Electronic Supplementary Material (ESI) for RSC Advances.


# Supporting Information

## Palladium-Catalyzed Tandem Allylic Substitution/Cyclization and Cascade Hydrosilylated Reduction: The Influence of Reaction Parameters and Hydrosilanes on Stereoselectivity

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# 1. General Information

Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. For example, all the aldehydes recrystallized or distilled prior to use. Dichloromethane, toluene, were freshly distilled from $CaH_2$, THF was freshly distilled from sodium metal prior to use. Ether ($Et_2O$), tetrahydrofuran (THF) and 1, 4-dioxane were dried and distilled from metal sodium and benzophenone. Alcohol solvents were dried and distilled from metal magnesium. Other commercially available reagents and solvents were used directly without purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (200 - 300 mesh). $^{1}H$ , $^{13}C$， $^{19}F$ and $^{29}Si$ NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in $CDCl_3$. Multiplicities were given as: s(singlet); d (doublet); *dd* (doublets of doublet); t (triplet); q (quartet);or m (multiplets). Infrared spectra were recorded on a Nexus 870 FTIR

spectrometer. High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer. HPLC was carried out with a Agilent 1260 infinity using a chiralpak AD-H column, a chiralpak OJ-H column or a chiralcel OD-H column.

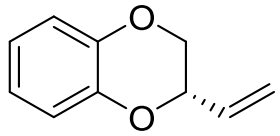
## 2. General procedure for the catalytic asymmetric tandem c yclization substitution in the presence of Pd/(*R*, *R*)-Fei-Phos.

Under argon atmosphere (*R, R*)-Fei-Phos (8.6 mg, 5 mol%) and $Pd_2(dba)_3$ (5.8mg, 2.5 mol%) were dissolved in 3 mL THF, and stirred at room temperature for about 30min. then Catechol **1a** (0.25 mmol) and (*Z*)-but-2-ene-1,4-diyl diacetate **2a** (60.2 mg, 0.35 mol) were added sequentially. The mixture was stirred at room temperature for 24 h. The solution was concentrated under reduced pressure and the residue was chromatographed on silica gel (PE:EA = 10:3) to give the cyclized product **3a**.

## 3. General procedure for the catalytic asymmetric tandem allylic cyclization which was reduced by $MePhSiH_2$ in the presence of Pd/(*R*, *R*)-Fei-Phos.

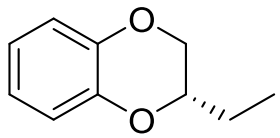
Under argon atmosphere (*R, R*)-Fei-Phos (8.6 mg, 5 mol%) and $Pd_2(dba)_3$ (5.8mg, 2.5 mol%) were dissolved in 3 mL THF, and stirred at room temperature for about 30min. then Catechol **1a** (27.5mg, 0.25 mmol), (*Z*)-but-2-ene-1,4-diyl diacetate **2a** (60.2 mg, 0.35 mol) and $MePhSiH_2$ (91.68 mg, 0.75 mmol) were added sequentially. The mixture was stirred at room temperature for 48 h and then was added TBAF(0,75 mmol, 1 mol/L in THF) which was stirred at room temperature for 6h, after which 2 mL $H_2O$ was added to quench the reaction. The water layer was extracted with EtOAc (5 mL×2). The organic layer was combined and washed by brine. The combined organic layer was dried over $Na_2SO_4$ and concentrated. The crude product was purified by silica gel chromatography (PE:EA = 10:3) to afford the product **4a**.

**(*S*)-2-vinyl-2,3-dihydrobenzo[b][1,4]dioxine(3a)**



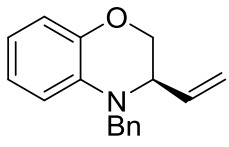
Colorless oil. Yield 85%. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.73 – 6.86 (m, 4H), 5.82 (ddd, *J* = 16.9, 10.7, 5.8 Hz, 1H), 5.43 (d, *J* = 17.3 Hz, 1H), 5.29 (d, *J* = 10.7 Hz, 1H), 4.47 – 4.62 (m, 1H), 4.16 (dd, *J* = 11.3, 2.4 Hz, 1H), 3.82 (dd, *J* = 11.3, 7.9 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.2, 143.1, 132.5, 121.6, 121.4, 119.1, 117.4, 117.0, 73.6, 67.6. HRMS(APCI): m/z: [M+H]+ calculated for $C_{10}H_{11}O_2$: 163.0754, Found: 163.0750. IR(KBr)$\nu_{max}$: 3431, 2961, 1641, 1493, 1261, 1022, 801, 747. Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 98:2, 1.0 mL/min, 280 nm); minor enantiomer tr = 7.357 min, major enantiomer tr = 7.036 min.

**(*S*)-2-ethyl-2,3-dihydrobenzo[b][1,4]dioxine(4a)**



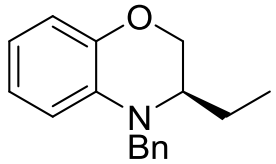
Colorless oil. Yield 99%. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.76 (ddt, *J* = 16.9, 7.1, 3.0 Hz, 4H), 4.14 (dd, *J* = 11.1, 1.8 Hz, 1H), 3.91 – 4.00 (m, 1H), 3.80 (dd, *J* = 11.1, 7.9 Hz, 1H), 1.66 (dt, *J* = 14.7, 7.4 Hz, 1H), 1.55 (dt, *J* = 13.8, 6.8 Hz, 1H), 0.99 (t, *J* = 15.0 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.6, 143.4, 121.4, 121.1, 117.3, 116.9, 74.3, 67.8, 24.2, 9.4. HRMS(APCI): m/z: [M + H]+ calculated for $C_{10}H_{12}O_2$: 165.0910, Found: 165.0906. IR(KBr)$\nu_{max}$: 3444, 2961, 1593, 1494, 1429, 1261, 1082, 794, 733, 699, 486, 433. Chiralpak OJ-H column (hexanes: 2-propanol = 99:1, 0.63 mL/min, 280 nm); minor enantiomer tr = 9.359 min, major enantiomer tr = 9.694 min.

**(*R*)-4-benzyl-3-vinyl-3,4-dihydro-2H-benzo[b][1,4]oxazine(3b)**



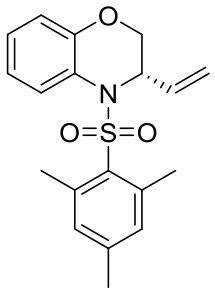
Colorless oil. Yield 90%. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.25 (m, 5H), 6.80 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.66 – 6.73 (m, 1H), 6.53 – 6.62 (m, 2H), 5.85 (ddd, *J* = 17.0, 10.6, 5.8 Hz, 1H), 5.35 (d, *J* = 17.3 Hz, 1H), 5.20 (d, *J* = 10.6 Hz, 1H), 4.50 – 4.63 (m, 1H), 4.35 (s, 2H), 3.22 (dd, *J* = 11.8, 2.6 Hz, 1H), 3.10 (dd, *J* = 11.8, 7.8 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.7, 138.1,

135.1, 135.0, 128.7, 127.22, 127.17, 121.6, 118.1, 117.8, 116.6, 112.6, 73.9, 55.10, 51.91. HRMS(APCI): m/z: [M + H]+ calculated for $C_{17}H_{18}NO$: 252.1383, Found: 252.1392. IR(KBr)$\nu_{max}$: 3525, 3403, 3064, 1605, 1503, 1452, 1355, 1261, 1123, 1048, 868, 793, 738, 698. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 98:2, 1.0 mL/min, 280 nm); minor enantiomer tr = 5.457 min, major enantiomer tr = 5.924 min.




**(*R*)-4-benzyl-3-ethyl-3,4-dihydro-2H-benzo[b][1,4]oxazine( 4b)**

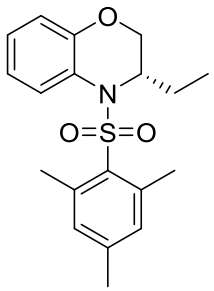
Colorless oil. Yield 80%. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.24 (m, 5H), 6.75 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.64 – 6.70 (m, 1H), 6.55 (dd, *J* = 14.2, 6.9 Hz, 2H), 4.31 – 4.36 (m, 2H), 3.96 (tdd, *J* = 8.1, 5.8, 2.5 Hz, 1H), 3.17 (dd, *J* = 11.6, 2.5 Hz, 1H), 3.03 (dd, *J* = 11.7, 8.0 Hz, 1H), 1.65 (dq, *J* = 15.0, 7.5 Hz, 1H), 1.51 (ddd, *J* = 13.9, 7.5, 5.7 Hz, 1H), 0.94 (t, *J* = 7.5 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 144.2, 138.4, 135.4, 134.2, 133.55, 133.48, 128.8, 127.3, 121.6, 118.0, 116.6, 112.5, 74.8, 55.2, 51.9, 26.2, 9.8. HRMS(APCI): m/z: [M + H]+ calculated for C17H20NO: 254.1539, Found: 252.1530. IR(KBr)$\nu_{max}$: 3466, 2964, 1605, 1504, 1455, 1356, 1253, 1049, 738, 698. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 98:2, 1.0 mL/min, 280 nm); minor enantiomer tr = 4.805 min, major enantiomer tr = 5.23 min.




**(*S*)-4-(mesitylsulfonyl)-3-vinyl-3,4-dihydro-2H-benzo[b][1,4]oxa zine(3c)**

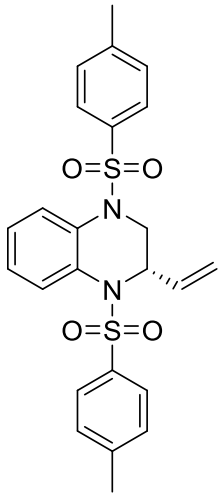
Yellow oil. Yield 67%. $^1$H NMR (400 MHz, $CDCl_3$) δ 6.89 – 6.97 (m, 4H), 6.86 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.66 – 6.72 (m, 1H), 5.78 (ddd, *J* = 17.0, 10.6, 6.0 Hz, 1H), 5.35 (d, *J* = 17.3 Hz, 1H), 5.25 (d, *J* = 10.6 Hz, 1H), 4.39 – 4.52 (m, 1H), 4.03 (dd, *J* = 14.3, 2.6 Hz, 1H), 3.03 (dd, *J* = 14.3, 9.6 Hz, 1H), 2.48 (s, 6H), 2.24 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 147.3, 143.3, 140.2, 133.8, 133.7, 132.4, 126.1, 124.2, 123.8, 120.6, 118.8, 117.7, 74.0, 47.3,

22.9, 21.0. HRMS(APCI): m/z: [M + H]+ calculated for $C_{19}H_{22}NO_3S$: 344.1315, Found:344.1310. IR(KBr)$\nu_{max}$: 2925, 2130, 1602, 1488, 1334, 1244, 1158, 1122, 1054, 868, 792, 754, 658, 584, 531. Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 96:4, 1.0 mL/min, 280 nm); minor enantiomer tr = 8.542 min, major enantiomer tr = 9.816 min.



**(*S*)-3-ethyl-4-(mesitylsulfonyl)-3,4-dihydro-2H-benzo[b][1,4]oxazine(4c)**

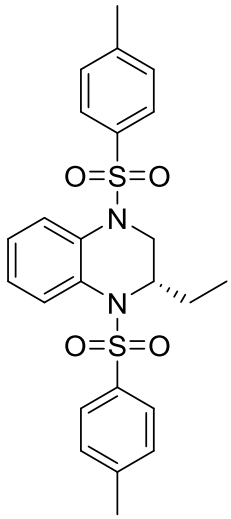
Yellow oil. Yield 88%. $^1$H NMR (400 MHz, $CDCl_3$) δ 6.97 – 7.05 (m, 4H), 6.87 – 6.91 (m, 1H), 6.74 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 4.10 (dd, *J* = 14.1, 2.3 Hz, 1H), 3.94 (ddt, *J* = 9.9, 6.6, 3.4 Hz, 1H), 3.07 (dd, *J* = 14.2, 9.5 Hz, 1H), 2.56 (s, 6H), 2.32 (s, 3H), 1.54 – 1.79 (m, 1H), 1.01 (t, J = 7.5 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 147.6, 143.2, 140.1, 134.1, 132.4, 125.8, 124.5, 123.4, 120.3, 117.6, 74.6, 47.0, 25.9, 22.9, 21.0, 9.2. HRMS(APCI): m/z: [M + H]+ calculated for $C_{19}H_{24}NO_3S$: 346.1471, Found: 346.1461. IR(KBr)$\nu_{max}$: 3466, 2936, 1603, 1489, 1459, 1334, 1251, 1208, 1159, 1126, 1075, 935, 903, 864, 793, 753, 658, 585, 529. Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 96:4, 1.0 mL/min, 280 nm); minor enantiomer tr = 8.105 min, major enantiomer tr = 9.28 min.



**(*S*)-1,4-ditosyl-2-vinyl-1,2,3,4-tetrahydroquinoxaline(3d)**

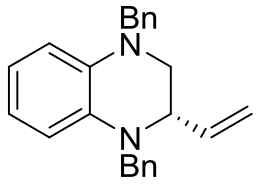
Colorless oil. Yield 90%. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.81 (m, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.17 – 7.25 (m, 4H), 6.98 – 7.08 (m, 1H), 5.61 (ddd, *J* = 17.0, 10.4, 4.8 Hz, 1H), 5.23 – 5.35 (m, 1H), 5.09 – 5.17 (m, 1H), 4.98 – 5.07 (m, 1H), 4.04 (dd, *J* = 12.8, 4.1 Hz, 1H), 3.29 (dd, *J* = 12.8, 4.5 Hz, 1H), 2.39 (d, *J* = 2.9 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ

144.23, 144.19, 136.5, 135.8, 133.5, 130.8, 129.9, 129.8, 127.3, 127.1, 126.1, 125.7, 123.8, 119.6, 118.8, 55.8, 48.0, 21.6. HRMS(ESI): m/z: [M + H]+ calculated for $C_{24}H_{25}N_2O_4S_2$: 469.1250, Found: 469.1260. IR(KBr)$\nu_{max}$: 3469, 2925, 1918, 1597, 1492, 1354, 1166, 934, 890, 813, 682, 576, 436. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 80:20, 1.0 mL/min, 280 nm); minor enantiomer tr = 12.176 min, major enantiomer tr = 10.78min.



**(*S*)-2-ethyl-1,4-ditosyl-1,2,3,4-tetrahydroquinoxaline(4d)**

Colorless oil. Yield 99%. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8Hz, 1H), 7.57 – 7.60 (dd, *J* = 8Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.20 (dd, *J*=8.1 Hz, 4H), 6.99 – 7.09 (m, 1H), 4.30 (dq, *J* = 10.4, 3.7, 3.0 Hz, 1H), 3.95 (dd, *J* = 12.5, 2.9 Hz, 1H), 3.09 (dd, *J* = 12.5, 4.2 Hz, 1H), 2.40 (s, 6H), 1.40 (m, 1H), 1.28 (m, 1H), 0.92 (t, *J* = 7.5 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 144.1, 144.0, 136.5, 135.9, 133.4, 133.3, 130.7, 129.8, 129.8, 127.8, 127.8, 127.7, 127.3, 127.0, 126.0, 124.6, 123.3, 118.8, 54.8, 47.4, 24.7, 21.58, 21.54, 10.2. HRMS(ESI): m/z: [M + H]+ calculated for $C_{24}H_{27}N_2O_4S_2$: 471.1407, Found: 469.1410. IR(KBr)$\nu_{max}$: 3512, 2966, 1598, 1492, 1456, 1353, 1263, 1167, 1090, 890, 813, 735, 669, 629, 564, 483. Enantiomeric excess was determined by HPLC with a Chiralpak OD-H column (hexanes: 2-propanol = 80:20, 1.0 mL/min, 280 nm); minor enantiomer tr = 11.09 min, major enantiomer tr = 12.5min.

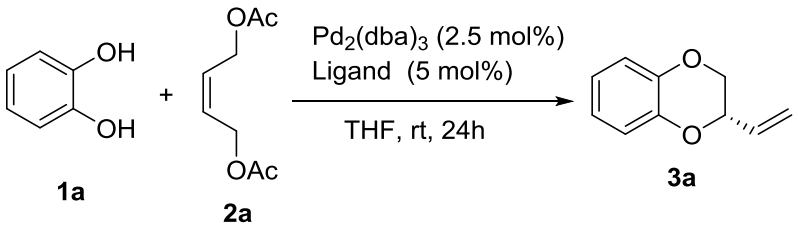


**(*S*)-1,4-dibenzyl-2-vinyl-1,2,3,4-tetrahydroquinoxaline(3e)**

Yellow oil. Yield 70%. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.24 (m, 8H), 7.10 – 7.17 (m, 2H), 6.48 (d, *J* = 7.6 Hz, 3H), 6.36 – 6.43 (m, 1H), 5.88 (ddd, *J* = 17.1, 10.3, 7.7 Hz, 1H), 5.06 – 5.09 (m, 1H), 5.03 (d, *J* = 9.8 Hz, 1H), 4.50 (d, *J* = 16.7 Hz, 1H), 4.38 (d, *J* = 15.9 Hz, 1H), 4.17 – 4.30 (T, *J*=16Hz, 2H), 3.81 (dt, *J* = 6.9, 3.2 Hz, 1H), 3.42 (dd, *J* =

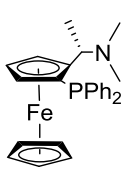
11.2, 3.4 Hz, 1H), 3.12 (dd, *J* = 11.2, 3.4 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.0, 138.8, 137.3, 135.6, 135.1, 128.7, 128.6, 127.4, 127.1, 126.92, 126.87, 118.7, 117.6, 117.0, 111.6, 111.4, 60.1, 55.8, 53.1, 52.6. HRMS(APCI): m/z: [M + H]+ calculated for $C_{24}H_{25}N_2$: 341.2012, Found: 341.2011. IR(KBr)$\nu_{max}$: 3456, 2846, 1593, 1510, 1451, 1354, 1242, 1169, 924, 731. Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 98:2, 1.0 mL/min, 280 nm); minor enantiomer tr = 12.146 min, major enantiomer tr =14.348min.

## Table S1. Ligand screen of Palladium-catalyzed asymmetric tandem allylic cyclization [a].

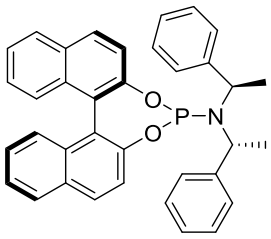



| Entry | Ligand | Yield(%)[c] | Ee(%)[b] |
|---|---|---|---|
| 1 | **L1** | n.r | - |
| 2 | **L2** | <5 | - |
| 3 | **L3** | 50 | 39 |
| 4 | **L4** | n.r | - |
| 5 | **L5** | n.r | - |
| 6 | **L6** | n.r | - |
| 7 | **L7** | n.r | - |
| 8 | **L8** | 30 | 25 |
| 9 | **L9** | n.r | - |
| 10 | **L10** | n.r | - |
| 11 | **L11** | n.r | - |
| 12 | **L12** | 60 | 39 |
| 13 | **L13** | n.r | - |
| 14 | **L14** | n.r | - |
| 15 | **L15** | n.r | - |
| 16 | **L16** | n.r | - |

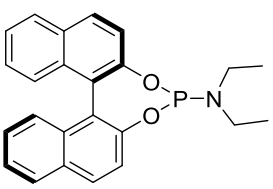
[a] The 1a (0.25mmol) and 2a (1.4 eq.) was carried out under $N_2$ at room temperature for 24 h by mixing metal cat (2.5 mol%) and the chiral ligand (5 mol%). [b] Determined by chiral HPLC. n.r is no reaction; trace represented <5% yield; n.d is not determined. [c] Isolated yield after purification on silica gel.



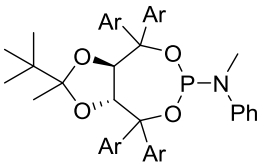

**L1**




**L2**

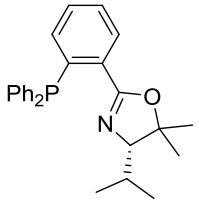



**L3**

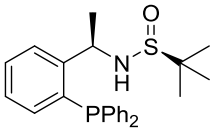



Ar=3,5-dimethylphenyl

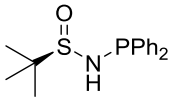
**L4**



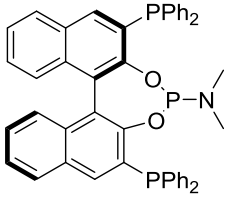

**L5**



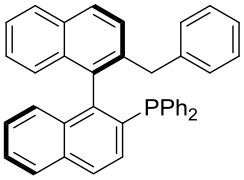

**L6**



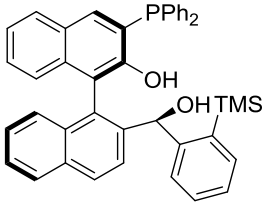

**L7**



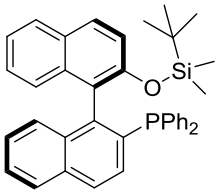

**L8**



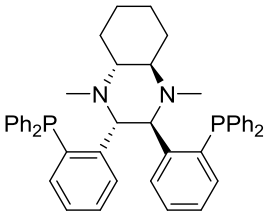

**L9**



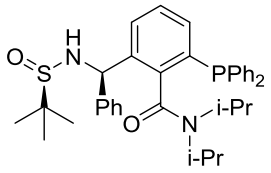

**L10**
**Tao-Phos**



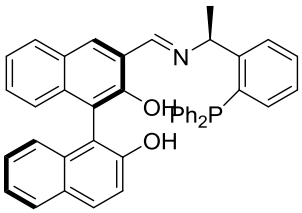

**L11**
**JSi-Phos**



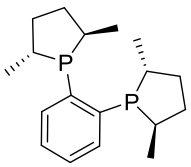

**L12**
**Fei-Phos**



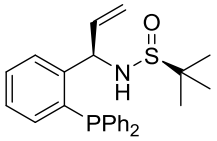

**L13**
**Xing-Phos**




**L14**
**HZNU-Phos**

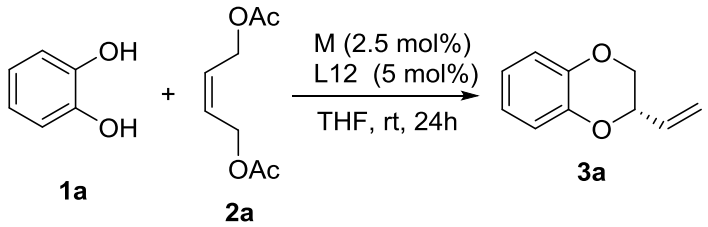



**L15**
**DuPhos**




**L16**

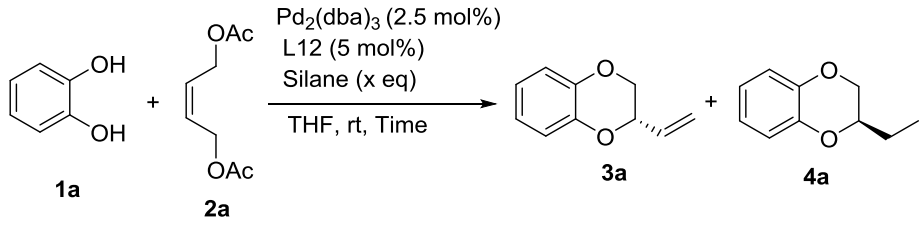
**Table S2. The effect of metal catalysts on the asymmetric tandem allylic cyclization.**[a]




| Entry | Cat | Yield(%) | Ee(%)[b] |
|---|---|---|---|
| 1 | $Pd(OAc)_2$ | n.r | - |
| 2 | $(Ph_3P)_4Pd$ | 21% | 19 |
| 3 | $PdCl_2(CH_3CN)_2$ | n.r | - |
| 4 | $PdCl_2(PhCN)_2$ | trace | - |
| 5 | $RhCl(PPh_3)$ | n.r | - |
| 6 | $[RhCl(coe)]_2$ | n.r | - |
| 7 | $[RhCl(cod)]_2$ | n.r | - |
| 8 | $[RhCl_2(pmcpd)]_2$ | n.r | - |
| 9 | $[RhCl(coe)_2]_2$ | n.r | - |
| 10 | $RuCl(PPh)_3$ | n.r | - |
| 11 | $[Ir(cod)OMe]_2$ | n.r | - |
| 12 | $[Pd(C_3H_5)Cl]_2$ | 58% | 35 |

[a]The 1a (0.25mmol) and 2a (1.4 eq.) was carried out under $N_2$ at room temperature for 24 h by mixing metal cat (2.5 mol%) and the chiral ligand (5 mol%). N.R is no reaction; trace represented <5% yield; N.D is not determined. [b] Determined by chiral HPLC.

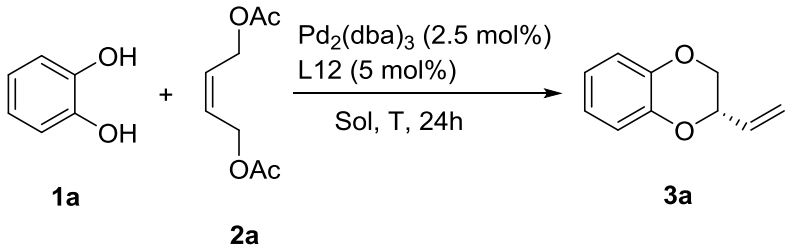
**Table S3. The influence of leaving group for asymmetric tandem allylic cyclization [a].**




| Entry | Leaving group | Ee(%)[b] |
|---|---|---|
| 1 | R'1(**2a**) | 39 |
| 2 | R'2(**2b**) | 27 |
| 3 | R'3(**2c**) | 31 |
| 4 | R'4(**2d**) | 20 |
| 5 | R'5(**2e**) | 41 |
| 6 | R'6(**2f**) | 45 |
| 7 | R'7(**2g**) | 23 |

[a] The reaction was carried out at room temperature for 24 h in THF by mixing $Pd_2(dba)_3$ (2.5 mol%) and the chiral ligand (5 mol%). [b] Determined by chiral HPLC.

**Table S4. The influence of temperature and solvent for asymmetric tandem allylic cyclization [a].**

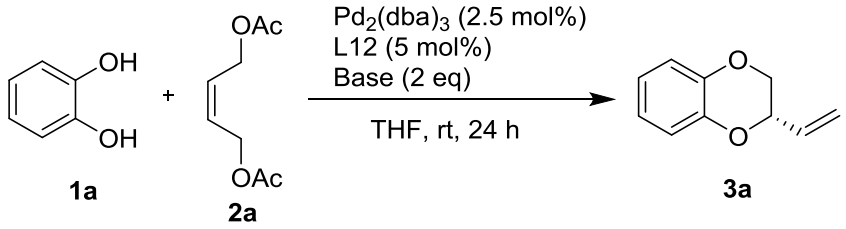



1a 2a 3a

| Entry | Temparature(°C) | Solvent | Yield(%)[b] | Ee(%)[c] |
|---|---|---|---|---|
| 1 | 0 | THF | 24% | 31 |
| 2 | -20 | THF | 5% | 33 |
| 3 | rt | Dioxane | 72% | 35 |
| 4 | rt | DCM | trace | - |
| 5 | rt | DCE | 12% | n.d |
| 6 | rt | DMSO | n.r | - |

[a] The 1a (0.25mmol) and 2a (1.4 eq.) was carried out under $N_2$ for 24 h by mixing metal cat (2.5 mol%) and the chiral ligand (5 mol%). [b] Isolated yield after purification on silica gel. [c] Determined by chiral HPLC. n.r is no reaction; trace represented <5% yield; n.d is not determined.

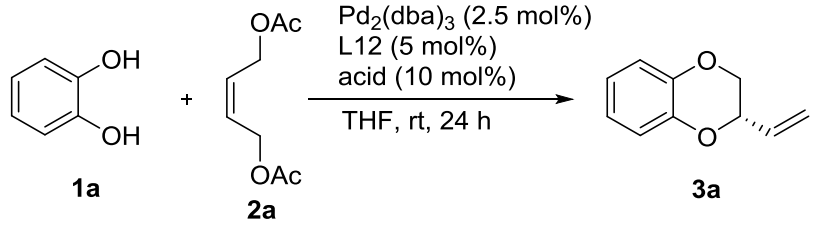
**Table S5. The influence of base for asymmetric tandem allylic cyclization** [a].




| Entry | Base | Yield(%)[c] | Ee(%)[b] |
|---|---|---|---|
| 1 | $K_2CO_3$ | 75% | 11 |
| 2 | $KHCO_3$ | 76% | 11 |
| 3 | $K_3PO_4$ | 68% | 9 |
| 4 | KF | 85% | 3 |
| 5 | $Na_2CO_3$ | 80% | 3 |
| 6 | $NaHCO_3$ | 62% | 27 |
| 7 | $Cs_2CO_3$ | 50% | 11 |
| 8 | HMDS | n.r | - |
| 9 | TMS-BA | trace | - |
| 10 | DBU | 75% | 7 |
| 11 | TEA | 69% | 19 |
| 12 | DIPEA | 74% | 37 |

[a] The 1a (0.25mmol) and 2a (1.4 eq.) was carried out at room temperature for 24 h by mixing $Pd_2(dba)_3$ (2.5 mol%) and the chiral ligand (5 mol%). n.r is no reaction; trace represented <5% yield; n.d is not determined. [b] Determined by chiral HPLC. [c] Isolated yield after purification on silica gel.

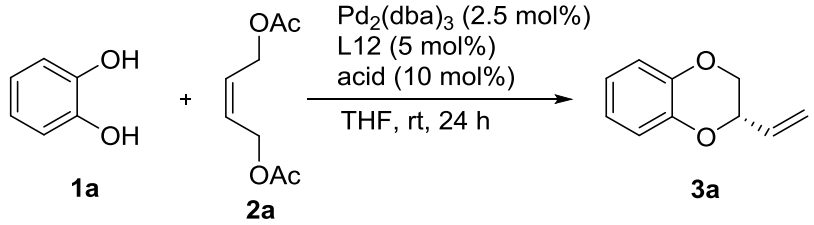
**Table S6. The influence of acid for asymmetric tandem allylic cyclization**[a].




| Entry | Acid | Ee(%)[b] |
|---|---|---|
| 1 | (*S*)-(+)-Mandelic acid | 5 |
| 2 | (R)-(-)-Mandelic acid | 9 |
| 3 | L-(-)-Proline | 25 |
| 4 | D-(+)-Proline | 17 |
| 5 | Benzoic acid | 3 |
| 6 | 2-methylbenzoic acid | 39 |
| 7 | Abietic acid | 19 |
| 8 | Ascorbic acid | 17 |
| 9 | Pivalic acid | 5 |
| 10 | Boric acid | 31 |
| 11 | Cyclopropylboronic acid | 15 |
| 12 | 2-naphthaleneacetic acid | 19 |
| 13 | Benzeneboronic acid | 51 |

[a] The 1a (0.25mmol) and 2a (1.4 eq.) was carried out at room temperature for 24 h by mixing $Pd_2(dba)_3$ (2.5 mol%) and the chiral ligand (5 mol%). [b] Determined by chiral HPLC.

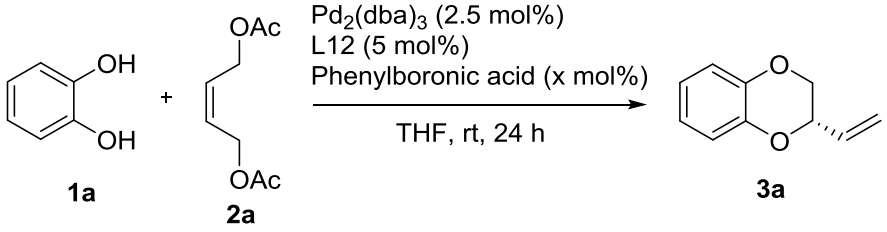
**Table S7. The influence of derivation of Phenylboronic acid for asymmetric tandem allylic cyclization**[a].




| Entry | Acid | Ee(%)[b] |
|---|---|---|
| 1 | Benzeneboronic acid | 51 |
| 2 | 2-Thiopheneboronic acid | n.d |
| 3 | 2-hydroxyphenylboronic acid | n.d |
| 5 | 2-trifluoromethylphenylboronic acid | 29 |
| 6 | 3-bromophenylboronic acid | 11 |
| 7 | 3,5-dimethylphenylboronic acid | 43 |
| 8 | 2-methoxyphenylboronic acid | 47 |
| 9 | 3,5-bis(trifluoromethyl)phenylboronic acid | 49 |
| 10 | 3-pyridineboronic acid | 21 |
| 11 | 3-methoxylphenylboronic acid | 45 |
| 12 | 4-pyridineboronic acid | 13 |
| 13 | 4-butylphenylboronic acid | 43 |
| 14 | 4-(trifluoromethoxy)phenylboronic acid | 21 |
| 15 | 4-ethoxylphenylboronic acid | 19 |
| 16 | 5-(Trifluoromethyl)dibenzothiophenium tetrafluoroborate | 11 |
| 17 | 5-pyrimidinylboronic acid | 17 |
| 18 | 4-fulorophenylboronic acid | 13 |
| 19 | 4-biphenylboronic acid | 20 |
| 20 | 9-anthraceneboronic acid | 9 |

[a] The 1a (0.25mmol) and 2a (1.4 eq.) was carried out at room temperature for 24 h by mixing $Pd_2(dba)_3$ (2.5 mol%) and the chiral ligand (5 mol%). N.R is no reaction; trace represented <5% yield; n.d is not determined. [b] Determined by chiral HPLC.

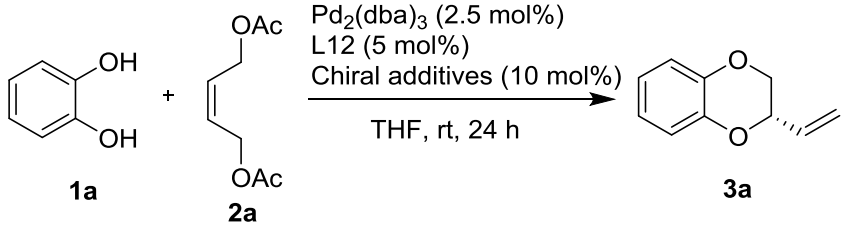
**Table S8. The influence of amount of Phenylboronic acid for asymmetric tandem allylic cyclization[a].**




| Entry | Phenylboronic acid | Yield(%)[f] | Ee(%)[e] |
|---|---|---|---|
| 1[b] | 10 mol% | 10 | 51 |
| 2[c] | 10 mol% | 40 | 47 |
| 3[d] | 10 mol% | 47 | 45 |
| 4[c] | 20 mol% | 43 | 45 |
| 5[c] | 30 mol% | n.d | 45 |
| 6[c] | 40 mol% | 21 | 45 |
| 7[c] | 50 mol% | 26 | 45 |
| 8[c] | 60 mol% | 24 | 45 |
| 9[c] | 70 mol% | 11 | 45 |
| 10[c] | 80 mol% | 38 | 47 |
| 11[c] | 90 mol% | 24 | 37 |
| 12[c] | 100 mol% | 16 | 45 |

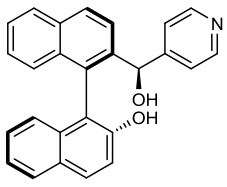
[a] The reaction was carried out at room temperature for 24h in THF by mixing $Pd_2(dba)_3$ (2.5 mol%) and the chiral ligand (5 mol%). [b] The 1a (0.25mmol) and 2a (1.4 eq.) was carried out. [c]The 1a (0.25mmol) and 2a (2 eq.) was carried out. [d] The 1a (0.25mmol) and 2a (3 eq.) was carried out. [e] Determined by chiral HPLC. [f] Isolated yield after purification on silica gel

**Table S9. The influence of additives for asymmetric tandem allylic cyclization[a].**

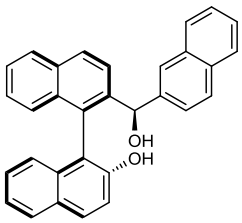



| Entry | Yield(%) | Ee(%)[i] |
|---|---|---|
| 1[b] | 67% | 38 |
| 2[c] | 80% | 41 |
| 3[d] | 75% | 43 |
| 4[e] | 72% | 43 |
| 5[f] | trace | - |
| 6[g] | 66% | 41 |
| 7[h] | 75% | 35 |

[a] The reaction was carried out at room temperature for 24 h in THF by mixing $Pd_2(dba)_3$ (2.5 mol%) and the chiral ligand (5 mol%). [b] The Benzaldehyde(10 mol%) was used. N.R is no reaction; trace represented <5% yield; N.D is not determined. [c] The *S*-BINOL(10 mol%) was used. [d]The *R*-BINOL(10 mol%) was used. [e] The *race*-BINOL(10 mol%) was used. [f] The TBAF(10 mol%) was used. [g] The A1(10 mol%) was used. [h] The A2(10 mol%) was used. [i] Determined by chiral HPLC.

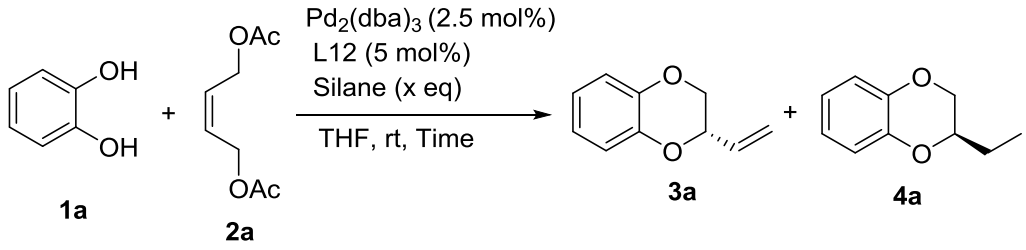



A1




A2

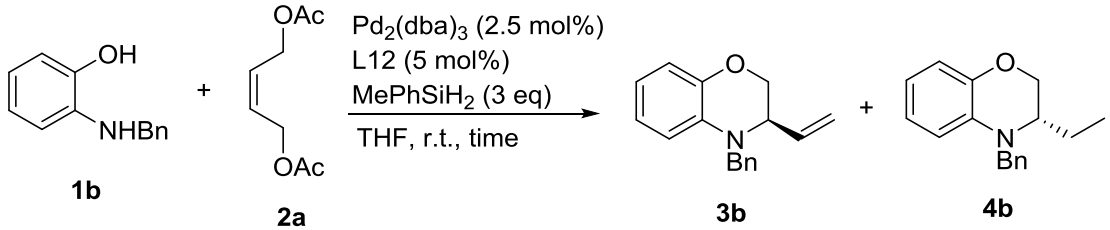
**Table S10. The influence of silane for asymmetric tandem allylic cyclization[a].**




| entry | Silane[b] | Yield(%) | 3a:4a[j] | Ee(%)[k] |
|---|---|---|---|---|
| 1 | PMHS | 99% | 1:0.48 | 39&43 |
| 2 | $Ph_2SiH_2$ | 99% | 1:0.59 | 39&43 |
| 3 | $MePhSiH_2$ | 99% | 0:1 | 45 |
| 4 | $MePhSiH_2$[c] | - | 3.6:1 | - |
| 5 | $MePhSiH_2$[d] | - | 1:1.4 | - |
| 6 | $MePhSiH_2$[e] | - | 1:8.7 | - |
| 7 | $MePhSiH_2$[f] | - | 1:1.5 | - |
| 8 | $MePhSiH_2$[g] | - | 1:22 | - |
| 9 | $PhSiH_3$ | n.r | - | - |
| 10[h] | $MePh_2SiH$ | 87% | 1:0 | 27 |
| 11[i] | $MePh_2SiH$ | 87% | 1:0 | 39 |

[a] The reaction was carried out at room temperature for 48 h in THF by mixing $Pd_2(dba)_3$ (2.5 mol%) and the chiral ligand (5 mol%). n.r is no reaction; trace represented <5% yield; n.d is not determined. [b] The silane (3 eq.) was used. [c] The silane (3 eq.) was used and the reaction time was 24h. [d] The silane(1 eq.) was used. [e] The silane (2 eq.) was used.[f]The silane(1 eq.) was used and the reaction time was 72h. [g] The silane (2 eq.) was used and the reaction time was 72 h. [h] The metal cat was $Cu(OAc)_2$ (5 mol%). [i]The *R*-BINOL(10 mol%) was added in presence of $Cu(OAc)_2$ (5 mol%). [j] Determined by GC-MS analysis. [k] Determined by chiral HPLC.

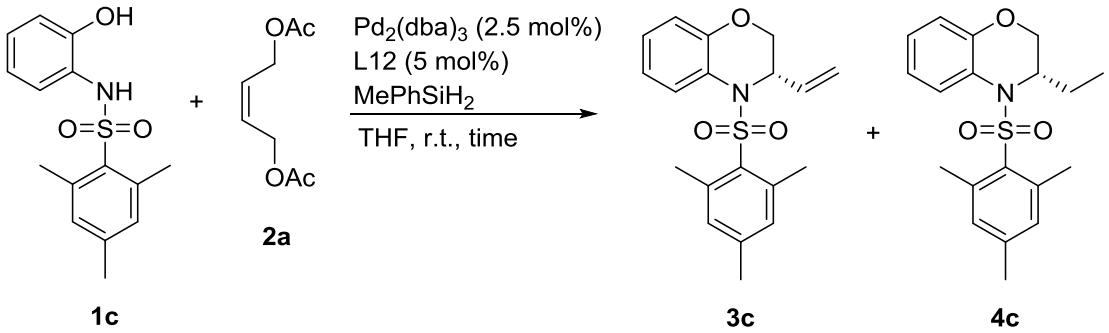
**Table S11. The influence of silane for asymmetric tandem allylic cyclization[a](4b).**




| Entry | Time | **3b:4b**[b] |
|---|---|---|
| 1 | 16 | 1:0.08 |
| 2 | 48 | 1:0.33 |
| 3 | 60 | 1:1.16 |
| 4 | 84 | >1:99 |
| 5 | 108 | 0:1 |

[a]The reaction was carried out at room temperature in THF by mixing $Pd_2(dba)_3$ (2.5 mol%) , $MePhSiH_2$ (3 eq.) and the chiral ligand (5 mol%). [b]Determined by GC-MS analysis.

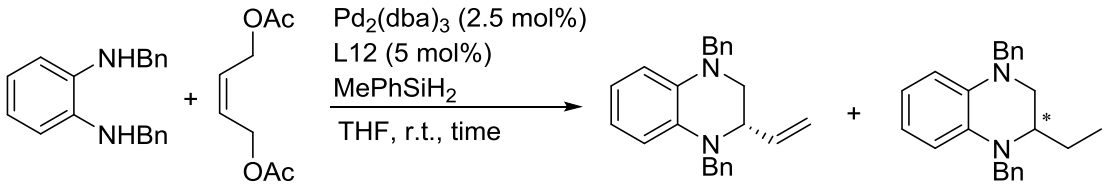
**Table S12. The influence of silane for asymmetric tandem allylic cyclization[a](4c).**




| entry | Time(h) | 3c:4c[c] |
|---|---|---|
| 1 | 12 | 1:0.07 |
| 2 | 36 | 1:2.9 |
| 3 | 60 | 1:3.3 |
| 4 | 88 | 1:3.1 |
| 5[b] | 144 | 0:1 |

[a] The reaction was carried out at room temperature in THF by mixing $Pd_2(dba)_3$ (2.5 mol%) , $MePhSiH_2$ (3 eq.) and the chiral ligand (5 mol%). [b] The $MePhSiH_2$ (4 eq) was used. [c] Determined by GC-MS analysis.

**Table S13. The influence of silane for asymmetric tandem allylic cyclization[a](4e).**

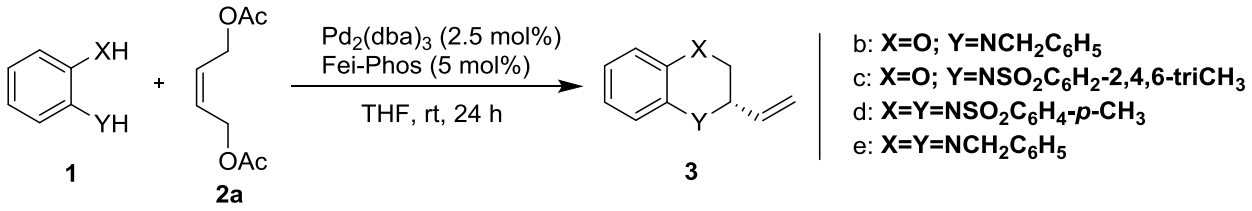


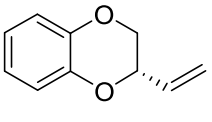

**1e** **2a** **3e** **4e**

| entry | Time(h) | 3e:4e[c] |
|---|---|---|
| 1 | 36 | 1:0 |
| 2 | 60 | 6.6:1 |
| 3 | 84 | 6.6:1 |
| 4 | 112 | 6.6:1 |
| 5[b] | 144 | 1:0 |

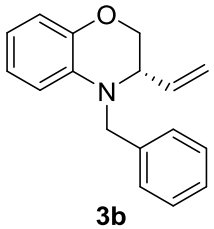
[a] The reaction was carried out at room temperature in THF by mixing $Pd_2(dba)_3$ (2.5 mol%) , $MePhSiH_2$ (3 eq.) and the chiral ligand (5 mol%). [b] The $MePhSiH_2$ (10 eq) was used. [c] Determined by GC-MS analysis.

## Scheme S1. Substrate scope (no additive)

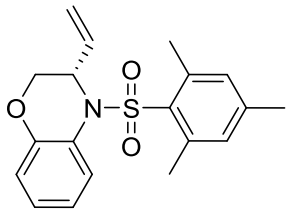


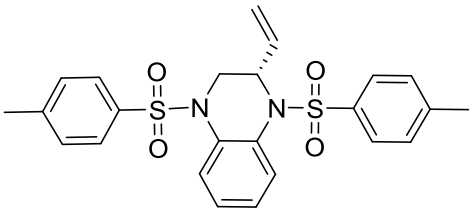
**3a**
60% yield, 39% *ee*



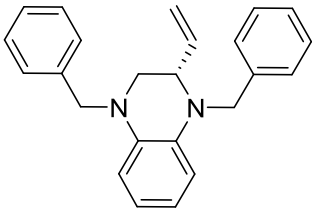
**3b**
90% yield, 35% *ee*



**3c**
67% yield, 7% *ee*

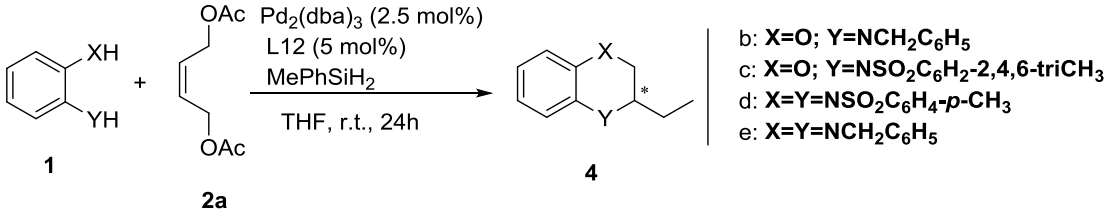


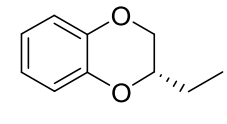
**3d**
90% yield, 15% *ee*



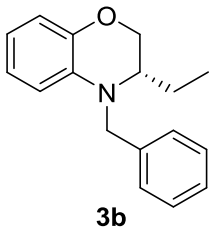
**3e**
70% yield, 27% *ee*

## Scheme S2. Reduced Substrate scope

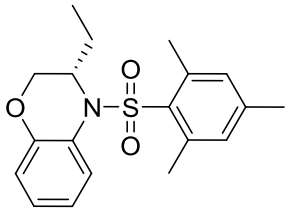


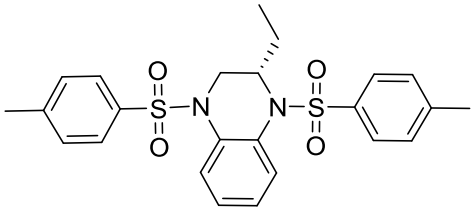
**3a**
99% yield, 45% *ee*



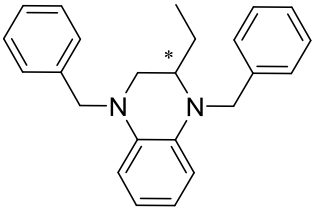
**3b**
76% yield, 46% *ee*



**3c**
88% yield, 11% *ee*

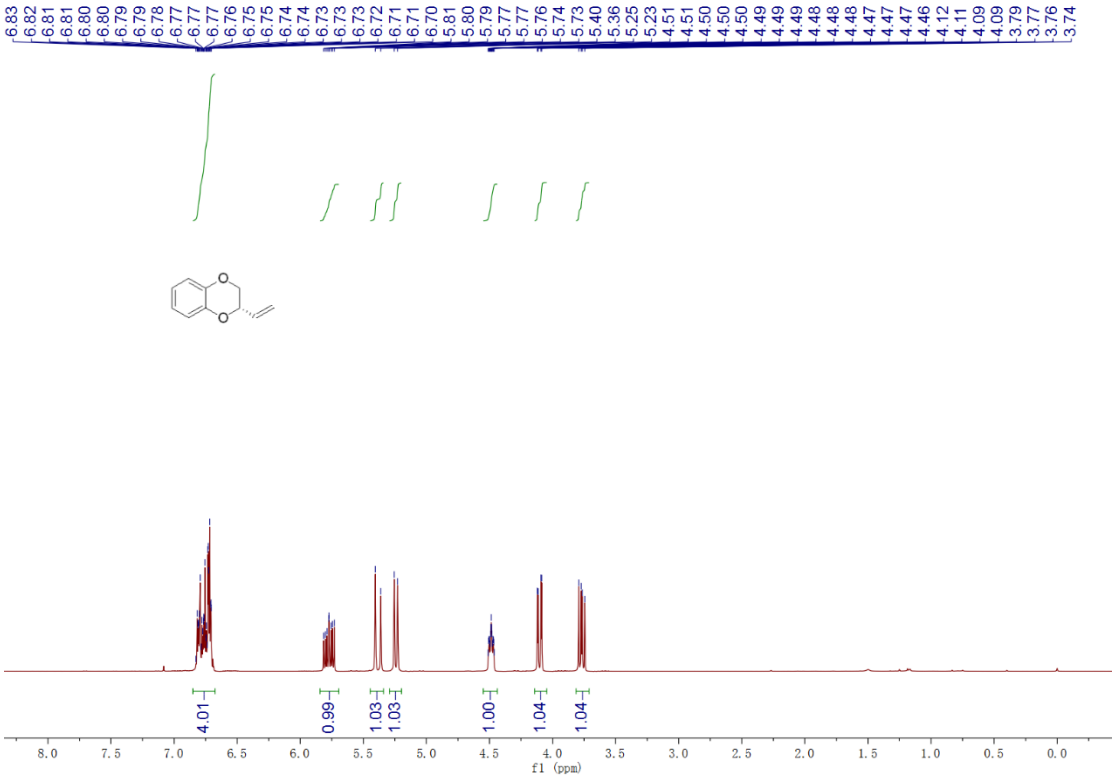


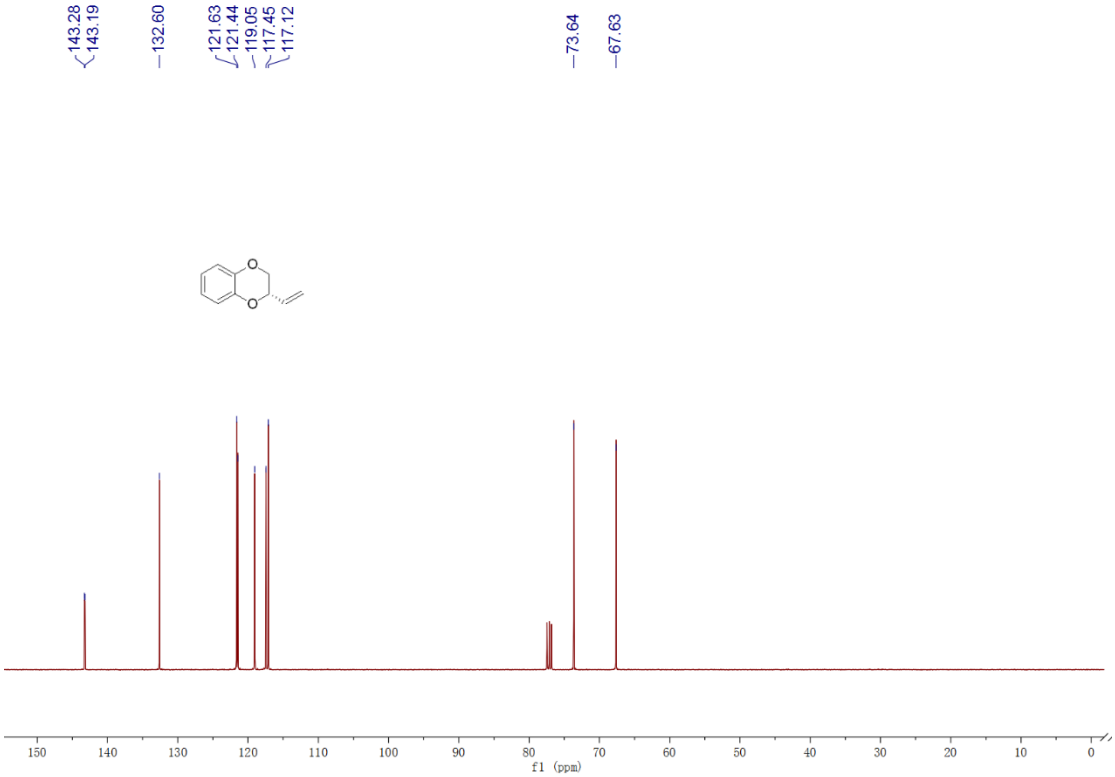
**3d**
97% yield, 15% *ee*

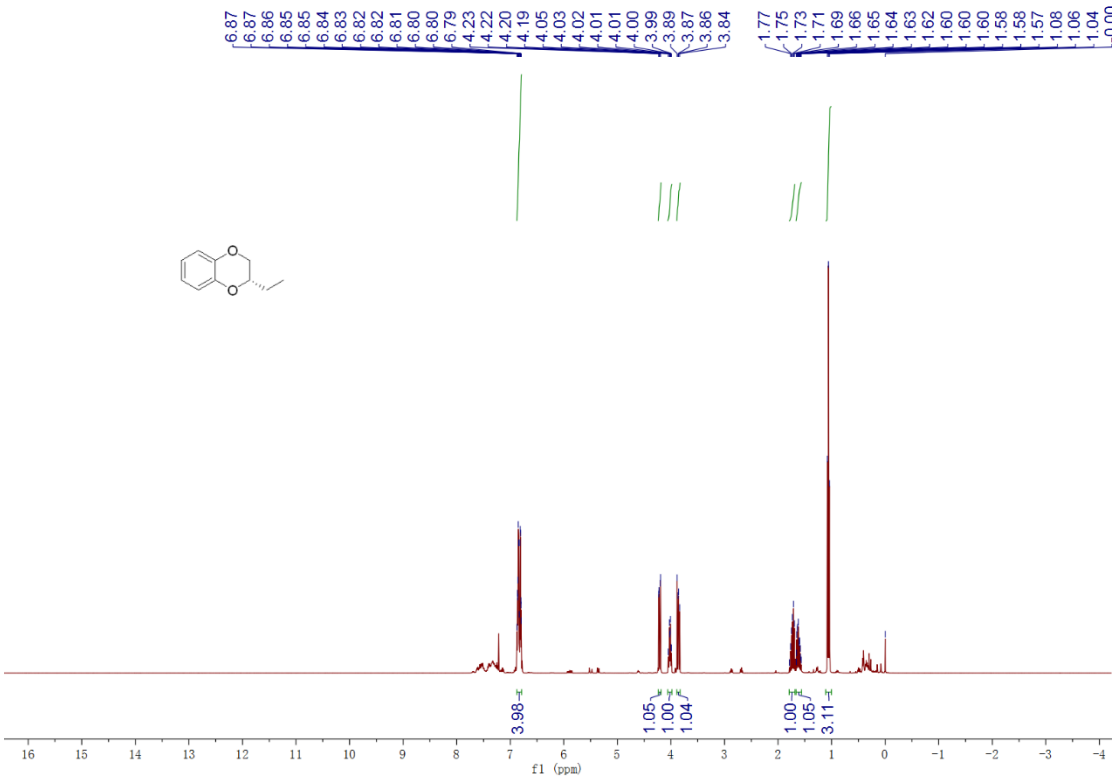


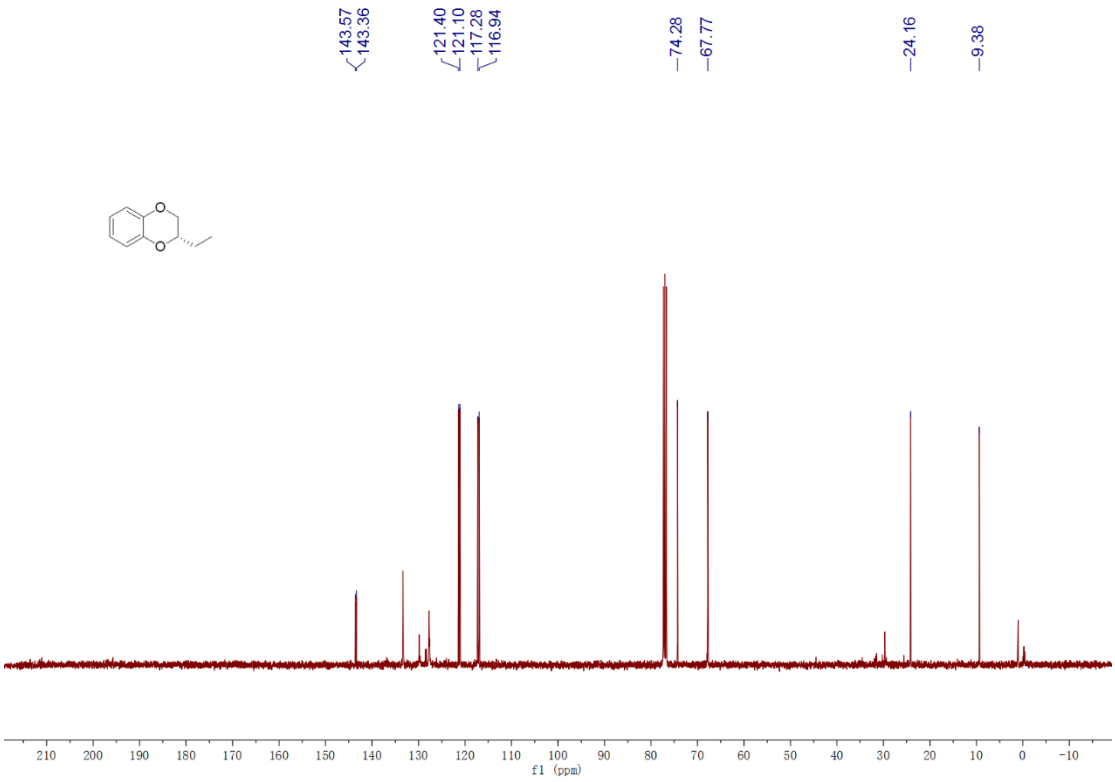
**3e**
n.r

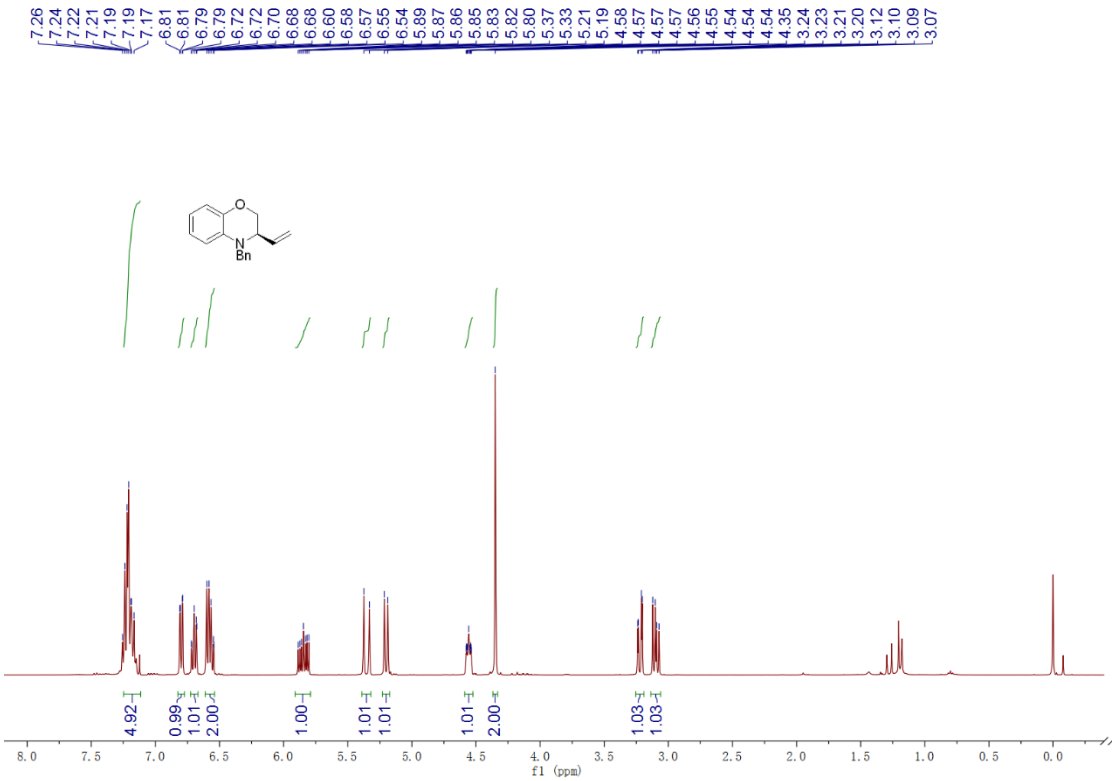
# 4. NMR Spectra

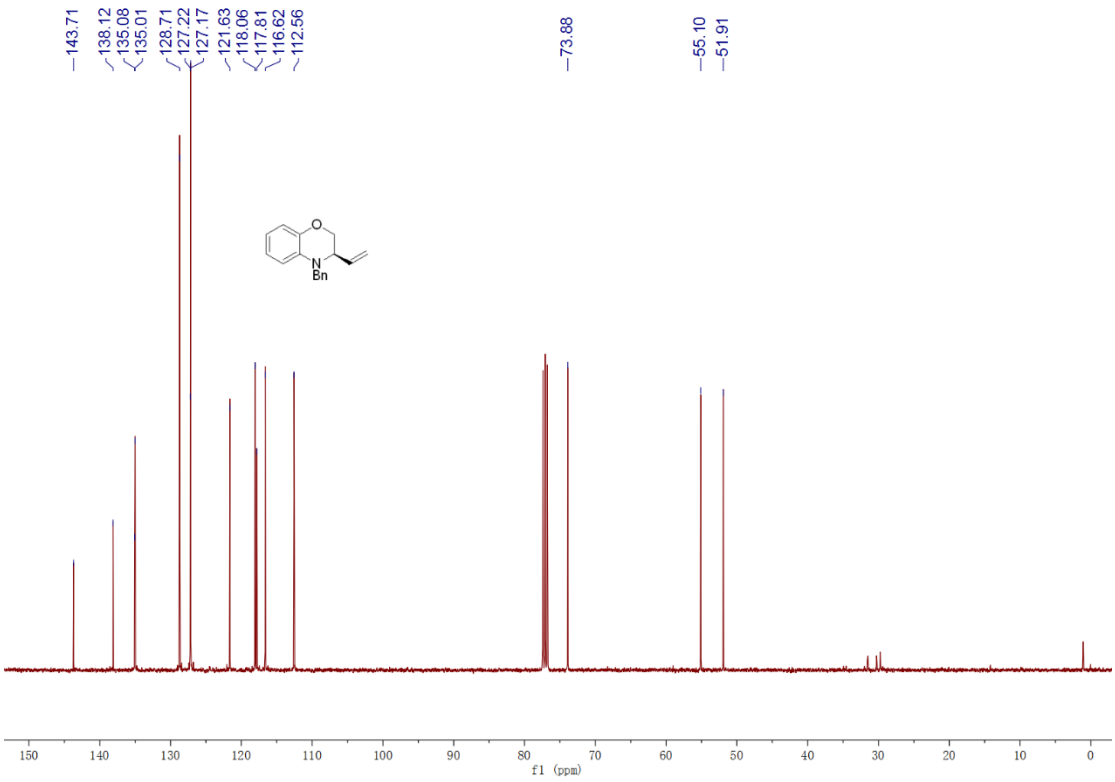


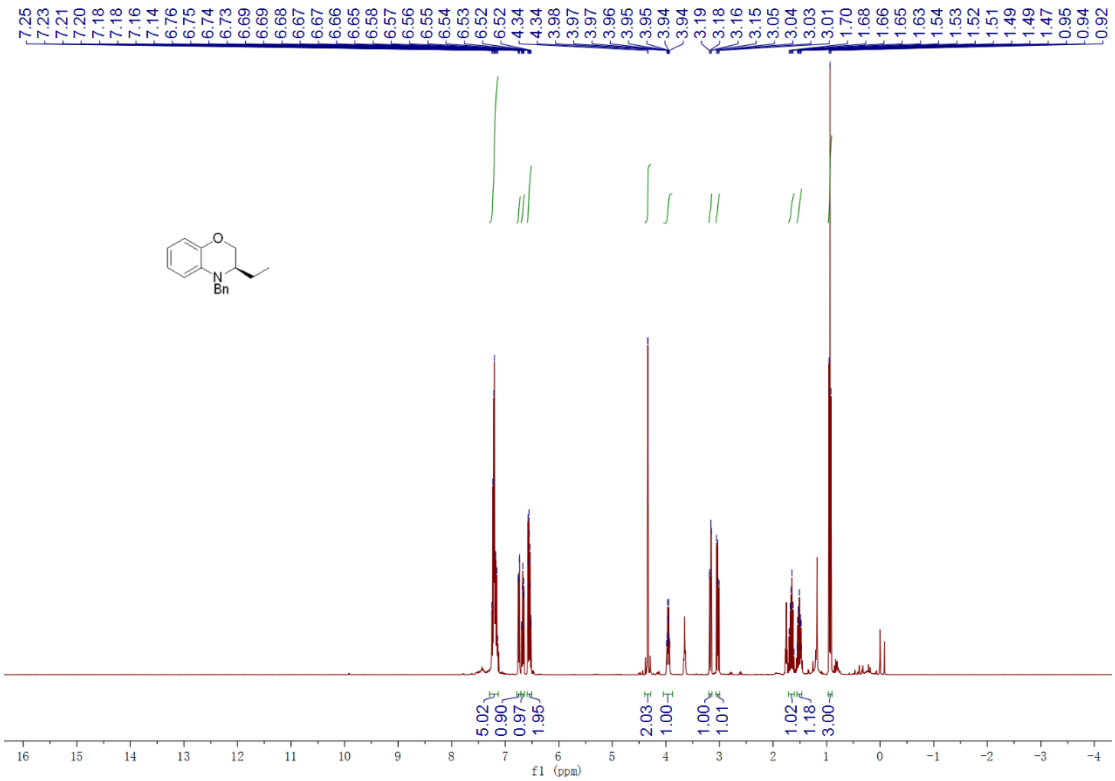



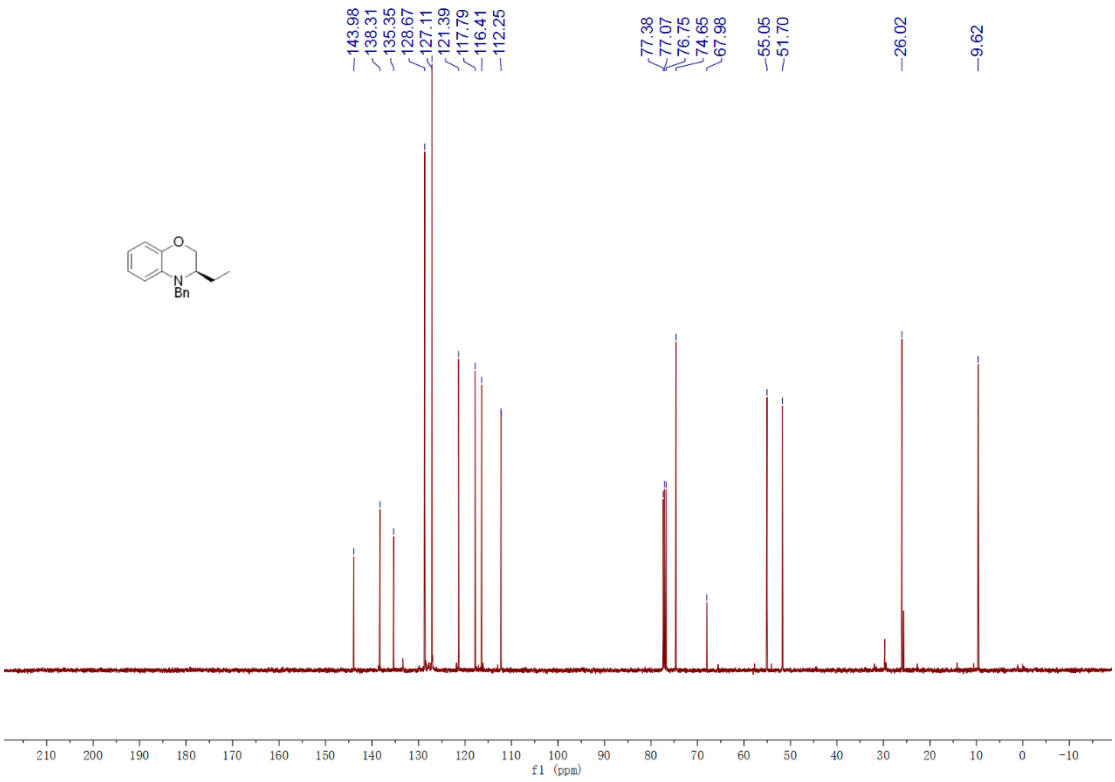

6.87
6.87
6.86
6.85
6.85
6.84
6.83
6.82
6.82
6.81
6.80
6.80
6.79
4.23
4.22
4.20
4.19
4.05
4.03
4.02
4.01
4.01
4.00
3.99
3.89
3.87
3.86
3.84
1.77
1.75
1.73
1.71
1.69
1.66
1.65
1.64
1.63
1.62
1.60
1.60
1.60
1.58
1.58
1.57
1.08
1.06
1.04
3.98
1.05
1.00
1.04
1.00
1.05
3.11
f1 (ppm)

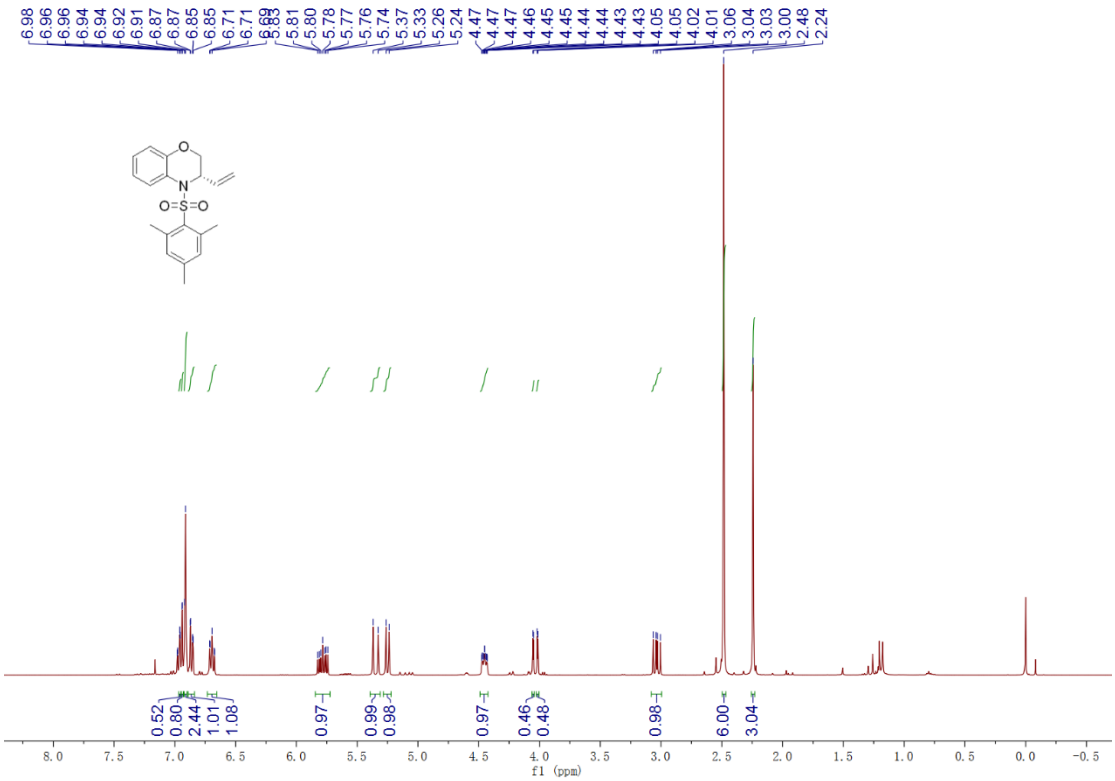

143.57
143.36
121.40
121.10
117.28
116.94
74.28
67.77
24.16
9.38
f1 (ppm)

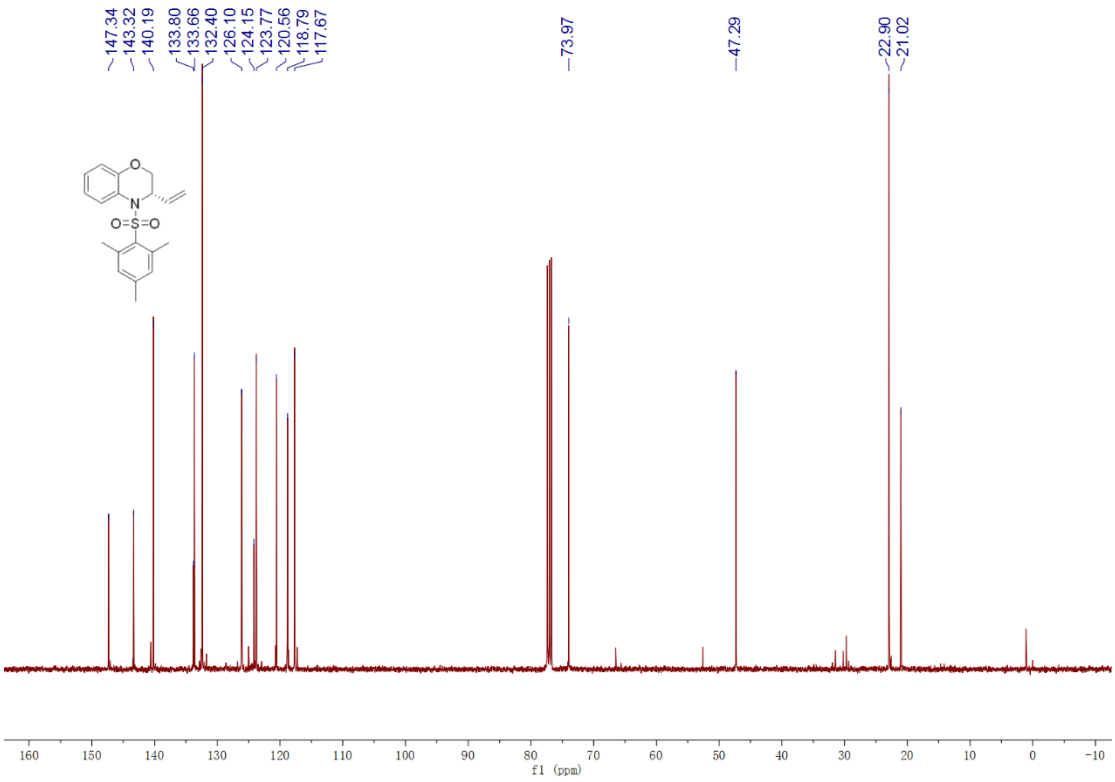

7.26
7.24
7.22
7.21
7.19
7.19
7.17
6.81
6.81
6.79
6.79
6.72
6.72
6.70
6.68
6.68
6.60
6.58
6.57
6.55
6.54
5.89
5.87
5.86
5.85
5.83
5.82
5.80
5.37
5.33
5.21
5.19
4.58
4.57
4.57
4.57
4.56
4.55
4.54
4.54
4.54
4.35
3.24
3.23
3.21
3.20
3.12
3.10
3.09
3.07
O
N
Bn
4.92
0.99
1.01
2.00
1.00
1.01
1.01
1.01
2.00
1.03
1.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

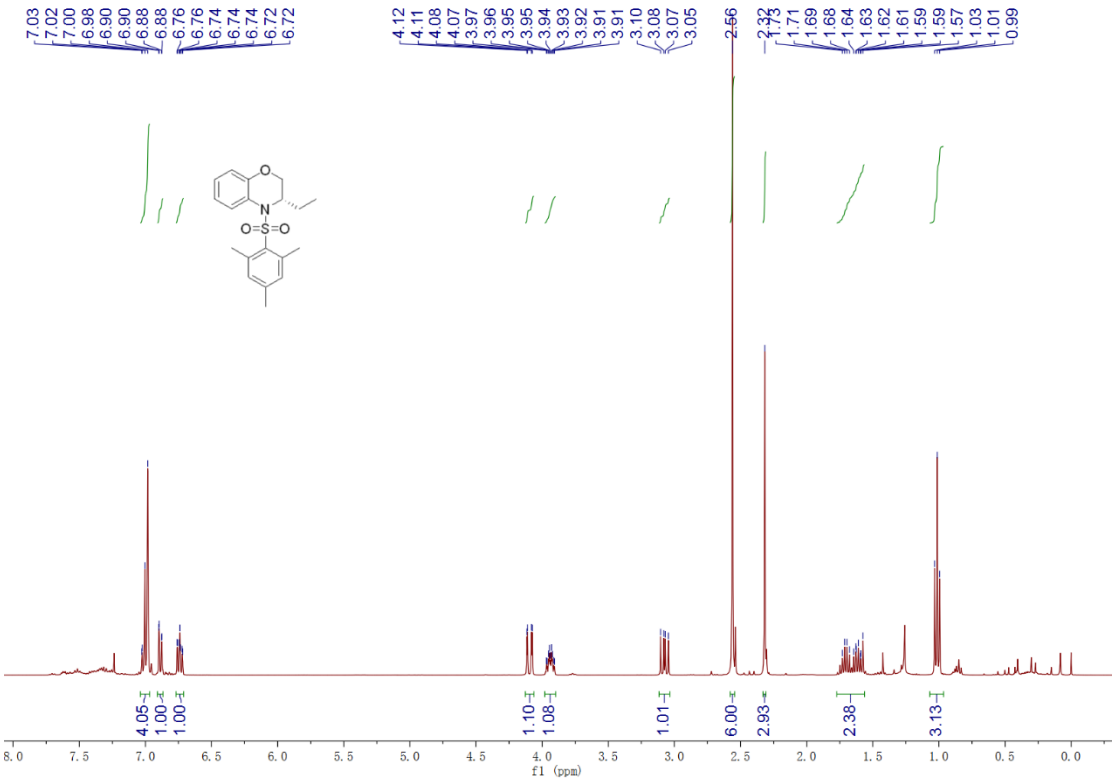

143.71
138.12
135.08
135.01
128.71
127.22
127.17
121.63
118.06
117.81
116.62
112.56
73.88
55.10
51.91
O
N
Bn
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

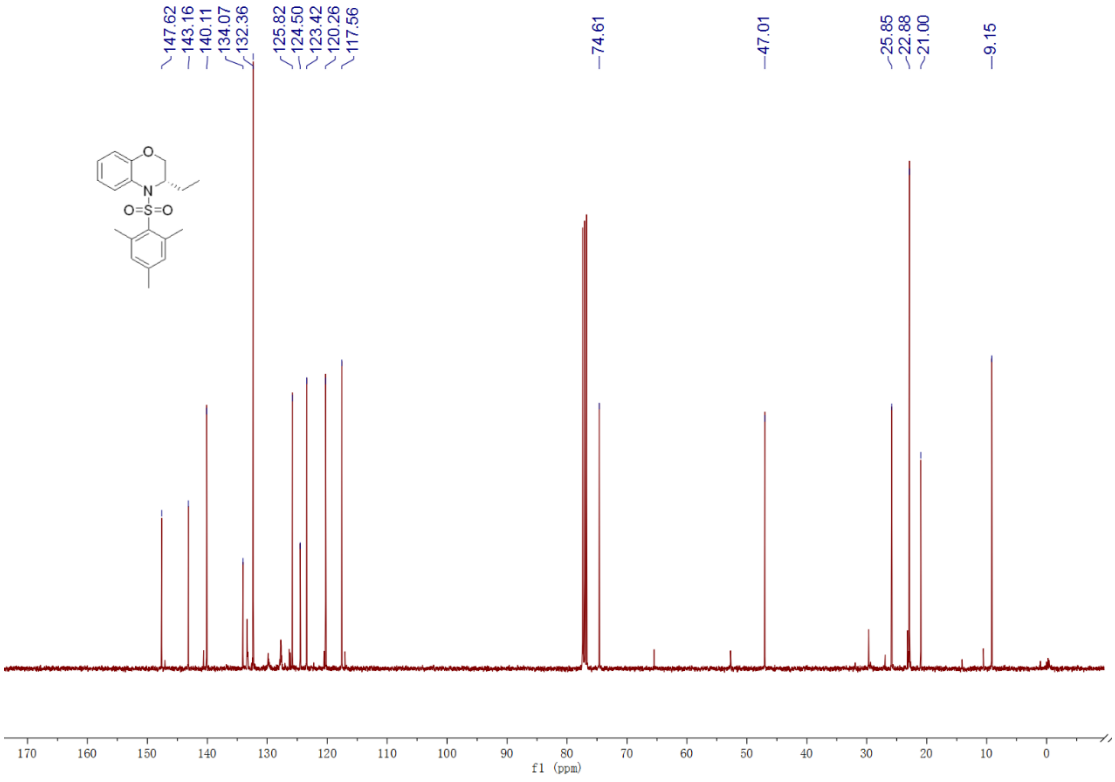

7.25
7.23
7.21
7.20
7.18
7.18
7.16
7.14
6.76
6.75
6.74
6.73
6.69
6.69
6.68
6.67
6.67
6.66
6.65
6.58
6.57
6.56
6.55
6.54
6.53
6.52
6.52
4.34
4.34
3.98
3.97
3.97
3.96
3.95
3.95
3.94
3.94
3.19
3.18
3.16
3.15
3.05
3.04
3.03
3.01
1.70
1.68
1.66
1.65
1.63
1.54
1.53
1.52
1.51
1.49
1.49
1.47
0.95
0.94
0.92
O
N
Bn
5.02
0.90
0.97
1.95
2.03
1.00
1.00
1.01
1.02
1.18
3.00
f1 (ppm)

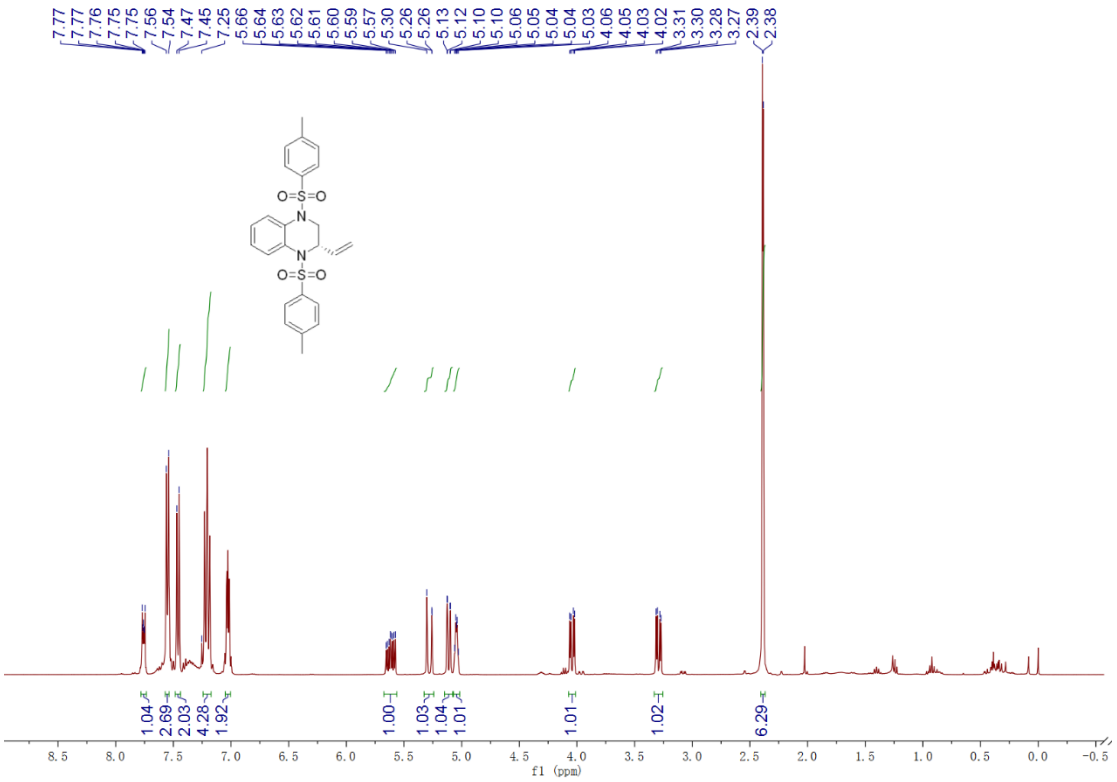

143.98
138.31
135.35
128.67
127.11
121.39
117.79
116.41
112.25
77.38
77.07
76.75
74.65
67.98
55.05
51.70
26.02
9.62
O
N
Bn
f1 (ppm)

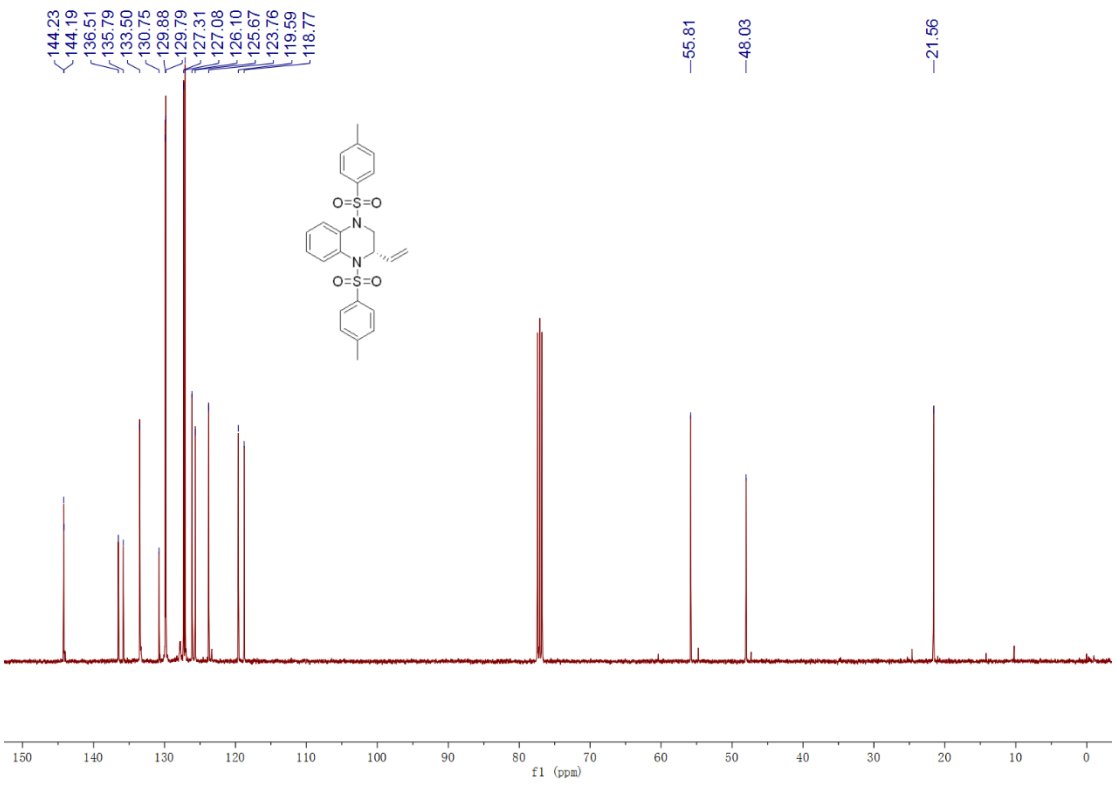

6.98
6.96
6.96
6.94
6.94
6.92
6.91
6.87
6.87
6.85
6.85
6.71
6.71
6.69
5.83
5.81
5.80
5.78
5.77
5.76
5.74
5.37
5.33
5.26
5.24
4.47
4.47
4.47
4.46
4.45
4.45
4.44
4.44
4.43
4.43
4.05
4.05
4.02
4.01
3.06
3.04
3.03
3.00
2.48
2.24
O
N
O=S=O
0.52
0.80
2.44
1.01
1.08
0.97
0.99
0.98
0.97
0.46
0.48
0.98
6.00
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

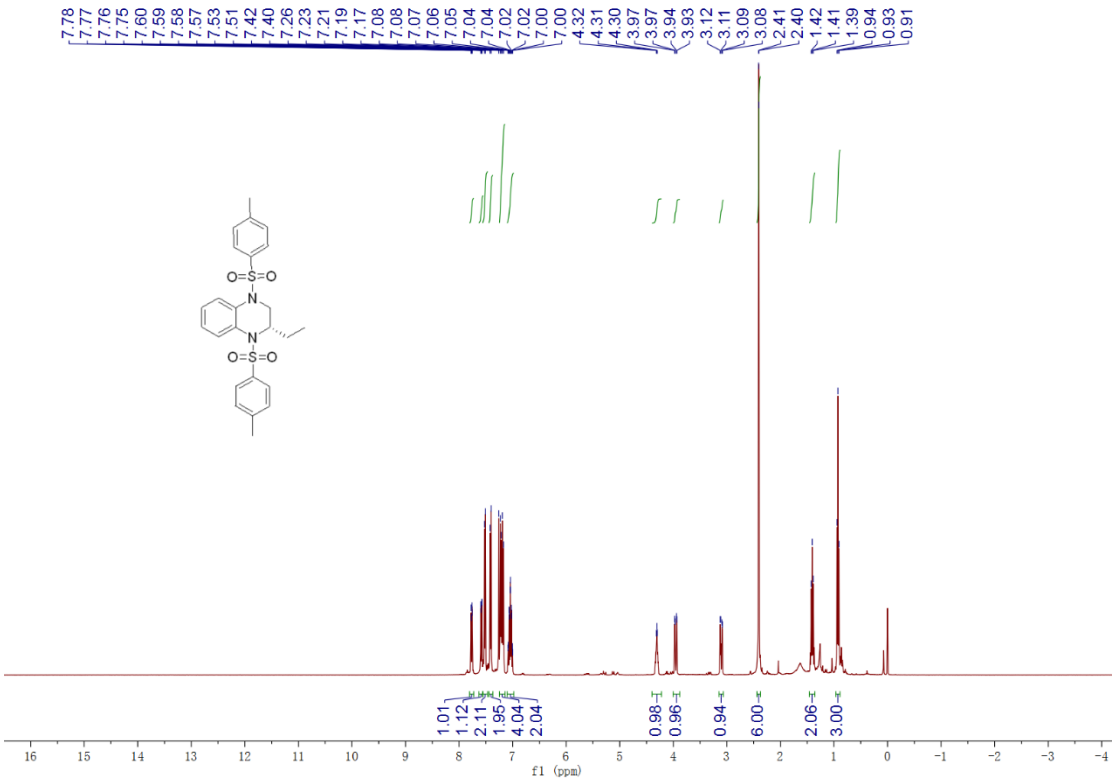

147.34
143.32
140.19
133.80
133.66
132.40
126.10
124.15
123.77
120.56
118.79
117.67
73.97
47.29
22.90
21.02
O
N
O=S=O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

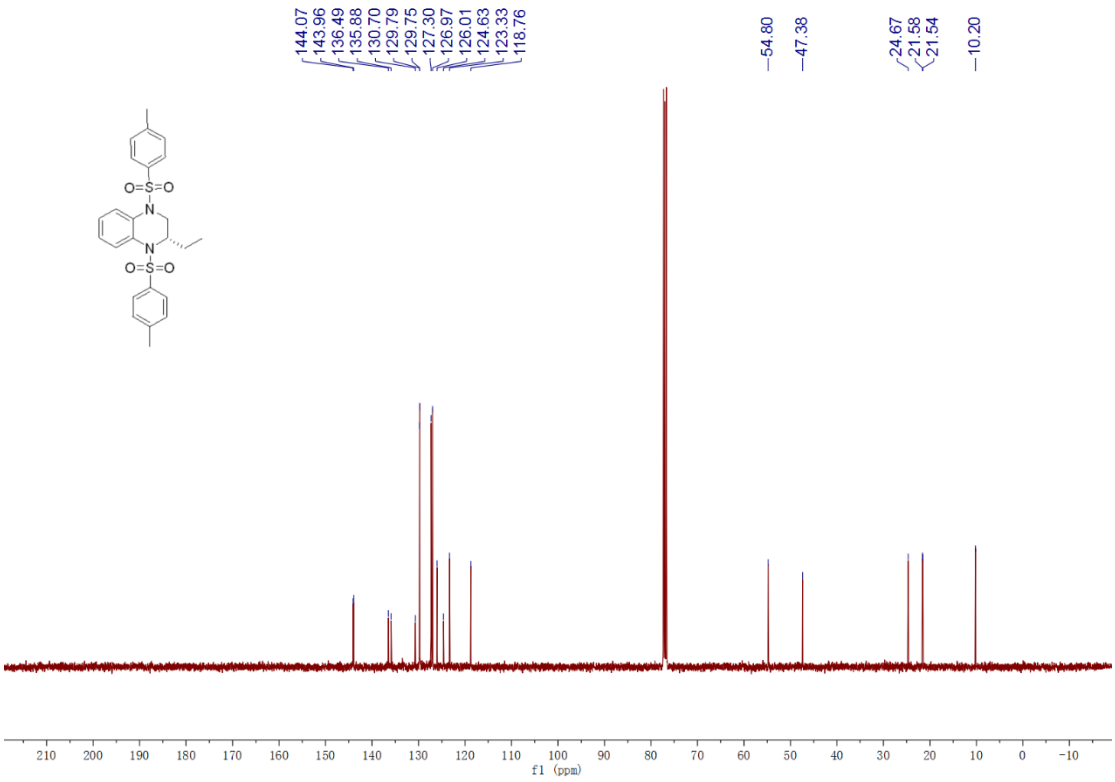

7.03
7.02
7.00
6.98
6.90
6.90
6.88
6.88
6.76
6.76
6.74
6.74
6.74
6.72
6.72
4.12
4.11
4.08
4.07
3.97
3.96
3.95
3.95
3.94
3.93
3.92
3.91
3.91
3.10
3.08
3.07
3.05
2.56
1.73
1.71
1.69
1.68
1.64
1.63
1.62
1.61
1.59
1.59
1.57
1.03
1.01
0.99
4.05
1.00
1.00
1.10
1.08
1.01
6.00
2.93
2.38
3.13
f1 (ppm)

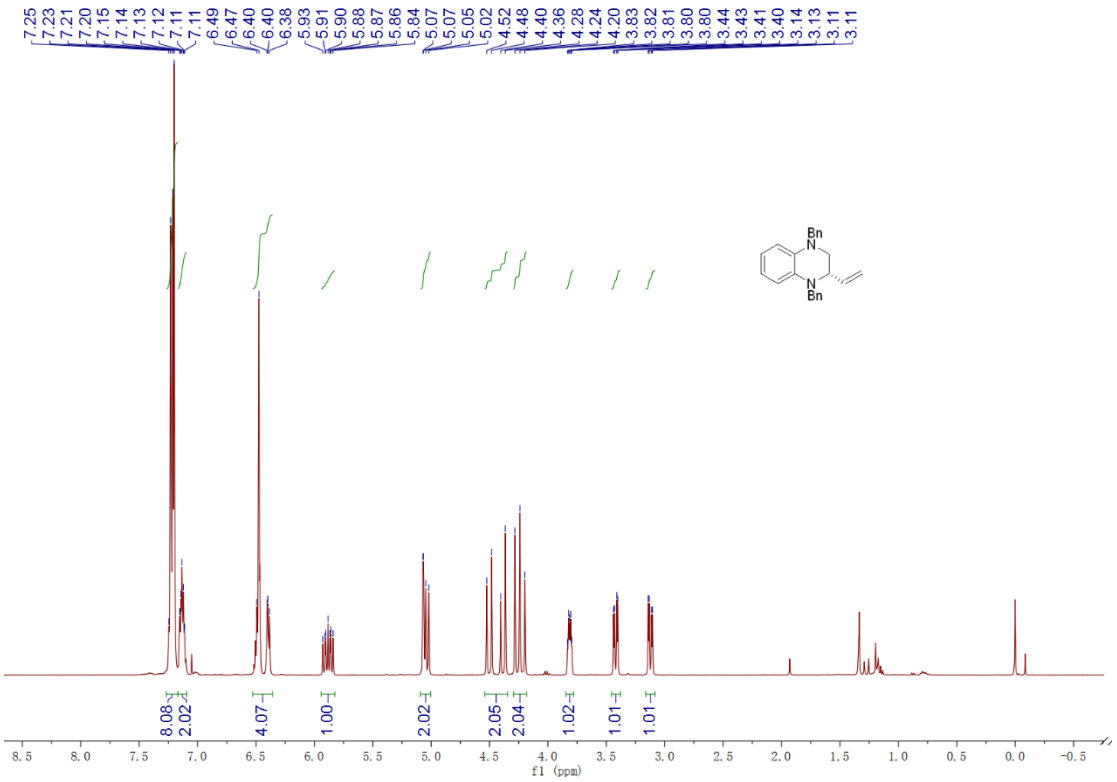

147.62
143.16
140.11
134.07
132.36
125.82
124.50
123.42
120.26
117.56
74.61
47.01
25.85
22.88
21.00
9.15
f1 (ppm)

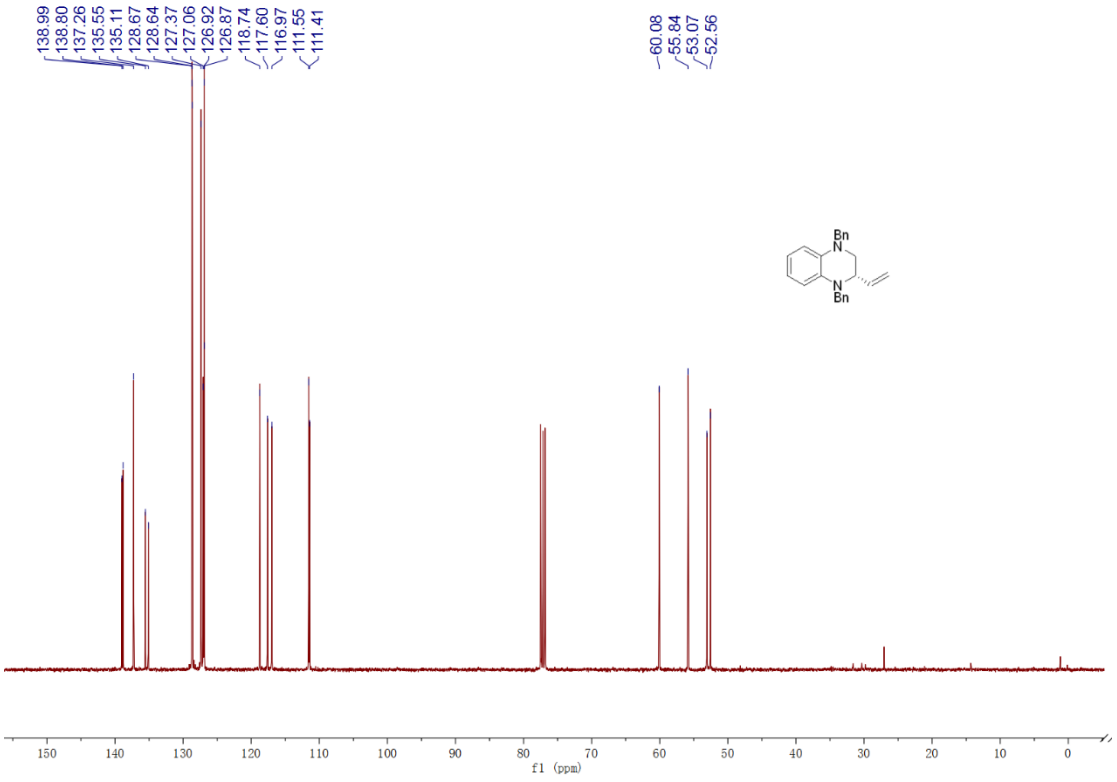

7.77
7.77
7.76
7.75
7.75
7.56
7.54
7.47
7.45
7.25
5.66
5.64
5.63
5.62
5.61
5.60
5.59
5.57
5.30
5.26
5.26
5.13
5.12
5.10
5.10
5.06
5.05
5.04
5.04
5.03
4.06
4.05
4.03
4.02
3.31
3.30
3.28
3.27
2.39
2.38
O=S=O
N
N
O=S=O
1.04
2.69
2.03
4.28
1.92
1.00
1.03
1.04
1.01
1.01
1.02
6.29
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


144.23
144.19
136.51
135.79
133.50
130.75
129.88
129.79
127.31
127.08
126.10
125.67
123.76
119.59
118.77
55.81
48.03
21.56
O=S=O
N
N
O=S=O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

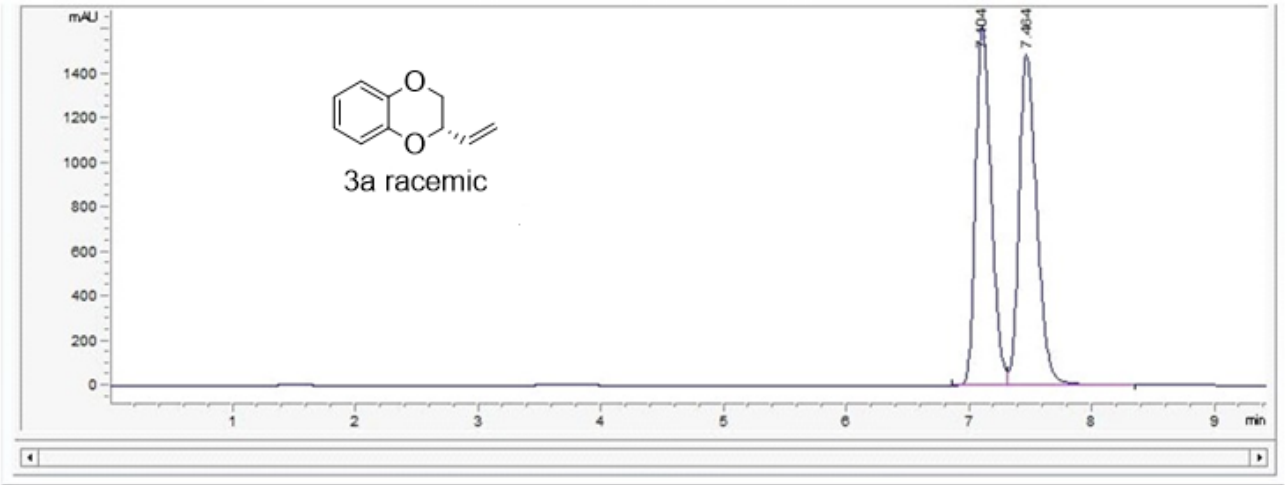

7.78
7.77
7.76
7.75
7.60
7.59
7.58
7.57
7.53
7.51
7.42
7.40
7.26
7.23
7.21
7.19
7.17
7.08
7.08
7.07
7.06
7.05
7.04
7.04
7.02
7.02
7.00
7.00
4.32
4.31
4.30
3.97
3.97
3.94
3.93
3.12
3.11
3.09
3.08
2.41
2.40
1.42
1.41
1.39
0.94
0.93
0.91
1.01
1.12
2.11
1.95
4.04
2.04
0.98
0.96
0.94
6.00
2.06
3.00
f1 (ppm)


144.07
143.96
136.49
135.88
130.70
129.79
129.75
127.30
126.97
126.01
124.63
123.33
118.76
54.80
47.38
24.67
21.58
21.54
10.20
f1 (ppm)

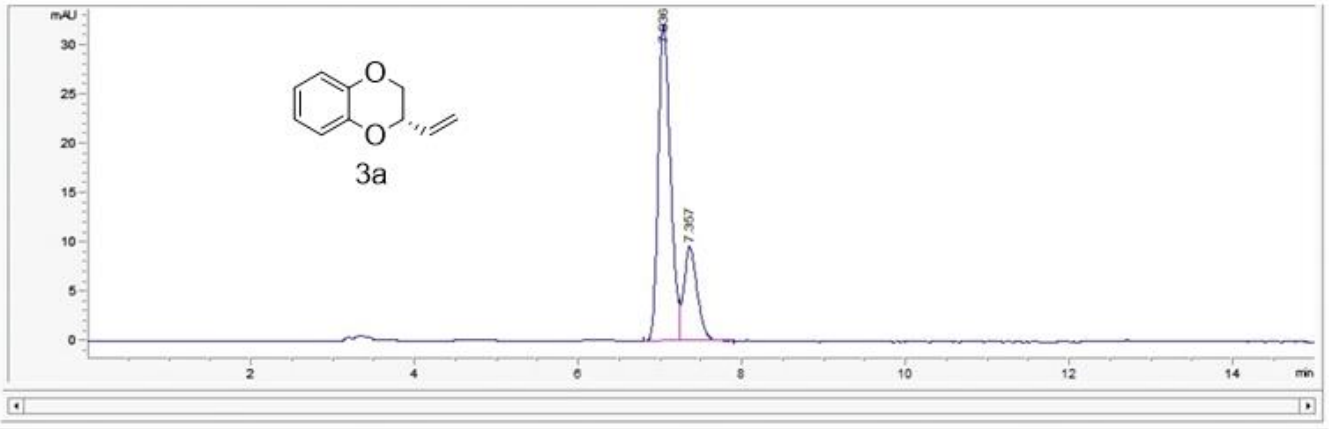

7.25
7.23
7.21
7.20
7.15
7.14
7.13
7.12
7.11
7.11
6.49
6.47
6.40
6.40
6.38
5.93
5.91
5.90
5.88
5.87
5.86
5.84
5.07
5.07
5.05
5.02
4.52
4.48
4.40
4.36
4.28
4.24
4.20
3.83
3.82
3.81
3.80
3.80
3.44
3.43
3.41
3.40
3.14
3.13
3.11
3.11
Bn
N
N
Bn
8.08
2.02
4.07
1.00
2.02
2.05
2.04
1.02
1.01
1.01
f1 (ppm)


138.99
138.80
137.26
135.55
135.11
128.67
128.64
127.37
127.06
126.92
126.87
118.74
117.60
116.97
111.55
111.41
60.08
55.84
53.07
52.56
Bn
N
N
Bn
f1 (ppm)

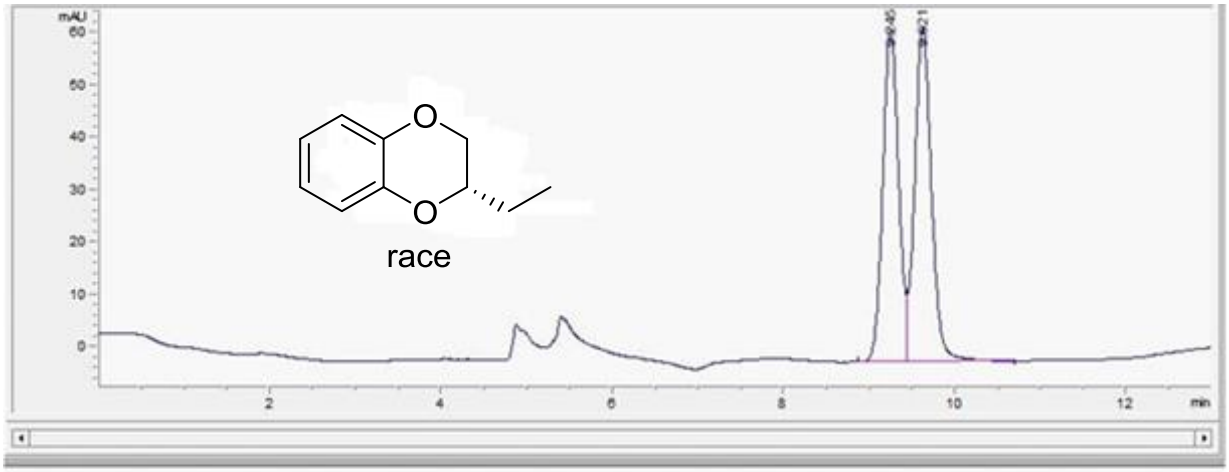
## 5. HPLC Spectra



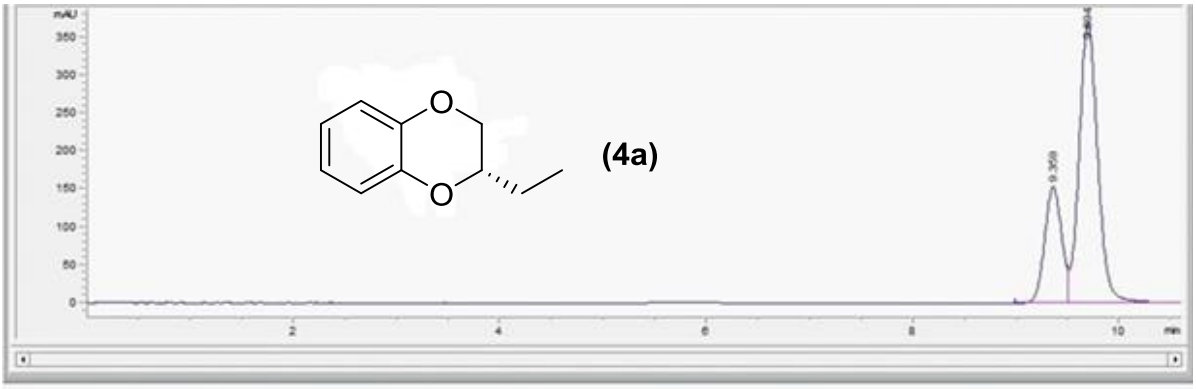

| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 7.104 | 14263.4 | 1608.6 | 0.1394 | 0.701 | 49.050 |
| 2 | 7.464 | 14815.8 | 1487.2 | 0.1522 | 0.649 | 50.950 |



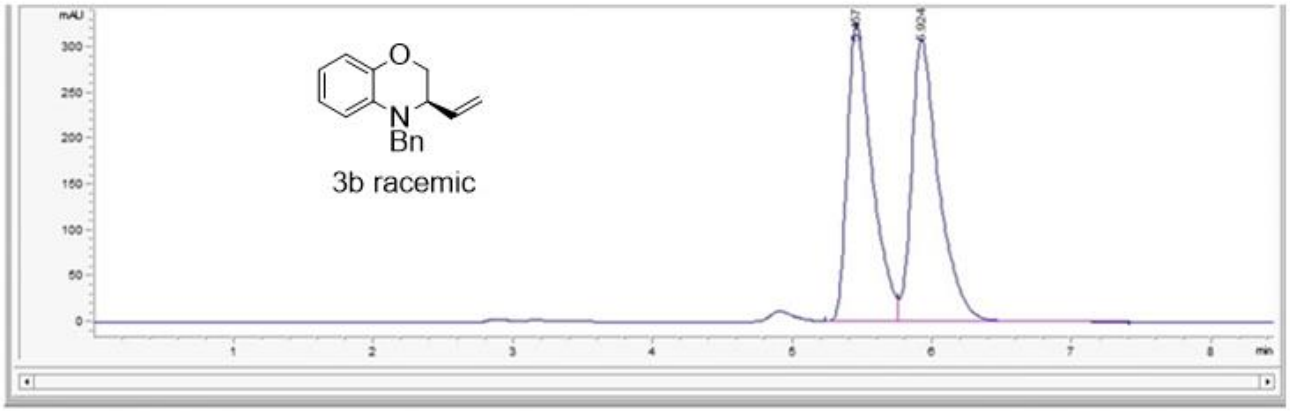

| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 7.036 | 335.8 | 32.2 | 0.1598 | 0.722 | 75.645 |
| 2 | 7.357 | 108.1 | 9.6 | 0.1699 | 0.718 | 24.355 |



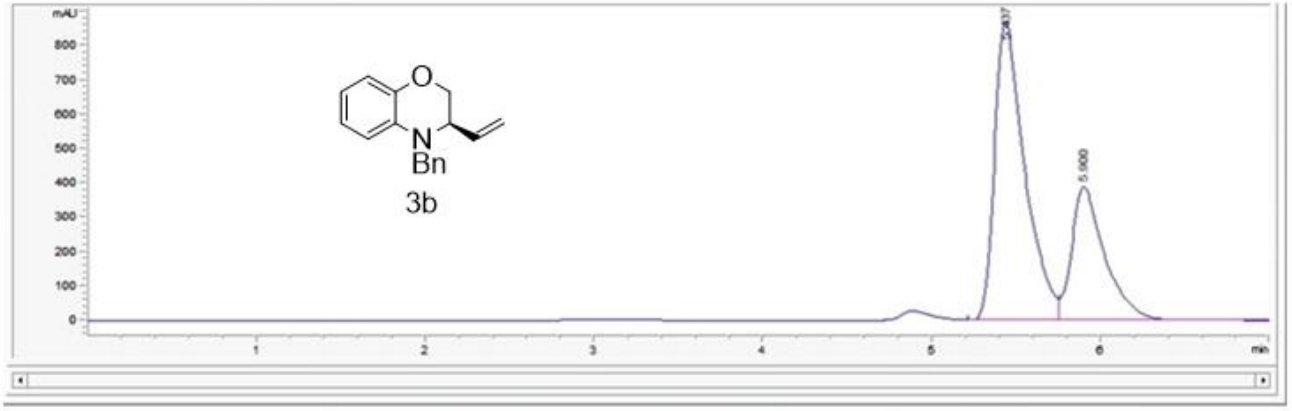

| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 9.245 | 813.3 | 63.6 | 0.1973 | 0.913 | 48.230 |
| 2 | 9.621 | 872.9 | 64 | 0.209 | 0.841 | 51.770 |



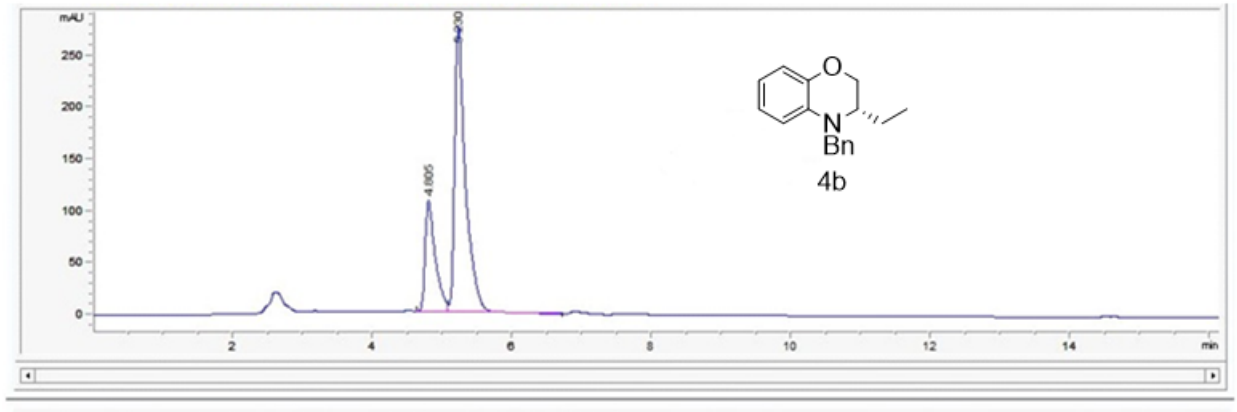

| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 9.359 | 1753 | 153.2 | 0.1775 | 0.966 | 27.478 |
| 2 | 9.694 | 4626.6 | 369.9 | 0.1919 | 0.818 | 72.522 |



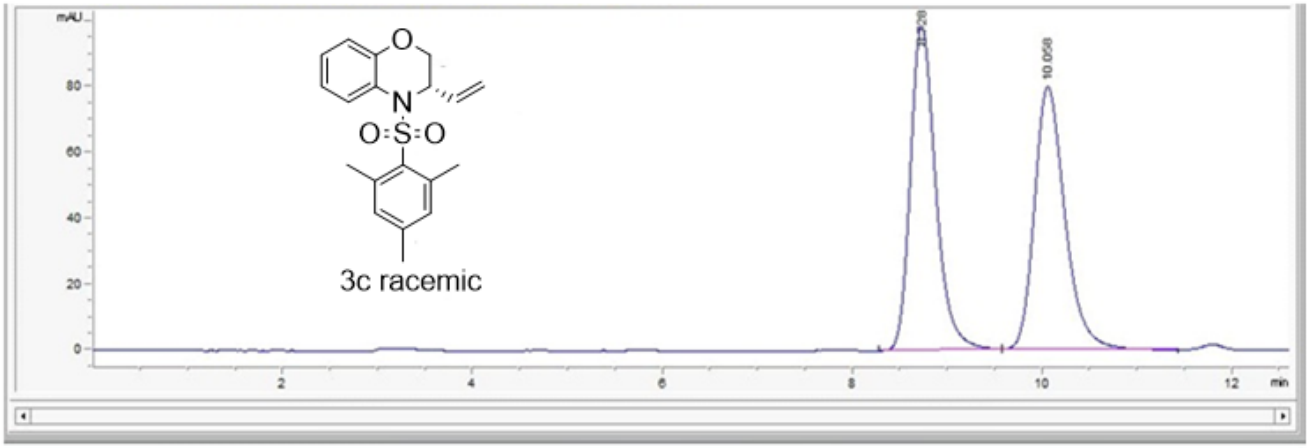

| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 5.457 | 4016.2 | 326.2 | 0.1817 | 0.539 | 49.043 |
| 2 | 5.924 | 4173 | 308.8 | 0.1977 | 0.531 | 50.957 |



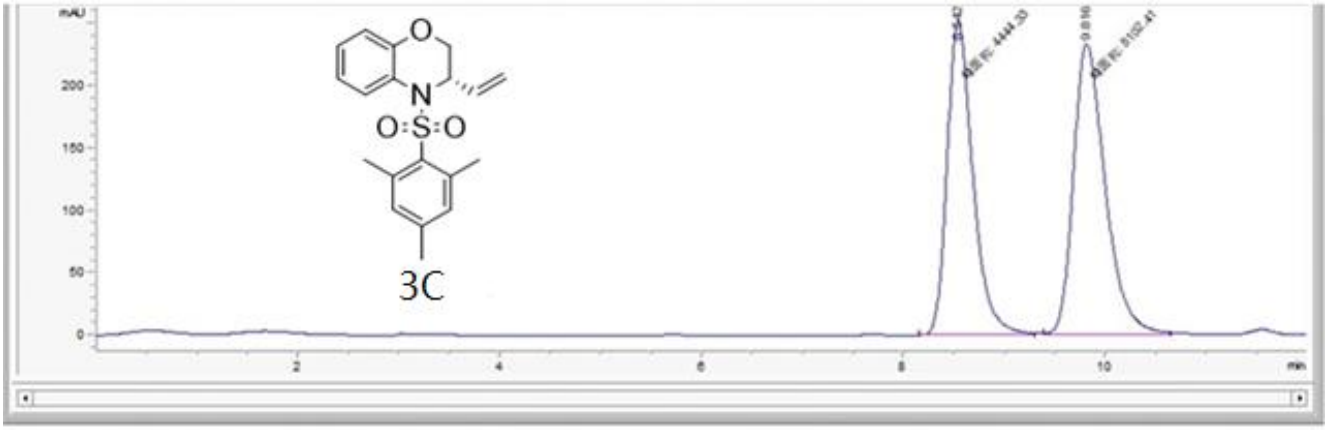

| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 5.437 | 10808.5 | 869.1 | 0.1831 | 0.526 | 67.038 |
| 2 | 5.9 | 5314.6 | 388.2 | 0.1997 | 0.54 | 32.962 |



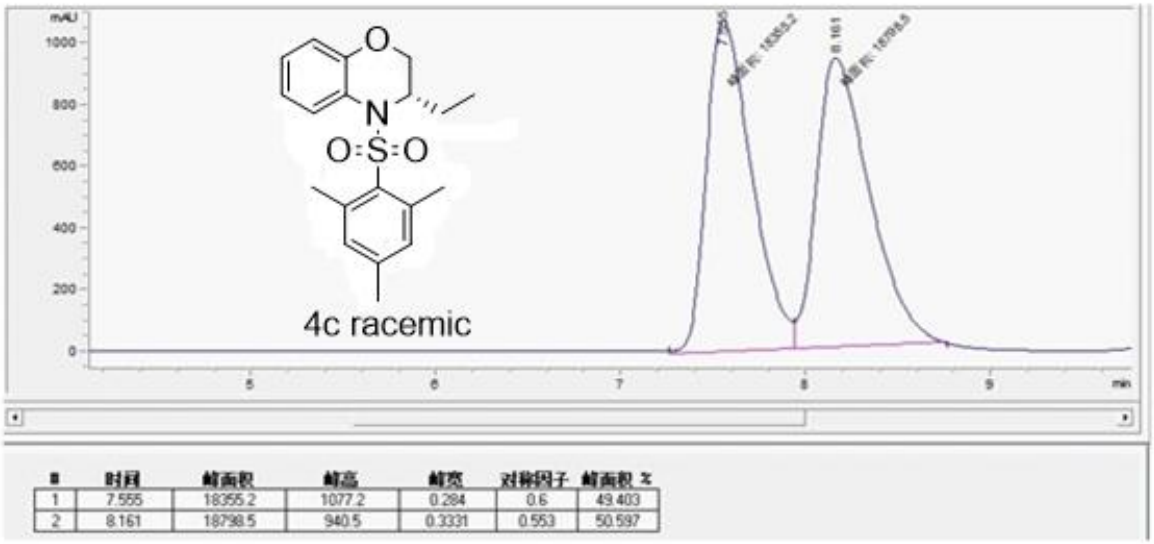

| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 4.805 | 1098.2 | 107.5 | 0.1472 | 0.477 | 26.812 |
| 2 | 5.23 | 2997.7 | 276.7 | 0.1544 | 0.456 | 73.188 |



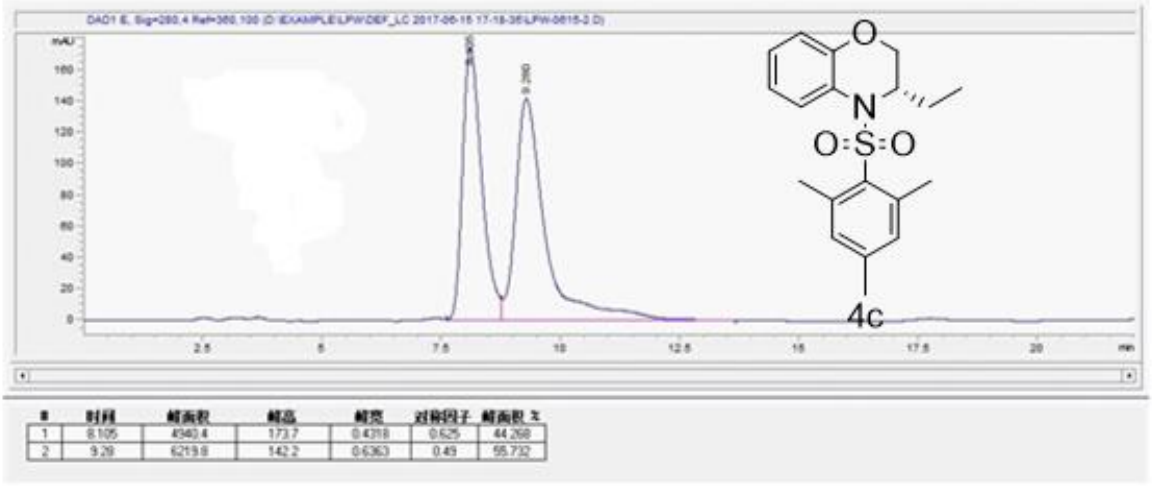

| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 8.728 | 1798 | 98.4 | 0.2792 | 0.738 | 50.051 |
| 2 | 10.058 | 1794.4 | 79.9 | 0.344 | 0.725 | 49.949 |



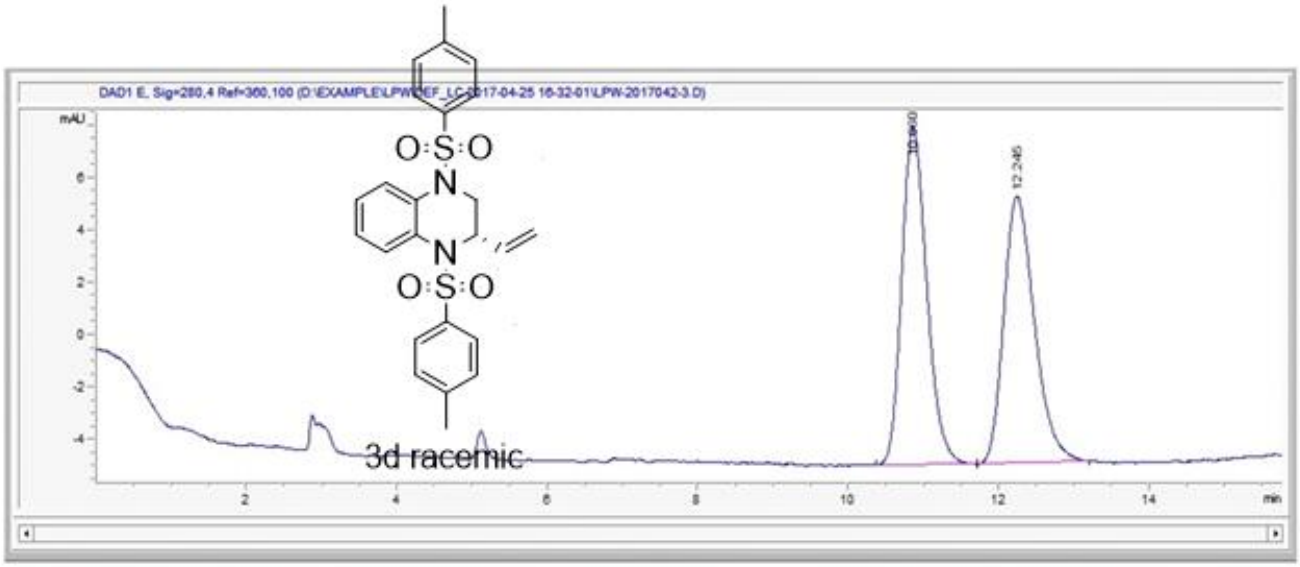

| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 8.542 | 4444.3 | 250.7 | 0.2955 | 0.7 | 46.553 |
| 2 | 9.816 | 5102.4 | 232.6 | 0.3656 | 0.676 | 53.447 |



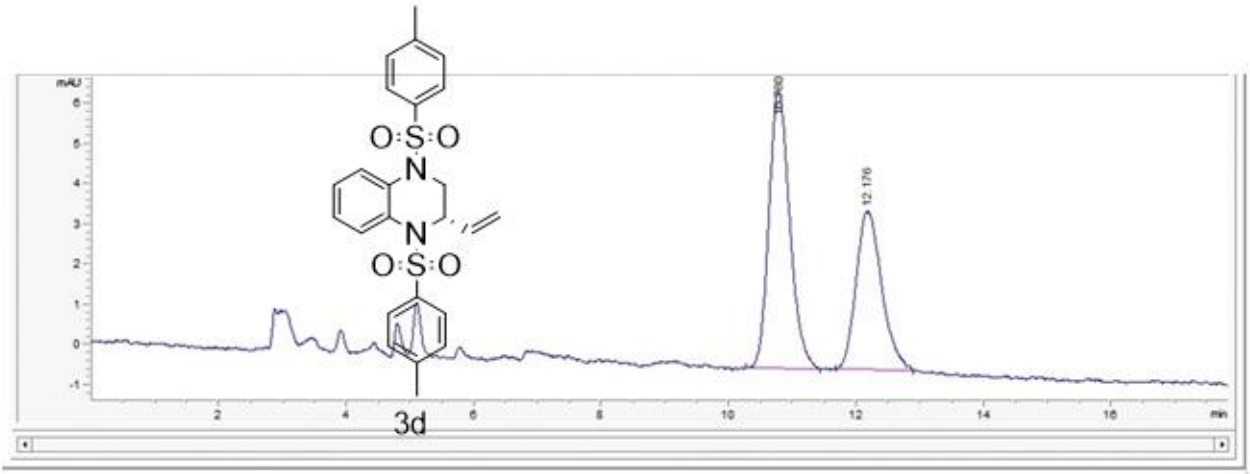

| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 7.555 | 18355.2 | 1077.2 | 0.284 | 0.6 | 49.403 |
| 2 | 8.161 | 18798.5 | 940.5 | 0.3331 | 0.553 | 50.597 |



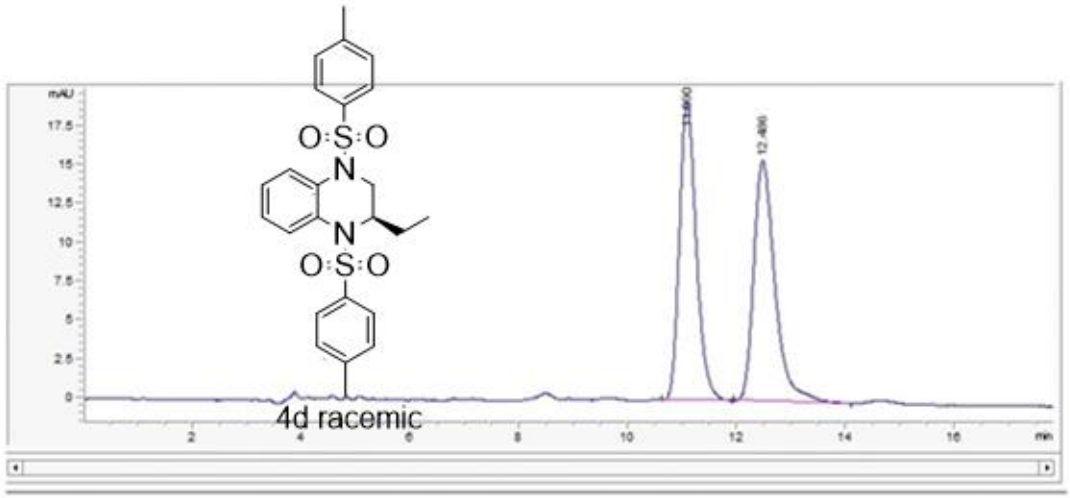

| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 8.105 | 4940.4 | 173.7 | 0.4318 | 0.625 | 44.268 |
| 2 | 9.29 | 6219.8 | 142.2 | 0.6363 | 0.49 | 55.732 |



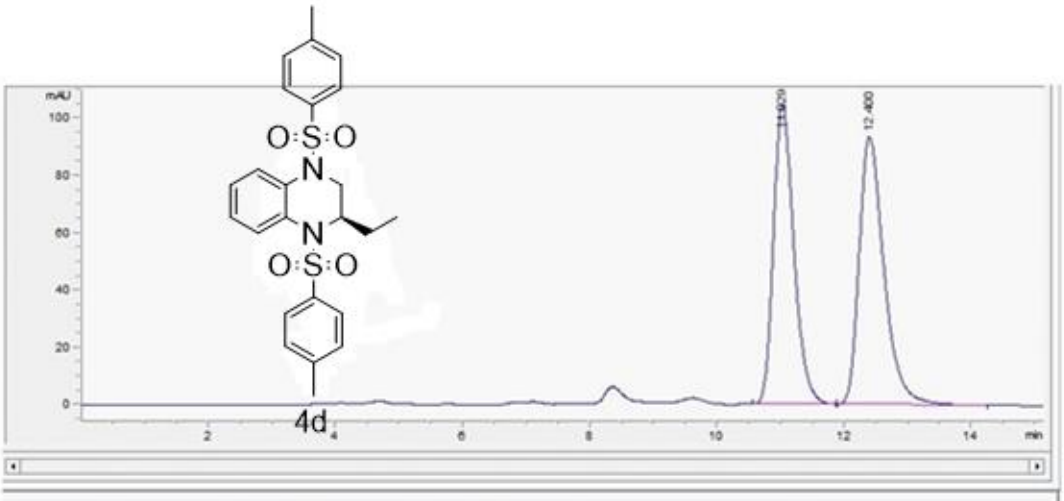

| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 10.86 | 297.8 | 12.9 | 0.3582 | 0.765 | 50.647 |
| 2 | 12.245 | 290.2 | 10.2 | 0.4257 | 0.725 | 49.353 |



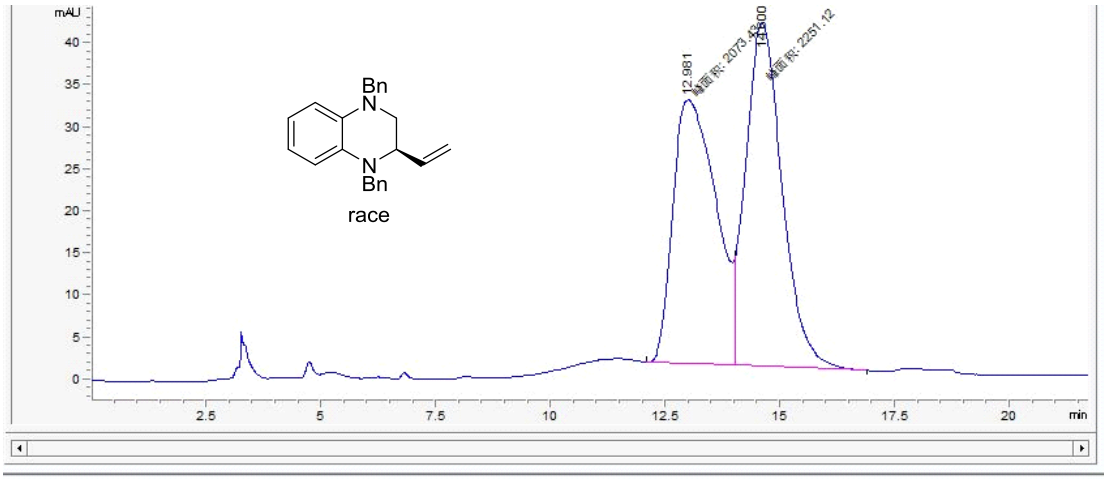

| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 10.78 | 157.4 | 6.9 | 0.33 | 0.796 | 58.644 |
| 2 | 12.176 | 111 | 4 | 0.3655 | 0.754 | 41.356 |



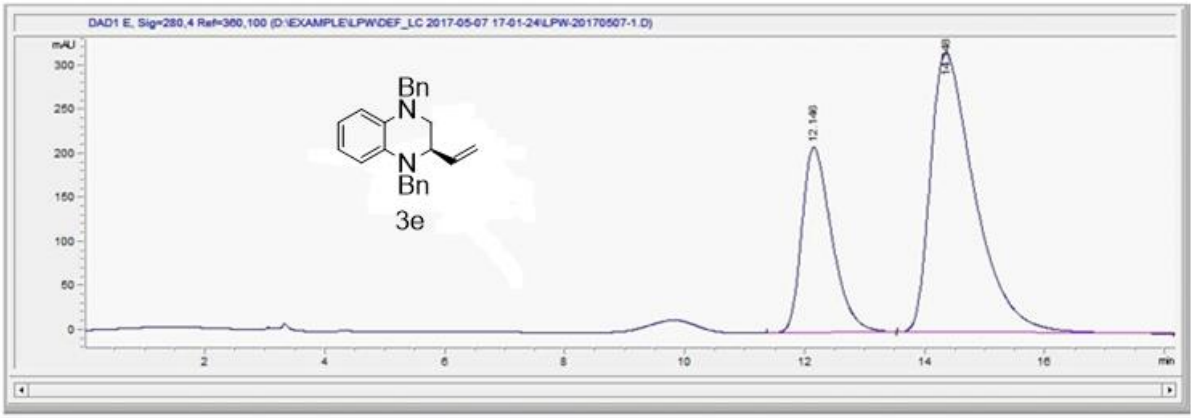

| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 11.09 | 413 | 19.2 | 0.3332 | 0.759 | 49.526 |
| 2 | 12.486 | 420.9 | 15.5 | 0.4113 | 0.676 | 50.474 |




| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 11.029 | 2334.3 | 104.7 | 0.342 | 0.731 | 47.831 |
| 2 | 12.4 | 2546 | 93.5 | 0.4135 | 0.651 | 52.169 |




| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 12.981 | 2073.4 | 31.4 | 1.1014 | 0 | 47.945 |
| 2 | 14.6 | 2251.1 | 40.8 | 0.9188 | 0.76 | 52.055 |




| # | 时间 | 峰面积 | 峰高 | 峰宽 | 对称因子 | 峰面积 % |
|---|---|---|---|---|---|---|
| 1 | 12.146 | 7308.5 | 210 | 0.532 | 0.626 | 30.950 |
| 2 | 14.348 | 16305.3 | 316.9 | 0.7763 | 0.492 | 69.050 |