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Organocatalytic Synthesis of Tetrahydroquinolines from α,β-Unsaturated Ketones *via* 1,5-Hydride Transfer/Cyclization

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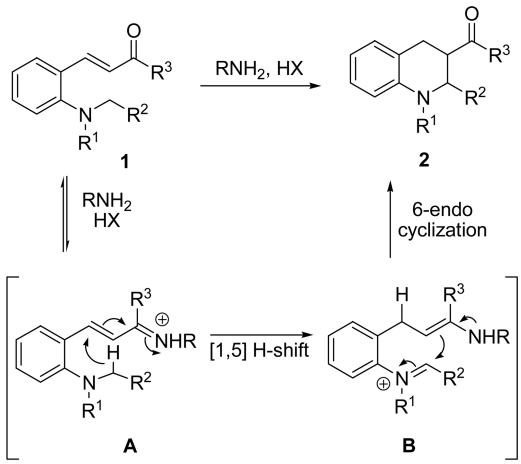
The development for direct functionalization of sp^3 C-H bonds has become an area of intense interest in synthetic organic chemistry. Because such reactions offer practical methods for the construction of structurally complex and biologically active organic molecules with atom- and step economy.[1] The 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. Sames group successfully applied the intramolecular 1,5-hydride transfer/cyclization strategy to the functionalization of ether, carbamate, and benzylic C-H bonds bearing unsaturated moieties.[2] This protocol includes the initial cleavage of a C-H bond in the context of a hydride transfer to give a zwitterionic intermediate, followed by ring closure to give the cyclic products. The *tert*-amino effect and related 1,5-hydride transfer/subsequent cyclization has attracted much attention due to its unique features to afford tetrahydroquinolines.[3,4] 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.[5] Therefore, the development of new and efficient synthetic routes for the preparation of tetrahydroquinoline analogues is of importance to both organic and medicinal chemistry.[6] Recently, several groups reported the synthesis of tetrahydroquinolines *via* intramolecular tandem hydride transfer/cyclization of *o*-dialkylamino-substituted alkylidene malonates, α,β-unsaturated aldehydes, acyl oxazolidinones using a metal complexes such as magnesium, cobalt, and gold complexes as well as organocatalysts such as phosphoric acids and diphenylprolinols.[7] To the best of our knowledge, there are no examples for organocatalytic synthesis of tetrahydroquinolines from α,β-unsaturated ketone derivatives *via* an internal redox reaction.

As part of the research program related to the development of synthetic methods for the formation of C-C bonds,[8] we recently reported the asymmetric internal redox reaction of cinnamaldehyde derivatives using secondary amines.[7b,7c] We envisioned that the formation of an iminium ion **A** through the reaction between α,β-unsaturated ketones **1** containing cyclic amine and amine catalysts would initiate a 1,5-hydride transfer to give iminium ion-enamine intermediate **B**, followed by 6-endo cyclization to give the tetrahydroquinolines **2**



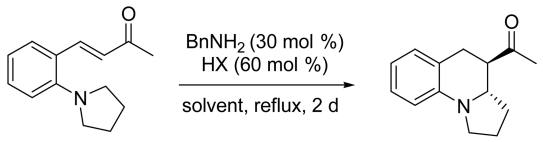
Scheme 1. Concept of the intramolecular redox reaction of enone.

(Scheme 1). Herein, we wish to report the organocatalytic synthesis of tetrahydroquinoline derivatives from β-(*o*-(dialkylamino)aryl)-α,β-unsaturated ketone derivatives *via* 1,5-hydride transfer/cyclization sequences.

To determine suitable reaction conditions for the organocatalytic intramolecular redox reactions of α,β-unsaturated ketones, we initially investigated the reaction system with (*E*)-4-(2-(pyrrolin-1-yl)phenyl)but-3-en-2-one (**1a**) in the presence of 30 mol % of benzyl amine as a catalyst and acid additive (60 mol %) in acetonitrile at reflux. We examined the reactivity with benzyl amine as a catalyst in the presence of different acids, such as 2,4-dinitrobenzensulfonic acid (DNBS), trifluoroacetic acid (TFA), $HClO_4$, and HBr as additives (entries 1-5). Among the additives probed, the best result (85% yield and 9:1 dr) was achieved when the reaction was conducted in trifluoromethanesulfonic acid (TfOH) (entry 1). A survey of the reaction media indicated that several common solvents, such as acetonitrile, dichloromethane, 1,1,2-trichloroethane, THF, and toluene were well tolerated in this intramolecular redox (entries 1 and 6-9). Among the solvents probed, the best result was achieved when the reaction was conducted in acetonitrile (entry 1).

With the optimized conditions in hand, we then explored the scope and limitations of the above reaction and the results are summarized in Table 2. The corresponding tetrahydroquinoline derivatives **2a-2h**, which incorporated five to nine-membered azacycles, were obtained in high yields

Table 1. Optimization of reaction conditions[a]



1a **2a**

Entry	HX	Solvent	Yield (%)[b]	Dr (%)[c]
1	TfOH	CH_3CN	85	9:1
2	DNBS	CH_3CN	56	7:3
3	TFA	CH_3CN	41	7:3
4	$HClO_4$	CH_3CN	54	6:4
5	HBr	CH_3CN	70	6:4
6	TfOH	CH_2Cl_2	65	6:4
7	TfOH	TCE	71	7:3
8	TfOH	THF	70	6:4
9	TfOH	PhMe	55	6:4

[a]Reactions were performed at a 0.3 mmol scale in 1.0 M solution of solvent. [b]Combined yield of both diastereomers. [c]Diastereomeric ratio was determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture.

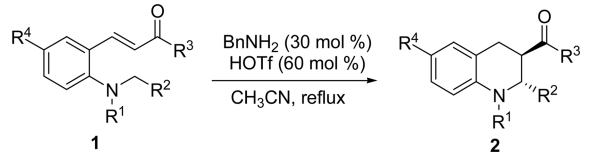
with moderate to high diastereoselectivities (73-95% yield, 9:1-1.1:1 dr). Other alipatic ketone derivatives such as (*E*)-1-(2-(azonan-1-yl)phenyl)pent-1-en-3-one (**1i**) and (*E*)-1-(2-(azonan-1-yl)phenyl)-5-phenylpent-1-en-3-one (**1j**) also afforded the corresponding tetrahydroquinoline derivatives **2i-2j** with high yields (78-95%). Aromatic ketone derivative, (*E*)-1-(2-(azonan-1-yl)phenyl)-3-(3-nitrophenyl)lprop-1-en-3-one (**1k**), also afforded the corresponding tetrahydroquinoline compound **2k** in moderate yield with diastereoselectivity. The relative configuration major diastereomer of **2** was established by comparison of the ^{1}H-NMR spectral data with previously reported data.[7b,7c]

In summary, we have presented the example of a organocatalytic enantioselective hydride transfer/cyclization reaction cascade from cyclic amines containing α,β-unsaturated ketones. The synthetically useful ring-fused tetrahydroquinoline derivatives were obtained in moderate to high yields with moderate to high diastereoselectivities. Further investigations for an asymmetric version of this organocatalytic intramolecular redox reaction of α,β-unsaturated ketones are currently underway in our laboratory.

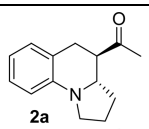
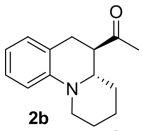
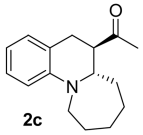
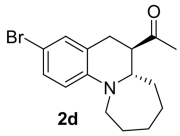
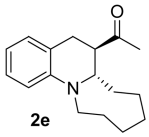
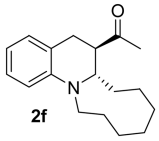
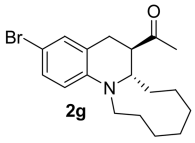
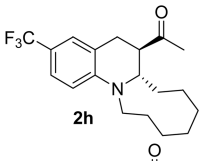
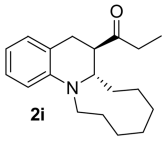
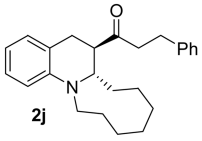
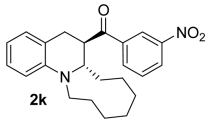
Experimental Section

General. All commercial reagents and solvents were used without purification. TLC analyses were carried out on precoated silica gel plates with F_{254} indicator. Visualization was accomplished by UV light (254 nm), I_2, *p*-anisaldehyde, ninhydrin, and phosphomolybdic acid solution as an indicator. Purification of reaction products was carried out by flash chromatography using E. Merck silica gel 60 (230-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) and AC 200 (200 MHz for ^{1}H, 50 MHz for ^{13}C). Chemical shift values (δ) are reported in ppm relative to Me_4Si (0.0 ppm).

Table 2. Organocatalytic synthesis of tetrahydroquinolines[a]



1 **2**

Entry	Time (h)	Product, **2**	Yield (%)[b]	Dr (%)[c]
1	48	 **2a**	85	9:1
2	36	 **2b**	73	9:1
3	24	 **2c**	85	7:1
4	24	 **2d**	84	8:1
5	12	 **2e**	85	4:1
6	12	 **2f**	92	1.1:1
7	12	 **2g**	95	1.1:1
8	10	 **2h**	93	1:1
9	12	 **2i**	95	2.3:1
10	24	 **2j**	78	2.5:1
11	24	 **2k**	72	1.7:1

[a]Reactions were performed at a 0.3 mmol scale in 1.0 M solution of CH_3CN. [b]Combined yield of both diastereomers. [c]Diastereomeric ratio was determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture.

General Procedure for the Catalytic Enantioselective 1,5-Hydride Transfer/Cyclization of β-(*o*-(Dialkylamino)-aryl)-α,β-unsaturated Ketones 1: To a stirred solution of β-(*o*-(dialkylamino)aryl)-α,β-unsaturated ketone **1** (0.3 mmol) and HOTf (16 μL, 0.18 mmol) in THF (0.3 mL) was added benzyl amine (9.8 μL, 0.09 mmol). The mixture was refluxed for 10-48 h, diluted with saturated $NaHCO_3$ solution (10 mL) and extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated, and purified by flash chromatography to afford tetrahydroquinoline derivatives **2**.

1-(1,2,3,3a,4,5-Hexahydropyrrolo[1,2-*a*]quinolin-4-yl)-ethanone (2a): Major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (td, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.03-7.02 (m, 1H), 6.58 (td, *J* = 7.2 Hz, 0.8 Hz, 1H), 6.45-6.43 (m, 1H), 3.49 (ddd, *J* = 15.2 Hz, 10.8 Hz, 5.2 Hz, 1H), 3.40 (ddd, *J* = 10.8 Hz, 9.2 Hz, 1.6 Hz, 1H), 3.19 (ddd, *J* = 18.8 Hz, 9.6 Hz, 7.6 Hz, 1H), 2.90-2.87 (m, 2H), 2.49 (ddd, *J* = 16.4 Hz, 9.6 Hz, 6.4 Hz, 1H), 2.29 (s, 3H), 2.25-1.87 (m, 3H), 1.50-1.37 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.21, 143.52, 128.45, 127.70, 119.83, 115.04, 110.14, 59.23, 50.37, 46.88, 31.96, 31.75, 30.53, 23.99.

1-(2,3,4,4a,5,6-Hexahydro-1*H*-pyrido[1,2-*a*]quinolin-5-yl)ethanone (2b): Major diastereomer. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.10-7.00 (m, 2H), 6.61-6.40 (m, 2H), 3.45-3.38 (m, 2H), 3.19-3.10 (m, 1H), 2.90-2.80 (m, 2H), 2.50-2,45 (m, 1H), 2.29 (s, 3H), 2.25-1.30 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.4, 143.3, 128.3, 127.5, 119.7, 115.1, 110.5, 59.3, 50.37, 49.8, 35.5, 31.9, 28.4, 26.5, 23.7.

1-(5,6,6a,7,8,9,10,11-Octahydroazepino[1,2-*a*]quinolin-6-yl)ethanone (2c): Major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06-7.00 (m, 2H), 6.58-6.53 (m, 2H), 3.80-3.74 (m, 2H), 3.15 (ddd, *J* = 15.2 Hz, 10.4 Hz, 4.8 Hz, 1H), 3.07-2.96 (m, 2H), 2.66-2.62 (m, 1H), 2.13 (s, 3H), 2.10-1.95 (m,1 H), 1.80-1.37 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.57, 144.01, 128.96, 127.47, 118.56, 115.32, 110.20, 58.92, 49.56, 49.23, 35.43, 28.17, 26.95, 26.69, 26.47, 25.59.

1-(3-Bromo-5,6,6a,7,8,9,10,11-octahydroazepino[1,2-*a*]-quinolin-6-yl)ethanone (2d): Major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.09 (m, 2H), 6.40-6.38 (m, 2H), 3.81-3.71 (m, 2H), 3.14 (ddd, *J* = 15.6 Hz, 11.6 Hz, 5.2 Hz, 1H), 3.04 (dd, *J* = 16.8 Hz, 3.6 Hz, 1H), 2.96 (dd, *J* = 16.8 Hz, 5.6 Hz, 1H), 2.65-2.62 (m, 1H), 2.13 (s, 3H), 2.07-1.95 (m, 1H), 1.80-1.30 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.87, 142.85, 131.35, 130.02, 120.60, 111.79, 106.90, 58.96, 49.41, 49.14, 35.39, 37.92, 26.56, 26.39, 25.72, 25.65.

1-(6,6a,7,8,9,10,11,12-Octahydro-5*H*-azocino[1,2-*a*]quinolin-6-yl)ethanone (2e): Major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08-7.04 (m, 1H), 7.01-6.99 (m, 1H), 6.59-6.53 (m, 2H), 3.79-3.70 (m, 2H), 3.24 (ddd, *J* = 14.8 Hz, 10.8 Hz, 3.6 Hz, 1H), 3.03 (d, *J* = 4.8 Hz, 2H), 2.66-2.63 (m, 1H), 2.10 (s, 3H), 2.00-1.40 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.57, 144.12, 128.98, 127.47, 118.53, 115.26, 111.11, 59.29, 52.60, 49.57, 33.67, 28.07, 27.70, 27.28, 26.72, 26.21, 25.94.

1-(5,6,6a,7,8,9,10,11,12,13-Decahydroazonino[1,2-*a*]-quinolin-6-yl)ethanone (2f): Major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.09 (m, 1H), 7.07-7.05 (m, 1H), 6.77-6.75 (m, 1H), 6.68 (td, *J* = 7.2 Hz, 0.8 Hz, 1H), 3.71-3.65 (m, 2H), 3.23 (ddd, *J* = 15.2 Hz, 7.2 Hz, 4.0 Hz, 1H), 3.07 (dd, *J* = 18.0 Hz, 14.8 Hz, 1H), 2.77-2.69 (m, 2H), 2.26 (s, 3H), 1.92-1.41 (m, 10H), 1.35-0.80 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.13, 144.65, 129.71, 127.16, 121.09, 116.87, 114.93, 60.44, 56.92, 48.58, 28.74, 28.04, 27.70, 27.30, 25.51, 25.11, 24.94, 24.70.

1-(3-Bromo-5,6,6a,7,8,9,10,11,12,13-decahydroazonino-[1,2-*a*]quinolin-6-yl)ethanone (2g): Major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.16 (m, 2H), 6.32-6.61 (m, 1H), 3.72-3.68 (m, 1H), 3.63 (ddd, *J* = 14.8 Hz, 7.6 Hz, 3.6 Hz, 1H), 3.23 (ddd, *J* = 15.2 Hz, 3.6 Hz, 7.2 Hz, 1H), 3.04 (dd, *J* = 18.0 Hz, 14.4 Hz, 1H), 2.73-2.66 (m, 2H), 2.26 (s, 3H), 1.92-1.40 (m, 10H), 1.30-1.20 (m, 1H), 1.17-0.80 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.49, 143.61, 131.99, 129.90, 123.19, 116.26, 108.62, 60.51, 56.89, 48.37, 28.75, 27.98, 27.53, 27.14, 25.57, 25.16, 24.92, 24.51.

1-(3-(Trifluoromethyl)-5,6,6a,7,8,9,10,11,12,13-decahydro-azonino[1,2-*a*]quinolin-6-yl)ethanone (2h): Major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 2H), 6.75-6.73 (m, 1H), 3.80-3.74 (m, 2H), 3.28 (ddd, *J* = 15.2 Hz, 7.2 Hz, 4.0 Hz, 1H), 3.09 (dd, *J* = 16.8 Hz, 13.6 Hz, 1H), 2.79 (dd, *J* = 16.8 Hz, 4.8 Hz, 1H), 2.71 (ddd, *J* = 13.2 Hz, 4.8 Hz, 3.2 Hz, 1H), 2.27 (s, 3H), 1.95-1.15 (m, 12H)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.23, 141.93, 126.67 (q, *J* = 4.0 Hz), 125.03 (q, *J* = 267.0 Hz), 124.35 (q, *J* = 4.0 Hz), 120.50, 118.02 (q, *J* = 32.0 Hz), 113.38, 61.06, 56.52, 48.76, 28.74, 28.47, 27.47, 26.83, 26.04, 25.62, 25.33, 24.74.

1-(5,6,6a,7,8,9,10,11,12,13-Decahydroazonino[1,2-*a*]-quinolin-6-yl)propan-1-one (2i): 2.3:1 Diastereomeric mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05-7.01 (m, 1H), 7.00-6.92 (m, 2H), 6.70-6.68 (m, 1H), 6.62-6.50 (m, 2H), 3.72-3.51 (m, 3H), 2.69-2.63 (m, 2H), 2.58-2.57 (m, 0.5H), 2.50-2.35 (m, 3H), 1.85-0.5 (m, 18H), 1.03 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.89, 210.61, 143.98, 143.64, 128.64, 127.90, 126.22, 126.07, 120.17, 118.33, 115.76, 114.90, 113.85, 112.09, 59.94, 59.53, 55.85, 55.58, 53.12, 53.05, 47.82, 46.59, 33.34, 32.27, 32.13, 27.33, 26.96, 26.67, 26.28, 25.93, 25.15, 25.12, 24.47, 24.07, 23.88, 23.68, 6.84, 6.69.

1-(5,6,6a,7,8,9,10,11,12,13-decahydroazonino[1,2-*a*]quinolin-6-yl)-3-phenylpropan-1-one (2j): Major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.18 (m, 5H), 7.11-7.07 (m, 1H), 7.06-7.03 (m, 1H), 6.75-6.73 (m, 1H), 6.67 (td, *J* = 7.2 Hz, 1.2 Hz, 1H), 3.67-3.58 (m, 2H), 3.21-3.14 (m, 1H), 3.13-3.06 (m, 1H), 3.05-3.00 (m, 1H), 2.99-2.93 (m, 2H), 2.87 (t, *J* = 7.2 Hz, 2H), 2.75-2.65 (m, 2H), 1.90-1.19 (m, 11H), 1.03-0.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.11, 144.64, 141.10, 129.69, 128.59, 128.42, 127.13, 126.25, 121.11, 116.87, 114.96, 60.39, 56.89, 40.08, 43.02, 29.74, 27.93, 27.68, 27.29, 25.48, 25.10, 24.84, 24.58.

(5,6,6a,7,8,9,10,11,12,13-Decahydroazonino[1,2-*a*]quinolin-6-yl)(3-nitrophenyl)methanone (2k): Major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71-8.70 (m, 1H), 8.43-8.41 (m, 1H), 8.20-8.17 (m, 1H), 7.70-7.16 (m, 1H), 7.12-

7.07 (m, 1H), 6.98-6.97 (m, 1H), 6.70-6.68 (m, 1H), 6.62 (td, J = 7.2 Hz, 0.8 Hz, 1H), 3.77-3.73 (m, 1H), 3.71-3.67 (m, 1H), 3.66-3.59 (m, 1H), 3.14 (dd, J = 16.8 Hz, 6.4 Hz, 1H), 3.06-2.97 (m, 2H), 1.90-1.40 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.53, 148.67, 144.79, 133.77, 130.09, 128.81, 127.32, 122.87, 119.46, 116.52, 113.46 (two aromatic carbons missing), 61.24, 56.57, 44.35, 32.89, 28.48, 27.18, 26.84, 25.90, 25.73, 24.93.

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