Iron Pentacarbonyl in Alkoxy- and Aminocarbonylation of Aromatic Halides

Matej Babjak,* Oľga Caletková, Diana Ďurišová, Tibor Gracza

Department of Organic Chemistry, Slovak University of Technology, Radlinského 9, 81237 Bratislava, Slovakia
Fax +421(2)52968560; E-mail: matej.babjak@stuba.sk

Received: 24.06.2014; Accepted after revision: 10.09.2014

Abstract: We have identified reaction conditions for a Heck-type carbonylation based on [$Fe(CO)_5$]. Preliminary optimization of alkoxycarbonylation on 2-bromonaphthalene defined functioning composition of the reaction mixture which was then applied on a small set of (hetero)aromatic halides. Respective aminocarbonylation of these halides with different amines, including aniline and benzotriazole, was accomplished with reasonable results.

Key words: aminocarbonylation, methoxycarbonylation, carbonylation, carbonyl complexes, iron, palladium catalysis

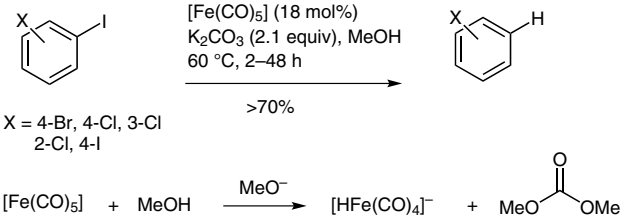
Heck carbonylation[1] represents a powerful alternative to other metalation-based transformations of aryl and heteroaryl halides to the corresponding carboxylates and carboxamides, such as lithiation followed by cyanoformate or carbon dioxide addition. Unfortunately, the reaction in its traditional form requires a presence of gaseous CO at high pressure, and as such invokes serious safety apprehensions. Therefore, several surrogates of CO have been introduced during last years, namely pivaloyl chloride,[2a] DMF[2b] or formates.[2c] Along with these methods, use of various metal carbonyls, particularly [$Mo(CO)_6$],[2e–i,2m] [$Cr(CO)_6$],[2j] and [$W(CO)_5$][2j–l] was reported with excellent results.

When pioneering this field, Larhed and co-workers made an early-stage finding that affordable carbonyls, such as [$Fe(CO)_5$] or [$Ni(CO)_4$], were unable to carbonylate the model substrate, 4-iodotoluene. Also Oshima and co-workers[3] had tested the precondition that [$Fe(CO)_5$] fails as a CO supply for the Heck carbonylation of iodides, and they identified [$CpFe(CO)_2]_2$ to be the optimal reagent for the task.

On the other hand, it is worth to note that [$Fe(CO)_5$] is the cheapest metal carbonyl compound available, produced in bulk scale (e.g., 9000 t/year by BASF),[4] liquid, nonvolatile, easy to handle, air and solution stable. Vapors of the compound are detectable by its characteristic odor, in contrast to odorless CO. Toxicity of metal carbonyls is in proportion with their volatility; in case of [$Fe(CO)_5$] (bp 105 °C at 1.013 bar) it is though reduced if compared with free CO or [$Ni(CO)_4$], but higher than the toxicity of solid carbonyls, for example, [$Mo(CO)_6$] or [$W(CO)_6$]. On the other hand, use of [$Mo(CO)_6$] or [$W(CO)_6$] introduces another toxic metal to the reaction environment in contrast with nontoxic iron.

SYNLETT 2014, 25, 2579–2584
Advanced online publication: 15.10.2014
DOI: 10.1055/s-0034-1379227; Art ID: st-2014-b0535-l

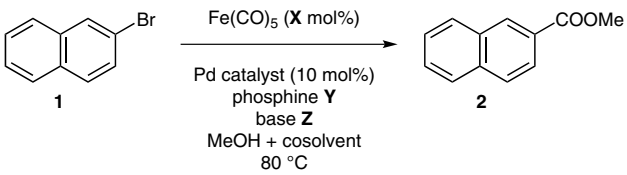
Considering the revelations of our predecessors,[2] we conceived an idea that [$Fe(CO)_5$] in the presence of acidic protons (i.e., from MeOH or other protic nucleophile) and a base could form a reactive hydride–iron complex, capable of a selective reductive cleavage of the iodine from the aromatic ring, similarly to the transformation, reported by Brunet[5] (Scheme 1), based on the combination of potassium carbonate and methanol. What was important for our plans, in situ formed iron hydride is too weak to harm other halogens (e.g., bromo or chloro substituents) or other reducible functional groups.



Scheme 1 Selective reduction of iodides with [$Fe(CO)_5$][5]

Here we presumed that the reaction of iodotoluene, studied by Larhed, afforded through similar reduction the toluene, which was then neglected in the toluene solution. In the analogy with the described Brunet reduction, we believed that reductive properties of carbonyl–iron hydrides are insufficient for the removal of the bromo substituent from the aromatic ring and at the same time, aryl bromides are well qualified to undergo the Heck carbonylation. Therefore we decided to repeat the Larhed experiment on selected aromatic bromides.[6]

Our initial model substrate was the 2-bromonaphthalene (**1**), as a cheap, solid, electron-rich substrate. Original conditions for the Heck methoxycarbonylation of bromobenzenes were chosen as the starting point, comprising 10 mol% of $Pd(OAc)_2$, 20 mol% of Ph_3P, triethylamine and methanol as cosolvent (Scheme 2).[7] Initial procedure was performed with one equivalent of iron pentacarbonyl.



Scheme 2 Model methoxycarbonylation with [$Fe(CO_5)$]

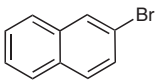
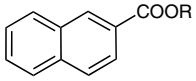
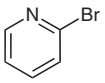
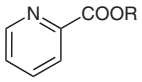
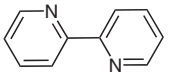
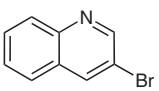
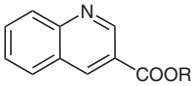
In the next step, the optimal reaction conditions were sought through the thorough variation of reaction conditions.[7] The amount of $[Fe(CO)_5]$ was reduced to 25 mol%, similarly to the published use of $[Mo(CO)_6]$ or $[CpFe(CO)_2]_2$. Acetonitrile was chosen as the optimal cosolvent and trialkyl amines, for example, triethylamine and DIPEA as the base. $Pd(OAc)_2$ was found to be the best supply of palladium. As a phosphine additive, Ph_3P and especially 1,1′-bis(diphenylphosphino)ferrocene (dppf) were qualified as the best ones, but it was essential to use it in amount at least of 36 mol%. This finding evoked simple hypothesis that at least one phosphine chelates the iron atom, releasing the CO from the ligand field. This hypothesis was then supported by the standalone reaction of Ph_3P and $[Fe(CO)_5]$ in stoichiometric ratio in MeCN–Et_3N.[7] Considering the known ability of iron compounds to undergo aryl bromine oxidative insertion, we have performed a control experiment without palladium catalyst, but with negative results. Small-scale experiments (0.1 mmol) with LC–MS monitoring were used for the initial optimization on 2-bromonaphthalene. A scaled-up reaction (1 mmol) under the optimized conditions with Ph_3P revealed that the isolated yield of **2** is lower than the HPLC estimation, mostly due to permanent interference of triphenylphosphine oxide and **2** during the flash chromatography (Ph_3P immobilized on polystyrene resin was tried without success[7]). To avoid this, the use of dppf was tested with positive results, bringing shorter reaction time as enjoyable bonus. The reaction with dppf furnished then the methylester **2** in 71% isolated yield after four hours (Table 1, entry 1).

It was found that the reaction can be interrupted (opened, analyzed, reclosed, and further heated), but the final yield will be lower than for the unopened run.[7] This can be simply explained by the escape of certain amount of free CO from the vessel. Therefore, an appropriate reaction time for each substrate must be determined iteratively, in our case, reactions of most substrates required equally 23 hours reaction time.

Thus, our optimized conditions for the methoxycarbonylation of 2-bromonaphthalene comprise 10 mol% of $Pd(OAc)_2$, 25 mol% of $[Fe(CO)_5]$, 36 mol% of phosphine, 10 equivalents of Et_3N, and heating at 80 °C in MeOH–MeCN. In comparison with similar methods, formation of methyl 2′-naphthoylformate,[8a–c] binaphtylketone or binaphthalene[8d–f] was not observed. These conditions were then used in the preparative manner for the transformation of 2-bromopyridine and 3-bromoquinoline to the corresponding methylcarboxylates (Table 1, entries 2 and 3). In the case of 2-bromopyridine, small amount of bipyridine was observed in the reaction mixture by LC–MS. Interestingly, switching from MeOH in MeCN to neat *n*-BuOH[9] led to further improvement, and in this case Ph_3P was a quite acceptable additive.

Rather mixed results in the oxycarbonylation series oriented us more towards the analogous aminocarbonylations, where we see the major potential of the method. In this case, all tested halides including heteroaryl bromides, such as 2-bromopyridine or bromoquinolines, furnished the corresponding amides in good yield, especially with reactive benzylamine (Table 2). Yields were seemingly independent from electron density on the aromatic ring of the bromide. *ortho*-Substituted bromide furnished an appropriate carbonylation product (Table 2, entry 8) as well. The cyclic amidine product **23**, isolated from the reaction of 2-bromonitrile **21**, was little surprising in the first mo-

Table 1 Carbonylation of Aryl Halides[a]

Entry	Bromide	Product[b]	Byproduct	Yield (%)[d]	Yield (%)[e]
1	 **1**	 **2** R = Me **3** R = *n*-Bu		**2** 71	**2** 36 **3** 52
2	 **4a**	 **5** R = Me **6** R = *n*-Bu	 **7**[c]	**5** (90) 25 **7** (10)	**5** (80) 6 **6** 39 **7** (13)
3	 **8**	 **9** R = Me **10** R = *n*-Bu		**9** 40	**10** 87

[a] The reactions were carried out as described in the general procedure.[11]
[b] Isolated yields; yields in parentheses are estimated yields (HPLC).[7]
[c] Compound **7** was observed only in reactions with MeOH.
[d] With dppf as phosphine additive.
[e] With Ph_3P as phosphine additive.

ment, but its formation is logical and already known.[10] As can be seen from entry 6 (Table 2), also an active heteroaryl chloride is capable to undergo the reaction. Naphthoylbenzotriazole **32** and anilides **12** and **18** represent then examples of products with unreactive amines. In the entire aminocarbonylation part, cheap Ph_3P was used instead of the dppf, with little disadvantage of extended reaction time in some cases. Nevertheless for less reactive bromide or amine part, the use of dppf is always an option. Buchwald–Hartwig reaction products were not observed during LC–MS analysis of the reaction mixtures.

Table 2 Overview of Aminocarbonylations with Various Aryl Bromides[a,11]

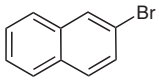
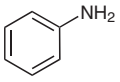
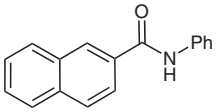
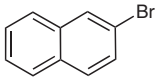
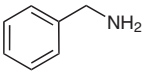
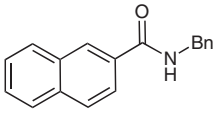
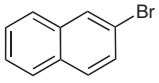
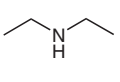
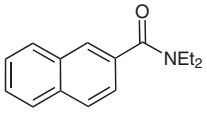
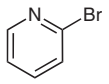
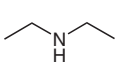
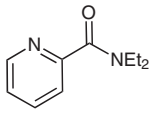
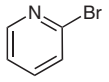
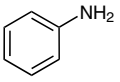
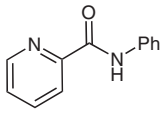
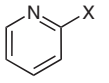
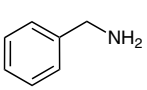
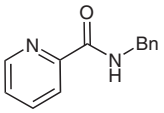
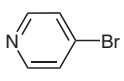
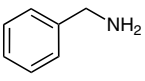
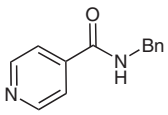
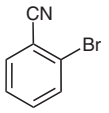
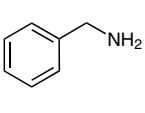
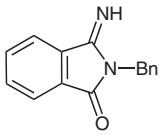
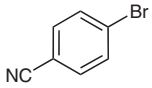
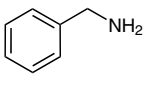
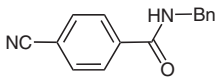
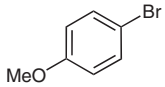
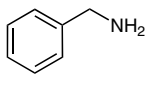
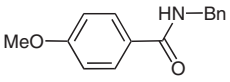
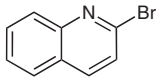
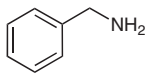
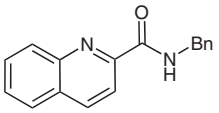
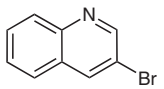
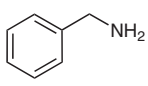
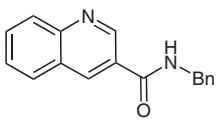
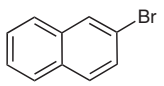
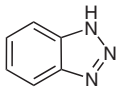
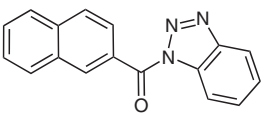
Entry	Bromide	Amine	Product (%)
1	 **1**	 **11**	 **12** 80
2	 **1**	 **13**	 **14** 84
3	 **1**	 **15**	 **16** 43
4	 **4a**	 **15**	 **17** 77
5	 **4a**	 **11**	 **18** 71
6	 **4a** X = Br **4b** X = Cl	 **13**	 **19** 46 (from **4a**, 32% from **4b**)
7	 **20**	 **13**	 **21** 62

Table 2 Overview of Aminocarbonylations with Various Aryl Bromides[a,11] (continued)

Entry	Bromide	Amine	Product (%)
8	 **22**	 **13**	 **23** 71
9	 **24**	 **13**	 **25** 86
10	 **26**	 **13**	 **27** 51
11	 **28**	 **13**	 **29** 87
12	 **8**	 **13**	 **30** 63
13	 **1**	 **31**	 **32** 36

[a] The reactions were carried out as described in references and notes.[11] Specified yields are after isolation.

In summary, we have developed a carbonylation method based on iron pentacarbonyl, in spite of implication, that this reagent represents unsuitable CO supply for the Heck-type carbonylation. LC–MS-monitored optimization of methoxycarbonylation of the 2-bromonaphthalene defined reasonable reaction conditions which were then applied on few aromatic bromides. In comparison with methoxycarbonylation, the butoxycarbonylation of these substrates was found to be slightly more practical. Similar aminocarbonylations of these bromides with different amines, including unreactive aniline and benzotriazole, were accomplished with good results. A successful aminocarbonylation with heteroaromatic chloride was achieved as well.

Acknowledgment

This work was supported by Slovak Grant Agencies (VEGA No. 1/0488/14, APVV-0203-10 and ASFEU, Bratislava, ITMS projects No. 26240120001, 26240120025).

Supporting Information for this article is available online at http://www.thieme-connect.com/products/ejournals/journal/10.1055/s-00000083.

References and Notes

(1) (a) Schoenberg, A.; Bartoletti, I.; Heck, R. F. *J. Org. Chem.* **1974**, *39*, 3318. (b) Schoenberg, A.; Bartoletti, I.; Heck, R. F. *J. Org. Chem.* **1974**, *39*, 3327. (c) Barnard, C. F. J. *Organometallics* **2008**, *27*, 5402.

(2) (a) Hermange, P.; Linhardt, A. T.; Taaning, R. H.; Bjerglund, K.; Lupp, D.; Skydstrup, T. *J. Am. Chem. Soc.* **2011**, *133*, 6061. (b) Wan, Y. Q.; Alterman, M.; Larhed, M.; Hallberg, A. *J. Org. Chem.* **2002**, *67*, 6232. (c) Morimoto, T.; Kaikuchi, K. *Angew Chem. Int. Ed.* **2004**, *43*, 5580. (d) Ueda, T.; Konishi, H.; Manabe, K. *Org. Lett.* **2013**, *15*, 5370. (e) Kaiser, N. F. K.; Hallberg, A.; Larhed, M. *J. Comb. Chem.* **2002**, *4*, 109. (f) Georgsson, J.; Hallberg, A.; Larhed, M. *J. Comb. Chem.* **2003**, *5*, 350. (g) Lagerlund, O.; Larhed, M. *J. Comb. Chem.* **2006**, *8*, 4. (h) Letavic, M. A.; Ly, K. S. *Tetrahedron Lett.* **2007**, *48*, 2339. (i) Odell, L. R.; Savmarker, J.; Larhed, M. *Tetrahedron Lett.* **2008**, *49*, 6115. (j) Wannberg, J.; Larhed, M. *J. Org. Chem.* **2003**, *68*, 5750. (k) Roberts, B.; Liptrot, D.; Alcaraz, L.; Luker, T.; Stocks, M. J. *Org. Lett.* **2010**, *12*, 4280. (l) Wieckowska, A.; Fransson, R.; Odell, L. R.; Larhed, M. *J. Org. Chem.* **2011**, *76*, 978. (m) Wei, R.; Motoki, Y. *J. Org. Chem.* **2010**, *64*, 8410.

(3) Nakaya, R.; Yorimitsu, H.; Oshima, K. *Chem. Lett.* **2011**, *40*, 904.

(4) Wildermuth, E.; Stark, H.; Friedrich, G.; Ebenhöch, F. L.; Kühborth, B.; Silver, J.; Rituper, R. *Iron Compounds, Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, **2000**.

(5) (a) Brunet, J.-J.; Taillefer, M. *J. Organomet. Chem.* **1988**, *348*, C5. (b) Brunet, J.-J.; Kindela, F. B.; Neibecker, D. *J. Organomet. Chem.* **1989**, *368*, 209.

(6) Babjak, M.; Karlubíková, O.; Gracza, T. *14th Blue Danube Symposium on Heterocyclic Chemistry Podbanské 2011 (Book of Abstracts)*; STU: Bratislava, **2011**, 34.

(7) See the Supporting Information.

(8) For the formation of 2′-aroyl formates via Heck reaction, see, for example: (a) Sakakura, T.; Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M. *J. Org. Chem.* **1987**, *52*, 5733. (b) Ozawa, F.; Kawasaki, N.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1985**, 567. (c) Tanaka, M.; Kobayashi, T.; Sakakura, T. *J. Chem Soc., Chem. Commun.* **1985**, *12*, 837. For the formation of diaryl ketones and diarenes under carbonylation conditions, see, for example: (d) Brunet, J. J.; Zaizi, A. E. *J. Organomet. Chem.* **1995**, *486*, 275. (e) Brunet, J.-J.; Zaizi, A. E. *Bull. Soc. Chim. Fr.* **1996**, *133*, 75. (f) Brunet, J. J.; Taillefer, M. *J. Organomet. Chem.* **1989**, *361*, C1.

(9) Jayasree, S.; Seayad, A.; Gupte, S. P.; Chaudhari, R. V. *Catal. Lett.* **1999**, *58*, 213.

(10) For spontaneous formation from *N*-benzyl-2-cyanobenzamide, see: (a) Valters, R. E.; Bace, A. E.; Valters, S. P. *Latvijas PSR Zinatnu Akademijas Vestis, Kimijas Serija* **1972**, 726. For physical and spectral characteristics of **22**, see: (b) Beaume, A.; Courillon, C.; Derat, E.; Malacria, M. *Chem. Eur. J.* **2008**, *14*, 1238.

(11) **General Procedure for the Carbonylation of Aryl Halides**

An aryl bromide (1 mmol), Ph_3P (94 mg, 0.36 mmol), and $Pd(OAc)_2$ (22 mg, 0.1 mmol) were weighed into screw cap vial equipped with a magnetic stir bar. Dry MeCN (5 mL) was added, followed by Et_3N (2.5 mL) and the corresponding amine (1.5 mmol). Neat iron pentacarbonyl (35 μL, 0.25 mmol) was added, and the vial was thoroughly closed and heated in the preheated oil bath or aluminum heating block (80 °C). The reaction mixture was stirred at the specified temperature for 23 h, then concentrated with approximately 1 g of silica, and the absorbed material was purified by gradient MPLC (hexanes–EtOAc in ratios 1:10 to 1:1). Methyl and *n*-butyl carboxylates, described in the article, were prepared in a similar manner; a mixture of MeCN with MeOH or *n*-BuOH in a ratio of 2:1 was used instead of pure MeCN, the identical amount of dppf (0.36 mmol) was used instead of Ph_3P in specified cases.

Methyl Naphthalene-2-carboxylate (2)

The compound was prepared according to the described general procedure with dppf as the ligand additive from 2-bromonaphthalene (**1**, 1.035 g, 5 mmol) of, isolated as a colorless oil (661 mg, 71%). All data, including ^{1}H NMR, ^{13}C NMR, LC–MS, and TLC data were identical with physical sample of **2**, purchased from Sigma-Aldrich.

***n*-Butyl Naphthalene-2-carboxylate (3)**

The compound was prepared according to the described general procedure with Ph_3P as the ligand additive from **1** (150 mg, 0.72 mmol), isolated as an off-white solid (164 mg, 52%). ^{1}H NMR, ^{13}C NMR, IR, ESI-MS, and TLC data of isolated **3** were in accordance with published data;[12a] mp 40–45 °C (EtOAcOEt); lit.:[12b] mp 41 °C.

Methyl Pyridine-2-carboxylate (5)

The compound was prepared according to the described general procedure with dppf as the ligand additive from 2-bromopyridine (**4a**, 150 mg, 0.95 mmol), isolated as a pale yellow oil (33 mg, 25%). HPLC yield in the reaction mixture was 90% according to the 254 nm peak-area calibration curve made from purchased sample. All data, including ^{1}H NMR, ^{13}C NMR, LC–MS, and TLC data were identical with physical sample of **5**, purchased from Sigma-Aldrich. The isolated sample was slightly colored in contrast with colorless commercial one.

***n*-Butyl Pyridine-2-carboxylate (6)**

The compound was prepared according to the described general procedure with Ph_3P as the ligand additive from **4a** (150 mg, 0.95 mmol), isolated as a pale yellow oil (66 mg, 39%). All data, including ^{1}H NMR, ^{13}C NMR, IR, ESI-MS, and TLC data were in accordance with the literature data.[13]

Methyl Quinoline-3-carboxylate (9)

The compound was prepared according to the described general procedure with dppf as the ligand additive from 3-bromoquinoline (**8**, 250 mg, 1.2 mmol), isolated as an off-white solid (90 mg, 40%). NMR and IR data were identical with the literature data;[14] mp 74–77 °C (EtOAc–hexanes); lit.:[14] mp 75–77 °C.

***n*-Butyl Quinoline-3-carboxylate (10)**

The compound was prepared according to the described general procedure with Ph_3P as the ligand additive from **8** (146 mg, 0.7 mmol), isolated as a thick yellow oil (140 mg, 87%). ^{1}H NMR, ^{13}C NMR, and IR data were in accordance with the literature data.[14]

***N*-Phenyl-2-naphthamide (12)**

The compound was prepared according to the described general procedure with Ph_3P as the ligand additive from 2-bromonaphthalene (**1**, 207 mg, 1 mmol), isolated as an off-white solid (198 mg, 80%); mp 166–168 °C (EtOAc); lit.:[15b] 170–171 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16 (br t, 1 H, *J* = 7.4 Hz), 7.38 (br t, 2 H, *J* = 7.9 Hz), 7.51–7.62 (m, 2 H), 7.70 (d, 2 H, *J* = 7.7 Hz, Ph), 7.85–7.95 (m, 4 H), 8.07 (br s, 1 H), 8.36 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 120.3, 123.5, 124.6, 126.9, 127.5, 127.8, 127.9, 128.7, 128.9, 129.1 (all d), 132.2, 132.6, 134.8, 138.0 (all s), 165.8

(s). IR spectra were in agreement with the literature data.[15a] NMR in DMSO can be found there as well. ESI-HRMS: *m/z* calcd for $C_{17}H_{13}NO$ + H [M + 1]: 248.1070; found: 248.1078.

***N*-Benzyl-2-naphthamide (14)**

The compound was prepared according to the described general procedure with Ph_3P as the ligand additive from 2-bromonaphthalene (**1**, 207 mg, 1 mmol), isolated as an off-white solid (220 mg, 84%). Spectral data (NMR, IR, MS) were in agreement with the literature data;[2m] mp 140–142 °C (EtOAc); lit.:[15a] mp 138–139 °C.

***N,N*-Diethyl-2-naphthamide (16)**

The compound was prepared according to the described general procedure with Ph_3P as the ligand additive from 2-bromonaphthalene (**1**, 207 mg, 1 mmol), isolated as a thick colorless oil (98 mg, 43%). All NMR and IR data were in accordance with the literature data.[16]

***N,N*-Diethylpicolinamide (17)**

The compound was prepared according to the described general procedure with Ph_3P as the ligand additive from 2-bromopyridine (**4a**, 158 mg, 1 mmol), isolated as a pale yellow oil (137 mg, 77%). All properties were in full accordance with the literature data.[17]

***N*-Phenyl-2-pyridinecarboxamide (18)**

The compound was prepared according to the described general procedure with Ph_3P as the ligand additive from **4a** (158 mg, 1 mmol), isolated as a yellowish solid (141 mg, 71%). All spectral data were in accordance with the literature data;[18a] mp 74–76 °C (EtOAc–hexanes); lit.[18b] mp 74–75 °C.

***N*-Benzyl-2-pyridinecarboxamide (19)**

The compound was prepared according to the described general procedure with Ph_3P as the ligand additive from bromide **4a** (158 mg, 1 mmol) or from chloride **4b** (114 mg, 1 mmol), isolated in both cases as a pale brown solid (98 mg, 46% from bromide **4a**, 68 mg, 32% from chloride **4b**). All spectral data were in agreement with the literature data;[19] mp 81–83 °C (EtOAc–hexanes); lit.[19] mp 81–84 °C.

***N*-Benzyl-4-pyridinecarboxamide (21)**

The compound was prepared according to the described general procedure with Ph_3P as the ligand additive from 4-bromopyridine (**20**, 158 mg, 1 mmol), isolated as an off-white solid (132 mg, 62%); mp 86–88 °C (EtOAc–hexanes; lit.[20b] mp 87–88 °C.

^{1}H NMR (300 MHz, CD_3OD): δ = 4.58 (s, 2 H), 7.34 (br s, 5 H), 7.82 (br s, 2 H), 8.71 (br s, 2 H), in rough agreement with the literature data.[20a] ^{13}C NMR (75 MHz, CD_3OD): δ = 44.7 (t), 123.2 (d, 2 C), 128.4, 128.7, 129.6 (all d), 139.7 (s), 143.9 (s), 151.0 (d, 2 C), 167.6 (s). IR (ATR): ν = 3300, 3064, 1645, 1542, 1196, 1172, 1126, 723, 660 cm^{-1}. ESI-HRMS: *m/z* calcd for $C_{13}H_{12}N_2O$ + H [M + 1]: 213.1022; found: 213.1018.

2-Benzyl-3-iminoisoindolin-1-one (23)

The compound was prepared according to the described general procedure with Ph_3P as the ligand additive from 2-bromobenzonitrile (**22**, 182 mg, 1 mmol), isolated as an off-white solid (168 mg, 71%); mp 123–124 °C (EtOAc); lit.[10b] mp 122–123 °C. NMR spectra were in accordance with the literature data.[10b] IR spectra were in accordance with the literature.[10a] ESI-HRMS: *m/z* calcd for $C_{15}H_{12}N_2O$ + H [M + 1]: 237.1022; found: 237.1019.

***N*-Benzyl-4-cyanobenzamide (25)**

The compound was prepared according to the described general procedure with Ph_3P as the ligand additive from 4-bromobenzonitrile (**24**, 182 mg, 1 mmol), isolated as an off-white solid (203 mg, 86%); mp 150–153 °C (EtOAc–hexanes); lit.[21b] mp 151 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.61 (d, 2 H, *J* = 5.7 Hz), 6.82 (br s, 1 H), 7.17–7.38 (m, 5 H), 7.67 (d, 2 H, *J* = 8.1 Hz), 7.87 (d, 2 H, *J* = 8.1 Hz), in fair accordance with the literature data.[21a] ^{13}C NMR (75 MHz, $CDCl_3$): δ = 44.3 (t), 115.0, 117.9 (all s), 127.2, 127.7, 127.8, 128.6, 128.8, 132.3 (all d), 137.5, 138.2 (all s), 165.6 (s). IR (ATR): ν = 3309, 3030, 2233, 1643, 1548, 1494, 1311, 719, 672 cm^{-1}. ESI-HRMS: *m/z* calcd for $C_{15}H_{12}N_2O$ + H [M + 1]: 237.1022; found: 237.1018.

***N*-Benzyl-4-methoxybenzamide (27)**

The compound was prepared according to the described general procedure with Ph_3P as the ligand additive from 4-bromoanisole (**26**, 187 mg, 1 mmol), isolated as a white solid (123 mg, 51%). Spectral data were in accordance with the literature data;[2m] mp 128–130 °C (EtOAc–hexanes); lit.[22] mp 129–130 °C.

***N*-Benzylquinoline-2-carboxamide (29)**

The compound was prepared according to the described general procedure with Ph_3P as the ligand additive from 2-bromoquinoline (**28**, 208 mg, 1 mmol), isolated as a white solid (228 mg, 87%). Spectral data were in full accordance with the literature data;[2m] mp 125–127 °C (EtOAc); lit.:[2m] 124–125 °C.

***N*-Benzylquinoline-3-carboxamide (30)**

The compound was prepared according to the described general procedure with Ph_3P as the ligand additive from 3-bromoquinoline (**8**, 208 mg, 1 mmol), isolated as a white solid (165 mg, 63%); mp 140–141 °C (EtOAc); lit.:[2c] 140 °C. NMR and IR data were in rough agreement with the literature data.[2c] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.69 (d, 2 H, *J* = 5.7 Hz), 6.94 (br s, 1 H), 7.22–7.40 (m, 5 H), 7.58 (ddd, 1 H, *J* = 1.0, 7.0, 8.0 Hz), 7.77 (ddd, 1 H, *J* = 1.4, 7.0, 8.4 Hz), 7.83 (br d, 1 H, *J* = 8.1 Hz, H-5), 8.10 (br d, 1 H, *J* = 8.4 Hz), 8.59 (br d, 1 H, *J* = 2.0 Hz), 9.26 (d, *J* = 2.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 44.2 (t), 126.8 (s), 127.5 (d), 127.7 (d), 128.0 (s), 128.7, 128.8, 129.3, 131.2, 135.6 (all d), 137.8 (s), 148.1 (d), 149.2 (s), 165.5 (s). IR (ATR): ν = 3257, 3059, 3028, 1659, 1620, 1542, 1500, 1430, 1302, 1250 740, 692 cm^{-1}. ESI-HRMS: *m/z* calcd for $C_{17}H_{14}N_2O$ + H [M + 1]: 263.1179; found: 263.1170.

1-(2-Naphthoyl)benzotriazole (32)

The compound was prepared according to the described general procedure with Ph_3P as the ligand additive from naphthalene **1** (207 mg, 1 mmol), isolated as a pale brown solid (98 mg, 36%). Spectral data were in full agreement with the literature data;[23a] mp 137–139 °C (EtOAc); lit.[23b] mp 140–142 °C.

(12) (a) Chan, A.; Maki, B. E.; Phillips, E. M.; Scheidt, K. A. *Org. Lett.* **2007**, *9*, 371. (b) Arrowsmith, G. B.; Jeffery, G. H.; Vogel, A. I. *J. Chem. Soc.* **1965**, 2072.

(13) Beller, M.; Maegerlein, W.; Indolese, A. F.; Fischer, C. *Synthesis* **2001**, 1098.

(14) Kim, H. J.; Jeong, E. M.; Lee, K.-J. *J. Heterocycl. Chem.* **2011**, *48*, 965.

(15) (a) Gonec, T.; Bobal, P.; Sujan, J.; Pesko, M.; Guo, J.; Kralova, K.; Pavlacka, L.; Vesely, L.; Kreckova, E.; Kos, J.; Coffey, A.; Kollar, P.; Imramovsky, A.; Placek, L.; Jampilek, J. *Molecules* **2012**, *17*, 613. (b) Collington, D. M.; Hey, D. H.; Rees, C. W. *J. Chem. Soc. C* **1968**, 1017.

(16) Niko, Y.; Hiroshige, Y.; Kawauchi, S.; Konishi, G.-I. *J. Org. Chem.* **2012**, *77*, 3986.

(17) Wang, X.; Wang, D.-Z. *Tetrahedron* **2011**, *67*, 3406.

(18) (a) Takács, A.; Jakab, B.; Petz, A.; Kollár, L. *Tetrahedron* **2007**, *63*, 10372. (b) Wang, Y.; Zhu, D.; Tang, L.; Wang, S.; Wang, Z. *Angew. Chem. Int. Ed.* **2011**, *50*, 8917.

(19) Gou, F.-R.; Wang, X.-C.; Huo, P.-F.; Bi, H.-P.; Guan, Z.-H.; Liang, Y.-M. *Org. Lett.* **2009**, *11*, 5726.

(20) (a) Epsztajn, J.; Bieniek, A.; Plotka, M. W. *J. Chem. Res.* **1986**, *1*, 442. (b) Kim, B. R.; Lee, H.-G.; Kang, S.-B.; Sung, G. H.; Kim, J.-J.; Park, J. K.; Lee, S.-G.; Yoon, Y.-J. *Synthesis* **2012**, *44*, 42.
(21) (a) Toshikatsu, M.; Kazuaki, I.; Hisashi, Y. *Org. Lett.* **2005**, *7*, 5043. (b) Ueda, T.; Konishi, H.; Manabe, K. *Org. Lett.* **2013**, *15*, 5370.
(22) Martinelli, J. R.; Clark, T. P.; Watson, D. A.; Munday, R. H.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2007**, *46*, 8460.
(23) (a) Katritzky, A. R.; Tala, S. R.; Abo-Dya, N. E.; Gyanda, K.; El-Gendy, B. E.-D. M.; Abdel-Samii, Z. K.; Steel, P. J. *J. Org. Chem.* **2009**, *74*, 7165. (b) El Khatib, M.; Elagawany, M.; Todadze, E.; Khelashvili, L.; El-Feky, S. A.; Katritzky, A. R. *Synlett* **2012**, *23*, 1384.

