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COPPER CORROLE CATALYZED ESTERIFICATION OF C(sp^3)-H WITH CARBOXYLIC ACIDS VIA CROSS-DEHYDROGENATIVE COUPLING REACTION

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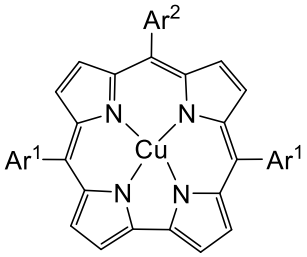
Abstract - Copper corrole complex was firstly used as catalyst for oxidative esterification of un-reactive C(sp^3)-H bond of cyclic ether and carboxylic acid via cross dehydrogenative coupling (CDC) reaction using di-*tert*-butyl peroxide (DTBP) as oxidant. A wide range of carboxylic acids can react with cyclic ether with good to excellent yields, showing copper corrole is a new kind of promising catalyst for CDC reaction. Under gram-level test, the turnover number (TON) may achieve 8400 with 84% yield at only 0.01% catalyst loading, demonstrating its practical uses.

INTRODUCTION

The construction of C-C and C-X (X = O, S, N, P) bond is one of the most important topic in organic synthesis.[1] Traditionally, the formation of C-C or C-X bond is achieved by Suzuki,[2] Hiyama [3] or Negishi coupling reactions.[4] Cross-Dehydrogenative Coupling (CDC) reaction is an alternative efficient method for the direct functionalization of C-H bond to construct C-X bond.[5] In recent years, much progress in activation of C(sp)-H and C(sp^2)-H by CDC reaction has been achieved,[6] but CDC reaction of un-reactive C(sp^3)-H bond lacks effective catalysts.[7] Coupling α-C(sp^3)-H with carboxylic acid is a convenient methods to prepare esters.[8] Many catalysts such as Bu_4NI,[9] iron[10] and copper[11] had been successfully applied to oxidative coupling of carboxylic acid with cyclic ether with the catalyst loadings around 20 mol%.

Recently, our group has successfully used copper and iron porphyrin in CDC reaction between carboxylic acid and cyclic ether.[12] Corrole is a trivalent anionic ligand having three pyrrole N-H protons in its inner

ring (Figure 1). Metal corrole catalysts demonstrate promising application for various organic reactions such as olefination of ketone,[13] hydration of terminal alkyne,[14] Suzuki coupling[15] and Diels-Alder reaction.[16] To the best of our knowledge, the use of metal corrole in CDC reaction has not been reported so far. Herein, we wish to report the activation of C(sp^3)-H by CDC reaction using copper corrole as catalyst. It turned out copper corrole has excellent performance in the CDC reaction. Significantly, the reaction achieved 84% yield with 8400 TON in gram level test at a low catalyst loading of only 0.01 mol%.



1: Ar^1=Ar^2=C_6H_5
2: Ar^1=C_6H_5,Ar^2=C_6F_5
3: Ar^1=C_6F_5,Ar^2=C_6H_5
4: Ar^1=Ar^2=C_6F_5

Figure 1. Molecular structure of copper corrole complexes

RESULTS AND DISCUSSION

X-Ray diffraction analysis showed that F_{10}C-Cu crystal had a triclinic structure of P-1 space group with a formulation unit in the cell without solvent molecules. All crystallographically independent atoms are in the usual position, except for the copper atom is located at the center of the corrole macrocycle (Figure 2). The 23-membered macrocyclic core of corrole is coplanar. The central copper atom is coordinated by four nitrogen atoms of corrole inner ring and forms a square planar structure. The Cu-N bond lengths range from 1.884 (4) to 1.897 (4) Å with an average value of 1.892 (4) Å.

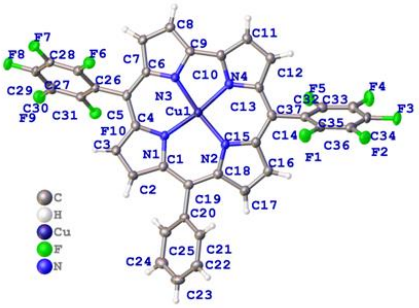
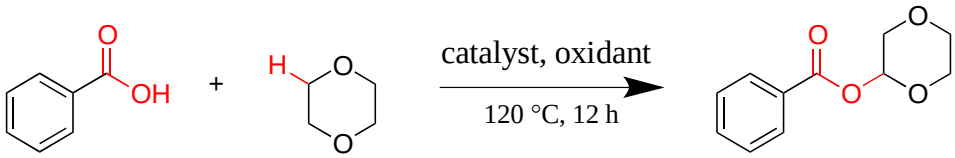


Figure 2. ORTEP plots of F_{10}C-Cu

We began our investigation of CDC reaction between benzoic acids and 1,4-dioxane using F_{15}C-Cu as the catalyst and DTBP as the oxidant, and found that the main product was 1,4-dioxan-2-yl benzoate as

indicated by NMR spectroscopy. The effect of catalyst concentration, reaction temperature and oxidants concentration was summarized in Table 1. When the catalyst loading of F_{15}C-Cu was 0.5 mol% (vs. benzoic acid), **1a** was obtained with a high isolated yield of 96% in 12 h. When the loading of F_{15}C-Cu decreased to 0.1 mol%, **1a** was obtained with an isolated yield of 70%. But with an increase of the loading of F_{15}C-Cu to 1.0 mol%, no improvement in the yield of **1a** could be observed. When using TBHP as the oxidant, the yield of **1a** sharply dropped to 44%. When DTBP was replaced by some stronger oxidants such as *m*-CPBA, PhIO, H_2O_2 and $PhI(OAc)_2$, no products could be detected. When F_{10}C-Cu, F_5C-Cu and F_0C-Cu were used at 0.5 mol% catalyst loading, the yield of **1a** was also decreased possibly because of the electron-donating effect of substitutes on the corrole periphery. Furthermore, the reaction could not proceed without the addition of the F_{15}C-Cu catalyst or DTBP oxidant. Combined of these observations, the optimal condition of current copper corrole catalyzed CDC reaction entry 2 of Table 1.

Table 1. Optimization of reaction conditions[a]

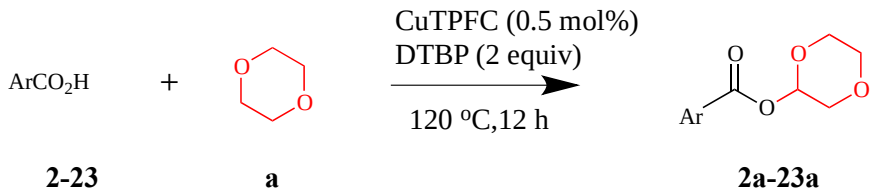


Entry`	Catalyst (mol%)	Oxidant (equiv.)	Yield(%)[b]
1	F_{15}C-Cu (0.5)	DTBP (2.0)	82[c]
2	F_{15}C-Cu (0.5)	DTBP (2.0)	96
3	F_{15}C-Cu (1.0)	DTBP (2.0)	98
4	F_{15}C-Cu (0.1)	DTBP (2.0)	70
5	F_{15}C-Cu (0.5)	DTBP (3.0)	88
6	F_{15}C-Cu (0.5)	TBHP (2.0)	44
7	F_{15}C-Cu (0.5)	*m*-CPBA (2.0)	N.D.[d]
8	F_{15}C-Cu (0.5)	H_2O_2 (2.0)	N.D.
9	F_{15}C-Cu (0.5)	$PhI(OAc)_2$ (2.0)	N.D.
10	F_0C-Cu (0.5)	DTBP (2.0)	57[c]
11	F_5C-Cu (0.5)	DTBP (2.0)	61[c]
12	F_{10}C-Cu (0.5)	DTBP (2.0)	75[c]
13	F_{15}C-Cu (0.5)	DTBP (2.0)	75[e]
14	F_{15}C-Cu (0.5)	-	N.D.
15	-	DTBP (2.0)	N.D.

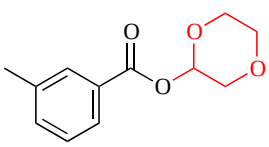
[a]Reaction condition: benzoic acid (0.5 mmol), 1,4-dioxane (2 mL), catalyst F_{15}C-Cu (0.5 mol%) and benzene at 120 °C for 12 h. [b]Isolated yield based on carboxylic acid. [c]6 h. [d]Not detected. [e]100 °C TBHP=*tert*-butyl hydroperoxide (70% in H_2O). *m*-CPBA=3-chloroperbenzoic acid. H_2O_2 (30% in H_2O). DTBP=di-*tert*-butyl peroxide.

To expand substrate scope of the reaction, a variety of derivatives of benzoic acid were used to react with 1,4-dioxane under the optimal reaction conditions, the results are summarized in Table 2. It could be seen that $F_{15}C$-Cu catalyzed CDC reaction of carboxylic acids and 1,4-dioxane CDC has a wide scope of substrates, benzoic acid derivatives bearing different groups such as methoxy, methyl, *tert*-butyl, phenyl, fluorine, chlorine and bromine may give good yields of 78~95%. *Ortho*-Substituted benzoic acid, *meta*-substituted benzoic acid and *para*-substituted benzoic acid all can react with 1,4-dioxane with good to excellent yields. The yield of *ortho*-substituted benzoic acid is slightly lower than that of *para*-substituted benzoic acid or *meta*-substituted benzoic acid, which may be ascribed to the steric hindrance effect (**4a**-**6a**). At the same time, we found that both electron-donating and electron-withdrawing aryl carboxylic acids can react with 1,4-dioxane and gave good yields of desired products. 4-Nitrobenzoic acid did not work under optimal condition, because the nitro group may quench oxygenic radical.[17] Interestingly, phenylpropanoid acid might react with 1,4-dioxane in the optimized conditions and gave desired product **18a** in 57% yield. However, the reaction could not progress when using furan-3-carboxylic acid and thiophene-3-carboxylic as substrates in this reaction (**19a**, **20a**).

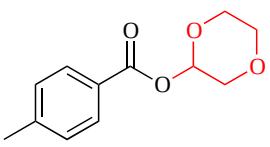
Table 2. Esterification of benzoic acid with C(sp^3)–H substrates[a]



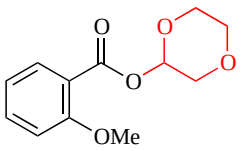
2-23 **a** **2a-23a**



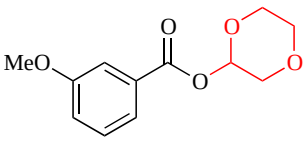
2a, 80%



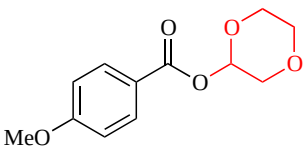
3a, 78%



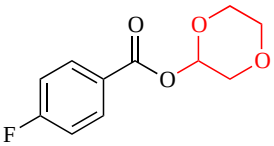
4a, 83%



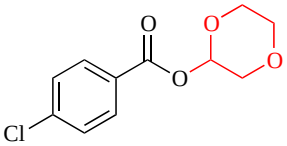
5a, 89%



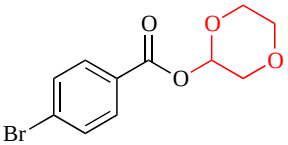
6a, 95%



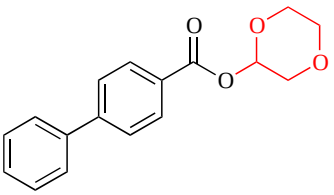
7a, 88%



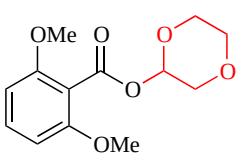
8a, 82%



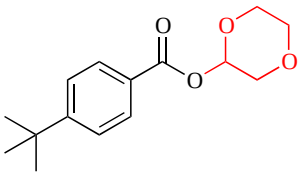
9a, 78%



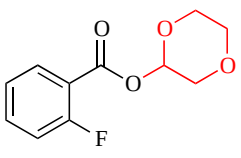
10a, 93%



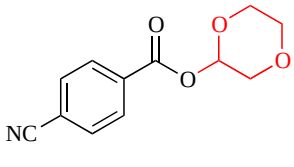
11a, 65%



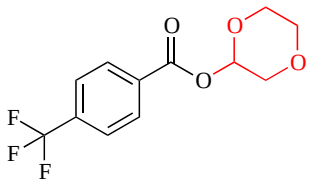
12a, 80%



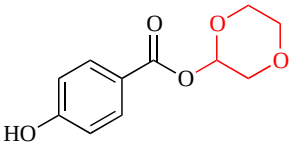
13a, 60%



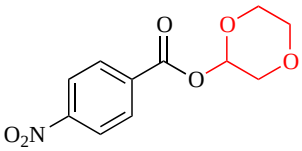
14a, 85%



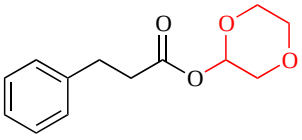
15a, 81%



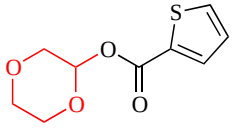
16a, N.D



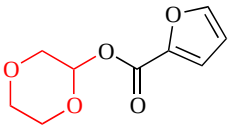
17a, N.D



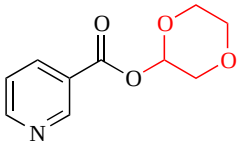
18a, 57%



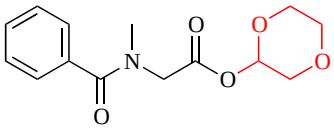
19a, N.D



20a, N.D



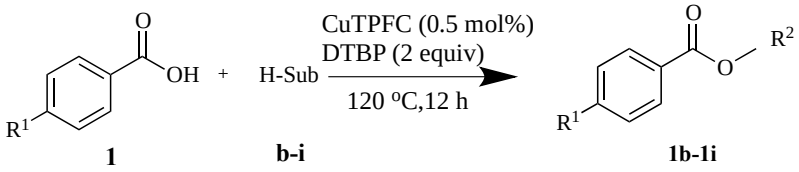
21a, N.D



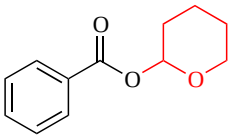
22a, N.D

[a]Reaction condition: benzoic acid (0.5 mmol), C(sp^3)–H substrates (1 mL) and catalyst F_{15}C-Cu (0.5 mol%) at 120 °C for 12 h. N.D. = not detected

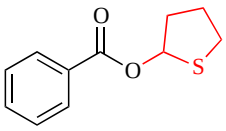
Table 3. Esterification of benzoic acid with C(sp^3)–H substrates[a]



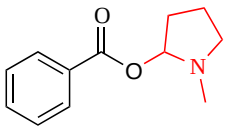
1 **b-i** **1b-1i**



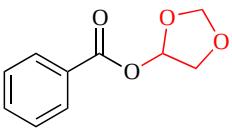
1b, N.D.



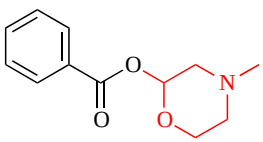
1c, N.D.



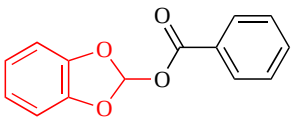
1d, N.D.



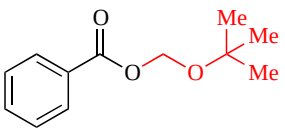
1e, 30%.



1f, N.D.



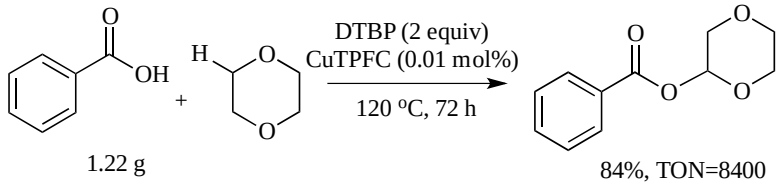
1g, N.D.



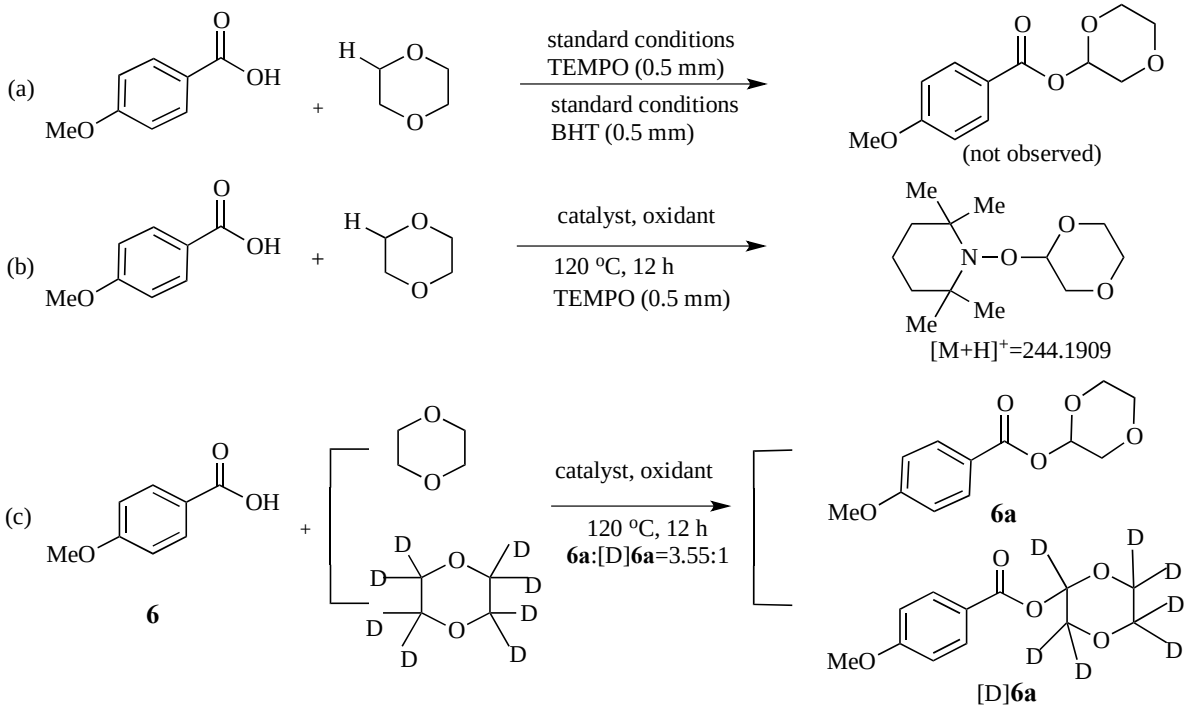
1h, 82%

[a]Reaction condition: benzoic acid (0.5 mmol), C(sp^3)–H substrates (1 mL) and catalyst F_{15}C-Cu (0.5 mol%) at 120 °C for 12 h. N.D. = not detected.

After using 1,4-dioxane as the substrate for the reaction, we had tried to extend the substrate scope to other C(sp^3)–H substrates as shown in Table 3. Disappointedly, when tetrahydrothiophene, tetrahydropyran and morpholine were used as the substrates, we could not get the products (**1b**, **1c**, **1f**). The coupling of benzoic acid and 1,3-dioxolane could give the expected product 1,3-dioxolan-4-yl 4-benzoate (**1e**) in 30% yield. When methyl *tert*-butyl ether was used as the substrate, the desired product (**1h**) was obtained in a satisfactory isolated yield 82%. Importantly, a high TON 8400 could be achieved when 0.01 mol% catalyst loading was used in the gram-level test of benzoic acid and 1,4-dioxane CDC reaction (Scheme 1).



Scheme 1. Gram-level reaction



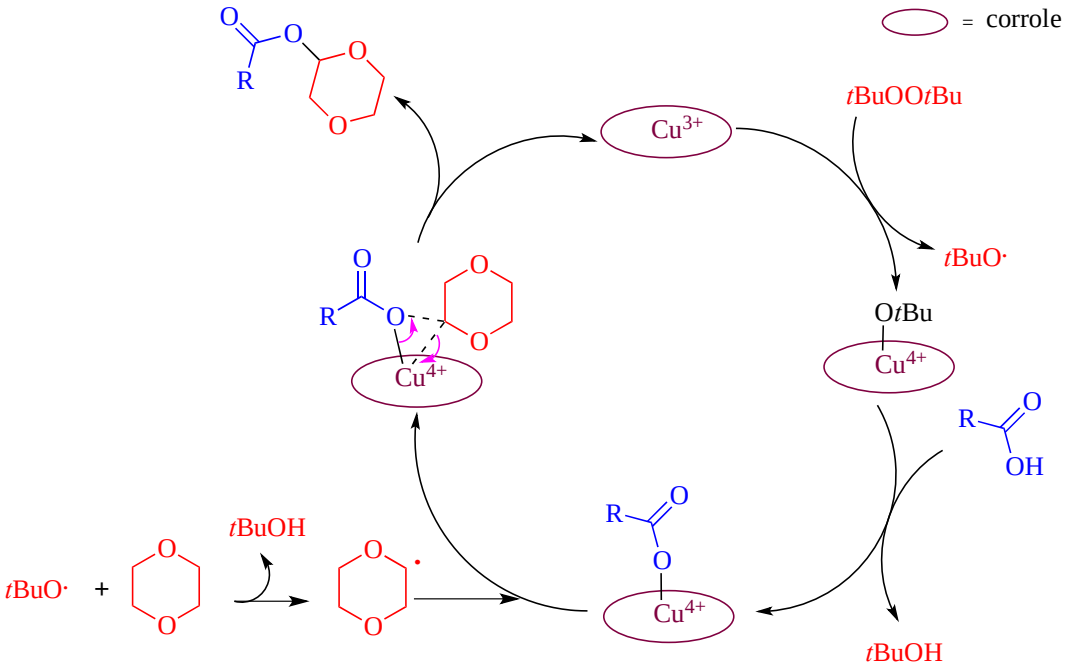
Scheme 2. Mechanistic investigation

To investigate the mechanism of copper corrole-catalyzed CDC esterification of ethers with carboxylic acids, we had conducted a series of control experiments. The desired product could not be detected when radical scavenger 2,2,6,6-tetramethylpyridine *N*-oxyl (TEMPO) or butylated hydroxytoluene (BHT) was

added to the reaction system (Scheme 2, a), this indicated that the oxidative coupling reaction processed through a radical involved pathway. When TEMPO was added to the reaction system, TEMPO-1,4-dioxane adduct (Scheme 2, b) could be detected by ESI-MS (Scheme S1), demonstrating the existence of 1,4-dioxane radical. We also have performed kinetic isotope effect (KIE) experiment to check the isotope effect of reaction, in which *p*-anisic acid was used to react with an equimolar mixture of 1,4-dioxane and 1,4-dioxane-d_8. The tested k_H/k_D was 3.55 according to the ratio of **6a** and [D]-**6a** in ^{1}H NMR spectroscopy (Scheme 2, c). This indicates that C(sp^3)–H bond cleavage is the rate-determining step. For electron paramagnetic resonance (EPR) experiment (Scheme S2), we had used radical scavenger TEMPO to capture the possible radical involved in the reaction. When TEMPO was mixed with benzoic acid, 1,4-dioxane and F_{15}C-Cu at 120 ℃, typical TEMPO EPR signal could by observed clearly as shown in Scheme S2 line a. When oxidant DTBP was added to the reaction system, the in situ generated intermediate radical was captured by TEMPO and thus the TEMPO EPR signal was significantly quenched (Scheme S2, line b). This indicated the reaction proceeded via radical pathway. It is noteworthy that the observed EPR signals correspond to mixture of TEMPO and copper corrole catalyst of the system, since the peaks position and intensity ratio is a little different from the initial higher concentration TEMPO. It had been reported that the copper corrole exhibited EPR around 3200-3600 gauss with hyperfine structure lines.[18]

Based on these experiments and previous literature,[19] the plausible mechanism for copper corrole catalyzed CDC esterification of ethers with carboxylic acids may be depicted in Scheme 3. Firstly, TPFCCu catalyze the homolysis of oxidant DTBP to generate *t*BuO· free radical and TPFCCuO*t*Bu intermediate complex. Then the *t*BuO· radical abstracts a hydrogen atom from dioxane and give dioxane radical. The TPFCCuO*t*Bu intermediate reacts with carboxylic acid to give TPFCCuO_2CR complex, which reacts with dioxane radical to give the desired product and furnish the catalytic cycle.

In summary, we have firstly used copper corrole in the catalyzed C(sp^3)-H activation for the construction of C-O bond via cross-dehydrogenative coupling of carboxylic acid and cyclic ether. Various carboxylic acids and ethers were well tolerated in this catalytic system and gave moderate to excellent yields. Importantly, in the gram-level test (0.01 mol% F_{15}C-Cu catalyst loading), the TON of the CDC reaction reached 8400. Mechanistic investigation showed that copper corrole catalyzed esterification of C(sp^3)-H bond and acid progressed by a radical mechanism. Further studies on metal corrole-catalyzed C-O and C-C bond construction via CDC reactions are currently underway in our laboratory.



Scheme 3. Proposed mechanism for esterification

EXPERIMENTAL

All reagents were purchased from commercial suppliers and were used without further purification. Silica gel (300-400 mesh size) was used for the column chromatography. The reaction was monitored by thin-layer chromatography on silica gel 60F254 (0.25 mm) under ultraviolet light. On the Bruker advanced 400M NMR spectrometer, ^{1}H, ^{13}C and ^{9}F NMR spectra were recorded in $CDCl_3$ with TMS as the internal standard.

Benzoic acids (0.5 mmol), 1,4-dioxane (1 mL), DTBP (1 mmol), and CuTPFC (0.5 mol%) were added to a Schlenk tube and stirred at 120 °C for 12 h. Then solvent of reaction mixture was removed in a rotary evaporator. The products were purified by silica gel (300–400 mesh size) column chromatography (hexane/CH_2Cl_2 =1:3).

1,4-Dioxan-2-yl benzoate (1a) yellow oil, yield: 99.8 mg (96%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 6.7 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 6.06 (s, 1H), 4.22 – 4.09 (m, 1H), 3.84 (s, 2H), 3.77 (d, *J* = 2.3 Hz, 2H), 3.61 (d, *J* = 11.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.16 (s), 133.39 (s), 129.88 (s), 129.76 (s),128.45 (s), 89.84 (s), 67.78 (s), 66.07 (s), 61.72 (s).

1,4-Dioxan-2-yl 3-methylbenzoate (2a) yellow oil, yield: 88.8 mg (80%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.36 (dt, *J* = 15.5, 7.5 Hz, 2H), 6.09 (s, 1H), 4.27 – 4.15 (m, 1H), 3.89 (s, 2H), 3.83 (d, *J* = 6.4 Hz, 2H), 3.67 (d, *J* = 11.8 Hz, 1H), 2.41 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.44 (s), 138.31 (s), 134.23 (s), 130.38 (s), 129.64 (s), 128.38 (s), 127.12 (s), 89.76 (s), 67.90 (s), 66.17 (s), 61.83 (s), 21.29 (s).

1,4-Dioxan-2-yl 4-methylbenzoate (3a) yellow oil, yield: 86.6 mg (78%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 6.09 (s, 1H), 4.27 – 4.12 (m, 1H), 3.89 (s, 2H), 3.82 (d, *J* = 6.3 Hz, 2H), 3.67 (d, *J* = 11.8 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.30 (s), 144.22 (s), 129.98 (s), 129.19 (s), 89.64 (s), 67.91 (s), 66.16 (s), 61.83 (s), 21.73 (s).

1,4-Dioxan-2-yl 2-methoxybenzoate (4a) yellow oil, yield: 98.8 mg (83%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.80 (m, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 6.97 (dd, *J* = 8.0, 5.5 Hz, 2H), 6.06 (s, 1H), 4.21 (dd, *J* = 12.1, 6.2 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 2H), 3.80 – 3.75 (m, 2H), 3.64 (d, *J* = 11.7 Hz, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 164.59 (s), 159.65 (s), 134.06 (s), 131.93 (s), 120.12 (s), 119.38 (s), 112.13 (s), 89.62 (s), 67.85 (s), 66.14 (s), 61.77 (s), 56.02 (d, *J* = 3.6 Hz).

1,4-Dioxan-2-yl 3-methoxybenzoate (5a) yellow oil, yield: 105.9 mg (89%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.0 Hz, 1H), 7.61 (s, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.11 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.07 (s, 1H), 4.29 – 4.09 (m, 1H), 3.88 (s, 2H), 3.84 (s, 3H), 3.81 (dd, *J* = 6.4, 2.4 Hz, 2H), 3.66 (d, *J* = 11.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.12 (s), 159.61 (s), 131.02 (s), 129.48 (s), 122.30 (s), 119.80 (s), 114.43 (s), 89.93 (s), 67.81 (s), 66.11 (s), 61.83 (s), 55.48 (s).

1,4-Dioxan-2-yl 4-methoxybenzoate (6a) yellow oil, yield: 111.6 mg (95%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.06 (s, 1H), 4.27 – 4.10 (m, 1H), 3.86 (d, *J* = 5.8 Hz, 5H), 3.80 (dd, *J* = 6.4, 2.3 Hz, 2H), 3.66 (d, *J* = 11.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.93 (s), 163.76 (s), 132.02 (s), 122.04 (s), 113.72 (s), 89.52 (s), 67.94 (s), 66.15 (s), 61.84 (s), 55.47 (s).

1,4-Dioxan-2-yl 4-fluorobenzoate (7a) yellow oil, yield: 99.4 mg (88%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 7.94 (m, 2H), 7.09 (t, *J* = 8.4 Hz, 2H), 6.04 (s, 1H), 4.25 – 4.03 (m, 1H), 3.87 – 3.72 (m, 4H), 3.63 (d, *J* = 11.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.26 (s), 164.73 (s), 164.21 (s), 132.49 (d, *J* = 9.4 Hz), 125.97 (s), 115.74 (s), 115.52 (s), 89.93 (s), 67.77 (s), 66.09 (s), 61.75 (s).

1,4-Dioxan-2-yl 4-chlorobenzoate (8a) yellow oil, yield: 99.2 mg (82%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 6.06 (s, 1H), 4.25 – 4.10 (m, 1H), 3.87 (s, 2H), 3.81 (d, *J* = 6.6 Hz, 2H), 3.66 (d, *J* = 11.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.40 (s), 139.91 (s), 131.30 (s), 128.84 (s), 128.19 (s), 90.05 (s), 67.78 (s), 66.12 (s), 61.78 (s).

1,4-Dioxan-2-yl 4-bromobenzoate (9a) yellow oil, yield: 111.5 mg (78%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 6.10 (s, 1H), 4.28 – 4.12 (m, 1H), 3.99 – 3.76 (m, 4H), 3.70 (d, *J* = 11.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.58 (s), 131.86 (s), 131.43 (s), 128.65 (s), 90.08 (s), 67.79 (s), 66.14 (s), 61.80 (s).

1,4-Dioxan-2-yl [1,1'-biphenyl]-4-carboxylate (10a) yellow oil, yield: 132.1 mg (93%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.0 Hz, 2H), 7.66 (dd, *J* = 21.2, 7.7 Hz, 4H), 7.55 – 7.34 (m, 3H), 6.13 (s, 1H), 4.31 – 4.18 (m, 1H), 3.94 – 3.79 (m, 4H), 3.70 (d, *J* = 11.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

165.17 (s), 146.19 (s), 139.93 (s), 130.49 (s), 128.99 (s), 128.28 (s), 127.25 (d, *J* = 17.2 Hz), 89.85 (s), 67.92 (s), 66.19 (s), 61.85 (s).

1,4-Dioxan-2-yl 2,6-dimethoxybenzoate (11a) yellow oil, yield: 87.1 mg (65%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 10.0 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 6.09 (s, 1H), 4.31 – 4.20 (m, 1H), 3.86 – 3.76 (m, 10H), 3.64 (d, *J* = 11.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.37 (s), 157.47 (s), 131.34 (s), 112.50 (s), 103.91 (s), 89.80 (s), 67.67 (s), 66.08 (s), 61.29 (s), 55.94 (s).

1,4-Dioxan-2-yl 4-(*tert*-butyl)benzoate (12a) yellow oil, yield: 105.6 mg (80%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 6.08 (s, 1H), 4.23 – 4.11 (m, 1H), 3.91 – 3.74 (m, 4H), 3.65 (d, *J* = 11.8 Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.21 (s), 157.14 (s), 129.84 (s), 126.96 (s), 125.44 (s), 89.62 (s), 67.89 (s), 66.14 (s), 61.77 (s), 35.13 (s), 31.11 (s).

1,4-Dioxan-2-yl 2-fluorobenzoate (13a) yellow oil, yield: 67.8 mg (60%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, *J* = 7.1 Hz, 1H), 7.59 – 7.48 (m, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 9.5 Hz, 1H), 6.10 (s, 1H), 4.31 – 4.14 (m, 1H), 3.90 – 3.77 (m, 4H), 3.66 (d, *J* = 11.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.49 (s), 163.07 (s), 160.89 (s), 134.99 (d, *J* = 9.1 Hz), 132.29 (s), 124.05 (d, *J* = 3.9 Hz), 117.22 (s), 116.99 (s), 90.20 (s), 67.69 (s), 66.12 (s), 61.76 (s).

1,4-Dioxan-2-yl 4-cyanobenzoate (14a) yellow oil, yield: 99.0 mg (85%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 6.06 (s, 1H), 4.05 (q, *J* = 7.1 Hz, 1H), 3.85 (s, 2H), 3.79 (d, *J* = 6.6 Hz, 2H), 3.64 (d, *J* = 11.7 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 163.67 (s), 133.60 (s), 132.30 (s), 130.37 (s), 117.84 (s), 116.84 (s), 90.64 (s), 67.64 (s), 66.08 (s), 61.77 (s).

1,4-Dioxan-2-yl 4-(trifluoromethyl)benzoate (15a) yellow oil, yield: 111.8 mg (81%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 6.10 (s, 1H), 4.27 – 4.11 (m, 1H), 3.96 – 3.77 (m, 4H), 3.67 (d, *J* = 11.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.08 (s), 134.96 (s), 134.64 (s), 133.00 (s), 130.30 (s), 125.51 (s), 122.22 (s), 90.37 (s), 61.75 (s).

1,4-Dioxan-2-yl 3-phenylpropanoate (18a) yellow oil, yield: 67.3 mg (57%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.19 (m, 5H), 5.88 (s, 1H), 4.11 – 3.99 (m, 1H), 3.75 (q, *J* = 12.0 Hz, 4H), 3.61 (d, *J* = 11.7 Hz, 1H), 3.03 (t, *J* = 7.7 Hz, 2H), 2.77 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.70 (s), 140.24 (s), 128.56 (s), 128.35 (s), 126.37 (s), 89.30 (s), 67.71 (s), 66.05 (s), 61.65 (s), 35.88 (s), 30.78 (s).

1,4-Dioxolan-4-yl benzoate (1e) yellow oil, yield: 29.1 mg (30%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 7.94 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 6.59 (dd, *J* = 4.1, 1.8 Hz, 1H), 5.20 (s, 1H), 5.15 (s, 1H), 4.15 (qd, *J* = 9.5, 3.0 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.85 (s), 133.53 (s), 129.82 (s), 128.47 (s), 95.95 (s), 94.71 (s), 70.73 (s).

***tert*-Butoxymethyl benzoate (1h)** yellow oil, yield: 85.3 mg (82%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 5.64 (s, 2H), 1.30 (s, 9H). ^{13}C NMR

(101 MHz, $CDCl_3$) δ 165.93 (s), 133.05 (s), 130.32 (s), 129.65 (s), 128.38 (s), 84.98 (s), 76.11 (s), 28.43 (s).

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