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Intramolecular Palladium-Catalyzed Oxidative Amination of Furans: Synthesis of Functionalized Indoles

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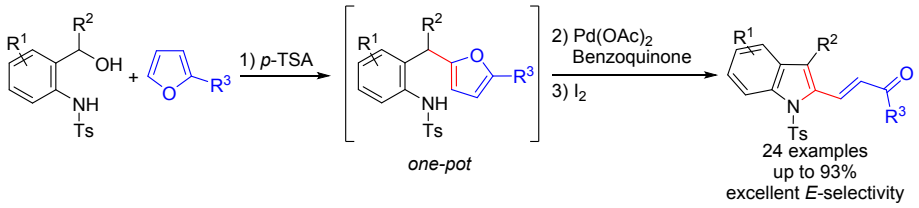


ABSTRACT

Unconventional modification of palladium-catalyzed oxidative amination where a furan ring serves as a masked olefin is described. The designed chemical process provides 2-(2-acylvinyl)indole derivatives with up to a 93% yield and excellent *E*-selectivity. A highly reactive α,β-unsaturated carbonyl moiety of the obtained compounds allows for accessing various heteroaromatic scaffolds through simple synthetic procedures.

Keywords: Furan; Indole; Catalysis; Palladium; Oxidative Amination

INTRODUCTION

Intramolecular transition metal-catalyzed oxidative amination[1] has become a powerful practical instrument being extensively exploited in organic synthesis to provide a wide range of nitrogen-containing heterocycles, starting from easily accessible substrates.[2] Among the variety of possible products the reaction of an olefin tethered to an amine functionality could end up with under oxidative amination conditions, the indole derivatives represent an important class of organic compounds due to their widespread use as active drug components, biologically significant natural products or substrates in the dye and agricultural industries.[3]

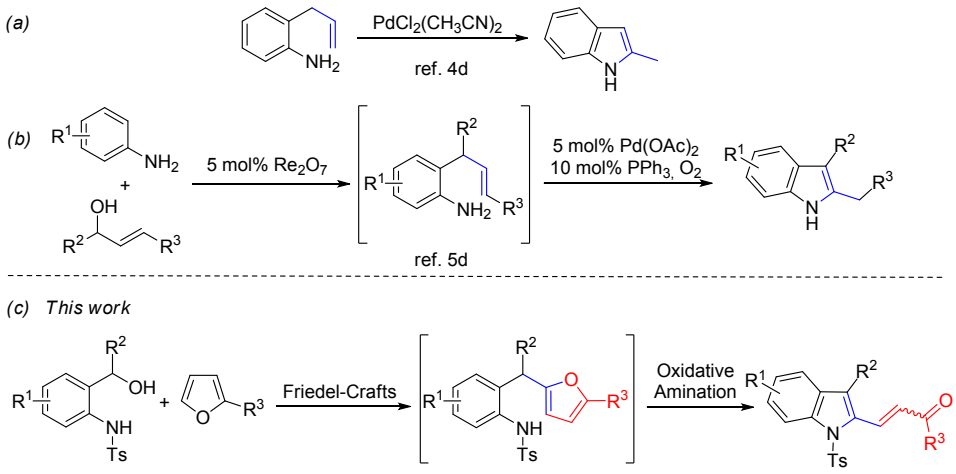
Starting from the pioneering works of Hegedus[4] (Scheme 1, *a*) the application of intramolecular oxidative amination catalyzed by transition metal complexes for the synthesis of substituted indoles has reached an impressive progress in terms of catalyst loading and conditions applied.[5] Thus, recently Ghorai *et al*. showed that 2-allylanilines underwent cyclization to form 2-benzylindoles with moderate to high yields in the presence of 5 mol% of $Pd(OAc)_2$ as a precatalyst and dioxygen as a terminal oxidant. Moreover, the authors also disclosed a *one-pot* protocol to obtain 2-benzylindoles starting from simple anilines and cinnamyl alcohols that reacted to form the intermediate 2-allylanilines under rhenium catalysis (Scheme 1, *b*).[5d]

The classical version of oxidative amination comprising the interaction of a weakly basic nitrogen with olefins in the presence of transition metal complexes and terminal oxidants is well-studied.[6] Undeniably, the utilization of conceptually new substrates containing masked alkene functionality for this reaction would greatly expand the scope and practical applicability of oxidative amination as a method to access important nitrogen-containing heterocycles. To the best of our knowledge, this possibility has not been explored to date.

Due to low resonance energy,[7] furan easily undergoes dearomatization reactions[8] under various conditions, thereby providing structurally diverse compounds. Despite its wide use as a masked 1,4-dicarbonyl compound,[9] furan could also act as an olefin equivalent exhibiting close reactivity to an isolated carbon-carbon double bond in some transition metal-catalyzed chemical transformations.[10] In consideration of this transformative aspect, we hypothesized that a benzylfuran possessing an amino group at *ortho*-position could be an ideal model substrate to study the possibility of intramolecular oxidative amination. Such a furyl-tethered amine would mimic the substrate for Hegedus indole synthesis reacting under oxidative amination conditions to furnish an indole core. Moreover, a target compound would contain a highly reactive enone functionality, which could be employed for further

modifications (Scheme 1, *c*).[11] Herein, we disclose a new variation of Hegedus indole synthesis *via* intramolecular oxidative amination of furans.

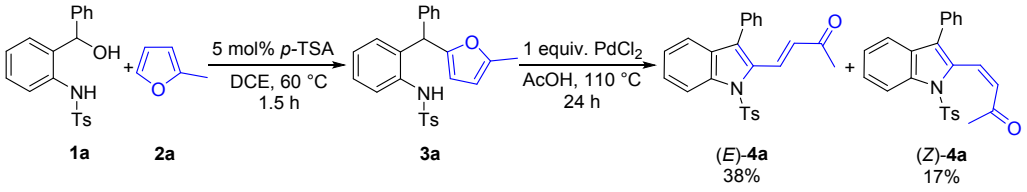
Scheme 1. Classic approaches to indoles *via* intramolecular oxidative amination and our work



RESULTS AND DISCUSSION

In order to check the initial hypothesis, we treated benzylfuran **3a**, obtained *via* Friedel-Crafts alkylation of 2-methylfuran (**2a**) with a corresponding benzyl alcohol **1a** in the presence of *para*-toluenesulfonic acid (*p*-TSA), with $PdCl_2$ upon heating in acetic acid and observed the formation of a target functionalized indole **4a** as a mixture of *Z* and *E* isomers with a moderate yield (Scheme 2).

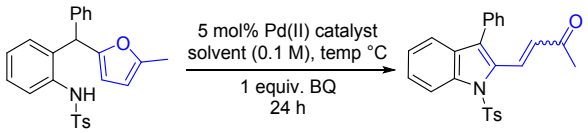
Scheme 2. Initial observation.



Encouraged by this result, we ran an optimization of the reaction conditions with benzylfuran **3a** as a model substrate. The optimization has revealed that a catalytic amount of a Pd(II) source could be employed so as to reach a complete conversion of the starting benzylfuran **3a**. We detected the formation of the target compound **4a** as a composite of geometrical isomers with 36% yield when 5 mol% $PdCl_2$ was added to the mixture of benzylfuran **3a** and benzoquinone (BQ) in acetic acid upon

heating at 110 °C (Table 1, entry 1). Other reoxidants such as $CuCl_2$, $Cu(OAc)_2$, $AgCO_3$, or dioxygen proved to be less efficient providing lower yields of **4a**. Next, we tested $PdCl_2$ complexes with PPh_3, PhCN, and MeCN and discovered that the combined yield of the target isomers could be increased up to 84% with the slight change of the isomeric ratio in favor of *E*-isomer (entries 2-4). Finally, we found that $Pd(OAc)_2$ in the amount of 5 mol% enabled to form an indole **4a** with 95% analytical yield, yet as a 1:2 *Z*/*E* mixture (entry 5). We screened different solvents in attempt to improve *Z*/*E* ratio; however, in all cases the yield of **4a** dropped significantly (entries 6-10). By further tuning the reaction parameters, we eventually determined that the optimal conditions for the formation of indole **4a** as a mixture of *Z*/*E* isomers with the highest possible yield could be achieved when the starting benzylfuran **3a** was heated in acetic acid in the presence of 5 mol% of $Pd(OAc)_2$/1 equiv. of BQ at 100 °C for 16 hours (entry 12). The presence of both $Pd(OAc)_2$ and BQ is required for the reaction to take place (entries 14-16).

Table 1. Optimization of the reaction conditions.[a]



3a **4a**

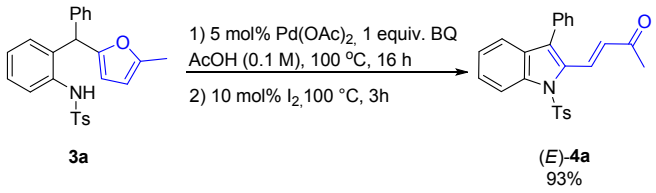
Entry	Catalyst	Solvent	temp (°C)	*Z*/*E* ratio[b]	Yield (%)[c]
1	$PdCl_2$	AcOH	110	1/4	36
2	$PdCl_2(PPh_3)_2$	AcOH	110	1/6	42
3	$PdCl_2(PhCN)_2$	AcOH	110	1/6	70
4	$PdCl_2(CH_3CN)_2$	AcOH	110	1/9	84
5	$Pd(OAc)_2$	AcOH	110	1/2	95
6	$Pd(OAc)_2$	toluene	110	3/1	62
7	$Pd(OAc)_2$	DMF	110	5/1	40
8	$Pd(OAc)_2$	1,4-dioxane	110	4/1	20
9	$Pd(OAc)_2$	CH_3CN	110	-	trace
10	$Pd(OAc)_2$	DCE	110	-	trace
11	$Pd(OAc)_2$	AcOH	100	1/2	95
12	**$Pd(OAc)_2$**[d]	**AcOH**	**100**	**1/2**	**95 (93)**[e]
13	$Pd(OAc)_2$[d]	AcOH	90	1/2	87

14	-[d]	AcOH	100	-	trace
15	$Pd(OAc)_2$[d,f]	AcOH	100	-	trace
16	-[d,f]	AcOH	100	-	N/R[g]

[a]*Reactions conditions*: a solution of benzylfuran **3a** (0.05 mmol), BQ (0.05 mmol) and a catalyst in a solvent (0.5 mL) were stirred at the indicated temperature for the indicated time. [b]*Z*/*E* ratios were determined by NMR. [c]NMR yields with CH_2Br_2 as an internal standard. [d]Reaction time – 16 h. [e]Isolated yield is given in parentheses, the reaction was run at 0.2 mmol scale. [f]No BQ. [g]0% conversion of **3a**.

The isomeric mixtures of α,β-unsaturated ketones could be selectively converted into *E*-isomer *via* iodine-catalyzed isomerization.[12] Indeed, the *Z*/*E*-mixture of indole **4a** obtained after palladium-catalyzed reaction of benzylfuran **3a** was smoothly transformed into (*E*)-2-(2-acetylvinyl)indole (*E*)-**4a** with quantitative yield after heating the substrate in acetic acid in the presence of 10 mol% I_2. Moreover, we found that this step could be combined with the previous one without any loss of efficiency (Scheme 3).

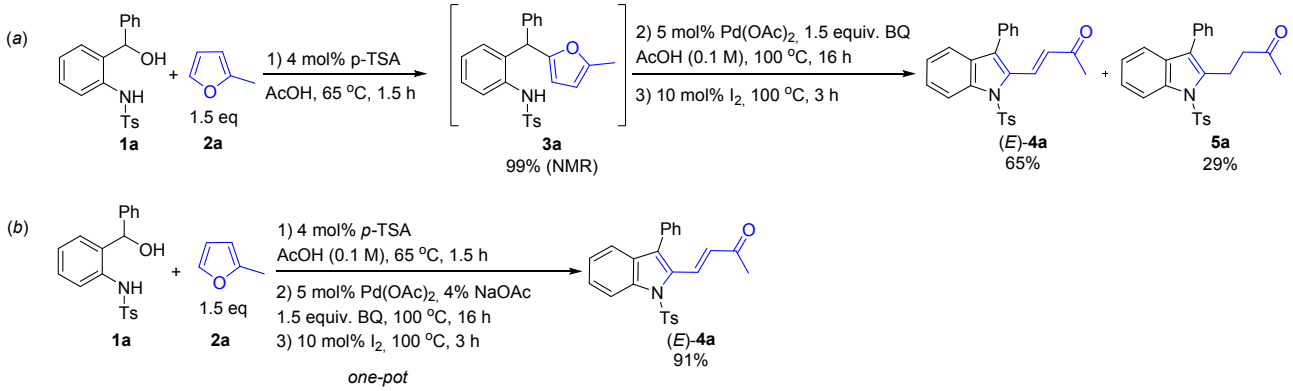
Scheme 3. *One-pot* synthesis of (*E*)-**4a** from **3a**



Ultimately, we decided to integrate the Friedel-Crafts alkylation step in order to design a convenient synthetic *one-pot* protocol toward (*E*)-2-(2-acylvinyl)indoles **4**. The reaction between benzyl alcohol **1a** and 1.5 equivalent of 2-methylfuran (**2a**) in acetic acid with 4 mol% of p-TSA as a catalyst at 65 °C led to a clean formation of an intermediate benzylfuran **3a** with quantitative analytical yield. However, heating the mixture at elevated temperature further with palladium catalyst/BQ followed by addition of molecular iodine resulted in the formation of the target indole (*E*)-**4a** with 65% yield, the other component being indole **5a** which possessed an oxoalkyl substituent at C-2 of an indole core (Scheme 4, *a*). Presumably, by-product **5a** was being formed by Brönsted acid-catalyzed rearrangement of benzylfuran **3a** under reaction conditions.[13] After some experimentation, we found that the addition of

sodium acetate equimolar to *p*-TSA totally prevented the noted side reaction: in that case the target indole (*E*)-**4a** was formed with 91% yield (Scheme 4, *b*). It should be pointed out that the amount of BQ should have been equal to the amount of the furan component as otherwise the excess of 2-methylfuran (**2a**) either reduced BQ or underwent conjugated addition to BQ[14] resulting in lower yield of the target indole (*E*)-**4a**.

Scheme 4. *One-pot* synthesis of (*E*)-**4a** from **1a**

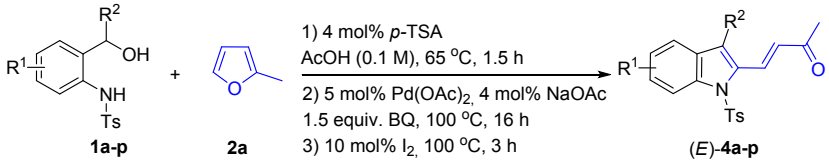


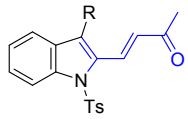
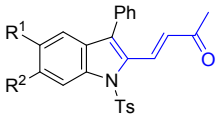
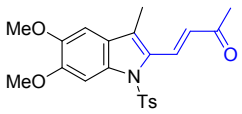
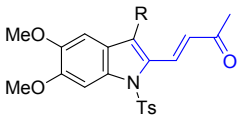
With the optimized conditions in hand, we explored the generality of the new *one-pot* method for the synthesis of functionalized indoles. First, the scope of the reaction of different benzyl alcohols **1** with 2-methylfuran (**2a**) was examined (Table 2). Thus, benzyl alcohols possessing various aryl substituents at α-position reacted smoothly providing corresponding indoles (*E*)-**4a-e** (entries 1-5) with high yields with the exempt of an alcohol **1f** which contained sterically hindered 2,5-dimethylphenyl group giving an indole (*E*)-**4f** with 61% yield (entry 6). When we switched to α-methyl substituted benzyl alcohol **1g**, we were able to isolate indole (*E*)-**4g** with 16% yield only. Supposedly, alcohol **1g** forms relatively less-stabilized and highly reactive benzylic cation[15] undergoing unwanted chemical processes that lowers the yield of the intermediate benzylfuran. In fact, when we ran this reaction starting from α-methylbenzylfuran obtained under milder conditions from an alcohol **1g** and 2-methylfuran (**2a**), we isolated a corresponding indole (*E*)-**4g** with 73% yield (entry 7). In contrast, more electron-rich benzyl alcohol **1h** reacted with 2-methylfuran (**2a**) with the formation of an indole (*E*)-**4h** with 85% yield (entry

8). This result could be explained by higher stabilization of the forming carbenium ion at the Friedel-Crafts step.

Other benzyl alcohols possessing different substituent at the aniline ring were also tested. We found that the presence of methyl or methoxy groups did not change the chemoselectivity of the studied reaction: the respective indoles (*E*)-**4i-m** were formed with 85-89% yield (entries 9-13). 4,5-Difluoro- and 4-bromo derivatives **1n,o** reacted with 2-methylfuran (**2a**) to form indoles (*E*)-**4n,o** with 55% and 45% yield accordingly that could be caused by deactivation properties of halogen substituents (entries 14,15). Finally, indole (*E*)-**4p** containing two methoxy groups at the aniline ring and 4-bromophenyl substituent at α-position was obtained with a 75% yield (entry 16).

Table 2. Scope of benzyl alcohols.[a]



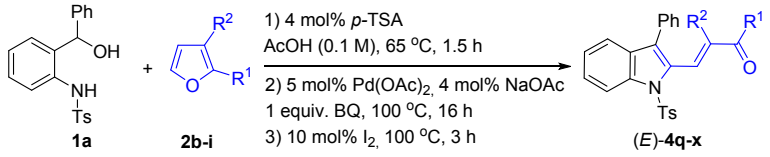
Entry	Product		Yield (%)	Entry	Product		Yield (%)
1		(*E*)-**4a** (Ph)	91 (83)[b]	9		(*E*)-**4i** (R^1 = Me, R^2 = H)	86
2		(*E*)-**4b** (4-MeC_6H_4)	87	10		(*E*)-**4j** (R^1 = OMe, R^2 = H)	87
3		(*E*)-**4c** (4-$MeOC_6H_4$)	85	11		(*E*)-**4k** (R^1 = H, R^2 = Me)	85
4		(*E*)-**4d** (4-FC_6H_4)	83	12		(*E*)-**4l** (R^1 =H, R^2 = OMe)	86
5		(*E*)-**4e** (2-MeC_6H_4)	84	13		(*E*)-**4m** (R^1 = R^2 = OMe)	89
6		(*E*)-**4f** (2,6-$Me_2C_6H_4$)	61	14		(*E*)-**4n** (R^1 = R^2 = F)	55
7		(*E*)-**4g** (Me)	16 (73)[c]	15		(*E*)-**4o** (R^1 = H, R^2 = Br)	45
8		(*E*)-**4h**	85[d]	16		(*E*)-**4p** (4-BrC_6H_4)	75

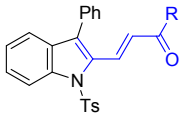
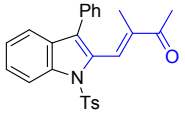
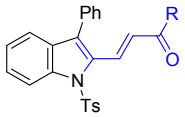
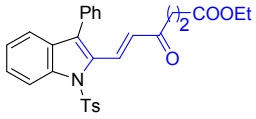
[a]*Reaction conditions*: benzyl alcohol **1** (1 equiv.), 2-methylfuran (**2a**) (1.5 equiv.), stepwise addition of reagents. [b]Reaction was performed at 3 mmol scale of benzyl alcohol **1a** and 4.5 mmol 2-methylfuran (**2a**). [c]Yield of indole (***E***)-**4g** obtained from the corresponding benzylfuran is given in parentheses. [d]First step – 45 min.

Further, we studied the scope of the reaction with regard to the furan component (Table 3). Since furans other than 2-methylfuran are much less volatile, one equivalent of the furan reaction partner

might be used, and, as a result, just one equivalent of BQ was needed. 2-Alkylfurans **2b,c** possessing *n*-butyl and *tert*-butyl groups reacted with benzyl alcohol **1a** to provide corresponding indoles (*E*)-**4q,r** with 84% and 78% yields respectively (entries 1,2). Reaction of 2,3-dimethylfuran (**2d**) gave indole (*E*)-**4s** with a moderate yield (entry 3), which was possibly caused by a steric hindrance posed by the second methyl group during an α,β-unsaturated carbonyl side chain forming step (see plausible mechanism, scheme 5). All tested 2-arylfurans **2e-h** were smoothly converted into 2-(2-benzoylvinyl)indoles (*E*)-**4t-w** with up to a 90% yield (entries 4-7). Noticeably, furan **2i** possessing an ester group in a side chain uneventfully reacted with benzyl alcohol **1a** producing an indole (*E*)-**4x** with high yield (entry 8).

Table 3. Scope of furans.[a]



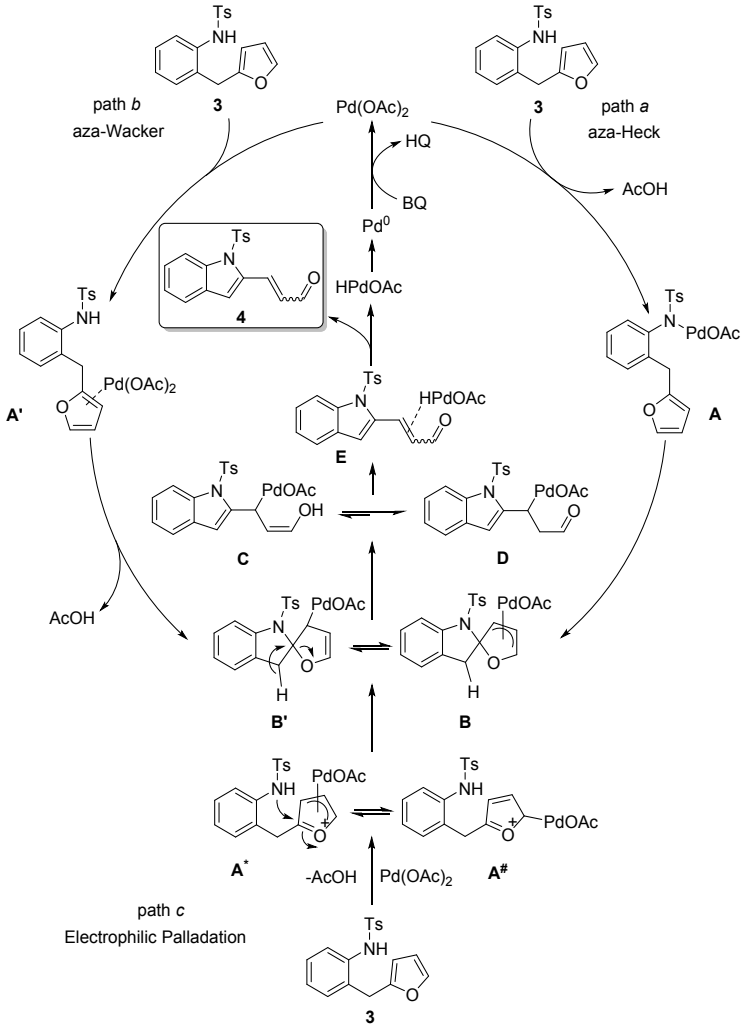
Entry	Product		Yield (%)
1		(*E*)-**4q** (*n*-Bu)	84
2		(*E*)-**4r** (*t*-Bu)	78
3		(*E*)-**4s**[b]	49
4		(*E*)-**4t** (Ph)	90
5		(*E*)-**4u** (4-ClC$_6$H$_4$)	81
6		(*E*)-**4v** (4-BrC$_6$H$_4$)	76
7		(*E*)-**4w** (naphth-1-yl)	84
8		(*E*)-**4x**	82

[a]*Reaction conditions*: benzyl alcohol **1a** (1 equiv.), furan **2** (1 equiv.), stepwise addition of reagents. [b]Indole (*E*)-**4s** was obtained from 2,3-dimethylfuran (**2d**) and benzyl alcohol **1a**.

Mechanistically, the reaction may proceed through three distinct pathways. One possibility may

include the formation of reactive species containing N-Pd bond (intermediate **A**, Scheme 5, aza-Heck path *a*). Further migratory insertion across a proximal furyl carbon-carbon double bond affords an intermediate **B** being in equilibrium with **B'**. Deprotonation of **B'** followed by furan ring opening leads to enole **C** which tautomerizes into ketone **D**. The latter upon β-hydride elimination furnishes reaction product **4**. Alternatively, the reaction could start with coordination of palladium species to the furan ring followed by aminopalladation (Scheme 5, aza-Wacker path *b*) or by electrophilic palladation of the furan ring followed by a nucleophilic addition (Scheme 5, path *c*) leading to intermediate **B**/**B'**.

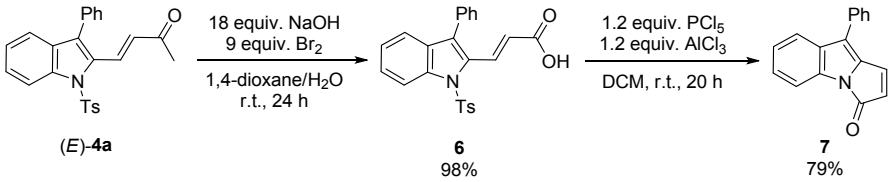
Scheme 5. Plausible mechanisms.



2-Vinylindoles represent an important class of organic compounds having been utilized as

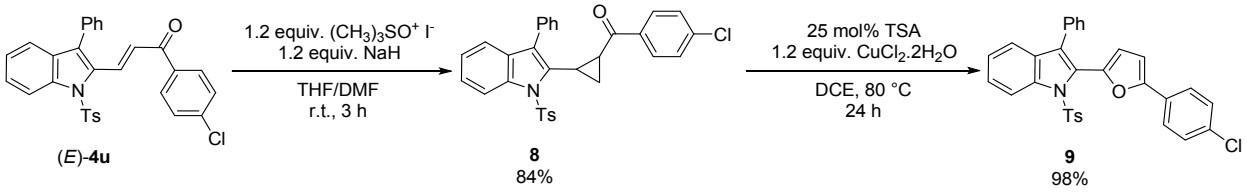
building-blocks in synthetic organic chemistry.[16] To further highlight the synthetic utility of obtained products we performed several transformations. Thus, oxidation of an indole (*E*)-**4a** with sodium hypobromite afforded acrylic acid **6** quantitatively. Surprisingly, **6** underwent detosylation followed by intramolecular nucleophilic substitution instead of electrophilic aromatic substitution in the presence of $PCl_5/AlCl_3$ to provide pyrroloindolone **7** in high yield (Scheme 6).

Scheme 6. Further transformations of indole (*E*)-**4a**.



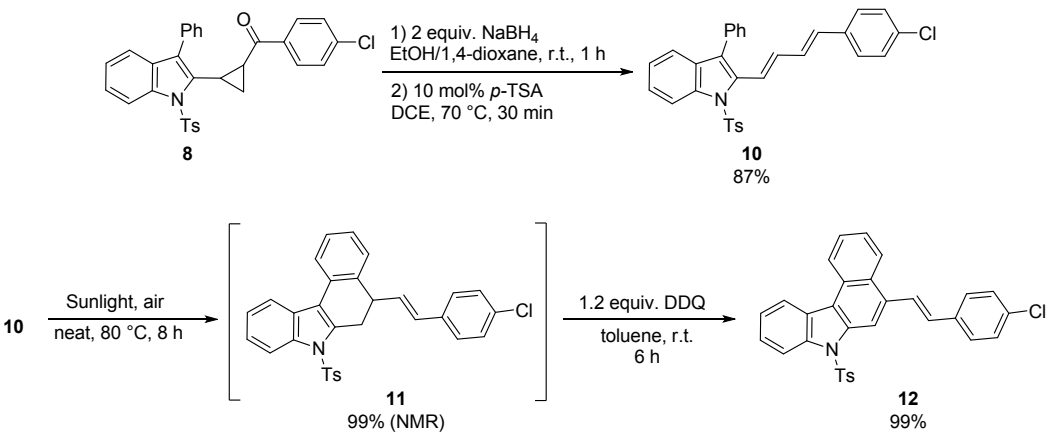
Next, cyclopropanation of indole (*E*)-**4u** under Corey-Chaykovsky reaction[17] conditions provided cyclopropane **8** with 84% yield. Heating the compound **8** in DCE in the presence of TSA and $CuCl_2$ led to the formation of indolylfuran **9** with excellent yield (Scheme 7).[18]

Scheme 7. Further transformations of indole (*E*)-**4u**.



Finally, reduction of cyclopropane **8** with sodium borohydride followed by treatment with TSA upon heating produced diene **10** with a high yield.[19] Diene **10** underwent spontaneous cyclization to form dihydrocarbazole **11** when stored on light. Heating diene **10** neat on sunlight led to a full conversion within 8 hours to produce compound **11** with quantitative analytical yield. Dihydrocarbazole **11** seemed to be pretty sensitive to air: it was rapidly oxidized into its unsaturated analogue **12**.[20] In order to convert a compound **11** into carbazole **12** in full, the mixture containing both heterocycles has been dissolved in toluene and treated with DDQ (Scheme 8).

Scheme 8. Synthesis of carbazole **12**.



CONCLUSION

In conclusion, we have showed that substituted furans can act as masked olefins under oxidative amination conditions. The synthetic protocol based on described reaction affords densely functionalized 2-(2-acylvinyl)indole derivatives with good-to-excellent yields and excellent *E*-selectivity from easily accessible starting materials. We have also demonstrated efficient transformations of the obtained indole products into a diverse range of heterocyclic scaffolds.

EXPERIMENTAL SECTION

General Information

^{1}H and ^{13}C NMR spectra were recorded with a «Bruker Avance III HD 400» (400 MHz for ^{1}H and 100 MHz for ^{13}C NMR) and Bruker Avance DRX-500 (500 MHz for ^{1}H and 125 MHz for ^{13}C NMR) or DPX-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C NMR) spectrometers at room temperature; the chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$, ^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.16 ppm; [D_6] DMSO, ^{1}H: δ = 2.50 ppm, ^{13}C: δ = 39.52 ppm). Coupling constants (*J*) are given in Hertz. Splitting patterns of an apparent multiplets associated with an averaged coupling constants were designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets) and br (broadened). All ^{13}C spectra were recorded with broadband proton decoupling. HRMS analysis was

performed on Micromass 70 VSE mass spectrometer. Anhydrous solvents purchased from Aldrich were additionally purified on PureSolv PS-400-4 by Innovative Technology, Inc. purification system and/or stored over calcium hydride. All starting materials were purchased from Strem Chemicals, Aldrich, TCI America, Oakwood Chemical, AK Sci., Alfa Aesar, Enamine, Combi-blocks or synthesized *via* known literature procedures. Palladium(II) chloride and palladium(II)acetate were purchased from Aldrich. Column chromatography was carried out employing Silicycle Silica-P flash silica gel (40-63 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. Data sets for X-Ray diffraction were collected with a «New Xcalibur, Ruby» diffractometer at room temperature.

General procedure for the synthesis of 2-(*N*-tosylamino)benzyl alcohols 1a-g[13]

To a solution of 2-(*N*-tosylamino)benzaldehyde[13] (413 mg, 1.5 mmol) in THF (8.0 mL) was added a solution of RMgBr (3.3 mmol, 2.2 equiv.) dropwise at -78 °C under argon. The resulting mixture was allowed to warm up to room temperature, and saturated NH_4Cl (5 mL) was added. The organic layer was separated, and the water layer was washed with ethyl acetate (2 × 10 mL). The combined organic solutions were dried over Na_2SO_4, and the solvents were evaporated. The resulted crude product was purified by column chromatography (petroleum ether/ethyl acetate, 30:1 to 10:1) to give alcohols **1a-g**.

***N*-{2-[Hydroxy(phenyl)methyl]phenyl}-4-methylbenzenesulfonamide (1a)**[21]**:**

Colorless oil; 509 mg, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (br s, 1H, NH), 7.50–7.45 (m, 3H, H_{Ar}), 7.31–7.13 (m, 8H, H_{Ar}), 7.04–7.00 (m, 1H, H_{Ar}), 6.94–6.92 (m, 1H, H_{Ar}), 5.69 (br s, 1H, CH), 2.76 (br s, 1H, OH), 2.38 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 143.7, 141.3, 136.9, 136.0, 133.4, 129.7 (2C), 129.2, 129.1, 128.8 (2C), 128.0, 127.4 (2C), 126.5 (2C), 124.7, 122.3, 74.9, 21.6 ppm.

***N*-{2-[Hydroxy(4-methylphenyl)methyl]phenyl}-4-methylbenzenesulfonamide (1b)**[13]**:**

Colorless oil; 523 mg, 95% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.07 (br s, 1H, NH), 7.48–7.46 (m, 3H, H_{Ar}), 7.22–7.19 (m, 1H, H_{Ar}), 7.14–7.09 (m, 4H, H_{Ar}), 7.02–6.99 (m, 3H, H_{Ar}), 6.92–6.90 (m, 1H, H_{Ar}), 5.60 (d, ^3J = 3.2 Hz, 1H, CH), 2.81 (d, ^3J = 3.2 Hz, 1H, OH), 2.38 (s, 3H, Me), 2.36 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 143.7, 138.2, 137.7, 136.7, 135.9, 133.3, 129.6 (2C), 129.4 (2C), 129.1, 129.0, 127.3 (2C), 126.4 (2C), 124.6, 122.1, 74.7, 21.6, 21.3 ppm.

***N*-{2-[Hydroxy(4-methoxyphenyl)methyl]phenyl}-4-methylbenzenesulfonamide (1c)[13]:**

Colorless oil; 512 mg, 89% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.18 (br s, 1H, NH), 7.45–7.47 (m, 3H, H_{Ar}), 7.21–7.18 (m, 1H, H_{Ar}), 7.13–7.11 (m, 2H, H_{Ar}), 7.05–6.98 (m, 3H, H_{Ar}), 6.91–6.89 (m, 1H, H_{Ar}), 6.80–6.78 (m, 2H, H_{Ar}), 5.59 (br s, 1H, CH), 3.79 (s, 3H, OMe), 3.11 (br s, 1H, OH), 2.36 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 159.3, 143.7, 136.6, 135.9, 133.3 (2C), 129.6 (2C), 129.0, 128.9, 127.7 (2C), 127.2 (2C), 124.6, 121.9, 114.0 (2C), 74.4, 55.4, 21.6 ppm.

***N*-{2-[(4-Fluorophenyl)(hydroxy)methyl]phenyl}-4-methylbenzenesulfonamide (1d)[13]:**

Colorless oil; 468 mg, 84% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.06 (s, 1H, NH), 7.48–7.46 (m, 1H, H_{Ar}), 7.44–7.42 (m, 2H, H_{Ar}), 7.24–7.21 (m, 1H, H_{Ar}), 7.13–7.08 (m, 4H, H_{Ar}), 7.05–7.02 (m, 1H, H_{Ar}), 6.94–6.90 (m, 3H, H_{Ar}), 5.71 (s, 1H, CH), 3.10 (br s, 1H, OH), 2.37 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 162.4 (d, J = 246.3 Hz), 143.9, 137.0, 136.5, 135.9, 133.2, 129.7 (2C), 129.3, 129.2, 128.0 (d, J = 8.1 Hz, 2C), 127.2 (2C), 124.8, 122.2, 115.4 (d, J = 21.6 Hz, 2C), 74.3, 21.6 ppm.

***N*-{2-[Hydroxy(2-methylphenyl)methyl]phenyl}-4-methylbenzenesulfonamide (1e):**

Colorless oil; 502 mg, 91% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.16 (br s, 1H, NH), 7.66–7.64 (m, 2H, H_{Ar}), 7.44–7.42 (m, 1H, H_{Ar}), 7.39–7.38 (m, 1H, H_{Ar}), 7.24–7.21 (m, 5H, H_{Ar}), 7.12–7.10 (m, 1H, H_{Ar}), 6.97–6.94 (m, 1H, H_{Ar}), 6.58–6.56 (m, 1H, H_{Ar}), 5.73 (d, ^3J = 4.0 Hz, 1H, CH), 2.96 (d, ^3J = 4.0 Hz, 1H, OH), 2.39 (s, 3H, Me), 1.78 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 144.0, 139.1, 137.0, 136.1, 135.5, 133.9, 130.6, 129.8 (2C), 129.0, 128.4, 128.1, 127.3 (2C), 126.5, 126.4,

125.6, 123.9, 70.7, 21.6, 18.8 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{21}H_{21}NO_3SNa$ $[M+Na]^+$ 390.1134; found 390.1132.

***N*-{2-[(2,6-Dimethylphenyl)(hydroxy)methyl]phenyl}-4-methylbenzenesulfonamide (1f):**

Colorless oil; 452 mg, 79% yield; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.11 (br s, 1H, NH), 7.68–7.66 (m, 2H, H_{Ar}), 7.64–7.61 (m, 1H, H_{Ar}), 7.24–7.21 (m, 3H, H_{Ar}), 7.15–7.11 (m, 1H, H_{Ar}), 7.02–7.00 (m, 2H, H_{Ar}), 6.91–6.87 (m, 1H, H_{Ar}), 6.44–6.42 (m, 1H, H_{Ar}), 5.82 (br s, 1H, CH), 2.75 (br s, 1H, OH), 2.38 (s, 3H, Me), 2.00 (s, 6H, Me) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 143.8, 137.6, 137.3 (2C), 137.0, 136.5, 131.0, 129.8 (2C), 129.5 (2C), 128.9, 128.3, 127.5, 127.1 (2C), 124.9, 123.6, 71.4, 21.6, 20.7 (2C) ppm; HRMS (ESI/TOF): m/z calcd. for $C_{22}H_{23}NO_3SNa$ $[M+Na]^+$ 404.1291; found 404.1291.

***N*-[2-(1-Hydroxyethyl)phenyl]-4-methylbenzenesulfonamide (1g)[13]:**

Colorless oil; 415 mg, 95% yield; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.42 (br s, 1H, NH), 7.70–7.68 (m, 2H, H_{Ar}), 7.44–7.42 (m, 1H, H_{Ar}), 7.23–7.17 (m, 3H, H_{Ar}), 7.09–7.07 (m, 1H, H_{Ar}), 7.05–7.03 (m, 1H, H_{Ar}), 4.84 (q, ^3J = 6.6 Hz, 1H, CH), 2.37 (s, 3H, Me), 1.36 (d, ^3J = 6.6 Hz, 3H, Me) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 143.9, 137.1, 135.9, 134.2, 129.8 (2C), 128.7, 127.3 (2C), 127.1, 124.8, 122.0, 69.9, 23.0, 21.7 ppm.

General procedure for the synthesis of 2-(*N*-tosylamino)benzyl alcohols 1h-p[22]

To a solution of the appropriate 2-aminobenzoic acid (3.5 mmol) in H_2O/THF (2:1 v/v) (30 mL) was added triethylamine (1.05 g, 1.47 mL, 10.5 mmol) at room temperature followed by *p*-toluenesulfonyl chloride (810 mg, 4.2 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 6 h. On completion, THF was removed and the aqueous solution was washed with diethyl ether (30 mL). The diethyl ether layer was discarded while the aqueous layer was acidified with hydrochloric acid (2 M, pH ca. 2) and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure.

The resulting solid was dried under vacuum overnight and used directly for the next step. The obtained solid was dissolved in CH_2Cl_2 (35 mL) and cooled to 0 °C under a nitrogen atmosphere. The solution was then treated with *N,O*-dimethylhydroxylamine·HCl (DMHA) (401 mg, 4.2 mmol) followed by *N*-methylmorpholine (NMM) (1.15 mL, 10.5 mmol). 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide) hydrochloride (EDC·HCl) (805 mg, 4.2 mmol) was then added portion-wise over a 15 min period. The reaction mixture was allowed to stir for further 3 h at 0 °C and an additional 15 h at room temperature. On completion, the reaction mixture was treated with saturated $NaHCO_3$ solution (30 mL). The organic and aqueous phases were separated and the aqueous phase was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were washed with 10% citric acid solution (20 mL) followed by brine (30 mL), dried over Na_2SO_2 and concentrated under reduced pressure. The solid product was washed with a mixture of 5% ethyl acetate/*n*-hexane solution and the resulting Weinreb amide was dried under vacuum overnight. The resulted amide was dissolved in anhydrous THF (25 mL) followed by the addition of the respective R^2MgBr (0.5 M, 1 M or 2 M THF solution, 7 mmol) at room temperature under a nitrogen atmosphere. The resulting mixture was then stirred for 18 h at room temperature. On completion, the reaction mixture was treated with saturated NH_4Cl or 2 M aqueous HCl solution (15 mL) and the resulting mixture was stirred at room temperature for 15 min before ethyl acetate (50 mL) was added. The phases were separated and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford a solid or oil, which was then dried under vacuum. The crude product formed after the third step was dissolved in MeOH (35 mL), cooled to 0 °C followed by portionwise addition of $NaBH_4$ (265 mg, 7 mmol). The reaction mixture was allowed to stir for further 1 h at 0 °C and an additional 2 h at room temperature. Upon completion, the reaction mixture was treated with saturated NH_4Cl, stirred for 15 min before ethyl acetate (20 mL) was added. The phases were separated and the

aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The target benzyl alcohols **1h-p** were purified then by column chromatography (petroleum ether/ethyl acetate, 30:1 to 10:1). Yields refer to the overall yields over 4 steps.

***N*-[2-(1-Hydroxyethyl)-4,5-dimethoxyphenyl]-4-methylbenzenesulfonamide (1h)[21]:**

Colorless oil; 898 mg, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (br s, 1H, NH), 7.61–7.59 (m, 2H, H_{Ar}), 7.22–7.20 (m, 2H, H_{Ar}), 6.70 (s, 1H, H_{Ar}), 6.68 (s, 1H, H_{Ar}), 4.83 (q, ^3J = 6.4 Hz, 1H, CH), 3.81 (s, 3H, OMe), 3.68 (s, 3H, OMe), 2.63 (br s, 1H, OH), 2.37 (s, 3H, Me), 1.27 (d, ^3J = 6.4 Hz, 3H, Me) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 148.4, 147.2, 143.9, 136.6, 130.4, 129.7 (2C), 127.5 (2C), 127.3, 109.7, 108.7, 67.6, 56.2, 56.0, 23.0, 21.6 ppm.

***N*-{2-[Hydroxy(phenyl)methyl]-4-methylphenyl}-4-methylbenzenesulfonamide (1i):**

Colorless oil; 887 mg, 69% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.02 (s, 1H, NH), 7.46–7.44 (m, 2H, H_{Ar}), 7.29–7.27 (m, 4H, H_{Ar}), 7.12–7.14 (m, 4H, H_{Ar}), 6.81 (br d, ^3J = 7.8 Hz, 1H, H_{Ar}), 6.77 (d, J = 7.8 Hz, 1H, H_{Ar}), 5.60 (s, 1H, CH), 2.88 (s, 1H, OH), 2.37 (s, 3H, Me), 2.26 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 143.7, 141.4, 139.2, 136.6, 135.7, 130.5, 129.6 (2C), 129.1, 128.7 (2C), 127.8, 127.3 (2C), 126.4 (2C), 125.4, 122.8, 74.5, 21.6, 21.3 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{21}H_{21}NO_3SNa$ $[M+Na]^+$ 390.1134; found 390.1135.

***N*-{2-[Hydroxy(phenyl)methyl]-4-methoxyphenyl}-4-methylbenzenesulfonamide (1j):**

Colorless oil; 980 mg, 73% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.14 (s, 1H, NH), 7.46–7.44 (m, 2H, H_{Ar}), 7.30 – 7.28 (m, 3H, H_{Ar}), 7.16–7.12 (m, 4H, H_{Ar}), 7.07 (d, ^4J = 2.5 Hz, 1H, H_{Ar}), 6.78 (d, ^3J = 8.5 Hz, 1H, H_{Ar}), 6.51 (dd, ^3J = 8.5, ^4J = 2.5 Hz, 1H, H_{Ar}), 5.61 (d, ^3J = 3.2 Hz, 1H, CH), 3.73 (s, 3H, OMe), 2.75 (d, ^3J = 3.2 Hz, 1H, OH), 2.37 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 160.1, 143.8, 141.5, 137.2, 136.5, 130.2, 129.7 (2C), 128.7 (2C), 127.8, 127.4 (2C), 126.4 (2C), 125.0, 109.9,

107.2, 74.6, 55.5, 21.7 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{21}H_{21}NO_4SNa$ $[M+Na]^+$ 406.1083; found 406.1075.

***N*-{2-[Hydroxy(phenyl)methyl]-5-methylphenyl}-4-methylbenzenesulfonamide (1k):**

Colorless oil; 952 mg, 74% yield; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.76 (s, 1H, NH), 7.48 – 7.46 (m, 2H, H_{Ar}), 7.30 – 7.28 (m, 3H, H_{Ar}), 7.26 (d, ^3J = 8.2 Hz, 1H, H_{Ar}), 7.15 – 7.13 (m, 4H, H_{Ar}), 7.00 (br d, ^3J = 8.2 Hz, 1H, H_{Ar}), 6.75 (br s, 1H, H_{Ar}), 5.65 (s, 1H, CH), 2.98 (br s, 1H, OH), 2.38 (s, 3H, Me), 2.21 (s, 3H, Me) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 143.7, 141.4, 136.6, 135.0, 134.3, 132.9, 129.8, 129.7 (2C), 129.5, 128.6 (2C), 127.8, 127.3 (2C), 126.4 (2C), 123.1, 74.2, 21.6, 21.0 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{21}H_{21}NO_3SNa$ $[M+Na]^+$ 390.1134; found 390.1126.

***N*-{2-[Hydroxy(phenyl)methyl]-5-methoxyphenyl}-4-methylbenzenesulfonamide (1l):**

Colorless oil; 953 mg, 71% yield; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.48–7.46 (m, 2H, H_{Ar}), 7.41 (s, 1H, NH), 7.29–7.22 (m, 3H, H_{Ar}), 7.16–7.11 (m, 4H, H_{Ar}), 7.11 (d, ^3J = 8.8 Hz, 1H, H_{Ar}), 6.67 (dd, ^3J = 8.8, ^4J = 2.8 Hz, 1H, H_{Ar}), 6.47 (d, ^4J = 2.8 Hz, 1H, H_{Ar}), 5.59 (s, 1H, CH), 3.63 (s, 3H, OMe), 3.21 (br s, 1H, OH), 2.37 (s, 3H, Me) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 157.6, 143.8, 141.4, 138.6, 136.5, 129.7 (2C), 128.6 (2C), 127.8, 127.6, 127.4 (2C), 126.5 (2C), 126.4, 114.8, 113.4, 73.1, 55.4, 21.6 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{21}H_{21}NO_4SNa$ $[M+Na]^+$ 406.1083; found 406.1081.

***N*-{2-[Hydroxy(phenyl)methyl]-4,5-dimethoxyphenyl}-4-methylbenzenesulfonamide (1m)[13,21]:**

Colorless oil; 1223 mg, 81% yield; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.52–7.50 (m, 2H, H_{Ar}), 7.31–7.27 (m, 4H, H_{Ar}+NH), 7.20–7.18 (m, 2H, H_{Ar}), 7.14–7.12 (m, 2H, H_{Ar}), 6.82 (s, 1H, H_{Ar}), 6.44 (s, 1H, H_{Ar}), 5.61 (d, ^3J = 3.5 Hz, 1H, CH), 3.74 (s, 3H, OMe), 3.67 (s, 3H, OMe), 2.72 (br s, 1H, OH), 2.40 (s, 3H, Me) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 148.8, 147.0, 143.9, 141.7, 136.5, 129.7 (2C), 128.9 (2C), 128.7 (2C), 127.9, 127.5 (2C), 126.5 (2C), 111.7, 108.8, 73.1, 56.1 (2C), 21.7 ppm.

***N*-{4,5-Difluoro-2-[hydroxy(phenyl)methyl]phenyl}-4-methylbenzenesulfonamide (1n)[13]:**

Colorless oil; 859 mg, 63% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.48–7.44 (m, 2H, H_{Ar}), 7.32–7.22 (m, 4H, H_{Ar}), 7.20–7.14 (m, 2H, H_{Ar}), 7.11–7.06 (m, 2H, H_{Ar}), 6.66 (dd, $^3J_{H\text{-}F}$ = 10.8 Hz, $^4J_{H\text{-}F}$ = 8.5 Hz, 1H, H_{Ar}), 5.53 (s, 1H, CH), 2.39 (s, 3H, Me) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 149.6 (dd, ^1J = 249.4 Hz, ^2J = 13.2 Hz), 147.2 (dd, ^1J = 247.1, ^2J = 12.7 Hz), 144.4, 140.5, 135.9, 131.9 (d, ^3J = 6.5 Hz), 131.1 (br s), 129.9 (2C), 128.9 (2C), 128.3, 127.2 (2C), 126.4 (2C), 117.7 (d, ^2J = 19.1 Hz), 112.3 (d, ^2J = 21.0 Hz), 73.3, 21.6 ppm.

***N*-{4-Bromo-2-[hydroxy(phenyl)methyl]phenyl}-4-methylbenzenesulfonamide (1o):**

Colorless oil; 1029 mg, 68% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.24 (s, 1H, H_{Ar}), 7.63 (d, ^4J = 1.7 Hz, 1H, H_{Ar}), 7.44–7.42 (m, 2H, H_{Ar}), 7.31–7.29 (m, 3H, H_{Ar}), 7.15–7.10 (m, 5H, H_{Ar}), 6.77 (d, ^3J = 8.2 Hz, 1H, H_{Ar}), 5.62 (d, ^3J = 3.4 Hz, 1H, CH), 3.03 (d, ^3J = 3.4 Hz, 1H, OH), 2.38 (s, 3H, Me) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 144.1, 140.6, 137.3, 136.1, 131.5, 130.5, 129.8 (2C), 128.9 (2C), 128.2, 127.3 (2C), 127.2, 126.3 (2C), 124.3, 122.7, 74.6, 21.7 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{20}H_{18}BrNO_3SNa$ $[M+Na]^+$ 454.0083; found 454.0085.

***N*-{2-[(4-Bromophenyl)(hydroxy)methyl]-4,5-dimethoxyphenyl}-4-methylbenzenesulfonamide (1p)**[11c]**:**

Colorless oil; 896 mg, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47–7.45 (m, 2H, H_{Ar}), 7.37–7.35 (m, 2H, H_{Ar}), 7.23 (br s, 1H, NH), 7.19–7.17 (m, 2H, H_{Ar}), 7.03–7.01 (m, 2H, H_{Ar}), 6.77 (s, 1H, H_{Ar}), 6.48 (s, 1H, H_{Ar}), 5.73 (br s, 1H, CH), 3.71 (s, 3H, OMe), 3.71 (s, 3H, OMe), 2.98 (br s, 1H, OH), 2.41 (s, 3H, Me) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 149.0, 147.2, 144.0, 141.2, 136.3, 131.5 (2C), 129.7 (2C), 128.9, 128.0 (2C), 127.9, 127.4 (2C), 121.5, 112.1, 108.7, 72.4, 56.2, 56.0, 21.6 ppm.

General procedure for the synthesis of benzylfurans 3a,g[11d]

To a solution of an appropriate benzyl alcohol **1a** or **1g** (2.0 mmol) and 2-methylfuran (**2a**) (3 mmol, 265 μL, 1.5 equiv.) in 1,2-DCE (10 mL) was added *p*-TSA (17 mg, 0.1 mmol). The resulting

mixture was stirred for 1.5 h at 60 °C. Upon completion, the reaction mixture was concentrated under reduced pressure. The target benzylfurans **3** were further purified by column chromatography (petroleum ether/ethyl acetate, 20:1).

4-Methyl-*N*-{2-[(5-methylfuran-2-yl)(phenyl)methyl]phenyl}benzenesulfonamide (3a)[11d]**:**

Colorless oil; 818 mg, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62–7.60 (m, 2H, H_{Ar}), 7.51–7.49 (m, 1H, H_{Ar}), 7.29–7.24 (m, 6H, H_{Ar}), 7.14–7.10 (m, 1H, H_{Ar}), 6.85–6.83 (m, 2H, H_{Ar}), 6.80–6.78 (m, 1H, H_{Ar}), 6.31 (br s, 1H, NH), 5.88 (d, ^3J = 2.9 Hz, 1H, H_{Fur}), 5.63 (d, ^3J = 2.9 Hz, 1H, H_{Fur}), 4.95 (br s, 1H, CH), 2.46 (s, 3H, Me), 2.27 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 152.5, 152.4, 143.9, 140.0, 137.2, 135.7, 134.4, 129.9 (2C), 129.7, 128.9 (2C), 128.8 (2C), 128.0, 127.4, 127.3 (2C), 126.5, 125.7, 110.1, 106.3, 46.2, 21.7, 13.7 ppm.

4-Methyl-*N*-{2-[1-(5-methylfuran-2-yl)ethyl]phenyl}benzenesulfonamide (3g)[11d]**:**

Colorless oil; 590 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61–7.59 (m, 2H, H_{Ar}), 7.40–7.38 (m, 1H, H_{Ar}), 7.24–7.14 (m, 5H, H_{Ar}), 6.77 (br s, 1H, NH), 5.83 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 5.79 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 3.86 (q, ^3J = 7.2 Hz, 1H, CH), 2.39 (s, 3H, Me), 2.21 (s, 3H, Me), 1.32 (d, ^3J = 7.2 Hz, 3H, Me) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 155.7, 151.6, 143.8, 137.2, 137.0, 134.3, 129.7 (2C), 127.8, 127.6, 127.4 (2C), 126.7, 125.2, 106.2, 106.0, 34.0, 21.6, 18.4, 13.6 ppm.

General procedure for the synthesis of indoles 4a-p

In a 3 mL Wheaton microreactor vial equipped with a Teflon pressure cap, a mixture of an appropriate benzyl alcohol **1** (0.2 mmol), 2-methylfuran (**2a**) (27 μL, 0.3 mmol, 1.5 equiv.), *p*-TSA (1.4 mg, 4 mol%) and acetic acid (2 mL) was stirred at 65 °C for 1.5 h. After that, $Pd(OAc)_2$ (2.3 mg, 5 mol%), benzoquinone (33 mg, 0.3 mmol, 1.5 equiv.) and NaOAc (0.7 mg, 4 mol%) was added, and the reaction mixture was stirred for an additional 16 h at 100 °C. Next, I_2 (5 mg, 10 mol%) was added, and the resulting mixture was stirred further for 3 h at 100 °C. Upon completion, the reaction mixture was

filtered through a pad of silica, the solvent was evaporated, and the residue was subjected to column chromatography (petroleum ether/ethyl acetate, 30:1 to 10:1) to afford a target indole derivative.

Procedure for the gram-scale synthesis of indole 4a

In a 100 mL RBF equipped with a rubber septum, a mixture of benzyl alcohol **1a** (1059 mg, 3 mmol), 2-methylfuran (**2a**) (405 μL, 4.5 mmol, 1.5 equiv.), *p*-TSA (21 mg, 4 mol%) and acetic acid (30 mL) was stirred at 65 °C for 1.5 h. After that, $Pd(OAc)_2$ (69 mg, 5 mol%), benzoquinone (990 mg, 4.5 mmol, 1.5 equiv.) and NaOAc (20 mg, 4 mol%) was added, and the reaction mixture was stirred for an additional 16 h at 100 °C. Next, I_2 (150 mg, 10 mol%) was added, and the resulting mixture was stirred further for 3 h at 100 °C. Upon completion, the reaction mixture was filtered through a pad of silica, the solvent was evaporated, and the residue was subjected to column chromatography (petroleum ether/ethyl acetate, 15:1) to afford indole **4a** as pale yellow oil (1035 mg, 83%).

(*E*)-4-(3-Phenyl-1-tosyl-1*H*-indol-2-yl)but-3-en-2-one (4a)[11c,d]**:**

Pale yellow oil; 76 mg, 91% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.30–8.28 (m, 1H, H_{Ar}), 8.13 (d, ^3J = 16.5 Hz, 1H, CH), 7.61–7.59 (m, 2H, H_{Ar}), 7.45–7.37 (m, 4H, H_{Ar}), 7.30–7.22 (m, 4H, H_{Ar}), 7.19–7.17 (m, 2H, H_{Ar}), 6.06 (d, ^3J = 16.5 Hz, 1H, CH), 2.34 (s, 3H, Me), 2.31 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 198.3, 145.4, 137.6, 135.0, 132.6, 132.6, 132.4, 131.7, 131.1, 129.9 (2C), 129.7 (2C), 129.2 (2C), 128.8, 128.4, 126.8 (3C), 124.6, 120.9, 115.7, 27.1, 21.7 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{25}H_{22}NO_3S$ $[M+H]^+$ 416.1315; found 416.1315.

(*E*)-4-[3-(4-Methylphenyl)-1-tosyl-1*H*-indol-2-yl]but-3-en-2-one (4b):

Pale yellow oil; 75 mg, 87% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.29–8.27 (m, 1H, H_{Ar}), 8.13 (d, ^3J = 16.5 Hz, 1H, CH), 7.60–7.58 (m, 2H, H_{Ar}), 7.42–7.39 (m, 1H, H_{Ar}), 7.30–7.28 (m, 1H, H_{Ar}), 7.24–7.21 (m, 3H, H_{Ar}), 7.18–7.14 (m, 4H, H_{Ar}), 6.11 (d, ^3J = 16.5 Hz, 1H, CH), 2.40 (s, 3H, Me), 2.33 (s, 6H, Me) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 198.5, 145.3, 138.3, 137.6, 135.0, 132.9, 132.5, 131.5,

131.2, 129.9 (2C), 129.8 (2C), 129.6 (2C), 129.3, 129.1, 126.8 (3C), 124.6, 121.0, 115.7, 27.0, 21.7, 21.5 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{26}H_{24}NO_3S$ $[M+H]^+$ 430.1471; found 430.1472.

(*E*)-4-[3-(4-Methoxyphenyl)-1-tosyl-1*H*-indol-2-yl]but-3-en-2-one (4c):

Pale yellow oil; 76 mg, 85% yield; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.29–8.27 (m, 1H, H_{Ar}), 8.13 (d, ^3J = 16.5 Hz, 1H, CH), 7.60–7.58 (m, 2H, H_{Ar}), 7.42–7.39 (m, 1H, H_{Ar}), 7.30–7.28 (m, 1H, H_{Ar}), 7.25–7.22 (m, 1H, H_{Ar}), 7.19–7.16 (m, 4H, H_{Ar}), 6.97–6.95 (m, 2H, H_{Ar}), 6.13 (d, ^3J = 16.5 Hz, 1H, CH), 3.85 (s, 3H, OMe), 2.33 (s, 6H, Me) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 198.5, 159.7, 145.3, 137.6, 135.0, 132.9, 132.3, 131.5, 131.3, 130.9 (2C), 129.9 (2C), 128.8, 126.8 (3C), 124.6, 124.3, 121.0, 115.8, 114.7 (2C), 55.4, 27.0, 21.7 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{26}H_{24}NO_4S$ $[M+H]^+$ 446.1421; found 446.1418.

(*E*)-4-[3-(4-Fluorophenyl)-1-tosyl-1*H*-indol-2-yl]but-3-en-2-one (4d):

Pale yellow oil; 72 mg, 83% yield; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.30–8.28 (m, 1H, H_{Ar}), 8.12 (d, ^3J = 16.5 Hz, 1H, CH), 7.62–7.60 (m, 2H, H_{Ar}), 7.43–7.41 (m, 1H, H_{Ar}), 7.26–7.23 (m, 4H, H_{Ar}), 7.19–7.17 (m, 2H, H_{Ar}), 7.15–7.12 (m, 2H, H_{Ar}), 6.04 (d, ^3J = 16.5 Hz, 1H, CH), 2.34 (s, 3H, Me), 2.33 (s, 3H, Me) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 198.2, 162.7 (d, $^1J_{C\text{-}F}$ = 248.1 Hz), 145.5, 137.5, 135.0, 132.7, 132.5, 131.8, 131.6 (d, $^3J_{C\text{-}F}$ = 8.1 Hz, 2C), 130.9, 129.9 (2C), 128.3, 127.5, 126.9, 126.8 (2C), 124.7, 120.7, 116.4 (d, $^2J_{C\text{-}F}$ = 21.6 Hz, 2C), 115.7, 27.1, 21.7 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{25}H_{21}FNO_3S$ $[M+H]^+$ 434.1221; found 434.1219.

(*E*)-4-[3-(2-Methylphenyl)-1-tosyl-1*H*-indol-2-yl]but-3-en-2-one (4e):

Pale yellow oil; 72 mg, 84% yield; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.30–8.28 (m, 1H, H_{Ar}), 8.17 (d, ^3J = 16.6 Hz, 1H, CH), 7.57–7.55 (m, 2H, H_{Ar}), 7.43–7.40 (m, 1H, H_{Ar}), 7.34–7.27 (m, 2H, H_{Ar}), 7.25–7.20 (m, 2H, H_{Ar}), 7.17–7.15 (m, 2H, H_{Ar}), 7.04–7.02 (m, 2H, H_{Ar}), 5.80 (d, ^3J = 16.6 Hz, 1H, CH), 2.33 (s, 3H, Me), 2.28 (s, 3H, Me), 1.84 (s, 3H, Me) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 198.5, 145.3,

137.8, 136.6, 134.8, 132.9, 131.8 (2C), 131.4, 131.0, 130.8, 129.8 (2C), 129.7, 129.2, 128.9, 127.0, 126.7 (2C), 126.6, 124.8, 121.0, 116.1, 26.8, 21.7, 19.5 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{26}H_{24}NO_3S$ $[M+H]^+$ 430.1471; found 430.1473.

(*E*)-4-[3-(2,6-Dimethylphenyl)-1-tosyl-1*H*-indol-2-yl]but-3-en-2-one (4f):

Pale yellow oil; 54 mg, 61% yield; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.32–8.30 (m, 1H, H_{Ar}), 8.21 (d, ^3J = 16.6 Hz, 1H, H_{Ar}), 7.53–7.51 (m, 2H, H_{Ar}), 7.44–7.41 (m, 1H, H_{Ar}), 7.23–7.20 (m, 2H, H_{Ar}), 7.14–7.12 (m, 2H, H_{Ar}), 7.11–7.09 (m, 2H, H_{Ar}), 6.96–6.94 (m, 1H, H_{Ar}), 5.68 (d, ^3J = 16.6 Hz, 1H, CH), 2.32 (s, 3H, Me), 2.28 (s, 3H, Me), 1.72 (s, 6H, Me) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 198.7, 145.3, 138.4, 136.5, 134.7, 133.1 (2C), 131.4, 131.1, 130.9, 129.8, 129.7 (2C), 129.0, 128.8, 128.1 (2C), 127.2, 126.6 (2C), 125.0, 120.7, 116.5, 26.7, 21.7, 19.8 (2C) ppm; HRMS (ESI/TOF): m/z calcd. for $C_{27}H_{26}NO_3S$ $[M+H]^+$ 444.1628; found 444.1631.

(*E*)-4-(3-Methyl-1-tosyl-1*H*-indol-2-yl)but-3-en-2-one (4g)[11c]**:**

Pale yellow oil; 12 mg, 16% yield; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.22–8.20 (m, 1H, H_{Ar}), 8.15 (d, ^3J = 16.6 Hz, 1H, CH), 7.53–7.51 (m, 2H, H_{Ar}), 7.45–7.43 (m, 1H, H_{Ar}), 7.40–7.37 (m, 1H, H_{Ar}), 7.29–7.26 (m, 1H, H_{Ar}), 7.12–7.10 (m, 2H, H_{Ar}), 6.34 (d, ^3J = 16.6 Hz, 1H, CH), 2.49 (s, 3H, Me), 2.30 (s, 3H, Me), 2.29 (s, 3H, Me). ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 198.8, 145.1, 137.4, 134.8, 134.4, 131.8, 131.7, 131.6, 129.8 (2C), 126.7, 126.6 (2C), 124.3, 124.0, 120.0, 115.6, 26.5, 21.6, 11.1 ppm.

(*E*)-4-(5,6-Dimethoxy-3-methyl-1-tosyl-1*H*-indol-2-yl)but-3-en-2-one (4h)[11c,d]**:**

Pale yellow oil; 70 mg, 85% yield; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, ^3J = 16.6 Hz, 1H, CH), 7.74 (s, 1H, H_{Ar}), 7.46–7.44 (m, 2H, H_{Ar}), 7.11–7.09 (m, 2H, H_{Ar}), 6.78 (s, 1H, H_{Ar}), 6.27 (d, ^3J = 16.6 Hz, 1H, H_{Ar}), 4.00 (s, 3H, OMe), 3.89 (s, 3H, OMe), 2.46 (s, 3H, Me), 2.29 (s, 3H, Me), 2.25 (s, 3H, Me) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 198.9, 149.8, 148.0, 145.1, 134.6, 134.6, 132.3, 130.7, 130.0, 129.7 (2C), 126.5 (2C), 125.1, 124.6, 100.8, 99.2, 56.5, 56.2, 26.4, 21.6, 11.5 ppm.

(*E*)-4-(5-Methyl-3-phenyl-1-tosyl-1*H*-indol-2-yl)but-3-en-2-one (4i):

Pale yellow oil; 74 mg, 86% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.16 (d, ^{3}J = 8.6 Hz, 1H, H_{Ar}), 8.12 (d, ^{3}J = 16.5 Hz, 1H, CH), 7.59–7.57 (m, 2H, H_{Ar}), 7.44–7.39 (m, 3H, H_{Ar}), 7.26–7.22 (m, 3H, H_{Ar}), 7.18–7.16 (m, 2H, H_{Ar}), 7.04 (br s, 1H, H_{Ar}), 6.04 (d, ^{3}J = 16.5 Hz, 1H, CH), 2.35 (s, 3H, Me), 2.34 (s, 3H, Me), 2.31 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 198.4, 145.2, 135.9, 134.9, 134.5, 132.8, 132.6, 132.3, 131.8, 131.3, 129.8 (2C), 129.7 (2C), 129.2 (2C), 128.9, 128.4 (2C), 126.8 (2C), 120.6, 115.5, 27.0, 21.7, 21.3 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{26}H_{24}NO_3S$ $[M+H]^+$ 430.1471; found 430.1470.

(*E*)-4-(5-Methoxy-3-phenyl-1-tosyl-1*H*-indol-2-yl)but-3-en-2-one (4j):

Pale yellow oil; 78 mg, 87% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.17 (d, ^{3}J = 9.2 Hz, 1H, H_{Ar}), 8.09 (d, ^{3}J = 16.5 Hz, 1H, CH), 7.56–7.54 (m, 2H, H_{Ar}), 7.45–7.38 (m, 3H, H_{Ar}), 7.25–7.23 (m, 2H, H_{Ar}), 7.17–7.15 (m, 2H, H_{Ar}), 7.02 (dd, ^{3}J = 9.2, ^{4}J = 2.5 Hz, 1H, H_{Ar}), 6.66 (d, ^{4}J = 2.5 Hz, 1H, H_{Ar}), 6.03 (d, ^{3}J = 16.5 Hz, 1H, CH), 3.73 (s, 3H, OMe), 2.34 (s, 3H, Me), 2.31 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 198.5, 157.4, 145.3, 134.7, 132.7, 132.5, 132.4, 132.3, 132.2, 129.8 (2C), 129.6 (2C), 129.3 (2C), 129.2, 128.5, 126.8 (2C), 122.5, 116.9, 116.2, 102.6, 55.7, 27.0, 21.7 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{26}H_{24}NO_4S$ $[M+H]^+$ 446.1421; found 446.1416.

(*E*)-4-(6-Methyl-3-phenyl-1-tosyl-1*H*-indol-2-yl)but-3-en-2-one (4k):

Pale yellow oil; 73 mg, 85% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.11 (d, ^{3}J = 16.5 Hz, 1H, CH), 8.10 (br s, 1H, H_{Ar}), 7.60–7.58 (m, 2H, H_{Ar}), 7.44–7.38 (m, 3H, H_{Ar}), 7.26–7.24 (m, 2H, H_{Ar}), 7.19–7.15 (m, 3H, H_{Ar}), 7.07 (d, ^{3}J = 8.0 Hz, 1H, H_{Ar}), 6.03 (d, ^{3}J = 16.5 Hz, 1H, CH), 2.52 (s, 3H, Me), 2.35 (s, 3H, Me), 2.30 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 198.4, 145.3, 138.1, 137.4, 135.1, 132.8, 132.6, 132.0, 131.0, 129.9 (2C), 129.7 (2C), 129.2 (2C), 129.1, 129.0, 128.4, 126.8 (2C), 126.2,

120.5, 115.8, 27.1, 22.4, 21.8 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{26}H_{24}NO_3S$ $[M+H]^+$ 430.1471; found 430.1470.

(*E*)-4-(6-Methoxy-3-phenyl-1-tosyl-1H-indol-2-yl)but-3-en-2-one (4l):

Pale yellow oil; 77 mg, 86% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.10 (d, ^3J = 16.5 Hz, 1H, CH), 7.82 (d, ^4J = 2.0 Hz, 1H, H_{Ar}), 7.60–7.58 (m, 2H, H_{Ar}), 7.44–7.36 (m, 3H, H_{Ar}), 7.25–7.23 (m, 2H, H_{Ar}), 7.19–7.17 (m, 2H, H_{Ar}), 7.15 (d, ^3J = 8.6 Hz, 1H, H_{Ar}), 6.86 (dd, ^3J = 8.6 Hz, ^4J = 2.0 Hz, 1H, H_{Ar}), 6.02 (d, ^3J = 16.5 Hz, 1H, CH), 3.93 (s, 3H, Me), 2.35 (s, 3H, Me), 2.29 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 198.4, 159.7, 145.4, 139.1, 135.0, 132.8, 132.6, 131.2, 130.5, 129.9 (2C), 129.7 (2C), 129.5, 129.2 (2C), 128.5, 126.8 (2C), 125.1, 121.6, 114.2, 99.7, 56.0, 27.0, 21.8 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{26}H_{24}NO_4S$ $[M+H]^+$ 446.1421; found 446.1414.

(*E*)-4-(5,6-Dimethoxy-3-phenyl-1-tosyl-1*H*-indol-2-yl)but-3-en-2-one (4m)[11c,d]**:**

Pale yellow oil; 85 mg, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (d, ^3J = 16.4 Hz, 1H, CH), 7.87 (s, 1H, H_{Ar}), 7.58–7.56 (m, 2H, H_{Ar}), 7.49–7.40 (m, 3H, H_{Ar}), 7.28–7.25 (m, 2H, H_{Ar}), 7.20–7.18 (m, 2H, H_{Ar}), 6.64 (s, 1H, H_{Ar}), 6.02 (d, ^3J = 16.5 Hz, 1H, CH), 4.06 (s, 3H, OMe), 3.80 (s, 3H, OMe), 2.37 (s, 3H, Me), 2.30 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 198.5, 150.0, 148.2, 145.3, 134.7, 132.7 (2C), 132.6, 130.7, 130.5, 130.0, 129.8 (2C), 129.6 (2C), 129.3 (2C), 128.5, 126.7 (2C), 124.4, 101.3, 99.2, 56.6, 56.2, 27.0, 21.7 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{27}H_{26}NO_5S$ $[M+H]^+$ 476.1526; found 476.1534.

(*E*)-4-(5,6-Difluoro-3-phenyl-1-tosyl-1*H*-indol-2-yl)but-3-en-2-one (4n):

Pale yellow oil; 50 mg, 55% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.17–8.14 (m, 1H, H_{Ar}), 8.06 (d, ^3J = 16.5 Hz, 1H, CH), 7.60–7.58 (m, 2H, H_{Ar}), 7.46–7.39 (m, 3H, H_{Ar}), 7.23–7.21 (m, 4H, H_{Ar}), 7.05–7.02 (m, 1H, H_{Ar}), 6.03 (d, ^3J = 16.5 Hz, 1H, CH), 2.37 (s, 3H, Me), 2.29 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 198.1, 150.2 (dd, $^1J_{C\text{-}F}$ = 248.3 Hz, $^2J_{C\text{-}F}$ = 14.8 Hz), 149.1 (dd, $^1J_{C\text{-}F}$ = 246.0 Hz,

$^{2}J_{C\text{-}F}$ = 14.6 Hz), 145.9, 134.7, 132.9, 132.8 (2C), 132.7, 131.7, 131.6, 130.1 (2C), 129.5 (2C), 129.4 (2C), 128.8, 127.8, 126.9 (2C), 107.8 (d, $^{2}J_{C\text{-}F}$ = 20.0 Hz), 104.9 (d, $^{2}J_{C\text{-}F}$ = 24.7 Hz), 27.2, 21.8 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{25}H_{20}F_2NO_3S$ $[M+H]^+$ 452.1126; found 452.1125.

(*E*)-4-(6-Bromo-3-phenyl-1-tosyl-1*H*-indol-2-yl)but-3-en-2-one (4o):

Pale yellow oil; 45 mg, 45% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.49 (d, ^{4}J = 1.6 Hz, 1H, H_{Ar}), 8.07 (d, ^{3}J = 16.5 Hz, 1H, CH), 7.63–7.61 (m, 2H, H_{Ar}), 7.45–7.39 (m, 3H, H_{Ar}), 7.36 (dd, ^{3}J = 8.4 Hz, ^{4}J = 1.6 Hz, 1H, H_{Ar}), 7.24–7.22 (m, 4H, H_{Ar}), 7.15 (d, ^{3}J = 8.4 Hz, 1H, H_{Ar}), 6.03 (d, ^{3}J = 16.5 Hz, 1H, CH), 2.37 (s, 3H, Me), 2.29 (s, 3H, Me) ppm; $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 198.1, 145.8, 138.1, 134.9, 133.0, 132.0, 131.9, 131.8, 130.1 (2C), 129.8, 129.7 (2C), 129.3 (2C), 128.7, 128.0 (2C), 126.9 (2C), 122.0, 120.7, 118.6, 27.2, 21.8 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{25}H_{21}BrNO_3S$ $[M+H]^+$ 494.0420; found 494.0419.

(*E*)-4-[3-(4-Bromophenyl)-5,6-dimethoxy-1-tosyl-1*H*-indol-2-yl]but-3-en-2-one (4p):

Pale yellow oil; 83 mg, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, ^{3}J = 16.5 Hz, 1H, CH), 7.84 (s, 1H, H_{Ar}), 7.58–7.53 (m, 4H, H_{Ar}), 7.18–7.12 (m, 4H, H_{Ar}), 6.57 (s, 1H, H_{Ar}), 6.00 (d, ^{3}J = 16.5 Hz, 1H, H_{Ar}), 4.02 (s, 3H, OMe), 3.78 (s, 3H, OMe), 2.34 (s, 3H, Me), 2.29 (s, 3H, Me) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 198.0, 150.2, 148.5, 145.4, 135.0, 132.6 (2C), 132.5, 132.3, 131.8, 131.3 (2C), 131.1, 130.6, 129.9 (2C), 128.0, 126.7 (2C), 124.0, 122.7, 101.2, 99.4, 56.6, 56.3, 27.0, 21.7 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{27}H_{25}BrNO_5S$ $[M+H]^+$ 554.0631; found 554.0622.

Alternative Synthesis of (*E*)-4-(3-methyl-1-tosyl-1*H*-indol-2-yl)but-3-en-2-one (4g)

In a 3 mL Wheaton microreactor vial, equipped with a Teflon pressure cap, a mixture of benzylfuran **3b** (71 mg, 0.2 mmol), $Pd(OAc)_2$ (2.3 mg, 5 mol%), benzoquinone (22 mg, 0.2 mmol, 1.0 equiv.) and acetic acid (2 mL) was stirred at 100 °C for 16 h. After that, I_2 (5 mg, 10 mol%) was added, and the resulting mixture was stirred further for 3 h at 100 °C. Upon completion, the reaction mixture

was filtered through a pad of silica, the solvent was evaporated, and the residue was subjected to a column chromatography (petroleum ether/ethyl acetate, 20:1) to afford target indole **4g** as a pale yellow oil (52 mg, 73%).

General procedure for the synthesis of indoles 4q-x

In a 3 mL Wheaton microreactor vial equipped with a Teflon pressure cap, a mixture of benzyl alcohol **1a** (71 mg, 0.2 mmol), furan **2** (0.2 mmol, 1.0 equiv.), *p*-TSA (1.4 mg, 4 mol%) and acetic acid (2 mL) was stirred at 65 °C for 1.5 h. After that, $Pd(OAc)_2$ (2.3 mg, 5 mol%), benzoquinone (22 mg, 0.2 mmol, 1.0 equiv.) and NaOAc (0.7 mg, 4 mol%) was added, and the reaction mixture was stirred for an additional 16 h at 100 °C. Next, I_2 (5 mg, 10 mol%) was added, and the resulting mixture was stirred further for 3 h at 100 °C. Upon completion, the reaction mixture was filtered through a pad of silica, the solvent was evaporated, and the residue was subjected to column chromatography (petroleum ether/ethyl acetate, 30:1 to 10:1) to afford a target indole derivative.

(*E*)-1-(3-Phenyl-1-tosyl-1*H*-indol-2-yl)hept-1-en-3-one (4q):

Pale yellow oil; 77 mg, 84% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.30–8.28 (m, 1H, H_{Ar}), 8.10 (d, ^3J = 16.4 Hz, 1H, H_{Ar}), 7.62–7.60 (m, 2H, H_{Ar}), 7.45–7.37 (m, 4H, H_{Ar}), 7.31–7.22 (m, 4H, H_{Ar}), 7.18–7.16 (m, 2H, H_{Ar}), 6.09 (d, ^3J = 16.4 Hz, 1H, CH), 2.53 (t, ^3J = 7.4 Hz, 2H, CH_2), 2.34 (s, 3H, Me), 1.58–1.52 (m, 2H, CH_2), 1.36–1.28 (m, 2H, CH_2), 0.91 (t, ^3J = 7.3 Hz, 3H, Me) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 200.5, 145.3, 137.6, 135.1, 132.6, 132.0, 131.9, 131.2, 131.0, 129.9 (2C), 129.8 (2C), 129.2 (2C), 128.5, 128.3, 126.9 (2C), 126.7, 124.6, 120.8, 115.7, 40.4, 26.7, 22.5, 21.8, 14.0 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{28}H_{28}NO_3S$ $[M+H]^+$ 458.1784; found 458.1783.

(*E*)-4,4-Dimethyl-1-(3-phenyl-1-tosyl-1*H*-indol-2-yl)pent-1-en-3-one (4r):

Pale yellow oil; 71 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.35–8.32 (m, 1H, H_{Ar}), 8.13 (d, ^3J = 15.7 Hz, 1H, CH), 7.68–7.66 (m, 2H, H_{Ar}), 7.47–7.36 (m, 4H, H_{Ar}), 7.32–7.29 (m, 3H, H_{Ar}), 7.26–7.22

(m, 1H, H_{Ar}), 7.19–7.17 (m, 2H, H_{Ar}), 6.50 (d, ^{3}J = 15.7 Hz, 1H, CH), 2.34 (s, 3H, Me), 0.94 (s, 9H, Me) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 203.3, 145.1, 137.7, 135.7, 133.3, 132.8, 130.8, 130.8, 130.0 (2C), 129.8 (2C), 129.2 (2C), 128.1, 128.0, 127.4, 127.1 (2C), 126.6, 124.4, 120.7, 115.7, 43.0, 26.0 (3C), 21.7 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{28}H_{28}NO_3S$ $[M+H]^+$ 458.1784; found 458.1787.

(*E*)-3-Methyl-4-(3-phenyl-1-tosyl-1*H*-indol-2-yl)but-3-en-2-one (4s):

Pale yellow oil; 42 mg, 49% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.34–8.32 (m, 1H, H_{Ar}), 7.92 (s, 1H, CH), 7.54–7.52 (m, 3H, H_{Ar}), 7.44–7.41 (m, 1H, H_{Ar}), 7.39–7.36 (m, 2H, H_{Ar}), 7.32–7.26 (m, 4H, H_{Ar}), 7.14–7.12 (m, 2H, H_{Ar}), 2.54 (s, 3H, Me), 2.31 (s, 3H, Me), 0.98 (s, 3H, Me) ppm; $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 202.0, 145.2, 142.8, 136.4, 136.0, 132.7, 131.9, 130.3 (2C), 129.8 (2C), 129.6, 129.0 (2C), 127.5 (2C), 127.4, 125.6, 124.6, 123.9, 122.8, 120.2, 114.7, 27.4, 21.8, 21.1 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{26}H_{24}NO_3S$ $[M+H]^+$ 430.1471; found 430.1472.

(*E*)-1-Phenyl-3-(3-phenyl-1-tosyl-1*H*-indol-2-yl)prop-2-en-1-one (4t):

Pale yellow oil; 86 mg, 90% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.36–8.34 (m, 1H, H_{Ar}), 8.30 (d, ^{3}J = 15.8 Hz, 1H, CH), 7.69–7.67 (m, 2H, H_{Ar}), 7.64–7.62 (m, 2H, H_{Ar}), 7.54–7.49 (m, 3H, H_{Ar}), 7.47–7.43 (m, 2H, H_{Ar}), 7.41–7.33 (m, 5H, H_{Ar}), 7.28–7.25 (m, 1H, H_{Ar}), 7.18–7.16 (m, 2H, H_{Ar}), 7.00 (d, ^{3}J = 15.8 Hz, 1H, H_{Ar}), 2.33 (s, 3H, Me) ppm; $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 189.6, 145.2, 137.9, 137.8, 135.2, 133.1, 132.9, 132.6, 132.4, 130.9, 130.1 (2C), 129.9 (2C), 129.4 (2C), 128.8, 128.6 (2C), 128.5 (2C), 128.3, 128.1, 127.0 (2C), 126.9, 124.6, 120.8, 115.8, 21.7 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{30}H_{24}NO_3S$ $[M+H]^+$ 478.1471; found 478.1470.

(*E*)-1-(4-Chlorophenyl)-3-(3-phenyl-1-tosyl-1*H*-indol-2-yl)prop-2-en-1-one (4u):

Pale yellow oil; 83 mg, 81% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.36–8.34 (m, 1H, H_{Ar}), 8.30 (d, ^{3}J = 15.8 Hz, 1H, CH), 7.68–7.66 (m, 2H, H_{Ar}), 7.57–7.55 (m, 2H, H_{Ar}), 7.53–7.42 (m, 4H, H_{Ar}), 7.37–7.32 (m, 5H, H_{Ar}), 7.28–7.24 (m, 1H, H_{Ar}), 7.18–7.16 (m, 2H, H_{Ar}), 6.96 (d, ^{3}J = 15.8 Hz, 1H, CH), 2.33 (s,

3H, Me) ppm; $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 188.3, 145.3, 139.4, 138.0, 136.3, 135.4, 133.2, 132.8, 132.6, 130.9, 130.1 (2C), 129.9 (2C), 129.8 (2C), 129.4 (2C), 129.2, 128.9 (2C), 128.3, 127.5, 127.1, 127.0 (2C), 124.6, 120.9, 115.9, 21.7 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{30}H_{23}ClNO_3S$ $[M+H]^+$ 512.1082; found 512.1085.

(*E*)-1-(4-Bromophenyl)-3-(3-phenyl-1-tosyl-1*H*-indol-2-yl)prop-2-en-1-one (4v):

Pale yellow oil; 85 mg, 76% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.35–8.33 (m, 1H, H_{Ar}), 8.30 (d, ^{3}J = 15.8 Hz, 1H, H_{Ar}), 7.67–7.65 (m, 2H, H_{Ar}), 7.54–7.43 (m, 8H, H_{Ar}), 7.36–7.32 (m, 3H, H_{Ar}), 7.28–7.25 (m, 1H, H_{Ar}), 7.18–7.16 (m, 2H, H_{Ar}), 6.94 (d, ^{3}J = 15.8 Hz, 1H, H_{Ar}), 2.33 (s, 3H, Me) ppm; $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 188.5, 145.3, 137.9, 136.7, 135.2, 133.2, 132.9, 132.5, 131.9 (2C), 130.9, 130.1 (2C), 130.0 (2C), 129.9 (2C), 129.4 (2C), 129.3, 128.4, 128.1, 127.4, 127.0 (3C), 124.6, 120.9, 115.9, 21.8 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{30}H_{23}BrNO_3S$ $[M+H]^+$ 556.0577; found 556.0579.

(*E*)-1-(Naphthalen-1-yl)-3-(3-phenyl-1-tosyl-1*H*-indol-2-yl)prop-2-en-1-one (4w):

Pale yellow oil; 89 mg, 84% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.34–8.31 (m, 2H, H_{Ar}), 8.17 (d, ^{3}J = 16.0 Hz, 1H, CH), 7.99–7.97 (m, 1H, H_{Ar}), 7.90–7.88 (m, 1H, H_{Ar}), 7.59–7.57 (m, 2H, H_{Ar}), 7.56–7.42 (m, 8H, H_{Ar}), 7.38–7.36 (m, 2H, H_{Ar}), 7.35–7.33 (m, 1H, H_{Ar}), 7.27–7.24 (m, 1H, H_{Ar}), 7.13–7.11 (m, 2H, H_{Ar}), 6.76 (d, ^{3}J = 16.0 Hz, 1H, CH), 2.31 (s, 3H, Me) ppm; $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 194.5, 145.2, 137.7, 136.3, 135.2, 134.0, 133.9, 132.9, 132.3, 132.2, 132.1, 130.8, 130.6, 130.0 (2C), 129.9 (2C), 129.3 (2C), 128.7, 128.6, 128.4, 127.7, 127.6, 126.9 (3C), 126.5, 125.8, 124.5, 124.5, 120.9, 115.6, 21.7 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{34}H_{26}NO_3S$ $[M+H]^+$ 528.1628; found 528.1628.

(*E*)-Ethyl 4-oxo-6-(3-phenyl-1-tosyl-1*H*-indol-2-yl)hex-5-enoate (4x):

Pale yellow oil; 82 mg, 82% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.31–8.29 (m, 1H, H_{Ar}), 8.18 (d, ^{3}J = 16.4 Hz, 1H, H_{Ar}), 7.63–7.61 (m, 2H, H_{Ar}), 7.45–7.37 (m, 4H, H_{Ar}), 7.30–7.22 (m, 4H, H_{Ar}), 7.19–7.17 (m, 2H, H_{Ar}), 6.12 (d, ^{3}J = 16.4 Hz, 1H, H_{Ar}), 4.15 (q, ^{3}J = 7.1 Hz, 2H, OCH_2), 2.88 (t, ^{3}J = 6.7 Hz, 2H,

CH_2), 2.61 (t, J = 6.7 Hz, 2H, CH_2), 2.34 (s, 3H, Me), 1.26 (t, ^3J = 7.1 Hz, 3H, Me) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 197.7, 172.8, 145.2, 137.5, 134.9, 132.3, 131.6, 131.1, 130.8, 129.9, 129.8 (2C), 129.6 (2C), 129.1 (2C), 128.7, 128.3, 126.8 (2C), 126.7, 124.5, 120.8, 115.6, 60.6, 34.9, 28.1, 21.6, 14.2 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{29}H_{28}NO_5S$ $[M+H]^+$ 502.1683; found 502.1680.

Synthesis of (*E*)-3-(1-tosyl-3-phenyl-1*H*-indol-2-yl)prop-2-enoic acid (6)

To a solution of NaOH (720 mg, 18.0 mmol, 18 equiv.) in H_20 (50 mL) was added Br_2 (465 μL, 9.0 mmol, 9 equiv.) dropwise at 0 °C. The resulting pale yellow solution was stirred at the same temperature for 0.5 h. Then, a solution of indole **4a** (414 mg, 1.0 mmol, 1 equiv.) in 1,4-dioxane (10 mL) was added dropwise over a period of ca. 5 min keeping the temperature at around 0 °C. The reaction was allowed to warm to room temperature and stirred for 24 h. Upon completion, the aqueous solution was washed with diethyl ether (20 mL). The diethyl ether layer was discarded while the aqueous layer was acidified with hydrochloric acid (2 M, pH ca. 2) and extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford acrylic acid **6** as a white solid with high NMR purity. If needed, the acid **6** could be recrystallized from acetone.

(*E*)-3-(1-Tosyl-3-phenyl-1*H*-indol-2-yl)prop-2-enoic acid (6):

White solid; Mp = 218−219 °C; 409 mg, 98% yield; ^1H NMR (400 MHz, DMSO) δ = 12.49 (br s, 1H, OH), 8.19–8.17 (m, 1H, H_{Ar}), 8.07 (d, ^3J = 16.1 Hz, 1H, CH), 7.66–7.64 (m, 2H, H_{Ar}), 7.52–7.43 (m, 4H, H_{Ar}), 7.37–7.33 (m, 4H, H_{Ar}), 7.31–7.27 (m, 1H, H_{Ar}), 7.24–7.22 (m, 1H, H_{Ar}), 5.73 (d, ^3J = 16.1 Hz, 1H, CH), 2.30 (s, 3H, Me) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, DMSO) δ = 166.4, 145.6, 136.3, 133.9, 132.2, 131.7, 131.2, 130.1 (2C), 130.0, 129.5 (2C), 129.0 (2C), 128.2, 127.3, 126.7, 126.3 (2C), 124.7, 124.6, 120.3, 114.9, 20.9 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{24}H_{19}NO_4SNa$ $[M+Na]^+$ 440.0927; found 440.0926.

Synthesis of 9-phenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (7)

To a solution of acrylic acid **6** (167 mg, 0.4 mmol) in DMC (7 mL) was added PCl_5 (100 mg, 0.48 mmol, 1.2 equiv.) at room temperature. The resulting mixture was stirred for 2 h followed by the addition of $AlCl_3$ (64 mg, 0.48 mmol, 1.2 equiv.). The mixture was additionally stirred for 18 h, then quenched with saturated aqueous solution of $NaHCO_3$ (2 mL) and filtered through Celite. The organic phase was separated; the aqueous phase was additionally extracted with CH_2Cl_2 (2 × 15 mL). Combined organic fractions were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to column chromatography (petroleum ether/CH_2Cl_2, 4:1) to afford pyrroloindolone **7**.

9-Phenyl-3*H*-pyrrolo[1,2-*a*]indol-3-one (7)[23]:

Yellow solid; Mp = 120−121 °C; 78 mg, 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71–7.75 (m, 1H, H_{Ar}), 7.62–7.58 (m, 3H, H_{Ar}), 7.53–7.49 (m, 2H, H_{Ar}), 7.45–7.42 (m, 1H, H_{Ar}), 7.35–7.31 (m, 1H, H_{Ar}), 7.26 (d, ^3J = 5.8 Hz, 1H, CH), 7.16–7.12 (m, 1H, H_{Ar}), 6.04 (d, ^3J = 5.8 Hz, 1H, CH) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 165.1, 137.9, 135.2, 134.8, 132.8, 132.1, 129.3 (2C), 128.7, 128.7 (2C), 128.1, 127.3, 123.5, 122.3, 112.8 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{17}H_{12}NO$ $[M+H]^+$ 246.0913; found 246.0907.

Synthesis of (4-chlorophenyl)[2-(3-phenyl-1-tosyl-1*H*-indol-2-yl)cyclopropyl]methanone 8

A suspension of NaH (60% w/w in mineral oil, 24 mg, 0.6 mmol, 1.2 equiv.) and trimethylsulfoxonium iodide (132 mg, 0.6 mmol, 1.2 equiv.) in THF/DMF (10 mL, 5:1) was stirred at 0 °C for 0.5 h followed by dropwise addition of the solution of indole **4u** (256 mg, 0.5 mmol, 1 equiv.) in THF (5 mL) at room temperature. The resulted suspension was stirred for 3 h, then quenched with saturated aqueous solution of NH_4Cl (3 mL). Ethyl acetate (25 mL) was added, the organic phase was separated, washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The

residue was subjected to column chromatography (petroleum ether/CH_2Cl_2 20:1 to 10:1) to give cyclopropane **8**.

(4-Chlorophenyl)[2-(3-phenyl-1-tosyl-1*H*-indol-2-yl)cyclopropyl]methanone (8):

White solid; Mp = 163−164 °C; 221 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.29–8.27 (m, 1H, H_{Ar}), 7.67–7.62 (m, 4H, H_{Ar}), 7.45–7.43 (m, 1H, H_{Ar}), 7.38–7.33 (m, 7H, H_{Ar}), 7.29–7.22 (m, 2H, H_{Ar}), 7.19–7.17 (m, 2H, H_{Ar}), 3.01–2.96 (m, 1H, CH), 2.68–2.64 (m, 1H, CH), 2.34 (s, 3H, Me), 1.65–1.61 (m, 1H, CH_2), 1.05–1.00 (m, 1H, CH_2) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 197.9, 145.0, 139.3, 137.0, 136.4, 136.1, 134.8, 133.1, 130.3 (2C), 130.0 (2C), 129.8, 129.7 (2C), 128.8 (2C), 128.7 (2C), 127.9, 126.6 (2C), 125.5, 125.4, 124.0, 119.8, 115.3, 28.4, 22.3, 22.2, 21.7 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{31}H_{25}ClNO_3S$ $[M+H]^+$ 526.1238; found 526.1241.

Synthesis of 2-[5-(4-chlorophenyl)furan-2-yl]-3-phenyl-1-tosyl-1*H*-indole 9

The solution of cyclopropane **8** (105 mg, 0.2 mmol, 1 equiv.), $CuCl_2{\cdot}H_2O$ (41 mg, 0.24 mmol, 1.2 equiv) and *p*-TSA (9 mg, 25 mol%) in 1,2-DCE (3 mL) was heated for 24 h at 80 °C. Upon completion, the reaction mixture was passed through a pad of silica, concentrated and subjected to a column chromatography (petroleum ether/CH_2Cl_2, 5:1) to afford furan **9**.

2-[5-(4-Chlorophenyl)furan-2-yl]-3-phenyl-1-tosyl-1*H*-indole (9):

Colorless oil; 103 mg, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38–8.36 (m, 1H, H_{Ar}), 7.61–7.55 (m, 3H, H_{Ar}), 7.46–7.44 (m, 3H, H_{Ar}), 7.34–7.26 (m, 8H, H_{Ar}), 7.14–7.12 (m, 2H, H_{Ar}), 6.66 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 6.48 (d, ^3J = 3.0 Hz, 1H, H_{Fur}), 2.32 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 153.7, 144.8, 143.5, 137.4, 135.8, 133.4, 132.5, 129.7 (2C), 129.6 (2C), 129.2, 129.0 (2C), 128.5 (2C), 127.9, 127.7, 127.2 (2C), 126.7, 126.2, 126.1, 125.4 (2C), 124.3, 120.7, 116.4, 115.9, 107.0, 21.7 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{31}H_{22}ClNO_3S$ $[M]^+$ 523.1003; found 523.1004.

Synthesis of 2-[(1*E*,3*E*)-4-(4-chlorophenyl)buta-1,3-dien-1-yl]-3-phenyl-1-tosyl-1*H*-indole (10)

To a solution of cyclopropane **8** (105 mg, 0.2 mmol, 1 equiv.) in EtOH/1,4-dioxane (15 mL, 4:1) was added $NaBH_4$ (15 mg, 0.4 mmol, 2 equiv.) in two portions at room temperature. In two hours, a saturated aqueous solution of NH_4Cl (5 mL) and ethyl acetate (20 ml) was added and the reaction mixture was stirred for additional 15 min. The organic phase was separated, washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was dissolved in 1,2-DCE (5 mL) followed by the addition of *p*-TSA (3.5 mg, 10 mo%). The resulted solution was heated at 70 °C for 30 min. Upon completion, the reaction mixture was concentrated under reduced pressure and subjected to column chromatography (petroleum ether/CH_2Cl_2 6:1) to give diene **10**. If needed, diene **10** could be recrystallized from petroleum ether/ethyl acetate in a form of yellow needles; *however, it should be done with care since diene **10** is unstable on sunlight.*

2-[(1*E*,3*E*)-4-(4-Chlorophenyl)buta-1,3-dien-1-yl]-3-phenyl-1-tosyl-1*H*-indole (10):

Yellow solid; Mp = 191−192 °C; 89 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.30–8.28 (m, 1H, H_{Ar}), 7.65–7.63 (m, 2H, H_{Ar}), 7.46–7.14 (m, 15H, H_{Ar}+CH), 6.87 (dd, ^3J = 15.4 Hz, ^3J = 10.8 Hz, 1H, CH), 6.27 (dd, ^3J = 15.4 Hz, ^3J = 10.8 Hz, 1H, CH), 6.22 (d, ^3J = 15.4 Hz, 1H, CH), 2.32 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 144.9, 137.1, 136.4, 135.7, 135.6, 134.7, 133.8, 133.6, 132.6, 131.5, 130.2 (2C), 129.8, 129.7 (2C), 129.0 (2C), 128.9 (2C), 127.8 (2C), 127.7, 127.0 (2C), 125.5, 124.6, 124.3, 121.9, 120.0, 115.8, 21.7 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{31}H_{24}ClNO_2S$ $[M]^+$ 509.1211; found 509.1211.

Synthesis of (*E*)-5-(4-chlorostyryl)-7-tosyl-7*H*-benzo[*c*]carbazole (12)

Diene **10** (51 mg, 0.1 mmol) was heated at 80 °C under the sunlight on air for 8 h. Upon full conversion of diene **10**, the solid was dissolved in toluene (5 mL) followed by the addition of DDQ (27 mg, 0.12 mmol, 1.2 equiv.). The formed solution was stirred for 6 h at room temperature, then diluted with ethyl acetate (10 mL) and washed with the aqueous solution of NaOH (1 M, 2 × 10 mL). Organic

phase was separated, while the aqueous phase was extracted with ethyl acetate (2 × 5 mL). Combined organic fractions were washed with brine (20 mL), dried over Na_2SO_4, concentrated under reduced pressure and subjected to column chromatography (petroleum ether/CH_2Cl_2, 5:1) in order to isolate carbazole **12**. If needed, the carbazole **12** could be recrystallyzed from MeOH/benzene or cyclohexane/ethyl acetate in a form of yellow needles.

(*E*)-5-(4-Chlorostyryl)-7-tosyl-7*H*-benzo[*c*]carbazole (12):

Pale yellow solid; Mp = 235−236 °C; 50 mg, 99% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.87 (s, 1H, H_{Ar}), 8.78–8.76 (m, 1H, H_{Ar}), 8.51–8.45 (m, 2H, H_{Ar}), 8.36–8.34 (m, 1H, H_{Ar}), 7.95 (d, ^3J = 15.8 Hz, 1H, CH), 7.74–7.69 (m, 3H, H_{Ar}), 7.62–7.58 (m, 3H, H_{Ar}), 7.55–7.47 (m, 2H, H_{Ar}), 7.43–7.41 (m, 2H, H_{Ar}), 7.27 (d, ^3J = 15.8 Hz, 1H, CH), 7.09–7.07 (m, 2H, H_{Ar}), 2.24 (s, 3H, Me) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 145.2, 138.7, 136.9, 136.2, 135.5, 135.4, 133.9, 131.6, 129.9 (2C), 129.5, 129.4, 129.2 (2C), 128.2 (2C), 127.5, 127.2, 127.0, 126.6 (2C), 126.4, 125.3, 125.2, 124.6, 124.4, 122.3, 120.1, 115.7, 112.8, 21.6 ppm; HRMS (ESI/TOF): m/z calcd. for $C_{31}H_{22}ClNO_2S$ $[M]^+$ 507.1054; found 507.1056.

SUPPORTING INFORMATION

The supporting information is available free of charge on the ACS Publications website at DOI: example of the optimization experiment, details of control experiments, X-ray crystallography data, and copies of ^{1}H and ^{13}C NMR spectra (PDF).

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