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Amide-Directed Intramolecular Co(III)-Catalyzed C-H Hydroarylation of Alkenes for the Synthesis of Dihydrobenzofurans with a Quaternary Center

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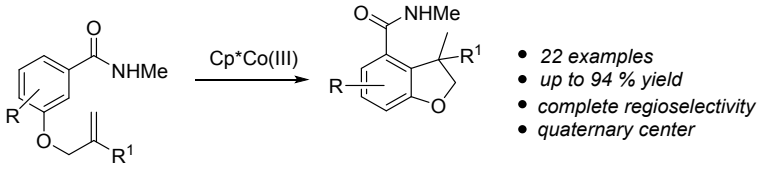
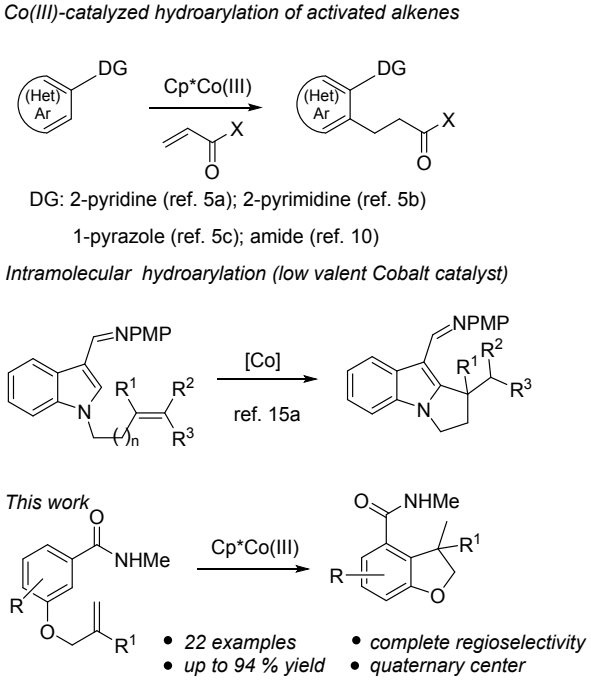


Abstract. The first example of Cp*Co(III)-catalyzed intramolecular hydroarylation of allyl aryl ethers using an amide directing group for the preparation of 3,3-disubstituted dihydrobenzofurans in high yields is described. The reaction of the unactivated alkene is completely selective for the formation of the quaternary center, allowing different substitution patterns on the aromatic ring and the alkene. The cyclization can also be extended to the formation of six-membered rings and to *N*-homoallylindoles.

Transition metal-catalyzed C-H activation / olefin hydroarylation reactions represent one of the most efficient and straightforward strategies to access complex multifunctional molecules related to pharmaceuticals, natural products, and materials.[1] Recently, the use of cheaper, more earth-abundant and

less toxic first row transition metals, such as cobalt, to replace palladium or rhodium complexes has started to attract significant attention.[2] Cobalt organometallic complexes are more nucleophilic than those of rhodium or iridium, as a result of the reduced electronegativity of cobalt, so improved chemo- or regioselectivities can be obtained, and also new reactivity can be devised. In this context, high-valent-cobalt-catalyzed dehydrogenative Heck-type reactions (DHR) have been described where the intermediate obtained after migratory insertion could be driven to β-hydride elimination or, alternatively, to protodemetalation affording alkylated products.[3] In this context, Cp*Co(III) complexes[4] have been applied for the intermolecular alkylation reaction of (hetero)arenes using different directing groups (e.g.: 2-pyridinyl, 2-pyrymidyl, pyrazole) with activated[5] or unactivated alkenes,[6] and also for enantioselective variants.[7] Weakly coordinating carbonyl directing groups (ketones, esters) have also been used in this type of C-H alkylation.[8] However, despite these advances, since the seminal work of Nakamura using low-valent cobalt catalysis,[9] the use of amide directing groups has been less explored.[10] Alternatively, Co(II) precatalysts that are oxidized *in situ* to Co(III) have been used in combination with bidentate directing groups, such as 8-aminoquinoline.[11] Thus, it has been possible to react unbiased alkenes driving the selectivity of the β-elimination step and resulting in an allylic selective DHR.[12] Intramolecular C-H activation/hydroarylation reactions with alkynes have been described. For example, benzofurans have been obtained through a Cp*Co(III) catalyzed 5-*exo*-dig intramolecular hydroarylation of aryl propargyl ethers bearing an amide directing group on the aromatic ring.[13] Alternatively, the alkyne has been also tethered to the directing group, i.e. the Cp*Co(III)-catalyzed C-H hydroarylation using alkyne-tethered hydroxamic esters as directing groups for the synthesis of isoquinolones.[14] However, cyclization reactions onto an alkene tethered to the (hetero)aromatic ring are underdeveloped, in contrast with the Pd(II) catalyzed reactions. To our knowledge, there are only examples of low-valent-cobalt-catalyzed intramolecular imine-directed C-2-alkylation of indoles (Scheme 1).[15] In a conceptually different approach, cobalt catalyzed radical cycloisomerization of unbiased alkenes generating cuaternary centers has been recently described.[16]



Scheme 1. Cobalt-catalyzed alkene hydroarylation.

Based on our recent findings on the Pd(II)-catalyzed intramolecular DHR, which provides a platform for the synthesis of nitrogen and oxygen heterocycles,[17] we sought to explore the possibility of an intramolecular high-valent-cobalt-catalyzed C-H alkylation with unactivated alkenes using an amide directing group. Herein, we describe for the first time a mild general Cp*Co(III)-catalyzed intramolecular C-H activation method for the selective hydroarylation of 3-allyloxybenzamides for the synthesis of the 2,3-dihydrobenzofuran core with a quaternary center at C-3 (Scheme 1).

Related Rh(III)-, Ir(I)-, and Ru-catalyzed protocols for the intramolecular hydroarylation of unactivated alkenes to access 2,3-dihydrobenzfurans have been described,[18] but they have some drawbacks (low natural abundance, toxicity, price). In contrast, our method features the use of a cheap and earth-abundant metal catalyst and a wide scope. Besides, the use of unactivated alkenes allows the formation of a quaternary center on C-3 of the 2,3-dihydrobenzfuran with complete regioselectivity, providing an complementary approach to the use of alkynes, which leads to the aromatic heterocycles, benzofurans.[13] Therefore, this work would represent an significant methodological advance in high-valent Co-catalyzed reactions.

Besides, it should be noted that 2,3-dihydrobenzofuran motif is present as structural core in several biologically active natural products[19] and pharmaceuticals.[20] In particular, 3,3-disubstituted 2,3-dihydrobenzofurans are potent selective cannabinoid receptor 2 agonists[21] and synthetic retinoids.[22]They are also important building blocks in the synthesis of more complex molecules, such as DNA-dependent protein kinase (DNA-PK) inhibitors[23] or non-structural protein 5B (NS5B) inhibitors used as antivirals in the treatment of chronic hepatitis C (HCVNS5B inhibitors)[24] (Figure 1).

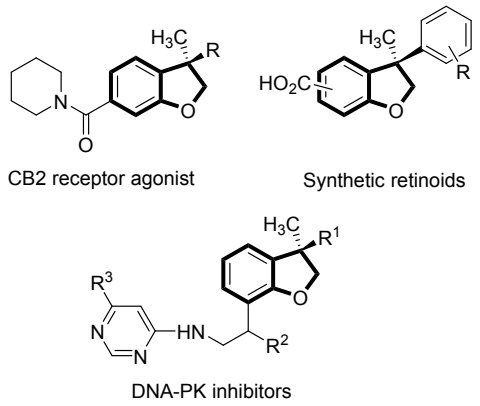
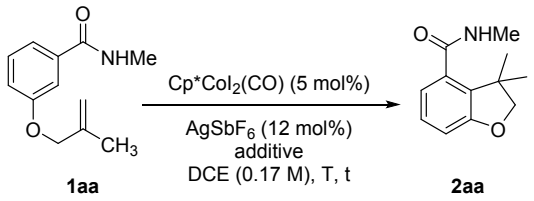


Figure 1. Biologically active 2,3-dhydrobenzofurans.

We started our study using amide **1aa** as substrate, and Cp*CoI_2(CO) (5 mol%) as precatalyst in the presence of $AgSbF_6$, which has been applied for intermolecular amide-directed hydroarylations.[10a,b,13] We began with the optimization of the reaction conditions utilizing KOAc as the carboxylate base (Table 1). When employing DCE as solvent at 80 ºC, benzofuran **2aa** could be isolated as the only reaction product, but a low conversion of the starting material was observed after 24 h (Table 1, entry 1). No improvement could be observed using a 10 mol% precatalyst loading (with the subsequent increase in the amount of base and silver salt) (Table 1, entry 2). The use of a larger amount of base was detrimental (Table 1, entry 3), while a stoichiometric amount of acetate with respect to cobalt[8] did not have an impact on reactivity (Table 1, entry 5). Different less hygroscopic acetate sources were also tested (Table 1, entries 5-10), but only NaOAc led to a comparable result (Table 1, entry 7), the rest allowing low conversions after 24 h, while *n*Bu_4N(OAc) completely shut down the reactivity (Table 1, entry 11).

Table 1. Optimization of reaction conditions



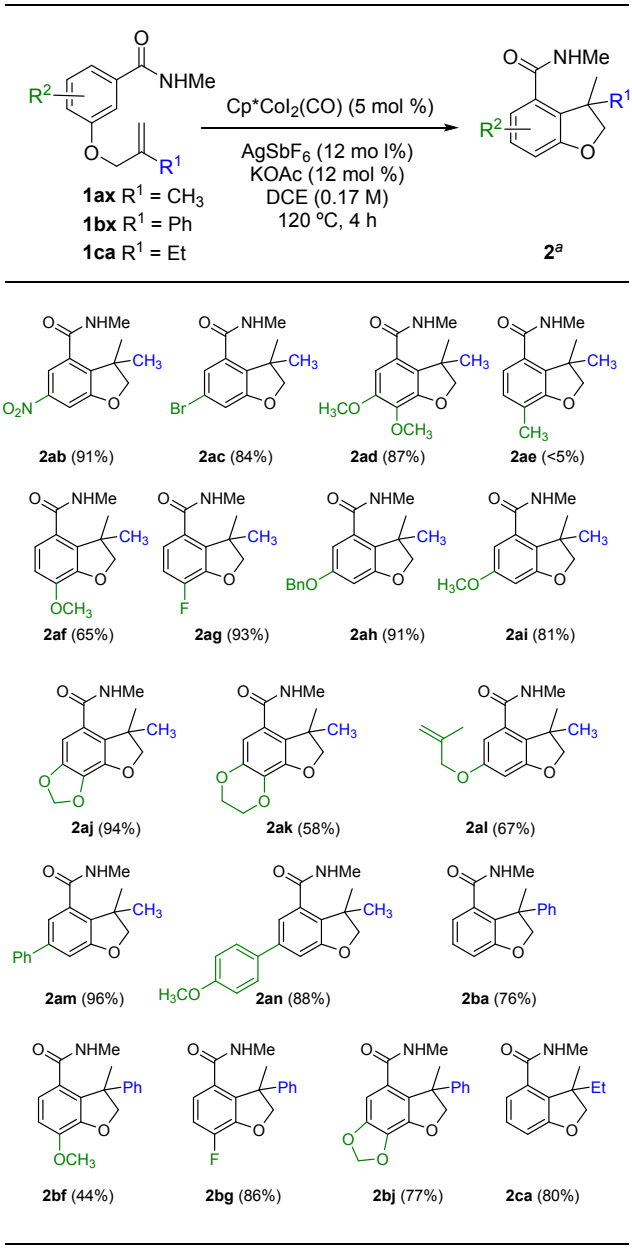
1aa **2aa**

entry	additive (mol %)	T (ºC)	time (h)	**2aa** (%)[a]
1	KOAc (12)	80	24	30
2[b]	KOAc (20)	80	24	31
3	KOAc (25)	80	24	10
4	KOAc (5)	80	24	33
5	$Cu(OAc)_2$ (12)	80	24	11
6	AgOAc (12)	80	24	4
7	NaOAc (12)	80	24	22
8	LiOAc (12)	80	24	13
9	CsOAc (12)	80	24	5
10	RbOAc (12)	80	24	13
11	nBu$_4$NOAc (12)	80	24	nr
12	NaOPiv (12)	80	24	6
13	KOCOPh (12)	80	24	25
14	AcOH (22)	80	24	6
15[c]	KOAc (12)	80	24	30
16	KOAc (12)	120	4	91
17[d]	KOAc (12)	120	4	nr
18[e]	KOAc (12)	120	4	nr
19	-	120	4	30

[a]Yield (%) of isolated pure compound. Reactions were carried out in a 0.2 to 0.3 mmol scale. [b]Cp*CoI_2(CO) (10 mol%) and $AgSbF_6$ (20 mol %) were used. [c][Cp*$Co(CH_3CN)_3$]$(SbF_6)_2$ (5 mol %) was used, with no $AgSbF_6$. [d]No Cp*CoI_2(CO) was used. [e]No $AgSbF_6$ was used. nr: no reaction; staring material recovered.

The use of different carboxylates (Table 1, entries 12-13) or acetic acid (Table 1, entry 14) was also unsuccessful. Besides, the reactivity was similar when a different cobalt precatalyst $[Cp^*Co(CH_3CN)_3](SbF_6)_2$ was used (Table 1, entry 15). Fortunately, an increase of the reaction temperature to 120 ºC resulted in a significant enhancement of the reactivity, leading to a complete conversion after just 4 hours, and furnishing the expected benzofuran **2aa** in excellent isolated yield (Table 1, entry 16). Control experiments were also carried out, confirming that both the presence of the cobalt precatalyst and the silver salt are required for reactivity (Table 1, entries 17-18). On the other hand, in the absence of the base (Table 1, entry 19), the reactivity is dramatically decreased, showing the importance of the carboxylate in assisting the C-H functionalization. It has been shown that the selectivity in the intermolecular hydroarylation of unbiased alkenes can be switched from the linear to the branched isomer by changing the additive used in the catalytic system, which results in a change in the C-H activation mechanism.[6] In our case, **2aa** was obtained with complete selectivity, through a 5-*exo* hydroarylation. Thus, for this intramolecular reaction, the type of carboxylate (and its absence) had an important impact on reactivity, but not on the regioselectivity of the transformation. Once the optimized reaction conditions were selected, the scope of the reaction was extended to different substitution patterns in both the arene and the alkene (Table 2). The electronic nature of the aromatic ring did not have a major impact on reactivity, as generally high yields of the dihydrobenzofurans **2** were obtained with electron-donating or electron-withdrawing substituents. However, **1ae** was almost unreactive, and lower yields were obtained in some of the examples with a substituent *ortho* to the allyl ether (**2af**, **2ak**, **2bf**), which could be attributed to unfavorable steric effects for the hydroarylation. In contrast to the use of ruthenium catalysts on related substrates[18d,f] a twofold hydroarylation of **1al** could also be hampered by steric effects, isolating **2al** as the only product in good yield. Different substituents on the alkene are also well tolerated (**2ba-2bj**, **2ca**).

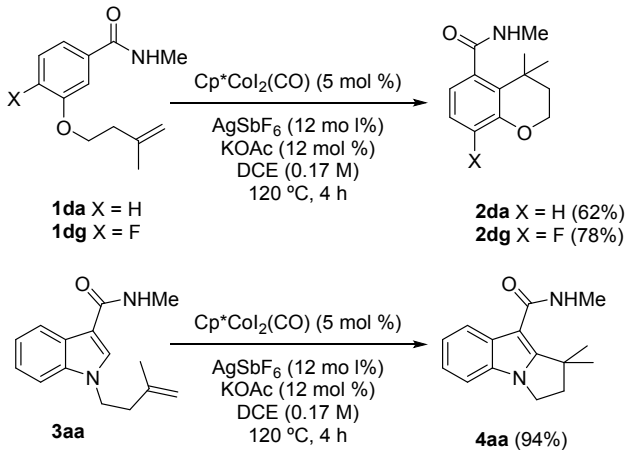
Table 2. Extension to the synthesis of benzofurans **2**



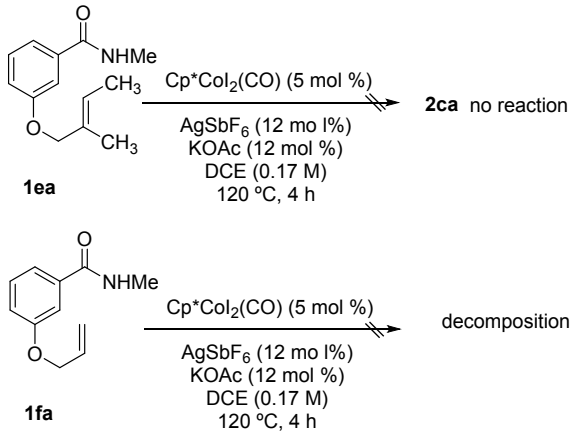
[a]Yield (%) of isolated pure product. Reactions were carried out in a 0.2 to 0.3 mmol scale in a 20 mL sealed reaction tube.

Under the same reaction conditions, the cyclization proceeded also efficiently through a 6-*exo* process for the formation of chromanes **2da, 2dg**. Besides, the cobaltation of the indole ring on **3aa** was also possible, leading to the formation of pyrroloindole **4aa** in excellent yield (Scheme 2). However, substitution on the terminal carbon of the alkene is not tolerated, probably due to steric reasons, as **1ea**

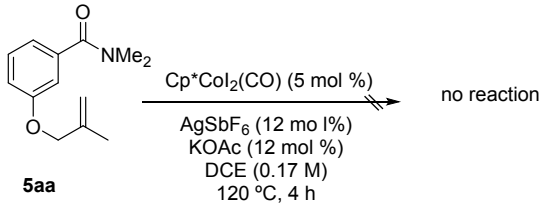
was unreactive under the standard reaction conditions. On the other hand, **1fa** led to decomposition products (Scheme 3).



Scheme 2. Extension to the synthesis of chromanes **2da,g** and pyrroloindole **4aa**



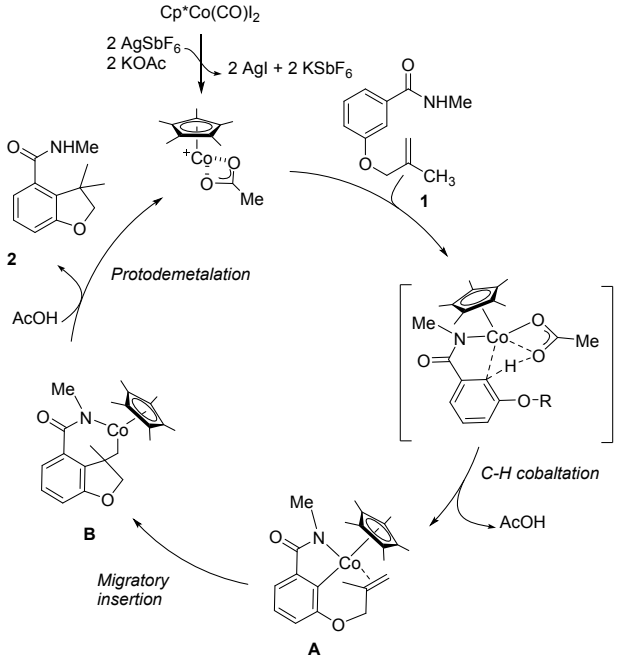
Scheme 3. Effect of the substitution on the alkene



Scheme 4. Effect of the directing group

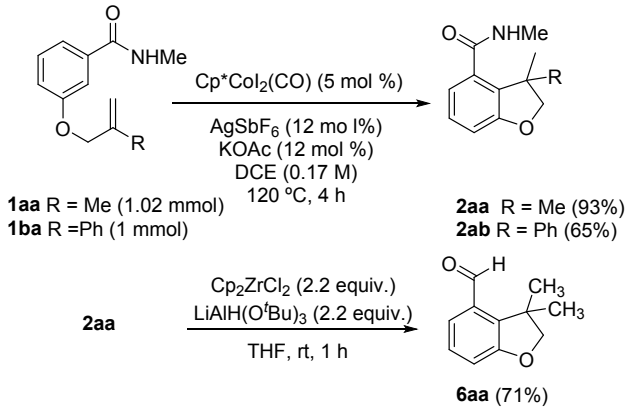
Finally, although dialkyl amides have been used as directing groups in related rhodium-,[18a] ruthenium-[18e] and iridium-[18g] mediated reactions, in this work, the presence of a N-H in the directing group is crucial for reactivity,[10,13,14] as **5aa** was completely unreactive (Scheme 4). Regarding the mode of action of the

amide directing group, C-H activation of benzamides through a Co-N binding mode has been proposed. In this context, cobaltacycles supporting that mechanism have been characterized.[25] On the other hand, the coordination of the Co(III)-center to the carbonyl oxygen has also been proposed for the intermolecular alkenylation of benzamides with activated alkenes.[26] It has also been shown that different substitution on the amide may result in different binding modes, as supported by DFT calculations.[10a,b] However, a Co-N activation pathway has also been proposed for related hydroarylation reactions[13,14,27] With all these considerations in mind, a schematic reaction mechanism proposal is depicted in Scheme 5. The C-H cobaltation of substrates **1** with the active $[Cp^*Co(OAc)]^+$ species, generated *in situ,* would take place to afford **A**, with the assistance of the acetate through a BIES[28] or a CMD[29] mechanism, as it has been proposed in similar transformations.[5d,6,8,10a,30] KIE experiments carried out in related systems[5b,5c,8] support that this C-H activation event is generally not the rate determining step. Subsequent selective migratory insertion would generate the seven-membered cobaltacycle **B** that would selectively undergo protodemetalation to afford **2**, regenerating the catalyst. An alternative pathway from **B** leading to aminoarylation products, as reported for related rhodium catalyzed systems,[18a] has not been observed, obtaining benzofurans with complete selectivity.



Scheme 5. Schematic mechanism proposal

Finally, the reaction was carried out in a 1 mmol scale with **1aa** and **1ba**, obtaining comparable yields (**2aa**, 93 *vs* 91%, and **2ba** 65 *vs* 76%) (Scheme 6). The possibility of transforming the directing group into other synthetically useful functional groups would allow further functionalization of the benzofurans obtained. With this purpose, the amide directing group could be reduced to an aldehyde using the Snieckus procedure for *in situ* generation of the Schwartz reagent (Scheme 6),[31] leading to aldehyde **6aa** in good yield, which has been further converted into a wide variety of derivatives.[18c]



Scheme 6. 1 mmol scale experiments and derivatization of **2aa**

In conclusion, the Cp*Co(III)-catalyzed intramolecular hydroarylation of unactivated alkenes takes place with complete selectivity for the generation of a quaternary center through an amide-directed cobaltation followed by migratory insertion and protodemetalation. The procedure allows the preparation of 3,3-disubstituted dihydrobenzofurans in high yields under relatively mild reaction conditions, and can also be extended to the synthesis of chromanes through the formation of 6-membred rings. Pyrroloindoles can also be obtained via C-H activation at C-2 of an indole moiety.

Experimental Section

General experimental methods. Melting points were determined in unsealed capillary tubes and are uncorrected. IR spectra were obtained using an ATR. NMR spectra were recorded at 20-25 ˚C, at 300 MHz for ^{1}H and 75.5 MHz for ^{13}C in $CDCl_3$ solutions. Mass spectra were recorded with an ESI^+ source. Exact mass was obtained using a TOF detector. TLC was carried out with 0.2 mm thick silica gel plates.

Visualization was accomplished by UV light. Flash column chromatography was performed on silica gel (230-400 mesh). Yields (%) are reported for pure isolated compounds after column chromatography, unless stated otherwise. Solids were crystallized after chromatography only for measuring the mp. All solvents used in reactions were anhydrous and purified according to standard procedures. All air- or moisture-sensitive reactions were performed under argon; the glassware was dried (130 ˚C) and purged with argon. Heating blocks with temperature control were used, when necessary, for the reactions that required heating. Cp*Co(III) catalysts were prepared and characterized according to literature procedures.[32] $Cp^*Co(CO)I_2$ was benchtop stable and could be stored (in the refrigerator at 5 ºC) for over 6 months. KOAc and NaOAc are hygroscopic and were kept in a sealed bottle in a dessecator. $AgSbF_6$ is hygroscopic and light-sentitive and was kept in a dark box.

Synthesis of amides 1. Substrates **1aa**,[18a] **1ab**, **1ad-1ag**,**1ai**, **1ak**,[18e] **1ba**, **1da**, **1ea**, **5aa** and **3aa**[18a] were prepared according to literature procedures, and **1ac**, **1ah**, **1aj**, **1al**, **1am**, **1an**, **1bf**, **1bg**, **1bj**, **1ca**, **1dg**, **1fa** using analogous synthetic routes (See supporting information Schemes S1 and S2). Preparation and characterization data for the non-described compunds **1** are given. The amides were obtained from the corresponding carboxylic acids according to the following General Procedure: Over a solution of the corresponding carboxylic acid (1 mmol) in dry CH_2Cl_2 (5 mL), one drop of DMF was added under argon atmosphere, followed by dropwise addition of oxalyl chloride (1.2 mmol). The mixture was stirred for 30 min at room temperature and the volatiles were evaporated *in vacuo*. The residue was redissolved in AcOEt (3.3 mL) and then, $CH_3NH_2 \cdot HCl$ (1.1 mmol), K_2CO_3 (2 mmol) and H_2O (1.7 mL) were subsequently added. The solution was stirred for 2 h and afterwards, the phases were separated. The aqueous phase was extracted with AcOEt (15 mL) and the combined organic extracts were washed with H_2O (15 mL) and brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The corresponding amides **1** were obtained without further purification or after purification by flash column chromatography (silica gel, petroleum ether/AcOEt).

5-Bromo-*N*-methyl-3-((2-methylallyl)oxy)benzamide (1ac). Prepared from 5-bromo-3-((2-methylallyl)oxy)benzoic acid (0.30 g, 1.1 mmol) and oxalyl chloride (0.11 mL, 1.3 mmol) in dry CH_2Cl_2

(5.5 mL); followed by $CH_3NH_2 \cdot HCl$ (81.2 mg, 1.2 mmol) and K_2CO_3 (0.30 g, 2.2 mmol) in AcOEt (3.7 mL) and H_2O (1.9 mL). After work-up, **1ac** was obtained as a solid without further purification (0.26 g, 84%): mp (CH_2Cl_2) 61-64 ºC; IR (ATR): 3310, 1637 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.35 (t, J = 1.5 Hz, 1H), 7.20 (t, J = 2.3, 1.7 Hz, 1H), 7.09 (dd, J = 2.3, 1.7 Hz, 1H), 6.41 (br s, 1H), 5.00 (br s, 1H), 4.92 (br s, 1H), 4.35 (s, 2H), 2.91 (d, J = 4.8 Hz, 3H), 1.73 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 166.8, 159.6, 139.9, 137.4, 122.8, 122.1, 121.0, 113.3, 112.5, 72.1, 27.0, 19.3; MS (ESI): *m/z* (%): 306.0 (MNa^+, 100), 286.0 (MH^+ + 2, 35), 285.0 (MH^+ + 1, 4), 284.0 (MH^+, 36), 148.1 (2); HRMS (ESI-TOF): *m/z* calcd. for $C_{12}H_{15}BrNO_2$: 284.0286 [MH^+]; found: 284.0287.

3-(Benzyloxy)-*N*-methyl-5-((2-methylallyl)oxy)benzamide (1ah). Prepared from 3-(benzyloxy)-5-((2-methylallyl)oxy)benzoic acid (0.14 g, 0.46 mmol) and oxalyl chloride (47.2 µL, 0.56 mmol) in dry CH_2Cl_2 (2.3 mL); followed by $CH_3NH_2 \cdot HCl$ (34.5 mg, 0.51 mmol) and K_2CO_3 (0.13 g, 0.93 mmol) in AcOEt (1.6 mL) and H_2O (0.79 mL). After work-up and purification by flash column chromatography (silica gel, petroleum ether/AcOEt 6/4), **1ah** was obtained as a solid (0.14 g, 96%): mp (CH_2Cl_2) 92-93 ºC; IR (ATR): 3243, 1631 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.47-7.29 (m, 5H), 7.00 (br s, 1H), 6.94 (br s, 1H), 6.68 (t, J = 2.1 Hz, 1H), 6.26 (br s, 1H), 5.21-4.88 (m, 4H), 4.43 (s, 2H), 2.98 (d, J = 4.8 Hz, 3H,), 1.83 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 168.0, 160.0, 140.5, 136.8, 136.5, 128.6, 128.1, 127.6, 113.0, 106.1, 105.8, 105.0, 72.0, 70.3, 26.9, 19.4; MS (ESI): *m/z* (%):334.1 (MNa^+, 100), 313.2 (MH^+ + 1, 9), 312.2 (MH^+, 55), 91.1 (2); HRMS (ESI-TOF): *m/z* calcd. for $C_{19}H_{22}NO_3$: 312.1600 [MH^+]; found: 312.1596.

***N*-Methyl-7-((2-methylallyl)oxy)benzo[*d*][*1,3*]dioxole-5-carboxamide (1aj).** Prepared from 7-((2-methylallyl)oxy)benzo[*d*][*1,3*]dioxole-5-carboxylic acid (0.31 g, 1.3 mmol) and oxalyl chloride (0.13 mL, 1.6 mmol) in dry CH_2Cl_2 (6.5 mL); followed by $CH_3NH_2 \cdot HCl$ (97.2 mg, 1.4 mmol) and K_2CO_3 (0.36 g, 2.6 mmol) in AcOEt (4.5 mL) and H_2O (2.2 mL). After work-up, **1aj** was obtained as a solid without further purification (0.29 g, 90%): mp (CH_2Cl_2) 99-101 ºC; IR (ATR): 3350, 1605 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.09 (d, J = 1.5 Hz, 1H), 6.89 (d, J = 1.5 Hz, 1H), 6.07 (br s, 1H), 6.04 (s, 2H), 5.11 (br s, 1H), 5.00 (br s, 1H), 4.58 (s, 2H), 2.99 (d, J = 4.9 Hz, 3H), 1.84 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5

MHz): δ 167.4, 149.0, 142.5, 140.3, 138.3, 129.1, 113.3, 109.7, 102.0, 100.9, 73.3, 26.9, 19.3; MS (ESI): *m/z* (%): 272.1 (MNa^+, 100), 250.1 (MH^+, 27), 193.1 (3); HRMS (ESI-TOF): *m/z* calcd. for $C_{13}H_{16}NO_4$: 250.1079 [MH^+]; found: 250.1077.

***N*-Methyl-3,5-bis((2-methylallyl)oxy)benzamide (1al).** Prepared from 3,5-bis((2-methylallyl)oxy)benzoic acid (0.31 g, 1.2 mmol) and oxalyl chloride (0.12 mL, 1.4 mmol) in dry CH_2Cl_2 (6.0 mL); followed by $CH_3NH_2 \cdot HCl$ (88.4 mg, 1.3 mmol) and K_2CO_3 (0.33 g, 2.4 mmol) in AcOEt (4.1 mL) and H_2O (2.1 mL). After work-up, **1al** was obtained as a solid without further purification (0.30 g, 91%): mp (CH_2Cl_2) 79-82 ºC; IR (ATR): 3250, 1595 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 6.93 (d, J = 2.3 Hz, 2H), 6.62-6.58 (m, 2H), 5.07 (br s, 2H), 4.97 (br s, 4H), 4.40 (s, 4H), 2.96 (d, J = 4.8 Hz, 3H), 1.80 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 168.1, 159.9, 140.5, 136.7, 112.9, 105.8, 104.9, 71.9, 26.9, 19.4; MS (ESI): *m/z* (%): 298.1 (MNa^+, 48), 276.2 (MH^+, 100), 245.1 (4), 219.1 (10); HRMS (ESI-TOF): *m/z* calcd. for $C_{16}H_{22}NO_3$: 276.1600 [MH^+]; found: 276.1601.

***N*-Methyl-5-((2-methylallyl)oxy)-[1,1´-biphenyl]-3-carboxamide (1am).** Prepared from 5-((2-methylallyl)oxy)-[1,1´-biphenyl]-3-carboxylic acid (0.20 g, 0.76 mmol) and oxalyl chloride (77.1 µL, 0.91 mmol) in dry CH_2Cl_2 (3.8 mL); followed by $CH_3NH_2 \cdot HCl$ (56.4 mg, 0.83 mmol) and K_2CO_3 (0.21 g, 1.5 mmol) in AcOEt (2.3 mL) and H_2O (1.3 mL). After work-up and purification by flash column chromatography (silica gel, petroleum ether/AcOEt 6/4), **1am** was obtained as a solid (0.20 g, 94%): mp (CH_2Cl_2) 99-101 ºC; IR (ATR): 3246, 1631 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.61-7.51 (m, 3H), 7.46-7.31 (m, 4H), 7.27-7.24 (m, 1H), 6.77 (br s, 1H), 5.12 (br s, 1H), 5.02 (br s, 1H), 4.49 (s, 2H), 2.99 (d, J = 4.8 Hz, 3H), 1.84 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 168.3, 159.3, 142.9, 140.5, 140.2, 136.5, 128.8, 127.8, 127.1, 118.1, 116.9, 113.0, 112.0, 71.9, 26.9, 19.4; MS (ESI): *m/z* (%): 304.1 (MNa^+, 97), 282.2 (MH^+, 85), 225.1 (3); HRMS (ESI-TOF): *m/z* calcd. for $C_{18}H_{20}NO_2$: 282.1494 [MH^+]; found: 282.1485.

4´-Methoxy-*N*-methyl-5-((2-methylallyl)oxy)-[1,1´-biphenyl]-3-carboxamide (1an). Prepared from 4´-methoxy-5-((2-methylallyl)oxy)-[1,1´-biphenyl]-3-carboxylic acid (0.30 g, 1.0 mmol) and oxalyl chloride (0.10 mL, 1.2 mmol) in dry CH_2Cl_2 (6.0 mL); followed by $CH_3NH_2 \cdot HCl$ (74.7 mg, 1.1 mmol)

and K_2CO_3 (0.28 g, 2.0 mmol) in AcOEt (4.0 mL) and H_2O (2.0 mL). After work-up, **1an** was obtained as a solid without further purification (0.30 g, 94%): mp (CH_2Cl_2) 120-122 ºC; IR (ATR): 3247, 1644 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.57-7.47 (m, 3H), 7.29 (br s, 1H), 7.22 (br s, 1H), 6.96 (d, J = 8.7 Hz, 2H), 6.53 (br s, 1H), 5.13 (br s, 1H), 5.02 (br s, 1H), 4.50 (s, 2H,), 3.84 (s, 3H), 3.01 (d, J = 4.8 Hz, 3H), 1.85 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 168.3, 159.5, 159.3, 142.5, 140.6, 136.5, 132.7, 128.2, 117.6, 116.5, 114.3, 113.0, 111.3, 71.9, 55.4, 26.9, 19.4; MS (ESI): *m/z* (%): 334.1 (MNa^+, 19), 312.2 (MH^+, 100), 255.1 (3); HRMS (ESI-TOF): *m/z* calcd. for $C_{19}H_{22}NO_3$: 312.1600 [MH^+]; found: 312.1601.

4-Methoxy-*N*-methyl-3-((2-phenylallyl)oxy)benzamide (1bf). Prepared from 4-methoxy-3-((2-phenylallyl)oxy)benzoic acid (0.18 g, 0.62 mmol) and oxalyl chloride (62.6 µL, 0.74 mmol) in dry CH_2Cl_2 (2.9 mL); followed by $CH_3NH_2 \cdot HCl$ (45.8 mg, 0.68 mmol) and K_2CO_3 (0.17 g, 1.2 mmol) in AcOEt (2.0 mL) and H_2O (1.0 mL). After work-up, **1bf** was obtained as a solid without further purification (0.16 g, 88%): mp (CH_2Cl_2) 114-117 ºC; IR (ATR): 3282, 1627 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.46-7.16 (m, 7H), 6.79 (d, J = 8.4 Hz, 1H), 6.03 (br s, 1H), 5.51 (br s, 1H), 5.40 (br s, 1H), 4.91 (s, 2H), 3.80 (s, 3H), 2.89 (d, J = 4.8 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 167.7, 152.5, 147.9, 142.7, 138.4, 128.5, 128.0, 127.2, 126.1, 120.2, 115.0, 113.4, 111.0, 70.9, 56.1, 26.8; MS (ESI): *m/z* (%): 320.1 (MNa^+, 54), 298.1 (MH^+, 100), 241.1 (8), 220.1 (8); HRMS (ESI-TOF): *m/z* calcd. for $C_{18}H_{20}NO_3$: 298.1443 [MH^+]; found: 298.1450.

4-Fluoro-*N*-methyl-3-((2-phenylallyl)oxy)benzamide (1bg). Prepared from 4-fluoro-3-((2-phenylallyl)oxy)benzoic acid (0.27 g, 1.0 mmol) and oxalyl chloride (0.10 mL, 1.2 mmol) in dry CH_2Cl_2 (5.0 mL); followed by $CH_3NH_2 \cdot HCl$ (74.8 mg, 1.1 mmol) and K_2CO_3 (0.28 g, 2.0 mmol) in AcOEt (3.4 mL) and H_2O (1.7 mL). After work-up, **1bg** was obtained as a solid without further purification (0.27 g, 95%): mp (CH_2Cl_2) 92-94 ºC; IR (ATR): 3310, 1634 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.57-7.46 (m, 3H), 7.43-7.23 (m, 4H), 7.11 (dd, J = 10.6, 8.4 Hz, 1H), 6.15 (br s, 1H), 5.64 (br s, 1H), 5.52 (br s, 1H), 5.02 (s, 2H), 3.00 (d, J = 4.9 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 167.2, 154.9 (d, J = 252.3 Hz), 146.7 (d, J = 11.2 Hz), 142.4, 138.1, 131.1 (d, J = 3.7 Hz), 128.5, 128.1, 126.1, 119.7 (d, J = 7.8 Hz), 116.1 (d, J = 19.3 Hz), 115.5, 115.2 (d, J = 2.8 Hz), 71.2, 26.9; MS (ESI): *m/z* (%):308.1 (MNa^+, 100), ,

286.1 (MH^+, 21), 208.1 (6); HRMS (ESI-TOF): *m/z* calcd. for $C_{17}H_{17}FNO_2$: 286.1243 [MH^+]; found: 286.1238.

***N*-Methyl-7-((2-phenylallyl)oxy)benzo[*d*][*1,3*]dioxole-5-carboxamide (1bj).** Prepared from 7-((2-phenylallyl)oxy)benzo[*d*][*1,3*]dioxole-5-carboxylic acid (0.15 g, 0.51 mmol) and oxalyl chloride (51.9 µL, 0.61 mmol) in dry CH_2Cl_2 (2.5 mL); followed by $CH_3NH_2 \cdot HCl$ (38.0 mg, 0.56 mmol) and K_2CO_3 (0.14 g, 1.0 mmol) in AcOEt (1.7 mL) and H_2O (0.87 mL). After work-up, **1bj** was obtained as a solid without further purification (0.15 g, 92%): mp (CH_2Cl_2) 118-121 ºC; IR (ATR): 3293, 1619 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.52-7.43 (m, 2H), 7.41-7.26 (m, 3H), 7.10 (br s, 1H), 6.93 (br s, 1H), 6.29 (br s, 1H), 6.00 (s, 2H), 5.61 (br s, 1H), 5.47 (br s, 1H), 5.03 (s, 2H), 2.96 (d, J = 4.7 Hz, 3H); $^{113}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 167.5, 149.1, 142.7, 142.1, 138.5, 138.1, 129.1, 128.5, 128.1, 126.1, 115.3, 110.2, 102.0, 101.4, 71.4, 26.9; MS (ESI): *m/z* (%):334.1 (MNa^+, 64), 312.1 (MH^+, 100), 255.1 (6), 234.1 (12); HRMS (ESI-TOF): *m/z* calcd. for $C_{18}H_{18}NO_4$: 312.1236 [MH^+]; found: 312.1239.

***N*-Methyl-3-(2-methylenebutoxy)benzamide (1ca).** Prepared from 3-(2-methylenebutoxy)benzoic acid (0.54 g, 2.6 mmol) and oxalyl chloride (0.26 mL, 3.1 mmol) in dry CH_2Cl_2 (12.4 mL); followed by $CH_3NH_2 \cdot HCl$ (0.19 mg, 2.9 mmol) and K_2CO_3 (0.72 g, 5.2 mmol) in AcOEt (8.4 mL) and H_2O (4.2 mL). After work-up, **1ca** was obtained as an oil without further purification (0.51 g, 90%): IR (ATR): 3317, 1637 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.32-7.29 (m, 1H), 7.23-7.17 (m, 2H), 7.04-6.86 (m, 1H), 6.35 (br s, 1H), 5.04 (br s, 1H), 4.91 (br s, 1H), 4.41 (s, 2H), 2.91 (d, J = 4.9 Hz, 3H), 2.07 (q, J = 7.4 Hz, 2H), 1.02 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 168.4, 158.9, 146.1, 135.9, 129.4, 119.1, 118.1, 113.3, 110.9, 70.9, 26.8, 25.8, 11.9; MS (ESI): *m/z* (%):, 242.1 (MNa^+, 78), 220.1 (MH^+, 100), 163.1 (5), 152.1 (7), 121.1 (5), 107.0 (5); HRMS (ESI-TOF): *m/z* calcd. for $C_{13}H_{18}NO_2$: 220.1338 [MH^+]; found: 220.1337.

4-Fluoro-*N*-methyl-3-((3-methylbut-3-en-1-yl)oxy)benzamide (1dg). Prepared from 4-fluoro-3-((3-methylbut-3-en-1-yl)oxy)benzoic acid (0.14 g, 0.63 mmol) and oxalyl chloride (63.5 µL, 0.75 mmol) in dry CH_2Cl_2 (3.1 mL); followed by $CH_3NH_2 \cdot HCl$ (46.4 mg, 0.69 mmol) and K_2CO_3 (0.17 g, 1.3 mmol) in AcOEt (2.1 mL) and H_2O (1.1 mL). After work-up and purification by flash column chromatography

(silica gel, petroleum ether/AcOEt 5/5), **1dg** was obtained as a solid (0.11 g, 77%): mp (CH_2Cl_2) 61-64 ºC; IR (ATR): 3389, 1637 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.57-7.45 (m, 1H), 7.30-7.20 (m, 1H), 7.15-7.00 (m, 1H), 6.42 (br s, 1H), 4.86 (br s, 1H), 4.80 (br s, 1H), 4.17 (t, J = 6.7 Hz, 2H), 2.99 (d, J = 4.7 Hz, 3H), 2.54 (t, J = 6.7 Hz, 2H), 1.81 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 167.3, 154.6 (d, J = 251.6 Hz), 147.2 (d, J = 11.0 Hz), 141.7, 131.1 (d, J = 3.7 Hz), 119.1 (d, J = 7.7 Hz), 115.9 (d, J = 19.3 Hz), 114.9 (d, J = 2.9 Hz), 112.3, 68.0, 37.0, 26.9, 22.8; MS (ESI): *m/z* (%):260.1 (MNa^+, 100), 238.1 (MH^+, 46), 170.1 (16); HRMS (ESI-TOF): *m/z* calcd. for $C_{13}H_{17}FNO_2$: 238.1243 [MH^+]; found: 238.1239.

3-(Allyloxy)-*N*-methylbenzamide (1fa). Prepared from 3-(allyloxy)benzoic acid (0.22 g, 1.2 mmol) and oxalyl chloride (0.12 mL, 1.5 mmol) in dry CH_2Cl_2 (5.8 mL); followed by $CH_3NH_2 \cdot HCl$ (90.3 mg, 1.3 mmol) and K_2CO_3 (0.34 g, 2.4 mmol) in AcOEt (3.9 mL) and H_2O (2.0 mL). After work-up, **1fa** was obtained as a solid without further purification (0.20 g, 85%): mp (CH_2Cl_2) 68-69 ºC; IR (ATR): 3342, 1633 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.34-7.14 (m, 3H), 6.93 (d, J = 7.8 Hz, 1H), 6.71 (br s, 1H), 5.93 (ddt, J = 15.8, 10.5, 5.2 Hz, 1H), 5.35-5.25 (m, 1H), 5.23-5.13 (m, 1H), 4.44 (d, J = 5.2 Hz, 2H), 2.87 (d, J = 4.8 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 167.2, 157.7, 135.0, 131.9, 128.5, 118.0, 117.2, 116.8, 112.1, 67.8, 25.8; MS (ESI): *m/z* (%):214.1 (MNa^+, 46), 192.1 (MH^+, 100), 107.0 (10); HRMS (ESI-TOF): *m/z* calcd. for $C_{11}H_{14}NO_2$: 192.1025 [MH^+]; found: 192.1027.

Co(III)-catalyzed intramolecular C-H alkylation of amides 1aa-1dg and 3aa. Synthesis of dihydrobenzofurans 2aa-2dg and indole 4aa. The corresponding amides **1aa-1dg** and **3aa** (1 equiv.), $AgSbF_6$ (0.12 equiv.), KOAc (0.12 equiv.) and Cp*Co(CO)I_2 (0.05 equiv.) were successively weighed in a 20-mL vial (23 × 72 mm). Then, 1,2-DCE (0.17 M) was added and the mixture was stirred at room temperature for 3 minutes before placing the reaction vessel in an oil bath preheated to 120 ºC. The reaction mixture was stirred at that temperature for 4 h and afterwards, it was diluted with AcOEt (20 mL). The volatiles were evaporated *in vacuo* and the residue was purified by flash column chromatography (silica gel, petroleum ether/AcOEt) to afford the corresponding benzofurans **2aa-2dg** and indole **4aa**.

***N*,3,3-Trimethyl-2,3-dihydrobenzofuran-4-carboxamide (2aa).** Prepared from benzamide **1aa** (62.7 mg, 0.31 mmol), $AgSbF_6$ (12.6 mg, 0.037 mmol), KOAc (3.6 mg, 0.037 mmol) and Cp*Co(CO)I_2 (7.3 mg, 0.015 mmol) in 1,2-DCE (1.8 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 6/4), **2aa** was obtained as a solid, whose data are coincidental to those reported[18a] (57.0 mg, 91%): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.10 (t, J = 7.8, 1H), 6.86-6.83 (m, 1H), 6.83-6.79 (m, 1H), 6.04 (br s, 1H), 4.17 (s, 2H), 2.95 (d, J = 4.9 Hz, 3H), 1.43 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 169.6, 160.3, 133.8, 133.6, 128.2, 112.0, 111.7, 85.3, 42.9, 26.6, 25.9.

***N*,3,3-Trimethyl-6-nitro-2,3-dihydrobenzofuran-4-carboxamide (2ab).** Prepared from benzamide **1ab** (62.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.030 mmol), KOAc (2.9 mg, 0.030 mmol) and Cp*Co(CO)I_2 (5.9 mg, 0.012 mmol) in 1,2-DCE (1.5 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 7/3), **2ab** was obtained as a solid, whose data are coincidental to those reported[18e] (56.9 mg, 91%): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.71 (d, J = 2.0 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 6.37 (br s, 1H), 4.28 (s, 2H), 2.98 (d, J = 4.9 Hz, 3H), 1.44 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 167.3, 161.2, 147.9, 141.6, 133.8, 114.8, 106.5, 86.2, 43.2, 26.8, 25.5.

6-Bromo-*N*,3,3-trimethyl-2,3-dihydrobenzofuran-4-carboxamide (2ac). Prepared from benzamide **1ac** (68.2 mg, 0.22 mmol), $AgSbF_6$ (9.0 mg, 0.027 mmol), KOAc (2.6 mg, 0.027 mmol) and Cp*Co(CO)I_2 (5.2 mg, 0.011 mmol) in 1,2-DCE (1.3 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 6/4), **3ac** was obtained as a solid (60.6 mg, 84%): mp (CH_2Cl_2) 138-139 ºC; IR (ATR): 3228, 1627 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.98 (s, 2H), 6.11 (br s, 1H), 4.19 (s, 2H), 2.95 (d, J = 4.9 Hz, 3H), 1.41 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 168.1, 161.3, 134.6, 133.3, 121.8, 120.9, 115.1, 85.8, 42.7, 26.7, 25.8; MS (ESI): *m/z* (%): 306.0 (MNa^+, 14), 286.0 (MH^+ + 2, 99), 285.0 (MH^+ + 1, 10), 284.0 (MH^+, 100); HRMS (ESI-TOF): *m/z* calcd. for $C_{12}H_{15}BrNO_2$: 284.0286 [MH^+]; found: 284.0294.

6,7-Dimethoxy-*N*,3,3-trimethyl-2,3-dihydrobenzofuran-4-carboxamide (2ad). Prepared from benzamide **1ad** (65.2 mg, 0.25 mmol), $AgSbF_6$ (10.1 mg, 0.029 mmol), KOAc (2.9 mg, 0.029 mmol) and Cp*Co(CO)I_2 (5.8 mg, 0.012 mmol) in 1,2-DCE (1.4 mL). After purification by flash column

chromatography (silica gel, petroleum ether/AcOEt 6/4), **2ad** was obtained as a solid, whose data are coincidental to those reported[18e] (57.0 mg, 87%): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.38 (s, 1H), 6.11 (br s, 1H), 4.18 (s, 2H), 3.90 (s, 3H), 3.77 (s, 3H), 2.92 (d, J = 4.9 Hz, 3H), 1.39 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 169.4, 152.2, 151.7, 134.9, 128.7, 127.1, 103.6, 86.3, 60.6, 56.4, 42.9, 26.6, 25.9.

7-Methoxy-*N*,3,3-trimethyl-2,3-dihydrobenzofuran-4-carboxamide (2af). Prepared from 4benzamide **1af** (65.8 mg, 0.28 mmol), $AgSbF_6$ (11.5 mg, 0.034 mmol), KOAc (3.3 mg, 0.034 mmol) and Cp*Co(CO)I_2 (6.7 mg, 0.014 mmol) in 1,2-DCE (1.6 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 5/5), **2af** was obtained as a solid, whose data are coincidental to those reported[18e] (41.2 mg, 65%): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.78 (d, J = 8.3 Hz, 1H), 6.60 (d, J = 8.3 Hz, 1H), 5.94 (br s, 1H), 4.15 (s, 2H), 3.79 (s, 3H), 2.86 (d, J = 4.9 Hz, 3H), 1.37 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 169.4, 148.4, 146.2, 135.3, 126.0, 120.2, 110.3, 86.0, 55.9, 43.7, 26.7, 25.8.

7-Fluoro-*N*,3,3-trimethyl-2,3-dihydrobenzofuran-4-carboxamide (2ag). Prepared from benzamide **1ag** (67.8 mg, 0.30 mmol), $AgSbF_6$ (12.5 mg, 0.036 mmol), KOAc (3.6 mg, 0.036 mmol) and Cp*Co(CO)I_2 (7.2 mg, 0.015 mmol) in 1,2-DCE (1.8 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 6/4), **2ag** was obtained as a solid, whose data are coincidental to those reported[18e] (62.9 mg, 93%): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.86 (d, J = 9.9, 8.4 Hz, 1H), 6.78 (d, J = 8.4, 4.3 Hz, 1H), 6.13 (br s, 1H), 4.25 (s, 2H), 2.92 (d, J = 4.9 Hz, 3H), 1.43 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 168.9, 148.6 (d, J = 255.9 Hz), 146.9 (d, J = 16.5 Hz), 137.9 (d, J = 3.2 Hz), 129.4 (d, J = 3.6 Hz), 119.8 (d, J = 5.9 Hz), 115.1 (d, J = 17.3 Hz), 86.5, 43.8 (d, J = 1.8 Hz), 26.6, 25.7.

6-(Benzyloxy)-*N*,3,3-trimethyl-2,3-dihydrobenzofuran-4-carboxamide (2ah). Prepared from benzamide **1ah** (68.2 mg, 0.22 mmol), $AgSbF_6$ (9.0 mg, 0.027 mmol), KOAc (2.6 mg, 0.027 mmol) and Cp*Co(CO)I_2 (5.2 mg, 0.011 mmol) in 1,2-DCE (1.3 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 6/4), **2ah** was obtained as a solid (62.1 mg, 91%): mp (CH_2Cl_2) 102-104 ºC; IR (ATR): 3307, 1612 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.46-7.27 (m, 5H),

6.49 (s, 2H), 6.15 (br s, 1H), 4.99 (s, 2H), 4.18 (s, 2H), 2.93 (d, J = 4.9 Hz, 3H), 1.42 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 169.4, 161.6, 159.1, 136.6, 133.7, 128.6, 128.1, 127.5, 126.3, 106.0, 98.8, 86.0, 70.4, 42.4, 26.6, 26.2; MS (ESI): *m/z* (%): 335.1 (MNa^+ + 1, 17), 334.1 (MNa^+, 100), 313.2 (MH^+ + 1, 6), 312.2 (MH^+, 36); HRMS (ESI-TOF): *m/z* calcd. for $C_{19}H_{22}NO_3$: 312.1600 [MH^+]; found: 312.1590.

6-Methoxy-*N*,3,3-trimethyl-2,3-dihydrobenzofuran-4-carboxamide (2ai). Prepared from benzamide **1ai** (68.2 mg, 0.29 mmol), $AgSbF_6$ (12.0 mg, 0.035 mmol), KOAc (3.4 mg, 0.035 mmol) and Cp*Co(CO)I_2 (6.9 mg, 0.014 mmol) in 1,2-DCE (1.7 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 5/5), **2ai** was obtained as a solid, whose data are coincidental to those reported[18e] (55.4 mg, 81%): ^1H NMR ($CDCl_3$, 300 MHz): δ 6.39 (d, J = 2.3 Hz, 1H), 6.36 (d, J = 2.3 Hz, 1H), 6.09 (br s, 1H), 4.16 (s, 2H), 3.73 (s, 3H), 2.92 (d, J = 4.9 Hz, 3H), 1.38 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 169.4, 161.6, 160.0, 133.6, 125.9, 104.9, 97.9, 86.0, 55.6, 42.4, 26.5, 26.1.

***N*,6,6-Trimethyl-6,7-dihydro-[*1,3*]dioxolo[*4,5-g*]benzofuran-5-carboxamide (2aj).** Prepared from benzamide **1aj** (64.2 mg, 0.26 mmol), $AgSbF_6$ (10.6 mg, 0.031 mmol), KOAc (3.0 mg, 0.031 mmol) and Cp*Co(CO)I_2 (6.1 mg, 0.013 mmol) in 1,2-DCE (1.5 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 6/4), **2aj** was obtained as a solid (60.5 mg, 94%): mp (CH_2Cl_2) 176-177 ºC; IR (ATR): 3307, 1649 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 6.41 (s, 1H), 5.96 (br s, 3H, NH), 4.24 (s, 2H), 2.94 (d, J = 4.9 Hz, 3H), 1.42 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 169.1, 148.5, 142.5, 131.7, 131.3, 126.0, 101.9, 100.1, 87.1, 43.2, 26.7, 25.7; MS (ESI): *m/z* (%): 273.1 (MNa^+ + 1, 10), 272.1 (MNa^+, 100), 251.1 (MH^+ + 1, 5), 250.1 (MH^+, 51), 193.1 (11); HRMS (ESI-TOF): *m/z* calcd. for $C_{13}H_{16}NO_4$: 250.1079 [MH^+]; found: 250.1077.

***N*,7,7-Trimethyl-2,3,7,8-tetrahydro-[*1,4*]dioxino[*2,3-g*]benzofuran-6-carboxamide (2ak).** Prepared from amide **1ak** (71.5 mg, 0.27 mmol), $AgSbF_6$ (11.2 mg, 0.033 mmol), KOAc (3.2 mg, 0.033 mmol) and Cp*Co(CO)I_2 (6.5 mg, 0.014 mmol) in 1,2-DCE (1.6 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 5/5), **2ak** was obtained as a solid, whose data are

coincidental to those reported[18e] (41.4 mg, 58%): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.44 (s, 1H), 5.93 (br s, 1H), 4.34-4.15 (m, 6H), 2.93 (d, J = 4.7 Hz, 3H), 1.42 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 169.0, 148.3, 143.2, 130.8, 127.9, 124.9, 108.2, 86.9, 64.6, 64.4, 43.3, 26.6, 26.0.

***N,3,3*-Trimethyl-6-((2-methylallyl)oxy)-2,3-dihydrobenzofuran-4-carboxamide (2al).** Prepared from benzamide **1al** (61.0 mg, 0.22 mmol), $AgSbF_6$ (9.1 mg, 0.027 mmol), KOAc (2.6 mg, 0.027 mmol) and Cp*Co(CO)I_2 (5.3 mg, 0.011 mmol) in 1,2-DCE (1.3 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 7/3), **2al** was obtained as an oil (40.8 mg, 67%): IR (ATR): 3300, 1648 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.35 (s, 2H), 5.88 (br s, 1H), 4.98 (br s, 1H), 4.90 (br s, 1H), 4.29 (s, 2H), 4.10 (s, 2H), 2.87 (d, J = 4.9 Hz, 3H), 1.72 (s, 3H), 1.33 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 169.4, 161.6, 159.2, 140.6, 133.6, 126.1, 112.9, 105.9, 98.7, 86.0, 72.1, 42.4, 26.6, 26.2, 19.4; MS (ESI): *m/z* (%): 298.1 (MNa^+, 40), 277.2 (MH^+ + 1, 13), 276.2 (MH^+, 100), 245.1 (4), 219.1 (19); HRMS (ESI-TOF): *m/z* calcd. for $C_{16}H_{22}NO_3$: 276.1600 [MH^+]; found: 276.1605.

***N*,3,3-Trimethyl-6-phenyl-2,3-dihydrobenzofuran-4-carboxamide (2am).** Prepared from amide **1am** (64.4 mg, 0.23 mmol), $AgSbF_6$ (9.4 mg, 0.028 mmol), KOAc (2.7 mg, 0.028 mmol) and Cp*Co(CO)I_2 (5.5 mg, 0.011 mmol) in 1,2-DCE (1.4 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 7/3), **2am** was obtained as a solid (62.0 mg, 96%): mp (CH_2Cl_2) 128-130 ºC; IR (ATR): 3246, 1631 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57-7.49 (m, 2H), 7.49-7.30 (m, 3H), 7.08 (s, 1H), 7.06 (s, 1H), 6.03 (br s, 1H), 4.23 (s, 2H), 2.96 (d, J = 4.9 Hz, 3H), 1.48 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 169.6, 161.0, 141.9, 140.3, 133.8, 132.9, 128.8, 127.6, 127.0, 118.2, 110.3, 85.6, 42.8, 26.6, 26.0; MS (ESI): *m/z* (%): 304.1 (MNa^+, 100), 282.1 (MH^+, 58), 225.1 (2); HRMS (ESI-TOF): *m/z* calcd. for $C_{18}H_{20}NO_2$: 282.1494 [MH^+]; found: 282.1492.

6-(4-Methoxyphenyl)-*N*,3,3-trimethyl-2,3-dihydrobenzofuran-4-carboxamide (2an). Prepared from amide **1an** (73.1 mg, 0.23 mmol), $AgSbF_6$ (9.7 mg, 0.028 mmol), KOAc (2.8 mg, 0.028 mmol) and Cp*Co(CO)I_2 (5.6 mg, 0.012 mmol) in 1,2-DCE (1.4 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 7/3), **2an** was obtained as a solid (64.4 mg, 88%): mp (CH_2Cl_2) 120-123 ºC; IR (ATR): 3349, 1637 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.45 (d, J = 8.7 Hz,

2H), 7.05-7.00 (m, 2H), 6.94 (d, J = 8.7 Hz, 2H), 6.09 (br s, 1H), 4.22 (s, 2H), 3.83 (s, 3H), 2.97 (d, J = 4.8 Hz, 3H), 1.47 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 169.7, 161.0, 159.4, 141.5, 133.8, 132.8, 132.3, 128.1, 117.7, 114.2, 109.8, 85.6, 55.3, 42.8, 26.6, 26.0; MS (ESI): *m/z* (%): 334.1 (MNa^+, 21), 312.2 (MH^+, 100), 255.1 (3); HRMS (ESI-TOF): *m/z* calcd. for $C_{19}H_{22}NO_3$: 312.1600 [MH^+]; found: 312.1603.

***N*,3-Dimethyl-3-phenyl-2,3-dihydrobenzofuran-4-carboxamide (2ba).** Prepared from *N*-methyl-3-((2-phenylallyl)oxy)benzamide **1ba** (70.0 mg, 0.26 mmol), $AgSbF_6$ (10.8 mg, 0.031 mmol), KOAc (3.1 mg, 0.031 mmol) and Cp*Co(CO)I_2 (6.2 mg, 0.013 mmol) in 1,2-DCE (1.5 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 6/4), **2ba** was obtained as a solid, whose data are coincidental to those reported[18a] (53.1 mg, 76%): ^1H NMR ($CDCl_3$, 300 MHz): δ 7.37-7.19 (m, 6H), 6.98-6.96 (m, 2H), 5.11 (br s, 1H), 4.54 (d, J = 8.6 Hz, 1H), 4.45 (d, J = 8.6 Hz, 1H), 2.49 (d, J = 4.9 Hz, 3H), 1.88 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 168.6, 160.4, 145.9, 133.9, 132.8, 129.1, 128.6, 126.8, 126.4, 120.4, 111.8, 87.2, 50.0, 26.1, 24.1.

7-Methoxy-*N*,3-dimethyl-3-phenyl-2,3-dihydrobenzofuran-4-carboxamide (2bf). Prepared from amide **1bf** (72.6 mg, 0.24 mmol), $AgSbF_6$ (10.1 mg, 0.029 mmol), KOAc (2.9 mg, 0.029 mmol) and Cp*Co(CO)I_2 (5.8 mg, 0.012 mmol) in 1,2-DCE (1.4 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 4/6), **2bf** was obtained as a solid (31.7 mg, 44%): mp (CH_2Cl_2) 124-125 ºC; IR (ATR): 3310 cm^{-1}, 1648 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.42-7.21 (m, 5H), 7.07 (d, J = 8.4 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 5.04 (br s, 1H), 4.60 (d, J = 8.7 Hz, 1H), 4.52 (d, J = 8.7 Hz, 1H), 3.96 (s, 3H), 2.50 (d, J = 4.9 Hz, 3H), 1.90 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 168.3, 148.6, 146.4, 145.8, 133.9, 128.7, 126.9, 126.3, 126.0, 122.0, 111.2, 87.8, 56.0, 50.8, 26.2, 23.9; MS (ESI): *m/z* (%): 320.1 (MNa^+, 43), 298.1 (MH^+, 100), 220.1 (6); HRMS (ESI-TOF): *m/z* calcd. for $C_{18}H_{20}NO_3$: 298.1443 [MH^+]; found: 298.1445.

7-Fluoro-*N*,3-Dimethyl-3-phenyl-2,3-dihydrobenzofuran-4-carboxamide (2bg). Prepared from amide **1bg** (73.3 mg, 0.26 mmol), $AgSbF_6$ (10.6 mg, 0.031 mmol), KOAc (3.0 mg, 0.031 mmol) and Cp*Co(CO)I_2 (6.1 mg, 0.013 mmol) in 1,2-DCE (1.5 mL). After purification by flash column

chromatography (silica gel, petroleum ether/AcOEt 6/4), **2bg** was obtained as a solid (63.2 mg, 86%): mp (CH_2Cl_2) 156-158 ºC; IR (ATR): 3339, 1652 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.44-7.19 (m, 5H), 7.08-6.88 (m, 2H), 5.08 (br s, 1H), 4.64 (s, J = 8.7 Hz, 1H), 4.56 (s, J = 8.7 Hz, 1H), 2.49 (d, J = 4.8 Hz, 3H), 1.91 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 167.7, 148.8 (d, J = 247.0 Hz), 147.1 (d, J = 7.0 Hz), 145.0, 136.7, 129.6 (d, J = 3.7 Hz), 128.7, 127.0, 126.4, 121.4 (d, J = 6.0 Hz), (d, J = 17.2 Hz), 116.0, 88.4, 50.9, 26.2, 23.9; MS (ESI): *m/z* (%): 308.1 (MNa^+, 100), 286.1 (MH^+, 27), 208.1 (5); HRMS (ESI-TOF): *m/z* calcd. for $C_{17}H_{17}FNO_2$: 286.1243 [MH^+]; found: 286.1242.

***N*,6-Dimethyl-6-phenyl-6,7-dihydro-[*1,3*]dioxolo[*4,5-g*]benzofuran-5-carboxamide (2bj).** Prepared from amide **1bj** (71.4 mg, 0.23 mmol), $AgSbF_6$ (9.5 mg, 0.028 mmol), KOAc (2.7 mg, 0.028 mmol) and Cp*Co(CO)I_2 (5.5 mg, 0.011mmol) in 1,2-DCE (1.4 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 6/4), **2bj** was obtained as a solid (54.9 mg, 77%): mp (CH_2Cl_2) 158-160 ºC; IR (ATR): 3285, 1640 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.46-7.16 (m, 5H), 6.58 (s, 1H), 6.04 (br s, 1H), 6.02 (br s, 1H), 5.07 (br s, 1H), 4.59 (d, J = 8.6 Hz, 1H), 4.50 (d, J = 8.6 Hz, 1H), 2.47 (d, J = 4.9 Hz, 3H), 1.87 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 168.0, 149.2, 145.7, 142.6, 131.9, 130.2, 128.7, 126.9, 126.6, 126.3, 102.2, 101.7, 88.8, 50.2, 26.2, 23.9; MS (ESI): *m/z* (%):334.1 (MNa^+, 50), 312.1 (MH^+, 100), 234.1 (7); HRMS (ESI-TOF): *m/z* calcd. for $C_{18}H_{18}NO_4$: 312.1236 [MH^+]; found: 312.1242.

3-Ethyl-*N*,3-trimethyl-2,3-dihydrobenzofuran-4-carboxamide (2ca). Prepared from amide **1ca** (60.0 mg, 0.27 mmol), $AgSbF_6$ (11.3 mg, 0.033 mmol), KOAc (3.2 mg, 0.033 mmol) and Cp*Co(CO)I_2 (6.5 mg, 0.014 mmol) in 1,2-DCE (1.6 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 6/4), **2ca** was obtained as an oil (47.9 mg, 80%): IR (ATR): 3317 1637 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.10 (t, J = 7.8 Hz, 1H), 6.83-6.79 (m, 2H), 6.03 (br s, 1H), 4.34 (d, J = 8.5 Hz, 1H), 4.09 (d, J = 8.5 Hz, 1H), 2.93 (d, J = 4.9 Hz, 3H), 2.04-1.87 (m, 1H), 1.74 (dq, J = 14.7, 7.5 Hz, 1H), 1.40 (s, 3H), 0.79 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 169.7, 160.8, 134.0, 132.4, 128.2, 119.0, 111.5, 82.3, 46.9, 31.5, 26.6, 24.6, 9.2; MS (ESI): *m/z* (%):242.1 (MNa^+, 12), 220.1

(MH$^+$, 100), 163.1 (3), 152.1 (2), 121.1 (2), 107.0 (2); HRMS (ESI-TOF): *m/z* calcd. for $C_{13}H_{18}NO_2$: 220.1338 [MH$^+$]; found: 220.1336.

***N*,4,4-Trimethylchroman-5-carboxamide (2da).** Prepared from *N*-methyl-3-((3-methylbut-3-en-1-yl)oxy)benzamide **1da** (61.5 mg, 0.28 mmol), $AgSbF_6$ (11.6 mg, 0.034 mmol), KOAc (3.3 mg, 0.034 mmol) and Cp*Co(CO)I_2 (6.7 mg, 0.014 mmol) in 1,2-DCE (1.5 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 6/4), **2da** was obtained as a solid, whose data are coincidental to those reported[18a] (38.0 mg, 62%): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.10 (dd, J = 8.2, 7.3 Hz, 1H), 6.82 (dd, J = 8.2, 1.4 Hz, 1H), 6.74 (dd, J = 7.3, 1.4 Hz, 1H), 5.91 (br s, 1H), 4.18-4.33 (m, 2H), 2.94 (d, J = 4.9 Hz, 3H), 1.71-1.85 (m, 2H), 1.45 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 172.9, 154.1, 138.1, 128.3, 127.0, 120.2, 118.9, 62.5, 39.5, 31.6, 29.3, 26.8.

8-Fluoro-*N*,4,4-trimethylchroman-5-carboxamide (2dg). Prepared from amide **1dg** (68.5 mg, 0.29 mmol), $AgSbF_6$ (11.9 mg, 0.035 mmol), KOAc (3.4 mg, 0.035 mmol) and Cp*Co(CO)I_2 (6.9 mg, 0.014 mmol) in 1,2-DCE (1.7 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 7/3) **2dg** was obtained as a solid (53.2 mg, 78%): mp (CH_2Cl_2) 179-181 ºC; IR (ATR): 3300, 1627 cm$^-$; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.10 (dd, J = 10.2, 8.3 Hz, 1H), 6.65 (dd, J = 8.3, 5.3 Hz, 1H), 6.06 (br s, 1H), 4.35-4.23 (m, 2H), 2.90 (d, J = 4.9 Hz, 3H), 1.72-1.85 (m, 2H), 1.43 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 172.1, 152.5 (d, J = 247.3 Hz), 142.7 (d, J = 10.1 Hz), 133.4 (d, J = 4.0 Hz), 131.2, 119.2 (d, J = 7.8 Hz), 113.0 (d, J = 18.6 Hz), 62.8, 39.0, 31.7 (d, J = 2.2 Hz), 29.0, 26.8; MS (ESI): *m/z* (%):260.1 (MNa$^+$, 83), 238.1 (MH$^+$, 100), 170.1 (5); HRMS (ESI-TOF): *m/z* calcd. for $C_{13}H_{17}FNO_2$: 238.1243 [MH$^+$]; found: 238.1237.

***N*,1,1-Trimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxamide (4aa).** Prepared from amide **3aa** (68.4 mg, 0.28 mmol), $AgSbF_6$ (11.6 mg, 0.034 mmol), KOAc (3.3 mg, 0.034 mmol) and Cp*Co(CO)I_2 (6.7 mg, 0.014 mmol) in 1,2-DCE (1.7 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 6/4), **4aa** was obtained as a solid, whose data are coincidental to those reported[18a] (64.3 mg, 94%): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.74-7.60 (m, 1H), 7.33-7.14 (m, 3H), 5.96 (br s, 1H), 4.09 (t, J = 7.0 Hz, 2H), 3.06 (d, J = 4.9 Hz, 3H), 2.46 (t, J = 7.0 Hz, 2H),

1.62 (s, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 166.1, 156.5, 131.7, 129.4, 121.3, 120.9, 119.0, 110.3, 102.4, 44.1, 42.7, 40.5, 26.5, 26.3.

1 mmol scale synthesis of 2aa. Prepared according to the general procedure using a 50-mL (25 × 150 mm) reaction tube from **1aa** (0.21 g, 1 mmol), $AgSbF_6$ (42.2 mg, 0.12 mmol), KOAc (12.1 mg, 0.12 mmol) and Cp*Co(CO)I_2 (24.4 mg, 0.05 mmol) in 1,2-DCE (6.0 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 6/4), **2aa** was obtained as a solid (0.20 mg, 93%).

1 mmol scale synthesis of 2ba Prepared according to the general procedure using a 50-mL (25 × 150 mm) reaction tube from **1ba** (0.27 g, 1 mmol), $AgSbF_6$ (41.2 mg, 0.12 mmol), KOAc (11.8 mg, 0.12 mmol) and Cp*Co(CO)I_2 (23.4 mg, 0.05 mmol) in 1,2-DCE (5.9 mL). After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 6/4), **2ba** was obtained as a solid (0.17 g, 65%).

Removal of the directing group. Synthesis of 6aa. To a solution of **2aa** (51.8 mg, 0.25 mmol) and Cp_2ZrCl_2 (0.16 g, 5.6 mmol) in dry THF (3 mL), a solution of $LiAlH(O^tBu)_3$ (1 M in THF) (0.56 mL, 5.6 mmol) was rapidly added under argon atmosphere. The reaction mixture was stirred at room temperature for 1 h and it was quenched by addition of H_2O (10 mL). A 0.5 M aqueous solution of HCl was added to adjust pH below 7 and the mixture was extracted with AcOEt (2 × 15 mL). The combined organic extracts were washed with brine (15 mL), dried (Na_2SO_4) and concentrated *in vacuo*. After purification by flash column chromatography (silica gel, petroleum ether/AcOEt 18/1), **6aa** was obtained as a solid, whose data are coincidental to those reported[18c] (31.7 mg, 71%): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.1 (s, 1H), 7.10 (t, J = 7.7, 1.1 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 6.95 (dd, J = 7.9, 1.1 Hz, 1H), 4.19 (s, 2H), 1.45 (s, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 191.4, 160.8, 136.7, 133.4, 128.6, 124.7, 115.6, 85.3, 43.3, 27.0.

Supporting Information Available. Copies of ^{1}H and ^{13}C NMR spectra of compounds **1-6**. This material is available free of charge via the Internet at http://pubs.acs.org.

FAIR Data is available as Supporting Information for Publication and includes the primary NMR FID files for compounds **1aa-1fa**; **2aa-2dg**; **3aa-6aa**

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Dedication. This paper is dedicatd to the memory of Prof. Killian Muñiz

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