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A concise approach for the synthesis of 3-iodoindoles and 3-iodobenzo[*b*]furans via Ph_3P-catalyzed iodocyclization

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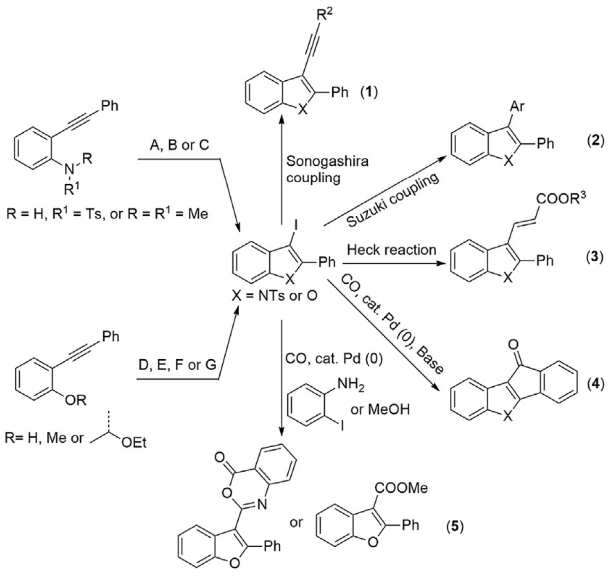
ABSTRACT

A variety of 3-iodoindole and 3-iodobenzo[*b*]furan derivatives were conveniently prepared from the corresponding 2-alkynylanilines and 2-alkynylphenols through Ph_3P-catalyzed iodocyclization in the presence of *N*-iodosuccinimide (NIS). This protocol provides a rapid access to 3-iodoindoles and 3-iodobenzo[*b*]furans in good to excellent yields under mild conditions.

1. Introduction

Indoles and benzo[*b*]furans are important structural motifs of many naturally occurring products and pharmaceutical molecules.[1] Therefore, numerous efficient synthetic approaches toward the indoles and benzo[*b*]furans have been developed.[2] Among these synthetic strategies, transition-metal-catalyzed aromatic C–N formation ranks as a powerful and reliable access to indole scaffolds.[3] Recently, remarkable progress has also been made on the synthesis of benzo[*b*]furans via cyclization of 2-alkynylphenol derivatives.[4] Moreover, due to the potential for further functionalization at the C–I bond by transition-metal-catalyzed cross coupling reactions, the development of new strategies to afford 3-iodoindoles and 3-iodobenzo[*b*]furans could be valuable. For example, Barluenga and co-workers have previously reported IPy_2BF_4 promoted intramolecular addition of 2-alkynylanilines to construct 3-iodoindole cores with moderate yields at low temperature (−60 °C) (Scheme 1, method A).[5a] Knight also established a simple strategy for the synthesis of 3-iodoindoles using 3.0 equiv I_2 and K_2CO_3 (Scheme 1, method B).[5e] Besides other strategies, iodine-mediated electrophilic cyclization of *N*,*N*-dialkyl-2-(1-alkynyl)anilines for the synthesis of 3-iodoindoles was accomplished by Larock (Scheme 1, method C).[5b] In other papers, Larock and Arcadi have demonstrated



A: IPy_2BF_4 (1.1 equiv), HBF_4 (1.0 equiv), -60 °C
B: I_2 (3.0 equiv), K_2CO_3 (3.0 equiv), 0-20 °C
C: I_2 (2.0 equiv)
D: I_2 (3.0 equiv), $NaHCO_3$ (3.0 equiv)
E: IC or I_2 (2.0 equiv)
F: $I(coll)_2PF_6$ (2.0 equiv), $BF_3{\cdot}Et_2O$ (2.0 equiv),
G: CuI (2.2 equiv), O_2, 135–140 °C

Scheme 1. Synthesis and application of 3-iodoindoles and 3-iodobenzo[*b*]furans.

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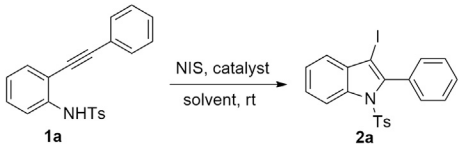
the preparation of 3-iodobenzo[*b*]furans by a related process involving iodocyclization (Scheme 1, method D, E).[5e,f] In 2008, the versatile synthesis of benzo[*b*]furans by iodocyclization of ethoxyethyl ether-substituted alkynes have been achieved by Wada and co-workers by using 2.0 equiv [I(coll)$_2$PF$_6$] (Scheme 1, method F).[5h] Under the Pyne conditions, the copper mediated cyclization–halogenation of *o*-alkynylphenols could afford 3-iodobenzofurans at higher reaction temperature (135–140 °C) (Scheme 1, method G).[5l] Furthermore, the functionalization of 3-iodoindoles and 3-iodobenzofurans can be accomplished by palladium-catalyzed coupling reactions at the C–I bond, such as the Sonogashira and Suzuki cross coupling processes and the Heck reactions (Scheme 1, Eqs. 1, 2 and 3).[5j,k] Larock also reported the synthesis of indole and benzofuran rings by the palladium-catalyzed cyclocarbonylation of 3-iodoindoles and 3-iodobenzofurans (Scheme 1, Eq. 4).[6] Another further elaboration of 3-iodobenzofurans was the cyclocarbonylation with 2-iodoaniline or methanol to afford the oxazine ring or benzo[*b*]furan-3-carboxylate (Scheme 1, Eq. 5).[5f] Owing to the considerable potential of 3-iodoindoles and 3-iodobenzo[*b*]furans, the rapid and practical approach to these heterocycles is still highly demanded.

Triphenylphosphine and its derivatives have been widely used in organic chemistry,[7] including several classic 'name' reactions, such as the Wittig reaction,[8] Staudinger reaction,[9] and Mitsunobu reaction.[10] In particular, phosphines also represent efficient catalysts for Michael,[11] Baylis–Hillman reactions,[12] among others. Given our recent success in the synthesis of indoles via NIS mediated cascade C–N bond formation/aromatization,[13] herein, we report a simple and efficient protocol for the synthesis of 3-iodoindole and 3-iodobenzo[*b*]furan derivatives through Ph$_3$P-catalyzed iodocyclization of the corresponding 2-alkynylanilines and 2-alkynylphenols.

2. Results and discussion

Initially, *N*-Ts-2-alkynylaniline **1a** was chosen as the model substrate to test the feasibility of the proposed transformation. We were delighted to find that the desired 3-iodoindole **2a** was formed in 63% yield after 48 h without any additives (Table 1, entry 1). When triphenylphosphine sulfide was used as catalyst, which could catalyze the iodocyclization process, the reaction time was reduced to 7 h and the yield of **2a** increased to 93% (Table 1, entry 2). It is note that using 1.2 equiv of NIS could diminish the yield of **2a** to 80% (Table 1, entry 3). We rationalized that the addition of Lewis base could promote the transformation, thus various triphenylphosphine derivatives were surveyed. Triphenylphosphine selenide was found to be active in catalyzing the iodocyclization reaction, and the product **2a** could be obtained in 95% yield, but triphenylphosphine oxide proved to be ineffective, and the yield significantly decreased to 21% (Table 1, entry 4 and 5). Remarkably, when triphenylphosphine was selected as catalyst, the reaction proceeded smoothly to give the product in 96% yield (Table 1, entry 6), and the reaction time was shortened to 4 h. In order to further optimize the reaction conditions, various solvents were also evaluated. As shown in Table 1, the reaction showed dramatic solvent effects. Gratifyingly, the use of dichloroethane as solvent gave the best result and furnished **2a** in 98% yield within 1.5 h (Table 1, entry 7). Further solvent screening showed that THF, toluene, and CH_3CN were not effective for this transformation, 1,4-dioxane as well as EtOAc led to lower yields, only provided product **2a** in 15% and 25% yields, respectively (Table 1, entries 8–12). In addition, other Lewis base also were examined, DMAP and DIPEA could generate 3-iodoindole **2a** in 29% and 27% yields (Table 1, entries 13 and 15). When DABCO was employed as catalyst, only afforded a trace amount of **2a** (Table 1, entry 14). Compared with NIS, iodine and NCS were sluggish to this reaction, no desired products were detected after 1.5 h (Table 1, entries 16 and 17). Additionally, the use of NBS could produce the 3-bromoindole in 65% yield (Table 1, entry 18).

Table 1
Optimization of reaction conditions[a]



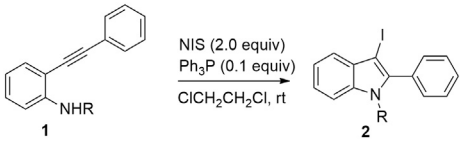
1a **2a**

Entry	Cat.	Solvent	Time (h)	Yield (%)[b]
1	—	CH_2Cl_2	48	63
2	Ph_3PS	CH_2Cl_2	7	93
3[c]	Ph_3PS	CH_2Cl_2	7	80
4	Ph_3PSe	CH_2Cl_2	7	95
5	Ph_3PO	CH_2Cl_2	7	21
6	Ph_3P	CH_2Cl_2	4	96
7	Ph_3P	Dichloroethane	1.5	98
8	Ph_3P	THF	1.5	35
9	Ph_3P	Toluene	1.5	51
10	Ph_3P	CH_3CN	1.5	43
11	Ph_3P	1,4-Dioxane	1.5	15
12	Ph_3P	EtOAc	1.5	25
13	DMAP	Dichloroethane	1.5	29
14	DABCO	Dichloroethane	1.5	Trace
15	DIPEA	Dichloroethane	1.5	27
16[d]	Ph_3P	Dichloroethane	1.5	ND
17[e]	Ph_3P	Dichloroethane	1.5	ND
18[f]	Ph_3P	Dichloroethane	1.5	65

[a] Reaction conditions:**1a** (0.10 mmol), NIS (2.0 equiv), catalyst (0.1 equiv), solvent (1.0 mL), rt under air.
[b] Isolated yield.
[c] 1.2 equiv of NIS was used.
[d] 2.0 equiv of I_2 was used instead of NIS.
[e] 2.0 equiv of NCS was used instead of NIS.
[f] 2.0 equiv of NBS was used instead of NIS. ND=Not detected. DMAP=4-dimethylaminopyridine; DABCO=1,4-Diazobicyclo[2.2.2]octane; DIPEA=*N*,*N*-Diisopropylethylamine.

Next, we investigated the effects of different *N*-protecting groups on 2-phenylanilines (Table 2). The results revealed that all sulfonamides could furnish the corresponding products in good to excellent yields under the standard conditions, while the *N*-Ms-protected substrate (**1f**) need longer reaction time (Table 2, entries 1–6). Meanwhile, under the same conditions, the substrate with *N*-acetyl (**1g**) also afforded the desired product in 45% yield after 12 h (Table 2, entry 7). However, the primary amine (**1h**) group in the substrate was not tolerated under the optimal reaction conditions, no desired product was observed after 5 h.

Table 2
Effects of protecting groups[a]



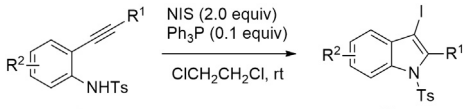
1 **2**

Entry	*R*	Time (h)	Yield (%)[b]
1	Ts (**1a**)	1.5	98 (**2a**)
2	$C_6H_5SO_2$ (**1b**)	1.5	78 (**2b**)
3	*p*-$BrC_6H_4SO_2$ (**1c**)	1.5	90 (**2c**)
4	*p*-$ClC_6H_4SO_2$ (**1d**)	1.5	80 (**2d**)
5	*p*-$NO_2C_6H_4SO_2$ (**1e**)	1.5	70 (**2e**)
6	Ms (**1f**)	12	85 (**2f**)
7	Ac (**1g**)	12	45 (**2g**)
8	H (**1h**)	5	ND

[a] Reaction conditions: Substrate **1** (0.1 mmol), NIS (2.0 equiv), Ph_3P (0.1 equiv), $ClCH_2CH_2Cl$ (1.0 mL), rt under air.
[b] Isolated yield. ND=Not detected.

With the optimized reaction conditions in hand, a series of 2-alkynylanilines were investigated. The substrates with electron-donating or -withdrawing group on the phenyl ring all could afford the desired products in good to excellent yields (Table 3, entries 1–8). Noteworthy, when the phenyl ring was appended with a strong electron-donating group at the *ortho*-position and *para*-position, the reactions are extremely efficient and high-yielding (Table 3, entries 4 and 5). Comparably, the reaction of the substrate with a *para*-chloro or fluoro group on the phenyl ring takes place in relatively slower rate but in good yield (Table 3, entries 6 and 7). A closer inspection revealed that the most strong electron-withdrawing group (e.g., $-CF_3$) appeared to have retarded the reaction to some extent, resulted in longer reaction time (24 h) and moderate yield (Table 3, entry 8). The substrates with a *tert*-butyl or cyclopropyl substituents were also successful, and the indoles **2p** and **2q** were uneventfully produced in 62% and 96% yields, respectively. However, when the R^1 were H or TMS groups, no desired products were isolated under the optimized conditions (not shown). Subsequently, we tested the various anilines. The result indicated that this method could be well applied to various substituted anilines. When the 2-alkynylanilines (**1r**–**1u**) were subjected to the reaction conditions, the corresponding 3-iodoindoles were obtained in 85–94% yields (Table 3, entries 11–14). The reaction of substrate carrying a ethyl ester group also have enough reactivity for the indole formation, which furnished the desired product in a 60% yield but required longer time (48 h), maybe attributed to the electron withdrawing effect of the ethyl ester group (Table 3, entry 15). Notably, as for the substrate with two substituents (**1w**), the presence of electron-donating group (−MeO) on the phenyl ring could improve the yield to 92%, meanwhile reduced the reaction time to 12 h (Table 3, entry 16). This method is also applicable to the direct synthesis of 6-substituted indoles. As a representative example, when the substrate **1x** was subjected to the reaction conditions, the 6-methyl-2-phenylindole **2x** was observed in 76% yield (Table 3, entry 17).

Table 3
Synthesis of 3-iodoindole derivatives[a]



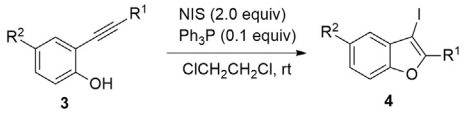
1 2

Entry	R^1	R^2	Time (h)	Yield (%)[b]
1	Ph (**1a**)	H	1.5	98 (**2a**)
2	4-MeC_6H_4 (**1i**)	H	1.5	97 (**2i**)
3	3-MeC_6H_4 (**1j**)	H	6	82 (**2j**)
4	4-MeOC_6H_4 (**1k**)	H	0.5	99 (**2k**)
5	2-MeOC_6H_4 (**1l**)	H	0.5	96 (**2l**)
6	4-Cl−C_6H_4 (**1m**)	H	5	92 (**2m**)
7	4-F−C_6H_4 (**1n**)	H	18	87 (**2n**)
8	4-CF_3−C_6H_4 (**1o**)	H	24	65 (**2o**)
9	*t*-Bu (**1p**)	H	48	62 (**2p**)
10	Cyclopropyl (**1q**)	H	1	96 (**2q**)
11	Ph (**1r**)	4-Me	2	88 (**2r**)
12	Ph (**1s**)	4-MeO	2	92 (**2s**)
13	Ph (**1t**)	4-Cl	2	94 (**2t**)
14	Ph (**1u**)	4-Br	4	85 (**2u**)
15	Ph (**1v**)	4-COOEt	48	60 (**2v**)
16	4-MeOC_6H_4 (**1w**)	4-COOEt	12	92 (**2w**)
17	Ph (**1x**)	5-Me	12	76 (**2x**)

[a] Reaction conditions: Substrate **1** (0.1 mmol), NIS (2.0 equiv), Ph_3P (0.1 equiv), $ClCH_2CH_2Cl$ (1.0 mL), rt under air.
[b] Isolated yield.

To further examine the substrates scope of the methodology, several diversely substituted 2-alkynylphenols were synthesized to be evaluated. We were delighted to find that this protocol was successfully applied to the synthesis of 3-iodobenzo[*b*]furans. As summarized in Table 4, the corresponding 3-iodobenzo[*b*]furans were generated in excellent isolated yields (up to 97%). The different substituents on the phenyl ring seemed to have posed little influence on the reactivities, all the substrates could be converted with high yields to desired products in a very short time (Table 4, entries 1–5). The substrates with alkyl substituents were well-tolerated. For example, the 2-alkynylphenols with *tert*-butyl and cyclopropyl moieties could produce the 3-iodobenzo[*b*]furans in high efficiency (Table 4, entries 6–7). On the other hand, the reaction of substituted phenol also proceeded smoothly to give product **4h** in 93% yield within 5 min.

Table 4
Synthesis of 3-iodobenzo[*b*]furan derivatives[a]



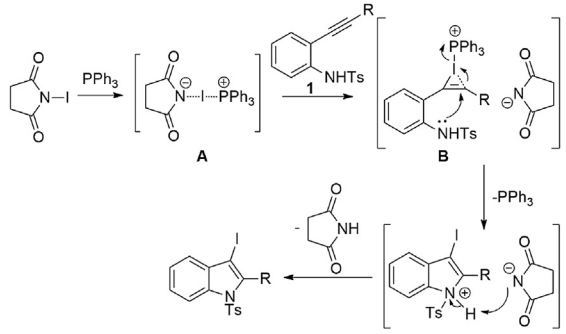
3 4

Entry	R^1	R^2	Time (min)	Yield (%)[b]
1	Ph (**3a**)	H	5	96 (**4a**)
2	4-MeC_6H_4 (**3b**)	H	5	90 (**4b**)
3	4-MeOC_6H_4 (**3c**)	H	5	97 (**4c**)
4	4-ClC_6H_4 (**3d**)	H	5	96 (**4d**)
5	4-FC_6H_4 (**3e**)	H	5	92 (**4e**)
6	*t*-Bu (**3f**)	H	10	91 (**4f**)
7	Cyclopropyl (**3g**)	H	30	89 (**4g**)
8	Ph (**3h**)	Br	5	93 (**4h**)

[a] Reaction conditions: Substrate **3** (0.1 mmol), NIS (2.0 equiv), Ph_3P (0.1 equiv), $ClCH_2CH_2Cl$ (1.0 mL), rt under air.
[b] Isolated yield.

2.1. Mechanism

On the basis of all the results described above, a plausible mechanism for the reaction is described in Scheme 2.[14] First, the iodine atom on NIS is likely activated by the Lewis basic triphenylphosphine to form intermediate **A**. The electrophilic I might then be delivered to alkyne **1** to form the intermediate **B**, which is subsequently attacked by the amino group to initiate the intramolecular amination to furnish the indole product.



Scheme 2. Proposed mechanism.

3. Conclusion

In summary, a practical protocol has been successfully established for the synthesis of 3-iodoindole and 3-iodobenzo[*b*]furan derivatives from the corresponding 2-alkynylanilines and 2-alkynylphenols. Using triphenylphosphine as a catalyst, the iodocyclization process is achieved high efficiently with a broad substrate scope. Considering the importance of indoles and benzo[*b*]furans as core structures in pharmacologically active substances, this method

should be attractive for both synthetic and medicinal chemistry. Further investigation in this direction is ongoing in our laboratory.

4. Experimental section

4.1. General information

All reactions were performed in standard glassware. Solvents were distilled prior to use. All commercially available reagents were used as purchased without further purification. ^{1}H and ^{13}C NMR spectra were obtained on 600 MHz spectrometer (150 MHz for ^{13}C NMR) or 400 MHz spectrometer (100 MHz for ^{13}C NMR) at 25 °C, using $CDCl_3$ with TMS or residual solvent as standard unless otherwise noted. Chemical-shift values were given in ppm and referenced to the internal standard TMS (tetramethylsilane). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; dd, doublet of doublets, and br s, broad singlet. The coupling constants (*J*) are reported in hertz (Hz). Infrared spectra were measured on an FT/IR instrument. Melting points were determined with a micromelting point apparatus without corrections. Low-resolution mass spectra were obtained using LS/MSD. High-resolution mass spectrometry (HRMS) was obtained on a Q-TOF microspectrometer. Flash column chromatography was performed over silica gel 200–300 mesh.

4.2. General procedure for the synthesis of 3-iodoindole, 3-iodobenzo[*b*]furan derivatives and characterization data

To a solution of substrate **1** or **3** (0.10 mmol) in dichloroethane (1.0 mL) were added Ph_3P (2.62 mg, 0.01 mmol) and NIS (45.0 mg, 0.20 mmol) under air. The resulting mixture was stirred at rt for the reported time, then the mixture was concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give the corresponding product.

*4.2.1. 3-Iodo-2-phenyl-1-(4-toluenesulfonyl)indole (**2a**).*[15] Reaction time: 1.5 h. Yield: 46.4 mg, 98%, light yellow solid, mp: 113–115 °C; R_f=0.32 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.31 (s, 3H), 7.08 (d, *J*=7.8 Hz, 2H), 7.30–7.48 (m, 10H), 8.31 (d, *J*=8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.5, 74.8, 114.9, 121.1, 123.6, 125.0, 125.8, 126.5, 128.3, 128.4, 130.5, 130.7, 131.2, 134.0, 135.9, 140.0, 144.0.

*4.2.2. 3-Iodo-N-(benzenesulfonyl)-2-phenylindole (**2b**).* Reaction time: 1.5 h. Yield: 35.8 mg, 78%, light yellow solid, mp: 102–104 °C; R_f=0.69 (20% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J*=7.2 Hz, 2H), 7.36 (d, *J*=6.6 Hz, 2H), 7.38–7.50 (m, 9H), 8.33 (d, *J*=8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 76.0, 116.0, 122.3, 124.8, 126.2, 126.9, 127.6, 128.9, 129.4, 131.4, 131.8, 132.2, 133.9, 137.0, 138.0, 141.0; IR (KBr) cm^{-1} 3065w, 2376w, 1721m, 1443s, 559s; mass spectrum (ESI): *m*/*e* (% relative intensity) 481.9 (100) $(M+Na)^+$; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{14}INO_2S$ $(M+H)^+$ 459.9868, found 459.9875.

*4.2.3. 3-Iodo-N-(4-bromophenylsulfonyl)-2-phenylindole (**2c**).* Reaction time: 1.5 h. Yield: 48.2 mg, 90%, white solid, mp: 165–167 °C; R_f=0.70 (20% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J*=7.2 Hz, 2H), 7.35–7.49 (m, 10H), 8.28 (d, *J*=7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 76.6, 116.0, 122.5, 125.0, 126.4, 127.7, 128.4, 129.3, 129.5, 131.2, 131.8, 132.2, 132.4, 136.7, 136.9, 140.9; IR (KBr) cm^{-1} 3049w, 1573s, 1444m, 1378s, 562s; mass spectrum (ESI): *m*/*e* (% relative intensity) 559.2 (100) $(M+Na)^+$; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{13}BrINO_2S$ $(M+Na)^+$ 559.8793, found 559.8821.

*4.2.4. 3-Iodo-N-(4-chlorophenylsulfonyl)-2-phenylindole (**2d**).* Reaction time: 1.5 h. Yield: 39.4 mg, 80%, light yellow solid, mp: 135–137 °C; R_f=0.45 (10% EtOAc in petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J*=8.8 Hz, 2H), 7.33–7.52 (m, 10H), 8.28 (d, *J*=8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 76.5, 116.0, 122.5, 125.0, 126.4, 127.7, 128.3, 129.2, 129.5, 131.3, 131.7, 132.4, 136.2, 136.9, 140.6, 140.9; IR (KBr) cm^{-1} 3049w, 1581m, 1445s, 1378s, 772s, 565s; mass spectrum (ESI): *m*/*e* (% relative intensity) 515.9 (100) $(M+Na)^+$; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{13}ClINO_2S$ $(M+Na)^+$ 515.9298, found 515.9299.

*4.2.5. 3-Iodo-N-Ns-2-phenylindole (**2e**).* Reaction time: 1.5 h. Yield: 35.2 mg, 70%, light yellow solid, mp: 175–177 °C; R_f=0.30 (10% EtOAc in petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J*=7.2 Hz, 2H), 7.40–7.52 (m, 6H), 7.59 (d, *J*=8.8 Hz, 2H), 8.14 (d, *J*=8.8 Hz, 2H), 8.28 (d, *J*=8.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 77.4, 116.0, 122.7, 124.1, 125.5, 126.8, 127.8, 128.2, 129.8, 130.9, 131.7, 132.6, 136.8, 140.7, 142.8, 150.6; IR (KBr) cm^{-1} 3117m, 1608m, 1530s, 1446s, 1383s, 1355s, 564s; mass spectrum (ESI): *m*/*e* (% relative intensity) 526.3 (100) $(M+Na)^+$; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{13}IN_2O_4S$ $(M+Na)^+$ 526.9538, found 526.9569.

*4.2.6. 3-Iodo-N-Ms-2-phenylindole (**2f**).* Reaction time: 12 h. Yield: 33.7 mg, 85%, light yellow solid, mp: 128–130 °C; R_f=0.27 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.85 (s, 3H),7.43–7.48 (m, 7H), 7.53 (d, *J*=6.6 Hz, 1H), 8.09 (d, *J*=7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 40.8, 75.5, 115.3, 122.5, 125.0, 126.4, 128.0, 129.6, 131.3, 131.4, 132.1, 136.7, 140.9; IR (KBr) cm^{-1} 3006w, 1446s, 1360s, 1174s, 514s; mass spectrum (ESI): *m*/*e* (% relative intensity) 420.1 (100) $(M+Na)^+$; HRMS (ESI): *m*/*z* calcd for $C_{15}H_{12}INO_2S$ $(M+Na)^+$ 419.9531, found 419.9533.

*4.2.7. 3-Iodo-N-Ac-2-phenylindole (**2g**).* Reaction time: 12 h. Yield: 16.2 mg, 45%, light yellow solid, R_f=0.16 (5% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.35 (s, 3H), 6.49 (d, *J*=7.8 Hz, 1H), 6.77 (d, *J*=7.8 Hz, 1H), 7.15 (d, *J*=7.8 Hz, 1H), 7.21 (d, *J*=7.2 Hz, 1H), 7.31–7.38 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.1, 74.7, 119.6, 125.3, 126.2, 126.6, 128.6, 129.3, 129.8, 130.6, 139.9, 141.8, 145.4, 158.4; IR (KBr) cm^{-1} 3050w, 1664s, 1455s, 635s; mass spectrum (ESI): *m*/*e* (% relative intensity) 362.7 (100) $(M+H)^+$; HRMS (ESI): *m*/*z* calcd for $C_{16}H_{12}INO$ $(M+Na)^+$ 383.9861, found 383.9856.

*4.2.8. 3-Iodo-N-Ts-2-p-tolylindole (**2i**).* Reaction time: 1.5 h. Yield: 47.2 mg, 97%, light yellow solid, mp: 125–127 °C; R_f=0.46 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.29 (s, 3H), 2.46 (s, 3H), 7.07 (d, *J*=7.8 Hz, 2H), 7.25–7.42 (m, 9H), 8.29 (d, *J*=8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6, 21.7, 75.8, 116.1, 122.1, 124.7, 126.0, 126.9, 127.0, 128.3, 128.6, 129.5, 131.6, 132.4, 135.0, 137.0, 139.3, 141.3, 145.0; IR (KBr) cm^{-1} 2917w, 1596s, 1498s, 1446s, 571s; mass spectrum (ESI): *m*/*e* (% relative intensity) 510.0 (100) $(M+Na)^+$; HRMS (ESI): *m*/*z* calcd for $C_{22}H_{18}INO_2S$ $(M+Na)^+$ 510.0001, found 509.9998.

*4.2.9. 3-Iodo-N-Ts-2-m-tolylindole (**2j**).* Reaction time: 6 h. Yield: 39.9 mg, 82%, light yellow solid, R_f=0.46 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.24 (s, 3H), 2.32 (s, 3H), 7.01 (d, *J*=9.0 Hz, 3H), 7.05 (d, *J*=7.2 Hz, 1H), 7.20–7.28 (m, 5H), 7.32–7.36 (m, 2H), 8.23 (d, *J*=8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.5, 21.6, 75.6, 116.0, 122.2, 124.6, 126.0, 127.0, 127.4, 128.8, 129.4, 130.1, 131.4, 132.2, 132.4, 135.2, 137.00, 137.03, 141.3, 145.0; IR (KBr) cm^{-1} 2964s, 1413s, 1261s, 587s; mass spectrum (ESI): *m*/*e* (% relative intensity) 510.2 (100) $(M+Na)^+$; HRMS (ESI): *m*/*z* calcd for $C_{22}H_{18}INO_2S$ $(M+Na)^+$ 510.0001, found 509.9989.

*4.2.10. 3-Iodo-N-Ts-2-(4-methoxyphenyl)indole (**2k**).* Reaction time: 0.5 h. Yield: 49.8 mg, 99%, light yellow solid, mp: 143–145 °C; R_f=0.31 (10% EtOAc in petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$)

δ 2.30 (s, 3H), 3.89 (s, 3H), 6.98 (d, *J*=8.8 Hz, 2H), 7.08 (d, *J*=8.0 Hz, 2H), 7.27–7.43 (m, 7H), 8.30 (d, *J*=8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 55.3, 75.7, 113.0, 116.1, 122.1, 123.6, 124.6, 125.9, 126.9, 129.5, 132.3, 133.2, 135.1, 137.0, 141.1, 145.0, 160.3; IR (KBr) cm^{-1} 3034w, 2916w, 1610s, 1501s, 1438s, 542s; mass spectrum (ESI): *m*/*e* (% relative intensity) 525.6 (100) $(M+Na)^+$; HRMS (ESI): *m*/*z* calcd for $C_{22}H_{18}INO_3S$ $(M+Na)^+$ 525.9950, found 525.9972.

*4.2.11. 3-Iodo-N-Ts-2-(2-methoxyphenyl)indole (**2l**).* Reaction time: 0.5 h. Yield: 48.3 mg, 96%, white solid, mp: 135–137 °C; R_f=0.33 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.71 (s, 3H), 6.97 (d, *J*=8.4 Hz, 1H), 7.04 (t, *J*=7.2 Hz, 1H), 7.11 (d, *J*=7.8 Hz, 2H), 7.15 (d, *J*=7.2 Hz, 1H), 7.34 (t, *J*=7.2 Hz, 1H), 7.38–7.43 (m, 4H), 7.50 (d, *J*=7.8 Hz, 1H), 8.23 (d, *J*=8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6, 55.4, 75.4, 110.8, 115.3, 119.7, 120.9, 121.9, 124.1, 125.6, 127.1, 129.4, 131.3, 132.0, 133.1, 135.7, 136.6, 138.3, 144.7, 158.4; IR (KBr) cm^{-1} 3478m, 1488m, 1444s, 1374s, 544s; mass spectrum (ESI): *m*/*e* (% relative intensity) 504.0 (100) $(M+H)^+$; HRMS (ESI): *m*/*z* calcd for $C_{22}H_{18}INO_3S$ $(M+Na)^+$ 525.9950, found 525.9949.

*4.2.12. 3-Iodo-N-Ts-2-(4-chlorophenyl)indole (**2m**).* Reaction time: 5 h. Yield: 46.5 mg, 92%, light yellow solid, mp: 168–170 °C; R_f=0.59 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.23 (s, 3H), 7.01 (d, *J*=7.8 Hz, 2H), 7.23 (d, *J*=7.8 Hz, 4H), 7.25–7.37 (m, 5H), 8.22 (d, *J*=8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6, 76.4, 116.1, 122.3, 124.9, 126.4, 126.8, 127.9, 129.6, 130.0, 132.2, 133.0, 134.9, 135.5, 137.1, 139.8, 145.3; IR (KBr) cm^{-1} 3058w, 1908w, 1597s, 1484s, 1381s, 571s; mass spectrum (ESI): *m*/*e* (% relative intensity) 507.6 (100) $(M+H)^+$; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{15}ClINO_2S$ $(M+Na)^+$ 529.9454, found 529.9430.

*4.2.13. 3-Iodo-N-Ts-2-(4-fluorophenyl)indole (**2n**).* Reaction time: 18 h. Yield: 42.7 mg, 87%, light yellow solid, mp: 183–185 °C; R_f=0.38 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.24 (s, 3H), 7.01 (d, *J*=7.8 Hz, 2H), 7.06 (t, *J*=8.4 Hz, 2H), 7.21–7.33 (m, 6H), 7.36 (t, *J*=7.2 Hz, 1H), 8.22 (d, *J*=8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.6, 75.1, 113.7 (d, *J*=21.6 Hz), 115.0, 121.2, 123.7, 125.2, 125.8, 126.4 (d, *J*=3.2 Hz), 128.5, 131.0, 132.6 (d, *J*=8.2 Hz), 134.0, 135.9, 138.9, 144.1, 163.0 (d, *J*=248.2 Hz); IR (KBr) cm^{-1} 3066w, 1597s, 1496s, 1375s, 540s; mass spectrum (ESI): *m*/*e* (% relative intensity) 490.5 (100) $(M+H)^+$; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{15}FINO_2S$ $(M+Na)^+$ 513.9750, found 513.9757.

*4.2.14. 3-Iodo-N-Ts-2-(4-trifluoromethyl)indole (**2o**).* Reaction time: 24 h. Yield: 35.1 mg, 65%, light yellow solid, mp: 153–155 °C; R_f=0.57 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.25 (s, 3H), 7.02 (d, *J*=7.2 Hz, 2H), 7.23 (d, *J*=7.8 Hz, 2H), 7.29–7.40 (m, 3H), 7.44 (d, *J*=7.8 Hz, 2H), 7.64 (d, *J*=7.8 Hz, 2H), 8.23 (d, *J*=8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.6, 115.0, 121.4, 122.1, 123.5 (q, *J*=3.5 Hz), 123.9, 125.6, 125.8, 128.6, 129.9, 130.1, 131.0, 131.2, 133.7, 134.2, 136.0, 138.3, 144.3; IR (KBr) cm^{-1} 3479m, 1617m, 1598s, 1381s, 571s; mass spectrum (ESI): *m*/*e* (% relative intensity) 563.6 (100) $(M+Na)^+$; HRMS (ESI): *m*/*z* calcd for $C_{22}H_{15}F_3INO_2S$ $(M+Na)^+$ 563.9718, found 563.9734.

*4.2.15. 3-Iodo-N-Ts-2-tert-butylindole (**2p**).* Reaction time: 48 h. Yield: 28.1 mg, 62%, light yellow solid, mp: 66–68 °C; R_f=0.52 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.79 (s, 9H), 2.23 (s, 3H), 6.94 (d, *J*=7.8 Hz, 2H), 7.10 (d, *J*=7.8 Hz, 1H), 7.15 (t, *J*=7.2 Hz, 1H), 7.19–7.25 (m, 3H), 7.92 (d, *J*=8.4 Hz, 1H); 13C NMR (150 MHz, CDCl3) δ 21.5, 31.9, 36.4, 80.3, 118.3, 121.9, 125.4, 125.7, 126.8, 128.5, 131.7, 136.4, 139.6, 144.2, 151.5; IR (KBr) cm^{-1} 3398m, 2962s, 1457s, 570s; mass spectrum (ESI): *m*/*e* (% relative intensity) 476.9 (100) $(M+Na)^+$; HRMS (ESI): *m*/*z* calcd for $C_{19}H_{20}INO_2S$ $(M+Na)^+$ 476.0157, found 476.0149.

*4.2.16. 3-Iodo-N-Ts-2-cyclopropylindole (**2q**).* Reaction time: 1 h. Yield: 41.9 mg, 96%, light yellow solid, mp: 89–91 °C; R_f=0.48 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.90–0.92 (m, 2H), 1.10–1.12 (m, 2H), 1.97–2.00 (m, 1H), 2.33 (s, 3H), 7.17 (d, *J*=7.8 Hz, 2H), 7.29 (d, *J*=7.8 Hz, 1H), 7.34 (d, *J*=7.2 Hz, 2H), 7.65 (d, *J*=7.8 Hz, 2H), 8.16 (d, *J*=8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 9.9, 10.4, 21.6, 73.5, 115.0, 121.8, 124.1, 125.7, 126.5, 129.8, 131.9, 136.3, 136.9, 140.5, 144.9; IR (KBr) cm^{-1} 3013w, 1596s, 1447s, 1367s, 542s; mass spectrum (ESI): *m*/*e* (% relative intensity) 459.3 (100) $(M+Na)^+$; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{16}INO_2S$ $(M+Na)^+$ 459.9844, found 459.9826.

*4.2.17. 3-Iodo-N-Ts-5-methyl-2-phenylindole (**2r**).* Reaction time: 2 h. Yield: 42.9 mg, 88%, light yellow solid, mp: 95–97 °C; R_f=0.47 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.47 (s, 3H), 7.07 (d, *J*=7.2 Hz, 2H), 7.18 (s, 1H), 7.22–7.24 (m, 2H), 7.30 (d, *J*=7.8 Hz, 2H), 7.37 (d, *J*=6.6 Hz, 2H), 7.43–7.49 (m, 3H), 8.17 (d, *J*=8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.3, 21.6, 75.9, 115.8, 122.0, 126.9, 127.5, 129.3, 129.5, 131.6, 131.7, 132.5, 134.6, 135.0, 135.2, 141.1, 144.9; IR (KBr) cm^{-1} 2916w, 1596m, 1467s, 1368s, 546s; mass spectrum (ESI): *m*/*e* (% relative intensity) 488.8 (100) $(M+H)^+$; HRMS (ESI): *m*/*z* calcd for $C_{22}H_{18}INO_2S$ $(M+H)^+$ 488.0181, found 488.0214.

*4.2.18. 3-Iodo-N-Ts-5-methoxy-2-phenylindole (**2s**).* Reaction time: 2 h. Yield: 46.3 mg, 92%, light yellow solid, mp: 70–72 °C; R_f=0.36 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.88 (s, 3H), 6.82 (s, 1H), 7.03 (d, *J*=7.8 Hz, 1H), 7.08 (d, *J*=7.8 Hz, 2H), 7.29 (d, *J*=7.8 Hz, 2H), 7.38 (d, *J*=7.2 Hz, 2H), 7.44–7.48 (m, 3H), 8.19 (d, *J*=9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6, 55.7, 76.0, 104.3, 115.1, 117.3, 126.9, 127.5, 129.3, 129.4, 131.4, 131.6, 131.7, 133.5, 134.8, 141.9, 144.9, 157.5; IR (KBr) cm^{-1} 2990w, 1609s, 1472s, 1434s, 542s; mass spectrum (ESI): *m*/*e* (% relative intensity) 525.8 (100) $(M+Na)^+$; HRMS (ESI): *m*/*z* calcd for $C_{22}H_{18}INO_3S$ $(M+Na)^+$ 525.9950, found 525.9944.

*4.2.19. 3-Iodo-N-Ts-5-chloro-2-phenylindole (**2t**).* Reaction time: 2 h. Yield: 47.7 mg, 94%, light yellow solid, mp: 129–131 °C; R_f=0.47 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.33 (s, 3H), 7.10 (d, *J*=7.8 Hz, 2H), 7.27 (d, *J*=7.8 Hz, 2H), 7.33 (d, *J*=7.2 Hz, 2H), 7.37–7.39 (m, 2H), 7.45 (t, *J*=7.2 Hz, 2H), 7.49 (d, *J*=7.2 Hz, 1H), 8.24 (d, *J*=8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.7, 74.2, 117.2, 121.9, 126.2, 126.9, 127.6, 129.6, 129.6, 130.6, 131.0, 131.7, 133.6, 134.8, 135.4, 142.5, 145.4; IR (KBr) cm^{-1} 3459m, 1597s, 1440s, 1370s, 544s; mass spectrum (ESI): *m*/*e* (% relative intensity) 529.6 (100) $(M+Na)^+$; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{15}ClINO_2S$ $(M+H)^+$ 507.9635, found 507.9650.

*4.2.20. 3-Iodo-N-Ts-5-bromo-2-phenylindole (**2u**).* Reaction time: 4 h. Yield: 46.8 mg, 85%, light yellow solid, R_f=0.37 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.33 (s, 3H), 7.10 (d, *J*=7.8 Hz, 2H), 7.28 (d, *J*=7.8 Hz, 2H), 7.33 (d, *J*=7.2 Hz, 2H), 7.45 (t, *J*=7.2 Hz, 2H), 7.48–7.52 (m, 2H), 7.55 (s, 1H), 8.18 (d, *J*=9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.7, 74.1, 117.5, 118.2, 124.9, 126.9, 127.6, 128.9, 129.5, 129.6, 131.0, 131.7, 134.0, 134.8, 135.8, 142.4, 145.4; IR (KBr) cm^{-1} 3068w, 1594s, 1438s, 1376s, 544s; mass spectrum (ESI): *m*/*e* (% relative intensity) 574.4 (100) $(M+Na)^+$; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{15}BrINO_2S$ $(M+Na)^+$ 573.8949, found 573.8925.

*4.2.21. 3-Iodo-N-Ts-2-phenyl-5-ethoxycarbonylindole (**2v**).* Reaction time: 48 h. Yield: 32.7 mg, 60%, light yellow solid, mp: 145–147 °C;

R_f=0.24 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.44 (t, J=7.2 Hz, 3H), 2.33 (s, 3H), 4.43 (q, J=6.6 Hz, 2H), 7.10 (d, J=7.8 Hz, 2H), 7.31 (d, J=7.8 Hz, 2H), 7.34 (d, J=7.2 Hz, 2H), 7.45 (t, J=7.2 Hz, 2H), 7.50 (t, J=7.2 Hz, 1H), 8.13 (d, J=8.4 Hz, 2H), 8.36 (d, J=8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.4, 21.6, 61.2, 75.5, 115.7, 124.3, 126.9, 127.0, 127.1, 127.6, 129.1, 129.5, 129.6, 131.1, 131.7, 132.1, 134.9, 139.6, 142.3, 145.4, 166.4; IR (KBr) cm^{-1} 2970w, 1709s, 1379s, 1311s, 1090s, 546s; mass spectrum (ESI): m/e (% relative intensity) 568.0 (100) $(M+Na)^+$; HRMS (ESI): m/z calcd for $C_{24}H_{20}INO_4S$ $(M+Na)^+$ 568.0055, found 568.0039.

*4.2.22. 3-Iodo-N-Ts-2-(4-methoxyphenyl)-5-ethoxycarbonylindole (**2w**).* Reaction time: 12 h. Yield: 52.9 mg, 92%, light yellow solid, mp: 105–107 °C; R_f=0.19 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.43 (t, J=7.2 Hz, 3H), 2.32 (s, 3H), 3.90 (s, 3H), 4.43 (q, J=6.6 Hz, 2H), 6.98 (d, J=7.8 Hz, 2H), 7.10 (d, J=7.8 Hz, 2H), 7.26–7.29 (m, 4H), 8.12 (d, J=10.2 Hz, 2H), 8.36 (d, J=8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.5, 21.7, 55.3, 61.2, 75.4, 113.0, 115.8, 123.0, 124.1, 126.9, 129.6, 132.2, 133.2, 134.9, 139.7, 142.4, 145.4, 160.5, 166.4; IR (KBr) cm^{-1} 2983w, 1715s, 1612s, 1501s; 1380s, 1097s, 545s; mass spectrum (ESI): m/e (% relative intensity) 598.6 (100) $(M+Na)^+$; HRMS (ESI): m/z calcd for $C_{25}H_{22}INO_5S$ $(M+Na)^+$ 598.0161, found 598.0151.

*4.2.23. 3-Iodo-N-Ts-6-methyl-2-phenylindole (**2x**).* Reaction time: 12 h. Yield: 37.0 mg, 76%, light yellow solid, mp: 178–180 °C; R_f=0.63 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.24 (s, 3H), 2.48 (s, 3H), 7.01 (d, J=7.8 Hz, 2H), 7.11 (d, J=7.8 Hz, 1H), 7.19–7.26 (m, 5H), 7.34–7.40 (m, 3H), 8.04 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.6, 21.1, 74.7, 115.0, 120.7, 125.0, 125.8, 126.4, 128.1, 128.4, 129.1, 130.6, 130.7, 134.1, 135.3, 136.3, 139.3, 143.9. IR (KBr) cm^{-1} 3052w, 1597w, 1371s, 1189s, 1032s, 801s, 578s; mass spectrum (ESI): m/e (% relative intensity) 510.0 (100) $(M+Na)^+$; HRMS (ESI): m/z calcd for $C_{22}H_{17}INO_2S$ $(M-H)^-$ 486.0019, found 486.0029.

*4.2.24. 3-Iodo-2-phenylbenzofuran (**4a**).*[5d] Reaction time: 5 min. Yield: 30.7 mg, 96%, light yellow oil, R_f=0.53 (100% petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, J=7.2 Hz, 1H), 7.35 (t, J=7.2 Hz, 1H), 7.40–7.50 (m, 5H), 8.18 (d, J=15.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 61.2, 111.2, 121.9, 123.6, 125.7, 127.5, 128.6, 129.3, 130.0, 132.5, 153.1, 153.9.

*4.2.25. 3-Iodo-2-(p-tolyl)benzofuran (**4b**).* Reaction time: 5 min. Yield: 30.1 mg, 90%, light yellow solid, R_f=0.55 (100% petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.41 (s, 3H), 7.28–7.34 (m, 4H), 7.43 (d, J=7.2 Hz, 1H), 7.46 (d, J=7.8 Hz, 1H), 8.06 (d, J=7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.5, 60.5, 111.1, 121.7, 123.5, 125.5, 127.2, 127.5, 129.3, 132.6, 139.4, 153.4, 153.9; IR (KBr) cm^{-1} 3494m, 2915w, 1498m, 492s; mass spectrum (ESI): m/e (% relative intensity) 334.7 (100) $(M+H)^+$; HRMS (ESI): m/z calcd for $C_{15}H_{11}IO$ $(M+H)^+$ 334.9933, found 334.9931.

*4.2.26. 3-Iodo-2-(4-methoxyphenyl)benzofuran (**4c**).*[5d] Reaction time: 5 min. Yield: 34.0 mg, 97%, light yellow solid, mp: 75–77 °C; R_f=0.50 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.86 (s, 3H), 7.01 (d, J=8.4 Hz, 2H), 7.27–7.33 (m, 2H), 7.41 (d, J=7.2 Hz, 1H), 7.45 (d, J=7.2 Hz, 1H), 8.12 (d, J=8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.4, 59.5, 111.0, 114.0, 121.6, 122.6, 123.4, 125.3, 129.1, 132.6, 153.3, 153.8, 160.4.

*4.2.27. 2-(4-Chlorophenyl)-3-iodobenzofuran (**4d**).* Reaction time: 5 min. Yield: 34.0 mg, 96%, light yellow solid, R_f=0.48 (100% petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (t, J=7.2 Hz, 1H), 7.37 (d, J=7.2 Hz, 1H), 7.42–7.47 (m, 4H), 8.12 (d, J=8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 61.7, 111.2, 122.0, 123.7, 126.0, 128.5, 128.6, 128.8, 132.4, 135.2, 151.9, 153.9; IR (KBr) cm^{-1} 3502w, 1482s, 1448s, 723s; mass spectrum (ESI): m/e (% relative intensity) 376.9 (100) $(M+Na)^+$; HRMS (ESI): m/z calcd for $C_{14}H_8ClIO$ $(M+H)^+$ 354.9387, found 354.9356.

*4.2.28. 2-(4-Fluorophenyl)-3-iodobenzofuran (**4e**).* Reaction time: 5 min. Yield: 31.1 mg, 92%, light yellow solid, R_f=0.50 (100% petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (t, J=8.4 Hz, 2H), 7.31 (t, J=7.2 Hz, 1H), 7.36 (t, J=7.2 Hz, 1H), 7.42 (d, J=7.8 Hz, 1H), 7.46 (d, J=7.8 Hz, 1H), 8.15 (t, J=5.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 61.0, 111.2, 115.8 (d, J=21.6 Hz), 121.9, 123.6, 125.8, 126.3 (d, J=3.2 Hz), 129.5 (d, J=8.4 Hz), 132.4, 152.3, 153.9, 163.9 (d, J=248.9 Hz); IR (KBr) cm^{-1} 3485w, 1602m, 1497s, 1408m, 742s; mass spectrum (ESI): m/e (% relative intensity) 338.1 (100) $(M+H)^+$; HRMS (ESI): m/z calcd for $C_{14}H_8FIO$ $(M+Na)^+$ 360.9502, found 360.9501.

*4.2.29. 2-(t-Butyl)-3-iodobenzofuran (**4f**).*[5h] Reaction time: 10 min. Yield: 27.3 mg, 91%, light yellow oil, R_f=0.89 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.45 (s, 9H), 7.14–7.18 (m, 2H), 7.27–7.29 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.5, 34.7, 57.7, 110.8, 121.2, 123.0, 124.6, 132.5, 152.9, 162.4.

*4.2.30. 2-Cyclopropyl-3-iodobenzofuran (**4g**).* Reaction time: 30 min. Yield: 25.2 mg, 89%, light yellow oil, R_f=0.91 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.04–1.06 (m, 2H), 1.13–1.14 (m, 2H), 2.16–2.19 (m, 1H), 7.23 (t, J=8.4 Hz, 2H), 7.30 (t, J=7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 7.8, 9.7, 61.1, 110.8, 120.2, 123.2, 124.2, 131.4, 153.3, 158.6; IR (KBr) cm^{-1} 3012m, 1754s, 1696s, 1589s, 744s; mass spectrum (ESI): m/e (% relative intensity) 284.2 (100) $(M+H)^+$; HRMS (ESI): m/z calcd for $C_{11}H_9IO$ $(M+Na)^+$ 306.9596, found 306.9610.

*4.2.31. 5-Bromo-3-iodo-2-phenylbenzofuran (**4h**).* Reaction time: 5 min. Yield: 36.9 mg, 93%, light yellow solid, R_f=0.53 (100% petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, J=8.4 Hz, 1H), 7.44 (t, J=7.8 Hz, 2H), 7.48 (t, J=7.8 Hz, 2H), 7.57 (s, 1H), 8.14 (d, J=7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 59.7, 112.7, 116.7, 124.6, 127.6, 128.5, 128.6, 129.5, 129.7, 134.5, 152.7, 154.3; IR (KBr) cm^{-1} 3485m, 1601m, 1487s, 1436s, 766s, 684s; mass spectrum (ESI): m/e (% relative intensity) 420.5 (100) $(M+Na)^+$; HRMS (ESI): m/z calcd for $C_{14}H_8BrIO$ $(M+H)^+$ 398.8881, found 398.8856.

*4.2.32. 3-Bromo-2-phenyl-1-(4-toluenesulfonyl)indole (**2a′**).*[16] Reaction time: 1.5 h. Yield: 27.2 mg, 64%, light yellow solid, R_f=0.72 (10% EtOAc in petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.30 (s, 3H), 7.07 (d, J=7.8 Hz, 2H), 7.30 (d, J=7.8 Hz, 2H), 7.37 (t, J=7.8 Hz, 1H), 7.43–7.49 (m, 7H), 8.35 (d, J=8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6, 103.8, 116.3, 120.0, 124.8, 126.2, 126.9, 127.6, 129.3, 129.5, 129.8, 130.1, 131.6, 134.6, 136.6, 137.6, 145.1.

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Supplementary data

Characterization data, general procedure for the synthesis of substrates, and ^{1}H and ^{13}C NMR spectra for substrates and products. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.09.005.

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