

Synthesis and Biological Evaluation of New Dihydrofuro[3,2-b]piperidine Derivatives as Potent α -Glucosidase Inhibitors

Haibo Wang^{1,2,3}, Xiaojiang Huang^{1,2}, Yang Pan^{1,2}, Guoqing Zhang¹, Senling Tang^{1,2}, Huawu Shao¹ and Wei Jiao^{1,*}

1 Natural Products Research Centre, Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu 610041, China; wanghb616@163.com (H.W.); huangxiaojiang22@mails.ucas.ac.cn (X.H.); 18685560668@163.com (Y.P.); guoqingzhanga@outlook.com (G.Z.); tangsl@cib.ac.cn (S.T.); shaohw@cib.ac.cn (H.S.)

2 University of Chinese Academy of Sciences, Beijing 100049, China

3 Zhejiang Hongyuan Pharmaceutical Co., Ltd., Linhai 317016, China

* Correspondence: jiaowei@cib.ac.cn

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Acetyl-2,3,5-tri-O-acetyl- β -D-arabinofuranoside(1)

Acetyl chloride (2 mL) was added dropwise to the solution of D-arabinose (5g, 33.4 mmol) in methanol at 0 °C. The mixture was stirred for 2.5 h and evaporated the solvent to obtain yellow residue, which was subsequently dissolved in pyridine (30 mL). Then, Ac₂O was added at 0 °C and the reaction was stirred for 8 h. The mixture was poured into cold water (50 mL), and extracted with EtOAc (3×50 mL). The organic layer was then washed with 1N HCl, brine, water and dried over Na₂SO₄, successively. The filtrate was concentrated *in vacuo*, and the obtained yellow residue was redissolved in Ac₂O (70 mL) and HOAc (20 mL), concentrated sulfuric acid (5 mL) was added dropwise to the solution at 0 °C. After work up and purification, the product was obtained as colorless syrup. Yield 89%. ¹H NMR (600MHz, CDCl₃) δ 5.37 (t, *J* = 7.1 Hz, 1H, O-CH), 5.15 (d, *J* = 3.2 Hz, 1H, O-CH), 5.02 (t, *J* = 6.5 Hz, 1H, O-CH), 4.71 (d, *J* = 3.2 Hz, 1H, O-CH), 3.98 (dd, *J* = 12.7, 2.5 Hz, 1H, OCH₂), 3.78 (dd, *J* = 12.6, 4.0 Hz, 1H, OCH₂), 3.43 (s, 3H, COCH₃), 2.12 (s, 3H, COCH₃), 2.11 (s, 3H, COCH₃), 2.04 (s, 3H, COCH₃).

1-C-Allyl-2,3,5-tri-O-acetyl- α -D-arabinofuranoside (2) (Figure S1, S2)

Compound 1 (10g, 31.5 mmol) was dissolved in anhydrous acetonitrile (100 mL), which Allyl-TMS (10mL, 60.3 mmol) was added to. Under argon atmosphere, Lewis acid TMSOTf was added at 0 °C and stirred the reaction for 8 h. Then, the mixture was poured into cold water (50 mL). After work up and purification, the product was obtained as colorless syrup. Yield 62%, Colorless syrup, $[\alpha]_D^{25} +23.3$ (c 0.99, CHCl₃). ¹H NMR (600 MHz, CDCl₃) δ 5.75–5.66 (m, 1H, =CH), 5.06–4.85 (m, 4H, 2 × O-CH, =CH₂), 4.20–4.12 (m, 2H, 2 × O-CH), 4.08 (dd, *J* = 12.6, 5.6 Hz, 1H, OCH₂), 4.01 (dd, *J* = 6.4, 4.8 Hz, 1H, OCH₂), 2.35–2.24 (m, 2H, =CHCH₂), 1.99 (s, 9H, 3 × COCH₃). ¹³C NMR (151 MHz, CDCl₃) δ 170.4(C=O), 169.8(C=O), 169.7(C=O), 133.1(=CH), 117.9(=CH₂), 82.2 (O-CH), 80.4 (O-CH), 80.0 (O-CH), 78.7 (O-CH), 63.2(OCH₂), 36.8(=CHCH₂), 20.7(CH₃), 20.6(CH₃), 20.6(CH₃). ESI-HRMS: *m/z* calcd for C₁₄H₂₀O₇Na [M+Na]⁺: 323.1101; found: 323.1091.

1-C-Allyl-2,3-di-O-acetyl-5-O-mesyl- α -D-arabinofuranoside (3)(Figure S3, S4)

A solution of compound 2 treated with 2 mL saturated MeONa in methanol at room temperature for 3h. The mixture was quenched with HOAc and evaporated the solvent to obtain yellow residue, which was subsequently dissolved in pyridine. Then, mesyl chloride (1.2 eq) was added dropwise at -20 °C and the solution was stirred for 48 h. Finally, Ac₂O was added to this reaction mixture and was stirred at room temperature for 5 h. The mixture was poured into cold water (40 mL), and extracted with EtOAc (3×50 mL). The organic layer was then washed with 1N HCl, brine, water and dried over Na₂SO₄, successively. The filtrate was concentrated *in vacuo*, and purified by silica gel flash column chromatography (petroleum ether/ethyl acetate, 3:1) to afford compound 3 as a colorless syrup. Yield 61%. $[\alpha]_D^{25} +22.2$ (c 1.0, CHCl₃). ¹H NMR (600 MHz, CDCl₃) δ 5.81–5.72 (m, 1H, =CH), 5.14–5.05 (m, 4H, 2 × O-CH, =CH₂), 4.44 (d, *J* = 11.2 Hz, 1H, CH₂OSO₂), 4.38 (d, *J* = 4.3 Hz, 1H, O-CH), 4.18 (d, *J* = 11.6 Hz, 1H, CH₂OSO₂), 4.09 (d, *J* = 9.3 Hz, 1H, O-CH), 3.05 (s, 3H, OSO₂CH₃), 2.41 (t, *J* = 6.4 Hz, 2H, =CHCH₂), 2.10 (s, 3H, COCH₃), 2.08 (s, 3H, COCH₃). ¹³C NMR (151 MHz, CDCl₃) δ 170.0(C=O), 169.9(C=O), 133.0 (=CH), 118.2(=CH₂), 82.4 (O-CH), 80.6 (O-CH), 79.8 (O-CH), 78.3 (O-CH), 68.4(CH₂OSO₂), 37.7(OSO₂CH₃), 36.6(=CHCH₂), 20.8(COCH₃), 20.7(COCH₃). ESI-HRMS: *m/z* calcd for C₁₃H₂₀O₈SNa [M+Na]⁺: 359.0771; found: 359.0761.

1-C-Allyl-2,3-di-O-acetyl-5-Azido-5-deoxy- α -D-arabinofuranoside (4)(Figure S5, S6)

A solution of 3 (2.7 mmol) in DMF (10 mL) was treated with NaN₃ (0.5 g, 8.2 mmol) at 80 °C for 8h. Then, the mixture was poured into cold water (30 mL), and extracted with EtOAc (3×40 mL). The organic layer was successively washed with water (2 × 50 mL), brine (3 × 100 mL), dried over anhydrous Na₂SO₄. The filtrate was concentrated to obtain a colorless syrup, which was subsequently subject to silica gel flash column chromatography (petroleum ether/ethyl acetate, 5:1) to afford compound 4 (0.6 g, 2.1 mmol, 90%) as a colorless syrup. $[\alpha]_D^{25} +85.5$ (c 0.91, CHCl₃). ¹H NMR (600 MHz, CDCl₃) δ 5.83–5.75 (m, 1H, =CH), 5.15–5.07 (m, 4H, 2 × O-CH, =CH₂), 4.13–4.05 (m, 2H, 2 × O-CH), 3.50 (dd, *J* = 13.0, 3.7 Hz, 1H, N₃CH₂), 3.43 (dd, *J* = 13.0, 5.8 Hz, 1H, N₃CH₂), 2.41 (t, *J* = 6.8 Hz, 2H, =CHCH₂), 2.11 (s, 3H, COCH₃), 2.07 (s, 3H, COCH₃). ¹³C NMR (151 MHz, CDCl₃) δ 170.1 (C=O), 170.0(C=O), 133.1 (=CH), 118.1 (=CH₂),

82.2 (O-CH), 81.9 (O-CH), 80.2 (O-CH), 79.1 (O-CH), 51.8(N₃CH₂), 36.6 (=CHCH₂), 20.8 (CH₃), 20.7 (CH₃). ESI-HRMS: *m/z* calcd for C₁₂H₁₇O₅N₃Na [M+Na]⁺: 306.1060; found: 306.1056.

1-C-Acetylmethyl-2,3-di-O-acetyl-5-Azido-5-deoxy- α -D-arabinofuranoside (5) (Figure S7, S8)

To a solution of **4** (1.5 mmol) and Hg(OAc)₂ (200 mg, 0.6 mmol) in acetone/water (4:1, 20 mL) was added dropwise a solution of Jones reagent (2 M, 6 mL) at 0 °C. The dark greenish brown mixture was stirred overnight at 0 °C to room temperature and then poured into cold water (40 mL). The aqueous mixture was extracted with EtOAc (3×60 mL). The organic layer was successively washed with water (2×50 mL), brine (5×100 mL), dried over anhydrous Na₂SO₄. The filtrate was concentrated *in vacuo* and the residue was purified by silica gel flash column chromatography (petroleum ether/ethyl acetate, 2:1, R_f = 0.3) to afford compound **5** as a colorless syrup. Yield 98%, [α]_D²⁵ +66.5 (*c* 1.3, CHCl₃). ¹H NMR (600 MHz, CDCl₃) δ 5.05 (dd, *J* = 8.5, 4.7 Hz, 1H, O-CH), 5.02 (br s, 1H, O-CH), 4.50–4.44 (m, 1H, O-CH), 4.10–4.05 (m, 1H, O-CH), 3.50–3.37 (m, 2H, N₃CH₂), 2.85–2.70 (m, 2H, COCH₂), 2.15 (s, 3H, COCH₃), 2.05 (s, 6H, 2 × COCH₃). ¹³C NMR (151 MHz, CDCl₃) δ 205.1 (C=O), 170.1 (C=O), 170.0 (C=O), 82.0 (O-CH), 80.5 (O-CH), 78.8 (O-CH), 78.7 (O-CH), 51.6 (N₃CH₂), 46.2 (COCH₂), 30.3 (CH₃), 20.7 (CH₃), 20.7 (CH₃). ESI-HRMS: *m/z* calcd for C₁₂H₁₇O₆N₃Na [M+Na]⁺: 322.1010; found: 322.0995.

1-C-Acetylmethyl-5-deoxy-5-amino- α -D-arabinopyranoside (6)(Figure S9, S10)

A solution of compound **5** (1 mmol) in 8mL methanol was bubbled with hydrogen in the presence Pd/C catalyst (200 mg) and stirred for 8h at room temperature. Then, the solution was filtered and evaporated to get a yellow syrup, which was immediately treated with 1% MeONa in methanol at room temperature for 8h. The reaction mixture was concentrated without disposal to obtain a yellow crude. Purified the crude with silica gel flash column chromatography (petroleum ether/acetone, 10:1→1:1) to afford the final product **6**. yellowish syrup, Yield 67%. ¹H NMR (600 MHz, MeOD) δ 4.02 (m, 1H, O-CH), 3.91 (s, 1H, O-CH), 3.80 (s, 1H, O-CH), 3.65 (s, 1H, NCH), 3.30–3.25 (m, 2H, NCH₂), 3.05–2.93 (m, 2H, COCH₂), 2.20 (s, 3H, COCH₃). ¹³C NMR (151 MHz, MeOD) δ 207.4 (C=O), 69.9 (O-CH), 69.6(O-CH), 63.6 (O-CH), 56.8 (NCH), 49.8 (NCH₂), 44.0 (COCH₂), 22.5 (CH₃). ESI-HRMS: *m/z* calcd for C₈H₁₆O₄N [M+H]⁺: 190.1074; found: 190.1075.

Acetyl-2,3,5-tri-O-acetyl- α/β -L-arabinofuranoside (7)

olorless syrup, Yield 93%, R_f = 0.3 (P.E./ EtOAc, 2:1). β :¹H NMR (600MHz, CDCl₃) δ 5.37 (t, *J* = 7.1 Hz, 1H,O-CH), 5.15 (d, *J* = 3.2 Hz, 1H, O-CH), 5.02 (t, *J* = 6.5 Hz, 1H,O-CH), 4.71 (d, *J* = 3.2 Hz, 1H, O-CH), 3.98 (dd, *J* = 2.5, 12.7 Hz, 1H, OCH₂), 3.78 (dd, *J* = 4.0, 12.6 Hz, 1H, OCH₂), 3.43 (s, 3H, COCH₃), 2.12 (s, 3H, COCH₃), 2.11 (s, 3H, COCH₃), 2.04 (s, 3H, COCH₃).

1-C-Allyl-2,3,5-tri-O-acetyl- α -L-arabinofuranoside (8)(Figure S11, S12)

The synthesized procedure was the same with compound **2**. Colorless syrup, Yield 91%, [α]_D²⁵ - 23.6 (*c* 0.40, CHCl₃). ¹H NMR (600 MHz, CDCl₃) δ 5.83–5.74 (m, 1H, =CH), 5.12–5.06 (m, 4H, 2 × O-CH, =CH₂), 4.24–4.21 (m, 2H, 2 × O-CH), 4.17–4.07 (m, 2H, O-CH₂), 2.42–2.26 (m, 2H, =CHCH₂), 2.14 (s, 9H, COCH₃). ¹³C NMR (151 MHz, CDCl₃) δ 170.7 (C=O), 170.0 (C=O), 169.9 (C=O), 133.1 (=CH), 118.0 (=CH₂), 82.3 (O-CH), 80.5 (O-CH), 80.1 (O-CH), 78.7 (O-CH), 63.4 (OCH₂), 36.9 (=CHCH₂), 20.8 (CH₃), 20.8 (CH₃), 20.8 (CH₃). ESI-HRMS: *m/z* calcd for C₁₄H₂₀O₇Na [M+Na]⁺: 323.1101; found: 323.1105.

1-C-Allyl-2,3-di-O-acetyl-5-O-mesyl- α -L-arabinofuranoside (9) (Figure S13, S14)

The synthesized procedure was the same with compound **3**. Colorless syrup, Yield 88%, [α]_D²⁵ -23.9 (*c* 0.93, CHCl₃). ¹H NMR (600 MHz, CDCl₃) δ 5.84–5.72 (m, 1H, =CH), 5.23–5.02 (m, 4H, 2 × O-CH, =CH₂), 4.41–4.36 (m, 2H, O-CH, CH₂OSO₂), 4.19 (d, *J* = 11.6 Hz, 1H, CH₂OSO₂), 4.12–4.05 (m, 1H, O-CH), 3.05 (s, 3H, OSO₂CH₃), 2.41 (dd, *J* = 15.8, 9.0 Hz, 2H, =CHCH₂), 2.08(s, 6H, 2 × COCH₃). ¹³C NMR (151 MHz, CDCl₃) δ 170.1 (C=O), 170.0 (C=O), 133.0 (=CH), 118.2 (=CH₂), 82.4 (O-CH), 80.6 (O-CH), 79.8 (O-CH), 78.3 (O-CH), 68.4 (CH₂OSO₂), 37.7(OSO₂CH₃), 36.6 (=CHCH₂), 20.8 (CH₃), 20.7 (CH₃). ESI-HRMS: *m/z* calcd for C₁₃H₂₀O₈SNa [M+Na]⁺: 359.0771; found: 359.0776.

1-C-Allyl-2,3-di-O-acetyl-5-Azido-5-deoxy- α -L-arabinofuranoside (10)(Figure S15, S16)

The synthesized procedure was the same with compound **4**. Colorless syrup, Yield 63%, [α]_D²⁵ - 84.2 (*c* 0.51, CHCl₃). ¹H NMR (600 MHz, CDCl₃) δ 5.85–5.78 (m, 1H, =CH), 5.25–5.02 (m, 4H, 2

\times O-CH, =CH₂), 4.18–4.08 (m, 2H, 2 \times O-CH), 3.52 (dd, J = 13.0, 3.7 Hz, 1H, N₃CH₂), 3.43 (dd, J = 13.0, 5.8 Hz, 1H, N₃CH₂), 2.42 (dd, J = 14.2, 7.5 Hz, 2H, =CHCH₂), 2.08 (s, 6H, 2 \times COCH₃). ¹³C NMR (151 MHz, CDCl₃) δ 170.1 (C=O), 170.0 (C=O), 133.1 (=CH), 118.1 (=CH₂), 82.2 (O-CH), 81.9 (O-CH), 80.2 (O-CH), 79.1 (O-CH), 51.8 (N₃CH₂), 36.6 (=CHCH₂), 20.8 (CH₃), 20.7 (CH₃). ESI-HRMS: m/z calcd for C₁₂H₁₇O₅N₃Na [M+Na]⁺: 306.1060; found: 306.1059.

1-C-Acetylmethyl-2,3-di-O-acetyl-5-Azido-5-deoxy- α -L-arabinofuranoside (11)(Figure S17, S18)

The synthesized procedure was the same with compound 5. Colorless syrup, Yield 98%, [α]_D²⁵ -66.4 (c 0.80, CHCl₃). ¹H NMR (600 MHz, CDCl₃) δ 5.08–5.00 (m, 2H, 2 \times O-CH), 4.53–4.46 (m, 1H, O-CH), 4.12–4.07 (m, 1H, O-CH), 3.48–3.41 (m, 2H, N₃CH₂), 2.82 (dd, J = 16.5, 8.2 Hz, 1H, COCH₂), 2.75 (dd, J = 16.4, 5.1 Hz, 1H, COCH₂), 2.16 (s, 3H, COCH₃), 2.07 (s, 6H, 2 \times COCH₃). ¹³C NMR (151 MHz, CDCl₃) δ 205.1 (C=O), 170.1 (C=O), 170.0 (C=O), 82.0(O-CH), 80.5(O-CH), 78.8(O-CH), 78.7(O-CH), 51.7 (N₃CH₂), 46.2 (COCH₂), 30.3 (CH₃), 20.8 (CH₃), 20.7 (CH₃). ESI-HRMS: m/z calcd for C₁₂H₁₇O₆N₃Na [M+Na]⁺: 322.1010; found: 322.1022.

1-C-Acetylmethyl-5-deoxy-5-amino- α -L-arabinopyranoside (12) (Figure S19, S20)

The synthesized procedure was the same with compound 6. Colorless syrup, Yield 65%. ¹H NMR (600 MHz, MeOD) δ 4.00 (d, J = 4.8 Hz, 1H, O-CH), 3.94–3.86 (m, 1H, O-CH), 3.78 (d, J = 4.1 Hz, 1H, O-CH), 3.64 (s, 1H, NCH), 3.50–3.35 (m, 1H, NCH₂), 3.02–2.91 (m, 2H, NCH₂, COCH₂), 2.82 (br dd, J = 11.6 Hz, 1H, COCH₂), 2.18 (s, 3H, COCH₃). ¹³C NMR (151 MHz, MeOD) δ 207.4 (C=O), 74.7 (O-CH), 71.2(O-CH), 68.7(O-CH), 63.5 (NCH), 49.8 (NCH₂), 44.0 (CH₂), 22.5 (CH₃). ESI-HRMS: m/z calcd for C₈H₁₆O₄N [M+H]⁺: 190.1074; found: 190.1081.

1. ^1H NMR and ^{13}C NMR spectra of intermediate compounds.

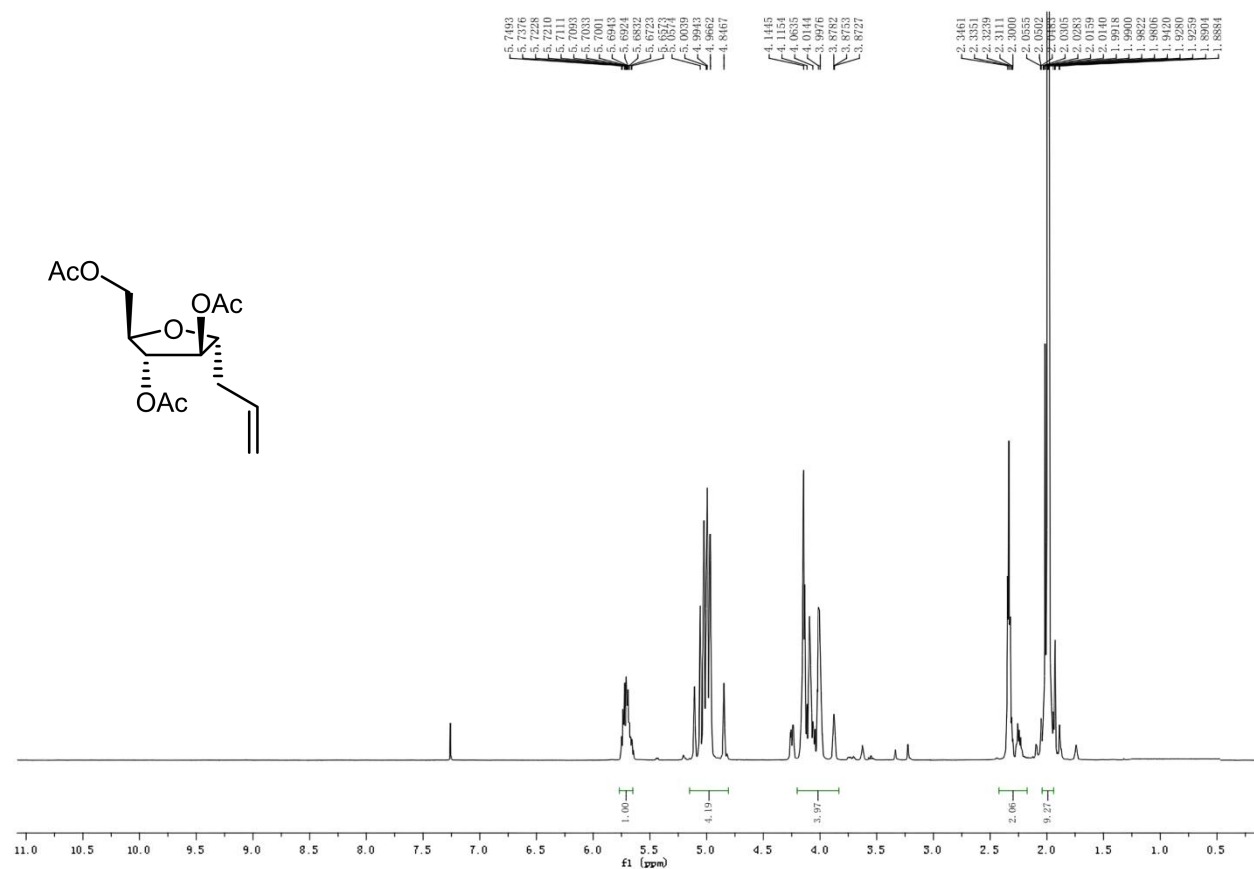


Figure S1. The ^1H NMR of compound 2.

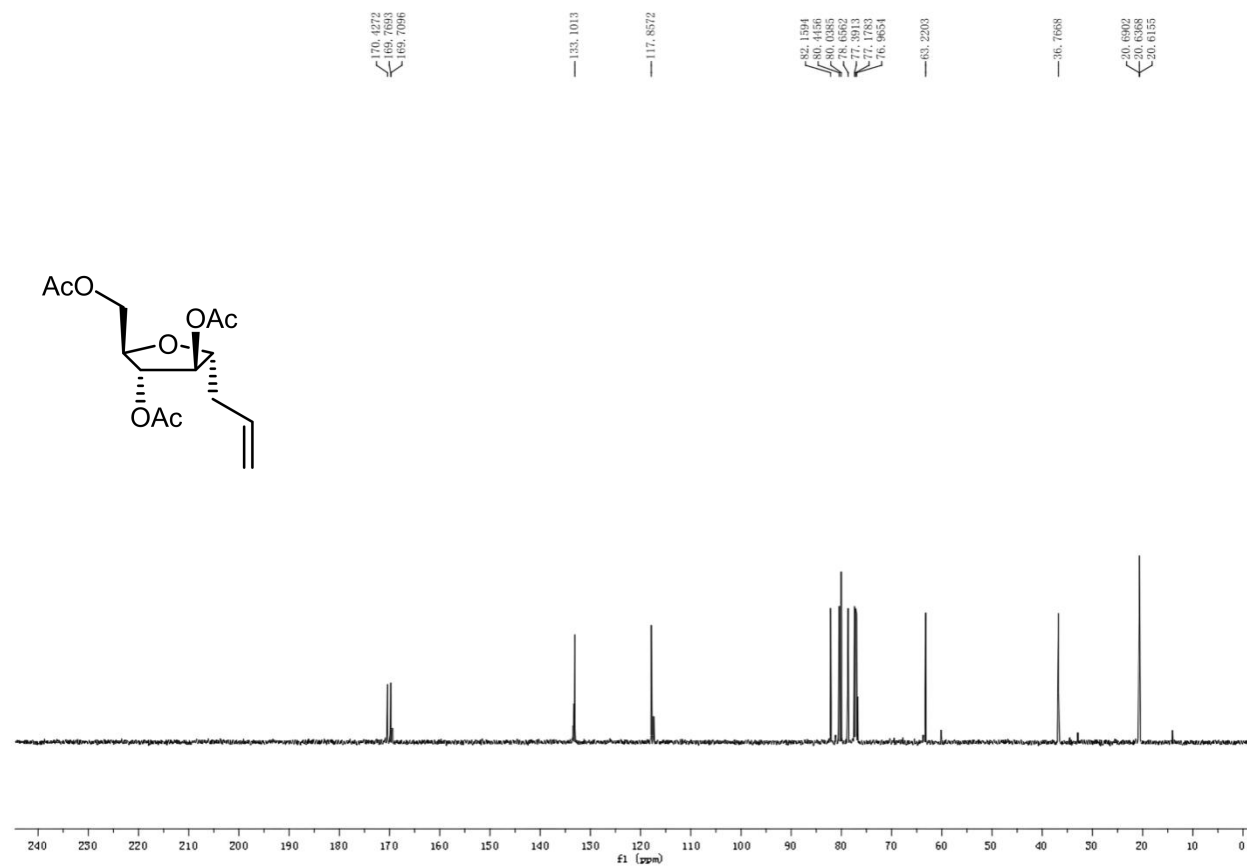


Figure S2. The ^{13}C NMR of Compound 2.

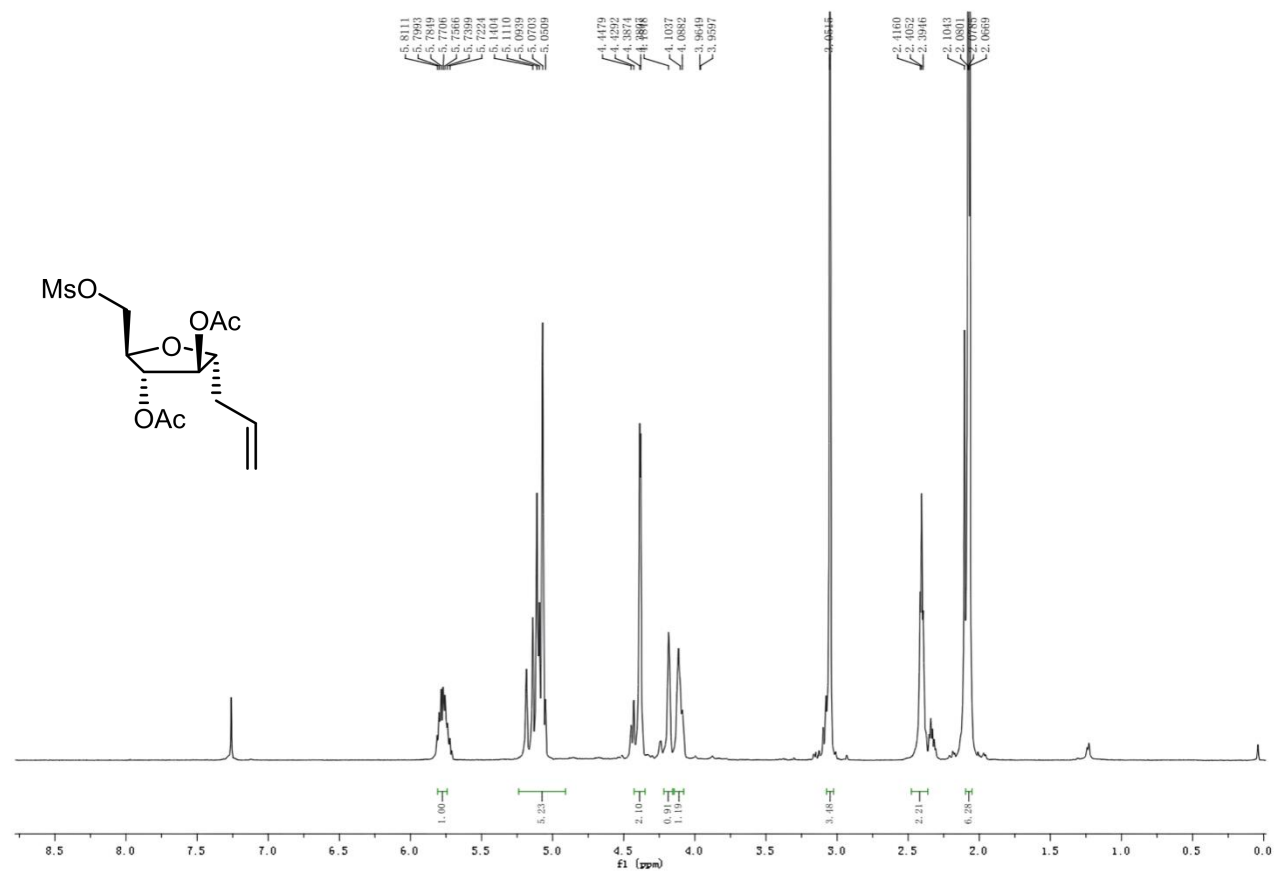


Figure S3. The ^1H NMR of compound 3.

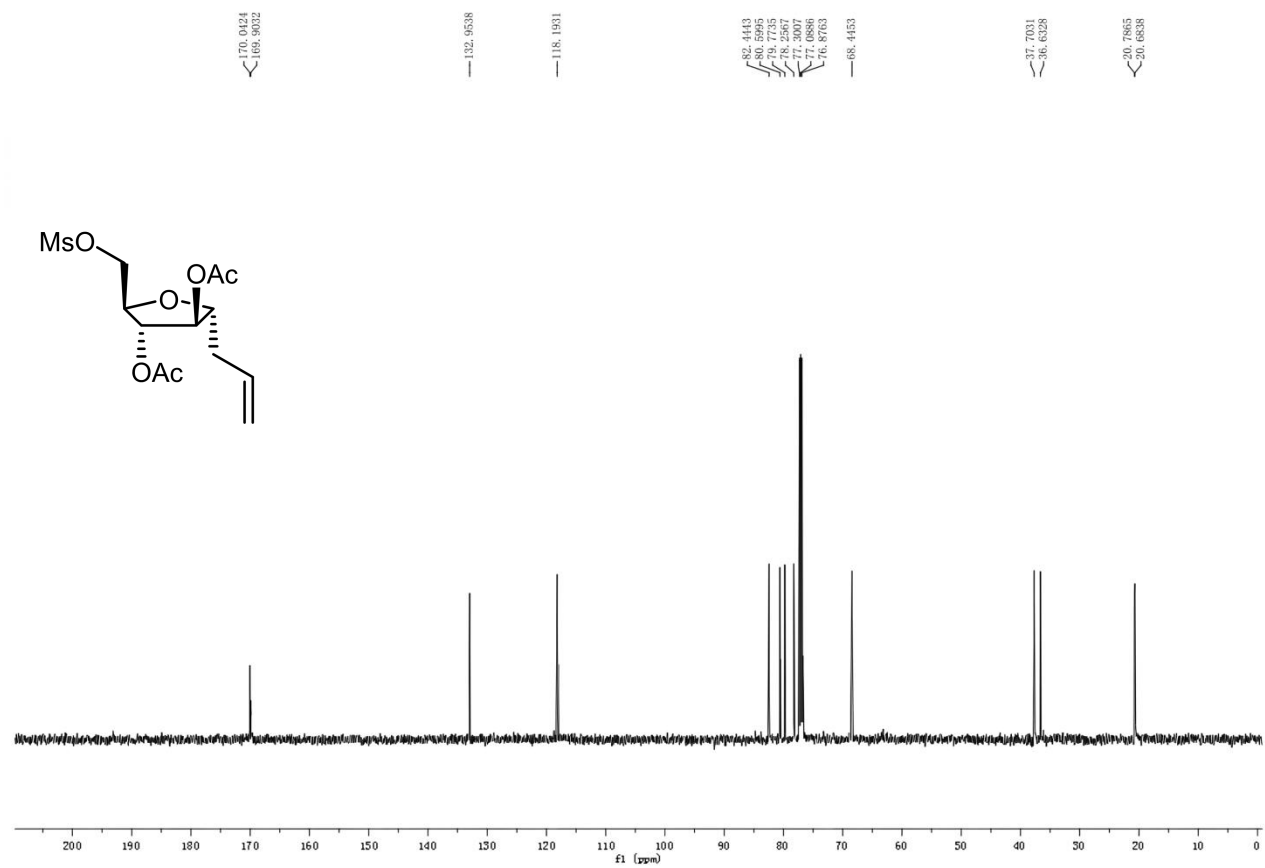


Figure S4. The ^{13}C NMR of Compound 3.

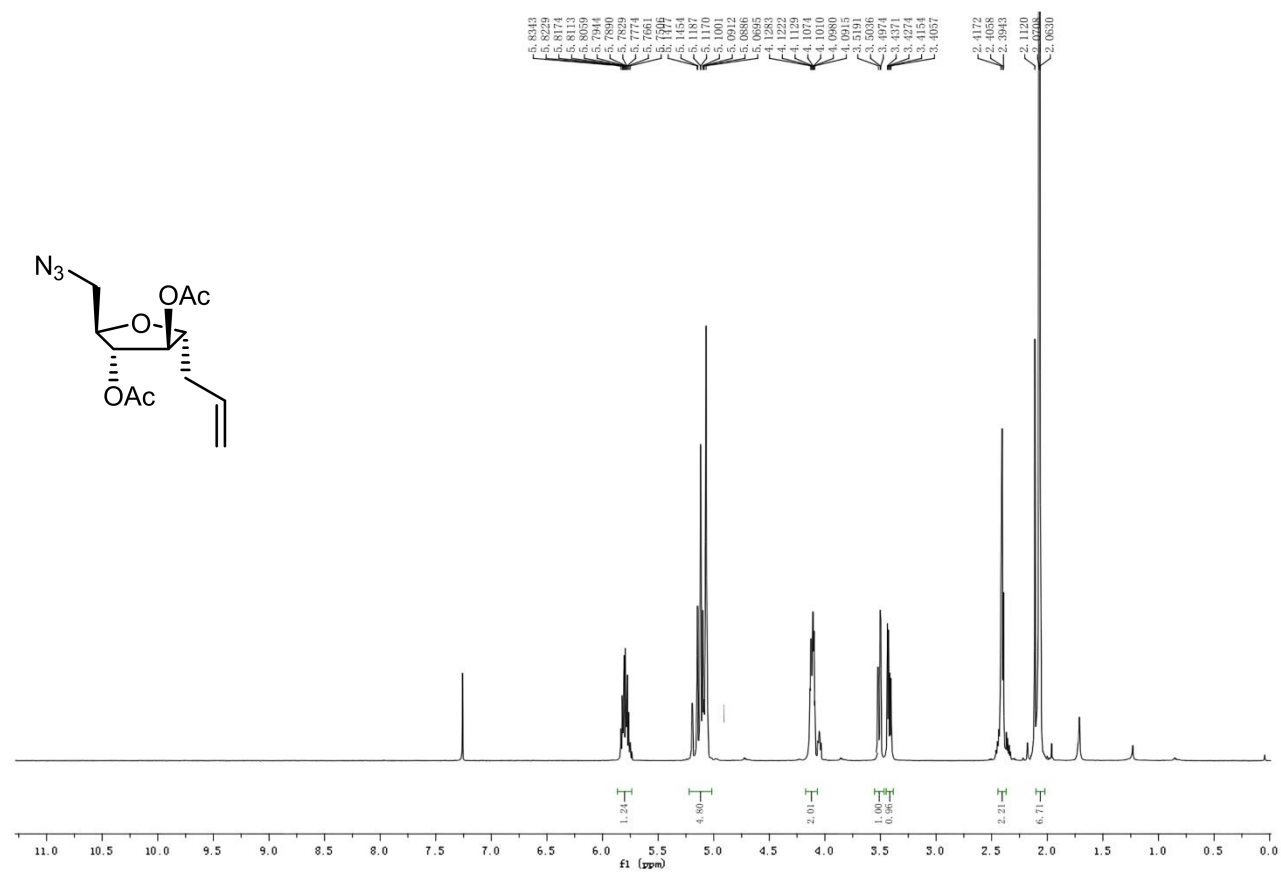


Figure S5. The ¹H NMR of compound 4.

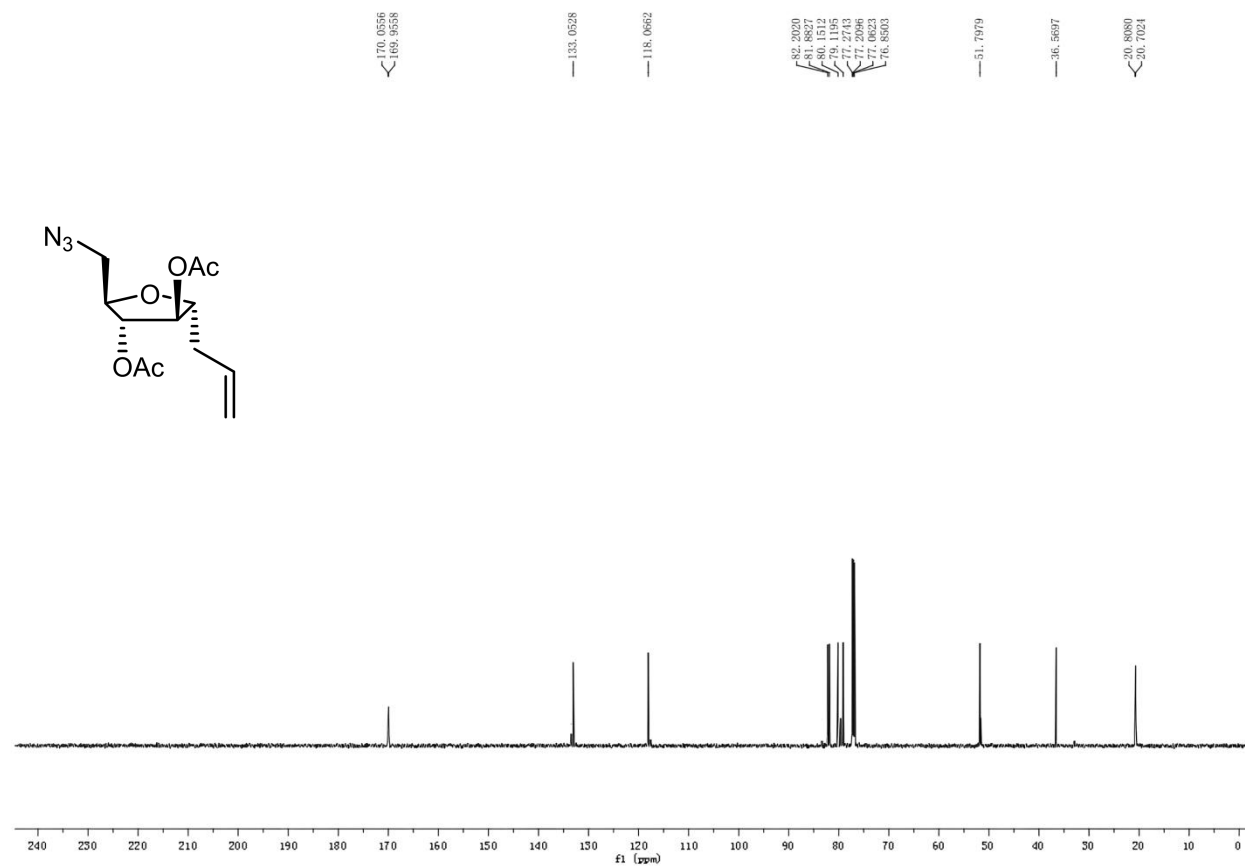


Figure S6. The ^{13}C NMR of Compound 4.

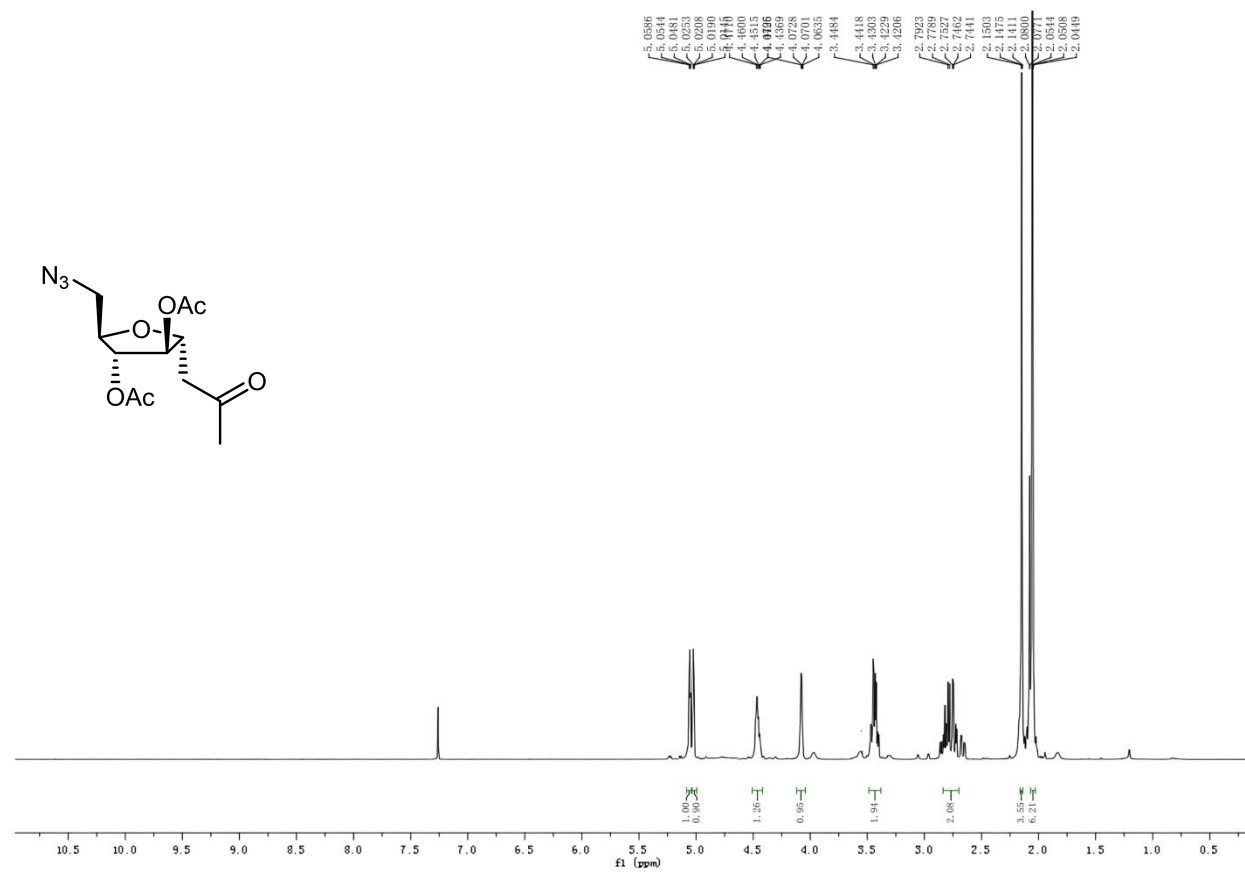


Figure S7. The ¹H NMR of compound 5.

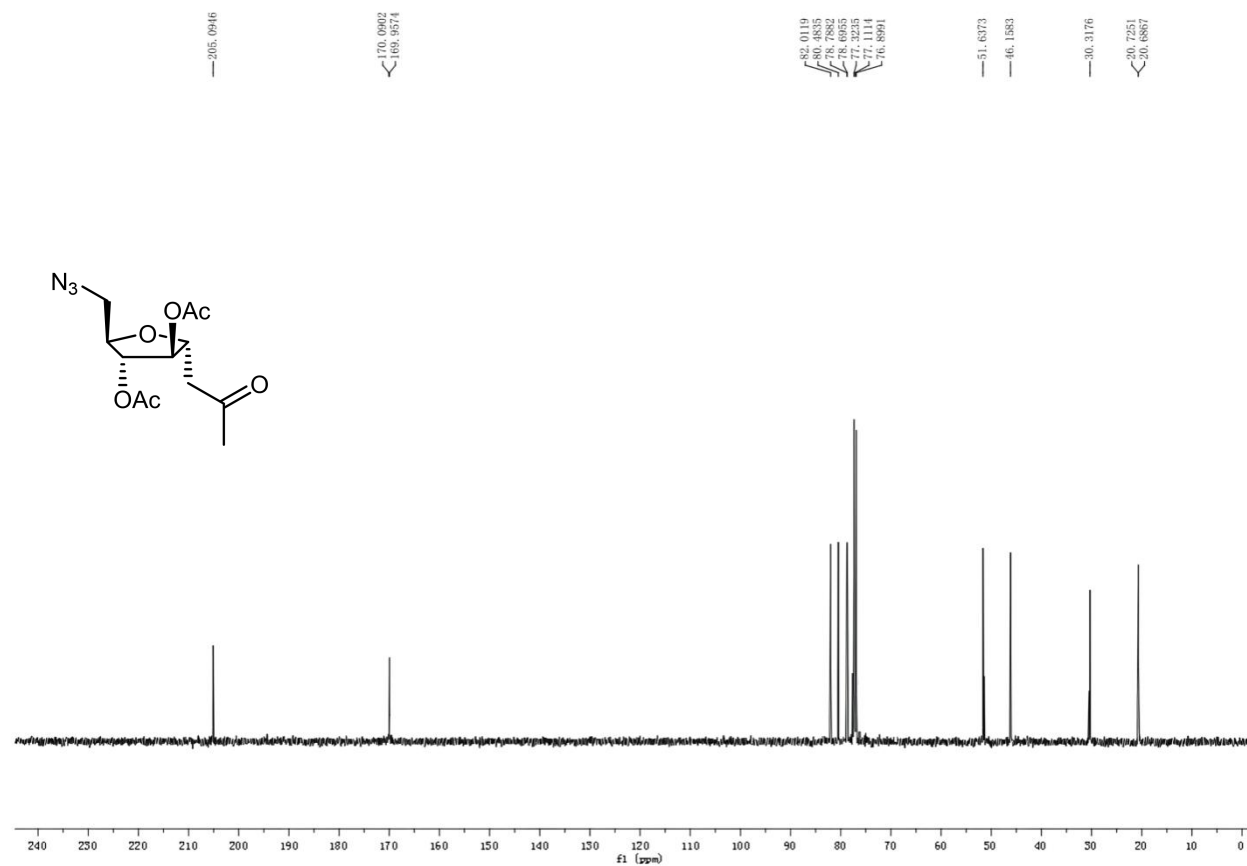


Figure S8. The ^{13}C NMR of Compound 5.

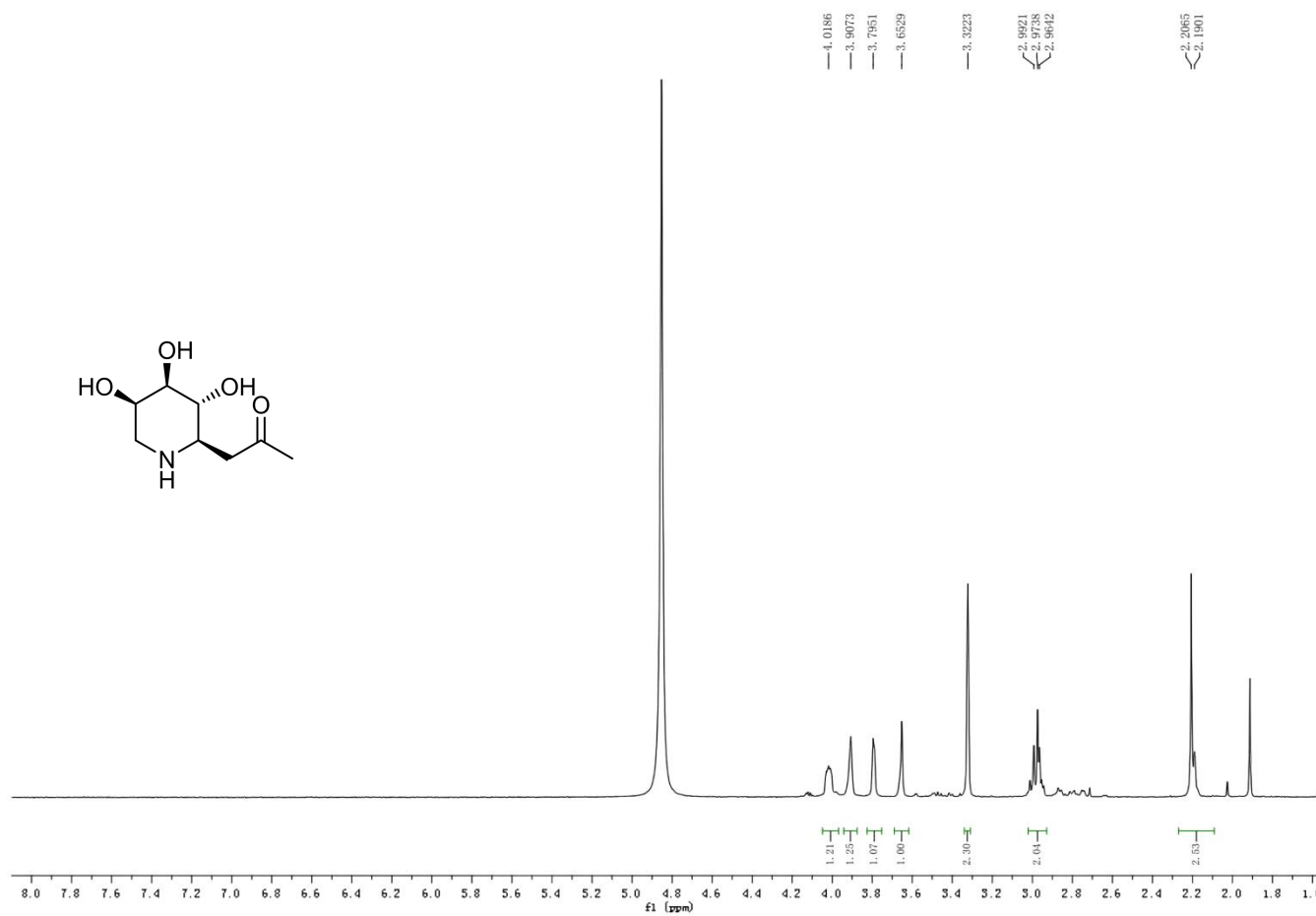


Figure S9. The ^1H NMR of compound 6.

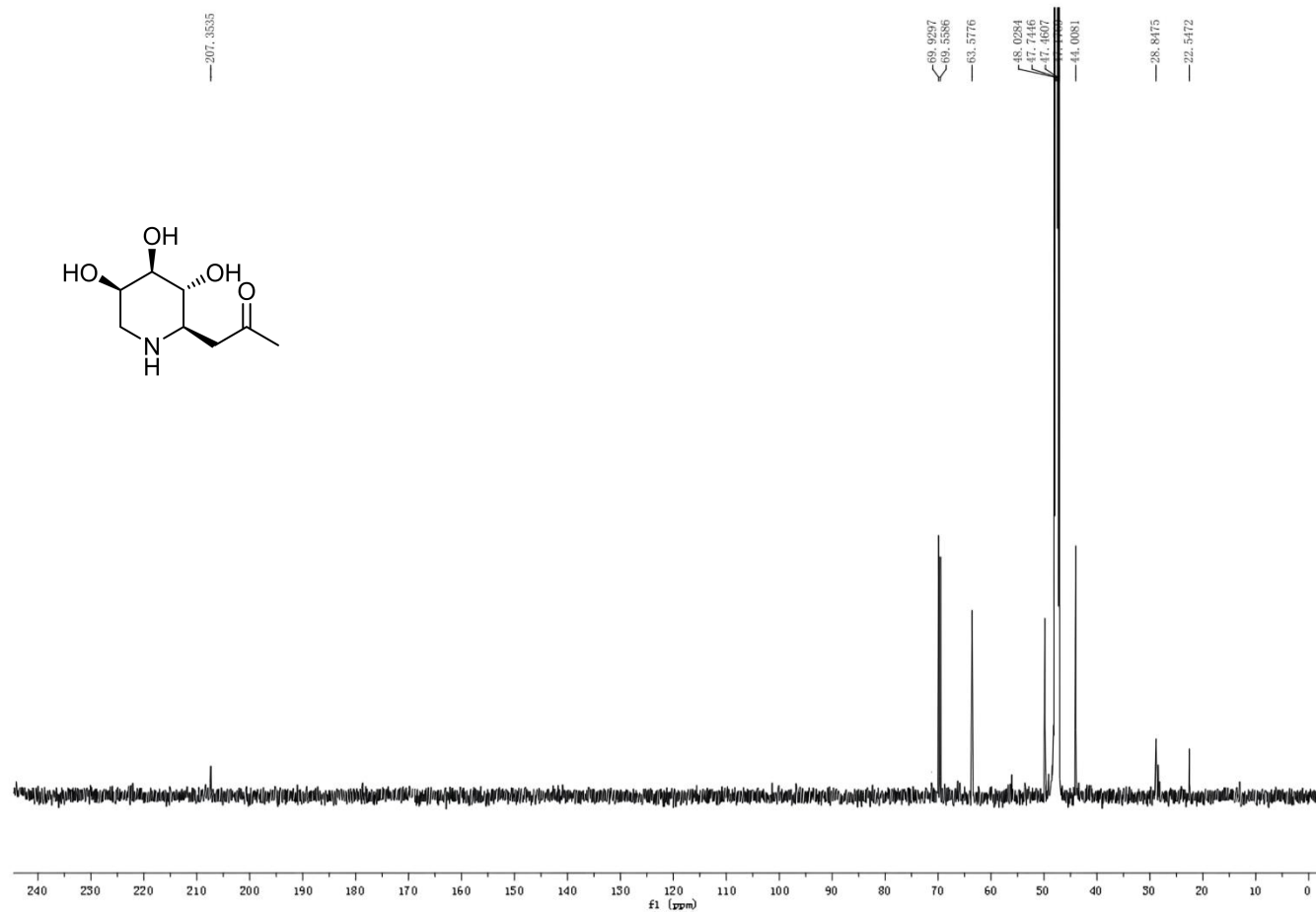


Figure S10. The ^{13}C -NMR of Compound 6.

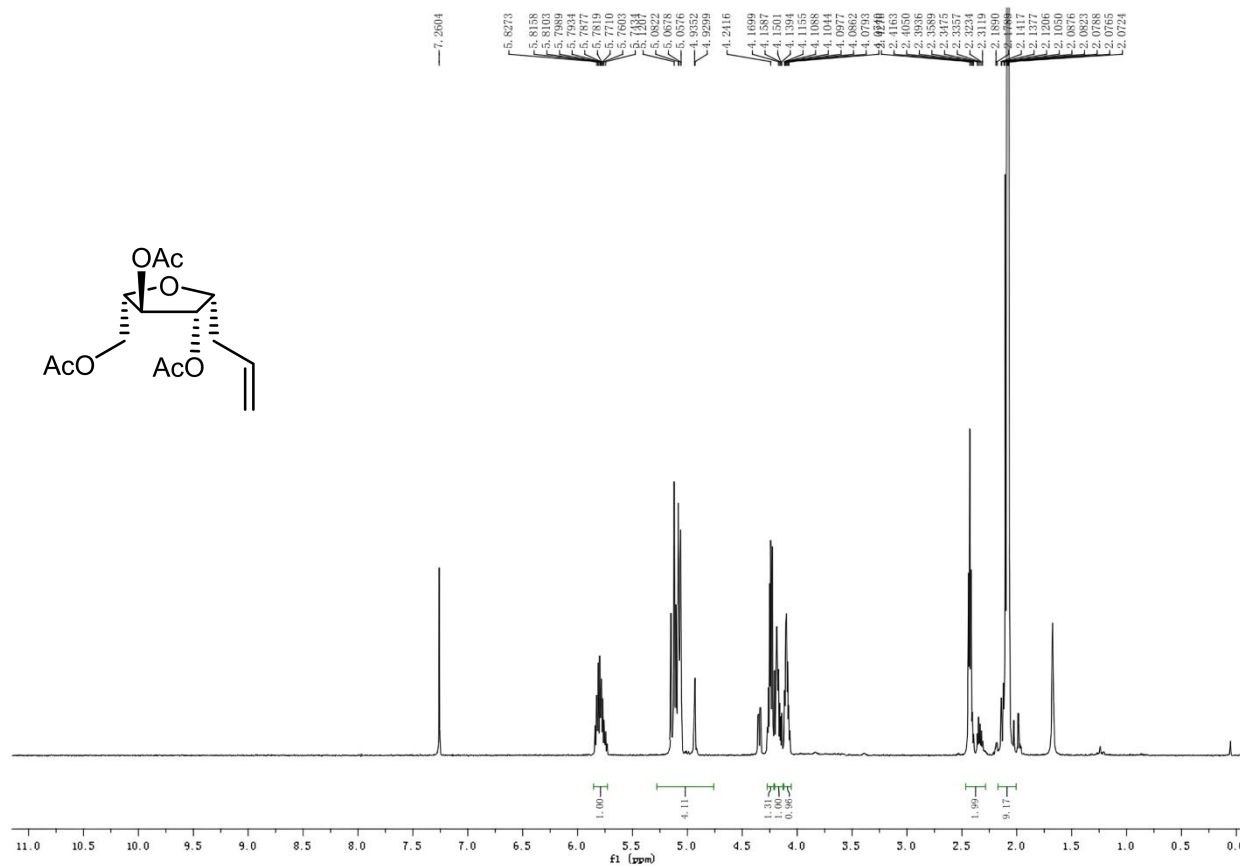


Figure S11. The ¹H NMR of compound 8.

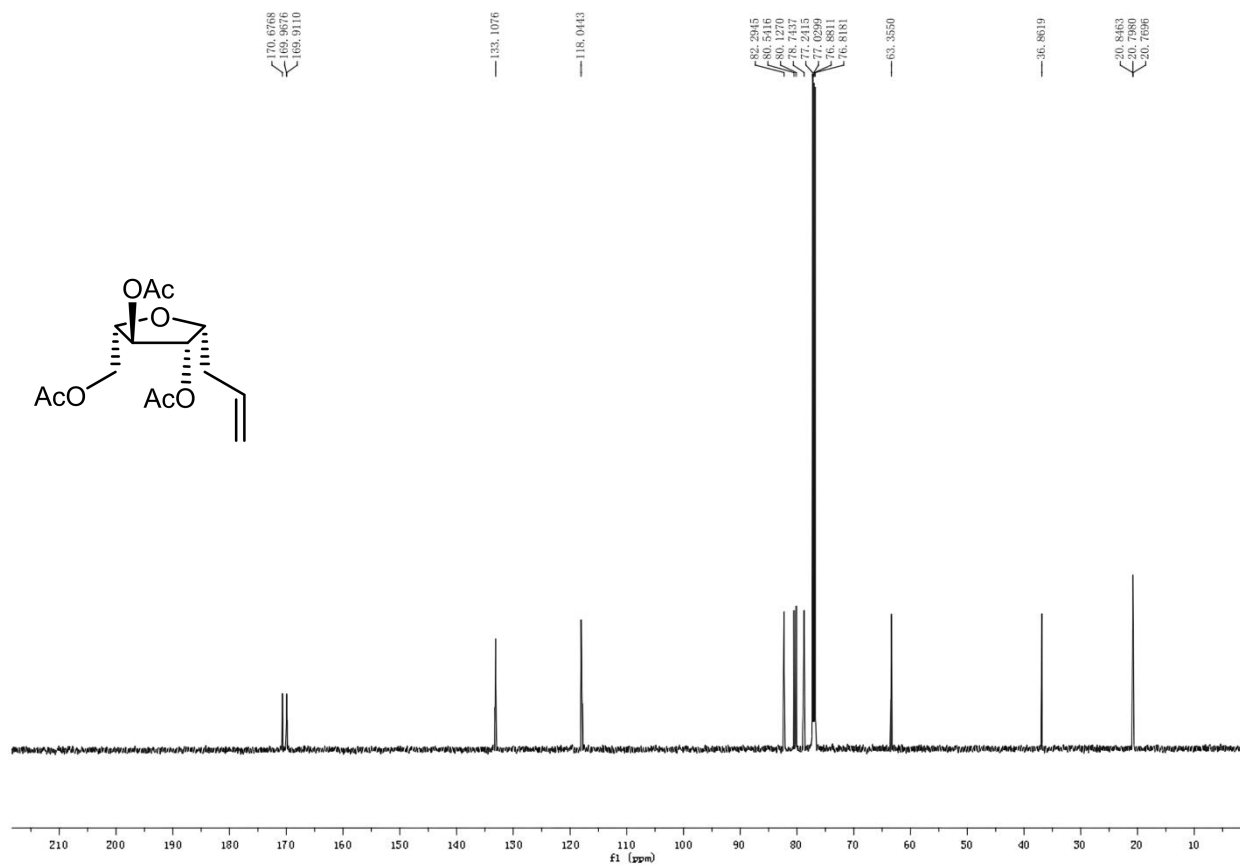


Figure S12. The ^{13}C NMR of Compound 8.

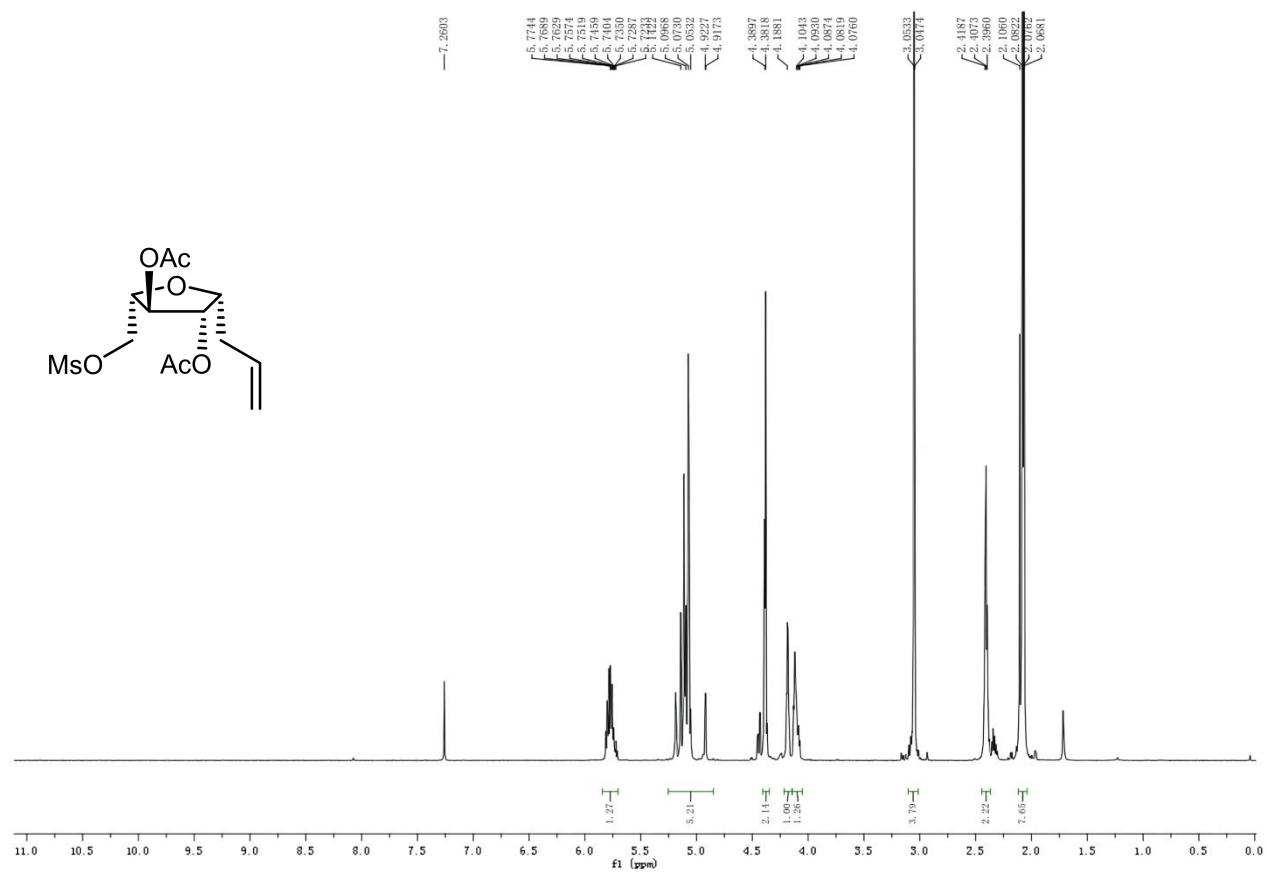


Figure S13. The ^1H NMR of compound 9.

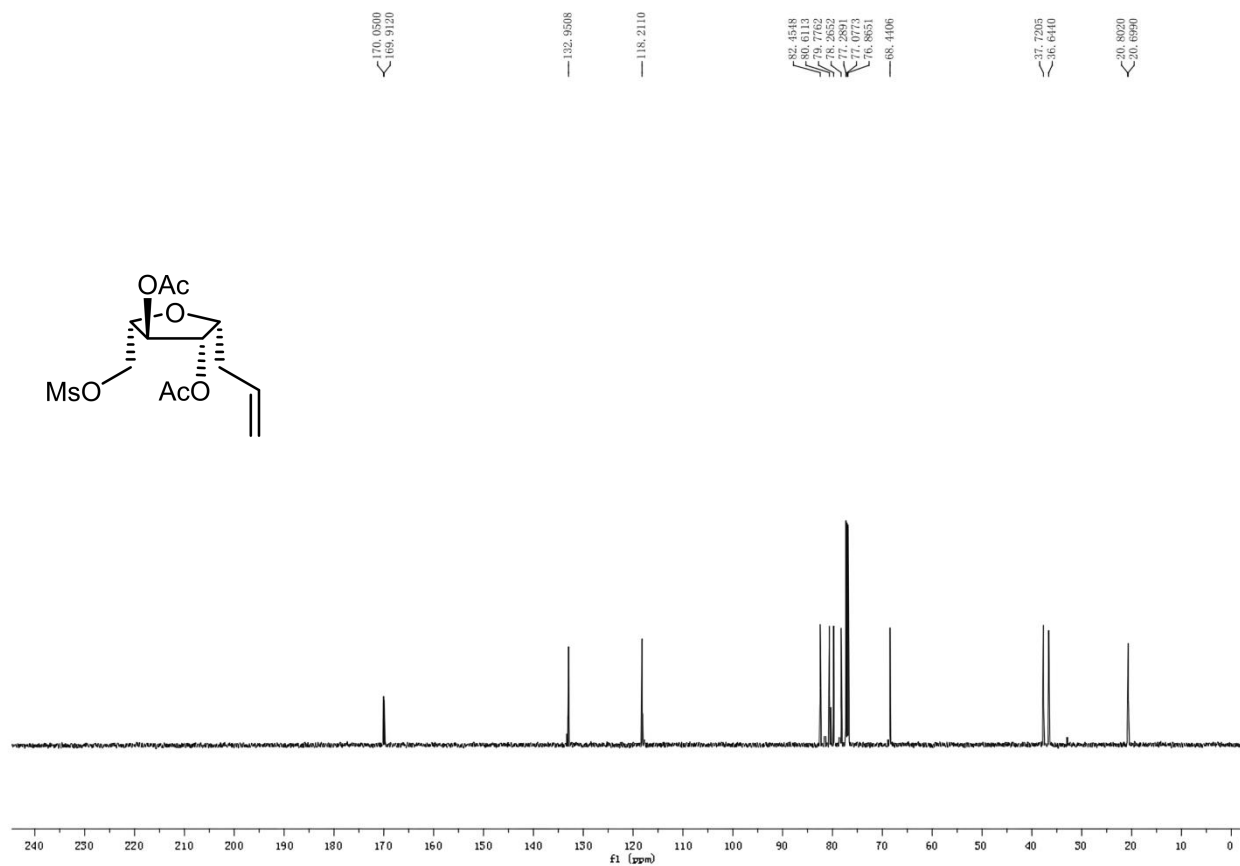


Figure S14. The ^{13}C NMR of Compound 9.

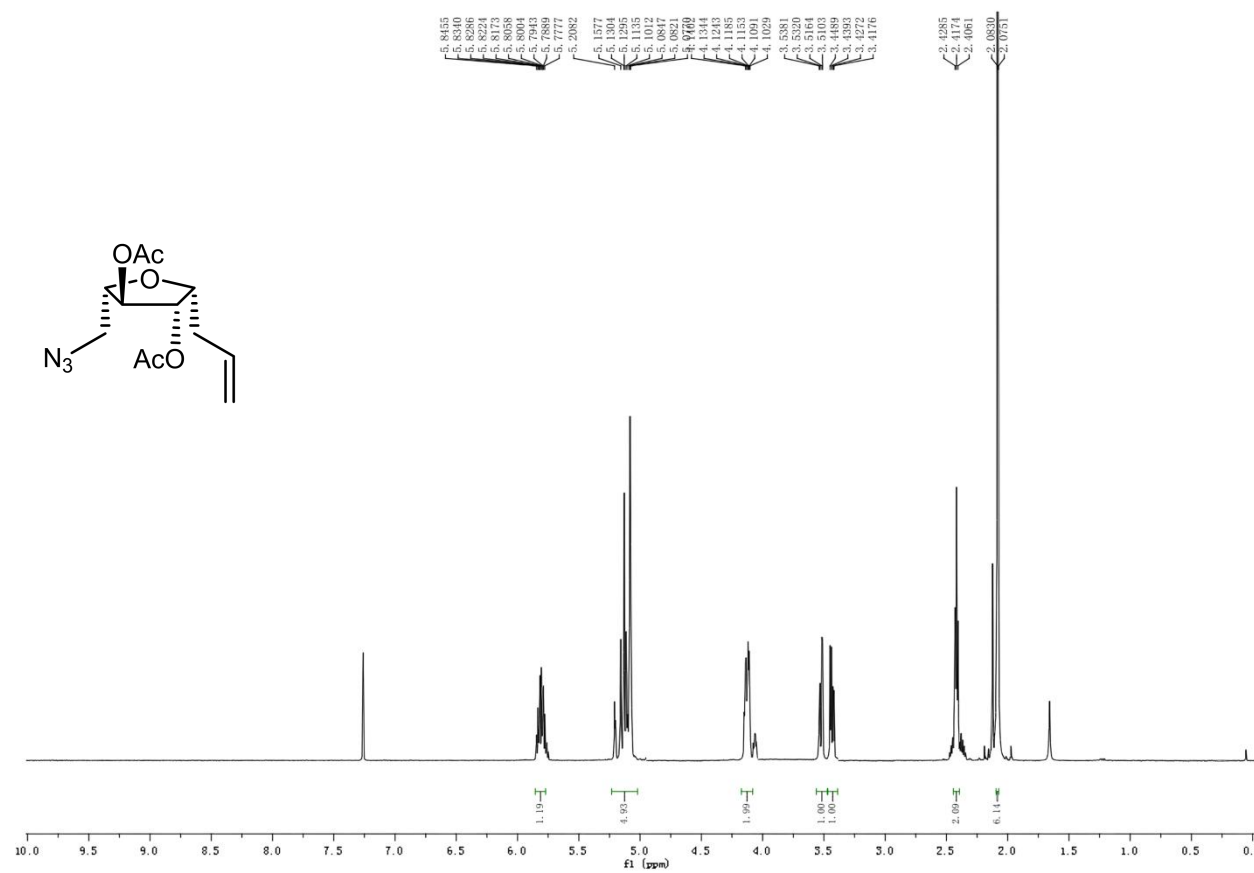


Figure S15. The ¹H NMR of compound 10.

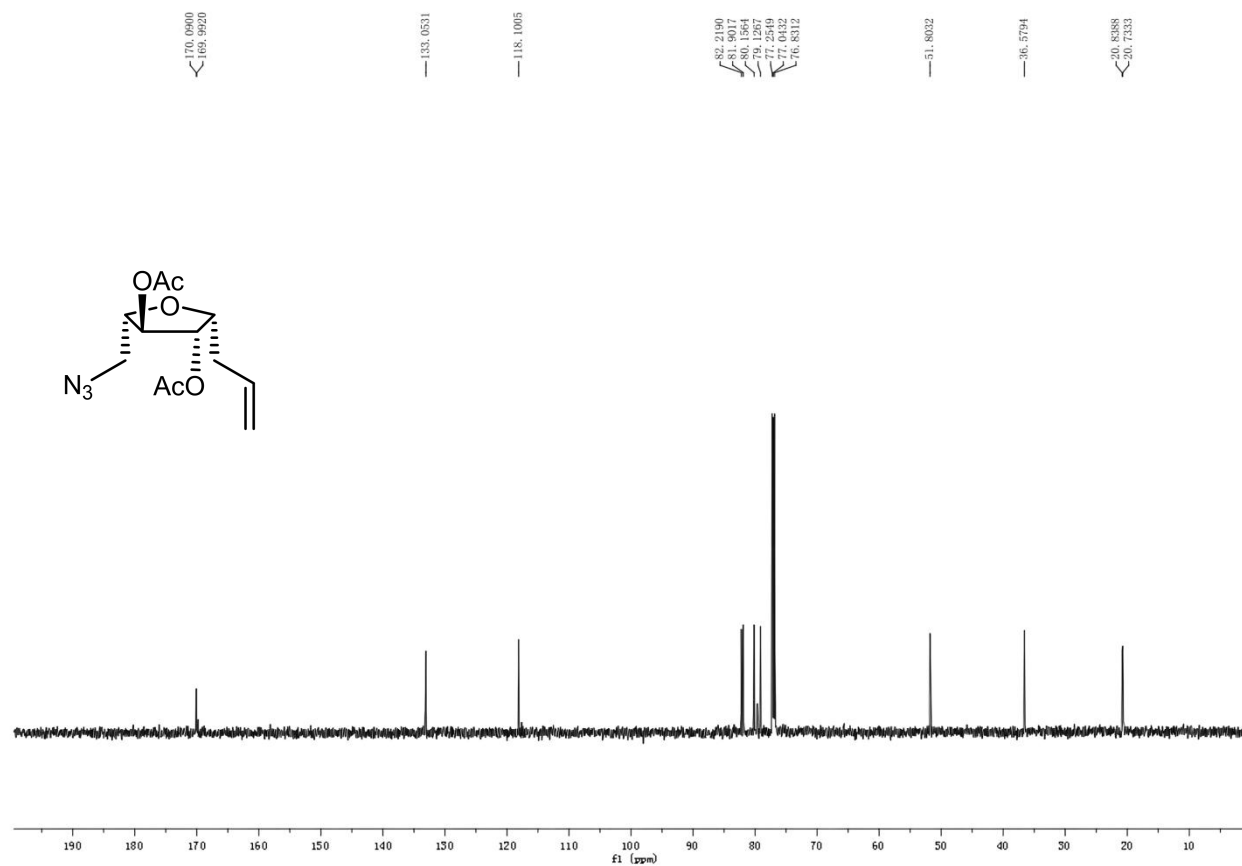


Figure S16. The ¹³C NMR of Compound 10.

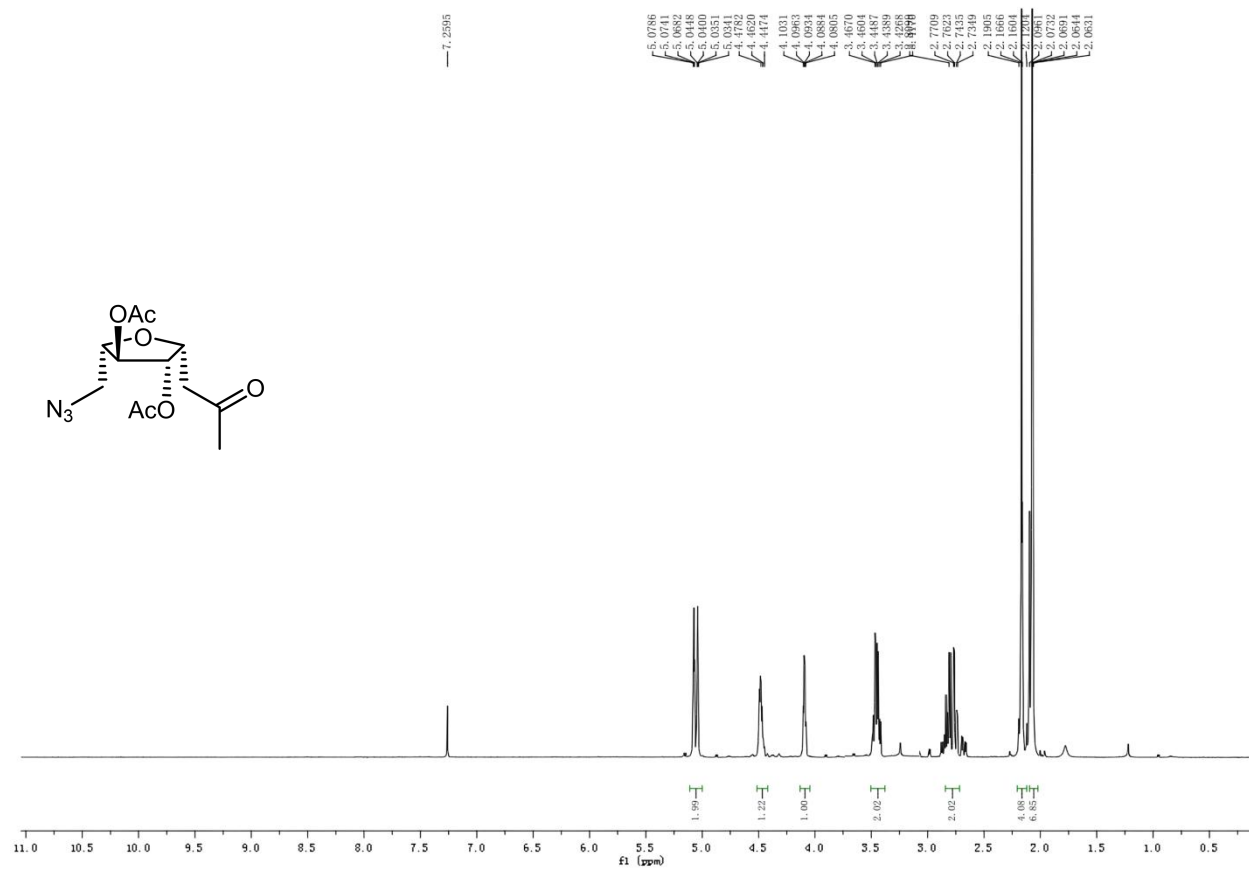


Figure S17. The ¹H NMR of compound 11.

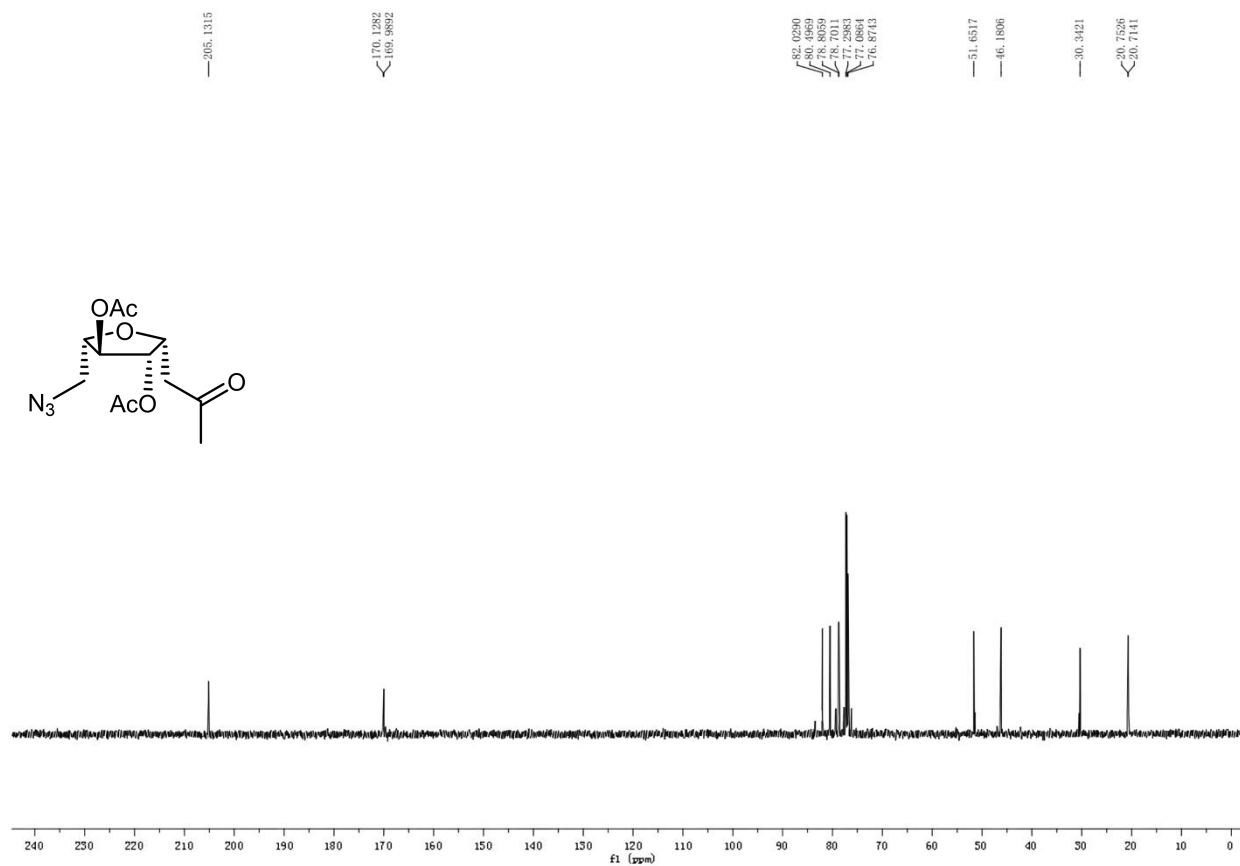


Figure S18. The ^{13}C NMR of Compound 11.

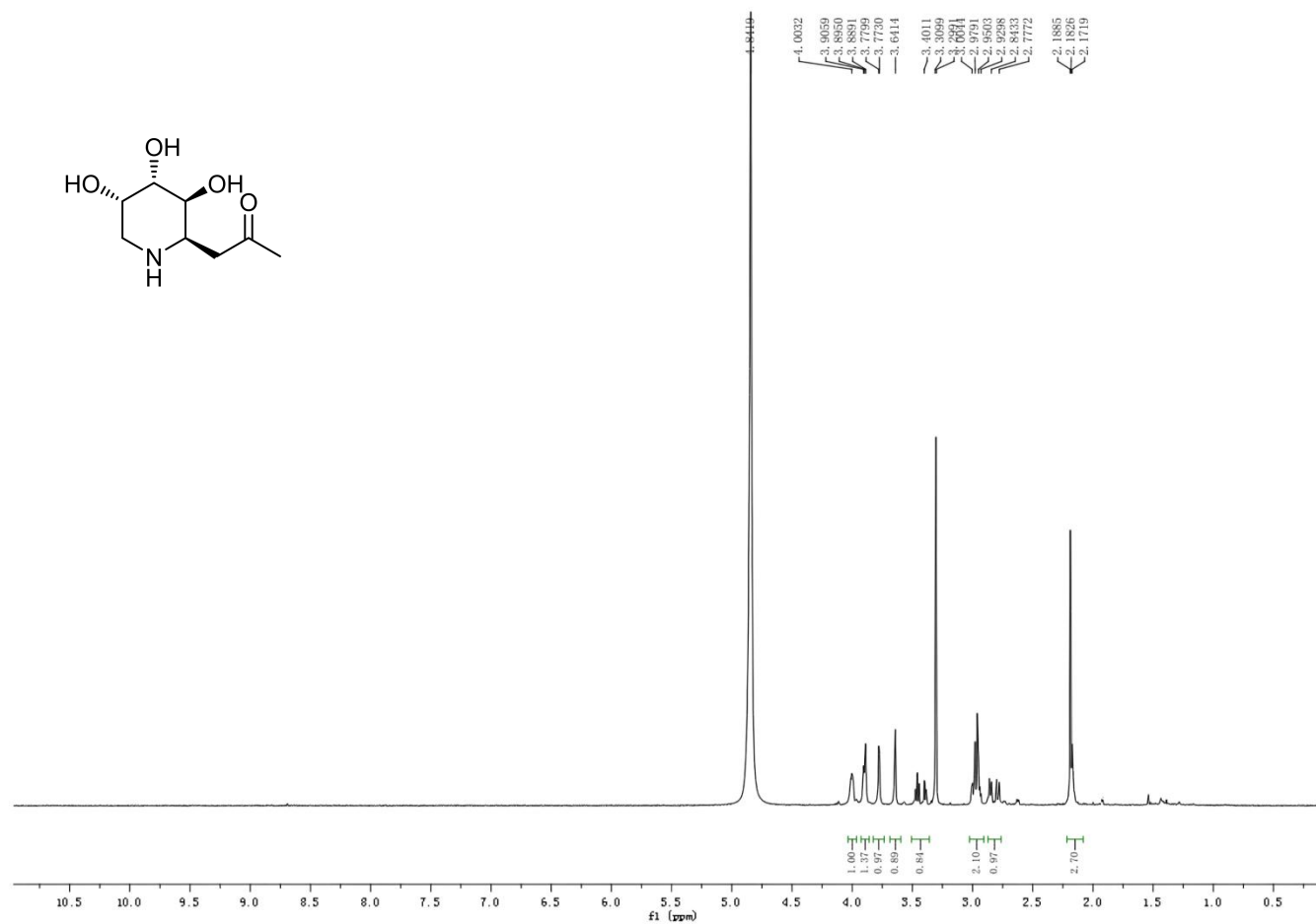


Figure S19. The ^1H NMR of compound 12.

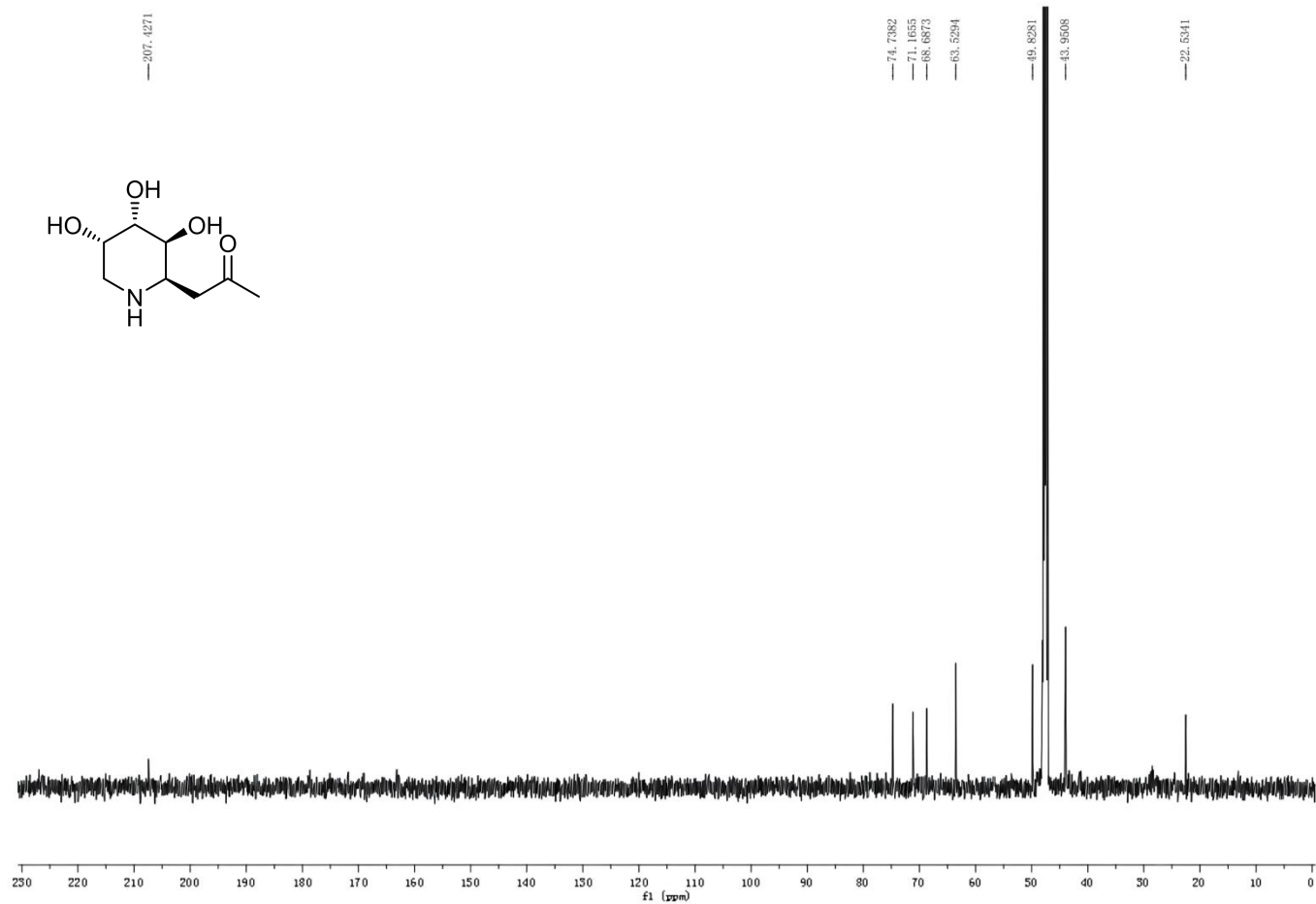


Figure S20. The ^{13}C -NMR of Compound 12.

2. ^1H NMR and ^{13}C NMR spectra of dihydrofuro[3,2-b]piperidine.

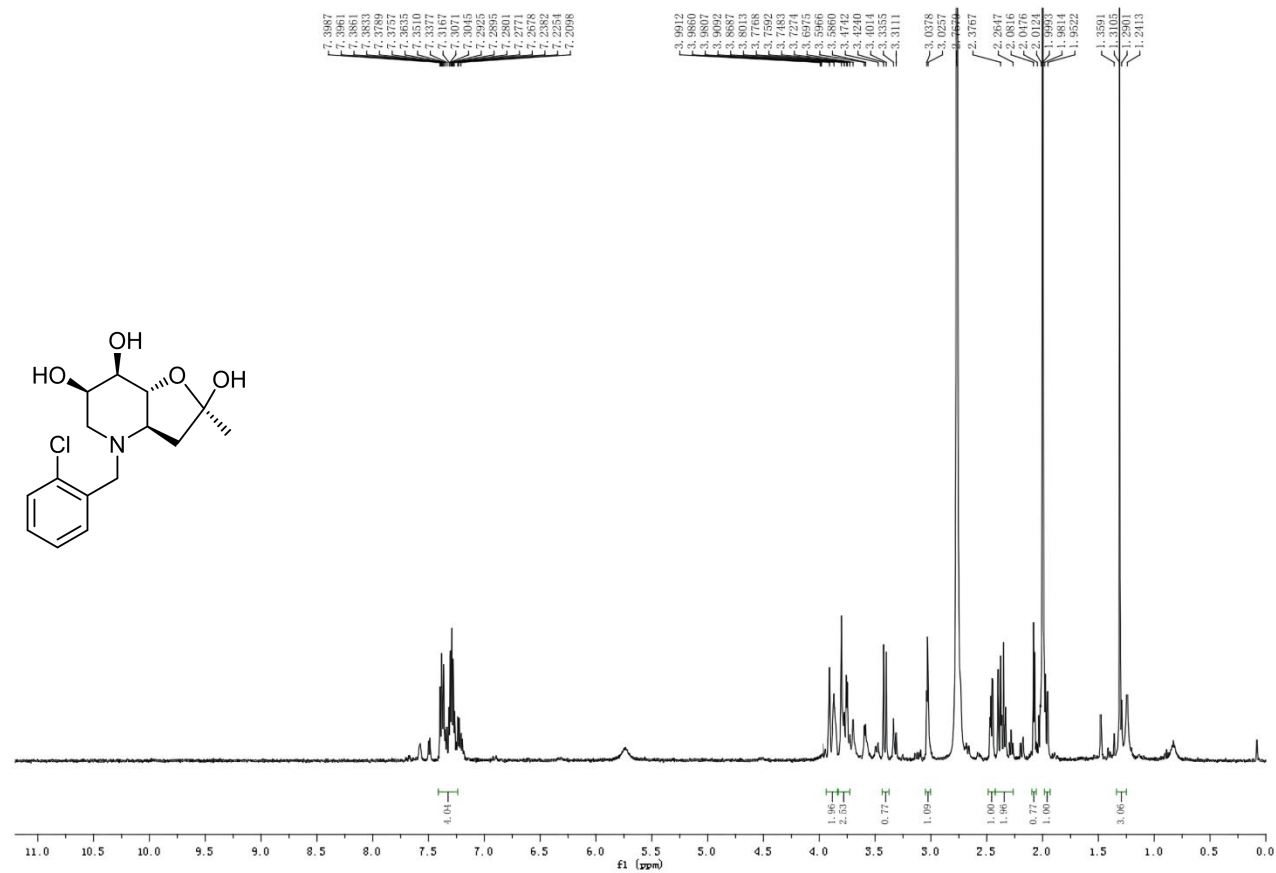


Figure S21. The ^1H NMR of compound 13.

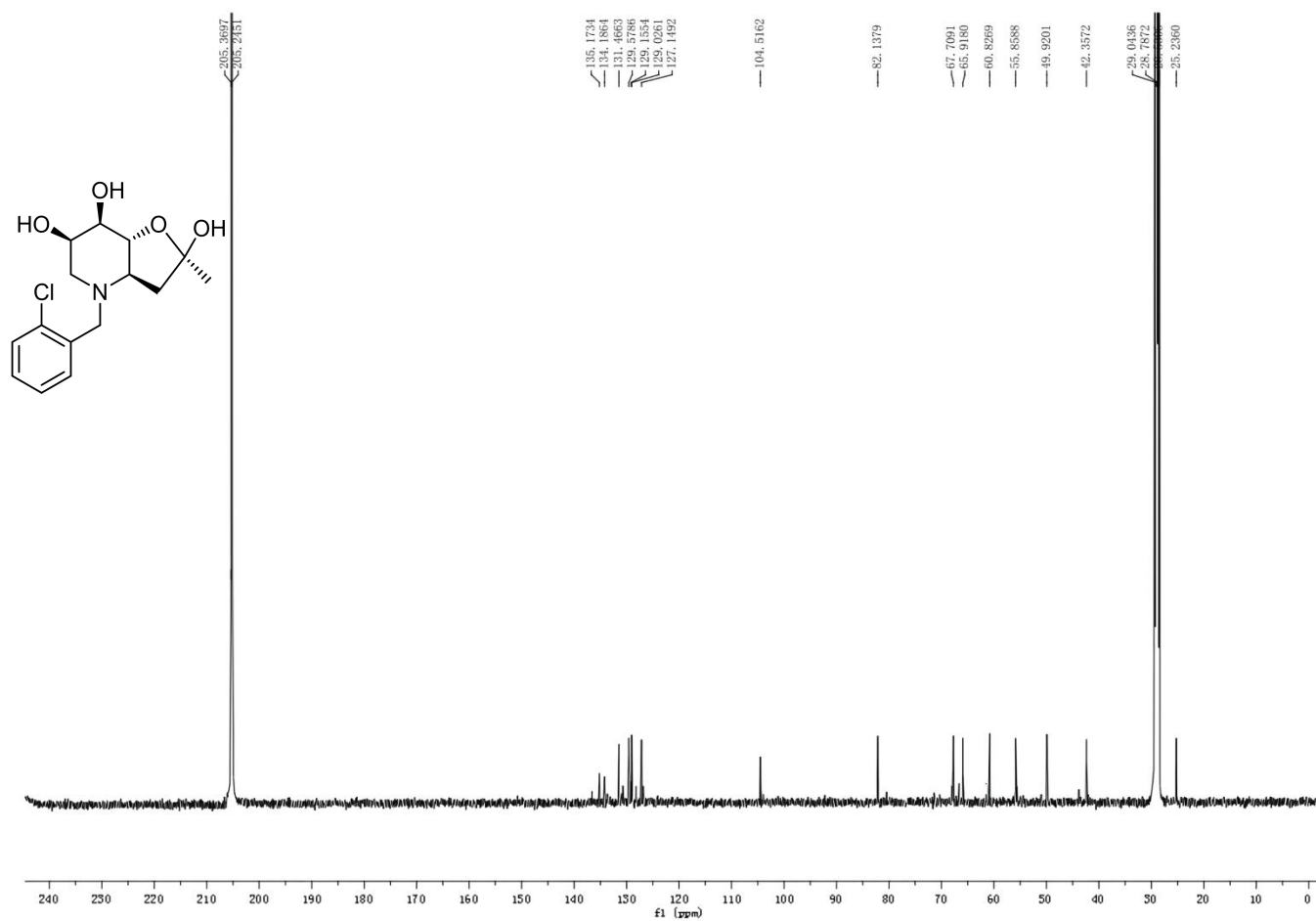


Figure S22. The ^{13}C -NMR of Compound 13.



Figure S23. The ¹H NMR of compound 14.

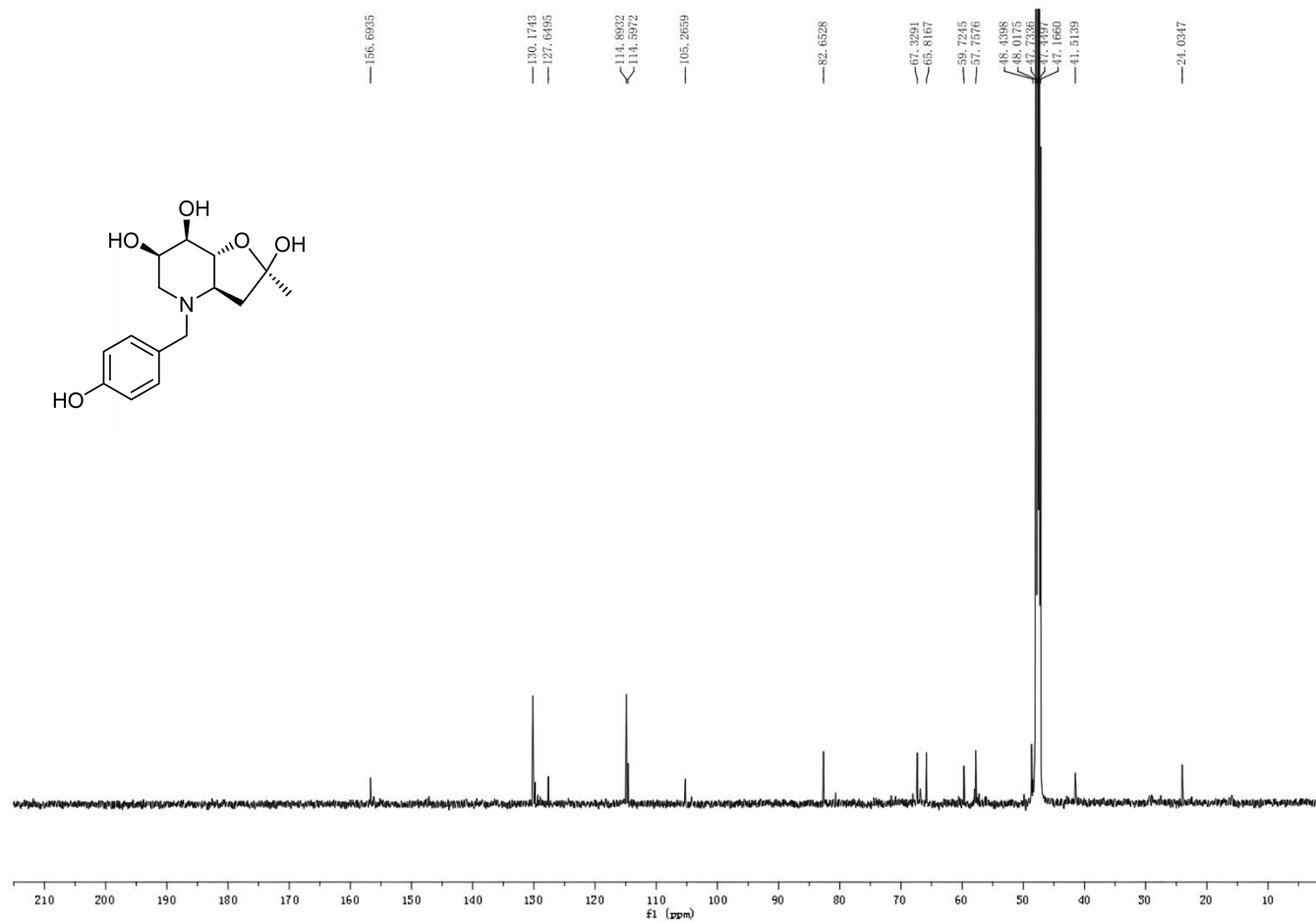


Figure S24. The ^{13}C -NMR of Compound 14.

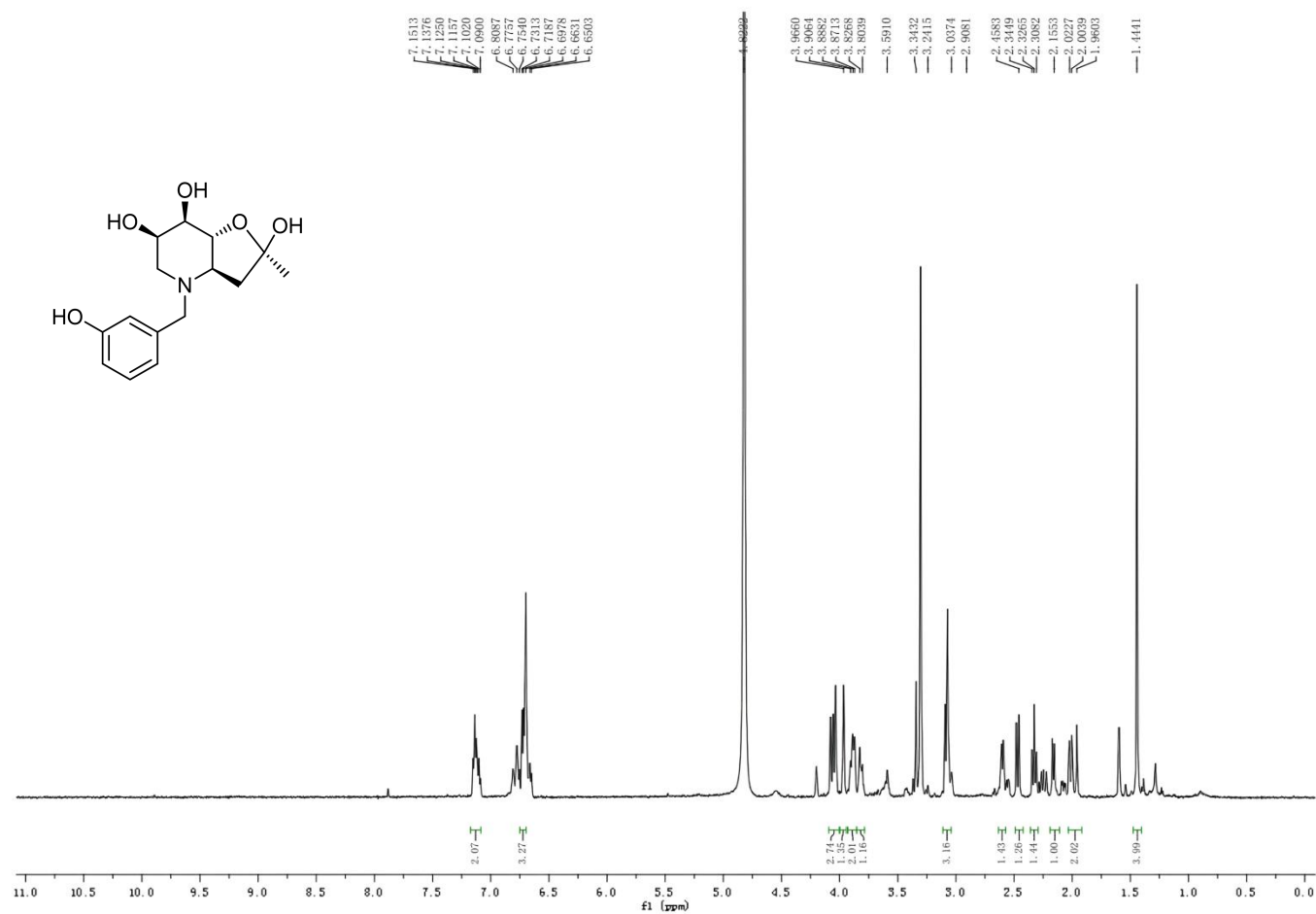


Figure S25. The ¹H NMR of compound 16.

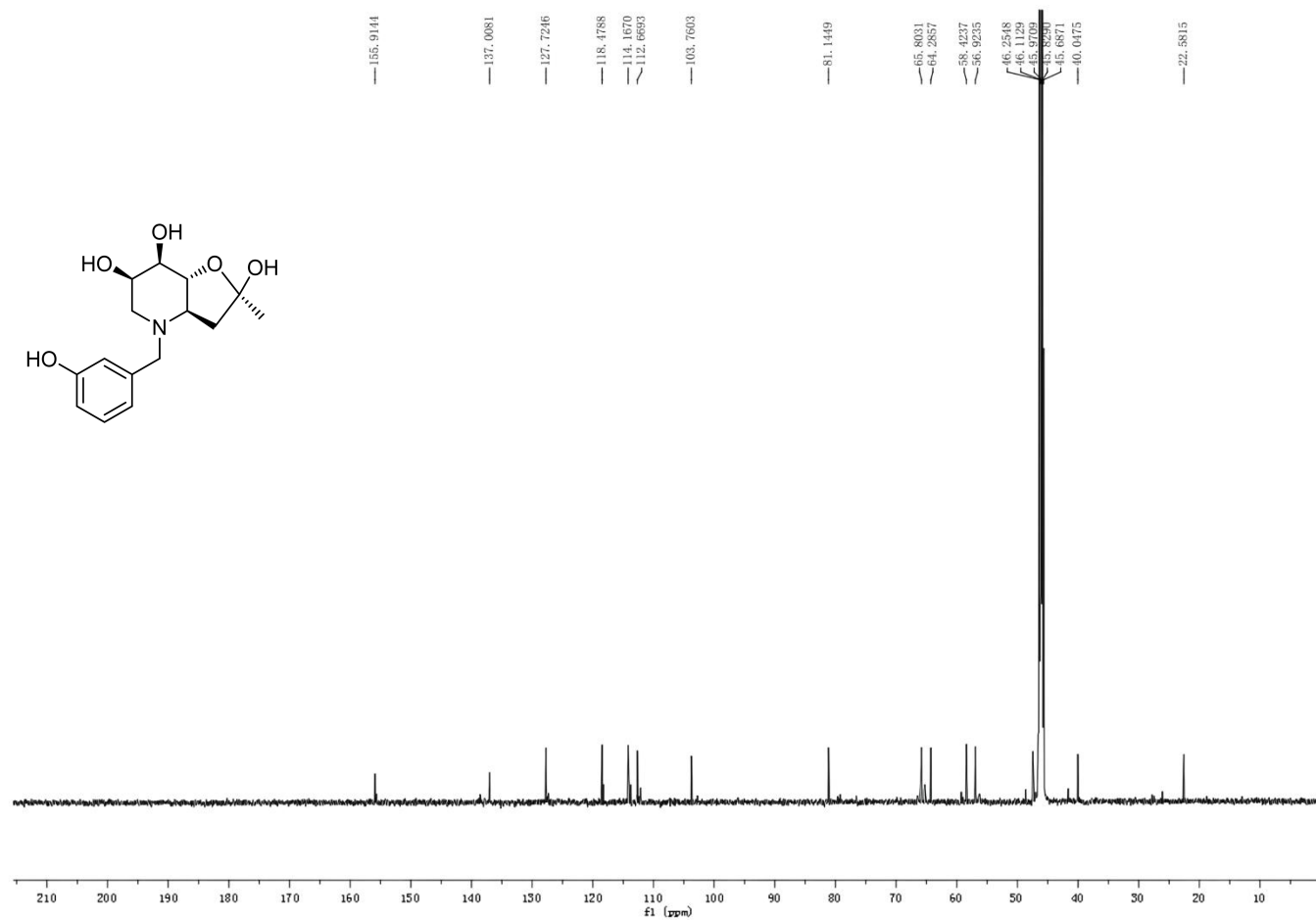


Figure S26. The ^{13}C -NMR of Compound 16.

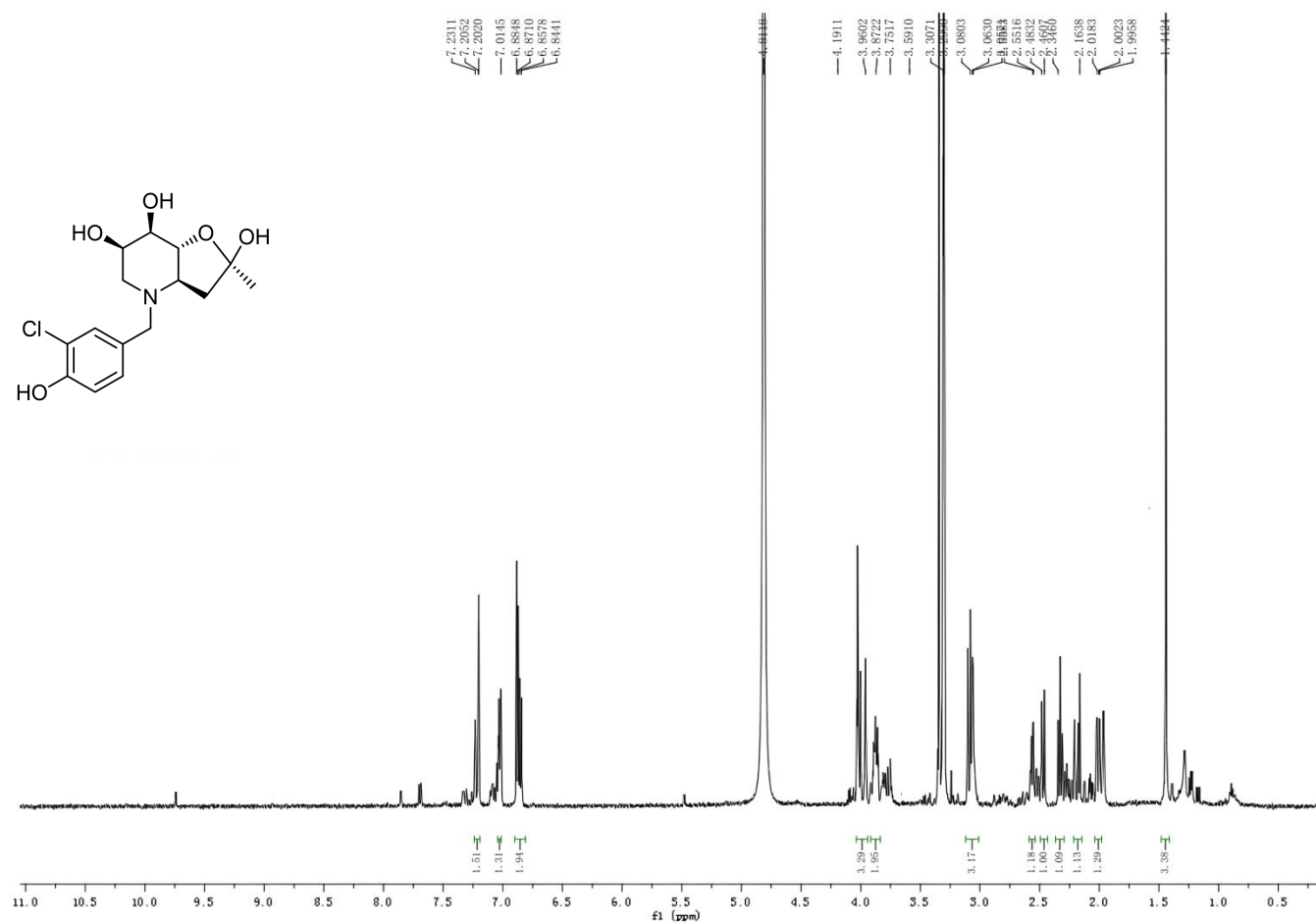


Figure S27. The ¹H NMR of compound 17.

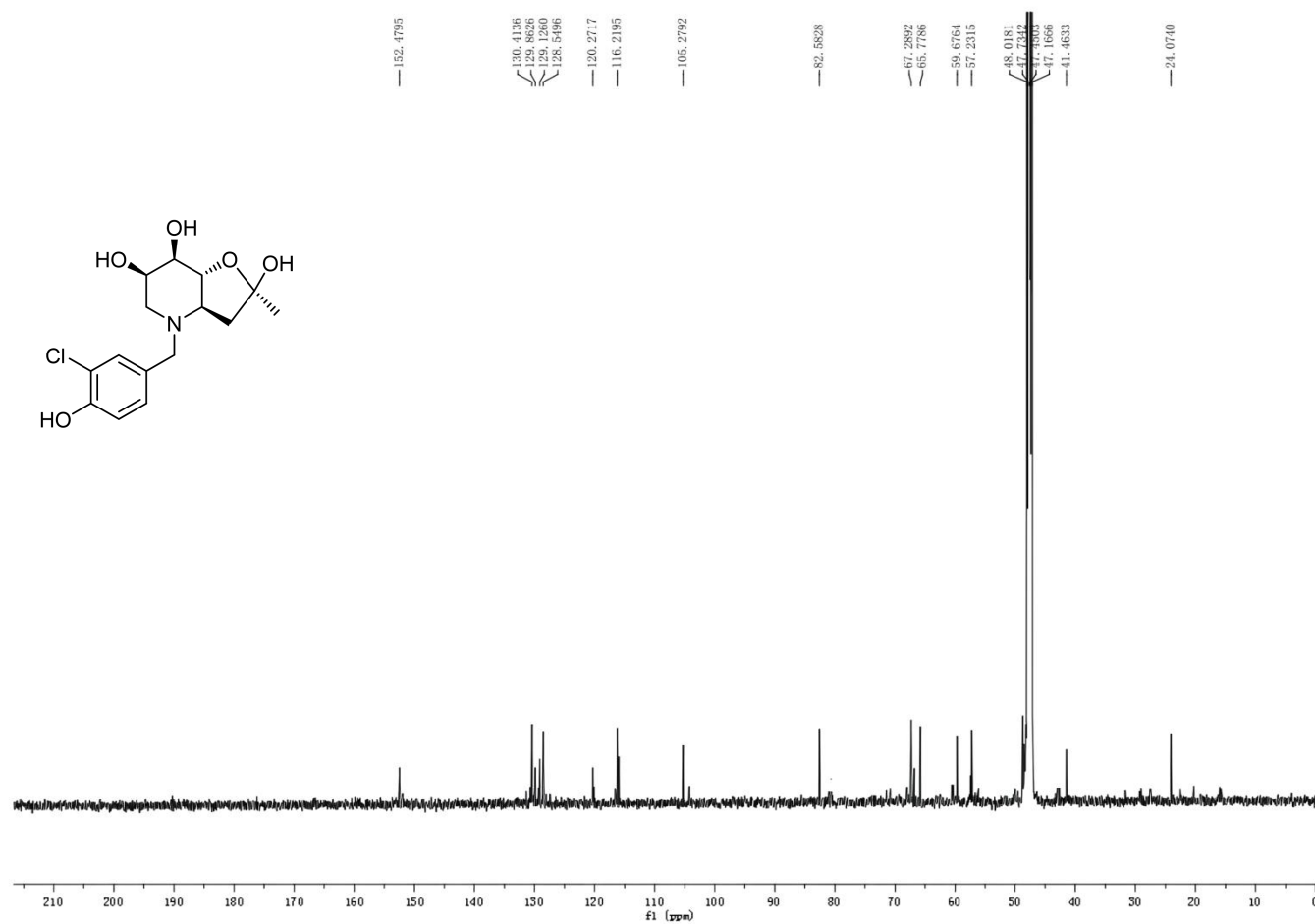


Figure S28. The ^{13}C -NMR of Compound 17.

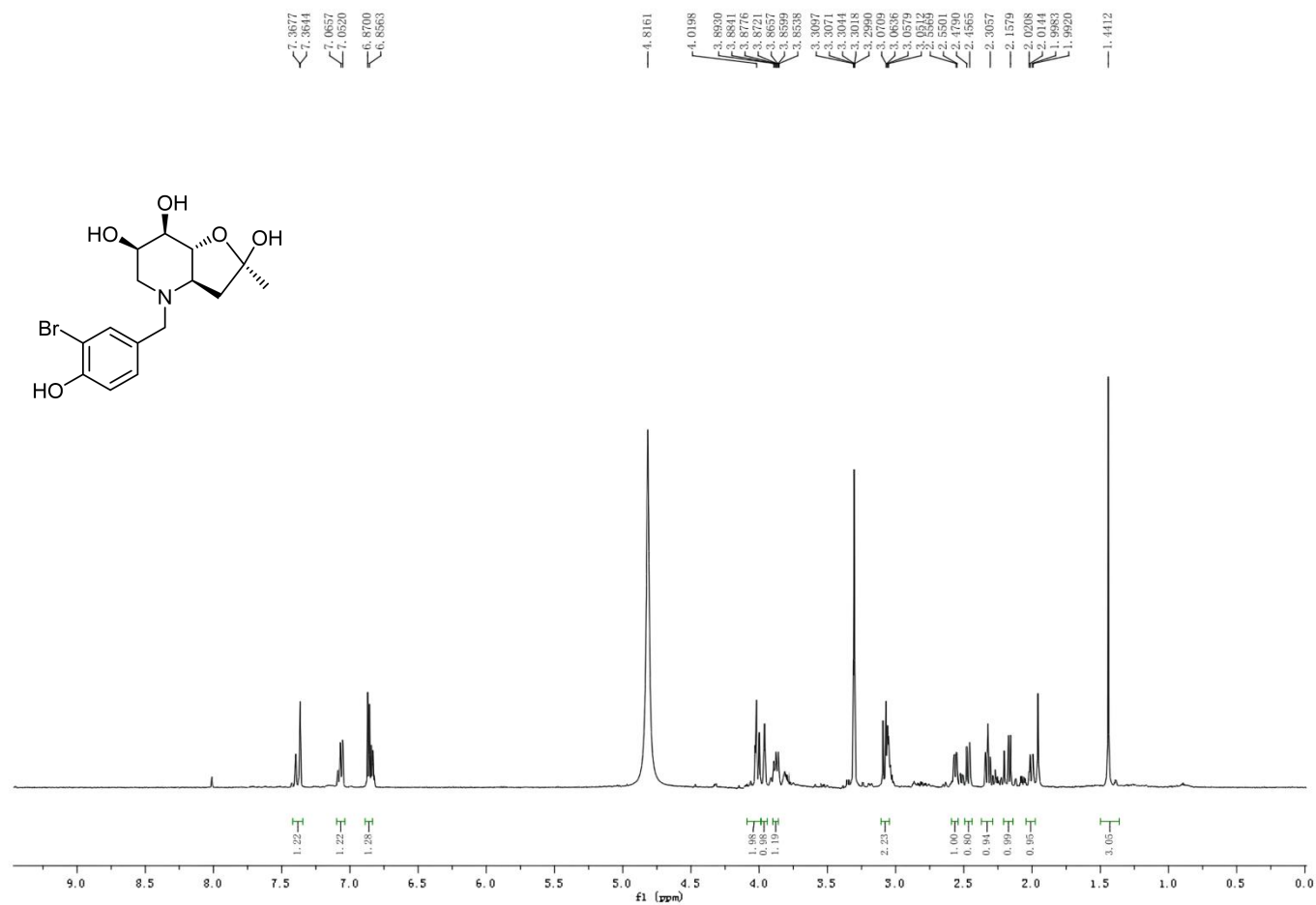


Figure S29. The ¹H NMR of compound 18.

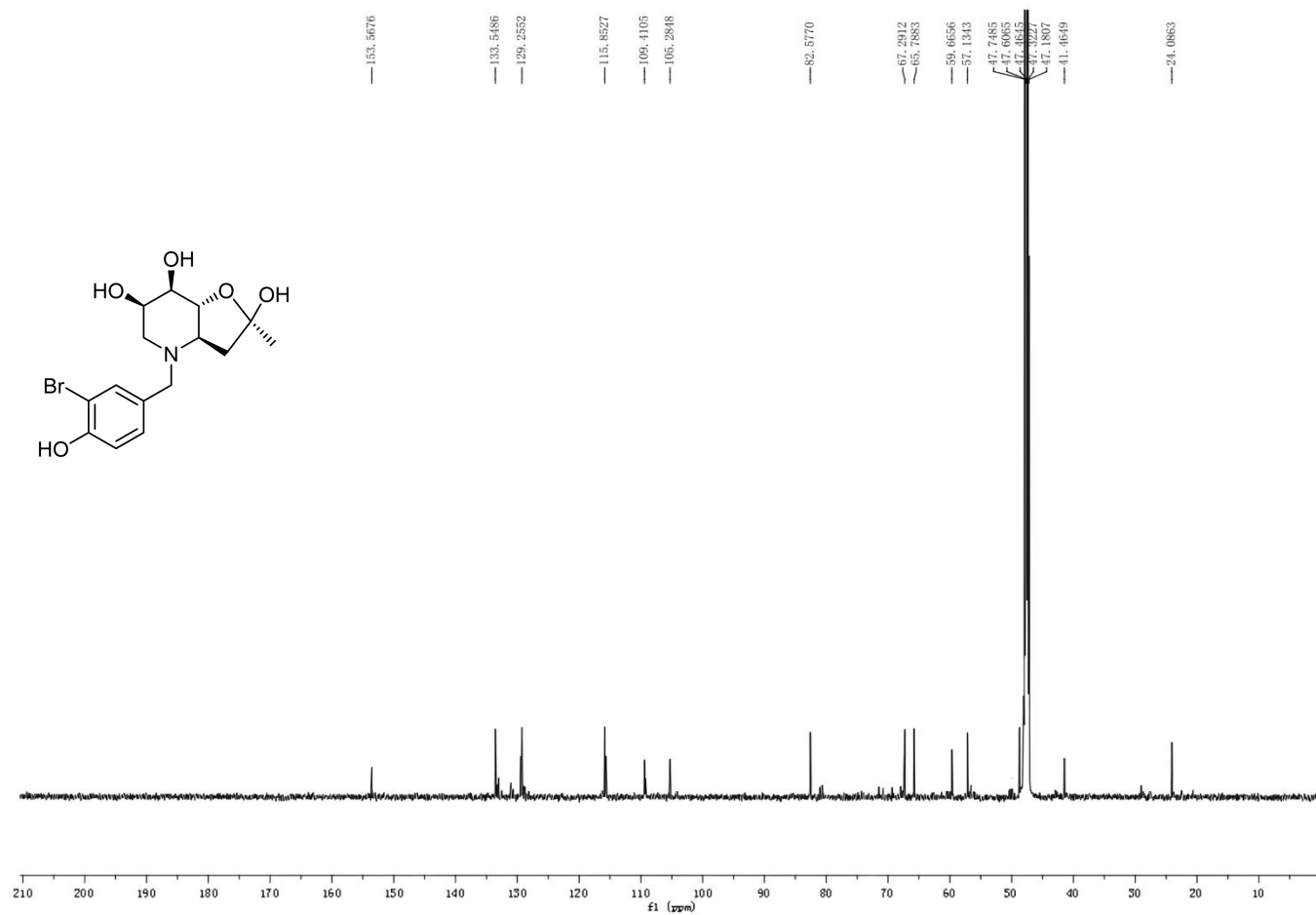


Figure S30. The ^{13}C -NMR of Compound 18.

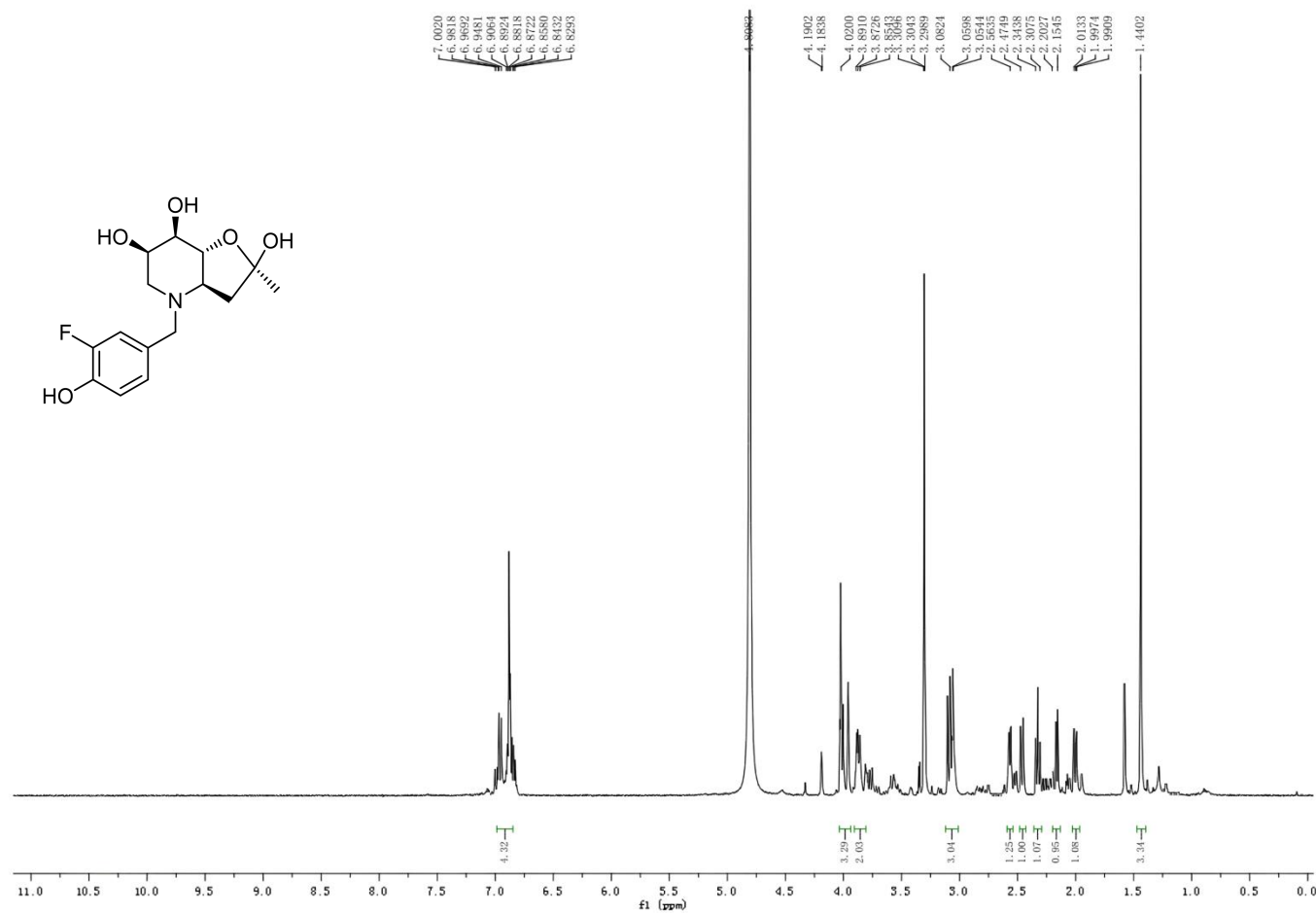


Figure S31. The ^1H NMR of compound 19.

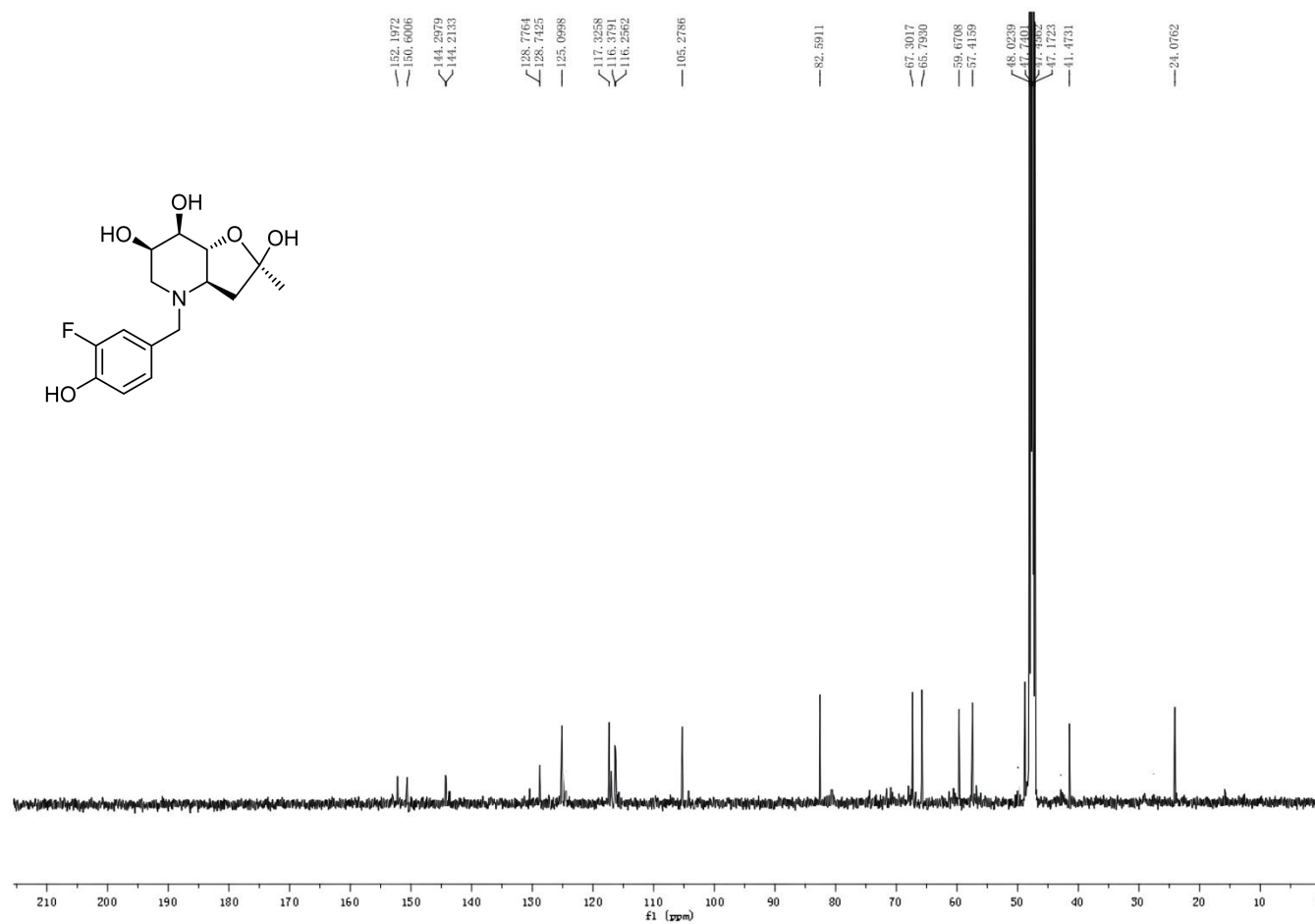


Figure S32. The ^{13}C -NMR of Compound 19.

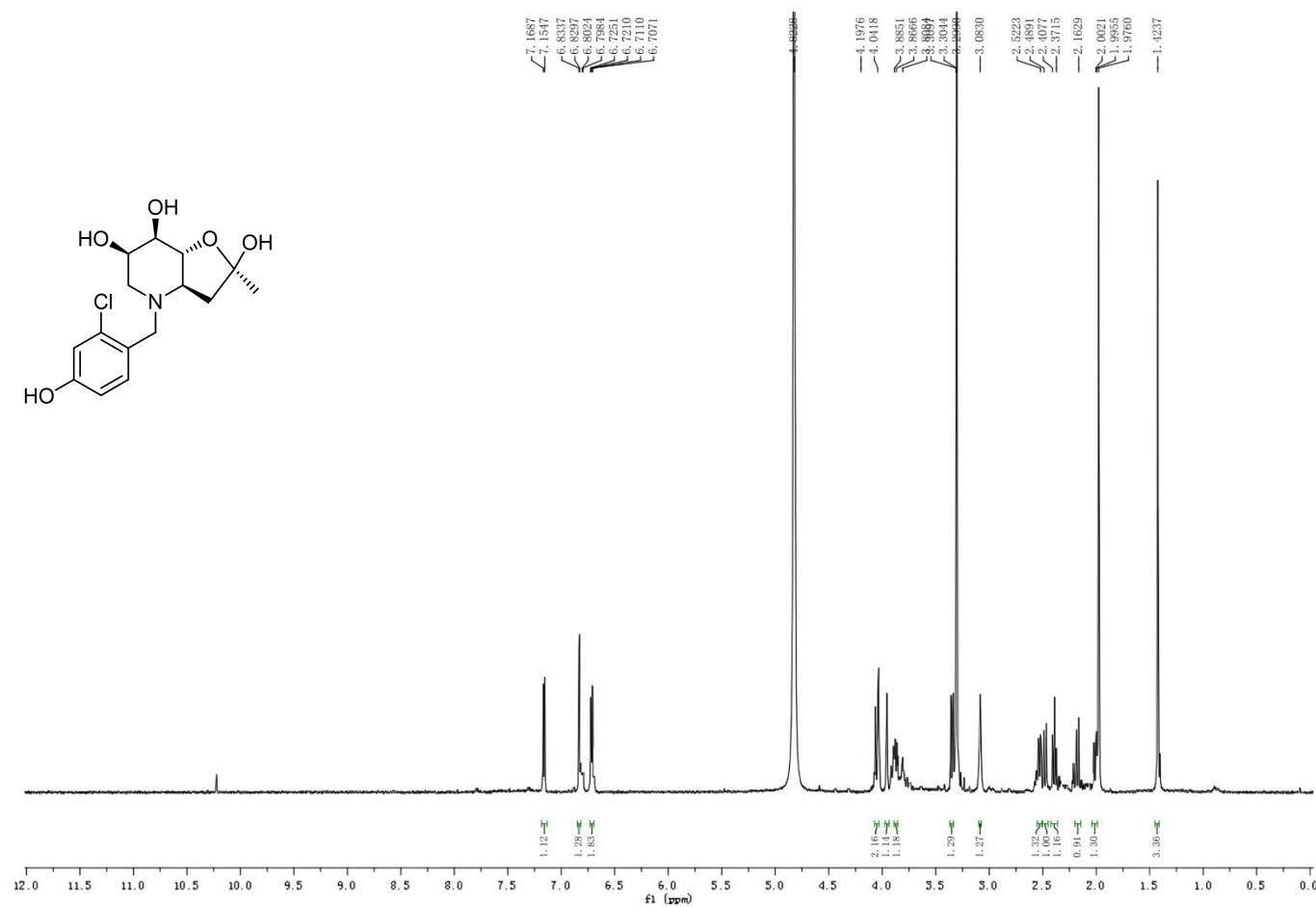


Figure S33. The ^1H NMR of compound 20.

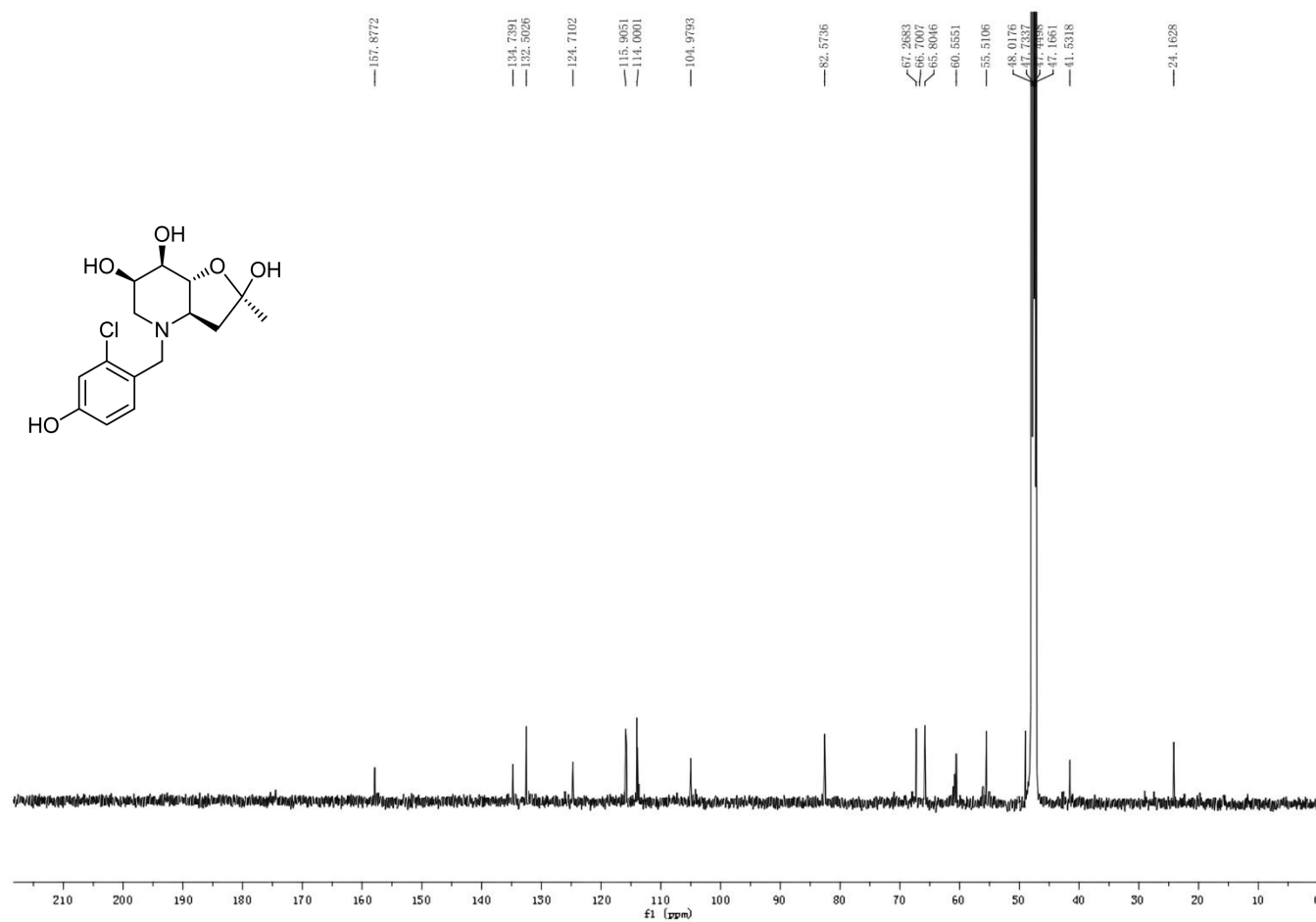


Figure S34. The ^{13}C -NMR of Compound 20.

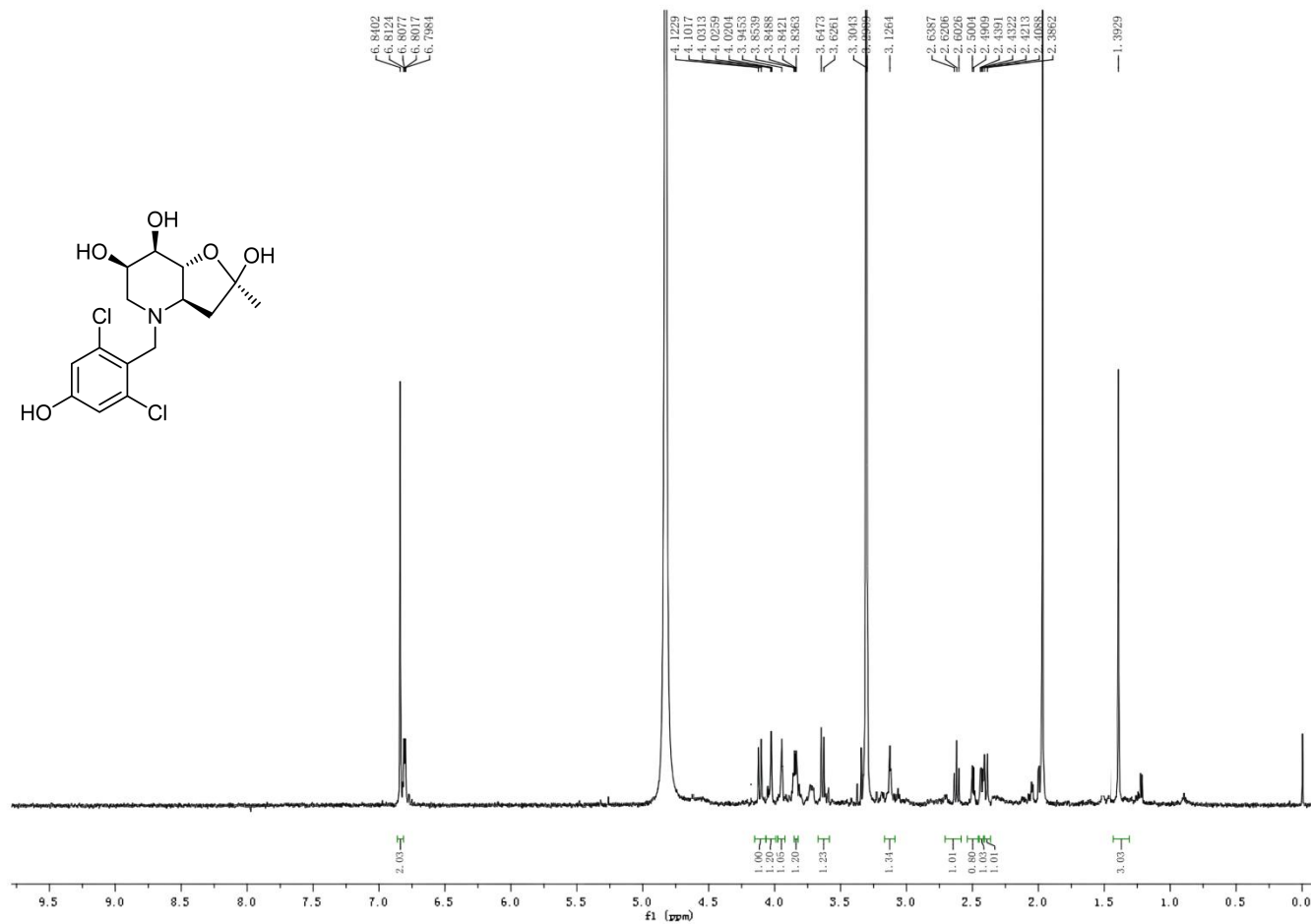


Figure S35. The ^1H NMR of compound **21**.

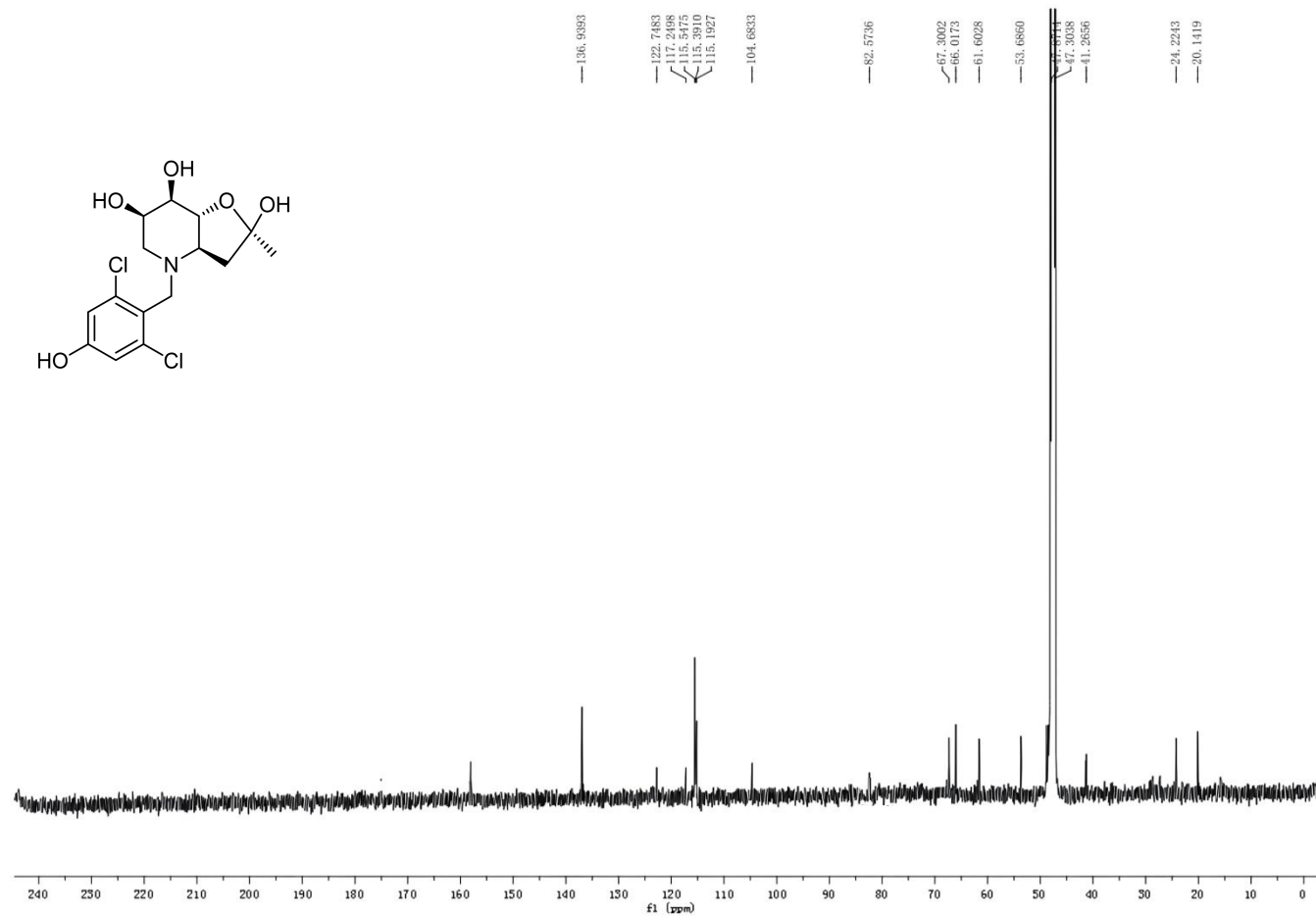


Figure S36. The ^{13}C -NMR of Compound 21.

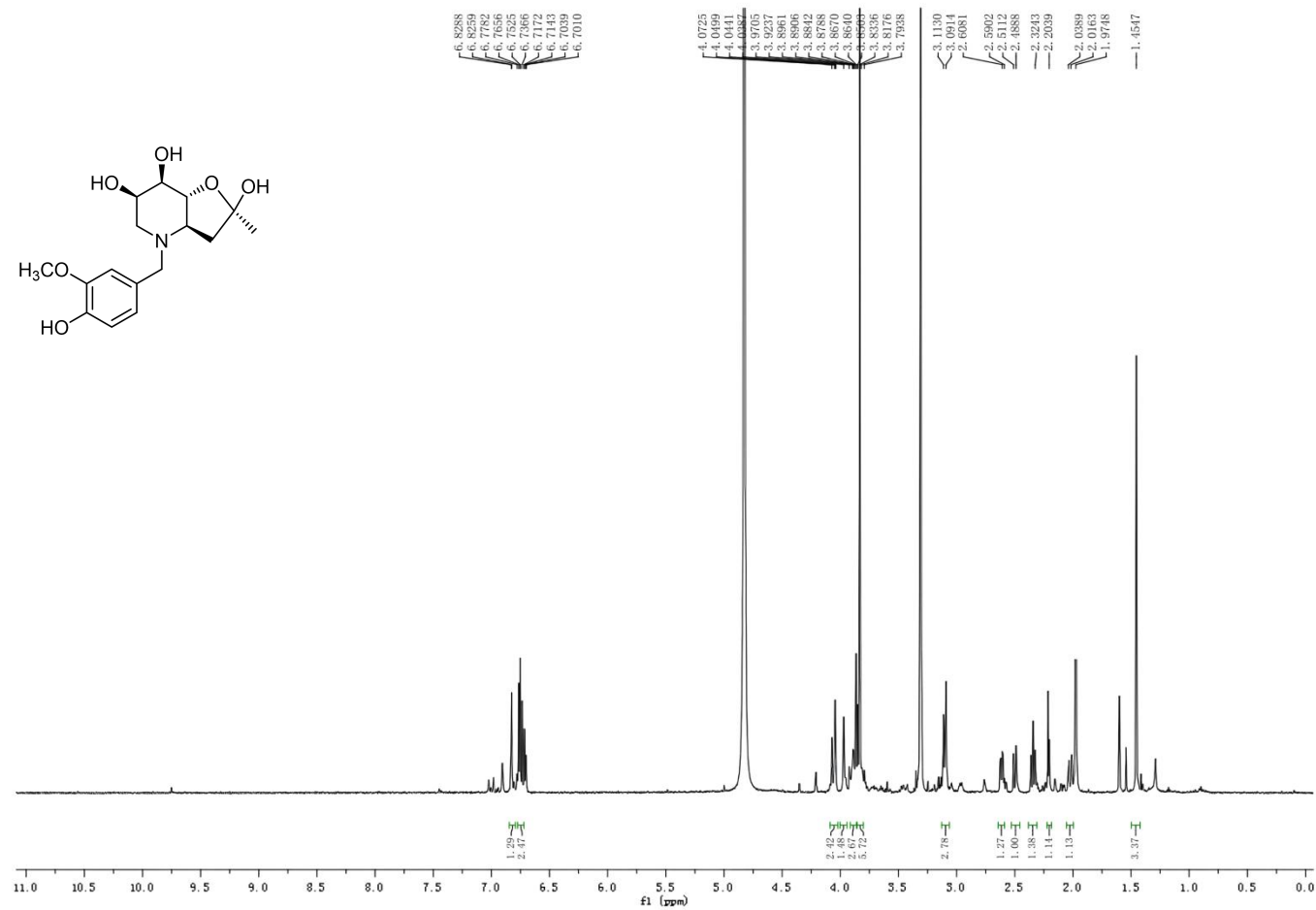


Figure S37. The ¹H NMR of compound 22.

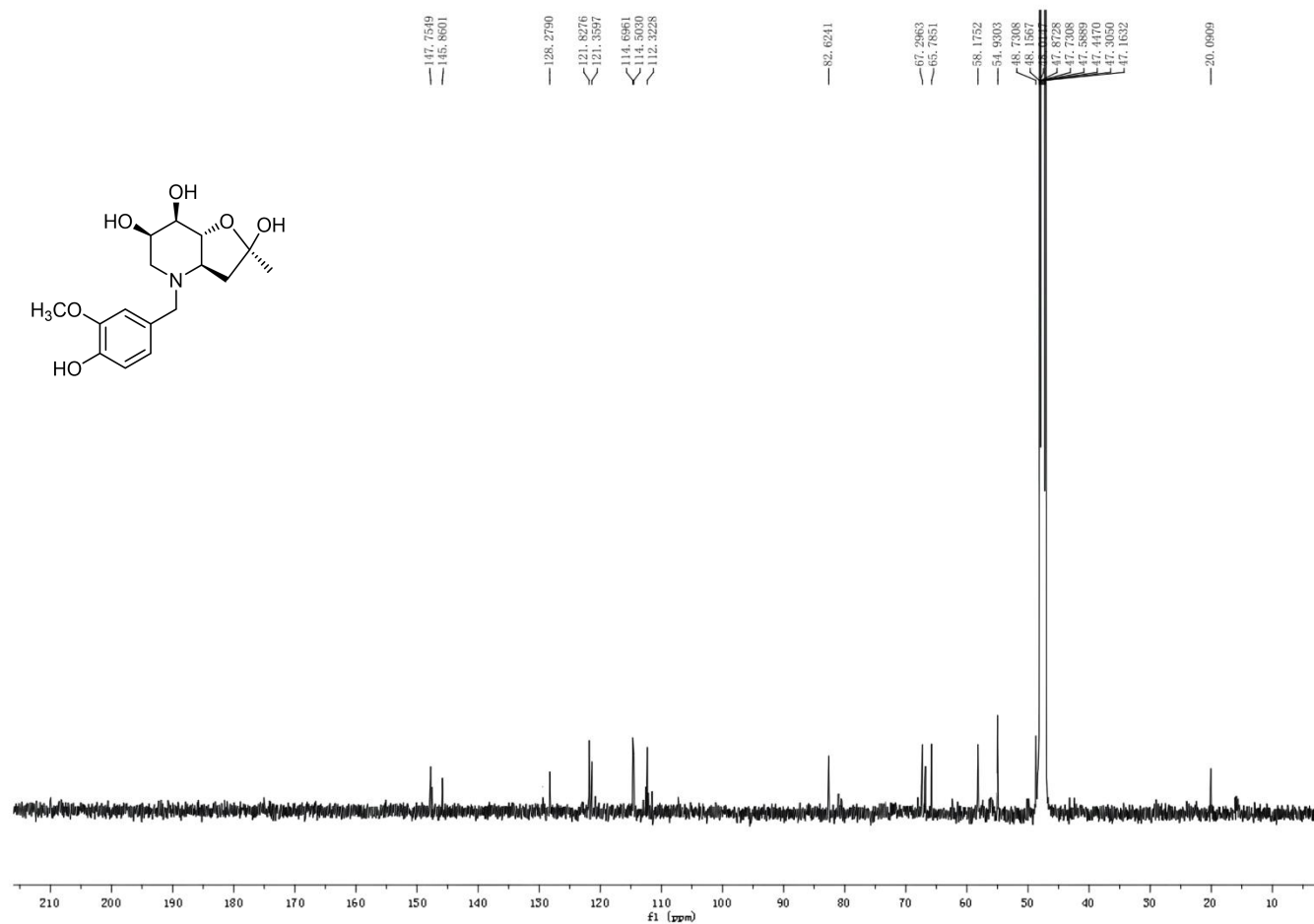


Figure S38. The ¹³C-NMR of Compound 22.

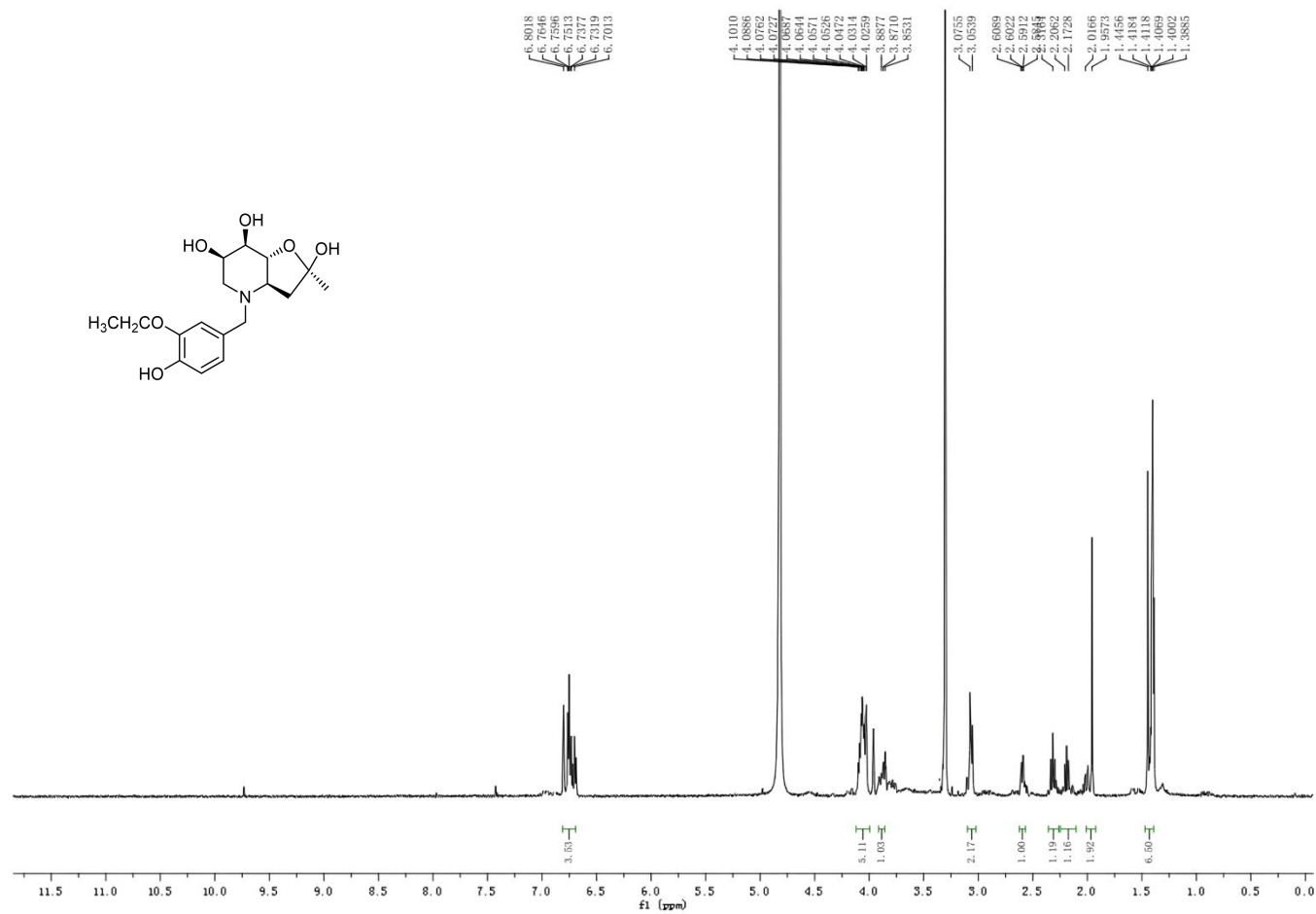


Figure S39. The ¹H NMR of compound 23.

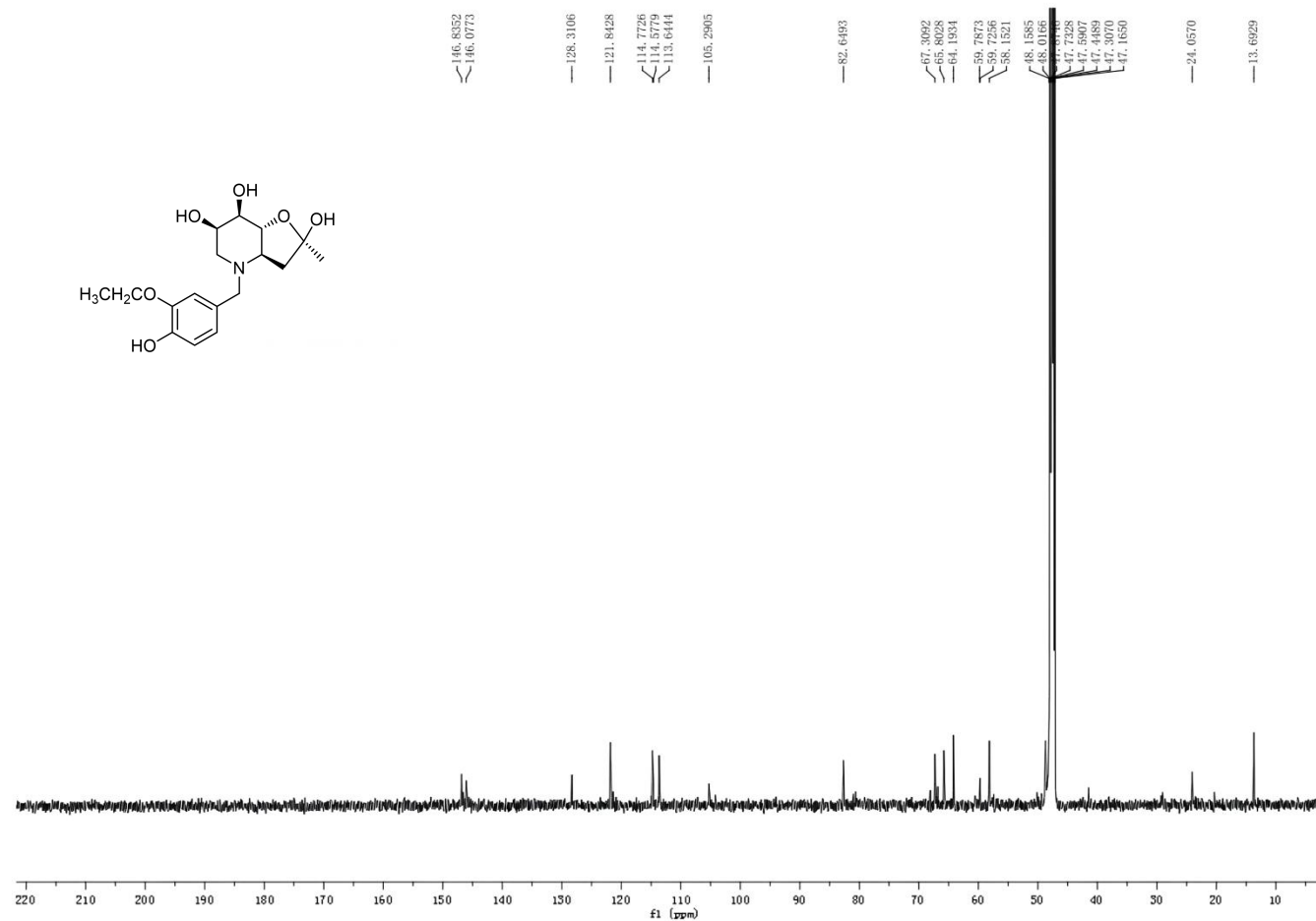


Figure S40. The ¹³C-NMR of Compound 23.

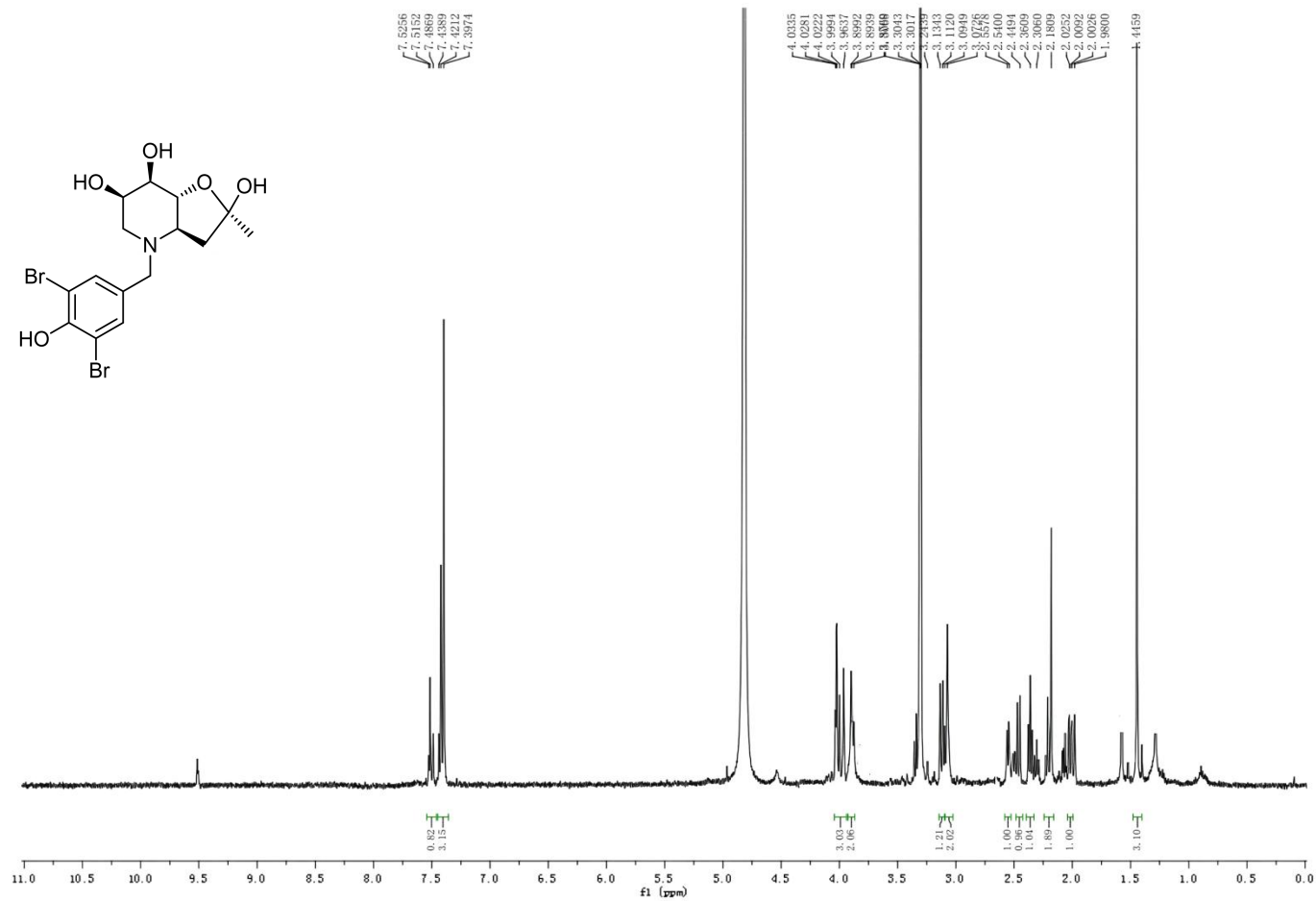


Figure S41. The ¹H NMR of compound 24.

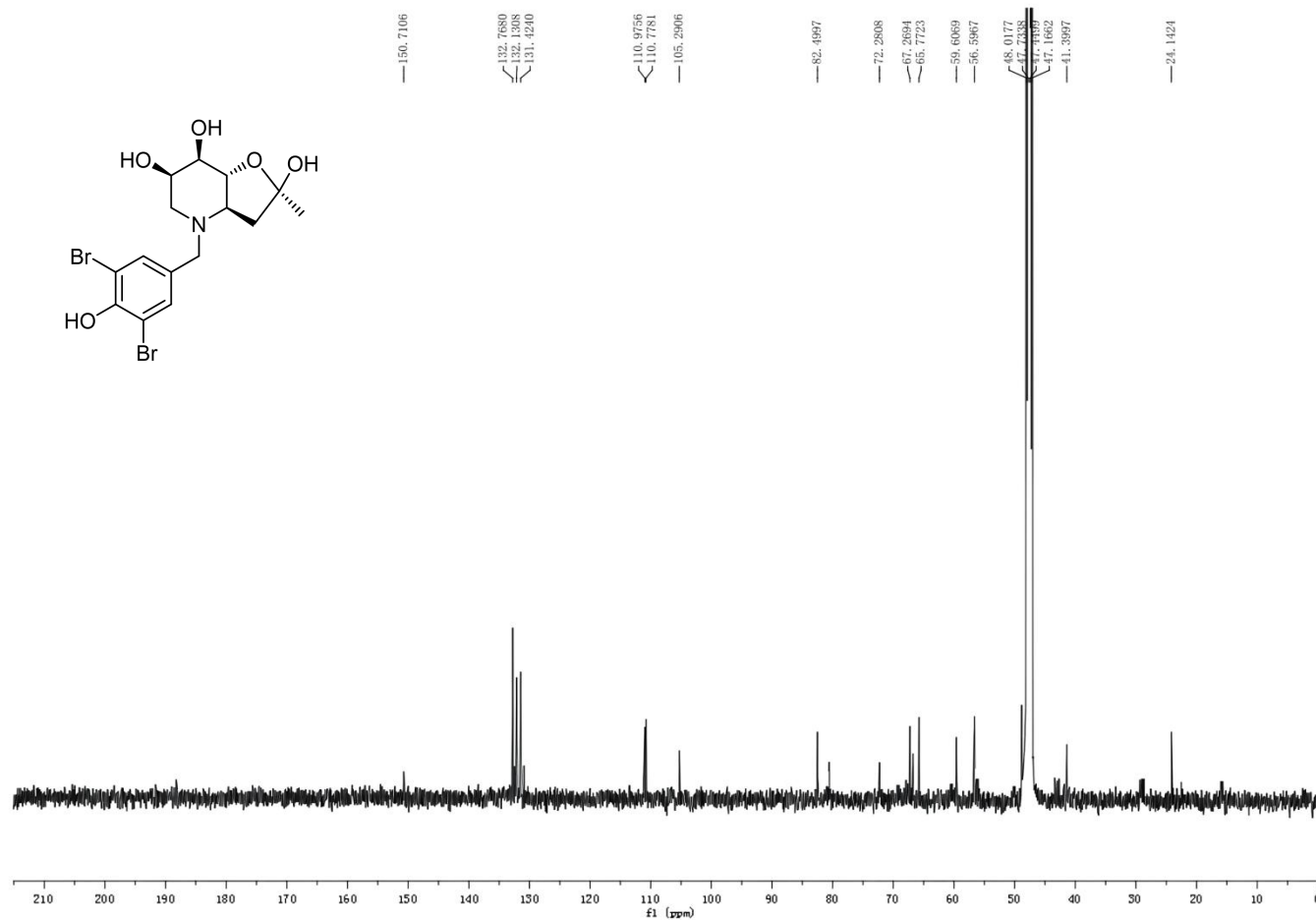


Figure S42. The ^{13}C -NMR of Compound 24.

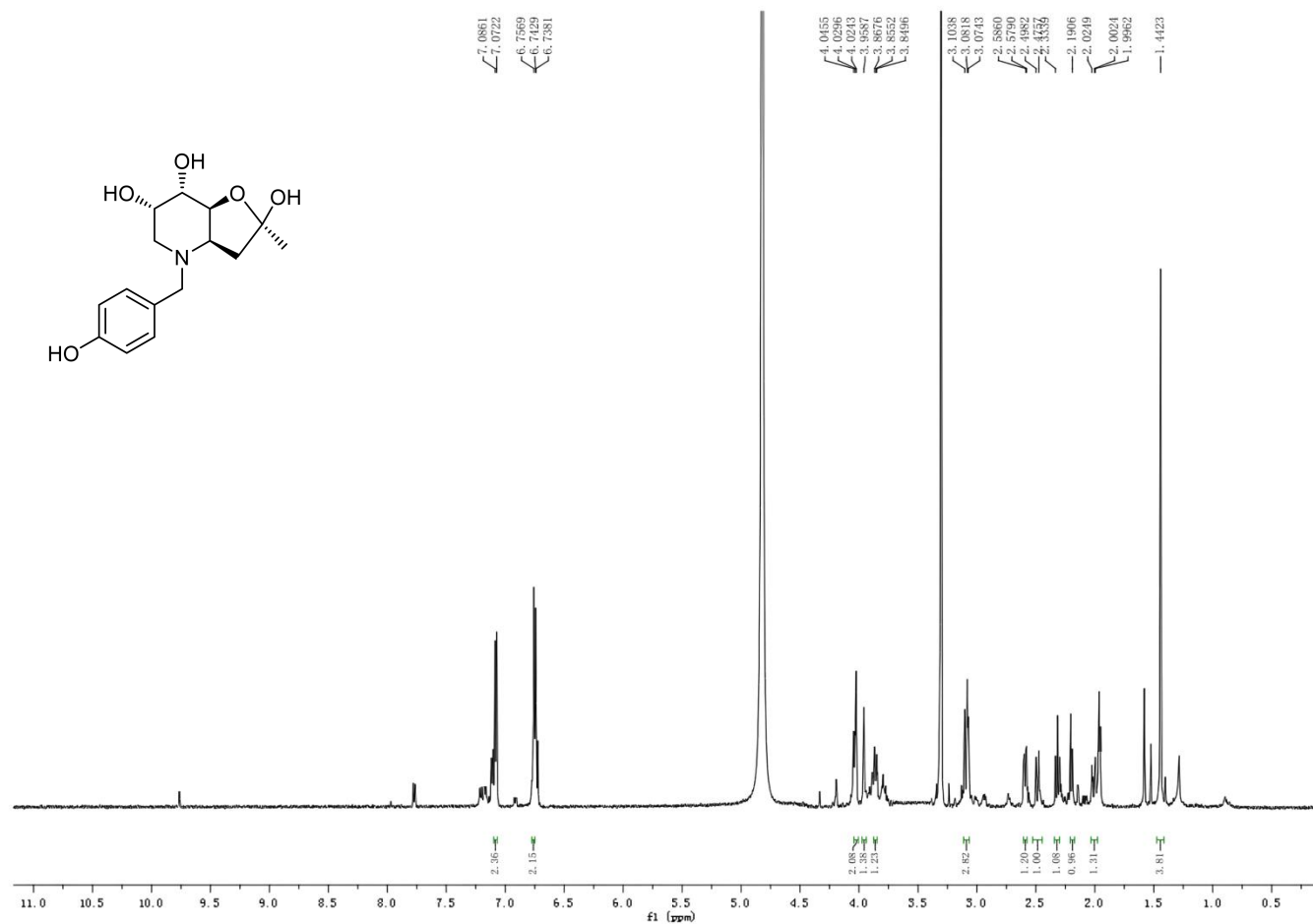


Figure S43. The ¹H NMR of compound 25.

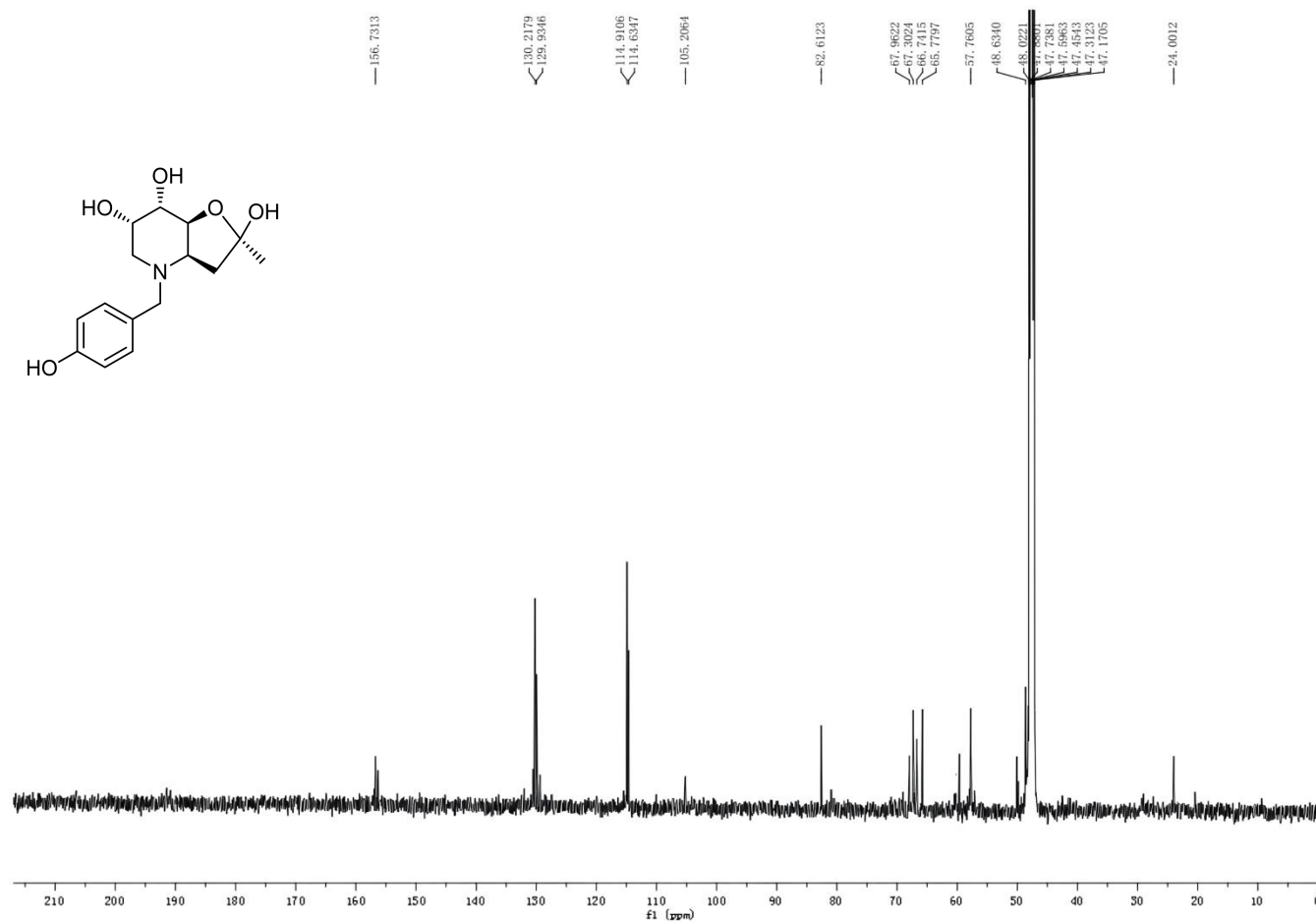


Figure S44. The ^{13}C -NMR of Compound 25.

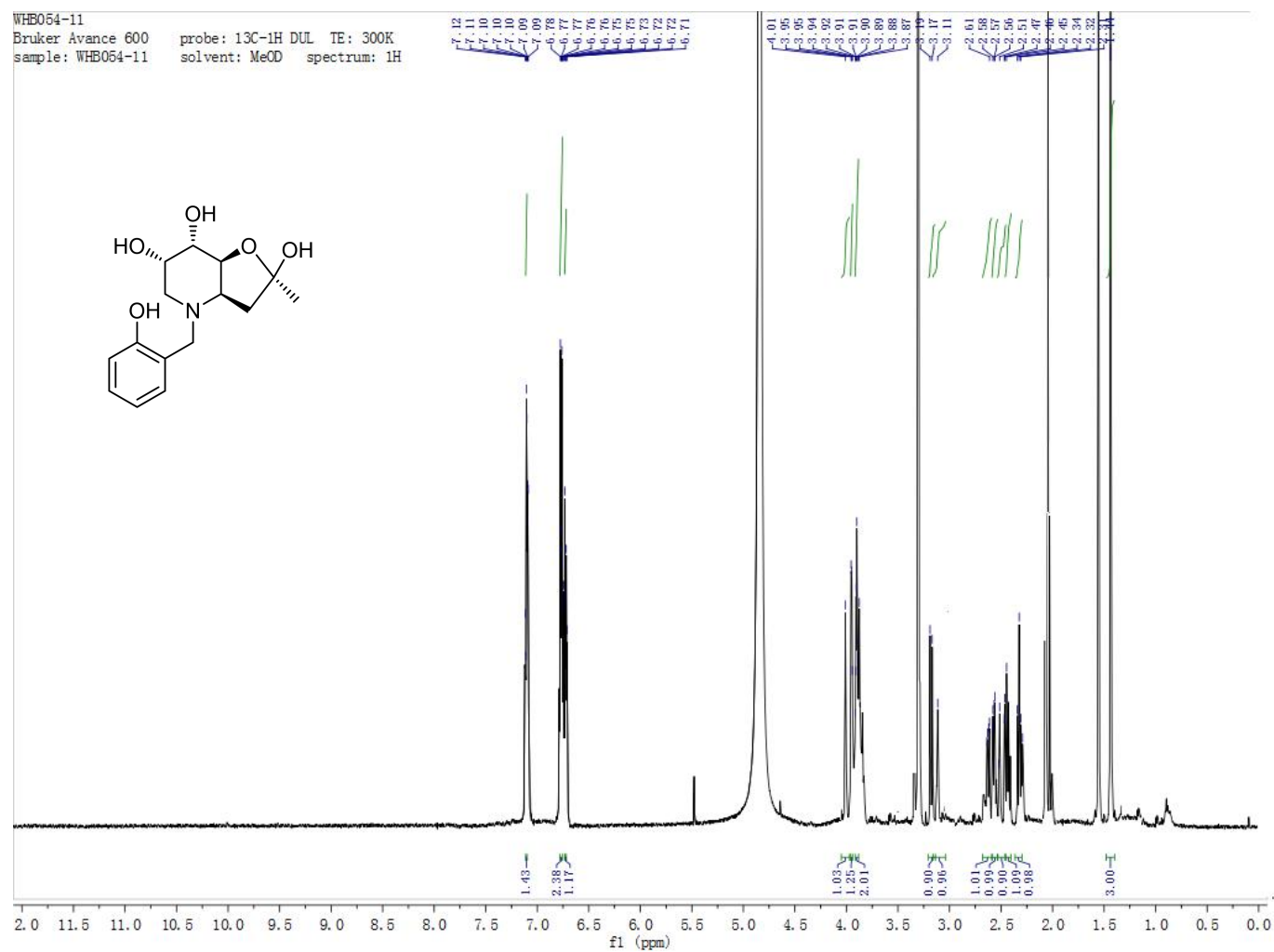


Figure S45. The ^1H NMR of compound 26.

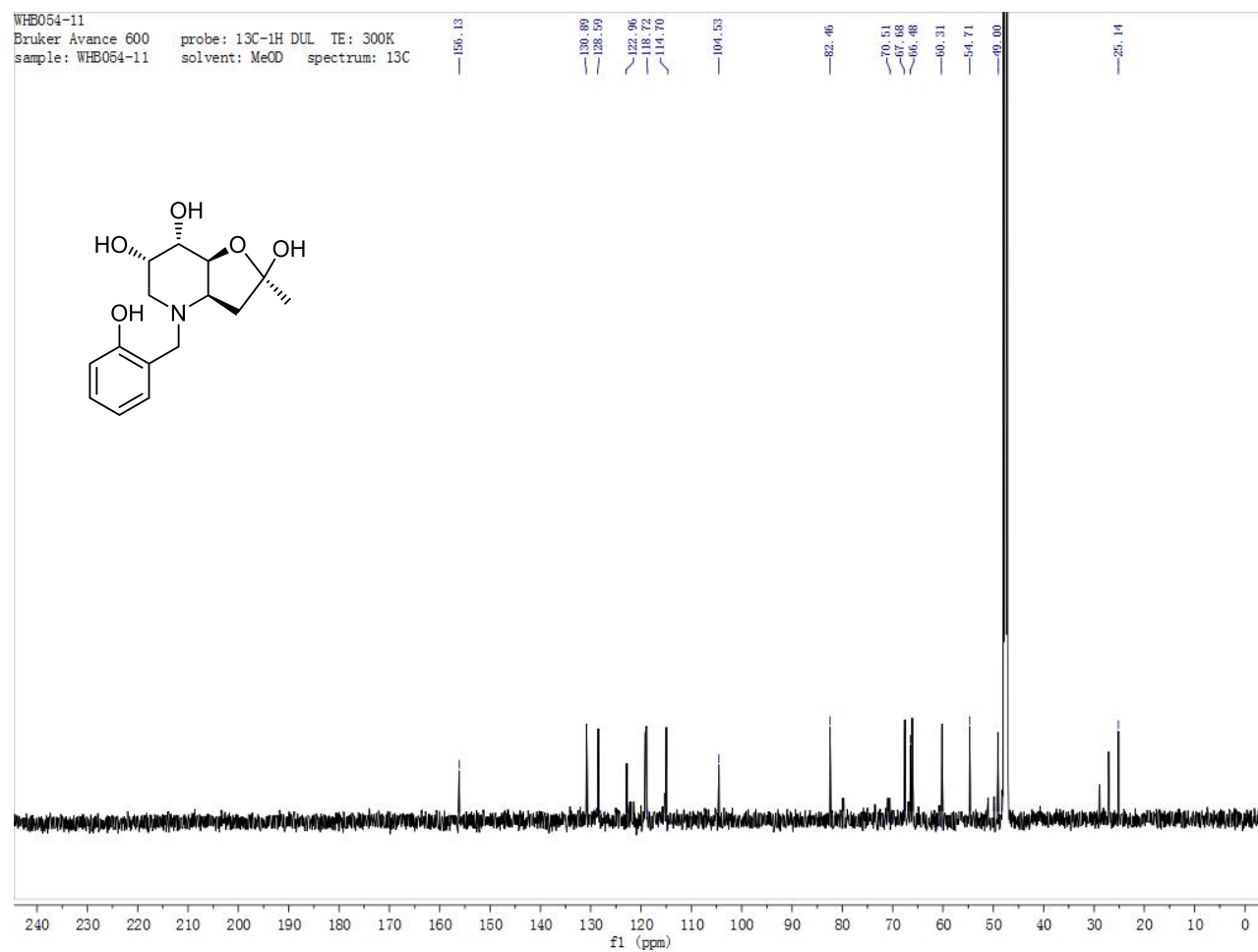


Figure S46. The ^{13}C -NMR of Compound 26.

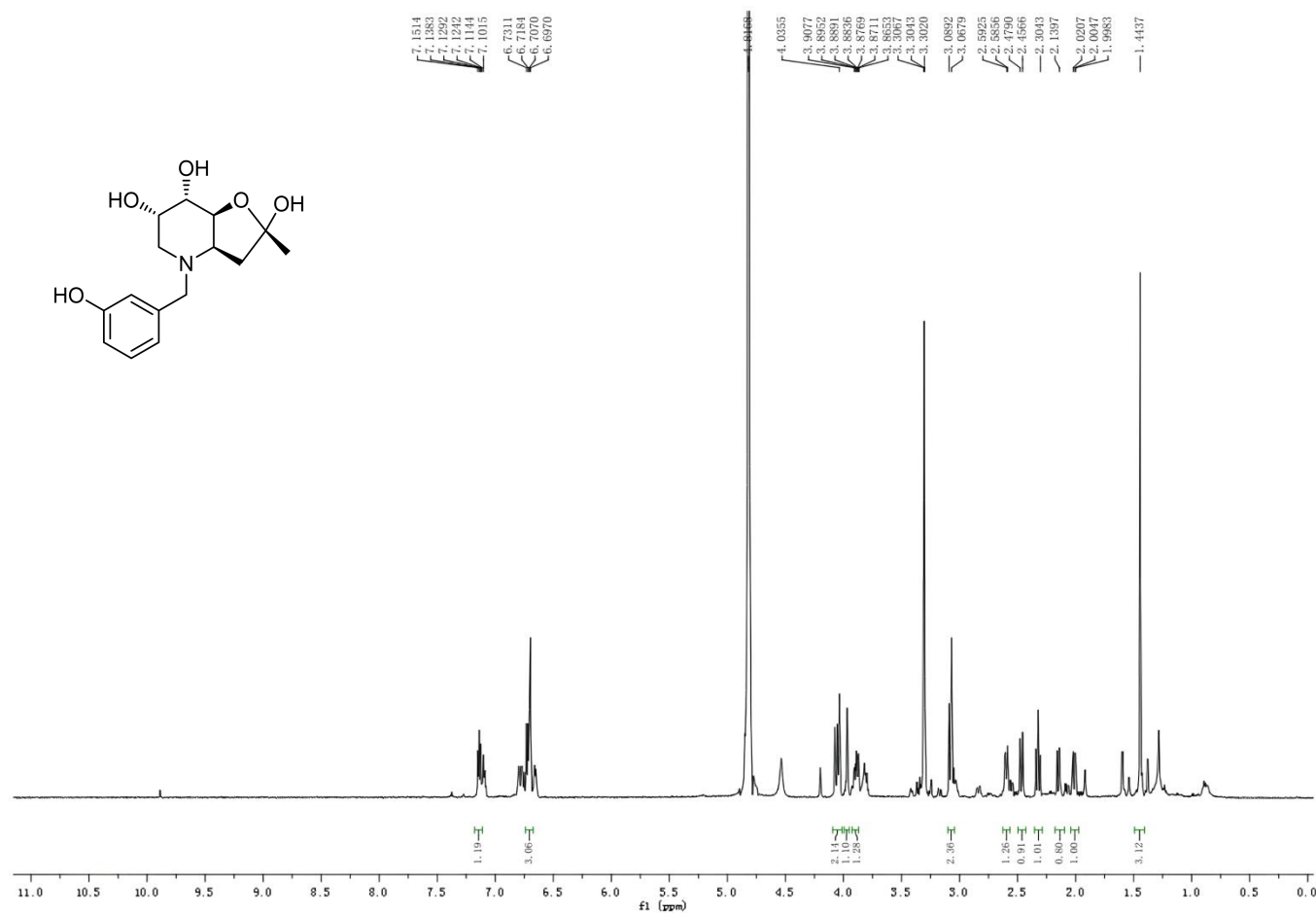


Figure S47. The ¹H NMR of compound 27.

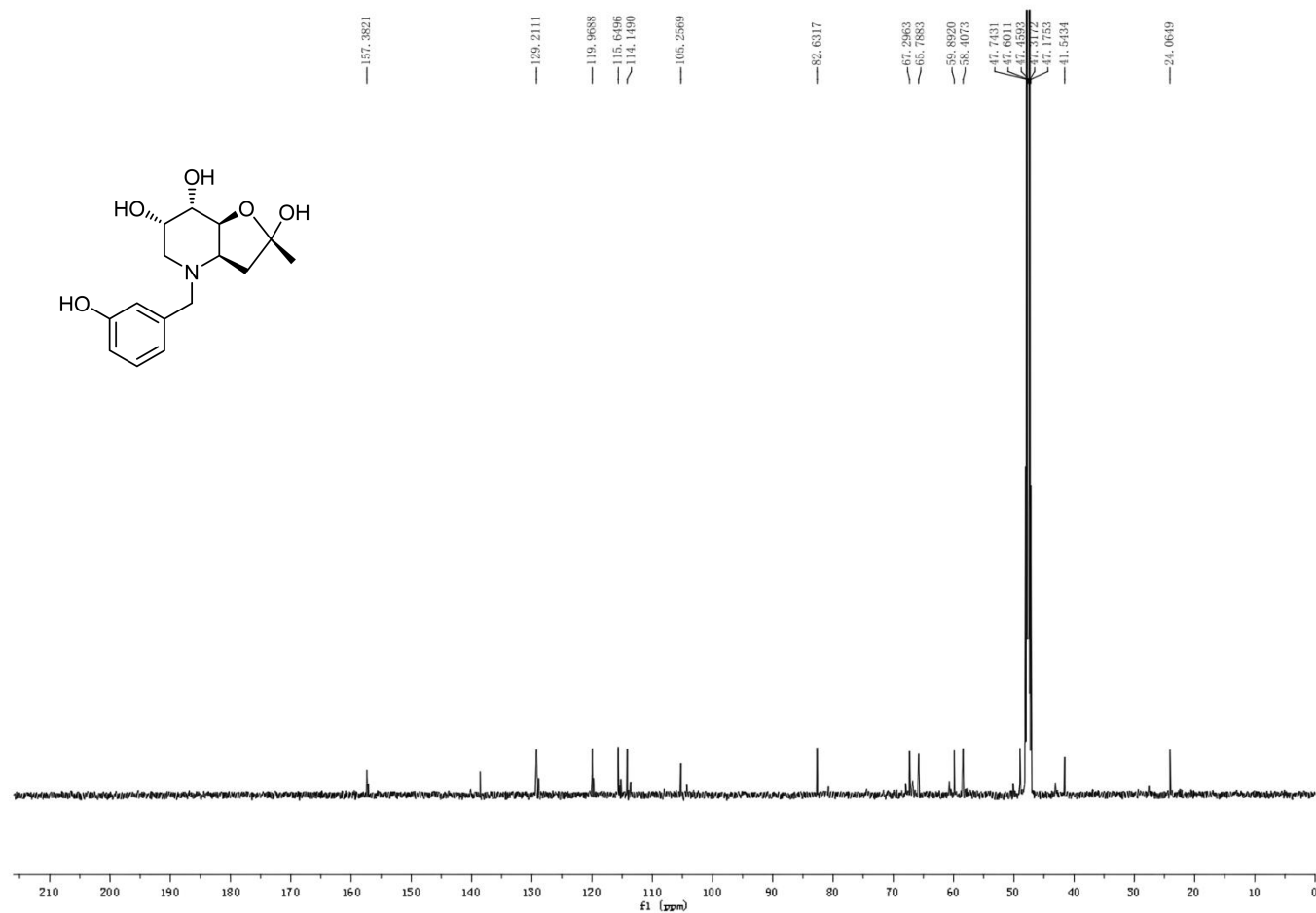


Figure S48. The ^{13}C -NMR of Compound 27.

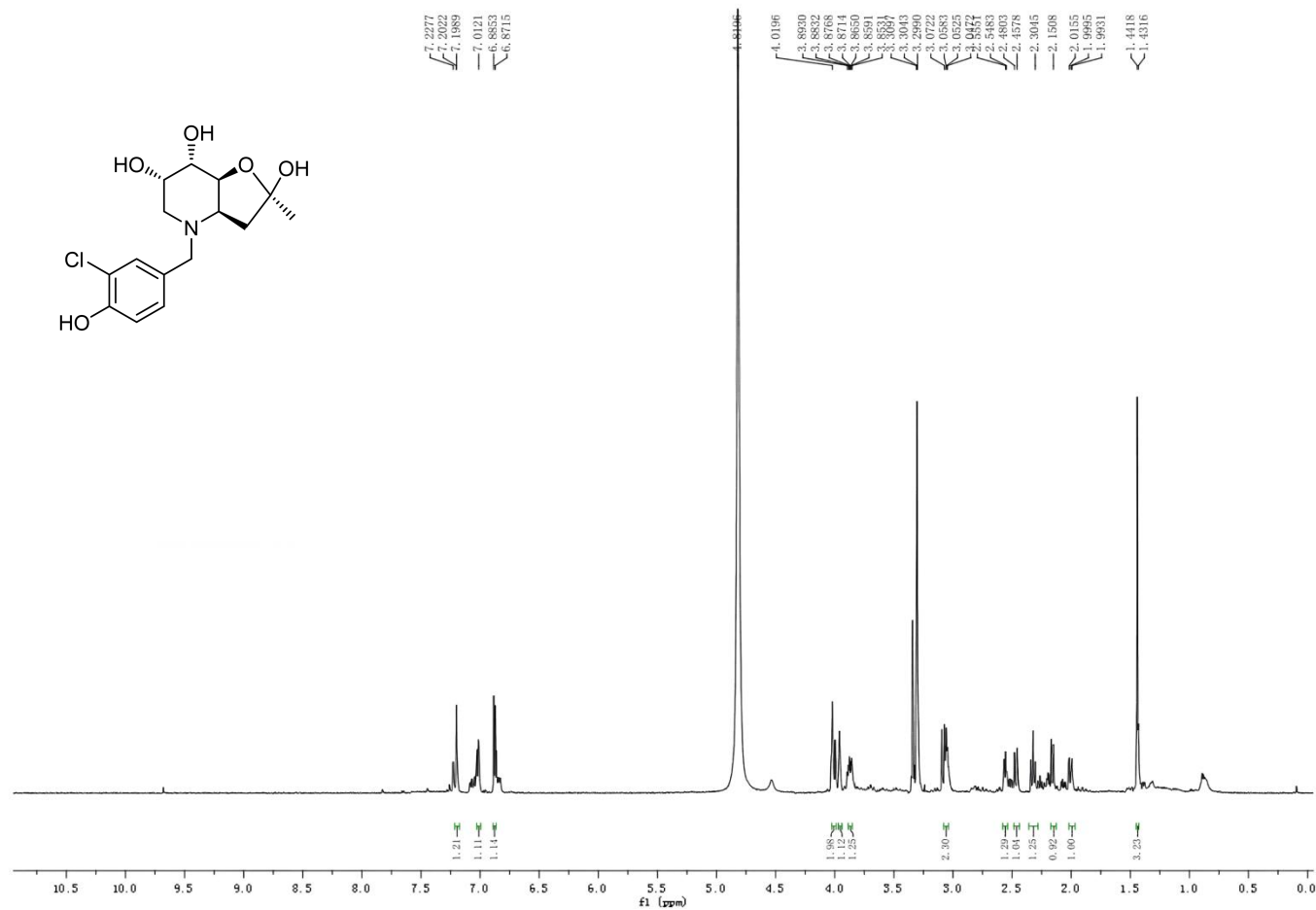


Figure S49. The ¹H NMR of compound 28.

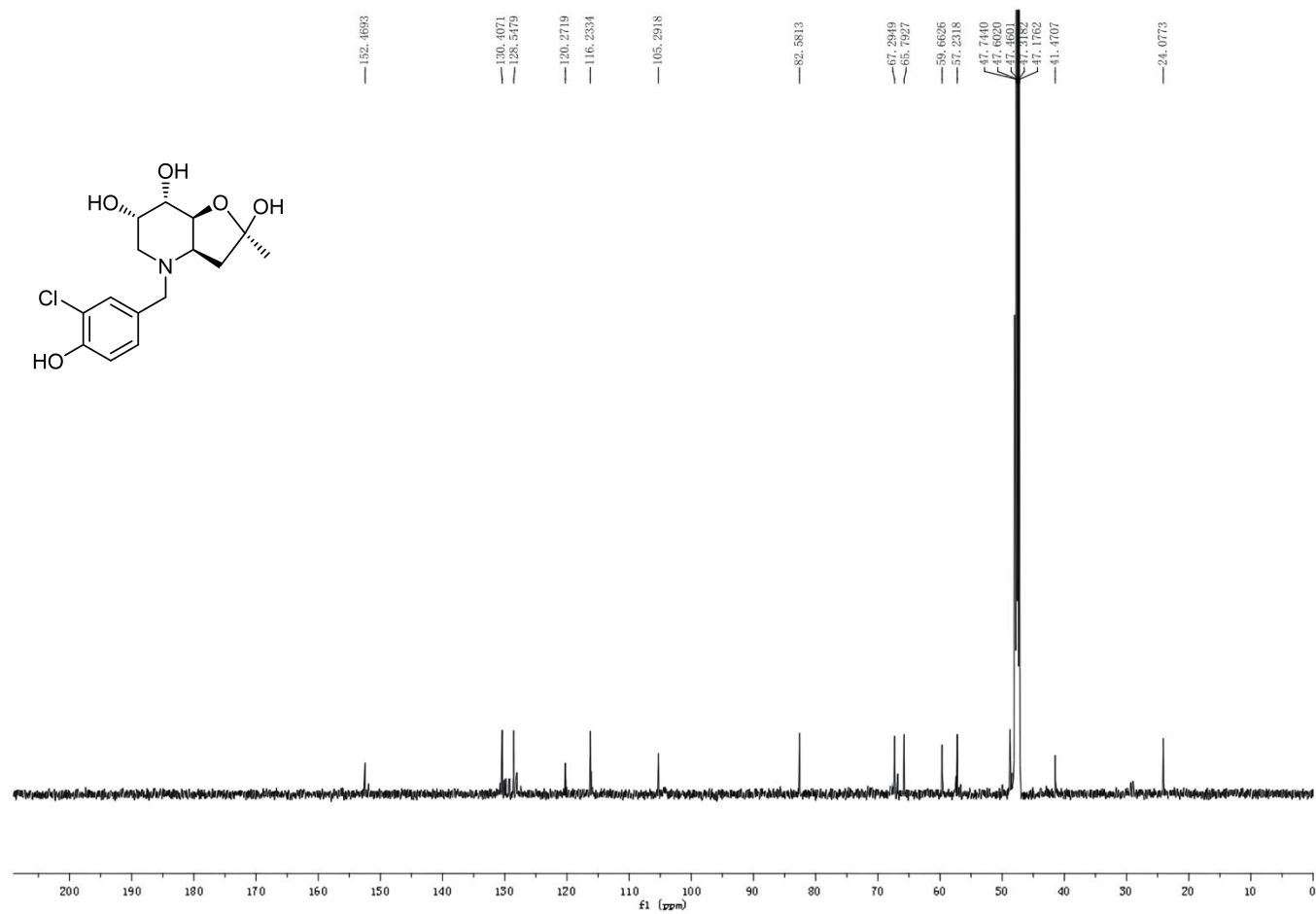


Figure S50. The ^{13}C -NMR of Compound 28.

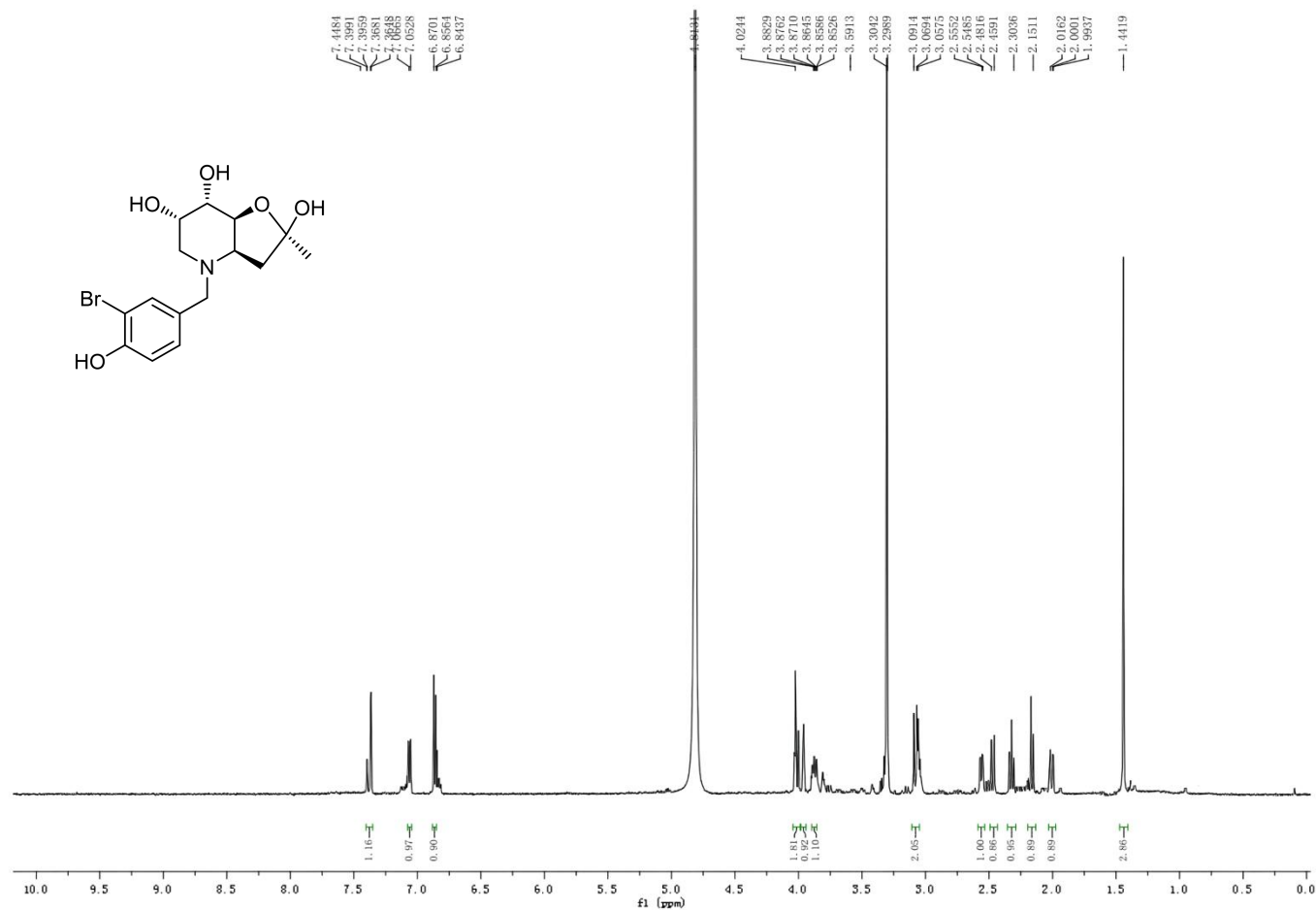


Figure S51. The ¹H NMR of compound 29.

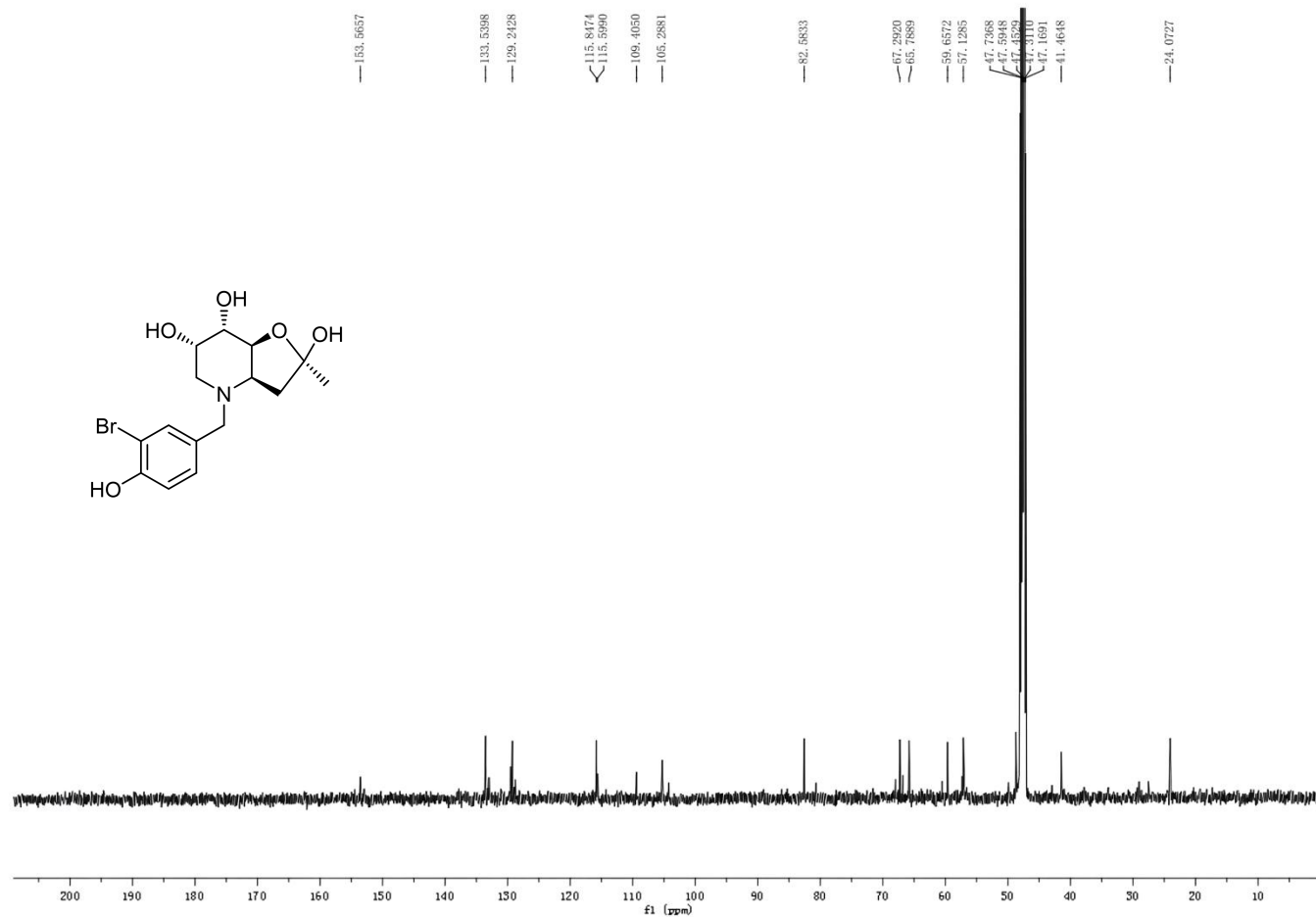


Figure S52. The ^{13}C -NMR of Compound 29.

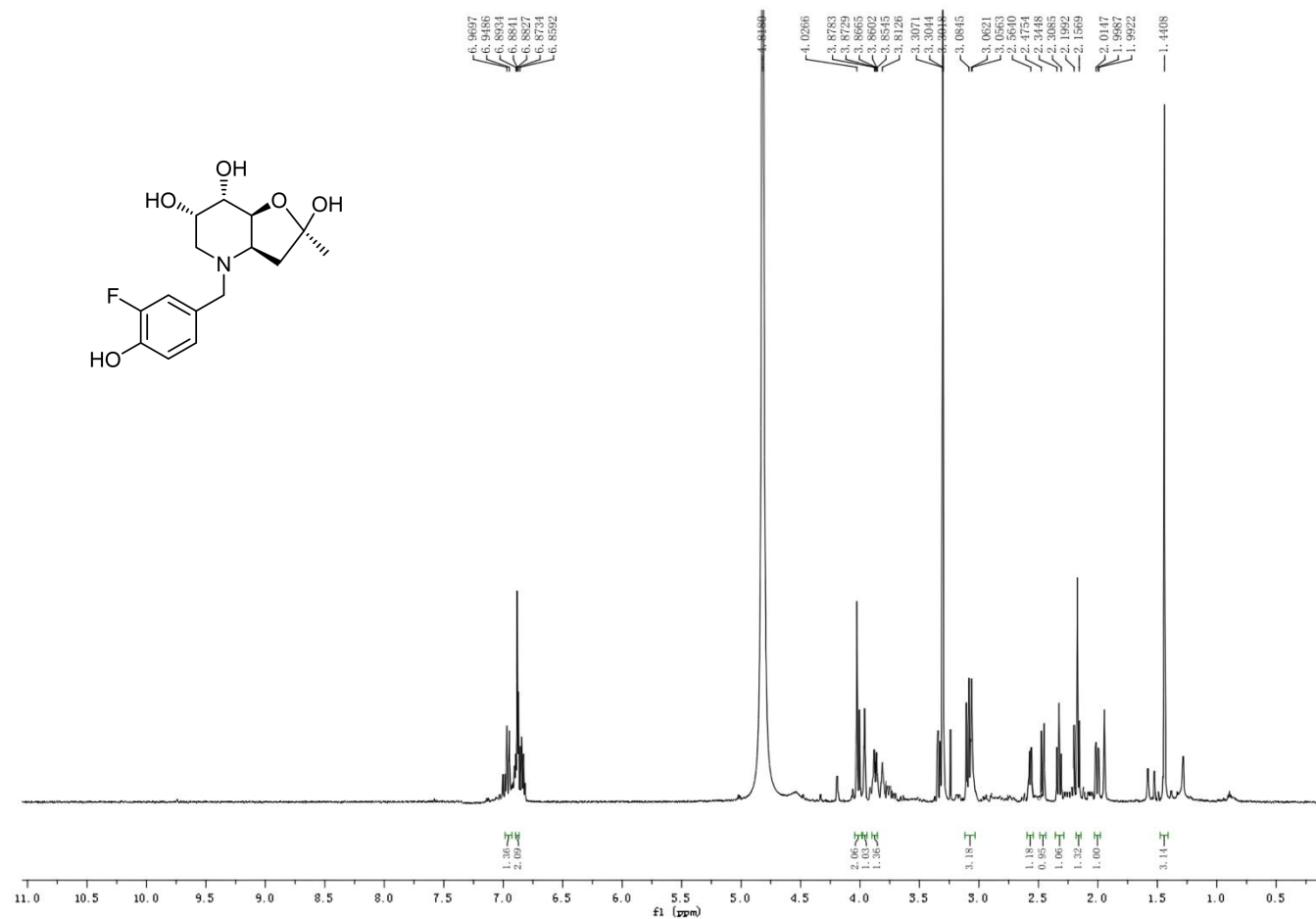


Figure S53. The ¹H NMR of compound 30.

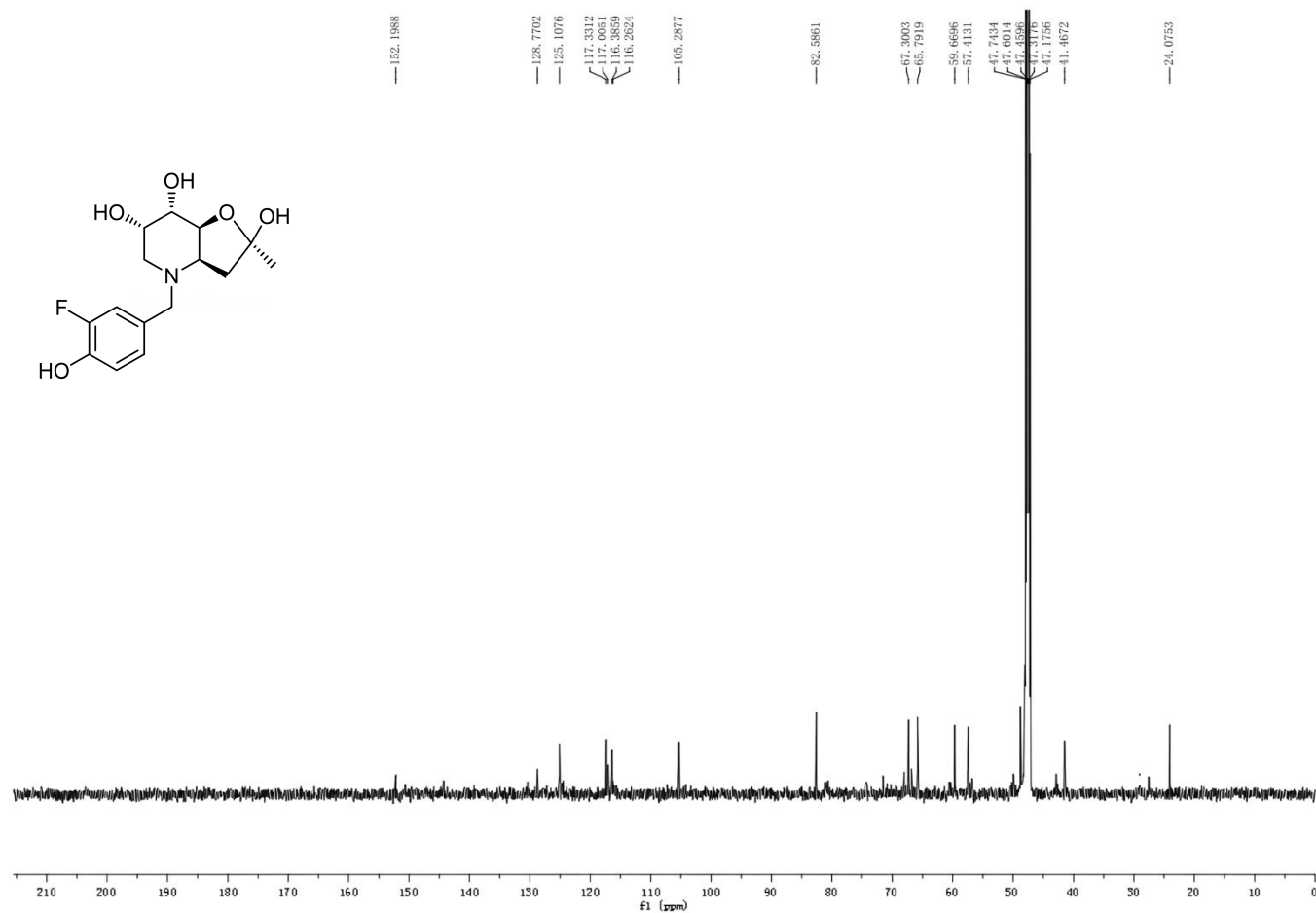


Figure S54. The ^{13}C -NMR of Compound 30.

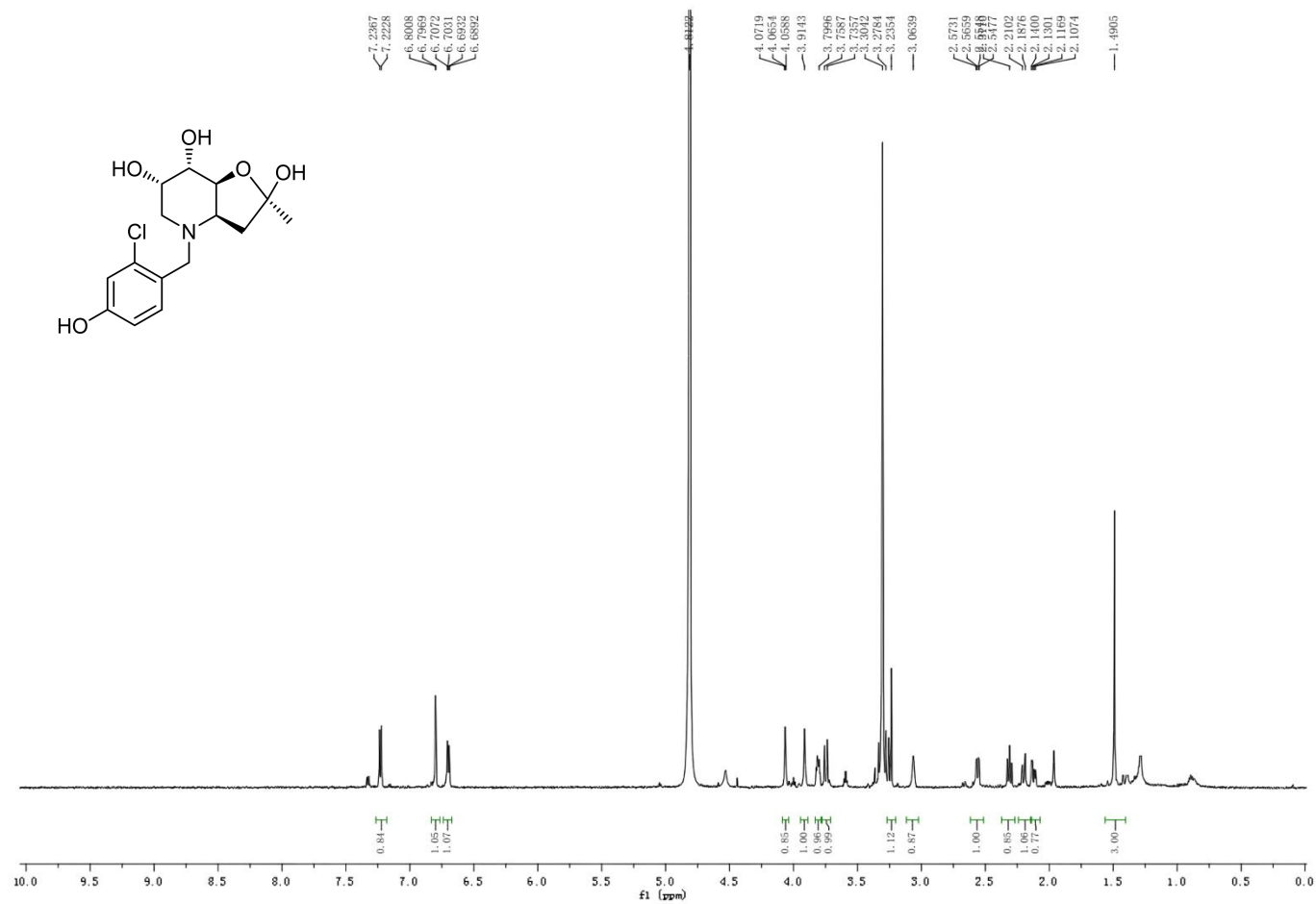


Figure S55. The ¹H NMR of compound 31.

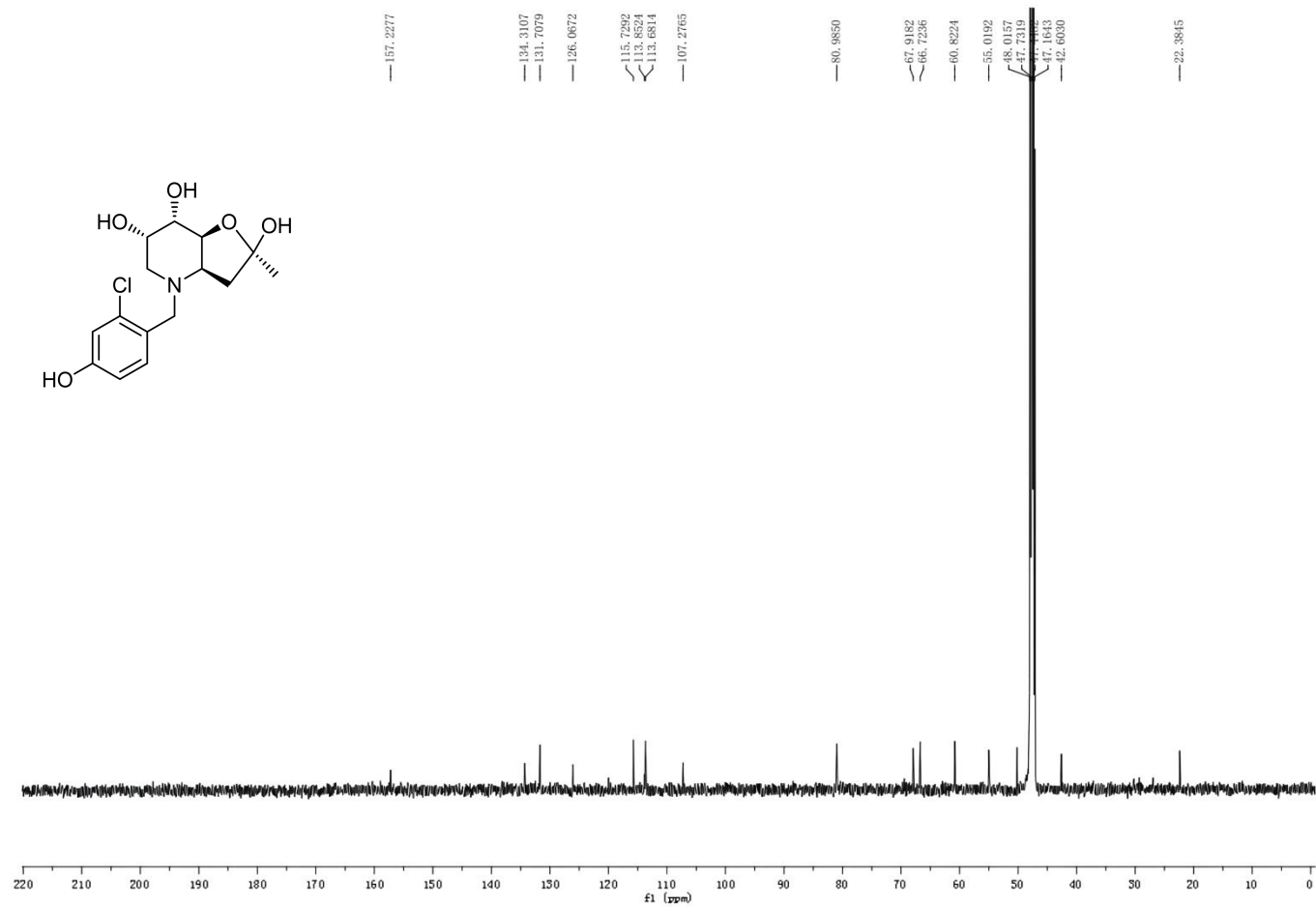


Figure S56. The ^{13}C -NMR of Compound 31.

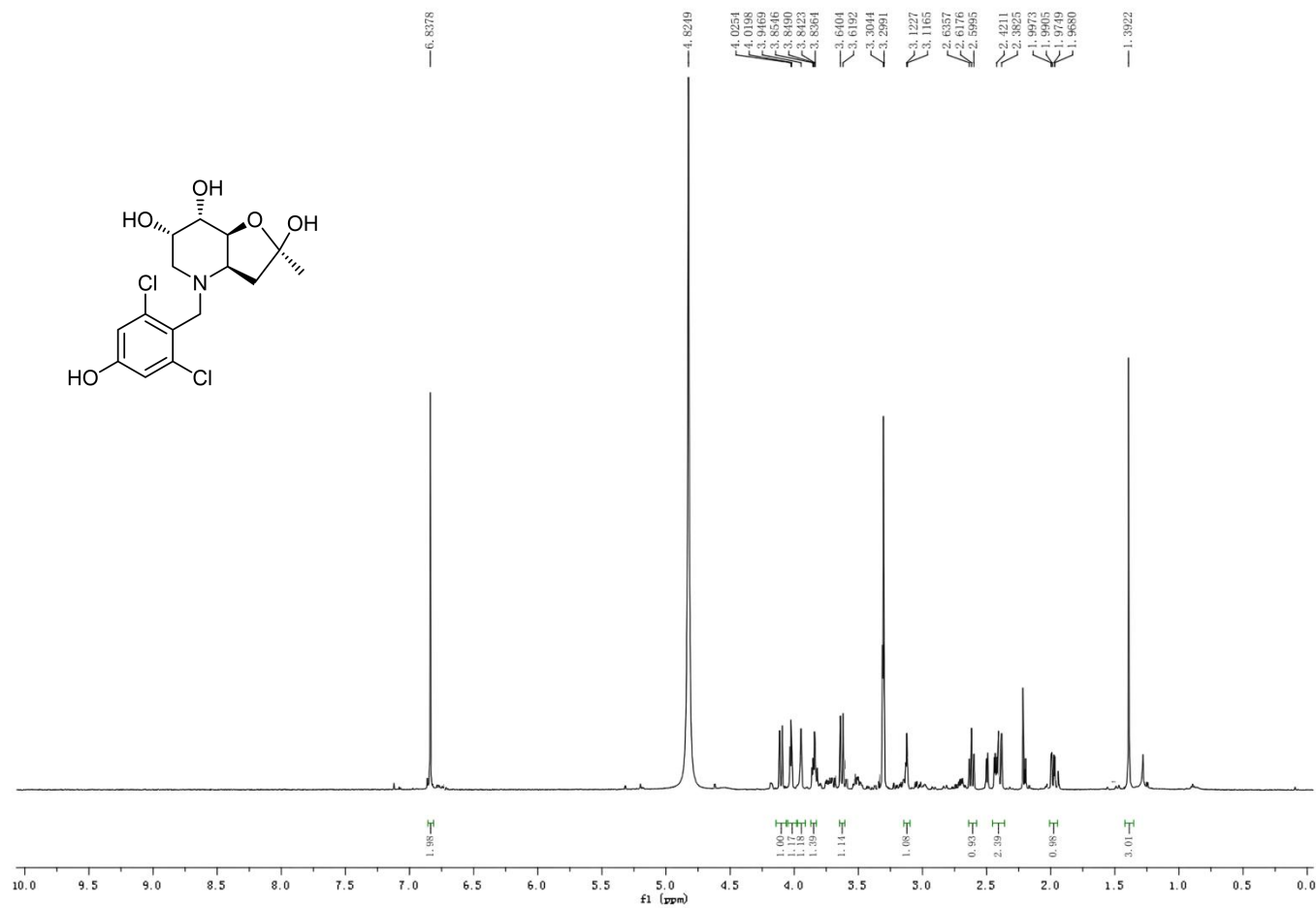


Figure S57. The ^1H NMR of compound 32.

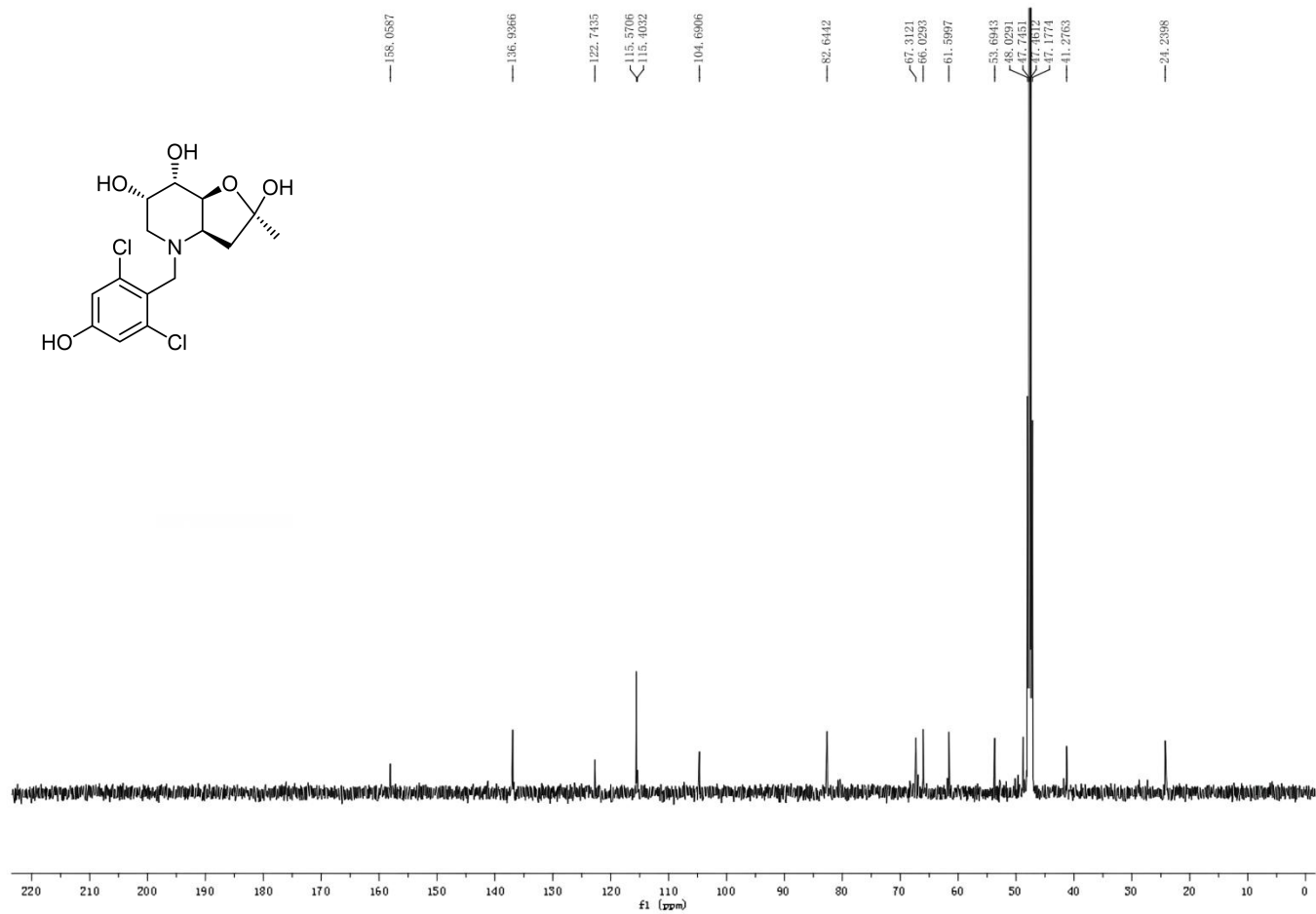


Figure S58. The ^{13}C -NMR of Compound 32.

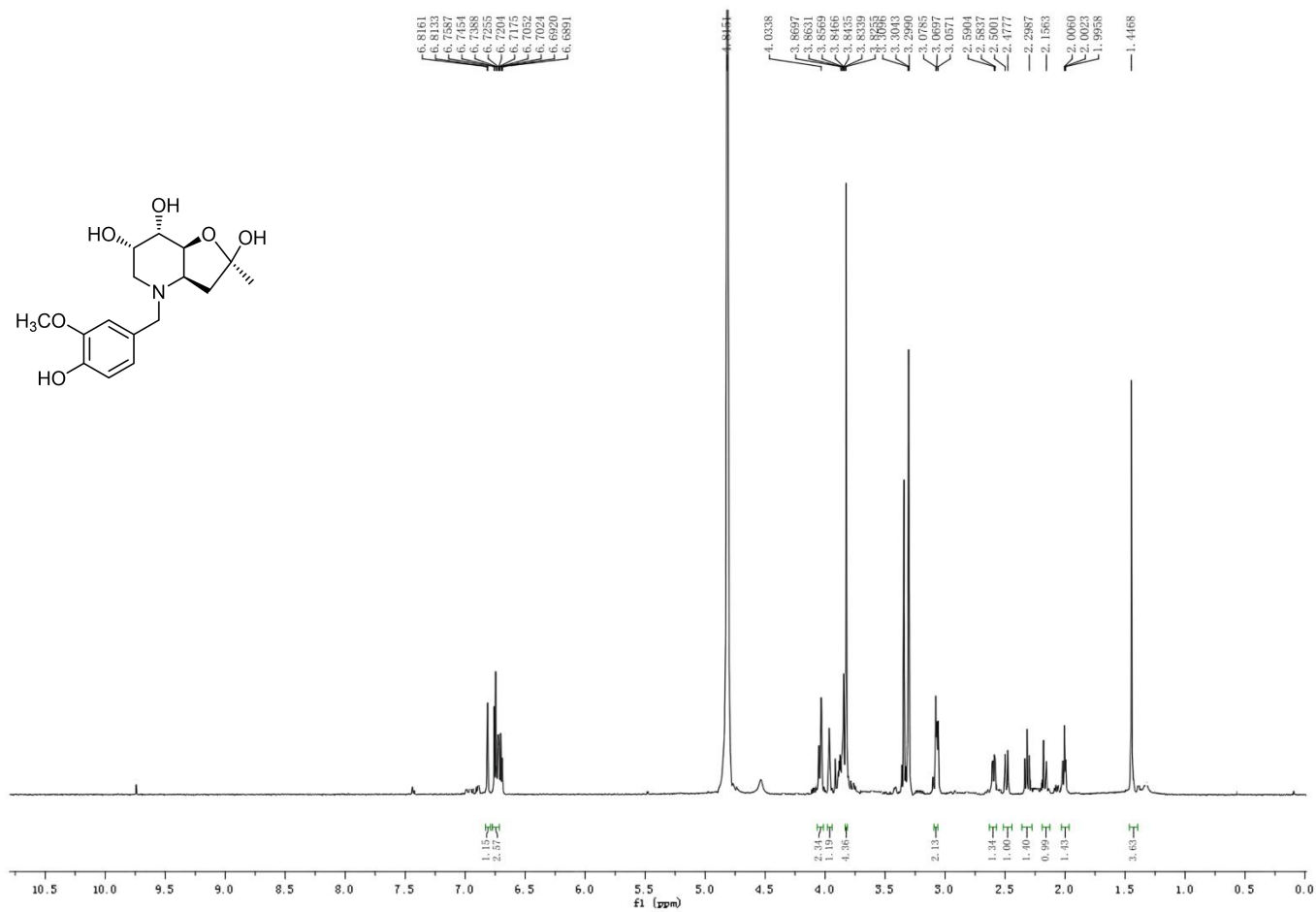


Figure S59. The ¹H NMR of compound 33.

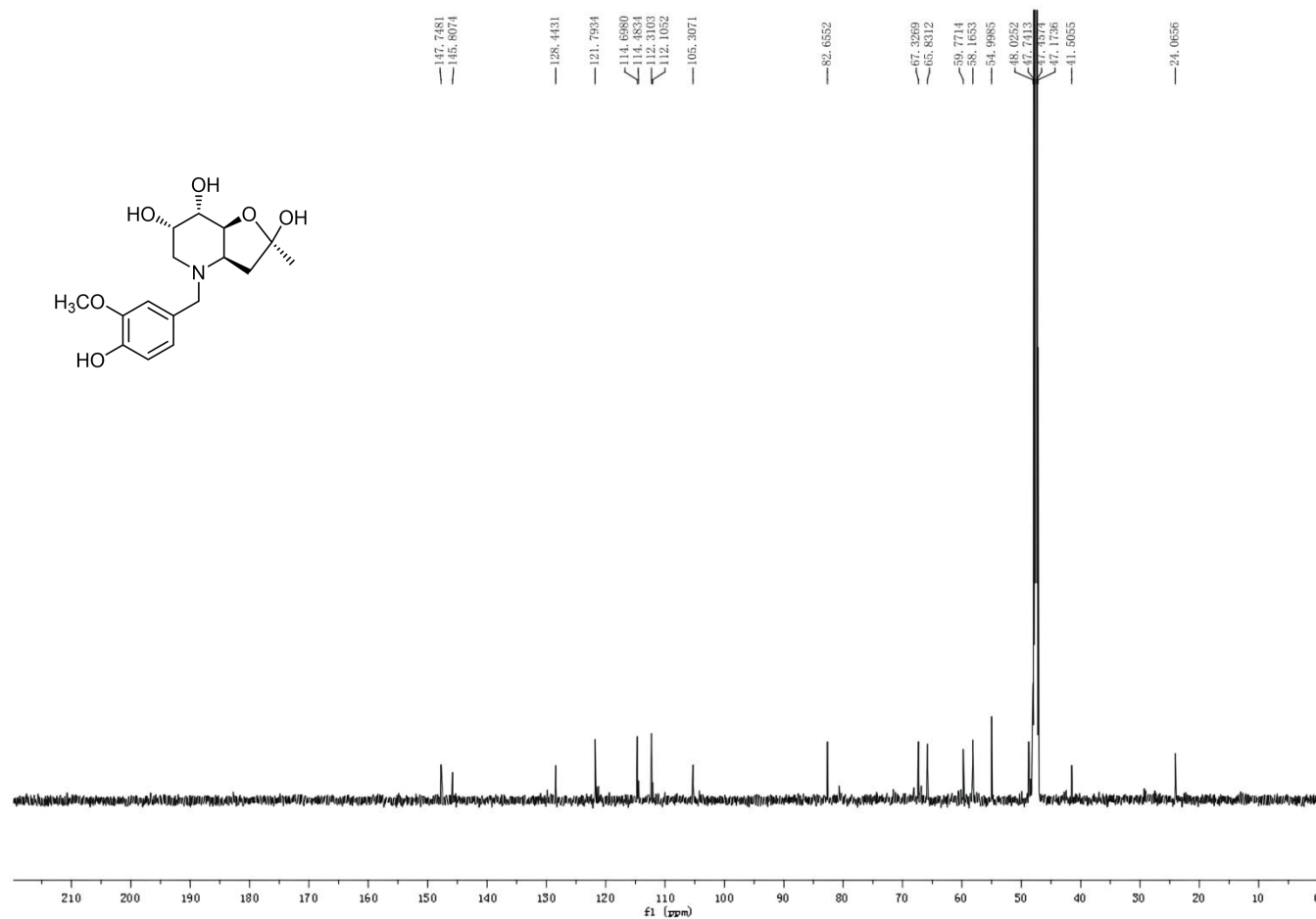


Figure S60. The ^{13}C -NMR of Compound 33.

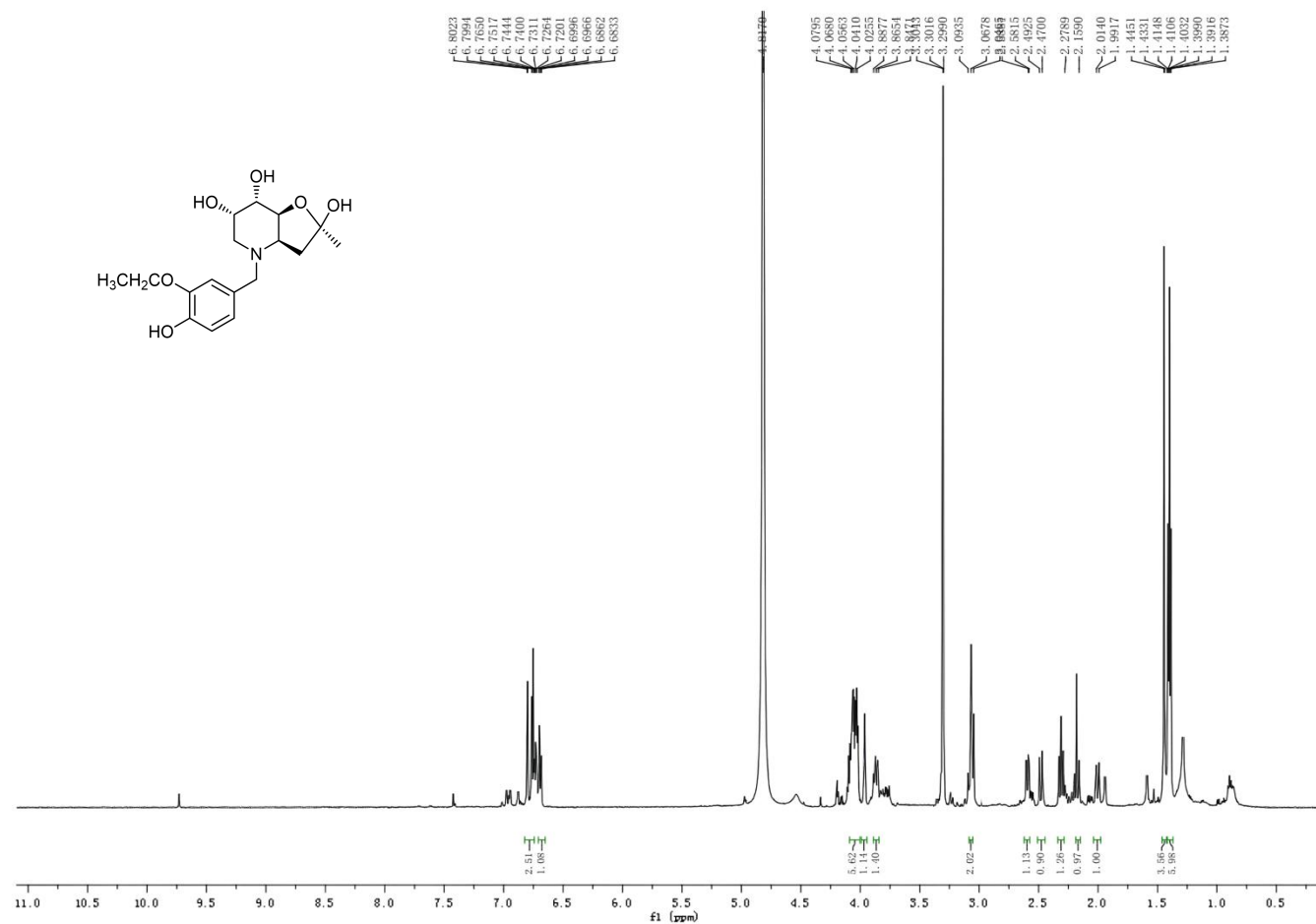


Figure S61. The ¹H NMR of compound 34.

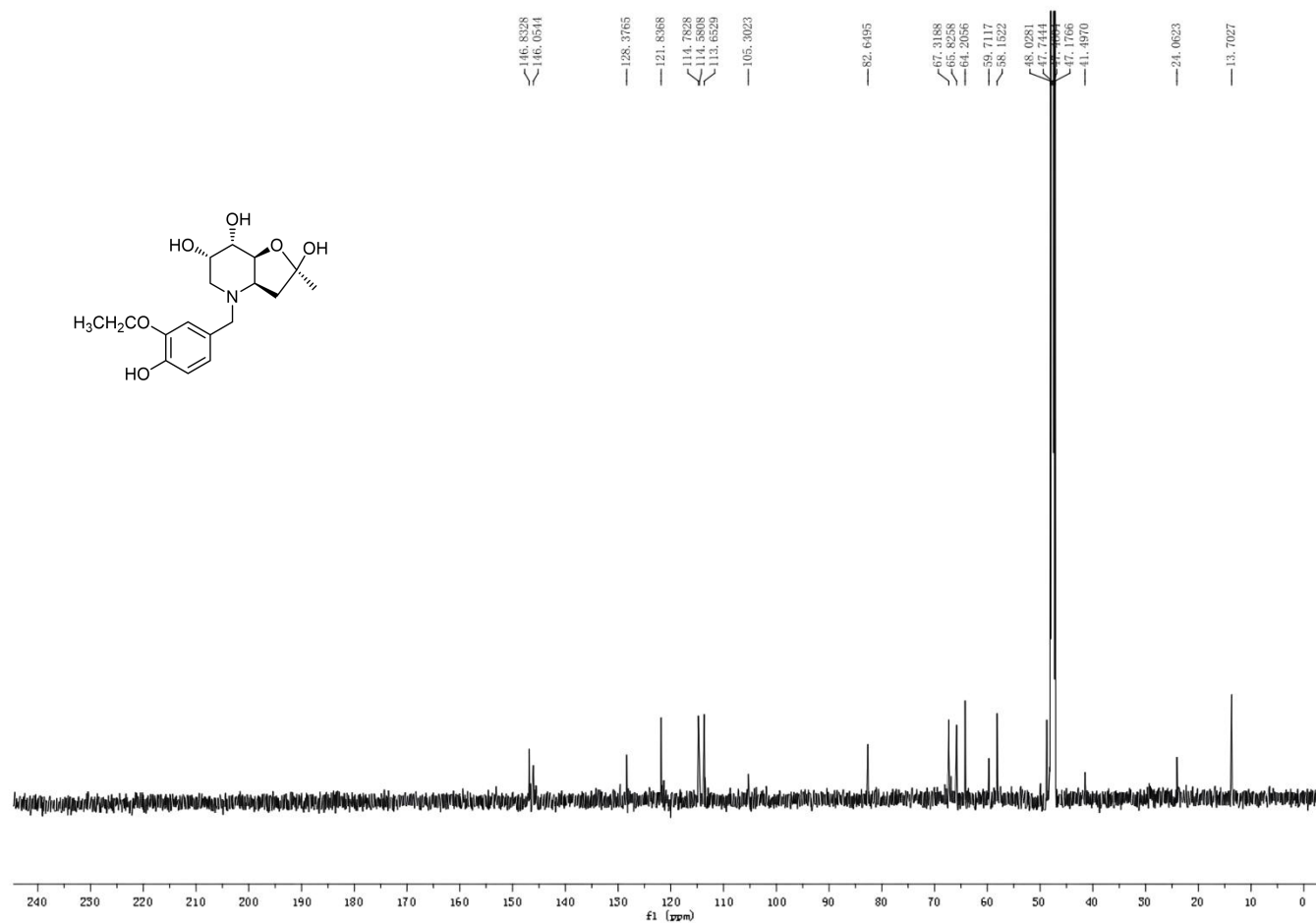


Figure S62. The ¹³C-NMR of Compound 34.