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

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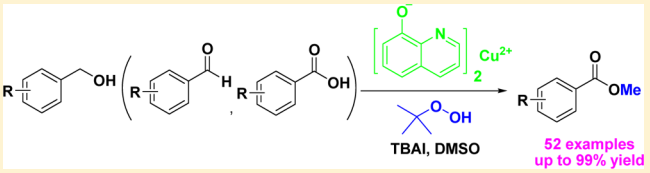
Supporting Information

ABSTRACT: The highly effective synthesis of methyl esters from benzylic alcohols, aldehydes, or acids via copper-catalyzed C−C cleavage from *tert*-butyl hydroperoxide is reported in this paper for the first time. Our protocol is easily accessible and practical, making it a possible supplement for the traditional way.



INTRODUCTION

It is well-known that esters are among the most important functional groups in chemistry. Among various types of esters, methyl esters frequently appear 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

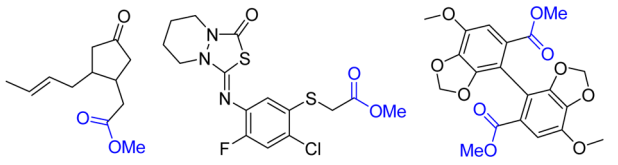
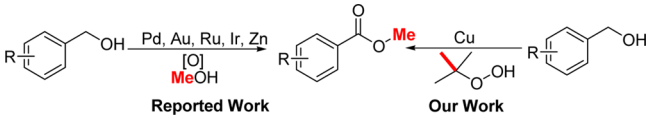


Figure 1. Representative organic compounds containing methyl ester moieties.

plant stress hormone, exhibiting anticancer activity on human cancer cells; fluthiacet-methyl (**B**)[4] is a postemergence herbicide mainly for control of certain annual broadleaf weeds in corn and soybeans; and biphenyldicarboxylate (**C**),[5] as a traditional Chinese medicine, exhibits antihapetotoxic (liver injury), anticonvulsive (cerebral protection), antitumor, anti-HIV, and antifungal activities.

Thus, substantial attention has been paid to approaches for acquiring methyl esters during the past several decades. Traditionally, methyl esters are prepared by the reaction of activated acid derivatives with methanol, which is a multistep process.[6] Since benzylic alcohols[7] are readily available, environmentally friendly, and simple to handle, they are usually employed as the substrates in the synthesis of methyl esters from methanol in many protocols. Recently, Beller and Lei independently reported some synthetically interesting Pd-catalyzed oxidative cross-esterifications 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 cross-esterification reactions of benzylic alcohols (Scheme 1).[9] In

Scheme 1. Strategies toward Methyl Esterification of Benzylic Alcohols



view of sustainable development in the future, low-cost, efficient metal catalysts need further investigation. With our ongoing interest in various cross-coupling reactions,[10] we describe our efforts on copper-catalyzed methyl esterification reactions with peroxides, which serve as both the oxidant and the source of the methyl group (Scheme 1). To the best of our knowledge, there have been few examples of copper-catalyzed direct esterification of benzylic alcohols in the absence of methanol to date. Furthermore, it was interesting to find that during the reaction the cleavage of C−C bonds occurs simultaneously. Actually, transition-metal-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.

RESULTS AND DISCUSSION

We began our investigation by examining the coupling of benzylic alcohol **1a** and *tert*-butyl hydroperoxide (TBHP) in the presence of a low-cost copper catalyst (Table 1, entry 1). However, no desired product was acquired. When tetrabutylammonium iodide (TBAI) was used as an additive, no reaction was observed (Table 1, entry 2). It was speculated that benzylic alcohols could not be oxidized in the current system.[13] Subsequently, a base was employed to assist the oxidation of

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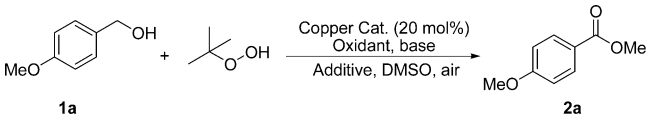
Table 1. Optimization of the Reaction Conditions for the Methyl Esterification of Benzylic Alcohol 1a[a]



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: **1a** (0.3 mmol), catalyst (0.06 mmol), oxidant (1.8 mmol), additive (0.12 mmol, 40 mol %), base (0.6 mmol, 2 equiv), solvent (2 mL), 120 °C, air, 24 h. [b]Based on **1a**. [c]DMF as the solvent. [d]TBHP (2.4 mmol). [e]Toluene as the solvent.

the benzylic alcohol, and KOH afforded a 27% yield of methyl 4-methoxybenzoate (**2a**) (Table 1, entry 3). Further optimization showed that the corresponding ester could be obtained in 79% yield when K_3PO_4 was used as the 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 di-*tert*-butyl peroxide (DTBP) or dicumyl peroxide (DCP) was used (Table 1, entries 11 and 12). Investigation of various solvents (Table 1, entries 13 and 14) showed that other solvents besides DMSO could hardly afford the ester. To our surprise, a 92% yield of the desired product **2a** was acquired when a larger 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 and 17). It can be seen that TBAI shows a key acceleration role in the methyl esterification. Actually, we also tried some other metals, including Fe, Ni, Co, and so on. However, their catalytic effects were very poor.

Under the optimized reaction conditions, various benzylic alcohol derivatives were examined, and related results are 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 yields of 70–92% when benzylic alcohols with the electron-donating methoxy group were used (Table 2, entries 1–4). For the methyl, isopropyl, and phenoxy groups, the desired esters **2e–g** were acquired in 74%, 61%, and 67% yield, respectively (Table 2, entries 5–7). It is noteworthy that an electron-withdrawing nitryl group gave a moderate yield of the corresponding ester **2h** (Table 2, entry 8).

During the methyl esterification of benzylic alcohols, the corresponding acids were detected as byproducts in the crude reaction mixtures by LC-MS, which suggested that the benzylic alcohol possibly was directly oxidized to the acid. In addition, we did not observe the corresponding aldehydes or any self-coupled products formed by reactions of the possible in situ-generated aldehydes and the unoxidized alcohols. After the successful application of the oxidative methyl esterification from benzylic alcohols, we tried to extend this methodology to aldehydes and carboxylic acids as substrates.[14] It was found that base was not necessary in the methyl esterification of aldehydes and that the amount of the oxidant could be reduced to 6 equiv. Subsequently, various aldehyde derivatives were examined, and representative results are listed in Table 3. Generally, it can be seen that the electronic and steric effects were not significant. In addition, substrates with electron-donating groups were superior to those with electron-withdrawing groups. Aldehydes substituted with an electron-donating group (methoxy) generated the methylation products in good to excellent yields under the optimized reaction conditions (Table 3, entries 1–6). The yield with 2-naphthaldehyde (96%) was better than that with 1-naphthaldehyde (72%) (Table 3, entries 7 and 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** and **4i** were obtained in satisfactory yields (Table 3, entries 12 and 13). It was observed that anthracene-10-carbaldehyde could give the desired ester **4j** in 70% yield using our system (Table 3, entry 14).

Compared with aldehydes, the corresponding acids are cheaper and more stable. At the same time, it was found that a smaller amount of TBHP (0.9 mmol) and a lower reaction temperature (100 °C) were suitable for the methyl esterification of acids. It is noteworthy that in this transformation, TBAI was not necessary. Thus, we can conclude that TBAI does show an acceleration role in the process of oxidation. Different substituted acids were subjected to the optimized conditions, as shown in Table 4. The results indicate that 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, acids with the strong electron-donating methoxy group generated the methylation products (**2a**, **2d**, and **6a–6c**) in good to excellent yields under the optimized reaction conditions. For the *tert*-butyl and methyl groups, the desired esters **6d** and **2e** were produced smoothly in 84% and 60% yield, respectively. Good yields were obtained when 1-naphthoic acid and 2-naphthoic acid were employed as the substrates (**4d** and **4e**). Substrates with a wide range of functional groups, including phenyl, benzoyl, ethanoyl, cyano, and nitro, all reacted smoothly under the optimized conditions (**2h**, **4g**, and **6e–6k**). 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 **6l**, **4h**, **6m**, and **6n** in moderate yields. 3-Hydroxy-2-naphthoic acid gave only an 18% yield of the corresponding product **6o** under the standard conditions. It is speculated that the hydroxyl group possibly is sensitive to oxidants. To our delight, 2-benzamidoacetic acid gave the

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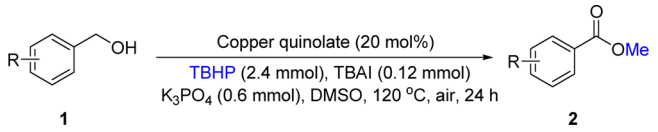
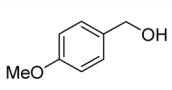
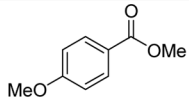
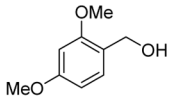
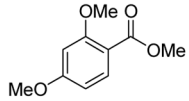
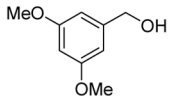
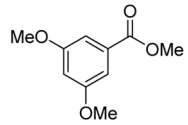
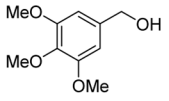
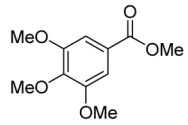
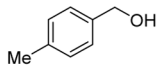
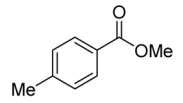
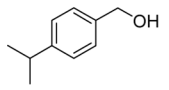
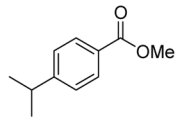
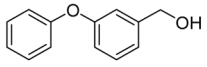
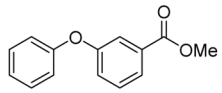
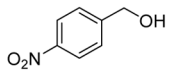
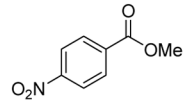
Table 2. Copper-Catalyzed Methyl Esterification of Various Benzylic Alcohols[a]



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]Based on benzylic alcohol.

desired ester **6p** in 73% yield without any protections. 2,2′-Dithiodibenzoic acid and adamantane-1-carboxylic acid did not afford the corresponding esters **6q** and **6r** under the standard conditions.

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

Further investigations of the mechanism were performed (Scheme 4). The reaction of sodium 4-methoxybenzoate with TBHP did not generate methyl 4-methoxybenzoate, indicating that no 4-methoxybenzoate anion and methyl cation are 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, a 96% yield of methyl 4-methoxybenzoate was obtained. ^{1}H NMR analysis showed that the product did not contain deuterium. This is an indirect proof that the methyl group of the 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 a great amount of acetophenone (**13**) was also isolated by column chromatography. This is a powerful proof to demonstrate that the methyl group of the product came from the oxidant. We believed that *tert*-butyl naphthalene-1-carboperoxoate may exist in the reaction system as an intermediate. To prove this hypothesis, this peroxide was synthesized and employed as the substrate for

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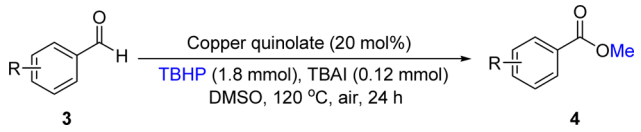
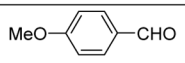
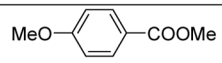
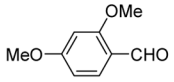
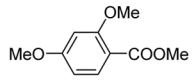
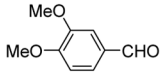
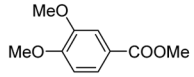
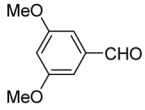
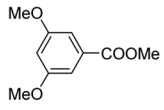
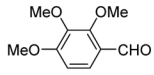
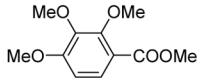
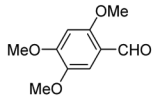
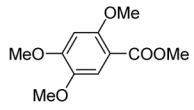
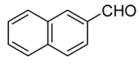
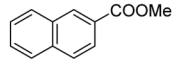
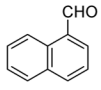
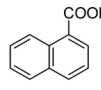
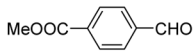
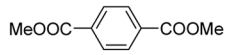
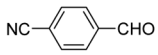
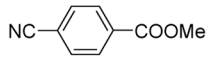
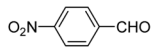
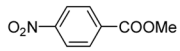
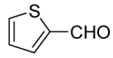
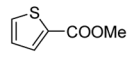
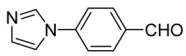
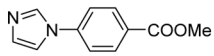
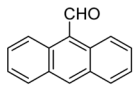
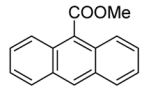
Table 3. Copper-Catalyzed Methyl Esterification of Various Aldehydes[a]



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 (0.3 mmol), copper quinolate (0.06 mmol), TBHP (1.8 mmol, 70% aqueous solution), TBAI (0.12 mmol), DMSO (2 mL), 120 °C, air, 24 h. [b]Based on aldehyde.

the reaction. As expected, methyl 1-naphthoate (**4e**) was obtained in 87% yield.[16]

On the basis of the above results and the literature, the tentative mechanism illustrated in Scheme 5 is proposed. Initially, TBHP decomposes to generate the *tert*-butoxyl and *tert*-butylperoxyl radicals in the presence of the copper catalyst.[17] Next, facile unimolecular decomposition of *tert*-butoxyl radical to acetone and a methyl radical occurs.[18] The benzylic alcohol is directly oxidized to benzoic acid in the presence of the oxidant and base, while the aldehyde is easily oxidized to benzoic acid using only the oxidant. Subsequently, the acyloxyl radical is generated from benzoic acid by the reaction with *tert*-butoxyl or *tert*-butylperoxyl radical. Finally, coupling of the acyloxyl and methyl radicals gives the desired ester.

■ CONCLUSIONS

In summary, we have successfully developed a novel, effective, and direct method of copper-catalyzed methyl esterification of benzylic alcohols, aldehydes, or acids via a C−C cleavage

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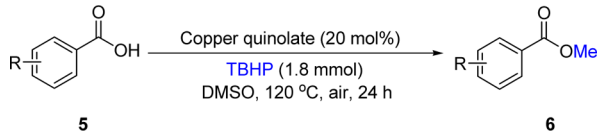
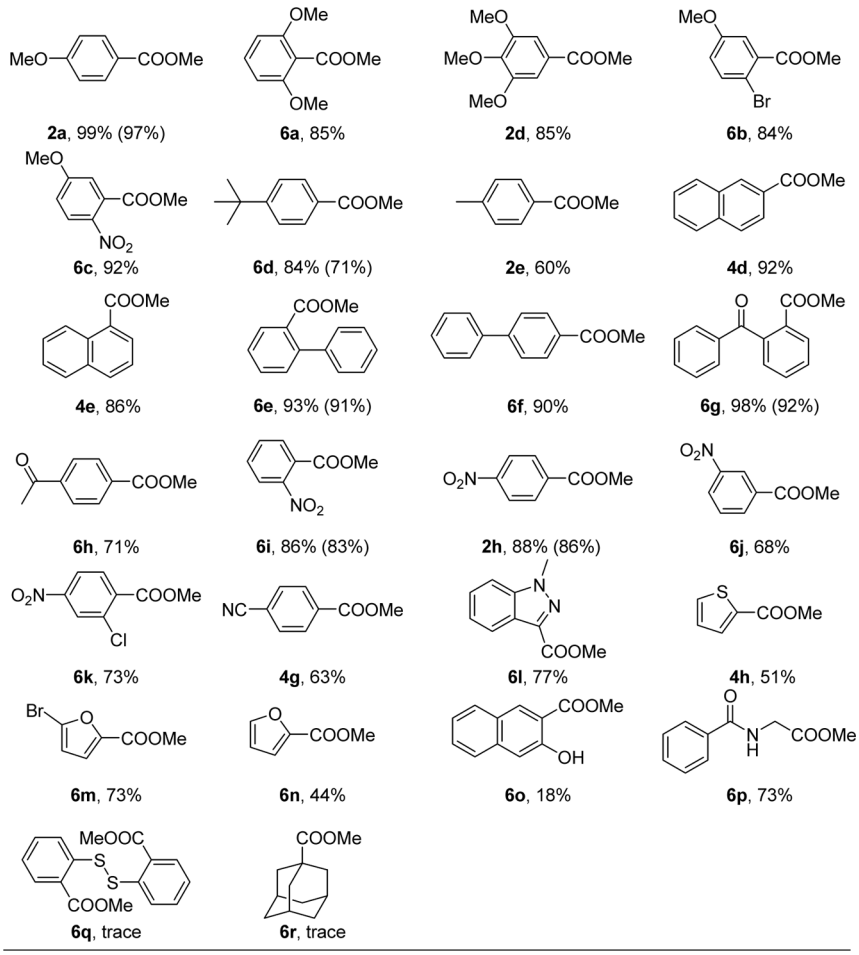
Table 4. Copper-Catalyzed Methyl Esterification of Various Acids[a]

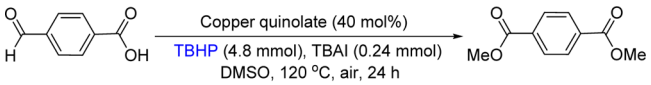


5 6



[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 yields in parentheses represent the results when a smaller amount of TBHP (0.9 mmol) and a lower reaction temperature (100 °C) were employed.

Scheme 2. Copper-Catalyzed Methyl Esterification of 4-Formylbenzoic Acid



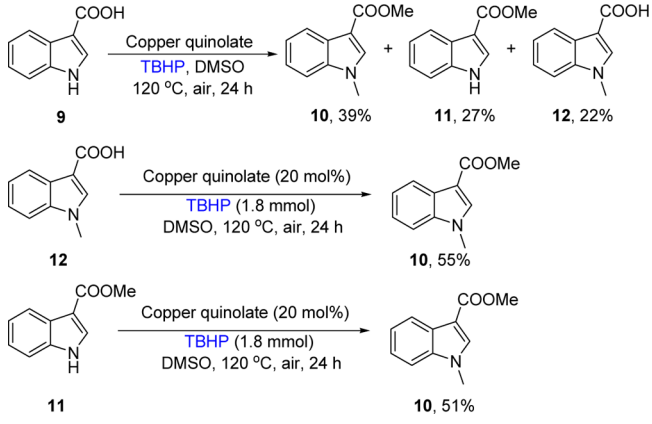
7 8, 60%

reaction. It is noteworthy that in this transformation, TBHP serves not only as the oxidant but also as the source of the methyl group. In general, the desired methyl esters were obtained in good to excellent yields. Thus, this catalytic protocol can tolerate a wide range of substrates and represents a practical and low-cost method for the preparation of methyl ester-based molecules. It could serve as a supplement for the traditional way in some cases. Further investigations of its applications are currently underway.

EXPERIMENTAL SECTION

General Experimental. All manipulations were carried out under an atmosphere of air. Benzylic alcohols, aldehydes, acids, *tert*-butyl

Scheme 3. Copper-Catalyzed Methylation or Methyl Esterification of 1*H*-Indole-3-Carboxylic Acid or Its Methyl Ester



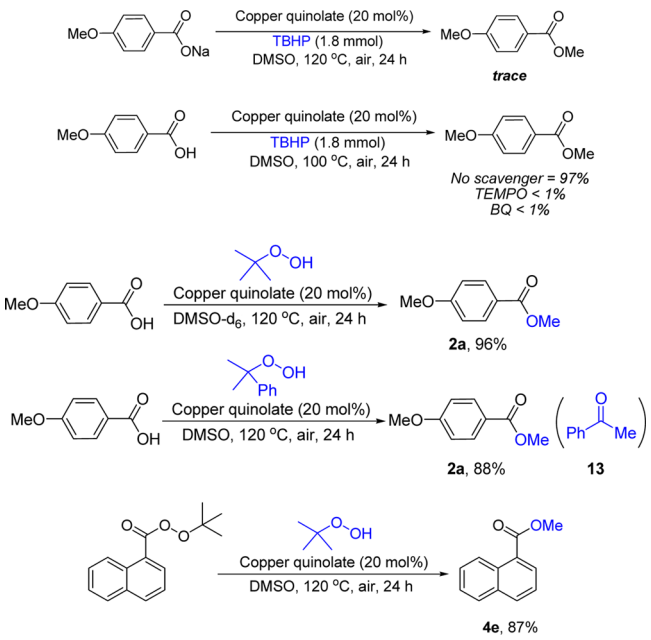
9 10, 39% 11, 27% 12, 22%

12 10, 55%

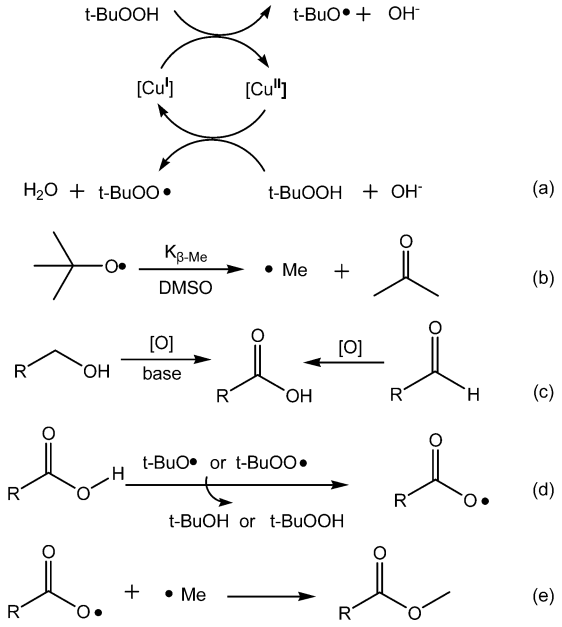
11 10, 51%

dx.doi.org/10.1021/jo4016387 | J. Org. Chem. 2013, 78, 9898−9905

Scheme 4. Control Experiments and Effect of Radical Inhibitors



Scheme 5. Possible Mechanism



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 reaction. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) data were recorded on 400 MHz spectrometers using $CDCl_3$ as the solvent. Chemical shifts (δ) are reported in parts per million and coupling constants (J) in hertz. ^{1}H NMR spectra were recorded with tetramethylsilane (δ = 0.00 ppm) as an internal reference; ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.00 ppm) as an internal reference.

General Procedure for Copper-Catalyzed Methyl Esterification of Benzylic Alcohols. 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, and the reaction mixture was heated in an oil bath at 120 °C for 24 h. The reaction was quenched with a saturated solution of Na_2SO_3 (for removal of excess TBHP), and the mixture was extracted with ethyl acetate. The organic solvent was removed under vacuum, and purification by chromatography on a silica gel column using a mixture of petroleum ether and ethyl acetate afforded the desired product.

General Procedure for Copper-Catalyzed Methyl Esterification of Aldehydes. 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, and the reaction mixture was heated in an oil bath at 120 °C for 24 h. The reaction was quenched with a saturated solution of Na_2SO_3 (for removal of excess TBHP), and the mixture was extracted with ethyl acetate. The organic solvent was removed under vacuum, and purification by chromatography on a silica gel column using a mixture of petroleum ether and ethyl acetate afforded the desired product.

General Procedure for Copper-Catalyzed Methyl Esterification of Acids. 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, and the reaction mixture was heated in an oil bath at 100−120 °C for 24 h. The reaction was quenched with a saturated solution of Na_2SO_3 (for removal of excess TBHP), and the mixture was extracted with ethyl acetate. The organic solvent was removed under vacuum, and purification by chromatography on a silica gel column 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 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 167.1, 154.2, 129.6, 127.7, 126.4, 51.9, 34.2, 30.8, 23.6; MS (m/z) calcd for $C_{11}H_{15}O_2$ 179.1, found 179.1 (M + H)$^+$.

Methyl 3,5-Dimethoxybenzoate. (51.3 mg, 96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 166.7, 160.5, 131.9, 107.0, 105.6, 55.4, 52.1; MS (m/z) calcd for $C_{10}H_{13}O_4$ 197.1, found 197.1 (M + H)$^+$.

Methyl 4-Nitrobenzoate. (47.8 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 165.4, 150.7, 135.7, 130.9, 123.7, 53.1; MS (m/z) calcd for $C_8H_8NO_4$ 182.0, found 182.0 (M + H)$^+$.

Methyl 4-Methylbenzoate. (33.3 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 166.1, 142.5, 128.5, 128.0, 126.4, 50.9, 20.6; MS (m/z) calcd for $C_9H_{11}O_2$ 151.1, found 151.1 (M + H)$^+$.

Methyl 3-Phenoxybenzoate. (45.9 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 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 (m/z) calcd for $C_{14}H_{13}O_3$ 229.1, found 229.1 (M + H)$^+$.

Methyl 2,4-Dimethoxybenzoate. (52.3 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 166.0, 164.2, 161.2, 133.7, 112.0, 104.5, 98.8, 55.8, 55.3, 51.6; MS (m/z) calcd for $C_{10}H_{13}O_4$ 197.1, found 197.1 (M + H)$^+$.

Methyl 3,4,5-Trimethoxybenzoate. (57.7 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 2H), 3.85 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 153.1, 142.2, 125.3, 106.9, 61.1, 56.4, 52.4; MS (m/z) calcd for $C_{11}H_{15}O_5$ 227.1, found 227.1 (M + H)$^+$.

Methyl 4-Methoxybenzoate. (49.3 mg, 99%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 167.0, 163.5, 131.8, 122.8, 113.8, 55.6, 52.0; MS (m/z) calcd for $C_9H_{11}O_3$ 167.1, found 167.1 (M + H)$^+$.

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Dimethyl Terephthalate. (34.9 mg, 60%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 4H), 3.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 134.1, 129.7, 110.0, 52.7; MS (m/z) calcd for $C_{10}H_{11}O_4$ 195.1, found 195.1 $(M + H)^+$.

Methyl 4-Cyanobenzoate. (34.3 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 165.3, 133.8, 132.2, 130.0, 117.9, 116.3, 52.7; MS (m/z) calcd for $C_9H_8NO_2$ 162.1, found 162.1 $(M + H)^+$.

Methyl 2-Naphthoate. (53.6 mg, 96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 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 (m/z) calcd for $C_{12}H_{11}O_2$ 187.1, found 187.1 $(M + H)^+$.

Methyl Thiophene-2-carboxylate. (21.7 mg, 51%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 162.9, 133.7, 133.6, 132.6, 128.0, 52.4; MS (m/z) calcd for $C_6H_7SO_2$ 143.0, found 143.0 $(M + H)^+$.

Methyl 3,4-Dimethoxybenzoate. (35.9 mg, 61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 167.1, 153.1, 148.8, 123.8, 122.8, 112.1, 110.4, 56.2, 52.2; MS (m/z) calcd for $C_{10}H_{13}O_4$ 197.1, found 197.1 $(M + H)^+$.

Methyl 1-Naphthoate. (40.2 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 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 (m/z) calcd for $C_{12}H_{11}O_2$ 187.1, found 187.1 $(M + H)^+$.

Methyl Anthracene-10-carboxylate. (49.6 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 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 (m/z) calcd for $C_{16}H_{13}O_2$ 237.1, found 237.1 $(M + H)^+$.

Methyl 2,3,4-Trimethoxybenzoate. (67.8 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 166.2, 157.3, 154.8, 143.1, 127.1, 124.4, 107.1, 62.0, 61.2, 56.2, 52.1; MS (m/z) calcd for $C_{11}H_{15}O_5$ 227.1, found 227.1 $(M + H)^+$.

Methyl 2,4,5-Trimethoxybenzoate. (57.7 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 165.9, 155.5, 153.4, 142.3, 114.1, 110.2, 97.4, 56.8, 56.2, 55.9, 51.7; MS (m/z) calcd for $C_{11}H_{15}O_5$ 227.1, found 227.1 $(M + H)^+$.

Methyl 4-(1H-Imidazol-1-yl)benzoate. (38.8 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 165.9, 140.5, 135.3, 131.4, 130.9, 128.8, 120.4, 117.6, 52.3; MS (m/z) calcd for $C_{11}H_{11}N_2O_2$ 203.1, found 203.1 $(M + H)^+$.

Methyl 2-Nitrobenzoate. (46.7 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 166.1, 133.2, 132.0, 130.0, 129.3, 127.7, 124.1, 53.5; MS (m/z) calcd for $C_8H_8NO_4$ 182.0, found 182.0 $(M + H)^+$.

Methyl 4-tert-Butylbenzoate. (48.4 mg, 84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 167.3, 156.7, 129.6, 127.6, 125.5, 52.2, 32.3, 31.3; MS (m/z) calcd for $C_{12}H_{17}O_2$ 193.1, found 193.1 $(M + H)^+$.

Methyl 3-Nitrobenzoate. (36.9 mg, 68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 165.1, 148.4, 135.5, 132.0, 129.9, 127.6, 124.8, 53.0; MS (m/z) calcd for $C_8H_8NO_4$ 182.1, found 182.1 $(M + H)^+$.

Methyl 2-Phenylbenzoate. (59.2 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 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 (m/z) calcd for $C_{14}H_{13}O_2$ 213.1, found 213.1 $(M + H)^+$.

Methyl 2-Benzoylbenzoate. (70.6 mg, 98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 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 (m/z) calcd for $C_{15}H_{13}O_3$ 241.1, found 241.1 $(M + H)^+$.

Methyl 5-Bromofuran-2-carboxylate. (44.7 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 158.2, 146.3, 127.7, 120.3, 114.1, 52.3; MS (m/z) calcd for $C_6H_6BrO_3$ 205.0, found 205.0 $(M + H)^+$.

Methyl 4-Acetylbenzoate. (37.9 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 197.4, 166.1, 140.1, 133.8, 129.7, 128.1, 52.4, 26.8; MS (m/z) calcd for $C_{10}H_{11}O_3$ 179.1, found 179.1 $(M + H)^+$.

Methyl 2,6-Dimethoxybenzoate. (50.0 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 167.3, 157.5, 131.3, 113.1, 104.1, 56.2, 52.7; MS (m/z) calcd for $C_{10}H_{13}O_4$ 197.1, found 197.1 $(M + H)^+$.

Methyl 5-Methoxy-2-nitrobenzoate. (58.3 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 166.8, 163.6, 140.0, 131.4, 126.9, 115.9, 114.3, 56.4, 53.6; MS (m/z) calcd for $C_9H_{10}NO_5$ 212.1, found 212.1 $(M + H)^+$.

Methyl 3-Hydroxy-2-naphthoate. (10.9 mg, 18%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 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 (m/z) calcd for $C_{12}H_{11}O_3$ 203.1, found 203.1 $(M + H)^+$.

Methyl 2-Bromo-5-methoxybenzoate. (61.5 mg, 84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 166.7, 158.7, 135.2, 132.8, 119.2, 116.4, 112.1, 55.8, 528; MS (m/z) calcd for $C_9H_{10}BrO_3$ 245.0, found 245.0 $(M + H)^+$.

Methyl 2-Chloro-4-nitrobenzoate. (47.1 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 164.8, 149.6, 135.9, 135.0, 132.2, 126.2, 121.6, 53.3; MS (m/z) calcd for $C_8H_7ClNO_4$ 216.0, found 216.0 $(M + H)^+$.

Methyl 1-Methyl-1H-indazole-3-carboxylate. (43.9 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 163.2, 141.1, 134.5, 127.1, 123.8, 123.3, 122.2, 109.7, 52.2, 36.6; MS (m/z) calcd for $C_{10}H_{11}N_2O_2$ 191.1, found 191.1 $(M + H)^+$.

Methyl 4-Phenylbenzoate. (57.3 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 167.2, 145.8, 140.2, 130.3, 129.2, 129.1, 128.4, 127.5, 127.3, 52.4; MS (m/z) calcd for $C_{14}H_{13}O_2$ 213.1, found 213.1 $(M + H)^+$.

Methyl Furan-2-carboxylate. (16.6 mg, 44%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 159.4, 146.5, 144.8, 118.2, 112.1, 52.2; MS (m/z) calcd for $C_6H_7O_3$ 127.1, found 127.1 $(M + H)^+$.

Methyl 2-Benzamidoacetate. (42.3 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 170.8, 167.9, 133.8, 132.0,

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128.8, 127.3, 52.6, 41.9; MS (m/z) calcd for $C_{10}H_{12}NO_3$ 194.1, found 194.1 $(M + H)^+$.

Methyl 1-Methyl-1H-indole-3-carboxylate. (31.2 mg, 55%); ^1H NMR (400 MHz, $CDCl_3$) δ 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 165.7, 137.4, 135.4, 126.8, 123.0, 122.1, 121.9, 110.0, 107.1, 51.2, 33.7; MS (m/z) calcd for $C_{11}H_{12}NO_2$ 190.1, found 190.1 $(M + H)^+$.

Methyl 1H-Indole-3-carboxylate. (14.2 mg, 27%); ^1H NMR (400 MHz, $CDCl_3$) δ 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 165.2, 136.8, 132.9, 126.1, 122.8, 121.7, 120.8, 112.8, 106.7, 51.1; MS (m/z) calcd for $C_{10}H_{10}NO_2$ 176.1, found 176.1 $(M + H)^+$.

1-Methyl-1H-Indole-3-carboxylic Acid. (11.6 mg, 22%); ^1H NMR (400 MHz, $CDCl_3$) δ 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 170.8, 142.1, 141.2, 131.5, 127.3, 126.4, 125.8, 115.7, 111.3, 38.1; MS (m/z) calcd for $C_{10}H_{10}NO_2$ 176.1, found 176.1 $(M + H)^+$.

Acetophenone. (90.1 mg, 42%); ^1H NMR (400 MHz, $CDCl_3$) δ 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 197.8, 136.7, 132.8, 128.3, 128.0, 26.3; MS (m/z) calcd for C_8H_9O 121.1, found 121.1 $(M + H)^+$.

■ ASSOCIATED CONTENT

Supporting Information

NMR spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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