Electronic Supplementary Information

Kinetic Resolution of Phosphoric Diester by Cinchona Alkaloid Derivatives Provided with a Guanidinium Unit

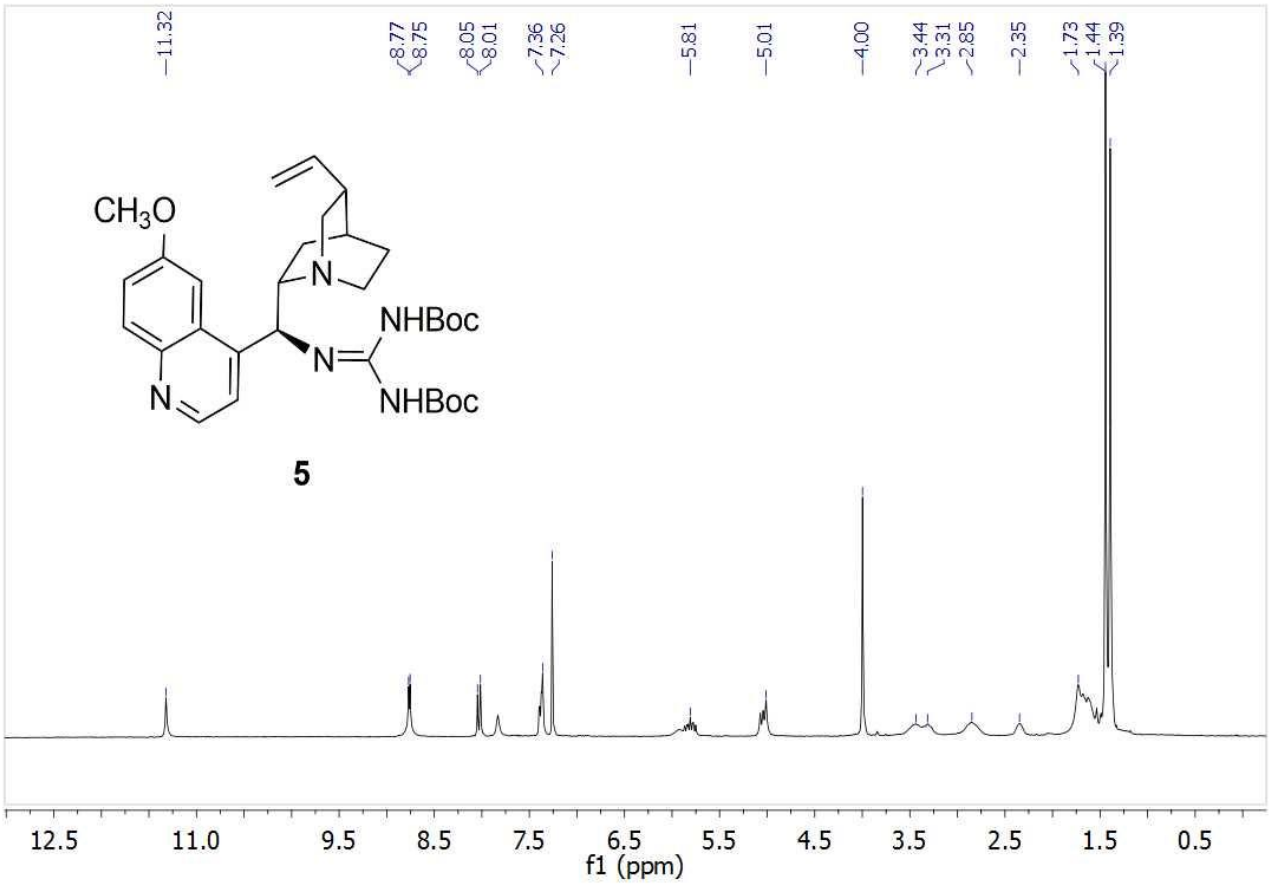
Riccardo Salvio,*[a,b] Mauro Moliterno,[a] Dario Caramelli,[a] Luca Pisciottani,[a] Achille Antenucci,[a] Melania D'Amico[a] and Marco Bella[a]

[a] Dipartimento di Chimica, Università La Sapienza, Roma, Italy

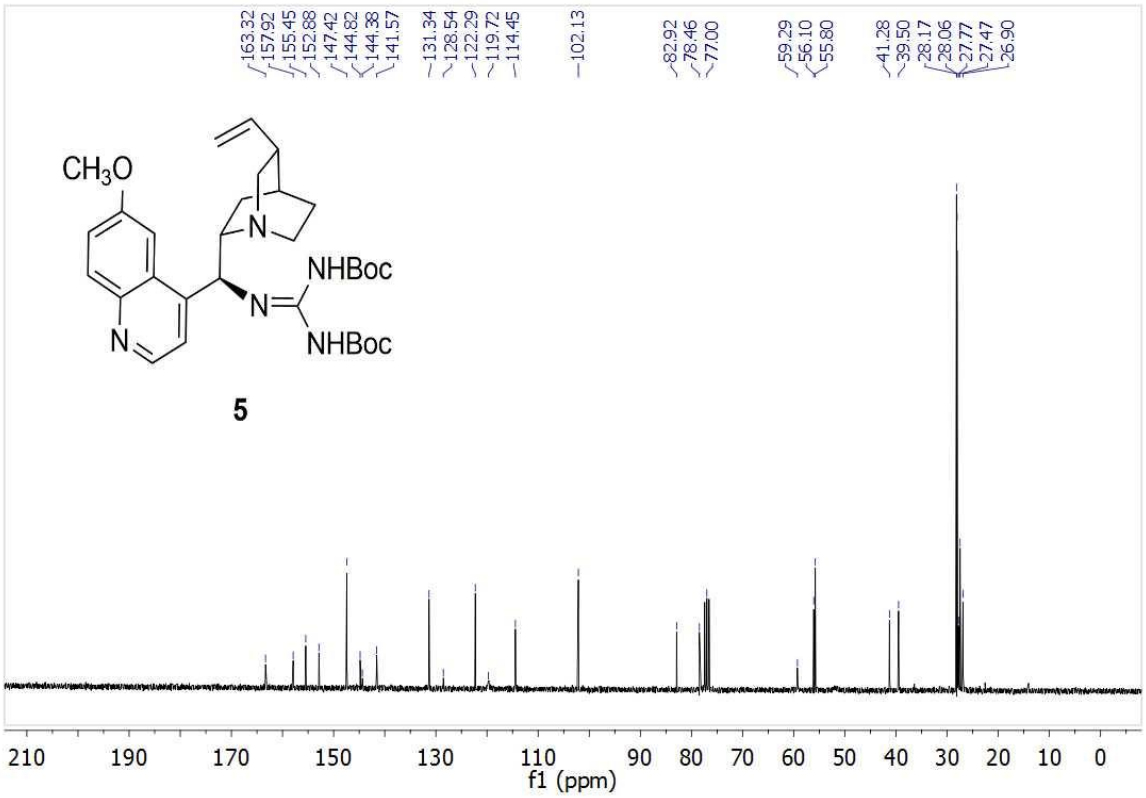
[b] IMC - CNR Sezione Meccanismi di Reazione, Università La Sapienza, 00185 Roma, Italy.

Table of Contents

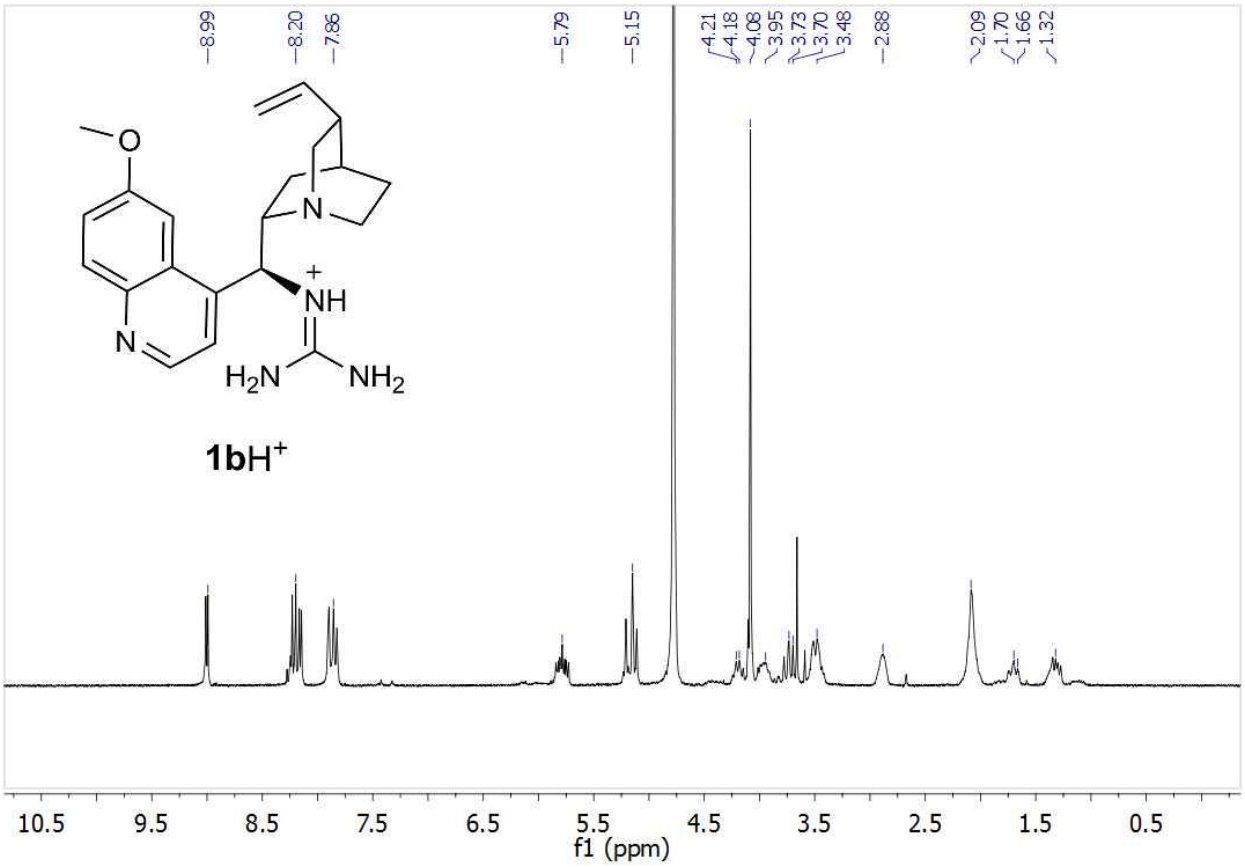
^{1}H NMR of **5** ($CDCl_3$, 300 MHz)



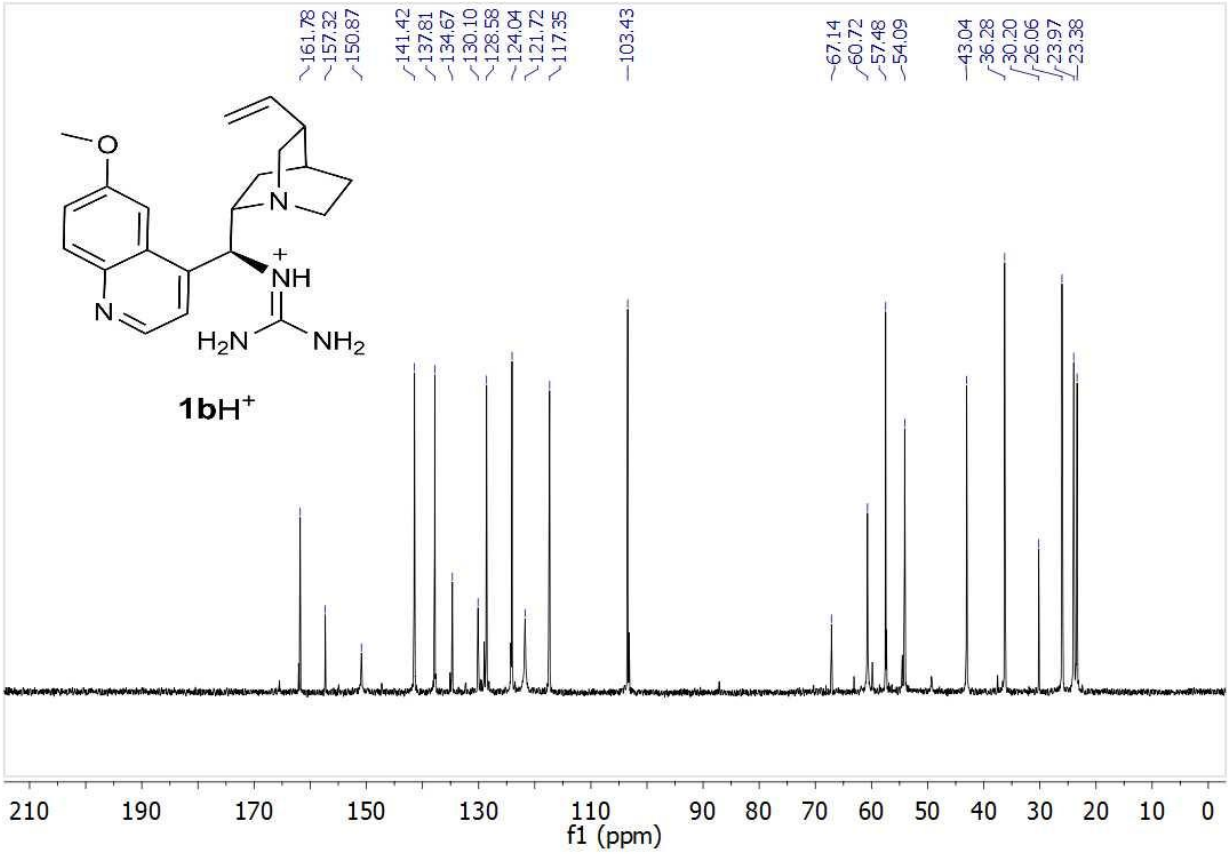
^{13}C NMR of **5** ($CDCl_3$, 75 MHz)



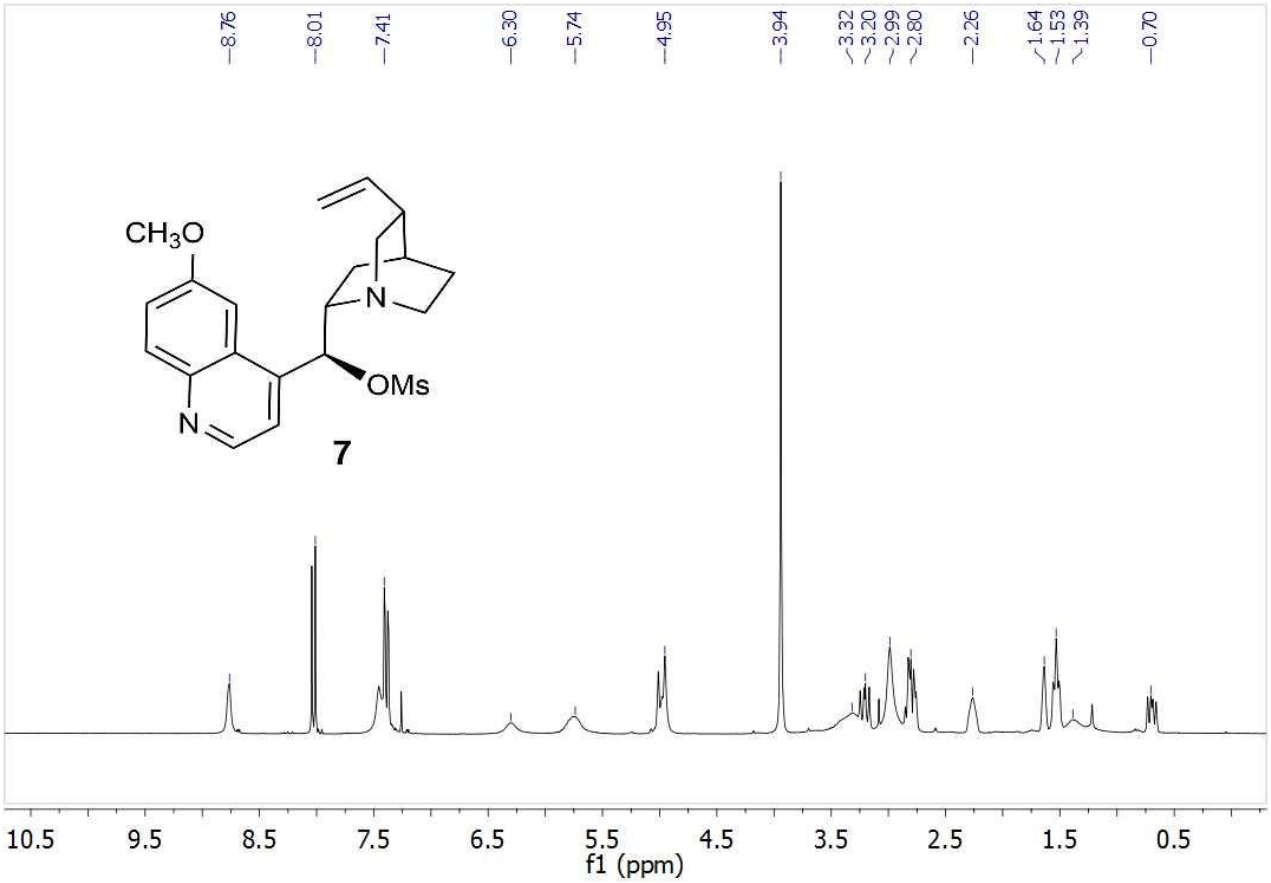
^{1}H NMR of **1b** (D_2O, 300 MHz)



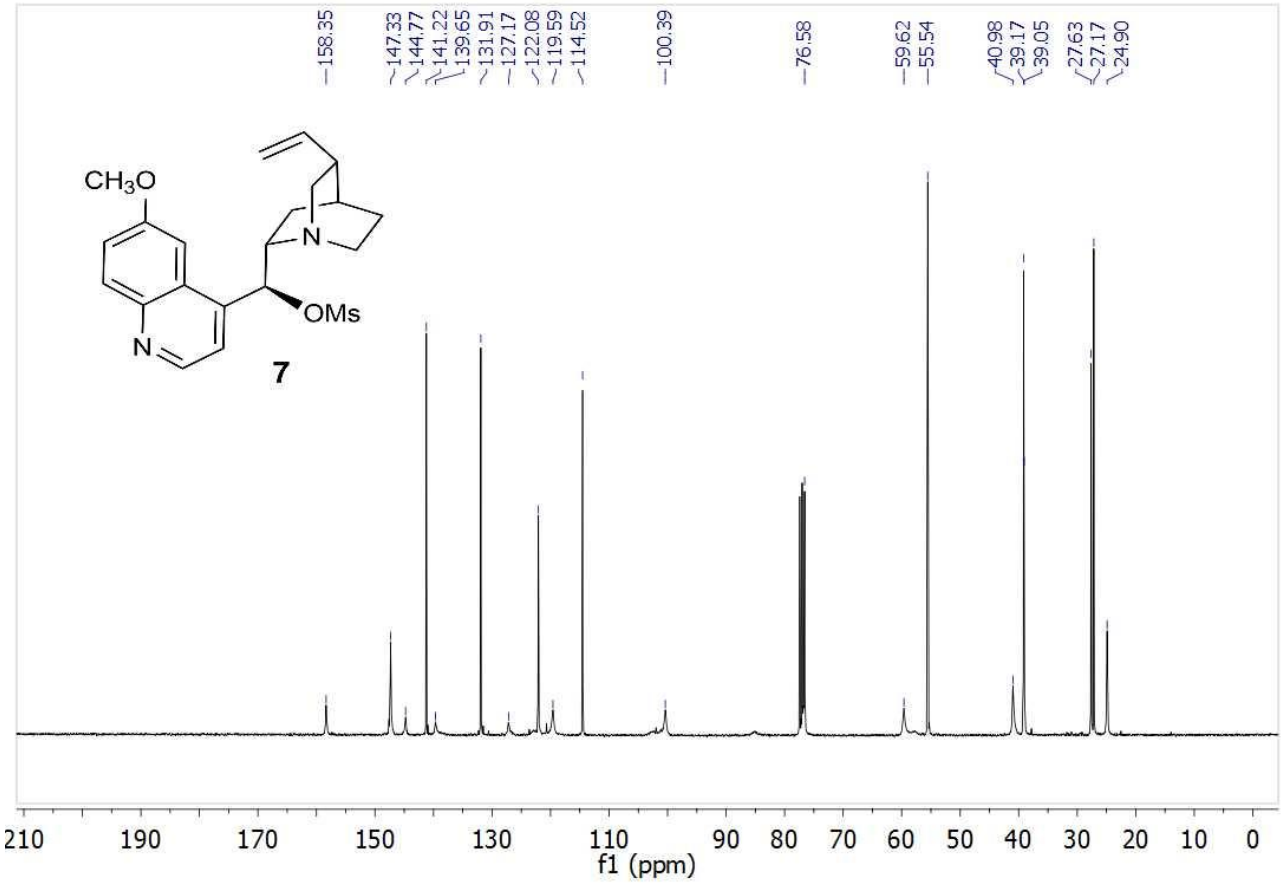
13C NMR of **1b** (D_2O, 75 MHz)



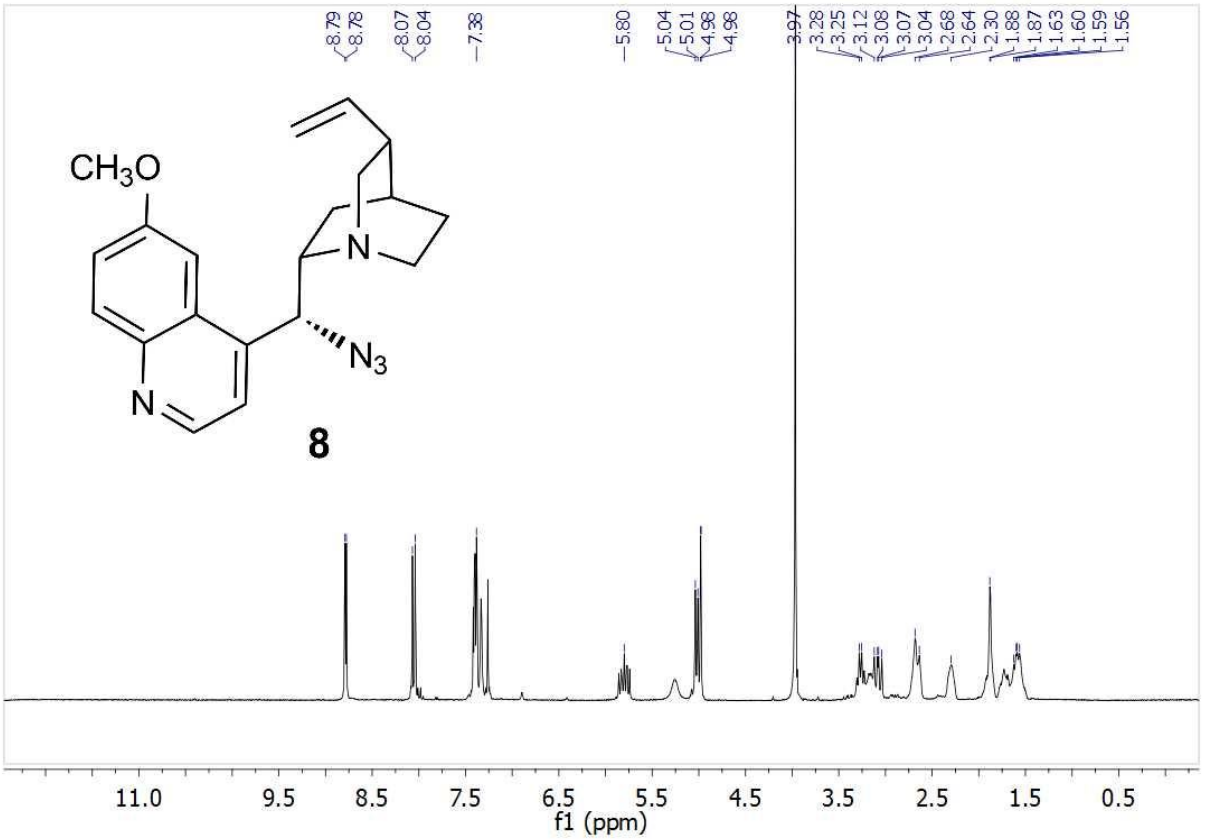
^{1}H NMR of **7** ($CDCl_3$, 300 MHz)



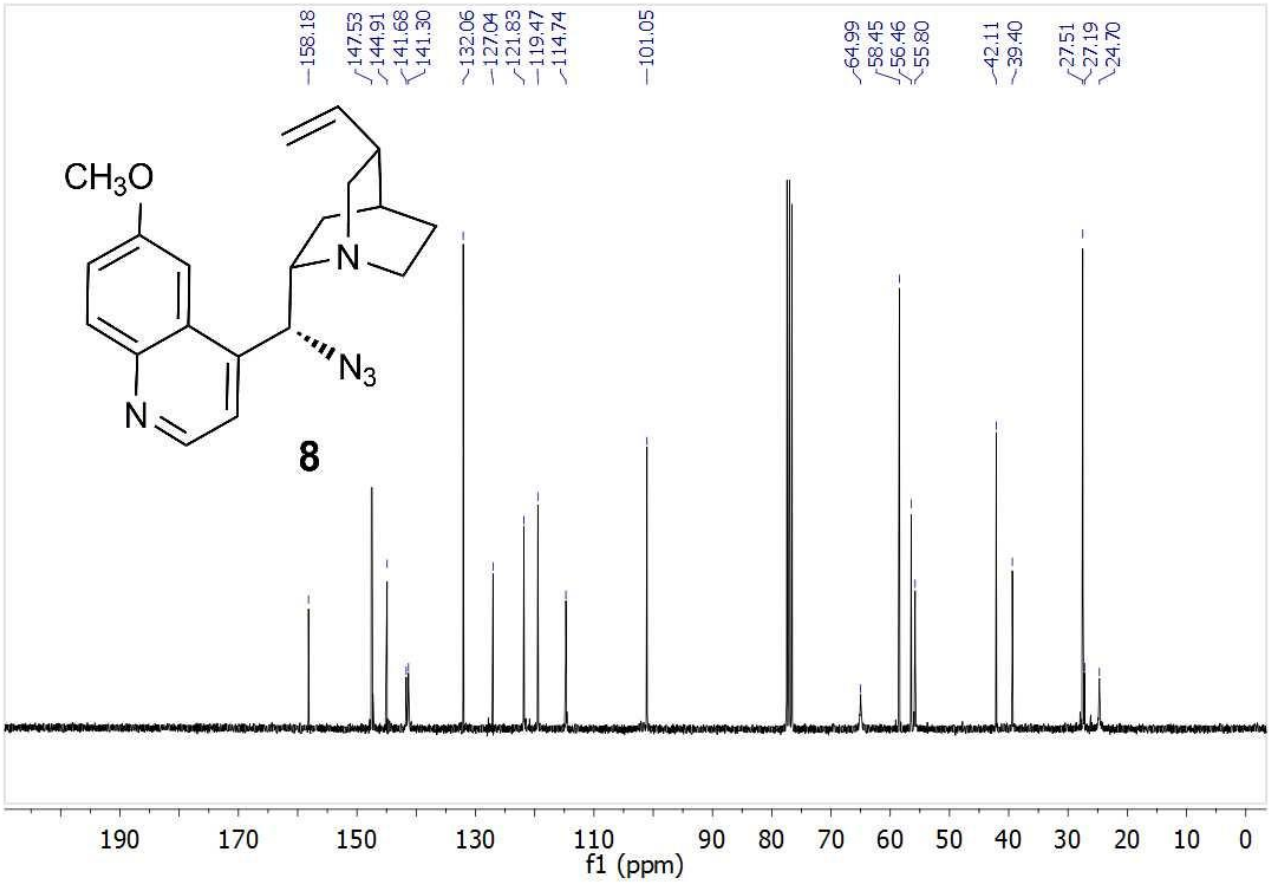
^{13}C NMR of **7** ($CDCl_3$, 75 MHz)



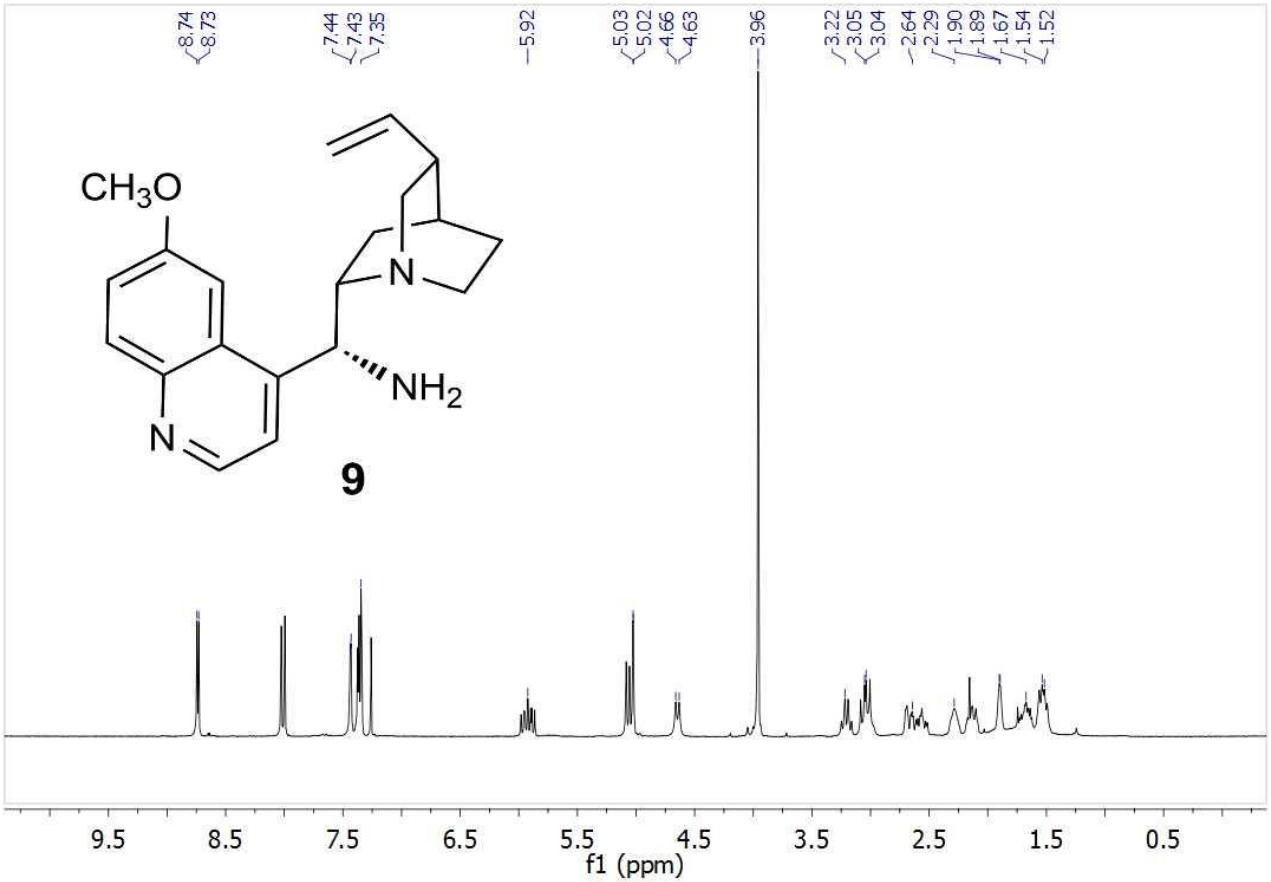
^{1}H NMR of **8** ($CDCl_3$, 300 MHz)



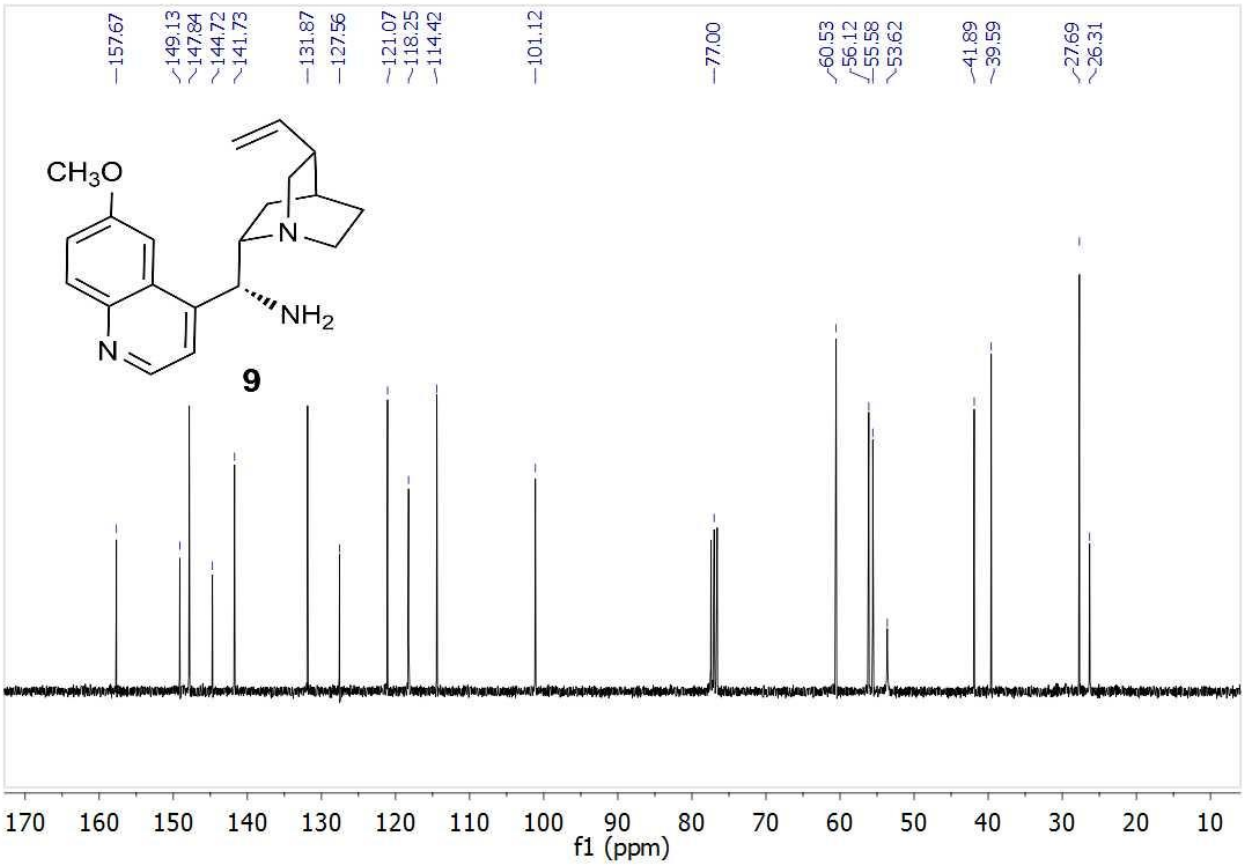
^{13}C NMR of **8** ($CDCl_3$, 75 MHz)



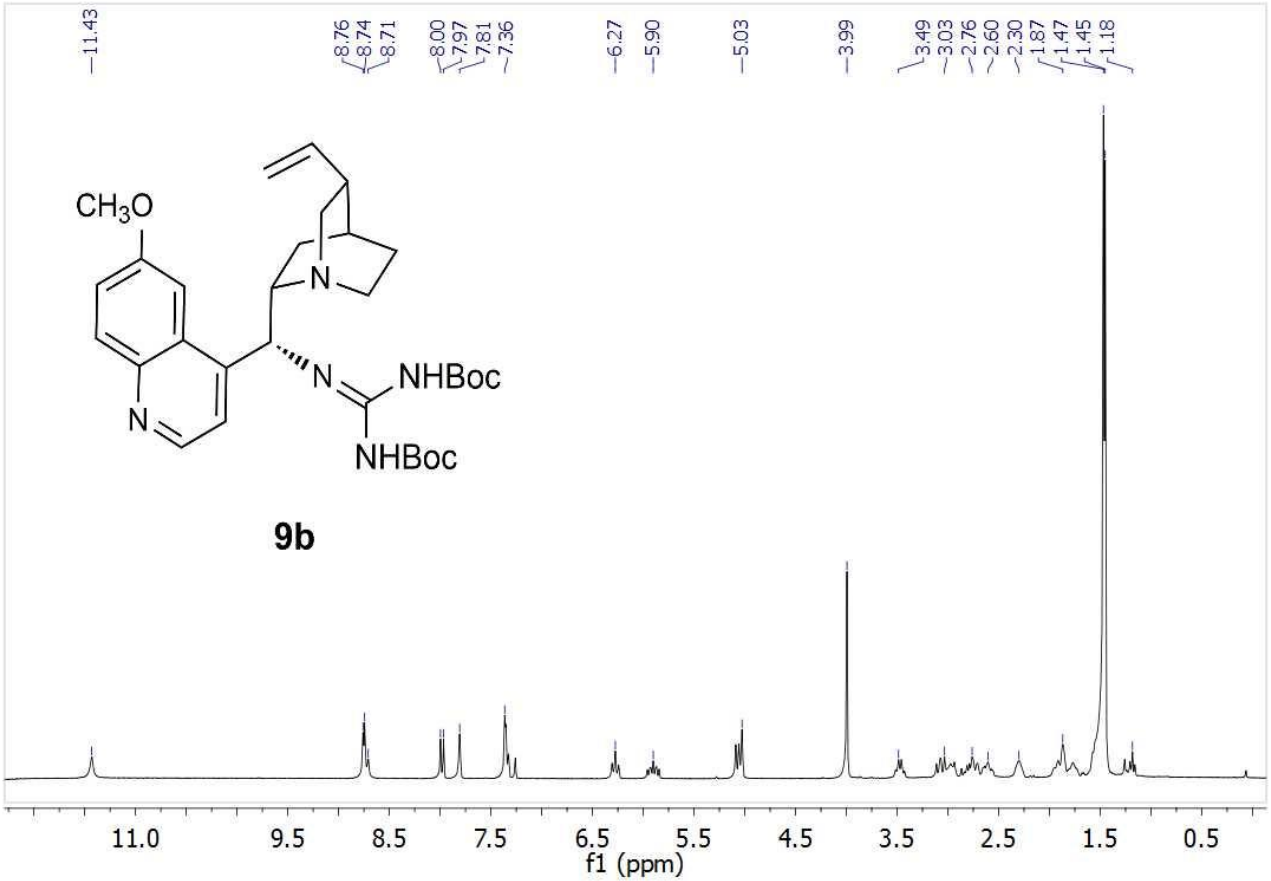
^{1}H NMR of **9** ($CDCl_3$, 300 MHz)



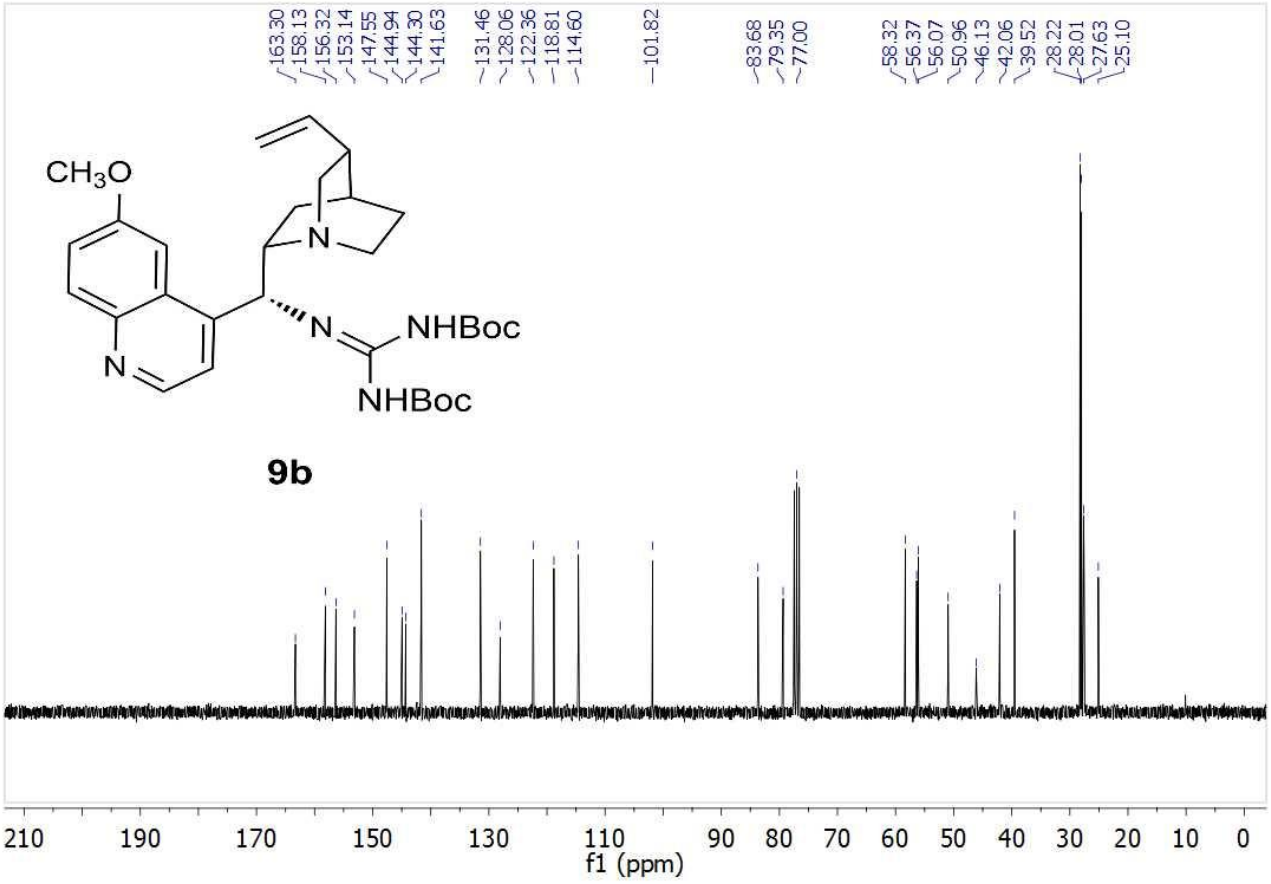
^{13}C NMR of **9** ($CDCl_3$, 75 MHz)



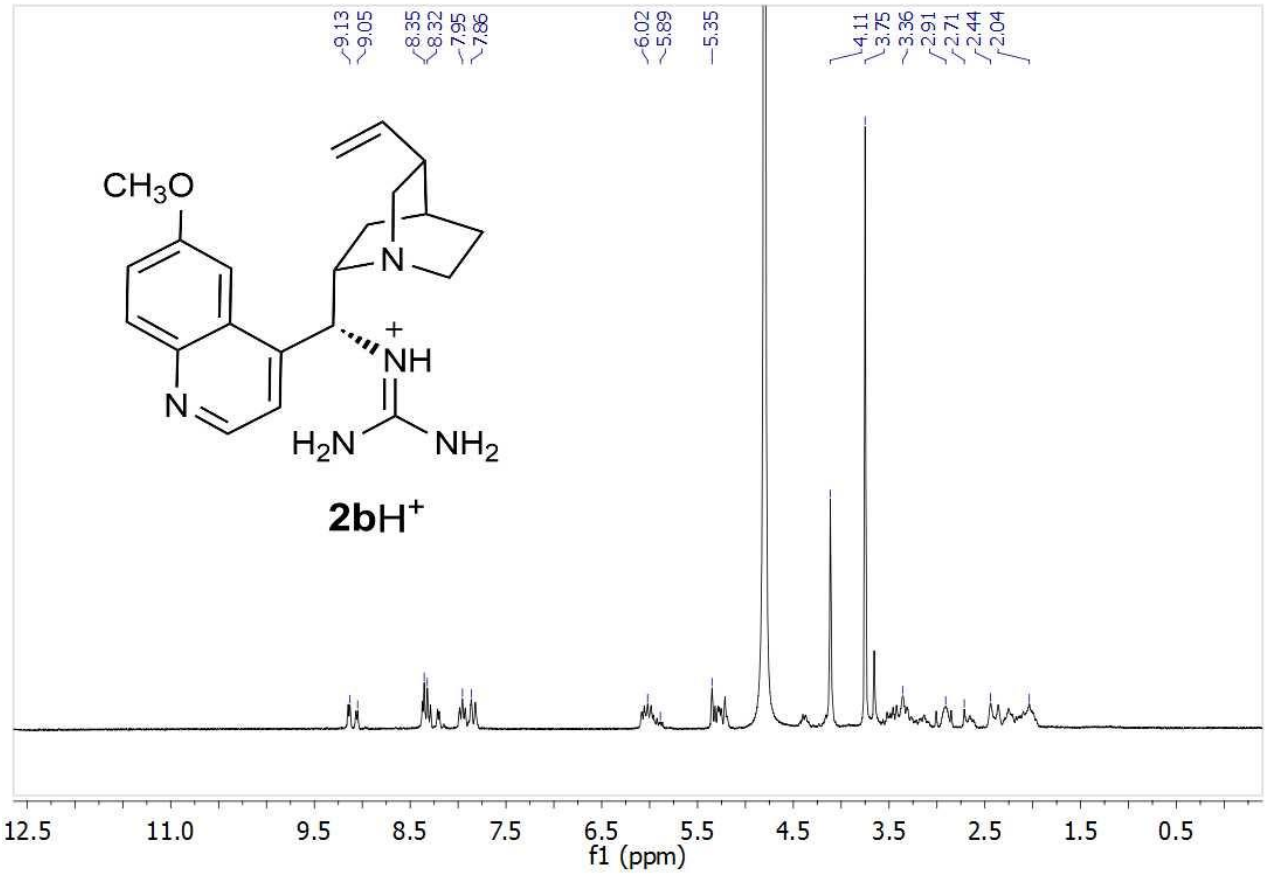
^{1}H NMR of **9b** ($CDCl_3$, 300 MHz)



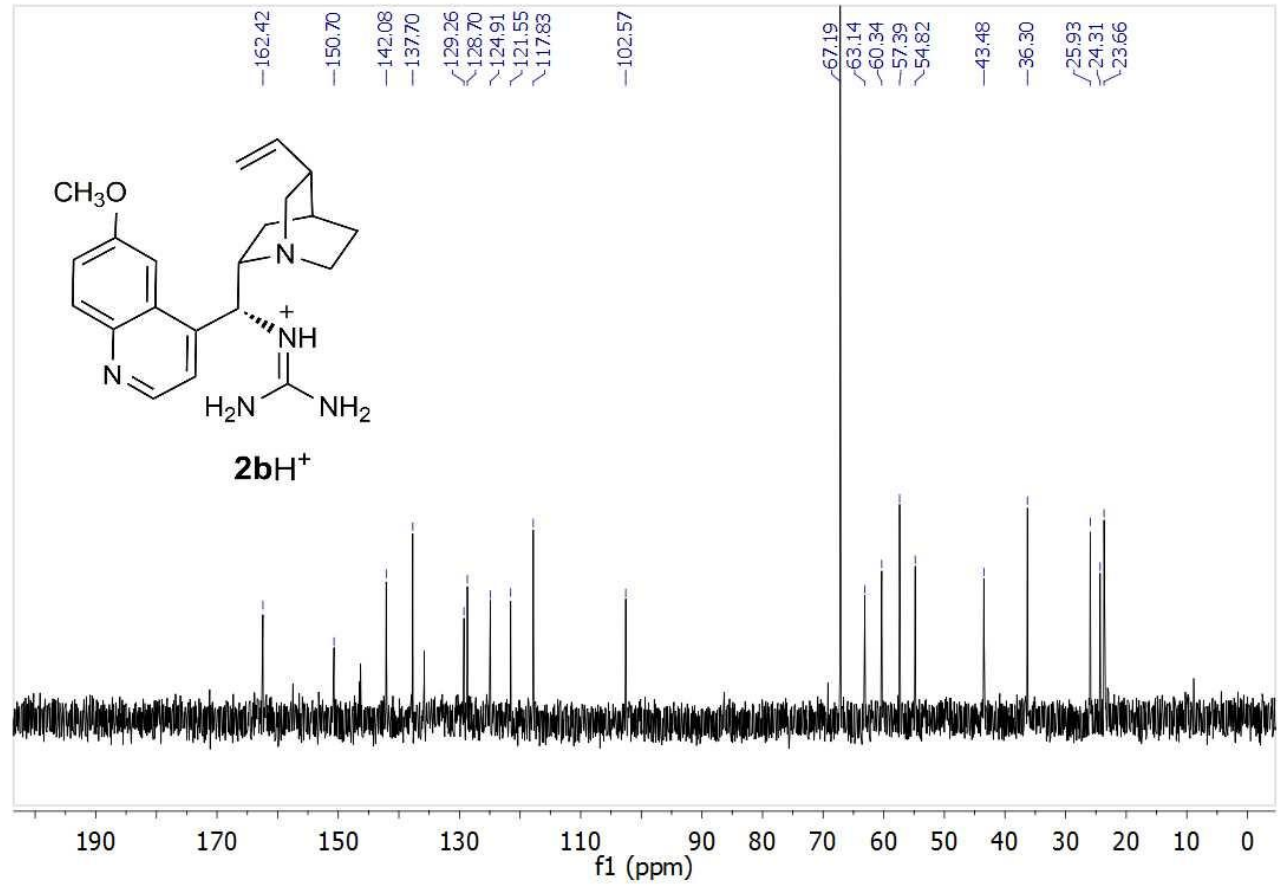
^{13}C NMR of **9b** ($CDCl_3$, 75 MHz)



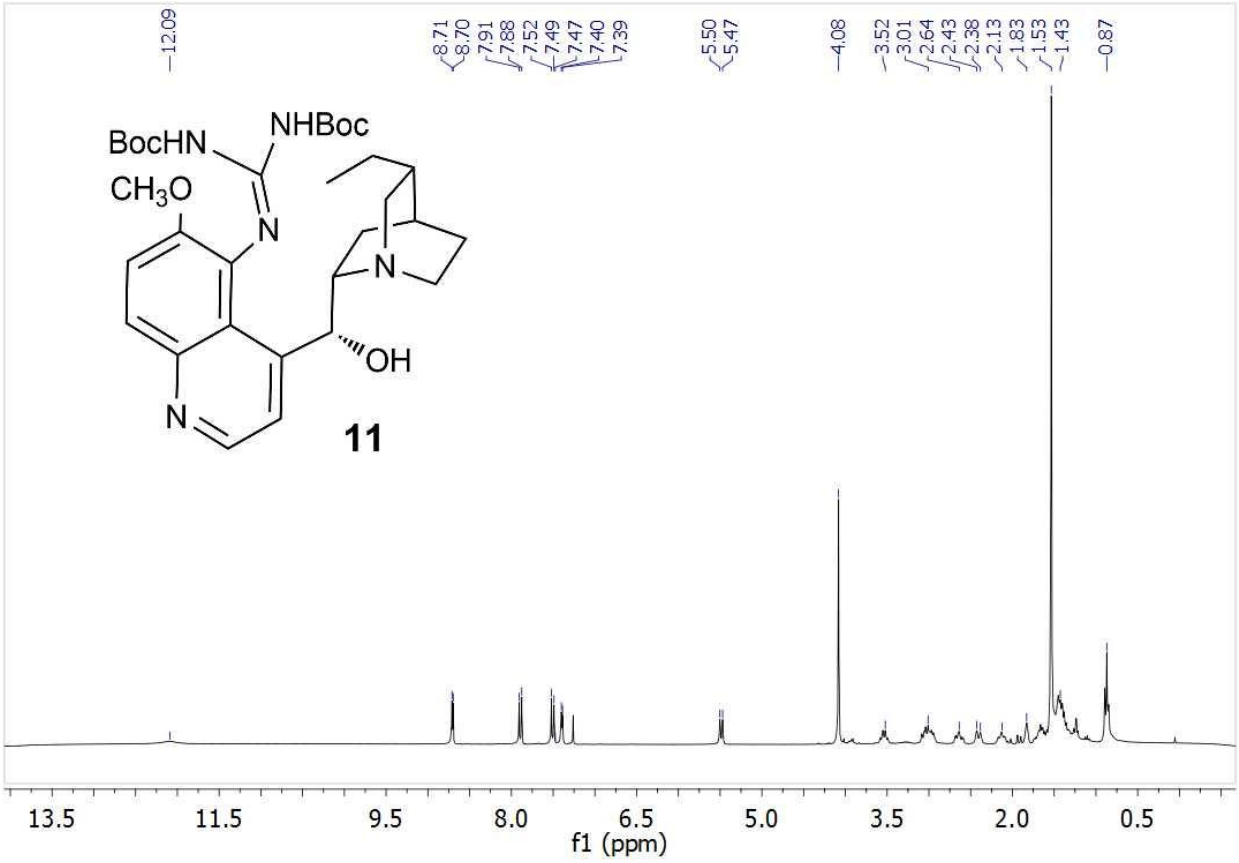
^{1}H NMR of **2b** (D_2O, 300 MHz, dioxane as internal standard)



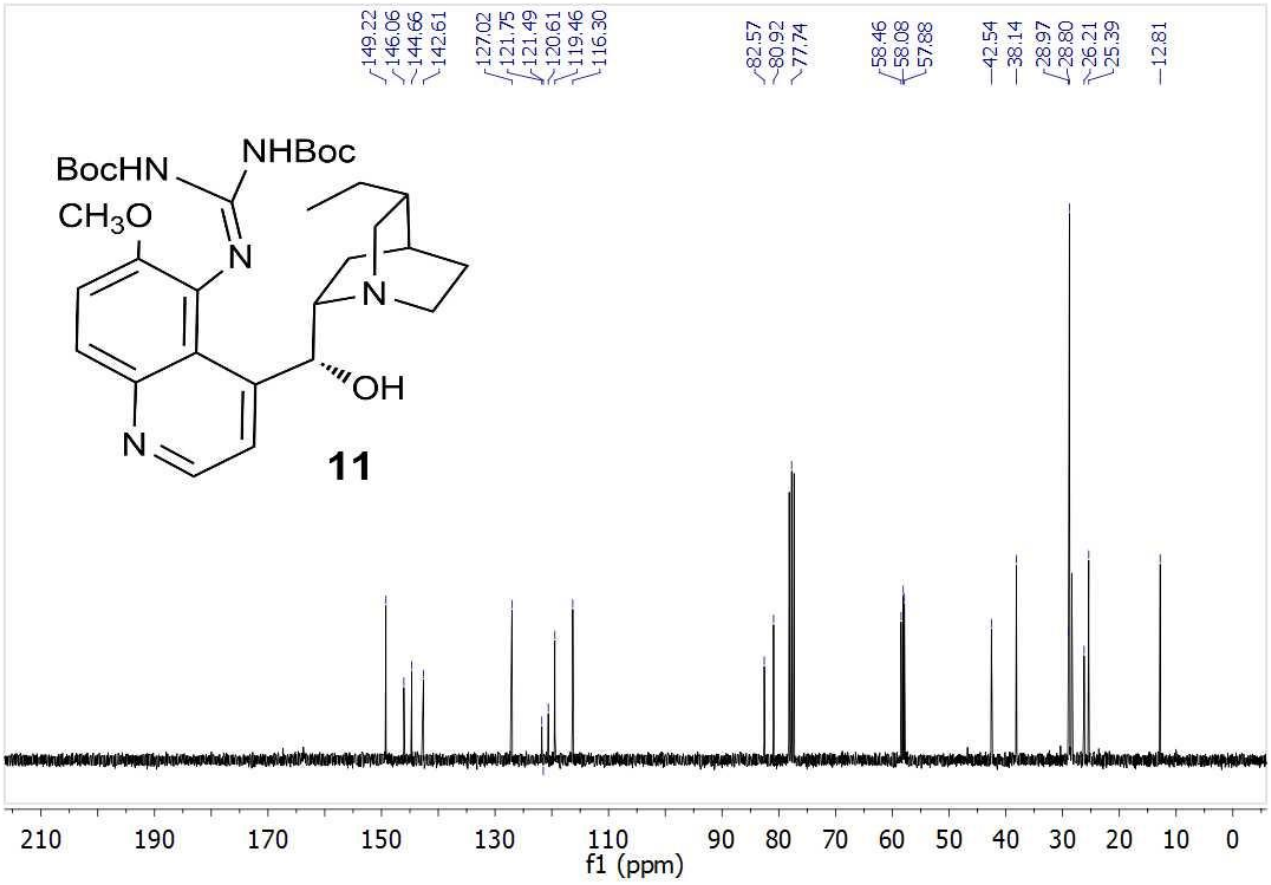
^{13}C NMR of **2b** (D_2O, 300 MHz, dioxane as internal standard)



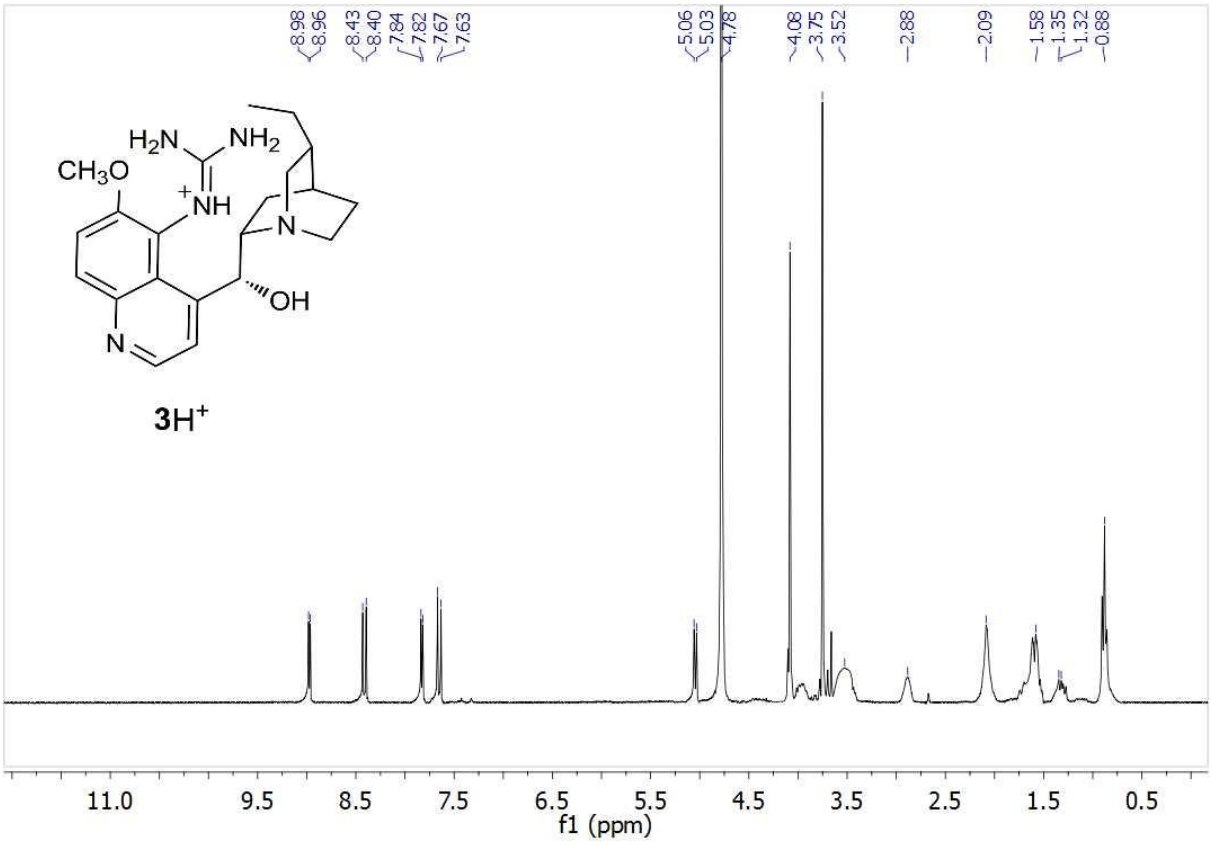
^{1}H NMR of **11** ($CDCl_3$, 300 MHz)



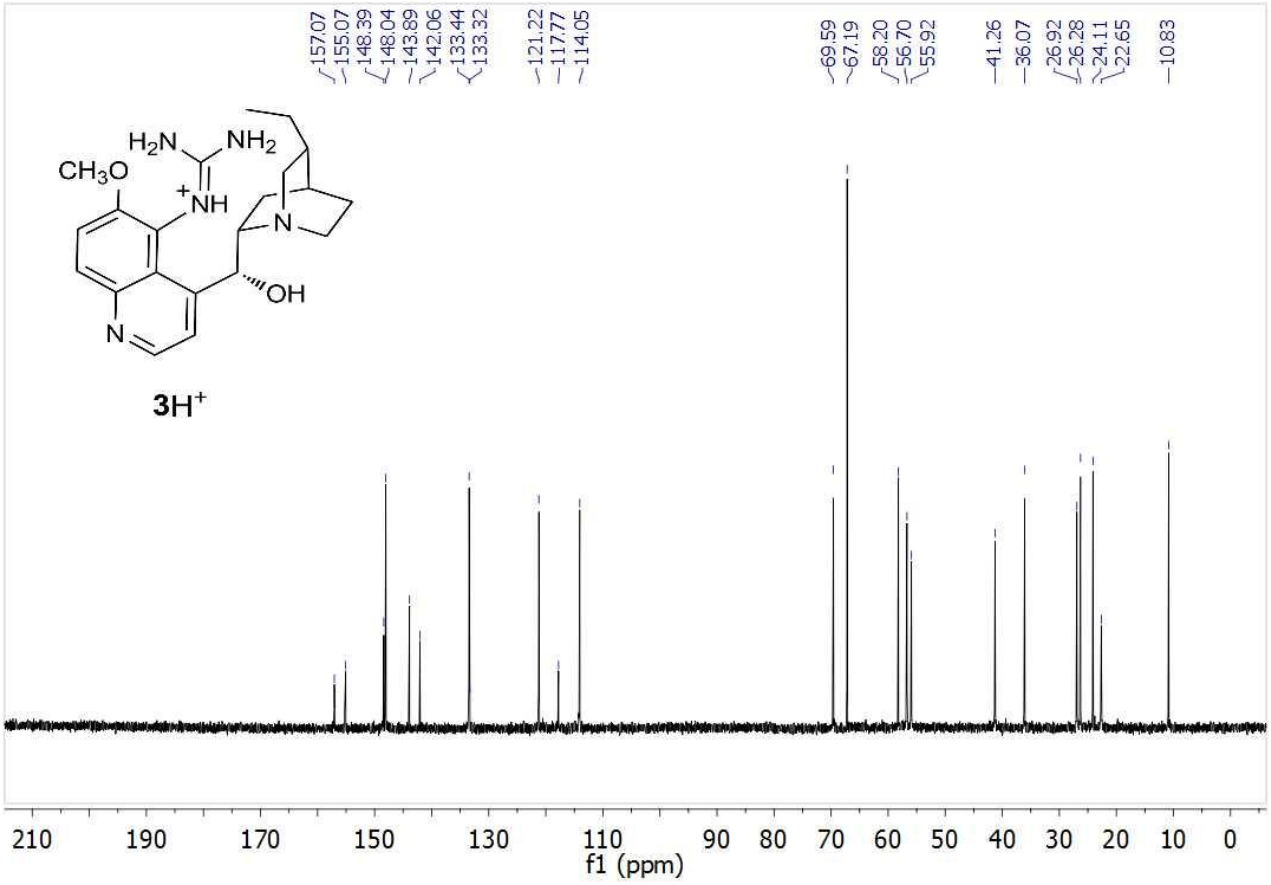
^{13}C NMR of **11** ($CDCl_3$, 75 MHz)



^{1}H NMR of **3** (D_2O, 300 MHz, dioxane as internal standard)



^{13}C NMR of **3** (D_2O, 75 MHz, dioxane as internal standard)



Distribution Diagrams

Distribution diagrams of the species **1b, 2b** and **3** as a function of pH under the conditions of the titration experiments in Figure 1 (see main text). Calculated on the basis of data in Table 1 with the program Hyperquad.[1]

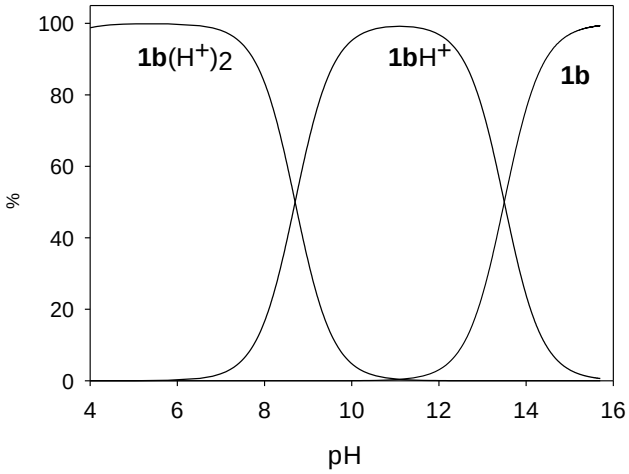


Figure 1S

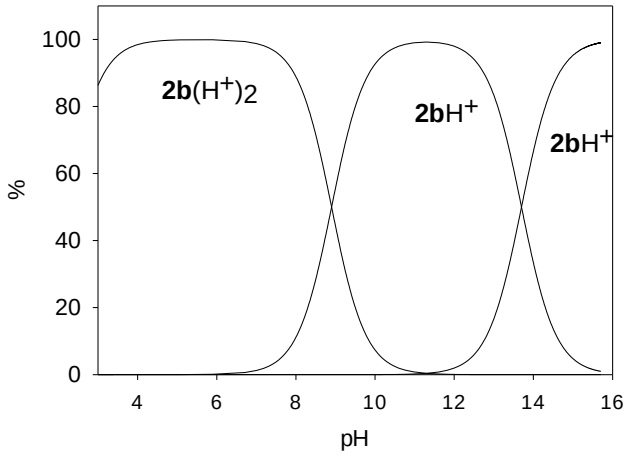


Figure 2S

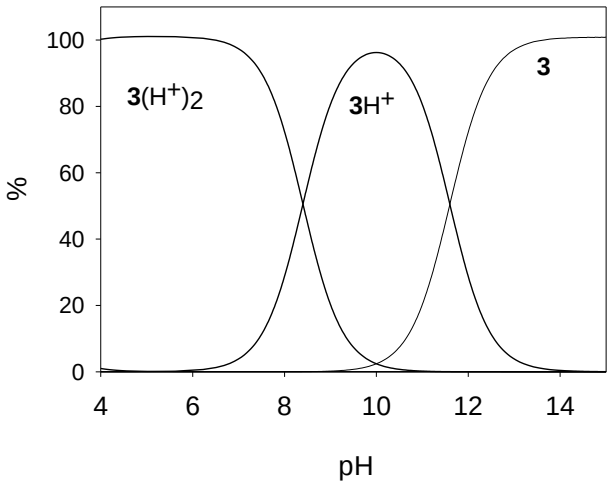


Figure 3S

Titration Experiments

Potentiometric titration plots of the chlorohydrates of the given compounds with $(CH_3)_4NOH$ in 80% DMSO, 25 °C, under the conditions of the titration experiments in Table 1 (main text).

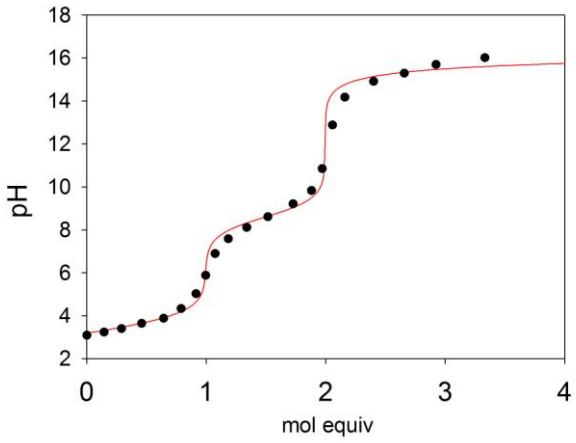


Figure 4S Compound **6b**

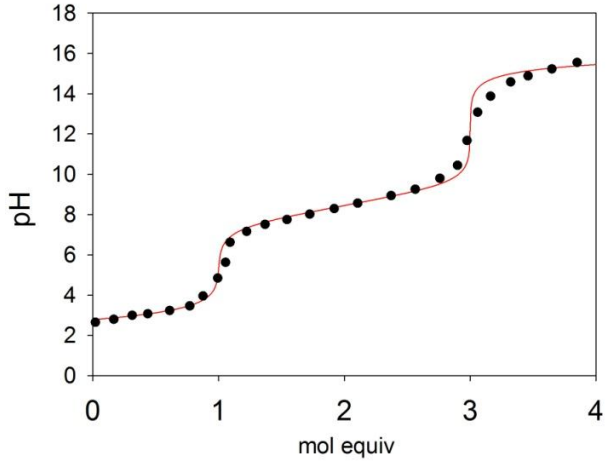


Figure 5S Compound **4**

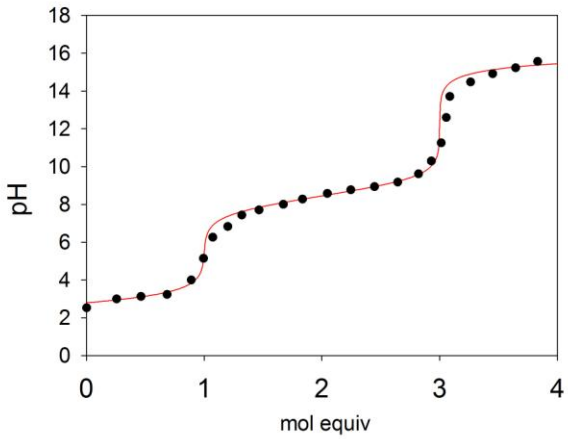


Figure 6S Compound **9**

Kinetic Experiments

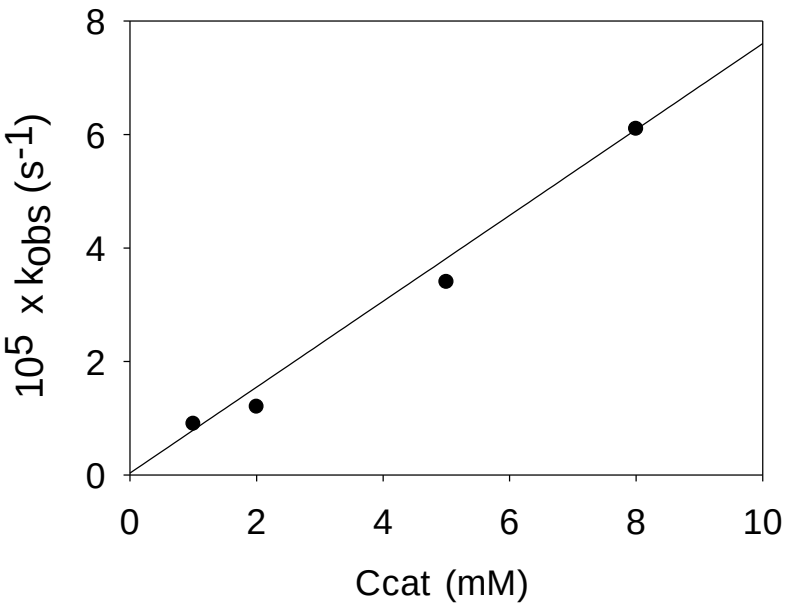


Figure 7S Plot of pseudo-first-order rate constants k_{obs} for the liberation of *p*-nitrophenol from 0.1 mM HPNP catalyzed by **1b** (80% DMSO, 25 ^{o}C, pH 8.7, 10 mM Me_4NClO_4) versus total catalyst concentration.

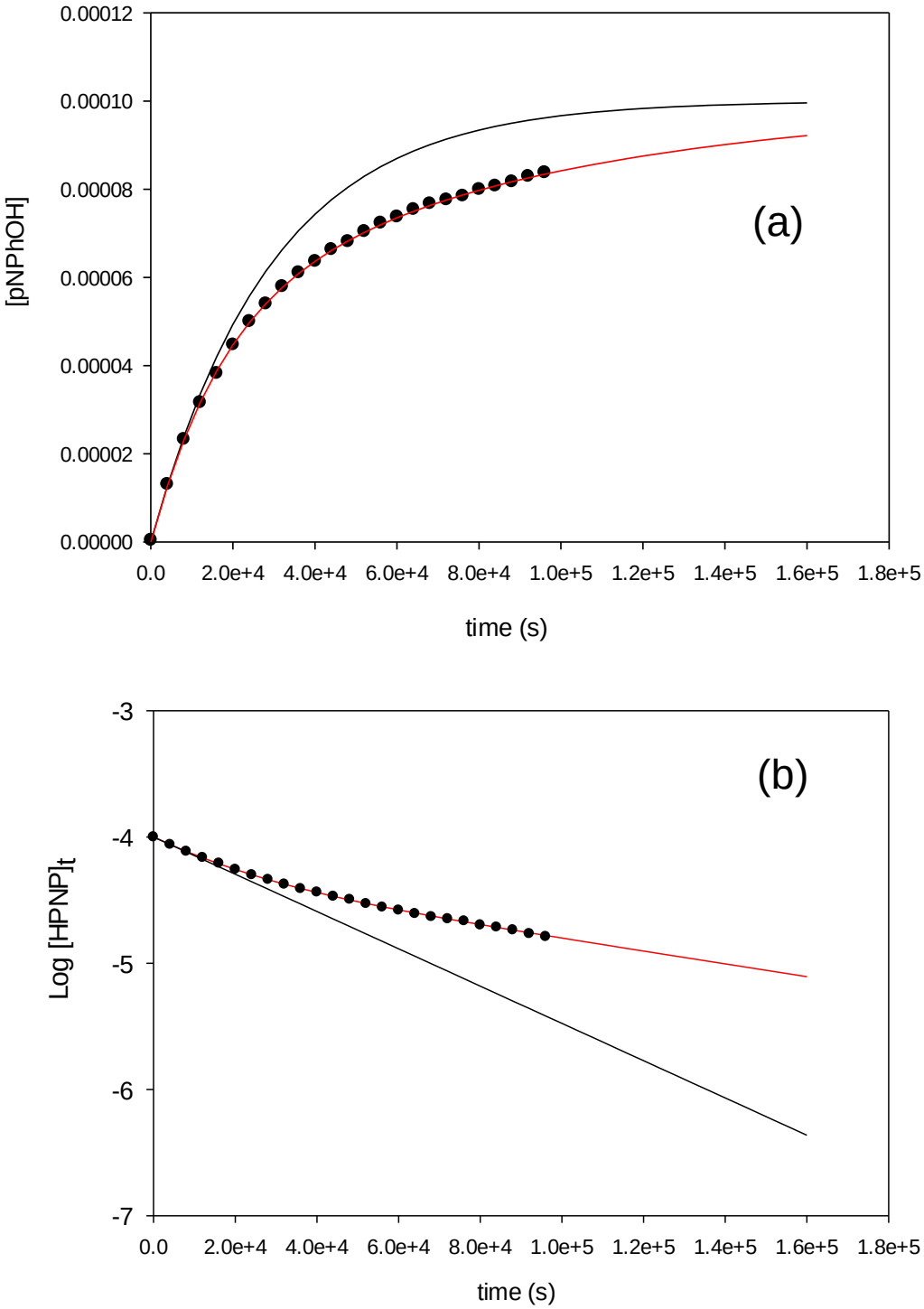
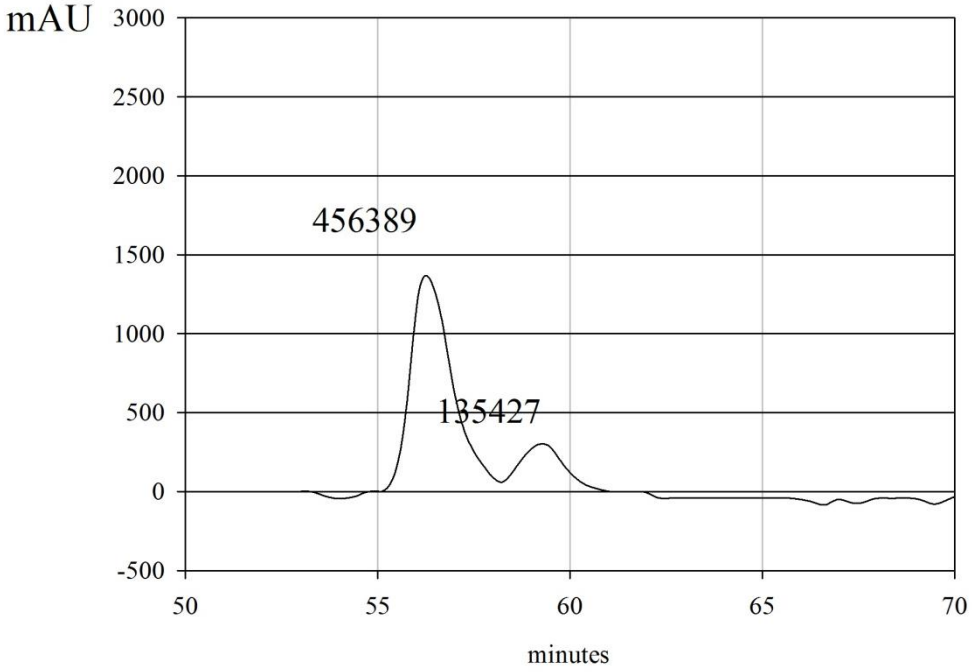


Figure 8S Data points for the HPNP transesterification catalyzed by 5.0 mM of **1b** (25 ^{o}C, 80% DMSO, pH 8.7). Linear (a) and logarithmic scale (b) plots. Data points are fitted to eq 4 in the main text (red line). As a comparison the ordinary first-order equation is reported (black line), calculated using eq 5 in the main text.

HPLC Data and Determination of the Absolute Configuration



Recovered substrate for the reaction of HPNP in presence of catalyst **1** in the conditions described in Table 2 (the reaction mixture was quenched with a 10 mM solution of $HClO_4$ at the indicated time interval).

ee= 54% Reaction time=8h18' Conversion=50%

Eluent=isopropanol/water(TFA-1mM). The column CHIRALPACK (Daicel Corporation) was irreversibly conditioned with H_2O:isopropanol 30:70. With this treatment the column is suitable for separation of polar analytes.

according to eq 1S,[2] k_{rel}=5.7. It is in agreement with the value determined by full-course UV-Vis measurements (Table 2, main text).

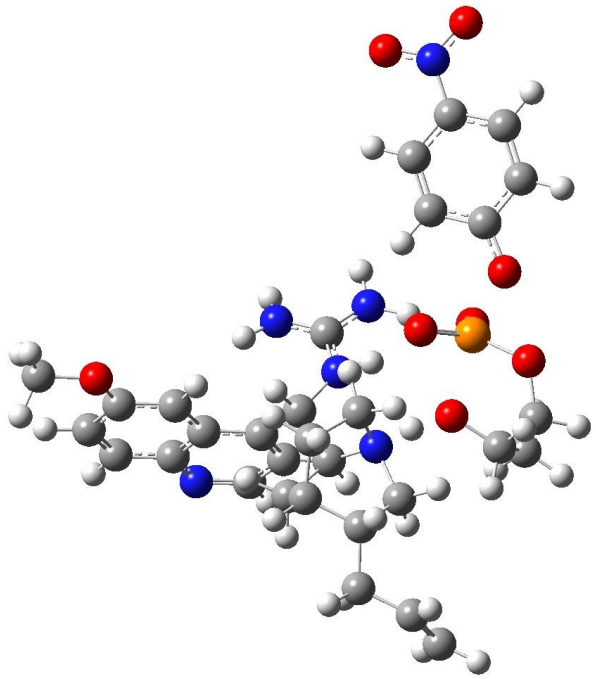
$$k_{rel} = \frac{\ln[(1-c)(1-ee)]}{\ln[(1-c)(1+ee)]} \qquad (1S)$$

Determination of the absolute configuration of HPNP.

The cleavage of HPNP catalyzed by catalyst **1b** in the conditions reported in Table 2 was quenched with a 10 mM solution of $HClO_4$. After chiral HPLC separation the unreacted substrate was separated from its less abundant enantiomer. Then the compound was treated with KOH 1 M, 100 ^oC for 24 h. After the exhaustive hydrolysis the (-)-1,2-propanediol (polarimetric measure) was obtained that has the (R) absolute configuration.[3] Consequently the most reactive HPNP enantiomer in the reaction promoted by the guanidine-functionalized catalyst **1b**, **2b** and **3** is (S).

Coordinates, energies and ZPVE from DFT calculations

Transition state of catalyst **1b**H^+ with (S)-HPNP



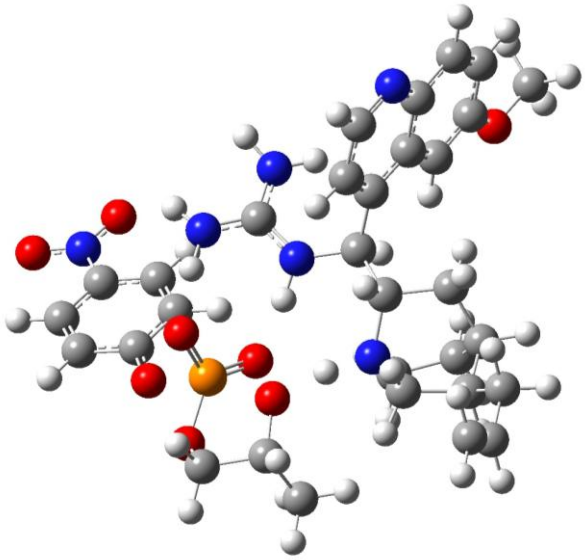
H	0.43841900	0.11501000	0.32350500
C	-4.27921100	-3.93669200	-0.84719700
C	-5.22144400	-4.39958900	0.10843600
C	-5.28516500	-3.80027200	1.34477200
C	-4.43152900	-2.72449600	1.69640700
C	-3.48598100	-2.24216600	0.72380200
C	-3.43375900	-2.88026800	-0.54037100
C	-2.64256900	-1.15290000	1.12479700
C	-2.77992400	-0.66403800	2.40705300
C	-3.74207700	-1.21698800	3.28229100
N	-4.54989800	-2.20502600	2.95241200
O	-4.13822500	-4.47054000	-2.08821400
H	-5.88719400	-5.22115100	-0.12462600
H	-5.99383400	-4.14343200	2.09112300
H	-2.73820800	-2.56657500	-1.30951900
C	-1.61402000	-0.50957200	0.18476400
H	-2.14377900	0.13923000	2.76442600
H	-3.83926500	-0.81610500	4.28935400
H	-1.60702000	-1.03947000	-0.77245000
N	-0.26049600	-0.52198200	0.75686400
C	-4.97603400	-5.56355900	-2.47148400
H	-4.68241500	-5.81598500	-3.49019400
H	-4.82080000	-6.43286500	-1.82363500
H	-6.03390400	-5.28020600	-2.45901500
C	-2.92103800	3.15761000	-1.98633300
C	-3.22770200	1.66624700	-2.23954400

C	-3.43855100	0.92999300	-0.90240400
C	-2.11648200	0.94595500	-0.07619500
N	-1.13013400	1.85583000	-0.77121500
C	-1.78053500	3.20834600	-0.94065200
H	-4.12331200	1.56443600	-2.85962700
H	-3.74988700	-0.09726800	-1.10639300
H	-4.24460100	1.38779000	-0.32412500
H	-2.26962200	1.41673100	0.89598500
C	-0.73859200	1.33298600	-2.12411200
C	-2.01256900	1.04397600	-2.95484800
H	-0.10100800	0.46362900	-1.97980700
H	-2.16005000	-0.03428300	-3.07370700
H	-1.90404100	1.46425700	-3.95884300
H	-2.55309900	3.58445800	-2.92757600
C	-4.14516000	3.99102500	-1.55298400
H	-0.98908300	3.90309100	-1.22670900
H	-0.11500500	2.10426500	-2.57909400
C	-3.82746700	5.45359100	-1.38973100
C	-3.96234200	6.14647900	-0.25751100
H	-2.14967400	3.50933700	0.04300600
H	-4.91941100	3.87049300	-2.32333400
H	-4.56178800	3.60069300	-0.61695600
H	-3.45312100	5.95989700	-2.28070100
H	-3.71511300	7.20265800	-0.20206100
H	-4.33280000	5.68273000	0.65404500
C	0.32310200	-1.54681900	1.41507500
N	1.48968800	-1.31699300	2.01860300
N	-0.22817400	-2.76697400	1.49533600
H	2.04645900	-2.10438500	2.31721700
H	1.93521800	-0.36653200	2.00965800
H	-1.05243300	-3.01787400	0.97488200
H	0.11954600	-3.44064500	2.16020500
O	4.23353400	1.45413900	-0.14332000
C	4.87852500	0.31268600	-0.29800700
C	4.28167500	-0.97533000	-0.26451100
C	5.05241600	-2.11030200	-0.44247600
C	6.43257100	-1.99686200	-0.66217300
C	7.04668300	-0.73546400	-0.70992600
C	6.27885900	0.39710100	-0.52934300
H	3.21301800	-1.05435300	-0.12666700
H	4.60017100	-3.09428700	-0.41993100
N	7.22558100	-3.18174000	-0.84496900
H	8.11339300	-0.66697600	-0.88273300
H	6.73196600	1.38252000	-0.55717800
O	0.63789900	2.39916700	0.96876500
C	0.77815700	3.75540500	1.32716800
C	1.88585400	4.27058900	0.40223100
O	2.87999900	3.25342500	0.26600600
P	2.52340700	1.65428400	0.48540100
O	1.81199700	0.82917400	-0.58699900
O	2.74643000	1.09335900	1.88637800

H	2.38856300	5.16455400	0.78476000
H	1.47933000	4.50030500	-0.59174200
H	-0.23098900	2.08008400	-0.04544800
O	8.44473500	-3.05889100	-1.04900300
O	6.66681400	-4.28988000	-0.79266900
C	1.10121900	3.91164700	2.81586900
H	0.29896900	3.47309100	3.41748900
H	2.03149500	3.39401100	3.06242300
H	1.19529900	4.96913600	3.08715700
H	-0.14438400	4.31439800	1.11187600

Total Energy= -2476.982814 ZPVE= 0.712568

Transition state of catalyst **1b**H^+ with (R)-HPNP



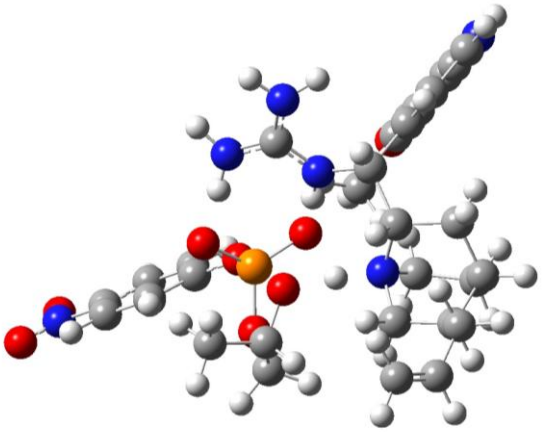
H	-0.52691900	-0.36475200	0.30116400
C	3.38801800	4.39853800	-0.96084600
C	4.14092500	5.12894800	-0.00468300
C	4.23054000	4.66424800	1.28677200
C	3.58814800	3.46831900	1.69497200
C	2.83536800	2.71771200	0.72451100
C	2.75273400	3.21941900	-0.59786800
C	2.20188200	1.51472400	1.18360000
C	2.33982100	1.17787100	2.51370200
C	3.10207900	1.99256600	3.38190600
N	3.71532900	3.09506600	3.00128400
O	3.23819100	4.78089300	-2.25539000
H	4.64186400	6.04814700	-0.28105900
H	4.79646800	5.20998800	2.03438300
H	2.19779700	2.70232600	-1.37113000
C	1.39603500	0.59142300	0.25601500
H	1.85635000	0.29375700	2.91609200
H	3.20281700	1.70782200	4.42740900
H	1.36628900	1.01449600	-0.75262200

N	0.02987500	0.39062500	0.75087100
C	3.86710500	5.98569000	-2.69937600
H	3.60857000	6.08083000	-3.75377000
H	3.49119600	6.85782000	-2.15390200
H	4.95605500	5.92956600	-2.59693600
C	3.71698400	-2.84628000	-1.40131800
C	3.73020900	-1.34302000	-1.74532400
C	3.58928600	-0.50981800	-0.45782600
C	2.19046600	-0.75022800	0.19707800
N	1.53863300	-1.91258800	-0.53135400
C	2.51695500	-3.06917400	-0.45542600
H	4.66039900	-1.07585100	-2.25539900
H	3.71353800	0.54582000	-0.70714000
H	4.37928300	-0.75350200	0.25620600
H	2.29691100	-1.10842400	1.22185100
C	1.24399000	-1.58172500	-1.96918500
C	2.52195800	-1.04794500	-2.65516300
H	0.40864000	-0.88207800	-1.97936900
H	2.44339500	0.02769700	-2.84122900
H	2.64824900	-1.53143000	-3.62799900
H	3.54065700	-3.40184300	-2.33098500
C	5.03616900	-3.37014200	-0.79704400
H	1.96484200	-3.97521900	-0.69264400
H	0.88817500	-2.50604500	-2.42673400
C	5.01311700	-4.85379800	-0.54121200
C	5.17574900	-5.42985200	0.65113300
H	2.83029900	-3.14324600	0.58878500
H	5.84215000	-3.13533700	-1.50594600
H	5.26570500	-2.84102800	0.13548200
H	4.84203800	-5.48288900	-1.41599000
H	5.14824500	-6.50893000	0.77163900
H	5.34957000	-4.84215800	1.54976700
C	-0.75968300	1.33670800	1.31529100
N	-1.84404600	0.92434700	1.96707700
N	-0.47949500	2.64585600	1.25943900
H	-2.59109100	1.58175000	2.13673200
H	-2.03788100	-0.10488000	2.03889700
H	0.24266600	3.01475400	0.66257100
H	-0.96353800	3.29688400	1.85932900
O	-4.11148500	-1.74982700	0.23732600
C	-4.70436600	-0.60515100	-0.03857200
C	-4.07806800	0.53558400	-0.61183000
C	-4.80880400	1.68110700	-0.87183900
C	-6.17877900	1.72833800	-0.57482600
C	-6.82565400	0.61396200	-0.01658000
C	-6.09797100	-0.52847100	0.24536900
H	-3.02700500	0.47227400	-0.85464300
H	-4.33483300	2.54999100	-1.31221700
N	-6.92742000	2.92298700	-0.84793000
H	-7.88422600	0.66678300	0.20539900

H	-6.57608900	-1.40013400	0.67996500
O	-0.47732400	-3.12481500	0.49275900
C	-0.65879300	-4.50484300	0.26530500
H	0.05244400	-5.09744500	0.86365200
C	-2.07781600	-4.75055600	0.77523900
O	-2.88360600	-3.69404500	0.24249900
P	-2.31756000	-2.16115900	0.48633900
O	-1.75426200	-1.28021000	-0.62787400
O	-2.22080800	-1.74495000	1.94989900
C	-0.55592000	-4.93193200	-1.20852900
H	-2.10947500	-4.72454000	1.87126300
H	-2.51282700	-5.69006900	0.42465700
H	0.59199700	-2.36083200	-0.05458100
O	-8.14299600	2.93927800	-0.58996400
O	-6.33674100	3.90287600	-1.33314600
H	-1.31436200	-4.41929800	-1.80721000
H	0.42221300	-4.71212700	-1.64261100
H	-0.71516900	-6.01223200	-1.30147200

Total Energy= -2.476.7794448 ZPVE= 0.713654

Transition state of catalyst **2b**H^+ with (S)-HPNP



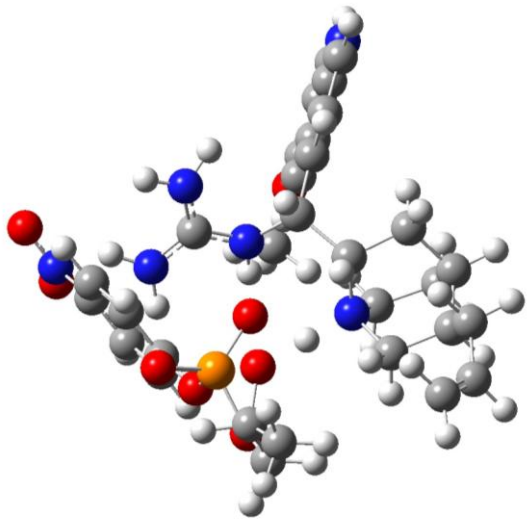
O	2.99077200	-0.53318500	-0.42970300
C	4.30458600	-0.41158100	-0.30212800
C	4.96126900	0.59993200	0.44482000
C	6.34294700	0.63529500	0.51001300
C	7.10339100	-0.33130700	-0.16256900
C	6.47802100	-1.34513800	-0.90362900
C	5.09911200	-1.38057900	-0.96913700
H	4.36924800	1.33004800	0.97777100
H	6.84977900	1.40462700	1.07942400
N	8.53991700	-0.28558300	-0.09041700
H	7.08187800	-2.08380800	-1.41557200
H	4.59223400	-2.15318800	-1.53755200
O	0.22040500	1.98863100	0.54892600

C	0.77437100	3.25535500	0.26215300
C	1.71362700	3.00427000	-0.92654600
O	2.31531000	1.71196700	-0.79122700
P	1.71153700	0.56388000	0.23109200
O	0.58283600	-0.37002000	-0.20878000
O	2.17095600	0.63580500	1.68350100
H	2.52386900	3.73744200	-0.99433100
H	1.15311800	3.02060400	-1.86974300
H	-0.92014900	1.61881600	-0.06803100
O	9.19492800	-1.15395500	-0.68912100
O	9.07670700	0.61998500	0.56775600
C	1.46998100	3.85595400	1.48695000
H	2.27444100	3.20378400	1.83366600
H	1.88027200	4.84492100	1.25409200
H	0.74831300	3.96795700	2.30227700
H	-0.00517300	3.95775300	-0.06292800
H	0.97964400	0.02235800	2.65391500
H	-0.61190800	-0.32455600	0.93836600
C	-1.30940100	-3.91650400	-1.19471300
C	-2.17507800	-5.03949200	-1.30314100
C	-3.39414700	-5.02357900	-0.68728900
C	-3.82398000	-3.89562300	0.06521500
C	-2.95744000	-2.74778200	0.17765600
C	-1.68415100	-2.79553800	-0.46704500
C	-3.46050000	-1.64558300	0.95309600
C	-4.70866900	-1.79632500	1.53939000
C	-5.47122600	-2.96580800	1.35677800
N	-5.05524800	-3.99082900	0.64132100
O	-0.13294000	-4.07784100	-1.85024000
H	-1.83784900	-5.89401900	-1.88030500
H	-4.07170200	-5.86828200	-0.75196300
H	-0.98741200	-1.97433400	-0.36759100
C	-2.77252400	-0.29802800	1.26618900
H	-5.12744400	-0.99852700	2.14611700
H	-6.45115700	-3.04863000	1.82314100
N	-1.37312000	-0.39154200	1.65755200
C	0.77482900	-2.97495700	-1.93338000
H	1.63427500	-3.34596400	-2.49313000
H	0.31830100	-2.13700300	-2.46990400
H	1.08727800	-2.61813300	-0.95085400
C	-3.73406500	2.95881500	-1.66115100
C	-4.22676400	1.51288200	-1.86005300
C	-4.37721000	0.79208400	-0.50872800
C	-3.07075900	0.94183300	0.31778400
N	-1.98039200	1.45200100	-0.60200300
C	-2.34480300	2.87222400	-0.97904400
H	-5.18635600	1.51266300	-2.38586100
H	-4.59331800	-0.25983200	-0.70516200
H	-5.22075600	1.18089700	0.06773300
H	-3.18459200	1.76921100	1.02100100

C	-1.86644300	0.63932300	-1.85796200
C	-3.17072800	0.75455100	-2.68643000
H	-1.64757800	-0.38462800	-1.56843800
H	-3.53784000	-0.24420500	-2.94083400
H	-2.98271600	1.28059200	-3.62754500
H	-3.59890700	3.39969600	-2.65589700
C	-4.72789100	3.85935600	-0.89293300
H	-1.55027100	3.22048200	-1.64078000
H	-0.99497100	1.01332100	-2.39723200
C	-4.29808500	5.30112100	-0.85744800
C	-4.04763700	6.00127300	0.25059200
H	-2.30270900	3.46739700	-0.06429200
H	-5.70270800	3.78288600	-1.39470700
H	-4.86864700	3.49613500	0.13180200
H	-4.18156800	5.78474100	-1.82844800
H	-3.73801800	7.04159100	0.21041700
H	-4.15172800	5.56028100	1.23953800
C	-0.99295100	-0.62492600	2.92319800
N	0.27466100	-0.44182000	3.27987700
N	-1.90550500	-0.99960500	3.85134100
H	0.58157200	-0.78904200	4.17615100
H	-2.70130300	-1.55222800	3.56704500
H	-1.59304800	-1.14702500	4.79972000
H	-3.29753000	0.02841900	2.16690000

Total Energy= -2476.978768 ZPVE= 0.713095

Transition state of catalyst **2b**H^+ with (*R*)-HPNP



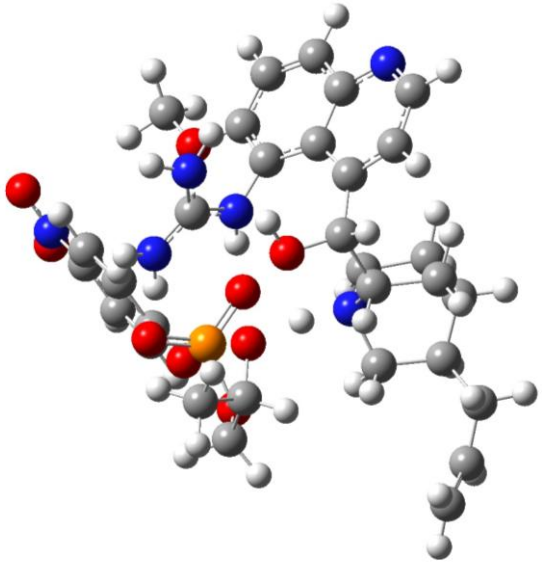
O	-2.55201800	-2.55444400	-0.70146900
C	-3.68038800	-1.89054700	-0.45927500
C	-3.92666400	-1.11154800	0.69264400
C	-5.14593500	-0.47451200	0.85434600
C	-6.13404400	-0.59206100	-0.13314900

C	-5.91183000	-1.35691200	-1.28556400
C	-4.69918900	-2.00181800	-1.43813600
H	-3.16410700	-1.04192100	1.45485700
H	-5.34765100	0.10998900	1.74470900
N	-7.40312300	0.07129600	0.04469400
H	-6.68652800	-1.42378100	-2.04507200
H	-4.50790000	-2.60537100	-2.31471700
O	1.12673700	-2.37185000	0.79272800
C	1.30400100	-3.76426300	0.83827000
H	0.67327600	-4.15385700	1.65537900
C	0.72071800	-4.29356200	-0.47108600
O	-0.50121700	-3.59625300	-0.75609100
P	-1.02441000	-2.32574100	0.15129500
O	-0.71655700	-0.89642200	-0.28494400
O	-1.40818000	-2.65126500	1.58874700
C	2.73077400	-4.23592800	1.09513400
H	0.49098600	-5.36472500	-0.44060600
H	1.41654100	-4.11362800	-1.30138500
C	-1.25100500	3.22267200	-1.32203400
C	-1.21163000	4.63845600	-1.44835100
C	-0.26768500	5.35775200	-0.77171100
C	0.69733800	4.71461400	0.05042000
C	0.67952500	3.27762200	0.16954700
C	-0.33294400	2.55261600	-0.52670400
C	1.69802700	2.69378700	1.00026300
C	2.56785200	3.56066000	1.64503900
C	2.48571600	4.95542600	1.46147500
N	1.58880400	5.52791400	0.68455700
O	-2.25145100	2.64037400	-2.02805400
H	-1.95062600	5.11886700	-2.08120300
H	-0.22420200	6.43976000	-0.83960000
H	-0.41216100	1.48020800	-0.41625600
C	1.95159000	1.19793900	1.29142900
H	3.34466300	3.17144200	2.29773100
H	3.18825000	5.60928300	1.97543100
N	0.76271700	0.42190900	1.61958600
H	0.25731800	-0.13142500	0.89302100
C	-2.36352200	1.21647100	-2.01270000
H	-3.24036200	0.98149100	-2.61667000
H	-1.47666500	0.74893500	-2.44692300
H	-2.49369900	0.83142000	-1.00073000
C	4.75224800	-0.70452000	-1.66938400
C	4.18218100	0.71748000	-1.86028400
C	3.85404700	1.37667200	-0.50997100
C	2.97943400	0.42887500	0.34788600
N	2.47516400	-0.69166500	-0.53809200
C	3.67356200	-1.52788100	-0.91731700
H	4.90097700	1.35885600	-2.38343300
H	3.32870100	2.30979600	-0.71550400
H	4.75649400	1.64726200	0.04094700
H	3.61993300	-0.10421500	1.05325900

C	1.83515000	-0.18493100	-1.79768800
C	2.86725600	0.59274100	-2.65532300
H	0.98739500	0.42939200	-1.51426200
H	2.47626700	1.58486300	-2.89673000
H	3.03988500	0.07345600	-3.60238900
H	4.88748000	-1.14602300	-2.66471900
C	6.12615800	-0.73206900	-0.96165500
H	3.29220600	-2.35469400	-1.52222900
H	1.43383200	-1.05800900	-2.31473600
C	6.73235000	-2.10710900	-0.90812400
C	7.03464600	-2.76955400	0.20918600
H	4.06960100	-1.95254900	0.00572500
H	6.79639000	-0.05988800	-1.51503400
H	6.04335200	-0.33073800	0.05470500
H	6.92334600	-2.57841400	-1.87248600
H	7.47025600	-3.76300400	0.18235600
H	6.86549800	-2.33726600	1.19256200
C	0.29907100	0.32579100	2.87383900
N	-0.57004800	-0.62799700	3.19429500
N	0.74780000	1.17484200	3.82908000
H	-1.04552800	-0.57215900	4.08246700
H	-0.80412000	-1.42511600	2.55579600
H	1.01889400	2.11182900	3.56720500
H	0.39226300	1.07322500	4.76824800
H	1.78679500	-1.51141500	0.06070700
H	2.52743000	1.23518800	2.21874900
H	3.39184400	-4.03873200	0.24692500
H	3.13400200	-3.72554800	1.97509900
H	2.75064200	-5.31379600	1.28942800
O	-8.26754900	-0.05628900	-0.83479900
O	-7.58412200	0.74225900	1.07325400

Total Energy=-2476.978561 ZPVE=0.7124563

Transition state of catalyst **3**H^+ with (*S*)-HPNP



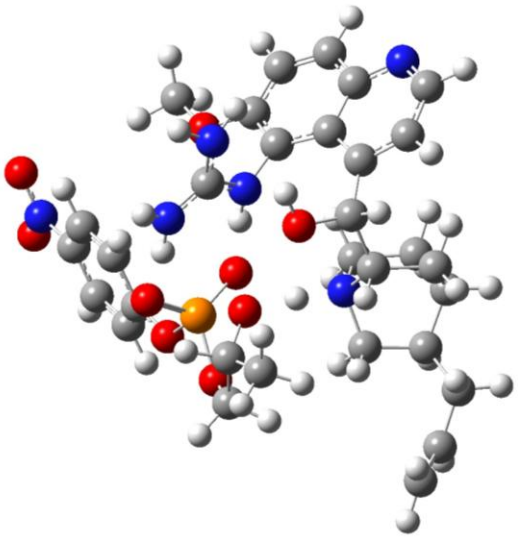
C	-3.80832200	-1.82836100	-0.41453600
C	-4.70405400	-2.33518800	-1.39423800
C	-5.91911200	-1.72715100	-1.63893000
C	-6.27619300	-0.58552600	-0.90514800
C	-5.41427900	-0.06651000	0.07186900
C	-4.19545700	-0.67342600	0.31638600
H	-6.59785900	-2.11427000	-2.38852000
H	-4.40587600	-3.21778000	-1.95031300
H	-3.53552000	-0.29491600	1.08467900
H	-5.72158300	0.80614600	0.63528600
N	-7.53987000	0.05338900	-1.15348500
O	-8.29135400	-0.42632100	-2.01827200
O	-7.83901200	1.06392500	-0.49608900
O	-2.67934400	-2.49071000	-0.23625500
O	0.70309400	-1.59807200	1.37410300
C	1.10904500	-2.79157300	2.00077300
C	1.06243700	-2.69897200	3.52650300
C	0.16716400	-3.90876000	1.45395600
O	-0.60858300	-3.38368900	0.37337500
P	-1.20147200	-1.85846800	0.64193700
O	-0.92120700	-0.71726300	-0.33059600
O	-1.80655300	-1.63436500	2.02529500
H	1.36208900	-3.64953100	3.98476800
H	0.04783700	-2.45568200	3.85320700
H	1.74269000	-1.91958400	3.88322300
H	2.14223000	-3.03266100	1.71038200
H	-0.50570000	-4.27140900	2.24109700
H	0.72321500	-4.76107700	1.05529900
H	1.57768800	-1.09516400	0.46279300
C	-0.74930800	3.25547200	-0.17755200
C	-0.64998900	4.40380400	-0.99425100
C	0.59211400	4.89854500	-1.28394100
C	1.77728300	4.28440700	-0.80816700
C	1.71635200	3.06599900	-0.02254800
C	0.39562600	2.59918000	0.30154400

C	3.00282100	2.49154300	0.34486700
C	4.12534300	3.23853000	0.01870700
C	4.05820400	4.43400300	-0.72036100
N	2.92531600	4.93751500	-1.15075500
O	-1.93504800	2.72899400	0.20854500
H	-1.53685000	4.89910700	-1.36681000
H	0.71206600	5.79387800	-1.88359200
C	3.38258300	1.16499000	1.05039900
H	5.10607500	2.89447500	0.32872800
H	4.97230900	4.97122100	-0.96537500
N	0.12381000	1.45010900	1.10793100
C	-3.14836400	3.34801900	-0.23292600
H	-3.95062400	2.74696800	0.19224000
H	-3.22676600	4.37631000	0.13402100
H	-3.22698000	3.33604600	-1.32442600
C	3.79499600	-2.08133300	-2.05872600
C	4.14816300	-0.58869400	-2.22891300
C	4.66630600	0.01551200	-0.91067300
C	3.59571200	-0.13106400	0.20865600
N	2.38651300	-0.83042400	-0.36562300
C	2.83133600	-2.19113700	-0.85027200
H	4.90637700	-0.46983000	-3.00920800
H	4.90061400	1.06762000	-1.08636100
H	5.59600500	-0.46337500	-0.59195200
H	3.95819600	-0.83044800	0.96659200
C	1.78888900	-0.09695800	-1.53398400
C	2.86239400	0.15920000	-2.61840600
H	1.35408100	0.82615200	-1.16635100
H	3.06698900	1.23073900	-2.70883900
H	2.50011800	-0.18459600	-3.59207700
H	3.26155100	-2.39592400	-2.96440600
C	5.02480400	-3.00271000	-1.90978500
H	1.92056600	-2.74710000	-1.08032200
H	0.96186800	-0.71274900	-1.88299300
C	4.65941400	-4.46208800	-1.85973100
C	4.92528700	-5.28701700	-0.84518800
H	3.31791800	-2.68744900	-0.00856900
H	5.68258500	-2.82258100	-2.77159200
H	5.59504700	-2.73723200	-1.01151000
H	4.12841000	-4.84745900	-2.73150500
H	4.63304800	-6.33290300	-0.86835200
H	5.45283300	-4.94671400	0.04320100
C	-0.08688900	1.56197900	2.42861300
N	-0.69806500	0.60458200	3.11070000
N	0.39008900	2.65300800	3.08771100
H	-0.72434800	0.66882500	4.11736400
H	0.60453700	3.47008000	2.53247500
H	0.00739000	2.85465700	4.00063000
H	4.41897500	1.35124500	1.36793700
O	2.63620800	0.80584000	2.19298800
H	-1.04440900	-0.28025800	2.66700800

H	-0.27562300	0.61507100	0.62244600
H	2.53491400	1.58694400	2.75655800

Total Energy= -2552.180495 ZPVE= 0.717283

Transition state of catalyst **3**H$^+$ with (*R*)-HPNP



C	-3.88943200	-1.83039200	-0.30182500
C	-4.80454200	-2.40306400	-1.22392100
C	-6.02220900	-1.80783200	-1.48850300
C	-6.35902300	-0.61384000	-0.83353500
C	-5.47609700	-0.02898900	0.08492400
C	-4.25499800	-0.62367100	0.34977300
H	-6.71748000	-2.24514700	-2.19397800
H	-4.52106100	-3.32571700	-1.71918300
H	-3.57837500	-0.19453900	1.07552700
H	-5.76785700	0.88505600	0.58759100
N	-7.62612600	0.01264400	-1.10257600
O	-8.39738200	-0.52608800	-1.91278700
O	-7.90623600	1.07072200	-0.51632300
O	-2.75819900	-2.48765700	-0.09943500
O	0.66730200	-1.50674800	1.43383600
C	0.85814500	-2.64312200	2.24087100
C	0.35583000	-3.81755800	1.38437500
O	-0.71772500	-3.36209500	0.54670400
P	-1.28265000	-1.81149400	0.70636300
O	-0.98305200	-0.73229100	-0.32740600
O	-1.86114200	-1.47544100	2.07970400
H	-0.00997100	-4.65193500	1.99406400
H	1.14970900	-4.19355400	0.72751300
H	1.54422900	-1.11017600	0.51455300
C	-0.71771500	3.27164800	-0.20138300
C	-0.61124000	4.40798300	-1.03404400

C	0.63413900	4.88830900	-1.33421000
C	1.81594100	4.26922800	-0.85609000
C	1.74696100	3.06054200	-0.05688900
C	0.42349800	2.61187100	0.28082200
C	3.02873900	2.47283000	0.30607500
C	4.15729200	3.20419400	-0.03423400
C	4.09854800	4.39499900	-0.78184500
N	2.96889400	4.90698800	-1.21088900
O	-1.90610800	2.76112900	0.19751800
H	-1.49508100	4.90643600	-1.40961000
H	0.75943200	5.77523600	-1.94518500
C	3.39722600	1.14389800	1.01480800
H	5.13653500	2.84968700	0.26881400
H	5.01705400	4.92002000	-1.03668500
N	0.14783000	1.48022100	1.10987000
C	-3.11591800	3.38542800	-0.24628800
H	-3.92159900	2.80013500	0.19428900
H	-3.18138900	4.42036600	0.10411000
H	-3.20173600	3.35627300	-1.33693500
C	3.70940800	-2.13331200	-2.06398200
C	4.06712400	-0.64653900	-2.26556500
C	4.61601700	-0.02813700	-0.96738500
C	3.57025500	-0.16207300	0.17692100
N	2.33793500	-0.84644500	-0.36239700
C	2.74119900	-2.21234500	-0.85622500
H	4.80918400	-0.54429900	-3.06367600
H	4.84632900	1.02196100	-1.15999600
H	5.55303300	-0.50354600	-0.66520400
H	3.94422300	-0.86232900	0.92848000
C	1.72861200	-0.10865400	-1.52018500
C	2.77730700	0.10324500	-2.63992600
H	1.33649000	0.83295600	-1.15269300
H	2.98984200	1.16961500	-2.76660900
H	2.38689700	-0.26382500	-3.59419600
H	3.17579800	-2.46534000	-2.96320200
C	4.93401600	-3.05846900	-1.89366800
H	1.81358000	-2.73388000	-1.09909100
H	0.87121800	-0.69988900	-1.83674500
C	4.55672700	-4.51383700	-1.81926400
C	4.80160900	-5.32031600	-0.78459700
H	3.20467600	-2.73534400	-0.01863700
H	5.59712900	-2.89850000	-2.75536700
H	5.50214100	-2.78188800	-0.99745000
H	4.03293700	-4.91227100	-2.68952500
H	4.50004300	-6.36380200	-0.79044800
H	5.32163300	-4.96712100	0.10320800
C	-0.03065700	1.61604900	2.43437500
N	-0.63689400	0.67866800	3.14457100
N	0.47664800	2.71185900	3.06298200
H	-0.66230000	0.77115000	4.14896000
H	0.68776700	3.51664900	2.48896500

H	0.11387200	2.93437900	3.97917400
H	4.44344500	1.31347900	1.30851200
O	2.66827300	0.81280400	2.17718900
H	-1.03731700	-0.19110900	2.71010100
H	-0.26735600	0.64482800	0.64932200
H	2.59597900	1.60263000	2.73319500
C	2.27333600	-2.83568300	2.77738600
H	2.60556100	-1.92428800	3.28134500
H	2.29642400	-3.65833200	3.50090400
H	2.99446300	-3.07345200	1.98911300
H	0.18721100	-2.54476000	3.10769400

Total Energy= -2552.179205 ZPVE= 0.717127

References

1) L. Alderighi, P. Gans, A. Ienco, D. Peters, A. Sabatini and A. Vacca, *Coord. Chem. Rev.*, 1999, **184**, 311.
2) J. M. Keith, J. F. Larrow and E. N. Jacobsen, *Adv. Synth. Catal.*, 2001, **343**, 5.
3) M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, 1978, **100**, 5491.