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Palladium-catalyzed, Copper(I)-promoted Methoxycarbonylation of Arylboronic Acids with O-methyl S-aryl thiocarbonates

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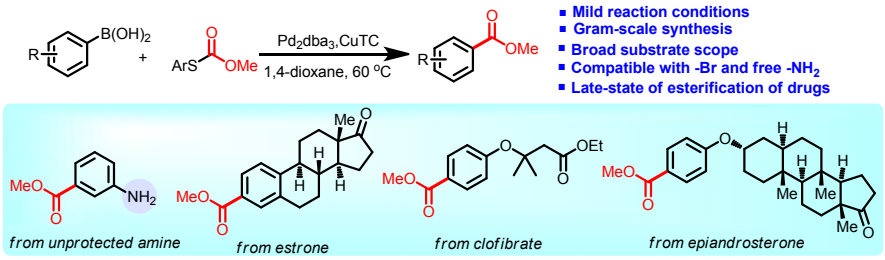


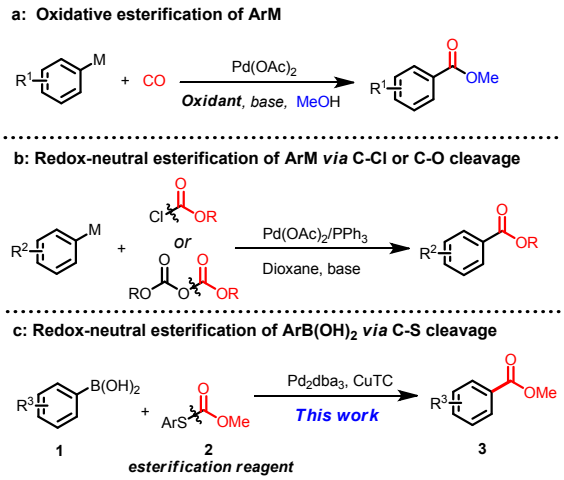
ABSTRACT: Here we report O-methyl S-aryl thiocarbonates as a versatile esterification reagent for palladium-catalyzed methoxycarbonylation of arylboronic acid in the presence of copper(I) thiophene-2-carboxylate (CuTC). The reaction condition is mild, and a variety of substituents including sensitive -Cl, -Br, and free -NH_2 could be tolerated. Further applications in the late-stage esterification of some pharmaceutical drugs demonstrate the broad utility of this method.

INTRODUCTION

Aryl carboxylate esters are important structural motifs found in pharmaceuticals, agrochemicals, and organic materials.[1] Many synthetic methods have been developed, including traditional condensation of carboxylic acids with alcohol, substitution of carbonate derivatives with Grignard reagents,[2] and carbonylation of aryl (pseudo)halides with CO.[3] Recently, Pd-catalyzed oxidative esterification from broadly accessible organometallic reagent has become a powerful alternative to traditional synthetic methods.[4] Conventionally, oxidative esterifications initiate the catalytic circle from Pd(II), and terminate with Pd(0) species. Thus stoichiometric amount external oxidant are required to regenerate the Pd(II) for catalytic turnover (Scheme 1a). In 2010, Lei developed a novel palladium-catalyzed aerobic oxidative carbonylation of arylboronate esters by using air as the sole oxidant.[5] Recently, Ge and coworkers successfully applied potassium oxalate monoesters in the esterification of potassium phenyltrifluoroborate in the present of 2 equiv. of $K_2S_2O_8$.[6] To obviate the need for external oxidant, redox-neutral coupling

of Ar–M with internally oxidative reagent would be an appealing strategy. However, this synthetic strategy is plagued by the limited repertoire of compatible esterification reagent. Jousseaume and Deng reported the Pd(0)-catalyzed oxidant-free esterification of arylorganotins and arylboronic acids with chloroformate (Scheme 1b).[7,8] Wu elegantly utilized the dialkyldicarbonates as esterification agents to furnish the arylboronic acids.[9] Recently, Kakiuchi, [10] Shi,[11] and Xu[12] reported Ru- and Pd-catalyzed C–H esterification with chloroformate and Boc_2O. Although these protocols are often effective, both chloroformate and dialkyldicarbonate are very reactive and susceptible to nucleophiles, such as free amines. Thus, the development of a practical and versatile esterification reagent would be highly desirable.

Scheme 1. Esterification of Organometallic Reagent



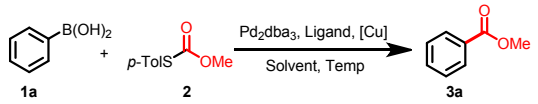
Thioesters are versatile building blocks in organic synthesis. Due to the feasibility of oxidative addition into the C(O)–S bond of thioester, transition-metal-catalyzed C–S bond activations of thioester have being one of the most important tools for the construction of carbon-carbon and carbon-heteroatom bonds.[13] For example, palladium-catalyzed C-acylations of organozinc and organoboronic reagents with thioester, namely Fukuyama and Liebeskind–Srogl reaction, have been widely applied in the ketone synthesis.[14] Fukuzawa reported the palladium-catalyzed C-formylation of arylzincs by utilizing the S-phenyl thioformate as a versatile formylating agent.[15] Very recently, Kambe, [16] Hosoya, [17] Sanford[18] reported Pd-, Rh-, Ni-catalyzed decarbonylative thioetherification and borylation of aromatic thioesters. Prompted by these reports, we questioned whether we could realize the palladium-catalyzed C-esterification of arylmetallic compounds with S-aryl thiocarbonate. Boronic acids are low toxic, relatively stable to air and moisture, commercially available, and broadly tolerant for functional group. Considering these practical advantages, we reported here the palladium-catalyzed methoxycarbonylation of aryl boronic acids with O-methyl S-aryl thiocarbonate under mild and redox-neutral conditions (Scheme 1c).

RESULTS AND DISCUSSION

We commenced our studies by treating aryl boronic acids **1a**, O-methyl S-*p*-toluenyl thiocarbonate **2** with 5 mol% $Pd_2(dba)_3$, 0.16 mmol CuTc, 20 mol% PCy_3 at 60 °C (Table 1). Gratifyingly, methoxycarbonylation of aryl boronic acids **1** occurred smoothly, giving the desired product **3a** in 10% yields (entry 1). Further screening of various phosphine ligands showed that PPh_3 and TFP could also promote the reaction, and TFP was the optimal choice (entry 2-5). Cu salts are proposed to form strong Cu–S bound with thioester, thus facilitating the transmetalation in Liebeskind-Srogl cross-coupling reaction. However, the yields decreased when we replaced CuTC with other Cu salts (entries 6-8). Lowering or increasing the reaction temperature lead to the decreased yield of esterated products (entries 9-11). The yield could be further improved to 80% by using 1,4-dioxane as the reaction solvent (Table 1, entry 12-17). For further investigation the effect of

different S-substituents, we screened a variety of electronically and sterically diverse O-methyl S-phenyl thiocarbonates, and found O-methyl S-*p*-toluenyl thiocarbonate **2** was the optimal esterification agent (see supporting information).

Table 1.Optimization of the Reaction Conditions[a]



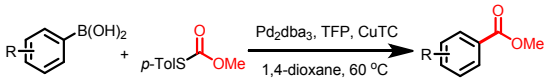
1a 2 3a

Entry	Ligand	[Cu]	Temp/°C	Solvent	Yield/%[c]
1	PCy_3	CuTC	60	THF	10
2	PPh_3	CuTC	60	THF	47
3	TFP	CuTC	60	THF	50
4	dppe	CuTC	60	THF	trace
5	Johnphos	CuTC	60	THF	18
6	TFP	CuOAC	60	THF	24
7	TFP	CuMeSal	60	THF	29
8	TFP	CuCl	60	THF	trace
9	TFP	CuTC	rt	THF	22
10	TFP	CuTC	40	THF	45
11	TFP	CuTC	80	THF	40
12	TFP	CuTC	60	Toluene	17
13	TFP	CuTC	60	DCE	15
14	TFP	CuTC	60	Acetonitrile	21
15	TFP	CuTC	60	DMSO	9
16	TFP	CuTC	60	Dioxane	75
17[b]	TFP	CuTC	60	Dioxane	80

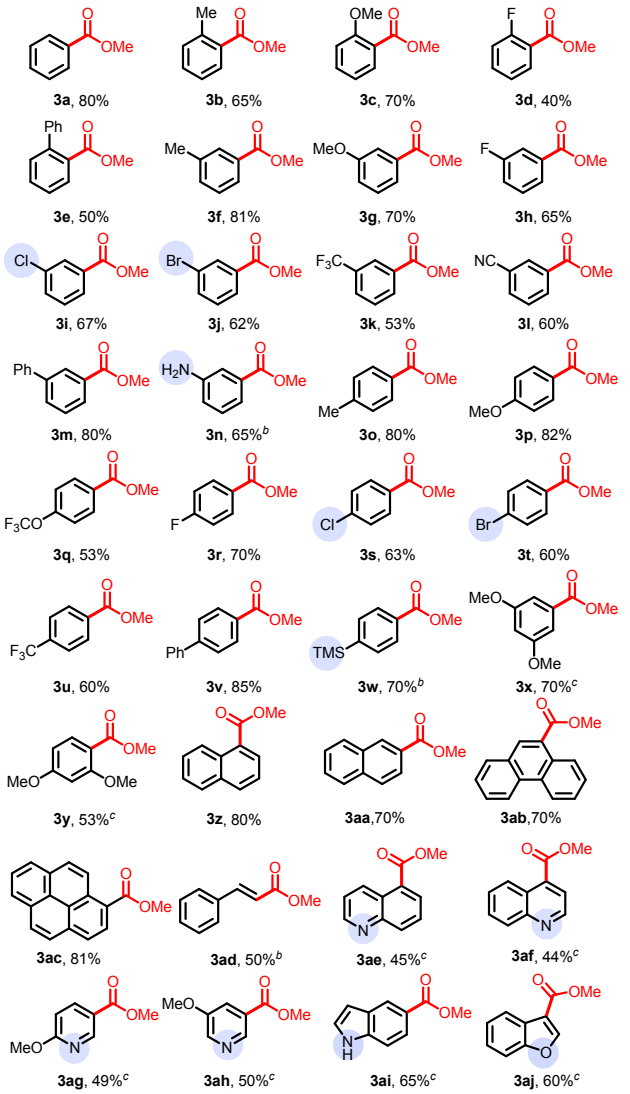
[a] Reaction conditions: **1a** (0.12 mmol), **2** (0.1 mmol), $Pd_2(dba)_3$ (5 mol%), Ligand (20 mol%), [Cu] (1.6 equiv.), Solvent (1 mL), temp, N_2, 16 h. TFP = Tri(2-furyl)phosphine. dppe = 1,2-Bis(diphenylphosphino)ethane, JohnPhos = (2-biphenyl)di-tert-butylphosphine.[b]**1a** (0.1 mmol), **2** (0.12 mmol). [c]The yield was determined by ^1H NMR analysis of crude product using CH_2Br_2 as internal standard.

With the optimized reaction conditions in hand, we examined the scope of various aryl boronic acids. As shown in Table 2, under the optimized conditions (5 mol% $Pd_2(dba)_3$, 20 mol% TFP, 0.16 mmol CuTc, 60 °C), the methoxycarbonylation of aryl boronic acid **1** with esterification agent **2** appeared to be quite general with respect to the substituents. Aryl boronic acid bearing electron-donating and -withdrawing groups (-Me, -OMe, $-OCF_3$, -Ph, -F, -Cl, -Br, -CN, $-CF_3$) were smoothly esterificated, giving the desired product **3a-3w** in moderate to good yields. Due to the mild and base-free reaction conditions, very sensitive -Br (**3j**, **3t**) and -TMS (**3w**) could be tolerated in the presence of Pd(0), thus offering additional opportunity for further functionalization. 3,5-, 2,4-dimethoxy phenylboronic acid gave the corresponding disubstituted methyl benzoate **3x**

Table 2. Substrate Scope of Arylboronic Acids[a]



1a-1aj 2 3a-3aj



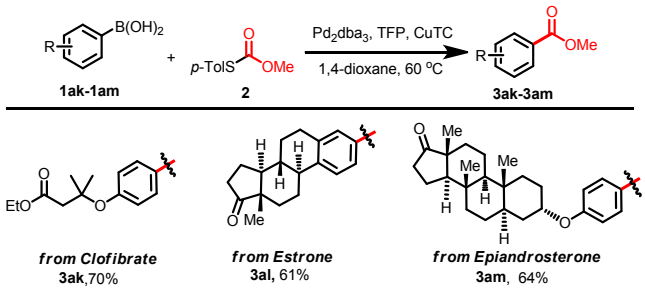
[a]Arylboronic acid **1** (0.1 mmol), **2** (0.12 mmol), $Pd_2(dba)_3$ (5 mol%), TFP (20 mol%), CuTC (0.16 mmol), 1,4-dioxane (1 mL), 60 °C, N_2,16 h. [b]**2** (0.2 mmol). [c] **2** (0.15 mmol).

and **3y** in 70% and 53% yields, respectively. It is worth noting that the substrates containing unprotected amine (**3n**, **3ai**) could be tolerated with the esterification reagents **2**. For polycyclic arene substrates, including naphthyl, phenanthrenyl, and pyrenylboronic acid, esterificated products **3z-3ac** were obtained in yields of 70-80%. When alkenyl boronic acid **1ad**

was employed in the reaction, the methyl cinnamate **3ad** could be obtained in 50% yield. To our delight, the protocol could be extended to heterocycle compounds, including quinolone, pyridine, unprotected indole, and benzofuran, giving the esterated products (**3ae-3aj**) in 44-65% yields.

To demonstrate the broad utility of this method, we further applied this protocol in the late-stage esterification of some drugs and bioactive molecules, including estrone, clofibrate, and epiandrosterone, furnishing the corresponding derivatives **3ak-3am** in 61-70% yields (Table 3).

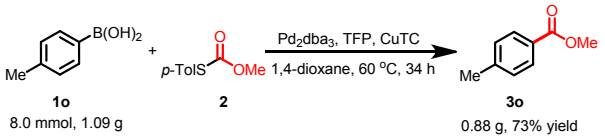
Table 3. Late-stage Esterification of Drugs Molecules[a]



[a] Reaction conditions: Arylboronic acid **1** (0.1 mmol), **2** (0.12 mmol), $Pd_2(dba)_3$ (5 mol%), TFP (20 mol%), CuTC (0.16 mmol), 1,4-dioxane (1 mL), 60 °C, N_2, 16 h.

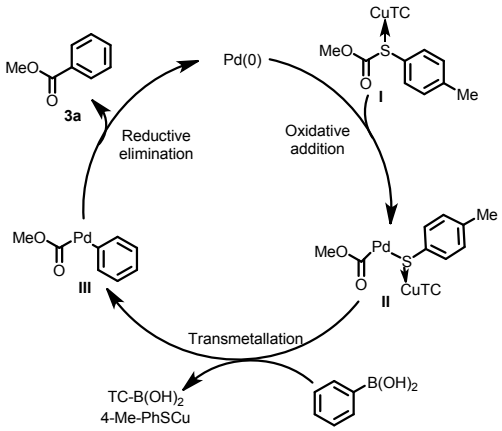
To illustrate the feasibility of this transformation for gram-scale reaction, we carried out the reaction of substrate **1o** with **2** on a 8.0 mmol scale. The desired product **3o** was isolated in 73% yields (Scheme 2).

Scheme 2. Gram-scale Synthesis



Based on the previous reports,[13,14d] a plausible mechanism for the methoxycarbonylation of aryl boronic acid is depicted in Scheme 3. First, O-methyl S-*p*-toluenyl thiocarbonate **2** coordinated with CuTC, forming the CuTC-bound thiolester complex **I**. Then palladium species **II** was formed by oxidative addition of Pd(0) into C(O)–S bond of thiolester. The coordinated copper salts were proposed to act as an activator to enhance the reactivity of **II** in the cross coupling. The subsequent transmetallation of arylboronic acid with intermediate **II** afforded the complex **III,** which then underwent the reductive elimination to furnish the final product **3a** with the regeneration of Pd(0) species.

Scheme 3. Possible Mechanism



CONCLUSIONS

In summary, we developed a palladium-catalyzed, copper-promoted methoxycarbonylation of aryl boronic acid with O-methyl S-*p*-toluenyl thiocarbonate. The reaction condition was mild and the substrate scope was broad. A variety of substituents including sensitive -Cl, -Br, and free -NH_2 groups could be tolerated. The protocol could also be applied to the late-stage esterification of some drugs, illustrating the broad utility of this method.

EXPERIMENTAL SECTION

General Information.

All commercial reagents were purchased from TCI, Sigma-Aldrich, Adamas-beta, and Energy Chemical of the highest purity grade. They were used without further purification unless specified. ^1H and ^{13}C NMR spectra were

recorded on Bruker AVANCE III 400, Bruker AVANCE III 500 instruments. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal. EI-double focus magnetic-sector high resolution MS (EI-DFS-HRMS) were recorded on a DFS-Thermofischer instrument at the Center for Mass Spectrometry, Shanghai Institute of Material Medica. S-*p*-toluenyl thiocarbonate **2**[19], **1ak**[20], **1al**[21], **1am**[20] are known products and synthesized according to the literature.

General Procedure for Palladium-Catalyzed Methoxycarbonylation.

To a 25 mL sealed tube was added substrates **1a** (0.1 mmol), Pd_2dba_3 (4.6 mg, 0.005 mmol, 5 mol%), CuTC (30.5 mg, 0.16 mmol, 1.6 equiv.), **2** (21.8 mg, 0.12 mmol, 1.2 equiv.) and 1,4-dioxane (1 mL). The reaction vessel was purged with nitrogen three times. Then the tube was placed in a preheated oil bath at 60 °C for 16 h. Upon completion, EtOAc was added to dilute the mixture and washed with $NH_3 \cdot H_2O$ and saturated NaCl (aq). The organic fraction was dried over anhydrous Na_2SO_4. Then the solvent was evaporated and the residue was purified by a silica gel packed flash chromatography column using ethyl acetate/hexane as the eluent.

Procedure for Gram-scale Synthesis

To a 250 mL round-bottomed flask was added substrates **1o** (1.09 g, 8 mmol), Pd_2dba_3 (0.37 g, 0.4 mmol, 5 mol%), CuTC (2.44 g, 12.8 mmol, 1.6 equiv.), 1,4-dioxane (80 mL) and **2** (1.75 g, 9.6 mmol, 1.2 equiv.). The reaction vessel was purged with nitrogen three times. Then the flask was placed in a preheated oil bath at 60 °C for 34 h. Upon completion, EtOAc was added to dilute the mixture and washed with $NH_3 \cdot H_2O$ and saturated NaCl (aq). The organic fraction was dried over anhydrous Na_2SO_4 The solvent was evaporated and the residue was purified by a silica gel packed flash chromatography column using ethyl acetate/hexane as the eluent.

*Methyl benzoate (**3a**)*.[22] Following the general procedure, the reaction was conducted with **1a** (12.2 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (10.9 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.00 (m, 2H), 7.59-7.48 (m, 1H), 7.44-7.40 (m, 2H), 3.90 (s, 3H).

*Methyl 2-methylbenzoate (**3b**)*.[23] Following the general procedure, the reaction was conducted with **1b** (13.6 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a colorless oil (9.8 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 8.0, 1.6 Hz, 1H), 7.42 (td, J = 8.0, 1.6 Hz, 1H), 7.33-7.18 (m, 2H), 3.92 (s, 3H), 2.63 (s, 3H).

*Methyl 2-methoxybenzoate (**3c**)*.[22] Following the general procedure, the reaction was conducted with **1c** (15.2 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (11.6 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 8.0, 2.0 Hz, 1H), 7.51-7.47 (m, 1H), 7.06-6.92 (m, 2H), 3.93 (s, 3H), 3.91 (s, 3H).

*Methyl 2-fluorobenzoate (**3d**)*. [32] Following the general procedure, the reaction was conducted with **1d** (14.0 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (6.2 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.92 (m, 1H), 7.59-7.43 (m, 1H), 7.25-7.07 (m, 2H), 3.94 (s, 3H).

*Methyl (1,1'-biphenyl)-2-carboxylate (**3e**).*[24] Following the general procedure, the reaction was conducted with **1e** (19.8 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (10.6 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.56 (td, *J* = 7.6, 1.6 Hz, 1H), 7.48-7.37 (m, 5H), 7.37-7.32 (m, 2H), 3.66 (s, 3H).

*1-Methoxycarbonyl-3-methylbenzene (**3f**).*[23] Following the general procedure, the reaction was conducted with **1f** (13.6 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (12.2 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.79 (m, 2H), 7.46-7.18 (m, 2H), 3.93 (s, 3H), 2.47-2.34 (m, 3H).

*Methyl 3-methoxybenzoate (**3g**).*[23] Following the general procedure, the reaction was conducted with **1g** (15.2 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (11.6 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.58 (dd, *J* = 2.8, 1.6 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.12 (ddd, *J* = 8.4, 2.8, 1.2 Hz, 1H), 3.94 (s, 3H), 3.88 (s, 3H).

*Methyl 3-fluorobenzoate (**3h**).*[25] Following the general procedure, the reaction was conducted with **1h** (14.0 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (10.1 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dt, *J* = 8.0, 1.2 Hz,1H), 7.74 (ddd, *J* = 9.2, 2.8, 1.6 Hz, 1H), 7.46-7.41 (m, 1H), 7.33-7.21 (m, 1H), 3.95 (s, 3H).

*Methyl 3-chlorobenzoate (**3i**).*[25] Following the general procedure, the reaction was conducted with **1i** (15.6 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (11.4 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (t, *J* = 2.0 Hz, 1H), 7.94 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.54 (ddd, *J* = 8.0, 2.0, 1.2 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 3.94 (s, 3H).

*Methyl 3-bromobenzoate (**3j**).*[22] Following the general procedure, the reaction was conducted with **1j** (20.1 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (13.3 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (t, *J* = 1.6 Hz, 1H), 7.99 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.70 (ddd, *J* = 8.0, 2.0, 1.2 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 3.95 (s, 3H).

*Methyl 3-(trifluoromethyl) benzoate (**3k**).*[26] Following the general procedure, the reaction was conducted with **1k** (19.0 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (10.8 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 1.6 Hz, 1H), 8.24 (d, *J* = 7.6 Hz, 1H), 7.89-7.73 (m, 1H), 7.67-7.53 (m, 1H), 3.97 (s, 3H).

*Methyl 3-cyanobenzoate (**3l**).*[27] Following the general procedure, the reaction was conducted with **1l** (14.7 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a white solid (9.7 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34-8.33 (m, 1H), 8.28 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.85 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.60 (td, *J* = 8.0, 0.8 Hz, 1H), 3.97 (s, 3H).

*Methyl 3-phenylbenzoate (**3m**).*[28] Following the general procedure, the reaction was conducted with **1m** (15.6 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (17.0 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 2.0 Hz, 1H), 8.09-8.00 (m, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.65

(dd, J = 7.2, 2.0 Hz, 2H), 7.56-7.47 (m, 3H), 7.43-7.39 (m, 1H), 3.97 (s, 3H).

*Methyl 3-aminobenzoate (**3n**).*[29] Following the general procedure, the reaction was conducted with **1n** (13.7 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (9.8 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dt, J = 7.6, 1.2 Hz, 1H), 7.37 (t, J = 2.0 Hz, 1H), 7.24 (t, J = 7.8 Hz, 1H), 6.88 (ddd, J = 8.0, 2.4, 1.2 Hz, 1H), 3.91 (s, 3H), 3.80 (s, 2H).

*Methyl 4-methylbenzoate (**3o**).*[22] Following the general procedure, the reaction was conducted with **1o** (13.6 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (12.0 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 3.91 (s, 3H), 2.41 (s, 3H).

*4-Methoxymethylbenzoate (**3p**).* [22] Following the general procedure, the reaction was conducted with **1p** (15.2 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (13.6 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-7.95 (m, 2H), 7.01-6.87 (m, 2H), 3.91 (s, 3H), 3.88 (s, 3H).

*Methyl 4-(trifluoromethoxy) benzoate (**3q**).*[30] Following the general procedure, the reaction was conducted with **1q** (20.6 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (11.7 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.03 (m, 2H), 7.30-7.27 (m, 2H), 3.95 (s, 3H).

*Methyl 4-flurobenzoate (**3r**).*[23] Following the general procedure, the reaction was conducted with **1r** (14.0 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (10.8 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11-7.99 (m, 2H), 7.16-7.06 (m, 2H), 3.91 (s, 3H).

*Methyl 4-chlorobenzoate (**3s**).*[22] Following the general procedure, the reaction was conducted with **1s** (15.6 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (10.7 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-7.93 (m, 2H), 7.48-7.37 (m, 2H), 3.94 (s, 3H).

*Methyl 4-bromobenzoate (**3t**).*[23] Following the general procedure, the reaction was conducted with **1t** (20.0 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (12.9 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.80 (m, 2H), 7.71-7.49 (m, 2H), 3.94 (s, 3H).

*Methyl 4-(trifluoromethyl) benzoate (**3u**).*[31] Following the general procedure, the reaction was conducted with **1u** (19.0 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (12.2 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.03 (m, 2H), 7.30-7.27 (m, 2H), 3.95 (s, 3H).

*Methyl 4-phenylbenzoate (**3v**).*[31] Following the general procedure, the reaction was conducted with **1v** (19.8 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (18.0 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.09 (m, 2H), 7.72-7.62 (m, 4H), 7.49 (t, J = 7.6 Hz, 2H), 7.45-7.39 (m, 1H), 3.97 (s, 3H).

*Methyl 4-(trimethylsilyl) benzoate (**3w**).*[32] Following the general procedure, the reaction was conducted with **1w** (19.4

mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (14.6 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 3.94 (s, 3H), 0.31 (s, 9H).

*Methyl methyl 3,5-dimethoxybenzoate (**3x**).*[33] Following the general procedure, the reaction was conducted with **1x** (18.2 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a white solid (13.7 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 2.4 Hz, 2H), 6.66 (t, *J* = 2.4 Hz, 1H), 3.92 (s, 3H), 3.84 (d, *J* = 0.8 Hz, 6H).

*Methyl 2, 4-dimethoxybenzoate (**3y**).*[33] Following the general procedure, the reaction was conducted with **1y** (18.2 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (10.4 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.84 (m, 1H), 6.51 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 3H), 3.87 (d, *J* = 1.2 Hz, 6H).

*Methyl 1-naphthoate (**3z**).*[33] Following the general procedure, the reaction was conducted with **1z** (17.2 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (14.9 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (dd, *J* = 8.8, 1.2 Hz, 1H), 8.22 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.04 (dt, *J* = 8.2, 1.2 Hz, 1H), 7.94-7.85 (m, 1H), 7.68-7.64 (m, 1H), 7.60-7.47 (m, 2H), 4.04 (s, 3H).

*Naphthalene-2-carboxylate (**3aa**).*[33] Following the general procedure, the reaction was conducted with **1aa** (17.2 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (13.0 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66-8.62 (m, 1H), 8.09 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.02-7.95 (m, 1H), 7.94-7.88 (m, 2H), 7.64-7.55 (m, 2H), 4.01 (s, 3H).

*Methyl phenanthrene-9-carboxylate (**3ab**).*[34] Following the general procedure, the reaction was conducted with **1ab** (22.2 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as an amorphous solid (16.5 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99-8.91 (m, 1H), 8.80-8.68 (m, 2H), 8.51 (s, 1H), 8.04-7.96 (m, 1H), 7.82-7.60 (m, 4H), 4.08 (s, 3H).

*1-Pyrenecarboxylic acid methyl ester (**3ac**).*[35] Following the general procedure, the reaction was conducted with **1ac** (24.6 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as an amorphous solid (21.1 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.29 (d, *J* = 9.5 Hz, 1H), 8.65 (d, *J* = 8.0 Hz, 1H), 8.30-8.22 (m, 3H), 8.17 (dd, *J* = 8.0, 3.2 Hz, 2H), 8.07 (dd, *J* = 8.0, 7.2 Hz, 2H), 4.14 (s, 3H).

*1-Phenylcclohexene (**3ad**).*[22] Following the general procedure, the reaction was conducted with **1ad** (14.8 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as a light yellow oil (8.1 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 16.0 Hz, 1H), 7.56-7.54 (m, 2H), 7.45-7.36 (m, 3H), 6.47 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H).

*Methyl qunoline-5-carboxylate (**3ae**).*[36] Following the general procedure, the reaction was conducted with **1ae** (17.3 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/40) as a light yellow oil (8.4 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (d, *J* =

6.0 Hz, 1H), 8.98 (d, *J* = 4.0 Hz, 1H), 8.39-8.2 (m, 2H), 7.78-7.74 (m, 1H), 7.54 (dd, *J* = 8.8, 4.0 Hz, 1H), 4.03 (s, 3H).

*Methyl quinoline-4-carboxylate (**3af**).*[37] Following the general procedure, the reaction was conducted with **1af** (17.3 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/40) as a light yellow oil (8.2 mg, 44%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.03 (d, *J* = 4.5 Hz, 1H), δ 8.77 (dd, *J* = 8.5, 0.8 Hz, 1H), 8.18 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.91 (d, *J* = 4.5 Hz, 1H), 7.80-7.76 (m, 1H), 7.68-7.65 (m, 1H), 4.05 (s, 3H).

*Methyl 2-methoxypyridine-5-carboxylate (**3ag**).*[38] Following the general procedure, the reaction was conducted with **1ag** (15.3 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/40) as a light yellow oil (8.2 mg, 49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (dd, *J* = 2.4, 0.8 Hz, 1H), 8.17 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.78 (dd, *J* = 8.8, 0.8 Hz, 1H), 4.02 (s, 3H), 3.93 (s, 3H).

*Methyl 5-methoxypyridine-3-carboxylate (**3ah**).*[39] Following the general procedure, the reaction was conducted with **1ah** (15.3 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/40) as a light yellow oil (8.4 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 1.6 Hz, 1H), 8.49 (d, *J* = 3.2 Hz, 1H), 7.78 (dd, *J* = 3.2, 1.6 Hz, 1H), 3.97 (s, 3H), 3.92 (s, 3H).

*Methyl indole-5-carboxylate (**3ai**).*[30] Following the general procedure, the reaction was conducted with **1ai** (16.1 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/40) as a white solid (11.4 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (brs, 1H) 8.45 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.94 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.43 (d, *J* = 4.0 Hz, 1H), 7.35-7.22 (m, 1H), 6.68-6.67 (m, 1H), 3.96 (s, 3H).

*Benzofuran-3-carboxylic acid methyl ester (**3aj**).*[40] Following the general procedure, the reaction was conducted with **1aj** (16.2 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/40) as light yellow oil (10.6 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.14-8.04 (m, 1H), 7.60-7.51 (m, 1H), 7.43-7.34 (m, 2H), 3.97 (s, 3H).

*Methyl 4-((1-ethoxy-2-methyl-1-oxopropan-2-yl) oxy) benzoate (**3ak**).* Following the general procedure, the reaction was conducted with **1ak** (25.2 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/100) as light yellow oil (18.6 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.91 (m, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 3H), 1.66 (s, 6H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 173.8, 166.8, 159.6, 131.2, 123.3, 117.3, 79.3, 61.7, 51.9, 25.4, 14.0. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{18}O_5^+$ 266.1149; Found 266.1150.

*Methyl (8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14, 15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3-carboxylate(**3al**).*[41] Following the general procedure, the reaction was conducted with **1al** (29.8 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/40) as an amorphous solid (19.0 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.77 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 3.92 (s, 3H), 3.02-2.93 (m, 2H), 2.60-2.43 (m, 2H), 2.39-2.33 (m, 1H), 2.26-1.96 (m, 4H), 1.71-1.47 (m, 6H), 0.94 (s, 3H).

*Methyl 4-(((3R,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclo penta[a]phenanthren-3-yl)oxy) benzoate(**3am**)* Following the general procedure, the reaction was conducted with **1am** (41.0 mg, 0.1 mmol). The product was obtained through silica gel chromatography (ethyl acetate/hexane 1/40) as a brown solid (27.2 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.93 (m, 2H), 6.96-6.87 (m, 2H), 4.64 (t, *J* = 2.8 Hz, 1H), 3.89 (s, 3H), 2.49-2.42 (m, 1H), 2.14-2.04 (m, 1H), 2.01-1.87 (m, 2H), 1.83-1.78 (m, 2H), 1.76-1.40 (m, 9H), 1.40-1.19 (m, 5H), 1.12-0.96 (m, 1H), 0.88 (d, *J* = 3.2 Hz, 7H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 166.9, 161.6, 131.6, 122.0, 115.2, 72.1, 54.2, 51.8, 51.4, 47.8, 39.6, 35.9, 35.8, 35.0, 32.5, 32.4, 31.5, 30.7, 28.1, 25.6, 21.7, 20.1, 13.8, 11.4. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{27}H_{36}O_4^+$ 424.2608; Found 424.2609.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge via the Internet at http://pubs.acs.org. Optimization of the Reaction Conditions for the Synthesis of **3a**, NMR spectra.

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Notes

The authors declare no competing financial interest.

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