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# Palladium-Catalyzed Oxidative Carbonylation of Aryl Hydrazines with CO and $O_2$ at Atmospheric Pressure **

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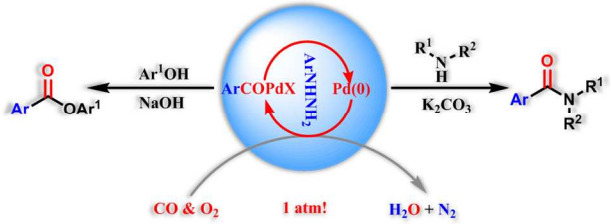
*Supporting Information*

**ABSTRACT:** Palladium-catalyzed aerobic oxidative aminocarbonylation and alkoxycarbonylation reactions with aryl hydrazines as coupling partners have been developed. The oxidative carbonylation of aryl hydrazines proceeded smoothly at atmospheric pressure CO, employing molecular oxygen as the terminal oxidant. The only by-products were nitrogen gas and water for both reactions. Notably, no double carbonylation was detected. Furthermore, aryl–halogen bonds, which are normally reactive in conventional Pd-catalyzed carbonylation reactions, remained intact.

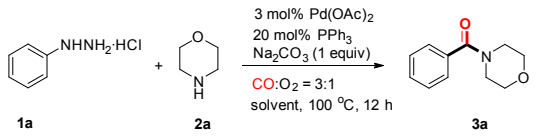



Increasing environmental concerns have stimulated the development of new synthetic transformations that minimize the generation of chemical waste. Palladium-catalyzed carbonylations using CO have evolved as attractive tools by which versatile, valuable carbonyl-containing molecules can be prepared from readily available feedstocks.[1] Among these strategies, the production of amides and esters via Pd-catalyzed amino-[2] and alkoxycarbonylations,[3] respectively, has attracted much attention. Conventional Pd-catalyzed carbonylation reactions employ aryl halides[2c,4] or pseudo-aryl halides (e.g., aryl triflates,[5] tosylates,[6] phosphates,[7] and other reagents[8]) as electrophilic coupling partners. However, stoichiometric chemical wastes as well as high reaction temperatures, high pressures, and poor chemoselectivity due to double carbonylation are notorious issues associated with these strategies. To overcome such disadvantages, Lei[9] and others[10] developed a series of oxidative carbonylations via C–H bond activation with the assistance of a directing group or the use of specific substrates. Although these efforts show some advantages over traditional carbonylations, they are intrinsically limited by the use of stoichiometric oxidant, assistance by directing groups, or substrate specificity. Environmentally friendly aryl halide surrogates that function under mild reaction conditions with excellent chemo- and regioselectivities are still in great demand. Recently, pioneering work by Loh *et al.* demonstrated that an aryl hydrazine could be transferred into palladium species under aerobic oxidative reaction conditions, with $N_2$ and $H_2O$ as the only by-products.[11]As appealing environmentally benign surrogates for aryl halides, aryl hydrazines have been employed in a number of Pd-catalyzed coupling reactions,[12] although the use of these compounds in lieu of aryl halides in organic transformations is still in its infancy. For example, aryl hydrazines have not yet been explored as coupling partners in transition-metal-catalyzed carbonylation reactions. Herein, we report the efficient production of amides and esters via the Pd-catalyzed oxidative amino- and alkoxycarbonylation reactions of aryl hydrazines under $O_2$ and CO at atmospheric pressure.

Amides are widely found in polymers, proteins, materials, agrochemicals, and pharmaceuticals;[13] indeed, up to 25% of all commercial pharmaceuticals and 67% of drug candidates contain amide bonds. Conventional amide syntheses often employ preactivated carboxyl components or coupling reagents and excess reactants, which increase both costs and chemical wastes.[14] We envisioned that aryl hydrazines could function as environmentally benign coupling partners in an oxidative aminocarbonylation reaction to provide amides in a greener chemical process.

We first examined the oxidative coupling of phenylhydrazine **1a** and morpholine **2b** to afford amide **3a** (Table 1). The reaction conditions were extensively optimized, and representative results

**Table 1. Optimization of Reaction Conditions**[a]




1a 2a 3a

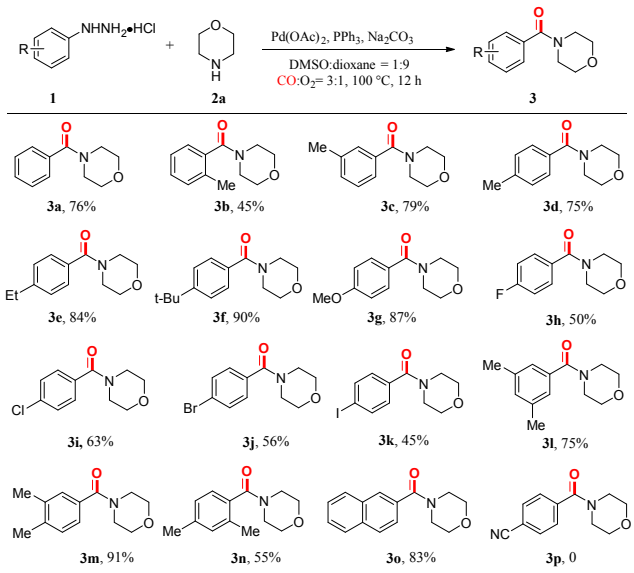
| entry | variation from standard conditions | solvent | yield[b] |
|---|---|---|---|
| 1 | none | PhMe | 42% |
| 2 | $Pd(CH_3CN)_2Cl_2$ instead of $Pd(OAc)_2$ | PhMe | 39% |
| 3 | $Pd(PPh_3)_4$ instead of $Pd(OAc)_2$ | PhMe | 13% |
| 4 | Dppe instead of $PPh_3$ | PhMe | 2% |
| 5 | 2,2′-dipyridyl instead of $PPh_3$ | PhMe | 17% |
| 6 | o-phenanthroline instead of $PPh_3$ | PhMe | 14% |
| 7 | $PhNHNH_2$ instead of 1a, without base | PhMe | 35% |
| 8 | none | dioxane | 66% |
| 9 | none | DMSO:dioxane (1:9) | 76% |

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), Pd catalyst (3 mol%), ligand (20 mol%), base (0.2 mmol), solvent (1 mL). [b]Isolated yield.

are summarized in Table 1 (for details, see the Supporting Information). Preliminary results showed that product **3a** could be obtained in moderate yield (42%) with 3 mol% $Pd(OAc)_2$, 20 mol% $PPh_3$, and 1 equiv $Na_2CO_3$ in toluene under a balloon of CO and $O_2$ (3:1) (entry 1). Variation of the Pd species or ligand did not afford any improvement in catalytic performance (entries 2–7). In contrast, the solvent had a significant effect: the yield increased to 66% with 1,4-dioxane as the solvent (entry 8), and to 76% when a mixed solvent system (1:9 DMSO:dioxane) was used (entry 9).

The generality of the reaction with various aryl hydrazines was evaluated (Scheme 1). Both electron-donating and weak electron-withdrawing substituents were compatible, although strong electron-withdrawing groups such as –CN (**3p**) and –$NO_2$ (not shown) were not tolerated. Hindered aryl hydrazines bearing an ortho methyl substituent were suitable substrates (**3b**, **3n**). For halogenated aryl hydrazines, the halogen–arene bonds were preserved and no double carbonylation was detected (**3h-3k**). Interestingly, the aryl–halogen bonds, which can also react under traditional Pd-catalyzed carbonylation conditions, remained intact.[15] The excellent chemoselectivity between the hydrazine and halides unambiguously illustrates the higher reactivity of the hydrazine functional group than the halides under these reaction conditions. This selectivity offers the opportunity for the further functionalization of the halogen-substituted amides.

**Scheme 1. Aryl hydrazine substrate scope for aminocarbonylation**[a]

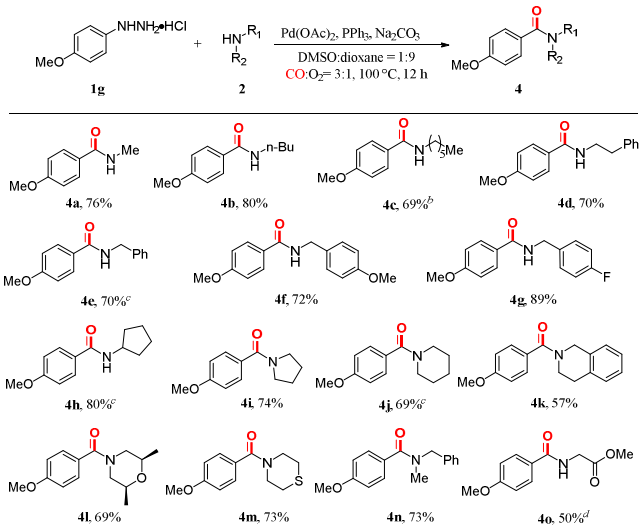



[a]Reaction conditions: aryl hydrazine hydrochloride **1** (0.4 mmol), **2a** (0.2 mmol), $Pd(OAc)_2$ (3 mol%), $PPh_3$ (20 mol%), $Na_2CO_3$ (0.2 mmol), DMSO:dioxane (1:9, 1 mL), a balloon of CO and $O_2$ (3:1). Isolated yield.

Variation of the amine was also examined, using 4-methoxyphenylhydrazine hydrochloride 1g as a model substrate (Scheme 2). Under the optimized reaction conditions, both primary (**4a**–**4h**) and secondary (**4i**–**4n**) amines participated in the reaction to smoothly provide the target amides in good to excellent yields. Hindered amines, including α-branched, cyclic, and acyclic secondary amines, were also compatible. Notably, the reaction substrate scope could be expanded to an α-amino ester (**4o**). Our efforts to apply this reaction to aryl amines such as aniline derivatives proved un- successful due to their low nucleophilicity. This feature highlights the selectivity possible between aryl and aliphatic amines.

These encouraging results prompted us to extend the reaction to alkoxycarbonylation. Unfortunately, only a trace amount of ester was obtained when the standard aminocarbonylation reaction conditions were applied to the alkoxycarbonylation. To our delight, slight modification of the reaction conditions provided a small amount of the desired product, and an extensive optimization study disclosed that the palladium species, ligand, and solvent significantly influence reaction efficiency. Ultimately, up to 79% yield of aryl ester could be isolated when the reaction was carried out in the presence of 3 mol% $PdCl_2$(dppp), tetramethyl-1,3-diaminopropane (TMDAP), and 1 equiv PhONa in (trifluoromethyl)-benzene (for optimization details, see the Supporting Information).

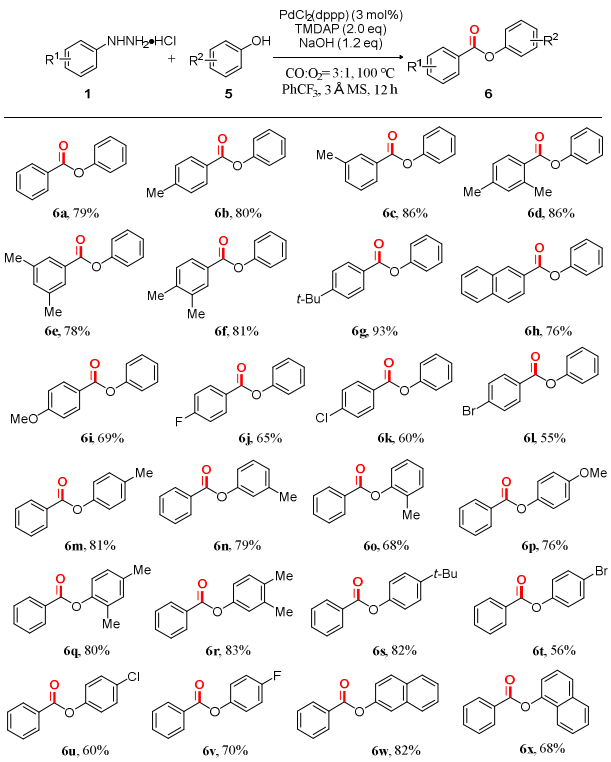
**Scheme 2. Amine substrate scope for aminocarbonylation**[a]




[a]Reaction conditions: **1g** (0.4 mmol), amine **2** (0.2 mmol), $Pd(OAc)_2$ (3 mol%), $PPh_3$ (20 mol%), $Na_2CO_3$ (0.2 mmol), DMSO:dioxane (1:9, 1 mL), a balloon of CO and $O_2$ (3:1). [b]36 h. [c]60 h. [d]Hydrochloride salt of amine and 2 eq. of $Na_2CO_3$ were used, 72 h. Isolated yield.

The substrate scope of the alkoxycarbonylation of aryl hydrazines was examined (Scheme 3). ArONa species were formed in situ by the treatment of ArOH with 1.2 equiv NaOH. Broad substrate scope with respect to both the aryl hydrazines and phenol derivatives was

**Scheme 3. Alkoxycarbonylation substrate scope**[a]



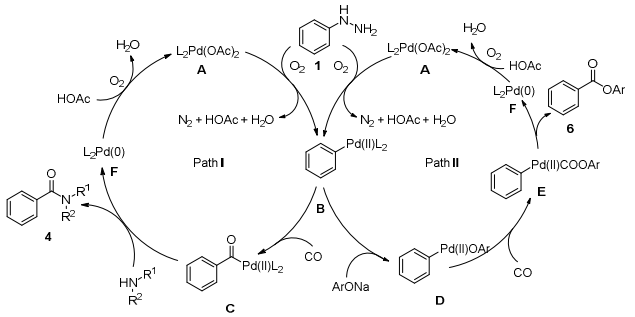

[a]Reaction conditions: **1** (0.8 mmol), ArOH (0.2 mmol), NaOH (0.24 mmol),

$PdCl_2$(dppp) (3 mol%), TMDAP (0.4 mmol), $PhCF_3$ (2.0 mL), 50 mg 3 Å MS, 100 °C, 12 h, a balloon of CO and $O_2$ (3:1). Isolated yield.

observed. Similarly to the aminocarbonylation reaction, electron-donating groups on the aryl hydrazine were beneficial. Here, too, halogen substituents (except iodine) were tolerated on both the aryl hydrazines and phenol derivatives, further confirming the greater reactivity of the hydrazine group. A hindered ortho methyl substituent was tolerated on either coupling partner, although strong electron-withdrawing groups had detrimental effects on reaction efficiency. For example, no reaction occurred when strong electron-withdrawing groups such as –CN or $–NO_2$ were present in either coupling partner. In addition, alcohols are not valid substrates for this transformation.

On the basis of previous research[11,12] and our experimental results, a plausible reaction mechanism is proposed for this transformation (Scheme 4). Phenylhydrazine is converted into palladium species B in the presence of oxygen and $Pd(OAc)_2$, accompanied by the release of $N_2$ and $H_2O$.[11] Palladium species B was detected and identified unambiguously by ESI-MS (see the Supporting Information), although the details of its formation is still kept elusive. CO insertion into the Pd–Ph bond, aminolysis, and reductive elimination lead to formation of the amide product with concomitant generation of Pd(0), which is oxidized to

**Scheme 4. A plausible reaction mechanism**




$Pd(OAc)_2$ by $O_2$ with the assistance of HOAc to complete the catalytic cycle (Path I). It is also possible that ligand exchange may occur before CO insertion (Path II). The second pathway was proven to be viable for the alkoxycarbonylation of aryl iodides with sodium alkoxide as the base by Lei and coworkers.[16] According to our experimental results, we believe that the aminocarbonylation of the aryl hydrazines in this work proceeds via path I, whereas the alkoxycarbonylation follows path II.

In summary, we report the first Pd-catalyzed oxidative carbonylation of aryl hydrazines, which offers environmentally friendly access to amides and esters with $N_2$ and $H_2O$ as the only by-products. The reaction was performed at atmospheric pressure in the presence of $O_2$ and CO, which act as the terminal oxidant and carbonyl source, respectively. High reaction efficiency was observed, with multiple bonds broken and formed in a single operation, and a broad range of coupling partners was tolerated. Using readily available starting materials, valuable amides and esters were produced in a practical manner. It is foreseeable that this environmentally friendly protocol will be an attractive strategy for the synthesis of amides and esters in future.

## ■ EXPERIMENTAL SECTION

All reactions were carried out in oven dried glassware. All Aryl hydrazine hydrochloride and phenol were obtained from commercial sources and used as received. All the reactions were monitored by thin-layer chromatography (TLC); products purification was done using silica gel column chromatography.

$^1H/^{13}C$ NMR spectra were recorded on Bruker avance 400 MHz and Bruker AMX 400 MHz spectrometer at 400/100 MHz, respectively, in $CDCl_3$ unless otherwise stated, using either TMS or the undeuterated solvent residual signal as the reference. Chemical shifts are given in ppm and are measured relative to $CDCl_3$ as an internal standard. Mass spectra were obtained by the electrospray ionization time-of-flight (ESI-TOF) mass spectrometry. GC yields were obtained using naphthalene as an internal standard. Flash column chromatography purification of compounds was carried out by gradient elution using ethyl acetate (EA) in light petroleum ether (PE).

**General procedure for aminocarbonylation of aryl hydrazine hydrochloride with amines:** Aryl hydrazine hydrochloride (0.4 mmol, 2.0 equiv.), $Pd(OAc)_2$ (1.3 mg, 0.006 mmol, 3 mol %), $PPh_3$ (10.5 mg, 0.04 mmol, 20 mol %) and $Na_2CO_3$ (21.2 mg, 0.2 mmol, 1.0 equiv.) were combined in an oven-dried Schlenk tube equipped with a stir-bar. After the addition of all soilde reagents, a balloon filled with CO and $O_2$ (the ratio is 3:1) was connected to the Schlenk tube via the side tube and purged 3 times. Then DMSO (0.1 mL), amine (0.2 mmol) and dioxane (0.9 mL) were added to the tube via a syringe. The Schlenk tube was heated at 100 ℃ for 12 h. After the reaction was completed (TLC), the contents were cooled to room temperature and then the balloon gas was released carefully. The reaction was quenched by water and extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous $Na_2SO_4$ and evaporated under vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel with petroleum ether/ ethyl acetate.

*Morpholino(phenyl)methanone* ***(3a)***[17] Purification by chromatography (petroleum ether/EtOAc = 8:1) afforded 3a as a yellow liquid (29 mg, 76%); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.45-7.36 (m, 5H), 3.77-3.46 (m, 8H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 170.5, 135.3, 129.9, 128.6, 127.1, 66.9(2C), 48.1, 42.5.

*Morpholino(o-tolyl)methanone* ***(3b)***[17] Purification by chromatography (petroleum ether/EtOAc = 8:1) afforded 3b as a colourless liquid (27 mg, 65%); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.30-7.27 (m, 1H), 7.23-7.20 (m, 2H), 7.16-7.15 (m, 1H), 3.83-3.77 (m, 4H), 3.61-3.54 (m, 2H), 3.28-3.18 (m, 2H), 2.32 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 170.1, 135.6, 134.2, 130.5, 129.1, 126.0, 125.8, 67.0(2C), 47.3, 41.2, 19.0.

*Morpholino(m-tolyl)methanone* ***(3c)***[17] Purification by chromatography (petroleum ether/EtOAc = 8:1) afforded 3c as a yellow liquid (32 mg, 79%); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.31-7.16 (m, 4H), 3.73-3.45 (m, 8H), 2.37 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 170.6, 138.5, 135.5, 130.6, 128.4, 127.7, 124.0, 66.9(2C), 48.2, 42.4, 21.4.

*morpholino(p-tolyl)methanone* ***(3d)***[17] Purification by chromatography (petroleum ether/EtOAc = 8:1) afforded 3d as a yellow liquid (31 mg, 75%); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 3.68-3.55 (m, 8H), 2.37 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 170.6, 140.1, 132.3, 129.1, 127.2, 66.9 (2C), 48.2, 42.4, 21.4.

*(4-ethylphenyl)(morpholino)methanone* ***(3e)*** Purification by chromatography (petroleum ether/EtOAc = 8:1) afforded 3e as a yellow liquid (37 mg, 84%); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 3.81 – 3.49 (m, 8H), 2.67 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 170.7, 146.4, 132.5, 128.0, 127.3, 66.9(2C), 48.2, 42.4, 28.7, 15.4. IR (KBr) ν̃ 2964, 1635, 1456, 1011, 839, 760 cm-1. HRMS (ESI-TOF) calcd for $C_{13}H_{17}NNaO_2$ (M + Na+) 242.1157, found 242.1159.

*(4-(tert-butyl)phenyl)(morpholino)methanone* ***(3f)*** Purification by chromatography (petroleum ether/EtOAc = 8:1) afforded 3f as a yellow liquid (44 mg, 90%); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 3.69-3.51 (m, 8H),

1.32 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.7, 153.2, 132.3, 127.0, 125.5, 66.9(2C), 48.4, 42.4, 34.8, 31.2. IR (KBr) ν̃ 2955, 1635, 1431, 1109, 835, 747 cm$^{-1}$. HRMS (ESI-TOF) calcd for $C_{15}H_{21}NNaO_2$ (M + Na$^+$) 270.1470, found 270.1472.

*(4-Methoxyphenyl)(morpholino)methanone* ***(3g)***[17] Purification by chromatography (petroleum ether/EtOAc = 6:1) afforded 3g as a yellow liquid (38 mg, 87%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 7.9 Hz, 2H), 3.84 (s, 3H), 3.70-3.61 (m, 8H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.4, 160.8, 129.1, 127.2, 113.7, 66.8 (2C), 55.3, 48.1, 43.1.

*(4-fluorophenyl)(morpholino)methanone* ***(3h)*** Purification by chromatography (petroleum ether/EtOAc = 8:1) afforded 3h as a yellow liquid (21 mg, 50%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.14 – 7.08 (m, 2H), 3.96 – 3.38 (m, 8H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.5, 164.7, 162.2, 131.3 (d, J = 3.5 Hz), 129.5 (d, J = 8.5 Hz), 115.8, 115.6, 66.9, 48.3, 42.8. IR (KBr) ν̃ 2959, 1637, 1450, 1011, 893, 756 cm-1. HRMS (ESI-TOF) calcd for $C_{11}H_{12}NNaO_2F$ (M + Na+) 232.0750, found 232.0744.

*(4-chlorophenyl)(morpholino)methanone* ***(3i)***[17] Purification by chromatography (petroleum ether/EtOAc = 8:1) afforded 3i as a yellow liquid (28 mg, 63%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 3.69-3.49 (m, 8H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.4, 136.1, 133.6, 128.9, 128.7, 66.8(2C), 48.1, 42.6.

*(4-bromophenyl)(morpholino)methanone* ***(3j)***[17] Purification by chromatography (petroleum ether/EtOAc = 8:1) afforded 3j as a yellow solid (30 mg, 56%). mp: 91−92 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 3.69-3.46 (m, 8H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.4, 134.1, 131.8, 128.9, 124.3, 66.8(2C), 48.1, 42.8.

*(4-iodophenyl)(morpholino)methanone* ***(3k)***[17] Purification by chromatography (petroleum ether/EtOAc = 8:1) afforded 3k as a yellow solid (29 mg, 45%). mp: 123−125 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.17 – 7.11 (m, 2H), 3.84 – 3.36 (m, 8H); $^{13}$C NMR (100 MHz, $CDCl_3$) 169.5, 137.7, 134.7, 128.8, 96.1, 66.8, 48.1, 42.5.

*(3,5-dimethylphenyl)(morpholino)methanone* ***(3l)***[17] Purification by chromatography (petroleum ether/EtOAc = 8:1) afforded 3l as a colorless oil (33 mg, 75%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 1H), 6.99 (s, 2H), 3.88 – 3.37 (m, 8H), 2.33 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.8, 138.3, 135.3, 131.4, 124.6, 66.9, 48.3, 42.6, 21.2.

*(3,4-dimethylphenyl)(morpholino)methanone* ***(3m)*** Purification by chromatography (petroleum ether/EtOAc = 8:1) afforded 3m as a yellow liquid (40 mg, 91%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 1H), 7.09-7.03 (m, 2H), 3.61-3.42 (m, 8H), 2.21-2.18 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.8, 138.7, 137.0, 132.8, 129.6, 128.4, 124.5, 66.9(2C), 48.3, 42.6, 19.7, 19.7. IR (KBr) ν̃ 2921, 1636, 1428, 1029, 822, 761 cm-1. HRMS (ESI-TOF) calcd for $C_{13}H_{17}NNaO_2$ (M + Na+) 242.1157, found 242.1158.

*(2,4-dimethylphenyl)(morpholino)methanone* ***(3n)*** Purification by chromatography (petroleum ether/EtOAc = 8:1) afforded 3n as a yellow liquid (28 mg, 65%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.06-7.01 (m, 3H), 3.81-3.76 (m, 4H), 3.60-3.52 (m, 2H), 3.28-3.21 (m, 2H), 2.32 (s, 3H), 2.28 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.4, 138.9, 134.1, 132.7, 131.2, 126.6, 125,9, 67.0(2C), 47.3, 42.0, 21.2, 19.0. IR (KBr) ν̃ 2961, 1635, 1429, 1020, 822, 761 cm-1. HRMS (ESI-TOF) calcd for $C_{13}H_{17}NNaO_2$ (M + Na+) 242.1157, found 242.1157.

*morpholino(naphthalen-2-yl)methanone* ***(3o)*** Purification by chromatography (petroleum ether/EtOAc = 8:1) afforded 3n as a red solid (40 mg, 83%), mp: 101-103 °C ; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.91-7.89 (m, 4H), 7.55-7.48 (m, 3H), 3.93-3.44 (s, 8H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.5, 133.8, 132.7, 132.6, 128.5, 128.4, 127.8, 127.2, 127.1, 126.8, 124.2, 67.0(2C), 48.3, 42.7. IR (KBr) ν̃ 2964, 1621, 1427, 1066, 839, 753 cm$^{-1}$. HRMS (ESI-TOF) calcd for $C_{15}H_{15}NNaO_2$ (M + Na$^+$) 264.1000, found 264.0999.

*4-methoxy-N-methylbenzamide* ***(4a)***[17] Purification by chromatography (petroleum ether/EtOAc = 6:1) afforded 4a as a yellow liquid (25 mg, 76%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.7 Hz, 2H), 6.89 (d, J = 7.7 Hz, 2H), 6.40 (bs, 1H), 3.83 (s, 3H), 2.97 (d, J = 2.9 Hz, 3H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.8, 162.1, 128.6, 127.1, 113.7, 55.3, 26.7.

*N-butyl-4-methoxybenzamide* ***(4b)***[17] Purification by chromatography (petroleum ether/EtOAc = 6:1) afforded 4b as a yellow liquid (33 mg, 80%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.19 (bs, 1H), 3.84 (s, 3H), 3.45-3.40 (m, 2H), 1.62-1.55 (m, 2H), 1.45-1.35 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.1, 162.0, 128.6, 127.1, 113.7, 55.4, 39.8, 31.8, 20.2, 13.8.

*N-hexyl-4-methoxybenzamide* ***(4c)***[17] Purification by chromatography (petroleum ether/EtOAc = 6:1) afforded 4c as a yellow solid (32 mg, 69%), mp: 62−64 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 6.11 (bs, 1H), 3.83 (s, 3H), 3.44-3.39 (m, 2H), 1.63-1.55 (m, 2H), 1.38-1.30 (m, 6H), 0.88 (t, *J* = 6.5 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.0, 162.0, 128.6, 127.2, 113.7, 55.4, 40.0, 31.5, 29.7, 26.7, 22.5, 14.0.

*4-methoxy-N-phenethylbenzamide* ***(4d)***[17] Purification by chromatography (petroleum ether/EtOAc = 6:1) afforded 4d as a yellow solid (36 mg, 70%). mp: 117−118 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.8 Hz, 2H), 7.35-7.31 (m, 2H), 7.27-7.23 (m, 3H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.21 (bs, 1H), 3.84 (s, 3H), 3.73-3.69 (m, 2H), 2.93 (t, *J* = 6.9 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.0, 162.1, 139.1, 128.8, 128.7, 128.6, 127.0, 126.5, 113.7, 55.4, 41.1, 35.8. IR (KBr) ν̃ 2931, 1637, 1456, 1028, 843, 750 cm$^{-1}$. HRMS (ESI-TOF) calcd for $C_{16}H_{17}NNaO_2$ (M + Na$^+$) 278.1157, found 278.1157.

*N-benzyl-4-methoxybenzamide* ***(4e)*** Purification by chromatography (petroleum ether/EtOAc = 6:1) afforded 4e as a yellow solid (34 mg, 70%). mp: 123−126 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.36 – 7.28 (m, 5H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.40 (bs, 1H), 4.62 (d, *J* = 5.7 Hz, 2H), 3.84 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.9, 162.3, 138.4, 128.8, 128.8, 127.9, 127.6, 126.7, 113.8, 55.4, 44.1. IR (KBr) ν̃ 2920, 1634, 1441, 1033, 845, 726 cm$^{-1}$. HRMS (ESI-TOF) calcd for $C_{15}H_{15}NNaO_2$ (M + Na$^+$) 264.1000, found 264.1005.

*4-methoxy-N-(4-methoxybenzyl)benzamide* ***(4f)*** Purification by chromatography (petroleum ether/EtOAc = 6:1) afforded 4e as a yellow solid (39 mg, 72%), mp: 160−162 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.90-6.85 (m, 4H), 6.45 (bs, 1H), 4.53 (d, *J* = 5.5 Hz, 2H), 3.82 (s, 3H), 3.78 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.8, 162.2, 159.1, 130.5, 129.3, 128.8, 126.7, 114.1, 113.7, 55.4, 55.3, 43.5. IR (KBr) ν̃ 2958, 1632, 1440, 1028, 846, 772 cm$^{-1}$. HRMS (ESI-TOF) calcd for $C_{16}H_{17}NNaO_3$ (M + Na$^+$) 294.1106, found 294.1109.

*N-(4-fluorobenzyl)-4-methoxybenzamide* ***(4g)*** Purification by chromatography (petroleum ether/EtOAc = 6:1) afforded 4e as a yellow solid (46 mg, 89%), mp: 134−136 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.7 Hz, 2H), 7.32-7.49 (m, 2H), 7.03-6.99 (m, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.47 (bs, 1H), 4.58 (d, *J* = 5.7 Hz, 2H), 3.84 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.9, 162.3, 162.2 (d, $J_{C\text{-}F}$ = 245.0), 134.3 (d, $J_{C\text{-}F}$ = 3.0), 129.5 (d, $J_{C\text{-}F}$= 8.0), 128.8, 126.5, 115.56 (d, $J_{C\text{-}F}$ = 22.0), 113.8, 55.4, 43.3. IR (KBr) ν̃ 2931, 1632, 1423, 1027, 843, 776 cm$^{-1}$. HRMS (ESI-TOF) calcd for $C_{15}H_{14}NNaO_2$ F(M + Na$^+$) 282.0906, found 282.0903.

*N-cyclopentyl-4-methoxybenzamide* ***(4h)***[17] Purification by chromatography (petroleum ether/EtOAc = 6:1) afforded 4h as a yellow solid (35 mg, 80%). mp: 150−152 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.00 (bs, 1H), 4.43-4.34 (m, 1H), 3.84 (s, 3H), 2.12-2.04 (m, 2H), 1.72-1.62 (m, 4H), 1.52-1.44 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.7, 162.0, 128.6, 127.3, 113.7, 55.4, 51.6, 33.3, 23.8.

*(4-methoxyphenyl)(pyrrolidin-1-yl)methanone* ***(4i)*** Purification by chromatography (petroleum ether/EtOAc = 6:1) afforded 4i as a yellow solid (30 mg, 74%). mp: 78−80 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 3.83 (s, 3H), 3.65-3.62 (m, 2H), 3.49-3.46 (m, 2H), 1.98-1.93 (m, 2H), 1.88-1.85 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.5, 160.8, 129.4, 129.1, 113.4, 55.3, 49.8, 46.3, 26.5, 24.4. IR (KBr) ν̃ 2926, 1608, 1425, 1032, 846, 765 cm-1. HRMS (ESI-TOF) calcd for C12H15NNaO2 (M + Na+) 228.1000, found 228.1001.

*(4-methoxyphenyl)(piperidin-1-yl)methanone****(4j)***[17] Purification by chromatography (petroleum ether/EtOAc = 6:1) afforded 4j as a yellow liquid (30 mg, 69%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 7.8 Hz, 2H), 6.90 (d, J = 7.8 Hz, 2H), 3.82 (s, 3H), 3.55-3.48 (m, 4H), 1.68-1.58 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.3, 160.5, 128.8, 128.6, 113.6, 55.3, 48.8, 43.2, 26.1, 26.3, 26.1, 24.6.

*(3,4-dihydroisoquinolin-2(1H)-yl)(4-methoxyphenyl)methanone* ***(4k)*** Purification by chromatography (petroleum ether/EtOAc = 5:1) afforded 4k as a yellow liquid (30 mg, 57%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.7 Hz, 2H), 7.19-7.15 (m, 4H), 6.93 (d, *J* = 8.7 Hz, 2H), 4.83-4.70 (m, 2H), 3.89-3.71 (m, 5H), 2.98-2.93 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.8, 160.9, 133.2, 129.1, 128.9, 128.8, 128.2, 126.7, 126.5, 113.8(2C), 55.4, 49.9, 45.1, 29.9. IR (KBr) ν̃ 2935, 1628, 1438, 1029, 841, 763 cm-1. HRMS (ESI-TOF) calcd for $C_{17}H_{17}NNaO_2$ (M + Na+) 290.1157, found 290.1156.

*((2S,6R)-2,6-dimethylmorpholino)(4-methoxyphenyl)methanone* ***(4l)*** Purification by chromatography (petroleum ether/EtOAc = 5:1) afforded 4l as a yellow liquid (34 mg, 69%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 6.94 – 6.90 (m, 2H), 3.84 (s, 3H), 3.60 (m, 2H), 3.02 – 2.29 (m, 2H), 1.87 – 1.48 (m, 2H), 1.36 – 1.06 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) 170.1, 160.8, 129.2, 127.6, 113.8, 71.9, 55.3, 53.5, 47.7, 18.7. IR (KBr) ν̃ 2935, 1628, 1438, 1029, 841, 763 cm-1. HRMS (ESI-TOF) calcd for $C_{14}H_{19}NNaO_3$ (M + Na+) 272.1263, found 272.1260.

*(4-methoxyphenyl)(thiomorpholino)methanone* ***(4m)*** Purification by chromatography (petroleum ether/EtOAc = 5:1) afforded 4m as a yellow liquid (35 mg, 73%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 3.86-3.81 (m, 7H), 2.70-2.60 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.8, 160.8, 128.9, 127.8, 113.9, 55.4, 48.6, 45.7, 27.7. IR (KBr) ν̃ 2920, 1634, 1456, 1027, 841, 763 cm-1. HRMS (ESI-TOF) calcd for $C_{12}H_{15}NNaO_2S$ (M + Na+) 260.0721, found 260.0725.

*N-benzyl-4-methoxy-N-methylbenzamide* ***(4n)*** Purification by chromatography (petroleum ether/EtOAc = 5:1) afforded 4n as a yellow liquid (37 mg, 73%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.8 Hz, 2H), 7.38-7.35 (m, 3H), 7.31-7.27 (m, 2H), 6.89 (d, J = 8.8 Hz, 2H), 4.72-4.59 (m, 2H), 3.81 (s, 3H), 2.96 (s, 3H). $^{13}$C (100MHz, $CDCl_3$) 160.72, 137.03, 128.98, 128.78, 128.27, 127.50, 126.70, 113.67, 77.42, 77.30, 77.10, 76.78, 65.58, 55.33, 51.03, 37.22, 33.48. IR (KBr) ν̃ 2924, 1634, 1453, 1073, 836, 734 cm-1. HRMS (ESI-TOF) calcd for $C_{16}H_{17}NNaO_2$ (M + Na+) 278.1157, found 278.1155.

*methyl 2-(4-methoxybenzamido)acetate* ***(4o)*** Purification by chromatography (petroleum ether/EtOAc = 6:1) afforded 4o as a yellow solid (22 mg, 50%). mp: 101−102 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.2 Hz, 2H), 6.65 (s, 1H), 4.24 (d, J = 4.1 Hz, 2H), 3.85 (s, 3H), 3.80 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.7, 167.0, 162.5, 129.0, 126.0, 113.8, 55.4, 52.5, 41.7. IR (KBr) ν̃ 2928, 1720, 1629, 1449, 1027, 846, 728 cm-1. HRMS (ESI-TOF) calcd for $C_{11}H_{13}NNaO_4$ (M + Na+) 246.0742, found 246.0749.

**General procedure for alkoxycarbonylation of aryl hydrazine hydrochloride with phenol derivatives:** Aryl hydrazine hydrochloride (0.8 mmol, 4.0 equiv.), $PdCl_2$(dppp) (3.5 mg, 0.006 mmol, 3 mol %), and NaOH (9.6 mg, 0.24 mmol, 1.2 equiv.) were combined in an oven-dried Schlenk tube equipped with a stir-bar. After the addition of all soilde reagents, a balloon filled with CO and $O_2$ (the ratio is 3:1) was connected to the Schlenk tube via the side tube and purged 3 times. Then TMDAP (67.8 μL, 0.4 mmol, 2.0 equiv), Ph-OH(17.6 μL, 0.4 mmol, 2.0 equiv) and 4-$CF_3$-Ph (2.0 mL) were added to the tube via a syringe. The Schlenk tube was heated at 100 ℃ for 12 h. After the reaction was completed (TLC), the contents were cooled to room temperature and then the balloon gas was released carefully. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel with petroleum ether/ ethyl acetate.

*phenyl benzoate* ***(6a)***[18] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6a as a white solid (31 mg, 79%). mp: 71−72 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.19 (m, 2H), 7.66 – 7.60 (m, 1H), 7.54 – 7.47 (m, 2H), 7.46 – 7.39 (m, 2H), 7.29 – 7.26 (m, 1H), 7.24 – 7.18 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.2, 151.0, 133.6, 130.2, 129.7, 129.5, 128.6, 125.9, 121.7.

*phenyl 4-methylbenzoate* ***(6b)***[19] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6b as a white solid (34 mg, 80%), mp: 77-78 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 2H), 7.45 – 7.38 (m, 2H), 7.32 – 7.27 (m, 2H), 7.26 – 7.18 (m, 3H), 2.45 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.3, 151.1, 144.4, 130.2, 129.5, 129.3, 126.9, 125.8, 121.8, 21.8.

*phenyl 3-methylbenzoate* ***(6c)***[19] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6c as a colorless oil (36 mg, 86%); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 2H), 7.46 – 7.38 (m, 4H), 7.29 – 7.25 (m, 1H), 7.24 – 7.19 (m, 2H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.4, 151.1, 138.4, 134.4, 130.7, 129.6, 129.5, 128.5, 127.4, 125.8, 121.8, 21.3.

*phenyl 2,4-dimethylbenzoate* ***(6d)*** Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6d as a colorless oil (39 mg, 86%); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.05 (m, 1H), 7.44 – 7.38 (m, 2H), 7.28 – 7.22 (m, 1H), 7.22 – 7.16 (m, 2H), 7.13 – 7.09 (m, 2H), 2.64 (s, 3H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.8, 151.1, 143.5, 141.5, 132.8, 131.4, 129.5, 126.7, 125.7, 125.7, 121.9, 22.0, 21.5; HRMS m/z(ESI) calcd for $C_{15}H_{14}NaO_2$ (M + Na+) 249.0886, found 249.0891.

*phenyl 3,5-dimethylbenzoate* ***(6e)*** Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6e as a colorless oil (35 mg, 78%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.44 – 7.39 (m, 2H), 7.29 – 7.23 (m, 2H), 7.22 – 7.18 (m, 2H), 2.40 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.5, 151.1, 138.3, 135.2, 129.5, 129.5, 127.9, 125.8, 121.8, 21.2; HRMS m/z(ESI) calcd for $C_{15}H_{14}NaO_2$ (M + Na+) 249.0886, found 249.0890.

*phenyl 3,4-dimethylbenzoate* ***(6f)***[20] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6e as a colorless oil (37 mg, 81%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 2H), 7.44 – 7.38 (m, 2H), 7.28 – 7.18 (m, 4H), 2.34 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.4, 151.1, 143.1, 137.0, 131.2, 129.9, 129.7, 127.8, 127.2, 125.8, 121.8, 20.1, 19.7.

*phenyl 4-(tert-butyl)benzoate* ***(6g)***[21] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6e as a white solid (47 mg, 93%), mp: 142-144 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.10 (m, 2H), 7.54 – 7.50 (m, 2H), 7.44 – 7.38 (m, 2H), 7.27 – 7.18 (m, 3H), 1.36 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.2, 157.4, 151.1, 130.1, 129.5, 126.9, 125.8, 125.6, 121.8, 35.2, 31.2.

*phenyl 2-naphthoate* ***(6h)***[22] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6h as a white solid (38 mg, 76%), mp: 95-97 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.81 – 8.77 (m, 1H), 8.22 – 8.18 (m, 1H), 8.03 – 7.98 (m, 1H), 7.96 – 7.90 (m, 2H), 7.65 – 7.56 (m, 2H), 7.48 – 7.42 (m, 2H), 7.30 – 7.24 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.4, 151.1, 135.9,

132.6, 131.9, 129.5, 129.5, 128.6(2C), 128.4, 127.9, 126.9, 125.9, 125.5, 121.8.

*phenyl 4-methoxybenzoate* ***(6i)***[19] Purification by chromatography (petroleum ether/EtOAc = 30:1) afforded 6i as a white solid (31 mg, 69%), mp: 73-75 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.11 (m, 2H), 7.45 – 7.38 (m, 2H), 7.29 – 7.17 (m, 3H), 7.01 – 6.94 (m, 2H), 3.89 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) 164.9, 163.9, 151.1, 132.3, 129.4, 125.7, 122.0, 121.8, 113.9, 55.5.

*phenyl 4-fluorobenzoate* ***(6j)***[19] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6j as a white solid (28 mg, 65%), mp: 64-66 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.19 (m, 2H), 7.46 – 7.40 (m, 2H), 7.30 – 7.24 (m, 1H), 7.23 – 7.16 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) 167.5, 164.9, 164.2, 150.9, 132.8, 132.7, 129.5, 126.0, 125.9, 125.9, 121.7, 115.9, 115.7.

*phenyl 4-chlorobenzoate* ***(6k)***[19] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6k as a white solid (28 mg, 60%), mp: 104-106 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.12 (m, 2H), 7.51 – 7.46 (m, 2H), 7.45 – 7.40 (m, 2H), 7.30 – 7.25 (m, 1H), 7.22 – 7.19 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) 164.3, 150.8, 140.2, 131.5, 129.5, 129.0, 128.1, 126.0, 121.6.

*phenyl 4-bromobenzoate* ***(6l)***[22] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6l as a white solid (30 mg, 55%), mp: 117-118 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H), 7.68 – 7.63 (m, 2H), 7.46 – 7.40 (m, 2H), 7.30 – 7.24 (m, 1H), 7.23 – 7.18 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) 164.5, 150.8, 132.0, 131.7, 129.5, 128.8, 128.6, 126.0, 121.6.

*p-tolyl benzoate* ***(6m)***[23] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6m as a white solid (34 mg, 81%), mp: 72-73 °C;$^1$H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.18 (m, 2H), 7.65 – 7.59 (m, 2H), 7.53 – 7.47 (m, 2H), 7.25 – 7.19 (m, 2H), 7.12 – 7.07 (m, 2H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.4, 148.8, 135.5, 133.5, 130.2, 130.0, 129.8, 128.5, 121.4, 20.9.

*m-tolyl benzoate* ***(6n)***[18] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6n as a colorless oil (33 mg, 79%); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.16 (m, 2H), 7.65 – 7.59 (m, 1H), 7.53 – 7.47 (m, 2H), 7.34 – 7.27 (m, 1H), 7.10 – 6.98 (m, 3H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.3, 151.0, 139.7, 133.5, 130.2, 129.7, 129.2, 128.6, 126.7, 122.3, 118.7, 21.4.

*o-tolyl benzoate* ***(6o)***[19] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6o as a colorless oil (29 mg, 68%); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.20 (m, 2H), 7.67 – 7.60 (m, 1H), 7.54 – 7.48 (m, 2H), 7.29 – 7.22 (m, 2H), 7.21 – 7.17 (m, 1H), 7.15 – 7.11 (m, 1H), 2.24 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) 164.9, 149.6, 133.6, 131.2, 130.3, 130.2, 129.6, 128.6, 127.0, 126.1, 122.0, 16.3.

*4-methoxyphenyl benzoate* ***(6p)***[18] Purification by chromatography (petroleum ether/EtOAc = 30:1) afforded 6p as a white solid (35 mg, 76%), mp: 87-88 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.09 (m, 2H), 7.58 – 7.52 (m, 1H), 7.46 – 7.40 (m, 2H), 7.07 – 7.04 (m, 2H), 6.88 – 6.84 (m, 2H), 3.75 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.5, 157.4, 144.5, 133.5, 130.1, 129.7, 128.5, 122.4, 114.6, 55.6.

*2,4-dimethylphenyl benzoate* ***(6q)***[24] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6q as a colorless oil (36 mg, 80%); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.18 (m, 2H), 7.66 – 7.60 (m, 2H), 7.54 – 7.47 (m, 2H), 7.09 – 6.98 (m, 3H), 2.33 (s, 3H), 2.19 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.1, 147.4, 135.6, 133.5, 131.8, 130.2, 129.9, 129.7, 128.6, 127.5, 121.7, 20.8, 16.2.

*3,4-dimethylphenyl benzoate* ***(6r)***[25] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6r as a white solid (37 mg, 83%), mp: 55-57 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.17 (m, 2H), 7.64 – 7.58 (m, 1H), 7.53 – 7.46 (m, 2H), 7.18 – 7.14 (m, 1H), 7.02 – 6.90 (m, 2H), 2.27 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.5, 148.9, 138.0, 134.2, 133.4, 130.4, 130.2, 129.8, 128.5, 122.6, 118.7, 19.9, 19.2.

*4-(tert-butyl)phenyl benzoate* ***(6s)***[26] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6s as a white solid (42 mg, 82%), mp: 77-78 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.17 (m, 2H), 7.65 – 7.60 (m, 1H), 7.54 – 7.48 (m, 2H), 7.46 – 7.41 (m, 2H), 7.16 – 7.11 (m, 2H), 1.34 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.4, 148.7, 148.6, 133.5, 130.2, 129.8, 128.6, 126.4, 121.0, 34.5, 31.5.

*4-bromophenyl benzoate* ***(6t)***[19] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6t as a white solid (31 mg, 56%), mp: 99-101 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.16 (m, 2H), 7.68 – 7.62 (m, 1H), 7.57 – 7.48 (m, 4H), 7.14 – 7.08 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) 164.9, 150.0, 133.8, 132.6, 130.2, 129.2, 128.7, 123.6, 119.0.

*4-chlorophenyl benzoate* ***(6u)***[18] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6u as a white solid (28 mg, 60%), mp: 87-89 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.19 (m, 2H), 7.70 – 7.64 (m, 1H), 7.58 – 7.51 (m, 2H), 7.45 – 7.39 (m, 2H), 7.23 – 7.16 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.0, 149.5, 133.8, 131.3, 130.2, 129.6, 129.2, 128.7, 123.1.

*4-fluorophenyl benzoate* ***(6v)***[19] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6v as a white solid (30 mg, 70%), mp: 47-48 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.16 (m, 2H), 7.66 – 7.60 (m, 1H), 7.54 – 7.47 (m, 2H), 7.21 – 7.14 (m, 2H), 7.13 – 7.07 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.2, 161.6, 159.1, 146.8, 146.8, 133.7, 130.2, 129.4, 128.6, 123.2, 123.1, 116.3, 116.0.

*naphthalen-2-yl benzoate* ***(6w)***[18] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6w as a white solid (41 mg, 82%), mp: 107-108 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.21 (m, 2H), 7.90 – 7.79 (m, 3H), 7.70 – 7.67 (m, 1H), 7.66 – 7.61 (m, 1H), 7.55 – 7.45 (m, 4H), 7.37 – 7.33 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.4, 148.7, 133.9, 133.7, 131.6, 130.3, 129.6, 129.5, 128.7, 127.9, 127.7, 126.6, 125.8, 121.3, 118.7.

*naphthalen-1-yl benzoate* ***(6x)***[19] Purification by chromatography (petroleum ether/EtOAc = 50:1) afforded 6x as a white solid (42 mg, 85%), mp: 57-58 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.30 (m, 2H), 7.97 – 7.86 (m, 2H), 7.80 – 7.75 (m, 1H), 7.70 – 7.65 (m, 1H), 7.59 – 7.53 (m, 2H), 7.51 – 7.47 (m, 3H), 7.39 – 7.35 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) 165.2, 146.9, 134.8, 133.8, 130.4, 129.5, 128.8, 128.1, 127.0, 126.5, 126.5, 126.1, 125.5, 121.3, 118.3.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedures and characterization data for all reactions and products, including $^1$H and $^{13}$C NMR spectra. 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 interests.

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