Synthesis X.-Y. Zhou, X. Chen Paper

Na_2CO_3-Catalyzed *N*-Acylation of Indoles with Alkenyl Carboxylates

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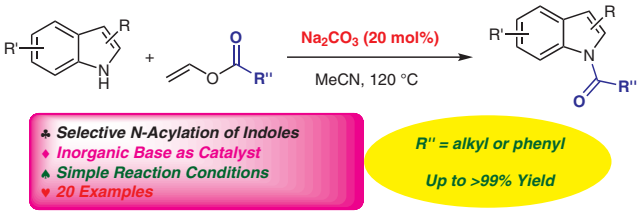

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Abstract The *N*-acylation of indoles has been accomplished via inorganic base catalysis. It provided an efficient and simple catalysis system for the preparation of *N*-acylindoles with alkenyl carboxylates as acylating agents. A broad variety of indoles undergo the smooth *N*-acylation using Na_2CO_3 as catalyst in MeCN at 120 °C to give the corresponding *N*-acylindoles in good to excellent yields.

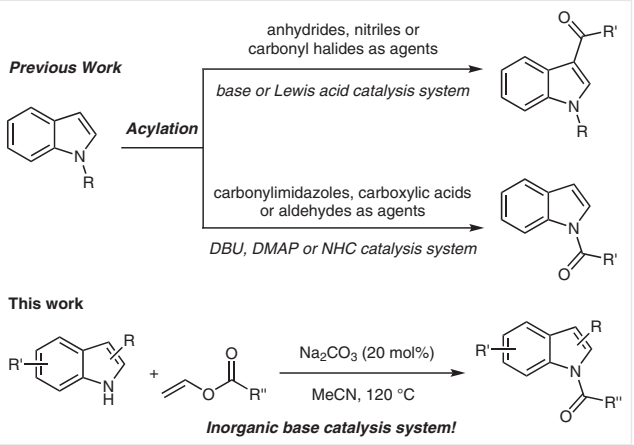
Key words inorganic base, catalysis, acylation, indole, alkenyl carboxylates

A wide range of natural products, pharmaceuticals, and fine chemicals contain indole moieties.[1] In order to utilize the indole skeletons in organic synthesis effectively, the transformation and functionalization of indole and its derivatives have attracted much attention. Oxidation,[2] reduction,[3] nucleophilic addition,[4] Friedel–Crafts reactions,[5] catalyzed oxidative cross-coupling reactions,[6] and C–H bond activation[7] have been reported widely. Besides, the acylation process has been recognized as a powerful strategy for the *N*-protection of indoles. Therefore, a series of acylating agents and catalysis systems have been sought for acylation of indoles.

The acylation in 2- or 3-position of indoles is a traditional method for the functionalization of indoles. 3-Acylindoles are obtained in many cases, such as in the dialkylaluminum chloride promoted 3-acylation of NH indoles in the presence of acyl chlorides,[8] anhydrides, nitriles or amino acid derivatives,[9] 1,5-diazabicyclo[4.3.0]non-5-ene (DBN)-[10] and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)-promoted[11] Friedel–Crafts acylation of indoles, copper-catalyzed intramolecular C–H oxidation/acylation of formyl-*N*-arylformamides,[12] Ru- and Fe-catalyzed C3-selective acylation of indoles with anilines,[13] and directed meta-acylation of aromatic compounds[14] and indoles[15] with nitrile as acylating agents. Unfortunately, *N*-acylation of indoles under mild reaction conditions are limited. The NBoc indoles were prepared by 4-(*N*,*N*-dimethylamino)pyridine (DMAP)-catalyzed acylation of indoles in the presence of di-*tert*-butyl dicarbonate (Boc_2O) with high selectivity. But this method is not suitable for the synthesis of other *N*-acylindoles.[2c] In 1998, Ottoni and his colleagues disclosed the methods of *N*-benzenesulfonylation, *N*-acetylation, *N*-methylation, and *N*-benzylation of indoles under strong basic conditions (NaOH, KOH, and Et_3N).[16] More specifically, 3-acylindoles are normal by-products in the synthesis of *N*-acylindoles and a highly regioselective method is necessary to be developed.

Recently, DBU-catalyzed *N*-acylation of indoles with carbonylimidazoles,[17] DMAP-catalyzed *N*-acylation of indoles with carboxylic acids and Boc_2O,[18] and *N*-heterocyclic carbene (NHC)-catalyzed *N*-acylation of indoles with aromatic and conjugated aldehydes[19] have been reported. In these methods, moderate to excellent yields have been achieved for the synthesis of *N*-acylindoles with high selectivity. In addition, transesterification and amination of esters is a direct strategy for the synthesis of esters and amides. With this in mind, we envisioned that this strategy could be applied to *N*-acylation of indoles, which would lead to a new method for late stage synthesis of *N*-acylindoles or *N*-acylindolines (Scheme 1).

To develop a method for the synthesis of *N*-acylindolines, a palladium-catalyzed *N*-acylation-transfer hydrogenation of indoles was carried out using indole (**1a**) and vinyl acetate (**2a**) as model starting materials, Pd/C (10 wt%) as catalyst, and sodium formate ($HCO_2Na{\cdot}2H_2O$, 200 mol%) as reductive base in acetonitrile at 100 °C. In this reaction, 1-(1*H*-indol-1-yl)ethanone (**3aa**) was isolated in 65% yield (Table 1, entry 1) and 31% starting material **1a** was recov-



Scheme 1 Selective acylation of indoles for the synthesis of acylindoles

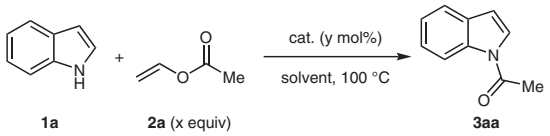
ered without the formation of the corresponding *N*-acylindoline and 3-acylindole. Therefore, we focused on the research about the selective *N*-acylation of indoles using vinyl esters as acylating agent. Then the catalyst, the amount of acylating agent, solvent, and temperature were evaluated to improve the yield of the product **3aa**, respectively. The results are shown in Table 1.

First, sodium formate as base was tested in MeCN at 100 °C without the Pd/C and 67% of **3aa** was isolated (Table 1, entry 2). It indicated that the metal catalyst was not necessary for the *N*-acylation of indoles. Then, the reactivity of other bases was tested, including Et_3N, NaOAc, K_2CO_3, MgO, and Na_2CO_3 (entries 3–7). Pleasingly, replacing $HCO_2Na{\cdot}2H_2O$ with Na_2CO_3 increased the yield to 73% (entry 7). To improve the yield further, the amount of base was optimized (entries 7–12) and 20 mol% Na_2CO_3 was found to be the optimized dosage (85% yield, entry 10). However, the *N*-acylation of indole cannot proceed smoothly without a base (entry 12). The dosage of acylating agent was optimized (entries 13–15) and the best result was obtained (92% yield, entry 15) when 4.0 equivalent **2a** was added. At last, other solvents and temperature were separately evaluated to improve the yield of the product **3aa**. The choice of solvent significantly influenced the yield (entries 15–19), with MeCN proving to be the optimal reaction medium, presumably due to solubility of Na_2CO_3. Especially, only trace amounts of the desired product **3aa** were observed when ethanol was used as the solvent (EtOH, entry 18). It is presumed that a transesterification had occurred between vinyl acetate and EtOH. To our delight, the reaction efficiency was further increased to 97% by elevating temperature to 120 °C (entry 21).

With optimized conditions in hand, we next sought to define the scope of carboxylates **2**. As shown in Table 2, the *N*-acylation of indole **1a** could proceed smoothly with alkenyl carboxylates **2a–f** and the moderate to excellent isolated yields (56–99%) of products **3** were obtained, respectively. While ethyl acetate was used as acylating agent to form **3aa**, no product was detected and the starting materials were recovered (Table 2, entry 7). It is important to note that the alkyl carboxylates are not suitable for the *N*-acylation of indole and it is considered to be due to the stability of alkyl carboxylates.

Subsequently, the substrate scope of indole for this *N*-acylation under the optimal reaction conditions was studied, as shown in Table 3. No target products were detected when indoles **1b–d** were utilized as the starting materials, respectively (Table 3, entries 1–3). We envision that the steric effect of Me, Ph, and CO_2Me at 2-position of indole inhib-

Table 1 Conditions for the Optimization for Base-Catalyzed *N*-Acylation of Indoles[a]

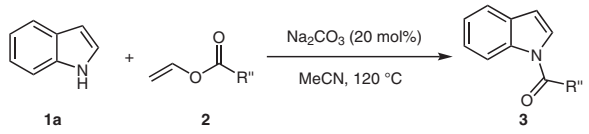


1a **2a** (x equiv) **3aa**

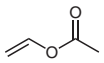
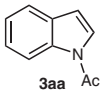
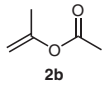
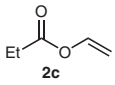
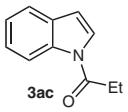
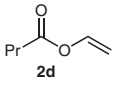
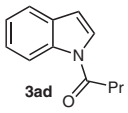
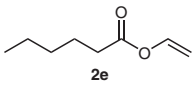
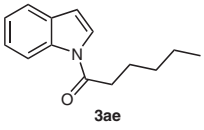
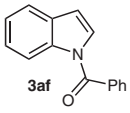
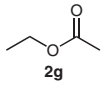
Entry	**2a** x (equiv)	Catalyst (y, mol%)	Solvent	Yield (%)[b]
1	2.0	Pd/C (10 wt%) $HCO_2Na{\cdot}2H_2O$ (200)	MeCN	65
2	2.0	$HCO_2Na{\cdot}2H_2O$ (200)	MeCN	67
3	2.0	Et_3N (200)	MeCN	59
4	2.0	NaOAc (200)	MeCN	21
5	2.0	K_2CO_3 (200)	MeCN	70
6	2.0	MgO (200)	MeCN	39
7	2.0	Na_2CO_3 (200)	MeCN	73
8	2.0	Na_2CO_3 (100)	MeCN	79
9	2.0	Na_2CO_3 (50)	MeCN	80
10	2.0	Na_2CO_3 (20)	MeCN	85
11	2.0	Na_2CO_3 (10)	MeCN	81
12	2.0	–	MeCN	trace
13	1.0	Na_2CO_3 (20)	MeCN	74
14	3.0	Na_2CO_3 (20)	MeCN	87
15	4.0	Na_2CO_3 (20)	MeCN	92
16	4.0	Na_2CO_3 (20)	toluene	11
17	4.0	Na_2CO_3 (20)	1,4-dioxane	40
18	4.0	Na_2CO_3 (20)	EtOH	trace
19	4.0	Na_2CO_3 (20)	THF	35
20[c]	4.0	Na_2CO_3 (20)	MeCN	42
21[d]	4.0	Na_2CO_3 (20)	MeCN	97

[a] Unless other stated, all reactions are carried out with **1a** (59 mg, 0.50 mmol), **2a** (x equiv), cat. (y mol%), solvent (3.0 mL), Temp (°C), 24 h.
[b] Isolated yield.
[c] Carried out at 80 °C.
[d] Carried out at 120 °C.

Table 2 Screen on the Scope of Substrate **2**[a]



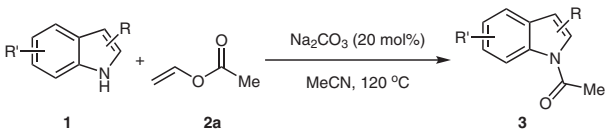
1a **2** **3**

Entry	Substrate **2**	Product **3**	Yield (%)[b]
1	 **2a**	 **3aa**	97
2	 **2b**	**3aa**	95
3	 **2c**	 **3ac**	75
4	 **2d**	 **3ad**	56
5	 **2e**	 **3ae**	77
6	 **2f**	 **3af**	>99
7	 **2g**	**3aa**	NR

[a] Unless otherwise stated, all reactions are carried out with **1a** (59 mg, 0.50 mmol), **2** (2.0 mmol, 4.0 equiv), Na_2CO_3 (10.6 mg, 0.10 mmol, 20 mol%) in MeCN (3.0 mL) at 120 °C for 24 h.
[b] Isolated yield. NR: No reaction.

ited the *N*-acylation process. As expected, 3-substituent and 5-substituent on indole were tolerated well under this procedure (61–99%, entries 4–10). 1*H*-Pyrrolo[2,3-b]pyridine (**1l**) and 2,3,4,9-tetrahydro-1*H*-carbazole (**1m**) were tested and the corresponding products were isolated in good yields (78% and 79%, entries 11 and 12). And substrate **1n** failed to give the corresponding product (entry 13), presumably due to steric effect.

Table 3 Screen on the Scope of Substrate **1**[a]



1 **2a** **3**

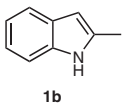
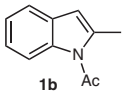
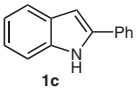
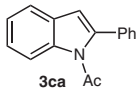
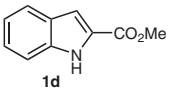
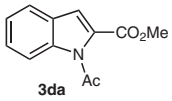
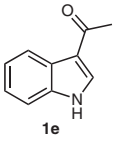
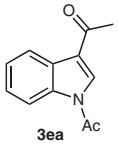
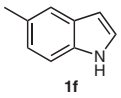
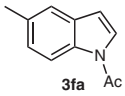
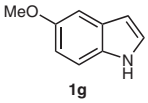
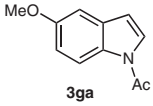
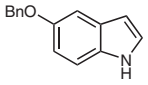
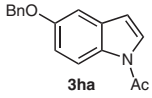
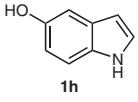
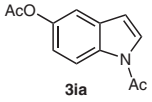
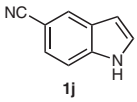
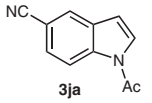
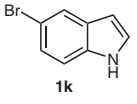
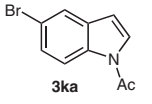
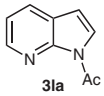
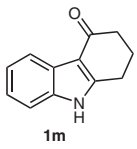
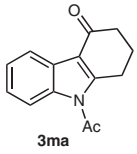
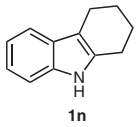
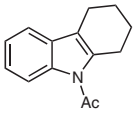
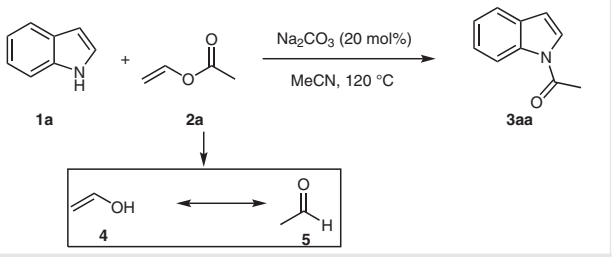
Entry	Substrate **1**	Product **3**	Yield (%)[b]
1	 **1b**	 **1b**	NR
2	 **1c**	 **3ca**	NR
3	 **1d**	 **3da**	NR
4	 **1e**	 **3ea**	82
5	 **1f**	 **3fa**	>99
6	 **1g**	 **3ga**	98
7	 **1h**	 **3ha**	61
8	 **1h**	 **3ia**	91
9	 **1j**	 **3ja**	91
10	 **1k**	 **3ka**	89
11	 **1l**	 **3la**	78

Table 3 (continued)

Entry	Substrate **1**	Product **3**	Yield (%)[b]
12	 **1m**	 **3ma**	79
13	 **1n**	 **3na**	NR

[a] Unless otherwise stated, all reactions are carried out with **1** (0.50 mmol), **2a** (172 mg, 2.0 mmol, 4.0 equiv), Na_2CO_3 (10.6 mg, 0.10 mmol, 20 mol%) in MeCN (3.0 mL) at 120 °C for 24 h.
[b] Isolated yield. NR: No reaction.

Based on the above results, the *N*-acylation of indoles can be achieved using alkenyl cayboxylates as acylation agents but not by using alkyl carboxylates. We predict that acetaldehyde (**5**), which was formed by the isomerization of ethenol **4**, was the driving force in the *N*-acylation of indoles and alkenyl cayboxylates, as shown in Scheme 2. While, EtOH was produced when alkyl carboxylates were utilized as agents and the reversed reaction inhibited the formation of *N*-acylindoles.



Scheme 2 The speculated reason for *N*-acylation of indoles

In summary, using alkenyl carboxylates as acylating agents, the Na_2CO_3-catalyzed *N*-acylation of indoles was successfully achieved in up to >99% yield. Equally important, it will play an important role in protecting group chemistry, especially in terms of *N*-protection of indoles.

Commercially available reagents were used throughout without further purification. The chemical shifts for ^{1}H NMR were recorded in ppm downfield from TMS with the solvent resonance as the internal standard. The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of $CDCl_3$ (77.23 ppm) as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. Flash column chromatography was performed on silica gel (200–300 mesh). TLC analysis was performed using glass-backed plates coated with 0.2 mm silica gel.

Na_2CO_3-Catalyzed *N*-Acylation of Indoles; General Procedure

A mixture of indole **1** (0.50 mmol), Na_2CO_3 (10.6 mg, 0.10 mmol, 20 mol%), and alkenyl carboxylate **2** (2.0 mmol, 4.0 equiv) in MeCN (3 mL) was added into a Schlenk flask (25 mL) and stirred at 120 °C until completion of the reaction. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (petroleum ether/EtOAc 20:1 to 5:1) to afford the desired acylindoles **3** (Tables 2 and 3).

1-(1*H*-Indol-1-yl)ethanone (3aa)[16]

Yield: 76.8 mg (97%); colorless oil; R_f = 0.67 (hexane/EtOAc 10:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 7.4 Hz, 1 H), 7.58 (d, *J* = 7.6 Hz, 1 H), 7.37–7.36 (m, 2 H), 7.31–7.28 (m, 1 H), 6.63 (d, *J* = 3.8 Hz, 1 H), 2.59 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.5, 135.3, 130.3, 125.1, 124.9, 123.5, 120.7, 116.4, 108.9, 23.7.

1-(1*H*-Indol-1-yl)propan-1-one (3ac)

Yield: 64.6 mg (75%); colorless oil; R_f = 0.66 (hexane/EtOAc 10:1).

IR (KBr): 2988, 2915, 1720, 1611, 1589, 1469, 1380, 1352, 1246, 1153, 1065, 982, 758 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 8.2 Hz, 1 H), 7.56 (d, *J* = 7.8 Hz, 1 H), 7.46 (d, *J* = 3.8 Hz, 1 H), 7.38–7.33 (m, 1 H), 7.28–7.25 (m, 1 H), 6.63 (d, *J* = 3.8 Hz, 1 H), 2.94 (t, *J* = 7.3 Hz, 2 H), 1.34 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 172.1, 135.5, 130.2, 125.0, 124.4, 123.5, 120.7, 116.5, 108.9, 29.1, 8.7.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{11}NONa$: 196.0738; found: 196.0741.

1-(1*H*-Indol-1-yl)butan-1-one (3ad)

Yield: 51.9 mg (56%); colorless oil; R_f = 0.68 (hexane/EtOAc 10:1).

IR (KBr): 2965, 2922, 1710, 1600, 1585, 1470, 1376, 1352, 1258, 1150, 1065, 980, 910, 752 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.2 Hz, 1 H), 7.56 (d, *J* = 7.7 Hz, 1 H), 7.46 (d, *J* = 3.7 Hz, 1 H), 7.35 (t, *J* = 7.7 Hz, 1 H), 7.28–7.25 (m, 1 H), 6.63 (d, *J* = 3.7 Hz, 1 H), 2.89 (t, *J* = 7.4 Hz, 2 H), 1.88 (m, 2 H), 1.08 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 171.4, 135.5, 130.2, 125.0, 124.6, 123.5, 120.7, 116.6, 108.9, 37.7, 18.1, 13.7.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{13}NONa$: 210.0895; found: 210.0896.

1-(1*H*-Indol-1-yl)hexan-1-one (3ae)

Yield: 82.6 mg (77%); colorless oil; R_f = 0.68 (hexane/EtOAc 10:1).

IR (KBr): 2978, 2933, 1700, 1605, 1580, 1473, 1379, 1346, 1250, 1151, 1070, 980, 910, 843, 752 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 8.2 Hz, 1 H), 7.54 (d, *J* = 7.7 Hz, 1 H), 7.41 (d, *J* = 3.8 Hz, 1 H), 7.35–7.30 (m, 1 H), 7.26–7.23 (m, 1 H), 6.60 (d, *J* = 3.8 Hz, 1 H), 2.85 (t, *J* = 7.5 Hz, 2 H), 1.84–1.78 (m, 2 H), 1.42–1.35 (m, 4 H), 0.92 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 171.6, 135.6, 130.3, 125.0, 124.6, 123.5, 120.7, 116.6, 108.9, 35.8, 31.3, 24.3, 22.4, 13.9.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{17}NONa$: 238.1208; found: 238.1210.

(1*H*-Indol-1-yl)(phenyl)methanone (3af)

Yield: 110.0 mg (>99%); white solid; mp 55–57 °C; R_f = 0.70 (hexane/EtOAc 10:1).

IR (neat): 2960, 2921, 1710, 1610, 1584, 1477, 1375, 1350, 1255, 1157, 1062, 980, 910, 836, 752 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 8.2 Hz, 1 H), 7.76–7.70 (m, 2 H), 7.61–7.58 (m, 2 H), 7.53–7.50 (m, 2 H), 7.40–7.24 (m, 3 H), 6.61 (d, *J* = 3.7 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.7, 136.0, 134.5, 131.8, 130.7, 129.5, 129.1, 128.5, 128.3, 127.6, 124.9, 123.9, 120.8, 116.3, 108.5.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{11}NONa$: 244.0738; found: 244.0738.

1,1′-(1*H*-Indole-1,3-diyl)diethanone (3ea)[16]

Yield: 82.5 mg (82%); white solid; mp 150–152 °C; R_f = 0.34 (hexane/EtOAc 5:1).

^1H NMR (500 MHz, $CDCl_3$): δ = 8.37–8.32 (m, 2 H), 8.01 (s, 1 H), 7.42–7.37 (m, 2 H), 2.71 (s, 3 H), 2.57 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 193.7, 168.6, 135.9, 131.1, 127.2, 126.2, 125.1, 122.4, 121.8, 116.1, 27.9, 24.0.

1-(5-Methyl-1*H*-indol-1-yl)ethanone (3fa)

Yield: 8.7 mg (>99%); white solid; mp 63–65 °C; R_f = 0.65 (hexane/EtOAc 10:1).

IR (neat): 2980, 2930, 1716, 1608, 1586, 1469, 1376, 1287, 1250, 1156, 1064, 987, 910, 836, 790, 763 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.29 (br s, 1 H), 7.33 (s, 2 H), 7.15 (d, *J* = 8.1 Hz, 1 H), 6.54 (d, *J* = 3.2 Hz, 1 H), 2.59 (s, 3 H), 2.43 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.4, 133.1, 130.6, 126.3, 125.2, 120.7, 116.1, 108.9, 23.8, 21.3.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{11}NONa$: 196.0738; found: 196.0736.

1-(5-Methoxy-1*H*-indol-1-yl)ethanone (3ga)

Yield: 92.8 mg (98%); white solid; mp 82–84 °C; R_f = 0.66 (hexane/EtOAc 10:1).

IR (neat): 2961, 2915, 1706, 1614, 1580, 1475, 1377, 1350, 1261, 1155, 1060, 985, 913, 841, 750 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.33 (d, *J* = 6.2 Hz, 1 H), 7.37 (s, 1 H), 7.02 (d, *J* = 2.4 Hz, 1 H), 6.95 (dd, *J* = 9.0, 2.4 Hz, 1 H), 6.56 (d, *J* = 3.7 Hz, 1 H), 3.85 (s, 3 H), 2.60 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.3, 156.4, 131.3, 130.2, 125.8, 117.2, 113.4, 109.0, 103.5, 55.6, 23.6.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{11}NO_2Na$: 212.0687; found: 212.0688.

1-[5-(Benzyloxy)-1*H*-indol-1-yl]ethanone (3ha)

Yield: 81.1 mg (61%); white solid; mp 127–129 °C; R_f = 0.61 (hexane/EtOAc 10:1).

IR (neat): 2960, 2925, 1700, 1605, 1581, 1482, 1380, 1355, 1260, 1150, 1062, 980, 908, 833 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.34 (d, *J* = 7.1 Hz, 1 H), 7.48–7.45 (m, 2 H), 7.40–7.38 (m, 3 H), 7.34–7.31 (m, 1 H), 7.10 (d, *J* = 2.2 Hz, 1 H), 7.04 (dd, *J* = 9.0, 2.2 Hz, 1 H), 6.56 (d, *J* = 3.7 Hz, 1 H), 5.11 (s, 2 H), 2.61 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.3, 155.6, 137.1, 128.6, 127.9, 127.5, 125.9, 117.3, 114.3, 109.0, 104.9, 70.5, 23.7.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{15}NO_2Na$: 288.1000; found: 288.1004.

1-Acetyl-1*H*-indol-5-yl Acetate (3ia)

Yield: 99.2 mg (91%); white solid; mp 133–135 °C; R_f = 0.58 (hexane/EtOAc 10:1).

IR (neat): 2960, 2920, 1705, 1611, 1587, 1480, 1379, 1353, 1250, 1160, 1061, 983, 912, 840, 748 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 8.7 Hz, 1 H), 7.44 (d, *J* = 3.7 Hz, 1 H), 7.28 (d, *J* = 2.2 Hz, 1 H), 7.06 (dd, *J* = 8.7, 2.2 Hz, 1 H), 6.61 (d, *J* = 3.7 Hz, 1 H), 2.62 (s, 3 H), 2.32 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.9, 168.4, 146.9, 133.2, 131.1, 126.3, 118.7, 117.2, 113.3, 109.0, 23.8, 21.1.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{11}NO_3Na$: 240.0637; found: 240.0641.

1-Acetyl-1*H*-indole-5-carbonitrile (3ja)

Yield: 84.0 mg (91%); white solid; mp 138–140 °C; R_f = 0.41 (hexane/EtOAc 10:1).

IR (neat): 2961, 2926, 2251, 1714, 1606, 1580, 1470, 1375, 1350, 1255, 1157, 1062, 981, 914, 832, 754 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.55 (d, *J* = 8.6 Hz, 1 H), 7.90 (s, 1 H), 7.61–7.55 (m, 2 H), 6.71 (d, *J* = 3.8 Hz, 1 H), 2.68 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.7, 137.3, 130.3, 128.2, 127.3, 125.6, 119.5, 117.4, 108.7, 107.1, 23.9.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_8N_2ONa$: 207.0534; found: 207.0533.

1-(5-Bromo-1*H*-indol-1-yl)ethanone (3ka)

Yield: 106.0 mg (89%); white solid; mp 111–113 °C; R_f = 0.60 (hexane/EtOAc 10:1).

IR (neat): 2962, 2920, 1700, 1603, 1580, 1475, 1378, 1261, 1145, 1068, 976, 841, 760, 643 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 8.5 Hz, 1 H), 7.68 (s, 1 H), 7.44–7.41 (m, 2 H), 6.57 (d, *J* = 3.3 Hz, 1 H), 2.63 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.5, 134.2, 127.9, 126.3, 123.5, 117.94, 116.9, 108.3, 23.8.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_8BrNONa$: 259.9687; found: 259.9690.

1-(1*H*-Pyrrolo[2,3-*b*]pyridin-1-yl)ethanone (3la)

Yield: 62.3 mg (78%); white solid; mp 165–167 °C; R_f = 0.31 (hexane/EtOAc 5:1).

IR (neat): 2979, 2922, 1730, 1621, 1592, 1460, 1368, 1343, 1257, 1152, 1059, 984, 843, 740 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.37 (dd, *J* = 4.8, 1.4 Hz, 1 H), 7.99 (d, *J* = 4.1 Hz, 1 H), 7.88 (dd, *J* = 7.8, 1.4 Hz, 1 H), 7.20 (dd, *J* = 7.8, 4.8 Hz, 1 H), 6.59 (d, *J* = 4.1 Hz, 1 H), 3.06 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.1, 147.8, 143.8, 129.3, 125.4, 123.7, 118.7, 105.7, 25.8.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_9H_8N_2ONa$: 183.0534; found: 183.0531.

9-Acetyl-2,3-dihydro-1*H*-carbazol-4(9*H*)-one (3ma)

Yield: 90.0 mg (79%); yellow solid; mp 136–138 °C; R_f = 0.33 (hexane/EtOAc 5:1).

IR (neat): 2972, 2930, 1773, 1750, 1609, 1589, 1501, 1366, 1343, 1250, 1153, 1060, 981, 912, 847, 743 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.38–8.29 (m, 1 H), 7.89–7.81 (m, 1 H), 7.38–7.33 (m, 2 H), 3.30 (t, *J* = 6.1 Hz, 2 H), 2.81 (s, 3 H), 2.61–2.57 (m, 2 H), 2.26–2.24 (m, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 222.7, 195.7, 170.4, 125.0, 124.7, 122.1, 114.3, 37.8, 27.5, 26.4, 23.5.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{13}NO_2Na$: 250.0844; found: 250.0845.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1609937.

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