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Acyl Cyanides as Bifunctional Reagent: Application in Copper-Catalyzed Cyanoamidation and Cyanoesterification Reaction

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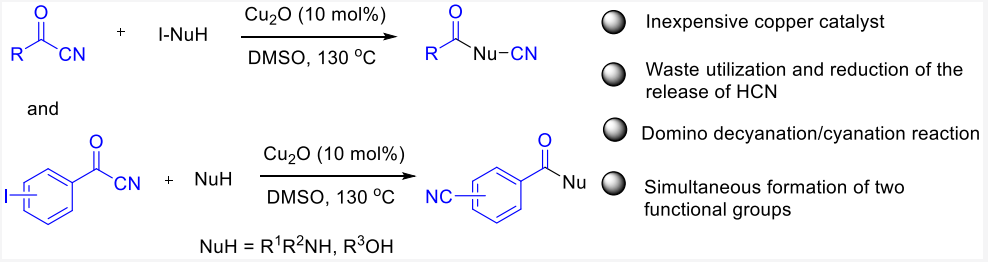

ABSTRACT: Cu-catalyzed domino decyanation and cyanation reaction of acyl cyanides with amines or alcohols have been developed. The cyano sources were generated in situ via C−CN cleavage yielding the corresponding cyano substituted amides or esters in moderate to excellent yields. This approach features a cheap copper catalyst, domino decyanation and cyanation reaction, readily available starting materials, broad substrate scope, operational simplicity, and the potential for further transformation of the cyano group.

Aryl nitriles are among the most prevalent structural motifs in natural products, pharmaceuticals, dyes, and electronic materials.[1] They have emerged as ubiquitous building blocks for various organic molecules such as amidines, amines, amides, aldehydes, tetrazoles, acids, and heterocyclic compounds.[2] Therefore, it has attracted extensive interest to develop new and efficient approaches for their preparation. Traditional protocols toward aryl nitriles include the Rosenmund−von Braun reaction and Sandmeyer reaction, which require a stoichiometric amount of highly toxic CuCN.[3] In recent years, transition-metal-catalyzed cyanation reaction of aryl halides has made remarkable progress due to several advantages, including wide substrate compatibility, mild reaction conditions, high efficiency, and excellent selectivity.[4] Compared to noble metal catalysts, copper catalysts are gaining more attention owing to their low cost, wide availability, exceptional reactivity, and sustainability.[5] The cyanating agents include a variety of metal cyanide sources, organic cyano-group sources, and combined cyano-group sources.[6] Although significant progress has been made toward the synthesis of aromatic nitriles, in view of the importance of cyano-containing molecules and the limitation of the reported approaches, further exploration of alternative and powerful transformations to yield cyano-containing molecules remains a challenge.

Acyl cyanides, as readily available and versatile building blocks, have been recognized as valuable substrates in organic synthesis. They have attracted much attention owing to their remarkable properties in acylcyanation of alkynes,[7] decarbonylative cyanation,[8] arylation,[9] cycloaddition,[10] Strecker-type addition reaction,[11] and Passerini condensation.[12] Although a variety of transformations based on C−CN cleavage or C−CN formation have been developed, the domino decyanation and cyanation reaction of acyl cyanides has not been disclosed.[13] This dual strategy meets today's criteria of sustainable synthesis and green chemistry, due to the simultaneous formation of two important functional groups with a one-pot operation from readily available materials. Herein, we described the first copper-catalyzed highly efficient synthesis of cyano substituted amides or esters via domino C−CN bond cleavage and formation from the coupling of acyl cyanides and amines or alcohols (Scheme 1).[14]

Initially, 2-iodoaniline **2a** was selected as the representative model substrate, and benzoyl cyanide **1a** was employed as the acylating agent and organic cyano-group source. As illustrated in Table 1, three common transition-metal catalysts were screened, and the cheap cupric oxide can furnish the *N*-(2-cyanophenyl)benzamide **3a** in good yield (Table 1, entries 1−3). Then a wide range of copper catalysts were examined. All of

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Scheme 1. Synthesis of Cyano Substituted Amides or Esters from Acyl Cyanides and Amines or Alcohols

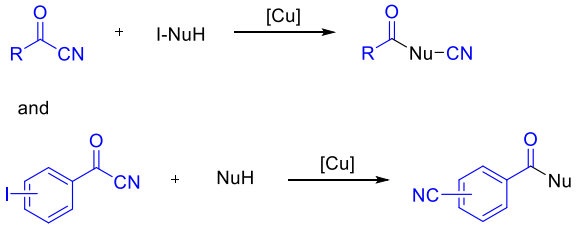
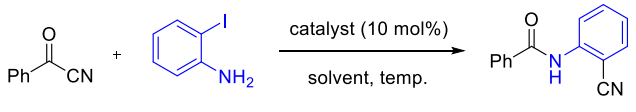


Table 1. Optimization of the Reaction Conditions[a]



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

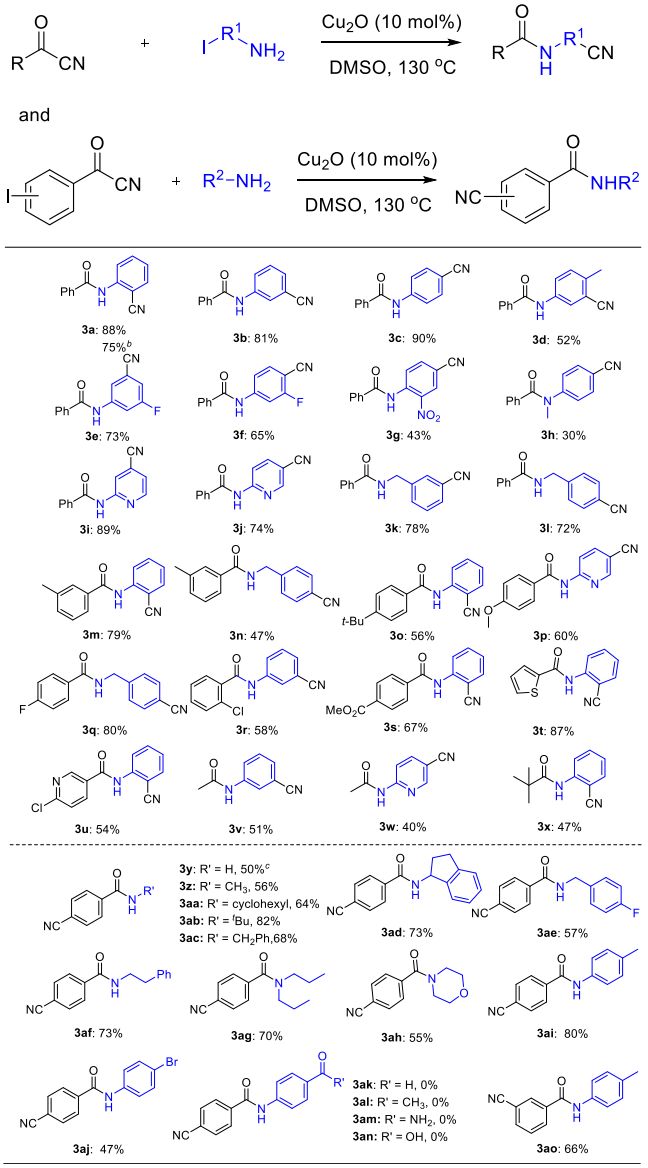
entry	catalyst	solvent	temp	yield[b] (%)
1	$Pd(PPh_3)_4$	DMF	130	62
2	$FeCl_3$	DMF	130	n.p.
3	CuO	DMF	130	65
4	Cu_2O	DMF	130	81
5	$Cu(OTf)_2$	DMF	130	47
6	$CuSO_4·5H_2O$	DMF	130	70
7	$Cu(OAc)_2$	DMF	130	37
8	$CuCl_2$	DMF	130	27
9	$CuBr_2$	DMF	130	38
10	CuI	DMF	130	42
11	$Cu(NO_3)_2·3H_2O$	DMF	130	41
12	–	DMF	130	n.p.
13	**Cu_2O**	**DMSO**	**130**	**91(88)**
14	Cu_2O	DMSO	110	51
15	Cu_2O	DMSO	70	10

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol) with catalyst (10 mol %) in solvent 1.0 mL for 10 h. [b]Determined by GC with mesitylene as internal standard. n.p. = no product.

the catalysts had some effect on the reaction. Among the catalyst tested, Cu_2O was the most effective and delivered the product in 81% yield (Table 1, entries 4−11). The reaction could not occur without a catalyst (Table 1, entry 12). Subsequently, a variety of solvents were investigated at 130 or 70 °C. The results revealed that the identity of the solvent was important; DMSO proved to be the optimal solvent, generating the desired product in 88% yield (Table S1 in the Supporting Information, entries 1−7). Lowering the temperature to 110 °C resulted in a lower yield, and a negligible yield was observed at 70 °C (Table 1, entries 14−15). Finally, because ligands can have a dramatic effect on the copper-catalyzed cyanation reaction, some common ligands were tried at 110 °C and found to be ineffective (Table S1 in the Supporting Information, entries 8−10). The optimized conditions for the synthesis of **3a** employed Cu_2O as the catalyst and DMSO as the solvent at 130 °C for 10 h (Table 1, entry 13).

To explore the scope of the copper-catalyzed domino decyanation and cyanation reaction, various substituted acyl cyanides and amines were coupled, and the results were summarized in Scheme 2. Benzoyl cyanide **1a** reacted efficiently with different iodo-substituted aromatic, heteroaromatic, and benzyl amines (**3a**−**3l**). Aniline with the iodo group at different positions had negligible effect on the product

Scheme 2. Substrate Scope of Acyl Cyanides and Amines[a]



[a]Reaction conditions: acyl cyanide (0.2 mmol), amine (0.2 mmol), Cu_2O (10 mol %) and DMSO (1.0 mL) at 130 °C for 10 h. [b]2 mmol scale. [c]3 equiv of 29% ammonia solution was used.

yields. The secondary aryl alkyl amine afforded **3h** in low yield. Substituted 2-aminopyridines reacted with **1a** to give **3i** and **3j** in 89% and 74% yields, respectively. Aroyl cyanides bearing either an electron-donating or an electron-poor group on the benzene ring were compatible and furnished the products in moderate to good yields (**3m**−**3s**). Heteroaroyl cyanides showed good reactivity to render the corresponding products in satisfactory yields (**3t** and **3u**). To our delight, the acetyl cyanide and sterically hindered alkynoyl cyanide reacted efficiently with aryl amines (**3v**−**3x**). Iodo-substituted benzoyl cyanides were also evaluated, and a set of amines were compatible under the standard conditions (**3y**−**3ao**). The challenging primary amide was formed in 50% yield, when an ammonia solution was employed as an amine source (**3y**). To our surprise, *tert*-butyl amine gave the product in high yield (**3ab**). The secondary amines led to the products in moderate yields (**3ag** and **3ah**). Besides, the desired products were

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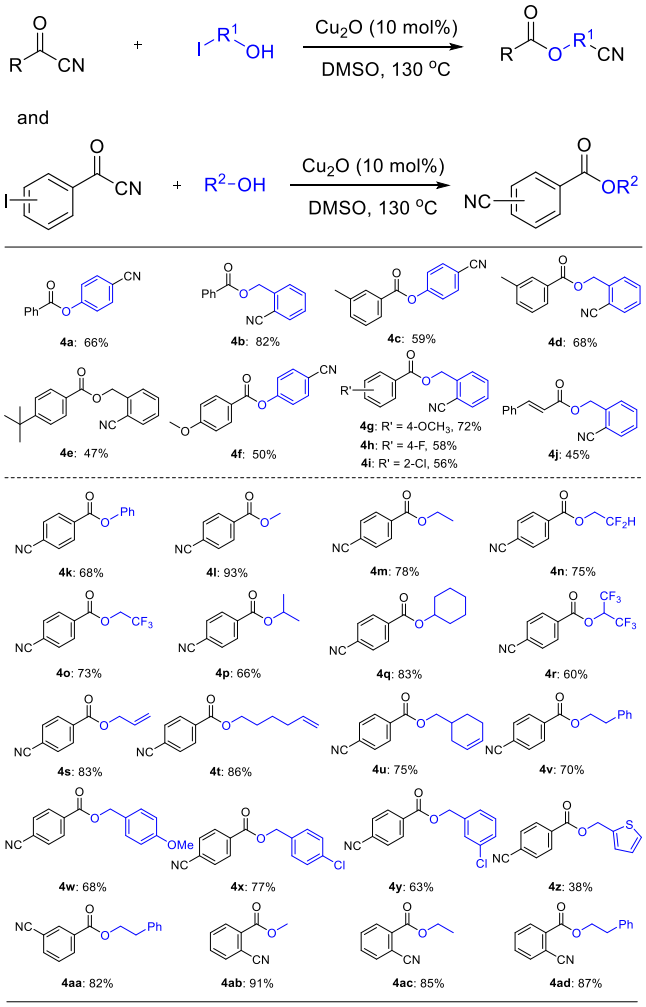
obtained in good yields from *p*-toluidine (**3ai** and **3ao**). Unluckily, aniline with functionalities like CHO, COMe, $CONH_2$, and COOH did not afford the corresponding products in this transformation (**3ak**–**3an**). To demonstrate the practicality, a large-scale synthesis was examined, and **3a** was formed in 75% yield.

To further illustrate the operational viability of our methodology, the coupling reaction of acyl cyanides with alcohols was explored. As shown in Scheme 3, both electron-rich and electron-deficient groups on the aroyl cyanide were compatible for this transformation (**4a**–**4i**). Remarkably, α,β-unsaturated acyl cyanide rendered the desired product in 45% yield (**4j**). Iodo-substituted benzyl alcohols were beneficial for the reaction compared to phenols (**4a**–**4g**). A variety of primary and secondary aliphatic alcohols reacted successfully with 4-iodo benzoyl cyanide (**4k**–**4z**). Significantly, TFE and HFIP can be used as nucleophilic reagents to afford the fluoro-containing products (**4o** and **4r**). The unsaturated long chain alcohol and cyclo alcohol delivered the products in satisfactory yields (**4t** and **4u**). Both 2-phenylethanol and phenylmethanol were tolerable in this cyanoesterification in spite of the electronic variations on the benzene rings (**4v**–**4x**). Ester **4z** could be obtained from the heteroaryl-substituted alcohol, albeit in relatively low yield. Moreover, 3-iodo benzoyl cyanide and sterically hindered 2-iodo benzoyl cyanide also led to the desired products in high yields (**4aa**–**4ad**). These results implied that the copper-catalyzed domino decyanation and cyanation reaction can be effective for the cyano-substituted amide and ester library.

Scheme 3. Substrate Scope of Acyl Cyanides and Alcohols[a]



[a]Reaction conditions: acyl cyanide (0.2 mmol), alcohol (0.2 mmol), Cu_2O (10 mol %), and DMSO (1.0 mL) at 130 °C for 10 h.

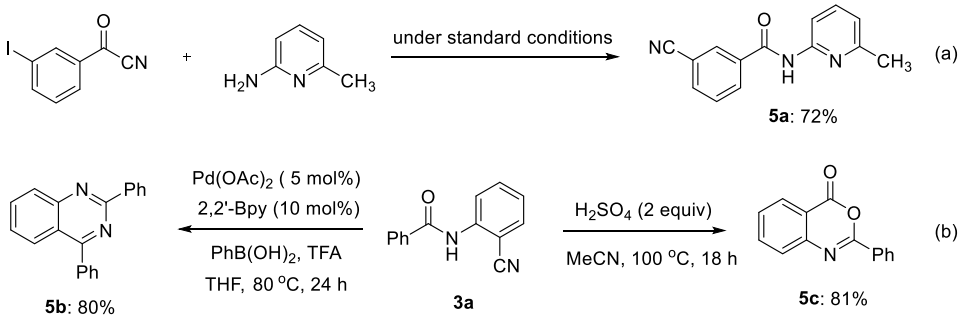
3-Cyano substituted pyridylamides are known to be an important mGluR5 antagonist template.[15] The target compound **5a** can be readily accessible via this copper-catalyzed cyanoamidation reaction (Scheme 4a). The synthetic utility of **3a** was demonstrated by preparation of the heterocycles, such as quinazoline (**5b**)[16] and benzoxazinone (**5c**),[17] in good yields (Scheme 4b).

Some control experiments were carried out to elucidate the reaction mechanism (Scheme 5). The reaction of benzoyl cyanide **1a** with 2-iodoaniline **2a** in the absence of a copper catalyst could generate iodoarene **6a** in excellent yield (Scheme 5a). Radical-trapping experiments were performed through the addition of TEMPO, DPE, and BHT to the reaction system in the standard conditions, and the formation of **3a** was not suppressed (Scheme 5b). These results inferred that this transformation did not occur via a radical mechanism.

A tentative mechanism was proposed and shown in Scheme 6 on the basis of previous results and our experimental observations. Initially, benzoyl cyanide **1a** underwent nucleophilic addition–elimination with 2-iodoaniline **2a** to lead to intermediate **6a**, in which the HCN was released through the cleavage of the C–CN bond.[13] It is noteworthy that the hydrocyanic acid can be confirmed by the cyanide-detecting test with a picric acid strip (Scheme S2 in the Supporting Information).[6d,18] Then the desired product **3a** was generated via a copper-catalyzed cyanation reaction from iodoarene and HCN.[19]

In summary, we have developed the first copper-catalyzed domino decyanation and cyanation reaction which allows the

Scheme 4. Synthetic Applications



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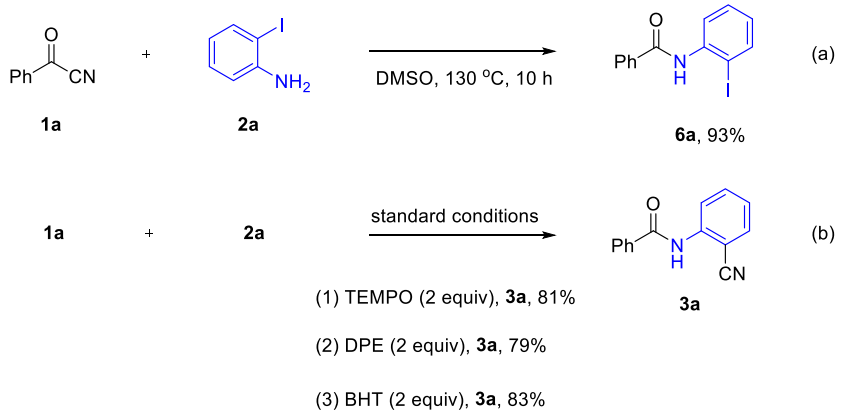
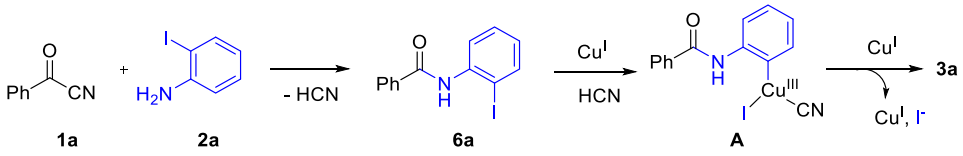
Scheme 5. Control Experiments



Scheme 6. Possible Reaction Mechanism



transfer of acyl cyanides to a series of cyano substituted amides as well as esters. This transformation utilized the release of hazardous HCN gas to generate valuable products. This dual strategy the paved way for a new synthetic protocol for the synthesis of bifunctional products in a one-pot operation. Further investigation to extend the synthetic application and detailed mechanism are currently ongoing in our laboratory.

EXPERIMENTAL SECTION

General Information. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were obtained on a 400 and 100 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and chloroform was used as the solvent with TMS as the internal standard unless otherwise noted. Melting point (mp) values were determined using a melting point instrument (uncorrected). Infrared (IR) spectra were collected from an infrared spectrometer (Bruker Tensor 27). Mass spectra were recorded on a GC-MS spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter, 0.25 mm; length, 30 m). High resolution mass spectra (HRMS) (TOF) were measured using electrospray ionization (ESI) mass spectrometry. Silica gel (300−400 mesh) was used for flash column chromatography, eluting (unless otherwise stated) with an ethyl acetate/petroleum ether (PE) (60−90 °C) mixture.

The amines, alcohols, and acyl cyanides **1a**, **1j** were commercially available from Sigma-Aldrich China. Substituted acyl cyanides **1b−1i**, **1k−1o** have been prepared using the literature procedure,[20] and data for known compounds have been compared with the reported data.[8−10,21] The typical experimental procedures for the preparation of starting materials are given below.

General Procedure for the Synthesis of Cyano Substituted Amides (3a−3aj). A mixture of acyl cyanide (0.2 mmol), amine (0.2 mmol) and Cu_2O (2.9 mg, 10 mol %) in DMSO (1.0 mL) was placed in a test tube (10 mL) equipped with a magnetic stirring bar. The tube was placed in a preheated oil bath at 130 °C, and the mixture was stirred vigorously for 10 h. After the reaction was finished, water (5 mL) was added. The solution was extracted with ethyl acetate (3 × 5 mL), and the combined extract was dried with anhydrous $MgSO_4$. Solvent was removed, and the residue was separated by column chromatography to give the pure sample.

Large Scale Synthesis. An oven-dried 25 mL screw cap test tube was charged with a magnetic stir bar, **1a** (262 mg, 2 mmol), **2a** (438 mg, 2 mmol), Cu_2O (28.8 mg, 10 mol %), and DMSO (6.0 mL). Then, the tube was placed in a preheated oil bath at 130 °C for 10 h. After the solution cooled to room temperature, water (10 mL) was added. The solution was extracted with ethyl acetate (3 × 10 mL), and the combined extract was dried with anhydrous $MgSO_4$. Solvent was removed, and the residue was separated by column chromatography (ethyl acetate/petroleum ether = 1:4) to give **3a** (333 mg, 75%).

*N-(2-Cyanophenyl)benzamide (**3a**).*[17] White solid (39 mg, 88%); mp 158−159 °C; R_f = 0.46 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (d, J = 8.5 Hz, 1H), 8.43 (s, 1H), 7.95−7.92 (m, 2H), 7.67−7.58 (m, 3H), 7.56−7.50 (m, 2H), 7.22 (td, J = 7.7, 1.0 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.4, 140.5, 134.3, 133.6, 132.6, 132.1, 129.0, 127.1, 124.2, 121.1, 116.4, 102.1. MS (EI) m/z: 222, 105, 77, 51, 39.

*N-(3-Cyanophenyl)benzamide (**3b**).*[22] White solid (36 mg, 81%); mp 138−139 °C; R_f = 0.32 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (s, 1H), 8.08−8.03 (m, 1H), 7.87 (dt, J = 8.4, 1.8 Hz, 3H), 7.60−7.55 (m, 1H), 7.51−7.47 (m, 2H), 7.45 (t, J = 5.6 Hz, 1H), 7.41 (dt, J = 7.7, 1.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 166.0, 138.8, 134.0, 132.3, 129.9, 128.8, 127.8, 127.1, 124.3, 123.3, 118.4, 112.9. MS (EI) m/z: 222, 105, 77, 51, 39.

*N-(4-Cyanophenyl)benzamide (**3c**).*[23] White solid (40 mg, 90%); mp 154−156 °C; R_f = 0.20 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 1H), 7.90−7.84 (m, 2H), 7.80 (d, J = 8.7 Hz, 2H), 7.64 (d, J = 8.7 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.9, 142.0, 134.0, 133.2, 132.4, 128.9, 127.1, 119.9, 118., 107.26. MS (EI) m/z: 222, 105, 77, 51, 39.

*N-(3-Cyano-4-methylphenyl)benzamide (**3d**).*[24] Yellow solid (24 mg, 52%); mp 174−176 °C; R_f = 0. 51 (petroleum ether/ethyl acetate = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (s, 1H), 7.96 (d, J = 2.1 Hz, 1H), 7.86 (d, J = 7.3 Hz, 2H), 7.75 (dd, J = 8.4, 2.1 Hz, 1H), 7.57 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.29 (d, J = 8.4 Hz, 1H), 2.52 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.8, 137.8, 136.2, 134.1, 132.2, 130.8, 128.8, 127.0, 124.5, 123.6, 117.7, 113.1, 19.8. MS (EI) m/z: 236, 105, 77, 51.

*N-(3-Cyano-5-fluorophenyl)benzamide (**3e**).*[25] Yellow solid (35 mg, 73%); mp 145−146 °C; R_f = 0.44 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (s, 1H), 7.93−7.82 (m, 3H), 7.70 (s, 1H), 7.61−7.54 (m, 1H), 7.47 (dd, J = 10.5, 4.7 Hz, 2H), 7.10 (ddd, J = 7.6, 2.4, 1.3 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz,

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$CDCl_3$): δ = 166.1, 162.4 (d, J = 247 Hz), 140.6 (d, J = 11 Hz), 133.6, 132.6, 128.9, 127.1, 119.0 (d, J = 4 Hz), 117.4 (d, J = 4 Hz), 114.5 (d, J = 25 Hz), 113.7 (d, J = 11 Hz), 112.2 (d, J = 26 Hz). MS (EI) *m/z*: 240, 207, 105, 77, 51, 39.

N-(4-Cyano-3-fluorophenyl)benzamide (**3f**). Yellow solid (31 mg, 65%); mp 132−134 °C; R_f = 0.23 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3289, 3101, 2921, 2234, 1667, 1595, 1521, 1446, 1177, 1117, 874, 831, 719; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (s, 1H), 7.95−7.83 (m, 3H), 7.61−7.52 (m, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.41 (dd, J = 8.6, 1.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 166.1, 163.8 (d, J = 256 Hz), 144.2 (d, J = 11 Hz), 133.7, 133.6 (d, J = 11 Hz), 132.7, 128.9, 127.1, 115.5 (d, J = 3 Hz), 114.2, 107.5 (d, J = 25 Hz), 95.9 (d, J = 16 Hz). MS (EI) *m/z*: 240, 207, 105, 77, 51, 39. HRMS (ESI): calcd for $C_{14}H_{10}FN_2O$ $[M + H]^+$ 241.0772; found 241.0775.

N-(4-Cyano-2-nitrophenyl)benzamide (**3g**).[26] Yellow solid (23 mg, 43%); mp = 145−147 °C; R_f = 0.57 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.55 (s, 1H), 9.25 (d, J = 8.9 Hz, 1H), 8.62 (d, J = 2.0 Hz, 1H), 7.99 (dd, J = 5.3, 3.3 Hz, 2H), 7.94 (dd, J = 8.9, 1.9 Hz, 1H), 7.70−7.63 (m, 1H), 7.61−7.55 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.7, 138.9, 138.5, 135.5, 133.3, 133.0, 130.3, 129.2, 127.4, 122.6, 116.5, 106.7. MS (EI) *m/z*: 267, 219, 105, 77, 51, 39.

N-(4-Cyanophenyl)-N-methylbenzamide (**3h**).[27] Yellow solid (14 mg, 30%); mp 90−91 °C; R_f = 0.38 (petroleum ether/ethyl acetate = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, J = 8.7 Hz, 2H), 7.30 (ddd, J = 10.0, 7.1, 1.9 Hz, 3H), 7.25−7.20 (m, 2H), 7.13 (d, J = 8.7 Hz, 2H), 3.52 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 170.5, 148.8, 135.0, 133.0, 130.4, 128.6, 128.1, 126.9, 118.1, 109.6, 38.0. MS (EI) *m/z*: 236, 129, 105, 77, 51, 39.

N-(4-Cyanopyridin-2-yl)benzamide (**3i**).[28] White solid (40 mg, 89%); mp 141−142 °C; R_f = 0.25 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.95 (s, 1H), 8.72−8.69 (m, 1H), 8.38 (d, J = 5.0 Hz, 1H), 7.91 (dd, J = 5.2, 3.3 Hz, 2H), 7.63−7.57 (m, 1H), 7.50 (dd, J = 10.4, 4.7 Hz, 2H), 7.28−7.25 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.8, 152.2, 149.0, 133.3, 132.7, 128.9, 127.2, 122.4, 121.1, 116.4, 116.1. MS (EI) *m/z*: 223, 194, 105, 77, 51, 39.

N-(5-Cyanopyridin-2-yl)benzamide (**3j**).[29] Yellow solid (33 mg, 74%); mp 187−189 °C; R_f = 0.43 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.88 (s, 1H), 8.55 (d, J = 8.3 Hz, 2H), 8.00 (dd, J = 8.9, 2.0 Hz, 1H), 7.97−7.87 (m, 2H), 7.62 (dd, J = 10.6, 4.2 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.7, 153.9, 151.6, 141.6, 133.2, 132.9, 129.0, 127.3, 116.7, 113.7, 105.1. MS (EI) *m/z*: 223, 194, 105, 77, 51, 39.

N-(3-Cyanobenzyl)benzamide (**3k**). White solid (37 mg, 78%); mp 108−110 °C; R_f = 0.34 (petroleum ether/ethyl acetate = 2:1); IR (KBr, cm^{-1}) 3305, 3059, 2936, 2226, 1635, 1578, 1533, 1488, 1424, 1312, 1161, 1076, 800, 725, 693; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86−7.76 (m, 2H), 7.62−7.48 (m, 4H), 7.46−7.34 (m, 3H), 7.00 (s, 1H), 4.63 (d, J = 6.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 167.6, 140.0, 133.6, 132.1, 131.8, 131.0, 130.9, 129.4, 128.6, 126.9, 118.6, 112.5, 43.0. MS (EI) *m/z*: 236, 131, 105, 77, 51, 39. HRMS (ESI): calcd for $C_{15}H_{13}N_2O$ $[M + H]^+$ 237.1022; found 237.1007.

N-(4-Cyanobenzyl)benzamide (**3l**).[30] White solid (34 mg, 72%); mp 153−155 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85−7.76 (m, 2H), 7.62 (d, J = 8.2 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.48−7.42 (m, 4H), 6.67 (s, 1H), 4.70 (d, J = 6.1 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 167.5, 143.8, 133.7, 132.5, 131.9, 128.7, 128.2, 126.9, 118.6, 111.3, 43.5. MS (EI) *m/z*: 236, 131, 105, 77, 51, 39.

N-(2-Cyanophenyl)-3-methylbenzamide (**3m**).[17] White solid (37 mg, 79%); mp 144−145 °C; R_f = 0.44 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (d, J = 8.5 Hz, 1H), 8.39 (s, 1H), 7.75 (s, 1H), 7.73−7.68 (m, 1H), 7.67−7.60 (m, 2H), 7.43−7.38 (m, 2H), 7.21 (td, J = 7.7, 1.0 Hz, 1H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.6, 140.6, 139.0, 134.3, 133.6, 133.4, 132.1, 128.9, 127.9, 124.1, 124.0, 121.1, 116.4, 102.0, 21.4. MS (EI) *m/z*: 236, 207, 192, 119, 91, 65, 39.

N-(4-Cyanobenzyl)-3-methylbenzamide (**3n**). Yellow solid (24 mg, 47%); mp 162−164 °C; R_f = 0.34 (petroleum ether/ethyl acetate = 2:1); IR (KBr, cm^{-1}) 3259, 3069, 2921, 2849, 2228, 1636, 1608, 1545, 1491, 1327, 1264, 1075, 795, 696, 542; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67−7.60 (m, 3H), 7.59−7.55 (m, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.34 (dd, J = 3.8, 2.0 Hz, 2H), 6.58 (s, 1H), 4.70 (d, J = 6.1 Hz, 2H), 2.40 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 167.7, 143.8, 138.6, 133.7, 132.6, 132.5, 128.5, 128.2, 127.7, 123.8, 118.6, 111.3, 43.4, 21.3. MS (EI) *m/z*: 250, 235, 119, 91, 65, 39. HRMS (ESI): calcd for $C_{16}H_{15}N_2O$ $[M + H]^+$ 251.1179; found 251.1185.

4-(tert-Butyl)-N-(2-cyanophenyl)benzamide (**3o**). White solid (31 mg, 56%); mp 129−130 °C; R_f = 0.46 (petroleum ether/ethyl acetate = 6:1); IR (KBr, cm^{-1}) 3223, 3033, 2966, 2223, 1659, 1611, 1581, 1535, 1509, 1477, 1448, 1316, 1126, 1022, 853, 765, 710, 569; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (d, J = 8.4 Hz, 1H), 8.42 (s, 1H), 7.92−7.84 (m, 2H), 7.68−7.59 (m, 2H), 7.57−7.50 (m, 2H), 7.20 (td, J = 7.7, 1.0 Hz, 1H), 1.36 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.3, 156.3, 140.7, 134.2, 132.0, 130.7, 127.0, 125.9, 124.0, 121.0, 116.4, 102.0, 35.0, 31.0. MS (EI) *m/z*: 278, 263, 245, 207, 192, 161, 146, 118, 91, 51, 41. HRMS (ESI): calcd for $C_{18}H_{19}N_2O$ $[M + H]^+$ 279.1492; found 279.1490.

N-(5-Cyanopyridin-2-yl)-4-methoxybenzamide (**3p**).[29] Yellow solid (30 mg, 60%); mp 144−146 °C; R_f = 0.26 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (s, 1H), 8.56−8.50 (m, 2H), 7.97 (dd, J = 8.8, 2.2 Hz, 1H), 7.92−7.88 (m, 2H), 7.02−6.97 (m, 2H), 3.89 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.1, 163.3, 154.2, 151.5, 141.5, 129.3, 125.3, 116.7, 114.2, 113.6, 104.8, 55.5. MS (EI) *m/z*: 253, 238, 135, 107, 92, 77, 64, 38.

N-(4-Cyanobenzyl)-4-fluorobenzamide (**3q**). White solid (40 mg, 80%); mp 148−149 °C; R_f = 0.51 (petroleum ether/ethyl acetate = 1:1); IR (KBr, cm^{-1}) 3269, 3070, 2921, 2849, 2235, 1633, 1578, 1506, 1454, 1319, 1301, 1154, 1094, 978, 886, 794, 597; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84−7.77 (m, 2H), 7.60−7.54 (m, 2H), 7.40 (d, J = 8.5 Hz, 2H), 7.12−7.05 (m, 2H), 6.93 (s, 1H), 4.64 (d, J = 6.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 166.5, 164.8 (d, J = 251 Hz), 143.8, 132.4, 129.8 (d, J = 3 Hz), 129.3 (d, J = 9 Hz), 128.1, 118.6, 115.7 (d, J = 22 Hz), 111.1, 43.4. MS (EI) *m/z*: 254, 224, 208, 123, 95, 75, 51, 39. HRMS (ESI): calcd for $C_{15}H_{12}FN_2O$ $[M + H]^+$ 255.0928; found 255.0927.

N-(3-Cyanophenyl)- 2-chlorobenzamide (**3r**). Brown solid (29 mg, 58%); mp 66−67 °C; R_f = 0.53 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3243, 3060, 2861, 2228, 1655, 1583, 1550, 1327, 1258, 1178, 1099, 1050, 894, 883, 682, 653, 460; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.03 (s, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.69−7.62 (m, 1H), 7.47−7.39 (m, 4H), 7.38−7.31 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.0, 138.4, 134.4, 132.0, 130.6, 130.4, 130.1, 129.9, 128.1, 127.3, 124.2, 123.2, 118.3, 113.0. MS (EI) *m/z*: 256, 221, 192, 164, 139, 111, 90, 75, 50. HRMS (ESI): calcd for $C_{14}H_{10}ClN_2O$ $[M + H]^+$ 257.0476; found 257.0472.

Methyl 4-((2-Cyanophenyl)carbamoyl)benzoate (**3s**). White solid (38 mg, 67%); mp 163−164 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 6:1); IR (KBr, cm^{-1}) 3265, 3065, 2956, 2230, 1716, 1655, 1603, 1580, 1533, 1494, 1285, 1106, 1019, 961, 777, 730, 502; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (d, J = 8.4 Hz, 1H), 8.47 (s, 1H), 8.17−8.13 (m, 2H), 8.00−7.95 (m, 2H), 7.63 (ddd, J = 8.9, 6.7, 1.2 Hz, 2H), 7.23 (td, J = 7.7, 0.9 Hz, 1H), 3.95 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.9, 164.6, 140.1, 137.3, 134.2, 133.6, 132.2, 130.1, 127.2, 124.6, 121.5, 116.2, 102.7, 52.4. MS (EI) *m/z*: 280, 249, 224, 207, 192, 163, 135, 103, 76, 50, 39. HRMS (ESI): calcd for $C_{16}H_{13}N_2O_3$ $[M + H]^+$ 281.0921; found 281.0924.

N-(2-Cyanophenyl)thiophene-2-carboxamide (**3t**).[31] Yellow solid (40 mg, 87%); mp 142−143 °C; R_f = 0.28 (petroleum ether/ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (d, J = 8.4 Hz, 1H), 8.30 (s, 1H), 7.70 (dd, J = 3.8, 1.0 Hz, 1H), 7.62 (ddd, J = 7.9, 6.4, 2.7 Hz, 3H), 7.23−7.17 (m, 1H), 7.15 (dd, J = 4.9, 3.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 159.7, 140.2, 138.1, 134.2, 132.1, 132.1, 129.0, 128.0, 124.2, 121.0, 116.3, 102.0. MS (EI) *m/z*: 228, 203, 111, 83, 63, 39.

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*6-Chloro-N-(2-cyanophenyl)nicotinamide (**3u**).* Yellow solid (28 mg, 54%); mp 171−172 °C; R_f = 0.46 (petroleum ether/ethyl acetate = 6:1); IR (KBr, cm^{-1}) 3283, 3060, 2228, 1652, 1582, 1532, 1478, 1448, 1316, 1139, 961, 908, 864, 765, 649, 502; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.96 (d, J = 2.1 Hz, 1H), 8.42 (d, J = 8.2 Hz, 2H), 8.18 (dd, J = 8.3, 2.6 Hz, 1H), 7.70−7.62 (m, 2H), 7.48 (dd, J = 8.3, 0.5 Hz, 1H), 7.29−7.25 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 162.8, 155.3, 148.6, 139.7, 137.6, 134.3, 132.3, 128.3, 125.1, 124.6, 122.0, 116.2, 103.2. MS (EI) m/z: 257, 231, 207, 193, 155, 140, 112, 76, 50, 39. HRMS (ESI): calcd for $C_{13}H_9ClN_3O$ $[M + H]^+$ 258.0429; found 258.0425.

*N-(3-Cyanophenyl)acetamide (**3v**).*[32] Yellow solid (16 mg, 51%); mp = 130−132 °C; R_f = 0.42 (petroleum ether/ethyl acetate = 1:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.34 (s, 1H), 7.96 (s, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.45−7.31 (m, 2H), 2.19 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.2, 138.9, 129.8, 127.5, 123.9, 122.9, 118.5, 112.5, 24.3. MS (EI) m/z: 160, 131, 118, 91, 63, 43.

*N-(5-Cyanopyridin-2-yl)acetamide (**3w**).*[33] Yellow solid (13 mg, 41%); mp 208−209 °C; R_f = 0.60 (petroleum ether/ethyl acetate = 1:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.54 (dd, J = 2.2, 0.7 Hz, 1H), 8.34 (d, J = 8.7 Hz, 1H), 8.26 (s, 1H), 7.93 (dd, J = 8.8, 2.2 Hz, 1H), 2.26 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 168.9, 153.7, 151.5, 141.6, 116.7, 113.4, 105.0, 24.8. MS (EI) m/z: 161, 119, 92, 64, 43.

*N-(2-Cyanophenyl)pivalamide (**3x**).* White solid (19 mg, 47%); mp 79−80 °C; R_f = 0.48 (petroleum ether/ethyl acetate = 6:1); IR (KBr, cm^{-1}) 3284, 3065, 2974, 2231, 1671, 1601, 1577, 1472, 1300, 1177, 1029, 940, 813, 755, 721, 629, 481; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, J = 8.3 Hz, 1H), 7.96 (s, 1H), 7.57 (dd, J = 12.8, 4.5 Hz, 2H), 7.14 (t, J = 7.6 Hz, 1H), 1.35 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 176.9, 140.7, 134.0, 131.8, 123.8, 121.0, 116.3, 102.0, 40.1, 27.3. MS (EI) m/z: 202, 187, 159, 145, 118, 85, 57, 41. HRMS (ESI): calcd for $C_{12}H_{15}N_2O$ $[M + H]^+$ 203.1179; found 203.1171.

*4-Cyanobenzamide (**3y**).*[6d] Yellow solid (15 mg, 50%); mp 224−225 °C; R_f = 0.2 (petroleum ether/ethyl acetate = 1:1); ^1H NMR (400 MHz, DMSO-*d6*): δ = 8.21 (s, 1H), 8.06−7.99 (m, 2H), 7.98−7.92 (m, 2H), 7.68 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-*d6*): δ = 166.4, 138.2, 132.3, 128.2, 118.3, 113.6. MS (EI) m/z: 146, 130, 102, 75, 50, 44.

*4-Cyano-N-methylbenzamide (**3z**).*[34] White solid (18 mg, 56%); mp 209−210 °C; R_f = 0.22 (petroleum ether/ethyl acetate = 1:1); ^1H NMR (400 MHz, DMSO-*d6*): δ = 8.72 (d, J = 4.0 Hz, 1H), 8.02−7.94 (m, 4H), 2.80 (d, J = 4.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 166.3, 138.4, 132.4, 127.5, 117.9, 114.9, 27.0. MS (EI) m/z: 160, 130, 102, 75, 51, 39.

*4-Cyano-N-cyclohexylbenzamide (**3aa**).*[35] White solid (29 mg, 64%); mp 183−184 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 4:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88−7.82 (m, 2H), 7.72 (d, J = 7.9 Hz, 2H), 6.03 (s, 1H), 4.02−3.90 (m, 1H), 2.08−1.97 (m, 2H), 1.82−1.72 (m, 2H), 1.66 (dd, J = 9.0, 3.9 Hz, 2H), 1.42 (dd, J = 24.9, 12.4 Hz, 2H), 1.24−1.13 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.8, 138.9, 132.3, 127.5, 118.0, 114.8, 49.1, 33.0, 25.4, 24.8. MS (EI) m/z: 228, 199, 185, 147, 130, 102, 82, 67, 41.

*N-(tert-Butyl)-4-cyanobenzamide (**3ab**).*[36] White solid (33 mg, 82%); mp 146−147 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 4:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.3 Hz, 2H), 7.71−7.59 (m, 2H), 6.10 (s, 1H), 1.45 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.0, 139.7, 132.2, 127.4, 118.0, 114.4, 52.0, 28.6. MS (EI) m/z: 202, 187, 147, 130, 102, 75, 56, 41.

*N-Benzyl-4-cyanobenzamide (**3ac**).*[37] White solid (32 mg, 68%); mp 150−151 °C; R_f = 0.62 (petroleum ether/ethyl acetate = 1:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.2 Hz, 2H), 7.67 (dd, J = 8.4, 1.5 Hz, 2H), 7.34 (dd, J = 8.0, 6.2 Hz, 2H), 7.32−7.27 (m, 3H), 6.85 (s, 1H), 4.60 (d, J = 5.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.5, 138.1, 137.4, 132.3, 128.7, 127.7, 127.7, 127.6, 117.9, 114.9, 44.2. MS (EI) m/z: 236, 219, 190, 157, 130, 102, 79, 51, 39.

*4-Cyano-N-(2,3-dihydro-1H-inden-1-yl)benzamide (**3ad**).* Gray solid (38 mg, 73%); mp 146−148 °C; R_f = 0.31 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3265, 3065, 2971, 2935, 2845, 2230, 1636, 1609, 1540, 1498, 1457, 1322, 1299, 1288, 1074, 1021, 906, 856, 756, 693; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.90−7.82 (m, 2H), 7.72−7.64 (m, 2H), 7.31 (d, J = 7.3 Hz, 1H), 7.26 (d, J = 3.7 Hz, 2H), 7.22 (dt, J = 8.6, 3.8 Hz, 1H), 6.67 (d, J = 8.1 Hz, 1H), 5.63 (q, J = 7.7 Hz, 1H), 3.02 (ddd, J = 15.9, 8.7, 4.0 Hz, 1H), 2.91 (dt, J = 16.0, 8.0 Hz, 1H), 2.71−2.60 (m, 1H), 1.92 (ddd, J = 15.9, 13.0, 8.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.4, 143.4, 142.4, 138.2, 132.3, 128.2, 127.6, 126.8, 124.9, 123.9, 117.9, 114.9, 55.3, 33.81, 30.2. MS (EI) m/z: 262, 244, 217, 190, 147, 130, 116, 102, 91, 51, 39. HRMS (ESI): calcd for $C_{17}H_{14}N_2NaO$ $[M + Na]^+$ 285.0998; found 285.0993.

*4-Cyano-N-(4-fluorobenzyl)benzamide (**3ae**).*[38] White solid (29 mg, 57%); mp 109−111 °C; R_f = 0.72 (petroleum ether/ethyl acetate = 1:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, J = 8.3 Hz, 2H), 7.74−7.64 (m, 2H), 7.29 (dd, J = 7.9, 5.7 Hz, 2H), 7.02 (t, J = 8.6 Hz, 2H), 6.73 (s, 1H), 4.58 (d, J = 5.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.5, 162.2 (d, J = 245 Hz), 138.0, 133.3 (d, J = 3 Hz), 132.4, 129.6 (d, J = 8 Hz), 127.6, 117.9, 115.7 (d, J = 22 Hz), 115.1, 43.5. MS (EI) m/z: 254, 224, 208, 190, 157, 130, 102, 75, 51, 39.

*4-Cyano-N-phenethylbenzamide (**3af**).*[38] White solid (36 mg, 73%); mp 115−117 °C; R_f = 0.72 (petroleum ether/ethyl acetate = 1:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.34 (t, J = 7.3 Hz, 2H), 7.30−7.25 (m, 1H), 7.22 (d, J = 7.3 Hz, 2H), 6.39 (s, 1H), 3.72 (q, J = 6.7 Hz, 2H), 2.94 (t, J = 6.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.6, 138.4, 132.3, 128.7, 128.6, 127.5, 126.7, 117.9, 114.8, 41.2, 35.3. MS (EI) m/z: 250, 207, 173, 159, 130, 104, 91, 65, 39.

*4-Cyano-N,N-dipropylbenzamide (**3ag**).*[39] Colorless liquid (32 mg, 70%); R_f = 0.35 (petroleum ether/ethyl acetate = 4:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72−7.67 (m, 2H), 7.48−7.43 (m, 2H), 3.51−3.38 (m, 2H), 3.17−3.04 (m, 2H), 1.72−1.66 (m, 2H), 1.58−1.46 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H), 0.74 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.6, 141.6, 132.3, 127.1, 118.1, 112.8, 50.5, 46.3, 21.8, 20.5, 11.3, 10.9. MS (EI) m/z: 230, 201, 159, 130, 102, 75, 51.

*4-(Morpholine-4-carbonyl)benzonitrile (**3ah**).*[40] Yellow solid (23 mg, 55%); mp 143−145 °C; R_f = 0. 32 (petroleum ether/ethyl acetate = 1:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.76−7.69 (m, 2H), 7.54−7.47 (m, 2H), 3.70 (d, J = 64.9 Hz, 6H), 3.37 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 168.2, 139.5, 132.4, 127.7, 117.9, 113.6, 66.6, 48.0, 42.5. MS (EI) m/z: 216, 185, 130, 102, 86, 56, 42.

*4-Cyano-N-(p-tolyl)benzamide (**3ai**).*[41] Yellow solid (38 mg, 80%); mp 177−179 °C; R_f = 0.36 (petroleum ether/ethyl acetate = 4:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.1 Hz, 3H), 7.74 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.2 Hz, 2H), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 163.8, 138.9, 134.9, 134.6, 132.5, 129.6, 127.7, 120.4, 117.9, 115.1, 20.9. MS (EI) m/z: 236, 207, 192, 130, 102, 77, 51, 39.

*N-(4-Bromophenyl)-4-cyanobenzamide (**3aj**).*[42] White solid (28 mg, 47%); mp 205−207 °C; R_f = 0. 64 (petroleum ether/ethyl acetate = 2:1); ^1H NMR (400 MHz, DMSO-*d6*): δ = 10.60 (s, 1H), 8.09 (d, J = 8.5 Hz, 2H), 8.02 (d, J = 8.4 Hz, 2H), 7.79−7.73 (m, 2H), 7.54 (d, J = 8.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-*d6*): δ = 164.69, 139.12, 138.61, 132.93, 131.99, 129.02, 122.75, 118.75, 116.30, 114.45. MS (EI) m/z: 300, 130, 102, 75, 63, 44.

*3-Cyano-N-(p-tolyl)benzamide (**3ao**).* Yellow solid (31 mg, 66%); mp 166−167 °C; R_f = 0.25 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3307, 3062, 2916, 2232, 1652, 1596, 1579, 1521, 1402, 1297, 1184, 1021, 935, 809, 795, 693, 518; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.16 (s, 1H), 8.14−8.03 (m, 2H), 7.80 (dt, J = 7.7, 1.2 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.50 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.3 Hz, 2H), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 163.5, 136.2, 134.9, 134.7, 134.7, 131.5, 130.7, 129.7, 129.6, 120.6, 118.0, 112.8, 20.9. MS (EI) m/z: 236, 205, 192, 165, 130, 102, 77, 51, 39. HRMS (ESI): calcd for $C_{15}H_{13}N_2O$ $[M + H]^+$ 237.1022; found 237.1016.

General Procedure for the Synthesis of Cyano Substituted Esters (4a−4ad). A mixture of acyl cyanide (0.2 mmol), alcohol (0.2

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mmol), and Cu_2O (2.9 mg, 10 mol %) in DMSO (1.0 mL) was placed in a test tube (10 mL) equipped with a magnetic stirring bar. The tube was placed in a preheated oil bath at 130 °C, and the mixture was stirred vigorously for 10 h. After the reaction was finished, water (5 mL) was added. The solution was extracted with ethyl acetate (3 × 5 mL), and the combined extract was dried with anhydrous $MgSO_4$. Solvent was removed, and the residue was separated by column chromatography to give the pure sample.

*4-Cyanophenyl Benzoate (**4a**).*[43] White solid (29 mg, 66%); mp 95−96 °C; R_f = 0.6 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23−8.16 (m, 2H), 7.79−7.72 (m, 2H), 7.71−7.65 (m, 1H), 7.57−7.51 (m, 2H), 7.41−7.35 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.3, 154.2, 134.1, 133.7, 130.2, 128.7, 122.9, 118.2, 116.4, 109.8. MS (EI) *m/z*: 223, 207, 193, 166, 140, 105, 77, 51, 39.

*2-Cyanobenzyl Benzoate (**4b**).* White solid (39 mg, 82%); mp 52−53 °C; R_f = 0.52 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3069, 2922, 2224, 1716, 1601, 1584, 1528, 1489, 1376, 1176, 1123, 1025, 765, 713, 559; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 7.2 Hz, 2H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 4.1 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 3H), 5.55 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.9, 139.4, 133.2, 133.0, 132.9, 129.7, 129.4, 129.4, 128.7, 128.4, 117.0, 112.1, 64.1. MS (EI) *m/z*: 237, 219, 192, 165, 132, 105, 77, 51, 39. HRMS (ESI): calcd for $C_{15}H_{12}NO_2$ $[M + H]^+$ 238.0863; found 238.0863.

*4-Cyanophenyl 3-Methylbenzoate (**4c**).* Yellow solid (28 mg, 59%); mp 62−64 °C; R_f = 0.63 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3103, 2917, 2849, 2231, 1729, 1600, 1585, 1500, 1458, 1278, 1212, 1087, 866, 833, 733, 681, 553; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04−7.96 (m, 2H), 7.78−7.71 (m, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.39−7.34 (m, 2H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.4, 154.2, 138.6, 134.9, 133.7, 130.7, 128.6, 128.5, 127.4, 122.9, 118.2, 109.7, 21.2. MS (EI) *m/z*: 237, 207, 178, 165, 139, 119, 91, 65, 39. HRMS (ESI): calcd for $C_{15}H_{12}NO_2$ $[M + H]^+$ 238.0863; found 238.0864.

*2-Cyanobenzyl 3-methylbenzoate (**4d**).* Colorless liquid (34 mg, 68%); R_f = 0.62 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3065, 2957, 2923, 2851, 2227, 1719, 1603, 1590, 1489, 1452, 1379, 1273, 1194, 1080, 1002, 763, 743, 682; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 6.9 Hz, 2H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 4.0 Hz, 2H), 7.49−7.42 (m, 1H), 7.40−7.30 (m, 2H), 5.55 (s, 2H), 2.40 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 166.2, 139.5, 138.3, 134.1, 133.1, 132.9, 130.3, 129.4, 128.7, 128.3, 126.9, 123.1, 117.0, 112.2, 64.0, 21.2. MS (EI) *m/z*: 251, 233, 222, 190, 160, 132, 119, 91, 65, 39. Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.20; H, 5.27; N, 5.65.

*2-Cyanobenzyl 4-(tert-butyl)benzoate (**4e**).* Colorless liquid (28 mg, 47%); R_f = 0.57 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3056, 2964, 2869, 2227, 1723, 1608, 1571, 1452, 1314, 1271, 1189, 1115, 1017, 854, 774, 707, 547; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07−7.95 (m, 2H), 7.76−7.66 (m, 1H), 7.61 (d, *J* = 4.2 Hz, 2H), 7.50−7.38 (m, 3H), 5.54 (s, 2H), 1.33 (d, *J* = 4.3 Hz, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 166.0, 157.0, 139.7, 133.1, 132.9, 129.7, 129.3, 128.6, 126.7, 125.4, 117.0, 112.1, 63.9, 35.1, 31.0. MS (EI) *m/z*: 293, 278, 260, 232, 218, 177, 161, 145, 116, 89, 51, 41. HRMS (ESI): calcd for $C_{19}H_{20}NO_2$ $[M + H]^+$ 294.1489; found 294.1486.

*4-Cyanophenyl 4-Methoxybenzoate (**4f**).*[44] White solid (25 mg, 50%); mp 109−110 °C; R_f = 0.47 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18−8.10 (m, 2H), 7.77−7.69 (m, 2H), 7.39−7.32 (m, 2H), 7.04−6.97 (m, 2H), 3.91 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.3, 164.0, 154.4, 133.6, 132.4, 122.9, 120.8, 118.3, 114.0, 109.5, 55.5. MS (EI) *m/z*: 253, 2326, 207, 184, 164, 135, 107, 92, 77, 64, 39.

*2-Cyanobenzyl 4-Methoxybenzoate (**4g**).* White solid (38 mg, 72%); mp 66−67 °C; R_f = 0.49 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3073, 2983, 2847, 2222, 1705, 1607, 1582, 1511, 1457, 1382, 1286, 1021, 846, 764, 695, 522; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07−8.01 (m, 2H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 4.0 Hz, 2H), 7.47−7.40 (m, 1H), 6.95−6.89 (m, 2H), 5.51 (s, 2H), 3.85 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.6, 163.6, 139.6, 133.0, 132.9, 131.8, 129.3, 128.6, 121.7, 117.0, 113.6, 112.0, 63.8, 55.3. MS (EI) *m/z*: 267, 224, 206, 180, 152, 135, 116, 92, 77, 64, 39. HRMS (ESI): calcd for $C_{16}H_{14}NO_3$ $[M + H]^+$ 268.0968; found 268.0962.

*2-Cyanobenzyl 4-Fluorobenzoate (**4h**).* White solid (30 mg, 58%); mp 62−64 °C; R_f = 0.54 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3066, 2918, 2849, 2226, 1724, 1604, 1506, 1487, 1457, 1270, 1124, 1010, 799, 763, 613; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16−8.05 (m, 2H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.66−7.58 (m, 2H), 7.50−7.43 (m, 1H), 7.16−7.08 (m, 2H), 5.53 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.9 (d, *J* = 253 Hz), 165.0, 139.2, 133.1 (d, *J* = 20 Hz), 132.4, 132.3, 129.5, 128.9, 125.7 (d, *J* = 3 Hz), 117.0, 115.6 (d, *J* = 22 Hz), 112.3, 64.3. MS (EI) *m/z*: 255, 237, 208, 183, 160, 132, 123, 116, 95, 75, 63, 39. HRMS (ESI): calcd for $C_{15}H_{10}FNNaO_2$ $[M + Na]^+$ 278.0588; found 278.0586.

*2-Cyanobenzyl 2-Chlorobenzoate (**4i**).* Brown solid (30 mg, 56%); mp 136−139 °C; R_f = 0.47 (petroleum ether/ethyl acetate = 1:1); IR (KBr, cm^{-1}) 3088, 2919, 2849, 2231, 1725, 1647, 1590, 1567, 1471, 1377, 1297, 1115, 1051, 768, 709, 551; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.76−7.69 (m, 1H), 7.64 (qd, *J* = 8.0, 3.7 Hz, 2H), 7.53−7.39 (m, 3H), 7.37−7.28 (m, 1H), 5.55 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.0, 139.0, 134.1, 133.1, 133.0, 132.9, 131.8, 131.2, 130.0, 129.2, 129.0, 126.7, 117.0, 112.4, 64.7. MS (EI) *m/z*: 271, 236, 190, 165, 139, 116, 75, 50, 39. HRMS (ESI): calcd for $C_{15}H_{11}ClNO_2$ $[M + H]^+$ 272.0473; found 272.0467.

*2-Cyanobenzyl Cinnamate (**4j**).* Yellow solid (24 mg, 45%); mp 61−62 °C; R_f = 0.47 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3088, 2919, 2849, 2231, 1725, 1590, 1590, 1567, 1471, 1253, 1115, 1051, 901, 768, 728, 651, 551; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 16.0 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.65−7.57 (m, 2H), 7.53 (dt, *J* = 7.9, 3.3 Hz, 2H), 7.45 (td, *J* = 7.4, 1.7 Hz, 1H), 7.41−7.36 (m, 3H), 6.50 (d, *J* = 16.0 Hz, 1H), 5.44 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 166.3, 145.9, 139.5, 134.2, 133.0, 132.9, 130.5, 129.4, 128.9, 128.7, 128.1, 117.1, 112.2, 99.9, 63.7. MS (EI) *m/z*: 263, 235, 219, 192, 148, 131, 103, 77, 51, 39. HRMS (ESI): calcd for $C_{17}H_{13}NNaO_2$ $[M + Na]^+$ 286.0838; found 286.0830.

*Phenyl 4-Cyanobenzoate (**4k**).*[43] White solid (30 mg, 68%); mp 165−166 °C; R_f = 0.64 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34−8.27 (m, 2H), 7.84−7.77 (m, 2H), 7.49−7.42 (m, 2H), 7.35−7.27 (m, 1H), 7.25−7.18 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 163.4, 150.3, 133.2, 132.2, 130.4, 129.5, 126.2, 121.3, 117.7, 116.7. MS (EI) *m/z*: 223, 193, 164, 130, 102, 75, 65, 51, 39.

*Methyl 4-Cyanobenzoate (**4l**).*[45] Yellow solid (30 mg, 93%); mp 62−63 °C; R_f = 0.54 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H), 3.94 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.3, 133.8, 132.1, 130.0, 117.8, 116.2, 52.6. MS (EI) *m/z*: 161, 130, 102, 75, 51, 38.

*Ethyl 4-Cyanobenzoate (**4m**).*[46] White solid (27 mg, 78%); mp 54−55 °C; R_f = 0.62 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.9, 134.2, 132.1, 130.0, 117.9, 116.2, 61.7, 14.2. MS (EI) *m/z*: 175, 147, 130, 102, 75, 51, 45.

*2,2-Difluoroethyl 4-Cyanobenzoate (**4n**).* White solid (32 mg, 75%); mp 54−55 °C; R_f = 0.50 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3103, 3053, 3020, 2973, 2232, 1736, 1609, 1566, 1501, 1460, 1372, 1274, 1020, 907, 868, 765, 691, 591, 485; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20−8.12 (m, 2H), 7.80−7.72 (m, 2H), 6.09 (tt, *J* = 54.8, 3.9 Hz, 1H), 4.54 (td, *J* = 13.7, 3.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.0, 132.5, 132.3, 130.3, 117.7, 117.0, 112.4 (t, *J* = 40 Hz), 63.2 (t, *J* = 29 Hz). MS (EI) *m/z*: 211, 147, 130, 102, 75, 51, 45. HRMS (ESI): calcd for $C_{10}H_8F_2NO_2$ $[M + H]^+$ 212.0518; found 212.0520.

*2,2,2-Trifluoroethyl 4-Cyanobenzoate (**4o**).* Gray solid (33 mg, 73%); mp 63−64 °C; R_f = 0.64 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3103, 3053, 3020, 2973, 2232, 1736, 1609,

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1566, 1527, 1460, 1372, 1274, 1020, 907, 868, 765, 691, 591; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, J = 8.3 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H), 4.73 (q, J = 8.3 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 163.3, 132.3, 132.0, 130.4, 122.7 (q, J = 75 Hz), 117.6, 117.2, 61.2 (q, J = 36 Hz). MS (EI) m/z: 229, 210, 180, 160, 130, 102, 75, 51, 38. HRMS (ESI): calcd for $C_{10}H_7F_3NO_2$ $[M + H]^+$ 230.0423; found 230.0425.

*Isopropyl 4-Cyanobenzoate (**4p**).*[47] White solid (25 mg, 66%); mp 49−51 °C; R_f = 0.71 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18−8.09 (m, 2H), 7.78−7.69 (m, 2H), 5.27 (hept, J = 6.3 Hz, 1H), 1.38 (d, J = 6.3 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.4, 134.6, 132.1, 130.0, 118.0, 116.1, 69.5, 21.8. MS (EI) m/z: 189, 174, 148, 130, 102, 75, 59, 43.

*Cyclohexyl 4-Cyanobenzoate (**4q**).*[48] White solid (38 mg, 83%); mp 61−62 °C; R_f = 0.75 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18−8.11 (m, 2H), 7.77−7.70 (m, 2H), 5.08−5.00 (m, 1H), 1.95 (dd, J = 12.0, 5.2 Hz, 2H), 1.79 (dd, J = 9.6, 3.3 Hz, 2H), 1.59 (ddd, J = 16.0, 10.9, 3.4 Hz, 4H), 1.51−1.39 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.3, 134.7, 132.1, 130.0, 118.0, 116.0, 74.1, 31.5, 25.3, 23.6. MS (EI) m/z: 229, 200, 188, 148, 130, 102, 82, 67, 55, 41.

*1,1,1,3,3,3-Hexafluoropropan-2-yl 4-cyanobenzoate (**4r**).* White solid (36 mg, 60%); mp 62−64 °C; R_f = 0.72 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3107, 3074, 2982, 2240, 1758, 1613, 1573, 1040, 1017, 908, 866, 762, 725, 695, 546; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, J = 8.5 Hz, 2H), 7.83 (d, J = 8.5 Hz, 2H), 6.01 (hept, J = 6.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 161.8, 132.6, 130.8, 130.4, 121.6 (m, J = 281 Hz), 117.3, 116.0, 67.3 (m, J = 35 Hz). MS (EI) m/z: 297, 258, 233, 214, 184, 151, 130, 102, 75, 51, 38. HRMS (ESI): calcd for $C_{11}H_5F_6NNaO_2$ $[M + Na]^+$ 320.0117; found 320.0115.

*Allyl 4-Cyanobenzoate (**4s**).*[49] Colorless liquid (31 mg, 83%); R_f = 0.67 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19−8.13 (m, 2H), 7.78−7.72 (m, 2H), 6.03 (ddt, J = 16.2, 10.5, 5.8 Hz, 1H), 5.42 (dq, J = 17.2, 1.4 Hz, 1H), 5.33 (dd, J = 10.4, 1.2 Hz, 1H), 4.85 (dt, J = 5.8, 1.3 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.5, 133.9, 132.2, 131.5, 130.1, 119.0, 117.9, 116.4, 66.3. MS (EI) m/z: 187, 148, 130, 102, 75, 51, 39.

*Hex-5-en-1-yl 4-Cyanobenzoate (**4t**).*[50] Colorless liquid (39 mg, 86%); R_f = 0.7 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16−8.10 (m, 2H), 7.77−7.71 (m, 2H), 5.80 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.06−4.95 (m, 2H), 4.35 (t, J = 6.6 Hz, 2H), 2.17−2.08 (m, 2H), 1.85−1.74 (m, 2H), 1.59−1.48 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.9, 138.0, 134.1, 132.1, 130.0, 117.9, 116.2, 114.9, 65.6, 33.1, 27.9, 25.1. MS (EI) m/z: 229, 199, 188, 148, 130, 102, 82, 67, 54, 41.

*Cyclohex-3-en-1-ylmethyl 4-Cyanobenzoate (**4u**).* Colorless liquid (36 mg, 75%); R_f = 0.72 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3024, 2921, 2840, 2231, 1724, 1610, 1570, 1437, 1406, 1274, 1177, 1044, 1019, 961, 861, 767, 657, 545; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20−8.09 (m, 2H), 7.80−7.68 (m, 2H), 5.75−5.64 (m, 2H), 4.26 (d, J = 6.5 Hz, 2H), 2.24−2.07 (m, 4H), 1.93−1.81 (m, 2H), 1.48−1.35 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.9, 134.2, 132.2, 130.0, 127.1, 125.2, 117.9, 116.3, 69.9, 33.0, 28.1, 25.3, 24.3. MS (EI) m/z: 241, 207, 193, 151, 130, 102, 94, 79, 66, 41. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.48; H, 6.17; N, 5.88.

*Phenethyl 4-Cyanobenzoate (**4v**).*[51] White solid (35 mg, 70%); mp 91−92 °C; R_f = 0.73 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15−8.07 (m, 2H), 7.78−7.69 (m, 2H), 7.37−7.30 (m, 2H), 7.30−7.23 (m, 3H), 4.57 (t, J = 7.0 Hz, 2H), 3.09 (t, J = 6.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.8, 137.4, 134.0, 132.1, 130.0, 128.8, 128.6, 126.7, 117.9, 116.3, 66.1, 35.0. MS (EI) m/z: 251, 207, 191, 151, 130, 104, 91, 65, 51, 39.

*4-Methoxybenzyl 4-Cyanobenzoate (**4w**).* White solid (36 mg, 68%); mp 69−70 °C; R_f = 0.53 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3068, 2987, 2957, 2834, 2227, 1613, 1589, 1517, 1467, 1381, 1246, 1109, 1037, 861, 765, 688, 576; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17−8.10 (m, 2H), 7.75−7.69 (m, 2H), 7.42−7.34 (m, 2H), 6.96−6.89 (m, 2H), 5.32 (s, 2H), 3.82 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.8, 159.9, 134.0, 132.1, 130.3, 130.1, 127.4, 117.9, 116.3, 114.0, 67.3, 55.2. MS (EI) m/z: 267, 224, 192, 164, 130, 121, 91, 51, 39. HRMS (ESI): calcd for $C_{16}H_{13}NNaO_3$ $[M + Na]^+$ 290.0788; found 290.0786.

*4-Chlorobenzyl 4-Cyanobenzoate (**4x**).* White solid (42 mg, 77%); mp 91−93 °C; R_f = 0.59 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3107, 3053, 2961, 2230, 1720, 1595, 1570, 1491, 1446, 1311, 1116, 1016, 860, 804, 727, 691, 535; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19−8.11 (m, 2H), 7.77−7.70 (m, 2H), 7.41−7.33 (m, 4H), 5.34 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.6, 134.5, 133.7, 133.6, 132.2, 130.1, 129.7, 128.8, 117.8, 116.5, 66.6. MS (EI) m/z: 271, 236, 218, 190, 165, 130, 102, 89, 51, 39. HRMS (ESI): calcd for $C_{15}H_{11}ClNO_2$ $[M + H]^+$ 272.0473; found 272.0466.

*3-Chlorobenzyl 4-Cyanobenzoate (**4y**).* White solid (34 mg, 63%); mp 86−87 °C; R_f = 0.62 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3066, 2961, 2920, 2227, 1724, 1604, 1576, 1481, 1405, 1379, 1176, 1109, 958, 864, 781, 694, 546; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19−8.14 (m, 2H), 7.78−7.72 (m, 2H), 7.43 (d, J = 1.0 Hz, 1H), 7.37−7.29 (m, 3H), 5.35 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.5, 137.2, 134.5, 133.5, 132.2, 130.1, 129.9, 128.7, 128.3, 126.3, 117.8, 116.5, 66.5. MS (EI) m/z: 271, 236, 218, 190, 165, 130, 102, 89, 51, 39. HRMS (ESI): calcd for $C_{15}H_{11}ClNO_2$ $[M + H]^+$ 272.0473; found 272.0474.

*Thiophen-2-ylmethyl 4-Cyanobenzoate (**4z**).* Yellow solid (18 mg, 38%); mp 72−74 °C; R_f = 0.61 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3086, 2919, 2849, 2229, 1724, 1609, 1457, 1375, 1214, 1105, 979, 848, 764, 712, 543; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 8.5 Hz, 2H), 7.36 (dd, J = 5.1, 1.0 Hz, 1H), 7.19 (d, J = 3.4 Hz, 1H), 7.02 (dd, J = 5.1, 3.5 Hz, 1H), 5.54 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.6, 137.1, 133.7, 132.2, 130.2, 128.6, 127.2, 126.9, 117.8, 116.5, 61.6. MS (EI) m/z: 243, 207, 191, 162, 130, 102, 97, 53, 45, 39. HRMS (ESI): calcd for $C_{13}H_{10}NO_2S$ $[M + H]^+$ 244.0427; found 244.0413.

*Phenethyl 3-Cyanobenzoate (**4aa**).* Yellow liquid (41 mg, 82%); R_f = 0.62 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3042, 2957, 2903, 2229, 1722, 1605, 1592, 1577, 1490, 1454, 1350, 1274, 1147, 993, 872, 759, 697, 490; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30−8.26 (m, 1H), 8.25−8.20 (m, 1H), 7.82 (dt, J = 7.7, 1.4 Hz, 1H), 7.57 (td, J = 7.9, 0.4 Hz, 1H), 7.34 (ddd, J = 7.1, 4.4, 1.6 Hz, 2H), 7.30−7.25 (m, 3H), 4.57 (t, J = 7.0 Hz, 2H), 3.10 (t, J = 7.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.4, 137.3, 135.8, 133.5, 133.1, 131.5, 129.3, 128.8, 128.5, 126.7, 117.8, 112.8, 66.1, 35.0. MS (EI) m/z: 251, 236, 204, 190, 165, 130, 104, 91, 65, 39. Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.23; H, 5.29; N, 5.50.

*Methyl 2-Cyanobenzoate (**4ab**).*[52] White solid (29 mg, 91%); mp 50−51 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18−8.09 (m, 1H), 7.84−7.76 (m, 1H), 7.72−7.62 (m, 2H), 3.99 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 164.4, 134.7, 132.6, 132.4, 132.2, 131.1, 117.4, 112.8, 52.7. MS (EI) m/z: 161, 130, 102, 75, 51, 39.

*Ethyl 2-Cyanobenzoate (**4ac**).*[52] White solid (30 mg, 85%); mp 64−66 °C; R_f = 0.56 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17−8.08 (m, 1H), 7.83−7.75 (m, 1H), 7.70−7.60 (m, 2H), 4.44 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 163.9, 134.6, 132.5, 132.5, 132.3, 131.0, 117.4, 112.7, 62.1, 13.9. MS (EI) m/z: 175, 147, 130, 102, 75, 51, 39.

*Phenethyl 2-Cyanobenzoate (**4ad**).* White solid (44 mg, 87%); mp 45−46 °C; R_f = 0.46 (petroleum ether/ethyl acetate = 4:1); IR (KBr, cm^{-1}) 3041, 2957, 2900, 2229, 1720, 1602, 1592, 1575, 1489, 1469, 1379, 1302, 1170, 1049, 1007, 800, 724, 574; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13−8.04 (m, 1H), 7.85−7.77 (m, 1H), 7.70−7.61 (m, 2H), 7.36−7.28 (m, 4H), 7.25 (ddd, J = 8.6, 5.0, 2.3 Hz, 1H), 4.62 (t, J = 7.2 Hz, 2H), 3.14 (t, J = 7.1 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 163.8, 137.3, 134.7, 132.6, 132.4, 132.3, 131.0, 128.9, 128.5, 126.6, 117.5, 112.8, 66.5, 34.7. MS (EI) m/z: 251,

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232, 204, 190, 165, 130, 104, 91, 65, 39. HRMS (ESI): calcd for $C_{16}H_{14}NO_2$ $[M + H]^+$ 252.1019; found 252.1019.

*N-(3-Cyano-6-methylpyridin-2-yl)benzamide (**5a**).*[15] White solid (34 mg, 72%); mp 87−89 °C; R_f = 0.27 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.80 (s, 1H), 8.23 (t, J = 1.5 Hz, 1H), 8.14 (dd, J = 6.8, 1.6 Hz, 2H), 7.87−7.77 (m, 1H), 7.70−7.56 (m, 2H), 6.96 (d, J = 7.5 Hz, 1H), 2.44 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 163.4, 157.0, 150.3, 138.9, 135.6, 135.1, 131.1, 129.7, 119.1, 117.7, 113.3, 111.2, 23.8. MS (EI) m/z: 237, 208, 130, 102, 75, 51, 39.

*2,4-Diphenylquinazoline (**5b**).*[16] Yellow solid (45 mg, 80%); mp 116−117 °C; R_f = 0.76 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.72 (dd, J = 8.0, 1.6 Hz, 2H), 8.15 (dd, J = 15.9, 8.4 Hz, 2H), 7.89 (ddd, J = 10.9, 8.0, 2.7 Hz, 3H), 7.65−7.58 (m, 3H), 7.58−7.49 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 168.2, 160.1, 151.9, 138.1, 137.6, 133.4, 130.4, 130.1, 129.8, 129.1, 128.6, 128.4, 126.9, 121.6. MS (EI) m/z: 282, 254, 226, 203, 178, 102, 77, 50, 39.

*2-Phenyl-4H-benzo[d][1,3]oxazin-4-one (**5c**).*[17] White solid (36 mg, 81%); mp 110−111 °C; R_f = 0.70 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.34−8.25 (m, 2H), 8.22 (dd, J = 7.9, 1.2 Hz, 1H), 7.80 (ddd, J = 8.2, 7.4, 1.5 Hz, 1H), 7.67 (dd, J = 8.1, 0.5 Hz, 1H), 7.58−7.53 (m, 1H), 7.52−7.46 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 159.4, 157.0, 146.8, 136.4, 132.5, 130.1, 128.6, 128.4, 128.2, 128.1, 127.1, 116.9. MS (EI) m/z: 223, 179, 146, 105, 77, 51, 39.

*N-(2-Iodophenyl)benzamide (**6a**).*[53] White solid (60 mg, 93%); mp 133−135 °C; R_f = 0. 72 (petroleum ether/ethyl acetate = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (dd, J = 8.3, 1.5 Hz, 1H), 8.30 (s, 1H), 8.02−7.95 (m, 2H), 7.82 (dd, J = 8.0, 1.4 Hz, 1H), 7.63−7.57 (m, 1H), 7.56−7.50 (m, 2H), 7.44−7.38 (m, 1H), 6.89 (td, J = 7.8, 1.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 165.2, 138.7, 138.2, 134.4, 132.1, 129.4, 128.9, 127.1, 126.0, 121.7, 90.2. MS (EI) m/z: 323, 196, 105, 77, 51.

■ ASSOCIATED CONTENT

Supporting Information

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^{1}H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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