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$GaCl_3$ Catalyzed C-H Cyanation of Indoles with *N*-Cyanosuccinimide

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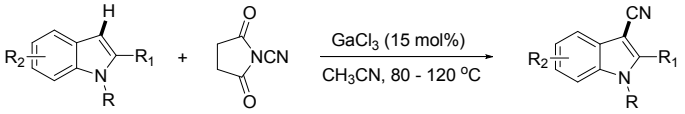


ABSTRACT: An efficient $GaCl_3$-catalyzed direct cyanation of indoles and pyrroles using bench-stable electrophilic cyanating agent *N*-cyanosuccinimide was achieved and afforded 3-cyanoindoles and 2-cyanopyrroles in good yields and excellent regioselectivities. Notably, this protocol exhibited high reactivity for unprotected indoles and was applicable to a broad range of indole and pyrrole substrates.

INTRODUCTION

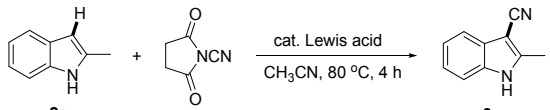
Nitrile is a fundamental functional group used in organic synthesis and ubiquitous in many organic compounds.[1] Aryl and heteroaryl nitriles account for the majority of nitrile bearing compounds with cyano group features in many therapeutic agents and natural products.[2] Indole framework is amenable to chemical transformation and forms integral parts of numerous useful chemical products.[3] Cyano indoles constitute an important class of aromatic compounds and serves as key intermediate to a variety of functional groups such as aldehydes, amines, amidines, tetrazoles, amides or other carboxy derivatives.[4] This prevalence prompted the development of many useful cyanation methods.[5] The synthesis and selective functionalization of indoles have been the focus of active research over the years. Classical methods of introducing cyano group into an aromatic ring rely on pre-functionalized arenes as precursors. For example, Sandmeyer reaction uses diazonium salts whereas Rosenmundvon Braun reaction and transition metal-catalyzed cross-couplings employ aryl halides.[6,7] Schmidt reaction uses aldehydes while dehydration reaction make use of primary carboxyamides and aldoximes,[8,9] amongst other methods.[10] More recently, oxidative cyanation through C-H bond activation has been demonstrated using various "CN" sources such as metal cyanides, CH_3NO_2, NCTS, TMSCN, TsCN, BrCN, Me_3SiN_3, and acetone cyanohydrin.[11-18] Moreover, transition metal catalyzed selective and controllable C-H cyanation of indoles has been extensively studied in recent years.[19]

To date, several efficient electrophilic cyanation methods have been developed using various cyano sources. While transition metal activation in direct C-H cyanation reaction is well established, Lewis acids mediation is not extensively investigated. In essence, Lewis acids were used in the classical Friedel-Crafts-Karrer type cyanation and relied primarily on stoichiometric amounts.[20] More recently, improved method based on catalytic amounts for cayanobromination has been reported.[16] In addition, electrophilic cyanation of five-membered heteroaromatic compounds in the presence of Lewis acids is also reported,[19d] mostly for *N*-protected indoles and pyroles (*i.e.* *N*-tosylindoles).[16b] However, direct cyanation of '*N*-H' free unprotected indoles remains relatively unexplored.[21]

RESULTS AND DISCUSSION

In continuation of our interest on the synthesis of nitrile compounds,[22] herein we report the direct $GaCl_3$-catalyzed cyanation of indoles through C-H bond cyanation using *N*–cyanosuccinimide as the cyanating agent. We began our investigation of the cyanation of unprotected 1*H*-indole (free '*N*-H') with *N*–cyanosuccinimide[23] using Lewis acids as catalysts (Table 1).

Table 1. Screening of Lewis Acid Catalysts[a]



Entry	Catalysts (mol%)	Solvent (mL)	Temperture (°C)	Yield (%)[b]
1	$BF_3.OEt_2$ (20)	CH_3CN (0.5)	80	NR[c]
2	$SnCl_2$ (20)	CH_3CN (0.5)	80	16
3	$AlCl_3$ (20)	CH_3CN (0.5)	80	NR
4	$GaCl_3$ (20)	CH_3CN (0.5)	80	80
5	$InCl_3$ (20)	CH_3CN (0.5)	80	NR
6	$NiCl_2$ (20)	CH_3CN (0.5)	80	NR
7	$Cu(OTf)_2$ (20)	CH_3CN (0.5)	80	NR
8	$ZnCl_2$ (20)	CH_3CN (0.5)	80	NR
9	$CoCl_2$ (20)	CH_3CN (0.5)	80	NR
10	$SmCl_3$ (20)	CH_3CN (0.5)	80	NR
11	$GaCl_3$ (20)	Dioxane (0.5)	80	43
12	$GaCl_3$ (20)	Toluene (0.5)	80	48
13	$GaCl_3$ (20)	DMF (0.5)	80	15
14	$GaCl_3$ (20)	DMSO (0.5)	80	12
15	$GaCl_3$ (20)	DMA (0.5)	80	27
16	$GaCl_3$ (20)	DCE (0.5)	80	25
17	$GaCl_3$ (20)	CH_3CN (0.5)	120	98
18	**$GaCl_3$ (15)**	**CH_3CN (0.5)**	**120**	**97**
19	$GaCl_3$ (10)	CH_3CN (0.5)	120	60
20	-	CH_3CN (0.5)	120	NR

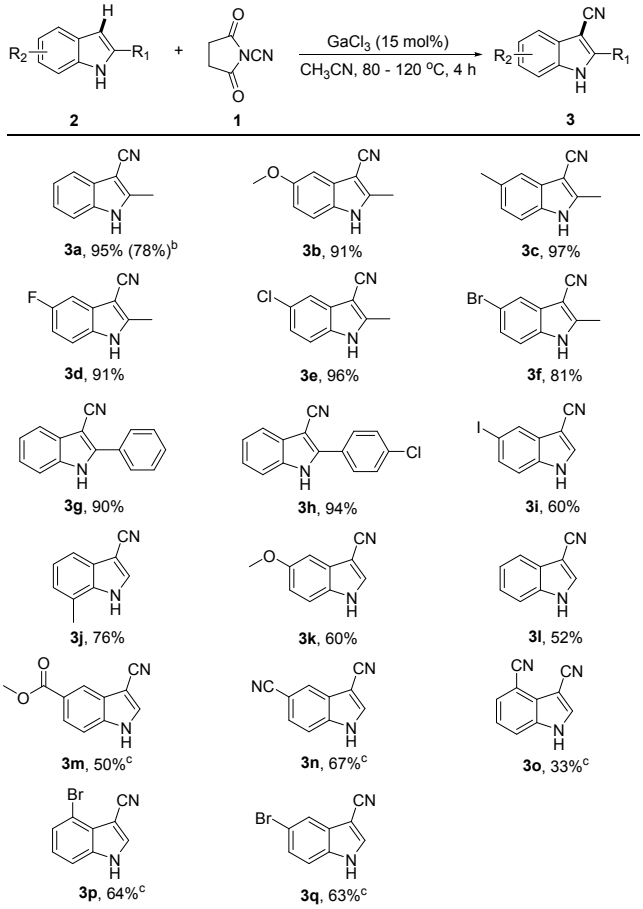
[a]Reaction conditions are as follows unless otherwise stated: **2a** (32.8 mg, 0.25 mmol, 1 equiv), *N*-cyanosuccinimide **1** (37.2 mg, 0.3 mmol, 1.2 equiv). [b]Yield determined based on GC analysis using *n*-Hexadecane as internal standard. [c]NR denotes no desired reaction.

After screening the activity of numerous Lewis acids, to our delight, we observed that a catalytic amount of $GaCl_3$ uniquely facilitated the desired cyanation of indole at the C3 position (Table 1, entry 4). Other conventionally used Lewis acids such as $BF_3.OEt_2$, $SnCl_2$, $AlCl_3$, $InCl_3$, $NiCl_2$, $Cu(OTf)_2$, $ZnCl_2$, $CoCl_2$, $SmCl_3$ (Table1, entry 1-3, entry 5-10) proved to be ineffective catalysts for this reaction. The desired cyanated products were formed only in 16% with $SnCl_2$ and only $GaCl_3$ provided 3-cyano-indole in 80%. Notably, cyanation does not take place when no catalyst is added to the reaction (Table 1, entry 20). $GaCl_3$ remarkably achieved mediation of the regioselective insertion of the cyano group into C3 position of indole substrates. Noteworthy, $GaCl_3$ catalyst showed excellent activity towards the desired product with 1*H*-indoles (free 'N-H'). In order to rationalize the activity of Lewis acids, through their corresponding cation's intrinsic properties (charge/ionic size) ratio, we performed in-situ ^{1}H NMR experiments using 1-*H*-indole with various Lewis acids (in CD_3CN). We found that the activity of the Lewis acid is in part associated with the cation's charge/size ratio of the metal. The observed downfield shift of indole N-H peak is pronounced with gallium chloride ($\delta_{N\text{-}H}$: 10.3 and 10.7 ppm) compared with other Lewis acids, suggesting strong interactions between $GaCl_3$ and 1*H*-indole possibly through coordination (free indole $\delta_{N\text{-}H}$ = 9.04 ppm, see Figures S-10 in supporting information).

Furthermore, we screened a range of solvents under various conditions and at different $GaCl_3$ molar ratios. For instance, solvents such as toluene, DMF, DMSO, *N*,*N*-dimethyl acetamide (DMA), and dioxane were examined and resulted in moderate to lower yields (Table 1, entry 11-15). Commonly used solvent DCE for this type reaction also resulted in lower yield (Table 1, entry 16). From all tested conventional solvents, we found that acetonitrile performed best for this reaction. The reaction temperature was also investigated and raising the temperature to 120 °C improved the yield significantly (98%). Lowering catalyst loading from 20 mol% to 15 mol% gave similar reaction yield (97%), while further reduction of catalyst loading to 10 mol% lowered significantly the yield to 60% (Table 1, entry 18-19). Finally, the optimized reaction conditions for this Ga-catalyzed cyanation of 2-methyl-1*H*-indole with *N*-cyanosuccinimide requires 15 mol% of $GaCl_3$ at 120 °C in CH_3CN to afford the desired cyanated product in 97% yield.

With the optimized reaction conditions in hands, we proceeded by examining $GaCl_3$-catalyzed cyanation reaction for a range of indole substrates (Scheme 1 & 2). It is noteworthy to mention that in most cases, the indole substrates were unprotected, in contrast to the commonly used method for C3 position electrophilic substitution (Scheme 1). Furthermore, reactions with C2-substituted 1*H*-indoles afforded the corresponding cyanated products in excellent yields. Methyl, phenyl and chlorophenyl substituents at the C2 position afforded the desired products in excellent yields (**3a**, **3g** and **3h**; 95%, 90% and 94%). In addition, indoles bearing electron-donating groups on the fused phenyl ring were transformed smoothly to the corresponding cyanated products with high yields (**3b**, **3c**; 91%, 97%). Indoles bearing halogen electron-withdrawing groups were also transformed easily to the corresponding cyanated products with high yields (**3d-f**, 81%-96%). More satisfyingly, we found that in the absence of substituent at the C2 position, the cyanation was also achieved regio-selectively to afford 3-cyanoindole products (**3i-3q**, 33%-76%, Scheme 1). Specifically, functional groups such as nitrile and ester substituted indole were transformed to the corresponding cyanated products with moderate yields (**3m**, **3n**; 50%, 67%). The reaction with 1*H*-indole-4-carbonitrile substrate provided cyanation product in lower yield (**3o**; 33%). 1*H*-indole bearing bromo substitution at either C4 or C5 position showed little effect, and afforded the corresponding cyanated products in good yields (**3p**, **3q**; 64%, 63%).

Scheme 1. $GaCl_3$-Catalyzed Cyanation of N-H Free Indoles[a]

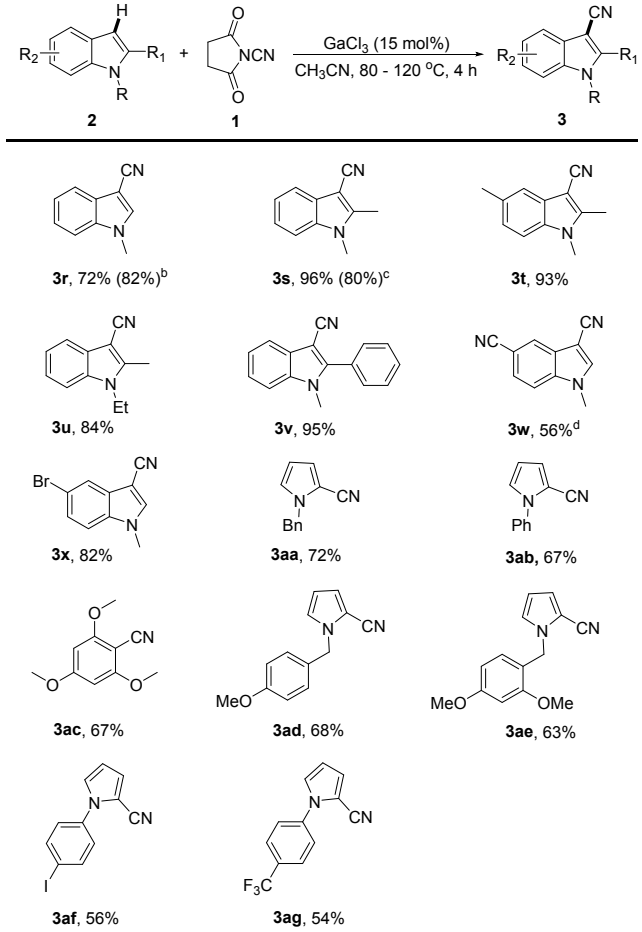


[a]Reaction conditions are as follows unless otherwise noted: **2** (0.25 mmol, 1 equiv), *N*-cyanosuccinimide **1** (37.2 mg, 0.3 mmol, 1.2 equiv), $GaCl_3$ (6.6 mg, 0.0375 mmol, 15 mol%) in CH_3CN (0.5 mL) at 120 °C for 4 h. [b]Reaction carried out at 80 °C for 4 h. [c]30 mol% $GaCl_3$ was used, reaction carried out at 80 °C for 12 h.

Following the results on the direct electrophilic cyanation for '*N*-H' free unprotected indoles, we then extended substrate scope to *N*-substituted indoles, pyrroles and arenes (Scheme 2). Gratifyingly, 1-methyl-1*H*-indole afforded the corresponding cyanated product in good yield (**3r**, 82%). 1,2-dimethyl-1*H*-indole and 1,2,5-trimethyl-1*H*-indole having methyl substituted C2 position also afforded **3s** and **3t** in excellent yields, 96% and 93%, respectively. Similarly, substituted indole with electron rich phenyl substituent at the C2 position gave the desired

cyanated product in good yield (**3v**, 95%). 1-ethlyl-2-methyl-1*H*-indole also provided the corresponding product in good yield (**3u**, 84%). Substituted indoles with electron-withdrawing nitrile substituent or bromide substituent at the C5 position were well tolerated (**3w**, 56% and **3x**, 82%). Furthermore we examined other substrates such as pyrroles and 1,3,5-trimethoxybenzene and regio-selective cyanation was observed in moderate reactivity (**3aa**, **3ab** and **3ac**; 72%, 67% and 67%). Pyrrole substrates were further investigated and afforded consistent regioselectivity and yield for **3ad**, **3ae**, **3af** and **3ag** in 68%, 63%, 56% and 54% yield, respectively. Gram-scale reactions of **2a** and **2s** were performed giving the corresponding prouducts in good to excellent yields, respectively (for details, see the Experimental section).

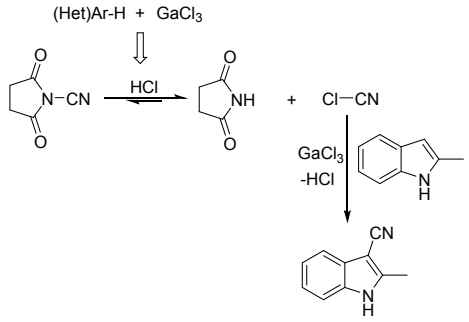
Scheme 2. $GaCl_3$-Catalyzed Cyanation of *N*-Substituted Indoles and other Substrates[a]



[a]Reaction conditions are as follows unless otherwise noted: **2** (0.25 mmol, 1 equiv), *N*-cyanosuccinimide **1** (37.2 mg, 0.3 mmol, 1.2 equiv), $GaCl_3$ (6.6 mg, 0.0375mmol, 15 mol%) in CH_3CN (0.5 mL) at 120 °C for 4 h. [b]Reaction was carried out at 120 °C for 8 h. [c]Reaction was carried out at 80 °C for 8 h. [d]30 mol% $GaCl_3$ was used, reaction was carried out at 80 °C for 12 h.

In order to probe possible actions mode involved and to account for plausible reaction pathway for this reaction, we performed in-situ ^{13}C NMR experiments under similar reaction conditions. We used 2-methyl-1*H*-indole as model substrate and examined its interaction with $GaCl_3$ and *N*-cyanosuccinimide in CD_3CN. As expected, the ^{13}C NMR spectra of the indole substrate with $GaCl_3$ showed significant change, consistent with indole C3 and $GaCl_3$ interaction/coordination releasing HCl (^{13}C NMR spectrum, see Figure S-3). The addition of $GaCl_3$ to *N*-cyanosuccinimide showed almost no change (^{13}C NMR spectrum, see Figure S-6). While after the addition of indole to this mixutre, clear changes of the carbonyl and CN signals of *N*-cyanosuccinimide were observed (^{13}C NMR spectrum, see Figure S-9). Hence, we propose that the presence of "free" HCl is important and it can react with the *N*-cyanosuccinimide reagent to produce the transient cyanogen chloride as the active CN source for indole substrates (Figure 1).[24]

Figure 1. Proposed Mechanism for $GaCl_3$ Catalyzed Cyanation.



CONCLUSIONS

In conclusion, we have developed $GaCl_3$-catalyzed procedure for efficient cyanation of indoles and pyrroles using a convenient and less toxic electrophilic cyanating agent *N*-cyanosuccinimide. We demonstrated that $GaCl_3$ is a superior catalyst compared with other Lewis acids. The procedure is broad in scope with respect to indole and pyrrole substrates. The method avoids the use of transition metal catalysts and is effective towards unexplored direct cyanation of 1*H*-indoles. It also provides a practical means for accessing 3-cyanoindoles and 2-cyanopyrroles. This methodology of $GaCl_3$-catalyzed aromatic C-H activation is currently pursued and applied to other heteroaromatic substrates.

EXPERIMENTAL SECTION

General Methods. ^1H NMR spectra were recorded with a BRUKER NMR (400 MHz). Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ and (δ = 2.5 ppm) in DMSO-d_6 as an internal standard. ^{13}C NMR spectra were obtained by the same NMR spectrometer and were calibrated with $CDCl_3$ (δ = 77.23 ppm) and DMSO-d_6 (δ = 39.52 ppm). Coupling constants are given in hertz (Hz). Reactions were monitored using thin-layer chromatography (TLC) on commercial silica gel plates (HSGF254). Visualization of the developed plates was performed under UV light (254 nm). 300-400 mesh silica gel (Qingdao, China) was used for flash column chromatography. High-resolution mass spectrometry (HRMS) was performed on an Agilent Q-TOF 6530 mass spectrometer at Suzhou Research Institute of LICP.

N-Cyanosuccinimide (**1**)[25], 1,2,5-Trimethyl-1*H*-indole (**2t**)[26], 1-(4-Methoxybenzyl)-1*H*-pyrrole (**2ad**)[27], 1-(2,4-Dimethoxybenzyl)-1*H*-pyrrole (**2ae**)[27] were prepared according to reported procedures. Other commercially obtained reagents were used without further purification.

General Experimental Procedure. In a glovebox, the catalyst $GaCl_3$ (6.6 mg, 15 mol%), substrates **2** (0.25 mmol, 1 equiv), *N*-cyanosuccinimide **1** (37.2 mg, 0.3 mmol, 1.2 equiv) and a stirring bar were added into a 10 mL oven-dried Schlenk tube under nitrogen atmosphere. Anhydrous CH_3CN (0.5 mL) were added. The Schlenk tube was sealed and brought out of the glovebox. The reaction was allowed to stir at 120 °C (Multi-well block heating system) for 4 h. The reaction solution was concentrated under vacuo and purified by column chromatography to afford the cyanated product **3**.

Experimental Procedure for cyanated product 3a (10 mmol scale). In a glovebox, the catalyst $GaCl_3$ (264 mg, 1.5 mmol), **2a** (1.312 g, 10 mmol, 1 equiv), *N*-cyanosuccinimide **1** (1.488g, 12 mmol, 1.2 equiv) and a stirring bar were added into a 75 mL sealing tube under nitrogen atmosphere. Anhydrous CH_3CN (10 mL) were added. The sealing tube was sealed and brought out of the glovebox. The reaction was allowed to stir at 120 °C (oil bath) for 4 h. The reaction solution was concentrated under vacuo, the crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford product **3a** (1.418 g, 91%).

Experimental Procedure for cyanated product 3s (10 mmol scale). In a glovebox, the catalyst $GaCl_3$ (264 mg, 1.5 mmol), **2s** (1.452 g, 10 mmol, 1 equiv), *N*-cyanosuccinimide **1** (1.488g, 12 mmol, 1.2 equiv) and a stirring bar were added into a 75 mL sealing tube under nitrogen atmosphere. Anhydrous CH_3CN (10 mL) were added. The sealing tube was sealed and brought out of the glovebox. The reaction was allowed to stir at 120 °C (oil bath) for 4 h. The reaction solution was concentrated under vacuo, the crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford product **3s** (1.358 g, 80%).

*2-Methyl-1H-indole-3-carbonitrile (**3a**)*.[13] Following the general procedure, a mixture of 2-methyl-1*H*-indole (32.8 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3a** (37.1 mg, 95%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.08 (br, 1H), 7.51 (dd, *J* = 6.9, 1.3 Hz, 1H), 7.43 (dd, *J* = 6.9, 1.3 Hz, 1H), 7.25-7.11 (m, 2H), 2.54 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 146.0, 134.9, 127.3, 122.7, 121.4, 117.8, 116.6, 112.1, 82.9, 12.6.

*5-Methoxy-2-methyl-1H-indole-3-carbonitrile (**3b**)*.[13] Following the general procedure, a mixture of 5-methoxy-2-methyl-1*H*-indole (42.5 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3b** (42.5 mg, 91%) as a light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.95 (br, 1H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.02 (d, *J* = 2.2 Hz, 1H), 6.85 (dd, *J* = 8.8, 2.2 Hz, 1H), 3.83 (s, 3H), 2.55 (s, 3H).; ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 155.1, 145.8, 129.6, 128.0, 116.7, 112.8, 112.4, 99.7, 82.7, 55.4, 12.6.

*2,5-Dimethyl-1H-indole-3-carbonitrile (**3c**)*.[28] Following the general procedure, a mixture of 2,5-dimethyl-1*H*-indole (37.5 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3c** (41.2 mg, 97%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.96 (br, 1H), 7.34 (d, *J* = 10.4 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 1H), 2.56-2.52 (m, 3H), 2.41 (d, *J* = 8.9 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 145.6, 133.1, 130.3, 127.5, 124.1, 117.4, 116.6, 111.7, 82.4, 21.0, 12.5.

5-Fluoro-2-methyl-1H-indole-3-carbonitrile (***3d***).[28] Following the general procedure, a mixture of 5-fluoro-2-methyl-1*H*-indole (39.3 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3d** (39.8 mg, 91%) as a light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.19 (br, 1H), 7.50-7.41 (m, 1H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.06 (t, *J* = 8.6 Hz, 1H), 2.55 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 158.2 (d, *J* = 234 Hz), 147.6, 131.4, 127.8, 116.0, 113.3 (d, *J* = 9.8 Hz), 110.7 (d, *J* = 26 Hz), 103.1 (d, *J* = 25 Hz), 83.3, 12.6.

*5-Chloro-2-methyl-1H-indole-3-carbonitrile (**3e**)*.[28] Following the general procedure, a mixture of 5-chloro-2-methyl-1*H*-indole (42.3 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3e** (45.7 mg, 96%) as a light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.27 (br, 1H), 7.51 (s, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 1H), 2.55 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 147.5, 133.3, 128.3, 126.1, 122.7, 117.0, 115.7, 113.5, 82.8, 12.6.

*5-Bromo-2-methyl-1H-indole-3-carbonitrile (**3f**)*. Following the general procedure, a mixture of 5-bromo-2-methyl-1*H*-indole (53.6 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3f** (47 mg, 81%) as a light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.26 (br, 1H), 7.63 (s, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.31 (dd, *J* = 8.6, 1.6 Hz, 1H), 2.53 (s, 3H).; ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 147.4, 133.6, 128.9, 125.3, 119.9, 115.7, 114.0, 82.7, 12.6. HRMS-ESI (m/z) [M+H$^+$] calcd for $C_{10}H_8BrN_2^+$ 234.9865, found 234.9875.

*2-Phenyl-1H-indole-3-carbonitrile (**3g**)*.[29] Following the general procedure, a mixture of 2-phenyl-1*H*-indole (49 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120

°C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3g** (49 mg, 90%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.60 (br, 1H), 7.99 (d, J = 7.2 Hz, 2H), 7.66-7.60 (m, 3H), 7.58-7.51 (m, 2H), 7.33-7.24 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 144.7, 135.6, 129.9, 129.4, 129.3, 128.3, 127.0, 123.9, 122.0, 118.4, 117.0, 112.7, 81.4.

*2-(4-Chlorophenyl)-1H-indole-3-carbonitrile (**3h**)*.[29] Following the general procedure, a mixture of 2-(4-chlorophenyl)-1*H*-indole (58 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3h** (59.3 mg, 94%) as a light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.62 (br, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.63 (dd, J = 11.1, 8.2 Hz, 3H), 7.54 (d, J = 8.4 Hz, 1H), 7.32-7.20 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 143.2, 135.6, 134.6, 129.3, 128.5, 128.3, 128.2, 124.0, 122.1, 118.4, 116.8, 112.7, 81.8.

*5-Iodo-1H-indole-3-carbonitrile (**3i**)*. Following the general procedure, a mixture of 5-iodo-1*H*-indole (62 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3i** (40.2 mg, 60%) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.35 (br, 1H), 8.25 (s, 1H), 7.95 (s, 1H), 7.55 (d, J = 7.2 Hz, 1H), 7.40 (d, J = 7.2 Hz, 1H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 135.4, 134.4, 131.6, 129.1, 126.7, 115.7, 115.3, 85.9, 83.6. HRMS-ESI (m/z) [M+H$^+$] calcd for $C_9H_6IN_2^+$ 268.9570, found 268.9568.

*7-Methyl-1H-indole-3-carbonitrile (**3j**)*. Following the general procedure, a mixture of 7-methyl-1*H*-indole (33.5 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3j** (29.7 mg, 76%) as a light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.23 (br, 1H), 8.28 (d, J = 2.6 Hz, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.16 (d, J = 7.7 Hz, 1H), 7.10 (d, J = 7.0 Hz, 1H), 2.54 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 134.8, 134.1, 126.6, 123.8, 122.4, 121.8, 116.5, 115.9, 84.6, 16.6. HRMS-ESI (m/z) [M+H$^+$] calcd for $C_{10}H_9N_2^+$ 157.0760, found 157.0761.

*5-Methoxy-1H-indole-3-carbonitrile (**3k**)*.[19i] Following the general procedure, a mixture of 5-methoxy-1*H*-indole (36.8 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (3:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3k** (25.8 mg, 60%) as a light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.06 (br, 1H), 8.16 (s, 1H), 7.44 (d, J = 8.9 Hz, 1H), 7.08 (s, 1H), 6.90 (d, J = 8.9 Hz, 1H), 3.81 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 155.3, 134.3, 130.0, 127.6, 116.6, 113.8, 99.7, 84.0, 55.4.

*1H-indole-3-carbonitrile (**3l**)*.[19f] Following the general procedure, a mixture of 1*H*-indole (29.6 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3l** (18.4 mg, 52%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.20 (br, 1H), 8.24 (s, 1H), 7.64 (d, J = 7.5 Hz, 1H), 7.59-7.54 (m, 1H), 7.31-7.20 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 135.2, 134.5, 126.7, 123.3, 121.7, 118.4, 116.4, 112.9, 84.2.

*Methyl 3-cyano-1H-indole-5-carboxylate (**3m**)*. Following the general procedure, a mixture of methyl 1*H*-indole-5-carboxylate (43.8 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (13.2 mg, 0.075 mmol) and 0.50 mL CH_3CN was heated to 80 °C for 12 h. The crude product was purified by flash column chromatography (3:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3m** (25.2 mg, 50%) as a light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.56 (br, 1H), 8.40 (s, 1H), 8.23 (s, 1H), 7.87 (d, J = 8.6 Hz, 1H), 7.64 (d, J = 8.6 Hz, 1H), 3.87 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 166.5, 137.8, 136.6, 126.4, 124.2, 123.2, 120.4, 115.7, 113.2, 85.7, 52.1. HRMS-ESI (m/z) [M+H$^+$] calcd for $C_{11}H_9N_2O_2^+$ 201.0659, found 201.0669.

*1H-indole-3,5-dicarbonitrile (**3n**)*.[19f] Following the general procedure, a mixture of 1*H*-indole-5-carbonitrile (35.6 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (13.2 mg, 0.075 mmol) and 0.50 mL CH_3CN was heated to 80 °C for 12 h. The crude product was purified by flash column chromatography (1:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3n** (28 mg, 67%) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.72 (br, 1H), 8.49 (s, 1H), 8.21 (s, 1H), 7.73 (d, J = 7.9 Hz, 1H), 7.65 (d, J = 7.9 Hz, 1H). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 137.5, 137.1, 126.4, 126.3, 124.2, 119.7, 115.3, 114.4, 104.2, 85.5. HRMS-ESI (m/z) [M+Na$^+$] calcd for $C_{10}H_5N_3Na^+$ 190.0376, found 190.0368.

*1H-indole-3,4-dicarbonitrile (**3o**)*. Following the general procedure, a mixture of 1*H*-indole-4-carbonitrile (35.6 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (13.2 mg, 0.075 mmol) and 0.50 mL CH_3CN was heated to 80 °C for 12 h. The crude product was purified by flash column chromatography (1:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3o** (13.6 mg, 33%) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.81 (br, 1H), 8.55 (s, 1H), 7.91 (d, J = 8.3 Hz, 1H), 7.75 (d, J = 7.4 Hz, 1H), 7.43 (t, J = 7.4 Hz, 1H). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 138.1, 135.4, 128.1, 125.2, 123.5, 118.6, 116.5, 114.7, 101.1, 83.9. HRMS-ESI (m/z) [M+Na$^+$] calcd for $C_{10}H_5N_3Na^+$ 190.0376, found 190.0370.

*4-Bromo-1H-indole-3-carbonitrile (**3p**)*. Following the general procedure, a mixture of 4-bromo-1*H*-indole (49 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (13.2 mg, 0.075 mmol) and 0.50 mL CH_3CN was heated to 80 °C for 12 h. The crude product was purified by flash column chromatography (3:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3p** (35.2 mg, 64%) as a light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.53 (br, 1H), 8.40 (d, J = 3.0 Hz, 1H), 7.56 (d, J = 8.2 Hz, 1H), 7.40 (d,

J = 7.6 Hz, 1H), 7.19 (t, *J* = 7.9 Hz, 1H); $^{13}C\{^1H\}$NMR (100 MHz, DMSO-d_6) δ 137.0, 136.2, 125.3, 124.9, 124.6, 116.2, 112.7, 112.6, 85.0. HRMS-ESI (m/z) [M+H$^+$] calcd for $C_9H_6BrN_2^+$ 220.9709, found 220.9707.

*7-Bromo-1H-indole-3-carbonitrile (**3q**)*. Following the general procedure, a mixture of 7-bromo-1*H*-indole (49 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (13.2 mg, 0.075 mmol) and 0.50 mL CH_3CN was heated to 80 °C for 12 h. The crude product was purified by flash column chromatography (3:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3q** (35 mg, 63%) as a light yellow solid. ^1H NMR (400 MHz, DMSO-d_6) δ 12.52 (br, 1H), 8.35 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H); $^{13}C\{^1H\}$NMR (100 MHz, DMSO-d_6) δ 135.8, 133.8, 128.3, 126.1, 123.2, 118.1, 115.8, 105.4, 85.9. HRMS-ESI (m/z) [M+H$^+$] calcd for $C_9H_6BrN_2^+$ 220.9709, found 220.9708.

*1-Methyl-1H-indole-3-carbonitrile (**3r**)*.[13] Following the general procedure, a mixture of 1-methyl-1*H*-indole (33 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 8 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3r** (32 mg, 82%) as a light yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 1H), 7.54 (s, 1H), 7.35 (dd, *J* = 21.1, 14.1 Hz, 3H), 3.84 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 136.2, 135.7, 127.9, 124.0, 122.3, 120.0, 116.1, 110.5, 85.6, 33.8.

*1,2-Dimethyl-1H-indole-3-carbonitrile (**3s**)*.[13] Following the general procedure, a mixture of 1,2-dimethyl-1*H*-indole (36.3 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3s** (41 mg, 96%) as a light yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.0 Hz, 1H), 7.24 (dd, *J* = 13.8, 5.6 Hz, 3H), 3.64 (s, 3H), 2.51 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 145.9, 136.4, 127.1, 123.1, 122.0, 119.0, 116.8, 109.9, 84.7, 30.3, 12.1.

*1,2,5-Trimethyl-1H-indole-3-carbonitrile (**3t**)*. Following the general procedure, a mixture of 1,2,5-trimethyl-1*H*-indole (40 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3t** (43 mg, 93%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.14 (d, *J* = 8.3 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 3.61 (s, 3H), 2.48 (s, 3H), 2.44 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 145.6, 134.8, 131.6, 127.3, 124.6, 118.7, 116.9, 109.6, 84.1, 30.3, 21.5, 12.0; HRMS-ESI (m/z) [M+H$^+$] calcd for $C_{12}H_{13}N_2^+$ 185.1073, found 185.1075.

*1-Ethyl-2-methyl-1H-indole-3-carbonitrile (**3u**)*.[11b] Following the general procedure, a mixture of 1-ethyl-2-methyl-1*H*-indole (40 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (20:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3u** (38.7 mg, 84%) as a white liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.3 Hz, 1H), 7.37-7.31 (m, 1H), 7.30-7.20 (m, 2H), 4.15 (q, *J* = 7.3 Hz, 2H), 2.58 (s, 3H), 1.38 (t, *J* = 7.3 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 145.1, 135.4, 127.4, 123.1, 122.0, 119.3, 116.9, 110.0, 85.1, 38.9, 15.1, 11.9.

*1-Methyl-2-phenyl-1H-indole-3-carbonitrile (**3v**)*.[13] Following the general procedure, a mixture of 1-methyl-2-phenyl-1*H*-indole (52.9 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (20:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3v** (55 mg, 95%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.58-7.46 (m, 5H), 7.43-7.26 (m, 3H), 3.72 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 148.2, 136.9, 123.0, 129.9, 129.1, 128.8, 127.6, 124.0, 122.5, 119.5, 116.8, 110.7, 85.5, 31.8.

*1-Methyl-1H-indole-3,5-dicarbonitrile (**3w**)*.[19h] Following the general procedure, a mixture of 1-methyl-1*H*-indole-5-carbonitrile (39.1 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (13.2 mg, 0.075 mmol) and 0.50 mL CH_3CN was heated to 80 °C for 12 h. The crude product was purified by flash column chromatography (3:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3w** (25.2 mg, 56%) as a yellow solid. ^1H NMR (400 MHz, CDCl3) δ 8.05 (s, 1H), 7.74 (s, 1H), 7.55 (dd, *J* = 27.1, 8.6 Hz, 2H), 3.95 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 138.0, 137.6, 127.5, 126.9, 125.2, 119.5, 114.5, 111.8, 105.8, 87.0, 34.2. HRMS-ESI (m/z) [M+Na$^+$] calcd for $C_{11}H_7N_3Na^+$ 204.0532, found 204.0524.

*5-Bromo-1-methyl-1H-indole-3-carbonitrile (**3x**)*.[19a] Following the general procedure, a mixture of 5-bromo-1-methyl-1*H*-indole (53.6 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3x** (48 mg, 82%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.51 (s, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 7.23 (d, *J* = 8.7 Hz, 1H), 3.83 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 136.5, 134.8, 129.3, 127.1, 122.4, 115.8, 115.3, 112.0, 85.2, 34.0.

*1-Benzyl-1H-pyrrole-2-carbonitrile (**3aa**)*.[13] Following the general procedure, a mixture of 1-benzyl-1*H*-pyrrole (40 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (20:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3aa** (32.7 mg, 72%) as a light yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 3H), 7.18 (d, *J* = 7.5 Hz, 2H), 6.82 (m, 2H), 6.21-6.17 (m, 1H), 5.19 (s, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 136.1, 129.2, 128.5, 127.6, 126.8, 120.5, 114.0, 110.1, 104.3, 52.6.

*1-Phenyl-1H-pyrrole-2-carbonitrile (**3ab**)*.[13] Following the general procedure, a mixture of 1-phenyl-1*H*-pyrrole (36.5 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$

(6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (20:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3ab** (28.1 mg, 67%) as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.39 (m, 5H), 7.08 (dd, *J* = 2.9, 1.6 Hz, 1H), 6.99 (dd, *J* = 3.9, 1.6 Hz, 1H), 6.35 (dd, *J* = 3.9, 2.9 Hz, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 138.4, 129.9, 128.5, 127.1, 124.3, 122.4, 114.0, 110.8, 104.2.

*2,4,6-Trimethoxybenzonitrile (**3ac**)*.[13] Following the general procedure, a mixture of 1,3,5-trimethoxybenene (42.5 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3ac** (32.4 mg, 67%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (s, 2H), 3.87 (d, *J* = 7.9 Hz, 9H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 165.5, 163.9, 114.8, 90.5, 84.1, 56.3, 55.9.

*1-(4-Methoxybenzyl)-1H-pyrrole-2-carbonitrile (**3ad**)*. Following the general procedure, a mixture of 1-(4-methoxybenzyl)-1*H*-pyrrole (46.8 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3ad** (36.2 mg, 68%) as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.7 Hz, 2H), 6.90-6.85 (m, 2H), 6.82 (dd, *J* = 2.6, 1.7 Hz, 1H), 6.80 (dd, *J* = 4.0, 1.7 Hz, 1H), 6.17 (dd, *J* = 4.0, 2.6 Hz, 1H), 5.11 (s, 2H), 3.78 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 159.6, 129.1, 128.0, 126.5, 120.3, 114.4, 114.0, 109.8, 103.9, 55.3, 52.0. HRMS-ESI (m/z) [M+Na$^+$] calcd for $C_{13}H_{12}N_2NaO^+$ 235.0842, found 235.0843.

*1-(2,4-Dimethoxybenzyl)-1H-pyrrole-2-carbonitrile (**3ae**)*. Following the general procedure, a mixture of 1-(2,4-dimethoxybenzyl)-1*H*-pyrrole (54.3 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3ae** (38.4 mg, 63%) as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.9 Hz, 1H), 6.86 (m, 1H), 6.76 (m, 1H), 6.47-6.42 (m, 2H), 6.11 (m, 1H), 5.12 (s, 2H), 3.82 (s, 3H), 3.79 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 161.4, 158.5, 130.7, 127.0, 119.9, 117.2, 114.4, 109.3, 104.4, 104.0, 98.8, 55.6, 55.5, 47.4. HRMS-ESI (m/z) [M+Na$^+$] calcd for $C_{14}H_{14}N_2NaO_2^+$ 265.0947, found 265.0949.

1-(4-Iodophenyl)-1H-pyrrole-2-carbonitrile **(3af)**. Following the general procedure, a mixture of 1-(4-iodophenyl)-1*H*-pyrrole (67.3 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3af** (41.2 mg, 56%) as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.09-6.96 (m, 2H), 6.40-6.33 (m, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 139.0, 138.0, 126.9, 126.0, 122.8, 113.8, 111.3, 104.2, 93.6. HRMS-ESI (m/z) [M+Na$^+$] calcd for $C_{11}H_7IN_2Na^+$ 316.9546, found 316.9548.

1-[4-(Trifluoromethyl)Phenyl]-1H-pyrrole-2-carbonitrile **(3ag)**. Following the general procedure, a mixture of 1-[4-(trifluoromethyl)phenyl]-1*H*-pyrrole (52.8 mg, 0.25 mmol), *N*-cyanosuccinimide (37 mg, 0.30 mmol), $GaCl_3$ (6.6 mg, 0.0375 mmol) and 0.50 mL CH_3CN was heated to 120 °C for 4 h. The crude product was purified by flash column chromatography (5:1 petroleum ether:ethyl acetate, visualized with UV) to afford cyanated product **3ag** (30.5 mg, 54%) as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.4 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.13 (s, 1H), 7.06 (s, 1H), 6.41 (s, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 141.1, 130.7, 130.4, 127.3 (d, *J* = 3.4 Hz), 127.0, 125.1, 124.5, 123.4, 113.7, 111.7, 104.2. HRMS-ESI (m/z) [M+Na$^+$] calcd for $C_{12}H_7F_3N_2Na^+$ 259.0454, found 259.0456.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via ACS Publications website at http://pubs.acs.org. Included in-situ NMR studies and recorded ^{1}H, ^{13}C NMR spectra for all compounds.

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Notes

The authors declare no competing financial interest.

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