

Pivalic anhydride mediated esterification of phenols with carboxylic acids through sodium thiosulfate catalysis

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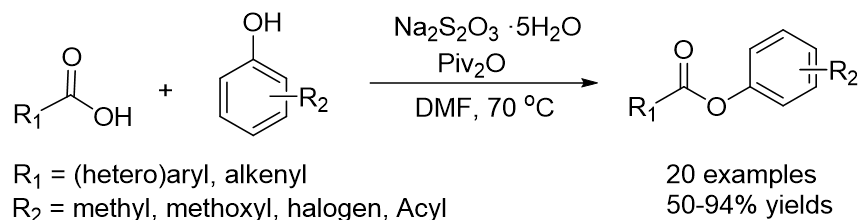
Received 10-20-2024

Accepted Manuscript 01-08-2025

Published on line 02-03-2025

Abstract

An improved method for the generation of acyl-Bunte salts has been developed by the reaction of carboxylic acids with sodium thiosulfate pentahydrate in the presence of inexpensive and easy to handle pivalic anhydride, which offers a simple and efficient pathway to generate phenolic esters from carboxylic acids and electron-rich phenols.



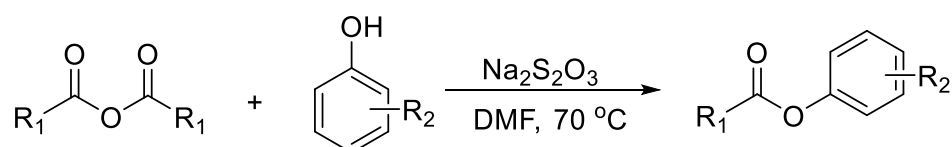
Keywords: Pivalic anhydride, sodium thiosulfate pentahydrate, esterification, phenolic esters

Introduction

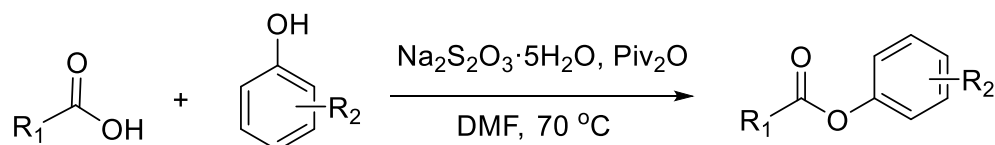
Phenolic esters are a versatile class of carboxylic acid derivatives that have found broad applications in medicinal chemistry¹⁻² and material science.³⁻⁴ Although various transition-metal catalyzed process have been developed,⁵⁻⁷ the most convenient and straightforward method for the preparation of phenolic esters is esterification of phenols. As phenol is generally less nucleophilic than alcohols, the esterification of phenols often requires more reactive anhydride⁸⁻¹¹, acyl halide¹²⁻¹⁵ and diacyl disulfide¹⁶⁻¹⁷ instead of carboxylic acids. To simplify the process, a variety of in situ activation method using carboxylic acids have also been developed over the years. However, the activation reagents, such as trifluoroacetic anhydride (TFAA),¹⁸⁻¹⁹ 2-chloro-1-methylpyridinium iodide,²⁰ BOP,²¹ DCC,²² PPE,²³ N,N-bis(2-oxo-3-oxazolidinyl) phosphordiamidic chloride,²⁴ CCl₄/PPh₃,²⁵ diphenyl(1,2-benzisoxazol-3-yl)phosphate,²⁶ Me₂NSO₂Cl,²⁷ montmorillonite-Ti⁴⁺,²⁸ metal triflates in [bmim]PF₆,²⁹ Mn(OAc)₃,³⁰ TiO(acac)₂,³¹ diarylammonium arensulfonate,³² were generally expensive, harmful or difficult-to-handle. Therefore, a simple process for the esterification of phenols with carboxylic acids remains highly desirable.

Recently, the Liang group reported that acyl-Bunte salts, generated via the reaction of symmetric anhydrides with sodium thiosulfate, could be nucleophilic attacked by phenols to form phenolic esters (Scheme 1a).³³ With the insight gained from this strategy, we questioned whether it would be possible to generate acyl-Bunte salts using carboxylic acids instead of symmetric anhydrides. We recognized that inexpensive and easy to handle pivalic anhydride might be a suitable activating agent as we have reported that the in situ generated pivaloyl mixed anhydride could undergo regioselective amidation by N-alkyl anilines.³⁴ Herein, we detail the successful execution of this idea and present a simple and practical sodium thiosulfate pentahydrate catalyzed esterification of phenols with carboxylic acids in the presence of pivalic anhydride (Scheme 1b). Compared with Liang group's work,³³ the formation of anhydride prior to effecting the esterification is unnecessary. The byproduct is nontoxic pivalic acid which could be removed by simple basic workup.

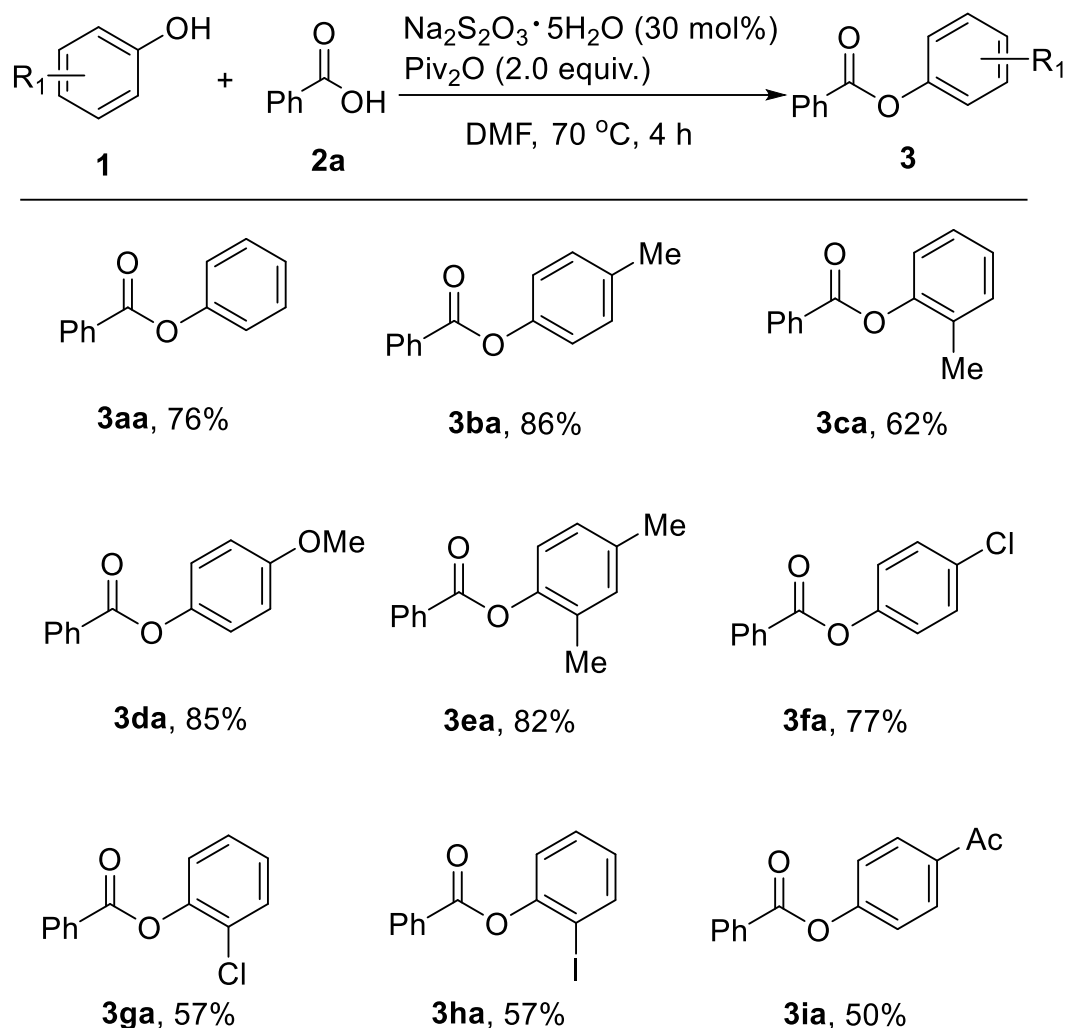
(a) Liang's work



(b) This work

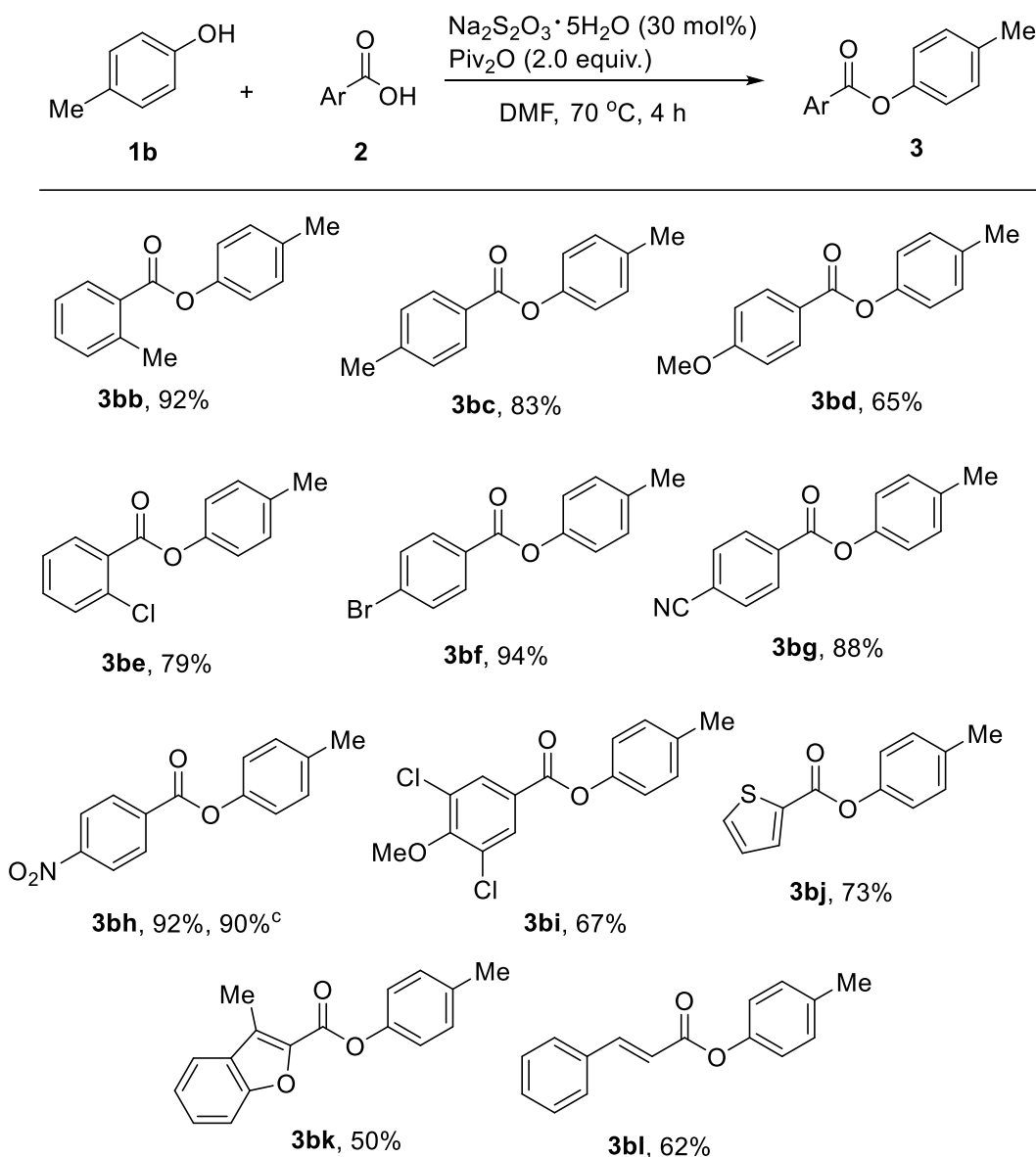


Scheme 1. Approaches for Phenolic ester formation.



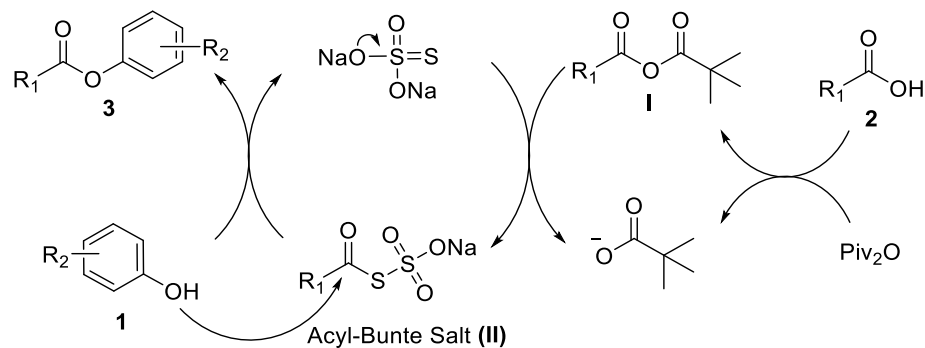
Scheme 2. Scope of the phenols. ^a Reaction conditions: **1** (1 mmol, 1 equiv.), **2a** (1.3 mmol, 1.3 equiv.), $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (0.3 mmol, 30 mol %) and Piv_2O (2.0 mmol, 2.0 equiv.) in 2 mL DMF at 70 °C for 4 h. ^b Isolated yield.

Next, the substrate scope of the reaction with respect to carboxylic acid substrates was explored. As shown in Scheme 3, the benzoic acids containing methyl **3bb-3bc**, methoxy **3bd**, halogen **3be-3bf** and strong electron-withdrawing cyanide **3bg**, nitro **3bh** groups have good tolerance to the system and corresponding phenolic ester products have been synthesized with moderate to excellent yields. Gram-scale preparation of **3bh** proceeded in 90% yield, testifying to the robustness and synthetic potential of this method. Generally, carboxylic acids bearing strong electron-withdrawing groups were more effective, due to the stronger nucleophilicity of the carbonyl groups of the resulted pivaloyl mixed anhydride intermediates. In addition, heterocyclic carboxylic acids, such as thiophene **3cj** and benzofuran **3ck**, were proved to be feasible coupling partners, providing the corresponding esters in 50-73% yields **3pa-3ra**. Besides aromatic acids, cinnamic acid was also found to be viable substrate, providing the corresponding phenolic ester **3cl** in 62% yield.



Scheme 3. Scope of the carboxylic acids ^a Reaction conditions: **1b** (1 mmol, 1 equiv.), **2** (1.3 mmol, 1.3 equiv.), $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (0.3 mmol, 30 mol %) and Piv_2O (2.0 mmol, 2.0 equiv.) in 2 mL DMF at 70 °C for 4 h. ^b Isolated yield. ^c Gram scale.

From the above experimental results and previous reports,**21-22** a plausible mechanism is proposed (Scheme 4). First, carboxylic acid **2** was in situ activated by Piv_2O to produce the pivaloyl mixed anhydride (I),³⁴ which then reacted with sodium thiosulfate pentahydrate to produce Acyl-Bunte salt (II).³³ Finally, the nucleophilic attack of phenols **1** to acyl-Bunte salt (II) to form phenolic esters **3** and regenerate sodium thiosulfate.



Scheme 4. Proposed mechanism.

Conclusions

In conclusion, we have developed a simple and efficient method for the synthesis of phenolic esters via esterification of phenols with carboxylic acids. The reactions are conducted using inexpensive and easy to handle pivalic anhydride and sodium thiosulfate pentahydrate and found to be compatible with a range of carboxylic acids and electron-rich phenols.

Experimental Section

General. Unless stated otherwise, all reactions were carried out under an air atmosphere. All commercial reagents were used without additional purification. Flash chromatography was carried out with silica gel (200–300 mesh). ^1H NMR and ^{13}C NMR spectra were recorded with 400 MHz and 101 MHz spectrometers in CDCl_3 by using tetramethylsilane (TMS) as the internal standard, respectively. High-resolution mass spectra (HRMS) were recorded using a positive-ion electrospray ionization (ESI+) source.

Experimental procedures and characterization of products. An 8 mL reaction flask was charged with phenols (1.0 mmol), carboxylic acid (1.3 mmol), sodium thiosulfate pentahydrate (0.3 mmol, 74.4 mg) in 2.0 mL of DMF at r.t. under an air atmosphere. Then, pivalic anhydride (2.0 mmol, 372.5 mg) was added and reacted in an air atmosphere at 70 °C for 4 h. At the end of the reaction, 30 mL of water was added and extracted with ethyl acetate (20 mL) for three times, and the organic phase was combined. The combined organic layers were washed with 2 M sodium hydroxide solution and brine, dried over Na_2SO_4 , filtered, and concentrated in vacuum. The residue was purified by column chromatography on silica gel to give the products **3**.

Benzoic acid phenyl ester (3aa). The reaction of **2a** (158.8 mg, 1.3 mmol) and **1a** (94.1 mg, 1.0 mmol) gives **3aa** as a white solid (150.6 mg, 76%); melting point: 65–68 °C (lit. mp 71–72 °C)³⁵; R_f = 0.43 (petroleum ether/ethyl acetate 20: 1); ^1H NMR (400 MHz, Chloroform- d) δ 8.21 (d, J 6.9 Hz, 2H), 7.62 (t, J 7.4 Hz, 1H), 7.50 (t, J 7.7 Hz, 2H), 7.45–7.39 (m, 2H), 7.29–7.24 (m, 1H), 7.23–7.19 (m, 2H). ^1H NMR is consistent with the literature precedent.³³

Benzoic acid 4-methylphenyl ester (3ba). The reaction of **2a** (158.8 mg, 1.3 mmol) and **1c** (108.1 mg, 1.0 mmol) gives **3ba** as a white solid (139.9 mg, 66%); melting point: 68–70 °C (lit. mp 72 °C)³⁶; R_f = 0.66 (petroleum ether/ethyl acetate 20: 1); ^1H NMR (400 MHz, Chloroform- d) δ 8.20 (dd, J 1.4, 8.4 Hz, 2H), 7.67–7.58 (m, 1H),

7.50 (t, *J* 7.6 Hz, 2H), 7.22 (d, *J* 8.0 Hz, 2H), 7.13-7.04 (m, 2H), 2.37 (s, 3H). ¹H NMR is consistent with the literature precedent.³⁷

Benzoic acid 2-methylphenyl ester(3ca). The reaction of **2a** (158.8 mg, 1.3 mmol) and **1b** (108.1 mg, 1.0 mmol) gives **3ca** as a light yellow liquid (132.2 mg, 62%); melting point: 60-61 °C(lit.mp 62-64 °C)³⁸; *R*_f = 0.63 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.23 (dd, *J* 1.4, 8.3 Hz, 2H), 7.63 (t, *J* 7.4 Hz, 1H), 7.51 (t, *J* 7.7 Hz, 2H), 7.30-7.22 (m, 2H), 7.19 (dd, *J* 1.4, 7.4 Hz, 1H), 7.14 (d, *J* 7.8 Hz, 1H), 2.23 (s, 3H). ¹H NMR is consistent with the literature precedent.³³

4-methoxyphenyl benzoate(3da). The reaction of **2a** (158.8 mg, 1.3 mmol) and **1d** (124.1 mg, 1.0 mmol) gives **3da** as a white solid (193.9 mg, 85%); melting point: 82-84 °C(lit.mp 87-88 °C)³¹; *R*_f = 0.47 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.24-8.16 (m, 2H), 7.62 (t, *J* 7.4 Hz, 1H), 7.50 (t, *J* 7.7 Hz, 2H), 7.16-7.10 (m, 2H), 6.96-6.92 (m, 2H), 3.81 (s, 3H). ¹H NMR is consistent with the literature precedent.³⁹

Phenol-2,4-dimethyl-1-benzoate(3ea). The reaction of **2a** (158.8 mg, 1.3 mmol) and **1e** (122.2 mg, 1.0 mmol) gives **3ea** as a colorless transparent liquid (185.1 mg, 82%); *R*_f = 0.59 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* 6.9 Hz, 2H), 7.62 (t, *J* 7.4 Hz, 1H), 7.50 (t, *J* 7.8 Hz, 2H), 7.07 (s, 1H), 7.04-6.98 (m, 2H), 2.33 (s, 3H), 2.19 (s, 3H). ¹H NMR is consistent with the literature precedent.³⁵

Benzoic acid 4-chlorophenyl ester(3fa). The reaction of **2a** (158.8 mg, 1.3 mmol) and **1f** (128.6 mg, 1.0 mmol) gives **3fa** as a white solid (178.1 mg, 77%); melting point: 82-85 °C(lit.mp 85-87 °C)⁴⁰; *R*_f = 0.53 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.18 (dd, *J* 1.4, 8.4 Hz, 2H), 7.64 (t, *J* 7.5 Hz, 1H), 7.50 (t, *J* 7.8 Hz, 2H), 7.38 (d, *J* 8.8 Hz, 2H), 7.16 (d, *J* 8.8 Hz, 2H). ¹H NMR is consistent with the literature precedent.⁴¹

Benzoic acid 2-chlorophenyl ester(3ga). The reaction of **2a** (158.8 mg, 1.3 mmol) and **1g** (128.6 mg, 1.0 mmol) gives **3ga** as a colorless transparent liquid (133.0 mg, 57%); melting point: 64-67 °C(lit.mp 66-67.5 °C)⁴¹; *R*_f = 0.50 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.28-8.21 (m, 2H), 7.69-7.63 (m, 1H), 7.57-7.47 (m, 3H), 7.33 (dd, *J* 1.5, 7.1 Hz, 1H), 7.28 (dd, *J* 1.8, 8.1 Hz, 1H), 7.25-7.21 (m, 1H). ¹H NMR is consistent with the literature precedent.⁴¹

Benzoic acid 2-iodophenyl ester(3ha). The reaction of **2a** (158.8 mg, 1.3 mmol) and **1h** (220.0 mg, 1.0 mmol) gives **3ha** as a light yellow liquid (183.2 mg, 57%); melting point: 58-59 °C(lit.mp 60-61 °C)⁴²; *R*_f = 0.50 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.30-8.24 (m, 2H), 7.86 (dd, *J* 1.5, 7.9 Hz, 1H), 7.64 (t, *J* 7.4 Hz, 1H), 7.52 (t, *J* 7.7 Hz, 2H), 7.43-7.37 (m, 1H), 7.24 (dd, *J* 1.6, 8.3 Hz, 1H), 7.00 (td, *J* 1.5, 7.6 Hz, 1H). ¹H NMR is consistent with the literature precedent.⁴³

Benzoic acid 2-iodophenyl ester(3ia). The reaction of **2a** (158.8 mg, 1.3 mmol) and **1h** (220.0 mg, 1.0 mmol) gives **3ia** as a white solid (156.2 mg, 50%); melting point: 130-132 °C(lit.mp 132-134 °C)⁴⁴; *R*_f = 0.50 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* 7.8 Hz, 2H), 8.05 (d, *J* 8.7 Hz, 2H), 7.66 (t, *J* 7.4 Hz, 1H), 7.53 (t, *J* 7.7 Hz, 2H), 7.34 (d, *J* 8.7 Hz, 2H), 2.63 (s, 3H). ¹H NMR is consistent with the literature precedent.³³

Benzoic acid 2-methyl-4-methylphenyl ester(3bb). The reaction of **2b** (177.0 mg, 1.3 mmol) and **1b** (108.1 mg, 1.0 mmol) gives **3bb** as a colorless transparent liquid (207.8 mg, 92%); *R*_f = 0.74 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* 7.2 Hz, 1H), 7.44 (t, *J* 6.8 Hz, 1H), 7.30 (d, *J* 8.2 Hz, 2H), 7.20 (d, *J* 8.2 Hz, 2H), 7.08 (d, *J* 8.1 Hz, 2H), 2.66 (s, 3H), 2.35 (s, 3H). ¹H NMR is consistent with the literature precedent.³³

Benzoic acid 4-methyl-4-methylphenyl ester(3bc). The reaction of **2c** (177.0 mg, 1.3 mmol) and **1b** (108.1 mg, 1.0 mmol) gives **3bc** as a white crystals (187.7 mg, 83%); melting point: 86-88 °C(lit.mp 89-89.5 °C)⁴⁵; *R*_f = 0.67 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* 8.2 Hz, 2H), 7.29 (d, *J* 8.0

H_z, 2H), 7.21 (d, *J* 8.2 Hz, 2H), 7.08 (d, *J* 8.5 Hz, 2H), 2.43 (s, 3H), 2.36 (s, 3H). ¹H NMR is consistent with the literature precedent.³³

Benzoic acid 4-methoxy-4-methylphenyl ester(3bd). The reaction of **2d** (197.8 mg, 1.3 mmol) and **1b** (108.1 mg, 1.0 mmol) gives **3bd** as a white crystals (156.8 mg, 65%); melting point: 62-65 °C(lit.mp 66-68 °C)⁴⁶; R_f = 0.56 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-d) δ 8.15 (d, *J* 8.7 Hz, 2H), 7.21 (d, *J* 8.1 Hz, 2H), 7.08 (d, *J* 8.3 Hz, 2H), 6.97 (d, *J* 8.8 Hz, 2H), 3.88 (s, 3H), 2.36 (s, 3H). ¹H NMR is consistent with the literature precedent.³³

Benzoic acid 2-chloro-4-methylphenyl ester(3be) The reaction of **2e** (203.5 mg, 1.3 mmol) and **1b** (108.1 mg, 1.0 mmol) gives **3be** as a light yellow viscous liquid (194.4 mg, 79%);melting point: 61-64 °C(lit.mp 67-69 °C)⁴⁷; R_f = 0.63 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-d) δ 8.01 (d, *J* 7.8 Hz, 1H), 7.52-7.42 (m, 2H), 7.39-7.33 (m, 1H), 7.21 (d, *J* 8.2 Hz, 2H), 7.14 (d, *J* 8.4 Hz, 2H), 2.36 (s, 3H). ¹H NMR is consistent with the literature precedent.³³

Benzoic acid 4-bromo-4-methylphenyl ester(3bf). The reaction of **2f** (261.3 mg, 1.3 mmol) and **1b** (108.1 mg, 1.0 mmol) gives **3bf** as a white crystals (274.6 mg, 94%); melting point: 112-115 °C(lit.mp 118-119 °C)⁴⁸; R_f = 0.67 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-d) δ 8.05 (d, *J* 8.6 Hz, 2H), 7.64 (d, *J* 8.5 Hz, 2H), 7.22 (d, *J* 8.2 Hz, 2H), 7.08 (d, *J* 8.4 Hz, 2H), 2.37 (s, 3H). ¹H NMR is consistent with the literature precedent.⁴⁸

Benzoic acid 4-cyano-4-methylphenyl ester(3bg). The reaction of **2g** (191.3 mg, 1.3 mmol) and **1b** (108.1 mg, 1.0 mmol) gives **3bg** as a white crystals (208.4 mg, 88%); melting point: 86-90 °C; R_f = 0.52 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-d) δ 8.30 (d, *J* 8.2 Hz, 2H), 7.81 (d, *J* 8.2 Hz, 2H), 7.24 (d, *J* 8.2 Hz, 2H), 7.09 (d, *J* 8.4 Hz, 2H), 2.38 (s, 3H). ¹H NMR is consistent with the literature precedent.⁴⁹

Benzoic acid 4-nitro-4-methylphenyl ester(3bh). The reaction of **2h** (217.3 mg, 1.3 mmol) and **1b** (108.1 mg, 1.0 mmol) gives **3bh** as a white solid (237.1 mg, 92%); melting point: 93-96 °C(lit.mp 98-99 °C)⁴⁵; R_f = 0.57 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-d) δ 8.41-8.33 (m, 4H), 7.24 (d, *J* 8.2 Hz, 2H), 7.11 (d, *J* 8.5 Hz, 2H), 2.39 (s, 3H). ¹H NMR is consistent with the literature precedent.⁵⁰

***p*-Tolyl 3,5-dichloro-4-methoxybenzoate(3bi).** The reaction of **2i** (287.4 mg, 1.3 mmol) and **1b** (108.1 mg, 1.0 mmol) gives **3bi** as a white solid (209.1 mg, 67%); melting point: 62-66 °C; R_f = 0.52 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-d) δ 8.13 (s, 2H), 7.22 (d, *J* 8.2 Hz, 2H), 7.06 (d, *J* 8.5 Hz, 2H), 3.98 (s, 3H), 2.37 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 163.0, 156.6, 148.4, 136.0, 130.8, 130.1, 129.8, 126.8, 121.2, 61.0, 20.9. HRMS (ESI) *m/z* calcd for C₁₅H₁₃Cl₂O₃⁺ (M+H)⁺ 311.0263, found 311.0260.

3-Thiophenecarboxylic acid 4-methylphenyl ester(3bj). The reaction of **2j** (166.6 mg, 1.3 mmol) and **1b** (108.1 mg, 1.0 mmol) gives **3bj** as a white crystals (159.5 mg, 73%); melting point: 78-83 °C; R_f = 0.41 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-d) δ 8.29 (dd, *J* 1.2, 3.1 Hz, 1H), 7.65 (dd, *J* 1.2, 5.1 Hz, 1H), 7.36 (m, 1H), 7.20 (d, *J* 7.9 Hz, 2H), 7.07 (d, *J* 8.5 Hz, 2H), 2.36 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 161.3, 148.5, 135.6, 134.0, 130.0, 128.3, 126.4, 121.4, 27.2, 21.0. HRMS (ESI) *m/z* calcd for C₁₂H₁₁O₂S⁺ (M+H)⁺ 219.0474, found 219.0475.

2-Benzofurancarboxylic acid 3-methyl-4-methylphenyl ester(3bk). The reaction of **2k** (229.0 mg, 1.3 mmol) and **1b** (108.1 mg, 1.0 mmol) gives **3bk** as a white solid (132.4 mg, 50%); melting point: 78-82 °C; R_f = 0.37 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-d) δ 7.66 (d, *J* 7.8 Hz, 1H), 7.58 (d, *J* 8.4 Hz, 1H), 7.51-7.45 (m, 1H), 7.32 (t, *J* 7.5 Hz, 1H), 7.23 (d, *J* 8.3 Hz, 2H), 7.14 (d, *J* 8.6 Hz, 2H), 2.65 (s, 3H), 2.37 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 159.10, 154.72, 147.97, 140.22, 135.87, 130.09, 129.05, 128.30, 127.61, 123.36, 121.44, 112.36, 27.18, 20.96, 9.63. HRMS (ESI) *m/z* calcd for C₁₇H₁₅O₃⁺ (M+H)⁺ 267.1016, found 267.1014.

2-Propenoic acid 3-phenyl-4-methylphenyl ester(3bl). The reaction of **2i** (192.6 mg, 1.3 mmol) and **1b** (108.1 mg, 1.0 mmol) gives **3ci** as a white solid (147.0 mg, 62%); melting point: 93–95 °C(lit.mp 96–97 °C)⁵¹; R_f = 0.33 (petroleum ether/ethyl acetate 20: 1); ¹H NMR (400 MHz, Chloroform-d) δ 7.86 (d, *J* 16.0 Hz, 1H), 7.58 (m, 2H), 7.44–7.38 (m, 3H), 7.20 (d, *J* 8.5 Hz, 2H), 7.05 (d, *J* 8.4 Hz, 2H), 6.62 (d, *J* 16.0 Hz, 1H), 2.35 (s, 3H). ¹H NMR is consistent with the literature precedent.⁵²

Acknowledgements

We thank the National Natural Science Foundation of Zhejiang Province (LY21B020008) for financial support.

Supplementary Material

Supplemental material for this article is available online.

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