Supporting Information

Concise syntheses of (–)-quinocarcinol methyl ester and (–)-oxa-quinocarcinol methyl ester

Tianhang Song[a] , Yifan Wu[a] , Jun Ren[a] , Zhongwen Wang*[a]

[a] *State Key Laboratory of Elemento-Organic Chemistry, Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, 94# Weijin Road, Tianjin 300071, China*

∗ Corresponding author.

E-mail address: wzwrj@nankai.edu.cn

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I. General Considerations

Unless otherwise noted in the experimental procedures, reactions were carried out in oven-dried glassware under a positive pressure of argon in anhydrous solvents using standard Schlenk techniques. Reaction temperatures above room temperature were monitored using liquid-in-glass thermometers. Reaction progress was monitored by thin-layer chromatography (TLC) on S-2 0.25 mm E. Merck silica gel plates (GF-254) and visualized by UV-light (254 and 365 nm)/$KMnO_4$/I_2/p-anisaldehyde. Organic solutions were concentrated under reduced pressure on an EYELA temperature-controlled rotary evaporator equipped with a dry ethanol condenser. All solvents were obtained from commercial sources and were purified according to standard procedures, and stored under an argon atmosphere. All reagents were purchased from the commercial sources and used without further purification. ^{1}H NMR and ^{13}C NMR data were recorded on Bruker AV400 using $CDCl_3$ as a solvent. Chemical shifts were reported in parts per million (δ) using the residual solvent signals ($CDCl_3$: δ 7.26 for ^{1}H NMR, δ 77.16 for ^{13}C NMR), coupling constants (*J*) in Hz. The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. HRMS were recorded on Varian 7.0T FTMS (Fourier transform ion cyclotron resonance mass spectrometer, ESI) and Agilent 6520 Q-TOF LC/MS (ESI). Single crystal X–ray diffraction measurements are carried out on a Rigaku 007 Saturn 70 diffractometer with Cu Kα radiation. The single crystals of **16** (CCDC 2365362) was obtained from dichloromethane and n-hexane by the method of solvent diffusion.

II. DFT Calculations

Computational methods

All calculations were carried out using Gaussian 16 package.[1] Geometry optimizations were performed using the B3LYP functional with Grimme's empirical dispersion-correction and 6-31G (d) basis set. Vibrational frequencies were calculated at the same level of theory to obtain the thermal correction and confirm the optimized geometries as minima (no imaginary frequencies) or transition structures (a single imaginary frequency) at the same level of theory. The intrinsic reaction coordinate calculations were performed to confirm that all obtained transition states connected the corresponding reactants and products. Solvation effects were introduced to all calculations, including the optimization and frequency analysis, by using the IEFPCM model with DMF as the solvent. For single-point energy calculations, the M06-2X functional was applied with Grimme's empirical dispersion-correction and def2-TZVP basis set. The solvation correction free energies were derived from the SMD model. Calculation of molecular thermodynamic quantities at 433.15K were carried out using Shermo program,[2] scale factor was applied to adjust for the errors arising from the harmonic oscillation assumption, quasi-rigid-rotor harmonic oscillator (quasi-RRHO) model was used to properly deal with low frequencies. Molecular structure figures were prepared using CYLview20.[3]

Cartesian coordinates of the optimized structures

INT1

Sum of electronic energy and thermal correction to G: -1149.710385 a.u.

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O	-2.24524500	1.97236200	-0.99259900
O	3.78725300	-0.85753900	-1.01619200
O	0.40935400	1.37888500	-2.01392500
O	-3.01305900	2.34388300	1.09169900
N	-0.35877400	-0.78254600	-0.47672900

C	1.94682000	-0.03822900	0.19557600
C	1.42156400	0.65953600	1.28530700
C	1.06400900	-0.66812700	-0.86179300
H	1.47257800	-1.66675000	-1.08101400
C	-3.11664400	0.10094000	0.23823900
C	3.65186900	1.15404200	2.07608600
H	4.31532200	1.61410800	2.80289900
C	-1.92074200	3.37487100	-1.09225700
H	-2.82940700	3.97537300	-1.01757300
H	-1.45363700	3.49029200	-2.06841900
H	-1.22628100	3.66033800	-0.29920400
C	-0.97284200	-1.97719900	-1.06672400
H	-0.46114800	-2.89818000	-0.73606700
H	-0.86268500	-1.92602800	-2.15526400
C	-0.07628300	0.70987500	1.43386800
H	-0.47012600	1.54303200	0.84616900
H	-0.35480200	0.88626400	2.47803000
C	3.34768100	-0.14360700	0.06485900
C	2.27328200	1.25232400	2.22624100
H	1.84718400	1.78258600	3.07349200
C	-2.19702300	-0.75684700	1.16448200
H	-2.41805300	-0.58348600	2.22236100
C	1.10021900	0.15244500	-2.17339600
H	2.13142000	0.37877200	-2.45155400
H	0.65638400	-0.44861300	-2.98351000
C	-2.46246300	-2.03920600	-0.70903000
H	-2.91771000	-2.91527100	-1.18182700
C	5.19067400	-1.02240600	-1.19037900
H	5.63858100	-1.54564700	-0.33741800
H	5.69085000	-0.05652400	-1.32732800
H	5.30986700	-1.62491400	-2.09162000
C	-2.79369000	1.57447700	0.17498800
C	-3.16272700	-0.71292500	-1.08167400
H	-4.19824200	-0.88606900	-1.38518700
H	-2.64782300	-0.20357000	-1.89627600
C	-0.67512500	-0.60922700	0.94616800
H	-0.20575400	-1.40390800	1.55493000
C	4.19954100	0.45243500	0.99832900
H	5.27505700	0.37507600	0.89771400
H	-0.43599200	1.12936400	-1.59036400
H	-4.09852500	0.06566800	0.71752900
N	-2.66678000	-2.08695300	0.74973200
C	-2.14853200	-3.24174900	1.46352500
H	-2.40047400	-3.14455200	2.52514700

H	-2.64069100	-4.14106200	1.07692300
H	-1.06097300	-3.39906200	1.39005500

INT2

Sum of electronic energy and thermal correction to G: -1149.7089442 a.u.

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O	3.75692200	2.13087300	1.02158600
O	-4.28403600	-1.08539400	0.17958100
O	-1.32136200	0.17452600	2.65428000
O	4.80677400	0.30835400	0.21344900
N	-0.11645700	-0.87061600	0.13025000
C	-2.35550500	0.23713800	-0.06973800
C	-1.74306500	1.44774000	-0.41243400
C	-1.54762100	-0.93479400	0.45441400
H	-1.98403200	-1.85409100	0.03355500
C	2.45745200	0.14251000	0.61037900
C	-3.89892000	2.41581100	-0.92226300
H	-4.50061800	3.25731100	-1.25367000
C	0.45932000	-2.18734200	-0.13461300
H	0.02832300	-2.65242500	-1.04133900
H	0.21877700	-2.85021900	0.70453200
C	-0.23771900	1.51255900	-0.36803500
H	0.10227400	1.74724900	0.64743400
H	0.12872600	2.30352200	-1.03137000
C	-3.75965800	0.12876300	-0.16421200
C	-2.51587500	2.53380100	-0.84374400
H	-2.02509500	3.46272900	-1.12020200
C	1.87549600	0.12853800	-0.84144300
H	2.23900900	0.95195100	-1.46649400
C	-1.71224100	-1.02216600	1.98961300
H	-2.75142400	-1.28710100	2.22670600
H	-1.05862100	-1.80910400	2.37710600
C	1.98681200	-2.07831100	-0.27029100
H	2.41362400	-3.07063500	-0.45065800
C	-5.69376000	-1.26385700	0.08314200
H	-6.04354500	-1.11763200	-0.94545800
H	-6.22778900	-0.57709800	0.75012900
H	-5.88449600	-2.29255000	0.39081000
C	3.72068300	0.96752600	0.65887400
C	2.60073700	-1.36706700	0.95155200
H	3.65078300	-1.64478800	1.05555600
H	2.07831000	-1.61193100	1.87940300
C	0.33308400	0.16330000	-0.79831400
H	-0.02570900	-0.02201400	-1.82856400

C	-4.53058000	1.21459600	-0.58861100
H	-5.60801800	1.13534900	-0.66300800
H	1.75604300	0.62765500	1.28667100
C	6.02850500	1.06737200	0.18260600
H	6.28970300	1.41217700	1.18598100
H	6.78771400	0.38393500	-0.19635100
H	5.92458400	1.93032600	-0.47963100
H	-1.87993700	0.88523900	2.29749600
N	2.37588300	-1.15424500	-1.34563500
C	2.03191400	-1.52191200	-2.70840700
H	2.39548500	-0.74348000	-3.38840000
H	2.54177600	-2.45884200	-2.95905200
H	0.95742400	-1.66361600	-2.90551400

INT3

Sum of electronic energy and thermal correction to G: -1130.3242503 a.u.

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O	2.47472600	-1.85098100	-1.79162000
O	2.48759200	1.15701700	1.44983500
O	-3.72914600	-1.10540800	0.65613300
O	-0.18684900	0.36685800	2.27614000
O	3.25263500	2.29159700	-0.33969000
N	0.39387100	-1.04817000	-0.03087000
C	-1.86895800	0.02762600	-0.22720100
C	-1.32474800	1.07318000	-0.97595000
C	-1.00626900	-1.01982900	0.44511100
H	-1.47855700	-1.99839400	0.27102600
C	3.20317500	-0.10504100	-0.46477900
C	-3.53404800	1.96479500	-1.38382200
H	-4.18206800	2.71327800	-1.83083900
C	2.26629900	2.41712600	2.11935300
H	3.21598300	2.93691900	2.25921200
H	1.81751900	2.15546500	3.07554700
H	1.58783500	3.04227300	1.53514800
C	0.93058500	-2.41069600	-0.03878300
H	0.37641400	-3.06109500	-0.73835400
H	0.83370300	-2.83852300	0.96467300
C	0.16871200	1.10058100	-1.17156700
H	0.63655800	1.60861600	-0.32396500
H	0.42958500	1.66299100	-2.07392200
C	-3.26968700	-0.04414100	-0.07410600
C	-2.15659400	2.03920800	-1.55618500
H	-1.71673200	2.84033600	-2.14363200
C	2.18636500	-0.46275000	-1.59597300

H	2.40714300	0.06515100	-2.52600000
C	-0.94460300	-0.79133500	1.97361500
H	-1.94924900	-0.65191200	2.37740100
H	-0.50906300	-1.68437600	2.45043500
C	2.39916400	-2.38012900	-0.45017500
H	2.81577800	-3.38874500	-0.47342200
C	-5.13540100	-1.24682500	0.82964100
H	-5.64543400	-1.36197800	-0.13393200
H	-5.55816600	-0.38828100	1.36434500
H	-5.27219000	-2.15013600	1.42519800
C	2.99263800	1.23370700	0.20119000
C	3.21481400	-1.38432200	0.40420500
H	4.23768100	-1.73669900	0.55633500
H	2.75576000	-1.22428400	1.37978400
C	0.68741200	-0.33224800	-1.27550700
H	0.17922400	-0.80763000	-2.13580900
C	-4.10136500	0.92157900	-0.64665400
H	-5.17654400	0.86956600	-0.52799100
H	0.63653200	0.26325100	1.75991600
H	4.16457800	-0.00418100	-0.97592900

INT4

Sum of electronic energy and thermal correction to G: -1130.3233529 a.u.

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O	-2.31457600	0.87490700	-1.76441000
O	-4.04575500	-1.55023800	1.46490600
O	4.20738500	1.10036700	-0.06997600
O	1.13738500	0.39471800	2.52323300
O	-4.81319900	-0.26605700	-0.22389900
N	0.04346000	0.91453600	-0.19423100
C	2.26941200	-0.22985200	-0.09465100
C	1.64911300	-1.47972900	-0.19623700
C	1.46557700	1.03131900	0.15695400
H	1.92706500	1.84209600	-0.42642500
C	-2.56220400	0.06637800	0.44684800
C	3.80262000	-2.54896000	-0.44396500
H	4.40054800	-3.44536300	-0.58126000
C	-0.50402700	2.13054000	-0.78452900
H	-0.07799300	2.33708200	-1.78448300
H	-0.26342200	2.98235300	-0.13859000
C	0.14227200	-1.52335100	-0.16886600
H	-0.21663600	-1.53331800	0.86701000
H	-0.22230500	-2.43384900	-0.65608900
C	3.67649000	-0.15420300	-0.17323400

C	2.41669900	-2.63750800	-0.37667300
H	1.92037300	-3.59945900	-0.46814400
C	-1.93905000	-0.24079300	-0.95117300
H	-2.33074300	-1.14418500	-1.42472100
C	1.58057900	1.42554200	1.64729100
H	2.61704100	1.71558900	1.86599700
H	0.93266500	2.28539000	1.84152500
C	-2.02254500	1.99724900	-0.91323000
H	-2.45061700	2.88647700	-1.38132000
C	5.62143700	1.24530500	-0.16209800
H	5.99519900	0.89031500	-1.12952900
H	6.12940200	0.70479800	0.64501100
H	5.81719100	2.31366600	-0.06482700
C	-3.86417400	-0.67011600	0.64348500
C	-2.69194200	1.61448900	0.42028700
H	-3.74003800	1.92012200	0.41370600
H	-2.19652100	2.06998400	1.28047900
C	-0.40487100	-0.29078200	-0.88291400
H	-0.05740300	-0.32051600	-1.93398200
C	4.44243400	-1.31020500	-0.34746000
H	5.52226800	-1.25700700	-0.40946300
H	-1.89360300	-0.25450800	1.24367800
C	-6.07928200	-0.94362000	-0.12769700
H	-6.51593100	-0.79644500	0.86297600
H	-6.71007200	-0.49423700	-0.89385200
H	-5.95421800	-2.01317000	-0.31267100
H	1.70237800	-0.37734000	2.35294600

INT5

Sum of electronic energy and thermal correction to G: -1137.294444 a.u.

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O	2.18481400	-1.35450100	-2.22729400
O	2.72649200	2.32662200	-0.00733700
O	-3.92818100	-1.13634900	0.78417700
O	0.05177900	-0.06191700	2.08250300
O	3.72094800	1.02508500	1.52271600
N	0.05282200	-1.02894000	-0.40997900
C	-2.14413000	0.11294600	-0.09720200
C	-1.64261300	1.27395000	-0.68978700
C	-1.24619900	-1.04690200	0.26986800
H	-1.78555200	-1.97561800	0.03654000
C	2.65908800	-0.03596400	-0.37254800
C	-3.86008400	2.24348500	-0.69969600
H	-4.52855800	3.06670200	-0.93605300

C	0.58960200	-2.34712700	-0.72449500
H	0.05707400	-2.81671000	-1.57245900
H	0.47204800	-3.00036900	0.14698500
C	-0.17236100	1.33675900	-1.00571400
H	0.40169500	1.67162600	-0.13622200
H	0.01366900	2.06329800	-1.80431500
C	-3.52069000	0.03098300	0.19723800
C	-2.50479600	2.33603500	-0.99564100
H	-2.10433500	3.22917800	-1.46774400
C	1.87093500	-0.05764700	-1.66594400
H	2.15496400	0.70525500	-2.39739200
C	-0.92444800	-1.04940800	1.79188600
H	-1.82050500	-0.83356300	2.37923000
H	-0.56540600	-2.05236000	2.07677600
C	2.07291800	-2.21704600	-1.08070400
H	2.48695600	-3.19097500	-1.35480500
C	-5.31155800	-1.29348200	1.07993900
H	-5.92226300	-1.23484600	0.17119500
H	-5.65404600	-0.53727700	1.79614600
H	-5.41111300	-2.28528500	1.52271400
C	2.99877800	1.10055800	0.28036100
C	2.87630400	-1.48612100	0.01753700
H	3.92640600	-1.80315100	-0.03165800
H	2.50455500	-1.73829600	1.01927600
C	0.33999300	-0.03208700	-1.44107300
H	-0.13855300	-0.30086800	-2.40266600
C	-4.38010600	1.09083700	-0.10319700
H	-5.43834700	1.03007200	0.11923100
H	0.67364700	-0.13586900	1.32305000
C	4.94339300	0.28446100	1.54634800
H	5.47166600	0.38139300	0.59126400
H	5.55483800	0.70446500	2.34924100
H	4.76703800	-0.77523400	1.75223900
Li	3.53446200	3.05803900	1.53604200

INT6

Sum of electronic energy and thermal correction to G: -1137.378367 a.u.

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O	2.31111700	2.35256800	1.35707500
O	3.81062600	-1.31623700	-0.89422200
O	-3.67325200	0.52615000	-1.45258100
O	0.41790000	-1.01665900	-1.46850800
O	2.30823900	-2.07576000	0.68520200
N	0.18597700	1.17287800	-0.09512600

C	-2.03617200	0.06626800	0.16606200
C	-1.64120000	-0.51704600	1.37158300
C	-1.05862500	0.77242200	-0.74755100
H	-1.56360000	1.64409100	-1.18183400
C	2.72690000	0.27444500	0.38632400
C	-3.89739300	-1.31631200	1.73782800
H	-4.62220700	-1.84675400	2.34888900
C	3.98239500	-2.67134200	-1.28265500
H	4.24906900	-3.31096500	-0.43529200
H	4.79889500	-2.66859100	-2.00946300
H	3.08756500	-3.08767900	-1.76388100
C	0.78891900	2.43146600	-0.53411800
H	0.24028500	3.29998800	-0.12607900
H	0.74327700	2.49073900	-1.62697200
C	-0.21035600	-0.37513000	1.81328500
H	0.41171100	-1.20966600	1.47518300
H	-0.15642700	-0.39061200	2.90803800
C	-3.37849600	-0.05740600	-0.25138000
C	-2.57768200	-1.20403400	2.15881000
H	-2.26209000	-1.64037300	3.10268300
C	1.94590700	0.95588700	1.50359900
H	2.21607800	0.64914700	2.52055800
C	-0.64561300	-0.17557600	-1.91883700
H	-1.47572300	-0.80543300	-2.24125700
H	-0.30023400	0.41845500	-2.77550000
C	2.25941600	2.52566700	-0.07147400
H	2.65003000	3.52137100	-0.30002500
C	-5.01604500	0.45976400	-1.92218200
H	-5.70542300	0.94944000	-1.22448900
H	-5.33202800	-0.57853600	-2.07663800
H	-5.02456100	0.98907400	-2.87563400
C	2.89906600	-1.05854000	0.14410100
C	3.14155300	1.37334300	-0.57512900
H	4.20057100	1.66891400	-0.50608000
H	2.94437900	1.12394200	-1.62521600
C	0.41050500	0.92678900	1.32695800
H	-0.00269100	1.75444500	1.93181300
C	-4.31053000	-0.74183100	0.53140400
H	-5.34274000	-0.83314500	0.21666400
H	0.97333500	-0.38387400	-0.92877700
Li	0.75945600	-2.57921200	-0.32543400

INT7

Sum of electronic energy and thermal correction to G: -1137.293226 a.u.

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O	2.31805500	-1.49590800	-2.02368600
O	3.57651300	0.41824300	2.05609400
O	-4.01617000	-0.97159900	0.46478200
O	-0.09515200	-0.36912300	2.17522900
O	2.98064400	1.92965500	0.46631000
N	0.05019600	-1.13782500	-0.38916700
C	-2.06021800	0.17424000	-0.15183100
C	-1.41020700	1.32933900	-0.59181400
C	-1.29961100	-1.08949000	0.18177700
H	-1.89369100	-1.94239200	-0.17477100
C	2.70892000	-0.40104700	-0.01653900
C	-3.52627100	2.49740500	-0.69972400
H	-4.09801300	3.39569900	-0.91541700
C	0.49947400	-2.46727200	-0.78481100
H	0.01906300	-2.80189800	-1.72296500
H	0.23589400	-3.18368400	0.00072100
C	0.08375400	1.28171200	-0.76611300
H	0.58548000	1.47178200	0.18776400
H	0.41512900	2.06082000	-1.46112500
C	-3.45948300	0.19645900	0.01962300
C	-2.14652800	2.48845600	-0.87199000
H	-1.62997300	3.37685000	-1.22530200
C	2.06050100	-0.22925400	-1.37160700
H	2.47117900	0.56000700	-2.00819400
C	-1.11476800	-1.24431100	1.71799700
H	-2.03921900	-1.00263800	2.24824500
H	-0.85912300	-2.29335000	1.94059700
C	2.01843100	-2.44663400	-0.98213000
H	2.37623800	-3.42467900	-1.31406700
C	-5.42804900	-1.02085100	0.63916600
H	-5.95282800	-0.83349600	-0.30511400
H	-5.76194100	-0.29476700	1.38978200
H	-5.65057200	-2.03079600	0.98570000
C	3.12050300	0.54229000	0.85884900
C	2.75167500	-1.89096500	0.25616900
H	3.77694200	-2.28450900	0.30491600
H	2.24741000	-2.17947500	1.18761200
C	0.52064900	-0.08306800	-1.28532200
H	0.12306100	-0.21688700	-2.30971700
C	-4.19438200	1.35297300	-0.25426100
H	-5.26963200	1.37282800	-0.12608300
H	0.59410400	-0.44520500	1.47785300
C	4.07418900	2.40414000	-0.32619200

H	4.08354000	1.91947500	-1.30826100
H	3.93702900	3.48045500	-0.45495100
H	5.03200300	2.21663900	0.17570900
Li	3.20132500	2.19636900	2.53797200

INT8

Sum of electronic energy and thermal correction to G: -1137.305513 a.u.

==========

O	2.50256000	-1.64944400	-1.95806500
O	3.28352900	0.90049100	1.89278400
O	-3.77182600	-1.04859200	0.79986100
O	0.34048900	-0.05276400	1.92230900
O	2.95893600	2.07647800	-0.06537700
N	0.18056600	-1.20377700	-0.43373600
C	-1.95738300	0.04414100	-0.21208500
C	-1.42021300	1.11906200	-0.92387300
C	-1.09550900	-1.10132100	0.26772100
H	-1.67192900	-2.02730000	0.14593300
C	2.73524300	-0.24715800	-0.11414700
C	-3.61352000	2.13070300	-1.06980000
H	-4.25945700	2.93672400	-1.40641900
C	0.71519700	-2.54668300	-0.61816200
H	0.27745200	-3.04378000	-1.50282200
H	0.47728800	-3.15375600	0.26156300
C	0.06063900	1.13302400	-1.19257000
H	0.59025500	1.54369900	-0.32747200
H	0.29204200	1.78613700	-2.04059100
C	-3.33591400	0.03070500	0.08138100
C	-2.25354000	2.15881900	-1.35838700
H	-1.82708300	2.98543600	-1.92000600
C	2.14971200	-0.31895600	-1.50605800
H	2.53864200	0.39723500	-2.23559400
C	-0.74695000	-0.96912000	1.78477600
H	-1.59638500	-0.59534700	2.35919800
H	-0.45904900	-1.95291300	2.18102000
C	2.23619200	-2.45549100	-0.79404400
H	2.66370900	-3.44603100	-0.97089200
C	-5.16002700	-1.13813900	1.10419400
H	-5.76550400	-1.17451100	0.19098800
H	-5.48659100	-0.29414000	1.72301600
H	-5.28364000	-2.06753300	1.66128800
C	3.00729100	0.86128500	0.63130700
C	2.89142800	-1.67721300	0.36498900
H	3.94421800	-1.97592000	0.48113900

H	2.39047600	-1.89782900	1.31784200
C	0.59351600	-0.26680400	-1.47856000
H	0.22950200	-0.59341800	-2.47025000
C	-4.16658700	1.06897300	-0.34777500
H	-5.22732000	1.06036800	-0.12944900
H	0.87522800	-0.21358600	1.09440800
Li	1.87369600	0.45463700	3.03730100
C	2.69817500	3.23212000	0.72246900
H	3.44408900	3.36637200	1.51059700
H	2.73046400	4.08012600	0.03416200
H	1.70252800	3.18547300	1.18623100

INT9

Sum of electronic energy and thermal correction to G: -1137.308679 a.u.

==========

O	2.32485000	1.48610700	1.83301800
O	4.47562100	-0.69262400	-0.00492000
O	-4.01592600	0.95799800	-0.85745500
O	-0.12385300	-0.52553200	-2.02442300
O	3.08830900	-1.59269100	-1.53092900
N	-0.15486100	1.15513000	0.53091300
C	-2.19394000	-0.14418300	0.14672600
C	-1.67431300	-1.20856200	0.88983800
C	-1.27624300	0.93592400	-0.37801000
H	-1.85342000	1.86964700	-0.42393700
C	2.27939400	0.21691400	-0.18904600
C	-3.88437200	-2.16326800	1.11314200
H	-4.54362300	-2.94075700	1.48930600
C	5.50296700	-1.62478200	-0.40943500
H	5.16549300	-2.65007500	-0.24502500
H	6.36215800	-1.39679900	0.21918500
H	5.74683000	-1.48069900	-1.46385100
C	0.43530900	2.46875400	0.66970500
H	0.08039800	2.98933700	1.58132000
H	0.15733000	3.08530300	-0.19096800
C	-0.18710900	-1.24237400	1.12797500
H	0.29710500	-1.63308300	0.22807300
H	0.05880300	-1.91279200	1.95847800
C	-3.57685300	-0.10860200	-0.11789800
C	-2.51968200	-2.21207600	1.37993500
H	-2.10208300	-3.02717100	1.96523400
C	1.90632100	0.20807300	1.32614200
H	2.39614000	-0.56435600	1.92436400

C	-0.82373300	0.63894600	-1.85028600
H	-1.75585900	0.68030800	-2.45633500
H	-0.23976200	1.54074000	-2.15363400
C	1.97114900	2.38318400	0.76315400
H	2.39677100	3.36231700	0.99893700
C	-5.40777700	1.05872400	-1.12985100
H	-5.99308900	1.13218500	-0.20508000
H	-5.76443900	0.20224600	-1.71490700
H	-5.53299900	1.97266800	-1.71232400
C	3.30694900	-0.77028900	-0.63707900
C	2.62402300	1.70429600	-0.44995400
H	3.70391200	1.87697000	-0.42677900
H	2.22647200	2.04924200	-1.40822000
C	0.36692400	0.15013800	1.43301600
H	0.12233600	0.39987200	2.48334800
C	-4.42269600	-1.11361700	0.36359200
H	-5.48740600	-1.08648200	0.16624100
H	1.38111100	-0.01932700	-0.76193500
Li	1.23731500	-1.55481900	-2.40007500

TS1

Sum of electronic energy and thermal correction to G: -1137.292756 a.u.

==========

O	2.44772300	-1.64776300	-1.84509200
O	3.40931700	0.71874400	1.92016000
O	-3.81963600	-0.87466800	0.98186200
O	0.36998800	0.15471300	1.75406300
O	3.38274300	1.79674900	-0.07745900
N	-0.15138600	-1.30885600	-0.78854000
C	-2.04134000	0.11669800	-0.19564000
C	-1.52486800	1.14942600	-0.98211300
C	-1.16420000	-1.04264200	0.22230800
H	-1.80940800	-1.92988200	0.28035200
C	2.32647300	-0.30472300	0.08780000
C	-3.68795900	2.23102500	-1.01189900
H	-4.33104500	3.04639100	-1.33150300
C	0.49228800	-2.61018900	-0.82569400
H	0.24468300	-3.14304100	-1.76202100
H	0.12433800	-3.22056800	0.00509300
C	-0.05753300	1.12337400	-1.31576500
H	0.49569000	1.53460500	-0.46397900
H	0.15501000	1.77002600	-2.17365200
C	-3.39329100	0.16314000	0.19651600
C	-2.35180100	2.20144500	-1.39770000

H	-1.93998300	2.99461100	-2.01605700
C	2.00561200	-0.34192900	-1.40238700
H	2.51894400	0.40625500	-2.01172800
C	-0.59722100	-0.85957200	1.66158100
H	-1.44239300	-0.64361100	2.33183300
H	-0.18161700	-1.83480400	1.97624800
C	2.02527400	-2.50102300	-0.76350300
H	2.48178200	-3.48329600	-0.91841800
C	-5.18496800	-0.89821200	1.38099100
H	-5.85407700	-0.93993700	0.51313300
H	-5.43816900	-0.02258700	1.99075000
H	-5.30614000	-1.80333100	1.97764600
C	3.11302400	0.71099000	0.69567000
C	2.53919300	-1.77277400	0.48966600
H	3.59817800	-2.00715600	0.65415800
H	1.98831100	-2.07120900	1.38830000
C	0.47509000	-0.28236100	-1.61264200
H	0.28689400	-0.51343200	-2.67676500
C	-4.21864900	1.21622800	-0.21049900
H	-5.26049700	1.25275400	0.08332400
H	1.20340300	-0.02283800	0.85173200
Li	1.77676200	0.43802400	2.99434000
C	3.88565800	2.95645400	0.60090200
H	4.84537100	2.74672500	1.07971100
H	4.00959700	3.71540800	-0.17229100
H	3.17477000	3.30251000	1.35708100

INT10

Sum of electronic energy and thermal correction to G: -1213.73103 a.u.

==========

O	1.96226500	-1.53667200	-1.99431100
O	3.57906300	0.75360000	1.69765900
O	-4.33654800	-1.03042600	0.50812400
O	-0.49577200	-0.33774900	2.25051900
O	2.64296300	2.06608200	0.06246100
N	-0.24773500	-1.11477100	-0.28886900
C	-2.40405400	0.14041700	-0.13571000
C	-1.77949900	1.29430600	-0.61430100
C	-1.62192200	-1.10058800	0.23299600
H	-2.18026000	-1.97240600	-0.13752700
C	2.47201200	-0.25409300	-0.14475500
C	-3.91895500	2.41805600	-0.74145500
H	-4.50908500	3.29908200	-0.97783300
C	0.23885000	-2.45537600	-0.60256500

H	-0.26192000	-2.87318100	-1.49489200
H	0.02813200	-3.11991900	0.24230700
C	-0.28744700	1.26847900	-0.81212800
H	0.22999900	1.51232200	0.12145700
H	0.01502900	2.02173300	-1.54726600
C	-3.80381500	0.13857300	0.03654500
C	-2.54045100	2.43062500	-0.92151200
H	-2.04323000	3.31830500	-1.30312800
C	1.69827000	-0.22259800	-1.44077900
H	2.03907700	0.52351500	-2.16443900
C	-1.48455000	-1.23729100	1.77620700
H	-2.43091300	-1.00726500	2.27095900
H	-1.21910100	-2.27907100	2.02082100
C	1.74488900	-2.39445300	-0.85711200
H	2.13238900	-3.38462300	-1.11025600
C	-5.74631200	-1.10274900	0.69106200
H	-6.27926200	-0.94708500	-0.25438700
H	-6.09039200	-0.36633500	1.42683800
H	-5.94753100	-2.10865500	1.06157200
C	2.91202400	0.81107300	0.60265100
C	2.49150100	-1.70480800	0.30931400
H	3.50315000	-2.12073100	0.41841000
H	1.97365100	-1.87662300	1.26283400
C	0.16259700	-0.11242100	-1.27518400
H	-0.28638800	-0.31872200	-2.26572200
C	-4.56259000	1.27251300	-0.26385200
H	-5.63764100	1.27381400	-0.13248800
H	0.18499000	-0.38209300	1.54146400
O	5.46099800	-0.42756400	-0.28818600
H	5.69325100	-1.33942500	-0.52394800
H	4.49246700	-0.34018800	-0.51037200
C	3.34018000	3.16286500	0.64535200
H	3.10844500	3.27233000	1.70898500
H	4.42629800	3.05866100	0.53254600
H	3.00266100	4.04841200	0.10219200
Li	5.27407300	-0.03393100	1.64506600

TS2

Sum of electronic energy and thermal correction to G: -1213.720091 a.u.

==========

O	1.95970300	-1.63250400	-1.93164300
O	3.60047600	0.77918600	1.67757900
O	-4.29273900	-1.04643800	0.49416700
O	-0.56146700	-0.19674600	2.35477100

O	2.51287500	2.04777900	0.14959900
N	-0.16665200	-1.09518700	-0.14118400
C	-2.35940900	0.12707000	-0.14242100
C	-1.74078200	1.26293100	-0.66826700
C	-1.56889900	-1.07612100	0.32298300
H	-2.09313300	-1.97501600	-0.03173800
C	2.67961600	-0.27094700	-0.23270900
C	-3.89331000	2.33259800	-0.93806600
H	-4.49090300	3.18548300	-1.24743500
C	0.29846900	-2.45654100	-0.41105200
H	-0.24835100	-2.90882400	-1.25731600
H	0.12107300	-3.07687900	0.47417200
C	-0.24240400	1.24934400	-0.81215800
H	0.23007600	1.54458100	0.12827500
H	0.07923300	1.97143100	-1.56969700
C	-3.76452300	0.10485700	-0.02295700
C	-2.50948000	2.36353900	-1.06961200
H	-2.01492000	3.23672100	-1.48633500
C	1.74871600	-0.28808000	-1.44201700
H	2.04317200	0.40477700	-2.23531800
C	-1.50232600	-1.14297400	1.87278900
H	-2.47676800	-0.91684000	2.31056000
H	-1.22280100	-2.16529100	2.17586200
C	1.78807000	-2.42546000	-0.73852600
H	2.15395600	-3.43117600	-0.95852300
C	-5.70744500	-1.14022600	0.62339000
H	-6.20290100	-1.04919200	-0.35038200
H	-6.09664800	-0.37203300	1.30188800
H	-5.90346100	-2.12830700	1.04145800
C	2.90712500	0.84150800	0.63275900
C	2.59464300	-1.68978100	0.35429900
H	3.58625200	-2.13989800	0.47948000
H	2.08309400	-1.73184400	1.32186500
C	0.22662400	-0.15118400	-1.19464500
H	-0.24995700	-0.41910500	-2.15684200
C	-4.53231800	1.20351400	-0.41726800
H	-5.61138200	1.18956500	-0.32581700
H	0.16168600	-0.27593600	1.69520600
O	5.27602800	-0.30609300	-0.61681200
H	5.50617600	-1.22293900	-0.83416600
H	3.99113200	-0.27947600	-0.62832500
C	2.98319300	3.20696800	0.85369600
H	2.63345100	3.20356400	1.88881500
H	4.07594300	3.25169700	0.84140600

H	2.56539000	4.05939800	0.31768400
Li	5.38492800	0.08143100	1.21697300

INT11

Sum of electronic energy and thermal correction to G: -1213.738482 a.u.

==========

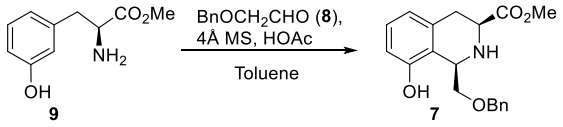
O	2.20193900	-1.65523600	-1.87942300
O	2.08165500	0.43025000	2.03342600
O	-4.17701800	-0.97589800	0.11209100
O	-0.73627100	-0.29733100	2.35698700
O	3.00816700	1.91868600	0.64020300
N	-0.00786500	-1.12568900	-0.17214900
C	-2.16174500	0.16458400	-0.29046100
C	-1.47282400	1.30791100	-0.70022600
C	-1.44808200	-1.09157300	0.16425100
H	-1.95971600	-1.94851600	-0.29926100
C	2.87951300	-0.36562500	-0.08613200
C	-3.56138200	2.47218800	-1.05253900
H	-4.10671900	3.36428800	-1.34702600
C	1.86997400	1.49526200	2.99085900
H	2.83005400	1.91036700	3.30112300
H	1.35643200	1.02309200	3.82552900
H	1.24989600	2.27771100	2.54986200
C	0.44036600	-2.48772200	-0.47401700
H	-0.07437100	-2.89488900	-1.36206400
H	0.20625700	-3.13719400	0.37600100
C	0.03123600	1.24632900	-0.75422400
H	0.43802500	1.49235900	0.23057100
H	0.42320500	1.98486300	-1.46158600
C	-3.57256700	0.18619600	-0.28084900
C	-2.17164200	2.45970900	-1.08342200
H	-1.61917200	3.33705000	-1.40831900
C	1.97952200	-0.33889000	-1.36401000
H	2.34748200	0.37828400	-2.10093800
C	-1.54233400	-1.25987900	1.69951200
H	-2.57217500	-1.12352400	2.03444100
H	-1.23201600	-2.28300300	1.96646200
C	1.94466000	-2.49072400	-0.73037300
H	2.29183800	-3.49662000	-0.97391300
C	-5.60013200	-1.02555500	0.12486300
H	-6.01299300	-0.85026700	-0.87544400
H	-6.01717000	-0.29139300	0.82404600
H	-5.85952800	-2.03183000	0.45570900
C	2.66421600	0.76113300	0.87821600

C	2.72757600	-1.81753100	0.41749000
H	3.70853600	-2.28062000	0.55192900
H	2.18493000	-1.88117500	1.36135700
C	0.46539600	-0.15829400	-1.16696800
H	0.02555600	-0.36378800	-2.16113900
C	-4.27215900	1.33577200	-0.65650400
H	-5.35488200	1.35513800	-0.64636800
H	0.12449100	-0.35221400	1.89810000
Li	4.28267400	2.36325900	-0.82102900
O	5.23627300	1.04632600	-1.52318700
H	4.82173500	0.68312900	-2.32057600
H	3.89182500	-0.17532000	-0.48392900

II. Experimental Procedures and Characterization Data

Synthesis of (–)-quinocarcinol methyl ester

Experimental Procedure for THIQ **7**



Compound **9** (CAS: 167935-97-9) is commercially available, it can be purchased from PUJIMEIHUA. Compound **9** can also be obtained from the esterification of commercially available L-*m*-tyrosine (CAS: 587-33-7, purchased from Leyan) with methanol in a quantitative yield.[4]

Based on a procedure reported by our group.[5] Acetic acid (70 μL, 0.1 mmol, 0.1 equiv) and 4 Å molecular sieves (12.00 g) were added sequentially to a solution of the amine **9** (2.14 g, 11.0 mmol, 1 equiv) in toluene (100 mL; substrate concentration ~0.1 M). The resulting solution was degassed by bubbling with argon for 30min. Then the solution was heated to 80 °C in an oil bath. A solution of benzyloxyacetaldehyde (CAS: 60656-87-3, purchased from Leyan, 1.80 g, 12.0 mmol, 1.1 equiv) in toluene (50 mL) was added slowly via syringe to the solution over 500 min (8.3 h). After 12 h at 80 °C (including the addition period), the reaction suspension was cooled to room temperature, and then filtered to remove the molecular sieves. Saturated aqueous sodium bicarbonate solution (20 mL) was added to the filtrate and the resulting biphasic solution was extracted with dichloromethane (4 × 40 mL). The combined organic extracts were dried over anhydrous sodium sulfate. The dried solution was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by flash-column chromatography (gradient elution 0.25% → 0.5% → 0.7% → 1% methanol–dichloromethane) to afford the THIQ **7** (2.52 g, 70% yield) as pale-yellow foam. The Pictet-Spengler reaction of compound **9** → **7** showed good *cis*-selectivity, no diasteromers of compound **7** were observed.

Compound **7**

R_f-value: 0.3 (20:1 DCM–MeOH)

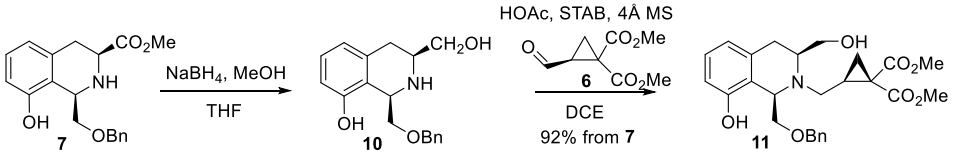
HRMS (ESI) m/z: Calculated for $C_{19}H_{21}NO_4$ $(M+H)^+$: 328.1545, found: 328.1558.

$[\alpha]^{26}_D$ = –34.4 (c 0.5, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39–7.28 (m, 5H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 7.8, 1H), 6.69 (d, *J* = 7.5 Hz, 1H), 4.62 (d, *J* = 11.7 Hz, 1H), 4.57 (t, *J* = 5.1 Hz, 1H), 4.53 (d, *J* = 11.7 Hz, 1H), 3.83–3.77 (m, 2H), 3.77 (s, 3H), 3.60 (dd, *J* = 11.2, 3.1 Hz, 1H), 3.02 (dd, *J* = 15.2, 3.1 Hz, 1H), 2.87 (dd, *J* = 15.2, 11.2 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.0, 154.4, 136.4, 135.9, 128.3, 127.9, 127.8, 127.6, 122.9, 120.8, 115.2, 75.8, 73.4, 54.4, 52.7, 52.0, 33.7.

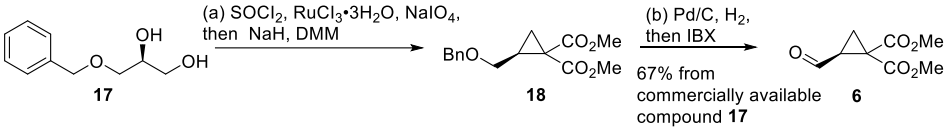
Experimental Procedure for Compound **11**



Reduction of **7**: T To a stirred solution of **7** (1.96 g, 6.0 mol, 1 equiv) in anhydrous THF (12 mL) was added sodium borohydride (2.22 g, 58.7 mol, 10 equiv) at 0°C. After 25min, MeOH (4.2 mL) was added dropwise. After gas evolution ceased, the mixture was stirred under reflux. After 40min, the suspension was concentrated under reduced pressure and water (20 mL) and ethyl acetate (40 mL) was carefully added to the resulting mixture at 0°C. The organic layer was washed with water (20 mL), dried over anhydrous sodium sulfate. The

dried solution was filtered and the filtrate was concentrated under reduced pressure to yield crude **10** which was used without further purification.

Kerr's synthetic route for cyclopropane **6:**



Reduction amination of **10** and **6**: Cyclopropane **6** (1.40 g, 7.5 mmol, 1.2 equiv, prepared using the literature procedure[6]) and 4 Å molecular sieves (6.20 g) were added to a solution of crude **10** in 1,2-dichloroethane (34 mL) and then treated with sodium triacetoxyborohydride (2.30 g, 10.9 mmol, 1.8 equiv) and HOAc (0.38 mL, 6.6 mmol, 1.1 equiv). The mixture was stirred at room temperature under an Ar atmosphere for 12 h until the reactants were consumed as determined by TLC. The reaction mixture was quenched by adding saturated aqueous sodium bicarbonate solution (20 mL), and the product was extracted with ethyl acetate (3 x 25 mL). The combined organic extracts were washed with brine (20 mL) and dried over anhydrous sodium sulfate. The dried solution was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by flash-column chromatography (gradient elution 10:1 → 4:1 petroleum ether–ethyl acetate) to afford compound **11** (2.60 g, 92% yield form **7**) as a white foam.

Compound **11**

R_f-value: 0.7 (50:50 PE–EA)

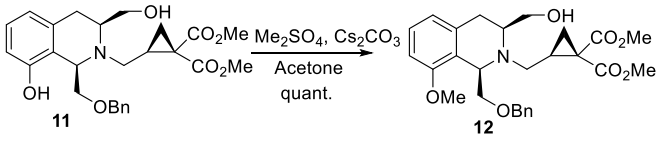
HRMS (ESI) m/z: Calculated for $C_{26}H_{32}N_2O_7$ $(M+H)^+$: 470.2173; Found: 470.2177.

$[\alpha]^{26}_D$ = +54.4 (c 0.5, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36–7.20 (m, 5H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.06 (s, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.74 (d, J = 7.4 Hz, 1H), 4.52 (s, 2H), 4.41 (dd, *J* = 10.2, 4.5 Hz, 1H), 3.84 (dd, J = 8.2, 4.5 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.64 (d, *J* = 11.1 Hz, 1H), 3.47 (t, *J* = 9.3 Hz, 1H), 3.32 (d, *J* = 11.1 Hz, 1H), 2.85 (dd, *J* = 14.0, 6.6 Hz, 1H), 2.89–2.71 (m, 3H), 2.63 (dd, *J* = 12.6, 6.0 Hz, 2H), 2.13 (p, *J* = 7.5 Hz, 1H), 1.55–1.44 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.3, 168.7, 153.9, 137.0, 136.5, 128.7, 128.3, 128.2, 127.9, 124.1, 120.4, 115.8, 77.0, 73.8, 62.9, 59.1, 55.6, 54.0, 53.02, 52.96, 32.7, 30.9, 26.8, 20.9.

Experimental Procedure for Compound **12**



To a solution of compound **11** (669.9 mg, 1.4 mmol, 1 equiv) in 14 mL of acetone, dimethyl sulfite (415 µL, 4.3 mmol, 3 equiv) and cesium carbonate (465.9 mg, 1.4 mmol, 1 equiv) were added sequentially at 0 °C. The mixture was stirred at room temperature for 6 h and then concentrated under reduced pressure. The residue so obtained was partitioned between ethyl acetate (20 mL) and water (10 mL). The two layers were separated, and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous sodium sulfate. The dried solution was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by flash-column chromatography (gradient elution 10:1 → 4:1 petroleum ether–ethyl acetate) to afford **12** (689.6 mg, quant. yield) as colorless oil.

Compound **12**

R_f-value: 0.35 (4:1 PE–EA)

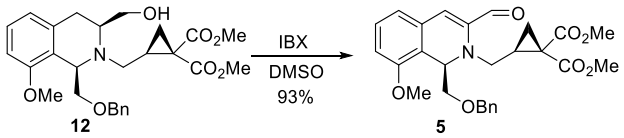
HRMS (ESI) m/z: Calculated for $C_{27}H_{34}NO_7$ $(M+H)^+$: 484.2330; Found: 484.2332.

$[\alpha]^{26}_D$ = +20.8 (c 0.5, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35–7.27 (m, 5H), 7.16 (t, *J* = 7.9 Hz, 1H), 6.74 (t, *J* = 8.5 Hz, 2H), 4.67 (dd, *J* = 8.9, 5.0 Hz, 1H), 4.53 (s, 2H), 3.80 (s, 3H), 3.75 (s, 3H), 3.67 (s, 3H), 3.67–3.63 (m, 1H), 3.47 (dd, *J* = 9.7, 5.0 Hz, 1H), 3.40 (d, *J* = 9.2 Hz, 1H), 3.32 (dd, *J* = 10.7, 2.4 Hz, 1H), 3.00–2.80 (m, 3H), 2.60 (dd, *J* = 14.9, 4.6 Hz, 1H), 2.51 (dd, *J* = 13.8, 7.7 Hz, 1H), 2.18 (qd, *J* = 8.1, 5.4 Hz, 1H), 1.48 (d, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.5, 168.6, 156.0, 138.6, 137.9, 128.4, 127.9, 127.6, 127.5, 124.1, 120.3, 108.2, 73.5, 72.8, 62.9, 59.7, 55.5, 55.1, 54.4, 52.8, 52.7, 32.4, 30.2, 27.2, 21.6.

Experimental Procedure for Compound **5**



12 **5**

The compound **12** (80.2 mg, 0.16 mmol, 1 equiv) was dissolved in DMSO (0.7 mL) and treated with iodoxybenzoic acid (111.0 mg, 0.40 mmol, 2.5 equiv). The mixture was stirred at room temperature under an Ar atmosphere for 2 h until the reactants were consumed as determined by TLC. The reaction mixture was diluted with water (1 mL) and filtered through a pad of Celite (washed with 5 mL of ethyl acetate). The resulting biphasic solution was extracted with dichloromethane (3 × 2 mL). The combined organic extracts were washed with water (1 mL), saturated aqueous sodium bicarbonate solution (1 mL) and brine (1 mL), dried over anhydrous sodium sulfate. The dried solution was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by flash-column chromatography (gradient elution 10:1 → 4:1 petroleum ether–ethyl acetate) to afford compound **5** (74.0 mg, 93%) as a yellow oil.

Compound **12**

R_f-value: 0.35 (4:1 PE–EA)

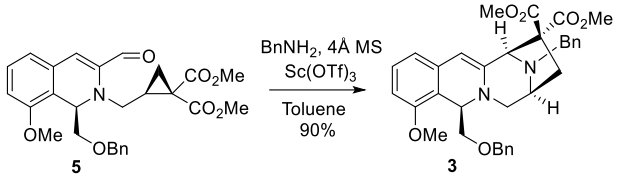
HRMS (ESI) m/z: Calculated for $C_{27}H_{30}NO_7$ $(M+H)^+$: 480.2017; Found: 480.2016.

$[\alpha]^{26}_D$ = –8.4 (c 0.5, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.29 (s, 1H), 7.37–7.13 (m, 5H), 6.81 (dd, *J* = 11.4, 7.9 Hz, 2H), 6.41 (s, 1H), 4.97 (dd, *J* = 8.7, 3.6 Hz, 1H), 4.50 (s, 2H), 3.89 (dd, *J* = 15.1, 8.6 Hz, 1H), 3.82 (s, 3H), 3.70 (s, 3H), 3.66 (s, 3H), 3.55 (dd, *J* = 15.0, 5.1 Hz, 1H), 3.54–3.44 (m, 1H), 3.23 (dd, *J* = 10.2, 3.6 Hz, 1H), 2.16 (dd, *J* = 8.4, 5.2 Hz, 1H), 1.46 (dd, *J* = 7.7, 4.8 Hz, 1H), 1.34 (dd, *J* = 9.1, 4.8 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.6, 170.5, 168.4, 155.0, 141.4, 132.5, 128.6, 128.4, 127.4, 124.6, 118.2, 111.2, 73.1, 70.5, 57.4, 55.5, 52.7, 52.6, 51.1, 32.7, 28.4, 20.7.

Experimental Procedure for Compound **3**



5 **3**

A mixture of compound **5** (797.1 mg, 1.66 mmol, 1 equiv), benzylamine (355.9 mg, 3.32 mmol, 2 equiv) in toluene (33 mL) were stirred in the presence of 4Å molecular sieves (3.70 g) at room temperature under argon for 10 min, then $Sc(OTf)_3$ (162.4 mg, 0.33 mmol, 0.2 equiv) was added. The mixture was stirred for another

30 min until the reactants were consumed as determined by TLC. The reaction suspension was filtered through a pad of Celite (washed with 20 mL of dichloromethane). The filtrate was concentrated under reduced pressure. The residue was purified by flash-column chromatography (gradient elution 20:1 → 10:1 petroleum ether–ethyl acetate) to afford compound **3** (850.4 mg, 90%) as white foam.

Compound **3**

R_f-value: 0.6 (4:1 PE–EA)

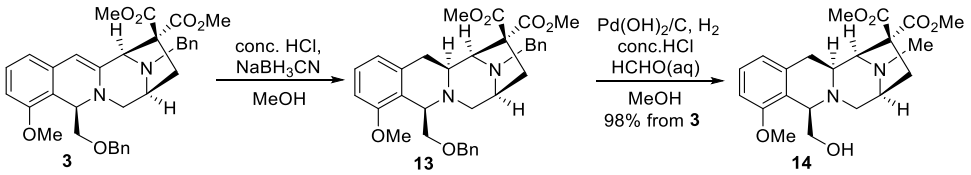
HRMS (ESI) m/z: Calculated for $C_{34}H_{37}N_2O_6$ $(M+H)^+$: 569.2648; Found: 569.2646.

$[\alpha]^{26}_D$ = +90.8 (c 0.5, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46–7.21 (m, 11H), 7.06 (t, *J* = 7.9 Hz, 1H), 6.54 (d, *J* = 8.3, 1H), 6.44 (d, *J* = 7.7, 1H), 4.94 (s, 1H), 4.86 (dd, *J* = 9.5, 2.5 Hz, 1H), 4.79 (d, *J* = 11.4 Hz, 1H), 4.43 (d, *J* = 11.4 Hz, 1H), 4.03 (s, 1H), 3.84 (t, *J* = 9.3 Hz, 1H), 3.80 (s, 2H), 3.79 (s, 3H), 3.75 (s, 3H), 3.67 (s, 3H), 3.58 (dd, *J* = 11.3, 3.1 Hz, 1H), 3.46–3.39 (m, 2H), 3.32 (d, *J* = 11.2, 1H), 3.23 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.04 (d, *J* = 13.6 Hz, 1H), 2.75 (dd, *J* = 13.5, 7.6 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.6, 168.5, 155.1, 139.2, 138.6, 138.0, 135.2, 128.6, 128.4, 128.2, 127.8, 127.4, 127.0, 115.7, 113.3, 106.3, 96.9, 73.3, 72.8, 65.1, 65.0, 56.6, 55.3, 53.0, 52.9, 51.4, 49.3, 36.3.

Experimental Procedure for Compound **14**



Sodium cyanoborohydride (446.4 mg, 7.10 mmol, 5.5 equiv) was added in small portions to a stirred solution of **3** (747.3 mg, 1.31 mmol, 1 equiv) and 37% aqueous hydrochloric acid (50 μL) in MeOH (50 ml) at 0°C. The reaction was maintained at 0 °C for 15 min, and then quenched with saturated aqueous sodium bicarbonate solution (25 mL) followed by dichloromethane (25 mL). The cloudy white mixture was vigorously stirred for 5 min. The biphasic mixture was extracted with dichloromethane (3 x 25 mL). The combined organic extracts were washed with brine (25 mL) and dried over anhydrous sodium sulfate. The dried solution was filtered and the filtrate was concentrated under reduced pressure. The crude product was re-dissolved in MeOH (16.5 mL), 37% aqueous hydrochloric acid (0.2 mL) and moist 10% w/w $Pd(OH)_2$ on carbon (≤50% water) (0.39 g, 0.28 mmol, 0.2 equiv) were then added. The flask was evacuated and purged with H_2 gas three times and a hydrogen balloon was attached. The reaction was maintained at 23 °C for 2 h, at which point a 37% w/w aqueous solution of formaldehyde (5 mL, 50 mmol, 50 equiv) were added via syringe. The reaction was maintained at 23 °C under hydrogen for an additional 2 h, and then filtered through a plug of Celite eluting with 10:1 CH_2Cl_2-MeOH (10 mL). The solvent was removed under reduced pressure and the residue was purified via flash-column chromatography (gradient elution 4:1 → 1:1 petroleum ether–ethyl acetate) to afford compound **14** (523.5 mg, 98% yield) as colorless oil.

Compound **14**

R_f-value: 0.2 (4:1 PE–EA)

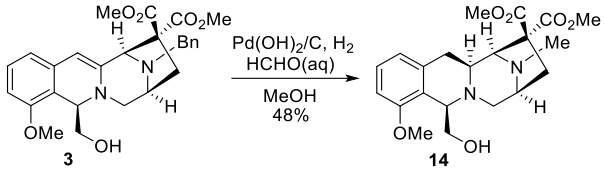
HRMS (ESI) m/z: Calculated for $C_{21}H_{29}N_2O_6$ $(M+H)^+$: 405.2020; Found: 405.2025.

$[\alpha]^{26}_D$ = –68.0 (c 0.5, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 (t, *J* = 7.9 Hz, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 3.92 (s, 1H), 3.83 (s, 2H), 3.79 (s, 3H), 3.75 (s, 3H), 3.72 (s, 3H), 3.50 (d, *J* = 22.1 Hz, 2H), 3.25 (d, *J* = 7.1 Hz, 1H), 3.15 (d, *J* = 12.1 Hz, 1H), 2.98 (d, *J* = 13.3 Hz, 1H), 2.90 (d, *J* = 11.1 Hz, 1H), 2.80 (d, *J* = 11.0

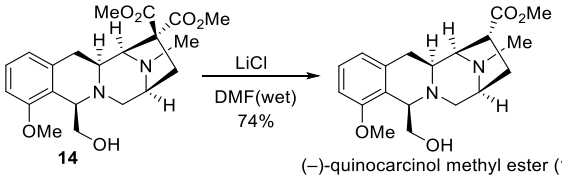
Hz, 1H), 2.61 (dd, *J* = 13.4, 7.1 Hz, 1H), 2.46 (s, 3H), 2.37 (d, *J* = 13.7 Hz, 1H), 2.28 (d, J = 12.9 Hz, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.7, 171.1, 156.0, 138.4, 127.3, 123.8, 119.9, 108.4, 69.1, 63.6, 62.5, 61.1, 59.4, 55.2, 53.9, 53.1, 53.0, 37.2, 36.1, 32.9.

Experimental Procedure for Compound 1**4** by One-pot Method



Compound **3** (850.4 mg, 1.5 mmol 1.0 equiv) was dissolved in MeOH (15 mL), and moist 10% w/w $Pd(OH)_2$ on carbon (≤50% water) (0.4 g, 0.28 mmol, 0.2 equiv) were then added. The flask was evacuated and purged with H_2 gas three times and a hydrogen balloon was attached. The reaction was maintained at 23 °C for 16 h, at which point a 37% w/w aqueous solution of formaldehyde (5.6 mL, 50 mmol, 50 equiv) were added via syringe. The reaction was maintained at 23 °C under hydrogen for an additional 8 h, and then filtered through a plug of Celite eluting with 10:1 CH_2Cl_2–MeOH (10 mL). The solvent was removed under reduced pressure and the residue was purified via flash-column chromatography (gradient elution 4:1 → 1:1 petroleum ether–ethyl acetate) to afford compound **14** (291.5 mg, 48% yield) as colorless oil.

Experimental Procedure for Compound **1**



A mixture of **14** (19.1 mg, 0.047 mmol, 1 equiv), LiCl (8.5 mg, 0.2 mmol, 4 equiv) and wet DMF (1% w/w water was added, 2 mL) was heated at 160 °C in an oil bath for 1 h. Then, the mixture was cooled to room temperature and diluted with water (2 mL) and extracted with ethyl ester (4 × 2 mL). The combined organic extracts were washed with water (2 mL) and brine (2 mL), dried over anhydrous sodium sulfate. The dried solution was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by flash-column chromatography (gradient elution 1% → 2% methanol–dichloromethane) to afford compound **1** (12.1 mg, 74% yield) as a pale-yellow oil.

<u>Compound **1**</u>

R_f-value: 0.2 (20:1 CH_2Cl_2–MeOH)

HRMS (ESI) m/z: Calculated for $C_{21}H_{29}N_2O_6$ $(M+H)^+$: 347.1965; Found: 347.1968.

IR (film): ν_{max} = 2949, 1732 (C=O), 1591, 1472, 1437, 1221, 1066 cm^{-1}. The value reported in the literature[7]: IR (neat): 1731 (C=O)

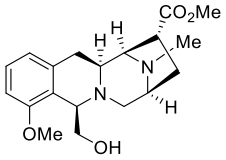
$[\alpha]^{28}_D$ = –90.0 (c 1.0, $CHCl_3$) The value reported in the literature[7]: $[\alpha]^{26}_D$ = –41.3 (c 0.61, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (t, *J* = 7.9 Hz, 1H), 6.71 (dd, *J* = 7.9, 4.9 Hz, 2H), 3.76–3.85 (m, 4H), 3.80 (s, 3H), 3.74 (s, 3H), 3.46 (s, 1H), 3.30 (br s, 1H), 3.18 (dd, *J* = 9.9, 5.7 Hz, 1H), 2.94–2.86 (m, 2H), 2.72–2.55 (m, 3H), 2.52 (dd, *J* = 15.3, 2.6 Hz, 1H), 2.36 (s, 3H), 1.98 (dd, *J* = 13.0, 9.7 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.3, 155.9, 137.0, 127.3, 123.8, 120.7, 108.3, 69.8, 62.3, 62.1, 60.2, 58.2, 56.2, 55.2, 52.2, 43.0, 40.3, 33.5, 29.9.

NMR data were identical to those reported in the literature.[7]

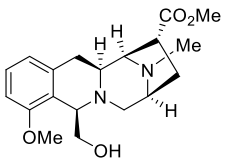
Table S1. Comparison of ^{1}H NMR data for published and synthetic **1**.



(–)-quinocarcinol methyl ester (**1**)

	Published δ_H **(ppm), 500 MHz, $CDCl_3$**	**Synthetic** δ_H **(ppm), 400 MHz, $CDCl_3$**	**Err** $\Delta\delta_H$ **(ppm)**
1	7.13 (dd, *J* = 8.0, 7.4 Hz, 1H)	7.13 (t, *J* = 7.9 Hz, 1H)	0.00
2	6.73–6.70 (m, 2H)	6.71 (dd, *J* = 7.9, 4.9 Hz, 2H)	-
3	3.84–3.73 (m, 4H)	3.76–3.85 (m, 4H)	-
4	3.80 (s, 3H)	3.80 (s, 3H)	0.00
5	3.74 (s, 3H)	3.74 (s, 3H)	0.00
6	3.47–3.45 (br m, 1H)	3.46 (s, 1H)	-
7	3.32–3.29 (br m, 1H)	3.30 (br s, 1H)	-
8	3.18 (dd, *J* = 9.7, 5.7 Hz, 1H)	3.18 (dd, *J* = 9.9, 5.7 Hz, 1H)	0.00
9	2.92–2.86 (m, 2H)	2.94–2.86 (m, 2H)	-
10	2.75–2.57 (m, 3H)	2.72–2.55 (m, 3H)	-
11	2.52 (dd, *J* = 15.2, 2.6 Hz, 1H)	2.52 (dd, *J* = 15.3, 2.6 Hz, 1H)	0.00
12	2.34 (s, 3H)	2.34 (s, 3H)	0.00
13	1.98 (dd, *J* = 13.2, 9.7 Hz, 1H)	1.98 (dd, *J* = 13.0, 9.7 Hz, 1H)	0.00

Table S2. Comparison of ^{13}C NMR data for published and synthetic **1**.



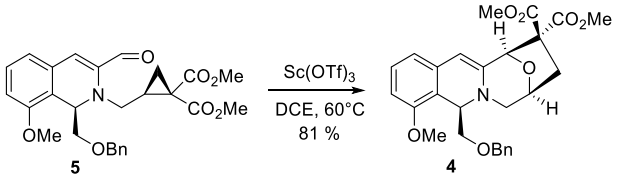
(–)-quinocarcinol methyl ester (**1**)

	Published Δ_C **(ppm), 125 MHz, $CDCl_3$**	**Synthetic** Δ_C **(ppm), 101 MHz, $CDCl_3$**	**Err** $\Delta\delta_C$ **(ppm)**
1	176.25	176.30	0.05
2	155.85	155.87	0.02
3	136.96	137.00	0.04
4	127.24	127.28	0.04
5	123.74	123.75	0.01
6	120.67	120.70	0.03
7	108.25	108.28	0.03

8	69.78	69.83	0.05
9	62.25	62.27	0.02
10	62.03	62.08	0.05
11	60.19	60.21	0.02
12	58.14	58.18	0.04
13	56.13	56.18	0.05
14	55.10	55.15	0.05
15	52.18	52.24	0.06
16	42.94	42.96	0.02
17	40.26	40.33	0.07
18	33.47	33.50	0.03
19	29.86	29.87	0.01

Synthesis of (–)-quinocarcinol methyl ester oxa-analogue

Experimental Procedure for Compound **4**



Compound **5** (508.7 mg, 1.06 mmol, 1 equiv) was dissolved in DCE (21 mL), then $Sc(OTf)_3$ (103.4 mg, 0.21 mmol, 0.2 equiv) was added to the solution at room temperature under argon. The mixture was then stirred at 60°C in an oil bath for another 30 min until the reactants were consumed as determined by TLC. The reaction suspension was filtered through a pad of Celite (washed with 20 mL of dichloromethane). The filtrate was concentrated under reduced pressure. The residue was purified by flash-column chromatography (gradient elution 20:1 → 10:1 petroleum ether–ethyl acetate) to afford compound **4** (412.9 mg, 81%) as white foam.

Compound **4**

R_f-value: 0.5 (4:1 PE–EA)

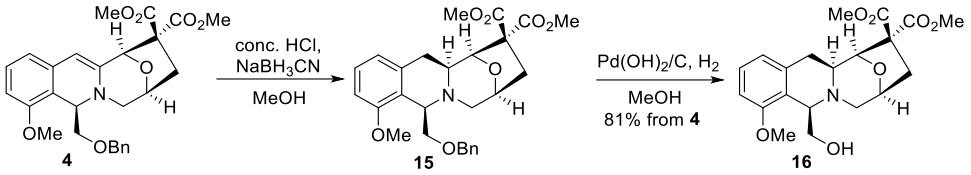
HRMS (ESI) m/z: Calculated for $C_{27}H_{29}NNaO_7$ $(M+Na)^+$: 502.1836; Found: 502.1842.

$[\alpha]^{30}_D = -11.2$ (c1.0, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 6.7 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.54 (d, *J* = 8.2 Hz, 1H), 6.47 (d, *J* = 7.7 Hz, 1H), 5.02 (d, *J* = 3.2 Hz, 2H), 4.83 (dd, *J* = 9.7, 2.5 Hz, 1H), 4.78 (d, *J* = 11.4 Hz, 1H), 4.57 (dd, *J* = 6.0, 1.9 Hz, 1H), 4.45 (d, *J* = 11.4 Hz, 1H), 3.82 (t, *J* = 9.3 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.71 (s, 3H), 3.54 (dd, *J* = 10.7, 3.2 Hz, 1H), 3.34 (dd, *J* = 10.7, 1.1 Hz, 1H), 3.27–3.18 (m, 2H), 2.59 (dd, *J* = 13.4, 7.9 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.1, 167.4, 155.2, 139.1, 137.8, 134.9, 128.5, 128.4, 127.8, 127.4, 116.1, 113.3, 107.0, 95.5, 79.3, 75.9, 73.4, 72.8, 66.9, 56.4, 55.3, 54.5, 53.3, 53.2, 35.5.

Experimental Procedure for Compound **16**



Sodium cyanoborohydride (237.0 mg, 3.80 mmol, 5.5 equiv) was added in small portions to a stirred solution of **3** (330.8 mg, 0.69 mmol, 1 equiv) and 37% aqueous hydrochloric acid (26 μL) in MeOH (26 ml) at 0°C. The reaction was maintained at 0 °C for 15 min, and then quenched with saturated aqueous sodium bicarbonate solution (10 mL) followed by dichloromethane (10 mL). The cloudy white mixture was vigorously stirred for 5 min. The biphasic mixture was extracted with dichloromethane (3 x 25 mL). The combined organic extracts were washed with brine (25 mL) and dried over anhydrous sodium sulfate. The dried solution was filtered and the filtrate was concentrated under reduced pressure. The crude product was re-dissolved in MeOH (8.7 mL), and moist 10% w/w $Pd(OH)_2$ on carbon (≤50% water) (0.57 g, 0.41 mmol, 0.6 equiv) were then added. The flask was evacuated and purged with H_2 gas three times and a hydrogen balloon was attached. The reaction was maintained at 23 °C for 2 h, and then filtered through a plug of Celite eluting with CH_2Cl_2 (10 mL). The solvent was removed under reduced pressure and the residue was purified via flash-column chromatography (gradient elution 4:1 → 1:1 petroleum ether–ethyl acetate) to afford compound **16** (218.3 mg, 81% yield) as white solid. m.p.: 157-160 °C

Compound **16**

R_f-value: 0.1 (4:1 PE–EA)

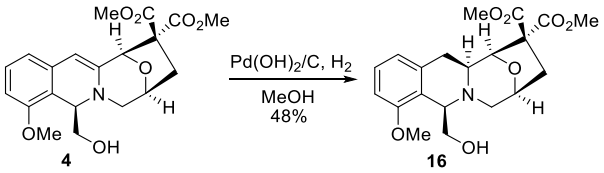
HRMS (ESI) m/z: Calculated for $C_{20}H_{26}NO_7$ $(M+H)^+$: 392.1704; Found: 392.1702.

$[\alpha]^{30}_D = -134.9$ (c 0.5, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 (t, *J* = 7.9 Hz, 1H), 6.71 (d, *J* = 8.3 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 4.86 (d, *J* = 1.9 Hz, 1H), 4.46 (dq, *J* = 7.7, 1.7 Hz, 1H), 3.86–3.80 (m, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 3.75 (s, 3H), 3.57 (td, *J* = 11.6, 10.6, 3.5 Hz, 1H), 3.39–3.32 (m, 1H), 3.11 (dd, *J* = 13.2, 1.3 Hz, 1H), 2.99 (ddd, *J* = 13.3, 10.8, 2.0 Hz, 2H), 2.81 (dd, *J* = 11.2, 2.2 Hz, 1H), 2.56–2.43 (m, 2H), 2.29–2.17 (m, 1H).

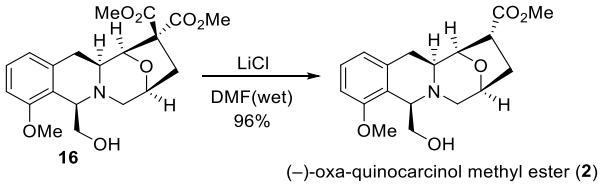
^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.8, 169.6, 156.0, 137.5, 127.4, 123.3, 119.9, 108.5, 81.8, 75.7, 63.6, 63.1, 60.7, 60.4, 58.2, 55.2, 53.2, 53.1, 37.9, 31.7.

Experimental Procedure for Compound 1**6** by One-pot Method



Following the experimental procedure for compound **14** by one-pot method, after column chromatography separation, 64.4 mg compound **16** was obtained from 169.4 mg compound **4** (47% yield).

Experimental Procedure for Compound **2**



A mixture of **16** (28.0 mg, 0.07 mmol, 1 equiv), LiCl (12.1 mg, 0.28 mmol, 4 equiv) and wet DMF (1% w/w water was added, 2 mL) was heated at 160 °C in an oil bath for 1 h. Then, the mixture was cooled to room temperature and diluted with water (2 mL) and extracted with ethyl ester (4 × 2 mL). The combined organic extracts were washed with water (2 mL) and brine (2 mL), dried over anhydrous sodium sulfate. The dried solution was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by flash-column chromatography (gradient elution 10:1 → 2:1 petroleum ether–ethyl acetate) to afford compound **2** (22.8 mg, 96% yield) as a white solid. m.p.: 133-137 °C

Compound **2**

R_f-value: 0.5 (1:1 PE–EA)

HRMS (ESI) m/z: Calculated for $C_{18}H_{24}NO_5$ $(M+H)^+$: 334.1649; Found: 334.1653.

IR (film): ν_{max} = 2924, 1733 (C=O), 1591, 1473, 1437, 1221, 1052 cm-1.

$[\alpha]^{30}_D$ = –73.6 (c 0.5, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 (t, *J* = 7.9 Hz, 1H), 6.72 (t, *J* = 8.2 Hz, 2H), 4.51 (dd, *J* = 7.2, 2.1 Hz, 1H), 4.46–4.41 (m, 1H), 3.84 (br s, 1H), 3.81 (s, 3H), 3.79–3.76 (m, 2H), 3.74 (s, 3H), 3.28 (dd, *J* = 9.6, 5.0 Hz, 1H), 2.90 (dd, *J* = 11.3, 1.8 Hz, 1H), 2.86 (ddd, *J* = 10.7, 3.5, 2.1 Hz, 1H), 2.68 (dd, *J* = 11.3, 2.2 Hz, 1H), 2.63–2.51 (m, 2H), 2.44 (ddd, *J* = 12.3, 7.2, 5.0 Hz, 1H), 2.13 (dd, *J* = 12.4, 9.6 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.0, 156.0, 136.7, 127.5, 123.4, 120.8, 108.5, 81.5, 75.9, 62.5, 60.4, 58.8, 56.5, 55.3, 52.4, 43.4, 32.7, 32.3.

2D NMR Correlations Analyses of Compound **2**:

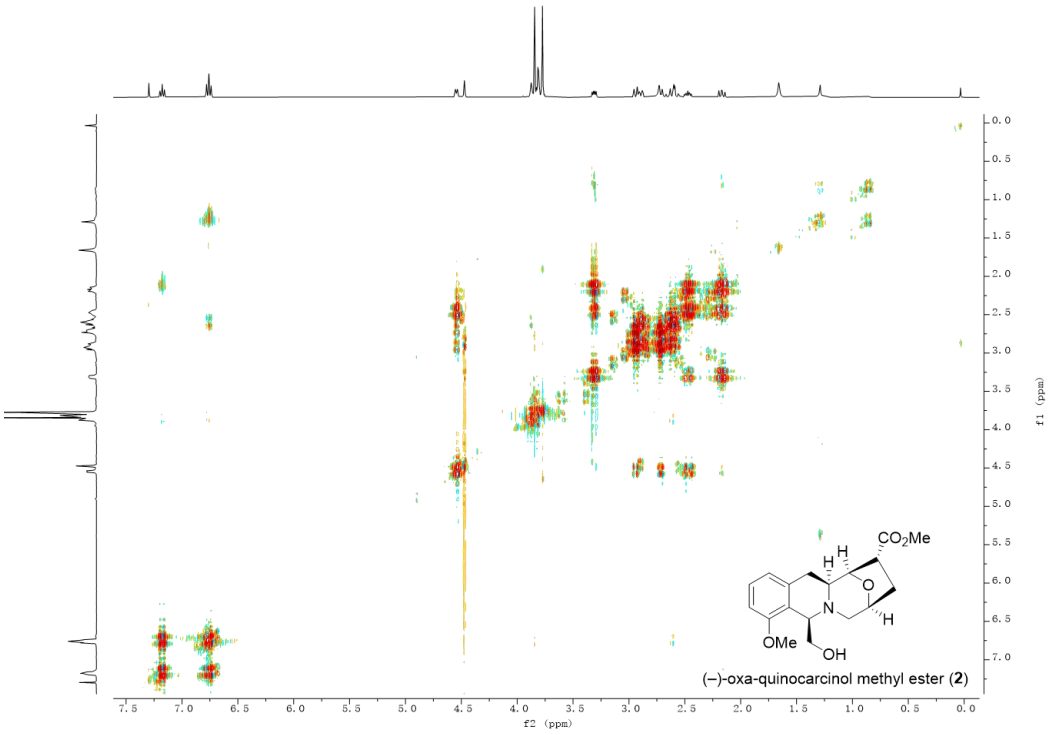


Fig. S1. ^{1}H-^{1}H COSY spectrum of compound **2**.

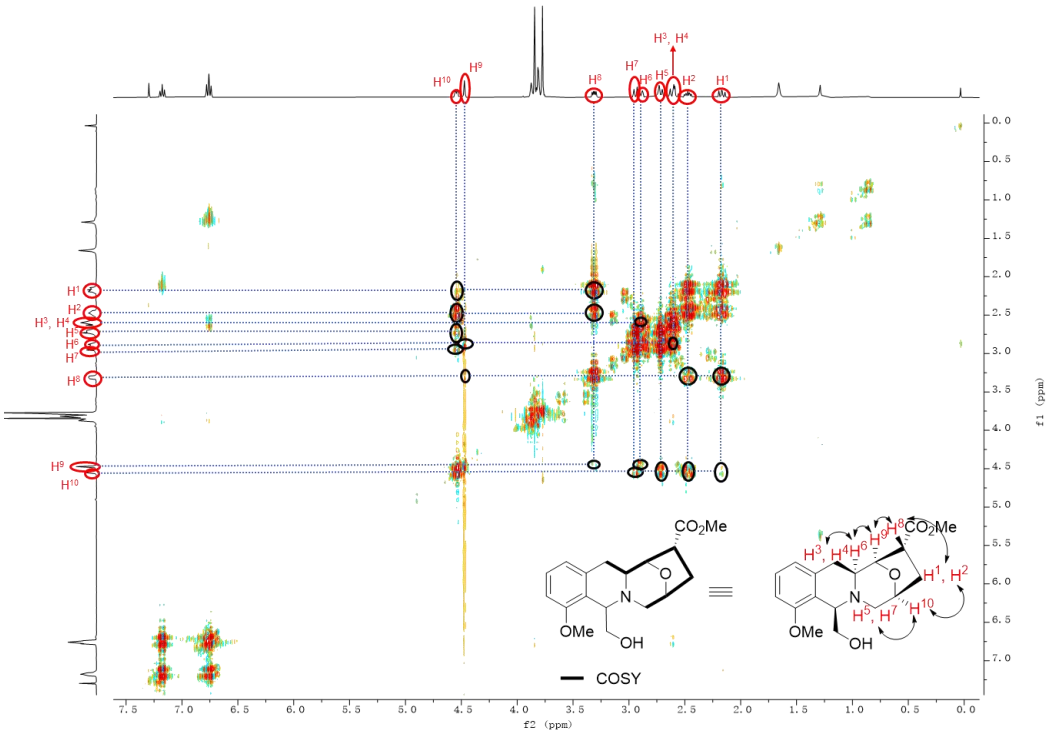


Fig. S2. Key COSY correlations observed for compound **2**.

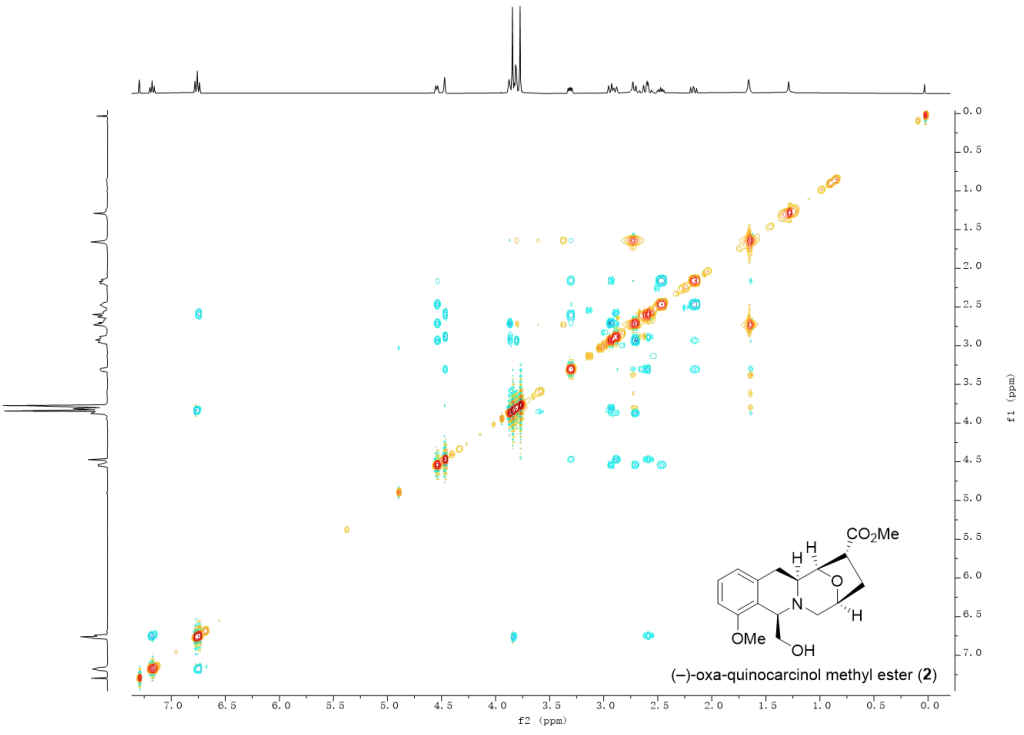


Fig. S3. NOE spectrum of compound **2**.

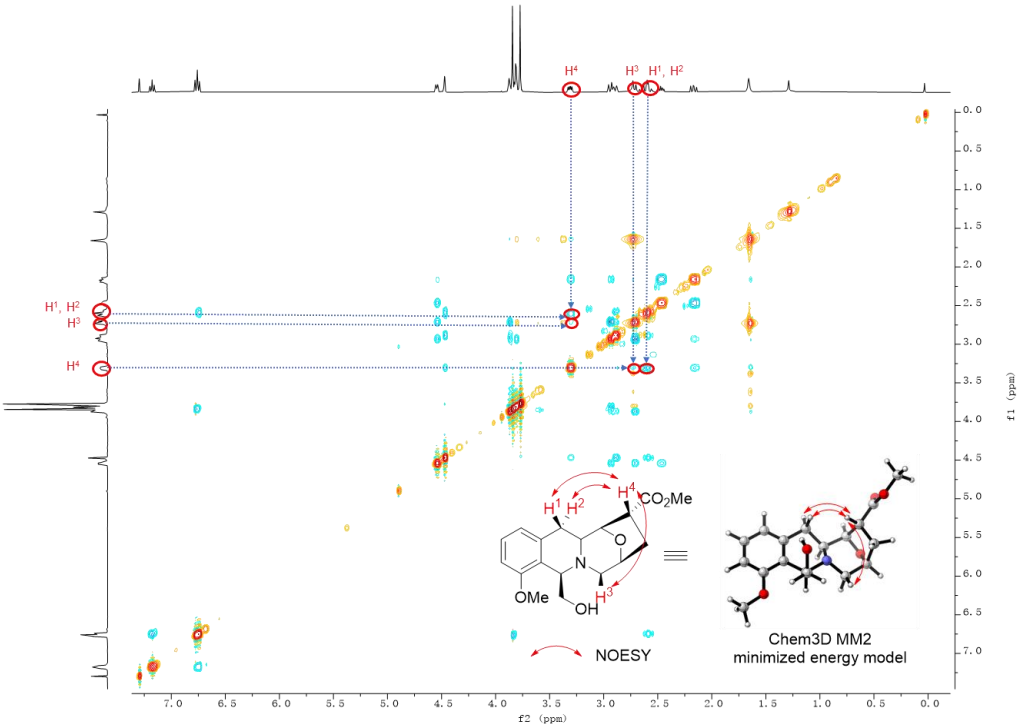


Fig. S4. Key NOE correlations observed for compound **2**.

III. X-ray Structural Analysis

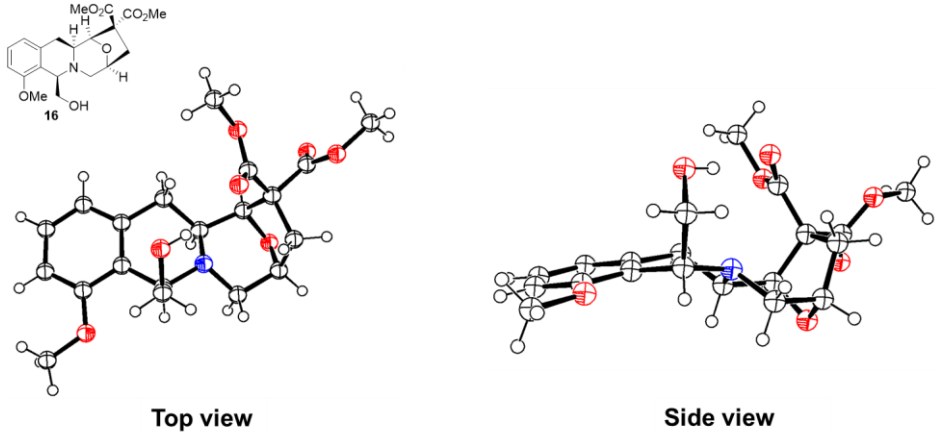


Fig. S5. Structural representation of compound **16**. The thermal ellipsoids are drawn at the 50% probability level.

Table S3. Crystal data and structure refinement for compound **16**.

Empirical formula	C81H102Cl2N4O28
Formula weight	1650.56
Temperature/K	138.15
Crystal system	monoclinic
Space group	P21
a/Å	11.21139(4)

b/Å	12.29166(6)
c/Å	29.87147(11)
α/°	90
β/°	90.6371(3)
γ/°	90
Volume/Å3	4116.23(3)
Z	2
ρcalcg/cm3	1.332
μ/mm-1	1.411
F(000)	1748.0
Crystal size/mm3	0.26 × 0.2 × 0.14
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.918 to 158.382
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -37 ≤ l ≤ 37
Reflections collected	174676
Independent reflections	17350 [Rint = 0.1080, Rsigma = 0.0367]
Data/restraints/parameters	17350/1/1053
Goodness-of-fit on F2	1.057
Final R indexes [I>=2σ (I)]	R1 = 0.0509, wR2 = 0.1391
Final R indexes [all data]	R1 = 0.0519, wR2 = 0.1405
Largest diff. peak/hole / e Å-3	0.49/-0.41
Flack parameter	0.008(17)

IV. NMR Spectra

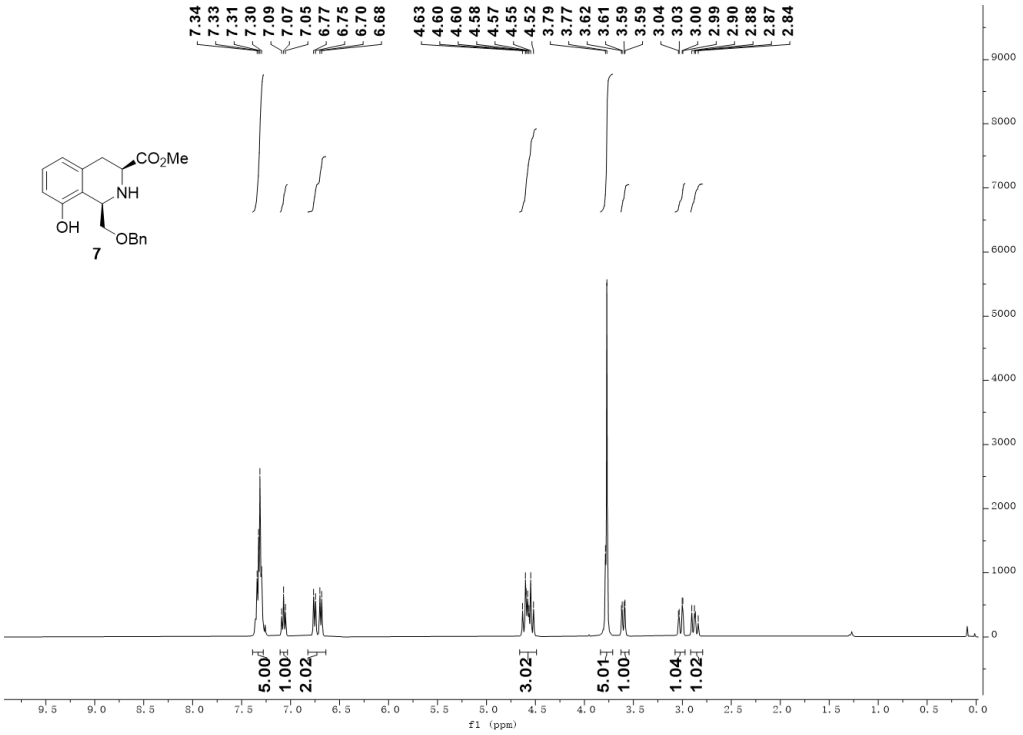


Fig. S6. ^{1}H NMR spectrum of compound **7** (400 MHz, $CDCl_3$).

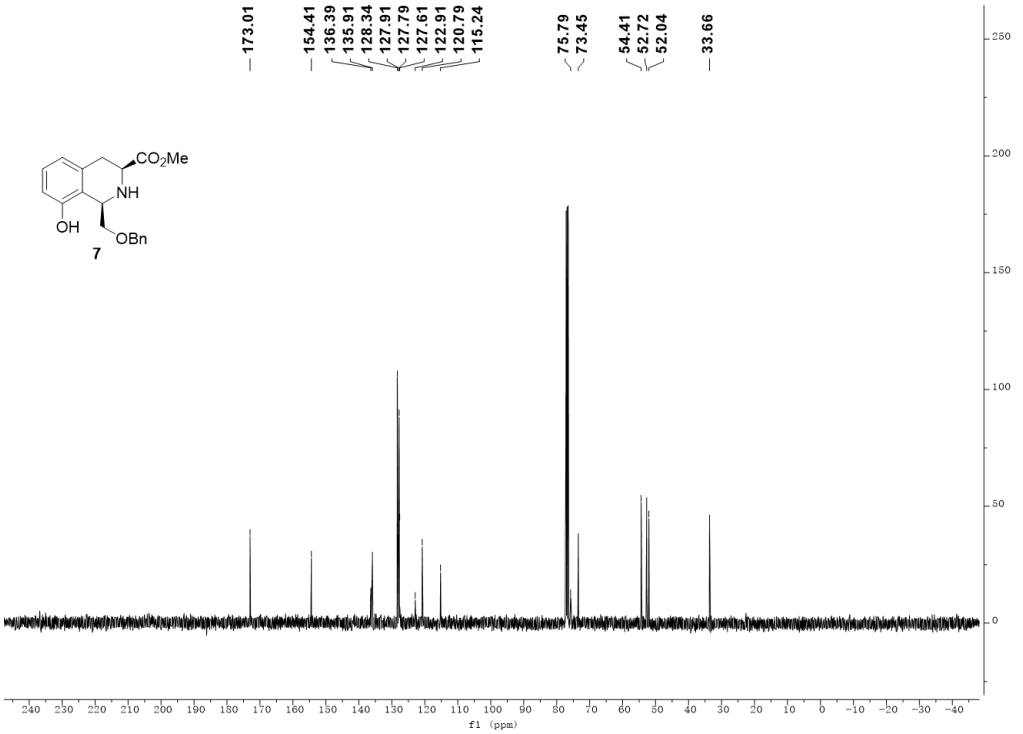


Fig. S7. ^{13}C NMR spectrum of compound **7** (100 MHz, $CDCl_3$).

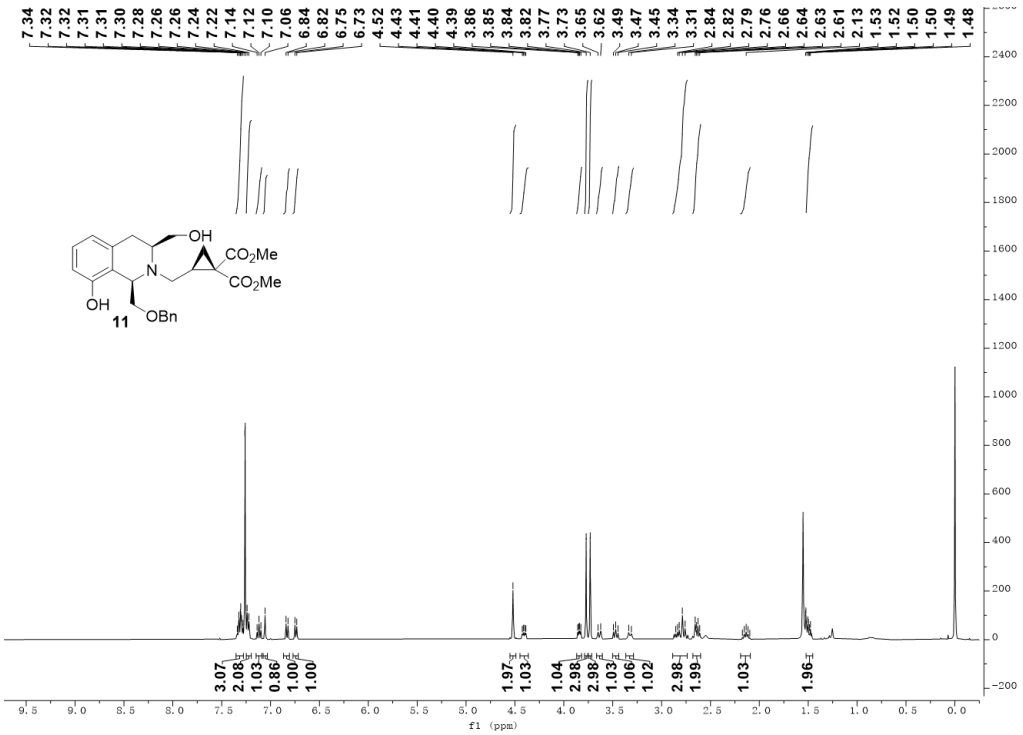


Fig. S8. ^{1}H NMR spectrum of compound **11** (400 MHz, $CDCl_3$).

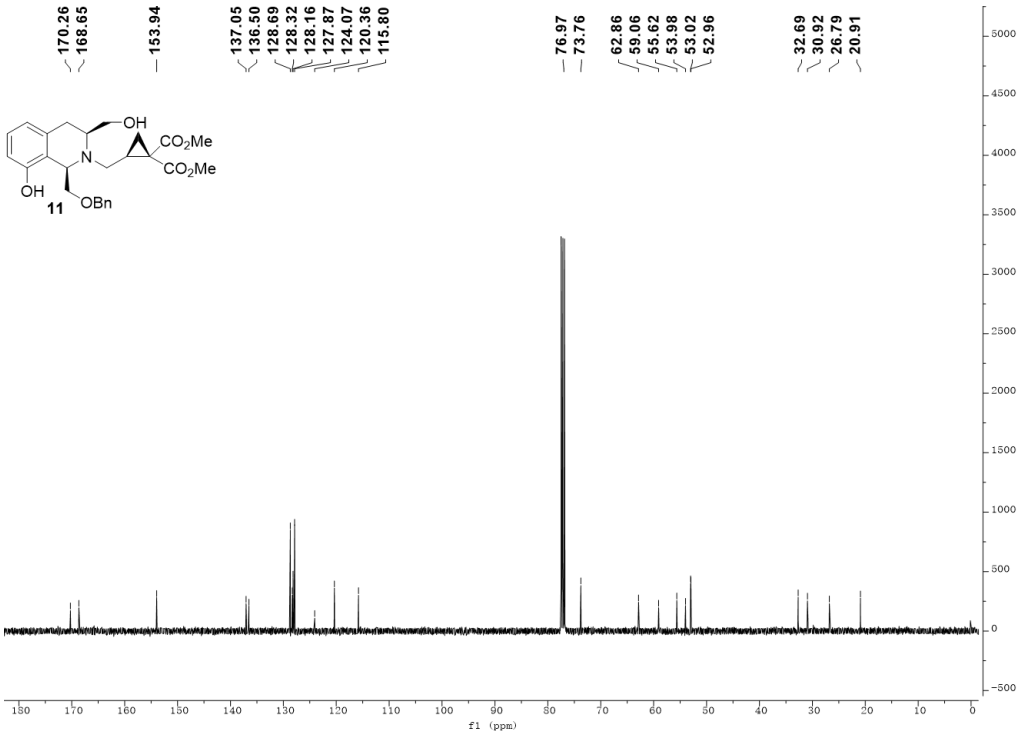


Fig. S9. ^{13}C NMR spectrum of compound **11** (100 MHz, $CDCl_3$).

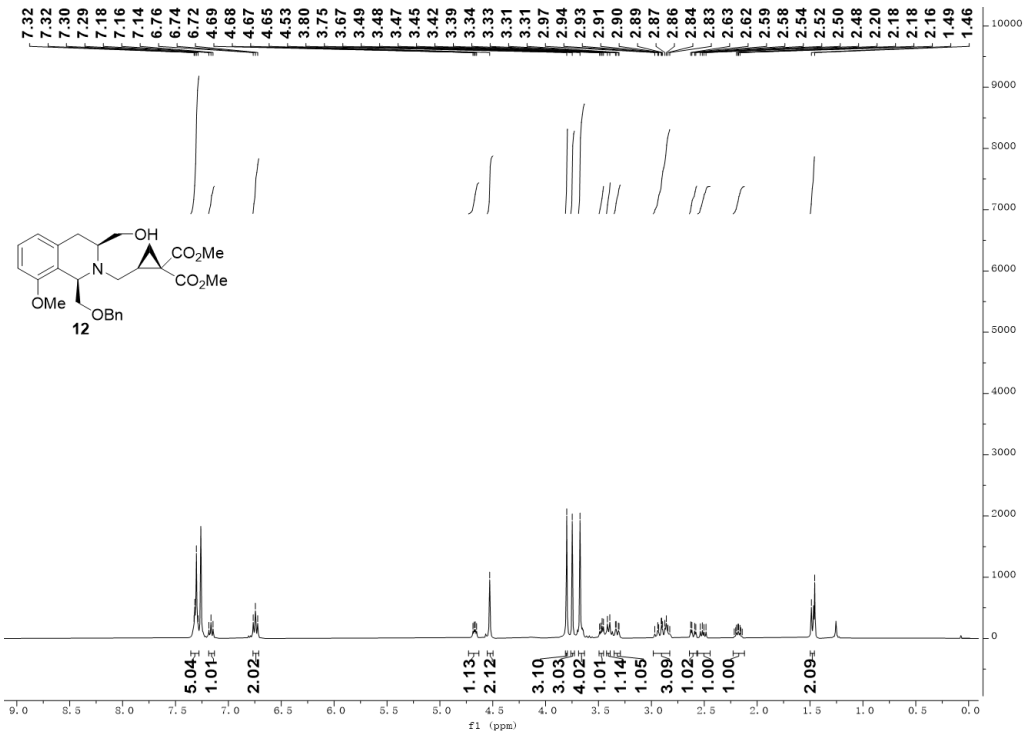


Fig. S10. ^{1}H NMR spectrum of compound **12** (400 MHz, $CDCl_3$).

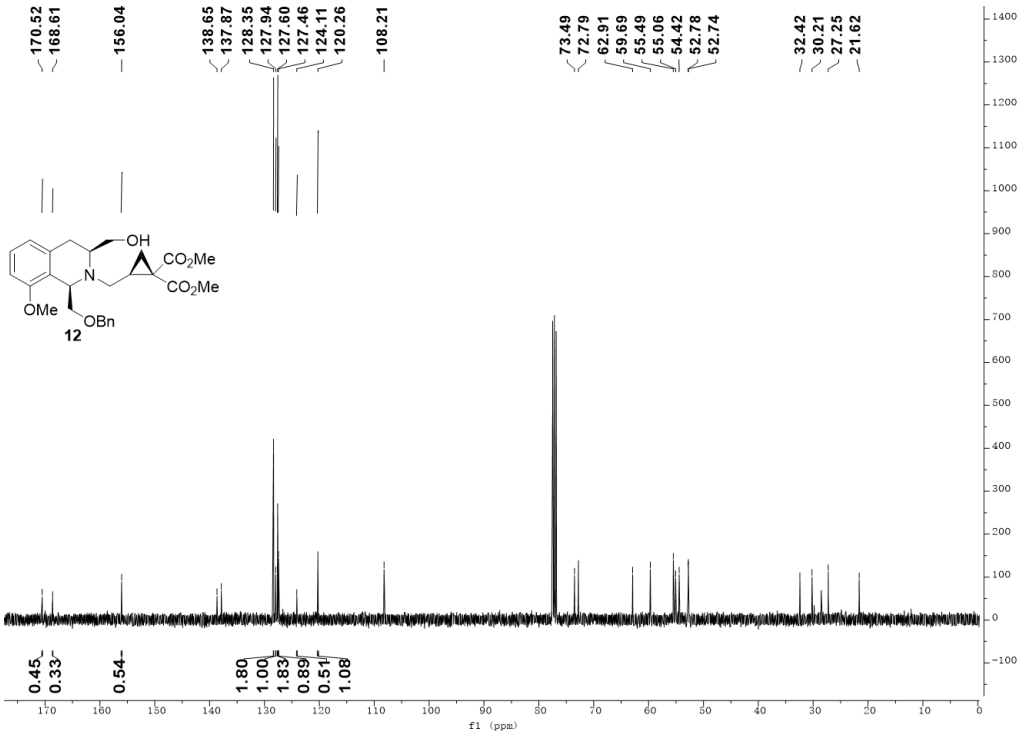


Fig. S11. ^{13}C NMR spectrum of compound **12** (100 MHz, $CDCl_3$).

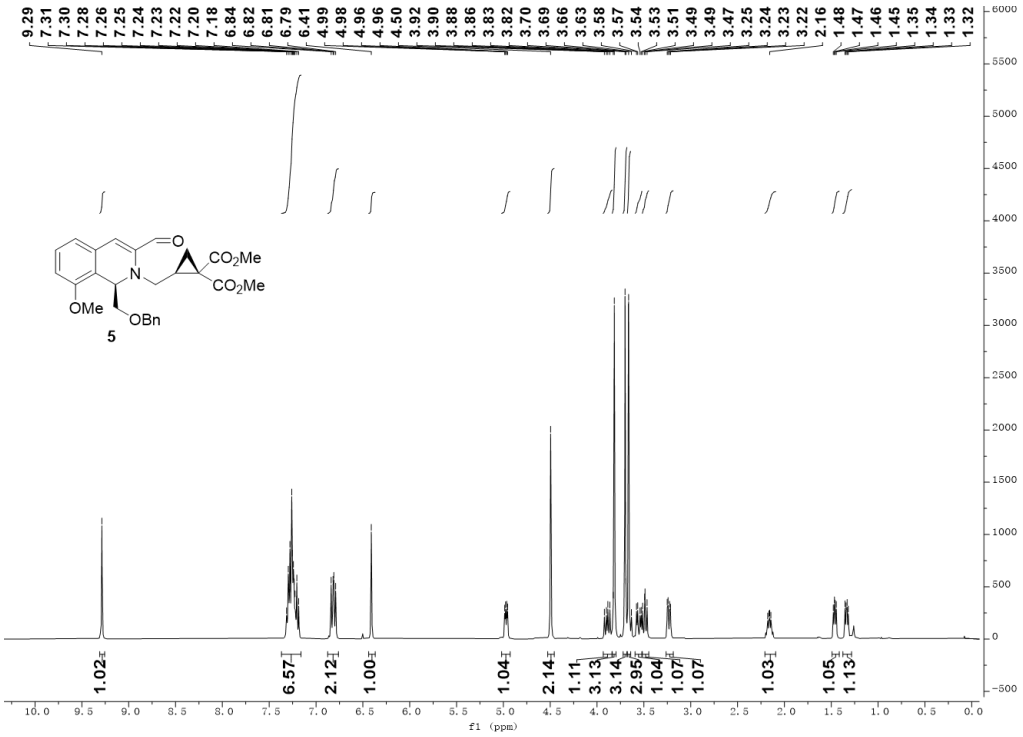


Fig. S12. ^{1}H NMR spectrum of compound **5** (400 MHz, $CDCl_3$).

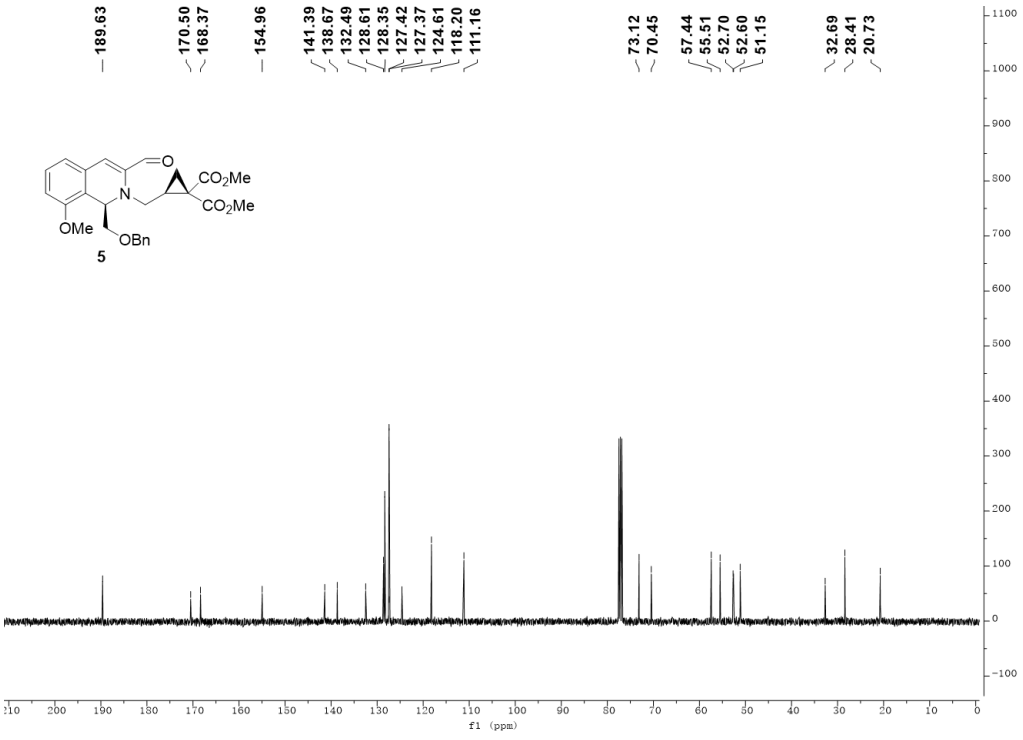


Fig. S13. ^{13}C NMR spectrum of compound **5** (101 MHz, $CDCl_3$).

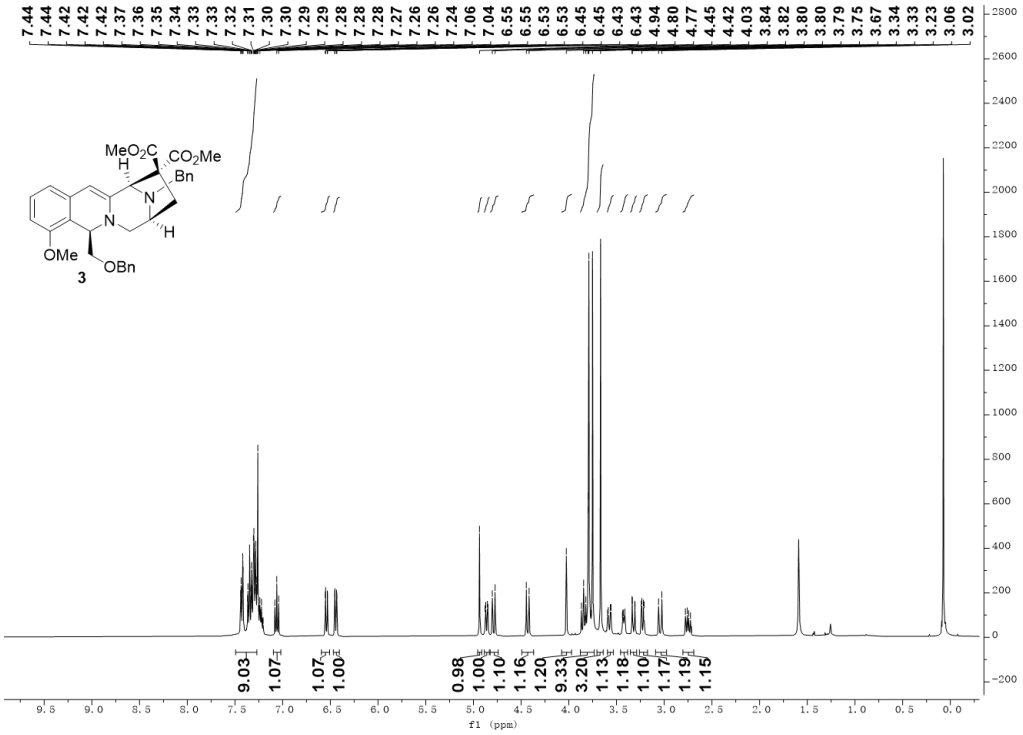


Fig. S14. ^{1}H NMR spectrum of compound **3** (400 MHz, $CDCl_3$).

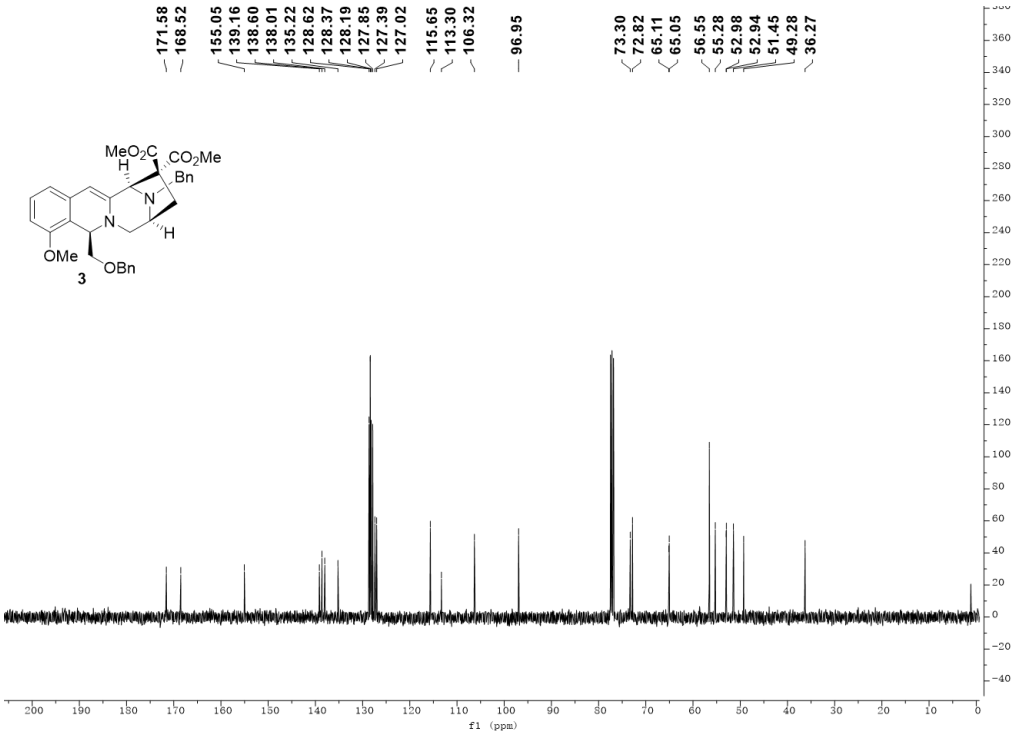


Fig. S15. ^{13}C NMR spectrum of compound **3** (101 MHz, $CDCl_3$).

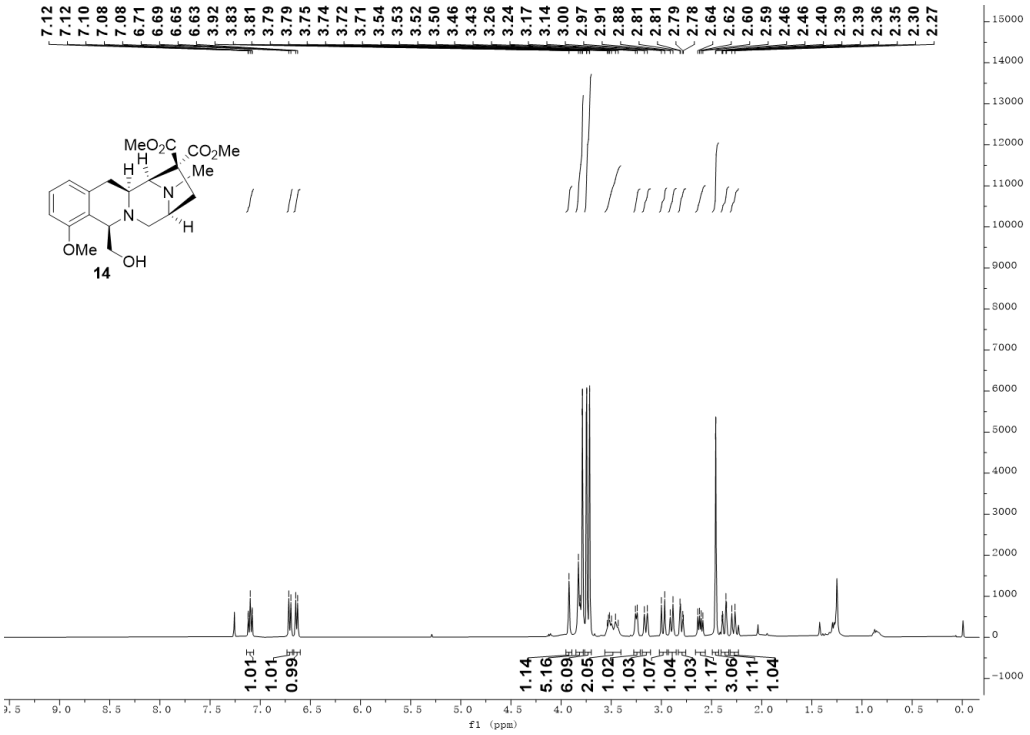


Fig. S16. ^{1}H NMR spectrum of compound **14** (400 MHz, $CDCl_3$).

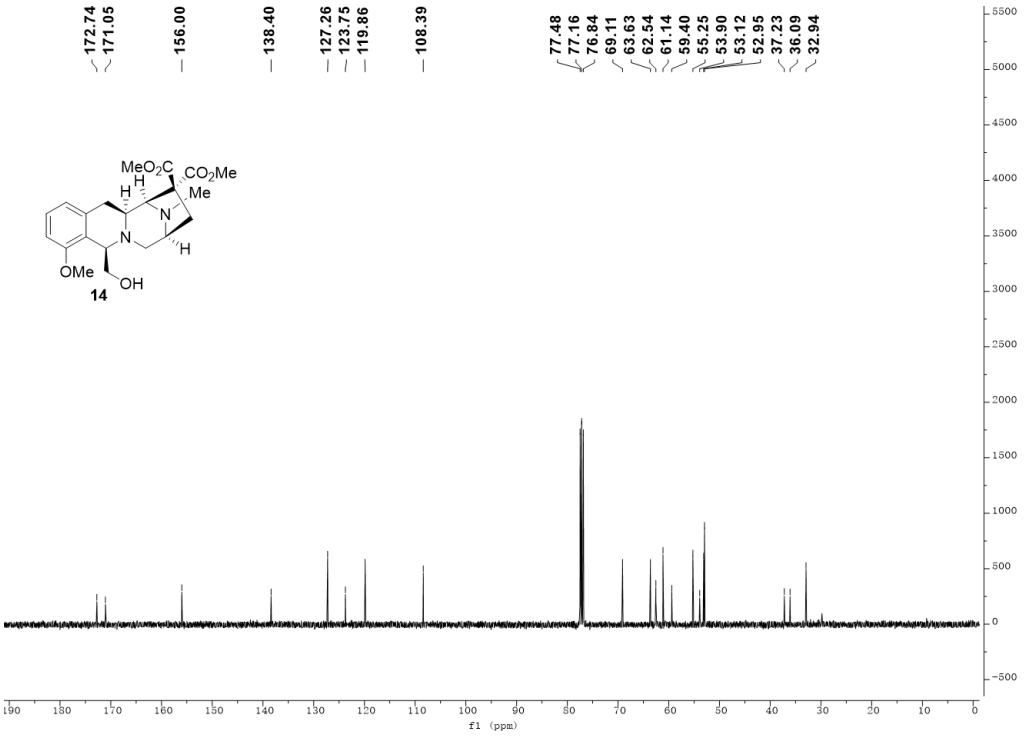


Fig. S17. ^{13}C NMR spectrum of compound **14** (101 MHz, $CDCl_3$).

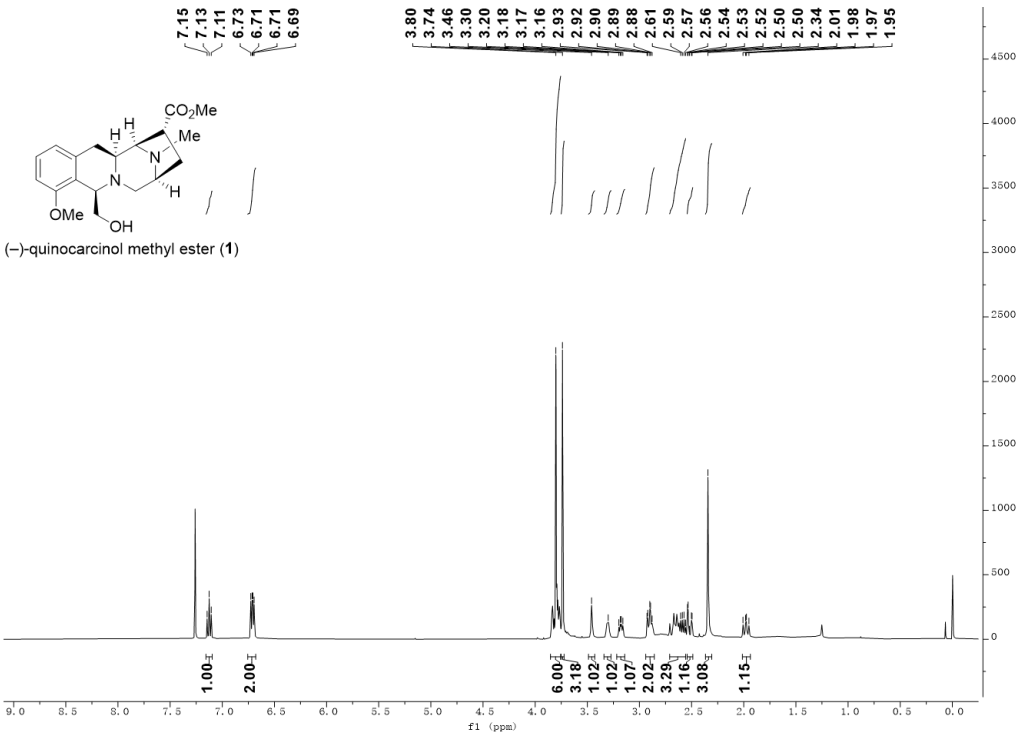


Fig. S18. ^{1}H NMR spectrum of compound **1** (400 MHz, $CDCl_3$).

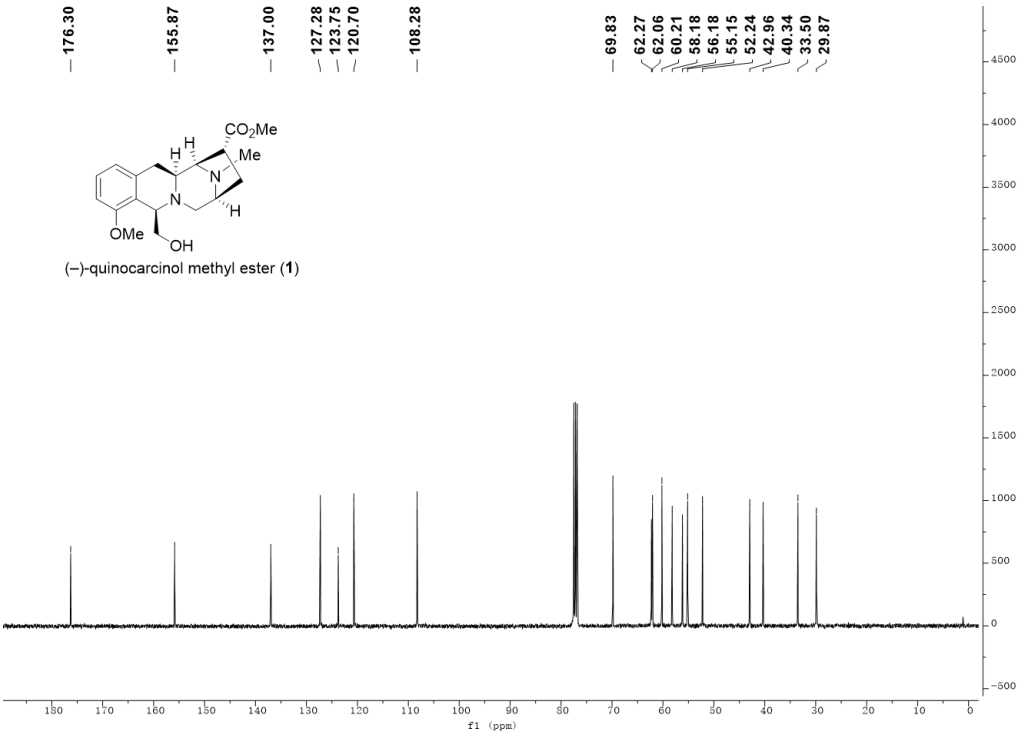


Fig. S19. ^{13}C NMR spectrum of compound **1** (101 MHz, $CDCl_3$).

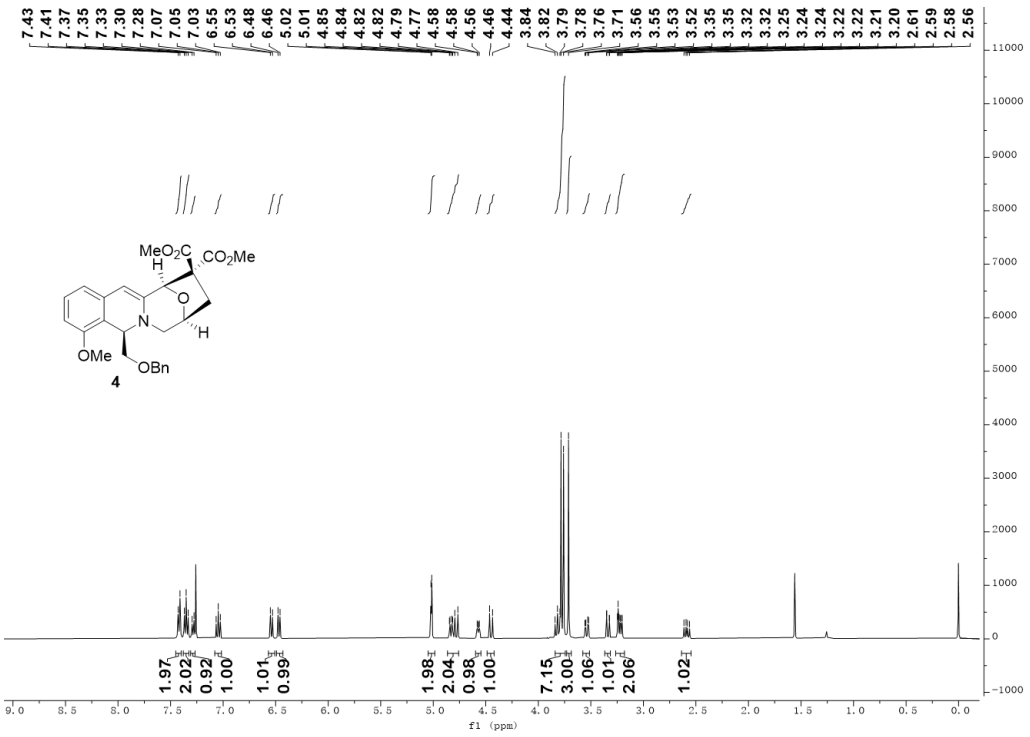


Fig. S20. ^{1}H NMR spectrum of compound **4** (400 MHz, $CDCl_3$).

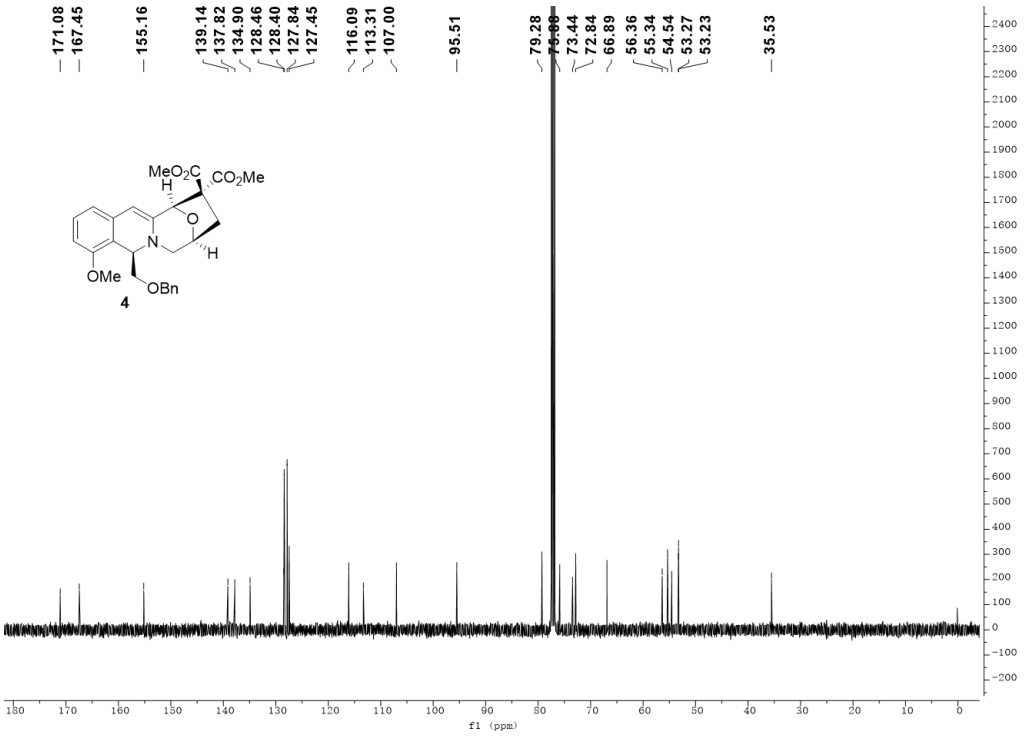


Fig. S21. ^{13}C NMR spectrum of compound **4** (101 MHz, $CDCl_3$).

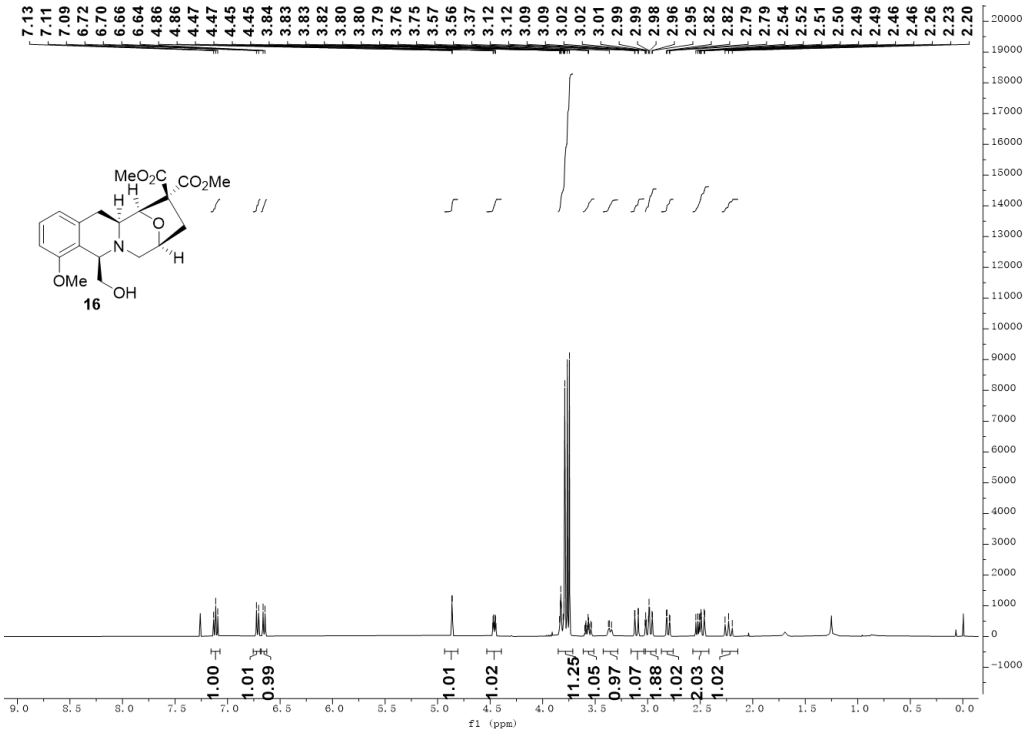


Fig. S22. ^{1}H NMR spectrum of compound **16** (400 MHz, $CDCl_3$).

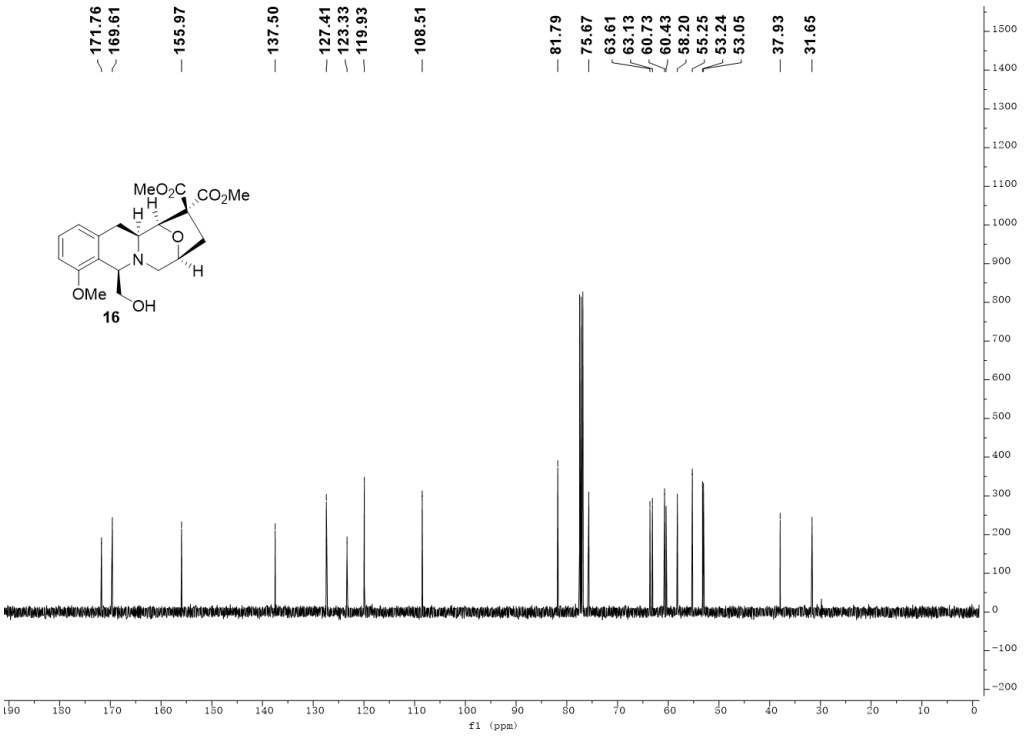


Fig. S23. ^{13}C NMR spectrum of compound **16** (101 MHz, $CDCl_3$).

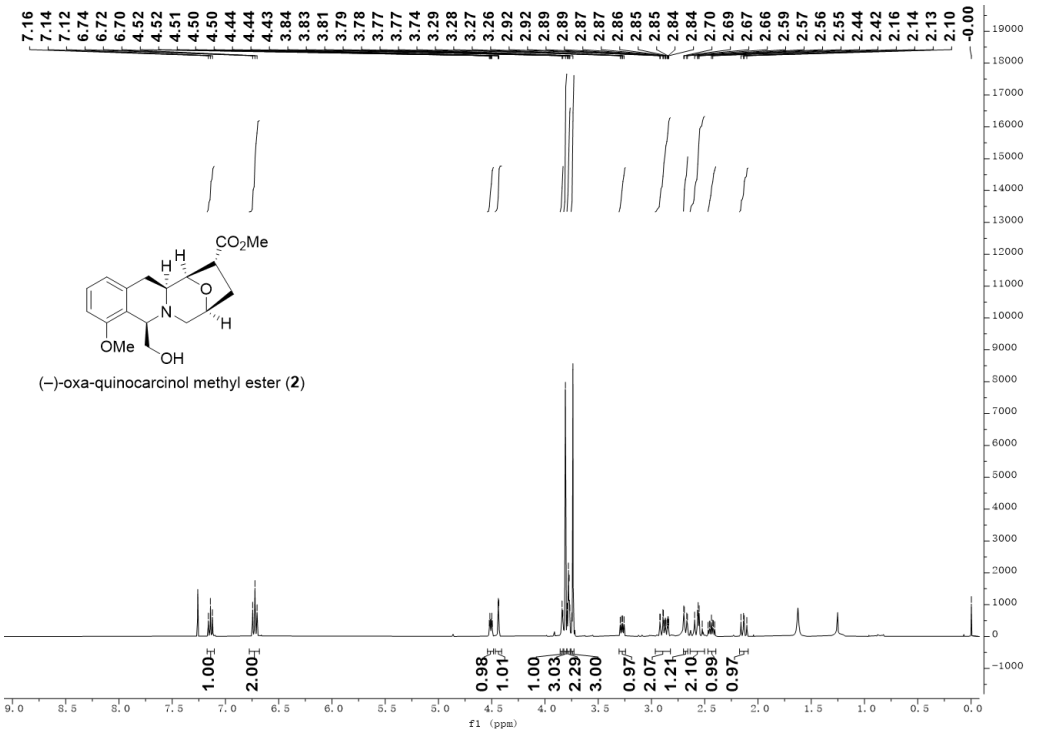


Fig. S24. ^{1}H NMR spectrum of compound **2** (400 MHz, $CDCl_3$).

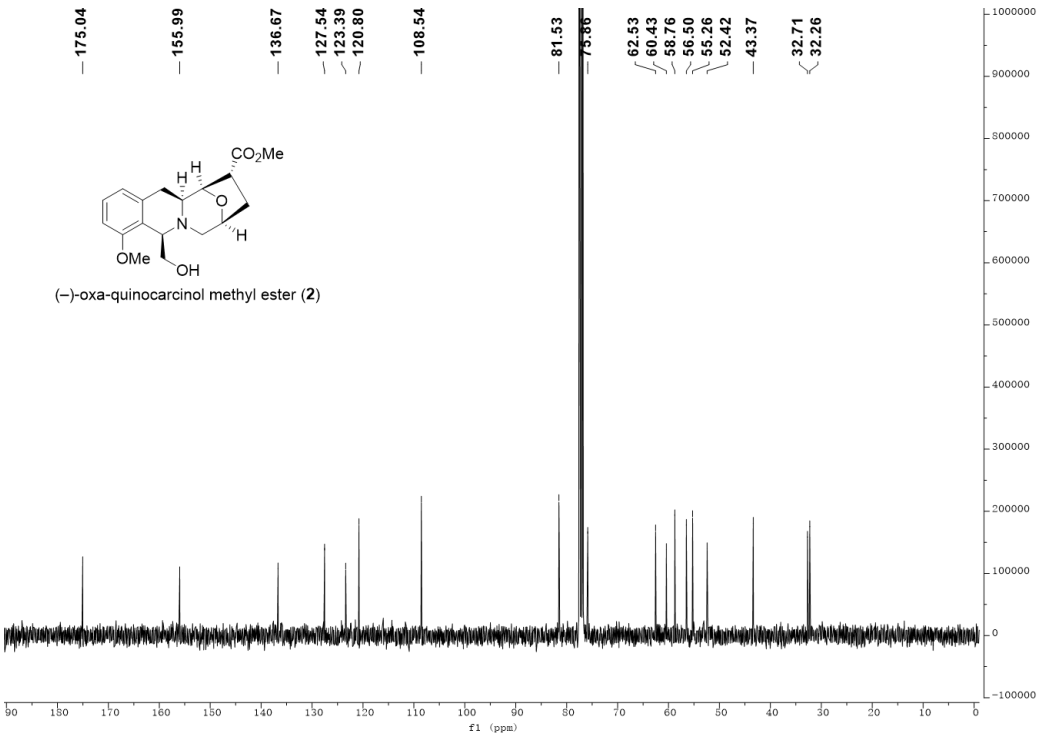


Fig. S25. ^{13}C NMR spectrum of compound **2** (101 MHz, $CDCl_3$).

V. Reference

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams,

F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Wallingford, CT, 2016.

[2] T. Lu and Q. *Chen, Comput. Theor. Chem.*, 2021, **1200**, 113249-113249.

[3] C. Y. Legault, CYLview20, Université de Sherbrooke, 2020 (http://www.cylview.org).

[4] B. Cao, D. Xiao and M. M. Joullié, *Org. Lett.*, 1999, **1**, 1799-1801.

[5] T.-H. Song, Y.-F. Wu, J. Ren and Z.-W. Wang, *Org. Lett.*, 2024, **26**, 7100-7104.

[6] C. A. Carson and M. A. Kerr, *Angew. Chem. Int. Ed.*, 2006, **45**, 6560-6563.

[7] H. Chiba, Y. Sakai, A. Ohara, S. Oishi, N. Fujii and H. Ohno, *Chem. Eur. J.*, 2013, **19**, 8875-8883.