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A Direct Access to Indoles via Ir(III)-Catalyzed C–H Functionalization of Acetanilides with Diazo Compounds

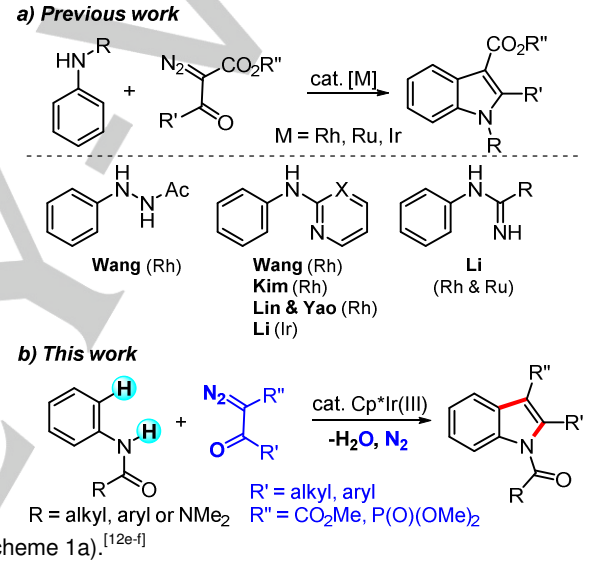
Pitambar Patel,* Gongutri Borah

Abstract: A one pot synthesis of indole derivatives from readily available acetanilide via Ir(III)-catalyzed C–H alkylation and annulations with diazo compounds have been developed. The reaction proceeds under mild conditions and generates molecular nitrogen and water as by-products. Various types of synthetically adaptable *N*-substituted indoles were accessed which includes *N*-acetyl, *N*-Pivolyl and *N*-Benzoyl groups.

Introduction

Indole represents one of the most abundant structural unit found in a wide range of biologically active compounds and drug molecules.[1] Because of their tremendous significant role in drug discovery various synthetic approaches have been established to access indole skeleton,[2] such as the Fischer indole synthesis,[3] heteroannulations/cyclization of 2-alkynylanilines[4] and metal-catalyzed coupling/condensation cascades.[5] However, general and efficient methods for the synthesis of functionalized indoles from easily available starting material is still of great interest. In the past decade the transition metal catalyzed C–H activations have emerged as one of the powerful efficient and straightforward tool for the construction of various heterocyclics from simple substrates.[6, 7] In this context, synthesis of indoles from the *N*-substituted anilines and alkynes via C–H annulation was reported by using Rhodium, palladium, ruthenium, nickel and cobalt catalysts.[8] However, most of these methods suffers in the regioselectivity with unsymmetrical alkynes to produce indoles.

More recently, metal-catalyzed carbenoid functionalization and annulations have been scrutinized as efficient and atom economic approach for the synthesis of various *N*-heterocyclic compounds.[9] In this context, Yu and co-worker documented the pioneering work on Rh(III)-catalyzed carbenoid functionalization of arenes.[9a] Following this results, the groups of Glorius,[10] Wang,[11] Li,[12] Kim[13] and others[14] have successfully demonstrated the synthesis of various heterocycles by same approach. Very recently, Wang et al. reported the Rh(III)-catalyzed carbenoid functionalization of 2-acetyl-1-arylhydrazines to afford 1-aminoindole derivatives (Scheme 1a).[11a] While Lin and Yao,[15] Kim[13b] and Wang[11c] independently documented the efficient synthesis of indoles using *N*-phenylpyrimidin-2-amine and diazo compounds via Rh (III)-catalyzed C–H bond activation (Scheme 1a). On the other hand, Li et al. disclosed the reaction of *N*-phenylpyrimidin-2-amine with diazo compounds under Ir(III)-catalytic conditions to afford *N*-pyrimidinyl indoles which is the only reports so far using Ir(III).[12d] Furthermore, Li and coworkers also demonstrated the synthesis of functionalized indoles from *N*-phenylacetimidamides via Rh(III) and Ru(III)- catalyzed C–H carbenoid functionalization (Scheme 1a).[12e-f]



Scheme 1. Synthesis of indole via metal catalyzed C–H activation

Inspite of these advancements, most of the methods are limited to Rh(III)-catalyst, where as only one literature precedent is available on indole synthesis via Ir(III)-catalyzed carbenoid functionalization.[12d, 16] To the best of our knowledge synthesis of indole from readily available acetanilide via metal catalyzed C–H carbenoid functionalization has not been realized till date.[17] In continuation of our ongoing study on Ir(III)-catalyzed of C–H annulations,[18] we recently reported the synthesis of oxindole from acetanilide and diazotized Meldrum's acid.[18c] At this stage, we envisioned the possible formation of indole derivatives when the diazotized Meldrum's acid is replaced with ethyl 2-diazo-3-oxobutanoate (Scheme 1b). Herein we report the results of Ir(III)-catalyzed carbenoid functionalization of acetanilide to obtain poly-substituted indole derivatives. Indole with various *N*-substitutions such as acetyl, pivolyl, and benzoyl can be synthesized easily using this protocol (Scheme 1b).

Results and Discussion

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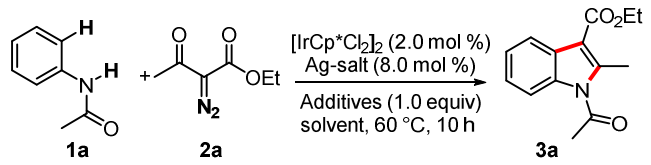
We initiated our optimization study with acetanilide **1a** and ethyl 2-diazo-3-oxobutanoate **2a** as model substrates. Use of $[IrCp^*Cl_2]_2$ (2.0 mol %), $AgNTf_2$ (8.0 mol %) as catalyst in 1,2-dichloroethane (1,2-DCE, 1 mL) at 60 ℃ for 10 h, did not promote the reaction of **1a** with **2a** (Table 1, entry 1). We then checked various additives and with AcOH (1.0 equiv) as additive, the desired ethyl 1-acetyl-2-methyl-1H-indole-3-carboxylate **3a** was obtained in 86% isolated yield (entry 2–5). Screening of various solvents indicated that 1,2-Dichloroethane was the best solvent (entries 6–7). Among the various silver salts tested, $AgNTF_2$ was found to be most effective (entries 9–10). Decreasing the catalyst loading (1.0 mol %) led to lower yield of **3a** (entries 11). Control experiments showed that both $[IrCp^*Cl_2]_2$ or $AgNTf_2$ were essential for this reaction (entries 12–13). It should be noted that the present C–H annulations did not proceed at all when $[RhCp^*Cl_2]_2$ and $[Ru(p\text{-Cymene})Cl_2]_2$ catalyst were employed (entries 14–15).

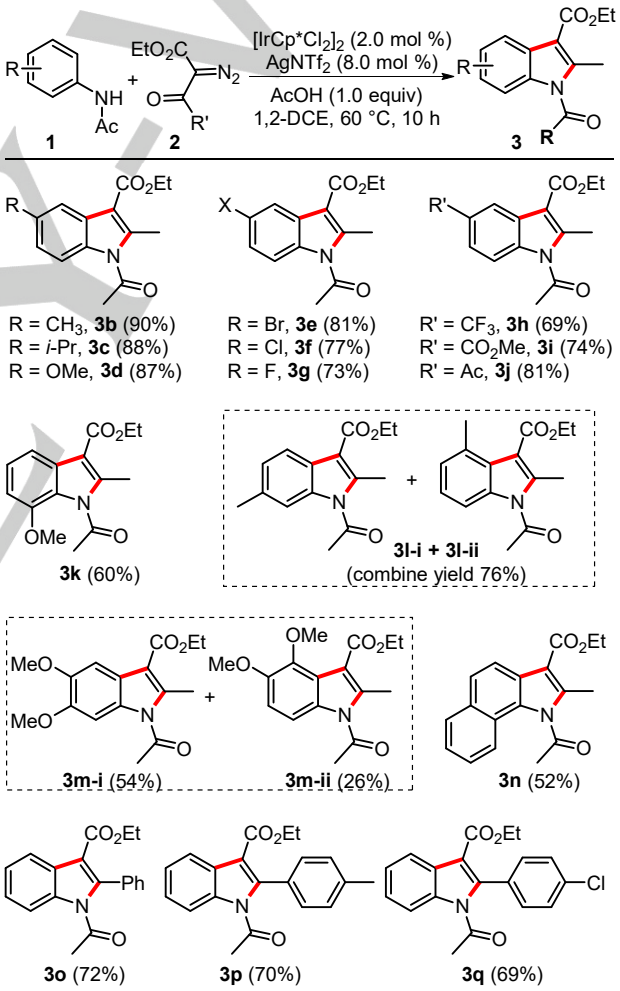
Table 1. Optimization of reaction parameters



entry	[Ag] salt	additive	solvent	yield (%)[b]
1	$AgNTf_2$	-	1,2-DCE	0
2	$AgNTf_2$	NaOAc	1,2-DCE	0
3	$AgNTf_2$	AcOH	1,2-DCE	88 (86)
4	$AgNTf_2$	PivOH	1,2-DCE	70
5[c]	$AgNTf_2$	AcOH	1,2-DCE	60
6	$AgNTf_2$	AcOH	MeOH	<10
7	$AgNTf_2$	AcOH	MeCN	15
8	$AgNTf_2$	AcOH	toluene	10
9	$AgSbF_6$	AcOH	1,2-DCE	72
10	AgOAc	AcOH	1,2-DCE	10
11[d]	$AgNTf_2$	AcOH	1,2-DCE	58
12[e]	$AgNTf_2$	AcOH	1,2-DCE	0
13	none	AcOH	1,2-DCE	12
14[f]	$AgNTf_2$	AcOH	1,2-DCE	0
15[g]	$AgNTf_2$	AcOH	1,2-DCE	0

[a]Reaction conditions: **1a** (0.15 mmol, 1.0 equiv), **2a** (0.18 mmol, 1.2 equiv), catalyst and additive in solvent (1 mL) at 60 ℃ for 10 h. [b]^1H NMR yield (CH_2Br_2 as internal standard); isolated yield in parentheses. [c] 0.5 equiv of AcOH was used. [d] 1.0 mol % of $[IrCp^*Cl_2]_2$ was used. [e] Reaction without $[IrCp^*Cl_2]_2$. [f] $[RhCp^*Cl_2]_2$ was used as catalyst. [g] $[Ru(p\text{-Cymene})Cl_2]_2$ was used as catalyst.

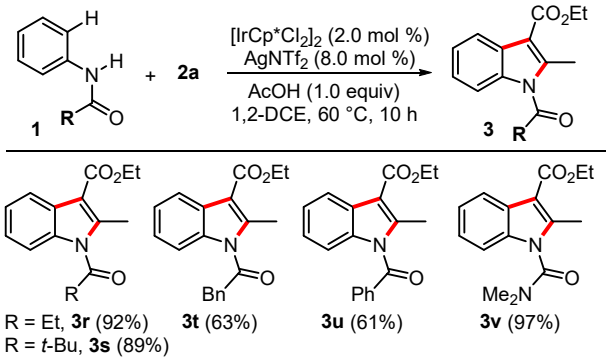
With the optimized reaction conditions, we then explored the scope of indole formation with differentially substituted acetanilides (Scheme 2). Acetanilides bearing electron-donating (**3b**-**3d**) and -withdrawing (**3e**-**3j**) substituents at *para*-position underwent the annulations reaction smoothly and furnished the desired indole derivative in good yields. It's worth noting that these alkylations are highly selective occurring at the *ortho*-position relative to the *N*-acetyl moiety even in the presence of other carbonyl chelating groups such as ester or ketone (**3i**, **3j**). Nevertheless, the reactions of *ortho*-substituted acetanilide gave relatively low yield of indole derivative (**3k**), likely due to low reactivity (steric reasons). Moreover, *m*-methyl acetanilide gave inseparable regiomeric products **3l-i** and **3l-ii**. Similarly, 3,4-dimethoxy acetanilide produced a mixture of **3m-i** and **3m-ii** in 3:1 ratio. Annulation of substrate containing fused arenes such as naphthyl (**3n**) was also smooth under the present conditions. Next we explored the substituent effect on the diazo compound by changing the carbonyl substituents. Pleasantly, reaction of ethyl 2-diazo-3-oxo-3-phenylpropanoate (**2b**) with **1a** under standard conditions furnished the desired ethyl 1-acetyl-2-phenyl-1H-indole-3-carboxylate (**3o**) in good yields. Similarly, diazo compounds having *para*-substituted aryl group such as methyl (**3p**) and chloro (**3q**) underwent annulations to furnish the desired product in high yields.



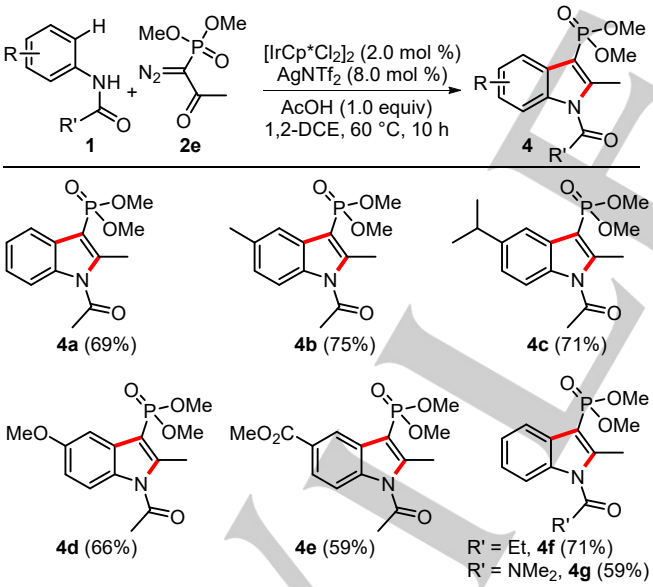
Scheme 2. Substrate scope for indole synthesis. Reaction conditions: **1** (0.15 mmol), **2** (1.2 equiv), in 1,2-DCE (1 mL); yields of isolated products are given.

Next, the scope of various types of *N*-substitutions was investigated (Scheme 3). We found that a range of synthetically useful *N*-substituents could readily be employed to furnish the

desired *N*-protected indole derivatives. Reaction of anilines having *N*-substitution such as propenoyl, pivolyl, phenyl acetyl group smoothly furnished the corresponding indole derivatives **3r**-**3t** in good to high yields. Similarly, *N*-phenylbenzamide gave exclusively the desired product **3u** in 62% yield. Further 1,1-dimethyl-3-phenylurea also gave the desired ethyl 1-(dimethylcarbamoyl)-2-methyl-1*H*-indole-3-carboxylate **3v** in excellent yield. Thus, various easily removable *N*-protected 2,3-disubstituted indole derivative could be synthesized through the present procedure, which offers synthetic flexibility in the utilization of the obtained products.

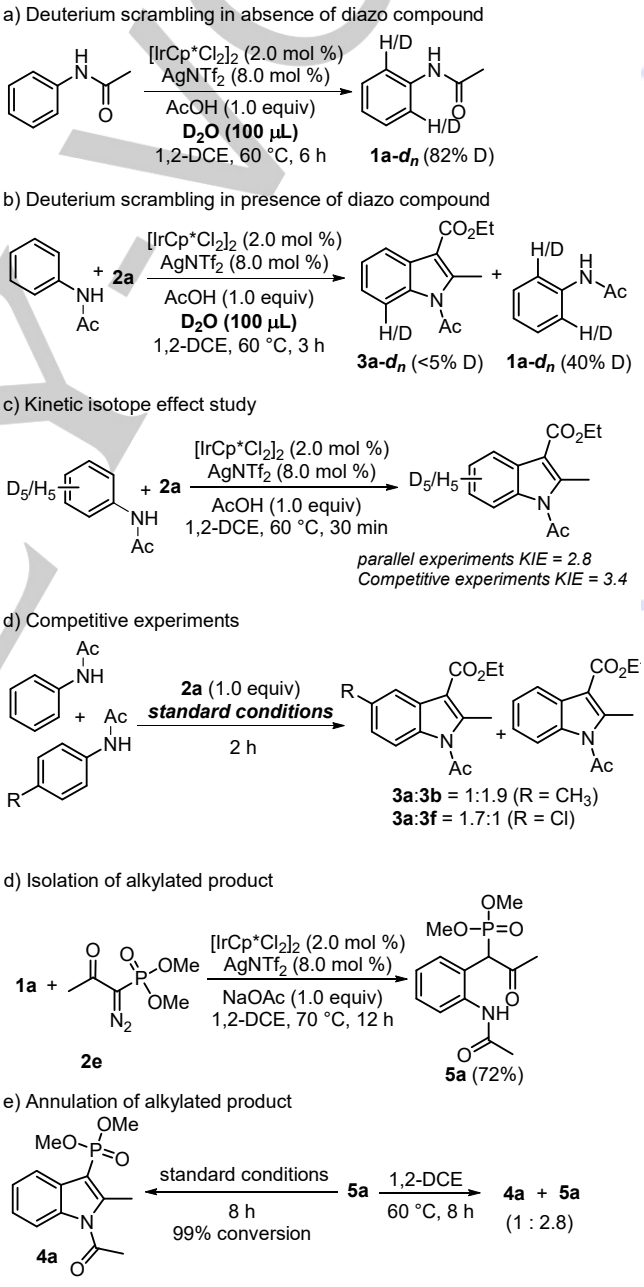


Scheme 3. Scope of various *N*-substitutions. Reaction conditions: **1** (0.15 mmol), **2a** (1.2 equiv), in 1,2-DCE (1 mL); yields of isolated products are given.



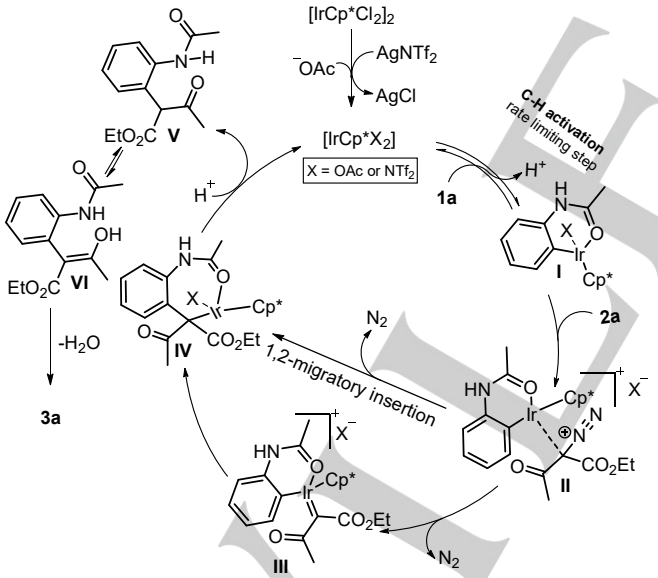
Scheme 4. Scope of diazo compounds. Reaction conditions: **1** (0.15 mmol), **2e** (1.2 equiv), in 1,2-DCE (1 mL); yields of isolated products are given.

With the successful exploration of substrate scope for *N*-aryl amides, we then investigate the feasibility of other diazo compounds. Gratifyingly, reaction of dimethyl (1-diazo-2-oxopropyl)phosphonate (**2e**) with **1a** under standard condition furnished the desired dimethyl (1-acetyl-2-methyl-1*H*-indol-3-yl)phosphonate (**4a**) in good yields (Scheme 4). It is important to note that, only alkylated product was observed with **2e** under Rh(III)-catalytic conditions.[15] Next we checked the scope of various *N*-arylamides for 3-phosphorylated indole synthesis. Overall it was observed that substrates having electron donating group gave higher yield as compared to substrates with electron-withdrawing group (**4b**-**4e**). Substrate with different *N*-substitutions such as *N*-phenylpropionamide and 1,1-dimethyl-3-phenylurea were compatible to present annulations reaction and furnished the desired indole derivatives **4f** and **4g** in good yield. Surprisingly, reaction with other diazo compound such as 3-diazopentane-2,4-dione and diethyl 2-diazomalonate were found to be sluggish.



Scheme 5 Preliminary mechanistic studies.

Several preliminary experiments were performed to shed light in to the reaction mechanism (Scheme 5). A notable deuterium scrambling of **1a** was observed when the reaction was performed using D_2O in the absence of diazo compound, indicating the reversibility of the C–H activation step (Scheme 5a). However, when the same step was performed in presence of **2a** no deuterium scrambling was observed in product **3a**, confirming that the C–C bond formation was faster than the back reaction (Scheme 5b). Next, a significant kinetic isotope effect (KIE) was observed both in parallel (2.8) and competitive experiments (3.4), which indicate the C–H activation to be the rate-determining step (Scheme 5c).[19] One pot intermolecular competitive experiment of **1a** with electron rich acetanilide **1b** or electron deficient acetanilide **1f** revealed that electron rich substrates were more efficient for the reaction (Scheme 5d). This also indicates the putative involvement of aromatic electrophilic mechanism. After a careful screening of the reaction parameters, the alkylated product **5a** was successfully isolated (Scheme 5e). When compound **5a** was stirred in 1,2-DCE at 60 °C for 8 hours, formation of desired annulated product **4a** was observed along with reamining **5a** (Scheme 5f). However, under standard conditions compound **5a** was completely converted to indole derivative **4a**. These results confirmed that the reaction proceeds via C–H alkylation followed by annulations to give the final product.



Scheme 6 Plausible catalytic cycle.

Based on the above results and literature precedents, a plausible mechanistic pathway is proposed in Scheme 6. The first step is the generation of a cationic Ir(III) species from the $[IrCp^*Cl_2]_2$ with $AgNTf_2$ and AcOH, which facilitates the key C–H bond activation to afford a six-membered iridacyclic intermediate **I**. Coordination of diazocompound to **I**, gave the diazonium intermediate **II**. Generation of the carbene intermediate **III** is assumed to take place before the subsequent migratory insertion of carbene to the C–Ir bond, leading to **IV**. Alternatively, intramolecular 1,2-migratory insertion of the aryl group would led to **IV**. Next, Protodemetalation of **IV** delivers the alkylated product **V**, and regenerates the active catalytic species. The enol intermediate **VI**, formed through keto–enol tautomerization of **V**, which undergo a dehydrative cyclization to furnish the indole product **3a**.

Conclusions

In summary, we developed a one step synthesis of functionalized indole from readily available acetanilides and α-diazocarbonyl compounds. The reaction proceeds under mild condition with high functional group tolerance and generate molecular nitrogen and water as side products. Using the present protocol, 3-phosphorylated indole derivative can be easily synthesized from aniline. The easily removable *N*-protecting group can also be used as directing group for further selective C7 functionalization.[20] Further studies on extension of present methods for sp3 C–H functionalization as well as extension of this methodology for synthesis of biologically active indole derivatives are on progress.

Experimental Section

General remarks

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F_{254} plates. Column chromatography was carried out by using spectrochem silica gel (100–200, 230–400 mesh). ^{1}H NMR spectra were recorded on Bruker AV 500 MHz spectrometers. TMS was used as an internal standard and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0.0 ppm) or $CDCl_3$ (7.27 ppm). In case of the peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J* is reported in Hertz (Hz). ^{13}C NMR spectra were obtained by Bruker AV (125 MHz) spectrometers and referenced to the internal solvent signals (central peak is 77.0 ppm in $CDCl_3$). For carbon appearing as doublet, its indicated as 'd'. High-resolution mass spectra (HRMS) were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump and WATER's XEVO G2 XS9T. All the *N*-aryl amides[8a] and diazo compounds[18] were prepared by following literature procedure.

Experimental Details

General procedure for Ir-catalyzed C–H annulations of acetanilides: To a 3 mL screw capped vial with a spinvane triangular-shaped Teflon stirbar were added acetanilide (0.15 mmol, 1.0 equiv), diazocompounds (0.18 mmol, 1.2 equiv), $[IrCp^*Cl_2]_2$ (2.0 mol %), $AgNTf_2$ (8.0 mol %), AcOH (9.0 mg, 1.0 equiv) and 1,2-dichloroethane (1.0 mL) under air. The reaction mixture was stirred at 60 °C for 10 h. After the completion of reaction, the reaction mixture was filtered through a pad of celite followed by washing of the pad with CH_2Cl_2 (10 mL x 2). The combined solvents were removed under reduced pressure and the residue was purified by column chromatography (EtOAc/hexane) to obtain the pure product.

Ethyl-1-acetyl-2-methyl-1*H*-indole-3-carboxylate (3a): White solid (31.8 mg, 86%); mp: 58-60 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (t, *J* = 7.1 Hz, 3H), 2.79 (s, 3H), 2.98 (s, 3H), 4.44 (q, *J* = 7.1 Hz, 2H), 7.28–7.40 (m, 2H), 7.82–7.94 (m, 1H), 8.12 (dd, *J* = 6.7, 2.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 15.2, 27.9, 60.3, 111.2, 114.2, 121.7, 123.9, 124.4, 127.4, 135.2, 144.8, 165.4, 171.0 ppm. HRMS (ESI+): calcd. for $C_{14}H_{16}O_3N$ $[M+H]^+$: 246.1125, found: 246.1124.

Ethyl 1-acetyl-2,5-dimethyl-1*H*-indole-3-carboxylate (3b): White solid (35.0 mg, 90%); mp: 85-88 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (t, *J* = 7.1 Hz, 3H), 2.48 (s, 3H), 2.77 (s, 3H), 2.95 (s, 3H), 4.42 (q, *J* = 7.1 Hz, 2H), 7.15 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.72 (s, 1H), 7.97 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 15.2, 22.0, 28.0, 60.3, 111.0, 114.5, 121.2, 124.9, 125.3, 134.4, 135.4, 144.0, 165.5, 171.1 ppm. HRMS (ESI+): calcd. for $C_{15}H_{18}O_3N$ $[M+H]^+$: 260.1281, found: 260.1280.

Ethyl-1-acetyl-5-isopropyl-2-methyl-1*H*-indole-3-carboxylate (3c): White solid; mp (38.0 mg, 88%): 93-94 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (d, *J* = 6.9 Hz, 6H), 1.48 (t, *J* = 7.2 Hz, 3H), 2.77 (s, 3H), 2.96 (s, 3H), 3.03 (sep, *J* = 6.9 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 7.20 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.78 (d, *J*=8.7 Hz, 1H), 8.00 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 15.3, 24.3, 27.9, 34.1, 60.2, 111.2, 114.0, 119.0, 123.2, 127.6, 133.6, 144.7, 144.9, 165.5, 170.9 ppm. HRMS (ESI+): calcd. for $C_{17}H_{20}O_3N$ $[M+H]^+$: 286.1438, found: 286.1440.

Ethyl-1-acetyl-5-methoxy-2-methyl-1*H*-indole-3-carboxylate (3d): White solid (36.0 mg, 87%); mp: 92-95 °C; NMR (500 MHz, $CDCl_3$) *δ* 1.47 (t, *J* = 7.2 Hz, 3H), 2.75 (s, 3H), 2.96 (s, 3H), 3.88 (s, 3H), 4.43 (q, *J* = 7.2 Hz, 2H), 6.91 (dd, *J* = 9.1, 2.7 Hz, 1H), 7.64 (d, *J* = 2.6 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 15.4, 27.8, 55.5, 60.3, 104.2, 111.0, 112.9, 115.2, 128.6, 129.9, 145.1, 156.5, 165.4, 170.7 ppm. HRMS (ESI+): calcd. for $C_{15}H_{18}O_4N$ $[M+H]^+$: 276.1230, found: 276.1229.

Ethyl 1-acetyl-5-bromo-2-methyl-1*H*-indole-3-carboxylate (3e): White solid (32.0 mg, 81%); mp: 82-85 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (t, *J* = 7.2 Hz, 3H), 2.76 (s, 3H), 2.97 (s, 3H), 4.44 (q, *J* = 7.2 Hz, 2H), 7.40 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 8.25 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 15.3, 27.9, 60.5, 110.6, 115.8, 117.5, 124.4, 127.3, 129.0, 134.0, 145.4, 164.8, 170.6 ppm. HRMS (ESI+): calcd. for $C_{14}H_{15}O_3NBr$ $[M+H]^+$: 324.0230 and 326.0209 (^{81}Br), found: 324.0229 and 326.0209 (^{81}Br).

Ethyl 1-acetyl-5-chloro-2-methyl-1*H*-indole-3-carboxylate (3f): White solid (32.5 mg, 77%); mp: 81-83 °C; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.48 (t, *J* = 7.2 Hz, 3H), 2.78 (s, 3H), 2.98 (s, 3H), 4.44 (q, *J* = 7.2 Hz, 2H), 7.22–7.32 (m, 1H), 7.84–7.93 (m, 1H), 8.07 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 14.4, 15.4, 28.0, 60.6, 110.5, 115.5, 121.2, 124.6, 128.4, 129.6, 133.5, 145.6, 164.9, 170.7 ppm. HRMS (ESI+): calcd. for $C_{14}H_{15}O_3NCl$ $[M+H]^+$: 280.0735, found: 280.0736.

Ethyl 1-acetyl-5-fluoro-2-methyl-1*H*-indole-3-carboxylate (3g): White solid (35.6 mg, 73%); mp: 75-79 °C; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.48 (t, *J* = 6.9 Hz, 3H), 2.78 (s, 3H), 2.99 (s, 3H), 4.43 (q, *J* = 7.0 Hz, 2H), 7.05 (td, *J* = 9.0, 2.2 Hz, 1H), 7.77 (dd, *J* = 9.5, 2.4 Hz, 1H), 7.94 (dd, *J* = 9.2, 4.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 15.4, 28.0, 60.5, 107.5 (d, *J* = 25.4 Hz), 110.9 (d, *J* = 4.5 Hz), 112.3 (d, *J* = 25.4 Hz), 115.6 (d, *J* = 9.1 Hz), 128.4 (d, *J*=10.9 Hz), 131.6, 145.9, 159.8 (d, *J* = 239.8 Hz), 165.0, 170.7 ppm. HRMS (ESI+): calcd. for $C_{14}H_{15}O_3NF$ $[M+H]^+$: 264.1030, found: 264.1028.

Ethyl-1-acetyl-2-methyl-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (3h): White solid (32.3 mg, 69%); mp: 67-69 °C; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.48 (t, *J* = 7.2 Hz,, 3H), 2.80 (s, 3H), 3.00 (s, 3H), 4.46 (q, *J* = 7.2 Hz, 2H), 7.55 (dd, *J* = 8.8, 1.6 Hz, 1H), 8.03 (d, *J*=8.9 Hz, 1H), 8.42 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 14.3, 15.2, 27.9, 60.6, 111.2, 114.6, 119.2 (q, *J* = 3.6 Hz), 121.2 (q, *J* = 3.6 Hz), 124.6 (q, *J* = 272.5 Hz), 126.2 (q, *J* = 32.7 Hz), 127.2, 136.8, 146.0, 164.7, 170.7 ppm. HRMS (ESI+): calcd. for $C_{15}H_{15}F_3NO_3$ $[M+H]^+$: 314.1004, found: 314.1001.

3-Ethyl-5-methyl-1-acetyl-2-methyl-1*H*-indole-3,5-dicarboxylate (3i): White solid (33.7 mg, 74%); mp: 113-115 °C; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.50 (t, *J* = 7.2 Hz, 3H), 2.81 (s, 3H), 2.99 (s, 3H), 3.96 (s, 3H), 4.47 (q, *J* = 7.2 Hz, 2H), 7.92–7.95 (m, 1H), 8.01 (dd, *J* = 8.9, 1.7 Hz, 1H), 8.82 (d, *J* = 0.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 15.2, 27.9, 52.1, 60.6, 111.5, 114.0, 123.9, 125.7, 125.8, 127.2, 137.7, 145.7, 164.9, 167.3, 170.8 ppm. HRMS (ESI+): calcd. for $C_{16}H_{18}O_5N$ $[M+H]^+$: 304.1179, found: 304.1178.

Ethyl-1,5-diacetyl-2-methyl-1*H*-indole-3-carboxylate (3j): White solid (35.0 mg, 81%); mp: 106-109 °C; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.50 (t, *J* = 7.1 Hz, 3H), 2.69 (s, 3H), 2.81 (s, 3H), 2.99 (s, 3H), 4.47 (q, *J* = 7.1 Hz, 2H), 7.93–7.99 (m, 2H), 8.77 (d, *J* = 0.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 14.4, 15.3, 26.7, 27.9, 60.6, 111.5, 114.2, 123.1, 124.4, 127.3, 133.1, 137.7, 145.9, 164.9, 170.7, 198.0 ppm. HRMS (ESI+): calcd. for $C_{16}H_{18}NO_4$ $[M+H]^+$: 288.1236, found: 288.1241.

Ethyl-1-acetyl-7-methoxy-2-methyl-1*H*-indole-3-carboxylate (3k): White solid (25.0 mg, 60%); mp: 117-119 °C; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.45 (t, *J* = 7.1 Hz, 3H), 2.56 (s, 3H), 2.76 (s, 3H), 3.94 (s, 3H), 4.41 (q, *J* = 7.2 Hz, 2H), 6.77 (d, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.7, 14.5, 28.6, 55.7, 60.0, 104.9, 107.9, 114.5, 124.0, 124.3, 129.5, 144.2, 146.1, 165.6, 174.3 ppm. HRMS (ESI+): calcd. for $C_{15}H_{18}O_4N$ $[M+H]^+$: 276.1236, found: 276.1236.

Ethyl-1-acetyl-2,6-dimethyl-1*H*-indole-3-carboxylate and ethyl-1-acetyl-2,7-dimethyl-1H-indole-3-carboxylate (3l-i+3l-ii): Colorless sticky liquid (29.5 mg, 76%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (t, *J* = 7.2 Hz, 0.9H), 1.48 (t, *J* = 7.2 Hz, 3H), 2.47 (s, 3H), 2.49 (s, 0.9H), 2.78 (s, 3.9 H), 2.96 (s, 0.9H), 2.96 (s. 3H), 4.4.–4.46 (m, 2.6H), 7.13–7.16 (m, 1.3H), 7.73 (s, 0.3 H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.91 (s, 1H), 7.98 (d, *J* = 8.1 Hz, 0.3H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 14.9, 14.9, 15.3, 15.4, 21.5, 22.0, 27.9, 28.0, 60.3, 60.3, 110.9, 111.0, 113.9, 114.5, 121.2, 121.5, 124.9, 125.3, 125.6, 127.5, 133.3, 133.5, 134.4, 135.4, 144.1, 144.8, 165.5, 171.0, 171.2 ppm. HRMS (ESI+): calcd. for $C_{15}H_{18}O_3N$ $[M+H]^+$: 260.1281, found: 260.1281.

Ethyl-1-acetyl-5,6-dimethoxy-2-methyl-1*H*-indole-3-carboxylate (3m-i): White solid (25.0 mg, 54%); mp: 124-129 °C; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.47 (t, *J* = 7.1 Hz, 3H), 2.73 (s, 3H), 2.94 (s, 3H), 3.94 (s, 3H), 3.96 (s, 3H), 4.43 (q, *J* = 7.1 Hz, 2H), 7.60 (s, 1H), 7.68 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 14.4, 15.5, 27.8, 55.9, 56.2, 60.2, 98.9, 102.9, 111.3, 120.3, 129.7, 141.7, 147.0, 147.5, 165.4, 170.9 ppm. HRMS (ESI+): calcd. for $C_{16}H_{20}O_5N$ $[M+H]^+$: 306.1336, found: 306.1337.

Ethyl-1-acetyl-6,7-dimethoxy-2-methyl-1*H*-indole-3-carboxylate (3m-ii): Sticky solid (8.0 mg, 26%); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.42 (t, *J* = 7.0 Hz, 3H), 2.67 (s, 3H), 2.71 (s, 3H), 3.89 (s, 3H), 3.91 (s, 3H), 4.43 (q, *J* = 7.1 Hz, 2H), 6.94 (d, *J* = 9.2 Hz, 1H), 7.66 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 14.3, 15.5, 27.5, 56.9, 60.9, 61.3, 110.5, 111.2, 113.8, 121.8, 131.4, 138.4, 140.8, 148.7, 166.4, 170.2 ppm. HRMS (ESI+): calcd. for $C_{16}H_{20}O_5N$ $[M+H]^+$: 306.1336, found: 306.1337.

Ethyl-1-acetyl-2-methyl-1*H*-benzo[g]indole-3-carboxylate (3n): White solid (23.0 mg, 52%); mp: 82-84 °C; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.49 (t,

J = 7.2 Hz, 3H), 2.63 (s, 3H), 2.85 (s, 3H), 4.46 (q, *J* = 7.2 Hz, 2H), 7.45–7.50 (m, 1H), 7.53–7.58 (m, 1H), 7.75 (t, *J* = 7.4 Hz, 2H), 7.98 (d, *J* = 8.1 Hz, 1H), 8.28 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 12.8, 14.5, 28.8, 60.2, 109.0, 120.8, 121.3, 121.5, 124.4, 124.7, 125.3, 126.2, 128.9, 129.4, 131.5, 142.3, 165.5, 175.4 ppm. HRMS (ESI+): calcd. for $C_{18}H_{18}O_3N$ $[M+H]^+$: 296.1281, found: 296.1277.

Ethyl-1-acetyl-2-phenyl-1*H*-indole-3-carboxylate (3o): White solid (33.0 mg, 72%); mp: 102-105 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.16 (t, *J* = 7.2 Hz, 3H), 1.91 (s, 3H), 4.20 (q, *J* = 7.2 Hz, 2H), 7.37–7.44 (m, 2H), 7.45–7.53 (m, 5H), 8.20–8.24 (m, 1H), 8.30–8.34 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 13.9, 27.8, 60.1, 112.4, 115.6, 121.6, 124.5, 125.7, 126.8, 128.3, 129.5, 130.3, 132.6, 136.2, 143.6, 164.2, 171.8 ppm. HRMS (ESI+): calcd. for $C_{19}H_{18}O_3N$ $[M+H]^+$: 308.1287, found: 308.1285.

Methyl-1-acetyl-2-(*p*-tolyl)-1*H*-indole-3-carboxylate (3p): White solid (34.0 mg, 70%); mp: 113-117 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.21 (t, *J* = 7.2 Hz, 3H), 1.58 (s, 3H), 1.93 (s, 3H), 2.45 (s, 3H), 4.23 (q, *J* = 7.2 Hz, 2H), 7.28–7.32 (m, 2H), 7.34–7.37 (m, 2H), 7.38–7.41 (m, 2H), 8.17–8.21 (m, 1H), 8.29–8.33 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 14.1, 21.5, 27.9, 60.2, 112.2, 115.6, 121.7, 124.5, 125.6, 126.8, 129.0, 129.5, 130.2, 136.2, 139.7, 144.1, 164.3, 172.0 ppm. HRMS (ESI+): calcd. for $C_{20}H_{20}O_3N$ $[M+H]^+$: 322.1443, found: 322.1441.

Ethyl-1-acetyl-2-(4-chlorophenyl)-1*H*-indole-3-carboxylate (3q); White solid (35.7 mg, 69%); mp: 124-129 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.22 (t, *J* = 7.1 Hz, 3H), 1.98 (s, 3H), 4.23 (q, *J* = 7.1 Hz, 2H), 7.39–7.45 (m, 4H), 7.46–7.51 (m, 2H), 8.19–8.22 (m, 1H), 8.28–8.31 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 14.0, 28.1, 60.3, 112.8, 115.6, 121.8, 124.7, 126.0, 126.7, 128.6, 131.0, 131.7, 135.8, 136.2, 142.2, 164.1, 171.3 ppm. HRMS (ESI+): calcd. for $C_{19}H_{17}O_3NCl$ $[M+H]^+$: 342.0897, found: 342.0896.

Ethyl-2-methyl-1-propionyl-1*H*-indole-3-carboxylate (3r): White solid (35.7 mg, 92%); mp: 92-94 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.37 (t, *J* = 7.2 Hz, 3H), 1.47 (t, *J* = 7.2 Hz, 3H), 2.97 (s, 3H), 3.06 (q, *J* = 7.3 Hz, 2H), 4.43 (q, *J* = 7.3 Hz, 2H), 7.29–7.32 (m, 2H), 7.81–7.85 (m, 1H), 8.11–8.14 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.4, 14.4, 15.2, 33.2, 60.3, 110.8, 113.9, 121.7, 123.7, 124.2, 127.4, 135.0, 144.8, 165.5, 175.3 ppm. HRMS (ESI+): calcd. for $C_{15}H_{18}O_3N$ $[M+H]^+$: 260.1281, found: 260.1282.

Ethyl-2-methyl-1-pivaloyl-1*H*-indole-3-carboxylate (3s): Sticky liquid (38.4 mg, 89%); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.37 (s, 9H), 1.46 (t, *J* = 7.2 Hz, 3H), 2.70 (s, 3H), 4.42 (q, *J* = 7.1 Hz, 2H), 7.17–7.21 (m, 1H), 7.22–7.26 (m, 2H), 8.06–8.16 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 13.6, 14.5, 28.0, 44.9, 59.8, 106.4, 111.1, 121.7, 122.4, 122.9, 126.4, 134.7, 142.8, 165.7, 186.5 ppm. HRMS (ESI+): calcd. for $C_{17}H_{22}O_3N$ $[M+H]^+$: 288.1594, found: 288.1595.

Ethyl-2-methyl-1-(2-phenylacetyl)-1*H*-indole-3-carboxylate (3t): Low melting solid (30.3 mg, 63%); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.46 (t, *J* = 7.1 Hz, 3H), 2.92 (s, 3H), 4.38 (s, 2H), 4.43 (q, *J* = 7.2 Hz, 2H), 7.25–7.28 (m, 2H), 7.30–7.33 (m, 3H), 7.34–7.38 (m, 2H), 7.77–7.89 (m, 1H), 8.10–8.17 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 14.9, 45.8, 60.3, 110.9, 113.7, 121.9, 123.9, 124.3, 127.5, 127.6, 128.9, 129.2, 132.9, 135.0, 144.8, 165.3, 172.5 ppm. HRMS (ESI+): calcd. for $C_{20}H_{20}O_3N$ $[M+H]^+$: 322.1443, found: 322.1444.

Ethyl-1-benzoyl-2-methyl-1*H*-indole-3-carboxylate (3u): Sticky liquid (28.0 mg, 61%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48 (t, *J* = 7.2 Hz, 3H), 2.72 (s, 3H), 4.45 (q, *J* = 7.1 Hz, 2H), 7.03–7.07 (m, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 7.24–7.30 (m, 1H), 7.49–7.54 (m, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 7.3 Hz, 2H), 8.14 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5, 14.5, 60.2, 110.0, 113.3, 121.5, 123.4, 123.5, 127.0, 129.0, 130.3, 134.1, 134.2, 136.0, 145.3, 165.5, 169.7 ppm. HRMS (ESI+): calcd. for $C_{19}H_{18}O_3N$ $[M+H]^+$: 308.1281, found: 308.1281.

Ethyl-1-(dimethylcarbamoyl)-2-methyl-1*H*-indole-3-carboxylate (3v): Sticky liquid (40.0 mg, 97%); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.46 (t, *J* = 7.2 Hz, 3H), 2.76 (s, 3H), 2.79 (br s., 3H), 3.27 (br s., 3H), 4.42 (q, *J* = 7.1 Hz, 2H), 7.21–7.23 (m, 1H), 7.24–7.27 (m, 2H), 8.12–8.14 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 12.6, 14.5, 36.7, 38.2, 59.8, 106.8, 110.4, 121.7, 122.6, 123.3, 126.5, 134.1, 143.4, 152.6, 165.6 ppm. HRMS (ESI+): calcd. for $C_{15}H_{19}O_3N_2$ $[M+H]^+$: 275.1396, found: 275.1398.

Dimethyl (1-acetyl-2-methyl-1*H*-indol-3-yl)phosphonate (4a): Sticky liquid (29.0 mg, 69%); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 2.81 (s, 3H), 2.97 (d, *J* = 2.3 Hz, 3H), 3.77 (s, 3H), 3.79 (s, 3H), 7.25–7.42 (m, 2H), 7.83–7.85 (m, 1H), 7.90–7.92 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 15.6, 27.9, 52.3, 52.34, 104.2 (d, *J* = 212.5 Hz), 114.5, 120.8, 123.9, 124.6, 129.0, *J* = 10.9 Hz), 135.7 (d, *J* = 12.7 Hz), 147.1 (d, *J* = 26.3 Hz), 170.7 ppm. HRMS (ESI+): calcd. for $C_{13}H_{17}O_4NP$ $[M+H]^+$: 282.0895, found: 282.0898

Dimethyl (1-acetyl-2,5-dimethyl-1*H*-indol-3-yl)phosphonate (4b): White solid (33.2 mg, 75%); mp: 99-103 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 2.45 (s, 3H), 2.78 (s, 3H), 2.93 (d, *J* = 2.3 Hz, 3H), 3.76 (s, 3H), 3.78 (s, 3H), 7.14 (d, *J* = 8.5 Hz, 1H), 7.64 (s, 1H), 7.76 (dd, *J* = 8.6, 1.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 15.6, 21.3, 27.8, 52.2, 52.2, 104.2 (d, *J* = 212.6 Hz), 114.2, 120.8, 125.8, 129.4 (d, *J* = 11.8 Hz), 133.6, 134.0 (d, *J* = 12.7 Hz), 147.1 (d, *J* = 26.3 Hz), 170.6 ppm. HRMS (ESI+): calcd. for $C_{14}H_{19}O_4NP$ $[M+H]^+$: 296.1046, found: 296.1045.

Dimethyl (1-acetyl-5-isopropyl-2-methyl-1*H*-indol-3-yl)phosphonate (4c): Sticky liquid (34.4 mg, 71%); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.30 (d, *J* = 6.9 Hz, 6H), 2.78 (s, 3H), 2.93 (d, *J* = 2.3 Hz, 3H), 3.03 (hept, *J* = 6.9 Hz, 1H), 3.77 (s, 3H), 3.79 (s, 3H), 7.21 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.69 (d, *J* = 1.7 Hz, 1H), 7.80 (dd, *J* = 8.7, 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 15.6, 24.3, 27.7, 34.0, 52.2, 52.3, 105.1 (d, *J* = 211.6 Hz), 114.3 118.3, 123.1, 129.3 (d, *J* = 11.8 Hz), 134.2 (d, *J* = 12.7 Hz), 144.8, 147.1 (d, *J* = 27.2 Hz), 170.6 ppm. HRMS (ESI+): calcd. for $C_{16}H_{22}O_4NP$ $[M+H]^+$: 324.1359, found: 324.1356.

Dimethyl (1-acetyl-5-methoxy-2-methyl-1*H*-indol-3-yl)phosphonate (4d): Sticky liquid (31.0 mg, 66%); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 2.77 (s, 3H), 2.93 (d, *J* = 1.5 Hz, 3H), 3.76 (s, 3H), 3.78 (s, 3H), 3.88 (s, 3H), 6.92 (dd, *J* = 9.1, 2.7 Hz, 1H), 7.35 (d, *J* = 2.6 Hz, 1H), 7.83 (dd, *J* = 9.2, 1.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 15.7, 27.7, 52.2, 52.3, 55.6, 103.4 104.2 (d, *J* = 210.7 Hz), 112.9, 115.5, 130.2 (d, *J* = 11.8 Hz), 130.4 (d, *J* = 12.7 Hz), 147.3 (d, *J* = 26.3 Hz), 156.5, 170.3 ppm. HRMS (ESI+): calcd. for $C_{14}H_{19}O_5NP$ $[M+H]^+$: 312.0995, found: 312.0992.

Methyl 1-acetyl-3-(dimethoxyphosphoryl)-2-methyl-1*H*-indole-5-carboxylate (4e): White solid (30.0 mg, 59%); mp: 117-120 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 2.82 (s, 3H), 2.97 (d, *J* = 2.1 Hz, 3H), 3.79 (s, 3H), 3.81 (s, 3H), 3.95 (s, 3H), 7.96 (dd, *J* = 8.8, 1.8 Hz, 1H), 8.01 - 8.04 (m, 1H), 8.51 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 15.5, 27.8, 52.2, 52.4, 52.5, 105.1 (d, *J* = 212.5 Hz), 114.3, 122.8, 125.8, 126.0, 128.8 (d, *J* = 10.9 Hz), 138.5 (d, *J* = 12.7 Hz), 148.1 (d, *J* = 27.2 Hz), 167.1, 170.5 ppm. HRMS (ESI+): calcd. for $C_{15}H_{19}O_6NP$ $[M+H]^+$: 340.0945, found: 340.0943.

Dimethyl (2-methyl-1-propionyl-1*H*-indol-3-yl)phosphonate (4f): Sticky liquid (31.6 mg, 71%); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.38 (t, *J* = 7.2 Hz, 3H), 2.95 (d, *J* = 2.3 Hz, 3H), 3.08 (q, *J* = 7.3 Hz, 2H), 3.76 (s, 3H), 3.78 (s, 3H), 7.25–7.40 (m, 2H), 7.78–7.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 9.3, 15.5, 33.0, 52.2, 52.3, 104.4 (d, *J* = 212.5 Hz), 114.3, 120.9,

123.7, 124.4, 129.1 (d, J = 10.9 Hz), 135.6 (d, J = 12.7 Hz), 147.1 (d, J = 26.3 Hz), 175.0 ppm. HRMS (ESI+): calcd. for $C_{14}H_{19}O_4NP$ $[M+H]^+$: 296.1046, found: 296.1043.

Dimethyl (1-(dimethylcarbamoyl)-2-methyl-1*H*-indol-3-yl)phosphonate (4g): White solid (27.5 mg, 59%); mp: 110-102 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.72 (s, 3H), 2.81 (br s, 3H), 3.27 (br s, 3H), 3.75 (br s, 3H), 3.77 (br s, 3H), 7.18–7.32 (m, 3H), 7.74–7.86 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.3, 36.8, 38.3, 52.2, 52.3, 98.9 (d, J = 216.2 Hz), 110.6, 120.8, 122.5, 123.5, 128.3 (d, J = 11.8 Hz), 135.0 (d, J = 13.6 Hz), 145.2 (d, J = 27.3 Hz), 152.6 ppm. HRMS (ESI+): calcd. for $C_{14}H_{19}O_4N_2P$ $[M+H]^+$: 310.1082, found: 310.1080.

Dimethyl (1-(2-acetamidophenyl)-2-oxopropyl)phosphonate (5a): To a 3 mL screw capped vial with a spinvane triangular-shaped Teflon stirbar were added acetanilide (30.0 mg, 1.0 equiv), diazocompounds **2e** (51.2 mg, 1.2 equiv), $[IrCp^*Cl_2]_2$ (3.5 mg, 2.0 mol %), $AgNTf_2$ (6.9 mg, 8.0 mol %), KOAc (18.2 mg, 1.0 equiv) and 1,2-dichloroethane (1.5 mL) under air. The reaction mixture was stirred at 70 ℃ for 12 h. Next, the reaction mixture was filtered through a pad of celite followed by washing of the pad with CH_2Cl_2 (10 mL x 2). The combined solvents were removed under reduced pressure and the residue was purified by column chromatography (EtOAc/hexane) to obtain the alkylated product **6a** as sticky liquid (48.0 mg, 72% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.02 (d, J = 1.5 Hz, 3H), 2.15 (s, 3H), 3.50 (d, J = 10.8 Hz, 3H), 3.94 (d, J = 11.1 Hz, 3H), 4.19 (d, J = 24.6 Hz, 1H), 7.22–7.26 (m, 1H), 7.27–7.30 (m, 1H), 7.39–7.49 (m, 1H), 7.70 (d, J = 8.1 Hz, 1H), 9.55 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.7, 28.9 (d, J = 8.2 Hz), 53.0 (d, J = 7.3 Hz), 54.7 (d, J = 7.3 Hz), 58.4 (d, J = 140.3 Hz), 124.3 (d, J = 7.3 Hz), 126.3, 127.4 (d, J = 2.7 Hz), 129.5 (d, J = 3.6 Hz), 132.0 (d, J = 7.3 Hz), 136.6 (d, J = 4.5 Hz), 169.6, 202.9 (d, J = 5.4 Hz) ppm; HRMS (ESI+): calcd. for $C_{13}H_{19}O_5NP$ $[M+H]^+$: 300.0995, found: 300.0995.

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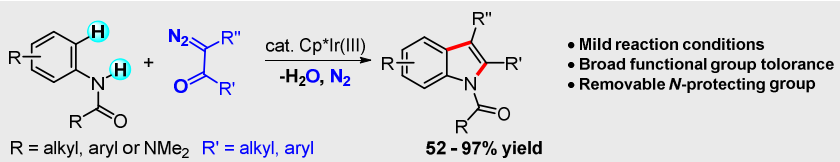

Here in we reported a one pot synthetic approach to poly-substituted indoles from readily available acetanilide via Ir(III)-catalyzed intermolecular C–H annulations with diazo compounds.

C–H Annulations

Pitambar Patel, Gangutri Borah*

Page No. – Page No.

A Direct Access to Indoles via Ir(III)-Catalyzed C-H Functionalization of Acetanilides with Diazo Compounds