# Supplementary Information

## Halogenation induced C−N bond activation enables the synthesis of 1,2-cis C-aryl furanosides via deaminative cyclization

Wenbo Wang,[a] Jiawei Wu,[a] Kaiyu Jiang,[a] Maochao Zhou[a] and Gang He*[ab]

[a]State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China
[b]Frontiers Science Center for New Organic Matter, Nankai University, Tianjin 300071, China

### Table of Contents

## 1. General Information

### 1.1 Reagents

All commercial materials were used as received unless otherwise noted. MeCN, DMSO and THF were purchased from J&K Chemical (dried by 4Å MS). HFIP and DCM (dried by 4Å MS) were purchased from Energy Chemical. TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching of UV fluorescence (λmax = 254 nm) or dipped with 10% $H_2SO_4$/EtOH solution then baked with heat gun until color develops. Flash chromatography was performed using Silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co. NBS (98%) and NCS (97%) were purchased from Bide pharm. Carbohydrates, amines, and potassium aryltrifluoroborates were purchased from Shanghai Bide pharm, Adamas-beta®, Macklin, Shanghai Haohong ScientificCo.Ltd, and others.

**Note**: Mixtures of $CH_2Cl_2$/MeOH/$H_2O$ were used for the silica gel column chromatography and TLC development. The mixture with water component produced concentrated spots on the TLC plates, whereas spots with significant tailing were observed if water was omitted. According to the polarity of different compounds, three ratios were used: $CH_2Cl_2$/MeOH/$H_2O$ = 30/2/0.3, 20/2/0.3, or 6/2/0.5. And all the mixtures used in this study were homogeneous.

### 1.2 Instruments

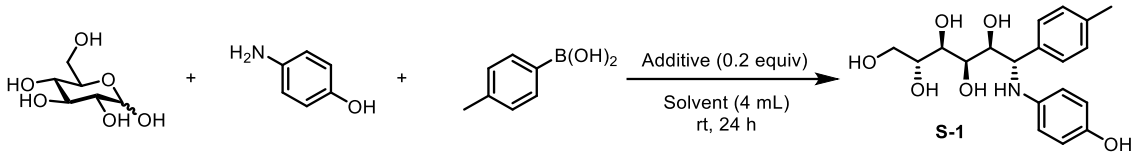
NMR spectra were recorded on Bruker AVANCE AV 600 or AV 400 instruments and all NMR experiments were reported in units, parts per million (ppm), using residual solvent peaks [$CDCl_3$: 7.26 ppm or 0.00 ppm (TMS) for $^1$H NMR and 77.16 ppm for $^{13}$C NMR; $CD_3OD$: 3.31 ppm for $^1$H NMR and 49.00 ppm for $^{13}$C NMR; acetone-$D_6$: 2.05 ppm for for $^1$H NMR and 29.84 ppm for $^{13}$C NMR]. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, m = multiplet. The HRMS data were collected on a

Thermo Q Exactive™ Focus instrument with Quadrupole-Orbitrap™ mass analyzer. The X-ray crystal structure was analysed on Rigaku XtaLAB P200 instrument. Reactions carried out at elevated temperature were heated using heating blocks.

## 2. Optimization of Petasis reaction

**General procedure for optimizing Petasis reaction**: unprotected glucose (36.0 mg, 0.2 mmol, 1.0 equiv), amine (0.2 mmol, 1.0 equiv), boronic reagents (1.0 or 1.2 equiv), additive and solvent (4 mL) were added into an 8 mL glass vial according the specific conditions listed below. The reaction mixture was stirred at rt or 60 °C. The resulting solution was concentrated *in vacuo*. The residue was dissolved in methanol and concentrated *in vacuo* (this manipulation was repeated for 3 times). The resulting residue was purified by silica gel flash chromatography to give the desired product.

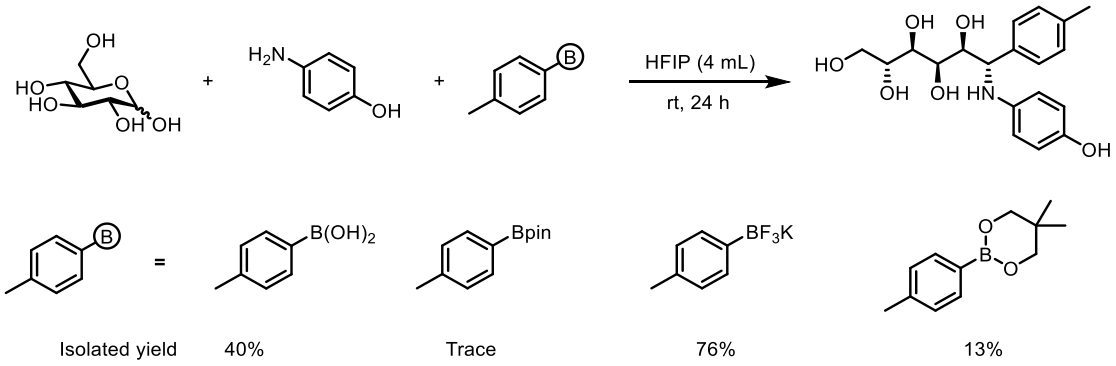
**2.1 Table S1.** Evaluation of solvents, additives and temperature




| Entry | Additive | Solvent | Yield (%)[a] |
|---|---|---|---|
| 1 | none | MeOH | N.D. |
| 2 | none | HFIP | 40 |
| 3 | none | DMSO | N.D. |
| 4 | none | THF | N.D. |
| 5 | none | DCM | N.D. |
| 6 | none | HFIP | 32[b] |
| 7 | none | $CH_3NO_2$ | N.D. |
| 8 | none | $PhCF_3$ | N.D. |
| 9 | aq. HCl (0.2 equiv) | MeCN | N.D. |
| 10 | $Pd(TFA)_2$ (0.2 equiv) | HFIP | 30 |
| 11 | NaOH (0.2 equiv) | HFIP | 20 |
| 12 | aq. HCl (0.2 equiv) | HFIP | 22 |
| 13 | $Sc(OTf)_3$ (0.2 equiv) | HFIP | 35 |

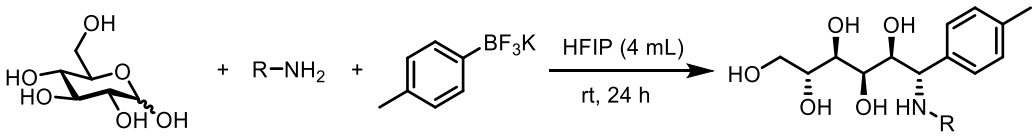
[a]Isolated yield. [b]Reaction was conducted at 60 °C. N.D.: not detected.

**2.2 Table S2.** Evaluation of boronic reagents

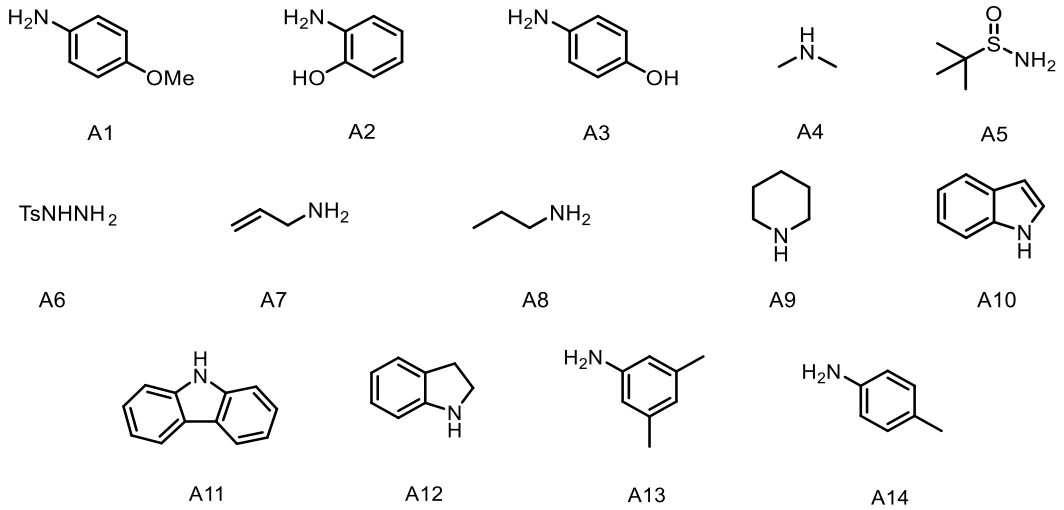



| Isolated yield | 40% | Trace | 76% | 13% |
|---|---|---|---|---|

**2.3 Table S3.** Evaluation of amines

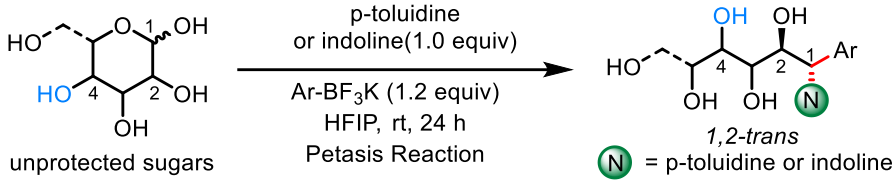



| Entry | Amine | Yield (%)[a] |
|---|---|---|
| 1 | A1 | 45[b] |
| 2 | A2 | 50[b] |
| 3 | A3 | 76 |
| 4 | A4 | N.D. |
| 5 | A5 | N.D. |
| 6 | A6 | N.D. |
| 7 | A7 | N.D. |
| 8 | A8 | N.D. |
| 9 | A9 | N.D. |
| 10 | A10 | N.D. |
| 11 | A11 | N.D. |
| 12 | A12 | 62 |
| 13 | A13 | 40 |
| 14 | A14 | 41 |
| 15 | A12 | 79[c] |
| 16 | A14 | 52[c] |
| 17 | A12 | 66[b,c] |
| 18 | A14 | N.D.[b,c] |

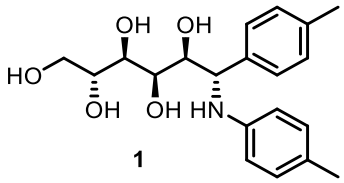



[a]Isolated yield. [b]p-Tolylboronic acid was used instead of potassium p-tolyltrifluoroborate. [c]1.2 equiv boronic reagent was employed. N.D.: not detected.

## 2.4 General procedure of Petasis reaction

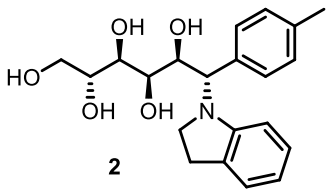



A solution of unprotected sugar (0.2 mmol, 1.0 equiv), amine (0.2 mmol, 1.0 equiv), and potassium aryltrifluoroborates (0.24 mmol, 1.2 equiv) in HFIP (4 mL) in an 8 mL glass vial was stirred at rt for 24 h and monitored by TLC analysis. The reaction mixture was concentrated *in vacuo*. The residue was dissolved in methanol and concentrated *in vacuo* (this manipulation was repeated for 3 times). The resulting residue was purified by silica gel flash chromatography to give the desired product.



**1**

White solid. ($R_f$ = 0.32, DCM/MeOH/$H_2O$ = 20/2/0.3)
Compound **1** was isolated in 52% yield (37.5 mg) following the general procedure of Petasis reaction.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.27 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.80 (d, *J* = 8.2 Hz, 2H), 6.46 (d, *J* = 8.4 Hz, 2H), 4.57 (d, *J* = 6.0 Hz, 1H), 4.00 – 3.92 (m, 2H), 3.72 (dd, *J* = 10.8, 2.9 Hz, 1H), 3.69 – 3.62 (m, 2H), 3.58 (dd, *J* = 10.8, 4.6 Hz, 1H), 2.26 (s, 3H), 2.11 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 146.7, 139.2, 137.6, 130.2, 129.8, 129.0, 127.0, 115.0, 77.0, 75.2, 73.0, 69.8, 64.7, 61.9, 21.1, 20.4.
**HRMS**: calculated for $C_{20}H_{28}NO_5^+$ [M+H$^+$]: 362.1962; **found**: 362.1955.



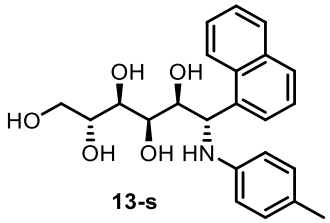
**2**

White solid. ($R_f$ = 0.41, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **2** was isolated in 79% yield (59.0 mg) following the general procedure of Petasis reaction.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.25 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.98 (td, *J* = 7.7, 1.2 Hz, 1H), 6.89 (dd, *J* = 7.2, 1.3 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.49 (td, *J* = 7.4, 0.9 Hz, 1H), 4.96 (d, *J* = 10.0 Hz, 1H), 4.52 (dd, *J* = 10.0, 1.8 Hz, 1H), 4.20 (t, *J* = 2.2 Hz, 1H), 3.81 – 3.76 (m, 2H), 3.76 – 3.71 (m, 1H), 3.64 (dd, *J* = 11.0, 5.3 Hz,

1H), 3.38 (td, *J* = 9.3, 3.6 Hz, 1H), 2.99 (td, *J* = 10.3, 8.6 Hz, 1H), 2.86 – 2.65 (m, 2H), 2.26 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 152.4, 137.9, 135.1, 130.5, 130.4, 129.6, 128.0, 125.2, 117.9, 108.5, 75.8, 73.3, 73.1, 69.8, 64.8, 61.2, 48.1, 29.1, 21.1.

**HRMS**: calculated for $C_{21}H_{27}NNaO_5^+$ [M+$Na^+$]: 396.1781; **found**: 396.1777.




**13-s**

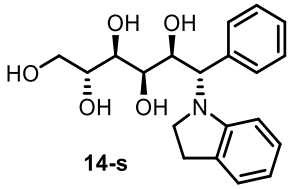
White solid. ($R_f$ = 0.31, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **13-s** was isolated in 57% yield (45.6 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 8.38 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 2H), 7.60 – 7.56 (m, 1H), 7.52 – 7.48 (m, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 2H), 6.40 (d, *J* = 8.4 Hz, 2H), 5.56 (d, *J* = 5.9 Hz, 1H), 4.22 (dd, *J* = 5.9, 1.5 Hz, 1H), 4.11 (t, *J* = 1.9 Hz, 1H), 3.69 – 3.60 (m, 2H), 3.57 – 3.49 (m, 2H), 2.10 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 146.8, 138.0, 135.4, 133.4, 130.3, 130.0, 128.7, 127.1, 126.7, 126.6, 126.4, 125.5, 124.0, 114.4, 76.7, 76.1, 72.8, 69.5, 64.6, 58.9, 20.4.

**HRMS**: calculated for $C_{23}H_{28}NO_5^+$ [M+$H^+$]: 398.1962; **found**: 398.1963.




**14-s**

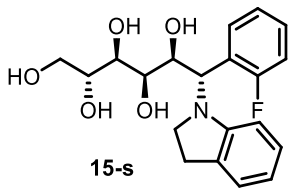
White solid. ($R_f$ = 0.46, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **14-s** was isolated in 65% yield (47.0 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.28 (d, *J* = 7.3 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.89 (t, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 7.1 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.40 (t, *J* = 7.3 Hz, 1H), 4.91 (d, *J* = 10.1 Hz, 1H), 4.46 (dd, *J* = 10.1, 1.7 Hz, 1H), 4.12 (t, *J* = 2.3 Hz, 1H), 3.75 – 3.60 (m, 3H), 3.54 (dd, *J* = 11.0, 5.4 Hz, 1H), 3.36 – 3.26 (m, 1H), 2.95 – 2.84 (m, 1H), 2.79 – 2.58 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 152.3, 138.1, 130.5, 130.5, 129.0, 128.3, 128.0, 125.3, 118.0, 108.5, 75.7, 73.3, 72.9, 69.7, 64.7, 61.4, 48.1, 29.1.

**HRMS**: calculated for $C_{20}H_{25}NNaO_5^+$ [M+$Na^+$]: 382.1625; **found**: 382.1623.




**15-s**

White solid. ($R_f$ = 0.42, DCM/MeOH/$H_2O$ = 20/2/0.3).

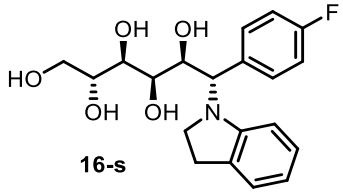
Compound **15-s** was isolated in 50% yield (38.0 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.55 – 7.47 (m, 1H), 7.27 – 7.20 (m, 1H), 7.16 – 7.10 (m, 1H), 7.07 – 7.00 (m, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.90 (d, J = 7.1 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.50 (t, *J* = 7.3 Hz, 1H), 5.31 (d, *J* = 10.2 Hz, 1H), 4.59 (d, *J* = 10.2 Hz, 1H), 4.16 (s, 1H), 3.81 – 3.70 (m, 3H), 3.63 (dd, *J* = 11.0, 5.2 Hz, 1H), 3.53 – 3.45 (m, 1H), 3.08 – 2.97 (m, 1H), 2.89 – 2.70 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 163.1 (d, *J* = 244.5 Hz), 151.9, 132.2 (d, *J* = 5.0 Hz), 130.0, 129.9 (d, *J* = 8.6 Hz), 128.0, 125.3 (d, *J* = 16.2 Hz), 125.1, 124.6 (d, *J* = 3.2 Hz), 118.1, 116.5, 116.3, 108.3, 101.3, 75.7, 73.3, 72.8, 72.7, 69.6, 64.7, 55.4, 48.4, 29.1.

**$^{19}$F NMR** (376 MHz, $CD_3OD$) δ -115.5.

**HRMS**: calculated for $C_{20}H_{25}FNO_5^+$ [M+$H^+$]: 378.1711; **found**: 378.1711.




**16-s**

White solid. ($R_f$ = 0.44, DCM/MeOH/$H_2O$ = 20/2/0.3).

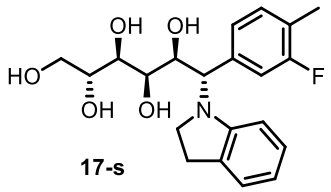
Compound **16-s** was isolated in 60% yield (45.0 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.29 (dd, *J* = 8.6, 5.5 Hz, 2H), 6.94 – 6.86 (m, 3H), 6.81 (d, *J* = 7.1 Hz, 1H), 6.69 (d, *J* = 7.9 Hz, 1H), 6.41 (t, *J* = 7.3 Hz, 1H), 4.91 (d, *J* = 10.0 Hz, 1H), 4.42 (dd, *J* = 9.9, 1.8 Hz, 1H), 4.10 (t, *J* = 2.1 Hz, 1H), 3.73 – 3.61 (m, 3H), 3.54 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.36 – 3.26 (m, 1H), 2.94 – 2.83 (m, 1H), 2.78 – 2.58 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 163.3 (d, *J* = 244.1 Hz), 152.1, 134.2 (d, *J* = 3.0 Hz), 132.1 (d, *J* = 7.6 Hz), 130.5, 128.1, 125.3, 118.2, 115.5 (d, *J* = 21.3 Hz),108.5, 75.6, 73.2, 73.0, 69.7, 64.7, 60.8, 48.0, 29.1.

**$^{19}$F NMR** (376 MHz, $CD_3OD$) δ -117.5.

**HRMS**: calculated for $C_{20}H_{25}FNO_5^+$ [M+$H^+$]: 378.1711; **found**: 378.1707.




**17-s**

White solid. ($R_f$ = 0.47, DCM/MeOH/$H_2O$ = 20/2/0.3).

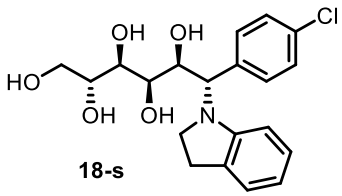
Compound **17-s** was isolated in 42% yield (33.0 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.12 (t, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 9.3 Hz, 2H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.91 (dd, *J* = 7.1, 1.2 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.51 (t, *J* = 7.3 Hz, 1H), 4.96 (d, *J* = 10.0 Hz, 1H), 4.50 (dd, *J* = 10.0, 1.8 Hz, 1H), 4.19 (t, *J* = 2.3 Hz, 1H), 3.81 – 3.76 (m, 2H), 3.76 – 3.71 (m, 1H), 3.65 (dd, *J* = 11.0, 5.4 Hz, 1H), 3.45 – 3.37 (m, 1H), 3.06 – 2.93 (m, 1H), 2.88 – 2.68 (m, 2H), 2.19 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 162.3 (d, *J* = 243.1 Hz), 152.2, 138.3 (d, *J* = 6.5 Hz), 131.9 (d, *J* = 5.1 Hz), 130.5, 128.1, 126.1(d, *J* = 3.1 Hz), 125.3, 124.5(d, *J* = 17.1 Hz), 118.2, 116.6 (d, *J* = 22.4 Hz), 108.5, 75.6, 73.3, 73.0, 69.7, 64.7, 60.9, 48.1, 29.1, 14.2 (d, *J* = 3.6 Hz).

**$^{19}$F NMR** (376 MHz, $CD_3OD$) δ -120.1.

**HRMS**: calculated for $C_{21}H_{27}FNO_5^+$ [M+H$^+$]: 392.1868; **found**: 392.1868.




**18-s**

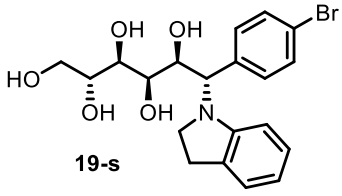
White solid. ($R_f$ = 0.43, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **18-s** was isolated in 62% yield (49.0 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.39 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.1 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.54 (t, *J* = 7.3 Hz, 1H), 5.02 (d, *J* = 9.9 Hz, 1H), 4.54 (dd, *J* = 9.9, 1.8 Hz, 1H), 4.21 (t, *J* = 2.2 Hz, 1H), 3.84 – 3.79 (m, 2H), 3.78 – 3.73 (m, 1H), 3.67 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.49 – 3.41 (m, 1H), 3.07 – 2.96 (m, 1H), 2.91 – 2.72 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 152.1, 137.1, 133.9, 132.0, 130.5, 129.0, 128.1, 125.4, 118.2, 108.5, 75.6, 73.2, 72.9, 69.7, 64.7, 60.8, 48.0, 29.1.

**HRMS**: calculated for $C_{20}H_{25}ClNO_5^+$ [M+H$^+$]: 394.1416; **found**: 394.1417.



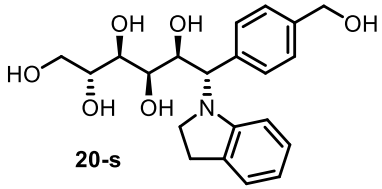

**19-s**

White solid. ($R_f$ = 0.42, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **19-s** was isolated in 69% yield (60.0 mg) following the general procedure of Petasis reaction.

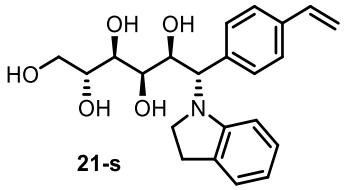
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.1 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.54 (t, *J* = 7.3 Hz, 1H), 5.00 (d, *J* = 10.0 Hz, 1H), 4.54 (dd, *J* = 9.9, 1.8 Hz, 1H), 4.21 (t, *J* = 2.2 Hz, 1H), 3.85 – 3.79 (m, 2H), 3.78 – 3.73 (m, 1H), 3.67 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.49 – 3.40 (m, 1H), 3.06 – 2.94 (m, 1H), 2.91 – 2.72 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 152.1, 137.5, 132.3, 132.0, 130.5, 128.1, 125.4, 122.0, 118.2, 108.5, 75.6, 73.2, 72.8, 69.7, 64.7, 60.9, 48.0, 29.1.
**HRMS**: calculated for $C_{20}H_{25}BrNO_5^+$ [M+H$^+$]: 438.0911; **found**: 438.0916.



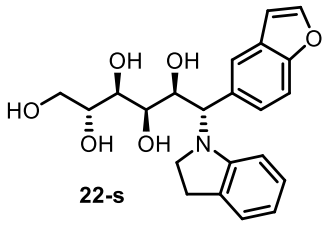
**20-s**

White solid. ($R_f$ = 0.22, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **20-s** was isolated in 78% yield (60.5 mg) following the general procedure of Petasis reaction.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.36 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.0 Hz, 1H), 6.83 – 6.76 (m, 1H), 6.49 (t, *J* = 7.3 Hz, 1H), 5.00 (d, *J* = 10.1 Hz, 1H), 4.60 – 4.47 (m, 3H), 4.21 (dd, *J* = 2.8, 1.8 Hz, 1H), 3.85 – 3.70 (m, 3H), 3.64 (dd, *J* = 10.9, 5.3 Hz, 1H), 3.44 – 3.35 (m, 1H), 3.05 – 2.92 (m, 1H), 2.86 – 2.74 (m, 1H), 2.74 – 2.64 (m, 1H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 152.3, 141.5, 137.1, 130.4, 128.0, 127.7, 125.2, 118.0, 108.5, 75.7, 73.2, 73.0, 69.7, 65.0, 64.7, 61.2, 48.0, 29.1.
**HRMS**: calculated for $C_{21}H_{28}NO_6^+$ [M+H$^+$]: 390.1911; **found**: 390.1911.



**21-s**

White solid. ($R_f$ = 0.45, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **21-s** was isolated in 62% yield (48.0 mg) following the general procedure of Petasis reaction.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.34 (s, 4H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.1 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.50 (t, *J* = 7.3 Hz, 1H), 5.71 (dd, *J* = 17.6, 1.2 Hz, 1H), 5.16 (dd, *J* = 10.9, 1.1 Hz, 1H), 5.00 (d, *J* = 10.0 Hz, 1H), 4.54 (dd, *J* = 10.0, 1.8 Hz, 1H), 4.26 – 4.15 (m, 1H), 3.83 – 3.70 (m, 3H), 3.64 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.44 – 3.36 (m, 1H), 3.04 – 2.94 (m, 1H), 2.86 – 2.68 (m, 2H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 152.3, 137.9, 137.9, 137.8, 130.6, 130.5, 128.0, 126.8, 125.3, 118.0, 113.8, 108.5, 75.7, 73.3, 73.0, 69.7, 64.7, 61.1, 48.1, 29.1.
**HRMS**: calculated for $C_{22}H_{28}NO_5^+$ [M+H$^+$]: 386.1962; found: 386.1962.




**22-s**

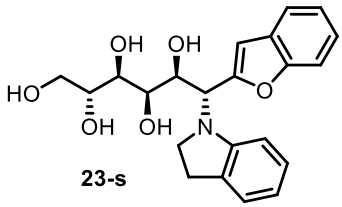
White solid. ($R_f$ = 0.45, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **22-s** was isolated in 79% yield (63.0 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.68 (d, *J* = 2.2 Hz, 1H), 7.66 (d, *J* = 1.7 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.32 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.05 – 6.96 (m, 1H), 6.90 (dd, *J* = 7.2, 1.3 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.79 (dd, *J* = 2.1, 1.1 Hz, 1H), 6.56 – 6.43 (m, 1H), 5.12 (d, *J* = 10.0 Hz, 1H), 4.60 (dd, *J* = 10.0, 1.9 Hz, 1H), 4.24 (dd, *J* = 2.7, 1.8 Hz, 1H), 3.83 – 3.80 (m, 1H), 3.80 – 3.72 (m, 2H), 3.65 (dd, *J* = 10.8, 5.3 Hz, 1H), 3.48 – 3.38 (m, 1H), 2.99 (q, *J* = 9.7, 9.2 Hz, 1H), 2.87 – 2.76 (m, 1H), 2.76 – 2.66 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 155.7, 152.4, 146.6, 132.7, 130.5, 128.6, 128.1, 127.0, 125.3, 122.9, 118.0, 111.5, 108.4, 107.7, 75.8, 73.3, 73.3, 69.8, 64.8, 61.5, 48.1, 29.1.

**HRMS**: calculated for $C_{22}H_{26}NO_6^+$ [M+H$^+$]: 400.1755; **found**: 400.1756.




**23-s**

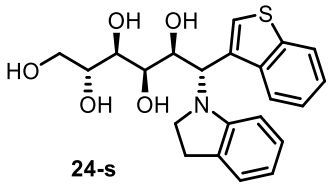
White solid. ($R_f$ = 0.45, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **23-s** was isolated in 79% yield (63.0 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.48 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.15 – 7.10 (m, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.94 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 6.73 (s, 1H), 6.56 (t, *J* = 7.3 Hz, 1H), 5.09 (d, *J* = 9.9 Hz, 1H), 4.60 (dd, *J* = 9.9, 1.7 Hz, 1H), 4.26 (dd, *J* = 3.0, 1.6 Hz, 1H), 3.84 – 3.79 (m, 2H), 3.78 – 3.73 (m, 1H), 3.66 (dd, *J* = 11.0, 5.4 Hz, 1H), 3.62 – 3.54 (m, 1H), 3.26 – 3.14 (m, 1H), 2.92 – 2.73 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 156.6, 156.0, 152.1, 130.6, 129.5, 128.0, 125.3, 124.8, 123.6, 121.8, 118.8, 111.9, 109.0, 107.1, 75.5, 73.3, 73.2, 69.4, 64.8, 56.9, 49.7, 29.2.

**HRMS**: calculated for $C_{22}H_{26}NO_6^+$ [M+H$^+$]: 400.1755; **found**: 400.1755.




**24-s**

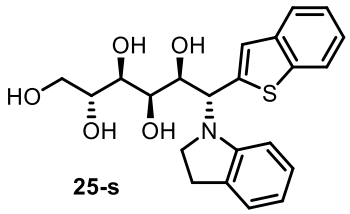
White solid. ($R_f$ = 0.44, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **24-s** was isolated in 74% yield (61.5 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.74 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.25 (m, 1H), 7.25 – 7.18 (m, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 7.1 Hz, 1H), 6.54 (t, *J* = 7.3 Hz, 1H), 5.32 (d, *J* = 9.0 Hz, 1H), 4.64 (dd, *J* = 9.0, 2.3 Hz, 1H), 4.15 (t, *J* = 1.9 Hz, 1H), 3.82 – 3.72 (m, 3H), 3.70 – 3.59 (m, 1H), 3.52 – 3.41 (m, 1H), 2.90 – 2.77 (m, 2H), 2.76 – 2.65 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 152.4, 141.3, 141.1, 134.2, 129.9, 128.3, 125.8, 125.4, 125.3, 125.0, 123.5, 123.5, 117.7, 107.2, 75.5, 74.1, 73.3, 70.1, 64.7, 55.2, 28.9.

**HRMS**: calculated for $C_{22}H_{26}NO_5S^+$ [M+H$^+$]: 416.1526; **found**: 416.1526.




**25-s**

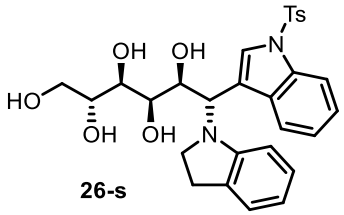
White solid. ($R_f$ = 0.44, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **25-s** was isolated in 65% yield (54.0 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.78 – 7.63 (m, 2H), 7.35 (s, 1H), 7.31 – 7.18 (m, 2H), 7.06 – 6.98 (m, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 6.64 – 6.46 (m, 1H), 5.22 (d, *J* = 9.4 Hz, 1H), 4.49 (dd, *J* = 9.4, 2.0 Hz, 1H), 4.25 (t, *J* = 2.4 Hz, 1H), 3.84 – 3.77 (m, 2H), 3.77 – 3.71 (m, 1H), 3.66 (dd, *J* = 11.0, 5.4 Hz, 1H), 3.53 – 3.44 (m, 1H), 3.29 – 3.20 (m, 1H), 3.03 – 2.75 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 151.9, 142.1, 140.8, 140.7, 130.6, 128.1, 125.4, 125.1, 125.0, 124.5, 124.2, 122.8, 118.8, 108.9, 75.4, 74.8, 73.3, 69.8, 64.8, 58.3, 29.1.

**HRMS**: calculated for $C_{22}H_{26}NO_5S^+$ [M+H$^+$]: 416.1526; **found**: 416.1528.



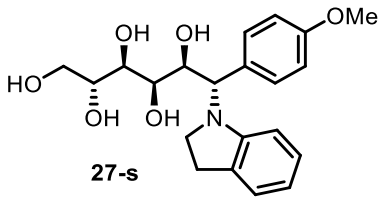

**26-s**

White solid. ($R_f$ = 0.42, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **26-s** was isolated in 73% yield (80.5 mg) following the general procedure of Petasis reaction.

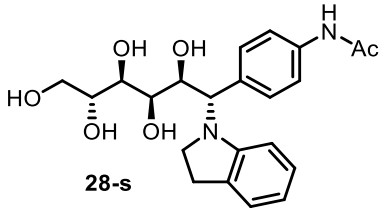
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.81 (s, 1H), 7.68 – 7.62 (m, 2H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.22 – 7.16 (m, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.06 – 6.97 (m, 2H), 6.88 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.52 (td, *J* = 7.4, 0.9 Hz, 1H), 5.13 (d, *J* = 8.9 Hz, 1H), 4.56 (dd, *J* = 8.9, 2.4 Hz, 1H), 4.14 (t, *J* = 2.2 Hz, 1H), 3.81 – 3.72 (m, 3H), 3.68 – 3.61 (m, 1H), 3.43 – 3.35 (m, 1H), 2.80 – 2.65 (m, 2H), 2.63 – 2.48 (m, 1H), 2.21 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 152.2, 146.4, 136.5, 135.9, 132.8, 130.8, 130.1, 128.2, 127.8, 127.2, 125.6, 125.4, 124.4, 121.7, 120.9, 118.0, 114.7, 107.8, 75.3, 74.1, 73.2, 70.1, 64.7, 54.2, 28.9, 21.4.
**HRMS**: calculated for $C_{29}H_{32}N_2NaO_7S^+$ [M+$Na^+$]: 575.1822; found: 575.1823.



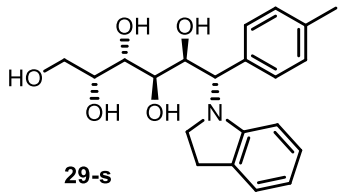
**27-s**

White solid. ($R_f$ = 0.42, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **27-s** was isolated in 85% yield (66.0 mg) following the general procedure of Petasis reaction.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.32 (d, *J* = 8.7 Hz, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.1 Hz, 1H), 6.89 – 6.82 (m, 2H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.52 (t, *J* = 7.2 Hz, 1H), 4.98 (d, *J* = 10.0 Hz, 1H), 4.53 (dd, *J* = 9.9, 1.8 Hz, 1H), 4.23 (t, *J* = 2.2 Hz, 1H), 3.85 – 3.75 (m, 3H), 3.74 (s, 3H), 3.67 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.45 – 3.36 (m, 1H), 3.06 – 2.95 (m, 1H), 2.88 – 2.69 (m, 2H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 160.2, 152.4, 131.5, 130.5, 130.1, 128.0, 125.3, 118.0, 114.4, 108.5, 75.7, 73.2, 73.2, 69.7, 64.7, 60.9, 55.6, 48.0, 29.1.
**HRMS**: calculated for $C_{21}H_{28}NO_6^+$ [M+$H^+$]: 390.1911; **found**: 390.1910.



**28-s**

White solid. ($R_f$ = 0.41, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **28-s** was isolated in 61% yield (50.5 mg) following the general procedure of Petasis reaction.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.46 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.1 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.60 – 6.38 (m, 1H), 4.97 (d, *J* = 10.0 Hz, 1H), 4.52 (dd, *J* = 10.0, 1.8 Hz, 1H), 4.27 – 4.14 (m, 1H), 3.82 – 3.76 (m, 2H), 3.76 – 3.71 (m, 1H), 3.63 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.46 – 3.36 (m, 1H), 3.08 – 2.95 (m, 1H), 2.87 – 2.69 (m, 2H), 2.08 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 171.6, 152.3, 138.8, 134.1, 130.9, 130.5, 128.0, 125.3, 120.8, 118.0, 108.5, 75.7, 73.3, 73.0, 69.7, 64.8, 61.0, 48.1, 29.1, 23.7.
**HRMS**: calculated for $C_{22}H_{29}N_2O_6^+$ [M+$H^+$]: 417.2020; **found**: 417.2020.




**29-s**

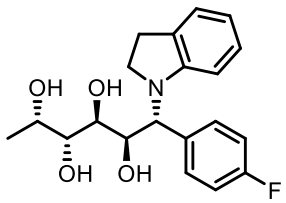
White solid. ($R_f$ = 0.41, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **29-s** was isolated in 81% yield (61.0 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.01 (t, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 7.1 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.50 (t, *J* = 7.3 Hz, 1H), 4.98 (d, *J* = 10.8 Hz, 1H), 4.68 (d, *J* = 10.7 Hz, 1H), 4.06 (d, *J* = 9.3 Hz, 1H), 4.01 – 3.95 (m, 1H), 3.75 (dd, *J* = 9.4, 1.6 Hz, 1H), 3.69 (d, *J* = 6.3 Hz, 2H), 3.48 – 3.40 (m, 1H), 3.08 – 2.98 (m, 1H), 2.91 – 2.70 (m, 2H), 2.30 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 152.4, 137.8, 135.6, 130.4, 130.3, 129.6, 128.0, 125.2, 117.7, 108.3, 71.8, 71.7, 70.5, 69.1, 65.1, 60.6, 47.6, 29.1, 21.1.

**HRMS**: calculated for $C_{21}H_{28}NO_5^+$ [M+H$^+$]: 374.1962; **found**: 374.1964.




**30-s**

White solid. ($R_f$ = 0.46, DCM/MeOH/$H_2O$ = 30/2/0.3).

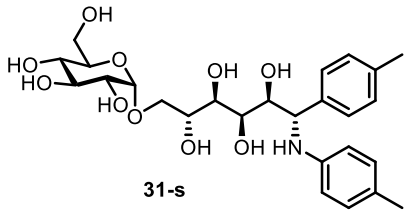
Compound **30-s** was isolated in 72% yield (52.0 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.41 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.07 – 6.99 (m, 3H), 6.92 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.52 (td, *J* = 7.4, 0.9 Hz, 1H), 5.02 (d, *J* = 10.7 Hz, 1H), 4.66 (dd, *J* = 10.7, 0.9 Hz, 1H), 4.16 – 4.09 (m, 1H), 4.02 (dd, *J* = 9.0, 0.9 Hz, 1H), 3.51 (dd, *J* = 9.1, 2.0 Hz, 1H), 3.49 – 3.42 (m, 1H), 3.02 (td, *J* = 10.3, 8.4 Hz, 1H), 2.91 – 2.81 (m, 1H), 2.81 – 2.72 (m, 1H), 1.28 (d, *J* = 6.5 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 162.0 (d, *J* = 243.8 Hz), 150.8, 133.5 (d, *J* = 3.3 Hz), 130.7 (d, *J* = 3.3 Hz), 129.0, 126.7, 124.0, 116.6, 114.1 (d, *J* = 21.3 Hz), 106.9, 73.6, 69.4, 68.1, 66.1, 58.9, 46.2, 27.7, 18.7.

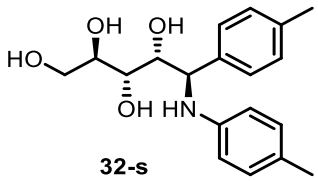
**$^{19}$F NMR** (376 MHz, $CD_3OD$) δ -117.8.

**HRMS**: calculated for $C_{20}H_{25}FNO_4^+$ [M+H$^+$]: 362.1762; **found**: 362.1753.



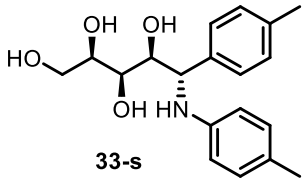

**31-s**

White solid. ($R_f$ = 0.42, DCM/MeOH/$H_2O$ = 6/2/0.5).
Compound **31-s** was isolated in 55% yield (57.6 mg) following the general procedure of Petasis reaction.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.31 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 6.82 (d, *J* = 8.1 Hz, 2H), 6.49 (d, *J* = 8.2 Hz, 2H), 4.81 (d, *J* = 3.7 Hz, 1H), 4.61 (d, *J* = 5.6 Hz, 1H), 4.07 – 4.00 (m, 2H), 3.97 (dd, *J* = 10.3, 4.1 Hz, 1H), 3.86 – 3.77 (m, 2H), 3.76 – 3.65 (m, 4H), 3.54 (dd, *J* = 10.3, 2.8 Hz, 1H), 3.43 (dd, *J* = 9.7, 3.7 Hz, 1H), 3.39 – 3.30 (m, 1H), 2.29 (s, 3H), 2.14 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 146.8, 139.2, 137.6, 130.2, 129.9, 129.0, 126.8, 115.0, 100.1, 77.3, 75.3, 74.6, 73.7, 73.5, 71.6, 71.1, 69.7, 69.3, 62.5, 62.1, 21.1, 20.4.
**HRMS**: calculated for $C_{26}H_{37}NNaO_{10}^+$ [M+$Na^+$]: 546.2310; **found**: 546.2314.



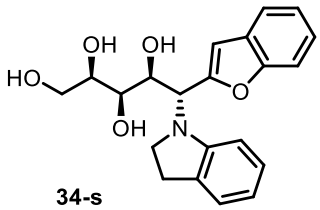
**32-s**

White solid. ($R_f$ = 0.32, DCM/MeOH/$H_2O$ = 30/2/0.3).
Compound **32-s** was isolated in 56% yield (36.5 mg) following the general procedure of Petasis reaction.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 8.2 Hz, 2H), 6.46 (d, *J* = 8.4 Hz, 2H), 4.59 (d, *J* = 7.3 Hz, 1H), 4.03 (dd, *J* = 7.3, 1.1 Hz, 1H), 3.83 – 3.74 (m, 2H), 3.73 – 3.66 (m, 1H), 3.60 (dd, *J* = 11.2, 5.8 Hz, 1H), 2.30 (s, 3H), 2.13 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 146.9, 140.1, 137.4, 130.2, 129.8, 128.8, 126.6, 114.8, 73.6, 73.2, 71.5, 65.0, 62.0, 21.1, 20.4.
**HRMS**: calculated for $C_{19}H_{26}NO_4^+$ [M+$H^+$]: 332.1856; **found**: 332.1848.



**33-s**

White solid. ($R_f$ = 0.33, DCM/MeOH/$H_2O$ = 30/2/0.3).
Compound **33-s** was isolated in 66% yield (43.8 mg) following the general procedure of Petasis reaction.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 6.49 (d, *J* = 8.4 Hz, 2H), 4.60 (d, *J* = 6.6 Hz, 1H), 3.94 (dd, *J* = 6.6, 2.0 Hz, 1H), 3.83 – 3.72 (m, 2H), 3.68 – 3.61 (m, 1H), 3.61 – 3.53 (m, 1H), 2.28 (s, 3H), 2.13 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 146.6, 139.4, 137.5, 130.2, 129.8, 128.9, 126.9, 115.0, 75.6, 75.0, 71.1, 64.2, 61.8, 21.1, 20.4.
**HRMS**: calculated for $C_{19}H_{26}NO_4^+$ [M+$H^+$]: 332.1856; **found**: 332.1853.




**34-s**

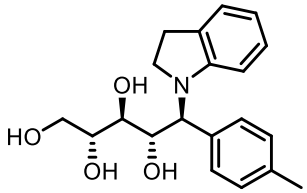
White solid. ($R_f$ = 0.48, DCM/MeOH/$H_2O$ = 30/2/0.3).

Compound **34-s-2** was isolated in 74% yield (54.5 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.51 – 7.45 (m, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.22 – 7.09 (m, 2H), 7.01 (t, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.72 (s, 1H), 6.61 – 6.49 (m, 1H), 5.07 (d, *J* = 10.1 Hz, 1H), 4.56 (dd, *J* = 10.1, 1.4 Hz, 1H), 4.08 (dd, *J* = 5.4, 1.4 Hz, 1H), 3.91 – 3.84 (m, 1H), 3.81 – 3.68 (m, 2H), 3.64 – 3.55 (m, 1H), 3.27 – 3.16 (m, 1H), 2.94 – 2.73 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 156.7, 155.9, 152.1, 130.6, 129.6, 128.0, 125.3, 124.8, 123.6, 121.7, 118.8, 111.9, 108.9, 107.0, 75.3, 71.2, 70.8, 64.1, 56.7, 49.6, 29.2.

**HRMS**: calculated for $C_{21}H_{24}NO_5^+$ [M+H$^+$]: 370.1649; **found**: 370.1649.




**35-s**

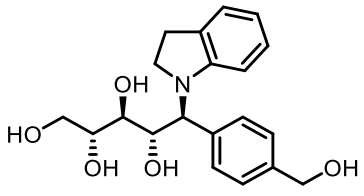
White solid. ($R_f$ = 0.45, DCM/MeOH/$H_2O$ = 30/2/0.3).

Compound **35-s** was isolated in 79% yield (54.0 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.93 (t, *J* = 7.7 Hz, 2H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.57 – 6.47 (m, 1H), 4.91 (d, *J* = 7.2 Hz, 1H), 4.43 (t, *J* = 6.7 Hz, 1H), 3.95 – 3.86 (m, 1H), 3.80 (dd, *J* = 11.3, 4.2 Hz, 1H), 3.76 (t, *J* = 5.9 Hz, 1H), 3.64 (dd, *J* = 11.3, 6.0 Hz, 1H), 3.59 – 3.47 (m, 1H), 3.20 (q, *J* = 9.3 Hz, 1H), 2.89 – 2.68 (m, 2H), 2.26 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 152.4, 137.9, 135.1, 131.1, 130.7, 129.5, 127.9, 125.2, 118.5, 109.1, 74.5, 74.3, 73.6, 64.2, 62.7, 49.7, 29.2, 21.1.

**HRMS**: calculated for $C_{20}H_{26}NO_4^+$ [M+H$^+$]: 344.1856; **found**: 344.1865.




**36-s**

White solid. ($R_f$ = 0.38, DCM/MeOH/$H_2O$ = 30/2/0.3).

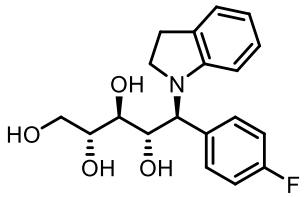
Compound **36-s** was isolated in 81% yield (58.0 mg) following the general procedure

of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.97 – 6.87 (m, 2H), 6.61 (d, *J* = 7.7 Hz, 1H), 6.52 (t, *J* = 7.3 Hz, 1H), 4.95 (d, *J* = 7.1 Hz, 1H), 4.55 (s, 2H), 4.45 (dd, *J* = 7.1, 6.2 Hz, 1H), 3.96 – 3.87 (m, 1H), 3.80 (dd, *J* = 11.3, 4.2 Hz, 1H), 3.75 (t, *J* = 6.0 Hz, 1H), 3.64 (dd, *J* = 11.3, 6.0 Hz, 1H), 3.61 – 3.52 (m, 1H), 3.24 (q, *J* = 9.3 Hz, 1H), 2.90 – 2.80 (m, 1H), 2.80 – 2.70 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 152.4, 141.6, 137.3, 131.1, 130.9, 127.9, 127.7, 125.2, 118.5, 109.1, 74.5, 74.2, 73.6, 65.0, 64.2, 62.8, 49.8, 29.2.

**HRMS**: calculated for $C_{20}H_{26}NO_5^+$ [M+H$^+$]: 360.1805; **found**: 360.1806.




**37-s**

White solid. ($R_f$ = 0.42, DCM/MeOH/$H_2O$ = 30/2/0.3).

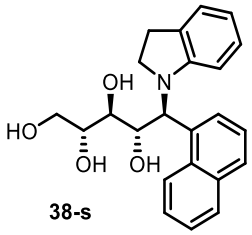
Compound **37-s** was isolated in 61% yield (42.5 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.54 – 7.36 (m, 2H), 7.06 – 6.95 (m, 2H), 6.94 (t, *J* = 7.4 Hz, 2H), 6.58 (d, *J* = 7.7 Hz, 1H), 6.53 (t, *J* = 7.3 Hz, 1H), 4.95 (d, *J* = 6.7 Hz, 1H), 4.42 (t, *J* = 6.6 Hz, 1H), 3.93 – 3.86 (m, 1H), 3.80 (dd, *J* = 11.4, 4.2 Hz, 1H), 3.70 (t, *J* = 6.1 Hz, 1H), 3.65 (dd, *J* = 11.3, 6.0 Hz, 1H), 3.64 – 3.53 (m, 1H), 3.25 (q, *J* = 9.1 Hz, 1H), 2.93 – 2.72 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 163.4 (d, *J* = 244.1 Hz), 152.3, 134.5 (d, *J* = 3.2 Hz), 132.6 (d, *J* = 7.8 Hz), 131.1, 128.0, 125.3, 118.5, 115.4 (d, *J* = 21.2 Hz), 108.9, 74.3, 74.2, 73.8, 64.2, 62.1, 49.8, 29.2.

**$^{19}$F NMR** (376 MHz, $CD_3OD$) δ -117.6.

**HRMS**: calculated for $C_{19}H_{23}FNO_4^+$ [M+H$^+$]: 348.1606; **found**: 348.1608.




**38-s**

White solid. ($R_f$ = 0.48, DCM/MeOH/$H_2O$ = 30/2/0.3).

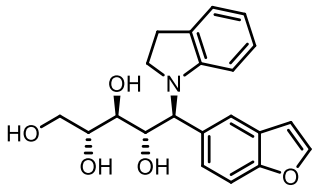
Compound **38-s** was isolated in 61% yield (46.5 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 8.16 (d, *J* = 7.2 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.86 – 7.72 (m, 2H), 7.46 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.42 – 7.32 (m, 2H), 6.98 (t, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.49 (t, *J* = 7.4 Hz, 1H), 5.76 (d, *J* = 5.2 Hz, 1H), 4.59 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.95 – 3.88 (m, 1H), 3.85 – 3.75 (m, 2H), 3.72 – 3.60 (m, 2H), 2.98 – 2.90 (m, 1H), 2.89 – 2.78 (m, 1H), 2.73 – 2.60 (m,

1H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 152.2, 135.4, 134.8, 134.6, 130.5, 129.7, 128.9, 128.6, 128.2, 127.0, 126.3, 125.9, 125.3, 125.0, 117.5, 106.9, 75.4, 75.1, 73.6, 64.3, 56.2, 50.1, 29.0.

**HRMS**: calculated for $C_{23}H_{26}NO_4^+$ [M+H$^+$]: 380.1856; **found**: 380.1857.




**39-s**

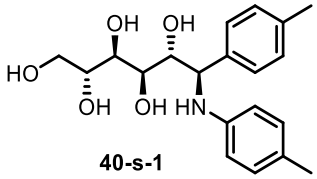
White solid. ($R_f$ = 0.44, DCM/MeOH/$H_2O$ = 30/2/0.3).

Compound **39-s** was isolated in 76% yield (56.0 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.73 (d, *J* = 1.3 Hz, 1H), 7.66 (d, *J* = 2.2 Hz, 1H), 7.40 (d, *J* = 1.1 Hz, 2H), 6.94 (t, *J* = 7.3 Hz, 2H), 6.76 (d, *J* = 2.2 Hz, 1H), 6.63 (d, *J* = 7.5 Hz, 1H), 6.52 (t, *J* = 7.4 Hz, 1H), 5.06 (d, *J* = 6.8 Hz, 1H), 4.49 (t, *J* = 6.6 Hz, 1H), 3.95 – 3.88 (m, 1H), 3.81 (dd, *J* = 11.3, 4.2 Hz, 1H), 3.75 (t, *J* = 6.1 Hz, 1H), 3.66 (dd, *J* = 11.4, 6.0 Hz, 1H), 3.63 – 3.56 (m, 1H), 3.25 (t, *J* = 9.1 Hz, 1H), 2.91 – 2.81 (m, 1H), 2.81 – 2.71 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 155.7, 152.5, 146.5, 132.9, 131.1, 128.6, 128.0, 127.3, 125.3, 123.4, 118.5, 111.4, 109.1, 107.7, 74.4, 74.4, 74.0, 64.2, 63.0, 49.9, 29.2.

**HRMS**: calculated for $C_{21}H_{24}NO_5^+$ [M+H$^+$]: 370.1649; **found**: 370.1649.




**40-s-1**

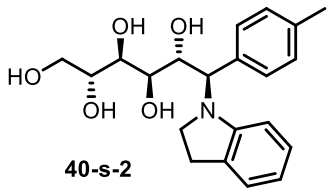
White solid. ($R_f$ = 0.31, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **40-s-1** was isolated in 61% yield (44.0 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.32 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.82 (d, *J* = 6.1 Hz, 2H), 6.53 (d, *J* = 6.4 Hz, 2H), 4.73 (d, *J* = 3.5 Hz, 1H), 4.04 (dd, *J* = 9.4, 3.5 Hz, 1H), 3.79 – 3.69 (m, 2H), 3.66 – 3.60 (m, 1H), 3.57 (dd, *J* = 10.9, 5.8 Hz, 1H), 3.49 (dd, *J* = 9.5, 1.0 Hz, 1H), 2.26 (s, 3H), 2.12 (s, 3H).

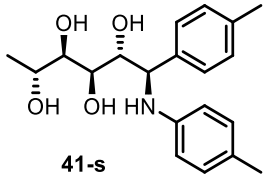
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 146.3, 137.6, 137.4, 130.3, 129.9, 129.5, 127.5, 115.7, 74.0, 73.0, 71.4, 71.0, 65.1, 60.1, 21.1, 20.4.

**HRMS**: calculated for $C_{20}H_{28}NO_5^+$ [M+H$^+$]: 362.1962; **found:** 362.1959.



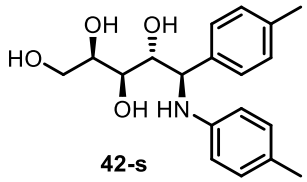

**40-s-2**

White solid. ($R_f$ = 0.42, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **40-s-2** was isolated in 81% yield (60.5 mg) following the general procedure of Petasis reaction.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.39 – 7.29 (m, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.97 – 6.87 (m, 2H), 6.58 – 6.50 (m, 2H), 4.82 (d, *J* = 6.0 Hz, 1H), 4.43 (dd, *J* = 7.9, 6.0 Hz, 1H), 3.88 – 3.81 (m, 2H), 3.77 (dd, *J* = 11.1, 3.5 Hz, 1H), 3.72 – 3.65 (m, 1H), 3.62 – 3.54 (m, 2H), 3.37 (q, *J* = 8.9 Hz, 1H), 2.91 – 2.74 (m, 2H), 2.28 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 152.5, 138.0, 135.3, 131.3, 130.9, 129.6, 127.9, 125.2, 118.7, 109.4, 73.0, 72.1, 72.0, 71.4, 65.0, 63.6, 50.4, 29.3, 21.1.
**HRMS**: calculated for $C_{21}H_{28}NO_5^+$ [M+H$^+$]: 374.1962; **found**: 374.1964.




**41-s**

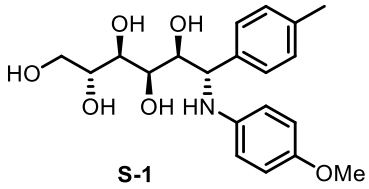
White solid. ($R_f$ = 0.34, DCM/MeOH/$H_2O$ = 30/2/0.3).
Compound **41-s** was isolated in 56% yield (39.0 mg) following the general procedure of Petasis reaction.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 2H), 6.53 (d, *J* = 8.4 Hz, 2H), 4.72 (d, *J* = 3.6 Hz, 1H), 4.03 (dd, *J* = 9.3, 3.6 Hz, 1H), 3.81 – 3.70 (m, 1H), 3.53 (dd, *J* = 9.3, 1.2 Hz, 1H), 3.47 (dd, *J* = 7.8, 1.2 Hz, 1H), 2.26 (s, 3H), 2.12 (s, 3H), 1.20 (d, *J* = 6.3 Hz, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 146.3, 137.7, 137.4, 130.3, 129.9, 129.5, 127.6, 115.8, 74.7, 74.2, 71.3, 68.8, 60.1, 21.1, 20.7, 20.5.
**HRMS**: calculated for $C_{20}H_{28}NO_4^+$ [M+H$^+$]: 346.2013; **found**: 346.2012.




**42-s**

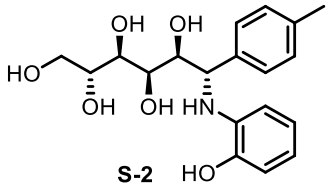
White solid. ($R_f$ = 0.36, DCM/MeOH/$H_2O$ = 30/2/0.3).
Compound **42-s** was isolated in 60% yield (40.0 mg) following the general procedure of Petasis reaction.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 2H), 6.53 (d, *J* = 8.4 Hz, 2H), 4.72 (d, *J* = 3.5 Hz, 1H), 4.05 (dd, *J* = 9.3, 3.6 Hz, 1H), 3.88 – 3.81 (m, 1H), 3.58 (dd, *J* = 11.0, 6.9 Hz, 1H), 3.53 (dd, *J* = 11.0, 5.7 Hz, 1H), 3.21 (dd, *J* = 9.3, 1.4 Hz, 1H), 2.25 (s, 3H), 2.11 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 146.2, 137.5, 137.5, 130.3, 129.9, 129.5, 127.6, 115.7, 74.1, 72.3, 71.6, 64.9, 60.0, 21.1, 20.5.
**HRMS**: calculated for $C_{19}H_{26}NO_4^+$ [M+H$^+$]: 332.1856; **found**: 332.1848.



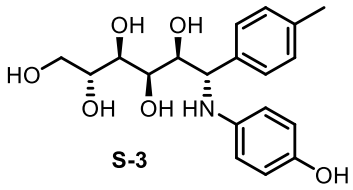
**S-1**

White solid. ($R_f$ = 0.34, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **S-1** was isolated in 45% yield (34.0 mg) following the general procedure of Petasis reaction.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.63 (d, *J* = 9.0 Hz, 2H), 6.55 (d, *J* = 8.9 Hz, 2H), 4.53 (d, *J* = 6.1 Hz, 1H), 3.98 (dd, *J* = 6.2, 3.2 Hz, 1H), 3.95 (dd, *J* = 3.2, 1.9 Hz, 1H), 3.72 (dd, *J* = 10.9, 2.9 Hz, 1H), 3.70 – 3.64 (m, 2H), 3.63 (s, 3H), 3.57 (dd, *J* = 10.8, 4.8 Hz, 1H), 2.26 (s, 3H).



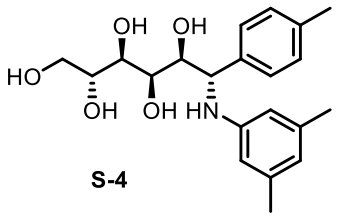
**S-2**

White solid. ($R_f$ = 0.21, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **S-2** was isolated in 50% yield (36.3 mg) following the general procedure of Petasis reaction.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.65 (d, *J* = 7.8 Hz, 1H), 6.56 – 6.50 (m, 1H), 6.48 – 6.42 (m, 2H), 4.66 (d, *J* = 5.4 Hz, 1H), 4.06 (dd, *J* = 5.5, 3.5 Hz, 1H), 3.88 (dd, *J* = 3.6, 1.7 Hz, 1H), 3.73 – 3.68 (m, 1H), 3.66 – 3.61 (m, 2H), 3.59 – 3.53 (m, 1H), 2.26 (s, 3H).



**S-3**

White solid. ($R_f$ = 0.22, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **S-3** was isolated in 76% yield (55.2 mg) following the general procedure of Petasis reaction.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.17 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.49 – 6.31 (m, 4H), 4.40 (d, *J* = 6.0 Hz, 1H), 3.94 – 3.81 (m, 2H), 3.62 (dd, *J* = 10.9, 2.8 Hz, 1H), 3.59 – 3.52 (m, 2H), 3.47 (dd, *J* = 11.2, 4.3 Hz, 1H), 2.17 (s, 3H).




**S-4**

White solid. ($R_f$ = 0.33, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **S-4** was isolated in 40% yield (30.0 mg) following the general procedure of Petasis reaction.

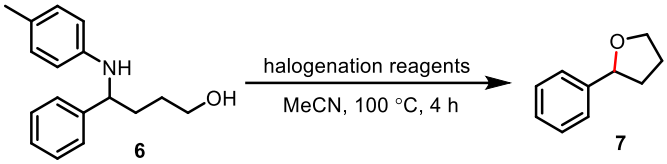
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.18 (d, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.09 (s, 3H), 4.49 (d, *J* = 6.0 Hz, 1H), 3.88 – 3.83 (m, 2H), 3.62 (dd, *J* = 10.8, 2.9 Hz, 1H), 3.57 (dd, *J* = 6.6, 3.9 Hz, 1H), 3.54 (d, *J* = 7.3 Hz, 1H), 3.47 (dd, *J* = 10.8, 4.8 Hz, 1H), 2.17 (s, 3H), 1.99 (s, 6H).

## 3. Synthesis of 1,2-cis C-aryl furanosides via deaminative cyclization.

### 3.1 Additional results on optimizing the deaminative cyclization using 6 as the model substrate.

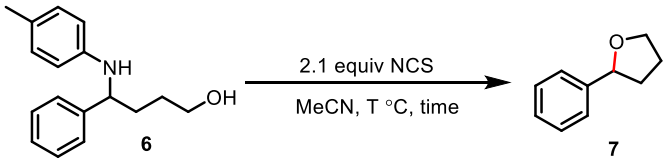
Amino alcohol substrate **6** (51.1 mg, 0.2 mmol, 1.0 equiv) was added into an 8 mL glass vial, then the solvent and reagents were added according the specific conditions listed below. After being cooled to rt, the reaction mixture was concentrated *in vacuo*. The resulting residue was dissolved in 0.5 mL of $CD_3OD$ along with 1,1,2,2-tetrachloroethane (33.6 mg, 0.2 mmol, 1.0 equiv, a singlet peak around 6.45 ppm was set as 1.00) as internal standard, and analyzed by $^1H$ NMR.

**3.1.1 Table S4.** Evaluation of halogenation reagents



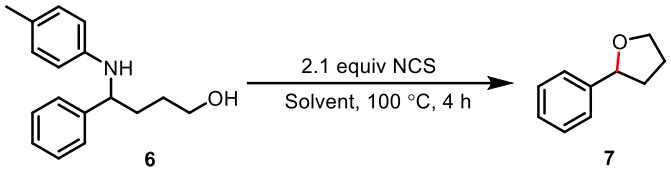

| Entry | Reaction conditions | NMR Yield (%) |
|---|---|---|
| 1 | 2.0 equiv NCS | 84 |
| 2 | 2.1 equiv NCS | 95 |
| 3 | 1.9 equiv NCS | 70 |
| 4 | 2.1 equiv NIS | 33 |
| 5 | 2.1 equiv NBS | 77 |
| 6 | 3.0 equiv NCS | 70 |
| 7 | Without NCS | N.D. |
| 8 | 2.0 equiv NFSI, 24 h | 40% |

**3.1.2 Table S5.** Evaluation of reaction temperature and time



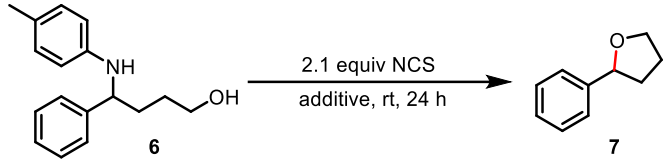

| Entry | Temperature and time | NMR Yield (%) |
|---|---|---|
| 1 | 15 °C, 24 h | trace |
| 2 | 40 °C, 24 h | 18 |
| 3 | 60 °C, 24 h | 78 |
| 4 | 80 °C, 9 h | 92 |
| 5 | 100 °C, 4 h | 95 |

**3.1.3 Table S6.** Evaluation of solvents



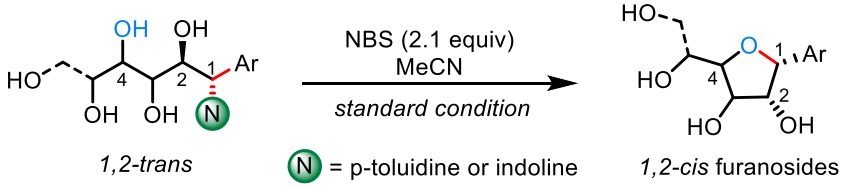

| Entry | Solvents | NMR Yield (%) |
|---|---|---|
| 1 | MeCN | 95 |
| 2 | HFIP | 76 |
| 3 | EtOH | 73 |
| 4 | THF | trace |
| 5 | Dioxane | trace |
| 6 | DCE | trace |
| 7 | Toluene | trace |

**3.1.4 Table S7.** Evaluation of additive



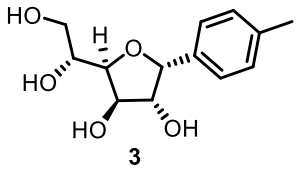

| Entry | Additive | NMR Yield (%) |
|---|---|---|
| 1 | None | 9 |
| 2 | 1.0 equiv TsOH | 66 |
| 3 | 1.0 equiv $La(OTf)_3$ | 73 |
| 4 | 1.0 equiv TFA | 13 |
| 5 | 1.0 equiv HCl (36% in water) | 61 |
| 6 | 1.0 equiv HBr (33% in AcOH) | 76 |
| 7 | 1.0 equiv BINOL phosphoric acid | 19 |
| 8 | 1.0 equiv HBr (40% in water) | 82 |
| 9 | 2.0 equiv HBr (40% in water) | 85 |
| 10 | 3.0 equiv HBr (40% in water) | 69 |
| 11 | 2.0 equiv HBr (40% in water) without NCS | N.D. |
| 12 | 2.0 equiv $Cu(OAc)_2$ | N.D. |

**3.2 General procedure for deaminative cyclization**



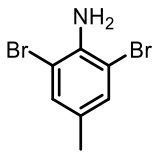

The linear 1-aryl polyhydroxy amines obtained from Petasis reaction (0.2 mmol, 1.0 equiv) was dissolved in MeCN (2 mL, 0.1 M) in an 8 mL glass vial. To the solution was

added NBS (74.8 mg, 0.42 mmol, 2.1 equiv). The mixture was stirred at 80 ℃ or 100 ℃ under air atmosphere and monitored by TLC analysis. After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure. The resulting residue was subjected to silica gel chromatography to give the desired product.



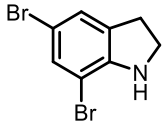

**3**

White solid. ($R_f$ = 0.22, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **3** was isolated in 85% yield (43.0 mg) from **1**, and 76% yield (38.8 mg) from **2** following the general procedure of deaminative cyclization.
**$^1$H NMR** (600 MHz, $CD_3OD$) δ 7.26 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), **5.21 (d, *J* = 3.2 Hz, 1H)**, 4.38 (d, *J* = 3.3 Hz, 1H), 4.23 (dd, *J* = 8.2, 3.4 Hz, 1H), 4.12 (d, *J* = 3.2 Hz, 1H), 4.06 – 3.95 (m, 1H), 3.88 (dd, *J* = 11.4, 3.3 Hz, 1H), 3.71 (dd, *J* = 11.5, 6.3 Hz, 1H), 2.33 (s, 3H).
**$^{13}$C NMR** (151 MHz, $CD_3OD$) δ 137.8, 136.0, 129.4, 128.2, 84.3, 81.8, 80.0, 78.6, 71.5, 65.6, 21.2.
**HRMS**: calculated for $C_{13}H_{18}NaO_5^+$ [M+$Na^+$]: 277.1046; **found**: 277.1047.




**4**

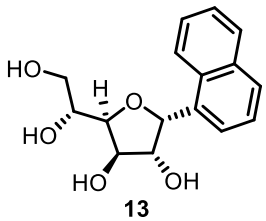
White solid. ($R_f$ = 0.31, hexane/ethyl acetate = 30/1)
Compound **4** is a known compound, and was obtained in 91% yield (48.0 mg) from the deaminative cyclization. The spectral data are consistent with those reported in literature[1].
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.20 (s, 2H), 4.38 (s, 2H), 2.21 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 139.7, 132.3, 129.5, 108.9, 20.0.




**5**

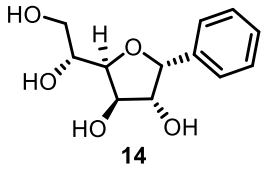
White solid. ($R_f$ = 0.39, hexane/ethyl acetate = 30/1)
Compound **5** is a known compound, and was obtained in 79% yield (44.0 mg) from the deaminative cyclization. The spectral data are consistent with those reported in literature[2].
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.28 (dt, *J* = 1.7, 0.8 Hz, 1H), 7.11 (d, *J* = 1.6 Hz, 1H),

3.62 (t, *J* = 8.5 Hz, 2H), 3.13 (t, *J* = 8.6 Hz, 2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 149.6, 132.3, 131.9, 126.7, 109.7, 103.2, 47.0, 30.9.



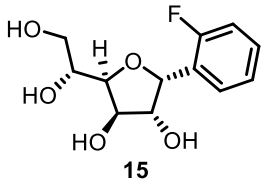
**13**

White solid. ($R_f$ = 0.21, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **13** was isolated in 82% yield (47.8 mg) following the general procedure of deaminative cyclization.
**$^{1}$H NMR** (400 MHz, $CD_3OD$) δ 8.02 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.77 (t, *J* = 8.3 Hz, 2H), 7.57 – 7.39 (m, 3H), **6.01 (d, *J* = 3.3 Hz, 1H)**, 4.51 (dd, *J* = 3.4, 1.2 Hz, 1H), 4.41 (dd, *J* = 3.2, 1.2 Hz, 1H), 4.29 (dd, *J* = 8.3, 3.2 Hz, 1H), 4.12 – 4.02 (m, 1H), 3.94 (dd, *J* = 11.5, 3.3 Hz, 1H), 3.77 (dd, *J* = 11.5, 6.2 Hz, 1H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 135.0, 134.6, 131.9, 129.8, 128.5, 126.9, 126.3, 125.8, 123.6, 81.6, 81.4, 79.2, 78.9, 71.5, 65.7.
**HRMS**: calculated for $C_{16}H_{18}NaO_5^+$ [M+$Na^+$]: 313.1046; **found**: 313.1046.



**14**

White solid. ($R_f$ = 0.23, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **14** was isolated in 70% yield (37.0 mg) following the general procedure of deaminative cyclization.
**$^{1}$H NMR** (400 MHz, $CD_3OD$) δ 7.41 – 7.30 (m, 4H), 7.25 (t, *J* = 7.1 Hz, 1H), **5.24 (d, *J* = 3.2 Hz, 1H)**, 4.37 (d, *J* = 3.1 Hz, 1H), 4.23 (dd, *J* = 8.3, 3.3 Hz, 1H), 4.16 (d, *J* = 3.1 Hz, 1H), 4.04 – 3.96 (m, 1H), 3.89 (dd, *J* = 11.5, 3.3 Hz, 1H), 3.71 (dd, *J* = 11.5, 6.2 Hz, 1H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 139.3, 128.8, 128.2, 84.4, 81.9, 80.0, 78.6, 71.5, 65.6.
**HRMS**: calculated for $C_{12}H_{16}NaO_5^+$ [M+$Na^+$]: 263.0890; **found**: 263.0891.



**15**

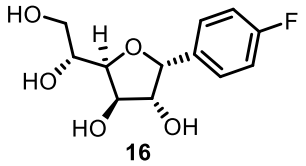
White solid. ($R_f$ = 0.27, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **15** was isolated in 64% yield (33.0 mg) following the general procedure of deaminative cyclization.
**$^{1}$H NMR** (400 MHz, $CD_3OD$) δ 7.59 – 7.51 (m, 1H), 7.29 – 7.21 (m, 1H), 7.16 – 7.09

(m, 1H), 7.05 – 6.97 (m, 1H), **5.45 (d, *J* = 3.4 Hz, 1H)**, 4.33 (dd, *J* = 3.1, 1.2 Hz, 1H), 4.30 – 4.27 (m, 1H), 4.17 (dd, *J* = 8.3, 3.1 Hz, 1H), 4.02 – 3.95 (m, 1H), 3.88 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.70 (dd, *J* = 11.5, 6.2 Hz, 1H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 161.0 (d, *J* = 243.5 Hz), 130.2 (d, *J* = 4.6 Hz), 129.6 (d, *J* = 8.2 Hz), 126.9 (d, *J* = 13.2 Hz), 124.7 (d, *J* = 3.3 Hz), 115.3 (d, *J* = 21.2 Hz), 81.5, 78.9, 78.9, 78.6, 71.4, 65.6.

**$^{19}$F NMR** (376 MHz, $CD_3OD$) δ -120.8.

**HRMS**: calculated for $C_{12}H_{15}FNaO_5^+$ [M+$Na^+$]: 281.0796; **found**: 281.0797.




**16**

White solid. ($R_f$ = 0.26, DCM/MeOH/$H_2O$ = 20/2/0.3).

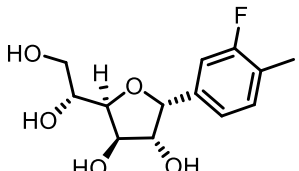
Compound **16** was isolated in 73% yield (39.0 mg) following the general procedure of deaminative cyclization.

**$^{1}$H NMR** (400 MHz, $CD_3OD$) δ 7.26 (dd, *J* = 8.5, 5.6 Hz, 2H), 6.93 (t, *J* = 8.8 Hz, 2H), **5.10 (d, *J* = 3.2 Hz, 1H)**, 4.25 (dd, *J* = 3.3, 1.2 Hz, 1H), 4.10 (dd, *J* = 8.3, 3.3 Hz, 1H), 4.00 (dd, *J* = 3.2, 1.3 Hz, 1H), 3.91 – 3.83 (m, 1H), 3.75 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.58 (dd, *J* = 11.5, 6.2 Hz, 1H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 163.5 (d, *J* = 243.1 Hz), 135.3 (d, *J* = 3.0 Hz), 130.0 (d, *J* = 8.0 Hz), 115.4 (d, *J* = 21.5 Hz), 83.8, 81.9, 79.9, 78.6, 71.5, 65.6.

**$^{19}$F NMR** (376 MHz, $CD_3OD$) δ -118.2.

**HRMS**: calculated for $C_{12}H_{15}FNaO_5^+$ [M+$Na^+$]: 281.0796; **found**: 281.0794.




**17**

White solid. ($R_f$ = 0.28, DCM/MeOH/$H_2O$ = 20/2/0.3).

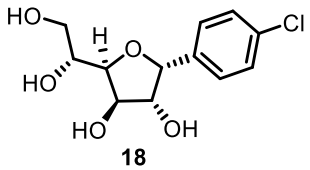
Compound **17** was isolated in 61% yield (33.0 mg) following the general procedure of deaminative cyclization.

**$^{1}$H NMR** (400 MHz, $CD_3OD$) δ 7.15 (t, *J* = 7.8 Hz, 2H), 7.09 – 6.97 (m, 1H), **5.17 (d, *J* = 3.2 Hz, 1H)**, 4.33 (dd, *J* = 3.3, 1.3 Hz, 1H), 4.19 (dd, *J* = 8.3, 3.3 Hz, 1H), 4.11 (dd, *J* = 3.2, 1.3 Hz, 1H), 4.01 – 3.92 (m, 1H), 3.85 (dd, *J* = 11.4, 3.3 Hz, 1H), 3.68 (dd, *J* = 11.5, 6.1 Hz, 1H), 2.23 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 162.5 (d, *J* = 242.3 Hz), 139.6 (d, *J* = 7.5 Hz), 131.8 (d, *J* = 5.3 Hz), 124.3 (d, *J* = 17.3 Hz), 123.5 (d, *J* = 3.2 Hz), 114.7 (d, *J* = 23.5 Hz), 83.7, 81.9, 80.0, 78.6, 71.5, 65.6, 14.2 (d, *J* = 3.7 Hz).

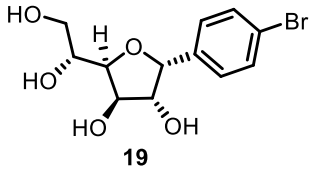
**$^{19}$F NMR** (376 MHz, $CD_3OD$) δ -120.8.

**HRMS**: calculated for $C_{13}H_{17}FNaO_5^+$ [M+$Na^+$]: 295.0952; **found**: 295.0959.



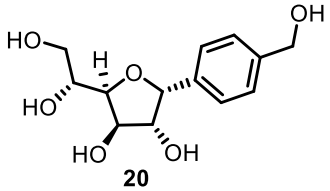
**18**

White solid. ($R_f$ = 0.24, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **18** was isolated in 77% yield (42.0 mg) following the general procedure of deaminative cyclization
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.38 – 7.28 (m, 4H), **5.19 (d, *J* = 3.2 Hz, 1H)**, 4.34 (dd, *J* = 3.3, 1.3 Hz, 1H), 4.20 (dd, *J* = 8.3, 3.2 Hz, 1H), 4.12 (dd, *J* = 3.3, 1.3 Hz, 1H), 4.00 – 3.93 (m, 1H), 3.85 (dd, *J* = 11.5, 3.3 Hz, 1H), 3.68 (dd, *J* = 11.4, 6.2 Hz, 1H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 138.4, 133.7, 129.8, 128.8, 83.8, 82.0, 79.9, 78.6, 71.5, 65.6.
**HRMS**: calculated for $C_{12}H_{15}ClNaO_5^+$ [M+$Na^+$]: 297.0500; **found**: 297.0502.



**19**

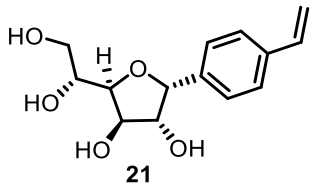
White solid. ($R_f$ = 0.29, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **19** was isolated in 79% yield (50.0 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), **5.18 (d, *J* = 3.2 Hz, 1H)**, 4.33 (dd, *J* = 3.3, 1.3 Hz, 1H), 4.20 (dd, *J* = 8.3, 3.3 Hz, 1H), 4.12 (dd, *J* = 3.2, 1.3 Hz, 1H), 4.04 – 3.91 (m, 1H), 3.85 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.68 (dd, *J* = 11.5, 6.2 Hz, 1H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 138.9, 131.8, 130.1, 121.7, 83.8, 82.0, 79.9, 78.6, 71.4, 65.6.
**HRMS**: calculated for $C_{12}H_{15}BrNaO_5^+$ [M+$Na^+$]: 340.9995; **found**: 340.9997.



**20**

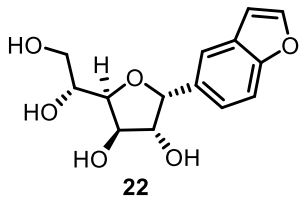
White solid. ($R_f$ = 0.23, DCM/MeOH/$H_2O$ = 5/1/0.3).
Compound **20** was isolated in 80% yield (43.0 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.38 – 7.27 (m, 4H), **5.22 (d, *J* = 3.2 Hz, 1H)**, 4.58 (s, 2H), 4.35 (dd, *J* = 3.3, 1.3 Hz, 1H), 4.21 (dd, *J* = 8.3, 3.3 Hz, 1H), 4.12 (dd, *J* = 3.2, 1.3 Hz, 1H), 4.02 – 3.94 (m, 1H), 3.86 (dd, *J* = 11.4, 3.3 Hz, 1H), 3.68 (dd, *J* = 11.5, 6.2 Hz, 1H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 141.5, 138.4, 128.2, 127.6, 84.2, 81.9, 80.0, 78.6, 71.5,

65.6, 65.1.
**HRMS**: calculated for $C_{13}H_{18}NaO_6^+$ [M+Na$^+$]: 293.0996; **found**: 293.0996.



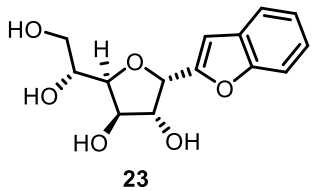
**21**

White solid. ($R_f$ = 0.23, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **21** was isolated in 75% yield (40.0 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.74 (dd, *J* = 17.7, 1.1 Hz, 1H), **5.20 (d, *J* = 3.4 Hz, 1H)**, 5.20 – 5.16 (m, 1H), 4.35 (dd, *J* = 3.3, 1.3 Hz, 1H), 4.21 (dd, *J* = 8.3, 3.3 Hz, 1H), 4.13 (dd, *J* = 3.3, 1.2 Hz, 1H), 4.01 – 3.94 (m, 1H), 3.86 (dd, *J* = 11.5, 3.3 Hz, 1H), 3.69 (dd, *J* = 11.5, 6.2 Hz, 1H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 139.1, 138.1, 138.0, 128.4, 126.7, 113.5, 84.2, 82.0, 80.0, 78.6, 71.5, 65.6.
**HRMS**: calculated for $C_{14}H_{18}NaO_5^+$ [M+Na$^+$]: 289.1046; **found**: 289.1046.



**22**

White solid. ($R_f$ = 0.25, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **22** was isolated in 71% yield (40.0 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.70 (d, *J* = 2.2 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.29 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.80 (dd, *J* = 2.2, 1.0 Hz, 1H), **5.33 (d, *J* = 3.1 Hz, 1H)**, 4.38 (dd, *J* = 3.3, 1.2 Hz, 1H), 4.25 (dd, *J* = 8.2, 3.3 Hz, 1H), 4.14 (dd, *J* = 3.1, 1.2 Hz, 1H), 4.04 – 3.96 (m, 1H), 3.88 (dd, *J* = 11.5, 3.3 Hz, 1H), 3.71 (dd, *J* = 11.5, 6.2 Hz, 1H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 155.9, 146.5, 133.7, 128.5, 124.7, 120.9, 111.3, 107.6, 84.5, 81.9, 80.1, 78.7, 71.5, 65.6.
**HRMS**: calculated for $C_{14}H_{16}NaO_6^+$ [M+Na$^+$]: 303.0839; **found**: 303.0838.



**23**

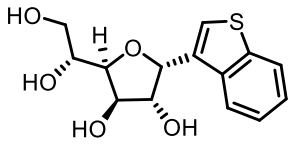
White solid. ($R_f$ = 0.25, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **23** was isolated in 70% yield (39.0 mg) following the general procedure of

deaminative cyclization.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.58 – 7.49 (m, 1H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.19 – 7.15 (m, 1H), 6.78 (s, 1H), **5.30 (d, *J* = 3.3 Hz, 1H)**, 4.37 (dd, *J* = 3.3, 1.5 Hz, 1H), 4.32 (dd, *J* = 3.5, 1.5 Hz, 1H), 4.23 (dd, *J* = 8.3, 3.3 Hz, 1H), 4.01 – 3.93 (m, 1H), 3.86 (dd, *J* = 11.5, 3.3 Hz, 1H), 3.69 (dd, *J* = 11.5, 6.2 Hz, 1H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 156.3, 156.1, 129.8, 124.7, 123.6, 121.8, 111.8, 105.7, 81.8, 79.3, 79.2, 78.4, 71.4, 65.5.

**HRMS**: calculated for $C_{14}H_{16}NaO_6^+$ [M+$Na^+$]: 303.0839; **found**: 303.0839.




**24**

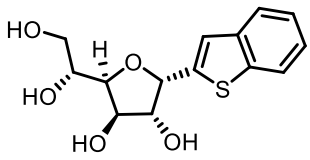
White solid. ($R_f$ = 0.27, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **24** was isolated in 69% yield (41.0 mg) following the general procedure of deaminative cyclization.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.94 – 7.85 (m, 1H), 7.85 – 7.79 (m, 1H), 7.58 (d, *J* = 1.1 Hz, 1H), 7.43 – 7.32 (m, 2H), **5.60 (dd, *J* = 2.8, 1.2 Hz, 1H)**, 4.42 (d, *J* = 2.9 Hz, 2H), 4.28 (dd, *J* = 8.4, 3.0 Hz, 1H), 4.08 – 4.01 (m, 1H), 3.92 (dd, *J* = 11.5, 3.2 Hz, 1H), 3.75 (dd, *J* = 11.5, 6.1 Hz, 1H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 142.0, 138.9, 134.0, 125.2, 124.9, 124.7, 123.7, 122.8, 81.2, 80.8, 78.9, 78.6, 71.4, 65.6.

**HRMS**: calculated for $C_{14}H_{16}NaO_5S^+$ [M+$Na^+$]: 319.0611; **found**: 319.0610.




**25**

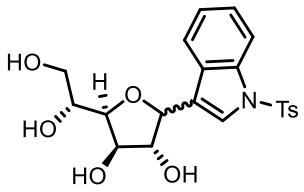
White solid. ($R_f$ = 0.27, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **25** was isolated in 74% yield (44.0 mg) following the general procedure of deaminative cyclization.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.82 – 7.78 (m, 1H), 7.75 – 7.70 (m, 1H), 7.34 – 7.22 (m, 3H), **5.49 (d, *J* = 2.8 Hz, 1H)**, 4.38 (dd, *J* = 3.4, 1.3 Hz, 1H), 4.22 (dd, *J* = 8.3, 3.4 Hz, 1H), 4.19 (dd, *J* = 3.1, 1.3 Hz, 1H), 4.01 – 3.93 (m, 1H), 3.85 (dd, *J* = 11.5, 3.3 Hz, 1H), 3.67 (dd, *J* = 11.5, 6.4 Hz, 1H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 143.3, 141.6, 140.9, 124.9, 124.8, 124.2, 123.0, 122.8, 81.9, 81.3, 80.1, 78.5, 71.5, 65.5.

**HRMS**: calculated for $C_{14}H_{16}NaO_5S^+$ [M+$Na^+$]: 319.0611; **found**: 319.0611.




**26** (α/β = 1/1)

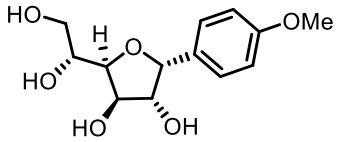
White solid. ($R_f$ = 0.26, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **26** was isolated in 70% yield (61.0 mg) following the general procedure of deaminative cyclization.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.93 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.80 – 7.71 (m, 2.5H), 7.66 (dd, *J* = 11.0, 1.1 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 0.5H), 7.33 – 7.25 (m, 1H), 7.25 – 7.16 (m, 3H), **5.42 (dd, *J* = 3.1, 1.2 Hz, 0.5H)**, 4.88 – 4.83 (m, 0.5H), 4.39 (dd, *J* = 3.4, 1.2 Hz, 0.5H), 4.30 – 4.22 (m, 1.5H), 4.18 (dd, *J* = 3.8, 1.4 Hz, 0.5H), 4.13 – 4.07 (m, 0.5H), 4.07 – 3.97 (m, 1H), 3.90 – 3.82 (m, 1H), 3.76 – 3.66 (m, 1H), 2.28 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 146.6, 146.5, 136.8, 136.5, 136.4, 136.3, 131.0, 130.9, 130.9, 130.5, 128.0, 127.9, 125.8, 125.7, 125.5, 124.8, 124.3, 124.2, 123.7, 121.6, 121.4, 121.0, 114.7, 114.5, 84.0, 82.8, 82.2, 81.3, 79.8, 79.1, 78.6, 78.6, 71.5, 65.5, 65.3, 21.4.

**HRMS**: calculated for $C_{21}H_{23}NNaO_7S^+$ [M+$Na^+$]: 456.1087; **found**: 456.1089.




**27α**

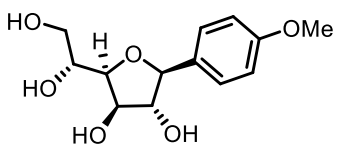
White solid. ($R_f$ = 0.28, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **27α** was isolated in 44% yield (24.0 mg) following the general procedure of deaminative cyclization.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.31 – 7.22 (m, 2H), 6.93 – 6.83 (m, 2H), **5.16 (d, *J* = 3.1 Hz, 1H)**, 4.34 (dd, *J* = 3.4, 1.3 Hz, 1H), 4.19 (dd, *J* = 8.3, 3.4 Hz, 1H), 4.06 (dd, *J* = 3.2, 1.3 Hz, 1H), 3.99 – 3.93 (m, 1H), 3.84 (dd, *J* = 11.5, 3.3 Hz, 1H), 3.77 (s, 3H), 3.67 (dd, *J* = 11.5, 6.3 Hz, 1H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 160.5, 131.0, 129.5, 114.3, 84.1, 81.8, 80.0, 78.6, 71.6, 65.6, 55.6.

**HRMS**: calculated for $C_{13}H_{18}NaO_6^+$ [M+$Na^+$]: 293.0996; **found**: 293.0997.




**27β**

White solid. ($R_f$ = 0.21, DCM/MeOH/$H_2O$ = 20/2/0.3).

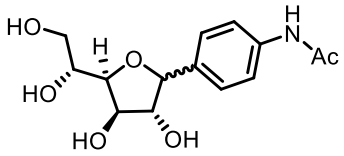
Compound **27β** was isolated in 22% yield (12.0 mg) following the general procedure of deaminative cyclization.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.39 – 7.33 (m, 2H), 6.89 – 6.85 (m, 2H), **4.53 (d, *J* =**

**4.2 Hz, 1H)**, 4.20 (dd, *J* = 3.9, 1.8 Hz, 1H), 4.05 (m, 1H), 3.99 – 3.94 (m, 2H), 3.83 (dd, *J* = 11.4, 3.4 Hz, 1H), 3.77 (s, 3H), 3.67 (dd, *J* = 11.5, 6.0 Hz, 1H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 160.7, 134.0, 128.9, 114.5, 88.6, 86.2, 82.1, 79.7, 71.5, 65.2, 55.7.

**HRMS**: calculated for $C_{13}H_{18}NaO_6^+$ [M+Na$^+$]: 293.0996; **found**: 293.0997.




**28** (α/β = 2/1)

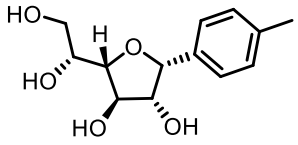
White solid. ($R_f$ = 0.26, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **28** was isolated in 72% yield (43.0 mg) following the general procedure of deaminative cyclization.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.54 – 7.45 (m, 2H), 7.39 (d, *J* = 8.6 Hz, 0.68H), 7.30 (d, *J* = 8.4 Hz, 1.34H), **5.18 (d, *J* = 3.1 Hz, 0.68H)**, **4.57 (d, *J* = 4.1 Hz, 0.34H)**, 4.35 (dd, *J* = 3.3, 1.3 Hz, 0.68H), 4.25 – 4.18 (m, 1H), 4.13 – 4.09 (m, 0.68H), 4.09 – 4.04 (m, 0.34H), 4.02 – 3.94 (m, 1.34H), 3.89 – 3.81 (m, 1H), 3.68 (dd, *J* = 11.5, 6.2 Hz, 1H), 2.10 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 171.6, 139.1, 138.8, 137.8, 135.1, 128.6, 127.9, 120.9, 120.7, 88.5, 86.1, 84.1, 82.2, 81.9, 80.0, 79.6, 78.6, 71.5, 71.4, 65.5, 65.2, 23.8, 23.8.

**HRMS**: calculated for $C_{14}H_{19}NNaO_6^+$ [M+Na$^+$]: 320.1105; **found**: 320.1105.




**29**

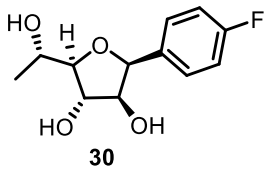
White solid. ($R_f$ = 0.27, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **29** was isolated in 75% yield (38.0 mg) following the general procedure of deaminative cyclization.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), **5.03 (d, *J* = 3.0 Hz, 1H)**, 4.24 (dd, *J* = 2.2, 1.1 Hz, 1H), 4.00 (t, *J* = 2.4 Hz, 1H), 3.90 (dd, *J* = 3.2, 1.1 Hz, 1H), 3.88 – 3.83 (m, 1H), 3.78 – 3.66 (m, 2H), 2.31 (s, 3H).

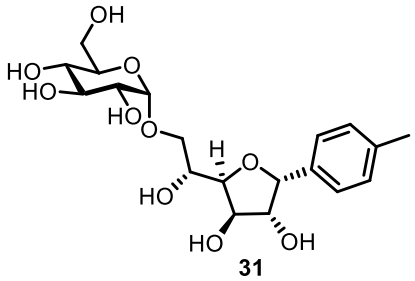
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 138.0, 135.3, 129.4, 128.2, 86.8, 84.7, 81.0, 80.0, 73.5, 64.4, 21.2.

**HRMS**: calculated for $C_{13}H_{18}NaO_5^+$ [M+Na$^+$]: 277.1046; **found**: 277.1045.



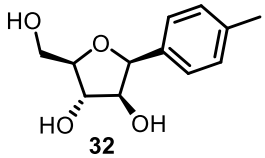

**30**

White solid. ($R_f$ = 0.24, DCM/MeOH/$H_2O$ = 30/2/0.3).
Compound **30** was isolated in 60% yield (29.1 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.44 (dd, *J* = 8.5, 5.7 Hz, 2H), 7.04 (t, *J* = 8.9 Hz, 2H), **5.06 (d, *J* = 3.1 Hz, 1H)**, 4.11 (dd, *J* = 2.3, 1.1 Hz, 1H), 4.04 – 3.96 (m, 1H), 3.92 (dd, *J* = 3.2, 1.1 Hz, 1H), 3.72 (dd, *J* = 4.3, 2.3 Hz, 1H), 1.32 (d, *J* = 6.5 Hz, 3H).
**$^{13}$C NMR** (151 MHz, $CD_3OD$) δ 163.0, 161.4, 133.1 (d, *J* = 2.7 Hz), 128.8 (d, *J* = 7.8 Hz), 114.0 (d, *J* = 21.6 Hz), 89.6, 82.7, 79.7, 78.8, 67.7, 18.6.
**$^{19}$F NMR** (376 MHz, $CD_3OD$) δ -117.9.
**HRMS**: calculated for $C_{12}H_{15}FNaO_4^+$ [M+$Na^+$]: 265.0847; **found**: 265.0847.



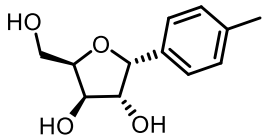
**31**

White solid. ($R_f$ = 0.22, DCM/MeOH/$H_2O$ = 6/2/0.5).
Compound **31** was isolated in 78% yield (65.0 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.23 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), **5.18 (d, *J* = 3.0 Hz, 1H)**, 4.45 – 4.33 (m, 2H), 4.16 – 4.03 (m, 3H), 3.90 – 3.66 (m, 5H), 3.63 (dd, *J* = 9.7, 2.1 Hz, 1H), 3.50 – 3.42 (m, 2H), 2.33 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 137.8, 136.0, 129.5, 128.2, 99.8, 84.3, 81.0, 80.2, 78.1, 75.3, 73.9, 73.2, 71.3, 70.0, 69.1, 62.1, 21.2.
**HRMS**: calculated for $C_{19}H_{28}NaO_{10}^+$ [M+$Na^+$]: 439.1575; **found**: 439.1576.



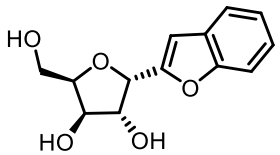
**32**

White solid. ($R_f$ = 0.25, DCM/MeOH/$H_2O$ = 30/2/0.3).
Compound **32** was isolated in 87% yield (39.0 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.31 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), **5.07 (d, *J* = 3.3 Hz, 1H)**, 4.14 (dd, *J* = 2.2, 1.1 Hz, 1H), 4.00 – 3.92 (m, 2H), 3.89 – 3.75 (m, 2H), 2.34 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 138.1, 135.3, 129.5, 128.4, 87.6, 84.8, 80.5, 80.2, 63.7, 21.2.
**HRMS**: calculated for $C_{12}H_{16}NaO_4^+$ [M+$Na^+$]: 247.0941; **found**: 247.0939.



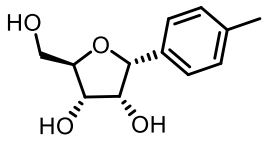
**33**

White solid. ($R_f$ = 0.21, DCM/MeOH/$H_2O$ = 30/2/0.3).
Compound **33** was isolated in 89% yield (40.1 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), **5.19 (d, *J* = 3.2 Hz, 1H)**, 4.43 – 4.34 (m, 1H), 4.29 (dd, *J* = 3.7, 1.4 Hz, 1H), 4.09 (dd, *J* = 3.3, 1.3 Hz, 1H), 3.94 – 3.77 (m, 2H), 2.34 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 137.9, 136.1, 129.5, 128.3, 84.0, 82.6, 80.3, 78.7, 62.0, 21.2.
**HRMS**: calculated for $C_{12}H_{16}NaO_4^+$ [M+$Na^+$]: 247.0941; **found**: 247.0939.



**34**

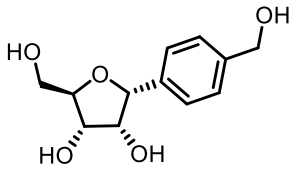
White solid. ($R_f$ = 0.22, DCM/MeOH/$H_2O$ = 30/2/0.3).
Compound **34** was isolated in 80% yield (40.1 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.56 – 7.50 (m, 1H), 7.47 – 7.38 (m, 1H), 7.27 – 7.12 (m, 2H), 6.80 (s, 1H), **5.29 (d, *J* = 3.5 Hz, 1H)**, 4.43 – 4.36 (m, 1H), 4.35 – 4.29 (m, 2H), 3.90 – 3.79 (m, 2H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 156.3, 156.2, 129.8, 124.8, 123.6, 121.8, 111.8, 105.8, 82.5, 79.5, 78.8, 78.4, 61.9.
**HRMS**: calculated for $C_{13}H_{14}NaO_5^+$ [M+$Na^+$]: 273.0733; **found**: 273.0734.



**35**

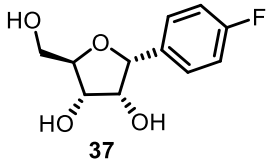
White solid. ($R_f$ = 0.25, DCM/MeOH/$H_2O$ = 30/2/0.3).
Compound **35** was isolated in 76% yield (34.1 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.26 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), **5.03 (d, *J* = 3.0 Hz, 1H)**, 4.31 (dd, *J* = 8.3, 4.4 Hz, 1H), 4.11 (dd, *J* = 4.3, 3.0 Hz, 1H), 4.07 – 4.00 (m, 1H), 3.85 (dd, *J* = 12.0, 2.7 Hz, 1H), 3.67 (dd, *J* = 12.0, 4.6 Hz, 1H), 2.31 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 137.9, 136.4, 129.4, 128.3, 84.2, 83.7, 75.4, 74.1, 63.3, 21.2.

**HRMS**: calculated for $C_{12}H_{16}NaO_4^+$ [M+Na$^+$]: 247.0941; **found**: 247.0940.



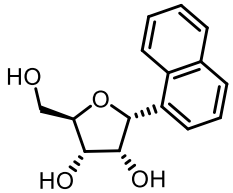

**36**

White solid. ($R_f$ = 0.21, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **36** was isolated in 77% yield (37.0 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), **5.08 (d, *J* = 3.0 Hz, 1H)**, 4.58 (s, 2H), 4.32 (dd, *J* = 8.3, 4.4 Hz, 1H), 4.15 (dd, *J* = 4.3, 3.1 Hz, 1H), 4.09 – 4.02 (m, 1H), 3.86 (dd, *J* = 12.0, 2.7 Hz, 1H), 3.68 (dd, *J* = 12.0, 4.6 Hz, 1H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 141.7, 138.6, 128.4, 127.5, 84.2, 83.8, 75.4, 74.2, 65.1, 63.3.
**HRMS**: calculated for $C_{12}H_{16}NaO_5^+$ [M+Na$^+$]: 263.0890; **found**: 263.0890.




**37**

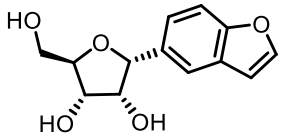
White solid. ($R_f$ = 0.27, DCM/MeOH/$H_2O$ = 30/2/0.3).
Compound **37** was isolated in 75% yield (34.0 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.44 – 7.34 (m, 2H), 7.10 – 6.96 (m, 2H), **5.06 (d, *J* = 3.0 Hz, 1H)**, 4.32 (dd, *J* = 8.4, 4.3 Hz, 1H), 4.13 (dd, *J* = 4.3, 3.1 Hz, 1H), 4.08 – 4.02 (m, 1H), 3.85 (dd, *J* = 12.0, 2.7 Hz, 1H), 3.67 (dd, *J* = 12.0, 4.6 Hz, 1H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 163.6 (d, *J* = 243.2 Hz), 135.6 (d, *J* = 3.0 Hz), 130.2 (d, *J* = 8.1 Hz), 115.4 (d, *J* = 21.5 Hz), 83.8, 83.7, 75.3, 74.1, 63.2.
**$^{19}$F NMR** (376 MHz, $CD_3OD$) δ -118.0.
**HRMS**: calculated for $C_{11}H_{13}FNaO_4^+$ [M+Na$^+$]: 251.0690; **found**: 251.0690.




**38**

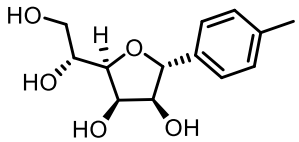
White solid. ($R_f$ = 0.25, DCM/MeOH/$H_2O$ = 30/2/0.3).
Compound **38** was isolated in 71% yield (37.0 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.87 (dd, *J* = 7.7, 1.8 Hz, 1H),

7.78 (d, *J* = 7.7 Hz, 2H), 7.54 – 7.38 (m, 3H), **5.88 (d, *J* = 3.0 Hz, 1H)**, 4.51 (dd, *J* = 4.5, 3.1 Hz, 1H), 4.46 (dd, *J* = 8.3, 4.4 Hz, 1H), 4.18 – 4.07 (m, 1H), 3.95 (dd, *J* = 12.0, 2.7 Hz, 1H), 3.76 (dd, *J* = 12.0, 4.7 Hz, 1H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 135.0, 134.9, 131.9, 129.7, 128.6, 126.9, 126.3, 126.3, 126.0, 123.7, 83.2, 81.3, 74.4, 74.2, 63.4.
**HRMS**: calculated for $C_{15}H_{16}NaO_4^+$ [M+Na$^+$]: 283.0941; **found**: 283.0940.



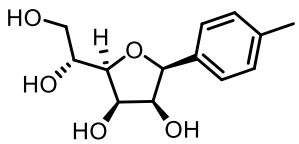
**39**

White solid. ($R_f$ = 0.24, DCM/MeOH/$H_2O$ = 30/2/0.3).
Compound **39** was isolated in 74% yield (37.0 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.71 (d, *J* = 2.2 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.44 (d, *J* = 8.6 Hz, 1H), 7.32 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.80 (dd, *J* = 2.3, 1.0 Hz, 1H), **5.18 (d, *J* = 3.0 Hz, 1H)**, 4.35 (dd, *J* = 8.4, 4.3 Hz, 1H), 4.16 (dd, *J* = 4.3, 3.0 Hz, 1H), 4.13 – 4.05 (m, 1H), 3.88 (dd, *J* = 12.0, 2.7 Hz, 1H), 3.70 (dd, *J* = 12.0, 4.6 Hz, 1H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 156.0, 146.5, 134.0, 128.5, 124.9, 121.1, 111.3, 107.6, 84.4, 83.8, 75.5, 74.2, 63.3.
**HRMS**: calculated for $C_{13}H_{14}NaO_5^+$ [M+Na$^+$]: 273.0733; **found**: 273.0733.



**40α**

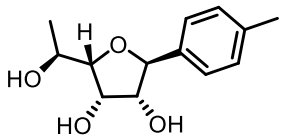
White solid. ($R_f$ = 0.28, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **40α** was isolated in 24% yield (12.0 mg) from **40-s-1**, and 28% yield (14.0 mg) from **40-s-2** following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), **4.72 (d, *J* = 8.5 Hz, 1H)**, 4.28 (t, *J* = 3.7 Hz, 1H), 4.12 (dd, *J* = 8.2, 3.3 Hz, 1H), 4.03 – 3.94 (m, 2H), 3.81 (dd, *J* = 11.5, 3.3 Hz, 1H), 3.64 (dd, *J* = 11.5, 6.0 Hz, 1H), 2.31 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 139.8, 138.3, 129.9, 127.1, 83.8, 81.6, 81.0, 73.7, 71.8, 64.9, 21.2.
**HRMS**: calculated for $C_{13}H_{18}NaO_5^+$ [M+Na$^+$]: 277.1046; **found**: 277.1047.



**40β**

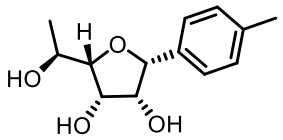
White solid. ($R_f$ = 0.21, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **40β** was isolated in 61% yield (31.0 mg) from **40-s-1**, and 43% yield (22.0 mg) from **40-s-2** following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), **4.51 (t, *J* = 5.5 Hz, 1H)**, 4.25 (t, *J* = 5.1 Hz, 1H), 4.14 – 4.06 (m, 1H), 3.89 (dd, *J* = 7.2, 5.8 Hz, 1H), 3.85 (dd, *J* = 11.5, 3.5 Hz, 1H), 3.70 (dd, *J* = 11.5, 6.1 Hz, 1H), 2.31 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 138.0, 135.9, 129.3, 128.6, 84.0, 80.5, 74.4, 74.0, 72.7, 64.9, 21.2.
**HRMS**: calculated for $C_{13}H_{18}NaO_5^+$ [M+Na$^+$]: 277.1046; **found**: 277.1045.



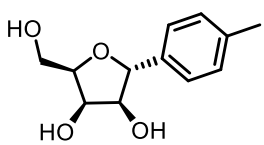
**41α**

White solid. ($R_f$ = 0.27, DCM/MeOH/$H_2O$ = 30/2/0.3).
Compound **41α** was isolated in 25% yield (12.0 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.27 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), **4.70 (d, *J* = 8.5 Hz, 1H)**, 4.29 (t, *J* = 3.8 Hz, 1H), 4.12 – 4.02 (m, 1H), 3.98 (dd, *J* = 8.6, 4.2 Hz, 1H), 3.92 – 3.84 (m, 1H), 2.31 (s, 3H), 1.29 (d, *J* = 6.4 Hz, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 139.8, 138.3, 129.9, 127.1, 85.8, 83.7, 81.1, 73.6, 67.3, 21.2, 20.4.
**HRMS**: calculated for $C_{13}H_{18}NaO_4^+$ [M+Na$^+$]: 261.1097; **found**: 261.1097.



**41β**

White solid. ($R_f$ = 0.22, DCM/MeOH/$H_2O$ = 30/2/0.3).
Compound **41β** was isolated in 52% yield (25.0 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.26 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), **4.81 (d, *J* = 4.8 Hz, 1H)**, 4.52 (t, *J* = 5.5 Hz, 1H), 4.29 – 4.13 (m, 2H), 3.66 (dd, *J* = 7.3, 6.0 Hz, 1H), 2.31 (s, 3H), 1.32 (d, *J* = 6.4 Hz, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 138.0, 136.0, 129.4, 128.6, 84.2, 83.8, 74.5, 74.2, 68.2, 21.2, 20.5.
**HRMS**: calculated for $C_{13}H_{18}NaO_4^+$ [M+Na$^+$]: 261.1097; **found**: 261.1099.



**42α**

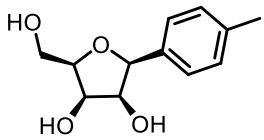
White solid. ($R_f$ = 0.29, DCM/MeOH/$H_2O$ = 30/2/0.3).

Compound **42α** was isolated in 20% yield (9.0 mg) following the general procedure of deaminative cyclization.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), **4.73 (d, *J* = 7.9 Hz, 1H)**, 4.33 – 4.27 (m, 1H), 4.24 (t, *J* = 4.2 Hz, 1H), 3.98 (dd, *J* = 7.9, 4.4 Hz, 1H), 3.89 – 3.74 (m, 2H), 2.31 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 139.6, 138.3, 129.9, 127.1, 83.9, 82.6, 80.7, 73.5, 62.3, 21.2.

**HRMS**: calculated for $C_{12}H_{16}NaO_4^+$ [M+$Na^+$]: 247.0941; **found**: 247.0940.




**42β**

White solid. ($R_f$ = 0.23, DCM/MeOH/$H_2O$ = 30/2/0.3).

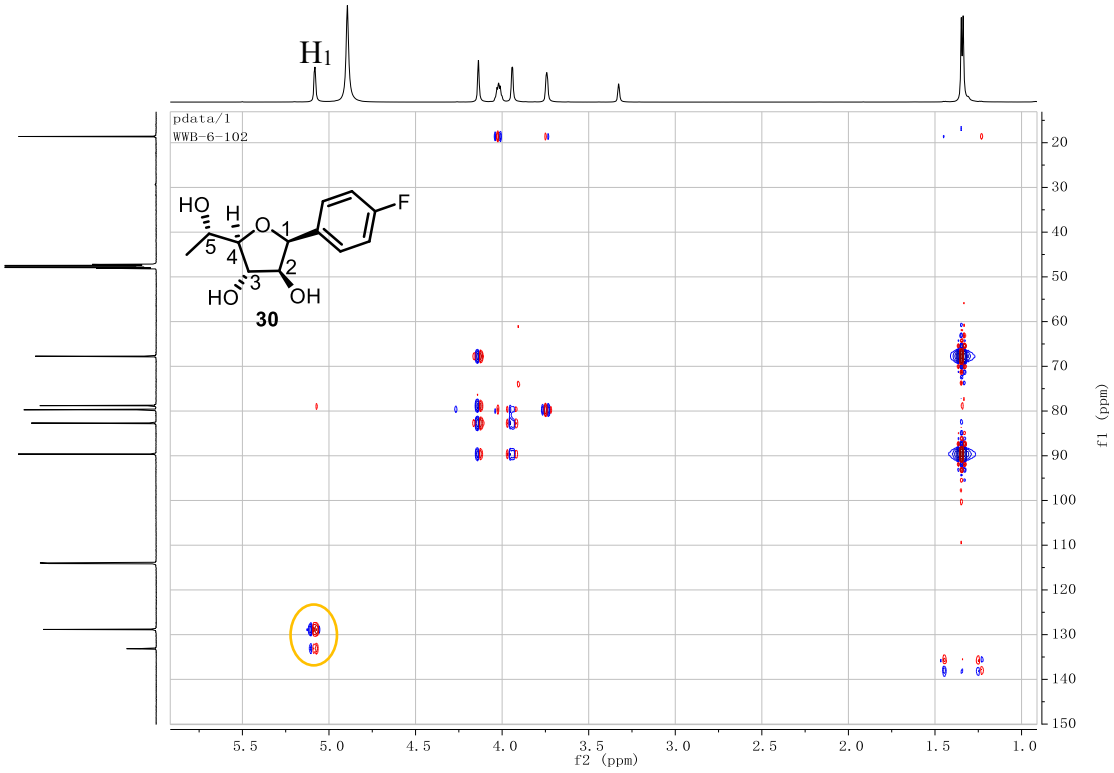
Compound **42β** was isolated in 51% yield (23.0 mg) following the general procedure of deaminative cyclization.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), **4.85 (1H)**, 4.58 (dd, *J* = 7.5, 5.0 Hz, 1H), 4.15 – 4.06 (m, 2H), 3.88 – 3.76 (m, 2H), 2.31 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 138.0, 135.9, 129.4, 128.5, 83.5, 81.2, 74.4, 74.2, 61.9, 21.2.

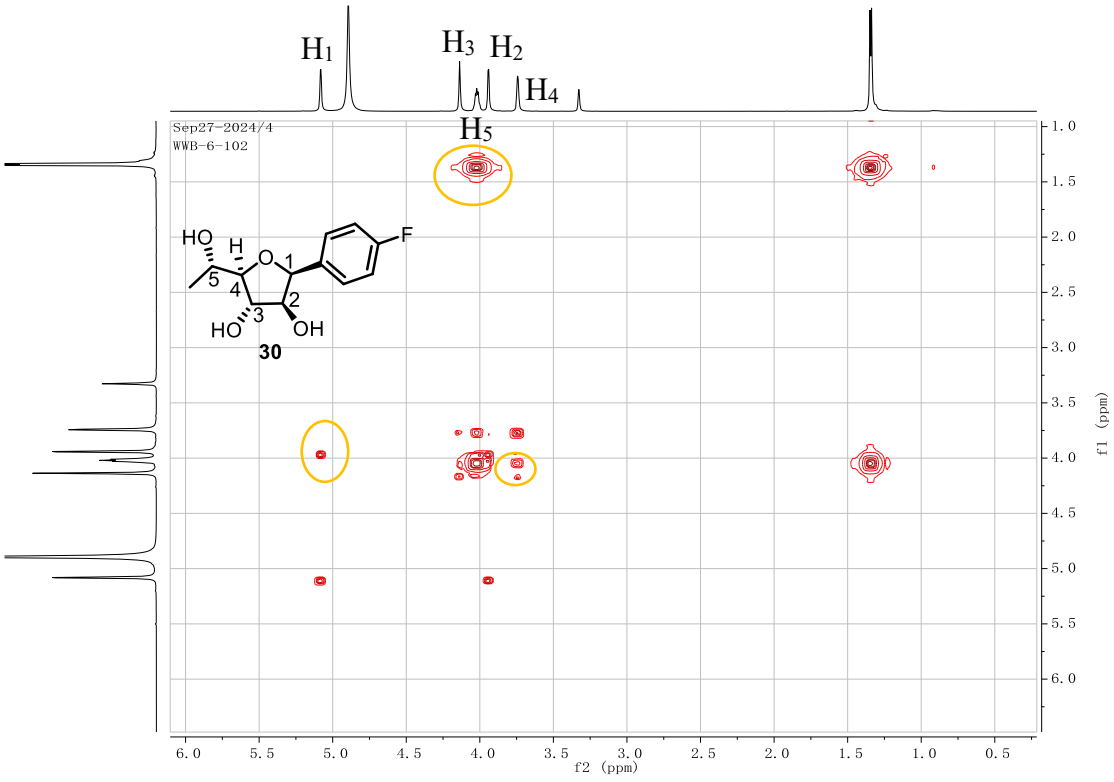
**HRMS**: calculated for $C_{12}H_{16}NaO_4^+$ [M+$Na^+$]: 247.0941; **found**: 247.0941.

### 3.3 stereochemical assignment of the products of deaminative cyclization



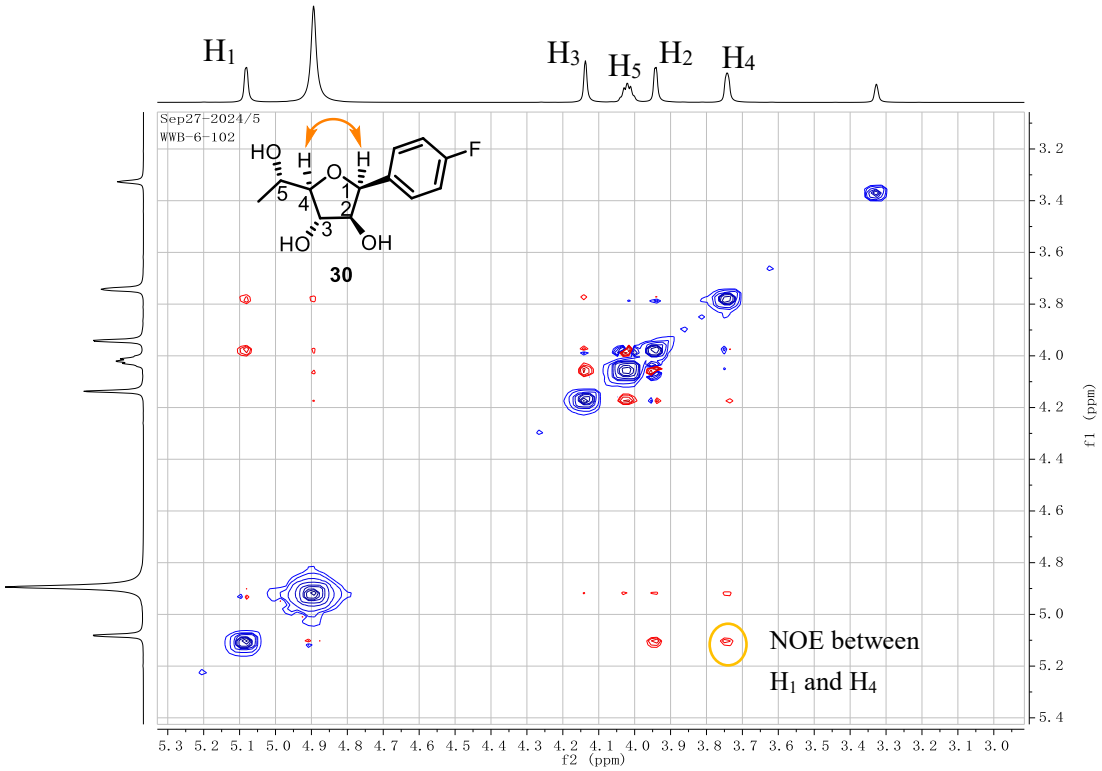

HMBC spectrum of compound **30** (600 MHz, $CD_3OD$)

$H_1$ was determined by HMBC spectrum.

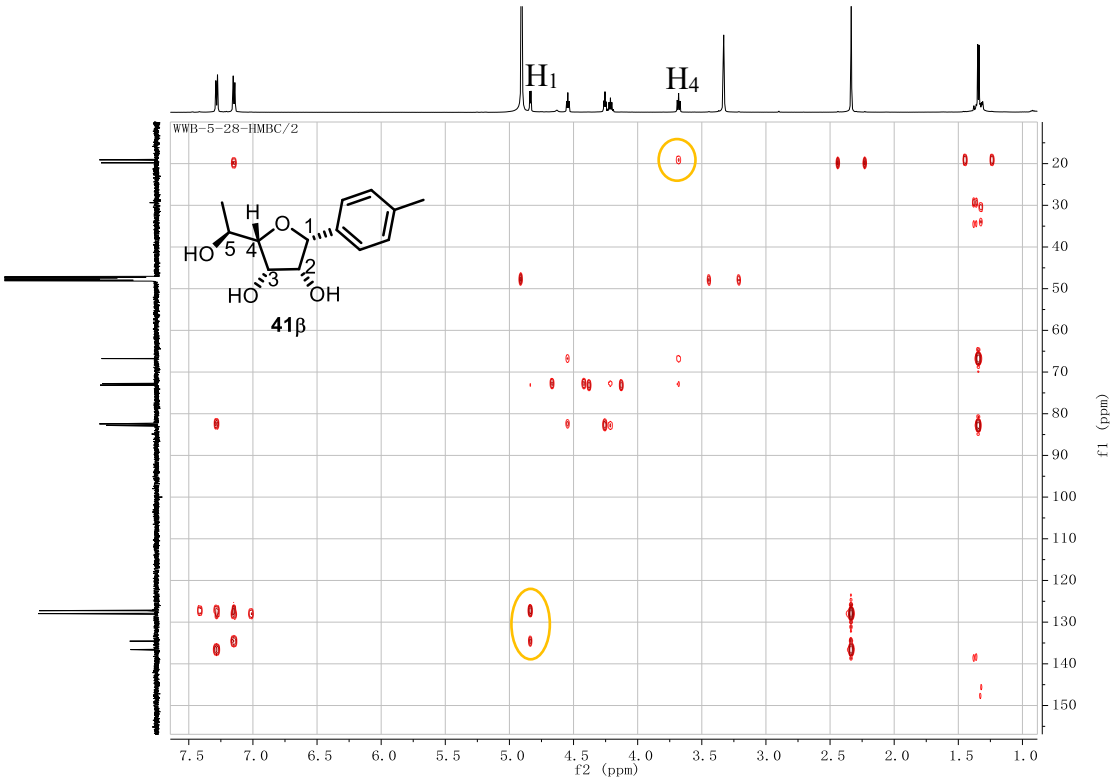



$^1H$-$^1H$ COSY spectrum of compound **30** (600 MHz, $CD_3OD$)

$H_{2\text{-}5}$ was determined by $^1H$-$^1H$ COSY spectrum.

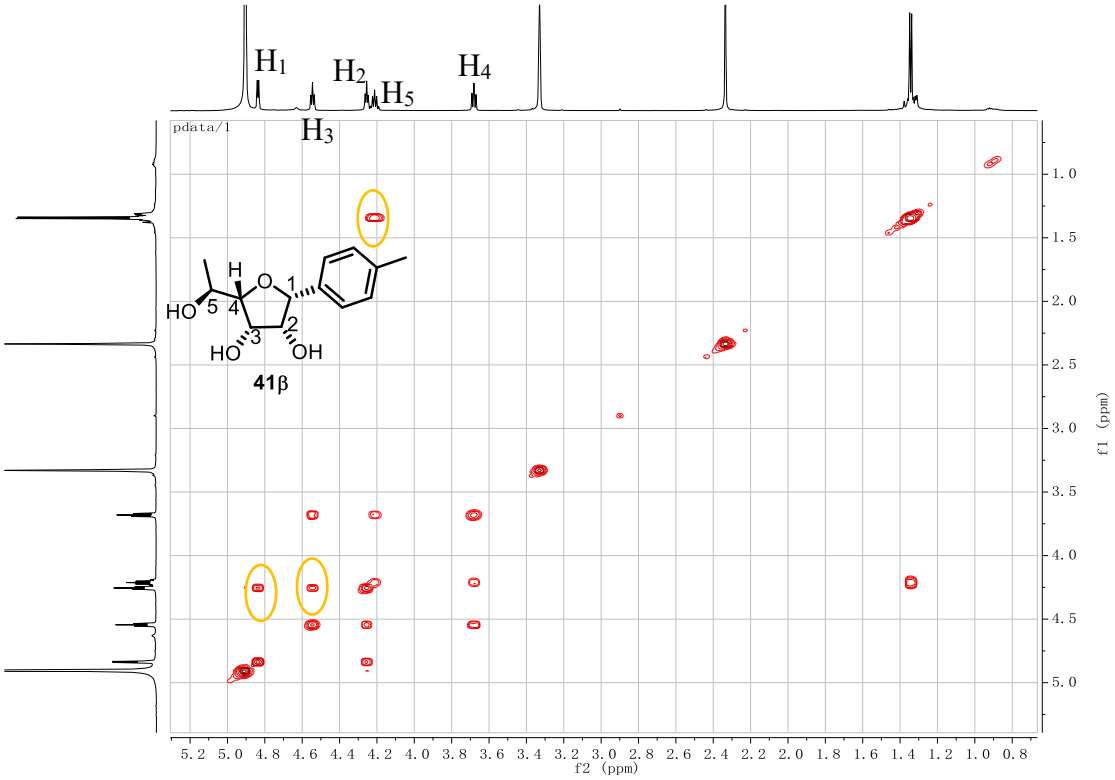



NOESY spectrum of compound **30** (600 MHz, $CD_3OD$)



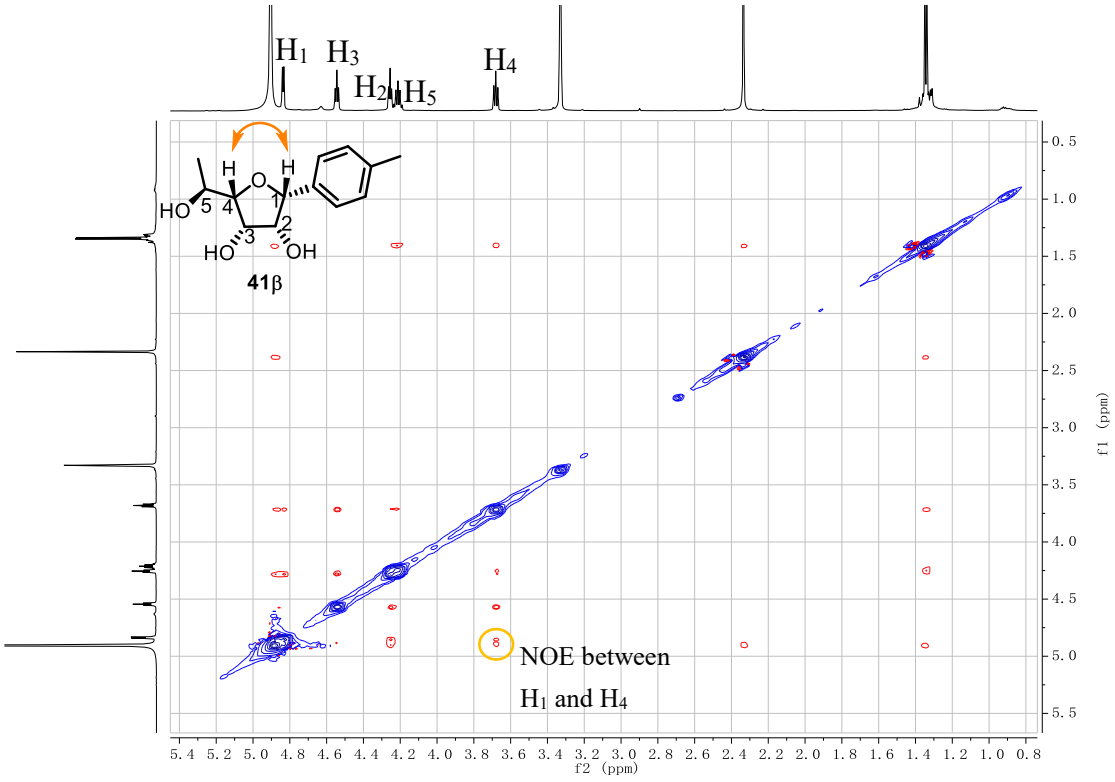

HMBC spectrum of compound **41β** (600 MHz, $CD_3OD$)

$H_1$ and $H_4$ was determined by HMBC spectrum.

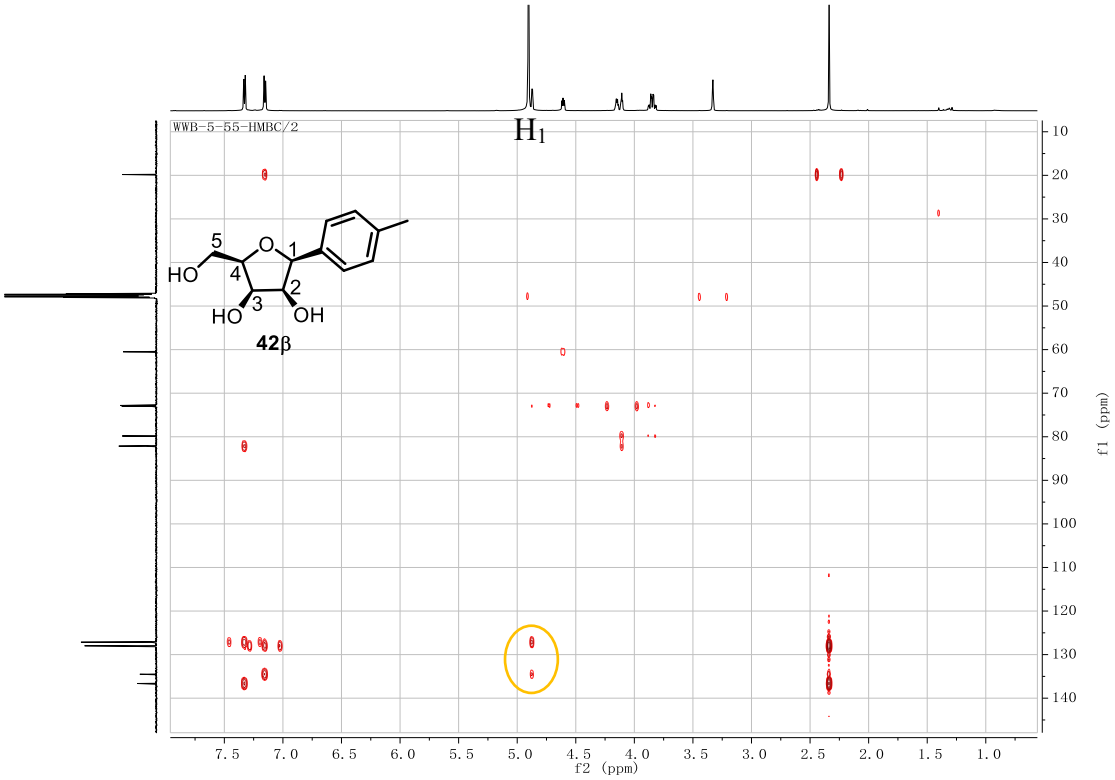



$^{1}$H-$^{1}$H COSY spectrum of compound **41β** (600 MHz, $CD_3OD$)

$H_{2\text{-}5}$ was determined by $^{1}$H-$^{1}$H COSY spectrum.

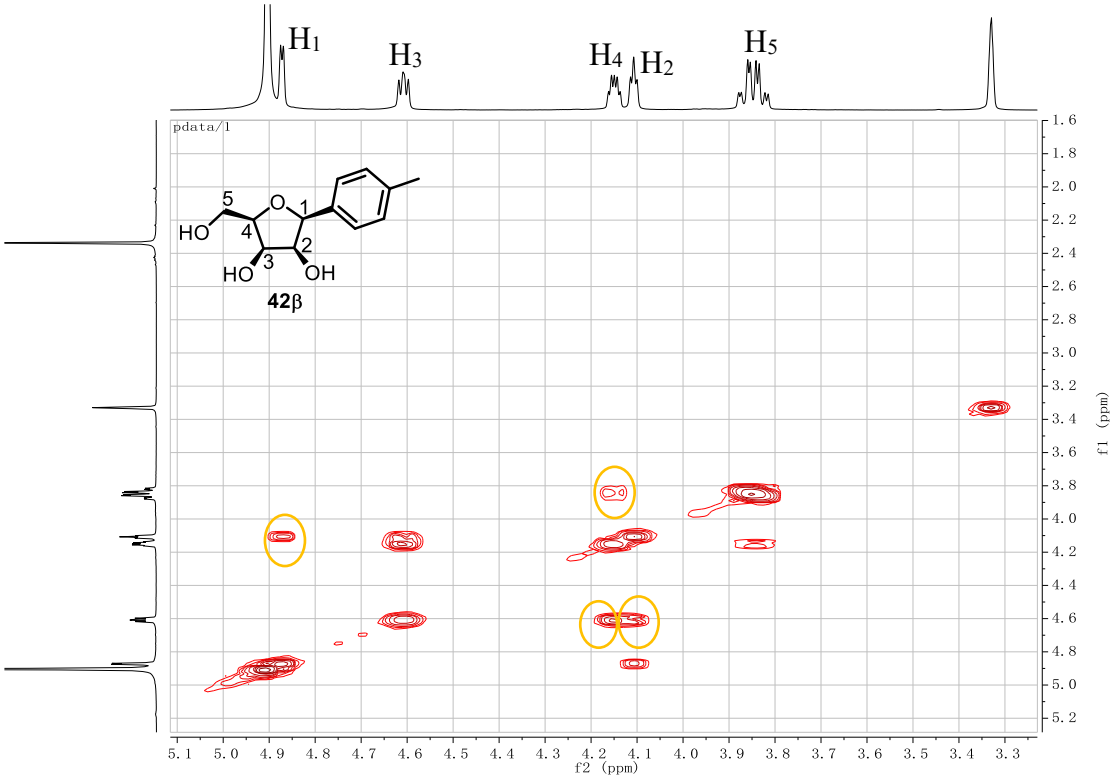



NOESY spectrum of compound **41β** (600 MHz, $CD_3OD$)



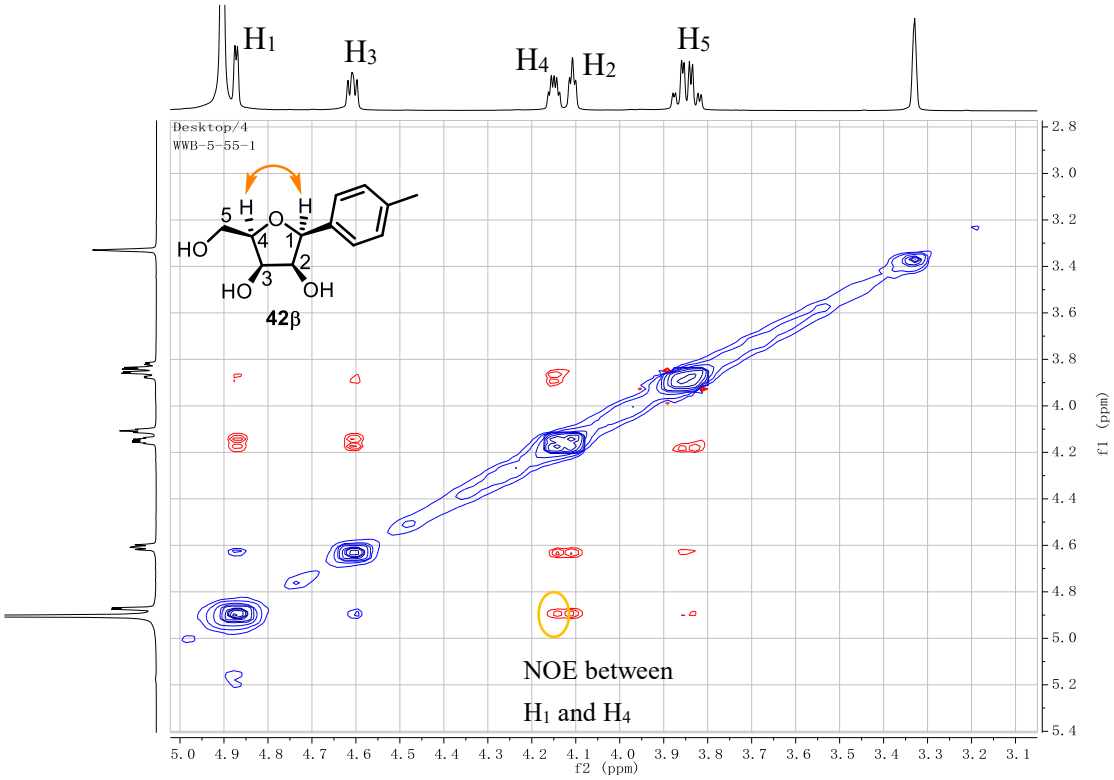

HMBC spectrum of compound **42β** (600 MHz, $CD_3OD$)

$H_1$ was determined by HMBC spectrum.

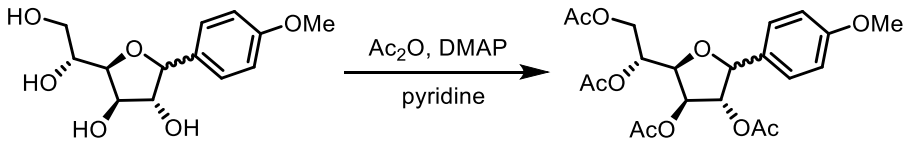



$^1H$-$^1H$ COSY spectrum of compound **42β** (600 MHz, $CD_3OD$)

$H_{2\text{-}5}$ was determined by $^1H$-$^1H$ COSY spectrum.




NOESY spectrum of compound **42β** (600 MHz, $CD_3OD$)



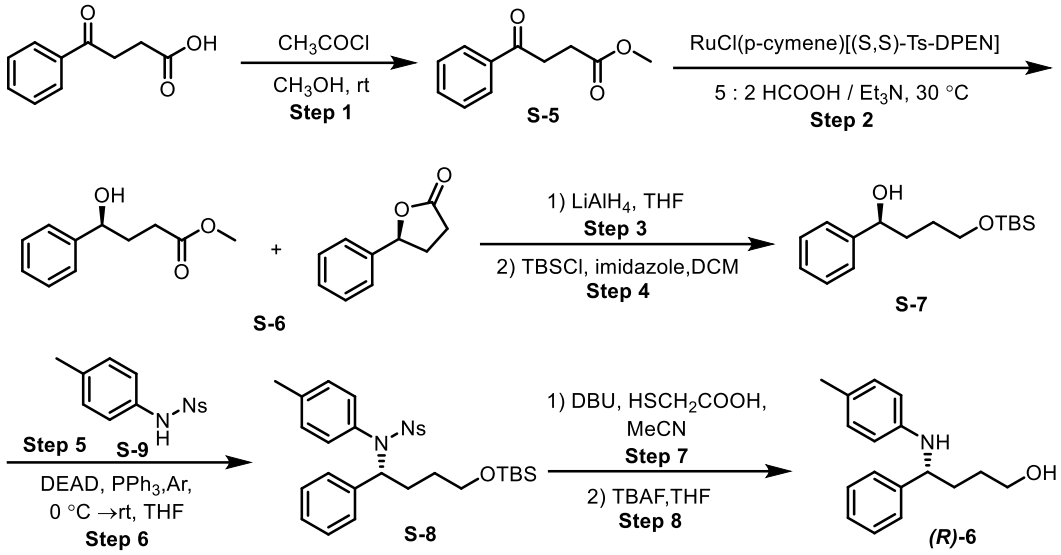

**27**, α/β = 2/1 **OAc-27**, α/β = 2/1

Compound **27** (54.1 mg, 0.2 mmol, 1.0 equiv, α/β= 2/1) was dissolved in pyridine (1 mL, 0.2 M) in an 8 mL glass vial. To the solution was added acetic anhydride (102.1 mg, 1.0 mmol, 5.0 equiv) and DMAP (2.5 mg, 0.02 mmol, 0.1 equiv). The mixture was stirred at rt under air atmosphere and monitored by TLC analysis. The reaction mixture was concentrated under reduced pressure. The resulting residue was subjected to silica gel chromatography to give the desired product **OAc-27**(71.0 mg, 81%, α/β= 2/1). White solid. ($R_f$ = 0.23, Hexane/ethyl acetate = 10/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.6 Hz, 2H, β-$H_{Ar}$), 7.20 (d, *J* = 8.5 Hz, 4H, α-$H_{Ar}$), 6.89 (d, *J* = 8.8 Hz, 2H, β-$H_{Ar}$), 6.85 (d, *J* = 8.8 Hz, 4H,α-$H_{Ar}$), 5.53 (dd, *J* = 3.7, 1.2 Hz, 2H, α-$H_3$), 5.45 – 5.38 (m, 2H,β-$H_3$, β-$H_5$), 5.36 (dd, *J* = 3.6, 1.2 Hz, 2H, α-$H_1$), 5.32 – 5.25 (m, 4H, α-$H_2$, α-$H_5$), 4.98 (dd, *J* = 3.0, 1.0 Hz, 1H, β-$H_1$), 4.89 (d, *J* = 3.0 Hz, 1H, β-$H_2$), 4.70 – 4.65 (m, 2H, α-$H_6$), 4.64 (d, *J* = 2.5 Hz, 1H, β-$H_6$), 4.56 (dd, *J* = 9.6, 3.7 Hz, 2H, α-$H_4$), 4.37 (dd, *J* = 9.2, 3.5 Hz, 1H, β-$H_4$), 4.21 (dd, *J* = 12.2, 5.5 Hz, 3H, α-$H_6$/β-$H_6$), 3.81 (s, 3H, β-OMe), 3.79 (s, 6H,α-OMe), 2.15 (s, 3H, β-OAc), 2.13 (s, 6H, α-OAc), 2.10 (s, 6H, α-OAc), 2.10 (s, 3H, β-OAc)2.03 (s, 3H, β-OAc), 2.02 (s, 6H, α-OAc), 1.97 (s, 3H, β-OAc), 1.78 (s, 6H, α-OAc). The spectral data are consistent with those reported in literature[14].

## 4. Mechanistic study using enantio-enriched amino alcohol *(R)*-6

### 4.1 Preparation of enantio-enriched amino alcohol *(R)*-6




**Step 1**: Phenylbutanoic acid (1.8 g, 10.0 mmol, 1.0 equiv) was dissolved in methanol. Acetyl chloride (942.0 mg, 12.0 mmol, 1.2 equiv) was added dropwise and the reaction mixture was stirred at rt for 10 h. The reaction mixture was diluted by dichloromethane, washed with Brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to obtain the corresponding methyl esters **S-5** (1.9 g, 98%). **S-5** was pure enough to use in the next step without further purification.

**Step 2**: **S-5** (1.2 g, 6.0 mmol, 1.0 equiv) was added to a solution of RuCl(p-cymene)[(S,S)-Ts-DPEN] (5 mol%) in a mixture of formic acid/triethylamine (5/2, 10 mL) under argon and stirred at 30 °C for 48 h. Saturated $NaHCO_3$ solution was added and the reaction mixture was extracted with DCM. The combined organic layers were washed with water and brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography to give a non-separable mixture of alcohol and lactone **S-6** (782.1 mg, approx 70%).

**Step 3**: $LiAlH_4$ (607.3 mg, 16.0 mmol, 4.0 equiv) was suspended in try THF (20 mL), and the mixture was cooled to 0 °C. The mixture of alcohol and lactone **S-6** (782.1 mg, approx 4.0 mmol total, 1.0 equiv) in try THF (5 mL) was added dropwise. The reaction mixture was allowing to warm to room temperature and stirred overnight. After 12 h, the reaction mixture was cooled to 0 °C and quenched by successive dropwise addition of $H_2O$, 15% NaOH (aq), and $H_2O$. After stirring at room temperature for another 1 h, $MgSO_4$ was added, and the mixture was filtered through a plug of celite (washing with THF). The filtrate was concentrated under reduced pressure to give a clear oil that solidified upon standing. A white solid was isolated and carried forward without purification. The **step 1-3** were following a reported procedure[3].

**Step 4**: Imidazole (816.8 mg, 12.0 mmol, 1.2 equiv) and TBSCl (1.8 g, 11.0 mmol, 1.1 equiv) were added to a solution of the product obtained in the **step 3** (1.7g, 10.0 mmol, 1.0 equiv) in $CH_2Cl_2$ (50 mL) at room temperature. After 9 h, the reaction was quenched by addition of saturated $NH_4Cl$ solution (50 mL). The reaction mixture was extracted with $CH_2Cl_2$. The organic extracts were dried over $Na_2SO_4$ and concentrated. Purification of the residue by flash column chromatography gave TBS ether **S-7** as a colorless oil (2.0 g, 71%).

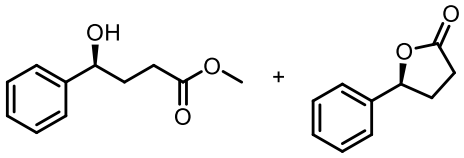
**Step 5**: Under nitrogen atmosphere, the mixture of p-toluidine (1.1 g, 10 mmol, 1.0 equiv) in pyridine (0.25 M) was stirred at 0 °C. 4-Nitrobenzenesulfonyl chloride (2.7 g, 12 mmol, 1.2 equiv) was added slowly, and then the mixture was stirred for 8 h at room temperature. The reaction solution was diluted with EtOAc (100 mL), and washed with 1N HCl (three times). The organic phase was washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography to afford the desired product **S-9** in quantitative yields (2.9 g).

**Step 6**: An oven-dried, three-necked round-bottomed flask was equipped with a Teflon-coated magnetic stir bar, an internal thermometer, a pressure-equalizing dropping funnel sealed with a rubber septum, and fitted with nitrogen gas inlet adaptor. The flask is evacuated and refilled with nitrogen three times, then charged with **S-9** (2.3 g, 7.7 mmol, 1.1 equiv), triphenylphosphine (2.4 g, 9.1 mmol, 1.3 equiv), and THF (30 mL). **S-7** (2.0 g, 7.0 mmol, 1.0 equiv) was added and the solution was stirred in an ice bath for 10 min. Diethyl azodicarboxylate (1.5 g, 8.4 mmol, 1.2 equiv) was added dropwise from dropping funnel over 20 min, such that the internal temperature does not exceed 0 °C. The solution becomes cloudy during the addition. The mixture was stirred at 0 °C overnight, then the solution is evaporated. *n*-Hexane was added at room temperature and the white solid that precipitates was removed in a sintered-glass Büchner funnel (diameter 80 mm) using suction filtration and washed with *n*-hexane, and the filtrate was evaporated to give of the crude product as a clear, yellow oil. This material was purified by silica gel column chromatography to give the desired product **S-8** (2.4 g, 70%).

**Step 7**: Thioglycolic acid (736.9 mg, 8.0 mmol, 2.0 equiv) was added to a solution of **S-8** (2.2 g, 4.0 mmol, 1.0 equiv) and 1,8-diazabicyclo(5.4.0)undec-7-ene (2.4 g, 16.0 mmol, 4.0 equiv) in MeCN (20 mL). The solution was stirred at rt for 2 h and concentrated *in vacuo*. Then DCM (20 mL) and 10% aqueous solution of $Na_2CO_3$ (20 mL) were added. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layers were dried over $MgSO_4$, filtered and evaporated under vacuum. A yellow solid was isolated and carried forward without purification.

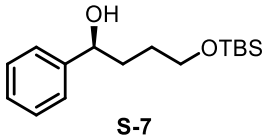
**Step 8**: To a stirred solution of the product obtained in the **step 7** (1.0 equiv) in dry THF (20 mL) was added tetrabutylammonium fluoride (TBAF, 5.0 g, 16 mmol, 4.0 equiv) at room temperature, and the resulting mixture was stirred for 9 h. The reaction mixture

was quenched with water and extracted with EtOAc. The organic extract was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography gave the desired product *(R)*-**6** (868.2 mg, 85%).



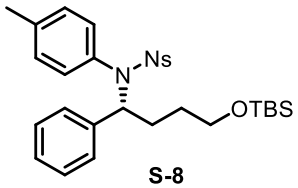
**S-6**

Ccolourles oil. ($R_f$ = 0.20, hexane/ethyl acetate = 10/1).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.08 (m, 5H), 5.61 – 5.41 (m, 0.4H), 4.88 – 4.63 (m, 0.6H), 3.66 (d, *J* = 5.9 Hz, 1.8H), 2.70 – 2.58 (m, 1.2H), 2.49 – 2.39 (m, 1.3H), 2.32 (d, *J* = 5.3 Hz, 0.6H), 2.24 – 2.14 (m, 0.5H), 2.11 – 2.01 (m, 1.3H).



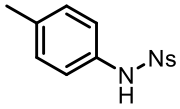
**S-7**

Ccolourles oil. ($R_f$ = 0.40, hexane/ethyl acetate = 10/1).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 4H), 7.30 – 7.20 (m, 1H), 4.70 (dd, *J* = 7.7, 5.0 Hz, 1H), 3.86 – 3.56 (m, 2H), 3.09 (s, 1H), 1.93 – 1.77 (m, 2H), 1.73 – 1.56 (m, 2H), 0.91 (s, 9H), 0.07 (s, 6H).



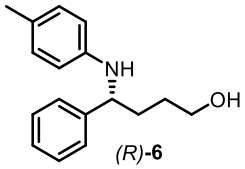
**S-8**

White solid. ($R_f$ = 0.30, hexane/ethyl acetate = 10/1).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.26 – 7.18 (m, 3H), 7.03 (d, *J* = 6.2 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.45 (d, *J* = 7.9 Hz, 2H), 5.53 (t, *J* = 7.8 Hz, 1H), 3.67 – 3.54 (m, 2H), 2.32 (s, 3H), 1.99 – 1.87 (m, 1H), 1.87 – 1.75 (m, 1H), 1.66 – 1.57 (m, 1H), 1.52 – 1.43 (m, 1H), 0.86 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H).



**S-9**

White solid. ($R_f$ = 0.30, hexane/ethyl acetate = 3/1).
$^1$H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.9 Hz, 2H), 7.90 (d, *J* = 8.9 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.75 (s, 1H), 2.30 (s, 3H). The spectral data are consistent with those reported in literature[4].




*(R)*-**6**

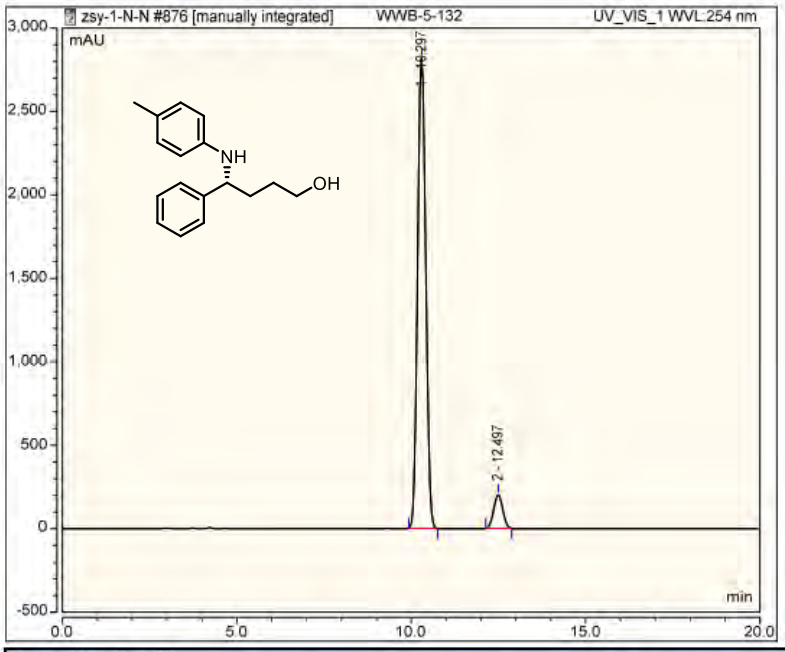
White solid. ($R_f$ = 0.20, hexane/ethyl acetate = 3/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 4H), 7.24 – 7.17 (m, 1H), 6.89 (d, *J* = 8.1 Hz, 2H), 6.44 (d, *J* = 8.4 Hz, 2H), 4.30 (t, *J* = 6.7 Hz, 1H), 3.65 (t, *J* = 6.3 Hz, 2H), 2.17 (s, 3H), 1.93 – 1.82 (m, 2H), 1.76 – 1.65 (m, 1H), 1.65 – 1.54 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 145.1, 144.2, 129.7, 128.7, 127.1, 126.7, 126.5, 113.7, 62.8, 58.6, 35.4, 29.7, 20.5.

The ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: $t_{minor}$ = 12.497 min, $t_{major}$ = 10.297 min, ee = 85%.

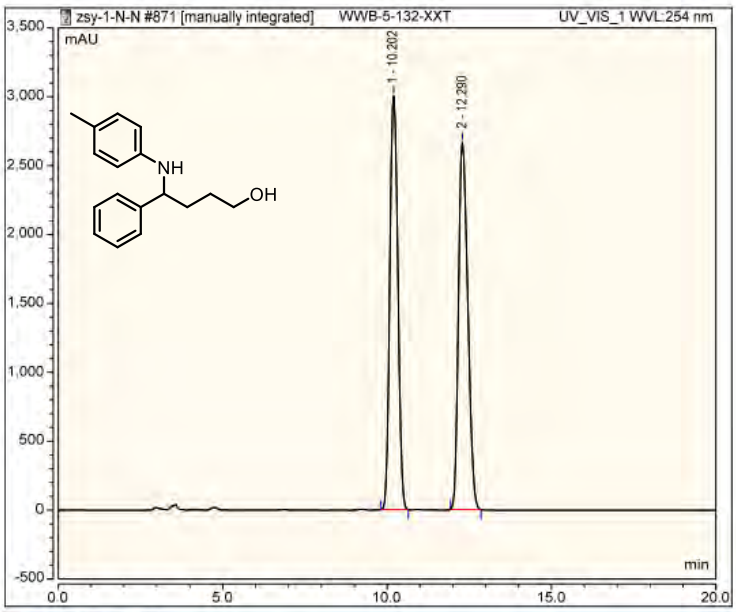
**HRMS**: calculated for $C_{17}H_{22}NO^+$ [M+H$^+$]: 256.1696; **found**: 256.1700.




**Integration Results**

| No. | Peak Nam | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | ee % |
|---|---|---|---|---|---|---|---|
| 1 | | 10.297 | 765.556 | 2817.594 | 92.69 | 93.31 | -85.39 |
| 2 | | 12.497 | 60.350 | 201.950 | 7.31 | 6.69 | |
| **Total:** | | | **825.906** | **3019.544** | **100.00** | **100.00** | |

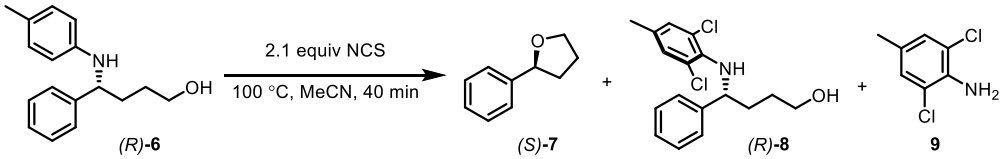
**Figure S1.** HPLC chromatogram of **(*R*)-6**




| Integration Results | | | | | | | |
|---|---|---|---|---|---|---|---|
| No. | Peak Nam | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | ee % |
| 1 | | 10.202 | 849.511 | 3004.376 | 49.31 | 53.01 | 1.38 |
| 2 | | 12.290 | 873.352 | 2662.929 | 50.69 | 46.99 | |
| **Total:** | | | **1722.864** | **5667.305** | **100.00** | **100.00** | |

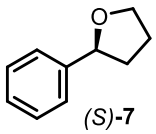
**Figure S2.** HPLC chromatogram of racemic **6**

### 4.2 Isolation and cyclization of the chlorinated intermediate




*(R)*-**6** *(S)*-**7** *(R)*-**8** **9**

Compound *(R)*-**6** (510.7 mg, 2 mmol, 1.0 equiv) was dissolved in MeCN (20 mL, 0.1 M) in a 50 mL glass vial. To the solution was added NCS (561.0 mg, 4.2 mmol, 2.1 equiv). The mixture was stirred at 100 °C under air atmosphere, and then cooled to room temperature after 40 minutes. The reaction mixture was concentrated under reduced pressure. The resulting residue was subjected to silica gel chromatography.




*(S)*-**7**

Colorless oil. ($R_f$ = 0.24, hexane/ethyl acetate = 30/1)

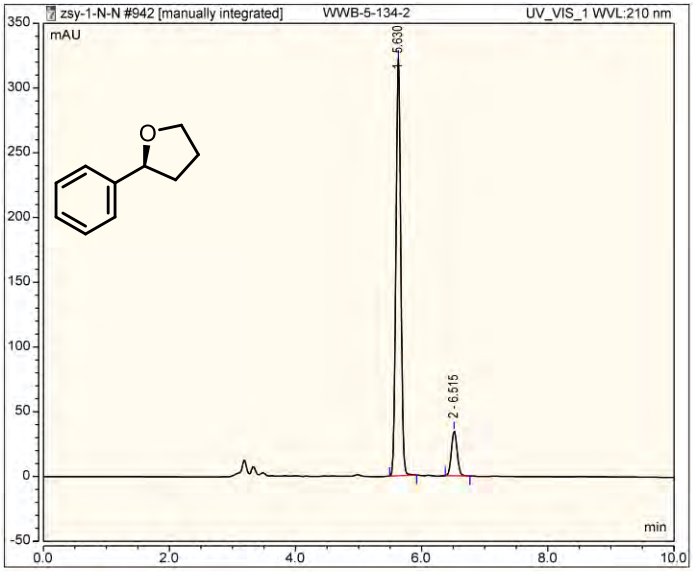
Compound *(S)*-**7** is a known compound, and was obtained in 28% yield (82.0 mg). The spectral data are consistent with those reported in literature[5].

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.28 – 7.19 (m, 1H), 4.89 (t, *J* = 7.2 Hz, 1H), 4.14 – 4.04 (m, 1H), 3.98 – 3.88 (m, 1H), 2.38 – 2.25 (m, 1H), 2.05 – 1.95

(m, 2H), 1.87 – 1.74 (m, 1H).

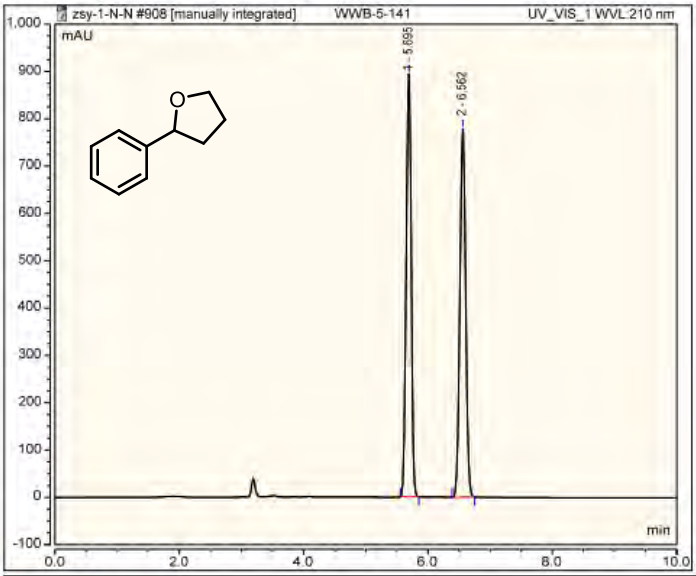
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.6, 128.4, 127.2, 125.8, 80.8, 68.8, 34.7, 26.2.

The ee value was determined by HPLC analysis (Chiralcel AD-H, i-PrOH/Hexane = 1/99, 1.0 mL/min, 215 nm), retention time: $t_{minor}$ = 6.515 min, $t_{major}$ = 5.630 min, ee = 78%.



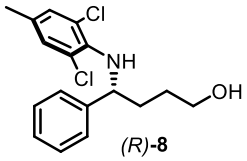

| Integration Results | | | | | | | |
|---|---|---|---|---|---|---|---|
| No. | Peak Nam | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | ee % |
| 1 | | 5.630 | 28.793 | 321.605 | 88.77 | 90.25 | -77.54 |
| 2 | | 6.515 | 3.643 | 34.741 | 11.23 | 9.75 | |
| **Total:** | | | **32.436** | **356.347** | **100.00** | **100.00** | |

**Figure S3.** HPLC chromatogram of **(*S*)-7**




| Integration Results | | | | | | | |
|---|---|---|---|---|---|---|---|
| No. | Peak Nam | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | ee % |
| 1 | | 5.695 | 83.845 | 893.641 | 49.96 | 53.45 | 0.07 |
| 2 | | 6.562 | 83.971 | 778.247 | 50.04 | 46.55 | |
| **Total:** | | | **167.816** | **1671.888** | **100.00** | **100.00** | |

**Figure S4.** HPLC chromatogram of racemic **7**




*(R)*-**8**

White solid. ($R_f$ = 0.29, hexane/ethyl acetate = 3/1).

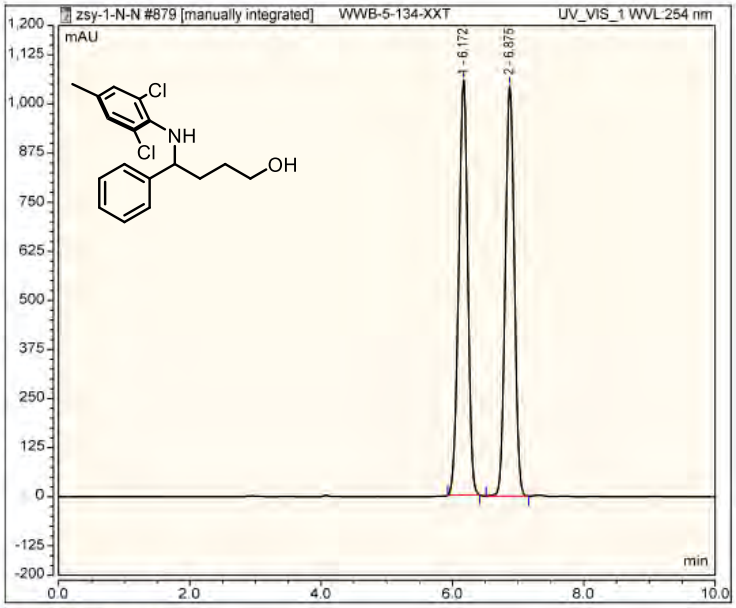
Compound *(R)*-**8** was isolated in 59% yield (380.0 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 4H), 7.21 – 7.12 (m, 1H), 6.94 (d, *J* = 0.8 Hz, 2H), 4.85 (t, *J* = 7.1 Hz, 1H), 3.63 (t, *J* = 6.4 Hz, 2H), 2.14 (s, 3H), 2.06 – 1.95 (m, 1H), 1.94 – 1.82 (m, 1H), 1.71 – 1.62 (m, 1H), 1.61 – 1.49 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.0, 138.7, 132.0, 129.3, 128.4, 127.3, 126.9, 126.1, 62.8, 60.5, 34.1, 30.0, 20.2.

The ee value was determined by HPLC analysis (Chiralcel AD-H, i-PrOH/Hexane = 10/90, 1.0 mL/min, 254 nm), retention time: $t_{minor}$ = 6.125 min, $t_{major}$ = 6.865 min, ee = 84%.

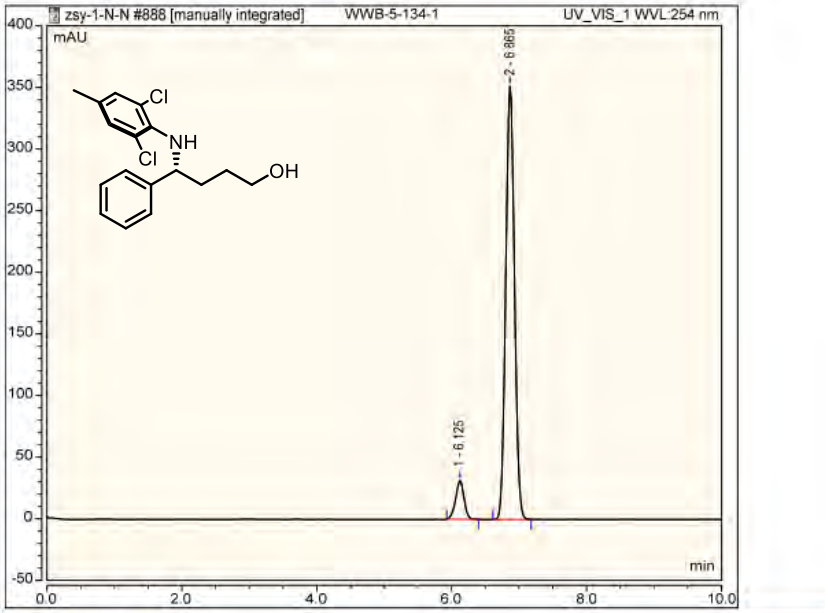
**HRMS**: calculated for $C_{17}H_{20}Cl_2NO^+$ [M+H$^+$]: 324.0916; **found**: 324.0917.




**Integration Results**

| No. | Peak Nam | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | ee % |
|---|---|---|---|---|---|---|---|
| 1 | | 6.172 | 169.350 | 1055.997 | 50.28 | 50.30 | -0.57 |
| 2 | | 6.875 | 167.444 | 1043.603 | 49.72 | 49.70 | |
| **Total:** | | | **336.794** | **2099.600** | **100.00** | **100.00** | |

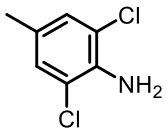
**Figure S5.** HPLC chromatogram of racemic **8**




**Integration Results**

| No. | Peak Nam | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | ee % |
|---|---|---|---|---|---|---|---|
| 1 | | 6.125 | 4.537 | 31.376 | 7.94 | 8.19 | 84.11 |
| 2 | | 6.865 | 52.580 | 351.537 | 92.06 | 91.81 | |
| **Total:** | | | **57.117** | **382.913** | **100.00** | **100.00** | |

**Figure S6.** HPLC chromatogram of **(*R*)-8**



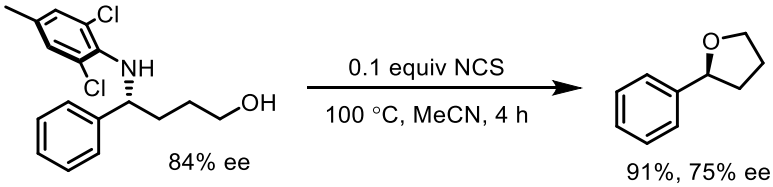

**9**

White solid. ($R_f$ = 0.33, hexane/ethyl acetate = 30/1)

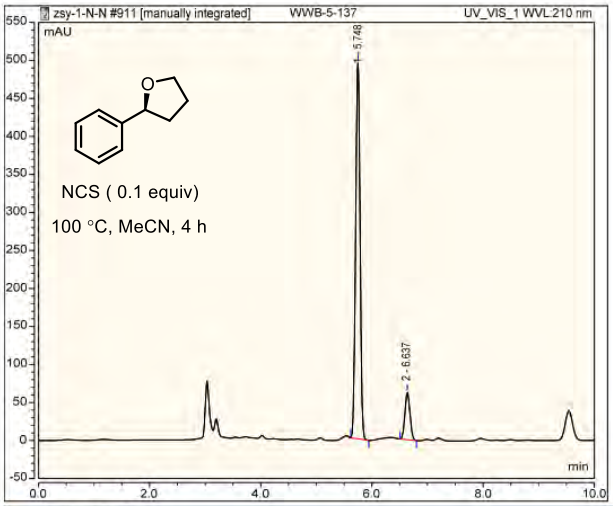
Compound **9** is a known compound, and was obtained in 31% yield (109.0 mg). The spectral data are consistent with those reported in literature[6].

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.00 (s, 2H), 4.28 (s, 2H), 2.21 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 137.7, 128.4, 119.6, 29.9, 20.2.



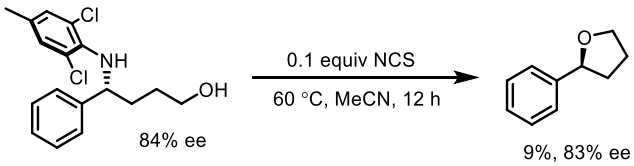

The ee value was determined by HPLC analysis (Chiralcel AD-H, i-PrOH/Hexane = 1/99, 1.0 mL/min, 210 nm), retention time: $t_{minor}$ = 6.637 min, $t_{major}$ = 5.748 min, ee = 75%.



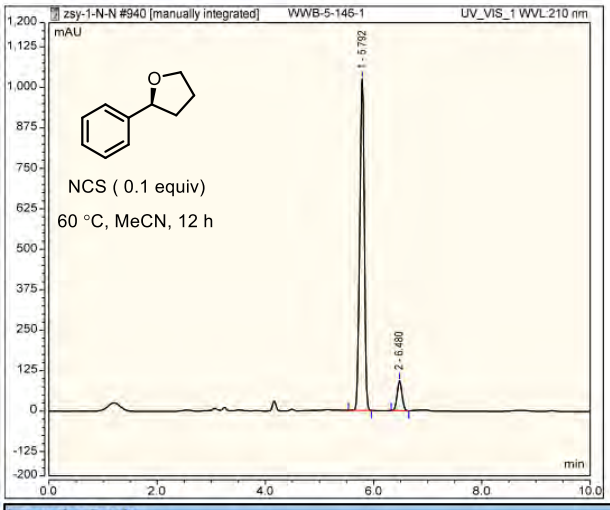

**Integration Results**

| No. | Peak Nam | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | ee % |
|---|---|---|---|---|---|---|---|
| 1 | | 5.748 | 45.768 | 494.857 | 87.48 | 88.83 | -74.96 |
| 2 | | 6.637 | 6.551 | 62.255 | 12.52 | 11.17 | |
| **Total:** | | | **52.320** | **557.112** | **100.00** | **100.00** | |

**Figure S7.** HPLC chromatogram of **(*S*)-7**



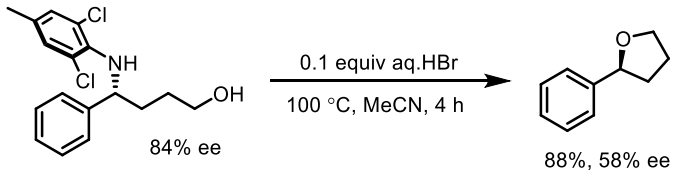

The ee value was determined by HPLC analysis (Chiralcel AD-H, i-PrOH/Hexane = 1/99, 1.0 mL/min, 210 nm), retention time: $t_{minor}$ = 6.480 min, $t_{major}$ = 5.792 min, ee = 83%.



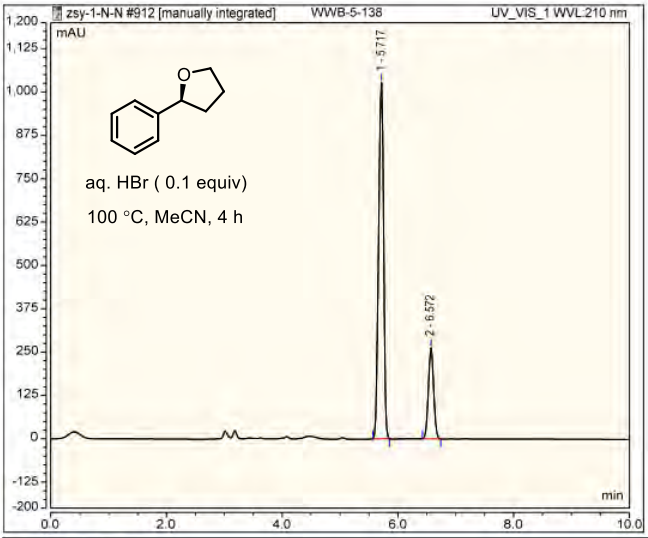

**Integration Results**

| No. | Peak Nam | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | ee % |
|---|---|---|---|---|---|---|---|
| 1 | | 5.792 | 101.520 | 1022.722 | 91.42 | 91.74 | -82.83 |
| 2 | | 6.480 | 9.531 | 92.125 | 8.58 | 8.26 | |
| **Total:** | | | **111.051** | **1114.848** | **100.00** | **100.00** | |

**Figure S8.** HPLC chromatogram of **(*S*)-7**



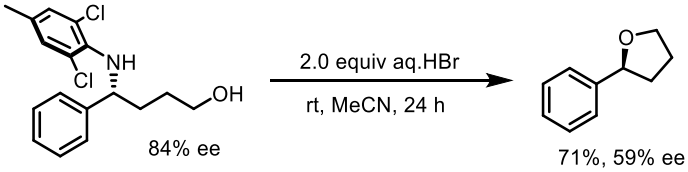

The ee value was determined by HPLC analysis (Chiralcel AD-H, i-PrOH/Hexane = 1/99, 1.0 mL/min, 210 nm), retention time: $t_{minor}$ = 6.572 min, $t_{major}$ = 5.717 min, ee = 58%.



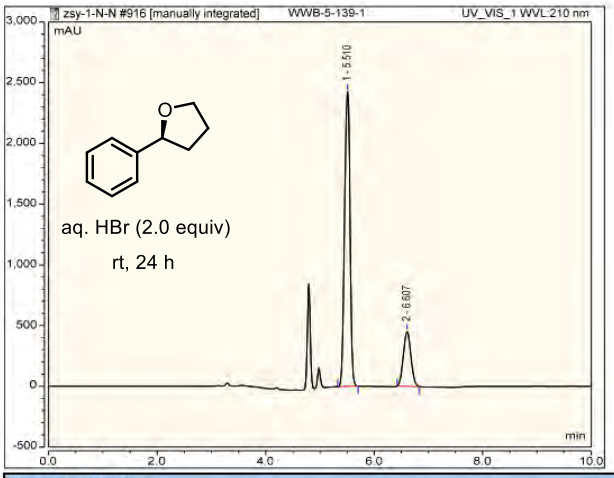

**Integration Results**

| No. | Peak Nam | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | ee % |
|---|---|---|---|---|---|---|---|
| 1 | | 5.717 | 103.481 | 1027.961 | 78.99 | 79.66 | -57.98 |
| 2 | | 6.572 | 27.523 | 262.441 | 21.01 | 20.34 | |
| **Total:** | | | **131.004** | **1290.402** | **100.00** | **100.00** | |

**Figure S9.** HPLC chromatogram of **(*S*)-7**



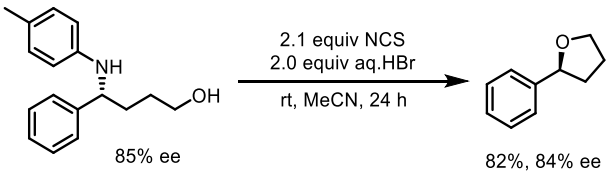

The ee value was determined by HPLC analysis (Chiralcel AD-H, i-PrOH/Hexane = 1/99, 1.0 mL/min, 210 nm), retention time: $t_{minor}$ = 6.607 min, $t_{major}$ = 5.510 min, ee = 59%.



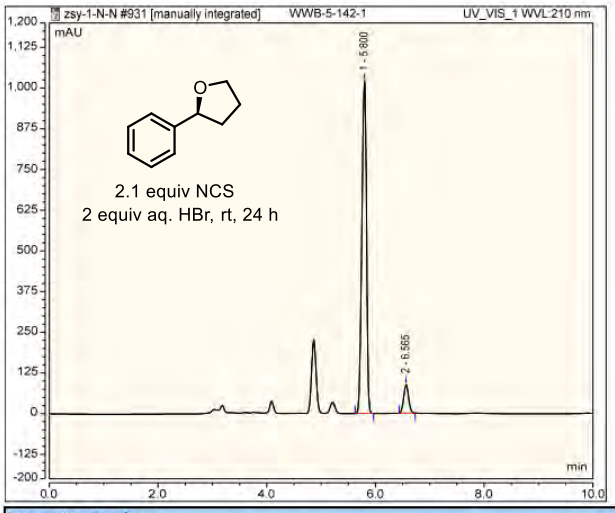

**Integration Results**

| No. | Peak Nam | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | ee % |
|---|---|---|---|---|---|---|---|
| 1 | | 5.510 | 282.888 | 2425.859 | 79.56 | 84.30 | -59.11 |
| 2 | | 6.607 | 72.691 | 451.823 | 20.44 | 15.70 | |
| Total: | | | 355.578 | 2877.682 | 100.00 | 100.00 | |

**Figure S10.** HPLC chromatogram of **(*S*)-7**




The ee value was determined by HPLC analysis (Chiralcel AD-H, i-PrOH/Hexane = 1/99, 1.0 mL/min, 210 nm), retention time: $t_{minor}$ = 6.565 min, $t_{major}$ = 5.800 min, ee = 84%.




**Integration Results**

| No. | Peak Nam | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | ee % |
|---|---|---|---|---|---|---|---|
| 1 | | 5.800 | 100.702 | 1020.053 | 91.77 | 92.08 | -83.53 |
| 2 | | 6.565 | 9.034 | 87.775 | 8.23 | 7.92 | |
| Total: | | | 109.736 | 1107.828 | 100.00 | 100.00 | |

**Figure S11.** HPLC chromatogram of **(*S*)-7**

### 4.3 Verification of N-Cl amine intermediate 9-X by $^1$H spectroscopy.

The 2,6-dichloro-4-toluidine (35.3 mg, 0.2 mmol, 1.0 equiv) was dissolved in $CD_2Cl_2$ (0.5 mL, 0.4 M) in a 4 mL glass vial. To the solution was added NCS (32.0 mg, 0.24 mmol, 1.2 equiv) and stir vigorously for 30 s. The solution was transferred into an oven dried NMR tube, and the reaction mixture was analyzed by $^1$H spectroscopy.

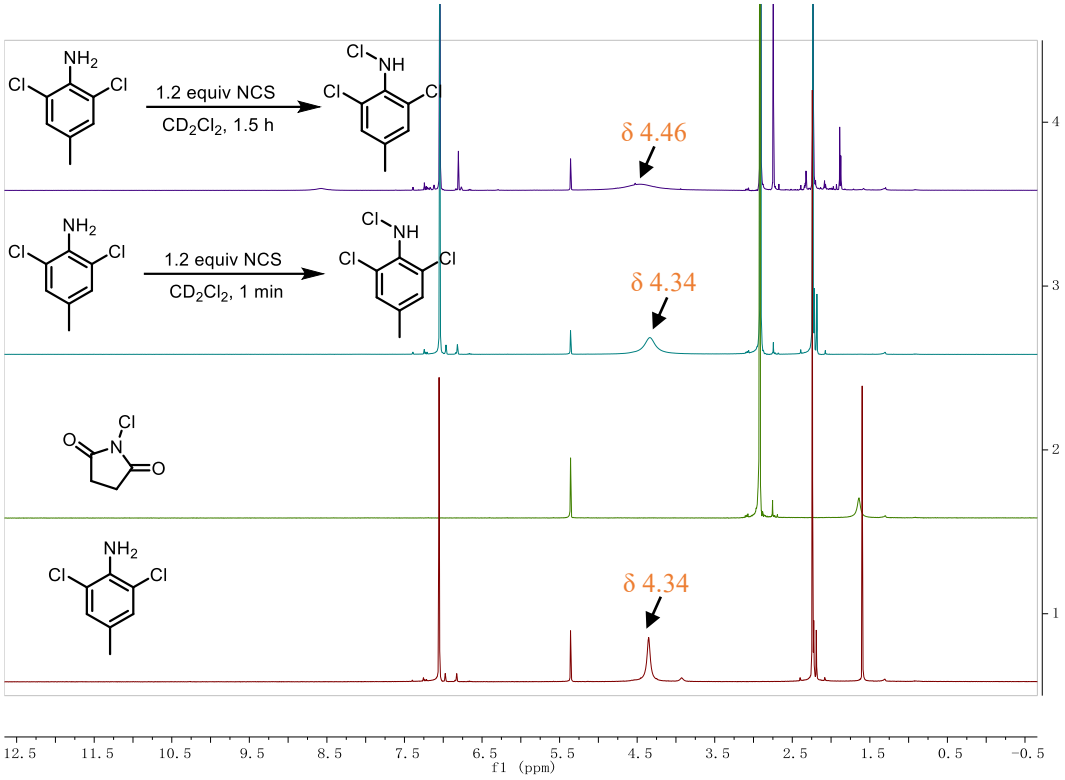
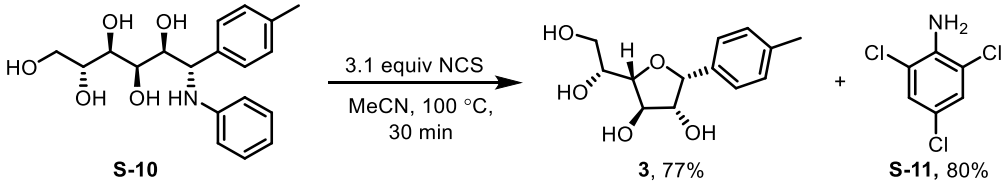


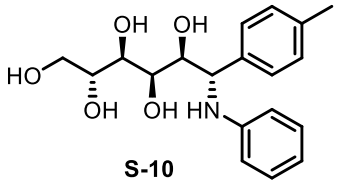

**Figure S12.** $^1$H NMR of N-Cl amine intermediate **9-X**

### 4.4 Verification experiment of another possible pathway.

There is another possible pathway for the deaminative cyclization process, in which halogenation occurs at the para position of the amino group, and the amine motif leaves in the form of an imine[15]. If the hypothesis is correct, the reaction would likely fail if aniline were used instead of toluidine. To test this hypothesis, aniline was employed as the amine source in the synthesis of C-aryl furanoside. The reaction afforded the desired C-aryl furanoside product **3** in 77% yield, along with 80% of 2,4,6-trichloroaniline. Thus, this pathway can be tentatively excluded.




**S-10** **3**, 77% **S-11**, 80%




**S-10**

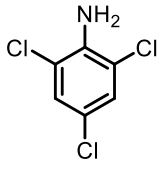
White solid. ($R_f$ = 0.44, DCM/MeOH/$H_2O$ = 20/2/0.3).

Compound **S-10** was isolated in 41% yield (28.5 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.97 (dd, *J* = 8.4, 7.3 Hz, 2H), 6.60 – 6.44 (m, 3H), 4.60 (d, *J* = 6.0 Hz, 1H), 3.97 (d, *J* = 4.9 Hz, 2H), 3.71 (dd, *J* = 10.9, 3.0 Hz, 1H), 3.69 – 3.62 (m, 2H), 3.57 (dd, *J* = 10.9, 4.9 Hz, 1H), 2.27 (s, 3H).

**$^{13}$C NMR** (151 MHz, $CD_3OD$) δ 147.8, 137.8, 136.2, 128.5, 128.3, 127.6, 116.3, 113.2, 75.7, 74.0, 71.6, 68.3, 63.3, 60.2, 19.7.

**HRMS**: calculated for $C_{19}H_{26}NO_5^+$ [M+H$^+$]: 348.1805; **found**: 348.1807.




**S-11**

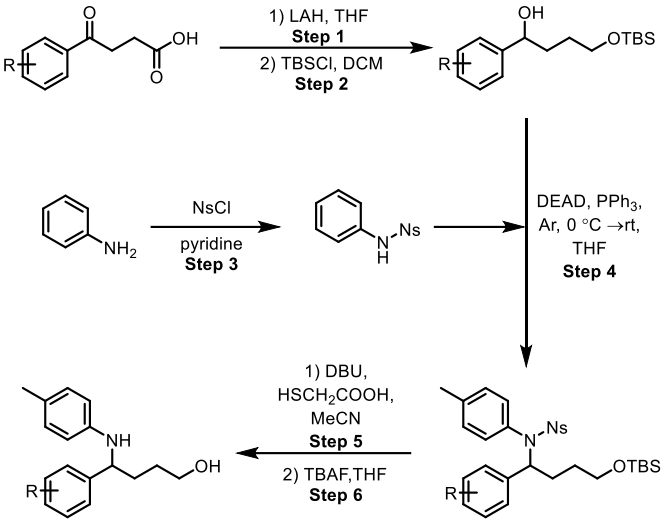
White solid. ($R_f$ = 0.51, hexane/ethyl acetate = 30/1)

Compound **S-11** is a known compound, and was obtained in 80% yield (31.4mg). The spectral data are consistent with those reported in literature[6].

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.19 (s, 2H), 4.43 (s, 2H).

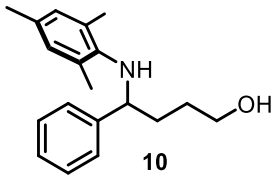
**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 139.0, 127.6, 121.9, 119.7.

## 5. Synthesis of amino alcohol substrates.



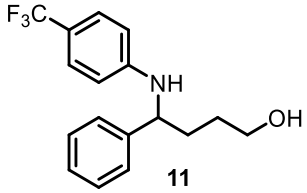

**Step 1**: $LiAlH_4$ (759.0 mg, 20.0 mmol, 4.0 equiv) was suspended in THF, and the mixture was cooled to 0 ºC. Benzoylpropionic acid (5.0 mmol, 1.0 equiv) in THF was added dropwise. The reaction mixture was stirred overnight, allowing to warm to room temperature. After 12 h, the reaction mixture was cooled to 0 °C and quenched by successive dropwise addition of $H_2O$, 15% NaOH (aq), and $H_2O$. The resulting mixture was stirred at room temperature for 1 h, then $MgSO_4$ was added, and the mixture was filtered through a plug of celite (washing with THF). The filtrate was concentrated under reduced pressure to give a clear oil that solidified upon standing. A white solid was isolated and carried forward without purification.

**Steps 2-6** were conducted following the same procedure as the **steps 4-8** for preparation of enantio-enriched amino alcohol substrate.



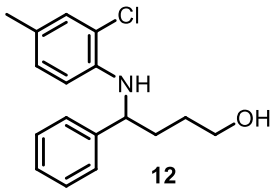
**10**

White solid (200.0 mg, 69%) ($R_f$ = 0.24, hexane/ethyl acetate = 3/1).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.17 (m, 3H), 7.15 (d, *J* = 6.3 Hz, 2H), 6.72 (s, 2H), 4.04 (t, *J* = 7.2 Hz, 1H), 3.63 (t, *J* = 5.6 Hz, 2H), 2.18 (s, 3H), 2.09 (s, 6H), 2.06 – 2.01 (m, 1H), 2.00 – 1.91 (m, 1H), 1.72 – 1.60 (m, 1H), 1.60 – 1.50 (m, 1H).
**HRMS**: calculated for $C_{19}H_{26}NO^+$ [M+H$^+$]: 284.2009; **found**: 284.2015.



**11**

White solid (330 mg, 82%) ($R_f$ = 0.27, hexane/ethyl acetate = 3/1).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 6H), 7.25 – 7.21 (m, 1H), 6.51 (d, *J* = 8.5 Hz, 2H), 4.36 (t, *J* = 6.8 Hz, 1H), 3.68 (td, *J* = 6.3, 1.8 Hz, 2H), 1.99 – 1.85 (m, 2H), 1.76 – 1.66 (m, 1H), 1.65 – 1.55 (m, 1H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 149.9, 143.1, 128.9, 127.5, 126.6 (q, *J* = 3.7 Hz), 126.4, 112.6, 62.6, 58.0, 35.1, 29.3.
**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -61.0.
**HRMS**: calculated for $C_{17}H_{19}F_3NO^+$ [M+H$^+$]: 310.1413; **found**: 310.1414.

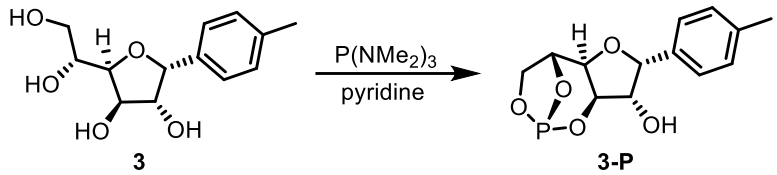


**12**

White solid (420 mg, 78%) ($R_f$ = 0.24, hexane/ethyl acetate = 3/1).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 7.24 – 7.18 (m, 1H), 7.06 (s, 1H), 6.75 (d, *J* = 8.6 Hz, 1H), 6.32 (d, *J* = 8.2 Hz, 1H), 4.35 (t, *J* = 6.8 Hz, 1H), 3.66 (t, *J* = 6.3 Hz, 2H), 2.15 (s, 3H), 1.98 – 1.88 (m, 2H), 1.80 – 1.68 (m, 1H), 1.66 – 1.56 (m, 1H).
**HRMS**: calculated for $C_{17}H_{21}ClNO^+$ [M+H$^+$]: 290.1306; **found**: 290.1306.

## 6. Derivation of the 1,2-*cis* C-aryl furanosides and synthetic applications.

### 6.1 Procedure for synthesis of 1,2-*cis* C-aryl furanosides' derivatives




3 3-P

Compound **3** (50.9 mg, 0.2 mmol, 1.0 equiv) was dissolved in pyridine (1 mL, 0.2 M) in an 8 mL glass vial. To the solution was added hexamethylphosphorous triamide (39.2 mg, 0.24 mmol, 1.2 equiv). The mixture was stirred at 100 ℃ under air atmosphere and monitored by TLC analysis. After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure. The resulting residue was subjected to silica gel chromatography to give the desired product **3-P** (30.0 mg, 53%).

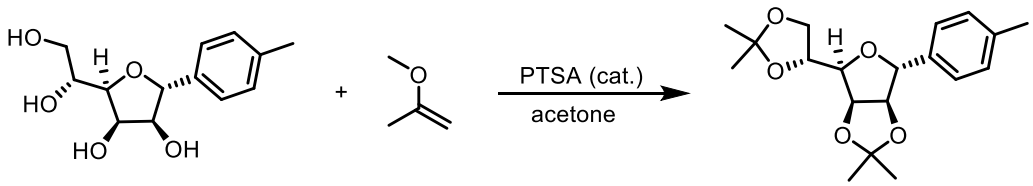
White solid. ($R_f$ = 0.23, Hexane/ethyl acetate = 5/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.54 (d, *J* = 2.6 Hz, 1H), 4.95 – 4.85 (m, 1H), 4.53 (d, *J* = 3.5 Hz, 1H), 4.33 – 4.24 (m, 2H), 4.15 (s, 1H), 4.02 – 3.85 (m, 1H), 2.36 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 138.3, 132.3, 129.7, 126.6, 84.2, 78.8, 78.7, 77.9, 77.2, 75.0, 75.0, 72.5, 72.5, 66.6, 66.5, 21.3.

**$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 117.6.

**HRMS**: calculated for $C_{13}H_{15}NaO_5P^+$ [M+$Na^+$]: 305.0549; **found**: 305.0549.



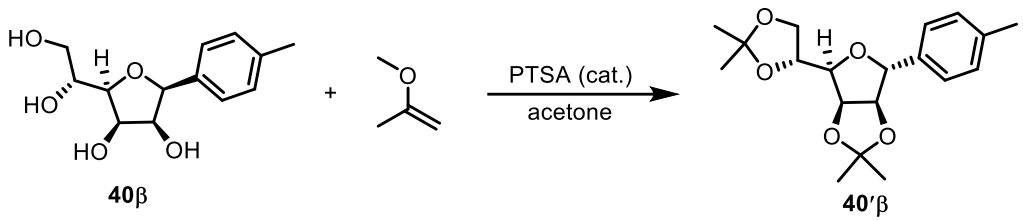

40α 40′α

Compound **40α** (45.8 mg, 0.18 mmol, 1.0 equiv) was dissolved in acetone(4 mL, 0.05 M) in an 8 mL glass vial. To the solution was added 2-methoxyproene (65.0 mg, 0.9 mmol, 5.0 equiv) and PTSA (3.1 mg, 0.018 mmol, 0.1 equiv). The mixture was stirred at room temperature under air atmosphere and monitored by TLC analysis. The reaction mixture was concentrated under reduced pressure. The resulting residue was subjected to silica gel chromatography to give the desired product **40'α** (45.0 mg, 75% yield).

White solid. ($R_f$ = 0.26, hexane/acetone = 10/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.09 (m, 4H), 5.17 (s, 1H), 4.96 (d, *J* = 5.9 Hz, 1H), 4.76 (dd, *J* = 6.0, 3.8 Hz, 1H), 4.58 – 4.43 (m, 1H), 4.28 – 4.10 (m, 2H), 3.86 (dd, *J* = 7.7, 3.7 Hz, 1H), 2.34 (s, 3H), 1.58 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H), 1.38 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 137.3, 135.4, 129.5, 125.6, 112.9, 109.3, 87.5, 85.0, 81.4, 81.2, 73.6, 67.2, 29.8, 27.0, 26.3, 25.3, 24.9, 21.2.



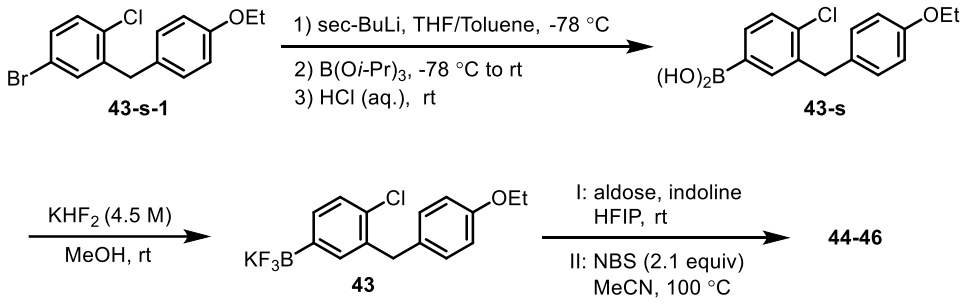

Compound **40'β** (71.1 mg, 0.28 mmol, 1.0 equiv) was synthesized in 80% yield (80.0 mg) following the same procedure as compound **40'α**.

White solid. ($R_f$ = 0.22, hexane/acetone = 10/1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.87 (dd, *J* = 6.0, 3.7 Hz, 1H), 4.78 (dd, *J* = 6.0, 3.7 Hz, 1H), 4.63 – 4.52 (m, 2H), 4.34 – 4.10 (m, 2H), 3.71 (dd, *J* = 7.2, 3.8 Hz, 1H), 2.36 (s, 3H), 1.51 (s, 3H), 1.49 (s, 3H), 1.44 (s, 3H), 1.31 (s, 3H).

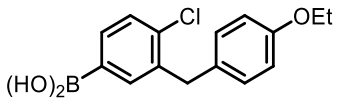
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 137.7, 132.4, 128.8, 127.5, 112.5, 109.1, 83.7, 82.4, 81.6, 80.9, 73.4, 67.1, 27.0, 25.7, 25.5, 24.3, 21.4.

## 6.2 Synthetic procedure for preparation the analogues of dapagliflozin



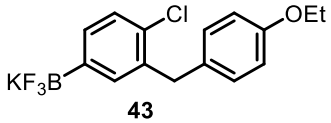

**Step 1**: To a solution of **43-s-1** (2.9 g, 9.0 mmol, 1.0 equiv) in dry THF (20 mL) was added a solution of sec-BuLi in n-hexane (1.3 M, 7 mL, 9.0 mmol, 1.0 equiv) dropwise at -78 ℃ under Ar. The reaction mixture was stirred for 30 min. To this mixture was added triisopropyl borate (935.0 mg, 9.0 mmol, 1.0 equiv) over 1 min, and the reaction mixture was warmed to rt. To this mixture was added 1M aq. HCl (10.0 mL), and the mixture was diluted with 10 mL of ether. The organic portion was separated and extracted with 1N NaOH (2 x 10 mL). The basic extracts were combined and acidified to pH 3 by the addition of 10% aqueous HCl. The mixture was extracted with ether (3×10 mL), and the organic layer was combined and concentrated *in vacuo* to afford **43-s** as a white solid (2.0 g, 6.9 mmol, 77%).

**Step 2**: To a stirred solution of **43-s** (2.0 g, 6.9 mmol, 1.0 equiv) in 10 mL of methanol was added $KHF_2$ (2.4 g, 31.0 mmol, 4.5 equiv), and the resulting mixture was stirred for 4 h at room temperature. Then the solvent was concentrated *in vacuo*. The solid was dissolved in 10 mL of hot acetonitrile and filtered. The filtrate was concentrated to afford **43** as a white solid (2.3 g, 93%).



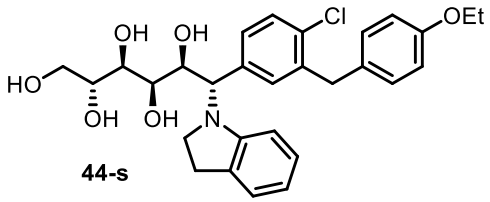

**43-s**

**$^{1}$H NMR** (400 MHz, DMSO-$D_6$) δ 8.15 (s, 1.5H), 7.84 – 7.58 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.1 Hz, 2H), 4.09 – 3.84 (m, 4H), 1.29 (t, *J* = 6.9 Hz, 3H).
**$^{13}$C NMR** (101 MHz, DMSO-$D_6$) δ 156.9, 137.6, 137.2, 135.1, 133.7, 131.4, 129.5, 128.4, 114.3, 62.9, 37.6, 14.7.



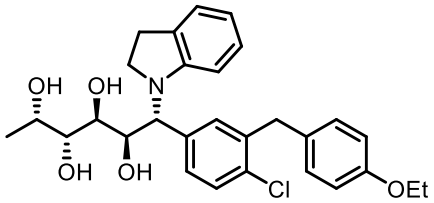

**43**

**$^{1}$H NMR** (400 MHz, MeOD) δ 7.44 – 7.39 (m, 1H), 7.34 – 7.29 (m, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 7.12 – 7.05 (m, 2H), 6.81 – 6.76 (m, 2H), 4.17 – 3.86 (m, 4H), 1.37 (t, *J* = 7.0 Hz, 3H).
**$^{13}$C NMR** (101 MHz, MeOD) δ 158.4, 138.0, 135.6, 133.8, 133.0, 132.0, 130.6, 128.8, 115.2, 64.3, 39.3, 15.2.
**$^{11}$B NMR** (128 MHz, MeOD) δ 4.5.
**$^{19}$F NMR** (376 MHz, MeOD) δ -143.3.




**44-s**

White solid. ($R_f$ = 0.42, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **44-s** was isolated in 58% yield (61.5 mg) following the general procedure of Petasis reaction.
**$^{1}$H NMR** (400 MHz, $CD_3OD$) δ 7.34 – 7.27 (m, 1H), 7.27 – 7.19 (m, 2H), 7.03 – 6.95 (m, 3H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.79 – 6.68 (m, 3H), 6.54 (t, *J* = 7.2 Hz, 1H), 4.96 (d, *J* = 10.1 Hz, 1H), 4.50 (dd, *J* = 10.0, 1.8 Hz, 1H), 4.21 (t, *J* = 2.2 Hz, 1H), 4.03 – 3.91 (m, 4H), 3.84 – 3.72 (m, 3H), 3.66 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.41 – 3.34 (m, 1H), 3.02 – 2.90 (m, 1H), 2.87 – 2.65 (m, 2H), 1.36 (t, *J* = 6.8 Hz, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 158.7, 152.1, 139.9, 137.1, 133.7, 133.4, 132.7, 130.8, 130.5, 129.8, 129.4, 128.1, 125.3, 118.2, 115.4, 108.7, 75.6, 73.2, 72.9, 69.6, 64.7, 64.4, 61.0, 48.0, 39.1, 29.1, 15.2.
**HRMS**: calculated for $C_{29}H_{35}ClNO_6^+$ [M+$H^+$]: 528.2147; **found**: 528.2151.




**45-s**

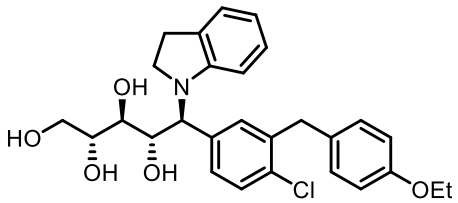
White solid. ($R_f$ = 0.44, DCM/MeOH/$H_2O$ = 30/2/0.3).

Compound **45-s** was isolated in 70% yield (71.5 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD/CDCl_3$) δ 7.32 – 7.26 (m, 1H), 7.22 – 7.13 (m, 2H), 7.05 – 6.93 (m, 4H), 6.80 – 6.73 (m, 2H), 6.68 (d, *J* = 7.9 Hz, 1H), 6.56 (td, *J* = 7.4, 0.9 Hz, 1H), 4.88 (d, *J* = 10.7 Hz, 1H), 4.59 – 4.52 (m, 1H), 4.37 (s, 2H), 4.08 – 3.99 (m, 3H), 3.98 (d, *J* = 4.0 Hz, 1H), 3.96 – 3.89 (m, 2H), 3.46 (dd, *J* = 8.5, 2.5 Hz, 1H), 2.99 (td, *J* = 10.3, 8.4 Hz, 1H), 2.89 – 2.72 (m, 2H), 1.40 (t, *J* = 7.0 Hz, 3H), 1.25 (d, *J* = 6.5 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CD_3OD/CDCl_3$) δ 157.5, 151.0, 139.1, 136.0, 133.2, 132.3, 131.7, 130.1, 129.6, 129.3, 128.2, 127.5, 124.8, 117.5, 114.7, 107.5, 74.5, 69.7, 68.4, 66.8, 63.8, 59.6, 46.8, 38.6, 28.4, 19.5, 15.0.

**HRMS**: calculated for $C_{29}H_{34}ClNNaO_5^+$ [M+$Na^+$]: 534.2018; **found**: 534.2024.




**46-s**

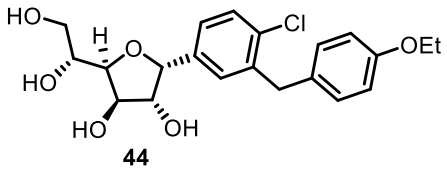
White solid. ($R_f$ = 0.46, DCM/MeOH/$H_2O$ = 30/2/0.3).

Compound **46-s** was isolated in 63% yield (63.0 mg) following the general procedure of Petasis reaction.

**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.34 – 7.22 (m, 3H), 6.98 – 6.88 (m, 4H), 6.75 – 6.69 (m, 2H), 6.53 (t, *J* = 7.1 Hz, 2H), 4.91 (d, *J* = 7.0 Hz, 1H), 4.40 (t, *J* = 6.6 Hz, 1H), 3.95 (d, *J* = 6.9 Hz, 1H), 3.91 (dd, *J* = 4.7, 2.3 Hz, 3H), 3.88 (td, *J* = 5.1, 4.2, 1.9 Hz, 1H), 3.79 (dd, *J* = 11.3, 4.2 Hz, 1H), 3.72 (t, *J* = 6.0 Hz, 1H), 3.64 (dd, *J* = 11.3, 6.0 Hz, 1H), 3.52 (td, *J* = 9.0, 5.3 Hz, 1H), 3.18 (q, *J* = 9.2 Hz, 1H), 2.87 – 2.68 (m, 2H), 1.33 (t, *J* = 7.0 Hz, 3H).

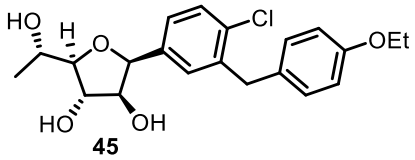
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 158.6, 152.1, 139.8, 137.3, 133.8, 133.7, 132.7, 131.1, 130.8, 129.9, 129.8, 128.0, 125.3, 118.6, 115.4, 109.2, 74.3, 74.2, 73.6, 64.4, 64.3, 62.3, 49.7, 39.2, 29.2, 15.2.

**HRMS**: calculated for $C_{28}H_{33}ClNO_5^+$ [M+$H^+$]: 498.2042; **found**: 498.2047.



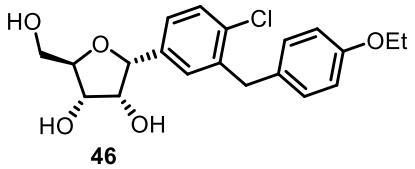
**44**

White solid. ($R_f$ = 0.24, DCM/MeOH/$H_2O$ = 20/2/0.3).
Compound **44** was isolated in 70% yield (57.0 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.31 (d, *J* = 8.2 Hz, 1H), 7.23 (d, *J* = 2.0 Hz, 1H), 7.19 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.85 – 6.72 (m, 2H), **5.14 (d, *J* = 3.1 Hz, 1H)**, 4.32 (dd, *J* = 3.3, 1.3 Hz, 1H), 4.17 (dd, *J* = 8.3, 3.3 Hz, 1H), 4.08 (dd, *J* = 3.2, 1.2 Hz, 1H), 4.02 – 3.91 (m, 5H), 3.83 (dd, *J* = 11.5, 3.2 Hz, 1H), 3.66 (dd, *J* = 11.4, 6.2 Hz, 1H), 1.34 (t, *J* = 7.0 Hz, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 158.8, 139.6, 138.5, 133.7, 132.9, 131.1, 130.8, 129.8, 127.7, 115.4, 83.8, 82.0, 79.9, 78.6, 71.5, 65.5, 64.4, 39.2, 15.2.
**HRMS**: calculated for $C_{21}H_{25}ClNaO_6^+$ [M+$Na^+$]: 431.1232; **found**: 431.1234.



**45**

White solid. ($R_f$ = 0.22, DCM/MeOH/$H_2O$ = 30/2/0.3).
Compound **45** was isolated in 60% yield (47.0 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.35 – 7.30 (m, 2H), 7.27 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.13 – 7.03 (m, 2H), 6.84 – 6.74 (m, 2H), **5.00 (d, *J* = 3.2 Hz, 1H)**, 4.09 (dd, *J* = 2.3, 1.1 Hz, 1H), 4.04 – 3.93 (m, 5H), 3.89 (dd, *J* = 3.3, 1.1 Hz, 1H), 3.70 (dd, *J* = 4.2, 2.3 Hz, 1H), 1.35 (t, *J* = 7.0 Hz, 3H), 1.28 (d, *J* = 6.4 Hz, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 158.8, 139.7, 137.7, 133.8, 132.9, 131.2, 130.8, 129.8, 127.8, 115.4, 91.0, 84.1, 81.0, 80.2, 69.1, 64.4, 39.2, 20.0, 15.2.
**HRMS**: calculated for $C_{21}H_{25}ClNaO_5^+$ [M+$Na^+$]: 415.1283; **found**: 415.1285.

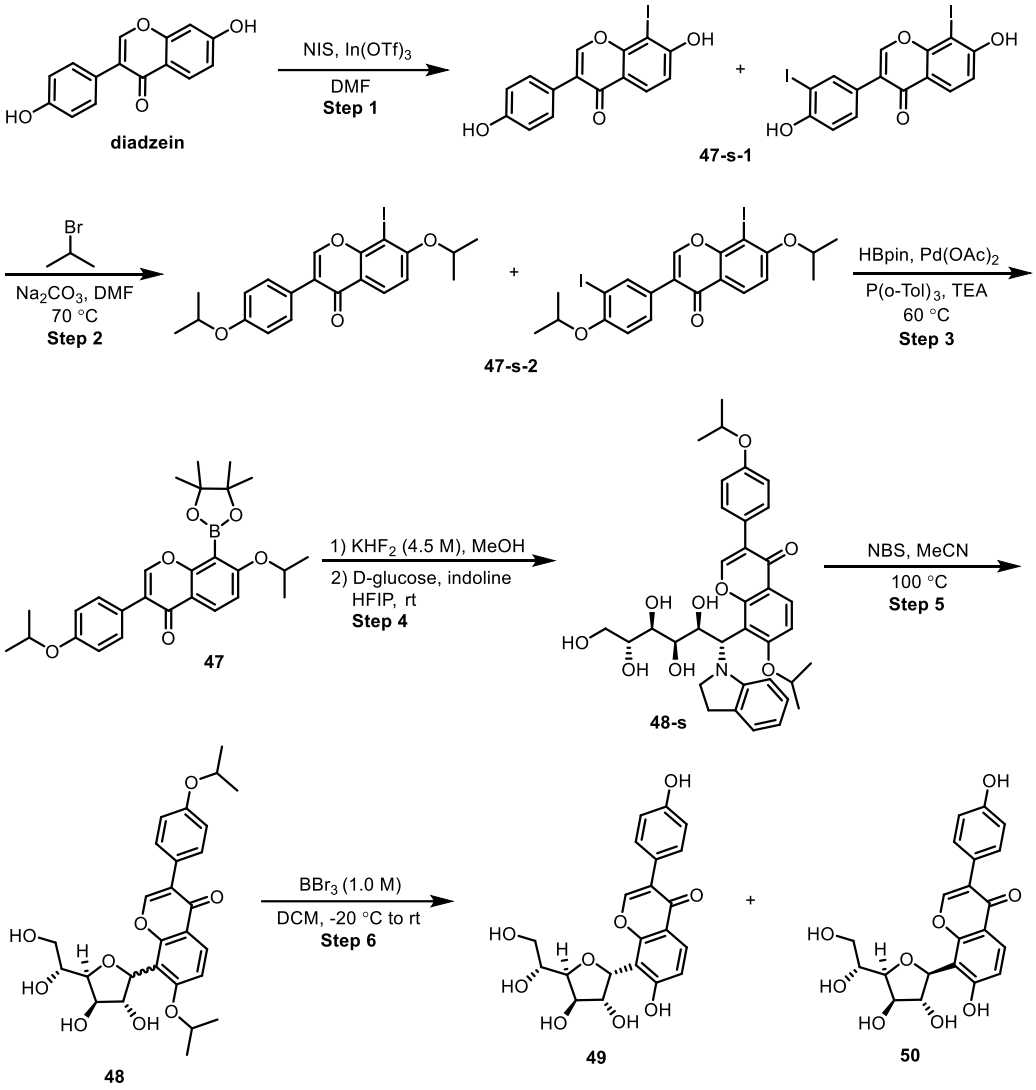


**46**

White solid. ($R_f$ = 0.25, DCM/MeOH/$H_2O$ = 30/2/0.3).
Compound **46** was isolated in 66% yield (50.0 mg) following the general procedure of deaminative cyclization.
**$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.31 (d, *J* = 8.2 Hz, 1H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.21 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.82 – 6.73 (m, 2H), **5.00 (d, *J* = 3.0 Hz, 1H)**, 4.29 (dd, *J* = 8.3, 4.3 Hz, 1H), 4.10 (dd, *J* = 4.4, 3.1 Hz, 1H), 4.05 – 3.99 (m, 3H), 3.96 (t, *J* = 7.0 Hz, 2H), 3.83 (dd, *J* = 12.0, 2.7 Hz, 1H), 3.65 (dd, *J* = 12.0, 4.6 Hz,

1H), 1.34 (t, $J$ = 7.0 Hz, 3H).
**$^{13}$C NMR** (101 MHz, $CD_3OD$) δ 158.8, 139.6, 138.8, 133.8, 133.0, 131.3, 130.8, 129.8, 127.9, 115.4, 83.8, 83.7, 75.2, 74.1, 64.4, 63.2, 39.3, 15.2.
**HRMS**: calculated for $C_{20}H_{23}ClNaO_5^+$ [M+Na$^+$]: 401.1126; **found**: 401.1126.

### 6.3 Synthesis of neopuerarin A and neopuerarin B




**Step 1**: A mixture of diadzein (5.0 g, 20.0 mmol, 1.0 equiv), NIS (5.0 g, 22.0 mmol, 1.1 equiv) and $In(OTf)_3$ (1.1 g, 2.0 mmol, 0.1 equiv) in DMF (300 mL) was stirred at rt in the dark (wrapped in foil) for 8 h. The reaction was monitored by TLC. After completion of the reaction, the mixture was diluted with water (300 mL) and extracted with ethyl acetate (3 x 200 mL). The combined organic phases were washed with water and brine. The organic layer was dried over $Na_2SO_4$ and concentrated *in vacuo.* The residue was purified by flash chromatography on silica gel to give a mixture of **47-s-1** (6.0 g) as a white solid.

**Step 2**: To a stirred solution of **47-s-1** (4.0 g, 1.0 equiv) in DMF (50 mL) was added

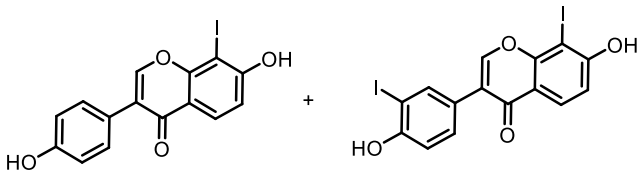
$K_2CO_3$ (4.6 g, 33.0 mmol, 3.0 equiv) at rt. The mixture was stirred for 10 min, then 2-bromopropane (4.1 g, 33.0 mmol, 3.0 equiv) was added. The resulting mixture was stirred at 65 °C for 9 h. The reaction progress was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature, diluted with water (300 mL) and extracted with ethyl acetate. The combined organic phases was washed with water and brine. The organic layer was dried over $Na_2SO_4$ and concentrated *in vacuo.* The residue was purified by flash chromatography on silica gel to give a mixture of **47-s-2** (4.0 g) as a white solid.

**Step 3**: A mixture of **47-s-2** (2.0 g, 1.0 equiv), $Pd(OAc)_2$ (44.9 mg, 0.2 mmol, 0.05 equiv), P(*o*-Tol)$_3$ (121.7 mg, 0.4 mmol, 0.1 equiv), TEA (1.4 mL, 10.0 mmol, 2.5 equiv) and dry THF (20 mL) was stirred at 0 ℃ under Ar atmosphere. HBpin (558.7 mg, 4.4 mmol, 1.1 equiv) was added slowly to the reaction mixture and the resulting mixture was stirred at 60 ºC for 5 h. The reaction mixture was cooled to rt, filtered thorough a pad of celite and concentrated *in vacuo*. The residue was diluted with water and extracted with EtOAc. The combined organic extracts were washed with water, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to give **47** (1.0 g) as a white solid.

**Step 4**: To a solution of pinacol ester **47** (464.0 mg, 1.0 mmol, 1.0 equiv) in methanol (3 mL) was added 4.5 M $KHF_2$ (aq) (1 mL, 4.5 mmol, 4.5 equiv). The resulting mixture was stirred until the pinacol ester were completely consumed monitoring by TLC, and then concentrated to dryness. The residue was used in the Petasis reaction without purification. Compound **48-s** was isolated in 66% yield (409.1 mg) following the general procedure of Petasis reaction.

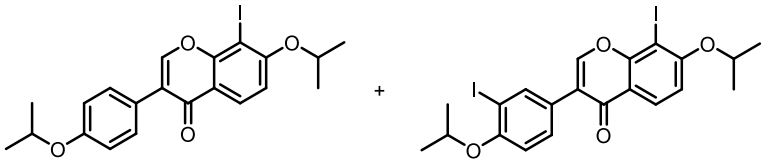
**Step 5**: Compound **48** was isolated in 56% yield (56.1 mg, α/β = 1/1) following the general procedure of deaminative cyclization.

**Step 6**: Compound **48** (23.1 mg, 0.05 mmol, 1.0 equiv) was dissolved in dry $CH_2Cl_2$ (1 mL) and $BBr_3$ (0.5 mL, 1.0 M in $CH_2Cl_2$, 0.5 mmol, 10.0 equiv) was added slowly at -20 ℃ under Ar. The solution was stirred for 9 h under Ar at rt. Upon completion, the reaction were quenched by the addition of MeOH (10 mL) under Ar at -20 ℃. The resulting mixture was stirred vigorously for 10 min at -20 ℃, and then concentrated to dryness. The residue was purified by semi-preparative HPLC (Waters Xselect CSH-C18 column, 2.1×50 mm, 2.5 μm), eluting with $H_2O$ (0.1% formic acid)-3% MeCN, 25% MeCN and 95% MeCN successively at 1.0 mL/min with a Shimadzu LC-10AT pump. The effluents were monitored at 250 nm using a Shimadzu SPD-10A UV detector. Compounds **49** (6.5 mg, 31%) and **50** (6.5 mg, 31%) were obtained as a white solid.



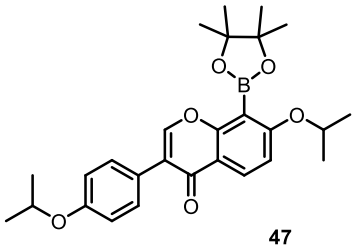
47-s-1

White solid. ($R_f$ = 0.22, hexane/ethyl acetate = 1/1).
**$^1$H NMR** (400 MHz, acetone-$D_6$) δ 8.31 (s, 1H), 8.08 (d, *J* = 8.7 Hz, 1H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H). The spectral data are consistent with those reported in literature[13].



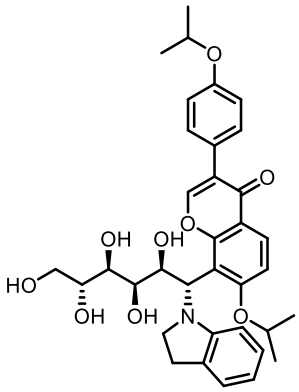
47-s-2

White solid. ($R_f$ = 0.46, hexane/ethyl acetate = 10/1).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.32-8.17 (m, 1H), 8.03 (s, 1H), 7.96 (d, *J* = 2.2 Hz, 0.3H), 7.56 – 7.43 (m, 1.7H), 7.01 – 6.85 (m, 3H), 4.84 – 4.73 (m, 1H), 4.65 – 4.54 (m, 1H), 1.47 (s, 3H), 1.46 (s, 3H), 1.42 (s, 1H), 1.41 (s, 1H), 1.37 (s, 2H), 1.35 (s, 2H).
**HRMS**: calculated for $C_{21}H_{21}NaO_4^+$ [M+$Na^+$]: 487.0377; **found**: 487.0378.



47

White solid. ($R_f$ = 0.32, hexane/ethyl acetate = 10/1).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.9 Hz, 1H), 7.90 (s, 1H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.00 – 6.90 (m, 3H), 4.76 – 4.66 (m, 1H), 4.64 – 4.53 (m, 1H), 1.43 (s, 12H), 1.39 (s, 3H), 1.37 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 176.2, 165.5, 160.0, 157.8, 152.5, 130.1, 129.7, 124.4, 124.2, 118.1, 115.8, 111.1, 84.4, 71.3, 69.9, 24.8, 22.2, 22.1.
**HRMS**: calculated for $C_{27}H_{34}BO_6^+$ [M+$H^+$]: 465.2443; **found**: 465.2450.



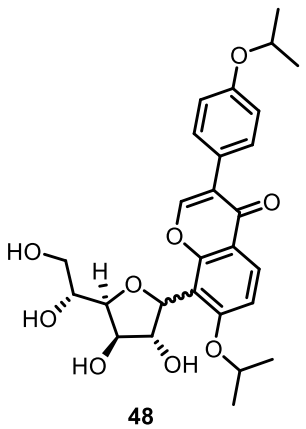
**48-s**

White solid. ($R_f$ = 0.39, DCM/MeOH/$H_2O$ = 20/2/0.3).

**$^1$H NMR** (400 MHz, acetone-$D_6$) δ 8.43 – 8.16 (m, 1H), 8.08 (d, *J* = 7.3 Hz, 1H), 7.63 – 7.41 (m, 2H), 7.16 (d, *J* = 9.1 Hz, 1H), 7.09 – 6.97 (m, 2H), 6.93 (d, *J* = 7.0 Hz, 2H), 6.87 (d, *J* = 7.2 Hz, 1H), 6.46 (d, *J* = 7.1 Hz, 1H), **6.02 (d, *J* = 10.4 Hz, 1H)**, 5.11 (d, *J* = 10.4 Hz, 1H), 4.97 – 4.74 (m, 1H), 4.68 – 4.59 (m, 1H), 4.13 (d, *J* = 2.7 Hz, 1H), 3.86 (dd, *J* = 7.2, 2.8 Hz, 1H), 3.82 – 3.72 (m, 3H), 3.64 (dd, *J* = 11.2, 5.5 Hz, 1H), 3.28 – 2.97 (m, 1H), 2.91 – 2.73 (m, 2H), 1.52 – 1.24 (m, 12H).

**$^{13}$C NMR** (101 MHz, acetone-$D_6$) δ 176.1, 162.1, 158.6, 157.7, 153.2, 152.6, 130.9, 128.8, 127.6, 127.1, 125.1, 124.6, 124.3, 118.9, 117.2, 116.1, 112.6, 108.9, 76.6, 73.5, 72.9, 72.6, 72.3, 71.8, 70.2, 69.2, 64.6, 52.8, 29.1, 22.3.

**HRMS**: calculated for $C_{35}H_{42}NO_9^+$ [M+$H^+$]: 620.2854; **found**: 620.2855.



**48**

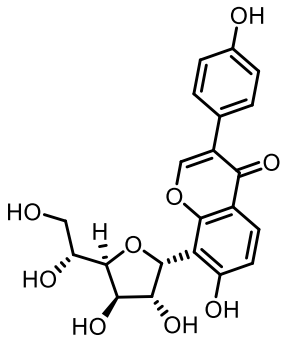
(α/β = 1/1)

White solid. ($R_f$ = 0.27, DCM/MeOH/$H_2O$ = 20/2/0.3).

**$^1$H NMR** (400 MHz, acetone-$D_6$) δ 8.26 (d, *J* = 4.8 Hz, 1H), 8.14 (dd, *J* = 18.6, 8.9 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.29 (d, *J* = 9.2 Hz, 0.5H), 7.26 – 7.21 (m, 0.5H), 6.96 (dd, *J* = 8.9, 2.5 Hz, 2H), **6.00 (d, *J* = 4.4 Hz, 0.5H)**, **5.33 (d, *J* = 6.8 Hz, 0.5H)**, 4.99 – 4.88 (m, 1H), 4.75 – 4.70 (m, 0.5H), 4.70 – 4.64 (m, 1H), 4.59 (s, 0.5H), 4.50 – 4.32 (m, 2H), 4.13 (s, 1H), 4.09 – 3.94 (m, 1.5H), 3.87 – 3.75 (m, 1H), 3.73 – 3.36 (m, 3.5H), 1.45 – 1.36 (m, 6H), 1.33 (s, 3H), 1.32 (s, 3H).

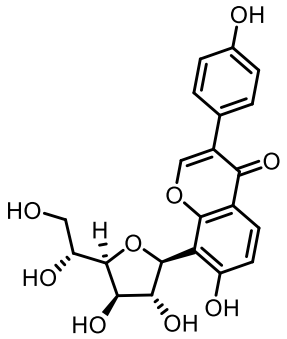
**$^{13}$C NMR** (151 MHz, acetone-$D_6$) δ 175.8, 161.7, 160.5, 158.8, 158.7, 157.2, 156.9, 153.7, 153.4, 131.0, 130.9, 128.0, 126.9, 125.4, 125.1, 124.6, 124.2, 119.5, 119.2, 116.2,

112.9, 112.2, 82.3, 81.4, 81.0, 80.1, 78.8, 78.4, 78.2, 72.8, 72.2, 71.6, 71.1, 70.2, 65.5, 64.8, 22.3, 22.2.
**HRMS**: calculated for $C_{27}H_{32}NaO_9^+$ [M+$Na^+$]: 523.1939; **found**: 523.1939.



**49**

**$^1$H NMR** (600 MHz, DMSO-$D_6$) δ 9.54 (s, 1H), 8.31 (s, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 2H), **5.71 (d, *J* = 3.2 Hz, 1H)**, 5.38 (d, *J* = 4.3 Hz, 1H), 4.70 (d, *J* = 6.0 Hz, 1H), 4.56 (s, 1H), 4.30 (d, *J* = 3.3 Hz, 1H), 4.27 – 4.21 (m, 1H), 4.18 (d, *J* = 3.6 Hz, 1H), 3.85 – 3.79 (m, 1H), 3.67 – 3.58 (m, 1H), 3.56 – 3.49 (m, 1H).
**$^{13}$C NMR** (151 MHz, DMSO-$D_6$) δ 174.9, 161.8, 157.3, 154.6, 152.6, 130.1, 125.6, 123.3, 122.5, 116.6, 115.7, 115.0, 109.6, 80.7, 79.7, 77.8, 75.1, 68.5, 64.0.
**HRMS**: calculated for $C_{21}H_{19}O_9^-$ [M-$H^+$]: 415.1035; **found**: 415.1042.



**50**

**$^1$H NMR** (600 MHz, DMSO-$D_6$) δ 9.56 (s, 1H), 8.34 (s, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 2H), 5.65 (s, 1H), **5.27 (d, *J* = 3.3 Hz, 1H)**, 4.17 (s, 1H), 4.11 (s, 1H), 3.88 – 3.76 (m, 2H), 3.65 – 3.56 (m, 1H), 3.47 – 3.41 (m, 1H).
**$^{13}$C NMR** (151 MHz, DMSO-$D_6$) δ 174.8, 157.3, 155.0, 152.6, 130.1, 126.4, 123.3, 122.5, 116.7, 116.1, 115.0, 111.6, 81.8, 80.6, 80.1, 77.0, 68.8, 63.8.
**HRMS**: calculated for $C_{21}H_{19}O_9^-$ [M-$H^+$]: 415.1035; **found**: 415.1041.

## 7. X-ray crystallographic data.

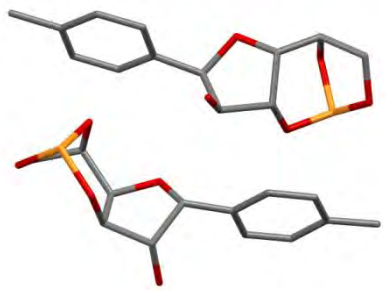


**Figure S13.** X-ray structure of compound **3-P**

Single crystals for X-ray studies were grown by slow evaporation of a solution of **compound 3-P** in hexane in 4 mL tube at room temperature. The X-ray data of is deposited in the Cambridge Crystallographic Data Centre with a number of CCDC 2297443 (DOI: 10.5517/ccdc.csd.cc2h3p2d).

**Table S8.** Crystal data and structure refinement for compound **3-P**.

| | |
|---|---|
| Identification code | compound **3-P** |
| Empirical formula | $C_{13}H_{15}O_5P$ |
| Formula weight | 282.22 |
| Temperature/K | 113.15 |
| Crystal system | Orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 5.7346(2) |
| b/Å | 17.6119(6) |
| c/Å | 25.8850(7) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2614.31(15) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.434 |
| μ/mm$^{-1}$ | 0.224 |
| F(000) | 1184.0 |
| Crystal size/mm$^3$ | 0.42 × 0.14 × 0.12 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.906 to 52.734 |
| Index ranges | $-7 \le h \le 7$, $-22 \le k \le 22$, $-32 \le l \le 32$ |
| Reflections collected | 27329 |
| Independent reflections | 5335 [$R_{int}$ = 0.0914, $R_{sigma}$ = 0.0517] |

| | |
|---|---|
| Data/restraints/parameters | 5335/0/348 |
| Goodness-of-fit on $F^2$ | 1.035 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0373, $wR_2$ = 0.0873 |
| Final R indexes [all data] | $R_1$ = 0.0418, $wR_2$ = 0.0914 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.21/-0.27 |
| Flack parameter | 0.01(6) |

**Table S9.** Fractional Atomic Coordinates ($x10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2×10^3$) for Compound **3-P**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{IJ}$ tensor.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| P001 | 2020.5(16) | 8333.8(5) | 4291.9(3) | 33.8(2) |
| P002 | 3032.9(16) | 5692.1(5) | 965.0(3) | 33.7(2) |
| O003 | 3565(4) | 8864.2(11) | 3911.7(7) | 26.7(5) |
| O004 | 8093(4) | 8891.9(11) | 2936.1(7) | 25.4(4) |
| O005 | 3497(3) | 6145.4(12) | 1501.7(7) | 28.2(5) |
| O006 | 570(4) | 6992.3(10) | 2589.5(7) | 26.6(5) |
| O007 | -225(4) | 5417.7(10) | 2189.2(7) | 27.7(5) |
| O008 | 4458(4) | 7699.0(10) | 3015.5(7) | 26.8(5) |
| O009 | 1066(4) | 5085.8(11) | 1153.8(7) | 30.5(5) |
| O00A | 4019(4) | 7948.0(12) | 4658.1(7) | 35.1(5) |
| O00B | 1712(4) | 7580.3(12) | 3930.0(8) | 35.7(5) |
| O00C | 1173(4) | 6242.5(13) | 672.3(7) | 35.2(5) |
| C00D | 1535(5) | 6472.7(15) | 1777.5(9) | 22.1(6) |
| C00E | 1255(5) | 5533.6(14) | 3072.9(9) | 22.1(6) |
| C00F | 5476(5) | 7728.0(15) | 3520.4(9) | 23.1(6) |
| C00G | 4286(5) | 8434.3(15) | 2237.6(9) | 21.6(6) |
| C00H | 2161(5) | 6490.0(15) | 2351.1(9) | 22.5(6) |
| C00I | 1723(5) | 5659.8(15) | 2506.8(9) | 22.7(6) |
| C00J | 4113(5) | 8462.5(14) | 2819.0(9) | 21.0(6) |
| C00K | 6199(5) | 8100.8(15) | 1993.0(10) | 25.6(6) |
| C00L | 5781(5) | 8947.5(15) | 3129.8(9) | 21.2(6) |
| C00M | 5630(5) | 8571.4(15) | 3662.5(10) | 21.8(6) |
| C00N | 609(7) | 5363.5(16) | 4142.2(10) | 33.5(7) |
| C00O | 2467(5) | 8712.3(16) | 1939.2(10) | 26.6(6) |
| C00P | 2941(6) | 5186.7(15) | 3373.4(10) | 26.6(6) |
| C00Q | -1006(5) | 5531.6(15) | 1275.7(9) | 23.3(6) |
| C00R | 6237(6) | 8041.8(16) | 1457.8(11) | 30.6(7) |
| C00S | -1087(6) | 5692.8(17) | 3835.9(11) | 34.7(7) |
| C00T | 4415(6) | 8310.0(17) | 1157.0(10) | 32.6(7) |
| C00U | -592(5) | 5956.3(15) | 1778.2(9) | 21.4(6) |
| C00V | 2624(6) | 5105.0(17) | 3904.7(10) | 32.1(7) |
| C00W | -797(6) | 5781.9(16) | 3308.0(11) | 28.5(6) |
| C00X | 4012(6) | 7247.5(16) | 3884.0(10) | 28.2(7) |

| | | | | |
|---|---|---|---|---|
| C00Y | 2528(6) | 8648.8(17) | 1402.0(10) | 31.2(7) |
| C00Z | 4940(7) | 7258.9(16) | 4431.8(11) | 34.8(8) |
| C010 | -1196(5) | 6070.0(17) | 817.3(10) | 28.1(6) |
| C011 | 257(8) | 5265(2) | 4719.2(12) | 55.2(11) |
| C012 | 4467(8) | 8217(2) | 573.2(11) | 53.7(11) |

**Table S10.** Anisotropic Displacement Parameters ($Å2\times10^3$) for Compound **3-P**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{23}$** | **$U_{13}$** | **$U_{12}$** |
|---|---|---|---|---|---|---|
| P001 | 36.2(5) | 39.6(5) | 25.6(3) | 8.8(3) | 7.1(3) | 1.7(4) |
| P002 | 27.7(4) | 50.2(5) | 23.1(3) | -7.7(3) | -1.3(3) | 2.0(4) |
| O003 | 33.5(12) | 24.3(9) | 22.2(9) | 2.0(8) | 6.9(8) | 4.0(9) |
| O004 | 21.6(10) | 25.1(9) | 29.4(9) | -6.1(8) | 4.2(9) | -5.5(9) |
| O005 | 21.9(11) | 40.3(11) | 22.3(9) | -2.8(8) | -1.4(8) | -3.2(9) |
| O006 | 29.3(12) | 21.9(9) | 28.6(10) | -6.6(8) | -2.9(8) | 0.5(9) |
| O007 | 39.2(12) | 24.6(10) | 19.5(8) | 4.4(8) | -10.1(9) | -11.9(9) |
| O008 | 43.9(13) | 19.4(9) | 17.2(8) | 1.9(7) | -8.1(9) | -7.2(9) |
| O009 | 33.5(12) | 27.6(10) | 30.5(10) | -7.7(8) | -8.9(9) | 6.2(10) |
| O00A | 49.3(14) | 36.4(11) | 19.5(9) | 2.1(9) | -2.7(9) | 2.1(11) |
| O00B | 33.9(13) | 41.4(12) | 31.7(11) | 10.5(9) | -4.8(10) | -11.3(11) |
| O00C | 32.0(12) | 50.6(13) | 23.1(9) | 7.8(9) | -4.1(9) | -8.6(11) |
| C00D | 24.5(16) | 21.4(12) | 20.3(12) | -0.7(10) | -1.2(10) | -1.1(12) |
| C00E | 30.6(16) | 17.0(12) | 18.6(11) | -2.5(10) | -2.1(11) | -1.2(12) |
| C00F | 30.2(16) | 20.4(13) | 18.7(12) | -0.5(10) | -5.9(12) | -0.7(12) |
| C00G | 25.8(15) | 19.7(12) | 19.3(12) | 2.7(10) | -0.7(11) | -3.2(12) |
| C00H | 24.0(15) | 22.7(13) | 20.8(12) | -3.2(10) | -2.4(11) | -2.7(12) |
| C00I | 26.9(16) | 21.9(13) | 19.2(11) | -3.2(10) | -5.7(11) | 1.6(12) |
| C00J | 22.9(14) | 20.7(13) | 19.6(12) | 3.5(10) | 0.1(10) | -0.9(12) |
| C00K | 28.9(16) | 24.0(13) | 24.0(12) | 1.7(11) | -0.7(11) | -0.6(12) |
| C00L | 24.3(15) | 18.0(12) | 21.3(12) | -1.2(10) | 2.6(11) | -1.2(12) |
| C00M | 24.0(15) | 21.0(12) | 20.4(12) | -1.2(10) | -0.8(11) | -0.8(12) |
| C00N | 56(2) | 22.6(14) | 21.8(13) | 0.1(11) | 2.1(14) | -2.9(15) |
| C00O | 27.7(17) | 26.6(14) | 25.4(13) | 5.6(11) | -2.0(11) | -2.0(12) |
| C00P | 34.2(16) | 22.9(13) | 22.7(12) | -2.8(10) | -3.6(12) | 3.2(13) |
| C00Q | 23.0(15) | 24.3(13) | 22.6(12) | 0.4(11) | -6.3(11) | 1.0(12) |
| C00R | 41.2(19) | 24.6(14) | 25.9(13) | -1.7(11) | 6.3(13) | -1.6(14) |
| C00S | 43(2) | 28.9(15) | 32.3(14) | -2.0(12) | 10.7(14) | 1.9(15) |
| C00T | 50(2) | 26.8(14) | 20.8(13) | 4.4(11) | -1.5(13) | -10.7(15) |
| C00U | 22.6(15) | 21.7(12) | 19.8(12) | 2.9(10) | -3.7(10) | -1.6(11) |
| C00V | 47(2) | 26.1(14) | 23.5(13) | 2.9(11) | -9.2(13) | 3.5(14) |
| C00W | 29.3(16) | 26.6(14) | 29.7(13) | 3.3(12) | 0.1(12) | 3.6(13) |
| C00X | 41.5(18) | 21.8(13) | 21.2(13) | 6.4(11) | -8.9(12) | -4.4(14) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C00Y | 37(2) | 30.7(15) | 25.7(13) | 10.7(12) | -10.1(13) | -6.4(13) |
| C00Z | 54(2) | 28.6(15) | 22.4(13) | 5.6(11) | -9.4(14) | 1.1(15) |
| C010 | 28.7(16) | 32.5(15) | 23.2(13) | 4.4(12) | -8.0(12) | -2.2(14) |
| C011 | 93(3) | 47(2) | 25.2(15) | 5.2(15) | 11.0(18) | 2(2) |
| C012 | 86(3) | 55(2) | 20.1(14) | 0.4(15) | -3.6(17) | -11(2) |

**Table S11.** Bond Lengths for compound **3-P**.

| **Atom** | **Atom** | **Length/Å** | **Atom** | **Atom** | **Length/Å** |
|---|---|---|---|---|---|
| P001 | O003 | 1.620(2) | C00E | C00W | 1.395(4) |
| P001 | O00A | 1.635(2) | C00F | C00M | 1.533(4) |
| P001 | O00B | 1.634(2) | C00F | C00X | 1.519(4) |
| P002 | O005 | 1.6241(19) | C00G | C00J | 1.509(3) |
| P002 | O009 | 1.628(2) | C00G | C00K | 1.397(4) |
| P002 | O00C | 1.628(2) | C00G | C00O | 1.387(4) |
| O003 | C00M | 1.444(3) | C00H | C00I | 1.537(4) |
| O004 | C00L | 1.420(3) | C00J | C00L | 1.514(4) |
| O005 | C00D | 1.452(3) | C00K | C00R | 1.389(4) |
| O006 | C00H | 1.413(3) | C00L | C00M | 1.532(3) |
| O007 | C00I | 1.451(3) | C00N | C00S | 1.382(5) |
| O007 | C00U | 1.441(3) | C00N | C00V | 1.386(5) |
| O008 | C00F | 1.432(3) | C00N | C011 | 1.517(4) |
| O008 | C00J | 1.451(3) | C00O | C00Y | 1.395(4) |
| O009 | C00Q | 1.459(3) | C00P | C00V | 1.395(4) |
| O00A | C00Z | 1.447(4) | C00Q | C00U | 1.519(3) |
| O00B | C00X | 1.448(4) | C00Q | C010 | 1.523(3) |
| O00C | C010 | 1.441(4) | C00R | C00T | 1.386(5) |
| C00D | C00H | 1.528(3) | C00S | C00W | 1.386(4) |
| C00D | C00U | 1.521(4) | C00T | C00Y | 1.389(5) |
| C00E | C00I | 1.506(3) | C00T | C012 | 1.520(4) |
| C00E | C00P | 1.383(4) | C00X | C00Z | 1.515(4) |

**Table S12.** Bond Angles for compound **3-P**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| O003 | P001 | O00A | 102.04(12) | O008 | C00J | C00L | 104.5(2) |
| O003 | P001 | O00B | 100.32(10) | C00G | C00J | C00L | 120.5(2) |
| O00B | P001 | O00A | 94.06(11) | C00R | C00K | C00G | 119.7(3) |
| O005 | P002 | O009 | 100.32(10) | O004 | C00L | C00J | 111.3(2) |
| O005 | P002 | O00C | 102.29(11) | O004 | C00L | C00M | 109.9(2) |
| O009 | P002 | O00C | 94.37(11) | C00J | C00L | C00M | 101.4(2) |
| C00M | O003 | P001 | 120.91(17) | O003 | C00M | C00F | 113.9(2) |
| C00D | O005 | P002 | 119.25(16) | O003 | C00M | C00L | 107.1(2) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C00U | O007 | C00I | 109.71(19) | C00L | C00M | C00F | 101.9(2) |
| C00F | O008 | C00J | 110.01(18) | C00S | C00N | C00V | 118.0(3) |
| C00Q | O009 | P002 | 106.02(16) | C00S | C00N | C011 | 121.3(3) |
| C00Z | O00A | P001 | 111.69(18) | C00V | C00N | C011 | 120.7(3) |
| C00X | O00B | P001 | 106.10(18) | C00G | C00O | C00Y | 120.5(3) |
| C010 | O00C | P002 | 111.76(17) | C00E | C00P | C00V | 120.6(3) |
| O005 | C00D | C00H | 107.7(2) | O009 | C00Q | C00U | 108.8(2) |
| O005 | C00D | C00U | 112.6(2) | O009 | C00Q | C010 | 103.0(2) |
| C00U | C00D | C00H | 101.5(2) | C00U | C00Q | C010 | 111.8(2) |
| C00P | C00E | C00I | 119.2(3) | C00T | C00R | C00K | 121.5(3) |
| C00P | C00E | C00W | 118.9(2) | C00N | C00S | C00W | 121.9(3) |
| C00W | C00E | C00I | 121.9(2) | C00R | C00T | C00Y | 118.5(3) |
| O008 | C00F | C00M | 106.1(2) | C00R | C00T | C012 | 120.5(3) |
| O008 | C00F | C00X | 108.7(2) | C00Y | C00T | C012 | 121.0(3) |
| C00X | C00F | C00M | 115.0(2) | O007 | C00U | C00D | 106.1(2) |
| C00K | C00G | C00J | 121.2(3) | O007 | C00U | C00Q | 109.3(2) |
| C00O | C00G | C00J | 119.6(3) | C00Q | C00U | C00D | 114.7(2) |
| C00O | C00G | C00K | 119.1(2) | C00N | C00V | C00P | 120.8(3) |
| O006 | C00H | C00D | 106.6(2) | C00S | C00W | C00E | 119.7(3) |
| O006 | C00H | C00I | 112.0(2) | O00B | C00X | C00F | 109.2(2) |
| C00D | C00H | C00I | 101.4(2) | O00B | C00X | C00Z | 103.7(2) |
| O007 | C00I | C00E | 111.8(2) | C00Z | C00X | C00F | 112.2(3) |
| O007 | C00I | C00H | 104.9(2) | C00T | C00Y | C00O | 120.6(3) |
| C00E | C00I | C00H | 115.1(2) | O00A | C00Z | C00X | 105.2(2) |
| O008 | C00J | C00G | 108.1(2) | O00C | C010 | C00Q | 105.5(2) |

**Table S13.** Torsion Angles for Compound **3-P**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| P001 | O003 | C00M | C00F | 33.6(3) | C00G | C00J | C00L | C00M | -158.6(2) |
| P001 | O003 | C00M | C00L | 145.49(18) | C00G | C00K | C00R | C00T | 0.3(4) |
| P001 | O00A | C00Z | C00X | 11.0(3) | C00G | C00O | C00Y | C00T | -0.3(4) |
| P001 | O00B | C00X | C00F | -74.1(2) | C00H | C00D | C00U | O007 | -32.5(3) |
| P001 | O00B | C00X | C00Z | 45.7(2) | C00H | C00D | C00U | C00Q | -153.3(2) |
| P002 | O005 | C00D | C00H | 151.59(18) | C00I | O007 | C00U | C00D | 11.7(3) |
| P002 | O005 | C00D | C00U | 40.5(3) | C00I | O007 | C00U | C00Q | 136.0(2) |
| P002 | O009 | C00Q | C00U | -73.2(2) | C00I | C00E | C00P | C00V | 175.9(3) |
| P002 | O009 | C00Q | C010 | 45.6(2) | C00I | C00E | C00W | C00S | -176.2(3) |
| P002 | O00C | C010 | C00Q | 10.9(3) | C00J | O008 | C00F | C00M | 3.8(3) |
| O003 | P001 | O00A | C00Z | -87.6(2) | C00J | O008 | C00F | C00X | 128.0(2) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| O003 | P001 | O00B | C00X | 67.35(17) | C00J | C00G | C00K | C00R | 176.0(3) |
| O004 | C00L | C00M | O003 | 160.6(2) | C00J | C00G | C00O | C00Y | -176.0(3) |
| O004 | C00L | C00M | C00F | -79.5(3) | C00J | C00L | C00M | O003 | -81.5(2) |
| O005 | P002 | O009 | C00Q | 67.26(17) | C00J | C00L | C00M | C00F | 38.4(3) |
| O005 | P002 | O00C | C010 | -87.2(2) | C00K | C00G | C00J | O008 | -52.2(3) |
| O005 | C00D | C00H | O006 | 163.9(2) | C00K | C00G | C00J | C00L | 67.6(3) |
| O005 | C00D | C00H | C00I | -78.8(3) | C00K | C00G | C00O | C00Y | 1.1(4) |
| O005 | C00D | C00U | O007 | 82.3(2) | C00K | C00R | C00T | C00Y | 0.5(4) |
| O005 | C00D | C00U | C00Q | -38.5(3) | C00K | C00R | C00T | C012 | -178.2(3) |
| O006 | C00H | C00I | O007 | 79.6(2) | C00M | C00F | C00X | O00B | 54.4(3) |
| O006 | C00H | C00I | C00E | -43.7(3) | C00M | C00F | C00X | C00Z | -60.1(3) |
| O008 | C00F | C00M | O003 | 88.3(3) | C00N | C00S | C00W | C00E | 0.1(5) |
| O008 | C00F | C00M | C00L | -26.7(3) | C00O | C00G | C00J | O008 | 124.8(3) |
| O008 | C00F | C00X | O00B | -64.4(3) | C00O | C00G | C00J | C00L | -115.4(3) |
| O008 | C00F | C00X | C00Z | -178.8(2) | C00O | C00G | C00K | C00R | -1.0(4) |
| O008 | C00J | C00L | O004 | 79.9(2) | C00P | C00E | C00I | O007 | 132.3(3) |
| O008 | C00J | C00L | C00M | -37.0(3) | C00P | C00E | C00I | C00H | -108.1(3) |
| O009 | P002 | O005 | C00D | -53.4(2) | C00P | C00E | C00W | C00S | 1.4(4) |
| O009 | P002 | O00C | C010 | 14.3(2) | C00R | C00T | C00Y | C00O | -0.4(4) |
| O009 | C00Q | C00U | O007 | -61.9(3) | C00S | C00N | C00V | C00P | 1.0(4) |
| O009 | C00Q | C00U | C00D | 57.1(3) | C00U | O007 | C00I | C00E | 139.5(2) |
| O009 | C00Q | C010 | O00C | -34.9(3) | C00U | O007 | C00I | C00H | 14.1(3) |
| O00A | P001 | O003 | C00M | 47.1(2) | C00U | C00D | C00H | O006 | -77.7(2) |
| O00A | P001 | O00B | C00X | -35.68(18) | C00U | C00D | C00H | C00I | 39.7(3) |
| O00B | P001 | O003 | C00M | -49.4(2) | C00U | C00Q | C010 | O00C | 81.8(3) |
| O00B | P001 | O00A | C00Z | 13.9(2) | C00V | C00N | C00S | C00W | -1.4(5) |
| O00B | C00X | C00Z | O00A | -35.1(3) | C00W | C00E | C00I | O007 | -50.1(3) |
| O00C | P002 | O005 | C00D | 43.4(2) | C00W | C00E | C00I | C00H | 69.4(3) |
| O00C | P002 | O009 | C00Q | -36.09(16) | C00W | C00E | C00P | C00V | -1.7(4) |
| C00D | C00H | C00I | O007 | -33.7(3) | C00X | C00F | C00M | O003 | -31.9(3) |
| C00D | C00H | C00I | C00E | -157.0(2) | C00X | C00F | C00M | C00L | -146.9(2) |
| C00E | C00P | C00V | C00N | 0.5(4) | C010 | C00Q | C00U | O007 | -175.0(2) |
| C00F | O008 | C00J | C00G | 150.6(2) | C010 | C00Q | C00U | C00D | -56.0(3) |
| C00F | O008 | C00J | C00L | 21.2(3) | C011 | C00N | C00S | C00W | -179.6(3) |
| C00F | C00X | C00Z | O00A | 82.7(3) | C011 | C00N | C00V | C00P | 179.2(3) |
| C00G | C00J | C00L | O004 | -41.7(3) | C012 | C00T | C00Y | C00O | 178.2(3) |

**Table S14.** Hydrogen Atom Coordinates (Å×$10^4$) and
Isotropic Displacement Parameters (Å2×$10^3$) for Compound **3-P**.

| **Atom** | ***X*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| H004 | 8860.39 | 9274.65 | 3028.55 | 38 |
| H006 | 1257.34 | 7238.85 | 2821.86 | 40 |
| H00D | 1145.28 | 6990.9 | 1645.17 | 26 |
| H00F | 7086.89 | 7512.14 | 3504.22 | 28 |
| H00H | 3817.82 | 6645.4 | 2409.63 | 27 |
| H00I | 3121.6 | 5353.98 | 2407.43 | 27 |
| H00J | 2490.45 | 8621.95 | 2909.84 | 25 |
| H00K | 7469.94 | 7914.95 | 2191.62 | 31 |
| H00L | 5249.17 | 9487.84 | 3143.27 | 25 |
| H00M | 7056.8 | 8678.74 | 3872.31 | 26 |
| H00O | 1169.85 | 8947.88 | 2101.71 | 32 |
| H00P | 4327.88 | 5002.38 | 3216.47 | 32 |
| H00Q | -2415.32 | 5199.54 | 1301.21 | 28 |
| H00R | 7541.77 | 7812.41 | 1294.21 | 37 |
| H00S | -2493.05 | 5862.79 | 3991.86 | 42 |
| H00U | -2004.66 | 6266.84 | 1859.47 | 26 |
| H00V | 3804.15 | 4869.17 | 4106.31 | 39 |
| H00W | -1989.99 | 6011.22 | 3106.84 | 34 |
| H00X | 3900.54 | 6714.09 | 3753.93 | 34 |
| H00Y | 1267.99 | 8838.96 | 1202.08 | 37 |
| H00A | 4398.05 | 6807.57 | 4625.71 | 42 |
| H00B | 6666.01 | 7265.73 | 4432.72 | 42 |
| H01D | -2034.2 | 5824.44 | 527.73 | 34 |
| H01E | -2040.2 | 6538.33 | 916 | 34 |
| H01F | 1022.86 | 5682.34 | 4903.29 | 83 |
| H01G | 935.59 | 4780.64 | 4829.36 | 83 |
| H01H | -1414.88 | 5268.24 | 4797.55 | 83 |
| H01A | 6051.52 | 8309.46 | 446.33 | 81 |
| H01B | 3393.63 | 8582.51 | 414.82 | 81 |
| H01C | 3987.46 | 7700.19 | 482.2 | 81 |

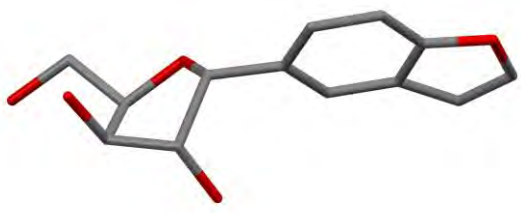


**Figure S14.** X-ray structure of **compound 34**

Single crystals for X-ray studies were grown by slow evaporation of a solution of

**compound 34** in Toluene/hexane in 4 mL tube at room temperature. The X-ray data of is deposited in the Cambridge Crystallographic Data Centre with a number of CCDC 2387663 (DOI: 10.5517/ccdc.csd.cc2l4kdq).

**Table S15. Crystal data and structure refinement for compound 34.**

| | |
|---|---|
| Identification code | compound **34** |
| Empirical formula | $C_{13}H_{14}O_5$ |
| Formula weight | 250.24 |
| Temperature/K | 100.00(10) |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 5.90450(10) |
| b/Å | 10.9096(2) |
| c/Å | 17.4397(3) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 1123.39(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.480 |
| μ/mm$^{-1}$ | 0.961 |
| F(000) | 528.0 |
| Crystal size/mm$^3$ | 0.26 × 0.23 × 0.17 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 9.562 to 148.396 |
| Index ranges | $-4 \le h \le 7$, $-13 \le k \le 13$, $-21 \le l \le 21$ |
| Reflections collected | 7591 |
| Independent reflections | 2145 [$R_{int}$ = 0.0153, $R_{sigma}$ = 0.0131] |
| Data/restraints/parameters | 2145/0/167 |
| Goodness-of-fit on $F^2$ | 1.053 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0266, $wR_2$ = 0.0704 |
| Final R indexes [all data] | $R_1$ = 0.0269, $wR_2$ = 0.0708 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.51/-0.15 |
| Flack parameter | -0.02(6) |

**Table S16.** Fractional Atomic Coordinates (x10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for Compound **34**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{IJ}$ tensor.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| O9 | 1263(2) | 4555.6(12) | 5448.9(7) | 19.2(3) |

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| O10 | 5588(2) | 3502.9(11) | 2239.4(7) | 15.5(3) |
| O16 | 8843(2) | 2521.9(13) | 555.5(7) | 19.5(3) |
| O17 | 4576(2) | 1073.7(11) | 2861.8(7) | 18.7(3) |
| O18 | 3242(2) | 2149.5(13) | 949.9(7) | 18.2(3) |
| C1 | 1582(3) | 4256.4(15) | 4691.0(10) | 16.0(4) |
| C2 | 17(3) | 4415.2(16) | 4115.5(10) | 17.8(4) |
| C3 | 662(3) | 4010.9(16) | 3389.8(10) | 16.5(4) |
| C4 | 2793(3) | 3474.7(16) | 3256.5(10) | 14.6(4) |
| C5 | 4341(3) | 3335.8(15) | 3849.1(10) | 14.3(3) |
| C6 | 3735(3) | 3740.3(15) | 4583.0(10) | 14.9(4) |
| C7 | 4779(3) | 3746.4(15) | 5334.0(10) | 17.1(4) |
| C8 | 3237(3) | 4223.6(16) | 5813.9(11) | 19.3(4) |
| C11 | 3349(3) | 3075.3(15) | 2449.1(10) | 13.6(4) |
| C12 | 3399(3) | 1699.3(15) | 2273.4(9) | 14.1(3) |
| C13 | 4757(3) | 1712.1(15) | 1522.4(9) | 14.2(4) |
| C14 | 6624(3) | 2629.8(15) | 1721.2(9) | 13.6(4) |
| C15 | 7654(3) | 3331.5(17) | 1055.9(10) | 17.0(4) |

**Table S17.** Anisotropic Displacement Parameters ($Å2\times10^3$) for Compound **34**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| O9 | 20.7(7) | 19.1(6) | 18.0(6) | -4.1(5) | 3.3(5) | 0.6(5) |
| O10 | 15.6(6) | 12.3(5) | 18.4(6) | -2.6(5) | 3.6(5) | -2.0(5) |
| O16 | 14.3(7) | 29.2(7) | 15.1(6) | -0.3(5) | 0.4(5) | 4.2(6) |
| O17 | 27.9(7) | 11.4(6) | 16.8(6) | 1.1(5) | -3.0(5) | 0.3(5) |
| O18 | 14.4(6) | 27.4(7) | 12.8(5) | 0.9(5) | -1.4(5) | 0.4(6) |
| C1 | 17.9(9) | 12.5(7) | 17.8(8) | -1.4(6) | 4.9(7) | -1.0(7) |
| C2 | 14.0(9) | 15.1(8) | 24.2(9) | -1.1(7) | 2.6(7) | 1.5(7) |
| C3 | 15.3(9) | 13.8(7) | 20.3(8) | 0.1(7) | -1.8(7) | -0.4(7) |
| C4 | 15.5(9) | 10.9(7) | 17.6(8) | -0.6(6) | 1.2(7) | -1.2(7) |
| C5 | 12.8(8) | 10.8(7) | 19.3(8) | -0.9(6) | 2.1(7) | 0.2(7) |
| C6 | 14.4(9) | 12.1(8) | 18.2(8) | 1.0(6) | -0.4(7) | -1.5(7) |
| C7 | 17.9(9) | 15.5(8) | 17.8(8) | -0.4(7) | -0.5(7) | -1.7(7) |
| C8 | 22.4(10) | 16.8(8) | 18.7(9) | -1.2(7) | -0.4(8) | -2.1(8) |
| C11 | 12.4(8) | 13.3(8) | 15.2(8) | 0.8(6) | 1.0(7) | -0.2(6) |
| C12 | 15.6(8) | 12.3(7) | 14.4(8) | 0.7(6) | -1.3(7) | -1.3(7) |
| C13 | 13.7(9) | 13.6(7) | 15.3(8) | -0.4(6) | -1.6(6) | 0.8(7) |
| C14 | 13.0(9) | 12.8(7) | 15.1(7) | -1.1(6) | 0.6(7) | 2.6(7) |
| C15 | 15.7(9) | 17.0(8) | 18.3(8) | 1.3(7) | 2.0(7) | -0.3(7) |

**Table S18.** Bond Lengths for compound **34**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| O9 | C1 | 1.374(2) | C3 | C4 | 1.407(3) |
| O9 | C8 | 1.377(2) | C4 | C5 | 1.388(3) |
| O10 | C11 | 1.449(2) | C4 | C11 | 1.510(2) |
| O10 | C14 | 1.449(2) | C5 | C6 | 1.400(2) |
| O16 | C15 | 1.426(2) | C6 | C7 | 1.448(3) |
| O17 | C12 | 1.415(2) | C7 | C8 | 1.342(3) |
| O18 | C13 | 1.423(2) | C11 | C12 | 1.532(2) |
| C1 | C2 | 1.375(3) | C12 | C13 | 1.536(2) |
| C1 | C6 | 1.403(3) | C13 | C14 | 1.529(2) |
| C2 | C3 | 1.393(3) | C14 | C15 | 1.517(2) |

**Table S19.** Bond Angles for compound **34**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C1 | O9 | C8 | 105.44(14) | C7 | C8 | O9 | 112.83(16) |
| C14 | O10 | C11 | 109.33(12) | O10 | C11 | C4 | 109.92(14) |
| O9 | C1 | C2 | 125.44(17) | O10 | C11 | C12 | 104.33(14) |
| O9 | C1 | C6 | 110.41(16) | C4 | C11 | C12 | 118.24(14) |
| C2 | C1 | C6 | 124.14(16) | O17 | C12 | C11 | 109.70(13) |
| C1 | C2 | C3 | 116.06(17) | O17 | C12 | C13 | 111.50(14) |
| C2 | C3 | C4 | 121.75(17) | C11 | C12 | C13 | 99.88(13) |
| C3 | C4 | C11 | 117.93(16) | O18 | C13 | C12 | 105.85(14) |
| C5 | C4 | C3 | 120.75(16) | O18 | C13 | C14 | 113.13(14) |
| C5 | C4 | C11 | 121.31(16) | C14 | C13 | C12 | 100.89(13) |
| C4 | C5 | C6 | 118.54(16) | O10 | C14 | C13 | 105.52(14) |
| C1 | C6 | C7 | 105.21(16) | O10 | C14 | C15 | 108.33(13) |
| C5 | C6 | C1 | 118.75(17) | C15 | C14 | C13 | 116.47(14) |
| C5 | C6 | C7 | 136.02(17) | O16 | C15 | C14 | 110.66(14) |
| C8 | C7 | C6 | 106.10(16) | | | | |

**Table S20.** Torsion Angles for Compound **34**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| O9 | C1 | C2 | C3 | -177.94(16) | C4 | C5 | C6 | C7 | 178.45(18) |
| O9 | C1 | C6 | C5 | 177.78(14) | C4 | C11 | C12 | O17 | -44.7(2) |
| O9 | C1 | C6 | C7 | -0.61(19) | C4 | C11 | C12 | C13 | -161.89(15) |
| O10 | C11 | C12 | O17 | 77.77(16) | C5 | C4 | C11 | O10 | -46.3(2) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| O10 | C11 | C12 | C13 | -39.45(15) | C5 | C4 | C11 | C12 | 73.3(2) |
| O10 | C14 | C15 | O16 | 175.75(14) | C5 | C6 | C7 | C8 | -177.06(19) |
| O17 | C12 | C13 | O18 | 169.25(13) | C6 | C1 | C2 | C3 | 0.9(3) |
| O17 | C12 | C13 | C14 | -72.68(16) | C6 | C7 | C8 | O9 | -0.9(2) |
| O18 | C13 | C14 | O10 | 80.03(16) | C8 | O9 | C1 | C2 | 179.07(17) |
| O18 | C13 | C14 | C15 | -40.2(2) | C8 | O9 | C1 | C6 | 0.08(18) |
| C1 | O9 | C8 | C7 | 0.55(19) | C11 | O10 | C14 | C13 | 8.12(17) |
| C1 | C2 | C3 | C4 | -0.1(3) | C11 | O10 | C14 | C15 | 133.53(14) |
| C1 | C6 | C7 | C8 | 0.91(19) | C11 | C4 | C5 | C6 | 179.12(15) |
| C2 | C1 | C6 | C5 | -1.2(3) | C11 | C12 | C13 | O18 | -74.88(15) |
| C2 | C1 | C6 | C7 | -179.62(17) | C11 | C12 | C13 | C14 | 43.19(16) |
| C2 | C3 | C4 | C5 | -0.3(3) | C12 | C13 | C14 | O10 | -32.59(16) |
| C2 | C3 | C4 | C11 | -179.44(16) | C12 | C13 | C14 | C15 | -152.79(14) |
| C3 | C4 | C5 | C6 | 0.1(3) | C13 | C14 | C15 | O16 | -65.57(19) |
| C3 | C4 | C11 | O10 | 132.79(16) | C14 | O10 | C11 | C4 | 147.77(13) |
| C3 | C4 | C11 | C12 | -107.65(19) | C14 | O10 | C11 | C12 | 20.04(16) |
| C4 | C5 | C6 | C1 | 0.7(2) | | | | | |

**Table S21.** Hydrogen Atom Coordinates (Å×$10^4$) and
Isotropic Displacement Parameters (Å2×$10^3$) for Compound **34**.

| **Atom** | ***X*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H16 | 10103.69 | 2344.24 | 749.11 | 29 |
| H17 | 4396.33 | 314.7 | 2808.38 | 28 |
| H18 | 3892.09 | 2141.55 | 521.47 | 27 |
| H2 | -1419.08 | 4779.13 | 4207.31 | 21 |
| H3 | -363.78 | 4099.8 | 2973.98 | 20 |
| H5 | 5780.45 | 2974.36 | 3758.8 | 17 |
| H7 | 6256.43 | 3468.58 | 5461.35 | 20 |
| H8 | 3481.89 | 4321.99 | 6348.8 | 23 |
| H11 | 2231.12 | 3467.72 | 2095.1 | 16 |
| H12 | 1840.87 | 1361.2 | 2197.21 | 17 |
| H13 | 5380.92 | 885.28 | 1393.28 | 17 |
| H14 | 7860.51 | 2188.99 | 1999.68 | 16 |
| H15A | 6439.76 | 3754.55 | 767.29 | 20 |
| H15B | 8708.7 | 3960.92 | 1254.88 | 20 |

**Figure S15.** X-ray structure of **compound 39**

Single crystals for X-ray studies were grown by slow evaporation of a solution of **compound 39** in EA/hexane in 4 mL tube at room temperature. The X-ray data of is deposited in the Cambridge Crystallographic Data Centre with a number of CCDC 2297325 (DOI: 10.5517/ccdc.csd.cc2h3k8g).

**Table S22.** Crystal data and structure refinement for compound **39**.

| | |
|---|---|
| Identification code | compound **39** |
| Empirical formula | $C_{13}H_{14}O_5$ |
| Formula weight | 250.24 |
| Temperature/K | 113.15 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 5.26399(4) |
| b/Å | 9.67070(7) |
| c/Å | 22.73664(17) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 1157.443(15) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.436 |
| μ/mm$^{-1}$ | 0.932 |
| F(000) | 528.0 |
| Crystal size/mm$^3$ | 0.25 × 0.22 × 0.16 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 7.776 to 157.854 |
| Index ranges | $-6 \le h \le 6$, $-12 \le k \le 12$, $-24 \le l \le 28$ |
| Reflections collected | 6827 |
| Independent reflections | 2401 [$R_{int}$ = 0.0176, $R_{sigma}$ = 0.0153] |
| Data/restraints/parameters | 2401/0/167 |
| Goodness-of-fit on F$^2$ | 1.050 |

| | |
|---|---|
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0283, $wR_2$ = 0.0759 |
| Final R indexes [all data] | $R_1$ = 0.0285, $wR_2$ = 0.0760 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.23/-0.13 |
| Flack parameter | 0.06(7) |

**Table S23.** Fractional Atomic Coordinates (x10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for Compound **39**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{IJ}$ tensor.

| **Atom** | ***X*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| O001 | 7235(2) | 3100.7(12) | 6095.4(5) | 26.4(3) |
| O002 | 3940(2) | 2593.2(13) | 5199.9(5) | 28.9(3) |
| O003 | 1807(2) | 7001.9(12) | 5082.8(6) | 31.6(3) |
| O004 | 4064(3) | 5602.9(12) | 6110.9(5) | 37.6(4) |
| O005 | 10666(3) | 5584.0(15) | 8436.6(6) | 37.8(3) |
| C00A | 7304(4) | 4466.8(17) | 8030.0(7) | 28.3(4) |
| C00B | 4604(3) | 3208.0(16) | 6233.4(7) | 22.3(3) |
| C00C | 7710(3) | 5918.2(18) | 6983.1(7) | 27.0(4) |
| C00D | 4025(3) | 4553.6(17) | 6557.9(7) | 25.6(3) |
| C00E | 5590(4) | 4197.5(17) | 7577.7(7) | 27.8(4) |
| C00F | 9410(3) | 6225.4(18) | 7430.9(8) | 29.1(4) |
| C00G | 9155(4) | 5474.2(17) | 7944.0(7) | 27.3(4) |
| C00H | 7753(5) | 3920(2) | 8612.2(8) | 41.0(5) |
| C00I | 9746(5) | 4605(2) | 8826.5(8) | 45.9(6) |
| C006 | 3516(3) | 4987.4(16) | 5552.1(7) | 23.3(3) |
| C007 | 1209(3) | 5637.8(16) | 5275.5(7) | 25.1(3) |
| C008 | 3111(3) | 3441.6(16) | 5670.1(7) | 22.0(3) |
| C009 | 5821(3) | 4914.5(16) | 7050.9(7) | 24.3(3) |

**Table S24.** Anisotropic Displacement Parameters (Å2×10$^3$) for Compound **39**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{23}$** | **$U_{13}$** | **$U_{12}$** |
|---|---|---|---|---|---|---|
| O001 | 19.7(6) | 28.4(6) | 31.1(6) | 1.9(5) | 3.7(5) | 4.6(5) |
| O002 | 25.2(5) | 33.5(6) | 28.1(6) | -10.8(5) | -1.6(5) | 3.4(5) |
| O003 | 30.7(6) | 25.9(6) | 38.2(6) | 9.5(5) | -4.5(6) | -0.6(5) |
| O004 | 61.1(9) | 22.1(6) | 29.7(6) | -1.0(5) | -18.5(6) | 5.4(6) |
| O005 | 43.5(8) | 40.6(7) | 29.4(6) | -7.4(5) | -7.8(6) | -5.6(7) |
| C00A | 37.4(10) | 23.9(8) | 23.7(7) | -2.1(6) | 0.7(7) | -0.4(7) |
| C00B | 19.8(7) | 22.5(7) | 24.4(7) | 1.9(6) | 3.8(6) | -0.7(6) |
| C00C | 28.8(9) | 27.6(8) | 24.7(7) | 1.5(6) | 4.6(7) | 4.2(7) |
| C00D | 25.3(7) | 28.4(8) | 23.1(7) | -1.6(6) | 0.2(6) | 6.2(7) |
| C00E | 32.9(9) | 25.8(7) | 24.8(7) | -1.6(6) | 0.3(7) | -3.7(7) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C00F | 27.9(9) | 26.9(8) | 32.3(8) | -3.0(6) | 5.8(7) | -1.8(7) |
| C00G | 29.8(8) | 27.0(8) | 25.1(7) | -7.5(6) | -2.2(7) | 2.0(7) |
| C00H | 60.5(14) | 38.0(10) | 24.5(8) | 3.0(7) | -5.6(9) | -9.1(10) |
| C00I | 65.7(15) | 46.4(11) | 25.4(8) | 0.4(8) | -11.6(9) | -5.1(11) |
| C006 | 23.4(8) | 24.0(7) | 22.6(7) | 0.4(6) | -0.7(6) | 0.0(6) |
| C007 | 24.9(8) | 24.0(7) | 26.3(7) | 3.1(6) | -0.3(6) | -0.6(6) |
| C008 | 20.1(7) | 22.8(7) | 23.0(7) | -1.3(6) | 2.6(6) | 1.5(6) |
| C009 | 25.0(8) | 24.0(7) | 23.8(7) | -3.2(6) | 1.4(6) | 6.5(7) |

**Table S25.** Bond Lengths for compound **39**.

| **Atom** | **Atom** | **Length/Å** | **Atom** | **Atom** | **Length/Å** |
|---|---|---|---|---|---|
| O001 | C00B | 1.4237(19) | C00B | C00D | 1.527(2) |
| O002 | C008 | 1.4164(18) | C00B | C008 | 1.519(2) |
| O003 | C007 | 1.4253(19) | C00C | C00F | 1.388(3) |
| O004 | C00D | 1.436(2) | C00C | C009 | 1.398(3) |
| O004 | C006 | 1.4325(19) | C00D | C009 | 1.507(2) |
| O005 | C00G | 1.378(2) | C00E | C009 | 1.389(2) |
| O005 | C00I | 1.384(3) | C00F | C00G | 1.381(2) |
| C00A | C00E | 1.393(2) | C00H | C00I | 1.333(3) |
| C00A | C00G | 1.392(3) | C006 | C007 | 1.505(2) |
| C00A | C00H | 1.445(2) | C006 | C008 | 1.534(2) |

**Table S26.** Bond Angles for compound **39**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C006 | O004 | C00D | 109.34(12) | O005 | C00G | C00F | 126.18(16) |
| C00G | O005 | C00I | 105.43(15) | C00F | C00G | C00A | 123.71(16) |
| C00E | C00A | C00H | 135.55(18) | C00I | C00H | C00A | 106.33(18) |
| C00G | C00A | C00E | 118.72(15) | C00H | C00I | O005 | 112.42(17) |
| C00G | C00A | C00H | 105.71(16) | O004 | C006 | C007 | 111.07(14) |
| O001 | C00B | C00D | 111.28(14) | O004 | C006 | C008 | 106.13(12) |
| O001 | C00B | C008 | 109.17(13) | C007 | C006 | C008 | 111.61(13) |
| C008 | C00B | C00D | 100.22(12) | O003 | C007 | C006 | 109.70(14) |
| C00F | C00C | C009 | 121.75(16) | O002 | C008 | C00B | 113.00(13) |
| O004 | C00D | C00B | 104.91(12) | O002 | C008 | C006 | 112.94(13) |
| O004 | C00D | C009 | 110.71(14) | C00B | C008 | C006 | 102.74(12) |
| C009 | C00D | C00B | 115.57(14) | C00C | C009 | C00D | 121.65(15) |
| C009 | C00E | C00A | 119.12(16) | C00E | C009 | C00C | 120.26(16) |
| C00G | C00F | C00C | 116.42(16) | C00E | C009 | C00D | 118.07(15) |
| O005 | C00G | C00A | 110.10(15) | | | | |

**Table S27.** Torsion Angles for Compound **39**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| O001 | C00B | C00D | O004 | 76.41(17) | C00E | C00A | C00G | C00F | -0.4(3) |
| O001 | C00B | C00D | C009 | -45.80(19) | C00E | C00A | C00H | C00I | 178.8(2) |
| O001 | C00B | C008 | O002 | 42.96(18) | C00F | C00C | C009 | C00D | -178.22(15) |
| O001 | C00B | C008 | C006 | -79.05(15) | C00F | C00C | C009 | C00E | 0.4(2) |
| O004 | C00D | C009 | C00C | -16.3(2) | C00G | O005 | C00I | C00H | -1.1(2) |
| O004 | C00D | C009 | C00E | 165.07(15) | C00G | C00A | C00E | C009 | 1.7(3) |
| O004 | C006 | C007 | O003 | 71.59(17) | C00G | C00A | C00H | C00I | 0.1(2) |
| O004 | C006 | C008 | O002 | -146.75(14) | C00H | C00A | C00E | C009 | -176.9(2) |
| O004 | C006 | C008 | C00B | -24.70(16) | C00H | C00A | C00G | O005 | -0.8(2) |
| C00A | C00E | C009 | C00C | -1.7(3) | C00H | C00A | C00G | C00F | 178.52(18) |
| C00A | C00E | C009 | C00D | 177.01(15) | C00I | O005 | C00G | C00A | 1.1(2) |
| C00A | C00H | C00I | O005 | 0.6(3) | C00I | O005 | C00G | C00F | -178.16(18) |
| C00B | C00D | C009 | C00C | 102.78(18) | C006 | O004 | C00D | C00B | 24.77(19) |
| C00B | C00D | C009 | C00E | -75.87(19) | C006 | O004 | C00D | C009 | 150.09(14) |
| C00C | C00F | C00G | O005 | 178.35(16) | C007 | C006 | C008 | O002 | 92.11(16) |
| C00C | C00F | C00G | C00A | -0.8(3) | C007 | C006 | C008 | C00B | -145.84(13) |
| C00D | O004 | C006 | C007 | 121.52(15) | C008 | C00B | C00D | O004 | -38.94(16) |
| C00D | O004 | C006 | C008 | 0.03(19) | C008 | C00B | C00D | C009 | -161.16(14) |
| C00D | C00B | C008 | O002 | 159.90(13) | C008 | C006 | C007 | O003 | -170.20(12) |
| C00D | C00B | C008 | C006 | 37.89(15) | C009 | C00C | C00F | C00G | 0.8(2) |
| C00E | C00A | C00G | O005 | -179.70(15) | | | | | |

**Table S28.** Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å2×10$^3$) for Compound **39**.

| **Atom** | ***X*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H001 | 7840.62 | 2390.49 | 6255.39 | 40 |
| H002 | 2706.11 | 2416.39 | 4977.97 | 43 |
| H003 | 459.06 | 7426.67 | 5002.04 | 47 |
| H00B | 3979.44 | 2381.5 | 6454.53 | 27 |
| H00C | 7833.33 | 6402.78 | 6620.72 | 32 |
| H00D | 2265.67 | 4495.09 | 6721.88 | 31 |
| H00E | 4280.69 | 3532.28 | 7628.62 | 33 |
| H00F | 10679.68 | 6915.56 | 7386.93 | 35 |
| H00H | 6814.09 | 3212.3 | 8804.15 | 49 |
| H00I | 10454.39 | 4440.84 | 9204.34 | 55 |
| H006 | 5008.73 | 5109.93 | 5285.13 | 28 |
| H00A | 642.7 | 5073.36 | 4936.72 | 30 |
| H00G | -193.03 | 5672.83 | 5565.37 | 30 |
| H008 | 1268.25 | 3265.77 | 5746.22 | 26 |

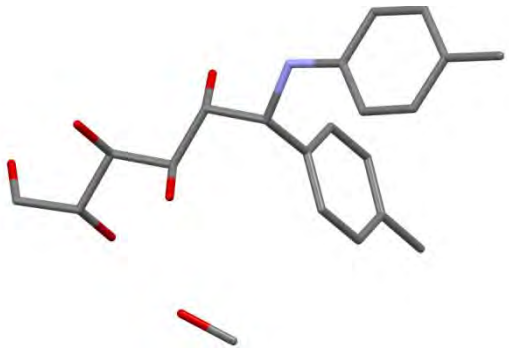


**Figure S16** X-ray structure of compound **40-s**

Single crystals for X-ray studies were grown by slow evaporation of a solution of **compound 40-s** in MeOD in 4 mL tube at room temperature. The X-ray data of is deposited in the Cambridge Crystallographic Data Centre with a number of CCDC 2297387 (DOI: 10.5517/ccdc.csd.cc2h3m8j).

**Table S29.** Crystal data and structure refinement for **40-s**.

| | |
|---|---|
| Identification code | Compound **40-s** |
| Empirical formula | $C_{21}H_{21}D_{10}NO_6$ |
| Formula weight | 403.53 |
| Temperature/K | 294.15 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 6.11364(4) |
| b/Å | 10.29889(7) |
| c/Å | 33.4418(2) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2105.62(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.273 |
| μ/mm$^{-1}$ | 0.742 |
| F(000) | 848.0 |
| Crystal size/mm$^3$ | 0.24 × 0.22 × 0.2 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.984 to 157.898 |
| Index ranges | $-6 \le h \le 7$, $-12 \le k \le 12$, $-42 \le l \le 41$ |
| Reflections collected | 20460 |
| Independent reflections | 4458 [$R_{int}$ = 0.0238, $R_{sigma}$ = 0.0197] |
| Data/restraints/parameters | 4458/2/270 |

| | |
|---|---|
| Goodness-of-fit on $F^2$ | 1.034 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0321, $wR_2$ = 0.0912 |
| Final R indexes [all data] | $R_1$ = 0.0330, $wR_2$ = 0.0920 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.25/-0.17 |
| Flack parameter | 0.05(5) |

**Table S30.** Fractional Atomic Coordinates ($x10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2×10^3$) for Compound **40-s**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{IJ}$ tensor.

| **Atom** | ***X*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| O001 | 4257(2) | 11432.6(12) | 5372.1(4) | 49.7(3) |
| D001 | 4970.22 | 12106.66 | 5364.7 | 75 |
| O002 | 2506(2) | 7335.1(15) | 5751.4(4) | 53.1(3) |
| D002 | 1795.7 | 7083.47 | 5558.4 | 80 |
| O003 | 4692(2) | 8443.1(14) | 4820.3(4) | 54.2(3) |
| D003 | 3850.05 | 7823.64 | 4815.29 | 81 |
| O004 | 7726(2) | 8717.0(12) | 5437.9(5) | 55.3(4) |
| D004 | 8321.73 | 9373.82 | 5523.55 | 83 |
| O005 | 1464(3) | 11078.7(14) | 4681.5(4) | 57.7(4) |
| D005 | 979.12 | 10646.2 | 4495.69 | 86 |
| N006 | 5558(3) | 5492.7(14) | 6050.7(5) | 46.1(3) |
| D006 | 4100(20) | 5410(20) | 6074(6) | 50(6) |
| C00A | 5446(3) | 8765.0(16) | 5526.4(5) | 40.2(3) |
| C00B | 6744(3) | 4758.6(16) | 6333.3(5) | 41.6(4) |
| C00C | 4853(3) | 10627.5(17) | 5042.7(5) | 44.1(4) |
| C00D | 4760(3) | 7386.4(17) | 5647.9(5) | 42.4(4) |
| C00E | 5301(4) | 9164.9(19) | 7088.2(6) | 52.2(4) |
| C00F | 8806(3) | 5123.7(19) | 6465.2(7) | 54.8(5) |
| C00G | 7462(3) | 8445.0(19) | 6524.3(6) | 49.6(4) |
| C00H | 6090(3) | 6879.8(16) | 6004.2(5) | 42.3(4) |
| C00I | 5912(3) | 3583.8(18) | 6468.8(6) | 49.7(4) |
| C00J | 3869(3) | 7638(2) | 6606.0(6) | 57.1(5) |
| C00K | 7101(4) | 2819(2) | 6729.9(6) | 54.9(5) |
| C00L | 7228(4) | 9174(2) | 6870.4(6) | 55.6(5) |
| C00M | 9967(3) | 4346(2) | 6725.0(7) | 55.1(5) |
| C00N | 3785(4) | 11103(2) | 4660.8(6) | 56.8(5) |
| C00O | 9149(4) | 3180.7(19) | 6865.6(6) | 51.8(4) |
| C00P | 3642(4) | 8374(2) | 6949.7(6) | 62.3(5) |
| C00Q | 5030(5) | 9981(3) | 7459.7(7) | 70.4(6) |
| C00R | 10478(5) | 2341(2) | 7143.6(8) | 71.6(6) |
| C008 | 5782(3) | 7669.4(16) | 6384.3(5) | 41.8(4) |
| C009 | 4204(3) | 9241.1(15) | 5157.0(5) | 38.4(3) |
| O007 | 10086(3) | 10813.9(17) | 5667.2(6) | 78.7(5) |

| | | | | |
|---|---|---|---|---|
| D007 | 11240(40) | 10980(30) | 5529(9) | 99(11) |
| C00S | 10553(9) | 11108(4) | 6060.9(10) | 132.0(18) |
| D00A | 11139.64 | 11970.75 | 6076.89 | 198 |
| D00B | 11605.91 | 10499.98 | 6162.49 | 198 |
| D00C | 9237.98 | 11056.59 | 6217.01 | 198 |

**Table S31.** Anisotropic Displacement Parameters ($Å2\times10^3$) for Compound **40-s**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{23}$** | **$U_{13}$** | **$U_{12}$** |
|---|---|---|---|---|---|---|
| O001 | 60.0(8) | 35.7(6) | 53.4(7) | -5.9(5) | 7.2(6) | -7.1(5) |
| O002 | 38.1(6) | 61.6(8) | 59.5(7) | 1.3(6) | -11.4(5) | -7.8(6) |
| O003 | 57.4(8) | 54.3(7) | 50.9(7) | -19.1(6) | 12.4(6) | -10.0(6) |
| O004 | 35.9(6) | 35.9(6) | 94.0(10) | -4.5(6) | -6.0(6) | -1.7(5) |
| O005 | 64.3(9) | 49.8(7) | 58.8(8) | -2.0(6) | -7.5(6) | 9.7(7) |
| N006 | 40.8(7) | 35.3(7) | 62.2(9) | 1.7(6) | -10.6(7) | -3.5(6) |
| C00A | 36.2(8) | 33.9(7) | 50.5(8) | -5.9(6) | -4.2(6) | 2.4(6) |
| C00B | 40.9(8) | 35.0(8) | 48.8(8) | -2.2(7) | -2.7(7) | 0.3(7) |
| C00C | 46.1(9) | 40.9(8) | 45.3(8) | -1.3(7) | 8.7(7) | -2.4(7) |
| C00D | 39.5(8) | 37.3(8) | 50.4(8) | -3.3(7) | -7.6(7) | -1.6(6) |
| C00E | 64.5(12) | 47.7(9) | 44.5(8) | 6.0(7) | -7.6(8) | 4.4(9) |
| C00F | 47.2(10) | 42.3(9) | 74.9(12) | 7.7(9) | -14.5(9) | -5.9(8) |
| C00G | 43.1(9) | 45.9(9) | 59.9(10) | -5.2(8) | -1.0(8) | -7.0(8) |
| C00H | 38.6(8) | 34.7(8) | 53.7(9) | -0.3(6) | -6.6(7) | -2.1(6) |
| C00I | 44.6(9) | 41.9(9) | 62.5(10) | 0.8(8) | -3.2(8) | -4.1(8) |
| C00J | 45.0(10) | 66.4(12) | 59.9(11) | -3.4(9) | -3.1(8) | -13.9(9) |
| C00K | 56.0(11) | 42.7(9) | 66.1(11) | 8.9(8) | -1.1(9) | -3.6(8) |
| C00L | 57.4(11) | 47.4(10) | 62.1(11) | -5.9(9) | -9.8(9) | -8.5(9) |
| C00M | 47.2(10) | 50.5(10) | 67.7(11) | 1.0(9) | -14.5(9) | 0.4(9) |
| C00N | 68.0(13) | 53.0(10) | 49.4(10) | 8.5(8) | 7.2(9) | -1.3(9) |
| C00O | 55.5(11) | 46.7(9) | 53.4(10) | -1.2(8) | -4.3(8) | 8.6(8) |
| C00P | 53.3(11) | 78.0(14) | 55.6(11) | 1.1(10) | 5.5(9) | -3.9(11) |
| C00Q | 94.2(17) | 68.6(13) | 48.2(10) | -0.6(10) | -3.8(10) | 6.1(13) |
| C00R | 77.9(16) | 62.0(13) | 75.0(14) | 12.0(11) | -21.8(12) | 7.1(12) |
| C008 | 38.9(8) | 36.8(8) | 49.7(8) | 3.6(7) | -8.1(7) | -1.4(7) |
| C009 | 38.3(8) | 37.2(7) | 39.7(7) | -6.7(6) | 3.6(6) | 1.2(6) |
| O007 | 68.8(10) | 60.5(9) | 106.7(14) | -21.7(9) | 30.0(10) | -16.6(8) |
| C00S | 189(5) | 120(3) | 87(2) | -26(2) | 47(3) | -80(3) |

**Table S32.** Bond Lengths for compound **40-s**.

| **Atom** | **Atom** | **Length/Å** | **Atom** | **Atom** | **Length/Å** |
|---|---|---|---|---|---|
| O001 | D001 | 0.8200 | C00D | C00H | 1.534(2) |

| | | | | | |
|---|---|---|---|---|---|
| O001 | C00C | 1.426(2) | C00E | C00L | 1.385(3) |
| O002 | D002 | 0.8200 | C00E | C00P | 1.380(3) |
| O002 | C00D | 1.422(2) | C00E | C00Q | 1.509(3) |
| O003 | D003 | 0.8200 | C00F | C00M | 1.379(3) |
| O003 | C009 | 1.4257(19) | C00G | C00L | 1.387(3) |
| O004 | D004 | 0.8200 | C00G | C008 | 1.383(2) |
| O004 | C00A | 1.426(2) | C00H | C008 | 1.521(2) |
| O005 | D005 | 0.8200 | C00I | C00K | 1.382(3) |
| O005 | C00N | 1.421(3) | C00J | C00P | 1.384(3) |
| N006 | D006 | 0.898(12) | C00J | C008 | 1.385(3) |
| N006 | C00B | 1.411(2) | C00K | C00O | 1.383(3) |
| N006 | C00H | 1.473(2) | C00M | C00O | 1.382(3) |
| C00A | C00D | 1.535(2) | C00O | C00R | 1.507(3) |
| C00A | C009 | 1.530(2) | O007 | D007 | 0.862(13) |
| C00B | C00F | 1.388(3) | O007 | C00S | 1.381(4) |
| C00B | C00I | 1.388(3) | C00S | D00A | 0.9600 |
| C00C | C00N | 1.516(3) | C00S | D00B | 0.9600 |
| C00C | C009 | 1.530(2) | C00S | D00C | 0.9600 |

**Table S33.** Bond Angles for Compound **40-s**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C00C | O001 | D001 | 109.5 | N006 | C00H | C008 | 113.77(15) |
| C00D | O002 | D002 | 109.5 | C008 | C00H | C00D | 113.69(14) |
| C009 | O003 | D003 | 109.5 | C00K | C00I | C00B | 120.69(18) |
| C00A | O004 | D004 | 109.5 | C00P | C00J | C008 | 121.08(19) |
| C00N | O005 | D005 | 109.5 | C00I | C00K | C00O | 121.98(19) |
| C00B | N006 | D006 | 113.5(14) | C00E | C00L | C00G | 121.54(19) |
| C00B | N006 | C00H | 118.47(14) | C00F | C00M | C00O | 122.18(19) |
| C00H | N006 | D006 | 108.9(15) | O005 | C00N | C00C | 112.54(16) |
| O004 | C00A | C00D | 106.85(13) | C00K | C00O | C00R | 122.4(2) |
| O004 | C00A | C009 | 109.18(15) | C00M | C00O | C00K | 116.73(18) |
| C009 | C00A | C00D | 111.99(13) | C00M | C00O | C00R | 120.9(2) |
| C00F | C00B | N006 | 122.33(16) | C00E | C00P | C00J | 121.9(2) |
| C00F | C00B | C00I | 117.71(17) | C00G | C008 | C00H | 119.99(17) |
| C00I | C00B | N006 | 119.84(16) | C00G | C008 | C00J | 117.36(17) |
| O001 | C00C | C00N | 110.67(16) | C00J | C008 | C00H | 122.64(16) |
| O001 | C00C | C009 | 106.46(13) | O003 | C009 | C00A | 110.42(14) |
| C00N | C00C | C009 | 113.60(16) | O003 | C009 | C00C | 106.63(13) |
| O002 | C00D | C00A | 111.31(14) | C00C | C009 | C00A | 111.84(14) |
| O002 | C00D | C00H | 108.17(15) | C00S | O007 | D007 | 107(2) |
| C00H | C00D | C00A | 112.05(13) | O007 | C00S | D00A | 109.5 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C00L | C00E | C00Q | 121.5(2) | O007 | C00S | D00B | 109.5 |
| C00P | C00E | C00L | 116.89(19) | O007 | C00S | D00C | 109.5 |
| C00P | C00E | C00Q | 121.6(2) | D00A | C00S | D00B | 109.5 |
| C00M | C00F | C00B | 120.71(18) | D00A | C00S | D00C | 109.5 |
| C008 | C00G | C00L | 121.22(19) | D00B | C00S | D00C | 109.5 |
| N006 | C00H | C00D | 107.13(14) | | | | |

**Table S34.** Torsion Angles for Compound **40-s**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| O001 | C00C | C00N | O005 | -61.1(2) | C00F | C00B | C00I | C00K | 0.7(3) |
| O001 | C00C | C009 | O003 | 177.04(14) | C00F | C00M | C00O | C00K | 0.6(3) |
| O001 | C00C | C009 | C00A | -62.16(18) | C00F | C00M | C00O | C00R | 178.9(2) |
| O002 | C00D | C00H | N006 | 66.12(18) | C00H | N006 | C00B | C00F | -22.8(3) |
| O002 | C00D | C00H | C008 | -60.45(19) | C00H | N006 | C00B | C00I | 161.48(17) |
| O004 | C00A | C00D | O002 | 178.71(14) | C00I | C00B | C00F | C00M | -0.6(3) |
| O004 | C00A | C00D | C00H | 57.43(19) | C00I | C00K | C00O | C00M | -0.5(3) |
| O004 | C00A | C009 | O003 | 55.36(17) | C00I | C00K | C00O | C00R | -178.7(2) |
| O004 | C00A | C009 | C00C | -63.21(17) | C00L | C00E | C00P | C00J | -1.0(3) |
| N006 | C00B | C00F | C00M | -176.4(2) | C00L | C00G | C008 | C00H | -179.90(17) |
| N006 | C00B | C00I | C00K | 176.65(18) | C00L | C00G | C008 | C00J | -0.8(3) |
| N006 | C00H | C008 | C00G | 127.91(18) | C00N | C00C | C009 | O003 | 55.0(2) |
| N006 | C00H | C008 | C00J | -51.2(2) | C00N | C00C | C009 | C00A | 175.79(15) |
| C00A | C00D | C00H | N006 | -170.82(14) | C00P | C00E | C00L | C00G | 1.4(3) |
| C00A | C00D | C00H | C008 | 62.62(19) | C00P | C00J | C008 | C00G | 1.2(3) |
| C00B | N006 | C00H | C00D | 173.43(16) | C00P | C00J | C008 | C00H | -179.69(19) |
| C00B | N006 | C00H | C008 | -60.0(2) | C00Q | C00E | C00L | C00G | -178.7(2) |
| C00B | C00F | C00M | C00O | -0.1(4) | C00Q | C00E | C00P | C00J | 179.1(2) |
| C00B | C00I | C00K | C00O | -0.2(3) | C008 | C00G | C00L | C00E | -0.5(3) |
| C00D | C00A | C009 | O003 | -62.77(18) | C008 | C00J | C00P | C00E | -0.4(4) |
| C00D | C00A | C009 | C00C | 178.66(13) | C009 | C00A | C00D | O002 | -61.78(18) |
| C00D | C00H | C008 | C00G | -109.10(19) | C009 | C00A | C00D | C00H | 176.94(14) |
| C00D | C00H | C008 | C00J | 71.8(2) | C009 | C00C | C00N | O005 | 58.6(2) |

**Table S35.** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å2×$10^3$) for Compound **40-s**.

| **Atom** | ***X*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H00A | 5191.24 | 9362.16 | 5749.72 | 48 |
| H00C | 6444.67 | 10662.48 | 5009.4 | 53 |
| H00D | 5006.39 | 6806.55 | 5419.9 | 51 |

| | | | | |
|---|---|---|---|---|
| H00F | 9411.48 | 5901.49 | 6377.44 | 66 |
| H00G | 8773.68 | 8478.35 | 6383.78 | 60 |
| H00H | 7639.17 | 6936.22 | 5930.85 | 51 |
| H00I | 4541.24 | 3308.78 | 6383.15 | 60 |
| H00J | 2718.78 | 7112.51 | 6522.57 | 69 |
| H00K | 6505.51 | 2037.27 | 6816.83 | 66 |
| H00L | 8391.29 | 9680.76 | 6958.23 | 67 |
| H00M | 11346.35 | 4613.58 | 6808.45 | 66 |
| H00B | 4264.32 | 11984.15 | 4607.48 | 68 |
| H00E | 4261.81 | 10562.48 | 4439.82 | 68 |
| H00P | 2334.25 | 8335.92 | 7091.27 | 75 |
| H00N | 6435.7 | 10128.18 | 7579.4 | 106 |
| H00O | 4103.12 | 9534.44 | 7646.3 | 106 |
| H00Q | 4379.72 | 10798.1 | 7389.89 | 106 |
| H00R | 9519.16 | 1906.9 | 7327.54 | 107 |
| H00S | 11489.9 | 2872.96 | 7289.61 | 107 |
| H00T | 11270.63 | 1707.62 | 6990.7 | 107 |
| H009 | 2628.85 | 9210.21 | 5210.3 | 46 |

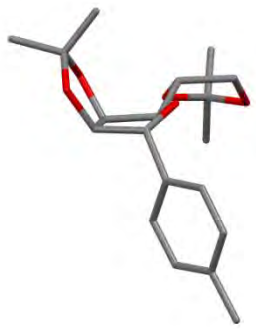


**Figure S17.** X-ray structure of **compound 40'α**

Single crystals for X-ray studies were grown by slow evaporation of a solution of **compound 40'α** in hexane in 4 mL tube at room temperature. The X-ray data of is deposited in the Cambridge Crystallographic Data Centre with a number of CCDC 2297359 (DOI: 10.5517/ccdc.csd.cc2h3lcl).

**Table S36.** Crystal data and structure refinement for compound **40'α**.

| | |
|---|---|
| Identification code | Compound **40'α** |
| Empirical formula | $C_{19}H_{26}O_5$ |
| Formula weight | 334.40 |
| Temperature/K | 294.15 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 5.85420(10) |

| | |
|---|---|
| b/Å | 10.33480(10) |
| c/Å | 29.2959(2) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 1772.46(4) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.253 |
| μ/mm$^{-1}$ | 0.732 |
| F(000) | 720.0 |
| Crystal size/mm$^3$ | 0.34 × 0.22 × 0.18 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 9.074 to 157.912 |
| Index ranges | -3 ≤ h ≤ 6, -12 ≤ k ≤ 12, -37 ≤ l ≤ 37 |
| Reflections collected | 16661 |
| Independent reflections | 3673 [$R_{int}$ = 0.0208, $R_{sigma}$ = 0.0156] |
| Data/restraints/parameters | 3673/0/223 |
| Goodness-of-fit on F$^2$ | 1.052 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0376, $wR_2$ = 0.1072 |
| Final R indexes [all data] | $R_1$ = 0.0383, $wR_2$ = 0.1080 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.28/-0.16 |
| Flack parameter | -0.04(4) |

**Table S37.** Fractional Atomic Coordinates (x10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for Compound **40'α**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *X* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| O001 | 3150(2) | 7462.2(13) | 6089.7(5) | 49.4(3) |
| O002 | 5183(3) | 10133.3(13) | 5813.2(5) | 56.6(4) |
| O003 | 2772(3) | 8621.1(18) | 7398.6(5) | 67.6(5) |
| O004 | 5148(4) | 8750.6(16) | 5209.1(5) | 70.2(5) |
| O005 | 4702(4) | 9903.6(18) | 6918.3(6) | 80.5(6) |
| C006 | 4545(3) | 6908.3(19) | 5730.6(6) | 47.0(4) |
| C007 | 5821(3) | 5738.7(18) | 5907.0(6) | 44.2(4) |
| C008 | 4614(4) | 8298.1(18) | 6343.1(6) | 45.1(4) |
| C009 | 4240(4) | 9955(2) | 5367.9(6) | 51.7(5) |
| C00A | 4769(4) | 4533(2) | 5897.0(7) | 52.5(5) |
| C00B | 3964(5) | 9817(2) | 7379.2(7) | 57.1(5) |
| C00C | 6076(4) | 8027(2) | 5570.9(6) | 51.1(5) |
| C00D | 6111(4) | 8964.6(19) | 5981.7(6) | 47.4(4) |
| C00E | 7989(4) | 5813(2) | 6101.9(7) | 52.7(5) |

| | | | | |
|---|---|---|---|---|
| C00F | 7931(5) | 3530(2) | 6281.8(7) | 59.4(6) |
| C00G | 9012(4) | 4724(2) | 6288.9(8) | 58.3(5) |
| C00H | 3186(4) | 9174(2) | 6638.2(7) | 56.5(5) |
| C00I | 5809(5) | 3455(2) | 6078.4(8) | 60.1(6) |
| C00J | 1680(5) | 8443(3) | 6978.4(8) | 66.3(7) |
| C00K | 5138(6) | 11002(3) | 5062.9(8) | 68.8(7) |
| C00L | 9041(7) | 2357(3) | 6495.4(11) | 90.6(10) |
| C00M | 2419(7) | 10936(3) | 7494.9(10) | 85.6(9) |
| C00N | 1701(5) | 9906(4) | 5389.0(10) | 89.5(10) |
| C00O | 5995(6) | 9761(4) | 7691.0(12) | 90.2(9) |

**Table S38.** Anisotropic Displacement Parameters ($Å2\times10^3$) for Compound **40'α**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{23}$** | **$U_{13}$** | **$U_{12}$** |
|---|---|---|---|---|---|---|
| O001 | 49.1(7) | 49.1(7) | 49.9(7) | -7.8(6) | 4.0(6) | -5.3(6) |
| O002 | 87.5(11) | 43.7(7) | 38.6(7) | 0.1(5) | -5.7(7) | -3.5(7) |
| O003 | 82.0(12) | 67.9(10) | 52.9(8) | 7.1(7) | 11.7(8) | -10.2(9) |
| O004 | 117.9(15) | 56.1(8) | 36.6(6) | -1.9(6) | -3.1(8) | 8.6(10) |
| O005 | 108.7(15) | 83.5(11) | 49.2(8) | -22.9(8) | 31.6(9) | -44.7(12) |
| C006 | 52.2(11) | 48.3(9) | 40.5(8) | -7.4(7) | -2.5(8) | -0.6(8) |
| C007 | 49.2(10) | 46.3(9) | 37.0(8) | -5.0(7) | 0.6(7) | -2.1(8) |
| C008 | 52.6(11) | 45.6(9) | 37.2(8) | -0.1(7) | 0.1(7) | -5.1(8) |
| C009 | 63.3(12) | 55.3(11) | 36.3(8) | 0.7(8) | 2.8(8) | -1.3(9) |
| C00A | 55.9(11) | 52.9(11) | 48.6(10) | -6.0(8) | -3.3(9) | -8.4(9) |
| C00B | 71.4(14) | 58.7(11) | 41.3(9) | -4.4(8) | 11.1(10) | -3.8(10) |
| C00C | 64.6(12) | 49.5(10) | 39.3(8) | -0.3(7) | 3.9(8) | -0.6(9) |
| C00D | 54.4(11) | 51.3(10) | 36.6(8) | 0.6(7) | 1.4(8) | -6.3(8) |
| C00E | 51.4(11) | 51.7(11) | 55.0(11) | -4.7(9) | -1.3(9) | -4.5(9) |
| C00F | 74.7(15) | 55.6(12) | 48.0(10) | 0.1(9) | 5.1(10) | 12.4(11) |
| C00G | 52.2(11) | 68.5(13) | 54.3(11) | -5.1(10) | -4.4(10) | 7.5(10) |
| C00H | 72.5(14) | 51.9(11) | 45.2(10) | -5.7(8) | 12.3(10) | -7.0(10) |
| C00I | 76.8(16) | 45.8(10) | 57.6(11) | -2.0(9) | 2.7(11) | -6.8(10) |
| C00J | 70.9(16) | 74.5(16) | 53.6(12) | -8.5(10) | 18.6(11) | -17.4(12) |
| C00K | 89.8(18) | 69.2(14) | 47.3(10) | 10.3(10) | 9.8(11) | 2.1(14) |
| C00L | 113(3) | 74.1(17) | 85.0(19) | 14.3(15) | -2.1(19) | 27.5(17) |
| C00M | 112(2) | 75.1(17) | 69.1(15) | -11.1(14) | 3.3(16) | 24.6(17) |
| C00N | 62.4(16) | 144(3) | 62.6(15) | -4.9(18) | 0.1(12) | -7.6(18) |
| C00O | 80.7(19) | 100(2) | 90(2) | -12.8(17) | -12.7(18) | 4.2(17) |

**Table S39.** Bond Lengths for compound **40'α**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| O001 | C006 | 1.450(2) | C008 | C00D | 1.537(3) |
| O001 | C008 | 1.425(2) | C008 | C00H | 1.505(3) |
| O002 | C009 | 1.428(2) | C009 | C00K | 1.499(3) |
| O002 | C00D | 1.413(2) | C009 | C00N | 1.489(4) |
| O003 | C00B | 1.421(3) | C00A | C00I | 1.376(3) |
| O003 | C00J | 1.399(3) | C00B | C00M | 1.507(4) |
| O004 | C009 | 1.431(3) | C00B | C00O | 1.500(4) |
| O004 | C00C | 1.406(3) | C00C | C00D | 1.545(3) |
| O005 | C00B | 1.420(2) | C00E | C00G | 1.387(3) |
| O005 | C00H | 1.424(3) | C00F | C00G | 1.387(4) |
| C006 | C007 | 1.512(3) | C00F | C00I | 1.380(4) |
| C006 | C00C | 1.536(3) | C00F | C00L | 1.511(3) |
| C007 | C00A | 1.390(3) | C00H | C00J | 1.530(3) |
| C007 | C00E | 1.394(3) | | | |

**Table S40.** Bond Angles for compound **40'α**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C008 | O001 | C006 | 106.17(14) | O003 | C00B | C00O | 109.3(2) |
| C00D | O002 | C009 | 110.93(15) | O005 | C00B | O003 | 104.02(17) |
| C00J | O003 | C00B | 107.66(18) | O005 | C00B | C00M | 110.4(2) |
| C00C | O004 | C009 | 111.15(14) | O005 | C00B | C00O | 109.9(2) |
| C00B | O005 | C00H | 108.97(18) | C00O | C00B | C00M | 111.6(2) |
| O001 | C006 | C007 | 110.24(15) | O004 | C00C | C006 | 113.8(2) |
| O001 | C006 | C00C | 104.62(15) | O004 | C00C | C00D | 105.00(16) |
| C007 | C006 | C00C | 114.68(18) | C006 | C00C | C00D | 104.04(15) |
| C00A | C007 | C006 | 119.36(18) | O002 | C00D | C008 | 113.85(18) |
| C00A | C007 | C00E | 117.46(19) | O002 | C00D | C00C | 105.00(15) |
| C00E | C007 | C006 | 123.10(18) | C008 | C00D | C00C | 104.36(16) |
| O001 | C008 | C00D | 104.81(14) | C00G | C00E | C007 | 120.7(2) |
| O001 | C008 | C00H | 109.27(17) | C00G | C00F | C00L | 120.8(3) |
| C00H | C008 | C00D | 116.26(17) | C00I | C00F | C00G | 117.8(2) |
| O002 | C009 | O004 | 105.39(17) | C00I | C00F | C00L | 121.4(3) |
| O002 | C009 | C00K | 108.41(19) | C00E | C00G | C00F | 121.3(2) |
| O002 | C009 | C00N | 110.6(2) | O005 | C00H | C008 | 107.7(2) |
| O004 | C009 | C00K | 107.68(18) | O005 | C00H | C00J | 104.17(17) |
| O004 | C009 | C00N | 110.8(2) | C008 | C00H | C00J | 113.38(19) |
| C00N | C009 | C00K | 113.6(3) | C00A | C00I | C00F | 121.3(2) |
| C00I | C00A | C007 | 121.4(2) | O003 | C00J | C00H | 104.2(2) |
| O003 | C00B | C00M | 111.3(2) | | | | |

**Table S41.** Torsion Angles for Compound **40'α**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| P001 | O003 | C00M | C00F | 33.6(3) | C00G | C00J | C00L | C00M | -158.6(2) |
| O001 | C006 | C007 | C00A | 86.5(2) | C00A | C007 | C00E | C00G | -1.7(3) |
| O001 | C006 | C007 | C00E | -90.4(2) | C00B | O003 | C00J | C00H | 28.3(3) |
| O001 | C006 | C00C | O004 | -91.12(19) | C00B | O005 | C00H | C008 | -129.9(2) |
| O001 | C006 | C00C | C00D | 22.6(2) | C00B | O005 | C00H | C00J | -9.2(3) |
| O001 | C008 | C00D | O002 | 90.11(19) | C00C | O004 | C009 | O002 | 15.9(3) |
| O001 | C008 | C00D | C00C | -23.8(2) | C00C | O004 | C009 | C00K | 131.4(2) |
| O001 | C008 | C00H | O005 | 174.37(16) | C00C | O004 | C009 | C00N | -103.8(2) |
| O001 | C008 | C00H | C00J | 59.7(2) | C00C | C006 | C007 | C00A | -155.76(17) |
| O004 | C00C | C00D | O002 | 0.3(2) | C00C | C006 | C007 | C00E | 27.4(2) |
| O004 | C00C | C00D | C008 | 120.35(19) | C00D | O002 | C009 | O004 | -15.6(2) |
| O005 | C00H | C00J | O003 | -11.5(3) | C00D | O002 | C009 | C00K | -130.7(2) |
| C006 | O001 | C008 | C00D | 39.62(19) | C00D | O002 | C009 | C00N | 104.2(3) |
| C006 | O001 | C008 | C00H | 164.87(15) | C00D | C008 | C00H | O005 | -67.3(2) |
| C006 | C007 | C00A | C00I | -176.10(19) | C00D | C008 | C00H | C00J | 178.00(19) |
| C006 | C007 | C00E | C00G | 175.19(19) | C00E | C007 | C00A | C00I | 1.0(3) |
| C006 | C00C | C00D | O002 | -119.59(18) | C00G | C00F | C00I | C00A | -1.4(3) |
| C006 | C00C | C00D | C008 | 0.5(2) | C00H | O005 | C00B | O003 | 26.4(3) |
| C007 | C006 | C00C | O004 | 147.99(16) | C00H | O005 | C00B | C00M | -93.1(3) |
| C007 | C006 | C00C | C00D | -98.30(19) | C00H | O005 | C00B | C00O | 143.3(2) |
| C007 | C00A | C00I | C00F | 0.6(3) | C00H | C008 | C00D | O002 | -30.6(2) |
| C007 | C00E | C00G | C00F | 1.0(3) | C00H | C008 | C00D | C00C | -144.53(19) |
| C008 | O001 | C006 | C007 | 84.47(18) | C00I | C00F | C00G | C00E | 0.6(3) |
| C008 | O001 | C006 | C00C | -39.32(19) | C00J | O003 | C00B | O005 | -34.4(3) |
| C008 | C00H | C00J | O003 | 105.2(2) | C00J | O003 | C00B | C00M | 84.4(2) |
| C009 | O002 | C00D | C008 | -103.98(19) | C00J | O003 | C00B | C00O | -151.8(2) |
| C009 | O002 | C00D | C00C | 9.6(2) | C00L | C00F | C00G | C00E | -178.7(2) |
| C009 | O004 | C00C | C006 | 103.1(2) | C00L | C00F | C00I | C00A | 177.9(2) |
| C009 | O004 | C00C | C00D | -10.0(3) | | | | | |

**Table S42.** Hydrogen Atom Coordinates (Å×$10^4$) and
Isotropic Displacement Parameters (Å2×$10^3$) for Compound **40'α**.

| **Atom** | ***X*** | ***y*** | ***Z*** | **U(eq)** |
|---|---|---|---|---|
| H006 | 3554.96 | 6642.18 | 5477.7 | 56 |
| H008 | 5593.93 | 7770.27 | 6540.23 | 54 |
| H00A | 3331.53 | 4453.6 | 5764.85 | 63 |
| H00C | 7617.52 | 7721.51 | 5497.39 | 61 |

| | | | | |
|---|---|---|---|---|
| H00D | 7670.32 | 9093.26 | 6094.42 | 57 |
| H00E | 8757.95 | 6599.88 | 6106.56 | 63 |
| H00G | 10449.39 | 4796.86 | 6421.48 | 70 |
| H00H | 2256.86 | 9752.25 | 6448.8 | 68 |
| H00I | 5066.48 | 2660.71 | 6063.64 | 72 |
| H00B | 147.61 | 8799.77 | 6984.31 | 80 |
| H00F | 1593.85 | 7532.16 | 6900.98 | 80 |
| H00J | 4654.84 | 11829.28 | 5176.33 | 103 |
| H00K | 4557.65 | 10879.91 | 4759.43 | 103 |
| H00L | 6776.34 | 10967.15 | 5057.48 | 103 |
| H00M | 10645.72 | 2359.1 | 6427.51 | 136 |
| H00N | 8357.29 | 1585.98 | 6374.17 | 136 |
| H00O | 8826.64 | 2381.04 | 6820.13 | 136 |
| H00P | 1139.21 | 10942.69 | 7290 | 128 |
| H00Q | 3250.38 | 11732.24 | 7465.48 | 128 |
| H00R | 1882.75 | 10845.83 | 7802.94 | 128 |
| H00S | 1235.98 | 9206.68 | 5583.78 | 134 |
| H00T | 1098.92 | 9771.28 | 5087.86 | 134 |
| H00U | 1129.72 | 10707.43 | 5508.88 | 134 |
| H00V | 5488.24 | 9628.53 | 7999.14 | 135 |
| H00W | 6826.19 | 10559.65 | 7672.08 | 135 |
| H00X | 6969.02 | 9058.29 | 7601.24 | 135 |

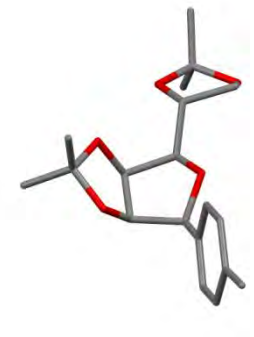


**Figure S18.** X-ray structure of **compound 40'β**

Single crystals for X-ray studies were grown by slow evaporation of a solution of **compound 40'β** in hexane in 4 mL tube at room temperature. The X-ray data of is deposited in the Cambridge Crystallographic Data Centre with a number of CCDC 2297392 (DOI: 10.5517/ccdc.csd.cc2h3mfp).

**Table S43.** Crystal data and structure refinement for compound **40'β**.

| | |
|---|---|
| Identification code | Compound **40'β** |
| Empirical formula | $C_{19}H_{26}O_5$ |
| Formula weight | 334.40 |
| Temperature/K | 294.15 |
| Crystal system | monoclinic |

| | |
|---|---|
| Space group | $P2_1$ |
| a/Å | 10.97750(10) |
| b/Å | 6.32230(10) |
| c/Å | 13.5853(2) |
| α/° | 90 |
| β/° | 98.8380(10) |
| γ/° | 90 |
| Volume/Å$^3$ | 931.67(2) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.192 |
| μ/mm$^{-1}$ | 0.697 |
| F(000) | 360.0 |
| Crystal size/mm$^3$ | 0.24 × 0.22 × 0.17 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 6.584 to 158.81 |
| Index ranges | -13 ≤ h ≤ 13, -7 ≤ k ≤ 7, -17 ≤ l ≤ 17 |
| Reflections collected | 17881 |
| Independent reflections | 3930 [$R_{int}$ = 0.0375, $R_{sigma}$ = 0.0284] |
| Data/restraints/parameters | 3930/1/223 |
| Goodness-of-fit on $F^2$ | 1.043 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0453, $wR_2$ = 0.1304 |
| Final R indexes [all data] | $R_1$ = 0.0473, $wR_2$ = 0.1337 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.21/-0.17 |
| Flack parameter | 0.08(10) |

**Table S44.** Fractional Atomic Coordinates (x10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for Compound **40'β**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{IJ}$ tensor.

| **Atom** | ***X*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| O001 | 5882.8(13) | 6088(3) | 3213.7(11) | 61.6(4) |
| O002 | 3744.2(14) | 3222(3) | 2255.2(13) | 76.5(5) |
| O003 | 5276.0(14) | 3545(3) | 1337.0(12) | 69.6(5) |
| O004 | 9311.6(17) | 6814(4) | 2751.2(16) | 90.6(7) |
| O005 | 8135.5(17) | 4780(4) | 1616.5(16) | 91.9(7) |
| C00A | 5873.8(19) | 2969(4) | 2293.8(15) | 61.1(5) |
| C00B | 4013(2) | 2980(4) | 1268.4(17) | 65.0(5) |
| C00C | 3395(2) | 5128(4) | 4682.5(16) | 60.2(5) |
| C00D | 2376(2) | 6241(4) | 4915.7(17) | 63.9(5) |
| C00E | 3574(2) | 7653(4) | 3410.6(16) | 61.6(5) |
| C00F | 6695.0(18) | 4755(4) | 2765.3(16) | 60.9(5) |
| C00G | 2579(2) | 8750(4) | 3659.6(18) | 65.3(5) |

| | | | | |
|---|---|---|---|---|
| C00H | 7315.6(19) | 6079(5) | 2058.8(18) | 69.9(6) |
| C00I | 3803(3) | 713(5) | 923(2) | 84.6(8) |
| C00J | 9375(2) | 5461(5) | 1942(2) | 77.6(7) |
| C00K | 8146(2) | 7794(6) | 2580(3) | 85.6(8) |
| C00L | 900(2) | 9319(5) | 4696(2) | 79.5(7) |
| C00M | 3256(3) | 4526(5) | 597(3) | 92.3(9) |
| C00N | 10175(4) | 3620(10) | 2303(4) | 126.1(15) |
| C00O | 9837(3) | 6624(9) | 1100(3) | 114.3(14) |
| C006 | 4005.2(17) | 5857(3) | 3926.4(13) | 52.2(4) |
| C007 | 1968.4(18) | 8069(4) | 4418.8(16) | 59.3(5) |
| C008 | 4833(2) | 2860(4) | 2933.3(16) | 62.6(5) |
| C009 | 5108.6(19) | 4685(4) | 3675.4(14) | 56.3(5) |

**Table S45.** Anisotropic Displacement Parameters ($Å2\times10^3$) for Compound **40'β**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{23}$** | **$U_{13}$** | **$U_{12}$** |
|---|---|---|---|---|---|---|
| O001 | 51.6(7) | 68.3(8) | 68.0(8) | -12.5(7) | 18.8(6) | -6.4(6) |
| O002 | 54.4(8) | 103.3(13) | 73.2(9) | -30.6(10) | 14.2(6) | -12.2(9) |
| O003 | 57.4(8) | 91.3(11) | 60.2(8) | -3.4(7) | 9.7(6) | -8.8(8) |
| O004 | 54.8(9) | 121.2(18) | 94.9(13) | -20.8(12) | 8.7(8) | -8.6(10) |
| O005 | 58.1(9) | 127.4(16) | 95.9(13) | -40.8(13) | 30.4(9) | -12.4(11) |
| C00A | 56.9(10) | 65.0(12) | 62.3(10) | -5.3(9) | 12.0(8) | 9.2(9) |
| C00B | 58.3(10) | 71.3(13) | 65.1(11) | -13.6(11) | 8.7(8) | -9.6(9) |
| C00C | 62.4(11) | 62.4(11) | 57.0(10) | 6.7(9) | 13.5(8) | -1.1(9) |
| C00D | 56.9(10) | 76.0(13) | 62.4(10) | 2.8(10) | 20.0(8) | -6.2(10) |
| C00E | 65.0(11) | 65.2(12) | 58.2(10) | 8.9(9) | 20.7(9) | -1.4(9) |
| C00F | 47.2(9) | 76.1(13) | 59.3(10) | -5.6(10) | 8.0(7) | 7.1(9) |
| C00G | 63.6(12) | 65.2(12) | 68.4(12) | 10.0(10) | 14.0(9) | 5.6(9) |
| C00H | 47.9(9) | 94.7(16) | 68.8(12) | -8.8(13) | 14.5(8) | -0.9(11) |
| C00I | 109(2) | 74.5(17) | 71.3(13) | -16.2(12) | 16.1(13) | -18.6(15) |
| C00J | 48.7(10) | 104(2) | 82.4(14) | -3.6(14) | 17.0(9) | 3.2(11) |
| C00K | 57.8(12) | 98(2) | 105.6(19) | -22.0(17) | 26.1(12) | -9.1(13) |
| C00L | 57.9(12) | 95.3(19) | 86.2(16) | -10.2(14) | 14.2(11) | 11.4(12) |
| C00M | 80.5(17) | 86.8(19) | 101(2) | -10.0(17) | -12.4(15) | 4.0(15) |
| C00N | 101(3) | 133(4) | 146(4) | 25(3) | 26(2) | 37(3) |
| C00O | 83(2) | 149(4) | 119(3) | 21(3) | 42.6(19) | 10(2) |
| C006 | 49.9(8) | 58.2(10) | 48.6(8) | -4.3(8) | 8.0(7) | -6.3(8) |
| C007 | 46.8(8) | 70.8(12) | 60.2(10) | -6.8(9) | 7.5(7) | -2.8(9) |
| C008 | 67.3(11) | 58.4(11) | 64.2(11) | -3.4(10) | 17.1(9) | -2.8(9) |
| C009 | 53.5(9) | 62.7(11) | 53.3(9) | -0.4(8) | 10.1(7) | -0.2(8) |

**Table S46.** Bond Lengths for compound **40'β**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| O001 | C00F | 1.429(3) | C00C | C00D | 1.399(3) |
| O001 | C009 | 1.438(3) | C00C | C006 | 1.388(3) |
| O002 | C00B | 1.424(3) | C00D | C007 | 1.378(4) |
| O002 | C008 | 1.411(3) | C00E | C00G | 1.379(3) |
| O003 | C00A | 1.411(3) | C00E | C006 | 1.379(3) |
| O003 | C00B | 1.420(3) | C00F | C00H | 1.512(4) |
| O004 | C00J | 1.403(4) | C00G | C007 | 1.382(3) |
| O004 | C00K | 1.408(4) | C00H | C00K | 1.520(4) |
| O005 | C00H | 1.419(3) | C00J | C00N | 1.495(5) |
| O005 | C00J | 1.430(3) | C00J | C00O | 1.512(5) |
| C00A | C00F | 1.524(3) | C00L | C007 | 1.510(3) |
| C00A | C008 | 1.540(3) | C006 | C009 | 1.503(3) |
| C00B | C00I | 1.515(4) | C008 | C009 | 1.531(3) |
| C00B | C00M | 1.498(4) | | | |

**Table S47.** Bond Angles for compound **40'β**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C00F | O001 | C009 | 105.75(17) | O005 | C00H | C00K | 103.67(18) |
| C008 | O002 | C00B | 108.65(17) | C00F | C00H | C00K | 113.3(2) |
| C00A | O003 | C00B | 107.86(18) | O004 | C00J | O005 | 105.46(19) |
| C00J | O004 | C00K | 107.0(2) | O004 | C00J | C00N | 108.3(3) |
| C00H | O005 | C00J | 109.3(2) | O004 | C00J | C00O | 111.1(3) |
| O003 | C00A | C00F | 110.9(2) | O005 | C00J | C00N | 110.5(3) |
| O003 | C00A | C008 | 104.53(17) | O005 | C00J | C00O | 109.0(3) |
| C00F | C00A | C008 | 103.79(16) | C00N | C00J | C00O | 112.2(3) |
| O002 | C00B | C00I | 110.5(2) | O004 | C00K | C00H | 103.1(3) |
| O002 | C00B | C00M | 109.0(2) | C00C | C006 | C009 | 120.08(19) |
| O003 | C00B | O002 | 104.63(16) | C00E | C006 | C00C | 118.83(19) |
| O003 | C00B | C00I | 111.0(2) | C00E | C006 | C009 | 121.09(18) |
| O003 | C00B | C00M | 108.7(2) | C00D | C007 | C00G | 118.0(2) |
| C00M | C00B | C00I | 112.6(2) | C00D | C007 | C00L | 121.6(2) |
| C006 | C00C | C00D | 119.6(2) | C00G | C007 | C00L | 120.5(2) |
| C007 | C00D | C00C | 121.5(2) | O002 | C008 | C00A | 104.59(16) |
| C00G | C00E | C006 | 120.83(19) | O002 | C008 | C009 | 111.69(18) |
| O001 | C00F | C00A | 104.41(16) | C009 | C008 | C00A | 104.42(17) |
| O001 | C00F | C00H | 108.4(2) | O001 | C009 | C006 | 110.23(18) |
| C00H | C00F | C00A | 116.02(18) | O001 | C009 | C008 | 104.36(16) |
| C00E | C00G | C007 | 121.3(2) | C006 | C009 | C008 | 115.85(17) |
| O005 | C00H | C00F | 109.0(2) | | | | |

**Table S48.** Torsion Angles for Compound **40'β**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| O001 | C00F | C00H | O005 | 179.35(16) | C00E | C006 | C009 | O001 | 25.0(2) |
| O001 | C00F | C00H | C00K | 64.5(2) | C00E | C006 | C009 | C008 | -93.2(2) |
| O002 | C008 | C009 | O001 | -91.4(2) | C00F | O001 | C009 | C006 | -164.59(15) |
| O002 | C008 | C009 | C006 | 30.0(3) | C00F | O001 | C009 | C008 | -39.6(2) |
| O003 | C00A | C00F | O001 | 84.9(2) | C00F | C00A | C008 | O002 | 120.79(19) |
| O003 | C00A | C00F | C00H | -34.3(3) | C00F | C00A | C008 | C009 | 3.3(2) |
| O003 | C00A | C008 | O002 | 4.4(2) | C00F | C00H | C00K | O004 | 93.1(3) |
| O003 | C00A | C008 | C009 | -113.0(2) | C00G | C00E | C006 | C00C | 2.1(3) |
| O005 | C00H | C00K | O004 | -24.9(3) | C00G | C00E | C006 | C009 | -178.4(2) |
| C00A | O003 | C00B | O002 | 31.8(3) | C00H | O005 | C00J | O004 | 13.8(3) |
| C00A | O003 | C00B | C00I | -87.3(2) | C00H | O005 | C00J | C00N | 130.6(3) |
| C00A | O003 | C00B | C00M | 148.2(2) | C00H | O005 | C00J | C00O | -105.6(3) |
| C00A | C00F | C00H | O005 | -63.6(2) | C00J | O004 | C00K | C00H | 34.4(3) |
| C00A | C00F | C00H | C00K | -178.5(2) | C00J | O005 | C00H | C00F | -114.0(2) |
| C00A | C008 | C009 | O001 | 21.1(2) | C00J | O005 | C00H | C00K | 6.9(3) |
| C00A | C008 | C009 | C006 | 142.48(19) | C00K | O004 | C00J | O005 | -30.7(3) |
| C00B | O002 | C008 | C00A | 15.0(3) | C00K | O004 | C00J | C00N | -149.0(3) |
| C00B | O002 | C008 | C009 | 127.3(2) | C00K | O004 | C00J | C00O | 87.3(3) |
| C00B | O003 | C00A | C00F | -133.56(19) | C006 | C00C | C00D | C007 | -0.8(3) |
| C00B | O003 | C00A | C008 | -22.3(2) | C006 | C00E | C00G | C007 | -1.2(4) |
| C00C | C00D | C007 | C00G | 1.7(3) | C008 | O002 | C00B | O003 | -28.9(3) |
| C00C | C00D | C007 | C00L | -177.6(2) | C008 | O002 | C00B | C00I | 90.7(2) |
| C00C | C006 | C009 | O001 | -155.54(17) | C008 | O002 | C00B | C00M | -145.0(2) |
| C00C | C006 | C009 | C008 | 86.3(2) | C008 | C00A | C00F | O001 | -26.9(2) |
| C00D | C00C | C006 | C00E | -1.1(3) | C008 | C00A | C00F | C00H | -146.1(2) |
| C00D | C00C | C006 | C009 | 179.5(2) | C009 | O001 | C00F | C00A | 42.0(2) |
| C00E | C00G | C007 | C00D | -0.6(4) | C009 | O001 | C00F | C00H | 166.23(15) |
| C00E | C00G | C007 | C00L | 178.6(2) | | | | | |

**Table S49.** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å2×$10^3$) for Compound **40'β**.

| **Atom** | ***X*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H00A | 6320.24 | 1627.29 | 2289.51 | 73 |
| H00C | 3663.04 | 3907.13 | 5032.06 | 72 |
| H00D | 1964.25 | 5735.68 | 5417.04 | 77 |

| | | | | |
|---|---|---|---|---|
| H00E | 3958.47 | 8129.61 | 2888.24 | 74 |
| H00F | 7323 | 4173.09 | 3285.45 | 73 |
| H00G | 2313.63 | 9972.63 | 3310.03 | 78 |
| H00H | 6697.07 | 6703.34 | 1543.66 | 84 |
| H00B | 4359.55 | -199.97 | 1340.33 | 127 |
| H00I | 3948.28 | 591.11 | 246.09 | 127 |
| H00J | 2968.9 | 312.37 | 963.1 | 127 |
| H00K | 8155.68 | 9031.66 | 2159.31 | 103 |
| H00L | 7882.39 | 8208.93 | 3201.83 | 103 |
| H00M | 183.22 | 9089.39 | 4205.82 | 119 |
| H00N | 1102.92 | 10797.1 | 4720.93 | 119 |
| H00O | 733.02 | 8866.56 | 5336.21 | 119 |
| H00P | 2396.31 | 4219.08 | 581.82 | 138 |
| H00Q | 3459.08 | 4414.15 | -62.96 | 138 |
| H00R | 3425.72 | 5935.49 | 843.74 | 138 |
| H00S | 10997.67 | 4108.3 | 2534.98 | 189 |
| H00T | 10189.47 | 2634.63 | 1767.68 | 189 |
| H00U | 9853.4 | 2936.35 | 2839.45 | 189 |
| H00V | 9380.9 | 7914.54 | 963.95 | 171 |
| H00W | 9726.57 | 5751.95 | 514.38 | 171 |
| H00X | 10695.95 | 6944.51 | 1286.27 | 171 |
| H008 | 4815.12 | 1492.84 | 3270.54 | 75 |
| H009 | 5582.1 | 4134.48 | 4292.61 | 68 |

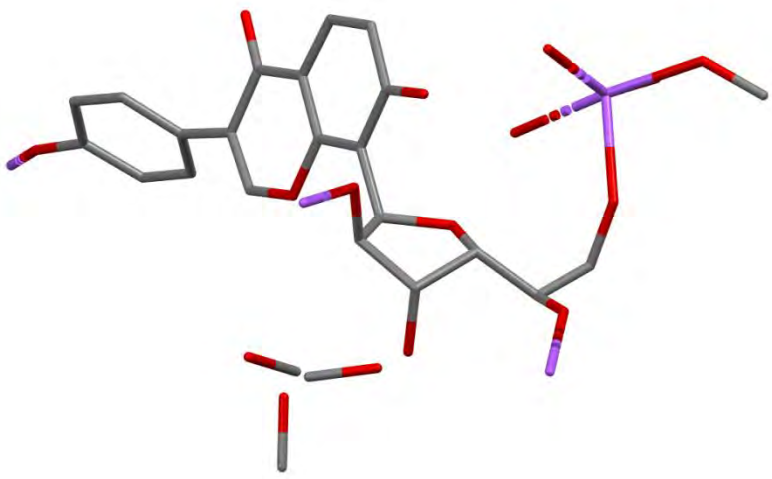


**Figure S19.** X-ray structure of **compound 49-Na**

Single crystals for X-ray studies were grown by slow evaporation of a solution of **compound 49-Na** in DCM/MeOH in 4 mL tube at room temperature. The X-ray data of is deposited in the Cambridge Crystallographic Data Centre with a number of CCDC 2337769 (DOI: 10.5517/ccdc.csd.cc2jgmxk).

**Table S50.** Crystal data and structure refinement for compound **49-Na**.

| | |
|---|---|
| Identification code | **49-Na** |
| Empirical formula | $C_{23.71}H_{29.83}NaO_{11.71}$ |
| Formula weight | 525.10 |
| Temperature/K | 113.15 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 7.8330(2) |
| b/Å | 9.9927(2) |
| c/Å | 32.0086(6) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2505.40(9) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.392 |
| μ/mm$^{-1}$ | 0.126 |
| F(000) | 1107.0 |
| Crystal size/mm$^3$ | 0.29 × 0.26 × 0.2 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.27 to 52.73 |
| Index ranges | -7 ≤ h ≤ 9, -10 ≤ k ≤ 12, -40 ≤ l ≤ 25 |
| Reflections collected | 12762 |
| Independent reflections | 5072 [$R_{int}$ = 0.0298, $R_{sigma}$ = 0.0372] |
| Data/restraints/parameters | 5072/76/380 |
| Goodness-of-fit on F$^2$ | 1.040 |
| Final R indexes [I>=2σ (I)] | $R_1$= 0.0379, w$R_2$ = 0.0888 |
| Final R indexes [all data] | $R_1$ = 0.0399, w$R_2$ = 0.0899 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.25/-0.19 |
| Flack parameter | 0.27(16) |

**Table S51.** Fractional Atomic Coordinates (x10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for Compound **49-Na**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{IJ}$ tensor.

| **Atom** | ***X*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| Na1 | 1875.0(12) | 4525.5(10) | 7274.5(3) | 15.3(2) |
| O002 | 5897(2) | 5764.6(16) | 6584.2(5) | 13.0(4) |
| O003 | 7344(2) | 3826.5(16) | 5606.7(5) | 14.5(4) |
| O004 | 6489(2) | 3221.2(17) | 7055.4(5) | 14.2(4) |
| O005 | 8563(2) | 7833.7(17) | 6535.2(5) | 19.8(4) |

| | | | | |
|---|---|---|---|---|
| O006 | 7964(2) | 562.7(19) | 3424.4(5) | 17.4(4) |
| O007 | 2973(2) | 6630.2(17) | 7277.5(5) | 16.4(4) |
| O008 | 6015(2) | 8390.3(19) | 7379.3(6) | 20.2(4) |
| O009 | 9320(2) | 4483.6(18) | 6952.1(5) | 17.5(4) |
| O00A | 5799(3) | 6.7(19) | 5351.5(6) | 26.7(5) |
| O00B | 488(3) | 4752(2) | 7904.0(6) | 31.6(5) |
| C00C | 6405(3) | 2773(2) | 6671.3(7) | 12.5(5) |
| C00D | 6841(3) | 3015(2) | 5931.4(7) | 12.3(5) |
| C00E | 6536(3) | 6528(2) | 6936.4(7) | 12.5(5) |
| C00F | 6875(3) | 3584(2) | 6329.3(7) | 12.3(5) |
| C00G | 8408(3) | 6764(2) | 6826.1(7) | 14.1(5) |
| C00H | 7411(3) | 3311(3) | 5217.8(7) | 15.7(5) |
| C00I | 7135(3) | 1616(2) | 4667.4(7) | 15.2(5) |
| C00J | 7312(3) | 5059(2) | 6380.5(7) | 12.6(5) |
| C00K | 5481(3) | 7799(2) | 6992.8(7) | 14.0(5) |
| C00L | 7683(3) | 876(3) | 3837.2(7) | 14.5(5) |
| C00M | 6666(4) | 1962(3) | 3929.4(8) | 20.0(6) |
| C00N | 6335(3) | 1691(3) | 5854.3(7) | 14.6(5) |
| C00O | 6391(4) | 2331(3) | 4342.1(8) | 18.9(6) |
| C00P | 6317(3) | 1152(3) | 5432.5(8) | 17.1(5) |
| C00Q | 6948(3) | 2059(2) | 5109.1(7) | 15.3(5) |
| C00R | 8106(3) | 491(3) | 4570.3(8) | 18.0(5) |
| C00S | 3565(4) | 7583(2) | 6978.9(7) | 14.9(5) |
| C00T | 5856(3) | 1434(3) | 6593.4(8) | 17.6(5) |
| C00U | 8374(3) | 117(3) | 4159.4(8) | 17.0(5) |
| C00V | 8902(3) | 5411(2) | 6634.3(7) | 14.2(5) |
| C00X | 5824(4) | 920(2) | 6199.1(8) | 18.5(6) |
| C00Z | -437(5) | 5857(3) | 8044.2(10) | 35.6(8) |
| O10 | 9805(4) | 6493(4) | 5338.9(10) | 39.7(10) |
| C010 | 8236(7) | 7053(5) | 5206.0(19) | 42.9(14) |
| O0AA | 11181(4) | 7695(3) | 6005.8(9) | 31.1(8) |
| C12 | 11689(12) | 8958(6) | 5871.3(17) | 81(3) |
| O11 | 7406(12) | 7702(7) | 5747(2) | 40(2) |
| C13 | 8600(30) | 7310(20) | 5439(6) | 84(5) |

**Table S52.** Anisotropic Displacement Parameters (Å2×$10^3$) for Compound **49-Na**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{23}$** | **$U_{13}$** | **$U_{12}$** |
|---|---|---|---|---|---|---|
| Na1 | 15.6(5) | 16.7(5) | 13.7(5) | -0.2(4) | -1.5(4) | 0.5(4) |
| O002 | 13.4(8) | 14.0(8) | 11.6(8) | -5.5(7) | 0.2(7) | 1.8(7) |
| O003 | 22.3(9) | 11.4(8) | 9.9(8) | -1.1(7) | 3.1(7) | -1.4(7) |
| O004 | 17.1(9) | 17.0(8) | 8.3(7) | -0.5(7) | 1.7(7) | -0.1(8) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O005 | 25.6(10) | 15.0(8) | 18.9(9) | -2.5(7) | 9.3(8) | -2.5(8) |
| O006 | 14.0(9) | 27.1(9) | 11.2(8) | -6.8(8) | 1.4(7) | 2.1(8) |
| O007 | 19.8(9) | 16.7(8) | 12.6(8) | -4.9(7) | 2.4(7) | -4.1(8) |
| O008 | 17.0(10) | 25.1(10) | 18.3(9) | -11.9(8) | 7.5(8) | -7.6(8) |
| O009 | 13.8(9) | 20.6(9) | 18.1(9) | 4.3(8) | -2.1(7) | -2.2(8) |
| O00A | 44.3(13) | 17.8(9) | 18.0(9) | -6.7(8) | 5.1(9) | -11.0(9) |
| O00B | 47.2(13) | 27.5(11) | 20.1(10) | 3.5(9) | 7.5(10) | 15.3(11) |
| C00C | 12.0(12) | 14.3(11) | 11.3(11) | -1.0(9) | -1.2(9) | 2.4(10) |
| C00D | 13.3(12) | 13.3(11) | 10.3(11) | 1.7(9) | 1.8(9) | 2.6(10) |
| C00E | 16.5(12) | 11.4(11) | 9.6(10) | -2.6(9) | -0.3(9) | -2.6(11) |
| C00F | 12.8(12) | 11.0(11) | 12.9(11) | -1.6(9) | 0.2(9) | 2.6(10) |
| C00G | 14.9(12) | 13.8(11) | 13.6(11) | -1.8(10) | 0.6(10) | -2.3(11) |
| C00H | 19.8(13) | 18.0(12) | 9.4(11) | -0.6(10) | 3.8(10) | 1.7(11) |
| C00I | 18.4(13) | 15.2(12) | 11.9(11) | -2.2(10) | 2.6(10) | -3.4(11) |
| C00J | 16.1(12) | 11.1(11) | 10.7(11) | 0.1(9) | 2.4(9) | 1.6(10) |
| C00K | 18.6(13) | 12.4(11) | 11.0(11) | -1.8(9) | 4.3(10) | 0.2(11) |
| C00L | 12.3(12) | 20.0(12) | 11.2(11) | -5.1(10) | 2.1(10) | -4.9(11) |
| C00M | 23.0(14) | 24.4(14) | 12.6(12) | 1.0(10) | -2.2(10) | 3.9(13) |
| C00N | 17.0(12) | 15.2(12) | 11.7(11) | -1.3(10) | 0.8(10) | 0.8(11) |
| C00O | 22.7(14) | 16.8(12) | 17.2(12) | -4.3(10) | 2.6(11) | 5.4(11) |
| C00P | 21.6(14) | 16.1(12) | 13.5(12) | -2.5(10) | 0.5(10) | -1.4(11) |
| C00Q | 16.6(13) | 17.3(12) | 11.9(11) | -1.8(10) | 0.0(10) | 2.4(11) |
| C00R | 22.0(13) | 17.9(12) | 14.0(12) | 1.3(10) | 0.0(10) | 1.0(12) |
| C00S | 18.6(13) | 12.9(11) | 13.3(11) | -2.4(9) | 0.0(10) | 3.3(10) |
| C00T | 23.4(14) | 16.1(12) | 13.2(11) | 4.9(10) | 1.7(10) | -2.4(11) |
| C00U | 18.8(13) | 15.3(12) | 17.0(12) | -2.7(10) | 3.0(10) | 1.7(11) |
| C00V | 14.4(12) | 15.1(12) | 13.0(11) | -0.7(10) | 1.7(9) | 0.1(10) |
| C00X | 26.1(14) | 10.9(11) | 18.6(13) | 0.1(10) | 0.9(11) | -4.3(12) |
| C00Z | 49(2) | 24.2(15) | 33.3(16) | 1.8(13) | 12.6(15) | 8.0(15) |
| O10 | 33.6(18) | 48(2) | 38.0(19) | -26.3(16) | -4.2(14) | 12.9(16) |
| C010 | 52(3) | 23(2) | 53(3) | -5(2) | -13(3) | 9(2) |
| O0AA | 34.6(18) | 35.9(17) | 22.8(15) | -8.3(13) | 7.5(13) | -4.6(14) |
| C12 | 140(7) | 67(4) | 37(3) | -13(3) | 28(4) | -69(5) |
| O11 | 72(6) | 24(4) | 25(4) | 10(3) | -1(4) | 9(4) |
| C13 | 105(11) | 79(10) | 68(9) | 12(9) | 4(9) | 1(10) |

**Table S53.** Bond Lengths for compound **49-Na**.

| **Atom** | **Atom** | **Length/Å** | **Atom** | **Atom** | **Length/Å** |
|---|---|---|---|---|---|
| Na1 | O006[1] | 2.396(2) | C00E | C00G | 1.527(4) |
| Na1 | O007 | 2.272(2) | C00E | C00K | 1.526(3) |
| Na1 | O008[2] | 2.291(2) | C00F | C00J | 1.522(3) |
| Na1 | O009[3] | 2.252(2) | C00G | C00V | 1.535(3) |
| Na1 | O00B | 2.300(2) | C00H | C00Q | 1.348(4) |

| | | | | | |
|---|---|---|---|---|---|
| O002 | C00E | 1.450(3) | C00I | C00O | 1.391(4) |
| O002 | C00J | 1.467(3) | C00I | C00Q | 1.489(3) |
| O003 | C00D | 1.376(3) | C00I | C00R | 1.392(4) |
| O003 | C00H | 1.348(3) | C00J | C00V | 1.528(3) |
| O004 | C00C | 1.310(3) | C00K | C00S | 1.517(4) |
| O005 | C00G | 1.423(3) | C00L | C00M | 1.378(4) |
| O006 | C00L | 1.376(3) | C00L | C00U | 1.390(4) |
| O007 | C00S | 1.426(3) | C00M | C00O | 1.388(3) |
| O008 | C00K | 1.433(3) | C00N | C00P | 1.454(3) |
| O009 | C00V | 1.414(3) | C00N | C00X | 1.405(3) |
| O00A | C00P | 1.242(3) | C00P | C00Q | 1.462(3) |
| O00B | C00Z | 1.395(4) | C00R | C00U | 1.383(3) |
| C00C | C00F | 1.411(3) | C00T | C00X | 1.363(3) |
| C00C | C00T | 1.428(4) | O10 | C010 | 1.416(6) |
| C00D | C00F | 1.395(3) | O0AA | C12 | 1.391(6) |
| C00D | C00N | 1.403(3) | O11 | C13 | 1.416(12) |

[1]-1/2+X,1/2-Y,1-Z; [2]1-X,-1/2+Y,3/2-Z; [3]-1+X,+Y,+Z

**Table S54.** Bond Angles for compound **49-Na**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| O007 | Na1 | O006[1] | 84.45(7) | C00Q | C00H | O003 | 125.6(2) |
| O007 | Na1 | O008[2] | 100.56(8) | C00O | C00I | C00Q | 121.1(2) |
| O007 | Na1 | O00B | 94.82(8) | C00O | C00I | C00R | 118.5(2) |
| O008[2] | Na1 | O006[1] | 100.17(7) | C00R | C00I | C00Q | 120.4(2) |
| O008[2] | Na1 | O00B | 88.03(8) | O002 | C00J | C00F | 110.1(2) |
| O009[3] | Na1 | O006[1] | 83.56(7) | O002 | C00J | C00V | 105.61(18) |
| O009[3] | Na1 | O007 | 110.83(8) | C00F | C00J | C00V | 117.6(2) |
| O009[3] | Na1 | O008[2] | 148.62(9) | O008 | C00K | C00E | 106.7(2) |
| O009[3] | Na1 | O00B | 89.06(8) | O008 | C00K | C00S | 111.9(2) |
| O00B | Na1 | O006[1] | 171.76(9) | C00S | C00K | C00E | 114.5(2) |
| C00E | O002 | C00J | 109.72(18) | O006 | C00L | C00M | 118.5(2) |
| C00H | O003 | C00D | 118.90(19) | O006 | C00L | C00U | 121.7(2) |
| C00L | O006 | Na1[4] | 148.03(16) | C00M | C00L | C00U | 119.7(2) |
| C00S | O007 | Na1 | 137.56(14) | C00L | C00M | C00O | 120.2(2) |
| C00K | O008 | Na1[5] | 146.35(16) | C00D | C00N | C00P | 121.1(2) |
| C00V | O009 | Na1[6] | 121.56(15) | C00D | C00N | C00X | 117.4(2) |
| C00Z | O00B | Na1 | 127.22(18) | C00X | C00N | C00P | 121.6(2) |
| O004 | C00C | C00F | 121.3(2) | C00M | C00O | C00I | 120.7(2) |
| O004 | C00C | C00T | 119.9(2) | O00A | C00P | C00N | 122.6(2) |

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C00F | C00C | C00T | 118.8(2) | O00A | C00P | C00Q | 122.3(2) |
| O003 | C00D | C00F | 116.4(2) | C00N | C00P | C00Q | 115.1(2) |
| O003 | C00D | C00N | 120.2(2) | C00H | C00Q | C00I | 119.7(2) |
| C00F | C00D | C00N | 123.4(2) | C00H | C00Q | C00P | 118.9(2) |
| O002 | C00E | C00G | 103.49(18) | C00P | C00Q | C00I | 121.4(2) |
| O002 | C00E | C00K | 110.04(19) | C00U | C00R | C00I | 120.9(2) |
| C00K | C00E | C00G | 114.8(2) | O007 | C00S | C00K | 113.4(2) |
| C00C | C00F | C00J | 122.1(2) | C00X | C00T | C00C | 121.4(2) |
| C00D | C00F | C00C | 118.0(2) | C00R | C00U | C00L | 119.9(2) |
| C00D | C00F | C00J | 119.8(2) | O009 | C00V | C00G | 110.36(19) |
| O005 | C00G | C00E | 110.4(2) | O009 | C00V | C00J | 114.9(2) |
| O005 | C00G | C00V | 112.25(19) | C00J | C00V | C00G | 102.1(2) |
| C00E | C00G | C00V | 101.42(19) | C00T | C00X | C00N | 121.0(2) |

[1]-1/2+X,1/2-Y,1-Z; [2]1-X,-1/2+Y,3/2-Z; [3]-1+X,+Y,+Z; [4]1/2+X,1/2-Y,1-Z; [5]1-X,1/2+Y,3/2-Z; [6]1+X,+Y,+Z

**Table S55.** Torsion Angles for Compound **49-Na**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| Na1[1] | O006 | C00L | C00M | -34.8(4) | C00E | O002 | C00J | C00V | 0.9(2) |
| Na1[1] | O006 | C00L | C00U | 144.2(2) | C00E | C00G | C00V | O009 | -82.9(2) |
| Na1 | O007 | C00S | C00K | -110.1(2) | C00E | C00G | C00V | C00J | 39.7(2) |
| Na1[2] | O008 | C00K | C00E | 72.4(3) | C00E | C00K | C00S | O007 | 56.2(3) |
| Na1[2] | O008 | C00K | C00S | -161.7(2) | C00F | C00C | C00T | C00X | 1.8(4) |
| Na1[3] | O009 | C00V | C00G | -78.6(2) | C00F | C00D | C00N | C00P | 179.7(2) |
| Na1[3] | O009 | C00V | C00J | 166.62(15) | C00F | C00D | C00N | C00X | 0.7(4) |
| O002 | C00E | C00G | O005 | 79.5(2) | C00F | C00J | C00V | O009 | -29.5(3) |
| O002 | C00E | C00G | C00V | -39.7(2) | C00F | C00J | C00V | C00G | -149.0(2) |
| O002 | C00E | C00K | O008 | 171.54(19) | C00G | C00E | C00K | O008 | -72.3(2) |
| O002 | C00E | C00K | C00S | 47.2(3) | C00G | C00E | C00K | C00S | 163.4(2) |
| O002 | C00J | C00V | O009 | 93.8(2) | C00H | O003 | C00D | C00F | 177.0(2) |
| O002 | C00J | C00V | C00G | -25.7(2) | C00H | O003 | C00D | C00N | -2.8(3) |
| O003 | C00D | C00F | C00C | -178.6(2) | C00I | C00R | C00U | C00L | 0.7(4) |
| O003 | C00D | C00F | C00J | 4.8(3) | C00J | O002 | C00E | C00G | 24.5(2) |
| O003 | C00D | C00N | C00P | -0.5(4) | C00J | O002 | C00E | C00K | 147.57(19) |
| O003 | C00D | C00N | C00X | -179.5(2) | C00K | C00E | C00G | O005 | -40.4(3) |
| O003 | C00H | C00Q | C00I | -178.4(2) | C00K | C00E | C00G | C00V | -159.59(19) |
| O003 | C00H | C00Q | C00P | -0.2(4) | C00L | C00M | C00O | C00I | 0.1(4) |

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| O004 | C00C | C00F | C00D | 176.5(2) | C00M | C00L | C00U | C00R | .1(4) |
| O004 | C00C | C00F | C00J | -6.9(4) | C00N | C00D | C00F | C00C | 1.2(4) |
| O004 | C00C | C00T | C00X | -177.2(2) | C00N | C00D | C00F | C00J | -175.4(2) |
| O005 | C00G | C00V | O009 | 159.2(2) | C00N | C00P | C00Q | C00H | -3.1(4) |
| O005 | C00G | C00V | C00J | -78.2(2) | C00N | C00P | C00Q | C00I | 175.2(2) |
| O006 | C00L | C00M | C00O | -178.3(2) | C00O | C00I | C00Q | C00H | -55.0(4) |
| O006 | C00L | C00U | C00R | 177.9(2) | C00O | C00I | C00Q | C00P | 126.8(3) |
| O008 | C00K | C00S | O007 | -65.3(3) | C00O | C00I | C00R | C00U | 2.1(4) |
| O00A | C00P | C00Q | C00H | 176.8(3) | C00P | C00N | C00X | C00T | 179.6(3) |
| O00A | C00P | C00Q | C00I | -5.0(4) | C00Q | C00I | C00O | C00M | 175.6(3) |
| C00C | C00F | C00J | O002 | -55.7(3) | C00Q | C00I | C00R | C00U | -176.0(2) |
| C00C | C00F | C00J | C00V | 65.2(3) | C00R | C00I | C00O | C00M | -2.5(4) |
| C00C | C00T | C00X | C00N | 0.1(4) | C00R | C00I | C00Q | C00H | 123.1(3) |
| C00D | O003 | C00H | C00Q | 3.2(4) | C00R | C00I | C00Q | C00P | -55.1(4) |
| C00D | C00F | C00J | O002 | 120.8(2) | C00T | C00C | C00F | C00D | -2.4(4) |
| C00D | C00F | C00J | C00V | -118.3(3) | C00T | C00C | C00F | C00J | 174.1(2) |
| C00D | C00N | C00P | O00A | -176.5(3) | C00U | C00L | C00M | C00O | 2.7(4) |
| C00D | C00N | C00P | C00Q | 3.4(4) | C00X | C00N | C00P | O00A | 2.5(4) |
| C00D | C00N | C00X | C00T | -1.4(4) | C00X | C00N | C00P | C00Q | -177.7(2) |
| C00E | O002 | C00J | C00F | 128.9(2) | | | | | |

[1]1/2+X,1/2-Y,1-Z; [2]1-X,1/2+Y,3/2-Z; [3]1+X,+Y,+Z

**Table S56.** Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å2×10$^3$) for Compound **49-Na**.

| Atom | *X* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H008 | 5240(40) | 8270(30) | 7545(10) | 21(8) |
| H005 | 9394.61 | 7687.92 | 6375.83 | 30 |
| H006 | 8900(50) | 90(30) | 3410(10) | 31(9) |
| H007 | 3100(40) | 7060(30) | 7500(6) | 25 |
| H009 | 8410(40) | 4080(30) | 7037(8) | 12(7) |
| H00B | 850(50) | 4190(40) | 8125(12) | 45(10) |
| H00E | 6462.18 | 5971.62 | 7195.52 | 15 |
| H00G | 9095.29 | 6947.36 | 7083.17 | 17 |
| H00H | 7819.38 | 3878.34 | 5001.72 | 19 |
| H00J | 7456.62 | 5448.8 | 6094.98 | 15 |
| H00K | 5788.54 | 8429.19 | 6762.23 | 17 |
| H00M | 6152.29 | 2459.58 | 3710.01 | 24 |
| H00O | 5686.61 | 3079.78 | 4403.04 | 23 |
| H00R | 8591.14 | -26.23 | 4789.16 | 22 |

| | | | | |
|---|---|---|---|---|
| H00A | 2986.53 | 8448.66 | 7030 | 18 |
| H00C | 3241.52 | 7276.5 | 6695.67 | 18 |
| H00T | 5505.97 | 890 | 6821.22 | 21 |
| H00U | 9029.68 | -658.28 | 4097.51 | 20 |
| H00V | 9898.8 | 5529.45 | 6442.71 | 17 |
| H00X | 5450.5 | 25.37 | 6156.84 | 22 |
| H00D | -1273.32 | 5567.66 | 8253.24 | 53 |
| H00F | -1032.44 | 6271.03 | 7807.96 | 53 |
| H00I | 344.44 | 6508.56 | 8169.81 | 53 |
| H10 | 10157.57 | 5950.77 | 5157.82 | 60 |
| H01A | 8392.42 | 7486.8 | 4934.09 | 64 |
| H01B | 7851.46 | 7716.62 | 5410.85 | 64 |
| H01C | 7378.25 | 6343.53 | 5181.04 | 64 |
| H0AA | 10763.33 | 7268.95 | 5803.94 | 47 |
| H12A | 12713.89 | 8875.28 | 5697.67 | 122 |
| H12B | 11941.04 | 9521.4 | 6114.22 | 122 |
| H12C | 10769.8 | 9366.71 | 5707.42 | 122 |
| H11 | 6834.72 | 8354.77 | 5658.21 | 60 |
| H13A | 8529.24 | 7916.46 | 5199.34 | 126 |
| H13B | 8346.86 | 6393.25 | 5347.16 | 126 |
| H13C | 9755.73 | 7339.83 | 5556.38 | 126 |

**Table S57.** Atomic Occupancy for **49-Na**.

| **Atom** | **Occupancy** | **Atom** | **Occupancy** | **Atom** | **Occupancy** |
|---|---|---|---|---|---|
| O10 | 0.707(4) | H10 | 0.707(4) | C010 | 0.707(4) |
| H01A | 0.707(4) | H01B | 0.707(4) | H01C | 0.707(4) |
| O0AA | 0.707(4) | H0AA | 0.707(4) | C12 | 0.707(4) |
| H12A | 0.707(4) | H12B | 0.707(4) | H12C | 0.707(4) |
| O11 | 0.293(4) | H11 | 0.293(4) | C13 | 0.293(4) |
| H13A | 0.293(4) | H13B | 0.293(4) | H13C | 0.293(4) |

## 8. References


[1]. K. Zhao, et al. Construction of Stable Helical Metal-Organic Frameworks with a Conformationally Rigid "Concave Ligand". *Chem.-Eur. J.* **27**, 10833-10838 (2021).

[2]. M. G. Ricardo, M. Schwark, D. Llanes, T. H. J. Niedermeyer, B. Westermann, Total Synthesis of Aetokthonotoxin, the Cyanobacterial Neurotoxin Causing Vacuolar Myelinopathy. *Chem.-Eur. J.* **27**, 12032-12035 (2021).

[3] A. Bunrit, et al. Brønsted Acid-Catalyzed Intramolecular Nucleophilic Substitution of the Hydroxyl Group in Stereogenic Alcohols with Chirality Transfer. *J. Am. Chem. Soc.* **137**, 4646-4649 (2015).

[4] X. Xiong, & Y.-Y. Yeung, Highly ortho-Selective Chlorination of Anilines Using a Secondary Ammonium Salt Organocatalyst. *Angew. Chem., Int. Ed.* **55**, 16101-16105 (2016).

[5]. S. Sun, Y. Yang, R. Zhao, D. Zhang, L. Liu, Site- and Enantiodifferentiating C($sp^3$)–H Oxidation Enables Asymmetric Access to Structurally and Stereochemically Diverse Saturated Cyclic Ethers. *J. Am. Chem. Soc.* **142**, 19346-19353 (2020).

[6]. Z. Lu, et al. CFBSA: a novel and practical chlorinating reagent. *Chem. Comm.* **51**, 14852-14855 (2015).

[7]. S. K. Rodrigo, H. Guan, Quick Installation of a 1,4-Difunctionality via Regioselective Nickel-Catalyzed Reductive Coupling of Ynoates and Aldehydes. *J. Org. Chem.* **77**, 8303-8309 (2012).

[8]. D. Rosas Vargas, S. P. Cook, Palladium nanoparticles: Chemoselective control for reductive Heck with aryl triflates and 2,3-dihydrofuran. *Tetrahedron* **74**, 3314-3317 (2018).

[9]. D. Liu, C. Liu, H. Li, A. Lei, Direct Functionalization of Tetrahydrofuran and 1,4-Dioxane: Nickel-Catalyzed Oxidative C($sp^3$)-H Arylation. *Angew. Chem., Int. Ed.* **52**, 4453-4456 (2013).

[10]. R. Lindroth, A. Ondrejková, C.-J. Wallentin, Visible-Light Mediated Oxidative Fragmentation of Ethers and Acetals by Means of Fe(III) Catalysis. *Org. Lett.* **24**, 1662-1667 (2022).

[11]. H. Shigehisa, et al. Catalytic Synthesis of Saturated Oxygen Heterocycles by Hydrofunctionalization of Unactivated Olefins: Unprotected and Protected Strategies. *J. Am. Chem. Soc.* **138**, 10597-10604 (2016).

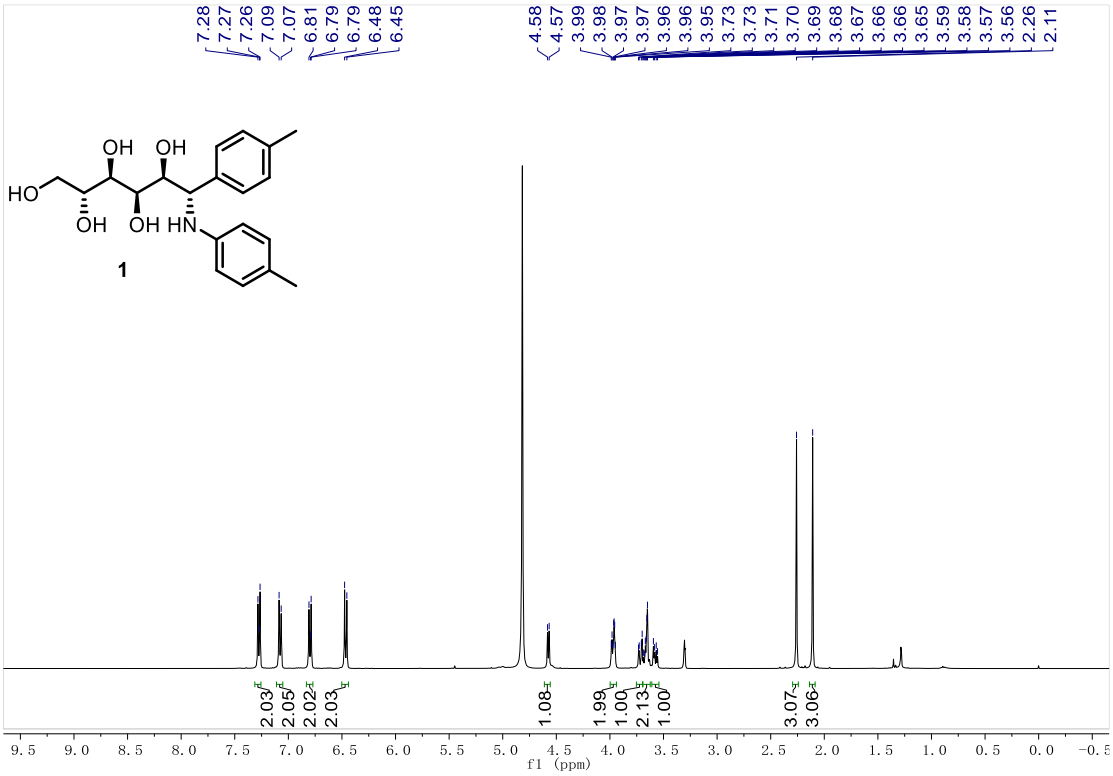
[12]. H. Im, D. Kang, S. Choi, S. Shin, S. Hong, Visible-Light-Induced C–O Bond Formation for the Construction of Five- and Six-Membered Cyclic Ethers and Lactones. *Org. Lett.* **20**, 7437-7441 (2018).

[13] C.-Y. Zhou, J. Li, S. Peddibhotla, D. Romo, Mild Arming and Derivatization of Natural Products via an $In(OTf)_3$-Catalyzed Arene Iodination. *Org. Lett*. **12**, 2104-2107 (2010).

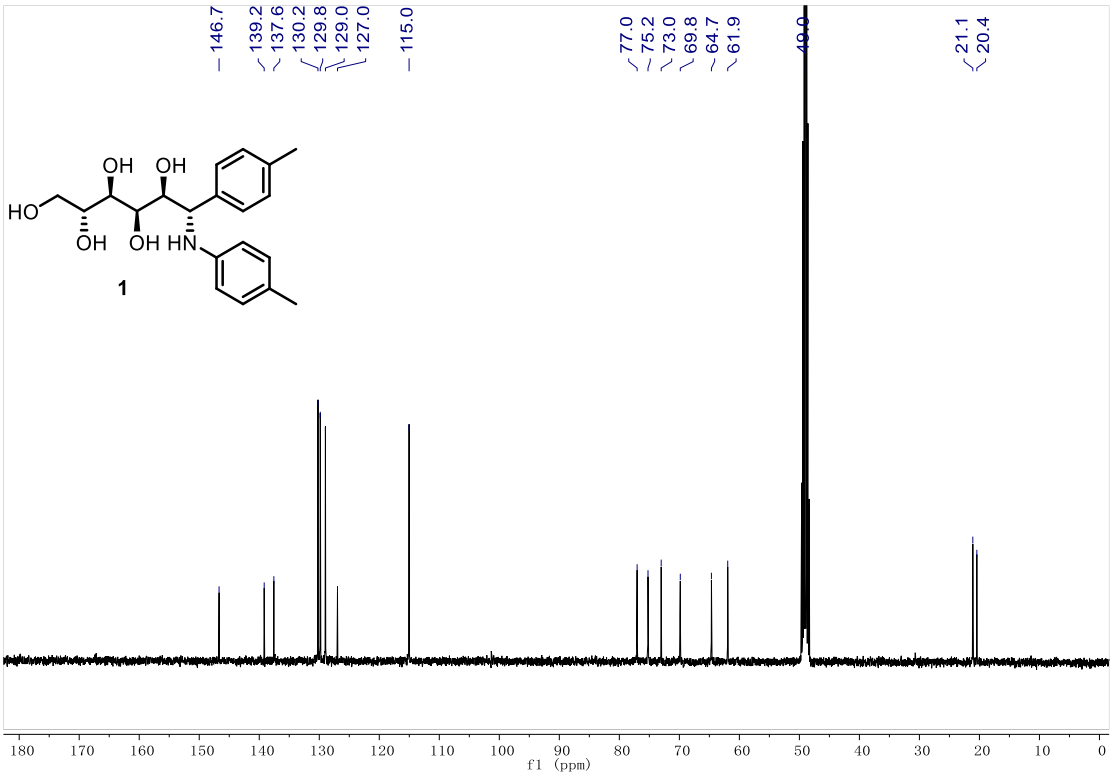
[14] Frick, W., Schmidt, R.R. Einfache Synthese Von Cβ-D-Glucopyranosylaromaten - Synthese Des 5,7,4′-Tri-O-Methylvitexins. *Liebigs Annalen der Chemie*, **1989**, 565-570 (1989).

[15] Qu, Z.-W., Zhu, H., Grimme, S. Mechanistic Insights for Aniline-Catalyzed Halogenation Reactions *ChemCatChem*, **12**, 5369-5373 (2020).

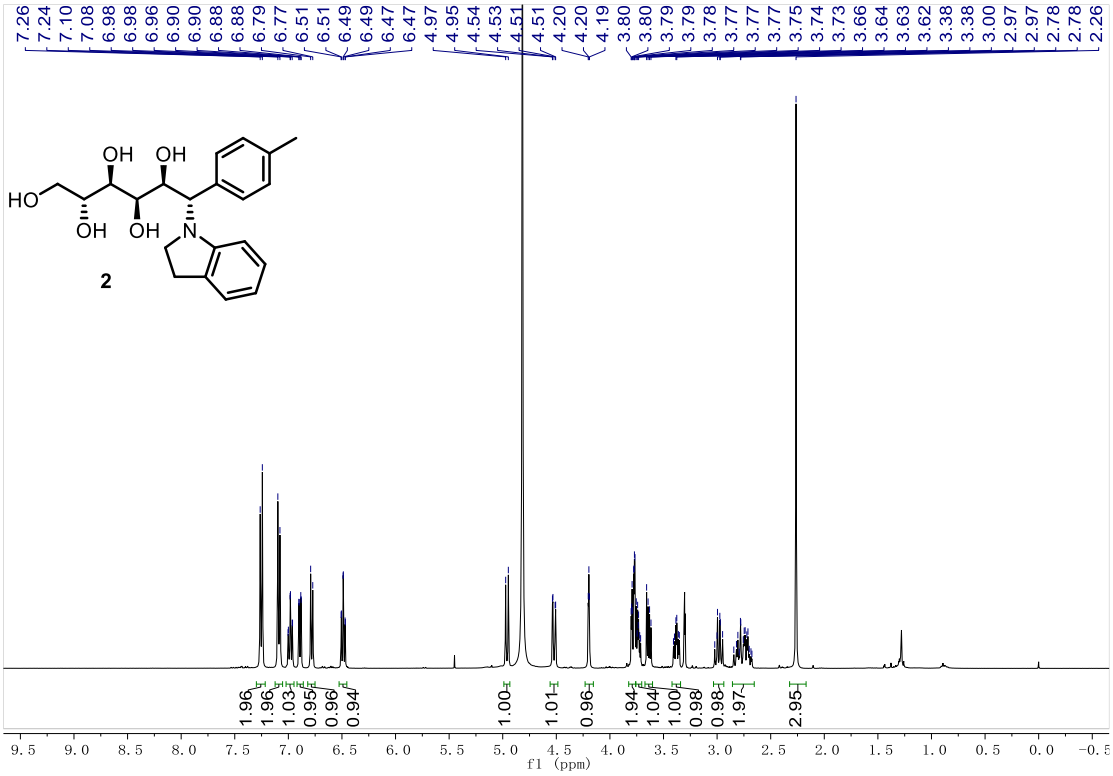
## 9. NMR Spectra



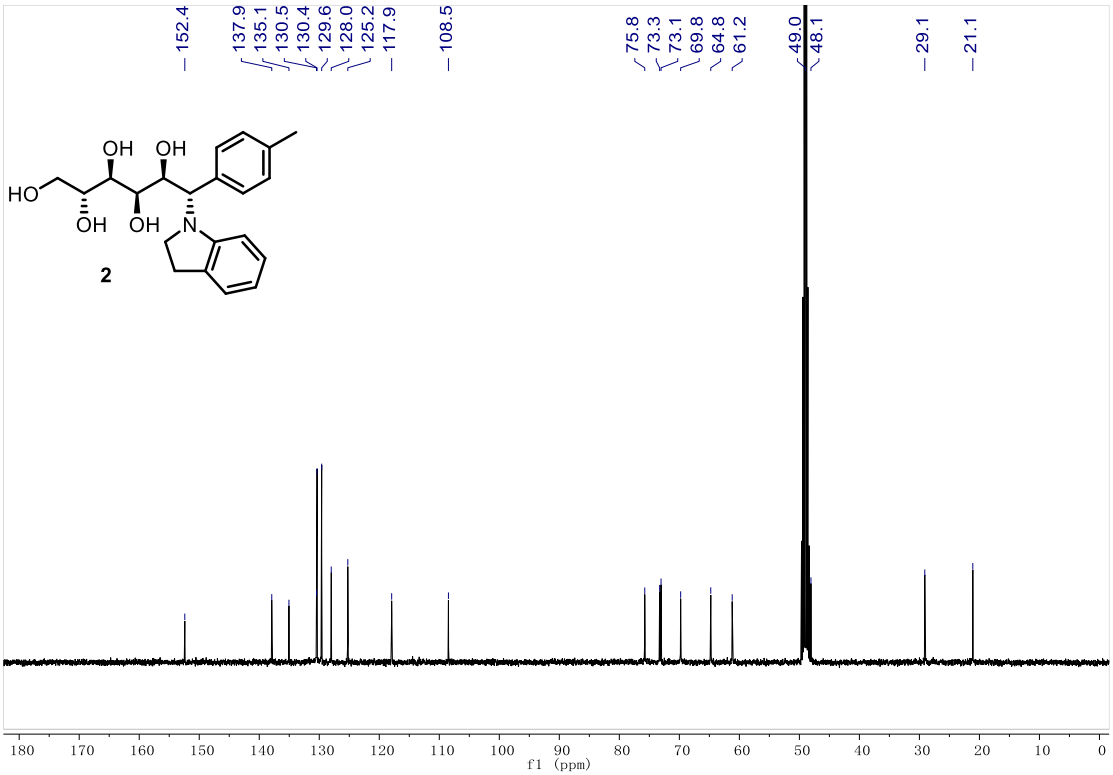

$^{1}$H NMR of compound **1** (400 MHz, $CD_3OD$)



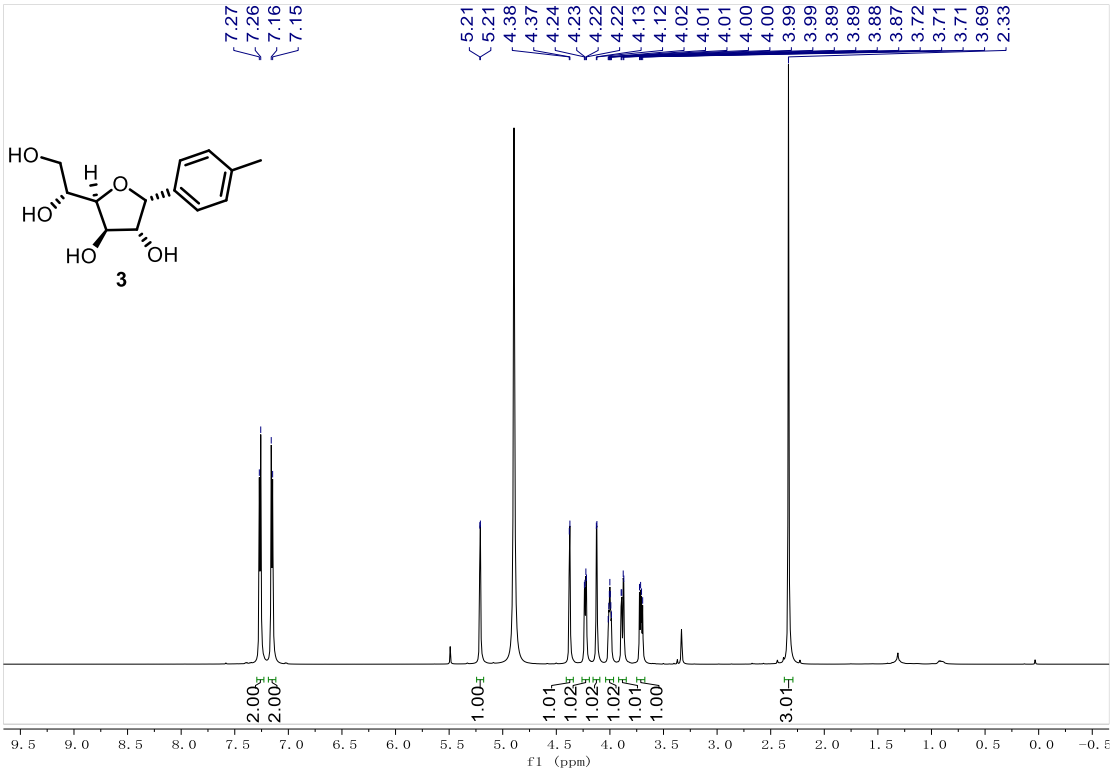

$^{13}$C NMR of compound **1** (101 MHz, $CD_3OD$)



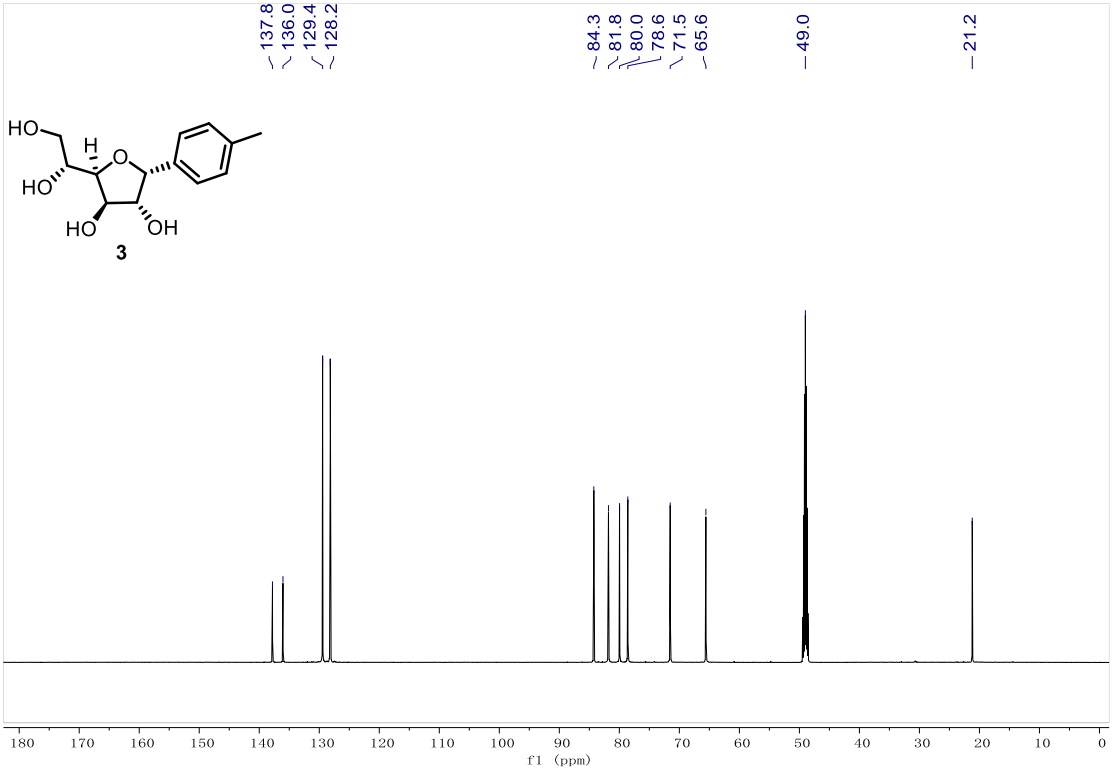

$^{1}$H NMR of compound **2** (400 MHz, $CD_3OD$)



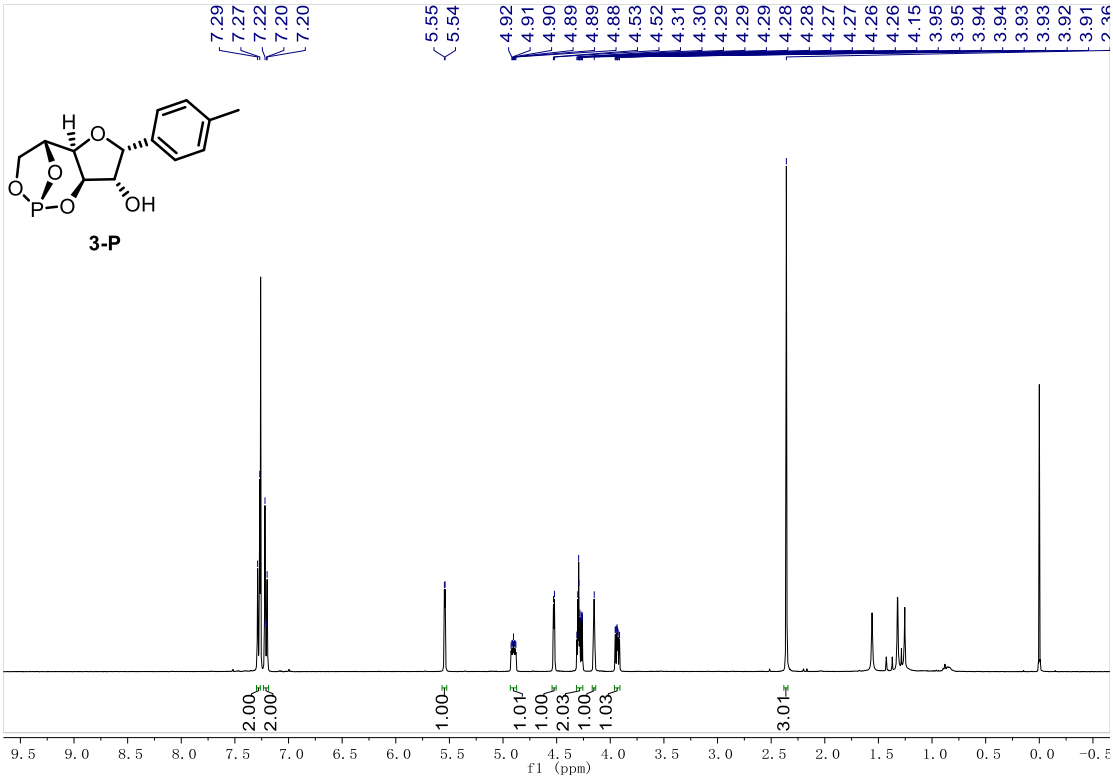

$^{13}$C NMR of compound **2** (101 MHz, $CD_3OD$)



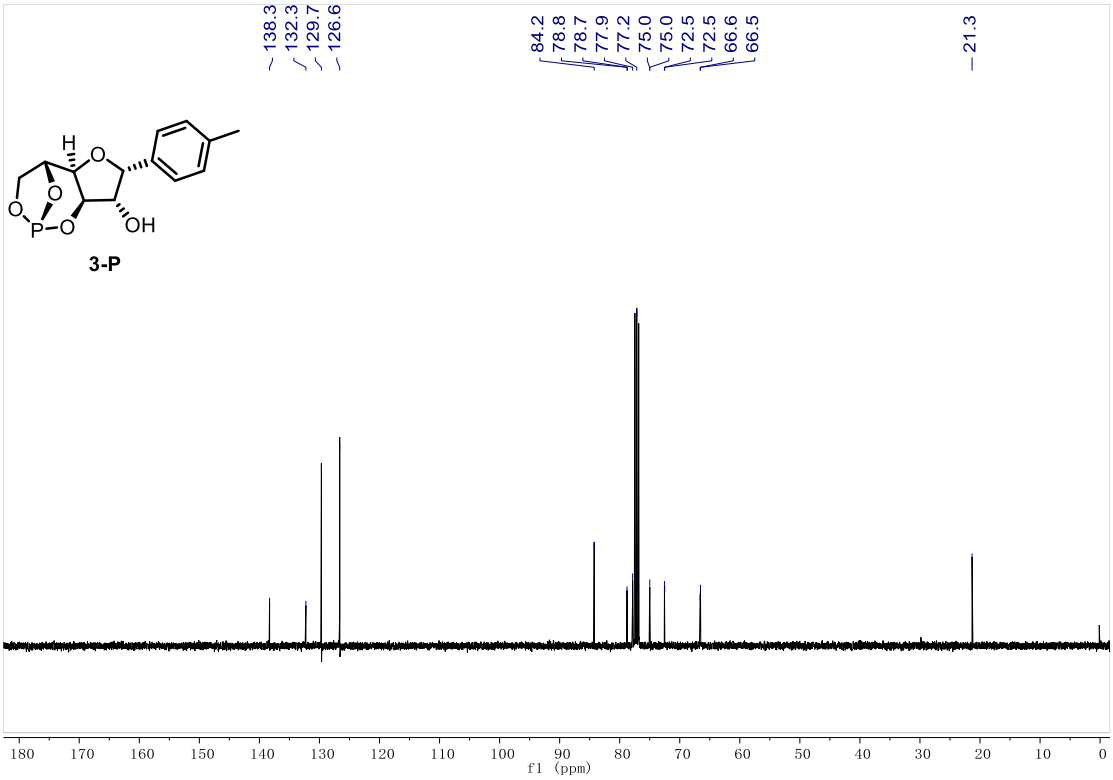

$^{1}$H NMR of compound **3** (600 MHz, $CD_3OD$)



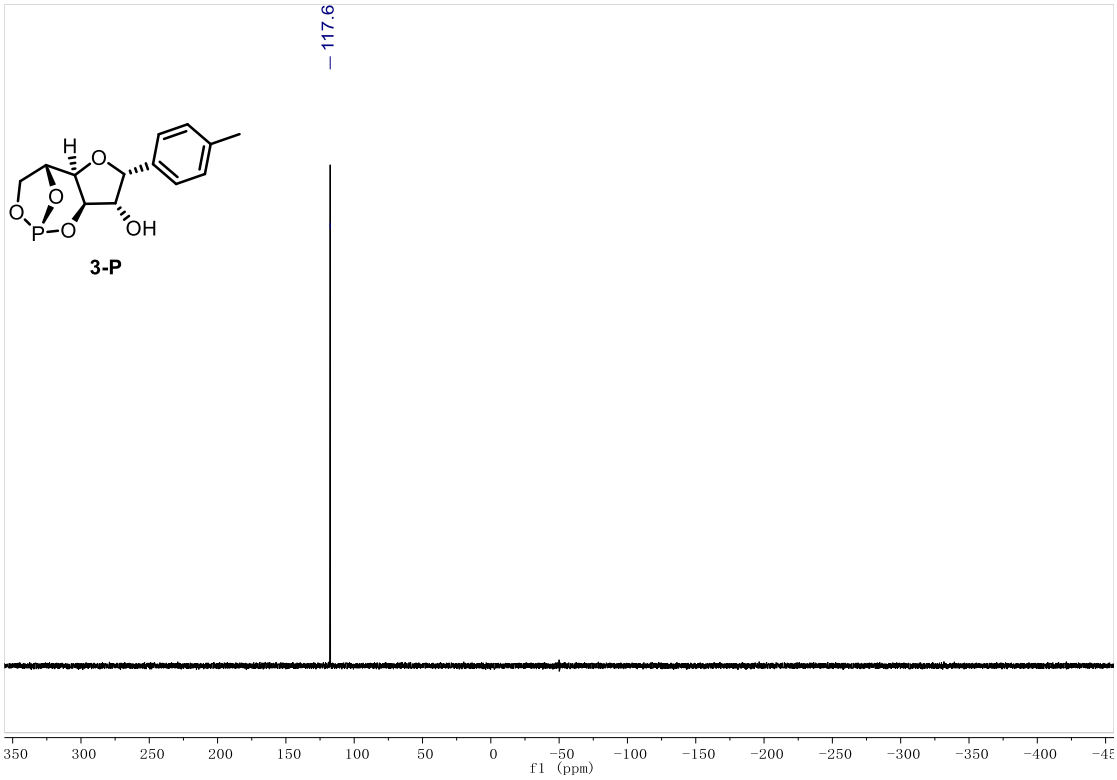

$^{13}$C NMR of compound **3** (151 MHz, $CD_3OD$)



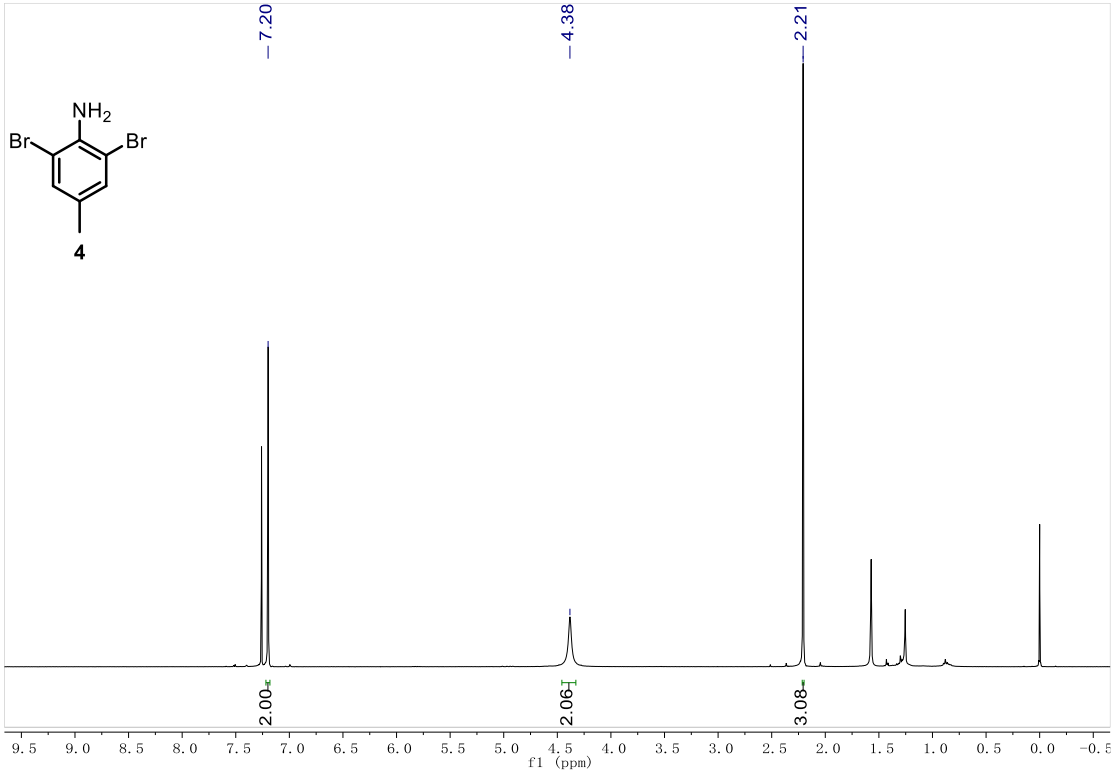

$^{1}$H NMR of compound **3-P** (400 MHz, $CDCl_3$)



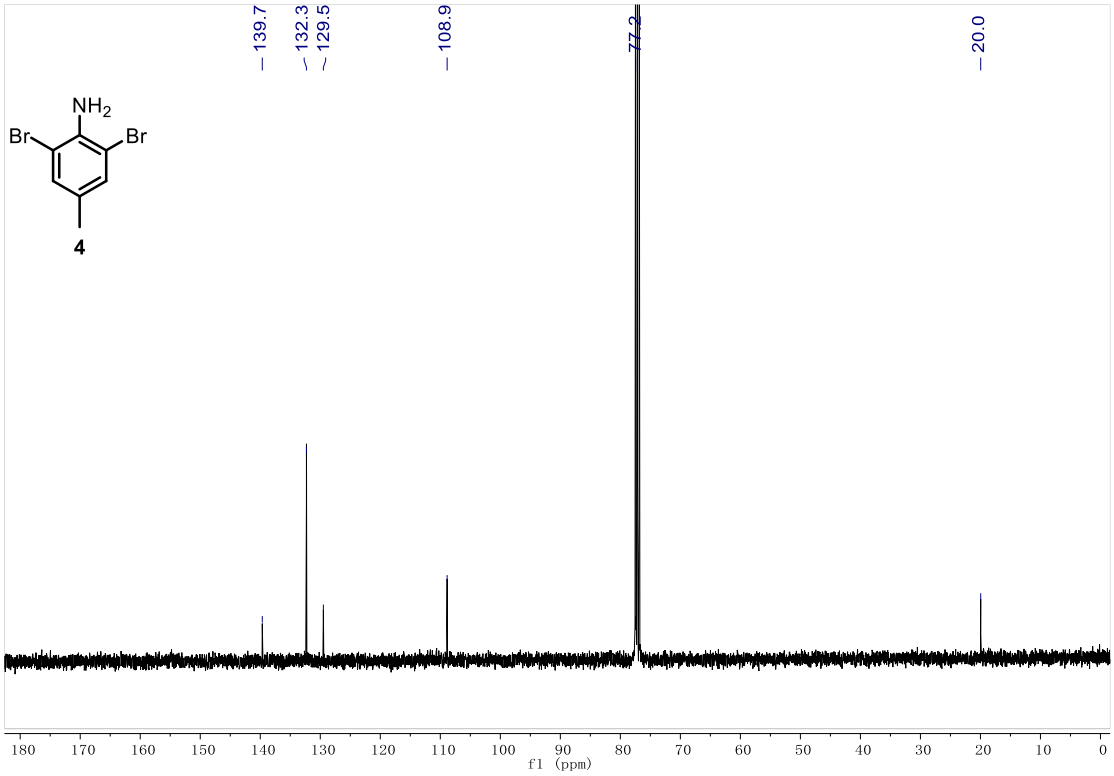

$^{13}$C NMR of compound **3-P** (101 MHz, $CDCl_3$)



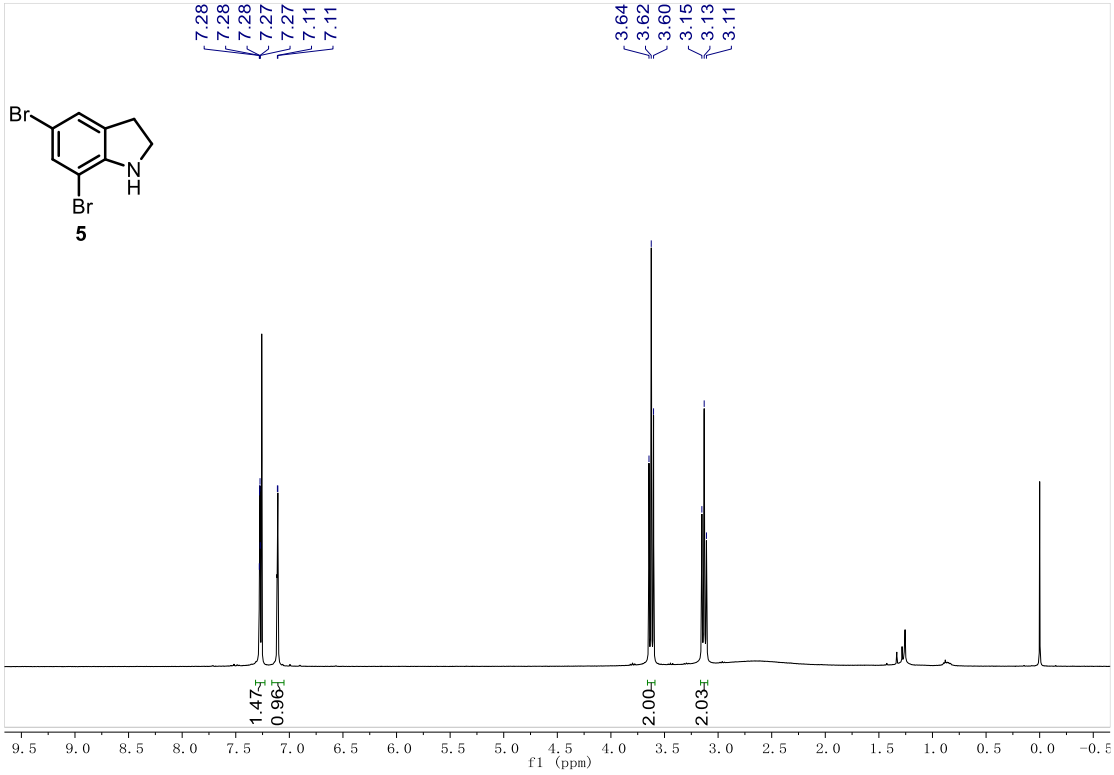

$^{31}$P NMR of compound **3-P** (162 MHz, $CDCl_3$)



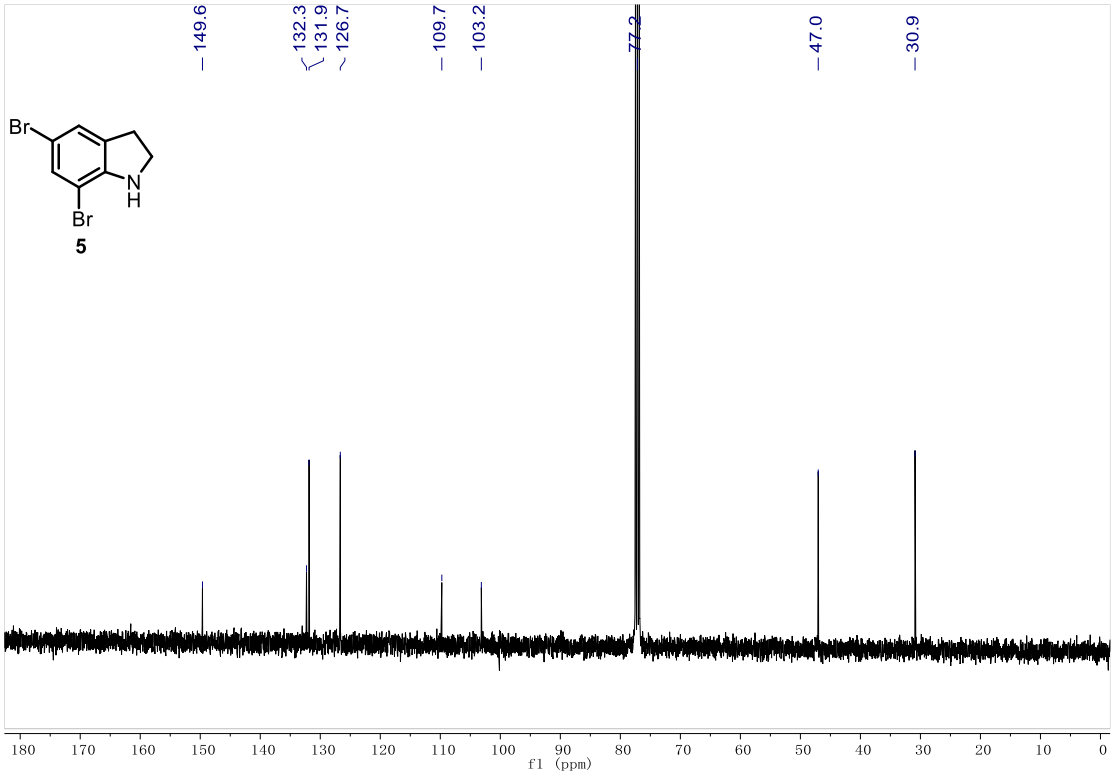

$^{1}$H NMR of compound **4** (400 MHz, $CDCl_3$)



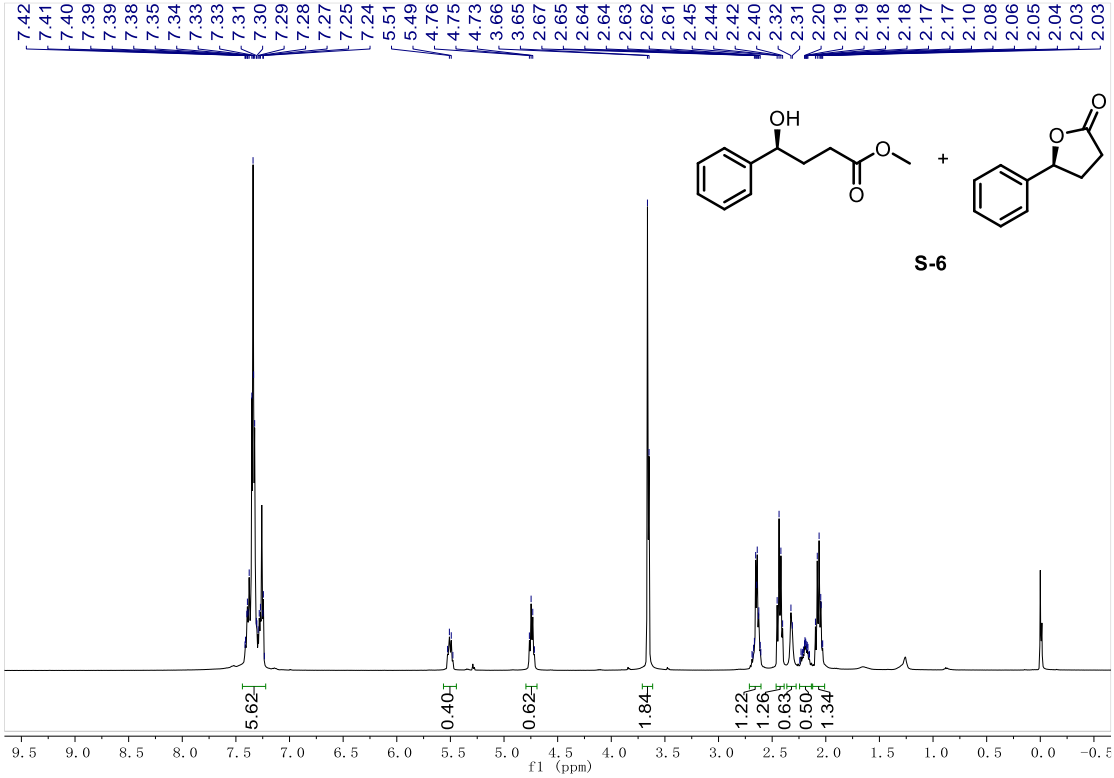

$^{13}$C NMR of compound **4** (101 MHz, $CDCl_3$)



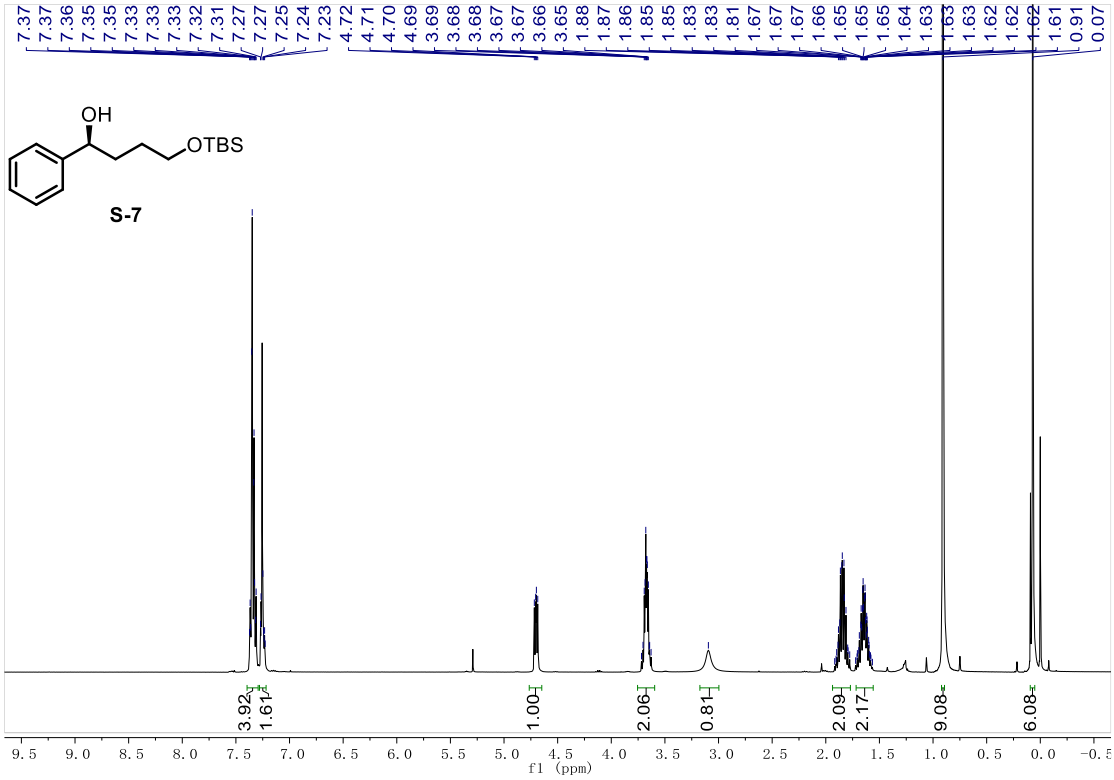

$^{1}$H NMR of compound **5** (400 MHz, $CDCl_3$)



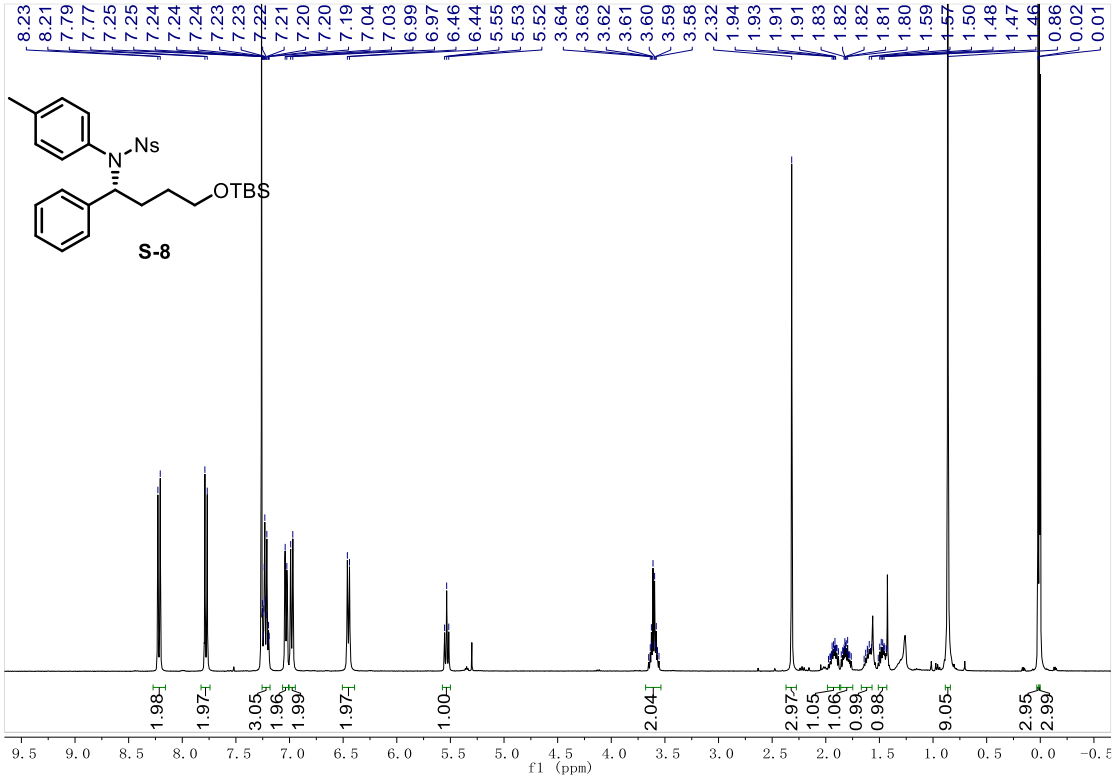

$^{13}$C NMR of compound **5** (101 MHz, $CDCl_3$)



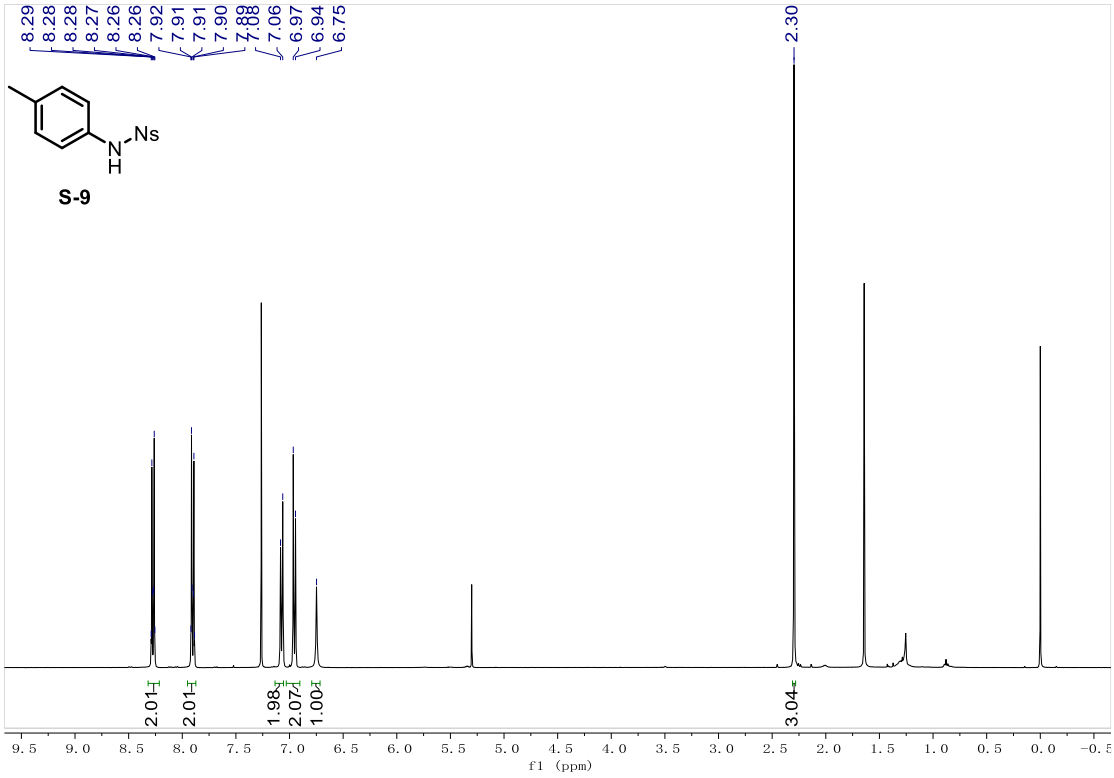

$^{1}$H NMR of compound **S-6** (400 MHz, $CDCl_3$)



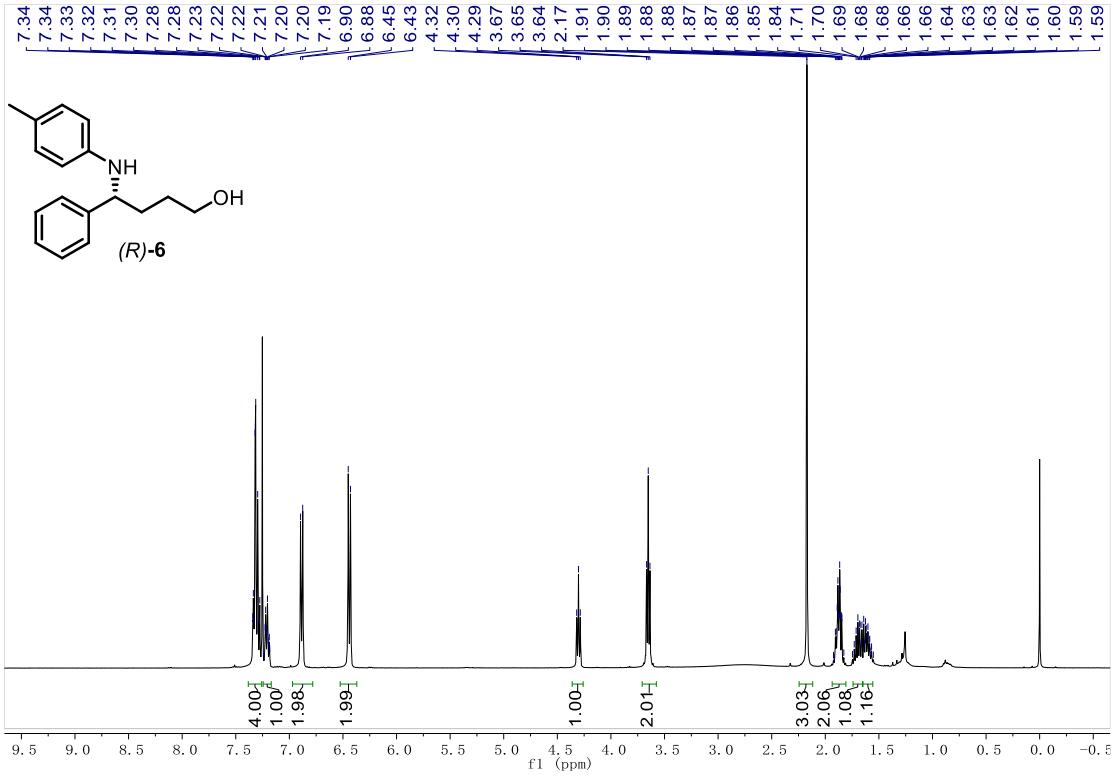

$^1$H NMR of compound **S-7** (400 MHz, $CDCl_3$)



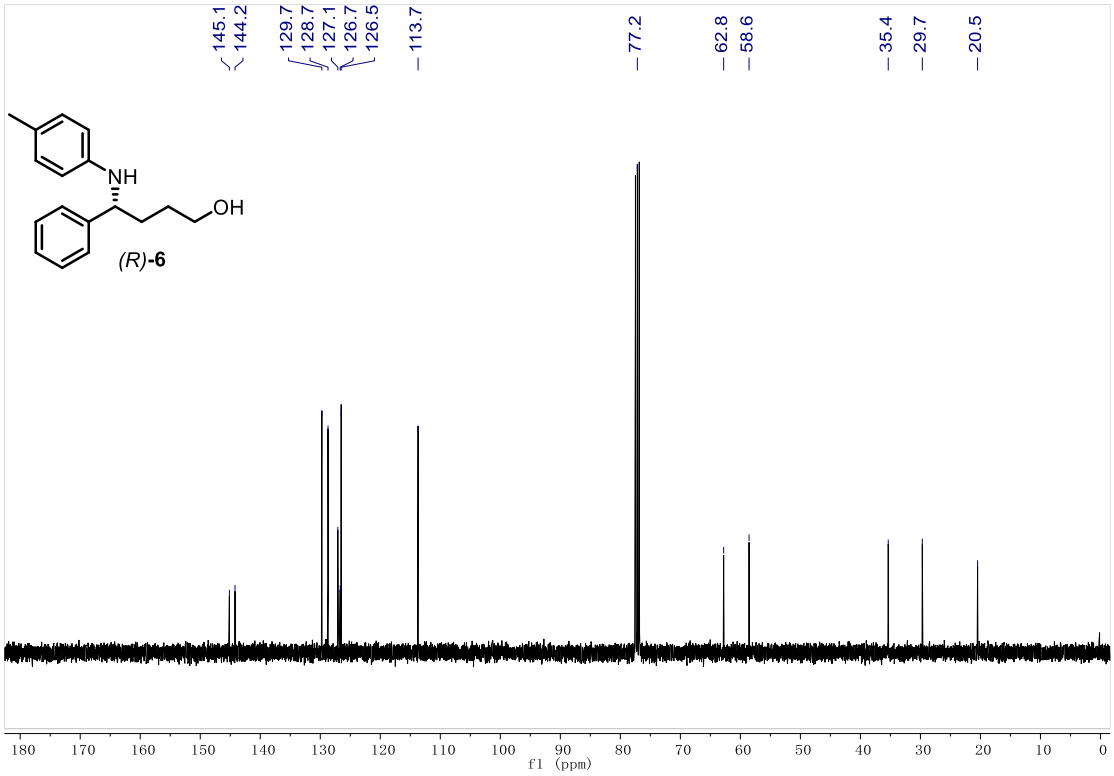

$^1$H NMR of compound **S-8** (400 MHz, $CDCl_3$)



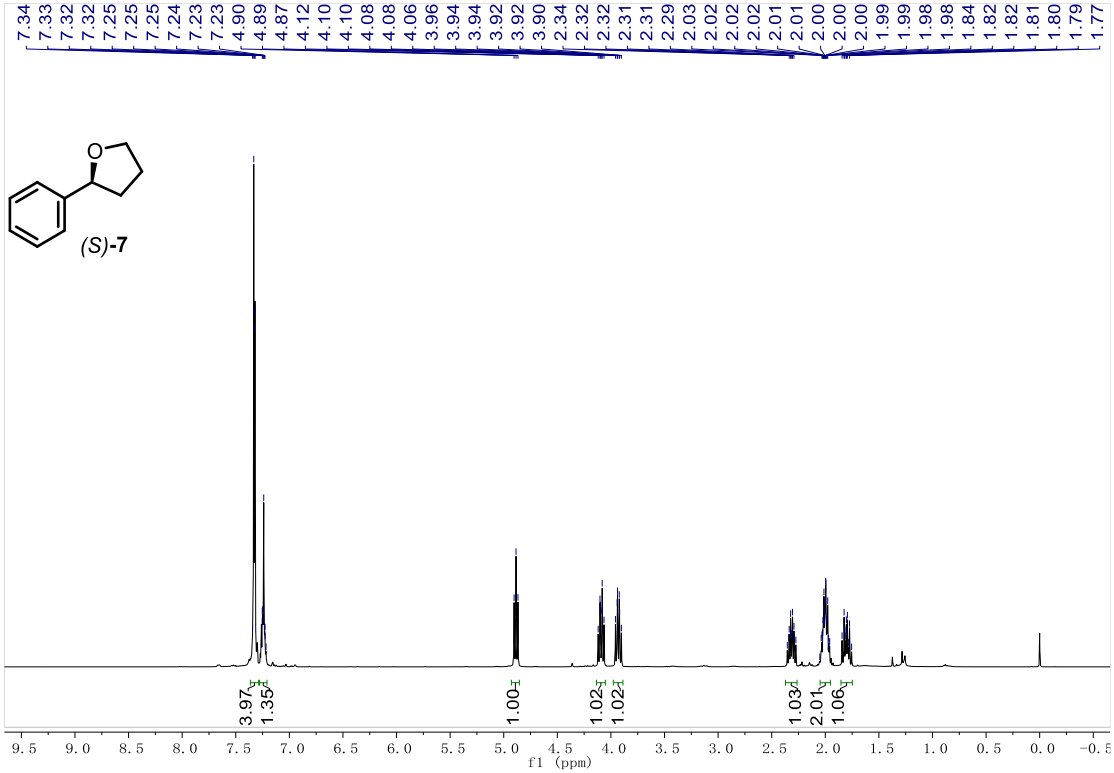

$^1$H NMR of compound **S-9** (400 MHz, $CDCl_3$)



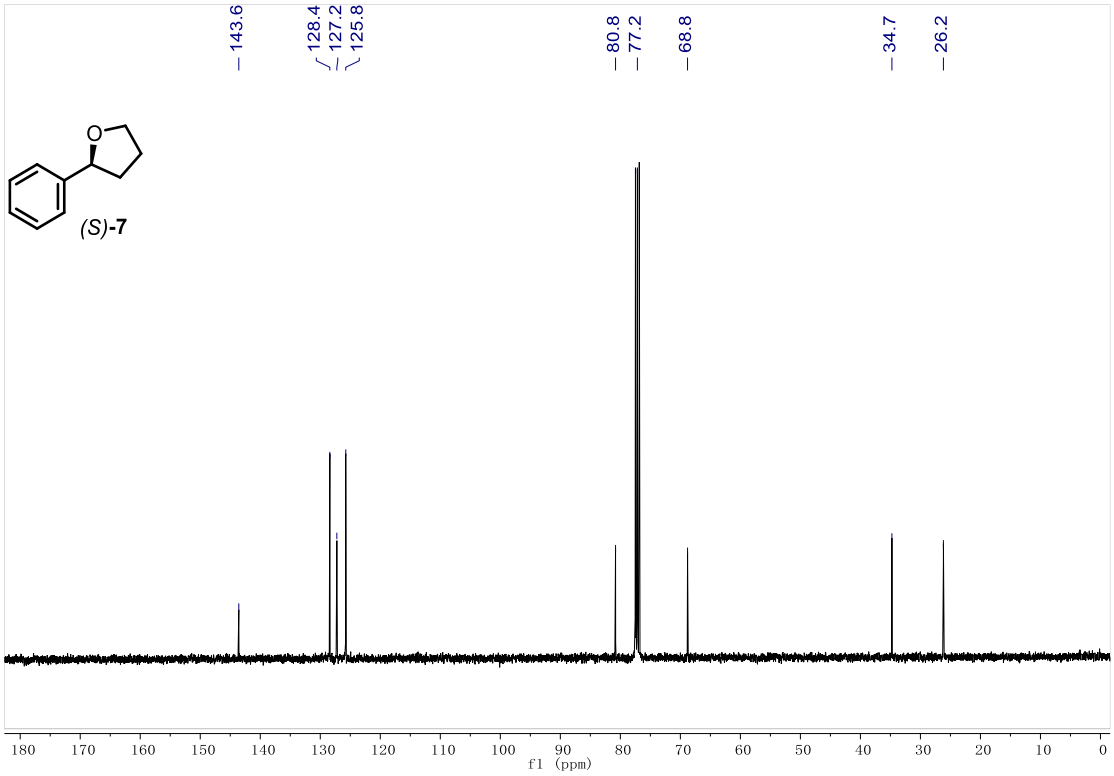

$^1$H NMR of compound *(R)*-**6** (400 MHz, $CDCl_3$)



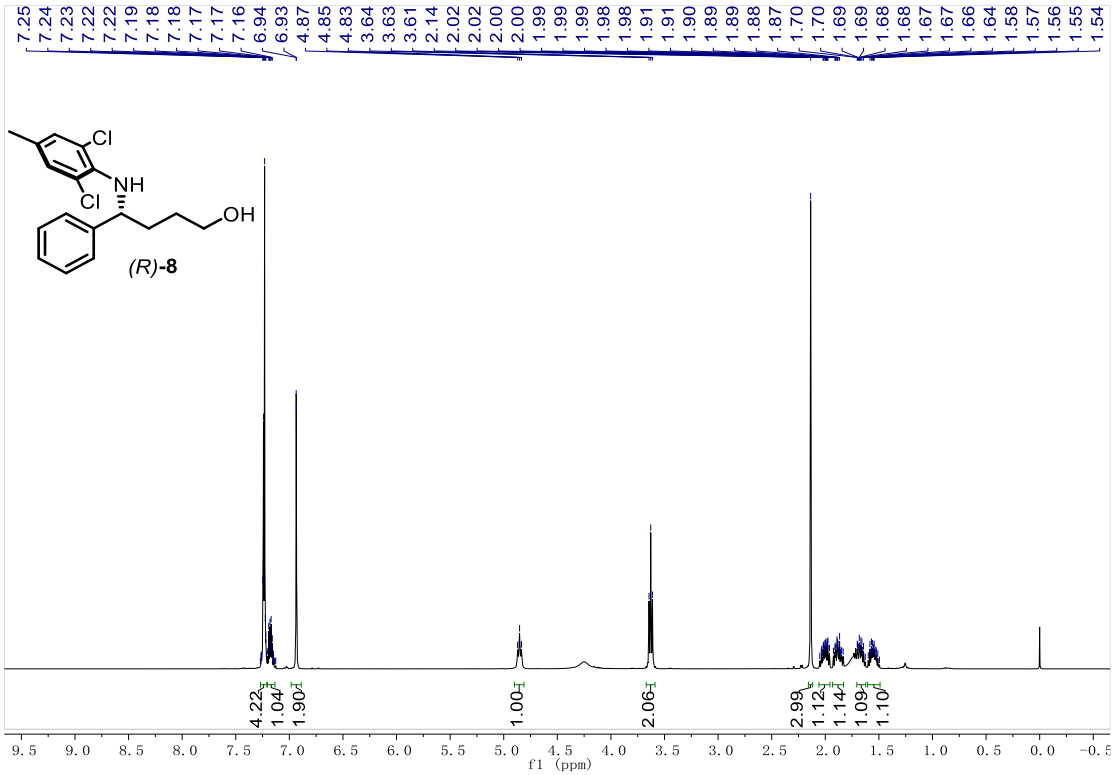

$^{13}$C NMR of compound *(R)*-**6** (101 MHz, $CDCl_3$)



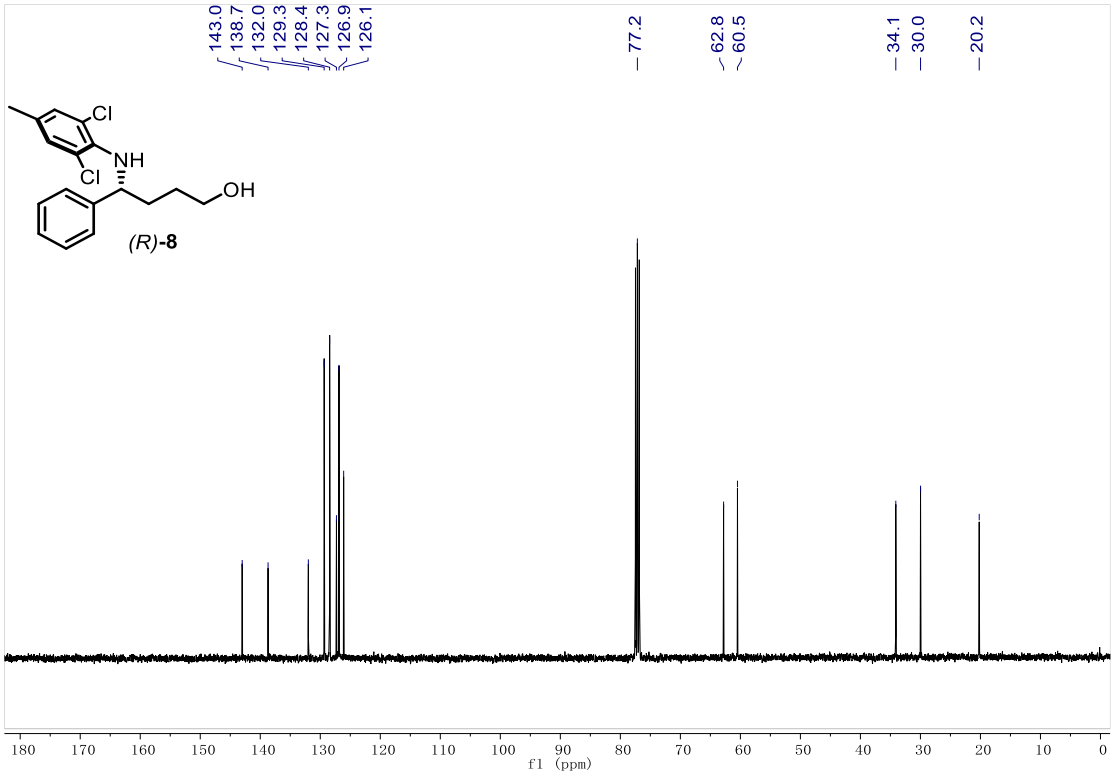

$^{1}$H NMR of compound *(S)*-**7** (400 MHz, $CDCl_3$)



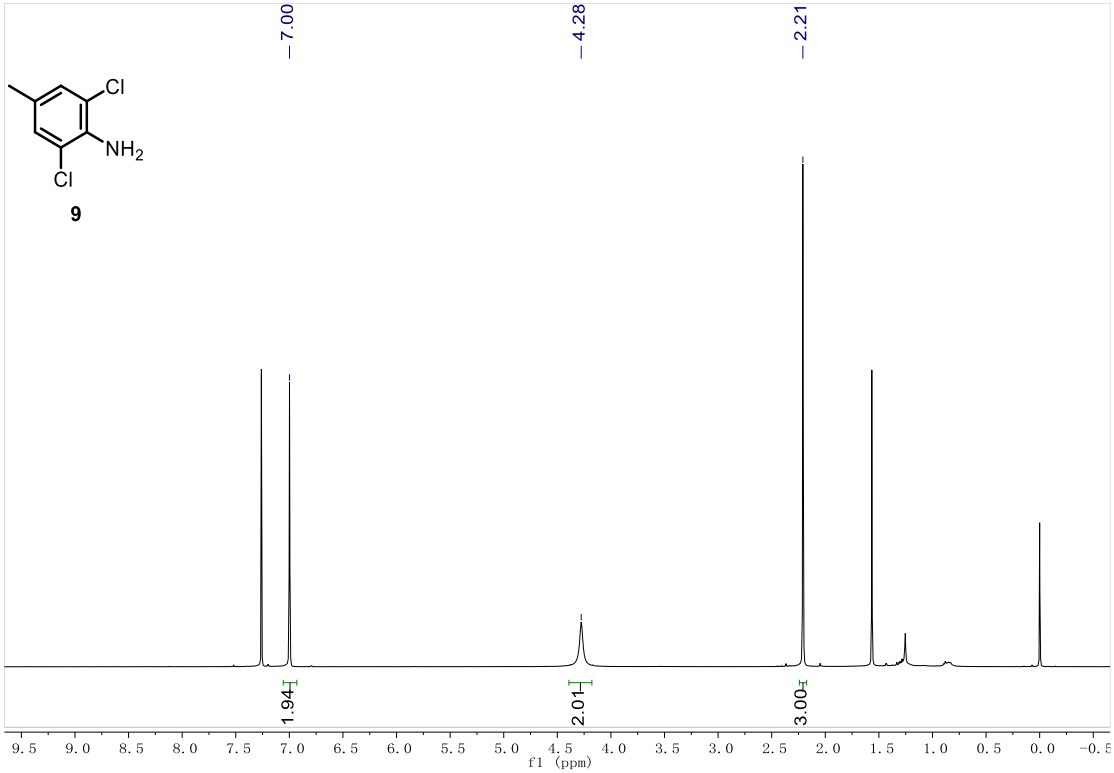

$^{13}$C NMR of compound *(S)*-**7** (101 MHz, $CDCl_3$)



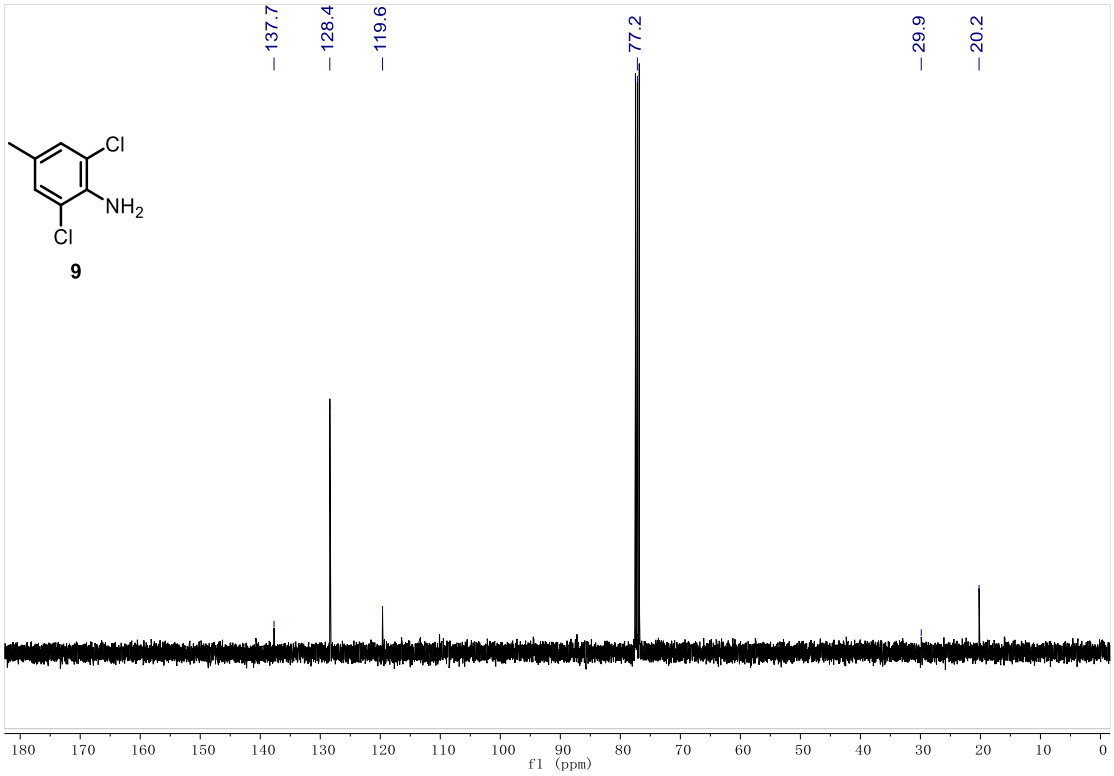

$^{1}$H NMR of compound *(R)*-**8** (400 MHz, $CDCl_3$)



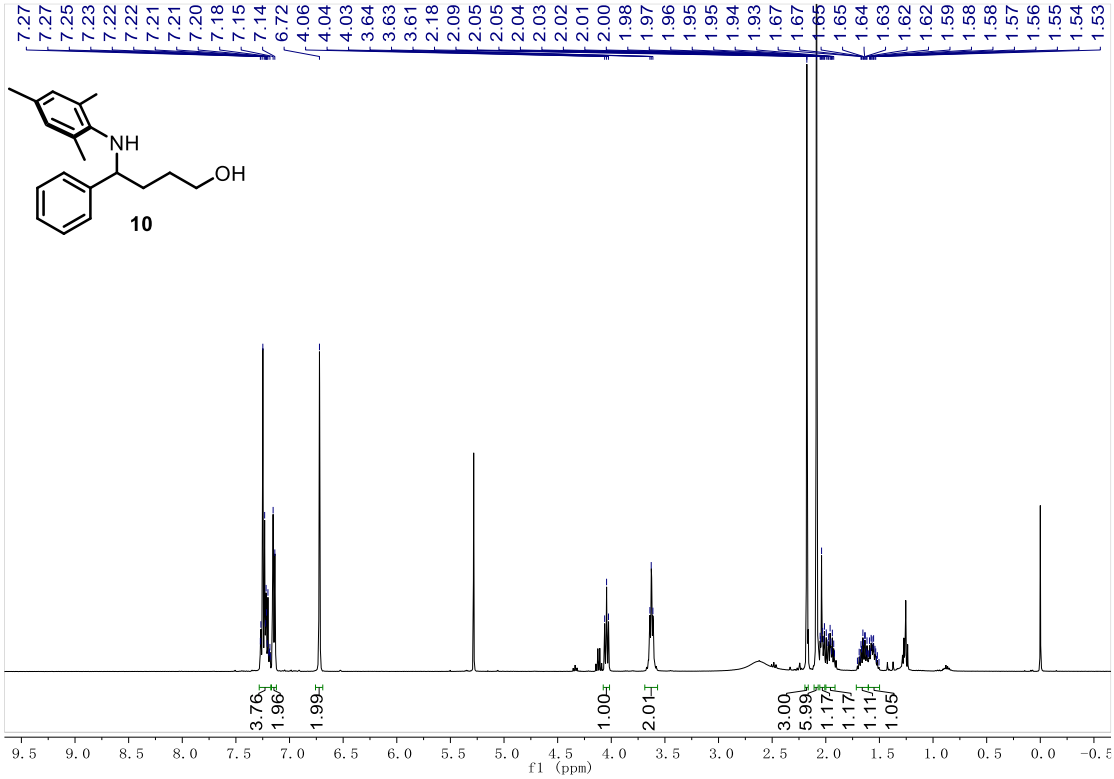

$^{13}$C NMR of compound *(R)*-**8** (101 MHz, $CDCl_3$)



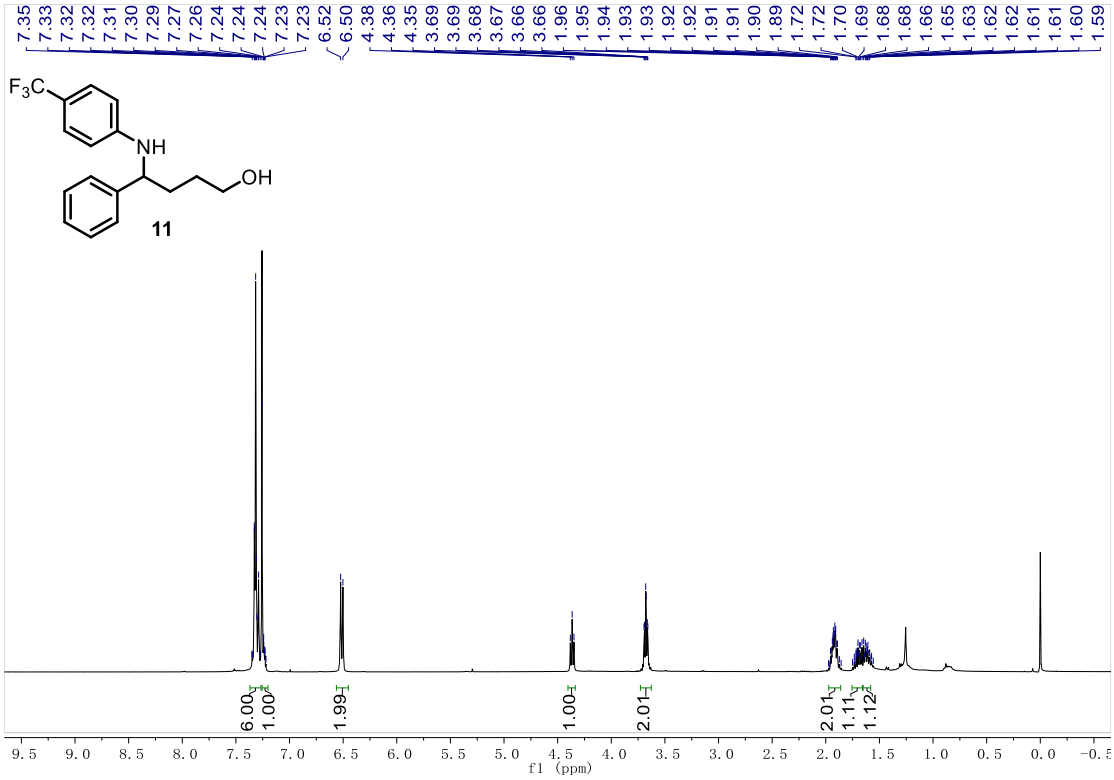

$^{1}$H NMR of compound **9** (400 MHz, $CDCl_3$)



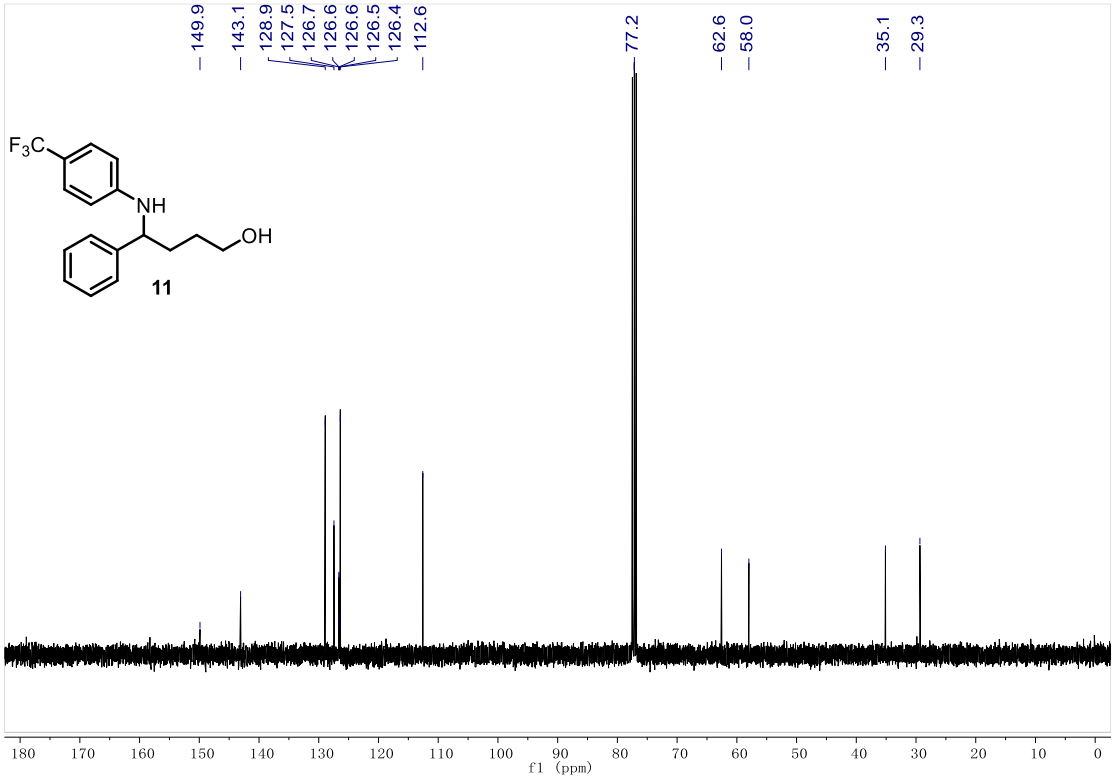

$^{13}$C NMR of compound **9** (101 MHz, $CDCl_3$)



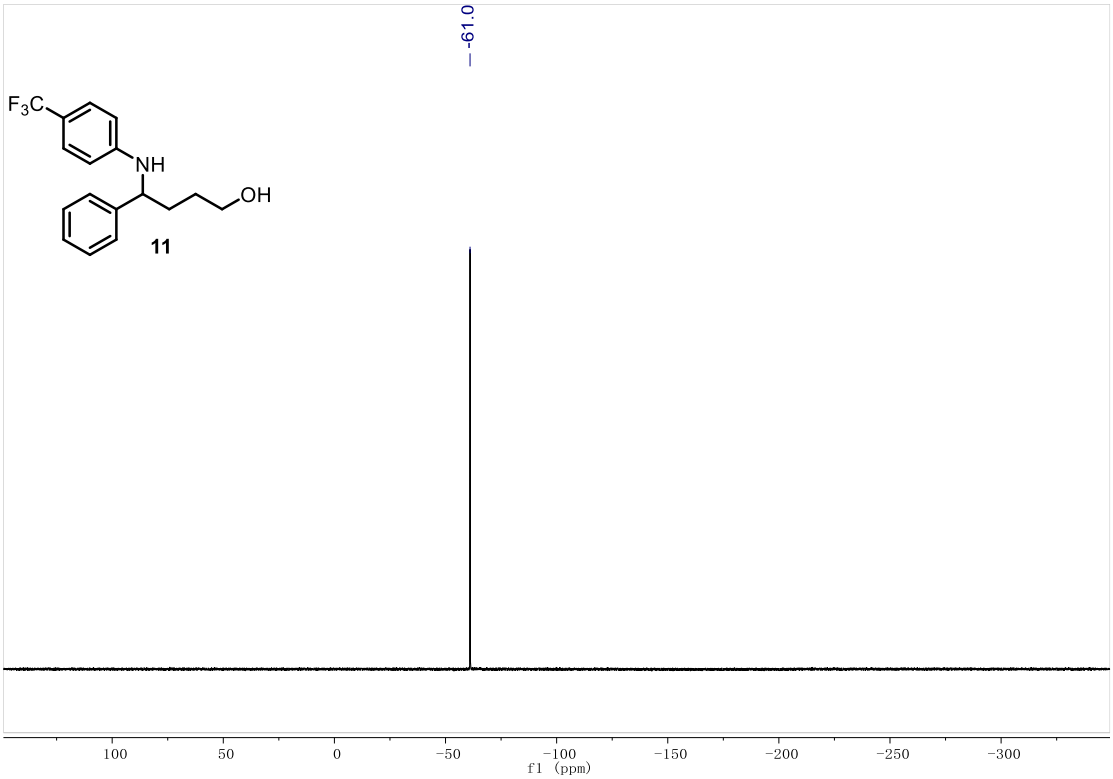

$^{1}$H NMR of compound **10** (400 MHz, $CDCl_3$)



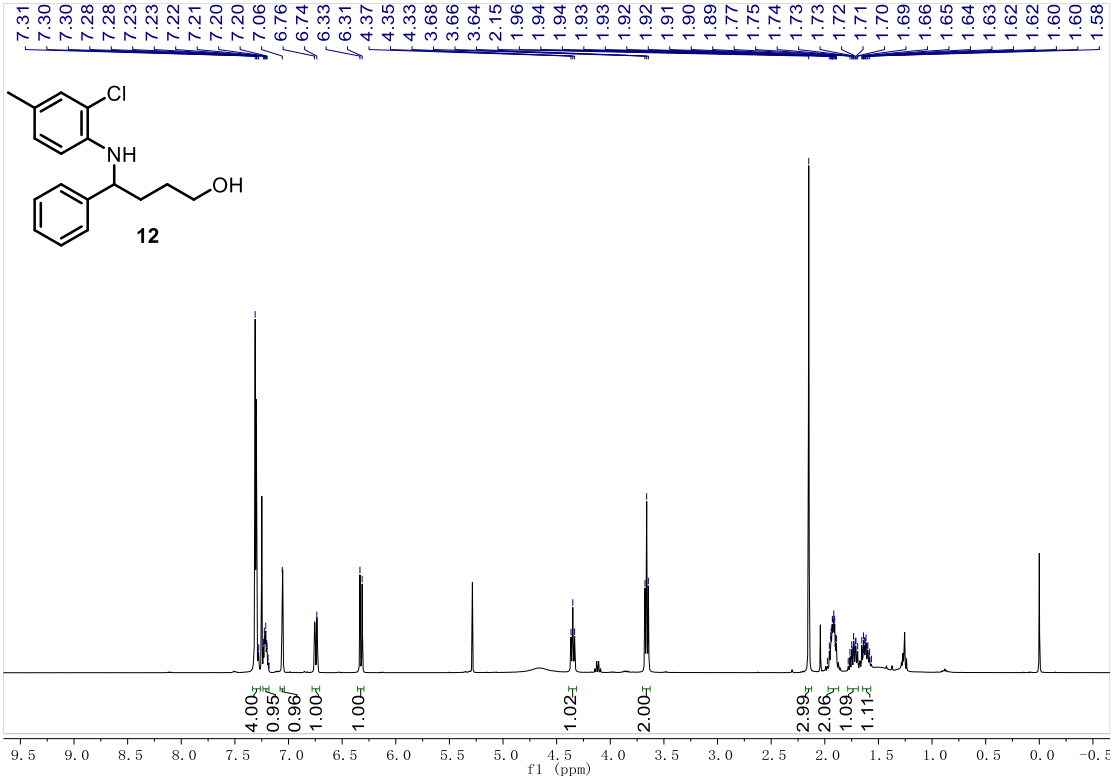

$^{1}$H NMR of compound **11** (400 MHz, $CDCl_3$)



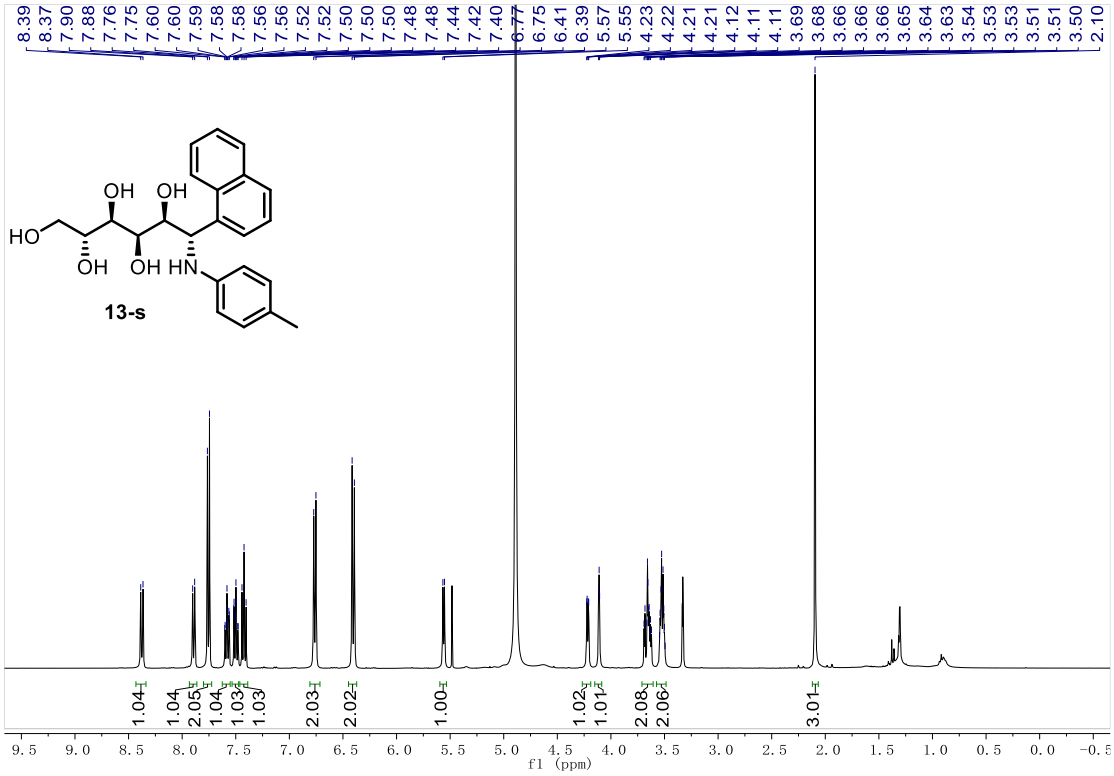

$^{13}$C NMR of compound **11** (101 MHz, $CDCl_3$)



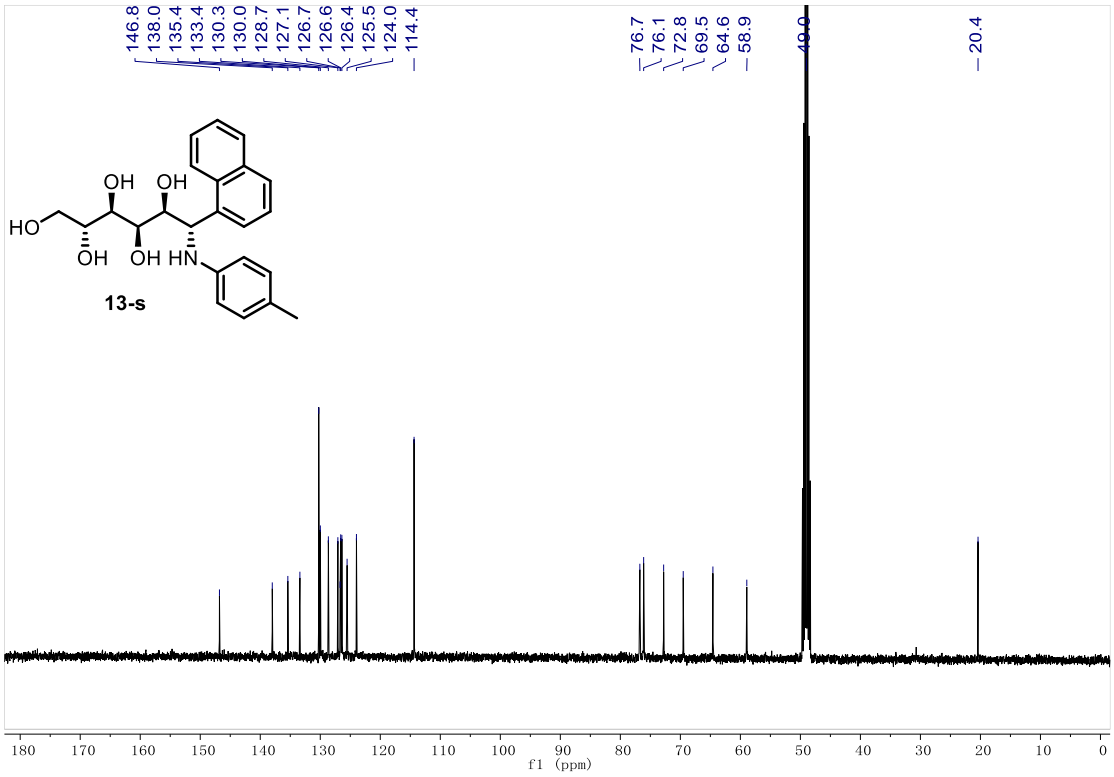

$^{19}$F NMR of compound **11** (376 MHz, $CDCl_3$)



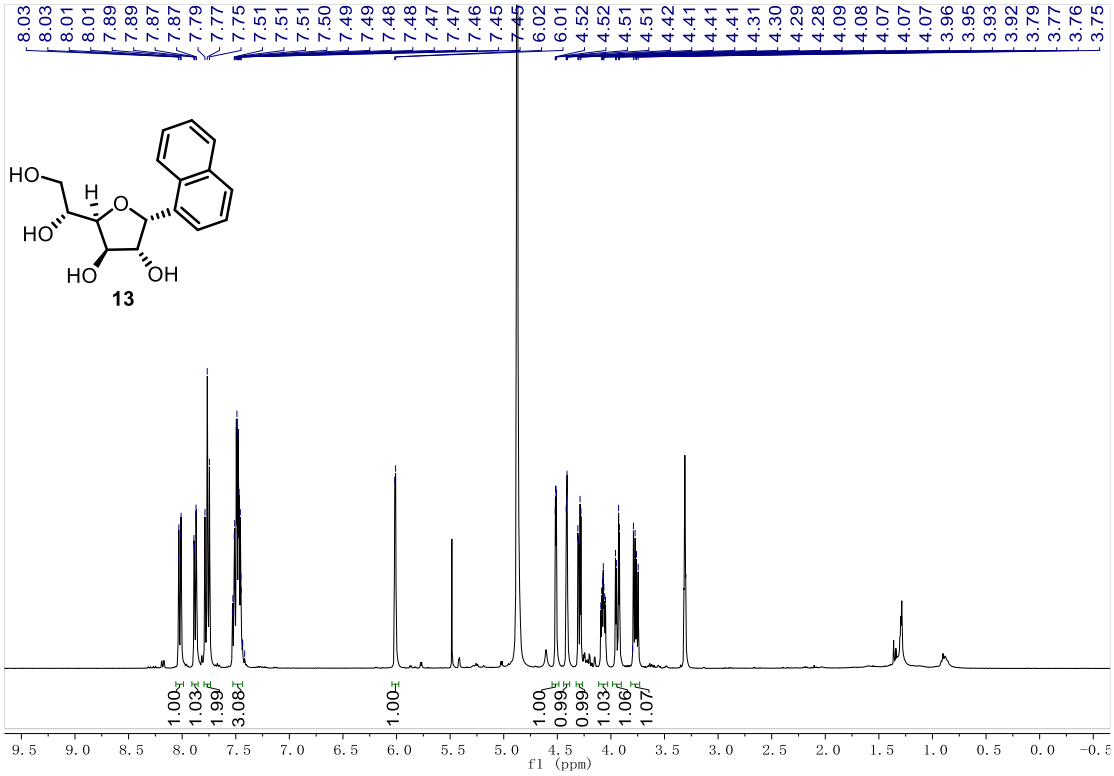

$^{1}$H NMR of compound **12** (400 MHz, $CDCl_3$)



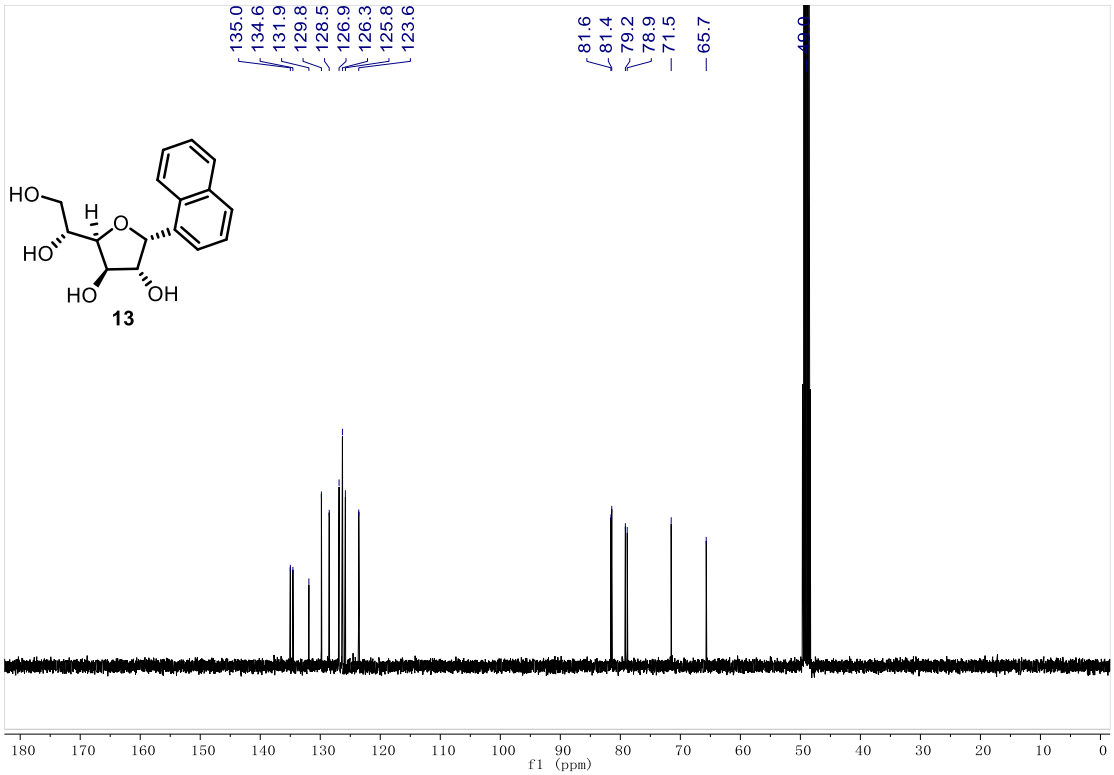

$^{1}$H NMR of compound **13-s** (400 MHz, $CD_3OD$)



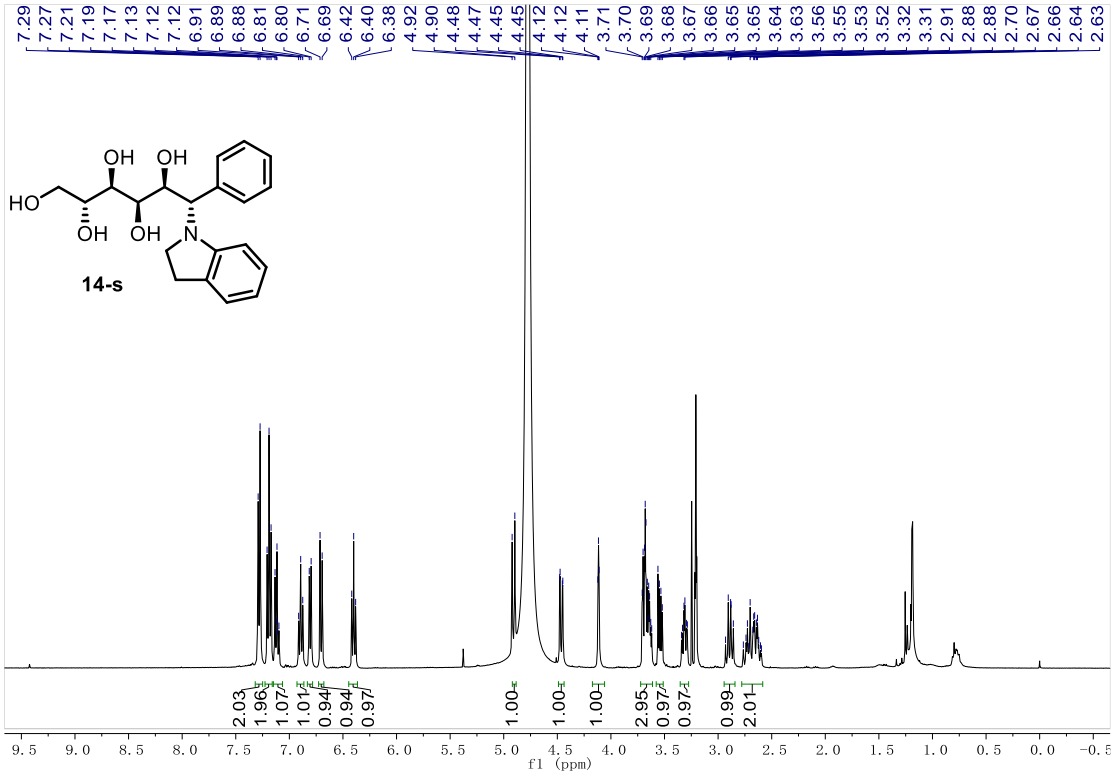

$^{13}$C NMR of compound **13-s** (101 MHz, $CD_3OD$)



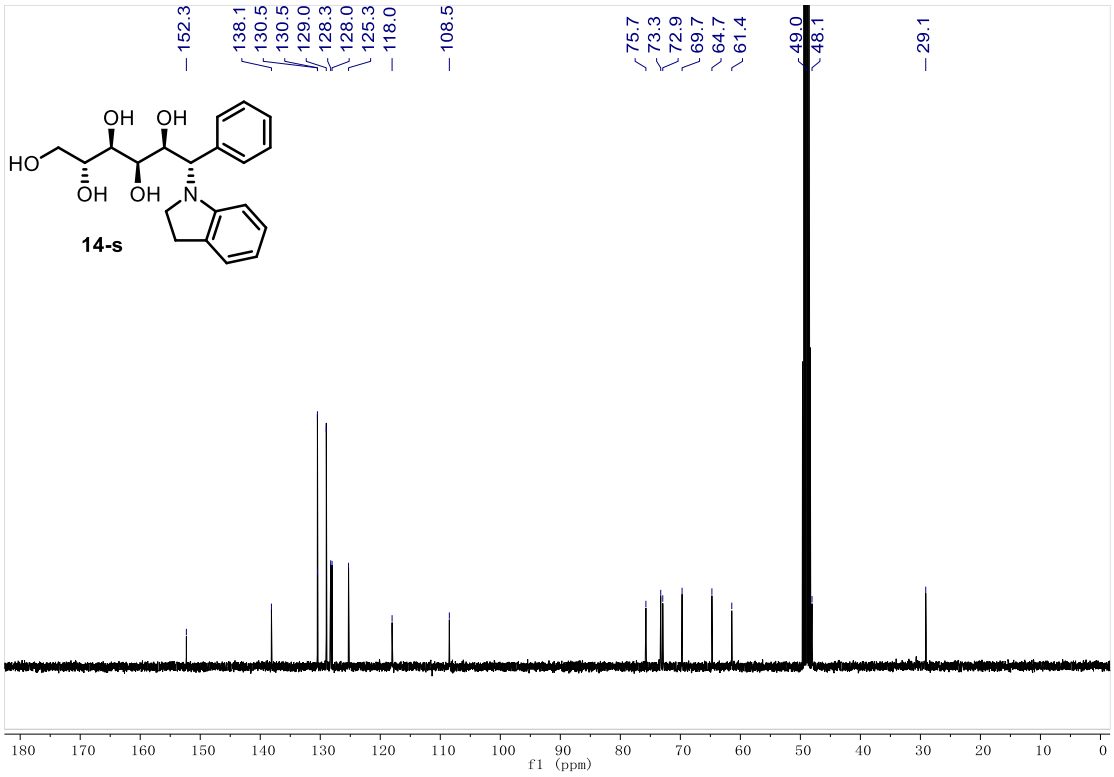

$^{1}$H NMR of compound **13** (400 MHz, $CD_3OD$)



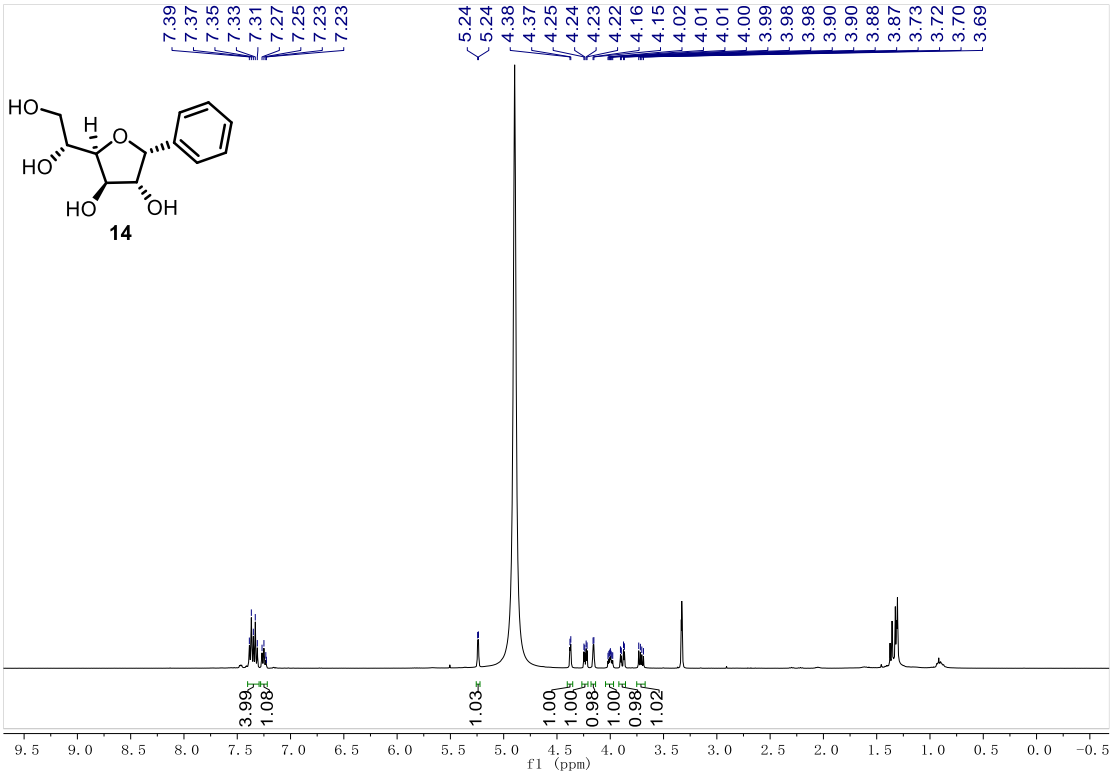

$^{13}$C NMR of compound **13** (101 MHz, $CD_3OD$)



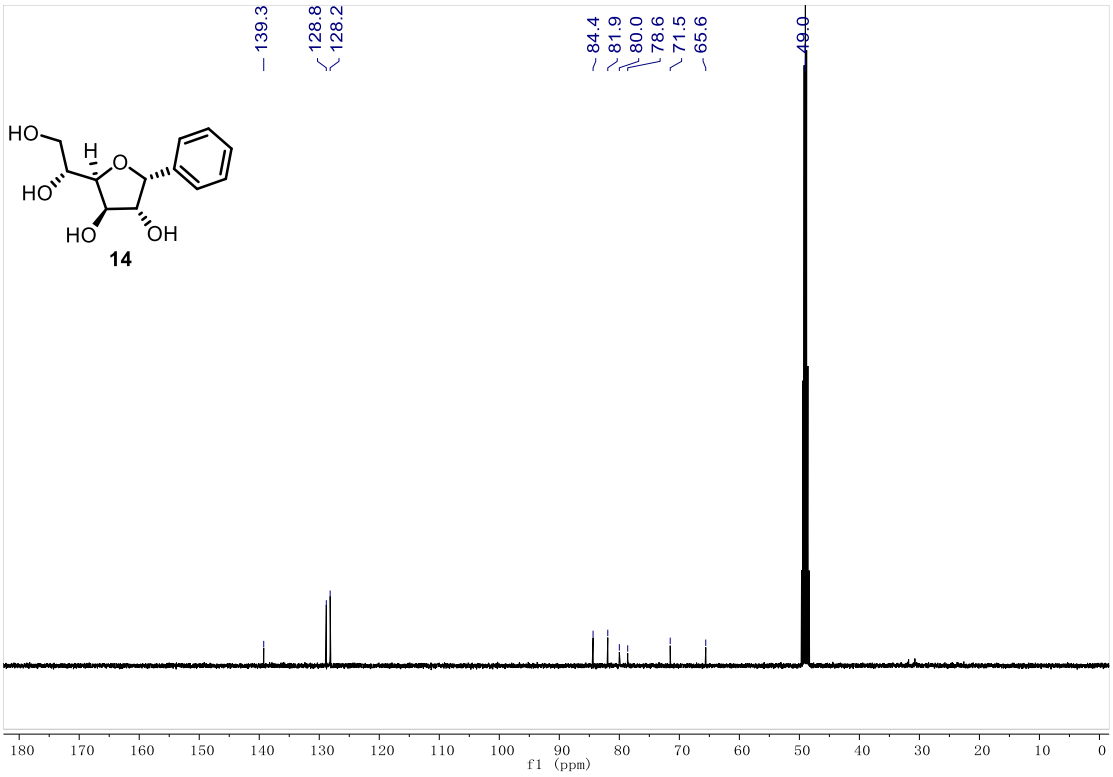

$^{1}$H NMR of compound **14-s** (400 MHz, $CD_3OD$)



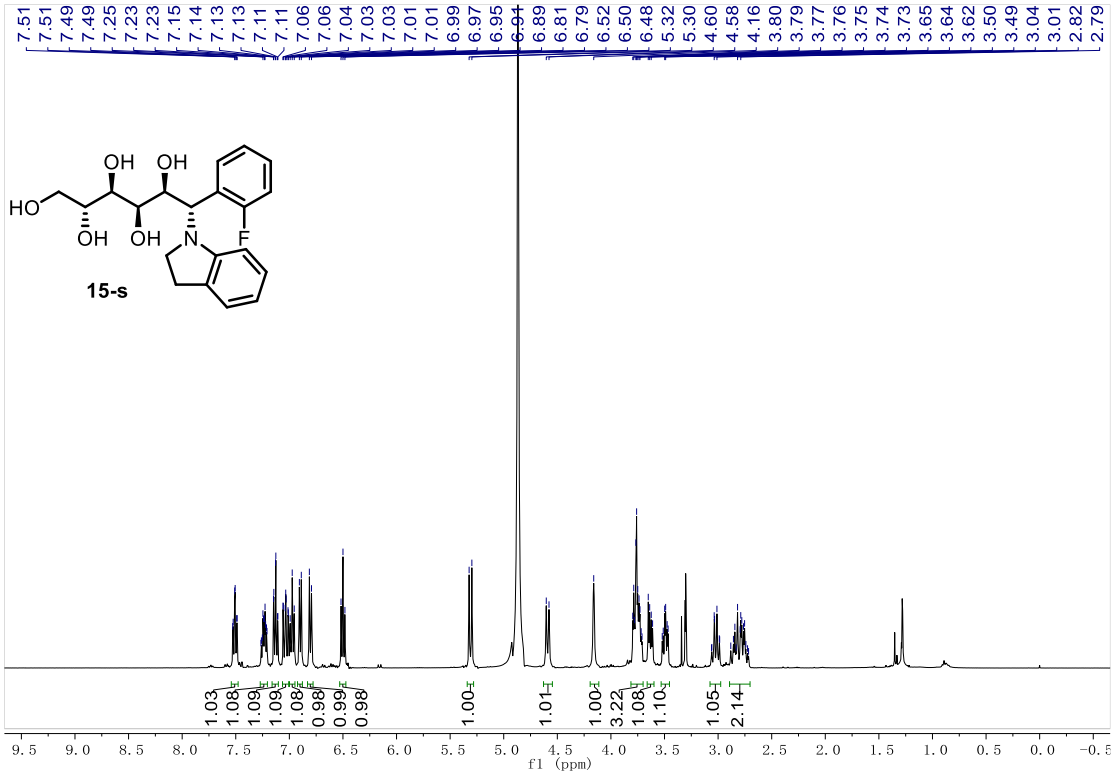

$^{13}$C NMR of compound **14-s** (101 MHz, $CD_3OD$)



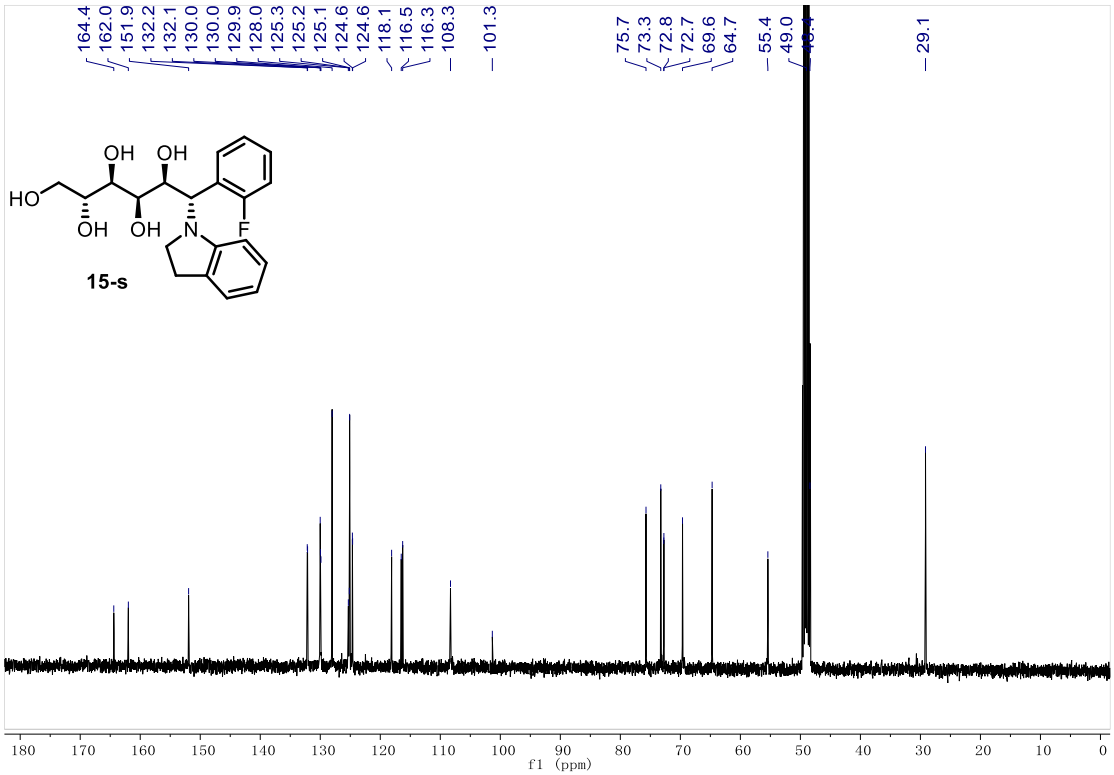

$^{1}$H NMR of compound **14** (400 MHz, $CD_3OD$)



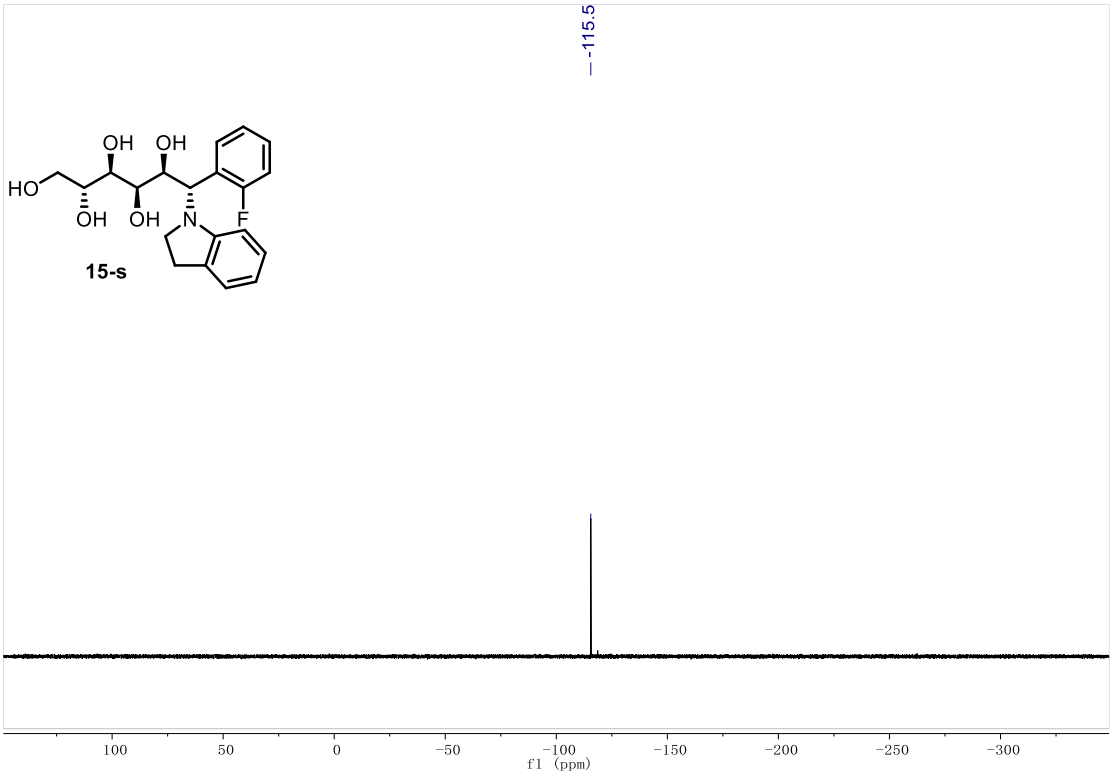

$^{13}$C NMR of compound **14** (101 MHz, $CD_3OD$)



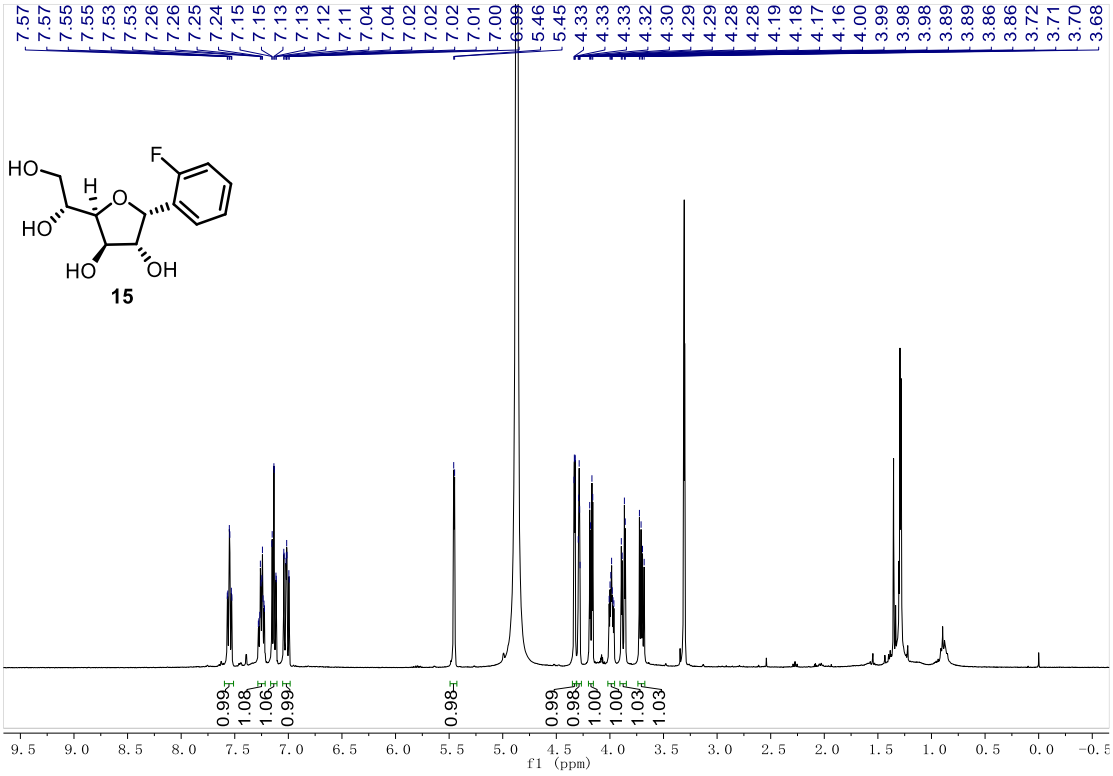

$^{1}$H NMR of compound **15-s** (400 MHz, $CD_3OD$)



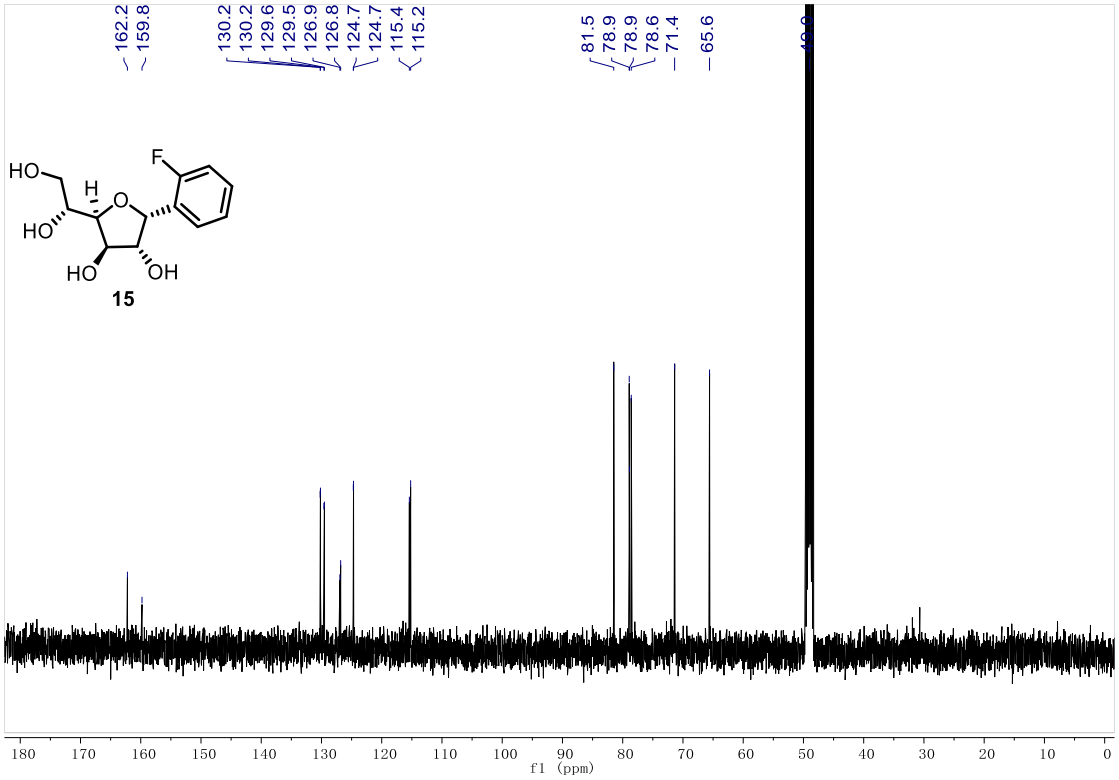

$^{13}$C NMR of compound **15-s** (101 MHz, $CD_3OD$)



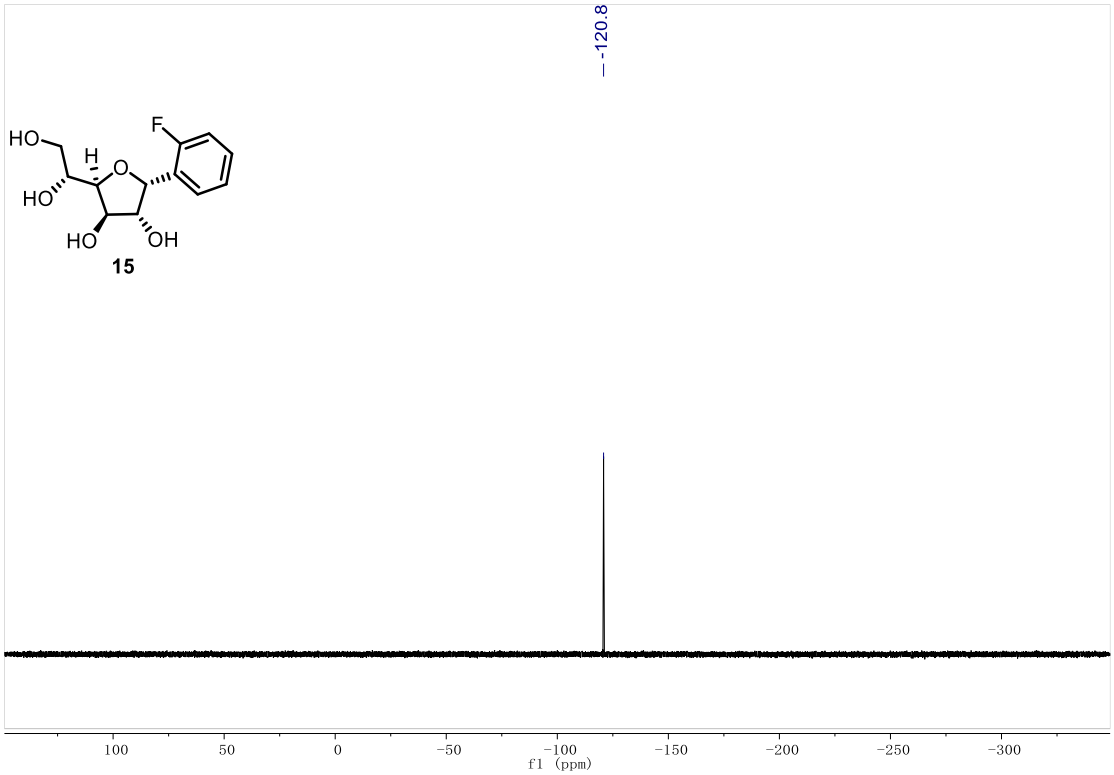

$^{19}$F NMR of compound **15-s** (376 MHz, $CD_3OD$)



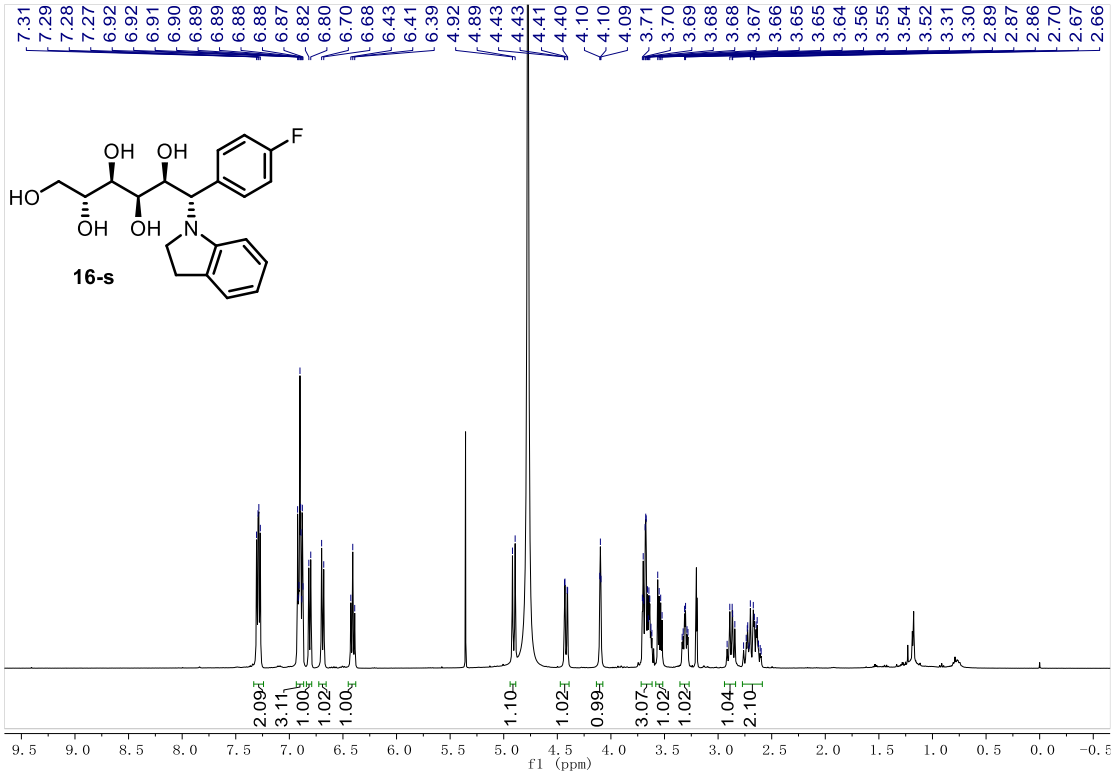

$^{1}$H NMR of compound **15** (400 MHz, $CD_3OD$)



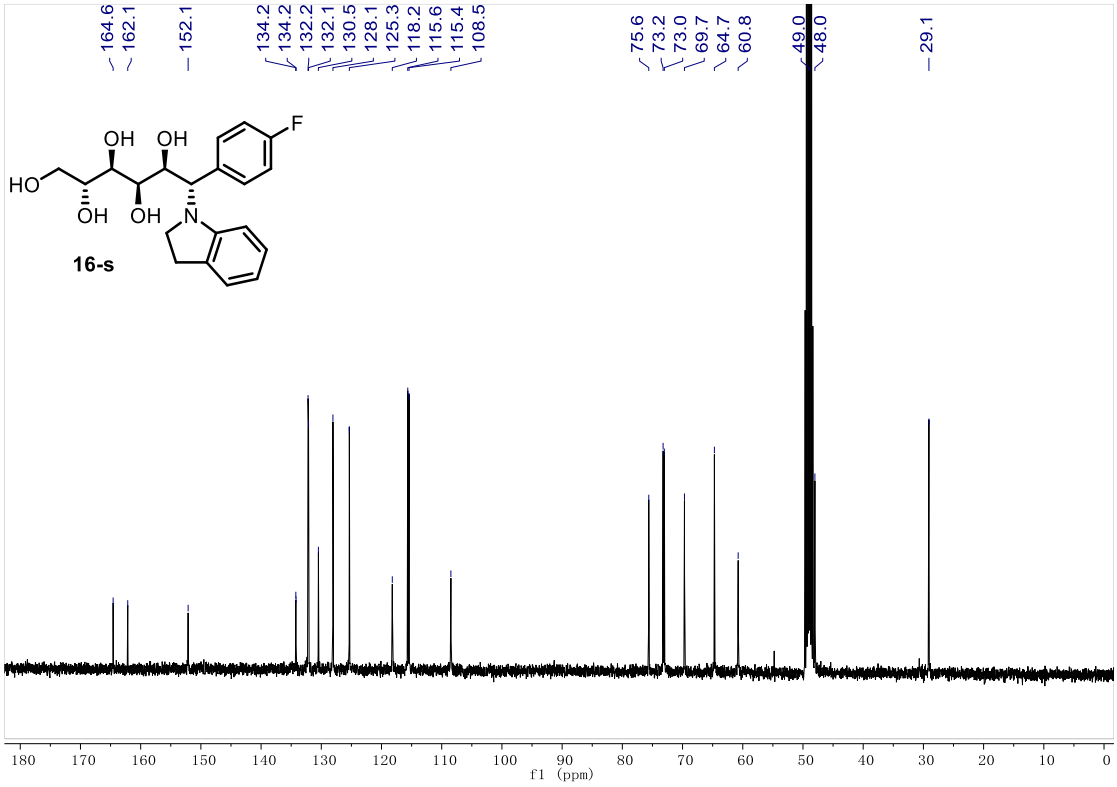

$^{13}$C NMR of compound **15** (101 MHz, $CD_3OD$)



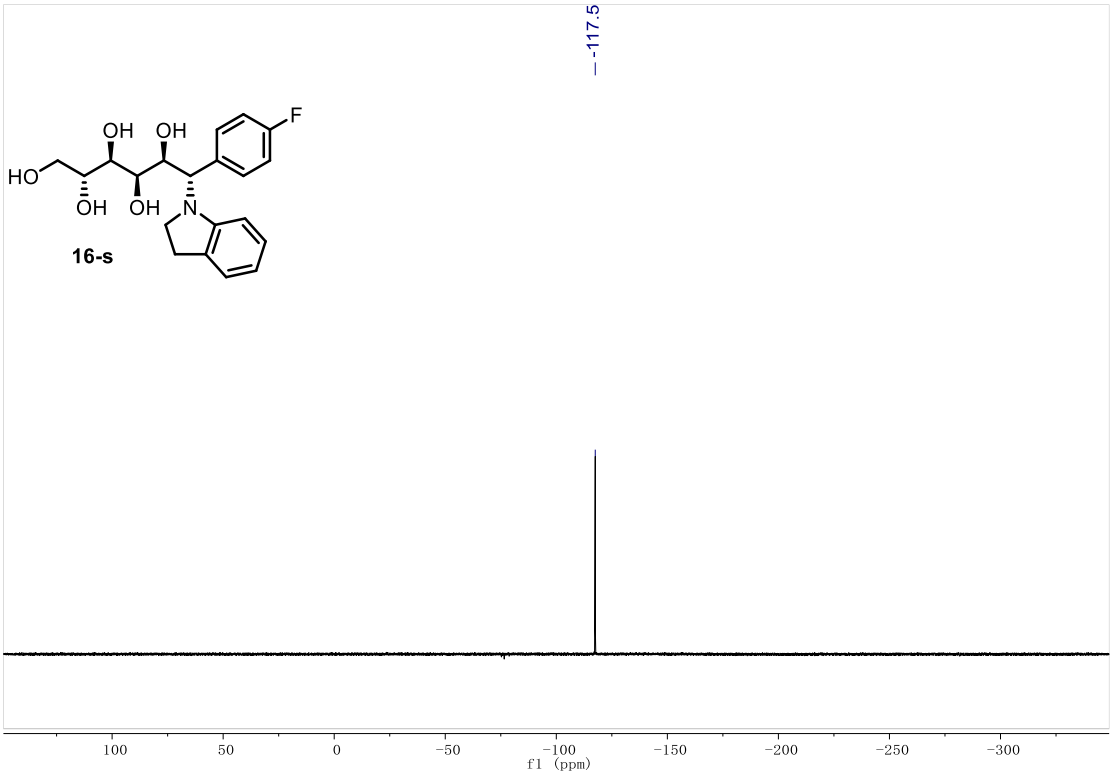

$^{19}$F NMR of compound **15** (376 MHz, $CD_3OD$)



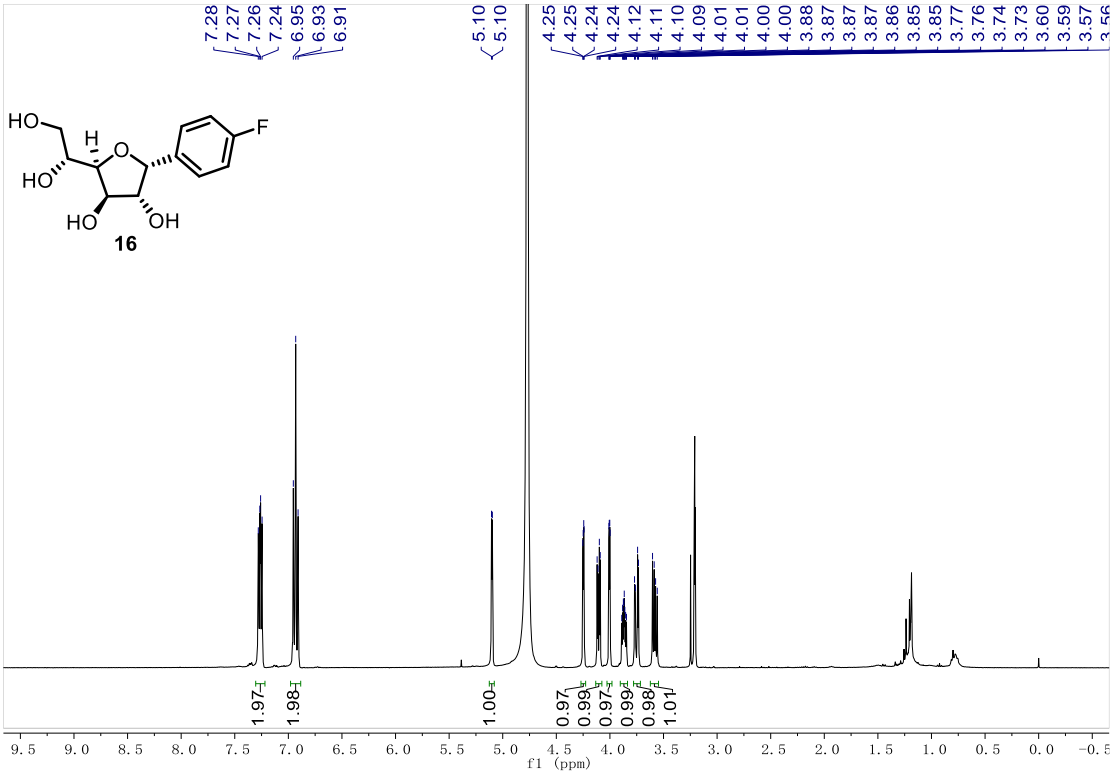

$^{1}$H NMR of compound **16-s** (400 MHz, $CD_3OD$)



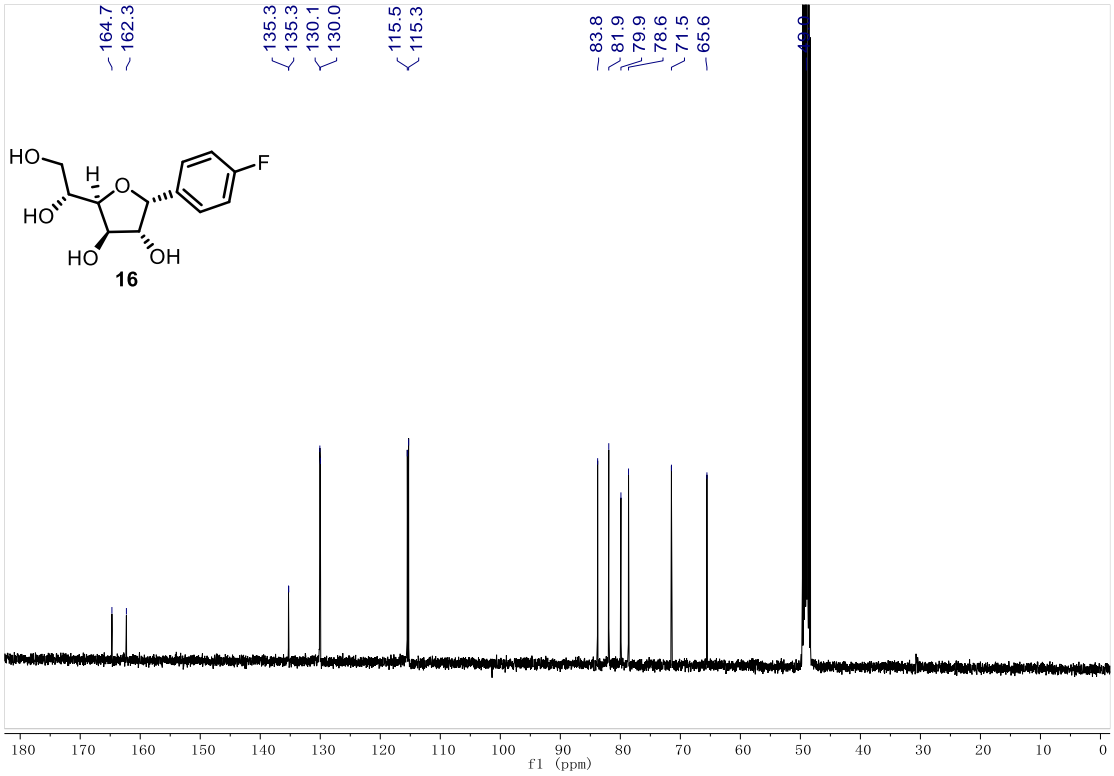

$^{13}$C NMR of compound **16-s** (101 MHz, $CD_3OD$)



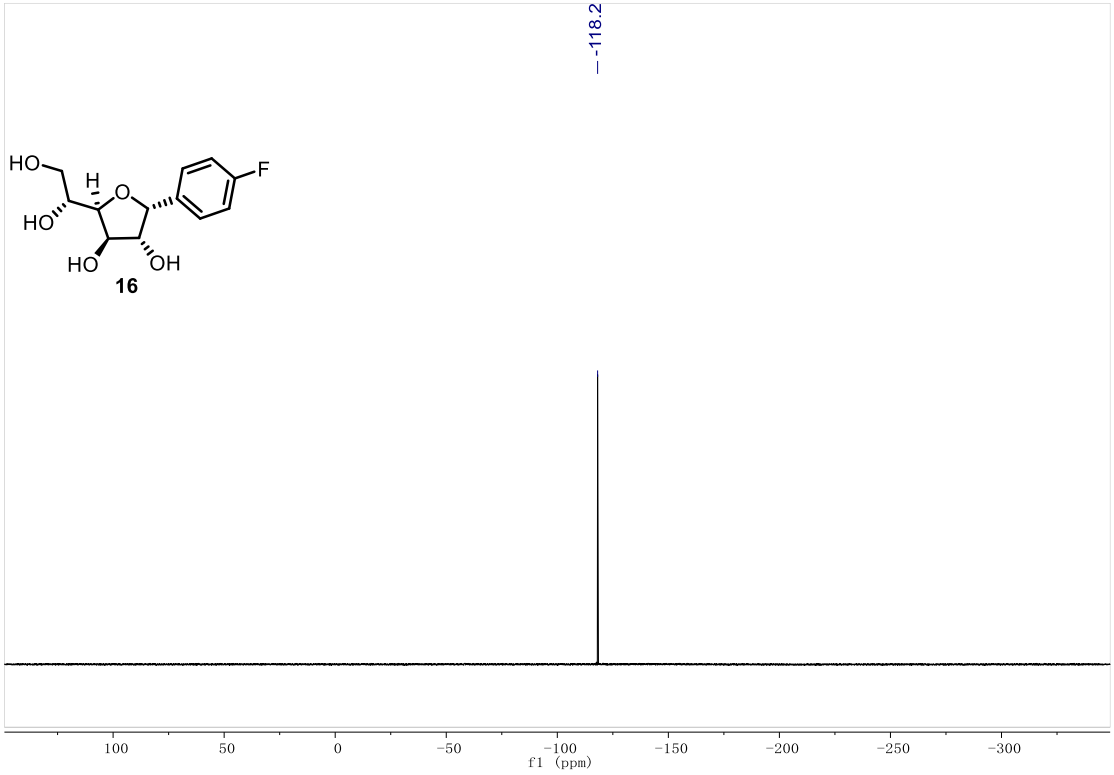

$^{19}$F NMR of compound **16-s** (376 MHz, $CD_3OD$)



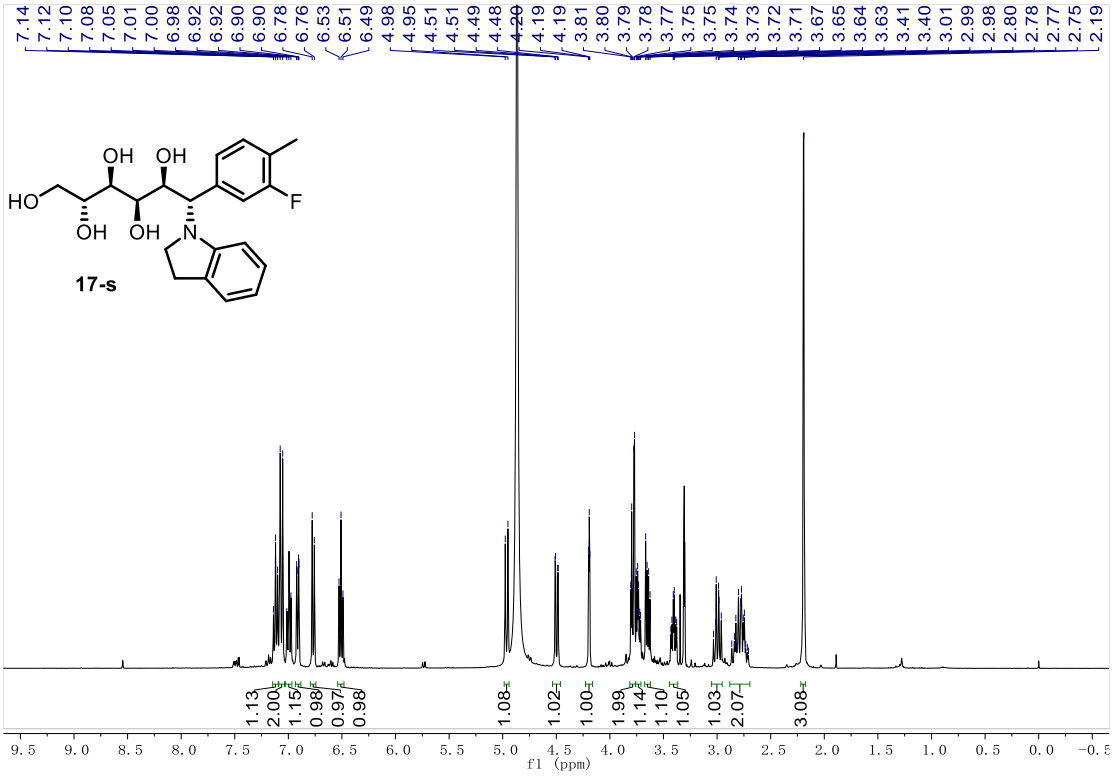

$^{1}$H NMR of compound **16** (400 MHz, $CD_3OD$)



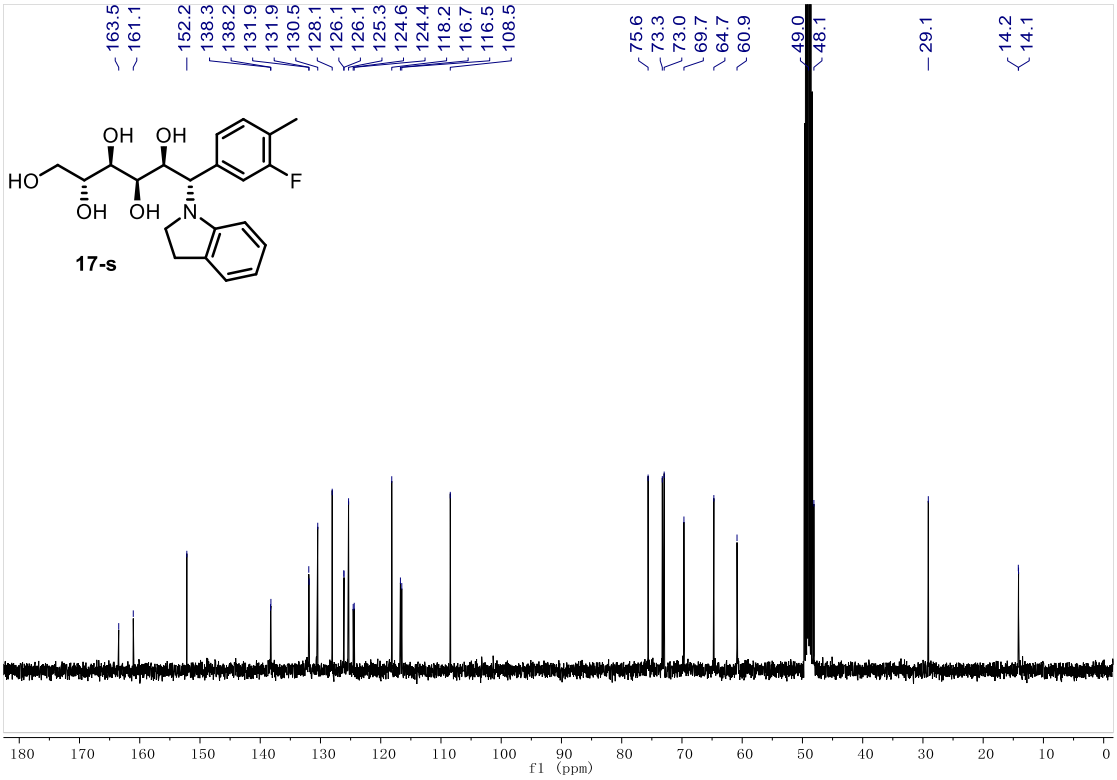

$^{13}$C NMR of compound **16** (101 MHz, $CD_3OD$)



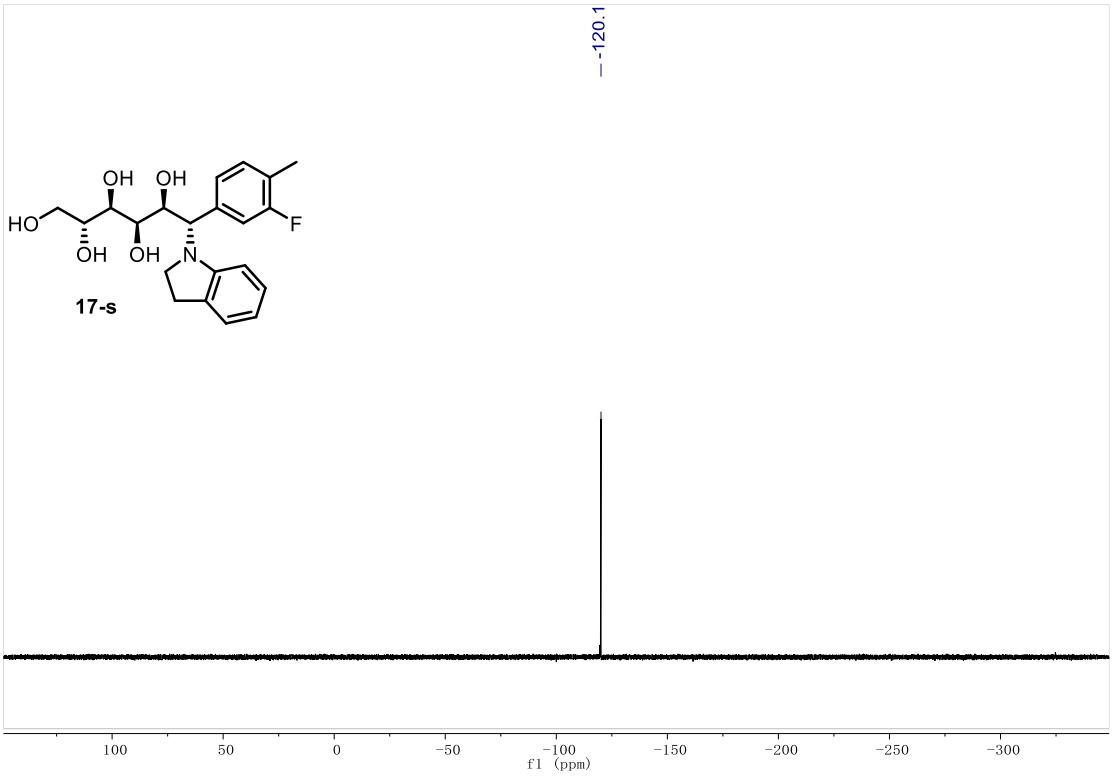

$^{19}$F NMR of compound **16** (376 MHz, $CD_3OD$)



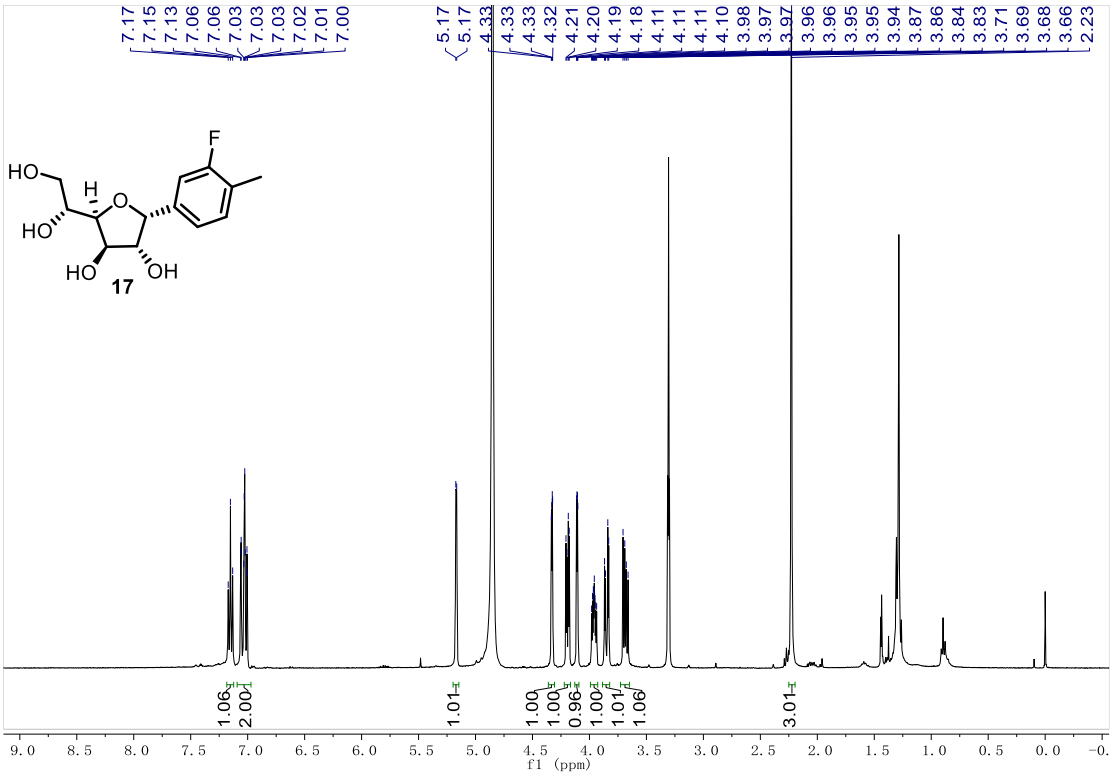

$^{1}$H NMR of compound **17-s** (400 MHz, $CD_3OD$)



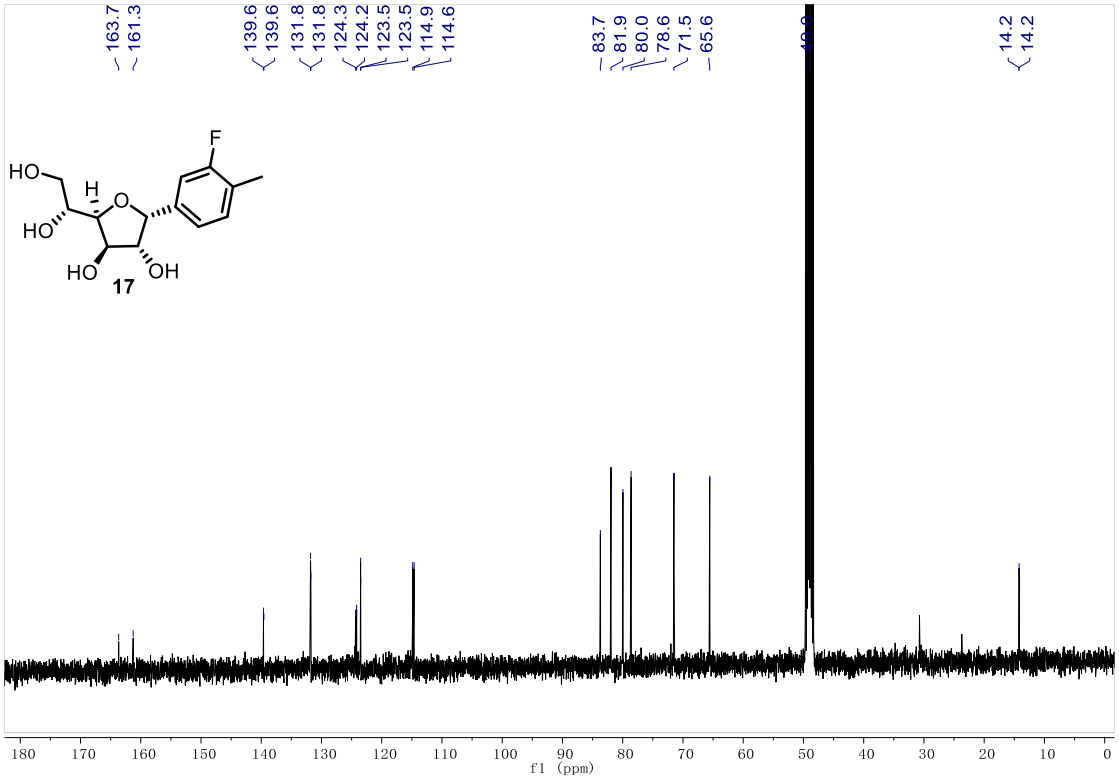

$^{13}$C NMR of compound **17-s** (101 MHz, $CD_3OD$)



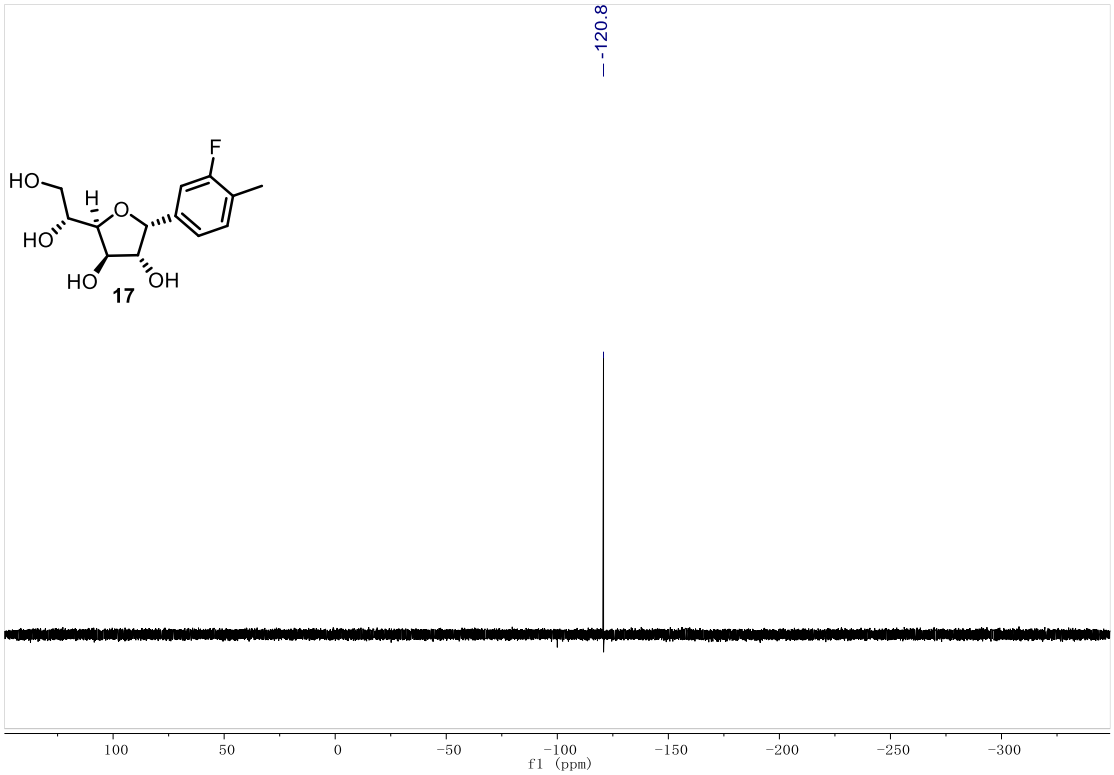

$^{19}$F NMR of compound **17-s** (376 MHz, $CD_3OD$)



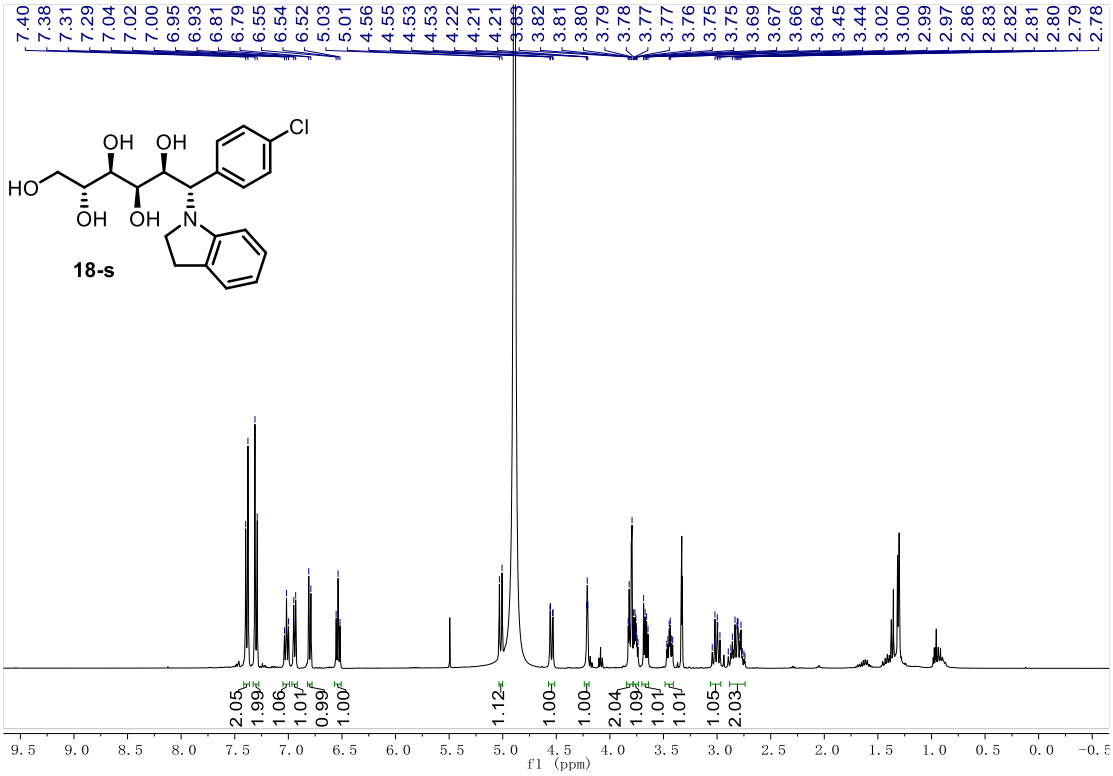

$^{1}$H NMR of compound **17** (400 MHz, $CD_3OD$)



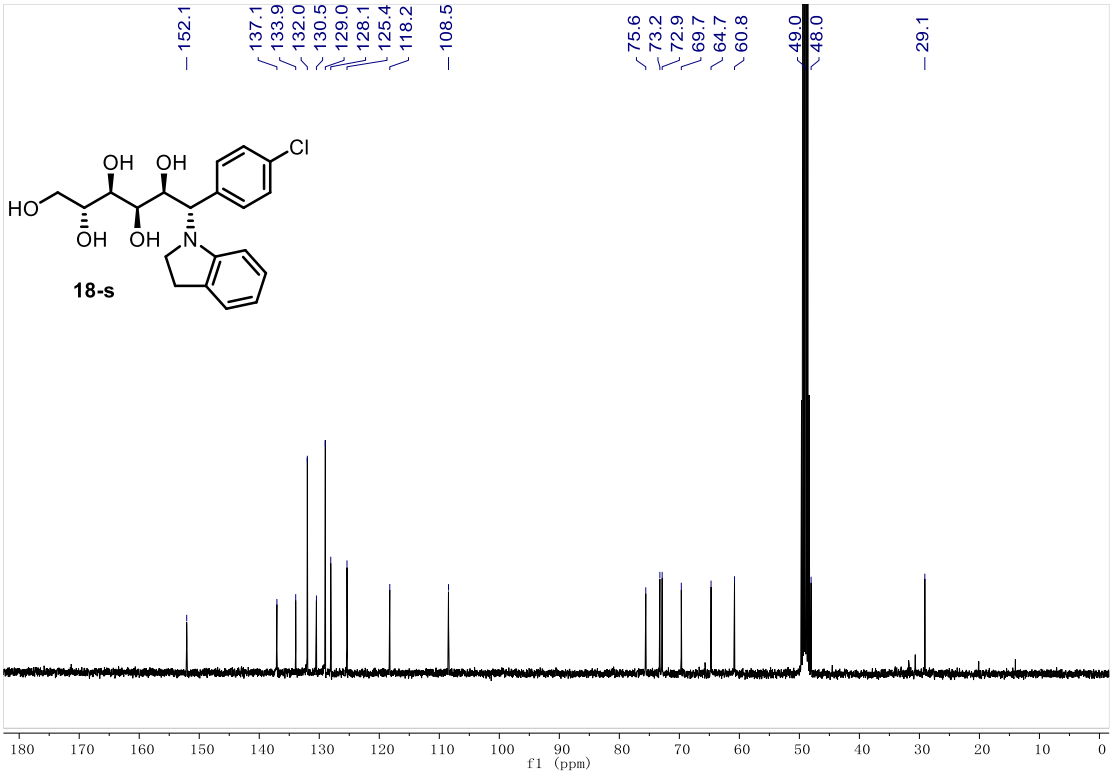

$^{13}$C NMR of compound **17** (101 MHz, $CD_3OD$)



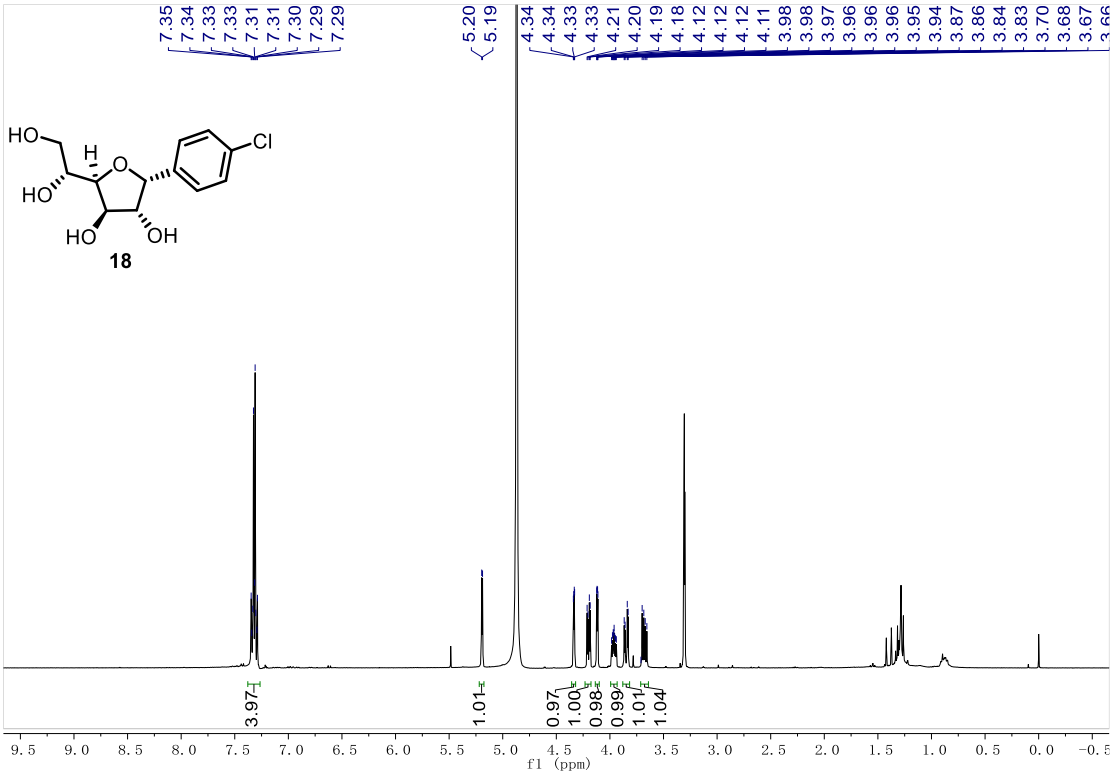

$^{19}$F NMR of compound **17** (376 MHz, $CD_3OD$)



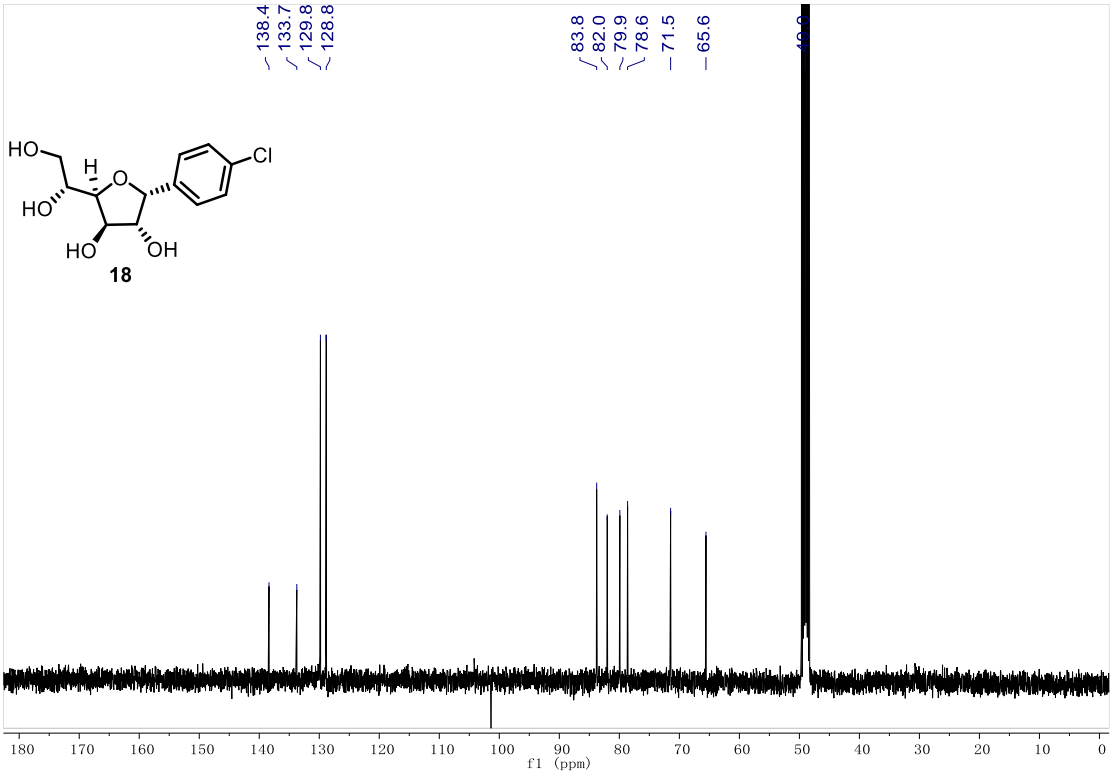

$^{1}$H NMR of compound **18-s** (400 MHz, $CD_3OD$)



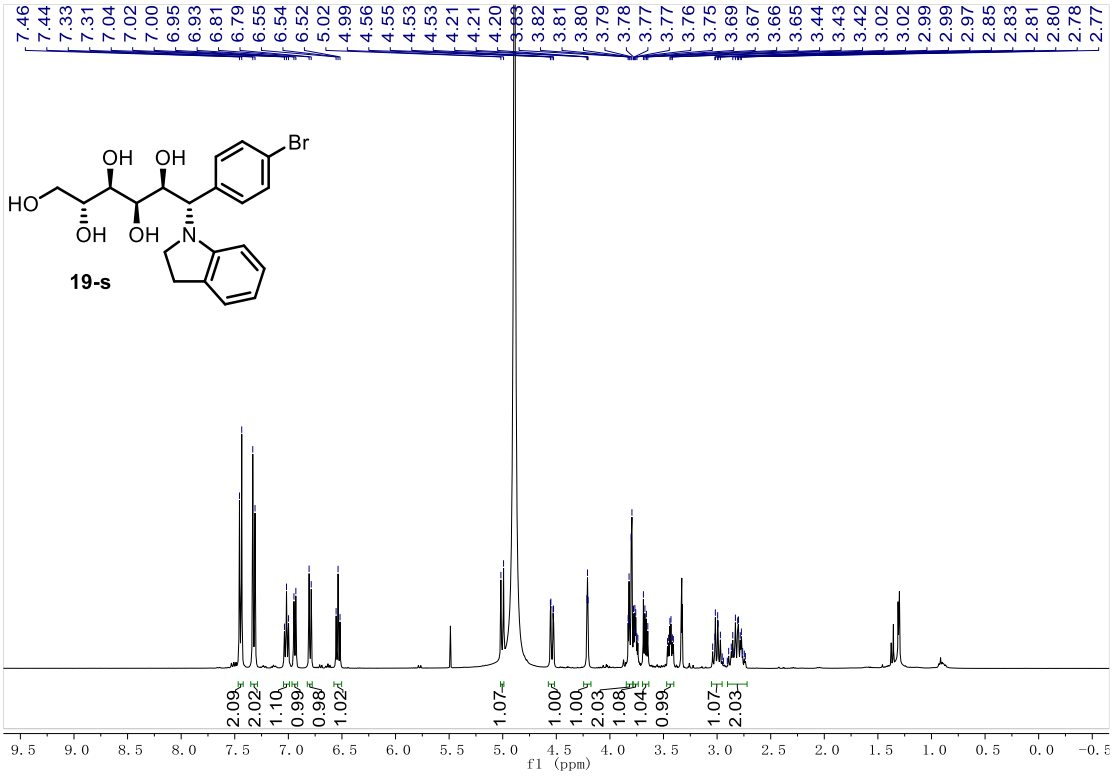

$^{13}$C NMR of compound **18-s** (101 MHz, $CD_3OD$)



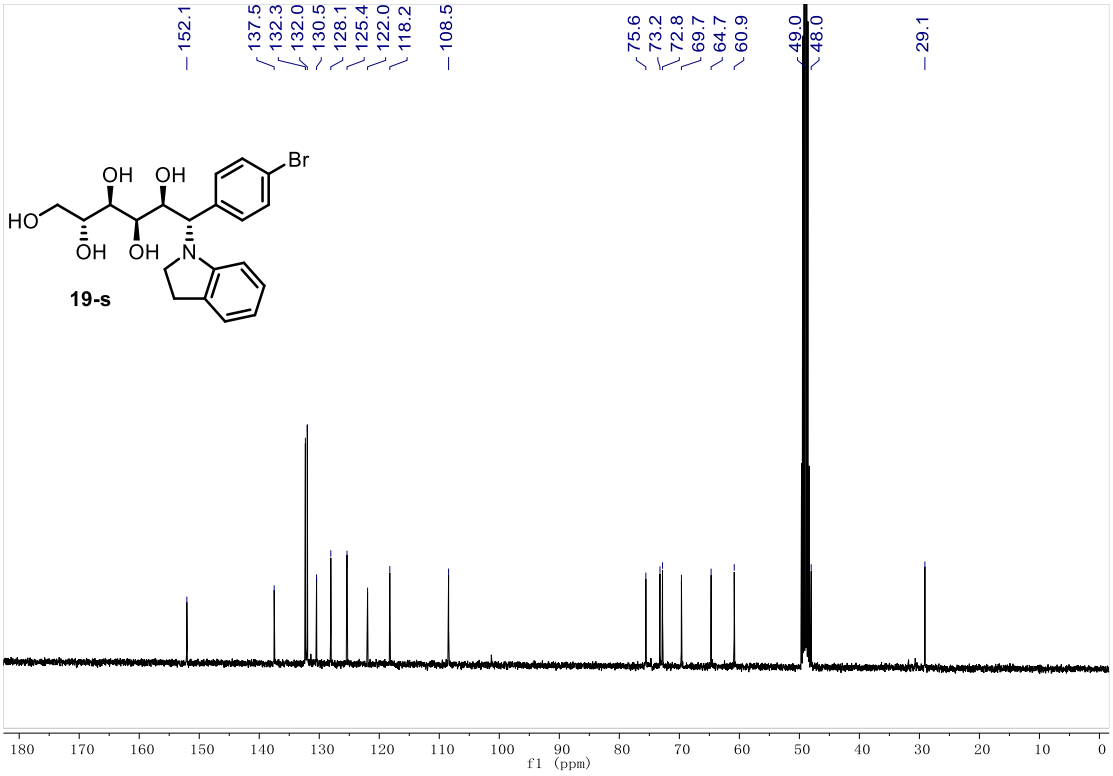

$^{1}$H NMR of compound **18** (400 MHz, $CD_3OD$)



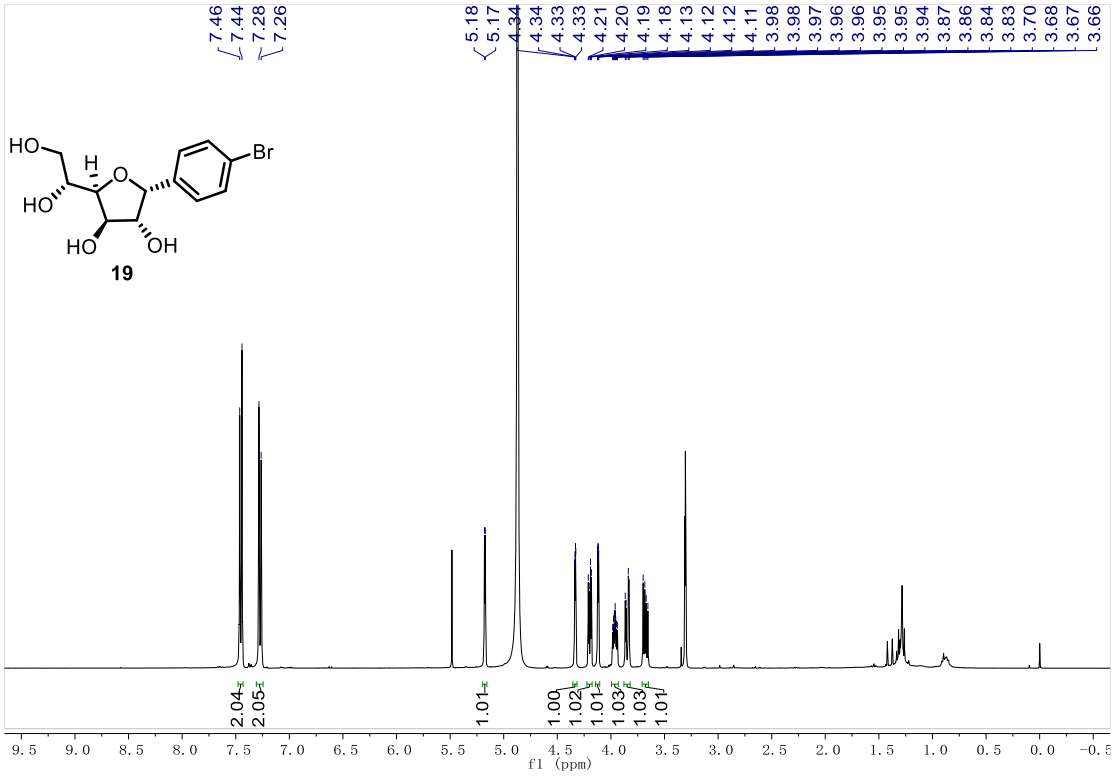

$^{13}$C NMR of compound **18** (101 MHz, $CD_3OD$)



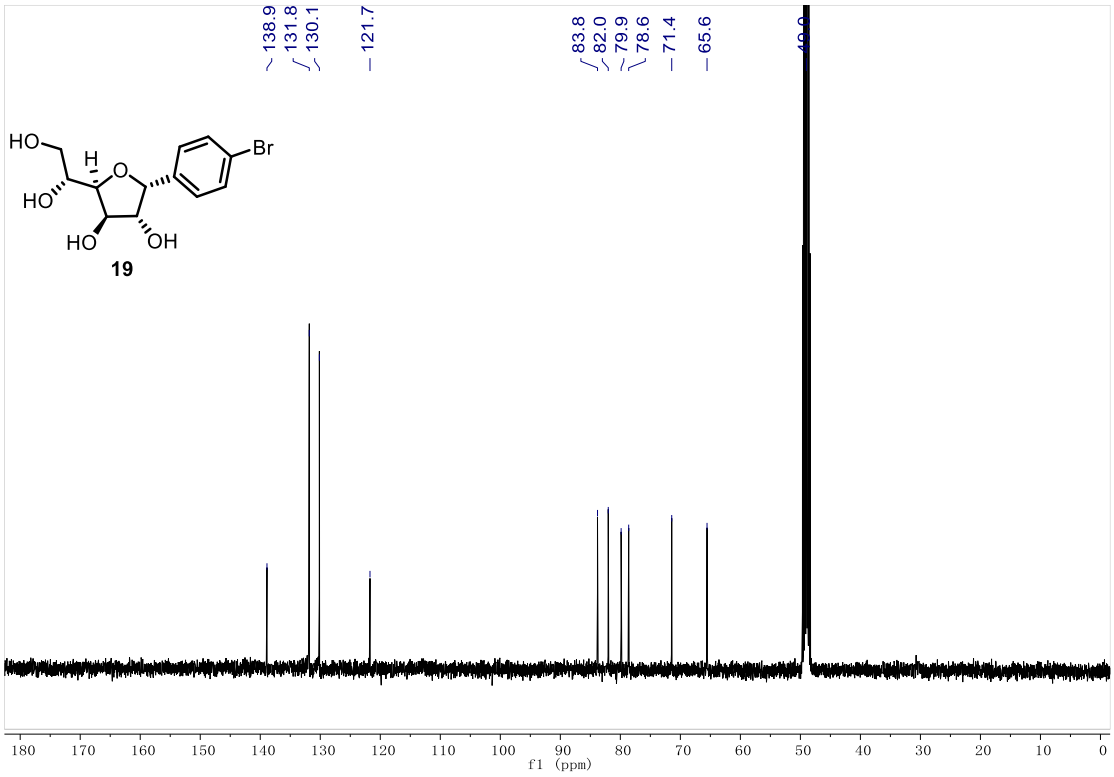

$^{1}$H NMR of compound **19-s** (400 MHz, $CD_3OD$)



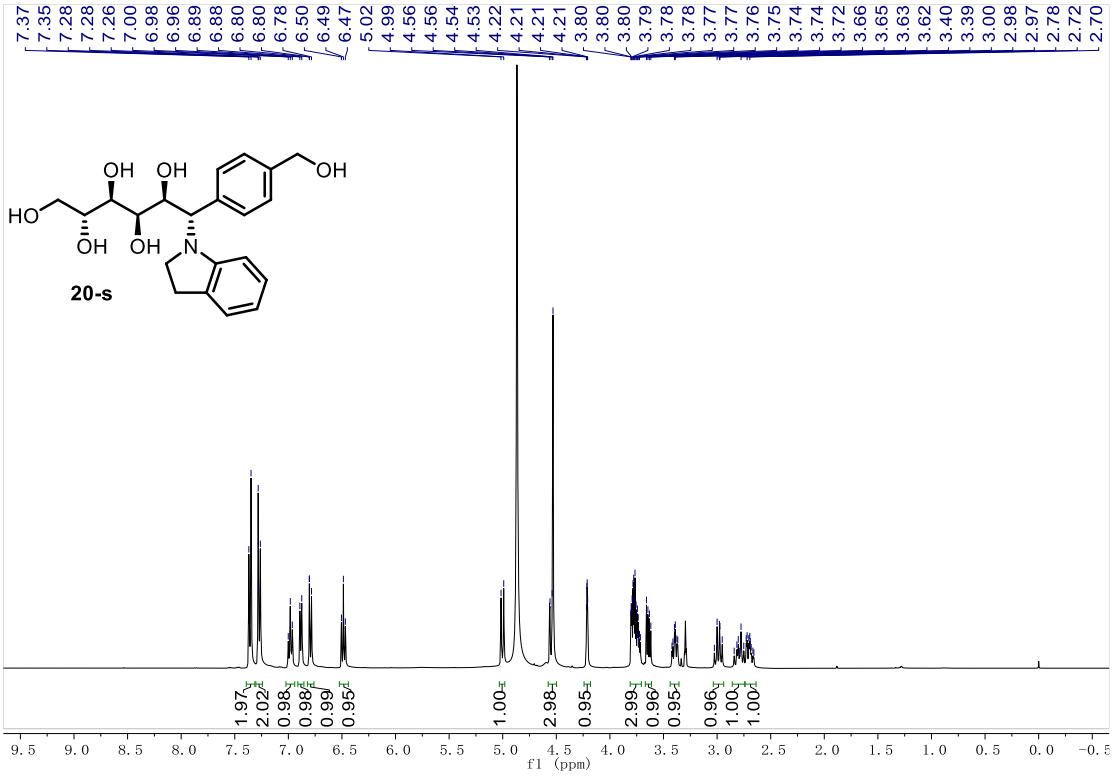

$^{13}$C NMR of compound **19-s** (101 MHz, $CD_3OD$)



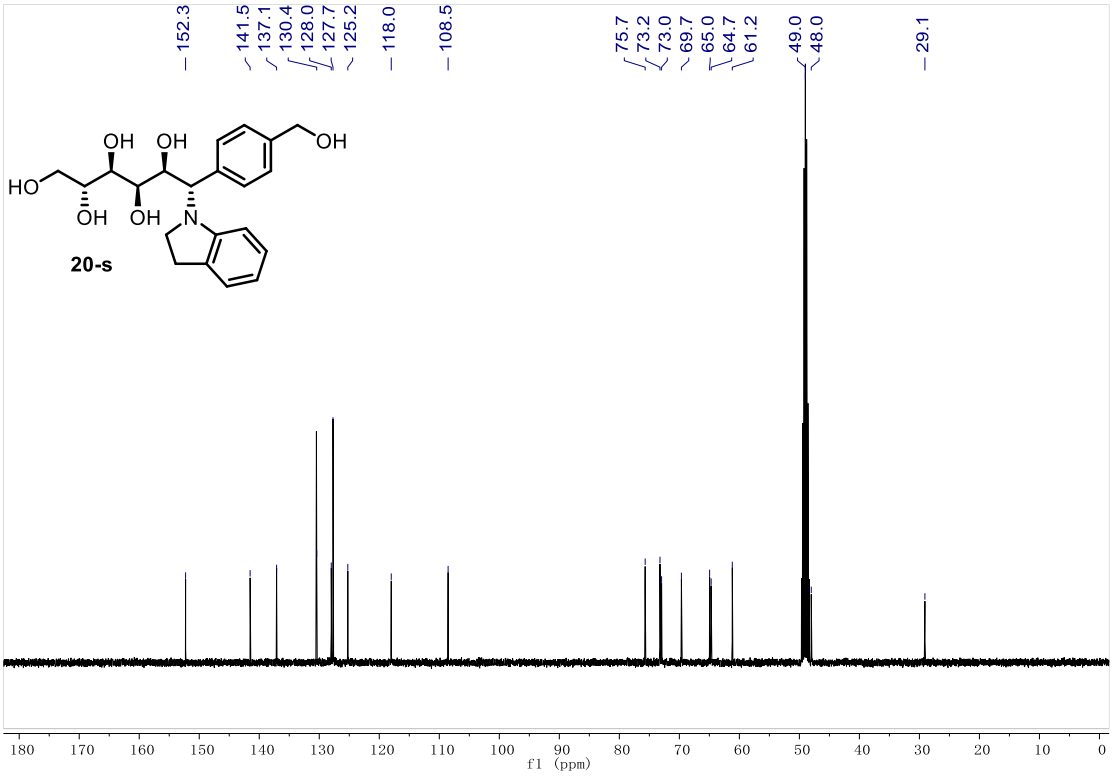

$^{1}$H NMR of compound **19** (400 MHz, $CD_3OD$)



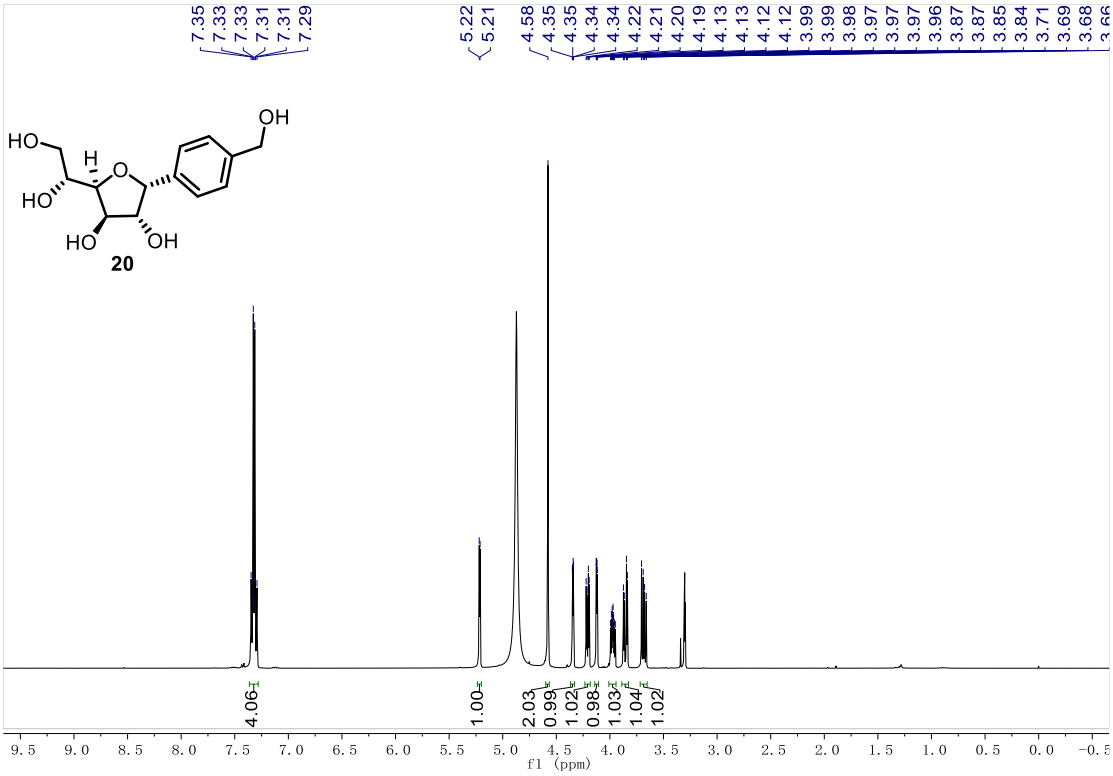

$^{13}$C NMR of compound **19** (101 MHz, $CD_3OD$)



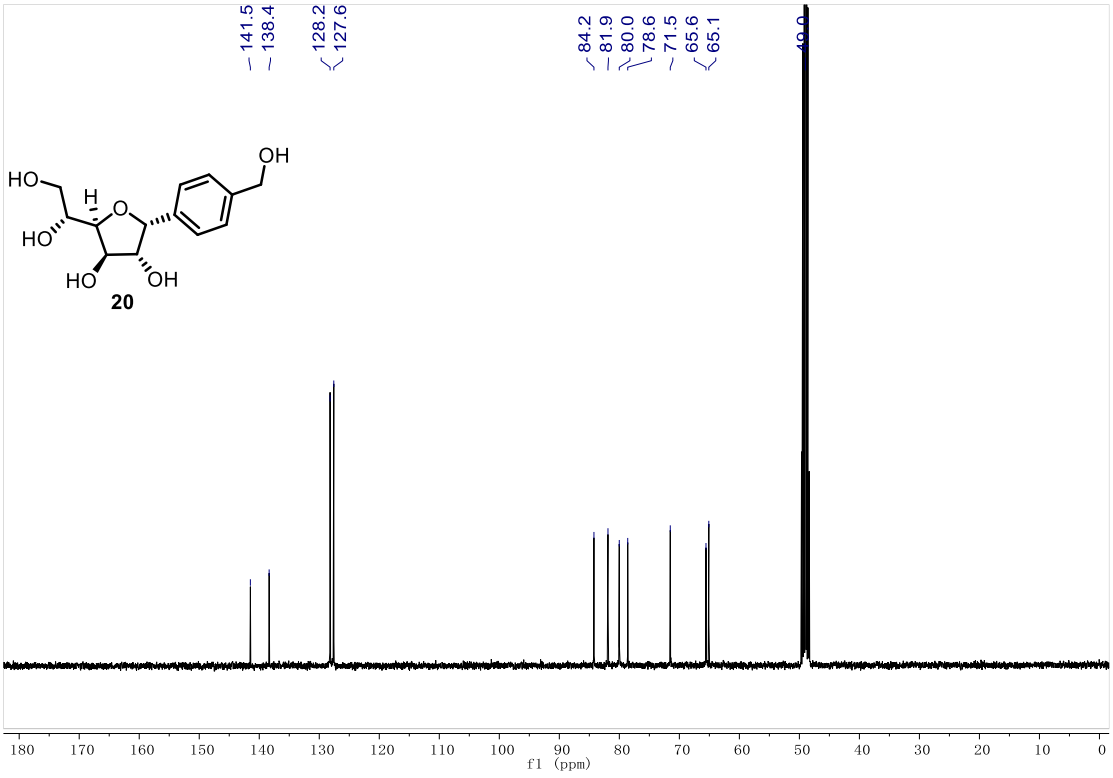

$^{1}$H NMR of compound **20-s** (400 MHz, $CD_3OD$)



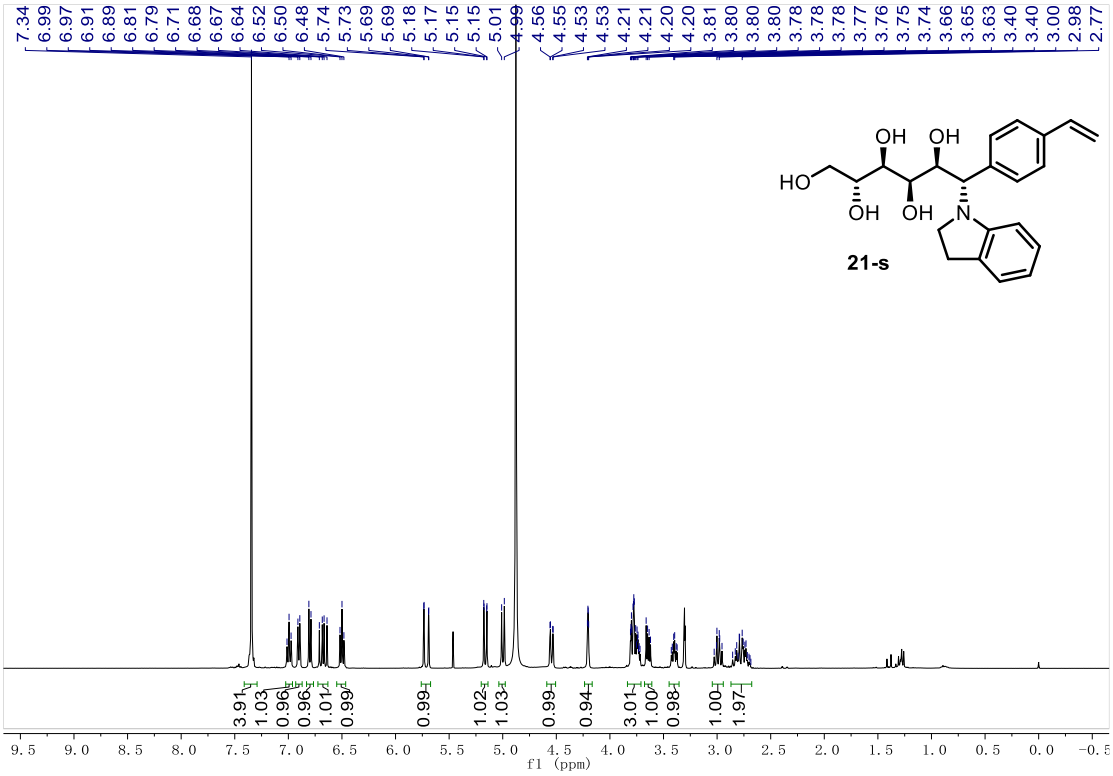

$^{13}$C NMR of compound **20-s** (101 MHz, $CD_3OD$)



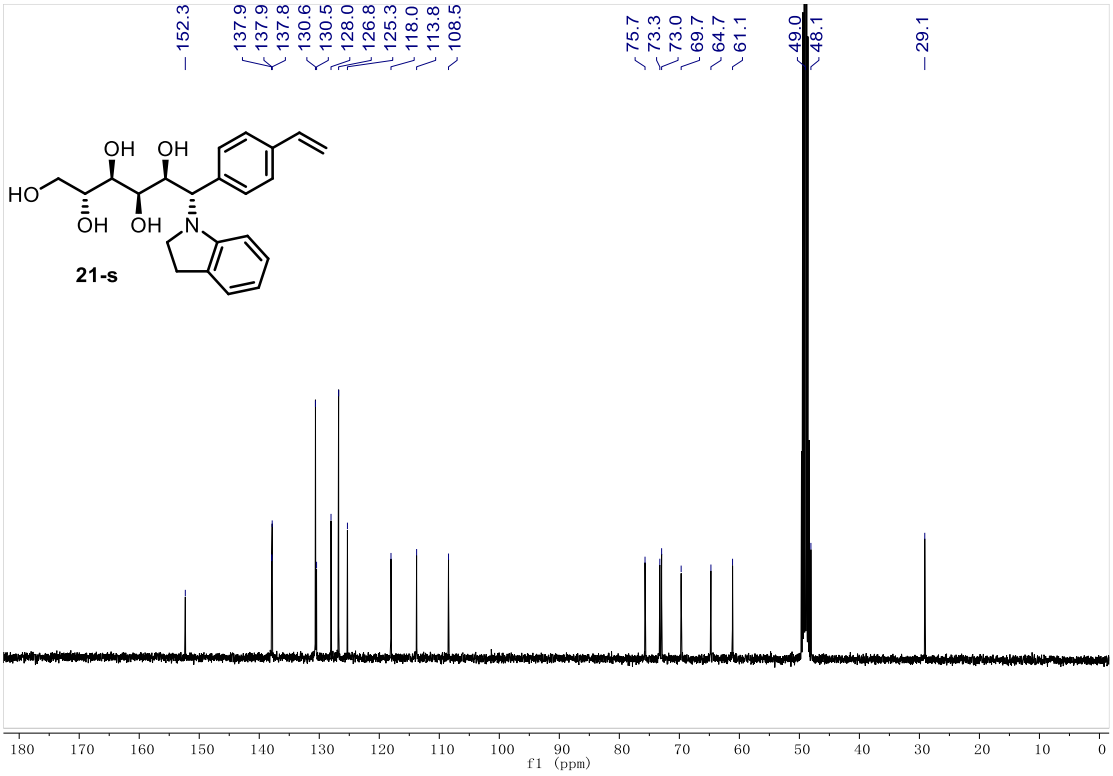

$^{1}$H NMR of compound **20** (400 MHz, $CD_3OD$)



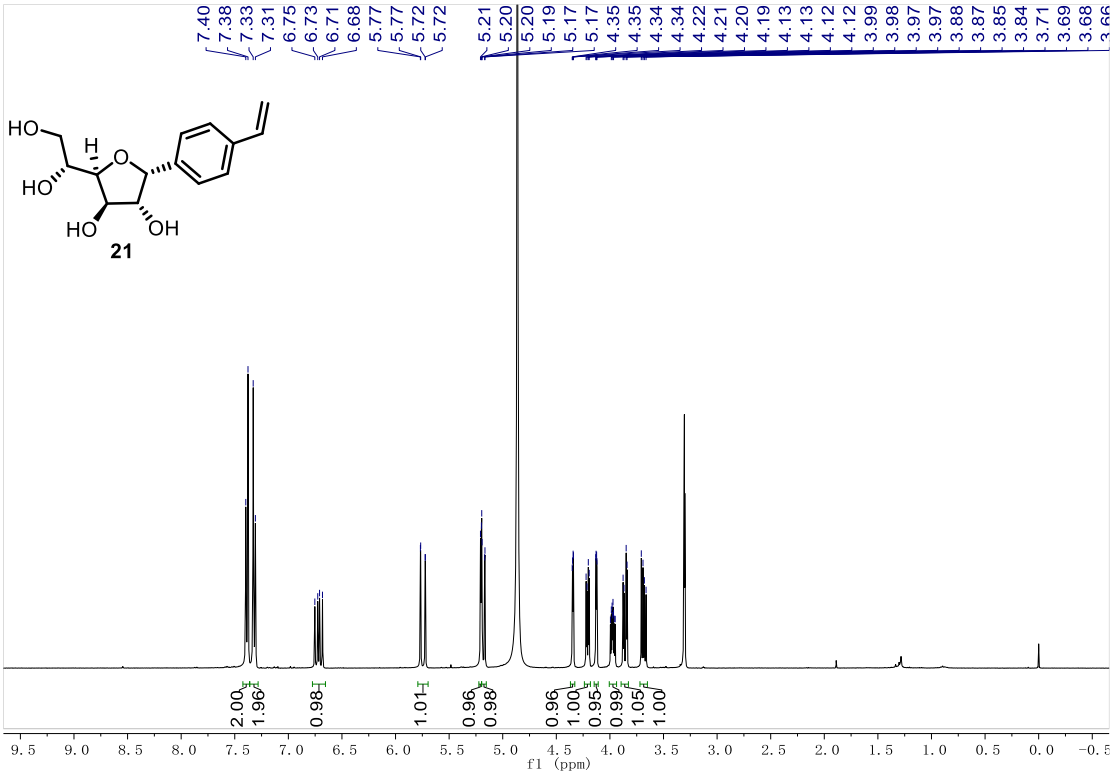

$^{13}$C NMR of compound **20** (101 MHz, $CD_3OD$)



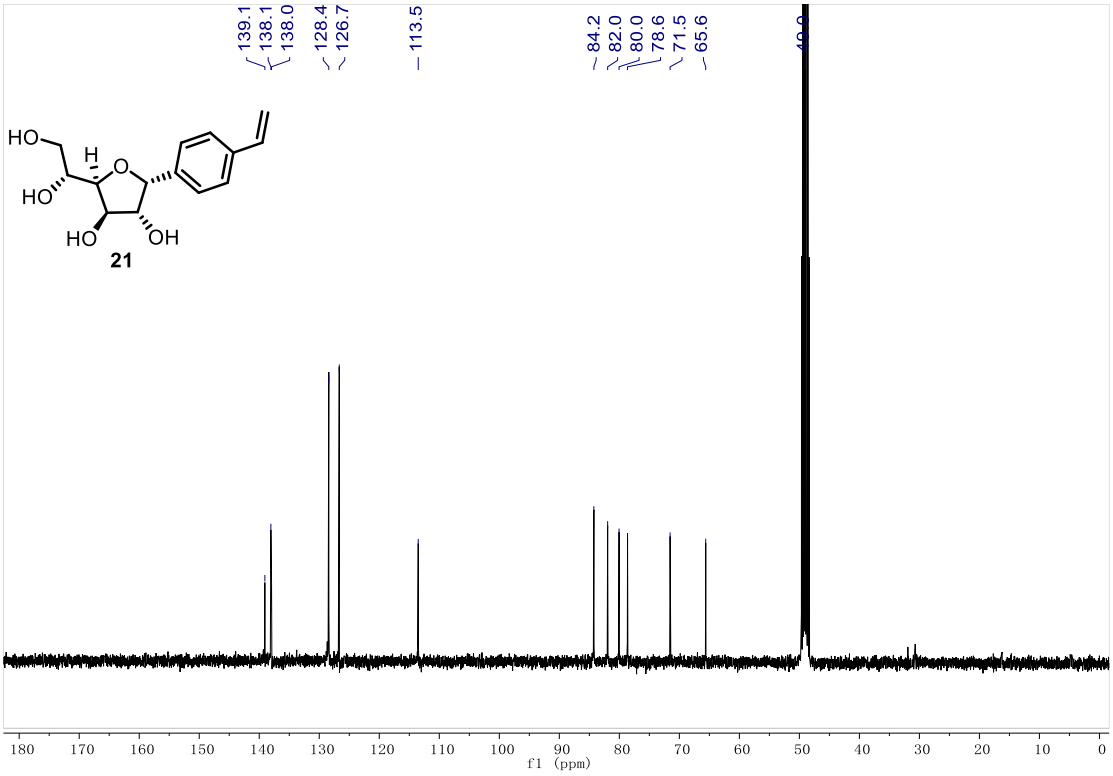

$^{1}$H NMR of compound **21-s** (400 MHz, $CD_3OD$)



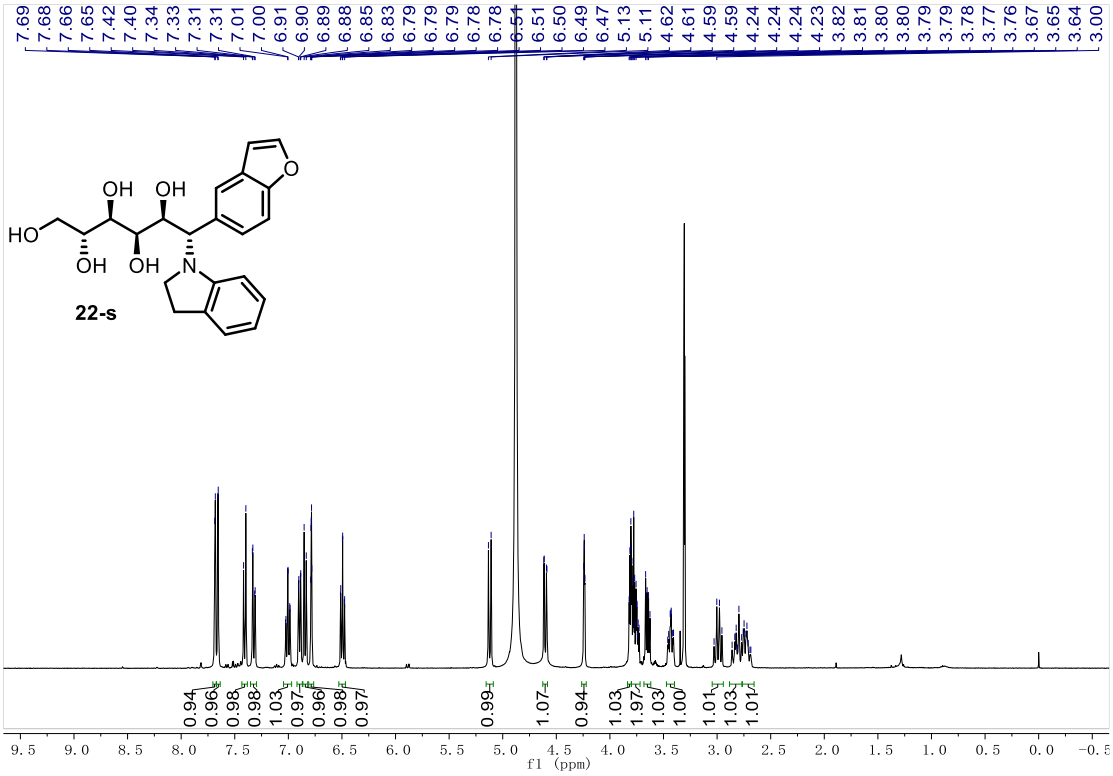

$^{13}$C NMR of compound **21-s** (101 MHz, $CD_3OD$)



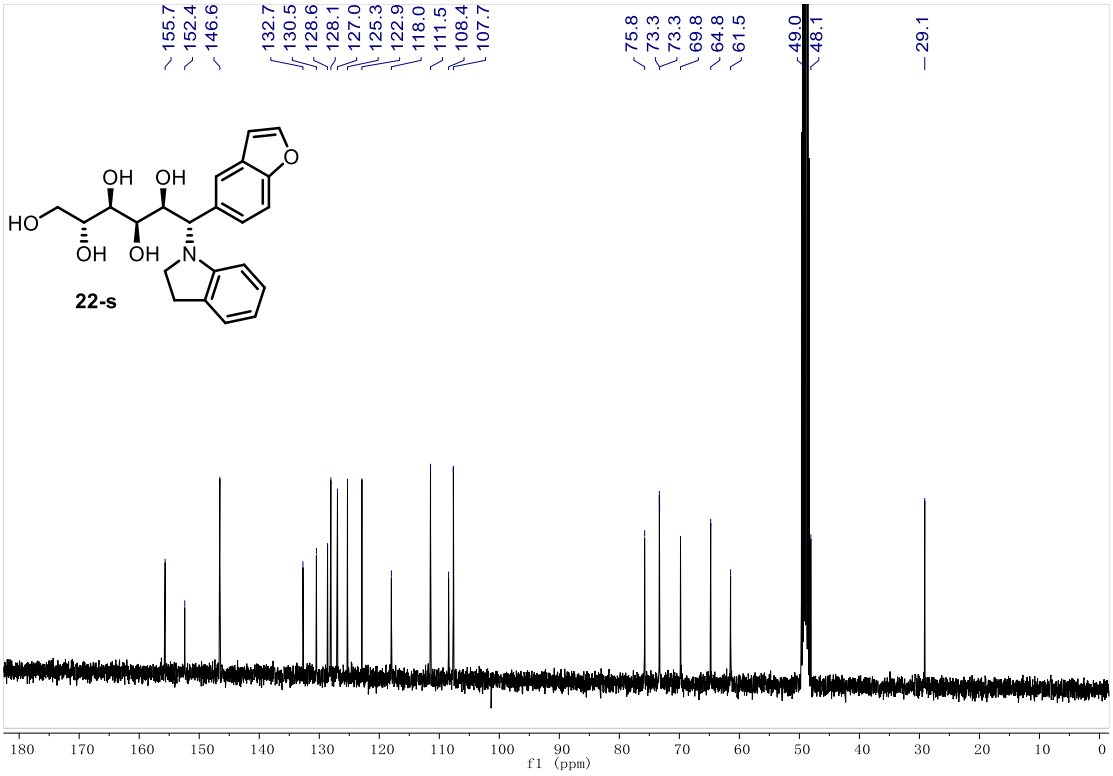

$^{1}$H NMR of compound **21** (400 MHz, $CD_3OD$)



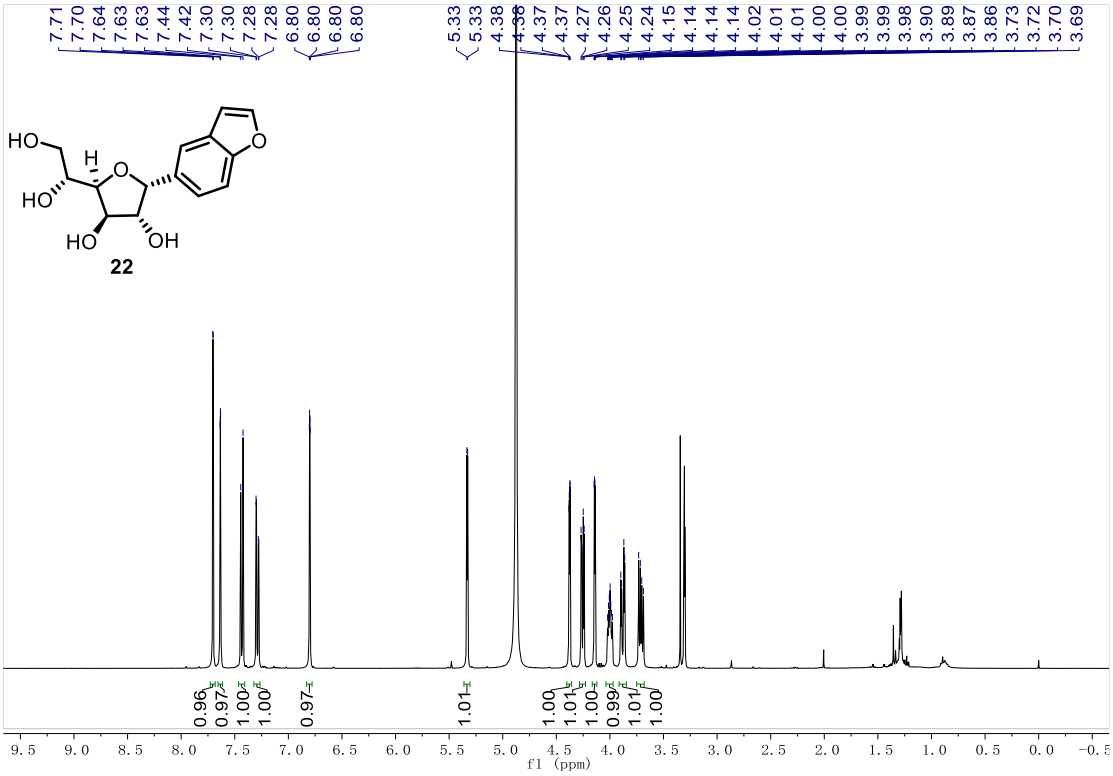

$^{13}$C NMR of compound **21** (101 MHz, $CD_3OD$)



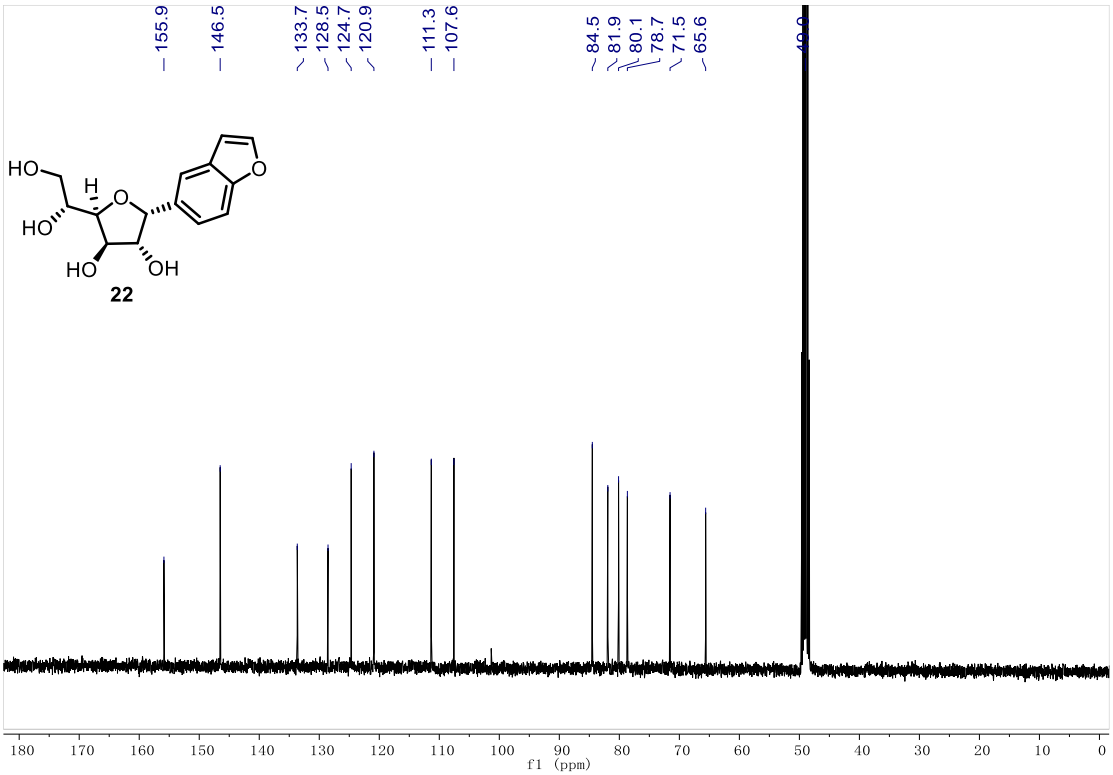

$^{1}$H NMR of compound **22-s** (400 MHz, $CD_3OD$)



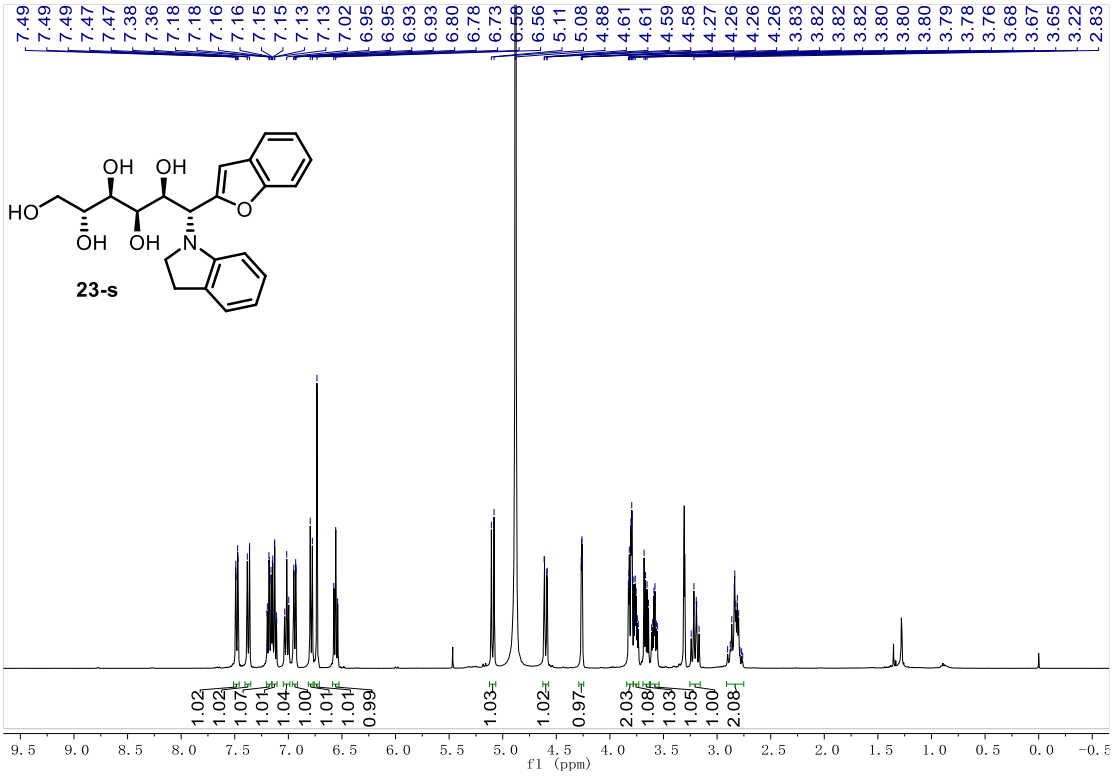

$^{13}$C NMR of compound **22-s** (101 MHz, $CD_3OD$)



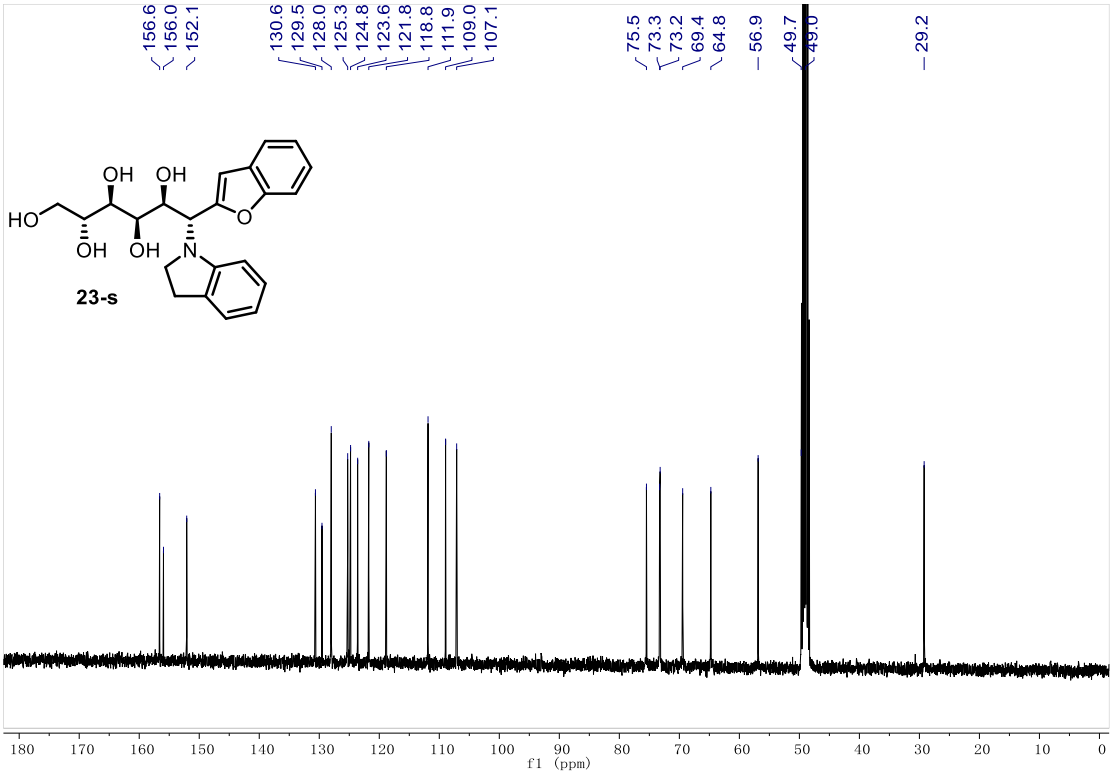

$^{1}$H NMR of compound **22** (400 MHz, $CD_3OD$)



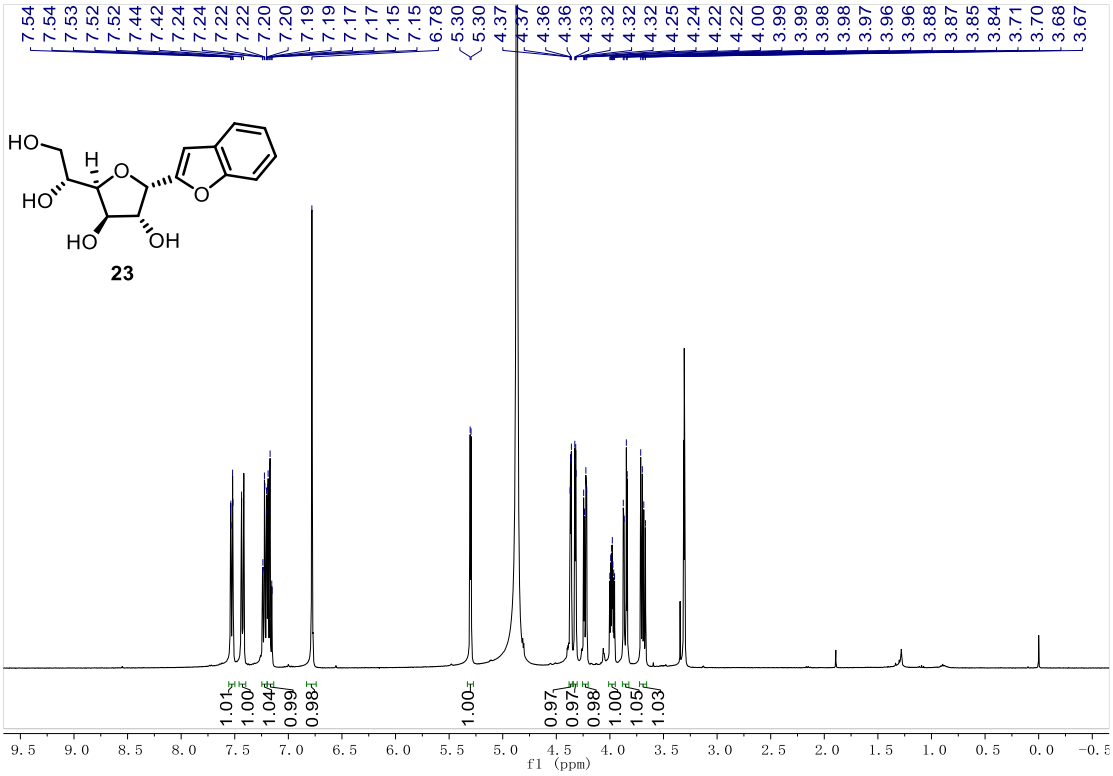

$^{13}$C NMR of compound **22** (101 MHz, $CD_3OD$)



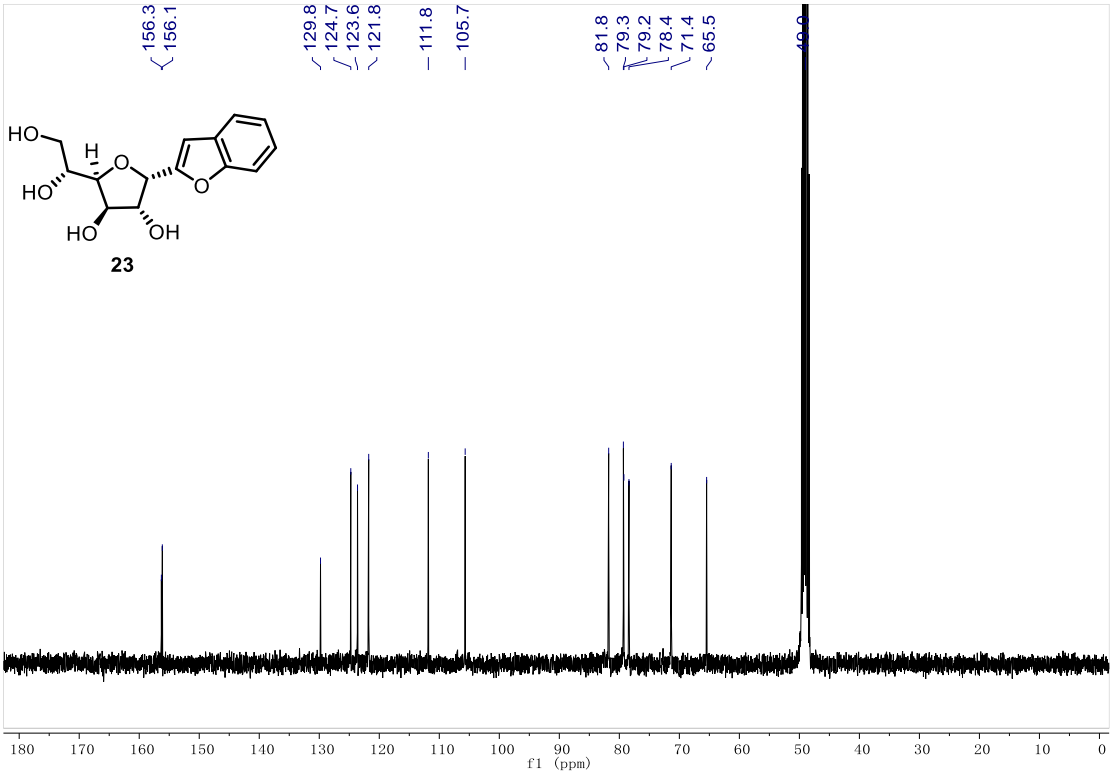

$^{1}$H NMR of compound **23-s** (400 MHz, $CD_3OD$)



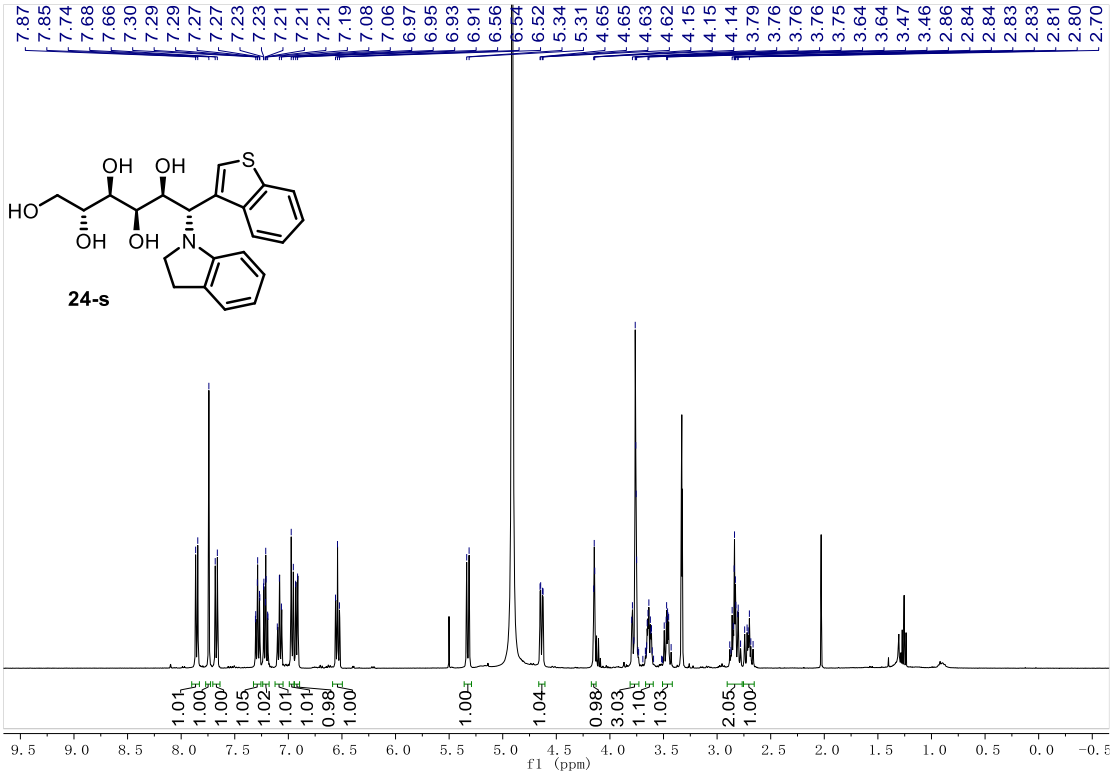

$^{13}$C NMR of compound **23-s** (101 MHz, $CD_3OD$)



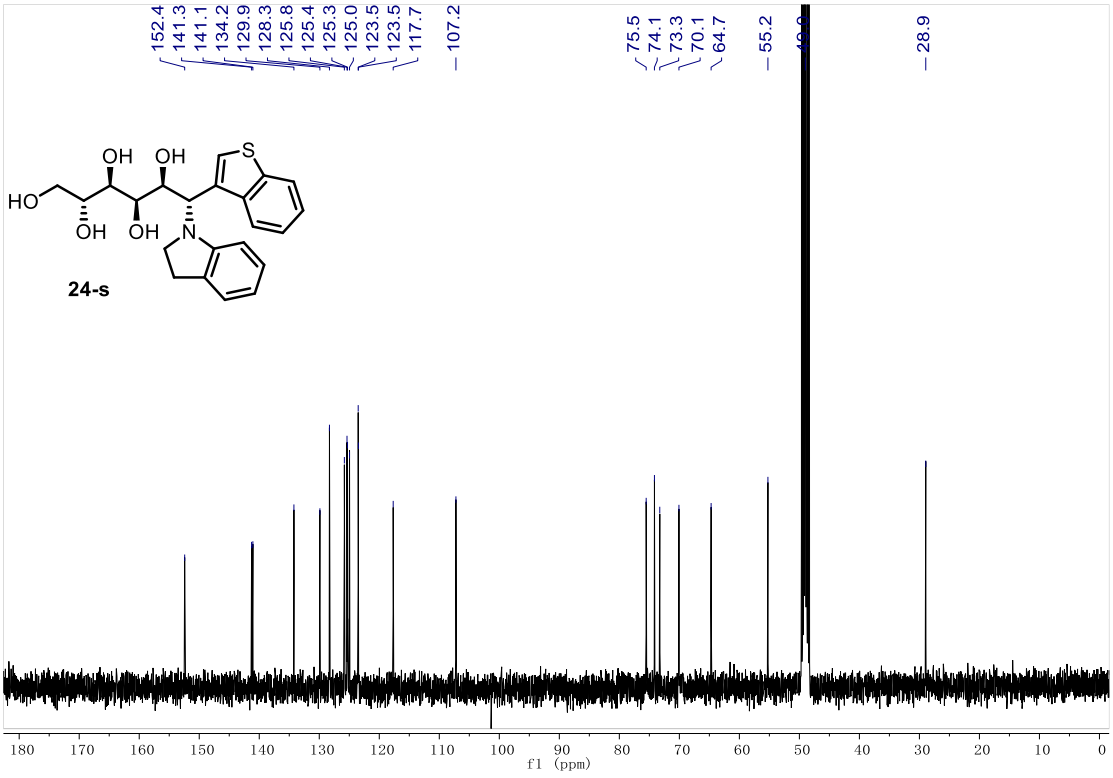

$^{1}$H NMR of compound **23** (400 MHz, $CD_3OD$)



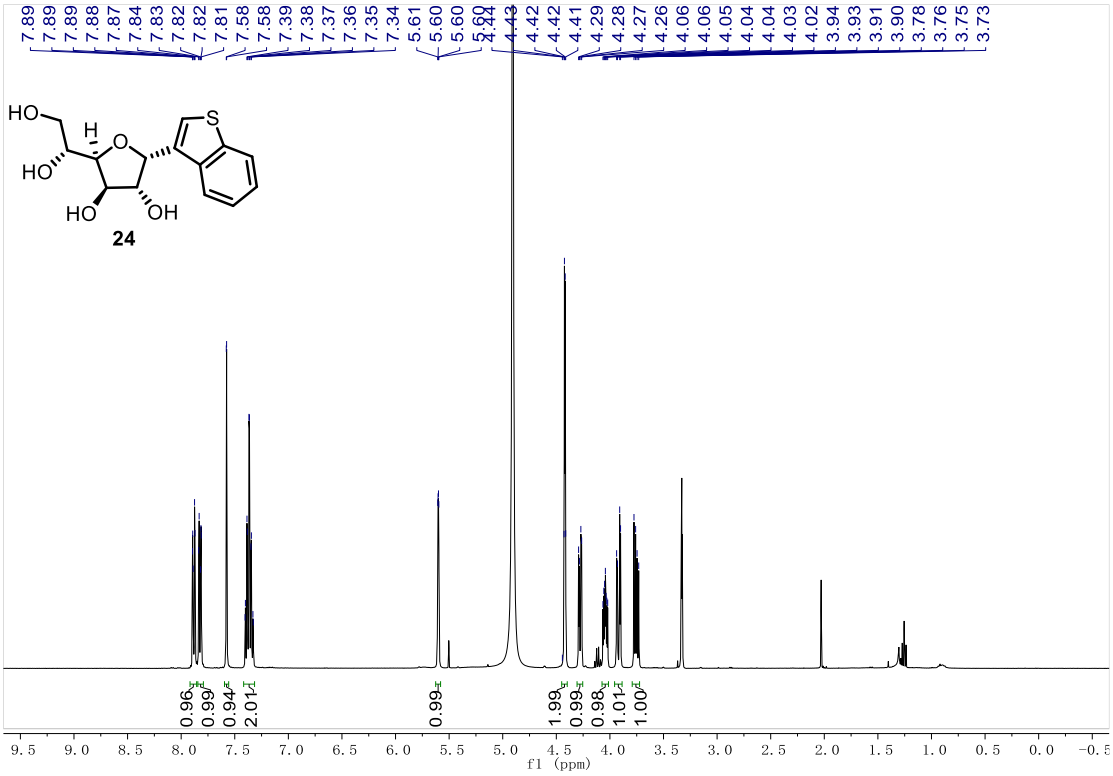

$^{13}$C NMR of compound **23** (101 MHz, $CD_3OD$)



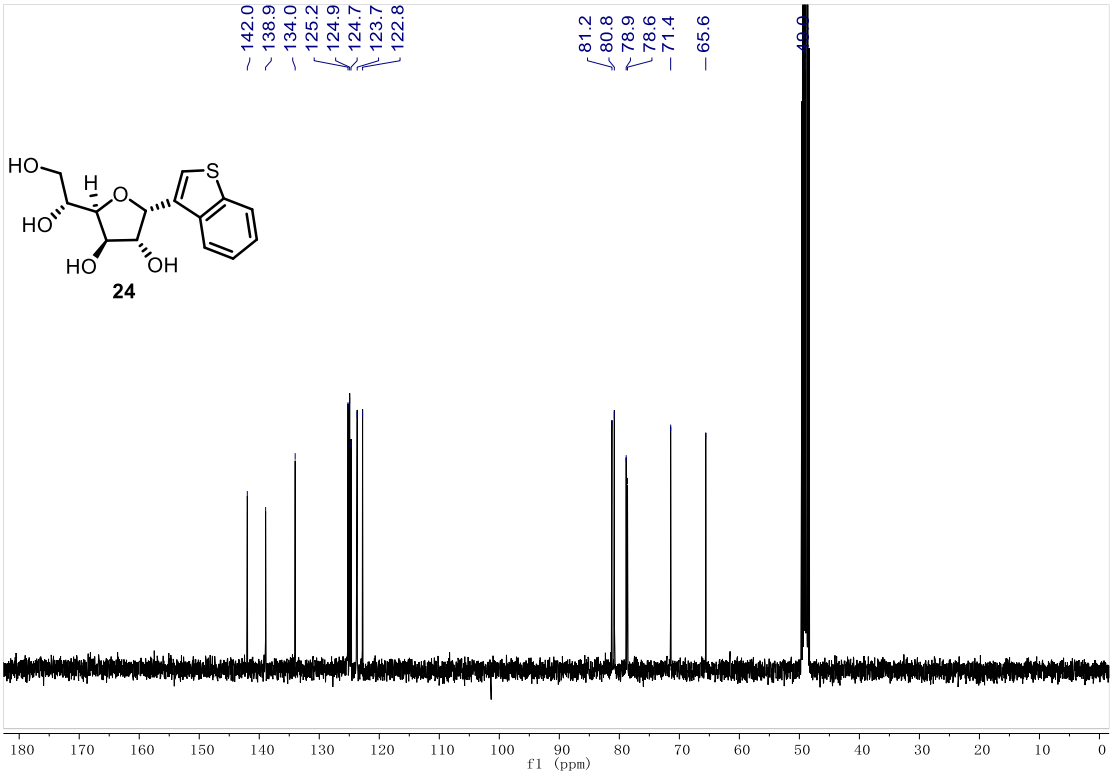

$^{1}$H NMR of compound **24-s** (400 MHz, $CD_3OD$)



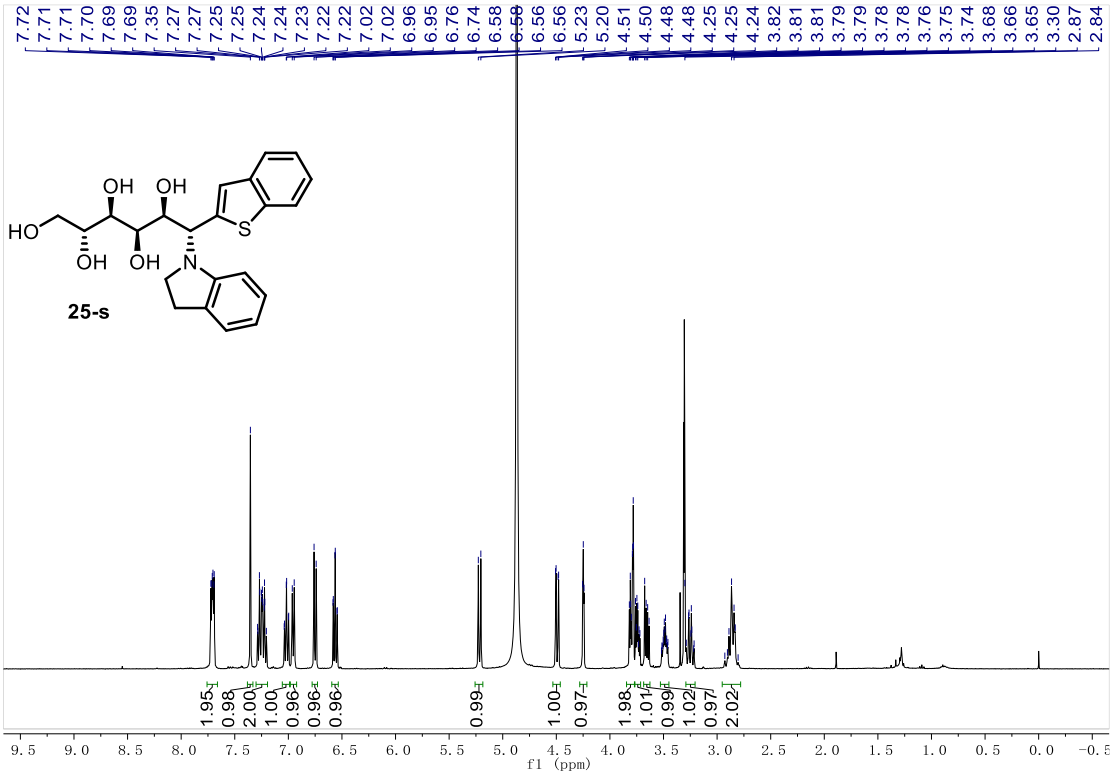

$^{13}$C NMR of compound **24-s** (101 MHz, $CD_3OD$)



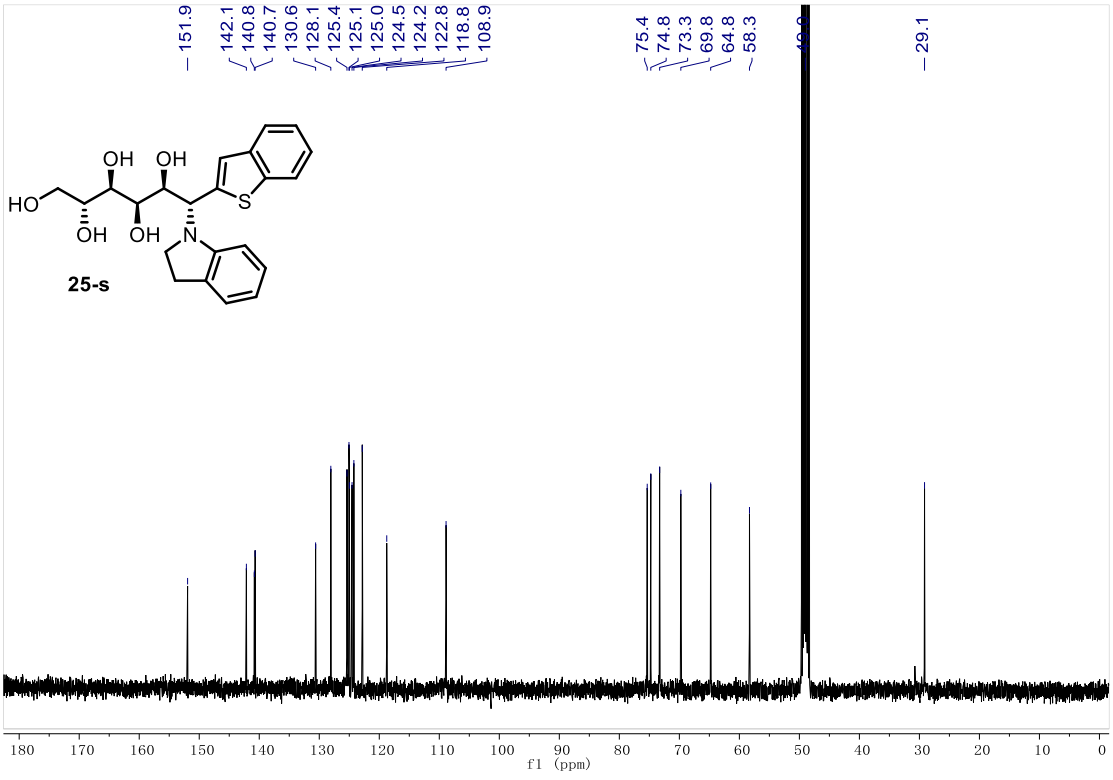

$^{1}$H NMR of compound **24** (400 MHz, $CD_3OD$)



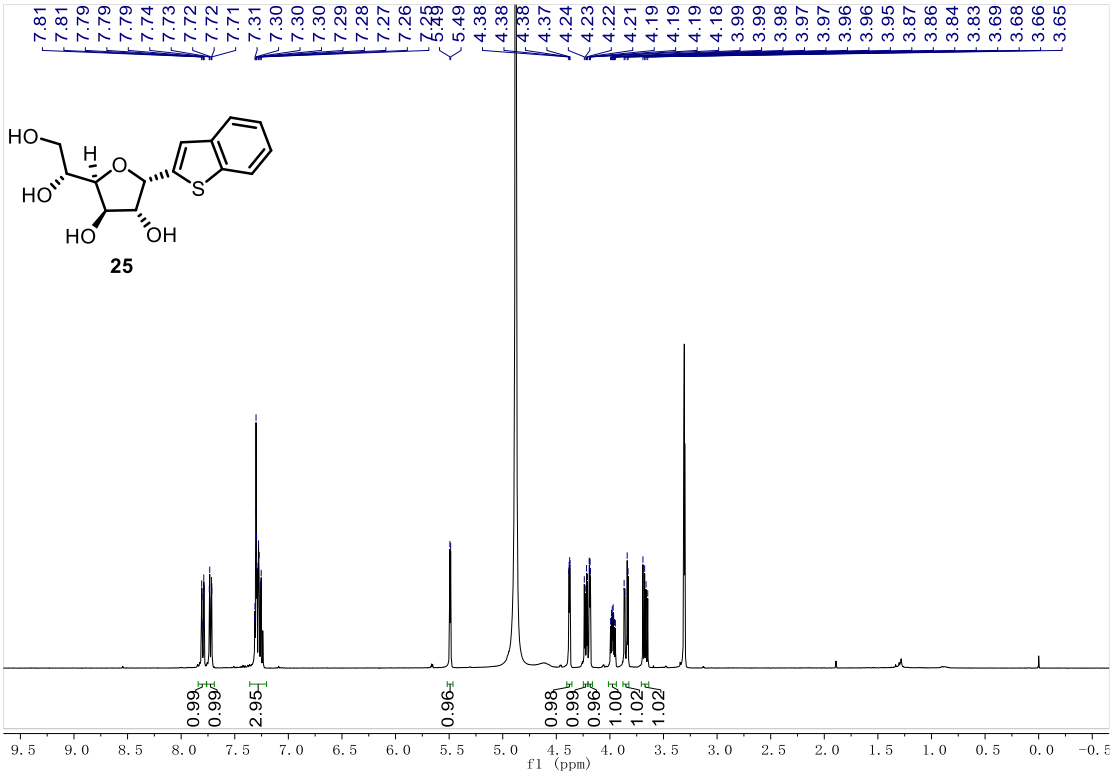

$^{13}$C NMR of compound **24** (101 MHz, $CD_3OD$)



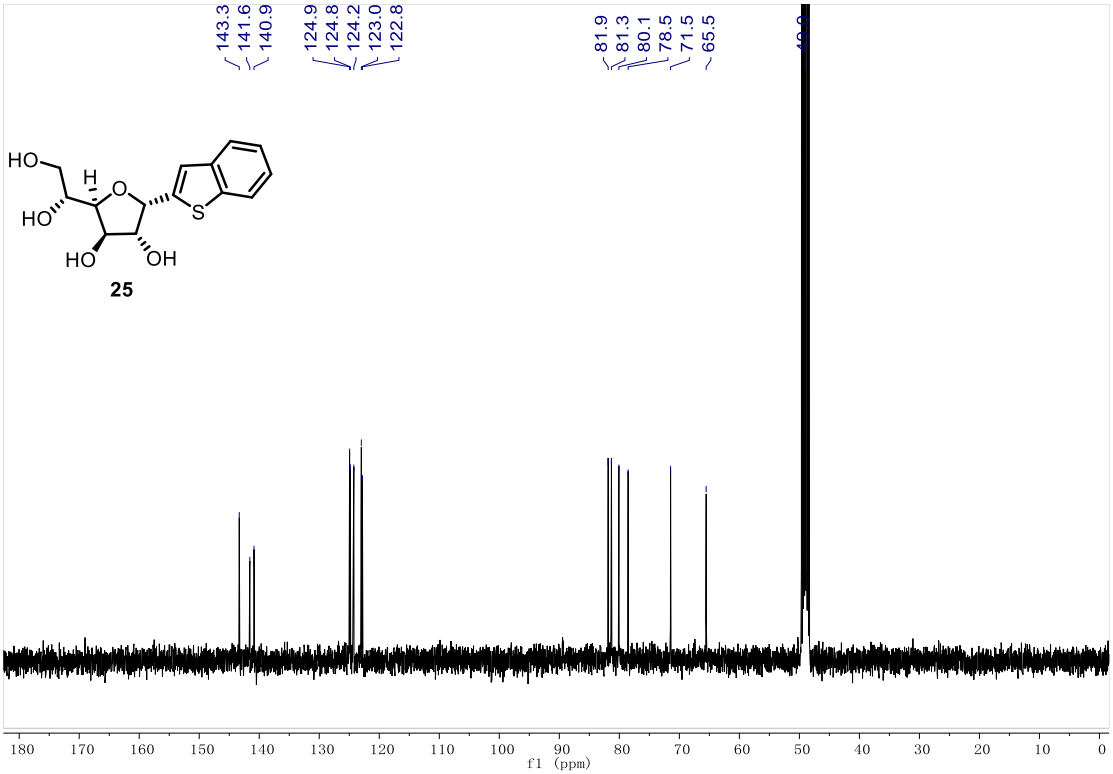

$^{1}$H NMR of compound **25-s** (400 MHz, $CD_3OD$)



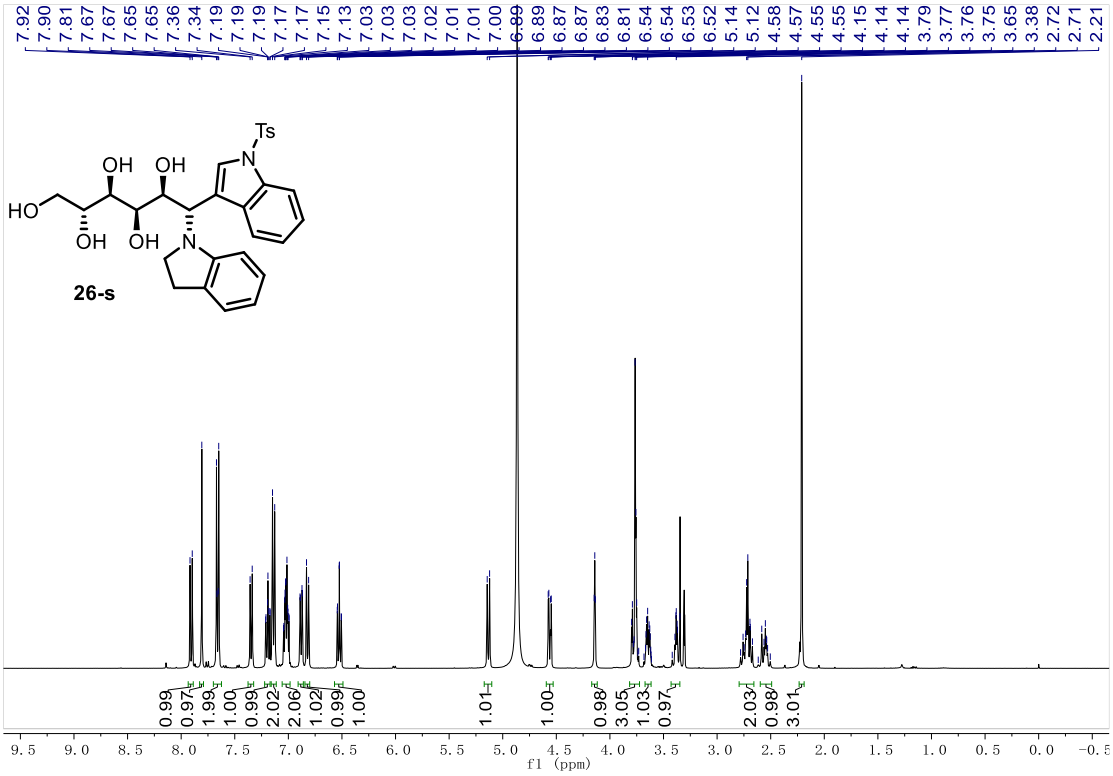

$^{13}$C NMR of compound **25-s** (101 MHz, $CD_3OD$)



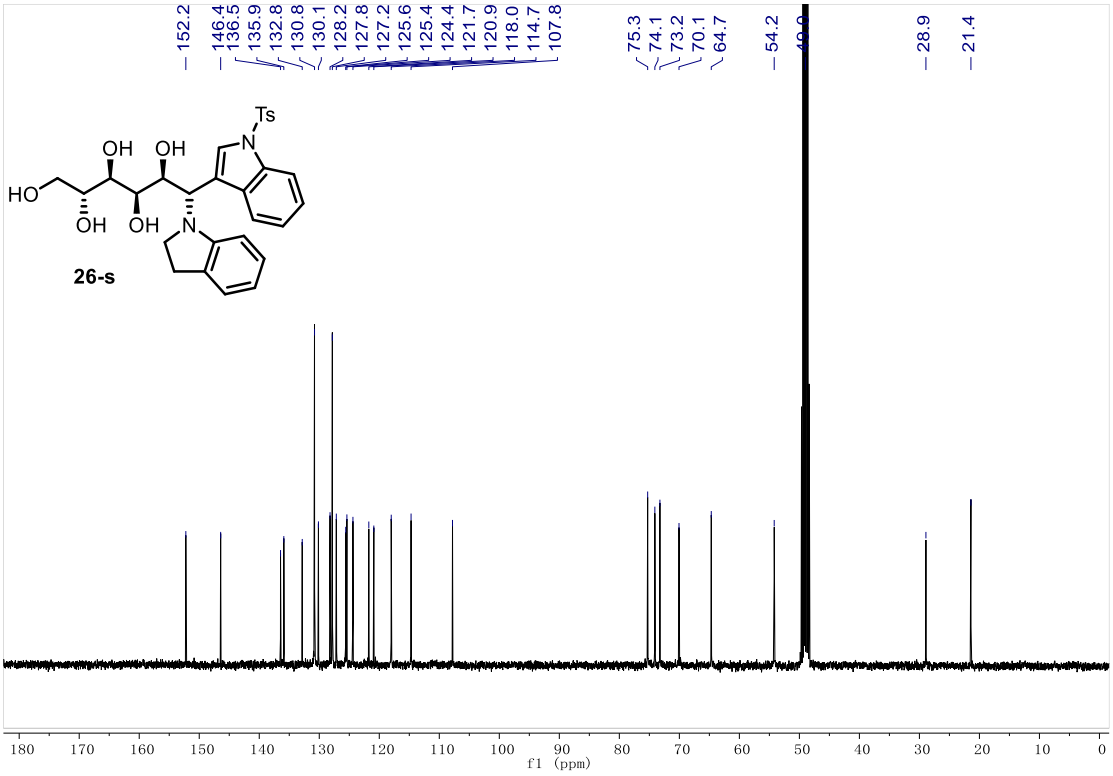

$^{1}$H NMR of compound **25** (400 MHz, $CD_3OD$)



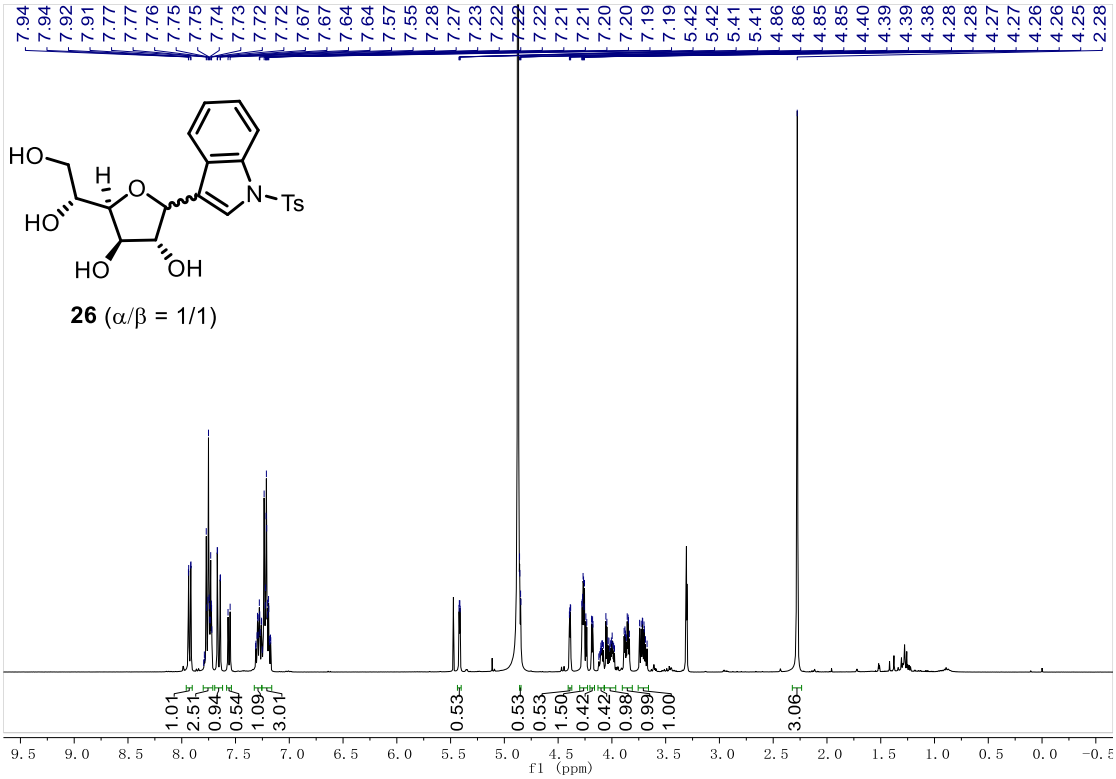

$^{13}$C NMR of compound **25** (101 MHz, $CD_3OD$)



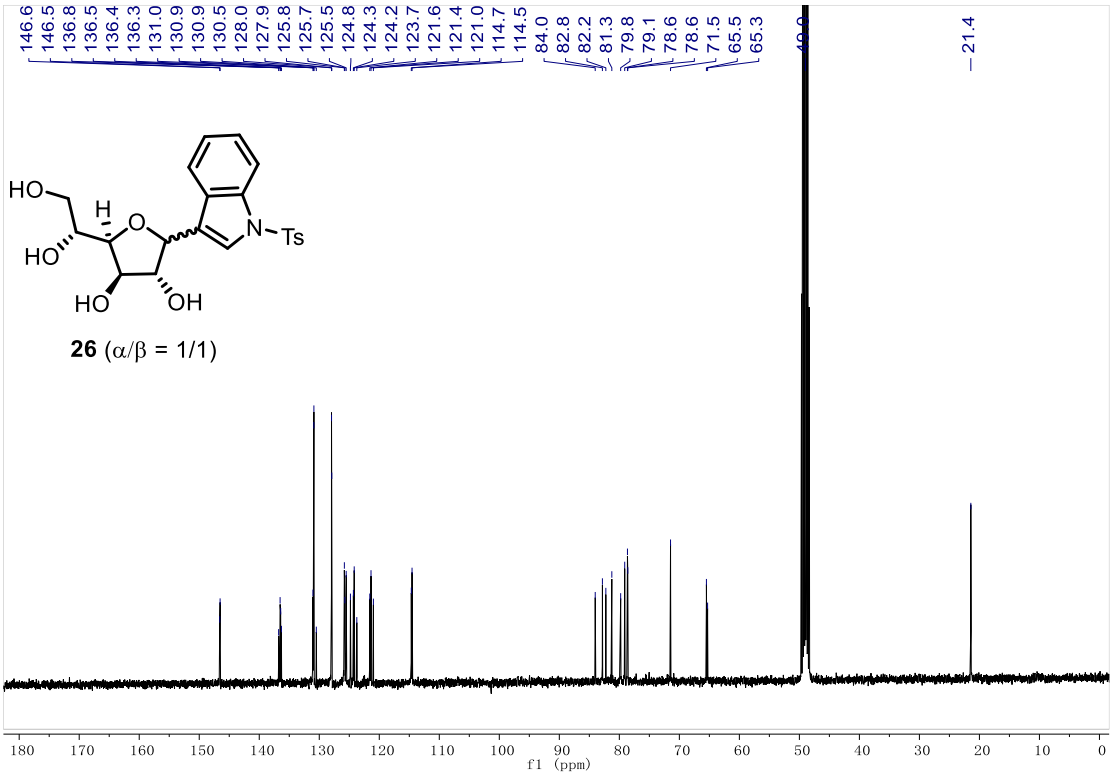

$^{1}$H NMR of compound **26-s** (400 MHz, $CD_3OD$)



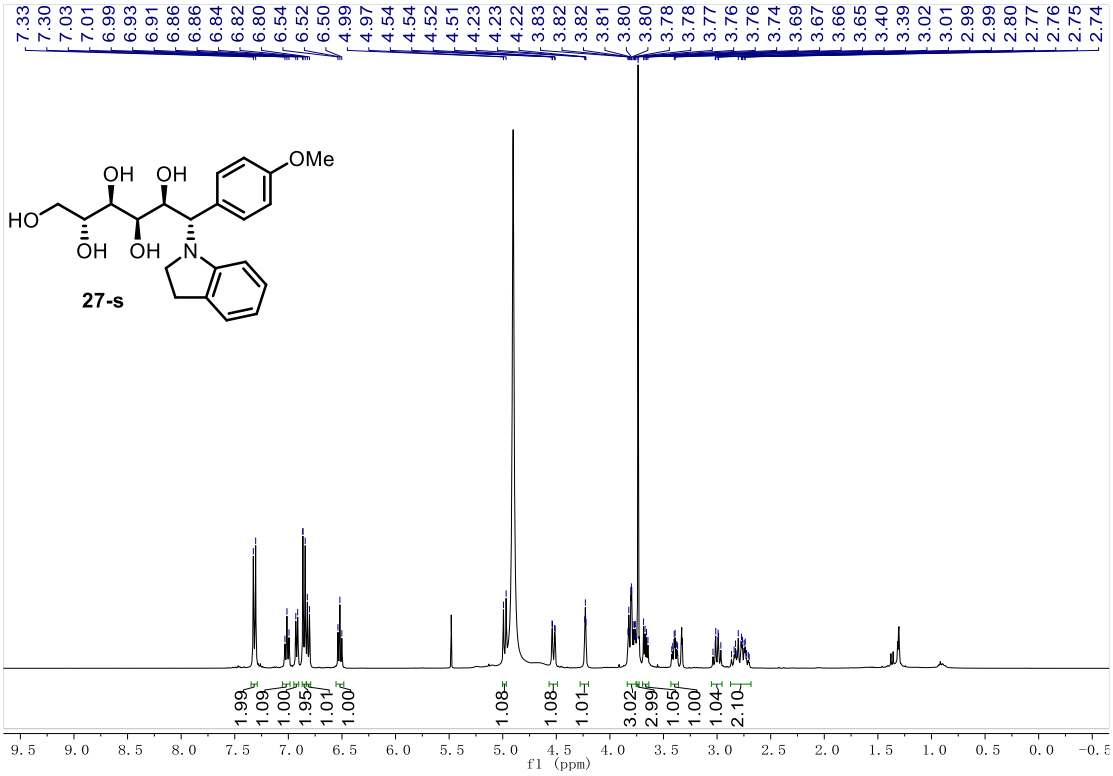

$^{13}$C NMR of compound **26-s** (101 MHz, $CD_3OD$)



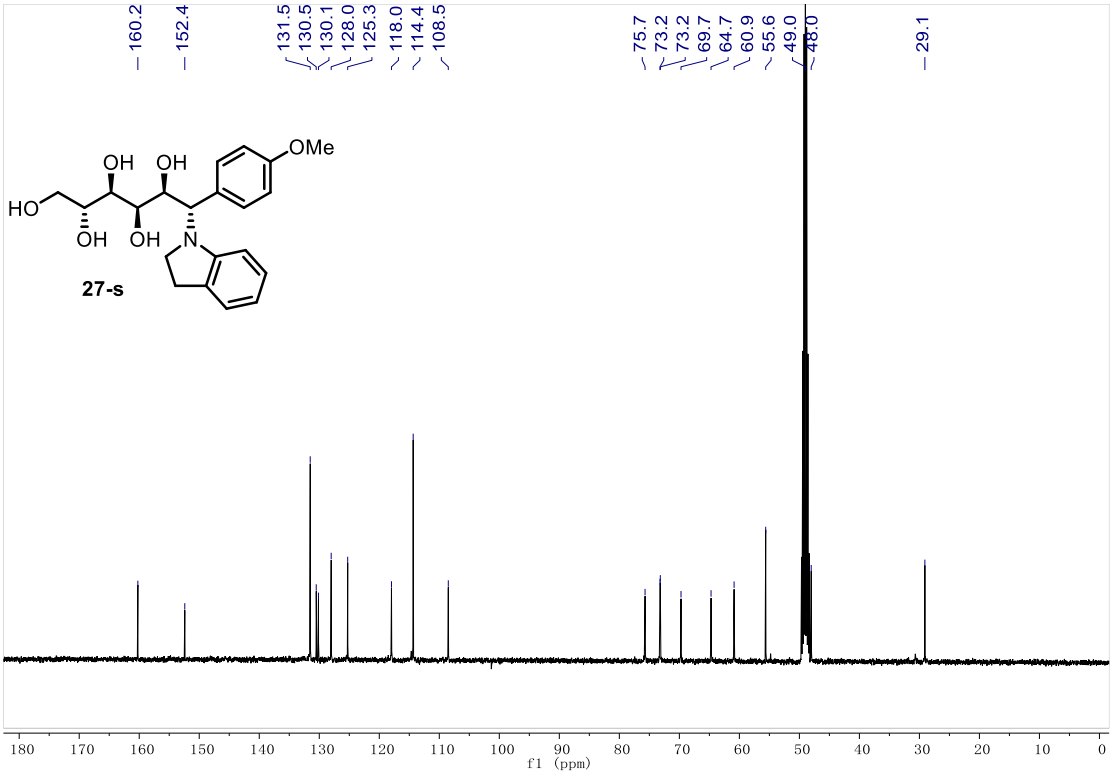

$^{1}$H NMR of compound **26 (α/β = 1/1)** (400 MHz, $CD_3OD$)



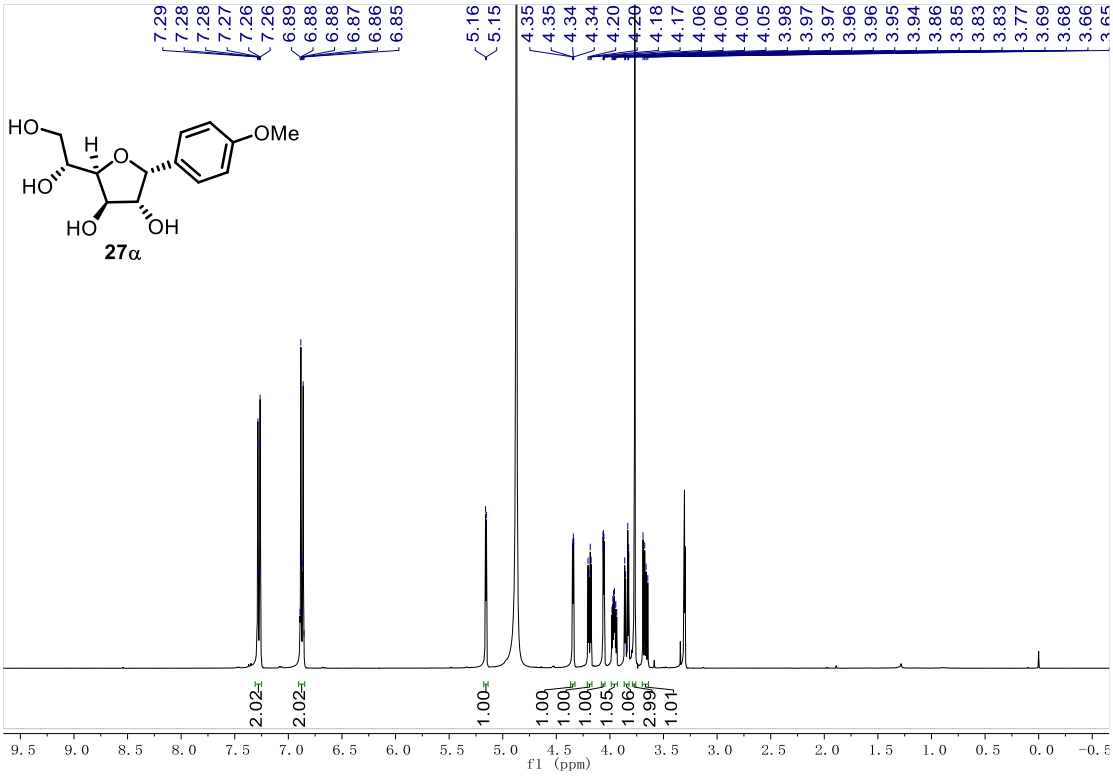

$^{13}$C NMR of compound **26 (α/β = 1/1)** (101 MHz, $CD_3OD$)



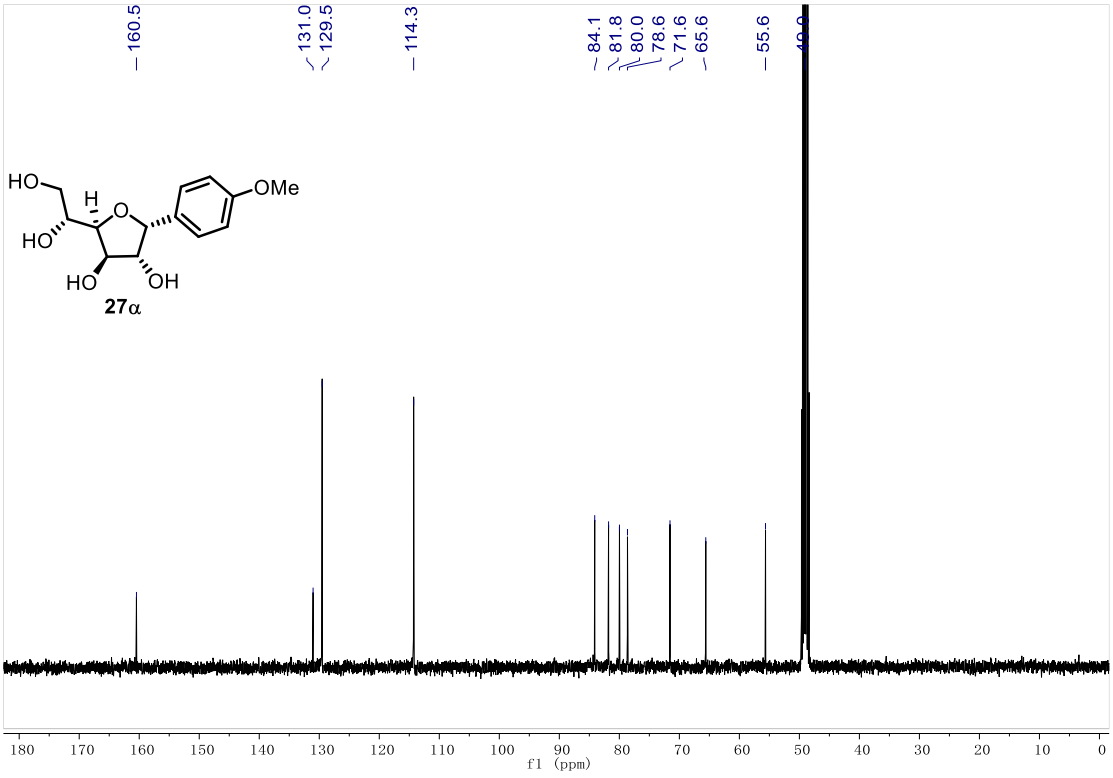

$^{1}$H NMR of compound **27-s** (400 MHz, $CD_3OD$)



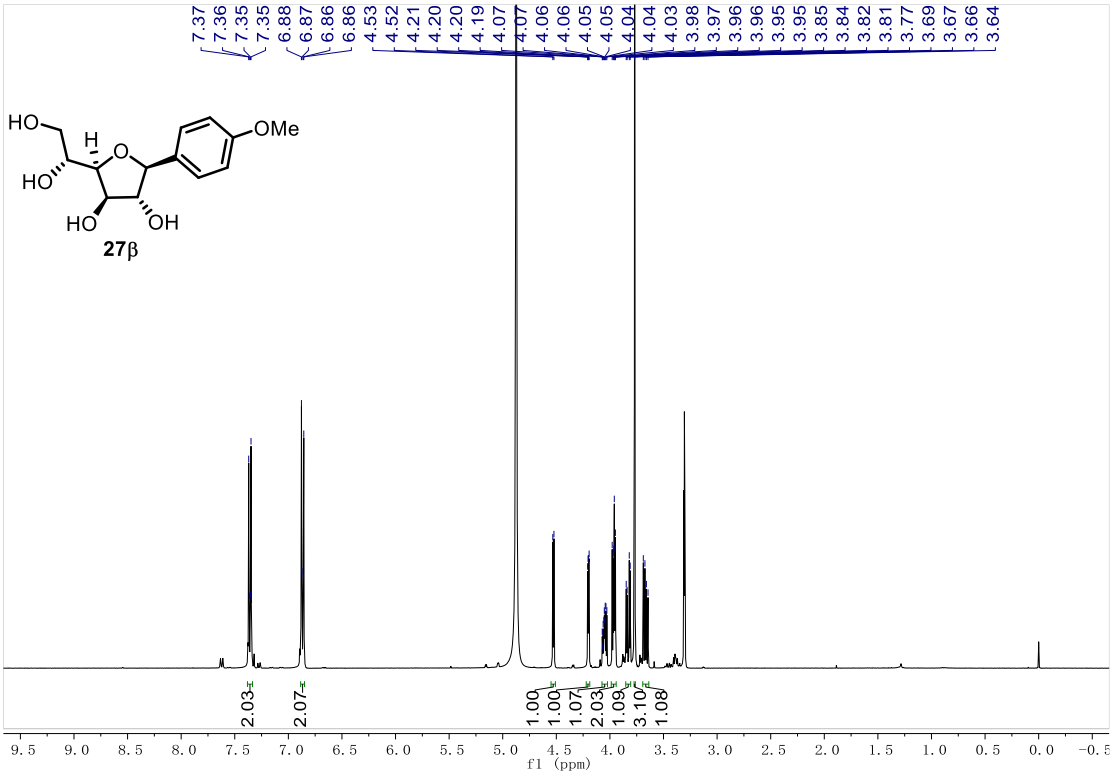

$^{13}$C NMR of compound **27-s** (101 MHz, $CD_3OD$)



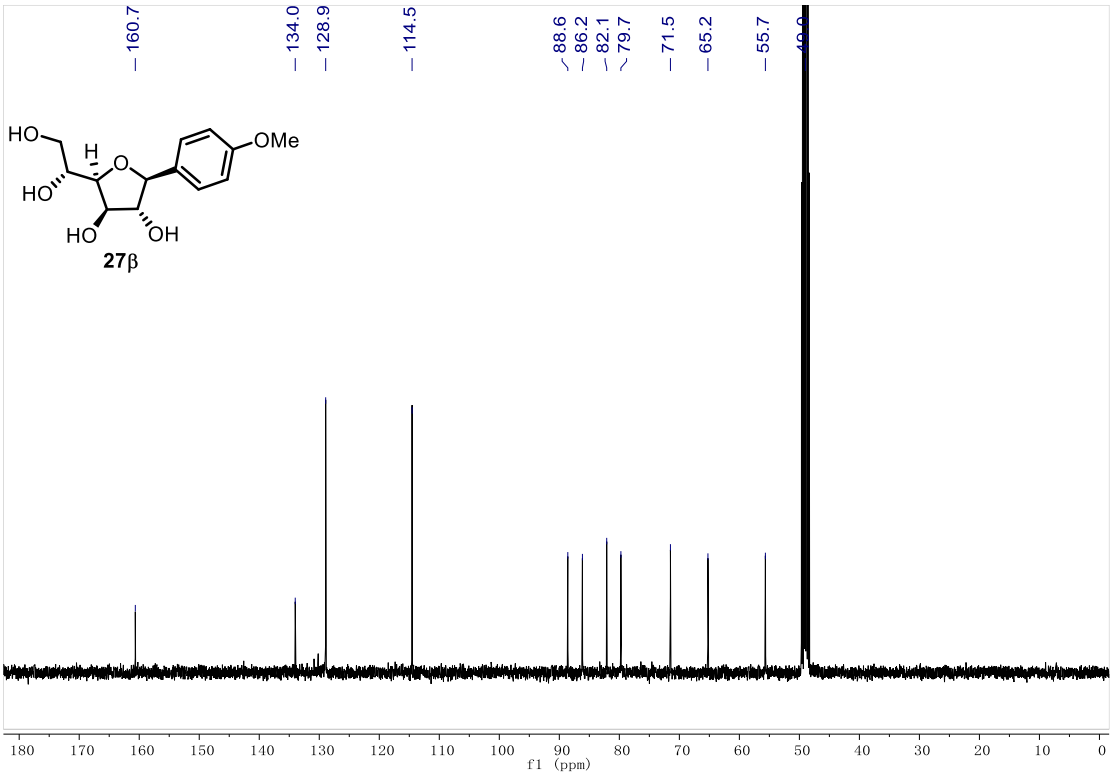

$^{1}$H NMR of compound **27α** (400 MHz, $CD_3OD$)



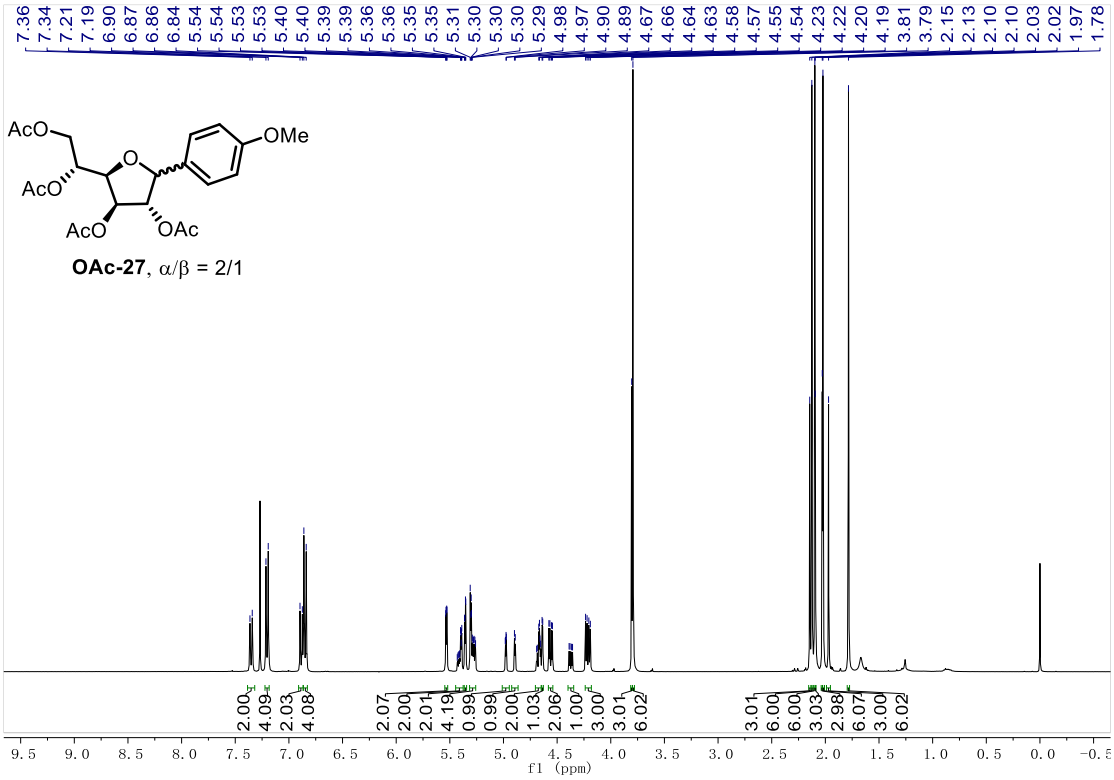

$^{13}$C NMR of compound **27α** (101 MHz, $CD_3OD$)



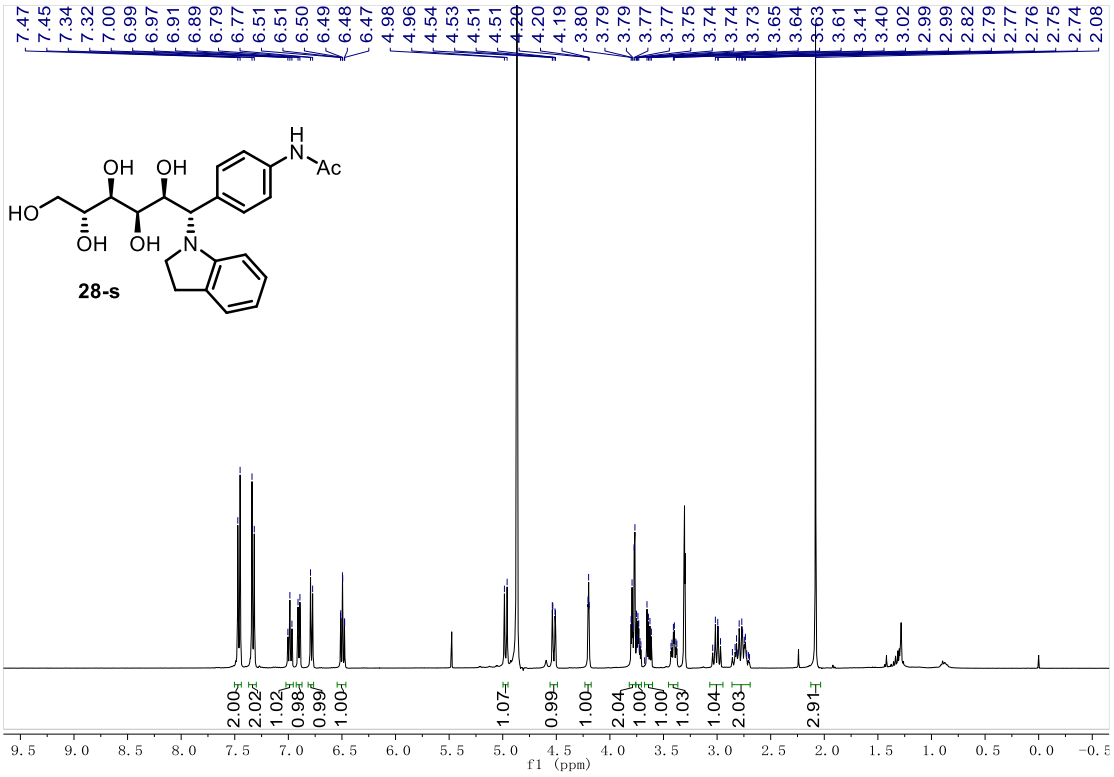

$^{1}$H NMR of compound **27β** (400 MHz, $CD_3OD$)



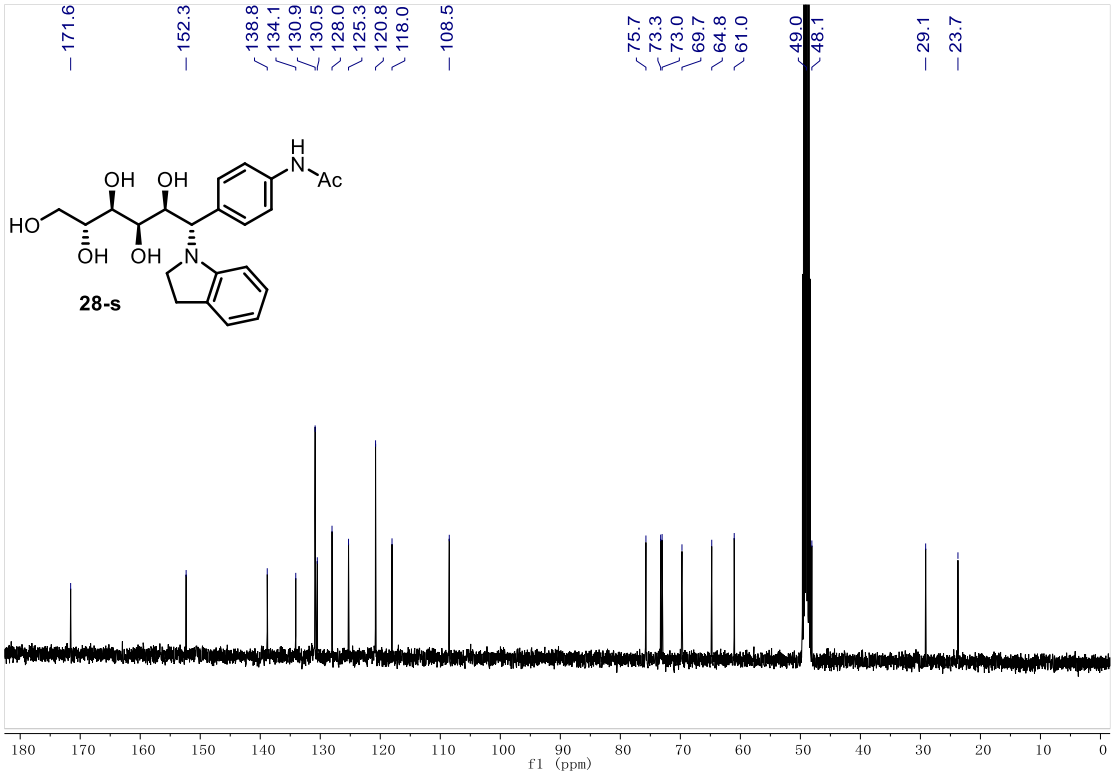

$^{13}$C NMR of compound **27β** (101 MHz, $CD_3OD$)



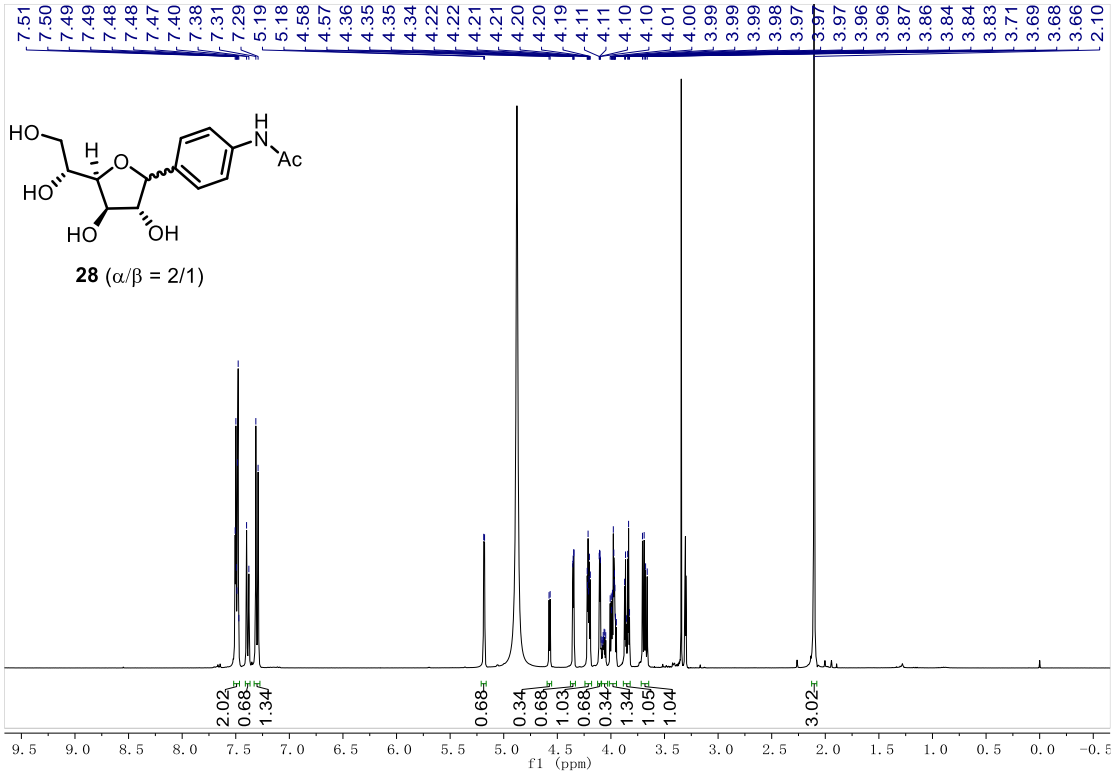

$^1$H NMR of compound **OAc-27 (α/β =2/1)** (400 MHz, $CDCl_3$)



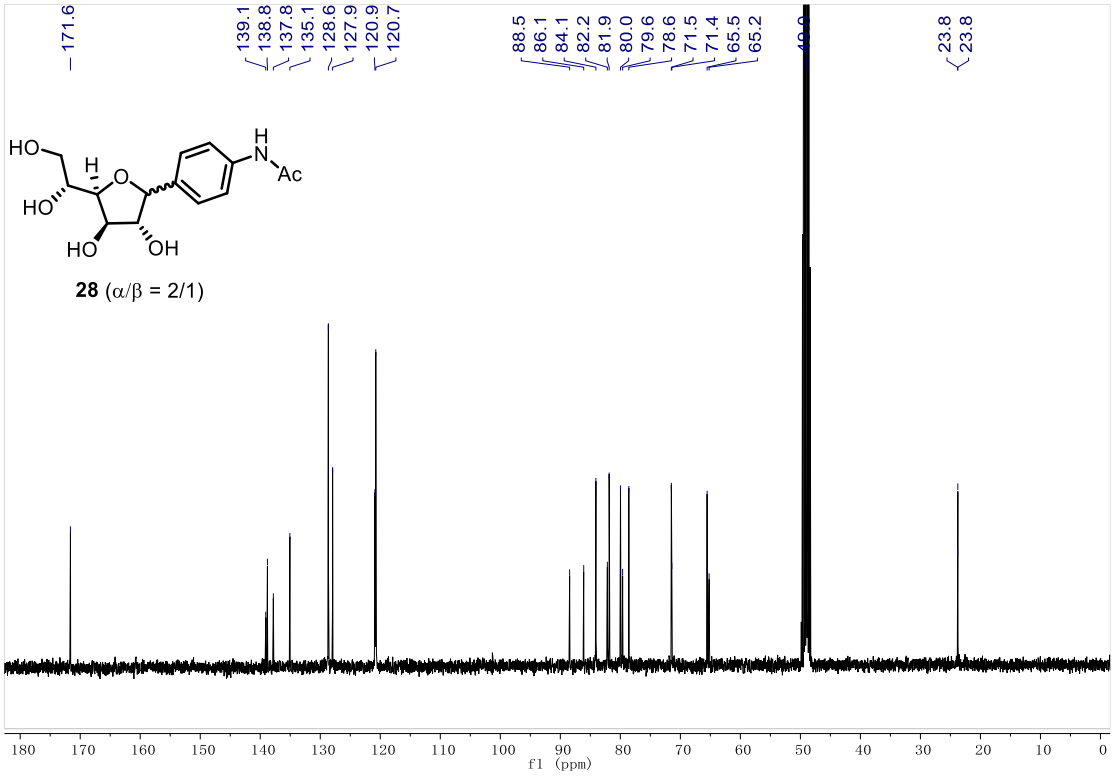

$^1$H NMR of compound **28-s** (400 MHz, $CD_3OD$)



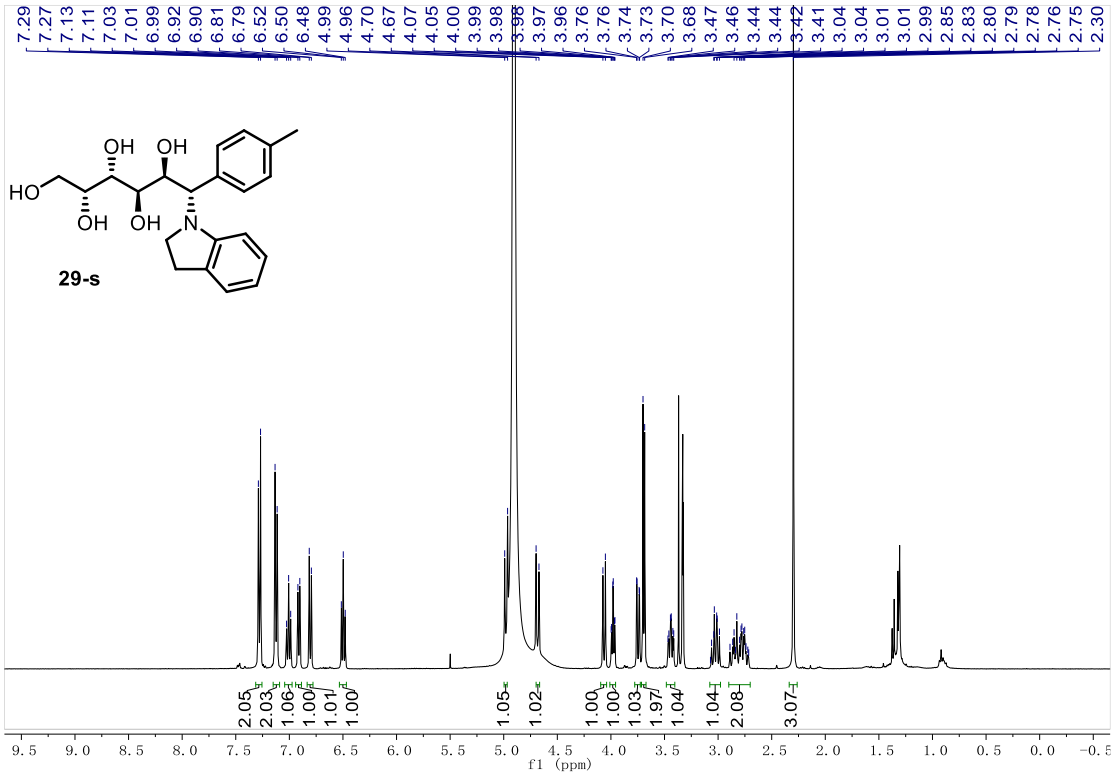

$^{13}$C NMR of compound **28-s** (101 MHz, $CD_3OD$)



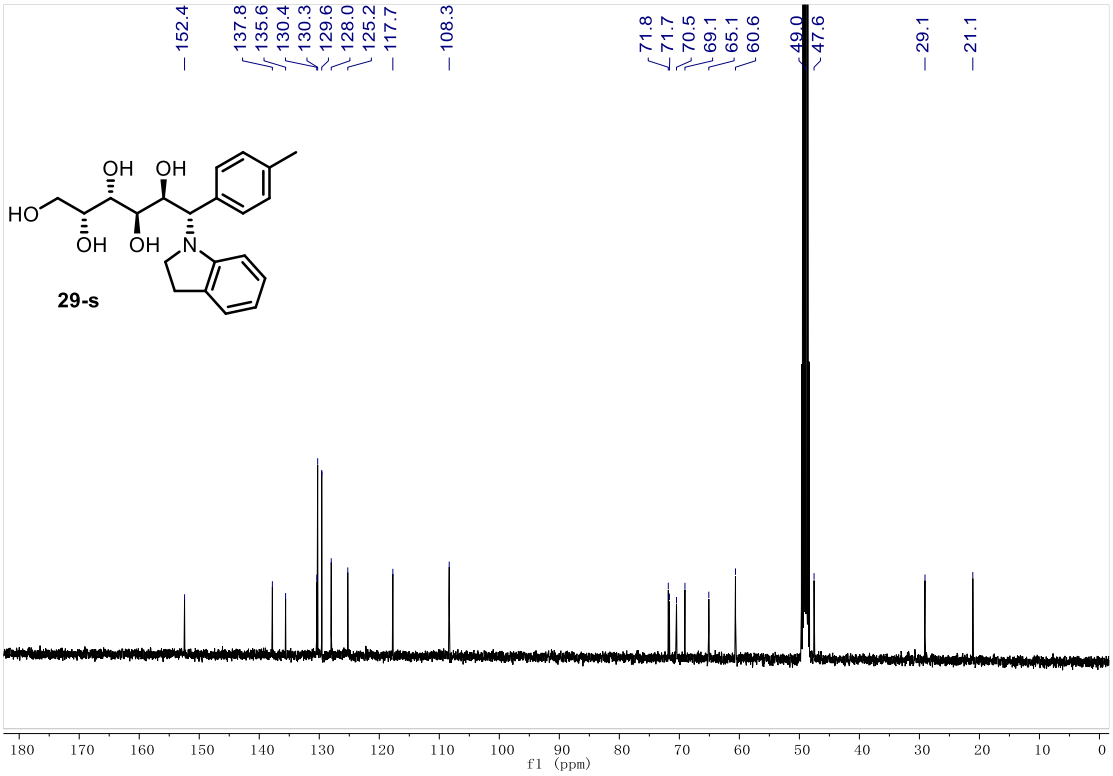

$^{1}$H NMR of compound **28 (α/β = 2/1)** (400 MHz, $CD_3OD$)



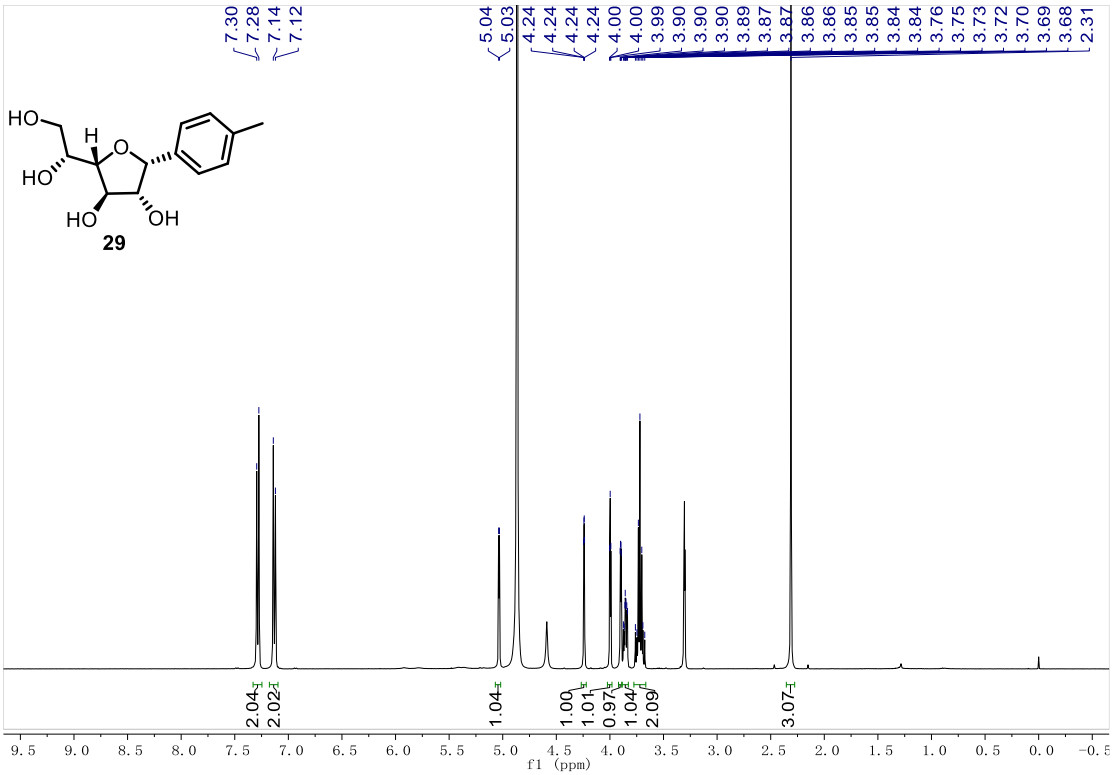

$^{13}$C NMR of compound **28 (α/β = 2/1)** (101 MHz, $CD_3OD$)



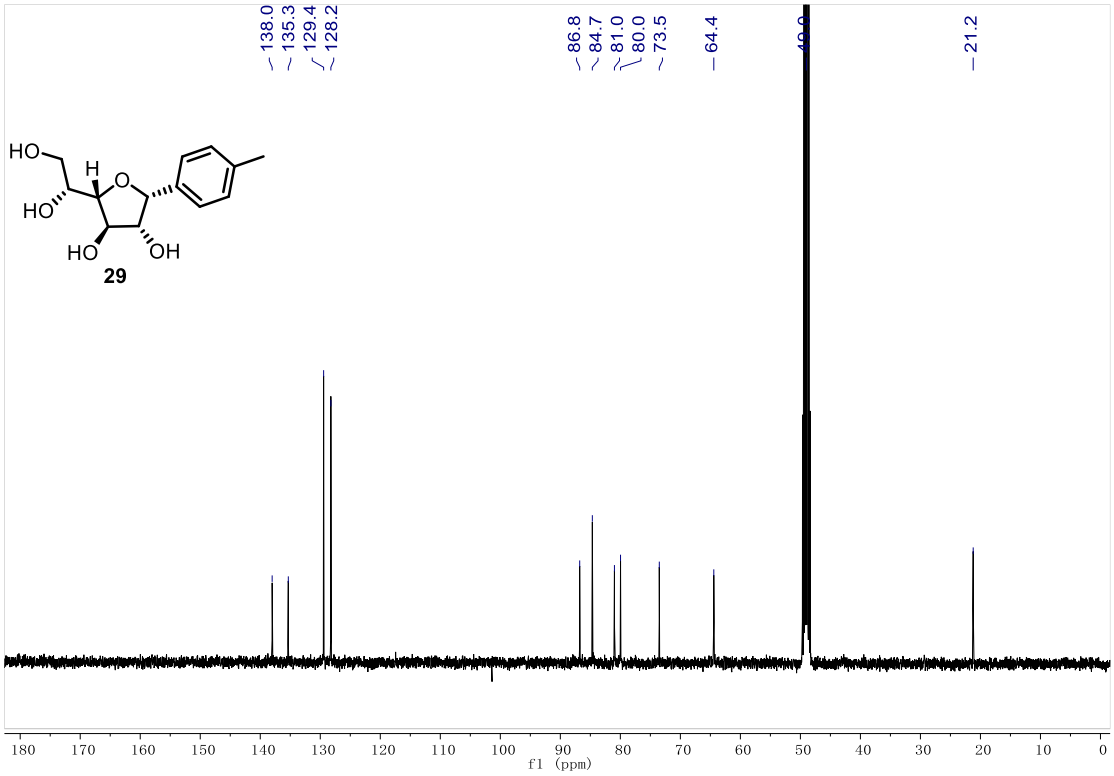

$^{1}$H NMR of compound **29-s** (400 MHz, $CD_3OD$)



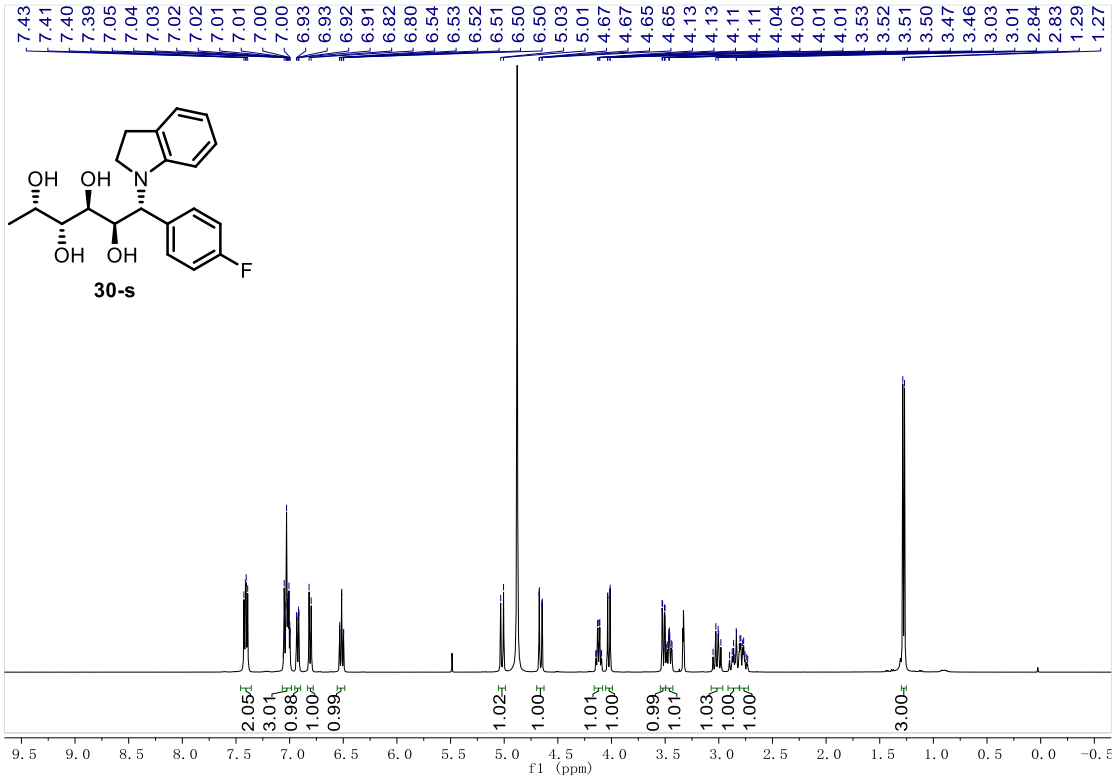

$^{13}$C NMR of compound **29-s** (101 MHz, $CD_3OD$)



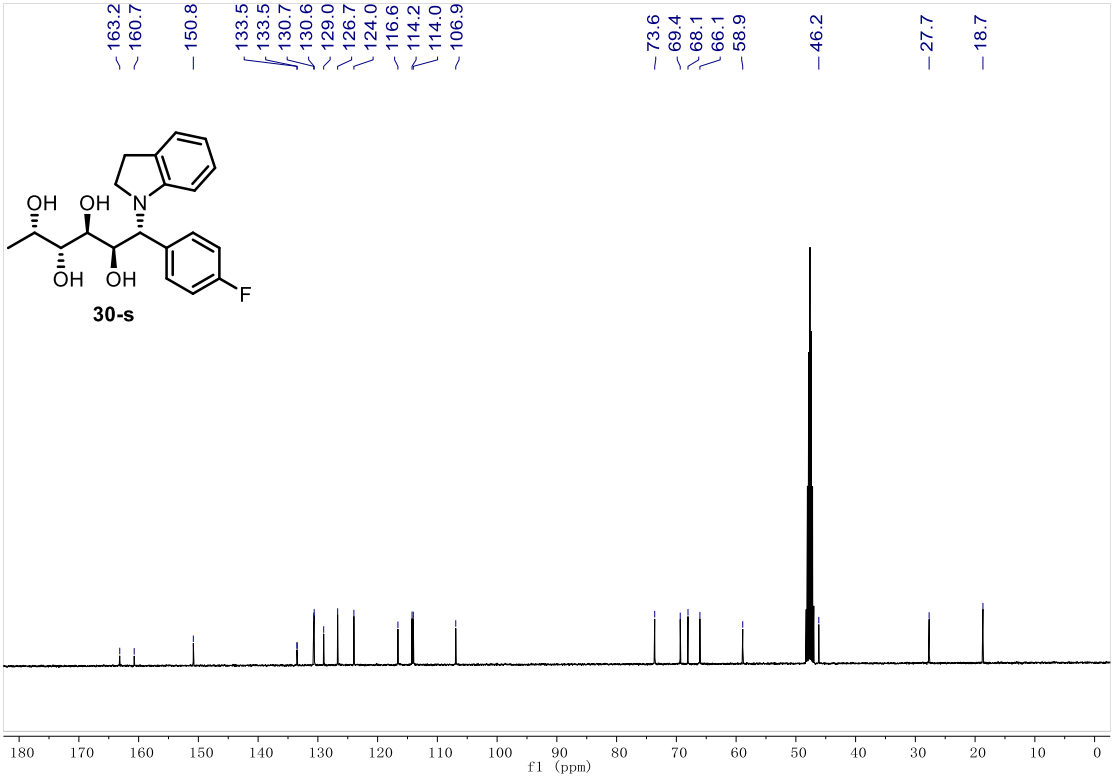

$^{1}$H NMR of compound **29** (400 MHz, $CD_3OD$)



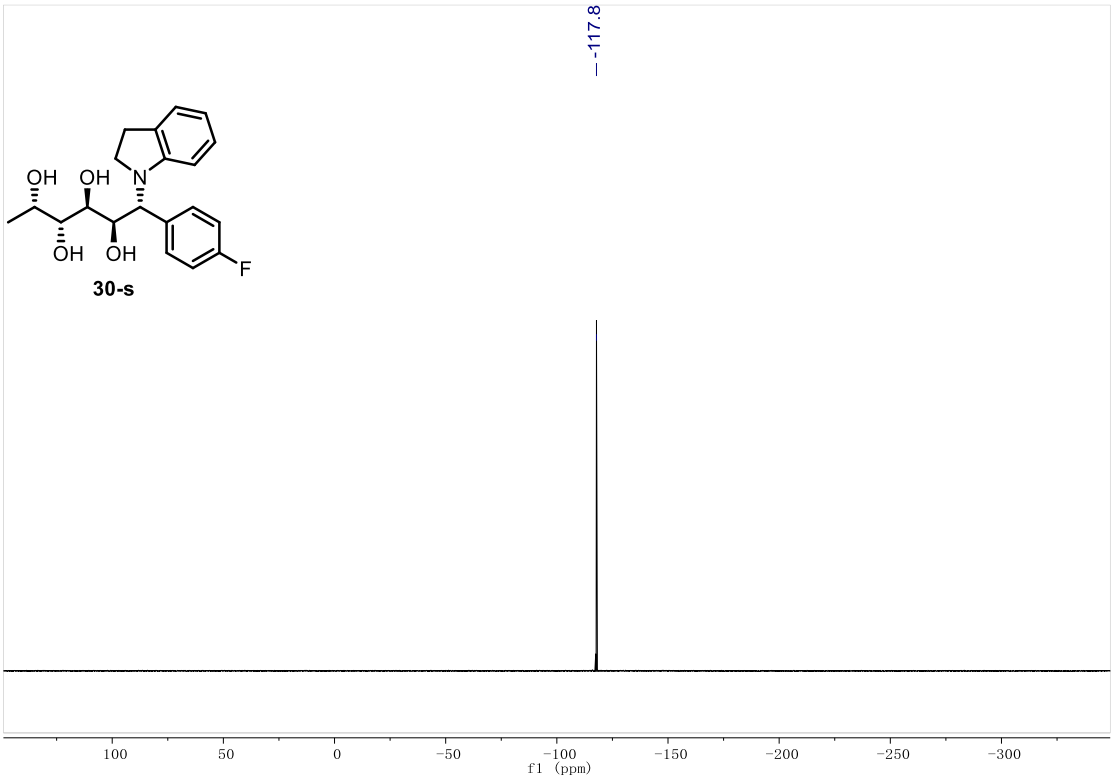

$^{13}$C NMR of compound **29** (101 MHz, $CD_3OD$)



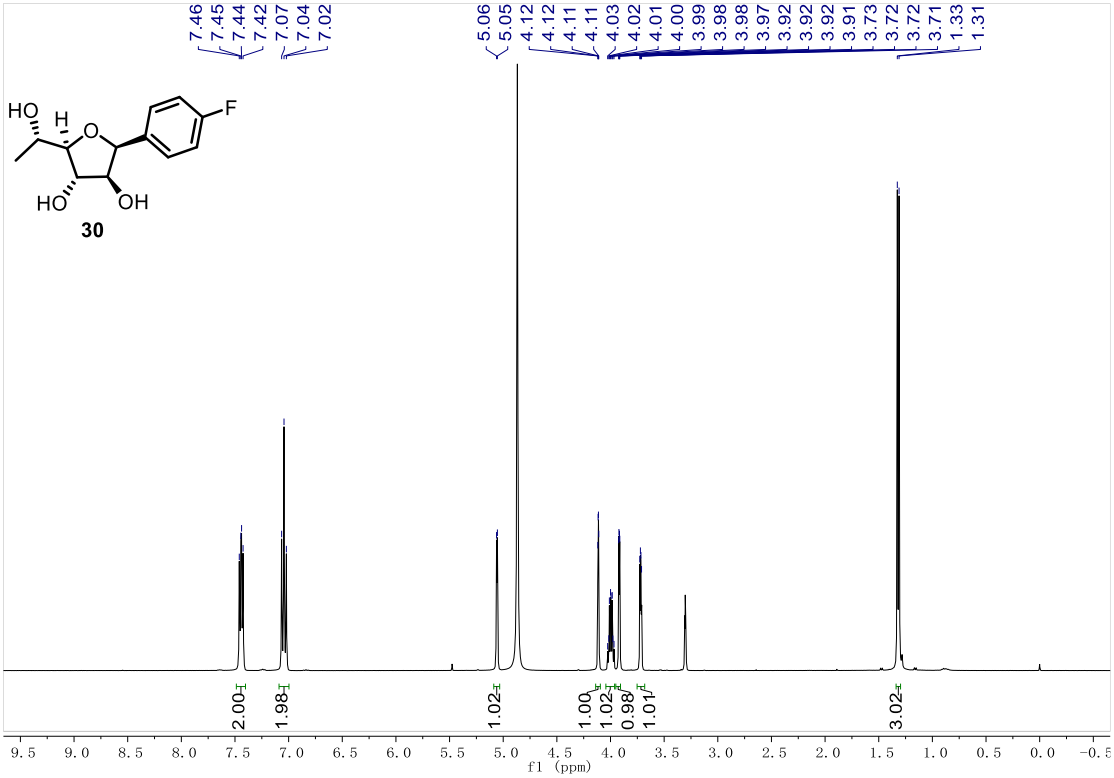

$^{1}$H NMR of compound **30-s** (400 MHz, $CD_3OD$)



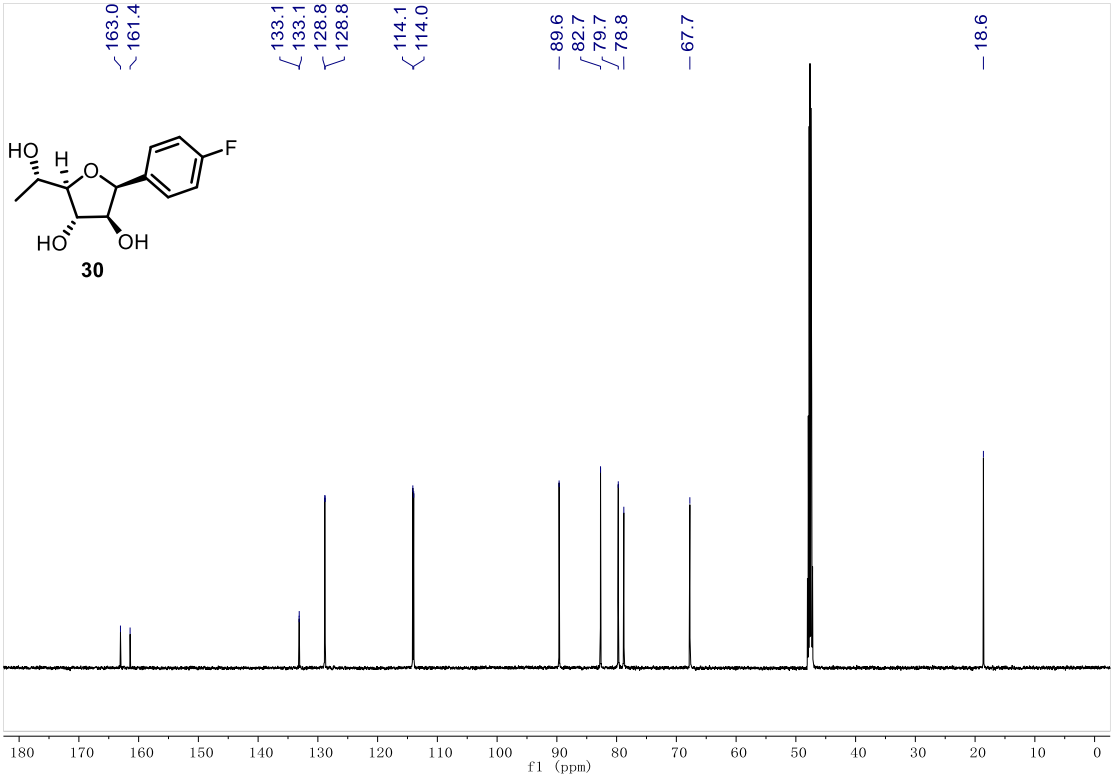

$^{13}$C NMR of compound **30-s** (101 MHz, $CD_3OD$)



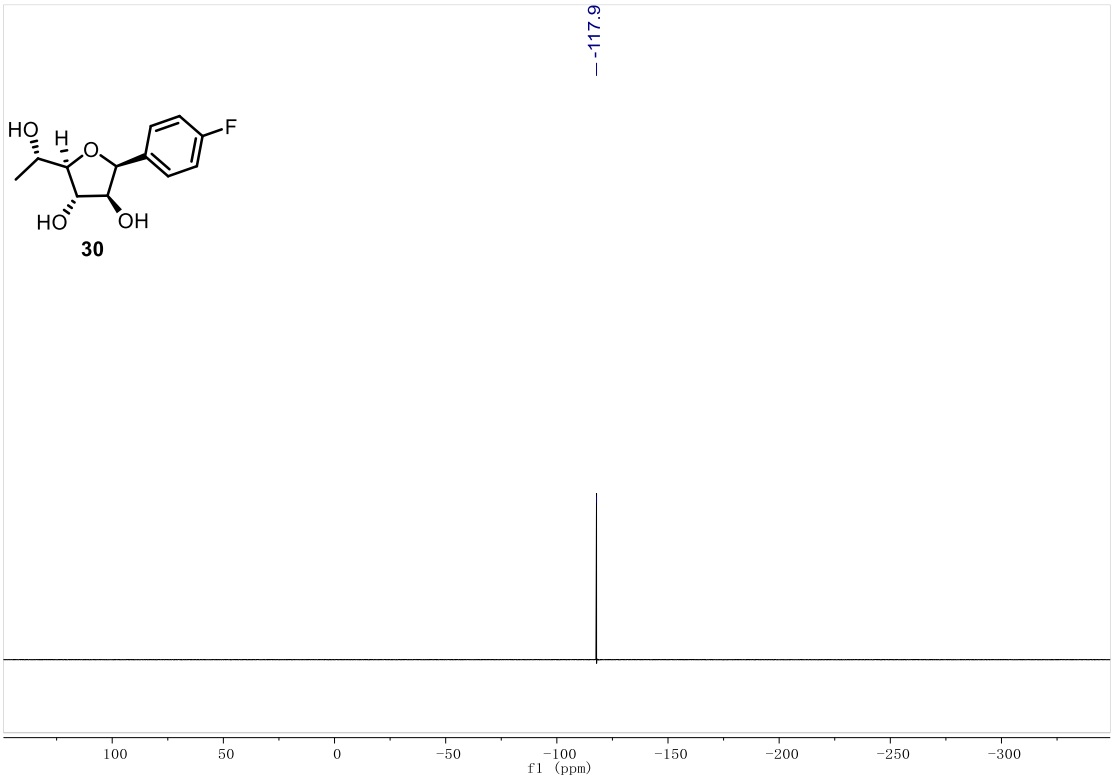

$^{19}$F NMR of compound **30-s** (376 MHz, $CD_3OD$)



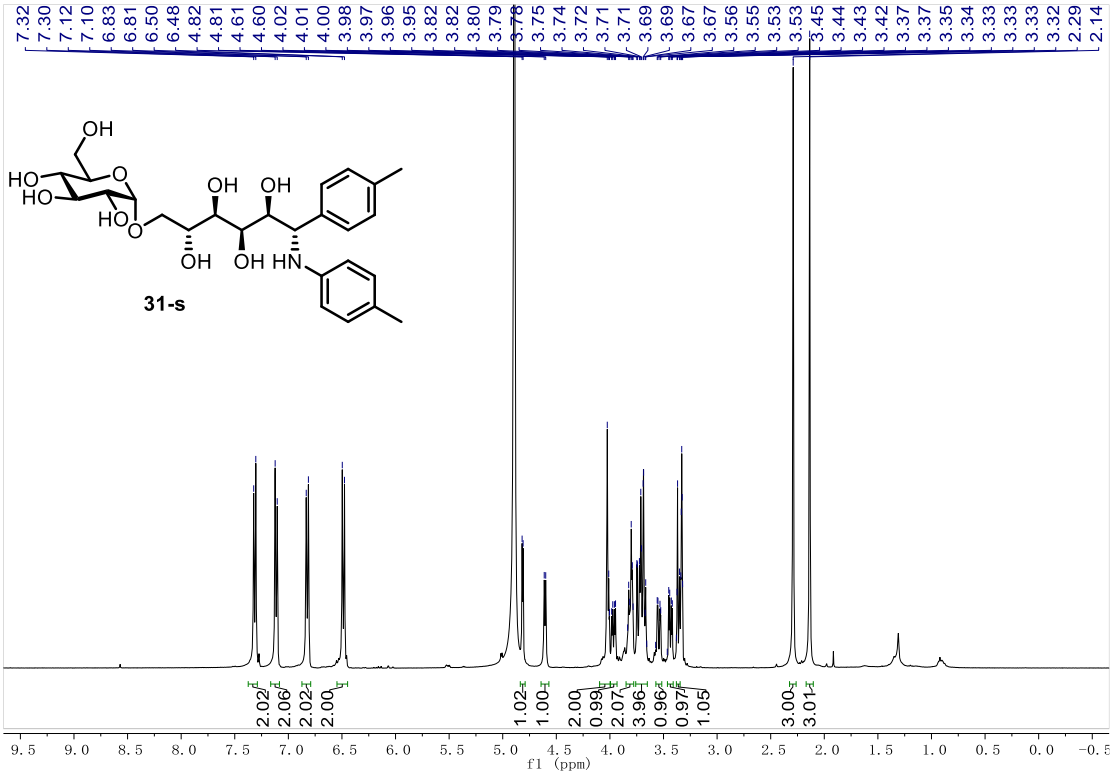

$^{1}$H NMR of compound **30** (400 MHz, $CD_3OD$)



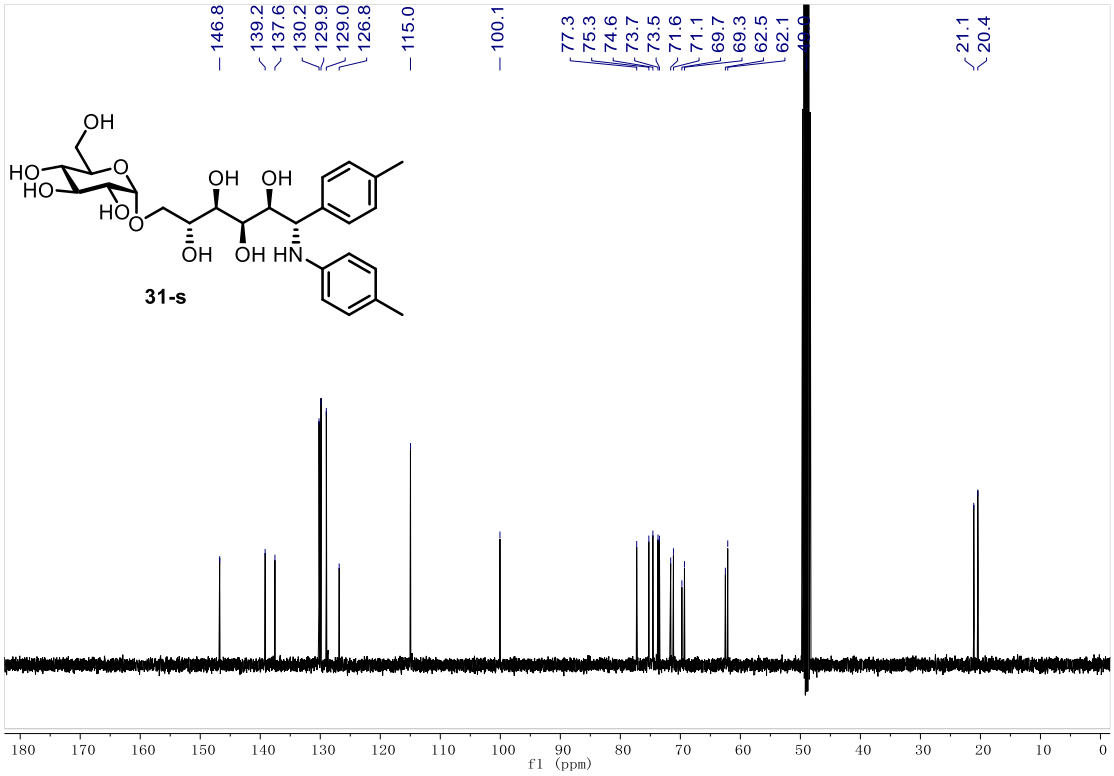

$^{13}$C NMR of compound **30** (101 MHz, $CD_3OD$)



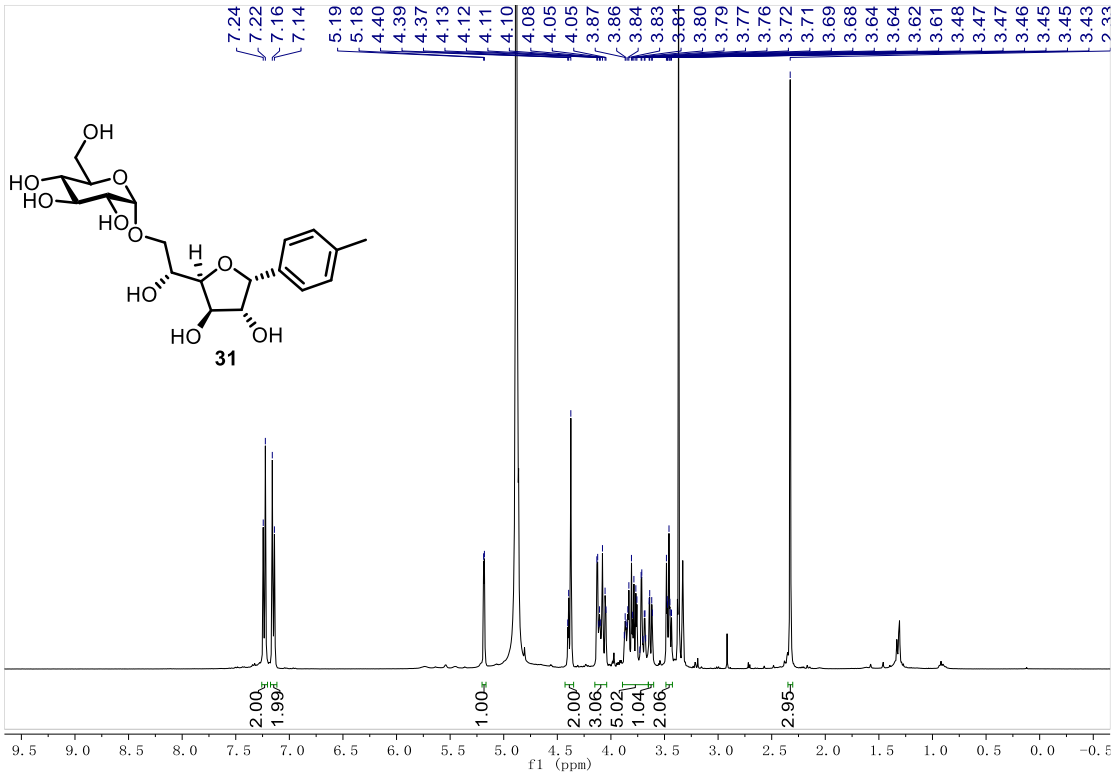

$^{19}$F NMR of compound **30** (376 MHz, $CD_3OD$)



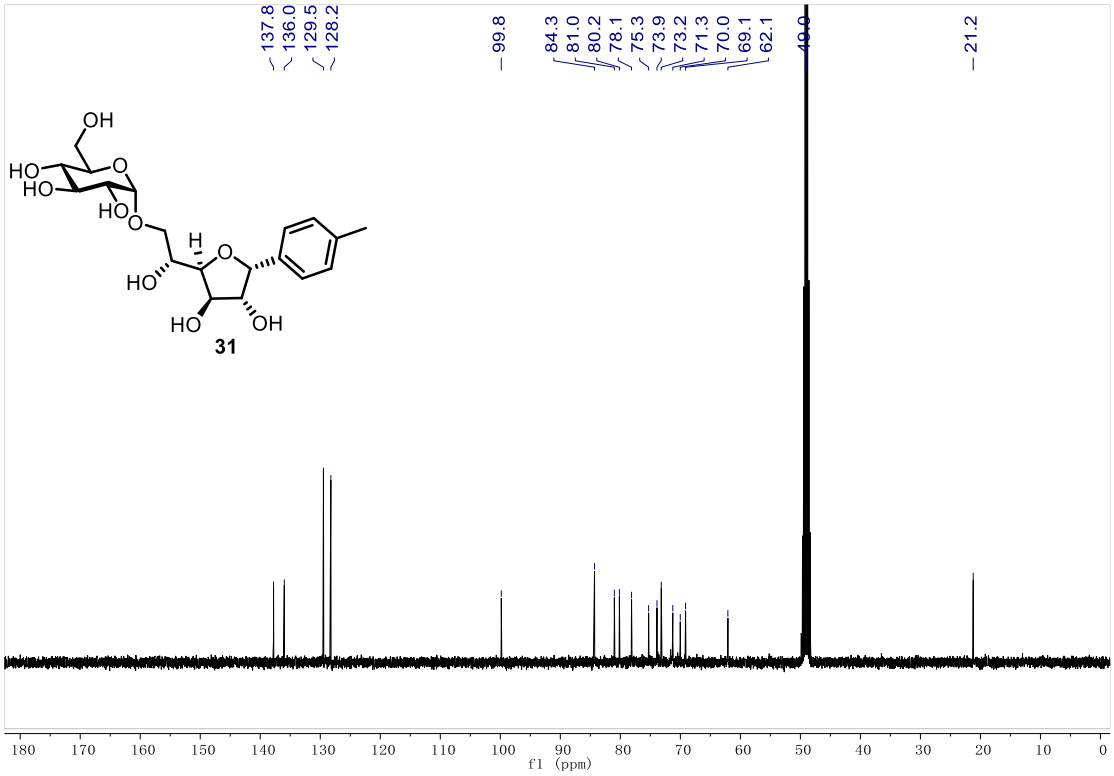

$^{1}$H NMR of compound **31-s** (400 MHz, $CD_3OD$)



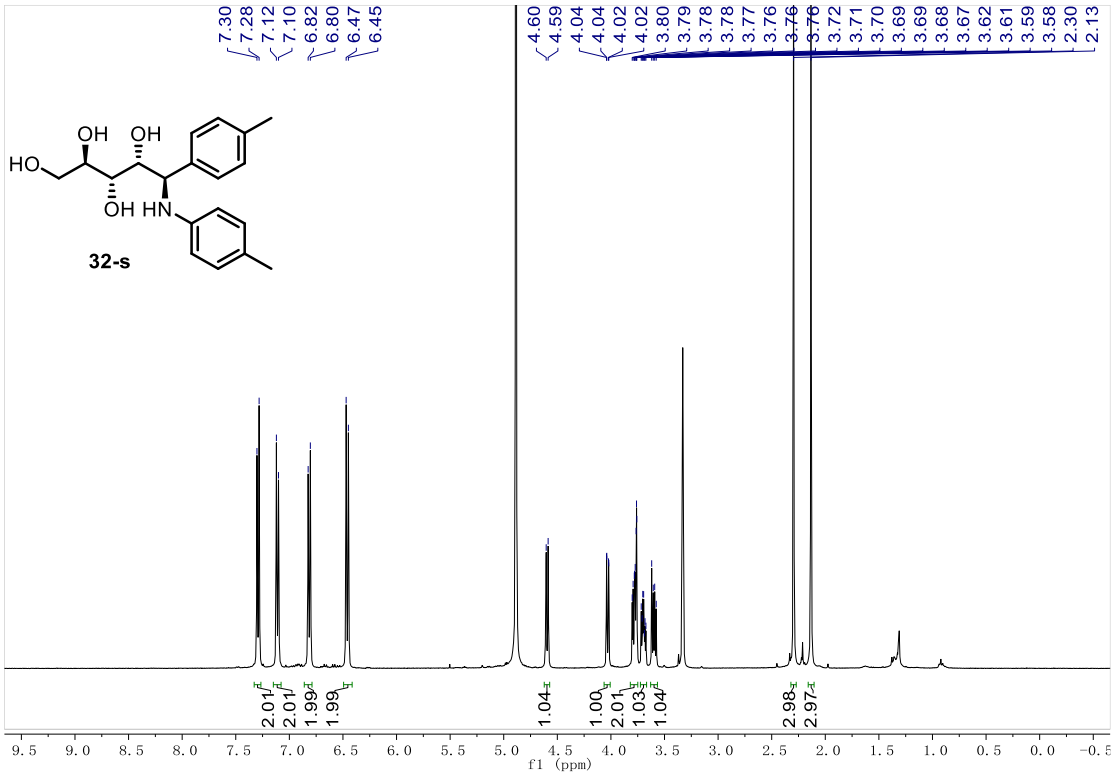

$^{13}$C NMR of compound **31-s** (101 MHz, $CD_3OD$)



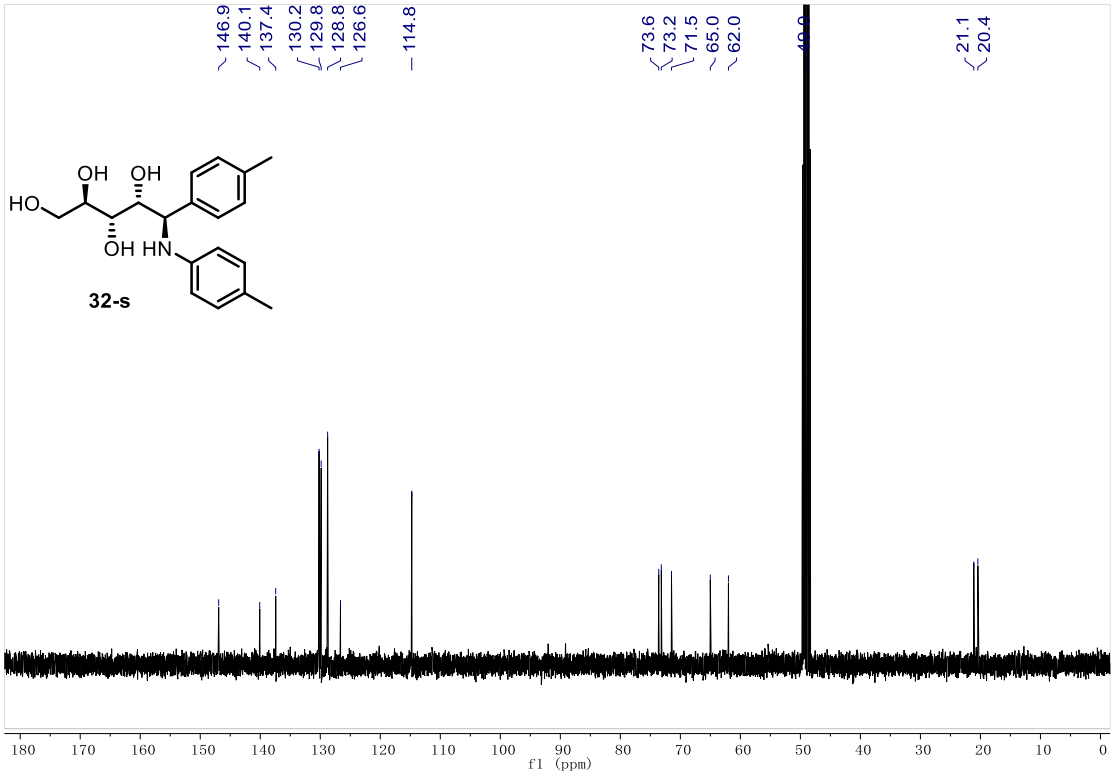

$^{1}$H NMR of compound **31** (400 MHz, $CD_3OD$)



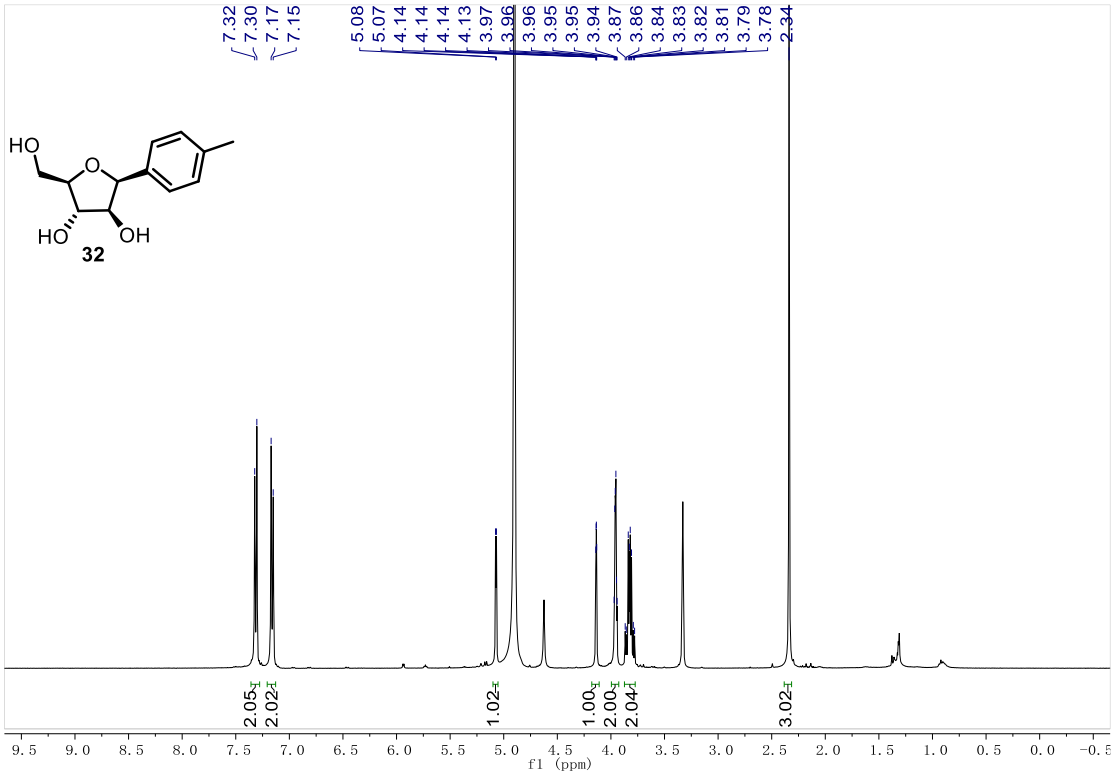

$^{13}$C NMR of compound **31** (101 MHz, $CD_3OD$)



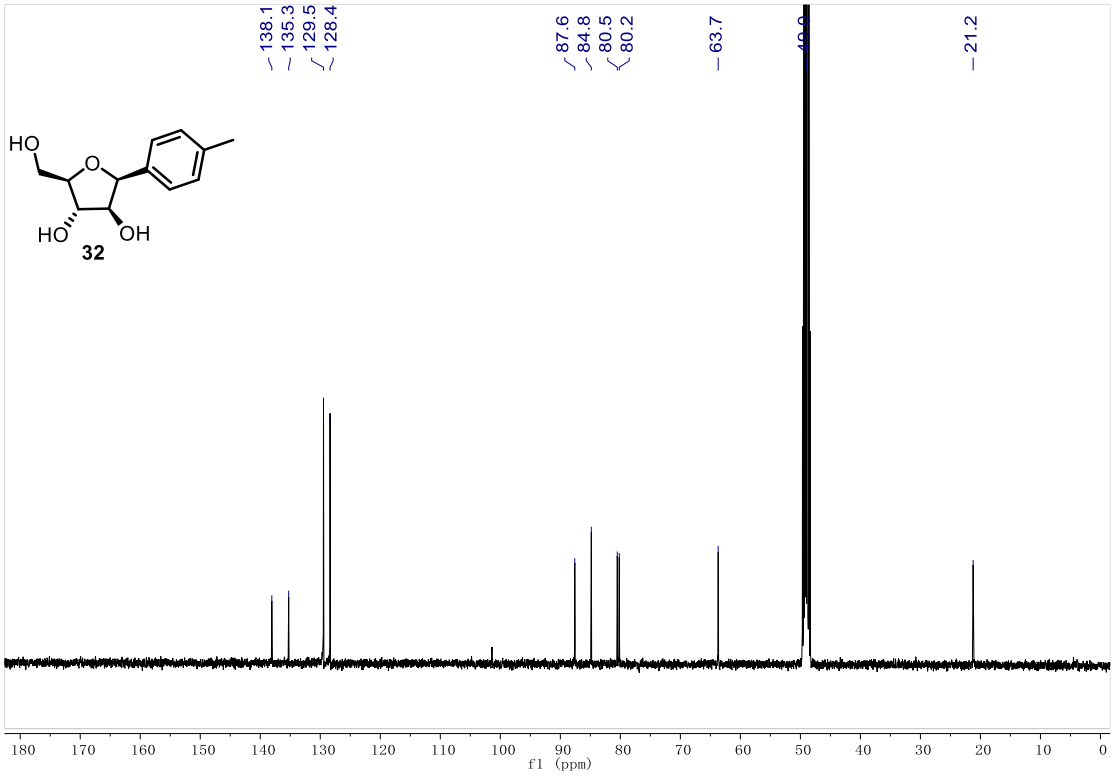

$^{1}$H NMR of compound **32-s** (400 MHz, $CD_3OD$)



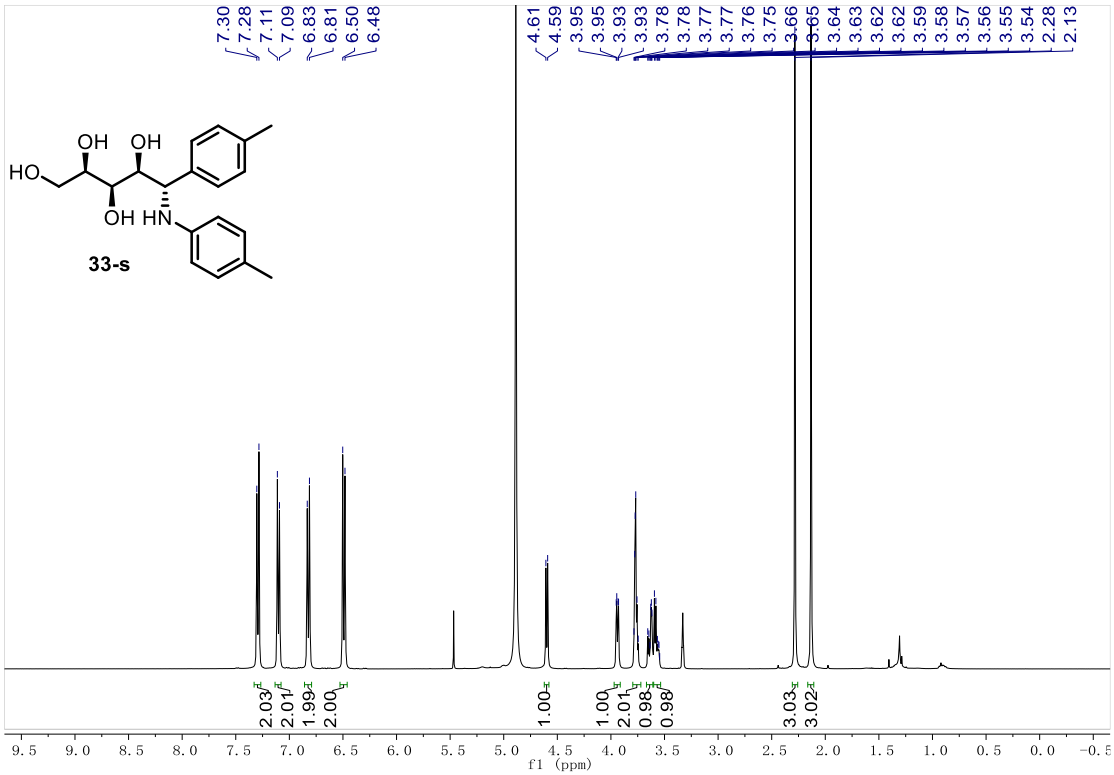

$^{13}$C NMR of compound **32-s** (101 MHz, $CD_3OD$)



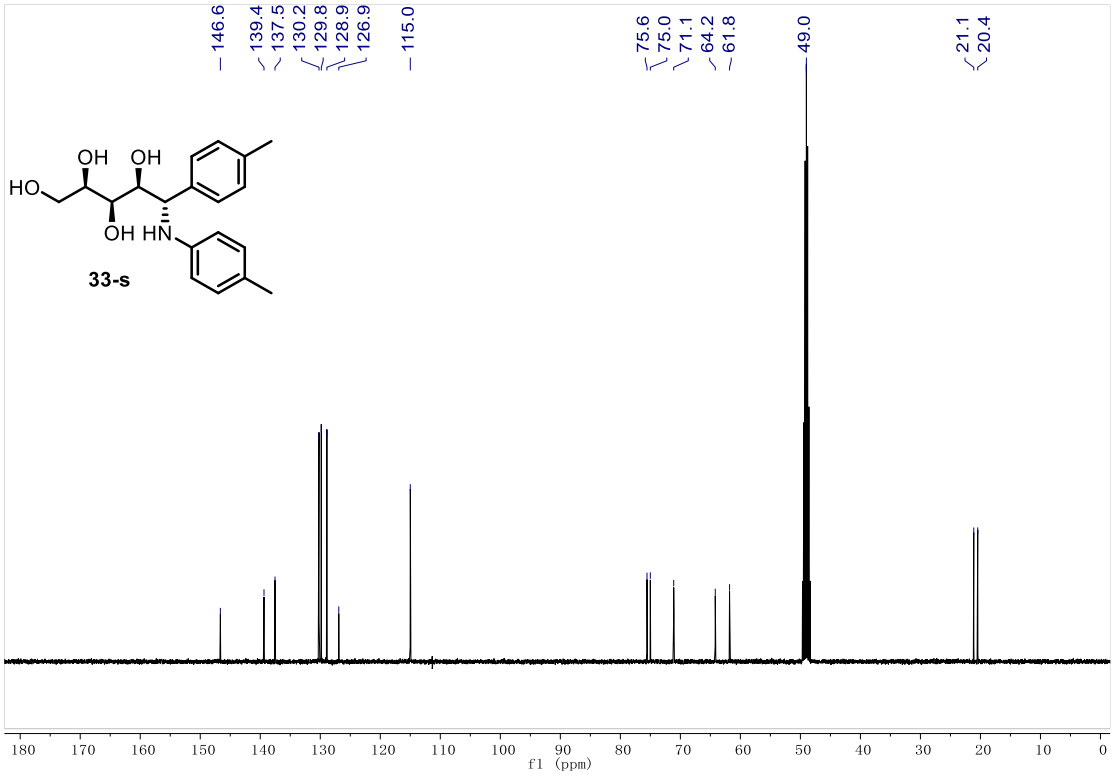

$^{1}$H NMR of compound **32** (400 MHz, $CD_3OD$)



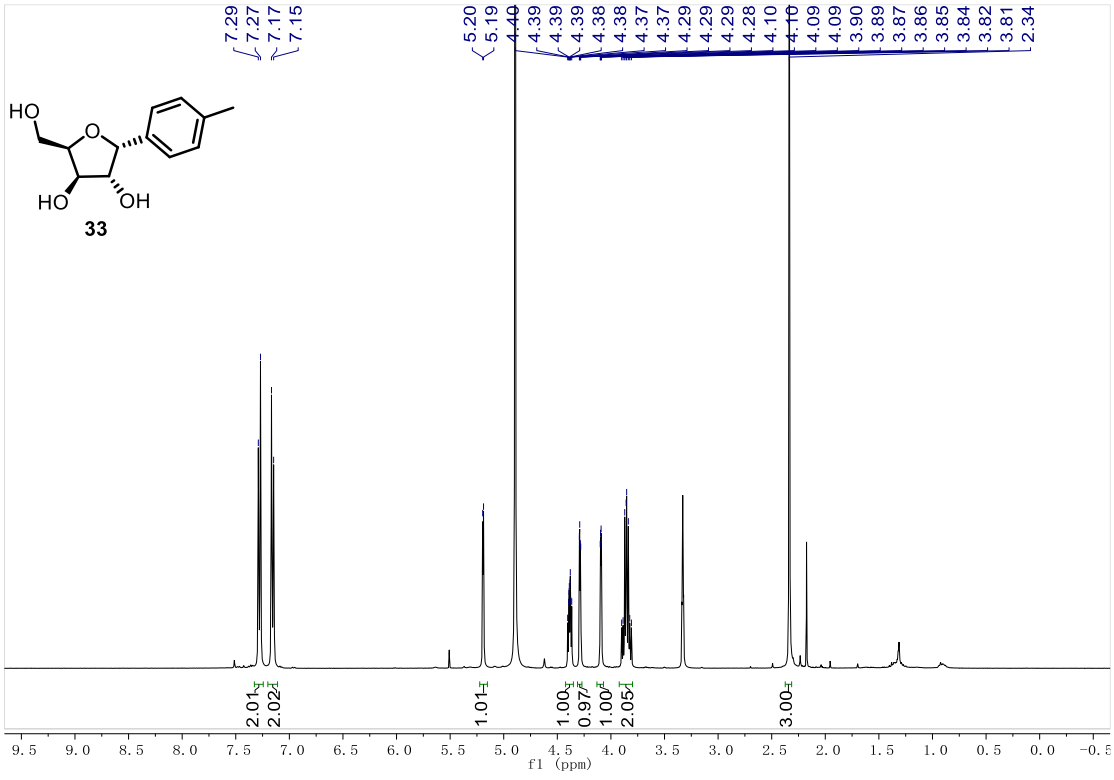

$^{13}$C NMR of compound **32** (101 MHz, $CD_3OD$)



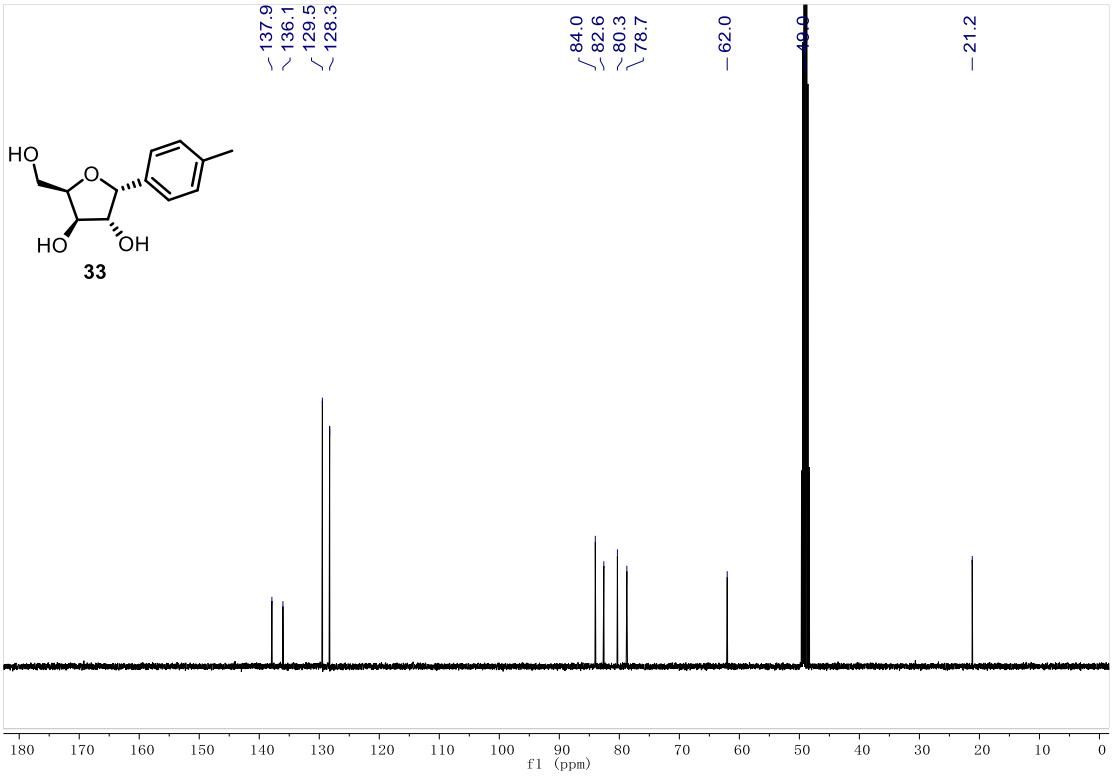

$^{1}$H NMR of compound **33-s** (400 MHz, $CD_3OD$)



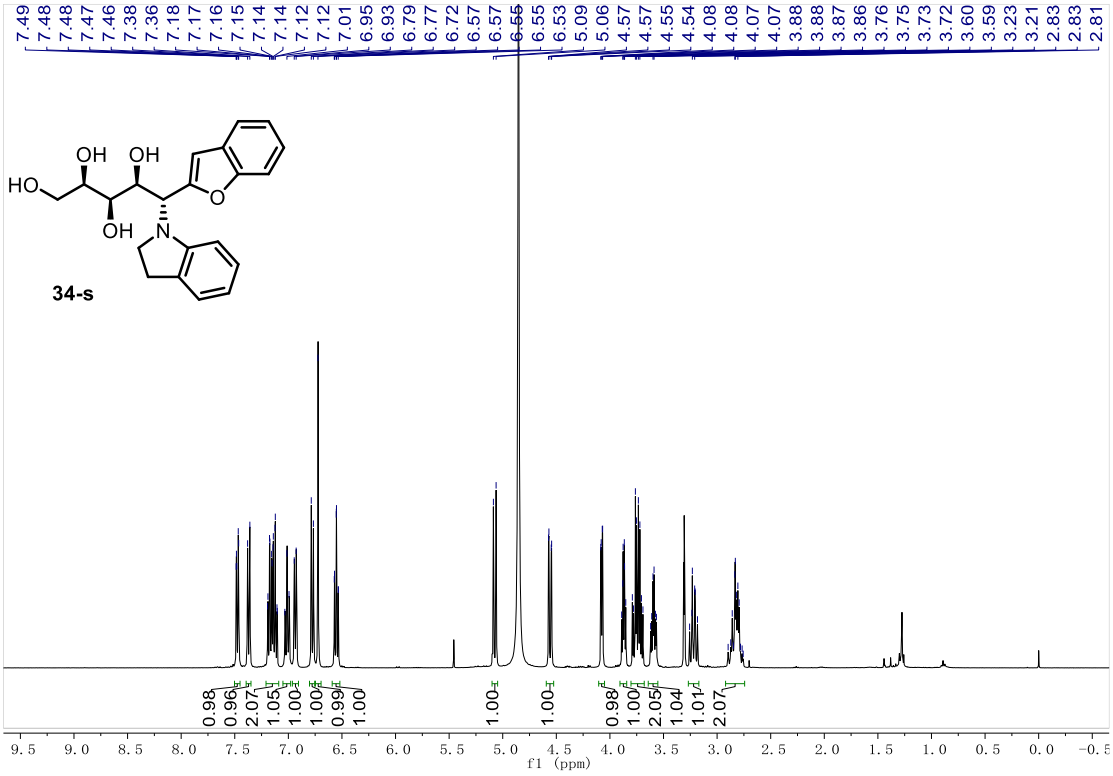

$^{13}$C NMR of compound **33-s** (101 MHz, $CD_3OD$)



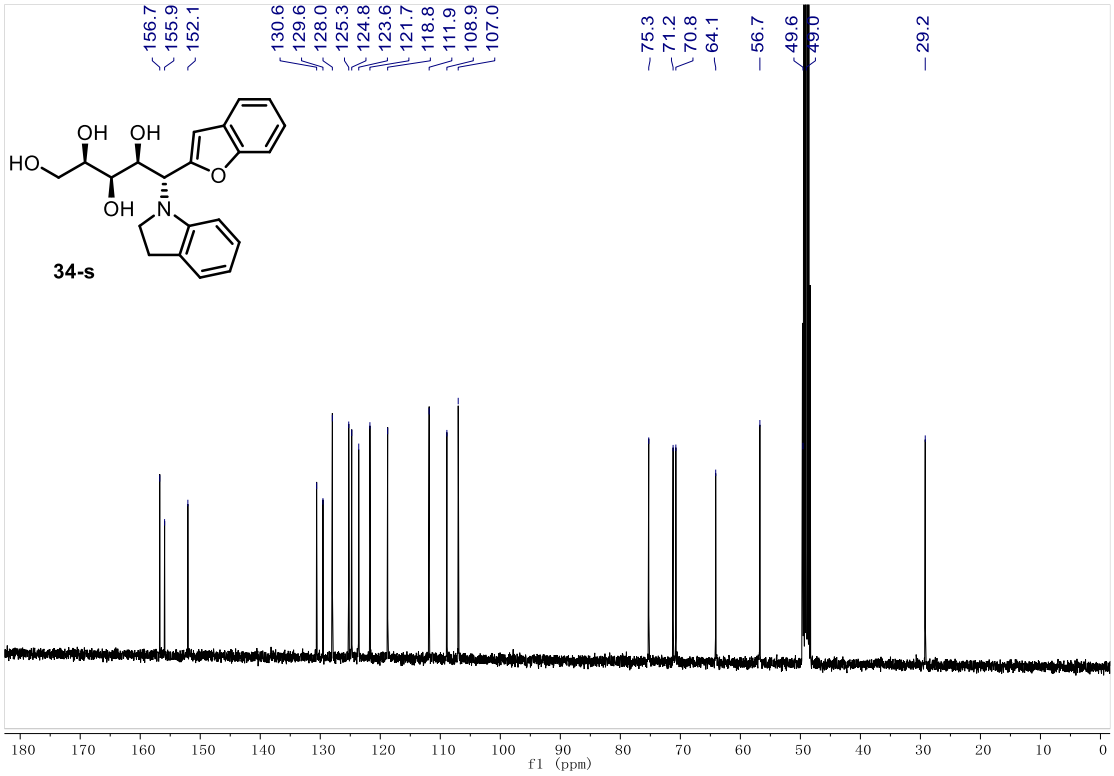

$^{1}$H NMR of compound **33** (400 MHz, $CD_3OD$)



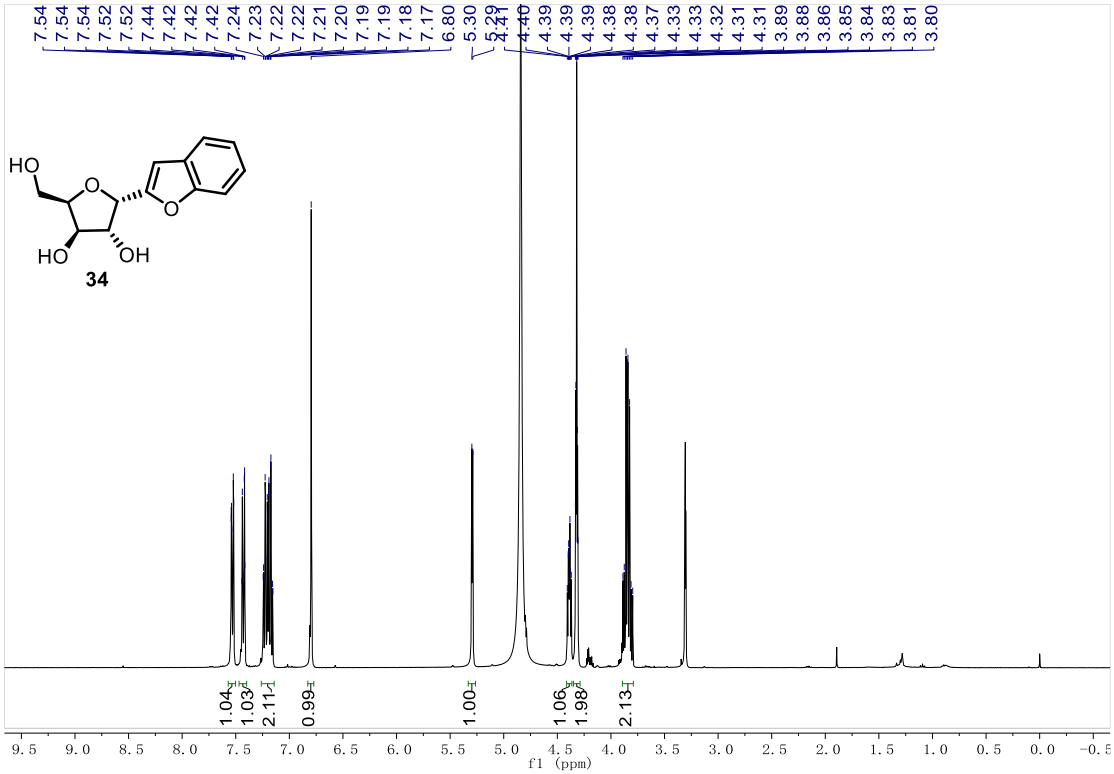

$^{13}$C NMR of compound **33** (101 MHz, $CD_3OD$)



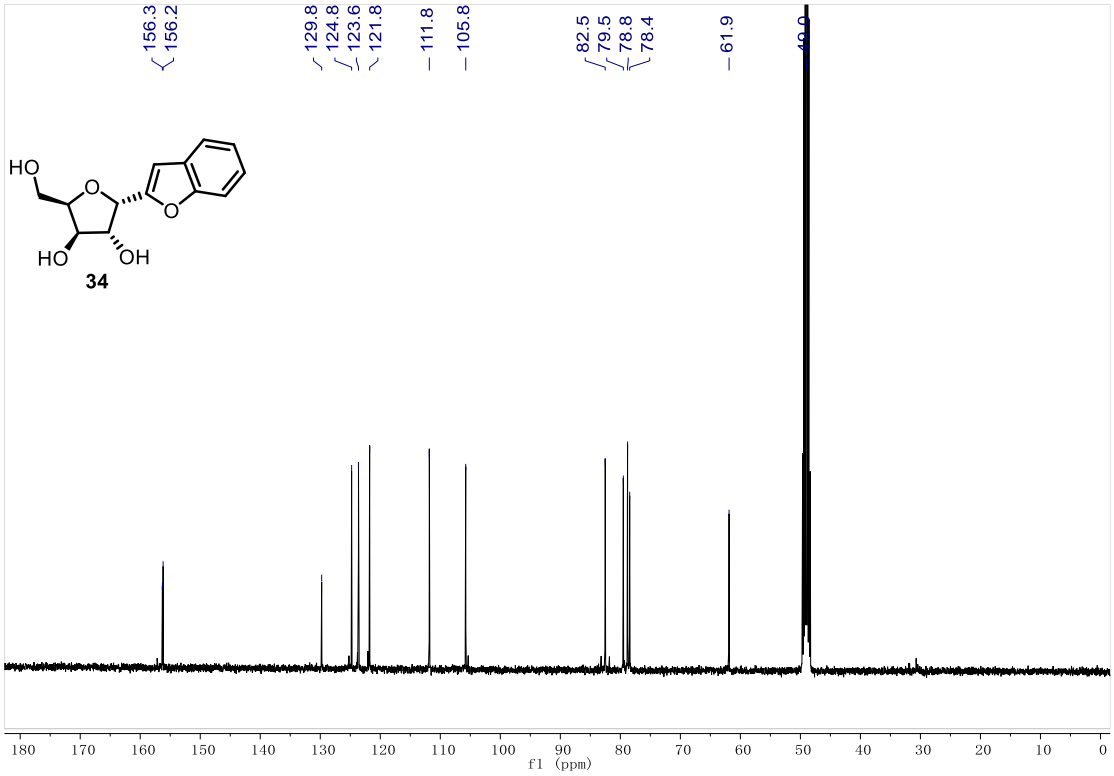

$^{1}$H NMR of compound **34-s** (400 MHz, $CD_3OD$)



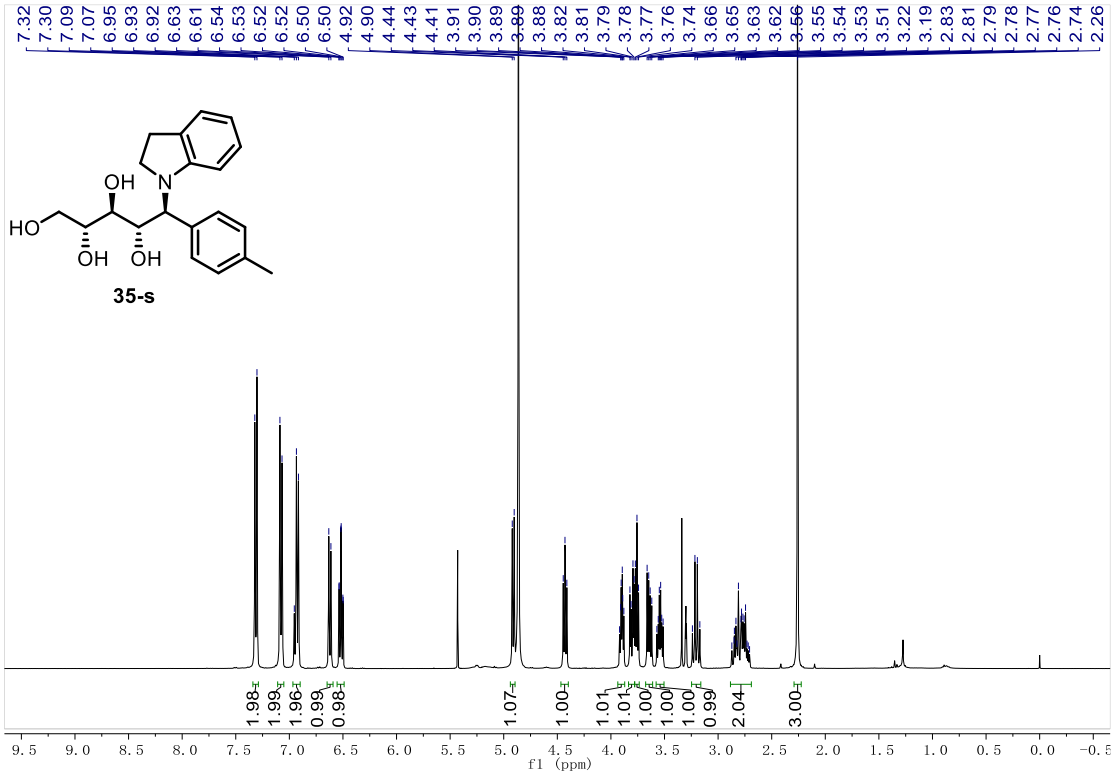

$^{13}$C NMR of compound **34-s** (101 MHz, $CD_3OD$)



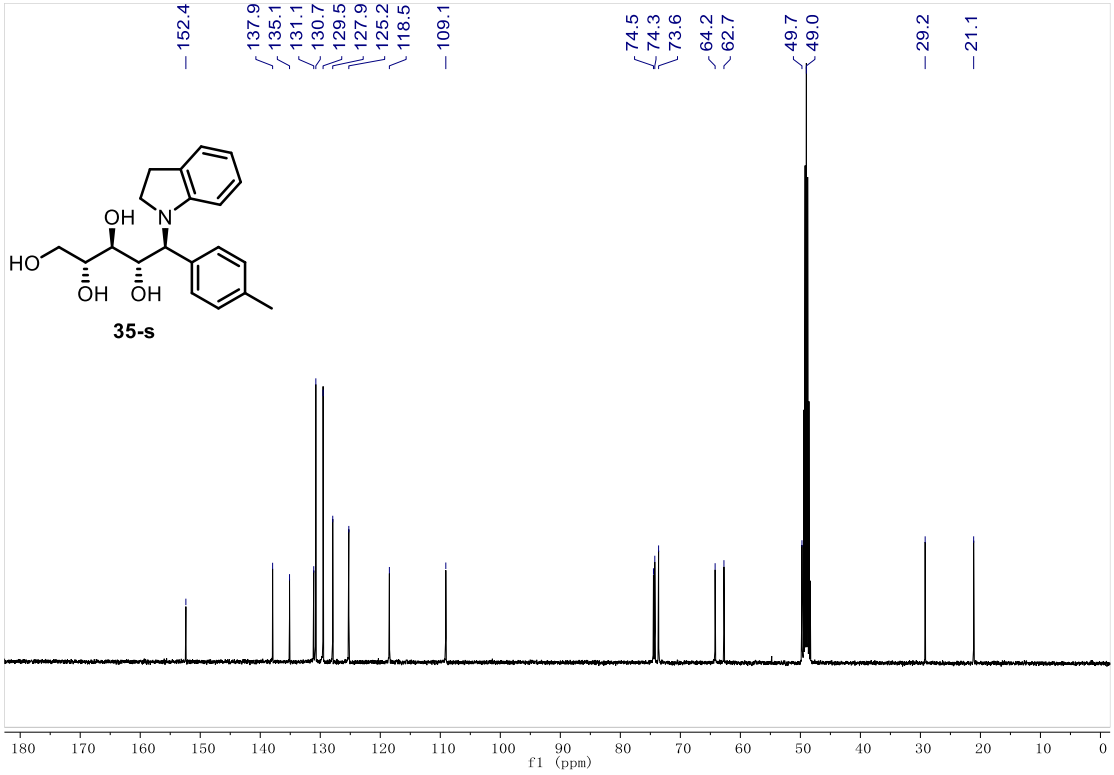

$^{1}$H NMR of compound **34** (400 MHz, $CD_3OD$)



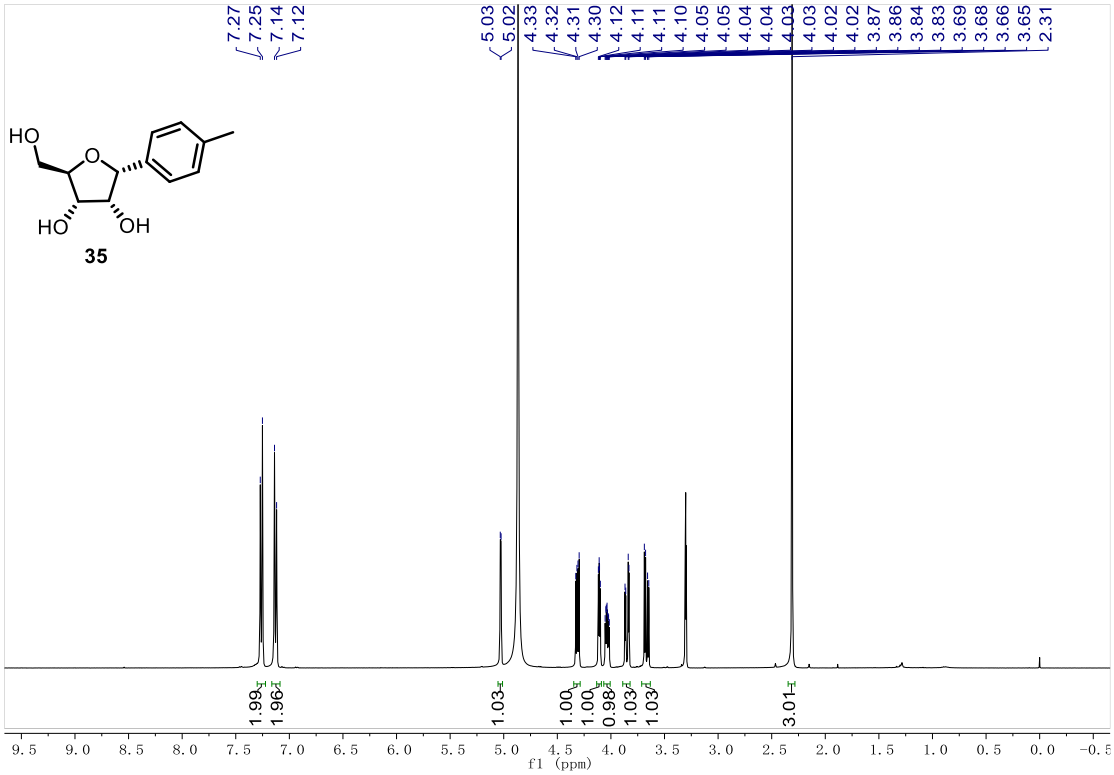

$^{13}$C NMR of compound **34** (101 MHz, $CD_3OD$)



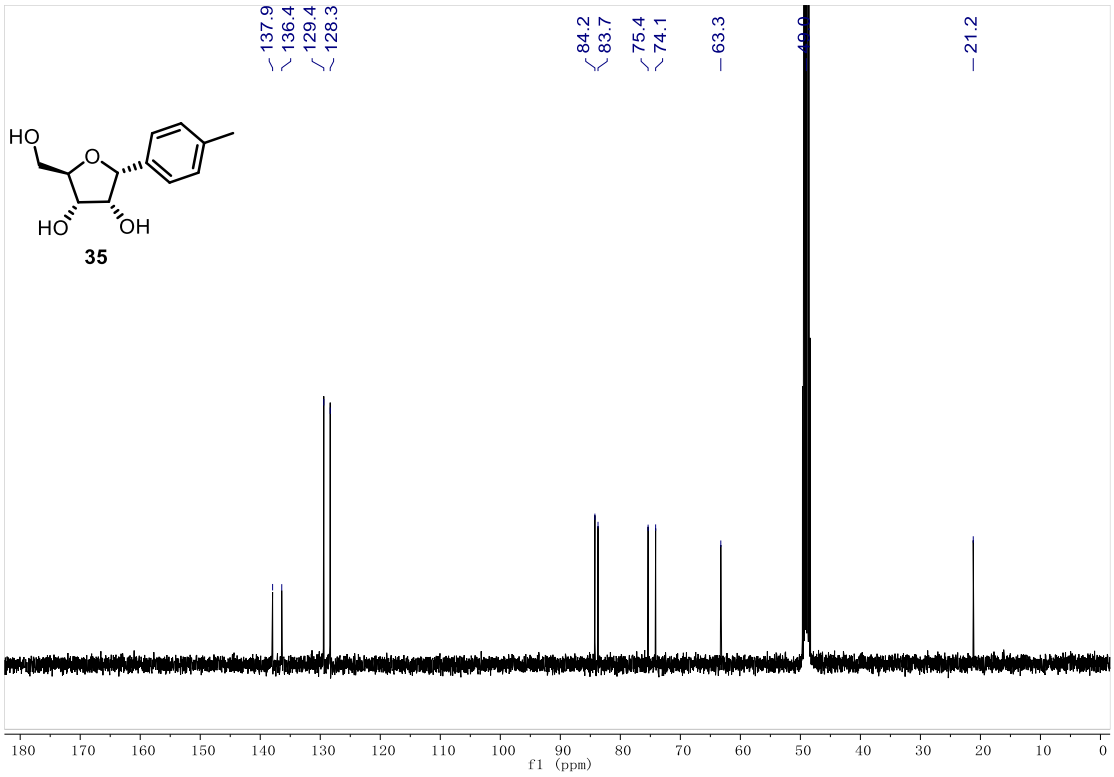

$^{1}$H NMR of compound **35-s** (400 MHz, $CD_3OD$)



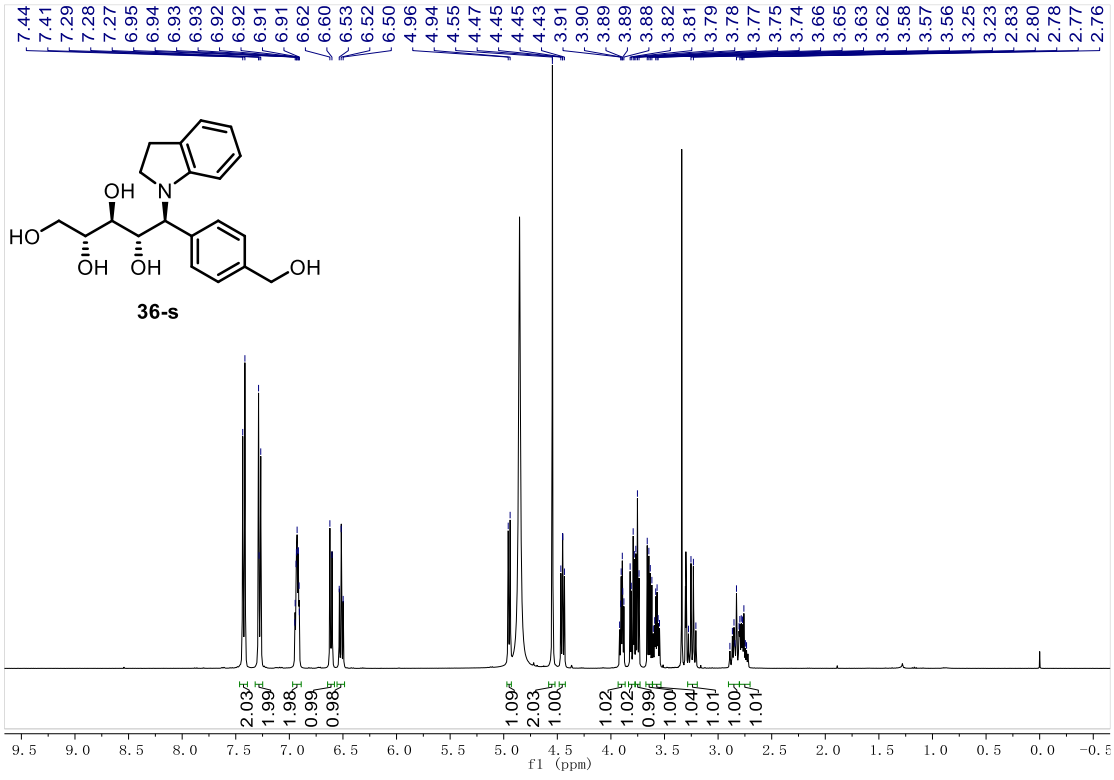

$^{13}$C NMR of compound **35-s** (101 MHz, $CD_3OD$)



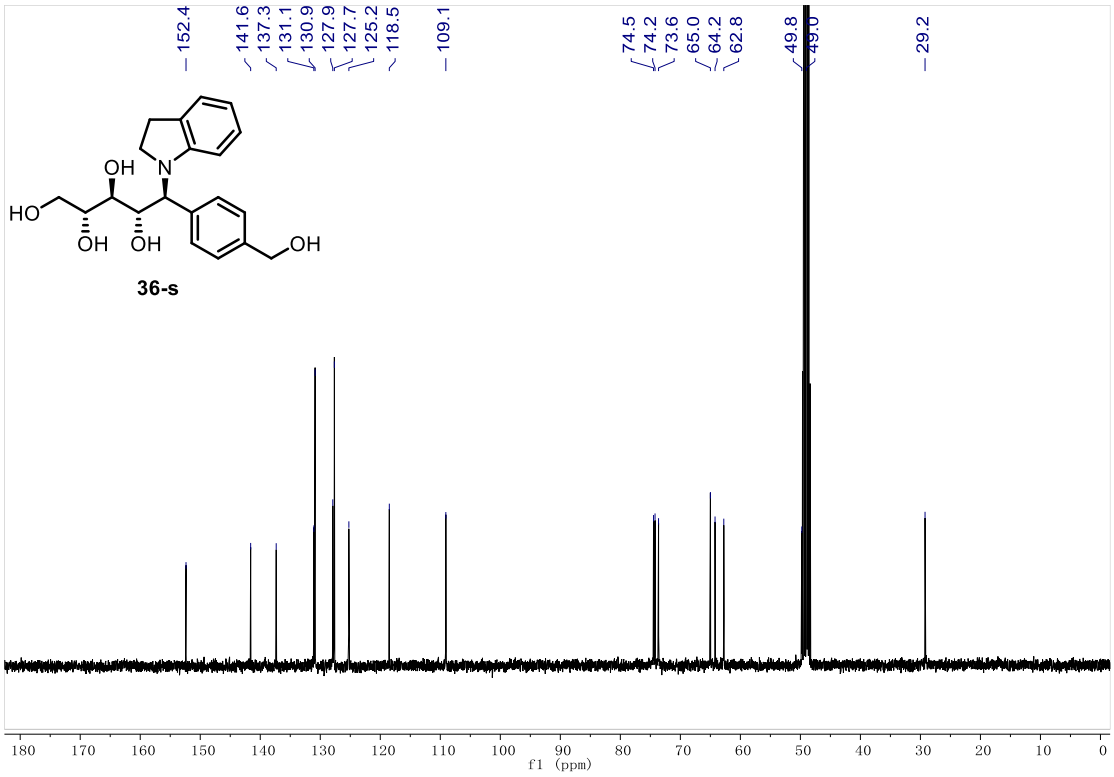

$^{1}$H NMR of compound **35** (400 MHz, $CD_3OD$)



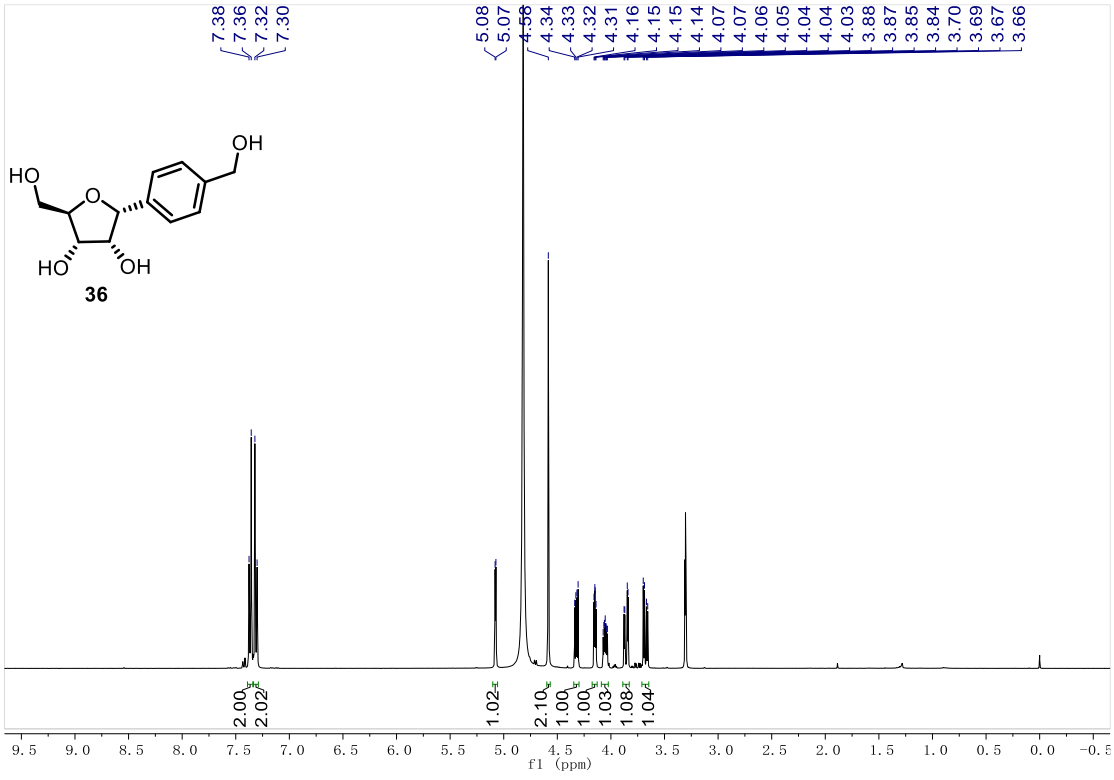

$^{13}$C NMR of compound **35** (101 MHz, $CD_3OD$)



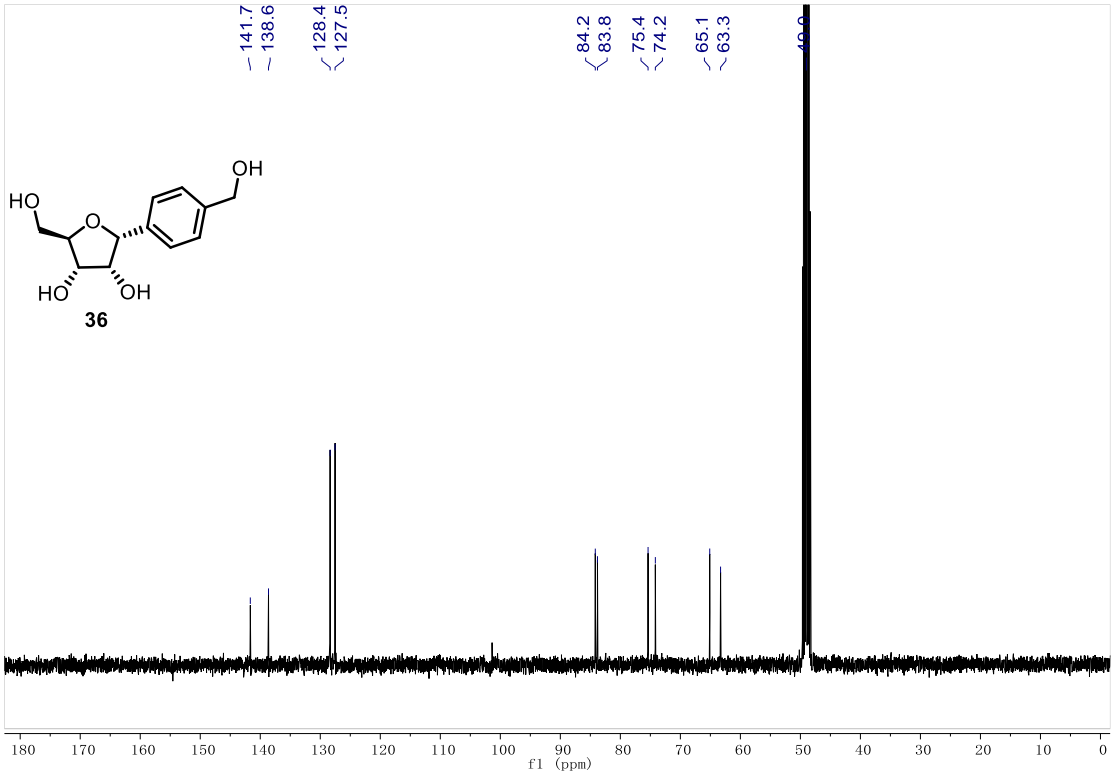

$^{1}$H NMR of compound **36-s** (400 MHz, $CD_3OD$)



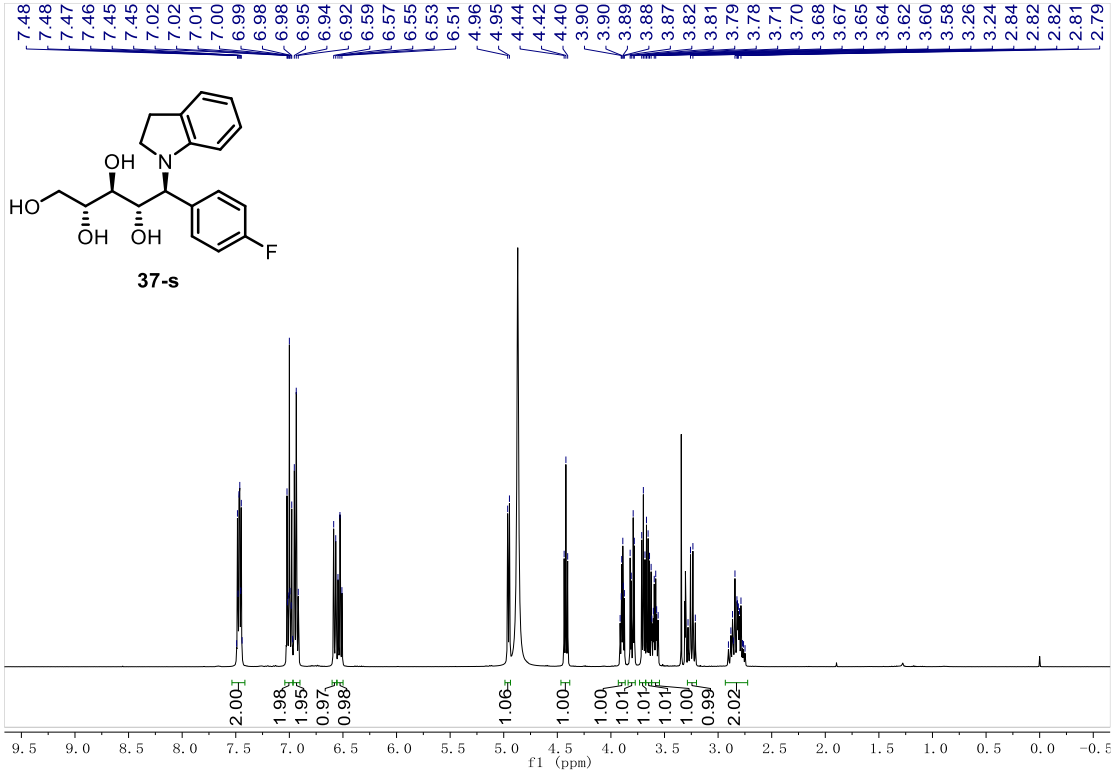

$^{13}$C NMR of compound **36-s** (101 MHz, $CD_3OD$)



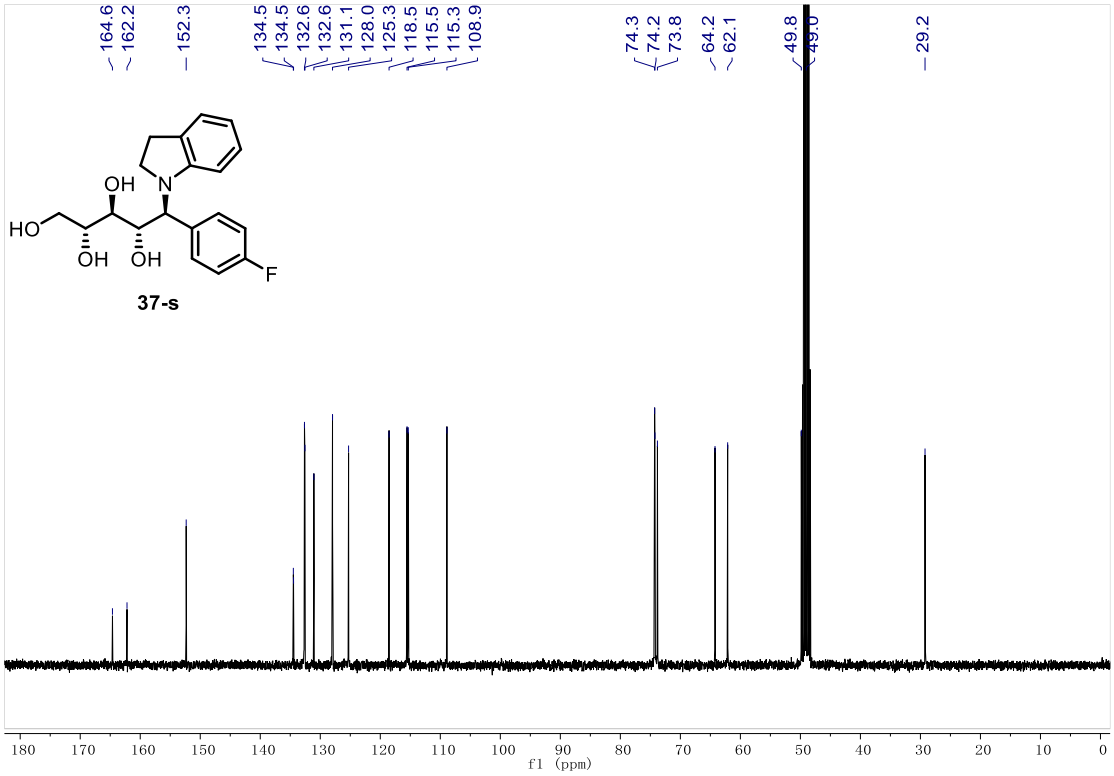

$^{1}$H NMR of compound **36** (400 MHz, $CD_3OD$)



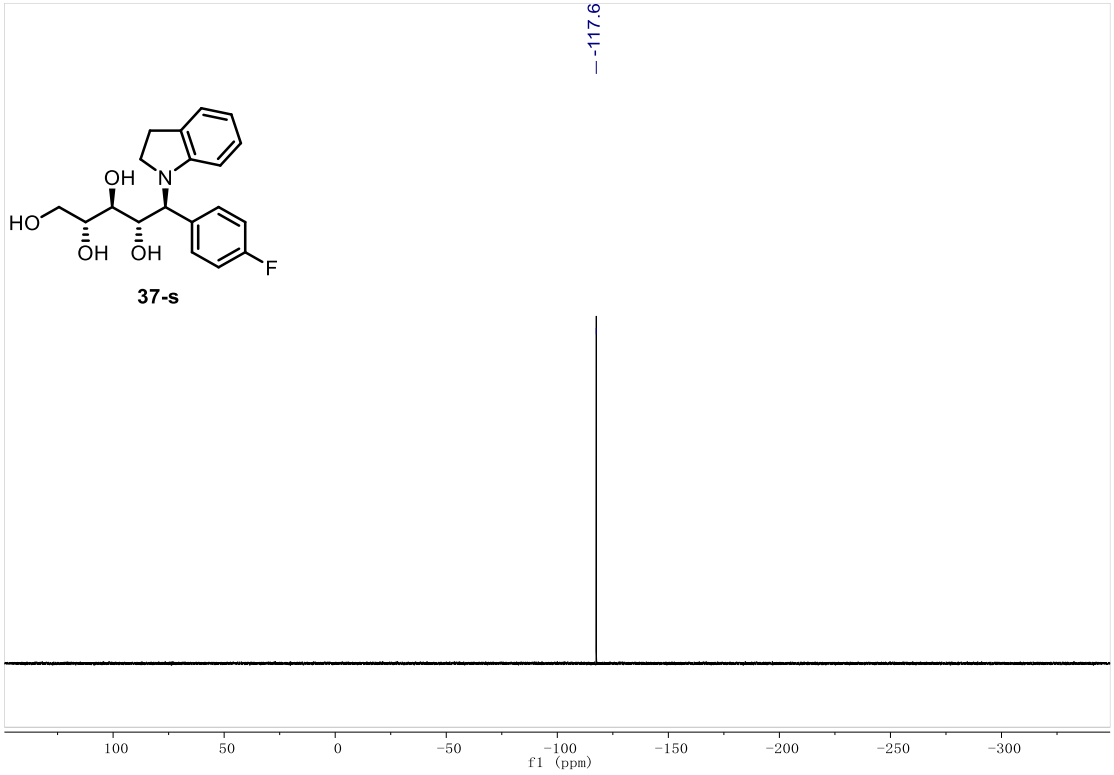

$^{13}$C NMR of compound **36** (101 MHz, $CD_3OD$)



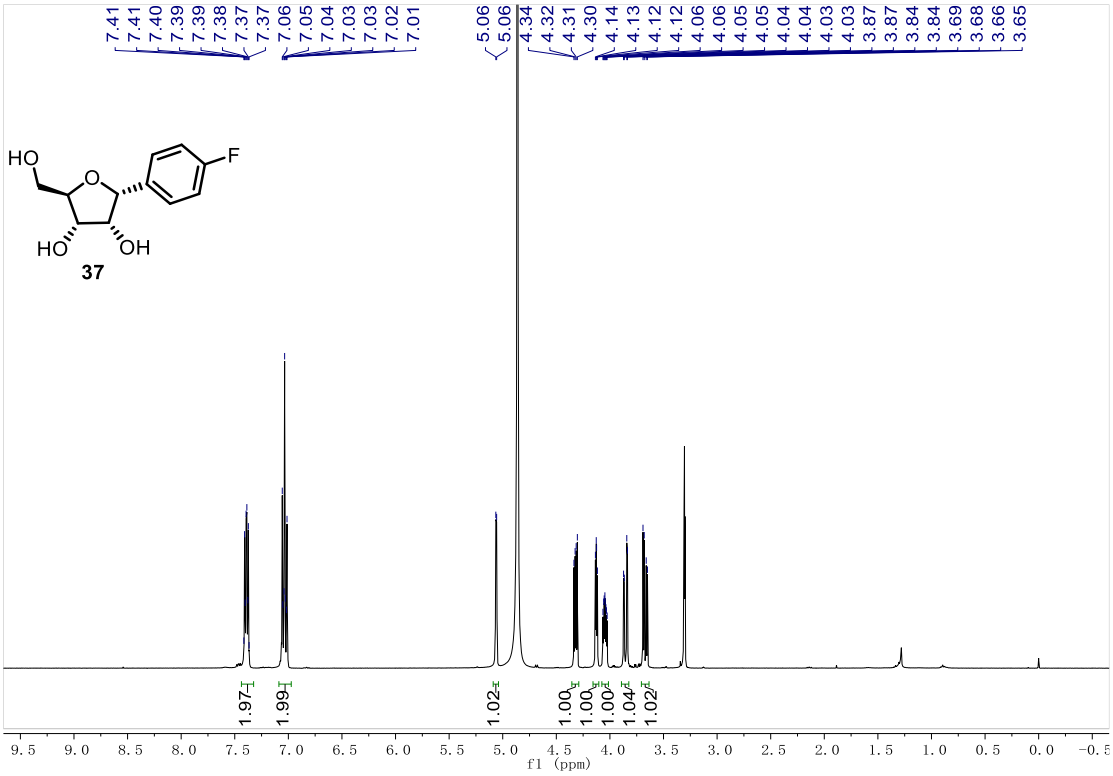

$^{1}$H NMR of compound **37-s** (400 MHz, $CD_3OD$)



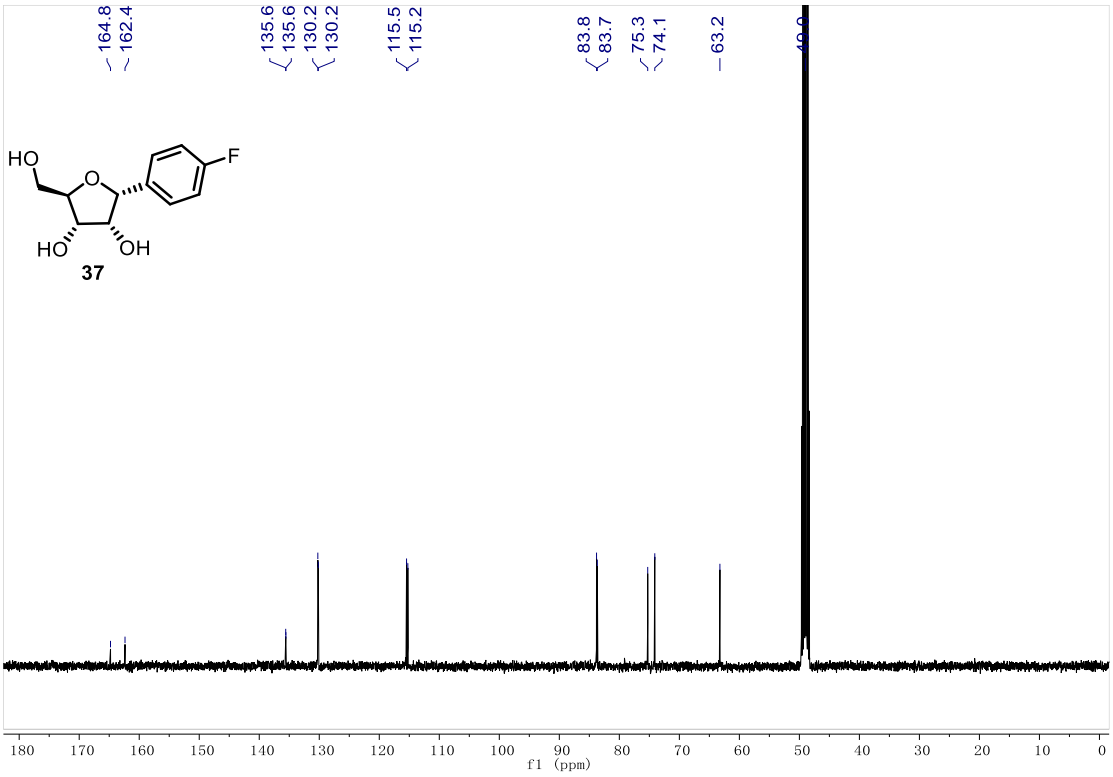

$^{13}$C NMR of compound **37-s** (101 MHz, $CD_3OD$)



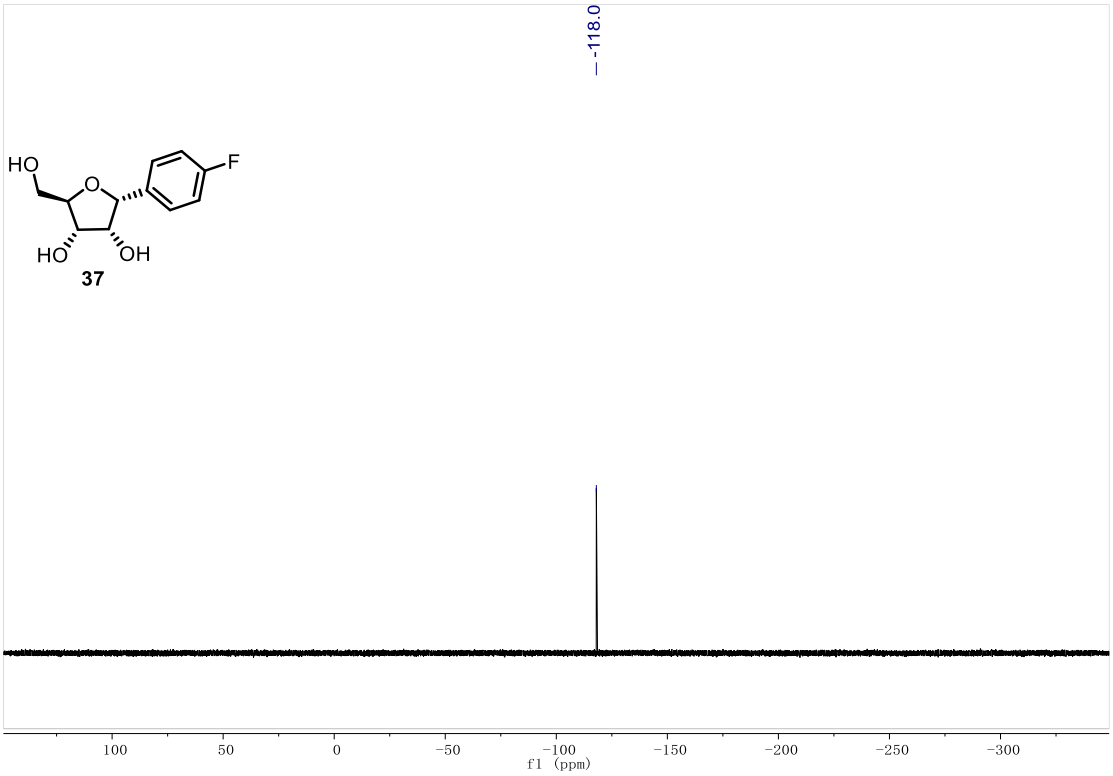

$^{19}$F NMR of compound **37-s** (376 MHz, $CD_3OD$)



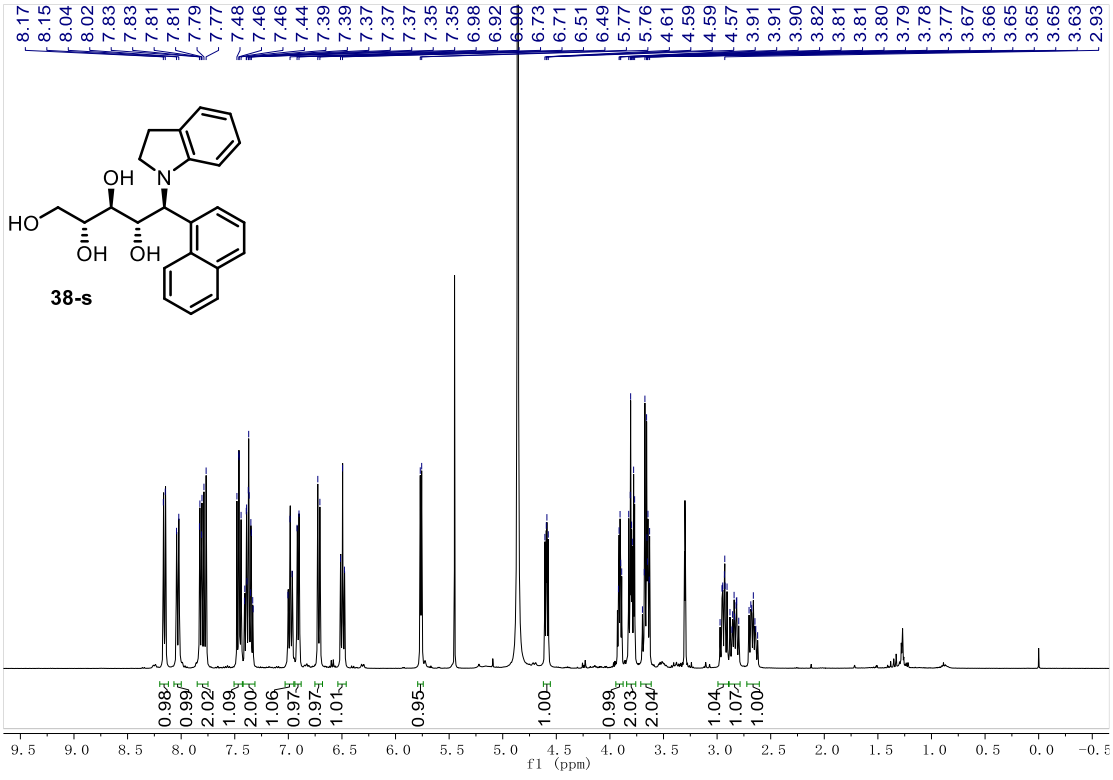

$^{1}$H NMR of compound **37** (400 MHz, $CD_3OD$)



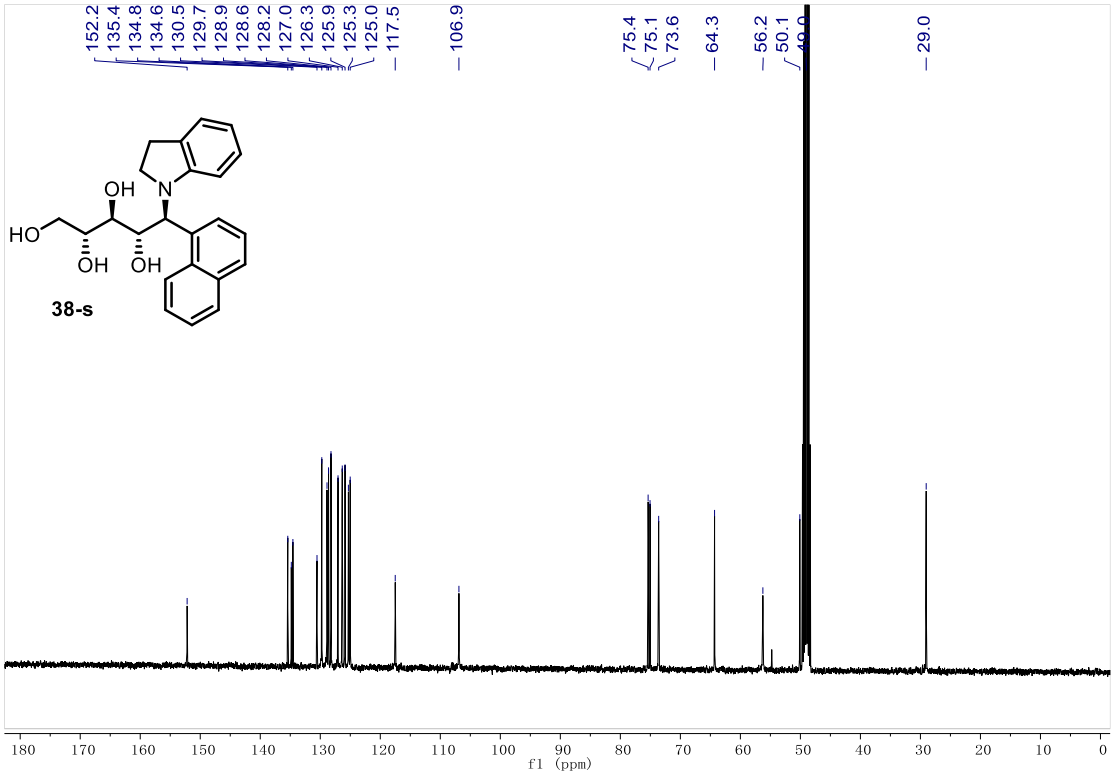

$^{13}$C NMR of compound **37** (101 MHz, $CD_3OD$)



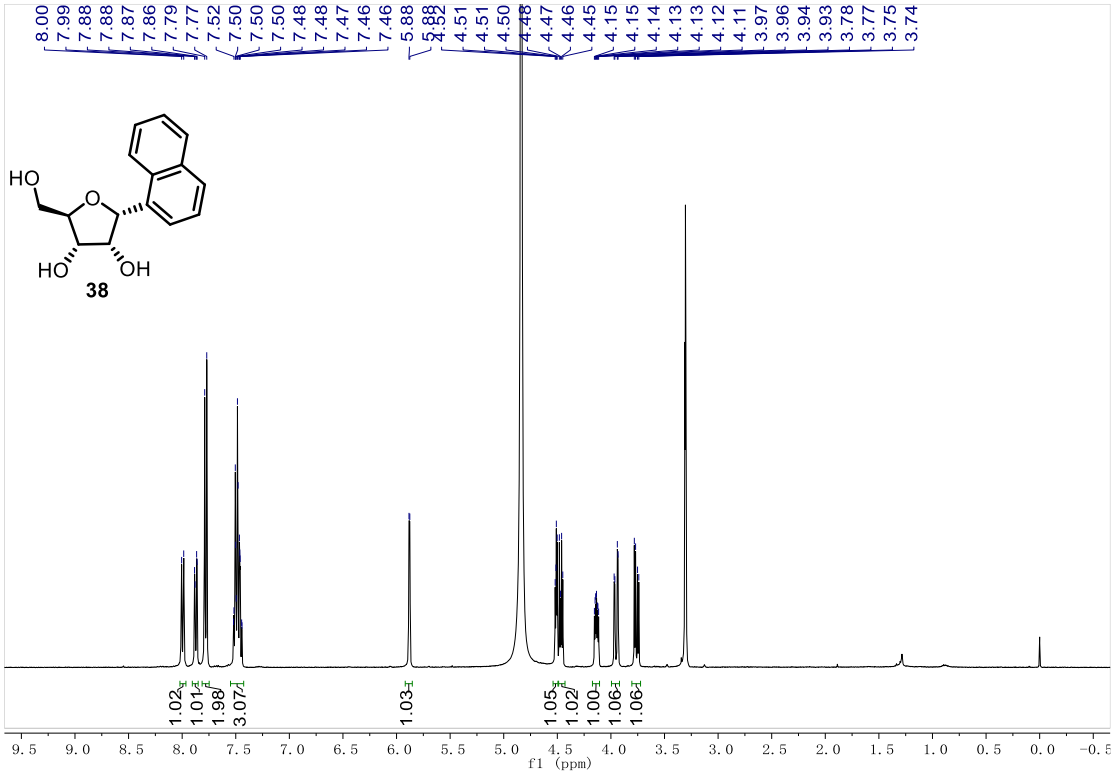

$^{19}$F NMR of compound **37** (376 MHz, $CD_3OD$)



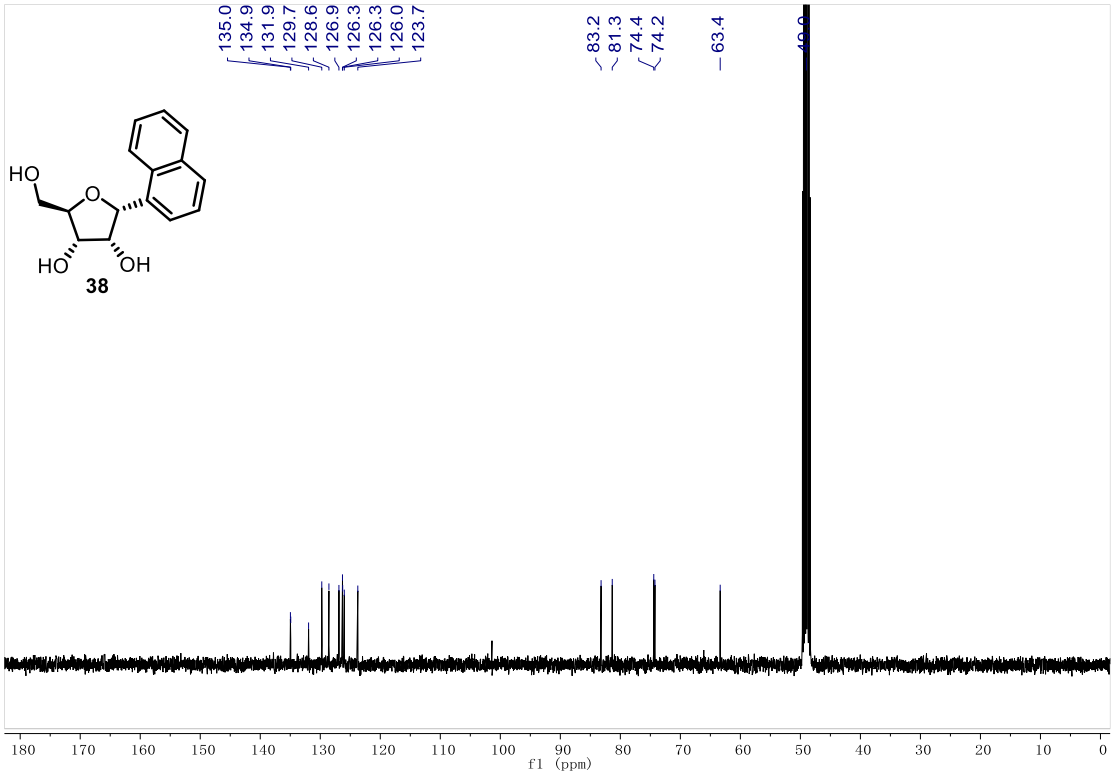

$^{1}$H NMR of compound **38-s** (400 MHz, $CD_3OD$)



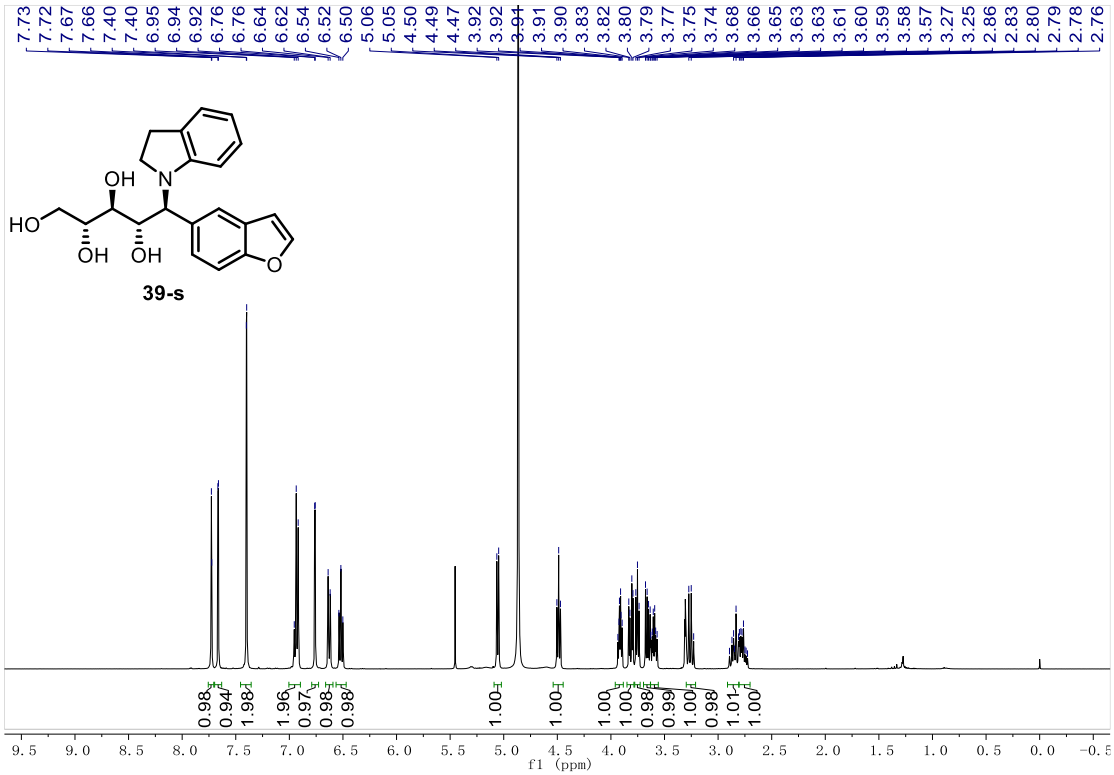

$^{13}$C NMR of compound **38-s** (101 MHz, $CD_3OD$)



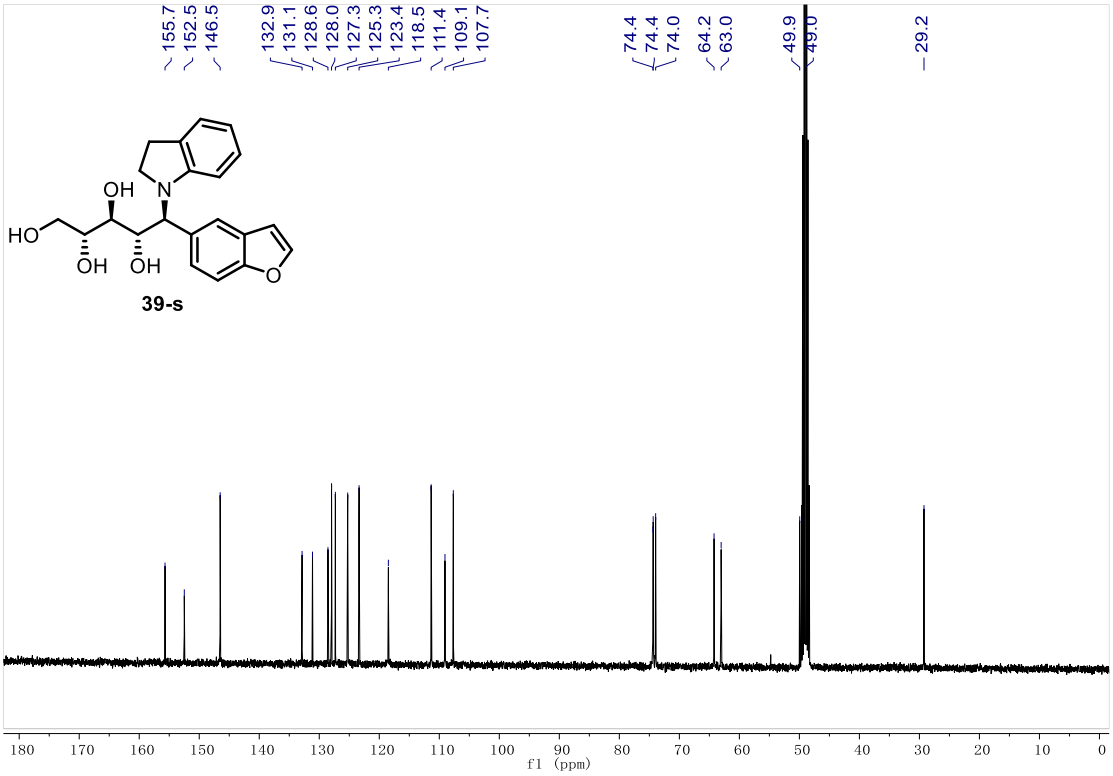

$^{1}$H NMR of compound **38** (400 MHz, $CD_3OD$)



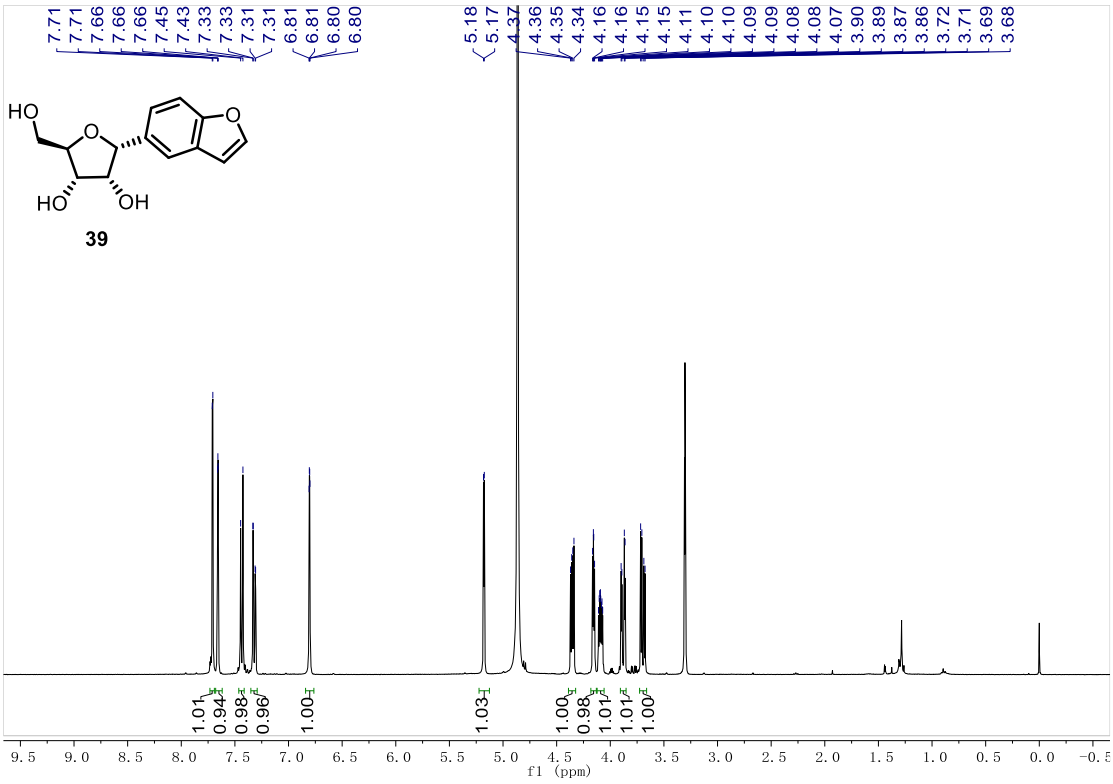

$^{13}$C NMR of compound **38** (101 MHz, $CD_3OD$)



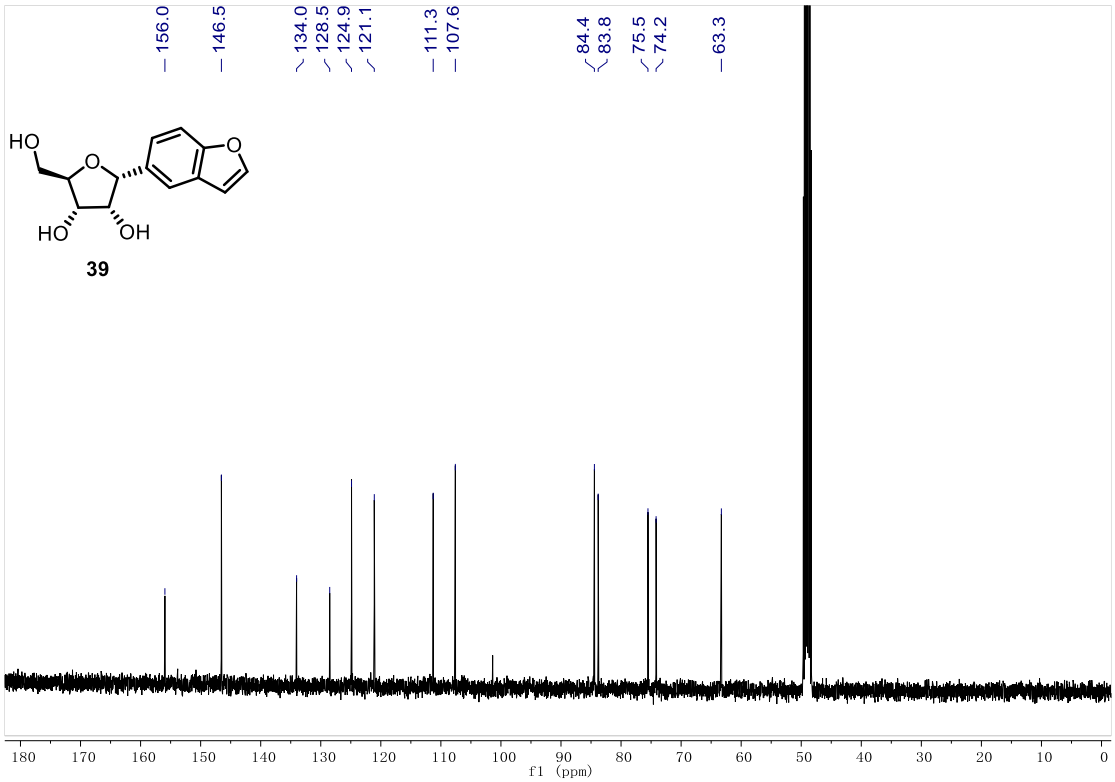

$^{1}$H NMR of compound **39-s** (400 MHz, $CD_3OD$)



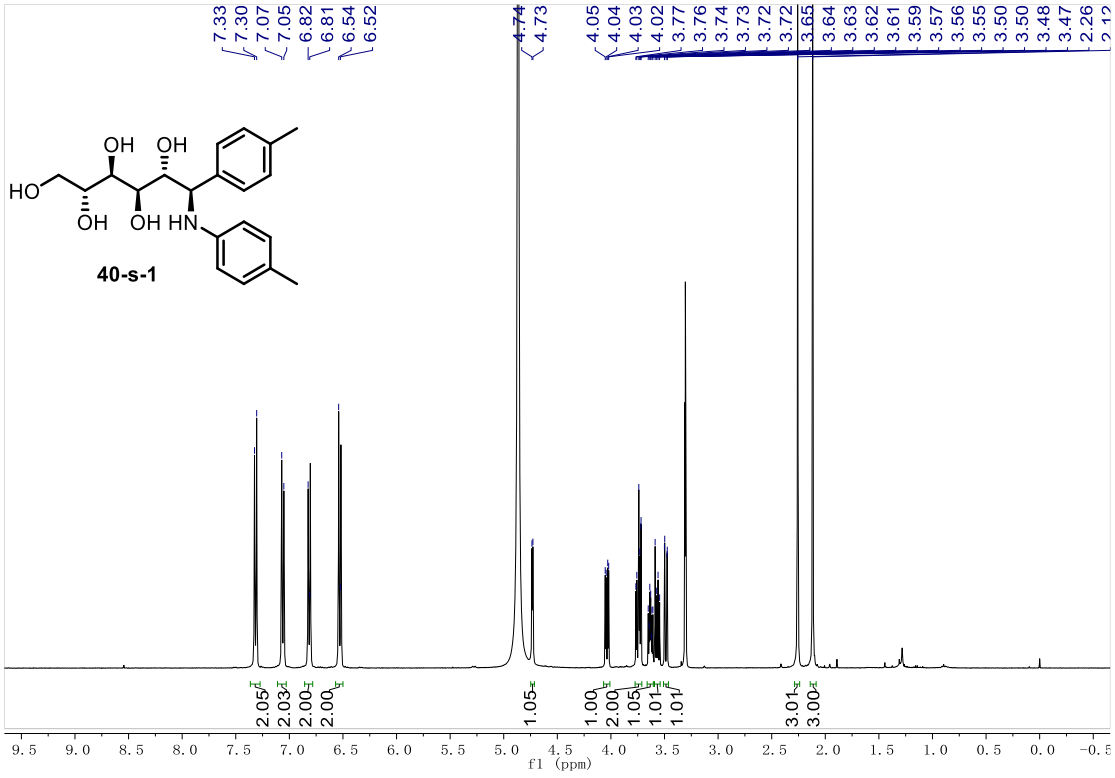

$^{13}$C NMR of compound **39-s** (101 MHz, $CD_3OD$)



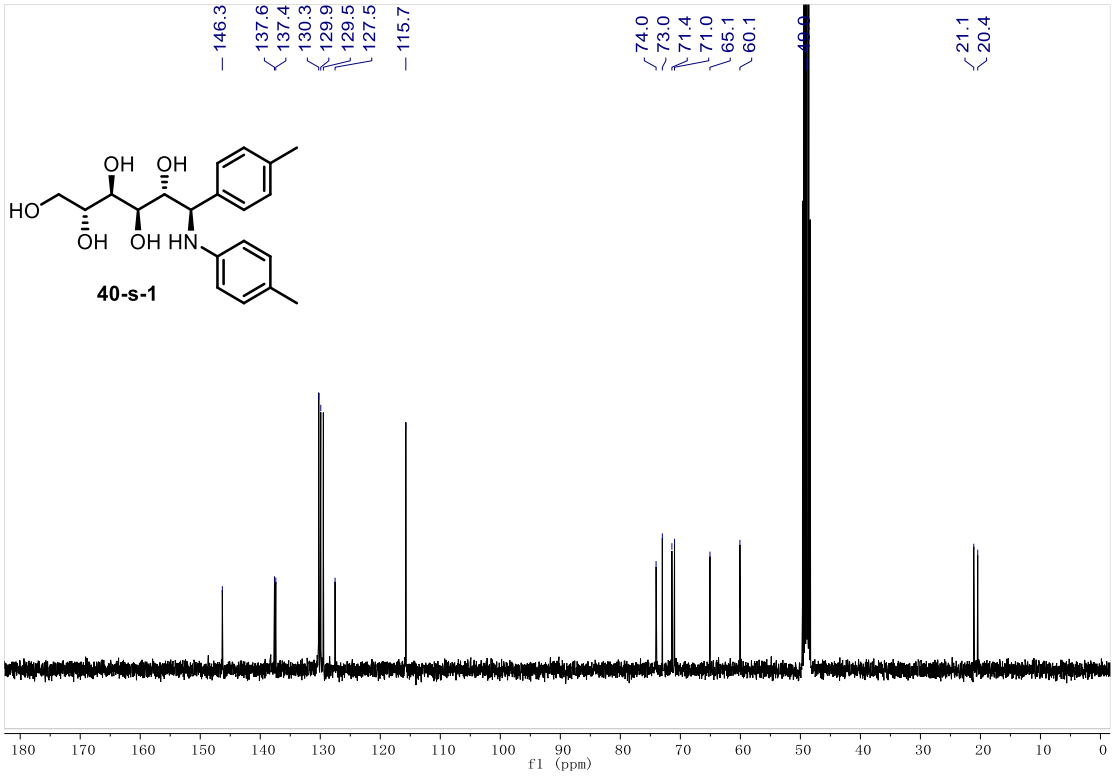

$^{1}$H NMR of compound **39** (400 MHz, $CD_3OD$)



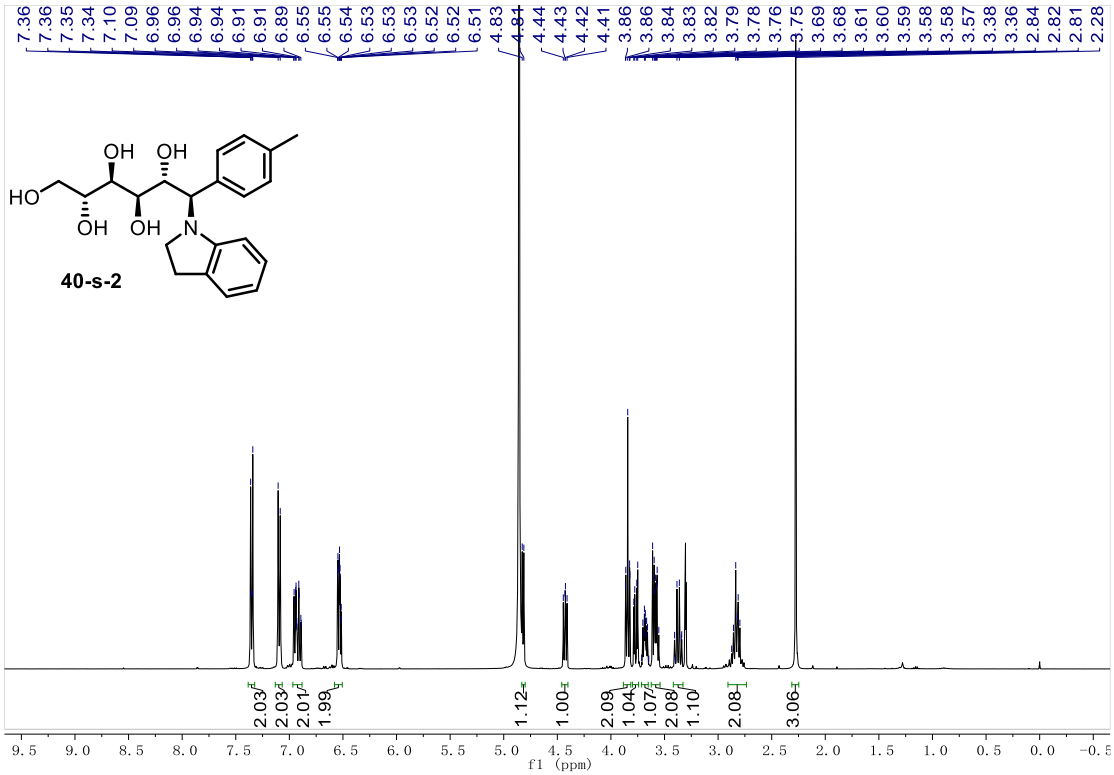

$^{13}$C NMR of compound **39** (101 MHz, $CD_3OD$)



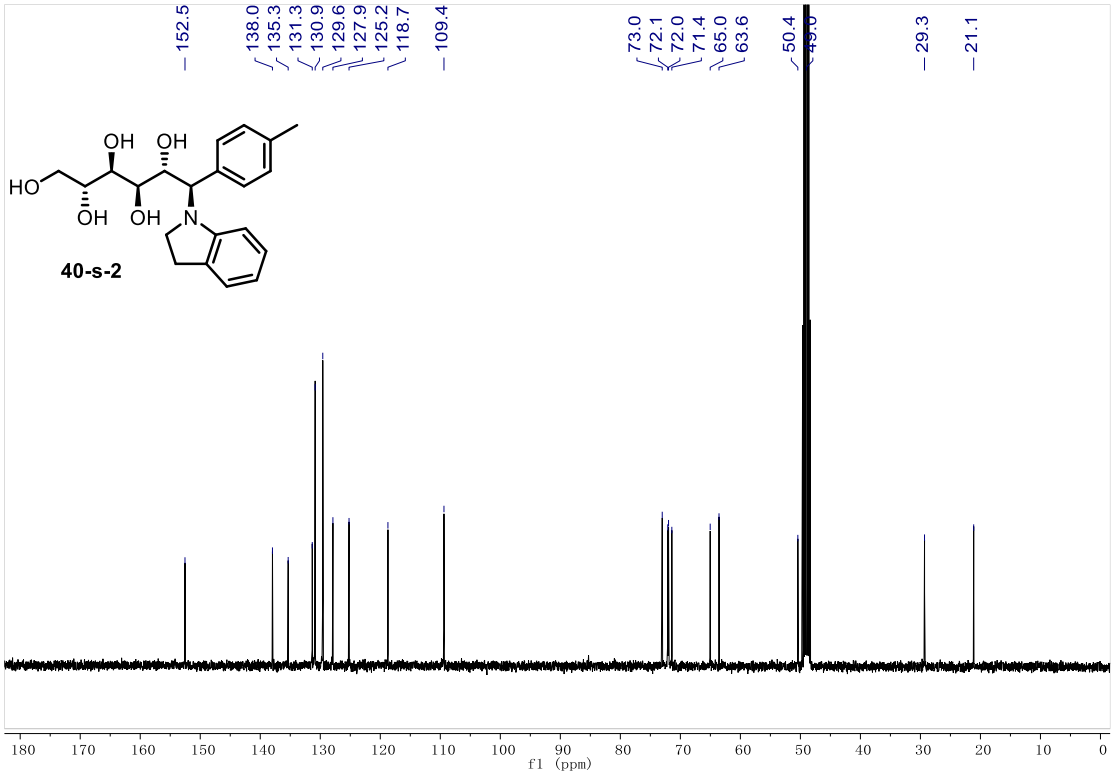

$^{1}$H NMR of compound **40-s-1** (400 MHz, $CD_3OD$)



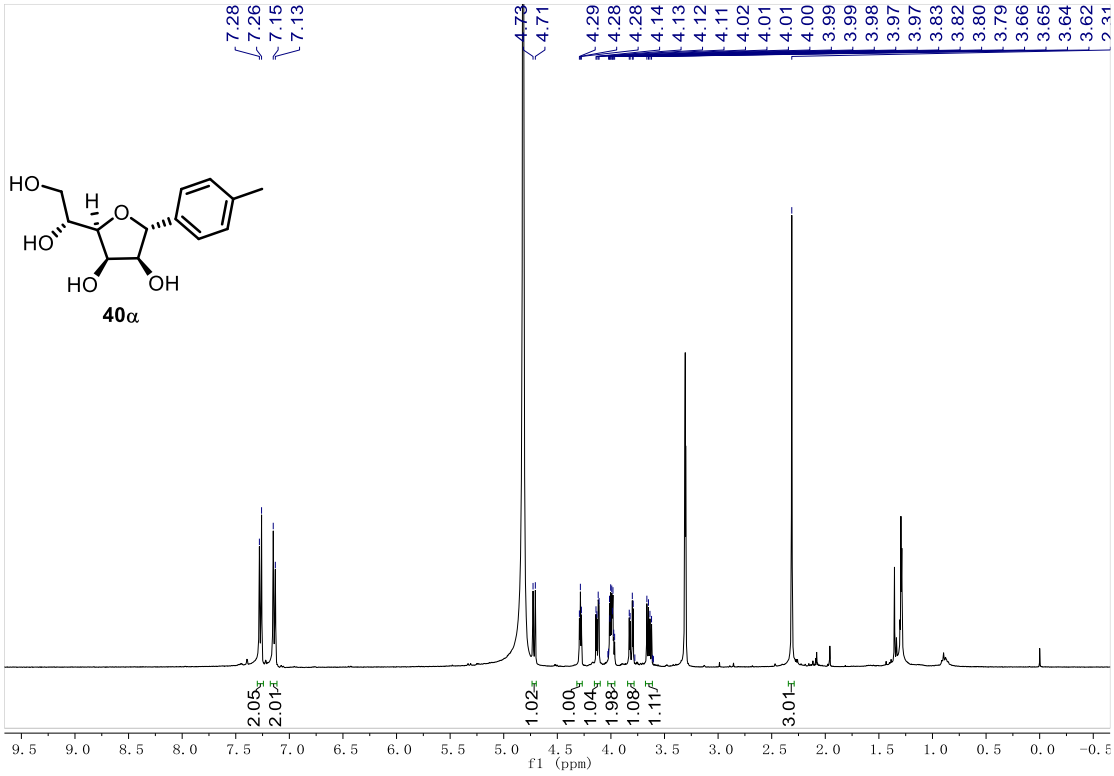

$^{13}$C NMR of compound **40-s-1** (101 MHz, $CD_3OD$)



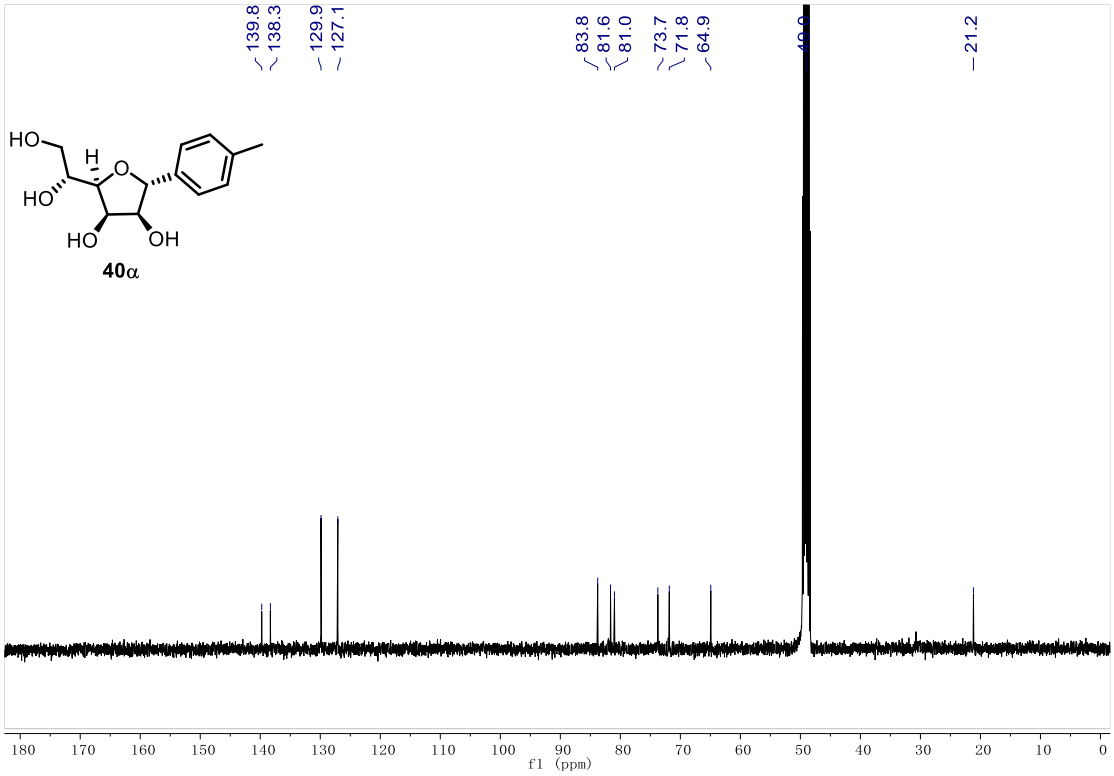

$^{1}$H NMR of compound **40-s-2** (400 MHz, $CD_3OD$)



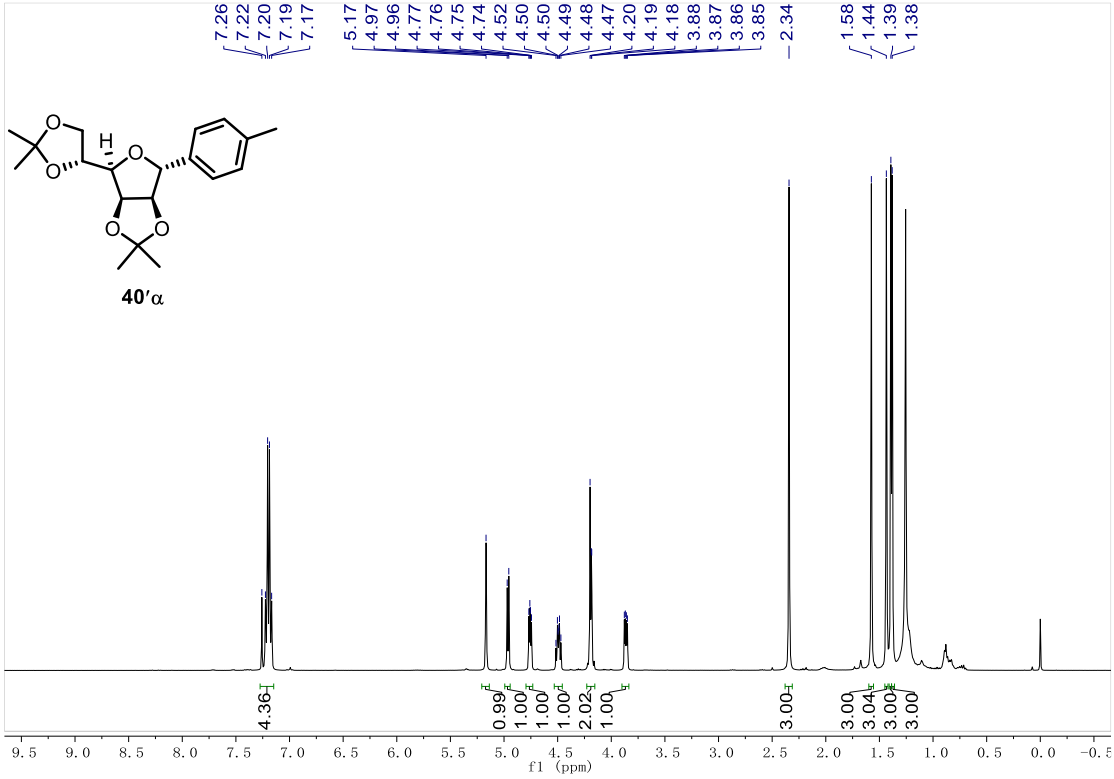

$^{13}$C NMR of compound **40-s-2** (101 MHz, $CD_3OD$)



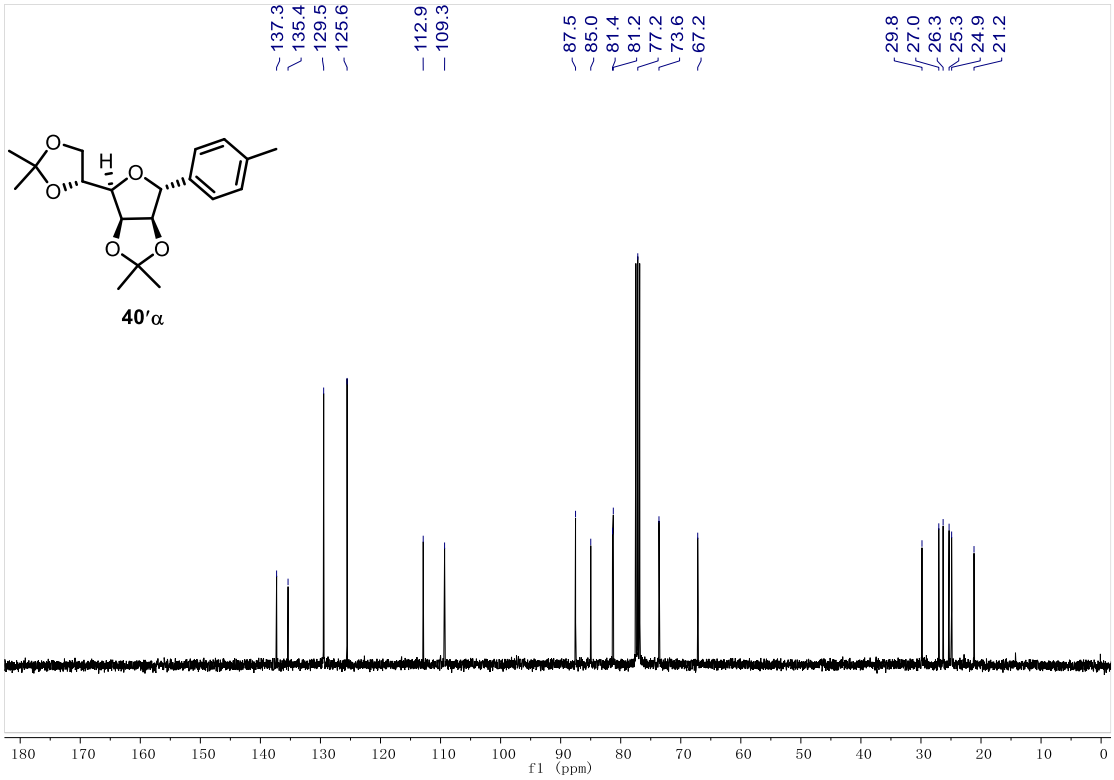

$^{1}$H NMR of compound **40α** (400 MHz, $CD_3OD$)



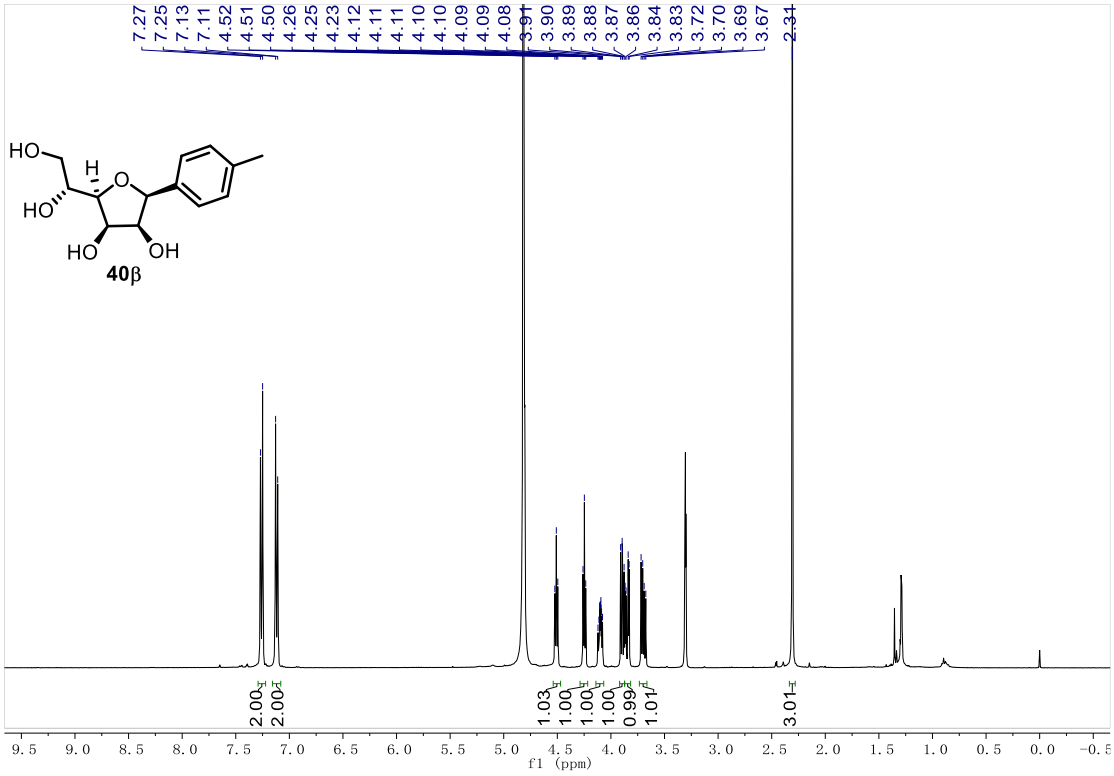

$^{13}$C NMR of compound **40α** (101 MHz, $CD_3OD$)



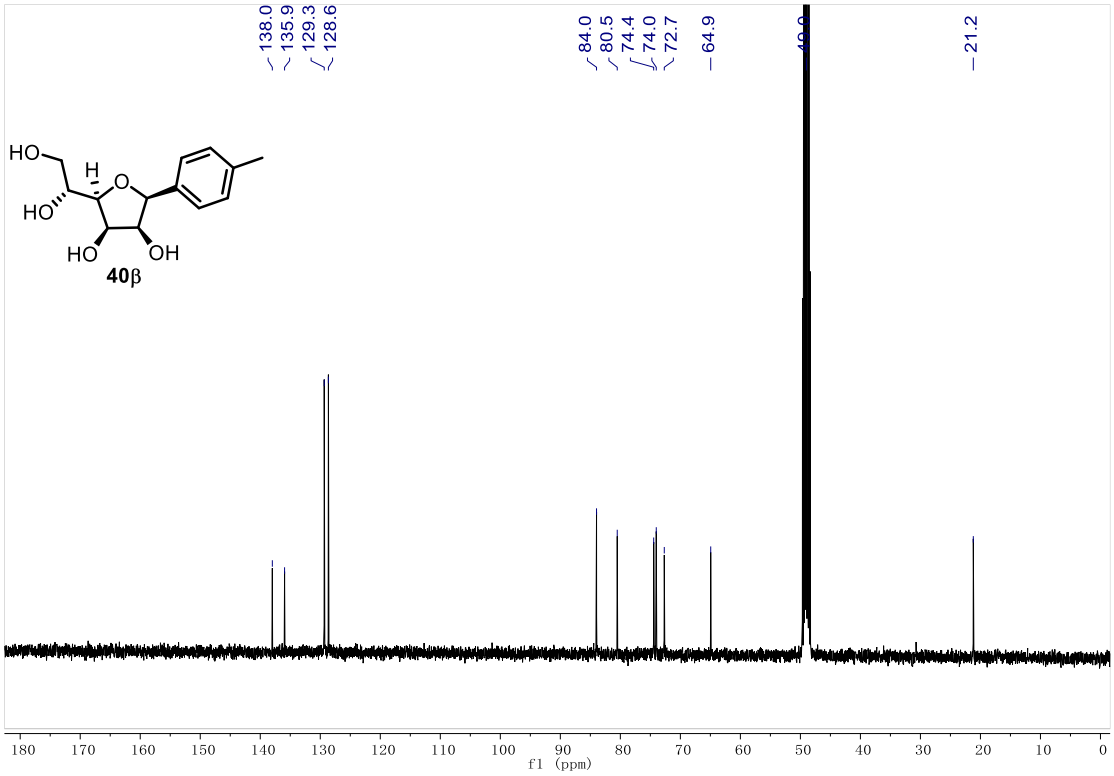

$^{1}$H NMR of compound **40'α** (400 MHz, $CDCl_3$)



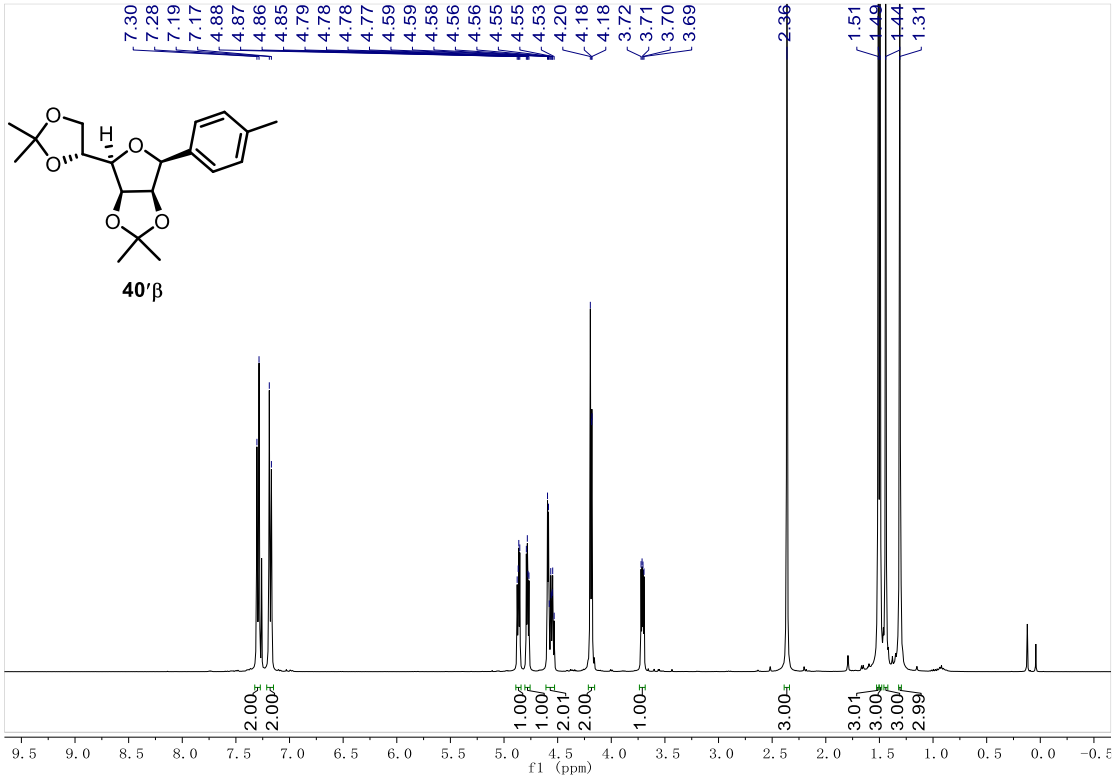

$^{13}$C NMR of compound **40'α** (101 MHz, $CDCl_3$)



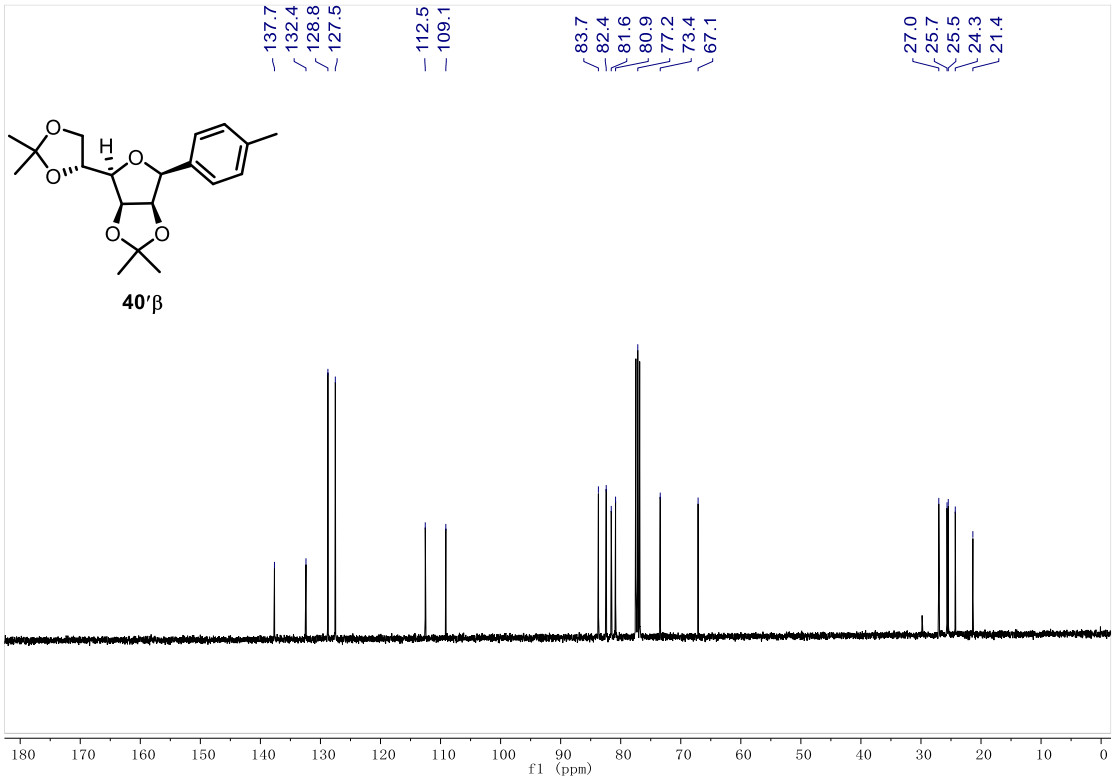

$^{1}$H NMR of compound **40β** (400 MHz, $CD_3OD$)



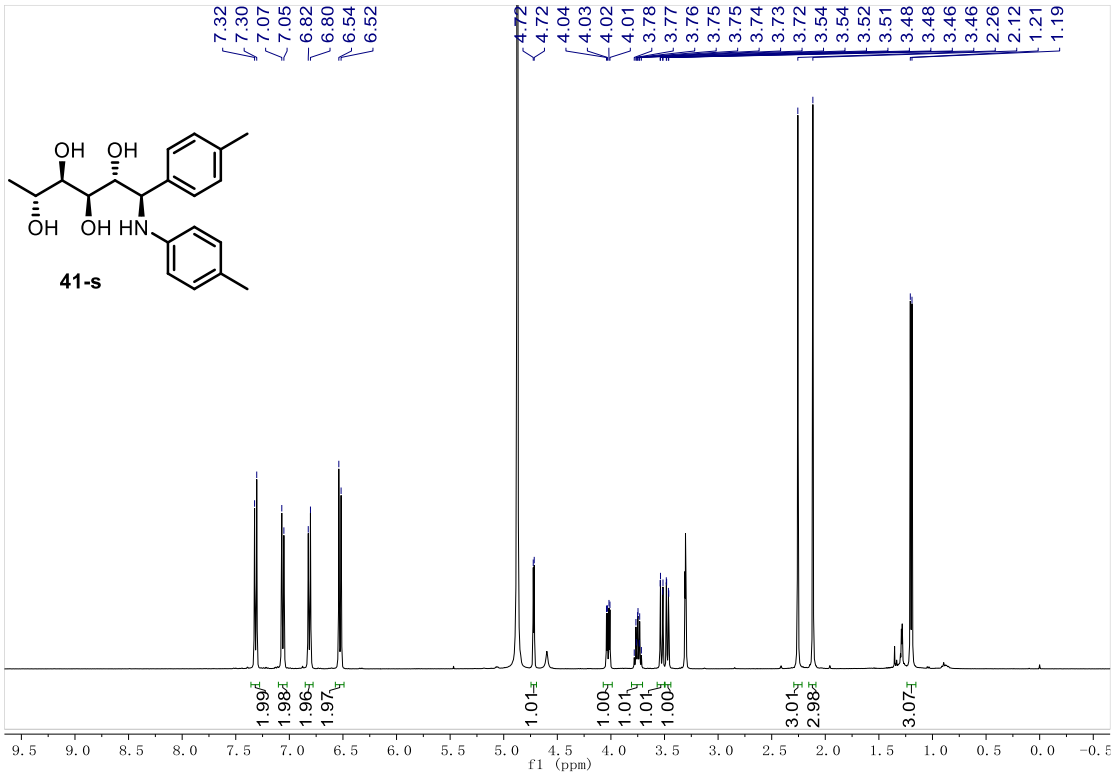

$^{13}$C NMR of compound **40β** (101 MHz, $CD_3OD$)



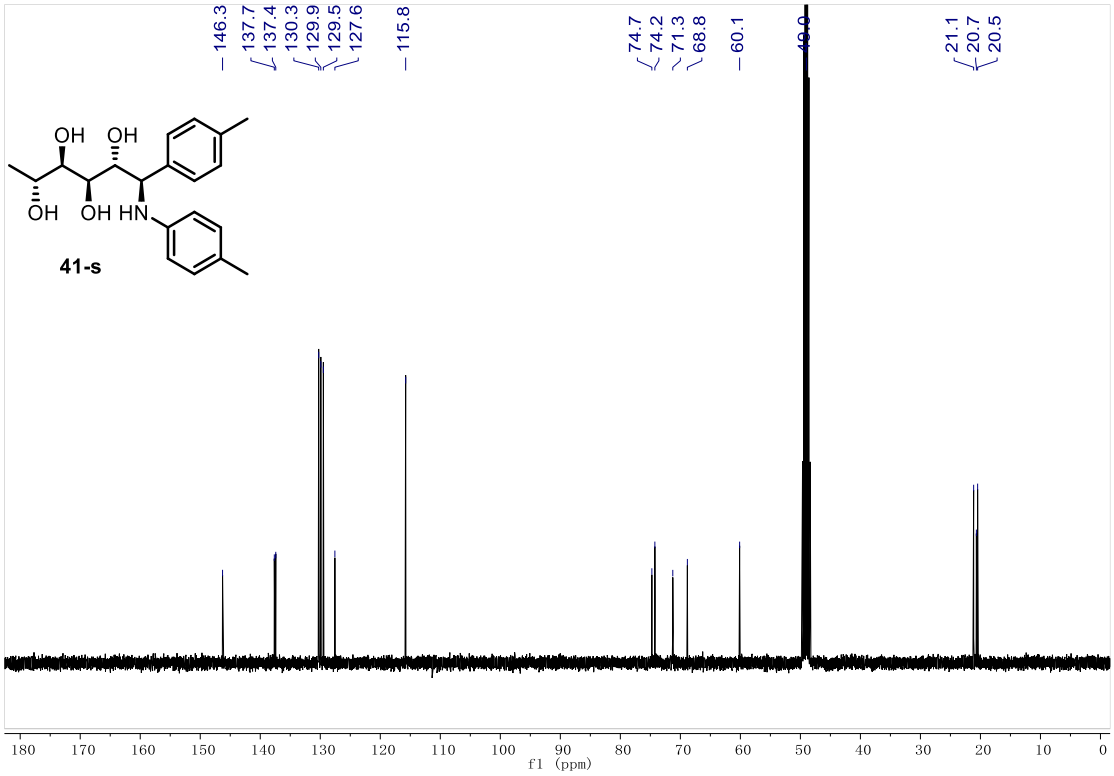

$^{1}$H NMR of compound **40'β** (400 MHz, $CDCl_3$)



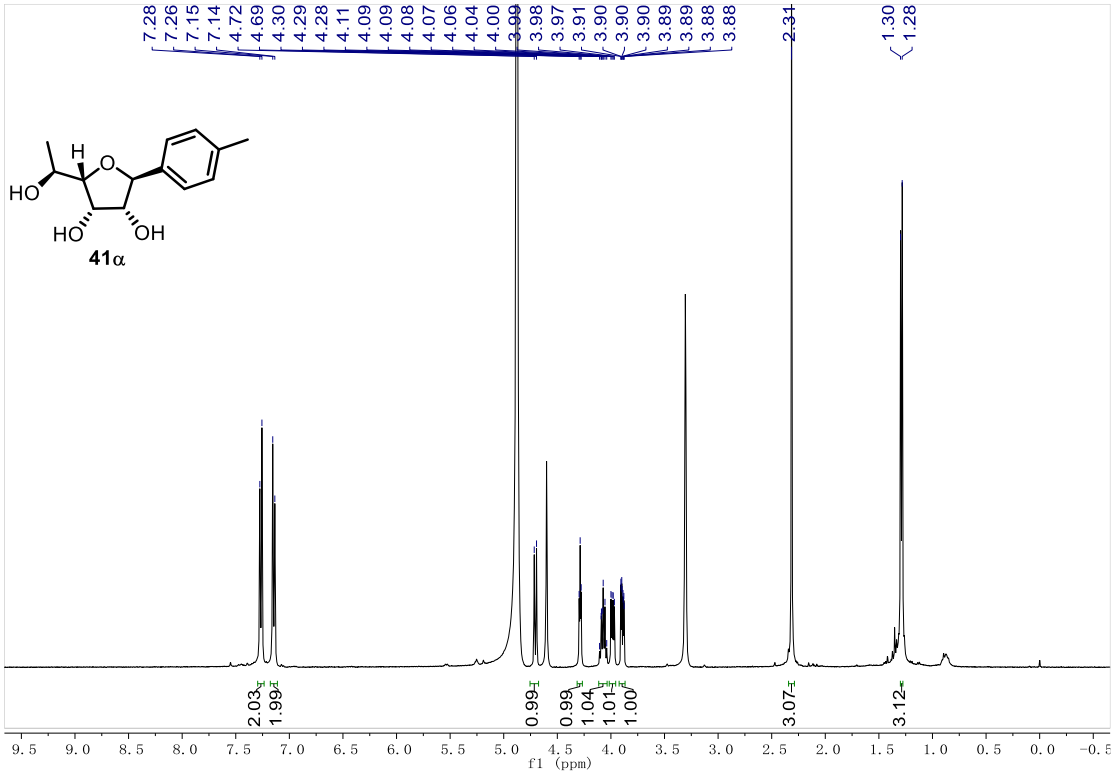

$^{13}$C NMR of compound **40'β** (101 MHz, $CDCl_3$)



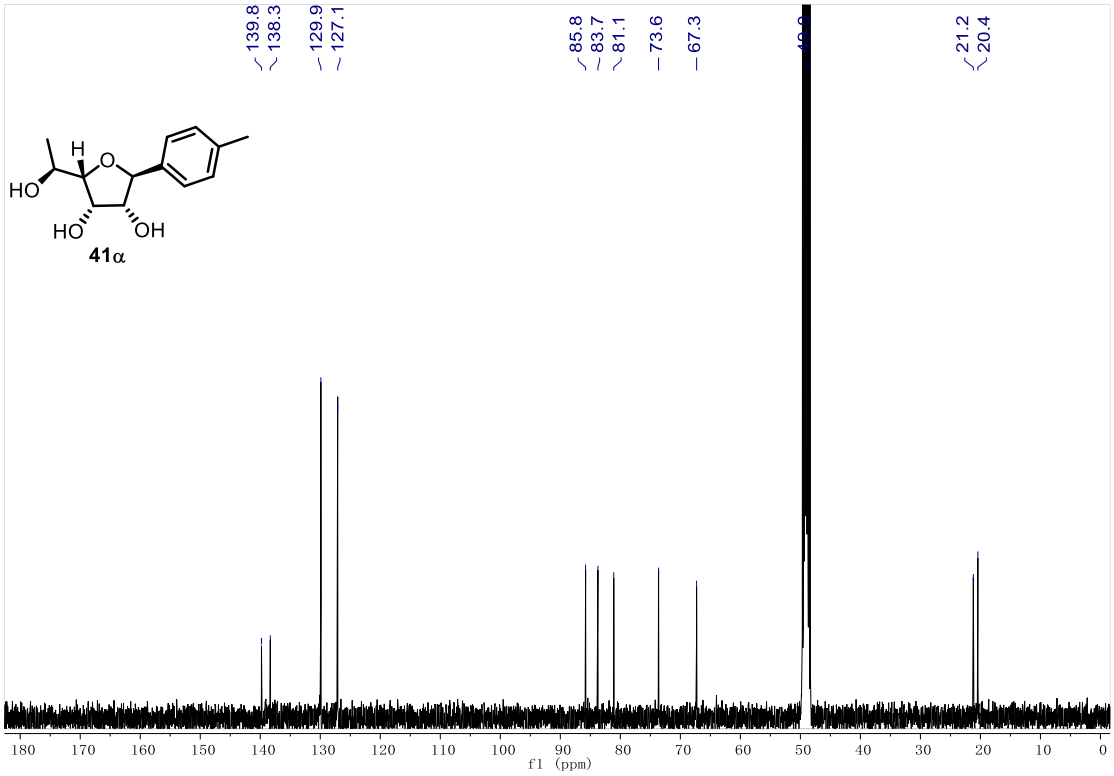

$^{1}$H NMR of compound **41-s** (400 MHz, $CD_3OD$)



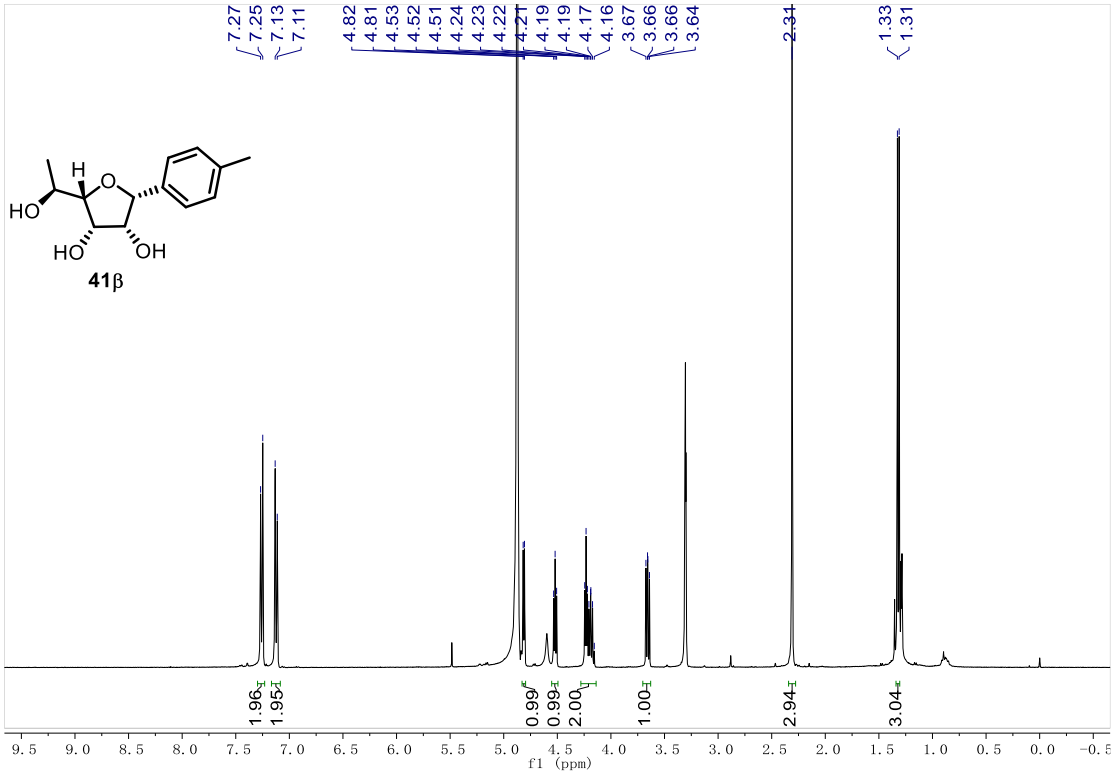

$^{13}$C NMR of compound **41-s** (101 MHz, $CD_3OD$)



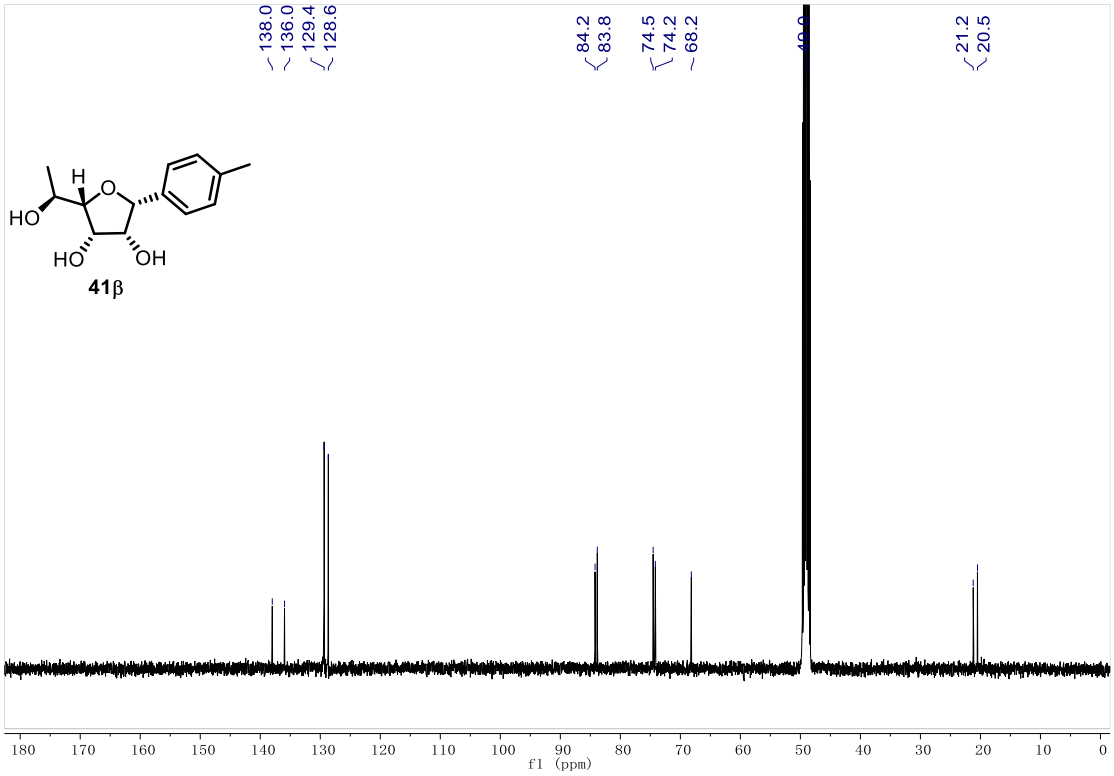

$^{1}$H NMR of compound **41α** (400 MHz, $CD_3OD$)



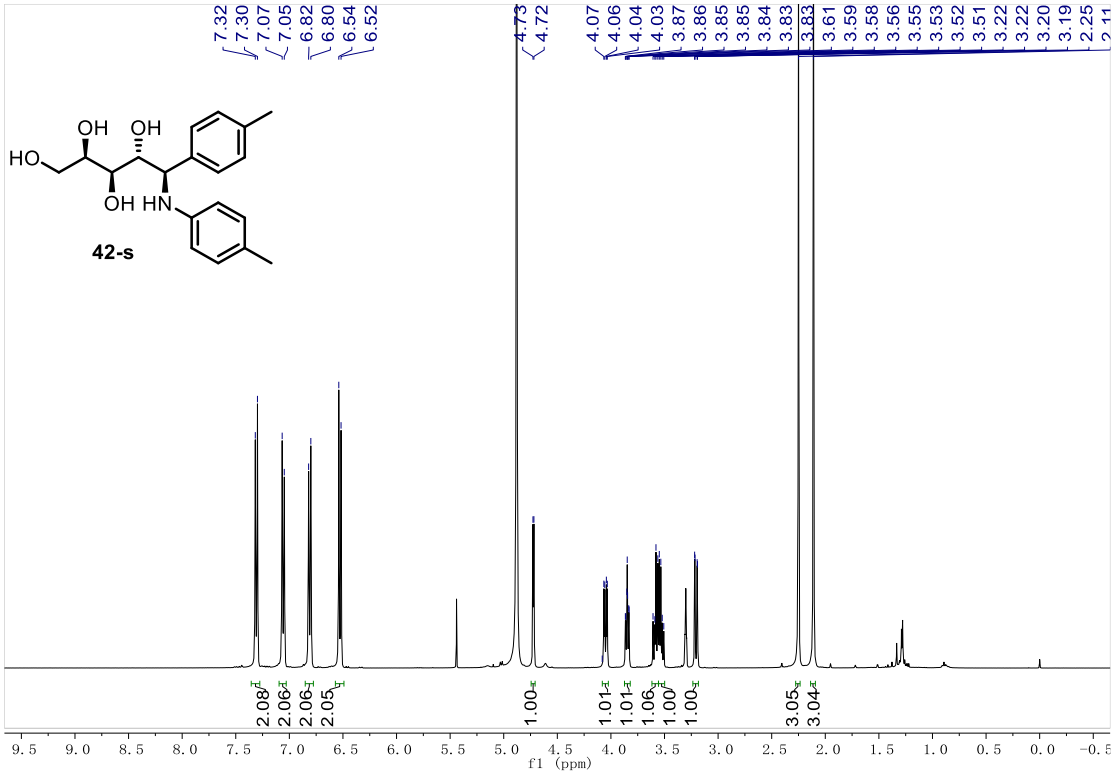

$^{13}$C NMR of compound **41α** (101 MHz, $CD_3OD$)



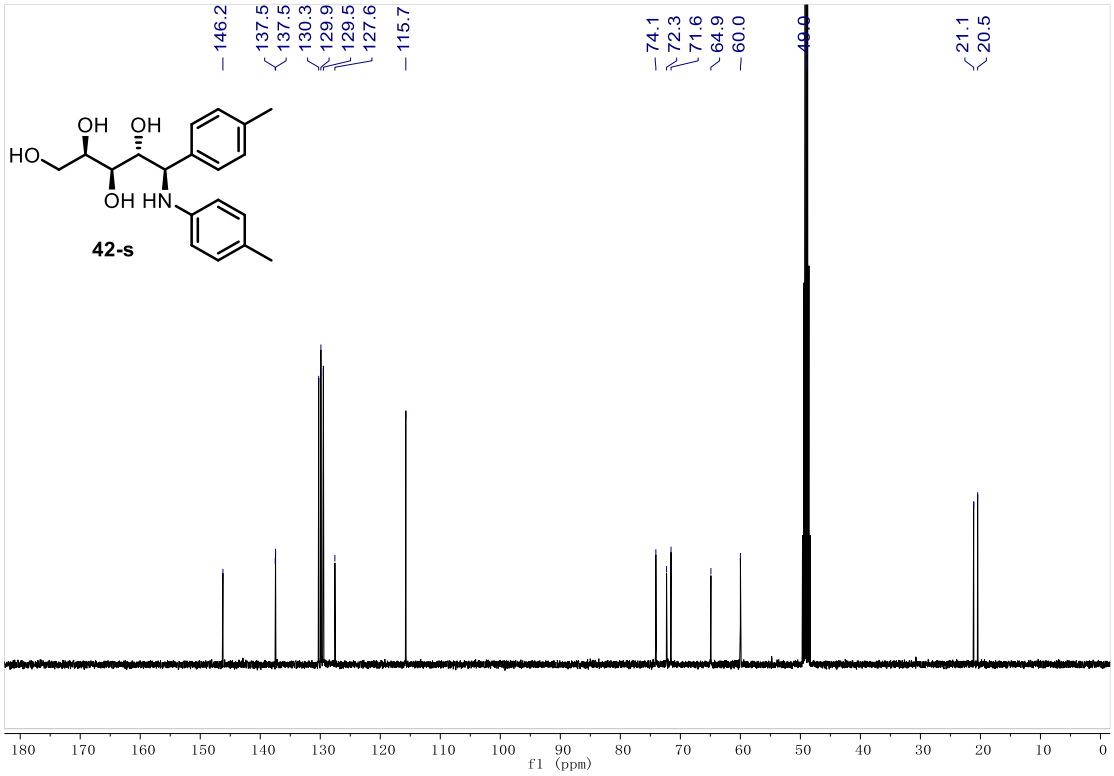

$^{1}$H NMR of compound **41β** (400 MHz, $CD_3OD$)



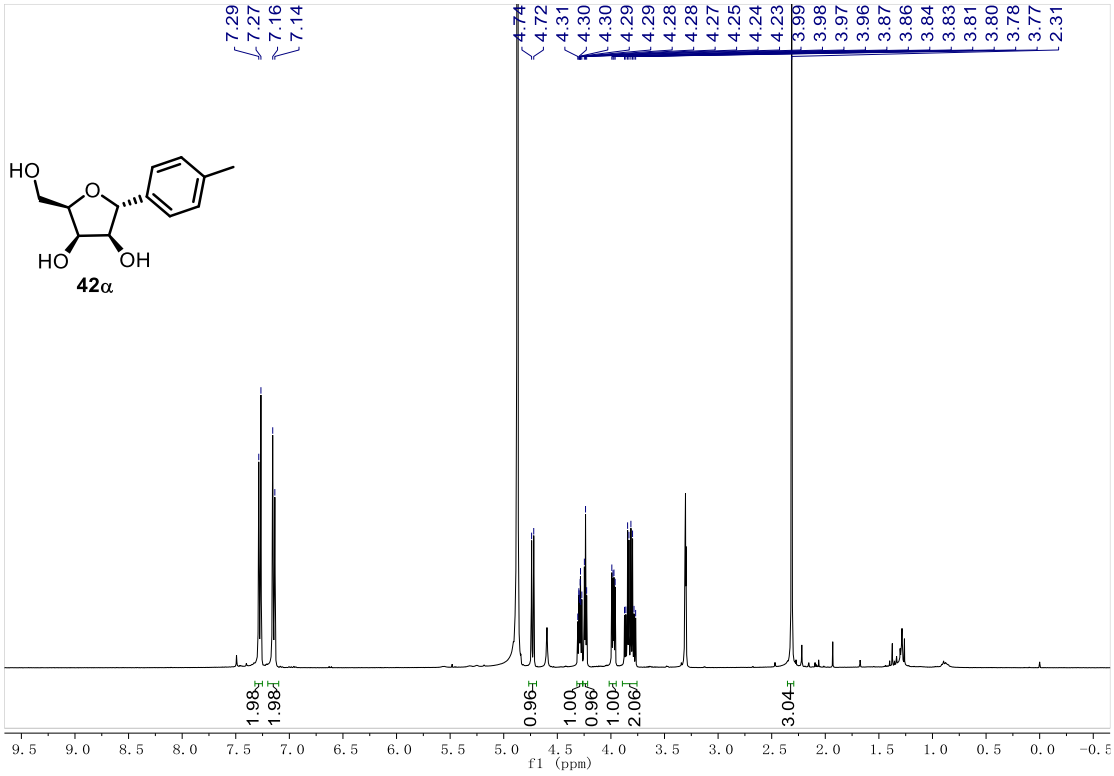

$^{13}$C NMR of compound **41β** (101 MHz, $CD_3OD$)



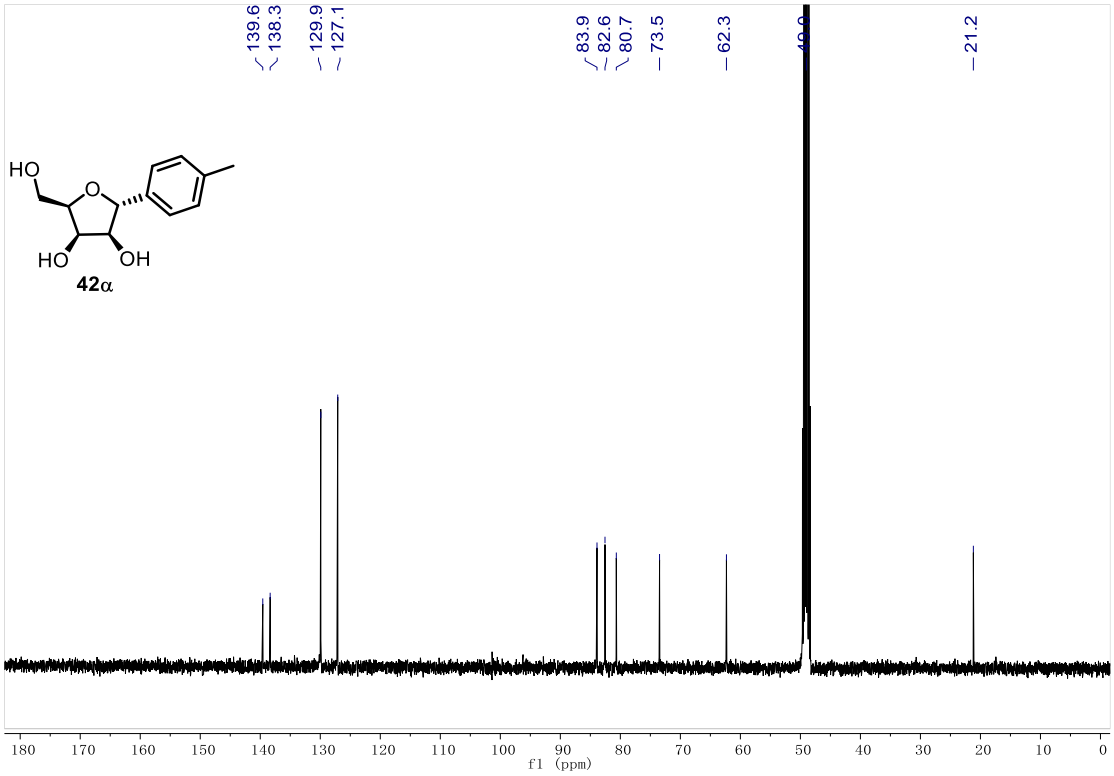

$^{1}$H NMR of compound **42-s** (400 MHz, $CD_3OD$)



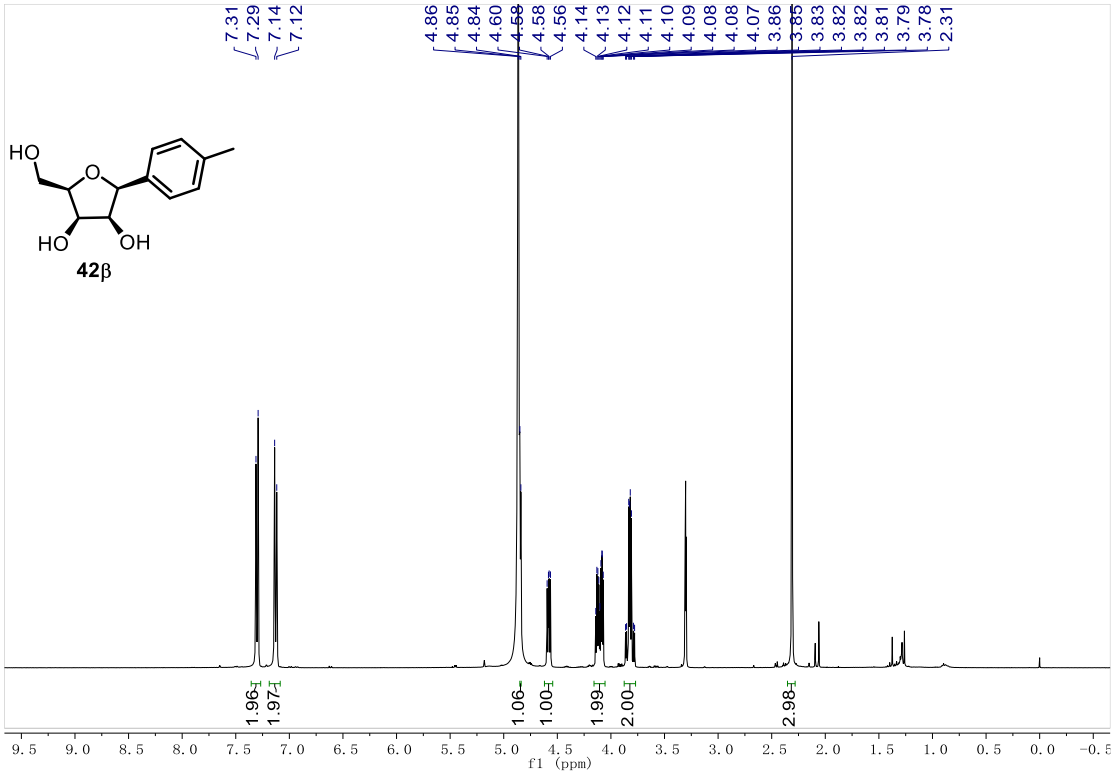

$^{13}$C NMR of compound **42-s** (101 MHz, $CD_3OD$)



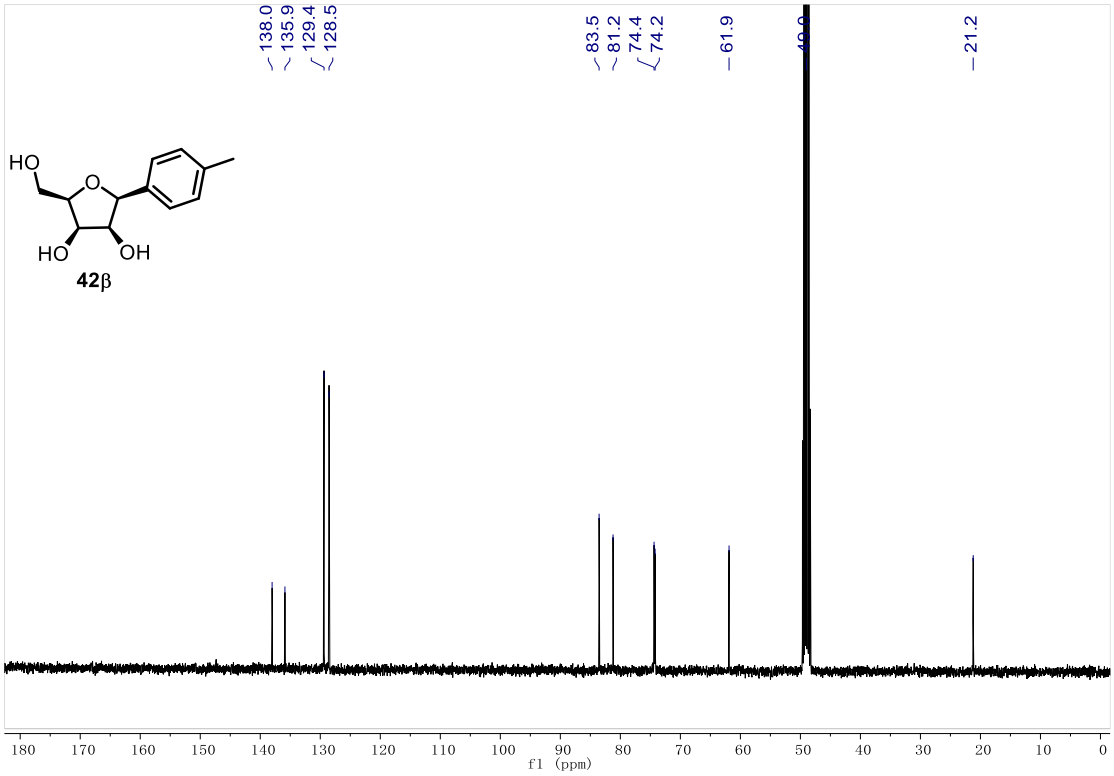

$^{1}$H NMR of compound **42α** (400 MHz, $CD_3OD$)



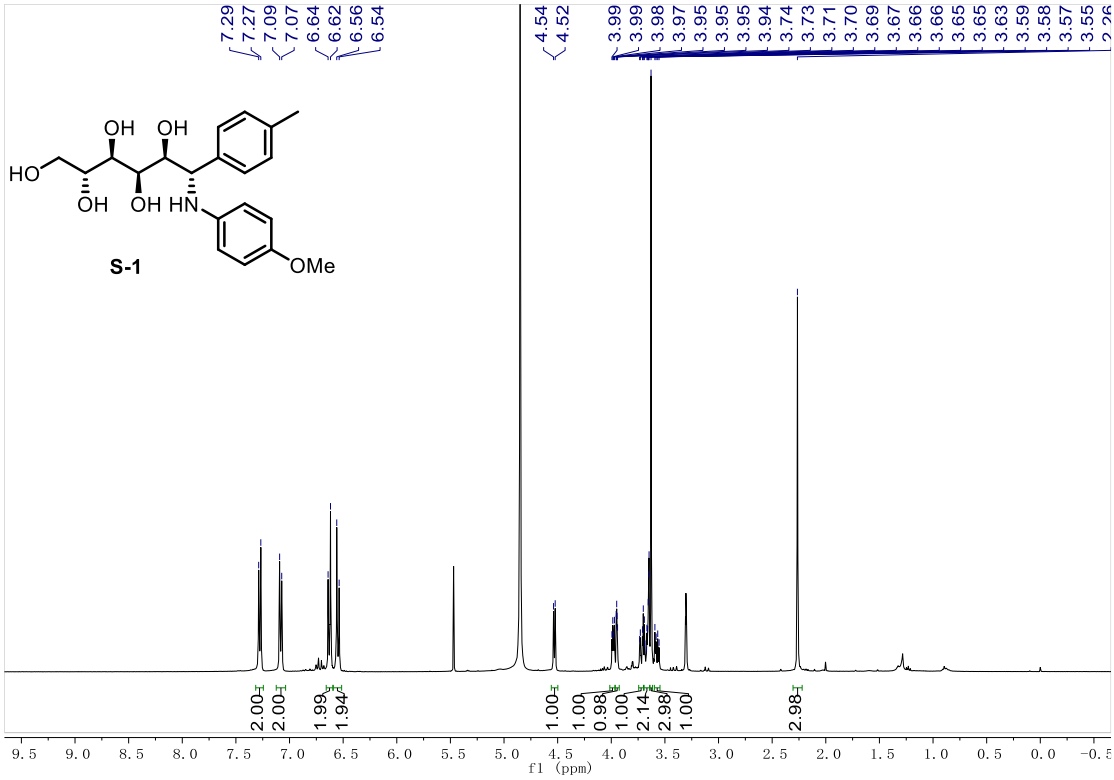

$^{13}$C NMR of compound **42α** (101 MHz, $CD_3OD$)



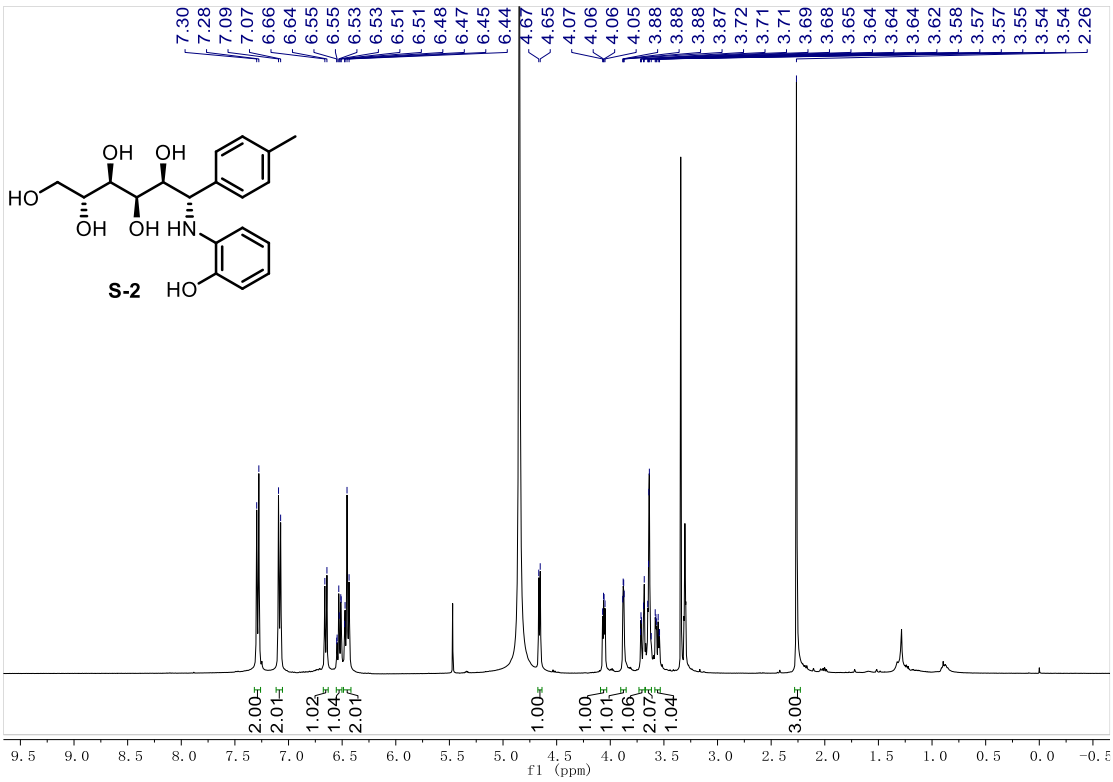

$^{1}$H NMR of compound **42β** (400 MHz, $CD_3OD$)



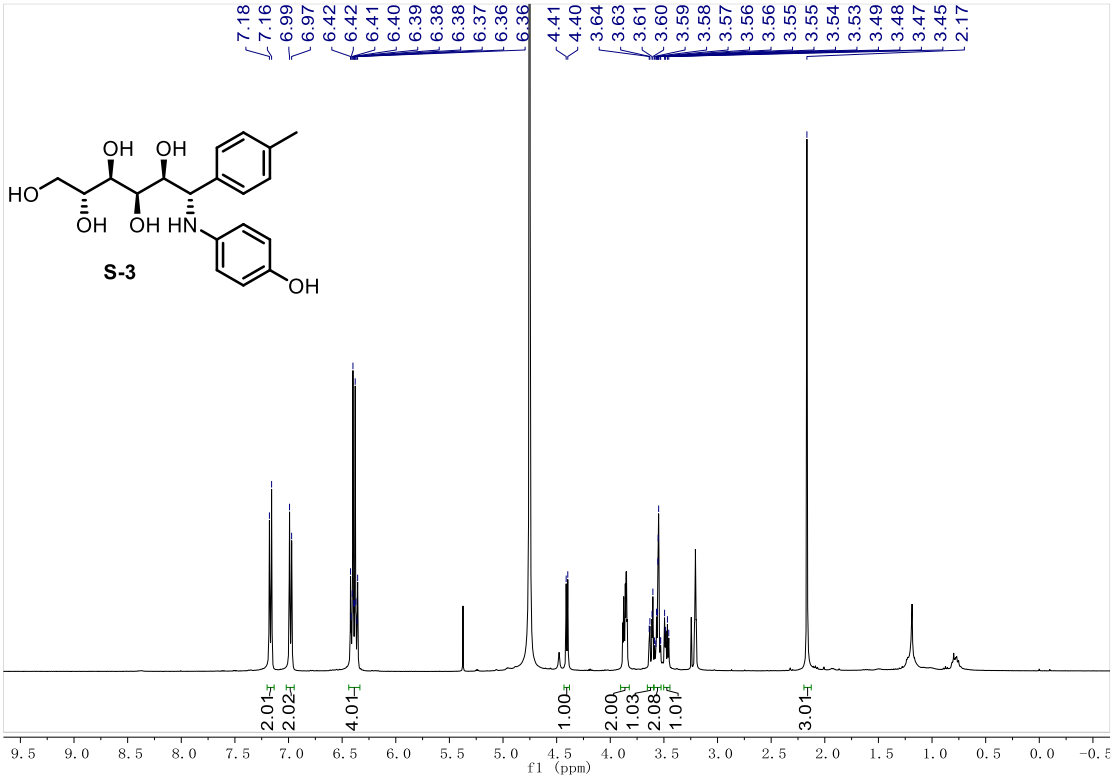

$^{13}$C NMR of compound **42β** (101 MHz, $CD_3OD$)



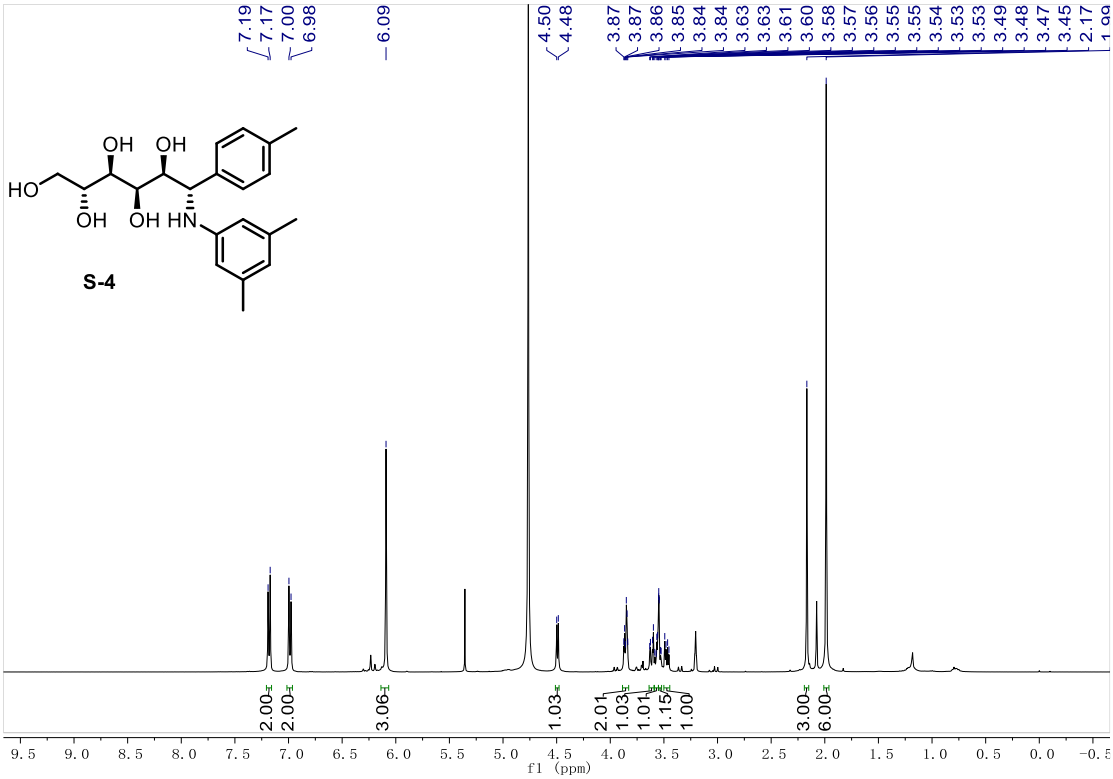

$^{1}$H NMR of compound **S-1** (400 MHz, $CD_3OD$)



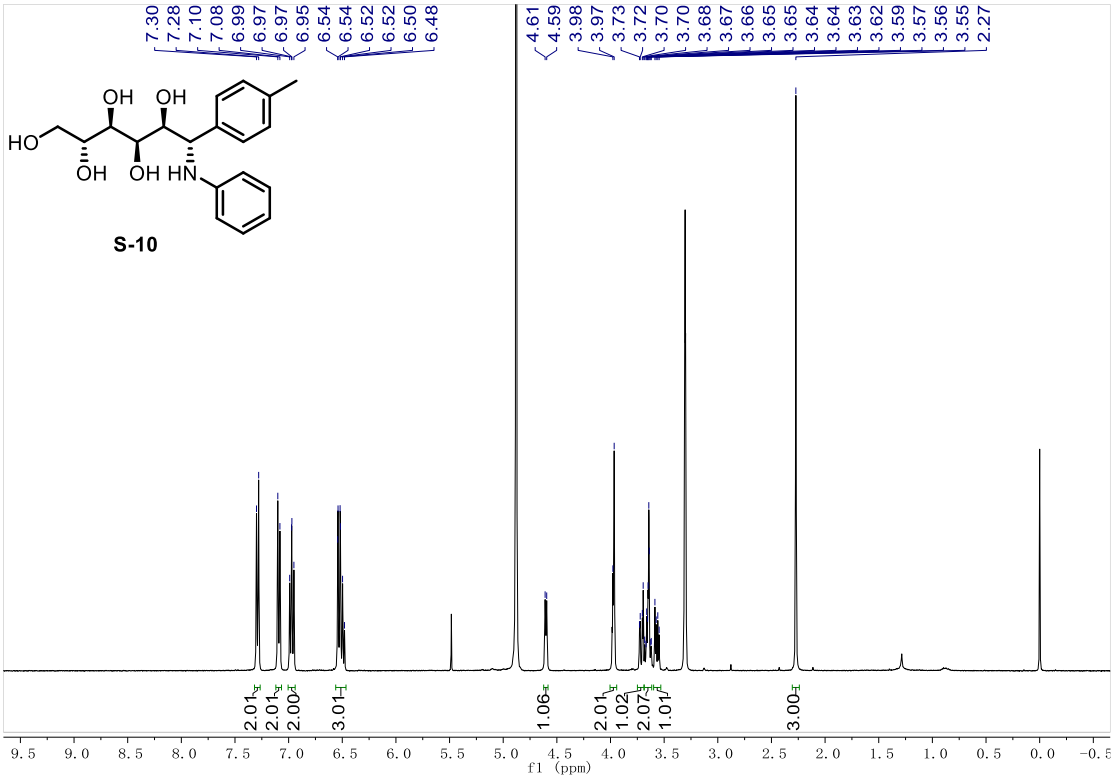

$^1$H NMR of compound **S-2** (400 MHz, $CD_3OD$)



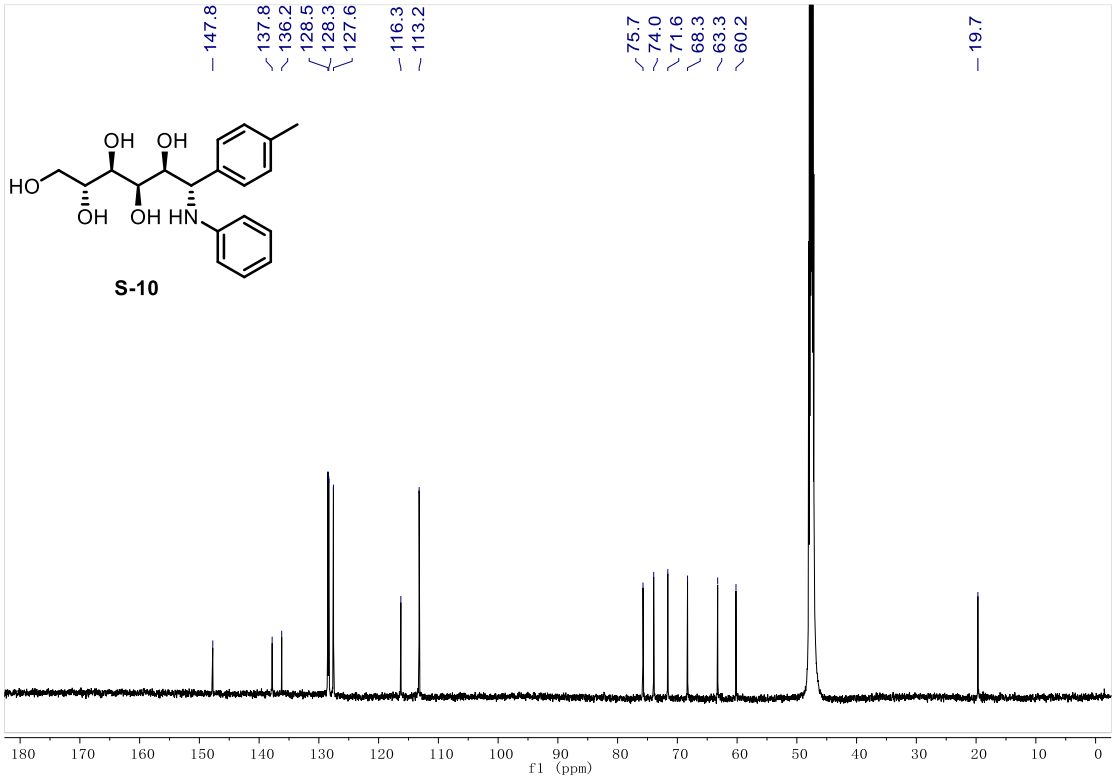

$^1$H NMR of compound **S-3** (400 MHz, $CD_3OD$)



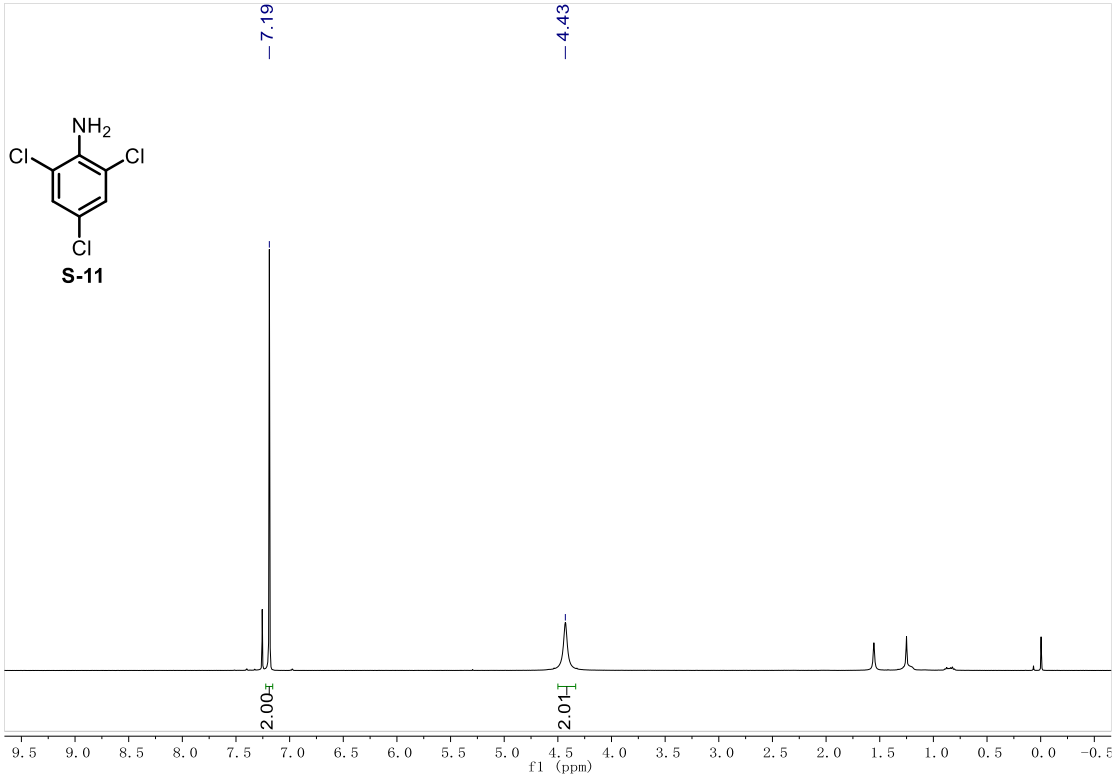

$^{1}$H NMR of compound **S-4** (400 MHz, $CD_3OD$)



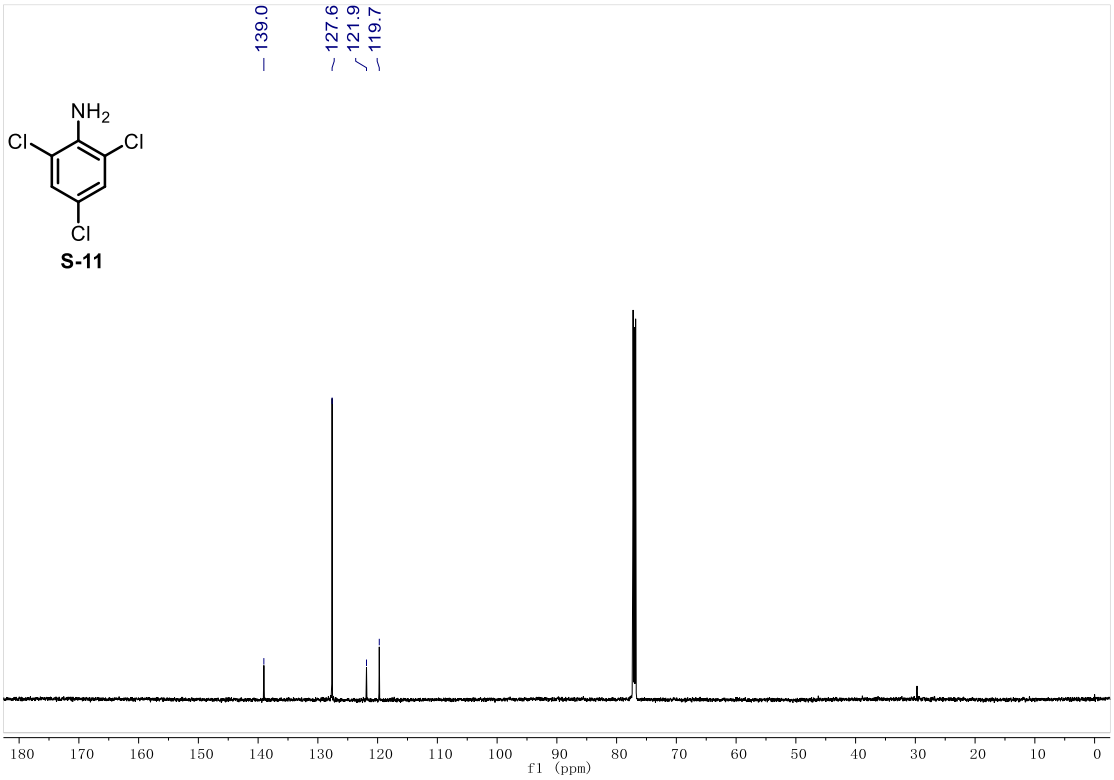

$^{1}$H NMR of compound **S-10** (400 MHz, $CD_3OD$)



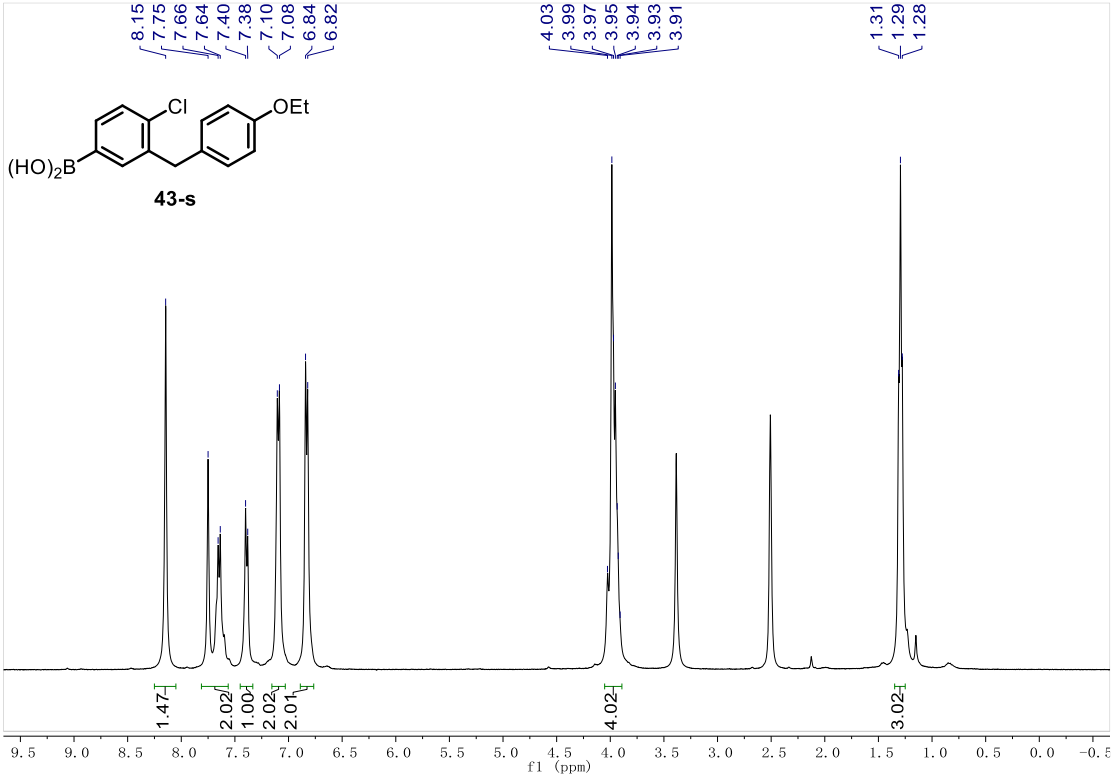

$^{13}$C NMR of compound **S-10** (151 MHz, $CD_3OD$)



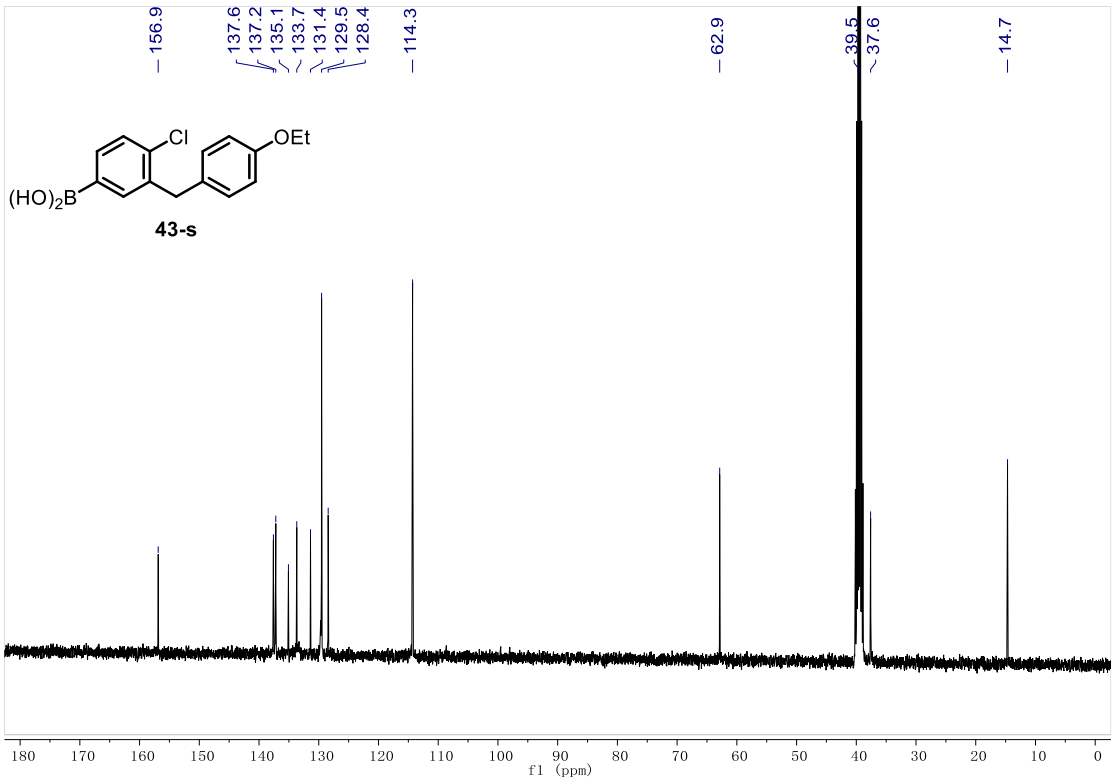

$^{1}$H NMR of compound **S-11** (400 MHz, $CDCl_3$)



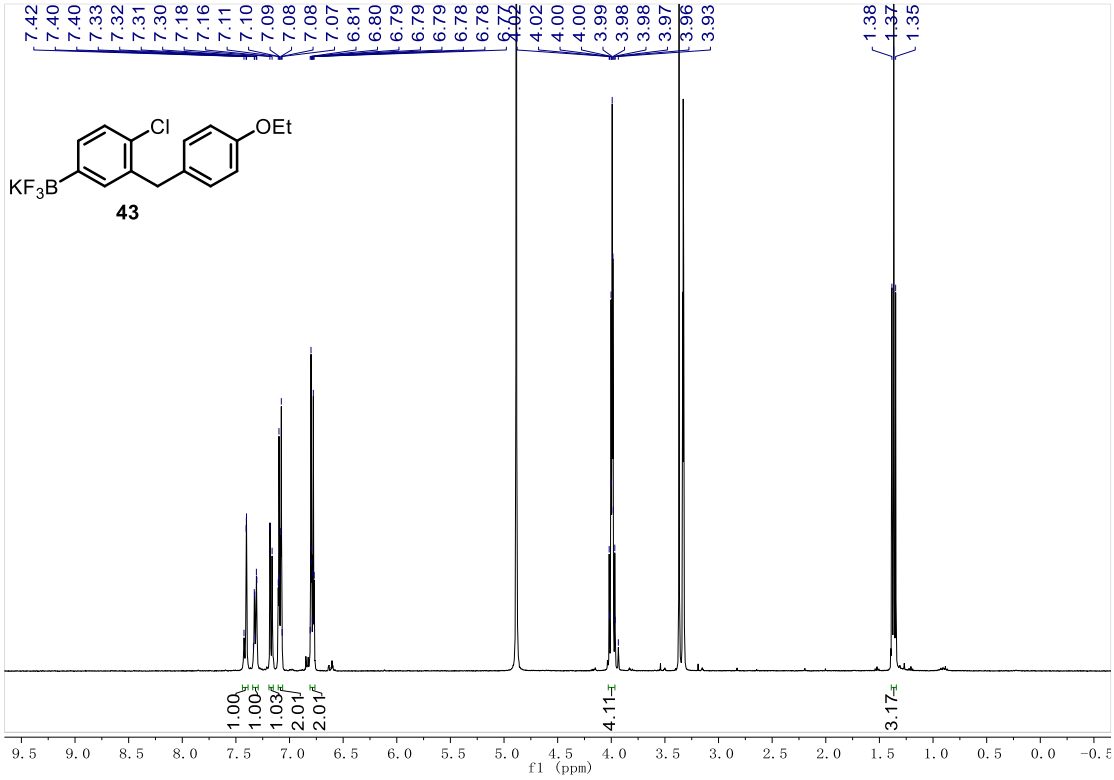

$^{13}$C NMR of compound **S-11** (151 MHz, $CDCl_3$)



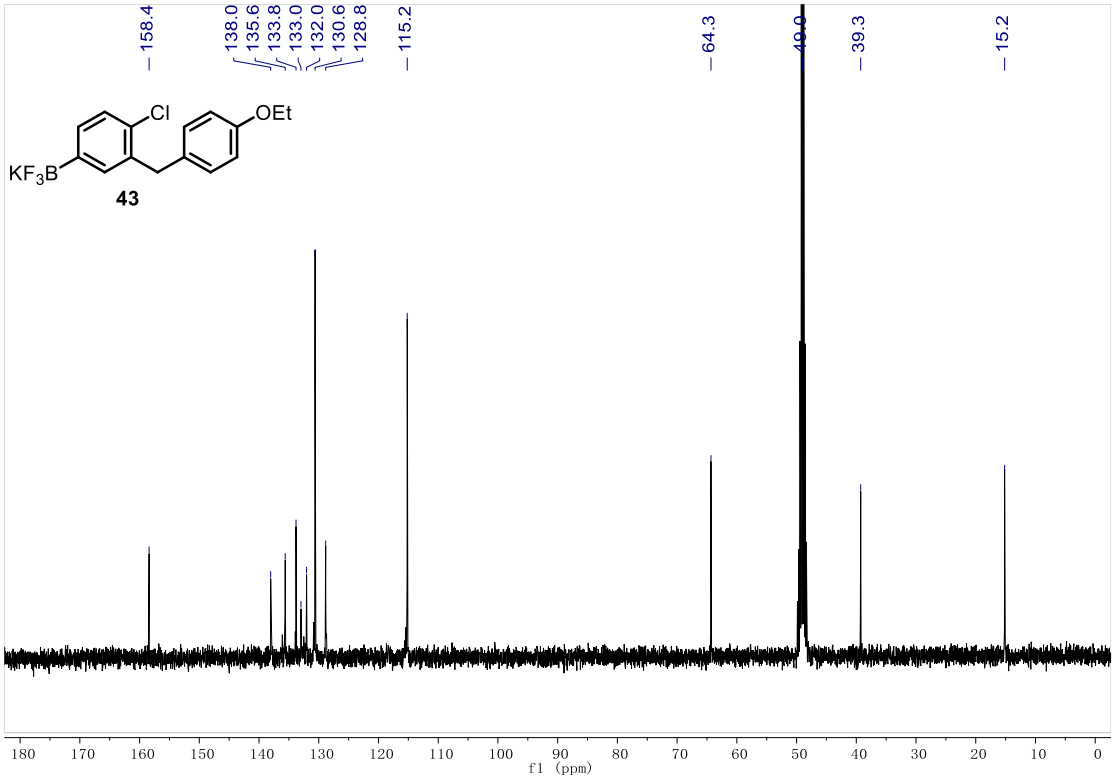

$^{1}$H NMR of compound **43-s** (400 MHz, DMSO-$D_6$)



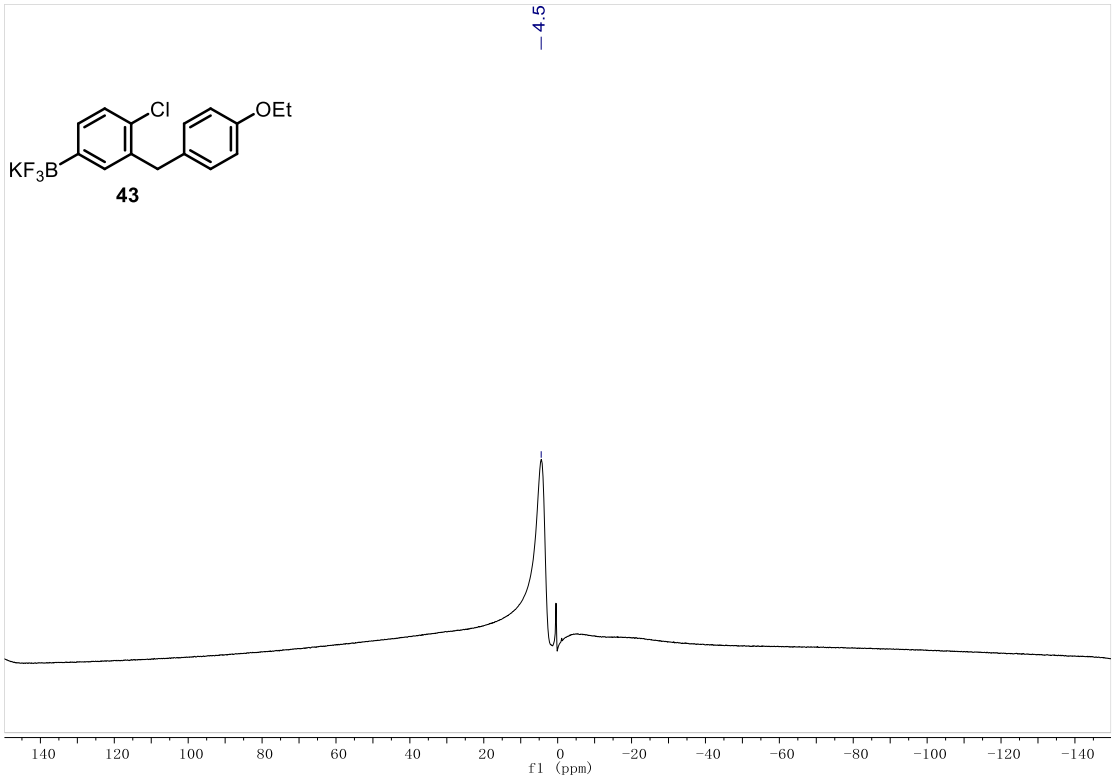

$^{13}$C NMR of compound **43-s** (101 MHz, DMSO-$D_6$)



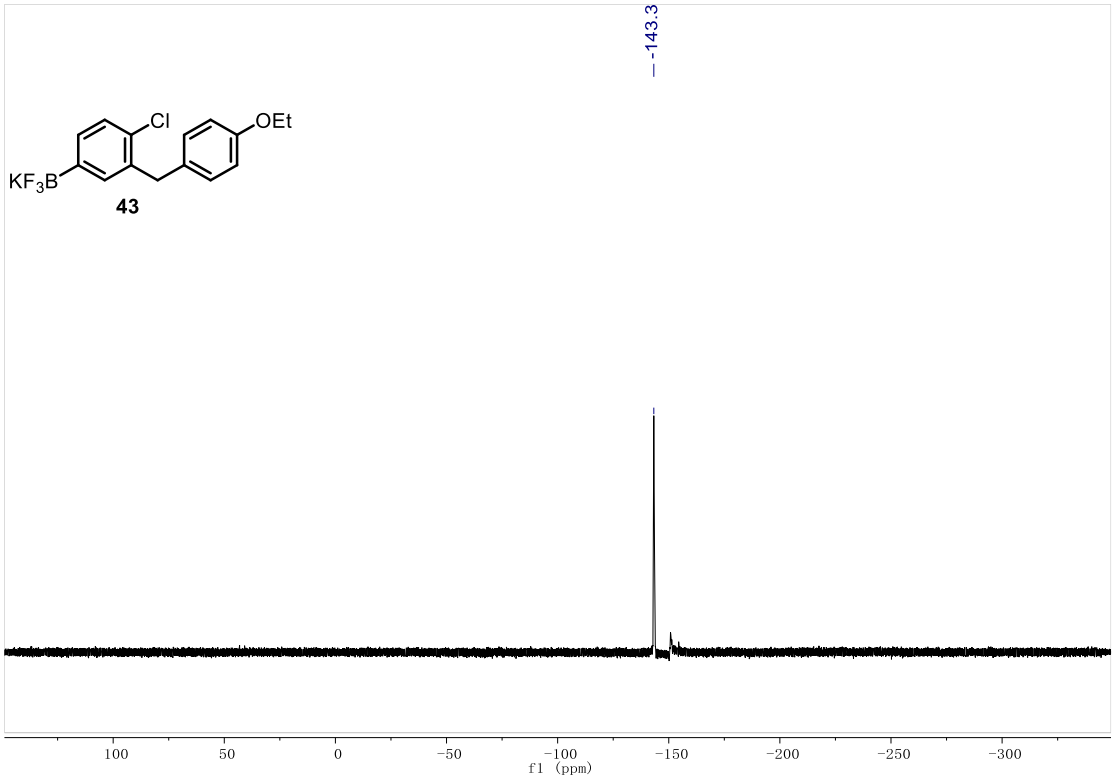

$^{1}$H NMR of compound **43** (400 MHz, $CD_3OD$)



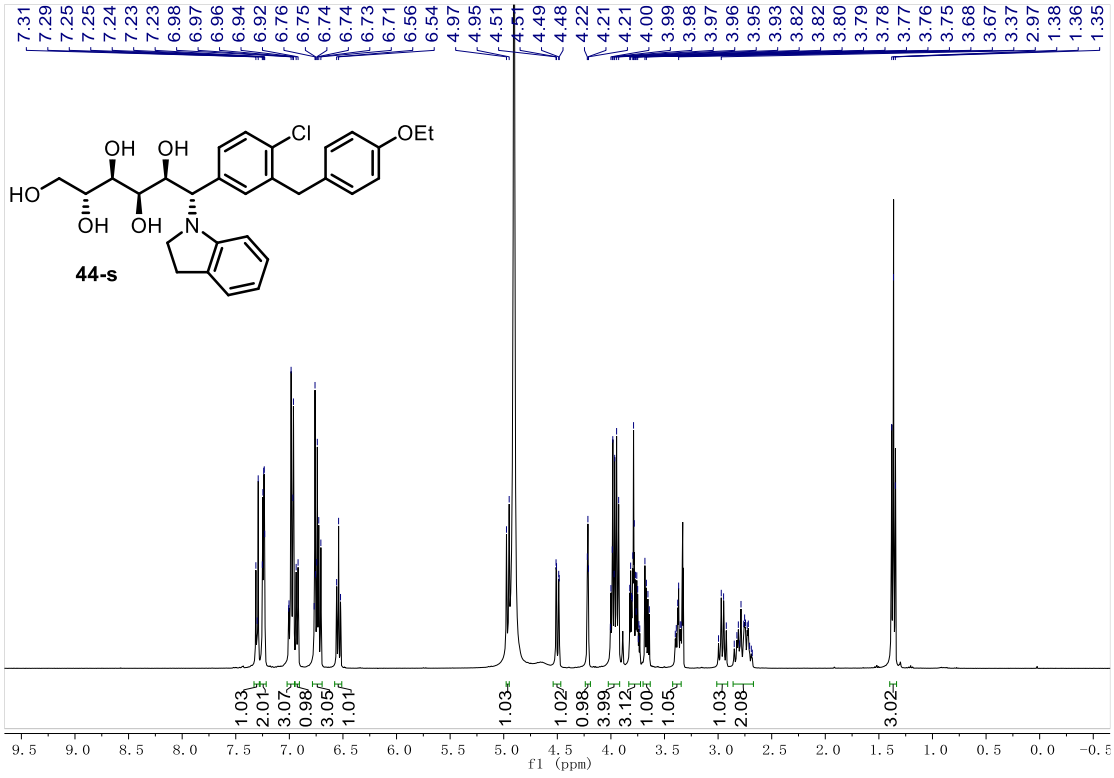

$^{13}$C NMR of compound **43** (101 MHz, $CD_3OD$)



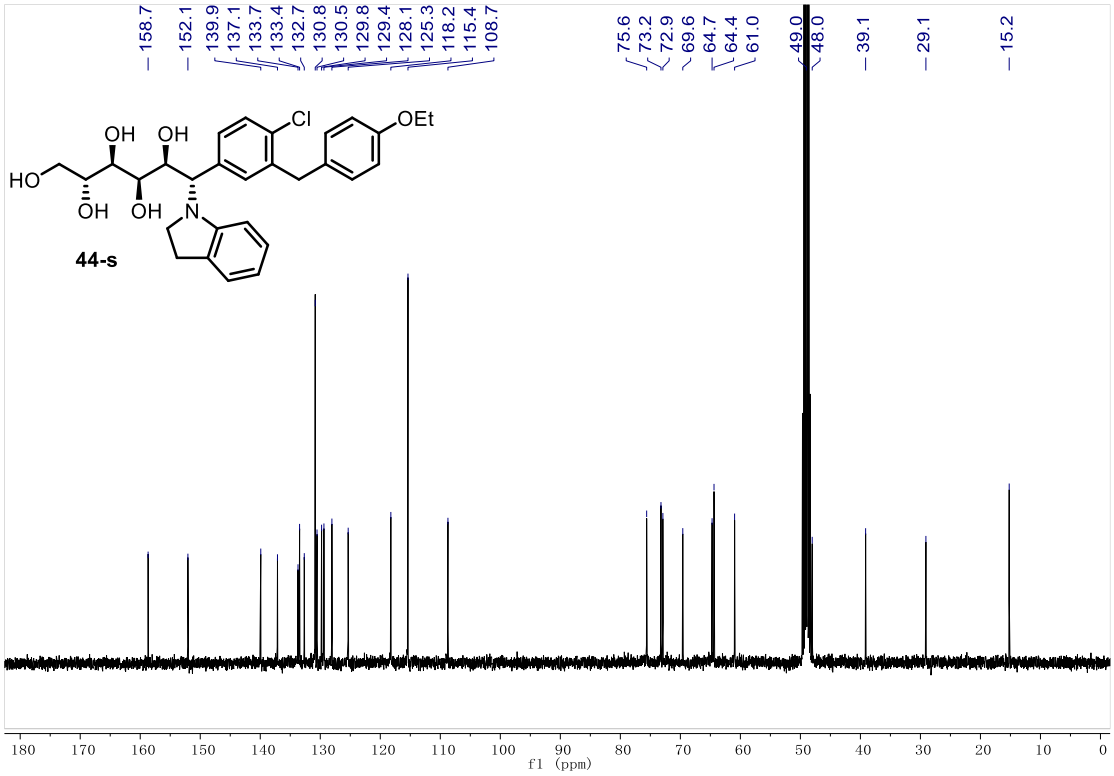

$^{11}$B NMR of compound **43** (128 MHz, $CD_3OD$)



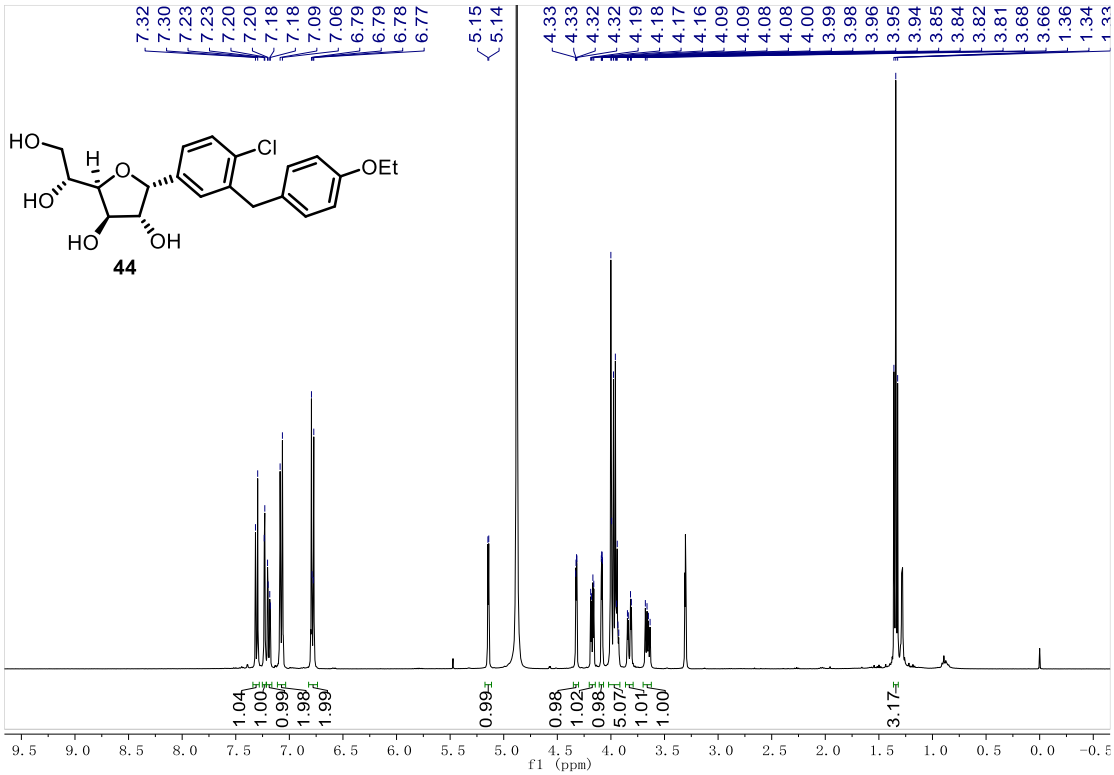

$^{19}$F NMR of compound **43** (376 MHz, $CD_3OD$)



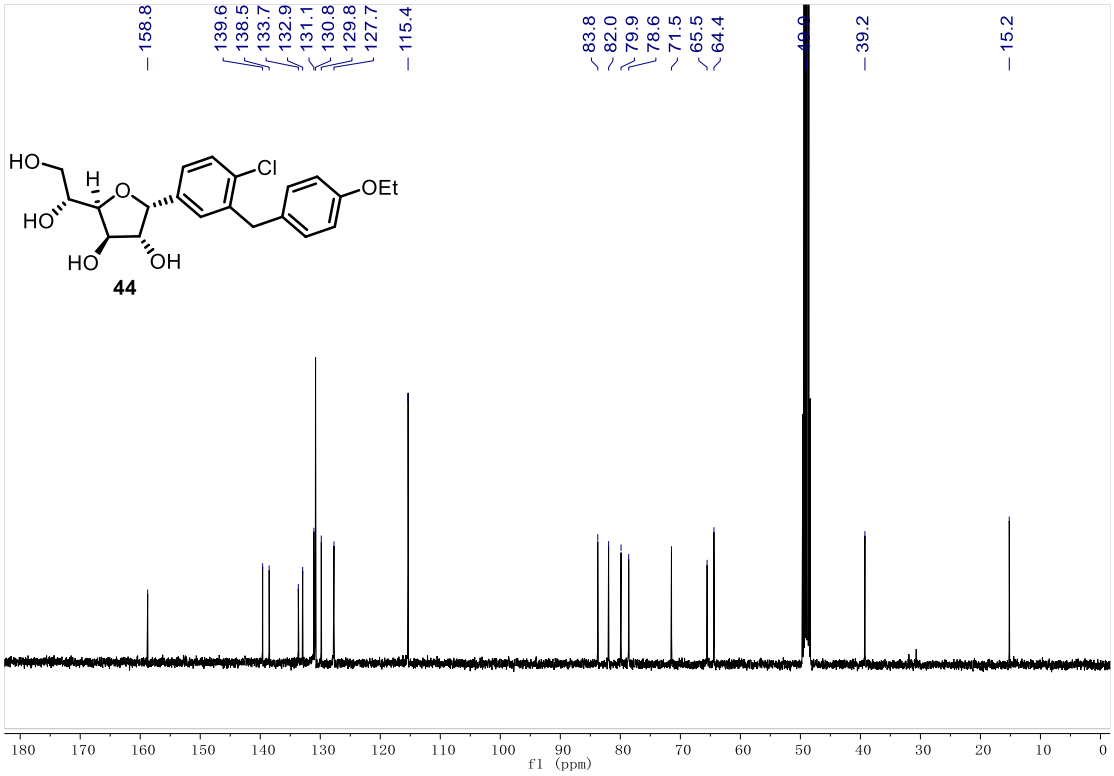

$^{1}$H NMR of compound **44-s** (400 MHz, $CD_3OD$)



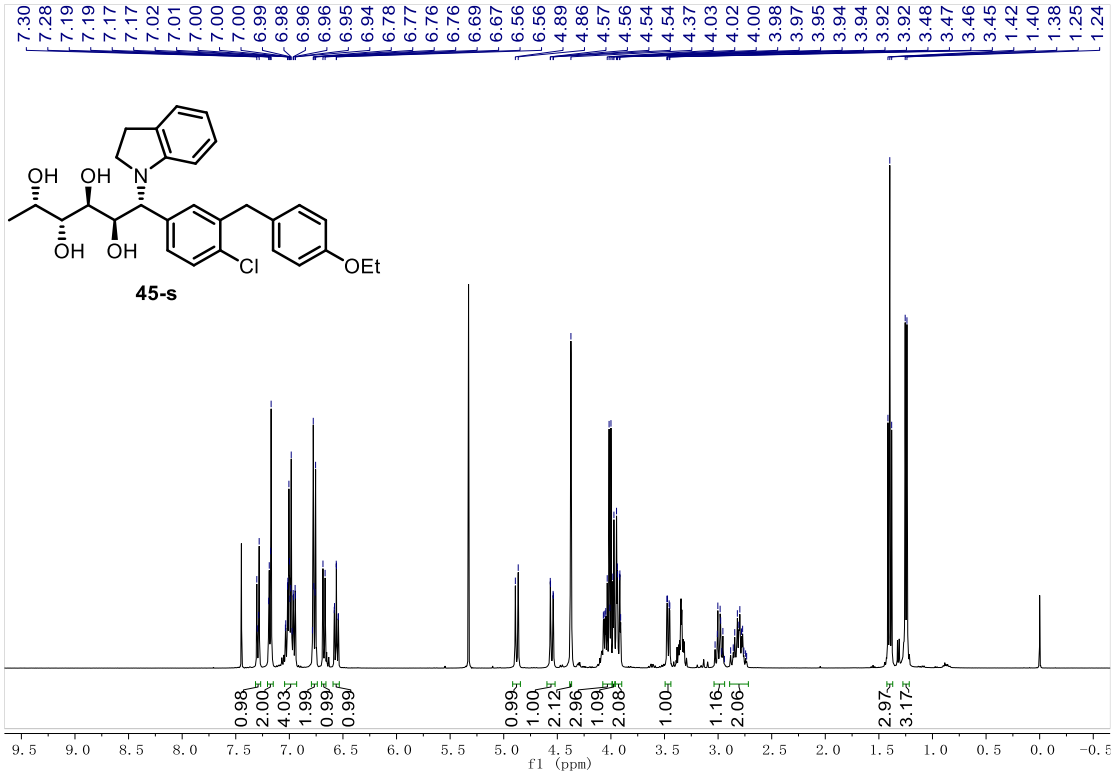

$^{13}$C NMR of compound **44-s** (101 MHz, $CD_3OD$)



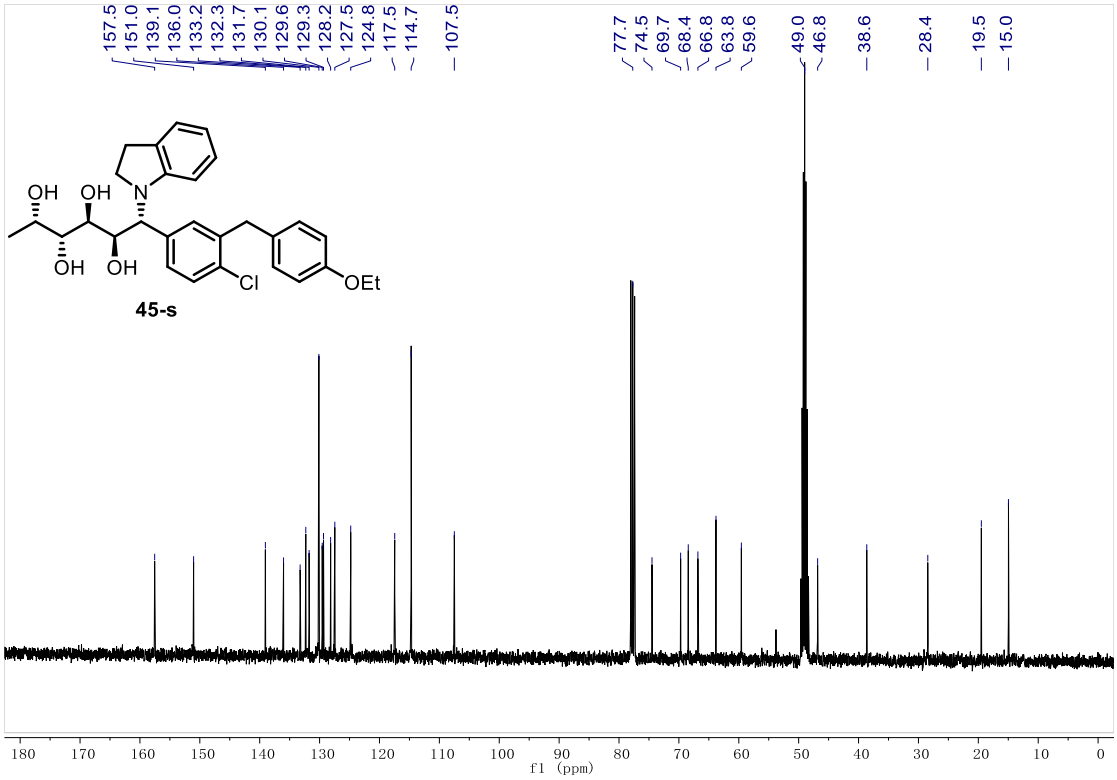

$^{1}$H NMR of compound **44** (400 MHz, $CD_3OD$)



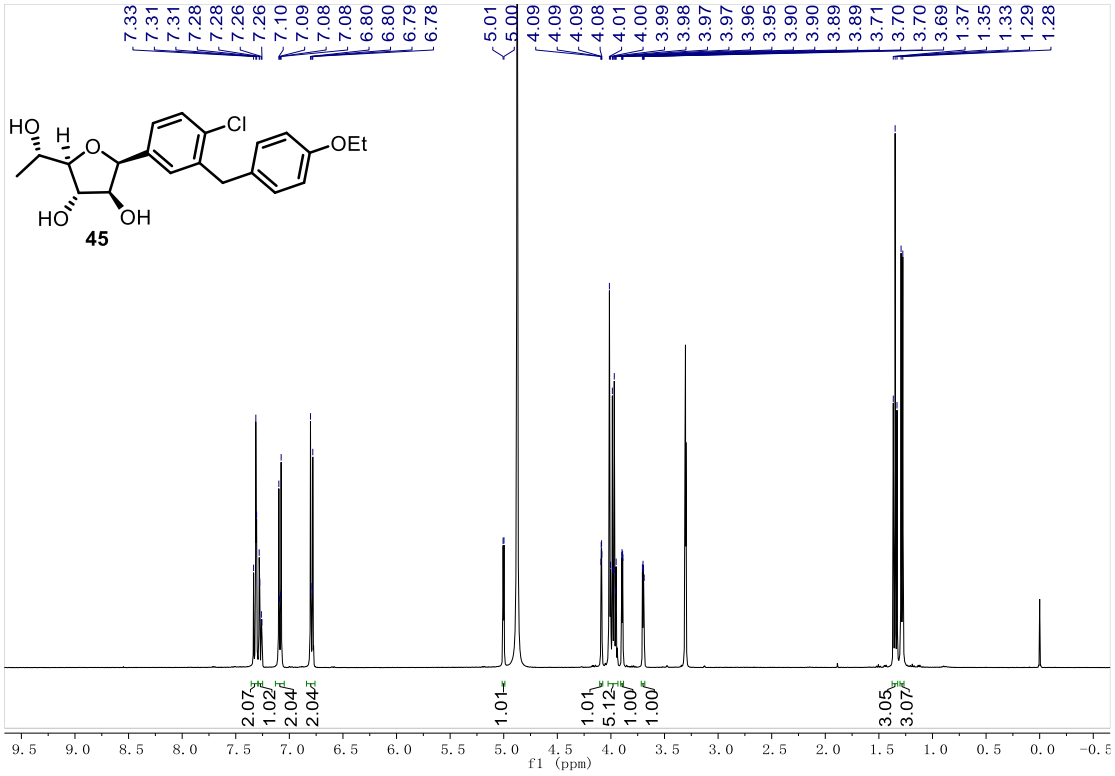

$^{13}$C NMR of compound **44** (101 MHz, $CD_3OD$)



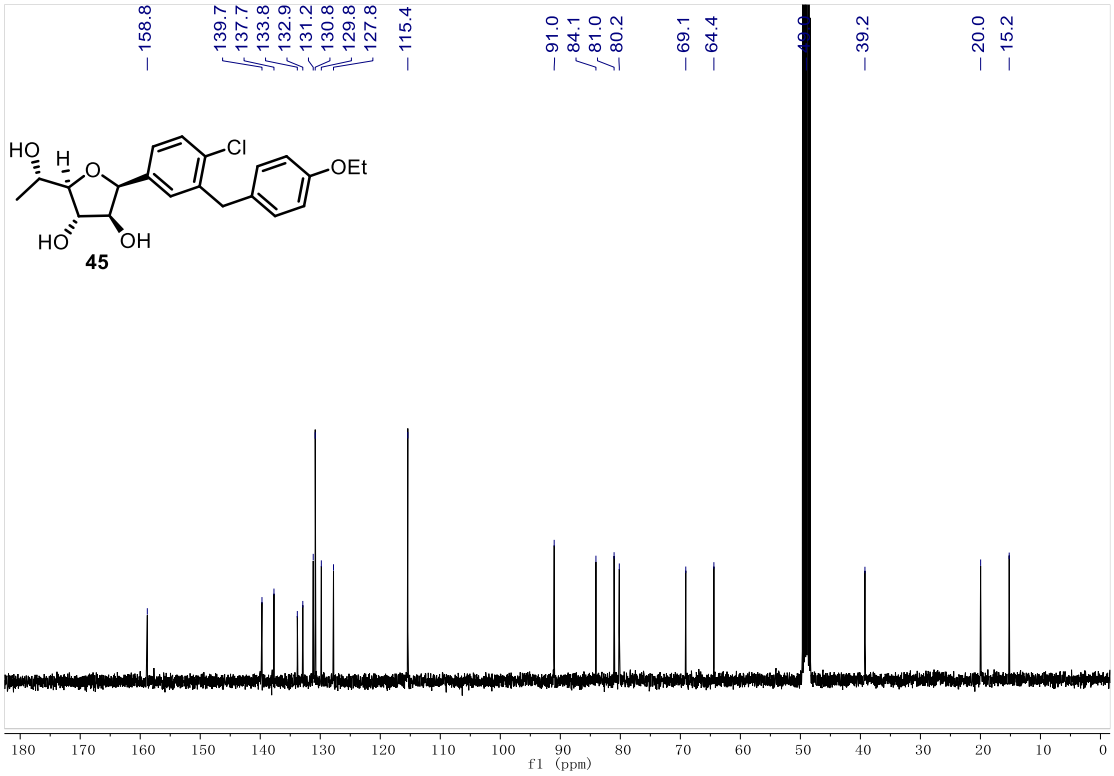

$^{1}$H NMR of compound **45-s** (400 MHz, $CD_3OD/CDCl_3$)



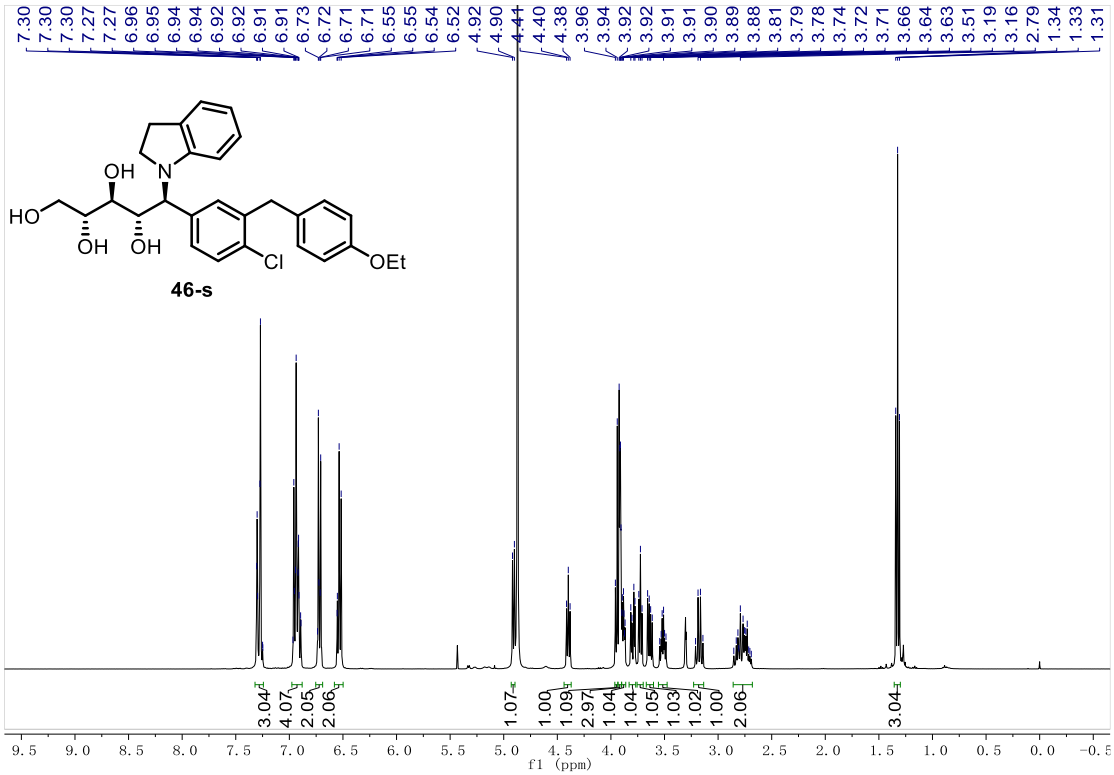

$^{13}$C NMR of compound **45-s** (101 MHz, $CD_3OD/CDCl_3$)



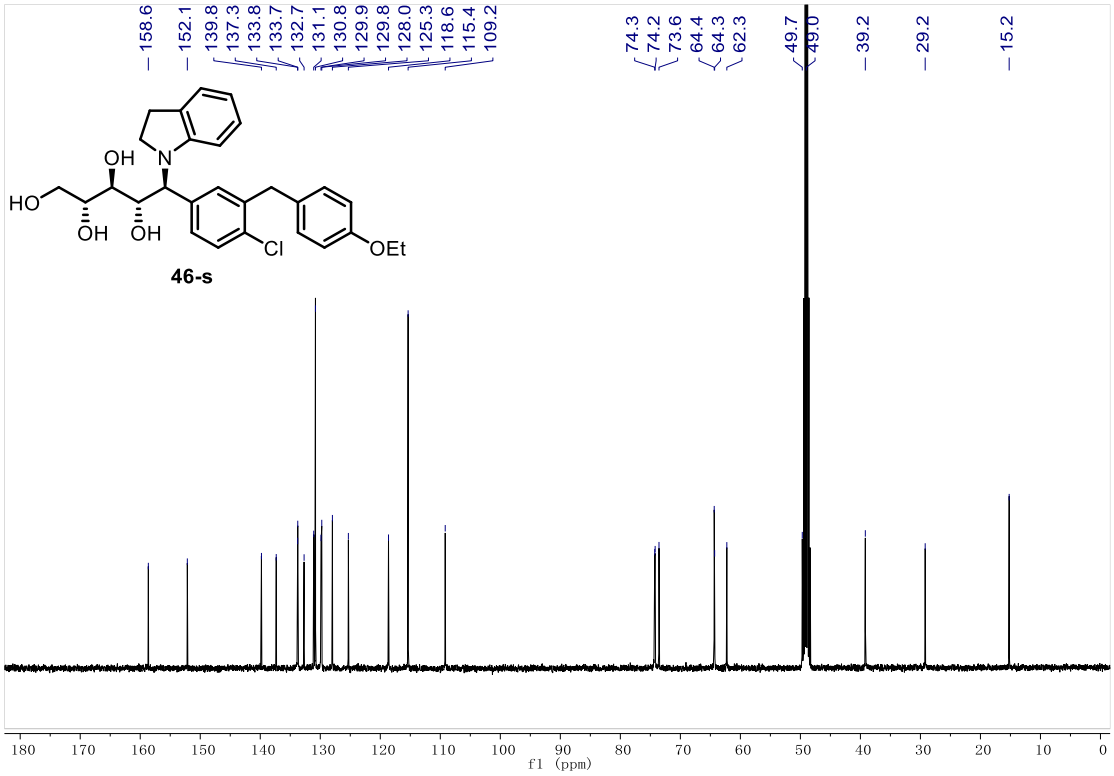

$^{1}$H NMR of compound **45** (400 MHz, $CD_3OD$)



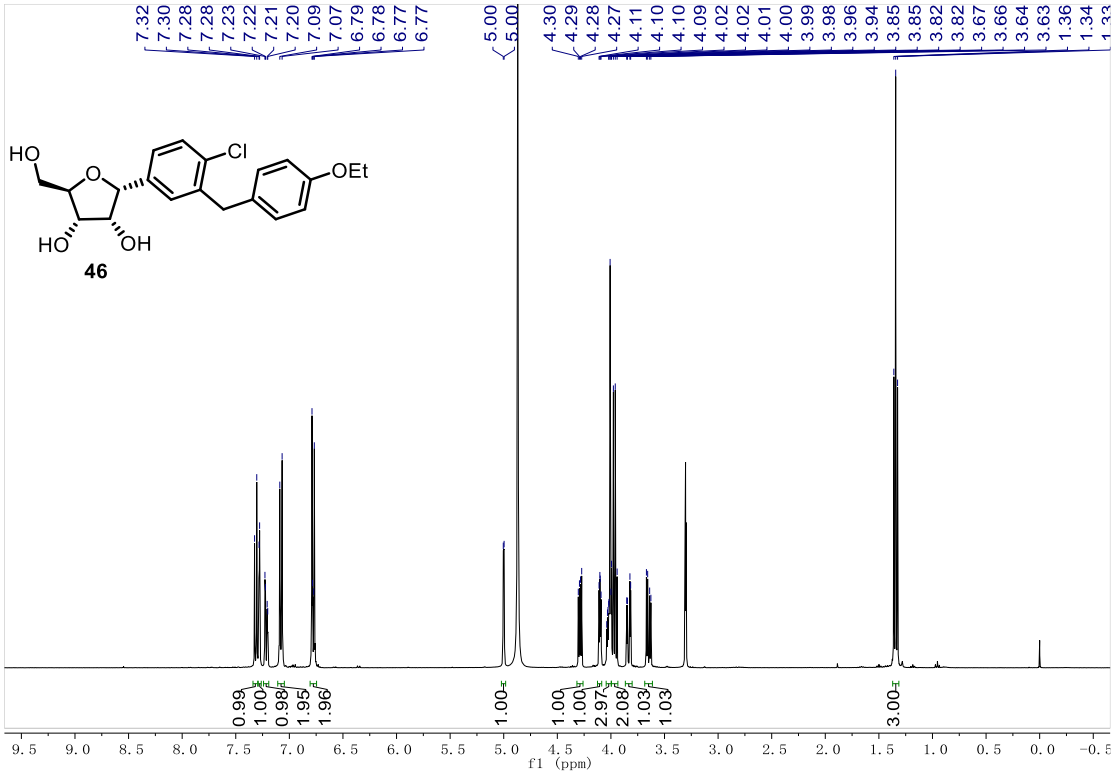

$^{13}$C NMR of compound **45** (101 MHz, $CD_3OD$)



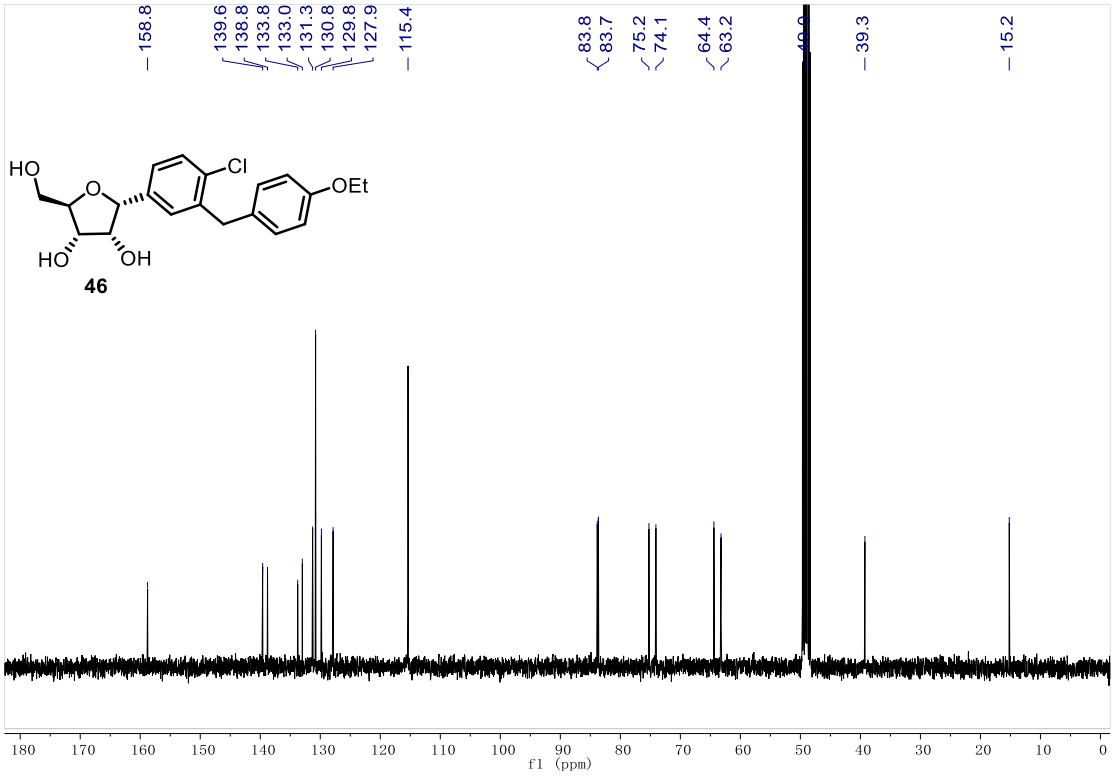

$^{1}$H NMR of compound **46-s** (400 MHz, $CD_3OD$)



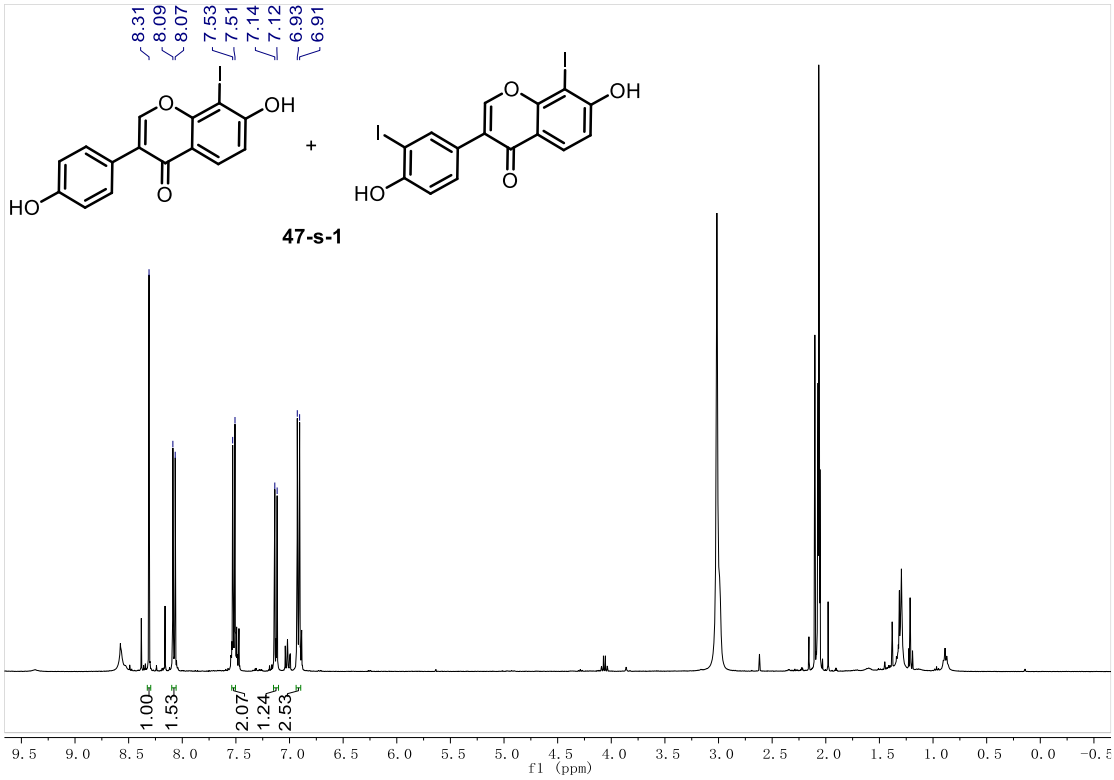

$^{13}$C NMR of compound **46-s** (101 MHz, $CD_3OD$)



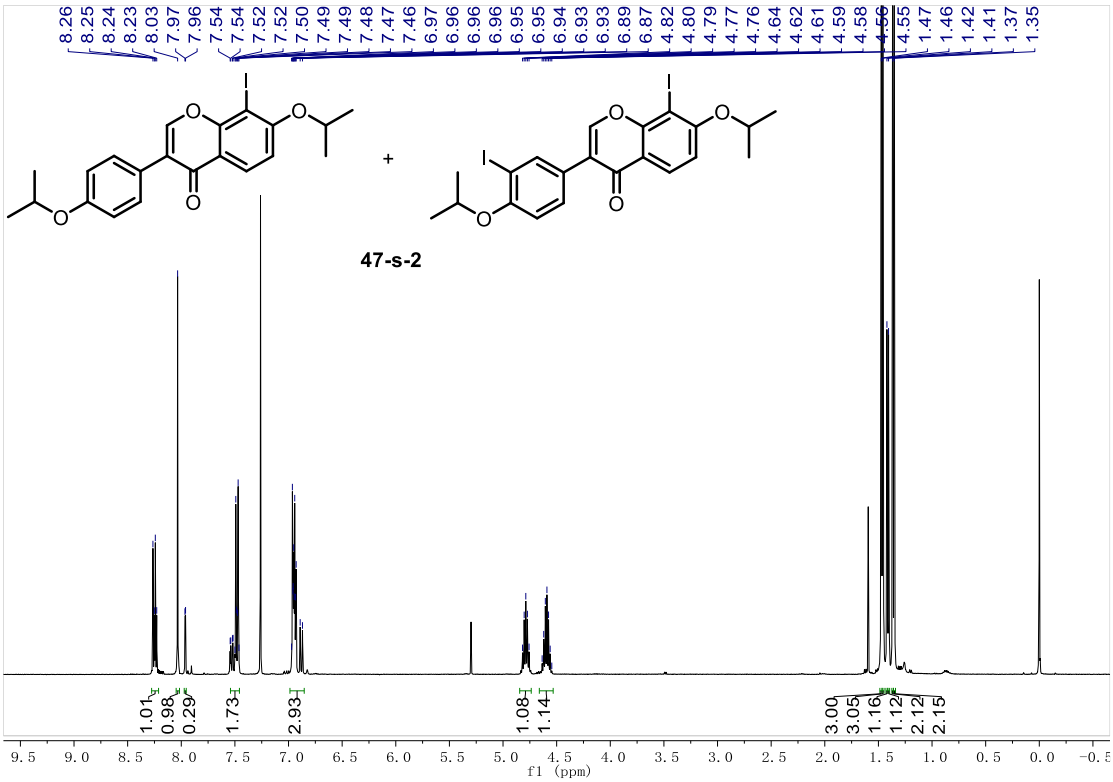

$^{1}$H NMR of compound **46** (400 MHz, $CD_3OD$)



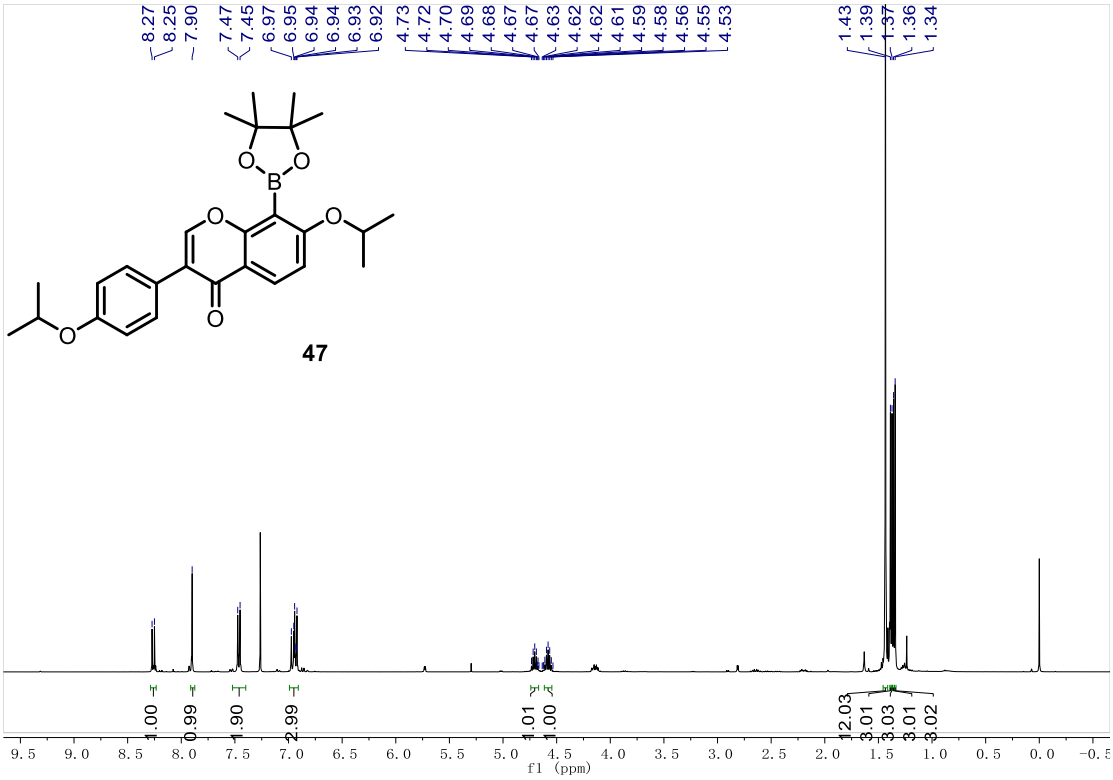

$^{13}$C NMR of compound **46** (101 MHz, $CD_3OD$)



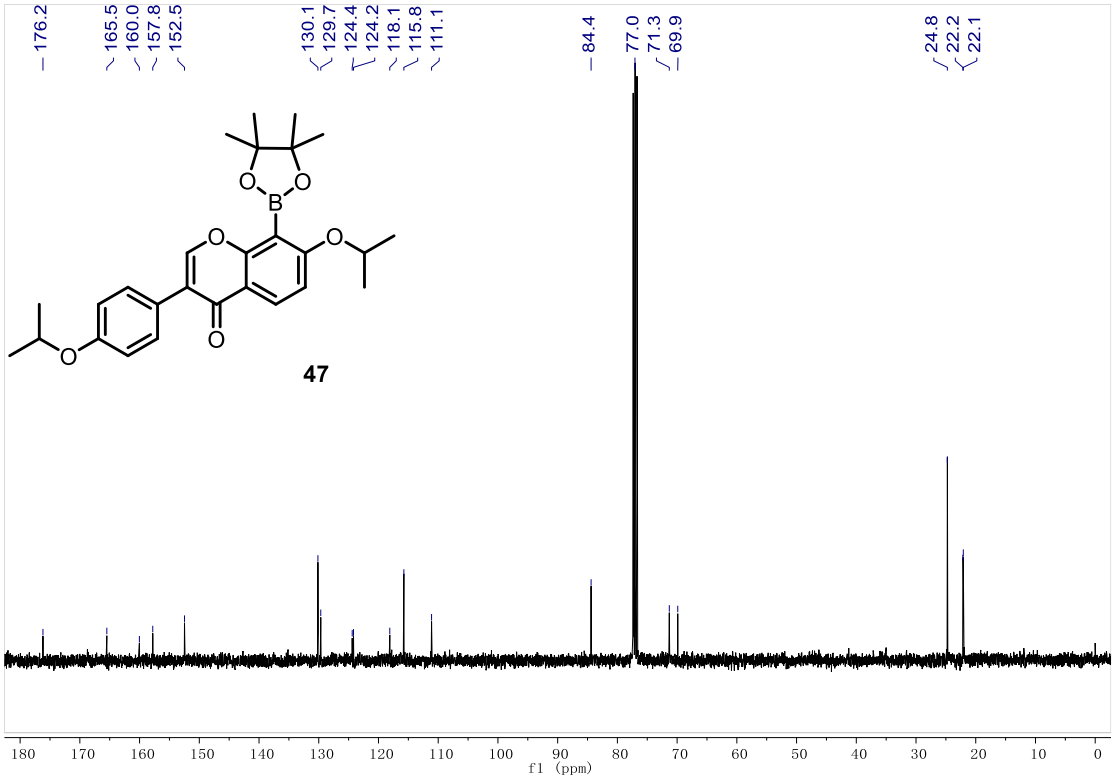

$^{1}$H NMR of compound **47-s-1** (400 MHz, acetone-$D_6$)



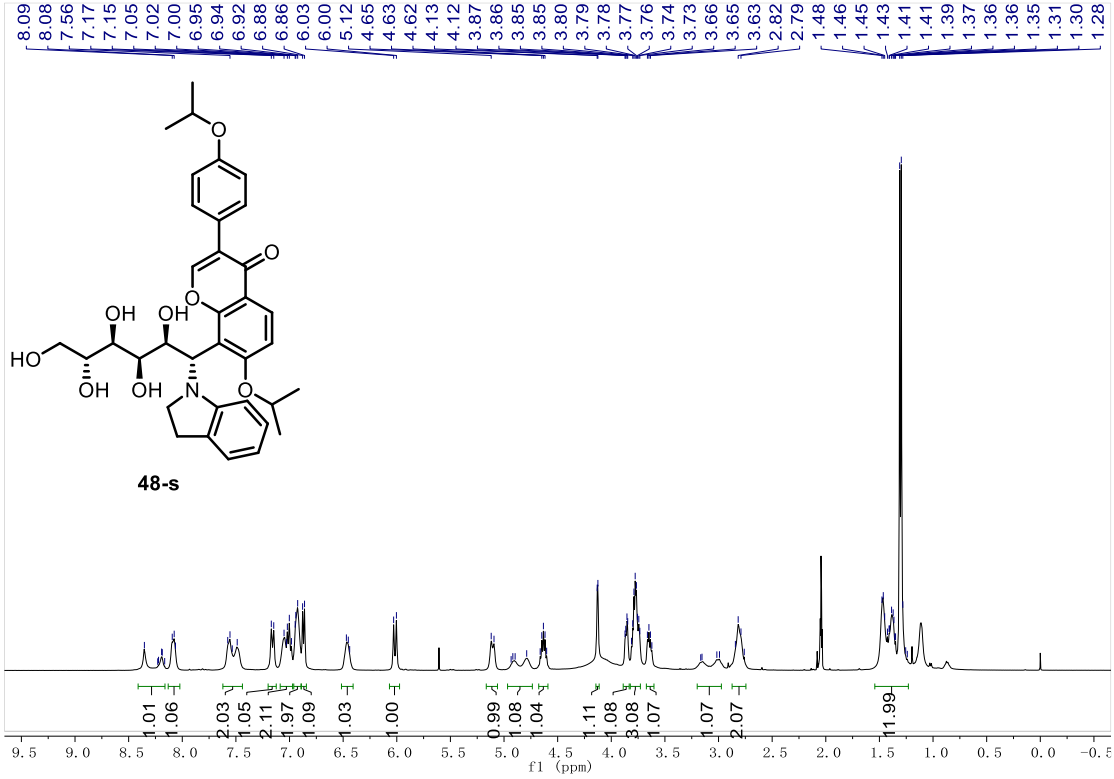

$^1$H NMR of compound **47-s-2** (400 MHz, $CDCl_3$)



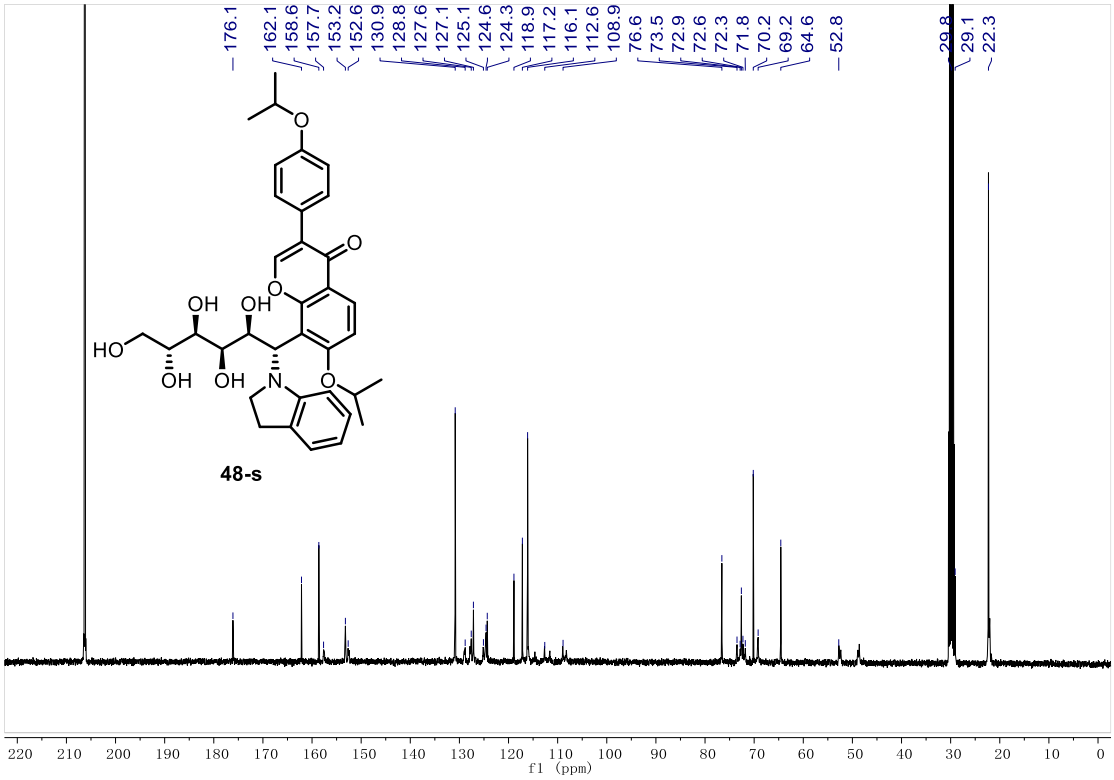

$^1$H NMR of compound **47** (400 MHz, $CDCl_3$)



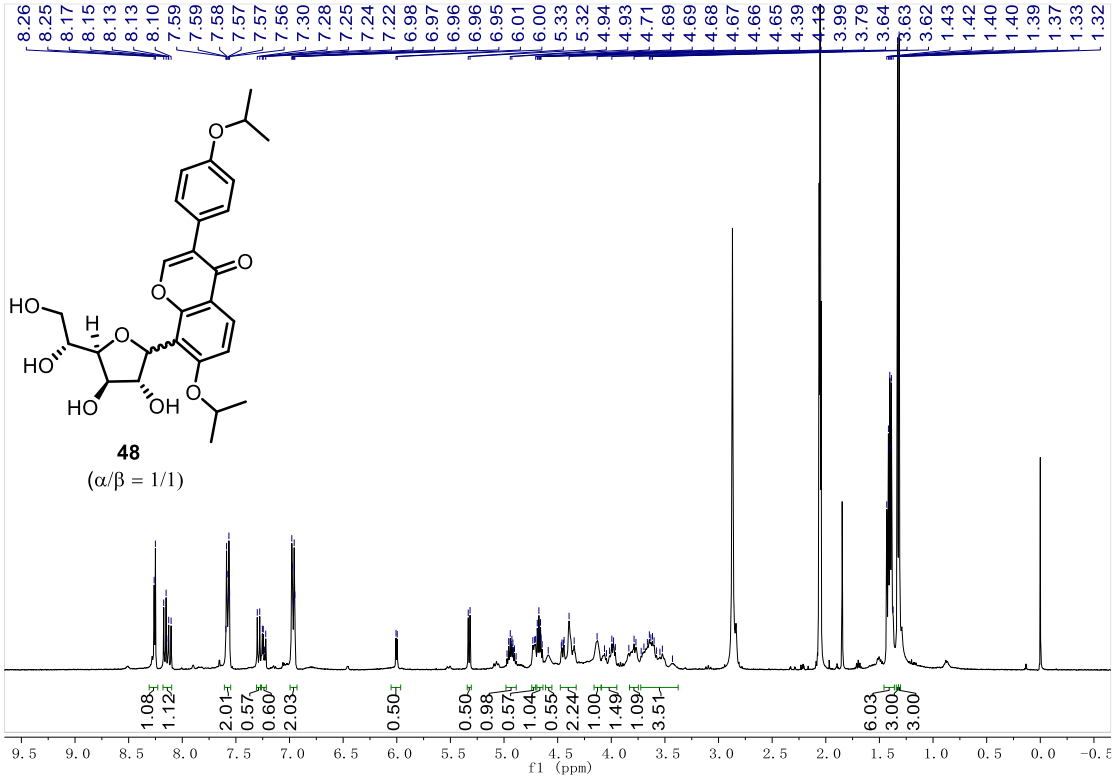

$^{13}$C NMR of compound **47** (101 MHz, $CDCl_3$)



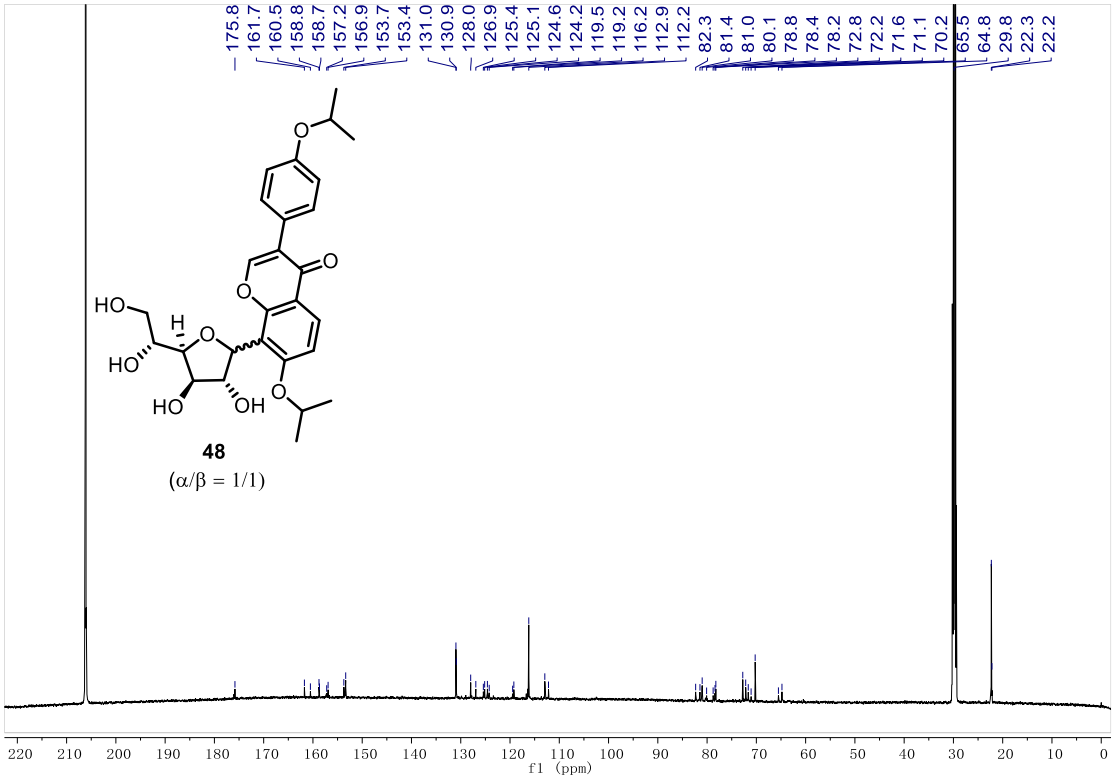

$^{1}$H NMR of compound **48-s** (400 MHz, acetone-$D_6$)



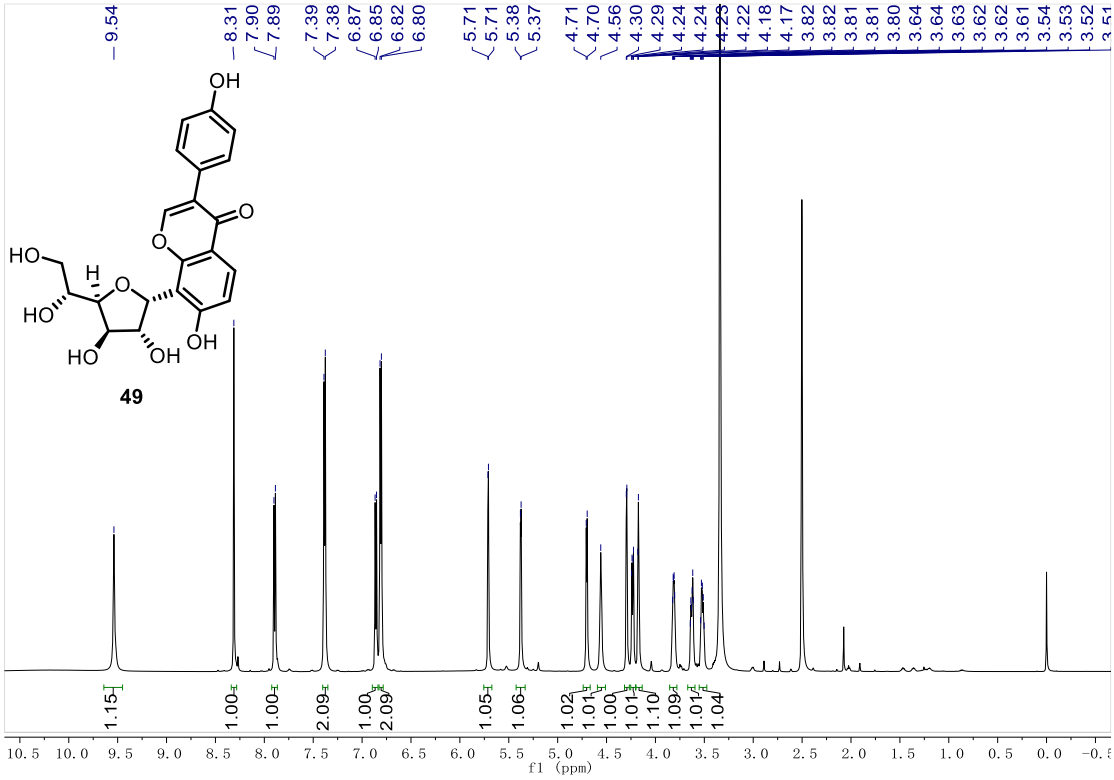

$^{13}$C NMR of compound **48-s** (101 MHz, acetone-$D_6$)



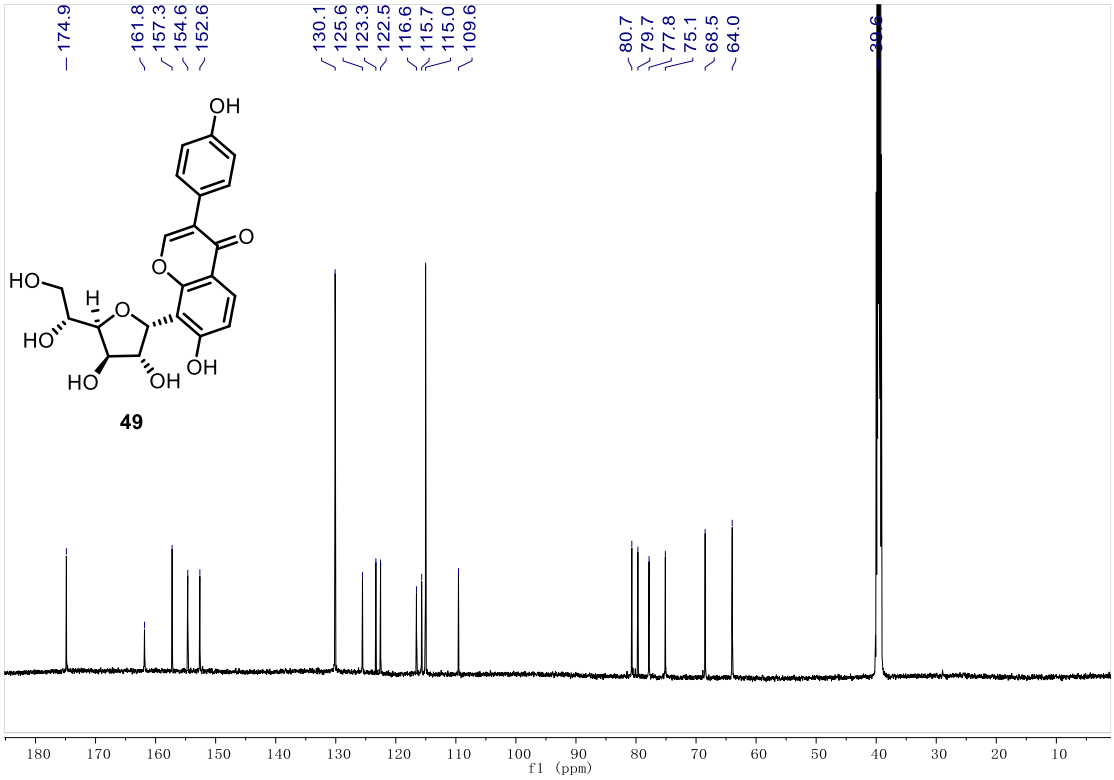

$^{1}$H NMR of compound **48 (α/β = 1/1)** (400 MHz, acetone-$D_6$)



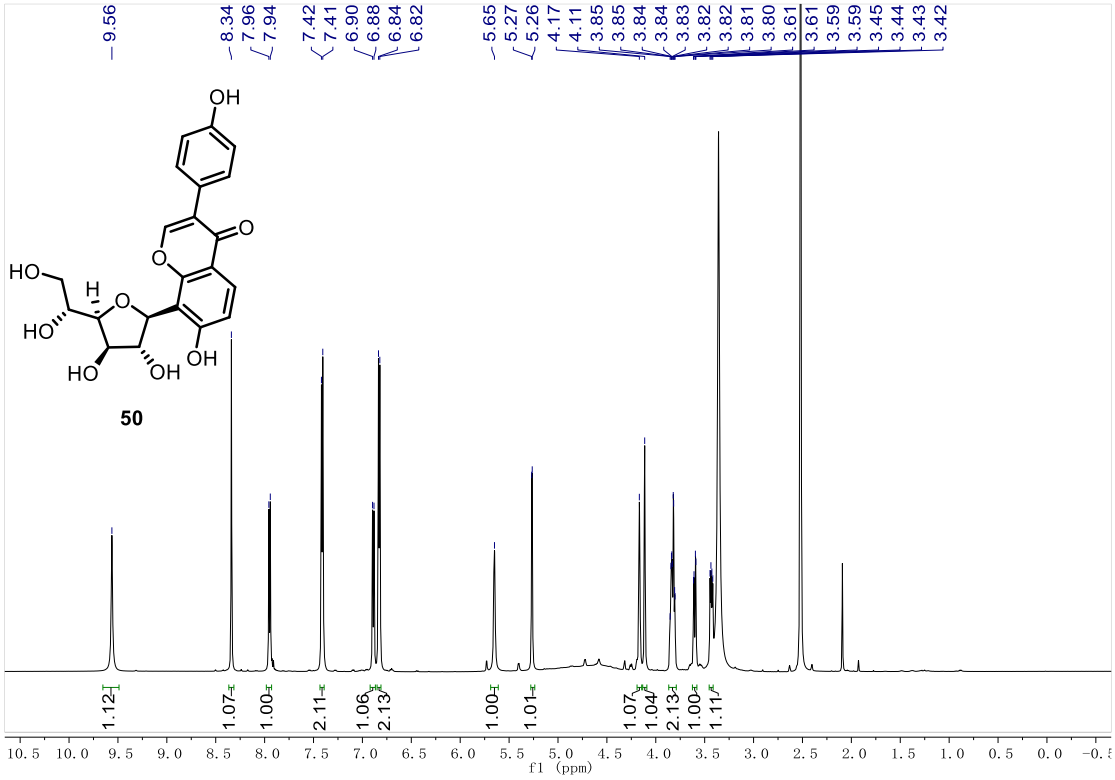

$^{13}$C NMR of compound **48 (α/β = 1/1)** (151 MHz, acetone-$D_6$)



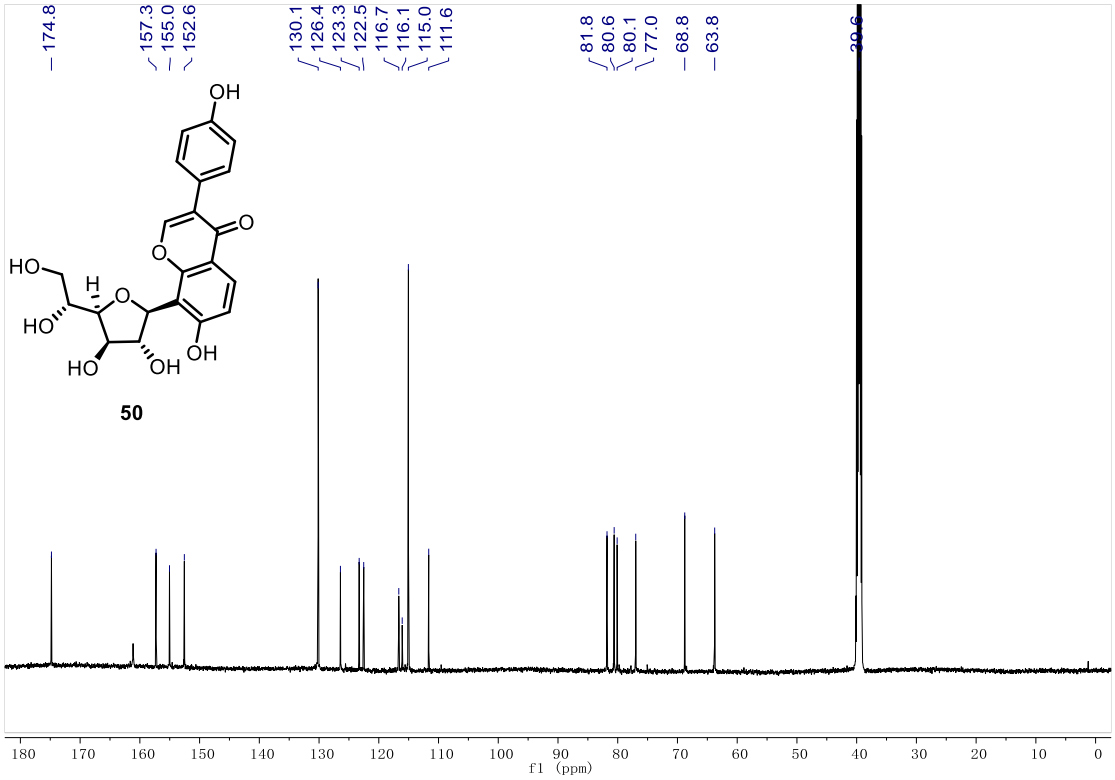

$^{1}$H NMR of compound **49** (600 MHz, DMSO-$D_6$)




$^{13}$C NMR of compound **49** (151 MHz, DMSO-$D_6$)




$^{1}$H NMR of compound **50** (600 MHz, DMSO-$D_6$)




$^{13}$C NMR of compound **50** (151 MHz, DMSO-$D_6$)