Electronic Supplementary Information (ESI)

A concise asymmetric total synthesis for structure elucidation of 5,6-secoiridoid from Incarvillea argute †

Jian-Jun Fu,‡[a] Zhi-Qian Liu,‡[b]Hui-Zi Jin,[c]Shou-De Zhang,[a] Qing-Yan Sun,*[d] and Wei-Dong Zhang*[abd]

[a] *Shanghai Key Laboratory of New Drug Design, School of Pharmacy, East China University of Science and Technology, Shanghai 200237, PRChina*

[b] *School of Pharmacy, Second Military Medical University, Shanghai200433, PRChina. E-mail:wdzhangy@hotmail.com; Tel/Fax: +86-21-81871244*

[c]*School of Pharmacy, Shanghai Jiao Tong University, Shanghai 200240, PR China*

[d]*Shanghai Institute of Pharmaceutical Industry, Shanghai 200040, PR China. E-mail:sqy_2000@163.com; Tel/Fax: +86-21-20572000-2028*

‡ These authors contributed equally to this work.

Contents

IX. Comparison of the Spectra of Natural and Synthetic Secoarguterin

I. General Experimental Procedures

NMR spectra were determined on500 MHz NMR instruments, for ^{1}H-NMR at 500 MHz and ^{13}C-NMR at125MHz. The following abbreviations are used in reporting NMR data: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dq, doublet of quartets; dt, doublet of triplets; qt, quartet of triplets; m, multiplets.ESI-MS spectra were recorded on Varian MAT-212 mass spectrometer.The time-of flight (TOF)-ESI spectra were carried out on a Q-Tofmicro YA019 mass spectrometer. IR spectra were recorded with a BrukerFTIR Vector 22 spectrometer. Optical rotations were obtained with a Perkin-Elmer 341 polarimeter. UV spectra were recorded with a Shimadzu UV-2550 spectrophotometer. Thin layer chromatography (TLC) was performed on $HSGF_{254}$ silica gel plates(10-40m m, Yantai, China), and were visualized with UV light and aqueous KMnO4 solution. Column chromatography was performed on silicagel (100-200, 200-300 mesh, Yantai, China), and silica gel H (10-40m m, Qingdao, China). HPLC was performed using a system composed ofa SHIMADZU LC-6AD pump, a SHIMADZU UV–VIS detector SPD-20A,a SHIMADZU 7725 injection port, and a preparative column (PRC-ODS,20 mm i.d.250 mm, 15 mm, Japan). A preparative column (ShimadzuPRC-ODS EV0233) was used for preparative HPLC (Shimadzu LC-6AD).Unless otherwise noted, all reactions were performed under an argon atmosphere using flame-dried glassware. Tetrahydrofuran (THF) and toluene weredistilled over sodium-benzophenone ketyl. Methylene chloride (CH_2Cl_2),and triethylamine (Et_3N) were distilled from calcium hydride (CaH_2) and stored under an argon atmosphere.Methanol (MeOH) was distilled from magnesium and stored under an argon atmosphere. Anhydrous N,N-dimethyl-Formamide (DMF), anhydrous Dimethyl Sulfoxide (DMSO), and other reagents werepurchased at the highest commercial quality and used without further purification, unless otherwisestated.

II. Plant Material

The roots of *I. arguta* were collected from Anning,Yunnan Province, P. R. China, in May 2006 and identified by Prof. Bao-kangHuang, School of Pharmacy, Second Military Medical University. Thevoucher specimens (LTM20060514) were deposited with the Herbarium ofthe School of Pharmacy, Shanghai Jiao Tong University, Shanghai, P. R.China.

III. Extraction and Isolation

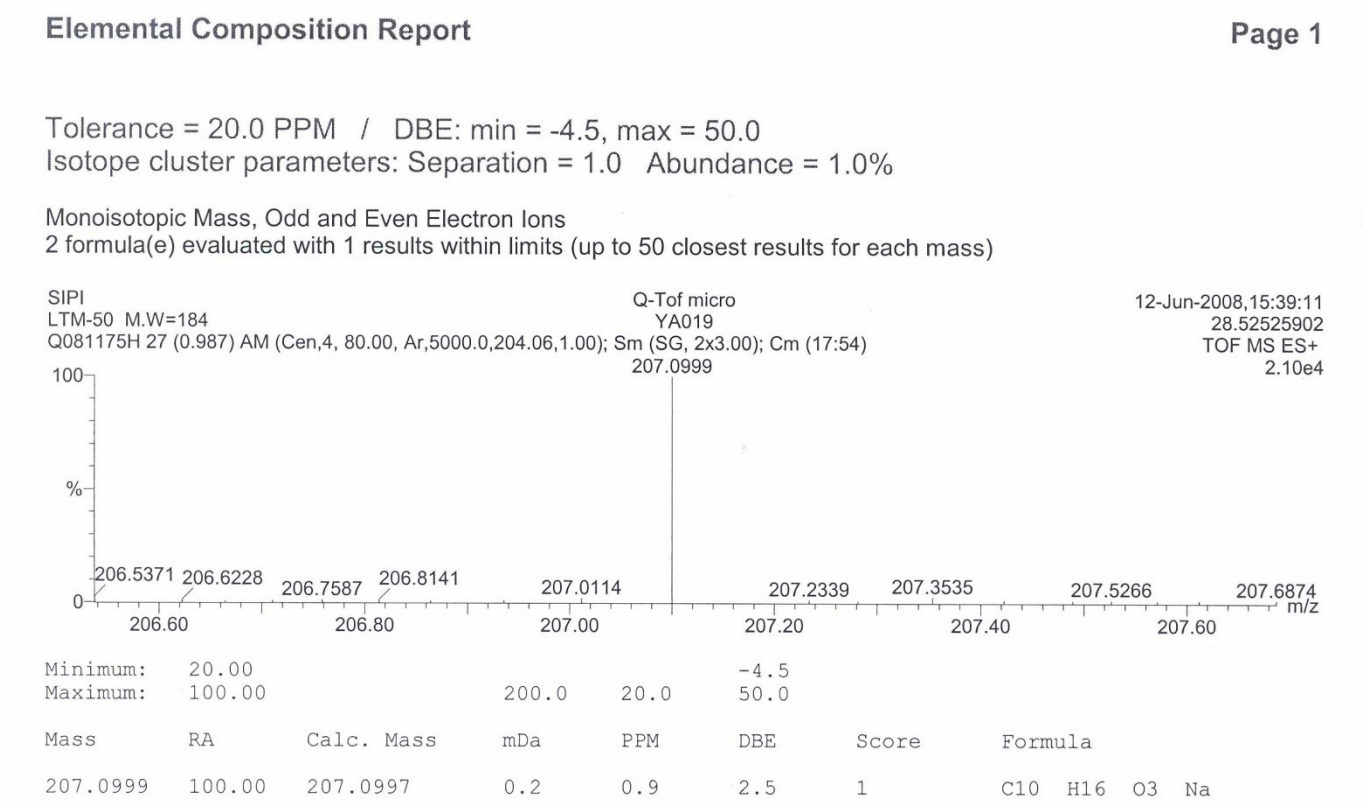
The dried roots (24.9 kg) of *I. arguta*were chopped and extracted with 80% EtOH at room temperature. The extract was dissolved in water to form a suspension and acidified to pH = 2 with 20% H_2SO_4 and filtered. The filtrate was basified to pH = 10 with saturated $NaHCO_3$aqueous solution and then extracted successively with $CHCl_3$. The $CHCl_3$ fraction was chromatographed over a silica gel column with a gradient CH_2Cl_2/MeOH (1:0→0:1) to give fourteen fractions 1-14. Fraction 7 was separated on a silica gel column (CH_2Cl_2/MeOH, 1:0→10:1) and further purified on preparative HPLC (MeOH/H_2O, 50:50) to yield **1** (5.5 mg).

IV. Cytotoxicity Assay

A cytotoxicity assay was carried out according to Denizot and Lang. Each cell(conc. 1×10^4) was seeded in each well containing 100 μl of DMEM (Dulbecco's modified Eagle'smedium). Subsequently, various concentrations of samples were added. The cells were incubated for 48 h at 37ºC inan atmosphere containing 5% of CO_2. Then 10 μl of FBS-free medium (FBS = fetal bovine serum)containing 5 mg/ml of MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium) solution wasadded to the wells. After 4 h of incubation at 37ºC, the medium was discarded, and the formazan blueformed in the cells was dissolved by adding 100 μl of DMSO. The optical density was measured at 570 nmwith a microplate reader.

V. Spectral of secoarguterin

Figure S1. The positive HR-ESI-MS spectrum of secoarguterin



Elemental Composition Report

Page 1

Tolerance = 20.0 PPM / DBE: min = -4.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

SIPI
LTM-50 M.W=184
Q081175H 27 (0.987) AM (Cen,4, 80.00, Ar,5000.0,204.06,1.00); Sm (SG, 2x3.00); Cm (17:54)

Q-Tof micro
YA019

12-Jun-2008,15:39:11
28.52525902
TOF MS ES+
2.10e4

Minimum:	20.00				-4.5		
Maximum:	100.00		200.0	20.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
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Figure S2. The ^{1}H NMR spectrum of secoarguterin (500 MHz, $CDCl_3$)

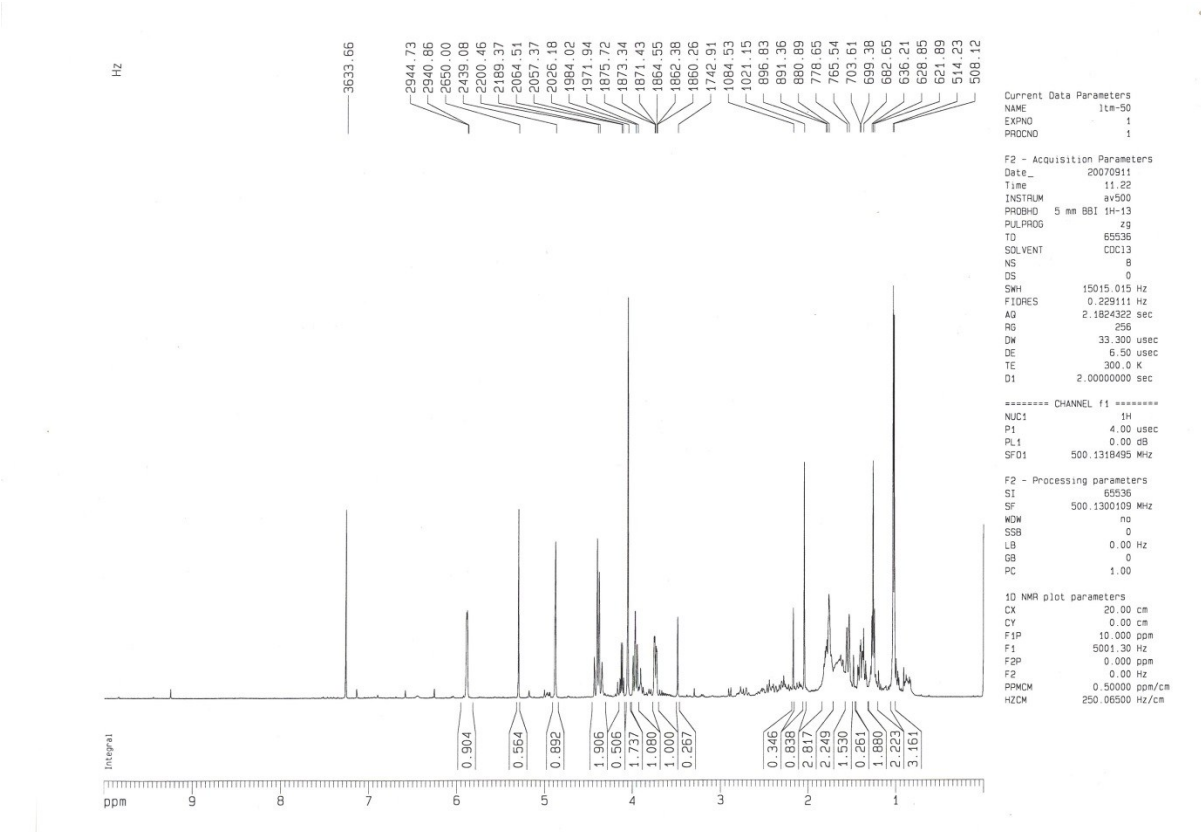


Figure S3. The ^{13}C NMR spectrum of secoarguterin (125MHz, $CDCl_3$)

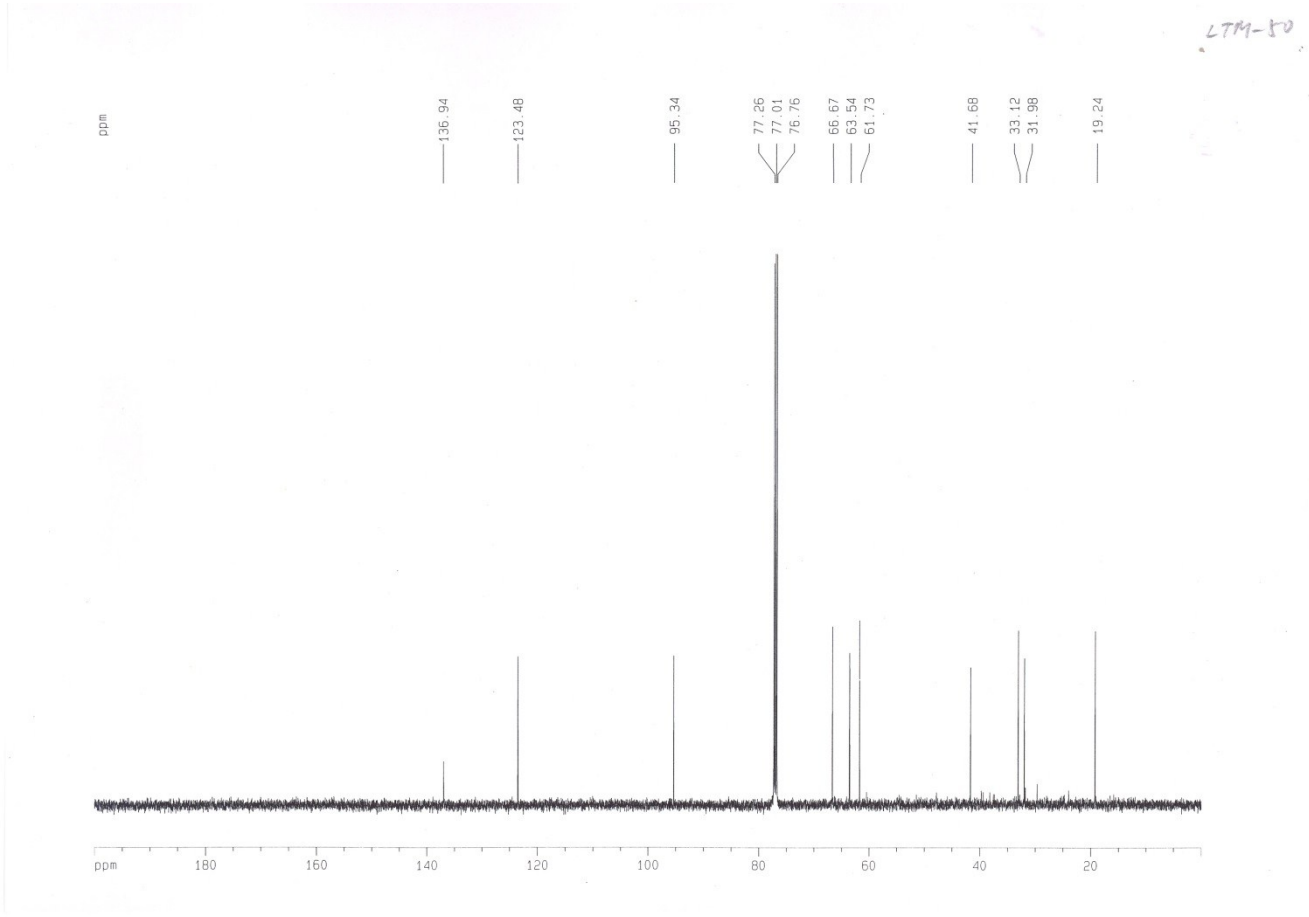


Figure S4. DEPT NMR spectrum of secoarguterin (125MHz, $CDCl_3$)

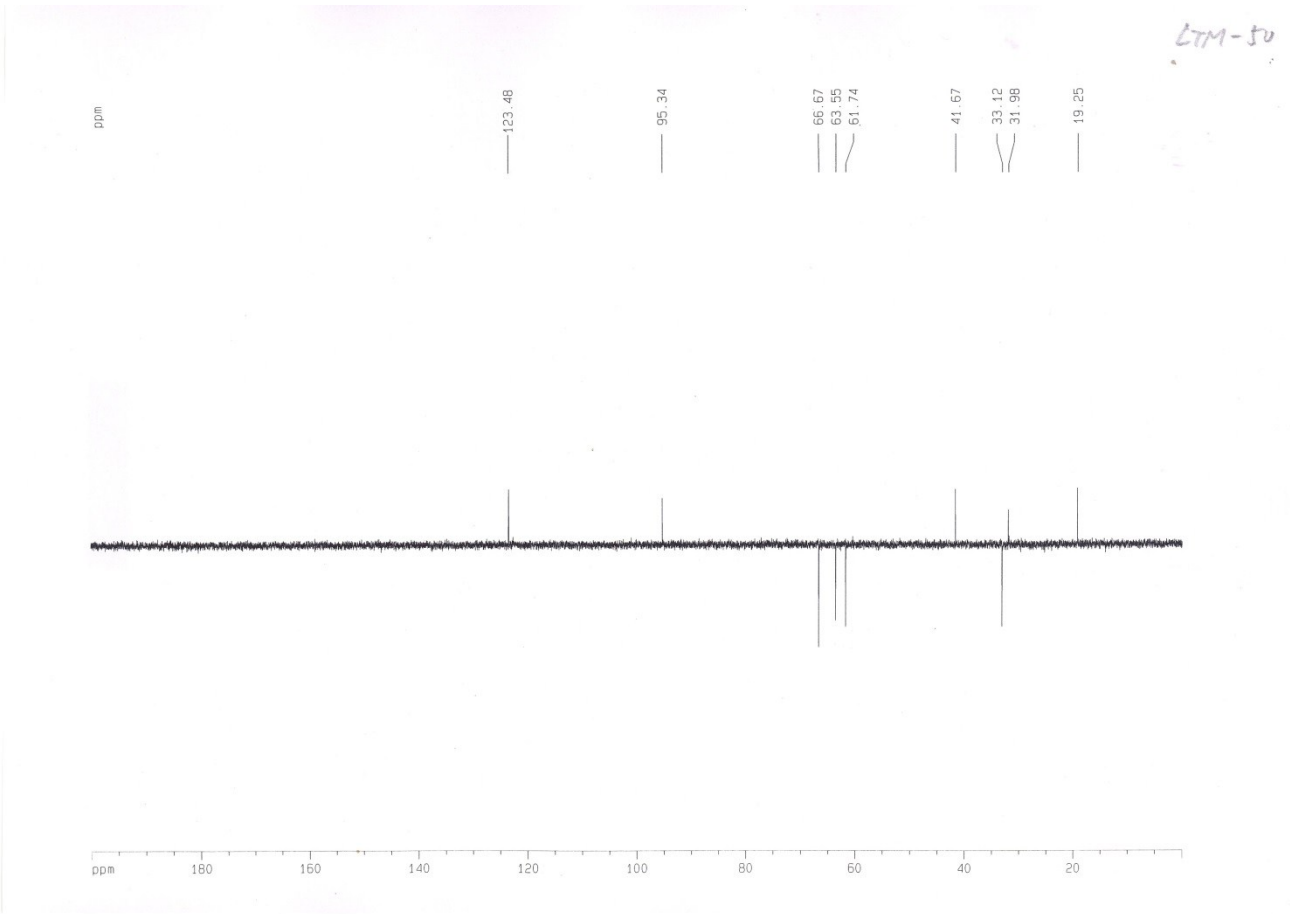


Figure S5. The ^{1}H-^{1}H COSY NMR spectrum of secoarguterin (500 MHz, $CDCl_3$)

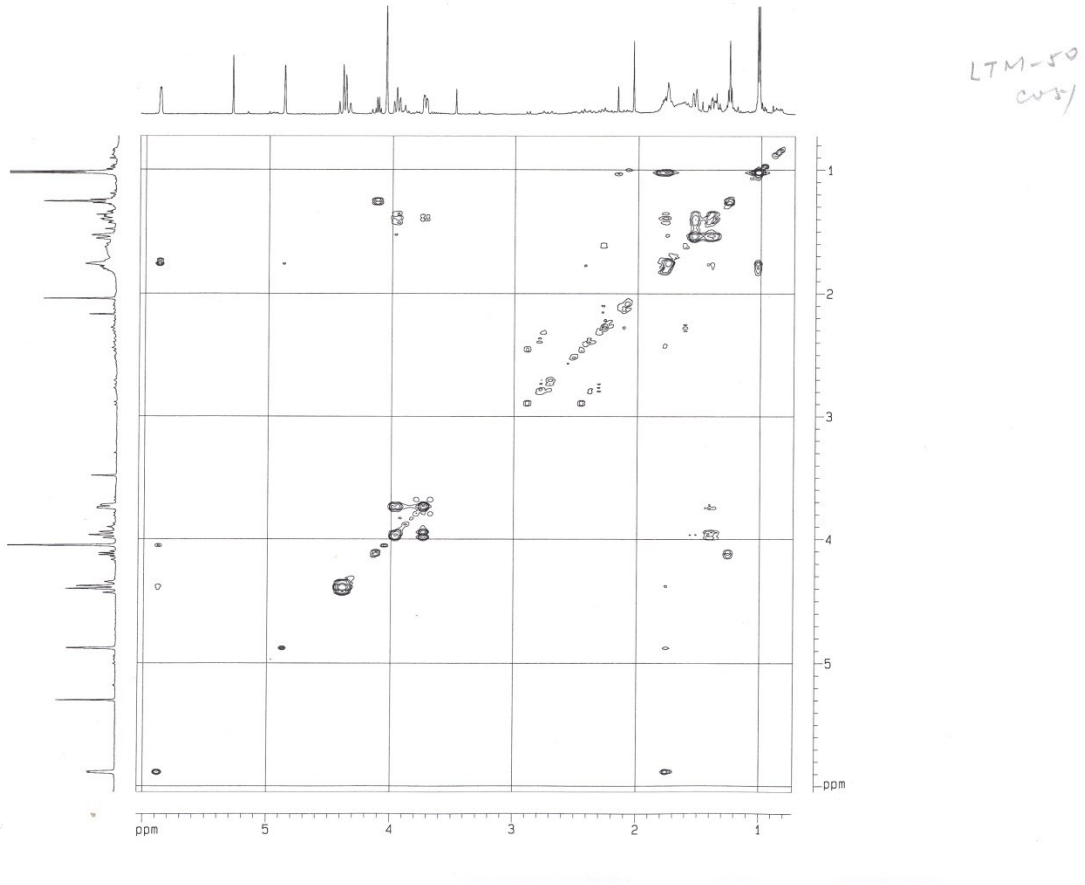


Figure S6. The HSQC spectrum of secoarguterin (500 MHz, $CDCl_3$)

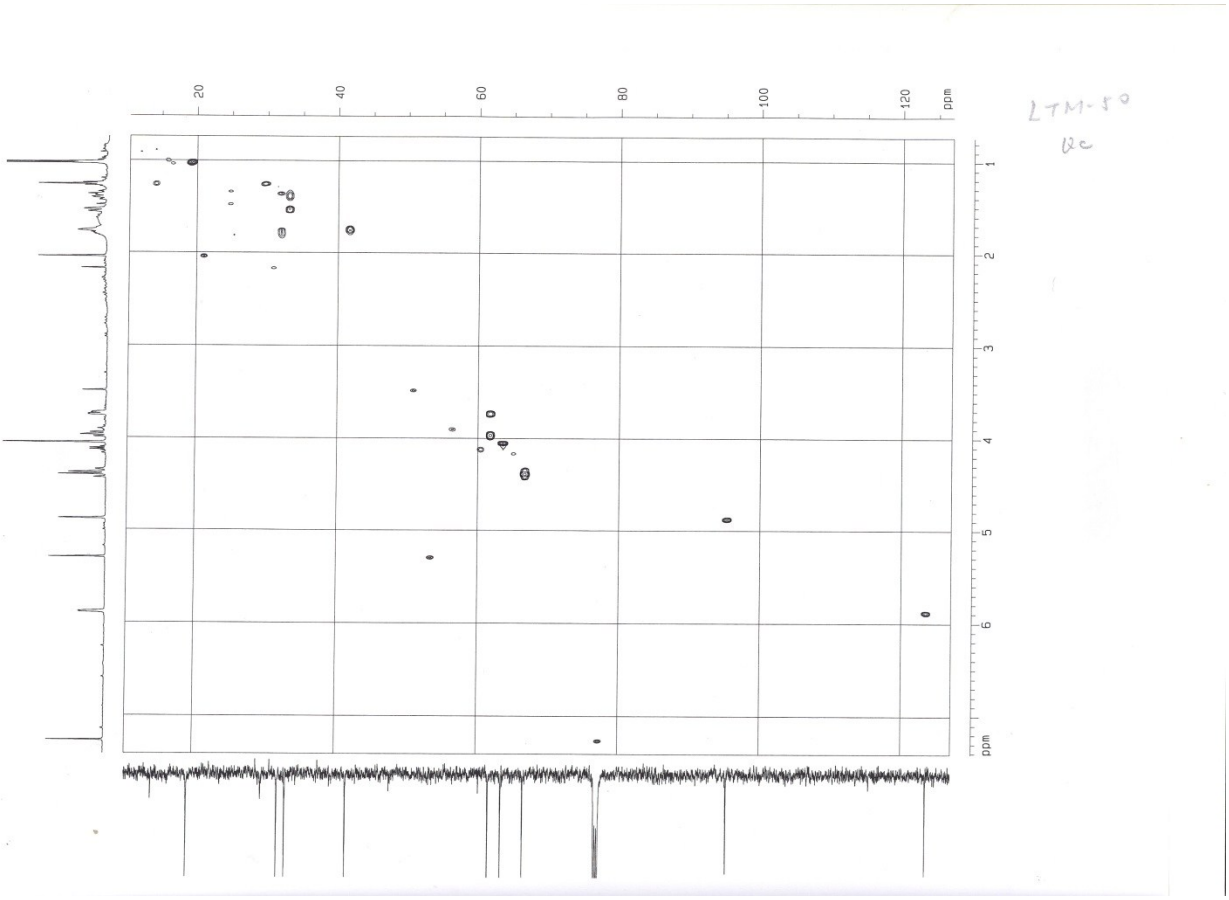


Figure S7. The HMBC spectrum of secoarguterin (500 MHz, $CDCl_3$)

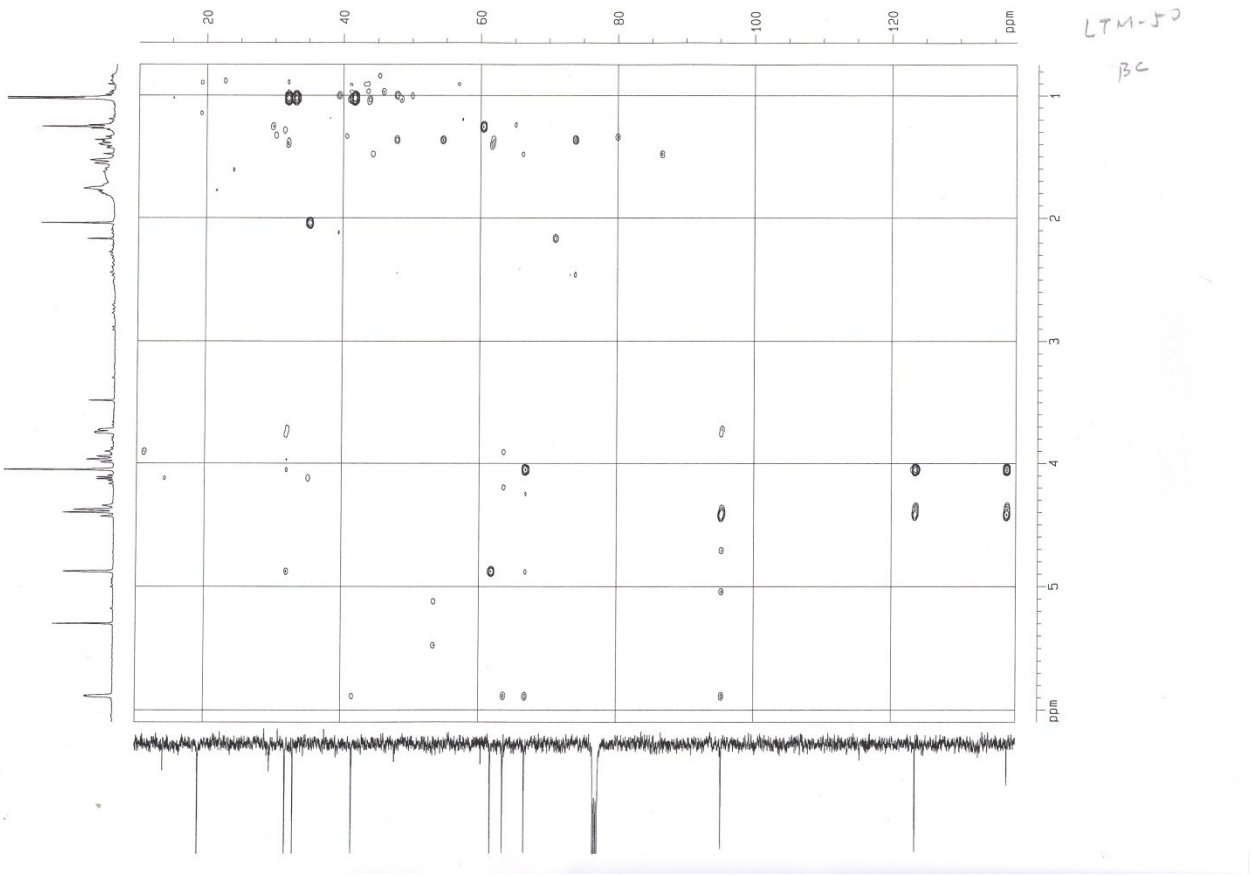
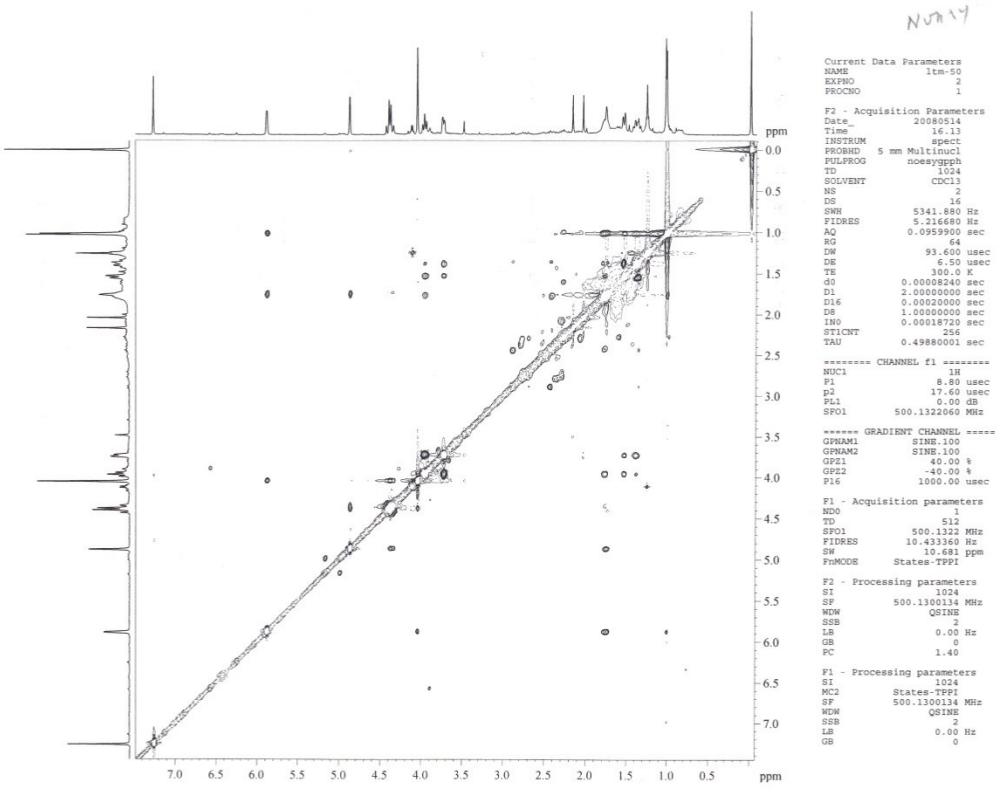
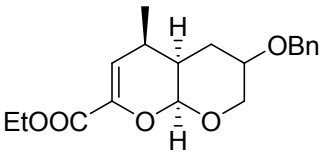


Figure S8. The NOESY spectrum of secoarguterin (500 MHz, $CDCl_3$)



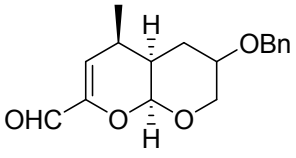
VI. Synthesis Experimental Procedures and Spectroscopic Data of Compounds

Compound **4**



1.5 ml of a 0.02M solution of [Cu((S,S)-t-Bu-box)]$(SbF_6)_2$ was treated at -40ºC with unsaturated ester **2**(6.5g, 45mmol) and **3** (26.7g, 140.5mmol). After the reaction was completed (TLC), the organic solvent was removed under reduced pressure. The residue was purified by column chromatography (petro ether/ethyl acetate = 6:1) to afford of compound **4**(15.6g, yield: 75%) as a colorless oil.$[\alpha]_D^{20}$-38 (c 0.17, $CHCl_3$);^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41 – 7.32 (m, 4H), 7.28 (dt, J = 7.6, 3.4 Hz, 1H), 5.73 (dd, J = 2.1, 1.4 Hz, 1H), 5.33 (s, 1H), 4.64 (d, J = 12.2 Hz, 1H), 4.54 (d, J = 12.2 Hz, 1H), 4.25 (qd, J = 7.1, 0.8 Hz, 2H), 4.04 (dd, J = 12.5, 1.4 Hz, 1H), 3.95 – 3.87 (m, 1H), 3.60 (s, 1H), 2.85 – 2.74 (m, 1H), 2.42 (d, J = 13.2 Hz, 1H), 1.84 (d, J = 10.7 Hz, 1H), 1.45 (td, J = 13.6, 2.9 Hz, 1H), 1.31 (t, J = 7.1 Hz, 3H), 1.00 (d, J = 7.4 Hz, 3H).^{13}C NMR (125MHz, $CDCl_3$) δ: 128.36, 127.53, 114.01, 97.65, 70.64, 62.28, 61.11, 30.50, 29.69, 22.10, 15.51, 14.18.HR-ESI-MS calcd for $C_{19}H_{24}NaO_5$ $[M+Na]^+$355.1515, found 355.1516.

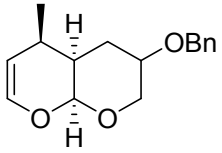
Compound **5**



To a solution of **4** (15.6g, 46.9mmol) in anhydrous CH_2Cl_2 (250mL) was added dropwise DIBAL-H (46.9mL, 1M in THF) at -78°C, then the solution was stirred at the same temperature for 2h. After the reaction was completed (TLC),a saturated aqueous solution of NH_4Cl (20 mL) was added. The mixture was extracted with ethyl acetate (3 × 25 mL). The combined organic layers were washed with brine (25 mL), and then dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 6:1 to 4:1) to give colorless oil product **5** (13.6 g, 65%).$[\alpha]_D^{20}$-45 (c 0.19, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (d, J = 2.9 Hz, 1H), 7.40 – 7.28 (m, 6H), 5.54 (dd, J = 2.4, 1.4 Hz, 1H), 5.35 (s, 1H), 4.65 (d, J = 12.1 Hz, 1H),

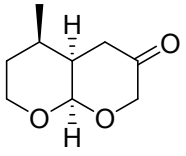
4.53 (d, J = 12.1 Hz, 1H), 4.03 (dd, J = 12.6, 1.3 Hz, 1H), 3.96 – 3.86 (m, 1H), 3.60 (s, 1H), 3.00 – 2.85 (m, 1H), 2.48 (s, 1H), 1.86 (dd, J = 13.8, 3.0 Hz, 1H), 1.40 (dt, J = 13.6, 2.6 Hz, 2H), 1.11 (d, J = 7.4 Hz, 1H), 1.06 (d, J = 7.5 Hz, 2H).^{13}C NMR (125MHz, $CDCl_3$) δ: 186.09, 128.38, 127.56, 125.13, 97.67, 70.80, 70.38, 62.15, 30.82, 30.37, 22.32, 15.24.HR-ESI-MS calcd for $C_{17}H_{20}NaO_4$ $[M+Na]^+$311.1253, found 311.1252.

Compound**6**



To a toluene solution (250mL) of the compound **5**(13.6g, 34.7mmol) was added $RhCl(PPh_3)_3$ (32.1g, 34.7mmol), and the mixture was heated to refluxed for 5h. The colour of the solution turned from red to yellow. The solution was concentrated and chromatographed on a silica column to afford compound **6**(9.7g, 75%) as a colorless oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.28 (m, 5H), 6.25 (dd, *J* = 5.5, 3.1 Hz, 1H), 5.26 (s, 1H), 4.70 – 4.48 (m, 3H), 4.34 (t, *J* = 7.5 Hz, 1H), 3.95 (d, *J* = 12.3 Hz, 1H), 3.83 (dd, *J* = 20.9, 12.5 Hz, 1H), 3.58 (d, *J* = 9.2 Hz, 1H), 2.75 – 2.62 (m, 1H), 2.48 – 2.29 (m, 1H), 1.81 (ddd, *J* = 31.5, 26.9, 13.7 Hz, 2H), 1.57 (td, *J* = 13.6, 2.4 Hz, 1H), 1.07 (d, *J* = 7.1 Hz, 1H), 1.00 – 0.83 (m, 3H).^{13}C NMR (125MHz, $CDCl_3$) δ 138.54, 134.44, 132.80 , 128.33, 127.51, 99.75, 98.22, 94.94, 92.44, 70.98, 69.60, 62.16, 38.32, 36.15, 33.13, 29.64, 26.27, 20.11, 17.60. HR-ESI-MS calcd for $C_{16}H_{20}NaO_3$ $[M+Na]^+$283.1304, found 283.1305.

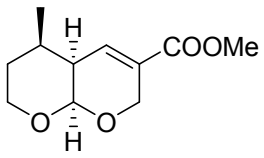
Compound **7**



The compound **6**(9.7g, 37.3mmol) and 10% Pd/C (1g) in CH_3OH (5 mL) was stirred at room temperature under a hydrogen atmosphere for 24h, filtered through a pad of celite, and concentrated. To a cooled (–78ºC) solution of oxalyl chloride (6.5mL, 74.6mmol) in CH_2Cl_2(200mL) was added dimethyl sulfoxide

(10.6 mL, 149.2mmol) followed by above crude product. The reaction mixture was allowed to stir for 1h at –78ºC, then triethylamine (76.0mL, 547mmol) was added. The solution was allowed to warm to 23ºC for 3h, and H_2O (100mL) was added. The aqueous layer was extracted with CH_2Cl_2(4×60mL), and the combined organic layers were washed with H_2O (3×30mL), and brine (50mL), dried over $MgSO_4$, and concentrated in vacuum. The resulting oil was purified by flash chromatography (hexane/ethyl acetate=5:1) to afford compound **7**(1.5g, 59%).^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.78 (d, J = 2.3 Hz, 1H), 4.29 (dd, J = 16.1, 0.5 Hz, 1H), 4.11 (ddd, J = 11.8, 5.0, 1.3 Hz, 1H), 3.95 (dd, J = 16.1, 1.7 Hz, 1H), 3.67 – 3.54 (m, 1H), 2.49 (dd, J = 16.5, 12.5 Hz, 1H), 2.34 (dd, J = 16.4, 5.5 Hz, 1H), 2.27 – 2.19 (m, 1H), 2.07 – 1.95 (m, 1H), 1.48 (dtd, J = 17.4, 12.4, 5.0 Hz, 1H), 1.39 – 1.29 (m, 1H), 0.90 (dd, J = 6.8, 2.9 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ: 207.12, 97.06, 68.20, 66.52, 39.74, 33.47, 31.65, 27.25, 17.45. HR-ESI-MS calcd for $C_9H_{14}NaO_3$ $[M+Na]^+$193.0835, found 193.0835.

Compound**8**

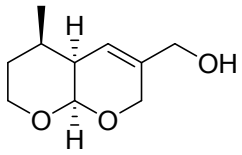


To a stirring solution of compound **7** (100mg, 0.588mmol) in 5 mL of THF, cooled to -78ºC, was added dropwise 2.5 mL (1.76mmol) of a 0.7 M solution of KHMDS in THF. After 1h, a solution of 252mg (0.706mmol) of N-phenyltrifluoro- methanesulfonimide in 4.5 mL of THF was added slowly. The solution was stirred at - -78ºC for 1h. Saturated aqueous NH_4Cl was added and the mixture was extracted with 10 mL of ether. The organic layer was washed with two 10-mL portions of water and then with 10 mL of saturated brine, dried, filtered, and concentrated to give a yellow-orange oil.

A solution of a mixture of above crude product (152mg, 0.503mmol), triethylamine(16.9mg, 0.167mmol), methanol (1.2ml), palladium(II) acetate (22.3mg, 0.1mmol), and triphenylphosphine (52.4mg, 0.2mmol) in 3mL of DMF was purged with carbon monoxide for 5 min, and then allowed to stir at room temperature under a balloon of carbon monoxide for 2h. The mixture was poured into 30 mL of ether and washed with two 30mL portions of water, 30 mL of saturated brine, dried, filtered and concentrated to give a brown oil. The crude product was purified by flash chromatography (hexane/ethyl acetate = 5:1) to give compound **8** (13.2mg, 16%) as a colorless oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (ddd, *J* = 15.9, 8.8, 7.1 Hz, 1H), 4.86 (d, *J* = 2.7 Hz, 1H), 4.63 (d, *J* = 16.6 Hz, 1H), 4.46 (dt, *J* = 16.6, 2.5 Hz, 1H), 3.96 (td, *J*

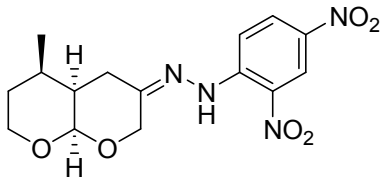
= 11.9, 2.4 Hz, 1H), 3.80 – 3.69 (m, 4H), 1.96 – 1.77 (m, 2H), 1.60 – 1.54 (m, 1H), 1.48 – 1.36 (m, 1H), 1.08 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (125MHz, $CDCl_3$) δ 165.12, 139.50, 129.21, 94.42, 65.20, 61.55, 51.66, 42.03, 32.96, 31.64, 30.86, 19.29.HR-ESI-MS calcd for $C_{11}H_{16}NaO_4$ $[M+Na]^+$235.0940, found 235.0941.

Compound**1**



To a solution of **8** (13.2mg, 0.062mmol) in anhydrous CH_2Cl_2 (5mL) was added dropwise DIBAL-H (0.18mL, 1M/L in THF) at room temperature, then the solution was stirred at the same temperature for 2h. After the reaction was complete (TLC). A saturated aqueous solution of NH_4Cl (20 mL) was added. The mixture was extracted with ethyl acetate (3 × 25 mL). The combined organic layers were washed with brine (25mL), and then dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 2:1) to give colorless oil product**1** (6.1mg, 57%). $[\alpha]_D^{20}$-105 (c 0.4, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87 (d, *J* = 2.7, 11.4 Hz, 1H), 4.87 (t, *J* = 6.3 Hz, 1H), 4.47 – 4.32 (m, 2H), 4.06 (d, *J* = 12.0 Hz, 2H), 4.01 – 3.91 (m, 1H), 3.78 – 3.69 (m, 1H), 1.85 – 1.72 (m, 2H), 1.56 – 1.50 (m, 1H), 1.45 – 1.34 (m, 1H), 1.02 (t, *J* = 5.6 Hz, 3H).^{13}C NMR (125MHz, $CDCl_3$) δ 136.81, 123.50, 95.30,66.66, 63.56, 61.73, 41.57, 33.07, 31.92, 19.25.HR-ESI-MS calcd for $C_{10}H_{16}NaO_3$ $[M+Na]^+$207.0997, found 207.0992

Compound**9**



To a CH_3CH_2OH solution (10 mL) of the compound **7**(20 mg, 0.118 mmol) was added 2,4-dinitrophenylhydrazine(23.3 mg, 0.118 mmol), and the mixture was heated to refluxed for 2h. When the solution was cooled, crystals appeared. Product was filtered (33 mg, 80%). $[\alpha]_D^{20}$-44 (c 0.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.19 (s, 1H), 9.13 (dd, J = 5.3, 2.6 Hz, 1H), 8.40 – 8.21 (m, 1H), 7.96 (d, J =

9.6 Hz, 1H), 4.82 (d, J = 2.1 Hz, 1H), 4.60 (d, J = 13.8 Hz, 1H), 4.27 (d, J = 13.8 Hz, 1H), 4.21 – 4.08 (m, 1H), 3.61 (td, J = 12.2, 2.7 Hz, 1H), 2.65 (dd, J = 15.2, 5.2 Hz, 1H), 2.42 (dd, J = 15.0, 12.5 Hz, 1H), 2.10 – 1.99 (m, 2H), 1.40 (d, J = 14.3 Hz, 1H), 1.05 (d, J = 6.8 Hz, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ 154.02, 145.20, 130.14, 123.39, 116.35, 98.04, 66.42, 64.25, 39.04, 31.89, 27.57, 19.69, 17.68. HR-ESI-MS calcd for $C_{15}H_{18}N_4O_6$ $[M+H]^+$ 351.1299, found 351.1299.

X. Spectra of compounds

Figure S9. The ^{1}H NMR spectrum of compound 4 (500 MHz, $CDCl_3$)

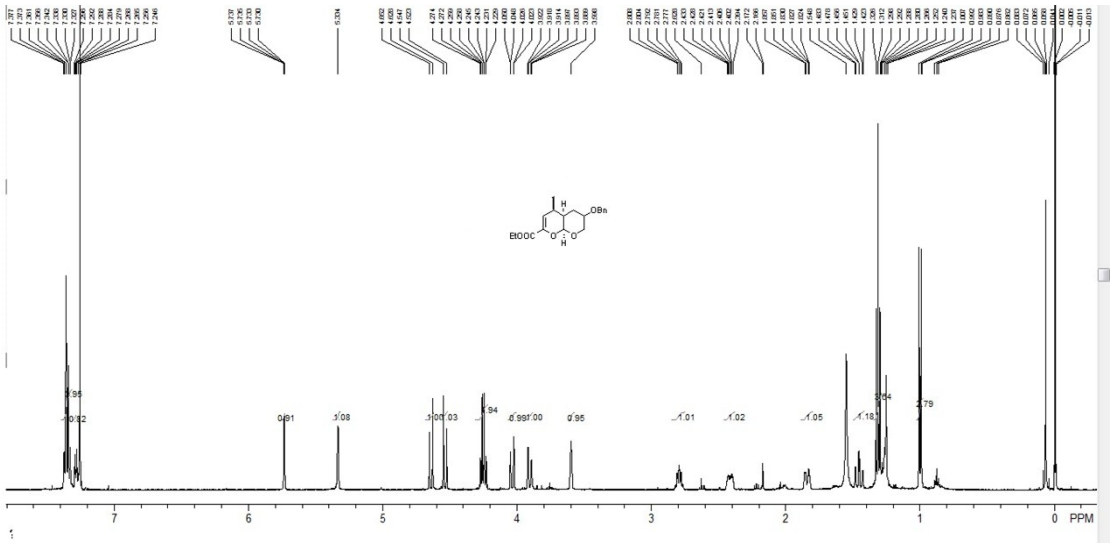


Figure S10. The ^{13}C NMR spectrum of compound 4 (125MHz, $CDCl_3$)

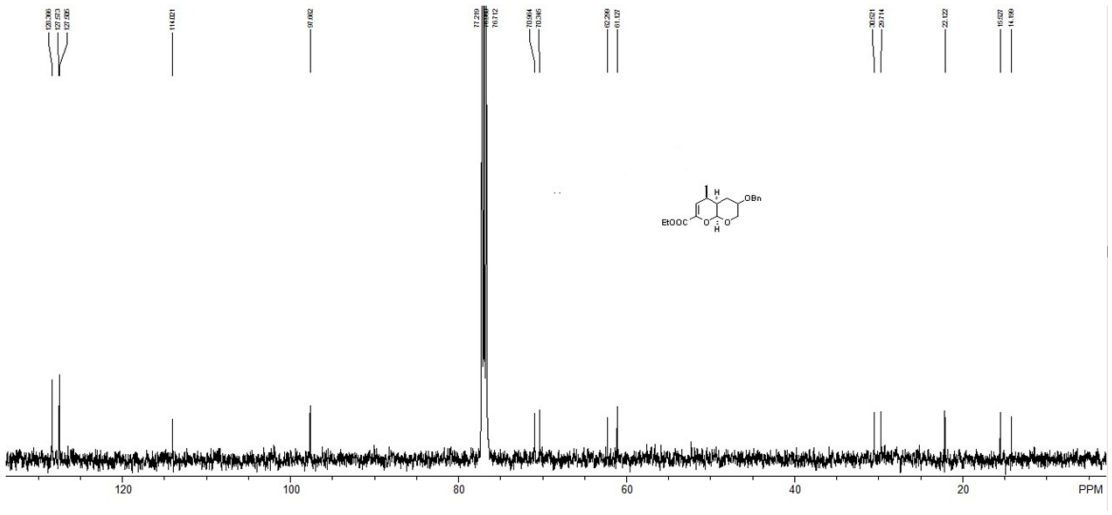


Figure S11. The ^{1}H NMR spectrum of compound 5 (500 MHz, $CDCl_3$)

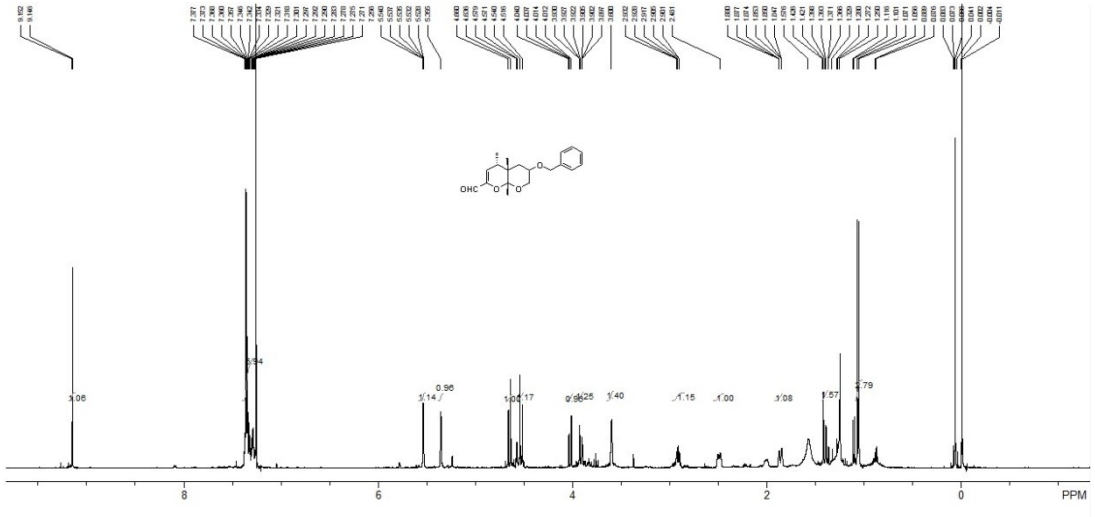


Figure S12. The ^{13}C NMR spectrum of compound 5 (125MHz, $CDCl_3$)

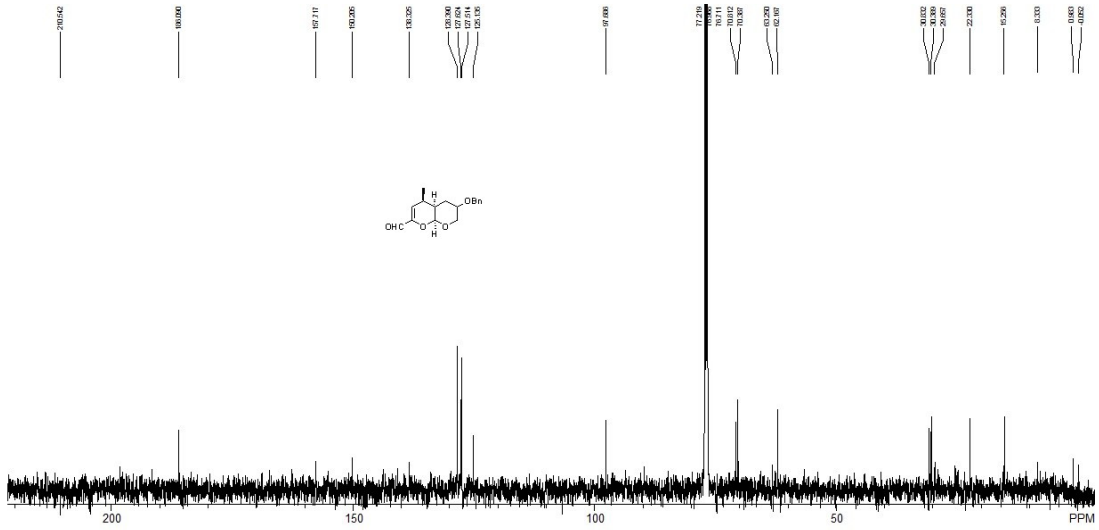


Figure S13. The ^{1}H NMR spectrum of compound 6 (500 MHz, $CDCl_3$)

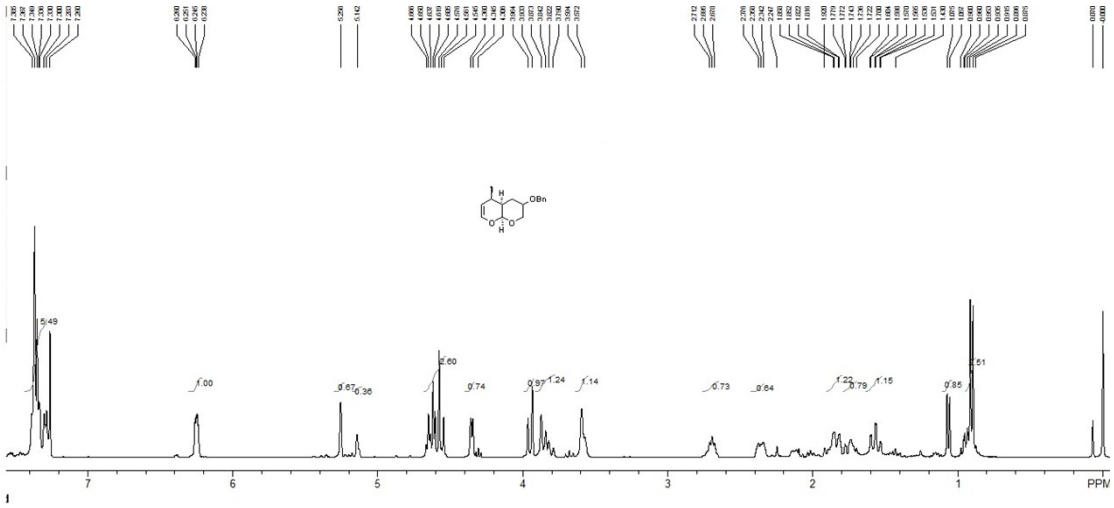


Figure S14. The ^{13}C NMR spectrum of compound 6 (125MHz, $CDCl_3$)

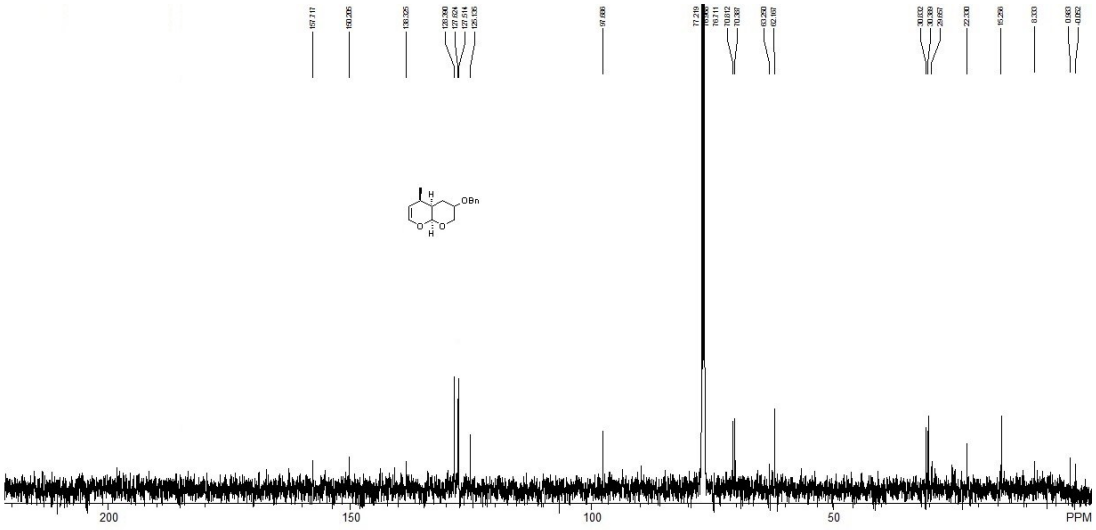


Figure S15. The ^{1}H NMR spectrum of compound 7 (500 MHz, $CDCl_3$)

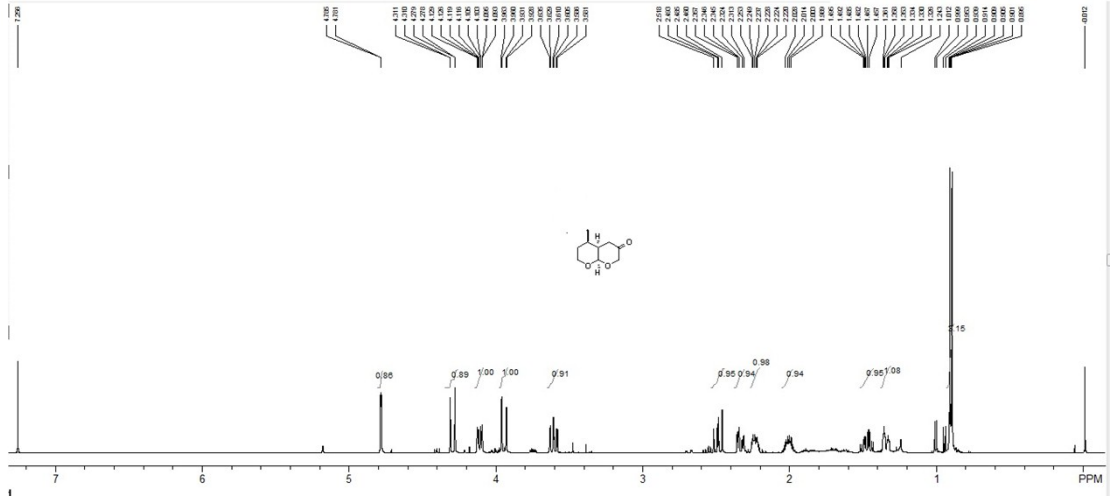


Figure S16. The ^{13}C NMR spectrum of compound 7 (125MHz, $CDCl_3$)

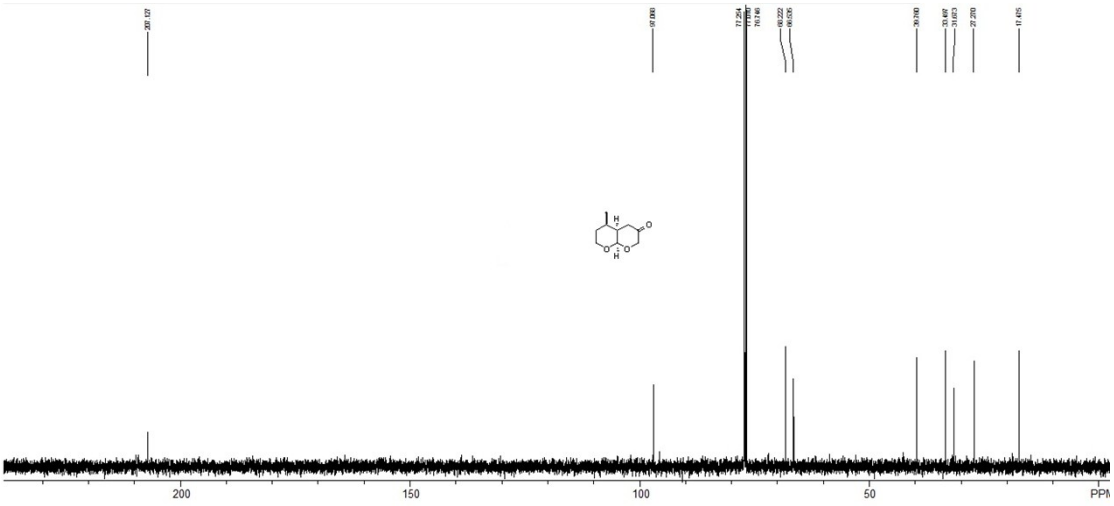


Figure S17. The ^{1}H NMR spectrum of compound 8 (500 MHz, $CDCl_3$)

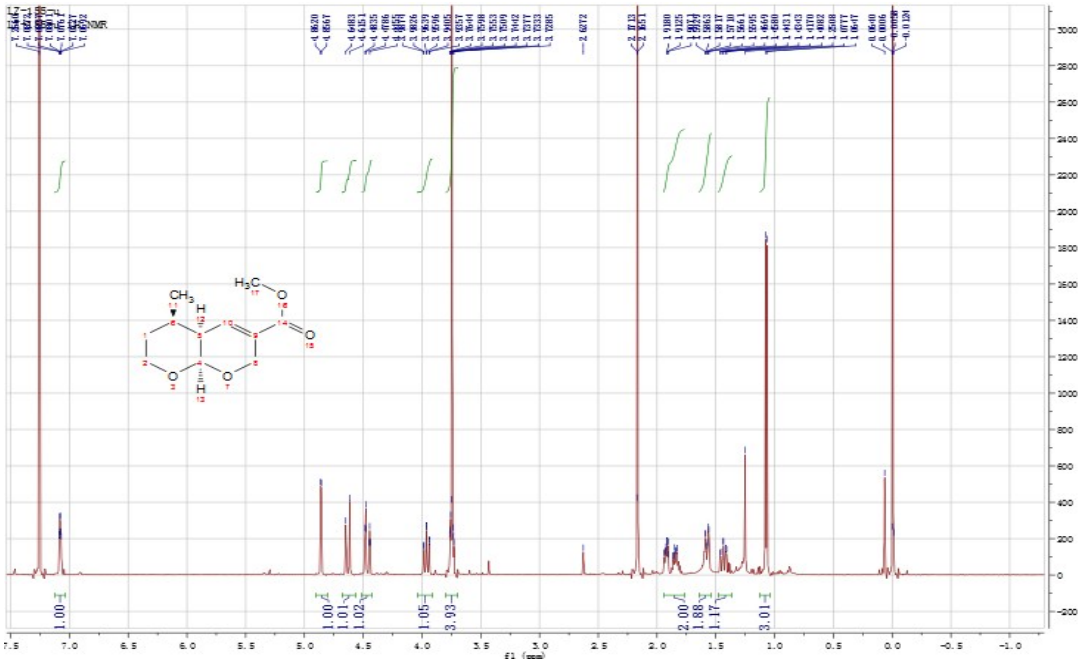


Figure S18. The ^{13}C NMR spectrum of compound 8 (125MHz, $CDCl_3$)

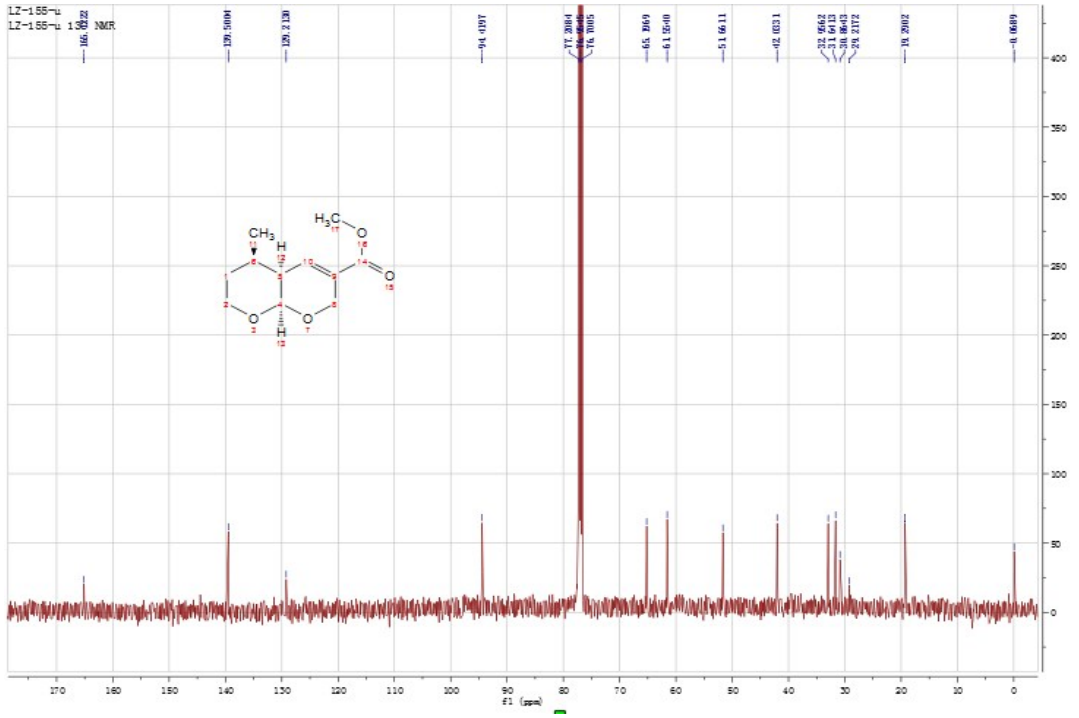


Figure S19. The ^{1}H NMR spectrum of compound 1 (500 MHz, $CDCl_3$)

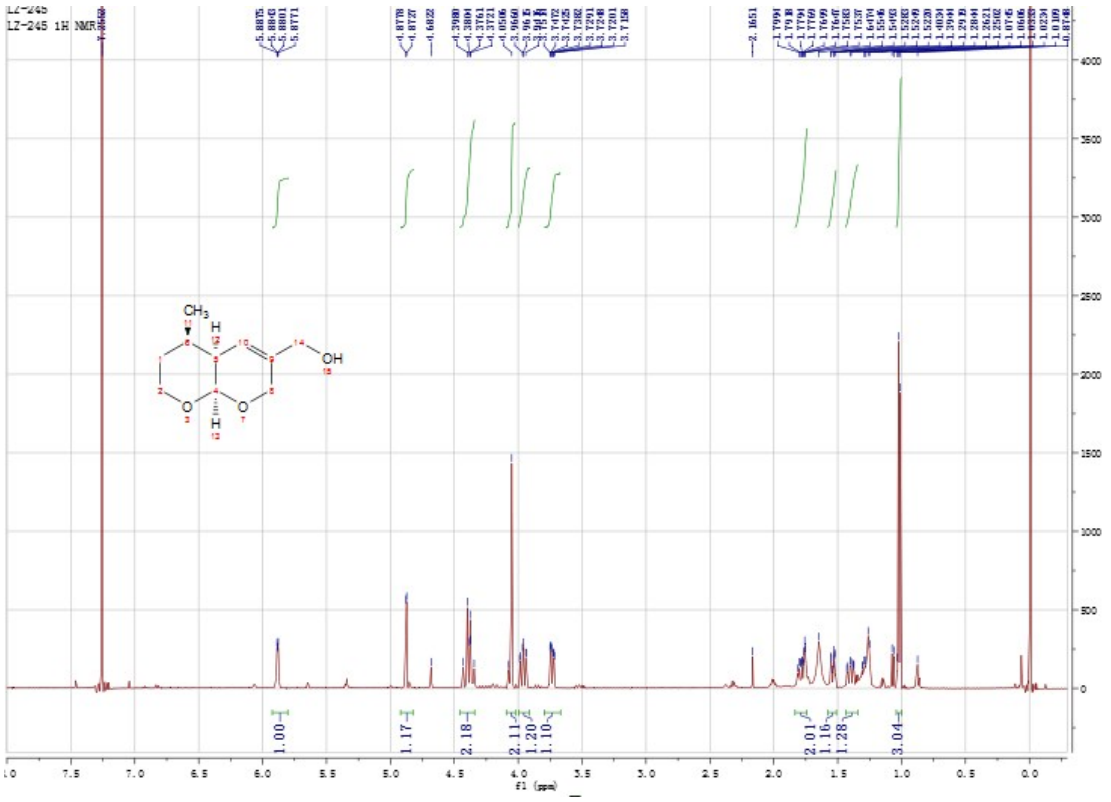


Figure S20. The ^{13}C NMR spectrum of compound 1 (125MHz, $CDCl_3$)

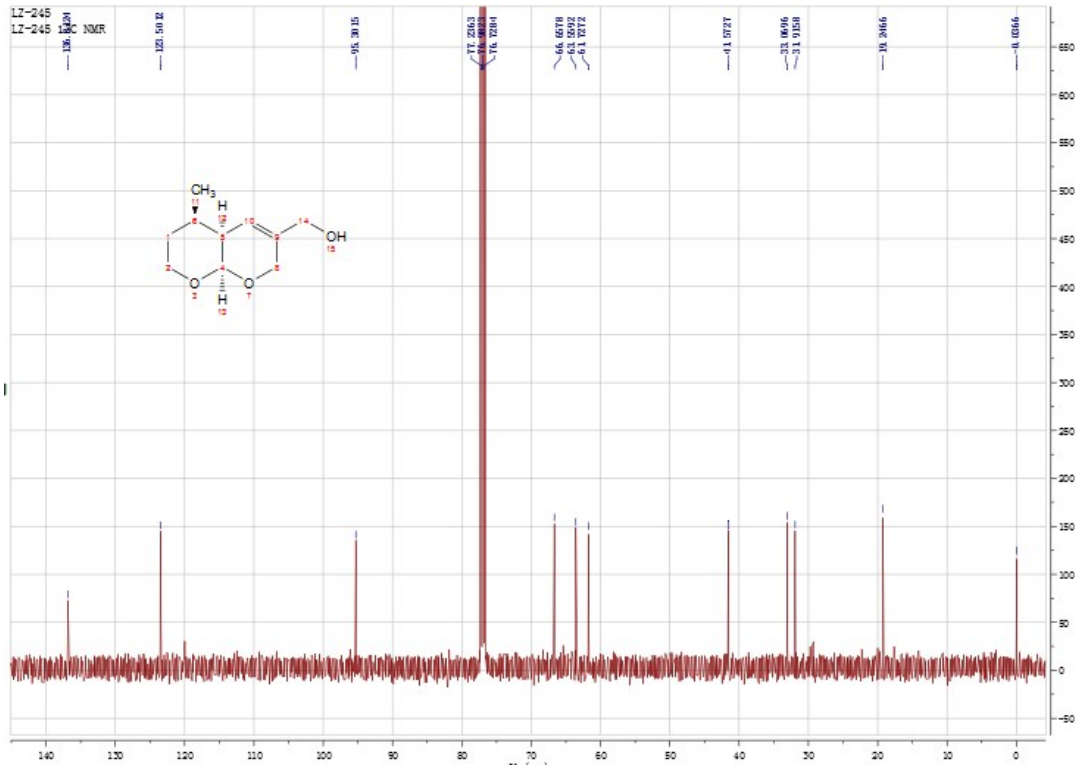


Figure S21. The ^{1}H NMR spectrum of compound 9 (500 MHz, $CDCl_3$)

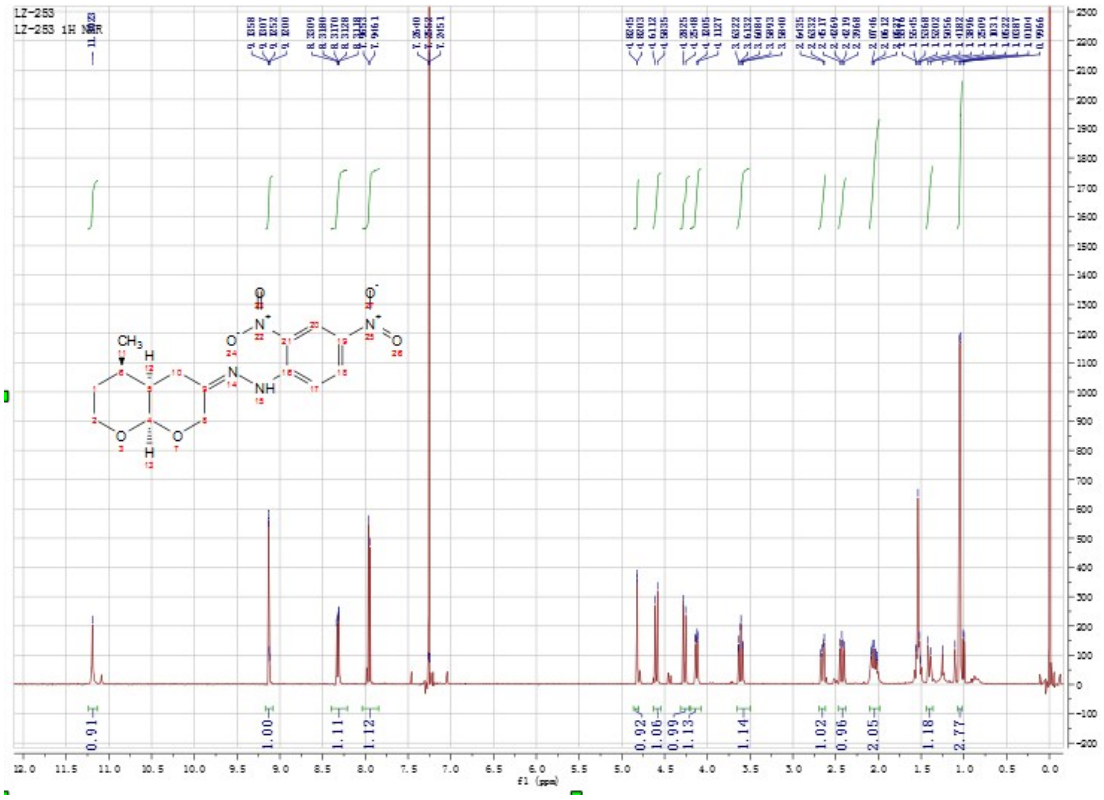
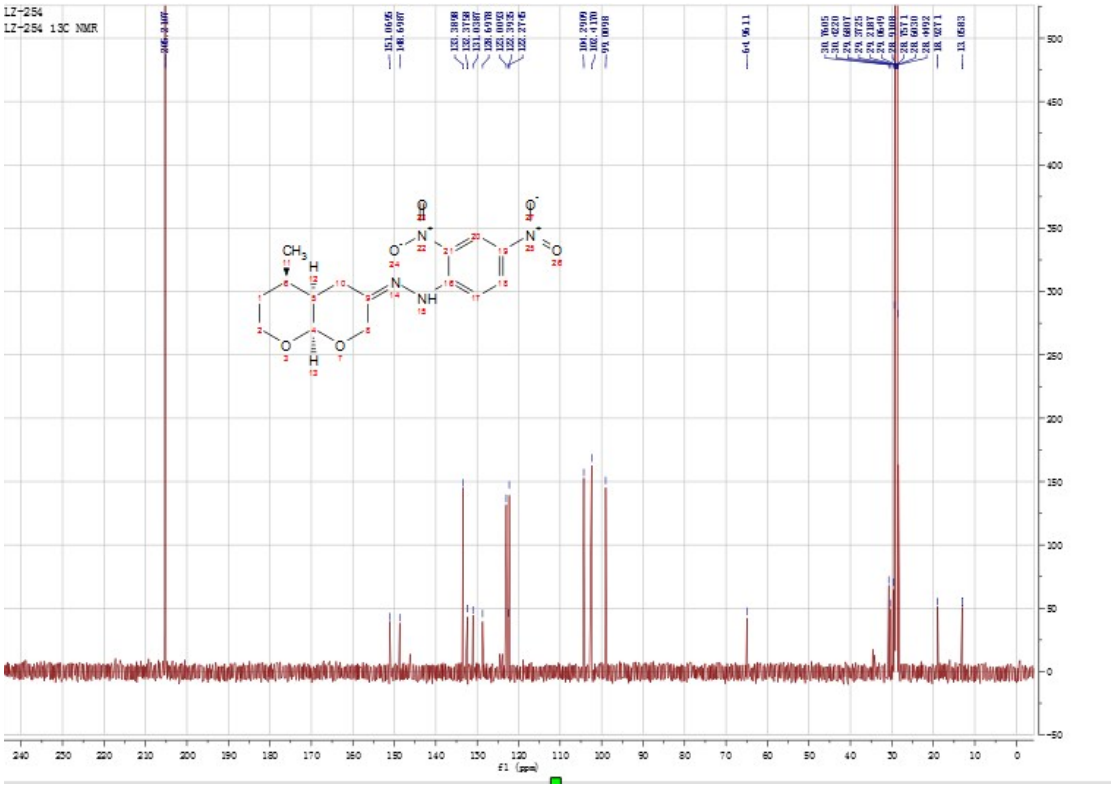


Figure S22. The ^{13}C NMR spectrum of compound 9 (125MHz, $CDCl_3$)



VIII. Crystal data and structure refinement of compound 9

Empirical formula	C15 H18 N4 O6
Formula weight	350.33
Temperature	140(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 5.76250(10) Å
	b = 23.3095(5) Å
	c = 11.9536(2) Å
Volume	1558.29(5) $Å^3$
Z	4
Density (calculated)	1.493 Mg/m^3
Absorption coefficient	0.995 mm^{-1}
F(000)	736
Crystal size	0.300 x 0.120 x 0.060 mm^3

Theta range for data collection	4.257 to 69.738°.
Index ranges	-6<=h<=6, -24<=k<=27, -14<=l<=14
Reflections collected	8065
Independent reflections	2854 [R(int) = 0.0488]
Completeness to theta = 67.679°	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7533 and 0.4285
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2854 / 12 / 228
Goodness-of-fit on F^2	1.180
Final R indices [I>2sigma(I)]	R1 = 0.0555, wR2 = 0.1462
R indices (all data)	R1 = 0.0629, wR2 = 0.1600
Extinction coefficient	0.0121(13)
Largest diff. peak and hole	0.800 and -0.851 e.$Å^{-3}$

Yellow prism crystals of **9**were obtained by recrystallization in ethyl acetate:acetone(1:4). Crystal data were obtained on Bruker SMART APEX II CCD area detector with graphite monochromated Cu-Kα radiation (λ =1.54178 Å) at 140(2) and operating in theΦ-ωscan mode. The structure was solved by direct methods and refined with full-matrix least-squares calculations of F^2using SHELX-97. The collected data were reduced by using the program SAINT and empirical ab sorption correction was made by using the SADABS program. The hydrogen atom positions were geometrically idealized and allowed to ride on their parent atoms. Crystallographic data for **9** have been deposited at the Cambridge Crystallographic Data Centre (deposition no. CCDC1402281). Copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK. [fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk].

IX. Comparison of the Spectra of Natural and Synthetic Secoarguterin (1)

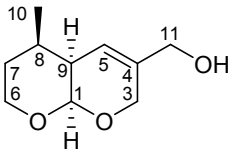


Table 1 ^{13}C and ^{1}H NMR spectroscopic datafor natural product and compound **1**

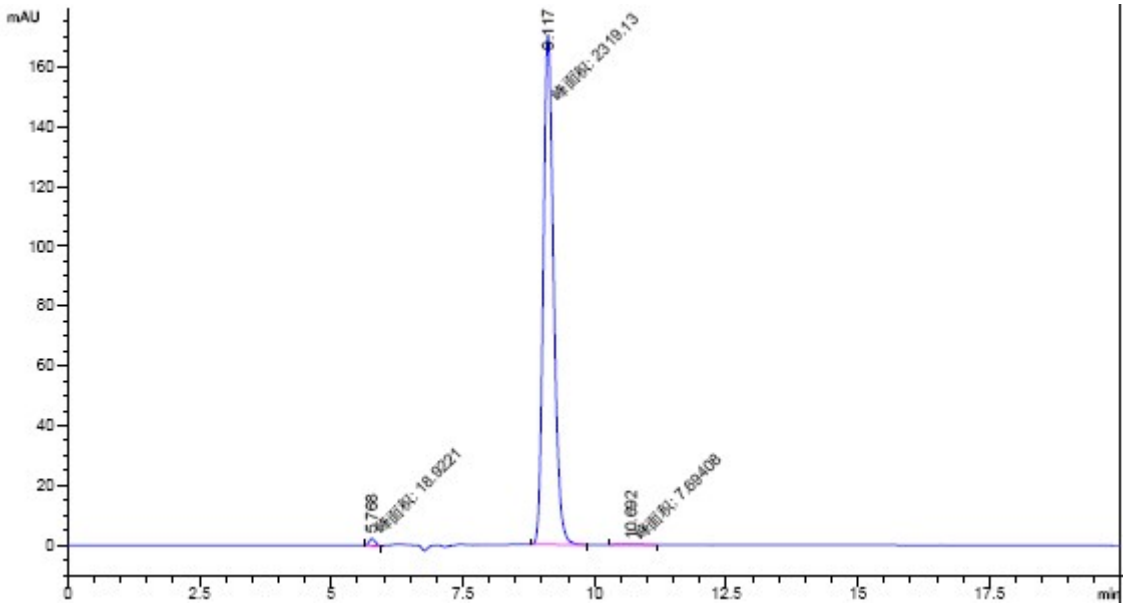
	Natural product		Synthsized compound**1**	
No.	$\delta_C{}^{b,c}$ mult.	$\delta_H{}^{a}$ mult. (*J* in Hz)	$\delta_C{}^{b,c}$ mult.	$\delta_H{}^{a}$ mult. (*J* in Hz)
1	95.3 *d*	4.88 (*d*, 3.0)	95.3 *d*	4.87 (*d*, 3.0)
3a	66.7 *t*	4.41 (*d,* 16.0)	65.7 *t*	4.41 (*d,* 16.0)
3b		4.36 (*d,* 16.0)		4.36 (*d,* 16.0)
4	136.9 *s*		137.4 *s*	
5	123.5 *d*	5.88 (*d*, 3.9)	123.5 *d*	5.88 (*dd,* 3.5, 1.5)
6a	61.7 *t*	3.97 (*t*, 11.0)	61.7 *t*	3.97 (*dt*, 11.5, 2.5)
6b		3.73 (*m*)		3.73 (*m*)
7a	33.1 *t*	1.54 (*d*, 13.1)	33.1 *t*	1.54 (*dd,* 13.0, 2.5)
7b		1.39 (*m*)		1.40 (*m*)
8	32.0 *d*	1.80 (*m*)	31.9 *d*	1.78 (*m*)
9	41.7 *d*	1.76 (*m*)	41.6 *d*	1.75 (*m*)
10	19.3 *q*	1.02 (*d*, 6.1)	19.3 *q*	1.02 (*d*, 6.0)
11	63.6 *t*	4.05 (*s*)	63.6 *t*	4.05 (*s*)

[a] Recorded at 500 MHz (in $CDCl_3$; δ in ppm); [b] Recorded at 125MHz; [c] Multiplicities inferred from by DEPT and HMQC experiments.

The NMR data of compound **1** were similar to those of natural product,with similar resonance structures corresponding to six-membered ring deduced by interpretation ofthe 2D NMR spectra of compound **1** (Table 1).

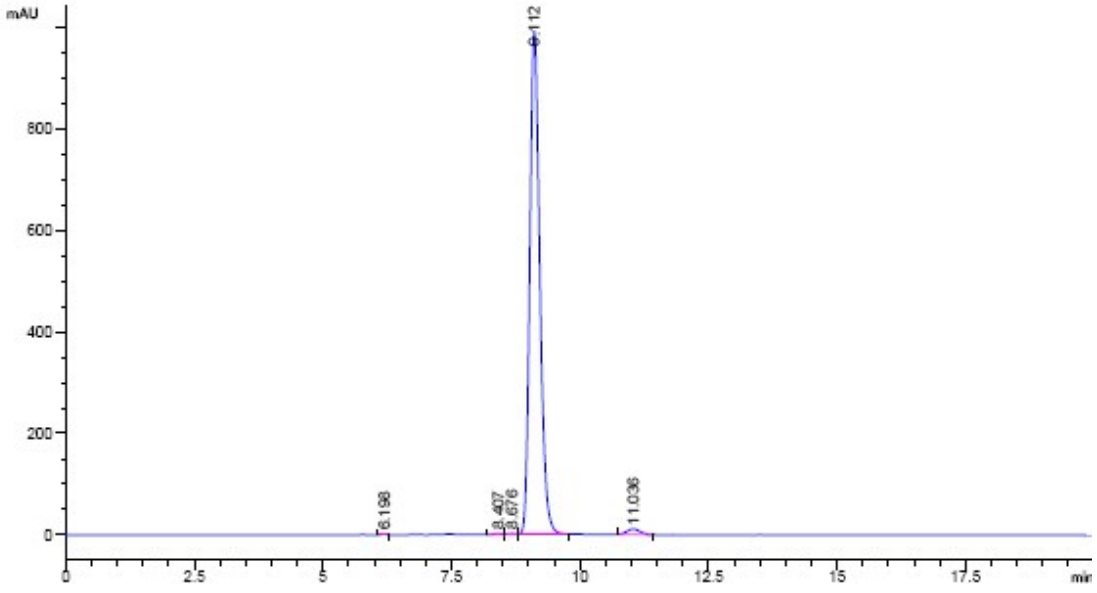
Chiralcel AD-H column, hexane : *i*PrOH = 200 : 1, 1.0 mL/min

Isolate 1



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	5.768	MM	0.1245	18.92206	2.53228	0.8067
2	9.117	MM	0.2267	2319.12524	170.49078	98.8653
3	10.692	MM	0.5081	7.69408	2.52367e-1	0.3280
总量 :				2345.74138	173.27543	

Synthesized compound 1



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	6.198	BV	0.0856	12.54611	2.19487	0.0920
2	8.407	VV	0.1565	18.83988	1.83065	0.1382
3	8.676	VV	0.2003	30.40620	2.32929	0.2230
4	9.112	MM	0.2250	1.33705e4	990.33740	98.0740
5	11.036	MM	0.3007	200.78229	11.12927	1.4728
总量 :				1.36331e4	1007.82148	