Synthesis X.-J. Shang, Z.-Q. Liu Special Topic

A Catalyzed Aerobic Intramolecular C–O Bond Formation: Facile Access to Ring-Fused Dihydrobenzoxazine Derivatives

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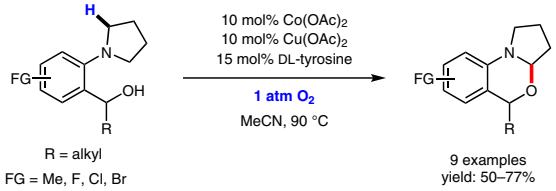

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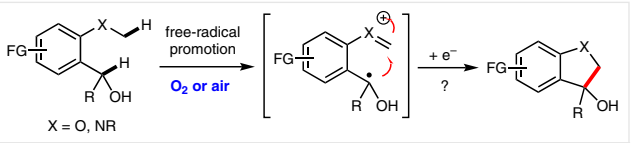
Abstract A catalyst comprising of catalytic cobalt(II) acetate/copper(II) acetate/DL-tyrosine with oxygen as the oxidant allows aerobic intramolecular C–O bond construction in [2-(pyrrolidin-1-yl)phenyl]methanol by free-radical promoted intramolecular selective functionalization of an (sp^3)C–H bond by the alcohol, thus providing an environmentally friendly approach to 5*H*-benzo[*d*]pyrrolo[2,1-*b*][1,3]oxazine derivatives.

Key words free radicals, C–H functionalization, cross-dehydrogenative coupling, aerobic oxidation, heterocycles

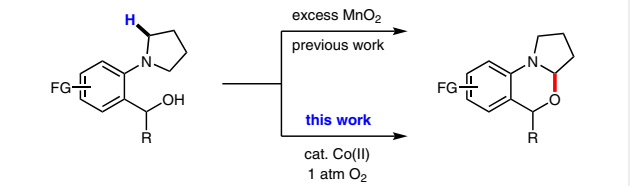
Carbon–carbon and/or carbon–heteroatom bond formation via cross-dehydrogenative coupling (CDC) strategy represents the most attractive and atom-economic conversion in synthetic organic chemistry.[1] In the past decades, efficient methods for C–X construction through direct (sp^3)C–H functionalization have been achieved.[2,3] However, stoichiometric oxidants, such as high-valent metal salts and peroxides, are generally required to remove the hydrogen atoms in most previous systems. Therefore, more efficient and waste-minimizing protocols are highly desirable.

Of particular interest is the exploration of novel CDC reactions for C–X bond formation; we have accomplished a series of efficient methods through free-radical promoted (sp^3)C–H functionalization.[4] In a continuous study on selective functionalization of the α-hydroxy-C–H with simple alcohols,[5] we began to hypothesize whether intramolecular (sp^3)C–C(sp^3) bond formation could be realized (Scheme 1). Furthermore, it would be very interesting if C–C bonds were formed by using oxygen and/or air as the terminal oxidant.[6]



Scheme 1 Hypothesis of free-radical promoted intramolecular C–C bond construction

However, the initial results indicated that it is not C–C bond construction but C–O bond construction that occurs under the present conditions (Scheme 2). As a result, ring-fused heterocycles,[7] 1,2,3,3a-tetrahydro-5*H*-benzo[*d*]pyrrolo[2,1-*b*][1,3]oxazines were isolated as the major product. This might be a consequence of the distance of the frontier molecular orbitals. Although an unexpected C–O bond forming heterocycle was obtained, the present approach to ring-fused dihydrobenzoxazine derivatives holds advantages over previous methods using excess metal salts.[8]

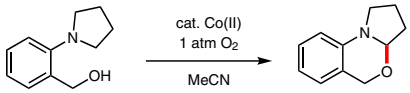


Scheme 2 Intramolecular C–O bond construction via (sp^3)C–H functionalization

Initially, we tested our hypothesis by using [2-(pyrrolidin-1-yl)phenyl]methanol as the model compound (Table 1). It can be seen from Table 1, factors such as volume of solvent, catalyst, and oxygen critically affect the reaction efficiency (entries 1–9). Interestingly, the yield of the desired product was improved to 71% by adding 15 mol% of

DL-tyrosine (entry 8). The amino acid might act as a ligand, which could activate the metal catalyst. However, no product was observed without O_2 (entry 9).

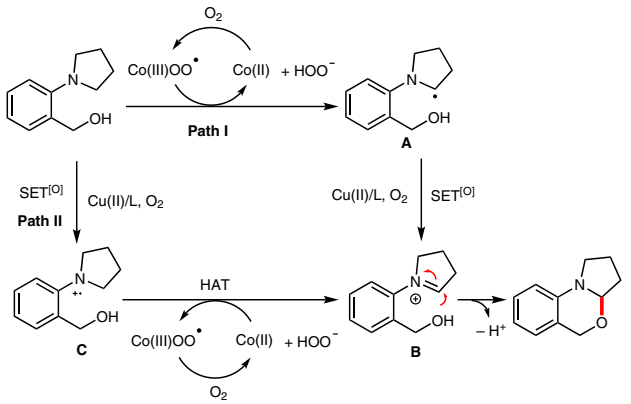
Table 1 Modification of the Typical Reaction Conditions[a]



Entry	Catalyst (10 mol%)	MeCN (mL)	Yield[b] (%)
1	$Co(OAc)_2$	5	27
2	$Co(OAc)_2/Cu(OAc)_2$	5	30
3	$Co(OAc)_2/Cu(OAc)_2$	15	39
4	$Co(OAc)_2/Cu(OAc)_2$	20	55
5	$Co(OAc)_2/Cu(OTf)_2$	20	-
6	$Co(OAc)_2/CuCl_2$	20	47
7	$Co(OAc)_2/CuBr$	20	46
8[c]	**$Co(OAc)_2/Cu(OAc)_2$**	**20**	**71**
9[d]	$Co(OAc)_2/Cu(OAc)_2$	20	–

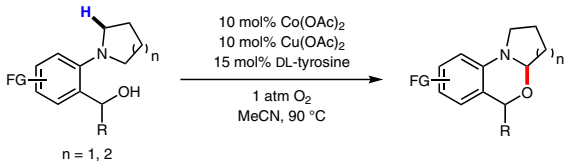
[a] Reaction conditions: [2-(pyrrolidin-1-yl)phenyl]methanol (0.2 mmol, 1 equiv), 1 atm. O_2 (bubble with an oxygen balloon), 90 °C, 10 h.
[b] Isolated yield.
[c] 15 mol% of DL-tyrosine was added.
[d] Without O_2.

Next we examined the scope of substrate. As depicted in Table 2, ring-fused dihydrobenzoxazine derivatives were isolated in moderate to good yields (entries 1–9). An array of substituted [2-(pyrrolidin-1-yl)phenyl]methanols with alkyl and halogen atoms (F, Cl, Br) in the aromatic core are amenable to this system (entries 1–5). Other secondary alcohols gave the corresponding products in moderate yields (entries 6–9). However, no reaction occurred with [2-(piperidin-1-yl)phenyl]methanol or (2-morpholinophenyl)methanol (entries 10 and 11). This might be due to the mismatching of the HOMO (lone pair of the oxygen atom) with LUMO (the antibonding π* of imine cation) in space.



Scheme 3 Suggested mechanism

Table 2 Examination of the Substrate[a]



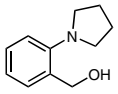
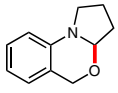
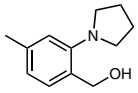
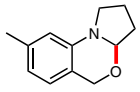
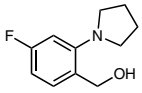
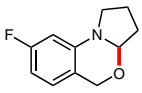
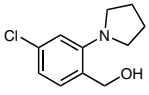
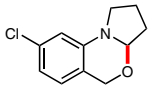
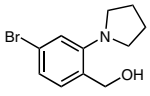
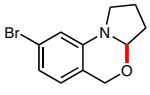
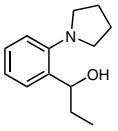
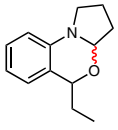
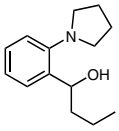
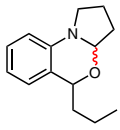
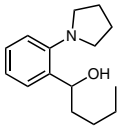
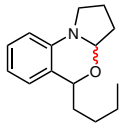
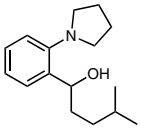
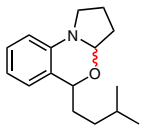
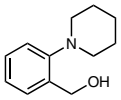
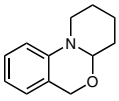
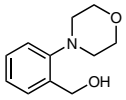
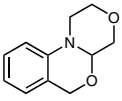
Entry	Substrate	Product	Yield[b] (%)
1			71
2			77
3			56
4			63
5			61
6			55[c]
7			53[c]
8			53[c]
9			50[c]

Table 2 (continued)

Entry	Substrate	Product	Yield[b] (%)
10			–
11			–

[a] Reaction conditions: substituted [2-(pyrrolidin-1-yl)phenyl]methanol (0.2 mmol, 1 equiv), $Co(OAc)_2$ (10 mol%), $Cu(OAc)_2$ (10 mol%), DL-tyrosine (15 mol%), 1 atm O_2 (bubble with an oxygen balloon), 90 °C, 10–20 h.
[b] Isolated yield.
[c] Diastereomers, ratio 7:3 (^{1}H NMR spectra).

As demonstrated in Scheme 3, two possible pathways might be involved in this reaction.[1c] In path I, a hydrogen atom transfer (HAT) would give radical intermediate **A**, which leads to the iminium **B** by single-electron oxidation. In contrast, path II might undergo SET first to form a radical cation **C**, then followed by HAT to give **B**. Finally an intramolecular nucleophilic addition followed by deprotonation affords the final product. The steric effect in the nucleophilic addition would be responsible for the ratio of diastereomers.

In summary, an aerobic intramolecular oxidative dehydrogenative C–O bond formation via selective functionalization of (sp^3)C–H bond with alcohols was developed, which allowed an environmentally benign access to ring-fused dihydrobenzoxazine derivatives.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 spectrometer in $CDCl_3$ with TMS as internal standard. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. HRMS data were measured on a Bruker Apex II. All products were identified by ^{1}H and ^{13}C NMR, MS, HRMS. The starting materials were purchased from Energy Chemicals, Alfa Aesar, Acros Organics, J&K Chemicals, Adamas, or Aldrich and used without further purification.

5*H*-Benzo[*d*]pyrrolo[2,1-*b*][1,3]oxazines; General Procedure

A solution of [2-(pyrrolidin-1-yl)phenyl]methanol (0.2 mmol, 1 equiv), $Co(OAc)_2$ (0.02 mmol, 10 mol%), $Cu(OAc)_2$ (0.02 mmol, 10 mol%), and DL-tyrosine (0.03 mmol, 15 mol%) in MeCN (20 mL) was stirred at 90 °C and bubbled with O_2 (equipped with an O_2 balloon) for 10–20 h. Sat. brine (15 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (hexane/EtOAc 20:1) to give the product.

1,2,3,3a-Tetrahydro-5*H*-benzo[*d*]pyrrolo[2,1-*b*][1,3]oxazine

Colorless oil; yield: 24.8 mg (71%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16(t, *J* = 8.0 Hz, 1 H), 6.94 (d, *J* = 7.2 Hz, 1 H), 6.76 (t, *J* = 7.2 Hz, 1 H) , 6.71 (d, *J* = 8.0 Hz, 1 H), 4.94–4.98 (m, 2 H), 4.78 (d, *J* = 14.0 Hz, 1 H), 3.60–3.65 (m, 1 H), 3.27 (q, *J* = 8.0 Hz, 1 H), 2.32–2.37 (m, 1 H), 2.04–2.10 (m, 1 H), 1.91–2.00 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.15, 127.68, 124.63, 121.58, 117.87, 115.19, 89.43, 68.22, 49.71, 32.41, 22.52.

MS (EI): *m*/*z* (%): 176 (10.1), 175 (84.2), 174 (100), 149 (18.3), 146 (23), 144 (20.8), 118 (39.0), 91 (23.1), 77 (17.5), 44 (31.2).

8-Methyl-1,2,3,3a-tetrahydro-5*H*-benzo[*d*]pyrrolo[2,1-*b*][1,3]oxazine

Colorless oil; yield: 29.1 mg (77%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84 (d, *J* = 0.8 Hz, 1 H), 6.60 (d, *J* = 0.8 Hz, 1 H), 6.55 (s, 1 H), 4.92–4.95 (m, 2 H), 4.76 (d, *J* = 1.6 Hz, 1 H), 3.59–3.64 (m, 1 H), 3.28 (q, *J* = 0.8 Hz, 1 H), 2.33 (s, 3 H), 2.30–2.35 (m, 1 H), 2.05–2.11 (m, 1 H), 1.92–2.01 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.04, 137.43, 124.53, 118.87, 118.78, 115.90, 89.44, 68.17, 49.76, 32.43, 22.56, 21.47.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{16}NO$: 190.1226; found: 190.1226.

8-Fluoro-1,2,3,3a-tetrahydro-5*H*-benzo[*d*]pyrrolo[2,1-*b*][1,3]oxazine

Colorless oil; yield: 21.6 mg (56%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.88 (td, *J* = 0.4, 0.8 Hz, 1 H), 6.66–6.71 (m, 2 H), 4.87–7.93 (m, 2 H), 4.73 (d, *J* = 1.6 Hz, 1 H), 3.59–3.63 (m, 1 H), 3.21 (q, *J* = 0.8 Hz, 1 H), 2.32–2.39 (m, 1 H), 2.04–2.09 (m, 1 H), 1.91–2.01 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.37, 155.01, 139.60, 123.51, 123.45, 117.42, 117.34, 114.35, 114.13, 111.42, 111.20, 89.56, 67.69, 67.67, 50.80, 32.43, 22.66.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{13}NOF$: 194.0976; found: 194.0984.

8-Chloro-1,2,3,3a-tetrahydro-5*H*-benzo[*d*]pyrrolo[2,1-*b*][1,3]oxazine

Colorless oil; yield: 26.3 mg (63%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 (dd, *J* = 0.4, 0.8 Hz, 1 H), 6.91 (d, *J* = 0.4 Hz, 1 H), 6.61 (d, *J* = 0.80 Hz, 1 H), 4.87–4.92 (m, 2 H), 4.72 (d, *J* = 1.6 Hz, 1 H), 3.56–5.61 (m, 1 H), 3.20–3.26 (m, 1 H), 2.31–2.38 (m, 1 H), 2.07–2.09 (m, 1 H), 1.93–1.98 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.75, 127.60, 124.54, 123.01, 122.76, 116.19, 89.47, 67.80, 49.76, 32.33, 22.48.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{13}NOCl$: 210.0680; found: 210.0685.

8-Bromo-1,2,3,3a-tetrahydro-5*H*-benzo[*d*]pyrrolo[2,1-*b*][1,3]oxazine

Colorless oil; yield: 30.9 mg (61%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (d, *J* = 0.8 Hz, 1 H), 7.04 (s, 1 H), 6.55 (d, *J* = 0.8 Hz, 1 H), 4.87–4.90 (m, 2 H), 4.72 (d, *J* = 1.6 Hz, 1 H), 3.55–3.60 (m, 1 H), 3.23 (q, *J* = 0.8 Hz, 1 H), 2.30–2.38 (m, 1 H), 2.04–2.09 (m, 1 H), 1.90–1.99 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.18, 130.47, 127.37, 123.39, 116.43, 109.83, 89.45, 67.74, 49.57, 32.32, 22.46.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{13}NOBr$: 254.1075; found: 254.1085.

5-Ethyl-1,2,3,3a-tetrahydro-5*H*-benzo[*d*]pyrrolo[2,1-*b*][1,3]oxazine

Colorless oil; yield: 22.3 mg (55%); diastereomers, ratio 7:3.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15–7.20 (m, 1 H), 7.04 (d, *J* = 0.80 Hz, 0.70 H), 7.00 (d, *J* = 0.8 Hz, 0.30 H), 6.69–6.80 (m, 2 H), 5.00–5.06 (m, 1 H), 4.89 (dd, *J* = 0.4, 0.8 Hz, 0.70 H), 4.66 (dd, *J* = 0.4, 1.2 Hz, 0.30 H), 3.56–3.66 (m, 1 H), 3.26–3.36 (m, 1 H), 2.29–2.37 (m, 1 H), 2.06–2.18 (m, 2 H), 1.91–1.99 (m, 2 H), 1.73–1.86 (m, 1 H), 1.13 (t, *J* = 0.8 Hz, 1 H), 1.04 (t, *J* = 0.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.91, 142.49, 127.49, 127.46, 125.68, 125.27, 125.08, 124.21, 117.85, 117.36, 115.12, 114.95, 88.55, 81.43, 49.59, 49.44, 32.57, 32.35, 28.90, 27.23, 22.45, 22.37, 10.16, 9.40.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{18}NO$: 204.1383; found: 204.1380.

5-Propyl-1,2,3,3a-tetrahydro-5*H*-benzo[*d*]pyrrolo[2,1-*b*][1,3]oxazine

Colorless oil; yield: 23.0 mg (53%); diastereomers, ratio 7:3.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14–7.19 (m, 1 H), 7.05 (d, *J* = 7.6 Hz, 0.69 H), 6.98 (d, *J* = 7.2 Hz, 0.31 H), 6.83–6.79 (m, 2 H), 5.06 (t, *J* = 4.8 Hz, 0.32 H), 5.01 (t, *J* = 4.8 Hz, 0.67 H), 4.92 (dd, *J* = 2.8, 8.0 Hz, 0.68 H), 4.78 (dd, *J* = 3.2, 10 Hz, 0.30 H), 3.56–5.65 (m, 1 H), 3.26–3.34 (m, 1 H), 2.32–2.35 (m, 1 H), 1.93–2.11 (m, 1 H), 1.51–1.76 (m, 3 H), 0.98–1.06 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.75, 142.50, 127.50, 127.41, 125.60, 125.54, 125.17, 124.16, 117.77, 117.36, 115.00, 114.97, 88.63, 81.45, 75.24, 49.62, 49.40, 38.11, 36.59, 32.56, 32.35, 22.46, 22.36, 18.68, 18.41, 14.23, 13.97.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{20}NO$: 218.1539; found: 218.1540.

5-Butyl-1,2,3,3a-tetrahydro-5*H*-benzo[*d*]pyrrolo[2,1-*b*][1,3]oxazine

Colorless oil; yield: 24.5 mg (53%); diastereomers, ratio 7:3.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.144–7.190 (m, 1 H), 7.05 (d, *J* = 7.6 Hz, 0.70 H), 6.99 (d, *J* = 7.6 Hz, 0.30 H), 6.74 (m, 2 H), 5.06 (t, *J* = 4.8 Hz, 0.3 H), 5.01 (t, *J* = 4.8 Hz, 0.70 H), 4.91 (dd, *J* = 2.8, 8 Hz, 0.71 H), 4.76 (dd, *J* = 4.0, 10.4 Hz, 0.3 H), 3.62–3.66 (m, 0.28 H), 3.56–3.61 (m, 0.7 H), 3.26–3.36 (m, 1 H), 2.11–2.35 (m, 1 H), 2.05–2.10 (m, 1.84 H), 1.93–2.00 (m, 2.32 H), 1.750–1.785 (m, 1 H), 1.39–1.55 (m, 4 H), 0.98 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.72, 142.47, 127.49, 127.41, 125.60, 125.24, 124.16, 117.85, 117.40, 115.05, 114.98, 88.65, 81.48, 76.48, 75.54, 49.61, 49.41, 35.72, 34.21, 32.55, 32.33, 27.69, 27.30, 22.89, 22.56, 22.43, 22.34, 14.09.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{22}NO$: 232.1696; found: 232.1704.

5-Isopentyl-1,2,3,3a-tetrahydro-5*H*-benzo[*d*]pyrrolo[2,1-*b*][1,3]oxazine

Colorless oil; yield: 24.5 mg (50%); diastereomers, ratio 7:3.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14–7.19 (m, 1 H), 7.05 (d, *J* = 8 Hz, 0.70 H), 6.99 (d, *J* = 8 Hz, 0.30 H), 6.68–6.79 (m, 2 H), 5.05 (t, *J* = 8 Hz, 0.33 H), 5.00 (t, *J* = 8 Hz, 0.66 H), 4.90 (dd, *J* = 4, 8 Hz, 0.67 H), 4.73 (dd, *J* = 4, 8 Hz, 0.33 H), 3.55–3.65 (m, 1 H), 3.25–3.35 (m, 1 H), 2.29–2.36 (m, 1 H), 2.05–2.12 (m, 2 H), 1.92–2.00 (m, 2 H), 1.73–1.80 (m, 1 H), 1.58–1.67 (m, 1 H), 1.35–1.46 (m, 1 H), 0.91–0.97 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.78, 142.46, 127.51, 127.45, 125.60, 125.52, 125.17, 124.16, 117.75, 117.34, 114.94, 114.91, 88.66, 81.43, 75.88, 49.59, 49.33, 34.63, 34.11, 33.87, 32.58, 32.33, 32.32, 28.27, 27.94, 22.87, 22.82, 22.44, 22.34.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{24}NO$: 246.1852; found: 246.1855.

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Supporting Information

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