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Copper-Catalyzed Methyl Esterification Reactions *via* C-C Bond Cleavage

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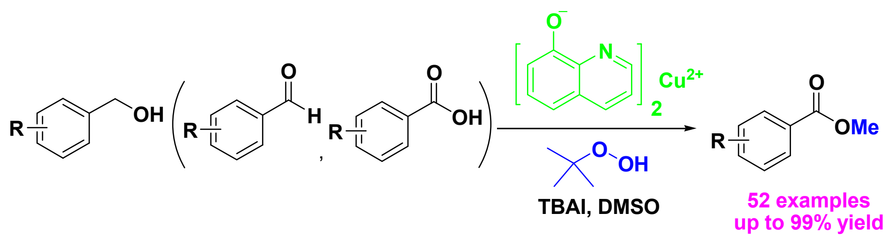
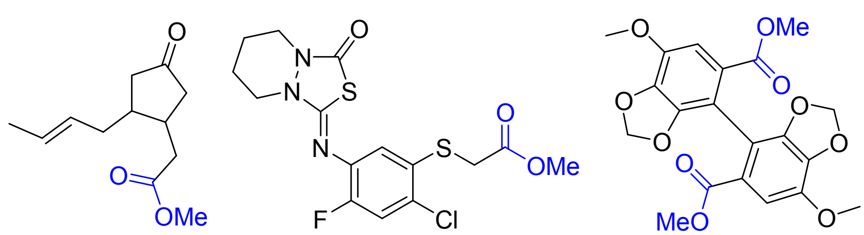


Highly effective synthesis of methyl esters from benzylic alcohols, aldehydes or acids was reported in this paper for the first time *via* copper-catalyzed C-C cleavage from *tert*-butyl hydroperoxide. Our protocol was easily accessible and practical, which will be the possible supplement for the traditional way.

Introduction

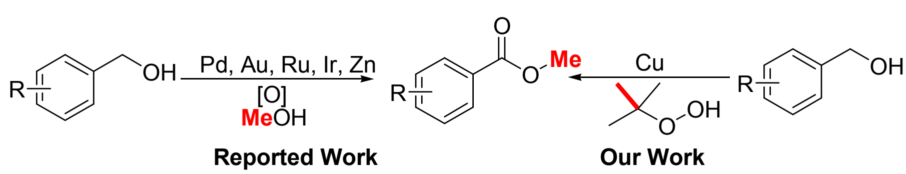


Methyl jasmonate (**A**) Fluthiacet-methyl (**B**) Biphenyldicarboxylate (**C**)

FIGURE 1. Representative organic compounds containing methyl ester moieties

As we know that the ester is one of the most important functional groups in chemicals. Among various types of esters, methyl one is frequently appeared as building blocks in various natural products and polymers.[1] It is noteworthy that many methyl esters have biological activities[2] (selected examples are shown in Figure 1). For example, methyl jasmonate (**A**)[3] is a plant stress hormone, exhibiting anti-cancer activity on human cancer cells; Fluthiacet-methyl (**B**)[4] is a post-emergence herbicide mainly for control of certain annual broadleaf weeds in corn and soybeans; Biphenyldicarboxylate (**C**)[5], as a traditional Chinese medicine, exhibits antihapetotoxic (liver injury), anticonvulsive (cerebral protection), antitumor, antiHIV and antifungal activities.

Thus, substantial attention has been paid on the approaches to acquire the methyl esters during the past several decades. Traditionally, methyl esters are prepared by the reaction of activated acid derivatives with methanol, which is a multi-step process.[6] Considering that benzylic alcohols[7] are readily available, environmental friendly and simple to handle, they are usually employed as the substrates to synthesize methyl esters from methanol in many protocols. Recently, Beller and Lei independently reported some synthetically interesting Pd-catalyzed oxidative cross-esterification of benzylic and aliphatic alcohols with methanol.[8] In addition, other transition metals such as Au, Ru, Ir and Zn also showed high efficiency for the cross-esterification reaction of benzylic alcohols (Scheme 1).[9] In view of the sustainable development in the future, the low-cost efficient metal catalysts need further investigation. With our ongoing interest in various cross-coupling reactions,[10] we describe our efforts on the copper-catalyzed methyl esterification reactions with peroxides, serving as both the oxidant and the source of methyl group (Scheme 1). To the best of our knowledge, there is few example of copper-catalyzed direct esterification of benzylic alcohols in the absence of methanol till now. Furthermore, during the reaction, it was interesting to find that the cleavage of C-C bonds occurred simultaneously. Actually, transition metals-catalyzed cleavage of C–C bonds as a versatile tool in modern organic synthesis has attracted much attention and emerged as a tremendous challenge during the past several years.[11] More recently, Li and co-workers reported a palladium-catalyzed methylation of aryl C-H bonds.[12] On the basis of our findings, we wish to develop a methodology of copper-catalyzed C-C bond cleavage followed by methyl esterification of benzylic alcohols.

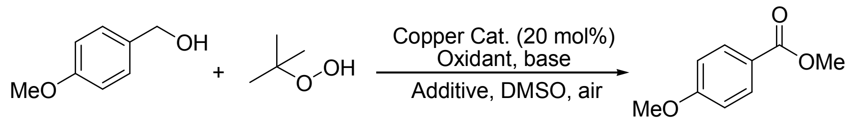


SCHEME 1. Strategies toward methyl esterification of benzylic alcohols

Result and discussion

Firstly, we began our investigation by examining the coupling of benzylic alcohol (**1a**) and TBHP in the presence of low-cost copper catalysis (Table 1, entry 1). However, no desired product was acquired. While TBAI (tetrabutylammonium iodide) was added into the system as the additive, no reaction was observed (Table 1, entry 2). It is speculated that benzylic alcohol could not be oxidized in the current system.[13] Subsequently, base was employed to assist the oxidation of benzylic alcohol, and KOH could afford 27% yield of methyl 4-methoxybenzoate (Table 1, entry 3). Further optimization showed that the corresponding ester could be obtained in 79% yield when K_3PO_4 was used as base (Table 1, entries 4-7). In addition, various copper sources were screened into the reaction (Table 1, entries 8-10) and copper quinolate was the best. Interestingly, no reaction occurred when *tert*-butyl peroxide and dicumyl peroxide were used (Table 1, entries 11-12). Investigation of the solvents (Table 1, entries 13-14) showed that other solvents except DMSO, could hardly afford the ester. To our surprise, a yield of 92% of the desired product (**2a**) was acquired when higher amount of the oxidant was used (Table 1, entry 15). Under the same conditions, the control experiment showed that the yield would be greatly reduced in the absence of catalyst or TBAI (Table 1, entries 16-17). It can be seen that TBAI shows a key acceleration role in the methyl esterification. Actually, we have also tried some other metals, including Fe, Ni, Co and et al. However, their catalytic effects were very poor.

TABLE 1. Optimization of reaction conditions for the methyl esterification of benzylic alcohol [a]



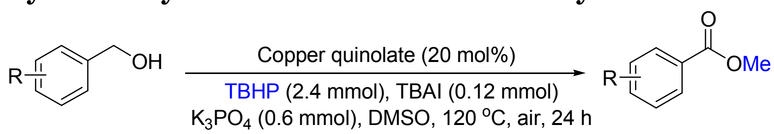
1a 2a

Entry	Cu Cat.	Oxidant	Additive	Base	Yield (%) [b]
1	Copper quinolate	TBHP	–	–	NR
2	Copper quinolate	TBHP	TBAI	–	NR
3	Copper quinolate	TBHP	TBAI	KOH	27
4	Copper quinolate	TBHP	TBAI	EtONa	67
5	Copper quinolate	TBHP	TBAI	^{t}BuOK	47
6	Copper quinolate	TBHP	TBAI	K_2CO_3	72
7	Copper quinolate	TBHP	TBAI	K_3PO_4	79
8	Copper powder	TBHP	TBAI	K_3PO_4	73
9	CuI	TBHP	TBAI	K_3PO_4	31
10	$Cu(OAc)_2.H_2O$	TBHP	TBAI	K_3PO_4	75
11	Copper quinolate	DTBP	TBAI	K_3PO_4	NR
12	Copper quinolate	DCP	TBAI	K_3PO_4	NR
13 [c]	Copper quinolate	TBHP	TBAI	K_3PO_4	NR
14 [d,e]	Copper quinolate	TBHP	TBAI	K_3PO_4	<5
15 [d]	Copper quinolate	TBHP	TBAI	K_3PO_4	92
16 [d]	–	TBHP	TBAI	K_3PO_4	42
17 [d]	Copper quinolate	TBHP	–	K_3PO_4	69

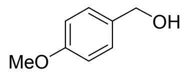
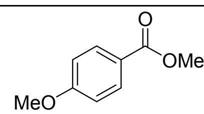
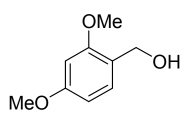
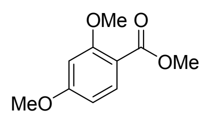
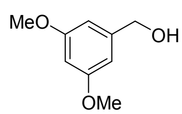
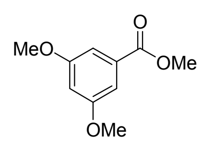
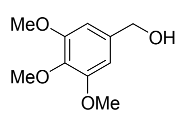
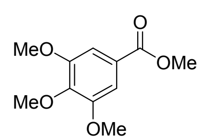
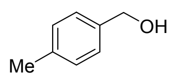
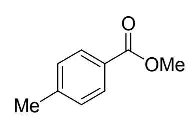
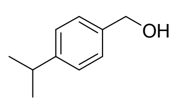
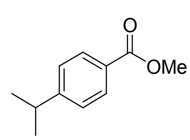
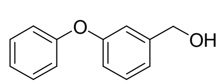
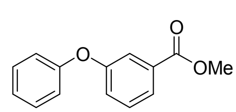
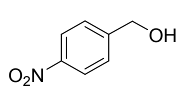
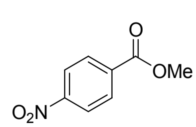
[a] Reaction conditions: methoxybenzylic alcohol (0.3mmol), catalyst (0.06 mmol), oxidant (1.8 mmol), additive (0.12mmol, 40 mol%), base (0.6 mmol, 2 equiv), solvent (2 mL), 120 ^oC, air, 24h. [b] The yield based on methoxybenzylic alcohol. [c] DMF as the solvent. [d] TBHP (2.4 mmol). [e] Toluene as the solvent.

Under the optimized reaction conditions, various benzylic alcohol derivatives were examined and related results were summarized in Table 2. It was shown that benzylic alcohols with electron-withdrawing or electron-donating groups were all well tolerated and the corresponding esters were obtained in moderate to excellent yields. The desired esters (**2**) were isolated in 70-92% yields when benzylic alcohols with the electron-donating methoxyl group were used (Table 2, entries 1-4). For the methyl, isopropyl, and phenoxy groups, the desired esters (**2e-2g**) were acquired with 74%, 61% and 67% yields, respectively (Table 2, entries 5-7). It was noteworthy that electron-withdrawing nitryl group gave moderate yield of the corresponding ester (**2h**) (Table 2, entry 8).

TABLE 2. Copper-catalyzed methyl esterification of various benzylic alcohols[a]



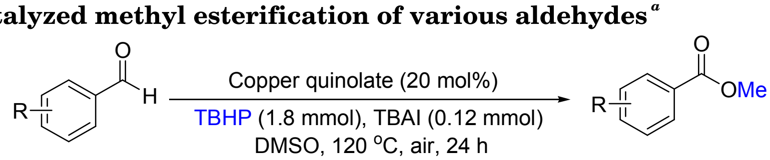
1 2

Entry	Benzylic Alcohol	Product		Yield (%)[b]
1			**2a**	92
2			**2b**	76
3			**2c**	80
4			**2d**	70
5			**2e**	74
6			**2f**	61
7			**2g**	67
8			**2h**	53

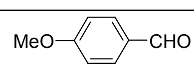
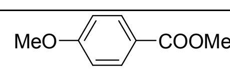
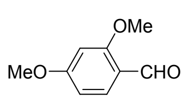
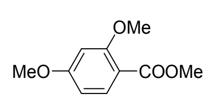
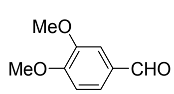
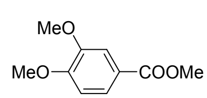
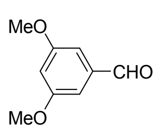
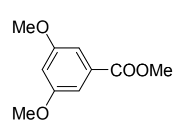
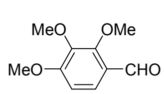
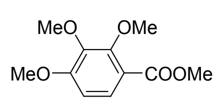
[a] Reaction conditions: benzylic alcohol (0.3 mmol), copper quinolate (0.06 mmol), TBHP (2.4 mmol, 70% aqueous solution), TBAI (0.12 mmol), K_3PO_4 (0.6 mmol), DMSO (2 mL), 120 °C, air, 24 h. [b] The yield based on benzylic alcohol.

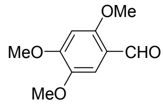
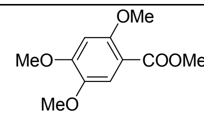
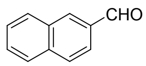
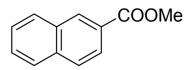
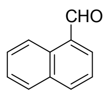
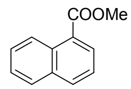
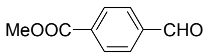
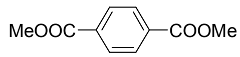
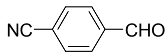
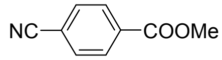
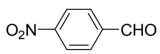
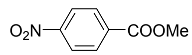
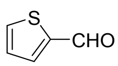
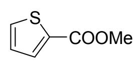
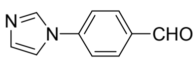
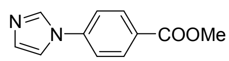
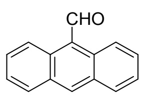
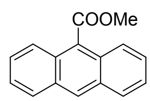
During the methyl esterification of benzylic alcohols, corresponding acid was detected as the by-product in the crude reaction mixture by LC-MS, which suggests that benzylic alcohol was directly oxidized to acid possibly. In addition, we did not observe corresponding aldehyde and any self coupled product by the possible *in situ* generated aldehyde and the unoxidized alcohol. After the successful application of the oxidative methyl esterification from benzylic alcohols, we tried to extend this methodology to the aldehydes or carboxylic acids as substrates.[14] It is found that base is not necessary in the methyl esterification of aldehyde and the amount of the oxidant could be reduced to six equivalents. Subsequently, various aldehyde derivatives were examined and representative results were listed in Table 3. Generally, it can be seen that the electronic effect and steric effect were not significant. In addition, substrates with electron-donating groups were superior to those with electron-withdrawing groups. The aldehydes substituted with the electron-donating group (methoxy) generated the methylation products in good to excellent yields under the optimized reaction conditions (Table 3, entries 1-6). 2-Naphthaldehyde was better than 1-naphthaldehyde, affording 96%, 72% yields, respectively (Table 3, entries 7-8). Furthermore, many electron-withdrawing groups, including cyano, nitro and ester, were well tolerated under the standard conditions (Table 3, entries 9-11). To show the synthetic utility of this method, heteroaryl aldehydes such as thiophene-2-carbaldehyde and 4-(1*H*-imidazol-1-yl) benzaldehyde, were subjected to the optimized conditions, and the desired esters (**4h-4i**) were obtained in satisfactory yields (Table 3, entries 12-13). It is observed that anthracene-10-carbaldehyde could give the desired ester (**4j**) in 70% yield using our system (Table 3, entry 14).

TABLE 3. Copper-catalyzed methyl esterification of various aldehydes[a]



3 **4**

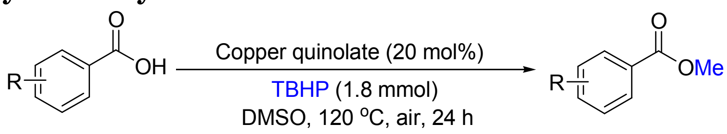
Entry	Aldehyde	Product		Yield (%)[b]
1			**2a**	95
2			**2b**	88
3			**4a**	61
4			**2c**	96
5			**4b**	94

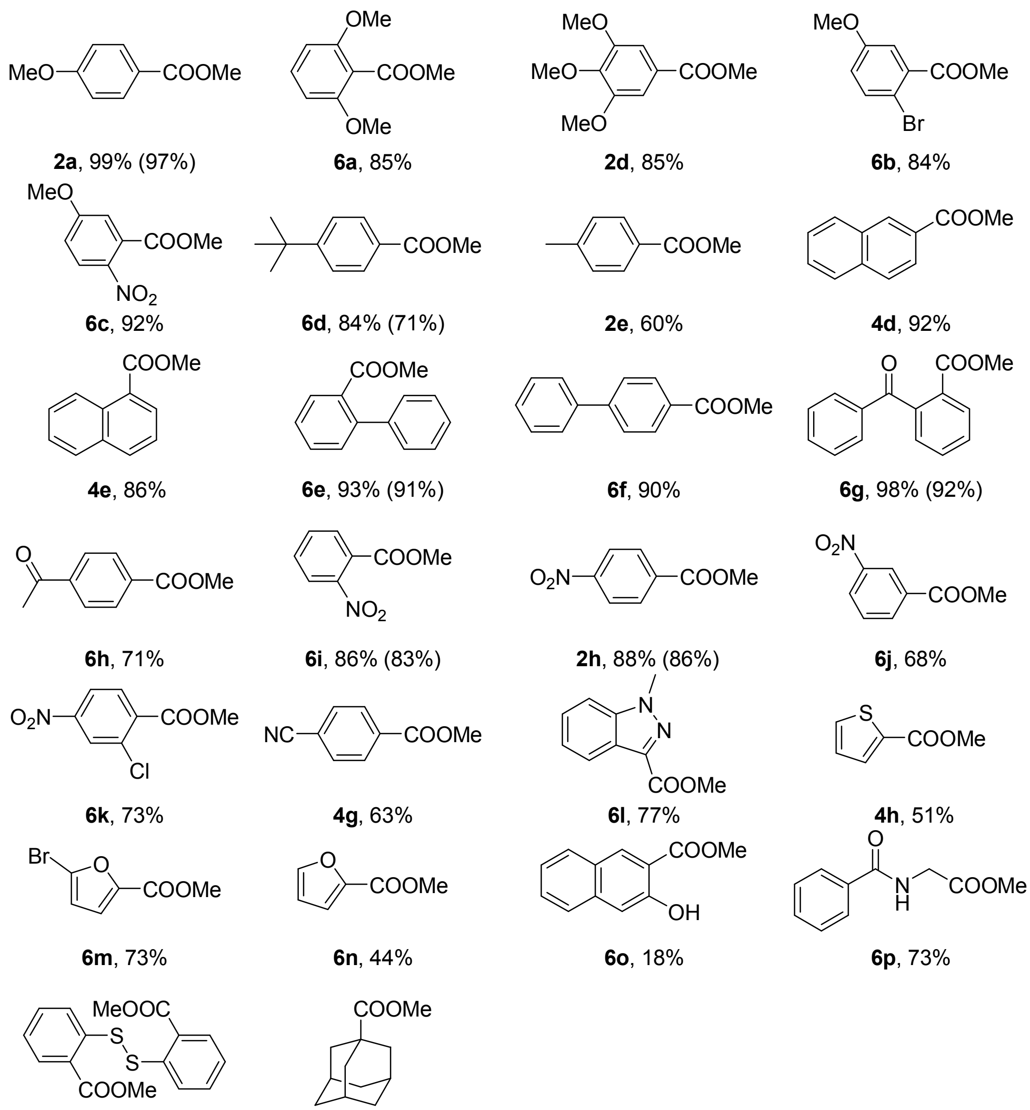
6			**4c**	85
7			**4d**	96
8			**4e**	72
9			**4f**	69
10			**4g**	71
11			**2h**	69
12			**4h**	65
13			**4i**	64
14			**4j**	70

[a] Reaction conditions: aldehyde (0.3mmol), copper quinolate (0.06 mmol), TBHP (1.8mmol, 70% aqueous solution), TBAI (0.12 mmol), DMSO (2 mL), 120^{o}C, Air, 24h. [b] The yield based on aldehyde.

Comparing with aldehydes, the corresponding acids are cheaper and more stable. At the same time, it was found that less amount of TBHP (0.9 mmol) and lower reaction temperature (100 ^{o}C) were suitable for the methyl esterification of acids. It is noteworthy that in this transformation, TBAI is not necessary. Thus, we can conclude that TABI do show acceleration role in the process of oxidation. Then, different substituted acids were subjected to the optimized conditions as shown in Table 4. The results indicated that the acids with electron-withdrawing or electron-donating groups were all well tolerated and provided the corresponding products in good to excellent yields. Similar to aldehydes, the acids with the strong electron-donating methoxyl group generated the methylation products in good to excellent yields under the optimized reaction conditions (**2a**, **2d** and **6a-6c**). For the tertiary butyl and methyl groups, the desired esters were produced smoothly in 84% and 60% yields respectively (**6d** and **2e**). Good yields were obtained when 1-naphthoic acid and 2-naphthoic acid were employed as the substrates (**4d** and **4e**). A wide range of functional groups, including phenyl, benzoyl, ethanoyl, cyano and nitro, all were performed smoothly under the optimized conditions (**2h**, **4g** and **6e-6l**). To expand the synthetic utility of the method, various heteroaryl acids such as 1-methyl-1*H*-indazole-3-carboxylic acid, thiophene-2-carboxylic acid, 5-bromofuran-2-carboxylic acid and furan-2-carboxylic acid, were subjected to the optimized conditions and afforded the desired esters in moderate yields (**4h**, **6m** and **6n**). 3-Hydroxy-2-naphthoic acid only gave 18% yield of the corresponding product (**6o**) under the standard condition. It is speculated that hydroxyl group is sensitive to oxidants possibly. To our delight, 2-benzamidoacetic acid could give the desired ester (**6p**) in 73% yield without any protections. 2,2′-Dithiodibenzoic acid and 1-adamantane carboxylic acid could not afford the corresponding esters (**6q-6r**) under the standard conditions.

TABLE 4. Copper-catalyzed methyl esterification of various acids[a]





2a, 99% (97%); **6a**, 85%; **2d**, 85%; **6b**, 84%

6c, 92%; **6d**, 84% (71%); **2e**, 60%; **4d**, 92%

4e, 86%; **6e**, 93% (91%); **6f**, 90%; **6g**, 98% (92%)

6h, 71%; **6i**, 86% (83%); **2h**, 88% (86%); **6j**, 68%

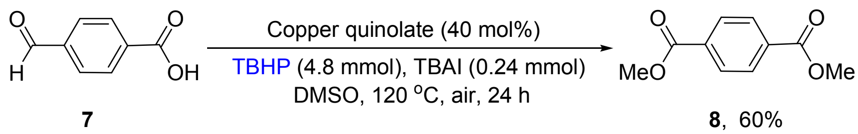
6k, 73%; **4g**, 63%; **6l**, 77%; **4h**, 51%

6m, 73%; **6n**, 44%; **6o**, 18%; **6p**, 73%

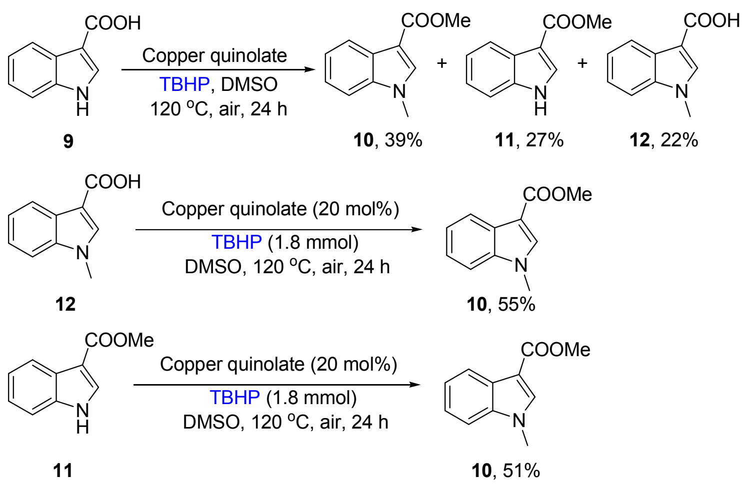
6q, trace; **6r**, trace

[a] Reaction conditions: Acid (0.3 mmol), copper quinolate (0.06 mmol), TBHP (1.8 mmol, 70% aqueous solution), DMSO (2 mL), 120 °C, air, 24 h. The value in the parenthesis represents the result when less amount of TBHP (0.9 mmol) and lower reaction temperature (100 °C) were employed.

Subsequently, 4-formylbenzoic acid (**7**) was subjected to the optimized conditions and afforded the desired dimethyl ester (**8**) in 60% yield (Scheme 2). Then 1*H*-indole-3-carboxylic acid was investigated and double-methylation product (**10**) (39%), mono-methylation product (**11**) (27%), *N*-methylation product (**12**) (22%) were formed respectively (Scheme 3). 1-Methyl-1*H*-indole-3-carboxylic acid (**12**) can give the desired ester (**10**) in 55% yield under the optimized condition, while 51% yield of *N*-methylation product (**10**) was formed by methyl 1*H*-indole-3-carboxylate.[15] Thus, it could be seen that our system can not only be used in the methyl esterification of alcohol, aldehyde and acid, but also provide a protection method of *N*-methylation.

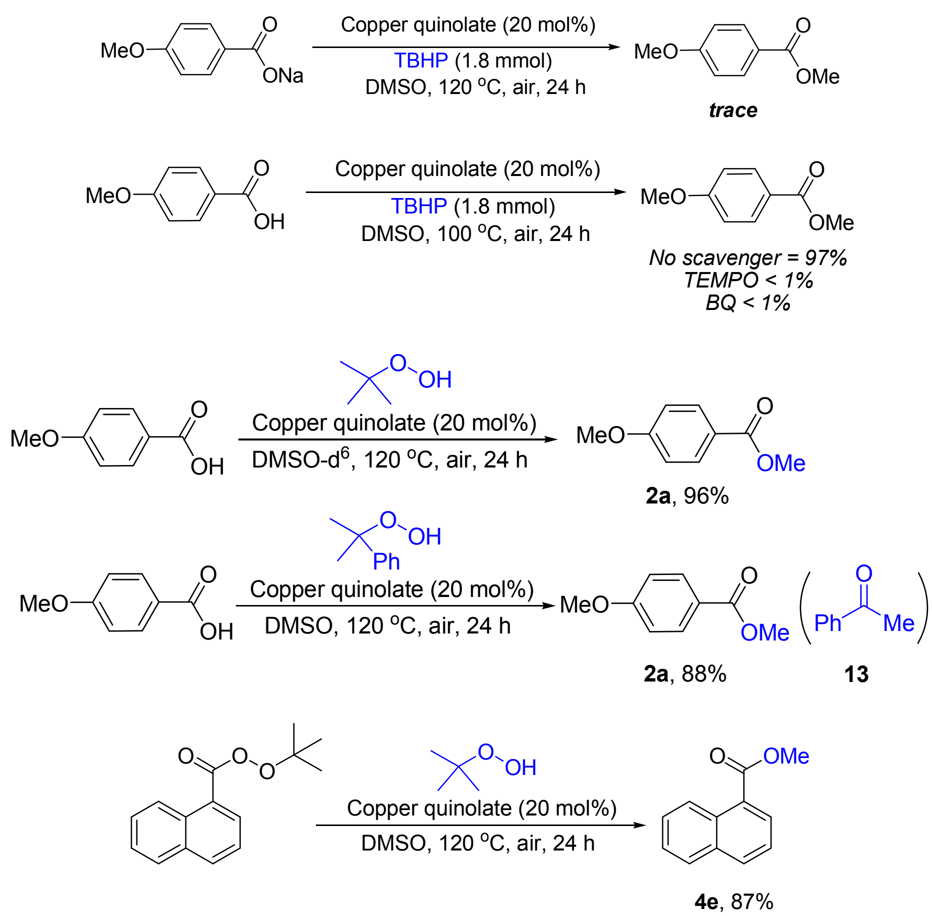


SCHEME 2. Copper-catalyzed methyl esterification of 4-formylbenzoic acid.



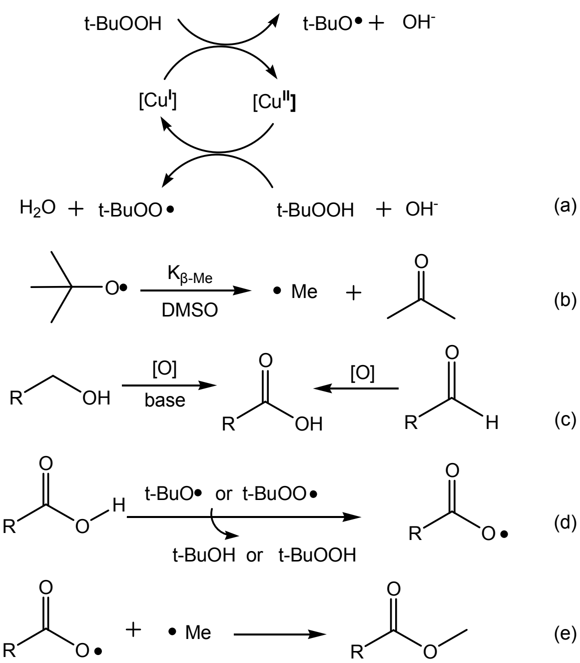
SCHEME 3. Copper-catalyzed methylation or methyl esterification of 1H-indole-3-carboxylic acid or its methyl ester.

Further investigations on the mechanism were performed (Scheme 4). The reaction of sodium 4-methoxybenzoate with TBHP did not generate the methyl 4-methoxybenzoate, indicating that no 4-methoxybenzoate anion and methyl cation were generated in the reaction system. In addition, it was observed that TEMPO could completely inhibit the reaction, which suggests that the reaction may involve acyloxy and methyl radicals in the catalytic cycle of the ester synthesis. When DMSO-d^{6} replaced the solvent DMSO, 96% yield of methyl 4-methoxybenzoate was obtained. ^{1}H NMR showed that the product did not contain deuterium. This is an indirect proof that the methyl group of product came from TBHP. When 1-(2-hydroperoxypropan-2-yl) benzene was employed instead of TBHP, methyl 4-methoxybenzoate was obtained in 88% yield. It is noteworthy that great amount of acetophenone (**13**) was also isolated by column chromatography. This is a powerful proof to demonstrate that the methyl group of product came from oxidant. We believed that *t*-butyl naphthalene-1-carboperoxoate may exist in the reaction system as an intermediate. In order to prove this hypothesis, this peroxide was synthesized and employed as the substrate for the reaction. As expected, the methyl 1-naphthoate (**4e**) was obtained in 87% yield.[16]



SCHEME 4. Control experiments and effect of radical inhibitor.

Based on the above results and literatures, a tentative mechanism is illustrated in Scheme 5. Initially, TBHP decomposes to generate the *tert*-butoxyl and *tert*-butylperoxy radicals in the presence of copper catalyst.[17] Then, a facile unimolecular decomposition of *tert*-butoxyl to acetone and a methyl radical occurred.[18] The benzylic alcohol was directly oxidized to benzoic acid in the presence of oxidant and base, while the aldehyde was easily oxidized to benzoic aicd only using oxidant. Subsequently, acyloxy radical was generated from benzoic acid in the function of *tert*-butoxyl or *tert*-butylperoxy radical. Finally, the coupling of acyloxy radical and methyl radical gave the desired ester.



SCHEME 5. The possible mechanism.

Conclusions

In summary, we have successfully developed a novel, effective and direct method of copper-catalyzed methyl esterification of benzyl alcohols, aldehydes or acids *via* C–C cleavage reaction. It is noteworthy that in this transformation, TBHP was used not only as the oxidant, but also as the source of methyl group. In general, the desired methyl esters could be obtained in good to excellent yields. Thus, this catalytic protocol could tolerate a wide range of substrates, which represents a practical and low-cost method for the preparation of methyl ester based molecules. It could be the possible supplement for the traditional way in some cases. Further investigations toward its applications are currently underway.

Experimental Section

General experimental: All manipulations were carried out under air atmosphere. Benzylic alcohols, aldehydes, acids, *tert*-butyl hydroperoxide (70% solution in water) and tetrabutylammonium iodide were commercially available and used without further purification. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) data were recorded on 400 M spectrometers using $CDCl_3$ as solvent. The chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. ^{1}H NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference.

General procedure for copper-catalyzed methyl esterification of benzyl alcohol: benzylic alcohol (0.3 mmol), copper quinolate (0.06 mmol, 20 mol %, 0.0210 g), K_3PO_4 (0.6 mmol, 2 equiv, 0.1274 g), TBAI (0.12 mmol, 40 mol %, 0.0443 g), TBHP (2.4 mmol, 0.33 mL of a 70% aqueous solution), and DMSO (2.0 mL) were added to a test tube in air. The reaction mixture was heated in an oil bath at 120 °C for 24 h and was quenched with a saturated solution of Na_2SO_3 (for removal of excess TBHP) and extracted with ethyl acetate. The organic solvent was removed under vacuum and purification by chromatography on a silica gel column by using a mixture of petroleum ether and ethyl acetate afforded the desired product.

General procedure for copper-catalyzed methyl esterification of aldehyde: aldehyde (0.3 mmol), copper quinolate (0.06 mmol, 20 mol %, 0.0210 g), TBAI (0.12 mmol, 40 mol %, 0.0443 g), TBHP (1.8 mmol, 0.25 mL of a 70% aqueous solution), and DMSO (2.0 mL) were added to a test tube in air. The reaction mixture was heated in an oil bath at 120 °C for 24 h and was quenched with a saturated solution of Na_2SO_3 (for removal of excess TBHP) and extracted with ethyl acetate. The organic solvent was removed under vacuum and purification by chromatography on a silica gel column by using a mixture of petroleum ether and ethyl acetate afforded the desired product.

General procedure for copper-catalyzed methyl esterification of acid: acid (0.3 mmol), copper quinolate (0.06 mmol, 20 mol %, 0.0210 g), TBHP (1.8 mmol, 0.25 mL of a 70% aqueous solution), and DMSO (2.0 mL) were added to a test tube in air. The reaction mixture was heated in an oil bath at 100-120 °C for 24 h and was quenched with a saturated solution of Na_2SO_3 (for removal of excess TBHP) and extracted with ethyl acetate. The organic solvent was removed under vacuum and purification by chromatography on a silica gel column by using a mixture of petroleum ether and ethyl acetate afforded the desired product.

Methyl 4-isopropylbenzoate (32.6 mg, 61%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.96 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 3.90 (s, 3H), 3.01-2.89 (m, 1H), 1.27 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.1, 154.2, 129.6, 127.7, 126.4, 51.9, 34.2, 30.8, 23.6; MS: Anal. Calcd. For $C_{11}H_{15}O_2$: 179.1, Found: 179.1 $(M+1)^+$.

Methyl 3,5-dimethoxybenzoate (51.3 mg, 96%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.18 (d, J = 4.0 Hz, 2H), 6.64 (t, J = 4,.0 Hz, 1H), 3.90 (s, 3H), 3.82 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.7, 160.5, 131.9, 107.0, 105.6, 55.4, 52.1; MS: Anal. Calcd. For $C_{10}H_{13}O_4$: 197.1, Found: 197.1 $(M+1)^+$.

Methyl 4-nitrobenzoate (47.8 mg, 88%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.26 (d, J =8.0 Hz, 2H), 8.18 (d, J = 8.0 Hz, 2H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.4, 150.7, 135.7, 130.9, 123.7, 53.1; MS: Anal. Calcd. For $C_8H_8NO_4$: 182.0, Found: 182.0 $(M+1)^+$.

Methyl 4-methylbenzoate (33.3 mg, 74%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.93 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 3.89 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.1, 142.5, 128.5, 128.0, 126.4, 50.9, 20.6; MS: Anal. Calcd. For $C_9H_{11}O_2$: 151.1, Found: 151.1 $(M+1)^+$.

Methyl 3-phenoxybenzoate (45.9 mg, 67%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.77 (d, J = 8.0 Hz, 1H), 7.66 (s, 1H), 7.37 (dt, J = 16.0, 7.9 Hz, 3H), 7.20 (d, J = 8.0 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 7.01 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.4, 157.4, 156.6, 131.8, 129.8, 129.7, 124.2, 123.7, 123.2, 119.5, 119.0, 52.2; MS: Anal. Calcd. For $C_{14}H_{13}O_3$: 229.1, Found: 229.1 $(M+1)^+$.

Methyl 2,4-dimethoxybenzoate (52.3 mg, 88%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.85 (d, J = 8.0 Hz, 1H), 6.51–6.45 (m, 2H), 3.89 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.0, 164.2, 161.2, 133.7, 112.0, 104.5, 98.8, 55.8, 55.3, 51.6; MS: Anal. Calcd. For $C_{10}H_{13}O_4$: 197.1, Found: 197.1 $(M+1)^+$.

Methyl 3,4,5-trimethoxybenzoate (57.7 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.24 (s, 2H), 3.85 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.8, 153.1, 142.2, 125.3, 106.9, 61.1, 56.4, 52.4; MS: Anal. Calcd. For $C_{11}H_{15}O_5$: 227.1, Found: 227.1 $(M+1)^+$.

Methyl 4-methoxybenzoate (49.3 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.99 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.0, 163.5, 131.8, 122.8, 113.8, 55.6, 52.0; MS: Anal. Calcd. For $C_9H_{11}O_3$: 167.1, Found: 167.1 $(M+1)^+$.

Dimethyl terephthalate (34.9 mg, 60%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.08 (s, 4H), 3.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.5, 134.07, 129.7, 110.0, 52.7; ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.5, 134.1, 129.7, 110.0, 52.7; MS: Anal. Calcd. For $C_{10}H_{11}O_4$: 195.1, Found: 195.1 $(M+1)^+$.

Methyl 4-cyanobenzoate (34.3 mg, 71%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.15 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.3, 133.8, 132.2, 130.0, 117.9, 116.3, 52.7; MS: Anal. Calcd. For $C_9H_8NO_2$: 162.1, Found: 162.1 $(M+1)^+$.

Methyl 2-naphthoate (53.6 mg, 96%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.59 (S, 1H), 8.05 (dd, J = 8.6, 1.4 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.58–7.49 (m, 2H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.5, 135.7, 132.7, 131.3, 129.6, 128.5, 128.4, 128.0, 127.6, 126.9, 125.4, 52.5; MS: Anal. Calcd. For $C_{12}H_{11}O_2$: 187.1, Found: 187.1 $(M+1)^+$.

Methyl thiophene-2-carboxylate (21.7 mg, 51%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.88 (dd, J = 3.7, 0.8 Hz, 1H), 7.63 (dd, J = 4.9, 0.8 Hz, 1H), 7.18 (dd, J = 4.7, 4.0 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 162.9, 133.7, 133.6, 132.6, 128.0, 52.4; MS: Anal. Calcd. For $C_6H_7SO_2$: 143.0, Found: 143.0 $(M+1)^+$.

Methyl 3,4-dimethoxybenzoate (35.9 mg, 61%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.68 (dd, J = 8.4, 1.9 Hz, 1H), 7.55 (d, J = 4.0 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 3.94 (s, 3H), 3.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.1, 153.1, 148.8, 123.8, 122.8, 112.1, 110.4, 56.2, 52.2; MS: Anal. Calcd. For $C_{10}H_{13}O_4$: 197.1, Found: 197.1 $(M+1)^+$.

Methyl 1-naphthoate (40.2 mg, 72%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.91 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.64–7.58 (m, 1H), 7.56–7.45 (m, 2H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)

(δ, ppm) 168.3, 134.0, 133.6, 131.5, 130.5, 128.8, 129.0, 127.3, 126.4, 126.0, 124.7, 52.4; MS: Anal. Calcd. For $C_{12}H_{11}O_2$: 187.1, Found: 187.1 $(M+1)^+$.

Methyl anthracene-10-carboxylate (49.6 mg, 70%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.51 (s, 1H), 8.01 (t, J = 8.0 Hz, 4H), 7.50 (dt, J = 14.7, 7.0 Hz, 4H), 4.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 170.3, 134.4, 133.7, 131.2, 129.7, 128.9, 128.7, 127.5, 127.3, 125.7, 125.3, 124.0, 122.5, 122.4, 121.3, 52.9; MS: Anal. Calcd. For $C_{16}H_{13}O_2$: 237.1, Found: 237.1 $(M+1)^+$.

Methyl 2,3,4-trimethoxybenzoate (67.8 mg, 94%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.56 (d, J = 8.0 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.2, 157.3, 154.8, 143.1, 127.1, 124.4, 107.1, 62.0, 61.2, 56.2, 52.1; MS: Anal. Calcd. For $C_{11}H_{15}O_5$: 227.1, Found: 227.1 $(M+1)^+$.

Methyl 2,4,5-trimethoxybenzoate (57.7 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.41 (s, 1H), 6.54 (s, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 3.88 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.9, 155.5, 153.4, 142.3, 114.1, 110.2, 97.4, 56.8, 56.2, 55.9, 51.7; MS: Anal. Calcd. For $C_{11}H_{15}O_5$: 227.1, Found: 227.1 $(M+1)^+$.

Methyl 4-(1H-imidazol-1-yl)benzoate (38.8 mg, 64%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.16 (d, J = 8.0 Hz, 2H), 7.97 (s, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.37 (s, 1H), 7.24 (s, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.9, 140.5, 135.3, 131.4, 130.9, 128.8, 120.4, 117.6, 52.3; MS: Anal. Calcd. For $C_{11}H_{11}N_2O_2$: 203.1, Found: 203.1 $(M+1)^+$.

Methyl 2-nitrobenzoate (46.7 mg, 86%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.92 (dd, J = 7.8, 1.1 Hz, 1H), 7.75 (dd, J = 7.5, 1.5 Hz, 1H), 7.67 (dtd, J = 17.0, 7.4, 1.5 Hz, 2H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.1, 133.2, 132.0, 130.0, 129.3, 127.7, 124.1, 53.5; MS: Anal. Calcd. For $C_8H_8NO_4$: 182.0, Found: 182.0 $(M+1)^+$.

Methyl 4-tert-butylbenzoate (48.4 mg, 84%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.97 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 3.90 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.3, 156.7, 129.6, 127.6, 125.5, 52.2, 32.3, 31.3; MS: Anal. Calcd. For $C_{12}H_{17}O_2$: 193.1, Found: 193.1 $(M+1)^+$.

Methyl 3-nitrobenzoate (36.9 mg, 68%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.88–8.83 (m, 1H), 8.45–8.40 (m, 1H), 8.40–8.35 (m, 1H), 7.68 (t, J = 8.0 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.1, 148.4, 135.5, 132.0, 129.9, 127.6, 124.8, 53.0; MS: Anal. Calcd. For $C_8H_8NO_4$: 182.1, Found: 182.1 $(M+1)^+$.

Methyl 2-phenylbenzoate (59.2 mg, 93%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.81 (dd, J = 7.7, 0.7 Hz, 1H), 7.50 (td, J = 7.5, 1.2 Hz, 1H), 7.37 (dt, J = 13.3, 6.8 Hz, 5H), 7.32–7.28 (m, 2H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 169.4, 142.7, 141.5, 131.5, 131.1, 131.0, 130.0, 128.5, 128.3, 127.5, 127.4, 52.2; MS: Anal. Calcd. For $C_{14}H_{13}O_2$: 213.1, Found: 213.1 $(M+1)^+$.

Methyl 2-benzoylbenzoate (70.6 mg, 98%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.04 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.63 (t, J = 8.0 Hz, 1H), 7.59–7.51 (m, 2H), 7.45–7.38 (m, 3H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 197.3, 166.6, 141.9, 137.3, 133.3, 132.7, 130.3, 129.9, 129.4, 129.3, 128.7, 128.0, 52.4; MS: Anal. Calcd. For $C_{15}H_{13}O_3$: 241.1, Found: 241.1 $(M+1)^+$.

Methyl 5-bromofuran-2-carboxylate (44.7 mg, 73%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.14 (d, J = 4.0 Hz, 1H), 6.47 (d, J = 4.0 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.2, 146.3, 127.7, 120.3, 114.1, 52.3; MS: Anal. Calcd. For $C_6H_6BrO_3$: 205.0, Found: 205.0 $(M+1)^+$.

Methyl 4-acetylbenzoate (37.9 mg, 71%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.12 (d, J = 8.0 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H), 3.95 (s, 3H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 197.4, 166.1, 140.1, 133.8, 129.7, 128.1, 52.4, 26.8; MS: Anal. Calcd. For $C_{10}H_{11}O_3$: 179.1, Found: 179.1 $(M+1)^+$.

Methyl 2,6-dimethoxybenzoate (50.0 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.25 (t, J = 8.0 Hz, 1H), 6.53 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H), 3.78 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.3, 157.5, 131.3, 113.1, 104.1, 56.2, 52.7; MS: Anal. Calcd. For $C_{10}H_{13}O_4$: 197.1, Found: 197.1 $(M+1)^+$.

Methyl 5-methoxy-2-nitrobenzoate (58.3 mg, 92%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.04–8.02 (m, 1H), 7.04–7.01 (m, 2H), 3.93 (s, 3H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.8, 163.6, 140.0, 131.4, 126.9, 115.9, 114.3, 56.4, 53.6; MS: Anal. Calcd. For $C_9H_{10}NO_5$: 212.1, Found: 212.1 $(M+1)^+$.

Methyl 3-hydroxy-2-naphthoate (10.9 mg, 18%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.44 (s, 1H), 8.49 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.50 (t, J = 8.0 Hz, 1H), 7.33 (d, J = 12.0 Hz, 2H), 4.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 169.3, 155.2, 136.9, 131.4, 128.2, 128.1, 126.0, 125.3, 122.9, 113.1, 110.6, 51.6; MS: Anal. Calcd. For $C_{12}H_{11}O_3$: 203.1, Found: 203.1 $(M+1)^+$.

Methyl 2-bromo-5-methoxybenzoate (61.5 mg, 84%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.49 (d, J = 9.0 Hz, 1H), 7.28 (d, J = 3.0 Hz, 1H), 6.86 (dd, J = 8.8, 3.1 Hz, 1H), 3.90 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.7, 158.7, 135.2, 132.8, 119.2, 116.4, 112.1, 55.8, 528; MS: Anal. Calcd. For $C_9H_{10}BrO_3$: 245.0, Found: 245.0 $(M+1)^+$.

Methyl 2-chloro-4-nitrobenzoate (47.1 mg, 73%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.31 (d, J = 2.0 Hz, 1H), 8.16 (dd, J = 8.6, 2.2 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.8, 149.6, 135.9, 135.0, 132.2, 126.2, 121.6, 53.3; MS: Anal. Calcd. For $C_8H_7ClNO_4$: 216.0, Found: 216.0 $(M+1)^+$.

Methyl 1-methyl-1H-indazole-3-carboxylate (43.9 mg, 77%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.21 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 4.0 Hz, 2H), 7.35–7.27 (m, 1H), 4.15 (s, 3H), 4.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.2, 141.1, 134.5, 127.1, 123.8, 123.3, 122.2, 109.7, 52.2, 36.6; MS: Anal. Calcd. For $C_{10}H_{11}N_2O_2$: 191.1, Found: 191.1 $(M+1)^+$.

Methyl 4-phenylbenzoate (57.3 mg, 90%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.12 (d, J = 8.0 Hz, 2H), 7.69–7.60 (m, 4H), 7.47 (t, J = 8.0 Hz, 2H), 7.40 (t, J = 8.0 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.2, 145.8, 140.2, 130.3, 129.2, 129.1, 128.4, 127.5, 127.3, 52.4; MS: Anal. Calcd. For $C_{14}H_{13}O_2$: 213.1, Found: 213.1 $(M+1)^+$.

Methyl furan-2-carboxylate (16.6 mg, 44%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.59 (s, 1H), 7.19 (d, J = 4.0 Hz, 1H), 6.55–6.50 (m, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 159.4, 146.5, 144.8, 118.2, 112.1, 52.2; MS: Anal. Calcd. For $C_6H_7O_3$: 127.1, Found: 127.1 $(M+1)^+$.

Methyl 2-benzamidoacetate (42.3 mg, 73%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.82 (d, J = 8.0 Hz, 2H), 7.49 (t, J = 8.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 2H), 7.15 (s, 1H), 4.21 (d, J = 8.0 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 170.8, 167.9, 133.8, 132.0, 128.8, 127.3, 52.6, 41.9; MS: Anal. Calcd. For $C_{10}H_{12}NO_3$: 194.1, Found: 194.1 $(M+1)^+$.

Methyl 1-methyl-1H-indole-3-carboxylate (31.2 mg, 55%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.17 (dd, J = 5.7, 3.1 Hz, 1H), 7.77 (s, 1H), 7.36–7.25 (m, 3H), 3.91 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.7, 137.4, 135.4, 126.8, 123.0, 122.1, 121.9, 110.0, 107.1, 51.2, 33.7; MS: Anal. Calcd. For $C_{11}H_{12}NO_2$: 190.1, Found: 190.1 $(M+1)^+$.

Methyl 1H-indole-3-carboxylate (14.2 mg, 27%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 9.21 (s, 1H), 8.18 (d, J = 4.5 Hz, 1H), 7.92 (s, 1H), 7.44 (s, 1H), 7.26 (s, 2H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, DMSO) (δ, ppm) 165.2, 136.8, 132.9, 126.1, 122.8, 121.7, 120.8, 112.8, 106.7, 51.1; MS: Anal. Calcd. For $C_{10}H_{10}NO_2$: 176.1, Found: 176.1 $(M+1)^+$.

1-Methyl-1H-indole-3-carboxylic acid (11.6 mg, 22%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.26–8.21 (m, 1H), 7.89 (s, 1H), 7.35 (dd, J = 20.9, 6.8 Hz, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, DMSO) (δ, ppm) 170.8, 142.1, 141.2, 131.5, 127.3, 126.4, 125.8, 115.7, 111.3, 38.1; MS: Anal. Calcd. For $C_{10}H_{10}NO_2$: 176.1, Found: 176.1 $(M+1)^+$.

Acetophenone (90.1 mg, 42%): ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.92 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 68.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 2H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 197.8, 136.7, 132.8, 128.3, 128.0, 26.3; MS: Anal. Calcd. For C_8H_9O: 121.1, Found: 121.1 $(M+1)^+$.

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Supporting Information Available: Procedural and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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