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Supplementary Information

Cu(I)-Catalyzed Asymmetric Intramolecular Addition of Aryl Pinacolboronic Esters to Unactivated Ketones: Enantioselective Synthesis of 2,3-Dihydrobenzofuran-3-ol Derivatives

Chunjie Ni,[a,b] Jihui Gao,[a] and Xianjie Fang*[a]

[a]School of Chemistry and Chemical Engineering, Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China

[b]School of Pharmacy, Yancheng Teachers University, Yancheng 224051, China

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1. General Information

Unless otherwise noted, all reagents were obtained commercially and used without further purification.

NMR spectrum: ^{1}H and ^{13}C spectra are recorded on the Bruker AVANCE spectrometer, operating at 400 MHz (500 MHz) for ^{1}H NMR and 100 MHz (125 MHz) for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm). Chemical shifts are reported downfield from $CDCl_3$ (δ: 7.26 ppm) and DMSO-d_6 (δ: 2.5 ppm) for ^{1}H NMR. Chemical shifts of ^{13}C NMR are reported in the scale relative to the solvent of $CDCl_3$ (δ: 77.0 ppm) and DMSO-d_6 (δ: 40.0 ppm) used as an internal reference. Multiplicities are recorded as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublet), q (quartet), m (multiplet). Coupling constants are reported in Hertz (Hz).

Mass spectroscopy: Mass spectra were in general recorded on Waters Micromass Q-TOF Premier Mass Spectrometer.

Infrared Spectrometer: Infrared spectra were obtained on Bruker TENSOR II instrument.

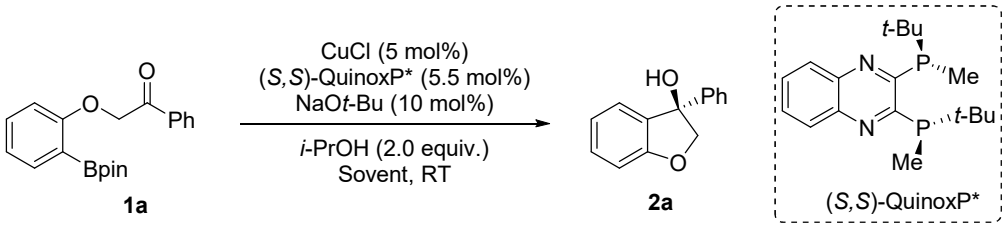
High Performance Liquid Chromatography: HPLC analysis was performed on Shimadzu 2030 equipment with Daicel Chiralpak OD-H or AD-H column.

Spectropolarimeter: Optical rotations were measured on Anton Paar MCP100 automatic polarimeter

Chromatography: Column chromatography was performed with silica gel (200-300 mesh ASTM).

2. Optimization of the Reaction Conditions

Table S1: Screening of Solvent[a]

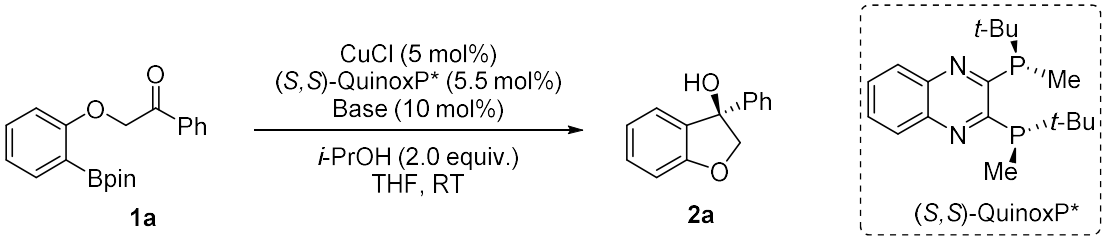


1a **2a**

entry	solvent	yield%[b]	ee%[c]
1	PhMe	74	94
2	DCM	62	31
3	DCE	61	96
4	Acetone	53	73
5	1,4-dioxane	56	71
6	MTBE	76	95
7	CH_3CN	38	66
8	DMF	trace	trace
9	THF	79	96
10[d]	THF	78	95

[a]Reaction conditions: The mixture of **1a** (33.8 mg, 0.1 mmol), CuCl (0.5 mg, 0.005 mmol), (*S,S*)-QuinoxP* (1.8 mg, 0.0055 mmol), NaO*t*-Bu (1 mg, 0.01 mmol) and *i*-PrOH (12.0 mg, 0.2 mmol) in solvent (0.5 mL) was stirred at RT for 16 h. [b]Isolated yield. [c]Determined by HPLC analysis. [d]Used 20 mol% NaO*t*-Bu.

Table S2: Screening of Base[a]

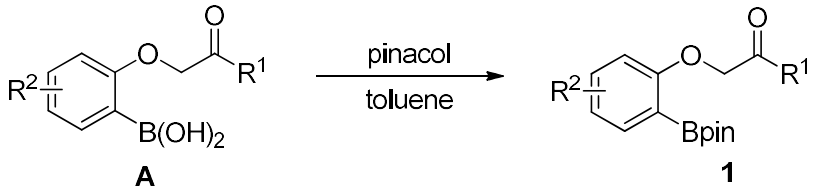


1a **2a**

entry	base	yield%[b]	ee%[c]
1	NaO*t*-Bu	79	96
2	LiO*t*-Bu	63	91
3	KOMe	55	73
4	NaOMe	51	74
5[d]	NaO*t*-Bu	66	96
6[e]	NaO*t*-Bu	71	95
7[f]	NaO*t*-Bu	70	96

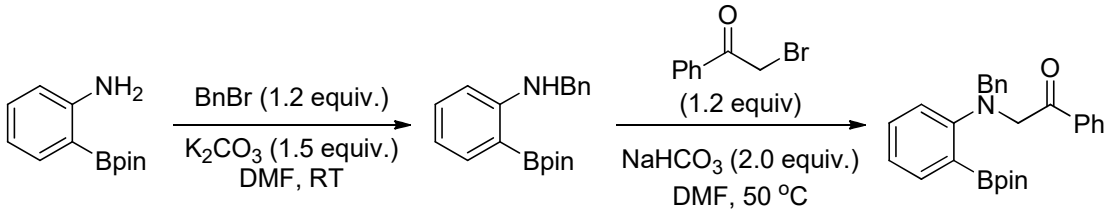
[a]Reaction conditions: The mixture of **1a** (33.8 mg, 0.1 mmol), CuCl (0.5 mg, 0.005 mmol), (*S,S*)-QuinoxP* (1.8 mg, 0.0055 mmol), Base (0.01 mmol) and *i*-PrOH (12.0 mg, 0.2 mmol) in THF (0.5 mL) was stirred at RT for 16 h. [b]Isolated yield. [c]Determined by HPLC analysis. [d] Used 1.0 equiv. *i*-PrOH. [e] Used 1.5 equiv. *i*-PrOH. [f]Used 2.5 equiv. *i*-PrOH.

3. General Procedure for the Preparation of Substrates



A 1

The mixture of compound **A** and equal equiv. pinacol was refluxed with Dean-Stark in toluene (2 mL/mmol A) for 2 hours. After complete consumption of compound A (monitored by GC), toluene was removed and the residue was used for next reaction without further purification. (*Note*: Compound A were prepared according to the reported literature.[1])



B C 3

To a 100 mL flask was added 2-aminophenylboronic acid pinacol ester (10 mmol), K_2CO_3 (2.08 g, 15 mmol), and DMF (30 mL) with stirring. After 15 minutes, BnBr (2.05 g, 12 mmol) was slowly added to the mixture over half an hour. After completion of the reaction (monitored by TLC), ethyl acetate (100 mL) and water (50 ml) were added to reaction mixture. The organic phase was separated and washed with water (3×50 mL). Then, the organic layer was concentrated under reduce pressure, which was directly used for the next step without further purification.

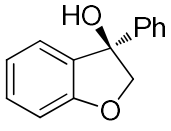
To a 100 mL flask was added **C**, 2-bromoacetophenone (2.39 g, 12 mmol), $NaHCO_3$ (1.68 g, 20 mmol), and DMF (30 mL). The reaction mixture was then heated to 50 °C. After completion of the reaction (monitored by TLC), ethyl acetate (100 mL) and water (50 ml) were added to reaction mixture. The organic phase was separated and washed with water (3×50 mL). Then, the organic layer was concentrated under reduce pressure and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give the substrate **3**.

4. General Procedure for the Cu-Catalyzed Reactions

To a 4 mL sealed tube was added substrate **1** (0.1 mmol), CuCl (0.5 mg, 0.005 mmol), (*S,S*)-QuinoxP* (1.8 mg, 0.0055 mmol), NaO*t*-Bu (1 mg, 0.01 mmol) and *i*-PrOH (12.0 mg, 0.2 mmol) in THF (0.5 mL) in glovebox. Then the mixture was stirred at RT for 16 h. After that time, the solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give the product **2**.

5. Data for the Products

(*R*)-3-phenyl-2,3-dihydrobenzofuran-3-ol(**2a**)



16.8 mg, 79% yield, oil.

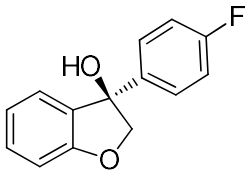
^{1}H NMR (500 MHz, DMSO) δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.38-7.31 (m, 2H), 7.30-7.22 (m, 2H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.95-6.87 (m, 2H), 6.21 (s, 1H), 4.56 (d, *J* = 9.9 Hz, 1H), 4.46 (d, J = 9.9 Hz, 1H).

^{13}C NMR (125 MHz, DMSO) δ 160.3, 145.4, 134.0, 130.1, 128.5, 127.4, 126.1, 125.2, 121.3, 110.5, 85.9, 81.3.

HRMS (ESI) Calcd for $C_{14}H_{11}O$ $[M-H_2O+H]^+$ 195.0810, found 195.0813.

$[\alpha]^{25}_D$ = -107.1 (c = 0.7 in CH_2Cl_2); 96% ee [Chiralcel OD-H column, *n*-hexane / isopropanol = 90:10, 0.8 mL/min, λ_{max} 254 nm, t_R = 8.8 min and 9.7 min].

(*R*)-3-(4-fluorophenyl)-2,3-dihydrobenzofuran-3-ol(**2b**)



18.4 mg, 80% yield, oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.46 (m, 2H), 7.36-7.30 (m, 1H), 7.13-7.04 (m, 3H), 6.97 (dd, *J* = 11.4, 4.3 Hz, 2H), 4.70 (d, *J* = 10.3 Hz, 1H), 4.48 (d, *J* = 10.3 Hz, 1H), 2.43 (s, 1H).

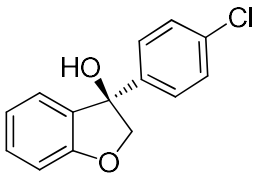
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 160.8 (d, *J* = 42.0 Hz), 138.3 (d, *J* = 3.0 Hz), 131.92, 130.77, 127.9 (d, *J* = 8.0 Hz), 124.3, 121.5, 115.1 (d, *J* = 22.0 Hz), 110.9, 86.0, 82.2.

IR (oil) *v* 3449 (br), 1593, 1472, 1057 cm^{-1}.

HRMS (ESI) Calcd for $C_{14}H_{10}FO$ $[M-H_2O+H]^+$ 213.0716, found 213.0725.

$[\alpha]^{25}_D$ = -78.0 (c = 0.9 in CH_2Cl_2); 96% ee [Chiralcel OD-H column, *n*-hexane / isopropanol = 90:10, 0.8 mL/min, λ_{max} 254 nm, t_R = 8.0 min and 9.5 min].

(*R*)-3-(4-chlorophenyl)-2,3-dihydrobenzofuran-3-ol(**2c**)



17.5 mg, 71% yield, oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.42 (m, 2H), 7.32 (dd, *J* = 15.8, 8.4 Hz, 3H), 7.07 (d, *J* = 7.4 Hz, 1H), 6.98-6.93 (m, 2H), 4.68 (d, *J* = 10.3 Hz, 1H), 4.46 (d, *J* = 10.3 Hz, 1H), 2.42 (s, 1H).

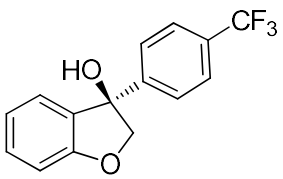
^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 141.2, 133.5, 131.8, 130.8, 128.4, 127.5, 124.2, 121.6, 110.9, 86.0, 82.2.

The spectral data are consistent with those reported in the literature.[1]

HRMS (ESI) Calcd for $C_{14}H_{10}ClO$ $[M-H_2O+H]^+$ 229.0420, found 229.0421.

$[\alpha]^{25}_D$ = -75.9 (c = 0.9 in CH_2Cl_2); 96% ee [Chiralcel OD-H column, *n*-hexane / isopropanol = 90:10, 0.8 mL/min, λ_{max} 254 nm, t_R = 8.2 min and 9.9 min].

(*R*)-3-(4-(trifluoromethyl)phenyl)-2,3-dihydrobenzofuran-3-ol(**2d**)



19.6 mg, 70% yield, oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.60 (m, 4H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.97 (dd, *J* = 17.4, 8.0 Hz, 2H), 4.71 (d, *J* = 10.4 Hz, 1H), 4.51 (d, *J* = 10.4 Hz, 1H), 2.43 (s, 1H).

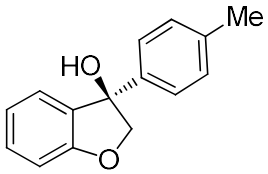
^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 146.7, 131.7, 131.0, 130.0, 129.7, 126.5, 125.2 (q, *J* = 3.8 Hz), 124.2, 121.7, 110.9, 86.0, 82.3.

The spectral data are consistent with those reported in the literature.[1]

HRMS (ESI) Calcd for $C_{15}H_{10}F_3O$ $[M-H_2O+H]^+$ 263.0684, found 263.0684.

$[\alpha]^{25}_D$ = -108.8 (c = 0.9 in CH_2Cl_2); 95% ee [Chiralcel OD-H column, *n*-hexane / isopropanol = 90:10, 0.8 mL/min, λ_{max} 254 nm, t_R = 7.5 min and 9.0 min].

(*R*)-3-(p-tolyl)-2,3-dihydrobenzofuran-3-ol(**2e**)



12.7 mg, 56% yield, oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.12-7.08 (m, 1H), 6.95 (dd, *J* = 14.0, 7.7 Hz, 2H), 4.68 (d, *J* = 10.2 Hz, 1H), 4.49 (d, *J* = 10.2 Hz, 1H), 2.37 (s, 3H), 2.33 (s, 1H).

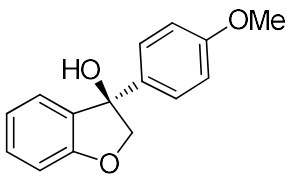
^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 139.6, 137.3, 132.3, 130.5, 128.9, 126.0, 124.3, 121.4, 110.7, 86.1, 82.5, 21.0.

The spectral data are consistent with those reported in the literature.[2]

HRMS (ESI) Calcd for $C_{15}H_{13}O$ $[M-H_2O+H]^+$ 209.0966, found 209.0969.

$[\alpha]^{25}_D$ = -127.3 (c = 0.4 in CH_2Cl_2); 96% ee [Chiralcel OD-H column, *n*-hexane / isopropanol = 90:10, 0.8 mL/min, λ_{max} 254 nm, t_R = 8.0 min and 9.2 min].

(*R*)-3-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-ol(**2f**)



15.0 mg, 62% yield, oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.33 (m, 2H), 7.27-7.21 (m, 1H), 7.05 (dd, *J* = 7.4, 0.8 Hz, 1H), 6.92-6.81 (m, 4H), 4.62 (d, *J* = 10.2 Hz, 1H), 4.40 (d, *J* = 10.2 Hz, 1H), 3.76 (s, 3H), 2.24 (s, 1H).

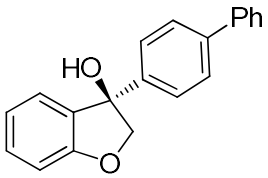
^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 159.0, 134.6, 132.3, 130.5, 127.3, 124.4, 121.4, 113.6, 110.8, 86.0, 82.3, 55.3.

The spectral data are consistent with those reported in the literature.[1]

HRMS (ESI) Calcd for $C_{15}H_{13}O_2$ $[M-H_2O+H]^+$ 225.0916, found 225.0915.

$[\alpha]^{25}_D$ = -41.5 (c = 0.4 in CH_2Cl_2); 97% ee [Chiralcel OD-H column, *n*-hexane / isopropanol = 90:10, 0.8 mL/min, λ_{max} 254 nm, t_R = 11.1 min and 13.6 min].

(*R*)-3-([1,1'-biphenyl]-4-yl)-2,3-dihydrobenzofuran-3-ol(**2g**)



20.0 mg, 69% yield, white foam.

^{1}H NMR (400 MHz, DMSO) δ 7.67-7.63 (m, 4H), 7.47 (dd, *J* = 15.1, 8.0 Hz, 4H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.29-7.24 (m, 1H), 7.08-7.03 (m, 1H), 6.97-6.89 (m, 2H), 6.27 (s, 1H), 4.59 (d, *J* = 9.9 Hz, 1H), 4.51 (d, *J* = 9.9 Hz, 1H).

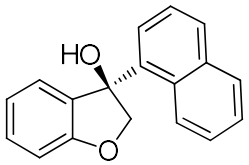
^{13}C NMR (100 MHz, DMSO) δ 160.3, 144.6, 140.3, 139.3, 133.9, 130.1, 129.4, 127.9, 127.1, 126.8, 126.8, 125.3, 121.3, 110.5, 85.9, 81.2.

IR (neat) *v* 3425 (br), 1601, 1460, 1126 cm^{-1}.

HRMS (ESI) Calcd for $C_{20}H_{15}O$ $[M-H_2O+H]^+$ 271.1123, found 271.1126.

$[\alpha]^{25}_D$ = -74.9 (c = 0.8 in CH_2Cl_2); 97% ee [Chiralcel OD-H column, *n*-hexane / isopropanol = 90:10, 0.8 mL/min, λ_{max} 254 nm, t_R = 11.1 min and 14.4 min].

(*R*)-3-(naphthalen-1-yl)-2,3-dihydrobenzofuran-3-ol(**2h**)



18.9 mg, 72% yield, oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.87-7.81 (m, 3H), 7.53-7.46 (m, 3H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 4.77 (d, *J* = 10.3 Hz, 1H), 4.62 (d, *J* = 10.3 Hz, 1H), 2.52 (s, 1H).

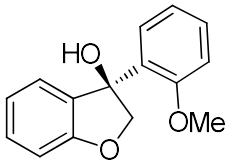
^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 139.8, 132.9, 132.6, 132.1, 130.7, 128.2, 128.1, 127.6, 126.4, 126.2, 124.8, 124.4, 124.2, 121.5, 110.8, 85.9, 82.7.

The spectral data are consistent with those reported in the literature.[2]

HRMS (ESI) Calcd for $C_{18}H_{13}O$ $[M-H_2O+H]^+$ 245.0966, found 245.0965.

$[\alpha]^{25}_D$ = -40.6 (c = 0.3 in CH_2Cl_2); 97% ee [Chiralcel OD-H column, *n*-hexane / isopropanol = 90:10, 0.8 mL/min, λ_{max} 254 nm, t_R = 12.8 min and 16.4 min].

(*R*)-3-(2-methoxyphenyl)-2,3-dihydrobenzofuran-3-ol(**2i**)



13.6 mg, 56% yield, oil.

^{1}H NMR (400 MHz, DMSO) δ 7.70 (d, *J* = 7.6 Hz, 1H), 7.32-7.27 (m, 1H), 7.21-7.14 (m, 1H), 7.04-6.92 (m, 2H), 6.86 (dd, *J* = 12.0, 7.7 Hz, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 5.98 (s, 1H), 4.64 (d, *J* = 9.4 Hz, 1H), 4.40 (d, *J* = 9.4 Hz, 1H), 3.43 (s, 3H).

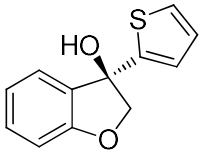
^{13}C NMR (100 MHz, DMSO) δ 160.5, 156.7, 134.0, 132.3, 129.4, 129.4, 127.3, 124.1, 120.4, 120.3, 112.8, 109.8, 83.9, 79.6, 56.0.

IR (oil) *v* 3457 (br), 1586, 1254, 849, 752 cm^{-1}.

HRMS (ESI) Calcd for $C_{15}H_{13}O_2$ $[M-H_2O+H]^+$ 225.0916, found 225.0912.

$[\alpha]^{25}_D$ = -164.1 (c = 0.2 in CH_2Cl_2); 85% ee [Chiralcel OD-H column, *n*-hexane / isopropanol = 90:10, 0.8 mL/min, λ_{max} 254 nm, t_R = 30.3 min and 33.1 min].

(*R*)-3-(thiophen-2-yl)-2,3-dihydrobenzofuran-3-ol(**2j**)



19.0 mg, 87% yield, oil. (Reactions was performed at 60 ºC.)

^{1}H NMR (500 MHz, DMSO) δ 7.47 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.29-7.18 (m, 1H), 7.21-7.18 (m, 1H), 6.99 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.93 (t, *J* = 7.3 Hz, 2H), 6.87 (dd, *J* = 3.5, 1.1 Hz, 1H), 6.57 (s, 1H), 4.60 (d, *J* = 9.9 Hz, 1H), 4.54 (d, *J* = 9.9 Hz, 1H).

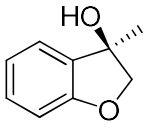
^{13}C NMR (125 MHz, DMSO) δ 159.9, 150.0, 133.0, 130.5, 127.5, 125.8, 125.1, 124.3, 121.3, 110.7, 85.4, 79.7.

IR (oil) *v* 3342 (br), 1621, 1468, 985 cm^{-1}.

HRMS (ESI) Calcd for $C_{12}H_9OS$ $[M-H_2O+H]^+$ 201.0374, found 201.0374.

$[\alpha]^{25}_D$ = -94.6 (c = 0.9 in CH_2Cl_2); 97% ee [Chiralcel OD-H column, *n*-hexane / isopropanol = 90:10, 0.8 mL/min, λ_{max} 254 nm, t_R = 15.8 min and 17.1 min].

(*R*)-3-methyl-2,3-dihydrobenzofuran-3-ol(**2k**)



7.8 mg, 52% yield, solid, mp 83-87 ºC. (Reactions was performed at 60 ºC.)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.4 Hz, 1H), 7.26-7.22 (m, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 4.50 (d, *J* = 10.0 Hz, 1H), 4.31 (d, *J* = 10.0 Hz, 1H), 2.01 (s, 1H), 1.69 (s, 3H).

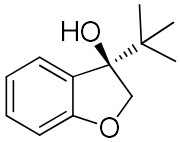
^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 131.9, 130.3, 122.9, 121.0, 110.7, 84.0, 77.9, 24.9.

The spectral data are consistent with those reported in the literature.[1]

HRMS (ESI) Calcd for C_9H_9O $[M-H_2O+H]^+$ 133.0653, found 133.0654.

$[\alpha]^{25}_D$ = -62.4 (c = 0.3 in CH_2Cl_2); 97% ee [Chiralcel OD-H column, *n*-hexane / isopropanol = 90:10, 0.8 mL/min, λ_{max} 254 nm, t_R = 7.4 min and 8.1 min].

(*R*)-3-(tert-butyl)-2,3-dihydrobenzofuran-3-ol(**2l**)



12.3 mg, 64% yield, solid, mp 80-84 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.5, 0.5 Hz, 1H), 7.26-7.22 (m, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 4.69 (d, *J* = 10.1 Hz, 1H), 4.23 (d, *J* = 10.1 Hz, 1H), 2.04 (s, 1H), 1.05 (s, 9H).

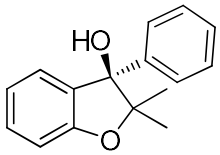
^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 130.0, 129.8, 125.0, 120.4, 110.5, 85.7, 80.5, 37.6, 24.8.

The spectral data are consistent with those reported in the literature.[3]

HRMS (ESI) Calcd for $C_{12}H_{15}O$ $[M-H_2O+H]^+$ 175.1123, found 175.1126.

$[\alpha]^{25}_D$ = -16.2 (c = 0.7 in CH_2Cl_2); 94% ee [Chiralcel OD-H column, *n*-hexane / isopropanol = 90:10, 0.8 mL/min, λ_{max} 254 nm, t_R = 6.0 min and 6.8 min].

(*R*)-2,2-dimethyl-3-phenyl-2,3-dihydrobenzofuran-3-ol (**2m**)



18.8 mg, 78% yield, white foam.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.48 (m, 2H), 7.42-7.25 (m, 5H), 6.98 (t, *J* = 10.0 Hz, 1H), 6.91 (d, *J* = 11.2 Hz, 1H), 2.09 (s, 1H), 1.62 (s, 3H), 0.88 (s, 3H)

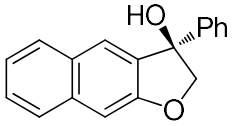
^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 130.1, 130.0, 125.0, 120.4, 110.5, 85.9, 80.6, 37.5, 24.8.

The spectral data are consistent with those reported in the literature.[4]

HRMS (ESI) Calcd for $C_{16}H_{17}O_2$ $[M+H]^+$ 241.1229, found 241.1236.

$[\alpha]^{25}_D$ = -104.2 (c = 0.6 in CH_2Cl_2); 94% ee [Chiralcel AD-H column, *n*-hexane / isopropanol = 90:10, 0.8 mL/min, λ_{max} 254 nm, t_R = 8.4 min and 9.4 min].

(*R*)-3-phenyl-2,3-dihydronaphtho[2,3-b]furan-3-ol(**2n**)



17.3 mg, 66% yield, oil.

^{1}H NMR (500 MHz, DMSO) δ 7.92-7.84 (m, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 1H), 7.27-7.21 (m, 3H), 6.47 (d, *J* = 1.1 Hz, 1H), 4.72 (d, *J* = 10.0 Hz, 1H), 4.57 (d, *J* = 9.9 Hz, 1H).

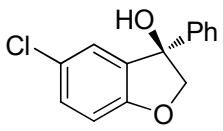
^{13}C NMR (125 MHz, DMSO) δ 158.4, 146.1, 131.8, 130.1, 130.0, 129.2, 128.6, 127.3, 127.0, 125.8, 123.6, 123.4, 123.0, 113.1, 87.7, 82.6.

IR (oil) *v* 3438 (br), 1627, 1489, 1150 cm^{-1}.

HRMS (ESI) Calcd for $C_{18}H_{13}O$ $[M-H_2O+H]^+$ 245.0966, found 245.0965.

$[\alpha]^{25}_D$ = -40.6 (c = 0.3 in CH_2Cl_2); 99% ee [Chiralcel OD-H column, *n*-hexane / isopropanol = 90:10, 0.8 mL/min, λ_{max} 254 nm, t_R = 13.1min and 33.0min].

(*R*)-5-chloro-3-phenyl-2,3-dihydrobenzofuran-3-ol(**2o**)



17.5 mg, 71% yield, oil.

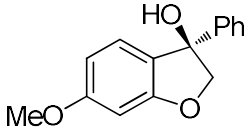
^{1}H NMR (500 MHz, DMSO) δ 7.41 (d, *J* = 7.4 Hz, 2H), 7.37 (dd, *J* = 10.4, 4.9 Hz, 2H), 7.32-7.26 (m, 2H), 6.97 (dd, *J* = 9.0, 5.0 Hz, 2H), 6.38 (s, 1H), 4.61 (d, *J* = 10.0 Hz, 1H), 4.53 (d, *J* = 10.0 Hz, 1H).

^{13}C NMR (125 MHz, DMSO) δ 159.1, 144.6, 136.1, 130.0, 128.6, 127.7, 126.1, 124.9, 124.7, 112.2, 86.5, 81.2.

HRMS (ESI) Calcd for $C_{14}H_{10}ClO$ $[M-H_2O+H]^+$ 229.0420, found 229.0422.

$[\alpha]^{25}_D$ = -43.6 (c = 0.4 in CH_2Cl_2); 86% ee [Chiralcel OD-H column, *n*-hexane / isopropanol = 90:10, 0.8 mL/min, λ_{max} 254 nm, t_R = 7.9 min and 9.0 min].

(*R*)-6-methoxy-3-phenyl-2,3-dihydrobenzofuran-3-ol(**2p**)



15.3 mg, 63% yield, oil.

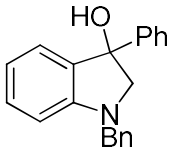
^{1}H NMR (400 MHz, DMSO) δ 7.43-7.38 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.25 (dd, *J* = 8.2, 6.2 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.53 (d, *J* = 2.2 Hz, 1H), 6.47 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.08 (s, 1H), 4.57 (d, *J* = 9.8 Hz, 1H), 4.45 (d, *J* = 9.8 Hz, 1H), 3.74 (s, 3H).

^{13}C NMR (100 MHz, DMSO) δ 161.9, 161.6, 145.6, 128.4, 127.3, 126.2, 126.1, 125.6, 107.6, 96.4, 86.9, 81.0, 55.9.

HRMS (ESI) Calcd for $C_{15}H_{13}O_2$ $[M-H_2O+H]^+$ 225.0916, found 225.0913.

$[\alpha]^{25}_D$ = -93.3 (c = 0.9 in CH_2Cl_2); 99% ee [Chiralcel AD-H column, *n*-hexane / isopropanol = 90:10, 0.8 mL/min, λ_{max} 254 nm, t_R = 14.3 min and 21.7 min].

1-benzyl-3-phenylindolin-3-ol(**4**)



19.0 mg, 64% yield, oil.

^{1}H NMR (400 MHz, DMSO) δ 7.55 (d, *J* = 6.7 Hz, 2H), 7.42-7.36 (m, 3H), 7.28 (d, *J* = 4.3 Hz, 4H), 7.23-7.18 (m, 1H), 7.15 (s, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.74 (t, *J* =

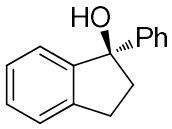
7.2 Hz, 1H), 6.65-6.57 (m, 2H), 4.58 (d, J = 16.3 Hz, 1H), 4.44 (d, J = 16.4 Hz, 1H), 3.36 (s, 2H).

^{13}C NMR (100 MHz, DMSO) δ 142.9, 142.9, 139.0, 134.6, 128.8, 128.7, 128.5, 127.5, 127.2, 126.4, 121.7, 117.5, 116.9, 112.3, 94.9, 57.4, 54.3.

IR (oil) v 3396 (br), 2628, 1479, 1251, 1026 cm^{-1}.

HRMS (ESI) Calcd for $C_{21}H_{18}N$ $[M-H_2O+H]^+$ 284.1439, found 284.1440.

(*R*)-1-phenyl-2,3-dihydro-1H-inden-1-ol(**6**)



9.3 mg, 44% yield, oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.20 (m, 8H), 7.11-7.08 (m, 1H), 3.24-3.13 (m, 1H), 3.01-2.90 (m, 1H), 2.52-2.47 (m, 2H), 2.10 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 146.1, 144.1, 128.6, 128.1, 127.0, 126.9, 125.6, 125.0, 124.2, 85.6, 44.8, 30.0.

The spectral data are consistent with those reported in the literature.[1]

HRMS (ESI) Calcd for $C_{15}H_{15}O$ $[M+H]^+$ 211.1123, found 211.1119.

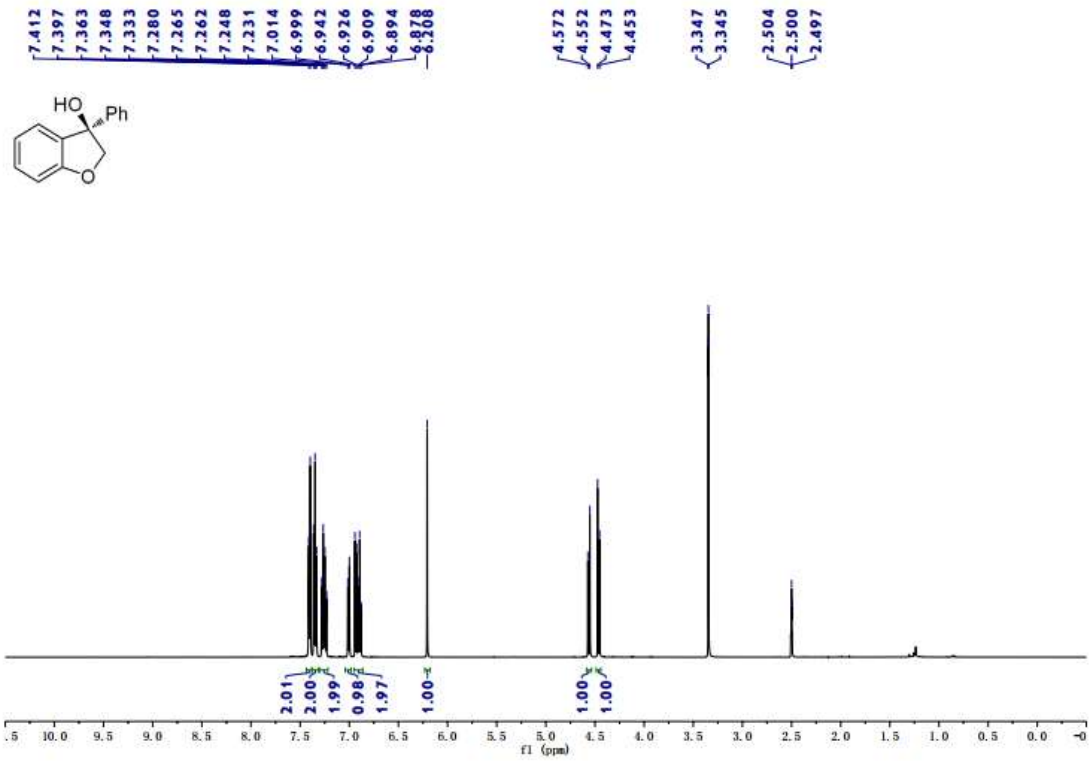
7% ee [Chiralcel AD-H column, *n*-hexane / isopropanol = 97:3, 0.8 mL/min, λ_{max} 254 nm, t_R = 12.5 min and 17.0 min].

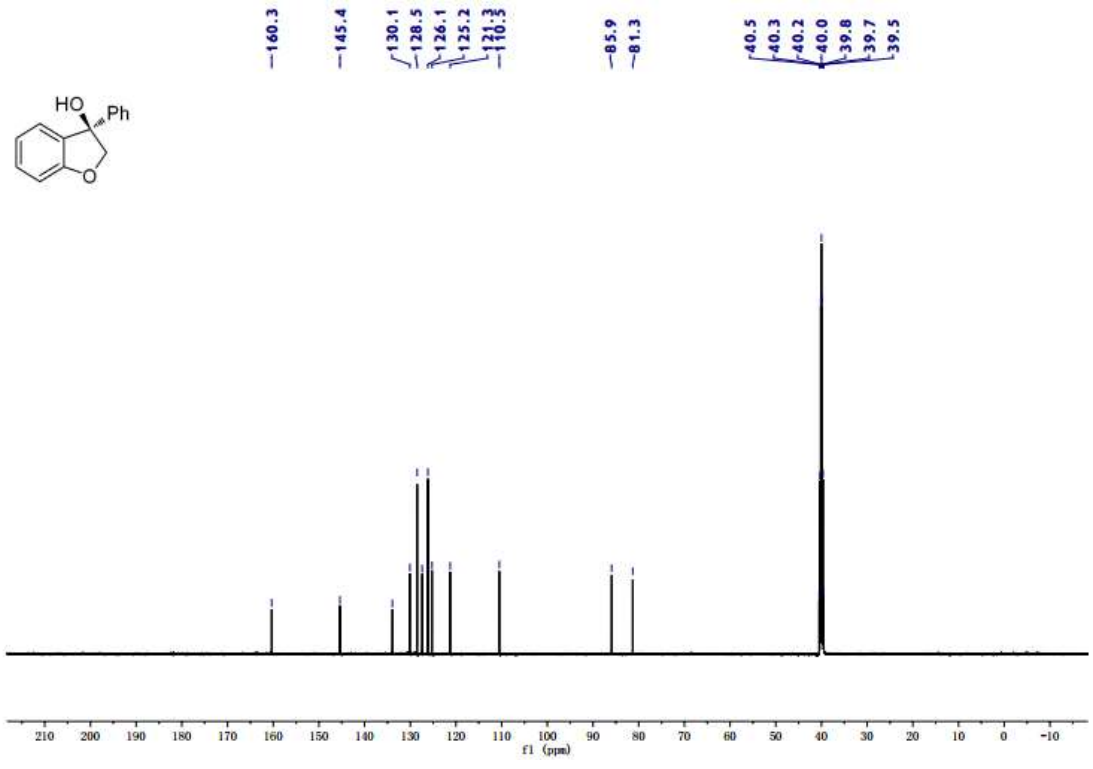
6. References

1. G. Liu and X. Lu, *J. Am. Chem. Soc.,* 2006, **128**, 16504.
2. D.-X. Zhu, W.-W. Chen and M.-H. Xu, *Tetrahedron,* 2016, **72**, 2637.
3. D. W. Low, G. Pattison, M. D. Wieczysty, G. H. Churchill and H. W. Lam, *Org. Lett.,* 2012, **14**, 2548.

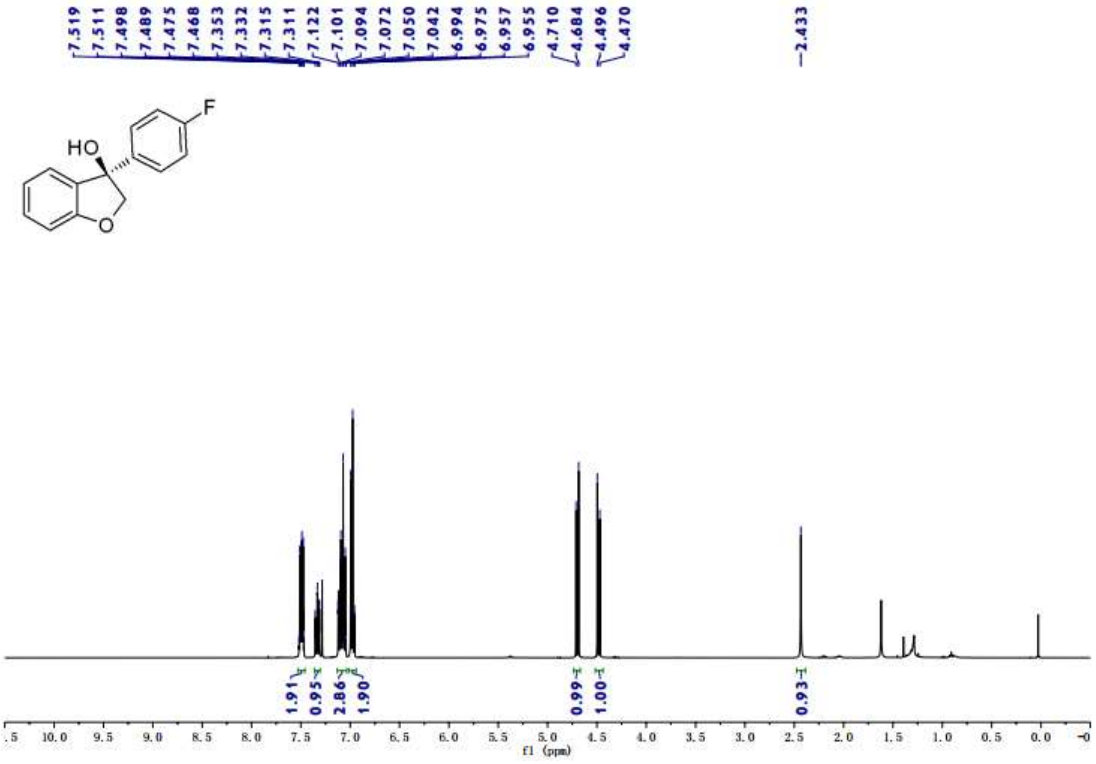
7. NMR and HPLC Spectra

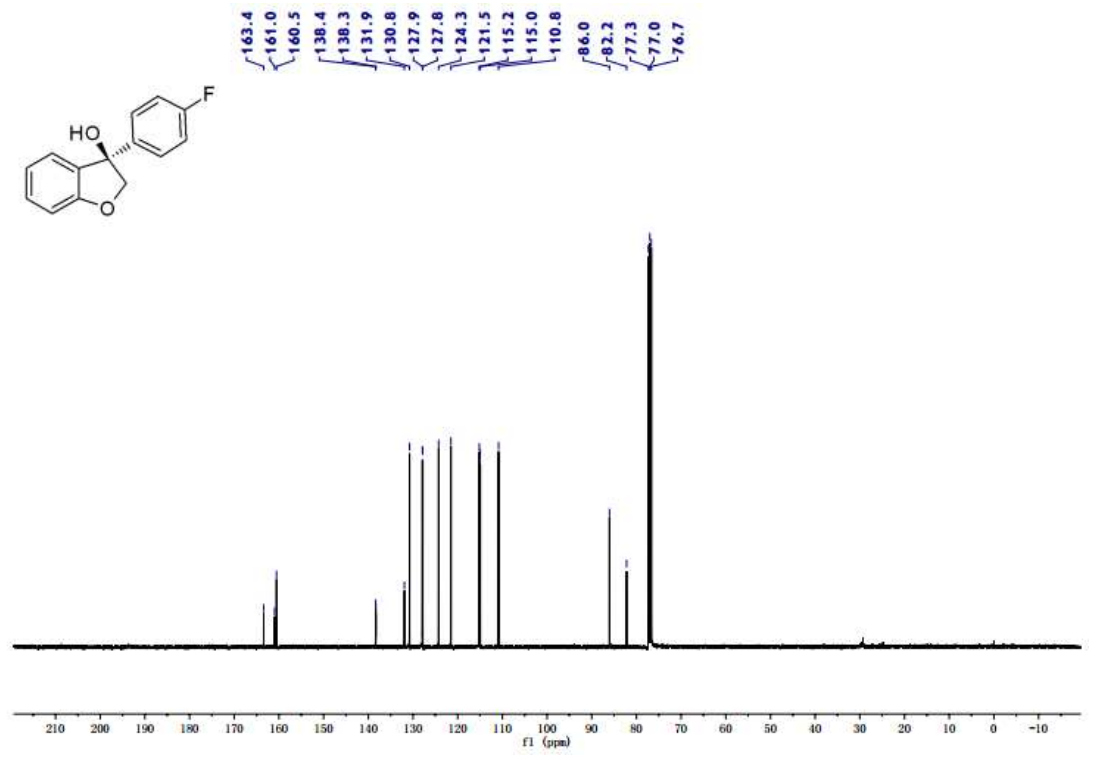
(*R*)-3-phenyl-2,3-dihydrobenzofuran-3-ol(**2a**)



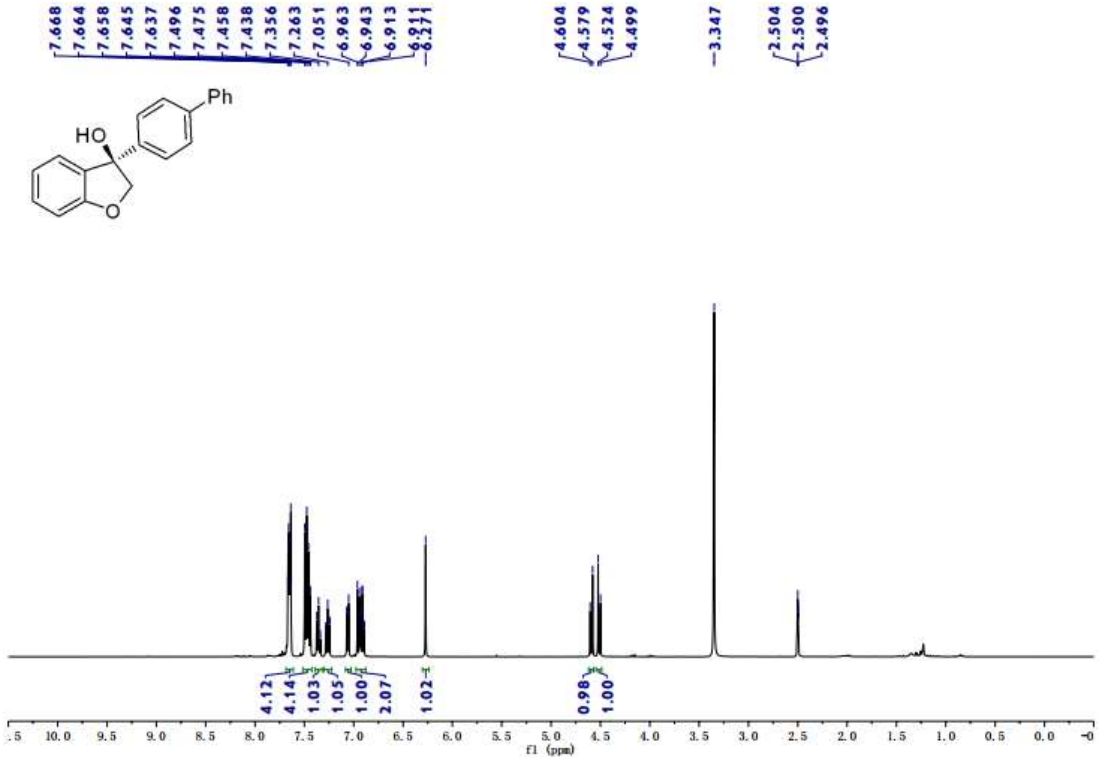


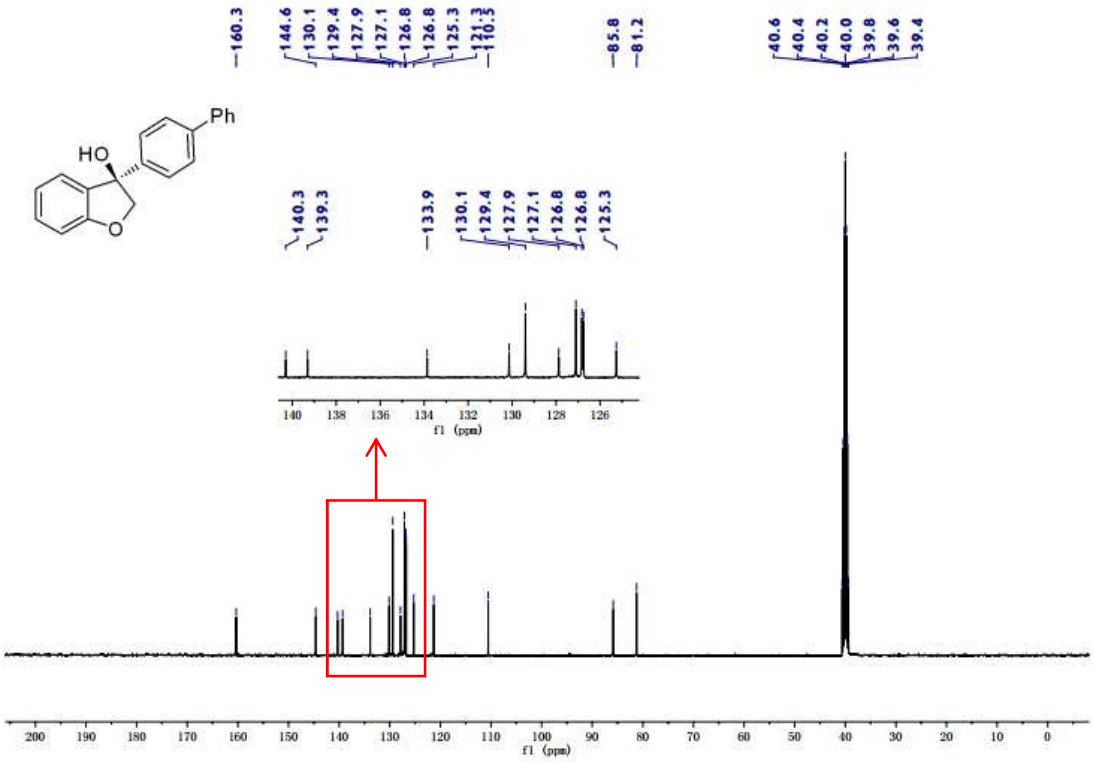
(*R*)-3-(4-fluorophenyl)-2,3-dihydrobenzofuran-3-ol(**2b**)



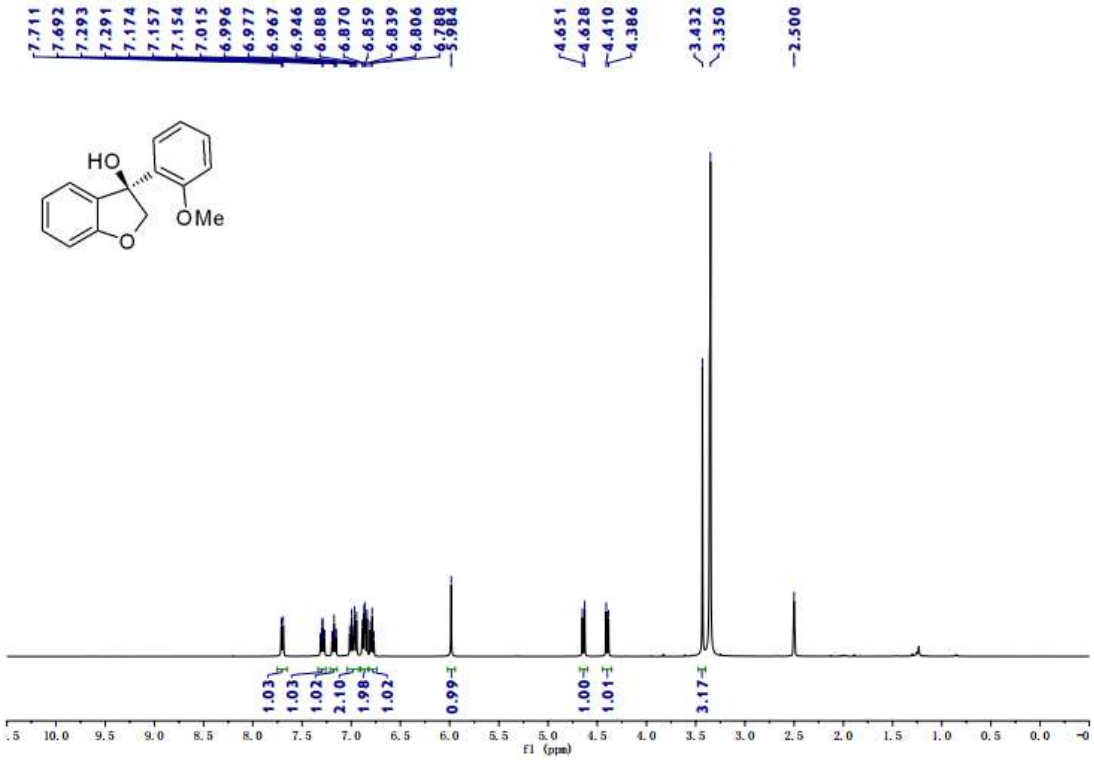


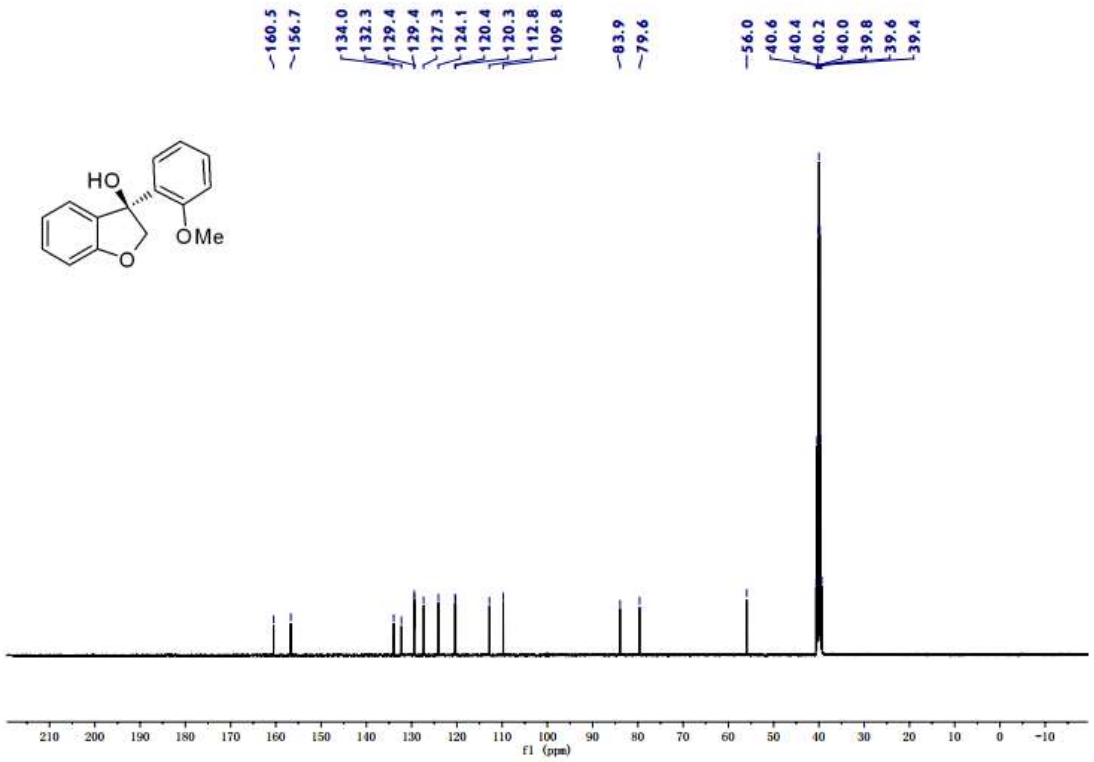
(*R*)-3-([1,1'-biphenyl]-4-yl)-2,3-dihydrobenzofuran-3-ol(**2g**)



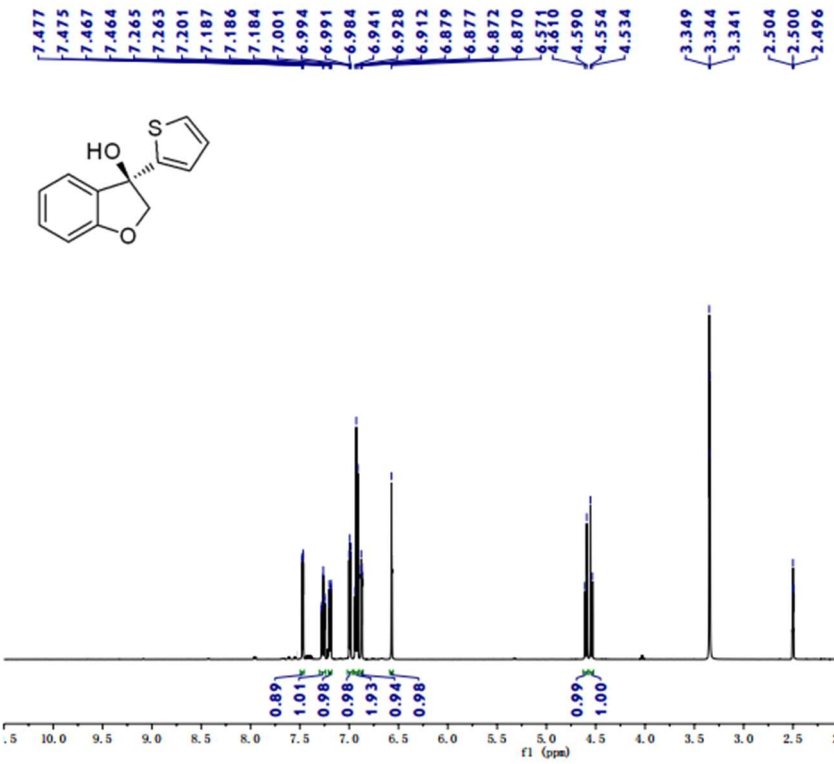


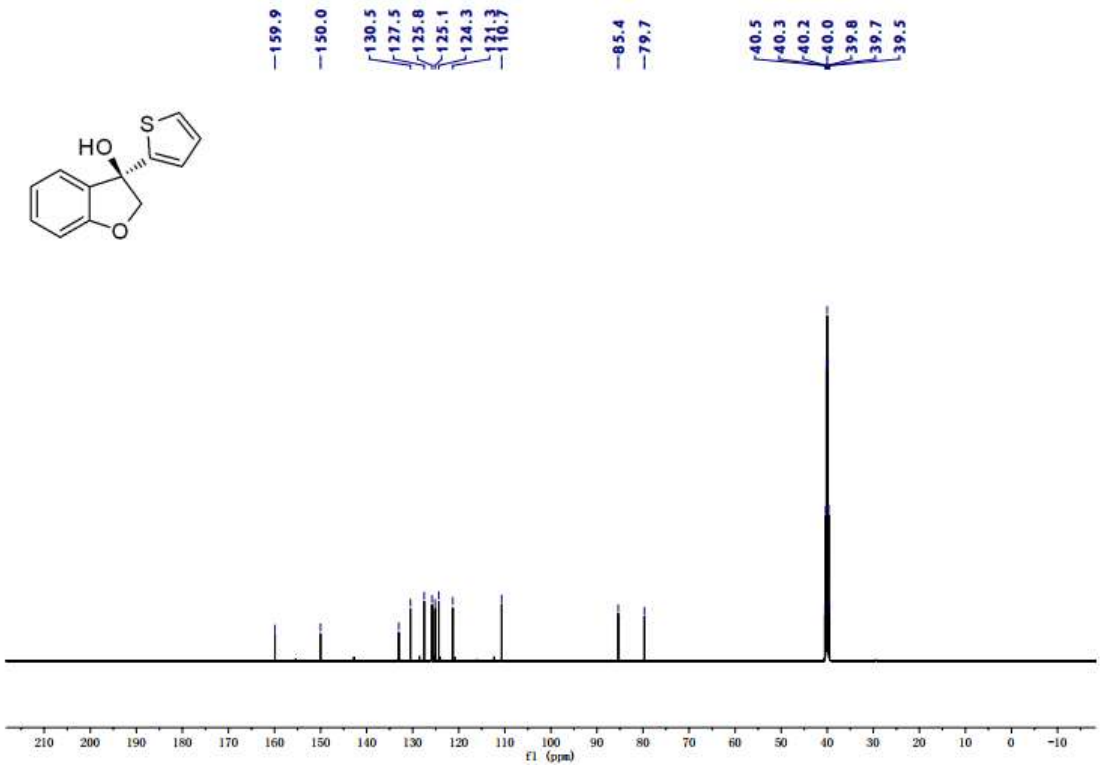
(*R*)-3-(2-methoxyphenyl)-2,3-dihydrobenzofuran-3-ol(**2i**)



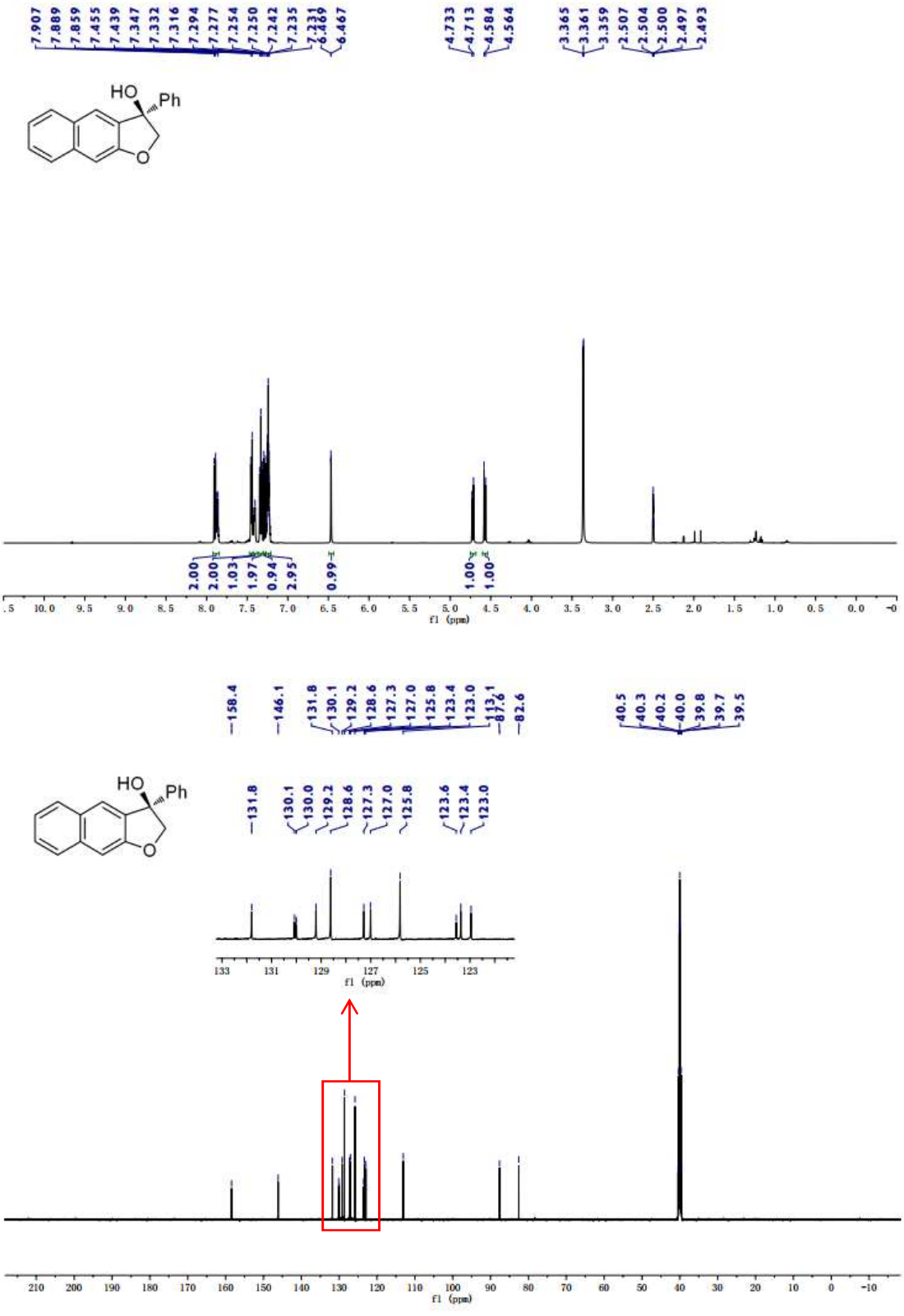


(*R*)-3-(thiophen-2-yl)-2,3-dihydrobenzofuran-3-ol(**2j**)

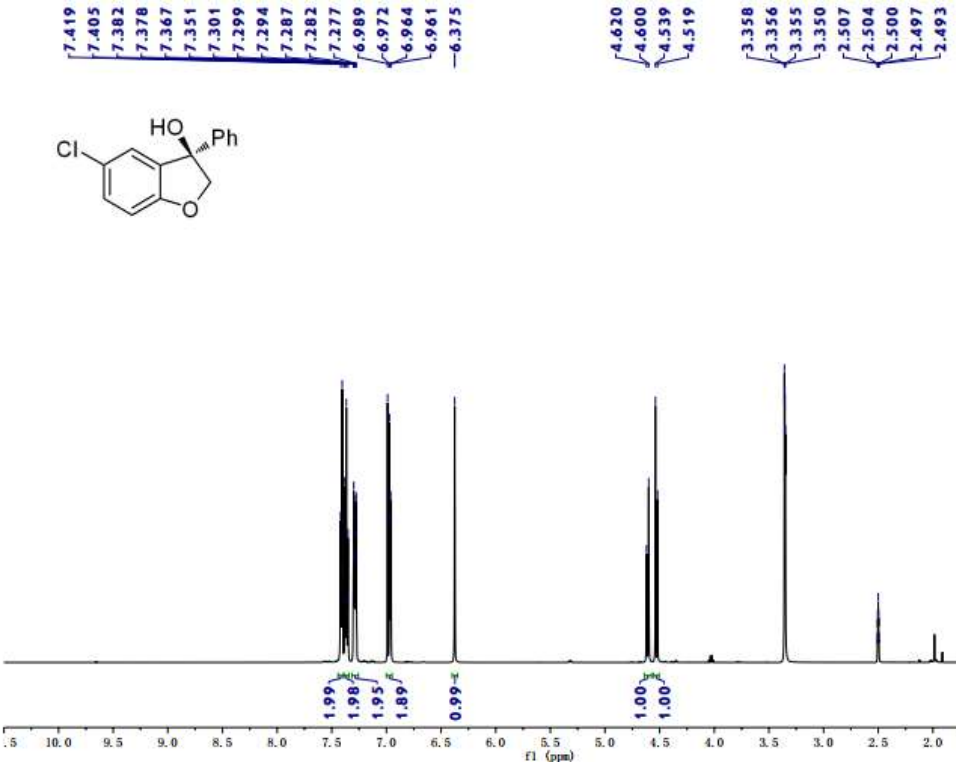


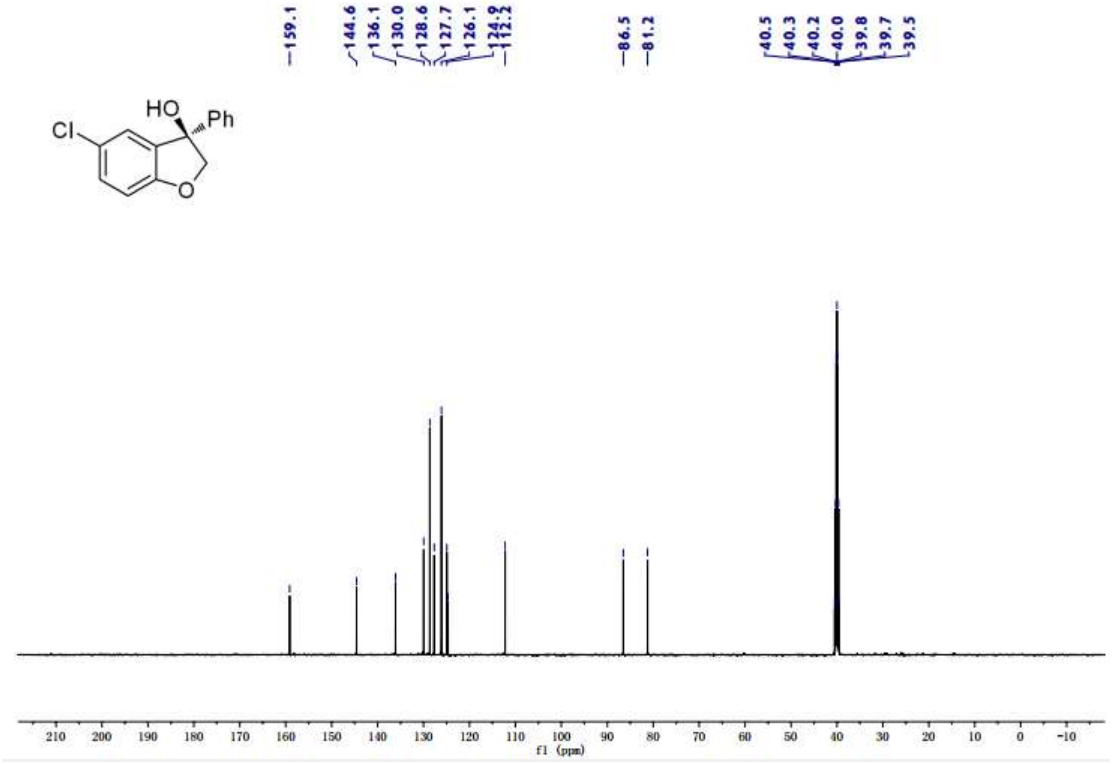


(*R*)-3-phenyl-2,3-dihydronaphtho[2,3-b]furan-3-ol(**2n**)

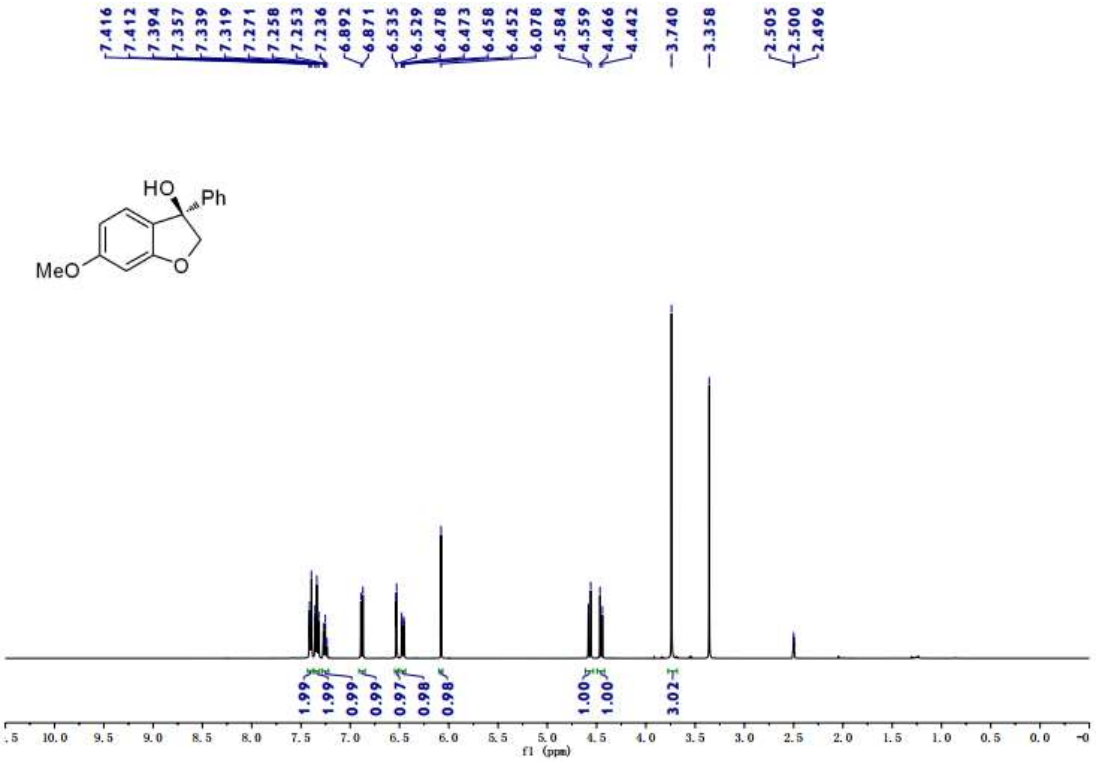


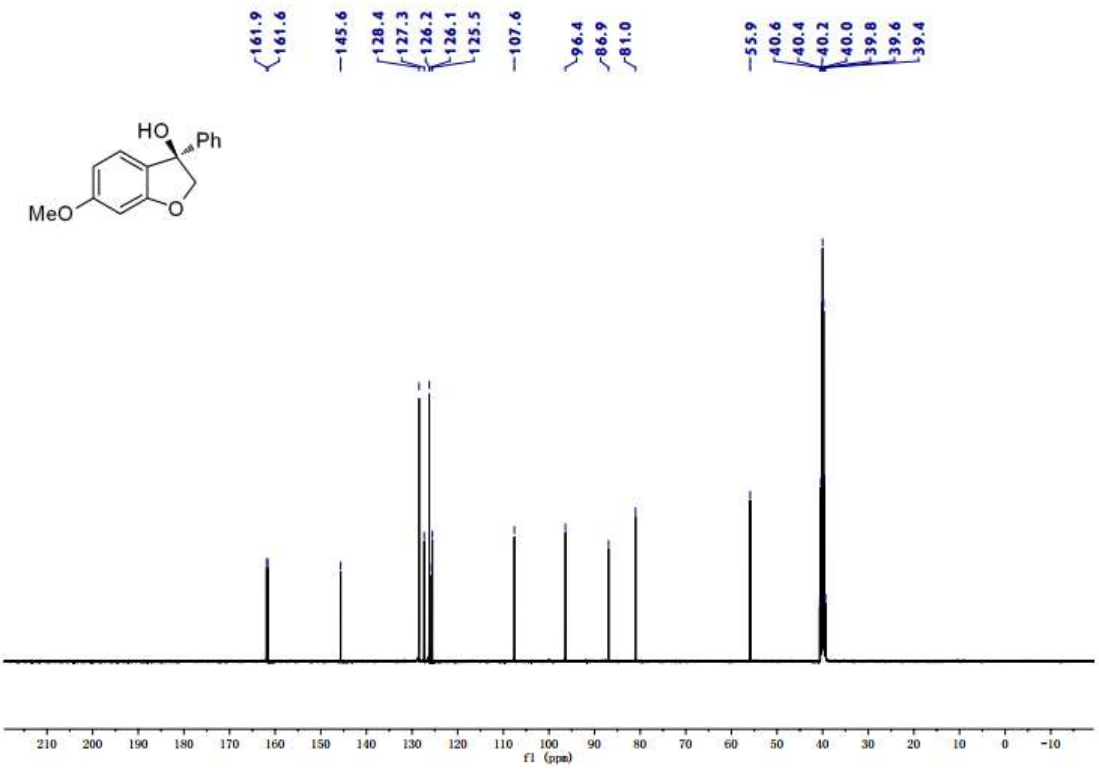
(*R*)-5-chloro-3-phenyl-2,3-dihydrobenzofuran-3-ol(**2o**)



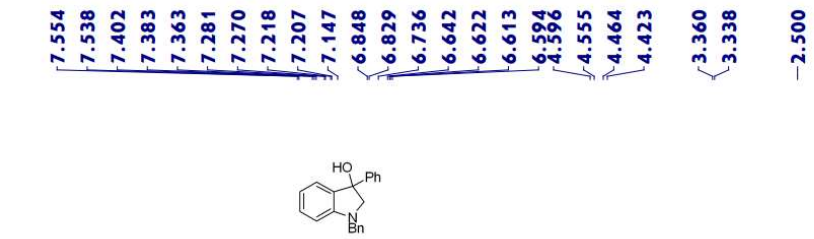


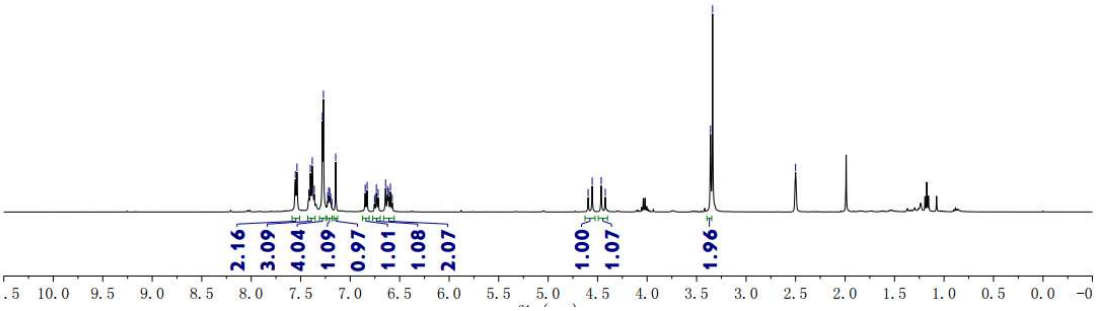
(*R*)-6-methoxy-3-phenyl-2,3-dihydrobenzofuran-3-ol(**2p**)

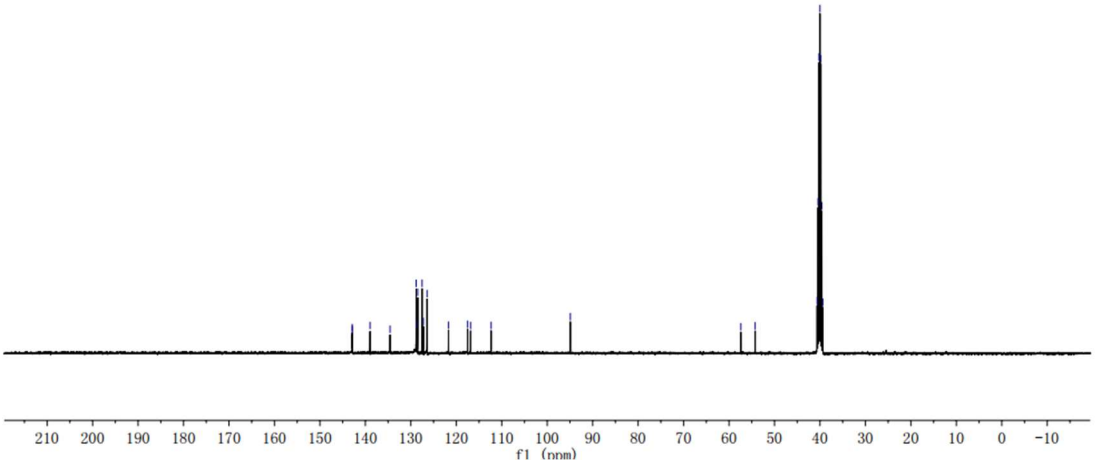




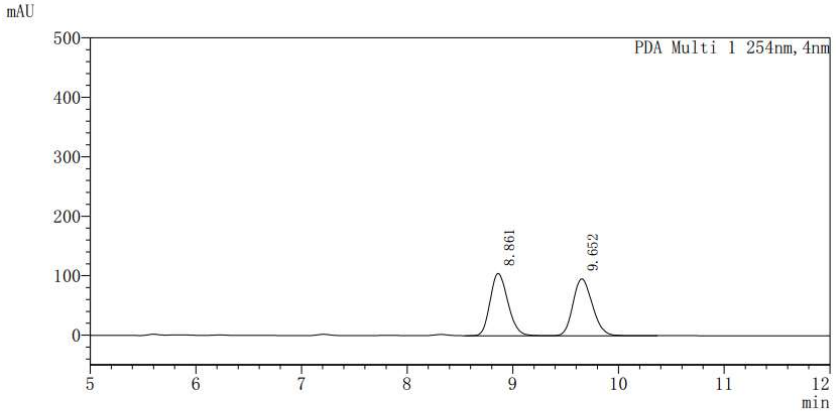
1-benzyl-3-phenylindolin-3-ol(**4**)





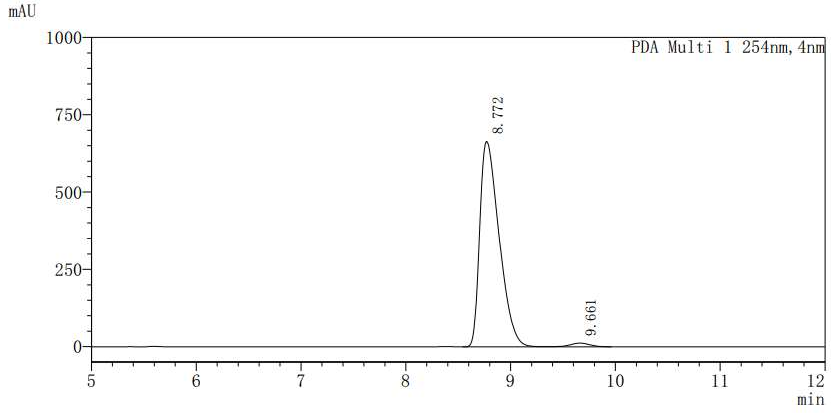


(*R*)-3-phenyl-2,3-dihydrobenzofuran-3-ol(**2a**)



PDA Ch1 254nm

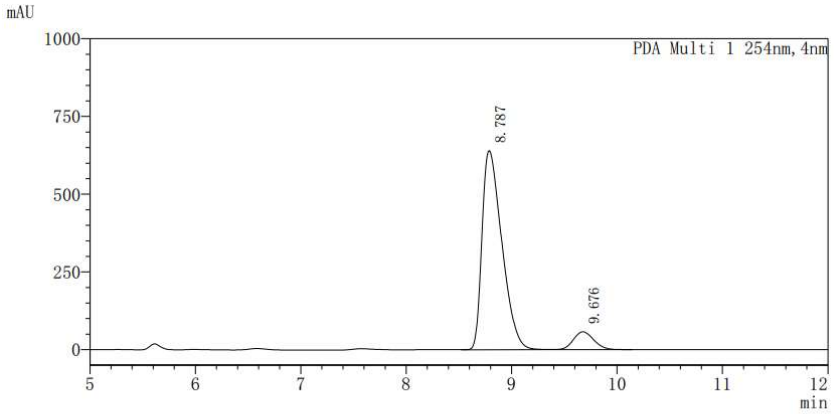
Peak	Time	Area	Height	Height%	Area%
1	8.861	1227570	104854	52.258	49.953
2	9.652	1229856	95794	47.742	50.047



PDA Ch1 254nm

Peak	Time	Area	Height	Height%	Area%
1	8.772	8559799	664731	98.207	98.135
2	9.661	162691	12137	1.793	1.865

(Reaction was performed at RT.)

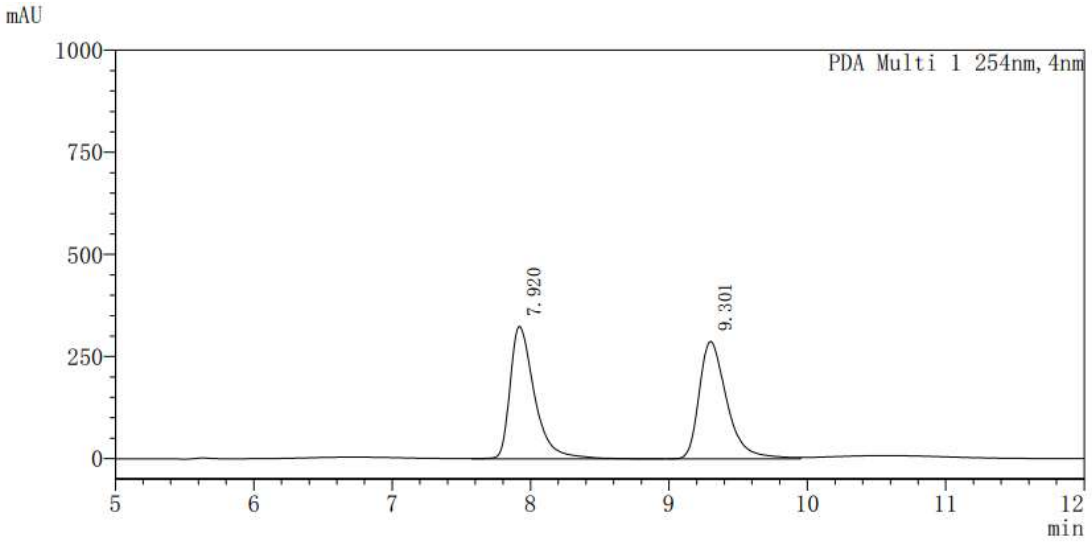


PDA Ch1 254nm

Peak	Time	Area	Height	Height%	Area%
1	8.787	8395954	640701	91.735	91.548
2	9.676	775112	57724	8.265	8.452

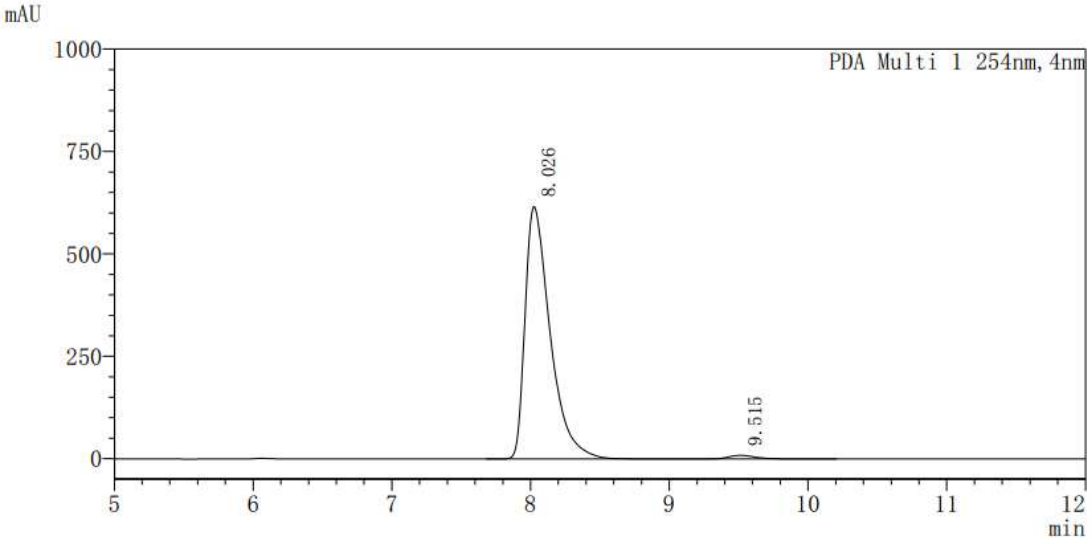
(Reaction was performed at 120 °C.)

(*R*)-3-(4-fluorophenyl)-2,3-dihydrobenzofuran-3-ol(**2b**)



PDA Ch1 254nm

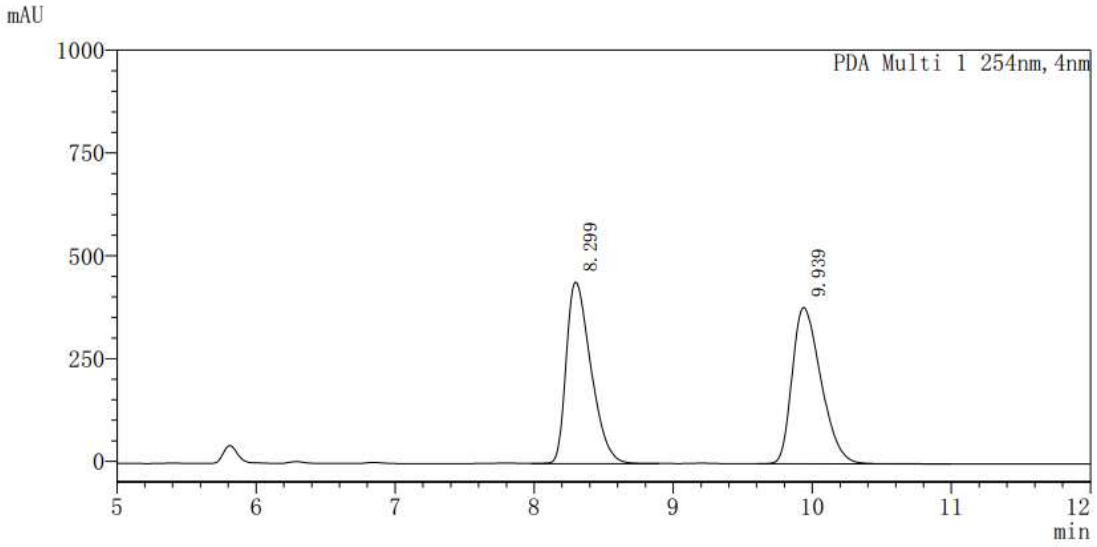
Peak	Time	Area	Height	Height%	Area%
1	7.920	3995009	324147	53.013	49.949
2	9.301	4003209	287298	46.987	50.051



PDA Ch1 254nm

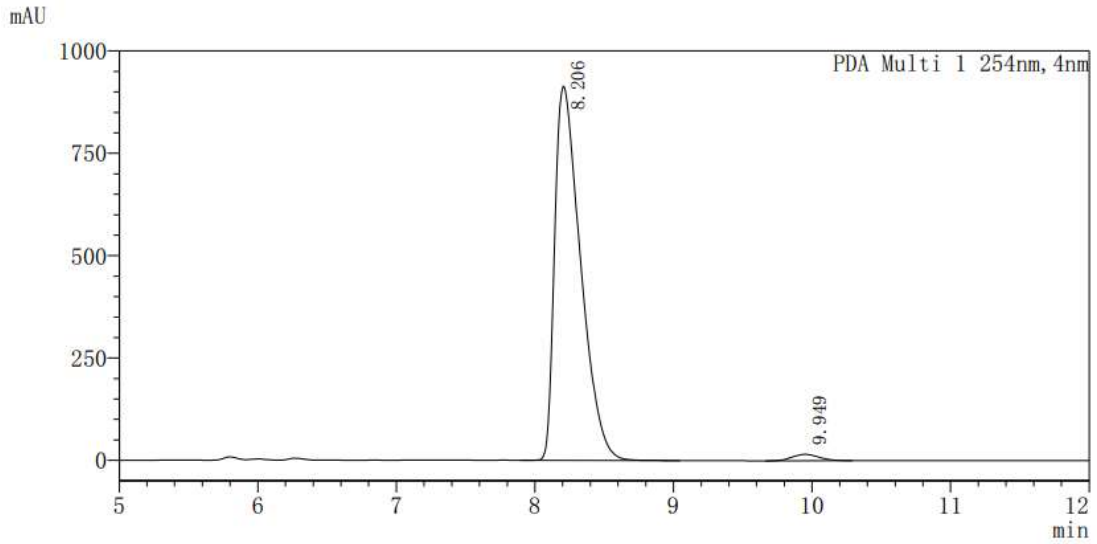
Peak	Time	Area	Height	Height%	Area%
1	8.026	7776938	616146	98.555	98.376
2	9.515	128413	9033	1.445	1.624

(*R*)-3-(4-chlorophenyl)-2,3-dihydrobenzofuran-3-ol(**2c**)



PDA Ch1 254nm

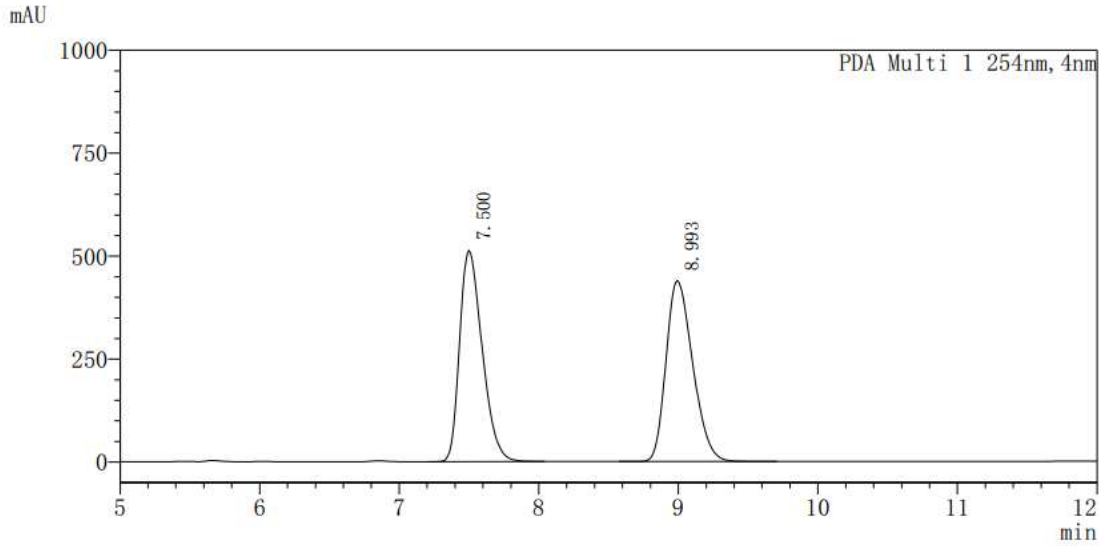
Peak	Time	Area	Height	Height%	Area%
1	8.299	5456256	441806	53.761	49.863
2	9.939	5486252	379986	46.239	50.137



PDA Ch1 254nm

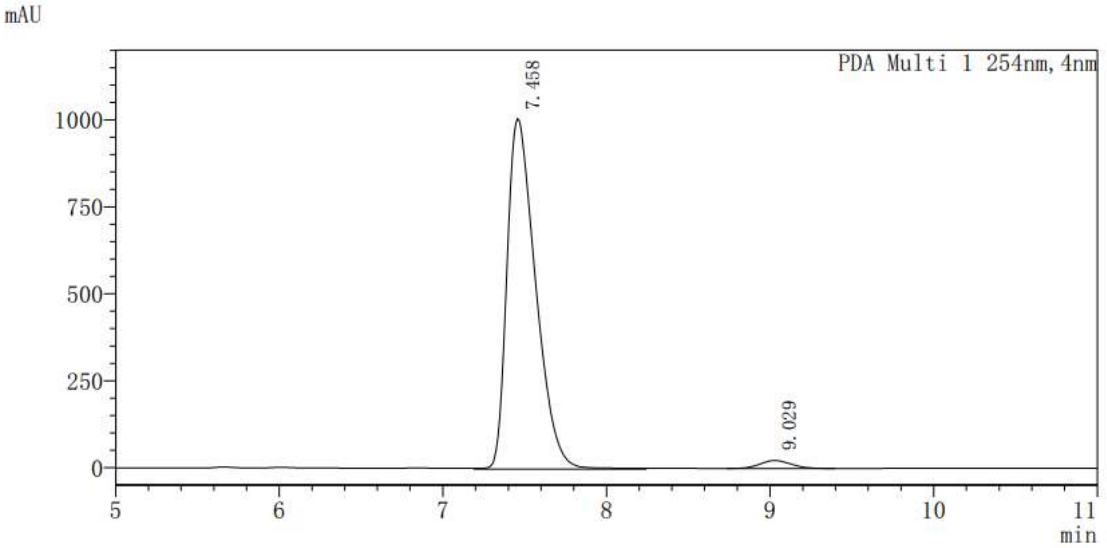
Peak	Time	Area	Height	Height%	Area%
1	8.206	11881082	914236	98.330	98.281
2	9.949	207795	15528	1.670	1.719

(*R*)-3-(4-(trifluoromethyl)phenyl)-2,3-dihydrobenzofuran-3-ol(**2d**)



PDA Ch1 254nm

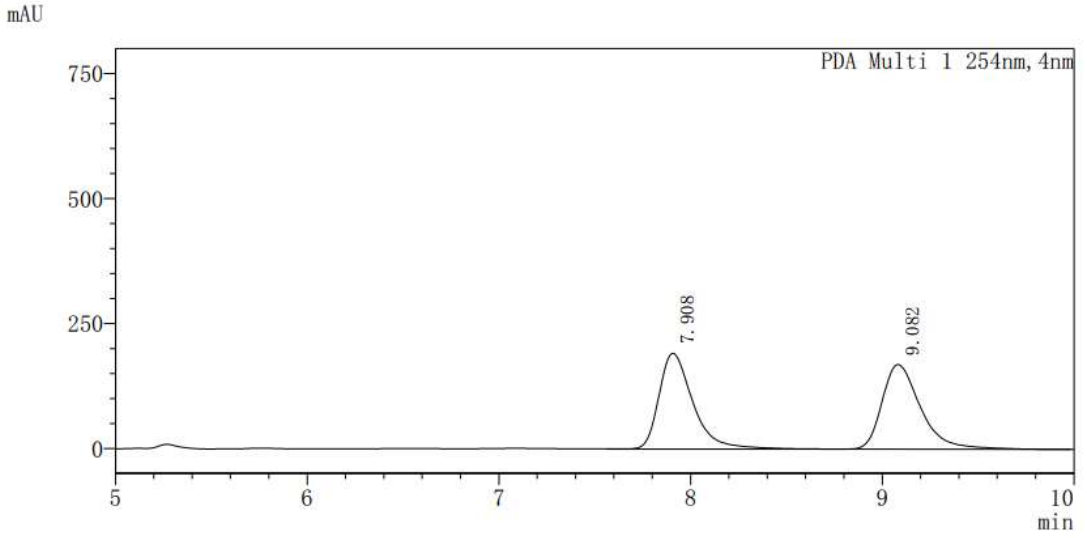
Peak	Time	Area	Height	Height%	Area%
1	7.500	5758843	512290	53.851	49.654
2	8.993	5839136	439021	46.149	50.346



PDA Ch1 254nm

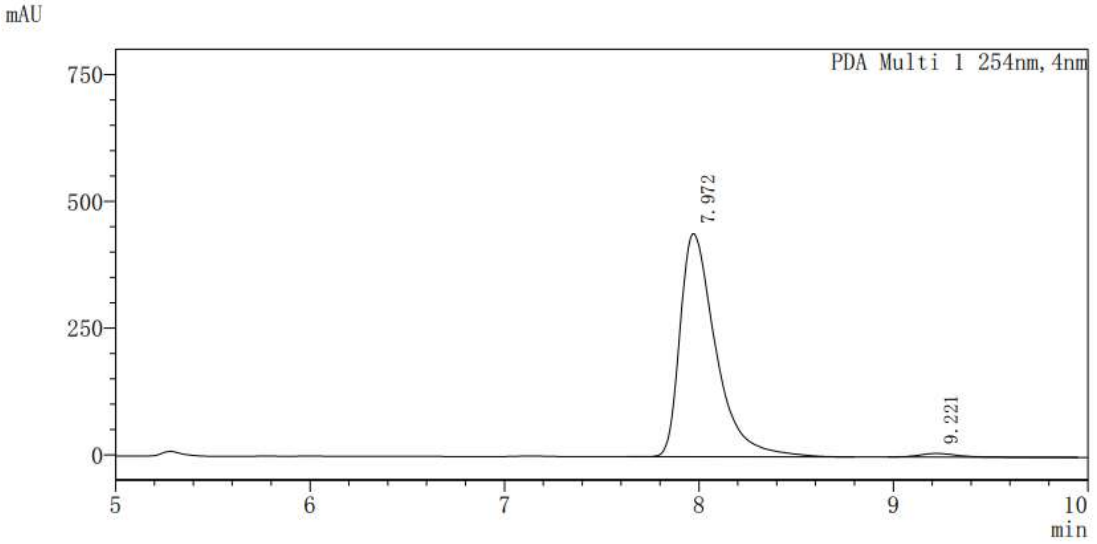
Peak	Time	Area	Height	Height%	Area%
1	7.458	12308795	1007696	97.816	97.635
2	9.029	298204	22499	2.184	2.365

(*R*)-3-(p-tolyl)-2,3-dihydrobenzofuran-3-ol(**2e**)



PDA Ch1 254nm

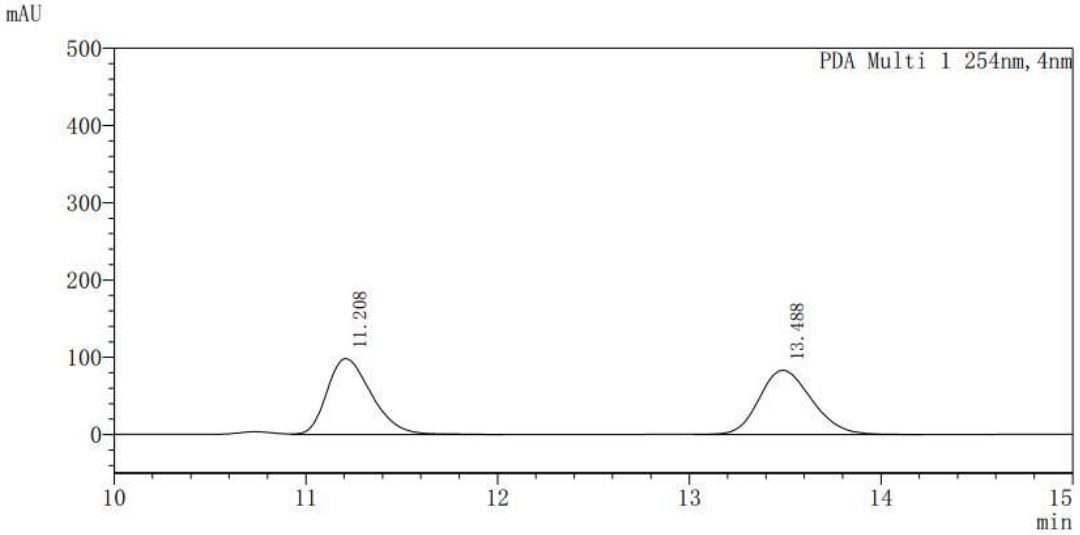
Peak	Time	Area	Height	Height%	Area%
1	7.908	2362844	191663	53.151	50.006
2	9.082	2362273	168940	46.849	49.994



PDA Ch1 254nm

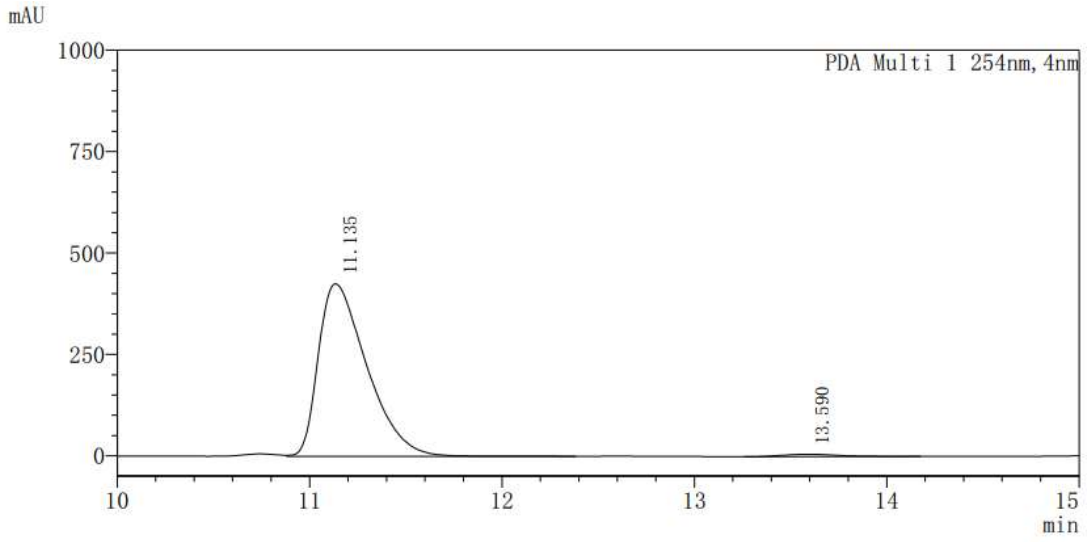
Peak	Time	Area	Height	Height%	Area%
1	7.972	5631016	440498	98.428	98.356
2	9.221	94141	7034	1.572	1.644

(*R*)-3-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-ol(**2f**)



PDA Ch1 254nm

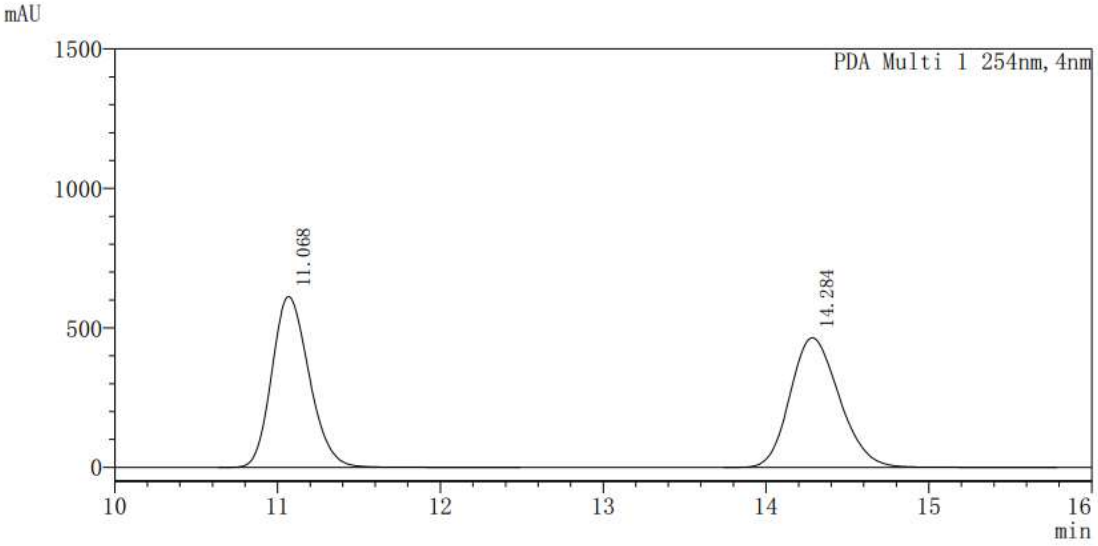
Peak	Time	Area	Height	Height%	Area%
1	11.208	1576319	98197	54.180	49.915
2	13.488	1581701	83043	45.820	50.085



PDA Ch1 254nm

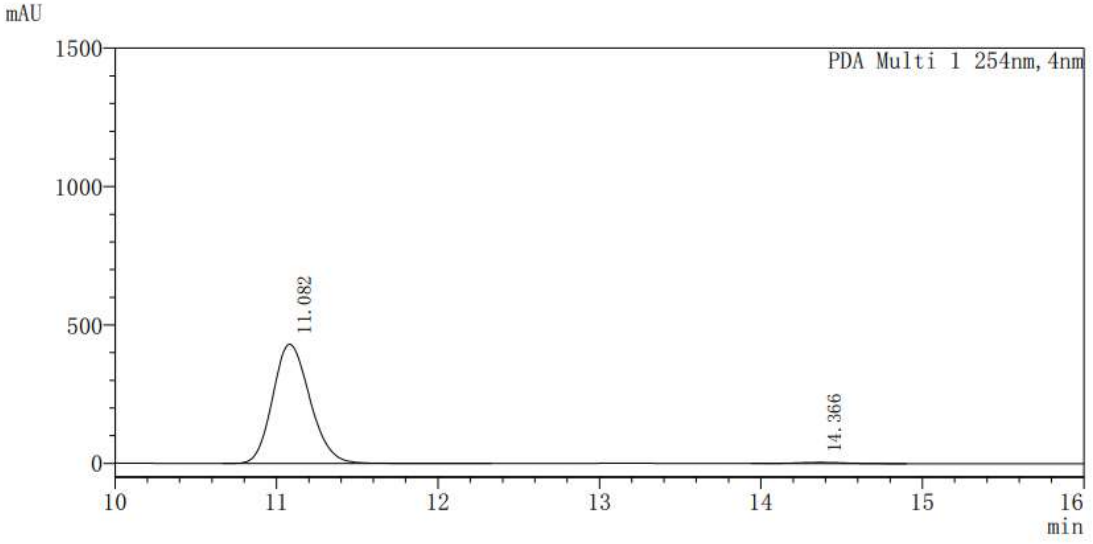
Peak	Time	Area	Height	Height%	Area%
1	11.135	7434644	425460	98.664	98.474
2	13.590	115217	5763	1.336	1.526

(*R*)-3-([1,1'-biphenyl]-4-yl)-2,3-dihydrobenzofuran-3-ol(**2g**)



PDA Ch1 254nm

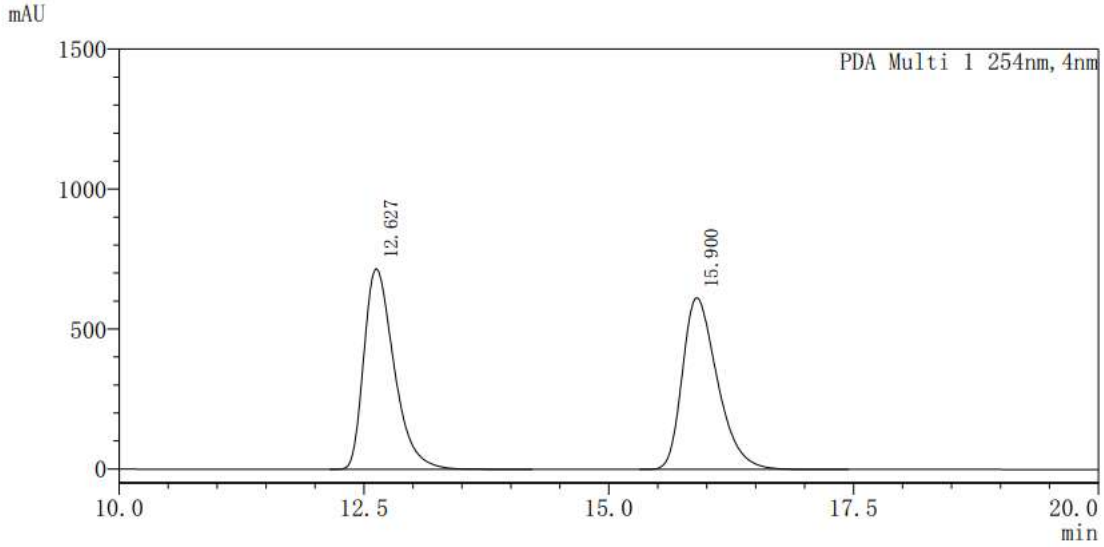
Peak	Time	Area	Height	Height%	Area%
1	11.068	9774210	612480	56.850	49.992
2	14.284	9777192	464876	43.150	50.008



PDA Ch1 254nm

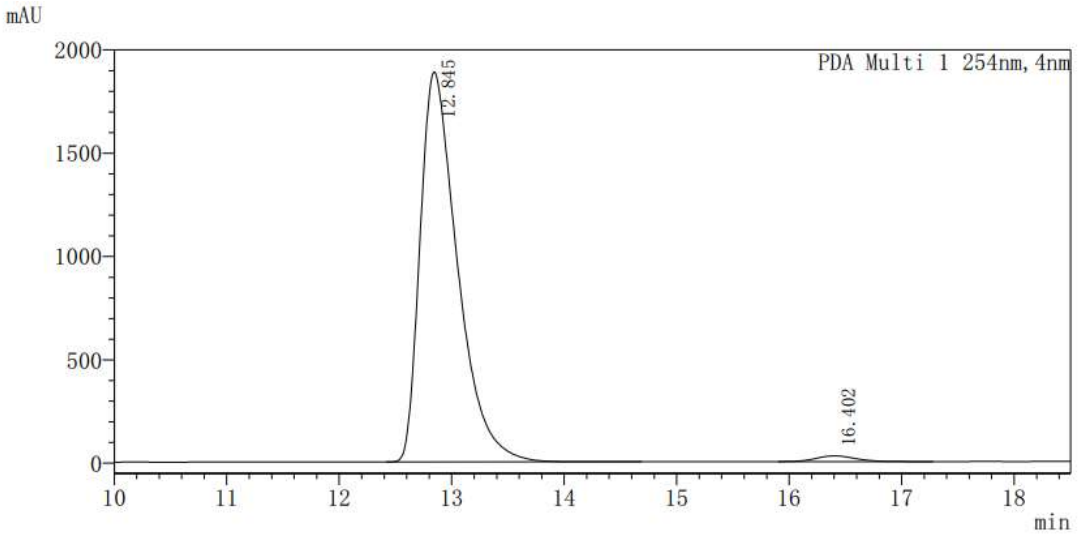
Peak	Time	Area	Height	Height%	Area%
1	11.082	6926634	431005	99.028	98.749
2	14.366	87751	4230	0.972	1.251

(*R*)-3-(naphthalen-1-yl)-2,3-dihydrobenzofuran-3-ol(**2h**)



PDA Ch1 254nm

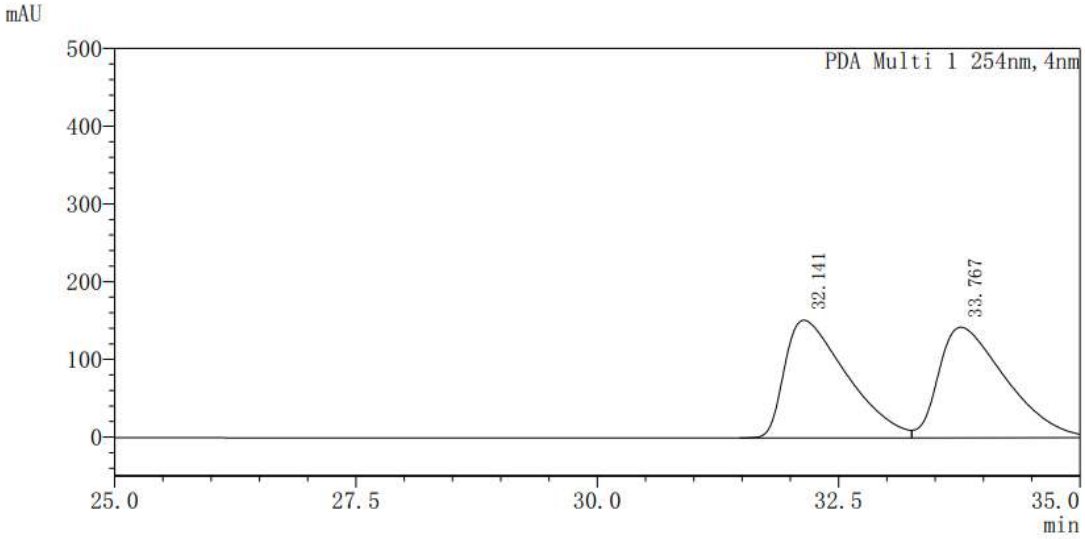
Peak	Time	Area	Height	Height%	Area%
1	12.627	15352227	716361	53.903	50.171
2	15.900	15247490	612617	46.097	49.829



PDA Ch1 254nm

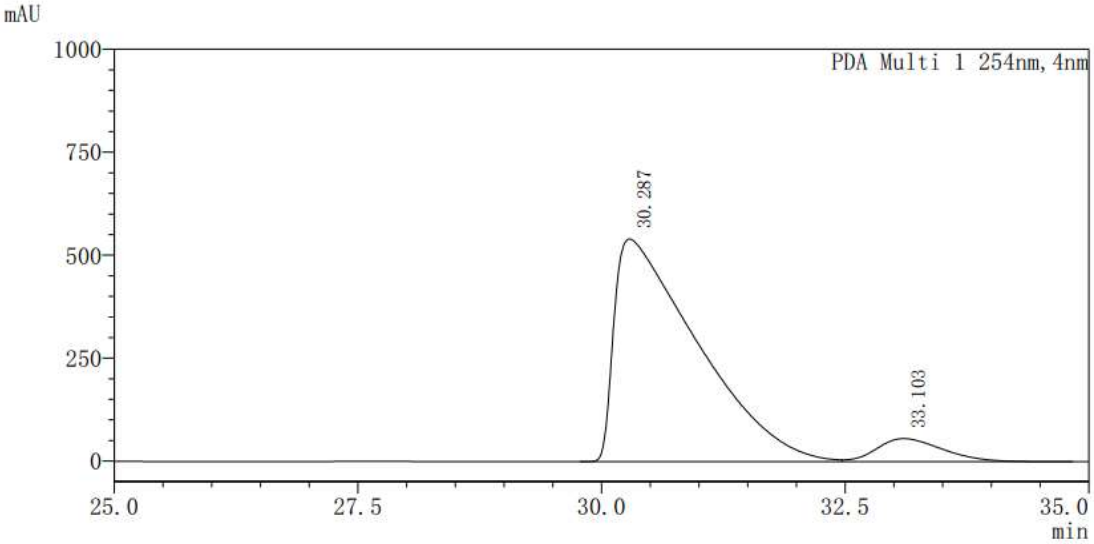
Peak	Time	Area	Height	Height%	Area%
1	12.845	43598473	1887230	98.542	98.454
2	16.402	684538	27924	1.458	1.546

(*R*)-3-(2-methoxyphenyl)-2,3-dihydrobenzofuran-3-ol(**2i**)



PDA Ch1 254nm

Peak	Time	Area	Height	Height%	Area%
1	32.141	6768028	151329	51.539	49.488
2	33.767	6908149	142290	48.461	50.512

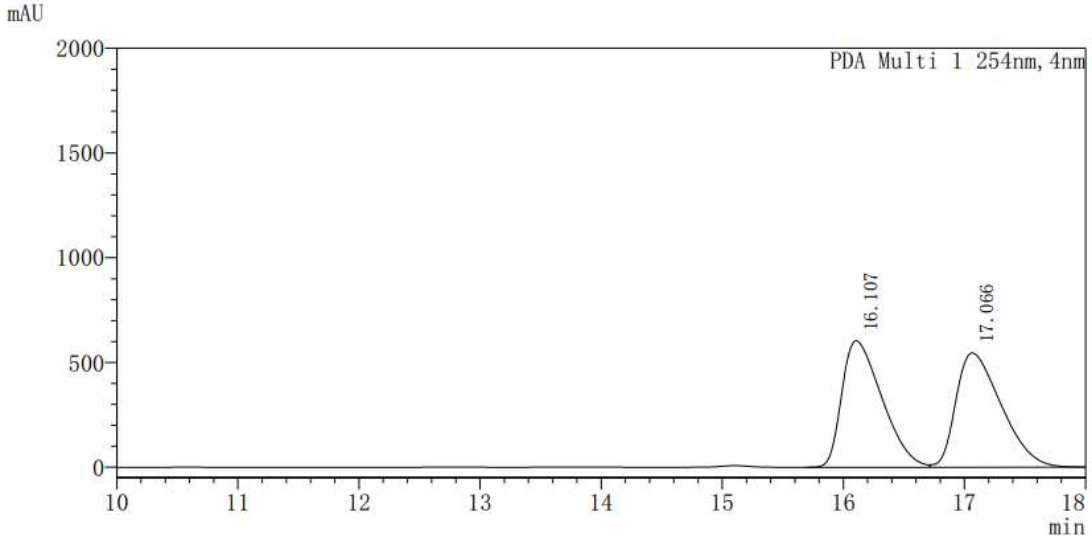


PDA Ch1 254nm

Peak	Time	Area	Height	Height%	Area%
1	30.287	32151953	540328	90.616	92.460
2	33.103	2622121	55956	9.384	7.540

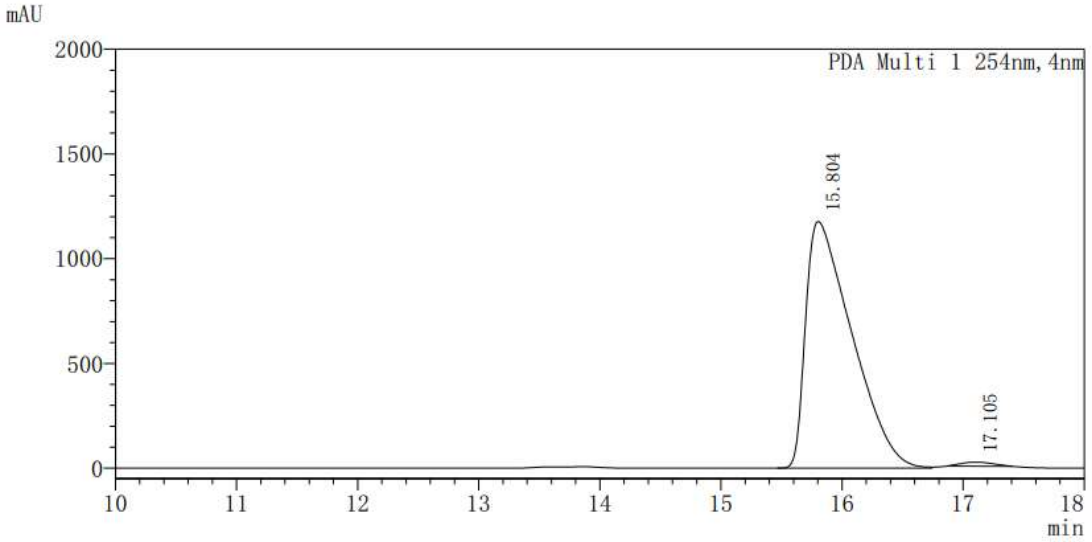
(*R*)-3-(thiophen-2-yl)-2,3-dihydrobenzofuran-3-ol(**2j**)

Reaction was performed at 60 °C.



PDA Ch1 254nm

Peak	Time	Area	Height	Height%	Area%
1	16.107	13921841	603791	52.538	49.477
2	17.066	14216046	545460	47.462	50.523

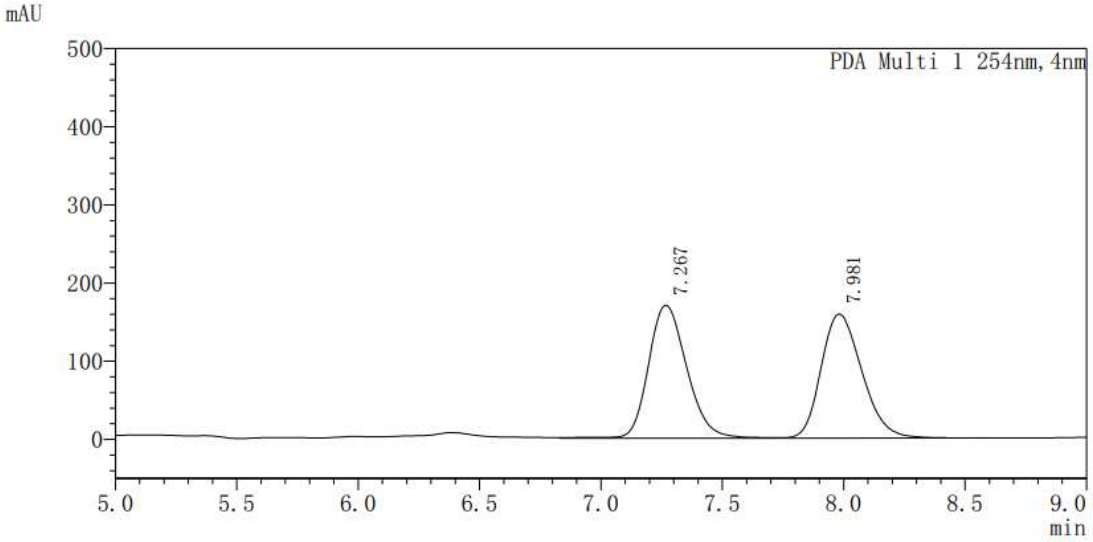


PDA Ch1 254nm

Peak	Time	Area	Height	Height%	Area%
1	15.804	31329082	1177886	98.402	98.869
2	17.105	358393	19127	1.598	1.131

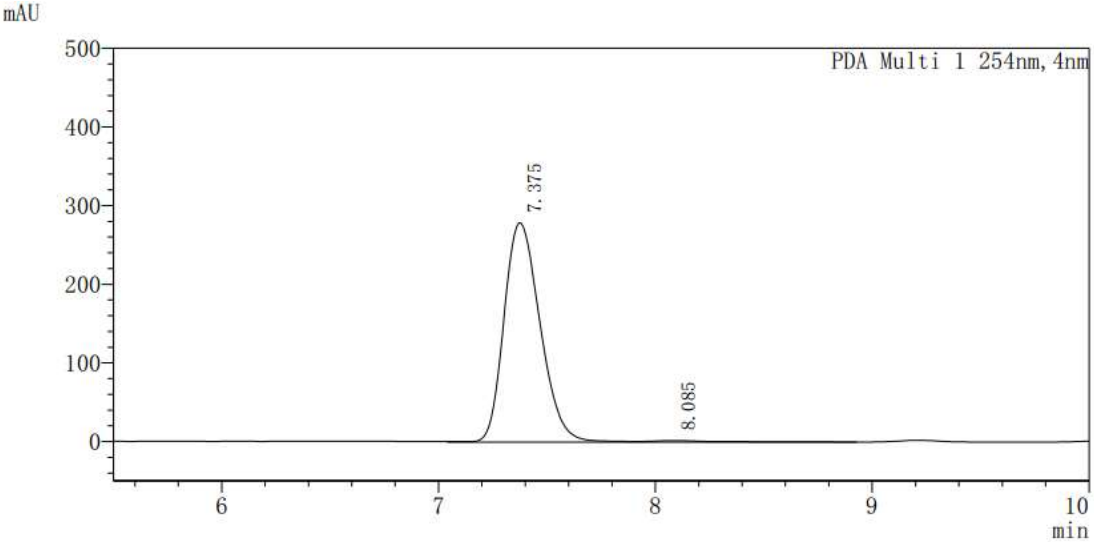
(*R*)-3-methyl-2,3-dihydrobenzofuran-3-ol(**2k**)

Reaction was performed at 60 °C.



PDA Ch1 254nm

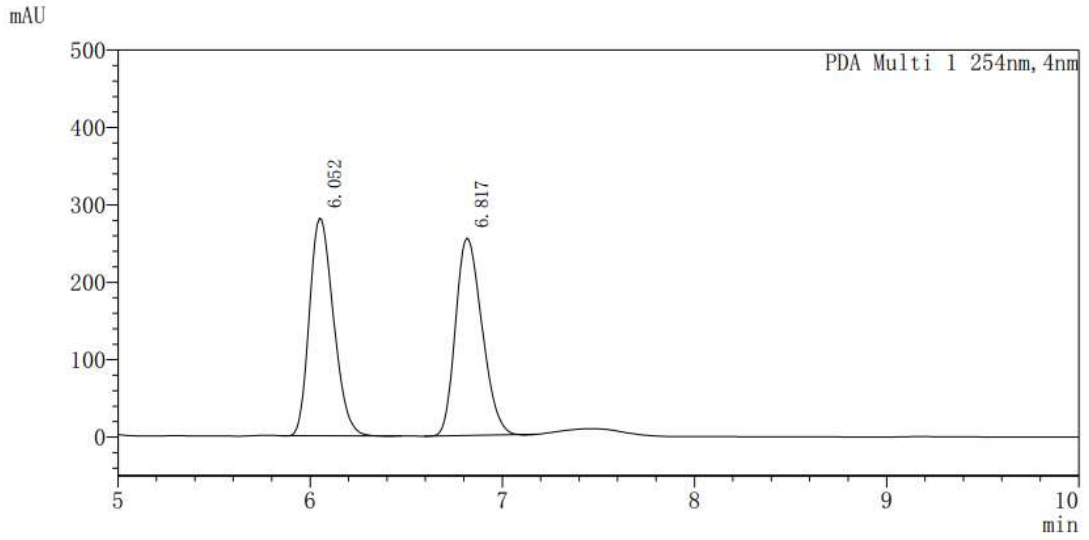
Peak	Time	Area	Height	Height%	Area%
1	7.267	1871229	170088	51.716	50.222
2	7.981	1854666	158801	48.284	49.778



PDA Ch1 254nm

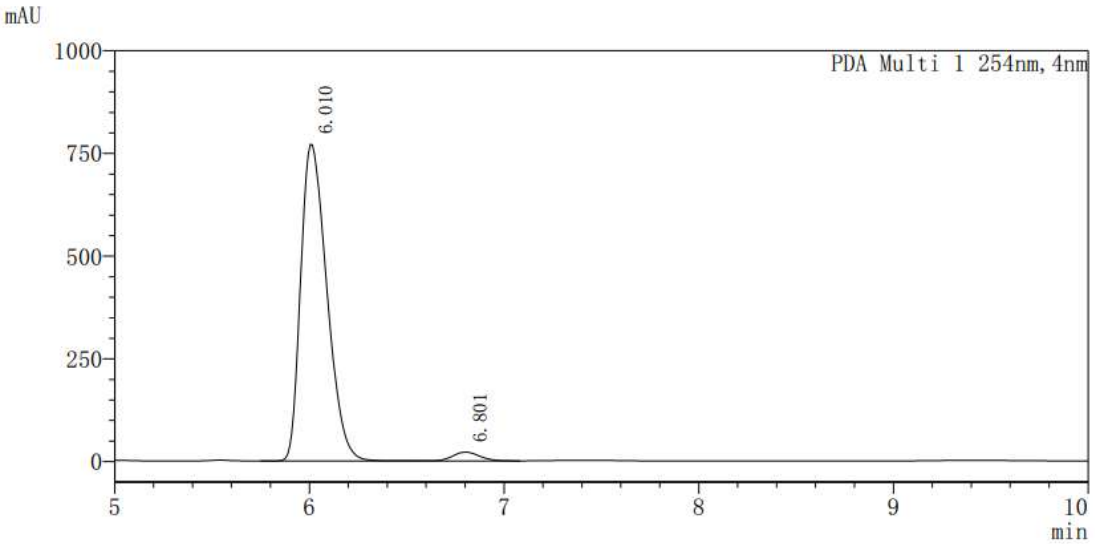
Peak	Time	Area	Height	Height%	Area%
1	7.375	3223280	278544	99.325	98.820
2	8.085	38487	1893	0.675	1.180

(*R*)-3-(tert-butyl)-2,3-dihydrobenzofuran-3-ol(**2l**)



PDA Ch1 254nm

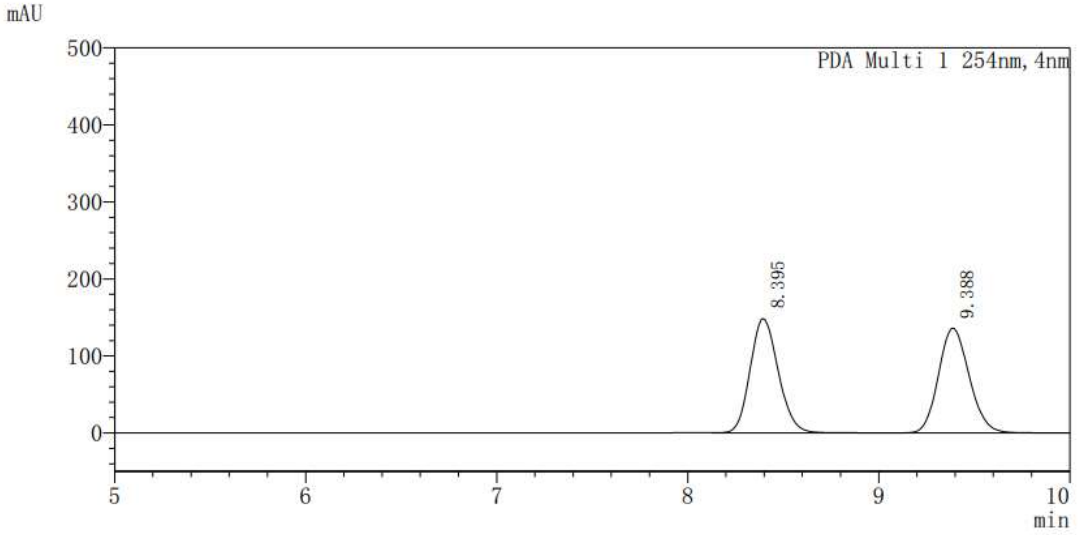
Peak	Time	Area	Height	Height%	Area%
1	6.052	2447934	280936	52.428	50.019
2	6.817	2446054	254915	47.572	49.981



PDA Ch1 254nm

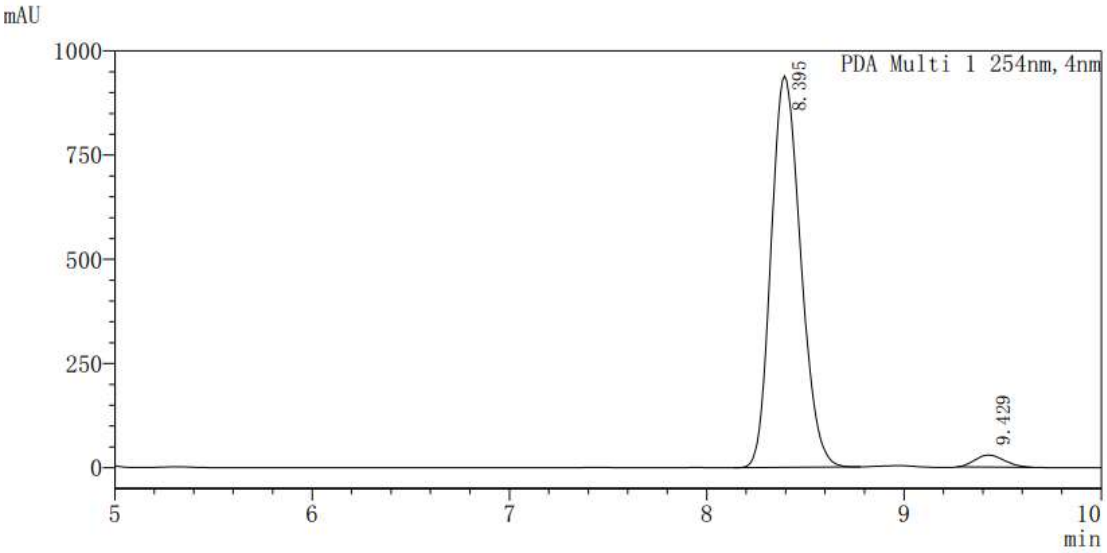
Peak	Time	Area	Height	Height%	Area%
1	6.010	7221349	771041	97.240	97.027
2	6.801	221287	21886	2.760	2.973

(*R*)-2,2-dimethyl-3-phenyl-2,3-dihydrobenzofuran-3-ol (**2m**)



PDA Ch1 254nm

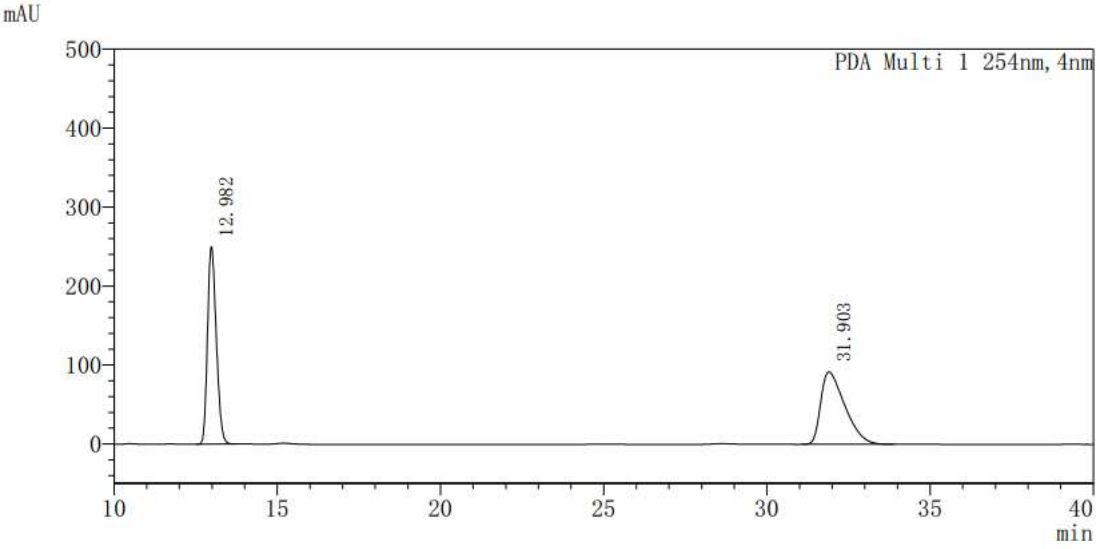
Peak	Time	Area	Height	Height%	Area%
1	8.395	1520408	148546	52.195	49.977
2	9.388	1521783	136051	47.805	50.023



PDA Ch1 254nm

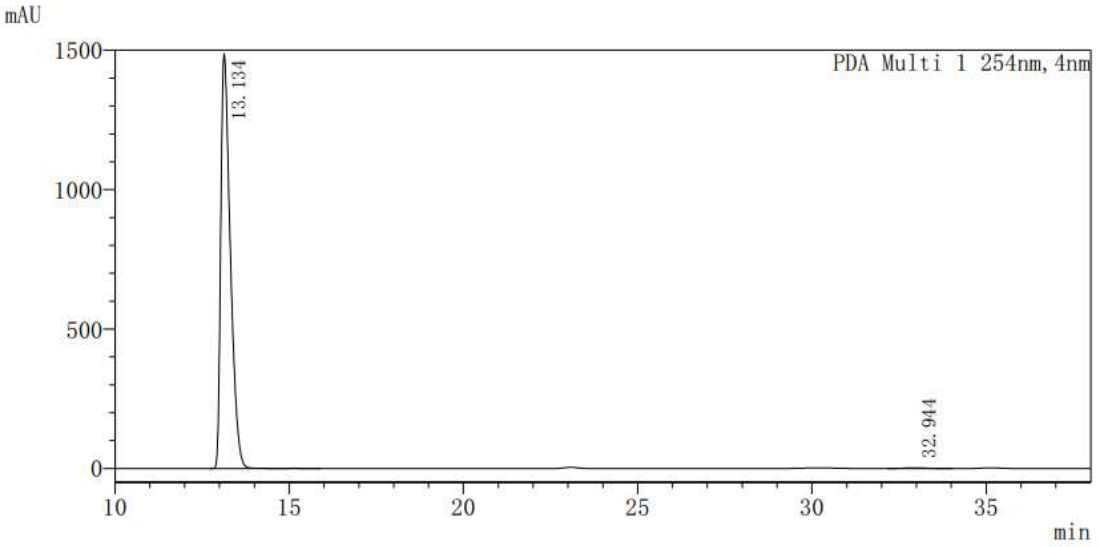
Peak	Time	Area	Height	Height%	Area%
1	8.395	9777961	939187	97.035	97.040
2	9.429	298221	28697	2.965	2.960

(*R*)-3-phenyl-2,3-dihydronaphtho[2,3-b]furan-3-ol(**2n**)



PDA Ch1 254nm

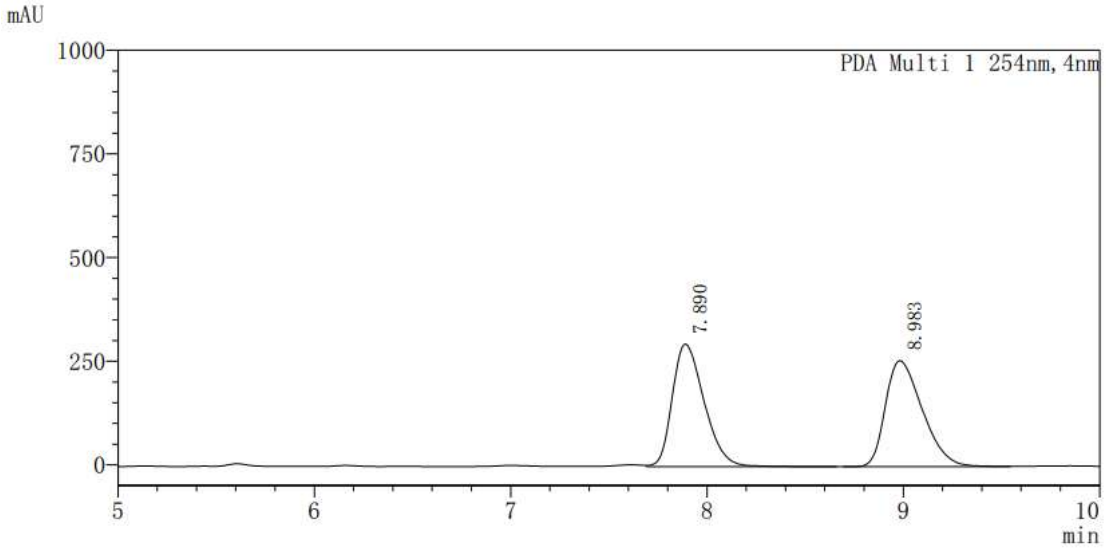
Peak	Time	Area	Height	Height%	Area%
1	12.982	4671466	250075	73.190	49.854
2	31.903	4698796	91603	26.810	50.146



PDA Ch1 254nm

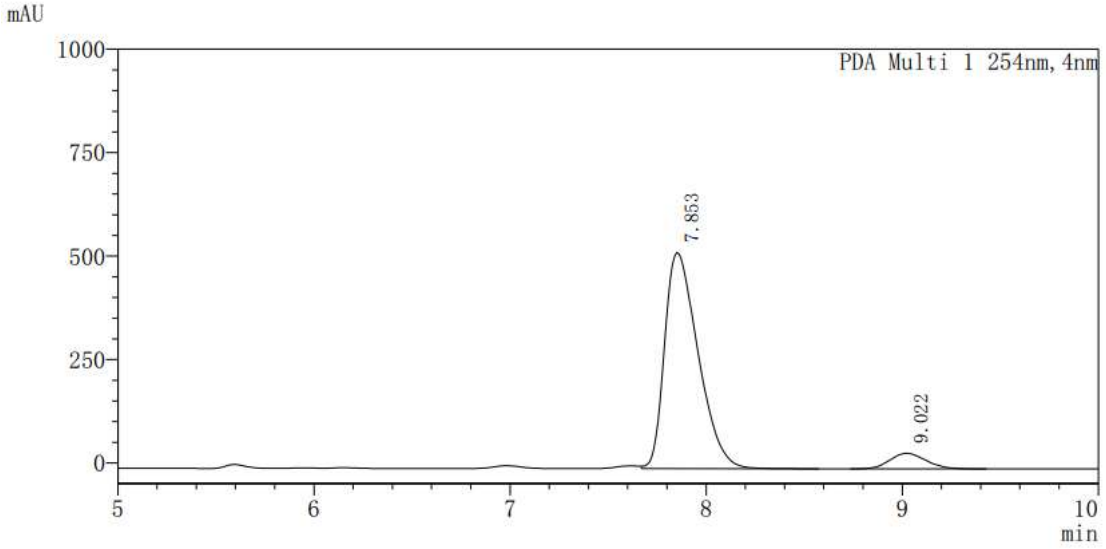
Peak	Time	Area	Height	Height%	Area%
1	13.134	28412231	1487401	99.831	99.598
2	32.944	114675	2524	0.169	0.402

(*R*)-5-chloro-3-phenyl-2,3-dihydrobenzofuran-3-ol(**2o**)



PDA Ch1 254nm

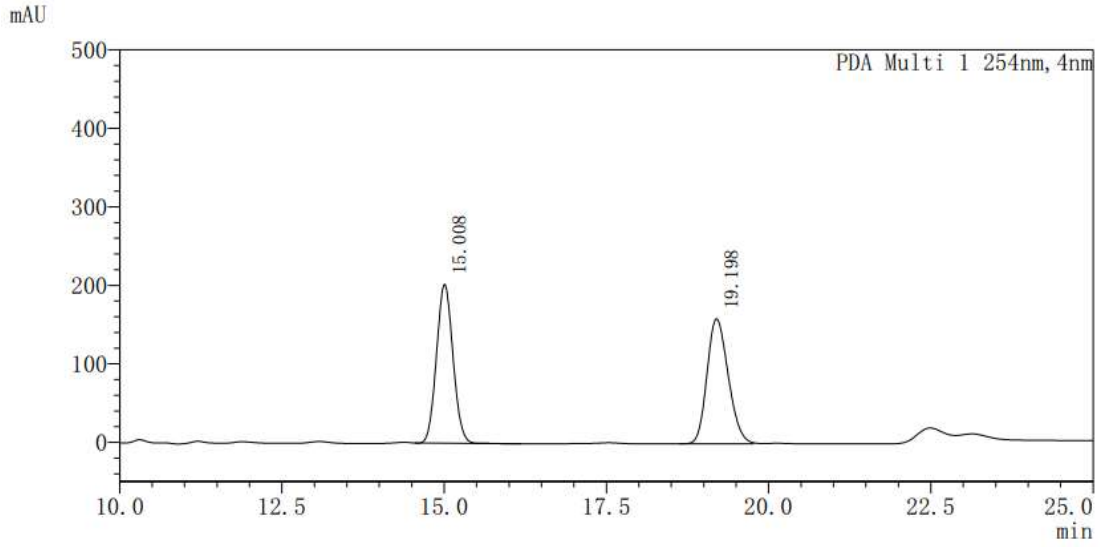
Peak	Time	Area	Height	Height%	Area%
1	7.890	3329584	295670	53.601	49.862
2	8.983	3348057	255938	46.399	50.138



PDA Ch1 254nm

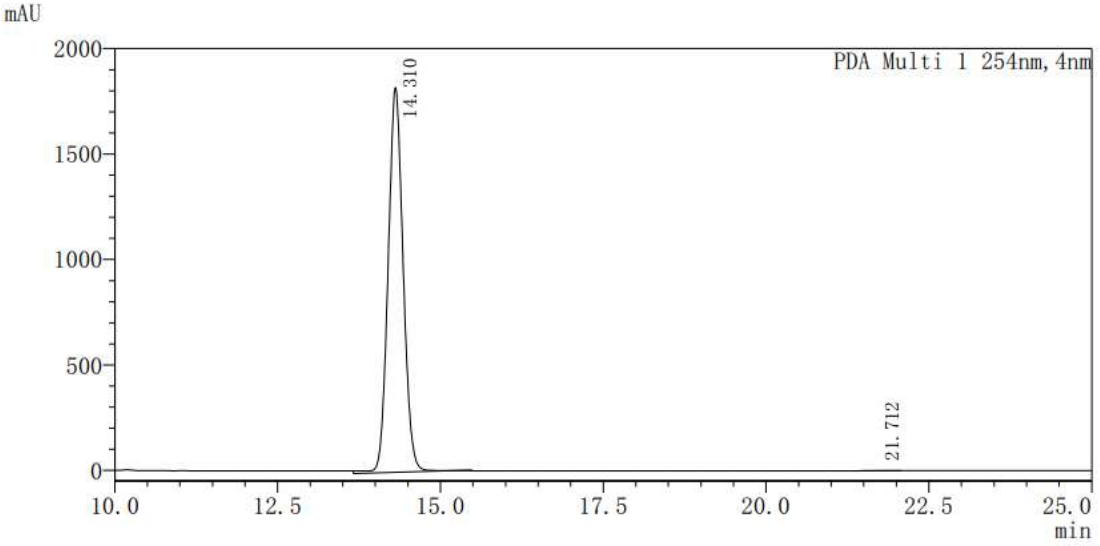
Peak	Time	Area	Height	Height%	Area%
1	7.853	6204558	522567	93.315	92.879
2	9.022	475691	37439	6.685	7.121

(*R*)-6-methoxy-3-phenyl-2,3-dihydrobenzofuran-3-ol(**2p**)



PDA Ch1 254nm

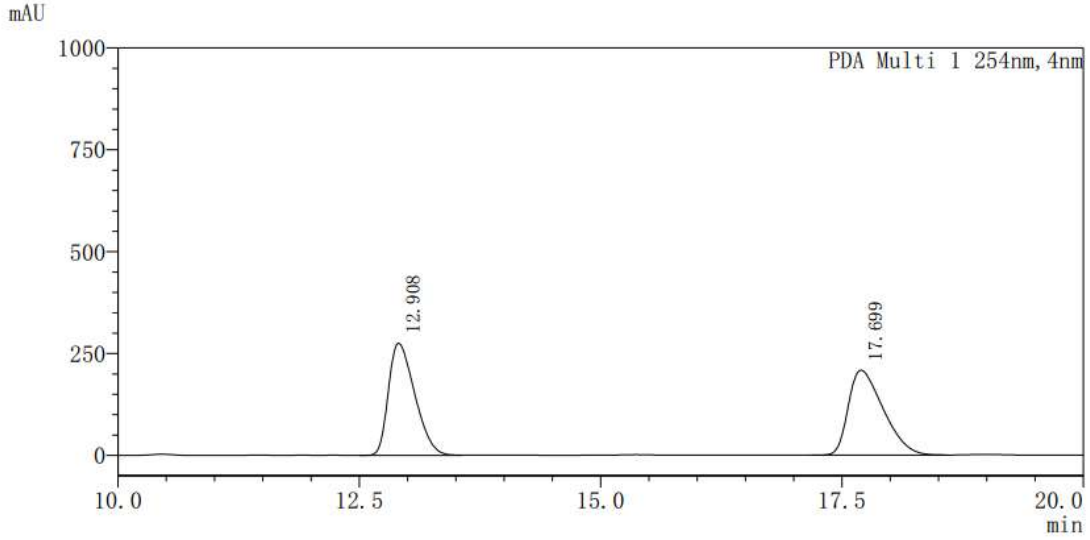
Peak	Time	Area	Height	Height%	Area%
1	15.008	3595799	202477	55.954	49.734
2	19.198	3634199	159386	44.046	50.266



PDA Ch1 254nm

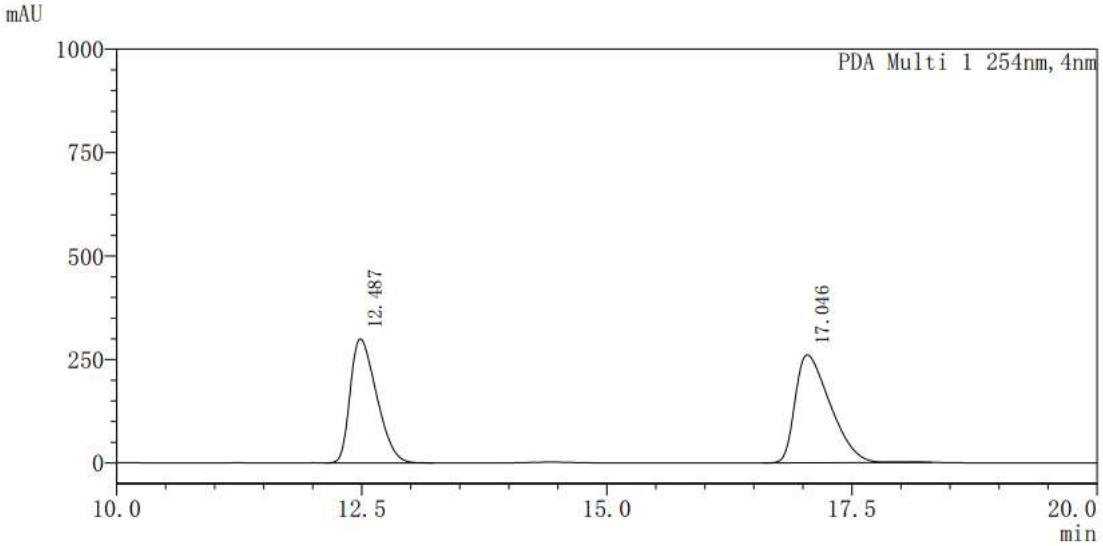
Peak	Time	Area	Height	Height%	Area%
1	14.310	29212206	1823746	99.977	99.970
2	21.712	8904	419	0.023	0.030

(*R*)-1-phenyl-2,3-dihydro-1H-inden-1-ol(**6**)



PDA Ch1 254nm

Peak	Time	Area	Height	Height%	Area%
1	12.908	5230935	275304	56.920	49.872
2	17.699	5257839	208362	43.080	50.128



PDA Ch1 254nm

Peak	Time	Area	Height	Height%	Area%
1	12.487	5610192	299543	53.453	46.359
2	17.046	6491378	260839	46.547	53.641