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Palladium-catalyzed N-heteroannulation of *N*-allyl- or *N*-benzyl-2-nitrobenzenamines: synthesis of 2-substituted benzimidazoles

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Abstract—A palladium-catalyzed reductive N-heteroannulation of *N*-allyl- or *N*-benzyl-2-nitrobenzenamines, using carbon monoxide as the ultimate reducing agent, affording 2-substituted benzimidazoles has been developed.

1. Introduction

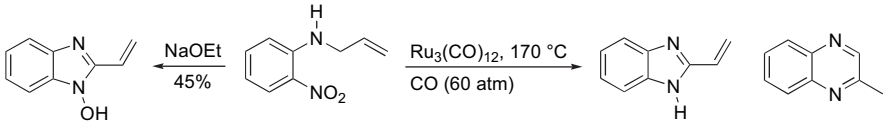
Transition metal-catalyzed reductive N-heteroannulations of 2-substituted nitroarenes are emerging as a powerful tool in the synthesis of a variety of nitrogen containing fused heterocyclic compounds.[1] Particularly useful and diverse are the palladium-catalyzed reactions using carbon monoxide as the ultimate reducing agent. Palladium-catalyzed reductive N-heteroannulation has been utilized in the synthesis of indoles,[2] 2*H*-indazoles,[2j] quinolines,[2j] 4(1*H*)-quinolones,[3] dihydroquinoxalines,[4] quinazolines,[5] 4(3*H*)-quinazolinones,[6] pyrrolines,[7] and 2,1-benzoisoxazole.[2j]

In contrast, annulation to form a benzimidazole has only been reported in a single case using a ruthenium-catalyst and *N*-allyl 2-nitrobenzenamine (**1**) as the substrate.[8] Reaction of **1** using triruthenium dodecacarbonyl (7 mol %) at elevated temperature and carbon monoxide pressure gave 2-ethenylbenzimidazole **2** (Scheme 1). It is interesting to note that both a higher yield of **2** and the formation of 2-methylquinoxaline (**3**) were observed using cyclooctene as the solvent.

Base mediated reactions of *N*-alkyl-, *N*-allyl- or *N*-benzyl-2-nitroaromatic compounds to give 2-substituted 1-hydroxy- or 1-alkoxybenzimidazoles have been reported in a number of cases.[9] For example, reaction of *N*-allyl-2-nitrobenzenamine with sodium ethoxide gave the corresponding 2-ethenyl-1-hydroxybenzimidazole (Scheme 1).[10] 1-Hydroxybenzimidazoles are readily reduced to benzimidazoles using, for example, Fe–HCl[10] or zinc dust in ethanol.[11]

2-Substituted benzimidazoles have also been prepared in low yields (6–40%) from *N*-alkyl and *N*-benzyl substituted 2-nitrobenzenamines using an excess of iron oxalate and lead shots at 220–240 °C.[12] It is not clear if the metal additives are actually involved in the reaction since pyrolysis of *N*-benzyl-2-nitrobenzenamine at 200–220 °C for 1 h in the absence of any catalyst or solvent gave benzaldehyde (26%), 2-nitrobenzenamine (50%), and 2-phenylbenzimidazole (48%).[13] In addition, heating *N*-benzyl-2-nitrobenzenamine in a mixture of benzylamine and benzyl alcohol gave 2-phenylbenzimidazole in 60% yield.[14]

The benzimidazole-forming reactions discussed above all require relatively harsh reaction conditions. Based on the relatively mild palladium-catalyzed N-heteroannulations to give indoles recently developed in our laboratories, we attempted to use similar reaction conditions for the formation of benzimidazoles. In our initial experiment, *N*-2-(propen-1-yl)benzenamine **5** was prepared by nucleophilic aromatic substitution of methyl 2-bromo-3-nitrobenzoate with



Scheme 1.

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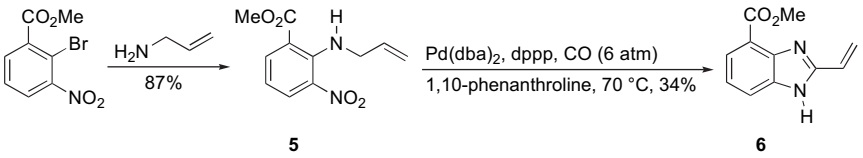
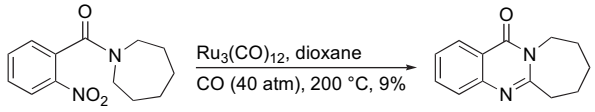


Scheme 2.



Scheme 3.

1-amino-2-propene. Reductive N-heteroannulation of **5** gave the 2-ethenyl substituted benzimidazole **6** in 34% yield (Scheme 2). To our knowledge, this represents only the third case of a transition metal-catalyzed reductive annulation of a nitrobenzene via the activation of the carbon–hydrogen bond of an sp^3-hybridized carbon. In addition to the single case shown in Scheme 1, Watanabe et al. reported the formation of 7,8,9,10-tetrahydroazepino[2,1-*b*]quinazolin-12(6*H*)-one albeit, in low isolated yield (Scheme 3).[6]

There are numerous methods for the preparation of 2-substituted benzimidazoles. The two most utilized are Philips synthesis involving a condensation of 1,2-diaminobenzenes with carboxylic acids or acid derivatives in the presence of an acid[15] and oxidative condensations of 1,2-diamines with aromatic aldehydes.[16] Encouraged by the result seen in Scheme 2, we decided to examine the scope and limitation of the palladium-catalyzed formation of 2-substituted benzimidazoles from *N*-allyl- or *N*-benzyl-2-nitrobenzenamines described in Scheme 2.

2. Results and discussion

In order to examine the palladium-catalyzed N-heteroannulation to give benzimidazoles, a variety of *N*-allyl- or *N*-benzyl-2-nitrobenzenamines were synthesized and the results of these reactions are summarized in Table 2. The annulation precursors were prepared by Buchwald–Hartwig type palladium-catalyzed amination of 2-halo-1-nitroarenes (entries 1, 7, 9–12, and 17–19),[17] reductive amination of 2-nitrobenzenamines with aldehydes (entries 6, 8, and 14),[18] nucleophilic aromatic substitution using 2-halo-1-nitroarenes and amines (entries 2, 3, and 15),[19,20] or according to literature procedures. Reactions forming either new compounds or alternative methods for the preparation of previously published compounds have yields reported in parenthesis in Table 2.

N-Benzyl-2-nitrobenzenamine (**10**) was used as a model substrate for the initial screening of the reaction conditions (Table 1). This compound was selected since the product 2-phenyl-benzimidazole (**26**) is substantially more stable compared to 2-ethenyl-benzimidazoles (such as **6**). The latter compounds are very prone to polymerization.[21] The screening reactions were performed at 120 °C for 20–24 h in all cases, and the amount of product was determined after purification by column chromatography. It should be noted

Table 1. Optimization of the reaction[a]

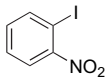
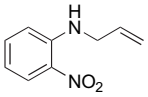
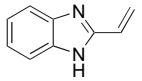
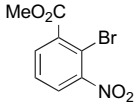
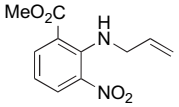
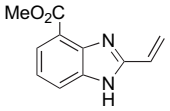
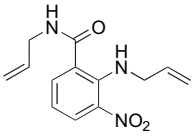
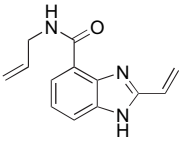
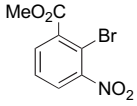
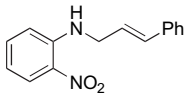
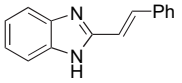
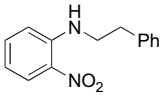
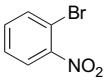
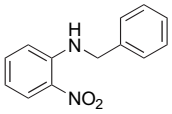
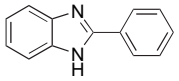
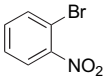
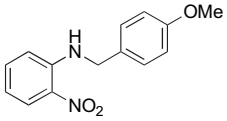
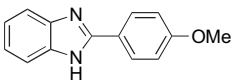
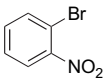
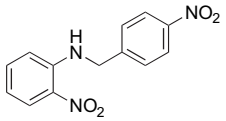
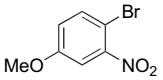
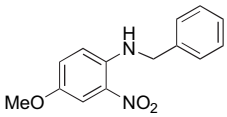
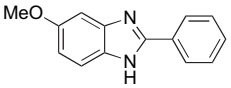
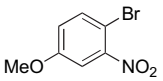
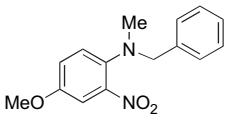
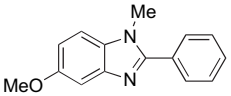
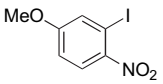
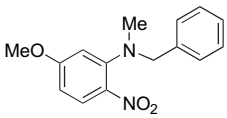
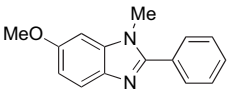
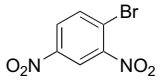
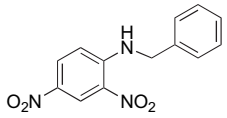
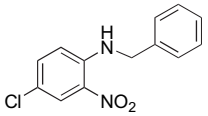
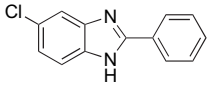
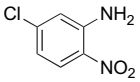
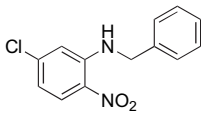
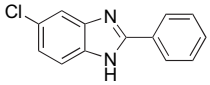
Entry	Catalyst	Ligands	Solvent	Pressure (atm)	Yield of **26** (%)
1	$Pd(dba)_2$	dppp/phen	DMF	6	20
2	**$Pd(dba)_2$**	**phen**	**DMF**	**6**	**59**
3	$Pd(OAc)_2$	phen	DMF	6	28
4	$Pd(dba)_2$	phen	DMF	1	19[b]
5	$Pd(dba)_2$	phen	DMF	3	33
6	$Pd(dba)_2$	phen	DMF	10	52
7	$Pd(dba)_2$	phen	DMF	14	40
8	$Pd(dba)_2$	dppp/phen	DMF	14	28
9	$Pd(dba)_2$	phen	DMF	20	23
10	—	phen	DMF	6	0[d]
11	$Pd(dba)_2$	phen	DMF	2[c]	0
12	$Pd(dba)_2$	phen	MeCN	6	26
13	$Pd(dba)_2$	phen	NMP	6	30
14	$Pd(dba)_2$	phen	PhMe	6	34

[a] The temperature was 120 °C for all reactions.
[b] 2-Nitrobenzenamine of 22% was also isolated.
[c] Argon was used in place of CO.
[d] Compound **10** in 96% yield was recovered. dba=bis(dibenzylidene)-acetone; dppp=bis(1,3-diphenylphosphino)propane; phen=1,10-phenanthroline.

that varying amounts of starting material (**10**) were obtained in most cases. Unfortunately, we were unable to quantify the amount of **10** since it co-elutes with bis(dibenzylidene)acetone. In our initial reaction both bis(1,3-diphenylphosphino)propane and 1,10-phenanthroline were used as ligands. This combination has previously been successfully employed in the synthesis of 1,2-dihydro-4(3*H*)-carbazolones[2h] and β-carbolines.[3] However, for the transformation of **10** to **26** a much higher yield was realized using only 1,10-phenanthroline as the ligand. Dimethyl formamide was shown to be a better solvent compared to, for example, acetonitrile, *N*-methylpyrrolidinone, and toluene (entries 2 and 12–14). DMF has previously been found by Davies et al. to be optimal for the cyclization of 2-nitro-1-alkenylarenes to give indoles.[2e] Palladium diacetate was examined as a catalyst but did not perform as well (entry 3). It should be noted that reaction of **10** in the absence of palladium bis(dibenzylideneacetone) resulted in a 96% recovery of the starting material (entry 10). No reaction was observed replacing carbon monoxide with an argon atmosphere (entry 11). A carbon monoxide pressure of 6 atm was found to be optimal for this catalyst system; lowering or raising the pressure only resulted in diminishing yields (entries 4–9). In contrast to the $Ru_3(CO)_{12}$ catalyst previously reported, we did not observe the formation of a quinoxaline under any reaction conditions, including using cyclooctene as the solvent employing compound **1** or any of the substrates examined (cf. Scheme 1). Reaction of **1** in cyclooctene resulted in quantitative recovery of the starting material.

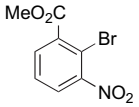
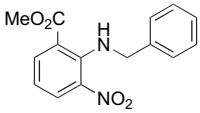
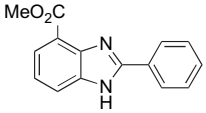
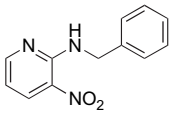
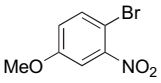
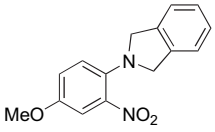
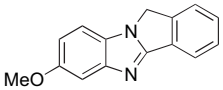
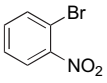
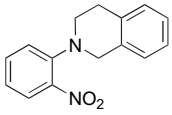
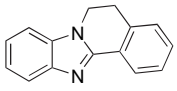
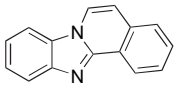
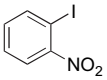
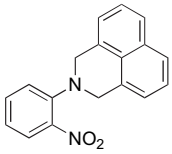
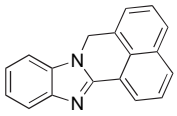
Using the conditions described above and with an array of substrates in hand, the scope and limitation of the annulation

Table 2. Synthesis and N-heterocyclization of *N*-benzyl-/*N*-allyl-2-nitroarenes

Entry	Nitrobenzene	*N*-Substituted-2-nitroarene[a,b]		Benzimidazole[a,b]	Yield
1			**1** (81%)		**2** (46%)
2			**5** (87%)		**6** (74%)
3			**7** (48%)		**24** (22%)
4			**8**[c]		**25** (54%)
5			**9**[c]	[d]	
6			**10** (83%)		**26** (83%)
7			**11** (92%)		**27** (56%)
8			**12** (25%)	[d]	
9			**13** (74%)		**28** (76%)
10			**14** (58%)		**29** (52%)
11			**15** (54%)		**30** (60%)[e]
12			**16** (83%)	[d]	
13			**17**[c]		**31** (64%)
14			**18** (35%)		**31** (58%)

(*continued*)

Table 2. (*continued*)

Entry	Nitrobenzene	*N*-Substituted-2-nitroarene[a,b]	Benzimidazole[a,b]	Yield
15			**19** (79%)		**32** (45%)
16			**20**[c]	[d]	
17			**21** (85%)		**33**[f]
18			**22** (68%)		**34** (44%)
					**35** (83%)
19			**23** (84%)		**36** (61%)

[a] See Section 3 for experimental details.
[b] Isolated yields of pure compound in parenthesis.
[c] Prepared according to a literature procedure.
[d] No benzimidazole, starting material, or any other identified products were observed.
[e] In addition, 28% of **15** was also isolated.
[f] Approximately 90% pure; the yield was not calculated.

reaction was examined next. Relatively long reaction times (2–8 d) were required for the reaction to go to completion as monitored by TLC. All four *N*-allylated 2-nitrobenzenamines examined underwent annulation to give 2-alkenyl-substituted benzimidazoles (Table 2, entries 1–4). *N*-Benzyl-2-nitroaminobenzene (**10**) and substrates having a functionalized *N*-benzyl substituent all but one reacted to form benzimidazole derivatives (entries 6, 7, and 17–19). No identifiable products or starting materials were obtained from the *N*-(4-nitrobenzyl) derivative (**12**, entry 8). It should be noted that *N*-4-nitrobenzyl-2-nitrobenzenamine (**16**) undergoes cyclization to give the corresponding 1-oxygenated benzimidazole under basic conditions described in Scheme 1.[22] Functional groups on the 2-nitrobenzenamine ring were also tolerated including methoxy-, chloro-, and carbomethoxy-groups. Although all starting materials were consumed, no product was identified using **16** having an electron-withdrawing nitro group (entry 12), or from reaction of the pyridine derivative **20**[23] (entry 16).

It is evident from the examples in Table 2 that in order for a methylene group to participate in the cyclization it must be activated by an adjacent aryl or alkenyl group. For example, *N*-(2-phenyl-1-ethyl)-2-nitrobenzenamine (**9**) did not produce the expected 2-benzylbenzimidazole[24] but produced minute quantities of a number of unidentified products (entry 5). No reaction on the methyl group of either **14** or **15** was observed (entries 10 and 11). When two different methylenes were present in the same molecule (**22**, entry 18), only the benzylic methylene reacted to form the benzimidazole nucleus.

The mechanism of the N-heteroannulation to form benzimidazoles is presently unclear. A metal-bound nitrene followed by carbon–hydrogen bond insertion was suggested for the two ruthenium-catalyzed reactions seen in Schemes 1 and 2. Ruthenium,[7,25] palladium,[2k] and selenium,[26] in the presence of carbon monoxide, have been shown to catalyze the formation of 2-arylbenzimidazoles from the 2-nitro-*N*-(phenylmethylene)benzenamine, the imine derived from reaction of 2-nitrobenzenamine and benzaldehyde. Thus, an oxidation of the amine to an imine ($NH–CH_2$ to N=CH) followed by cyclization was initially considered as a possible reaction path. However, reaction of preformed 2-nitro-*N*-(phenylmethylene)benzenamine under our reaction conditions did not produce the corresponding 2-phenylbenzimidazole (**26**) but only resulted in hydrolysis of the imine back to the original starting materials. Another mechanistic possibility is a base mediated cyclization to form an *N*-hydroxybenzimidazole followed by a palladium-catalyzed deoxygenation. This does not appear to be the case since no reaction is observed in the absence of palladium and the starting material is recovered unchanged even after prolonged reaction times. We were unable to identify any

intermediates by quenching the reaction prior to complete consumption of the starting material. Only starting material and product were observed.

In summary, we have developed a relatively mild and expedient palladium-catalyzed synthesis of 2-alkenyl- or 2-aryl-substituted benzimidazoles starting from readily available *N*-allyl- or *N*-benzyl-2-nitrobenzenamines. The reaction involves, at least formally, an unusual insertion into an sp^3-hybridized carbon–hydrogen bond. The reaction sequence is flexible and a variety of functional groups are tolerated. Although numerous methods for the preparation of benzimidazoles exist, the presented reaction may offer an advantage when acid sensitive or oxidation prone functional groups are present in the target molecule. Present studies are focused on the synthesis of more complex polycyclic benzimidazoles.

3. Experimental section

3.1. General procedures

All NMR spectra were determined in $CDCl_3$ at 600 MHz (^1H NMR) and 150 MHz (^{13}C NMR). The chemical shifts are expressed in δ values relative to Me_4Si (0.00, ^1H and ^{13}C) or $CDCl_3$ (77.00, ^{13}C) internal standards. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Toluene, hexanes, and EtOAc were distilled from calcium hydride. Chemicals prepared according to literature procedures have been footnoted the first time used; all other reagents were obtained from commercial sources and used as received. All reactions were performed in oven-dried glassware under an argon atmosphere unless otherwise stated. Solvents were removed from crude reaction mixtures and products on a rotary evaporator at water aspirator pressure. Melting points were determined on a MelTemp and are uncorrected. Elemental analyses were performed in the Department of Chemical Engineering, College of Engineering and Mineral Resources, West Virginia University.

3.1.1. *N*-(2-Propen-1-yl)-2-nitrophenylamine (1). A solution of 1-iodo-2-nitrobenzene (124 mg, 0.498 mmol), *N*-(2-propen-1-yl)amine (50 μL, 0.666 mmol), palladium diacetate ($Pd(OAc)_2$, 11.7 mg, 0.052 mmol), 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (binap, 47.1 mg, 0.076 mmol), and cesium carbonate (228 mg, 0.700 mmol) in toluene (6 mL) was stirred (30 min) under argon atmosphere followed by heating at 80 °C (44.75 h). The mixture was cooled to ambient temperature, diluted with EtOAc (6 mL), filtered (Celite), and the Celite was washed with a few milliliter of EtOAc. The solvents were removed on a rotary evaporator at water aspirator pressure and the crude product was purified by column chromatography on silica (hexanes/EtOAc, 9:1) to give **1** (72.2 mg, 0.405 mmol, 81%) as an orange oil. Analytical data are in complete agreement with published values.[20]

3.1.2. Methyl 3-nitro-2-(*N*-(2-propen-1-yl))aminobenzoate (5). To a solution of methyl 2-bromo-3-nitrobenzoate (1.12 g, 4.31 mmol) in dichloromethane (50 mL) was added 2-propen-1-ylamine (350 mL, 4.66 mmol) and the reaction mixture was stirred at ambient temperature (23 h). Concentrated sulfuric acid (5 drops) was added and three portions of 2-propen-1-ylamine (330 mL, 4.40 mmol) were added (immediately, after 21.5 h, and after 24 h). The solution was heated at 50 °C for this entire period and for an additional 23 h after the last addition. The solvents were removed on a rotary evaporator at water aspirator pressure and the residue was purified by chromatography (hexanes/EtOAc, 9:1) to give **5** (890 mg, 3.77, 87%) as a pale brown solid. Mp 60–61 °C; ^1H NMR: δ 8.56 (br s, 1H), 8.08 (dd, J=7.2, 1.2 Hz, 1H), 7.97 (dd, J=7.8, 1.8 Hz, 1H), 6.69 (t, J=7.8 Hz, 1H), 5.85–5.91 (m, 1H), 5.32 (d, J=16.8 Hz, 1H), 5.22 (d, J=10.2 Hz, 1H), 3.91 (s, 3H), 3.61 (s, 2H); ^{13}C NMR: δ 167.7, 145.3, 137.4, 136.9, 133.6, 131.5, 118.0, 116.8, 114.6, 52.4, 49.1; IR (neat): 1687, 1523, 1344, 1121 cm^{-1}; Anal. Calcd for $C_{11}H_{12}N_2O_4$: C, 55.93; H, 5.12. Found: C, 56.05; H, 5.58; HRMS calcd for $C_{11}H_{13}N_2O_4$ ($M+H^+$): 237.0875, found: 237.0870.

3.1.3. *N*-(2-Propen-1-yl) 2-(*N*-(2-propen-1-yl))amino-3-nitrobenzamide (7). To a solution of 2-bromo-3-nitrobenzoic acid (2.06 g, 8.37 mmol) in benzene (20 mL) at 0 °C was added oxalyl chloride (4.0 mL, 45.9 mmol) via syringe. The resulting solution was stirred (0 °C, 10 min, ambient temperature, 1 h, and at reflux, 1 h), and the solvent and excess reagents were removed. The crude product was dissolved in benzene (20 mL), *N*-(2-propen-1-yl)amine (2.0 mL, 26.7 mmol) in benzene (10 mL) was added via pipette, and the resulting solution was stirred at ambient temperature (68 h). The solvent was removed on a rotary evaporator at water aspirator pressure and the crude product was purified by chromatography (hexanes/EtOAc, 6:4) to give **7** (1.05 g, 4.02 mmol, 48%) as a yellow solid followed by *N*-(2-propen-1-yl) 2-bromo-3-nitrobenzamide (740 mg, 2.60, 31%) as a yellow solid. Data for **7**: mp 59–60 °C; ^1H NMR: δ 8.16 (dd, J=9.0, 1.2 Hz, 1H), 7.76 (dd, J=7.8, 1.2 Hz, 1H), 7.64 (br s, 1H), 6.85 (t, J=7.8 Hz, 1H), 6.72 (br s, 1H), 5.96–5.84 (m, 2H), 5.29–5.25 (m, 2H), 5.23–5.18 (m, 2H), 4.07 (t, J=6.0 Hz, 2H), 3.80 (t, J=6.0 Hz, 2H); ^{13}C NMR: δ 167.2, 143.7, 137.8, 136.4, 133.8, 133.4, 128.7, 126.6, 117.6, 117.5, 117.5, 50.6, 42.5; IR (neat): 3311, 1637, 1488, 1270, 925 cm^{-1}; Anal. Calcd for $C_{13}H_{15}N_3O_3$: C, 59.76; H, 5.79. Found: C, 59.43; H, 6.06.

3.1.4. *N*-Benzyl-2-nitrobenzenamine (10). To a solution of 2-nitrobenzenamine (300 mg, 2.17 mmol), benzaldehyde (420 μL, 4.13), glacial acetic acid (750 μL, 13.1 mmol), and dichloromethane (10 mL) was added sodium triacetoxyborohydride (1.29 g, 6.09 mmol) and the reaction mixture was stirred at ambient temperature (90.5 h). Additional benzaldehyde (210 μL, 2.06 mmol) was added and the solution was stirred at ambient temperature (28.75 h). Additional sodium triacetoxyborohydride (648 mg, 3.06 mmol) was added and the solution was stirred at ambient temperature (23.5 h). The mixture was diluted with sodium bicarbonate (aqueous 10 mL) and washed with EtOAc (4×10 mL). The combined organic phases were dried ($MgSO_4$), filtered, and the solvents were removed on a rotary evaporator at water aspirator pressure. The crude product was purified by chromatography (hexanes then hexanes/EtOAc, 95:5) to give **10** (409 mg, 1.80 mmol, 83%) as an orange solid. Mp 73–74 °C (lit.[27] 72 °C)

3.1.5. *N*-(4-Methoxybenzyl)-2-nitrobenzenamine (11). A solution of 2-bromo-1-nitrobenzene (230 mg, 1.14 mmol), 4-methoxybenzylamine (170 μL, 1.31 mmol), $Pd(OAc)_2$ (23.6 mg, 0.105 mmol), binap (94.0 mg, 0.151 mmol), and cesium carbonate (460 mg, 1.41 mmol) in toluene (6 mL) was reacted, as described for **1** (rt, 30 min; 80 °C, 28.5 h), to give after purification by chromatography (hexanes/EtOAc, 9:1) **11** (270 mg, 1.05 mmol, 92%) as a yellow solid. Mp 94–95 °C (lit.[28] 81–82 °C).

3.1.6. *N*-4-Nitrobenzyl-2-nitrobenzenamine (12). A solution of 2-nitrobenzenamine (552 mg, 4.00 mmol), 4-nitrobenzaldehyde (605 mg, 4.01 mmol), and benzene (50 mL) was heated at reflux (110 °C, 47 h followed by 130 °C for 67 h) while removing water via a Dean–Stark trap. After cooling to ambient temperature, dichloromethane (20 mL) and sodium triacetoxyborohydride (2.37 g, 11.2 mmol) were added and the reaction mixture was stirred at ambient temperature (23.25 h). Workup as described for **10** gave after chromatography (hexanes/EtOAc, 9:1) **12** (270 mg, 0.988 mmol, 25%) as a yellow solid. Mp 127–129 °C (lit.[22] 133–135 °C).

3.1.7. *N*-Benzyl-4-methoxy-2-nitrobenzenamine (13). Reaction of 4-bromo-3-nitro-1-methoxybenzene (461 mg, 2.00 mmol), benzylamine (290 μL, 2.66 mmol), $Pd(OAc)_2$ (45.1 mg, 0.201 mmol), binap (188 mg, 0.302 mmol), and cesium carbonate (914 mg, 2.81 mmol) in toluene (6 mL), as described for **1** (30 min at rt, 16.5 h at 80 °C), gave after dilution, filtration, and chromatography (hexanes then hexanes/EtOAc, 98:2) **13** (380 mg, 1.48 mmol, 74%) as a red solid. Mp 104–105 °C (lit.[29] 105–106 °C); ^{1}H NMR: δ 8.35 (br s, 1H), 7.65 (d, J=2.4 Hz, 1H), 7.37–7.33 (m, 4H), 7.29 (t, J=6.6 Hz, 1H), 7.08 (dd, J=9.6, 3.0 Hz, 1H), 6.78 (d, J=9.6 Hz, 1H), 4.54 (d, J=5.4 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR: δ 149.9, 141.1, 137.6, 131.4, 128.9, 127.6, 127.1, 127.0, 115.6, 107.3, 55.9, 47.3; IR (neat): 1569, 1515, 1281, 1031 cm^{-1}; Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.11; H, 5.46. Found: C, 65.01; H, 5.73.

3.1.8. *N*-Benzyl-*N*-methyl-4-methoxy-2-nitrobenzenamine (14). A solution of 2-bromo-5-methoxy-1-nitrobenzene (500 mg, 2.16 mmol), *N*-benzyl-*N*-methyl amine (370 μL, 2.87 mmol), $Pd(OAc)_2$ (49.3 mg, 0.220 mmol), binap (202 mg, 0.325 mmol), and cesium carbonate (984 mg, 3.02 mmol) in toluene (6 mL), as described for **1** (30 min at rt, 19.75 h at 80 °C), gave after dilution, filtration, and chromatography (hexanes/EtOAc, 95:5) **14** (340 mg, 1.25 mmol, 58%) as a dark red oil. ^{1}H NMR: δ 7.29–7.27 (m, 4H), 7.22–7.20 (m, 2H), 7.11 (d, J=9.6 Hz, 1H), 6.98 (dd, J=9.0, 3.0 Hz, 1H), 4.14 (s, 2H), 3.73 (s, 3H), 2.64 (s, 3H); ^{13}C NMR: δ 154.0, 143.9, 139.7, 137.5, 128.2, 128.0, 127.1, 123.4, 119.8, 109.0, 60.2, 55.6, 41.1; IR (neat): 1519, 1496, 1452, 1292, 1033, 863, 696 cm^{-1}; Anal. Calcd for $C_{15}H_{16}N_2O_3$: C, 66.16; H, 5.92. Found: C, 66.31; H, 6.21.

3.1.9. *N*-Benzyl-(5-methoxy-2-nitrophenyl)-*N*-methylamine (15). Reaction of 2-iodo-4-methoxy-1-nitrobenzene (500 mg, 1.79 mmol), *N*-benzyl-*N*-methyl amine (300 μL, 2.33 mmol), $Pd(OAc)_2$ (40.7 mg, 0.181 mmol), binap (168 mg, 0.269 mmol), and cesium carbonate (819 mg, 2.51 mmol) in toluene (6 mL), as described for **1** (45.5 h at 80 °C, 23.25 h at 120 °C), gave after dilution, filtration, and chromatography (hexanes/EtOAc, 98:2) **15** (262 mg, 0.962 mmol, 54%) as a yellow solid. Mp 97–99 °C; ^{1}H NMR: δ 7.85 (d, J=9.6 Hz, 1H), 7.32–7.22 (m, 5H), 6.45 (d, J=1.8 Hz, 1H), 6.38 (dd, J=9.6, 2.4 Hz, 1H), 4.33 (s, 2H), 3.74 (s, 3H), 2.74 (s, 3H); ^{13}C NMR: δ 163.4, 148.3, 136.8, 133.8, 128.9, 128.4, 127.4, 127.2, 105.0, 104.0, 58.5, 55.5, 40.3; IR (neat): 1613, 1567, 1501, 1450, 1415, 1216 cm^{-1}; Anal. Calcd for $C_{15}H_{16}N_2O_3$: C, 66.16; H, 5.92. Found: C, 65.94; H, 6.22.

3.1.10. *N*-Benzyl-2,4-dinitrobenzenamine (16). Reaction of 1-bromo-2,4-dinitrobenzene (494 mg, 2.00 mmol), benzylamine (290 μL, 2.66 mmol), $Pd(OAc)_2$ (45.5 mg, 0.203 mmol), binap (197 mg, 0.316 mmol), and cesium carbonate (914 mg, 2.81 mmol) in toluene (6 mL), as described for **1** (30 min at rt, 19.5 h at 80 °C), gave after dilution, filtration, and chromatography (hexanes/EtOAc, 9:1 then 8:2) **16** (454 mg, 1.66 mmol, 83%) as a yellow solid. Mp 115–117 °C (lit.[30] 115–116 °C).

3.1.11. *N*-Benzyl-5-chloro-2-nitrobenzenamine (18). 5-Chloro-2-nitrobenzenamine (599 mg, 3.47 mmol), benzaldehyde (68 μL, 6.68 mmol), and acetic acid (1.2 mL, 21.0 mmol), in dichloromethane (20 mL) with sodium triacetoxyborohydride (2.07 g, 9.77 mmol), were reacted as described for **7**. Additional benzaldehyde (340 μL, 3.34 mmol, after 19.75 h), sodium triacetoxyborohydride (1.03 g, 4.86 mmol, after 20 h), benzaldehyde (340 μL, 3.34 mmol, after 26.5 h), and triacetoxyborohydride (1.03 g, 4.86 mmol, after 27 h) were added, and the reaction mixture was stirred for an additional 20.25 h. Workup as described for **10** gave after chromatography (hexanes then hexanes/EtOAc, 98:2) **18** (322 mg, 1.23 mmol, 35%) as an orange solid. Mp 96–98 °C (lit.[31] 100–101 °C).

3.1.12. Methyl 2-(*N*-benzylamino)-3-nitrobenzoate (19).[32] A solution of methyl 2-bromo-3-nitrobenzoate (261 mg, 1.00 mmol) and benzylamine (230 μL, 2.11 mmol) in dichloromethane (10 mL) was stirred at ambient temperature (23 h). Additional benzylamine (12 μL, 1.10 mmol) was added and the solution was stirred at ambient temperature (24 h). The solution was washed with sodium carbonate (4×10 mL) and then the organic phase was dried ($MgSO_4$), filtered, and the solvents were removed on a rotary evaporator at water aspirator pressure. Purification by chromatography (hexanes/EtOAc, 9:1) gave **19** (225 mg, 0.791 mmol, 79%) as a yellow solid. Mp 96–97 °C; ^{1}H NMR: δ 8.77 (br s, 1H), 8.09 (dd, J=7.8, 1.8 Hz, 1H), 7.99 (dd, J=8.4, 1.8 Hz, 1H), 7.34 (t, J=7.8 Hz, 2H), 7.30–7.28 (m, 3H), 6.71 (t, J=7.8 Hz, 1H), 4.16 (d, J=4.2 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR: δ 167.7, 145.3, 137.6, 137.3, 136.9, 131.6, 128.9, 127.9, 127.9, 116.9, 114.7, 52.4, 51.0; IR (neat): 1699, 1577, 1490, 1259, 1105 cm^{-1}; Anal. Calcd for $C_{15}H_{14}N_2O_4$: C, 62.93; H, 4.93. Found: C, 63.28; H, 5.30.

3.1.13. 2-(4-Methoxy-2-nitrophenyl)-2,3-dihydro-1*H*-isoindole (21). Reaction of 2-bromo-5-methoxy-1-nitrobenzene (375 mg, 1.62 mmol), isoindoline (255 mg, 2.14 mmol), $Pd(OAc)_2$ (36.2 mg, 0.161 mmol), binap (151 mg, 0.242 mmol), and cesium carbonate (738 mg, 2.27 mmol) in toluene (6 mL), as described for **1** (30 min at rt, 19.5 h at 80 °C) gave after dilution, filtration, and chromatography

(hexanes/EtOAc, 9:1) **21** (374 mg, 1.38 mmol, 85%) as a red solid. Mp 103–104 °C (lit.[33] 112 °C).

3.1.14. 2-(2-Nitro-1-phenyl)-1,2,3,4-tetrahydroisoquinoline (22). Reaction of 2-bromo-1-nitrobenzene (404 mg, 2.00 mmol), 1,2,3,4-tetrahydroisoquinoline (330 μL, 2.64 mmol), $Pd(OAc)_2$ (45.5 mg, 0.203 mmol), binap (187 mg, 0.301 mmol), and cesium carbonate (915 mg, 2.81 mmol) in toluene (6 mL), as described for **1** (6 h at rt, 40.75 h at 80 °C), gave after dilution, filtration, and chromatography (hexanes/EtOAc, 95:5) **22** (344 mg, 1.35 mmol, 68%) as an orange solid. Mp 98–100 °C (lit.[34] 100–102 °C).

3.1.15. 2-(2-Nitrophenyl)-2,3-dihydro-1*H*-benzo[*de*]isoquinoline (23). Reaction of 2-iodonitrobenzene (124 mg, 0.498 mmol), 2,3-dihydro-1*H*-benzo[*de*]isoquinoline (109 mg, 0.644 mmol), $Pd(OAc)_2$ (11.8 mg, 0.053 mmol), binap (46.7 mg, 0.075 mmol), and cesium carbonate (229 mg, 0.703 mmol) in toluene (6 mL), as described for **1** (30 min at rt, 91.25 h at 80 °C), gave after dilution, filtration, and chromatography (hexanes/EtOAc, 6:4) **23** (121 mg, 0.417 mmol, 84%) as a yellow solid. Mp 104–108 °C; ^{1}H NMR: δ 7.77 (d, J=7.8 Hz, 1H), 7.71 (d, J=8.4 Hz, 2 h), 7.41 (t, J=7.8 Hz, 2H), 7.31 (t, J=8.4 Hz, 1H), 7.21 (d, J=6.6 Hz, 2H), 7.14 (d, J=9.0 Hz, 1H), 6.96 (t, J=7.8 Hz, 1H), 4.63 (s, 4H); ^{13}C NMR: δ 145.3, 143.3, 133.4, 132.1, 128.0, 126.6, 126.0, 125.8, 121.8, 121.7, 121.7, 55.2; IR (neat): 1602, 1520, 1355, 1214, 802, 752 cm^{-1}; Anal. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86. Found: C, 74.23; H, 5.23.

3.1.16. 2-Ethenyl-1*H*-benzimidazole (2). To a threaded ACE Glass pressure tube were added **1** (72.2 mg, 0.405 mmol), bis(dibenzylideneacetone)palladium ($Pd(dba)_2$, 14.1 mg, 0.025 mmol), and 1,10-phenanthroline monohydrate (8.40 mg, 0.047 mmol) in DMF (6 mL). The tube was fitted with a pressure head and after the solution was saturated with CO (four cycles to 6 atm of CO) the reaction mixture was heated at 120 °C under CO (6 atm, 47 h). The mixture was diluted with EtOAc (10 mL) and washed with water (4×10 mL). The combined organic phases were dried ($MgSO_4$), filtered, and the solvents were removed on a rotary evaporator at water aspirator pressure. Purification by chromatography (hexanes/EtOAc, 2:8) gave **2** (27.1 mg, 0.188 mmol, 46%) as a pale brown solid. Mp 149–153 °C (lit.[21b] 184 °C).

3.1.17. Methyl 2-ethenyl-1*H*-benzimidazole-4-carboxylate (6). Reaction of **5** (37.8 mg, 0.160 mmol), $Pd(dba)_2$ (7.30 mg, 0.013 mmol), and 1,10-phenanthroline monohydrate (4.0 mg, 0.022 mmol) in DMF (6 mL), as described for **2** (CO, 120 °C, 70.5 h), gave after extraction and chromatography (hexanes/EtOAc, 7:3) **6** (24.1 mg, 0.119 mmol, 74%) as a red solid. Mp 64–71 °C; ^{1}H NMR: δ 7.94 (dd, J=7.8, 0.6 Hz, 1H), 7.88 (dd, J=7.8, 1.2 Hz, 1H), 7.29 (t, J=7.8 Hz, 1H), 6.85 (dd, J=18.0, 11.4 Hz, 1H), 6.26 (d, J=18.0 Hz, 1H), 5.73 (d, J=11.4 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR: δ 167.0, 151.3, 144.5, 134.4, 126.1, 125.0, 125.0, 121.9, 121.7, 113.2, 52.1; IR (neat): 1702, 1431, 1291, 1137, 931 cm^{-1}; HRMS calcd for $C_{11}H_{11}N_2O_2$ (M+H$^+$): 203.0821, found: 203.0815.

3.1.18. *N*-(2-Propen-1-yl) 2-ethenyl-1*H*-benzimidazole-4-carboxamide (24). Reaction of **7** (261 mg, 1.00 mmol), $Pd(dba)_2$ (34.8 mg, 0.061 mmol), and 1,10-phenanthroline monohydrate (21.7 mg, 0.120 mmol) in DMF, (6 mL) as described for **2** (CO, 120 °C, 47 h), gave after extraction and chromatography (hexanes/EtOAc, 6:4) **24** (50.1 mg, 0.221 mmol, 22%) as a 7:1 mixture of rotamers as a pale yellow solid. Mp 192–195 °C; major rotamer: ^{1}H NMR (DMSO-d_6): δ 13.11 (br s, 1H), 9.91 (br s, 1H), 7.86 (d, J=7.8 Hz, 1H), 7.68 (d, J=7.8 Hz, 1H), 7.33 (t, J=7.8 Hz, 1H), 6.85 (dd, J=18.0, 11.4 Hz, 1H), 6.38 (d, J=14.4 Hz, 1H), 6.01 (10-line ddt, J=17.4, 10.8, 5.4 Hz, 1H), 5.80 (d, J=11.4 Hz, 1H), 5.30 (dd, J=17.4, 1.2 Hz, 1H), 5.15 (dd, J=10.2, 1.2 Hz, 1H), 4.09 (t, J=5.4 Hz, 2H); ^{13}C NMR: δ 164.3, 151.2, 140.8, 135.3, 134.5, 126.1, 122.8, 122.6, 122.5, 122.0, 115.0, 114.8, 41.1; IR (neat): 1637, 1610, 1554, 1429, 1251 cm^{-1}; Anal. Calcd for $C_{13}H_{13}N_2O$: C, 68.70; H, 5.77. Found: C, 68.81; H, 6.01. Minor rotamer: ^{1}H NMR (DMSO-d_6): δ 12.42 (br s, 1H), 8.81 (br s, 1H), 7.73 (t, J=8.4 Hz, 2H), 7.22 (t, J=7.8 Hz, 1H), 6.96 (dd, J=18.0, 11.4 Hz, 1H), 6.43 (d, J=17.4 Hz, 1H), 5.60–5.92 (m, 1H), 5.62 (d, J=11.4 Hz, 1H), 5.21 (d, J=17.4 Hz, 1H), 5.11 (d, J=10.2 Hz, 1H), 3.98 (br s, 2H).

3.1.19. 2-(2-Phenyl-1-ethenyl)-1*H*-benzimidazole (25). Reaction of **8** (267 mg, 1.05 mmol),[35] $Pd(dba)_2$ (37.0 mg, 0.064 mmol), and 1,10-phenanthroline monohydrate (22.8 mg, 0.127 mmol) in DMF (6 mL), as described for **2** (CO, 120 °C, 92.75 h), gave after extraction and chromatography (hexanes/EtOAc, 6:4) **25** (126 mg, 0.570 mmol, 54%) as a yellow-brown solid. Mp 202–204 °C (lit.[36] 201–202 °C).

3.1.20. 2-Phenyl-1*H*-benzimidazole (26). Reaction of **10** (114 mg, 0.502 mmol), $Pd(dba)_2$ (17.7 mg, 0.031 mmol), and 1,10-phenanthroline monohydrate (10.4 mg, 0.058 mmol) and DMF (6 mL), as described for **2** (CO, 120 °C, 139.75 h), gave after extraction and chromatography (hexanes/EtOAc, 9:1) **26** (80.7 mg, 0.416 mmol, 83%) as a white solid. Mp 302–303 °C (lit.[37,38] 285–286 °C).

3.1.21. 2-(4-Methoxyphenyl)-1*H*-benzimidazole (27). Reaction of **11** (250 mg, 0.968 mmol), $Pd(dba)_2$ (33.7 mg, 0.059 mmol), and 1,10-phenanthroline monohydrate (21.3 mg, 0.118 mmol) in DMF (6 mL), as described for **2** (CO, 120 °C, 65.5 h), gave after extraction and chromatography (hexanes/EtOAc, in order 8:2, 1:1) **27** (121 mg, 0.540 mmol, 56%) as a pale brown solid. Mp 222–225 °C (lit.[37] 222–225 °C).

3.1.22. 5-Methoxy-2-phenyl-1*H*-benzimidazole (28). Reaction of **13** (128 mg, 0.498 mmol), $(Pd)dba)_2$ (17.7 mg, 0.031 mmol), 1,10-phenanthroline monohydrate (10.7 mg, 0.060 mmol) in DMF (6 mL), as described for **2** (CO, 120 °C, 193.75 h), gave after extraction and chromatography (hexanes/EtOAc, 7:3) **28** (85.5 mg, 0.378 mmol, 76%) as a faint yellow solid. Mp 142–143 °C (lit.[39] 143–144 °C).

3.1.23. 5-Methoxy-1-methyl-2-phenyl-1*H*-benzimidazole (29). Reaction of **14** (136 mg, 0.499 mmol), $Pd(dba)_2$ (17.8 mg, 0.031 mmol), and 1,10-phenanthroline monohydrate (10.9 mg, 0.061 mmol) in DMF (6 mL), as described for **2** (CO, 120 °C, 67.75 h), gave after extraction and

chromatography (hexanes/EtOAc, 9:1 then 1:1) **29** (61.4 mg, 0.258 mmol, 52%) as a white solid.[40] Mp 123–126 °C; ^{1}H NMR: δ 7.75 (d, J=7.8 Hz, 2H), 7.53–7.48 (m, 3H), 7.30 (s, 1H), 7.27 (d, J=9.0 Hz, 1H), 6.98 (d, J=8.4 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H); ^{13}C NMR: δ 156.4, 153.9, 143.6, 131.3, 130.2, 129.6, 129.3, 128.6, 112.8, 110.0, 101.9, 55.8, 31.7; IR (neat): 1467, 1158, 1025, 833, 803, 770 cm^{-1}; Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.92. Found: C, 75.49; H, 6.42; HRMS calcd for $C_{15}H_{15}N_2O$ (M+H$^+$): 239.1184, found: 239.1179.

3.1.24. 6-Methoxy-1-methyl-2-phenyl-1*H*-benzimidazole (30). Reaction of **15** (134 mg, 0.492 mmol), Pd(dba)$_2$ (17.4 mg, 0.030 mmol), and 1,10-phenanthroline monohydrate (10.6 mg, 0.059 mmol) in DMF (6 mL), as described for **2** (CO, 120 °C, 115.5 h), gave after extraction and chromatography (hexanes/EtOAc, in order 9:1, 7:3, 3:7) **15** (38.1 mg, 0.140 mmol, 28%) followed by **30** (70.6 mg, 0.296 mmol, 60%) as a white solid. Mp 145–147 °C; ^{1}H NMR: δ 7.70 (t, J=7.2 Hz, 3H), 7.48–7.43 (m, 3H), 6.93 (dd, J=9.0, 2.4 Hz, 1H), 6.78 (s, 1H), 3.85 (s, 3H), 3.74 (s, 3H); ^{13}C NMR: δ 156.6, 152.8, 137.3, 130.2, 129.3, 129.1, 128.5, 120.1, 111.5, 93.1, 55.7, 31.5; IR (neat): 1462, 1216, 1084, 1023, 809 cm^{-1}; Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.92. Found: C, 75.38; H, 6.43. HRMS calcd for $C_{15}H_{15}N_2O$ (M+H$^+$): 239.1184, found: 239.1179.

3.1.25. 5-Chloro-2-phenyl-1*H*-benzimidazole (31). Reaction of *N*-benzyl-4-chloro-2-nitrobenzenamine (**17**)[41] (131 mg, 0.499 mmol), Pd(dba)$_2$ (17.2 mg, 0.030 mmol), and 1,10-phenanthroline monohydrate (11.0 mg, 0.061 mmol) in DMF (6 mL), as described for **2** (CO, 120 °C, 46.5 h), gave after extraction and chromatography (hexanes/EtOAc, 9:1 then 1:1) **31** (72.9 mg, 0.319 mmol, 64%) as a pale brown solid. Mp 210–212 °C (lit.[37] 206–210 °C).

Alternative procedure: reaction of **18** (131 mg, 0.499 mmol), Pd(dba)$_2$ (18.0 mg, 0.031 mmol), and 1,10-phenanthroline monohydrate (11.6 mg, 0.064 mmol) in DMF (6 mL), as described for **2** (CO, 120 °C, 74 h), gave after extraction and chromatography (hexanes/EtOAc, 1:1) **31** (67.4 mg, 0.295 mmol, 59%) as a pale brown solid.

3.1.26. Methyl 2-phenyl-1*H*-benzimidazole-4-carboxylate (32). Reaction of **19** (143 mg, 0.503 mmol), Pd(dba)$_2$ (17.6 mg, 0.031 mmol), and 1,10-phenanthroline monohydrate (11.0 mg, 0.061 mmol) in DMF (6 mL), as described for **2** (CO, 120 °C, 139.5 h), gave after extraction and chromatography (hexanes/EtOAc, 9:1 then 7:3) **32** (56.7 mg, 0.225 mmol, 45%) as a pale brown solid. Mp 123–126 °C (lit.[42] 125–127 °C).

Alternative method: reaction of **19** (99.3 mg, 0.349 mmol), Pd(dba)$_2$ (12.6 mg, 0.022 mmol), 1,10-phenanthroline monohydrate (7.8 mg, 0.043 mmol), and 1,3-bis(diphenylphosphino)propane (8.9 mg, 0.022 mmol) in DMF (5 mL), as described for **2** (CO, 120 °C, 138.5 h), gave after extraction and chromatography (hexanes/EtOAc, 9:1 then 7:3) **32** (47.4 mg, 0.188 mmol, 54%) as a pale brown solid.

3.1.27. 7-Methoxy-11*H*-isoindolo[2,1-*a*]benzimidazole (33). Reaction of **21** (113 mg, 0.418 mmol), Pd(dba)$_2$ (15.1 mg, 0.026 mmol), and 1,10-phenanthroline monohydrate (8.9 mg, 0.050 mmol) in DMF (6 mL), as described for **2** (CO, 120 °C, 76 h), gave after extraction and chromatography (hexanes/EtOAc, 7:3) **33** (34.3 mg, approximately 90% pure by ^{1}H NMR).[43] Spectral data from impure **33**: ^{1}H NMR: δ 7.96 (d, J=7.2 Hz, 1H), 7.49 (d, J=7.2 Hz, 1H), 7.46 (t, J=7.2 Hz, 1H), 7.41 (dt, J=7.2, 1.2 Hz, 1H), 7.26 (d, J=2.4 Hz, 1H), 7.24 (dd, J=7.2, 1.8 Hz, 1H), 6.87 (dd, J=6.6, 1.8 Hz, 1H), 4.91 (s, 2H), 3.84 (s, 3H); ^{13}C NMR: δ 158.7, 156.1, 149.1, 143.3, 129.4, 129.2, 128.6, 127.3, 123.9, 121.7, 112.6, 109.8, 103.2, 55.8, 47.3; HRMS calcd for $C_{15}H_{13}N_2O$ (M+H$^+$): 237.1028, found: 237.1023.

3.1.28. 5,6-Dihydrobenz[4,5]imidazo[2,1-*a*]isoquinoline (34) and benz[4,5]imidazo[2,1-*a*]isoquinoline (35). Reaction of **22** (127 mg, 0.499 mmol), Pd(dba)$_2$ (17.3 mg, 0.030 mmol), and 1,10-phenanthroline monohydrate (11.1 mg, 0.062 mmol) in DMF (6 mL), as described for **2** (CO, 120 °C, 67.5 h), gave after extraction and chromatography (hexanes/EtOAc, 9:1) **35** (6.6 mg, 0.030 mmol, 6%) as a pale yellow solid followed by **34** (48.9 mg, 0.222 mmol, 44%) as a pale brown solid.[40] Data for **35**: mp 107–108 °C (lit.[44,45] 129–130 °C). Data for **34**: mp 148–149 °C; ^{1}H NMR: δ 8.30 (dd, J=7.8, 1.8 Hz, 1H), 7.84–7.81 (m, 1H), 7.42–7.34 (m, 3H), 7.31–7.25 (m, 3H), 4.32 (t, J=7.2 Hz, 2H), 3.27 (t, J=7.2 Hz, 2H); ^{13}C NMR: δ 149.1, 144.0, 134.7, 134.2, 130.1, 128.0, 127.7, 126.7, 125.6, 122.6, 122.4, 119.8, 109.0, 40.4, 28.2; IR (neat): 1482, 1448, 1326, 775, 734 cm^{-1}; Anal. Calcd for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49. Found: C, 81.49; H, 5.92.

3.1.29. 7*H*-Benzimidazo[2,1-*a*]benz[*de*]isoquinoline (36). Reaction of **23** (102 mg, 0.351 mmol), Pd(dba)$_2$ (11.3 mg, 0.020 mmol), and 1,10-phenanthroline monohydrate (8.0 mg, 0.044 mmol) in DMF (6 mL), as described above for **2** (CO, 120 °C, 112 h), gave after extraction and chromatography (hexanes/EtOAc, 7:3 then 1:1) **36** (54.9 mg, 0.214 mmol, 61%) as a yellow solid. Mp 210–212 °C (lit.[46] 212–213 °C).

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