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Copper(I) Bromide-Catalyzed Carbonylative Coupling of Aryl Halides with Phenols, Alcohols and Amines using Sodium Cyanide as C_1 Source: A Synthesis of Carboxylic Acid Derivatives

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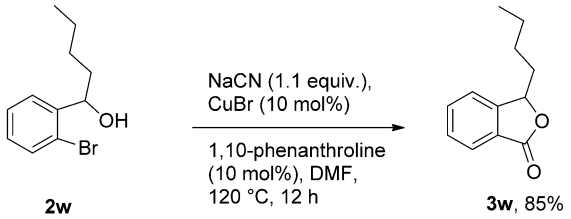
Abstract: A new "carbon monoxide-free" synthesis of carboxylate derivatives *via* carbonylative coupling of aryl bromides with phenols, alcohols, amines and acids in the presence of copper(I) bromide as catalyst and sodium cyanide in a stoichiometric amount has been developed. Its intramolecular version provides for the preparation of lactones (e.g., isochroman-1-ones and isobenzfuranones), imides, anhydrides and lactams in excellent yields (73–96%).

Keywords: anhydrides; C_1 building blocks; isochroman-1-ones; lactams; lactones

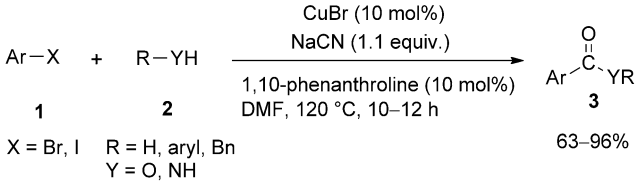
Aromatic and heteroaromatic carboxylate derivatives such as esters, amides, lactones, lactams, anhydrides, etc. are versatile raw materials in the manufacture of agrochemicals, dyes, pharmaceuticals, photosensitizers and other industrial products.[1] Their preparation directly from aryl halides begins with halogen-metal exchange by alkyllithium or Grignard reagents followed by reaction with CO_2 to produce carboxylic acids, which can subsequently be condensed with phenols, alcohols or amines.[2] Alternatively, an efficient and complementary methodology is the emergence of Pd-catalyzed Heck carbonylation of aryl halides with alcohols or amines, which is highly attractive due to its high atom economy.[3] However, the use of highly specialized equipment capable of withstanding elevated pressure has often been necessary to enable safe handling of CO in the standard laboratory equipment. Recent improvements[4] in this strategy focus on alkoxy/aryloxy carbonylation, oxidative esterification *via* NHC catalysis[5] and aminocarbonylation in ionic liquids.[6] Still, there is continuing interest in easier and cost-effective alternative methods that avoid the use of CO gas and organometallic reagents.

The classical reaction of bromobenzene derivatives with a stoichiometric amount of CuCN in DMF at reflux temperature (Rosenmund–Von Braun reaction)[7] generally affords the corresponding cyanobenzene derivatives. Subsequently, nickel[8,9] and palladium[10] complexes as catalysts in the cyanation of aryl bromides using KCN and NaCN[11] as CN source were introduced. Many other variants followed later including zinc cyanide,[12] trimethylsilyl cyanide,[13] tributyltin cyanide,[14] dialkylcyanoboronates,[15] potassium hexacyanoferrate(II)[16] and acetone cyanohydrin.[17] However, the high cost of these metals/reagents and the need to use expensive and toxic phosphines as ligands necessitated the development of other methods. The copper-catalyzed cyanation of aryl and heteroaryl bromides in toluene at around 110–130 °C has also been reported.[18] However, this method requires the use of a ten-fold amount of the rather expensive ligand *N*,*N*′-dimethylethylenediamine relative to the copper salt. This feature is thus less attractive for large-scale applications. As a consequence, the search for more practical methods involving copper catalysis appears necessary to meet the demands of contemporary chemical synthesis, that is, less waste and the use of catalytic processes wherever possible.

Recently, we have reported a new method for the CuCN-mediated one-pot cyclization of 4-(2-bromophenyl)-2-butenoates that provides for an efficient synthesis of substituted naphthalene amino esters.[19] In analogy with this, we reasoned that subjecting 2-bromobenzylic alcohol (**2w**) to the same reaction conditions should afford the corresponding aryl cyanide, which can be elaborated after hydrolysis, to construct the corresponding butylphthalide (**3w**), an anticonvul-



Scheme 1. CuBr-catalyzed synthesis of butylphthalide from 2-bromobenzyl alcohol.



Scheme 2. CuBr-catalyzed carbonylative coupling of aryl halides with NaCN and nucleophiles.

sant drug for the treatment of stroke. Gratifyingly, phthalide **3w** (85%) was isolated in a single step directly from bromo alcohol **2w** (Scheme 1).

In this communication, we wish to describe a new Cu-catalyzed one-pot methodology for the preparation of several carboxylate derivatives directly from aryl halides (**1**) with phenols, alcohols, amines and H_2O as the nucleophiles (**2**) using NaCN as C_1 source under neutral reaction conditions (Scheme 2).

For determining the optimal conditions (Table 1), bromobenzene and phenol were treated with CuCN (1 equiv.) in DMF at 150 °C, which gave the corresponding phenyl ester **3a** in 28% yield. The yield of **3a** was significantly improved to 45% when the CuCN quantity was increased (2 equiv.) under otherwise the same reaction conditions. However, a remarkable increase in yield of **3a** (74%) was realized when the CuCN concentration was further increased (3 equiv.). On lowering the temperature (120 °C), the product yield was reduced (46%). A brief evaluation of solvents showed that DMF was the most suitable one. In order to provide a catalytic process, we have carried out the carbonylative coupling with CuBr as the catalyst and NaCN, a relatively easy to handle solid as the CN source. Thus, by using CuBr (10 mol%) along with NaCN (1.1 equiv.), **3a** was obtained in low yield (24%, entry 4). In order to improve the yield, a series of N-based ligands was screened along with CuBr (10 mol%) and NaCN (1.1 equiv.), which allowed the reaction to proceed at 120 °C giving **3a** in reasonably good yields (entries 5–10). After several experimentations, it was thus found that a combination of bromobenzene, phenol, NaCN (1.1 equiv.), CuBr (10 mol%), and 1,10-phenanthroline (10 mol%) in DMF at 120 °C for 12 h represented the optimised conditions for achieving **3a** in high yields (74%, entry 6). The observed ligand-based acceleration can be rationalized by the fact that Cu(I) is electronically enriched when associated to bipyridine-type ligands thus facilitating oxidative addition of ArX onto Cu(I).[20] Lowering the CuBr concentration (5 mol%) afforded **3a** in low yields (37%). Employing $K_4[Fe(CN)_6]$[20e,21] as the cyanide source was not useful either.

With the optimized reaction conditions in hand, next we sought to examine the scope and limitations

Table 1. CuBr-catalyzed carbonylative coupling of bromobenzene with phenol using NaCN as C_1 source: optimization studies.[a]

No.	Catalyst (10 mol%)	Ligand/Additive (10 mol%)	CN source (equiv.)	Temp. [°C]	Yield of **3a** [%][b]
1	–	–	CuCN (3)	150	74 (28,[c] 45[d])
2	–	–	CuCN (3)	120	46
3	CuCN	–	NaCN (1.1)	120	19
4	CuBr	–	NaCN (1.1)	120	24
5	CuBr	L-proline	NaCN (1.1)	120	70
6	CuBr	1,10-phenanthroline	NaCN (1.1)	120	74 (37,[e] trace[f])
7	CuI	1,10-phenanthroline	NaCN (1.1)	120	76
8	CuBr	ethylenediamine	NaCN (1.1)	120	38
9	CuBr	*N*,*N*-dimethylethylenediamine	NaCN (1.1)	120	32
10	CuBr	*N*,*N*-diisopropylethylenediamine	NaCN (1.1)	120	27
11	$Cu(OAc)_2$	KI	$K_4[Fe(CN)_6]$ (0.5)	150	trace[g]

[a] PhBr (3 mmol), PhOH (3 mmol), DMF, 12 h.
[b] Isolated yield after column chromatographic purification.
[c] 1 equiv. of CuCN used.
[d] 2 equiv. of CuCN used.
[e] 5 mol% of CuBr used.
[f] Toluene used.
[g] DMF + H_2O (1:1) used.

Table 2. CuBr-catalyzed carbonylative coupling of haloaromatics with nucleophiles.[a]

No.	Substrate (**1**) (ArX)	Nucleophiles (**2a–k**) (RYH)	Product (**3a–k**)	Yields [%][b]
a	bromobenzene	phenol	phenyl benzoate	74
b	bromobenzene	4-nitrophenol	4-nitrophenyl benzoate	71
c	bromobenzene	4-methoxybenzyl alcohol	4-methoxybenzyl benzoate	76
d	bromobenzene	aniline	benzanilide	68
e	bromobenzene	2-chloroaniline	2-chlorobenzanilide	70
f	bromobenzene	4-methoxyaniline	4-methoxybenzanilide	63
g	bromobenzene	2-chlorobenzylamine	2-chlorobenzylbenzamide	71
h	bromobenzene	water	benzoic acid	70
i	3-bromotoluene	phenol	3-methylphenyl benzoate	68
j	4-methoxybromobenzene	phenol	4-methoxyphenyl benzoate	71
k	4-nitroiodobenzene	phenol	4-nitrophenyl benzoate	71

[a] *Reaction conditions:* NaCN (3.3 mmol), CuBr (10 mol%), substrate (3 mmol), nucleophile (3 mmol), 1,10-phenanthroline (10 mol%), DMF, 120 °C, 12 h.
[b] Isolated yield after column chromatographic purification.

of the reaction with various bromides and amine nucleophiles. Table 2 illustrates a number of representative aryl halides that have been coupled with a variety of phenols and amines, indicative of considerable generality. Noteworthy among these are the aryl halides bearing NO_2 and OMe groups that were successful under these conditions. Electron-rich and electron-deficient nucleophiles such as phenols, alcohols, anilines, benzylamine, etc. gave good yields of the corresponding carboxylic esters and amides (63–76%). Other minor products isolated in these cases were the corresponding aryl nitriles, unreacted nucleophiles (alcohol or amine) and traces of benzoic acid. Also, benzoic acid was obtained (70%) when water was used. However, in the case of 1-bromooctane, only 1-cyanooctane (80%) was obtained under reaction conditions while long-chain aliphatic alcohols (C_8 and C_{16}) when reacted with bromobenzene, gave benzoic acid as the sole product, which may be a limitation of the catalytic process.

Next, its intramolecular versions were examined, which allowed for the synthesis of lactones, lactams,[24] anhydrides and other heterocycles. As can be seen from Table 3, several substituted 2-bromophenethyl alcohol derivatives (**2l–q**), were subjected to Cu-catalyzed intramolecular coupling with NaCN (1.1 equiv.) that afforded the corresponding isochroman-1-ones (**3l–q**) in excellent yields (84–88%). Similarly, 2-bromobenzylic alcohol derivatives (**2s–w**) gave the corresponding isobenzfuranones (phthalides), (**3s–w**) in 78–92% yields. Interestingly, phthalic anhydride (**3x**) was also obtained in 96% yields from 2-iodobenzoic acid. Simple coumarin (entry **3r**) was also obtained in 81% yield from vinylic dibromophenol **2r.**[23,24] The dicarbonylative coupling of *ortho*-dibromobenzene into phthalimide **3y**[24] in a single step is remarkable.

Also, aryl nitriles can be employed instead of aryl halides as substrates giving the desired products (**3**), although the reaction fails in the absence of a Cu(I) catalyst. Mechanistically, Ar–X on oxidative addition with CuX forms arylCuX, which subsequently undergoes nucleophilic displacement with NaCN to generate ArCuCN (**I**).[18,25] Reductive elimination of ArCuCN produces ArCN (**II**) (isolated and characterized) which on σ-bond metathesis with nucleophiles (e.g., alcohols, phenols and amines) gives imine (**III**),[26] hydrolysis of which affords **3a–z** (Figure 1).

In summary, we have developed a simple Cu-catalyzed protocol for the carbonylative coupling of aryl halides with a variety of nucleophiles and NaCN as C_1 source using 1,10-phenanthroline as ligand that provides for the synthesis of carboxylic acid derivatives in high yields. Incorporation of the carbonyl moiety into organic molecules using a three-component matrix with CN, an organic halide and a nucleophilic component constitutes a simple and diverse approach to the formation of benzoic acid derivatives. This transformation is very practical, as it could be conducted under air. We believe that this "CO-free" catalytic process will find tremendous applications in the commercial production of large volume chemicals such as aromatic carboxylic acids, esters, amides, lactones, anhydrides, coumarins, etc.

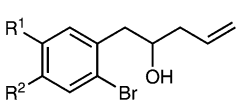
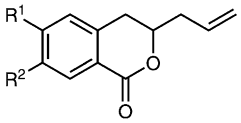
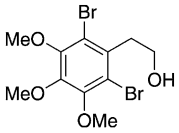
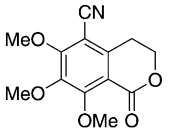
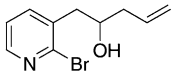
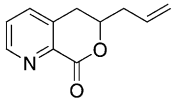
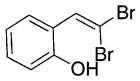
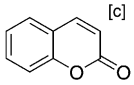
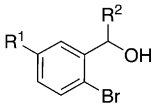
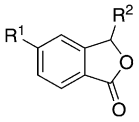
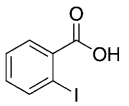
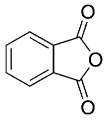
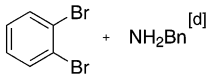
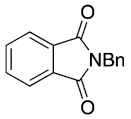
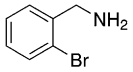
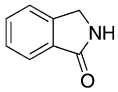
Experimental Section

NB: *Sodium cyanide is "highly toxic" and must be handled with due care.*

General Experimental Procedure for the Preparation of 1-(2-bromophenyl)alkenols (2l–q) and (2s–u)

To a stirred solution of substituted 2-bromobenzaldehyde or 2-(2-bromophenyl)acetaldehyde[8] (5 mmol) in CH_3CN:H_2O (40 mL:10 mL) at 0 °C were added allyl bromide (6 mmol), activated Zn dust (6 mmol) and saturated NH_4Cl solution (10 mL). The reaction mixture was allowed to stir at room temperature for 2–3 h (monitored by TLC). The reaction

Table 3. CuBr-catalyzed intramolecular carbonylative coupling: substrate scope.[a]

Substrate (**2l–z**)[b]		Product (**3l–z**), Yield	
	$R^1=H$, $R^2=H$; (**2l**) $R^1=H$, $R^2=Me$; (**2m**) $R^1=OMe$, $R_2=H$; (**2n**) $R^1=F$, $R^2=H$; (**2o**)		$R^1=H$, $R^2=H$; (**3l**), 84% $R^1=H$, $R^2=Me$; (**3m**), 86% $R^1=OMe$, $R^2=H$; (**3n**), 87% $R^1=F$, $R^2=H$; (**3o**), 88%
	(**2p**)		(**3p**), 84%
	(**2q**)		(**3q**), 84%
	(**2r**)		[c] (**3r**), 81%
	$R^1=F$, $R^2=$allyl; (**2s**) $R^1=OMe$, $R^2=$allyl; (**2t**) $R^1=Br$, $R^2=$allyl; (**2u**) $R^1=H$, $R^2=$heptyl; (**2v**)		$R^1=F$, $R^2=$allyl; (**3s**), 92% $R^1=OMe$, $R^2=$allyl; (**3t**), 85% $R^1=Br$, $R^2=$allyl; (**3u**), 78% $R^1=H$, $R^2=$heptyl; (**3**), 91%
	(**2x**)		(**3x**), 96%
	(**2y**)		(**3y**), 73%
	(**2z**)		(**3z**), 81%

[a] For reaction conditions, see footnote under Table 2.
[b] The corresponding aldehydes were trapped with allyl bromide under Barbier allylation[22] conditions (see Experimental Section).
[c] Concomitant reduction of one of the Br atoms to H takes place.[23]
[d] 2 equiv.of NaCN used, 1 equiv. of benzylamine used as nucleophile.

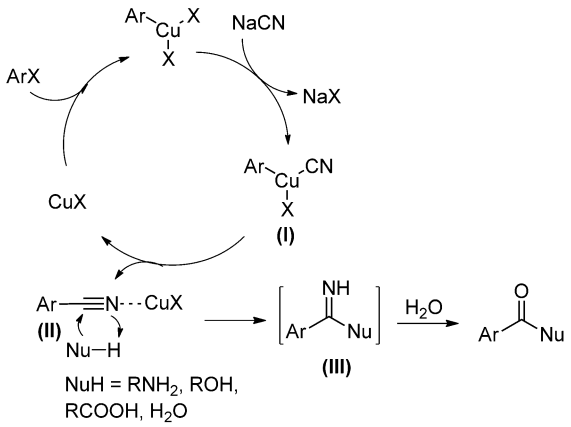


Figure 1. Proposed catalytic cycle for CuBr-catalyzed carbonylative coupling of aryl halides with NaCN and nucleophiles.

mixture was then cooled to 0 °C and excess Zn was quenched with aqueous NH_4Cl. Solvent was evaporated under reduced pressure and aqueous layer was diluted with EtOAc. The organic layer was separated and the aqueous layer was extracted with EtOAc (3×20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give crude products which were purified by column chromatography [silica gel (230–400 mesh) and petroleum ether:EtOAc (7:3) as an eluent] to afford the corresponding 1-(2-bromophenyl)alkenols (**2k–p**) and (**2r–t**); yield: 80–92%.

General Experimental Procedure for the Preparation of Carboxylic Acid Derivatives (3a-3k) *via* an Intermolecular Reaction

To a stirred solution of haloarenes **1a–k** (3 mmol) and nucleophiles **2a–k** (3 mmol) in dry DMF (15 mL) were added NaCN (3.3 mmol), CuBr (0.3 mmol) and 1,10-phenanthroline (0.3 mmol). The entire reaction mixture was heated to

120 °C while being stirred under N_2 for 12 h (monitored by TLC). The reaction mixture was then cooled to room temperature and excess cyanide was quenched with aqueous $NaClO_2$, diluted with water (10 mL) and EtOAc (15 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3×20 mL). The aqueous layer after extraction was poured into aqueous $KMnO_4$ solution and then disposed of. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give crude products which were purified by column chromatography [silica gel (230–400 mesh) and petroleum ether:EtOAc (7:3) as an eluent] to afford the corresponding esters and amides (**3a–k**); yield: 63–74%.

General Experimental Procedure for the Preparation of Carboxylic Acid Derivatives (3l–3z) *via* an Intramolecular Reaction

To a stirred solution of haloarenes **2k–y** (3 mmol) in dry DMF (15 mL) were added NaCN (3.3 mmol), CuBr (0.3 mmol) and 1,10-phenanthroline (0.3 mmol). The entire reaction mixture was heated to 120 °C while being stirred under N_2 for 12 h (monitored by TLC). The reaction mixture was then cooled to room temperature and excess cyanide was quenched with aqueous $NaClO_2$, diluted with water (10 mL) and EtOAc (15 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3×20 mL). The aqueous layer after extraction was poured into aqueous $KMnO_4$ solution and then disposed of. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give crude products which was purified by column chromatography [silica gel (230–400 mesh) and petroleum ether:EtOAc (7:3) as an eluent] to afford the corresponding esters and imides (**3l–z**); yield: 73–96%.

Phenyl benzoate (3a): Yield: 0.440 g (2.222 mmol, 74%); colorless solid; mp 70 °C; IR ($CHCl_3$): υ_{max} = 690, 1080, 1260, 1500, 1718, 2980 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.18–7.30 (m, 3H) 7.39–7.53 (m, 4H) 7.58–7.67 (m, 1H), 8.20 (td, J = 1.7 and 6.9 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 121.7, 125.8, 128.5, 129.4, 129.7, 130.2, 133.5, 151.0, 164.9; Aanalysis: $C_{13}H_{10}O_2$ requires C 78.77, H 5.09, O 16.14; found: C 78.56, H 5.34, O 16.10%.

4-Nitrophenyl benzoate (3b): Yield: 0.517 g (2.127 mmol, 71%); colorless solid; mp 141 °C; IR ($CHCl_3$): $\upsilon_{max=}$ 695, 1060, 1206, 1340, 1530,1740, 3010 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.43 (td, J = 3.2 and 8.9 Hz, 2H) 7.50–7.61 (m, 2H) 7.55 (dt, J = 1.6 and 7.6 Hz, 1H) 7.70 (tt, J = 1.6 and 7.6 Hz, 1H), 8.19–8.24 (m, 2H), 8.34 (td, J = 3.2 and 8.9 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 122.6, 125.2, 128.6, 128.8, 130.3, 134.2, 145.4, 155.7, 164.0; analysis: $C_{13}H_9NO_4$ requires C 64.20, H 3.73, N 5.76, O 26.31; found: C 64.46, H 3.54, N 5.67, O 26.33%.

4-Methoxybenzyl benzoate (3c): Yield: 0.552 g (2.280 mmol, 76%); colorless solid; mp 91 °C; IR ($CHCl_3$): υ_{max} = 693, 1075, 1270, 1500, 1720, 2990 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 3.80 (s, 3H), 5.28 (s, 2H), 6.89 (td, J = 2.9 and 8.6 Hz, 2H), 7.35–7.45 (m, 4H), 7.53 (tt, J = 1.7 and 7.1 Hz, 1H), 8.04 (td, J = 1.7 and 7.1 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.1, 66.4, 113.9, 128.2, 129.5, 129.6, 130.0, 130.3, 132.8, 159.6, 166.2; analysis: $C_{15}H_{14}O_3$ requires C 74.36, H 5.82, O 19.81; found: C 74.35, H 5.78, O 19.87%.

***N*-Phenylbenzamide (3d):** Yield: 0.402 (2.040 mmol, 68%); colorless solid; mp 163 °C; IR ($CHCl_3$): υ_{max} = 690, 780, 1305, 1430, 1530, 1600, 1670, 3330 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 6.63–6.77 (m, 2H), 7.13 (tt, J = 1.6 and 8.4 Hz, 2H), 7.32–7.65 (m, 5H), 7.86 (td, J = 1.6 and 6.4 Hz, 2H); ^{13}C NMR(100 MHz, $CDCl_3$): δ = 115.1, 118.6, 120.2, 124.6, 127.1, 128.8, 129.1, 129.3, 131.8, 135.1, 138.0, 146.3, 165.5; analysis: $C_{13}H_{11}NO$ requires C 79.17, H 5.62, N 7.10, O 8.11; found: C 79.95, H 5.54, N 7.13, O 7.38%.

***N*-(2-Chlorophenyl)benzamide (3e):** Yield: 0.486 g (2.099 mmol, 70%); colorless solid; mp 101 °C; IR ($CHCl_3$): υ_{max} = 690, 788, 1310, 1415, 1510, 1600, 1680, 3310 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.07 (dt, J = 1.3 and 7.4 Hz, 1H), 7.29–7.59 (m, 5H), 7.93 (td, J = 1.3 and 6.1 Hz, 2H), 8.45 (br. s., 1H), 8.58 (dd, J = 1.6 and 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 121.5, 122.9, 124.6, 127.1, 127.9, 128.9, 128.9, 132.1, 134.6, 134.8, 165.0; analysis: $C_{13}H_{10}ClNO$ requires C 67.40, H 4.35, Cl 15.30, N 6.05, O 6.91; found: C 67.87, H 4.23, Cl 15.18, N 6.20, O 6.52%.

***N*-(2-Chlorobenzyl)benzamide (3g):** Yield: 0.523 g (2.130 mmol, 71%); colorless solid; mp 99 °C; IR ($CHCl_3$): υ_{max} = 688, 785, 1316, 1400, 1520, 1678, 3320 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 4.70 (d, J = 5.4 Hz, 2H), 6.73 (br. s., 1H) 7.20–7.26 (m, 2H) 7.35–7.52 (m, 5H) 7.77 (dd, J = 1.6 and 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.0, 127.0, 127.1, 128.6, 128.9, 129.6, 130.4, 131.5, 133.7, 134.3, 135.7, 167.2; analysis: $C_{14}H_{12}ClNO$ requires C 68.44, H 4.92, Cl 14.43, N 5.70, O 6.51; found: C 68.87, H 4.23, Cl 14.78, N 5.20, O 6.92%.

Benzoic acid (3h): Yield: 0.256 g (2.098 mmol, 70%); colorless solid; mp 123 °C; IR ($CHCl_3$): υ_{max} = 700, 1280, 1320, 1410, 1690, 3200 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6): δ = 7.43–7.48 (m, 2H), 7.50–7.55 (m, 1H), 7.93–7.96 (m, 2H); ^{13}C NMR (50 MHz, acetone-d_6): δ = 30.2, 128.3, 129.1, 132.1, 135.3, 169.1; analysis: $C_7H_6O_2$ requires C 68.85, H 4.95, O 26.20; found: C 68.82, H 4.97, O 26.21%.

Phenyl 3-methylbenzoate (3i): Yield: 0.433 g (2.041 mmol, 68%); colorless oil; ^1H NMR (200 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 7.16 −7.30 (m, 3H), 7.34–7.46 (m, 4H), 7.98–8.01 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.0, 121.5, 125.5, 127.0, 128.2, 129.1, 129.2, 130.4, 134.0, 137.9, 150.8, 164.7; analysis: $C_{14}H_{12}O_2$ requires C 79.23, H 5.70, O 15.08; found: C 79.12, H 5.97, O 14.91%.

Phenyl 4-methoxybenzoate (3j): Yield: 0.485 g (2.130 mmol, 71%); colorless solid; mp 70 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 3.89 (s, 3H), 6.97 (td, J = 3.5 Hz and 9.1 Hz, 2H), 7.15–7.29 (m, 3H), 7.35–7.46 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.4, 113.8, 121.8, 123.2, 125.7, 129.4, 132.3, 151.1, 163.9, 164.7; analysis: $C_{14}H_{12}O_3$ requires C 73.67, H 5.30, O 21.03; found: C 73.75, H 5.13, O 21.12%.

Phenyl 4-nitrobenzoate (3k): Yield: 0.518 g (2.130 mmol, 71%); colorless solid; mp 128 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.16–7.50 (m, 5H), 8.36 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 122.8, 123.8, 129.8, 131.3, 131.9, 134.6, 148.9, 151.0, 162.9; analysis: $C_{13}H_9NO_4$ requires C 64.20, H 3.73, N 5.76, O 26.31; found: C 64.38, H 3.52, N 5.81, O 26.29%.

3-Allylisochroman-1-one (3l): Yield: 0.474 g (2.521 mmol (86%); colorless oil; IR ($CHCl_3$): υ_{max} = 745, 917, 1118, 1281,

1723, 2918, 3077 ; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.45–2.72 (m, 2H) 2.87–3.07 (m, 2H) 4.51–4.62 (m, 1H), 5.13–5.24 (m, 2H), 5.79–5.97 (m, 1H) 7.21–7.56 (m, 3H), 8.07 (dd, J = 0.8 and 7.7 Hz, 1H); ^{13}C NMR (125 MHz,) $CDCl_3$: δ = 32.5, 39.2, 77.6, 118.8, 125.2, 127.3, 127.6, 130.3, 132.3, 133.6, 138.9, 164.9; HR-MS (ESI$^+$): m/z = 211.0730, calcd. for $(C_{12}H_{12}O_2)^+$ [(M+Na)$^+$]: 211.0727; analysis: $C_{12}H_{12}O_2$ requires C 76.57, H 6.43, O 17.00; found: C 76.58, H 6.33, O 17.09%.

3-Allyl-7-methylisochroman-1-one (3m): Yield: 0.521 g (2.579 mmol, 86%); colorless oil; IR ($CHCl_3$): υ_{max} = 774, 921, 1082, 1194, 1723, 2923, 3078 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.39 (s, 3H), 2.51–2.68 (m, 2H), 2.82–2.94 (m, 2H), 4.48–4.61 (m, 1H), 5.12–5.23 (m, 2H), 5.77–6.00 (m, 1H) 7.10 (d, J = 7.7 Hz, 1H) 7.32 (d, J = 7.7 Hz, 1H), 7.90 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.9, 32.1, 39.2, 77.7, 118.7, 124.8, 127.2, 130.4, 132.4, 134.4, 135.9, 137.3, 165.2; HR-MS (ESI$^+$): m/z = 225.0886, calcd. for $(C_{13}H_{14}O_2)^+$ [(M+Na)$^+$]: 225.0884; analysis: $C_{13}H_{14}O_2$ requires C 77.20, H 6.98, O 15.82; found: C 77.38, H 6.83, O 15.79%.

3-Allyl-6-methoxyisochroman-1-one (3n): Yield: 0.569 g (2.610 mmol, 87%); colorless oil; IR ($CHCl_3$): υ_{max} = 778, 917, 1027, 1260, 1606, 1716, 2920, 3076 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.48–3.04 (m, 4H), 3.86 (s, 3H), 4.49–4.60 (m, 1H), 5.16–5.24 (m, 2H), 5.83–6.00 (m, 1H), 6.70 (d, J = 2.4 Hz, 1H), 6.87 (dd, J = 2.4 and 8.3 Hz, 1H), 8.02 (d, J = 8.3 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 32.7, 39.1, 55.4, 77.4, 112.0 113.4, 117.5, 118.7, 132.3, 132.4, 141.2, 163.7, 165.3; HR-MS (ESI$^+$): m/z = 241.0835, calcd. for $(C_{13}H_{14}O_3)^+$ [(M+Na)$^+$]: 241.0831; analysis: $C_{13}H_{14}O_3$ requires C 71.54, H 6.47, O 21.99; found: C 71.58, H 6.53, O 21.89%.

3-Allyl-6-fluoroisochroman-1-one (3o): Yield: 0.536 g (2.640 mmol, 88%); colorless oil; IR ($CHCl_3$): υ_{max} = 667, 755, 1107, 1267, 1615, 1725, 2919, 3079 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.45–2.72 (m, 2H) 2.84–3.08 (m, 2H), 4.51- 4.65 (m, 1H), 5.16–5.25 (m, 2H), 5.78–5.99 (m, 1H), 6.93 (dd, J = 2.3 and 8.1 Hz, 1H), 7.06 (dt, J = 2.3 and 8.1 Hz, 1H), 8.10 (dd, J = 5.6 and 8.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 32.6, 39.1, 77.5, 114.3, 115.3, 119.1, 121.5, 132.1, 133.3, 141.9, 164.0, 166.8; HR-MS (ESI$^+$): m/z = 229.0635, calcd. for $(C_{12}H_{11}O_2F)^+$ [(M+Na)$^+$]: 229.0632; analysis: $C_{12}H_{11}O_2F$ requires C 69.89, H 5.38, F 9.21, O 15.52; found: C 69.95, H 5.54, F 9.13, O 15.38%.

6,7,8-Trimethoxy-1-oxoisochromane-5-carbonitrile (3p): Yield: 0.663 g (2.520 mmol, 84%); yellowish solid; mp 107 °C; IR ($CHCl_3$): υ_{max} = 802, 1036, 1130, 1579, 1677, 1713, 2922, 2949 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.31 (t, J = 8.5 Hz, 2H), 3.85 (s, 3H), 3.95 (s, 3H), 4.04 (s, 3H), 4.65 (t, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.4, 61.4, 61.8, 62.2, 65.7, 100.3, 113.8, 115.2, 141.2, 145.1, 159.6, 159.7, 161.2; HR-MS (ESI$^+$): m/z = 286.0693, calcd. for $(C_{13}H_{13}NO_5)^+$ [(M+Na)$^+$]: 286.0691; analysis: $C_{13}H_{13}NO_5$ requires C 59.31, H 4.98, N 5.32, O 30.39; found: C 58.95, H 4.57, N 5.27, O 31.21%.

6-Allyl-5,6-dihydro-8*H*-pyrano[3,4-*b*]pyridin-8-one (3q): Yield: 0.476 g (2.518 mmol, 84%); yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.29–2.73 (m, 4H), 5.05–5.19 (m, 2H), 5.23 (s, 1H), 5.79–5.96 (m, 1H), 7.27 (dd, J = 4.9 and 7.6 Hz, 1H), 7.92 (dd, J = 1.5 Hz and 7.6 Hz, 1H), 8.28 (dd, J = 1.5 and 4.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 40.4, 42.0, 69.3, 118.9, 122.4, 133.3, 134.0, 140.4, 147.7, 151.5; analysis: $C_9H_6O_2$ requires C 73.97, H 4.14, O 21.89; found: C 73.94, H 4.17, O 21.89%.

2*H*-Chromen-2-one (3r): Yield: 0.355 g (2.430 mmol, 81%); colorless liquid; IR ($CHCl_3$): υ_{max} = 820, 1104, 1180, 1610, 1710, 3030 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.43 (d, J = 9.4 Hz, 1H), 7.28–7.57 (m, 4H), 7.77 (d, J = 9.4 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 116.7, 116.9, 118.8, 124.4, 127.8, 131.8, 143.5, 154.0, 160.8; analysis: $C_9H_6O_2$ requires C 73.97, H 4.14, O 21.89; found: C 73.94, H 4.17, O 21.89%.

3-Allyl-5-fluoroisobenzofuran-1(3*H*)-one (3s): Yield: 0.530 g (2.760 mmol, 92%); colorless oil; IR ($CHCl_3$): υ_{max} = 988, 1100, 1247, 1483, 1604, 1624, 1766, 3100 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.62–2.78 (m, 2H), 5.12–5.25 (m, 2H), 5.48 (t, J = 6.1 Hz, 1H), 5.65–5.86 (m, 1H), 7.12–7.28 (m, 2H), 7.89 (dd, J = 4.8 and 8.1 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 38.2, 79.2, 109.3, 117.2, 119.8, 122.2, 127.8, 130.6, 151.9, 163.6, 168.7; analysis: $C_{11}H_9FO_2$ requires C 68.75, H 4.72, F 9.89, O 16.65; found: C 68.82, H 4.97, O, 26.21%.

3-Allyl-5-methoxyisobenzofuran-1(3*H*)-one (3t): Yield: 0.518 g (2.551 mmol, 85%); colorless oil; IR ($CHCl_3$): υ_{max} = 692, 1073, 1103, 1259, 1605, 1744, 2997 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.56–2.81 (m, 2H), 3.91 (s, 3H), 5.15–5.25 (m, 2H), 5.42 (t, J = 6.1 Hz, 1H), 5.68- 5.89 (m, 1H), 6.87 (d, J = 1.6 Hz, 1H), 7.02 (dd, J = 1.6 and 8.5 Hz, 1H), 7.80 (d, J = 8.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 38.8, 55.7, 79.3, 106.1, 116.2, 118.7, 119.6, 127.2, 131.3, 152.0, 164.5, 169.8; analysis: $C_{12}H_{12}O_3$ requires C 70.58, H 5.92, O 23.50; found: C 70.61, H 5.67, O 23.72%.

5-Bromoisobenzofuran-1(3*H*)-one (3u): Yield: 0.498 g (2.338 mmol (78%); colorless solid; mp 162 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.30 (s, 2H), 7.68 (t, J = 3.7 Hz, 2H), 7.77–7.81 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 68.8, 124.9, 125.6, 127.1, 129.2, 132.7, 148.2, 169.7; analysis: $C_8H_5BrO_2$ requires C 45.11, H 2.37, Br 37.51, O 15.02; found: C 45.65, H 2.24, Br 38.13, O 13.98%.

3-Heptylisobenzofuran-1(3*H*)-one (3v): Yield: 0.633 g (2.728 mmol, 91%); colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, J = 3.5 Hz, 3H), 1.27–1.47 (m, 10H), 1.66–1.82 (m, 1H), 1.96–2.12 (m, 1H), 5.46 (dd, J = 4.0 and 7.4 Hz, 1H), 7.41–7.55 (m, 2H), 7.66 (dt, J = 1.6 and 7.6 Hz, 1H). 7.88 (d, J = 7.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0, 22.5, 24.8, 29.0, 29.3, 31.7, 34.7, 81.2, 121.6, 125.6, 126.2 128.9, 133.8, 150.0, 170.3; analysis: $C_{15}H_{20}O_2$ requires C 77.55, H 8.68, O 13.77; found: C 77.58, H 8.71, O 13.71%.

3-Butylisobenzofuran-1(3*H*)-one (3w): Yield: 0.496 g (2.610 mmol, 87%); colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.91 (t, J = 6.3 Hz, 3H), 1.26–1.52 (m, 4H), 1.71–1.82 (m, 1H), 1.98–2.12 (m, 1H), 5.46 (dd, J = 4.1 and 7.2 Hz, 1H), 7.50 (dd, J = 7.2 and 9.8 Hz, 2H), 7.67 (t, J = 7.2 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8, 22.4, 26.8, 34.4, 81.1, 121.6, 125.6, 126.2, 128.9, 133.8,150.0, 170.2; analysis: $C_{12}H_{14}O_2$ requires C 75.76, H 7.42, O 16.82; found: C 75.54, H 7.57, O 16.89%.

Isobenzofuran-1,3-dione (3x): Yield: 0.426 g (2.878 mmol, 96%); colorless solid; mp 131 °C; IR ($CHCl_3$): υ_{max} = 667, 758, 1052, 1307, 1604, 1748, 1772, 2924 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.77 (dd, J = 2.0 and 6.0 Hz, 2H), 7.89 (dd, J = 2.0 and 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.6, 132.7, 134.3, 167.7; HR-MS (ESI$^+$): m/z = 149.0233, calcd. for $(C_8H_5O_3)^+$: 149.0232; analysis: $C_8H_4O_3$

requires C 64.87, H 2.72, O 32.40; found: C 64.82, H 2.77, O 32.41%.

2-Benzylisoindoline-1,3-dione (3y): Yield: 0.396 g (2.187 mmol, 73%); colorless solid; mp 115 °C; IR ($CHCl_3$): υ_{max} = 717, 1062, 1331, 1391, 1453, 1715, 1764, 2853, 2924 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 4.84 (s, 2H), 7.24–7.45 (m, 5H), 7.69 (dd, J = 2.9 and 5.6 Hz, 2H), 7.84 (dd, J = 2.9 and 5.6 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 41.6, 123.3, 127.8, 128.7, 132.2, 133.9, 136.4, 167.9; HR-MS (ESI$^+$): m/z = 260.0682, calcd. for $(C_{15}H_{11}O_2NNa)^+$ [(M+Na)$^+$]: 260.0678; analysis: $C_{15}H_{11}NO_2$ requires C 75.94, H 4.67, N 5.90, O 13.49; found: C 75.87, H 4.33, N 5.98, O 13.82%.

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References

[1] a) J. S. Dewar, P. S. Goldberg, *J. Org. Chem.* **1970**, *35*, 2711–2715; b) C. Khoo, P. H. Chen, M. V. Wood, M. Y. Shih, *Chem. Phys.* **1999**, *245*, 517–531; c) S. Neelakantan, R. Padmasani, T. R. Seshadri, *Tetrahedron* **1965**, *21*, 3531–3536.

[2] a) I. I. F. Boogaerts, S. P. Nolan, *Chem. Commun.* **2011**, *47*, 3021–3024; b) H. Gilman, J. W. Morton Jr, *Org. React.* **1954**, *8*, 258; c) M. S. Kharasch, O. Reinmuth, *Grignard Reactions of Nonmetallic Substances,* Prentice-Hall, New York, **1954**, p 5.

[3] a) R. Grigg, S. P. Mutton, *Tetrahedron* **2010**, *66*, 5515; b) C. F. J. Barnard, *Organometallics* **2008**, *27*, 5402–5422.

[4] a) T. T. Dang, Y. Zhu, J. S. Y. Ngiam, S. C. Ghosh, A. Chen, A. M. Seayad, *ACS Catal.* **2013**, *3*, 1406–1410; b) A. Brennfuhrer, H. Neumann, M. Beller, *Angew. Chem.* **2009**, *121*, 4176–4196; *Angew. Chem. Int. Ed.* **2009**, *48*, 4114–4133; c) T. Hama, X. Liu, D. A. Culkin, J. F. Hartwig, *J. Am. Chem. Soc.* **2003**, *125*, 11176–11177; d) T. Ueda, K. Hideyuki, K. Manabe, *Org. Lett.* **2012**, *14*, 12; e) J. R. Martinelli, D. A. Watson, D. M. Freckmann, T. E. Barder, S. L. Buchwald, *J. Org. Chem.* **2008**, *73*, 7102–7107; f) P. Nordeman, L. R. Odell, M. Larhed, *J. Org. Chem.* **2012**, *77*, 11393–11398.

[5] a) K. Zeitler, *Angew. Chem.* **2005**, *117*, 7674; *Angew. Chem. Int. Ed.* **2005**, *44*, 7506; b) B. E. Maki, K. A. Scheidt, *Org. Lett.* **2008**, *10*, 4331; c) M. Yoshida, Y. Katagiri, W. B. Zhu, K. Shishido, *Org. Biomol. Chem.* **2009**, **7**, 4062; d) C. A. Rose, K. Zeitler, *Org. Lett.* **2010**, *12*, 4552; e) C. Qin, H. Wu, J. Chen, M. Liu, J. Cheng, W. J. Su, *Org. Lett.* **2008**, *10*, 1537; f) M. Zhang, S. Zhang, G. Zhang, F. Chen, J. Cheng, *Tetrahedron Lett. Tetrahedron Lett* **2011**, *52*, 2480–2483.

[6] M. V. Khedkar, T. Sasaki, B. M. Bhanage, *ACS Catal.* **2013**, *3*, 287–293.

[7] C. F. Koelsch, A. G. Whitney, *J. Org. Chem.* **1941**, *6*, 795–803.

[8] a) L. Cassar, *J. Organomet. Chem.* **1973**, *54*, C57–C58; b) L. Cassar, M. Fo, F. Montanari, G. P. Mainelli, *J. Organomet. Chem.* **1979**, *173*.

[9] a) Y. Sakakibara, F. Okuda, A. Shimoyabashi, K. Kirino, M. Sakai, N. Uchino, K. Takagi, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1985–1990; b) Y. Sakakibara, Y. Ido, K. Sasaki, M. Sakai, N. Uchino, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2776–2778.

[10] M. Sundermeier, A. Zapf, M. Beller, *Eur. J. Inorg. Chem.* **2003**, 3513–3526, and references cited therein.

[11] a) B. A. Anderson, E. C. Bell, F. O. Ginah, K. Harn, L. M. Pagh, J. P. Wepsiec, *J. Org. Chem.* **1998**, *63*, 8224–8228; b) M. Sundermeier, A. Zapf, M. Beller, J. Sans, *Tetrahedron Lett.* **2001**, *42*, 6707–6710; c) M. Sundermeier, A. Zapf, S. Mutyala, W. Baumann, J. Sans, S. Weiss, M. Beller, *Chem. Eur. J.* **2003**, *9*, 1828–1836.

[12] a) D. M. Tschaen, R. Desmond, A. O. King, M. C. Fortin, B. Pipik, S. King, T. R. Verhoeven, *Synth. Commun.* **1994**, *24*, 887–890; b) T. Okano, J. Kiji, Y. Toyooka, *Chem. Lett.* **1998**, 425–426; c) P. E. Maligres, M. S. Waters, F. Fleitz, D. Askin, *Tetrahedron Lett.* **1999**, *40*, 8193–8195; d) F. Jin, P. N. Confalone, *Tetrahedron Lett.* **2000**, *41*, 3271–3273; e) M. Alterman, A. Hallberg, *J. Org. Chem.* **2000**, *65*, 7984–7989; f) A. W. Shaw, J. deSolms, *Tetrahedron Lett.* **2001**, *42*, 7173–7176; g) J. Ramnauth, N. Bhardwaj, P. Renton, S. Rakhit, S. P. Maddaford, *Synlett* **2003**, 2237–2239; h) R. Chidambaran, *Tetrahedron Lett.* **2004**, *45*, 1441–1444.

[13] a) N. Chatani, T. Hanafusa, *J. Org. Chem.* **1986**, *51*, 4714–4716; b) M. Sundermeier, S. Mutyala, A. Zapf, A. Spannenberg, M. Beller, *J. Organomet. Chem.* **2003**, *684*, 50–55.

[14] C. Yang, M. Williams, *Org. Lett.* **2004**, *6*, 2837–2840.

[15] B. Jiang, Y. Kan, A. Zhang, *Tetrahedron* **2001**, *57*, 1581–1584.

[16] T. Schareina, A. Zapf, M. Beller, *Chem. Commun.* **2004**, 1388–1389.

[17] H.-J. Cristau, A. Ouali, J.-F. Spindler, M. Taillefer, *Chem. Eur. J.* **2005**, *11*, 2483–2492.

[18] J. Zanon, A. Klapars, S. L. Buchwald, *J. Am. Chem. Soc.* **2003**, *125*, 2890–2891.

[19] R. R. Santhosh, P. K. Prasad, B. B. Bhushan, A. Sudalai, *J. Org. Chem. J. Org.Chem.* **2013**, *78*, 5045–5050.

[20] a) M. Taillefer, H.-J. Cristau, P. P. Cellier, J.-F. Spindler, A. Ouali, *Patent* WO 03/101966, **2003**; b) H.-J. Cristau, A. Ouali, J.-F. Spindler, M. Taillefer, *Chem. Eur. J.* **2005**, *11*, 2483; c) A. Ouali, J.-F. Spindler, A. Jutand, M. Taillefer, *Adv. Synth. Catal.* **2007**, *349*, 1906; d) T. Schareina, A. Zapf, W. Mägerlein, N. Müller, M. Beller, *Synlett* **2007**, 555; e) T. Schareina, A. Zapf, W. Mägerlein, N. Müller, M. Beller, *Chem. Eur. J.* **2007**, *13*, 6249; f) T. Schareina, A. Zapf, M. Beller, *Tetrahedron Lett.* **2005**, *46*, 2585.

[21] C. DeBlase, N. E. Leadbeater, *Tetrahedron* **2010**, *66*, 1098–1101.

[22] a) J. X. Wang, X. F. Jia, T. J. Meng, L. Xin, *Synthesis* **2005**, 2838–2844; b) W. Chung, S. Higashiya, Y. Oba, J. T. Welch, *Tetrahedron* **2003**, *59*, 10031–10036.

[23] One of the Br atoms is converted to CN while the other is reduced to H during work-up (unpublished results).
[24] a) H. Cao, H. Alper, *Org. Lett.* **2010**, *12*, 18; b) W. Ren, M. Yamane, *J. Org. Chem.* **2010**, *75*, 8410–8415; c) K. Sasano, J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2013**, *135*, 10954–10957.
[25] a) H.-J. Cristau, P. P. Cellier, J.- F. Spindler, M. Taillefer, *Chem. Eur. J.* **2004**, *10*, 5607; b) R. A. Altman, E. D. Koval, S. L. Buchwald, *J. Org. Chem.* **2007**, *72*, 6190; c) A. Ouali, J.-F. Spindler, H.-J. Cristau, M. Taillefer, *Adv. Synth. Catal.* **2006**, *348*, 499; d) A. Ouali, M. Taillefer, J.-F. Spindler, A. Jutand, *Organometallics* **2007**, *26*, 65; e) E. R. Strieter, D. G. Blackmond, S. L. Buchwald, *J. Am. Chem. Soc.* **2005**, *127*, 4120; f) S.-L. Zhang, L. Liu, Y. Fu, Q.-X. Guo, *Organometallics* **2007**, *26*, 4546; g) R. A. Altman, A. M. Hyde, X. Huang, S. L. Buchwald, *J. Am. Chem. Soc.* **2008**, *130*, 9613; h) J. W. Tye, Z. Weng, A. M. Johns, C. D. Incarvito, J. F. Hartwig, *J. Am. Chem. Soc.* **2008**, *130*, 9971; i) L. M. Huffman, S. S. Stahl, *J. Am. Chem. Soc.* **2008**, *130*, 9196; j) H. Kaddouri, V. Vicente, A. Ouali, F. Ouazzani, M. Taillefer, *Angew. Chem.* **2009**, *121*, 339; *Angew. Chem. Int. Ed.* **2009**, *48*, 333; k) G. Lefèvre, G. Franc, A. Tlili, C. Adamo, M. Taillefer, I. Ciofini, A. Jutand, *Organometallics* **2012**, *31*, 7694; l) G. Lefèvre, A. Tlili, M. Taillefer, C. Adamo, I. Ciofini, A. Jutand, *Dalton Trans.* **2013**, *42*, 5348; m) A. Ouali, M. Taillefer, in: *Science of Synthesis*, vol. 2, (Ed.: P. V. Leeuwen), Georg Thieme Verlag, Stuttgart, **2013**, pp 95–125.
[26] R. S. Reddy, C. K. Indukurunaga, A. Sudalai, *Org. Biomol. Chem.* **2012**, *10*, 3655.