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Csp^2–N Bond Formation via Ligand-Free Pd-Catalyzed Oxidative Coupling Reaction of *N*-Tosylhydrazones and Indole Derivatives

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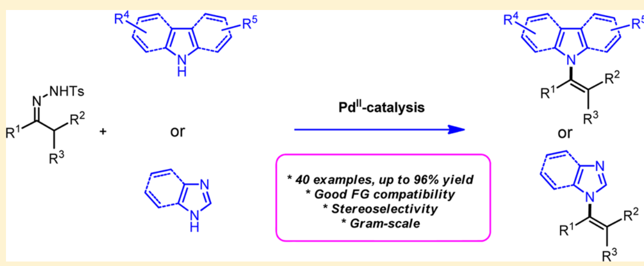
Supporting Information

ABSTRACT: In a fresh approach to the synthesis of *N*-vinylazoles, a ligand-free palladium catalytic system was found to promote the Csp^2–N bond-forming reaction utilizing *N*-tosylhydrazones and N-H azoles. This process shows functional group tolerance; di-, tri-, and tetrasubstituted *N*-vinylazoles were obtained in high yields. Under the optimized conditions, the reaction proceeds with high stereoselectivity depending on the nature of the coupling partners.



INTRODUCTION

N-Vinylazoles are important classes of building blocks in organic synthesis and are also key structural motifs in medicinal chemistry.[1] They have been found to display antifungal activity.[2] *N*-Vinylazoles have been shown to serve as monomers for the synthesis of poly(*N*-vinylazoles).[3] These latter have been utilized as semiconductors and photosensitive materials. There are several methods for the preparation of *N*-vinylazoles. The most conventional route is the condensation of *N*-H azoles with carbonyl compounds in the presence of a water scavenger and a Brønsted or Lewis acid (Scheme 1a).[4] The relatively harsh reaction conditions generally required for this transformation cause low functional group tolerance and prompted the emergence of alternative methods.[5] Recently, with the development of modern organometallic chemistry, transition-metal-catalyzed coupling reactions offer a more reliable approach to the preparation of *N*-vinylazoles by coupling *N*-H azoles with vinyl halides or vinyl triflates (Scheme 1b).[1,6] The major limitation of this method is that multiple steps are generally required for the preparation of the vinyl halide. A more attractive approach is the amination of alkynes (Scheme 1c).[7] Intermolecular addition of amines to alkynes has been well-studied.[8] However, the addition of N-heterocycles onto alkynes remains elusive, and the regioselectivity issue is always a daunting task.[7a,9] Therefore, it would be desirable to develop a new type of coupling reaction to form *N*-vinylazoles that may circumvent these drawbacks.[10]

Over the past years, *N*-tosylhydrazones have attracted extensive attention because of their various useful applications in organic synthesis. In particular, they are valuable and readily available reagents in C–C,[11] C–S,[12] C–O,[13] and C–B[14] bond-forming reactions through metal-catalyzed and metal-free processes. In this area, we reported the Cu-catalyzed Csp^3–N bond-forming reaction between *N*-tosylhydrazones and aliphatic amines, giving rise to the reductive coupling products (Scheme 2a).[15] Herein, we further report the oxidative Pd-catalyzed cross-coupling of *N*-tosylhydrazones and *N*-H azoles, which constitutes a highly efficient and practical approach for Csp^2–N bond formation (Scheme 2b).

In the course of our interest of sulfonylhydrazones as versatile coupling partners,[16] very recently, we developed a novel Pd-catalyzed three-component reaction (MCR) between *N*-tosylhydrazones, dihaloarenes, and amines (e.g., anilines, aliphatic amines), producing nitrogen-containing 1,1′-diarylethylenes of biological interest through a faster C═C bond formation and an efficient intermolecular C–N cross-coupling.[17] To expand the scope of this catalytic MCR to a wider variety of new coupling partners (e.g., *N*-H azoles), we decided to study the employ of indoles **2** as nucleophilic components in the cross coupling process of *N*-tosylhydrazone **1a** and 1-chloro-4-iodobenzene **3a**. However, to our surprise, under optimized conditions, the 1,1′-diarylethylene containing an indole unit **5** was never detected and, instead, *N*-vinylindole **4a** was isolated in a good 70% yield (Scheme 3).

On the basis of this unexpected result, we have explored this new type coupling reaction that allows an expeditious and easy access to *N*-vinylindole derivatives. To the best of our knowledge, this is the first report describing the palladium-catalyzed Csp^2–N bond formation through the oxidative coupling of *N*-H azoles and *N*-tosylhydrazones (Scheme 2b). Mechanistically, this Csp^2–N bond-forming reaction is fundamentally different from those classically reported in the literature.[5] Moreover, the use of *N*-tosylhydrazones represents a

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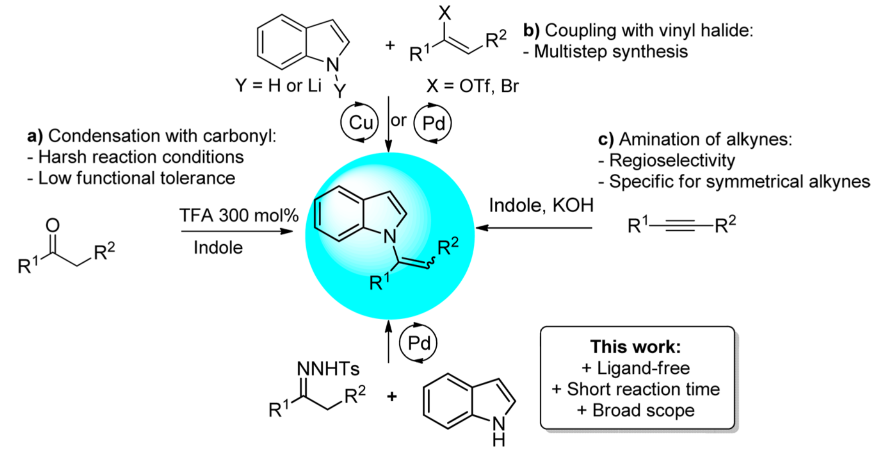
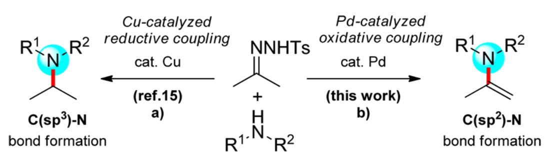
Scheme 1. Synthetic Approaches Toward *N*-Vinylindoles



Scheme 2. Transition-Metal-Catalyzed C−N Bond-Forming Reactions of *N*-Tosylhydrazones with Amines



very convenient methodology for the unconventional modification of carbonyl compounds.

■ RESULTS AND DISCUSSION

We began the exploration of this new transformation with *N*-tosylhydrazone **1a** and indole **2a** as a model substrate (Table 1; see the Supporting Information for the complete study). Since the final product **4a** of the MCR depicted in Scheme 3 did not incorporate the aryl unit of **3a**, we carried out the coupling, without the addition of halogenated derivative **3a** (Table 1, entry 1). Under these conditions, no trace of **4a** was detected. In this case, thermolysis of hydrazone **1a** provides the formation of two concomitant byproducts: (i) the Bamford−Stevens[18] alkene (1,3,5-trimethoxy-2-vinylbenzene), resulting from the evolution of the diazo intermediate, and (ii) the reductive etherification product (2-(1-(*tert*-butoxy)ethyl)-1,3,5-trimethoxybenzene)[13] derived from the reaction between the carbene complex and base (NaO*t*Bu). This result suggests that **3a** plays the role of the oxidant for this coupling. For the next experiments, we found that simply using iodobenzene as the oxidant serves as an effective alternative to **3a**. Next, the reaction without ligand Xphos was performed (entry 2). Gratifyingly, the desired *N*-vinylindole **4a** was obtained as the sole reaction product in a very promising 75% isolated yield. Other combinations of palladium source, base, and solvents were then examined. The base of choice for this transformation was NaO*t*Bu (see, entries 2−4). On the basis of the results obtained in entries 2 and 6, commercially available $Pd_2(dba)_3\cdot CHCl_3$ was fixed as the source of palladium. Screening of the solvent source demonstrates that fluorobenzene (PhF) and cyclopentylmethyl ether (CPME) give the best results (entries 6 and 9). Under optimal conditions, clean and full conversion of the starting material was achieved to give **4a** in nearly quantitative yield upon isolation (Table 1, entry 9). Notably, a low conversion was observed when iodobenzene was changed to bromobenzene, and no reaction occurred in the presence of O_2 or 1,4-benzoquinone (1,4-BQ) (entries 11−12). It should be noted that the coupling of hydrazone **1a** with indole **2a** is not limited to a small scale (0.75 mmol) as it could be conveniently performed on a 2.5 g scale for **1a** (6.6 mmol), giving rise to **4a** in 90% yield.

We next explored the scope of this useful cross-coupling of *N*-tosylhydrazones and indoles (Table 2). The reaction is general with various hydrazones derived from acetophenones and 4,5,6,7-substituted indoles (compounds **4b**−**4m**). The reaction displays no dependence upon the electronic nature and position of the substituent on the aromatic ring of the indole or hydrazone moiety. Electron-rich and electron-poor indoles or hydrazones all reacted completely and effectively within 1 h (compounds **4b**−**4i**). It is noteworthy that functional groups, such as amine, nitrile, and alkyne, are well-tolerated (compounds **4k**−**4m**).

Scheme 3. Pd(II)-Catalyzed Csp^2−N Bond Formation through the Oxidative Coupling of Indole 2a and *N*-Tosylhydrazone 1a

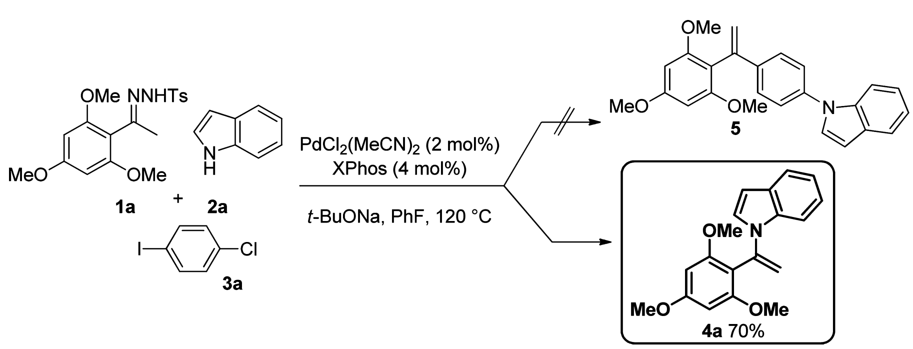
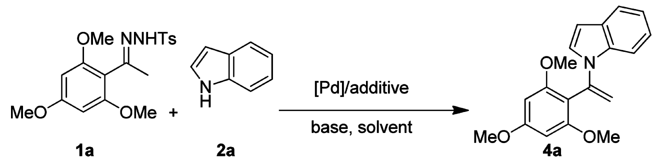


Table 1. Selected Optimization Experiments for the Coupling of *N*-Tosylhydrazones 1a with Indole 2a[a]



entry	[Pd]	additive	solvent	base	yield (%)[b]
1	$PdCl_2(MeCN)_2$		PhF	NaO*t*Bu	0[c]
2	$PdCl_2(MeCN)_2$	PhI	PhF	NaO*t*Bu	75
3	$PdCl_2(MeCN)_2$	PhI	PhF	LiO*t*Bu	18
4	$PdCl_2(MeCN)_2$	PhI	PhF	Cs_2CO_3	14
5	$PdCl_2(PPh_3)_2$	PhI	PhF	NaO*t*Bu	16[d]
6	$Pd_2(dba)_3·CHCl_3$	PhI	PhF	NaO*t*Bu	95
7	$Pd_2(dba)_3·CHCl_3$	PhI	PhMe	NaO*t*Bu	87
8	$Pd_2(dba)_3·CHCl_3$	PhI	dioxane	NaO*t*Bu	75
9	**$Pd_2(dba)_3·CHCl_3$**	**PhI**	**CPME**	**NaO*t*Bu**	**97**
10	$Pd_2(dba)_3·CHCl_3$	PhBr	CPME	NaO*t*Bu	66
11	$Pd_2(dba)_3·CHCl_3$	O_2	CPME	NaO*t*Bu	0
12	$Pd_2(dba)_3·CHCl_3$	1,4-BQ	CPME	NaO*t*Bu	0

[a]Reaction conditions: *N*-tosylhydrazone **1a** (0.75 mmol), indole **2a** (0.5 mmol), additive (0.6 mmol), [Pd] (2 mol %), base (1.4 mmol), solvent (4 mL) at reflux for 2 h. [b]Yield of isolated product **4a**. [c]Coupling was performed in the presence of Xphos ligand (4 mol %). [d]In this case, coupling between hydrazone **1a** and iodobenzene gives the corresponding olefin, mainly (1,3,5-trimethoxy-2-(1-phenylvinyl)benzene).

To further expand the scope of this reaction, we studied the coupling with various hydrazone partners (compounds **4n**–**4v**). As depicted in Table 2, the coupling of *N*-tosylhydrazones derived from aliphatic ketones, aldehydes, chromanones, and tetralones with different indoles led to the expected *N*-vinylindole products in excellent yields. The reaction was also extended to hindered tosylhydrazones. Substrates containing a secondary carbon atom α to the hydrazone function were successfully coupled with 5-halo-indole, to provide tetrasubstituted vinylindoles **4q** and **4r** having a cycloalkylidene unit in good yields.

In this study, we also examined the stereoselectivity issue. Interestingly, the coupling reaction of a hydrazone derived from propiophenone, which features a methoxy group in the *ortho*-position, afforded mainly the *Z*-olefin **4m** (*E*/*Z* 10/90). More interestingly, coupling between indoles and hydrazones derived from 1,2-diphenylethanone compounds afforded exclusively the *Z*-vinylindoles **4s** and **4t**, whereas the reaction with the hydrazone derived from 3-pentanone provided a 45/55 mixture of the *E*/*Z* isomers (compound **4o**).

To highlight the power of this vinylation of indoles, the Pd-catalyzed Csp^2–N bond formation reaction was applied to other types of substrates (Table 3). 2- or 3-Substituted indoles showed excellent reactivity (compounds **4w**–**4ae**). Gratifyingly, sterically hindered *N*-tosylhydrazones featuring *ortho*/*ortho'*-substituents on the aromatic ring could be installed efficiently (compounds **4w**, **4x**, **4z**, and **4ab**). The use of 2,3-disubstituted indole also delivered the corresponding product in a good 88% yield (compound **4ae**). It should be noted that the chemoselectivity of this reaction must be underlined since tryptamine was selectively coupled with hydrazone, giving rise to compound **4aa** in a good 78% yield.

Encouraged by the results obtained with substituted indoles, we proceeded to apply this catalytic system to other *N*-H azoles. To our delight, it was found that the reaction is applicable to carbazoles (compounds **4af**–**4ah**), including 3,6-dibromocarbazole, which can be subjected to a further functionalization (C–Br bonds). The resulting compound **4ah** may be used for the synthesis of some multiaryl compounds by stepwise cross-coupling reactions.[10]

Also, coupling worked well for other *N*-H azoles, such as 1,2,3,4-tetrahydrocarbazole, pyrrole, 1,5,6,7-tetrahydro-4*H*-indol-4-one, benzimidazole, and imidazole. Thus, the corresponding *N*-vinylazoles (compounds **4ai**–**4an**) were obtained in yields ranging from 35% to 80%.

A plausible mechanism for this Pd-catalyzed oxidative coupling is depicted in Scheme 4. Iodobenzene acts as a viable oxidant for this transformation, and its dehalogenation leads to the formation of unreactive benzene that becomes part of the solvent.[19] The reaction is initiated by the oxidation of Pd(0) to Pd(II) species by iodobenzene, which reacts with the in situ generated diazo substrate **I** to give Pd–carbene complex **III**.[20] Ligand exchange between complex **III** and indole leads to the formation of species **IV**, which undergoes a migratory insertion of the indole unit to furnish the alkyl palladium complex **V**. Further β-hydride elimination provides the cross-coupling product **4** and species **VI**, which regenerates the Pd(0) catalyst after reductive elimination.

To obtain additional information on the reaction mechanism, the coupling between d_2-deuterated **6**[21] and indole **2a** has been performed under our optimized catalytic conditions using 3,4,5-trimethoxyiodobenzene **7** as the oxidant instead of iodobenzene. According to the mechanism depicted in Scheme 4, we can expect the formation, through a reductive elimination step, of trimethoxydeuterobenzene **8**. As shown in Scheme 5, as expected, the reaction product **4ao** isolated from this experiment contains a significant amount of deuterium at the vinyl carbon β to indole. In addition, we isolated compound **8** in which the carbon–I bond of **7** was replaced by a C–deuterium bond. This result is an agreement with the formation of **4** by β-hydrogen elimination and the role played by aryl iodide **7** as the oxidant.

The *Z*-stereoselectivity observed for compounds **4r** and **4s** was rationalized by performing a computational chemistry study.[22] Specifically, we were interested in the *syn*-β-hydrogen elimination step, which would be involved in the control of the

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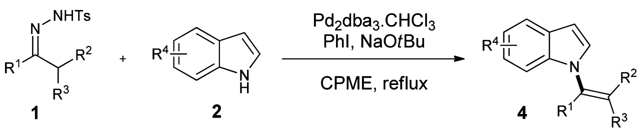
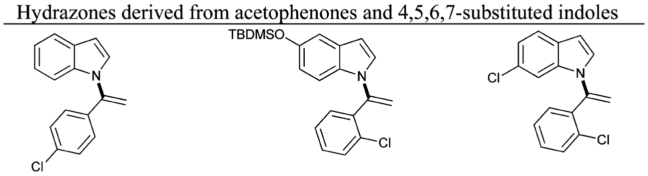
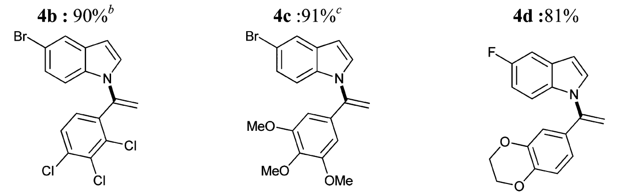
Table 2. Scope of the Pd-Catalyzed Cross-Coupling of Hydrazones 1 and Indole Derivatives 2[a,b,c,d]



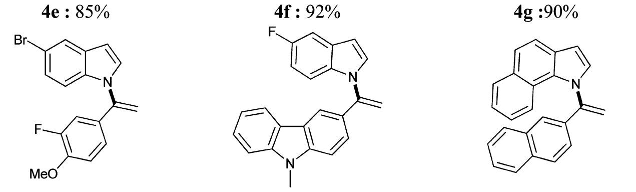
Hydrazones derived from acetophenones and 4,5,6,7-substituted indoles



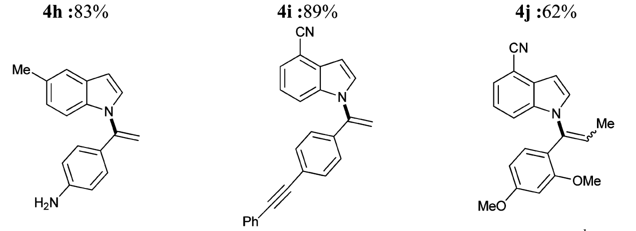
4b : 90%[b] | **4c** :91%[c] | **4d** :81%



4e : 85% | **4f** : 92% | **4g** :90%

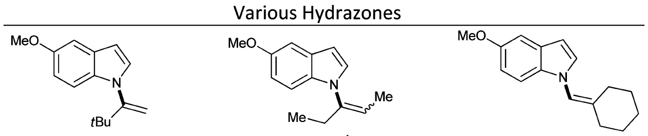


4h :83% | **4i** :89% | **4j** :62%

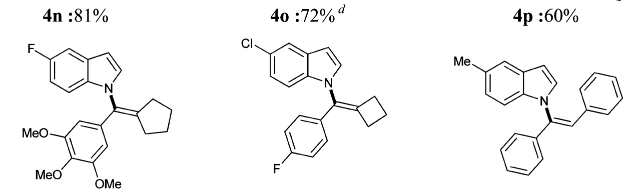


4k :70% | **4l** :72% | **4m** :78%[d]

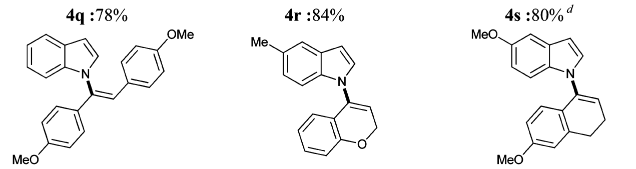
Various Hydrazones



4n :81% | **4o** :72%[d] | **4p** :60%



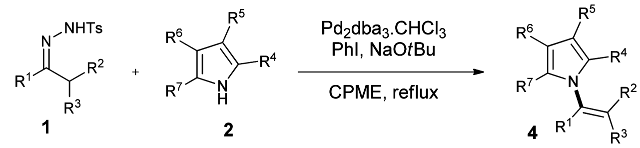
4q :78% | **4r** :84% | **4s** :80%[d]



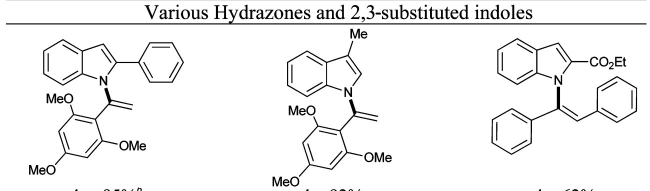
4t :90%[d] | **4u** :72% | **4v** :86%

[a]Reaction conditions: *N*-tosylhydrazone **1** (0.75 mmol), indole **2** (0.5 mmol), PhI (0.6 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (2 mol %), NaO*t*Bu (1.4 mmol), CPME (4 mL) at reflux for 1 h. [b]Yield of isolated product. [c]Coupling with unprotected 5-hydroxyindole does not proceed. [d]Compound **4m** was obtained as a 10:90 mixture of *E*/*Z* isomers. Compound **4o** was obtained as a 45:55 mixture of *E*/*Z* isomers. Compounds **4s** and **4t** were obtained as single *Z* isomers. *E*/*Z* ratio was determined by [1]HNMR.

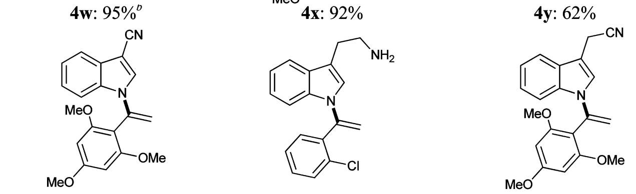
Table 3. Scope of the Pd-Catalyzed Cross-Coupling of Hydrazones 1 and Indole Derivatives 2[a,b]



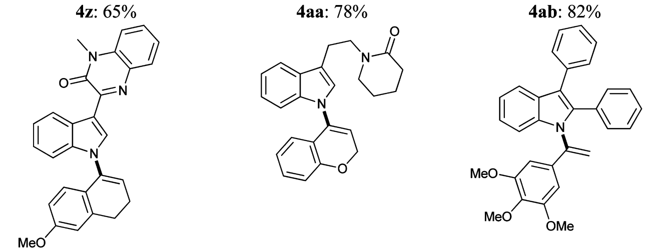
Various Hydrazones and 2,3-substituted indoles



4w: 95%[b] | **4x**: 92% | **4y**: 62%

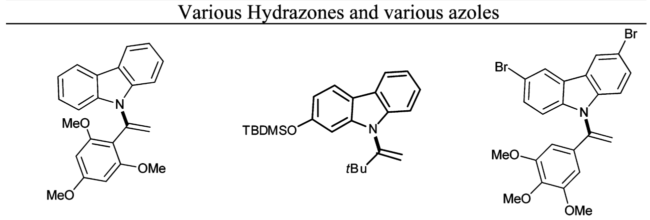


4z: 65% | **4aa**: 78% | **4ab**: 82%

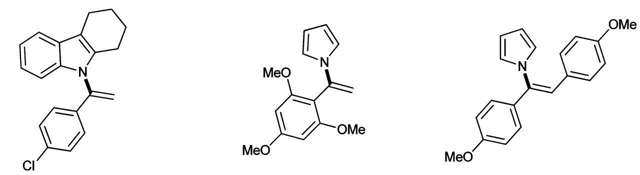


4ac: 90% | **4ad**: 78% | **4ae**: 88%

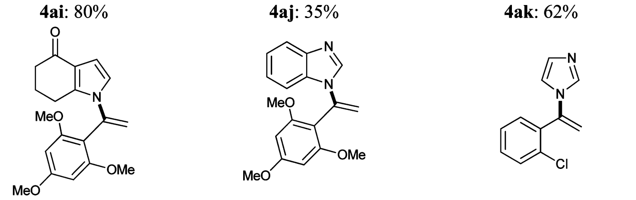
Various Hydrazones and various azoles



4af: 96% | **4ag**: 73% | **4ah**: 74%



4ai: 80% | **4aj**: 35% | **4ak**: 62%

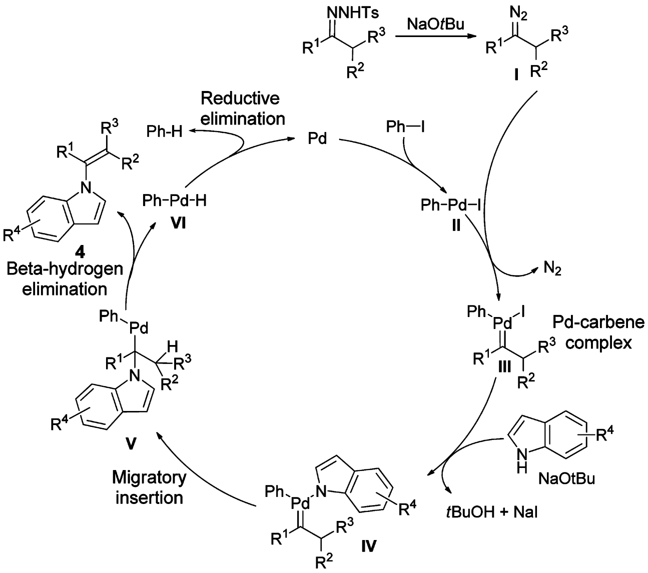


4al: 55% | **4am**: 40% | **4an**: 43%

[a]Reaction conditions: *N*-tosylhydrazone **1** (0.75 mmol), indole **2** (0.5 mmol), PhI (0.6 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (2 mol %), NaO*t*Bu (1.4 mmol), CPME (4 mL) at reflux for 1 h. [b]Yield of isolated product.

stereochemistry of the double bond. Starting from the alkyl palladium complex **A** (Scheme 6), we compute for the *β*-hydrogen elimination step both the transition states **TS-*Z*** and **TS-*E*** that lead to the *Z* and *E* double bonds, respectively (isomers **B-*Z*** and **B-*E***). The examination of the molecular models of transition states shows similar arrangements of the phenyl and indole substituents. In both cases, the indole moeity (in red in Scheme 6) is almost orthogonal relative to the plane formed by the incipient double bond, with its six-membered

Scheme 4. Proposed Mechanism for Pd-Catalyzed Cross-Coupling of *N*-Tosylhydrazones with Indoles



ring anti to the metal. This conformation minimizes the steric interaction for indole and induces an almost coplanar position of the phenyl group (in blue in Scheme 6) and the incipient double bond. In this situation, the steric hindrance of the phenyl group (in blue) close to the incipient double bond exceeds that of the indole (in red). The phenyl substituent located on the alkyl chain (in green in Scheme 6) has, therefore, lower steric interaction when located *trans* to this phenyl group (in blue). Consequently, the transition state leading to the *Z* isomer (**TS-*Z***) is 2.5 kcal·mol^{-1} lower in energy than **TS-*E***, explaining that the formation of the *Z* isomer is clearly favored.

■ CONCLUSION

In summary, we have described a new procedure for the preparation of *N*-vinylazole compounds by free-ligand Pd-catalyzed cross-coupling between *N*-tosylhydrazones and various azole reagents. This reaction, which involves an unprecedented indole migratory insertion of a palladium carbene, was used to obtain a variety of *N*-vinylazoles, including trisubstituted compounds, in a stereoselective manner. Unlike established methods for *N*-vinylazole formation, the current methodology requires no additional organometallic reagent. Moreover, the *N*-tosylhydrazones used are readily available from the corresponding ketones or aldehydes and are easy to handle. All of these features make this method a useful extension of palladium-catalyzed coupling reactions for *N*-vinylazole synthesis.

■ EXPERIMENTAL SECTION

General Methods. Solvent peaks were used as reference values, with $CDCl_3$ at 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR. Chemical shifts δ are given in parts per million, and the following abbreviations are used: singlet (s), doublet (d), doublet of doublet (dd), triplet (t), multiplet (m), and broad singlet (bs). Reaction courses and product mixtures were routinely monitored by TLC on silica gel, and compounds were visualized with phosphomolybdic acid/Δ, anisaldehyde/Δ, or vanillin/Δ. Flash chromatography was performed using silica gel 60 (40−63 mm, 230−400 mesh) at medium pressure (200 mbar). Fluorobenzene was used as received; dioxane, dichloromethane, cyclohexane, and tetrahydrofuran were dried using the procedures described in *Purification of Laboratory Chemicals*.[23] Organic extracts were, in general, dried over $MgSO_4$ or Na_2SO_4. High-resolution mass spectra were recorded with the aid of a MicrOTOF-Q II. All products reported showed ^{1}H and ^{13}C NMR spectra in agreement with the assigned structures.

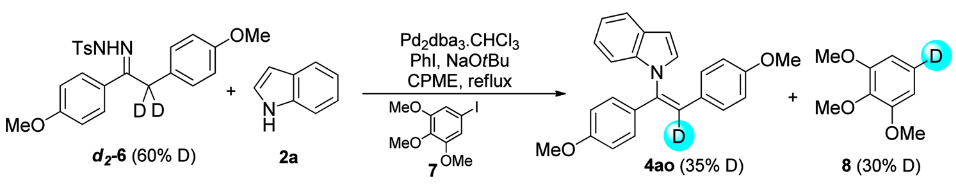
General Procedure for Preparation of Hydrazones.[24] To a rapidly stirred suspension of *p*-toluenesulphonohydrazide (5 mmol) in dry methanol (10 mL) at 60 °C, the ketone (5 mmol) was added dropwise. Within 5−60 min, the *N*-tosylhydrazone began to precipitate. The mixture was cooled to 0 °C, and the product was collected on a Büchner funnel, washed with petroleum ether, and then dried in vacuo to afford the pure product. The reaction provides the *N*-tosylhydrazone derivatives in about 88−99% yields.

Typical Pd-Catalyzed Oxidative Cross-Coupling of Hydrazones and Indole Derivatives. A 10 mL round-bottom flask with a condenser under an argon atmosphere was charged with *N*-tosylhydrazone (1.5 equiv), iodobenzene (1.2 equiv), $Pd_2(dba)_3$·$CHCl_3$ (2 mol %), NaO*t*Bu (2.8 equiv), and indole (1 equiv). A 4 mL portion of CPME was then added via syringe at room temperature. The flask was put into a preheated oil bath and stirred at reflux for 1 h. The crude reaction mixture was allowed to cool to room temperature. EtOAc was added to the mixture, which was filtered through Celite. The solvents were evaporated under reduced pressure, and the crude residue was purified by flash chromatography on silica gel.

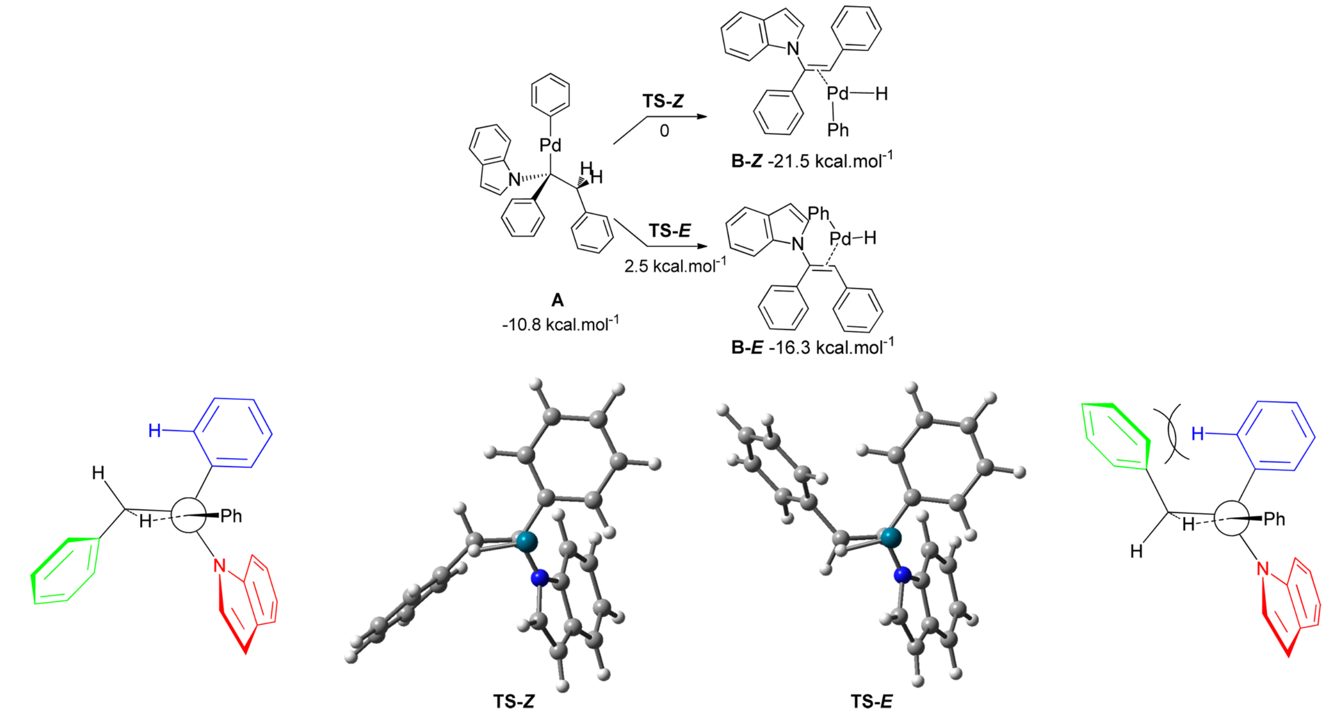
*1-(1-(2,4,6-Trimethoxyphenyl)vinyl)-1H-indole **4a**.* Flash chromatography on silica gel (EtOAc/cyclohexane 2/98) afforded 150 mg of **4a** (0.49 mmol, yield 97%); white solid, mp: 134−136 °C; TLC: R_f = 0.58 (EtOAc/cyclohexane, 20/80, SiO_2); IR (neat) 1641, 1604, 1582, 1453, 1414; ^{1}H NMR (300 MHz, CD_3COCD_3) δ (ppm) 7.52 (m, 1H), 7.36 (m, 1H), 7.17 (d, J = 3.3 Hz, 1H), 7.02 (m, 2H), 6.44 (d, J = 3.3 Hz, 1H), 6.29 (s, 2H), 5.56 (s, 1H), 5.08 (s, 1H), 3.85 (s, 3H), 3.66 (s, 6H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm) 163.0 (C), 160.4 (2C), 138.3 (C), 136.6 (C), 130.5 (C), 128.7 (CH), 122.4 (CH), 121.3 (CH), 120.4 (CH), 112.5 (CH), 109.6 (C), 109.4 (CH_2), 102.8 (CH), 91.8 (2CH), 56.3 ($2CH_3$), 55.7 (CH_3); HRMS (ESI) (M + H)$^+$: m/z calcd for $C_{19}H_{20}NO_3$ 310.1443; found 310.1431.

*1-(1-(4-Chlorophenyl)vinyl)-1H-indole **4b**.* Flash chromatography on silica gel (pentane) afforded 114 mg of **4b** (0.45 mmol, yield 90%); white solid, mp: 69−70 °C; TLC: R_f = 0.30 (cyclohexane, SiO_2); IR (neat) 1491, 1455, 1338, 1215; ^{1}H NMR (300 MHz, C_6D_6) δ (ppm) 7.65 (dt, J = 7.7, 1.1 Hz, 1H), 7.12 (m, 3H), 6.92 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 3.3 Hz, 1H), 6.76 (d, J = 8.7 Hz, 2H), 6.53 (d, J = 3.1 Hz, 1H), 5.03 (s, 1H), 4.93 (s, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ (ppm) 144.1 (C), 136.8 (C), 135.6 (C), 135.1 (C), 129.9 (C), 128.9 (2CH), 128.4 (2CH), 128.2 (CH), 122.5 (CH), 121.4 (CH), 120.8 (CH), 112.0 (CH), 108.2 (CH_2), 103.8 (CH); HRMS (APCI) (M + H)$^+$: m/z calcd for $C_{16}H_{13}ClN$ 254.0737; found 254.0762.

Scheme 5. Cross-Coupling in the Presence of Deuterated Hydrazone d_2-6



Scheme 6. DFT-Computed Relative Free Energy Values, Transition State Conformations for the β-Hydrogen Elimination (Palladium Aryl Ligand Has Been Omitted for Clarity), and Their Newman Projection Along the Pd−C$_{alkyl}$ Bond



*5-((tert-Butyldimethylsilyl)oxy)-1-(1-(2-chlorophenyl)vinyl)-1H-indole **4c**.* Flash chromatography on silica gel (Et_2O/pentane 2/98) afforded 174 mg of **4c** (0.46 mmol, yield 91%); colorless oil; TLC: R_f = 0.71 (EtOAc/cyclohexane, 10/90, SiO_2); IR (neat) 1739, 1571, 1467, 1294, 1194; ^1H NMR (300 MHz, C_6D_6) δ (ppm) 7.28 (d, J = 2.2 Hz, 1H), 7.19 (d, J = 0.5 Hz, 2H), 7.18−7.00 (m, 2H), 6.95−6.74 (m, 3H), 6.45 (dd, J = 3.3, 0.6 Hz, 1H), 5.26 (s, 1H), 4.97 (s, 1H), 1.08 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (75 MHz, C_6D_6) δ (ppm) 150.4 (C), 143.1 (C), 137.0 (C), 133.9 (C), 132.2 (C), 131.6 (CH), 131.4 (C), 130.5 (CH), 130.2 (CH), 128.4 (CH), 127.0 (CH), 116.8 (CH), 112.5(CH), 111.1 (CH), 107.8 (CH_2), 104.0 (CH), 26.0 ($3CH_3$), 18.5 (C), −4.3($2CH_3$); HRMS (APCI) $(M + H)^+$: m/z calcd for $C_{22}H_{27}ClNOSi$ 384.1550; found 384.1564.

*6-Chloro-1-(1-(2-chlorophenyl)vinyl)-1H-indole **4d**.* Flash chromatography on silica gel (pentane) afforded 116 mg of **4d** (0.41 mmol, yield 81%); colorless oil; TLC: R_f = 0.26 (cyclohexane, SiO_2); IR (neat) 1516, 1461, 1444, 1351, 1211; ^1H NMR (300 MHz, C_6D_6) δ (ppm) 7.43 (m, 1H), 7.30 (d, J = 8.4 Hz, 1H), 7.13 (m, 1H), 6.96 (m, 2H), 6.72 (m, 3H), 6.34 (dd, J = 3.4, 0.8 Hz, 1H), 5.07 (d, J = 0.7 Hz, 1H), 4.87 (d, J = 0.7 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ (ppm) 142.6 (C), 136.8 (C), 136.4 (C), 133.8 (C), 131.6 (CH), 130.5 (CH), 130.4 (CH), 129.0 (C), 128.7 (C), 128.4 (CH), 127.0 (CH), 122.4 (CH), 121.7 (CH), 112.1 (CH), 109.4 (CH_2), 104.3 (CH); HRMS (APCI) $(M + H)^+$: m/z calcd for $C_{16}H_{12}Cl_2N$ 288.0347; found 288.0349.

*5-Bromo-1-(1-(2,3,4-trichlorophenyl)vinyl)-1H-indole **4e**.* Flash chromatography on silica gel (pentane) afforded 170 mg of **4d** (0.43 mmol, yield 85%); colorless oil; TLC: R_f = 0.23 (cyclohexane, SiO_2); IR (neat) 1518, 1453, 1367, 1207; ^1H NMR (300 MHz, CD_3COCD_3) δ (ppm) 7.78 (m, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.24 (m, 2H), 7.17 (d, J = 8.8 Hz, 1H), 6.61 (dd, J = 3.4, 0.7 Hz, 1H), 5.75 (d, J = 1.2 Hz, 1H), 5.51 (d, J = 1.2 Hz, 1H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm) 142.5 (C), 137.8 (C), 135.4 (C), 135.3 (C), 132.5 (C), 131.4 (CH), 130.2 (C), 130.2 (CH), 130.0 (CH), 125.9 (CH), 124.3 (CH), 116.0 (C), 114.2 (C), 113.9 (CH), 111.3 (CH_2), 104.5 (CH); HRMS (APCI) $(M + H)^+$: m/z calcd for $C_{16}H_{10}BrCl_3N$ 399.9062; found 399.9082.

*5-Bromo-1-(1-(3,4,5-trimethoxyphenyl)vinyl)-1H-indole **4f**.* Flash chromatography on silica gel (EtOAc/cyclohexane, 2/98) afforded 178 mg of **4f** (0.46 mmol, yield 92%); colorless oil; TLC: R_f = 0.26 (EtOAc/cyclohexane, 20/80, SiO_2); IR (neat) 1736, 1581, 1504, 1449, 1412, 1370, 1335, 1230; ^1H NMR (300 MHz, CD_3COCD_3) δ (ppm) 7.79 (m, 1H), 7.37 (d, J = 3.3 Hz, 1H), 7.20 (dd, J = 8.8, 1.9 Hz, 1H), 7.06 (d, J = 8.8 Hz, 1H), 6.63 (dd, J = 3.3, 0.7 Hz, 1H), 6.61 (s, 2H), 5.72 (d, J = 0.6 Hz, 1H), 5.36 (d, J = 0.6 Hz, 1H), 3.76 (s, J = 11.2 Hz, 3H), 3.72 (s, 6H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm) 154.5 (2C), 145.4 (C), 140.5 (C), 136.1 (C), 133.0 (C), 132.1 (C), 131.2 (CH), 125.4 (CH), 124.1 (CH), 114.3 (CH), 113.8 (C), 108.9 (CH_2), 105.4 (2CH), 103.4 (CH), 60.7 (CH_3), 56.5 ($2CH_3$); HRMS (ESI) $(M + H)^+$: m/z calcd for $C_{19}H_{19}NO_3Br$ 388.0548; found 388.0552.

*1-(1-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)vinyl)-5-fluoro-1H-indole **4g**.* Flash chromatography on silica gel (EtOAc/cyclohexane, 2/98) afforded 133 mg of **4g** (0.45 mmol, yield 90%); white solid; mp: 129−131 °C; TLC: R_f = 0.38 (EtOAc/cyclohexane, 10/90, SiO_2); IR (neat) 1581, 1507, 1284, 1066; ^1H NMR (300 MHz, CD_3COCD_3) δ (ppm) 7.37 (d, J = 3.2 Hz, 1H), 7.32 (dd, J = 9.6, 2.5 Hz, 1H), 7.04 (dd, J = 9.0, 4.5 Hz, 1H), 6.88 (dd, J = 9.2, 2.5 Hz, 1H), 6.83 (m, 1H), 6.75 (m, 2H), 6.62 (d, J = 3.2 Hz, 1H), 5.61 (s, 1H), 5.29 (s, 1H), 4.27 (m, 4H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm) 160.4 (C), 157.3 (C), 145.8 (C), 145.2 (C), 144.7 (C), 132.3 (C, d, J = 254 Hz), 131.6 (CH), 130.9 (C), 130.8 (C), 120.6 (CH), 118.2 (CH), 116.3 (CH), 113.5 (CH, d, J = 10 Hz), 110.7 (CH, d, J = 26 Hz), 108.1 (CH_2), 106.3 (CH, d, J = 24 Hz), 103.7 (CH, d, J = 4 Hz), 65.3 (CH_2), 65.1 (CH_2); HRMS (ESI) $(M + H)^+$: m/z calcd for $C_{18}H_{15}NO_2F$ 296.1087; found 296.1082.

*5-Bromo-1-(1-(3-fluoro-4-methoxyphenyl)vinyl)-1H-indole **4h**.* Flash chromatography on silica gel (Et_2O/cyclohexane, 2/98) afforded 145 mg of **4h** (0.42 mmol, yield 83%); white solid; mp: 83−84 °C; TLC: R_f = 0.51 (EtOAc/cyclohexane, 20/80, SiO_2); IR (neat) 1630, 1514, 1452, 1365, 1330, 1274, 1202; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.79 (d, J = 1.7 Hz, 1H), 7.21 (m, 2H), 7.07 (dd, J = 12.1, 1.9 Hz, 1H), 7.95 (m, 3H), 6.58 (d, J = 3.2 Hz, 1H), 5.54 (s, 1H), 5.31 (s, 1H), 3.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 152.5 (C, d, J = 247 Hz), 148.8 (C, d, J = 11 Hz), 143.6 (C), 135.2 (C), 131.1 (C), 129.9 (CH), 129.8 (C), 125.1 (CH), 123.6 (CH), 123.0 (CH, d, J = 3.1 Hz), 114.8 (CH, d, J = 20 Hz), 113.7 (C), 113.4 (2CH), 108.1 (CH_2), 102.9 (CH), 56.4 (CH_3); HRMS (ESI) $(M + Na)^+$: m/z calcd for $C_{17}H_{13}BrFNNaO$ 368.0062; found 368.0060.

3-(1-(5-Fluoro-1H-indol-1-yl)vinyl)-9-methyl-9H-carbazole **4i**. Flash chromatography on silica gel (EtOAc/cyclohexane, 2/98) afforded 151 mg of **4i** (0.45 mmol, yield 89%); white solid; mp: 137−139 °C; TLC: R_f = 0.56 (EtOAc/cyclohexane, 20/80, SiO_2); IR (neat) 2927, 1601, 1469, 1446, 1369, 1247, 1188; ^{1}H NMR (300 MHz, CD_3COCD_3) δ (ppm) 8.16 (dd, *J* = 1.8, 0.7 Hz, 1H), 8.08 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.67−7.41 (m, 4H), 7.35 (ddd, *J* = 8.6, 3.9, 2.2 Hz, 2H), 7.20 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 7.01 (ddt, *J* = 9.0, 4.5, 0.7 Hz, 1H), 6.87−6.72 (m, 1H), 6.66 (dd, *J* = 3.3, 0.8 Hz, 1H), 5.67 (s, 1H), 5.34 (s, 1H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 158.2 (C, d, *J* = 235 Hz), 146.0 (C), 141.7 (C), 133.3 (C), 130.6 (CH), 130.0 (C), 129.8 (C), 128.0 (C), 126.4 (CH), 125.1 (CH), 123.1 (C), 122.8 (C), 120.7 (CH), 119.5 (CH), 119.3 (CH), 113.0 (CH, d, *J* = 9 Hz), 110.5 (CH, d, *J* = 21 Hz), 108.9 (CH), 108.6 (CH), 106.3 (CH_2), 105.8 (d, *J* = 23 Hz), 103.0 (CH, d, *J* = 4 Hz), 29.2 (CH_3); HRMS (APCI) (M + H)$^+$: *m/z* calcd for $C_{23}H_{18}FN_2$ 341.1454; found 341.1446.

1-(1-(Naphthalen-2-yl)vinyl)-1H-benzo[g]indole **4j**. Flash chromatography on silica gel (pentane) afforded 100 mg of **4j** (0.31 mmol, yield 62%); white solid; mp: 105−107 °C; TLC: R_f = 0.20 (cyclohexane, SiO_2); IR (neat) 1737, 1498, 1443, 1400, 1348, 1328, 1232; ^{1}H NMR (300 MHz, C_6D_6) δ (ppm) 8.41 (m, 1H), 7.78 (m, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.30 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.11 (m, 10H), 6.80 (d, *J* = 3.0 Hz, 1H), 5.70 (s, 1H), 5.24 (s, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ (ppm) 147.7 (C), 134.4 (C), 134.0 (C), 133.8 (C), 132.1 (C), 130.9 (C), 129.7 (CH), 129.4 (CH), 129.1 (CH), 129.0 (CH), 126.9 (CH), 126.6 (CH), 126.5 (C), 125.8 (CH), 125.4 (CH), 123.9 (CH), 123.3 (CH), 122.6 (CH), 121.8 (CH), 121.4 (CH), 113.0 (CH_2), 104.6 (CH); HRMS (APCI) (M + H)$^+$: *m/z* calcd for $C_{24}H_{18}N$ 320.1439; found 320.1451.

4-(1-(5-Methyl-1H-indol-1-yl)vinyl)aniline **4k**. Flash chromatography on silica gel (DCM/cyclohexane, 40/60) afforded 87 mg of **4k** (0.35 mmol, yield 70%); colorless oil; TLC: R_f = 0.30 (EtOAc/cyclohexane, 30/70, SiO_2); IR (neat) 1621, 1515, 1475, 1365, 1331; ^{1}H NMR (300 MHz, MeOD) δ (ppm) 7.34 (m, 1H), 7.17 (d, *J* = 3.2 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.84 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.64 (d, *J* = 8.7 Hz, 2H), 6.46 (dd, *J* = 3.3, 0.7 Hz, 1H), 5.35 (s, 1H), 5.06 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, MeOD) δ 150.3 (C), 147.1 (C), 136.3 (C), 131.1 (C), 130.1 (C), 129.8 (CH), 129.0 (2CH), 127.6 (C), 124.2 (CH), 121.3 (CH), 115.8 (2CH), 112.7 (CH), 104.2 (CH_2), 103.1 (CH), 21.4 (CH_3); HRMS (ESI) (M + H)$^+$: *m/z* calcd for $C_{17}H_{17}N_2$ 249.1392; found 249.1390.

1-(1-(4-(Phenylethynyl)phenyl)vinyl)-1H-indole-4-carbonitrile **4l**. Flash chromatography on silica gel (EtOAc/cyclohexane, 2/98) afforded 124 mg of **4l** (0.36 mmol, yield 72%); white solid; mp: 113−115 °C; TLC: R_f = 0.52 (EtOAc/cyclohexane, 20/80, SiO_2); IR (neat) 2223, 1628, 1510, 1432, 1332; ^{1}H NMR (300 MHz, C_6D_6) δ 7.52 (m, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.12 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.00 (m, 3H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.73 (dd, *J* = 3.3, 0.8 Hz, 1H), 6.73 (m, 2H), 5.09 (d, *J* = 0.6 Hz, 1H), 4.77 (d, *J* = 0.6 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 143.8 (C), 136.3 (C), 136.1 (C), 132.3 (2CH), 132.0 (2CH), 131.1 (C),131.1 (CH), 128.9 (CH), 128.8 (2CH), 126.9 (2CH), 125.7 (CH), 125.0 (CH), 123.5 (C), 122.1 (C), 118.4 (CH), 116.1 (C), 110.0 (CH_2), 104.6 (C), 102.5 (CH), 92.0 (C), 89.4 (C); HRMS (ESI) (M + H)$^+$: *m/z* calcd for $C_{25}H_{17}N_2$ 345.1392; found 345.1390.

1-(1-(2,4-Dimethoxyphenyl)prop-1-en-1-yl)-1H-indole-4-carbonitrile **4m**. Flash chromatography on silica gel (EtOAc/cyclohexane, 2/98) afforded 125 mg of **4m** (0.39 mmol, yield 78%); yellow oil; TLC: R_f = 0.42 (EtOAc/cyclohexane, 10/90, SiO_2); IR (neat) 2225, 1736, 1609, 1576, 1503, 1433, 1337, 1303, 1240, 1208. Data for *Z* major isomer: ^{1}H NMR (400 MHz, CD_3COCD_3,) δ (ppm) 7.50 (dd, *J* = 7.3, 0.7 Hz, 1H), 7.46 (d, *J* = 3.2 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.23 (m, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.75 (dd, *J* = 3.2, 0.7 Hz, 1H), 6.53 (d, *J* = 2.4 Hz, 1H), 6.46 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.32 (q, *J* = 7.0 Hz, 1H), 3.78 (s, 3H), 3.59 (s, 3H), 1.58 (d, *J* = 7.0 Hz, 3H). Data for *Z* major isomer: ^{13}C NMR (101 MHz, CD_3COCD_3,) δ 162.2 (C), 159.5 (C), 137.1 (C), 135.2 (C), 133.0 (CH), 131.0 (CH), 130.2 (C), 125.9 (CH), 125.6 (CH), 122.3 (CH), 120.5 (C), 119.0 (C), 117.0 (CH), 105.7 (CH), 103.6 (C), 101.0 (CH), 99.6 (CH), 55.9 (CH_3), 55.7 (CH_3), 13.8 (CH_3); HRMS (ESI) (M + H)$^+$: *m/z* calcd for $C_{20}H_{19}N_2O_2$ 319.1447; found 319.1443.

1-(3,3-Dimethylbut-1-en-2-yl)-5-methoxy-1H-indole **4n**. Flash chromatography on silica gel (cyclohexane) afforded 93 mg of **4n** (0.41 mmol, yield 81%); colorless oil; TLC: R_f = 0.20 (cyclohexane, SiO_2); IR (neat) 1639, 1478, 1447, 1288, 1269, 1209, 1162, 1146; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.21 (d, *J* = 8.9 Hz, 1H), 7.09 (m, 2H), 6.86 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.50 (d, *J* = 3.1 Hz, 1H), 5.52 (s, 1H), 5.14 (s, 1H), 3.88 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 154.5 (C), 154.1 (C), 133.6 (C), 129.5 (CH), 128.1(C), 113.4 (CH_2), 112.2 (CH), 112.0 (CH), 102.1 (CH), 101.0 (CH), 56.0 (CH_3), 38.0 (C), 29.5 ($3CH_3$); HRMS (APCI) (M + H)$^+$: *m/z* calcd for $C_{15}H_{20}NO$ 230.1545; found 230.1541.

5-Methoxy-1-(pent-2-en-3-yl)-1H-indole **4o**. Flash chromatography on silica gel (EtOAc/cyclohexane, 5/95) afforded 77 mg of **4o** (0.36 mmol, yield 72%); colorless oil; TLC: R_f = 0.28 (EtOAc/cyclohexane, 2/98, SiO_2); IR (neat) 1476, 1436, 1239, 1215, 1193, 1167, 1147; Data for *Z* and *E* isomers: ^{1}H NMR (300 MHz, C_6D_6) δ (ppm) 7.28 (d, *J* = 8.8 Hz, 1H), 7.16 (m, 2H), 7.12 (d, *J* = 8.8 Hz, 1H), 7.11 (d, *J* = 8.8 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 1H), 6.91 (d, *J* = 3.1 Hz, 1H), 6.81 (d, *J* = 3.1 Hz, 1H), 6.58 (dd, *J* = 3.1, 0.7 Hz, 1H), 6.55 (dd, *J* = 3.1, 0.7 Hz, 1H), 5.39 (q, *J* = 7.0 Hz, 1H), 5.29 (qt, *J* = 6.8, 1.2 Hz, 1H), 3.55 (s, 3H), 3.55 (s, 3H), 2.24 (q, *J* = 7.5 Hz, 2H), 2.15 (qt, *J* = 7.4, 1.3 Hz, 2H), 1.46 (d, *J* = 7.0 Hz, 3H), 1.25 (dt, *J* = 6.8, 1.4 Hz, 3H), 0.73 (t, *J* = 7.3 Hz, 3H), 0.68 (t, *J* = 7.3 Hz, 3H). Data for *Z* and *E* isomers: ^{13}C NMR (75 MHz, C_6D_6) δ 155.0 (C), 155.0 (C), 139.8 (C), 139.7 (C), 129.7 (C), 129.1 (C), 127.4 (C), 127.3 (C), 120.0 (CH), 119.4 (CH), 112.8 (CH), 112.7 (CH), 111.8 (CH), 111.6 (CH), 102.8 (CH), 102.7 (CH), 102.4 (CH), 102.0 (CH), 55.3 (CH_3), 55.3 (CH_3), 29.9 (CH_2), 23.5 (CH_2), 12.7 (CH_3), 12.4 (CH_3), 12.0 (CH_3), 11.7 (CH_3); HRMS (ESI) (M + H)$^+$: *m/z* calcd for $C_{14}H_{18}NO$ 216.1388; found 216.1380.

1-(Cyclohexylidenemethyl)-5-methoxy-1H-indole **4p**. Flash chromatography on silica gel (cyclohexane) afforded 72 mg of **4p** (0.30 mmol, yield 60%); colorless oil; TLC: R_f = 0.33 (EtOAc/cyclohexane, 5/95, SiO_2); IR (neat) 1605, 1510, 1442, 1244, 1176; ^{1}H NMR (300 MHz, CD_3COCD_3) δ 7.19 (d, *J* = 8.8 Hz, 1H), 7.10 (d, *J* = 13.5 Hz, 1H), 7.09 (d, *J* = 12.7 Hz, 1H), 6.81 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.62 (s, 1H), 6.44 (dd, *J* = 3.1, 0.8 Hz, 1H), 3.80 (s, 3H), 2.33 (m, 2H), 2.17 (m, 2H), 1.65 (m, 4H), 1.53 (m, 2H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ 155.5 (C), 140.2 (2C), 132.9 (C), 129.7 (CH), 117.8 (CH), 112.7 (CH), 111.6 (CH), 103.2 (CH), 102.4 (CH), 55.9 (CH_3), 33.9 (CH_2), 29.0 ($2CH_2$), 28.1 (CH_2), 27.1 (CH_2); HRMS (ESI) (M + H)$^+$: *m/z* calcd for $C_{16}H_{20}NO$ 242.1545; found 242.1543.

1-(Cyclopentylidene(3,4,5-trimethoxyphenyl)methyl)-5-fluoro-1H-indole **4q**. Flash chromatography on silica gel (EtOAc/cyclohexane, 2/98) afforded 149 mg of **4q** (0.39 mmol, yield 78%); white solid; mp: 125−127 °C; TLC: R_f = 0.37 (EtOAc/cyclohexane, 20/80, SiO_2); IR (neat) 1581, 1506, 1474, 1448, 1413, 1341, 1237, 1128; ^{1}H NMR (300 MHz, C_6D_6) δ 7.39 (dd, *J* = 9.3, 2.3 Hz, 1H), 7.05 (m, 1H), 6.96 (m, 2H), 6.49 (dd, *J* = 3.1, 0.7 Hz, 1H), 6.41 (s, 2H), 3.80 (s, 3H), 3.29 (s, 6H), 2.51 (t, *J* = 7.0 Hz, 2H), 2.03 (t, *J* = 7.2 Hz, 2H), 1.51 (m, 2H), 1.36 (m, 2H); ^{13}C NMR (75 MHz, C_6D_6) δ 158.82 (C, d, *J* = 234 Hz), 154.0 (2C), 144.8 (C), 134.1 (C), 133.2 (C), 130.1 (CH), 129.1 (C, d, *J* = 10 Hz), 128.7 (C), 111.7 (CH, d, *J* = 10 Hz), 110.9 (CH, d, *J* = 26 Hz), 106.3 (CH, d, *J* = 23 Hz), 105.9 (2CH), 102.8 (C, d, *J* = 5 Hz), 60.5 (CH_3), 55.9 ($2CH_3$), 33.1 (CH_2), 32.4 (CH_2), 27.9 (CH_2), 26.1 (CH_2); HRMS (ESI) (M + Na)$^+$: *m/z* calcd for $C_{23}H_{24}FNNaO_3$ 404.1638; found 404.1615.

5-Chloro-1-(cyclobutylidene(4-fluorophenyl)methyl)-1H-indole **4r**. Flash chromatography on silica gel (pentane) afforded 130 mg of **4r** (0.42 mmol, yield 84%); white solid; mp: 71−74 °C; TLC: R_f = 0.47 (cyclohexane, SiO_2); IR (neat) 1602, 1507, 1454, 1370, 1328, 1231, 1208, 1159; ^{1}H NMR (300 MHz, C_6D_6) δ (ppm) 7.68 (m, 1H), 7.17 (m, 1H), 6.86 (d, *J* = 8.7 Hz, 1H), 6.74 (d, *J* = 3.2 Hz, 1H), 6.69 (m, 4H), 6.39 (dd, *J* = 3.2, 0.8 Hz, 1H), 2.66 (m, 2H), 2.30 (m, 2H), 1.64 (m, 2H). ^{13}C NMR (75 MHz, C_6D_6) δ (ppm) 162.3 (C, d, *J* = 247 Hz), 142.0 (C), 135.0 (C), 133.0 (C), 132.9 (C), 129.9 (C), 129.6 (CH), 128.2 (2CH), 126.3 (C), 122.9 (CH), 121.0 (CH), 115.7 (2CH, d, *J* = 21.6 Hz), 112.1 (CH), 102.7 (CH), 31.6 (CH_2), 30.4

(CH_2), 17.4 (CH_2); HRMS (ESI) (M + H)$^+$: *m/z* calcd for $C_{19}H_{16}ClFN$ 312.0955; found 312.0939.

(Z)-1-(1,2-Diphenylvinyl)-5-methyl-1H-indole **4s**. Flash chromatography on silica gel (pentane) afforded 124 mg of **4s** (0.40 mmol, yield 80%); white solid; mp: 100−102 °C; TLC: R_f = 0.33 (cyclohexane, SiO_2); IR (neat) 1474, 1448, 1391, 1211; ^{1}H NMR (300 MHz, C_6D_6) δ 7.45 (m, 1H), 7.12 (m, 2H), 7.02 (m, 4H), 6.84 (m, 7H), 6.78 (d, *J* = 3.2 Hz, 1H), 6.58 (dd, *J* = 3.2, 0.8 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 139.0 (C), 136.9 (C), 135.4 (C), 134.6 (C), 129.9 (C), 129.8 (C), 129.1 (2CH), 128.9 (2CH), 128.7 (2CH), 126.6 (2CH), 125.0 (CH), 124.5 (CH), 121.2 (CH), 111.9 (CH), 104.0 (CH), 21.5 (CH_3); HRMS (ESI) (M + H)$^+$: *m/z* calcd for $C_{23}H_{20}N$ 310.1596; found 310.1568.

(Z)-1-(1,2-Diphenylvinyl)-5-methyl-1H-indole **4t**. Flash chromatography on silica gel (EtOAc/cyclohexane, 1/99) afforded 160 mg of **4t** (0.45 mmol, yield 90%); white solid; mp: 109−100 °C; TLC: R_f = 0.39 (EtOAc/cyclohexane, 10/90, SiO_2); IR (neat) 1735, 1606, 1512, 1456, 1301, 1244, 1216, 1175; ^{1}H NMR (300 MHz, CD_3COCD_3) δ (ppm) 7.84−7.51 (m, 1H), 7.22−6.94 (m, 7H), 6.91−6.82 (m, 2H), 6.79−6.70 (m, 3H), 6.64 (d, *J* = 9.0 Hz, 2H), 3.79 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm).161.0 (C), 160.1 (C), 136.4 (C), 134.4 (C), 132.0 (C), 130.9 (2CH), 129.8 (C), 129.3 (CH), 128.5(C), 127.7 (2CH), 124.1 (CH), 122.9 (CH), 121.6 (CH), 120.9 (CH), 114.9 (2CH), 114.5 (2CH), 112.1 (CH), 104.3 (CH), 55.7 (CH_3), 55.4 (CH_3); HRMS (ESI) (M + H)$^+$: *m/z* calcd for $C_{24}H_{22}NO_2$ 356.1651; found 356.1649.

1-(2H-Chromen-4-yl)-5-methyl-1H-indole **4u**. Flash chromatography on silica gel (Et_2O/cyclohexane, 1/99) afforded 94 mg of **4u** (0.36 mmol, yield 72%); colorless oil; TLC: R_f = 0.56 (EtOAc/cyclohexane, 5/95, SiO_2); IR (neat) 1648, 1484, 1385, 1335, 1224, 1173, 1121; ^{1}H NMR (300 MHz, CD_3COCD_3) δ (ppm) 7.42 (m, 1H), 7.26 (d, *J* = 3.2 Hz, 1H), 7.22 (td, *J* = 7.8, 1.6 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.93 (m, 2H), 6.82 (td, *J* = 7.6, 1.1 Hz, 1H), 6.57 (m, 2H), 6.04 (t, *J* = 3.9 Hz, 1H), 5.04 (d, *J* = 3.9 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm) 156.2 (C), 154.0 (C), 134.4 (C), 131.1 (CH), 130.2 (C), 130.0 (C), 129.3 (CH), 124.4 (CH), 124.4 (CH), 122.2 (CH), 122.0 (C), 121.4 (CH), 118.8 (CH), 117.1 (CH), 111.6 (CH), 103.4 (CH), 66.0 (CH_2), 21.4 (CH_3); HRMS (APCI) (M + H)$^+$: *m/z* calcd for $C_{18}H_{16}NO$ 262.1232; found 262.1239.

5-Methoxy-1-(6-methoxy-3,4-dihydronaphthalen-1-yl)-1H-indole **4v**. Flash chromatography on silica gel (EtOAc/cyclohexane, 2/98) afforded 131 mg of **4v** (0.43 mmol, yield 86%); colorless oil; TLC: R_f = 0.44 (EtOAc/cyclohexane, 20/80, SiO_2); IR (neat) 3391, 3293, 1604, 1476, 1280, 1252; ^{1}H NMR (300 MHz, C_6D_6) δ 7.18 (d, *J* = 2.3 Hz, 1H), 7.13 (m, 1H), 7.06 (d, *J* = 3.1 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.69 (d, *J* = 2.6 Hz, 1H), 6.62 (m, 2H), 6.30 (dd, *J* = 8.5, 2.6 Hz, 1H), 5.65 (t, *J* = 4.7 Hz, 1H), 3.52 (s, 3H), 3.24 (s, 3H), 2.54 (t, *J* = 7.9 Hz, 2H), 2.11−1.93 (m, 2H); ^{13}C NMR (75 MHz, C_6D_6) δ 160.1 (C), 155.3 (C), 138.4 (C), 136.9 (C), 132.7 (C), 129.9 (C), 129.2 (CH), 125.6 (C), 125.2 (CH), 121.7 (CH), 114.7 (CH), 112.9 (CH), 112.6 (CH), 111.2 (CH), 103.0 (CH), 102.6 (CH), 55.5 (CH_3), 54.8 (CH_3), 28.3 (CH_2), 22.9 (CH_2); HRMS (ESI) (M + H)$^+$: *m/z* calcd for $C_{20}H_{20}NO_2$ 306.1494; found 306.1499.

2-Phenyl-1-(1-(2,4,6-trimethoxyphenyl)vinyl)-1H-indole **4w**. Flash chromatography on silica gel (EtOAc/cyclohexane 2/98) afforded 182 mg of **4w** (0.48 mmol, yield 95%); white solid ; mp: 114−117 °C; TLC: R_f = 0.61 (EtOAc/cyclohexane, 20/80, SiO_2); IR (neat) 1603, 1581, 1454, 1413, 1332, 1226, 1204; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.62 (d, *J* = 7.2 Hz, 1H), 7.49 (m, 3H), 7.19 (m, 5H), 6.55 (s, 1H), 5.86 (s, 2H), 5.66 (s, 1H), 5.59 (s, 1H), 3.73 (s, 3H), 3.38 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 161.2 (C), 159.3 (2C), 141.2 (C), 139.7 (C), 135.5 (C), 133.9 (C), 128.9 (2CH), 128.4 (C), 127.5 (2CH), 126.8 (CH), 121.7 (CH), 120.1 (CH), 119.9 (CH), 116.6 (CH_2), 111.8 (CH), 109.7 (C), 103.5 (CH), 90.5 (2CH), 55.6 ($2CH_3$), 55.4 (CH_3); HRMS (ESI) (M + Na)$^+$: *m/z* calcd for $C_{25}H_{23}NNaO_3$ 408.1576; found 408.1549.

3-Methyl-1-(1-(2,4,6-trimethoxyphenyl)vinyl)-1H-indole **4x**. Flash chromatography on silica gel (EtOAc/cyclohexane 2/98) afforded 149 mg of **4x** (0.46 mmol, yield 92%); white solid; mp: 134−136 °C; TLC: R_f = 0.35 (EtOAc/cyclohexane, 10/90, SiO_2); IR (neat) 1604, 1582, 1496, 1453, 1414, 1355, 1225, 1204; ^{1}H NMR (300 MHz, CD_3COCD_3) δ (ppm) 7.47 (m, 1H), 7.32 (m, 1H), 7.03 (m, 2H), 6.94 (d, *J* = 1.1 Hz, 1H), 6.29 (s, 2H), 5.49 (s, 1H), 4.96 (s, 1H), 3.85 (s, 3H), 3.66 (s, 6H), 2.24 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm) 163.0 (C), 160.4 (2C), 138.2 (C), 136.9 (C), 130.9 (C), 129.7 (C), 126.1 (CH), 122.5 (CH), 119.9 (CH), 119.4 (CH), 112.5 (CH), 111.7 (C), 107.6 (CH_2), 91.8 (2CH), 56.3 ($2CH_3$), 55.8 (CH_3), 9.6 (CH_3); HRMS (ESI) (M + H)$^+$: *m/z* calcd for $C_{20}H_{22}NO_3$ 324.1600; found 324.1594.

(Z)-Ethyl 1-(1,2-Diphenylvinyl)-1H-indole-2-carboxylate **4y**. Flash chromatography on silica gel (EtOAc/cyclohexane 1/99) afforded 114 mg of **4y** (0.31 mmol, yield 62%); white solid ; mp: 124−126 °C; TLC: R_f = 0.57 (EtOAc/cyclohexane, 10/90, SiO_2); IR (neat) 1712, 1524, 1448, 1406, 1237, 1210, 1193; ^{1}H NMR (300 MHz, C_6D_6) δ (ppm) 7.61 (m, 2H), 7.17 (m, 4H), 7.01 (m, 5H), 6.91 (m, 2H), 6.81 (m, 3H), 3.85 (qq, *J* = 10.8, 7.1 Hz, 2H), 0.80 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ (ppm) 160.6 (C), 139.8 (C), 138.9 (C), 136.1 (C), 135.5 (C), 129.6 (C), 128.9 (2CH), 128.8 (2CH), 128.8 (2CH), 128.5 (CH), 127.3 (C), 126.8 (CH), 126.1 (CH), 125.8 (2CH), 122.8 (CH), 122.0 (CH), 112.3 (CH), 112.2 (CH), 60.5 (CH_2), 14.0 (CH_3) ; HRMS (ESI) (M + Na)$^+$: *m/z* calcd for $C_{25}H_{21}NNaO_2$ 390.1470; found 390.1471.

1-(1-(2,4,6-Trimethoxyphenyl)vinyl)-1H-indole-3-carbonitrile **4z**. Flash chromatography on silica gel (EtOAc/cyclohexane 5/95) afforded 110 mg of **4z** (0.33 mmol, yield 65%); white solid; mp: 116−118 °C; TLC: R_f = 0.33 (EtOAc/cyclohexane, 20/80, SiO_2); IR (neat) 1647, 1581, 1496, 1314, 1226, 1205, 1158; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.77 (m, 1H), 7.69 (s, 1H), 7.52 (m, 1H), 7.30 (m, 2H), 6.19 (s, 2H), 5.76 (s, 1H), 5.46 (s, 1H), 3.89 (s, 3H), 3.73 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 162.4 (C), 159.5 (2C), 136.1 (C), 135.5 (C), 135.3 (CH), 128.1 (C), 123.9 (CH), 122.2 (CH), 119.7 (CH), 116.2 (C), 114.0 (CH_2), 112.7 (CH), 107.3 (C), 90.9 (2CH), 86.5 (C), 56.0 ($2CH_3$), 55.6 (CH_3); HRMS (ESI) (M + Na)$^+$: *m/z* calcd for $C_{20}H_{18}N_2NaO_3$ 357.1215; found 357.1187.

2-(1-(1-(2-Chlorophenyl)vinyl)-1H-indol-3-yl)ethanamine **4aa**. Flash chromatography on silica gel (MeOH/DCM 2/98) afforded 115 mg of **4aa** (0.39 mmol, yield 78%); yellow oil ; TLC: R_f = 0.47 (MeOH/DCM, 10/90, SiO_2); IR (neat) 3467, 1735, 1455, 1376, 1225, 1046; ^{1}H NMR (300 MHz, MeOD) δ (ppm) 7.55 (m, 2H), 7.38 (m, 3H), 7.06 (m, 3H), 6.95 (s, 1H), 5.53 (d, *J* = 0.5 Hz, 1H), 5.25 (d, *J* = 0.4 Hz, 1H), 2.90 (m, 4H); ^{13}C NMR (75 MHz, MeOD) δ (ppm) 144.5 (C), 137.9 (C), 137.6 (C), 134.5 (C), 132.8 (CH), 131.6 (CH), 131.2 (CH), 130.6 (C), 128.4 (CH), 126.7 (CH), 123.4 (CH), 121.1 (CH), 119.9 (CH), 115.7 (C), 112.6 (CH), 108.3 (CH_2), 42.5 (CH_2), 28.9 (CH_2); HRMS (ESI) (M + H)$^+$: *m/z* calcd for $C_{18}H_{18}ClN_2$ 297.1159; found 297.1139.

2-(1-(1-(2,4,6-Trimethoxyphenyl)vinyl)-1H-indol-3-yl)acetonitrile **4ab**. Flash chromatography on silica gel (EtOAc/cyclohexane 5/95) afforded 143 mg of **4ab** (0.41 mmol, yield 82%); yellow solid; mp: 161−163 °C; TLC: R_f = 0.27 (EtOAc/cyclohexane, 20/80, SiO_2); IR (neat) 1641, 1604, 1582, 1455, 1415, 1366, 1226; ^{1}H NMR (300 MHz, CD_3COCD_3) δ 7.61 (m, 1H), 7.41 (m, 1H), 7.23 (s, 1H), 7.12 (m, 2H), 6.29 (s, 2H), 5.59 (s, 1H), 5.13 (s, 1H), 3.97 (d, *J* = 0.9 Hz, 3H), 3.85 (s, 3H), 3.67 (s, 6H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ 163.2 (C), 160.4 (2C), 137.9 (C), 137.1 (C), 128.6 (C), 127.4 (C), 127.4 (CH), 123.3 (CH), 120.7 (CH), 119.2 (CH), 112.9 (CH), 110.1 (CH_2), 109.2 (C), 106.0 (C), 91.8 (2CH), 56.3 ($2CH_3$), 55.8 (CH_3), 14.0 (CH_2) ; HRMS (ESI) (M + H)$^+$: *m/z* calcd for $C_{21}H_{21}N_2O_3$ 349,1552; found 349.1553.

3-(1-(6-Methoxy-3,4-dihydronaphthalen-1-yl)-1H-indol-3-yl)-1-methylquinoxalin-2(1H)-one **4ac**. Flash chromatography on silica gel (DCM/cyclohexane 50/50) afforded 195 mg of **4ac** (0.45 mmol, yield 90%); yellow solid; mp: 190−191 °C; TLC: R_f = 0.61 (DCM, SiO_2); IR (neat) 1738, 1650, 1535, 1497, 1455, 1307, 1253, 1200, 1167; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.09 (d, *J* = 8.0 Hz, 1H), 9.00 (s, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.51 (m, 1H), 7.38 (m, 3H), 7.25 (m, 2H), 6.83 (s, 1H), 6.57 (m, 2H), 6.20 (t, *J* = 4.6 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 2.99 (t, *J* = 7.8 Hz, 2H), 2.60 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 159.7 (C), 154.7 (C), 151.0 (C), 138.2 (C), 137.4 (C), 136.6 (CH), 136.0 (C), 134.0 (C), 131.9 (C), 129.6 (CH), 128.5(CH), 127.5 (C), 124.8 (C), 124.7 (CH), 123.7 (CH), 123.7 (CH), 123.5 (CH), 123.2 (CH), 122.1 (CH), 114.3 (CH), 113.6 (CH), 112.6 (C), 111.6 (CH), 111.2 (CH), 55.4 (CH_3), 29.3 (CH_3), 28.2 (CH_2), 22.9 (CH_2); HRMS (ESI) $(M + H)^+$: m/z calcd for $C_{28}H_{24}N_3O_2$ 434.1869; found 434.1868.

1-(2-(1-(2H-Chromen-4-yl)-1H-indol-3-yl)ethyl)piperidin-2-one ***4ad***. Flash chromatography on silica gel (MeOH/DCM 2/98) afforded 145 mg of **4ad** (0.39 mmol, yield 78%); colorless oil; TLC: R_f = 0.67 (MeOH/DCM, 5/95, SiO_2); IR (neat) 1736, 1640, 1606, 1486, 1459, 1395, 1224; ^{1}H NMR (300 MHz, CD_3COCD_3) δ 7.75 (m, 1H), 7.17 (m, 5H), 6.91 (dd, J = 8.1, 0.9 Hz, 1H), 6.82 (td, J = 7.6, 1.1 Hz, 1H), 6.60 (dd, J = 7.7, 1.6 Hz, 1H), 6.03 (t, J = 3.9 Hz, 1H), 5.03 (d, J = 3.9 Hz, 2H), 3.65 (m, 2H), 3.27 (m, 2H), 3.04 (m, 2H), 2.24 (m, 2H), 1.71 (m, 4H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ 169.2 (C), 156.2 (C), 137.9 (C), 134.3 (C), 131.1 (CH), 129.6 (C), 126.9 (CH), 124.4 (CH), 123.0 (CH), 122.2 (CH), 122.0 (C), 120.6 (CH), 120.1 (CH), 118.7 (CH), 117.1 (CH), 115.2 (C), 111.8 (CH), 66.0 (CH_2), 49.0 (CH_2), 48.5 (CH_2), 33.1 (CH_2), 24.1 (CH_2), 23.6 (CH_2), 22.2 (CH_2); HRMS (ESI) $(M + Na)^+$: m/z calcd for $C_{24}H_{24}N_2O_2Na$ 395.1735; found 395.1728.

2,3-Diphenyl-1-(1-(3,4,5-trimethoxyphenyl)vinyl)-1H-indole ***4ae***. Flash chromatography on silica gel (EtOAc/cyclohexane 1/99) afforded 203 mg of **4ae** (0.44 mmol, yield 88%); white solid ; mp: 149−151 °C; TLC: R_f = 0.40 (EtOAc/cyclohexane, 20/80, SiO_2); IR (neat) 1581, 1504, 1454, 1413, 1368, 1323, 1238; ^{1}H NMR (300 MHz, CD_3COCD_3) δ 7.73 (m, 1H), 7.34 (m, 7H), 7.21 (m, 6H), 6.37 (s, 2H), 6.04 (s, 1H), 5.42 (s, 1H), 3.67 (s, 3H), 3.63 (s, 6H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ 154.3 (2C), 144.0 (C), 139.1 (C), 138.7 (C), 135.8 (C), 133.8 (C), 133.0 (C), 131.8 (2CH), 130.9 (2CH), 129.2 (2CH), 128.7 (2CH), 128.5 (CH), 128.4 (C), 126.9 (CH), 125.0 (C), 123.6 (CH), 121.8 (CH), 120.2 (CH), 117.5 (C), 114.6 (CH_2), 112.2 (CH), 104.7 (2CH), 60.6 (CH_3), 56.5 ($2CH_3$); HRMS (ESI) $(M + H)^+$: m/z calcd for $C_{31}H_{28}NO_3$ 462.2069; found 462.2045.

9-(1-(2,4,6-Trimethoxyphenyl)vinyl)-9H-carbazole ***4af***. Flash chromatography on silica gel (EtOAc/cyclohexane 1/99) afforded 172 mg of **4af** (0.48 mmol, yield 96%); white solid; mp: 134−136 °C; TLC: R_f = 0.48 (EtOAc/cyclohexane, 20/80, SiO_2); IR (neat) 1604, 1581, 1451, 1414, 1332, 1226, 1204; ^{1}H NMR (300 MHz, C_6D_6) δ (ppm) 8.06 (dd, J = 7.7, 0.7 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 7.39 (ddd, J = 8.3, 7.2, 1.2 Hz, 2H), 7.21 (td, J = 7.6, 0.9 Hz, 2H), 5.92 (s, 2H), 5.75 (s, 1H), 5.71 (s, 1H), 3.24 (s, 3H), 3.00 (s, 6H); ^{13}C NMR (75 MHz, C_6D_6) δ (ppm) 162.0 (C), 160.2 (2C), 141.6 (2C), 135.7 (C), 125.8 (2CH), 123.9 (2C), 120.3 (2CH), 119.7 (2CH), 117.2 (CH_2), 111.6 (2CH), 109.1 (C), 91.2 (2CH), 55.2 ($2CH_3$), 54.7 (CH_3); HRMS (ESI) $(M + Na)^+$: m/z calcd for $C_{23}H_{21}NNaO_3$ 382.1419; found 382.1396.

2-((tert-Butyldimethylsilyl)oxy)-9-(3,3-dimethylbut-1-en-2-yl)-9H-carbazole ***4ag***. Flash chromatography on silica gel (EtOAc/cyclohexane 1/99) afforded 139 mg of **4ag** (0.37 mmol, yield 73%); colorless oil; TLC: R_f = 0.69 (EtOAc/cyclohexane, 5/95, SiO_2); IR (neat) 1625, 1599, 1495, 1457, 1345, 1284, 1253, 1224; ^{1}H NMR (300 MHz, C_6D_6) δ 8.98 (m, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.33 (m, 1H), 7.25 (m, 2H), 7.02 (d, J = 1.9 Hz, 1H), 6.93 (dd, J = 8.4, 2.1 Hz, 1H), 5.31 (s, 1H), 4.87 (s, 1H), 1.06 (s, 9H), 1.03 (s, 9H), 0.25 (s, 3H), 0.24 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 155.1 (C), 153.7 (C), 144.1 (C), 143.1 (C), 124.8 (CH), 123.8 (C), 121.1 (CH), 119.8 (CH), 119.8 (CH), 118.2 (C), 116.7 (CH_2), 113.4 (CH), 111.0 (CH), 102.3 (CH), 39.0 (C), 30.4 (CH_3), 26.0 ($3CH_3$), 18.6 (C), −4.1 (CH_3), −4.2 (CH_3); HRMS (ESI) $(M + H)^+$: m/z calcd for $C_{24}H_{34}NOSi$ 380.2410; found 380.2409.

3,6-Dibromo-9-(1-(3,4,5-trimethoxyphenyl)vinyl)-9H-carbazole ***4ah***. Flash chromatography on silica gel (EtOAc/cyclohexane 2/98) afforded 191 mg of **4ah** (0.37 mmol, yield 74%); white solid; mp: 134−136 °C; TLC: R_f = 0.19 (EtOAc/cyclohexane, 10/90, SiO_2); IR (neat) 1581, 1468, 1433, 1412, 1365, 1282, 1234; ^{1}H NMR (300 MHz, CD_3COCD_3) δ (ppm) 8.45 (d, J = 1.8 Hz, 2H), 7.54 (dd, J = 8.8, 1.9 Hz, 2H), 7.24 (d, J = 8.7 Hz, 2H), 6.57 (s, 2H), 6.24 (s, 1H), 5.60 (s, 1H), 3.73 (s, 3H), 3.64 (s, 6H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm) 154.7 (2C), 142.7 (C), 140.8 (2C), 140.5 (C), 132.2 (C), 130.2 (CH), 125.0 (2C), 124.3 (2CH), 113.9 (CH_2), 113.7 (2CH), 113.6 (2C), 104.7 (2CH), 60.6 (CH_3), 56.5 ($2CH_3$); HRMS (ESI) $(M + H)^+$: m/z calcd for $C_{23}H_{20}Br_2NO_3$ 517.9792; found 517.9789.

9-(1-(4-Chlorophenyl)vinyl)-2,3,4,9-tetrahydro-1H-carbazole ***4ai***. Flash chromatography on silica gel (cyclohexane) afforded 123 mg of **4ai** (0.4 mmol, yield 80%); colorless oil; TLC: R_f = 0.30 (cyclohexane, SiO_2); IR (neat) 1490, 1458, 1371, 1228; ^{1}H NMR (300 MHz, C_6D_6) δ (ppm) 7.62 (dd, J = 7.4, 1.1 Hz, 1H), 7.22 (m, 3H), 6.91 (m, 2H), 6.73 (m, 2H), 5.38 (s, 1H), 4.96 (s, 1H), 2.70 (m, 2H), 2.20 (m, 2H), 1.63 (m, 4H); ^{13}C NMR (75 MHz, C_6D_6) δ 142.3 (C), 138.1 (C), 136.4 (C), 135.7 (C), 134.9 (C), 129.1 (2CH), 128.7 (C), 127.7 (2CH), 122.0 (CH), 120.3 (CH), 118.4 (CH), 112.4 (CH_2), 111.7 (C), 110.8 (CH), 23.7 (CH_2), 23.5 (CH_2), 23.2 (CH_2), 21.5 (CH_2); HRMS (APCI) $(M + H)^+$: m/z calcd for $C_{20}H_{19}ClN$ 308.1206; found 308.1223.

1-(1-(2,4,6-Trimethoxyphenyl)vinyl)-1H-pyrrole ***4aj***. Flash chromatography on silica gel (EtOAc/cyclohexane 2/98) afforded 45 mg of **4aj** (0.18 mmol, yield 35%); orange oil ; TLC: R_f = 0.57 (EtOAc/cyclohexane, 20/80, SiO_2); IR (neat) 1648, 1605, 1582, 1413, 1334, 1226; ^{1}H NMR (300 MHz, CD_3COCD_3) δ 6.75 (m, 2H), 6.30 (s, 2H), 6.03 (m, 2H), 5.39 (s, 1H), 4.54 (s, 1H), 3.86 (s, 3H), 3.71 (s, 6H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ 163.1 (C), 160.4 (2C), 138.7 (C), 119.4 (2CH), 109.6 (2CH), 101.6 (CH_2), 91.6 (2CH), 56.2 ($2CH_3$), 55.7 (CH_3); HRMS (ESI) $(M + H)^+$: m/z calcd for $C_{15}H_{18}NO_3$ 260.1287; found 260.1280.

(Z)-1-(1,2-Bis(4-methoxyphenyl)vinyl)-1H-pyrrole ***4ak***. Flash chromatography on silica gel (EtOAc/cyclohexane 1/99) afforded 95 mg of **4ak** (0.31 mmol, yield 62%); white solid; mp: 134−136 °C; TLC: R_f = 0.67 (EtOAc/cyclohexane, 20/80, SiO_2); IR (neat) 1605, 1510, 1442, 1244; ^{1}H NMR (300 MHz, CD_3COCD_3) δ 7.30 (m, 4H), 7.08 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.5 Hz, 2H), 6.94 (m, 2H), 6.71 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ 159.6 (C), 144.8(C), 141.0(C), 133.6(C), 132.3 (2CH), 131.6 (2CH), 131.1 (C), 129.0(2CH), 128.1 (2CH), 128.0 (CH), 115.1 (2CH), 114.3 (2CH), 55.5 (CH_3), 55.5 (CH_3); HRMS (ESI) $(M + H)^+$: m/z calcd for $C_{20}H_{20}NO_2$ 306.1494; found 306.1495.

1-(1-(2,4,6-Trimethoxyphenyl)vinyl)-6,7-dihydro-1H-indol-4(5H)-one ***4al***. Flash chromatography on silica gel (MeOH/cyclohexane 2/98) afforded 92 mg of **4al** (0.28 mmol, yield 55%); white solid; mp: 167−170 °C ; TLC: R_f = 0.75 (MeOH/DCM, 10/90, SiO_2); IR (neat) 1656, 1604, 1584, 1495, 1462, 1414, 1368, 1228; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.61 (d, J = 3.1 Hz, 1H), 6.51 (d, J = 3.1 Hz, 1H), 6.14 (s, 2H), 5.44 (s, 1H), 5.25 (s, 1H), 3.85 (s, 3H), 3.72 (s, 6H), 2.65 (t, J = 6.1 Hz, 2H), 2.45 (m, 2H), 2.07 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0 (C), 162.1 (C), 159.3 (2C), 144.0 (C), 136.6 (C), 123.0 (CH), 121.1 (C), 113.6 (CH_2), 108.1 (C), 105.2 (CH), 90.9 (2CH), 56.1 ($2CH_3$), 55.5 (CH_3), 37.9 (CH_2), 24.4 (CH_2), 23.0 (CH_2); HRMS (ESI) $(M + H)^+$: m/z calcd for $C_{19}H_{22}NO_4$ 328.1549; found 328.1553.

1-(1-(2,4,6-Trimethoxyphenyl)vinyl)-1H-benzo[d]imidazole ***4am***. Flash chromatography on silica gel (MeOH/DCM 1/99) afforded 62 mg of **4am** (0.20 mmol, yield 40%); white solid; mp: 167−170 °C; TLC: R_f = 0.35 (MeOH/DCM, 5/95, SiO_2); IR (neat) 1739, 1608, 1586, 1454, 1228, 1205; ^{1}H NMR (300 MHz, CD_3COCD_3) δ 7.98 (s, 1H), 7.63 (m, 1H), 7.29 (m, 1H), 7.15 (m, 2H), 6.30 (s, 2H), 5.73 (s, 1H), 5.22 (s, 1H), 3.84 (s, 3H), 3.69 (s, 6H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ 163.4 (C), 160.4 (2C), 145.4 (C), 143.9 (CH), 135.8 (C), 123.5 (CH), 122.5 (CH), 120.7 (CH), 112.4 (CH), 111.8 (CH_2), 107.7 (C), 91.8 (2CH), 56.3 ($2CH_3$), 55.8 (CH_3); HRMS (ESI) $(M + H)^+$: m/z calcd for $C_{18}H_{19}N_2O_3$ 311.1396; found 311.1396.

1-(1-(2-Chlorophenyl)vinyl)-1H-imidazole ***4an***. Flash chromatography on silica gel (MeOH/DCM 2/98) afforded 44 mg of **4an** (0.22 mmol, yield 43%); colorless oil ; TLC: R_f = 0.43 (MeOH/DCM, 5/95, SiO_2); IR (neat) 1649, 1487, 1432, 1375, 1321, 1245; ^{1}H NMR (300 MHz, CD_3COCD_3) δ 7.53 (m, 5H), 7.21 (s, 1H), 7.03 (s, 1H), 5.74 (d, J = 1.4 Hz, 1H), 5.13 (d, J = 1.4 Hz, 1H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ 141.5 (C), 135.6 (C), 133.9 (C), 132.9 (CH), 132.1 (2CH), 130.9 (CH), 130.3 (CH), 128.5 (CH), 118.7 (CH), 107.2

(CH_2); HRMS (APCI) $(M + H)^+$: m/z calcd for $C_{11}H_{10}ClN_2$ 205.0533; found 205.0533.

Synthesis of *d*2-Deuterated *N*-Tosylhydrazone 6. *Synthesis of d_2-Deuterated Ketone.* To an Emrys Optimizer 2−5 mL pyrex reaction vessel were added 1-methoxy-4-[(4-methoxyphenyl)ethynyl]-benzene (1 mmol, 238 mg) and PTSA·H_2O (0.3 mmol, 57 mg) in CD_3OD (3 mL). The reaction vessel was then placed in the Emrys Optimizer and exposed to microwave irradiation according to the following specifications: 120 °C during 30 min; fixed hold time, on; sample absorption, high; prestirring, 60 s. After cooling to room temperature, H_2O (5 mL) was added and the mixture was extracted with EtOAc (3 × 5 mL). Organic layers were dried and concentrated, and the crude was purified by column chromatography on silica gel (EtOAc/cyclohexane 5/95) to afford 224 mg of d_2-deuterated ketone (225 mg, 0.87 mmol, yield 87%); ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.99 (d, J = 8.9 Hz, 2H), 7.19 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 3.85 (s, 3H), 3.78 (s, 3H).

*d_2-Deuterated N-Tosylhydrazone **6**.* Prepared according to the general procedure with d_2-deuterated ketone (2 mmol, 516 mg) to give the corresponding tosylhydrazone; 481 mg (60% deuterated according to NMR integration) (1.13 mmol, yield 57%); ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.68 (m, 4H), 7.53 (bs, 1H), 7.27 (m, 2H), 6.88 (m, 4H), 6.73 (d, J = 8.6 Hz, 2H), 3.92 (m, 0.8H), 3.82 (s, 3H), 3.80 (s, 3H), 2.43 (s, 3H).

***4ao**.* Prepared according to the general procedure to give the corresponding product 144 mg (35% deuterated according to NMR integration) (0.41 mmol, yield 81%); ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.69 (d, J = 7.7 Hz, 1H), 7.13 (m, 3H), 7.07 (d, J = 7.2 Hz, 1H), 7.03 (d, J = 3.2 Hz, 1H), 6.98 (d, J = 8.2 Hz, 1H), 6.96 (s, 0.75H), 6.84 (d, J = 8.8 Hz, 2H), 6.67 (m, 5H), 3.81 (s, 3H), 3.72 (s, 3H).

*1,2,3-Trimethoxybenzene-d (Compound **8**).* Isolated from the crude mixture of coupling between deuterated hydrazone, indole, and 5-iodo-1,2,3-trimethoxybenzene as oxidant; ^1H NMR (300 MHz, CD_3COCD_3) δ (ppm) 6.97 (t, J = 8.4 Hz, 0.7H), 6.64 (m, 2H), 3.80 (s, 6H), 3.72 (s, 3H).

Computational Methods. Calculations have been carried out with the Gaussian 09 package of programs.[25] Full geometry optimizations for all compounds were carried out with the use of the B3LYP[26] density functional level of theory and with the following basis set denoted as BS1. A 6-31G(d) basis set was employed for the first- (H) and second-row (C, N) elements. The standard LANL2DZ small-core relativistic effective-core potential with a valence shell of double-ζ quality was used on palladium.[27] To get accurate energies and Gibbs free energies, the SCF convergence criterion has been systematically tightened to 10^{-8} a.u., and the force minimizations were carried out until the rms force becomes smaller than (at least) 1×10^{-5} a.u. Frequency analyses were carried out to confirm that the reported structures are minima or transition states on the B3LYP/BS1 potential energy surface, and to evaluate the thermal and entropic contributions necessary for the calculation of Gibbs free energies G. Intrinsic reaction coordinate (IRC) calculations have been performed to ascertain the identity of the transition structure under consideration. The validity of this level of calculation has been demonstrated in previous studies on Pd(II) complexes.[28] This is confirmed for the energetic data examined in this study by comparison with improved energies. These energies were obtained by single-point calculations, at the B3LYP/BS1 geometries, at the B3LYP and M06L[29] density functional levels of theory, with the extended def2-TZVPP basis set and its associated ECP for Pd,[30] denoted as BS2, which has been retrieved from the EMSL Basis Set Library.[31]

ASSOCIATED CONTENT

Supporting Information

Details for experimental conditions and copies of ^1H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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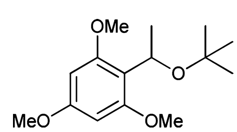

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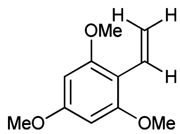

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