Copper-Catalyzed C–N Cross-Coupling of Substituted 2-Halobenzoates with Secondary Acyclic Amides

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Abstract: The copper-catalyzed C–N cross-coupling of poorly nucleophilic acyclic secondary amides with sterically hindered substituted 2-halobenzoates has been demonstrated with 1,4-dimethyl-3,4-dihydro-1*H*-benzo[*e*][1,4]diazepin-5(2*H*)-one (DMBDO) as ligands for the first time. The protocol is effective for the synthesis of hindered tertiary amides. We also found that the alkoxycarbonyl (CO_2R) group has a strong *ortho*-substituent effect on a Goldberg-type C–N coupling reaction.

Key words: copper, N-arylation, cross-coupling, amides, halobenzoates

The amide moiety is an important structural motif in a great number of biologically active compounds and functional molecules.[1] Copper-catalyzed C–N cross-coupling reactions are among the most powerful and versatile tools to construct this structural motif. However, the classic Ullmann reaction[2] and the related Goldberg reaction[3] often require drastic reaction conditions, for example, stoichiometric amounts of copper salts, high temperatures (>150 °C), and the use of polar solvents such as *N*,*N*-dimethylformamide, collidine, and pyridine. In the past few years, a wide range of ligands, including diamines,[4] diimines,[5] amino acids,[6] β-keto esters,[7] ethylene glycols,[8] heptadiones,[9] xantphos, or Xphos[10] have been exploited for these catalytic processes in the presence of catalytic amounts of the copper or palladium catalysts. Although these processes display increased activity and substrate scope relative to their predecessors, a significant limitation to these processes is that they are mostly restricted to primary amides or lactams, and the use of *ortho*-substituted coupling partners in intermolecular reactions is rare. For secondary acyclic amides (which are known to be challenging cross-coupling substrates due to their steric hindrance[10a] and poor nucleophilicity[11]) or sterically hindered coupling partners, only a few isolated examples involving either palladium or copper as catalysts have been described until recently.[9,10a,b,11,12] In continuation of our endeavors devoted to the development of copper-catalyzed coupling reactions,[13] herein we wish to report a copper-catalyzed C–N cross-coupling reaction of secondary acyclic amides with sterically hindered 2-halobenzoates, for which 1,4-dimethyl-3,4-dihydro-1*H*-benzo[*e*][1,4]diazepin-5(2*H*)-one (DMBDO) has been used as a ligand for the first time.

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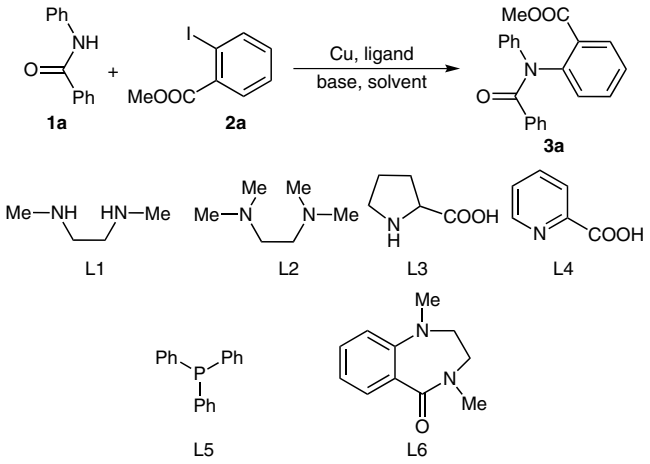
Our initial investigation was based on the reaction of *N*-phenylbenzamide (**1a**) with methyl 2-iodobenzoate (**2a**) in the presence of 20 mol% of copper(II) bromide in toluene at 130 °C under air (Table 1). With cesium carbonate as base, the reaction was observed to give the product methyl 2-(*N*-phenylbenzamido)benzoate (**3a**) in 35% yield after 24 hours in the presence of 40 mol% *N*,*N*′-dimethylethylenediamine (DMEDA; entry 1). The structure of the products was confirmed by an X-ray single-crystal diffraction analysis of **3a** (Figure 1).[14] After screening of various bases and solvents, it was observed that potassium carbonate and xylene are effective for this reaction (entries 2 and 3). Encouraged by these results, we screened a series of common ligands including *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, triphenylphosphine, L-proline, and picolinic acid. However, they all led to lower yields (entries 4–7). Finally, we were pleased to find that the use of 1,4-dimethyl-3,4-dihydro-1*H*-benzo[*e*][1,4]diazepin-5(2*H*)-one (DMBDO) furnished a good isolated yield of coupling product **3a** (entry 8). Further studies revealed that copper(I) iodide exhibited superior catalytic efficiency compared to the other examined copper catalysts (entries 9–11). The catalyst loading could be decreased to 10 mol% without any loss in yield (entry 12), and it could be further decreased to 5 mol% with a slightly decreased yield (entry 13). It is noteworthy that the reaction gave a slightly lower yield under nitrogen atmosphere as compared to air atmosphere (entry 15). Control experiments revealed that no **3a** was obtained in the absence of a copper catalyst (entry 16) and the reaction was very sluggish in the absence of a ligand (entry 17). Additionally, the base potassium phosphate and the solvent dioxane, although suitable for numerous N-arylation reactions,[15] are less effective under our reaction conditions (entry 18). After optimization of the reaction conditions, the following conditions were selected as the standard ones: amide **1** (0.25 mmol), 2-halobenzoate **2** (0.5 mmol), copper(I) iodide (0.025 mmol), ligand L6 (0.05 mmol), and potassium carbonate (3 equiv) in xylene (2 mL) at 130 °C for 24 hours in the presence of air.

A number of *N*-arylbenzamides could be coupled by using this methodology (Table 2). Coupling of substrates bearing methoxy and methyl substituents is efficient (entries 1–3), whereas stronger electron-withdrawing substituents are not tolerated (entry 4). A number of halogenated benzamides reacted with methyl 2-iodobenzoate (**2a**) to give the tertiary acyclic amides in good yields (entries 5–8). These groups can facilitate subsequent chemoselective processes. It was also noted that sterically hindered sec-

Table 1 Optimization of Reaction Conditions[a]



Entry	Cu cat. (mol%)	Ligand	Solvent	Base	Yield[b] (%)
1	$CuBr_2$ (20)	L1	toluene	Cs_2CO_3	35
2	$CuBr_2$ (20)	L1	DMF	K_2CO_3	22
3	$CuBr_2$ (20)	L1	xylene	K_2CO_3	70
4	$CuBr_2$ (20)	L2	xylene	K_2CO_3	37
5	$CuBr_2$ (20)	L3	xylene	K_2CO_3	68
6	$CuBr_2$ (20)	L4	xylene	K_2CO_3	49
7	$CuBr_2$ (20)	L5	xylene	K_2CO_3	64
8	$CuBr_2$ (20)	L6	xylene	K_2CO_3	75
9	CuI (20)	L6	xylene	K_2CO_3	84
10	CuCl (20)	L6	xylene	K_2CO_3	19
11	CuO (20)	L6	xylene	K_2CO_3	0
12	CuI (10)	L6	xylene	K_2CO_3	85
13	CuI (5)	L6	xylene	K_2CO_3	78
14	CuI (10)	L6	xylene	K_2CO_3	29[c]
15	CuI (10)	L6	xylene	K_2CO_3	79[d]
16	none	L6	xylene	K_2CO_3	0
17	CuI (10)	none	xylene	K_2CO_3	<5
18	CuI (10)	L6	dioxane	K_3PO_4	55

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), base (3 equiv), cat., solvent (2 mL), 130 °C, 24 h, under air.
[b] Isolated yield.
[c] Reaction run at 130 °C for 8 h.
[d] Under N_2 atmosphere.

ondary acyclic amides are tolerated under these reaction conditions (entries 8 and 9). Next we examined the effect of the benzamide group on the efficiency of the reaction. Both electron-rich and electron-deficient amide groups were well tolerated, leading to excellent isolated yields of the desired products (entries 10–14). In contrast to electron-rich groups, electron-deficient substrates gave slightly better yields, except with the starting compound derived from 4-nitrobenzoic acid (entry 14). Thus, we were able to perform the coupling of *N*-arylarylamides substituted with electron-donating or electron-withdrawing groups on the aromatic rings (entries 15 and 16). The cross-coupling reaction was also extended to an *N*-alkylarylamide (entry 17) and *N*-arylacetamide (entry 18) with 2-halobenzoates, the corresponding coupling products being obtained in good isolated yields. In the case of *N*-(2-chlorophenyl)benzamide (entry 8), coupling with **2a** gave a mixture of two stereoisomeric tertiary amides, as demonstrated by NMR spectroscopy of **3i** under different temperatures.[14] The products **3j**, **3n** and **3s** (entries 9, 13, 18) also were isomer mixtures. The slower rate of configurational change may derive from rotational barriers in these compounds.

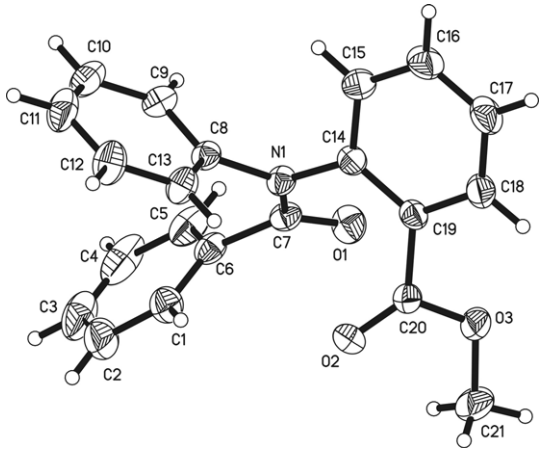


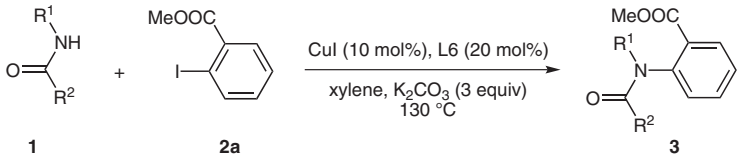
Figure 1 ORTEP representation of the crystal structure of **3a**

The reaction scope was also studied with respect to different substituted 2-halobenzoates, and the results are summarized in Table 3. Among the three methyl 2-halobenzoates (X = I, Br, Cl), methyl 2-iodobenzoate showed the best results, affording methyl 2-(*N*-phenylbenzamido)benzoate in excellent yield, whereas methyl 2-chlorobenzoate failed to give the desired products under the standard conditions (entries 1–3). Good isolated yields of the desired coupling products could be obtained when ethyl 2-iodobenzoate (entry 4), cyclohexyl 2-iodobenzoate (entry 5), and butyl 2-iodobenzoate (entry 6) were used as the electrophiles. It indicated that the steric hindrance of the ester functional groups have little effect on the reaction. Moreover, substituted 2-halobenzoates were also tolerated (entry 7).

When *meta*- and *para*-substituted halobenzoates were used (methyl 3-iodobenzoate and methyl 4-iodobenzoate), low yields of corresponding coupling products were obtained (35% and 39% respectively). It indicated that the *ortho* ester functional groups have an accelerating effect on the reaction. The proposed mechanism, based on the above date and previous literature,[16] is shown in Scheme 1. First, the copper(I) species **A** coordinates to the carbonyl group of **2**; this is followed by oxidative addition to give a copper(III)–aryl species **B**, just as illustrated by Ma

for similar copper-catalyzed C–O coupling reactions.[16e] After reaction of **B** with amide **1** and base to give a copper(III) complex **C**, reductive elimination occurs to afford the expected compound **3** and regenerate the catalytic copper(I) species **A** in the process.

Table 2 N-Arylation of Various Amides with Methyl 2-Iodobenzoate[a]



1 **2a** **3**

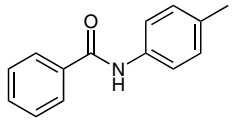
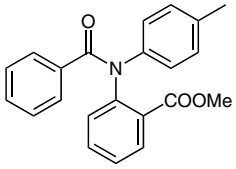
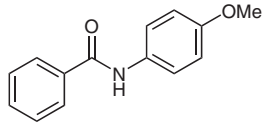
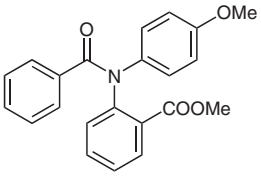
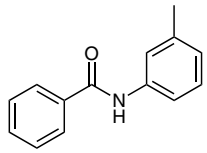
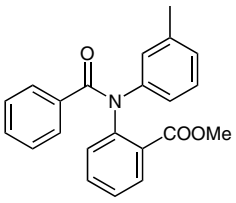
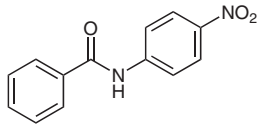
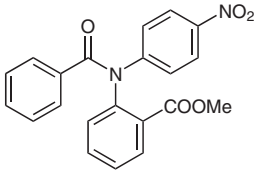
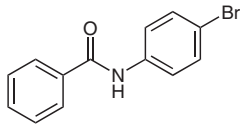
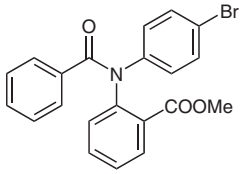
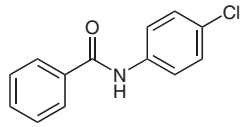
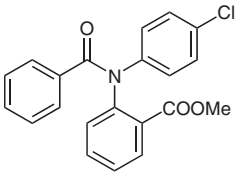
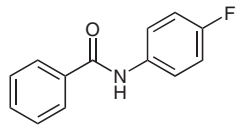
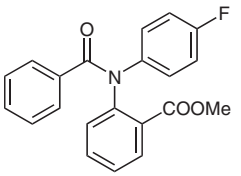
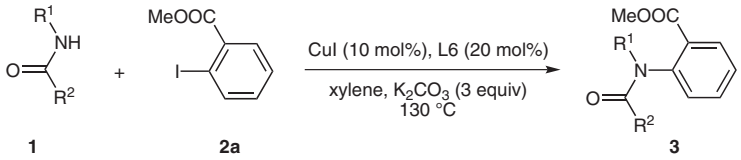
Entry	**1**	**3**	Yield (%)[b]
1		**3b** 	81
2		**3c** 	93
3		**3d** 	68
4		**3e** 	0
5		**3f** 	88
6		**3g** 	83
7		**3h** 	87

Table 2 N-Arylation of Various Amides with Methyl 2-Iodobenzoate[a] (continued)



1 **2a** **3**

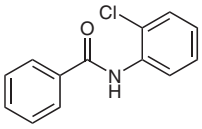
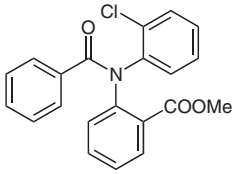
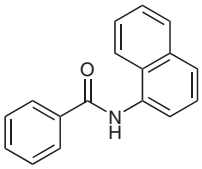
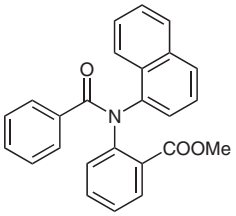
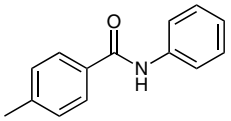
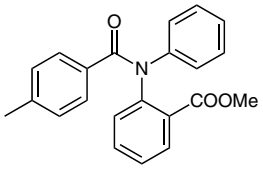
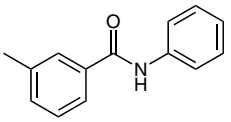
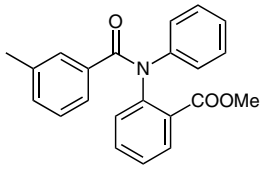
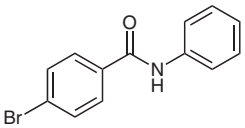
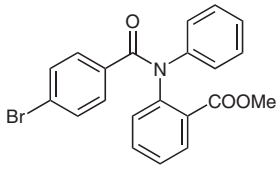
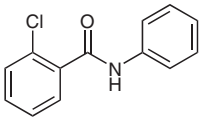
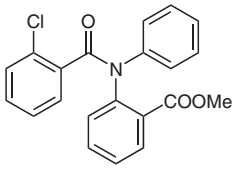
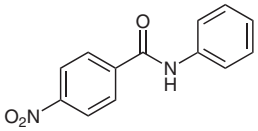
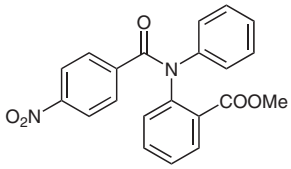
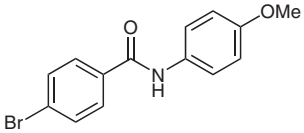
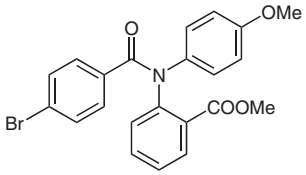
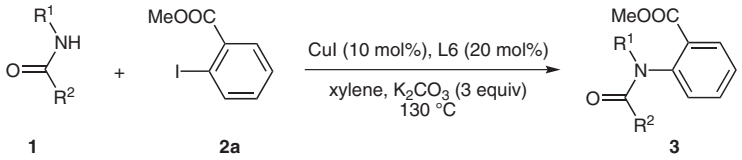
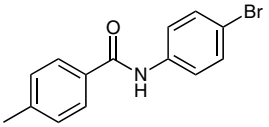
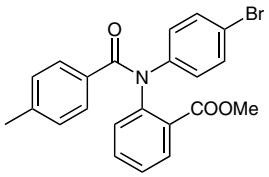
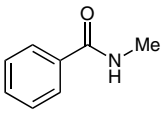
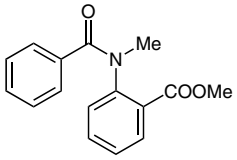
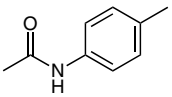
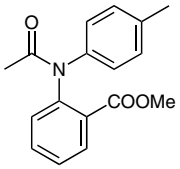
Entry	**1**	**3**	Yield (%)[b]
8			37
9			60
10			75
11			68
12			85
13			77
14			59
15			78

Table 2 N-Arylation of Various Amides with Methyl 2-Iodobenzoate[a] (continued)

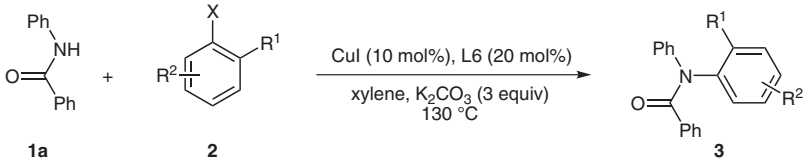


1 2a 3

Entry	1	3	Yield (%)[b]
16		**3q** 	68
17		**3r** 	70
18		**3s** 	80

[a] Reaction conditions: **1** (0.25 mmol), **2a** (0.5 mmol), base (3 equiv), CuI (0.025 mmol), L (0.05 mmol), xylene (2 mL), 130 °C, 24 h, under air.
[b] Yields of isolated products after chromatographic purification.

Table 3 The Reaction Scope for the Synthesis of 2-Halobenzoates[a]



1a 2 3

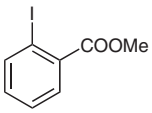
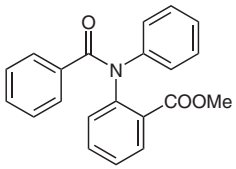
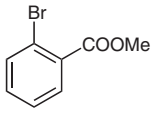
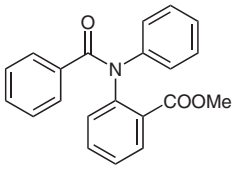
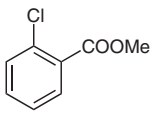
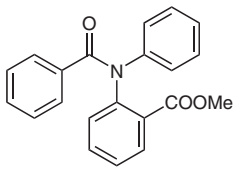
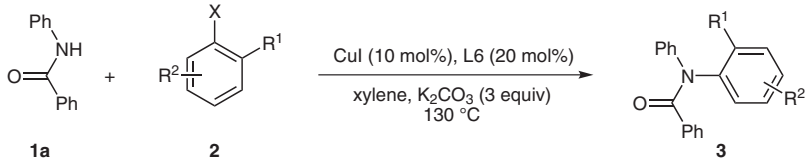
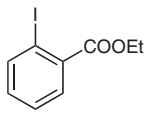
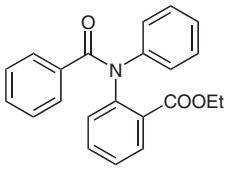
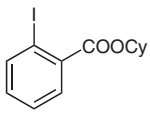
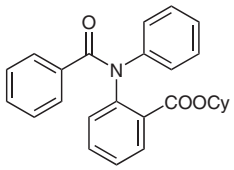
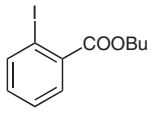
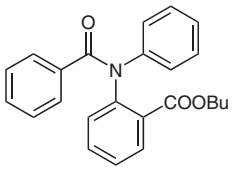
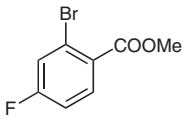
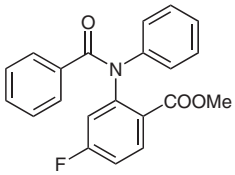
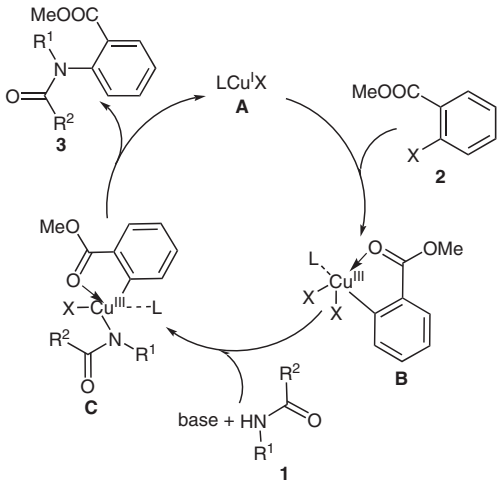
Entry	2	3	Yield (%)[b]
1		**3a** 	85
2		**3a** 	64
3		**3a** 	0

Table 3 The Reaction Scope for the Synthesis of 2-Halobenzoates[a] (continued)



Entry	2	3	Yield (%)[b]
4		**3t** 	80
5		**3u** 	80
6		**3v** 	83
7		**3w** 	53

[a] Reaction conditions: **1a** (0.25 mmol), **2** (0.5 mmol), base (3 equiv), CuI (0.025 mmol), L (0.05 mmol), xylene (2 mL), 130 °C, 24 h, under air.
[b] Yields of isolated products after chromatographic purification



Scheme 1 Proposed reaction mechanism

In conclusion, we have developed a C–N cross-coupling method for the reaction of synthetically useful aromatic and aliphatic secondary amides with substituted 2-halobenzoates. We also found that the CO_2R group has a strong *ortho*-substituent effect on the Goldberg-type C–N coupling reaction. This protocol provides a novel synthetic route to an array of hindered tertiary amides, with inexpensive copper as the catalyst. Further efforts for the applications of this catalytic system are ongoing in our laboratory, along with further mechanistic studies.

All reactions were carried out under an air atmosphere in oven-dried glassware with magnetic stirring. Unless otherwise noted, all materials were obtained from commercial suppliers and were used without further purification. Amides[9] and L6[17] were prepared according to the reported procedures. All solvents were reagent grade. Dichloromethane, toluene and xylene were freshly distilled from CaH_2 prior to use. DMF was dried over 4 Å molecular sieves overnight prior to use. 1,4-Dioxane were freshly distilled from sodium/benzophenone under nitrogen prior to use. Unless otherwise noted, organic extracts were dried with Na_2SO_4, filtered through a fritted glass funnel, and concentrated with a rotary evaporator (20–30 mmHg). Flash chromatography was performed with silica gel (200–300 mesh) using the mobile phase indicated. Unless otherwise noted, NMR spectra were recorded for ^{1}H NMR at 400 MHz or 500 MHz, and ^{13}C NMR at 100 MHz or 125 MHz using TMS as internal stan-

dard. Mass spectrometry data were collected on an HRMS-APCI instrument or a low-resolution MS instrument using EI or ESI ionization. Melting points were measured with a micro melting point apparatus.

2-Amidobenzoates 3 by N-Arylation of Secondary Acyclic Amides 1; General Procedure

The 2-halobenzoate **2** (0.5 mmol, 2 equiv) was added under air to a mixture of the amide **1** (0.25 mmol, 1 equiv), CuI (5 mg, 0.025 mmol, 10 mol%), K_2CO_3 (0.1 g, 0.75 mmol, 3 equiv), and L6 (0.05 mmol, 20 mol%) in anhyd xylene (2 mL) in a 25 mL reaction tube. The tube was sealed and the mixture was allowed to stir electromagnetically in an oil bath at 130 °C for 24 h. After the mixture had cooled to r.t., H_2O (10 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic phase was dried (Na_2SO_4), filtered, and concentrated. The residue was purified by flash column chromatography (silica gel, EtOAc–PE); this afforded the corresponding product **3**.

Methyl 2-(*N*-Phenylbenzamido)benzoate (3a)

Yield: 70.3 mg (85%); white solid; mp 130–132 °C.

IR (KBr): 1726, 1662, 1598, 1489, 1455, 1337, 1283, 1087, 956, 760, 691, 620 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.93 (s, 1 H), 7.47 (dd, *J* = 18.3, 7.4 Hz, 3 H), 7.36–7.02 (m, 10 H), 3.80 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.6, 166.4, 143.8, 143.2, 135.9, 132.9, 131.1, 130.1, 129.1, 128.9, 127.8, 127.5, 126.8, 126.2, 52.4.

ESI-MS: *m*/*z* = 332.0 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{21}H_{17}NO_3$: 331.1208; found: 331.1205.

Methyl 2-(*N*-*p*-Tolylbenzamido)benzoate (3b)

Yield: 69.9 mg (81%); yellow oil.

IR (KBr): 1724, 1659, 1489, 1335, 1293, 1256, 1085, 757, 718, 623 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.97 (s, 1 H), 7.47 (dd, *J* = 17.3, 8.0 Hz, 3 H), 7.23 (dt, *J* = 34.3, 7.4 Hz, 4 H), 7.15–6.75 (m, 5 H), 3.80 (s, 3 H), 2.27 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.58, 166.44, 143.22, 141.30, 136.10, 136.00, 132.88, 131.05, 130.01, 129.57, 129.07, 128.75, 127.76, 127.48, 126.69, 126.00, 52.36, 20.97.

ESI-MS: *m*/*z* = 346.0 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{22}H_{19}NO_3$: 345.1365; found: 345.1361.

Methyl 2-[*N*-(4-Methoxyphenyl)benzamido]benzoate (3c)

Yield: 83.9 mg (93%); white solid; mp 154–155 °C.

IR (KBr): 1720, 1659, 1507, 1343, 1247, 1083, 1028, 700, 624 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.97 (s, 1 H), 7.47 (s, 3 H), 7.36–7.15 (m, 5 H), 7.08 (d, *J* = 32.2 Hz, 2 H), 6.71 (s, 2 H), 3.82 (s, 3 H), 3.74 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.59, 166.51, 157.82, 136.01, 132.85, 130.98, 129.94, 129.01, 127.78, 126.64, 114.19, 55.36, 52.38.

ESI-MS: *m*/*z* = 362.1 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{22}H_{19}NO_4$: 361.1314; found: 361.1319.

Methyl 2-(*N*-*m*-Tolylbenzamido)benzoate (3d)

Yield: 58.7 mg (68%); yellow oil.

IR (KBr): 1724, 1654, 1598, 1343, 1275, 1084, 756, 701, 632 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 20.6 Hz, 1 H), 7.56–7.37 (m, 3 H), 7.34–7.23 (m, 2 H), 7.19 (t, *J* = 7.5 Hz, 2 H), 7.16–7.03 (m, 2 H), 6.95 (s, 3 H), 3.80 (s, 3 H), 2.24 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.58, 166.42, 143.72, 143.22, 138.88, 135.98, 132.89, 131.04, 130.06, 129.05, 128.77, 128.62, 128.05, 127.73, 127.12, 126.72, 124.90, 52.35, 21.25.

ESI-MS: *m*/*z* = 346.0 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{22}H_{19}NO_3$: 345.1365; found: 345.1368.

Methyl 2-[*N*-(4-Bromophenyl)benzamido]benzoate (3f)

Yield: 90.2 mg (88%); pale yellow solid; mp 153–155 °C.

IR (KBr): 1716, 1665, 1599, 1483, 1344, 1282, 1271, 813, 713, 622 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.91 (s, 1 H), 7.46 (d, *J* = 6.7 Hz, 3 H), 7.31 (dd, *J* = 16.1, 8.3 Hz, 4 H), 7.22 (t, *J* = 7.4 Hz, 2 H), 7.11 (d, *J* = 7.8 Hz, 1 H), 7.04 (d, *J* = 20.2 Hz, 2 H), 3.79 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.38, 166.14, 142.84, 137.98, 135.48, 133.09, 132.01, 131.30, 130.38, 129.03, 128.83, 127.95, 127.20, 119.70, 52.43.

ESI-MS: *m*/*z* = 409.9 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{21}H_{16}BrNO_3$: 409.0314; found: 409.0314.

Methyl 2-[*N*-(4-Chlorophenyl)benzamido]benzoate (3g)

Yield: 75.8 mg (83%); white solid; mp 135–137 °C.

IR (KBr): 1717, 1665, 1488, 1329, 1288, 1271, 1088, 714, 625 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.91 (s, 1 H), 7.47 (d, *J* = 6.9 Hz, 3 H), 7.31 (dd, *J* = 15.9, 8.3 Hz, 2 H), 7.21 (dd, *J* = 18.0, 10.6 Hz, 4 H), 7.14–7.01 (m, 3 H), 3.80 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.45, 166.18, 142.89, 135.51, 133.08, 131.80, 131.29, 130.37, 129.05, 128.83, 128.54, 127.95, 127.18, 52.44.

ESI-MS: *m*/*z* = 366.0 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{21}H_{16}ClNO_3$: 365.0819; found: 365.0833.

Methyl 2-[*N*-(4-Fluorophenyl)benzamido]benzoate (3h)

Yield: 75.9 mg (87%); pale yellow solid; mp 123–124 °C.

IR (KBr): 1724, 1659, 1506, 1449, 1334, 1277, 1082, 819, 718, 623 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.95 (s, 1 H), 7.46 (d, *J* = 7.0 Hz, 3 H), 7.29 (t, *J* = 7.4 Hz, 2 H), 7.25–7.03 (m, 5 H), 6.92 (s, 2 H), 3.81 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.51, 166.32, 161.68, 159.72 (d, *J* = 245.0 Hz), 135.65, 133.00, 131.17, 130.22, 128.99, 128.78 (d, *J* = 26.3 Hz), 127.89, 127.02, 115.92, 115.74 (d, *J* = 22.5 Hz), 52.42.

ESI-MS: *m*/*z* = 350.0 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{21}H_{16}FNO_3$: 349.1114; found: 349.1125.

Methyl 2-[*N*-(2-Chlorophenyl)benzamido]benzoate (3i)

Yield: 33.8 mg (37%); mixture of two isomers (100:61); white solid; mp 124–127 °C.

IR (KBr): 1722, 1667, 1598, 1476, 1331, 1259, 1087, 760, 710, 623 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 7.6 Hz, 1 H), 7.59 (d, *J* = 7.4 Hz, 2 H), 7.51–7.39 (m, 2 H), 7.38–7.00 (m, 8 H), 3.86 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 171.06, 166.61, 142.10, 141.55, 141.29, 135.84, 133.02, 132.52, 131.17, 131.02, 130.57, 130.29, 129.32, 129.04, 128.77, 128.32, 128.19, 127.87, 127.73, 127.51, 126.70, 52.39.

ESI-MS: *m*/*z* = 366.2 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{21}H_{16}ClNO_3$: 365.0819; found: 365.0810.

Methyl 2-(*N*-1-Naphthylbenzamido)benzoate (3j)
Yield: 57.2 mg (60%); mixture of two isomers (100:22); yellow oil.

IR (KBr): 1722, 1663, 1597, 1447, 1320, 1264, 1094, 775, 700 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.33 (s, 1 H), 8.00 (dd, *J* = 7.5, 1.4 Hz, 1 H), 7.87–7.74 (m, 1 H), 7.70 (t, *J* = 10.7 Hz, 1 H), 7.56–7.38 (m, 4 H), 7.38–7.16 (m, 5 H), 7.03 (t, *J* = 7.5 Hz, 2 H), 6.85 (d, *J* = 6.9 Hz, 1 H), 3.88 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 172.26, 167.28, 142.41, 139.75, 136.47, 134.65, 132.56, 130.74, 130.17, 129.40, 128.27, 128.08, 127.81, 127.65, 127.33, 126.40, 126.13, 125.90, 125.64, 125.29, 123.78, 52.47.

ESI-MS: *m*/*z* = 382.1 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{25}H_{19}NO_3$: 381.1365; found: 381.1360.

Methyl 2-(4-Methyl-*N*-phenylbenzamido)benzoate (3k)
Yield: 64.7 mg (75%); yellow oil.

IR (KBr): 1724, 1660, 1491, 1339, 1293, 1257, 1084, 758, 605 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (s, 1 H), 7.44 (t, *J* = 7.4 Hz, 1 H), 7.38 (d, *J* = 7.9 Hz, 2 H), 7.29 (t, *J* = 7.4 Hz, 1 H), 7.22 (s, 2 H), 7.17–7.04 (m, 4 H), 7.00 (d, *J* = 8.0 Hz, 2 H), 3.78 (s, 3 H), 2.27 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.63, 166.41, 144.01, 143.39, 140.45, 132.90, 131.10, 129.27, 128.88, 128.46, 127.44, 126.71, 126.08, 52.34, 21.42.

ESI-MS: *m*/*z* = 346.0 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{22}H_{19}NO_3$: 345.1365; found: 345.1366.

Methyl 2-(3-Methyl-*N*-phenylbenzamido)benzoate (3l)
Yield: 58.7 mg (68%); pale yellow solid; mp 132–134 °C.

IR (KBr): 1713, 1651, 1590, 1382, 1350, 762, 738, 699 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (s, 1 H), 7.45 (t, *J* = 7.3 Hz, 1 H), 7.34 (s, 1 H), 7.31 (d, *J* = 6.9 Hz, 1 H), 7.20 (d, *J* = 7.3 Hz, 3 H), 7.17–7.01 (m, 6 H), 3.80 (s, 3 H), 2.24 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.73, 166.42, 143.84, 143.19, 137.60, 135.76, 132.87, 131.07, 130.90, 129.80, 128.87, 127.52, 126.77, 126.19, 52.37, 21.25.

ESI-MS: *m*/*z* = 346.0 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{22}H_{19}NO_3$: 345.1365; found: 345.1361.

Methyl 2-(4-Bromo-*N*-phenylbenzamido)benzoate (3m)
Yield: 87.1 mg (85%); yellow oil.

IR (KBr): 1723, 1661, 1589, 1491, 1341, 1258, 1084, 758, 696 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.97 (s, 1 H), 7.46 (d, *J* = 7.0 Hz, 1 H), 7.36 (dd, *J* = 15.7, 8.5 Hz, 5 H), 7.29–6.91 (m, 7 H), 3.80 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.63, 166.27, 142.95, 137.04, 134.84, 133.09, 131.72, 131.55, 131.19, 131.08, 130.78, 129.09, 128.60, 127.62, 127.05, 126.50, 124.70, 52.41.

ESI-MS: *m*/*z* = 410.2 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{21}H_{16}BrNO_3$: 409.0314; found: 409.0313.

Methyl 2-(2-Chloro-*N*-phenylbenzamido)benzoate (3n)
Yield: 70.4 mg (77%); mixture of two isomers (100:30); white solid; mp 155–156 °C.

IR (KBr): 1725, 1662, 1592, 1492, 1437, 1262, 1089, 961, 770, 699, 621 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.97 (dd, *J* = 7.8, 1.1 Hz, 1 H), 7.51 (td, *J* = 7.8, 1.2 Hz, 1 H), 7.39 (ddd, *J* = 25.1, 11.4, 4.3 Hz, 3 H), 7.32–7.18 (m, 4 H), 7.18–6.99 (m, 4 H), 3.94–3.80 (m, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.51, 166.58, 142.78, 141.45, 136.20, 132.88, 131.61, 130.64, 129.96, 129.52, 129.13, 129.09, 128.95, 128.89, 127.61, 127.11, 127.09, 126.27, 52.46.

ESI-MS: *m*/*z* = 366.1 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{21}H_{16}ClNO_3$: 365.0819; found: 365.0822.

Methyl 2-(4-Nitro-*N*-phenylbenzamido)benzoate (3o)
Yield: 55.5 mg (59%); yellow oil.

IR (KBr): 1723, 1665, 1596, 1522, 1343, 1085, 734, 710 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.9 Hz, 3 H), 7.68 (d, *J* = 6.7 Hz, 2 H), 7.51 (s, 1 H), 7.34 (d, *J* = 44.2 Hz, 2 H), 7.12 (t, *J* = 36.1 Hz, 5 H), 3.86 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.58, 166.21, 148.22, 142.95, 142.29, 133.30, 131.15, 129.95, 129.36, 128.89, 128.22, 127.85, 127.37, 127.15, 123.11, 52.49.

ESI-MS: *m*/*z* = 377.0 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{21}H_{16}N_2O_5$: 376.1059; found: 376.1063.

Methyl 2-[4-Bromo-*N*-(4-methoxyphenyl)benzamido]benzoate (3p)
Yield: 85.8 mg (78%); yellow oil.

IR (KBr): 1724, 1654, 1588, 1508, 1343, 1247, 1084, 833, 746, 627 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (s, 1 H), 7.63–7.27 (m, 6 H), 7.20–6.96 (m, 3 H), 6.73 (s, 2 H), 3.82 (s, 3 H), 3.75 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.62, 166.43, 158.01, 142.92, 137.01, 136.57, 135.58, 135.00, 131.06, 130.71, 128.98, 128.83, 128.66, 126.78, 124.43, 114.36, 55.37, 52.40.

ESI-MS: *m*/*z* = 440.0 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{22}H_{18}BrNO_4$: 439.0419; found: 439.0422.

Methyl 2-[*N*-(4-Bromophenyl)-4-methylbenzamido]benzoate (3q)
Yield: 72.1 mg (68%); yellow oil.

IR (KBr): 1724, 1662, 1486, 1327, 1293, 1070, 745, 607 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 (s, 1 H), 7.45 (t, *J* = 7.4 Hz, 1 H), 7.41–7.26 (m, 5 H), 7.10 (d, *J* = 7.9 Hz, 1 H), 7.07–6.83 (m, 4 H), 3.77 (s, 3 H), 2.28 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.44, 166.17, 143.04, 140.77, 137.94, 133.05, 132.49, 131.98, 131.28, 129.20, 128.83, 128.62, 127.05, 126.00, 119.52, 52.39, 21.45.

ESI-MS: *m*/*z* = 424.1 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{22}H_{18}BrNO_3$: 423.0470; found: 423.0475.

Methyl 2-(*N*-Methylbenzamido)benzoate (3r)
Yield: 47.1 mg (70%); yellow oil.

IR (KBr): 1723, 1648, 1598, 1490, 1366, 1259, 1077, 701 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.78–7.72 (m, 1 H), 7.45 (t, *J* = 7.2 Hz, 1 H), 7.28–7.16 (m, 5 H), 7.11 (t, *J* = 7.5 Hz, 2 H), 3.87 (s, 3 H), 3.44 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.51, 165.92, 144.83, 135.73, 133.08, 131.54, 129.82, 129.61, 128.36, 127.61, 127.27, 52.49, 38.33.

ESI-MS: *m*/*z* = 270.0 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{16}H_{15}NO_3$: 269.1052; found: 269.1056.

Methyl 2-(*N*-*p*-Tolylacetamido)benzoate (3s)
Yield: 56.6 mg (80%); mixture of two isomers (100:40); yellow oil.

IR (KBr): 1726, 1674, 1509, 1488, 1291, 1086, 761, 589 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.00–7.82 (m, 1 H), 7.61–7.30 (m, 3 H), 7.28–7.22 (m, 1 H), 7.18 (t, *J* = 11.4 Hz, 1 H), 7.15–7.01 (m, 2 H), 3.92–3.82 (m, 3 H), 2.38–2.24 (m, 3 H), 2.02 (m, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 171.28, 166.77, 142.08, 141.06, 137.76, 132.69, 130.56, 130.23, 129.30, 128.63, 128.56, 128.06, 126.49, 125.80, 52.28, 23.21, 21.07.

ESI-MS: *m*/*z* = 284.0 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{17}H_{17}NO_3$: 283.1208; found: 283.1205.

Ethyl 2-(*N*-Phenylbenzamido)benzoate (3t)
Yield: 69.1 mg (80%); white solid; mp 90–92 °C.

IR (KBr): 2987, 1719, 1655, 1598, 1490, 1346, 1258, 1080, 757, 701, 625 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.90 (s, 1 H), 7.49 (d, *J* = 7.6 Hz, 2 H), 7.43 (t, *J* = 7.0 Hz, 1 H), 7.35–7.24 (m, 3 H), 7.19 (t, *J* = 7.6 Hz, 4 H), 7.12 (d, *J* = 7.6 Hz, 3 H), 4.26 (d, *J* = 6.3 Hz, 2 H), 1.27 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.49, 165.96, 143.82, 143.17, 135.98, 132.77, 131.00, 130.11, 129.35, 129.12, 128.90, 127.79, 127.53, 126.87, 126.22, 61.39, 14.20.

ESI-MS: *m*/*z* = 346.0 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{22}H_{19}NO_3$: 345.1365; found: 345.1364.

Cyclohexyl 2-(*N*-Phenylbenzamido)benzoate (3u)
Yield: 77.8 mg (78%); yellow oil.

IR (KBr): 2936, 2857, 1716, 1663, 1596, 1491, 1339, 1255, 1082, 757, 696, 625 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 7.0 Hz, 1 H), 7.50 (d, *J* = 7.4 Hz, 2 H), 7.42 (t, *J* = 7.3 Hz, 1 H), 7.34–7.07 (m, 10 H), 4.89 (s, 1 H), 1.86 (s, 2 H), 1.69 (s, 2 H), 1.50 (dd, *J* = 26.0, 17.4 Hz, 2 H), 1.39–1.30 (m, 2 H), 1.25 (dd, *J* = 14.1, 8.4 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.34, 165.27, 143.79, 143.17, 136.09, 132.52, 130.88, 129.96, 129.90, 129.11, 128.78, 127.72, 126.85, 126.08, 73.76, 31.49, 26.92, 25.37, 23.74.

ESI-MS: *m*/*z* = 400.3 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{26}H_{25}NO_3$: 399.1834; found: 399.1831.

Butyl 2-(*N*-Phenylbenzamido)benzoate (3v)
Yield: 77.4 mg (83%); yellow oil.

IR (KBr): 2959, 2872, 1720, 1663, 1597, 1491, 1339, 1255, 1082, 757, 696, 624 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 7.4 Hz, 1 H), 7.57–7.40 (m, 3 H), 7.35–7.03 (m, 10 H), 4.20 (s, 2 H), 1.72–1.56 (m, 2 H), 1.37 (d, *J* = 6.7 Hz, 2 H), 0.90 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.47, 165.92, 143.77, 143.23, 135.97, 132.72, 130.95, 130.07, 129.35, 129.11, 128.83, 128.60, 127.75, 127.47, 126.85, 126.16, 65.21, 30.57, 19.13, 13.69.

ESI-MS: *m*/*z* = 374.1 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{24}H_{23}NO_3$: 373.1678; found: 373.1680.

Methyl 4-Fluoro-2-(*N*-phenylbenzamido)benzoate (3w)
Yield: 46.3 mg (53%); yellow oil.

IR (KBr): 1725, 1664, 1593, 1495, 1334, 1259, 1109, 755, 700, 414 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 6.5 Hz, 1 H), 7.49 (d, *J* = 7.5 Hz, 2 H), 7.32–7.20 (m, 5 H), 7.15 (dd, *J* = 17.4, 9.9 Hz, 3 H), 7.01 (t, *J* = 7.2 Hz, 1 H), 6.81 (d, *J* = 8.9 Hz, 1 H), 3.80 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.60, 166.05, 165.51, 164.02 (d, *J* = 253.8 Hz), 143.42, 135.50, 133.32, 133.24 (d, *J* = 10.0 Hz), 130.39, 129.16, 127.88, 127.60, 126.66, 125.04, 116.81, 114.11, 113.94 (d, *J* = 21.3 Hz), 52.43.

ESI-MS: *m*/*z* = 350.0 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{21}H_{16}FNO_3$: 349.1114; found: 349.1112.

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