

Supporting Information

Palladium catalyzed decarboxylative β -C-glycosylation of glycals with oxazol-5-(4*H*)-ones as acceptors

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1. General information

Chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040-0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm). ^1H and ^{13}C NMR spectra were recorded on Bruker 400 MHz or 500 MHz spectrometer in CDCl_3 , acetone- d_6 or DMSO- d_6 with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^1H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; p = pentet; m = multiplet; brs = broad singlet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ , ppm). The enantiomeric excess values were determined by chiral HPLC with an Agilent instrument and a Daicel CHIRALCEL and CHIRALPAK column. High resolution mass spectroscopy (HRMS) analyses were performed at a Q-Exactive (Thermo Scientific) Inc mass instrument.

2. Substrates involved in the manuscript

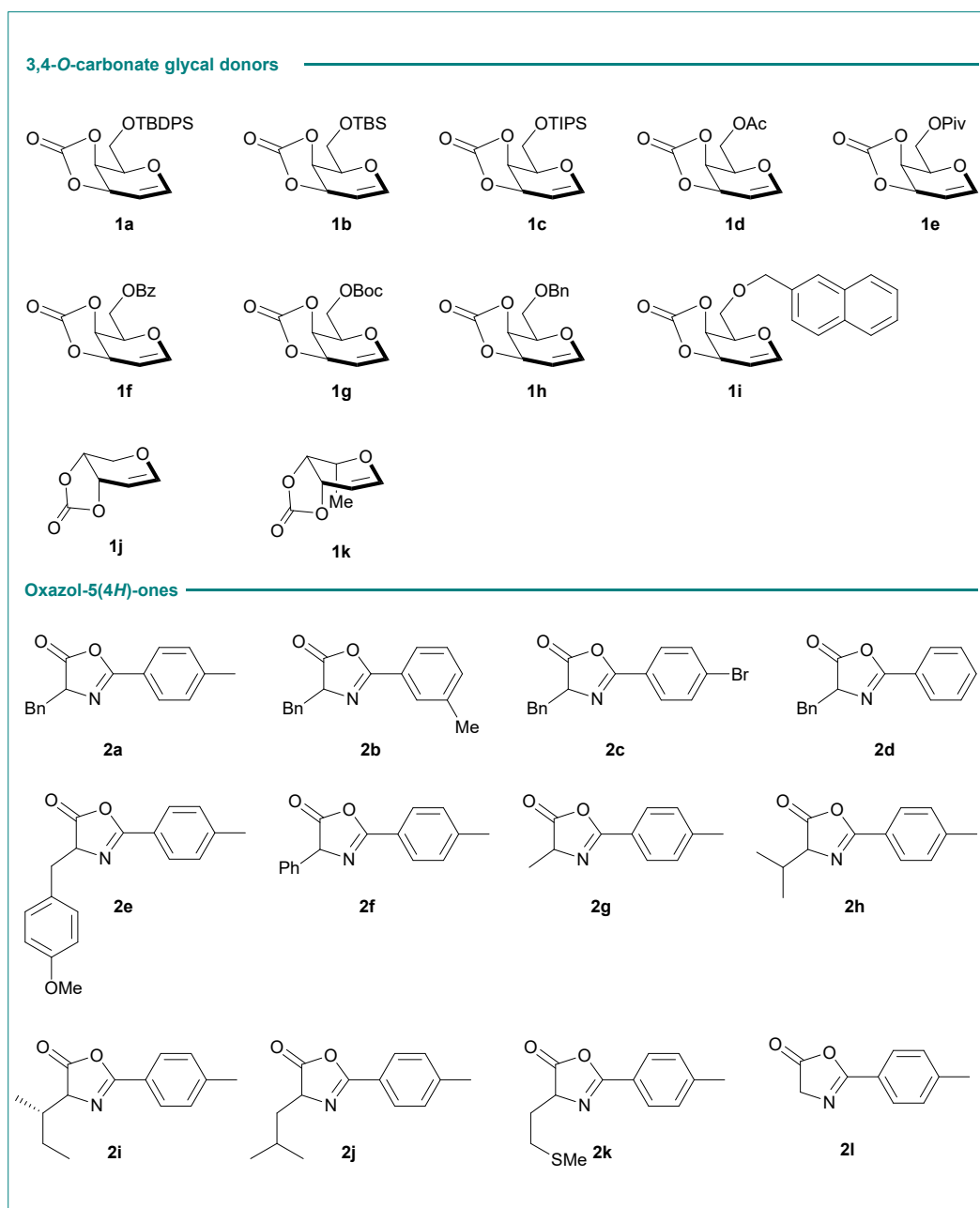
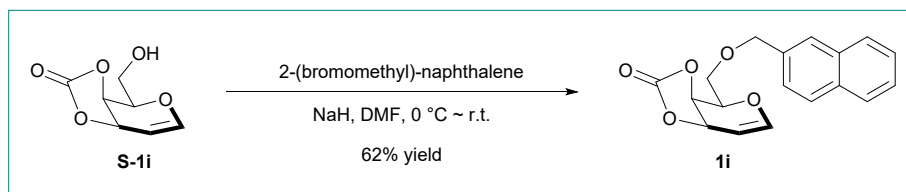


Figure S1. Substrates were investigated in the manuscript

3. Procedures for the preparation of substrates 1 and 2

3.1 Procedures for the preparation of 3,4-*O*-carbonate glycal donor 1

Galactal donors **1a-1h** were prepared according to the corresponding literatures¹ and **1i** was obtained as the following procedure.



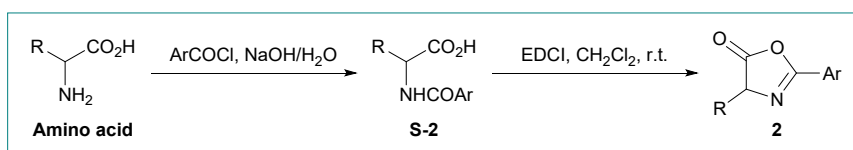
A solution of carbonate derivative **S-1i**^{1b} (226 mg, 1.3 mmol) in anhydrous DMF (2 mL) was slowly treated with sodium hydride (78 mg, 1.95 mmol) at 0 °C (ice bath). Ten minutes later, 2-(Bromomethyl)-naphthalene (431 mg, 1.95 mmol) was added, and the resulting mixture was stirred at room temperature overnight. The starting material was consumed completely indicated by TLC chromatography. The reaction mixture was cooled to 0 °C and quenched by NH₄Cl aqueous, then extracted by EtOAc (10 mL × 2), the combined organic phases were washed with water (15 mL) and brine (15 mL). The separated organic phase was dried over Na₂SO₄ and concentrated to provide the crude product which was purified by silica column chromatography (EtOAc/petroleum ether = 1/3). Galactal donor **1i** could be afforded as a white powder (62% yield), m.p. 69-71 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.86 – 7.83 (m, 3H), 7.78 (s, 1H), 7.51 – 7.44 (m, 3H), 6.68 (d, *J* = 6.3 Hz, 1H), 5.15 (ddd, *J* = 7.7, 3.1, 1.1 Hz, 1H), 4.96 – 4.91 (m, 2H), 4.75 (t, *J* = 12.4 Hz, 2H), 4.10 (td, *J* = 6.7, 1.6 Hz, 1H), 3.88 – 3.78 (m, 2H);

¹³C NMR (100 MHz, CDCl₃) δ 154.0, 149.2, 134.6, 133.2, 133.1, 128.4, 127.9, 127.7, 126.8, 126.3, 126.1, 125.6, 98.0, 73.9, 73.2, 72.5, 68.8, 68.0;

HRMS (ESI) *m/z*: [M+Na] calcd. for C₁₈H₁₆O₅Na, 335.0895; found, 335.0891.

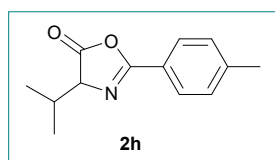
3.2 Procedures for the preparation of oxazol-5(4*H*)-ones 2



Oxazol-5(4*H*)-ones **2** were prepared according to the literature method.

Step 1, synthesis of *N*-benzoyl amino acid.² The corresponding commercially available amino acid (40 mmol, 1 equiv) was slowly dissolved in 2 N NaOH (50 mL, 100 mmol, 2.5 equiv) under 0 °C, benzoyl chloride (1.05 equiv) was added dropwise at this temperature. After the addition was complete, the mixture was stirred for additional 30 min at 0 °C. Subsequently, the mixture was allowed to warm to room temperature or 75 °C (for Val, Leu, Ile, Met) and was stirred for two additional hours. After cooling to 0 °C with ice bath, the reaction mixture was acidified with 6 N HCl to give a white precipitation. The total mixture was kept at 0 °C for an hour, after which a solid was collected, washed with cold water, and air-dried. Without further purification, the crude product was used for next step.

Step 2, synthesis of oxazol-5(4*H*)-ones **2.**³ To a suspension of *N*-benzoyl amino acid (10 mmol) in anhydrous CH₂Cl₂ (30 mL) was added EDCI•HCl (2.5 g, 13 mmol, 1.3 equiv) at room temperature. The reaction mixture was washed with water (20 mL) and brine (20 mL), then dried with Na₂SO₄. Removal of the solvent under reduced pressure to give crude product which was purified by silica column chromatography to provide desire oxazolone derivatives **2**. The NMR spectroscopic data of oxazol-5(4*H*)-ones **2a-2g** were identical to those in the previous report.

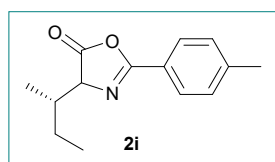


White powder, 79% yield, m.p. 47-49 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.30 (d, *J* = 4.4 Hz, 1H), 2.45 (s, 3H), 2.45 – 2.36 (m, 1H), 1.16 (d, *J* = 6.9 Hz, 3H), 1.04 (d, *J* = 6.9 Hz, 3H);

¹³C NMR (100 MHz, CDCl₃) δ 178.0, 161.7, 143.4, 129.5, 127.8, 123.1, 70.6, 31.2, 21.7, 18.7, 17.5;

HRMS (ESI) *m/z*: [M+H] calcd. for C₁₃H₁₆NO₂, 218.1181; found, 218.1177.



Colorless oil, 95% yield.

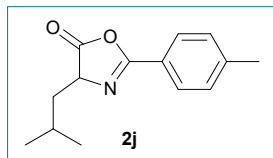
¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.88 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 4.40 (dz, *J* = 3.9 Hz, 0.54 H), 4.35 (d, *J* = 4.3 Hz, 0.46 H),

2.43 (s, 3H), 2.18 – 2.08 (m, 1H), 1.74 – 1.33 (m, 2H), 1.17 – 0.90 (m, 6H);

¹³C NMR (100 MHz, CDCl₃) δ 178.7, 177.9, 161.7, 161.6, 143.3, 129.5, 129.5, 127.8, 127.8,

123.1, 69.7, 69.1, 37.7, 26.2, 25.0, 21.7, 15.4, 14.4, 11.8, 11.7;

HRMS (ESI) m/z : $[M+H]$ calcd. for $C_{14}H_{18}NO_2$, 232.1338; found, 232.1332.

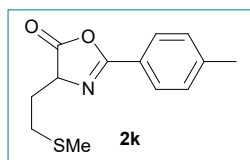


White powder, 87% yield, m.p. 58-60 °C.

1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, $J = 8.3$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 4.40 (dd, $J = 8.9, 5.7$ Hz, 1H), 2.43 (s, 3H), 2.11 – 2.01 (m, 1H), 1.83 (ddd, $J = 13.6, 7.8, 5.7$ Hz, 1H), 1.71 – 1.64 (m, 1H), 1.03 (d, $J = 6.7$ Hz, 3H), 1.01 (d, $J = 6.7$ Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 161.4, 143.3, 129.5, 127.8, 123.2, 63.9, 40.8, 25.2, 22.7, 22.0, 21.7;

HRMS (ESI) m/z : $[M+H]$ calcd. for $C_{14}H_{18}NO_2$, 232.1338; found, 232.1333.

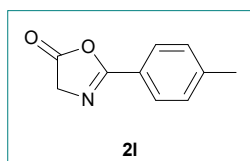


White powder, 79% yield, m.p. 139-141 °C.

1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 4.58 (dd, $J = 7.2, 5.8$ Hz, 1H), 2.73 (t, $J = 7.1$ Hz, 2H), 2.43 (s, 3H), 2.30 (dtd, $J = 14.1, 7.0, 5.8$ Hz, 1H), 2.18 – 2.09 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 162.1, 143.5, 129.5, 127.9, 123.0, 63.6, 30.5, 30.0, 21.7, 15.1;

HRMS (ESI) m/z : $[M+H]$ calcd. for $C_{13}H_{16}NO_2S$, 250.0902; found, 250.0897.



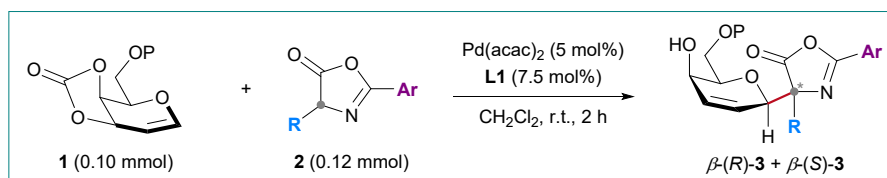
White powder, 75% yield, m.p. 92-94 °C.

1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, $J = 8.3$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 4.41 (s, 2H), 2.43 (s, 3H);

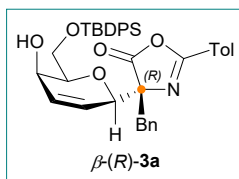
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 163.5, 143.6, 129.5, 127.8, 123.0, 55.0, 21.7;

HRMS (ESI) m/z : $[M+H]$ calcd. for $C_{10}H_{10}NO_2$, 176.0712; found, 176.0707.

4. β -C-glycosylation of glycols with oxazol-5-(4H)-ones



Under argon atmosphere, a resealable Schlenk tube equipped with a magnetic stir bar was charged with Pd(acac)₂ (1.5 mg, 5 mol%), ligand **L1** (4.1 mg, 7.5 mol%) and 3,4-*O*-carbonate glycol donor **1** (0.1 mmol) and oxazol-5(4*H*)-ones **2** (0.12 mmol). Then anhydrous CH₂Cl₂ (2 mL) was added and the resulting mixture was degassed and refilled in three cycles. The reaction mixture was stirred at room temperature and monitored by TLC until the glycol donor was consumed completely in two hours. The solvent was removed under reduced pressure to afford a crude product which was purified by preparative TLC (EtOAc/petroleum ether or CH₂Cl₂/MeOH) to yield 4-hydroxyl 2,3-unsaturated C-glycoside β -(*R*)-**3** and β -(*S*)-**3**. (*Note*: DABCO (1.2 equiv) was needed for substrates **2g-2i**).

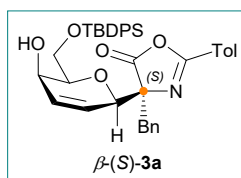


Compound β -(*R*)-**3a** was obtained as colorless syrup in 29% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.76 – 7.70 (m, 6H), 7.45 – 7.37 (m, 6H), 7.27 (d, J = 7.9 Hz, 2H), 7.20 – 7.12 (m, 5H), 6.26 (ddd, J = 10.4, 5.7, 2.0 Hz, 1H), 6.08 (dd, J = 10.3, 1.5 Hz, 1H), 4.60 (d, J = 2.0 Hz, 1H), 4.00 – 3.93 (m, 2H), 3.87 – 3.79 (m, 2H), 3.42 (d, J = 13.5 Hz, 1H), 3.31 (d, J = 13.5 Hz, 1H), 3.22 (d, J = 9.5 Hz, 1H), 2.36 (s, 3H), 0.99 (s, 9H);

^{13}C NMR (100 MHz, acetone- d_6) δ 177.5, 161.4, 144.3, 136.3, 136.3, 135.4, 134.4, 134.2, 131.9, 131.2, 130.5, 130.2, 128.8, 128.6, 128.5, 127.8, 123.7, 79.6, 78.0, 77.6, 64.5, 62.4, 39.5, 27.1, 21.5, 19.7;

HRMS (ESI) m/z : [M+Na] calcd. for $\text{C}_{39}\text{H}_{41}\text{NO}_5\text{SiNa}$, 654.2652; found, 654.2662.

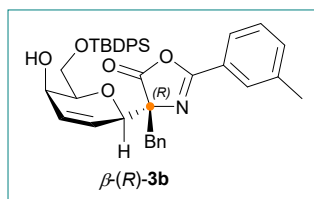


Compound β -(*S*)-**3a** was obtained as colorless syrup in 63% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.76 – 7.71 (m, 6H), 7.46 – 7.38 (m, 6H), 7.30 – 7.27 (m, 2H), 7.21 – 7.11 (m, 5H), 6.30 (ddd, J = 10.2, 5.8, 2.0 Hz, 1H), 6.14 (dd, J = 10.3, 1.8 Hz, 1H), 4.70 (d, J = 1.9 Hz, 1H), 3.96 (ddt, J = 7.5, 5.7, 1.7 Hz, 1H), 3.90 – 3.79 (m, 3H), 3.40 (d, J = 13.3 Hz, 1H), 3.31 (d, J = 13.3 Hz, 1H), 2.84 (d, J = 9.9 Hz, 1H), 2.37 (s, 3H), 1.04 (s, 9H);

^{13}C NMR (100 MHz, acetone- d_6) δ 177.9, 162.0, 144.4, 136.3, 136.2, 135.1, 134.3, 134.1, 131.8, 131.8, 131.2, 130.5, 130.3, 128.8, 128.6, 128.5, 128.5, 127.9, 127.8, 123.7, 79.3, 78.0, 77.8, 64.5, 62.4, 39.5, 27.1, 21.5, 19.7.;

HRMS (ESI) m/z : [M+Na] calcd. for $\text{C}_{39}\text{H}_{41}\text{NO}_5\text{SiNa}$, 654.2652; found, 654.2660.

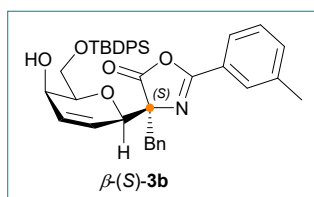


Compound β -(R)-**3b** was obtained as colorless syrup in 30% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.75 (dd, $J = 7.4, 1.8$ Hz, 2H), 7.71 – 7.69 (m, 2H), 7.65 – 7.62 (m, 2H), 7.45 – 7.31 (m, 8H), 7.22 – 7.11 (m, 5H), 6.28 (ddd, $J = 10.3, 5.7, 2.0$ Hz, 1H), 6.14 (dd, $J = 10.3, 1.6$ Hz, 1H), 4.61 (d, $J = 2.2$ Hz, 1H), 4.00 – 3.92 (m, 2H), 3.87 – 3.78 (m, 2H), 3.41 (d, $J = 13.5$ Hz, 1H), 3.34 (d, $J = 13.5$ Hz, 1H), 3.08 (d, $J = 9.2$ Hz, 1H), 2.33 (s, 3H), 0.98 (s, 9H);

^{13}C NMR (100 MHz, acetone- d_6) δ 177.5, 161.4, 139.4, 136.3, 136.3, 135.4, 134.4, 134.2, 134.1, 131.9, 131.2, 130.5, 130.5, 129.5, 128.9, 128.8, 128.6, 127.9, 126.5, 125.7, 79.6, 78.1, 77.7, 64.5, 62.4, 39.5, 27.0, 21.1, 19.6;

HRMS (ESI) m/z : [M+Na] calcd. for $\text{C}_{39}\text{H}_{41}\text{NO}_5\text{SiNa}$, 654.2652; found, 654.2658.

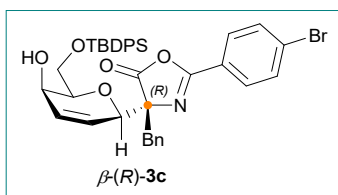


Compound β -(S)-**3b** was obtained as colorless syrup in 63% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.76 – 7.73 (m, 4H), 7.65 – 7.63 (m, 2H), 7.44 – 7.34 (m, 8H), 7.22 – 7.14 (m, 5H), 6.30 (ddd, $J = 10.3, 5.8, 1.9$ Hz, 1H), 6.15 (dd, $J = 10.3, 1.6$ Hz, 1H), 4.70 (d, $J = 2.0$ Hz, 1H), 3.99 – 3.95 (m, 1H), 3.91 – 3.79 (m, 3H), 3.41 (d, $J = 13.3$ Hz, 1H), 3.32 (d, $J = 13.3$ Hz, 1H), 2.81 (d, $J = 9.9$ Hz, 1H), 2.35 (s, 3H), 1.04 (s, 9H);

^{13}C NMR (100 MHz, acetone- d_6) δ 177.9, 162.0, 139.5, 136.3, 136.3, 135.1, 134.4, 134.3, 134.2, 131.8, 131.2, 130.5, 130.5, 129.6, 128.9, 128.8, 128.6, 128.6, 127.9, 127.8, 126.5, 125.7, 79.4, 78.1, 77.9, 64.6, 62.4, 39.5, 27.1, 21.1, 19.7;

HRMS (ESI) m/z : [M+Na] calcd. for $\text{C}_{39}\text{H}_{41}\text{NO}_5\text{SiNa}$, 654.2652; found, 654.2657.

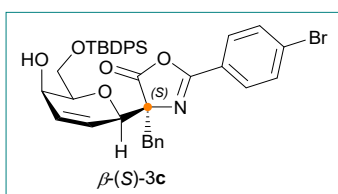


Compound β -(R)-3c was obtained as colorless syrup in 40% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.76 – 7.64 (m, 8H), 7.45 – 7.36 (m, 6H), 7.21 – 7.11 (m, 5H), 6.27 (ddd, J = 10.4, 5.6, 2.0 Hz, 1H), 6.16 (dd, J = 10.3, 1.5 Hz, 1H), 4.62 (d, J = 2.2 Hz, 1H), 4.00 – 3.91 (m, 2H), 3.88 – 3.75 (m, 2H), 3.42 (d, J = 13.5 Hz, 1H), 3.35 (d, J = 13.5 Hz, 1H), 3.13 (d, J = 9.0 Hz, 1H), 0.97 (s, 9H);

^{13}C NMR (100 MHz, acetone- d_6) δ 177.1, 160.6, 136.3, 136.3, 135.2, 134.3, 134.1, 132.9, 131.9, 131.1, 130.5, 130.5, 130.2, 128.8, 128.5, 127.9, 127.7, 127.7, 125.7, 79.7, 77.9, 77.8, 64.6, 62.4, 39.4, 27.0, 19.6;

HRMS (ESI) m/z : [M+Na] calcd. for $\text{C}_{38}\text{H}_{38}\text{BrNO}_5\text{SiNa}$, 718.1600; found, 718.1602.

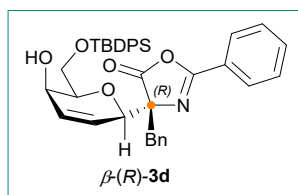


Compound β -(S)-3c was obtained as colorless syrup in 32% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.77 – 7.68 (m, 8H), 7.46 – 7.38 (m, 6H), 7.20 – 7.12 (m, 5H), 6.29 (ddd, J = 10.4, 5.7, 1.9 Hz, 1H), 6.18 (dd, J = 10.2, 1.6 Hz, 1H), 4.70 (d, J = 2.0 Hz, 1H), 3.98 – 3.95 (m, 1H), 3.89 – 3.77 (m, 3H), 3.43 (d, J = 13.4 Hz, 1H), 3.31 (d, J = 13.4 Hz, 1H), 2.87 (d, J = 8.8 Hz, 1H), 1.03 (s, 9H);

^{13}C NMR (100 MHz, acetone- d_6) δ 177.5, 161.2, 136.3, 136.3, 135.0, 134.3, 134.1, 133.0, 131.8, 131.2, 130.5, 130.3, 128.8, 128.6, 128.6, 128.0, 127.9, 127.7, 125.7, 79.5, 78.3, 77.9, 64.6, 62.4, 39.5, 27.1, 19.7;

HRMS (ESI) m/z : [M+Na] calcd. for $\text{C}_{38}\text{H}_{38}\text{BrNO}_5\text{SiNa}$, 718.1600; found, 718.1602.

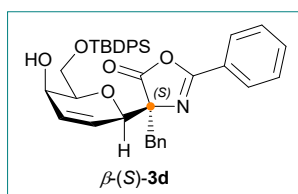


Compound $\beta(R)$ -**3d** was obtained as colorless syrup in 29% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.85 – 7.82 (m, 2H), 7.76 – 7.69 (m, 4H), 7.59 – 7.55 (m, 1H), 7.48 – 7.36 (m, 8H), 7.22 – 7.10 (m, 5H), 6.27 (ddd, $J = 10.3, 5.7, 2.1$ Hz, 1H), 6.13 (dd, $J = 10.3, 1.7$ Hz, 1H), 4.62 (d, $J = 1.9$ Hz, 1H), 4.00 – 3.92 (m, 2H), 3.88 – 3.79 (m, 2H), 3.43 (d, $J = 13.5$ Hz, 1H), 3.34 (d, $J = 13.5$ Hz, 1H), 3.17 (d, $J = 9.3$ Hz, 1H), 0.98 (s, 9H);

^{13}C NMR (100 MHz, acetone- d_6) δ 178.0, 162.0, 159.7, 144.4, 136.3, 136.3, 134.3, 134.2, 132.3, 131.8, 130.5, 130.3, 128.6, 128.6, 128.5, 127.8, 126.8, 123.8, 114.1, 79.3, 78.2, 77.8, 64.5, 62.4, 55.3, 38.7, 27.1, 21.5, 19.7;

HRMS (ESI) m/z : $[M+Na]$ calcd. for $\text{C}_{38}\text{H}_{39}\text{NO}_5\text{SiNa}$, 640.2495; found, 640.2502.

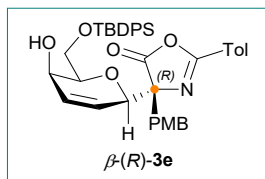


Compound $\beta(S)$ -**3d** was obtained as colorless syrup in 58% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.84 (dd, $J = 8.0, 1.4$ Hz, 2H), 7.76 – 7.73 (m, 4H), 7.62 – 7.58 (m, 1H), 7.50 – 7.38 (m, 8H), 7.22 – 7.13 (m, 5H), 6.30 (ddd, $J = 10.3, 5.7, 2.0$ Hz, 1H), 6.16 (dd, $J = 10.2, 1.6$ Hz, 1H), 4.70 (d, $J = 1.9$ Hz, 1H), 3.97 (ddd, $J = 9.8, 5.7, 1.7$ Hz, 1H), 3.91 – 3.80 (m, 3H), 3.43 (d, $J = 13.3$ Hz, 1H), 3.32 (d, $J = 13.3$ Hz, 1H), 2.85 (d, $J = 9.8$ Hz, 1H), 1.04 (s, 9H);

^{13}C NMR (100 MHz, acetone- d_6) δ 177.8, 161.9, 136.3, 136.3, 135.1, 134.3, 134.1, 133.6, 131.8, 131.2, 130.5, 130.5, 129.6, 128.8, 128.6, 128.5, 128.5, 127.9, 127.8, 126.6, 79.4, 78.1, 77.8, 64.6, 62.4, 39.5, 27.1, 19.7;

HRMS (ESI) m/z : $[M+Na]$ calcd. for $\text{C}_{38}\text{H}_{39}\text{NO}_5\text{SiNa}$, 640.2495; found, 640.2499.

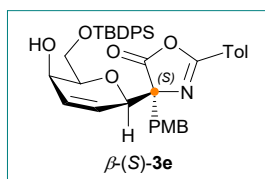


Compound β -(R)-3e was obtained as colorless syrup in 29% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.76 – 7.70 (m, 6H), 7.47 – 7.37 (m, 6H), 7.27 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 6.72 (d, J = 8.5 Hz, 2H), 6.26 (ddd, J = 10.3, 5.7, 2.0 Hz, 1H), 6.07 (dd, J = 10.3, 1.6 Hz, 1H), 4.58 (d, J = 2.2 Hz, 1H), 3.99 – 3.93 (m, 2H), 3.89 – 3.75 (m, 2H), 3.66 (s, 3H), 3.35 (d, J = 13.7 Hz, 1H), 3.25 (d, J = 13.7 Hz, 1H), 3.18 (d, J = 9.5 Hz, 1H), 2.36 (s, 3H), 1.00 (s, 9H);

^{13}C NMR (100 MHz, acetone- d_6) δ 177.6, 161.4, 159.7, 144.3, 136.3, 136.3, 134.4, 134.1, 132.2, 131.8, 130.5, 130.5, 130.2, 128.6, 128.5, 127.9, 127.0, 123.8, 114.1, 79.5, 78.0, 77.8, 64.5, 62.4, 55.3, 38.7, 27.1, 21.5, 19.7;

HRMS (ESI) m/z : [M+Na] calcd. for $\text{C}_{40}\text{H}_{43}\text{NO}_6\text{SiNa}$, 684.2757; found, 684.2765.

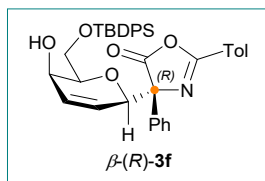


Compound β -(S)-3e was obtained as colorless syrup in 64% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.76 – 7.72 (m, 6H), 7.46 – 7.38 (m, 6H), 7.30 – 7.28 (m, 2H), 7.11 – 7.09 (m, 2H), 6.71 (d, J = 8.3 Hz, 2H), 6.30 (ddd, J = 10.5, 5.9, 2.0 Hz, 1H), 6.13 (dd, J = 10.4, 1.6 Hz, 1H), 4.67 (s, 1H), 3.98 – 3.94 (m, 1H), 3.90 – 3.79 (m, 3H), 3.66 (s, 3H), 3.33 (d, J = 13.5 Hz, 1H), 3.25 (d, J = 13.5 Hz, 1H), 2.83 (d, J = 10.1 Hz, 1H), 2.37 (s, 3H), 1.05 (s, 9H);

^{13}C NMR (100 MHz, acetone- d_6) δ 178.0, 162.0, 159.7, 144.4, 136.3, 136.3, 134.3, 134.2, 132.3, 131.8, 130.5, 130.3, 128.6, 128.6, 128.5, 127.8, 126.8, 123.8, 114.1, 79.3, 78.2, 77.8, 64.5, 62.4, 55.3, 38.7, 27.1, 21.5, 19.7;

HRMS (ESI) m/z : [M+Na] calcd. for $\text{C}_{40}\text{H}_{43}\text{NO}_6\text{SiNa}$, 684.2757; found, 684.2761.

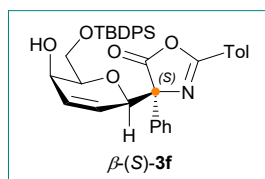


Compound β -(R)-**3f** was obtained as colorless syrup in 21% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.92 (d, J = 8.1 Hz, 2H), 7.78 – 7.75 (m, 2H), 7.70 – 7.68 (m, 2H), 7.63 – 7.61 (m, 2H), 7.49 – 7.33 (m, 11H), 6.19 (ddd, J = 10.3, 5.8, 2.2 Hz, 1H), 5.63 (dd, J = 10.3, 1.6 Hz, 1H), 4.83 (d, J = 2.0 Hz, 1H), 3.93 (ddt, J = 7.5, 5.8, 1.8 Hz, 1H), 3.85 (dd, J = 8.9, 4.1 Hz, 1H), 3.78 – 3.71 (m, 2H), 2.68 (d, J = 9.4 Hz, 1H), 2.39 (s, 3H), 0.93 (s, 9H);

^{13}C NMR (100 MHz, acetone- d_6) δ 176.2, 161.7, 144.5, 136.3, 136.3, 135.4, 134.3, 134.0, 131.9, 130.5, 130.3, 129.6, 129.5, 128.8, 128.6, 128.5, 127.7, 127.2, 123.9, 79.9, 79.4, 78.4, 64.3, 62.2, 27.0, 21.6, 19.6;

HRMS (ESI) m/z : [M+Na] calcd. for $\text{C}_{38}\text{H}_{39}\text{NO}_5\text{SiNa}$, 640.2495; found, 640.2505.

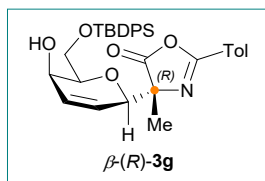


Compound β -(S)-**3f** was obtained as colorless syrup in 69% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.97 (d, J = 8.0 Hz, 2H), 7.80 – 7.78 (m, 2H), 7.72 – 7.68 (m, 4H), 7.49 – 7.37 (m, 11H), 6.19 (ddd, J = 10.2, 5.8, 1.9 Hz, 1H), 5.60 (dd, J = 10.4, 1.7 Hz, 1H), 5.01 (d, J = 2.0 Hz, 1H), 3.95 – 3.90 (m, 1H), 3.87 – 3.80 (m, 2H), 3.74 – 3.70 (m, 1H), 2.81 (d, J = 9.4 Hz, 1H), 2.43 (s, 3H), 1.02 (s, 9H);

^{13}C NMR (100 MHz, acetone- d_6) δ 177.6, 162.4, 144.7, 136.2, 136.2, 135.8, 134.3, 134.0, 131.3, 130.5, 130.4, 130.4, 129.6, 129.6, 128.8, 128.6, 128.5, 127.2, 127.1, 123.9, 80.7, 79.4, 77.3, 64.5, 62.1, 27.1, 21.6, 19.6;

HRMS (ESI) m/z : [M+Na] calcd. for $\text{C}_{38}\text{H}_{39}\text{NO}_5\text{SiNa}$, 640.2495; found, 640.2498.

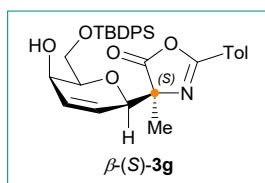


Compound β -(R)-3g was obtained as colorless syrup in 32% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.85 (d, J = 8.0 Hz, 2H), 7.73 – 7.70 (m, 2H), 7.67 – 7.65 (m, 2H), 7.46 – 7.32 (m, 8H), 6.24 (ddd, J = 10.3, 5.7, 2.1 Hz, 1H), 6.05 (dd, J = 10.3, 1.6 Hz, 1H), 4.45 (d, J = 2.0 Hz, 1H), 3.97 – 3.93 (m, 1H), 3.90 – 3.85 (m, 1H), 3.77 – 3.72 (m, 2H), 2.89 (d, J = 9.4 Hz, 1H), 2.39 (s, 3H), 1.56 (s, 3H), 0.96 (s, 9H);

^{13}C NMR (100 MHz, acetone- d_6) δ 178.7, 161.3, 144.2, 136.3, 136.3, 134.3, 134.1, 131.6, 130.5, 130.5, 130.2, 128.6, 128.5, 127.8, 124.2, 79.3, 78.6, 72.8, 64.3, 62.3, 27.0, 21.5, 19.8, 19.6;

HRMS (ESI) m/z : [M+Na] calcd. for $\text{C}_{33}\text{H}_{37}\text{NO}_5\text{SiNa}$, 578.2339; found, 578.2342.

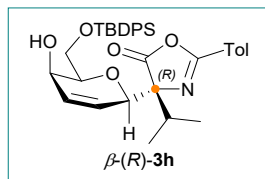


Compound β -(S)-3g was obtained as colorless syrup in 56% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.85 (d, J = 7.9 Hz, 2H), 7.72 – 7.69 (m, 4H), 7.45 – 7.34 (m, 8H), 6.27 (ddd, J = 10.4, 5.8, 1.9 Hz, 1H), 6.13 (dd, J = 10.2, 1.7 Hz, 1H), 4.53 (d, J = 2.0 Hz, 1H), 3.96 – 3.91 (m, 1H), 3.83 – 3.76 (m, 2H), 3.73 – 3.67 (m, 1H), 2.73 (d, J = 9.8 Hz, 1H), 2.41 (s, 3H), 1.56 (s, 3H), 1.01 (s, 9H);

^{13}C NMR (100 MHz, acetone- d_6) δ 179.5, 161.8, 144.3, 136.3, 136.2, 134.3, 134.1, 131.4, 130.5, 130.3, 128.6, 128.6, 128.5, 127.6, 124.2, 79.1, 78.5, 72.8, 64.4, 62.3, 27.1, 21.6, 19.7, 19.6;

HRMS (ESI) m/z : [M+H] calcd. for $\text{C}_{33}\text{H}_{38}\text{NO}_5\text{Si}$, 556.2519; found, 556.2519.

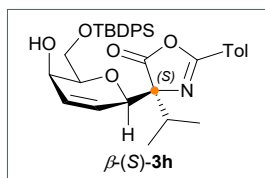


Compound β -(*R*)-**3h** was obtained as colorless syrup in 21% yield.

¹H NMR (400 MHz, acetone-*d*₆) δ 7.87 (d, J = 8.0 Hz, 2H), 7.70 – 7.68 (m, 2H), 7.65 – 7.63 (m, 2H), 7.45 – 7.32 (m, 8H), 6.24 (ddd, J = 10.4, 5.7, 2.1 Hz, 1H), 6.03 (dd, J = 10.3, 1.5 Hz, 1H), 4.66 (d, J = 2.0 Hz, 1H), 3.94 – 3.90 (m, 1H), 3.86 – 3.79 (m, 1H), 3.76 – 3.70 (m, 2H), 2.75 (d, J = 9.6 Hz, 1H), 2.49 (hept, J = 7.1 Hz, 1H), 2.39 (s, 3H), 1.09 (d, J = 6.8 Hz, 3H), 0.94 (s, 9H), 0.90 (d, J = 6.7 Hz, 3H);

¹³C NMR (100 MHz, acetone-*d*₆) δ 178.5, 161.8, 144.3, 136.3, 134.3, 134.0, 131.9, 130.5, 130.3, 128.7, 128.5, 127.2, 123.9, 80.2, 79.4, 76.5, 64.4, 62.4, 32.1, 27.0, 21.5, 19.6, 17.3, 17.0;

HRMS (ESI) m/z : [M+Na] calcd. for C₃₅H₄₁NO₅SiNa, 606.2652; found, 606.2658.

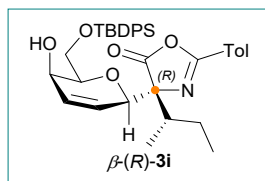


Compound β -(*S*)-**3h** was obtained as colorless syrup in 59% yield.

¹H NMR (400 MHz, acetone-*d*₆) δ 7.89 (d, J = 8.0 Hz, 2H), 7.76 – 7.73 (m, 4H), 7.48 – 7.38 (m, 8H), 6.25 (ddd, J = 10.2, 5.9, 1.9 Hz, 1H), 5.85 (dd, J = 10.2, 1.7 Hz, 1H), 4.74 (d, J = 1.9 Hz, 1H), 3.94 – 3.78 (m, 4H), 2.61 (hept, J = 7.1 Hz, 1H), 2.57 (d, J = 10.4 Hz, 1H), 2.43 (s, 3H), 1.07 – 1.04 (m, 12H), 0.96 (d, J = 6.8 Hz, 3H);

¹³C NMR (100 MHz, acetone-*d*₆) δ 178.7, 162.4, 144.6, 136.3, 136.3, 134.3, 134.2, 132.2, 130.5, 130.5, 128.7, 128.6, 127.7, 123.7, 79.7, 79.2, 75.3, 64.5, 62.3, 31.7, 27.1, 21.6, 19.7, 17.1, 16.7;

HRMS (ESI) m/z : [M+Na] calcd. for C₃₅H₄₁NO₅SiNa, 606.2652; found, 606.2656.

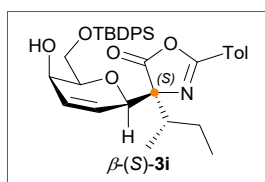


Compound β -(*R*)-**3i** was obtained as colorless syrup in 28% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.87 (d, J = 7.9 Hz, 2H), 7.69 – 7.67 (m, 2H), 7.63 – 7.60 (m, 2H), 7.43 – 7.31 (m, 8H), 6.26 (ddd, J = 10.4, 5.8, 2.0 Hz, 1H), 6.09 (d, J = 10.4 Hz, 1H), 4.68 (d, J = 2.0 Hz, 1H), 3.91 (dd, J = 9.1, 6.3 Hz, 1H), 3.84 – 3.77 (m, 1H), 3.73 – 3.67 (m, 2H), 2.59 (d, J = 9.7 Hz, 1H), 2.38 (s, 3H), 2.18 (ddt, J = 10.4, 7.0, 3.5 Hz, 1H), 1.12 – 1.00 (m, 5H), 0.92 – 0.86 (m, 12H);

^{13}C NMR (100 MHz, acetone- d_6) δ 178.9, 161.6, 144.2, 136.2, 134.3, 134.0, 131.9, 130.5, 130.3, 128.6, 128.5, 128.5, 127.1, 124.0, 80.9, 79.3, 76.5, 64.3, 62.4, 38.9, 27.0, 24.9, 21.5, 19.6, 13.2, 11.9;

HRMS (ESI) m/z : [M+Na] calcd. for $\text{C}_{36}\text{H}_{43}\text{NO}_5\text{SiNa}$, 620.2808; found, 620.2814.

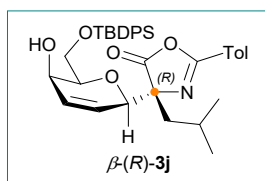


Compound β -(*S*)-**3i** was obtained as colorless syrup in 49% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.88 (d, J = 8.0 Hz, 2H), 7.74 – 7.72 (m, 4H), 7.45 – 7.37 (m, 8H), 6.26 (ddd, J = 10.2, 5.9, 1.9 Hz, 1H), 5.90 (dd, J = 10.2, 1.7 Hz, 1H), 4.81 (d, J = 2.0 Hz, 1H), 3.91 (dd, J = 10.4, 6.0 Hz, 1H), 3.86 – 3.80 (m, 3H), 2.57 (d, J = 10.5 Hz, 1H), 2.43 (s, 3H), 2.33 (dq, J = 10.1, 7.0, 3.1 Hz, 1H), 1.68 (dq, J = 15.0, 7.4, 2.9 Hz, 1H), 1.19 (ddd, J = 13.4, 10.4, 7.1 Hz, 1H), 1.03 (s, 9H), 0.99 (d, J = 6.9 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H);

^{13}C NMR (100 MHz, acetone- d_6) δ 178.6, 162.4, 144.6, 136.3, 136.3, 134.2, 134.1, 132.1, 130.5, 130.4, 128.6, 128.6, 128.6, 127.7, 123.7, 79.8, 79.1, 75.3, 64.5, 62.3, 38.0, 27.1, 23.8, 21.6, 19.6, 12.7, 11.9;

HRMS (ESI) m/z : [M+Na] calcd. for $\text{C}_{36}\text{H}_{43}\text{NO}_5\text{SiNa}$, 620.2808; found, 620.2812.

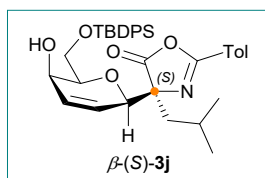


Compound β -(*R*)-**3j** was obtained as colorless syrup in 32% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.88 (d, J = 8.0 Hz, 2H), 7.72 – 7.69 (m, 2H), 7.66 – 7.64 (m, 2H), 7.46 – 7.32 (m, 8H), 6.23 (ddd, J = 10.3, 5.7, 2.1 Hz, 1H), 6.03 (dd, J = 10.4, 1.1 Hz, 1H), 4.46 (d, J = 2.3 Hz, 1H), 3.93 (dd, J = 8.9, 6.1 Hz, 1H), 3.85 (dt, J = 9.9, 5.0 Hz, 1H), 3.76 – 3.70 (m, 2H), 2.83 (d, J = 9.4 Hz, 1H), 2.39 (s, 3H), 2.14 (dd, J = 14.0, 4.9 Hz, 1H), 1.83 (dd, J = 14.0, 8.0 Hz, 1H), 1.68 – 1.59 (m, 1H), 0.95 (s, 9H), 0.91 (d, J = 6.7 Hz, 3H), 0.82 (d, J = 6.6 Hz, 3H);

^{13}C NMR (100 MHz, acetone- d_6) δ 179.1, 161.3, 144.3, 136.3, 136.3, 134.3, 134.0, 131.8, 130.5, 130.5, 130.3, 128.6, 128.5, 127.6, 124.1, 79.3, 78.9, 76.2, 64.3, 62.3, 42.1, 27.0, 25.4, 24.4, 23.0, 21.5, 19.6;

HRMS (ESI) m/z : [M+Na] calcd. for $\text{C}_{36}\text{H}_{43}\text{NO}_5\text{SiNa}$, 620.2808; found, 620.2808.

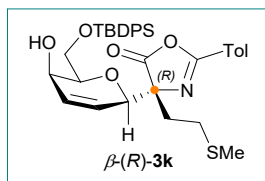


Compound β -(*S*)-**3j** was obtained as colorless syrup in 45% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.87 (d, J = 8.0 Hz, 2H), 7.73 – 7.71 (m, 4H), 7.45 – 7.36 (m, 8H), 6.24 (ddd, J = 10.4, 5.8, 1.9 Hz, 1H), 6.06 (dd, J = 10.3, 1.6 Hz, 1H), 4.50 (d, J = 2.0 Hz, 1H), 3.93 – 3.89 (m, 1H), 3.83 – 3.71 (m, 3H), 2.68 (d, J = 9.8 Hz, 1H), 2.42 (s, 3H), 2.08 (dd, J = 14.1, 6.0 Hz, 1H), 1.92 (dd, J = 14.1, 6.6 Hz, 1H), 1.64 – 1.55 (m, 1H), 1.02 (s, 9H), 0.88 (d, J = 6.6 Hz, 3H), 0.85 (d, J = 6.6 Hz, 3H);

^{13}C NMR (100 MHz, acetone- d_6) δ 179.4, 161.9, 144.5, 136.3, 136.3, 134.3, 134.1, 131.6, 130.5, 130.4, 128.6, 128.6, 128.5, 127.9, 124.0, 79.2, 78.7, 76.6, 64.4, 62.3, 42.0, 27.1, 25.5, 24.2, 23.6, 21.6, 19.6;

HRMS (ESI) m/z : [M+Na] calcd. for $\text{C}_{36}\text{H}_{43}\text{NO}_5\text{SiNa}$, 620.2808; found, 620.2814.

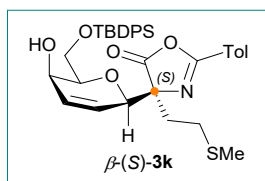


Compound β -(*R*)-**3k** was obtained as colorless syrup in 36% yield.

¹H NMR (400 MHz, acetone-*d*₆) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.73 – 7.71 (m, 2H), 7.68 – 7.66 (m, 2H), 7.46 – 7.32 (m, 8H), 6.24 (ddd, *J* = 10.3, 5.8, 2.1 Hz, 1H), 6.02 (dd, *J* = 10.7, 1.7 Hz, 1H), 4.50 (d, *J* = 2.0 Hz, 1H), 3.96 – 3.92 (m, 1H), 3.90 – 3.85 (m, 1H), 3.79 – 3.71 (m, 2H), 2.97 (d, *J* = 9.3 Hz, 1H), 2.58 – 2.51 (m, 1H), 2.46 – 2.28 (m, 6H), 2.00 (s, 3H), 0.97 (s, 9H);

¹³C NMR (100 MHz, acetone-*d*₆) δ 178.4, 162.3, 144.4, 136.3, 136.3, 134.3, 134.1, 131.9, 130.5, 130.5, 130.3, 128.7, 128.5, 127.5, 124.1, 79.4, 78.3, 75.5, 64.3, 62.3, 32.4, 29.2, 27.0, 21.6, 19.6, 14.8;

HRMS (ESI) *m/z*: [M+Na] calcd. for C₃₅H₄₁NO₅SSiNa, 638.2372; found, 638.2374.

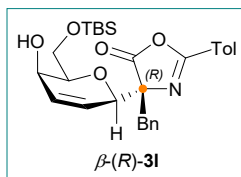


Compound β -(*S*)-**3k** was obtained as colorless syrup in 49% yield.

¹H NMR (400 MHz, acetone-*d*₆) 7.87 (d, *J* = 8.0 Hz, 2H), 7.74 – 7.72 (m, 4H), 7.46 – 7.35 (m, 8H), 6.25 (ddd, *J* = 10.4, 5.7, 1.9 Hz, 1H), 6.06 (dd, *J* = 10.3, 1.6 Hz, 1H), 4.57 (d, *J* = 2.0 Hz, 1H), 3.95 – 3.91 (m, 1H), 3.86 – 3.73 (m, 3H), 2.75 (d, *J* = 9.7 Hz, 1H), 2.55 – 2.48 (m, 1H), 2.44 – 2.31 (m, 6H), 2.01 (s, 3H), 1.03 (s, 9H);

¹³C NMR (100 MHz, acetone-*d*₆) δ 178.8, 162.7, 144.5, 136.3, 136.3, 134.3, 134.1, 131.8, 130.5, 130.4, 128.7, 128.6, 128.5, 127.7, 124.0, 79.3, 78.1, 76.0, 64.4, 62.3, 32.7, 28.9, 27.1, 21.6, 19.6, 14.9;

HRMS (ESI) *m/z*: [M+Na] calcd. for C₃₅H₄₁NO₅SSiNa, 638.2372; found, 638.2377.

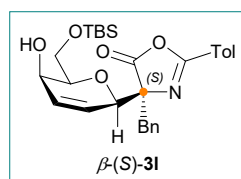


Compound β -(*R*)-**3I** was obtained as colorless syrup in 32% yield.

¹H NMR (400 MHz, acetone-*d*₆) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.10 (m, 5H), 6.27 (ddd, *J* = 10.4, 5.8, 2.0 Hz, 1H), 6.11 (dd, *J* = 10.2, 1.6 Hz, 1H), 4.59 (d, *J* = 2.1 Hz, 1H), 3.93 – 3.89 (m, 1H), 3.85 (dd, *J* = 10.5, 5.6 Hz, 1H), 3.72 (dd, *J* = 10.5, 6.3 Hz, 1H), 3.61 (ddd, *J* = 7.1, 4.0, 1.5 Hz, 1H), 3.40 (d, *J* = 13.4 Hz, 1H), 3.33 (d, *J* = 13.5 Hz, 1H), 2.99 (d, *J* = 9.4 Hz, 1H), 2.38 (s, 3H), 0.84 (s, 9H), 0.00 (s, 6H);

¹³C NMR (100 MHz, acetone-*d*₆) δ 177.6, 161.3, 144.3, 135.3, 132.0, 131.2, 130.2, 128.8, 128.5, 127.8, 127.7, 123.8, 79.6, 78.0, 77.7, 63.7, 62.2, 39.6, 26.2, 21.5, 18.8, -5.1, -5.4;

HRMS (ESI) *m/z*: [M+Na] calcd. for C₂₉H₃₇NO₅SiNa, 530.2339; found, 530.2342.

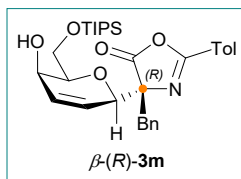


Compound β -(*S*)-**3I** was obtained as colorless syrup in 67% yield.

¹H NMR (400 MHz, acetone-*d*₆) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.12 (m, 5H), 6.30 (ddd, *J* = 10.3, 5.9, 1.9 Hz, 1H), 6.13 (dd, *J* = 10.2, 1.7 Hz, 1H), 4.66 (d, *J* = 2.0 Hz, 1H), 3.90 – 3.86 (m, 1H), 3.77 (dd, *J* = 10.1, 5.6 Hz, 1H), 3.71 – 3.62 (m, 2H), 3.40 (d, *J* = 13.3 Hz, 1H), 3.28 (d, *J* = 13.3 Hz, 1H), 2.69 (d, *J* = 10.0 Hz, 1H), 2.39 (s, 3H), 0.89 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H);

¹³C NMR (100 MHz, acetone-*d*₆) δ 177.9, 162.0, 144.4, 135.1, 131.9, 131.2, 130.3, 128.8, 128.5, 127.9, 127.7, 123.8, 79.2, 78.1, 77.8, 63.5, 62.1, 39.5, 26.2, 21.5, 18.8, -5.2, -5.4;

HRMS (ESI) *m/z*: [M+H] calcd. for C₂₉H₃₈NO₅Si, 508.2519; found, 508.2517.

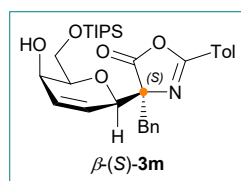


Compound β -(R)-3m was obtained as colorless syrup in 33% yield.

$^1\text{H NMR}$ (400 MHz, acetone- d_6) δ 7.72 (d, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.21 – 7.10 (m, 5H), 6.28 (ddd, $J = 10.4, 5.8, 2.0$ Hz, 1H), 6.08 (dd, $J = 10.3, 1.6$ Hz, 1H), 4.61 (d, $J = 2.0$ Hz, 1H), 3.98 – 3.93 (m, 2H), 3.83 (dd, $J = 10.2, 6.2$ Hz, 1H), 3.66 (td, $J = 6.0, 1.7$ Hz, 1H), 3.42 (d, $J = 13.4$ Hz, 1H), 3.32 (d, $J = 13.5$ Hz, 1H), 3.02 (d, $J = 9.5$ Hz, 1H), 2.38 (s, 3H), 1.11 – 0.97 (m, 21H);

$^{13}\text{C NMR}$ (100 MHz, acetone- d_6) δ 177.6, 161.3, 144.3, 135.3, 132.0, 131.2, 130.2, 128.8, 128.5, 127.8, 127.7, 123.8, 79.7, 78.1, 77.8, 64.0, 62.3, 39.6, 21.5, 18.3, 12.6;

HRMS (ESI) m/z : $[M+Na]$ calcd. for $\text{C}_{32}\text{H}_{43}\text{NO}_5\text{SiNa}$, 572.2808; found, 572.2813.

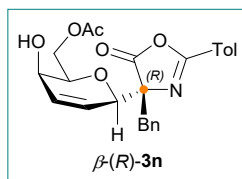


Compound β -(S)-3m was obtained as colorless syrup in 65% yield.

$^1\text{H NMR}$ (400 MHz, acetone- d_6) δ 7.73 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 7.9$ Hz, 2H), 7.21 – 7.12 (m, 5H), 6.31 (ddd, $J = 10.3, 5.9, 1.9$ Hz, 1H), 6.13 (dd, $J = 10.2, 1.7$ Hz, 1H), 4.68 (d, $J = 2.0$ Hz, 1H), 3.94 – 3.85 (m, 2H), 3.79 (dd, $J = 10.1, 6.2$ Hz, 1H), 3.69 (td, $J = 6.1, 1.6$ Hz, 1H), 3.40 (d, $J = 13.3$ Hz, 1H), 3.29 (d, $J = 13.3$ Hz, 1H), 2.73 (d, $J = 10.1$ Hz, 1H), 2.39 (s, 3H), 1.15 – 1.01 (m, 21H);

$^{13}\text{C NMR}$ (100 MHz, acetone- d_6) δ 177.9, 162.0, 144.4, 135.2, 132.0, 131.2, 130.3, 128.8, 128.5, 127.9, 127.7, 123.8, 79.3, 78.1, 77.8, 63.9, 62.2, 39.5, 21.5, 18.3, 18.3, 12.6;

HRMS (ESI) m/z : $[M+H]$ calcd. for $\text{C}_{32}\text{H}_{44}\text{NO}_5\text{Si}$, 550.2989; found, 550.2993.

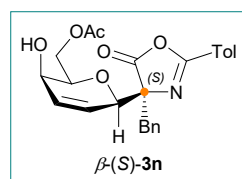


Compound β -(R)-3n was obtained as colorless syrup in 34% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.74 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.22 – 7.11 (m, 5H), 6.24 (ddd, J = 10.3, 5.6, 2.1 Hz, 1H), 6.12 (dd, J = 10.3, 1.7 Hz, 1H), 4.54 (d, J = 2.0 Hz, 1H), 4.30 (dd, J = 11.6, 7.6 Hz, 1H), 4.16 (dd, J = 11.6, 4.7 Hz, 1H), 3.93 (ddt, J = 7.7, 5.7, 2.1 Hz, 1H), 3.80 (ddd, J = 7.2, 4.7, 2.2 Hz, 1H), 3.51 (d, J = 9.2 Hz, 1H), 3.39 (d, J = 13.5 Hz, 1H), 3.34 (d, J = 13.5 Hz, 1H), 2.39 (s, 3H), 1.89 (s, 3H);

^{13}C NMR (100 MHz, acetone- d_6) δ 177.3, 170.8, 161.5, 144.3, 135.3, 131.4, 131.2, 130.2, 128.8, 128.5, 127.8, 127.8, 123.8, 77.7, 77.4, 76.7, 64.3, 62.3, 39.2, 21.5, 20.6;

HRMS (ESI) m/z : [M+H] calcd. for $\text{C}_{25}\text{H}_{26}\text{NO}_6$, 436.1760; found, 436.1763.

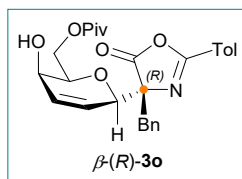


Compound β -(S)-3n was obtained as colorless syrup in 60% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.74 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 7.23 – 7.13 (m, 5H), 6.26 (ddd, J = 10.3, 5.7, 1.9 Hz, 1H), 6.14 (dd, J = 10.3, 1.6 Hz, 1H), 4.63 (d, J = 2.2 Hz, 1H), 4.21 – 4.12 (m, 2H), 3.92 – 3.88 (m, 1H), 3.82 (ddd, J = 7.0, 4.8, 1.8 Hz, 1H), 3.42 (d, J = 13.3 Hz, 1H), 3.27 (d, J = 13.3 Hz, 1H), 3.08 (d, J = 9.6 Hz, 1H), 2.39 (s, 3H), 2.01 (s, 3H);

^{13}C NMR (100 MHz, acetone- d_6) δ 177.1, 170.0, 161.2, 143.6, 134.3, 130.5, 130.4, 129.5, 128.0, 127.7, 127.1, 127.0, 123.0, 77.1, 76.7, 75.7, 63.6, 61.5, 38.7, 20.7, 19.9;

HRMS (ESI) m/z : [M+H] calcd. for $\text{C}_{25}\text{H}_{26}\text{NO}_6$, 436.1760; found, 436.1757.

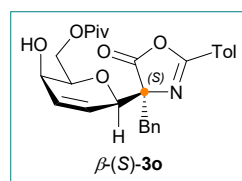


Compound β -(R)-**3o** was obtained as colorless syrup in 35% yield.

¹H NMR (400 MHz, acetone-*d*₆) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.29 – 7.11 (m, 5H), 6.25 (ddd, *J* = 10.4, 5.5, 2.0 Hz, 1H), 6.14 (dd, *J* = 10.3, 1.5 Hz, 1H), 4.55 (d, *J* = 2.1 Hz, 1H), 4.28 (dd, *J* = 11.3, 7.7 Hz, 1H), 4.18 (dd, *J* = 11.6, 4.5 Hz, 1H), 3.96 – 3.92 (m, 1H), 3.82 (ddd, *J* = 7.2, 4.5, 2.0 Hz, 1H), 3.46 (d, *J* = 9.2 Hz, 1H), 3.40 (d, *J* = 13.5 Hz, 1H), 3.33 (d, *J* = 13.5 Hz, 1H), 2.38 (s, 3H), 1.08 (s, 9H);

¹³C NMR (100 MHz, acetone-*d*₆) δ 177.3, 176.5, 160.6, 143.4, 134.5, 130.6, 130.3, 129.4, 128.0, 127.7, 127.0, 123.0, 77.1, 76.7, 76.0, 63.6, 61.6, 38.5, 38.3, 26.4, 20.7;

HRMS (ESI) *m/z*: [M+Na] calcd. for C₂₈H₃₁NO₆Na, 500.2049; found, 500.2053.

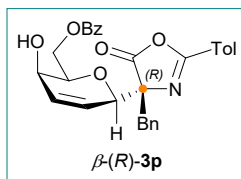


Compound β -(S)-**3o** was obtained as colorless syrup in 63% yield.

¹H NMR (400 MHz, acetone-*d*₆) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.21 – 7.12 (m, 5H), 6.27 (ddd, *J* = 10.4, 5.6, 1.9 Hz, 1H), 6.18 (dd, *J* = 10.3, 1.5 Hz, 1H), 4.65 (d, *J* = 2.1 Hz, 1H), 4.21 (dd, *J* = 11.5, 7.5 Hz, 1H), 4.14 (dd, *J* = 11.5, 4.7 Hz, 1H), 3.91 (ddd, *J* = 9.5, 5.3, 2.2 Hz, 1H), 3.85 (ddd, *J* = 7.1, 4.7, 1.8 Hz, 1H), 3.41 (d, *J* = 13.3 Hz, 1H), 3.28 (d, *J* = 13.3 Hz, 1H), 3.10 (d, *J* = 9.6 Hz, 1H), 2.38 (s, 3H), 1.19 (s, 9H);

¹³C NMR (100 MHz, acetone-*d*₆) δ 178.1, 177.8, 161.9, 144.4, 135.1, 131.3, 131.2, 130.3, 128.8, 128.5, 127.9, 127.9, 123.8, 77.9, 77.8, 76.6, 64.3, 62.4, 39.4, 39.2, 27.4, 21.5;

HRMS (ESI) *m/z*: [M+Na] calcd. for C₂₈H₃₁NO₆Na, 500.2049; found, 500.2050.

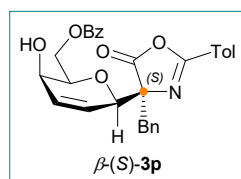


Compound β -(R)-3p was obtained as colorless syrup in 40% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.91 (d, J = 7.5 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.63 – 7.59 (m, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.21 – 7.10 (m, 5H), 6.28 (ddd, J = 10.5, 5.5, 2.0 Hz, 1H), 6.19 (dd, J = 10.4, 1.4 Hz, 1H), 4.59 (d, J = 2.0 Hz, 1H), 4.55 – 4.47 (m, 2H), 4.06 (ddd, J = 9.4, 5.1, 2.4 Hz, 1H), 3.99 (ddd, J = 7.3, 4.9, 2.1 Hz, 1H), 3.57 (d, J = 9.0 Hz, 1H), 3.37 (t, J = 13.9 Hz, 2H), 2.38 (s, 3H);

^{13}C NMR (100 MHz, acetone- d_6) δ 177.3, 166.5, 161.5, 144.2, 135.3, 133.7, 131.4, 131.2, 131.1, 130.2, 130.1, 129.2, 128.8, 128.4, 127.9, 127.8, 123.8, 77.8, 77.4, 76.8, 65.0, 62.4, 39.2, 21.5;

HRMS (ESI) m/z : [M+H] calcd. for $\text{C}_{30}\text{H}_{28}\text{NO}_6$, 498.1917; found, 498.1921.

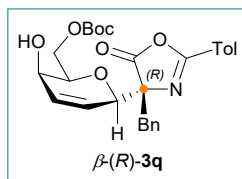


Compound β -(S)-3p was obtained as colorless syrup in 56% yield.

^1H NMR (400 MHz, acetone- d_6) δ 8.06 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 7.22 – 7.12 (m, 5H), 6.30 (ddd, J = 10.5, 5.5, 1.9 Hz, 1H), 6.18 (dd, J = 10.3, 1.6 Hz, 1H), 4.68 (d, J = 2.0 Hz, 1H), 4.49 (dd, J = 11.6, 4.6 Hz, 1H), 4.42 (dd, J = 11.5, 7.4 Hz, 1H), 4.04 – 4.01 (m, 2H), 3.44 (d, J = 13.3 Hz, 1H), 3.27 (d, J = 13.4 Hz, 1H), 3.22 (d, J = 9.6 Hz, 1H), 2.38 (s, 3H);

^{13}C NMR (100 MHz, acetone- d_6) δ 177.9, 166.6, 162.0, 144.4, 135.1, 133.9, 131.3, 131.3, 131.1, 130.3, 130.2, 129.3, 128.7, 128.5, 127.9, 127.9, 123.8, 77.9, 77.6, 76.6, 65.1, 62.5, 39.5, 21.5;

HRMS (ESI) m/z : [M+H] calcd. for $\text{C}_{30}\text{H}_{28}\text{NO}_6$, 498.1917; found, 498.1919.

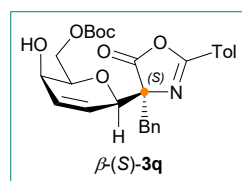


Compound β -(R)-3q was obtained as colorless syrup in 41% yield.

¹H NMR (400 MHz, acetone-*d*₆) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.22 – 7.11 (m, 5H), 6.25 (ddd, *J* = 10.5, 5.6, 2.0 Hz, 1H), 6.10 (dd, *J* = 10.3, 1.5 Hz, 1H), 4.58 (d, *J* = 2.2 Hz 1H), 4.28 (dd, *J* = 11.5, 7.5 Hz, 1H), 4.20 (dd, *J* = 11.5, 4.2 Hz, 1H), 3.94 (ddd, *J* = 8.8, 5.5, 2.5 Hz, 1H), 3.82 (ddd, *J* = 7.0, 4.1, 1.9 Hz, 1H), 3.46 (d, *J* = 9.2 Hz, 1H), 3.40 (d, *J* = 13.5 Hz, 1H), 3.33 (d, *J* = 13.5 Hz, 1H), 2.38 (s, 3H), 1.38 (s, 9H);

¹³C NMR (100 MHz, acetone-*d*₆) δ 177.4, 161.4, 154.2, 144.3, 135.3, 131.4, 131.2, 130.3, 128.8, 128.5, 127.9, 127.8, 123.8, 81.9, 77.7, 77.5, 76.7, 67.3, 62.4, 39.4, 27.8, 21.5;

HRMS (ESI) *m/z*: [M+H] calcd. for C₂₈H₃₂NO₇, 494.2179; found, 494.2182.

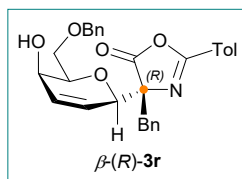


Compound β -(S)-3q was obtained as colorless syrup in 53% yield.

¹H NMR (400 MHz, acetone-*d*₆) δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.10 (m, 5H), 6.27 (ddd, *J* = 9.9, 5.5, 1.6 Hz, 1H), 6.13 (dd, *J* = 10.3, 1.2 Hz, 1H), 4.64 (d, *J* = 2.1 Hz, 1H), 4.21 (dd, *J* = 11.6, 7.4 Hz, 1H), 4.15 (dd, *J* = 11.5, 4.3 Hz, 1H), 3.92 – 3.88 (m, 1H), 3.85 – 3.81 (m, 1H), 3.41 (d, *J* = 13.3 Hz, 1H), 3.28 (d, *J* = 13.3 Hz, 1H), 3.03 (d, *J* = 9.8 Hz, 1H), 2.39 (s, 3H), 1.45 (s, 9H);

¹³C NMR (100 MHz, acetone-*d*₆) δ 177.9, 162.1, 154.2, 144.4, 135.1, 131.3, 131.3, 130.3, 128.8, 128.5, 127.9, 127.8, 123.8, 82.0, 77.9, 77.4, 76.5, 67.2, 62.4, 39.5, 27.8, 21.5;

HRMS (ESI) *m/z*: [M+H] calcd. for C₂₈H₃₂NO₇, 494.2179; found, 494.2182.

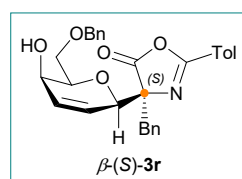


Compound β -(R)-**3r** was obtained as colorless syrup in 31% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.77 – 7.74 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.27 – 7.11 (m, 10H), 6.25 (ddd, J = 10.3, 5.6, 2.1 Hz, 1H), 6.16 (dd, J = 10.4, 1.6 Hz, 1H), 4.58 (q, J = 1.9 Hz, 1H), 4.53 (d, J = 12.4 Hz, 1H), 4.46 (d, J = 12.3 Hz, 1H), 3.91 (d, J = 6.6 Hz, 1H), 3.79 (ddd, J = 6.7, 4.5, 2.1 Hz, 1H), 3.74 (dd, J = 10.6, 4.5 Hz, 1H), 3.60 (dd, J = 10.6, 6.9 Hz, 1H), 3.39 (q, J = 13.4 Hz, 1H), 3.35 (q, J = 13.5 Hz, 1H), 3.16 (d, J = 9.1 Hz, 1H), 2.39 (s, 3H);

^{13}C NMR (100 MHz, acetone- d_6) δ 177.5, 161.3, 144.3, 139.9, 135.4, 131.7, 131.2, 130.3, 128.9, 128.8, 128.5, 128.0, 127.9, 127.8, 127.7, 123.9, 78.7, 77.9, 77.6, 73.7, 70.9, 62.7, 39.3, 21.5;

HRMS (ESI) m/z : [M+H] calcd. for $\text{C}_{30}\text{H}_{30}\text{NO}_5$, 484.2124; found, 484.2127.

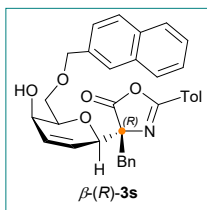


Compound β -(S)-**3r** was obtained as colorless syrup in 58% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.73 (d, J = 8.3 Hz, 2H), 7.37 – 7.12 (m, 12H), 6.27 (ddd, J = 10.3, 5.8, 2.0 Hz, 1H), 6.14 (dd, J = 10.3, 1.7 Hz, 1H), 4.67 (q, J = 1.9 Hz, 1H), 4.55 (s, 2H), 3.88 (ddt, J = 9.6, 5.8, 1.9 Hz, 1H), 3.82 (ddd, J = 6.8, 4.8, 1.9 Hz, 1H), 3.66 (dd, J = 10.4, 4.9 Hz, 1H), 3.56 (dd, J = 10.4, 6.8 Hz, 1H), 3.42 (d, J = 13.3 Hz, 1H), 3.28 (d, J = 13.3 Hz, 1H), 2.82 (d, J = 9.8 Hz, 1H), 2.38 (s, 3H);

^{13}C NMR (100 MHz, acetone- d_6) δ 178.1, 161.9, 144.4, 139.8, 135.2, 131.7, 131.2, 130.3, 129.0, 128.8, 128.5, 128.2, 128.0, 127.9, 127.7, 123.8, 78.1, 78.0, 77.7, 73.5, 70.6, 62.6, 39.5, 21.5;

HRMS (ESI) m/z : [M+H] calcd. for $\text{C}_{30}\text{H}_{30}\text{NO}_5$, 484.2124; found, 484.2127.

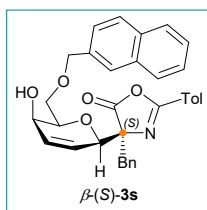


Compound β -(R)-**3s** was obtained as colorless syrup in 32% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.86 – 7.81 (m, 2H), 7.77 – 7.74 (m, 3H), 7.70 (s, 1H), 7.50 – 7.44 (m, 2H), 7.33 (dd, J = 8.5, 1.7 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.23 – 7.11 (m, 5H), 6.26 (ddd, J = 10.3, 5.6, 2.1 Hz, 1H), 6.18 (dd, J = 10.3, 1.6 Hz, 1H), 4.71 (dd, J = 12.6, 0.9 Hz, 1H), 4.63 (dd, J = 12.6, 0.9 Hz, 1H), 4.59 (q, J = 1.9 Hz, 1H), 3.94 (ddt, J = 9.2, 5.5, 1.9 Hz, 1H), 3.85 – 3.79 (m, 2H), 3.70 – 3.64 (m, 1H), 3.38 (s, 2H), 3.19 (d, J = 9.1 Hz, 1H), 2.36 (s, 3H);

^{13}C NMR (100 MHz, acetone- d_6) δ 177.5, 161.3, 144.3, 137.6, 135.4, 134.2, 133.7, 131.7, 131.2, 130.3, 128.8, 128.6, 128.5, 128.5, 128.4, 127.8, 127.7, 126.7, 126.4, 126.4, 126.4, 123.9, 78.8, 77.9, 77.6, 73.9, 71.0, 62.7, 39.3, 21.5;

HRMS (ESI) m/z : [M+H] calcd. for $\text{C}_{34}\text{H}_{32}\text{NO}_5$, 534.2280; found, 534.2286.

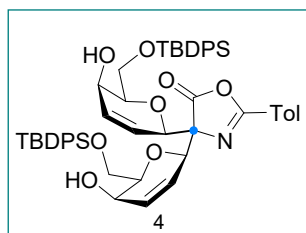


Compound β -(S)-**3s** was obtained as colorless syrup in 60% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.89 – 7.84 (m, 4H), 7.70 (d, J = 8.3 Hz, 2H), 7.52 – 7.45 (m, 3H), 7.27 – 7.11 (m, 7H), 6.27 (ddd, J = 10.3, 5.7, 2.0 Hz, 1H), 6.15 (dd, J = 10.3, 1.6 Hz, 1H), 4.75 – 4.71 (m, 2H), 4.69 (q, J = 1.8 Hz, 1H), 3.92 – 3.84 (m, 2H), 3.70 (dd, J = 10.5, 4.6 Hz, 1H), 3.60 (dd, J = 10.5, 6.8 Hz, 1H), 3.42 (d, J = 13.3 Hz, 1H), 3.29 (d, J = 13.3 Hz, 1H), 2.84 (d, J = 9.8 Hz, 1H), 2.35 (s, 3H);

^{13}C NMR (100 MHz, acetone- d_6) δ 178.1, 161.9, 144.4, 137.4, 135.2, 134.2, 133.8, 131.7, 131.2, 130.3, 128.8, 128.7, 128.6, 128.5, 128.4, 127.9, 127.7, 126.8, 126.7, 126.5, 126.5, 123.8, 78.1, 78.0, 77.8, 73.5, 70.7, 62.7, 39.5, 21.5;

HRMS (ESI) m/z : [M+H] calcd. for $\text{C}_{34}\text{H}_{32}\text{NO}_5$, 534.2280; found, 534.2281.

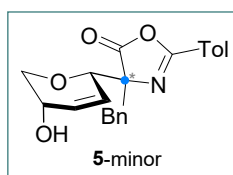


Compound **4** was obtained as colorless syrup in 83% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.69 – 7.62 (m, 8H), 7.41 – 7.31 (m, 12H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.32 – 6.28 (m, 1H), 6.27 – 6.22 (m, 1H), 5.92 (d, *J* = 10.2 Hz, 1H), 5.61 (dd, *J* = 10.1, 1.9 Hz, 1H), 4.89 (d, *J* = 8.1 Hz, 2H), 3.98 (d, *J* = 6.2 Hz, 1H), 3.93 – 3.68 (m, 7H), 2.82 (brs, 1H), 2.36 (brs, 1H and s, 3H), 1.00 (s, 18H);

¹³C NMR (100 MHz, CDCl₃) δ 175.7, 163.7, 144.2, 135.6, 135.6, 135.6, 133.5, 133.4, 132.7, 131.4, 129.7, 129.6, 129.6, 128.3, 127.7, 127.6, 127.4, 125.9, 121.9, 78.6, 77.8, 77.6, 74.6, 63.0, 62.8, 61.6, 61.3, 26.7, 26.7, 21.7, 19.2, 19.2;

HRMS (ESI) *m/z*: [M+H] calcd. for C₅₄H₆₂NO₈Si₂, 908.4014; found, 908.4008.

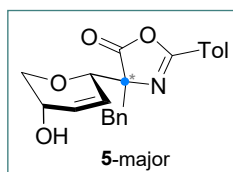


Compound **5-minor** ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, 30:1, $R_f = 0.6$) was obtained as colorless syrup in 39% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.74 (d, $J = 8.2$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.17 – 7.12 (m, 5H), 6.21 – 6.14 (m, 2H), 4.55 (d, $J = 1.9$ Hz, 1H), 3.91 (ddd, $J = 7.9, 3.6, 2.3$ Hz, 1H), 3.77 (dd, $J = 11.5, 3.2$ Hz, 1H), 3.71 (dd, $J = 11.4, 3.3$ Hz, 1H), 3.51 (d, $J = 8.0$ Hz, 1H), 3.39 (d, $J = 13.3$ Hz, 1H), 3.26 (d, $J = 13.3$ Hz, 1H), 2.39 (s, 3H);

^{13}C NMR (100 MHz, acetone- d_6) δ 178.2, 161.6, 144.3, 135.2, 132.1, 131.1, 130.3, 128.8, 128.5, 127.9, 126.6, 123.9, 78.7, 76.8, 70.4, 62.2, 39.5, 21.5;

HRMS (ESI) m/z : $[\text{M}+\text{H}]$ calcd. for $\text{C}_{22}\text{H}_{22}\text{NO}_4$, 364.1549; found, 364.1541.

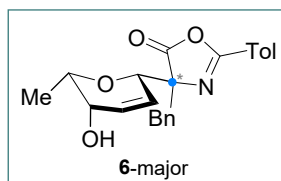


Compound **5-major** ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, 30:1, $R_f = 0.55$) was obtained as colorless syrup in 44% yield.

^1H NMR (400 MHz, acetone- d_6) δ 7.74 (d, $J = 8.3$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.21 – 7.12 (m, 5H), 6.16 (ddd, $J = 10.6, 4.2, 2.2$ Hz, 1H), 6.01 (dd, $J = 10.4, 1.8$ Hz, 1H), 4.44 (d, $J = 2.0$ Hz, 1H), 3.96 – 3.91 (m, 2H), 3.77 – 3.71 (m, 2H), 3.42 (d, $J = 13.5$ Hz, 1H), 3.31 (d, $J = 13.5$ Hz, 1H), 2.39 (s, 3H);

^{13}C NMR (100 MHz, acetone- d_6) δ 177.6, 161.0, 144.3, 135.5, 132.3, 131.1, 130.3, 128.8, 128.4, 127.8, 126.7, 123.8, 77.8, 76.9, 70.7, 62.3, 39.7, 21.5;

HRMS (ESI) m/z : $[\text{M}+\text{H}]$ calcd. for $\text{C}_{22}\text{H}_{22}\text{NO}_4$, 364.1549; found, 364.1542.

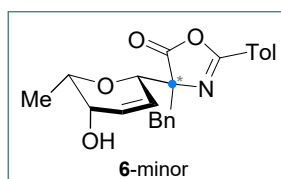


Compound **6-major** (CH₂Cl₂/MeOH, 30:1, R_f = 0.7) was obtained as colorless syrup in 63% yield.

¹H NMR (400 MHz, acetone-*d*₆) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.11 (m, 5H), 6.28 (ddd, *J* = 10.3, 5.8, 2.0 Hz, 1H), 6.12 (dd, *J* = 10.3, 1.8 Hz, 1H), 4.62 (d, *J* = 1.9 Hz, 1H), 3.72 (qd, *J* = 6.4, 1.8 Hz, 1H), 3.62 (ddt, *J* = 10.2, 5.7, 1.8 Hz, 1H), 3.38 (d, *J* = 13.4 Hz, 1H), 3.28 (d, *J* = 13.3 Hz, 1H), 2.61 (d, *J* = 10.3 Hz, 1H), 2.38 (s, 3H), 1.14 (d, *J* = 6.4 Hz, 3H);

¹³C NMR (100 MHz, acetone-*d*₆) δ 178.1, 161.8, 144.4, 135.2, 132.3, 131.2, 130.3, 128.7, 128.4, 127.9, 127.3, 123.8, 78.2, 77.9, 74.2, 64.6, 39.4, 21.5, 17.0;

HRMS (ESI) *m/z*: [M+H] calcd. for C₂₃H₂₄NO₄, 378.1705; found, 378.1698.



Compound **6-minor** (CH₂Cl₂/MeOH, 30:1, R_f = 0.6) was obtained as colorless syrup in 29% yield.

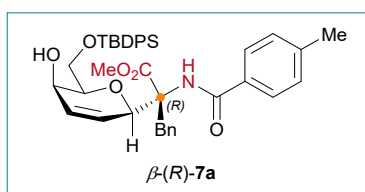
¹H NMR (400 MHz, acetone-*d*₆) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.10 (m, 5H), 6.25 (ddd, *J* = 10.2, 5.6, 2.2 Hz, 1H), 6.08 (dd, *J* = 10.3, 1.7 Hz, 1H), 4.53 (d, *J* = 2.0 Hz, 1H), 3.71 – 3.64 (m, 2H), 3.39 (d, *J* = 13.5 Hz, 1H), 3.32 (d, *J* = 13.5 Hz, 1H), 2.96 (d, *J* = 9.7 Hz, 1H), 2.39 (s, 3H), 1.18 (d, *J* = 6.4 Hz, 3H);

¹³C NMR (100 MHz, acetone-*d*₆) δ 177.6, 161.3, 144.3, 135.5, 132.4, 131.1, 130.3, 128.8, 128.4, 127.8, 127.4, 123.9, 78.0, 77.7, 74.5, 64.7, 39.4, 21.5, 17.0;

HRMS (ESI) *m/z*: [M+H] calcd. for C₂₃H₂₄NO₄, 378.1705; found, 378.1699.

5. Synthetic transformations of β -C-glycoside **3a**

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with β -(*R*)-**3a** or β -(*S*)-**3a** (63 mg, 0.1 mmol) and anhydrous MeOH (1 mL). Then, MeONa (27 μ L, 0.15 mmol, 30% in MeOH) was added and the reaction mixture was stirred at room temperature for 20 min. Upon completion (monitored by TLC), the mixture was diluted with H₂O (15 mL) and extracted with EtOAc (10 mL \times 2). The combined organic layer was washed with brine and dried over Na₂SO₄, then concentrated under reduced pressure. The residue was purified by silica column chromatography to give β -(*R*)-**7a** or β -(*S*)-**7a** respectively.

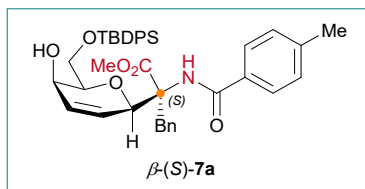


Compound β -(*R*)-**7a** was obtained as a colorless syrup in 85% yield.

¹H NMR (400 MHz, acetone-*d*₆) δ 7.79 – 7.77 (m, 4H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.51 (s, 1H), 7.48 – 7.40 (m, 6H), 7.30 – 7.27 (m, 2H), 7.22 – 7.16 (m, 5H), 6.35 (dd, *J* = 10.5, 1.5 Hz, 1H), 6.02 (ddd, *J* = 10.4, 5.6, 2.2 Hz, 1H), 4.73 (d, *J* = 1.9 Hz, 1H), 3.98 – 3.97 (m, 2H), 3.92 (ddt, *J* = 7.7, 5.7, 1.9 Hz, 1H), 3.82 – 3.74 (m, 5H), 3.50 (d, *J* = 13.0 Hz, 1H), 3.14 (d, *J* = 7.8 Hz, 1H), 2.32 (s, 3H), 1.04 (s, 9H);

¹³C NMR (100 MHz, acetone-*d*₆) δ 171.2, 167.3, 142.2, 136.6, 136.3, 134.3, 134.2, 133.0, 131.2, 130.7, 130.5, 130.5, 129.6, 129.2, 128.9, 128.6, 128.0, 127.6, 79.7, 76.3, 67.1, 65.2, 62.6, 52.2, 39.0, 27.2, 21.3, 19.6;

HRMS (ESI) *m/z*: [M+H] calcd. for C₄₀H₄₆NO₆Si, 664.3094; found, 664.3093.



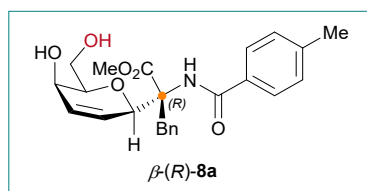
Compound β -(*S*)-**7a** was obtained as a colorless syrup in 79% yield.

¹H NMR (400 MHz, acetone-*d*₆) δ 7.89 – 7.84 (m, 4H), 7.71 (d, *J* = 7.9 Hz, 2H), 7.52 – 7.48 (m, 6H), 7.41 (s, 1H), 7.29 – 7.23 (m, 4H), 7.18 – 7.14 (m, 3H), 6.24 (d, *J* = 10.4 Hz, 1H), 6.04

(ddd, $J = 10.3, 5.5, 2.1$ Hz, 1H), 4.58 (d, $J = 2.2$ Hz, 1H), 4.11 – 3.92 (m, 4H), 3.84 – 3.81 (m, 1H), 3.72 (s, 3H), 3.67 (d, $J = 13.6$ Hz, 1H), 3.20 (d, $J = 8.1$ Hz, 1H), 2.37 (s, 3H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, acetone- d_6) δ 171.4, 167.3, 142.5, 137.7, 136.3, 136.3, 134.3, 134.2, 132.9, 131.6, 130.6, 130.5, 130.1, 129.7, 128.8, 128.7, 128.0, 127.2, 80.4, 76.0, 66.8, 65.4, 62.7, 52.4, 35.9, 27.2, 21.3, 19.7;

HRMS (ESI) m/z : [M+H] calcd. for $\text{C}_{40}\text{H}_{46}\text{NO}_6\text{Si}$, 664.3094; found, 664.3091.

To a solution of β -(*R*)-**7a** (63 mg) or β -(*S*)-**7a** (48 mg) in THF was added TBAF (1.2 eq., 0.5 M in THF) at room temperature, then the reaction mixture was stirred for 15 min. Upon completion (monitored by TLC), the mixture was concentrated under reduced pressure to give a crude product which was purified *via* preparative TLC to yield β -(*R*)-**8a** or β -(*S*)-**8a** respectively.

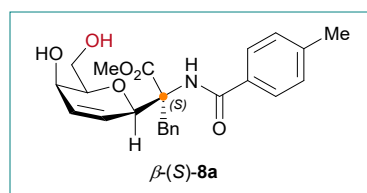


Compound β -(*R*)-**8a** was obtained as a colorless syrup in 82% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 8.2$ Hz, 2H), 7.22 – 7.19 (m, 5H), 7.13 (s, 1H), 7.10 – 7.08 (m, 2H), 6.20 (dd, $J = 10.4, 1.4$ Hz, 1H), 6.14 (ddd, $J = 10.3, 5.5, 2.0$ Hz, 1H), 4.98 (d, $J = 1.9$ Hz, 1H), 3.90 (t, $J = 7.1$ Hz, 1H), 3.82 – 3.70 (m, 6H), 3.57 – 3.52 (m, 2H), 2.64 (s, 1H), 2.37 (s, 3H), 2.36 (s, 1H);

^{13}C NMR (100 MHz, CDCl_3) δ 171.3, 167.6, 142.2, 135.5, 132.0, 130.1, 129.3, 129.3, 128.4, 128.3, 127.1, 127.0, 77.2, 75.8, 68.2, 62.9, 62.8, 52.6, 36.9, 21.5;

HRMS (ESI) m/z : [M+H] calcd. for $\text{C}_{24}\text{H}_{28}\text{NO}_6$, 426.1917; found, 426.1913.



Compound β -(*S*)-**8a** was obtained as a colorless syrup in 84% yield.

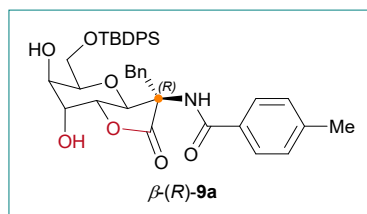
^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.1$ Hz, 2H), 7.26 – 7.18 (m, 5H), 7.12 – 7.09 (m,

2H), 7.01 (s, 1H), 6.15 (ddd, $J = 10.3, 5.7, 2.1$ Hz, 1H), 6.05 (dd, $J = 10.2, 1.5$ Hz, 1H), 5.15 (d, $J = 1.8$ Hz, 1H), 4.08 (d, $J = 13.8$ Hz, 1H), 3.93 (dd, $J = 11.3, 6.4$ Hz, 2H), 3.83 – 3.82 (m, 4H), 3.71 (ddd, $J = 6.7, 4.7, 1.6$ Hz, 1H), 3.57 (d, $J = 13.8$ Hz, 1H), 2.39 (s, 3H), 2.16 (s, 1H), 1.99 (d, $J = 9.7$ Hz, 1H);

^{13}C NMR (100 MHz, CDCl_3) δ 171.8, 167.1, 142.4, 135.9, 131.9, 130.0, 129.4, 129.1, 129.0, 128.3, 127.0, 126.9, 77.6, 76.1, 68.3, 62.8, 53.1, 35.4, 21.5;

HRMS (ESI) m/z : $[M+H]$ calcd. for $\text{C}_{24}\text{H}_{28}\text{NO}_6$, 426.1917; found, 426.1913.

To a solution of β -(*R*)-**3a** (63 mg, 0.1 mmol) or β -(*S*)-**3a** (63 mg, 0.1 mmol) in acetone/ H_2O (1 mL/0.2 mL, 5:1) was added $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$ (1.8 mg, 5 mol%) and NMO (35 mg, 0.3 mmol) at room temperature, then the reaction mixture was stirred for 24 hours. Upon completion (monitored by TLC), the mixture was extracted with EtOAc (5 mL \times 2), the combined organic layer was washed with brine and dried over Na_2SO_4 . Removal of the solvent under reduced pressure followed by purification *via* preparative TLC to afford β -(*R*)-**9a** or β -(*S*)-**9a** respectively.

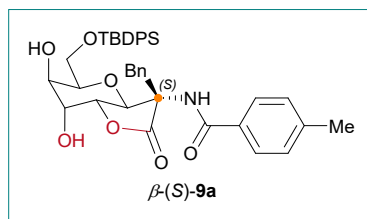


Compound β -(*R*)-**9a** was obtained as a colorless syrup in 92% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.62 – 7.56 (m, 4H), 7.49 (d, $J = 8.0$ Hz, 2H), 7.45 – 7.34 (m, 4H), 7.29 – 7.22 (m, 7H), 7.07 (d, $J = 7.9$ Hz, 2H), 6.30 (s, 1H), 4.73 (dd, $J = 9.8, 2.4$ Hz, 1H), 4.47 (s, 1H), 4.31 – 4.28 (m, 2H), 4.10 (d, $J = 3.7$ Hz, 1H), 3.95 – 3.86 (m, 3H), 3.50 (d, $J = 13.9$ Hz, 1H), 3.30 (d, $J = 13.9$ Hz, 1H), 3.16 (brs, 1H), 2.31 (s, 3H), 0.94 (s, 9H);

^{13}C NMR (100 MHz, CDCl_3) δ 171.9, 166.7, 142.5, 135.5, 135.4, 134.3, 132.5, 132.0, 130.5, 130.3, 130.1, 130.0, 129.3, 128.6, 127.9, 127.9, 127.6, 127.1, 76.6, 75.9, 75.7, 72.6, 66.7, 65.4, 60.0, 41.3, 26.6, 21.5, 19.1;

HRMS (ESI) m/z : $[M+H]$ calcd. for $\text{C}_{39}\text{H}_{44}\text{NO}_7\text{Si}$, 666.2887; found, 666.2887.



Compound β -(S)-**9a** was obtained as a white acicular crystal in 90% yield, m. p. 142-143 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.78 – 7.76 (m, 2H), 7.71 – 7.68 (m, 2H), 7.47 – 7.32 (m, 13H), 7.14 – 7.12 (m, 2H), 6.34 (s, 1H), 5.28 (d, $J = 10.3$ Hz, 1H), 4.59 (dd, $J = 10.3, 2.5$ Hz, 1H), 4.51 – 4.49 (m, 1H), 4.23 (d, $J = 3.6$ Hz, 1H), 4.13 (dd, $J = 11.2, 4.0$ Hz, 1H), 4.06 – 3.98 (m, 2H), 3.83 (s, 1H), 3.52 (d, $J = 14.1$ Hz, 1H), 3.30 (d, $J = 14.1$ Hz, 1H), 2.33 (s, 3H), 2.04 (s, 1H), 1.08 (s, 9H);

^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 166.8, 142.5, 135.7, 135.5, 133.1, 132.3, 132.2, 130.9, 130.3, 130.0, 130.0, 129.2, 128.9, 128.0, 127.9, 127.9, 126.9, 75.7, 74.2, 72.8, 67.3, 65.6, 62.0, 34.2, 26.7, 21.4, 19.1;

HRMS (ESI) m/z : $[\text{M}+\text{H}]$ calcd. for $\text{C}_{39}\text{H}_{44}\text{NO}_7\text{Si}$, 666.2887; found, 666.2884.

6. Crystal data and structure refinement for β -(S)-9a

Compound β -(S)-9a: The crystal structure of compound β -(S)-9a has been deposited at the Cambridge Crystallographic Data Centre (CCDC 2201062). The data is available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

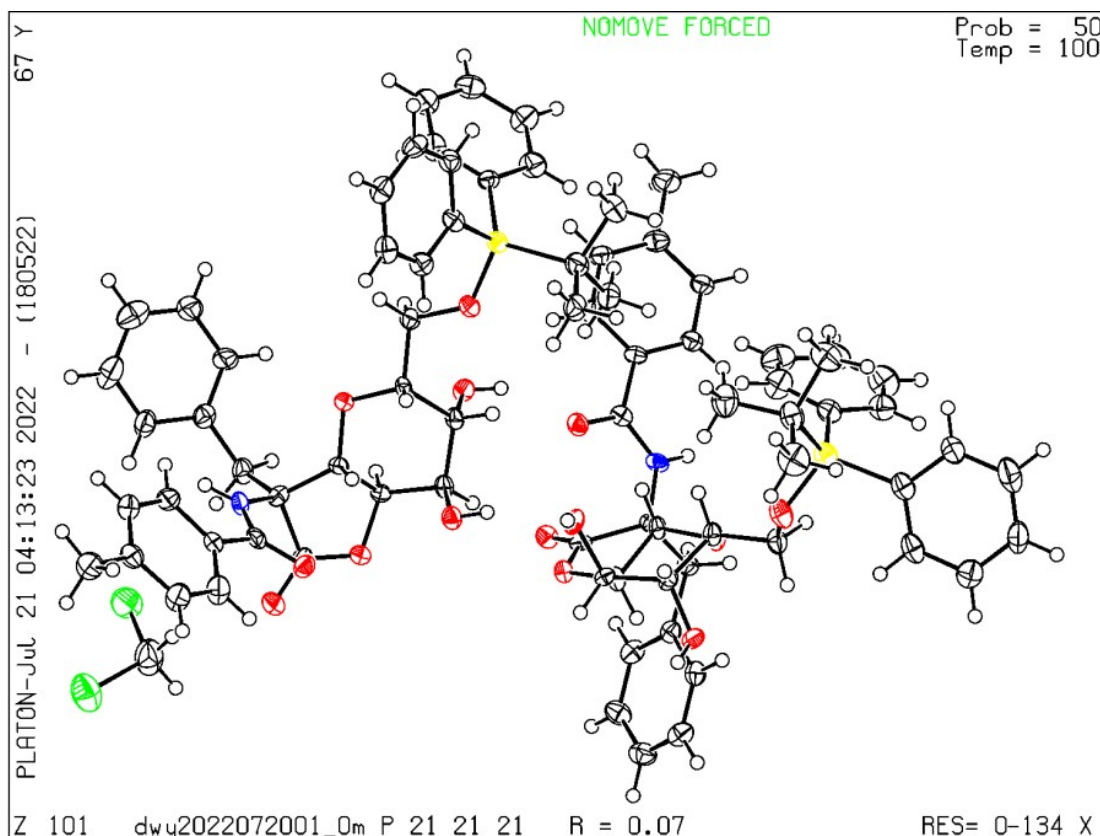


Table 1. Crystal data and structure refinement for β -(S)-9a.

Identification code	β -(S)-9a
Empirical formula	C _{39.5} H ₄₄ ClNO ₇ Si
Formula weight	708.29
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	13.5432(8)
b/Å	15.8899(17)
c/Å	34.626(3)
α /°	90
β /°	90
γ /°	90

Volume/Å ³	7451.5(12)
Z	8
ρ _{calc} /g/cm ³	1.263
μ/mm ⁻¹	1.620
F(000)	3000.0
Crystal size/mm ³	0.2 × 0.08 × 0.04
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	5.104 to 138.074
Index ranges	-12 ≤ h ≤ 16, -17 ≤ k ≤ 18, -35 ≤ l ≤ 41
Reflections collected	47446
Independent reflections	13362 [R _{int} = 0.0907, R _{sigma} = 0.0786]
Data/restraints/parameters	13362/2/904
Goodness-of-fit on F ²	1.078
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0705, wR ₂ = 0.1731
Final R indexes [all data]	R ₁ = 0.0795, wR ₂ = 0.1790
Largest diff. peak/hole / e Å ⁻³	0.66/-0.71
Flack parameter	0.087(13)

Table 2. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for β-(S)-9a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Cl1	7322.2(17)	4303.4(17)	7957.0(7)	58.2(6)
Cl2	5395.8(16)	4625.1(14)	7616.9(6)	48.1(5)
Si1	5016.3(13)	6356.1(11)	4248.1(5)	21.9(4)
Si2	7157.7(14)	1818.0(13)	3013.3(6)	28.2(4)
O1	5091(4)	5769(3)	4636.9(13)	25.3(10)
O2	5242(3)	5528(3)	5673.1(12)	20.3(9)
O3	6356(3)	3566(3)	5396.7(13)	23.7(10)
O4	5455(3)	3530(3)	6146.0(12)	23.1(10)
O5	7667(3)	4388(3)	6237.3(13)	25.3(10)
O6	6066(4)	3717(3)	6737.9(14)	30.9(11)
O7	3981(3)	4455(3)	5119.3(13)	22.6(10)
O8	5470(3)	1125(3)	4133.9(12)	22.0(10)
O9	7406(3)	1479(3)	3451.4(13)	30.7(11)
O10	3639(3)	1900(3)	5265.0(13)	23.6(10)
O11	5218(3)	1761(3)	5122.4(12)	19.1(9)

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for β -(S)-9a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
O12	3972(3)	3183(3)	4627.6(13)	24.3(10)
O13	6696(3)	2706(3)	4701.7(13)	22.8(10)
O14	7390(3)	543(3)	4415.2(13)	23.6(10)
N1	6628(4)	5378(4)	6470.0(15)	22.3(12)
C2	8407(5)	5555(4)	6557.6(18)	22.7(14)
N3	3371(4)	1956(3)	4407.5(16)	21.6(11)
C1	1917(5)	7688(5)	4163(2)	34.2(17)
C79	2096(5)	6932(5)	3967(2)	35.8(17)
C3	2998(5)	6529(5)	3993(2)	33.4(17)
C4	3774(5)	6872(4)	4202.6(19)	22.0(13)
C5	4934(5)	6007(4)	5029.8(18)	22.5(14)
C6	5408(5)	5315(4)	5272.5(17)	18.5(13)
C7	5705(5)	4883(4)	5892.9(18)	18.1(13)
C8	5758(5)	4956(4)	6333(2)	21.6(14)
C9	7551(5)	5066(4)	6405.8(18)	22.3(14)
C10	8336(5)	6415(4)	6648(2)	26.8(15)
C11	9152(5)	6822(5)	6802(2)	28.4(15)
C12	10031(5)	6417(4)	6866.4(19)	27.5(15)
C13	10922(6)	6842(5)	7032(2)	37.6(18)
C14	7357(5)	8488(4)	4405(2)	29.8(16)
C15	7459(5)	7729(5)	4597(2)	29.8(16)
C16	6765(5)	7102(4)	4542(2)	27.2(15)
C17	5964(5)	7205(4)	4292.6(18)	22.6(14)
C18	5905(5)	7964(4)	4092(2)	27.1(15)
C19	6594(5)	8593(4)	4147(2)	28.9(15)
C20	5023(4)	4441(4)	5156.7(18)	19.1(12)
C21	5333(5)	3743(4)	5438.6(18)	21.8(14)
C22	5140(5)	4076(4)	5834.3(18)	18.8(13)
C23	5811(5)	4000(4)	6435(2)	22.7(14)
C24	10088(6)	5574(5)	6765(2)	36.4(17)
C25	9277(5)	5154(5)	6612(2)	35.2(18)
C26	4833(5)	5287(4)	6541(2)	27.2(15)
C27	4723(5)	6234(4)	6554(2)	26.3(15)
C28	4182(5)	6655(5)	6283(2)	31.9(17)
C29	4063(6)	7526(5)	6299(2)	38.7(18)
C30	4495(6)	7976(5)	6585(3)	43(2)

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for β -(S)-9a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
C31	5065(6)	7568(5)	6863(3)	44(2)
C32	5159(6)	6692(5)	6856(2)	34.6(17)
C33	2692(6)	8030(5)	4372(2)	32.8(16)
C34	3600(5)	7642(5)	4395(2)	32.1(16)
C35	5358(5)	5578(5)	3856(2)	29.1(15)
C36	4737(6)	4774(5)	3876(2)	33.7(17)
C37	6445(5)	5340(5)	3904(2)	33.3(17)
C38	5225(6)	5984(5)	3454(2)	37.0(18)
C39	225(6)	4600(5)	3647(2)	40.2(19)
C40	1060(5)	4141(4)	3834(2)	28.5(16)
C41	1306(5)	3320(4)	3721(2)	27.8(15)
C42	2062(5)	2886(4)	3906(2)	24.7(14)
C43	2578(4)	3261(4)	4206.4(18)	20.0(13)
C44	3350(5)	2803(4)	4427.3(19)	20.6(13)
C45	4105(4)	1450(4)	4603.7(17)	17.0(12)
C46	5142(4)	1605(4)	4448.8(18)	19.6(13)
C47	6408(5)	1456(4)	4023.6(18)	21.5(13)
C48	6726(5)	975(4)	3661(2)	26.0(15)
C49	5819(5)	1995(4)	2982(2)	28.6(15)
C50	5202(6)	1487(5)	2747(2)	35.1(17)
C51	4192(6)	1537(6)	2758(3)	45(2)
C52	3721(6)	2102(6)	3003(3)	47(2)
C53	7960(6)	-415(5)	2180(2)	40.9(19)
C54	8041(6)	-499(5)	2575(2)	37.4(18)
C55	7816(5)	181(5)	2814(2)	32.6(17)
C56	7500(5)	950(5)	2668(2)	31.6(16)
C57	7440(6)	1024(5)	2263(2)	40.3(19)
C58	7661(7)	350(6)	2020(2)	49(2)
C59	7163(5)	1407(4)	4352.5(18)	21.9(13)
C60	6793(5)	1812(4)	4731.8(19)	20.1(13)
C61	5787(4)	1433(4)	4794.7(18)	20.0(13)
C62	3735(5)	528(4)	4591.5(19)	22.5(14)
C63	4132(5)	-78(4)	4893.2(19)	21.6(13)
C64	4971(5)	-559(4)	4819(2)	24.6(14)
C65	5304(5)	-1131(4)	5095(2)	28.9(16)
C66	4814(5)	-1230(5)	5435(2)	33.1(17)

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for β -(S)-9a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
C67	3977(5)	-754(5)	5510(2)	30.5(16)
C68	3648(5)	-178(4)	5235(2)	26.4(15)
C69	4270(4)	1748(4)	5029.1(19)	19.3(13)
C70	1613(5)	4507(4)	4127(2)	28.1(15)
C71	2354(5)	4084(4)	4309.4(19)	23.0(14)
C72	5311(6)	2573(5)	3216(2)	38.4(18)
C73	4286(6)	2619(6)	3242(3)	48(2)
C74	7951(6)	2773(5)	2956(2)	35.2(17)
C75	9039(6)	2508(6)	2983(3)	46(2)
C76	7753(7)	3409(5)	3286(2)	45(2)
C77	7745(6)	3213(5)	2564(2)	42.7(19)
C78	6549(7)	4084(7)	7568(3)	59(3)

Table 3. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for β -(S)-9a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	46.5(12)	81.9(17)	46.1(13)	-9.5(11)	-4.7(10)	-0.9(11)
Cl2	43.4(11)	57.0(13)	43.8(11)	1.2(10)	2.4(9)	7.6(10)
Si1	20.8(8)	25.0(9)	19.7(9)	0.7(7)	0.6(7)	0.2(7)
Si2	22.5(9)	36.7(11)	25.6(10)	-0.9(8)	-0.6(8)	-1.7(8)
O1	33(3)	26(2)	17(2)	1.5(18)	1(2)	1(2)
O2	25(2)	18(2)	18(2)	0.8(17)	-3.8(18)	0.9(18)
O3	21(2)	28(2)	22(2)	-4(2)	-1.9(19)	0.8(19)
O4	29(2)	21(2)	20(2)	2.6(18)	-2.6(19)	1.4(19)
O5	23(2)	23(2)	29(3)	-5(2)	-2(2)	3.5(19)
O6	42(3)	30(3)	21(2)	3(2)	-3(2)	0(2)
O7	18(2)	23(2)	27(2)	-3.1(19)	-1.8(19)	0.5(18)
O8	19(2)	26(2)	20(2)	-3.8(18)	2.2(19)	-1.8(18)
O9	23(2)	46(3)	24(2)	-3(2)	0(2)	-5(2)
O10	21(2)	29(2)	22(2)	1.0(19)	2.3(19)	-0.1(19)
O11	15(2)	24(2)	18(2)	-2.5(17)	1.1(17)	-1.7(17)
O12	21(2)	28(2)	24(2)	-3.5(19)	-5.8(19)	1.3(19)
O13	20(2)	20(2)	29(3)	-6.2(19)	5.0(19)	-5.6(18)
O14	23(2)	18(2)	30(3)	-1.6(18)	-2(2)	2.7(18)
N1	20(3)	30(3)	16(3)	-6(2)	-2(2)	2(2)

Table 3. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for β -(S)-9a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C2	28(3)	25(3)	16(3)	0(3)	-3(3)	2(3)
N3	15(3)	25(3)	24(3)	3(2)	-8(2)	1(2)
C1	25(4)	39(4)	39(4)	9(3)	0(3)	3(3)
C79	26(4)	33(4)	49(5)	-4(3)	-3(3)	0(3)
C3	24(4)	36(4)	40(4)	0(3)	-7(3)	-1(3)
C4	22(3)	20(3)	24(3)	1(3)	-2(3)	3(3)
C5	23(3)	26(3)	19(3)	-1(3)	2(3)	5(3)
C6	22(3)	21(3)	12(3)	-1(2)	2(3)	-4(2)
C7	19(3)	17(3)	18(3)	3(2)	-2(2)	0(2)
C8	22(3)	18(3)	25(4)	-1(3)	4(3)	1(2)
C9	24(3)	30(4)	13(3)	1(3)	1(3)	4(3)
C10	23(3)	31(4)	27(4)	-1(3)	1(3)	8(3)
C11	29(4)	29(4)	28(4)	-4(3)	0(3)	-2(3)
C12	27(3)	32(4)	23(3)	2(3)	1(3)	-3(3)
C13	29(4)	40(4)	44(5)	-5(4)	-10(4)	2(3)
C14	23(3)	29(4)	38(4)	-6(3)	-2(3)	-6(3)
C15	23(4)	37(4)	30(4)	-5(3)	0(3)	-4(3)
C16	24(4)	29(4)	28(4)	0(3)	0(3)	1(3)
C17	21(3)	30(4)	18(3)	3(3)	6(3)	-1(3)
C18	28(4)	30(4)	23(4)	0(3)	1(3)	3(3)
C19	31(4)	21(3)	35(4)	2(3)	6(3)	-2(3)
C20	15(3)	23(3)	20(3)	-3(2)	-4(3)	-3(2)
C21	20(3)	25(3)	21(3)	-4(3)	-3(3)	-3(3)
C22	20(3)	18(3)	18(3)	4(2)	1(3)	-1(2)
C23	21(3)	22(3)	25(4)	-3(3)	1(3)	-2(3)
C24	27(4)	38(4)	44(4)	-11(3)	-8(3)	5(3)
C25	29(4)	41(4)	35(4)	-10(3)	-1(3)	1(3)
C26	25(4)	34(4)	23(4)	-6(3)	3(3)	2(3)
C27	26(4)	28(4)	25(4)	-2(3)	7(3)	2(3)
C28	30(4)	35(4)	31(4)	0(3)	-1(3)	15(3)
C29	49(5)	37(4)	29(4)	2(3)	3(4)	11(4)
C30	40(5)	33(4)	56(5)	4(4)	17(4)	3(3)
C31	33(4)	38(4)	61(6)	-20(4)	-3(4)	2(4)
C32	32(4)	35(4)	36(4)	-14(3)	-5(3)	8(3)
C33	29(4)	37(4)	32(4)	-1(3)	2(3)	3(3)
C34	26(4)	39(4)	31(4)	-6(3)	0(3)	0(3)
C35	28(4)	34(4)	25(4)	0(3)	1(3)	5(3)

Table 3. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for β -(S)-9a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C36	40(4)	31(4)	29(4)	-4(3)	4(3)	-4(3)
C37	31(4)	40(4)	29(4)	-7(3)	3(3)	8(3)
C38	36(4)	46(5)	30(4)	1(3)	-3(3)	-3(4)
C39	37(4)	38(4)	46(5)	-1(4)	-15(4)	9(3)
C40	22(3)	28(4)	35(4)	4(3)	-3(3)	3(3)
C41	31(4)	25(4)	27(4)	3(3)	-9(3)	2(3)
C42	26(4)	24(3)	24(3)	2(3)	-5(3)	1(3)
C43	16(3)	21(3)	22(3)	5(3)	-1(3)	0(2)
C44	15(3)	26(3)	20(3)	3(3)	1(3)	0(3)
C45	17(3)	20(3)	14(3)	-1(2)	-4(2)	3(2)
C46	16(3)	26(3)	16(3)	-5(2)	2(2)	0(2)
C47	19(3)	26(3)	20(3)	-5(3)	1(3)	0(3)
C48	30(4)	27(4)	21(4)	-3(3)	-1(3)	-7(3)
C49	35(4)	30(4)	21(4)	6(3)	6(3)	-3(3)
C50	32(4)	35(4)	39(4)	2(3)	-3(3)	-2(3)
C51	30(4)	56(5)	50(5)	-1(4)	-9(4)	-4(4)
C52	24(4)	56(6)	61(6)	12(4)	-8(4)	1(4)
C53	42(5)	46(5)	35(4)	-18(4)	-4(4)	2(4)
C54	31(4)	39(4)	41(5)	-5(4)	0(3)	1(3)
C55	25(4)	50(5)	23(4)	-4(3)	1(3)	-3(3)
C56	29(4)	41(4)	25(4)	-1(3)	1(3)	-2(3)
C57	48(5)	45(5)	28(4)	-5(3)	-7(4)	9(4)
C58	47(5)	71(6)	28(4)	-13(4)	-2(4)	5(5)
C59	23(3)	19(3)	24(3)	-4(3)	1(3)	3(3)
C60	21(3)	16(3)	23(3)	0(3)	0(3)	4(2)
C61	15(3)	27(3)	18(3)	-4(3)	1(3)	-5(3)
C62	22(3)	22(3)	24(3)	1(3)	-4(3)	1(3)
C63	19(3)	21(3)	25(3)	-2(3)	-1(3)	-3(2)
C64	23(3)	26(3)	25(3)	-3(3)	1(3)	-4(3)
C65	20(3)	25(4)	42(4)	-2(3)	-3(3)	0(3)
C66	31(4)	32(4)	37(4)	6(3)	-8(3)	-1(3)
C67	29(4)	38(4)	25(4)	7(3)	3(3)	-1(3)
C68	25(3)	23(3)	31(4)	0(3)	6(3)	-1(3)
C69	18(3)	16(3)	24(3)	5(3)	1(3)	4(2)
C70	29(4)	22(3)	32(4)	1(3)	-7(3)	4(3)
C71	22(3)	24(3)	24(3)	-2(3)	0(3)	0(3)
C72	27(4)	40(4)	48(5)	-6(4)	1(4)	-1(3)

Table 3. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for β -(S)-9a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C73	41(5)	46(5)	57(6)	5(4)	7(4)	5(4)
C74	36(4)	43(4)	26(4)	-2(3)	4(3)	-4(3)
C75	28(4)	52(5)	56(5)	0(4)	-3(4)	-13(4)
C76	45(5)	45(5)	43(5)	-7(4)	1(4)	-11(4)
C77	37(4)	51(5)	39(5)	9(4)	-2(4)	-8(4)
C78	49(5)	74(7)	54(6)	-23(5)	-8(5)	21(5)

Table 4. Bond Lengths for β -(S)-9a.

Atom	Atom	Length/ \AA	Atom	Atom	Length/ \AA
C11	C78	1.742(10)	C17	C18	1.395(9)
C12	C78	1.791(9)	C18	C19	1.381(10)
Si1	O1	1.641(5)	C20	C21	1.537(9)
Si1	C4	1.878(7)	C21	C22	1.492(9)
Si1	C17	1.868(7)	C24	C25	1.390(11)
Si1	C35	1.894(7)	C26	C27	1.513(10)
Si2	O9	1.644(5)	C27	C28	1.366(10)
Si2	C49	1.838(8)	C27	C32	1.405(10)
Si2	C56	1.882(8)	C28	C29	1.395(11)
Si2	C74	1.870(8)	C29	C30	1.354(12)
O1	C5	1.428(7)	C30	C31	1.392(12)
O2	C6	1.445(7)	C31	C32	1.399(11)
O2	C7	1.422(7)	C33	C34	1.377(10)
O3	C21	1.422(8)	C35	C36	1.532(10)
O4	C22	1.449(7)	C35	C37	1.529(10)
O4	C23	1.339(8)	C35	C38	1.544(10)
O5	C9	1.235(8)	C39	C40	1.493(10)
O6	C23	1.191(8)	C40	C41	1.401(10)
O7	C20	1.417(7)	C40	C70	1.389(10)
O8	C46	1.403(7)	C41	C42	1.391(9)
O8	C47	1.428(8)	C42	C43	1.387(9)
O9	C48	1.420(8)	C43	C44	1.486(9)
O10	C69	1.207(8)	C43	C71	1.389(9)
O11	C61	1.467(7)	C45	C46	1.523(9)
O11	C69	1.325(8)	C45	C62	1.550(9)
O12	C44	1.246(8)	C45	C69	1.563(9)
O13	C60	1.431(8)	C46	C61	1.508(9)

Table 4. Bond Lengths for β -(S)-9a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O14	C59	1.424(8)	C47	C48	1.531(9)
N1	C8	1.436(8)	C47	C59	1.532(9)
N1	C9	1.364(9)	C49	C50	1.417(10)
C2	C9	1.491(9)	C49	C72	1.406(11)
C2	C10	1.407(10)	C50	C51	1.372(11)
C2	C25	1.352(10)	C51	C52	1.391(13)
N3	C44	1.348(8)	C52	C73	1.394(13)
N3	C45	1.447(8)	C53	C54	1.379(12)
C1	C79	1.401(11)	C53	C58	1.397(13)
C1	C33	1.386(11)	C54	C55	1.393(11)
C79	C3	1.382(10)	C55	C56	1.390(11)
C3	C4	1.390(10)	C56	C57	1.412(10)
C4	C34	1.412(10)	C57	C58	1.393(11)
C5	C6	1.525(9)	C59	C60	1.546(9)
C6	C20	1.537(8)	C60	C61	1.505(8)
C7	C8	1.529(9)	C62	C63	1.518(9)
C7	C22	1.507(9)	C63	C64	1.392(9)
C8	C23	1.563(9)	C63	C68	1.362(10)
C8	C26	1.538(9)	C64	C65	1.393(10)
C10	C11	1.387(10)	C65	C66	1.360(11)
C11	C12	1.371(10)	C66	C67	1.387(10)
C12	C13	1.497(10)	C67	C68	1.396(10)
C12	C24	1.388(10)	C70	C71	1.364(9)
C14	C15	1.385(10)	C72	C73	1.393(12)
C14	C19	1.376(10)	C74	C75	1.534(11)
C15	C16	1.383(10)	C74	C76	1.549(11)
C16	C17	1.396(10)	C74	C77	1.553(11)

Table 5. Bond Angles for β -(S)-9a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Si1	C4	111.9(3)	C31	C32	C27	119.3(7)
O1	Si1	C17	107.5(3)	C34	C33	C1	122.0(7)
O1	Si1	C35	101.7(3)	C33	C34	C4	120.7(7)
C4	Si1	C35	116.3(3)	C36	C35	Si1	112.2(5)
C17	Si1	C4	107.9(3)	C36	C35	C38	109.1(6)
C17	Si1	C35	111.3(3)	C37	C35	Si1	108.5(5)
O9	Si2	C49	107.8(3)	C37	C35	C36	108.5(6)

Table 5. Bond Angles for β -(S)-9a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O9	Si2	C56	107.2(3)	C37	C35	C38	108.3(6)
O9	Si2	C74	104.3(3)	C38	C35	Si1	110.2(5)
C49	Si2	C56	108.5(3)	C41	C40	C39	121.0(7)
C49	Si2	C74	115.9(4)	C70	C40	C39	121.4(7)
C74	Si2	C56	112.6(3)	C70	C40	C41	117.7(6)
C5	O1	Si1	128.5(4)	C42	C41	C40	120.6(7)
C7	O2	C6	106.0(4)	C43	C42	C41	120.1(6)
C23	O4	C22	109.3(5)	C42	C43	C44	122.0(6)
C46	O8	C47	106.8(4)	C42	C43	C71	119.1(6)
C48	O9	Si2	121.6(4)	C71	C43	C44	118.8(6)
C69	O11	C61	108.4(5)	O12	C44	N3	119.8(6)
C9	N1	C8	121.9(5)	O12	C44	C43	121.7(6)
C10	C2	C9	122.1(6)	N3	C44	C43	118.5(6)
C25	C2	C9	118.7(6)	N3	C45	C46	112.2(5)
C25	C2	C10	119.1(7)	N3	C45	C62	106.9(5)
C44	N3	C45	123.0(5)	N3	C45	C69	111.9(5)
C33	C1	C79	117.3(7)	C46	C45	C62	116.1(5)
C3	C79	C1	121.2(7)	C46	C45	C69	98.7(5)
C79	C3	C4	121.4(7)	C62	C45	C69	111.0(5)
C3	C4	Si1	123.4(5)	O8	C46	C45	118.6(5)
C3	C4	C34	117.3(6)	O8	C46	C61	109.6(5)
C34	C4	Si1	119.3(5)	C61	C46	C45	103.0(5)
O1	C5	C6	105.8(5)	O8	C47	C48	106.6(5)
O2	C6	C5	107.1(5)	O8	C47	C59	112.1(5)
O2	C6	C20	114.2(5)	C48	C47	C59	113.4(5)
C5	C6	C20	111.4(5)	O9	C48	C47	108.7(5)
O2	C7	C8	119.9(5)	C50	C49	Si2	121.9(6)
O2	C7	C22	108.5(5)	C72	C49	Si2	123.3(6)
C22	C7	C8	102.9(5)	C72	C49	C50	114.5(7)
N1	C8	C7	113.9(5)	C51	C50	C49	122.6(8)
N1	C8	C23	109.9(5)	C50	C51	C52	120.7(8)
N1	C8	C26	110.7(5)	C51	C52	C73	119.4(8)
C7	C8	C23	98.9(5)	C54	C53	C58	120.0(7)
C7	C8	C26	117.1(6)	C53	C54	C55	119.7(8)
C26	C8	C23	105.2(5)	C56	C55	C54	122.3(7)
O5	C9	N1	120.7(6)	C55	C56	Si2	119.4(5)
O5	C9	C2	121.5(6)	C55	C56	C57	116.8(7)
N1	C9	C2	117.8(6)	C57	C56	Si2	123.8(6)

Table 5. Bond Angles for β -(S)-9a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	C10	C2	119.0(6)	C58	C57	C56	121.6(8)
C12	C11	C10	122.3(7)	C57	C58	C53	119.4(8)
C11	C12	C13	123.4(7)	O14	C59	C47	107.8(5)
C11	C12	C24	117.4(7)	O14	C59	C60	110.0(5)
C24	C12	C13	119.2(7)	C47	C59	C60	113.2(5)
C19	C14	C15	119.5(6)	O13	C60	C59	112.4(5)
C16	C15	C14	119.5(7)	O13	C60	C61	108.9(5)
C15	C16	C17	122.0(7)	C61	C60	C59	104.5(5)
C16	C17	Si1	120.0(5)	O11	C61	C46	104.2(5)
C18	C17	Si1	123.0(5)	O11	C61	C60	116.4(5)
C18	C17	C16	117.0(6)	C60	C61	C46	109.7(5)
C19	C18	C17	121.2(7)	C63	C62	C45	117.8(5)
C14	C19	C18	120.6(7)	C64	C63	C62	120.7(6)
O7	C20	C6	110.4(5)	C68	C63	C62	120.1(6)
O7	C20	C21	109.9(5)	C68	C63	C64	119.2(6)
C21	C20	C6	113.2(5)	C63	C64	C65	119.8(6)
O3	C21	C20	110.1(5)	C66	C65	C64	120.7(7)
O3	C21	C22	109.5(5)	C65	C66	C67	119.9(7)
C22	C21	C20	106.2(5)	C66	C67	C68	119.3(7)
O4	C22	C7	105.0(5)	C63	C68	C67	121.1(6)
O4	C22	C21	114.8(5)	O10	C69	O11	121.3(6)
C21	C22	C7	109.7(5)	O10	C69	C45	126.6(6)
O4	C23	C8	110.8(6)	O11	C69	C45	111.9(5)
O6	C23	O4	123.5(6)	C71	C70	C40	121.9(7)
O6	C23	C8	125.5(6)	C70	C71	C43	120.4(6)
C12	C24	C25	121.0(7)	C73	C72	C49	123.9(8)
C2	C25	C24	121.0(7)	C72	C73	C52	118.6(9)
C27	C26	C8	115.7(6)	C75	C74	Si2	108.9(6)
C28	C27	C26	121.3(7)	C75	C74	C76	107.4(7)
C28	C27	C32	119.0(7)	C75	C74	C77	110.5(7)
C32	C27	C26	119.7(6)	C76	C74	Si2	110.6(5)
C27	C28	C29	121.3(7)	C76	C74	C77	108.6(7)
C30	C29	C28	120.2(8)	C77	C74	Si2	110.8(5)
C29	C30	C31	119.9(8)	C11	C78	C12	110.8(5)
C30	C31	C32	120.2(8)				

Table 6. Torsion Angles for β -(S)-9a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Si1	O1	C5	C6	-162.5(4)	C22	C7	C8	N1	149.5(5)
Si1	C4	C34	C33	-179.0(6)	C22	C7	C8	C23	32.9(6)
Si1	C17	C18	C19	176.6(5)	C22	C7	C8	C26	-79.3(7)
Si2	O9	C48	C47	-117.1(5)	C23	O4	C22	C7	22.4(6)
Si2	C49	C50	C51	171.3(7)	C23	O4	C22	C21	142.9(6)
Si2	C49	C72	C73	-169.2(7)	C23	C8	C26	C27	168.3(6)
Si2	C56	C57	C58	-177.2(7)	C25	C2	C9	O5	-19.1(10)
O1	Si1	C4	C3	-93.5(6)	C25	C2	C9	N1	158.8(7)
O1	Si1	C4	C34	85.3(6)	C25	C2	C10	C11	-1.9(10)
O1	Si1	C17	C16	20.8(6)	C26	C8	C23	O4	99.9(6)
O1	Si1	C17	C18	-157.8(5)	C26	C8	C23	O6	-75.3(8)
O1	Si1	C35	C36	52.3(6)	C26	C27	C28	C29	178.6(7)
O1	Si1	C35	C37	-67.6(5)	C26	C27	C32	C31	179.1(7)
O1	Si1	C35	C38	174.0(5)	C27	C28	C29	C30	0.7(12)
O1	C5	C6	O2	-178.8(5)	C28	C27	C32	C31	-2.8(11)
O1	C5	C6	C20	-53.3(7)	C28	C29	C30	C31	0.3(13)
O2	C6	C20	O7	75.6(6)	C29	C30	C31	C32	-2.6(13)
O2	C6	C20	C21	-48.1(7)	C30	C31	C32	C27	3.9(12)
O2	C7	C8	N1	-90.0(7)	C32	C27	C28	C29	0.5(11)
O2	C7	C8	C23	153.5(5)	C33	C1	C79	C3	2.4(12)
O2	C7	C8	C26	41.3(8)	C35	Si1	O1	C5	178.7(6)
O2	C7	C22	O4	-163.4(5)	C35	Si1	C4	C3	22.7(7)
O2	C7	C22	C21	72.7(6)	C35	Si1	C4	C34	-158.4(5)
O3	C21	C22	O4	-56.7(7)	C35	Si1	C17	C16	-89.7(6)
O3	C21	C22	C7	61.3(7)	C35	Si1	C17	C18	91.7(6)
O7	C20	C21	O3	163.7(5)	C39	C40	C41	C42	-177.8(7)
O7	C20	C21	C22	-77.8(6)	C39	C40	C70	C71	177.6(7)
O8	C46	C61	O11	-164.1(5)	C40	C41	C42	C43	0.6(11)
O8	C46	C61	C60	70.6(6)	C40	C70	C71	C43	-0.2(11)
O8	C47	C48	O9	156.2(5)	C41	C40	C70	C71	-1.7(11)
O8	C47	C59	O14	68.8(6)	C41	C42	C43	C44	176.2(6)
O8	C47	C59	C60	-53.1(7)	C41	C42	C43	C71	-2.5(10)
O9	Si2	C49	C50	-112.0(6)	C42	C43	C44	O12	162.1(6)
O9	Si2	C49	C72	61.0(7)	C42	C43	C44	N3	-17.8(9)
O9	Si2	C56	C55	4.6(7)	C42	C43	C71	C70	2.4(10)
O9	Si2	C56	C57	-176.6(6)	C44	N3	C45	C46	-64.9(8)
O9	Si2	C74	C75	62.6(6)	C44	N3	C45	C62	166.7(6)
O9	Si2	C74	C76	-55.2(6)	C44	N3	C45	C69	45.0(8)
O9	Si2	C74	C77	-175.7(5)	C44	C43	C71	C70	-176.4(6)

Table 6. Torsion Angles for β -(S)-9a.

O13 C60 C61 O11	-54.7(7)	C45 N3 C44 O12	-1.3(10)
O13 C60 C61 C46	63.3(6)	C45 N3 C44 C43	178.5(6)
O14 C59 C60 O13	171.1(5)	C45 C46 C61 O11	-36.9(6)
O14 C59 C60 C61	-70.9(6)	C45 C46 C61 C60	-162.3(5)
N1 C8 C23 O4	-140.9(5)	C45 C62 C63 C64	-91.8(7)
N1 C8 C23 O6	43.9(9)	C45 C62 C63 C68	90.6(8)
N1 C8 C26 C27	49.7(8)	C46 O8 C47 C48	-175.7(5)
C2 C10 C11 C12	0.5(11)	C46 O8 C47 C59	59.7(6)
N3 C45 C46 O8	-88.2(7)	C46 C45 C62 C63	76.3(7)
N3 C45 C46 C61	150.7(5)	C46 C45 C69 O10	165.9(6)
N3 C45 C62 C63	-157.5(6)	C46 C45 C69 O11	-19.0(6)
N3 C45 C69 O10	47.7(8)	C47 O8 C46 C45	173.9(5)
N3 C45 C69 O11	-137.3(5)	C47 O8 C46 C61	-68.3(6)
C1 C79 C3 C4	-2.5(12)	C47 C59 C60 O13	-68.2(7)
C1 C33 C34 C4	0.1(12)	C47 C59 C60 C61	49.8(7)
C79 C1 C33 C34	-1.2(12)	C48 C47 C59 O14	-51.9(7)
C79 C3 C4 Si1	-179.9(6)	C48 C47 C59 C60	-173.9(5)
C79 C3 C4 C34	1.3(11)	C49 Si2 O9 C48	32.5(6)
C3 C4 C34 C33	-0.1(11)	C49 Si2 C56 C55	-111.5(6)
C4 Si1 O1 C5	-56.5(6)	C49 Si2 C56 C57	67.2(7)
C4 Si1 C17 C16	141.6(5)	C49 Si2 C74 C75	-179.1(5)
C4 Si1 C17 C18	-37.0(6)	C49 Si2 C74 C76	63.1(7)
C4 Si1 C35 C36	-69.5(6)	C49 Si2 C74 C77	-57.4(7)
C4 Si1 C35 C37	170.6(5)	C49 C50 C51 C52	0.4(13)
C4 Si1 C35 C38	52.2(6)	C49 C72 C73 C52	-4.4(14)
C5 C6 C20 O7	-45.9(7)	C50 C49 C72 C73	4.3(12)
C5 C6 C20 C21	-169.6(5)	C50 C51 C52 C73	-0.3(14)
C6 O2 C7 C8	174.1(5)	C51 C52 C73 C72	2.2(14)
C6 O2 C7 C22	-68.3(6)	C53 C54 C55 C56	0.6(12)
C6 C20 C21 O3	-72.3(7)	C54 C53 C58 C57	-0.3(13)
C6 C20 C21 C22	46.2(7)	C54 C55 C56 Si2	177.3(6)
C7 O2 C6 C5	-179.1(5)	C54 C55 C56 C57	-1.6(11)
C7 O2 C6 C20	57.1(6)	C55 C56 C57 C58	1.6(12)
C7 C8 C23 O4	-21.4(7)	C56 Si2 O9 C48	-84.1(5)
C7 C8 C23 O6	163.4(7)	C56 Si2 C49 C50	3.8(7)
C7 C8 C26 C27	-83.1(7)	C56 Si2 C49 C72	176.7(6)
C8 N1 C9 O5	-2.6(9)	C56 Si2 C74 C75	-53.3(7)
C8 N1 C9 C2	179.5(6)	C56 Si2 C74 C76	-171.1(6)

Table 6. Torsion Angles for β -(S)-9a.

C8 C7 C22 O4	-35.3(6)	C56 Si2 C74 C77	68.4(6)
C8 C7 C22 C21	-159.3(5)	C56 C57 C58 C53	-0.7(14)
C8 C26 C27 C28	94.1(8)	C58 C53 C54 C55	0.4(12)
C8 C26 C27 C32	-87.8(8)	C59 C47 C48 O9	-80.0(7)
C9 N1 C8 C7	-62.3(8)	C59 C60 C61 O11	-175.0(5)
C9 N1 C8 C23	47.6(8)	C59 C60 C61 C46	-57.0(6)
C9 N1 C8 C26	163.3(6)	C61 O11 C69 O10	171.7(6)
C9 C2 C10 C11	177.6(6)	C61 O11 C69 C45	-3.6(7)
C9 C2 C25 C24	-177.9(7)	C62 C45 C46 O8	35.2(8)
C10 C2 C9 O5	161.4(6)	C62 C45 C46 C61	-86.0(6)
C10 C2 C9 N1	-20.7(9)	C62 C45 C69 O10	-71.6(8)
C10 C2 C25 C24	1.7(11)	C62 C45 C69 O11	103.4(6)
C10 C11 C12 C13	-180.0(7)	C62 C63 C64 C65	-177.9(6)
C10 C11 C12 C24	1.2(11)	C62 C63 C68 C67	177.5(6)
C11 C12 C24 C25	-1.5(11)	C63 C64 C65 C66	0.6(10)
C12 C24 C25 C2	0.1(13)	C64 C63 C68 C67	-0.2(10)
C13 C12 C24 C25	179.6(8)	C64 C65 C66 C67	-0.4(11)
C14 C15 C16 C17	0.8(11)	C65 C66 C67 C68	0.0(11)
C15 C14 C19 C18	2.9(11)	C66 C67 C68 C63	0.3(11)
C15 C16 C17 Si1	-176.9(5)	C68 C63 C64 C65	-0.3(9)
C15 C16 C17 C18	1.8(10)	C69 O11 C61 C46	25.5(6)
C16 C17 C18 C19	-2.1(10)	C69 O11 C61 C60	146.4(6)
C17 Si1 O1 C5	61.7(6)	C69 C45 C46 O8	153.8(5)
C17 Si1 C4 C3	148.5(6)	C69 C45 C46 C61	32.7(6)
C17 Si1 C4 C34	-32.7(6)	C69 C45 C62 C63	-35.3(8)
C17 Si1 C35 C36	166.4(5)	C70 C40 C41 C42	1.5(11)
C17 Si1 C35 C37	46.6(6)	C71 C43 C44 O12	-19.2(9)
C17 Si1 C35 C38	-71.9(6)	C71 C43 C44 N3	161.0(6)
C17 C18 C19 C14	-0.2(11)	C72 C49 C50 C51	-2.2(11)
C19 C14 C15 C16	-3.1(11)	C74 Si2 O9 C48	156.2(5)
C20 C21 C22 O4	-175.6(5)	C74 Si2 C49 C50	131.7(6)
C20 C21 C22 C7	-57.6(6)	C74 Si2 C49 C72	-55.4(7)
C22 O4 C23 O6	175.3(6)	C74 Si2 C56 C55	118.7(6)
C22 O4 C23 C8	-0.1(7)	C74 Si2 C56 C57	-62.5(8)

Table 7. Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for β -(S)-9a.

Atom	x	y	z	U(eq)
H3	6470.04	3409.24	5169.34	36
H7	3812.72	4163	4928.06	34
H13	7254.86	2922.11	4666.73	34
H14A	7939.02	503.6	4526.58	35
H1	6562.72	5851.67	6599.4	27
H3B	2918.23	1698.92	4268.76	26
H1A	1290.12	7954.76	4153.46	41
H79	1588.26	6692.9	3812.55	43
H3A	3088.33	6005.76	3864.81	40
H5A	4218.77	6048.35	5086.17	27
H5B	5245.97	6557.36	5084.34	27
H6	6136.07	5327.68	5224.2	22
H7A	6389.75	4801.67	5791.9	22
H10	7737.68	6713.15	6605.16	32
H11	9100.48	7402.77	6864.97	34
H13A	10784.41	7442.46	7067.04	56
H13B	11480.96	6772.6	6855.17	56
H13C	11083.44	6588.22	7282.1	56
H14	7810.4	8932.86	4451.03	36
H15	8001.19	7638.91	4766.37	36
H16	6835.47	6585.35	4677.28	33
H18	5382.43	8048.97	3913.02	33
H19	6539.8	9104.01	4006.26	35
H20	5306.47	4301.41	4897.83	23
H21	4934.13	3222.7	5391.97	26
H22	4417.53	4192.17	5862.39	23
H24	10691.87	5279.03	6799.62	44
H25	9334.29	4576.41	6544.59	42
H26A	4243.73	5047.71	6412.59	33
H26B	4841.59	5072.86	6809.66	33
H28	3880.7	6348.05	6078.93	38
H29	3677.05	7805.18	6109.12	46
H30	4410.25	8569.36	6596.26	52
H31	5391.14	7886.3	7056.78	53
H32	5513.37	6409.2	7054.22	41
H33	2594.86	8547.74	4503.93	39
H34	4113.54	7894.37	4541.11	39
H36A	4793.81	4526.81	4134.52	51
H36B	4976.54	4370.08	3683.6	51

Table 7. Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for β -(*S*)-9a.

H36C	4044.35	4909.06	3823.22	51
H37A	6851.51	5849.96	3893.8	50
H37B	6640.49	4958.32	3695.38	50
H37C	6538.41	5060.63	4153.42	50
H38A	4533.8	6152.34	3420.09	56
H38B	5405.24	5577.13	3253.48	56
H38C	5650.25	6480.98	3433.44	56
H39A	159.76	4414.07	3377.98	60
H39B	356.88	5206.31	3652.73	60
H39C	-388.03	4480.74	3786.35	60
H41	952.27	3057.49	3517.47	33
H42	2226.88	2331.43	3825.96	30
H46	5202.88	2213.93	4380.22	24
H47	6318.76	2061.05	3952.54	26
H48A	7039.8	435.83	3735.04	31
H48B	6141.99	849.2	3499.15	31
H50	5501.31	1097.14	2575.09	42
H51	3808.72	1181.81	2595.59	54
H52	3020.43	2135.43	3008.37	57
H53	8109.21	-878.17	2016.66	49
H54	8248.36	-1017.96	2684.29	45
H55	7880.34	115.43	3085.18	39
H57	7243.11	1544.96	2152.71	48
H58	7608.2	411.32	1747.86	59
H59	7778.14	1703.75	4269.47	26
H60	7242.62	1662.36	4950.36	24
H61	5860.69	810.36	4825.43	24
H62A	3006.8	536.45	4614.37	27
H62B	3895.23	295.53	4333.68	27
H64	5313.95	-497.36	4581.93	30
H65	5879.51	-1454.86	5045.08	35
H66	5045.24	-1623.78	5620.38	40
H67	3631.55	-820.83	5747.25	37
H68	3077.31	150.79	5286.74	32
H70	1470.02	5069.23	4202.5	34
H71	2719.33	4353.49	4508.22	28
H72	5689.91	2955.4	3366.48	46

Table 7. Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for β -(*S*)-9a.

H73	3978.54	2995.55	3417.67	58
H75A	9160.76	2245.16	3234.66	68
H75B	9461.12	3005.67	2955.37	68
H75C	9189.57	2105.78	2777.07	68
H76A	7101.69	3665.45	3249.54	67
H76B	8260.69	3849.07	3281.32	67
H76C	7772.76	3116.21	3534.46	67
H77A	7965.29	2849.34	2352	64
H77B	8103.83	3748.07	2553.43	64
H77C	7035.14	3319.64	2538.21	64
H78A	6428.68	3470.7	7553.46	71
H78B	6874.41	4260.69	7324.61	71

7. Copies of NMR spectra

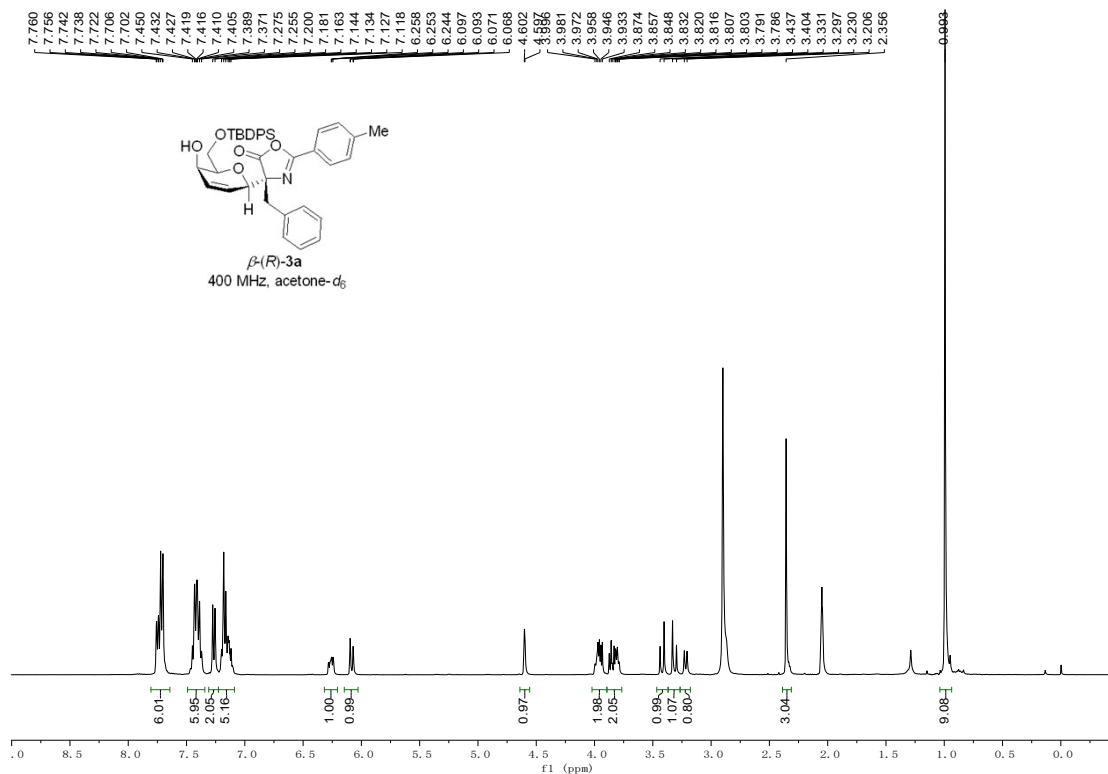


Figure S2. ^1H NMR spectrum of β -(R)-3a

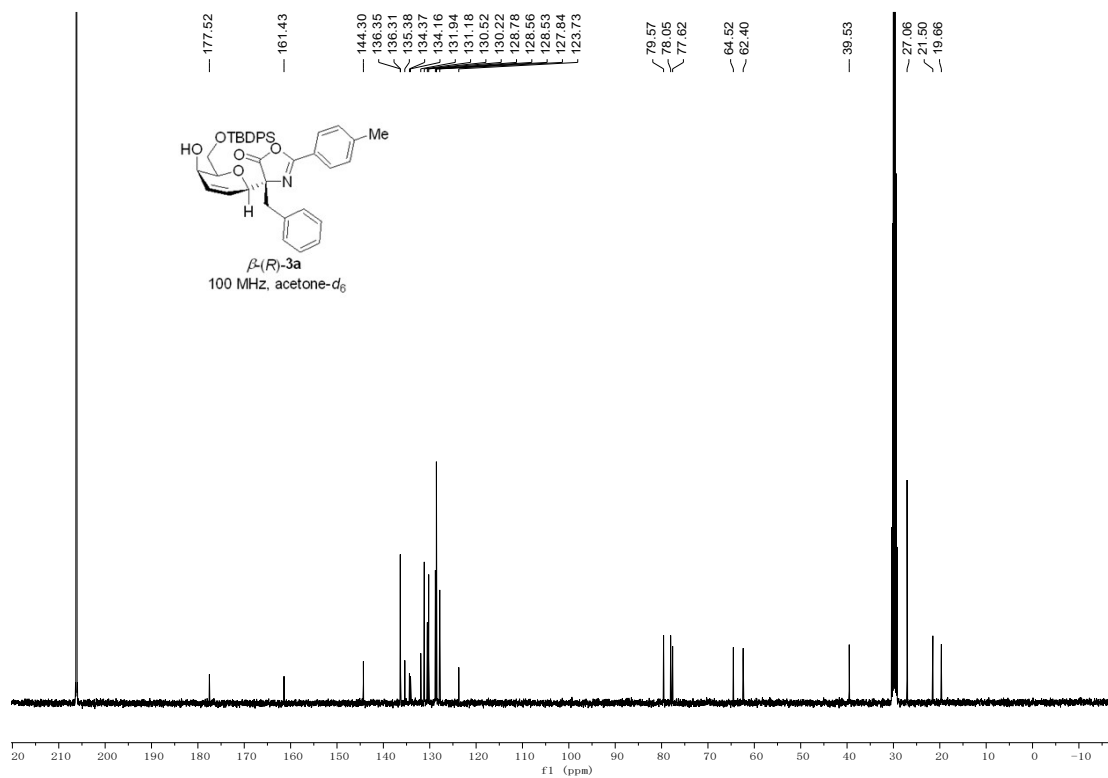


Figure S3. ^{13}C NMR spectrum of β -(R)-3a

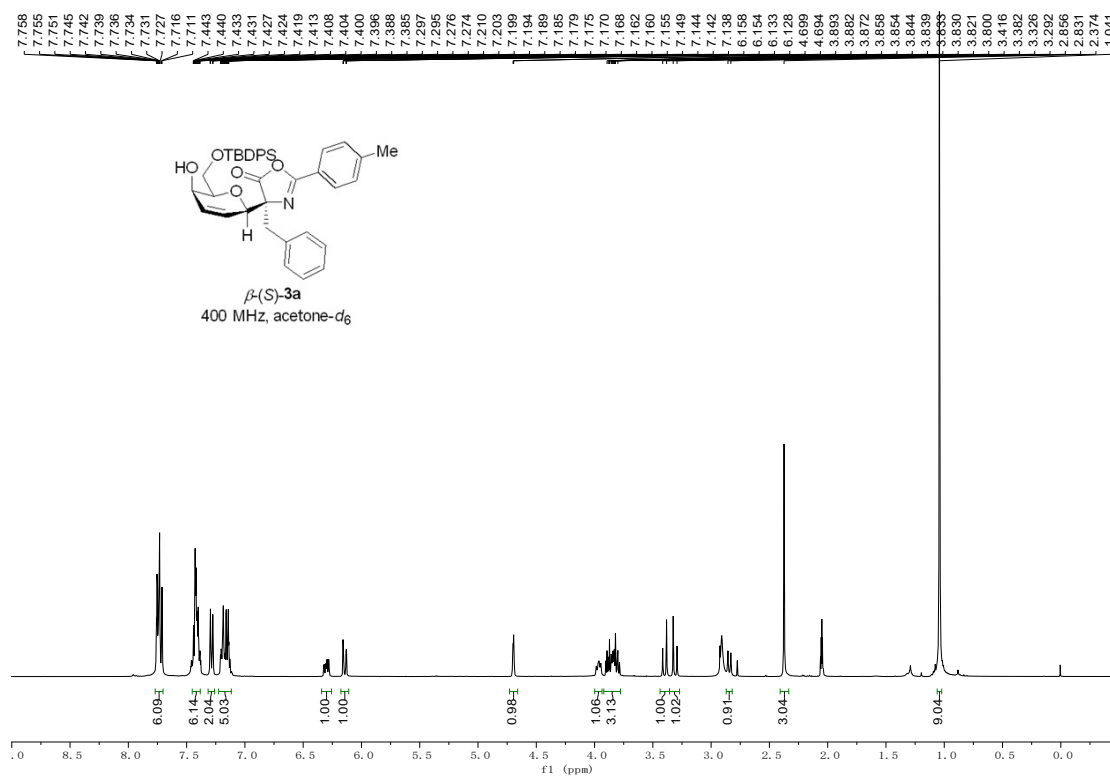


Figure S4. ^1H NMR spectrum of β -(S)-3a

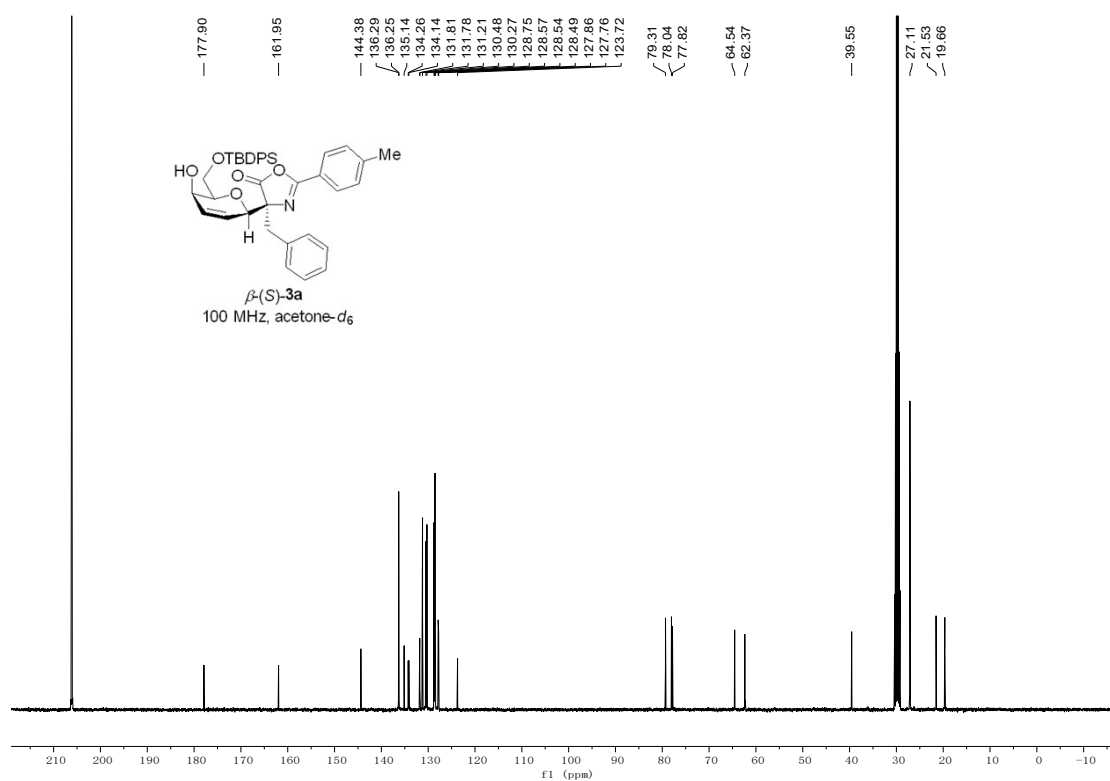


Figure S5. ^{13}C NMR spectrum of β -(S)-3a

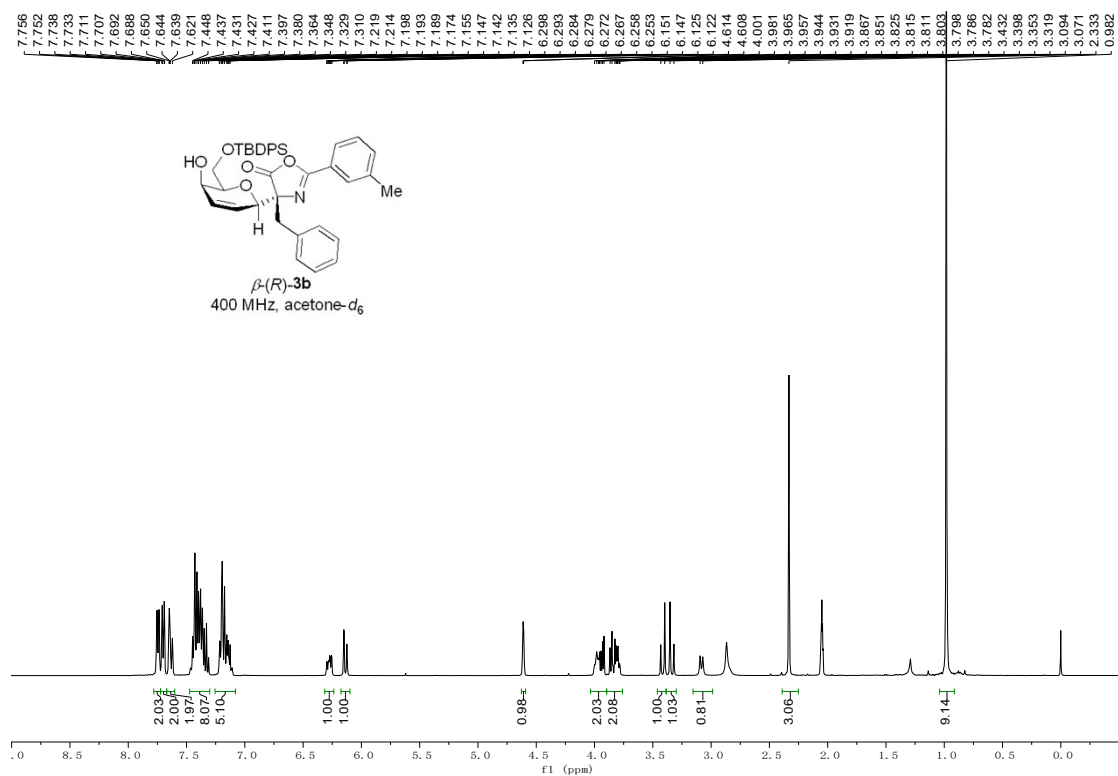


Figure S6. ^1H NMR spectrum of β -(R)-3b

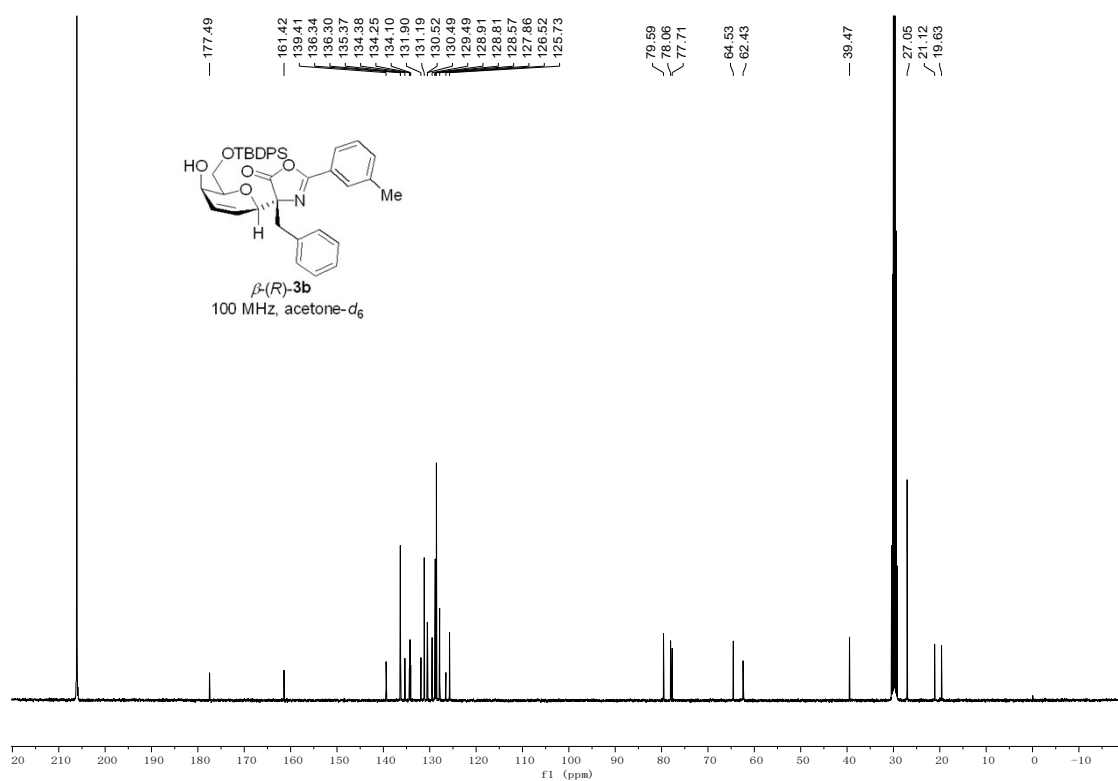


Figure S7. ^{13}C NMR spectrum of β -(R)-3b

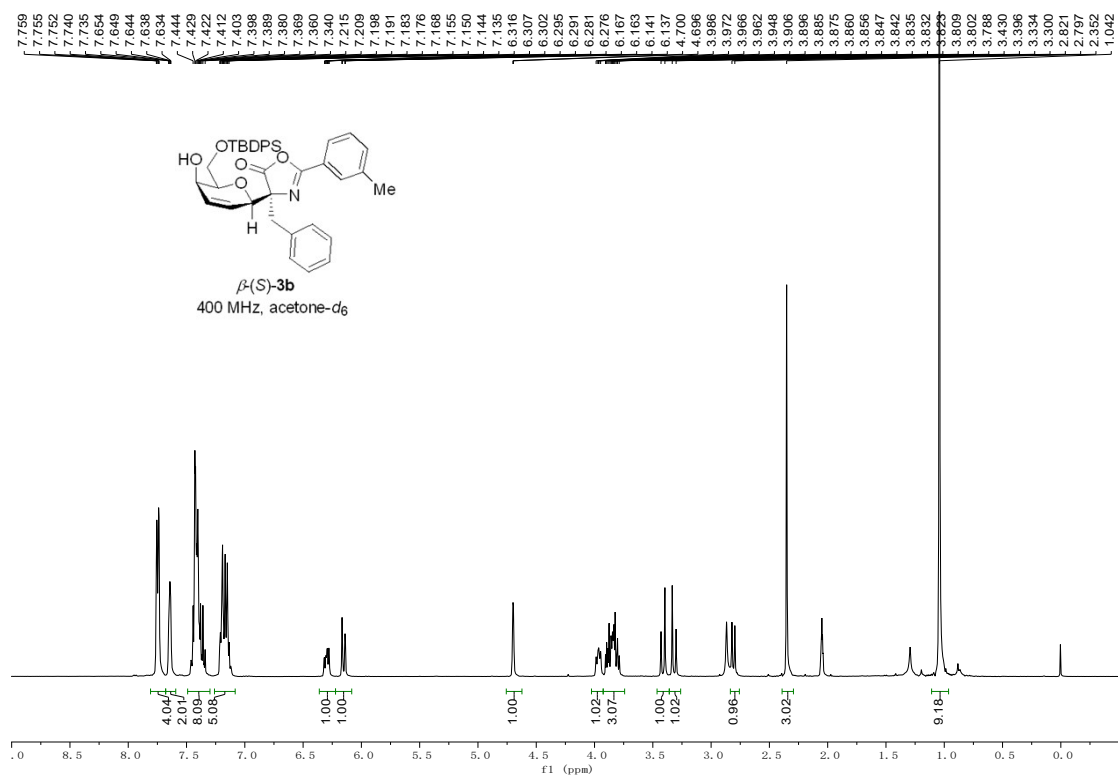


Figure S8. ^1H NMR spectrum of β -(S)-3b

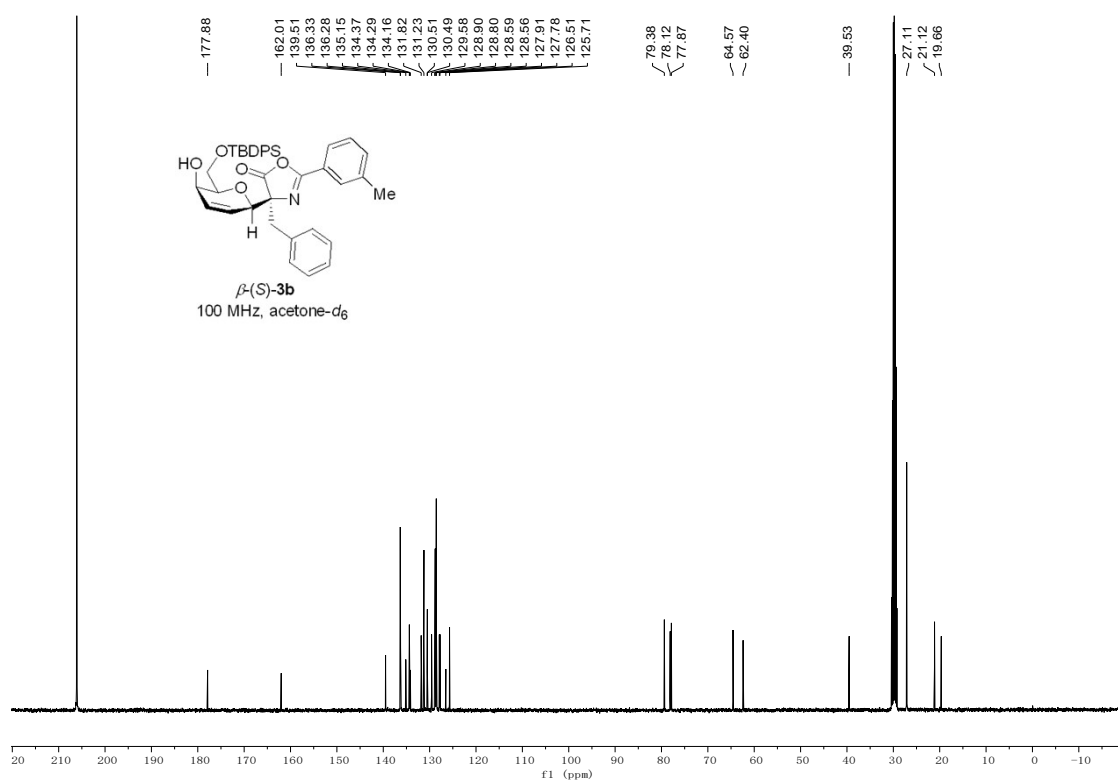


Figure S9. ^{13}C NMR spectrum of β -(S)-3b

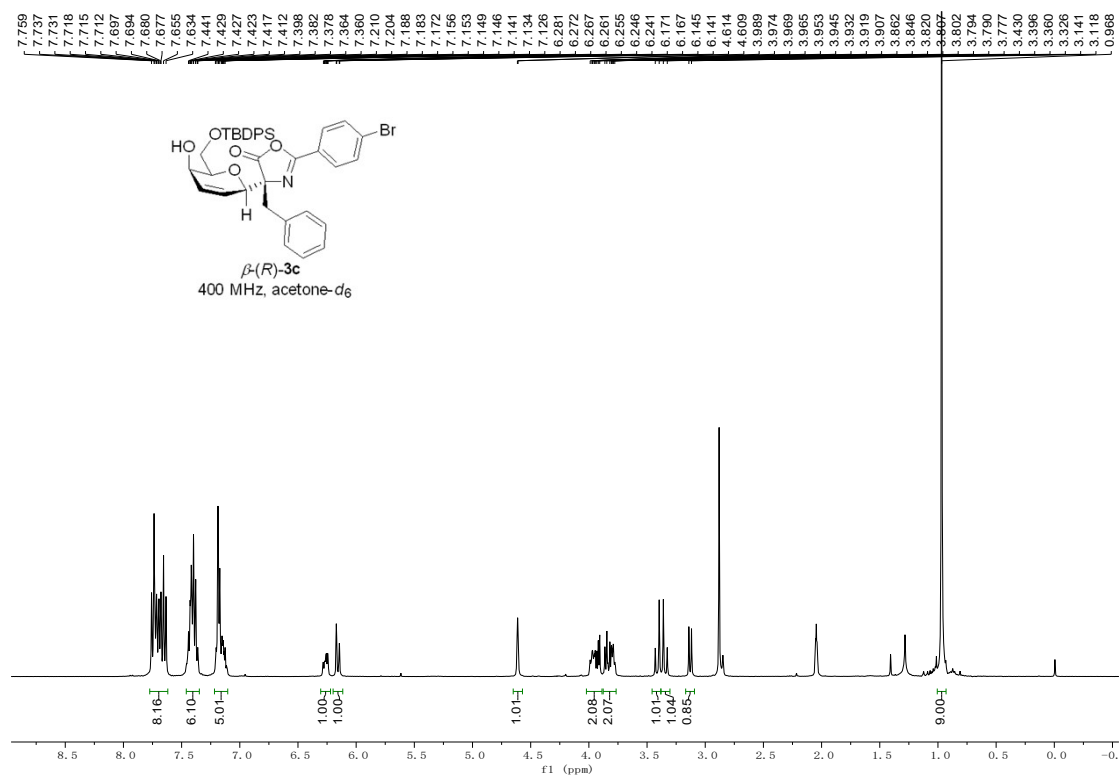


Figure S10. ^1H NMR spectrum of β -(R)-3c

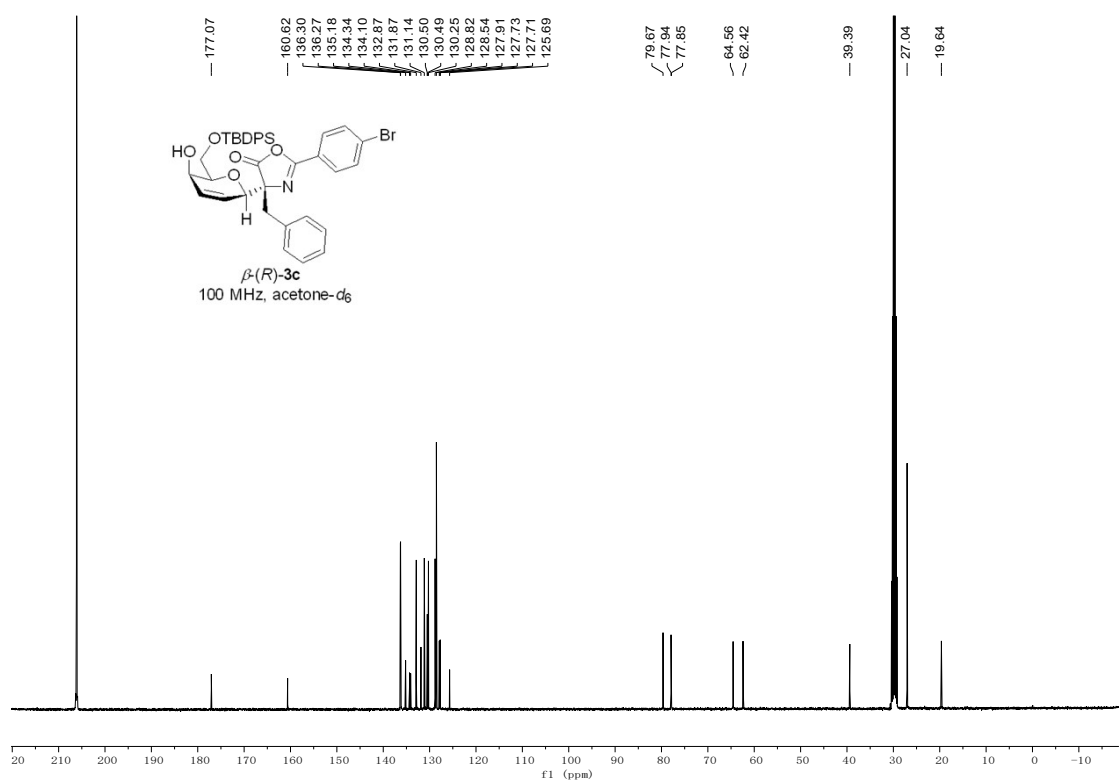


Figure S11. ^{13}C NMR spectrum of β -(R)-3c

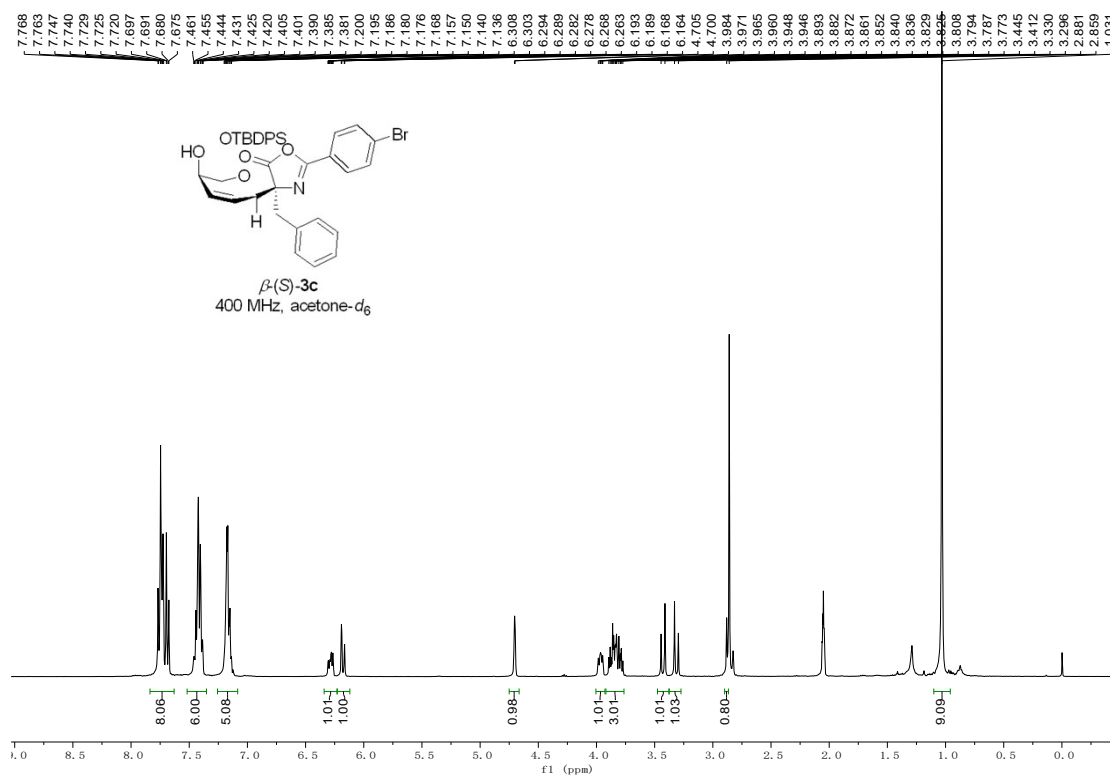


Figure S12. ^1H NMR spectrum of β -(S)-**3c**

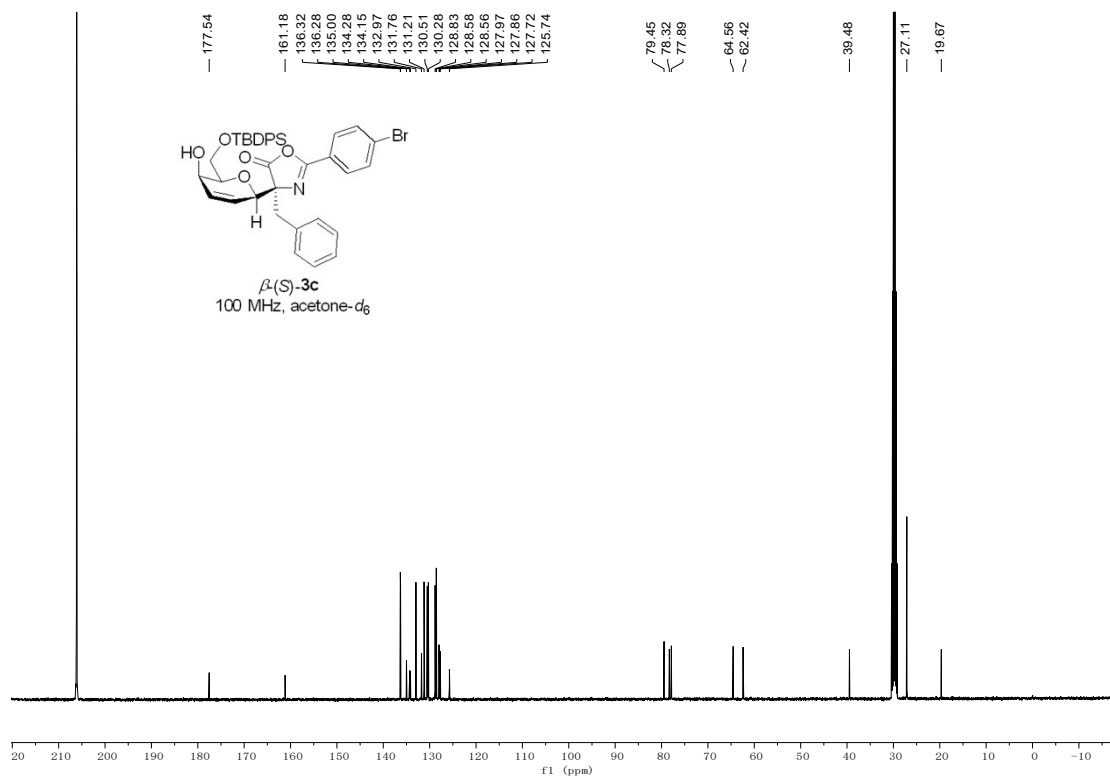


Figure S13. ^{13}C NMR spectrum of β -(S)-**3c**

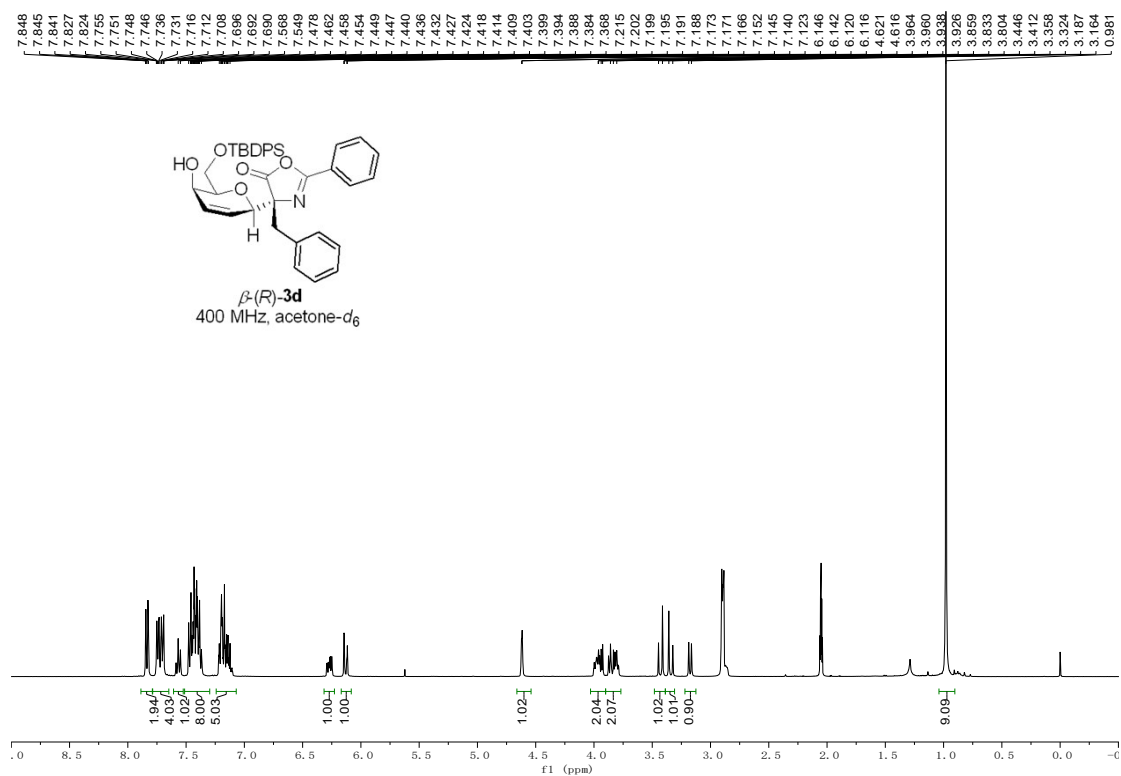


Figure S14. ^1H NMR spectrum of β -(R)-3d

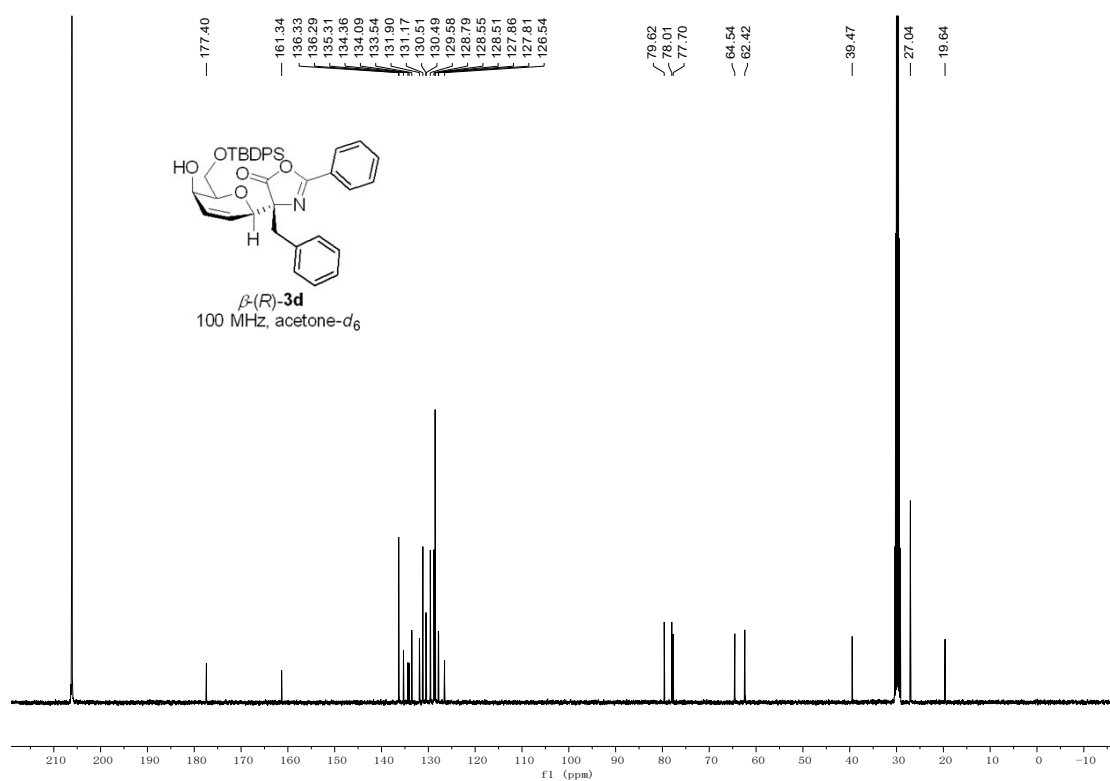


Figure S15. ^{13}C NMR spectrum of β -(R)-3d

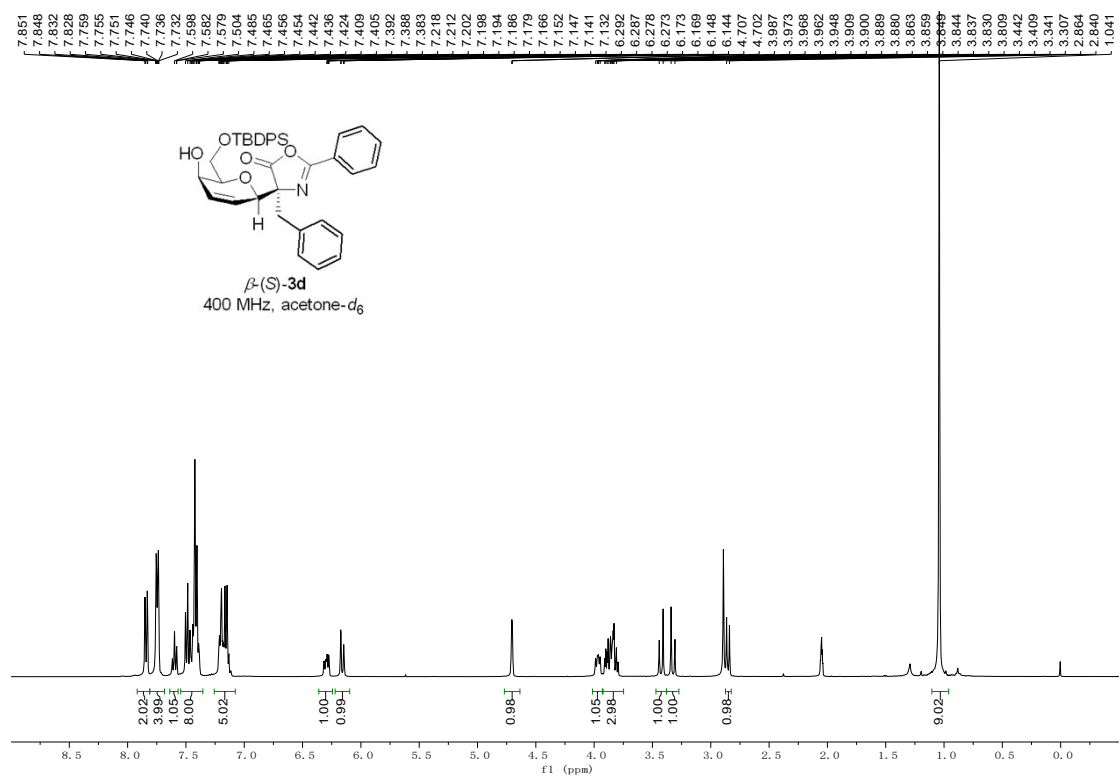


Figure S16. ^1H NMR spectrum of β -(S)-3d

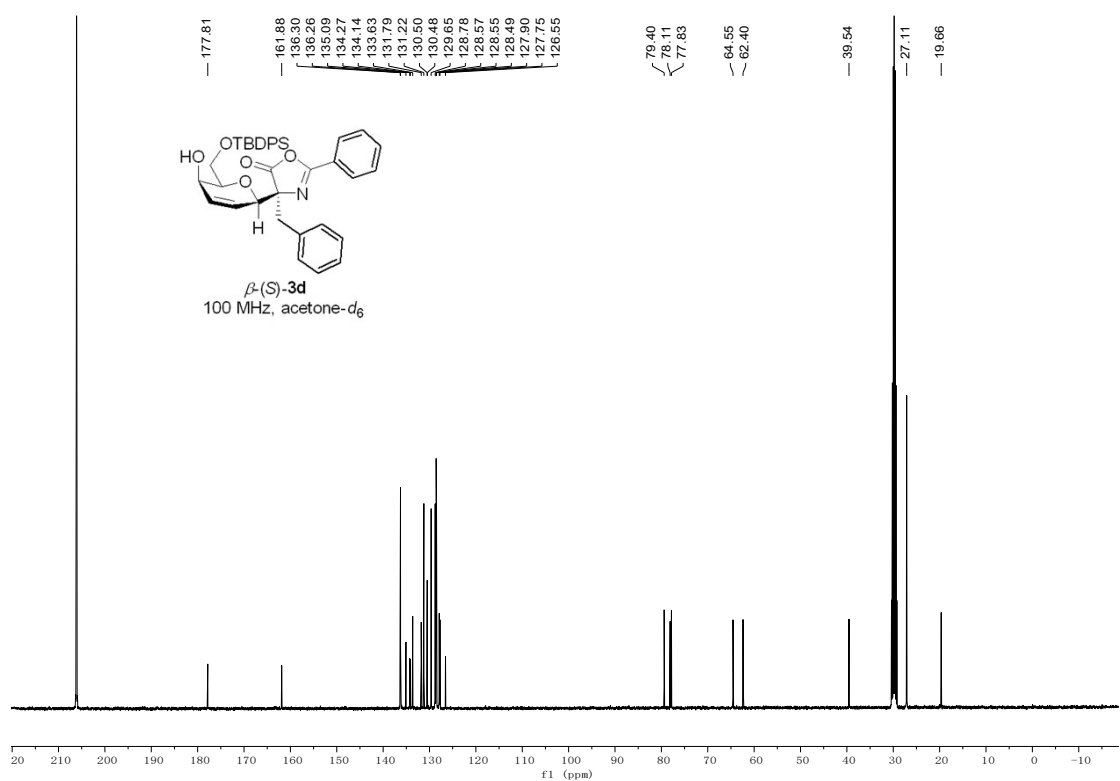


Figure S17. ^{13}C NMR spectrum of β -(S)-3d

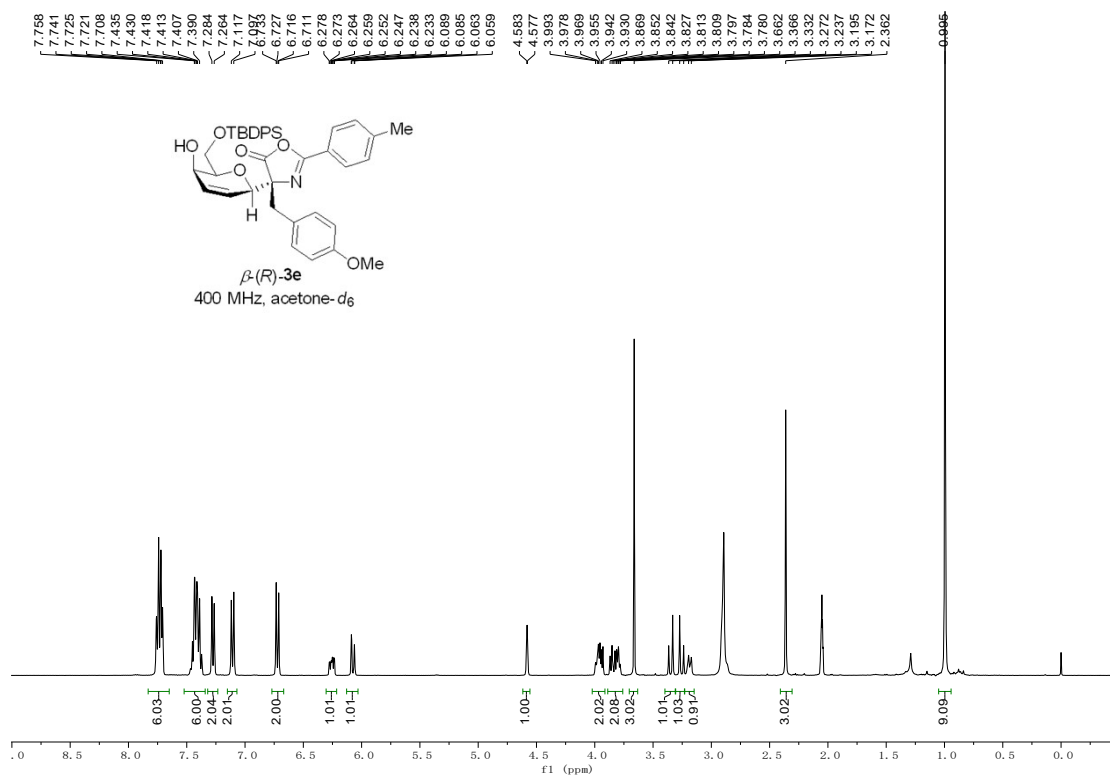


Figure S18. ^1H NMR spectrum of β -(R)-3e

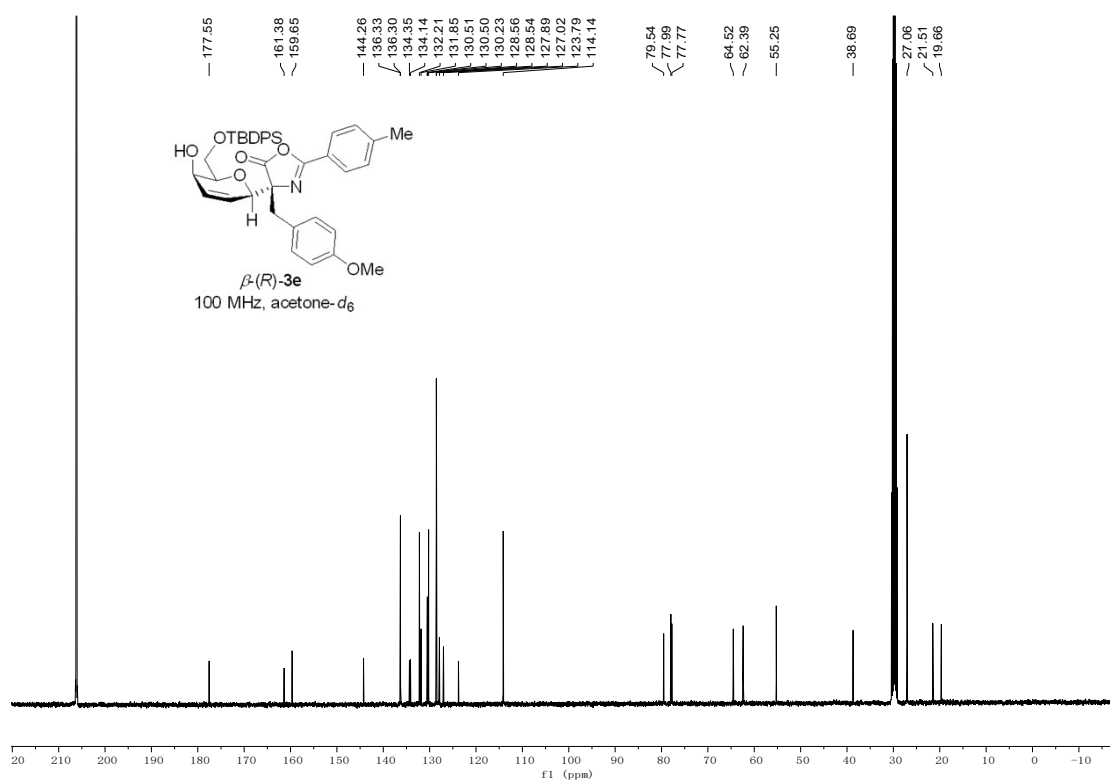


Figure S19. ^{13}C NMR spectrum of β -(R)-3e

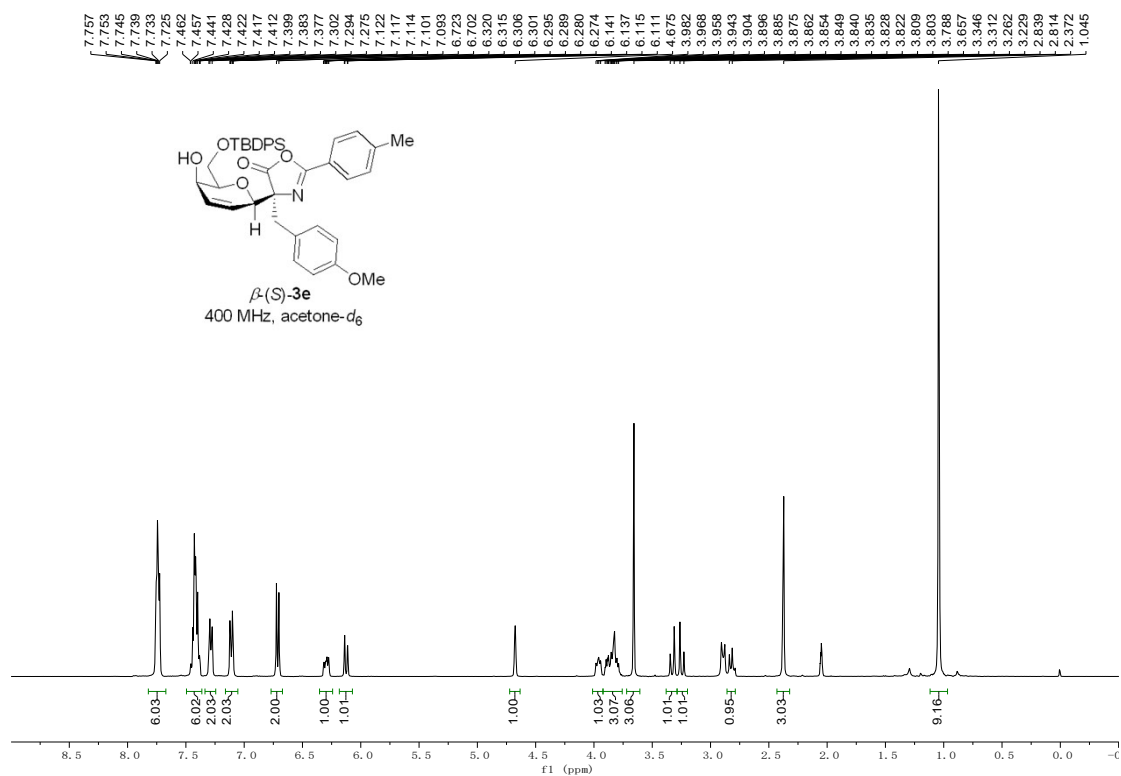


Figure S20. ^1H NMR spectrum of β -(S)-3e

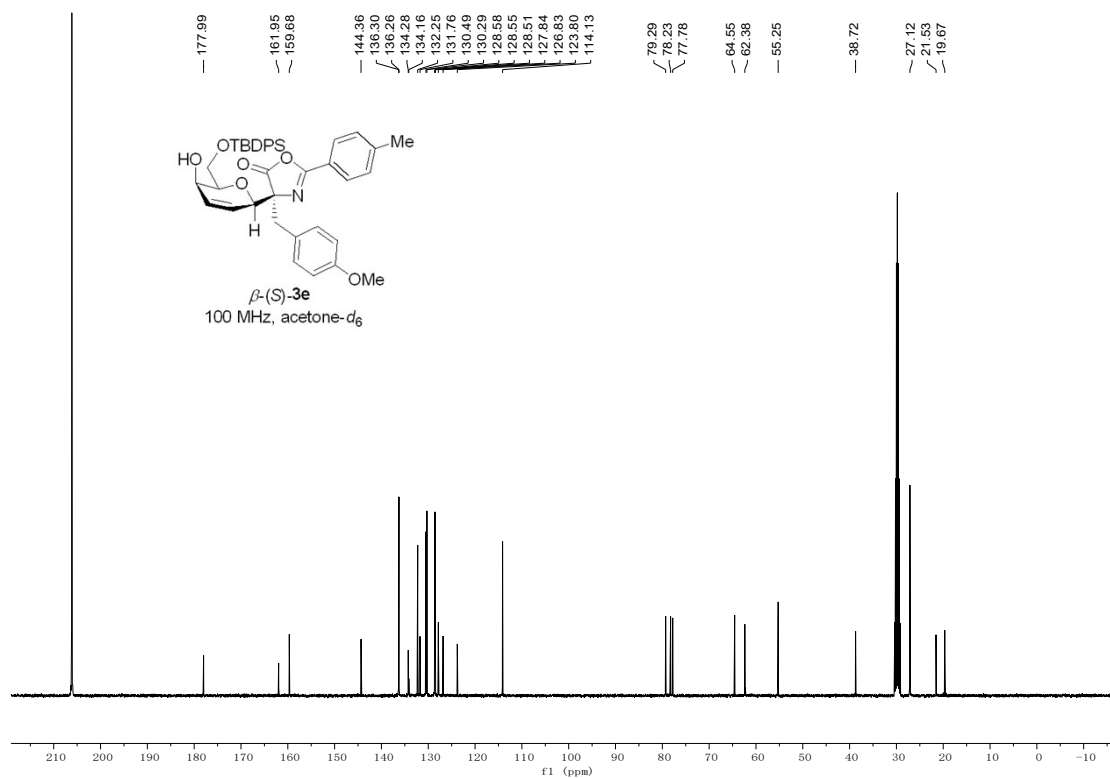


Figure S21. ^{13}C NMR spectrum of β -(S)-3e

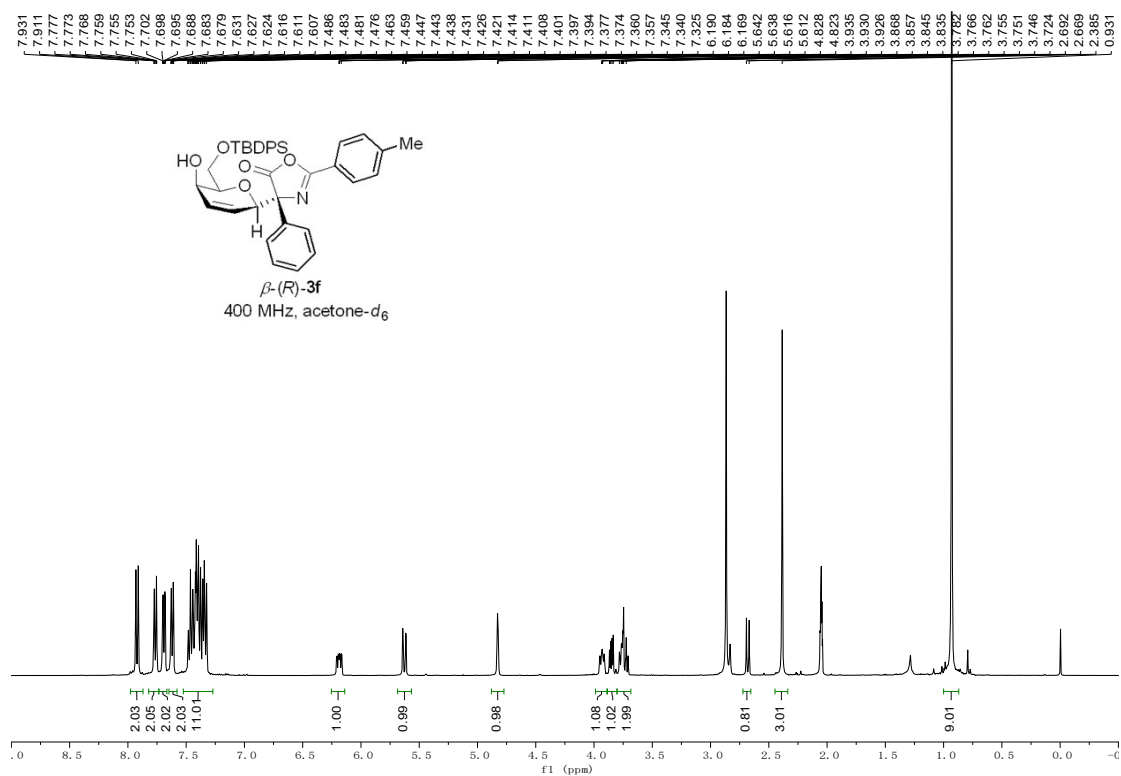


Figure S22. ^1H NMR spectrum of β -(R)-3f

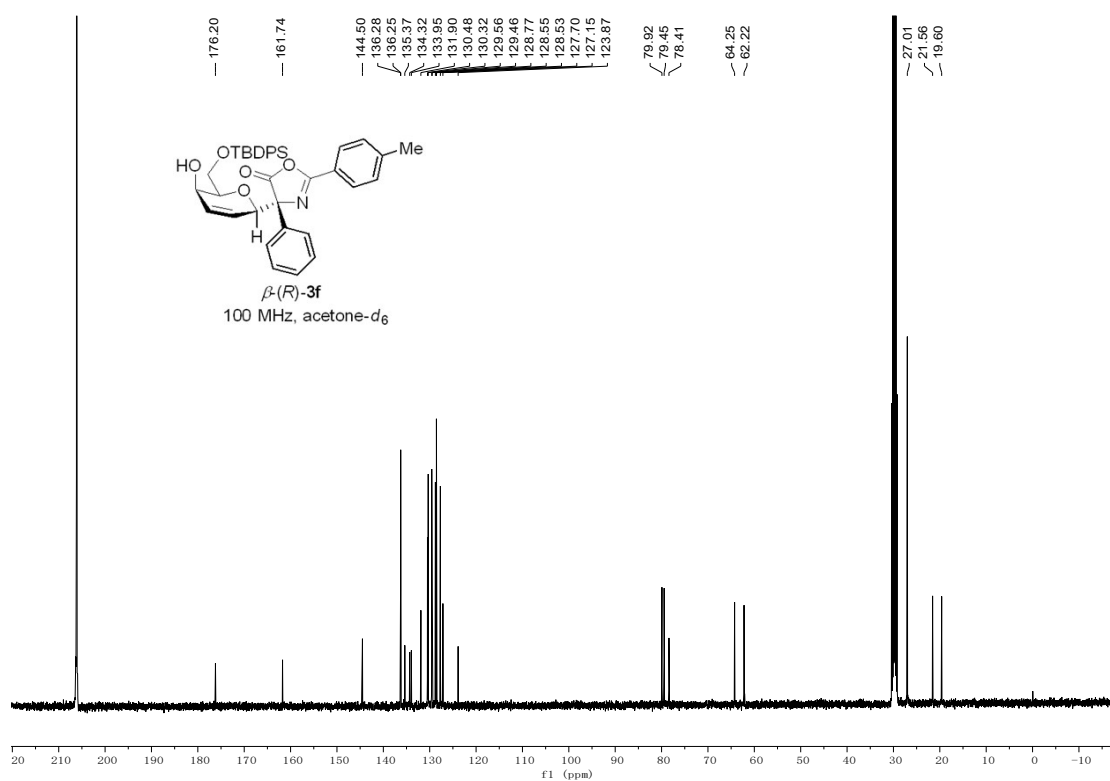


Figure S23. ^{13}C NMR spectrum of β -(R)-3f

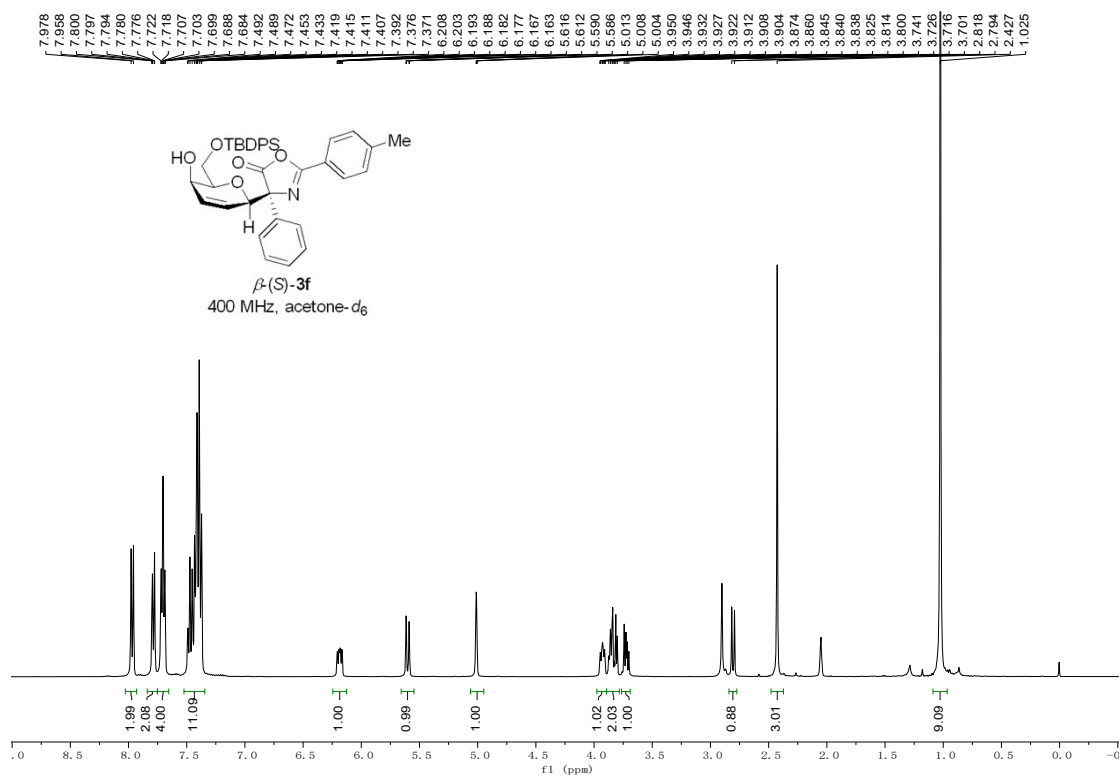


Figure S24. ^1H NMR spectrum of β -(S)-3f

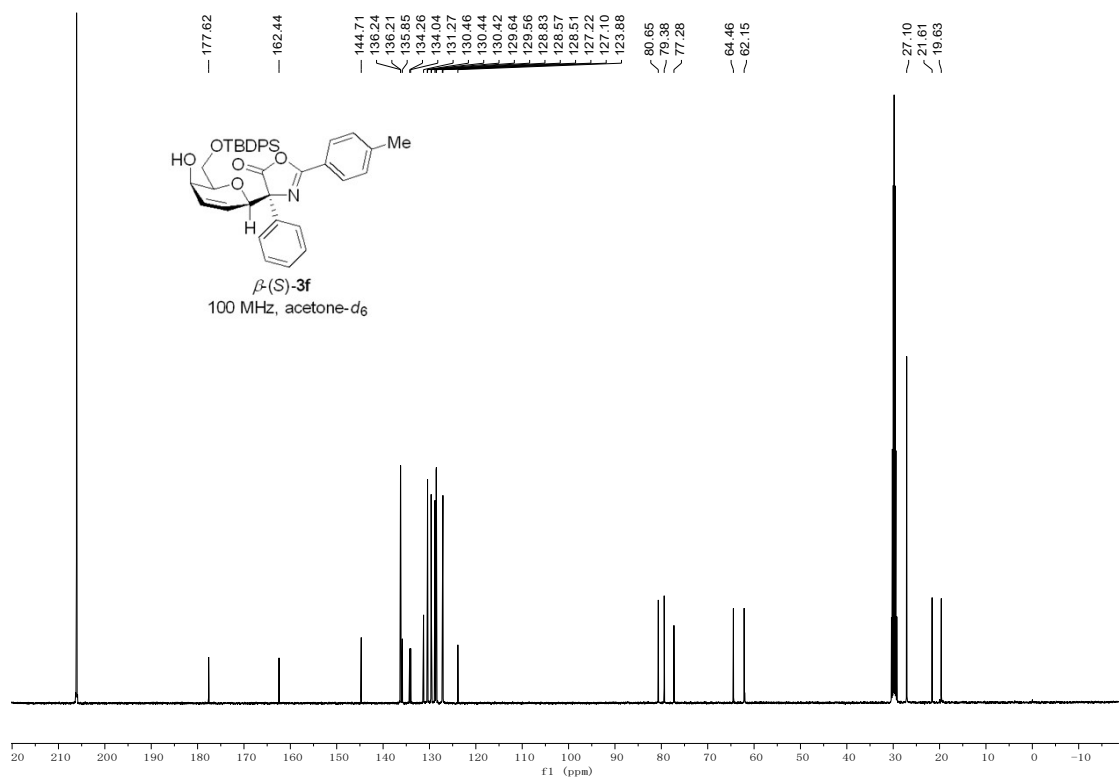


Figure S25. ^{13}C NMR spectrum of β -(S)-3f

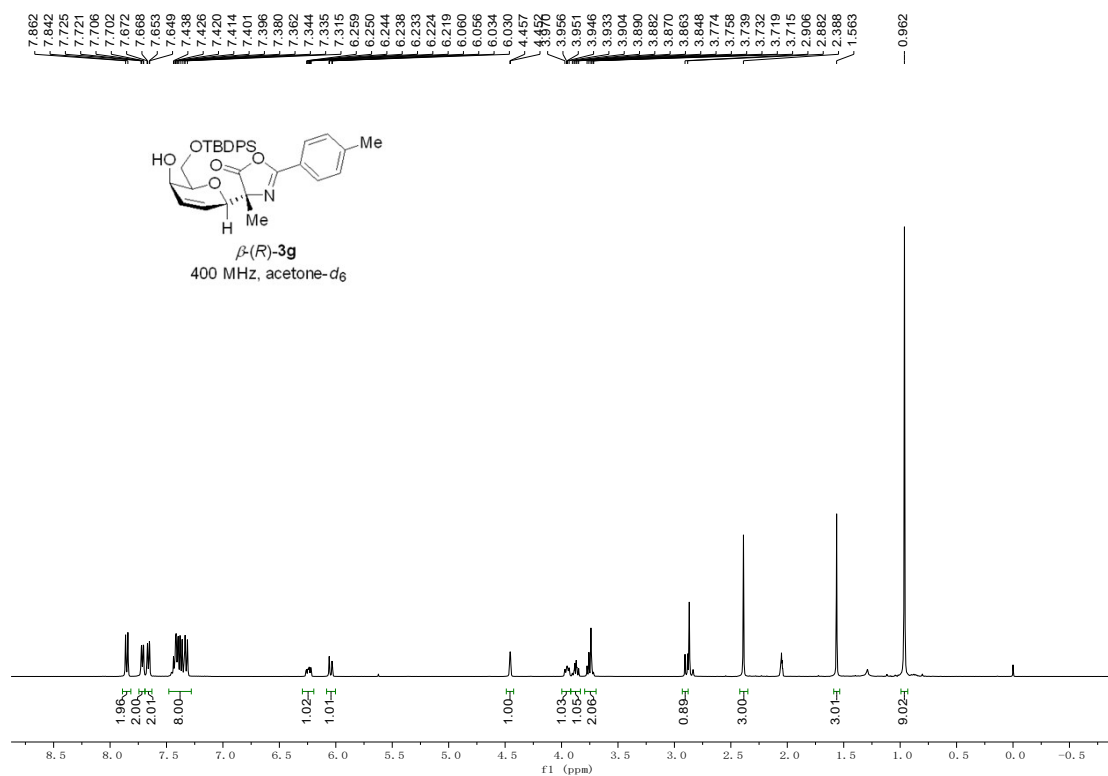


Figure S26. ^1H NMR spectrum of β -(R)-3g

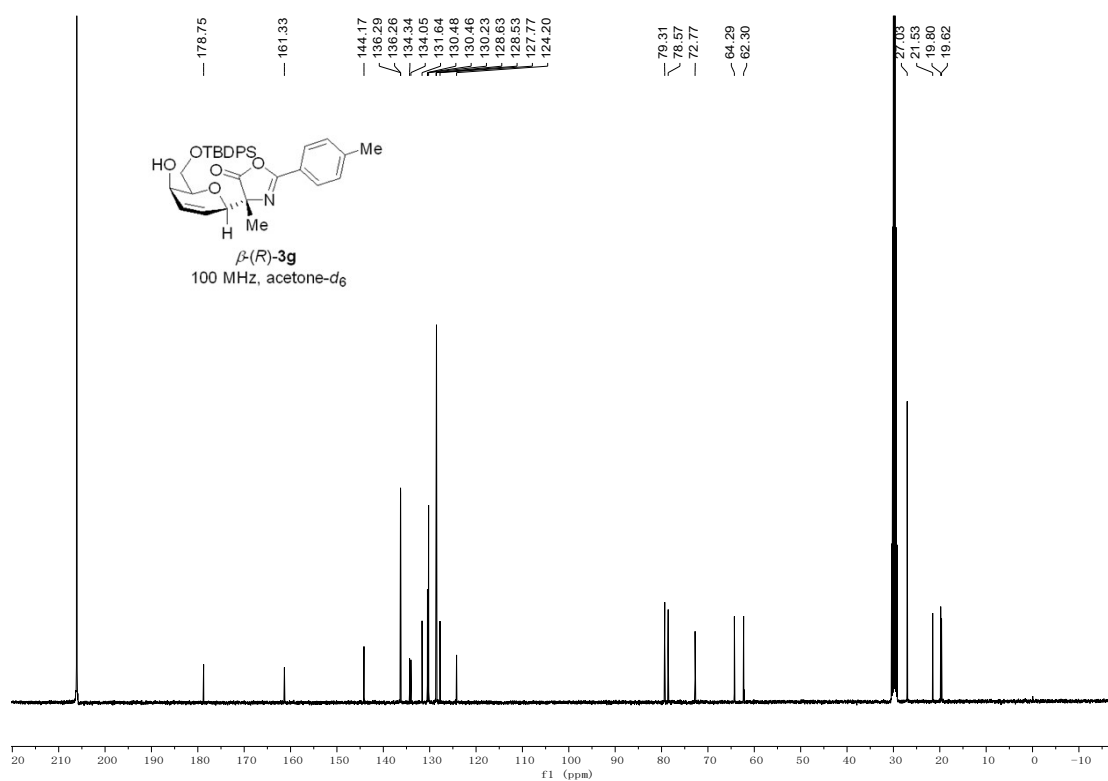


Figure S27. ^{13}C NMR spectrum of β -(R)-3g

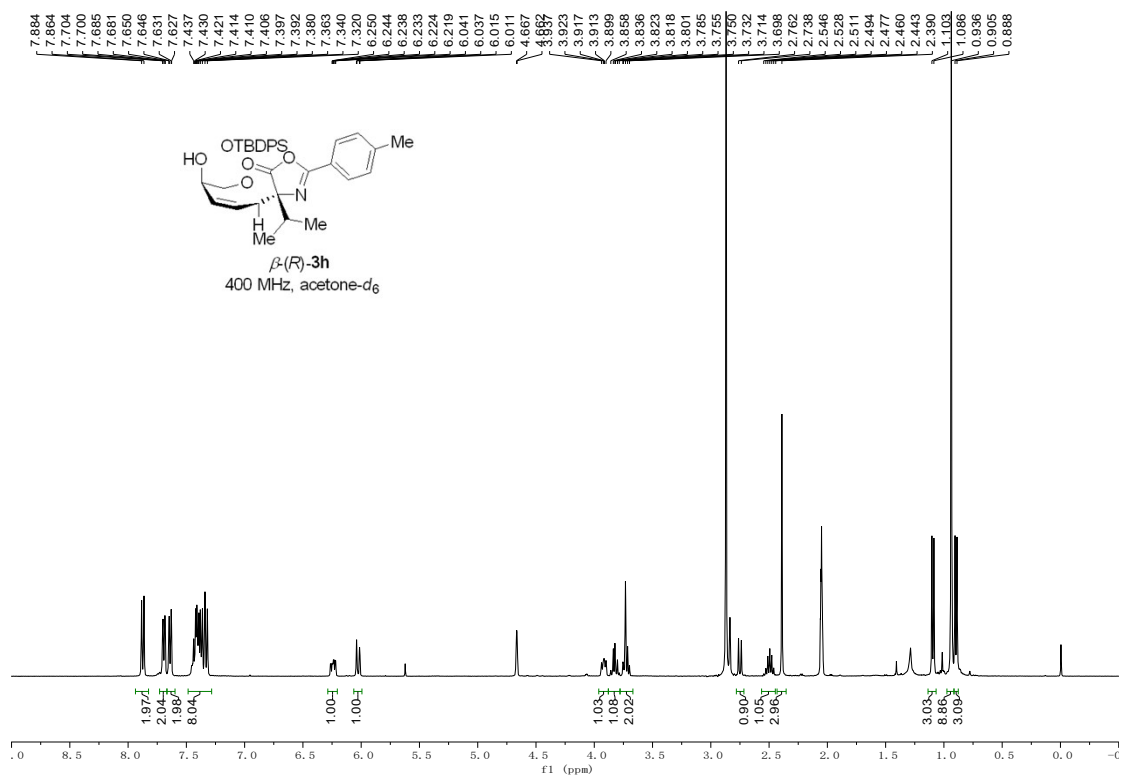


Figure S30. ^1H NMR spectrum of β -(R)-3h

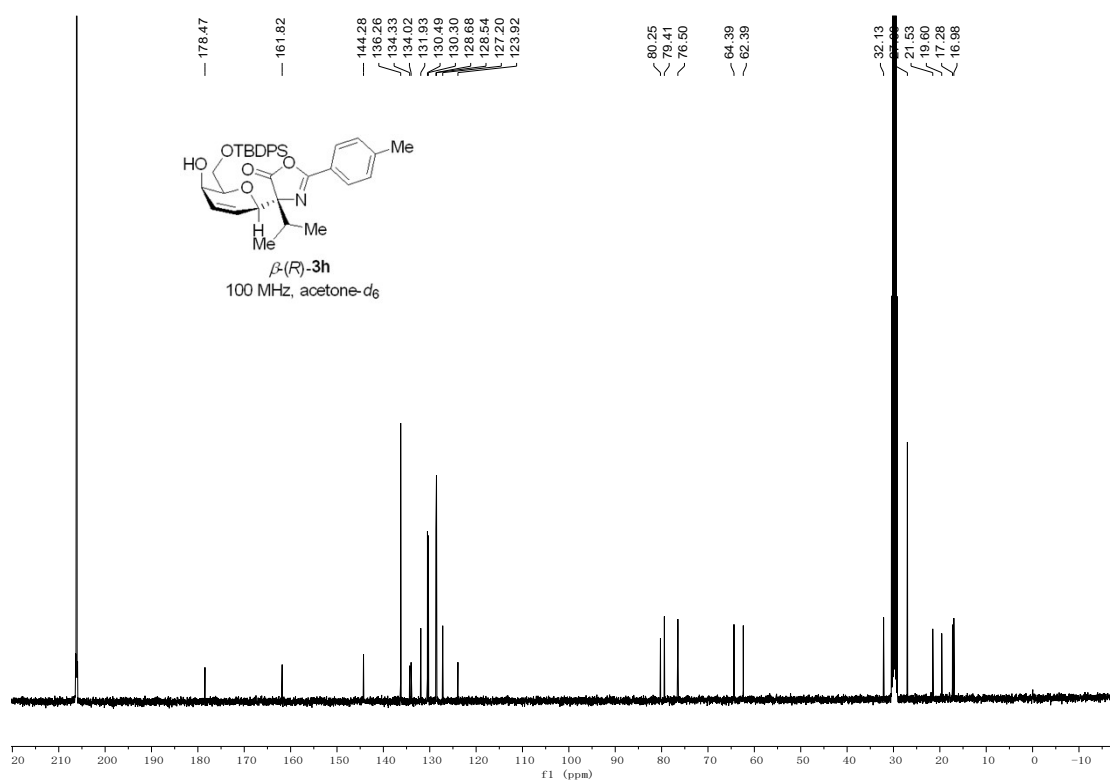


Figure S31. ^{13}C NMR spectrum of β -(R)-3h

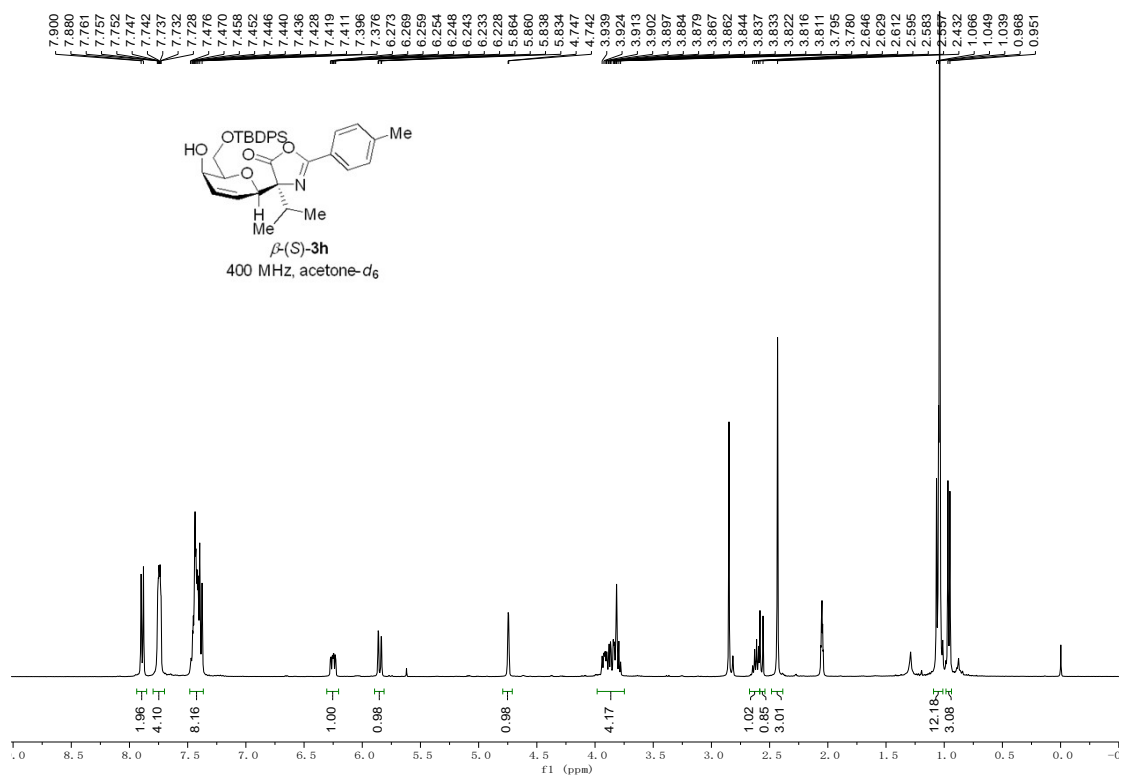


Figure S32. ^1H NMR spectrum of β -(S)-3h

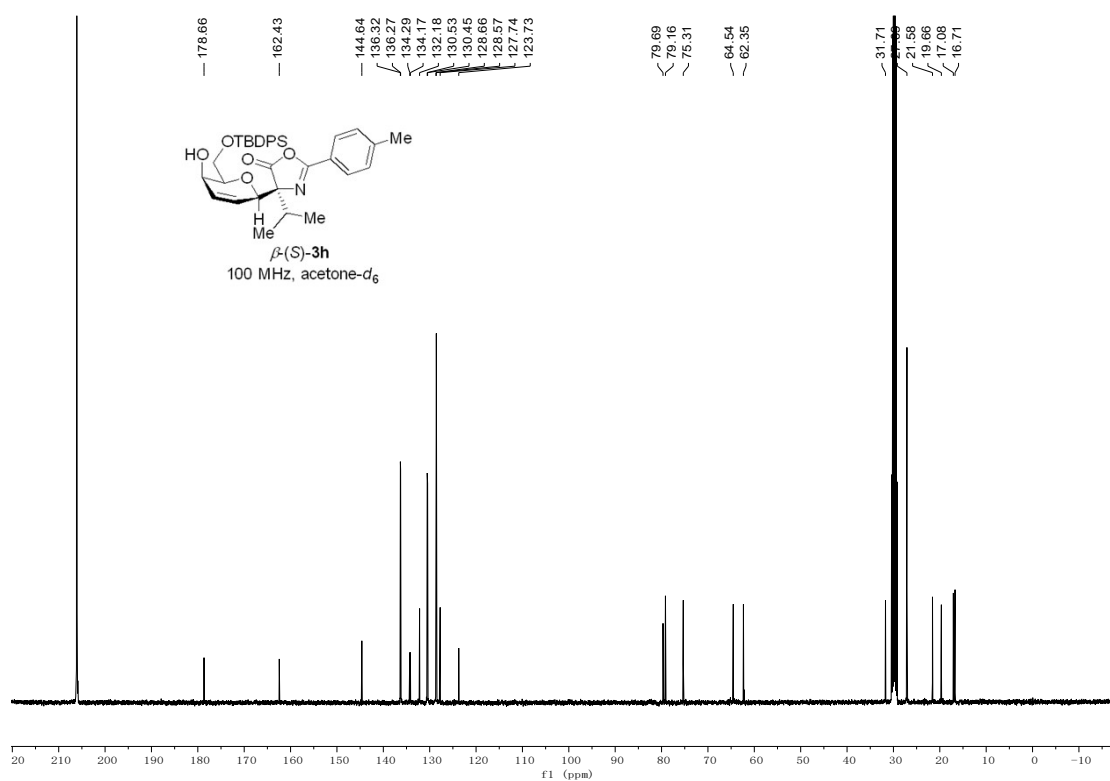


Figure S33. ^{13}C NMR spectrum of β -(S)-3h

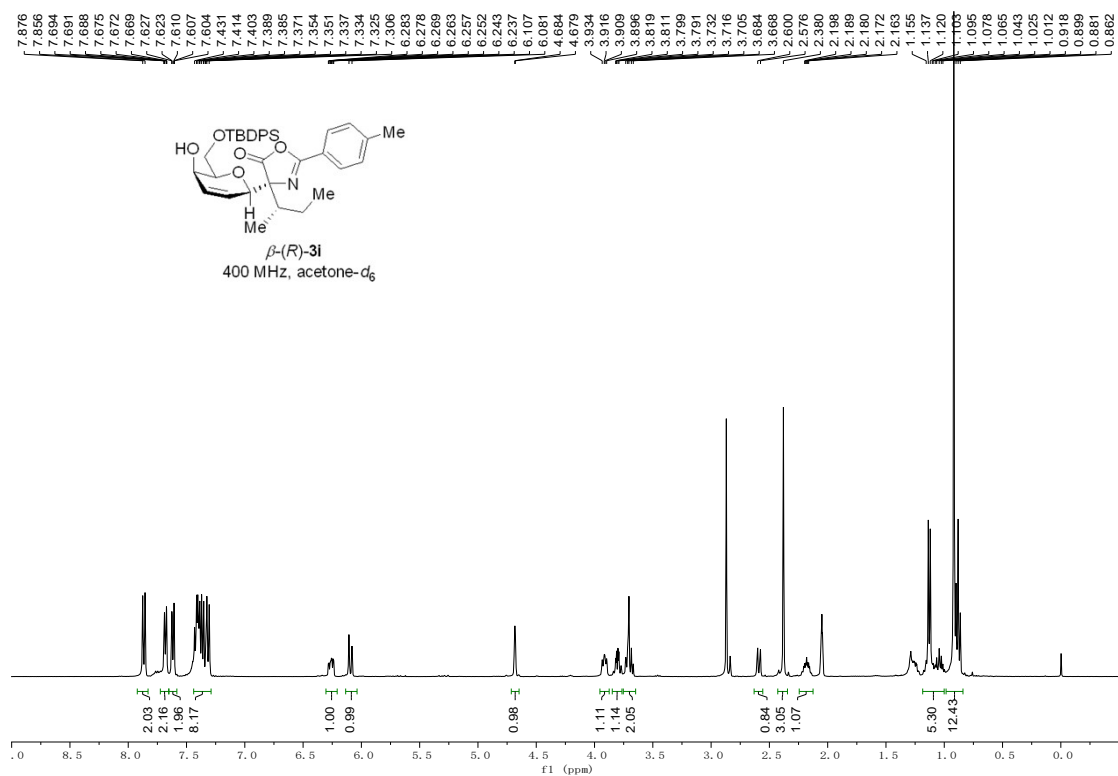


Figure S34. ^1H NMR spectrum of β -(*R*)-3i

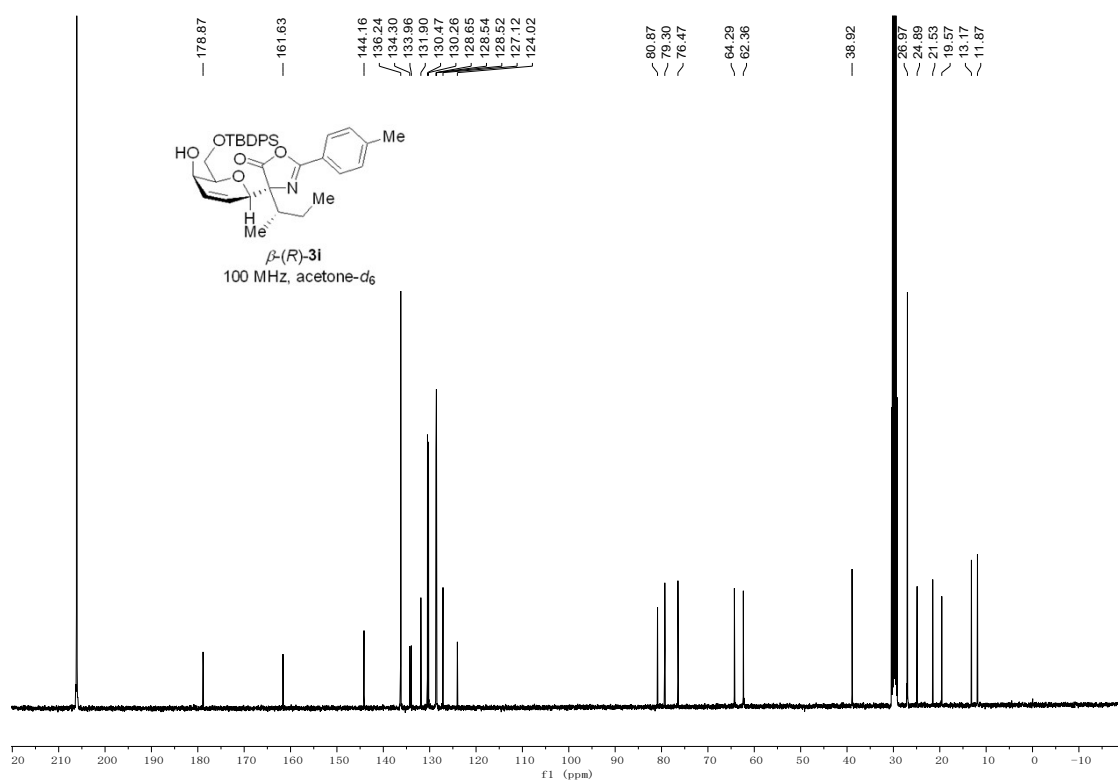


Figure S35. ^{13}C NMR spectrum of β -(*R*)-3i

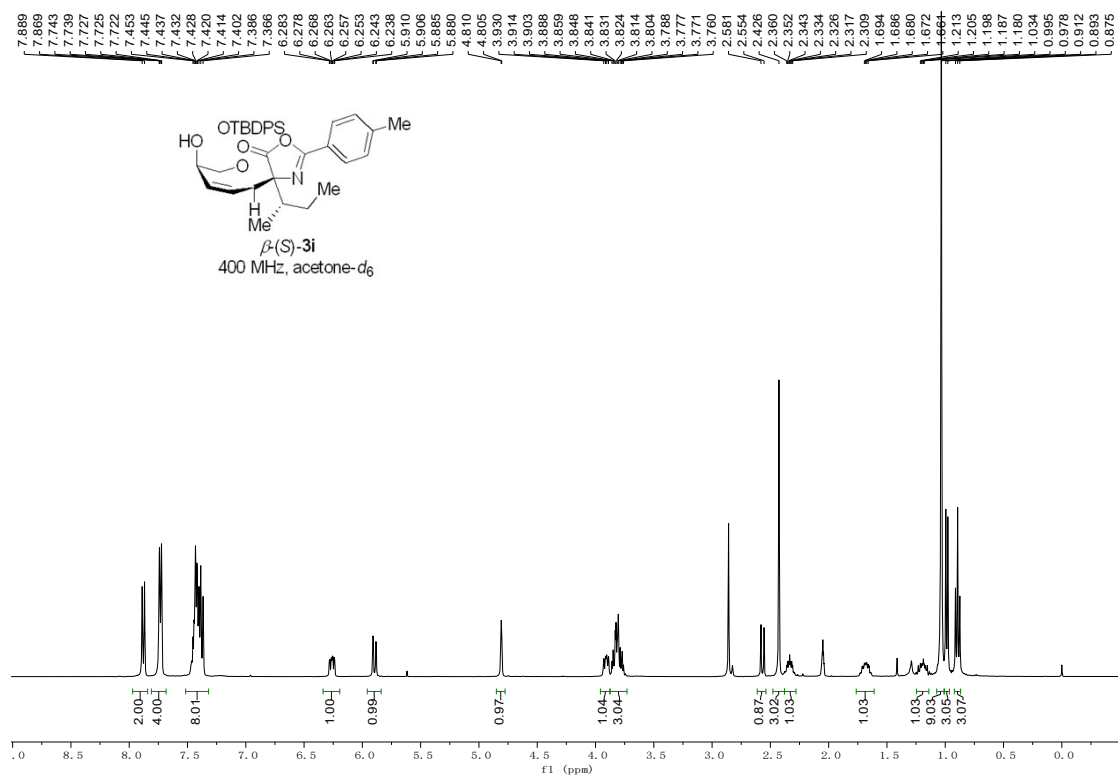


Figure S36. ^1H NMR spectrum of β -(S)-3i

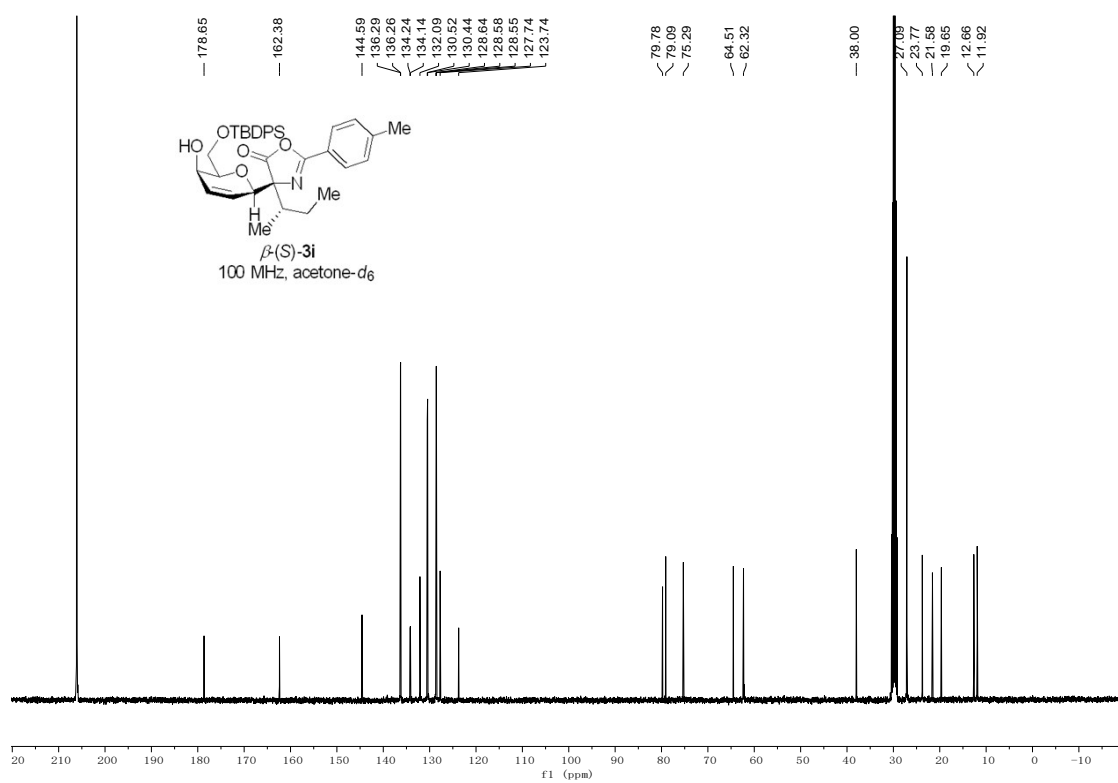


Figure S37. ^{13}C NMR spectrum of β -(S)-3i

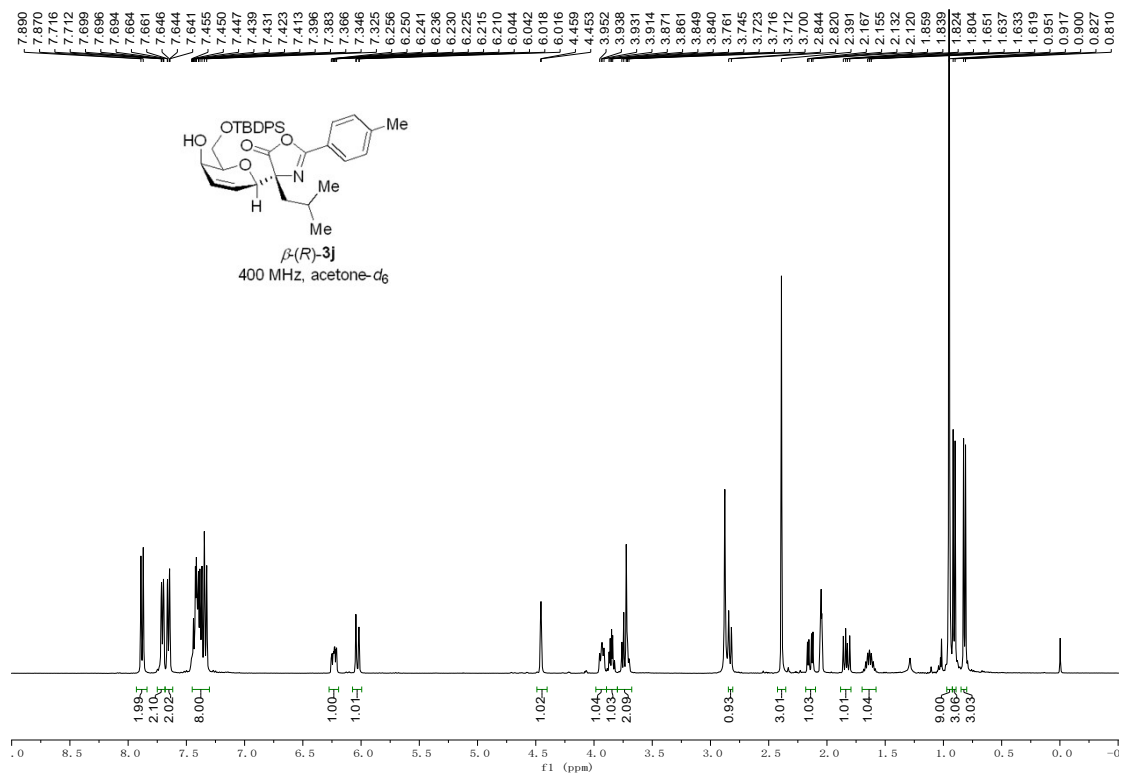


Figure S38. ^1H NMR spectrum of β -(R)-3j

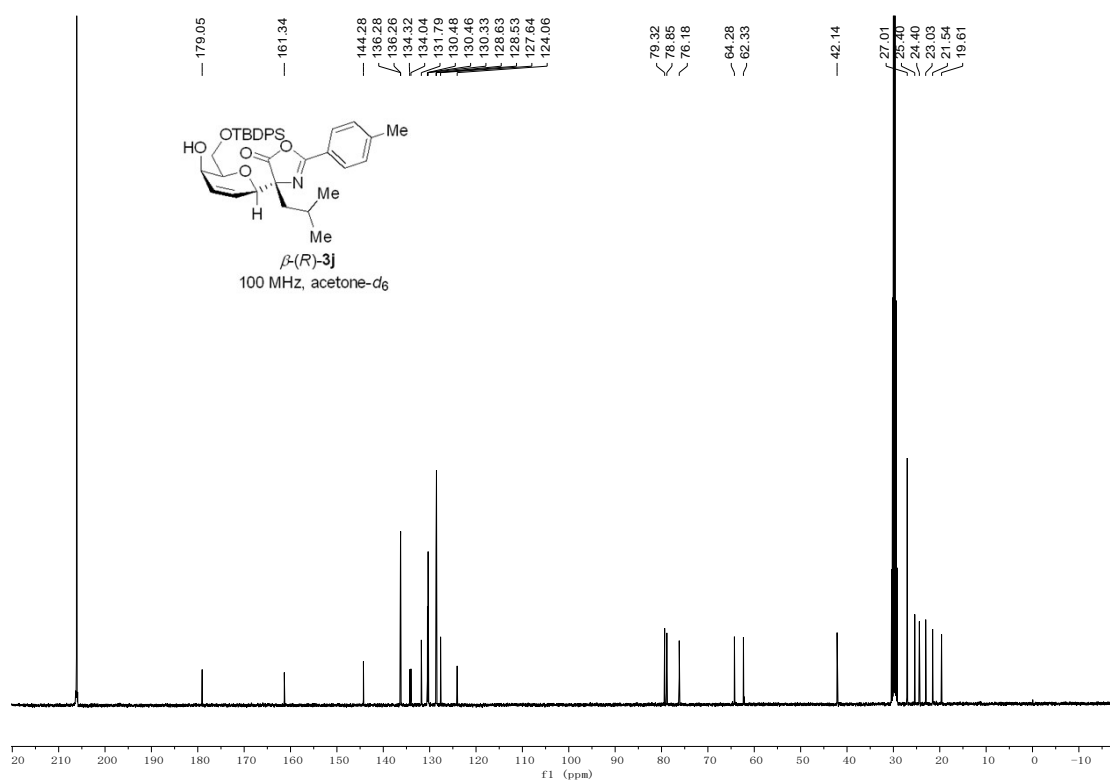


Figure S39. ^{13}C NMR spectrum of β -(R)-3j

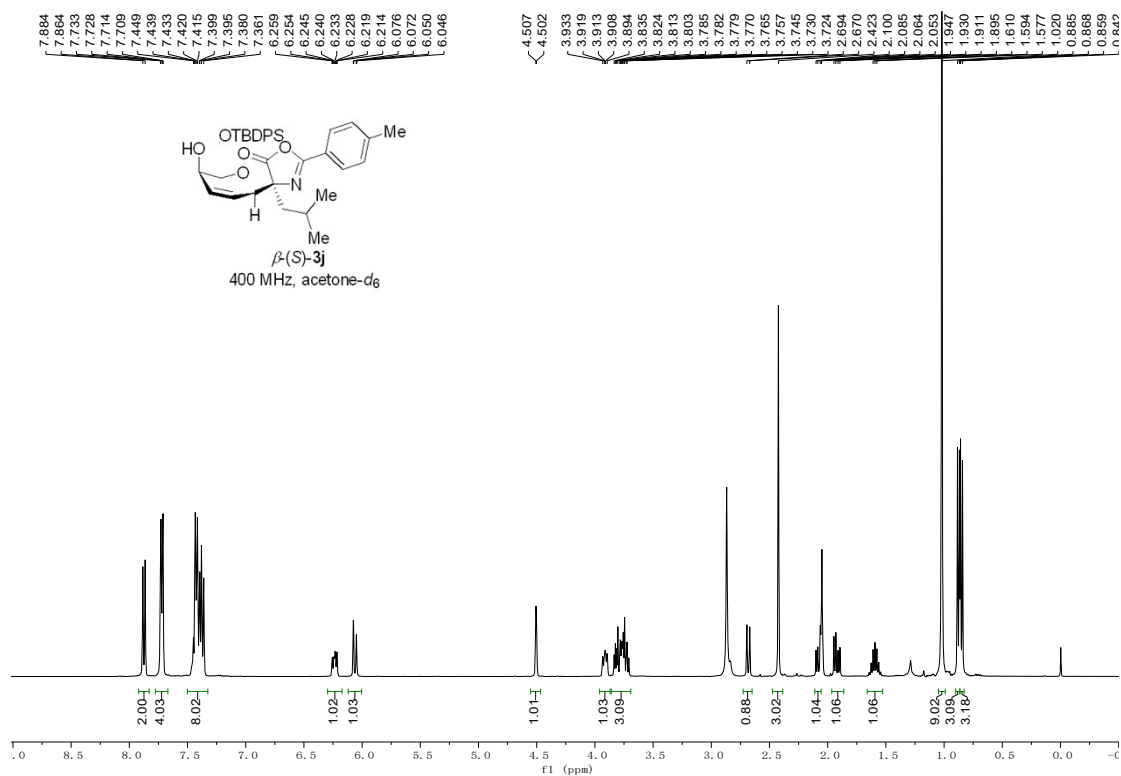


Figure S40. ^1H NMR spectrum of β -(S)-3j

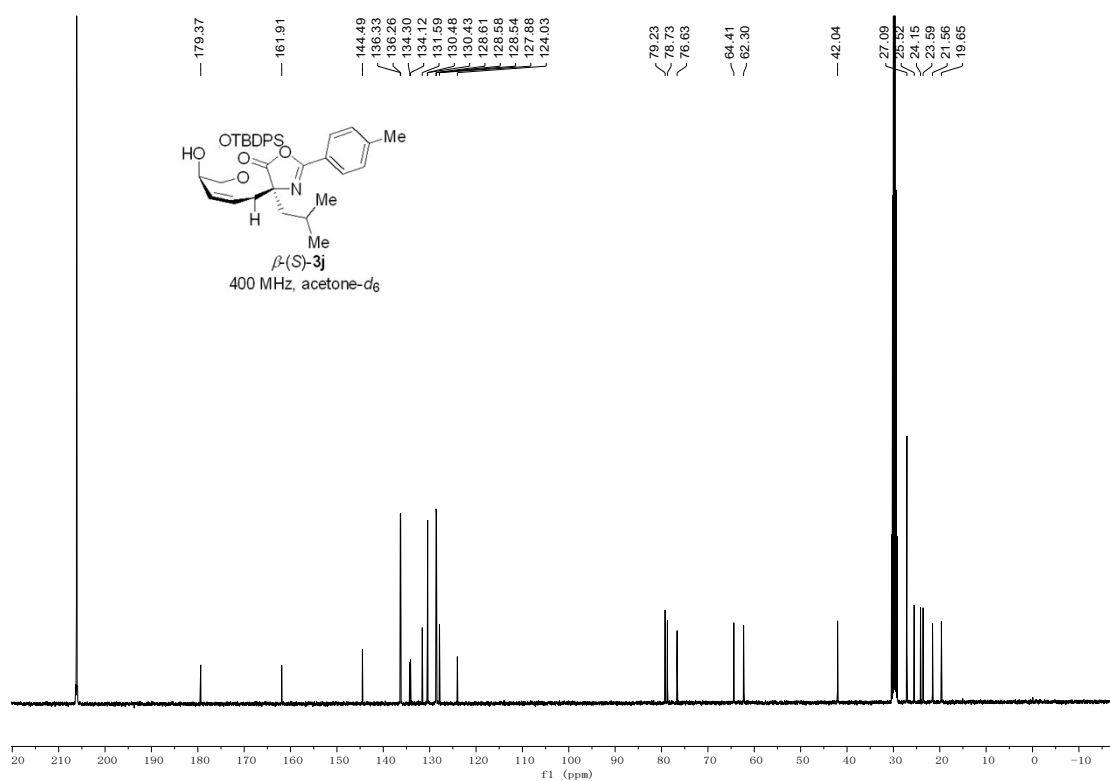


Figure S41. ^{13}C NMR spectrum of β -(S)-3j

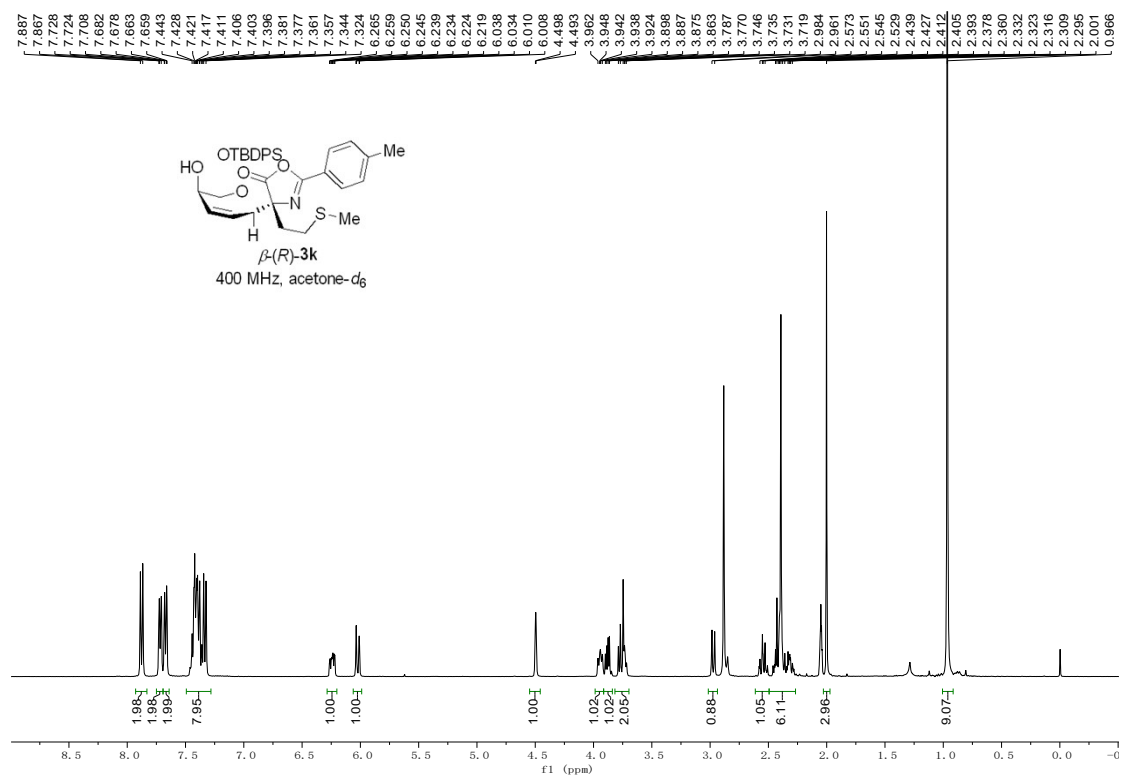


Figure S42. ^1H NMR spectrum of β -(R)-3k

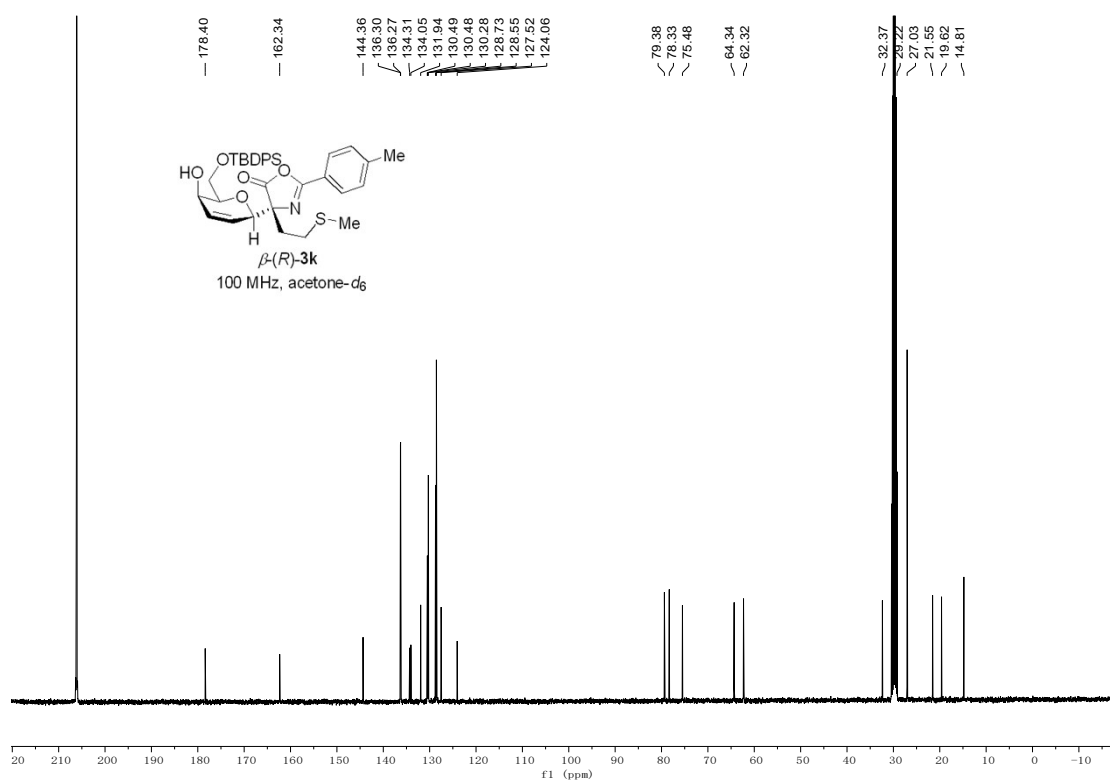


Figure S43. ^{13}C NMR spectrum of β -(R)-3k

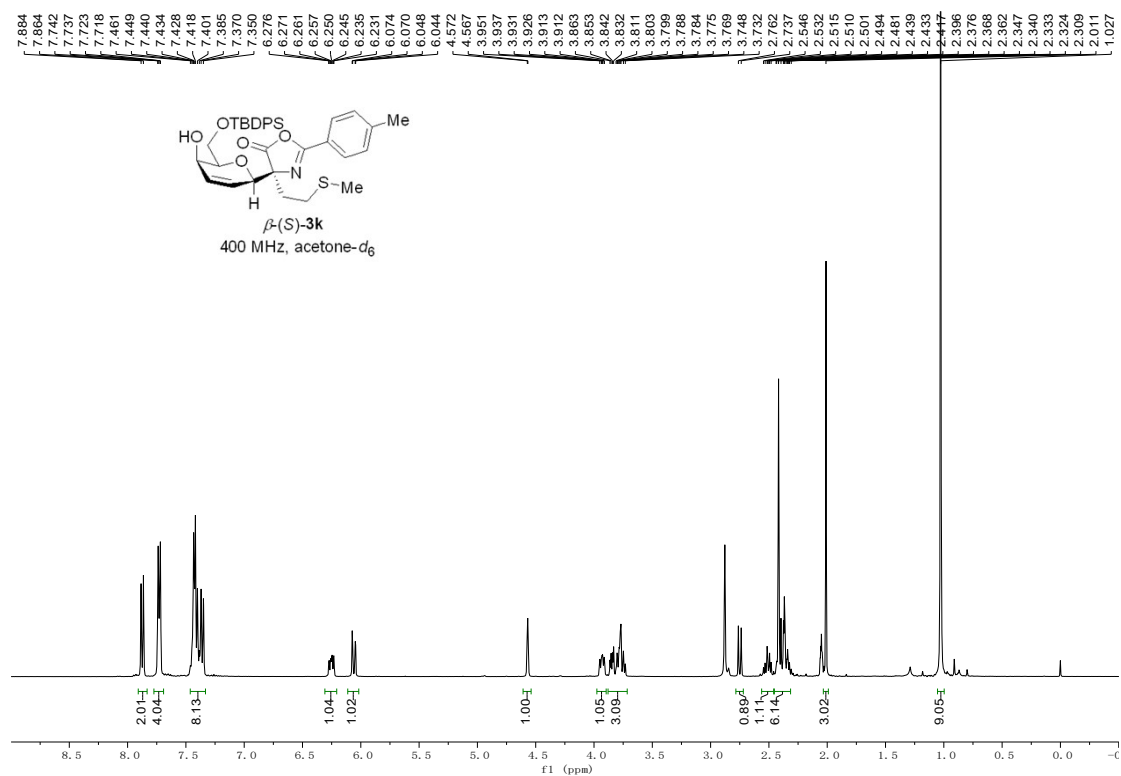


Figure S44. ^1H NMR spectrum of β -(S)-3k

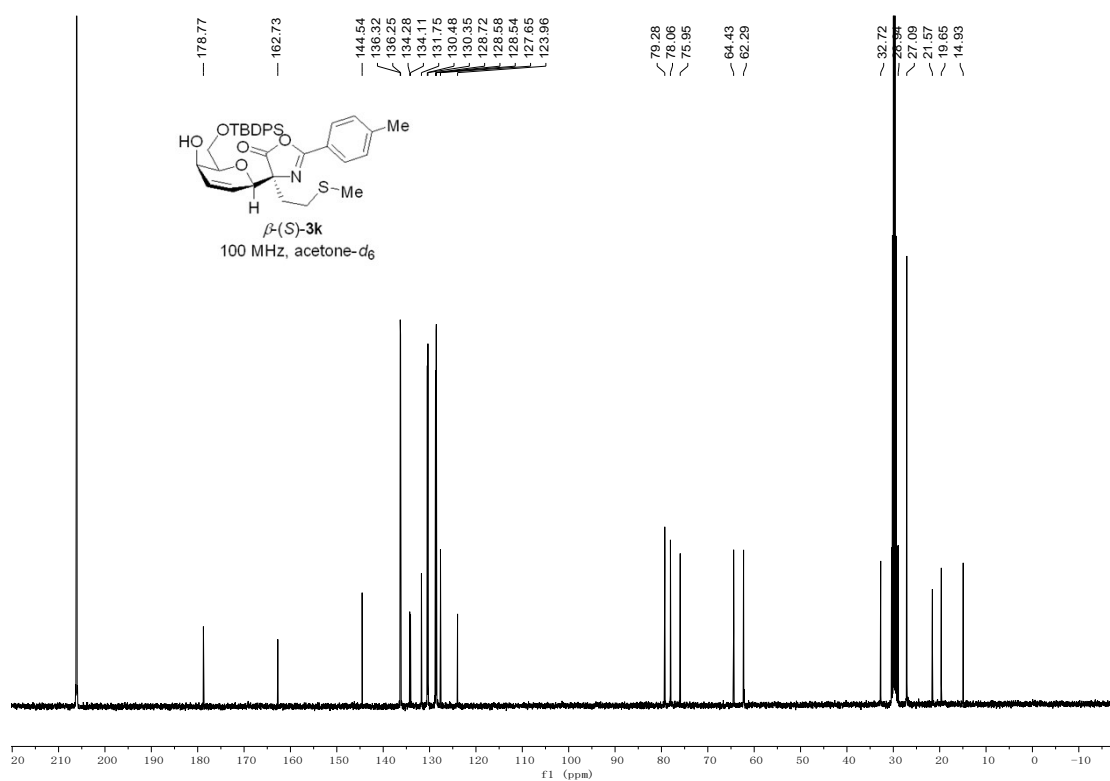


Figure S45. ^{13}C NMR spectrum of β -(S)-3k

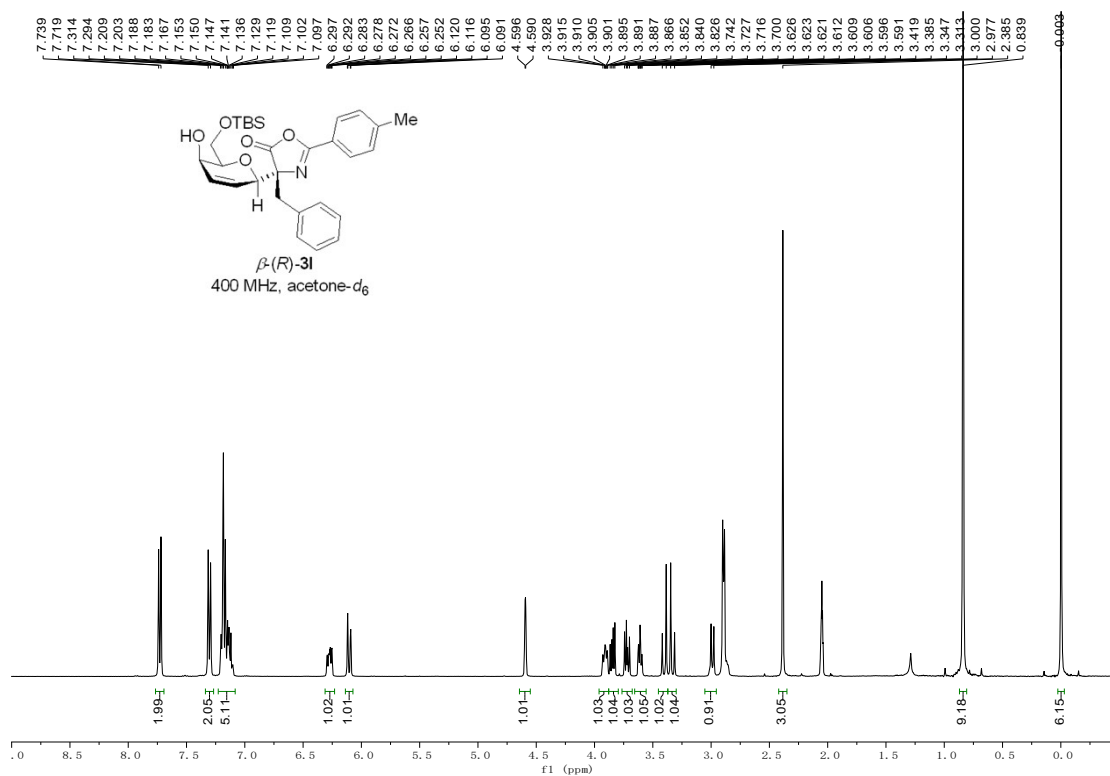


Figure S46. ^1H NMR spectrum of β -(R)-31

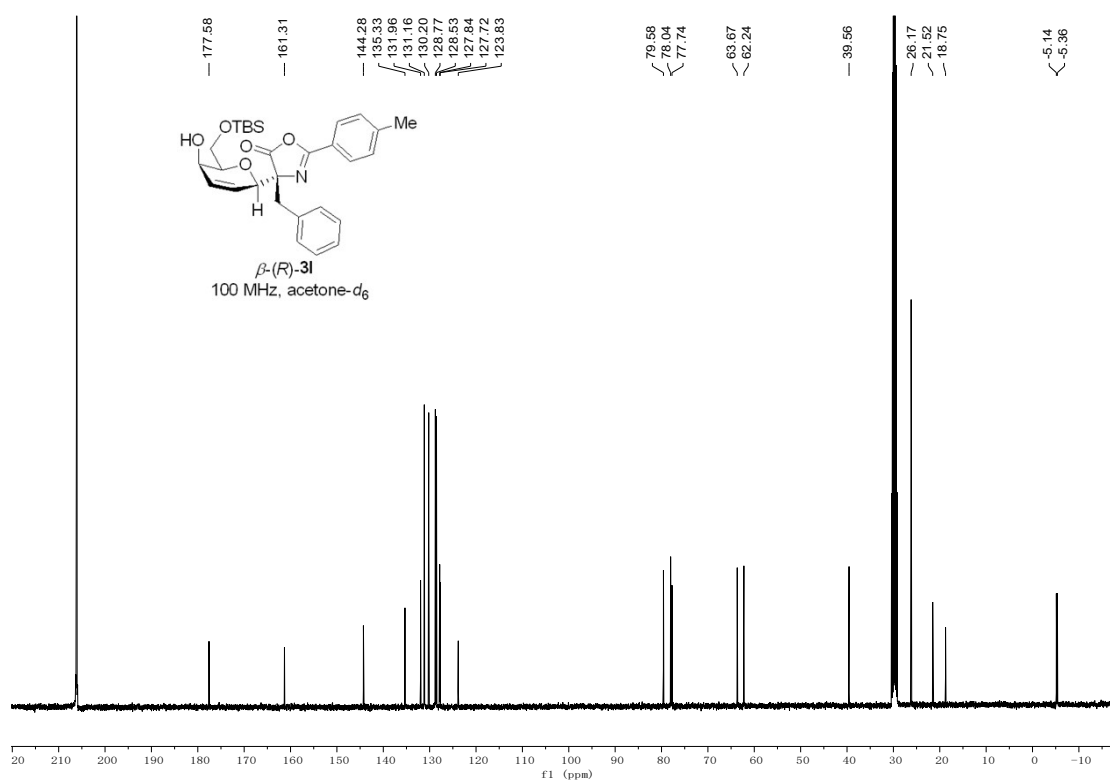


Figure S47. ^{13}C NMR spectrum of β -(R)-31

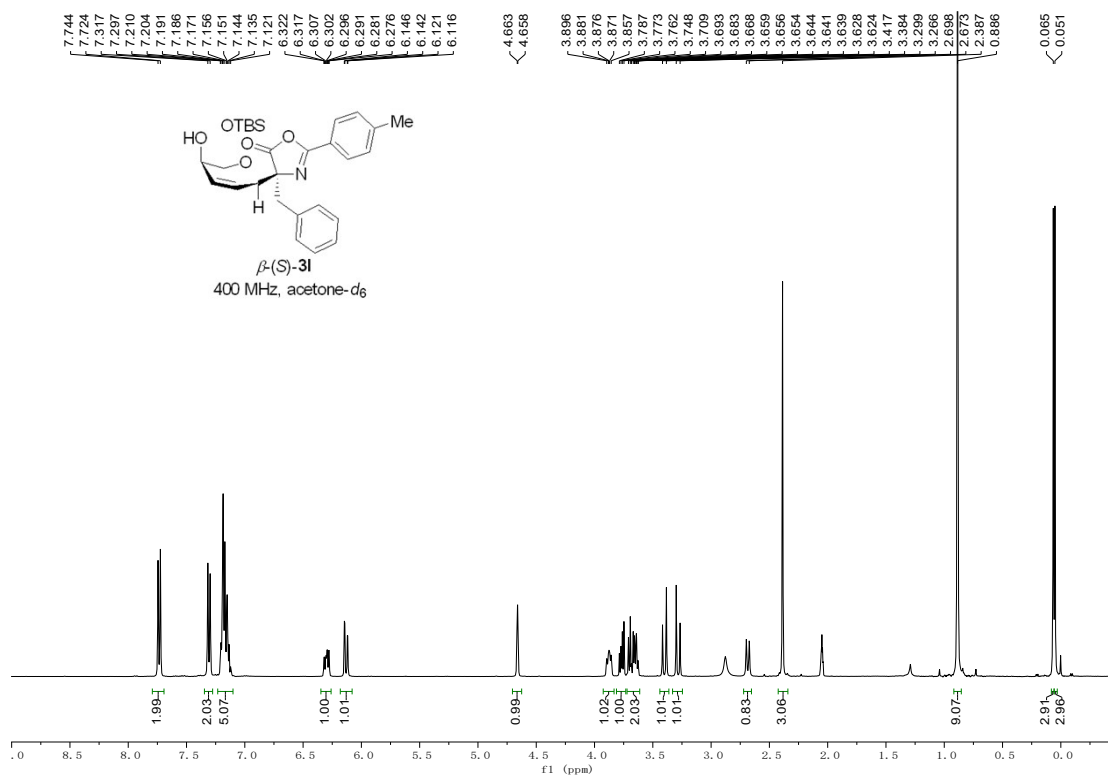


Figure S48. ^1H NMR spectrum of β -(S)-31

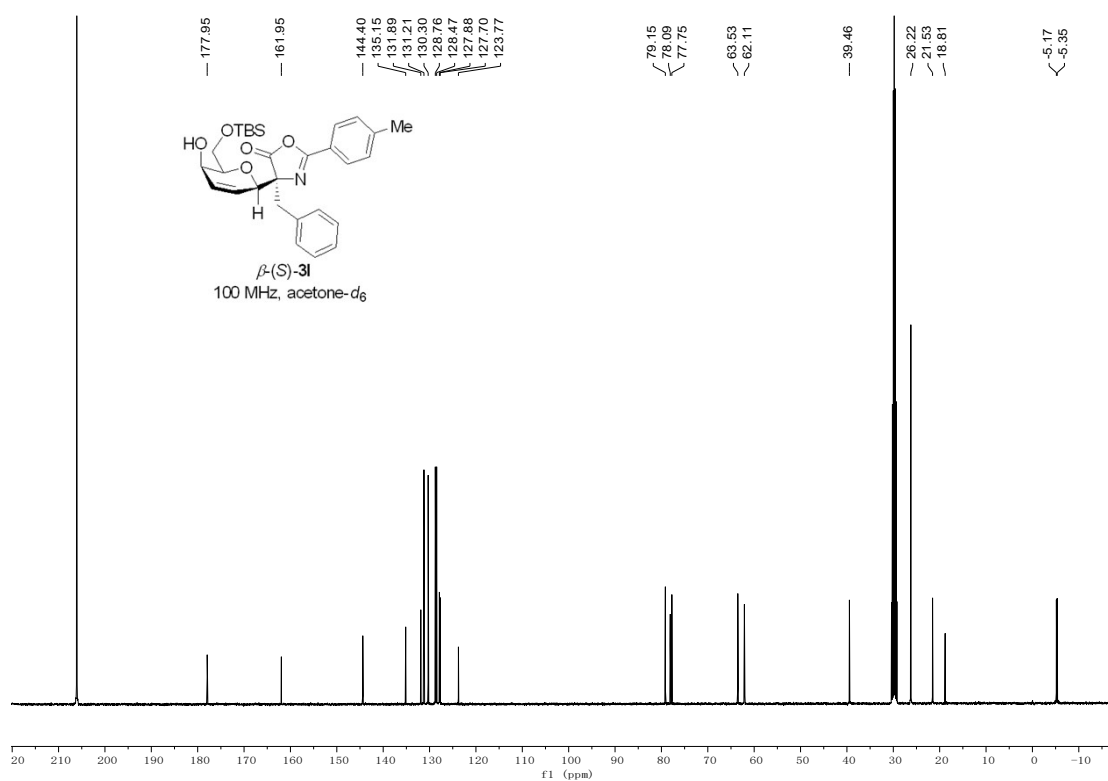


Figure S49. ^{13}C NMR spectrum of β -(S)-31

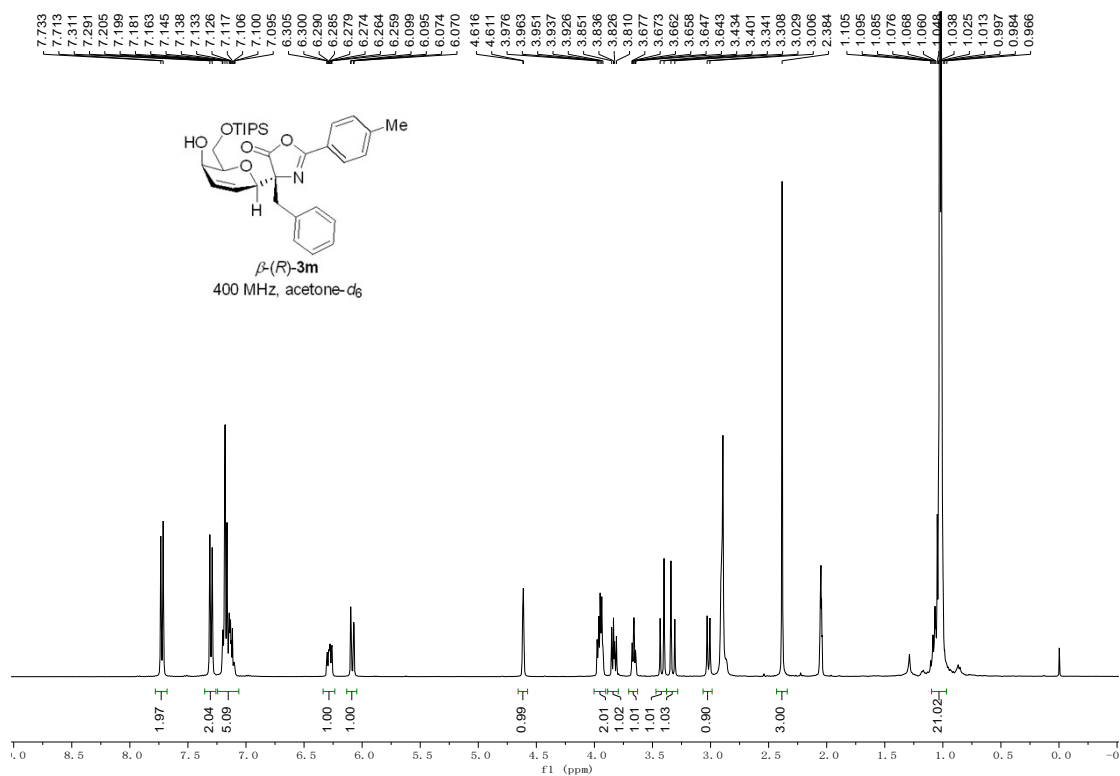


Figure S50. ^1H NMR spectrum of β -(R)-3m

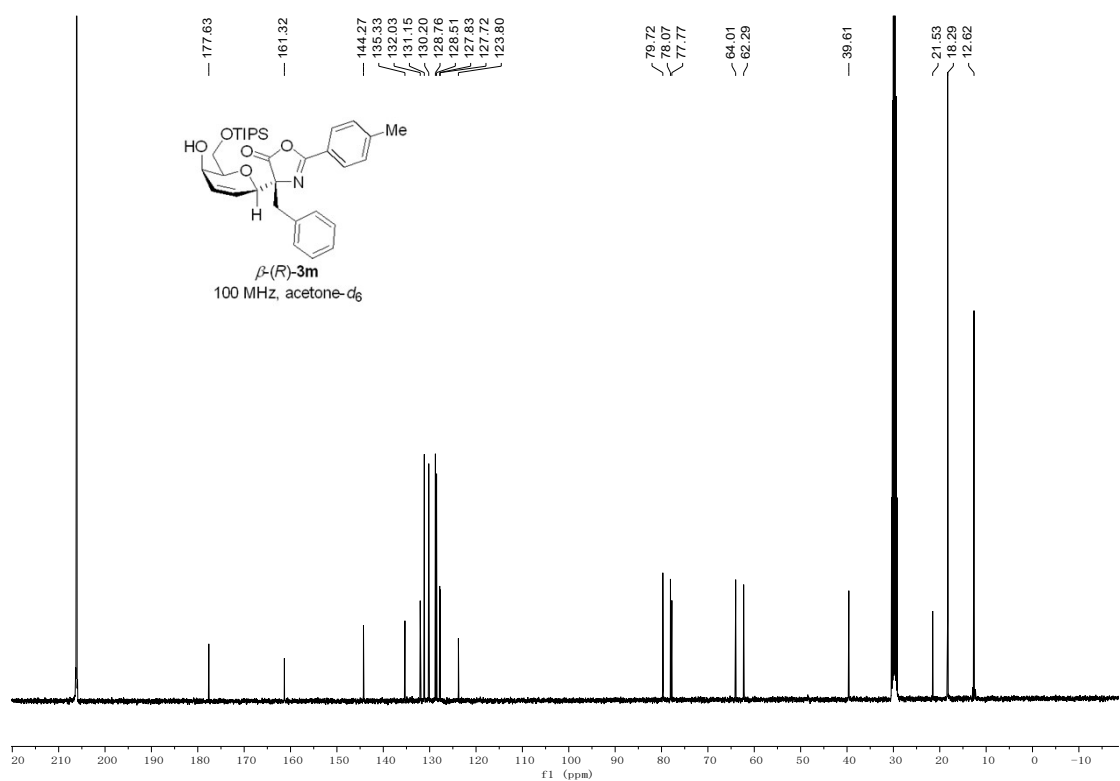


Figure S51. ^{13}C NMR spectrum of β -(R)-3m

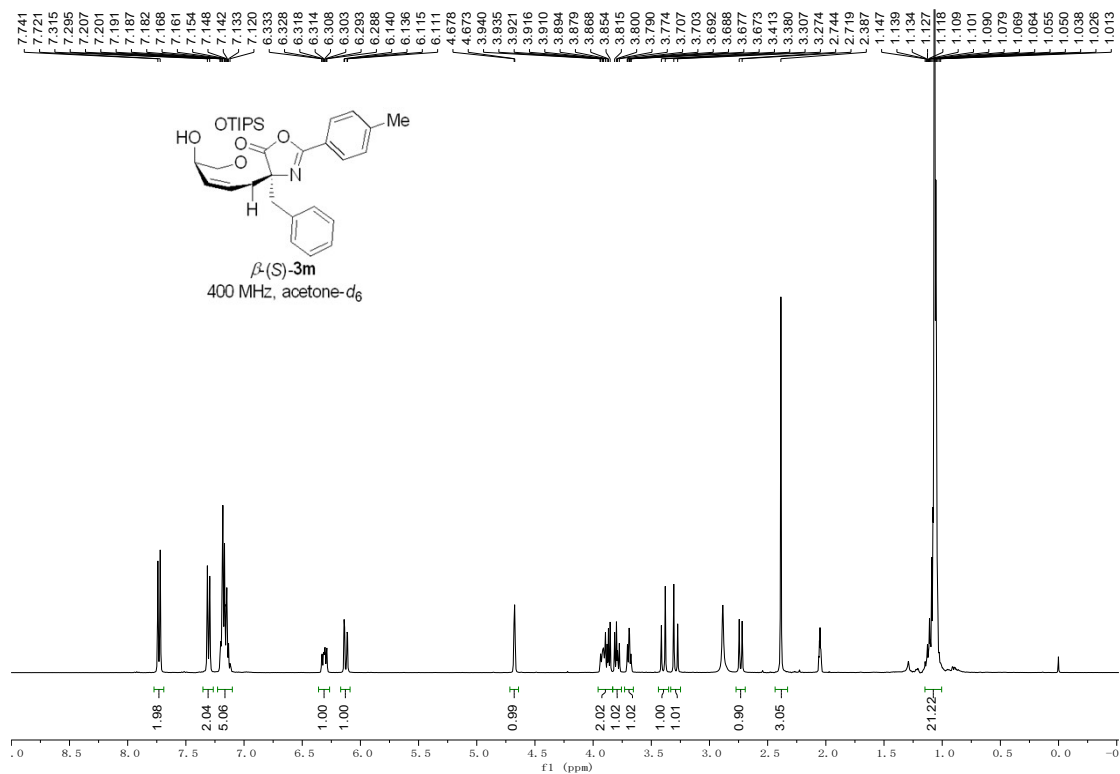


Figure S52. ^1H NMR spectrum of β -(S)-3m

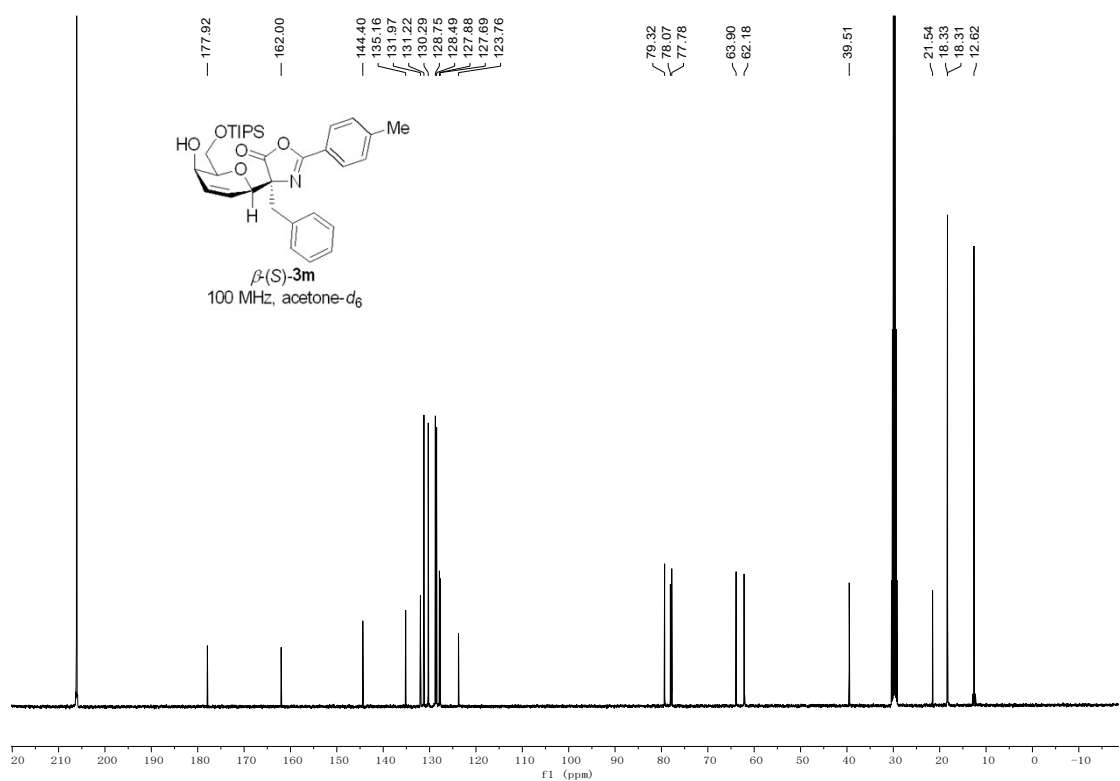


Figure S53. ^{13}C NMR spectrum of β -(S)-3m

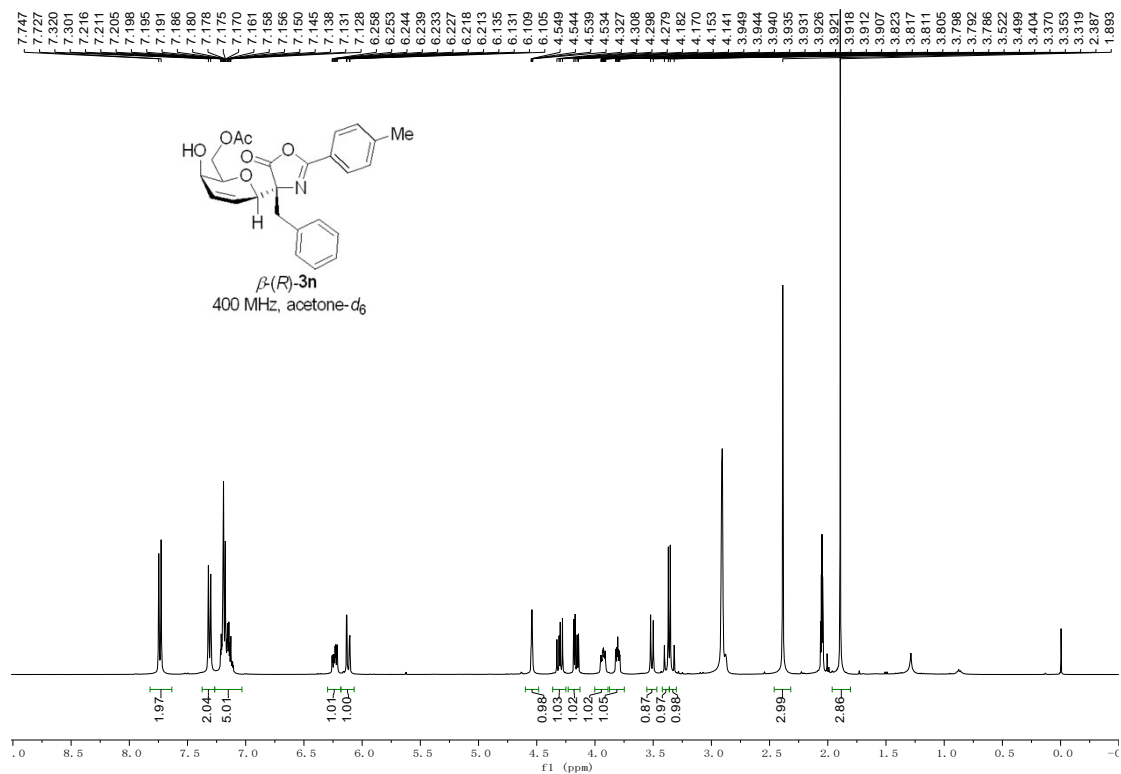


Figure S54. ^1H NMR spectrum of β -(R)-3n

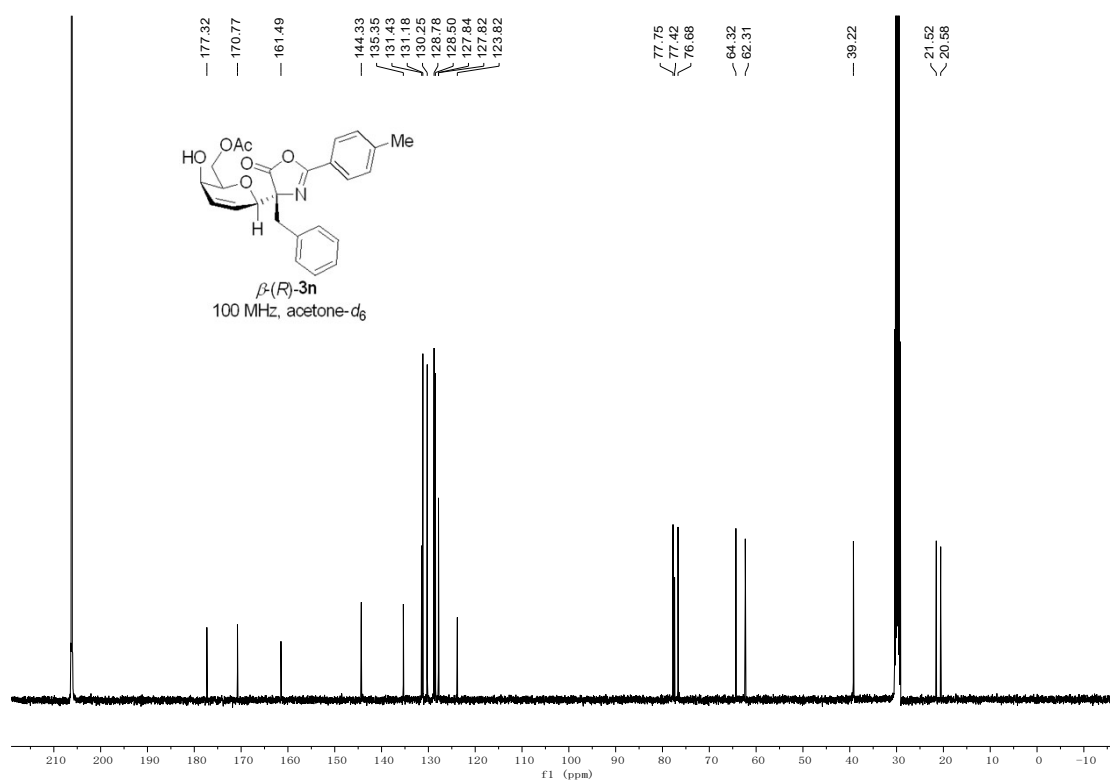


Figure S55. ^{13}C NMR spectrum of β -(R)-3n

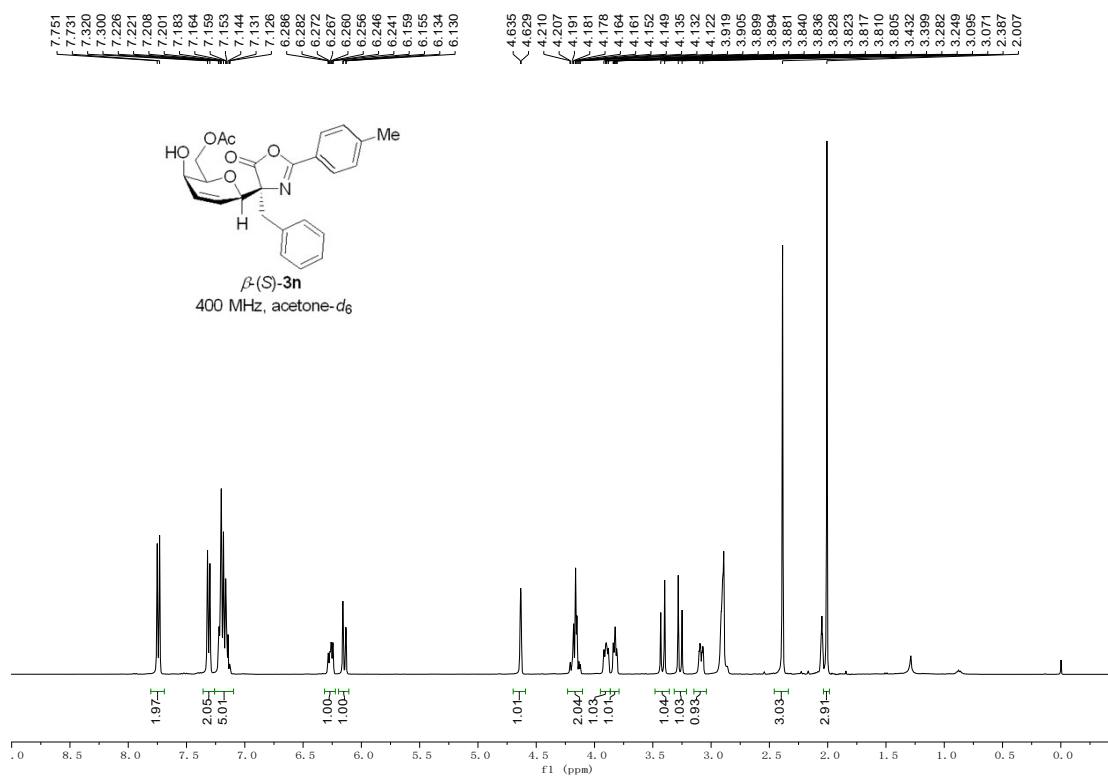


Figure S56. ^1H NMR spectrum of β -(S)-3n

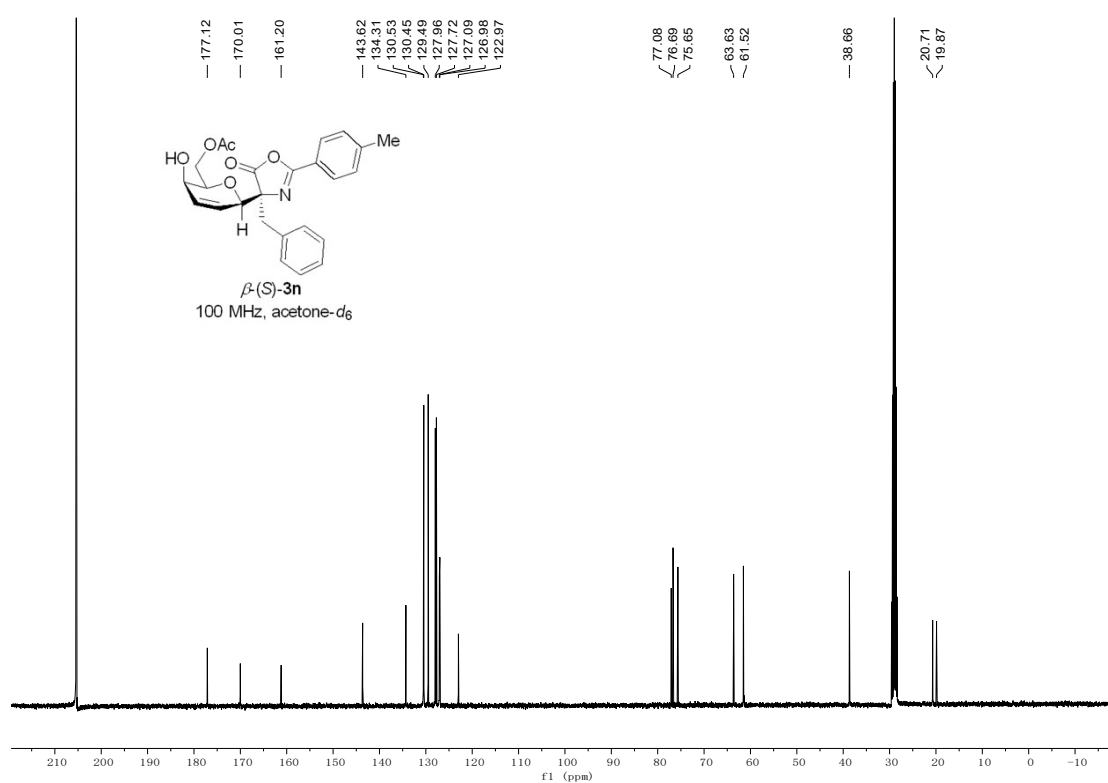


Figure S57. ^{13}C NMR spectrum of β -(S)-3n

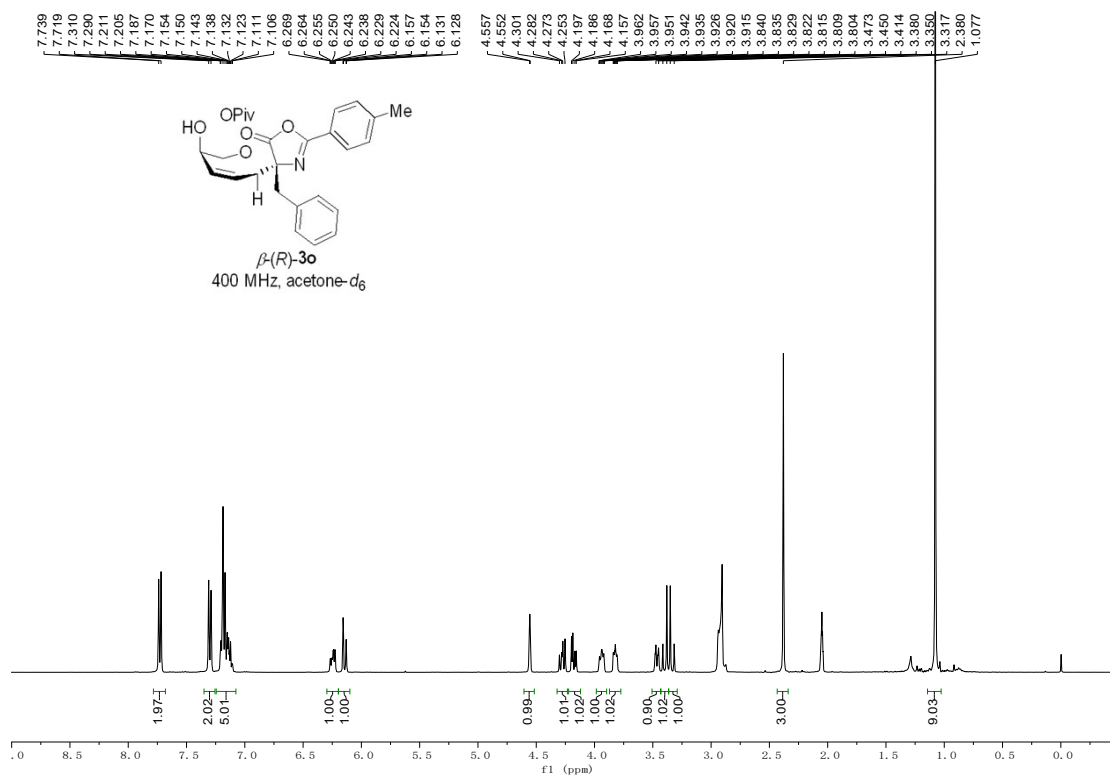


Figure S58. ^1H NMR spectrum of β -(R)-3o

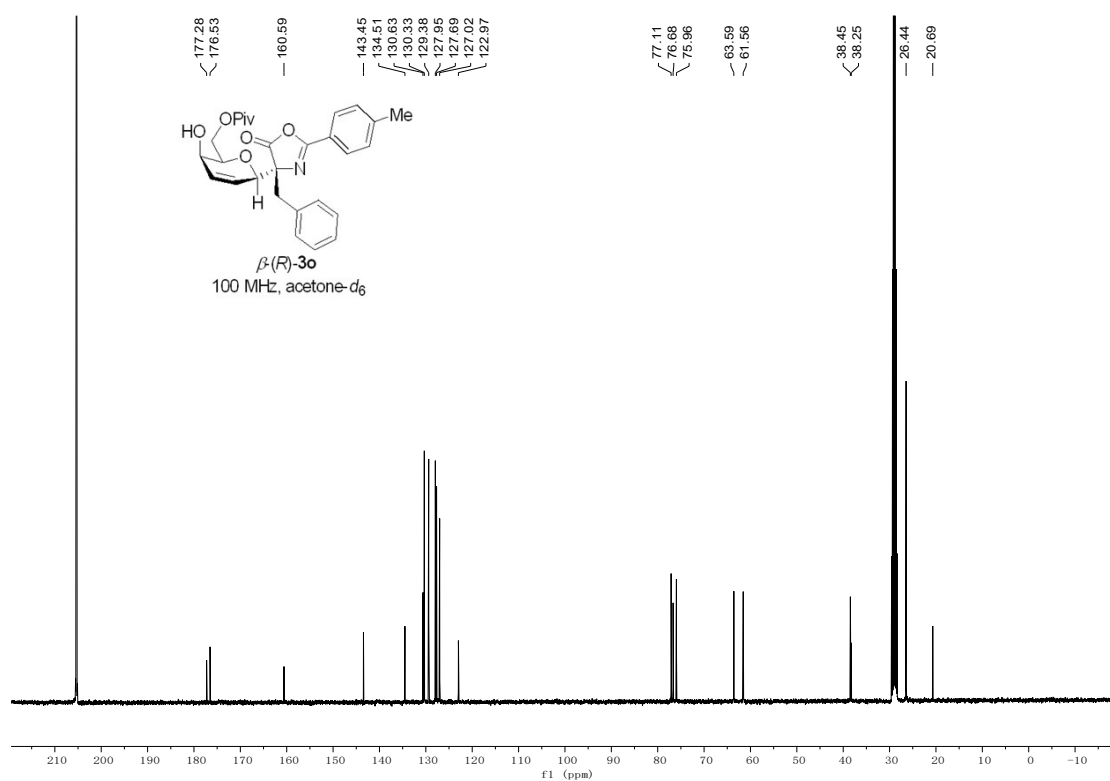


Figure S59. ^{13}C NMR spectrum of β -(R)-3o

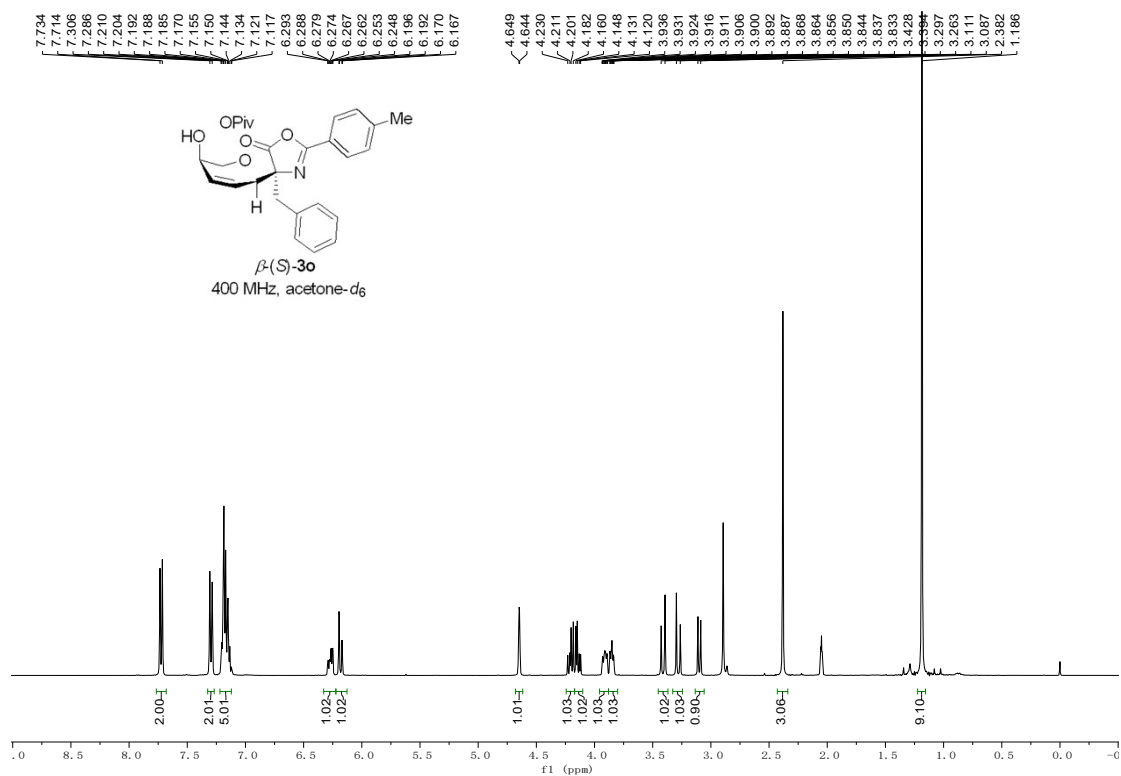


Figure S60. ^1H NMR spectrum of β -(S)-3o

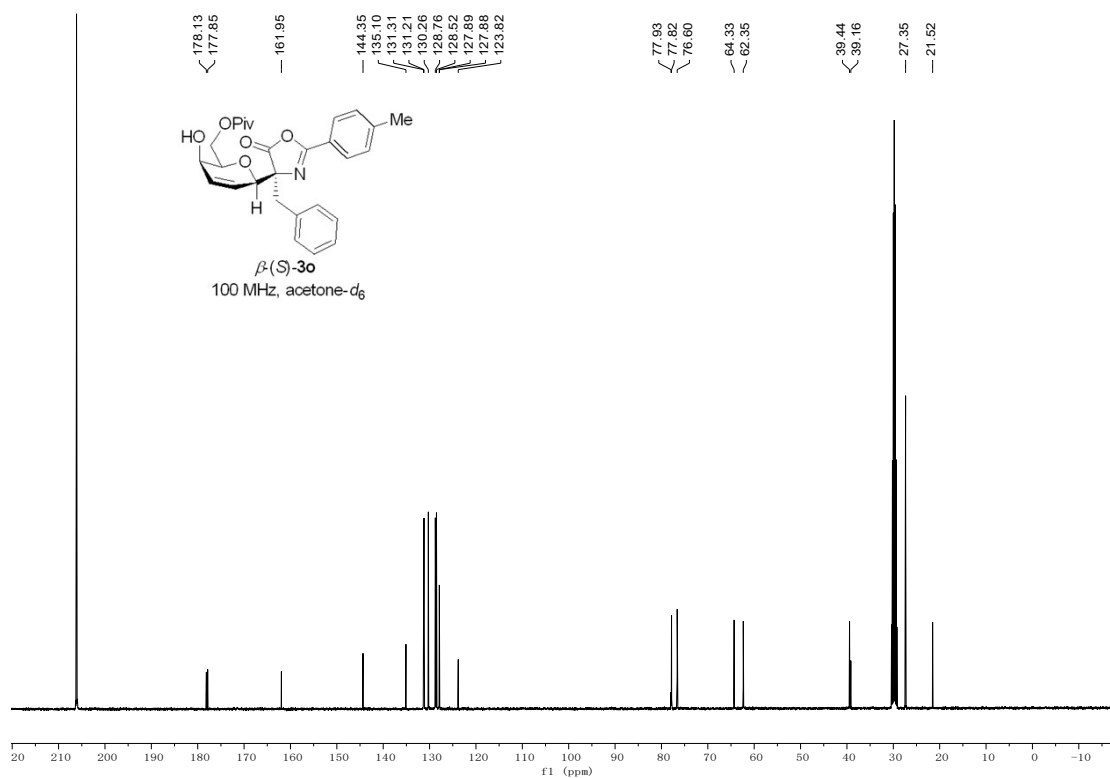


Figure S61. ^{13}C NMR spectrum of β -(S)-3o

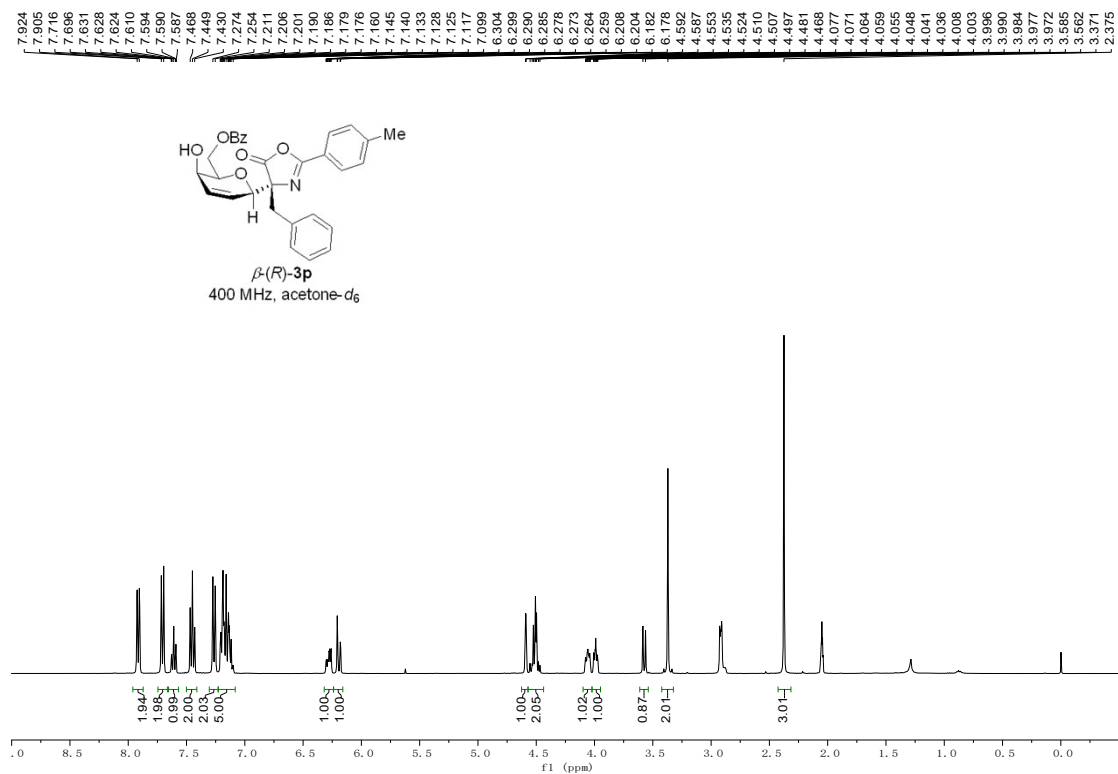


Figure S62. ¹H NMR spectrum of β -(*R*)-**3p**

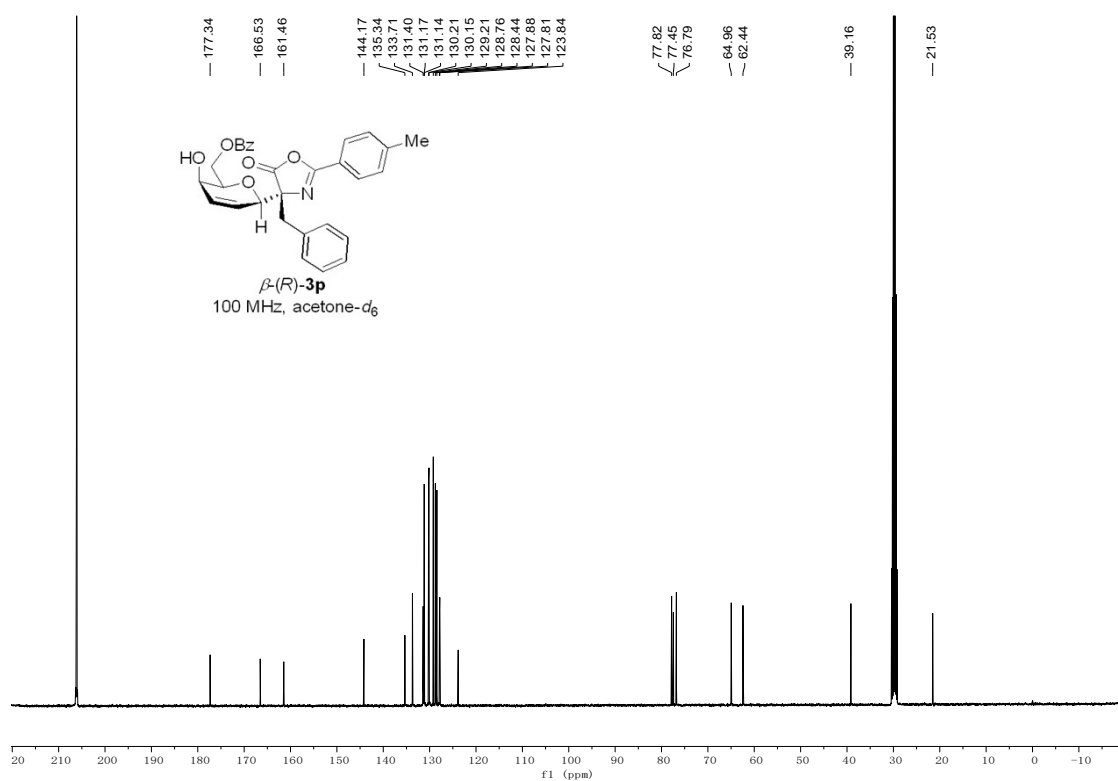


Figure S63. ¹³C NMR spectrum of β -(*R*)-**3p**

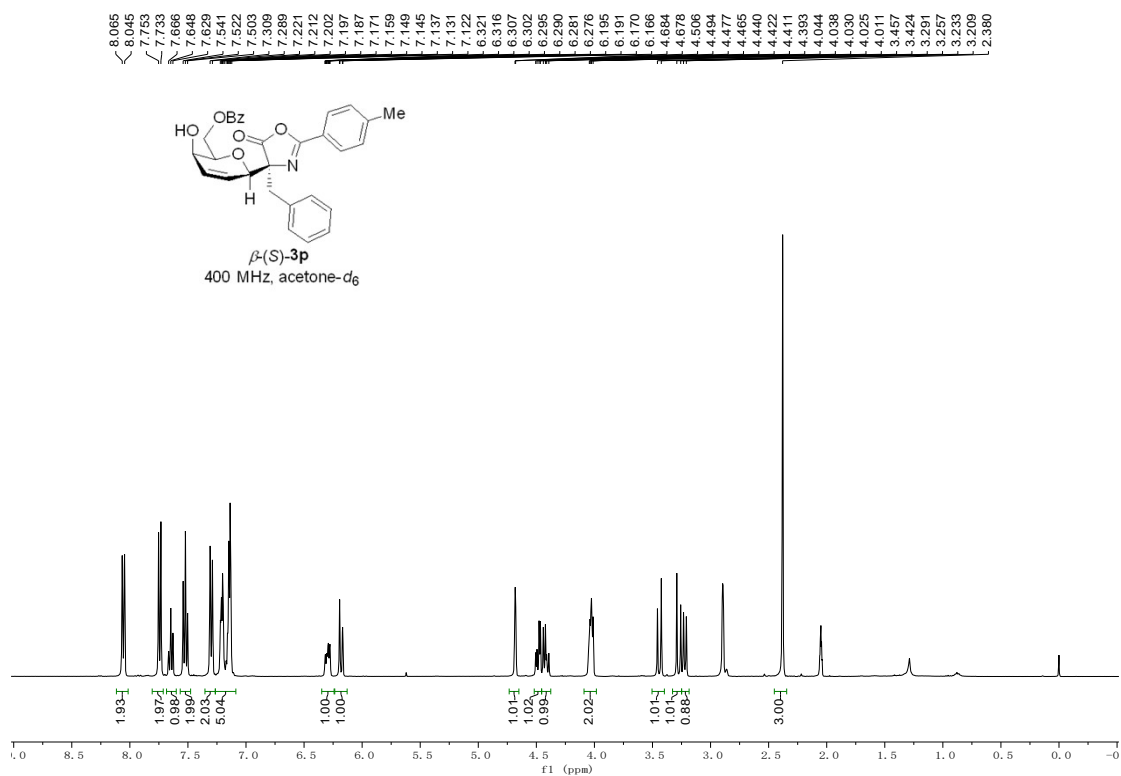


Figure S64. ^1H NMR spectrum of β -(S)-3p

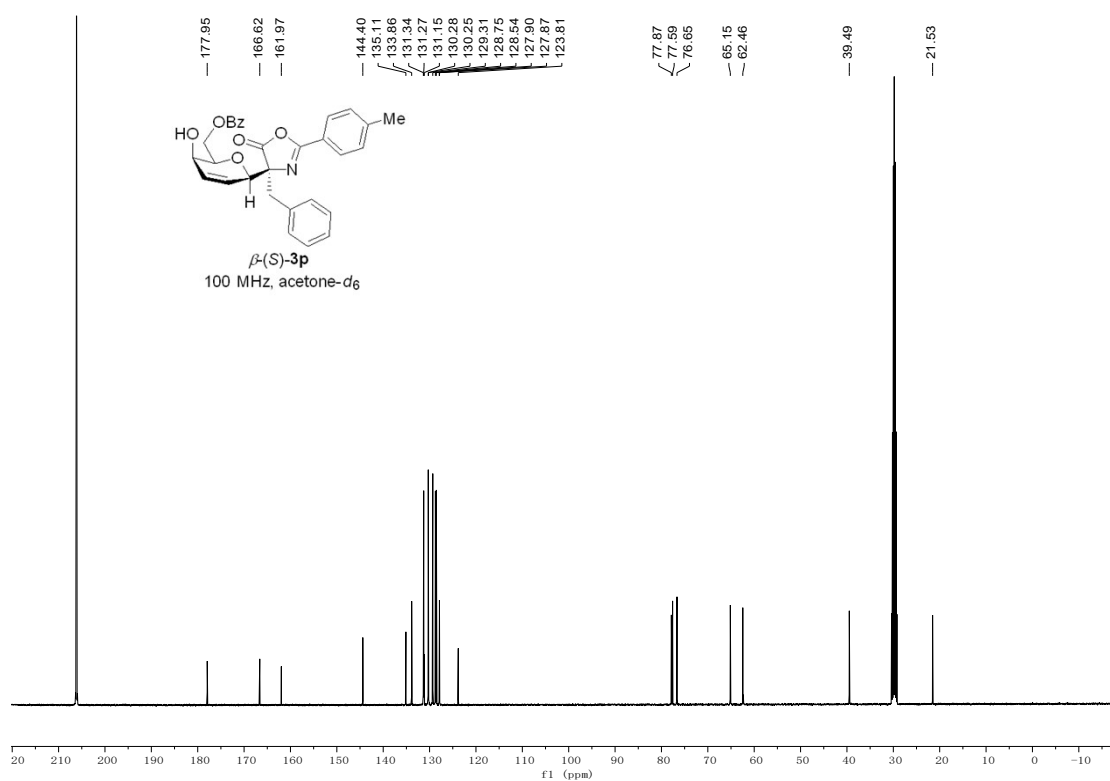


Figure S65. ^{13}C NMR spectrum of β -(S)-3p

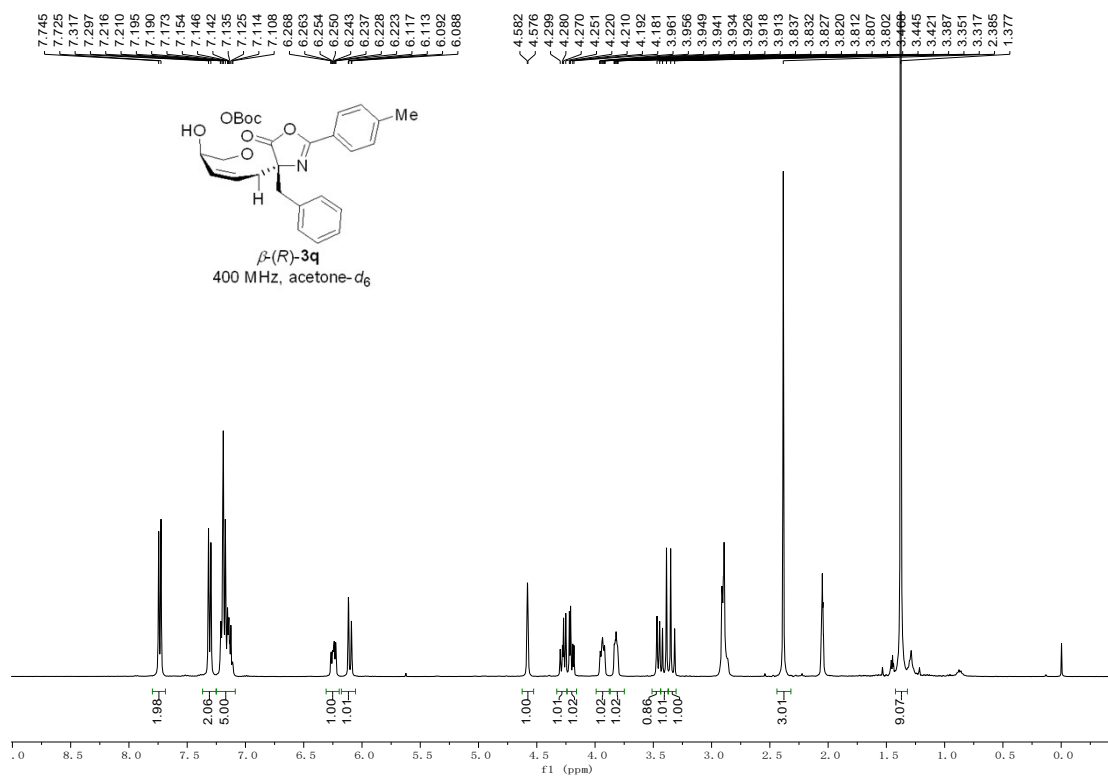


Figure S66. ¹H NMR spectrum of β -(*R*)-3q

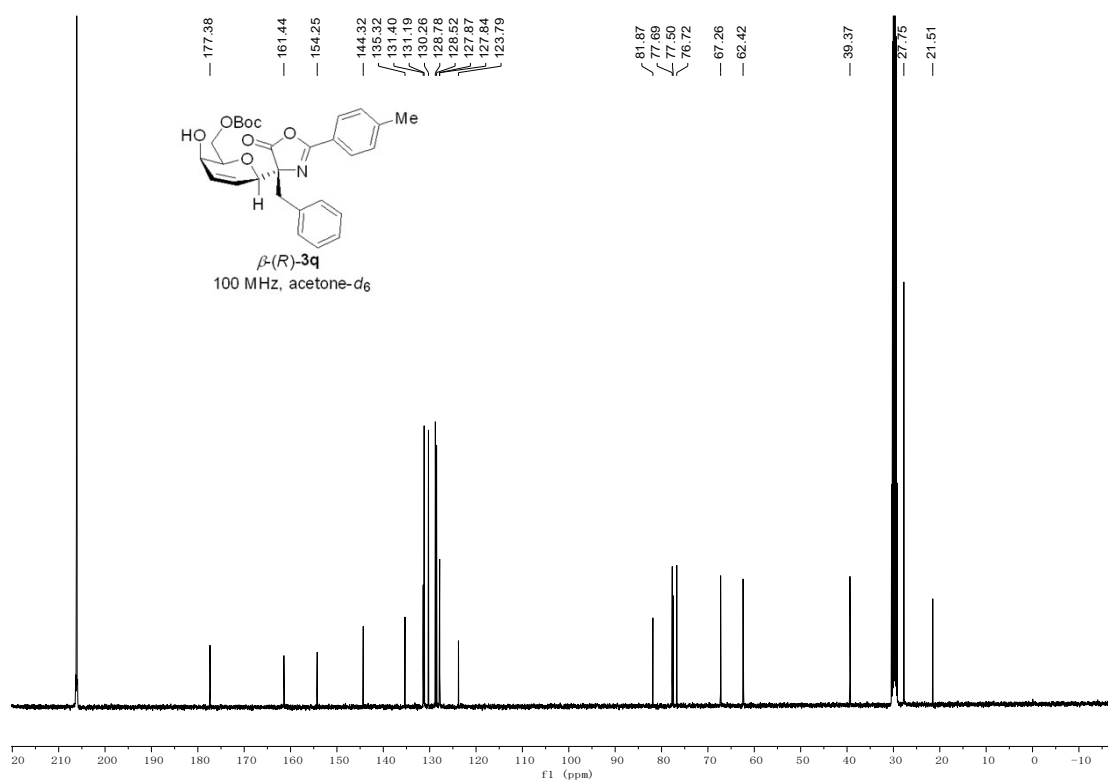


Figure S67. ¹³C NMR spectrum of β -(*R*)-3q

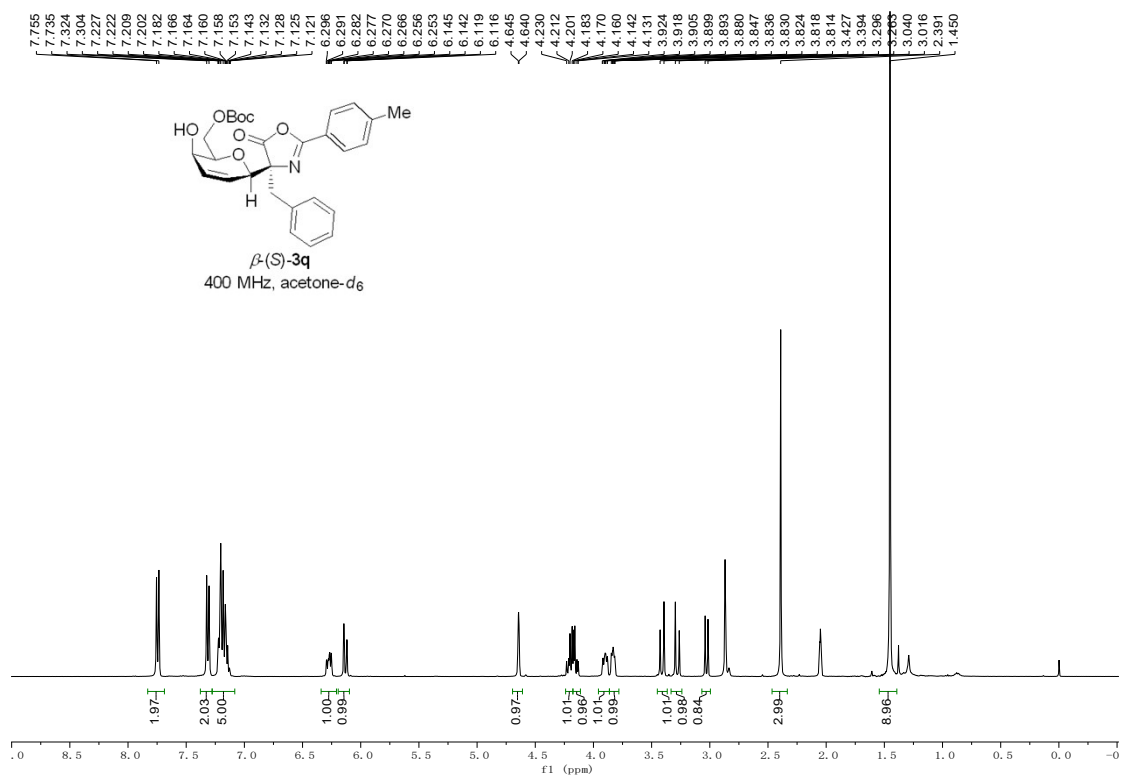


Figure S68. ^1H NMR spectrum of β -(S)-3q

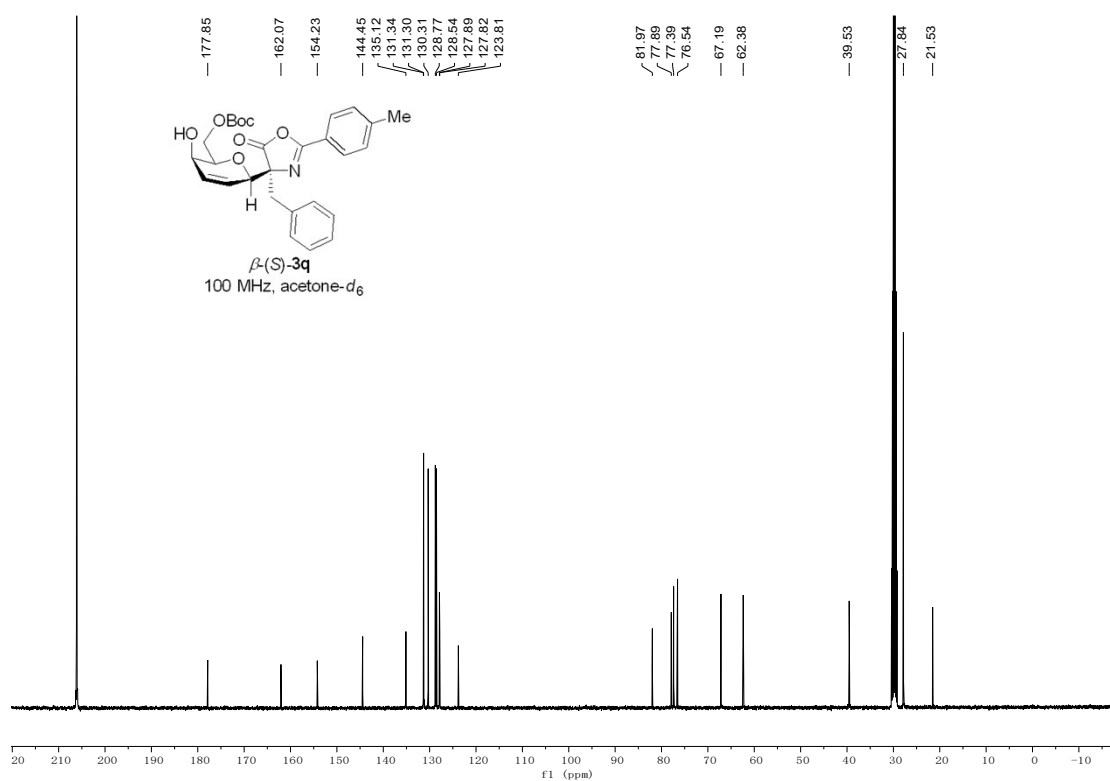


Figure S69. ^{13}C NMR spectrum of β -(S)-3q

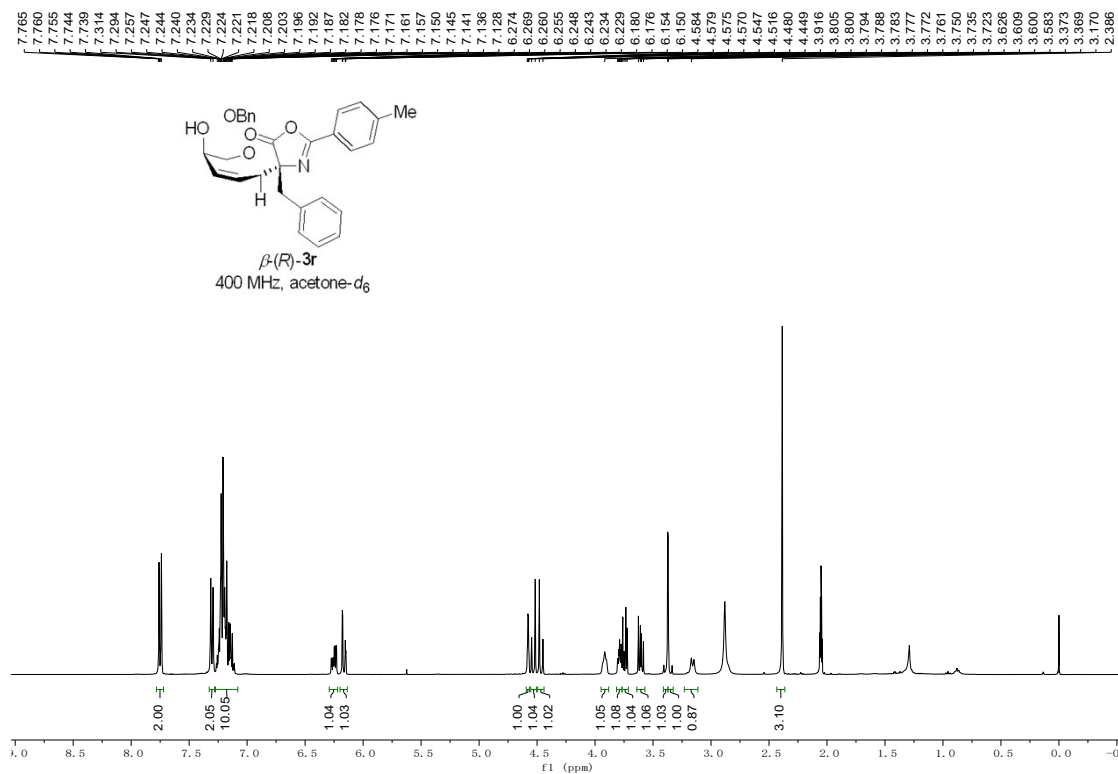


Figure S70. ^1H NMR spectrum of β -(*R*)-**3r**

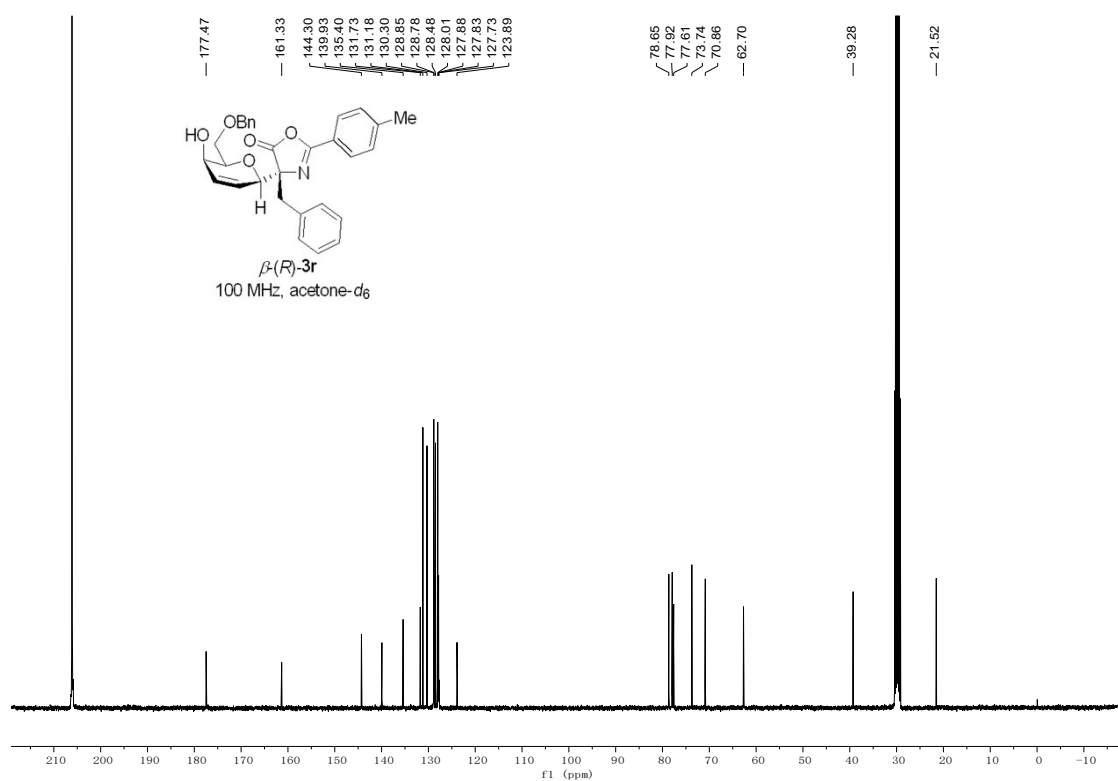


Figure S71. ^{13}C NMR spectrum of β -(*R*)-**3r**

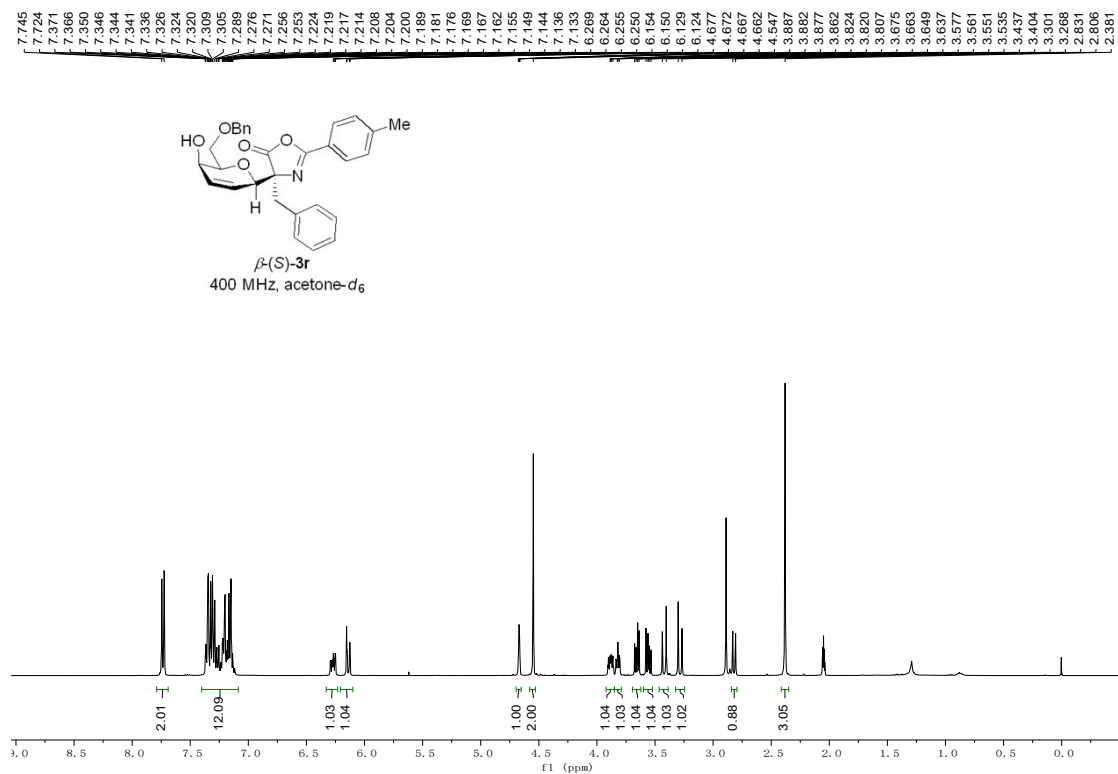


Figure S72. ^1H NMR spectrum of β -(S)-3r

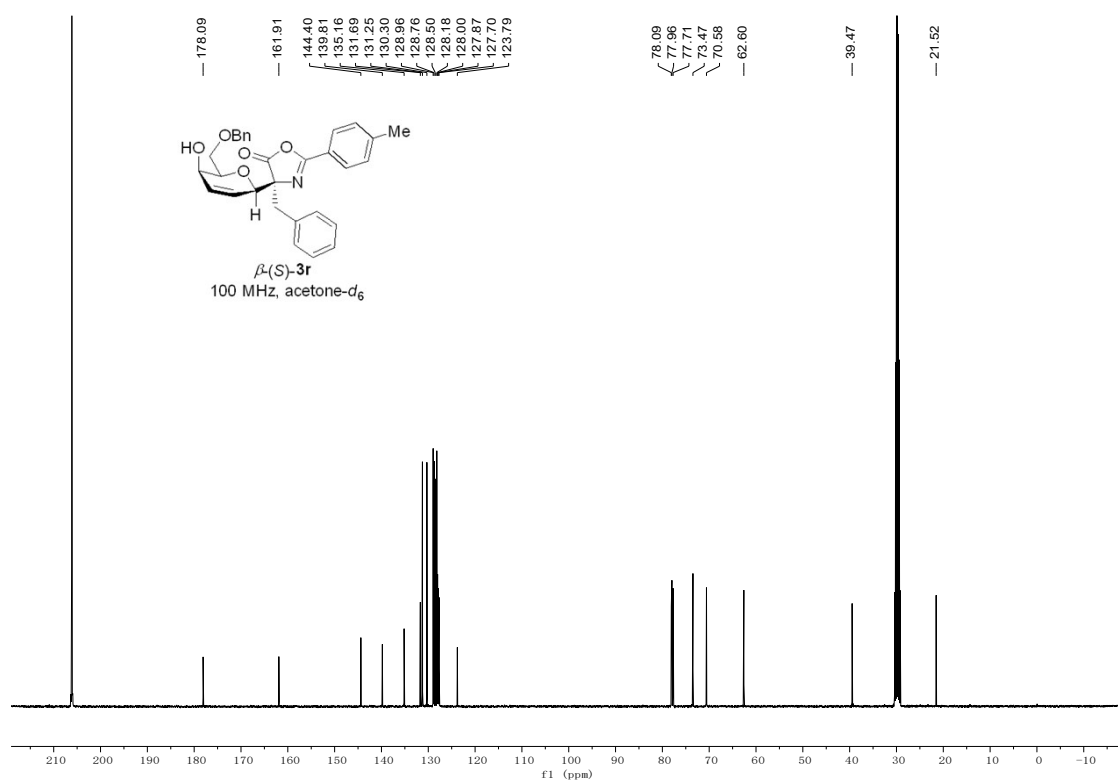


Figure S73. ^{13}C NMR spectrum of β -(S)-3r

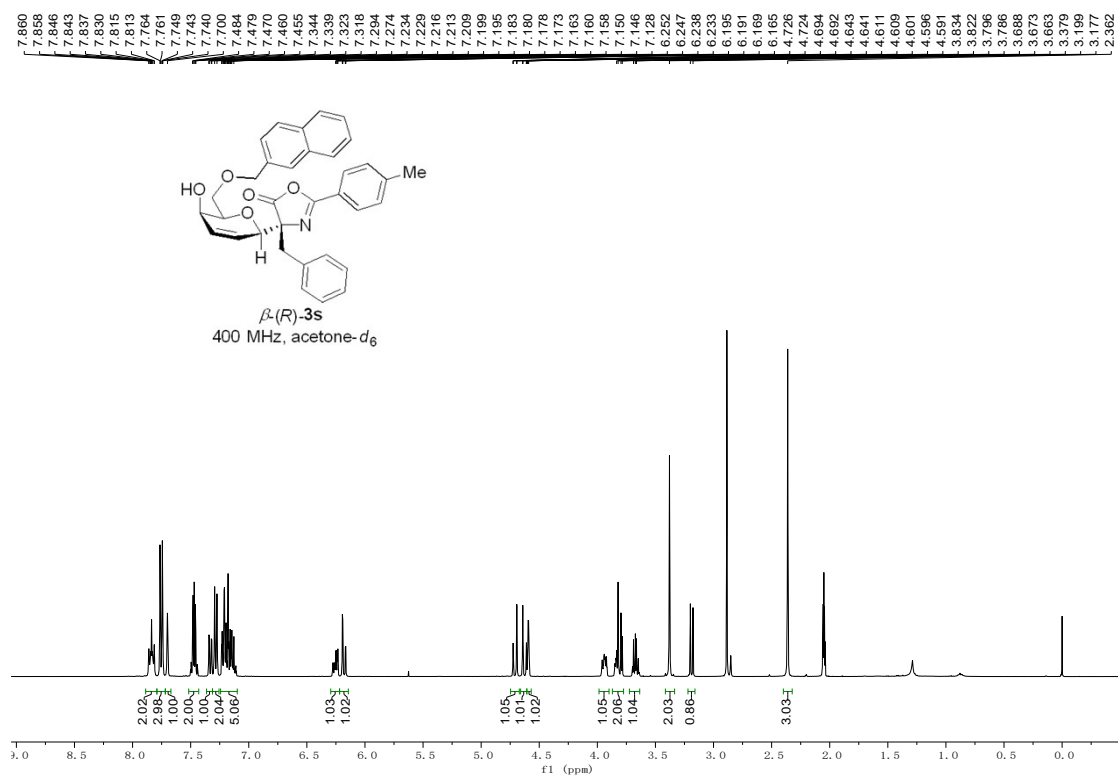


Figure S74. ^1H NMR spectrum of β -(*R*)-**3s**

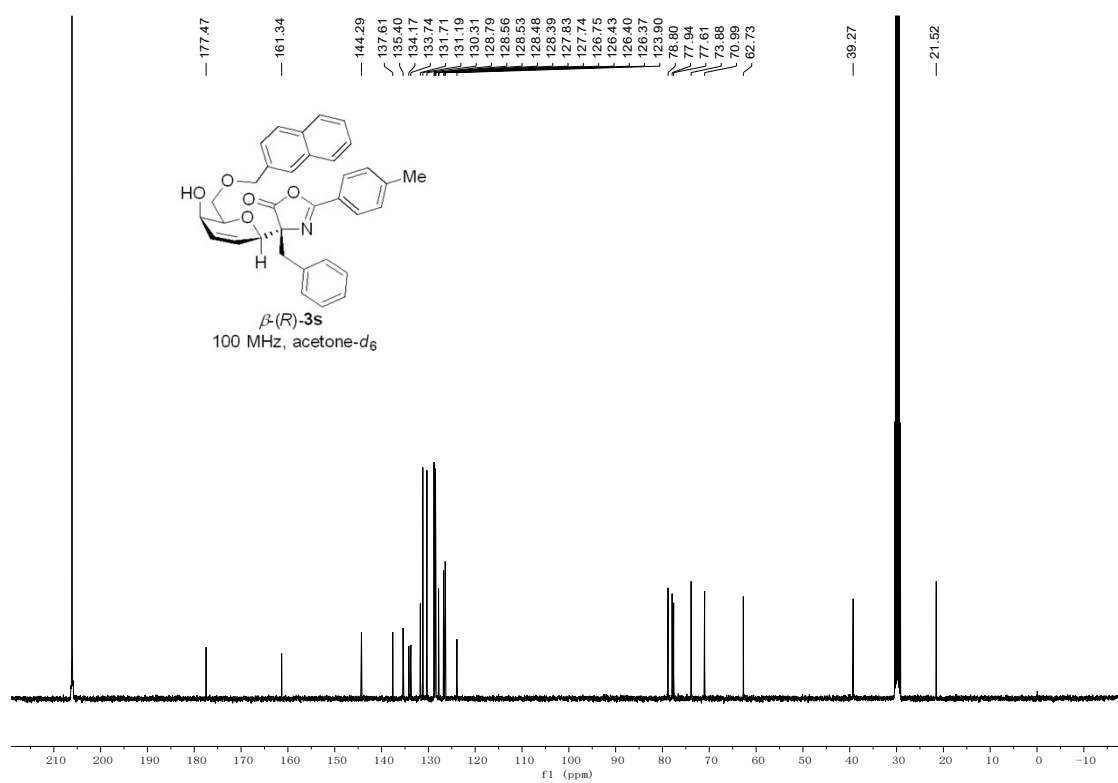


Figure S75. ^{13}C NMR spectrum of β -(*R*)-**3s**

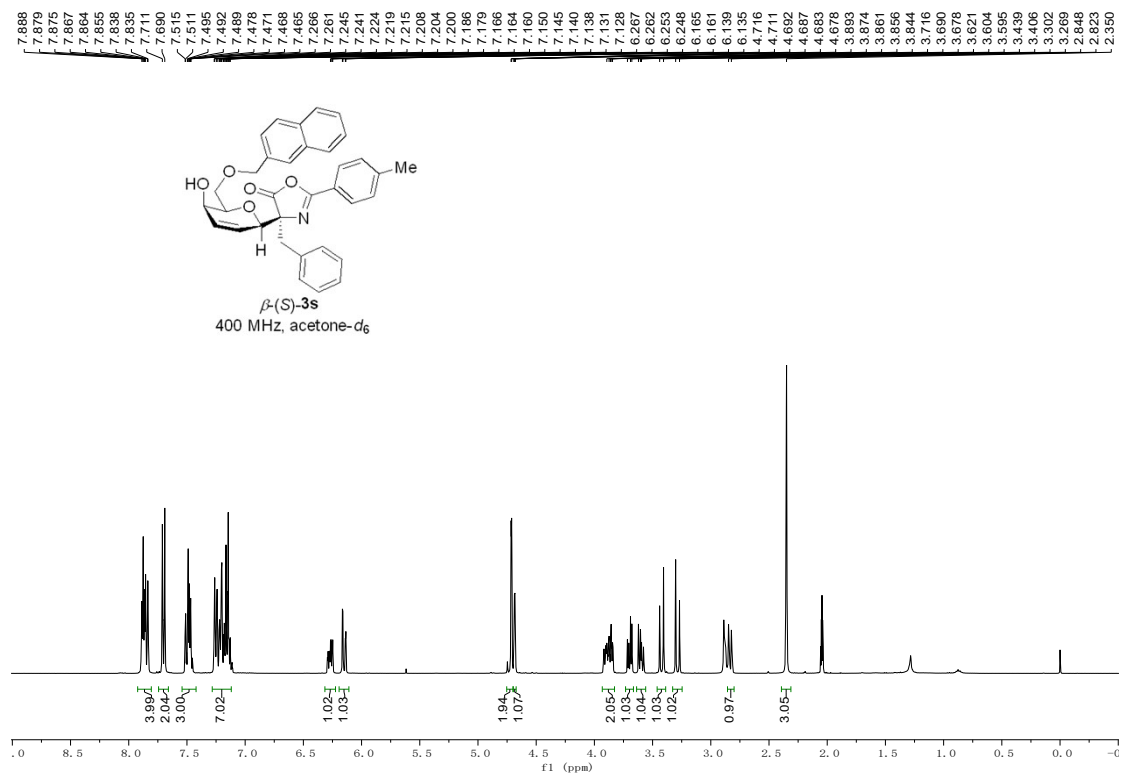


Figure S76. ^1H NMR spectrum of β -(S)-3s

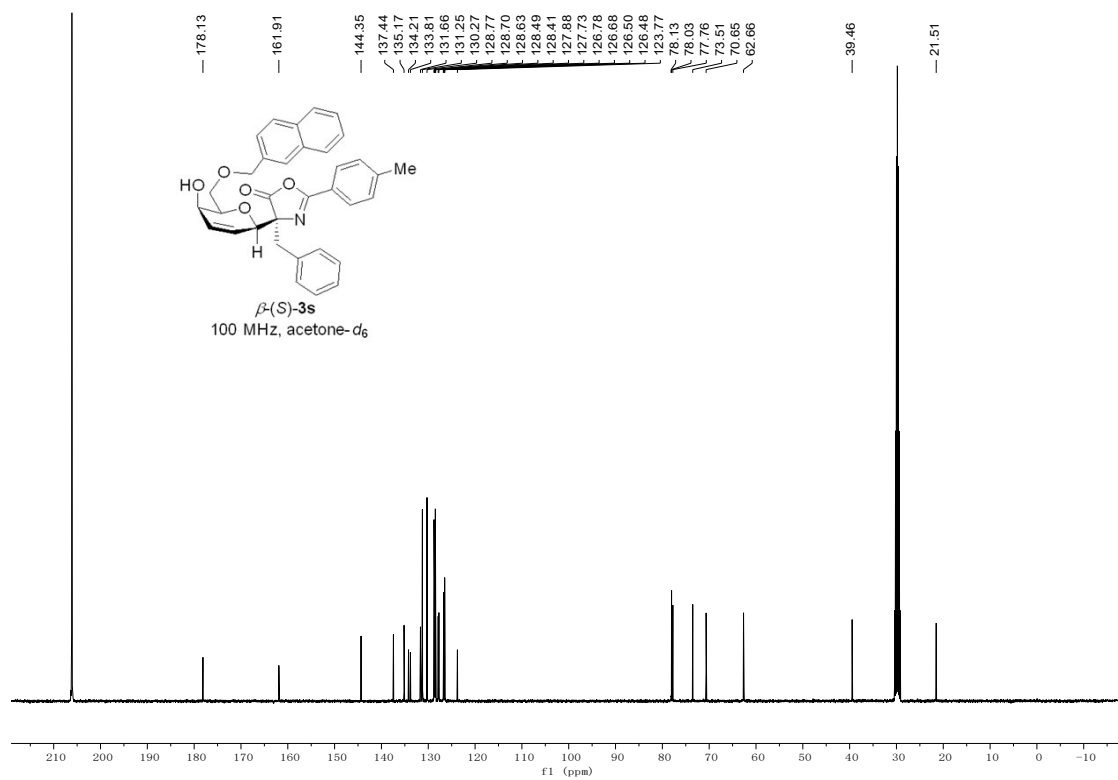


Figure S77. ^{13}C NMR spectrum of β -(S)-3s

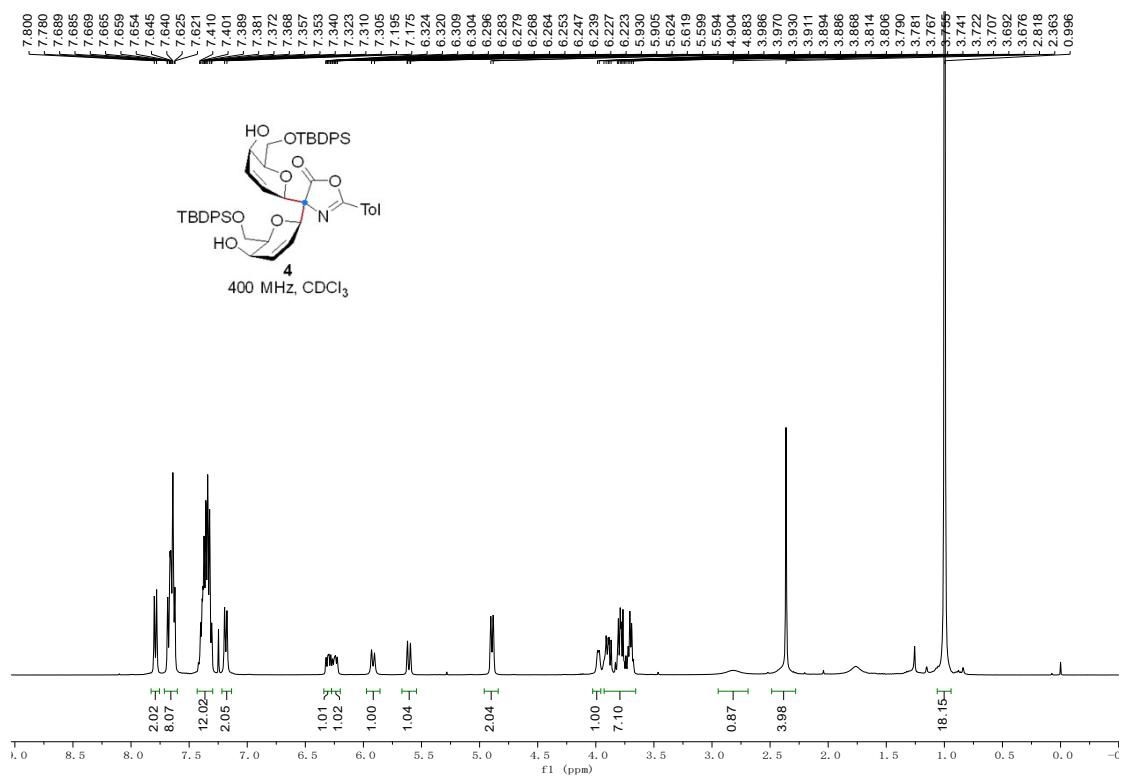


Figure S78. ¹H NMR spectrum of **4**

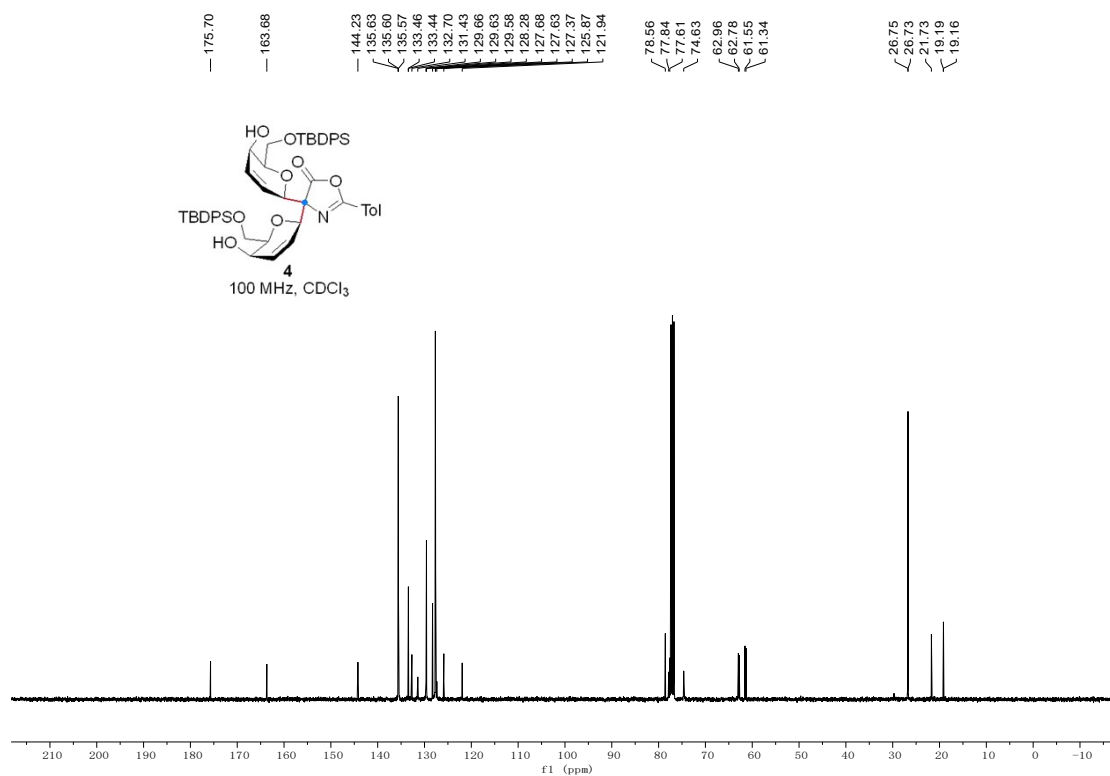


Figure S79. ¹³C NMR spectrum of **4**

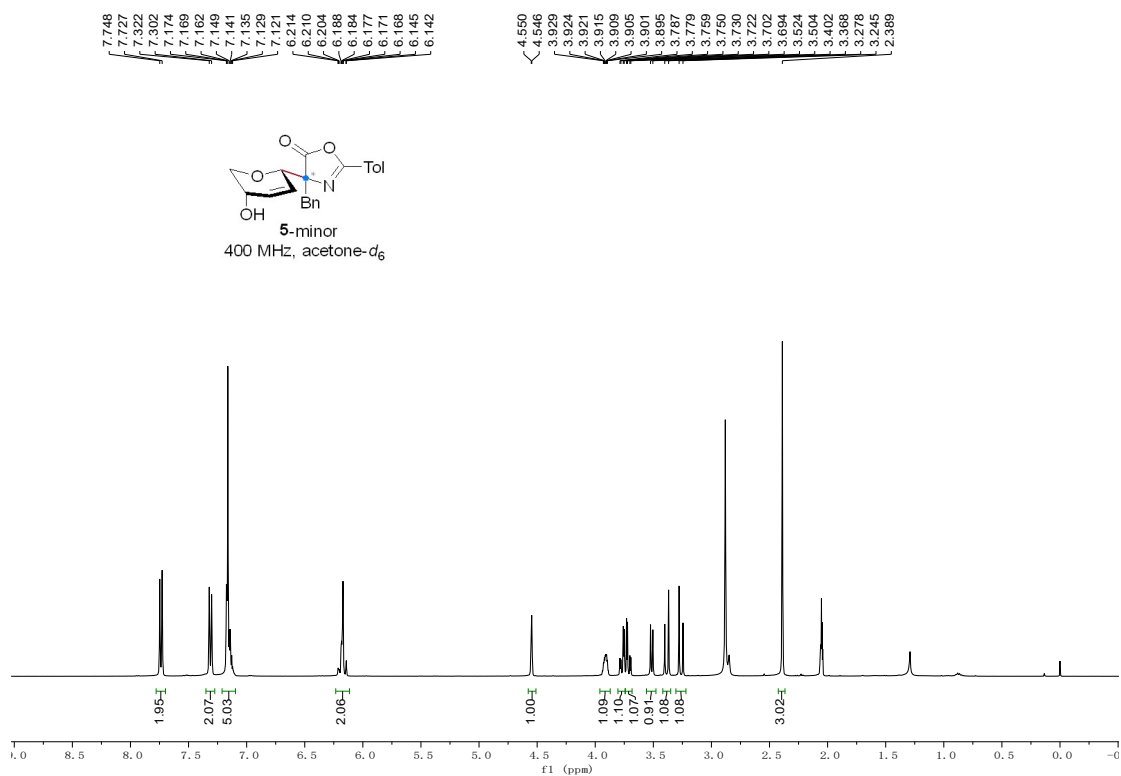


Figure S80. ^1H NMR spectrum of **5-minor**

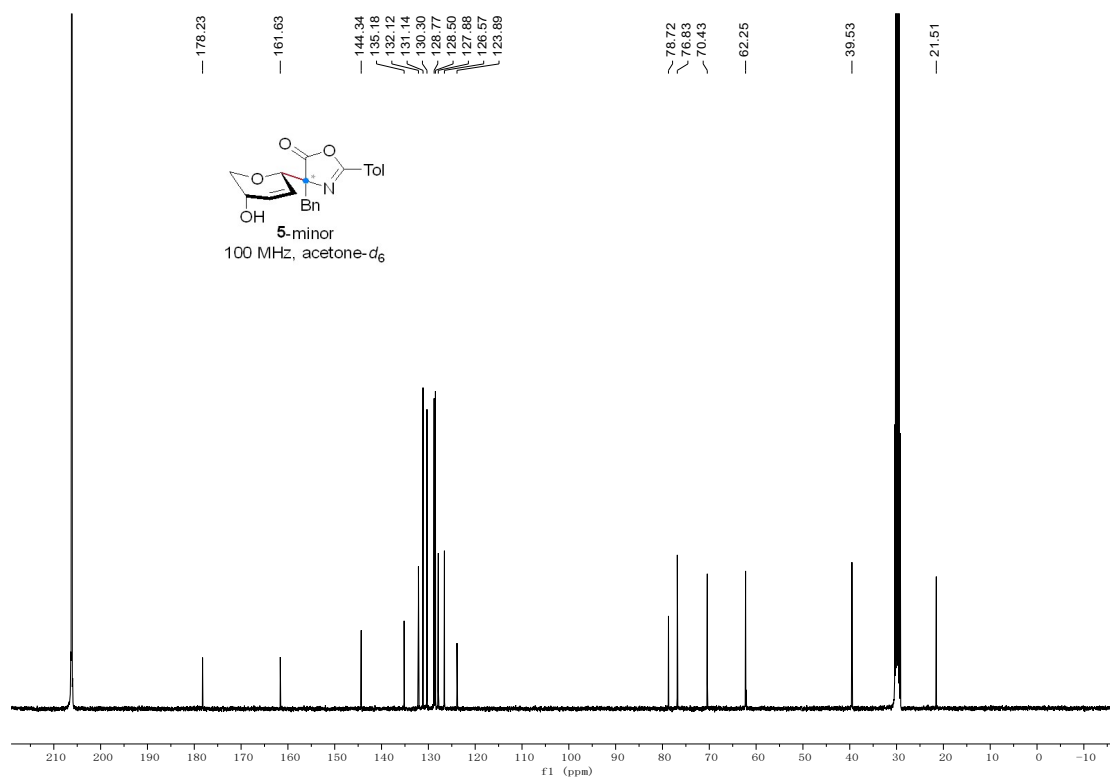


Figure S81. ^{13}C NMR spectrum of **5-minor**

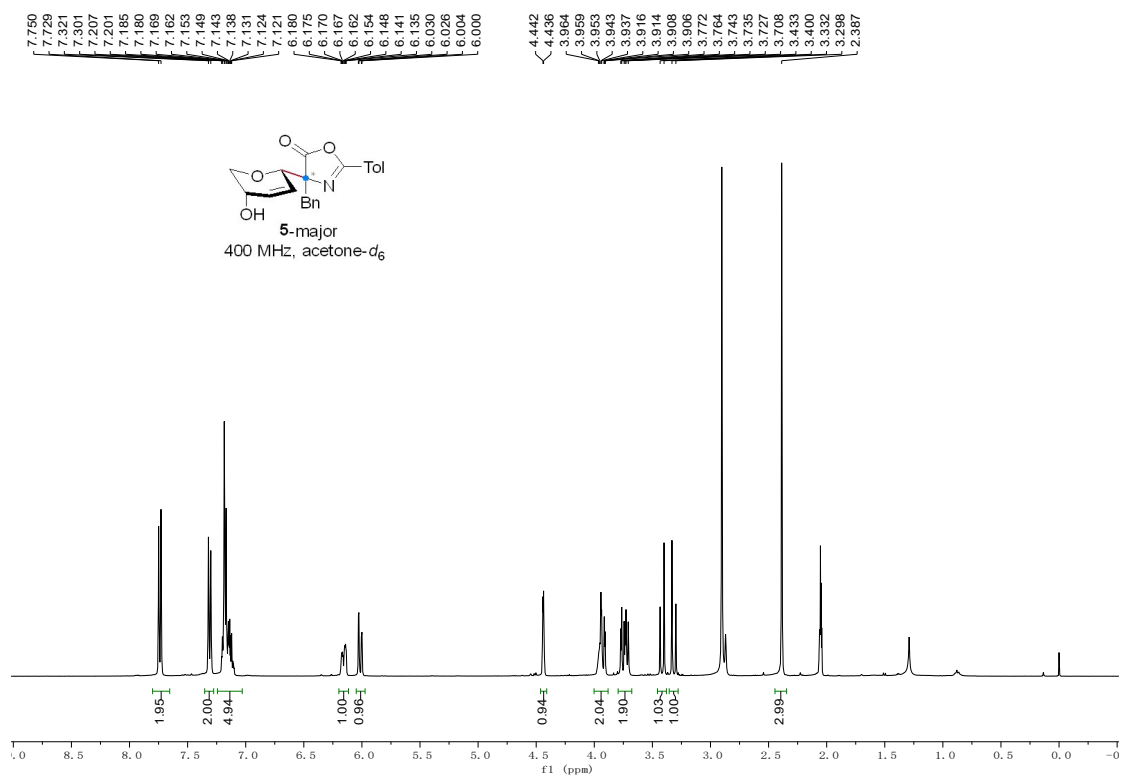


Figure S82. ^1H NMR spectrum of **5-major**

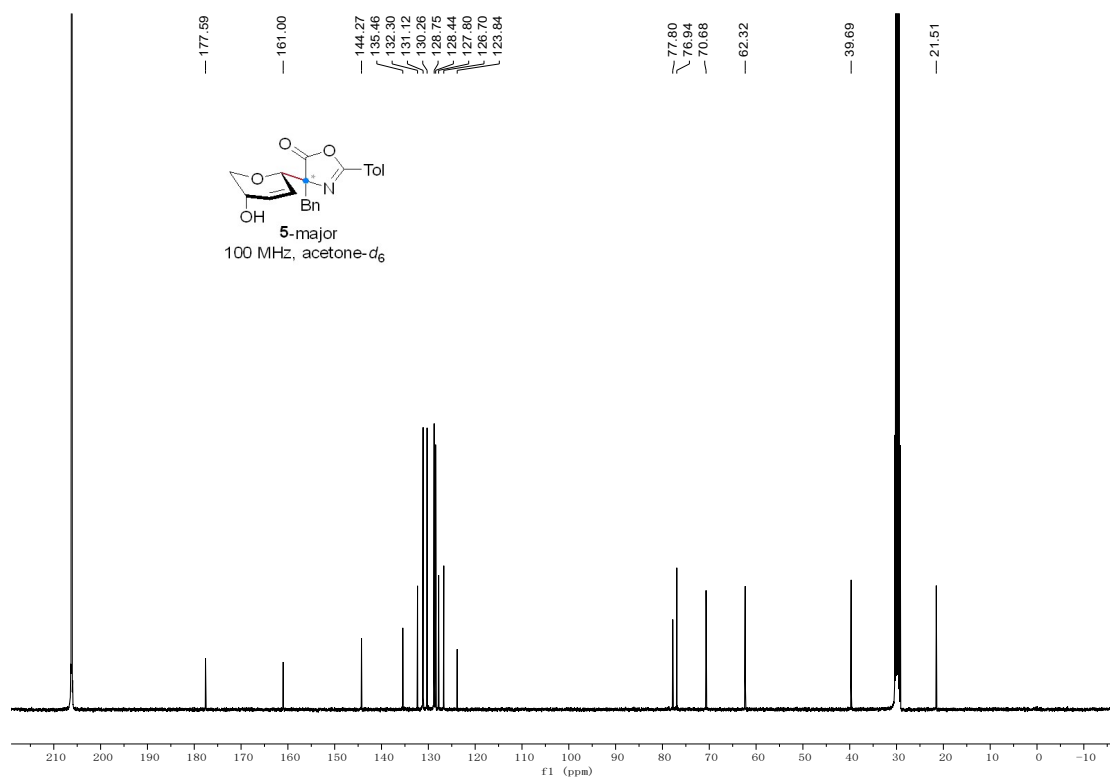


Figure S83. ^{13}C NMR spectrum of **5-major**

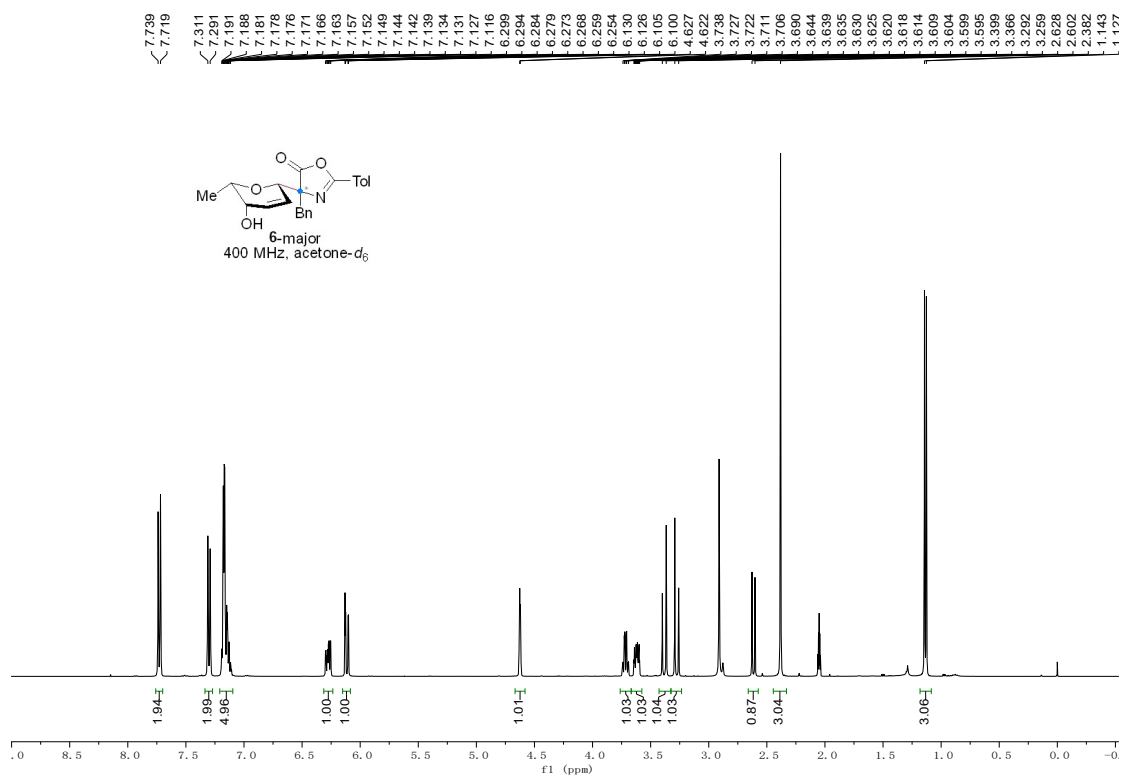


Figure S84. ¹H NMR spectrum of **6-major**

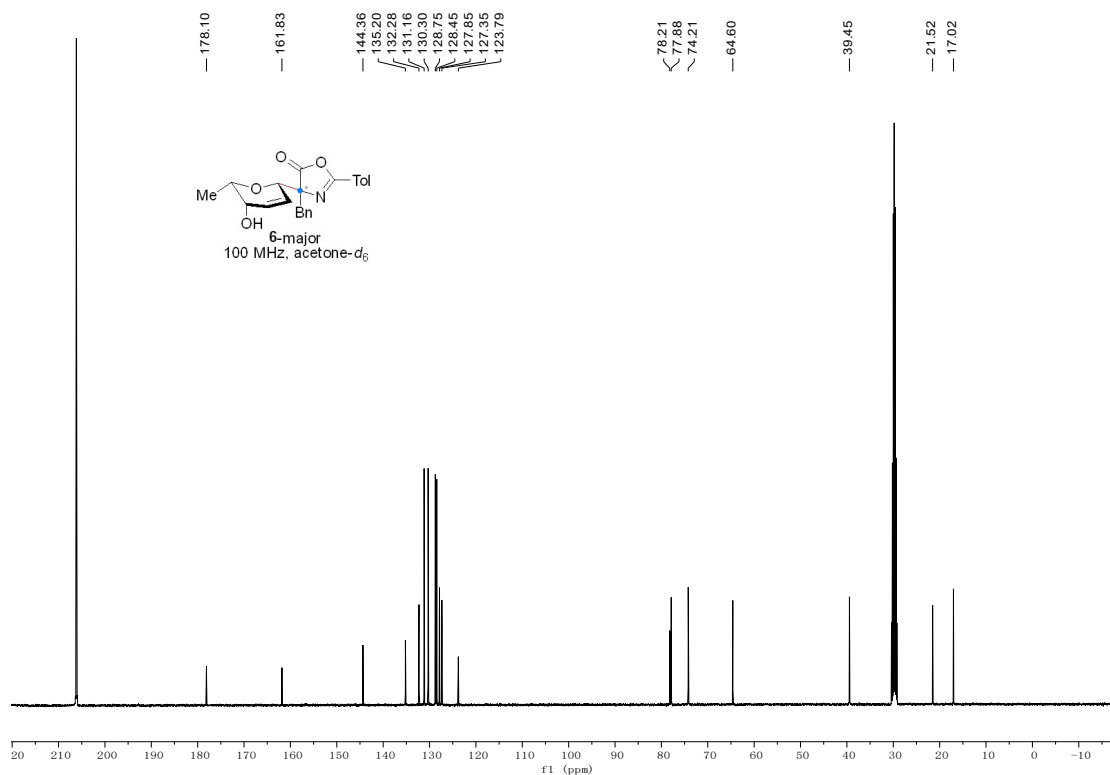


Figure S85. ¹³C NMR spectrum of **6-major**

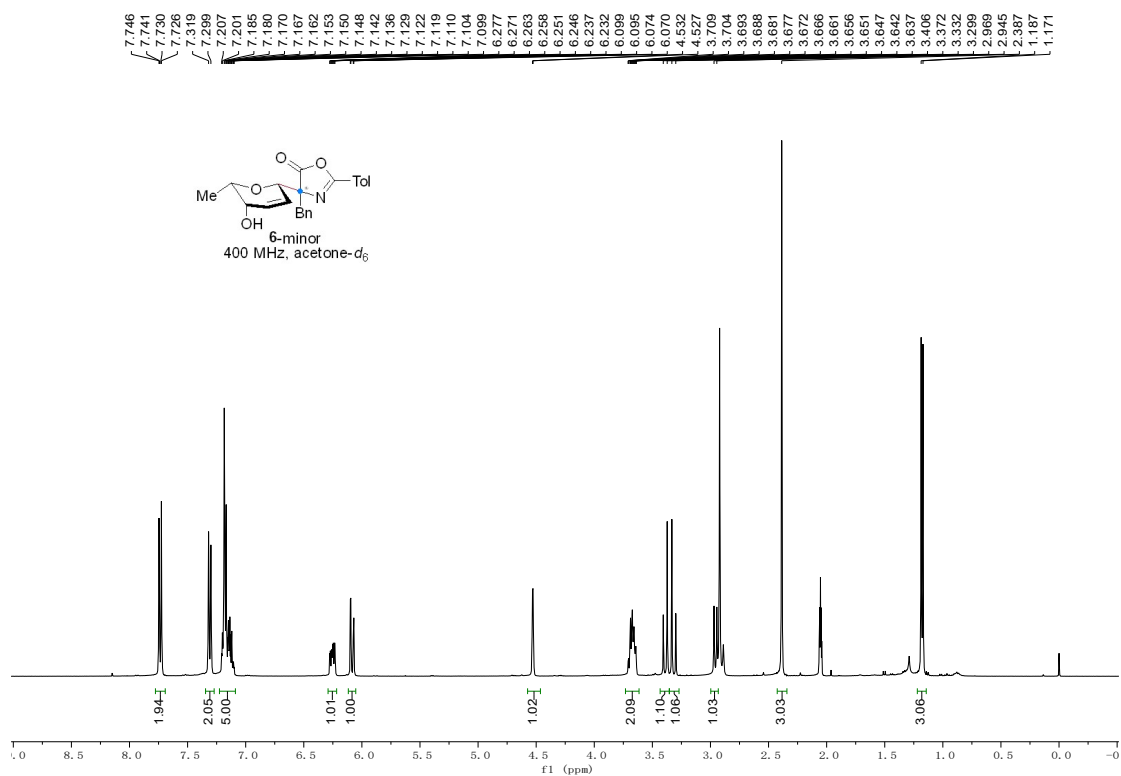


Figure S86. ¹H NMR spectrum of 6-minor

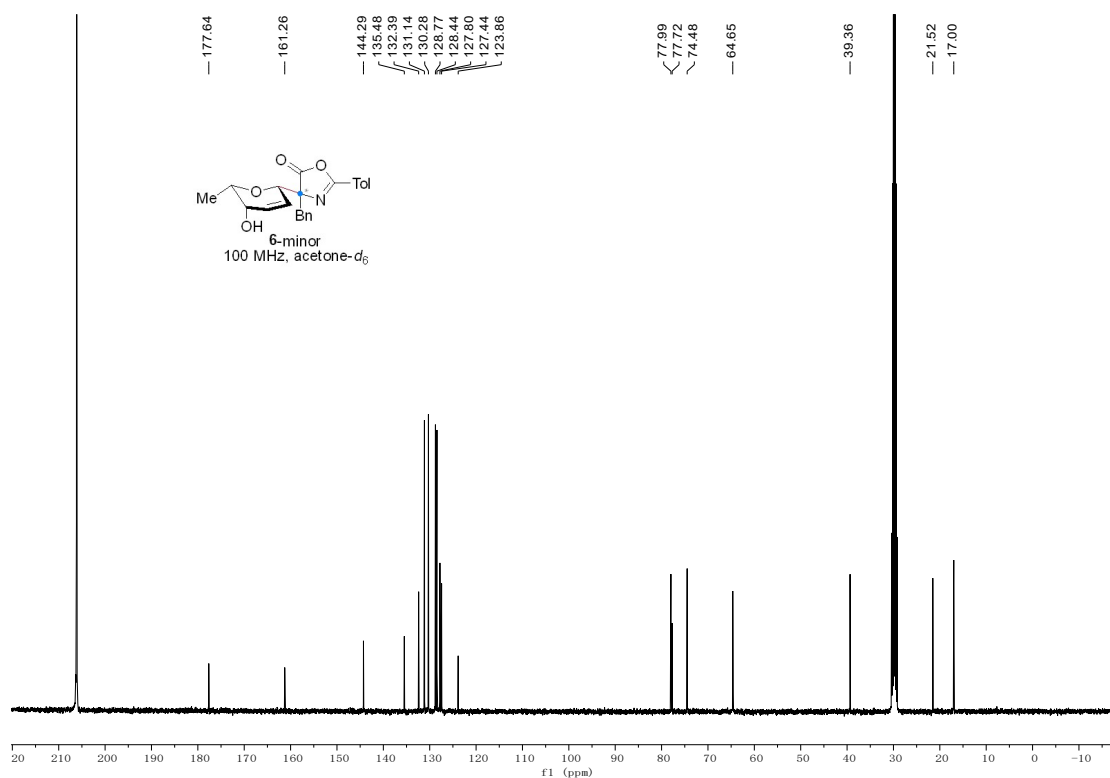


Figure S87. ¹³C NMR spectrum of 6-minor

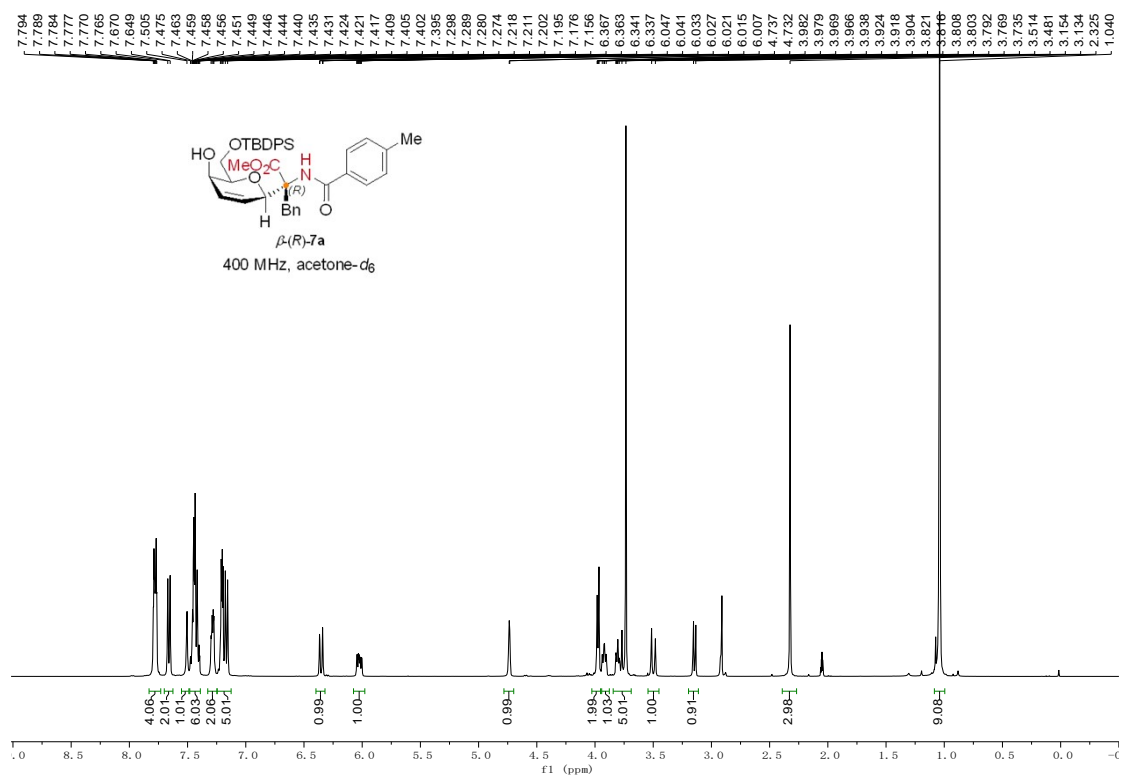


Figure S88. ^1H NMR spectrum of β -(*R*)-7a

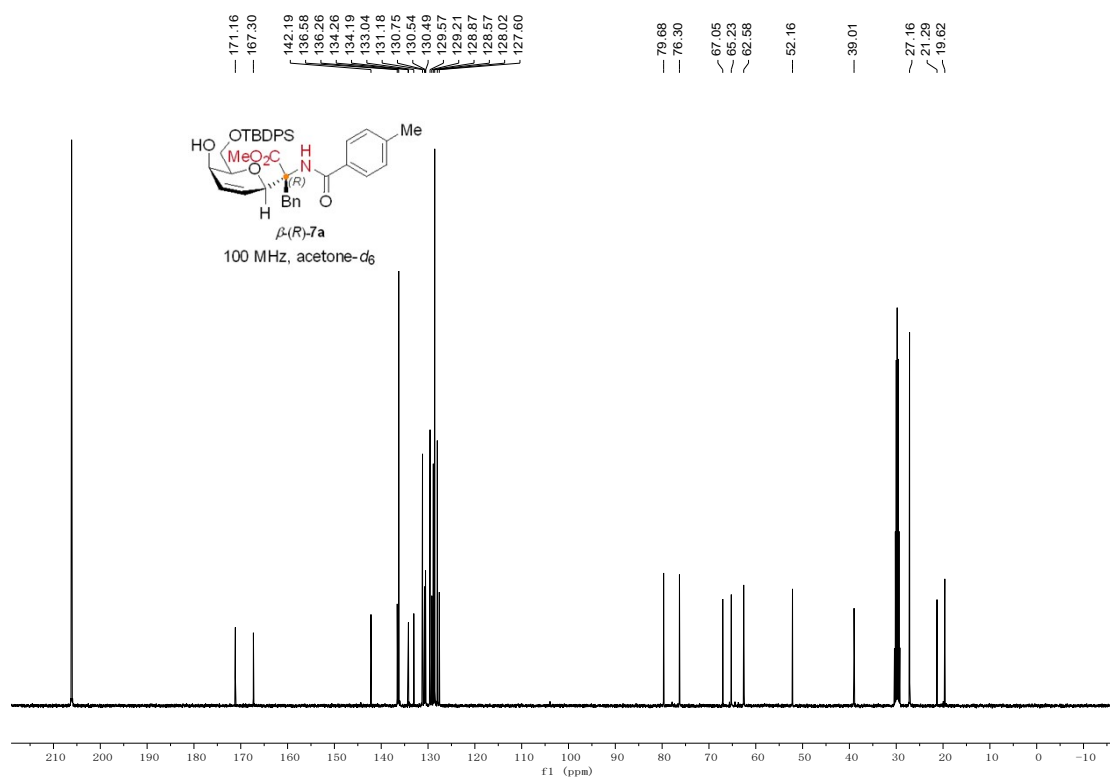


Figure S89. ^{13}C NMR spectrum of β -(*R*)-7a

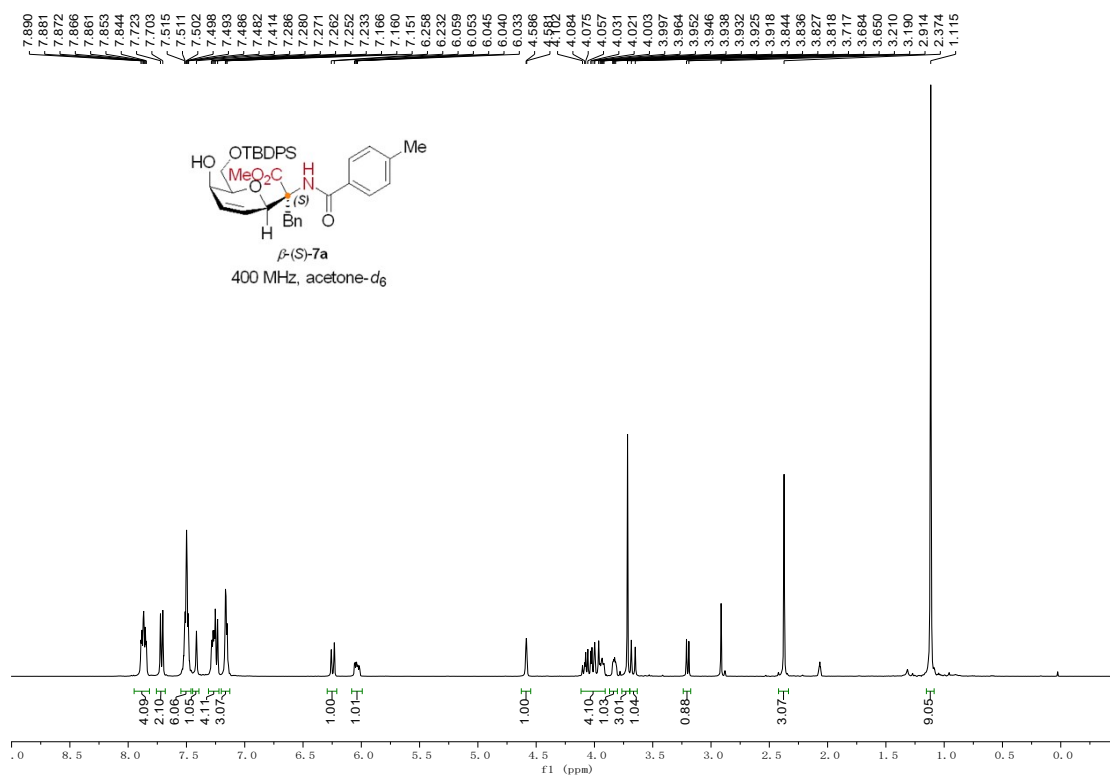


Figure S90. ¹H NMR spectrum of β -(S)-7a

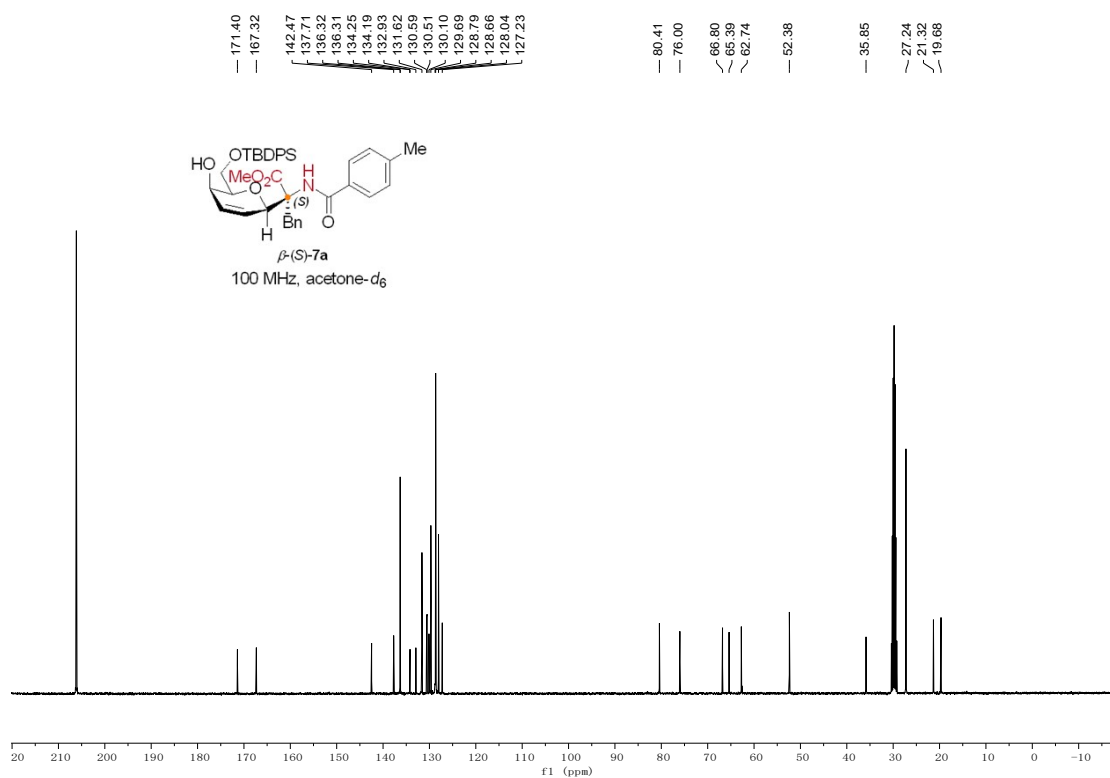


Figure S91. ¹³C NMR spectrum of β -(S)-7a

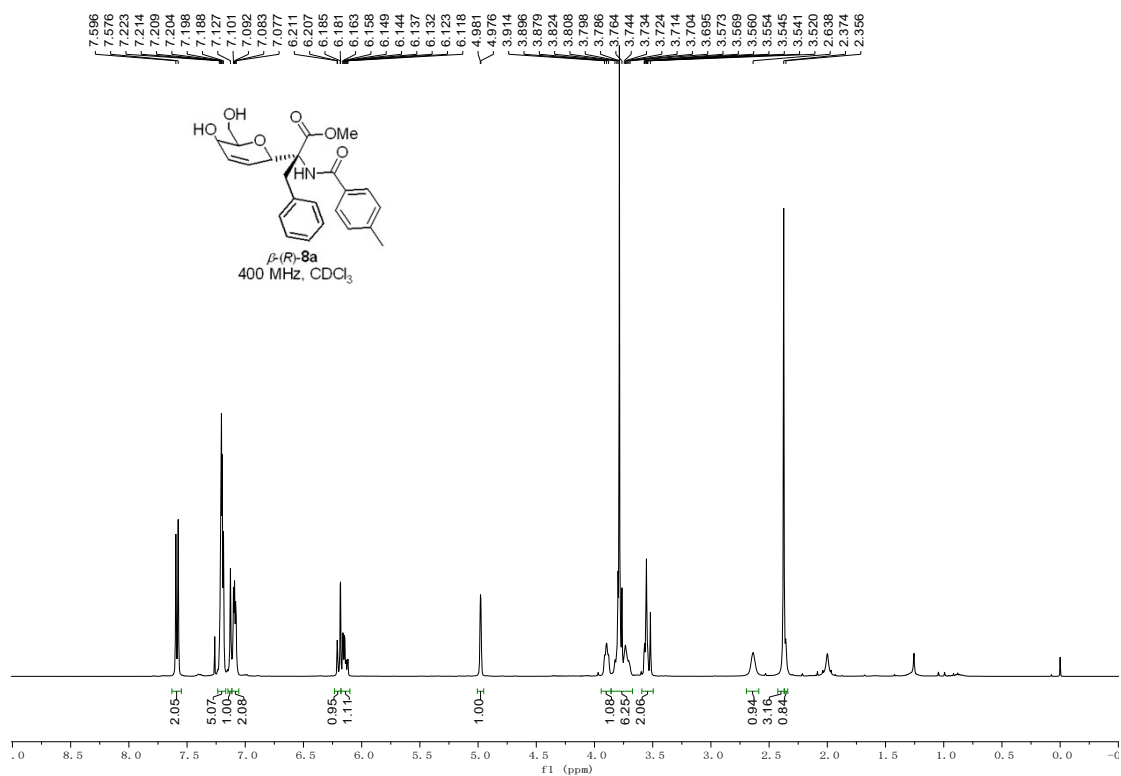


Figure S92. ¹H NMR spectrum of β -(R)-8a

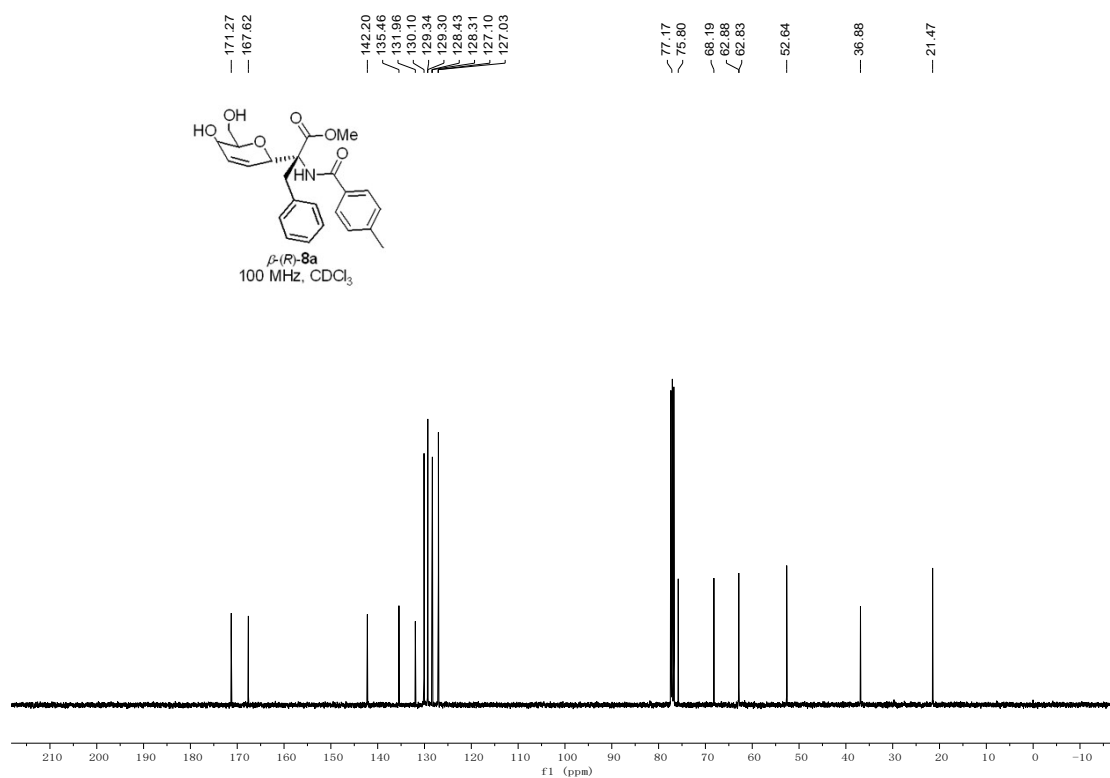


Figure S93. ¹³C NMR spectrum of β -(R)-8a

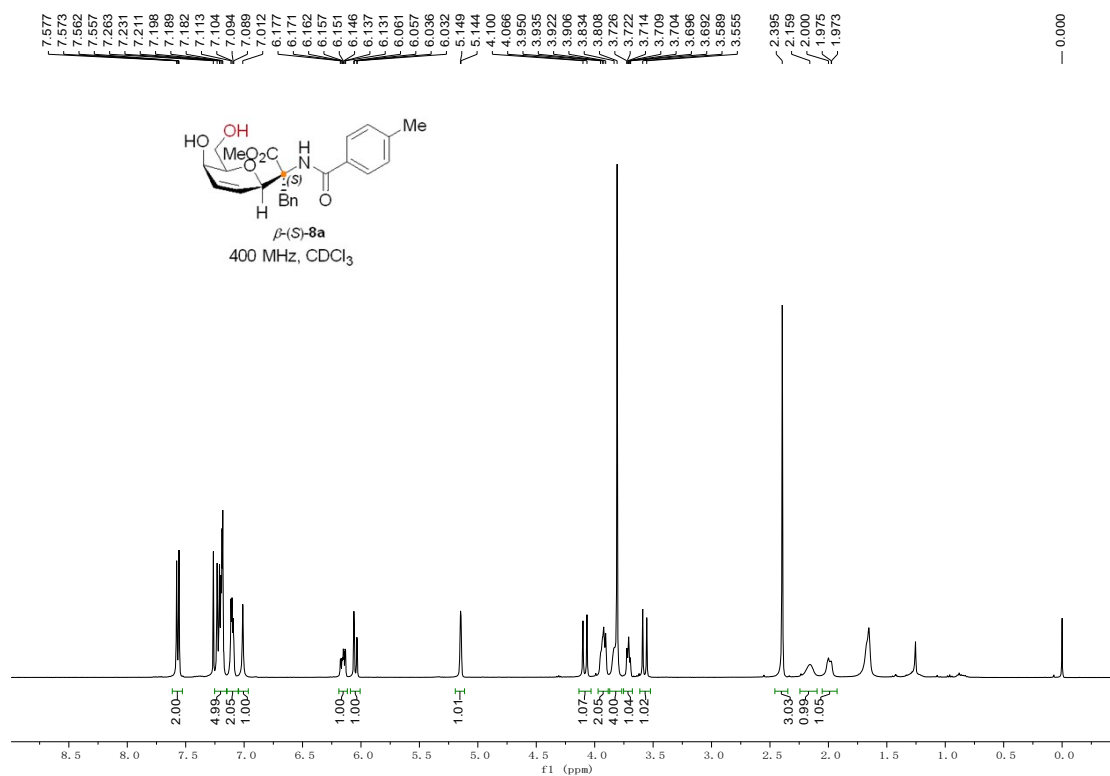


Figure S94. ^1H NMR spectrum of β -(S)-8a

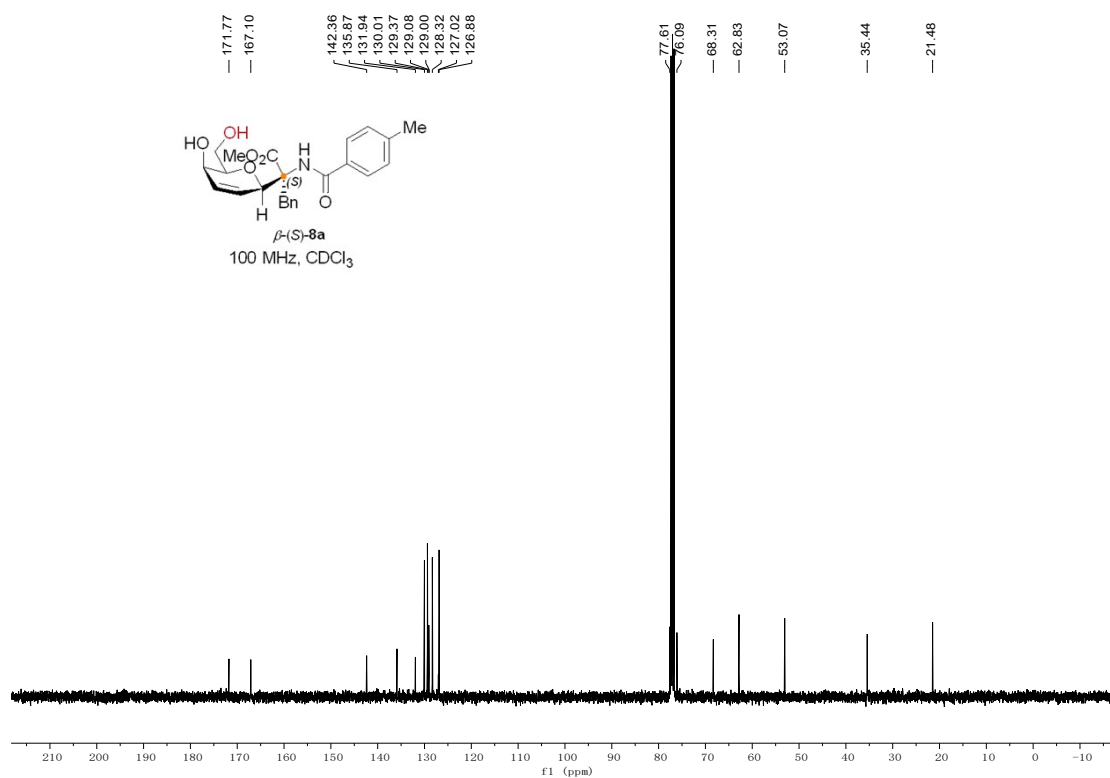


Figure S95. ^{13}C NMR spectrum of β -(S)-8a

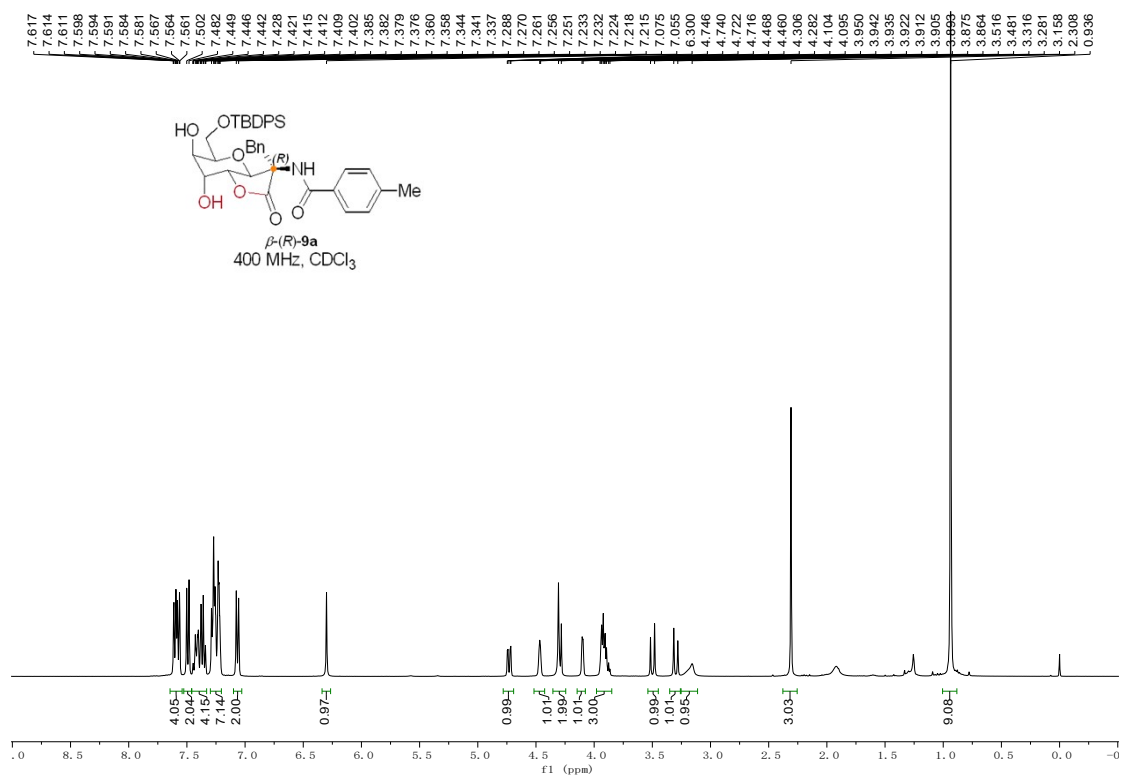


Figure S96. ^1H NMR spectrum of β -(R)-9a

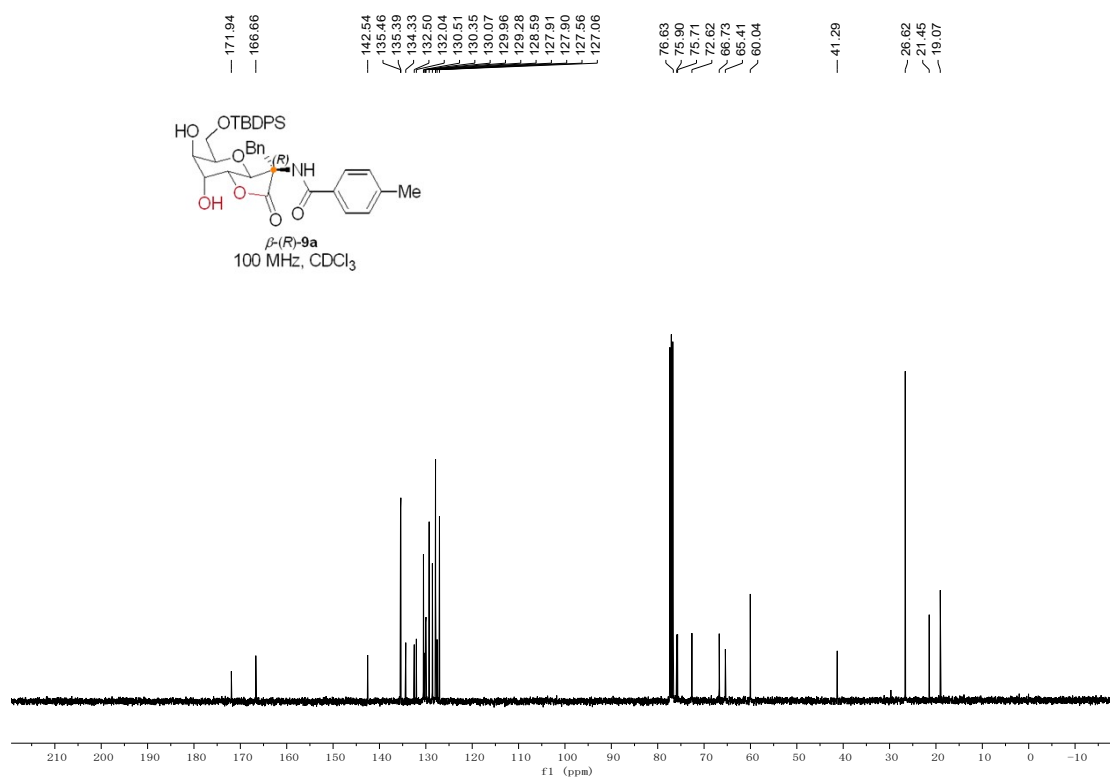


Figure S97. ^{13}C NMR spectrum of β -(R)-9a

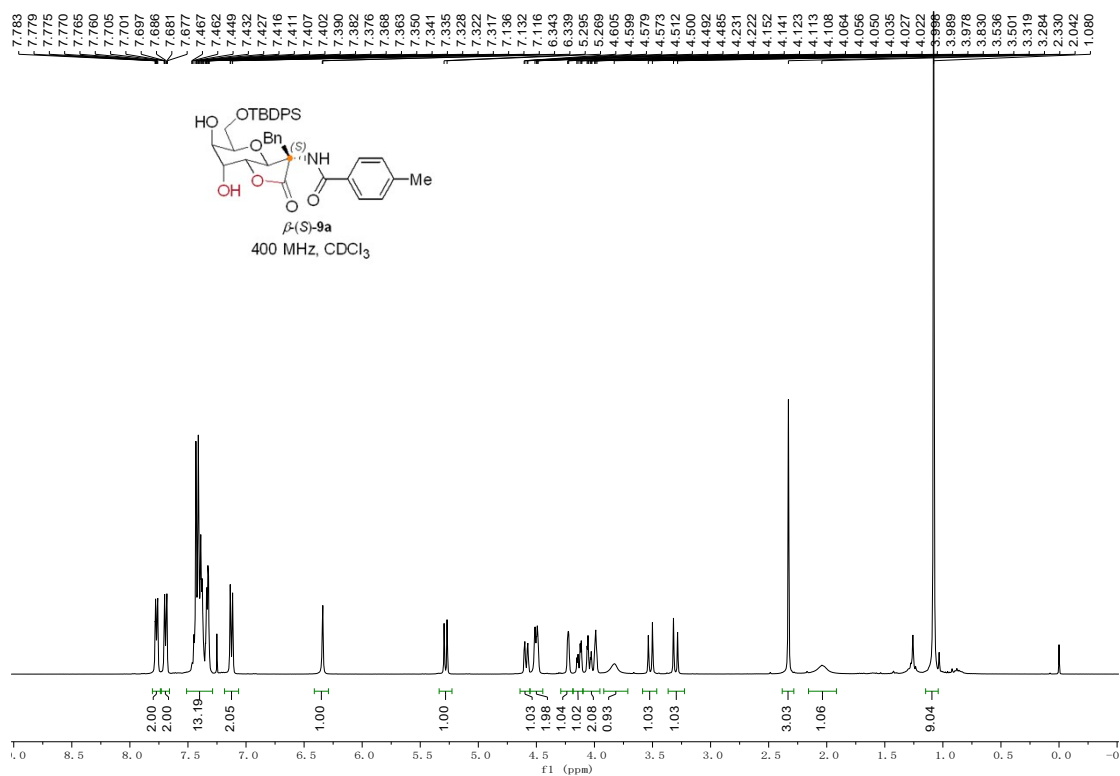


Figure S98. ¹H NMR spectrum of β -(S)-9a

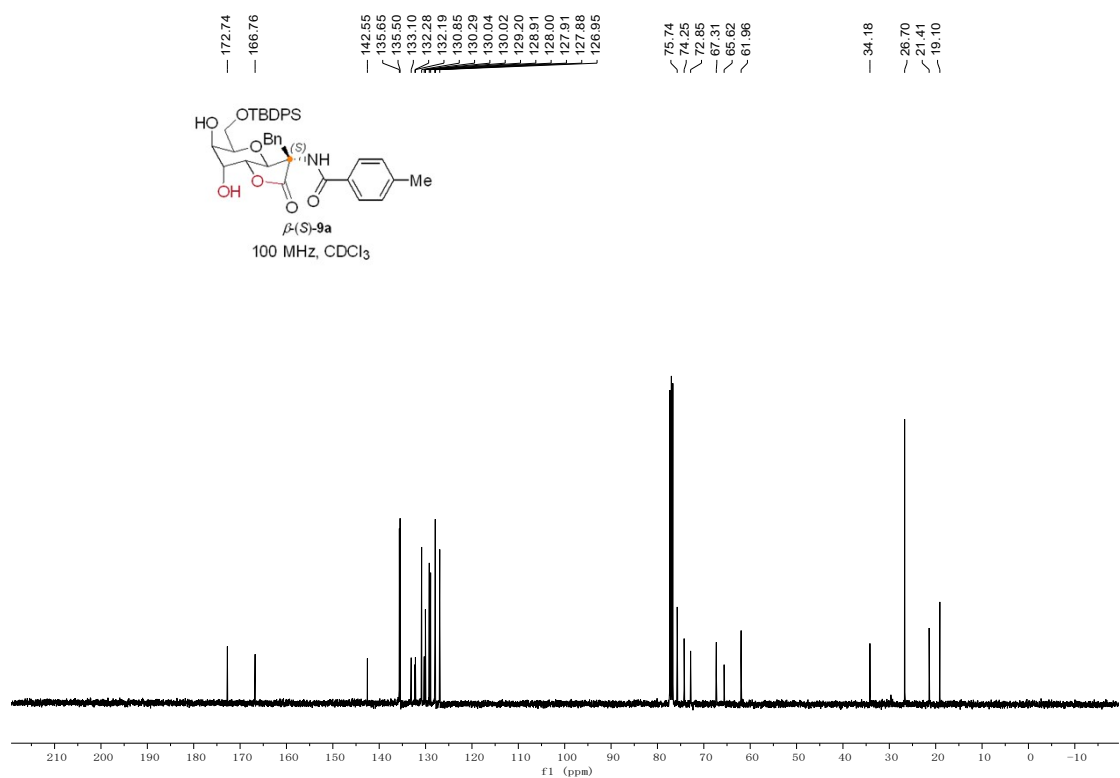


Figure S99. ¹³C NMR spectrum of β -(S)-9a

8. β -selectivity at anomeric center determined by 2D-NMR

8.1 β -selectivity of β -(*R*)-3a determined by 2D-NMR

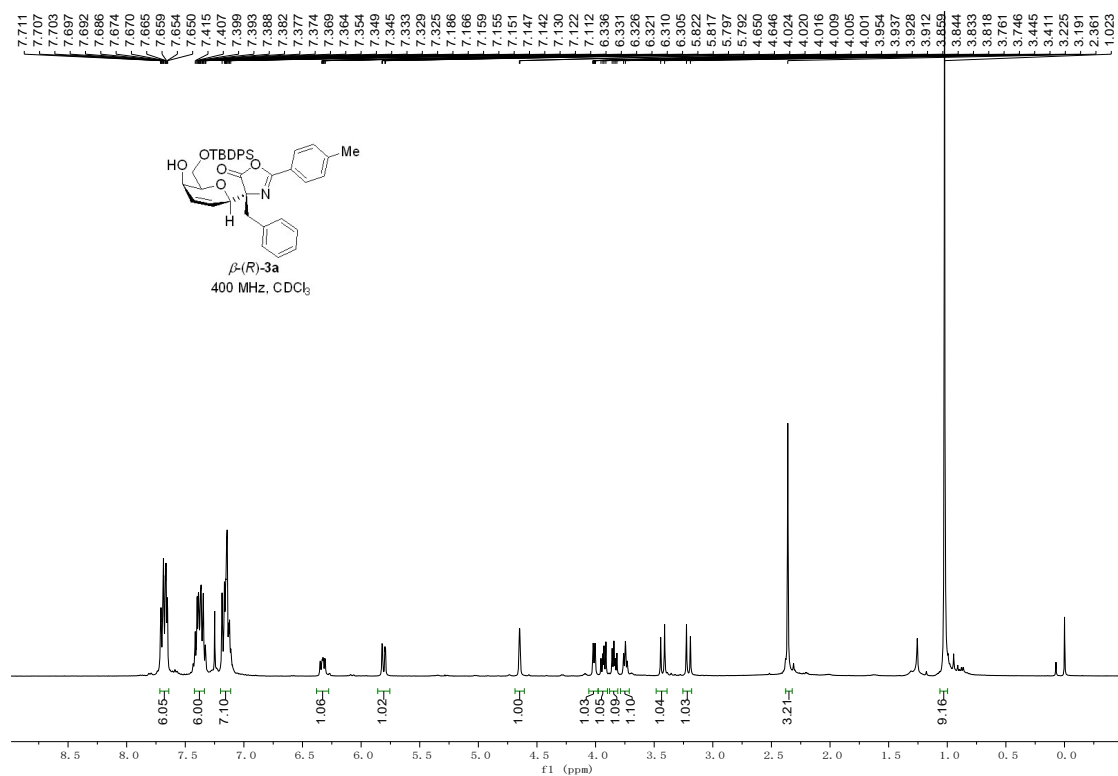


Figure S100. ¹H NMR spectrum of β -(*R*)-3a

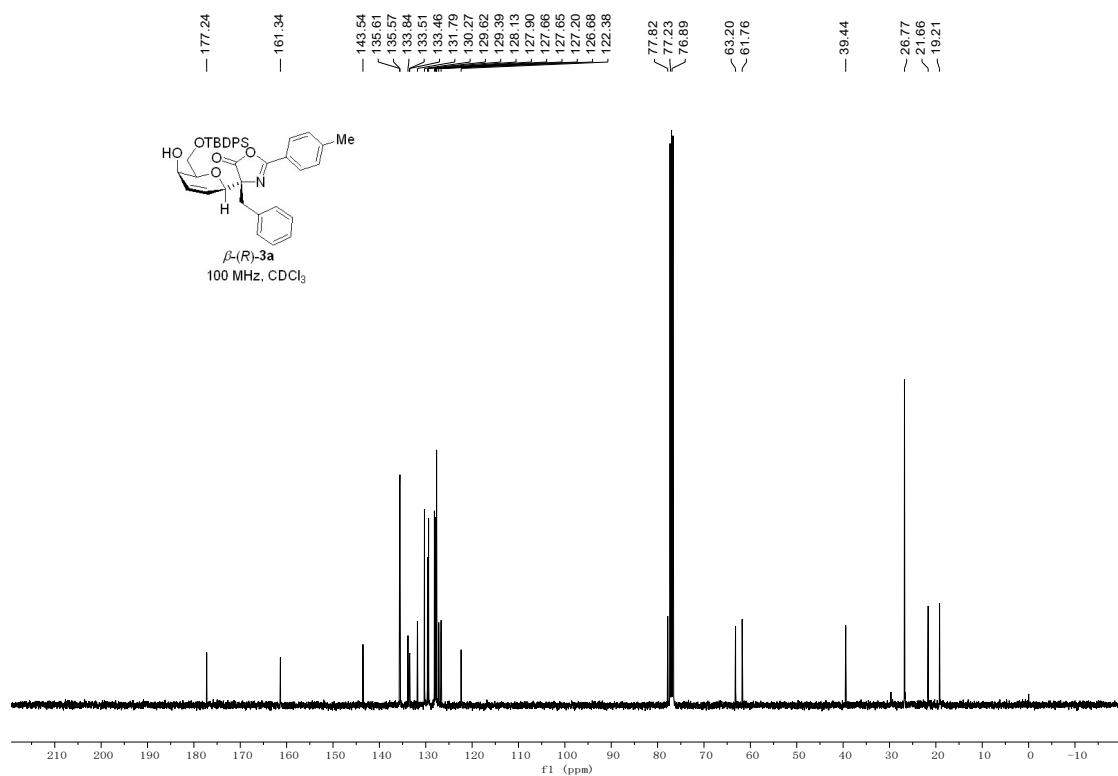


Figure S101. ¹³C NMR spectrum of β -(*R*)-3a

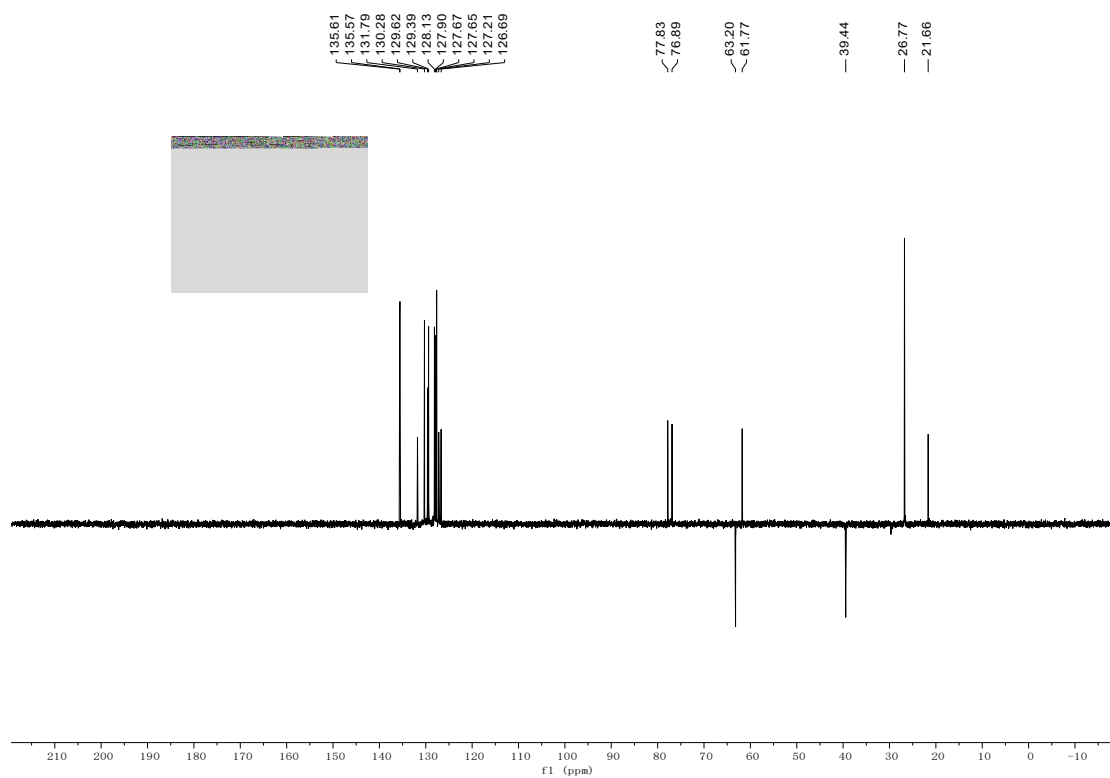


Figure S102. DEPT135 NMR spectrum of β -(*R*)-**3a**

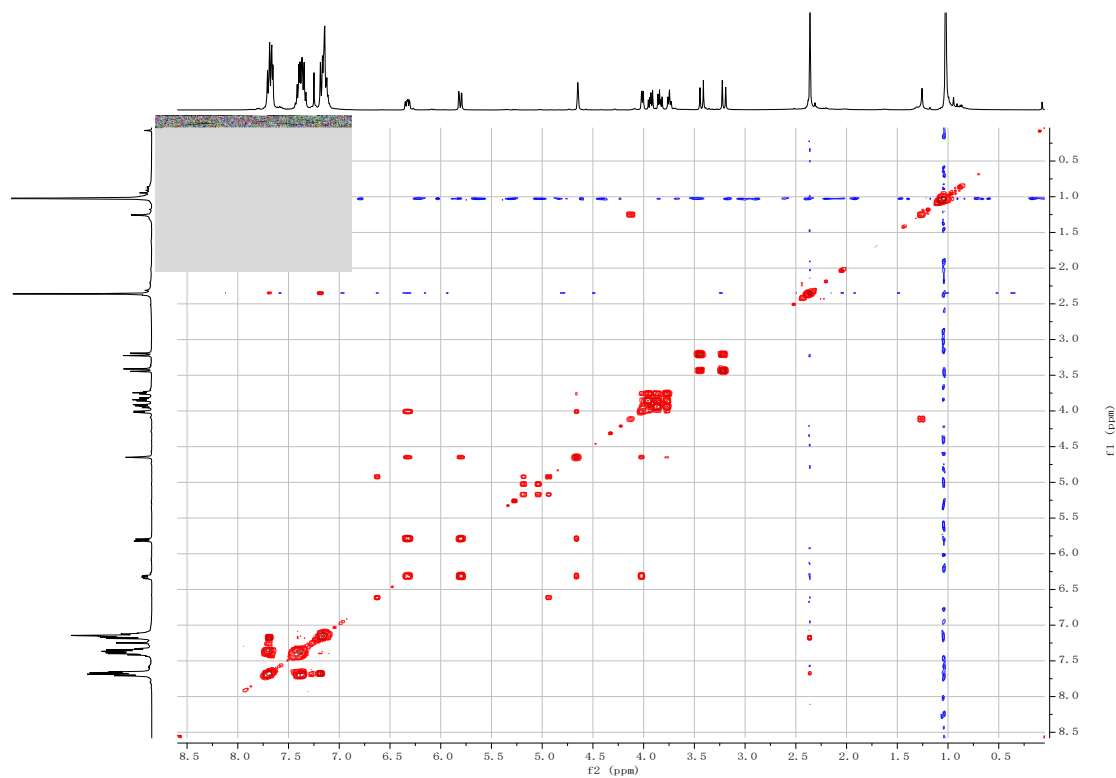


Figure S103. ^1H - ^1H COSY spectrum of β -(*R*)-**3a**

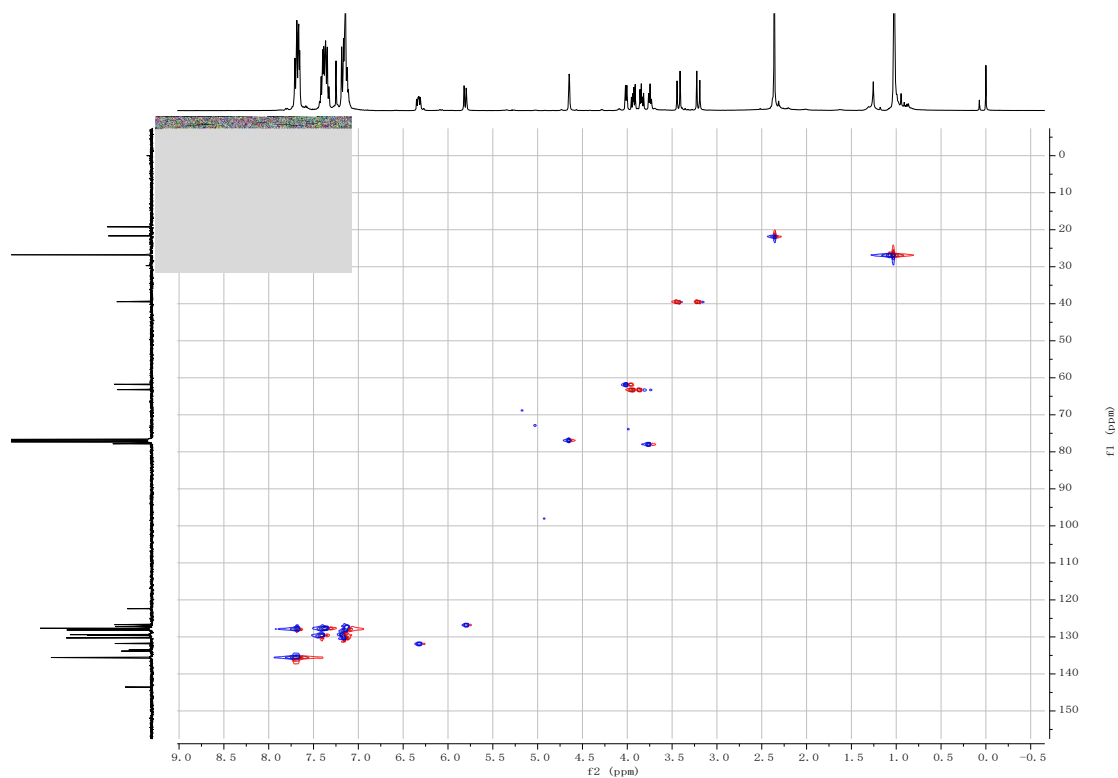


Figure S104. HSQC spectrum of β -(*R*)-**3a**

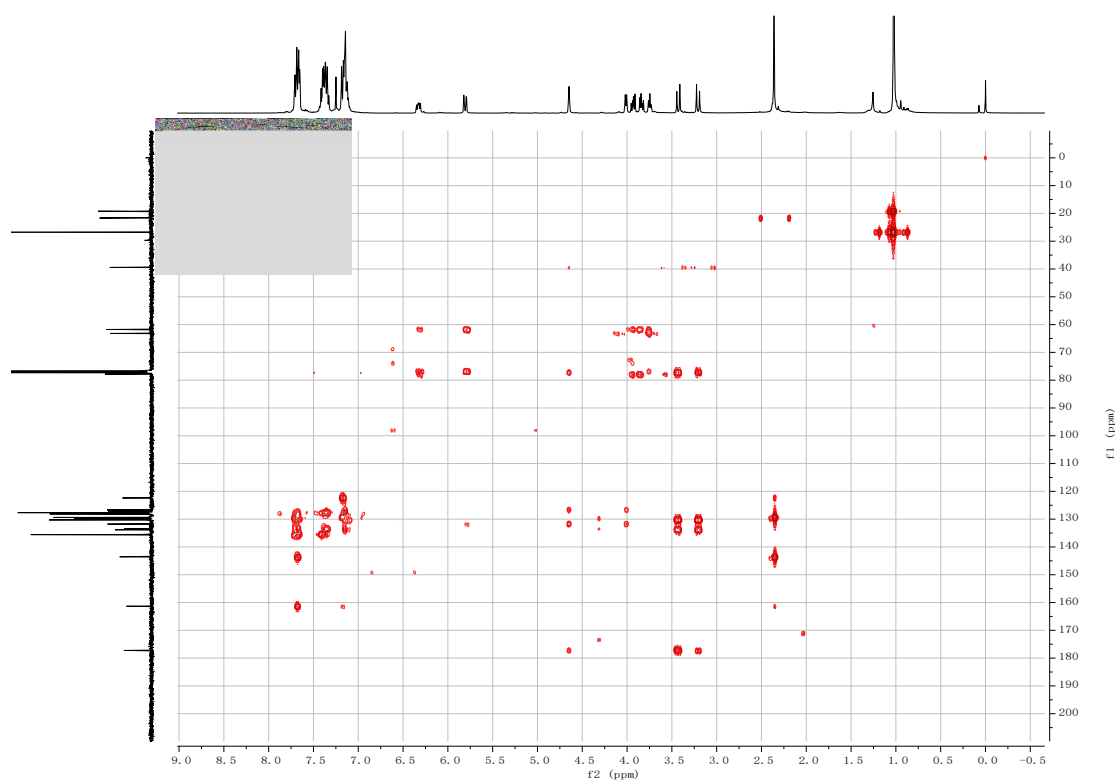


Figure S105. HMBC spectrum of β -(*R*)-**3a**

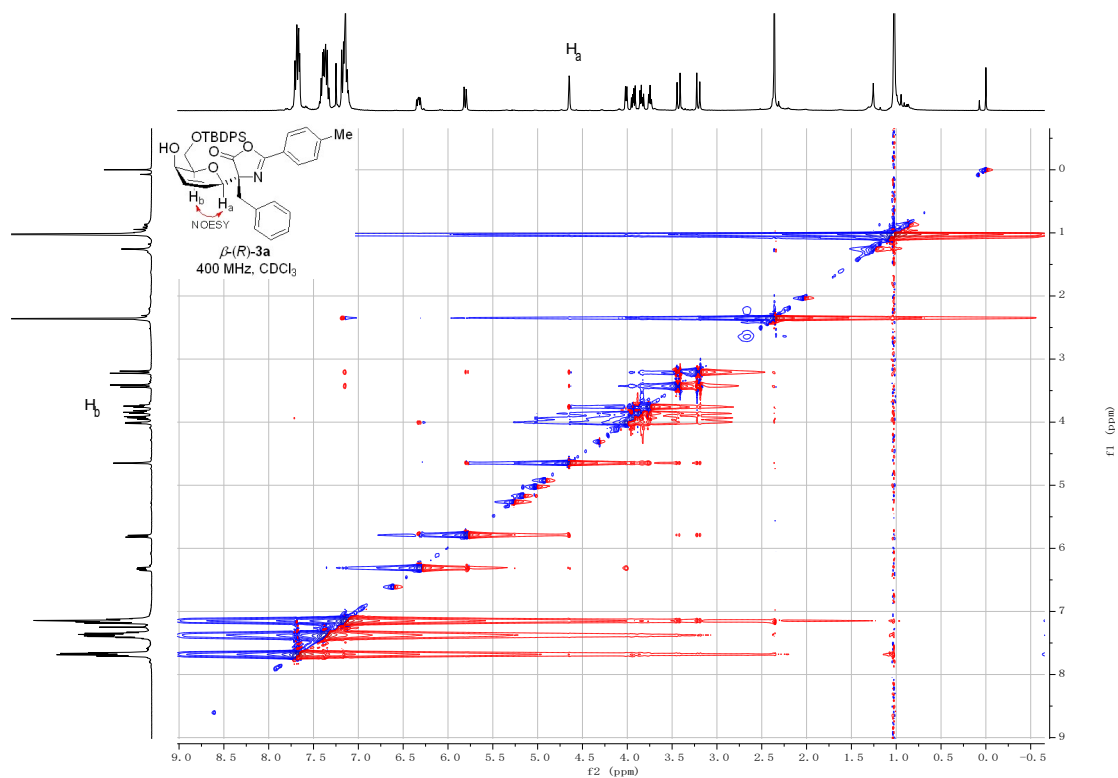


Figure S106. NOESY spectrum of β -(*R*)-3a

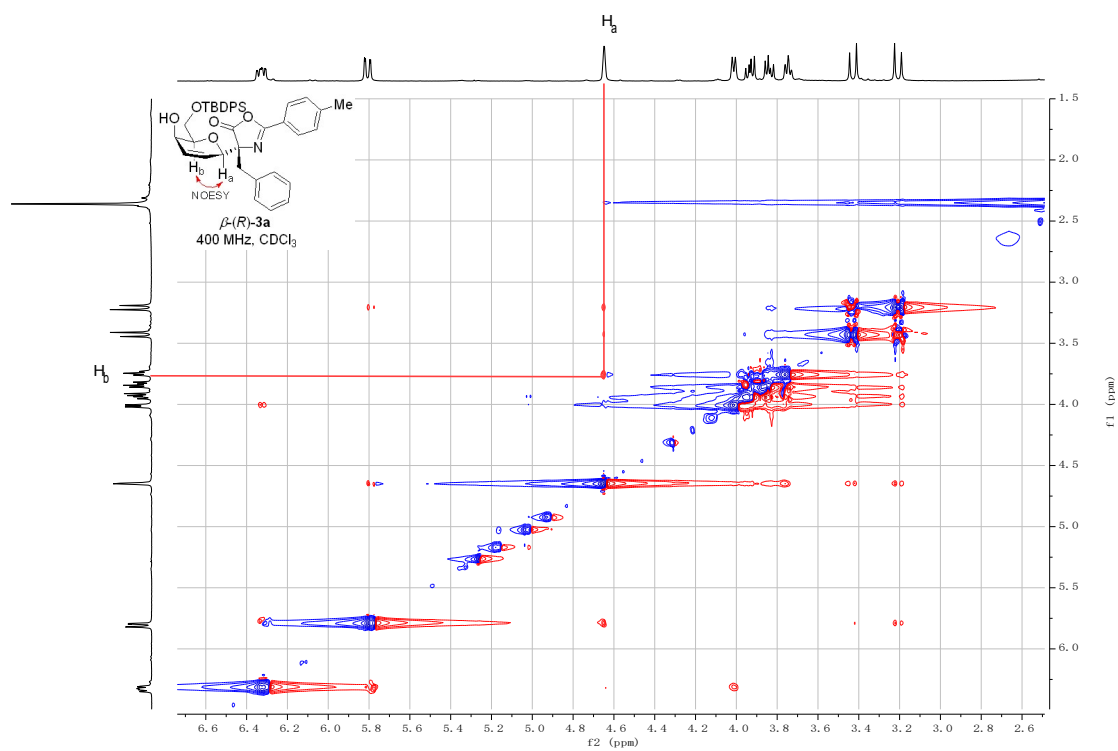


Figure S107. The enlarged NOESY spectrum of β -(*R*)-3a

8.2 β -selectivity of β -(S)-3a determined by 2D-NMR

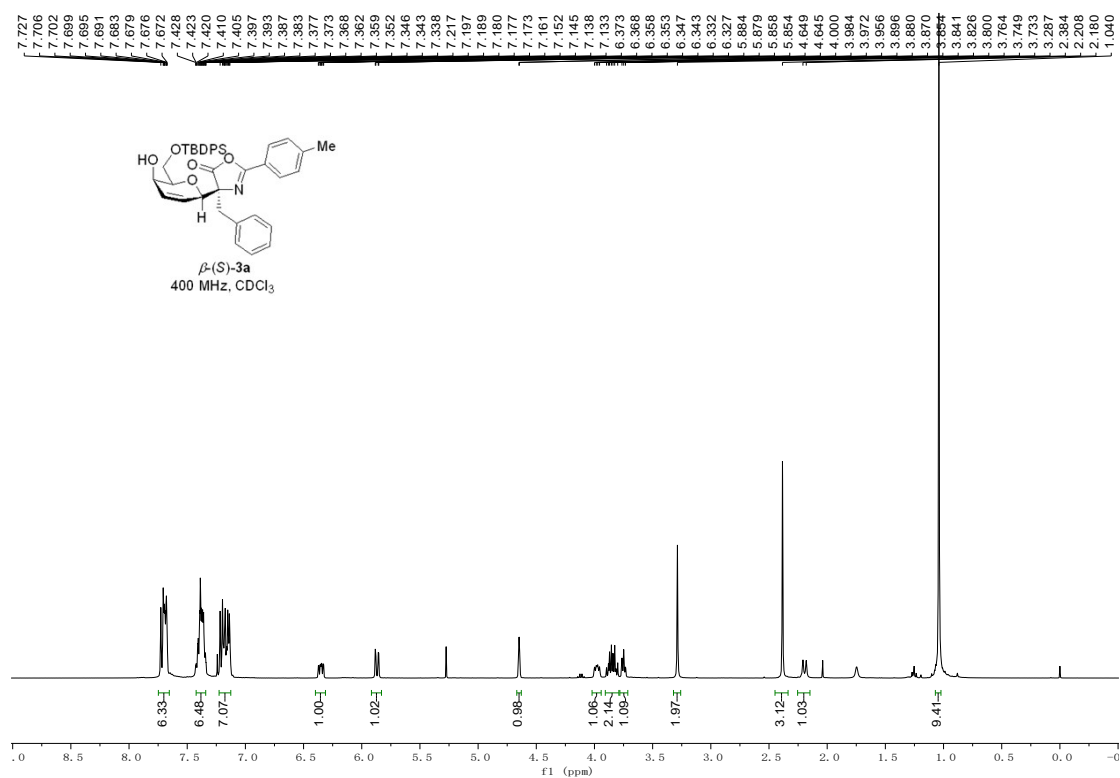


Figure S108. ¹H NMR spectrum of β -(S)-3a

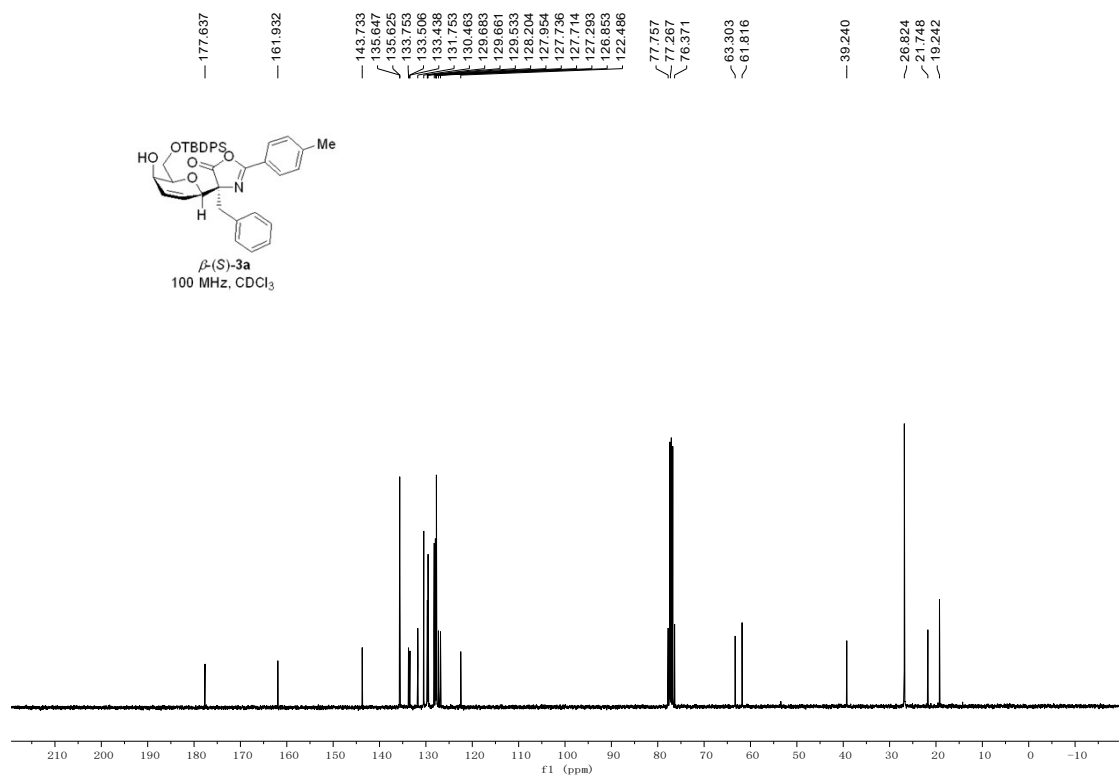


Figure S109. ¹³C NMR spectrum of β -(S)-3a

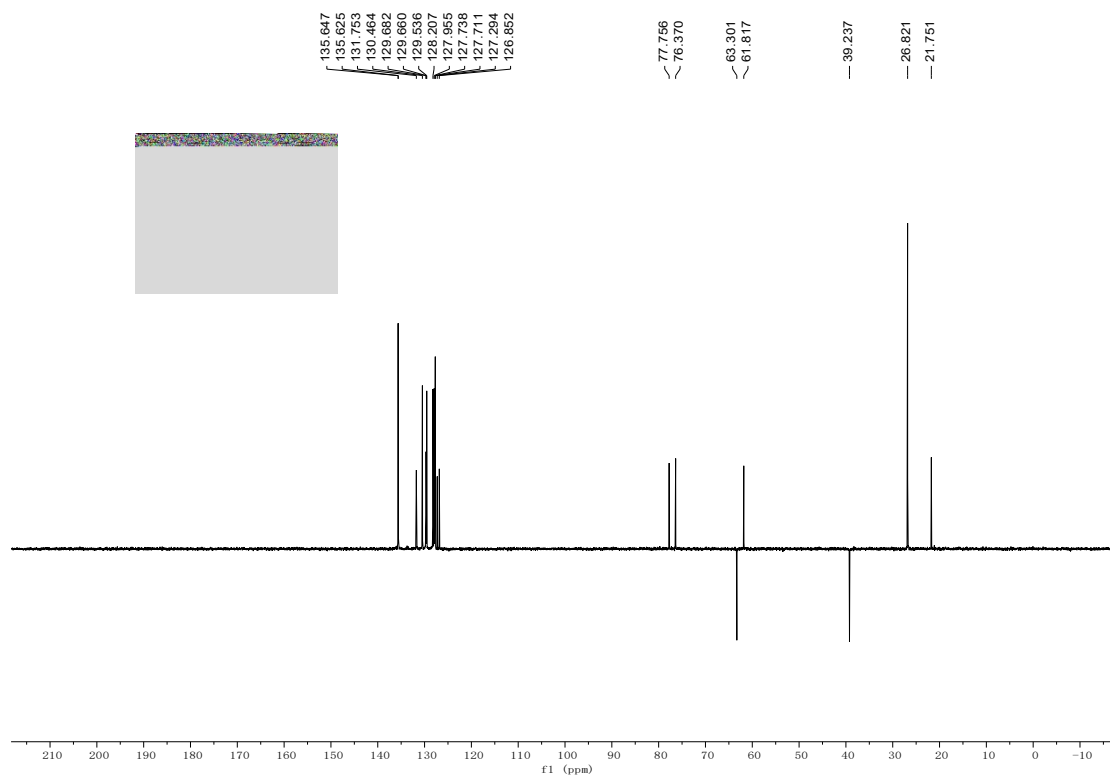


Figure S110. DEPT135 spectrum of β -(*S*)-**3a**

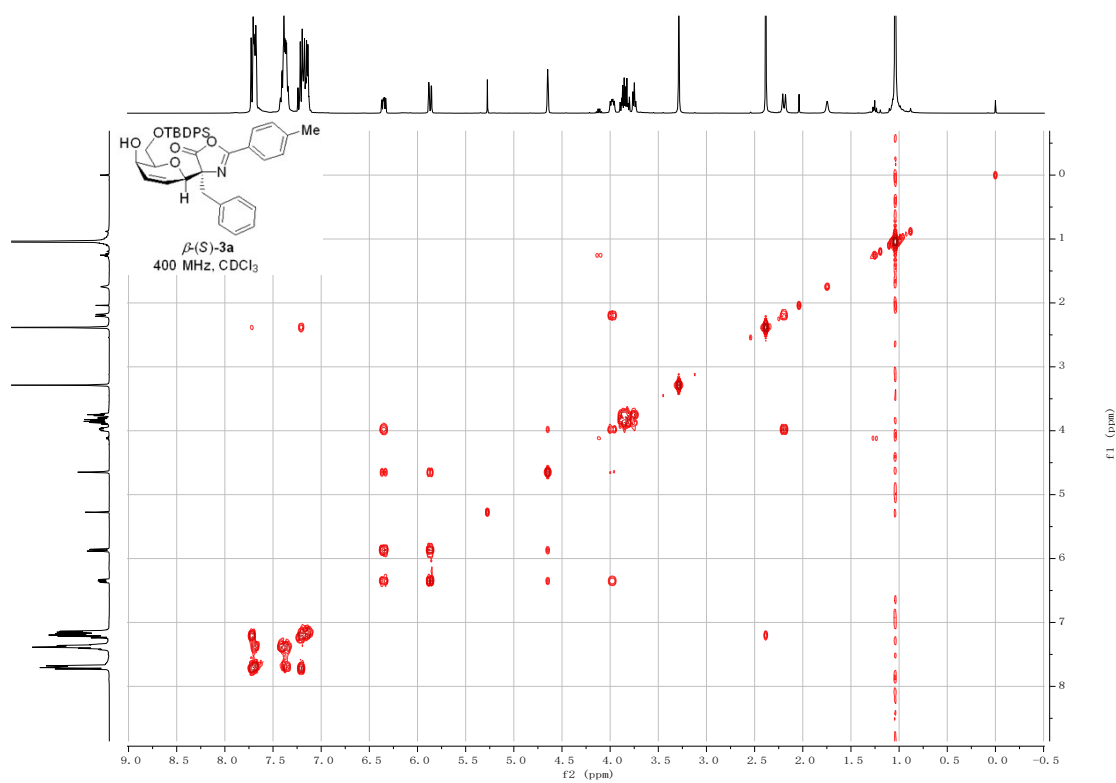


Figure S111. ¹H-¹H COSY spectrum of β -(*S*)-**3a**

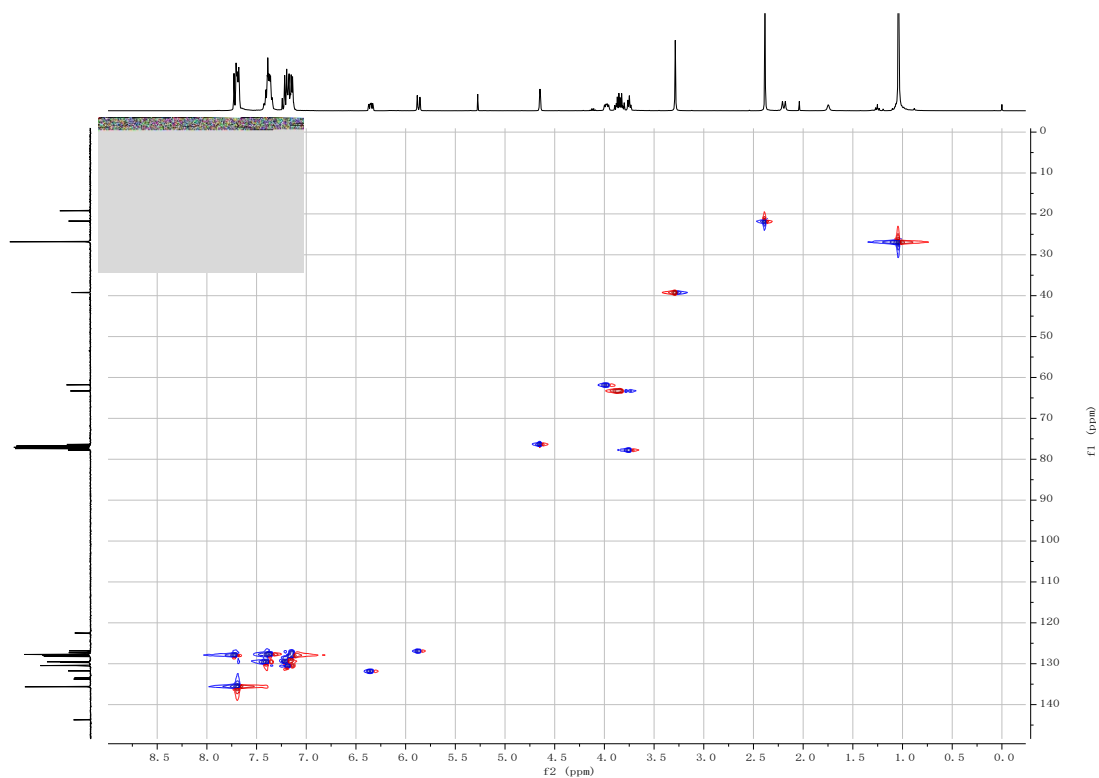


Figure S112. HSQC spectrum of β -(*S*)-**3a**

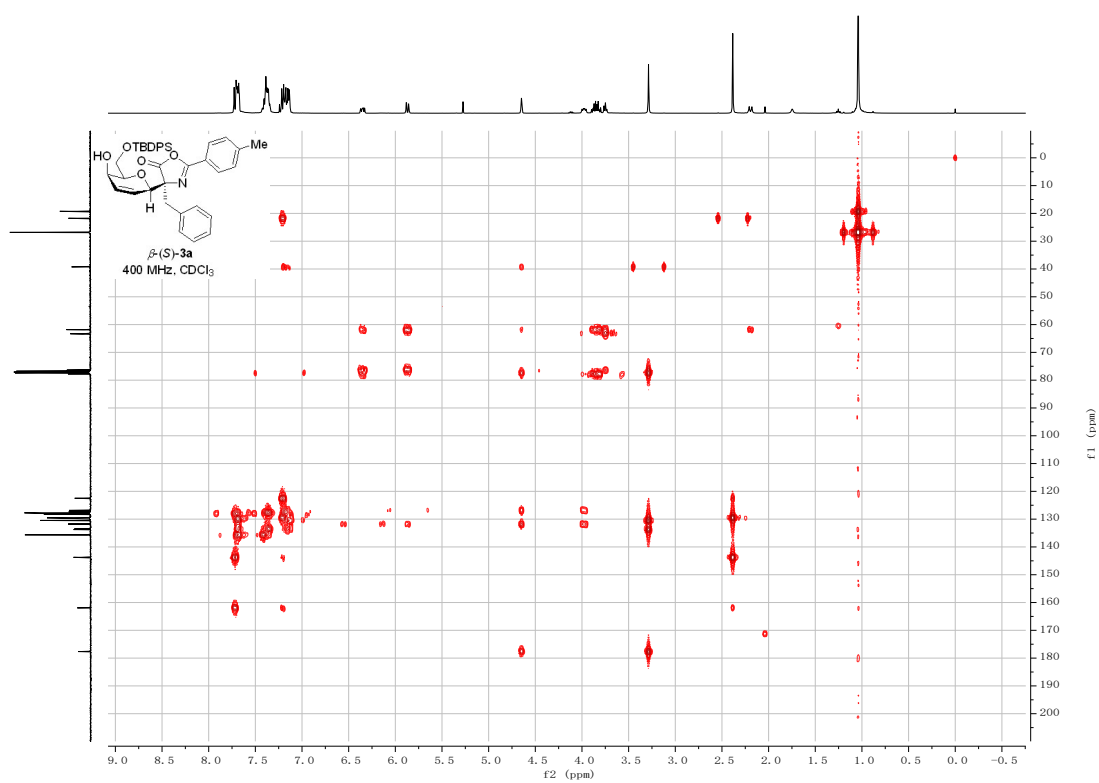


Figure S113. HMBC spectrum of β -(*S*)-**3a**

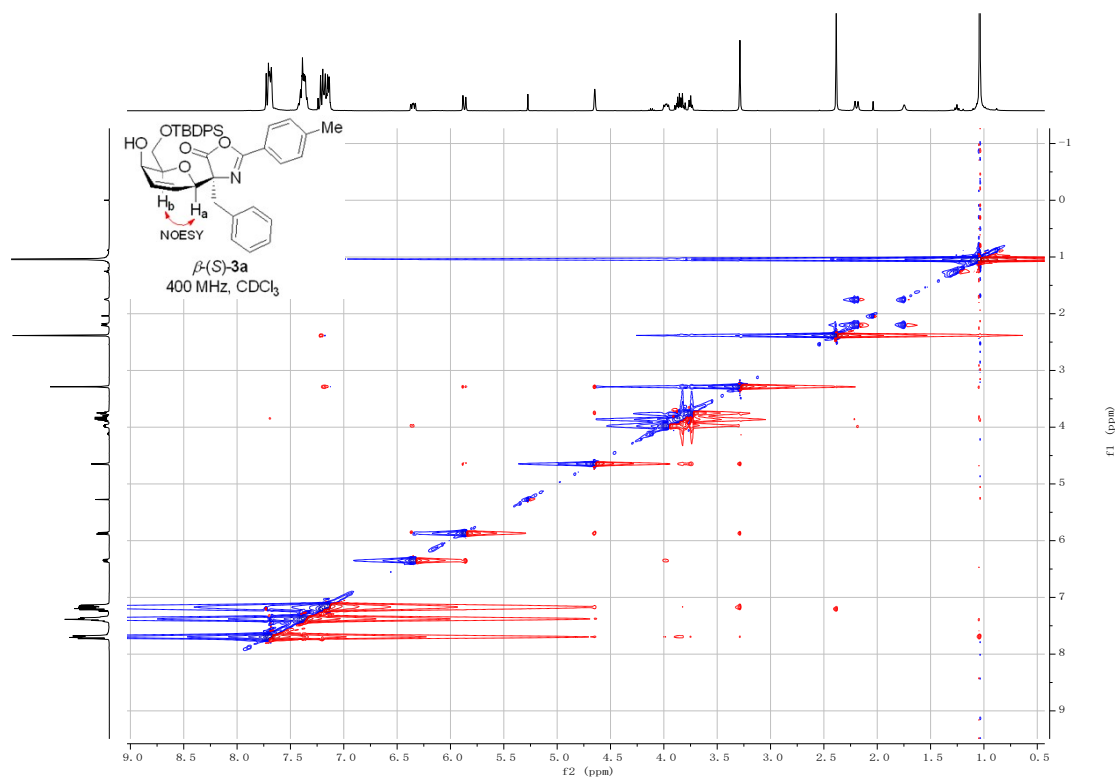


Figure S114. NOESY spectrum of β -(S)-3a

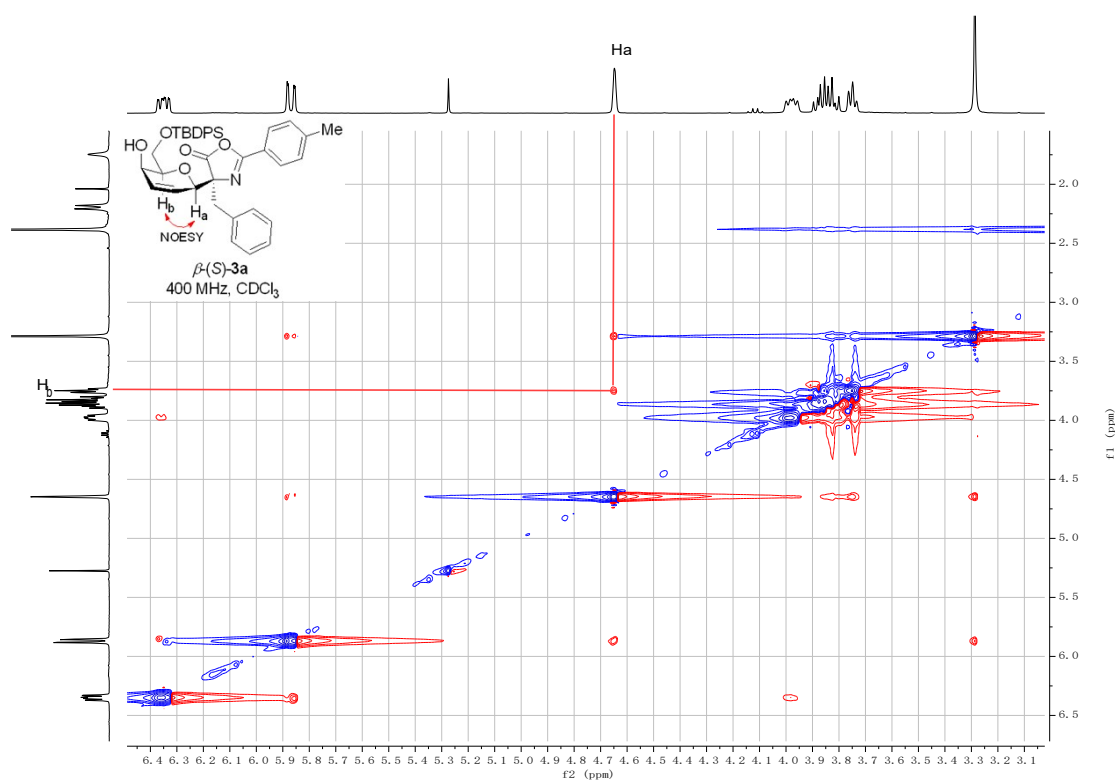


Figure S115. The enlarged NOESY spectrum of β -(S)-3a

9. Supplementary references

(1) (a) Dai, Y.; Tian, B.; Chen, H.; Zhang, Q. *ACS Catalysis* **2019**, *9*, 2909-2915; (b) Dai, Y.; Zheng, J.; Zhang, Q. *Organic Letters* **2018**, *20*, 3923-3927; (c) Meng, S.; Zhong, W.; Yao, W.; Li, Z. *Organic Letters* **2020**, *22*, 2981-2986.

(2) (a) Badiola, E.; Fiser, B.; Gómez-Bengoa, E.; Mielgo, A.; Olaizola, I.; Urruzuno, I.; García, J. M.; Odriozola, J. M.; Razkin, J.; Oiarbide, M.; Palomo, C. *Journal of the American Chemical Society* **2014**, *136*, 17869-17881; (b) Gerwick, W. H.; Fenical, W. *The Journal of Organic Chemistry* **1983**, *48*, 3325-3329.

(3) de Mello, A. C.; Momo, P. B.; Burtoloso, A. C. B.; Amarante, G. W. *The Journal of Organic Chemistry* **2018**, *83*, 11399-11406.