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Organocatalytic Oxidative Enamine Catalysis and 1,5-Hydride Transfer/Cyclization: Synthesis of Tetrahydroquinoline Derivatives

Mi Hyun Kim and Dae Young Kim*

*Department of Chemistry, Soonchunhyang University, Chungnam 336-745, Korea. *E-mail: dyoung@sch.ac.kr*
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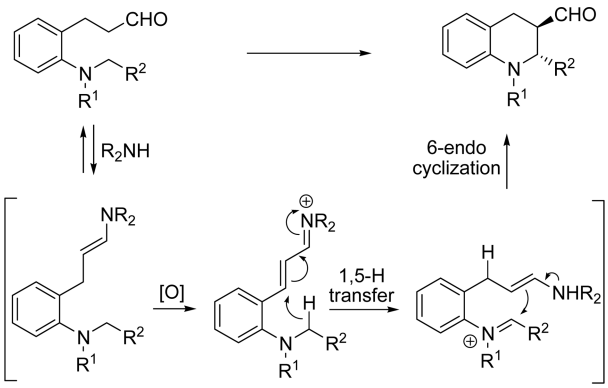
The development of C-C bond formation *via* C-H bonds activation has become an area of intense interest in synthetic organic chemistry. Because such reactions offer efficient methods for the construction of structurally complex and biologically active compounds.[1] Direct oxidative β-functionalization of simple aldehydes to β-functionalized ones is highly desirable, given this highly atom-economic, highly efficient, and waste reduced process.[2] However, the enantioselective routes for the oxidative β-functionalization of simple aldehydes have been rare.[3] Recently, three examples of organocatalytic enantioselective β-functionalization of aldehydes were reported by Wang,[4] Hayashi,[5] and Enders[6] groups. In this oxidative enamine catalysis, organic oxidants were converting the enamines to iminium ions in the presence of the amine catalyst, which facilitated the further nucleophilic addition to afford the β-functionalized products. The 1,5-hydride transfer and subsequent cyclization process is a well-known sp^3 C-H bond functionalization strategy and has attracted considerable interest for its application in the synthesis of heterocyclic compounds.[7] The *tert*-amino effect and related 1,5-hydride transfer and subsequent cyclization has attracted much attention due to its unique features to afford tetrahydroquinolines.[8,9] Tetrahydroquinoline derivatives have attracted considerable attention in organic synthesis and medicinal chemistry due to their importance as building blocks and diverse array of biological activities.[10] Therefore, the development of new and efficient synthetic routes for the preparation of tetrahydroquinoline analogues is of importance to both organic synthetic and medicinal chemistry.[11] Recently, several groups reported the synthesis of tetrahydroquinolines *via* intramolecular tandem hydride transfer/cyclization of *o*-dialkylamino-substituted alkylidene malonates, α,β-unsaturated aldehydes, and acyl oxazolidinones using a metal complexes such as magnesium, cobalt, and gold complexes as well as organocatalysts such as phosphoric acids and pyrrolidine.[12]

As part of the research program related to the development of synthetic methods for the formation of C-C bonds,[13] we recently reported the asymmetric internal redox reaction of cinnamaldehyde derivatives using secondary amines.[14] We became interested in an oxidation protocol where the saturated aldehyde is converted *in situ* into the corresponding α,β-unsaturated aldehyde which can then be manipulated with

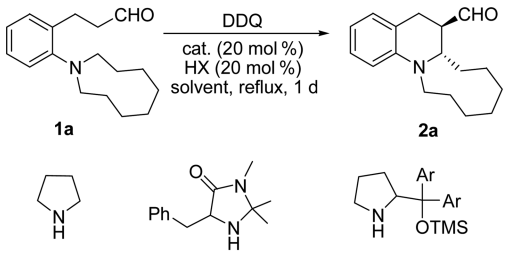


Scheme 1. Organocatalytic oxidative enamine catalysis and intramolecular redox reaction.

1,5-hydride transfer/cyclization. To the best of our knowledge, there are no examples for organocatalytic synthesis of tetrahydroquinolines from saturated aldehyde derivatives *via* oxidative enamine catalysis and internal redox reaction. Herein, we describe the first intramolecular version of oxidative enamine catalysis and 1,5-hydride transfer/cyclization sequences towards the asymmetric synthesis of tetrahydroquinolines (Scheme 1).

To determine suitable reaction conditions for the organocatalytic oxidative enamine catalysis and intramolecular redox reactions of saturated aldehydes, we initially investigated the reaction system with 3-(2-(azonan-1-yl)phenyl)propanal (**1a**) in the presence of 2,3-dichloro-5,6-dicyanoquinone (DDQ) as oxidant and nonchiral secondary amines **I-III** as organocatalysts in dichloromethane at reflux. Diarylprolinol silyl ether **III** effectively promoted this reaction in high yield with diasteroselectivity (71% yield, 80:20 dr, Table 1, entry 3). We then examined the reactivity with catalyst **III** in the presence of different acids, such as trifluoromethanesulfonic acid (TfOH), trifluoroacetic acid (TFA), and 2,4-dinitrobenzensulfonic acid (DNBS) as additives (Table 1, entries 3-5). Among the additives probed, the best result (84% yield and 86:14 dr) was achieved when the reaction was conducted in DNBS (Table 1, entry 5). A survey of the reaction media indicated that several common solvents, such as dichloromethane, chloroform, THF, and toluene were well tolerated in this intramolecular redox (Table 1, entries 5-8).

Table 1. Optimization of the reaction conditions[a]



Entry	Cat.	HX	Solvent	Yield (%)[b]	dr (%)[c]
1	**I**	HOTf	CH_2Cl_2	55	60:40
2	**II**	HCl	CH_2Cl_2	45	75:25
3	**III**	HOTf	CH_2Cl_2	71	80:20
4	**III**	TFA	CH_2Cl_2	66	80:20
5	**III**	DNBS	CH_2Cl_2	84	86:14
6	**III**	DNBS	$CHCl_3$	72	78:22
7	**III**	DNBS	THF	61	80:20
8	**III**	DNBS	PhMe	57	80:20

[a]Reactions were carried out with **1a** (0.3 mmol), oxidant (1.0 equiv.) catalyst (0.06 mmol), and additive (0.06 mmol) in solvent (1.0 mL). [b]Combined yield of both diastereomers. [c]Diastereomeric ratio is determined by ^{1}H NMR spectroscopic analysis.

Among the solvents probed, the best result was achieved when the reaction was conducted in dichloromethane (Table 1, entry 5).

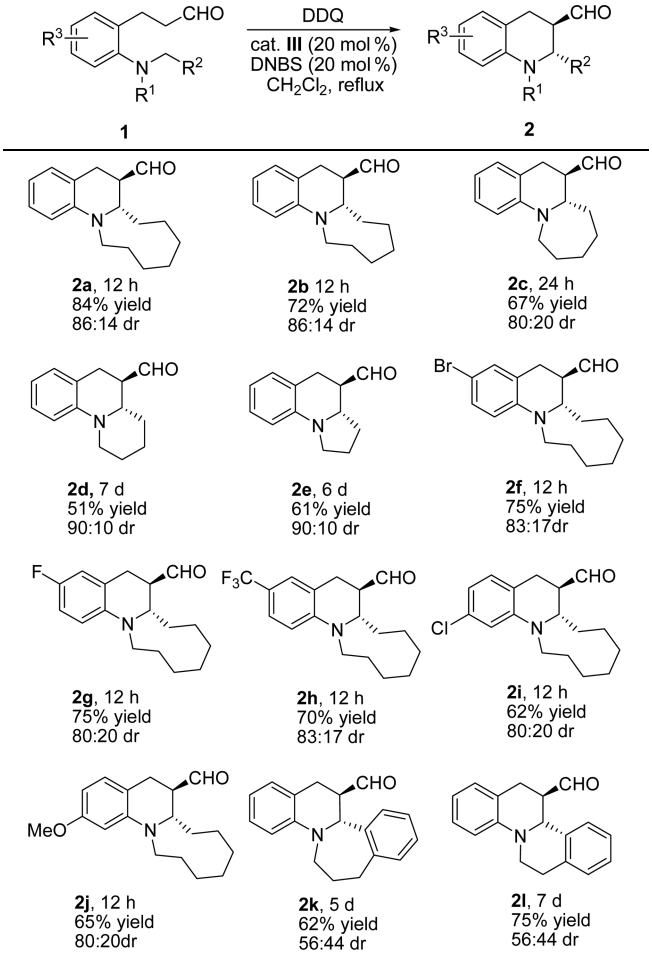
With optimal reaction conditions in hand, the scope of the reaction was explored as seen in Table 2. Organocatalyst **I**-catalyzed enantioselective oxidative enamine catalysis and intramolecular redox reactions of 3-arylpropanals **1** proved to be a general approach for the synthesis of versatile chiral-tetrahydroquinolines **2**. Products **2a-2j** which incorporated five to nine-membered azacycles were formed with moderate to high yields and high diastereoselectivities (62-84% yields, 80:20-90:10 dr, Table 2). A range of electron-withdrawing and electron-donating substitutions on the aryl ring of 3-arylpropanal derivatives **1** provided corresponding products **2f-2j** in moderate yields and high diastereoselectivities (62-75% yields, 80:20-83:17 dr, Table 2). However, products **2k-2l** which incorporated bicyclic azacycles were formed with low diastereoselectivities (1.2:1 dr, Table 2). The relative configuration major diastereomer of **2** was established by comparison of the ^{1}H-NMR spectral data with previously reported data.[14]

In summary, we have presented the first example of a organocatalytic oxidative enamine catalysis and hydride transfer/ring closure reaction cascade. The synthetically useful ring-fused tetrahydroquinoline derivatives were obtained in moderate yields and high levels of diastereoselectivities. Further investigations for the asymmetric version of this organocatalytic oxidative enamine catalysis and internal redox reaction are under way.

Experimental

General Procedure for the Synthesis of Tetrahydroquinoline Derivatives 2: To a stirred solution of 3-(*o*-(dialkylamino)aryl)propanals **1** (0.3 mmol) in CH_2Cl_2 (1.0 mL) was added DDQ (68.1 mg, 0.3 mmol), racemic diarylprolinol silylether catalyst **III** (35.9 mg, 0.06 mmol), and DNBS (14.9 mg, 0.06 mmol). The mixture was refluxed for 0.5-7 d, diluted with saturated $NaHCO_3$ solution (10 mL) and extracted with ethyl acetate (2 × 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated, and purified by flash chromatography (EtOAc/hexane = 1:10) to afford tetrahydroquinoline derivatives **2**.

Table 2. Catalytic oxidative enamine catalysis and hydride transfer/cyclization[a-c]



[a]Reactions were carried out with 3-arylpropanals **1** (0.3 mmol), DDQ (0.3 mmol), catalyst III (0.06 mmol), and DNBS (0.06 mmol) in CH_2Cl_2 (1.0 mL). [b]Combined yield of both diastereomers. [c]Diastereomeric ratio was determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture.

(6*R*,6a*S*)-5,6,6a,7,8,9,10,11,12,13-Decahydroazonino[1,2-*a*]quinoline-6-carbaldehyde (2a): Major diastereomer; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (d, J = 0.8 Hz, 1H), 7.14-7.07 (m, 2H), 6.80-6.77 (m, 1H), 6.70 (td, J = 7.2 Hz, 1.2 Hz, 1H), 3.76 (dt, J = 10.8 Hz, 2.4 Hz, 1H), 3.67 (ddd, J = 14.8 Hz, 8.0 Hz, 3.6 Hz, 1H), 3.22 (ddd, J = 14.8 Hz, 6.8 Hz, 3.6 Hz, 1H), 3.05-2.98 (m, 1H), 2.87 (dd, J = 16.8 Hz, 5.6 Hz, 1H), 2.70-2.65 (m, 1H), 1.84-1.10 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.21, 144.97, 129.77, 127.35, 120.33, 117.04, 115.24, 58.88, 56.79, 48.00, 28.87, 27.62, 27.25,

25.44, 25.09, 24.74, 23.33; EI-MS: *m/z* 258.1 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{17}H_{24}NO$ $[M+H]^+$: 258.1861; found 258.1858.

(6*R*,6a*R*)-6,6a,7,8,9,10,11,12-Octahydro-5*H*-azocino[1,2-*a*]quinoline-6-carbaldehyde (2b): Major diastereomer; ^1H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, *J* = 0.4 Hz, 1H), 7.08-7.03 (m, 2H, 6.61-6.54 (m, 2H), 3.84-3.79 (m, 2H), 3.24-3.21 (m, 1H), 3.20-3.06 (m, 2H), 2.54-2.51 (m, 1H), 2.01-1.32 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.32, 143.98, 129.52, 127.54, 117.37, 115.53, 111.33, 55.45, 53.15, 48.65, 33.90, 27.82, 26.91, 26.26, 26.09, 24.17; EI-MS: *m/z* 244.1 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{16}H_{22}NO$ $[M+H]^+$: 244.1701; found 244.1697.

(6*R*,6a*S*)-5,6,6a,7,8,9,10,11-Octahydroazepino[1,2-*a*]quinoline-6-carbaldehyde (2c): Major diastereomer; ^1H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.06-7.01 (m, 2H), 6.52-6.54 (m, 1H), 6.40-6.48 (m, 1H), 3.85 (dd, *J* = 6.0 Hz, 3.0 Hz, 1H), 3.82-3.79 (m, 1H), 3.22-3.09 (m, 2H), 3.02 (dd, *J* = 8.0 Hz, 6.5 Hz, 1 H), 2.54-2.52 (m, 1H), 1.81-1.95 (m, 1H), 1.67-1.57 (m, 6H), 1.37-1.34 (m, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.17, 144.90, 129.50, 127.53, 117.15, 115.67, 110.39, 58.26, 49.58, 47.95, 35.02, 26.63, 26.13, 25.94, 23.80; EI-MS: *m/z* 230.1 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{15}H_{20}NO$ $[M+H]^+$: 230.1545; found 230.1541.

(4a*S*,5*R*)-2,3,4,4a,5,6-Hexahydro-1*H*-pyrido[1,2-*a*]quinoline-5-carbaldehyde (2d): Major diastereomer; ^1H NMR (400 MHz, $CDCl_3$) δ 9.63 (d, *J* = 1.6 Hz, 1H), 7.10 (td, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.03-7.01 (m, 1H), 6.78-6.76 (m, 1H), 6.67 (td, *J* = 7.2 Hz, 0.8 Hz, 1H), 3.95-3.91 (m, 1H), 3.45 (ddd, *J* = 10.8 Hz, 5.2 Hz, 2.0 Hz, 1H), 2.99 (dd, *J* = 15.2 Hz, 6.4 Hz, 1H), 2.90-2.84 (m, 2H), 2.63-2.58 (m, 1H), 1.90-1.50 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.72, 145.73, 128.89, 127.65, 122.10, 117.62, 112.60, 56.53, 52.01, 48.39, 31.26, 25.99, 24.98, 24.06; EI-MS: *m/z* 216.1 $[M+H]^+$.

(3a*S*,4*R*)-1,2,3,3a,4,5-Hexahydropyrrolo[1,2-*a*]quinoline-4-carbaldehyde (2e): Major diastereoisomer; ^1H NMR (400 MHz, $CDCl_3$) δ 9.91 (d, *J* = 2.0 Hz, 1H), 7.11-7.08 (m, 1H), 7.35 (d, *J* = 7.0 Hz, 1H), 6.60-6.57 (m, 1H), 6.44 (d, *J* = 8.0 Hz, 1H) 3.49 (ddd, *J* = 10.4 Hz, 10.1 Hz, 4.9 Hz, 1H), 3.38 (ddd, *J* = 11.1 Hz, 8.9 Hz, 2.1 Hz, 1H), 3.22-3.17 (m, 1H), 2.93-2.91 (m, 2H), 2.50-2.41 (m, 1H), 2.32-2.28 (m, 1H), 2.13-2.10 (m, 1H), 1.97-1.95 (m, 1H), 1.58-1.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.99, 143.89, 128.70, 127.76, 119.06, 115.48, 110.45, 57.75, 50.35, 46.64, 31.62, 28.59, 24.02; EI-MS: *m/z* 202.1 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{13}H_{16}NO$ $[M+H]^+$: 202.1232; found 202.1238.

(6*R*,6a*S*)-3-Bromo-5,6,6a,7,8,9,10,11,12,13-decahydroazonino[1,2-*a*]quinoline-6-carbaldehyde (2f): Major diastereomer; ^1H NMR (400 MHz, $CDCl_3$) δ 9.81 (d, *J* = 0.8 Hz, 1H), 7.19-7.17 (m, 2H), 6.65-6.62 (m, 1H), 3.76 (dt, *J* = 10.4 Hz, 2.8 Hz, 1H), 3.61 (ddd, *J* = 14.8 Hz, 7.6 Hz, 3.2 Hz, 1H), 3.21 (ddd, *J* = 14.8 Hz, 6.8 Hz, 3.2 Hz, 1H), 3.01 (dd, *J* = 16.8 Hz, 13.6 Hz, 1H), 2.82 (dd, *J* = 17.2 Hz, 5.6 Hz, 1H), 2.67-2.61 (m, 1H), 1.90-1.10 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.46, 143.95, 132.07, 130.11, 122.40, 116.58, 108.80, 58.92, 56.75, 47.82, 28.81, 27.46, 27.10, 25.51, 25.16, 24.74, 23.15; EI-MS: *m/z* 336.0 $[M+H]^+$.

(6*R*,6a*S*)-3-Fluoro-5,6,6a,7,8,9,10,11,12,13-decahydroazonino[1,2-*a*]quinoline-6-carbaldehyde (2g): Major diastereomer; ^1H NMR (400 MHz, $CDCl_3$) δ 9.82 (d, *J* = 0.4 Hz, 1H), 6.86-6.77 (m, 2H), 6.71 (dd, *J* = 8.8 Hz, 4.8 Hz, 1H), 3.75 (dt, *J* = 11.2 Hz, 2.8 Hz, 1H), 3.54 (ddd, *J* = 14.8 Hz, 8.4 Hz, 3.6 Hz, 1H), 3.21 (ddd, *J* = 14.8 Hz, 6.4 Hz, 3.2 Hz, 1H), 3.03 (dd, *J* = 16.4 Hz, 13.6 Hz, 1H), 2.82 (dd, *J* = 16.8 Hz, 5.2 Hz, 1H), 2.70-2.64 (m, 1H), 1.90-1.25 (m, 11H), 1.15-1.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.77, 155.38 (d, *J* = 234.7 Hz), 141.38, 121.78 (d, *J* = 7.1 Hz), 116.55 (d, *J* = 8.4 Hz), 115.62 (d, *J* = 21.7 Hz), 114.08 (d, *J* = 22.0 Hz), 58.20, 57.21, 47.47, 28.52, 27.53, 27.44, 24.89, 24.55, 24.31, 23.38; EI-MS: *m/z* 276.1 $[M+H]^+$.

(6*R*,6a*S*)-3-(Trifluoromethyl)-5,6,6a,7,8,9,10,11,12,13-decahydroazonino[1,2-*a*]quinoline-6-carbaldehyde (2h): Major diastereomer; ^1H NMR (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.30-7.28 (m, 2H), 6.66-6.64 (m, 1H), 3.92-3.88 (m, 1H), 3.72 (ddd, *J* = 12.4 Hz, 6.4 Hz, 3.2 Hz, 1H), 3.27 (ddd, *J* = 15.2 Hz, 7.6 Hz, 3.2 Hz, 1H), 3.18-3.14 (m, 1H), 3.12-3.10 (m, 1H), 2.61 (dt, *J* = 6.4 Hz, 2.4 Hz, 1H), 1.90-1.30 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.31, 147.19, 126.57 (q, *J* = 3.6 Hz), 124.60 (q, *J* = 4.1 Hz), 123.81 (q, *J* = 265.2), 117.19, 116.99 (q, *J* = 32.2 Hz), 110.71, 59.84, 56.65, 48.75, 33.22, 30.92, 27.69, 26.57, 26.39, 25.35, 23.75; EI-MS: *m/z* 326.1 $[M+H]^+$.

(6*R*,6a*S*)-2-Chloro-5,6,6a,7,8,9,10,11,12,13-decahydroazonino[1,2-*a*]quinoline-6-carbaldehyde (2i): Major diastereomer; ^1H NMR (400 MHz, $CDCl_3$) δ 9.81 (d, *J* = 0.4 Hz, 1H), 6.98-6.96 (m, 1H), 6.72-6.70 (m, 1H), 6.64 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 3.77 (dt, *J* = 10.8 Hz, 2.4 Hz, 1H), 3.64 (ddd, *J* = 15.2 Hz, 7.2 Hz, 3.6 Hz, 1H), 3.22 (ddd, *J* = 14.8 Hz, 7.2 Hz, 3.6 Hz, 1H), 3.02-2.94 (m, 1H), 2.82 (dd, *J* = 17.2 Hz, 5.6 Hz, 1H), 2.64 (ddd, *J* = 13.6 Hz, 5.2 Hz, 4 Hz, 1H), 1.90-1.10 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.53, 145.92, 132.75, 130.66, 118.62, 116.85, 114.40, 58.98, 56.75, 48.11, 29.06, 27.40, 17.10, 25.60, 25.24, 24.77, 22.87; EI-MS: *m/z* 292.1 $[M+H]^+$.

(6*R*,6a*S*)-2-Methoxy-5,6,6a,7,8,9,10,11,12,13-decahydroazonino[1,2-*a*]quinoline-6-carbaldehyde (2j): Major diastereomer; ^1H NMR (400 MHz, $CDCl_3$) δ 9.81 (d, *J* = 0.8 Hz, 1H), 7.00-6.98 (m, 1H), 6.31-6.29 (m, 2H), 3.78 (s, 3H), 3.73-3.64 (m, 2H), 3.22 (ddd, *J* = 15.2 Hz, 7.2 Hz, 3.6 Hz, 1H), 3.00-2.94 (m, 2H), 2.82 (dd, *J* = 16.0 Hz, 5.2 Hz, 2.68-2.63 (m, 1H), 1.90-1.10 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.26, 159.20, 145.91, 130.24, 113.04, 102.10, 100.95, 59.19, 56.80, 55.19, 48.52, 29.02 27.63, 27.16, 25.62, 25.30, 24.86, 22.69; EI-MS: *m/z* 288.1 $[M+H]^+$.

(12b*R*,13*R*)-6,7,8,12b,13,14-Hexahydrobenzo[3,4]azepino[1,2-*a*]quinoline-13-carbaldehyde (2k): Major diastereomer. ^1H NMR (400 MHz, $CDCl_3$) δ 9.64 (d, *J* = 1.6 HZ, 1H), 7.18-7.02 (m, 6H), 6.67-6.58 (m, 2H), 5.05 (d, *J* = 6.4 Hz, 1H), 2.99-2.90 (m, 2H), 2.65 (dt, *J* = 14 Hz, 4.8 Hz, 1H), 2.27-2.19 (m, 1H), 1.68-1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.02, 143.42, 139.63, 139.28, 130.80, 129.28, 127.86, 127.65, 127.16, 126.54, 119.34, 116.07, 110.66, 63.26, 49.49, 46.33, 31.88, 26.72, 24.73; EI-MS: *m/z* 278.1

$[M+H]^+$.

(11b*R*,12*R*)-7,11b,12,13-Tetrahydro-6*H*-isoquinolino[2,1-*a*]quinoline-12-carbaldehyde (2l): Major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.33-7.28 (m, 2H), 7.24-7.19 (m, 2H), 7.14-7.10 (m, 2H), 6.85-6.83 (m, 1H), 6.79 (td, J = 7.2 Hz, 0.8 Hz, 1H), 4.66-4.67 (m, 1H), 4.01-3.97 (m, 1H), 3.41 (d, J = 16.8 Hz, 1H), 3.29 (dt, J = 7.2 Hz, 1.6 Hz, 1H), 3.17 (dd, J = 16.4 Hz, 6.8 Hz, 1H), 3.08-3.04 (m, 1H), 3.02-2.99 (m, 1H), 2.93-2.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.02, 146.38, 135.36, 134.98, 129.86, 128.81, 126.95, 126.83, 126.24, 121.32, 118.87, 112.11 (one aromatic carbon missing), 57.61, 51.21, 42.06, 29.89, 27.67; EI-MS: *m/z* 264.1 $[M+H]^+$.

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