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Double Palladium Catalyzed Reductive Cyclizations. Synthesis of 2,2′-, 2,3′-, and 3,3′-Bi-1*H*-indoles, Indolo[3,2-*b*]indoles, and Indolo[2,3-*b*]indoles

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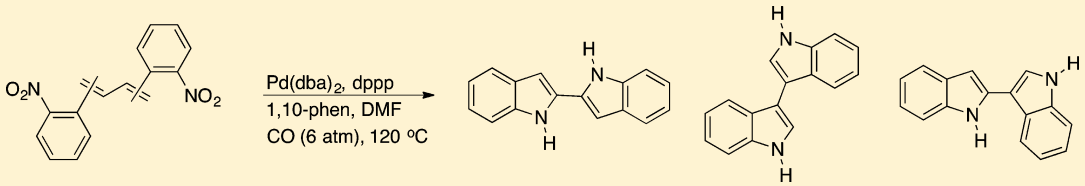
Supporting Information



ABSTRACT: A palladium catalyzed, carbon monoxide mediated, double reductive cyclization of 1,4-, 1,3-, and 2,3-bis(2-nitroaryl)-1,3-butadienes to afford 2,2′-, 2,3′-, and 3,3′-biindoles, respectively, was developed. In contrast, reductive cyclizations of 1,2-bis(2-nitroaryl)ethenes were nonselective, affording mixtures of monocyclized indoles, indolo[3,2-*b*]indole, indolo[1,2-*c*]quinazolin-6(5*H*)-ones, and 5,11-dihydro-6*H*-indolo[3,2-*c*]quinolin-6-ones. Nonselective product formation was also observed from reductive cyclization of 1,1-bis(2-nitroaryl)ethenes, producing indolo[2,3-*b*]indoles and indolo[2,3-*c*]quinolin-6-ones. Carbon monoxide insertion to give the carbonyl containing products was the major or sole reaction path starting from 1,1- or 1,2-bis(2-nitroaryl)ethenes.

INTRODUCTION

Reductive cyclization of 2-nitrostyrenes and 2-nitrobiphenyls to give indoles and carbazoles, respectively, can be accomplished using a number of reagents. The more commonly employed reducing agents are trialkyl phosphites or triphenylphosphine, at elevated temperatures, reactions originally described by Cadogan[1] and Sundberg.[2] More recently, reductive cyclizations using transition metal catalysts in the presence of carbon monoxide, as the ultimate reducing agent, have been developed. Palladium complexes are the most commonly used catalysts for this transformation, and this very facile cyclization has been used in total synthesis of a number of indole alkaloids.[3] We envisioned this cyclization as an expedient methodology for the synthesis of a variety of compounds containing two indole units, either connected via a single bond or fused together. Five different types of substrates, three bis(2-nitrophenyl)butadienes and two bis(2-nitrophenyl)ethenes were selected as biindole precursors (Figure 1). The formation of 2,2′-, 3,3′-, and 2,3′-biindoles from 1,4-, 2,3-, and 1,3-bis(2-nitroaryl)-1,3-butadienes, respectively, was anticipated via a cyclization onto each of the two double bonds of the butadiene (A−C, Figure 1). In related reactions, successful reductive cyclizations of 1,2-bis(2-nitroaryl)ethenes and 1,1-bis(2-nitroaryl)ethenes onto a shared alkene would furnish indolo[3,2-*b*]indoles and indolo[2,3-*b*]indoles (D−E, Figure 1).

We report herein short and efficient synthetic sequences to a variety of substituted biindoles using a double reductive cyclization of 1,4-, 2,3-, and 1,3-bis(2-nitroaryl)-1,3-butadienes as the ultimate and key step forming both indole rings. Also discussed below are nonselective reactions of 1,2-bis(2-nitroaryl)ethenes and 1,1-bis(2-nitroaryl)ethenes leading to mixtures of products.

RESULT AND DISCUSSION

The first type of cyclization studied was the reaction of 1,4-bis(2-nitroaryl)buta-1,3-dienes (cyclization A in Figure 1). The parent compound, 1,4-bis(2-nitrophenyl)-1,3-butadiene (**6**), was prepared following the procedure of Lowinger et al.[4] via a Wittig reaction of 2-nitrocinnamaldehyde (**4**) with 2-nitrobenzyl triphenylphosphonium bromide (**45**) in the presence of a base (Table 1). To our delight, subjecting compound **6** to a palladium catalyzed reductive cyclization using a bis(dibenzylideneacetone)palladium-1,3-bis(diphenyl)propane-1,10-phenanthroline catalyst system, in the presence of carbon monoxide (*p*CO = 6 atm, 120 °C) in *N*,*N*-dimethylformamide, afforded 2-(1*H*-indol-2-yl)-1*H*-indole (**11**)[5] in good isolated yield (Table 1).

2,2′-Indoles not also connected in the 3,3′-position have not to date been isolated from natural sources. However, a number of synthetic pathways to these biindoles have been reported in the literature. For example, the parent compound 2,2′-bi-1*H*-indole (**11**) has been prepared by iridium,[6] gold,[7] and base[8] catalyzed cyclization of the diamine corresponding to **6**, Cadogan−Sundberg type cyclizations of **6** using triphenylphosphine,[9] or triethylphosphite,[10] and a double Madelung cyclization.[11] Pertinent to the current methodology, Cenini et al. reported a Pd(TMB)$_2$-TMphenantroline[12] catalyzed carbon

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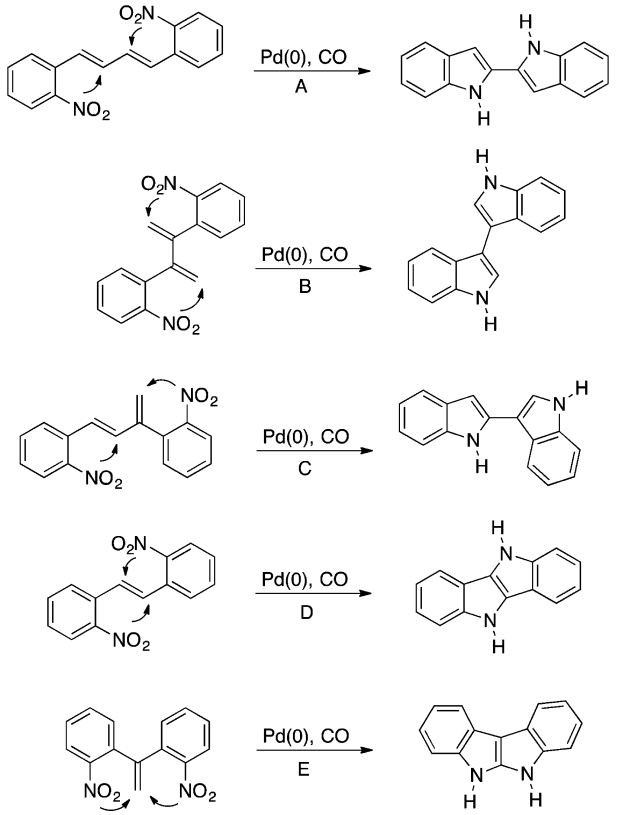


Figure 1. Possible cyclizations (A–E) of bis(2-nitrophenyl)butadienes and -ethenes.

monoxide (pCO = 40 atm, 140 °C) mediated cyclization of **6** to give **11** (40%) in addition to the monocyclized product 2-(2-nitrophenyl)indole (26%).[13] A related transformation has also been described by Davies et al. using a palladium catalyst but without experimental details or yields.[14]

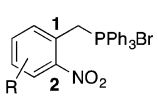
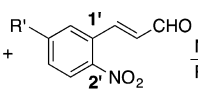
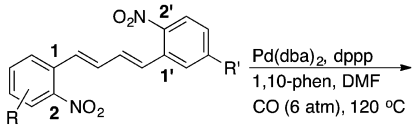
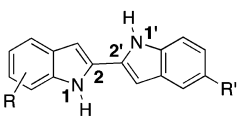
Four additional cyclization substrates (**7**–**10**, Table 1) were synthesized by treatment of Wittig salts **1**–**3**, prepared in 55–75% yield from the corresponding benzyl bromides, with 2-nitrocinnamaldehyde (**4**) or 5-bromo-2-nitrocinnamaldehyde (**5**) in the presence of a base. 5-Bromo-2-nitrocinnamaldehyde (**5**) was obtained by reaction of 5-bromo-2-nitrobenzaldehyde with (formylmethyl)triphenylphosphonium chloride in the presence of 4-(*N*,*N*-dimethylamino)pyridine (DMAP, Scheme 1). A fair amount of dienal **16**, derived from two consecutive Wittig reactions, was also isolated in addition to **5**. The dienes (**7**–**10**) were smoothly transformed into the corresponding 2,2′-bi-1*H*-indoles **12**–**15** under the same conditions used for **6** (Table 1). A good to excellent yield of product was observed for all substrates examined.

Encouraged by the results shown in Table 1, double cyclizations of 2,3-bis(2-nitrophenyl)-1,3-butadienes to give 3,3′-biindoles (cyclization B, Figure 1) were examined next, and the results are summarized in Table 2. The parent cyclization precursor 2,3-bis(2-nitrophenyl)-1,3-butadiene (**27**) has previously been prepared using a palladium catalyzed double cross-coupling of 2-nitrophenylboronic acid with 1,4-bis(methoxycarbonyloxy)-2-butyne.[15] We have recently reported the formation of **28** (Table 2), a substituted analogue of **27**, as side product in a Kosugi–Migita–Stille reaction of **23** with an aryl bromide.[16] It seemed plausible that homocoupling of **23**, and related alkenyltin reagents, would be the major reaction path in the absence of a cross-coupling partner. In order to examine this idea, tributyl(1-(2-nitrophenyl)ethenyl)tin (**22**) was prepared from 1-ethynyl-2-nitrobenzene (**17**) in excellent isolated yield using the regioselective palladium catalyzed hydrostannation developed by Alami and co-workers.[17] As expected, the β-isomer was not detected by ^{1}H NMR of the crude reaction mixture. To our delight, palladium catalyzed homocoupling of **22** proceeded smoothly in DMF to give homocoupling product **27**. With the cyclization precursor in hand, exposure of **27** to the reductive cyclization protocol resulted in the formation of 3,3′-biindole **32**[18] as the sole product (Table 2).

3,3′-Biindoles are relatively rare in nature, but a few examples of halogenated and/or sulfur containing alkaloids of this type have been isolated from algea.[19−22] In addition, the unsubstituted 3,3′-biindole **32** (Table 2) was isolated from a terrestrial fungus.[23] Recent synthesis of 3,3′-biindoles include, for example, a Masuda indole borylation–Suzuki arylation sequence,[24] a tellurium tetrachloride mediated,[25] and palladium catalyzed oxidative dimerizations of indoles.[26]

To briefly examine the scope of the double cyclization, four additional 1-(2-nitrophenyl)ethenyl)tin derivatives (**23**–**26**) were prepared in a similar fashion to **22**. Palladium catalyzed homocoupling of **23** gave the expected product **28** in good yield.

Table 1. Synthesis of 2,2′-Bi-1*H*-indoles from 1,4-Bis(2-nitrophenyl)-1,3-butadienes

Phosphane	Aldehyde	Diene[a,b]	2,2′-Bi-1*H*-indole[a]
			
		6 (R=R′=H)	**11** (R=R′=H, 73%)
1 (R=6-Cl)	**4** (R=H)	**7** (R=6-Cl, R′=H, 55%)	**12** (R=4-Cl, R′=H, 94%)
2 (R=3-OMe)	**4** (R=H)	**8** (R=3-OMe, R′=H, 64%)	**13** (R=7-OMe, R′=H, 93%)
3 (R=4-Br)	**4** (R=H)	**9** (R=4-Br, R′=H, 73%)	**14** (R=6-Br, R′=H, 74%)
3 (R=4-Br)	**5** (R′=5-Br)	**10** (R=4-Br, R′=5-Br, 75%)	**15** (R=6-Br, R′=5-Br, 71%)

[a]Isolated yield of pure product after chromatography. [b]Mixtures of *EE*/*EZ* isomers were obtained for **8**–**10**.

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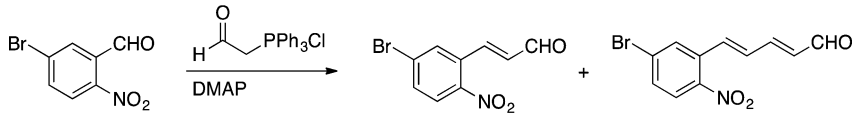
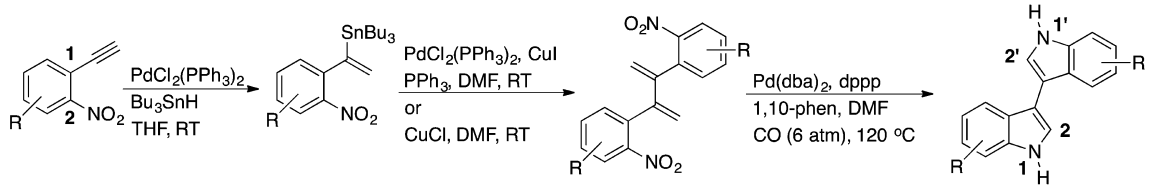
Scheme 1. Synthesis of 5-Bromo-2-nitrocinnamaldehyde (5)



5 (51%) **16** (21%)

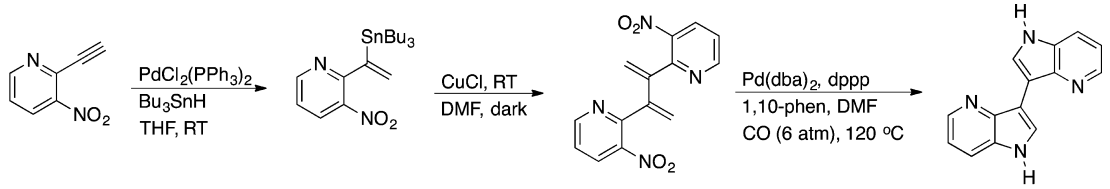
Table 2. Synthesis of 3,3′-Biindoles from 2,3-Bis(2-nitrophenyl)-1,3-butadienes



Alkyne	Vinyltin[a]	Diene[a]	3,3′-bi-1(*H*)indole[a]
17 (R=H)	**22** (95%)	**27** (67%)[b]	**32** (R=H, 89%)
18 (R=5-OBn)	**23** (96%)	**28** (78%)[b]	**33** (R=5,5′-diOBn, 87%)
19 (R=4-Cl)	**24** (96%)	**29** (36%,[b] 80%[c])	**34** (R=6,6′-diCl, 100%)
20 (R=4-CO_2Me)	**25** (78%)	**30** (92%[c])	**35** (R=6,6′-diCO_2Me, 100%)
21 (R=4-OMe)	**26** (90%)	**31** (98%[c])	**36** (R=6,6′-diOMe, 64%)

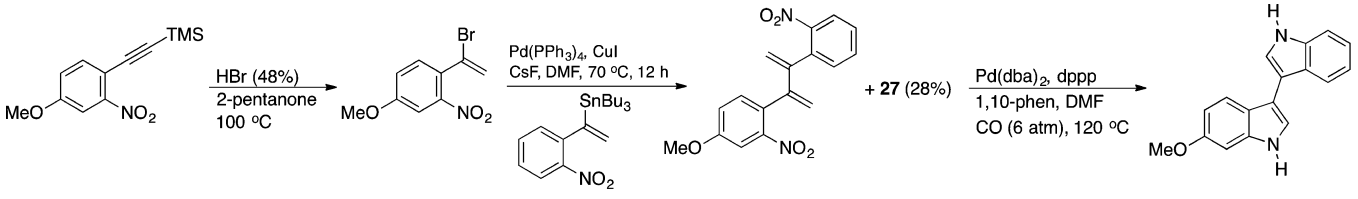
[a]Isolated yield of pure products after chromatography. [b]$PdCl_2(PPh_3)_2$ was used. [c]CuCl was used.

Scheme 2. Synthesis of 4,4′-Diaza-3,3′-bi-1*H*-indole (40)



37 **38** (61%) **39** (54%) **40**(74%)

Scheme 3. Synthesis of the Unsymmetrically Substituted 3,3′-Bi-1*H*-indole 44



41 **42** (57%) **22** **43** (61%) **44** (100%)

However, the yield of the chloro-substituted dimer **29** was low using this type of reaction and a different methodology was pursued. Homocoupling of organotin reagents has been reported using an excess CuCl in DMF,[27] an excess of $CuNO_3$ in THF,[28] or a catalytic amount of $CuCl_2$ in the presence of 0.5 equiv of iodine in DMF.[29] In our hands, treatment of tin derivatives **24**–**26** with 2.5 equiv of CuCl in DMF at ambient temperature furnished 1,3-butadienes **29**–**31** in excellent yields (Table 2). Double reductive cyclizations of **28**–**31** gave the expected 3,3′-biindoles **33**–**36** in 64–100% isolated yield.

An example of a synthesis of a 3,3′-diazaindole was pursued using the hydrostannation, dimerization, cyclization sequence discussed above. Thus, 4,4′-diaza-3,3′-bi-1*H*-indole (**40**) was prepared in three steps from the previously reported 2-ethynyl-3-nitropyridine (**37**) (Scheme 2).

An unsymmetric 2,3-bis(2-nitrophenyl)-1,3-butadiene was also prepared (Scheme 3). Treatment of **41** with HBr in 3-pentanone as the solvent furnished vinyl bromide **42**.[30] Kosugi–Migita–Stille cross-coupling of **42** with ethenyltin **22** gave 1,3-butadiene **43**. Tin impurities from the cross-coupling were removed by chromatography using a 9:1 SiO_2/K_2CO_3 stationary phase as described by Harrowven et al.[31] Double cyclization

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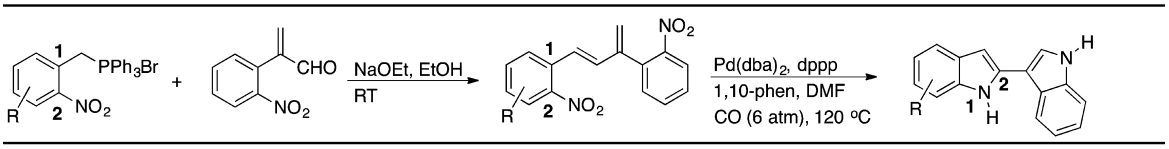
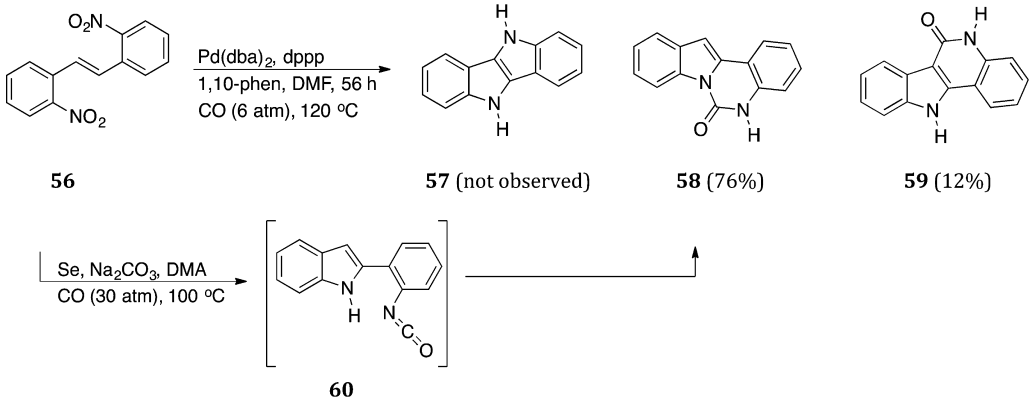
Table 3. Synthesis of 2,3′-Bi-1*H*-indoles from 1,3-Bis(2-nitrophenyl)-1,3-butadienes



Phosphane		Diene[a]	2,3′-bi-1(*H*)indole[a]
45 (R=H)	**47**	**48** (R=H, 41%)	**52** (R=H, 61%)
2 (R=3-OMe)	**47**	**49** (R=3-OMe, 38%)	**53** (R=7-OMe, 72%)
3 (R=4-Br)	**47**	**50**(R=4-Br, 21%)	**54** (R=6-Br, 66%)
46 (R=5-Br)	**47**	**51** (R=5-Br, 22%)	**55** (R=5-Br, 67%)

[a]Isolated yield of pure products after chromatography.

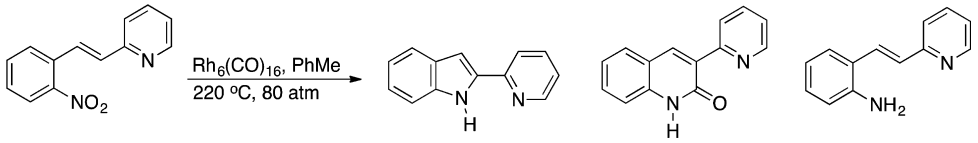
Scheme 4. Reductive Cyclization of 1,2-Bis(2-nitrophenyl)ethene (56)



56 **57** (not observed) **58** (76%) **59** (12%)

60

Scheme 5



61 **62** (35%) **63** (17%) **64** (5%)

smoothly transformed **43** to the expected 3,3′-biindole **44** in quantitative yield.[32]

The third permutation of the double cyclization of substituted 1,3-butadienes is the synthesis of 2,3′-bi-1*H*-indoles from 1,3-bis(2-nitrophenyl)-1,3-butadienes (cyclization C, Figure 1). 2,3′-Bi-1*H*-indoles have previously been prepared, for example, via the Fischer indole synthesis,[33] acid mediated reaction of 3-bromoindole with indole,[34] and Lewis acid mediated dimerization to give 2,3-dihydro-2,3′-bisindole, followed by oxidation.[35] To date, only four natural products containing a 2,3′-bisindole have been isolated.[36] All four compounds are connected by an ethylene bridge between the 2 and 3′ carbons of the respective indoles.

The parent cyclization precursor **48** was prepared in moderate yield by a Wittig reaction of **45** with 2-(2-nitrophenyl)-2-propenal (**47**, Table 3).[37] Three additional 1,3-bis(2-nitrophenyl)-1,3-butadienes (**49**–**51**) were prepared in a similar fashion by reaction of Wittig salts **2**, **3**, and **46** with **47** under basic conditions. Low to moderate yields of products were isolated. Treatment of **48**–**51** with carbon monoxide, under the palladium catalyzed conditions described above, gave the anticipated 2,3′-bi-1*H*-indoles (**52**–**55**) in 61–72% yield.

The fourth variation of a double cyclization (cyclization D in Figure 1) is the cyclization of two adjacent 2-nitroaryl groups onto a single alkene with the anticipated formation of an indolo[3,2-*b*]indole. In the event, subjecting the known parent compound 1,2-bis(2-nitrophenyl)ethene (**56**)[38] to the palladium catalyzed reductive cyclization conditions for 56 h did not furnish the double cyclization product indolo[3,2-*b*]indole (**57**)[39] but gave two isomeric tetracyclic compounds, indolo-[1,2-*c*]quinazolin-6(5*H*)-one (**58**) and 5,11-dihydro-6*H*-indolo-[3,2-*c*]quinolin-6-one (**59**) (Scheme 4). The products were identified by 2D NMR experiments and by comparison of analytical data with reported values. It should be noted that Nishiyama et al. have reported a reductive cyclization, related to the transition metal catalyzed reactions. For example, treatment of **56** with a catalytic amount of selenium (40 mol %) under 30 atm of carbon monoxide at 100 °C gave **58** in 60% yield (Scheme 4).[40]

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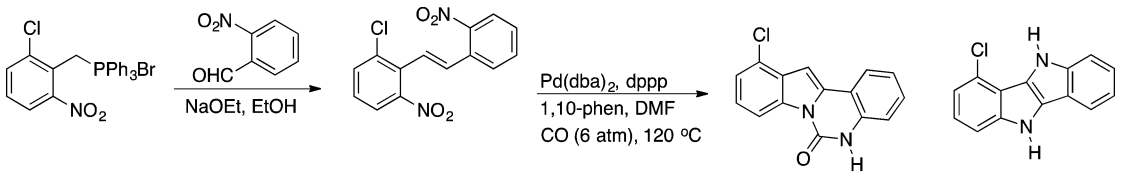
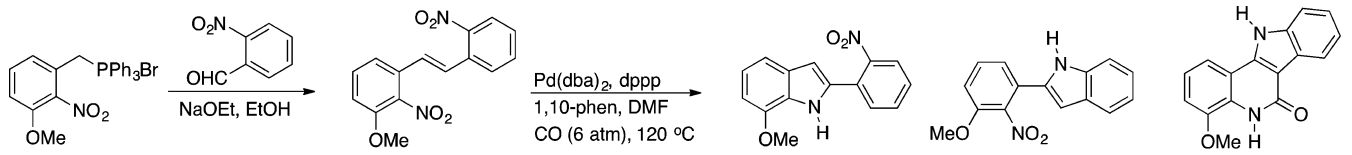
Scheme 6. Synthesis and Reductive Cyclization of 65



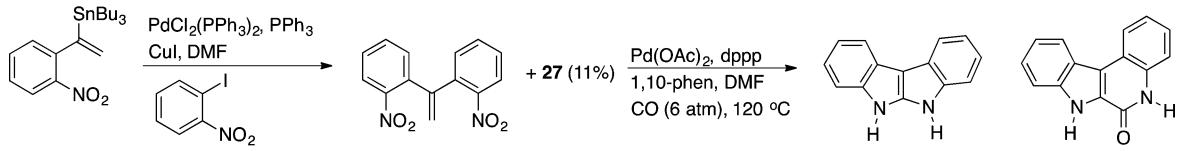
1 **65** (28%) **66** (69%) **67**(13%)

Scheme 7. Synthesis and Reductive Cyclization of 68



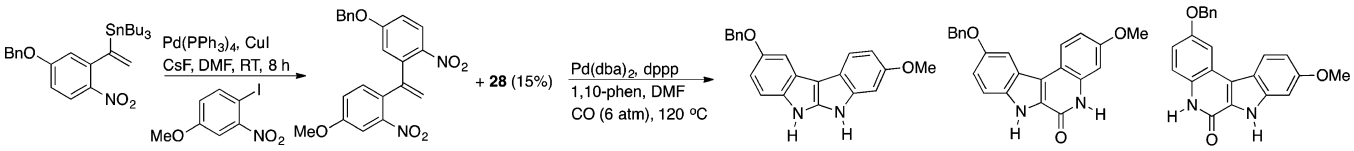
2 **68** (90%) **69** (10%) **70** (74%) **71** (6%)

Scheme 8. Formation of Indolo[2,3-*b*]indole (73) and Indolo[2,3-*c*]quinolinone (74)



22 **72** (62%) **73** (14%) **74**(58%)

Scheme 9. Formation of Indolo[2,3-*b*]indole 77 and Indolo[2,3-*c*]quinolinones 78 and 79



23 **75** **76** (69%) **77** (30%) **78** (38%) **79** (31%)

Carbon monoxide insertion to form an isocyanate (**60**) was suggested as a possible intermediate in the selenium catalyzed transformation, followed by reaction with the indole N−H (Scheme 4). Isocyanate **60** has previously been reported as an intermediate in a Curtius rearrangement of the corresponding acid, affording a 1:1 mixture of **58** and **59**.[41] Compound **59** was not observed in the selenium-catalyzed reactions. Products derived from insertion of carbon monoxide have been isolated in a few additional cases from transition metal catalyzed reductive cyclizations of nitro aromatic compounds.[42] For example, rhodium catalyzed reductive cyclization of **61** afforded in addition to indole **62** as the major product, quinolinone **63** and amine **64** (Scheme 5).[43]

In order to evaluate the palladium catalyzed double reductive cyclization of 1,2-bis(2-nitrophenyl)alkenes as a general methodology toward indolo[1,2-*c*]quinazolin-6(5*H*)-ones, two additional substrates **65** and **68** were prepared by Wittig reactions of **1** and **2** with 2-nitrobenzaldehyde (Schemes 6 and 7). Upon reductive cyclization of the chloro-substituted compound **65**, both an indolo[1,2-*c*]quinazolin-6(5*H*)-one (**66**) and an indolo[3,2-*b*]indole (**67**) were isolated (Scheme 6). The latter compound represents the first case of the formation of an indolo[3,2-*b*]indole from a transition metal catalyzed reductive cyclization, although the yield was very low. In contrast to **65**, the methoxy-substituted substrate **68** did not participate in a double cyclization as readily as **56** and **65**. In the event, two monocyclized products **69** and **70** were isolated in 10% and 74%, respectively, together with a minor amount of the indolo[3,2-*c*]quinolin-6-one **71** (Scheme 7). Indole **70** was presumed to be the immediate precursor to the tetracyclic compound **71**; however, only a miniscule amount of **71** (2%) was isolated from an attempted cyclization of **70** under identical reaction conditions. Although all of the starting material was consumed in the reaction, no other product could be identified.

Finally, a synthesis of indolo[2,3-*b*]indoles was envisioned starting from 1,1-bis(2-nitrophenyl)ethenes (cyclization E in Figure 1). Kosugi−Migita−Stille cross-coupling of 1-iodo-2-nitrobenzene with **22** afforded cyclization precursor **72** in good yield.[44] As observed in previous palladium catalyzed reactions involving stannane **22**, dimer **27** was also isolated as a minor product in 11% yield. Palladium catalyzed reductive cyclization of **72** gave the anticipated indolo[2,3-*b*]indole (**73**), although in a very low isolated yield together with indolo[2,3-*c*]quinolinone **74** as the major product (Scheme 8). Formation of the latter compound is perhaps not so surprising in light of the results discussed above using 1,2-bis(2-nitrophenyl)ethenes. It should be noted that Cadogan−Sundberg type cyclizations of 3-(2-

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nitrophenyl)indoles using PPh_3[45] or $P(OEt)_3$[46] to afford indolo[3,2-*b*]indoles have been reported.

The reaction sequence seen in Scheme 8 represents a very short route to indolo[2,3-*c*]quinolin-6-ones starting from a symmetrical substrate like **72**. A number of methodologies have been developed for the construction of the indoloquinolin-6-one skeleton. This includes cyclizations of *N*-arylindole-2-carboxamides utilizing a Heck reaction,[47] photochemical cyclizations of indole-2-carboxylic acid arylamides[48] and 3-(2-azidophenyl)-*N*-phenylacrylamides,[49] oxidative cyclizations of 3-arylindole-2-carboxamides,[50] and a platinum catalyzed reduction of ethyl 3-(2-nitrophenyl)-1*H*-indole-2-carboxylates.[51]

The unsymmetrically substituted substrate **76** containing a methoxy group meta to one of the nitro groups and a benzyloxy group para to the second nitro group was also prepared via a Kosugi−Migita−Stille reaction of **23** with 2-nitro-4-methoxy-1-iodobenzene (**75**, Scheme 9).

Compound **76** was subjected to the cyclization conditions, and three different products were obtained after chromatography, an indolo[2,3-*b*]indole **77** and two isomeric indolo[2,3-*c*]quinolin-6-ones **78** and **79** in an approximately 1:1:1 ratio. The structures of the isomeric tetracycles **78**−**79** were elucidated using 2D NMR experiments. Apparently, there is little preference for the initial (presumed) cyclization to form the indole skeleton prior to the second cyclization.

While the use of an unsymmetrical cyclization precursor probably will furnish two isomeric indolo[2,3-*c*]quinolin-6-ones, the present methodology may be of synthetic value employing symmetrical starting materials.

SUMMARY

Short synthetic routes to 2,2′-, 2,3′-, and 3,3′-biindoles have been developed clearly demonstrating the palladium catalyzed reductive cyclization as a potentially useful methodology toward these ring systems. On the basis of the results shown in Schemes 4 and 6−9 and from the selenium catalyzed reactions reported in the literature, it appears that general syntheses of indolo[3,2-*b*]indoles and indolo[2,3-*b*]indoles via a palladium catalyzed carbon monoxide mediated double reductive cyclization of 1,2-bis(2-nitrophenyl)ethenes or 1,1-bis(2-nitrophenyl)ethenes, respectively, are not feasible. Monocyclized products and products derived from carbon monoxide insertion are the major products seen in these reactions.

EXPERIMENTAL SECTION

General Procedures. All NMR spectra were recorded in $CDCl_3$ at 600 MHz (^{1}H NMR) and 150 MHz (^{13}C NMR, ^{1}H-broadband decoupled) at ambient temperature unless otherwise stated. The chemical shifts are expressed in δ values relative to Me_4Si (0.0 ppm, ^{1}H and ^{13}C) or $CDCl_3$ (77.0 ppm, ^{13}C) internal standards. HRMS data were obtained via ESI with an ion trap mass analyzer in positive ion mode unless otherwise stated.

THF was purified/dried via two consecutive columns composed of activated alumina and Q5 catalyst on a Glass Contours solvent purification system. Dichloromethane and toluene was purified/dried via two consecutive columns composed of activated alumina on a Glass Contours solvent purification system.

Chemicals prepared according to literature procedures have been footnoted first time used; all other reagents were obtained from commercial sources and used as received. All reactions were performed under a nitrogen atmosphere in oven-dried glassware unless otherwise stated. Solvents were removed from reaction mixtures and products on a rotary evaporator at water aspirator pressure unless otherwise stated.

[(6-Chloro-2-nitrophenyl)methyl]triphenylphosphonium Bromide (1). To a solution of 2-chloro-6-nitrobenzylbromide (3.03 g, 12.1 mmol) in toluene (36 mL) was added, in portions, triphenylphosphine (PPh_3, 3.49 g, 13.3 mmol). The resulting solution was stirred under a nitrogen atmosphere, at 100 °C, for 12 h. A precipitate started to form after 15 min. The mixture was cooled to ambient temperature, the precipitate was removed by filtration, the solid was washed with Et_2O, and the solvents were removed to afford **1** (6.21 g, 12.1 mmol, 100%) as a white solid. mp = 235−243 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.96 (d, J = 8.4 Hz, 1H), 7.89−7.85 (m, 4H), 7.73−7.66 (m, 12H), 7.63 (td, J = 7.8, 1.8 Hz, 1H), 5.34 (d, J = 14.4 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 149.7 (d, J^{CP} = 4.5 Hz), 136.4 (d, J^{CP} = 6.0 Hz), 135.4 (d, J^{CP} = 3.0 Hz), 135.1 (d, J^{CP} = 3.0 Hz), 133.8 (d, J^{CP} = 10.5 Hz), 131.3 (d, J^{CP} = 3.0 Hz), 130.0 (d, J^{CP} = 13.5 Hz), 124.9 (d, J^{CP} = 3.0 Hz), 123.5 (d, J^{CP} = 9.0 Hz), 117.9 (d, J^{CP} = 85.5 Hz), 25.9 (d, J^{CP} = 51.0 Hz); IR (ATR) 1533, 1434, 1355, 1107, 748 cm^{-1}; HRMS (ESI, negative ion mode) calcd for $C_{25}H_{20}BrClNO_2P$ (M^-) 511.0104, found 511.0133.

[(3-Methoxy-2-nitrophenyl)methyl]triphenylphosphonium Bromide (2). Treatment of 3-methoxy-2-nitrobenzylbromide (1.48 g, 6.05 mmol) with PPh_3 (1.74 g, 6.64 mmol) in toluene (15 mL) as described for **1** (100 °C, 12 h) gave, after workup, **2** (2.67 g, 5.26 mmol, 87%) as a white solid. mp = 213−215 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.92 (t, J = 7.8 Hz, 3H), 7.74 (dt, J = 7.8, 3.6 Hz, 6H), 7.63 (dd, J = 8.4, 7.2 Hz, 6H), 7.42 (t, J = 8.4 Hz, 1H), 7.35 (d, J = 9.0 Hz, 1H), 6.66 (dd, J = 8.4, 2.4 Hz, 1H), 5.10 (d, J = 15.0 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 151.4 (d, J^{CP} = 2.2 Hz), 140.9(d, J^{CP} = 6.9 Hz), 135.3 (d, J^{CP} = 3.4 Hz), 133.9 (d, J^{CP} = 10.2 Hz), 132.1 (d, J^{CP} = 3.4 Hz), 130.2 (d, J^{CP} = 12.6 Hz), 123.1 (d, J^{CP} = 4.6 Hz), 121.8 (d, J^{CP} = 7.9 Hz), 117.1 (d, J^{CP} = 84.6 Hz), 114.3 (d, J^{CP} = 2.2 Hz), 57.0, 25.3 (d, J^{CP} = 49.2 Hz); IR (ATR) 1536, 1433, 1281, 1108, 685 cm^{-1}; HRMS (ESI, negative ion mode) calcd for $C_{26}H_{23}BrNO_3P$ (M^-) 507.0599, found 507.0628.

[(4-Bromo-2-nitrophenyl)methyl]triphenylphosphonium Bromide (3). Treatment of 4-bromo-2-nitrobenzylbromide (208 mg, 0.705 mmol) with PPh_3 (203 mg, 0.774 mmol) in toluene (8 mL) as described for **1** (100 °C, 8 h) gave, after workup, **3** (393 mg, 0.705 mmol, 100%) as a white solid. mp = 242−244 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.24 (d, J = 2.0 Hz, 1H), 7.97−7.90 (m, 3H), 7.92(d, J = 1.6 Hz, 1H), 7.77−7.72 (m, 6H), 7.66−7.61 (m, 6H), 7.31 (dd, J = 8.0, 2.4 Hz, 1H), 5.42 (d, J = 15.2 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 148.8 (d, J^{CP} = 6.1 Hz), 137.3 (d, J^{CP} = 3.0 Hz), 135.3 (d, J^{CP} = 3.0 Hz), 133.9 (d, J^{CP} = 10.6 Hz), 130.3 (d, J^{CP} = 12.1 Hz), 128.4 (d, J^{CP} = 2.3 Hz), 123.1 (d, J^{CP} = 8.4 Hz), 122.6 (d, J^{CP} = 4.5 Hz), 117.4, 116.6, 26.4 (d, J^{CP} = 49.3 Hz); IR (ATR) 1521, 1367, 1346, 1284, 1066, 852 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{20}Br_2NO_2P$ (M − Br) 476.0415, found 476.0416.

3-(5-Bromo-2-nitrophenyl)-2-propenal (5) and *E,E*-5-(5-Bromo-2-nitrophenyl)-2,4-pentadienal (16). A mixture of 5-bromo-2-nitrobenzaldehyde (600 mg, 2.61 mmol), (formylmethyl)-triphenylphosphonium chloride (1.78 mg, 5.22 mmol), and DMAP (956 mg, 7.82 mmol) in $CHCl_3$ (36 mL) was stirred at ambient temperature for 4 h, followed by heating at reflux for 3 h. After cooling to ambient temperature, the solvent was removed under reduced pressure and the resulting crude product was purified by chromatography (hexane/EtOAc, 95:5) to afford, in order of elution, **5** (337 mg, 1.32 mmol, 51%) and **16** (153 mg, 0.542 mmol, 21%), both as pale yellow solids. Analytical data for **5**: mp = 135−137 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.78 (d, J = 7.2 Hz, 1H), 8.01 (d, J = 3.0 Hz, 1H), 7.99 (d, J = 9.6 Hz, 1H), 7.80 (d, J = 1.8 Hz, 1H), 7.73 (dd, J = 9.0, 1.8 Hz, 1H), 6.61 (dd, J = 15.5, 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.5, 146.5, 145.7, 133.9, 133.4, 132.0, 131.9, 128.8, 126.7; IR (ATR) 1675, 1521, 1345, 1098, 834 cm^{-1}; HRMS (ESI, negative ion mode) calcd for $C_9H_6BrNO_3$ (M^-) 254.9531, found 254.9530.

Analytical data for **16**: mp = 127−129 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.68 (d, J = 7.8 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 2.4 Hz, 1H), 7.62 (dd, J = 9.0, 2.4 Hz, 1H), 7.50 (d, J = 15.6 Hz, 1H), 7.30 (dd, J = 15.6, 10.8 Hz, 1H), 6.96 (dd, J = 15.6, 11.4 Hz, 1H), 6.36 (dd, J = 15.6, 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.2, 149.8, 146.6, 135.0, 134.1, 133.1, 132.5, 131.8, 131.4, 128.4, 126.6; IR (ATR) 3417, 1676, 1512, 1345, 1334, 1117, 983 cm^{-1}; HRMS (ESI,

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negative ion mode) calcd for $C_{11}H_8BrNO_3$ (M^-) 280.9688, found 280.9709.

***E,E*-1-(2-Chloro-6-nitrophenyl)-4-(2-nitrophenyl)-1,3-butadiene (7).** A solution of freshly prepared sodium ethoxide (NaOEt, 1.5 M in EtOH, 6 mL, 9.0 mmol) was added dropwise to a solution of **4** (389 mg, 2.20 mmol) and **1** (1.13 g, 2.20 mmol) in absolute EtOH (9 mL) at ambient temperature. The reaction mixture turned dark purple, slowly changing to red. After 36 h at ambient temperature, water (30 mL) was added, and the mixture was extracted with EtOAc (3 × 15 mL). The combined organic phases were dried ($MgSO_4$) and filtered, and the solvents were removed under reduced pressure. The residue was purified by chromatography (hexane/EtOAc, 9:1, then 8:2) to give **7** (399 mg, 1.21 mmol, 55%) as an orange solid. mp = 153−155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 8.0, 0.8 Hz, 1H), 7.90 (dd, J = 8.4, 1.2 Hz, 1H), 7.82 (dd, J = 8.4, 1.2 Hz, 1H), 7.73−7.63 (m, 3H), 7.60 (td, J = 7.2, 0.4 Hz, 1H), 7.51 (td, J = 8.0, 0.8 Hz, 1H), 7.46−7.32 (m, 6H), 7.19 (d, J = 15.2 Hz, 1H), 7.17 (d, J = 15.2 Hz, 1H), 6.93 (dd, J = 13.4, 10.0 Hz, 1H), 6.83 (d, J = 15.6 Hz, 1H), 6.73−6.59 (m, 3H), 6.40 (dd, J = 15.2, 10.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.7, 150.3, 147.9, 147.8, 136.6, 135.7, 135.1, 133.7, 133.6, 133.2, 133.0, 133.0, 132.9, 132.2, 132.0, 130.8, 130.2, 130.2, 129.7, 128.9, 128.4, 128.4, 128.3, 128.3, 127.9, 127.7, 125.8, 124.7, 124.6, 124.3, 122.5, 122.4; IR (ATR) 1515, 1343, 986, 751, 725 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{12}ClN_2O_4$ ($M + H^+$) 331.0486, found 331.0480.

***EE/ZE*-1-(3-Methoxy-2-nitrophenyl)-4-(2-nitrophenyl)-1,3-butadiene (8).** Treatment of a solution of **4** (300 mg, 1.69 mmol) and **2** (861 mg, 1.69 mmol) in EtOH (18 mL) with NaOEt (1.7 M, 11 mL, 18.7 mmol), as described for **7** (24 h), gave, after workup and chromatography (hexane/EtOAc, 8:2, then 7:3), **8** (354 mg, 1.08 mmol, 64%, *EE*/*ZE* = 1:1) as an orange solid. mp = 130−135 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.97−7.95 (m, 3H), 7.76 (dd, J = 7.9, 1.4 Hz, 1H), 7.71 (dd, J = 7.8, 1.3 Hz, 1H), 7.68 (dd, J = 7.9, 1.3 Hz, 1H), 7.59 (t, J = 8.3 Hz, 1H), 7.56−7.51 (m, 4H), 7.41−7.30 (m, 3H), 7.25 (dd, J = 8.3, 0.8 Hz, 1H), 7.17 (d, J = 15.2 Hz, 1H), 7.16 (d, J = 7.9 Hz, 1H), 7.13 (d, J = 15.2 Hz, 1H), 7.03 (dd, J = 15.2, 11.5 Hz, 1H), 6.73 (t, J = 11.4 Hz, 1H), 6.59 (d, J = 15.5 Hz, 1H), 6.45 (d, J = 11.3 Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, major and minor) δ 150.3, 150.2, 147.9, 147.8, 139.9, 139.7, 134.4, 133.9, 133.6, 133.5, 133.2, 131.6, 131.3, 130.9, 130.9, 130.8, 129.3, 129.1, 129.1, 128.9, 128.7, 128.3, 128.2, 127.7, 125.5, 124.4, 124.4, 124.1, 121.9, 117.4, 112.8, 112.5, 56.7, 56.7; IR (ATR) 1519, 1369, 1343, 1285, 1063 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{15}N_2O_5$ ($M + H^+$) 327.0981, found 327.0976.

***EE/EZ*-1-(4-Bromo-2-nitrophenyl)-4-(2-nitrophenyl)-1,3-butadiene (9).** Treatment of a solution of **4** (51 mg, 0.29 mmol) and **3** (155 mg, 0.278 mmol) in EtOH (7 mL) with NaOEt (1.7 M, 7 mL, 11.9 mmol), as described for **7** (36 h), gave, after workup and chromatography (hexane/EtOAc, 9:1), **9** (78.4 mg, 0.209 mmol, 73%, *EE*/*EZ* = 1:2) as an orange solid. NMR data from the *EE*/*EZ* = 1:2 mixture of **9**: mp = 141−142 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.32 (d, J = 2.1 Hz, 1H), 8.19 (d, J = 2.1 Hz, 0.5H), 7.99−7.94 (m, 3H), 7.91 (dd, J = 8.6, 2.0 Hz, 0.5H), 7.78 (dd, J = 8.0, 1.3 Hz, 1H), 7.72 (t, J = 6.7 Hz, 0.5H), 7.65 (dd, J = 7.4, 0.7 Hz, 1H), 7.54−7.50 (m, 3H), 7.38 (dd, J = 15.1, 10.5 Hz, 0.5H), 7.31 (dd, J = 14.9, 10.6 Hz, 0.5H), 7.17−7.14 (m, 1.5H), 7.05−6.98 (m, 1.5H), 6.79 (d, J = 11.4 Hz, 1H), 7.73 (t, J = 11.2 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 148.3, 148.2, 147.9, 147.8, 136.3, 135.8, 134.6, 134.0, 133.7, 133.3, 133.2, 131.8, 130.9, 130.7, 130.4, 130.2, 129.3, 129.0, 128.9, 128.9, 128.5, 128.2, 128.2, 127.7, 127.2, 127.1, 126.9, 122.4, 124.3, 120.7, 120.6;[52] IR (ATR) 3027, 1520, 1347, 1217, 748 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{12}BrN_2O_4$ ($M + H^+$) 374.9980, found 374.9975.

***EZ/EE*-1-(4-Bromo-2-nitro-nitrophenyl)-4-(5-bromo-2-nitrophenyl)-1,3-butadiene (10).** Treatment of a solution of **5** (320 mg, 1.25 mmol) with **3** (696 mg, 1.25 mmol) with NaOEt (2.0 M in EtOH, 2.81 mL, 5.62 mmol) in EtOH (16 mL), as described for **7** (24 h), gave, after workup and chromatography (hexane/EtOAc, 9:1), **10** (424 mg, 0.934 mmol, 75%, *EZ*/*EE* = 7:1) as an orange solid. mp = 159−162 °C; ^{1}H NMR data from the *EZ*/*EE* = 7:1 mixture of **10**, major isomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (d, J = 1.8 Hz, 1H), 7.83 (d, J = 8.6 Hz, 1H), 7.78 (dd, J = 8.3, 1.8 Hz, 1H), 7.60 (d, J = 2.0 Hz, 1H), 7.51 (dd, J = 8.8, 1.9 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.22 (d, J = 15.3 Hz, 1H), 6.90 (d, J = 11.2 Hz, 1H), 6.78 (dd, J = 15.2, 11.2 Hz, 1H), 6.64 (t, J = 11.4 Hz, 1H); partial ^{1}H NMR data for minor isomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, J = 1.6 Hz, 1H), 7.87 (d, J = 2.5 Hz, 1H), 7.73 (dd, J = 9.1, 1.8 Hz, 1H), 7.62 (d, J = 8.3 Hz. 1H), 7.54 (dd, J = 8.6, 1.7 Hz, 1H), 7.02−6.96 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 148.1, 148.0, 146.4, 146.3, 136.3, 136.2, 134.4, 134.2, 134.0, 133.7, 133.6, 131.5, 131.4, 131.0, 130.9, 130.8, 130.0, 129.5, 129.3, 129.2, 128.8, 128.6, 128.1, 128.1, 128.0, 127.8, 126.5, 126.4, 126.4, 126.3, 121.9, 121.7; IR (ATR) 3381, 1589, 1517, 1335, 748 cm^{-1}; HRMS (ESI, negative ion mode) calcd for $C_{16}H_{10}Br_2N_2O_4$ (M^-) 451.9007, found 451.9018.

2,2′-Bi-1*H*-indole (11). 1,4-Di(2-nitrophenyl)-1,3-butadiene (**6**)[53] (51 mg, 0.17 mmol), $Pd(dba)_2$ (6 mg, 0.01 mmol), dppp (4 mg, 0.01 mmol), and phen (5 mg, 0.02 mmol) were dissolved in anhydrous DMF (1 mL) in a threaded ACE glass pressure tube. The tube was fitted with a pressure head, and the solution was saturated with carbon monoxide (four cycles of 6 atm of CO). The reaction mixture was heated at 120 °C under CO (6 atm) until all starting material was consumed (60 h), as judged by TLC (hexanes/EtOAc, 9:1). Brine (10 mL) was added, and the red-brown solution was extracted with EtOAc (3 × 20 mL). The combined organic phases were dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by chromatography (hexane/EtOAc, 19:1) to afford **11** (29 mg, 0.13 mmol, 73%) as a white solid. mp 310−313 °C (lit.[54] mp 310−312 °C).

4-Chloro-2,2′-bi-1*H*-indole (12). Treatment of a solution of **7** (297 mg, 0.898 mmol) in DMF (2 mL) with $Pd(dba)_2$ (36 mg, 0.063 mmol), dppp (26 mg, 0.063 mmol), and phen (23 mg, 0.126 mmol), as described for **11** (6 atm CO, 120 °C, 40 h), gave, after workup and chromatography (hexane/EtOAc, 9:1), **12** (226 mg, 0.846 mmol, 94%) as a white solid. mp = 186−187 °C; ^{1}H NMR (400 MHz, Acetone-d_6) δ 11.03 (br s, 1H), 10.81 (br, s, 1H), 7.60 (dd, J = 7.6, 0.8 Hz, 1H), 7.46 (dd, J = 8.0, 0.8 Hz, 1H), 7.39 (ddd, J = 7.2, 2.4, 0.8 Hz, 1H), 7.18 (td, J = 7.6, 0.4 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.14−7.05 (m, 4H), 7.01 (dd, J = 2.4, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 138.9, 138.3, 133.3, 131.5, 129.8, 128.6, 125.7, 123.5, 123.2, 121.2, 120.7, 120.1, 111.9, 110.8, 100.2, 97.6; IR (ATR) 3409, 3063, 1334, 1185, 747 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{12}ClN_2$ ($M + H^+$) 267.0689, found 267.0686.

7-Methoxy-2,2′-bi-1*H*-indole (13). Treatment of a solution of **8** (86 mg, 0.26 mmol) in DMF (2 mL) with $Pd(dba)_2$ (11 mg, 0.018 mmol), dppp (8 mg, 0.018 mmol), and phen (23 mg, 0.126 mmol), as described for **11** (CO 6 atm, 120 °C, 72 h), gave, after workup and chromatography (hexane/EtOAc, 9:1), **13** (64 mg, 0.24 mmol, 93%) as a white solid. mp = 228−229 °C; ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.68, (br, s, 1H), 10.58 (br, s, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.42 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 7.13 (td, J = 6.8, 1.2 Hz, 1H), 7.11 (d, J = 1.2 Hz, 1H), 7.04 (td, J = 6.8, 1.2 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.94 (d, J = 2.4 Hz, 1H), 6.68 (d, J = 7.6 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 147.2, 138.1, 132.3, 132.1, 131.3, 130.0, 128.3, 122.7, 121.2, 121.0, 120.5, 113.8, 111.8, 103.7, 100.2, 100.0, 55.6; IR (ATR) 3346, 1580, 1344, 1252, 1094, 729 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{15}N_2O$ ($M + H^+$) 263.1184, found 263.1184.

6-Bromo-2,2′-bi-1*H*-indole (14). Treatment of a solution of **9** (72 mg, 0.19 mmol) in DMF (1.5 mL) with $Pd(dba)_2$ (8 mg, 0.013 mmol), dppp (6 mg, 0.013 mmol), and phen (5 mg, 0.027 mmol), as described for **11** (CO 6 atm, 120 °C, 49 h), gave, after workup and chromatography (hexane/EtOAc, 1:9), **14** (44 mg, 0.142 mmol, 74%) as a white solid. mp = 251−252 °C; ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.93 (s, 1H), 10.79 (s, 1H), 7.58 (s, 1H), 7.57 (d, J = 8.8 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.41 (dd, J = 7.6, 0.8 Hz, 1H), 7.17 (dd, J = 8.8, 2.0 Hz, 1H), 7.14 (dd, J = 8.4, 1.2 Hz, 1H), 7.04 (t with further fine splittings, J = 7.2 Hz, 1H), 6.96 (br s, 2H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 138.9, 138.2, 133.4, 131.7, 129.8, 129.0, 123.6, 123.1, 122.5, 121.1, 120.6, 115.6, 114.5, 111.9, 100.0, 99.5; IR (ATR) 3425, 1386, 1338, 1218, 741 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{12}BrN_2$ ($M + H^+$) 311.0183, found 311.0176.

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5,6′-Dibromo-2,2′-bi-1*H*-indole (15). Treatment of a solution of **10** (100 mg, 0.220 mmol) in the presence of $Pd(dba)_2$ (8.9 mg, 0.015 mmol), dppp (6.4 mg, 0.015 mmol), and phen (5.6 mg, 0.031 mmol) in DMF (1.5 mL) with CO (6 atm), as described for **11** (120 °C, 58 h), gave, after workup and chromatography (hexane/EtOAc, 9:1), **15** (61.3 mg, 0.157 mmol, 71%) as a white solid. mp = 275−276 °C; ^{1}H NMR (600 MHz, $CDCl_3$/DMSO-d_6) δ 11.73 (br, s, 1H), 11.69 (br, s, 1H), 7.74 (s, 1H), 7.53 (s, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.34 (d, J = 9.0 Hz, 1H), 7.19 (dd, J = 8.4, 1.8 Hz, 1H), 7.12 (dd, J = 8.4, 1.8 Hz, 1H), 6.94 (s, 1H), 6.90 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$/DMSO-d_6) δ 137.8, 135.6, 132.2, 131.6, 130.2, 127.3, 124.1, 122.3, 122.1, 121.6, 114.4, 113.5, 112.8, 111.9, 99.0, 98.3; IR (ATR) 3416, 1599, 1437, 1332, 802 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{11}Br_2N_2$ ($M + H^+$) 388.9289, found 388.9286.

Tributyl(1-(2-nitrophenyl)ethenyl)tin (22). Tributyltin hydride (742 mg, 2.55 mmol) was added dropwise, at ambient temperature, to a solution of $PdCl_2(PPh_3)_2$ (119 mg, 0.170 mmol) and 1-ethynyl-2-nitrobenzene (**17**)[55] (250 mg, 1.70 mmol) in THF (5 mL). The dark brown reaction mixture was stirred for 34 h, followed by removal of the solvent under reduced pressure. Purification by chromatography (hexane/EtOAc, 95:5) gave **22** (707 mg, 1.61 mmol, 95%) as a pale green oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (dd, J = 8.4, 1.2 Hz, 1H), 7.52 (dt, J = 7.8, 1.2 Hz, 1H), 7.31 (dt, J = 7.2, 1.2 Hz, 1H), 7.11 (dd, J = 7.8, 1.2 Hz, 1H), 5.74 (d, J = 3.0 Hz, 1H), 5.45 (d, J = 2.4 Hz, 1H), 1.43−1.48 (m, 6H), 1.26 (sext, J = 7.8 Hz, 6H), 0.91−0.94 (m, 6H), 0.86 (t, J = 7.2 Hz, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.6, 146.0, 144.3, 133.2, 129.7, 126.3, 126.0, 124.3, 28.8, 27.3, 13.6, 10.9; IR (ATR) 2922, 1518, 1339, 1038 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{34}NO_2{}^{120}Sn$ ($M + H^+$) 440.1606, found 440.1607.

Tributyl(1-(5-benzyloxy-2-nitrophenyl)ethenyl)tin (23). Treatment of **18**[16] (1.30 g, 5.15 mmol) in dry THF (15 mL) with tributyltin hydride (2.30 g, 7.90 mmol) in the presence of $PdCl_2(PPh_3)_2$ (362 mg, 0.515 mmol), as described for **22** (24 h), gave, after solvent removal and chromatography (hexane/EtOAc, 9:1), **23** (2.70 g, 4.96 mmol, 96%) as a brown viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 9.2 Hz, 1H), 7.45−7.33 (m, 5H), 6.86 (dd, J = 9.2, 2.4 Hz, 1H), 6.63 (d, J = 2.0 Hz, 1H), 5.72 (d, J = 2.4 Hz, 1H), 5.41 (d, J = 2.0 Hz, 1H), 5.14 (s, 2H), 1.56−1.37 (m, 6H), 1.27 (sext, J = 7.2 Hz, 6H), 0.95−0.84 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 155.7, 147.6, 139.1, 135.6, 128.7, 128.4, 127.5, 127.1, 124.8, 114.6, 112.7,70.5, 28.8, 27.3, 13.6, 11.0; IR (ATR) 2954, 2922, 1567, 1329, 1283, 1243, 1228, 694 cm^{-1}; HRMS calcd for $C_{27}H_{40}NO_3{}^{120}Sn$ ($M + H^+$) 546.2030, found 546.2030.

Tributyl(1-(4-chloro-2-nitrophenyl)ethenyl)tin (24). Treatment of a solution of **19**[56] (215 mg, 1.18 mmol) in THF (3 mL) with tributyltin hydride (577 mg, 1.78 mmol) in the presence of $PdCl_2(PPh_3)_2$ (83.1 mg, 0.118 mmol), as described for **22** (24 h), gave, after solvent removal and chromatography (hexane/EtOAc, 19:1), **24** (537 mg, 1.13 mmol, 96%) as a brown viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 2.0 Hz, 1H), 7.48 (dd, J = 8.4, 2.4 Hz, 1H), 7.05 (d, J = 8.0, Hz, 1H), 5.73 (d, J = 2.4 Hz, 1H), 5.46 (d, J = 2.4 Hz, 1H), 1.51−1.43 (m, 6H), 1.30 (sext, J = 8.0 Hz, 6H), 0.99−0.82 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 146.1, 142.8, 133.2, 131.8, 130.8, 126.8, 124.2, 28.8, 27.2, 13.6, 10.9; IR (ATR) 2954, 2922, 1567, 1329, 1283, 1243, 1228, 694 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{33}ClNO_2{}^{120}Sn$ ($M + H^+$) 474.1222, found 474.1225.

Tributyl(1-(4-carbomethoxy-2-nitrophenyl)ethenyl)tin (25). Treatment of a solution of **20**[57] (100 mg, 0.487 mmol) in THF (2 mL) with tributyltin hydride (213 mg, 0.731 mmol) in the presence of $PdCl_2(PPh_3)_2$ (34 mg, 0.049 mmol), as described for **22** (35 h), gave, after solvent removal and chromatography (hexane/EtOAc, 19:1), **25** (189 mg, 0.380 mmol, 78%) as a brown viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 1.6 Hz, 1H), 8.15 (dd, J = 7.6, 1.6 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 5.75 (d, J = 2.8 Hz, 1H), 5.48 (d, J = 2.8 Hz, 1H), 3.96 (s, 3H), 1.51−1.43 (m, 6H), 1.25 (sext, J = 7.2 Hz, 6H), 0.94−0.90 (m, 6H), 0.85 (t, J = 6.8 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 154.1, 148.7, 145.8, 133.5, 129.9, 128.6, 126.4, 125.6, 52.4, 28.7, 27.2, 13.6, 11.0; IR (ATR) 2954, 2922, 1567, 1329, 1283, 1243, 1228, 694 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{36}NO_4{}^{120}Sn$ ($M + H^+$) 498.1666, found 498.1670.

Tributyl(1-(4-methoxy-2-nitrophenyl)ethenyl)tin (26). Treatment of a solution of **21**[58] (1.10 g, 6.21 mmol) in THF (130 mL) with tributyltin hydride (2.71 g, 9.31 mmol) in the presence of $PdCl_2(PPh_3)_2$ (436 mg, 0.621 mmol), as described for **22** (32 h), gave, after solvent removal and chromatography (hexane/EtOAc, 9:1), **26** (2.62 g, 5.58 mmol, 90%) as a brown viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 2.8 Hz, 1H), 7.10 (dd, J = 8.4, 2.8 Hz, 1H), 7.01 (d, J = 8.0,Hz, 1H), 5.72 (d, J = 2.4 Hz, 1H), 5.42 (d, J = 2.8 Hz, 1H), 3.86 (s, 3H), 1.51−1.32 (m, 6H), 1.26 (sext, J = 7.6 Hz,, 6H), 0.98−0.82 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 154.3, 146.1, 136.8, 130.7, 126.1, 120.6, 108.2, 55.8, 28.8, 27.3, 13.6, 10.8; IR (ATR) 2924, 1521, 1341, 1303, 1034 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{26}NO_3{}^{120}Sn$ ($M + H^+ - C_4H_8$) 412.0935, found 412.0931.

2,3-Di(2-nitrophenyl)-1,3-butadiene (27).[16] To a solution of **22** (348 mg, 0.794 mmol) in DMF (10 mL) were added $PdCl_2(PPh_3)_2$ (28 mg, 0.040 mmol), PPh_3 (21 mg, 0.080 mmol), and CuI (113 mg, 0.595 mmol). The reaction was stirred at ambient temperature for 36 h. Et_2O (30 mL) was added, and the organic phase was washed with NH_4OH (10%, aqueous, 3 × 30 mL), H_2O (30 mL), and brine (30 mL). The organic phase was dried ($MgSO_4$) and filtered, and the solvents were removed under reduced pressure. The resulting solid was purified by chromatography (hexane/EtOAc, 95:5) to afford **27** (78 mg, 0.263 mmol, 67%) as a dark yellow solid. mp = 122−124 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (dd, J = 8.4, 1.2 Hz, 2H), 7.66 (dt, J = 7.8, 1.2 Hz, 2H), 7.61 (dd, J = 7.8, 1.2 Hz, 2H), 7.52 (dt, J = 7.2, 1.2 Hz, 2H), 5.15 (s, 2H), 4.92 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.0, 145.2, 135.3, 132.9, 132.4, 128.7, 124.0, 118.3; IR (ATR) 1514, 1332, 911, 790, 749, 697 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{12}N_2NaO_4$ ($M + Na^+$) 319.0695, found 319.0690.

2,3-Di(5-benzyloxy-2-nitrophenyl)-1,3-butadiene (28). Treatment of **23** (103 mg, 0.189 mmol) in DMF (1.5 mL) with $Pd(dba)_2$ (7.2 mg, 0.013 mmol), PPh_3 (14 mg, 0.053 mmol), and CuI (36 mg, 0.189 mmol), as described for **27** (28 h), gave, after workup and chromatography[59] (hexane/EtOAc, 9:1), **28** (37.6 mg, 0.074 mmol, 78%) as a white solid. mp = 158−160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 9.2, Hz, 1H), 7.48−7.36 (m, 5H), 7.17 (d, J = 2.8 Hz, 1H), 7.02 (dd, J = 9.6, 3.2 Hz, 1H), 5.19 (s, 2H), 5.08 (s, 1H), 4.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 145.6, 141.7, 138.3, 135.5, 128.7, 128.4, 127.8, 126.8, 117.5, 117.1, 114.9, 70.7; IR (ATR) 1573, 1513, 1343, 1230, 1007 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{25}N_2O_6$ ($M + H^+$) 509.1713, found 509.1715.

2,3-Di(4-chloro-2-nitrophenyl)-1,3-butadiene (29). To a slurry of copper chloride (210 mg, 2.12 mmol) in DMF (2 mL) in a round-bottom flask covered with aluminum foil to exclude light was added a solution of **24** (400 mg, 0.846 mmol) in DMF (2 mL). The resulting mixture was stirred at ambient temperature for 1 h. A saturated solution of NH_4Cl (aqueous, 4 mL) was added, and the mixture was allowed to stir for an additional hour. The mixture was diluted with EtOAc (30 mL) and was washed with H_2O (3 × 30 mL) and brine (20 mL). The organic phase was dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure. The residue was purified by chromatography[59] (hexane/EtOAc, 9:1), affording **29** (124 mg, 0.340 mmol, 80%) as a white solid. mp = 182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 2.0, Hz, 1H), 7.64 (dd, J = 8.0, 1.6 Hz 1H), 7.54 (d, J = 8.4 Hz, 1H), 5.15 (s, 1H), 4.92 (s, 1H); ^{13} C NMR (100 MHz, DMSO-d_6) δ 149.2, 143.4, 133.5, 133.3, 133.2, 132.6, 124.1, 119.4; IR (ATR) 3086, 1523, 1344, 914, 700 cm^{-1}; HRMS (ESI, negative ion mode) calcd for $C_{16}H_{10}Cl_2N_2O_4$ (M^-) 364.0018, found 364.0048.

2,3-Di(4-carbomethoxy-2-nitrophenyl)-1,3-butadiene (30). Treatment of **25** (400 mg, 0.806 mmol) with CuCl (207 mg, 2.10 mmol) in DMF (2 mL), as described for **29** (3 h), gave, after workup and chromatography[59] (hexane/EtOAc, 9:1), **30** (306 mg, 0.742 mmol, 92%) as a white solid. mp = 187−188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 1.2, Hz, 1H), 8.29 (dd, J = 7.6, 1.2 Hz 1H), 7.68 (d, J = 8.0 Hz, 1H), 5.18 (s, 1H), 5.20 (s, 2H), 4.92 (s, 1H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 148.9, 144.2, 139.0, 133.5, 132.6, 131.2, 125.3, 118.9, 52.8; IR (ATR) 1721, 1532, 1358, 1288, 1219 cm^{-1}; HRMS (ESI, negative ion mode) calcd for $C_{20}H_{16}N_2O_8$ (M^-) 412.0907, found 412.0937.

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2,3-Di(4-methoxy-2-nitrophenyl)-1,3-butadiene (31). Treatment of **26** (100 mg, 0.214 mmol) in the presence of CuCl (55 mg, 0.56 mmol), in DMF (1.5 mL), as described for **29** (2 h), gave, after workup and chromatography[59] (hexane/EtOAc, 9:1), **31** (37.1 mg, 0.104 mmol, 98%) as a white solid. mp = 163.5−164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 9.2, Hz, 1H), 7.47 (d, J = 2.4, Hz 1H), 7.17 (dd, J = 8.8 2.8 Hz, 1H), 5.09 (s, 1H), 4.90 (s, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 149.5, 145.3, 133.2, 127.6, 119.3, 118.0, 108.8, 55.9; IR (ATR) 1521, 1340, 1308, 1278, 1028 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{17}N_2O_6$ (M + H$^+$) 357.1087, found 357.1081.

3,3′-Bi-1*H*-indole (32).[60] Treatment of a solution of **27** (93.0 mg, 0.314 mmol) in the presence of $Pd(dba)_2$ (18.1 mg, 0.031 mmol), dppp (13.0 mg, 0.031 mmol), and phen (11.4 mg, 0.063 mmol) in DMF (1.5 mL) with CO (6 atm), as described for **11** (120 °C, 36 h), gave, after chromatography (hexane/EtOAc, 7:3), **32** (65.1 mg, 0.280 mmol, 89%) as a white solid. All data in accordance with previously reported values.

5,5′-Dibenzyloxy-3,3′-bi-1*H*-indole (33). Treatment of a solution of **28** (100 mg, 0.197 mmol) in the presence of $Pd(dba)_2$ (9 mg, 0.016 mmol), dppp (6 mg, 0.016 mmol), and phen (6 mg, 0.031 mmol) in DMF (2 mL) with CO (6 atm), as described for **11** (72 h), gave, after workup and chromatography (hexane/EtOAc; 7:3), **33** (76.3 mg, 0.172 mmol, 87%) as a white solid. mp = 125−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (br, s, 1H), 7.46 (d, J = 6.8, Hz, 2H), 7.39−7.31 (m, 6H), 7.02 (dd, J = 8.8, 2.4 Hz, 1H), 5.07 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 137.6, 131.6, 128.4, 127.7, 127.6, 127.3, 122.4, 113.2, 111.9, 110.7, 103.6, 71.0; IR (ATR) 3406, 1452, 1186, 1151, 794 cm^{-1}; HRMS (ESI, negative mode) calcd for $C_{30}H_{24}N_2O_2$ (M$^-$) 444.1838, found 444.1834.

6,6′-Dichloro-3,3′-bi-1*H*-indole (34). Treatment of a solution of **29** (23 mg, 0.064 mmol) in the presence of $Pd(dba)_2$ (4 mg, 0.006 mmol), dppp (4 mg, 0.006 mmol), and phen (2 mg, 0.013 mmol) in DMF (1.5 mL) with CO (6 atm), as described for **11** (72 h), gave, after workup and chromatography (hexane/EtOAc, 7:3), **34** (190 mg, 0.063 mmol, 100%) as a white solid. mp = 225−226 °C; ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.52 (s, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 2.4 Hz, 1H), 7.53 (d, J = 2.0 Hz, 1H), 7.09 (dd, J = 8.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 138.1, 127.9, 126.3, 123.9, 121.7, 120.4, 112.2, 111.1; IR (ATR) 3411, 1448, 1376, 1227, 914, 802 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{11}Cl_2N_2$ (M + H$^+$) 301.0299, found 301.0292.

6,6′-Carbomethoxy-3,3′-bi-1*H*-indole (35). Treatment of a solution of **30** (100 mg, 0.243 mmol) in the presence of $Pd(dba)_2$ (10 mg, 0.017 mmol), dppp (7 mg, 0.017 mmol), and phen (6 mg, 0.034 mmol) in DMF (2 mL) with CO (6 atm), as described for **11** (44 h), gave, after workup and chromatography (hexane/EtOAc, 1:1), **35** (84.3 mg, 0.242 mmol, 100%) as a white solid. mp = 300−301 °C; ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ 11.67 (br, s, 1H), 8.13 (s with further fine splittings, 1H), 7.96 (d, J = 2.4 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.69 (dd, J = 8.4, 1.6 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6) δ 167.1, 135.5, 129.2, 125.7, 122.3, 119.5, 118.9, 113.6, 109.5, 51.4; IR (ATR) 3305, 1689, 1436, 1319, 1227 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{17}N_2O_4$ (M + H$^+$) 349.1188, found 349.1182.

6,6′-Dimethoxy-3,3′-bi-1*H*-indole (36). Treatment of a solution of **31** (421 mg, 1.18 mmol) in the presence of $Pd(dba)_2$ (47 mg, 0.083 mmol), dppp (34 mg, 0.083 mmol), and phen (30 mg, 0.17 mmol) in DMF (2.5 mL) with CO (6 atm), as described for **11** (30 h), gave, after workup and chromatography (hexane/EtOAc, 1:1), **36** (221 mg, 0.757 mmol, 64%) as a white solid. mp = 282−284 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.90 (s, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.46 (d, J = 2.0 Hz, 1H), 6.92 (d, J = 2.4 Hz, 1H), 6.70 (dd, J = 8.4, 1.6 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.5, 137.1, 120.3, 120.2, 120.1, 109.8, 108.9, 94.5, 55.1; IR (ATR) 3379, 1626, 1298, 1155, 1026 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{17}N_2O_2$ (M + H$^+$) 293.1290, found 293.1284.

Tributyl(1-(3-nitro-2-pyridyl)ethenyl)tin (38). Treatment of a solution of **37**[61] (100 mg, 0.675 mmol) in THF (2 mL) with tributyltin hydride (295 mg, 1.01 mmol) in the presence of $PdCl_2(PPh_3)_2$ (47 mg, 0.068 mmol), as described for **22** (36 h), gave, after solvent removal and chromatography (hexane/EtOAc, 9:1), **38** (181 mg, 0.412 mmol, 61%) as a brown viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, J = 4.8, 1.6 Hz, 1H), 8.10 (dd, J = 8.4, 1.6 Hz, 1H), 7.24 (dd, J = 8.0, 4.4 Hz, 1H), 5.95 (d, J = 2.8 Hz, 1H), 5.64 (d, J = 2.4 Hz, 1H), 1.49−1.43 (m, 6H), 1.30−125 (m, 6H), 1.00−0.83 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 153.4, 152.0, 143.8, 131.8, 129.1, 120.7, 28.7, 27.2, 13.6, 10.9; (ATR) 2956, 2924, 1526, 1352, 808 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{33}N_2O_2{}^{120}$Sn (M + H$^+$) 441.1564, found 441.1558.

2,3-Di(3-nitro-2-pyridyl)-1,3-butadiene (39). Treatment of **38** (500 mg, 1.14 mmol) with CuCl (282 mg, 2.85 mmol) in DMF (3 mL), as described for **29** (5 h), gave, after workup and chromatography[59] (hexane/EtOAc, 1:1), **39** (91.4 mg, 0.306 mmol, 54%) as a white solid. mp = 198−199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (dd, J = 4.8, 1.6 Hz, 1H), 8.22 (dd, J = 8.4, 1.6 Hz 1H), 7.48 (dd, J = 8.4, 4.8 Hz, 1H), 5.40 (s, 1H), 5.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 152.4, 146.4, 143.6, 132.0, 123.2, 120.0; IR (ATR) 3019, 1522, 1361, 1217, 932 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{11}N_4O_4$ (M + H$^+$) 299.0780, found 299.0774.

3,3′-Bi-1*H*-pyrrolo[3,2-*b*]pyridine (40). Treatment of a solution of **39** (90 mg, 0.302 mmol) in the presence of $Pd(dba)_2$ (12 mg, 0.021 mmol), dppp (9 mg, 0.021 mmol), and phen (8 mg, 0.042 mmol) in DMF (2 mL) with CO (6 atm), as described for **11** (36 h), gave, after workup and chromatography (EtOAc), **40** (52.3 mg, 0.223 mmol, 74%) as a white solid. mp = 309−310 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.26 (s, 1H), 8.63 (d, J = 2.4 Hz, 1H), 8.44 (dd, J = 4.8, 1.6 Hz, 1H), 7.81 (dd, J = 8.0, 1.2 Hz, 1H), 7.16 (dd, J = 8.4, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 143.7, 142.1, 128.6, 125.6, 118.5, 116.3, 108 0.9; IR (ATR) 3088, 3019, 1522, 1361, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{11}N_4$ (M + H$^+$) 235.0984, found 235.0978.

2-(1-Bromo-1-ethenyl)-5-methoxy-1-nitrobenzene (42). A mixture of 2-(2-trimethylsilyl-1-ethynyl)-5-methoxy-1-nitrobenzene (**41**)[62] (756 mg, 3.03 mmol) and HBr (aq.-48%, 1.10 mL) in 3-pentanone (7 mL) was stirred at 100 °C for 2 h. After cooling to ambient temperature, the dark brown solution was diluted with EtOAc (15 mL) and the organic phase was washed with water (3 × 15 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated under reduced pressure. The resulting brown oil was purified by chromatography (hexane/EtOAc, 95:5) to give **42** (446 mg, 1.73 mmol, 57%) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 2.0 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.10 (dd, J = 8.4, 2.8 Hz, 1H), 5.84 (d, J = 2.4 Hz, 1H), 5.82 (d, J = 2.4 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 148.2, 132.2, 127.5, 124.3, 121.2, 118.8, 109.4, 56.0; IR (ATR) 1611, 1526, 1352, 1245, 1029 cm^{-1}; HRMS (ESI) calcd for $C_9H_9BrNO_3$ (M + H$^+$) 257.9765, found 257.9763.

2-(4-Methoxy-2-nitrophenyl)-3-(2-nitrophenyl)-1,3-butadiene (43). To a mixture of **42** (320 mg, 1.24 mmol), CuI (307 mg, 1.61 mmol), CsF (382 mg, 2.52 mmol), and $Pd(PPh_3)_4$ (143 mg, 0.124 mmol) in DMF (3 mL) was added, under a N_2 atmosphere, a solution of **22** (706 mg, 1.61 mmol) in DMF (3 mL). The resulting mixture was stirred at 70 °C for 12 h. The mixture was cooled to ambient temperature, and EtOAc (30 mL) was added. The mixture was washed with water (5 × 20 mL) and brine (20 mL), the organic phase was dried ($MgSO_4$) and filtered, and the filtrate was concentrated under reduced pressure. The resulting brown oil was purified by chromatography[59] (hexane/EtOAc, 95:5) to give, in order of elution, **27** (66 mg, 0.22 mmol, 28%) as a white solid and **43** (247 mg, 0.756 mmol, 61%) as a yellow solid. mp = 91−95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 8.4, 1.2 Hz, 1H), 7.65 (dt, J = 8.4, 1.2 Hz, 1H), 7.59 (dd, J = 8.0, 1.6 Hz, 1H), 7.52−7.47 (m, 3H), 7.19 (dd, J = 8.4, 2.8 Hz, 1H), 5.12 (d, J = 2.8 Hz, 2H), 4.93 (s, 1H), 4.88 (s, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 149.4,148.9, 145.4, 145.0, 135.4, 133.1, 132.9, 132.3, 128.6, 127.3, 123.9, 119.2, 118.1, 117.9, 108.8, 55.8; IR (ATR) 1520, 1351, 1233, 1027, 910 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{15}N_2O_5$ (M + H$^+$) 327.0981, found 327.0979.

6-Methoxy-3,3′-bi-1*H*-indole (44). Treatment of a solution of **43** (200 mg, 0.613 mmol) in the presence of $Pd_2(dba)_3$ (56 mg, 0.061 mmol), dppp (26 mg, 0.063 mmol), and phen (22 mg, 0.123 mmol) in DMF (1.5 mL) with CO (6 atm), as described for **11** (30 h), gave, after

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workup and chromatography (hexane/EtOAc, 7:3 then 1:1), **44** (161 mg, 0.613 mmol, 100%) as a white solid. mp = 252 °C (dec.); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.11 (br s, 1H), 10.93 (br s, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 2.4 Hz, 1H), 7.49 (d, J = 2.4 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.13 (t, J = 7.2 Hz, 1H), 7.05 (t, J = 7.2 Hz, 1H), 6.94 (d, J = 2.4 Hz, 1H), 6.72 (dd, J = 8.4, 2.4 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.6, 137.1, 136.4, 126.0, 121.6, 121.2, 120.4, 120.3, 120.2, 119.6, 118.8, 111.5, 109.9, 109.7, 108.9, 94.5, 55.2; IR (ATR) 3395, 1629, 1454, 1239, 1105 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{15}N_2O$ ($M + H^+$) 263.1184, found 263.1180.

[(5-Bromo-2-nitrophenyl)methyl]triphenylphosphonium Bromide (46).[63] Treatment of 5-bromo-2-nitrobenzyl bromide (486 mg, 1.65 mmol) with PPh_3 (519 mg, 1.977 mmol) in toluene (6 mL), as described for **1** (100 °C, 10 h), gave, after workup, **46** (918 mg, 1.647 mmol, 100%) as a white solid. mp = 249−250 °C, ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.97 (d, J = 9.0 Hz, 1H), 7.93 (td, J = 8.4, 1.8 Hz, 3H), 7.87 (dt, J = 7.2, 2.4 Hz, 1H), 7.75 (dt, J = 8.4, 3.6 Hz, 6H), 7.67−7.64 (m, 6H), 7.56 (d, J = 2.4 Hz, 1H), 5.47 (d, J = 15.0 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 147.3 (d, J^{CP} = 5.7 Hz), 136.3 (d, J^{CP} = 10.3 Hz), 136.3, 135.4, 134.0 (d, J^{CP} = 10.3 Hz), 133.3, 127.9 (d, J^{CP} = 4.5 Hz), 127.8, 125.9 (d, J^{CP} = 9.1 Hz), 116.9 (d, J^{CP} = 85.8 Hz), 26.6 (d, J^{CP} = 49.2 Hz); IR 1519, 1330, 1109, 884, 754 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{20}Br_2NO_2P$ (M-Br) 476.0415, found 476.0416.

***EZ/EE*-1,3-Di(2-nitrophenyl)-1,3-butadiene (48).** Treatment of a solution of 2-(2-nitrophenyl)propenal **47**[64] (250 mg, 1.41 mmol) and **45** (810 mg, 1.69 mmol) in EtOH (10 mL) with NaOEt (1.8 M in EtOH, 5.5 mL, 9.90 mmol), as described for **7** (24 h), gave, after workup and chromatography (hexane/EtOAc, 17:3), **48** (171 mg, 0.579 mmol, 41%, *EZ*/*EE* = 10:1) as a faint yellow solid. mp = 132−138 °C; Data from the mixture of isomers of **48**, major isomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (dd, J = 7.9, 1.3 Hz, 1H), 7.53 (dd, J = 8.0, 1.3 Hz, 1H), 7.22−7.06 (m, 6H), 6.83 (d, J = 12.1 Hz, 1H), 6.58 (d, J = 12.3 Hz, 1H), 5.51 (d, J = 0.8 Hz, 1H), 5.20 (d, J = 0.4 Hz 1H); partial data of minor isomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (dd, J = 8.2, 1.1 Hz, 1H), 7.90 (dd, J = 8.2, 1.3 Hz, 1H), 7.68−7.65 (m, 2H), 7.57 (t with further fine splittings, J = 7.2 Hz, 1H), 7.43 (dd, J = 7.6, 1.3 Hz, 1H), 7.37 (dt, J = 7.8, 1.4 Hz, 1H), 6.99 (d, J = 16.0 Hz, 1H), 5.59 (s, 1H), 5.30 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.6, 147.8, 147.6, 146.9, 144.6, 142.0, 135.4, 134.4, 134.2, 133.2, 133.1, 132.5, 132.4, 132.3, 132.1, 132.1, 132.0, 131.0, 131.0, 128.9, 128.4, 128.2, 128.0, 127.9, 127.5, 126.8, 127.7, 124.3, 123.8, 123.7, 122.4, 120.2; IR (ATR) 1568, 1514, 1339, 912, 786 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{13}N_2O_4$ ($M + H^+$) 297.0875, found 297.0870.

***E*-1-(3-Methoxy-2-nitrophenyl)-3-(2-nitrophenyl)-1,3-butadiene (49).** Treatment of a solution of **47** (69.7 mg, 0.393 mmol) and **2** (200 mg, 0.393 mmol) in absolute EtOH (2 mL) with NaOEt (2 M, 1.1 mL, 2.2 mmol), as described for **7** (30 h), gave, after workup and chromatography (hexane/EtOAc, 85:15), **49** (49.1 mg, 0.150 mmol, 38%) as a yellow-orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, J = 8.4, 1.6 Hz, 1H), 7.27−7.23 (m, 1H), 7.21−7.15 (m, 2H), 6.92 (t, J = 8.0 Hz, 1H), 6.74 (dt, J = 7.6, 1.2 Hz, 1H), 6.67 (d, J = 8.4 Hz, 1H), 6.55 (d, J = 12.4 Hz, 1H), 6.44 (d, J = 12.0 Hz 1H), 6.52 (d, J = 0.8 Hz, 1H), 5.23 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.2, 150.2, 148.2, 141.6, 139.8, 135.0, 133.8, 131.9, 131.4, 130.5, 129.9, 128.0, 123.7, 123.6, 123.0, 121.9, 56.4; IR (ATR) 1522, 1337, 1107, 8333, 756, 721, 690 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{15}N_2O_5$ ($M + H^+$) 327.0981, found 327.0977.

***E*-1-(4-Bromo-2-nitrophenyl)-3-(2-nitrophenyl)-1,3-butadiene (50).** Treatment of a solution of **47** (320 mg, 1.80 mmol) with **3** (1.20 g, 2.23 mmol) with NaOEt (2.0 M, 4.2 mL, 8.41 mmol) in EtOH (15 mL), as described for **7** (26 h), gave, after workup and chromatography (hexane/EtOAc, 9:1), **50** (139 mg, 0.370 mmol, 21%) as a faint yellow solid. mp = 119−121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 2.0 Hz, 1H), 7.58 (dd, J = 7.2, 1.2 Hz, 1H), 7.27−7.19 (m, 3H), 7.10−7.05 (m, 2H), 6.74 (d, J = 12.0 Hz, 1H), 6.60 (d, J = 12.4 Hz, 1H), 5.54 (s, 1H), 5.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 147.2, 141.7, 135.2, 135.1, 133.3, 132.2, 131.8, 131.3, 131.1, 128.1, 126.8, 126.3, 123.9, 123.0, 121.0; IR (ATR) 1517, 1338, 1147, 859, 784 cm^{-1}; HRMS (ESI, negative ion mode) calcd for $C_{16}H_{11}BrN_2O_4$ (M^-) 373.9902, found 373.9898.

***E*-1-(5-Bromo-2-nitrophenyl)-3-(2-nitrophenyl)-1,3-butadiene (51).** Treatment of a solution of **47** (246 mg, 1.39 mmol) and **46** (850 mg, 1.53 mmol) in EtOH (8 mL) with NaOEt (2.0 M, 3.1 mL, 6.24 mmol), as described for **7** (26 h), gave, after workup and chromatography (hexane/EtOAc, 9:1), **51** (113 mg, 0.301 mmol, 22%) as a yellow solid. mp = 129−134 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, J = 8.4 Hz, 1H), 7.60 (dd, J = 8.4, 1.2 Hz, 1H), 7.29 (d, J = 2.4 Hz, 1H), 7.24 (dd, J = 7.2, 1.2 Hz, 1H), 7.20 (dd, J = 9.0, 2.4 Hz, 1H), 7.13 (td, J = 8.4, 1.8 Hz, 1H), 7.08 (dd, J = 7.8, 1.8 Hz, 1H), 6.78 (d, J = 12.0 Hz, 1H), 6.63 (d, J = 12.6 Hz, 1H), 5.58 (s, 1H), 5.28 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.7, 145.6, 141.8, 135.1, 135.1, 133.8, 132.3, 132.0, 130.9, 130.8, 128.2, 127.3, 125.8, 125.3, 124.0, 123.4; IR (ATR) 1598, 1518, 1340, 855, 754 cm^{-1}; HRMS (ESI, negative ion mode) calcd for $C_{16}H_{11}BrN_2O_4$ (M^-) 373.9902, found 373.9898.

2,3′-Bi-1*H*-indole (52). Treatment of a solution of **48** (200 mg, 0.675 mmol) in the presence of $Pd(dba)_2$ (19 mg, 0.034 mmol), dppp (14 mg, 0.034 mmol), and phen (12 mg, 0.067 mmol) in DMF (2 mL) with CO (6 atm), as described for **11** (41 h), gave, after workup and chromatography (hexane/EtOAc, 7:3), **52** (96 mg, 0.41 mmol, 61%) as a white solid. mp = 206−207 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.32 (s, 1H), 11.14 (s, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.85 (d, J = 1.8 Hz, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.18 (t, J = 6.0 Hz, 1H), 7.16 (t, J = 6.0 Hz, 1H), 7.03 (t, J = 7.2 Hz, 1H), 6.96 (t, J = 7.2 Hz, 1H), 6.74 (d, J = 1.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.6, 135.9, 134.1, 129.1, 124.6, 123.0, 121.5, 120.1, 119.6, 119.6, 118.9, 118.7, 111.8, 110.3, 108.4, 96.7; IR (ATR) 3405, 3054, 1596, 1456, 1308, 743 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{13}N_2$ ($M + H^+$) 233.1078, found 233.1073.

7-Methoxy-2,3′-bi-1*H*-indole (53). Reaction of a solution of **49** (46 mg, 0.14 mmol) in the presence of $Pd(dba)_2$ (8.1 mg, 0.014 mmol), dppp (6.0 mg, 0.015 mmol), and phen (5.1 mg, 0.028 mmol) in DMF (0.8 mL) with CO (6 atm), as described for **11** (120 °C, 48 h), gave, after workup and chromatography (hexane/EtOAc, 7:3), **53** (26.7 mg, 0.102 mmol, 72%) as a yellowish-brown oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (br s, 1H), 8.29 (br s, 1H), 7.48 (d, J = 2.6 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.29 (dt, J = 7.0, 1.2 Hz, 1H), (7.25−7.23 (m, 3H), 7.05 (t, J = 7.9 Hz, 1H), 6.77 (d, J = 2.2 Hz, 1H), 6.66 (d, J = 7.6 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.7, 136.4, 132.8, 130.7, 126.3, 125.4, 122.9, 121.3, 120.7, 120.3, 120.0, 112.9, 111.5, 110.4, 101.6, 99.7, 55.4; IR (ATR) 3395, 1703, 1598, 1576, 1254, 1094, 789, 742 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{15}N_2O$ ($M + H^+$) 263.1184, found 263.1182.

6-Bromo-2,3′-bi-1*H*-indole (54). Reaction of a solution of **50** (50 mg, 0.133 mmol) in the presence of $Pd(dba)_2$ (4.6 mg, 0.008 mmol), dppp (3.3 mg, 0.008 mmol), and phen (3 mg, 0.016 mmol) in DMF (1.5 mL) with CO (6 atm), as described for **11** (120 °C, 43 h), gave, after workup and chromatography (hexane/EtOAc, 7:3), **54** (27.4 mg, 0.088 mmol, 66%) as a white solid. mp = 205−206 °C; ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ 11.41 (br, s, 1H), 11.34 (br, s, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 2.4 Hz, 1H), 7.67 (d, J = 1.8 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.22−7.13 (m, 3H), 6.77 (d, J = 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6) δ 136.9, 136.6, 135.2, 128.2, 124.5, 123.4, 121.7, 121.5, 120.5, 119.8, 119.4, 112.8, 112.6, 111.9, 107.9, 96.8; IR (ATR) 3410, 3381, 1588, 1317, 747 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{12}BrN_2$ ($M + H^+$) 311.0184, found 311.0181.

5-Bromo-2,3′-bi-1*H*-indole (55). Reaction of a solution of **51** (121 mg, 0.323 mmol) in the presence of $Pd(dba)_2$ (13 mg, 0.023 mmol), dppp (9.4 mg, 0.023 mmol), and phen (8.2 mg, 0.045 mmol) in DMF (1.5 mL) with CO (6 atm), as described for **11** (120 °C, 44 h), gave, after workup and chromatography (hexane/EtOAc, 7:3), **55** (67.3 mg, 0.216 mmol, 67%) as a white solid. mp = 205−206 °C ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.46 (br, s, 1H), 11.42 (br, s, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 2.4 Hz, 1H), 7.67 (d, J = 1.8 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.22−7.15 (m, 3H), 7.14 (dd, J = 7.8, 1.8 Hz, 1H), 7.27 (d, J = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 136.6, 135.8, 134.7, 131.2, 124.5, 123.7, 122.6, 121.9, 121.1, 119.9, 119.5, 112.3, 112.0, 111.3, 107.9, 96.4; IR (ATR)

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3412, 3356, 1589, 1234, 748 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{12}BrN_2$ ($M + H^+$) 311.0184, found 311.0182.

Indolo[1,2-*c*]quinazolin-6(5*H*)-one (58)[46] and 5,11-Dihydro-6*H*-indolo[3,2-*c*]quinolin-6-one (59).[65] Treatment of a solution of *trans*-2,2′-di(2-nitrophenyl)ethene (**56**)[66] (200 mg, 0.740 mmol) in the presence of $Pd(dba)_2$ (25.6 mg, 0.044 mmol), dppp (18.3 mg, 0.044 mmol), and phen (16 mg, 0.089 mmol) in DMF (2 mL) with CO (6 atm), as described for **11** (120 °C, 56 h), gave, after workup and chromatography (hexane/EtOAc, 9:1, 8:2, and 1:1), in order of elution, **58** (132 mg, 0.565 mmol, 76%) and **59** (21 mg, 0.090 mmol, 12%), both as white solids. Analytical data for **58**: mp = 320−321 °C; ^{1}H NMR (600 MHz, $CDCl_3$/DMSO-d_6) δ 11.23 (br, s, 1H), 8.56−8.55 (m, 1H), 7.96 (d, J = 9.6 Hz, 1H), 7.68−7.66 (m, 1H), 7.34 (t, J = 8.4 Hz, 1H), 7.31−7.27 (m, 2H), 7.24 (d, J = 8.4 Hz, 1H), 7.19−7.15 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$/DMSO-d_6) δ 147.0, 134.1, 133.9, 133.3, 129.4, 128.9, 123.1, 123.0, 122.5, 122.5, 119.8, 115.4, 115.2, 113.5, 97.7; IR (ATR) 2920, 1697, 1596, 1339, 739 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{11}N_2O$ ($M + H^+$) 235.0871, found 235.0868.

Analytical data for **59**: mp = 396−397 °C (dec.); ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.55 (br, s, 1H), 11.42 (br, s, 1H), 8.20 (dd, J = 7.8, 1.2 Hz, 2H), 7.62 (d, J = 7.8 Hz, 1H), 7.51 (td, J = 8.4, 1.2 Hz, 1H), 7.47(dd, J = 8.4, 0.6 Hz, 1H), 7.38−7.35 (m, 1H), 7.30−7.25 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 159.8, 140.7, 137.9, 137.7, 129.1, 124.4, 124.0, 122.1, 121.5, 121.0, 120.7, 116.0, 111.9, 111.7, 106.4; IR (ATR) 3050, 2925, 1698, 1596, 1395 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{11}N_2O$ ($M + H^+$) 235.0871, found 235.0869.

1-(5-Chloro-2-nitrophenyl)-2-(2-nitrophenyl)ethene (65). Treatment of a solution of 2-nitrobenzaldehyde (531 mg, 3.51 mmol) with **1** (2.20 mg, 4.29 mmol) in EtOH (18 mL) in the presence of NaOEt (1.8 M, 10.5 mL, 18.9 mmol), as described for **7** (24 h), gave, after workup and chromatography (hexane/EtOAc, 1:1), **65** (300 mg, 0.985 mmol, 28%) as a faint yellow solid. mp = 139−140 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 9.6 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.68 (t, J = 7.8 Hz, 1H), 7.50 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 8.4 Hz, 1H), 7.30 (d, J = 16.8 Hz, 1H), 7.09 (d, J = 16.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.4, 147.7, 135.5, 133.9, 133.6, 132.3, 132.1, 130.8, 129.2, 129.1, 128.8, 125.5, 124.8, 122.6; IR (ATR) 1525, 1347, 1217, 738 cm^{-1}; HRMS (ESI, negative ion mode) calcd for $C_{14}H_9ClN_2O_4$ (M^-) 304.0251, found 304.0272.

2-(2-Nitro-6-chlorophenyl)indole (66) and 4-Chloro-5,10-dihydroindolo[3,2-*b*]indole (67). Reaction of **65** (250 mg, 0.822 mmol) in the presence of $Pd(dba)_2$ (23.6 mg, 0.041 mmol), dppp (16.9 mg, 0.041 mmol), and phen (14.8 mg, 0.082 mmol) in DMF (2 mL), as described for **11** (120 °C, 76 h), gave, after workup and chromatography (hexane/EtOAc, 9:1, 8:2, 1:1), in order of elution, **67** (26 mg, 0.107 mmol, 13%) and **66** (153 mg, 0.570 mmol, 69%), both as white solids. Analytic data for **66**: mp = 269−270 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.52 (br, s, 1H), 8.52 (dd, J = 8.2, 0.8 Hz, 1H), 8.24 (dd, J = 7.6, 1.2 Hz, 1H), 7.48−7.44 (m, 3H), 7.35 (t, J = 8.2 Hz, 1H), 7.28 (d, J = 8.2 Hz, 1H), 7.26 (t, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.8, 135.2, 134.4, 134.0, 130.0, 128.2, 124.1, 124.0, 123.8, 123.1, 123.0, 115.4, 114.4, 113.2, 96.0; IR (ATR) 3053, 1712, 1419, 1398, 748 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{10}ClN_2O$ ($M + H^+$) 269.0482, found 269.0475.

Analytic data for **67**: mp = 182−183 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.33 (br, s, 1H), 11.05 (br, s, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.11−7.04 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 141.0, 140.7, 125.9, 123.3, 122.6, 122.0, 122.0, 118.2, 117.7, 117.4, 113.9, 113.5, 112.5, 110.9; IR (ATR) 3424, 1455, 1391, 1322, 730 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_9ClN_2$ (M^+) 240.0454, found 240.0447.

***Z*/*E*-1-(3-Methoxy-2-nitrophenyl)-2-(2-nitrophenyl)ethene (68).** Treatment of a solution of 2-nitrobenzaldehyde (500 mg, 3.31 mmol) with **2** (1.68 mg, 3.31 mmol) in EtOH (16 mL) in the presence of NaOEt (1.8 M, 12 mL, 21.6 mmol), as described for **7** (ambient temperature, 24 h), gave, after workup and chromatography (hexane/EtOAc, 7:3 then 1:1), **68** (891 mg, 2.97 mmol, 90%, Z/E = 1.8:1) as an orange solid. NMR data from the E/Z = 1.8:1 mixture of **68**, major isomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10−8.08 (m, 1H), 7.17 (d, J = 7.5 Hz, 1H), 7.48 (t, J = 8.3 Hz, 1H), 7.40−7.36 (m, 2H), 7.09 (t, J = 8.5 Hz, 1H), 6.87 (d, J = 8.3 Hz, 1H), 6.68 (d, J = 11.7 Hz, 1H), 6.48 (d, J = 7.7 Hz, 1H), 3.89 (s, 3H); minor isomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 15.7 Hz, 1H), 7.63 (t, J = 8.2 Hz, 1H), 7.45 (d, J = 8.2 Hz, 1H), 7.19−7.16 (m, 2H), 7.11 (d, J = 12.1 Hz, 1H), 7.01 (d, J = 8.2 Hz, 1H), 6.88 (d, J = 15.8 Hz, 1H), 3.92 (s, 3H); Analytical data for both isomers from the mixture: mp = 135−140 °C; ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.0, 150.8, 148.0, 147.9, 141.1, 140.7, 133.5, 133.3, 132.4, 132.4, 132.1, 132.0, 131.1, 130.6, 130.3, 130.0, 129.4, 129.0, 128.8, 128.7, 125.4, 124.9, 124.7, 124.6, 122.1, 118.1, 112.1, 111.5, 56.5, 56.4; IR (ATR) 1518, 1342, 1285, 1063, 852 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{13}N_2O_5$ ($M + H^+$) 301.0824, found 301.0817.

7-Methoxy-2-(2-nitrophenyl)indole (69), 2-(3-Methoxy-2-nitrophenyl)indole (70), and 5,11-Dihydro-4-methoxy-6*H*-indolo[3,2-*c*]quinolin-6-one (71). Reaction of **68** (439 mg, 1.46 mmol) in the presence of $Pd(dba)_2$ (50.4 mg, 0.088 mmol), dppp (36.2 mg, 0.088 mmol), and phen (31.6 mg, 0.175 mmol) in DMF (3 mL) with CO (6 atm), as described for **11** (120 °C, 56 h), gave, after workup and chromatography (hexane/EtOAc, 9:1, 8:2, 1:1, 3:7), in order of elution, **69** (38 mg, 0.14 mmol, 10%) as a viscous oil, **70** (290 mg, 1.08 mmol, 74%) as a yellow solid, and **71** (23.2 mg, 0.088 mmol, 6%) as a white solid.

Analytic data for **69**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 7.2 Hz, 1H), 8.11 (br s, 1H), 7.71 (dd, J = 6.8, 2.4 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.42−7.36 (m, 2H), 7.17 (t, J = 8.0 Hz, 1H), 7.09 (s, 1H), 6.91 (d, J = 8.0 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.3, 134.0, 133.4, 129.6, 123.8, 123.5, 123.2, 123.0, 120.2, 115.6, 115.3, 114.1, 110.7, 98.4, 56.0; IR (ATR) 3424, 2230, 1611, 1535, 1052 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{13}N_2O_3$ ($M + H^+$) 269.0926, found 269.0919.

Analytic data for **70**: mp = 158−160 °C; ^{1}H NMR (600 MHz, $CDCl_3$/DMSO-d_6) δ 11.57 (br s, 1H), 7.59 (t, J = 8.4 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.04 (t, J = 8.0 Hz, 1H), 6.54 (d, J = 1.6 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$/DMSO-d_6) δ 150.4, 139.1, 137.0, 131.0, 130.6, 128.2, 125.2, 122.4, 120.4, 120.3, 119.6, 112.0, 111.5, 101.1, 56.5; IR (ATR) 3402, 1609, 1527, 1275, 1112 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{13}N_2O_3$ ($M + H^+$) 269.0926, found 269.0919.

Analytic data for **71**: mp = 355−360 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.57 (br, s, 1H), 10.16 (br, s, 1H), 8.20 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.37 (td, J = 8.4, 1.2 Hz, 1H), 7.28−7.25 (m, 2H), 7.17 (d, J = 7.8 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.1, 146.3, 140.7, 137.7, 127.6, 124.4, 124.1, 121.7, 121.1, 120.8, 113.9, 112.4, 111.7, 110.0, 106.7, 56.1; IR (ATR) 3407, 1523, 1377, 1275, 1110 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{13}N_2O_2$ ($M + H^+$) 265.0977, found 265.0971.

1,1-Bis(2-nitrophenyl)ethene (72) and 2,3-Di(2-nitrophenyl)-1,3-butadiene (27). To a solution of 2-iodonitrobenzene (473 mg, 1.90 mmol) in DMF (10 mL) were added **22** (1.00 g, 2.28 mmol), $PdCl_2(PPh_3)_2$ (67 mg, 0.095 mmol), PPh_3 (50 mg, 0.190 mmol), and CuI (271 mg, 1.43 mmol). The reaction was stirred at ambient temperature for 24 h. Et_2O (30 mL) was added, and the organic phase was washed with NH_4OH (10%-aqueous, 3 × 30 mL), H_2O (30 mL), and brine (30 mL). The organic phase was dried ($MgSO_4$) and filtered, and the solvents were removed under reduced pressure. The residue was purified by chromatography (hexane/EtOAc, 9:1) to afford, in order of elution, **27** (30 mg, 0.10 mmol, 11%) and **72** (320 mg, 1.18 mmol, 62%), both as a white solid. mp = 132−134 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.62 (s, 2H), 7.43−7.46 (m, 2H), 7.58−7.59 (m, 4H), 7.71 (dt, J = 7.8, 0.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 121.3, 123.9, 129.1, 132.4, 133.1, 133.9, 142.4, 148.7; IR (ATR) 716, 774, 1351, 1516 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{10}N_2NaO_4$ ($M + Na^+$) 293.0538, found 293.0534.

Indolo[2,3-*b*]indole (73) and 6*H*-Indolo[2,3-*c*]quinolin-6-one (74).[67] Reaction of **72** (210 mg, 0.777 mmol) in the presence of $Pd(OAc)_2$ (17.5 mg, 0.078 mmol), dppp (32 mg, 0.078 mmol), phen (28 mg, 0.155 mmol), and CO (6 atm) in DMF (3 mL), as described

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for **11** (41 h), gave, after chromatography (hexane/EtOAc, 4:6), in order of elution, **73** (22.6 mg, 0.110 mmol, 14%) and **74** (106 mg, 0.451 mmol, 58%), both as white solids. Analytical data for **73**: mp 340−343 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.35 (br, s, 1H), 7.79 (d, J = 7.2 Hz, 1H), 7.40 (d, J = 7.8 Hz, 1H), 7.10 (dt, J = 7.2, 0.6 Hz, 1H),; 7.05 (dt, J = 8.4, 1.8 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6)) δ 144.5, 138.6, 121.9, 119.2, 119.0, 117.4, 111.5, 99.7; IR (ATR) 3413, 3363, 1450, 736, 696 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{11}N_2$ (M + H$^+$) 207.0922, found 207.0917.

Analytical data for **74**: mp 312−314 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.34 (br s, 1H), 11.85 (br s, 1H), 8.47 (d, J = 7.8 Hz, 1H), 8.44 (d, J = 7.2 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.47 (t, J = 7.8 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H), 7.34 (t, J = 7.2 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H) ; ^{13}C NMR (150 MHz, DMSO-d_6) δ 155.7, 138.8, 134.9, 127.6, 125.9, 125.7, 123.0, 122.3, 122.3, 122.2, 120.7, 118.2, 118.0, 116.1, 113.0, ; IR (ATR) 3316, 3158, 1648, 1620, 1328, 729 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{11}N_2O$ (M + H$^+$) 235.0871, found 235.0867.

1-(5-Benzyloxy-2-nitrophenyl)-2-(4-methoxy-2-nitrophenyl)ethene (76). To a solution of **75** (500 mg, 1.79 mmol) in DMF (4 mL) were added CuI (34 mg, 0.18 mmol), CsF (546 mg, 3.62 mmol), Pd(PPh$_3$)$_4$ (124 mg, 0.108 mmol), and **23** (1.10 g, 2.01 mmol). The mixture was stirred at 50 °C under N_2 for 8 h. After cooling to ambient temperature, the crude mixture was diluted with EtOAc (35 mL) and washed with H_2O (3 × 35 mL) and brine (2 × 35 mL). The organic layer was dried ($MgSO_4$) and filtered, and the solvents were removed under reduced pressure. The residue was purified by chromatography on SiO_2/K_2CO_3 (9:1) using (hexane/EtOAc, 9:1 then 85:15) to give, in order of elution, **28** (69.2 mg, 0.136 mmol, 15%) and **76** (503 mg, 1.24 mmol, 69%), both as white solids. Analytical data for **76**: mp = 127−128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 9.2 Hz, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.45−7.34 (m, 5H), 7.17 (d, J = 2.8 Hz, 1H), 7.11 (d, J = 2.8 Hz, 1H), 7.09 (dd, J = 8.8, 2.8 Hz, 1H), 6.95 (dd, J = 8.8, 2.4 Hz, 1H), 5.55 (s, 1H), 5.52 (s, 1H), 5.16 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 159.5, 149.1, 142.8, 141.6, 137.2, 135.5, 134.2, 128.7, 128.4, 127.7, 126.7, 126.0, 120.3, 119.1, 118.5, 114.7, 108.7, 70.7, 55.8; IR (ATR) 1515, 1348, 1228, 1004, 826 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{19}N_2O_6$ (M + H$^+$) 407.1243, found 407.1236.

6-Methoxy-indolo[2,3-*b*]-5-benzyloxyindole (77), 2-Benzyloxy-5,7-dihydro-9-methoxy-6*H*-indolo[2,3-*c*]quinolin-6-one (78), and 10-Benzyloxy-5,7-dihydro-3-methoxy-6*H*-indolo[2,3-*c*]quinolin-6-one (79). Reaction of **76** (300 mg, 0.738 mmol) in the presence of Pd(dba)$_2$, dppp (29.7 mg, 0.0527 mmol), and phen (21.3 mg, 0.052 mmol) in DMF (2.5 mL), as described for **11** (pCO = 6 atm, 41 h), gave, after chromatography (hexane/EtOAc, in order 7:3, 1:1, 3:7, 2:8), in order of elution, **77** (75.8 mg, 0.221 mmol, 30%), **79** (84.7 mg, 0.229 mmol, 31%), and **78** (104 mg, 0.281 mmol, 38%), all as white solids.

Analytical data for **77**: mp = 206−207 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.59 (s, 1H), 10.50 (s, 1H), 8.16 (d, J = 8.4 Hz, 1H), 8.01−797 (m, 2H), 7.95 (d, J = 2.8 Hz, 1H), 7.87−7.81 (m, 2H), 7.79−7.75 (m, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.47 (d, J = 2.4 Hz, 1H), 7.25 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 7.22 (dd, J = 9.2, 2.4 Hz, 1H), 5.65 (s, 2H), 4.26 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.9, 152.6, 144.9, 139.6, 138.0, 133.3, 128.3, 127.6, 127.6, 122.2, 117.8, 116.2, 111.7, 107.4, 107.0, 102.8, 99.6, 96.9, 69.9, 55.3; IR (ATR) 3373, 1577, 1452, 1148, 1022 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{18}N_2O_2$ (M$^+$) 342.1368, found 342.1361.

Analytical data for **78**: mp = 285−286 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.05 (s, 1H), 11.66 (s, 1H), 8.34 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 2.4 Hz, 1H), 7.56 (d, J = 6.8 Hz, 2H), 7.53 (d, J = 9.2 Hz, 1H), 7.42 (t, J = 7.2 Hz, 2H), 7.34 (tt, J = 6.8, 1.2 Hz, 1H), 7.19 (dd, J = 9.2, 2.4 Hz, 1H), 7.05 (d, J = 2.8 Hz, 1H), 6.95 (dd, J = 8.4, 2.4 Hz, 1H), 5.27 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.5, 155.9, 153.2, 137.5, 136.3, 134.2, 128.4, 127.8, 127.7, 126.6, 124.2, 122.0, 118.3, 117.0, 113.8, 111.9, 110.2, 104.8, 99.8, 70.1, 55.2; IR (ATR) 3437, 3026, 1621, 1288, 811 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{19}N_2O_3$ (M + H$^+$) 371.1396, found 371.1389.

Analytical data for **79**: mp = 276−277 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.16 (s, 1H), 11.65 (s, 1H), 8.27 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 2.8 Hz, 1H), 7.56 (d, J = 7.2 Hz, 2H), 7.44−7.40 (m, 3H), 7.34 (t, J = 7.6 Hz, 1H), 7.12 (dd, J = 8.8, 2.4 Hz, 1H), 7.05 (d, J = 2.4 Hz, 1H), 6.94 (dd, J = 8.8, 2.4 Hz, 1H), 5.29 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.3, 154.9, 153.7, 140.2, 137.4, 129.4, 128.4, 127.8, 127.7, 127.2, 123.1, 118.4, 118.4, 117.2, 116.2, 115.0, 111.5, 106.7, 94.8, 69.8, 55.2; IR (ATR) 3448, 1652, 1458, 1264, 1228 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{19}N_2O_3$ (M + H$^+$) 371.1396, found 371.1389.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01987.

Copies of ^{1}H NMR and ^{13}C NMR spectra of all new compounds including 1D and 2D NMR experiments to secure the structure of isomers **78** and **79** (PDF)

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Notes

The authors declare no competing financial interest.

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