Nickel-Catalyzed Cross-Electrophile Coupling of 1,2,3-Benzotriazin-4(3H)-ones with Aryl Bromides

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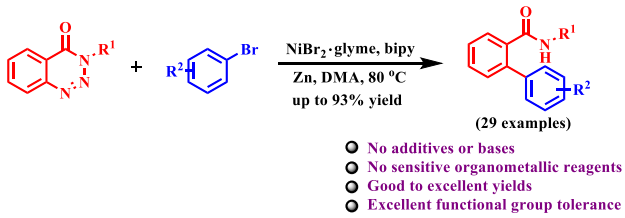
Supporting Information Placeholder



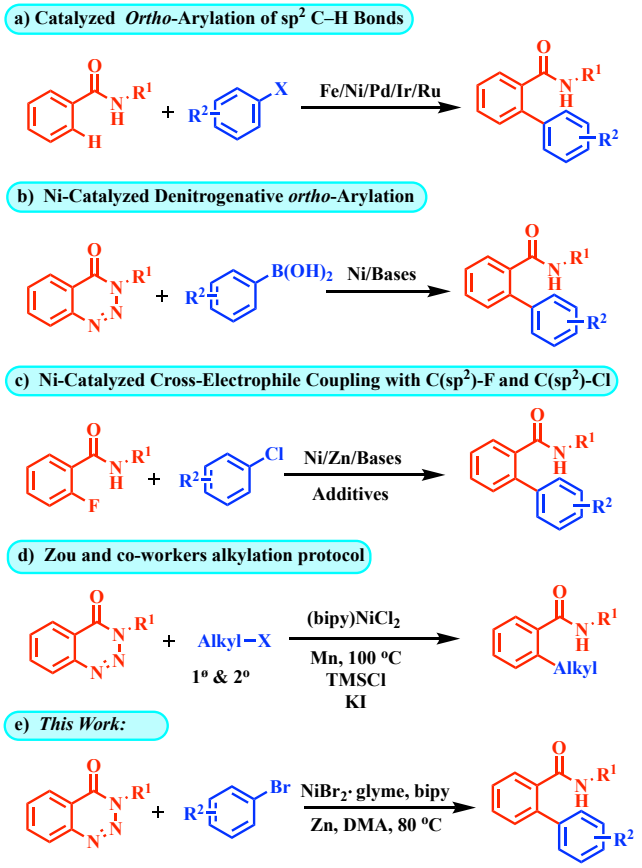
ABSTRACT: The nickel-catalyzed cross-electrophile coupling of 1,2,3-benzotriazin-4(3H)-ones with aryl bromides to generate a diverse array of *ortho*-arylated benzamide derivatives has been developed. The reaction displayed good functional group tolerance with Zn as the reductant. The key to this transformation is the ring opening of benzotriazinones, which undergo a denitrogenative process to obtain various benzamide derivatives (29 examples, 42−93% yield). The scalability of this transformation is demonstrated.

INTRODUCTION

Benzamide derivatives are important building blocks commonly found in pesticides[1] and medications.[2] They are also useful precursors for the preparation of supramolecular polymers.[3] In addition, benzamide derivatives act as chelating ligands that coordinate to transition metals.[4] Due to their popularity, the development of efficient and versatile methods to synthesize *ortho*-arylated benzamide derivatives remains desirable.

The methods for *ortho*-arylation of benzamide derivatives often rely on the ability of this group to coordinate to metals. As a result, the transition-metal-catalyzed (including Fe,[5] Ni,[6] Pd,[7] Ir,[8] Ru[9]) directed *ortho*-arylation of sp^2 C–H bonds has seen extensive development (Scheme 1a). A less common approach is the nickel-catalyzed denitrogenative *ortho*-arylation of benzotriazinones (Scheme 1b). In 2018, Cheng,[10] Mannathan[11] and their coworkers developed nickel-catalyzed denitrogenative cross-coupling reactions of 1,2,3-benzotriazin-4(3H)-ones with organoboronic reagents to provide *ortho*-arylated benzamides. Like other couplings using boronic acid derivatives, these reactions require base. The denitrogenative strategy can be applied to the preparation of isoquinolones and isoindolinones by using various unsaturated substrates instead of boronic acids, such as alkene,[12] alkyne[13] and isocyanides.[14] More recently, Chatani[15] and coworkers advanced a nickel-catalyzed cross-electrophile coupling reaction between benzamides bearing a 2-F or 2-Cl in the presence of base, reductant and additives (Scheme 1c). Of note, in the final stages of submission of this work, Zou[16] and co-workers reported a related *ortho-alkylation* of 1,2,3-benzotriazin-4(3H)-ones (Scheme 1d).

Inspired by the elegant efforts in Schemes 1a-c, and with our interests in cross-electrophile coupling reactions,[17] we report herein the nickel-catalyzed denitrogenative cross-coupling of 1,2,3-benzotriazin-4(3H)-ones with aryl bromides under reductive conditions (Scheme 1e). This method was employed to generate a diverse array of *ortho*-arylated benzamide derivatives. The method circumvents the use of organometallic reagents and bases. This reaction not only broadens the classes of electrophiles in cross-electrophile coupling reactions but also provides a new route for the construction of *ortho*-arylated benzamides.



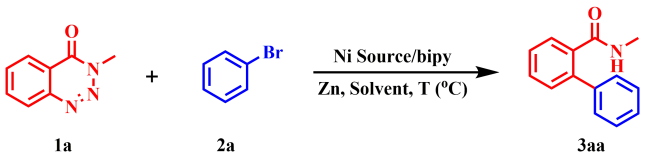
Scheme 1. Transition-Metal-Catalyzed *Ortho*-Arylation of Benzamide Derivatives

RESULTS AND DISCUSSION

Motivated by our previous studies on nickel-catalyzed cross-electrophile coupling reactions,[17a, 17b, 18] we initiated our research by choosing Ni(COD)$_2$/bipy as catalyst precursors, 3-methylbenzo[d][1,2,3]triazin-4(3H)-one **1a** and bromobenzene **2a** as model substrates. Zn powder was employed as the reductant with *N,N*-dimethylacetamide (DMA) as the solvent at 60 ºC for 12 h. We were pleased to find that the denitrogenative *ortho*-arylated product **3aa** was produced in 56% isolated yield (Table 1, entry 1). Next, we screened different nickel sources using bipy as ligand (Table 1, entries 2–6). From these experiments, we observed that NiBr$_2$•glyme provided the most improved yield of the denitrogenative cross-coupling product **3aa** (68% yield, Table 1, entry 6). Other nickel sources [NiBr$_2$, NiI$_2$, NiBr$_2$•DME, NiCl$_2$(PPh$_3$)$_2$] proved less effective (Table 1, entries 2–5, for details on nickel sources and ligands screening see the Supporting Information). Based on these results, NiBr$_2$•glyme was used as catalyst.

We next moved to study the effect of solvent on the coupling yield (Table 1, entries 7–9). It was observed that when tetrahydrofuran (THF) was used, the cross-coupled product **3aa** was obtained in 20% isolated yield (Table 1, entry 7). Non-coordinating toluene provided **3aa** in only 17% isolated yield (Table 1, entry 8), while CH$_3$CN did not afford the desired cross-coupling product (Table 1, entry 9). To increase the yield of **3aa**, we next examined the impact of temperature. Increasing the temperature from 60 to 80 °C resulted in an increase in the desired product to 87% isolated yield (Table 1, entry 10). Further increasing the temperature from 80 to 100 °C, however, led to a decrease in the yield to 73% (Table 1, entry 11). It should be noted that aryl bromides are the most suitable electrophiles in the system (for details on aryl electrophile screening see the Supporting Information). Control experiments revealed that NiBr$_2$•glyme and Zn powder were crucial for this reaction; no reaction occurred in their absence (Table 1, entries 12 and 13). Ultimately, our optimized conditions for this transformation were 3-methylbenzo[d][1,2,3]triazin-4(3H)-one (**1a**, 1.0 equiv), bromobenzene (**2a**, 2.0 equiv), Zn powder (2 equiv), NiBr$_2$•glyme (10 mol %) and bipy (15 mol %) in DMA (0.5 M) at 80 °C for 12 h.

Table 1. Optimization of the Reaction Conditions[a]



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

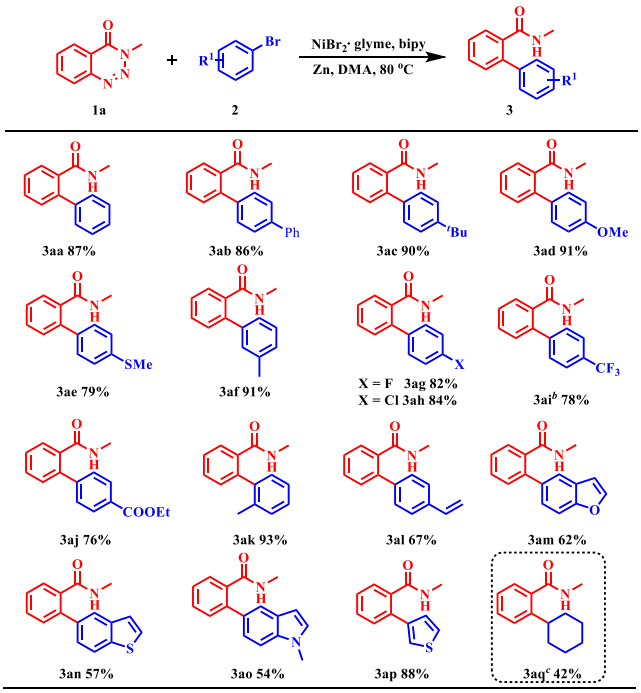
Entry	Ni source	Solvent	Temp (ºC)	Yield[b] (%)
1	Ni(COD)$_2$	DMA	60	56
2	NiBr$_2$	DMA	60	17
3	NiI$_2$	DMA	60	54
4	NiBr$_2$·DME	DMA	60	42
5	NiCl$_2$(PPh$_3$)$_2$	DMA	60	27
6	NiBr$_2$·glyme	DMA	60	68
7	NiBr$_2$·glyme	THF	60	20
8	NiBr$_2$·glyme	toluene	60	17
9	NiBr$_2$·glyme	CH$_3$CN	60	trace
10	NiBr$_2$·glyme	DMA	80	87
11	NiBr$_2$·glyme	DMA	100	73
12	no NiBr$_2$·glyme			0
13	no Zn powder			0

[a]Reactions were conducted on a 0.1 mmol scale using **1a** (1 equiv), **2a** (2 equiv), Ni source (10 mol %), and bipy (15 mol %), solvent (0.5 M). [b]Isolated yields. Trace means the yield was <5%.

With the optimized reaction conditions in hand (Table 1, entry 10), we next investigated the scope of aryl bromides in the cross-electrophile coupling reaction. A wide range of aryl bromides with different substituents reacted smoothly with 3-methylbenzo[d][1,2,3]triazin-4(3H)-one **1a** to afford the corresponding *ortho*-arylated benzamide derivatives in good to excellent yields (54–93%) (Table 2). As noted, the parent bromobenzene **2a** reacted to give the cross-coupling product **3aa** in 87% isolated yield. Aryl bromides containing electron-neutral and donating groups, such as 4-Ph, 4-^{t}Bu, 4-OMe, 4-SMe and 3-Me exhibited good to excellent reactivities, affording **3ab**–**3af** in 79–91% yields. In addition, this transformation is amenable to substrates bearing electronegative and electron-withdrawing groups, such as 4-F, 4-Cl, 4-CF$_3$ and 4-CO$_2$Et affording the corresponding products **3ag**–**3aj** with excellent chemoselectivity in 76–84% yield. A more sterically hindered aryl bromide, 2-bromotoluene, was a viable coupling partner, providing the product **3ak** in 93% yield. The reaction was found to be chemoselective; when an aryl bromide containing an olefin was employed in this transformation, no Heck-type products were observed and the cross-coupling product was obtained in 67% yield. To our delight, heterocyclic-containing coupling partners, including benzofuran, benzothiophene, indole, and

thiophene, were tolerated under our standard conditions, generating the arylated products **3am**–**3ap** in 54–88% yields. Although the Zou group reported the denitrogenative alkylation reaction (Scheme 1d), we were curious if our conditions would also lead to alkyl coupling. Therefore, we checked our reaction conditions with cyclohexyl bromide and **1a** and obtained the alkylated product with 42% isolated yield.

Table 2. Substrate Scope of Aryl Bromides[a]

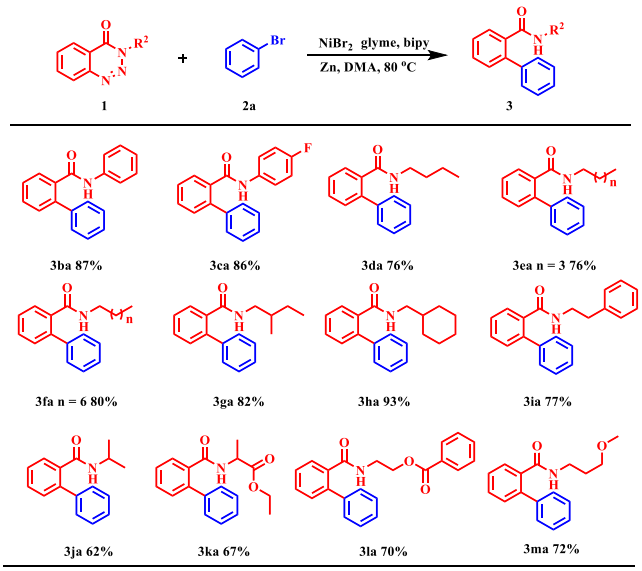


[a]Reactions performed on a 0.1 mmol scale using **1a** (1 equiv), **2** (2 equiv), $NiBr_2$•glyme (10 mol %), bipy (15 mol %), Zn powder (2 equiv) and DMA (0.5 M) under 80 °C for 12h. [b]3.0 equiv of aryl bromide was used. [c]Cyclohexyl bromide was used as electrophile.

This protocol was also successfully applied in the cross-coupling of various 1,2,3-benzotriazin-4(3H)ones with bromobenzene, providing the *ortho*-arylated benzamide derivatives **3ba**–**3ma** in 62–93% yield (Table 3). *N*-Aryl-substituted 1,2,3-benzotriazin-4(3H)-ones **2b** and **2c** were examined. It was found that these substrates participated in this transformation affording **3ba** and **3ca** in 87% and 86% yield, respectively.

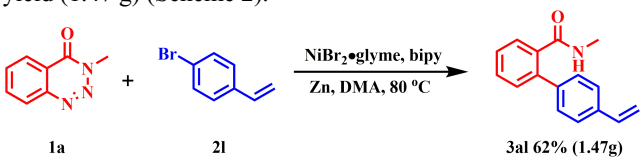
N-Alkyl-substituted benzotriazinones **2d**–**2i** were also examined. Coupling partners with primary *N*-alkyl-groups coupled with bromobenzene to afford **3da**–**3ia** in 76 – 93% isolated yield. Secondary *N*-alkyl-substituted 1,2,3-benzotriazin-4(3H)-one was also compatible under the standard conditions, providing **3ja** in 62% yield. In addition, more challenging functionalized *N*-alkyl-substituted benzotriazinones bearing esters and ether were compatible under standard conditions, providing the corresponding products **3ka**–**3ma** in 67 – 72% yields.

Table 3. Substrate Scope of 1,2,3-Benzotriazin-4(3H)-ones[a]



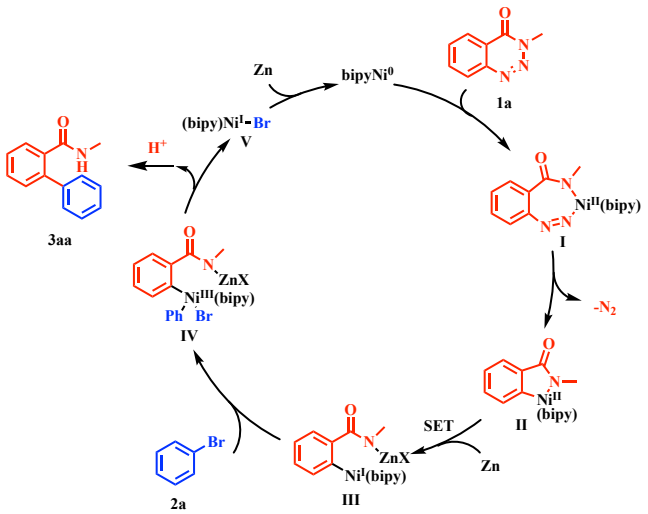
[a]Reactions performed on a 0.1 mmol scale using **1** (1 equiv), **2a** (2 equiv), $NiBr_2$•glyme (10 mol %), bipy (15 mol %), Zn powder (2 equiv) and DMA (0.5 M) under 80 °C for 12h.

To test the scalability of this transformation, 10.0 mmol of **1a** was coupled with 4-bromostyrene **2l** under the standard conditions**.** The cross-coupling product **3al** was isolated in 62% yield (1.47 g) (Scheme 2).



Scheme 2. Scale-up to 10.0 mmol

A plausible mechanism is advanced in Scheme 3. Initially triazine **1** reacts with L_nNi^0 via N–N oxidative addition to form a seven-membered aza-nickelacyclic intermediate **I**.[13e] This step is followed by the extrusion of N_2 to produce intermediate **II**. The five-membered aza-nickelacycle intermediate (**II**) is proposed to be reduced to a L_nNi^I species (**III**) that undergoes oxidative addition of the aryl bromide **2**. The resulting intermediate (**IV**) subsequently undergoes reductive elimination to afforded *ortho*-arylated benzamide derivative **3aa** and an L_nNi^I–Br species **V**. Intermediate **V** is converted to L_nNi^0 by Zn powder to close the catalytic cycle.



Scheme 3. Proposed Mechanism

CONCLUSIONS

In summary, we have developed a cross-electrophile coupling reaction involving 1,2,3-benzotriazin-4(3H)-ones with aryl bromides. This method has the advantage of circumventing the use of preformed organometallic reagents, which can be air and water sensitive, and avoiding the use of base. Our method is general, scalable, and affords an array of *ortho*-arylated benzamide derivatives in 54–91% yields. We anticipate that this method could be readily adapted for use in the synthesis of fine chemicals and medicinal relevant compounds.

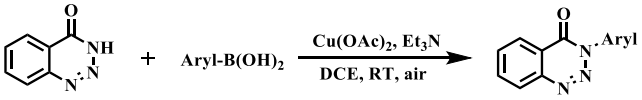
EXPERIMENTAL SECTION

General Information. All reactions were carried out under an atmosphere of dry nitrogen. Anhydrous DMA was purchased from J&K and used without further purification. Zn powder was purchased from Sigma-Aldrich (median ＜10 micron) and used as received. Unless otherwise stated, reagents were commercially available and used as purchased. Chemicals were obtained from Sigma-Aldrich, Acros, Innochem, Energy Chemical, TCI China or Alfa Aesar. The progress of reactions was monitored by thin-layer chromatography using TLC plates and visualized by bromocresol green solution. Flash chromatography was performed with Qingdao Haiyang flash silica gel (200–300 mesh). The NMR spectra were obtained using a Brüker 400 MHz Fourier-transform NMR spectrometer. Chemical shifts were reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants were reported in hertz. The infrared spectra were obtained with KBr plates using a IS10 FT-IR Spectrometer (ThermoFisher Corporation). High resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (Xevo G2-XS QTof) using electrospray ionization (ESI) in positive or negative mode. Melting points were measured using a WRS-1C Melt-Temp apparatus and were uncorrected. Although we have not had any issues with the 1,2,3-benzotriazin-4(3H)-ones, care should always be used when handling compounds with multiple contiguous nitrogen atoms. All reactions were heated in oil baths.

General Procedure A. Synthesis of N-alkyl substituted 1,2,3-triazin-4-ones

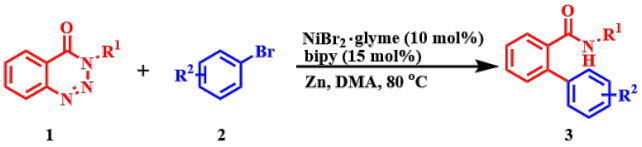
***General Procedure A*:** To an oven-dried microwave vial (50 mL) equipped with a stir bar (20 × 5 mm) was added 1,2,3-benzotriazin-4(3H)-one (6.8 mmol) and K_2CO_3 (1.41g, 10 mmol) under air atmosphere. The microwave vial was sealed with a cap containing a rubber septum and evacuated used a vacuum pump with a hose fitted with a needle that was poked through the septum. The vial was charged with N_2 by balloon. This process was repeated three times to remove most of the dioxygen. Next, 10 mL of DMF was added via syringe through the septum and the vial was cooled in an ice bath. The alkyl/aryl bromide (11 mmol) was then added to the reaction mixture at 0 °C via syringe. Once addition was complete, the vial was removed from the ice bath and allowed to warm to room temperature and stirred (~400 rpm) at room temperature for 18 h under nitrogen. After the reaction period, the resulting colorless solution was quenched by addition of 10 mL of water via syringe through the septum and the vial opened to air. The resulting solution was extracted with EtOAc (3 x 20 mL). The combined organic extracts were washed with water, brine, dried over $MgSO_4$ and filtered. The resulting solution was subjected to reduced pressure and the residue was purified by flash chromatography (200–300 mesh) on silica gel to afford the corresponding product.

General Procedure B. Synthesis of N-aryl substituted 1,2,3-triazin-4-ones



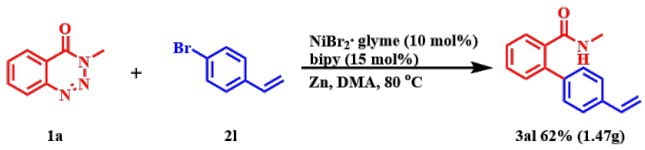
***General procedure B*:** To an oven-dried microwave vial (50 mL) equipped with a stir bar (20 × 5 mm) was added 1,2,3-benzotriazin-4(3H)-one (5.0 mmol) and phenylboronic acid (7.5 mmol) under air atmosphere. Next, anhydrous $Cu(OAc)_2$ (5.0 mmol) and Et_3N (10.0 mmol) in DCE (30 mL) were added. The microwave vial was sealed, and stirred at ambient temperature for 2.0 h. After the reaction period, the resulting colorless solution was quenched by addition of 10 mL of water via syringe through the septum and the vial opened to air. The resulting solution was extracted with EtOAc (3 x 20 mL). The combined organic extracts were washed with water, brine, dried over $MgSO_4$ and filtered. The resulting solution was subjected to reduced pressure and the residue was purified by flash chromatography on silica gel (200–300 mesh) to afford the corresponding product.

General Procedure for the Synthesis of *ortho*-Arylated Benzamide Derivatives



***General Procedure*:** To an oven-dried microwave vial (10 mL) equipped with a stir bar (10 × 5 mm) was added $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 1,2,3-benzotriazin-4(3H)-ones (**1**) (0.10 mmol, 1.0 equiv.), aryl bromide (**2**) (0.2 mmol, 2.0 equiv.) and Zn (13.1 mg, 0.2 mmol, 2 equiv.) under an nitrogen atmosphere inside a glove box at 25 °C. Next, 0.2 mL of dry DMA was added via syringe. The microwave vial was sealed with a cap containing a rubber septum and removed from the glove box. The reaction mixture was stirred (~800 rpm) at 80 °C in an oil bath for 12 h. The resulting gray solution was cooled to RT, quenched by addition of 5 drops 2M HCl via syringe through the septum and then the vial opened to air. The reaction mixture was passed through a short flash column chromatography in silica gel (200–300 mesh) and rinsed with 5 mL of ethyl acetate to afford a yellow solution. The solvent and volatile materials were removed by rotary evaporator. The crude residue was purified by flash column chromatography in silica gel to yield the corresponding product.

Scale-up Transformation to 10.0 mmol for the Synthesis of 3al



1a 2l 3al 62% (1.47g)

To an oven-dried microwave vial (10 mL) equipped with a stir bar (10 × 5 mm) was added $NiBr_2$·glyme (350 mg, 1.0 mmol), bipy (230 mg, 1.5 mmol), 3-methylbenzo[d][1,2,3]triazin-4(3H)-one (**1a**) (1.61 g, 10.0 mmol), 1-bromo-4-ethenylbenzene (**2l**) (3.27 mL, 20 mmol) and Zn (1.31 g, 20 mmol, 2 equiv) under an argon atmosphere inside a glove box at 25 °C. Next, 20 mL of dry DMA was added via syringe. The microwave vial was sealed with a cap containing a rubber septum and removed from the glove box. The reaction mixture was stirred (~800 rpm) at 80 °C in an oil bath for 12 h. The resulting gray solution was cooled to RT, quenched by addition of 15 drops 2M HCl via syringe through the septum and then the vial opened to air. The reaction mixture was passed through a short flash column chromatography in silica gel (200–300 mesh) and rinsed with 15 mL of ethyl acetate to afford a yellow solution. The solvent and volatile materials were removed by rotary evaporator. The crude residue was purified by flash column chromatography in silica gel to obtain the corresponding product **3al** with 62% yield.

N-methyl-[1,1'-biphenyl]-2-carboxamide (3aa). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-methylbenzo[d][1,2,3]triazin-4(3H)-one (**1a**) (16.1 mg, 0.10 mmol), bromobenzene (**2a**) (21.1 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (18.4 mg, 87% yield) as a white solid. R_f = 0.5 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, J = 8.1 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.42 – 7.39 (m, 5H), 7.38 – 7.35 (m, 2H), 5.30 (s, 1H), 2.66 (d, J = 4.9 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 170.3, 140.1, 139.3, 135.6, 130.1, 130.0, 128.7, 128.54, 128.52, 127.7, 127.5, 26.6 ppm. The spectroscopic data for this product match the literature data.[19]

N-methyl-[1,1':4',1''-terphenyl]-2-carboxamide (3ab). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-methylbenzo[d][1,2,3]triazin-4(3H)-one (**1a**) (16.1 mg, 0.10 mmol), 4-bromobiphenyl (**2b**) (46.6 mg, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (24.7 mg, 86% yield) as a white solid. R_f = 0.42 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 – 7.62 (m, 5H), 7.48 (dd, J = 7.9, 6.1 Hz, 5H), 7.44 – 7.40 (m, 2H), 7.37 (t, J = 7.4 Hz, 1H), 5.38 (s, 1H), 2.70 (d, J = 4.9 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 170.4, 140.4, 140.3, 138.9, 138.8, 135.7, 130.1, 130.0, 129.0, 128.8, 128.7, 127.8, 127.5, 127.1, 126.9, 26.7 ppm.The spectroscopic data for this product match the literature data.[19]

4'-(Tert-butyl)-N-methyl-[1,1'-biphenyl]-2-carboxamide (3ac). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-methylbenzo[d][1,2,3]triazin-4(3H)-one (**1a**) (16.1 mg, 0.10 mmol), 1-bromo-4-(*tert*-butyl)benzene (**2c**) (34.7 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (24.1 mg, 90% yield) as a white solid. Mp: 115.8 – 116.4 °C. R_f = 0.57 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 – 7.67 (m, 1H), 7.47 – 7.42 (m, 3H), 7.40 – 7.33 (m, 4H), 5.22 (s, 1H), 2.67 (d, J = 4.9 Hz, 3H), 1.35 (s, 9H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 170.4, 150.7, 139.2, 137.0, 135.5, 130.09, 130.07, 128.8, 128.3, 127.4, 125.5, 34.6, 31.3, 26.6 ppm. IR(neat): 2963, 2904, 2868, 1636, 1540, 1408, 838, 581 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{22}NO$ 268.1701; Found 268.1703.

4'-Methoxy-N-methyl-[1,1'-biphenyl]-2-carboxamide (3ad). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-methylbenzo[d][1,2,3]triazin-4(3H)-one (**1a**) (16.1 mg, 0.10 mmol), 4-bromoanisole (**2d**) (25.0 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (22.0 mg, 91% yield) as a white solid. R_f = 0.40 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 – 7.63 (m, 1H), 7.46 – 7.42 (m, 1H), 7.38 – 7.31 (m, 4H), 6.97 – 6.93 (m, 2H), 5.29 (s, 1H), 3.84 (s, 3H), 2.70 (d, J = 4.9 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 170.5, 159.3, 138.9, 135.5, 132.4, 130.1, 130.0, 129.7, 128.7, 127.2, 113.9, 55.2, 26.6 ppm. The spectroscopic data for this product match the literature data.[20]

N-methyl-4'-(methylthio)-[1,1'-biphenyl]-2-carboxamide (3ae). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-methylbenzo[d][1,2,3]triazin-4(3H)-one (**1a**) (16.1 mg, 0.10 mmol), 4-bromothioanisole (**2e**) (27.0 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (20.3 mg, 79 % yield) as a white solid. R_f = 0.41 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 – 7.63 (m, 1H), 7.47 (td, J = 7.5, 1.5 Hz, 1H), 7.40 (dd, J = 7.6, 1.4 Hz, 1H), 7.37 – 7.33 (m, 3H), 7.30 – 7.27 (m, 2H), 5.30 (s, 1H), 2.72 (d, J = 4.9 Hz, 3H), 2.52 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 170.3, 138.6, 138.3, 136.5, 135.6, 130.1, 130.0, 128.9, 128.7, 127.5, 126.2, 26.7, 15.5 ppm. The spectroscopic data for this product match the literature data.[19]

N,3'-dimethyl-[1,1'-biphenyl]-2-carboxamide (3af). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-methylbenzo[d][1,2,3]triazin-4(3H)-one (**1a**) (16.1 mg, 0.10 mmol), 3-bromotoluene (**2f**) (24.3 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (20.5 mg, 91% yield) as a white solid. R_f = 0.63 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (dd, J = 7.6, 1.5 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.41 – 7.35 (m, 2H), 7.30 (t, J = 7.5 Hz, 1H), 7.23 – 7.17 (m, 3H), 5.21 (s, 1H), 2.68 (d, J = 4.9 Hz, 3H), 2.39 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 170.3, 140.1, 139.4, 138.2, 135.5, 130.1, 130.0, 129.2, 128.8, 128.51, 128.45, 127.5, 125.7, 26.6, 21.4 ppm. The spectroscopic data for this product match the literature data.[5]

4'-Fluoro-N-methyl-[1,1'-biphenyl]-2-carboxamide (3ag). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-methylbenzo[d][1,2,3]triazin-4(3H)-one (**1a**) (16.1 mg, 0.10 mmol), 4-bromofluorobenzene (**2g**) (22.0 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with

Petroleum ether:EtOAc = 5:1) to give the product (18.9 mg, 82 % yield) as a white solid. R_f = 0.47 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.43 – 7.32 (m, 6H), 5.35 (s, 1H), 2.73 (d, *J* = 4.9 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 170.2, 162.4 (d, $J^1_{C\text{-}F}$ = 248.5 Hz), 138.2, 136.1 (d, $J^4_{C\text{-}F}$ = 3.5 Hz), 135.8, 130.2, 130.13, 130.06, 128.1 (d, $J^2_{C\text{-}F}$ = 91.7 Hz), 115.5 (d, $J^3_{C\text{-}F}$ = 21.5 Hz), 26.6 ppm. One resonance was not observed due to overlapping resonances. The spectroscopic data for this product match the literature data.[21]

4'-Chloro-N-methyl-[1,1'-biphenyl]-2-carboxamide (3ah). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-methylbenzo[d][1,2,3]triazin-4(3H)-one **(1a)** (16.1 mg, 0.10 mmol), 4-chlorobromobenzene (**2h**) (23.2 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (20.6 mg, 84% yield) as a white solid. R_f = 0.45 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 – 7.61 (m, 1H), 7.50 – 7.45 (m, 1H), 7.44 – 7.39 (m, 2H), 7.36 (dd, *J* = 9.4, 6.6 Hz, 4H), 5.32 (s, 1H), 2.73 (d, *J* = 4.9 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 170.2, 138.5, 138.0, 135.9, 133.8, 130.2, 130.0, 129.8, 128.7, 128.6, 127.8, 26.7 ppm. The spectroscopic data for this product match the literature data.[19]

N-methyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide (3ai). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-methylbenzo[d][1,2,3]triazin-4(3H)-one **(1a)** (16.1 mg, 0.10 mmol), 4-bromobenzotrifluoride (**2i**) (28.0 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (21.9 mg, 78% yield) as a white solid. R_f = 0.45 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.37 (t, *J* = 6.8 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 5.33 (s, 1H), 2.66 (d, *J* = 4.9 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 170.0, 143.7, 137.9, 136.0, 130.2, 130.1, 128.8, 128.4, 128.2, 125.4 (q, $J_{C\text{-}F}$ = 4.0 Hz), 124.1 (q, $J_{C\text{-}F}$ = 270 Hz), 26.7 ppm. The spectroscopic data for this product match the literature data.[19]

Ethyl 2'-(methylcarbamoyl)-[1,1'-biphenyl]-4-carboxylate (3aj). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-methylbenzo[d][1,2,3]triazin-4(3H)-one **(1a)** (16.1 mg, 0.10 mmol), 4-(ethoxycarbonyl)-1-bromobenzene (**2j**) (26.2 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (21.5 mg, 76% yield) as a white solid. Mp: 264.4 – 266.1 ºC. R_f = 0.32 (Petroleum ether:EtOAc = 5:1).^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 – 8.07 (m, 2H), 7.66 – 7.63 (m, 1H), 7.51 – 7.47 (m, 3H), 7.46 – 7.38 (m, 2H), 5.38 (s, 1H), 4.41 (t, *J* = 7.1 Hz, 2H), 2.71 (d, *J* = 4.9 Hz, 3H), 1.42 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 170.1, 166.3, 144.6, 138.3, 135.9, 130.2, 130.0, 129.7, 129.6, 128.6, 128.2, 61.1, 26.7, 14.3 ppm. One resonance was not observed due to overlapping resonances. IR(neat): 2987, 2983, 2936, 1736, 1646, 1472, 1108, 747, 659, 521 cm^{-1}. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{17}H_{18}NO_3$ 284.1287; Found 284.1292.

N,2'-dimethyl-[1,1'-biphenyl]-2-carboxamide (3ak). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-methylbenzo[d][1,2,3]triazin-4(3H)-one **(1a)** (16.1 mg, 0.10 mmol), 2-bromotoluene (**2k**) (24.1 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (21.0 mg, 93% yield) as a white solid. R_f = 0.70 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.31 – 7.26 (m, 3H), 7.21 – 7.17 (m, 2H), 5.26 (s, 1H), 2.62 (d, *J* = 4.8 Hz, 3H), 2.11 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 168.9, 140.0, 139.0, 136.0, 134.7, 130.3, 130.32, 130.29, 129.2, 129.0, 128.1, 127.6, 126.1, 26.7, 19.9 ppm. The spectroscopic data for this product match the literature data.[5]

N-methyl-4'-vinyl-[1,1'-biphenyl]-2-carboxamide (3al). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-methylbenzo[d][1,2,3]triazin-4(3H)-one **(1a)** (16.1 mg, 0.10 mmol), 1-bromo-4-ethenylbenzene (**2l**) (32.7 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (15.9 mg, 67% yield) as a colorless liquid. R_f = 0.46 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 – 7.66 (m, 1H), 7.49 – 7.45 (m, 3H), 7.42 – 7.36 (m, 4H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.81 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.31 (dd, *J* = 10.9, 0.8 Hz, 1H), 5.25 (s, 1H), 2.70 (d, *J* = 5.0 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 170.3, 139.5, 138.8, 136.9, 136.2, 135.6, 130.1, 130.0, 128.8, 127.6, 126.4, 114.4, 26.7 ppm. One resonance was not observed due to overlapping resonances. IR(neat): 2962, 2954, 2864, 1636, 1409, 1318, 764, 568 cm^{-1}. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{16}H_{16}NO$ 238.1232; Found 238.1234.

2-(Benzofuran-5-yl)-N-methylbenzamide (3am). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), **1a** (16.1 mg, 0.10 mmol), 5-bromo-1-benzofuran (**2m**) (39.4 mg, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (15.6 mg, 62% yield) as a white solid. Mp: 164.2 – 165.8 ºC. R_f = 0.35 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 – 7.67 (m, 2H), 7.65 – 7.64 (m, 1H), 7.55 – 7.52 (m, 1H), 7.50 – 7.46 (m, 1H), 7.42 – 7.38 (m, 2H), 7.34 – 7.31 (m, 1H), 6.82 – 6.79 (m, 1H), 5.24 (s, 1H), 2.63 (d, *J* = 4.9 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 170.4, 154.5, 145.7, 139.5, 135.8, 135.0, 130.5, 130.0, 128.8, 127.8, 127.4, 125.2, 121.1, 111.4, 106.7, 26.6 ppm. IR(neat): 2998, 2952, 2876, 1637, 1463, 1110, 757, 529 cm^{-1}. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{16}H_{14}NO_2$ 252.1025; Found 252.1021.

2-(Benzo[b]thiophen-5-yl)-N-methylbenzamide (3an). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), **1a** (16.1 mg, 0.10 mmol), 5-bromobenzo[b]thiophene (**2n**) (25.8 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (15.2 mg, 57% yield) as a white solid. Mp: 180.2 – 181.3 ºC. R_f = 0.32 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 – 7.79 (m, 2H), 7.63 – 7.60 (m, 1H), 7.43 – 7.39 (m, 2H), 7.37 – 7.32 (m, 2H), 7.32 – 7.28 (m, 2H), 5.21 (s, 1H), 2.55 (d, *J* = 4.9 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 170.3, 139.8, 139.22, 139.15, 136.4, 135.8, 130.5, 130.1, 128.8, 127.5, 127.3, 125.1, 123.9, 123.4, 122.5, 26.6 ppm. IR(neat): 2972, 2911, 2853, 1640, 1410, 1260, 752, 552

cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}NOS$ 268.0796; Found 268.0798.

N-methyl-2-(1-methyl-1H-indol-5-yl)benzamide (3ao). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), **1a** (16.1 mg, 0.10 mmol), 5-bromo-1-methyl-1H-indole (**2o**) (42.0 mg, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (14.3 mg, 54% yield) as a white solid. Mp: 189.6 – 190.2 ºC. R_f = 0.32 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 – 7.71 (m, 1H), 7.66 (d, *J* = 1.8 Hz, 1H), 7.49 – 7.31 (m, 4H), 7.25 (s, 1H), 7.09 (d, *J* = 3.2 Hz, 1H), 6.51 (dd, *J* = 3.2, 1.0 Hz, 1H), 5.24 (s, 1H), 3.81 (s, 3H), 2.59 (d, *J* = 4.9 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 170.5, 140.5, 136.2, 135.4, 131.3, 130.7, 129.9, 129.6, 129.0, 128.6, 126.9, 122.7, 120.8, 109.3, 101.2, 32.9, 26.6 ppm. IR(neat): 2952, 2924, 2890, 1636, 1410, 1334, 750, 560 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}N_2O$ 265.1341; Found 265.1346.

N-methyl-2-(thiophen-3-yl)benzamide (3ap). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), **1a** (16.1 mg, 0.10 mmol), 3-bromothiophene (**2p**) (18.7 μL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (19.1 mg, 88% yield) as a white solid. Mp: 123.0 – 123.8 ºC. R_f = 0.5 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 – 7.58 (m, 1H), 7.44 – 7.40 (m, 2H), 7.38 – 7.35 (m, 3H), 7.18 – 7.16 (m, 1H), 5.46 (s, 1H), 2.76 (d, *J* = 4.9 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 170.4, 140.5, 135.6, 133.7, 129.9, 129.7, 128.5, 128.1, 127.5, 125.9, 122.8, 26.7 ppm. IR(neat): 2957, 2924, 2852, 1640, 1543, 1325, 753, 690, 518 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{12}NOS$ 218.0640; Found 218.0642.

2-Cyclohexyl-N-methylbenzamide (3aq). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), **1a** (16.1 mg, 0.10 mmol), cyclohexyl bromide (**2q**) (24.6 μL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (9.1 mg, 42% yield) as a colorless oil. R_f = 0.82 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, *J* = 6.4 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.21 – 7.11 (m, 1H), 6.04 – 5.74 (m, 1H), 2.96 (d, *J* = 4.8 Hz, 3H), 1.86 – 1.72 (m, 6H), 1.47 – 1.35 (m, 4H), 1.30 – 1.19 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 171.2, 145.5, 136.3, 129.7, 126.6, 126.5, 125.5, 40.4, 34.4, 26.7, 26.6, 26.1 ppm. The spectroscopic data for this product match the literature data.[16]

N-phenyl-[1,1'-biphenyl]-2-carboxamide (3ba). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-phenylbenzo[d][1,2,3]triazin-4(3H)-one **(1b)** (22.3 mg, 0.10 mmol), bromobenzene (**2a**) (21.1 μL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (23.8 mg, 87% yield) as a white solid. R_f = 0.52 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.49 – 7.40 (m, 7H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.96 (s, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 167.1, 139.8, 139.5, 137.4, 135.2, 130.6, 130.3, 129.5, 128.9, 128.7, 128.0, 127.8, 127.0, 124.4, 119.9 ppm. The spectroscopic data for this product match the literature data.[22]

N-(4-fluorophenyl)-[1,1'-biphenyl]-2-carboxamide (3ca). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-(4-fluorophenyl)benzo[d][1,2,3]triazin-4(3H)-one **(1c)** (24.1 mg, 0.10 mmol), bromobenzene (**2a**) (21.1 μL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (25.1 mg, 86% yield) as a white solid. R_f = 0.5 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.61 – 7.47 (m, 2H), 7.48 – 7.38 (m, 6H), 7.05 – 7.00 (m, 2H), 6.93 (d, *J* = 8.7 Hz, 1H), 6.94 – 6.86 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 167.2, 159.4 (d, $J^4_{C\text{-}F}$ = 245.0 Hz), 139.7 (d, $J^4_{C\text{-}F}$ = 38.8 Hz), 134.9, 131.8, 130.7, 130.2, 129.4, 128.9, 128.7, 128.1, 127.9, 127.0, 121.8 (d, $J^4_{C\text{-}F}$ = 7.9 Hz), 115.4 (d, $J^4_{C\text{-}F}$ = 22.7 Hz) ppm. The spectroscopic data for this product match the literature data.[23]

N-butyl-[1,1'-biphenyl]-2-carboxamide (3da). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-butylbenzo[d][1,2,3]triazin-4(3H)-one **(1d)** (20.3 mg, 0.10 mmol), bromobenzene (**2a**) (21.1 μL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (19.3 mg, 76% yield) as a white solid. R_f = 0.63 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, *J* = 7.5 Hz, 1H), 7.48 – 7.45 (m, 1H), 7.43 – 7.36 (m, 7H), 5.19 (s, 1H), 3.17 – 3.12 (m, 2H), 1.18 – 1.10 (m, 2H), 1.03 – 0.97 (m, 2H), 0.77 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 169.3, 140.2, 139.2, 135.8, 130.1, 129.9, 128.8, 128.6, 128.5, 127.7, 127.5, 39.4, 30.8, 19.7, 13.6 ppm. The spectroscopic data for this product match the literature data.[10]

N-pentyl-[1,1'-biphenyl]-2-carboxamide (3ea). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.1 mmol), bipy (2.3 mg, 0.015 mmol), 3-pentylbenzo[d][1,2,3]triazin-4(3H)-one **(1e)** (21.7 mg, 0.10 mmol), bromobenzene (**2a**) (21.1 μL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (20.3 mg, 76% yield) as a white solid. Mp: 118.4 – 119.2 ºC. R_f = 0.56 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.46 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.42 (d, *J* = 4.4 Hz, 5H), 7.39 – 7.35 (m, 2H), 5.21 (s, 1H), 3.16 – 3.10 (m, 2H), 1.20 – 1.12 (m, 4H), 0.98 – 0.91 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 169.3, 140.3, 139.3, 135.9, 130.1, 129.9, 128.8, 128.7, 128.6, 127.7, 127.6, 39.7, 28.8, 28.5, 22.2, 13.8 ppm. IR(neat): 2960, 2923, 2850, 1639, 1453, 1315, 1196, 764, 564 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{22}NO$ 268.1701; Found 268.1697.

N-octyl-[1,1'-biphenyl]-2-carboxamide (3fa). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-hexylbenzo[d][1,2,3]triazin-4(3H)-one **(1f)** (23.1 mg, 0.10 mmol), bromobenzene (**2a**) (21.1 μL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (22.5 mg, 80% yield) as

a white solid. R_f = 0.54 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.45 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.41 – 7.33 (m, 7H), 5.27 (s, 1H), 3.14 – 3.09 (m, 2H), 1.29 – 1.25 (m, 2H), 1.22 – 1.12 (m, 8H), 0.98 (dd, *J* = 9.4, 6.7 Hz, 2H), 0.87 (d, *J* = 7.2 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 169.2, 140.2, 139.2, 135.8, 130.0, 129.8, 128.7, 128.6, 128.5, 127.7, 127.4, 39.7, 31.6, 29.1, 29.0, 28.7, 26.6, 22.5, 14.0 ppm. The spectroscopic data for this product match the literature data.[10]

N-(2-methylbutyl)-[1,1'-biphenyl]-2-carboxamide (3ga). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-(2-methylbutyl)benzo[d][1,2,3]triazin-4(3H)-one (**1g**) (21.7 mg, 0.10 mmol), bromobenzene (**2a**) (21.1 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (21.9 mg, 82% yield) as a white solid. Mp: 143.3 – 144.7 ºC. R_f = 0.53 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.42 – 7.34 (m, 7H), 5.24 (s, 1H), 3.08 (dd, *J* = 13.4, 6.1 Hz, 1H), 2.94 (dd, *J* = 12.6, 6.5 Hz, 1H), 1.22 (d, *J* = 12.5 Hz, 1H), 1.06 – 0.98 (m, 1H), 0.84 (dd, *J* = 14.0, 5.9 Hz, 1H), 0.73 (t, *J* = 7.3 Hz, 3H), 0.57 (d, *J* = 6.7 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 169.5, 140.3, 139.3, 135.9, 130.2, 129.9, 128.9, 128.69, 128.66, 127.8, 127.6, 45.5, 34.2, 26.7, 16.8, 11.1 ppm. IR(neat): 2960, 2923, 2850, 1639, 1453, 1315, 1196, 764, 564 cm^{-1}. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{18}H_{22}NO$ 268.1701; Found 268.1707.

N-(cyclohexylmethyl)-[1,1'-biphenyl]-2-carboxamide (3ha). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-(cyclohexylmethyl)benzo[d][1,2,3]triazin-4(3H)-one (**1h**) (24.3 mg, 0.10 mmol), bromobenzene (**2a**) (21.1 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (27.3 mg, 93% yield) as a white solid. Mp: 132.0 – 132.7 ºC. R_f = 0.70 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.46 – 7.35 (m, 8H), 5.33 (s, 1H), 2.98 (t, *J* = 6.3 Hz, 2H), 1.61 – 1.55 (m, 3H), 1.30 – 1.25 (m, 2H), 1.13 – 1.02 (m, 4H), 0.68 – 0.57 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 169.4, 140.3, 139.2, 135.9, 130.1, 129.9, 128.8, 128.7, 128.6, 127.7, 127.5, 46.0, 37.3, 30.5, 26.2, 25.7 ppm. IR(neat): 3060, 2921, 2850, 1640, 1541, 1276, 915, 747, 698, 541 cm^{-1}. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{20}H_{24}NO$ 294.1858; Found 294.1860.

N-phenethyl-[1,1'-biphenyl]-2-carboxamide (3ia). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-phenethylbenzo[d][1,2,3]triazin-4(3H)-one (**1i**) (25.1 mg, 0.10 mmol), bromobenzene (**2a**) (21.1 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (23.2 mg, 77% yield) as a white solid. R_f = 0.58 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.42 (d, *J* = 16.5 Hz, 8H), 7.20 (q, *J* = 6.8, 5.4 Hz, 3H), 6.98 – 6.86 (m, 2H), 5.40 – 5.18 (m, 1H), 3.50 – 3.37 (m, 2H), 2.50 (t, *J* = 7.0 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 169.5, 140.1, 139.2, 138.5, 135.8, 130.1, 129.9, 128.7, 128.6, 128.5, 128.4, 127.7, 127.5, 126.3, 40.7, 34.9 ppm. One resonance was not observed due to overlapping resonances. The spectroscopic data for this product match the literature data.[24]

N-isopropyl-[1,1'-biphenyl]-2-carboxamide (3ja). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-isopropylbenzo[d][1,2,3]triazin-4(3H)-one (**1j**) (18.9 mg, 0.10 mmol), bromobenzene (**2a**) (21.1 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (14.8 mg, 62% yield) as a white solid. Mp: 127.4 – 129.3 ºC. R_f = 0.55 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 – 7.70 (m, 1H), 7.49 – 7.43 (m, 1H), 7.43 – 7.34 (m, 7H), 4.94 (s, 1H), 4.04 – 3.96 (m, 1H), 0.84 (d, *J* = 6.5 Hz, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 168.4, 140.3, 139.4, 135.9, 130.0, 129.9, 128.84, 128.78, 128.6, 127.7, 127.6, 41.5, 22.1 ppm. IR(neat): 2993, 2921, 2849, 1636, 1448, 1318, 1074, 745, 576 cm^{-1}. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{16}H_{17}NO$ 240.1388; Found 240.1392.

Ethyl ([1,1'-biphenyl]-2-carbonyl)alaninate (3ka). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), ethyl 2-(4-oxobenzo[d][1,2,3]triazin-3(4H)-yl)propanoate (**1k**) (24.7 mg, 0.10 mmol), bromobenzene (**2a**) (21.1 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (19.9 mg, 67% yield) as a white solid. Mp: 58.0 – 59.7 ºC. R_f = 0.30 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.50 – 7.35 (m, 8H), 5.86 (s, 1H), 4.56 – 4.49 (m, 1H), 4.14 – 4.16 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 7.1 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 172.5, 168.6, 140.1, 139.8, 135.1, 130.23, 130.15, 128.7, 128.5, 127.7, 127.5, 61.3, 48.2, 17.8, 14.0 ppm. One resonance was not observed due to overlapping resonances. IR(neat): 2993, 2983, 2936, 1738, 1646, 1525, 1207, 747, 701, 521 cm^{-1}. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{18}H_{20}NO_3$ 298.1443; Found 298.1439.

2-([1,1'-Biphenyl]-2-carboxamido)ethyl benzoate (3la). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 2-(4-oxobenzo[d][1,2,3]triazin-3(4H)-yl)ethyl benzoate (**1l**) (29.5 mg, 0.10 mmol), bromobenzene (**2a**) (21.1 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (24.2 mg, 70% yield) as a colorless liquid. R_f = 0.26 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.71 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.50 – 7.42 (m, 4H), 7.37 (dd, *J* = 6.4, 1.6 Hz, 3H), 7.27 – 7.20 (m, 3H), 5.64 (s, 1H), 4.10 – 4.07 (m, 2H), 3.60 – 3.56 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 169.6, 166.2, 139.9, 139.4, 135.4, 133.1, 130.24, 130.15, 129.6, 128.8, 128.6, 128.5, 128.3, 127.9, 127.6, 63.6, 38.7 ppm. One resonance was not observed due to overlapping resonances. IR(neat): 2955, 2920, 2888, 2848, 1716, 1656, 1645, 1532, 1274, 1071, 747, 712, 517 cm^{-1}. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{22}H_{20}NO_3$ 346.1443; Found 346.1446.

N-(3-methoxypropyl)-[1,1'-biphenyl]-2-carboxamide (3ma). The reaction was performed following the General Procedure with $NiBr_2$·glyme (3.5 mg, 0.01 mmol), bipy (2.3 mg, 0.015 mmol), 3-(3-ethoxypropyl)benzo[d][1,2,3]triazin-4(3H)-one (**1m**) (23.3 mg, 0.10 mmol), bromobenzene (**2a**) (21.1 µL, 0.2 mmol) and Zn (13.1 mg, 0.2 mmol, 2 equiv). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product

(19.4 mg, 72% yield) as a colorless liquid. R_f = 0.35 (Petroleum ether:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.46 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.43 – 7.40 (m, 4H), 7.40 – 7.35 (m, 3H), 5.72 (s, 1H), 3.28 – 3.23 (m, 2H), 3.16 (s, 3H), 3.12 (t, *J* = 5.9 Hz, 2H), 1.50 – 1.44 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 169.6, 140.4, 139.4, 136.2, 130.2, 130.0, 128.82, 128.80, 128.6, 127.8, 127.7, 71.1, 58.7, 38.1, 28.7 ppm. IR(neat): 2954, 2921, 2850, 1636, 1275, 1119, 749, 699, 521 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{20}NO_2$ 270.1494; Found 270.1491.

ASSOCIATED CONTENT

DATA AVAILABILITY STATEMENT

The data underlying this study are available in the published article and its online supplementary material.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Supporting Information. (Experimental details, characterization data and NMR spectra)

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Notes

The authors declare no competing financial interest.

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