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Metal-free direct cyanoisopropylation/arylation of *N*-arylacrylamides or *N*-alkyl-*N*-(arylsulfonyl)acrylamides with AIBN: a simple and mild approach to cyano-containing oxindoles†

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A simple and metal-free direct cyanoisopropylation/arylation of *N*-arylacrylamides or *N*-alkyl-*N*-(arylsulfonyl)acrylamides with AIBN has been developed with cheap and readily available CH_3NO_2 as both the solvent and the oxidant. This reaction provides an efficient approach to cyano-containing oxindoles, which are highly valued synthetic intermediates of biologically active molecules. A series of *N*-alkyl-*N*-(arylsulfonyl)acrylamide substrates could be converted into the corresponding oxindoles in good yields and with excellent chemoselectivity via one-pot cyanoisopropylation/aryl migration/desulfonylation and C(sp^2)-N bond formation. In contrast to previous reports, the mild conditions together with no need for any metal catalysts and additional oxidants make this protocol very easy to handle and practical.

Introduction

The incorporation of cyano or cyano-containing functional groups into organic molecules is of great important in organic synthesis because the nitrile moiety can serve as versatile building block for various organic transformations.[1] Thus far, considerable efforts have been made on the development of new synthetic procedures for the construction of cyano-containing compounds.[2,3] Among them, transition-metal-catalyzed or -mediated cyanation of arenes and heteroarenes are undoubtedly the most effective strategies to introduce the nitrile moiety into organic molecules.[2] Despite formidable advances, however, the introduction of cyano species into valuable heterocyclic molecules such as oxindoles is a worthwhile and challenging goal in synthesis chemistry. In particular, these cyano-containing oxindoles, including (3-methyl-3-cyanomethyl)indolin-2-ones, are highly valued synthetic intermediates of inhibitor derivatives of acetyl- and butyrylcholinesterase such as esermethole and physostigmine.[4] One early approach to cyano-containing oxindoles through a domino intramolecular Heck-cyanation reaction using potassium ferro(II) cyanide as a cyanide donor.[5] An intriguing entry to these highly valuable molecules was reported by Takemoto et al.,[6] this discovery presents an effective strategy for the enantioselective cyanoamidation of olefins. Unfortunately, these methodologies often require prefunctionalization of the starting materials. In contrast, direct C-H functionalization/cyclization of alkenes could circumvent this limitation. In 2011, Liu et al. reported a pioneering work for access to cyano-containing oxindoles by Pd-catalyzed oxidative cyanoalkylation/cyclization of alkenes using alkyl nitriles as the nitrile source.[7] Later on, You and Zhao independently achieved the copper-catalyzed cyanomethylation/cyclization of activated alkenes with acetonitrile using DTBP as the oxidant[8] and the $Mn(OAc)_3$-mediated cyanomethylation/cyclization of activated alkenes with acetonitrile in the presence of a stoichiometric amount of arylboronic acid[9] for the preparation of cyano-containing oxindoles, respectively.

Azobisisobutyronitrile (AIBN) is widely known as a radical initiator.[10] However, in 2008, Punta pioneered the application of AIBN as a "$C(Me)_2CN$" source in the synthesis of important organic molecules: β-hydroxynitriles.[11] Until recently, the groups of Wang and Tang successfully achieved the oxidative, copper-catalyzed synthesis of cyano-containing oxindoles from activated alkenes through a free radical cyanoisopropylation/cyclization cascade reaction by using AIBN as a source of $C(Me)_2CN$ radical.[12,13] These reports were closely followed by an independent publication by Kuang et al. in which the essentially identical transformation was described with superstoichiometric amounts of DTBP as the oxidant.[14] Nevertheless, these cyanoisopropylation/cyclization approaches suffered from one or more limitations including limited functional group tolerance (e.g., chemosensitive OH group and steric hindrance large NPhth group are not compatible with these potocols), poor substrate scope, the use of superstoichiometric amounts of external-oxidants (e.g., DTBP, $K_2S_2O_8$), and/or the metal catalysts, which may limit their applicability in synthetic chemistry.

We sought to develop a general, mild, practical and cost-effective cyanoisopropylation/cyclization approach toward cyano-containing oxindoles. As a part of our continuing interest in the metal-free C-H functionalization/cyclization reactions.[15,16] Herein we present an operationally simple and highly efficient cyanoisopropylation/arylation without using any metal catalysts and additional oxidants, thus becoming a powerful alternative for accessing cyano-

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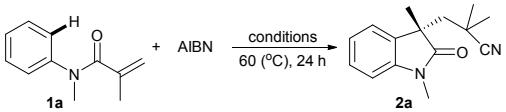
containing oxindoles in a direct manner. Compared with previous reports, the significance of the present finding is twofold: (1) This transformation exhibits good generality: the substrate scope is not only applicable to *N*-arylacrylamides, but also to *N*-alkyl-*N*-(arylsulfonyl)acrylamides. In particular, *N*-alkyl-*N*-(arylsulfonyl) acrylamides could be efficiently converted into the desired oxindoles in good yields and with excellent chemoselectivity via one-pot cyanoisopropylation/aryl migration/desulfonylation and C(sp^2)-N bond formation. (2) Mild reaction conditions (60 °C) and good functional group compatibility utilizing cheap and readily available CH_3NO_2 as both the solvent and the oxidant, thus becoming a practical and expeditious protocol for cyanoisopropylation/arylation. Moreover, this transformation could also be conducted on gram-scale.

Results and discussion

Inspired by the work of Xu,[17] who demonstrated that thermal decomposition of AIBN in CH_3NO_2 generates 2-cyanoprop-2-yl radical, which can mediate the oxidative cleavage of *gem*-disubstituted alkenes. We hypothesized that AIBN/CH_3NO_2 combined strategy, could be applied to C-H cyanoisopropylation/ cyclization of alkenes under metal-free conditions. When the reaction of *N*-arylacrylamide **1a** with AIBN (1.5 equiv.) was carried out in CH_3NO_2 at 60 °C under a N_2 atmosphere for 24 h, much to our delight the desired cyano-containing oxindole **2a** was produced in 61% yield (Table 1, entry 1). With continued use of CH_3NO_2 as solvent, a series of external oxidants, such as O_2, $K_2S_2O_8$, and $(NH_4)_2S_2O_8$ were tested, the results showed that the presence of additional oxidants in this reaction system are definitely disadvantageous (Table 1, entries 2-4). Furthermore, temperature

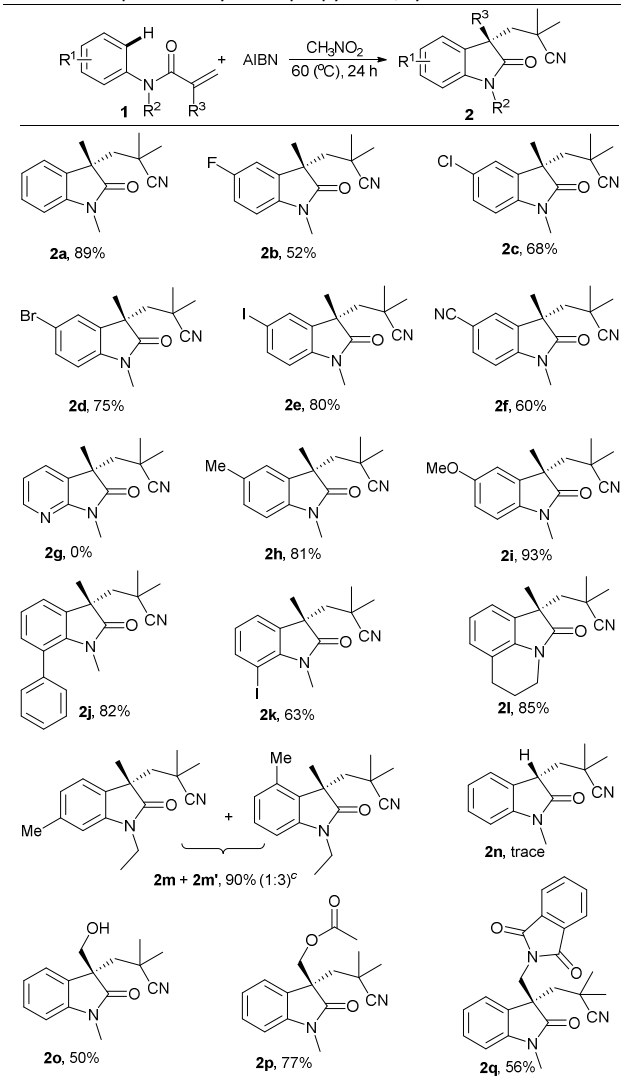
Table 1 Optimization of the reaction conditions[a]



Entry	AIBN (equiv.)	Oxidant (equiv.)	Solvent	Convn[b] (%)	Yield[c] (%)
1	1.5	none	CH_3NO_2	63	61
2	1.5	O_2 (balloon)	CH_3NO_2	10	trace
3	1.5	$K_2S_2O_8$ (2.0)	CH_3NO_2	86	58
4	1.5	$(NH_4)_2S_2O_8$ (2.0)	CH_3NO_2	85	54
5[d]	1.5	none	CH_3NO_2	52	49
6[e]	1.5	none	CH_3NO_2	68	64
7	3.0	none	CH_3NO_2	95	89
8	4.0	none	CH_3NO_2	>95	86
9	3.0	none	DMSO	>95	31
10	3.0	none	DMF	32	trace
11	3.0	none	toluene	60	15
12	3.0	none	CH_3CN	67	12

[a]Reaction conditions: *N*-arylacrylamide **1a** (0.2 mmol), solvent (1.0 mL), 60 °C, under N_2 atmosphere. [b]Conversion based on TLC analysis and amount of recovered starting material. [c]Yield of isolated product. [d]Temperature: 80 °C. [e]Reaction time: 48 h.

Table 2 Scope of the cyanoisopropylation/cyclization reaction[a,b]



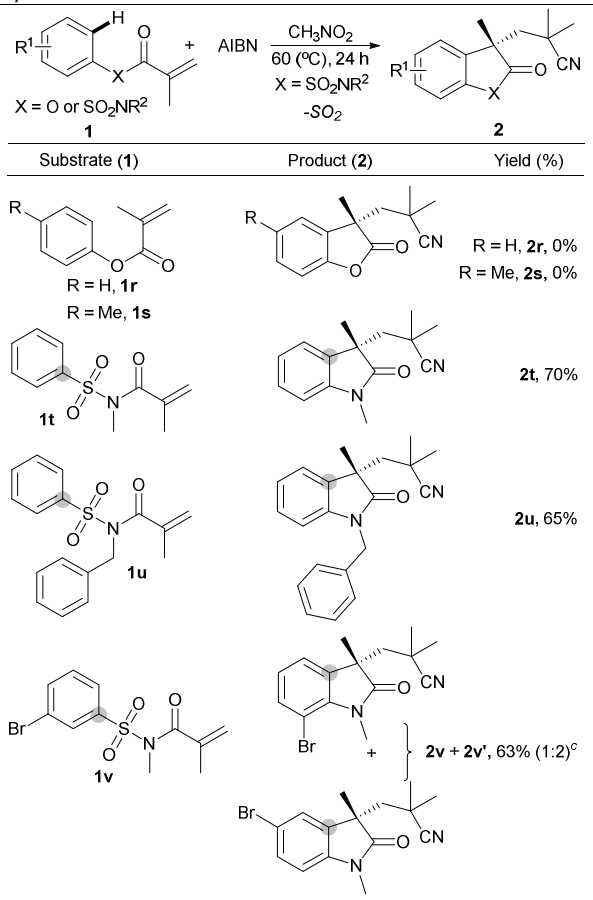
[a]Reaction conditions: *N*-arylacrylamides **1** (0.2 mmol), AIBN (0.6 mmol), and CH_3NO_2 (1.0 mL) at 60 °C under a N_2 atmosphere for 24 h. [b]Yield of isolated product. [c]Determined by ^1H NMR.

also has great influence on decomposition rate of AIBN.[18] Increasing the reaction temperature to 80 °C decreased the yield to 49% (Table 1, entry 5). Regarding the reaction time, we found that prolonging the reaction time did not improve the reaction efficiency drastically (Table 1, entry 6). The best yield (89%) was achieved when increasing the amount of AIBN to 3.0 equiv. (Table 1, entry 7), while further increase of AIBN dropped the yield (Table 1, entry 8). Encouraged by these results, various solvents such as DMSO, DMF, toluene, and CH_3CN were then screened in the presence of 3.0 equiv. of AIBN (Table 1, entries 9-12). The results showed that CH_3NO_2 to be the best choice for this transformation. In addition, when reactions performed in new, acid-washed schlenk tubes, similar yields were obtained, thereby excluding the influence of trace metals (from the old flasks) on this conversion. Finally, this reaction was repeated three times, and three runs were almost

consistent in conversions and yields (see Figure S1 in the Supporting Information). From these experiments, we determined the optimized conditions to be AIBN (3.0 equiv.), CH_3NO_2 (1.0 mL), 60 °C, N_2 atmosphere, 24 h.

With the optimized reaction conditions in hand, we first investigated the substrate scope and the limitations of the cyanoisopropylation/cyclization reaction (Table 2). Substrates with halo substitutions, such as F, Cl, Br, and I, exhibited good reactivity, generating 52-80% yields of the cyano-containing oxindoles (**2b**-**2e**). Electron-withdrawing substituents, such as a CN group, on the *N*-aryl moiety resulted in a good yield of product **2f**, whereas interestingly, *N*-pyridineacrylamide, which is a heterocyclic compound, gave no conversion at all (**2g**). To our delight, electron-donating groups, such as Me and OMe, were well-tolerated on the aryl ring, providing the corresponding products in good to high yields (**2h** and **2i**). Gratifyingly, the sterically congested *ortho*-substituted substrates were also effectively reacted with AIBN to give products **2j** and **2k** in 82% and 63% yield, respectively. Furthermore, a tetrahydroquinoline derivative was also viable as a substrate to furnish tricyclic product **2l** in 85% yield. It worth noting that substrate at which the *N*-methyl group is replaced by an ethyl substituent was also compatible with the reaction conditions. For example, substrate bearing *meta*-methyl substituent afforded a mixture of two regioselective products (**2m**/**2m'** in a ratio of 1:3). Finally, the substituent effect on olefin (at the R^3 position) was investigated. Unfortunately, mono-substituent olefin (R^3 = H), which is sensitive to this system, gave a complex mixture and only a trace amount of the desired product was detected by GC-MS (**2n**). Gratifyingly, several *α*-substituted olefins bearing different functional group, such as, alcohol (**1o**), ester (**1p**), and phthalimide (**1q**), were also compatible reaction partners in this protocol, and all reactions provided desired oxindoles **2o**-**2q** in moderate to good yields.

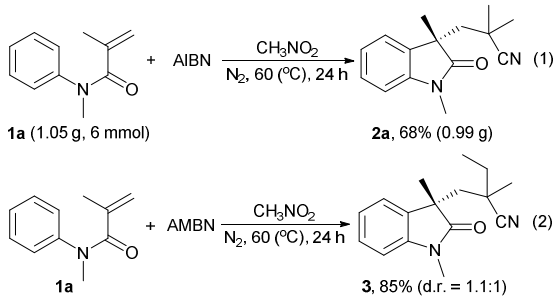
Table 3 Substrate scopes of various *N*-alkyl-*N*-(arylsulfonyl) acrylamides[a,b]



[a]Reaction conditions: *N*-alkyl-*N*-(arylsulfonyl)acrylamides **1** (0.2 mmol), AIBN (0.6 mmol), and CH_3NO_2 (1.0 mL) at 60 °C under a N_2 atmosphere for 24 h. [b]Yield of isolated product. [c]Determined by ^{1}H NMR.

Encouraged by the aforementioned cyanoisopropylation/cyclization reaction of *N*-arylacrylamides with AIBN, we next turned our attention toward expanding the substrate scope to phenyl methacrylates and *N*-alkyl-*N*-(arylsulfonyl)acrylamides (Table 3). When **1r** and **1s** were subjected to the standard reaction conditions, no desired products **2r** and **2s** were observed. Much to our surprise, the conjugated tosyl amide substrates, which underwent a cascade transformation to give CF_3-containing oxindoles using $TMSCF_3$ recently reported by Liu's group,[16o] could also be converted into the desired cyano-containing oxindoles in this metal-free system. For example, *N*-tosyl substrates bearing different substituents at the *N*-atoms were well-tolerated in this transformation, and all reactions proceeded selectively and provided corresponding desired oxindoles in good yields (**2t** and **2u**). Interestingly, when the substituent is placed at the *meta* position relative to the sulfonyl group does the reaction provides a mixture of regioisomers (**2v**/**2v'** in a ratio of 1:2), which is consistent with a certain regioselectivity of a previously reported copper-catalyzed trifluoromethylation reaction.[19]

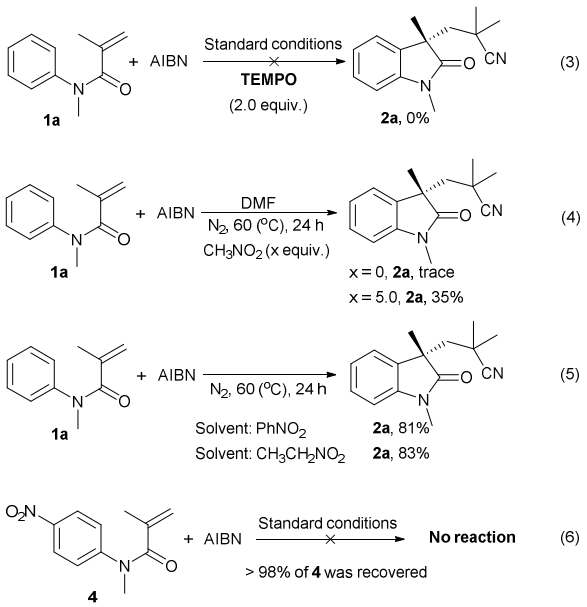
To demonstrate the preparative practicality of this metal-free reaction, we carried out the cyanoisopropylation/cyclization reaction of *N*-arylacrylamide **1a** with AIBN on a gram scale. Reaction of 1.05 g (6 mmol) of *N*-arylacrylamide **1a** with 3.0 equiv. of AIBN in CH_3NO_2 afforded **2a** in 68% (0.99 g) yield (eqn (1)). Finally, the generality of this operationally simple protocol has been further demonstrated. As shown in eqn (2), the reaction of *N*-arylacrylamide **1a** with 2,2'-(diazene-1,2-diyl)bis(2-methylbutanenitrile) (AMBN) provided the corresponding oxindole **3** in 85% yield (d.r. = 1.1:1).



Though the exact mechanism is still not clear at present, some information has been gathered. First, when 2.0 equiv. of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, a radical-trapping reagent)

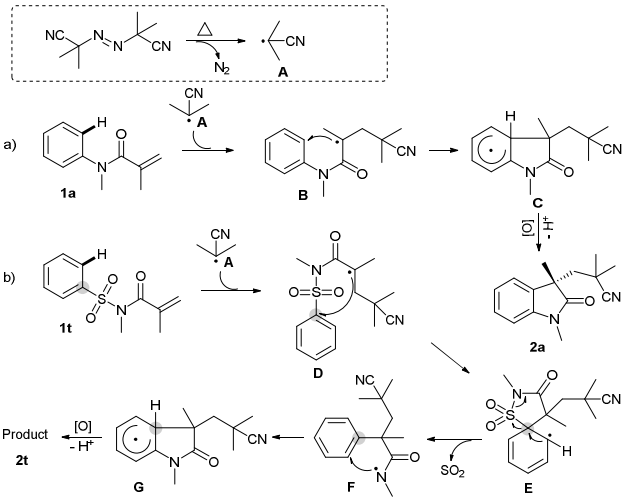
was added to the present reaction system, the cyanoisopropylation /cyclization reaction was totally suppressed (Scheme 1, eqn (3)). This observation implied that the reaction presumably underwent a radical pathway. Second, only a trace amount of **2a** was observed when the reaction performed in DMF (Table 1, entry 10). In contrast, in the presence of 5.0 equiv. of CH_3NO_2, a markedly increased yield was obtained (Scheme 1, eqn (4)). These observations confirmed the key role of CH_3NO_2 in this transformation. Since the nitro compounds such as CH_3NO_2 and $PhNO_2$ can be used as the single-electron oxidants in the field of photocatalysis,[20,21] we could not immediately rule out possible mechanisms involving the oxidation process. Hence, we reasoned that other oxidizing nitro compounds should also facilitate our transformation. Accordingly, when $PhNO_2$ and $CH_3CH_2NO_2$ were used instead of CH_3NO_2 under otherwise identical conditions, good yields of **2a** were also isolated (Scheme 1, eqn (5)). These results could provide support in favor of the above-mentioned possibility. Particularly noteworthy was that when *para*-NO_2 substituted amide **4**, which is a productive reaction partner in Wang's $CuBr/K_2S_2O_8$ catalytic oxidation system,[12] was submitted to the reaction conditions, it was recovered unchanged (Scheme 1, eqn (6)). It was suspected that the presence of a strong electron-withdrawing nitro group on the aryl ring is detrimental to the reaction process in the present reaction system.

In order to better understand the reaction mechanism, we also tried to capture more information by GC-MS analysis. More importantly, after the reaction, the potential byproduct isobutyronitrile ($CH(Me)_2CN$) was not observed. This result implied that a 2-cyanoprop-2-yl radical-related hydrogen abstraction process involved in the reaction mechanism seems unlikely.



Scheme 1 Control experiments

On the basis of these preliminary results and previous related reports, a possible mechanism for our methodology is depicted in Scheme 2. Initially, thermal decomposition of AIBN would result in the generation of radical **A** with the release of nitrogen.[17,18] Subsequently, the 2-cyanoprop-2-yl radical **A** selectively added to the carbon-carbon double bond of *N*-arylacrylamide **1a** affording radical intermediate **B**, which underwent an intramolecular radical cyclization to furnish intermediate **C**.[16,22] Further single electron oxidation of **C** by oxidizing CH_3NO_2[20] affording the corresponding carbocation which lost H^+ to produce the cyano-contained oxindole **2a** (Path a).[14,16c] On the other hand, addition of radical **A** to the carbon-carbon double bond of conjugated tosyl amide **1t** furnishes *α*-alkyl radical intermediate **D**.[16o,19,23] Subsequently, the intramolecular *ipso*-cyclization of intermediate **D** occurs to give a spirocyclic intermediate **E**.[19,23] Intermediate **E** undergoes rapid desulfonylation to selectively form a nitrogen-centered radical intermediate **F**,[16o,19,23] which had also been proposed by Zhou et al.[24] in a metal-free cascade reaction. Through further radical cyclization, this intermediate **F** would convert to cyclized radical intermediate **G**.[16o,19,24] The validity of this proposal can also be supported by the reaction results of *N*-alkyl-*N*-(arylsulfonyl)acrylamides (Table 3). Finally, the **G** would undergo single electron oxidation and proton loss ($-H^+$) processes to afford the desired product **2t** (Path b).[14,16c,20]



Scheme 2 Possible mechanism

Conclusions

In summary, we have developed a general and highly efficient synthesis approach for the cyanoisopropylation/arylation of alkenes toward the cyano-containing oxindoles under simple and mild conditions. Such a general and efficient protocol, which exhibits a broad substrate scope and good functional group compatibility, is an interesting and competitive alternative to the known approaches for preparing these highly valuable compounds. Further studies on the clarification of the reaction mechanism and application of this transformation are undergoing.

Experimental

General remarks

N-Arylacrylamides **1a**-**q** and **4**[7,25] and *N*-alkyl-*N*-(arylsulfonyl) acrylamides **1t**-**v**[19,23,26] were prepared according to literature procedures. Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. All solvents were dried and distilled prior to use according to the standard protocols. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ with TMS as internal standard (400 MHz ^{1}H, 100 MHz ^{13}C) at room temperature. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quintet), m (multiplet) and coupling constants (*J*) are reported in hertz. HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. IR measurements were performed with a FTIR SHIMADZU DR-8000 spectrometer that was fitted with a Pike Technologies MIRacle Single Reflection ATR adapter. Melting points were determined using XT-4 apparatus and are uncorrected.

General procedure for the synthesis of cyano-containing oxindoles through metal-free direct cyanoisopropylation/arylation of alkenes with AIBN

To an oven-dried Schlenk tube was added substrate **1** (0.2 mmol), AIBN (0.6 mmol), and CH_3NO_2 (1 mL). The tube was then charged with nitrogen, and the mixture was stirred at 60 ^{o}C for 24 h. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography (petroleum ether-ethyl acetate = 6:1) to give the desired product **2**.

Acknowledgements

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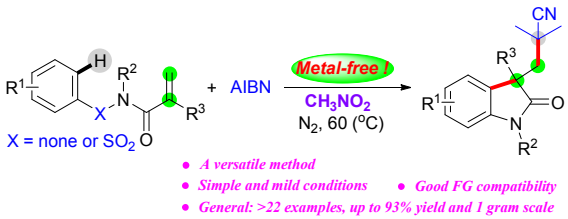
Graphic for Abstract



A general, highly efficient approach to cyano-containing oxindoles is presented that is achieved by a metal-free direct cyanoisopropylation/arylation of *N*-arylacrylamides or *N*-alkyl-*N*-(arylsulfonyl)acrylamides with AIBN.