Chemospecific synthesis of 2-acetoxyindole-3-carbonitriles catalyzed by $Cu(acac)_2$*

*Shanyan Mo, Jianzhuo Tu, and Jiaxi Xu**

State Key Laboratory of Chemical Engineering Resource, Department of Organic Chemistry, Faculty of Science, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China. Fax: +(86) 106 443 5565. E-mail: jxxu@mail.buct.edu.cn

A chemospecific one-pot synthesis of easily isolable 2-acetoxyindole-3-carbonitriles was described. The intermediate 2-oxindole-3-carbonitriles successfully prepared from 2-cyanodiazoacetanilides without isolation were treated with acetyl chloride and triethylamine to give 2-acetoxyindole-3-carbonitriles. The developed one-pot approach showed broad substrate scope.

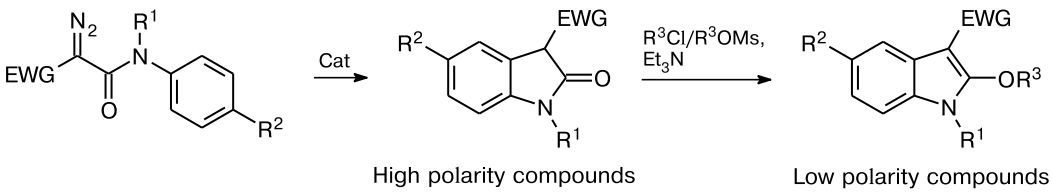
Key words: indole, diazoacetanilide, insertion reactions, $Cu(acac)_2$, oxindole.

The indole skeleton is one of the most significant and valuable heterocycles due to its wide and extensive application in chemical, medicinal, and materials science.[1] Therefore, the synthetic methods to access indole derivatives have attracted much attention. Numerous synthetic approaches have been developed during the last decades.[2,3] Among them, the intramolecular cyclization of α-diazoacetanilides through carbene insertion into the aromatic C—H bond is one of the most efficient routes to prepare oxindole derivatives with broad substrate scope.[4] However, this reaction requires the use of the expensive catalysts, such as dirhodium tetracarboxylates and tetracarboxamidates, and can proceed with different chemoselectivities (carbene insertion into aromatic or aliphatic C—H bonds, cyclopropanation, and even 1,3-dipolar cycloaddition).[5] Thus, recent efforts have been devoted to the improvement of chemoselectivity and application of inexpensive catalysts.[6,7]

As a part of our ongoing project to develop green-chemistry approaches involving catalysis with low cost transition metals to synthesize heterocyclic compounds,[8] we were interested in the synthesis of oxindoles from 2-cyanodiazoacetanilides. Padwa and co-workers[5] noted that substituted 2-oxindoles bearing the electron-withdrawing group (EWG) at the 3-position are very difficult to isolate due to their strong polarity. The obtained products were amorphous substances and cannot be recrystallized from any solvents. Moreover, the attempts to purify ethyl 2-oxindole-3-carboxylates by silica gel column chromatography resulted in their decomposition.[5]

To solve the isolation problem, a strategy based on transformation of oxindoles into 2-hydroxyindoles in the presence of base and hydroxy group protecting reagents, such as chlorosilanes and benzoyl chloride, was developed (Scheme 1).[5] Using this approach, 2-trialkylsilyloxy- and 2-benzoyloxyindoles were prepared. Gener-

Scheme 1



High polarity compounds — Low polarity compounds

EWG (electron-withdrawing group) = CO_2Et, SO_2Ph, CN
R^1 = Me, R^2 = H; R^3 = $(Pr^i)_3Si$ (TIPS), Bu^tMe_2Si (TBDMS), PhCO
Cat is catalyst.

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ally, they have very low polarity and, therefore, can be easily isolated.

Herein, we report a chemospecific one-pot synthesis of easily isolable 2-acetoxyindole-3-carbonitriles from 2-cyanodiazoacetanilides.

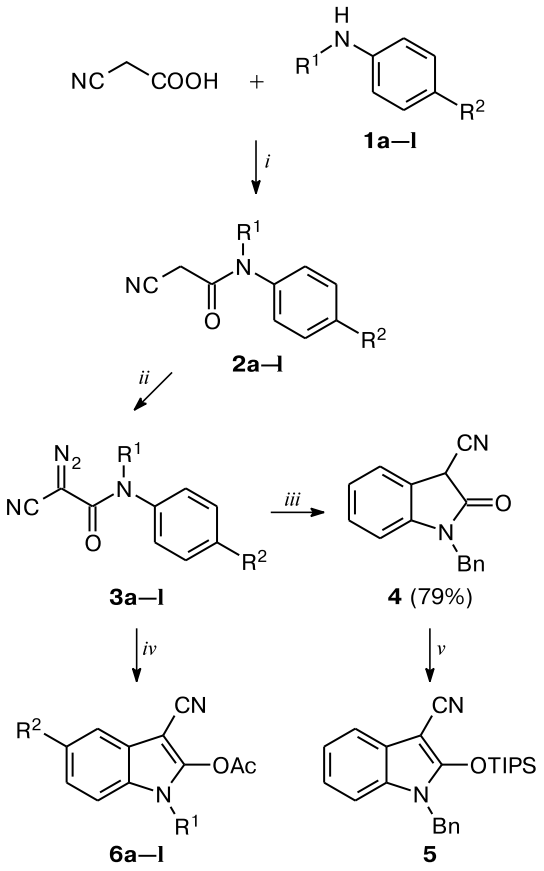
Results and Discussion

In our previous studies on the chemospecific intramolecular Buchner reaction,[8a] we applied catalysis with inexpensive Cu^{II} complexes, for instance $Cu(acac)_2$, to realize the chemospecific synthesis of 5,7-bicyclic cycloheptapyrrolones from *N*-benzyl-2-cyanodiazoacetamides. Now, we pursued to realize chemospecific synthesis of 2-oxindole-3-carbonitriles from 2-cyanodiazoacetanilides in the presence of Cu^{II} catalysts. Note that to date the only one example was reported for the synthesis of 1-methyl-2-oxindoline-3-carbonitrile from 2-cyano-2-diazo-*N*-methylacetanilide under the catalysis of dirhodium(II) tetra(perfluorobutyramidate).[5a] The aim of the present investigation is the replacement of precious metal salts with inexpensive $Cu(acac)_2$ and the improvement of reaction chemoselectivity.

Condensation of cyanoacetic acid with various secondary amines **1a**—**l** using *N,N´*-dicyclohexylcarbodiimide (DCC) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) as coupling reagents gave a series of cyanoacetanilides **2a**—**l** (Scheme 2). By the reaction with triflic azide as the diazo transfer agent, cyanoacetanilides **2a**—**l** were converted into the desired starting materials, cyanodiazoacetanilides **3a**—**l**. We selected *N*-benzyl-2-cyano-2-diazoacetanilide (**3a**) as a model compound. Starting from compound **3a**, we successfully obtained 1-benzyl-2-oxoindoline-3-carbonitrile (**4**) in 79% yield under the $Cu(acac)_2$ catalysis. However, the product **4** was difficult to isolate by column chromatography because of its strong polarity even using $MeOH—CHCl_3$ as an eluent. Next, triisopropylsilyl chloride (TIPSCl) in the presence of triethylamine was attempted to protect the hydroxy group generating 1-benzyl-2-triisopropylsilyloxyindole-3-carbonitrile (**5**). Product **5** was easily isolated by silica gel column chromatography but it was contaminated with TIPSCl used in the reaction in an excess due to its very close polarity to **5**. Because the reaction was conducted in small scale, this mixture cannot be subjected to vacuum distillation, which can be regarded as an efficient purification method for the large-scale syntheses.

Since the synthesis involving TIPSCl was unsuccessful, AcCl was selected as the protecting reagents for the hydroxy groups of compounds **3a**—**l** with an advantage that the excessive AcCl can be easily removed by washings with water. After functionalization of the C—H aromatic bond by carbene insertion, AcCl and TEA were added *in situ* into the reaction mixture. According to ^1H NMR spectral data, 2-acetoxy-3-cyanoindole **6a** was obtained

Scheme 2



Reagents: *i*. DCC, DMAP, CH_2Cl_2; *ii*. $CF_3SO_2N_3$, Et_3N; *iii*. $Cu(acac)_2$, $ClCH_2CH_2Cl$; *iv*. 1) $Cu(acac)_2$ (5 mol.%), $ClCH_2CH_2Cl$, 2) AcCl, Et_3N; *v*. $(Pr^i)_3SiCl$ (TIPSCl), Et_3N.

Compounds **1**—**3** and **6**	R^1	R^2	Yield of **6** (%)
a	Bn	H	50
b	Me	H	44
c	*cyclo*-Hex	H	40
d	Pr	H	63
e	$CH_2CH=CH_2$	H	40
f	4-$O_2NC_6H_4CH_2$	H	30
g	2-$ClC_6H_4CH_2$	H	42
h	3-$ClC_6H_4CH_2$	H	41
i	4-$ClC_6H_4CH_2$	H	40
j	Ph	H	52
k	Bn	Me	47
l	Bn	OMe	50

with high purity. 2,5-Diacetoxy-3-cyano-4,6,7-trimethylindoles were prepared previously[9] *via* the reaction of trimethylbenzoquinone and cyanoacetamides in the presence of sodium methoxide.

Next, we explored the scope of substrates **3** in the carbene insertion reaction (see Scheme 2). Substrates **3b**—**i** bearing different *N*-alkyl groups afforded the corresponding 2-acetoxy-1-alkylindole-3-carbonitriles **6b**—**i** regardless the *N*-alkyl group nature (linear, branched, cyclic, or

aromatic). No product of carbene insertion into the C—H aliphatic bond was observed showing chemospecific formation of 2-acetoxyindole-3-carbonitriles.

N-Allyl-substituted substrate **3e** produced the target product in low yield (40%); however, even in this case products of neither cyclopropanation nor 1,3-dipolar cycloaddition to the allyl group were observed. Substrate **3j** bearing two *N*-phenyl groups was also attempted and the target indole product was obtained in 52% yield without formation of the corresponding Buchner reaction product. Substrates **3k**,**l** bearing the electron-donating methyl and methoxy groups at the 4-position of the phenyl ring produced the corresponding carbonitriles **6k**,**l** in moderate yields. It should be noted that the unambiguous conclusion about effect of electronic nature of the substituent on the reaction yield cannot be drawn from the obtained results.

In summary, we have developed a practical protocol to synthesize 2-acetoxyindole-3-carbonitriles from 2-cyano-2-diazoacetanilides. The distinguished features of the developed chemospecific approach are the catalysis with inexpensive $Cu(acac)_2$, the one-pot reaction, and the easiness of the target product isolation. The one-pot reaction sequence involved insertion of carbene into the aromatic C—H bond, aromatization, and protection of the hydroxy group using AcCl in the presence of TEA. The methodology showed broad substrate scope and excellent chemospecificity.

Experimental

1,2-Dichloroethane was dried over $CaCl_2$, refluxed over CaH_2 under nitrogen, and freshly distilled prior to use. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker 400 spectrometer in $CDCl_3$ relative to Me_4Si (an internal standard). IR spectra were recorded in dichloromethane on a Nicolet Avatar 300 FTIR spectrometer. High resolution electrospray ionization mass spectrometry was performed with Bruker Apex IV LC/MSD TOF instrument. Melting points were measured with a Yanaco MP-500 apparatus and are uncorrected. Silica gel GF_{254} plates were used for TLC; spots were visualized with UV light or iodine vapors. Column chromatography was performed on silica gel (200—300 mesh) using gradient elution with petroleum ether (b.p 60—90 °C)—ethyl acetate.

Synthesis of 2-cyanoacetanilides (general procedure).[10] A solution of DCC (2.27 g, 11 mmol) and DMAP (61 mg, 0.5 mmol) in CH_2Cl_2 (20 mL) was added to a solution of secondary amine **1** (10 mmol) and 2-cyanoacetic acid (936 mg, 11 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The resulting solution was stirred for 1 h. During this period, a white solid (1,3-dicyclohexylurea) was precipitated, which was subsequently filtrated. The solvent was removed under reduced pressure. The resulting crude product was recrystallized from EtOH to afford pure amides **2a—l**.

***N*-Benzyl-2-cyano-*N*-phenylacetamide (2a).** Colorless crystals. Yield 1.25 g (50%), m.p. 94—97 °C (*cf.* Ref. 11: 91—94 °C). ^1H NMR, δ: 7.38—7.37 (m, 3 H); 7.32—7.22 (m, 3 H); 7.22—7.11 (m, 2 H); 7.07—6.91 (m, 2 H); 4.89 (s, 2 H); 3.21 (s, 2 H). ^{13}C NMR, δ: 161.7, 140.6, 136.1, 130.2, 129.2, 129.1, 128.5, 128.2, 127.9, 114.1, 53.7, 25.7. IR, ν/cm^{-1}: 2259 (CN), 1664 (C=O).

2-Cyano-*N*-methyl-*N*-phenylacetamide (2b). Colorless crystals. Yield 1.43 g (82%), m.p. 87—89 °C (*cf.* Ref. 11: 76—79 °C). ^1H NMR, δ: 7.51—7.47 (m, 2 H); 7.45—7.41 (m, 1 H); 7.26—7.23 (m, 2 H); 3.32 (s, 3 H); 3.25 (s, 2 H). ^{13}C NMR, δ: 161.6, 142.3, 130.4, 128.9, 127.0, 114.1, 37.8, 25.3. IR, ν/cm^{-1}: 2259 (CN), 1668 (C=O).

2-Cyano-*N*-cyclohexyl-*N*-phenylacetamide (2c). Colorless crystals. Yield 2.13 g (88%), m.p. 158—159 °C. ^1H NMR, δ: 7.50—7.46 (m, 3 H); 7.15—7.13 (m, 2 H); 4.55 (tt, 1 H, J = 12.0 Hz, J = 3.6 Hz); 3.07 (s, 2 H); 1.86 (d, 2 H, J = 12.8 Hz); 1.75 (d, 2 H, J = 13.6 Hz); 1.58 (d, 1 H, J = 13.2 Hz); 1.39 (ddddd, 2 H, J = 13.6 Hz, J = 13.2 Hz, J = 12.8 Hz, J = 3.6 Hz, J = 3.2 Hz); 1.05 (dddd, 2 H, J = 12.8 Hz, J = 12.8 Hz, J = 12.0 Hz, J = 3.6 Hz); 0.91 (dtt, 1 H, J = 13.2 Hz, J = 13.2 Hz, J = 3.6 Hz). ^{13}C NMR, δ: 161.1, 137.6, 129.9, 129.8, 129.3, 114.3, 55.4, 31.2, 26.2, 25.5, 25.1. IR, ν/cm^{-1}: 2261 (CN), 1667 (C=O). MS (ESI), *m/z*: 243.1495 $[M + H]^+$. Calculated for $C_{15}H_{19}N_2O$: 243.1492 $[M + H]^+$.

2-Cyano-*N*-phenyl-*N*-propylacetamide (2d). Colorless crystals. Yield 1.84 g (91%), m.p. 60—64 °C. ^1H NMR, δ: 7.51—7.42 (m, 3 H); 7.23—7.21 (m, 2 H); 3.69 (t, 2 H, J = 7.6); 3.19 (s, 2 H); 1.56 (sext, 2 H, J = 7.6 Hz); 0.91 (t, 3 H, J = 7.6 Hz). ^{13}C NMR, δ: 161.4, 140.9, 130.3, 129.0, 127.9, 114.2, 51.5, 25.7, 20.6, 11.0. IR, ν/cm^{-1}: 2254 (CN), 1670 (C=O). MS (ESI), *m/z*: 203.1180 $[M + H]^+$. Calculated for $C_{12}H_{15}N_2O$: 203.1179 $[M + H]^+$.

***N*-Allyl-2-cyano-*N*-phenylacetamide (2e).**[12] Colorless crystals. Yield 1.76 g (88%). ^1H NMR, δ: 7.50—7.42 (m, 3 H); 7.21 (d, 2 H, J = 7.2 Hz); 5.85 (ddt, 1 H, J = 16.8 Hz, J = 10.0 Hz, J = 6.4 Hz); 5.18 (d, 1 H, J = 10.0 Hz); 5.11 (d, 1 H, J = 16.8 Hz); 4.32 (d, 2 H, J = 6.4 Hz); 3.25 (s, 2 H). ^{13}C NMR, δ: 162.0, 140.5, 131.4, 130.3, 129.3, 127.9, 119.4, 113.9, 53.0, 25.6. IR, ν/cm^{-1}: 2260 (CN), 1743 (C=O).

***N*-Benzyl-2-cyano-*N*-(4-nitrophenyl)acetamide (2f).** Colorless crystals. Yield 2.40 g (81%), m.p. 183—185 °C. ^1H NMR, δ: 8.25 (d, 2 H, J = 8.8 Hz); 7.34—7.27 (m, 3 H, J = 2.7 Hz); 7.27—7.21 (m, 2 H); 7.20—7.13 (m, 2 H); 4.95 (s, 2 H); 3.28 (s, 2 H). ^{13}C NMR, δ: 161.1, 147.6, 146.0, 135.2, 129.4, 128.9, 128.4, 125.5, 113.5, 53.8, 26.0. IR, ν/cm^{-1}: 2261 (CN), 1677 (C=O). MS (ESI), *m/z*: 296.1033 $[M + H]^+$. Calculated for $C_{16}H_{14}N_3O_3$: 296.1030 $[M + H]^+$.

***N*-(2-Chlorobenzyl)-2-cyano-*N*-phenylacetamide (2g).** Colorless crystals. Yield 0.97 g (34%), m.p. 103—104 °C. ^1H NMR, δ: 7.38—7.31 (m, 4 H); 7.29—7.26 (m, 1 H); 7.22—7.17 (m, 2 H); 7.07—7.03 (m, 2 H); 5.08 (s, 2 H); 3.26 (s, 2 H). ^{13}C NMR, δ: 161.8, 140.1, 134.0, 133.4, 130.9, 130.1, 129.5, 129.2, 128.0, 127.0, 114.0, 50.5, 25.7. IR, ν/cm^{-1}: 2259 (CN), 1674 (C=O). MS (ESI), *m/z*: 285.0795 $[M + H]^+$. Calculated for $C_{16}H_{14}ClN_2O$: 285.0789 $[M + H]^+$.

***N*-(3-Chlorobenzyl)-2-cyano-*N*-phenylacetamide (2h).** Colorless crystals. Yield 1.49 g (54%), m.p. 98—99 °C. ^1H NMR, δ: 7.42—7.39 (m, 3 H); 7.27—7.19 (m, 3 H); 7.08—7.07 (m, 1 H); 7.04—7.01 (m, 2 H); 4.85 (s, 2 H); 3.24 (s, 2 H). ^{13}C NMR, δ: 161.9, 140.3, 138.1, 134.3, 130.3, 129.8, 129.3, 128.9, 128.1, 128.0, 127.1, 113.9, 53.1, 25.7. IR, ν/cm^{-1}: 2258 (CN), 1657 (C=O). MS (ESI), *m/z*: 285.0794 $[M + H]^+$. Calculated for $C_{16}H_{14}ClN_2O$: 285.0789 $[M + H]^+$.

***N*-(4-Chlorobenzyl)-2-cyano-*N*-phenylacetamide (2i).** Colorless crystals. Yield 2.05 g (72%), m.p. 131—132 °C. ^1H NMR, δ: 7.42—7.39 (m, 3 H); 7.25 (dd, 2 H, J = 7.2 Hz, J = 2.0 Hz); 7.08 (dd, 2 H, J = 7.2 Hz, J = 2.0 Hz); 7.04—7.01 (m, 2 H); 4.85 (s, 2 H); 3.24 (s, 2 H). ^{13}C NMR, δ: 161.8, 140.3, 134.6, 133.8, 130.4, 130.3, 129.3, 128.7, 128.1, 113.9, 53.0, 25.7. IR, ν/cm^{-1}: 2259

(CN), 1676 (C=O). MS (ESI), *m/z*: 285.0795 $[M + H]^+$. Calculated for $C_{16}H_{14}ClN_2O$: 285.0789 $[M + H]^+$.

2-Cyano-*N*,*N*-diphenylacetamide (2j). Colorless crystals. Yield 2.00 g (88%), m.p. 161—162 °C (*cf.* Ref. 12: 154—156 °C). ^{1}H NMR, δ: 7.47—7.23 (m, 10 H); 3.41 (s, 2 H). ^{13}C NMR, δ: 161.6, 141.4, 130.5, 129.1, 128.4, 126.9, 125.8, 113.9, 26.7. IR, ν/cm^{-1}: 2260 (CN), 1676 (C=O).

***N*-Benzyl-2-cyano-*N*-(4-methylphenyl)acetamide (2k).** Colorless crystals. Yield 2.53 g (96%), m.p. 104—106 °C. ^{1}H NMR, δ: 7.29—7.25 (m, 3 H); 7.19—7.15 (m, 4 H); 6.87—6.84 (m, 2 H); 4.86 (s, 2 H); 3.21 (s, 2 H); 2.35 (s, 3 H). ^{13}C NMR, δ: 161.8, 139.3, 137.9, 136.2, 130.8, 129.0, 128.5, 127.9, 127.8, 114.1, 53.7, 25.7, 21.1 IR, ν/cm^{-1}: 2259 (CN), 1670 (C=O). MS (ESI), *m/z*: 265.1339 $[M + H]^+$. Calculated for $C_{17}H_{17}N_2O$: 265.1335 $[M + H]^+$.

***N*-Benzyl-2-cyano-*N*-(4-methoxyphenyl)acetamide (2l).** Colorless crystals. Yield 2.21 g (79%), m.p. 108—110 °C. ^{1}H NMR, δ: 7.29—7.25 (m, 3 H); 7.19—7.16 (m, 2 H); 6.90—6.84 (m, 4 H); 4.84 (s, 2 H); 3.79 (s, 3 H); 3.21 (s, 2 H). ^{13}C NMR, δ: 162.1, 159.7, 136.2, 133.0, 129.2, 129.0, 128.5, 127.8, 115.2, 114.2, 55.4, 53.7, 25.6. IR, ν/cm^{-1}: 2260 (CN), 1670 (C=O). MS (ESI), *m/z*: 281.1287 $[M + H]^+$. Calculated for $C_{17}H_{17}N_2O_2$: 281.1285 $[M + H]^+$.

Synthesis of 2-cyano-2-diazoacetanilides 3a—l (general procedure).[13] Sodium azide (2.34 g, 36 mmol) was dissolved in a mixture of H_2O (10 mL) and CH_2Cl_2 (5 mL) and the resulting solution was cooled to 0 °C in an ice-water bath. To this vigorously stirred solution, triflic anhydride (1 mL, 6 mmol) was added dropwise through a syringe over 10 min. After 2 h stirring at 0 °C, the organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (5 mL). The combined organics were washed with aqueous $NaHCO_3$ (10 mL), dried with Na_2SO_4, and immediately used on the next step. To a 0 °C solution of amide **2a—l** (5 mmol) in MeCN (10 mL), freshly prepared solution of $CF_3SO_2N_3$ in CH_2Cl_2 was added under nitrogen followed by addition of TEA (758 mg, 7.5 mmol). The resulting mixture was stirred at room temperature for 18 h and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (gradient elution with ethyl acetate—petroleum ether (1 : 4 → 4 : 1, v/v) to give pure products **3a—l**.

***N*-Benzyl-2-cyano-2-diazo-*N*-phenylacetamide (3a).** Yellow crystals. Yield 1.24 g (90%), m.p. 46—47 °C. ^{1}H NMR, δ: 7.45—7.40 (m, 1 H), 7.38—7.34 (m, 2 H); 7.30—7.26 (m, 3 H); 7.21—7.19 (m, 2 H); 7.07—7.05 (m, 2 H); 4.93 (s, 2H). ^{13}C NMR, δ: 159.3, 139.5, 136.1, 129.9, 129.7, 128.9, 128.5, 128.0, 127.9, 107.0, 54.9. IR, ν/cm^{-1}: 2215 (CN), 2121 (CN_2), 1638 (C=O). MS (ESI), *m/z*: 277.1092 $[M + H]^+$. Calculated for $C_{16}H_{13}N_4O$: 277.1084 $[M + H]^+$.

2-Cyano-2-diazo-*N*-methyl-*N*-phenylacetamide (3b).[5a] Yellow oil. Yield 0.90 g (90%). ^{1}H NMR, δ: 7.48—7.44 (m, 3 H); 7.29—7.24 (m, 2 H); 3.37 (s, 3 H). ^{13}C NMR, δ: 159.2, 141.2, 130.1, 129.5, 127.7, 107.2, 39.1. IR, ν/cm^{-1}: 2180 (CN), 2135 (CN_2), 1729 (C=O).

2-Cyano-*N*-cyclohexyl-2-diazo-*N*-phenylacetamide (3c). Yellow oil. Yield 1.07 g (80%). ^{1}H NMR, δ: 7.52 (t, 1 H, *J* = 7.6 Hz); 7.44 (dd, 2 H, *J* = 8.0 Hz, *J* = 7.6 Hz); 7.17 (d, 2 H, *J* = 8.0 Hz); 4.55 (tt, 1 H, *J* = 12.0 Hz, *J* = 3.6 Hz); 1.87 (d, 2 H, *J* = 12.4 Hz); 1.77 (d, 2 H, *J* = 13.6 Hz); 1.59 (d, 1 H, *J* = 12.8 Hz); 1.39 (ddddd, 2 H, *J* = 13.6 Hz, *J* = 13.2 Hz, *J* = 12.8 Hz, *J* = 3.6 Hz, *J* = 3.2 Hz); 1.15 (dddd, 2 H, *J* = 12.8 Hz, *J* = 12.4 Hz, *J* = 12.0 Hz, *J* = 3.6 Hz); 0.93 (dtt, 1 H, *J* = 13.2 Hz, *J* = 12.8 Hz, *J* = 3.6 Hz). ^{13}C NMR, δ: 158.6, 136.3, 131.2, 130.2, 129.4, 107.0, 56.7, 31.3, 25.7, 25.1. IR, ν/cm^{-1}: 2213 (CN), 2125 (CN_2), 1724 (C=O). MS (ESI), *m/z*: 269.1399 $[M + H]^+$. Calculated for $C_{15}H_{17}N_4O$: 269.1397 $[M + H]^+$.

2-Cyano-2-diazo-*N*-phenyl-*N*-propylacetamide (3d). Yellow oil. Yield 1.02 g (90%). ^{1}H NMR, δ: 7.48—7.43 (m, 3 H); 7.26—7.21 (m, 2 H); 3.72 (t, 2 H, *J* = 7.6 Hz); 1.59 (sext, 2 H, *J* = 7.6 Hz); 0.92 (t, 3 H, *J* = 7.6 Hz). ^{13}C NMR, δ: 158.9, 139.7, 130.0, 129.6, 128.7, 107.2, 52.8, 20.8, 11.0. IR, ν/cm^{-1}: 2216 (CN), 2125 (CN_2), 1729 (C=O). MS (ESI), *m/z*: 229.1083 $[M + H]^+$. Calculated for $C_{12}H_{13}N_4O$: 229.1084 $[M + H]^+$.

***N*-Allyl-2-cyano-2-diazo-*N*-phenylacetamide (3e).** Yellow oil. Yield 0.7 g (62%). ^{1}H NMR, δ: 7.54—7.38 (m, 3 H); 7.26—7.22 (m, 2 H); 5.93—5.83 (m, 1 H); 5.19 (d, 1 H, *J* = 10.4 Hz); 5.14 (d, 1 H, *J* = 18.4 Hz); 4.35 (d, 2 H, *J* = 4.8 Hz). ^{13}C NMR, δ: 159.0, 139.7, 131.8, 129.9, 129.7, 128.7, 119.1, 107.1, 54.1. IR, ν/cm^{-1}: 2232 (CN), 2123 (CN_2), 1701 (C=O). MS (ESI), *m/z*: 227.0922 $[M + H]^+$. Calculated for $C_{12}H_{11}N_4O$: 227.0927 $[M + H]^+$.

2-Cyano-2-diazo-*N*-(4-nitrobenzyl)-*N*-phenylacetamide (3f). Yellow crystals. Yield 1.44 g (90%), m.p. 132—134 °C. ^{1}H NMR, δ: 8.16 (d, 2 H, *J* = 8.7 Hz); 7.47—7.39 (m, 5 H); 7.08 (d, 2 H, *J* = 8.7 Hz); 5.02 (s, 2 H). ^{13}C NMR, δ: 159.8, 147.6, 143.3, 139.2, 130.2, 130.1, 129.7, 128.6, 123.8, 106.7, 54.2. IR, ν/cm^{-1}: 2217 (CN), 2123 (CN_2), 1638 (C=O). MS (ESI), *m/z*: 322.0937 $[M + H]^+$. Calculated for $C_{16}H_{12}N_5O_3$: 322.0935 $[M + H]^+$.

***N*-(2-Chlorobenzyl)-2-cyano-2-diazo-*N*-phenylacetamide (3g).** Yellow oil. Yield 1.41 g (91%). ^{1}H NMR, δ: 7.43—7.28 (m, 5 H); 7.24—7.19 (m, 2 H); 7.11—7.09 (m, 2 H); 5.12 (s, 2 H). ^{13}C NMR, δ: 159.5, 139.2, 133.8, 133.5, 130.4, 129.8, 129.8, 129.6, 129.2, 128.8, 127.0, 107.0, 51.7. IR, ν/cm^{-1}: 2215 (CN), 2122 (CN_2), 1734 (C=O). MS (ESI), *m/z*: 311.0691 $[M + H]^+$. Calculated for $C_{16}H_{12}ClN_4O$: 311.0694 $[M + H]^+$.

***N*-(3-Chlorobenzyl)-2-cyano-2-diazo-*N*-phenylacetamide (3h).** Yellow oil. Yield 1.13 g (73%). ^{1}H NMR, δ: 7.47—7.37 (m, 3 H); 7.27—7.19 (m, 3 H); 7.08—7.06 (m, 3 H); 4.89 (s, 2 H). ^{13}C NMR, δ: 159.4, 139.3, 138.1, 134.4, 130.0, 129.8, 129.8, 128.9, 128.8, 128.1, 127.0, 106.9, 54.3. IR, ν/cm^{-1}: 2213 (CN), 2123 (CN_2), 1767 (C=O). MS (ESI), *m/z*: 311.0696 $[M + H]^+$. Calculated for $C_{16}H_{12}ClN_4O$: 311.0694 $[M + H]^+$.

***N*-(4-Chlorobenzyl)-2-cyano-2-diazo-*N*-phenylacetamide (3i).** Yellow crystals. Yield 1.46 g (94%), m.p. 67—68 °C. ^{1}H NMR, δ: 7.47—7.42 (m, 1 H); 7.41—7.36 (m, 2 H); 7.27—7.24 (m, 2 H); 7.16—7.13 (m, 2 H); 7.07—7.04 (m, 2 H); 4.89 (s, 2 H). ^{13}C NMR, δ: 159.4, 139.3, 134.6, 133.9, 130.4, 130.0, 129.8, 128.9, 128.7, 106.9, 54.2. IR, ν/cm^{-1}: 2213 (CN), 2121 (CN_2), 1763 (C=O). MS (ESI), *m/z*: 311.0700 $[M + H]^+$. Calculated for $C_{16}H_{12}ClN_4O$: 311.0694 $[M + H]^+$.

2-Cyano-2-diazo-*N*,*N*-diphenylacetamide (3j). Yellow crystals. Yield 1.20 g (92%), m.p. 96—99 °C. ^{1}H NMR, δ: 7.43—7.38 (m, 4 H); 7.36—7.33 (m, 2 H); 7.28—7.25 (m, 4 H). ^{13}C NMR, δ: 159.8, 141.3, 129.7, 128.1, 127.4, 106.9. IR, ν/cm^{-1}: 2218 (CN), 2129 (CN_2), 1735 (C=O). MS (ESI), *m/z*: 263.0925 $[M + H]^+$. Calculated for $C_{15}H_{11}N_4O$: 263.0927 $[M + H]^+$.

***N*-Benzyl-2-cyano-2-diazo-*N*-(4-methylphenyl)acetamide (3k).** Yellow crystals. Yield 1.00 g (69%), m.p. 95—96 °C. ^{1}H NMR, δ: 7.29—7.25 (m, 3 H); 7.21—7.19 (m, 2 H); 7.15 (d, 2 H, *J* = 8.0 Hz); 6.92 (d, 2 H, *J* = 8.0 Hz); 4.89 (s, 2 H); 2.37 (s, 3 H). ^{13}C NMR, δ: 159.4, 140.0, 136.8, 136.2, 130.4, 128.9, 128.6, 128.5, 127.8, 107.2, 54.9, 21.2. IR, ν/cm^{-1}: 2213 (CN), 2124

(CN_2), 1724 (C=O). MS (ESI), *m/z*: 291.1244 $[M + H]^+$. Calculated for $C_{17}H_{15}N_4O$: 291.1240 $[M + H]^+$.

***N*-Benzyl-2-cyano-2-diazo-*N*-(4-methylphenyl)acetamide (3l).** Yellow oil. Yield 1.47 g (96%). ^1H NMR, δ: 7.29—7.27 (m, 3 H); 7.20—7.18 (m, 2 H); 6.95—6.91 (m, 2 H); 6.85—6.82 (m, 2 H); 4.87 (s, 2 H); 3.80 (s, 3 H). ^{13}C NMR, δ: 160.6, 159.6, 136.1, 132.0, 130.2, 129.0, 128.5, 127.9, 114.9, 107.1, 55.5, 54.9. IR, ν/cm^{-1}: 2217 (CN), 2123 (CN_2), 1637 (C=O). MS (ESI), *m/z*: 307.1195 $[M + H]^+$. Calculated for $C_{17}H_{15}N_4O_2$: 307.1190 $[M + H]^+$.

1-Benzyl-2-oxoindoline-3-carbonitrile (4). A solution of 2-cyanodiazoacetamide **3** (276 mg, 1 mmol) in 1,2-dichloroethane (5 mL) was added dropwise *via* syringe over 40 min to a refluxing solution of $Cu(acac)_2$ (13 mg, 0.05 mmol) in 1,2-dichloroethane (5 mL) under nitrogen. The reaction course was monitored by TLC. After complete consumption of the starting material, the reaction mixture was concentrated under reduced pressure. Product **4** was purified by silica gel column chromatography (successive elution with the ethyl acetate—petroleum ether gradient (1 : 1 → 100 : 0, v/v) and methanol). Colorless crystals. Yield 0.196 g (79%), m.p. 97—98 °C. ^1H NMR, δ: 7.45—7.43 (m, 1 H); 7.36—7.25 (m, 6 H); 7.15—7.11 (m, 1 H); 6.81—6.79 (m, 1 H); 4.96 (d, 1 H, *J* = 7.4 Hz); 4.89 (d, 1 H, *J* = 7.4 Hz); 4.63 (s, 1 H). ^{13}C NMR, δ: 167.2, 142.9, 134.5, 130.3, 129.0, 128.1, 127.4, 124.9, 123.8, 120.1, 113.9, 110.2, 44.7, 36.6. IR, ν/cm^{-1}: 2203 (CN), 1726 (C=O). MS (ESI), *m/z*: 271.0852 $[M + H]^+$. Calculated for $C_{16}H_{12}N_2NaO$: 271.0842 $[M + H]^+$.

Synthesis of compounds 6 (general procedure). A solution of 2-cyanoacetamide **3** (1 mmol) in 1,2-dichloroethane (5 mL) was added dropwise *via* syringe over 40 min to a refluxing solution of $Cu(acac)_2$ (13 mg, 0.05 mmol) in 1,2-dichloroethane (5 mL) under nitrogen. The reaction course was monitored by TLC. After complete consumption of the starting material, the reaction mixture was cooled to 0 °C and treated with triethylamine (121 mg, 1.2 mmol) and then a solution of AcCl (94 mg, 1.2 mmol) in 1,2-dichloroethane (5 mL) was added dropwise *via* syringe over 30 min. After 1 h, the solution was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (elution with ethyl acetate—petroleum ether (1 : 9 → 1 : 1, v/v) to afford pure products **6**.

1-Benzyl-3-cyano-1*H*-indol-2-yl acetate (6a). Colorless crystals. Yield 148 mg (51%), m.p. 143—144 °C. ^1H NMR, δ: 7.69 (d, 1 H, *J* = 7.6 Hz); 7.33—7.21 (m, 6 H); 7.10 (d, 2 H, *J* = 6.8 Hz); 5.21 (s, 2 H); 2.35 (s, 3 H). ^{13}C NMR, δ: 165.9, 147.3, 134.9, 131.5, 129.0, 128.2, 126.5, 125.2, 123.7, 122.7, 119.5, 113.9, 110.7, 76.3, 46.5, 20.2. IR, ν/cm^{-1}: 2221 (CN), 1784 (C=O). MS (ESI), *m/z*: 291.1130 $[M + H]^+$. Calculated for $C_{18}H_{15}N_2O_2$: 291.1128 $[M + H]^+$.

3-Cyano-1-methyl-1*H*-indol-2-yl acetate (6b). Colorless crystals. Yield 94 mg (44%), m.p. 61—63 °C. ^1H NMR, δ: 7.66 (d, 1 H, *J* = 7.2 Hz); 7.34—7.26 (m, 3 H); 3.59 (s, 3 H); 2.47 (s, 3 H). ^{13}C NMR, δ: 166.4, 147.5, 132.0, 125.0, 123.5, 122.6, 119.4, 114.0, 110.0, 75.4, 28.9, 20.2. IR, ν/cm^{-1}: 2206 (CN), 1729 (C=O). MS (ESI), *m/z*: 237.0633 $[M + H]^+$. Calculated for $C_{12}H_{10}N_2NaO_2$: 237.0634 $[M + H]^+$.

3-Cyano-1-cyclohexyl-1*H*-indol-2-yl acetate (6c). Colorless crystals. Yield 113 mg (40%), m.p. 77—81 °C. ^1H NMR, δ: 7.69—7.65 (m, 1 H); 7.52—7.47 (dd, 1 H, *J* = 6.4 Hz, *J* = 2.6 Hz); 7.30—7.23 (dd, 2 H, *J* = 5.9 Hz, *J* = 2.5 Hz); 4.11 (tt, 1 H, *J* = 12.4 Hz, *J* = 3.8 Hz); 2.48 (s, 3 H); 2.08 (dddd, 2 H, *J* = 12.8 Hz, *J* = 12.4 Hz, *J* = 12.0 Hz, *J* = 3.6 Hz); 2.00—1.89 (m, 4 H); 1.81 (d, 1 H, *J* = 12.8 Hz); 1.42 (ddddd, 2 H, *J* = 13.2 Hz, *J* = 13.2 Hz, *J* = 12.8 Hz, *J* = 3.6 Hz, *J* = 3.2 Hz); 1.30 (dtt, 1 H, *J* = 13.2 Hz, *J* = 12.8 Hz, *J* = 3.8 Hz). ^{13}C NMR, δ: 166.4, 147.1, 130.7, 125.5, 123.0, 122.1, 119.6, 114.1, 111.8, 76.1, 56.1, 31.2, 26.1, 25.3, 20.5. IR, ν/cm^{-1}: 2217 (CN), 1797 (C=O). MS (ESI), *m/z*: 305.1264 $[M + H]^+$. Calculated for $C_{17}H_{18}N_2NaO_2$: 305.1260 $[M + H]^+$.

3-Cyano-1-propyl-1*H*-indol-2-yl acetate (6d). Colorless oil. Yield 150 mg (63%). ^1H NMR, δ: 7.68—7.66 (m, 1 H); 7.33—7.25 (m, 3 H); 3.97 (t, 2 H, *J* = 7.2 Hz); 2.46 (s, 3 H); 1.80 (sext, 2 H, *J* = 7.2 Hz); 0.92 (t, 3 H, *J* = 7.2 Hz). ^{13}C NMR, δ: 166.1, 147.2, 131.3, 125.2, 123.4, 122.4, 119.4, 114.1, 110.3, 75.5, 44.6, 22.6, 20.3, 11.2. IR, ν/cm^{-1}: 2219 (CN), 1797 (C=O). MS (ESI), *m/z*: 265.0946 $[M + H]^+$. Calculated for $C_{14}H_{14}N_2NaO_2$: 265.0947 $[M + H]^+$.

1-Allyl-3-cyano-1*H*-indol-2-yl acetate (6e). Colorless oil. Yield 96 mg (40%). ^1H NMR, δ: 7.70—7.68 (m, 1 H); 7.30—7.26 (m, 3 H); 5.87 (ddt, 1 H, *J* = 17.2 Hz, *J* = 10.2 Hz, *J* = 5.2 Hz); 5.23 (d, 1 H, *J* = 10.2 Hz); 5.08 (d, 1 H, *J* = 17.2 Hz); 4.63 (d, 2 H, *J* = 5.2 Hz); 2.44 (s, 3 H). ^{13}C NMR, δ: 166.1, 147.1, 131.4, 131.0, 125.1, 123.6, 122.6, 119.5, 118.2, 113.9, 110.5, 76.1, 45.2, 20.3. IR, ν/cm^{-1}: 2219 (CN), 1798 (C=O). MS (ESI), *m/z*: 263.0793 $[M + H]^+$. Calculated for $C_{14}H_{12}N_2NaO_2$: 263.0791 $[M + H]^+$.

3-Cyano-1-(4-nitrobenzyl)-1*H*-indol-2-yl acetate (6f). Colorless crystals. Yield 134 mg (40%), m.p. 188—192 °C. ^1H NMR, δ: 8.16 (d, 2 H, *J* = 8.4 Hz); 7.72 (d, 1 H, *J* = 7.6 Hz); 7.33—7.25 (m, 4 H); 7.13 (d, 1 H, *J* = 7.6 Hz); 5.33 (s, 2 H); 2.40 (s, 3 H). ^{13}C NMR, δ: 166.0, 147.7, 147.1, 142.0, 131.2, 127.2, 125.2, 124.3, 124.2, 123.1, 119.8, 113.5, 110.3, 71.7, 45.7, 20.2. IR, ν/cm^{-1}: 2203 (CN), 1727 (C=O). MS (ESI), *m/z*: 336.0985 $[M + H]^+$. Calculated for $C_{18}H_{14}N_3O_4$: 336.0979 $[M + H]^+$.

1-(2-Chlorobenzyl)-3-cyano-1*H*-indol-2-yl acetate (6g). Colorless oil. Yield 130 mg (40%). ^1H NMR, δ: 7.73 (d, 1 H, *J* = 7.2 Hz); 7.43 (d, 1 H, *J* = 7.9 Hz); 7.32—7.29 (m, 1 H); 7.27—7.22 (m, 2 H); 7.19 (d, 1 H, *J* = 7.7 Hz); 7.12 (t, 1 H, *J* = 7.7 Hz); 6.65 (d, 1 H, *J* = 7.7 Hz); 5.33 (s, 2 H); 2.37 (s, 3 H). ^{13}C NMR, δ: 166.0, 147.4, 132.4, 132.2, 131.5, 129.7, 129.4, 127.5, 127.5, 125.2, 124.0, 122.9, 119.7, 113.7, 110.5, 76.7, 43.9, 20.2 IR, ν/cm^{-1}: 2222 (CN), 1801 (C=O). MS (ESI), *m/z*: 325.0732 $[M + H]^+$. Calculated for $C_{18}H_{14}ClN_2O_2$: 325.0738 $[M + H]^+$.

1-(3-Chlorobenzyl)-3-cyano-1*H*-indol-2-yl acetate (6h). Colorless oil. Yield 133 mg (41%). ^1H NMR, δ: 7.77—7.68 (m, 1 H); 7.31—7.18 (m, 6 H); 6.95 (d, 1 H, *J* = 7.2 Hz); 5.18 (s, 2 H); 2.38 (s, 3 H). ^{13}C NMR, δ: 165.9, 147.2, 136.9, 135.0, 131.4, 130.4, 128.5, 126.7, 125.2, 124.6, 124.0, 122.9, 119.7, 113.7, 110.5, 77.2, 45.9, 20.2. IR, ν/cm^{-1}: 2210 (CN), 1738 (C=O). MS (ESI), *m/z*: 325.0739 $[M + H]^+$. Calculated for $C_{18}H_{14}ClN_2O_2$: 325.0738 $[M + H]^+$.

1-(4-Chlorobenzyl)-3-cyano-1*H*-indol-2-yl acetate (6i). Colorless crystals. Yield 136 mg (42%), m.p. 143—146 °C. ^1H NMR, δ: 7.70 (dd, 1 H, *J* = 6.9 Hz, *J* = 1.2 Hz), 7.31—7.23 (m, 4 H); 7.16 (dd, 1 H, *J* = 7.2 Hz, *J* = 1.2 Hz); 7.04 (d, 2 H, *J* = 8.4 Hz); 5.18 (s, 2 H); 2.38 (s, 3 H). ^{13}C NMR, δ: 166.0, 147.2, 134.1, 133.4, 131.4, 129.2, 127.8, 125.2, 123.9, 122.9, 119.7, 113.7, 110.5, 76.6, 45.8, 20.2. IR, ν/cm^{-1}: 2222 (CN), 1800 (C=O). MS (ESI), *m/z*: 325.0731 $[M + H]^+$. Calculated for $C_{18}H_{14}ClN_2O_2$: 325.0738 $[M + H]^+$.

3-Cyano-1-phenyl-1*H*-indol-2-yl acetate (6j). Yellow crystals. Yield 144 mg (52%), m.p. 125—128 °C. ^1H NMR, δ: 7.74

(d, 1 H, J = 7.6 Hz); 7.59—7.52 (m, 3 H); 7.38—7.36 (m, 2 H); 7.32 (td, 1 H, J = 7.6 Hz, J = 1.2 Hz); 7.27 (td, 1 H, J = 7.6 Hz, J = 1.2 Hz); 7.19 (d, 1 H, J = 8.0 Hz); 2.21 (s, 3 H). ^{13}C NMR, δ: 166.4, 147.1, 133.7, 132.8, 129.8, 129.3, 127.0, 124.9, 124.1, 123.1, 119.5, 113.6, 111.1, 77.4, 20.0. IR, ν/cm^{-1}: 2220 (CN), 1794 (C=O). MS (ESI), m/z: 299.0792 $[M + H]^+$. Calculated for $C_{17}H_{12}N_2NaO_2$: 299.0791 $[M + H]^+$.

1-Benzyl-3-cyano-5-methyl-1*H*-indol-2-yl acetate (6k). Colorless crystals. Yield 143 mg (47%), m.p. 107—111 °C. ^{1}H NMR, δ: 7.49 (s, 1 H); 7.33—7.27 (m, 3 H); 7.11—7.04 (m, 4 H); 5.18 (s, 2 H); 2.44 (s, 3 H); 2.35 (s, 3 H). ^{13}C NMR, δ: 166.0, 147.2, 135.0, 132.4, 129.8, 129.0, 128.1, 126.5, 125.4, 125.2, 119.3, 114.0, 110.4, 75.8, 46.5, 21.4, 20.2. IR, ν/cm^{-1}: 2216 (CN), 1798 (C=O). MS (ESI), m/z: 305.1290 $[M + H]^+$. Calculated for $C_{19}H_{17}N_2O_2$: 305.1285 $[M + H]^+$.

1-Benzyl-3-cyano-5-methoxy-1*H*-indol-2-yl acetate (6l). Colorless crystals. Yield 160 mg (50%), m.p. 114—116 °C. ^{1}H NMR, δ: 7.33—7.28 (m, 3 H); 7.14—7.08 (m, 4 H); 6.86 (dd, 1 H, J = 8.8 Hz, J = 2.4 Hz); 5.17 (s, 2 H); 3.84 (s, 3 H); 2.35 (s, 3 H). ^{13}C NMR, δ: 166.0, 156.2, 147.1, 135.0, 129.0, 128.2, 126.5, 126.1, 126.0, 114.1, 114.0, 111.7, 101.2, 76.2, 55.7, 46.6, 20.2. IR, ν/cm^{-1}: 2216 (CN), 1794 (C=O). MS (ESI), m/z: 343.1038 $[M + H]^+$. Calculated for $C_{19}H_{16}N_2NaO_3$: 343.1053 $[M + H]^+$.

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