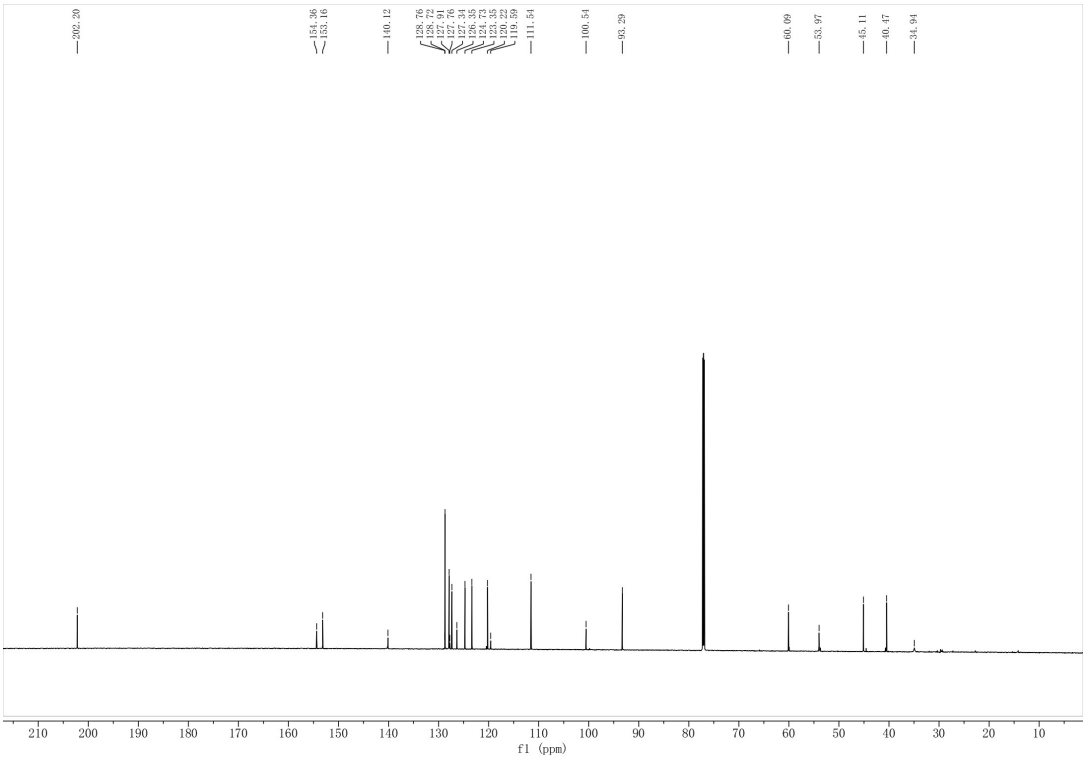


Figure S82. ^{13}C NMR spectrum of compound **4** in $CDCl_3$ at 201 MHz.

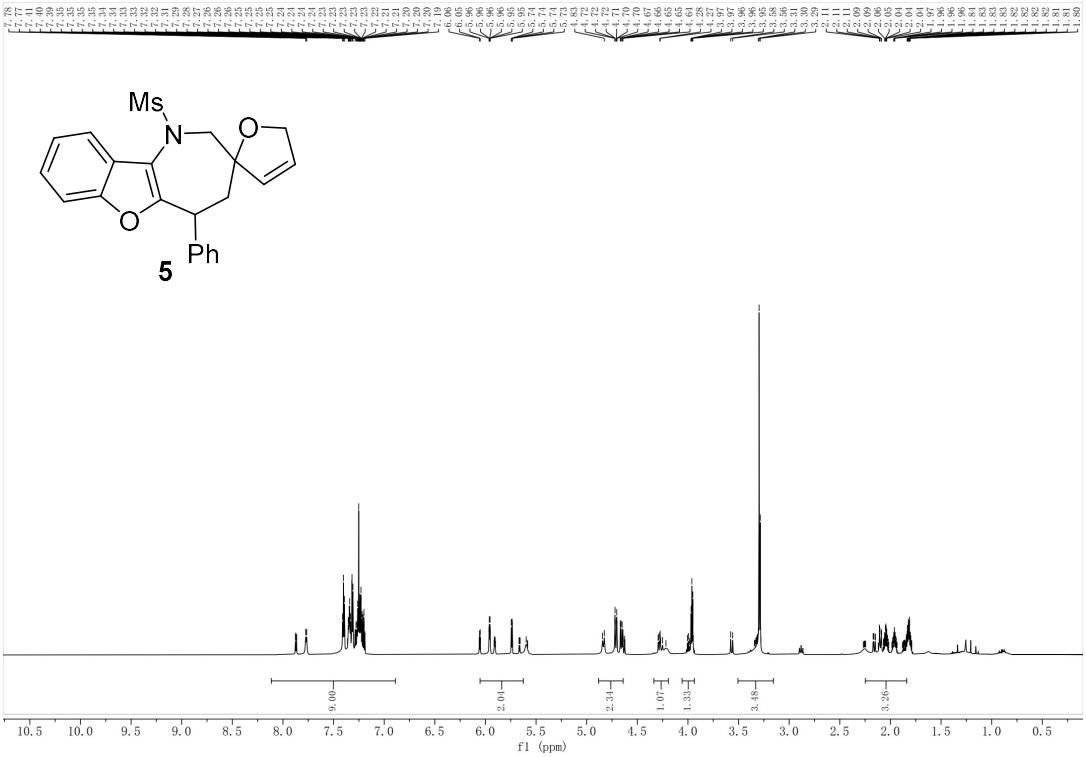


Figure S83. ^{1}H NMR spectrum of compound **5** in $CDCl_3$ at 800 MHz.

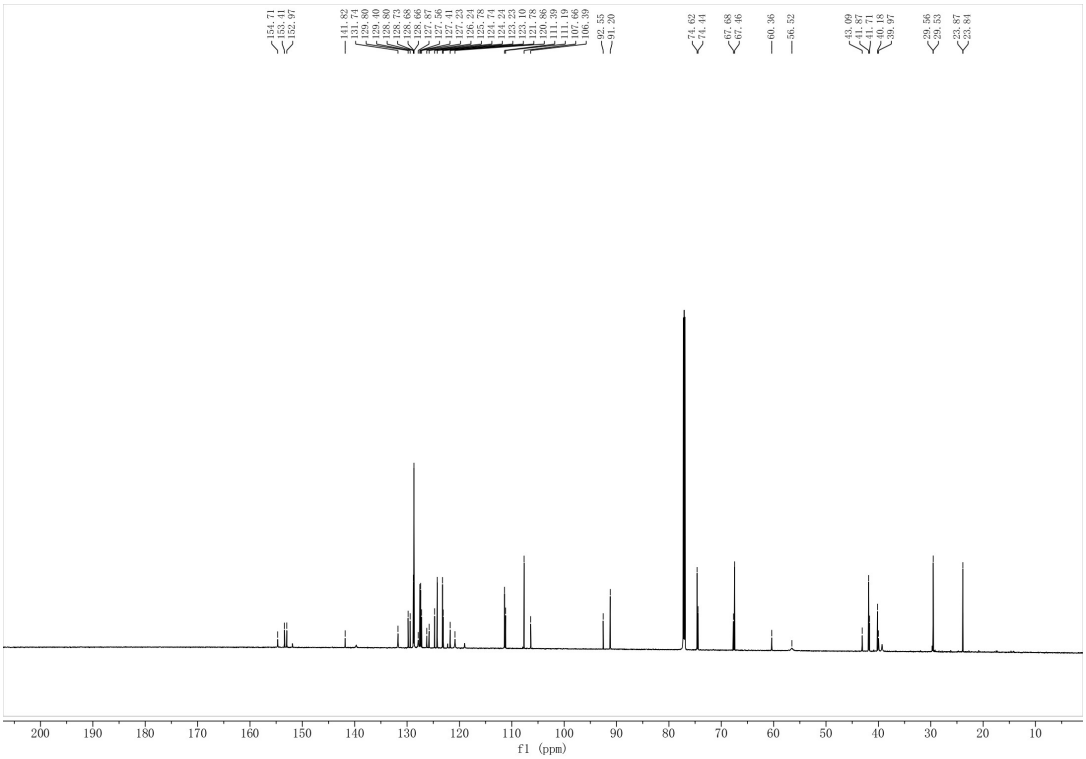


Figure S84. ^{13}C NMR spectrum of compound **5** in $CDCl_3$ at 201 MHz.

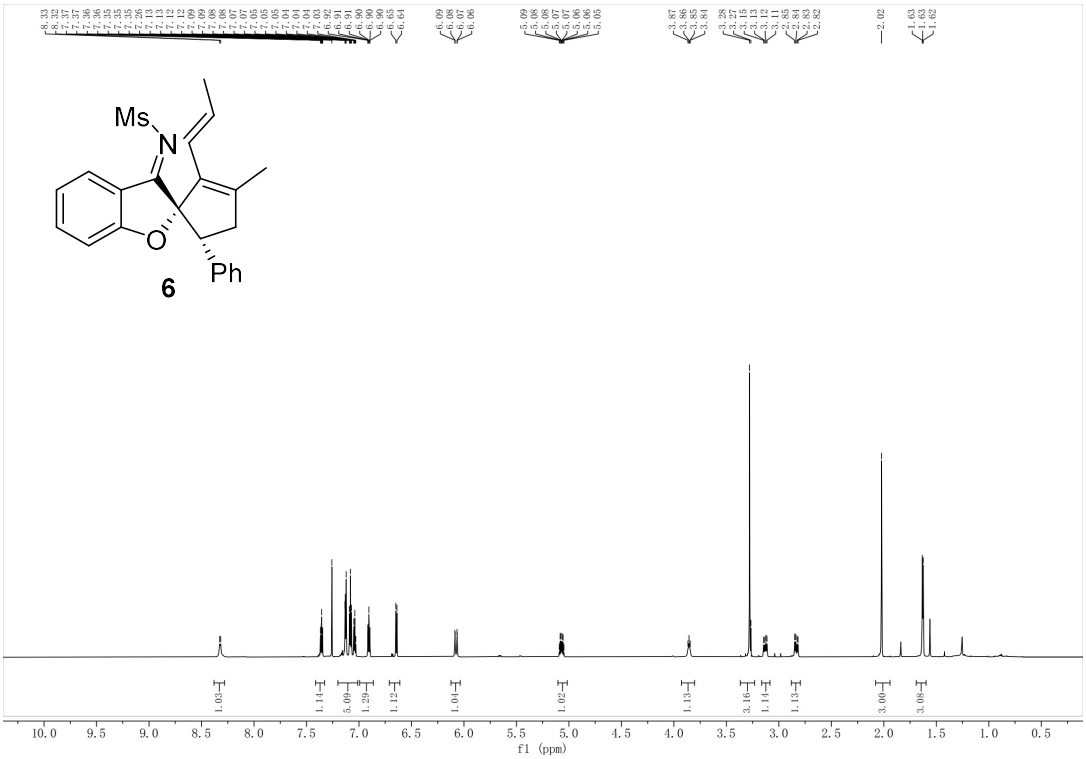


Figure S85. ^{1}H NMR spectrum of compound **6** in $CDCl_3$ at 800 MHz.

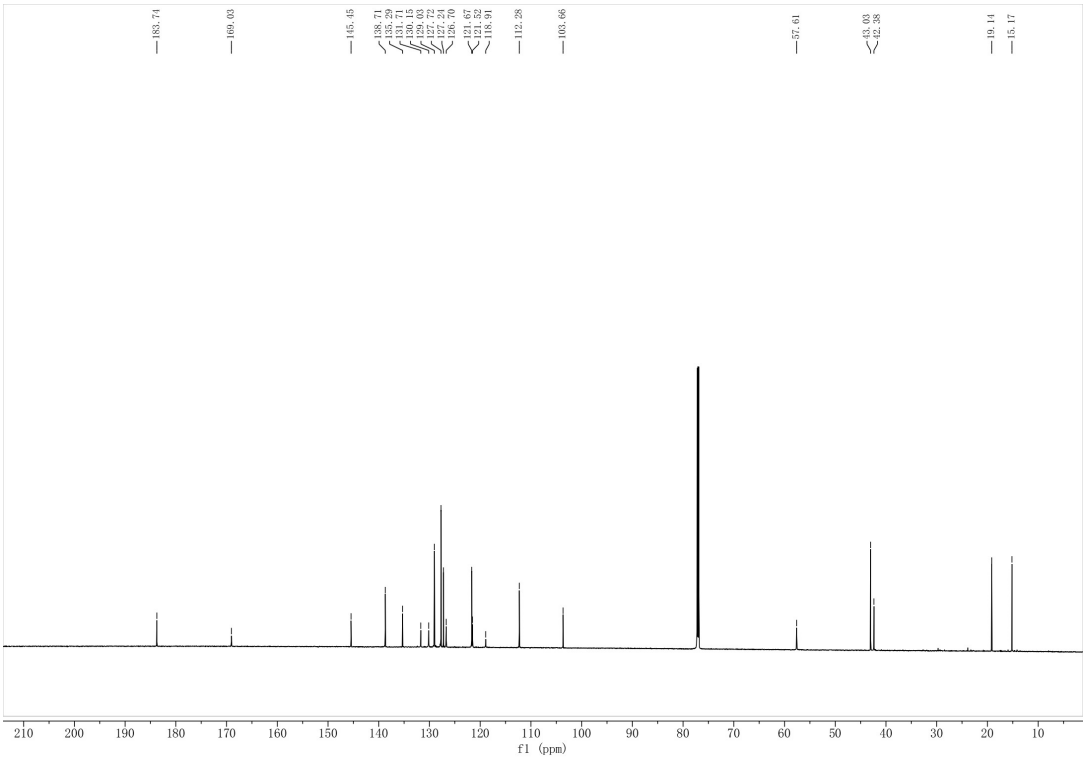
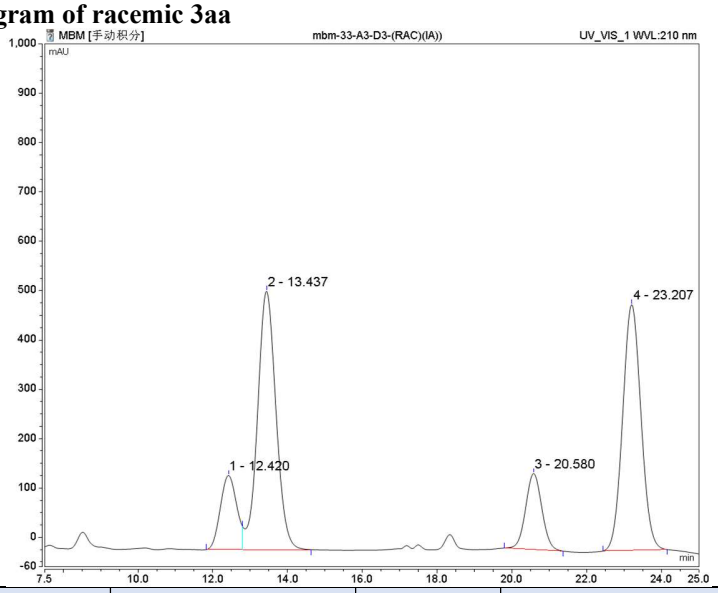


Figure S86. ^{13}C NMR spectrum of compound **6** in $CDCl_3$ at 201 MHz.

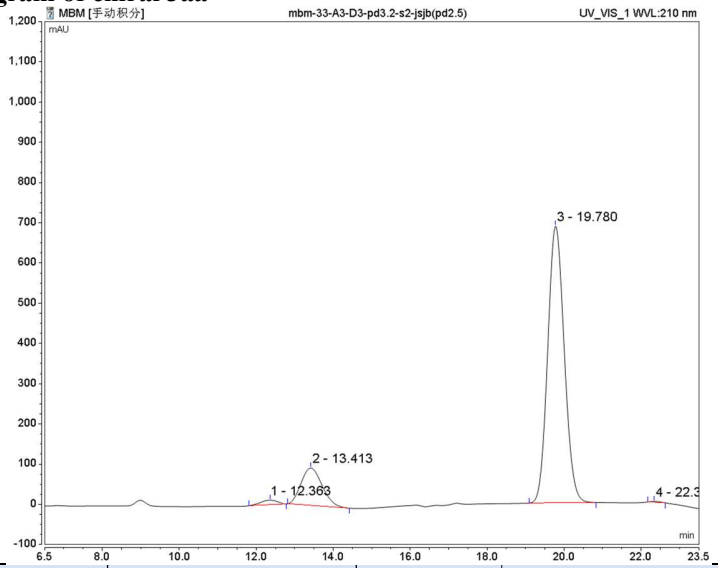
HPLC Chromatograms of All Products

HPLC chromatogram of racemic 3aa



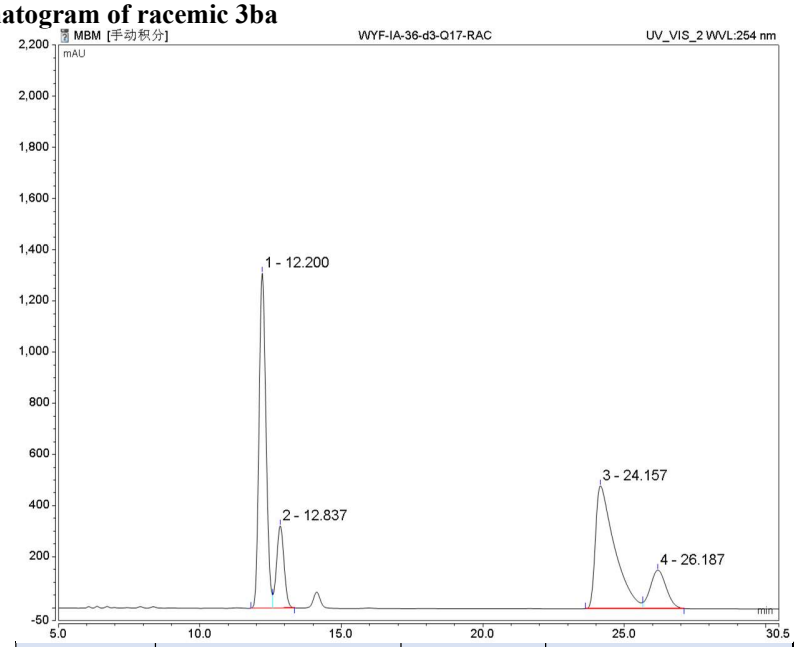
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	12.42	75.319	10.26
2	13.437	299.394	40.77
3	20.58	77.221	10.52
4	23.207	282.383	38.46
Total:		734.317	100

HPLC chromatogram of chiral 3aa



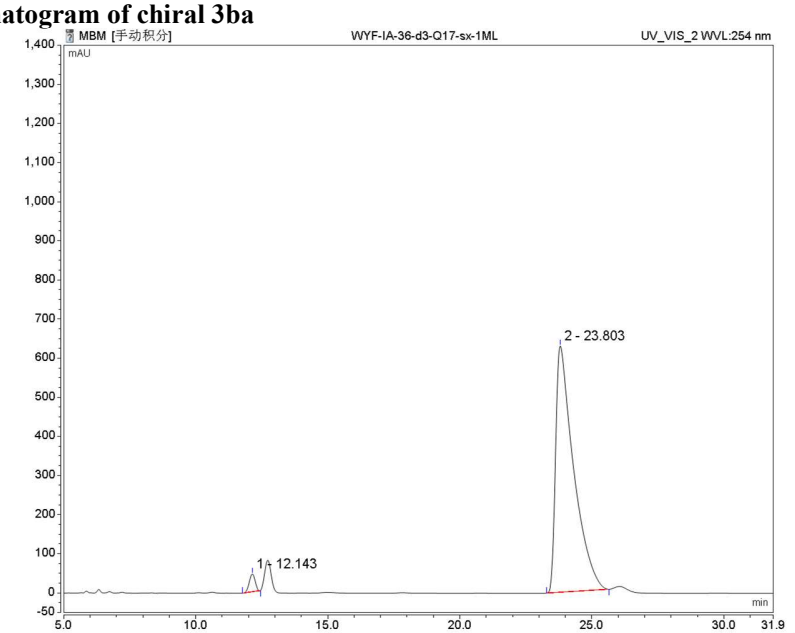
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	12.363	5.717	1.4
2	13.413	58.978	14.46
3	19.78	342.556	83.99
4	22.347	0.608	0.15
Total:		407.858	100

HPLC chromatogram of racemic 3ba



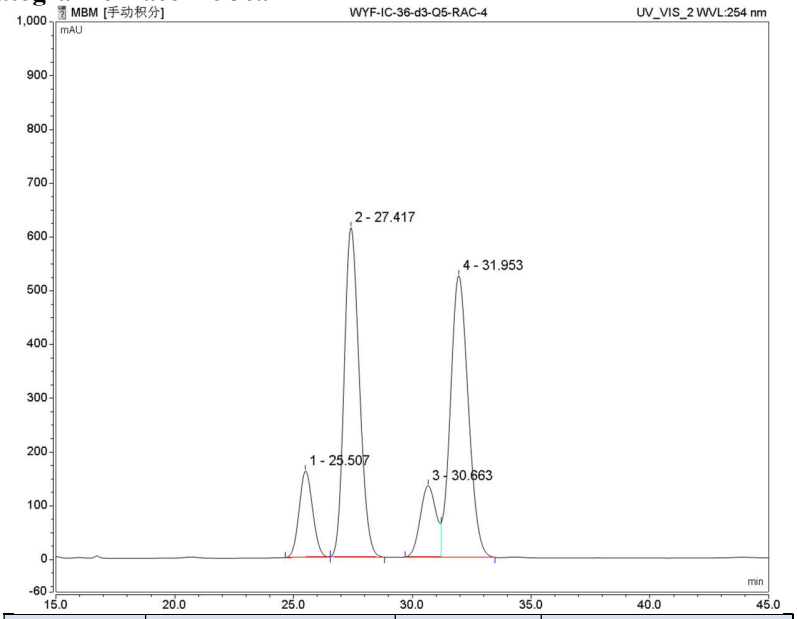
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	12.2	372.79	39.54
2	12.837	98.302	10.43
3	24.157	374.348	39.71
4	26.187	97.266	10.32
Total:		942.707	100

HPLC chromatogram of chiral 3ba



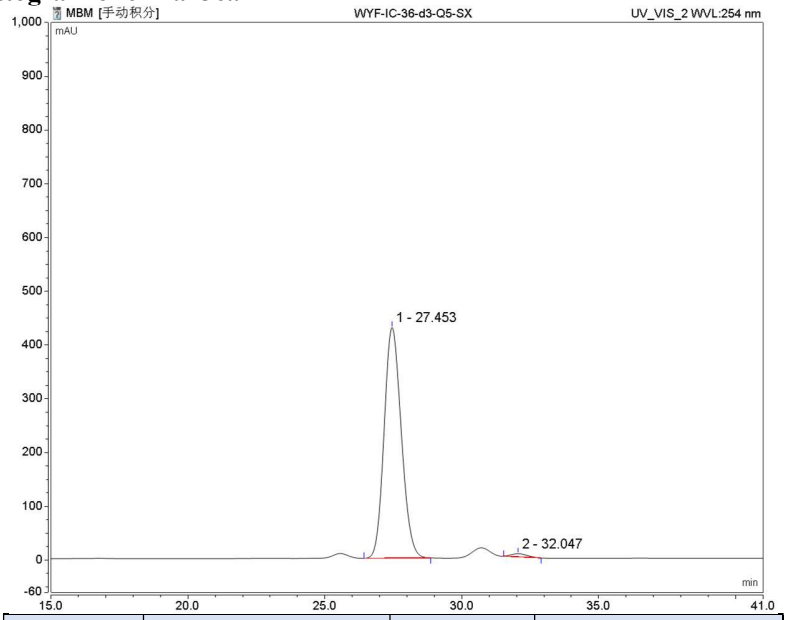
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	12.143	11.663	2.3
2	23.803	495.681	97.7
Total:		507.345	100

HPLC chromatogram of racemic 3ca



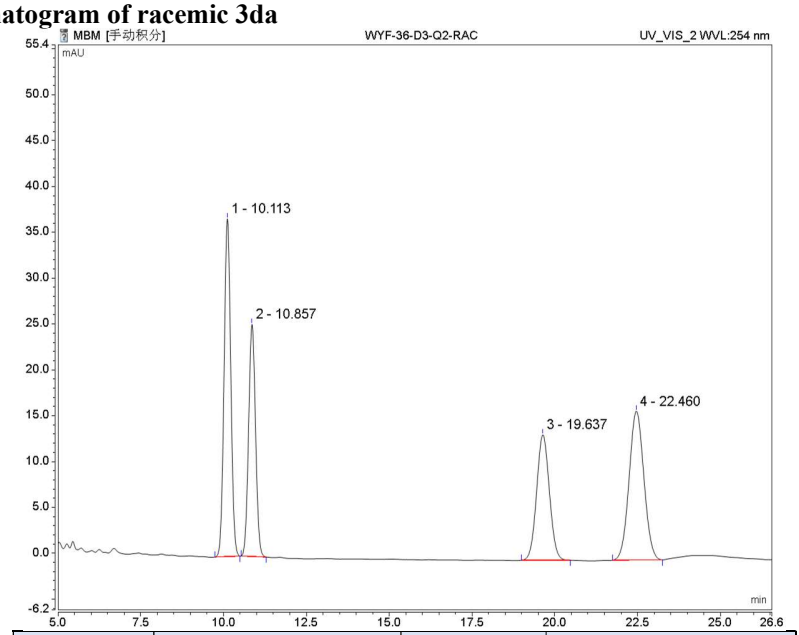
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	25.507	105.218	9.42
2	27.417	451.669	40.45
3	30.663	103.055	9.23
4	31.953	456.572	40.89
Total:		1116.515	100

HPLC chromatogram of chiral 3ca



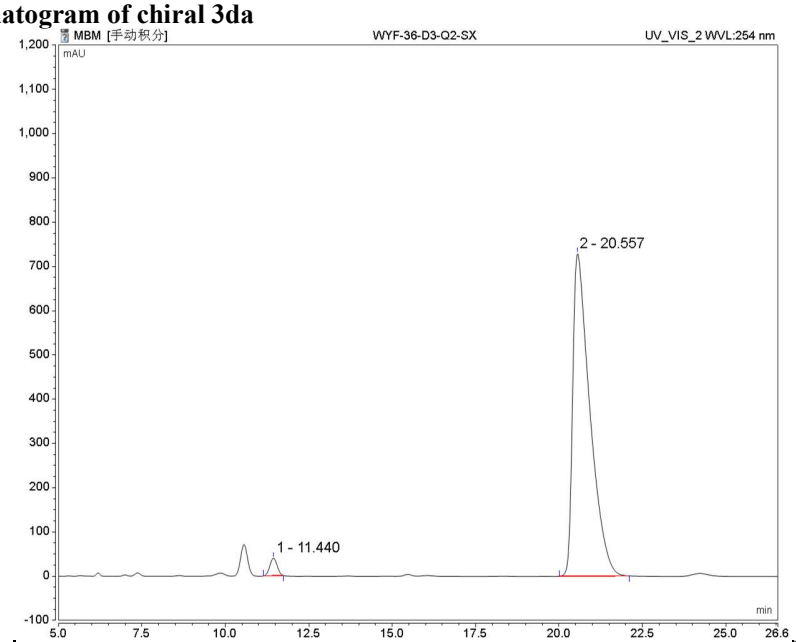
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	27.453	311.58	98.76
2	32.047	3.919	1.24
Total:		315.499	100

HPLC chromatogram of racemic 3da



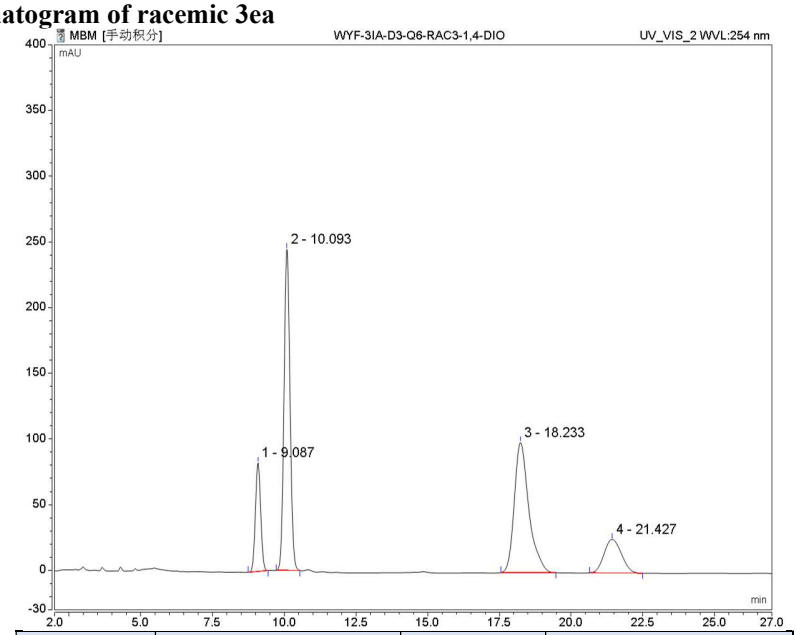
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	10.113	8.584	29.36
2	10.857	6.131	20.97
3	19.637	6.109	20.9
4	22.46	8.41	28.77
Total:		29.235	100.00

HPLC chromatogram of chiral 3da



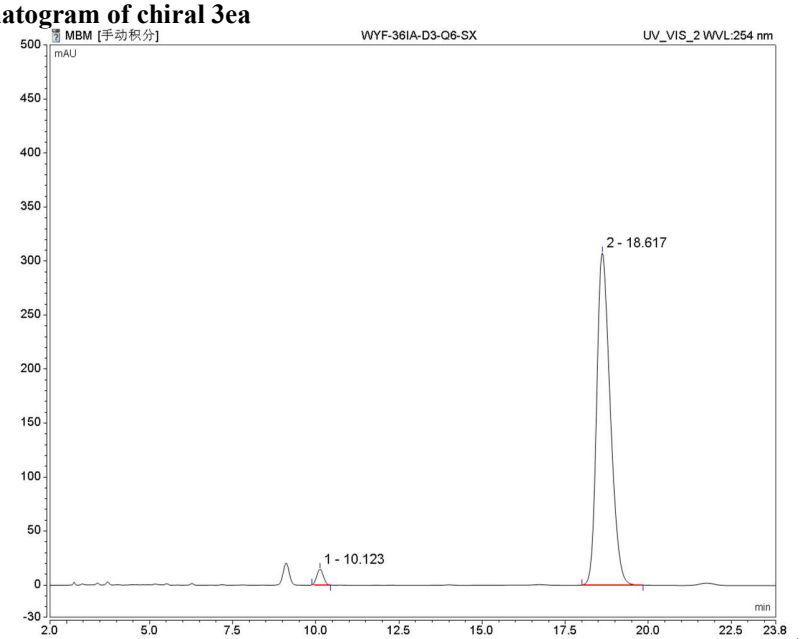
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	11.44	10.107	2.27
2	20.557	434.756	97.73
Total:		444.863	100

HPLC chromatogram of racemic 3ea



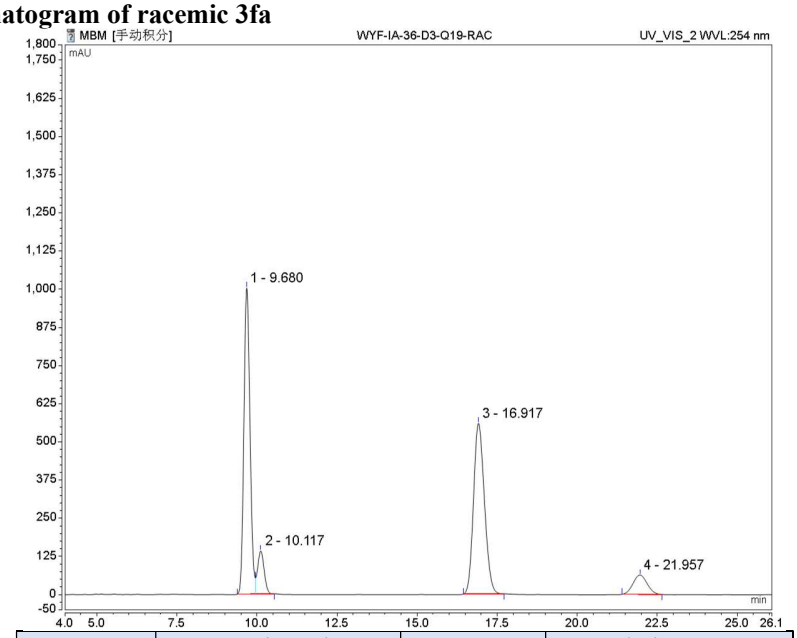
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	9.087	17.701	11.57
2	10.093	59.042	38.6
3	18.233	58.292	38.11
4	21.427	17.932	11.72
Total:		152.968	100

HPLC chromatogram of chiral 3ea



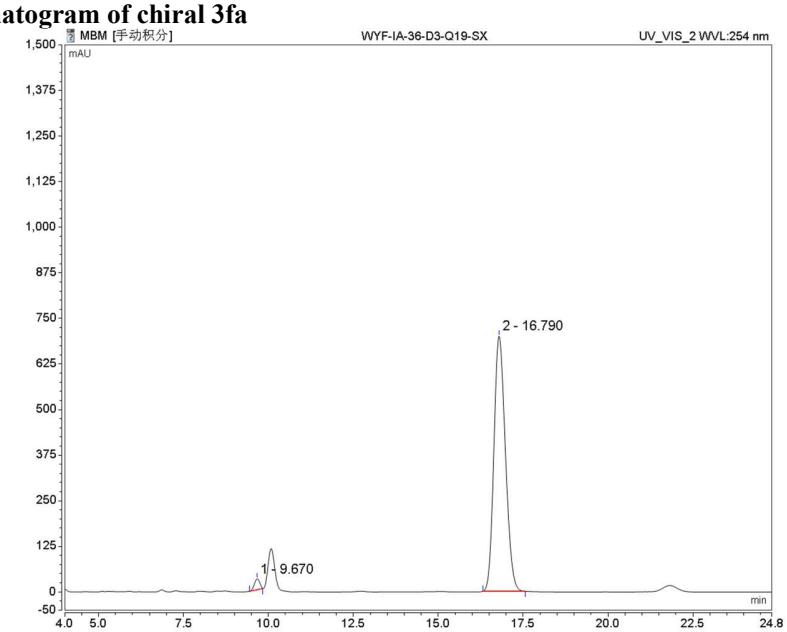
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	10.123	3.404	2.29
2	18.617	145.287	97.71
Total:		148.69	100

HPLC chromatogram of racemic 3fa



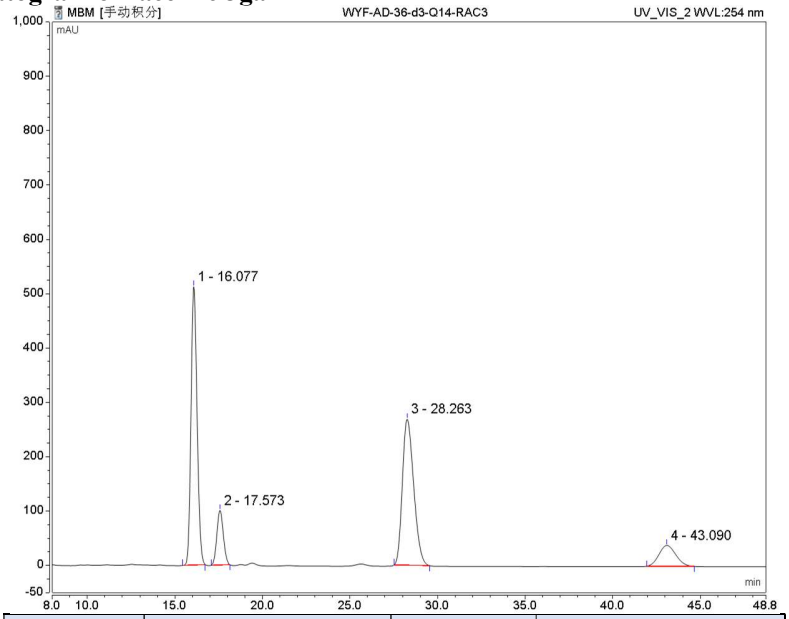
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	9.68	221.348	43.65
2	10.117	33.168	6.54
3	16.917	220.385	43.46
4	21.957	32.242	6.36
Total:		507.142	100

HPLC chromatogram of chiral 3fa



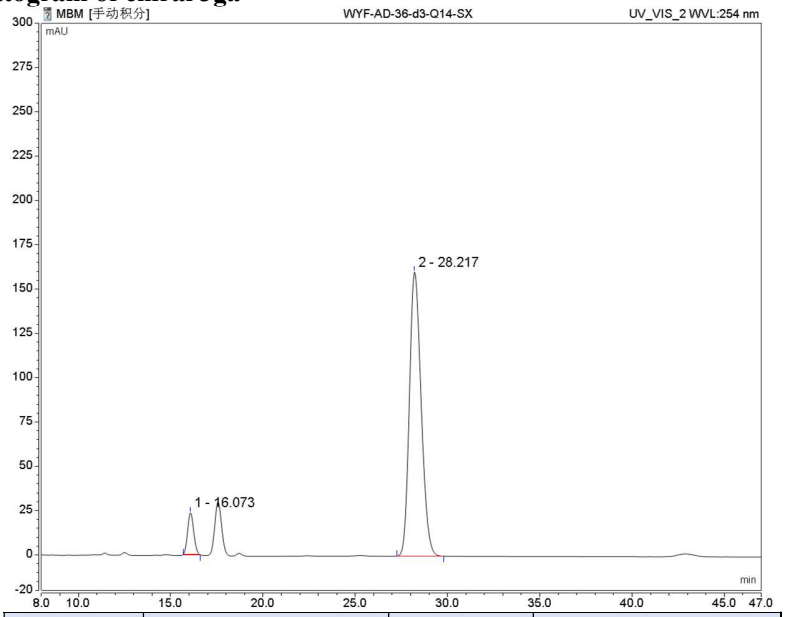
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	9.67	5.55	1.98
2	16.79	275.159	98.02
Total:		280.709	100

HPLC chromatogram of racemic 3ga



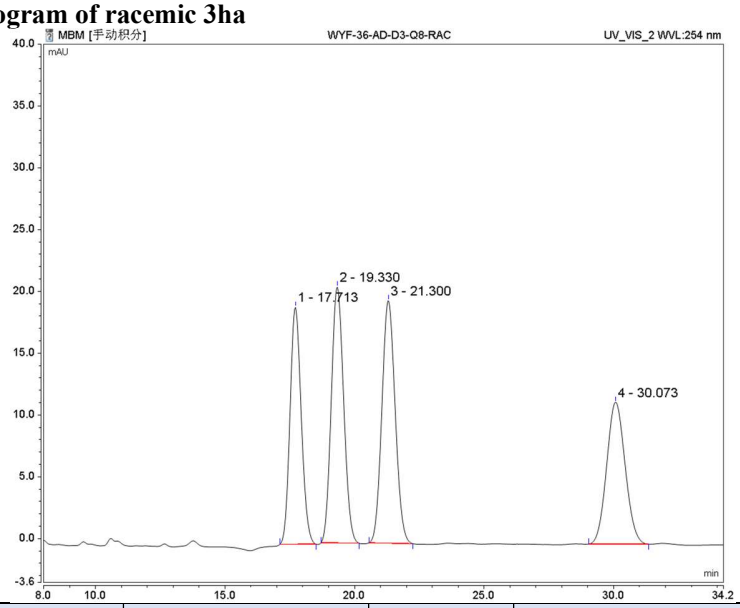
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	16.077	204.098	41.55
2	17.573	43.045	8.76
3	28.263	201.216	40.97
4	43.09	42.82	8.72
Total:		491.179	100

HPLC chromatogram of chiral 3ga



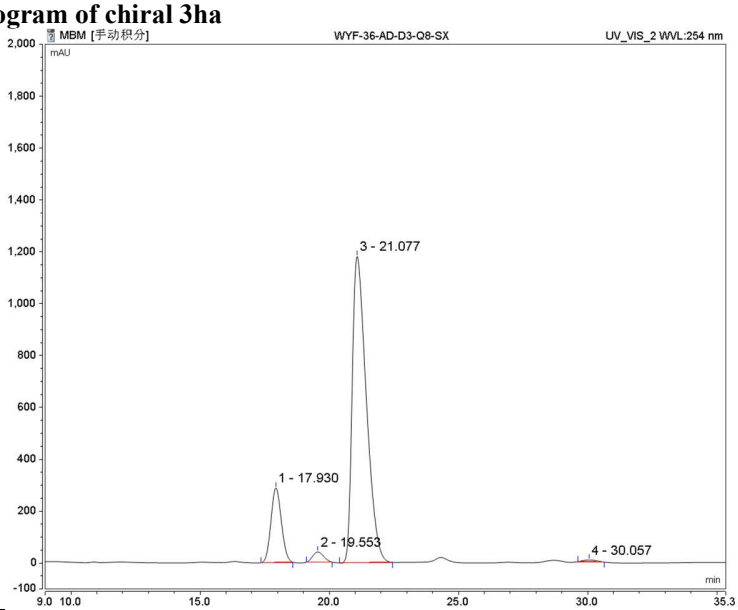
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	16.073	9.069	7.13
2	28.217	118.135	92.87
Total:		127.204	100

HPLC chromatogram of racemic 3ha



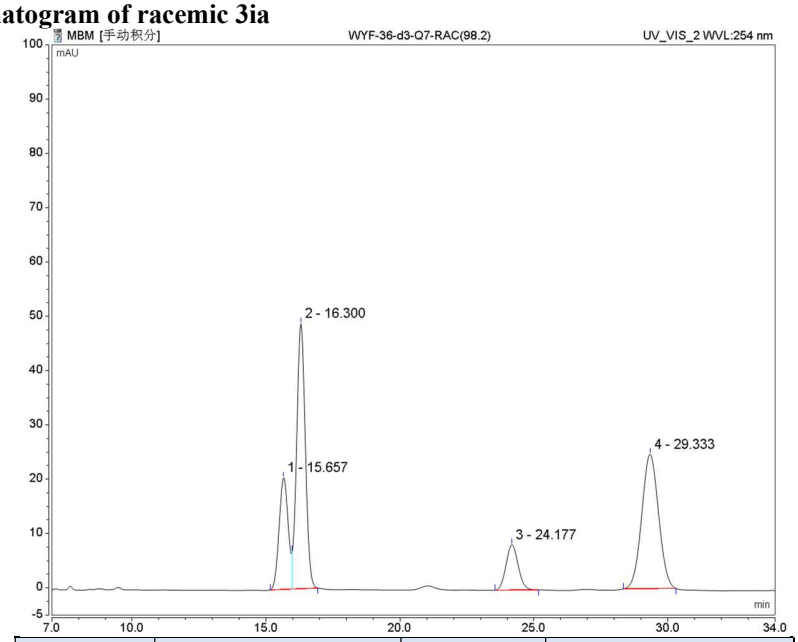
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	17.713	9.597	22.75
2	19.33	11.449	27.14
3	21.3	11.657	27.63
4	30.073	9.48	22.47
Total:		42.183	100

HPLC chromatogram of chiral 3ha



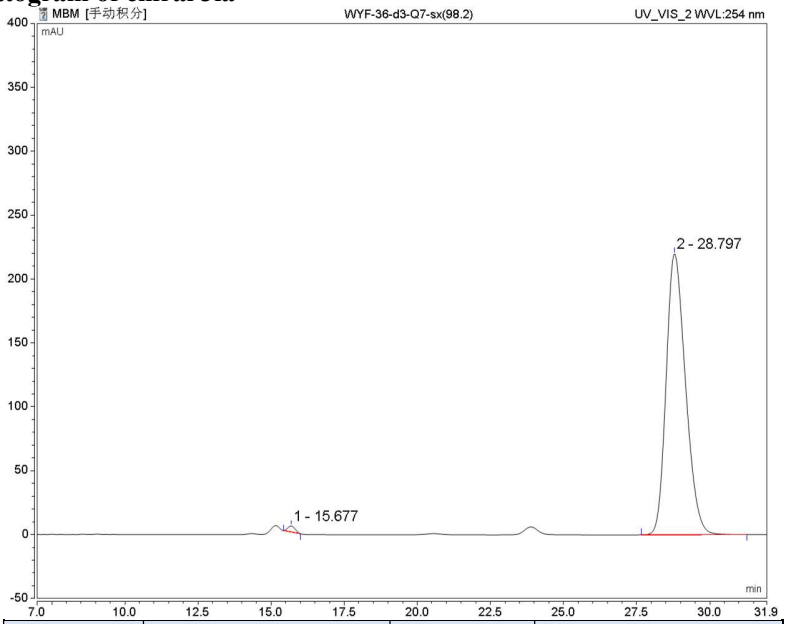
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	17.93	134.428	14.86
2	19.553	19.228	2.13
3	21.077	746.401	82.53
4	30.057	4.312	0.48
Total:		904.369	100

HPLC chromatogram of racemic 3ia



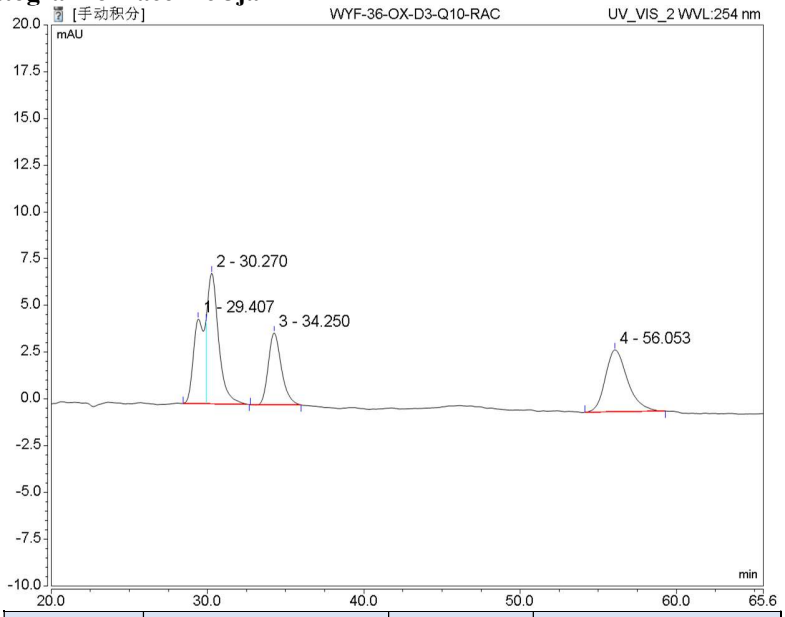
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	15.657	8.217	16.84
2	16.3	18.176	37.25
3	24.177	4.398	9.01
4	29.333	17.998	36.89
Total:		48.79	100

HPLC chromatogram of chiral 3ia



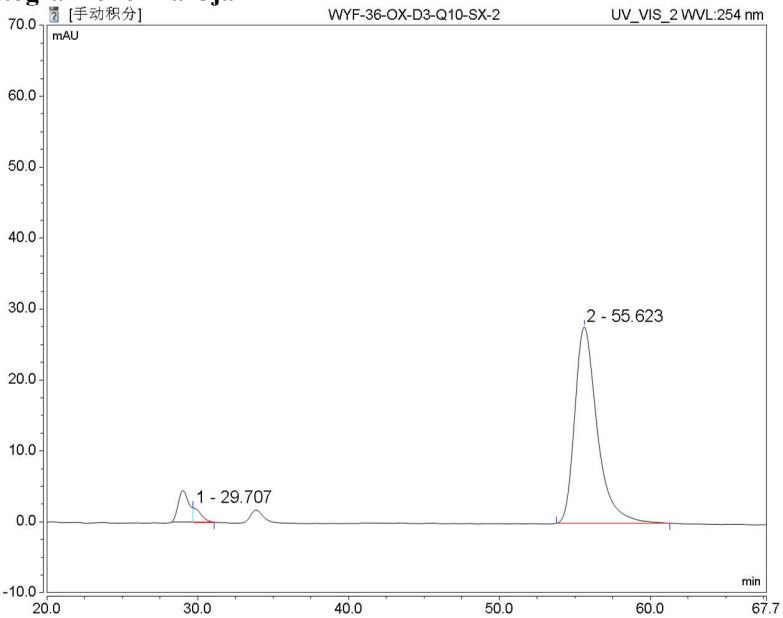
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	15.677	1.352	0.8
2	28.797	168.695	99.2
Total:		170.047	100

HPLC chromatogram of racemic 3ja



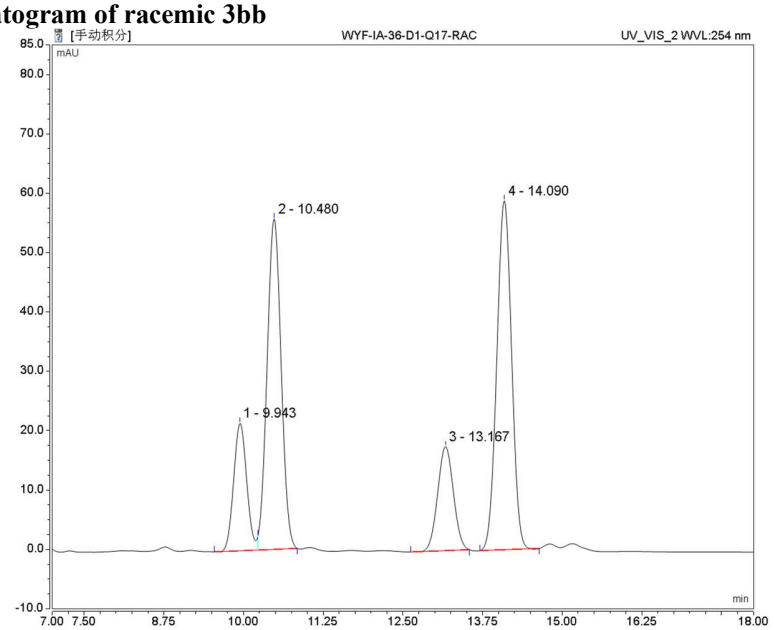
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	29.407	3.689	19.62
2	30.27	5.91	31.44
3	34.25	3.74	19.89
4	56.053	5.459	29.04
Total:		18.798	100

HPLC chromatogram of chiral 3ja



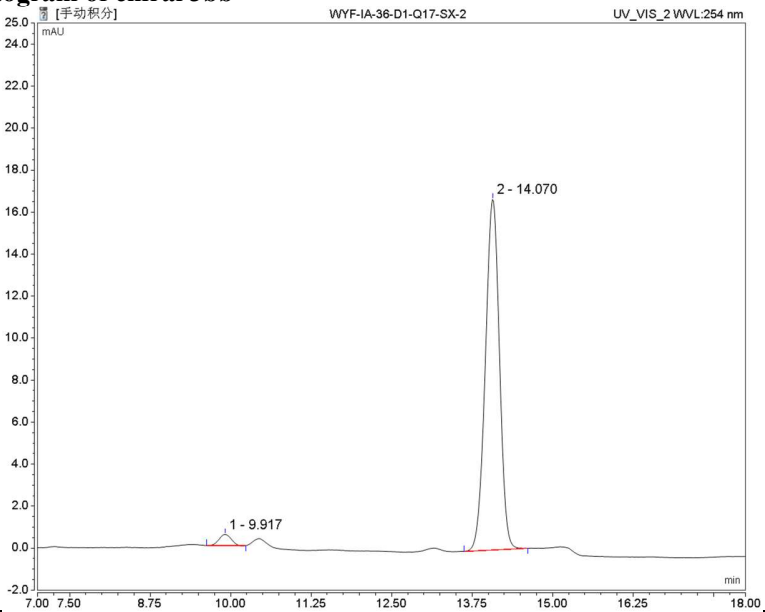
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	29.707	1.165	2.37
2	55.623	47.927	97.63
Total:		49.092	100

HPLC chromatogram of racemic 3bb



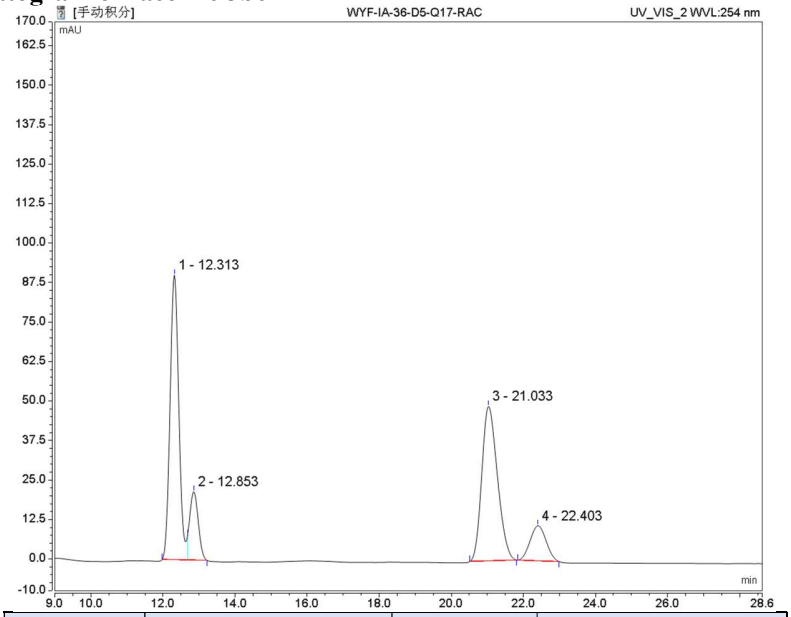
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	9.943	5.115	12.75
2	10.48	14.211	35.43
3	13.167	5.015	12.5
4	14.09	15.767	39.31
Total:		40.107	100

HPLC chromatogram of chiral 3bb



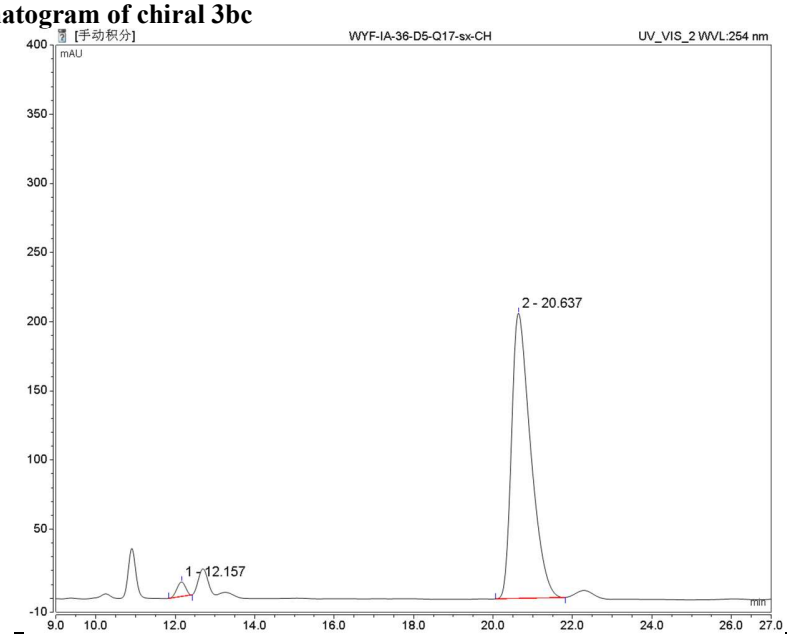
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	9.917	0.115	2.66
2	14.07	4.23	97.34
Total:		4.345	100

HPLC chromatogram of racemic 3bc



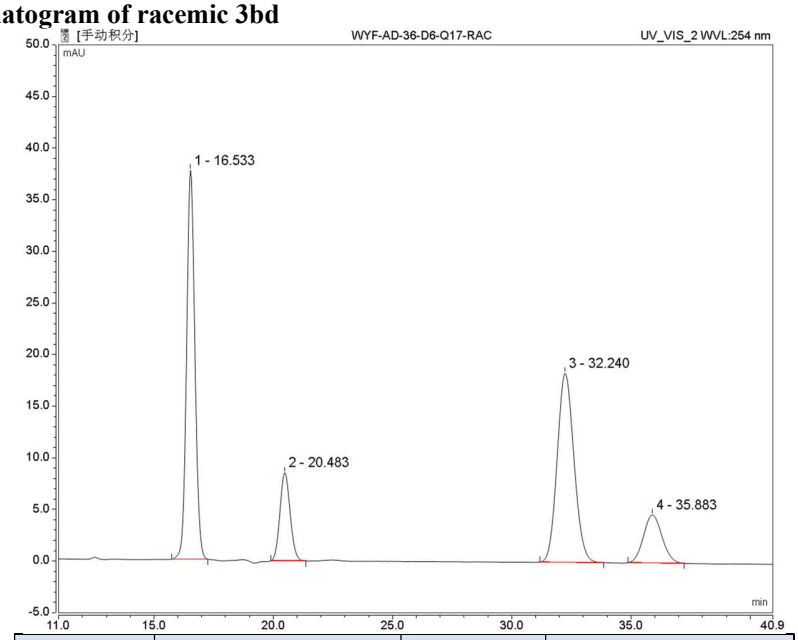
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	12.313	25.278	41.17
2	12.853	5.935	9.67
3	21.033	24.486	39.88
4	22.403	5.699	9.28
Total:		61.398	100

HPLC chromatogram of chiral 3bc



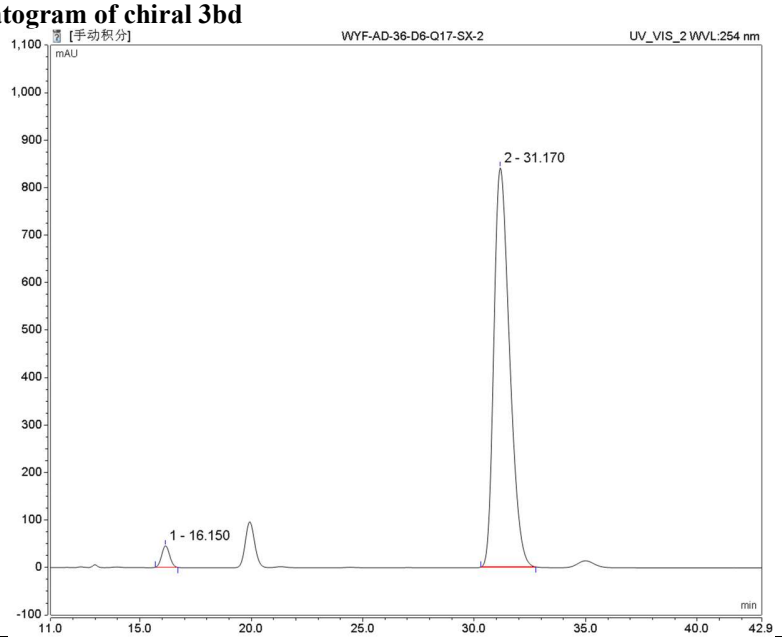
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	12.157	2.662	2.27
2	20.637	114.528	97.73
Total:		61.398	100

HPLC chromatogram of racemic 3bd



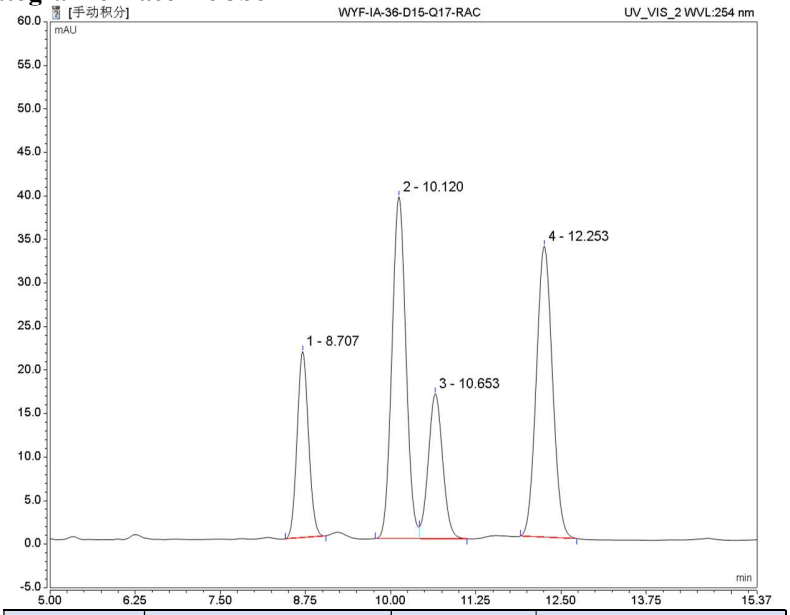
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	16.533	15.149	39.37
2	20.483	4.21	10.94
3	32.24	14.939	38.82
4	35.883	4.181	10.87
Total:		38.478	100

HPLC chromatogram of chiral 3bd



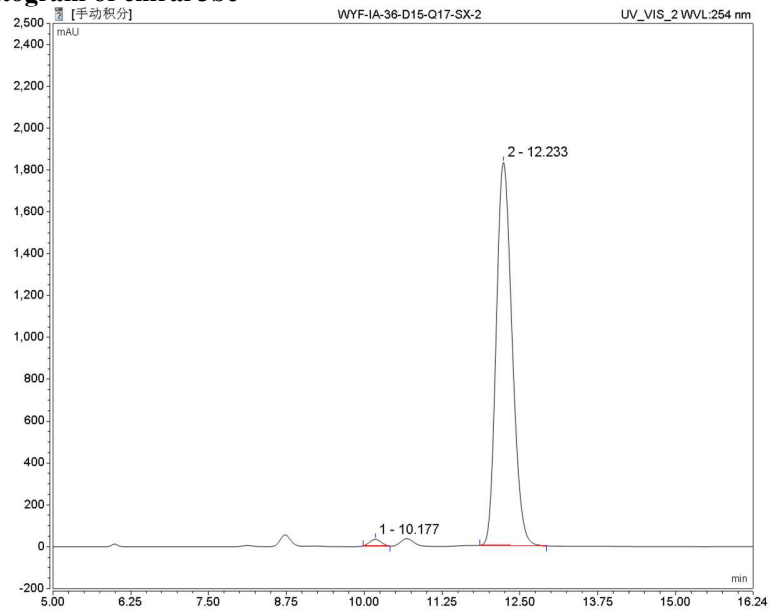
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	16.15	18.825	2.67
2	31.17	685.862	97.33
Total:		704.688	100

HPLC chromatogram of racemic 3be



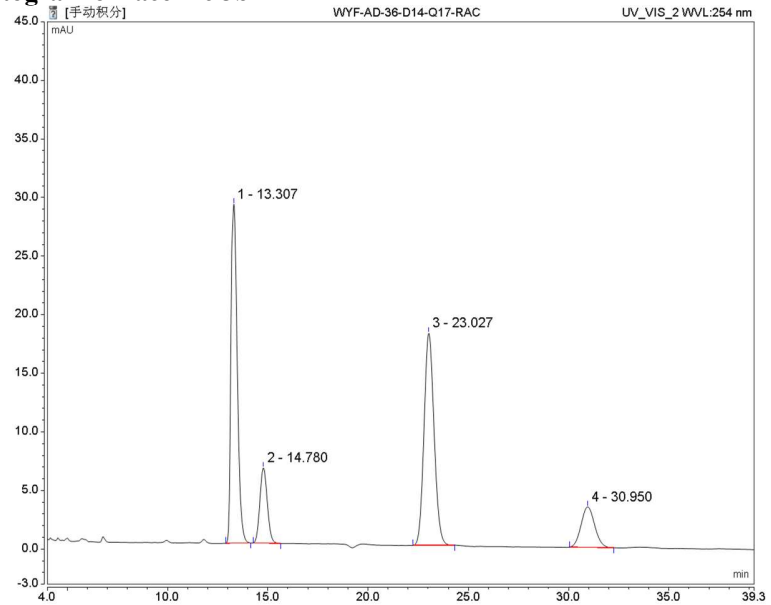
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	8.707	4.142	15.51
2	10.12	9.336	34.96
3	10.653	4.057	15.19
4	12.253	9.169	34.34
Total:		26.704	100

HPLC chromatogram of chiral 3be



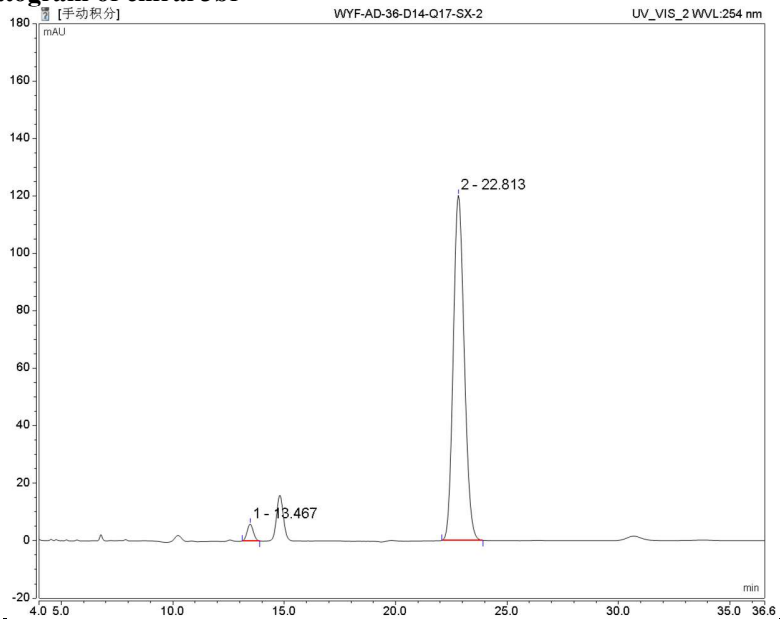
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	10.177	6.737	1.23
2	12.233	539.436	98.77
Total:		546.173	100

HPLC chromatogram of racemic 3bf



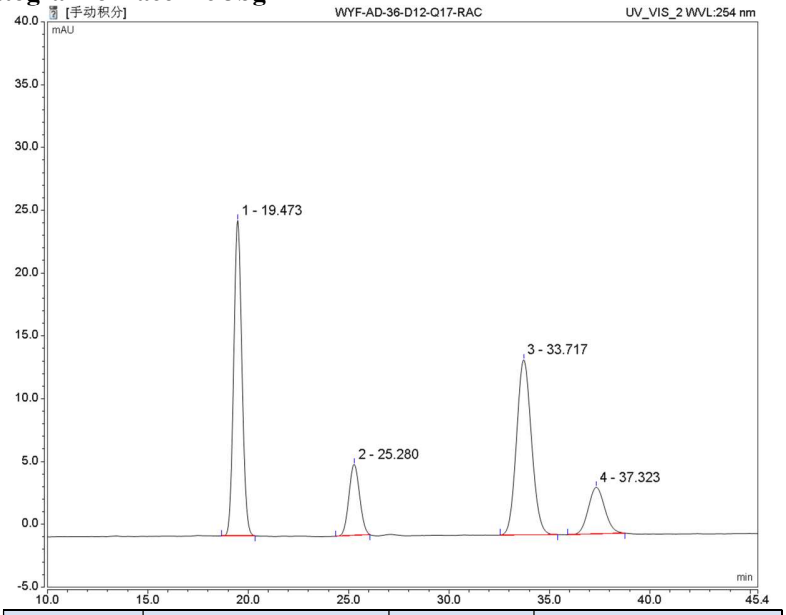
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	13.307	10.503	39.7
2	14.78	2.741	10.36
3	23.027	10.496	39.68
4	30.95	2.714	10.26
Total:		26.454	100

HPLC chromatogram of chiral 3bf



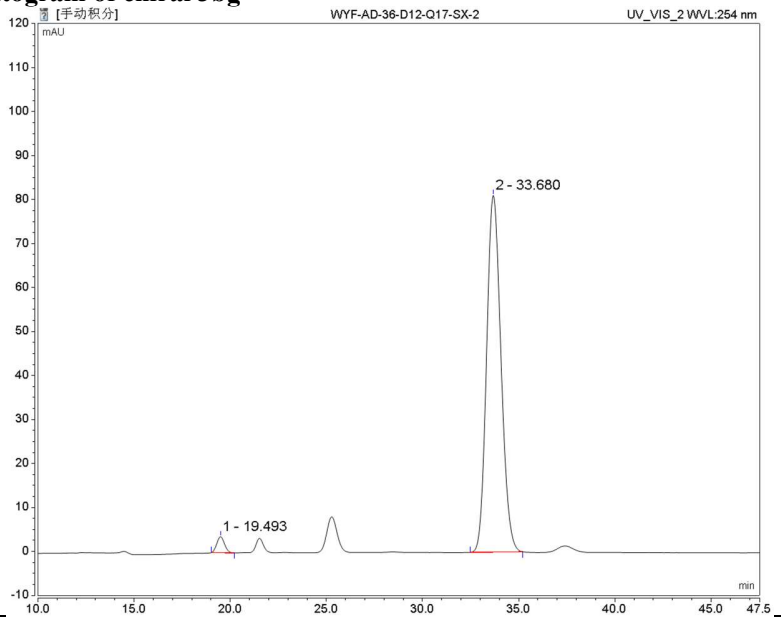
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	13.467	1.878	2.67
2	22.813	68.378	97.33
Total:		70.255	100

HPLC chromatogram of racemic 3bg



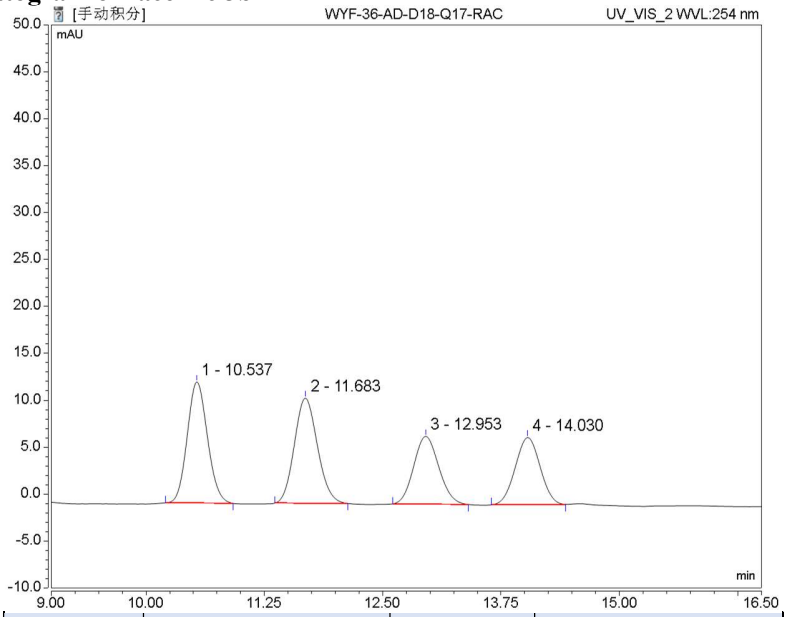
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	19.473	11.901	38.49
2	25.28	3.488	11.28
3	33.717	12.033	38.91
4	37.323	3.502	11.32
Total:		30.923	100

HPLC chromatogram of chiral 3bg



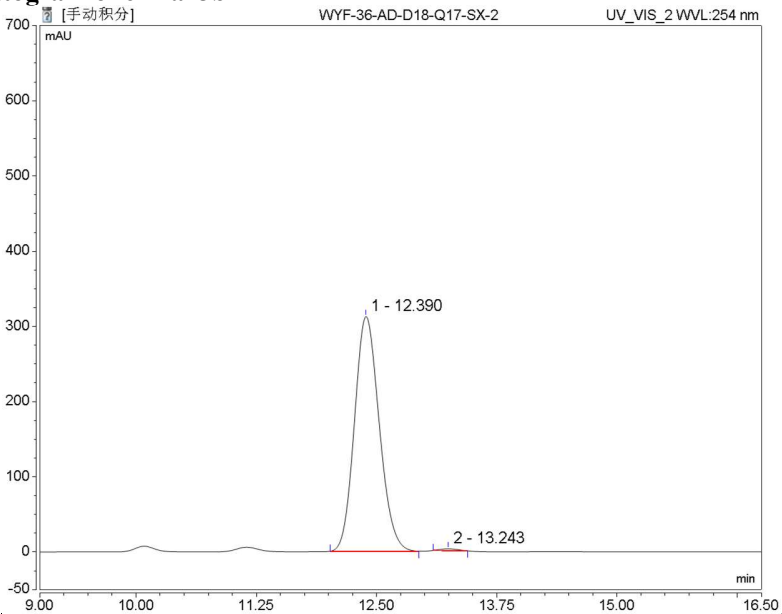
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	19.493	1.685	2.34
2	33.68	70.17	97.66
Total:		71.855	100

HPLC chromatogram of racemic 3bh



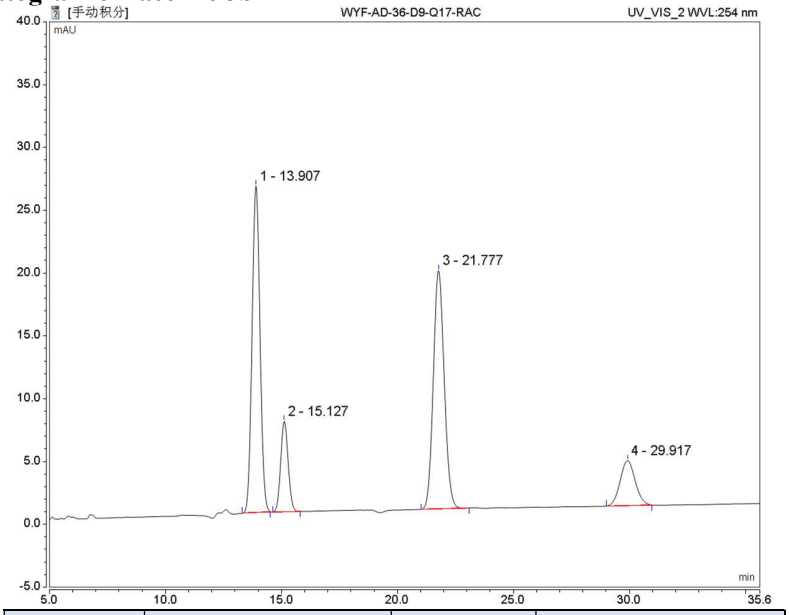
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	10.537	3.19	29.69
2	11.683	3.165	29.46
3	12.953	2.218	20.64
4	14.03	2.17	20.2
Total:		10.743	100

HPLC chromatogram of chiral 3bh



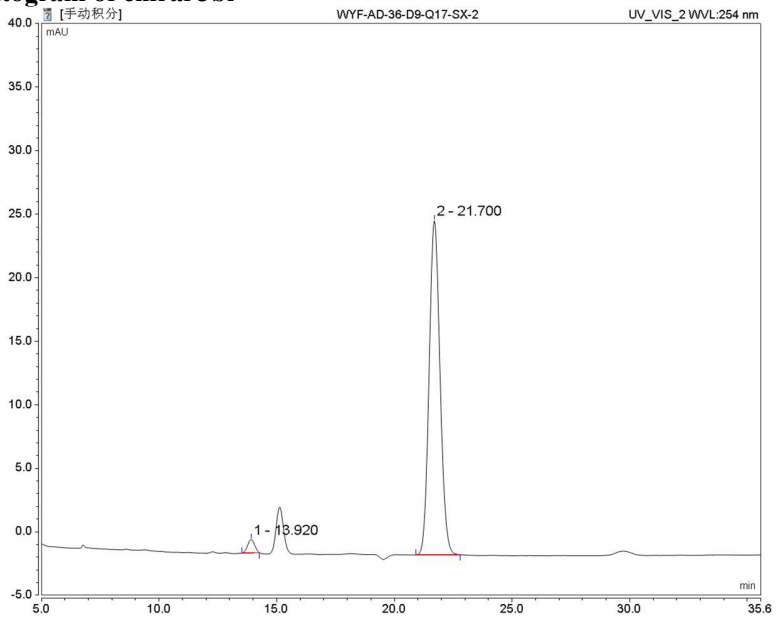
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	12.39	92.964	99.44
2	13.243	0.519	0.56
Total:		93.483	100

HPLC chromatogram of racemic 3bi



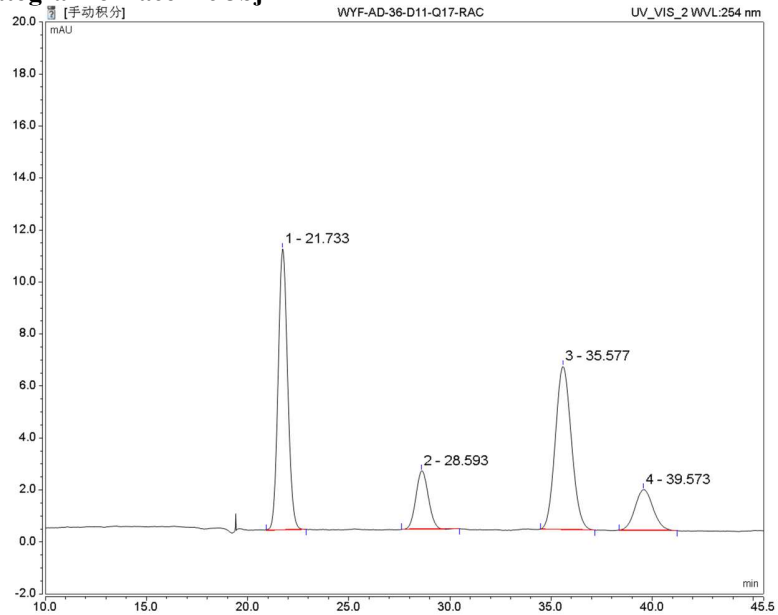
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	13.907	10.29	39.57
2	15.127	2.694	10.36
3	21.777	10.329	39.72
4	29.917	2.69	10.34
Total:		26.002	100

HPLC chromatogram of chiral 3bi



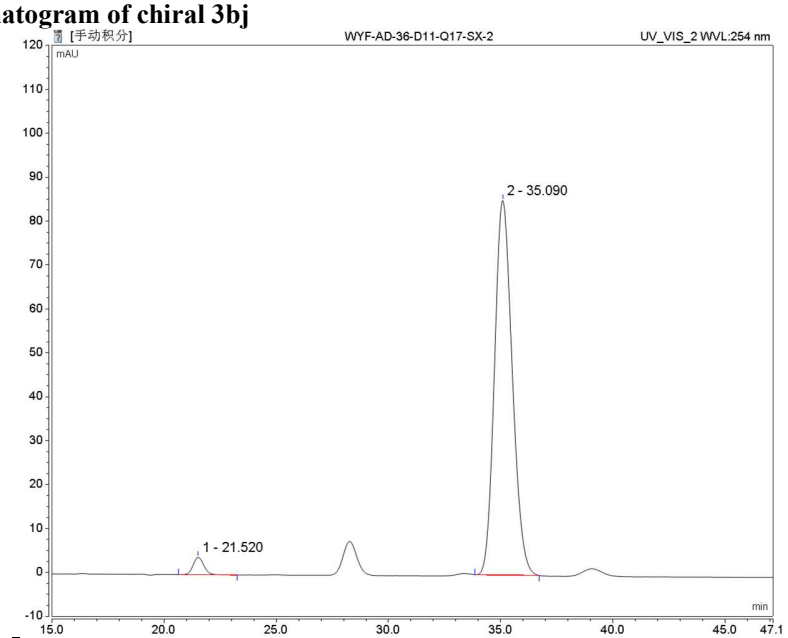
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	13.92	0.365	2.52
2	21.7	14.093	97.48
Total:		14.458	100

HPLC chromatogram of racemic 3bj



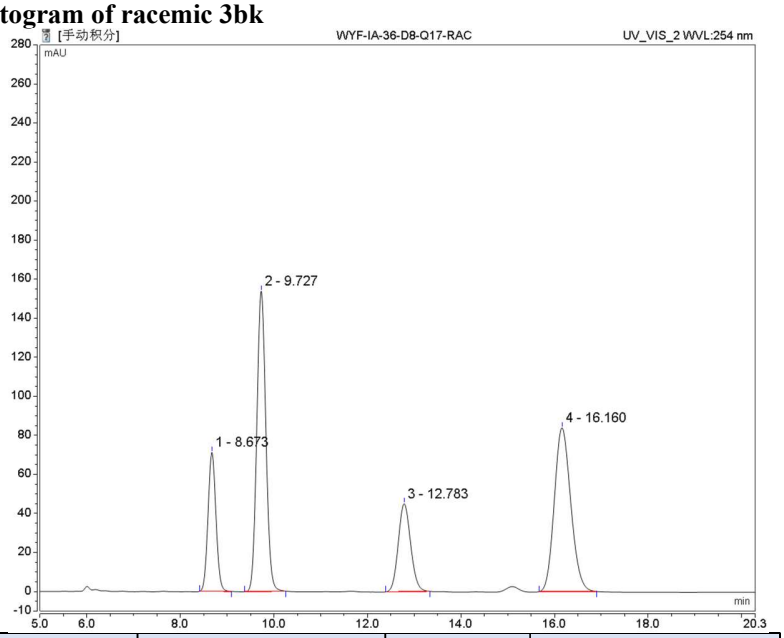
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	21.733	5.857	39.47
2	28.593	1.587	10.69
3	35.577	5.781	38.95
4	39.573	1.616	10.89
Total:		14.841	100

HPLC chromatogram of chiral 3bj



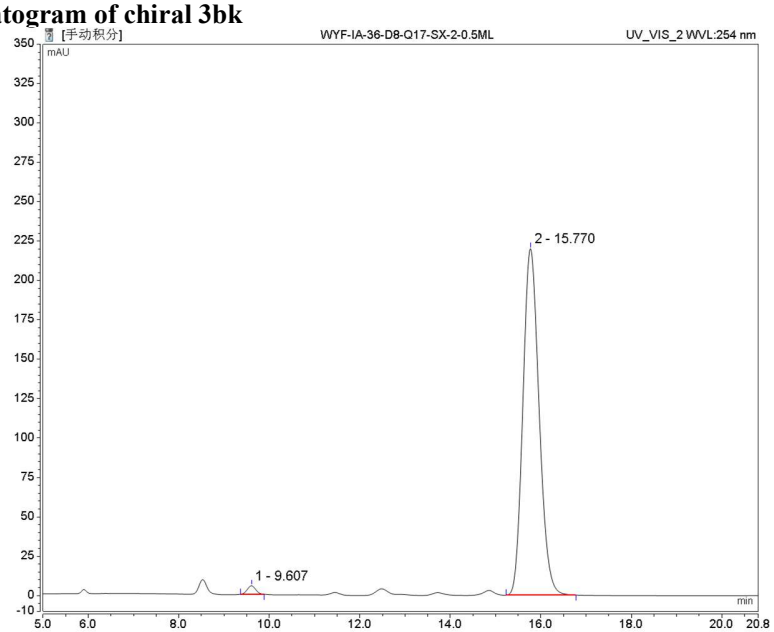
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	21.52	2.198	2.74
2	35.09	78.141	97.26
Total:		80.339	100

HPLC chromatogram of racemic 3bk



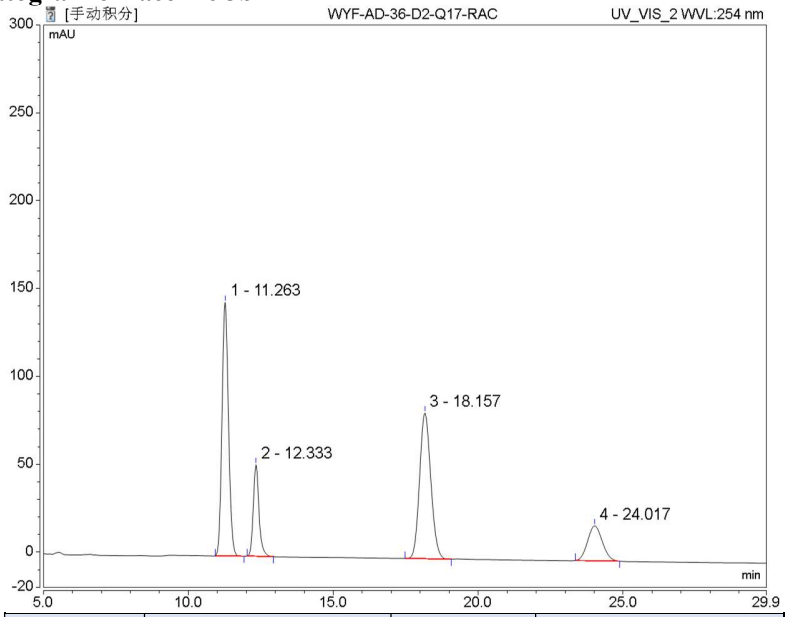
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	8.673	13.962	14.47
2	9.727	34.475	35.73
3	12.783	13.851	14.36
4	16.16	34.197	35.44
Total:		96.486	100

HPLC chromatogram of chiral 3bk



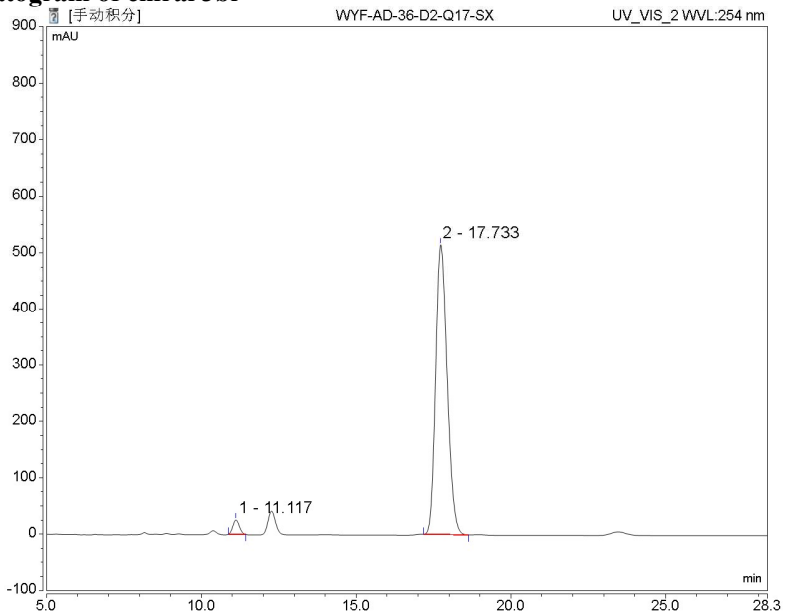
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	9.607	1.171	1.27
2	15.77	90.993	98.73
Total:		92.164	100

HPLC chromatogram of racemic 3bl



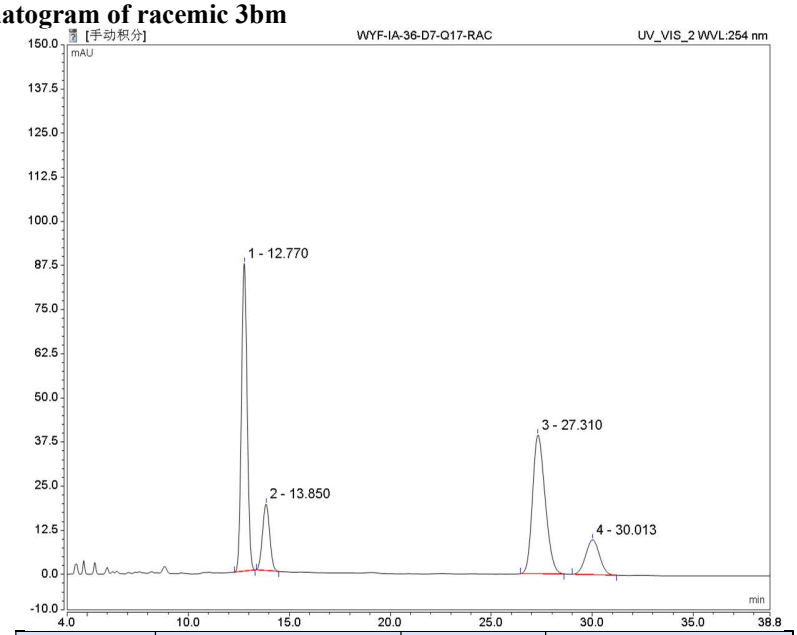
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	11.263	37.189	37.94
2	12.333	11.942	12.19
3	18.157	37.153	37.91
4	24.017	11.723	11.96
Total:		98.007	100

HPLC chromatogram of chiral 3bl



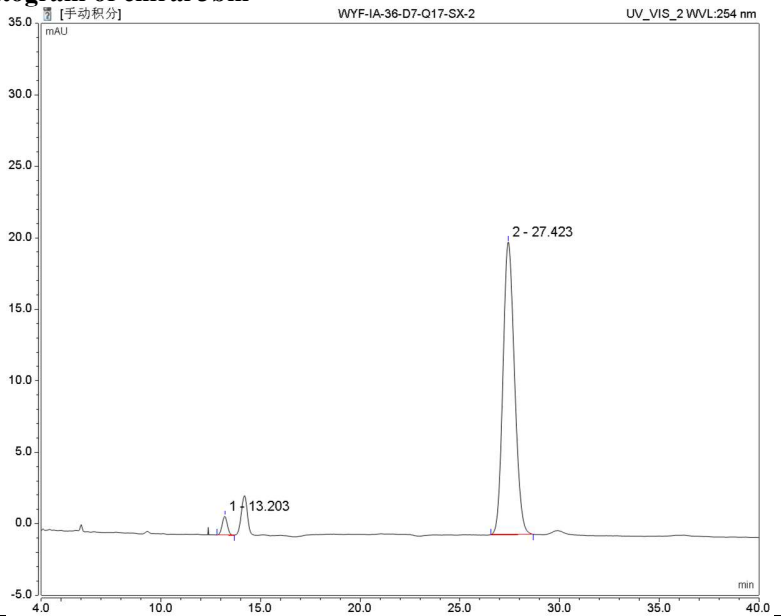
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	11.117	6.328	2.77
2	17.733	221.949	97.23
Total:		228.277	100

HPLC chromatogram of racemic 3bm



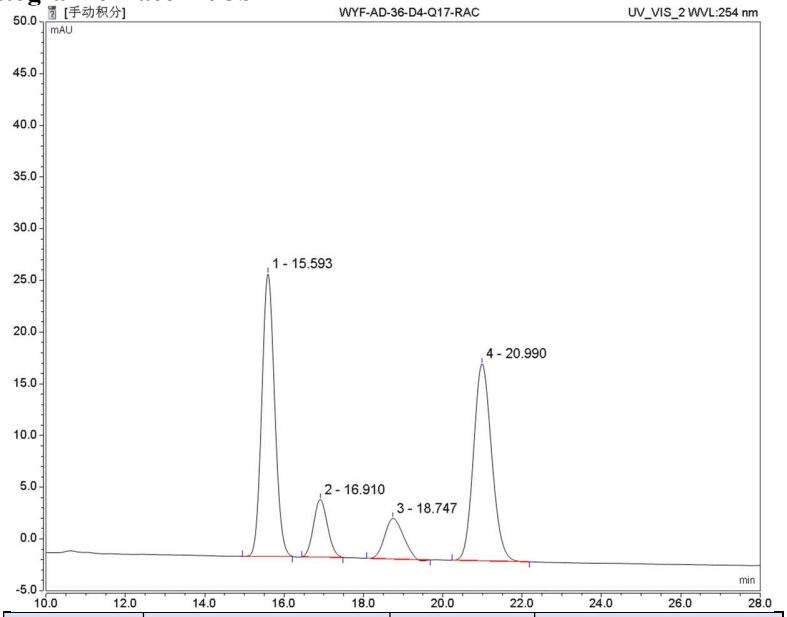
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	12.77	28.535	39.33
2	13.85	7.736	10.66
3	27.31	28.439	39.19
4	30.013	7.848	10.82
Total:		72.557	100

HPLC chromatogram of chiral 3bm



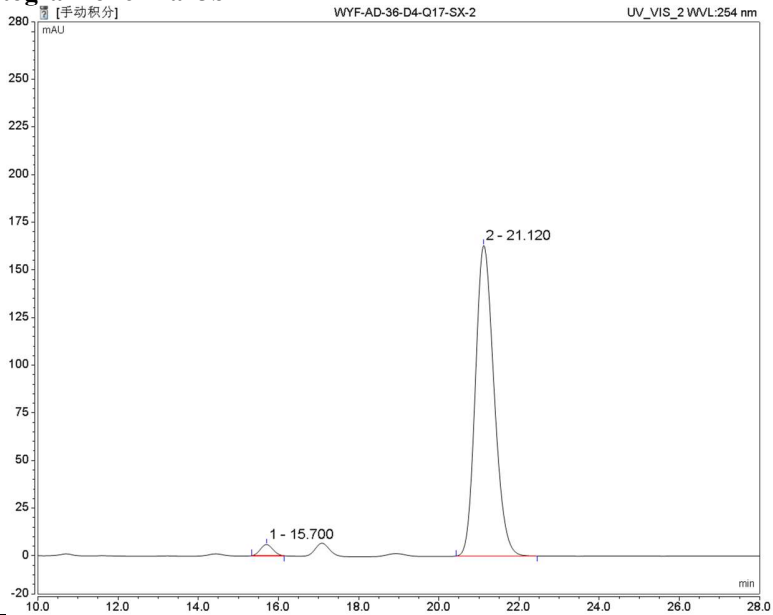
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	13.203	0.391	2.77
2	27.423	13.722	97.23
Total:		14.114	100

HPLC chromatogram of racemic 3bn



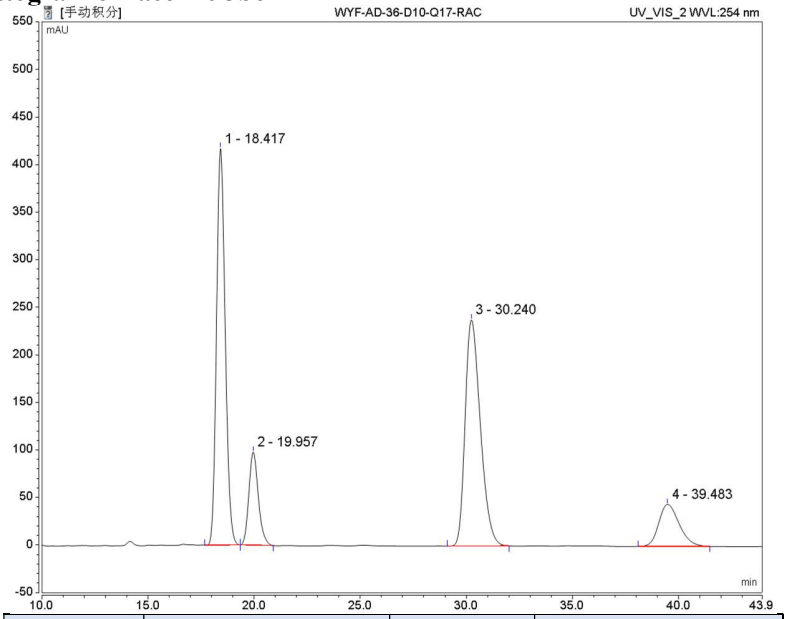
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	15.593	10.248	41.39
2	16.91	2.27	9.17
3	18.747	2.136	8.63
4	20.99	10.109	40.82
Total:		24.763	100

HPLC chromatogram of chiral 3bn



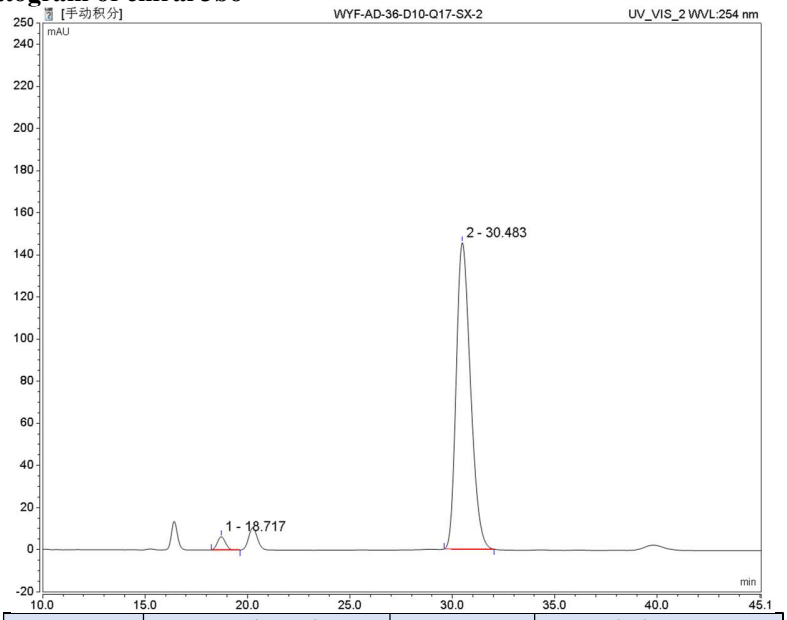
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	15.7	2.134	2.37
2	21.12	87.808	97.63
Total:		89.942	100

HPLC chromatogram of racemic 3bo



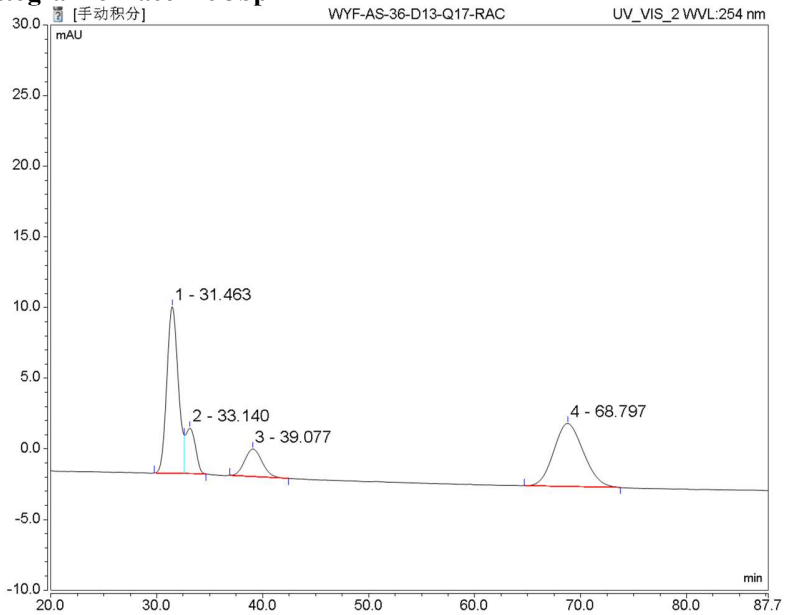
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	18.417	197.635	39.91
2	19.957	50.748	10.25
3	30.24	197.746	39.94
4	39.483	49.025	9.9
Total:		495.154	100

HPLC chromatogram of chiral 3bo



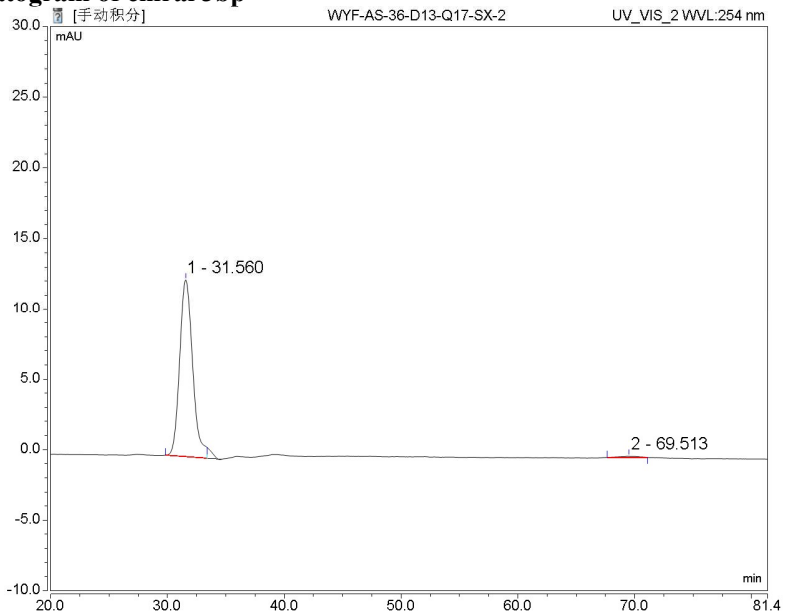
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	18.717	2.82	2.34
2	30.483	117.605	97.66
Total:		120.425	100

HPLC chromatogram of racemic 3bp



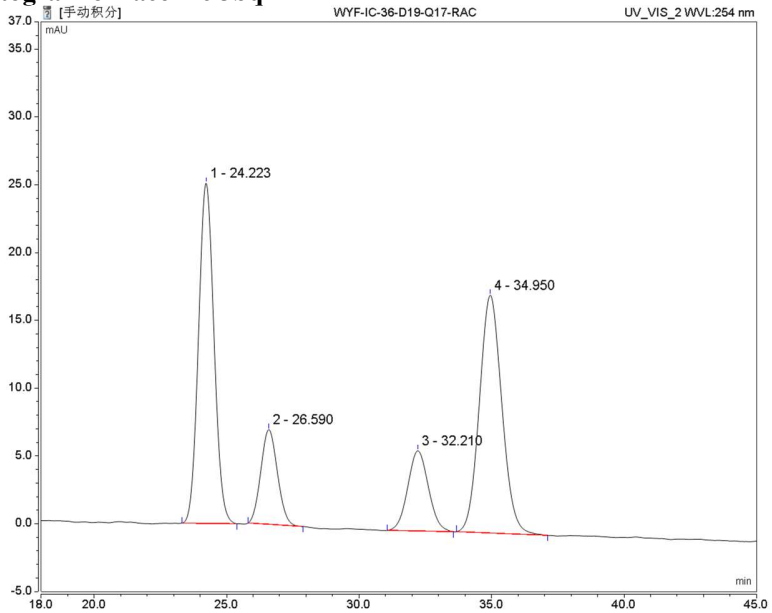
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	31.463	14.704	40.3
2	33.14	3.56	9.76
3	39.077	3.734	10.23
4	68.797	14.488	39.71
Total:		36.486	100

HPLC chromatogram of chiral 3bp



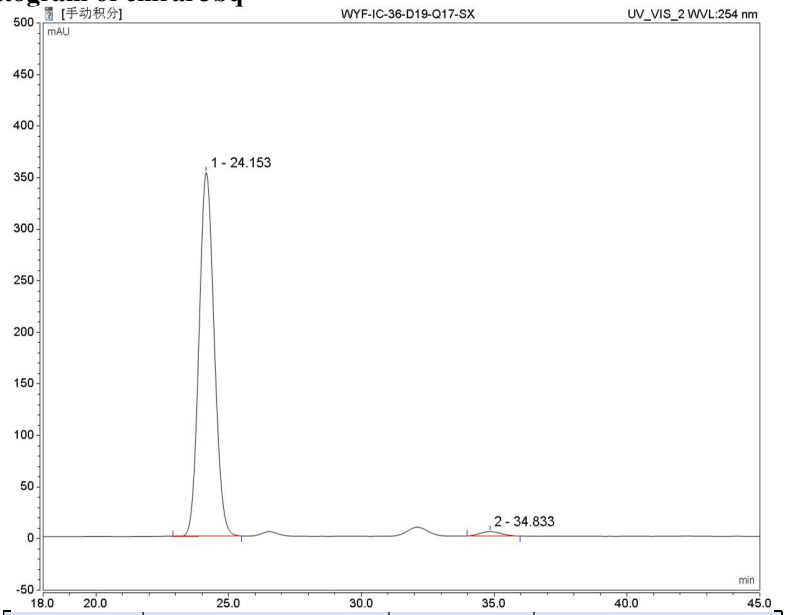
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	31.56	16.122	99.04
2	69.513	0.156	0.96
Total:		16.278	100

HPLC chromatogram of racemic 3bq



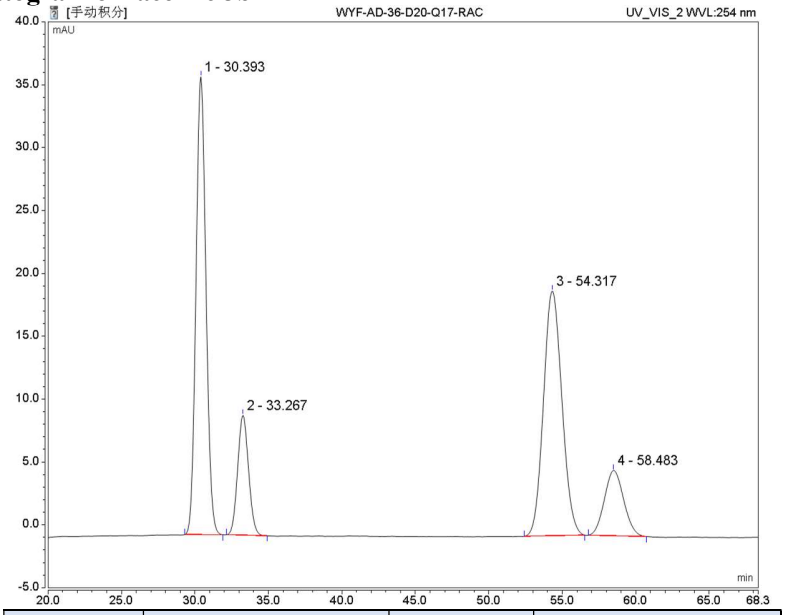
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	24.223	16.977	38.07
2	26.59	5.067	11.36
3	32.21	5.334	11.96
4	34.95	17.222	38.61
Total:		44.599	100

HPLC chromatogram of chiral 3bq



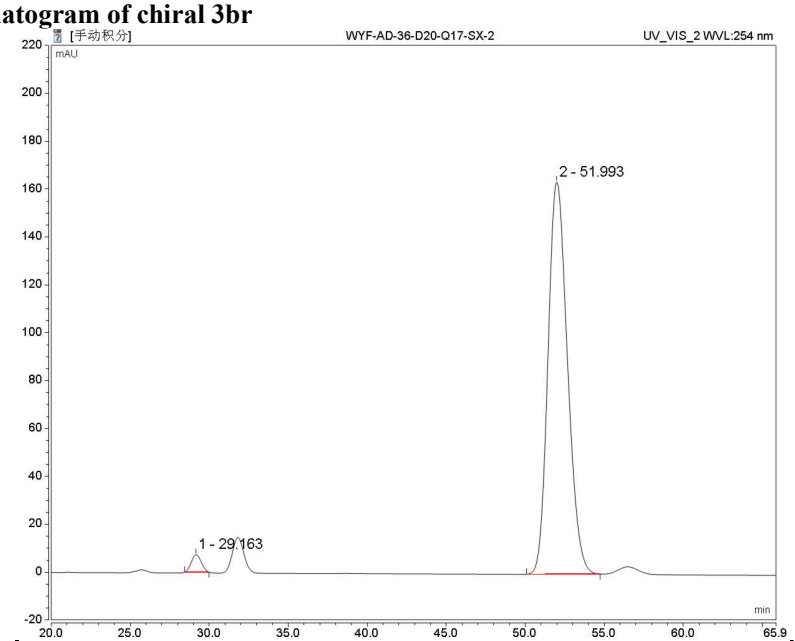
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	24.153	233	98.37
2	34.833	3.862	1.63
Total:		236.862	100

HPLC chromatogram of racemic 3br



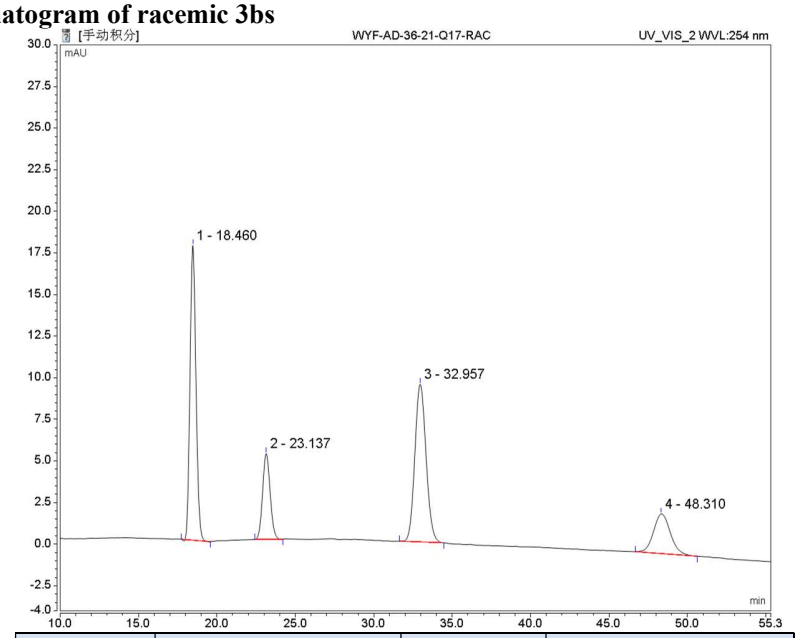
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	30.393	28.629	39.21
2	33.267	8.185	11.21
3	54.317	28.312	38.77
4	58.483	7.896	10.81
Total:		73.022	100

HPLC chromatogram of chiral 3br



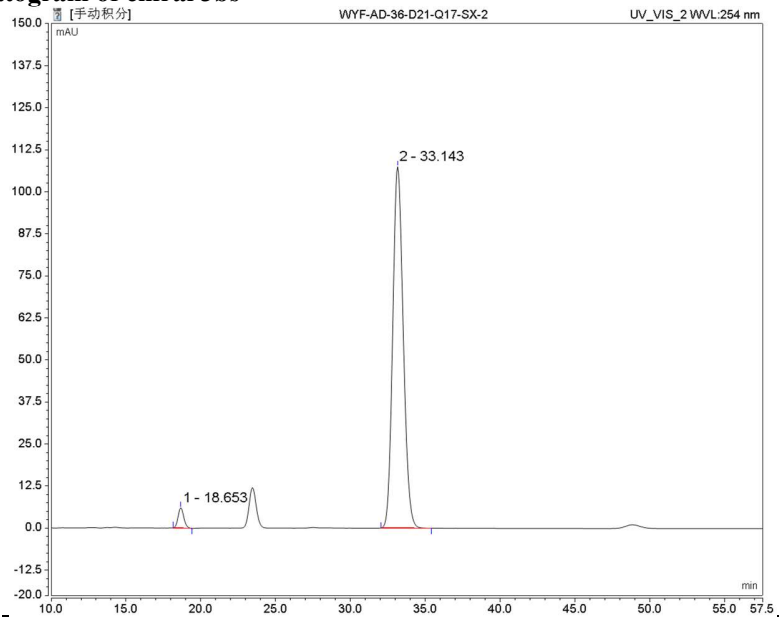
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	29.163	5.243	2.2
2	51.993	233.616	97.8
Total:		238.859	100

HPLC chromatogram of racemic 3bs



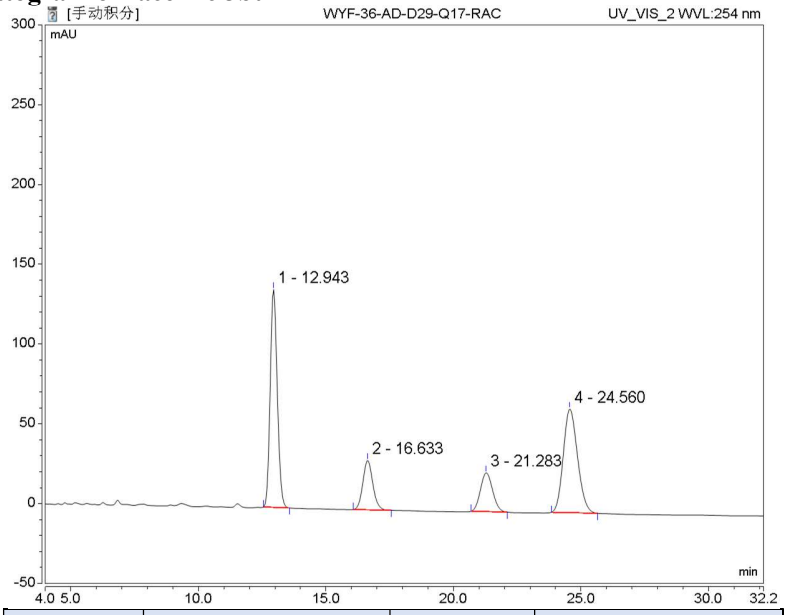
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	18.46	7.786	36.25
2	23.137	2.867	13.35
3	32.957	7.85	36.55
4	48.31	2.977	13.86
Total:		21.48	100

HPLC chromatogram of chiral 3bs



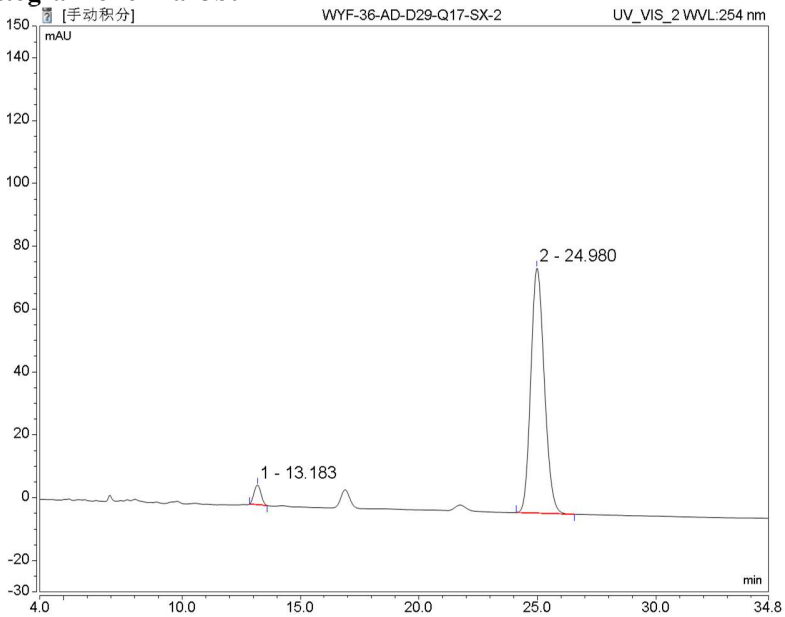
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	18.653	2.674	2.96
2	33.143	87.531	97.04
Total:		90.204	100

HPLC chromatogram of racemic 3bt



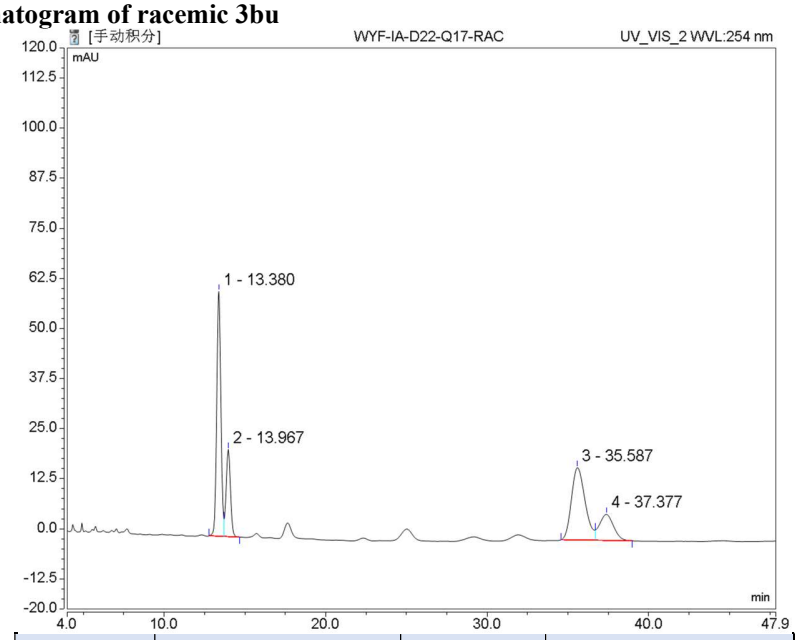
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	12.943	43.689	38.63
2	16.633	14.023	12.4
3	21.283	13.377	11.83
4	24.56	42.008	37.14
Total:		113.097	100

HPLC chromatogram of chiral 3bt



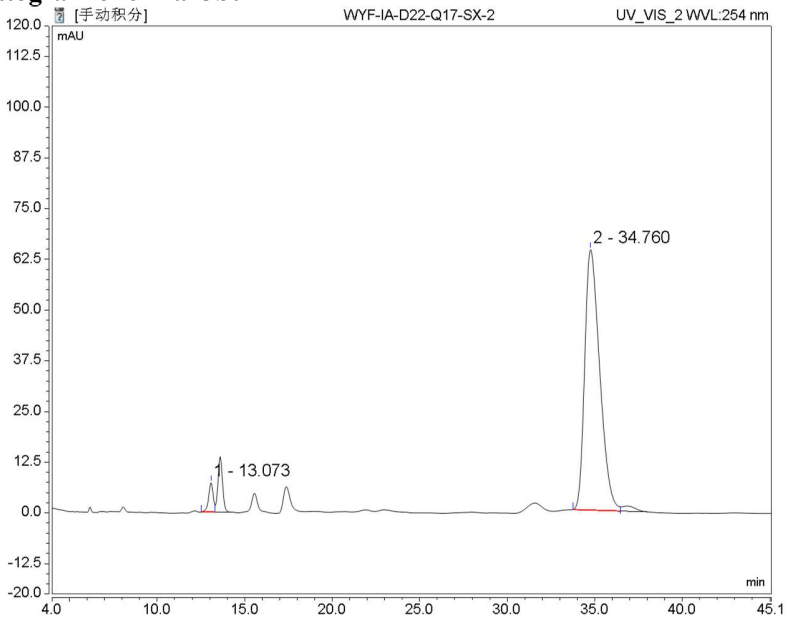
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	13.183	2.151	4.01
2	24.98	51.495	95.99
Total:		53.646	100

HPLC chromatogram of racemic 3bu



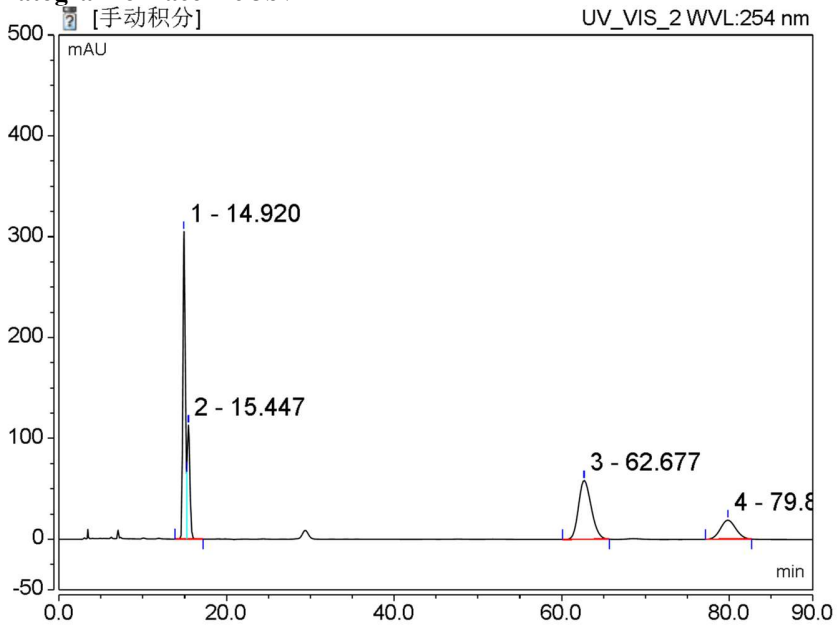
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	13.38	18.097	36.79
2	13.967	6.785	13.79
3	35.587	17.755	36.1
4	37.377	6.553	13.32
Total:		49.19	100

HPLC chromatogram of chiral 3bu



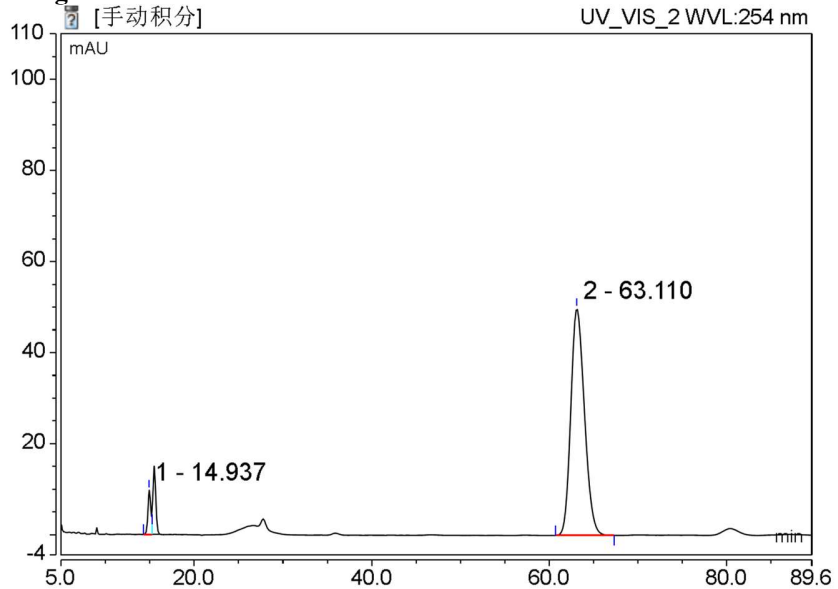
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	13.073	2.155	3.27
2	34.76	63.838	96.73
Total:		65.992	100

HPLC chromatogram of racemic 3bv



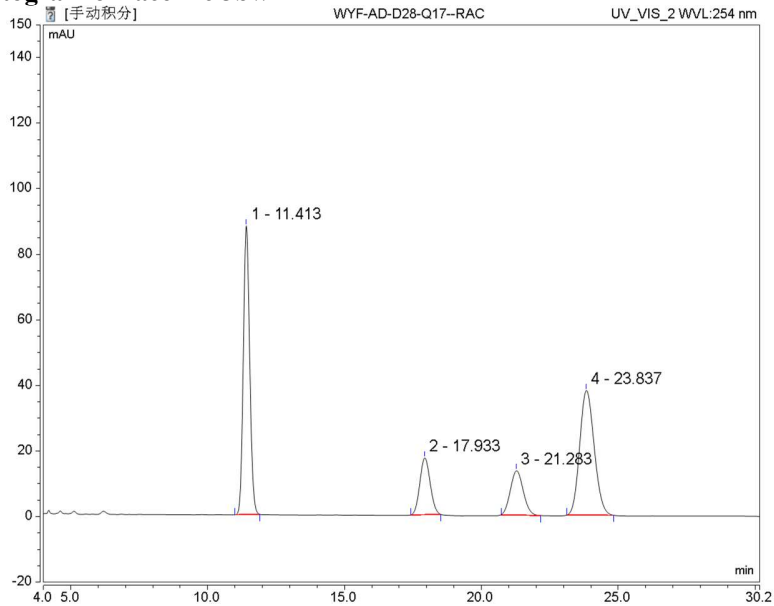
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	14.92	104.107	36.2
2	15.447	40.51	14.09
3	62.677	102.839	35.76
4	79.827	40.099	13.94
Total:		287.555	100

HPLC chromatogram of chiral 3bv



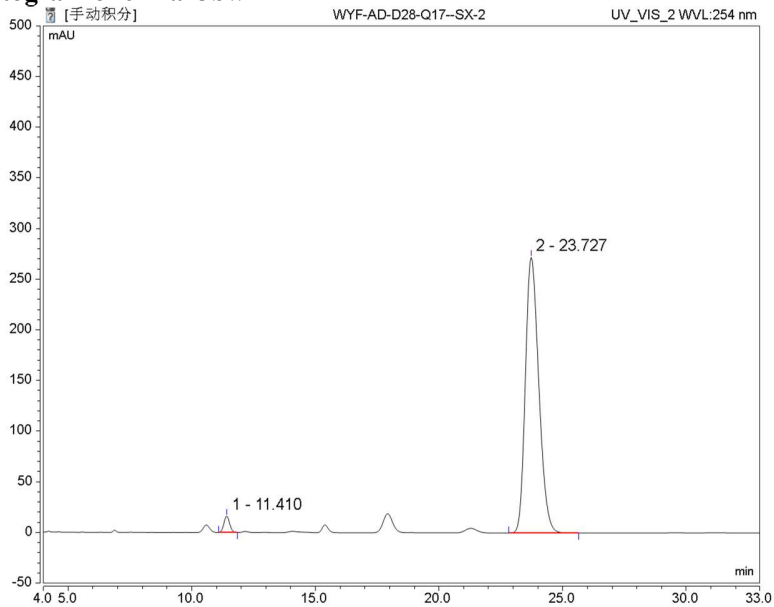
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	14.937	3.616	3.91
2	63.11	88.817	96.09
Total:		92.433	100

HPLC chromatogram of racemic 3bw



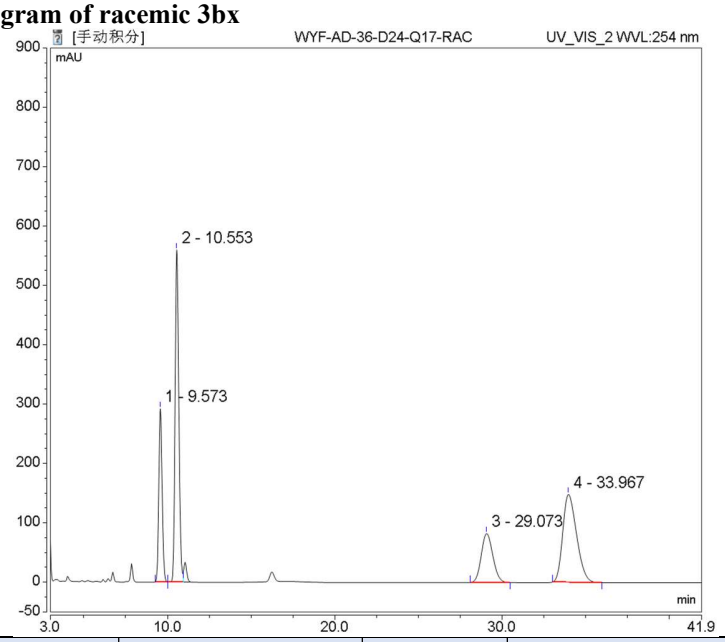
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	11.413	23.69	38.17
2	17.933	7.591	12.23
3	21.283	7.377	11.89
4	23.837	23.403	37.71
Total:		62.061	100

HPLC chromatogram of chiral 3bw



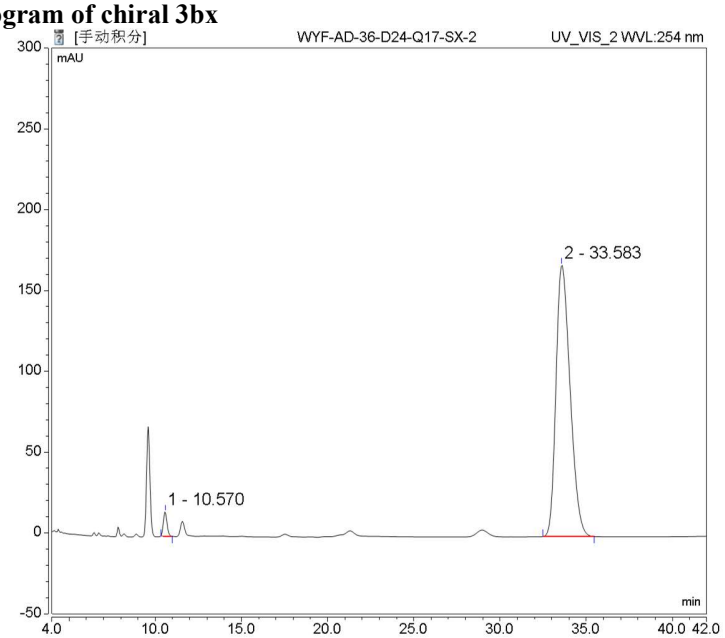
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	11.41	4.312	2.46
2	23.727	171.082	97.54
Total:		175.395	100

HPLC chromatogram of racemic 3bx



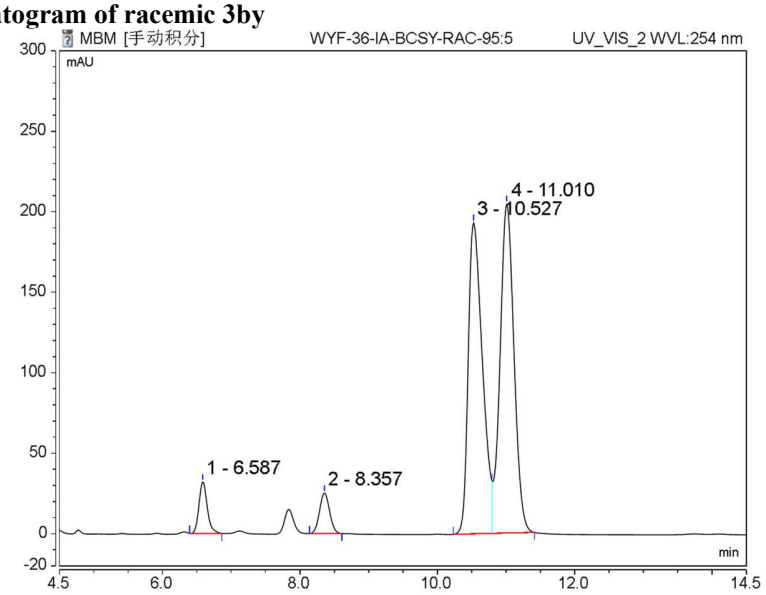
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	9.573	67.008	16.07
2	10.553	143	34.3
3	29.073	65.978	15.83
4	33.967	140.927	33.8
Total:		416.914	100

HPLC chromatogram of chiral 3bx



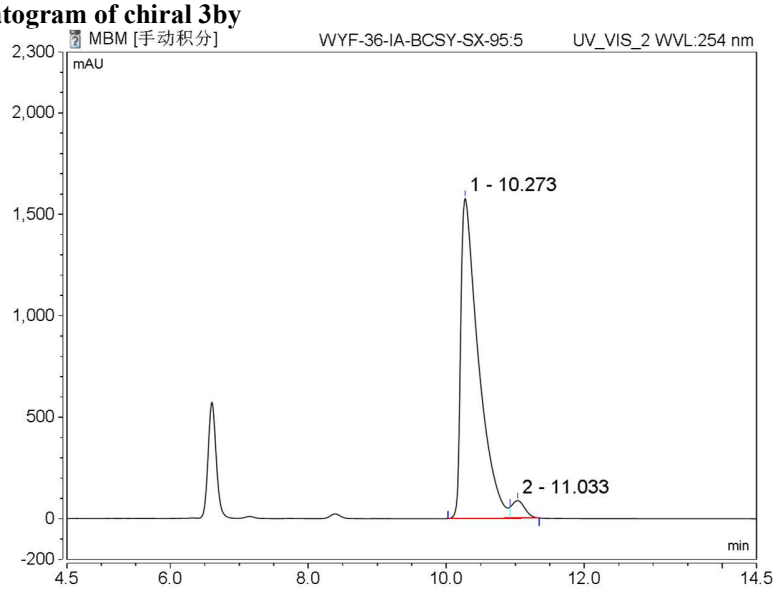
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	10.57	3.685	2.26
2	33.583	159.314	97.74
Total:		162.999	100

HPLC chromatogram of racemic 3by



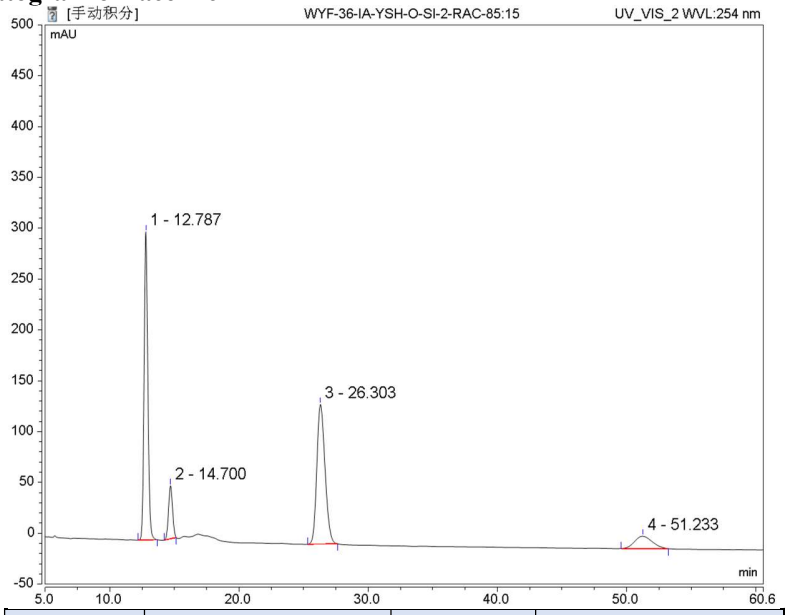
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	6.587	4.454	4.32
2	8.357	4.281	4.15
3	10.527	46.11	44.72
4	11.01	48.274	46.81
Total:		103.119	100

HPLC chromatogram of chiral 3by



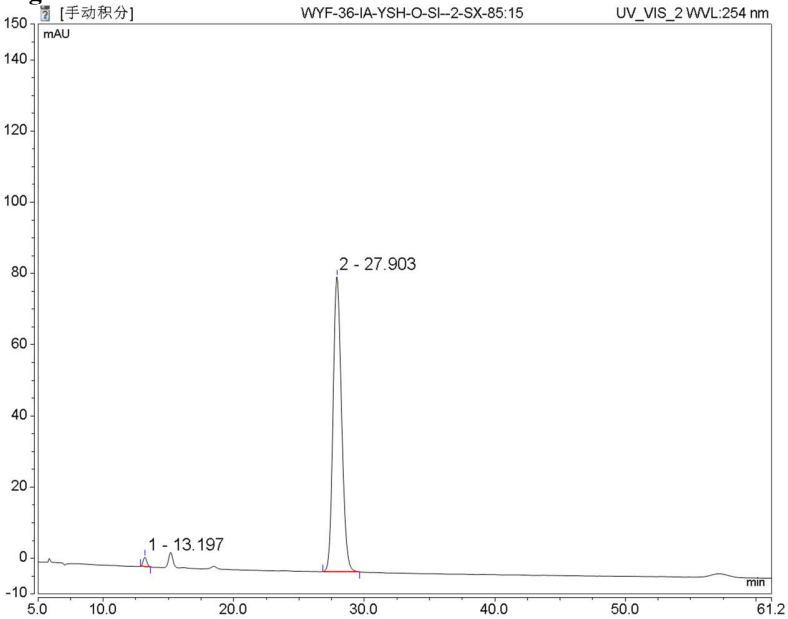
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	10.273	471.073	96.21
2	11.033	18.539	3.79
Total:		489.611	100

HPLC chromatogram of racemic 4



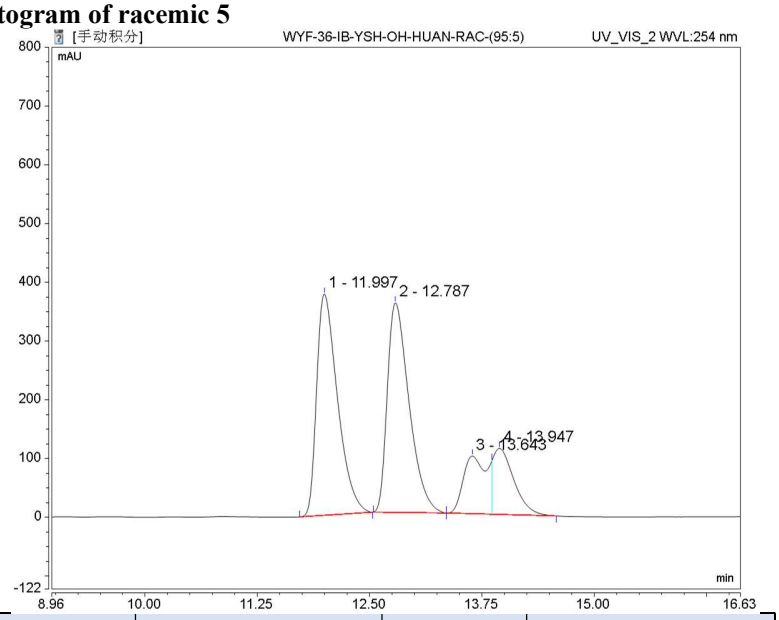
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	12.787	101.27	42.13
2	14.7	18.788	7.82
3	26.303	101.084	42.05
4	51.233	19.248	8.01
Total:		240.39	100

HPLC chromatogram of chiral 4



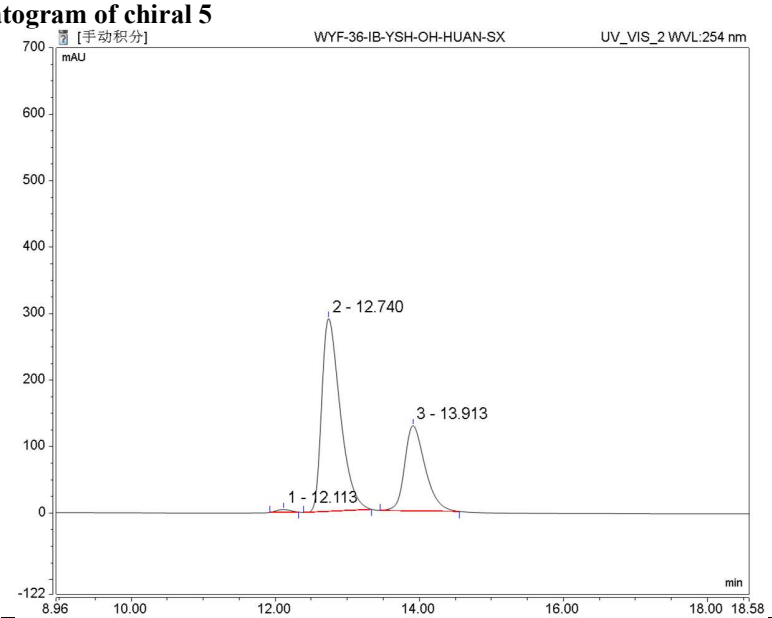
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	13.197	0.851	1.34
2	27.903	62.59	98.66
Total:		63.441	100

HPLC chromatogram of racemic 5



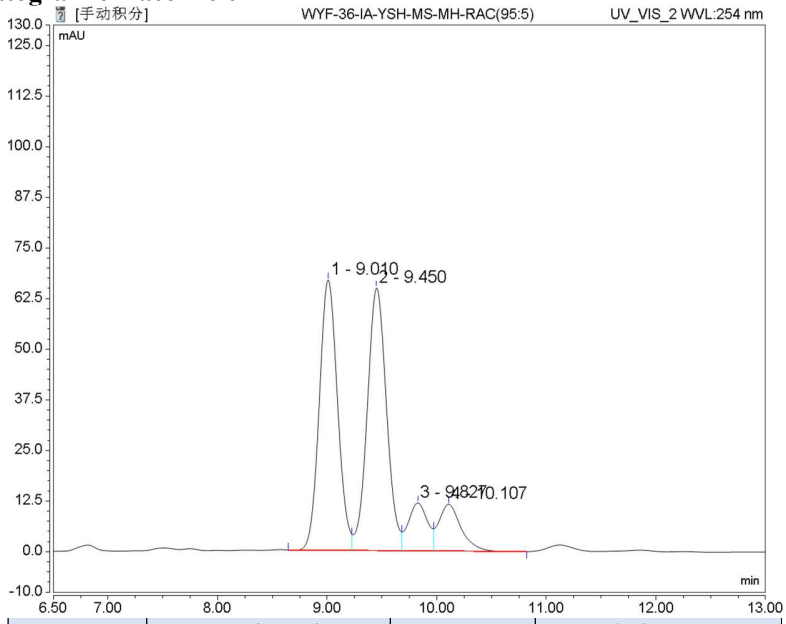
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	11.997	101.49	38.8
2	12.787	100.257	38.32
3	13.643	30.063	11.49
4	13.947	29.791	11.39
Total:		261.6	100

HPLC chromatogram of chiral 5



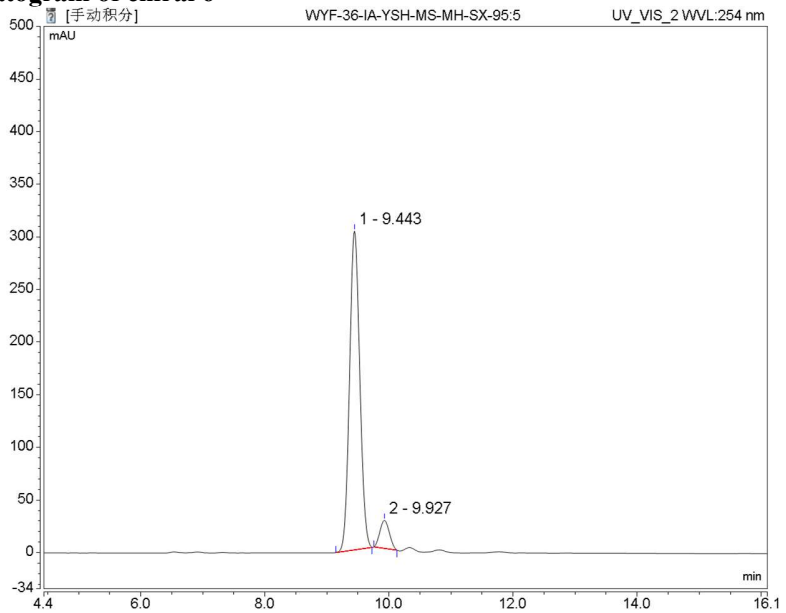
No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	12.113	0.881	0.68
2	12.74	86.299	66.69
3	13.913	42.214	32.62
Total:		129.394	100

HPLC chromatogram of racemic 6



No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	9.01	12.858	41.22
2	9.45	13.199	42.31
3	9.827	2.419	7.75
4	10.107	2.718	8.71
Total:		31.194	100

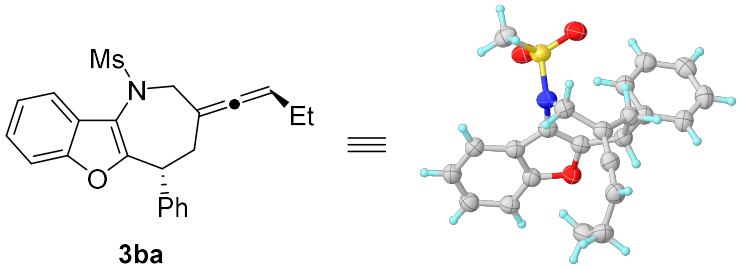
HPLC chromatogram of chiral 6



No.	Retention Time	Area	Relative Area
	min	mAU*min	%
1	9.443	57.694	92.44
2	9.927	4.718	7.56
Total:		62.412	100

X-Ray Crystallographic Data of 3ba and 6

Crystallographic data for **3ba** have been deposited with the Cam-bridge Crystallographic Data Centre as deposition number CCDC 2335107. These data can be obtained free of charge via www.ccdc.cam. ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.



3ba

X-ray structure of **3ba**

Table 1 Crystal data and structure refinement for 3ba.

Identification code	3ba
Empirical formula	$C_{23}H_{23}NO_3S$
Formula weight	393.48
Temperature/K	150.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.9922(2)
b/Å	11.1557(2)
c/Å	16.1415(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1979.36(6)
Z	4
ρ_{calc}g/cm^3	1.320
μ/mm^{-1}	1.645
F(000)	832.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.638 to 149.2
Index ranges	$-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $-17 \leq l \leq 20$
Reflections collected	16934
Independent reflections	3987 [R_{int} = 0.0278, R_{sigma} = 0.0303]
Data/restraints/parameters	3987/0/255
Goodness-of-fit on F^2	1.133

Final R indexes [I>=2σ (I)]	R_1 = 0.0588, wR_2 = 0.1291
Final R indexes [all data]	R_1 = 0.0589, wR_2 = 0.1293
Largest diff. peak/hole / e Å^{-3}	0.63/-0.26
Flack parameter	0.030(4)

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

Atom	*x*	*y*	*z*	U(eq)
S001	751.5(5)	2875.2(5)	7699.0(4)	45.1(2)
O002	3468.8(16)	3478.9(16)	5484.6(12)	46.5(4)
O003	1286(2)	4035(2)	7808.2(12)	56.8(5)
O004	1171(2)	1910(2)	8210.7(13)	59.1(5)
C005	4542(2)	1723(2)	6873.3(16)	44.8(5)
C006	1608(2)	4272(2)	5791.1(16)	44.5(5)
N007	882(2)	2547.4(19)	6710.7(13)	45.2(5)
C008	1774(2)	3157(2)	6226.1(15)	44.0(5)
C009	2883(2)	2728(2)	6027.2(15)	44.6(5)
C00A	3532(2)	1585(2)	6232.8(16)	45.4(5)
C00B	6385(3)	947(3)	7494(2)	55.9(6)
C00C	5528(2)	933(2)	6859.8(18)	50.7(6)
C00D	2627(2)	611(2)	6538.2(16)	46.9(5)
C00E	1145(3)	-418(3)	4623.3(18)	54.6(6)
C00F	1449(2)	621(2)	6050.3(17)	46.0(5)
C00G	695(2)	5133(2)	5733.8(16)	48.9(5)
C00H	1297(3)	66(2)	5344.6(16)	48.9(5)
C00I	425(2)	1380(2)	6407.1(17)	47.7(5)
C00J	1968(3)	6225(2)	4759.7(17)	51.7(6)
C00K	2887(3)	5381(2)	4811.7(16)	48.1(5)
C00L	889(3)	6109(2)	5217.6(17)	51.4(6)
C00M	4452(2)	2543(3)	7521.1(16)	48.6(5)
C00N	2683(2)	4417(2)	5340.5(15)	45.3(5)
C00O	1453(3)	208(3)	3818.9(19)	64.9(8)
C00P	1998(3)	1431(4)	3936(2)	66.9(8)
C00Q	5325(3)	2560(3)	8146.7(18)	52.4(6)
C00R	6282(3)	1751(3)	8137.7(19)	54.8(6)
C00S	-836(2)	2987(3)	7834.3(19)	55.3(6)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3ba. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S001	43.8(3)	50.7(3)	40.8(3)	-1.7(2)	2.60(19)	-4.5(2)
O002	46.1(9)	46.9(8)	46.4(9)	4.4(7)	2.8(7)	1.3(7)
O003	58.4(10)	62.8(11)	49.1(10)	-10.4(8)	5.2(8)	-12.2(9)
O004	60.3(11)	69.9(12)	47.1(10)	6.3(9)	1.5(8)	1.3(10)
C005	44.1(11)	43.6(10)	46.7(12)	4.0(9)	2.9(10)	-0.5(9)
C006	47.3(12)	46.2(11)	40.0(11)	-1.6(9)	-0.1(9)	-1.7(10)
N007	48.8(10)	45.3(10)	41.6(10)	-1.8(8)	3.7(8)	-5.3(8)
C008	46.7(11)	45.8(11)	39.5(11)	-0.7(9)	0.4(9)	-1.6(9)
C009	47.2(11)	45.2(11)	41.5(11)	0.7(9)	0.0(9)	-3.3(10)
C00A	48.0(12)	43.6(11)	44.6(12)	0.6(9)	1.5(9)	0.8(10)
C00B	44.4(12)	51.4(13)	71.9(18)	5.9(12)	-2.4(11)	4.1(10)
C00C	46.3(12)	45.7(11)	60.2(14)	-0.6(10)	1.1(11)	1.1(10)
C00D	50.1(12)	43.6(10)	46.9(11)	1.6(9)	-2.1(10)	-1.3(9)
C00E	60.7(15)	49.7(12)	53.3(14)	-6.8(10)	-4.2(11)	3.8(11)
C00F	49.9(12)	42.8(11)	45.2(11)	1.3(9)	0.1(10)	-4.3(10)
C00G	49.3(13)	49.5(12)	47.9(12)	-1.4(10)	2.5(10)	3.5(10)
C00H	50.4(12)	43.8(11)	52.4(13)	2.1(10)	-1.7(10)	-1.6(10)
C00I	48.1(12)	46.7(12)	48.1(12)	-3.0(10)	0.4(10)	-4.4(10)
C00J	62.1(15)	46.0(12)	47.1(12)	3.2(10)	0.9(11)	0.9(11)
C00K	50.9(13)	49.2(12)	44.1(12)	3.0(10)	2.0(10)	-1.9(10)
C00L	56.8(14)	47.9(12)	49.5(12)	-0.1(10)	-0.7(11)	8.4(11)
C00M	46.9(11)	47.1(12)	51.7(13)	1.4(10)	0.7(10)	1.2(10)
C00N	46.6(11)	45.4(12)	43.9(11)	-0.8(9)	-1.3(9)	1.9(10)
C00O	71.4(18)	78.5(19)	44.8(13)	-6.1(14)	-1.3(12)	13.7(16)
C00P	66.6(18)	80(2)	54.3(15)	15.6(15)	6.6(14)	7.4(16)
C00Q	51.3(13)	57.0(13)	48.8(13)	1.8(11)	1.0(10)	-5.3(11)
C00R	47.7(12)	60.4(14)	56.3(15)	11.3(12)	-3.1(11)	-8.0(12)
C00S	42.6(12)	67.3(16)	56.0(14)	-9.5(12)	6.9(10)	-2.8(11)

Table 4 Bond Lengths for 3ba.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S001	O003	1.432(2)	C00A	C00D	1.553(4)
S001	O004	1.433(2)	C00B	C00C	1.391(4)
S001	N007	1.643(2)	C00B	C00R	1.377(5)
S001	C00S	1.763(3)	C00D	C00F	1.515(4)
O002	C009	1.373(3)	C00E	C00H	1.294(4)
O002	C00N	1.377(3)	C00E	C00O	1.513(4)

Table 4 Bond Lengths for 3ba.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C005	C00A	1.525(3)	C00F	C00H	1.307(4)
C005	C00C	1.397(4)	C00F	C00I	1.522(4)
C005	C00M	1.393(4)	C00G	C00L	1.387(4)
C006	C008	1.440(3)	C00J	C00K	1.384(4)
C006	C00G	1.392(4)	C00J	C00L	1.404(4)
C006	C00N	1.397(3)	C00K	C00N	1.391(4)
N007	C008	1.427(3)	C00M	C00Q	1.393(4)
N007	C00I	1.479(3)	C00O	C00P	1.502(6)
C008	C009	1.348(4)	C00Q	C00R	1.386(5)
C009	C00A	1.498(3)			

Table 5 Bond Angles for 3ba.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O003	S001	O004	118.41(14)	C009	C00A	C005	114.3(2)
O003	S001	N007	106.55(11)	C009	C00A	C00D	111.2(2)
O003	S001	C00S	109.08(14)	C00R	C00B	C00C	120.4(3)
O004	S001	N007	111.35(12)	C00B	C00C	C005	120.5(3)
O004	S001	C00S	107.48(15)	C00F	C00D	C00A	112.2(2)
N007	S001	C00S	102.86(13)	C00H	C00E	C00O	123.4(3)
C009	O002	C00N	106.13(19)	C00D	C00F	C00I	116.0(2)
C00C	C005	C00A	119.4(2)	C00H	C00F	C00D	123.9(2)
C00M	C005	C00A	121.5(2)	C00H	C00F	C00I	120.0(2)
C00M	C005	C00C	118.8(2)	C00L	C00G	C006	118.1(2)
C00G	C006	C008	136.1(2)	C00E	C00H	C00F	176.3(3)
C00G	C006	C00N	119.6(2)	N007	C00I	C00F	111.4(2)
C00N	C006	C008	104.3(2)	C00K	C00J	C00L	121.5(3)
C008	N007	S001	119.09(17)	C00J	C00K	C00N	116.5(2)
C008	N007	C00I	118.1(2)	C00G	C00L	C00J	121.2(2)
C00I	N007	S001	119.21(18)	C00Q	C00M	C005	120.3(3)
N007	C008	C006	126.3(2)	O002	C00N	C006	110.8(2)
C009	C008	C006	107.8(2)	O002	C00N	C00K	126.2(2)
C009	C008	N007	125.6(2)	C00K	C00N	C006	123.1(2)
O002	C009	C00A	116.0(2)	C00P	C00O	C00E	113.6(3)
C008	C009	O002	111.0(2)	C00R	C00Q	C00M	120.4(3)
C008	C009	C00A	132.8(2)	C00B	C00R	C00Q	119.6(3)
C005	C00A	C00D	108.8(2)				

Table 6 Torsion Angles for 3ba.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S001	N007	C008	C006	-88.6(3)	C00C	C005	C00A	C009	-151.9(2)
S001	N007	C008	C009	98.6(3)	C00C	C005	C00A	C00D	83.2(3)
S001	N007	C00I	C00F	-117.7(2)	C00C	C005	C00M	C00Q	-0.8(4)
O002	C009	C00A	C005	79.4(3)	C00C	C00B	C00R	C00Q	-0.8(4)
O002	C009	C00A	C00D	-157.0(2)	C00D	C00F	C00I	N007	42.6(3)
O003	S001	N007	C008	20.7(2)	C00G	C006	C008	N007	6.4(5)
O003	S001	N007	C00I	179.0(2)	C00G	C006	C008	C009	-179.7(3)
O004	S001	N007	C008	-109.8(2)	C00G	C006	C00N	O002	179.6(2)
O004	S001	N007	C00I	48.5(2)	C00G	C006	C00N	C00K	-1.5(4)
C005	C00A	C00D	C00F	166.4(2)	C00H	C00E	C00O	C00P	2.1(5)
C005	C00M	C00Q	C00R	-0.9(4)	C00H	C00F	C00I	N007	-134.7(3)
C006	C008	C009	O002	-0.3(3)	C00I	N007	C008	C006	112.9(3)
C006	C008	C009	C00A	-175.3(3)	C00I	N007	C008	C009	-59.9(3)
C006	C00G	C00L	C00J	0.5(4)	C00J	C00K	C00N	O002	179.9(3)
N007	C008	C009	O002	173.7(2)	C00J	C00K	C00N	C006	1.2(4)
N007	C008	C009	C00A	-1.3(4)	C00K	C00J	C00L	C00G	-0.8(4)
C008	C006	C00G	C00L	-179.1(3)	C00L	C00J	C00K	C00N	-0.1(4)
C008	C006	C00N	O002	-0.5(3)	C00M	C005	C00A	C009	34.3(3)
C008	C006	C00N	C00K	178.3(2)	C00M	C005	C00A	C00D	-90.5(3)
C008	N007	C00I	C00F	40.8(3)	C00M	C005	C00C	C00B	1.7(4)
C008	C009	C00A	C005	-105.8(3)	C00M	C00Q	C00R	C00B	1.7(4)
C008	C009	C00A	C00D	17.8(4)	C00N	O002	C009	C008	-0.1(3)
C009	O002	C00N	C006	0.4(3)	C00N	O002	C009	C00A	175.8(2)
C009	O002	C00N	C00K	-178.4(2)	C00N	C006	C008	N007	-173.4(2)
C009	C00A	C00D	C00F	39.8(3)	C00N	C006	C008	C009	0.5(3)
C00A	C005	C00C	C00B	-172.2(2)	C00N	C006	C00G	C00L	0.6(4)
C00A	C005	C00M	C00Q	173.0(2)	C00R	C00B	C00C	C005	-0.9(4)
C00A	C00D	C00F	C00H	84.5(3)	C00S	S001	N007	C008	135.4(2)
C00A	C00D	C00F	C00I	-92.7(3)	C00S	S001	N007	C00I	-66.3(2)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3ba.

Atom	*x*	*y*	*z*	U(eq)
H00A	3912.94	1282.15	5710.61	54
H00B	7045.72	398.4	7482.8	67
H00C	5614.42	383.06	6414.44	61
H00D	3011.99	-187.69	6486.64	56
H00E	2444.13	748.09	7131.3	56

Table 7 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for 3ba.

Atom	*x*	*y*	*z*	U(eq)
H00F	822.21	-1206.78	4597.56	65
H00G	-38.98	5055.02	6039.46	59
H00H	-197.84	1518.48	5974.66	57
H00I	34.88	942.56	6869.71	57
H00J	2070.24	6898.51	4406.09	62
H00K	3618.9	5455.28	4502.68	58
H00L	280.01	6709.92	5173.19	62
H00M	3792.73	3093.12	7536.25	58
H00N	2033.27	-295.36	3504.2	78
H00O	703.36	284.17	3483.08	78
H00P	2074.38	1829.04	3397.35	100
H00Q	2804.3	1354.11	4189.9	100
H00R	1471.19	1909.07	4298	100
H00S	5263.43	3129.46	8582.25	63
H00T	6862.87	1750.32	8573.22	66
H00U	-1016.46	3166.8	8415.78	83
H00V	-1219.98	2226.32	7680.07	83
H00W	-1154.39	3630.54	7482.29	83

Crystallographic data for **6** have been deposited with the Cam-bridge Crystallographic Data Centre as deposition number CCDC 2335108. These data can be obtained free of charge via www.ccdc.cam. ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

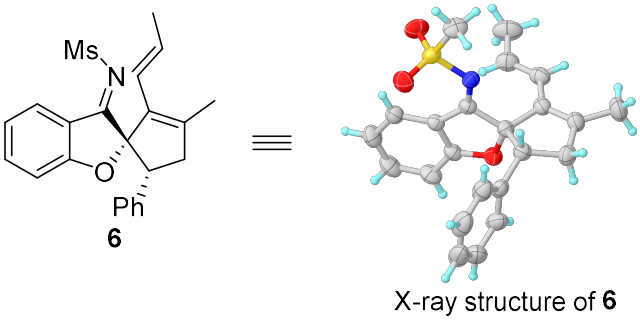


Table 1 Crystal data and structure refinement for 6.

Identification code	6
Empirical formula	$C_{23}H_{23}NO_3S$
Formula weight	393.48
Temperature/K	293(2)

Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.79420(10)
b/Å	10.27180(10)
c/Å	25.9536(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2077.86(5)
Z	4
ρ_{calc}g/cm^3	1.258
μ/mm^{-1}	1.567
F(000)	832.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.812 to 136.644
Index ranges	$-9 \leq h \leq 9$, $-10 \leq k \leq 12$, $-27 \leq l \leq 31$
Reflections collected	18670
Independent reflections	3774 [R_{int} = 0.1448, R_{sigma} = 0.0799]
Data/restraints/parameters	3774/0/257
Goodness-of-fit on F^2	1.152
Final R indexes [I>=2σ (I)]	R_1 = 0.0729, wR_2 = 0.1902
Final R indexes [all data]	R_1 = 0.0770, wR_2 = 0.1940
Largest diff. peak/hole / e Å^{-3}	0.45/-0.53
Flack parameter	-0.04(4)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 6. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S25	231.3(15)	4184.8(10)	7301.3(5)	38.1(4)
O9	3902(4)	3886(3)	5757.3(12)	40.9(8)
O27	1499(5)	4788(4)	7616.6(15)	55.3(10)
O26	-91(5)	2831(3)	7386.1(16)	56.4(10)
N24	615(5)	4455(4)	6687.0(15)	38.1(9)
C13	945(6)	4075(5)	5502.6(18)	39.9(11)
C1	2264(6)	4473(5)	5904.2(18)	35.7(10)
C8	4567(6)	3294(4)	6181.0(19)	37.0(10)
C4	4033(6)	2711(5)	7065(2)	42.7(11)
C3	3502(6)	3342(4)	6613.7(18)	34.2(10)
C14	3941(7)	6641(5)	6036.3(19)	43.6(12)
C2	2002(5)	4063(4)	6462.5(18)	34.5(10)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 6. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C12	674(6)	5071(5)	5172(2)	45.1(12)
C6	6624(7)	2056(6)	6633(2)	55.7(15)
C5	5577(7)	2075(5)	7069(2)	52.7(14)
C20	260(7)	2774(5)	5459(2)	46.8(12)
C11	1718(7)	6245(5)	5305(2)	48.1(13)
C10	2320(6)	5979(5)	5856.5(19)	39.9(11)
C15	3859(9)	7532(6)	6441(2)	57.7(15)
C19	5520(8)	6427(6)	5809(2)	56.0(14)
C21	559(7)	1760(5)	5759(2)	52.0(13)
C23	-460(9)	5072(7)	4709(2)	67.0(18)
C7	6142(6)	2663(6)	6182(2)	50.1(13)
C28	-1689(8)	5037(5)	7360(3)	55.5(15)
C18	6972(9)	7037(8)	5989(3)	75(2)
C16	5325(11)	8154(7)	6611(3)	76(2)
C22	-184(9)	437(6)	5686(3)	71.0(18)
C17	6863(11)	7917(8)	6386(3)	84(3)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 6. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S25	40.2(6)	32.1(6)	41.8(7)	0.9(5)	4.7(5)	-0.3(4)
O9	35.3(16)	46.4(19)	41.0(18)	-0.7(15)	3.5(14)	6.8(14)
O27	57(2)	59(2)	50(2)	-9.2(18)	-8.8(18)	-6.5(18)
O26	60(2)	32.1(17)	77(3)	10.8(17)	8(2)	-4.2(16)
N24	37.0(19)	38(2)	39(2)	4.3(17)	2.6(16)	1.9(18)
C13	37(2)	45(2)	38(2)	-1(2)	-1(2)	1(2)
C1	33(2)	35(2)	39(3)	1.5(19)	0.0(18)	4.2(19)
C8	32(2)	33(2)	46(3)	-3(2)	-2.0(19)	1(2)
C4	42(2)	40(3)	47(3)	4(2)	-2(2)	0(2)
C3	30.7(19)	31(2)	41(3)	-1.5(19)	-1.0(19)	1.7(18)
C14	54(3)	42(3)	35(3)	7(2)	-2(2)	-10(2)
C2	34(2)	30(2)	40(3)	-2.8(19)	-0.2(18)	-2(2)
C12	41(3)	52(3)	42(3)	1(2)	-5(2)	4(2)
C6	39(2)	53(3)	75(4)	-7(3)	-11(3)	14(3)
C5	49(3)	49(3)	60(3)	4(2)	-11(3)	13(3)
C20	42(2)	51(3)	47(3)	-8(2)	-1(2)	-8(2)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 6. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C11	53(3)	44(3)	47(3)	8(2)	-5(2)	4(2)
C10	41(2)	38(2)	41(3)	1(2)	0(2)	1(2)
C15	78(4)	51(3)	44(3)	0(3)	-2(3)	-13(3)
C19	55(3)	60(3)	52(3)	3(3)	4(3)	-18(3)
C21	51(3)	45(3)	60(3)	-8(3)	3(2)	-7(3)
C23	68(4)	73(4)	60(4)	8(3)	-27(3)	-6(3)
C7	36(2)	56(3)	59(3)	-8(3)	3(2)	8(2)
C28	54(3)	47(3)	65(4)	-4(3)	17(3)	6(2)
C18	63(4)	90(5)	71(4)	20(4)	-9(3)	-32(4)
C16	112(6)	70(4)	44(3)	-1(3)	-15(4)	-31(5)
C22	70(4)	50(3)	93(5)	-15(3)	15(4)	-18(3)
C17	99(6)	92(5)	60(4)	22(4)	-29(4)	-56(5)

Table 4 Bond Lengths for 6.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S25	O27	1.425(4)	C3	C2	1.439(6)
S25	O26	1.430(3)	C14	C10	1.509(7)
S25	N24	1.646(4)	C14	C15	1.394(8)
S25	C28	1.741(6)	C14	C19	1.382(8)
O9	C1	1.463(5)	C12	C11	1.495(8)
O9	C8	1.359(6)	C12	C23	1.493(8)
N24	C2	1.292(6)	C6	C5	1.395(8)
C13	C1	1.520(7)	C6	C7	1.378(8)
C13	C12	1.352(7)	C20	C21	1.321(7)
C13	C20	1.443(7)	C11	C10	1.531(7)
C1	C2	1.523(7)	C15	C16	1.381(9)
C1	C10	1.552(7)	C19	C18	1.376(9)
C8	C3	1.398(7)	C21	C22	1.489(8)
C8	C7	1.388(7)	C18	C17	1.374(12)
C4	C3	1.402(7)	C16	C17	1.355(12)
C4	C5	1.369(7)			

Table 5 Bond Angles for 6.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O27	S25	O26	117.2(2)	C15	C14	C10	119.3(5)

Table 5 Bond Angles for 6.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O27	S25	N24	110.9(2)	C19	C14	C10	122.8(5)
O27	S25	C28	109.1(3)	C19	C14	C15	117.9(5)
O26	S25	N24	110.2(2)	N24	C2	C1	117.1(4)
O26	S25	C28	108.9(3)	N24	C2	C3	135.8(4)
N24	S25	C28	99.0(3)	C3	C2	C1	107.0(4)
C8	O9	C1	107.8(3)	C13	C12	C11	112.3(4)
C2	N24	S25	122.4(3)	C13	C12	C23	127.2(5)
C12	C13	C1	109.7(4)	C23	C12	C11	120.5(5)
C12	C13	C20	126.4(5)	C7	C6	C5	121.5(5)
C20	C13	C1	123.6(4)	C4	C5	C6	121.0(5)
O9	C1	C13	107.5(4)	C21	C20	C13	128.2(5)
O9	C1	C2	104.5(3)	C12	C11	C10	103.8(4)
O9	C1	C10	111.4(4)	C14	C10	C1	116.6(4)
C13	C1	C2	119.2(4)	C14	C10	C11	117.7(4)
C13	C1	C10	103.5(4)	C11	C10	C1	104.1(4)
C2	C1	C10	110.8(4)	C16	C15	C14	120.4(6)
O9	C8	C3	114.0(4)	C18	C19	C14	121.0(6)
O9	C8	C7	123.3(5)	C20	C21	C22	125.1(6)
C7	C8	C3	122.7(5)	C6	C7	C8	117.1(5)
C5	C4	C3	119.1(5)	C17	C18	C19	120.2(7)
C8	C3	C4	118.7(4)	C17	C16	C15	120.8(7)
C8	C3	C2	106.4(4)	C16	C17	C18	119.7(7)
C4	C3	C2	134.9(4)				

Table 6 Torsion Angles for 6.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S25	N24	C2	C1	-175.1(3)	C2	C1	C10	C14	75.0(5)
S25	N24	C2	C3	1.4(8)	C2	C1	C10	C11	-153.5(4)
O9	C1	C2	N24	-179.5(4)	C12	C13	C1	O9	-101.7(4)
O9	C1	C2	C3	3.0(5)	C12	C13	C1	C2	139.8(5)
O9	C1	C10	C14	-41.0(6)	C12	C13	C1	C10	16.3(5)
O9	C1	C10	C11	90.5(4)	C12	C13	C20	C21	176.5(6)
O9	C8	C3	C4	177.2(4)	C12	C11	C10	C1	24.2(5)
O9	C8	C3	C2	-1.4(5)	C12	C11	C10	C14	155.1(5)
O9	C8	C7	C6	-177.3(5)	C5	C4	C3	C8	0.3(7)
O27	S25	N24	C2	61.4(4)	C5	C4	C3	C2	178.5(5)
O26	S25	N24	C2	-70.0(4)	C5	C6	C7	C8	0.0(8)
C13	C1	C2	N24	-59.5(6)	C20	C13	C1	O9	72.0(6)

Table 6 Torsion Angles for 6.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C13	C1	C2	C3	123.0(4)	C20	C13	C1	C2	-46.5(6)
C13	C1	C10	C14	-156.2(4)	C20	C13	C1	C10	-170.0(5)
C13	C1	C10	C11	-24.7(5)	C20	C13	C12	C11	-174.3(5)
C13	C12	C11	C10	-15.3(6)	C20	C13	C12	C23	3.7(9)
C13	C20	C21	C22	-179.3(6)	C10	C1	C2	N24	60.3(5)
C1	O9	C8	C3	3.4(5)	C10	C1	C2	C3	-117.2(4)
C1	O9	C8	C7	-178.4(4)	C10	C14	C15	C16	-179.7(6)
C1	C13	C12	C11	-0.8(6)	C10	C14	C19	C18	-179.1(5)
C1	C13	C12	C23	177.2(5)	C15	C14	C10	C1	-118.6(5)
C1	C13	C20	C21	3.9(8)	C15	C14	C10	C11	116.5(6)
C8	O9	C1	C13	-131.4(4)	C15	C14	C19	C18	2.4(9)
C8	O9	C1	C2	-3.8(4)	C15	C16	C17	C18	-0.7(11)
C8	O9	C1	C10	115.9(4)	C19	C14	C10	C1	62.9(7)
C8	C3	C2	N24	-177.9(5)	C19	C14	C10	C11	-61.9(7)
C8	C3	C2	C1	-1.1(5)	C19	C14	C15	C16	-1.2(9)
C4	C3	C2	N24	3.8(9)	C19	C18	C17	C16	1.9(11)
C4	C3	C2	C1	-179.4(5)	C23	C12	C11	C10	166.6(5)
C3	C8	C7	C6	0.8(8)	C7	C8	C3	C4	-1.0(7)
C3	C4	C5	C6	0.5(8)	C7	C8	C3	C2	-179.6(4)
C14	C15	C16	C17	0.4(10)	C7	C6	C5	C4	-0.7(9)
C14	C19	C18	C17	-2.8(10)	C28	S25	N24	C2	175.9(4)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 6.

Atom	*x*	*y*	*z*	U(eq)
H4	3345.57	2723.92	7358.21	51
H6	7672.23	1624.58	6647.53	67
H5	5932.19	1648.69	7366.93	63
H20	-485.63	2631.85	5184.82	56
H11A	1026.75	7029.45	5289.16	58
H11B	2686.57	6336.51	5073.27	58
H10	1404.99	6304.63	6081.08	48
H15	2811.44	7708.37	6597.45	69
H19	5600.84	5861.77	5529.75	67
H21	1290.14	1881.86	6037.92	62
H23A	218.86	5219.27	4405.54	101
H23B	-1300.12	5750.32	4741.08	101
H23C	-1029.47	4245.67	4680.91	101

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 6.

Atom	*x*	*y*	*z*	U(eq)
H7	6839.9	2649.37	5891.9	60
H28A	-2103.39	4965.63	7707.44	83
H28B	-2522.42	4677.53	7127.77	83
H28C	-1501.49	5936.6	7277.9	83
H18	8031.77	6853.23	5840.83	89
H16	5255.6	8742.54	6881.99	91
H22A	-924.2	439.59	5390.08	107
H22B	-831.75	199.08	5985.91	107
H22C	724.88	-179.77	5634.01	107
H17	7841.02	8347.65	6500.71	100