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Effective Nitration of Anilides and Acrylamides by *tert*-Butyl Nitrite

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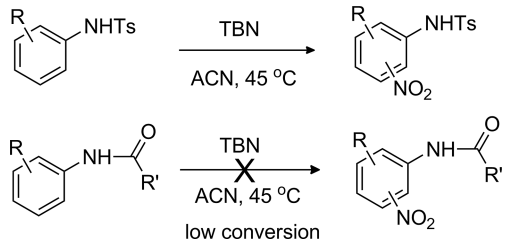
Nitro compounds are important intermediates in synthetic organic chemistry and the chemical industry. Herein, the efficient copper-catalyzed [10 % $Cu(NO_3)_2 \cdot 3H_2O$] nitration of anilides was developed by using TBN (*tert*-butyl nitrite) as a nitrating reagent to give the corresponding nitro-substituted aromatic products in good to excellent yields. The use of TBN also led to the selective nitration of acrylamides at room temperature to afford only the (*E*) isomer of the nitration product. A series of anilides and acrylamides with a broad array of functional groups were well-tolerated by this procedure. This synthetic method has many advantages, which include inexpensive starting materials, mild reaction conditions, a fast reaction rate, and high yields. A mechanistic investigation indicates that a nitro radical, which is generated from the thermal homolysis of TBN, is involved in the two nitration processes.

Introduction

Direct and selective functionalizations of alkyl, alkenyl, and aryl C–H bonds have been a long-standing challenge in synthetic chemistry.[1] The relatively low cost and ubiquity of hydrocarbons make the C–H bond functionalization an attractive alternative to classical cross-couping reactions, which usually require organohalides and organometallic reagents.[2] In addition, C–H activation provides an atom-economical synthetic strategy with a decreased production of toxic byproducts, which contributes to the growing field of reactions with decreased environmental impact.[3]

Nitroarenes and nitroolefins have been widely used as key intermediates in synthetic organic chemistry and for the generation of explosives, dyes, and pharmaceuticals.[4] The mixed acid system (HNO_3/H_2SO_4)[5] and N_2O_5[6] are usually used as the nitrating reagents in the classical electrophilic nitration reaction. However, these protocols suffer a lot of problems such as low regioselectivity, harsh reaction conditions, and limited functional group tolerance.[5,6] Therefore, mild and simple methods for a selective nitration have been the focus of such research. Several strategies such as using directing groups,[7] an *ipso*-nitration reaction,[8] the nitro-demetalation of C–B[9] and C–Li[10] bonds, and the indirect nitration of amines and azides through *ipso*-oxidation and nitro-decarboxylation[11] with high regioselectivity have been developed under mild conditions to afford nitroarenes in good yields. The syntheses of nitro-olefins have also been achieved by different methods such as the direct nitration of olefinic C–H bonds[12] or acetylene bonds[13] and the nitro-decarboxylation of aromatic α,β-unsaturated carboxylic acids.[14] However, there are much fewer reports of the selective nitration of anilides[15] and acrylamides.[16]

As a metal-free nitrating reagent, *tert*-butyl nitrite (TBN) has an advantage in being both inexpensive and easy handled. It has been shown that TBN is an effective chemoselective nitrating reagent for phenols.[17] Recently, a selective nitration of aromatic sulfonamides was achieved by using TBN as the nitrating reagent.[18] However, the nitration of aromatic amides did not occur under the same conditions (Scheme 1). Herein, we report the use of a combination of TBN and a catalytic amount of a copper salt for the efficient aryl nitration of aromatic amides (Scheme 2). This method exhibits chemoselectivity towards aryl amides in the presence of other activating functional groups. In particular, TBN leads to the exclusive alkenyl nitration of acrylamides in the absence of a metal additive even at room temperature (Scheme 2) to produce nitro-substituted olefins in high yields, which solely have the (*E*) configuration. Sub-



Scheme 1. Selective nitration of aromatic sulfonamides (Ts = *p*-tolylsulfonyl, ACN = acetonitrile).

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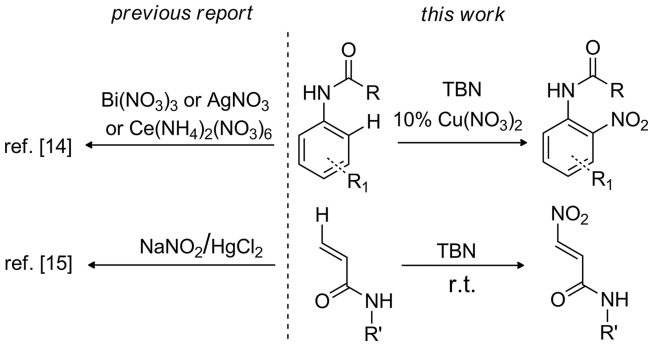
strates that contain both electron-donating and electron-withdrawing groups are well-tolerated in both of these nitration processes.



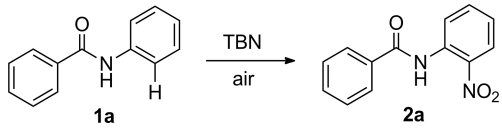
Scheme 2. Effective introduction of nitro group to aromatic rings and alkenyl units.

Results and Discussion

Initially, the nitration of *N*-phenyl benzamide (**1a**) was chosen as a model substrate, and a survey of the reaction conditions, including additives, solvents, temperature, and reaction time, was conducted in air. The reaction was first examined without any additive in CH_3CN for 12 h (Table 1, Entries 1 and 2). When the reaction temperature was increased to 80 °C, compound **2a** was detected in 23% yield (Table 1, Entry 2). If 5% of $Cu(NO_3)_2{\cdot}3H_2O$ was added, the yield of **2a** increased in 2 h to 70% (Table 1, Entry 3), whereas the addition of other metal salts such as $Cu(OAc)_2$, $CuCl_2{\cdot}2H_2O$, $CuSO_4$, CuCl $FeCl_3{\cdot}6H_2O$, and $NiCl_2{\cdot}6H_2O$ resulted in lower yields (Table 1, Entries 4–9). If the amount of the additive $Cu(NO_3)_2{\cdot}3H_2O$ was increased from 5 to 10%, the yield further improved to 76% (Table 1, Entry 10), but employing 15% of $Cu(NO_3)_2{\cdot}3H_2O$ resulted in no significant change (Table 1, Entry 11). A lower reaction temperature decelerated the reaction rate (Table 1, Entry 12). The nature of the solvent also had a dramatic effect on the yield (Table 1, Entries 13–18). CH_3CN was determined to be the best solvent (76% yield, Table 1, Entry 10), whereas the reaction did not occur in EtOH (Table 1, Entry 15). The lower yields that resulted from carrying out the reaction in $PhCH_3$ or 1,2-dichloroethane (DCE) may be a consequence of the low solubility of the catalyst in such solvents (Table 1, Entries 13 and 14).

With the optimized reaction conditions in hand, the scope of the amide substrate was investigated (Table 2). A variety of amide substrates smoothly underwent an *ortho*-nitration to generate the desired products (42–98% yield, Table 2, **2a**–**2h** and **2k**–**2t**). The *para*-substituted substrates afforded excellent yields of the *ortho*-nitration products, as the competing *para*-nitration process was prevented (Table 2, **2b**–**2d**). Substrates with an electron-donating R_1 group (Table 2, **2f** and **2g**) at the *meta* position had better reactivity than those with an electron-withdrawing group (Table 2, **2e**). An electron-withdrawing R_1 group also led to an increased yield of the *para*-nitration product. The

Table 1. Optimization of reaction conditions for *ortho*-nitration of **1a**.[a]



Entry	Additive [%]	Solvent	*T* [h]	*T* [°C][b]	% **2a**[c]
1	–	CH_3CN	12	45	trace
2	–	CH_3CN	12	80	23
3	$Cu(NO_3)_2{\cdot}3H_2O$ (5)	CH_3CN	2	80	70
4	$Cu(OAc)_2$ (5)	CH_3CN	2	80	62
5	$CuCl_2{\cdot}2H_2O$ (5)	CH_3CN	2	80	54
6	$CuSO_4$ (5)	CH_3CN	2	80	52
7	CuCl (5)	CH_3CN	2	80	46
8	$FeCl_3{\cdot}6H_2O$ (5)	CH_3CN	2	80	38
9	$NiCl_2{\cdot}6H_2O$ (5)	CH_3CN	2	80	32
10	$Cu(NO_3)_2{\cdot}3H_2O$ (10)	CH_3CN	2	80	76
11	$Cu(NO_3)_2{\cdot}3H_2O$ (15)	CH_3CN	2	80	77
12	$Cu(NO_3)_2{\cdot}3H_2O$ (10)	CH_3CN	2	60	56
13	$Cu(NO_3)_2{\cdot}3H_2O$ (10)	$PhCH_3$	2	80	29
14	$Cu(NO_3)_2{\cdot}3H_2O$ (10)	DCE	2	80	54
15	$Cu(NO_3)_2{\cdot}3H_2O$ (10)	EtOH	2	80	0
16	$Cu(NO_3)_2{\cdot}3H_2O$ (10)	DMF[d]	2	80	trace
17	$Cu(NO_3)_2{\cdot}3H_2O$ (10)	THF[d]	2	65	12
18	$Cu(NO_3)_2{\cdot}3H_2O$ (10)	DCM[d]	2	reflux	trace

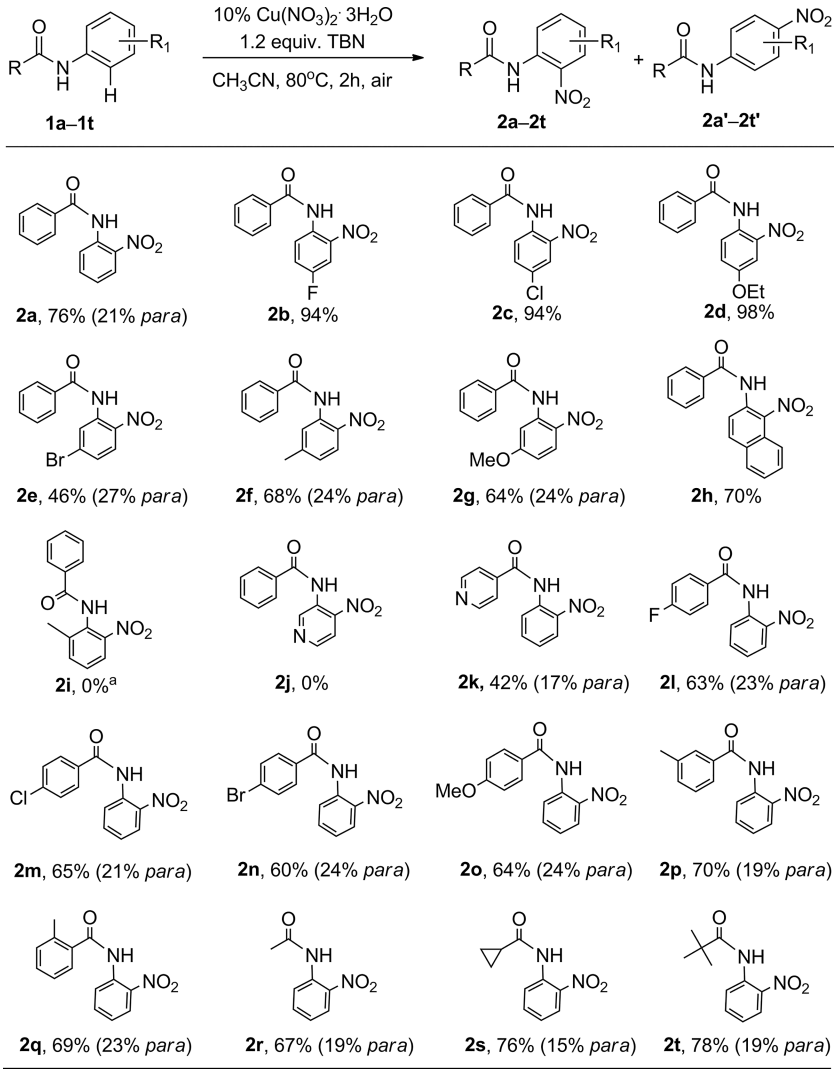
[a] Reagents and conditions: **1a** (0.2 mmol) and TBN (0.24 mmol) in solvent (3.0 mL), unless otherwise noted. [b] Oil bath temperature. [c] GC yield. The *ortho*/*para* product ratio was approximately 3:1. [d] DMF = *N*,*N*-dimethylformamide, THF = tetrahydrofuran, DCM = dichloromethane.

naphthalene ring underwent the *ortho*-nitration reaction to give the corresponding product in 70% yield (Table 2, **2h**). The steric hindrance in **1i** could inhibit its *ortho*-nitration, and its reaction led to the *para*-nitration product instead (Table 2, **2i**). The substrate that contained a pyridyl ring did not undergo the nitration (Table 2, **2j**). Substrates with different R groups (other aryl or alkyl groups) showed similar reactivity (60–78% yield, Table 2, **2l**–**2t**), but the exception was that which contained a pyridyl group for R. In this case, a lower yield resulted, even when the reaction time was increased to 24 h (42% yield, Table 2, **2k**). Thus, these anilide substrates have similar reactivities to those reported for the nitration of phenols.[17]

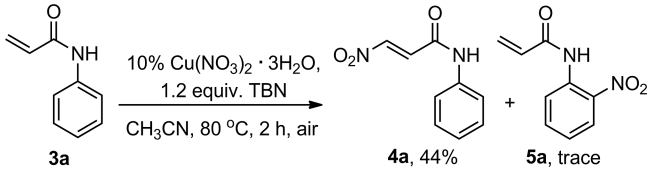
To extend the scope of the substrates, the nitration of **3a**, which contained two different sp^2-hybridized C–H bonds (i.e., the arene and the olefin), was examined under the standard reaction conditions. Surprisingly, nitration of the olefin occurred, and product **4a** was isolated in a yield of 44% with selectivity for the (*E*) isomer. Only a trace amount of *ortho*-nitration product **5a** was detected (Scheme 3). This prompted us to conduct an intensive study of this reaction to determine whether we could control the nitration to obtain a chemoselective result. However, under all of the examined reaction conditions, nitration mainly occurred at the olefinic bond.

The reaction conditions for the olefinic nitration of acrylamide were also optimized (Table 3). The addition of the copper salt $Cu(NO_3)_2{\cdot}3H_2O$ had no effect on the yield (Table 3, Entry 1 vs. 2). The yield increased to 51% when

Table 2. *ortho*-Nitration of anilide derivatives by TBN.



[a] The *para*-substituted nitration product was detected in 46% yield.

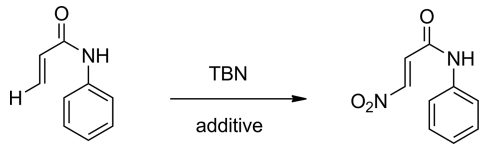


Scheme 3. A new nitration result by using **3a** as the substrate.

the amount of TBN was increased to 2.4 equiv. (Table 3, Entry 3). The nitration could also occur at room temperature to give a yield of 59% of **4a** in 2 h (Table 3, Entry 4). The increase in the yield of the product when the reaction was conducted at room temperature may result from the inhibition of any further transformation of the olefinic nitration product or the reaction intermediates. Monitoring the nitration process by TLC provided the actual reaction time of 6 h. Increasing the reaction time to 10 h gave only a slightly improved yield (Table 3, Entries 5 and 6). Different solvents were also examined. No reaction occurred in EtOH (Table 3, Entry 7). Employing DCM, THF, $PhCH_3$, or DCE resulted in lower yields (Table 3, Entries 8–11). Ultimately, CH_3CN afforded the most favorable result (73%, Table 3, Entry 5).

To explore this interesting stereoselective olefinic nitration process, the scope of the acrylamide substrate was examined. The aryl group (for R) that contained either an electron-donating or electron-withdrawing unit was well-tolerated under the reaction conditions to give the corresponding product in good yield (65–76% yield, Table 4, **4a**–**4h**). This demonstrates that the electronic properties have little effect on the nitration at the olefinic unit. The substrates that contained an alkyl group (for R) such as *n*-butyl, cyclohexyl, and *tert*-butyl gave rise to better yields (81–86% yield, Table 4, **4i**–**4k**). However, (*E*)-*N*-phenylbut-2-enamide resulted in a lower conversion (36% yield,

Table 3. Optimization of reaction conditions for olefinic nitration of **3a**.[a]



3a **4a**

Entry	Additive [%]	Solvent	*T* [h]	*T* [°C]	% **4a**
1[b]	$Cu(NO_3)_2 \cdot 3H_2O$ (10)	CH_3CN	2	80	44
2[b]	–	CH_3CN	2	80	43
3[c]	–	CH_3CN	2	80	51
4	–	CH_3CN	2	r.t.	59
5	–	CH_3CN	6	r.t.	73
6	–	CH_3CN	10	r.t.	75
7	–	EtOH	6	r.t.	0
8	–	DCE	6	r.t.	60
9	–	DCM	6	r.t.	24
10	–	THF	6	r.t.	18
11	–	$PhCH_3$	6	r.t.	31

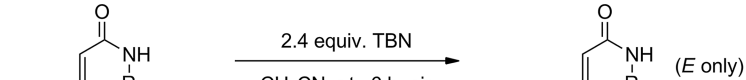
[a] Reagents and conditions: **3a** (0.2 mmol) and TBN (0.48 mmol) in solvent (3.0 mL), unless otherwise noted. [b] TBN (1.2 equiv.) was used. [c] TBN (2.4 equiv.) was used.

Table 4, **4l**), even with an increased temperature (40 °C) and longer reaction time (24 h). The unsubstituted acrylamide afforded **4m** in good yield (79% yield, Table 4).

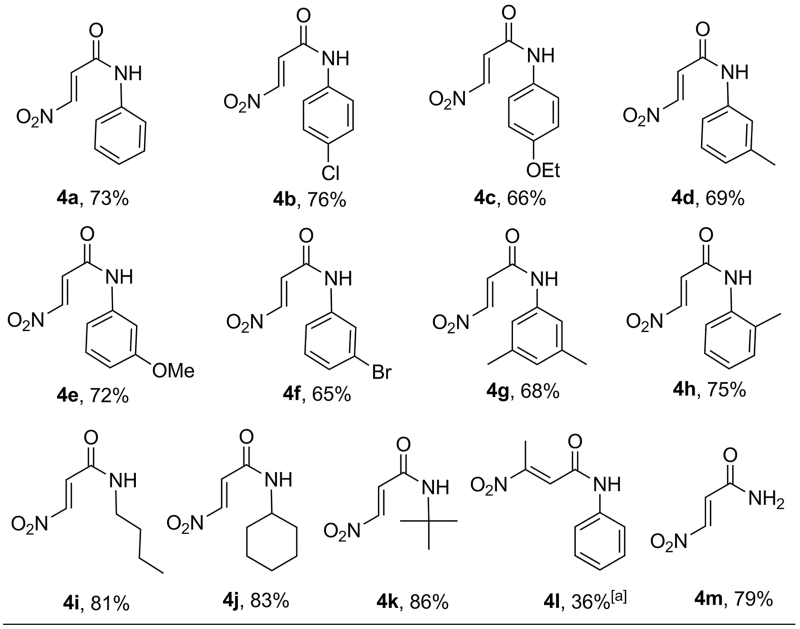
To gain insight into the two nitration processes, radical capture experiments were performed. The radical trapping reagent TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) was employed in individual nitration reactions that led to only 9% of **2a** or 4% of **4a** [Scheme 4, Equations (1) and (2)]. If the radical trapping reagent 1,1-diphenylethene was used, **2a** and **4a** were not detected, but instead adduct **4n** with a nitro group and 1,1-diphenylethene unit was isolated in almost quantitative yields in both cases, as confirmed by NMR, MS, and X-ray crystal structure analyses [Scheme 4, Equations (3) and (4) and Supporting Information]. These experiments demonstrate that the two processes may proceed by radical mechanisms with the existence of a nitro radical. Additionally, no nitration occurred when an *N*-methyl-protected anilide was used [Scheme 4, Equation (5)]. N-substitution may prevent the formation of an anilide radical intermediate (according to Arn's mechanism[18]) upon the one-electron oxidation by the Cu^{II} species.

On the basis of above experimental evidence and related literature,[12,19–22] the plausible reaction mechanisms of these nitration processes are proposed in Scheme 5. First, TBN undergoes a thermal homolysis to liberate the alkoxyl and nitric oxide radicals.[19] Then NO· is oxidized by air to afford NO_2·.[20] In the arene nitration process, it is assumed that the initial one-electron oxidation of the anilide by copper(II) results in the formation of anilide radical **A**.[21] Subsequently, **A** undergoes a reversible transformation followed by the attack of the NO_2 radical at the *ortho* or *para* positions of the aromatic ring to generate the corresponding nitration products.[22] In the olefin nitration process, according to Jiao's work,[20c] NO_2· attacks the alkenyl unit

Table 4. Olefinic nitration of acrylamide derivatives.



3a–3m **4a–4m**

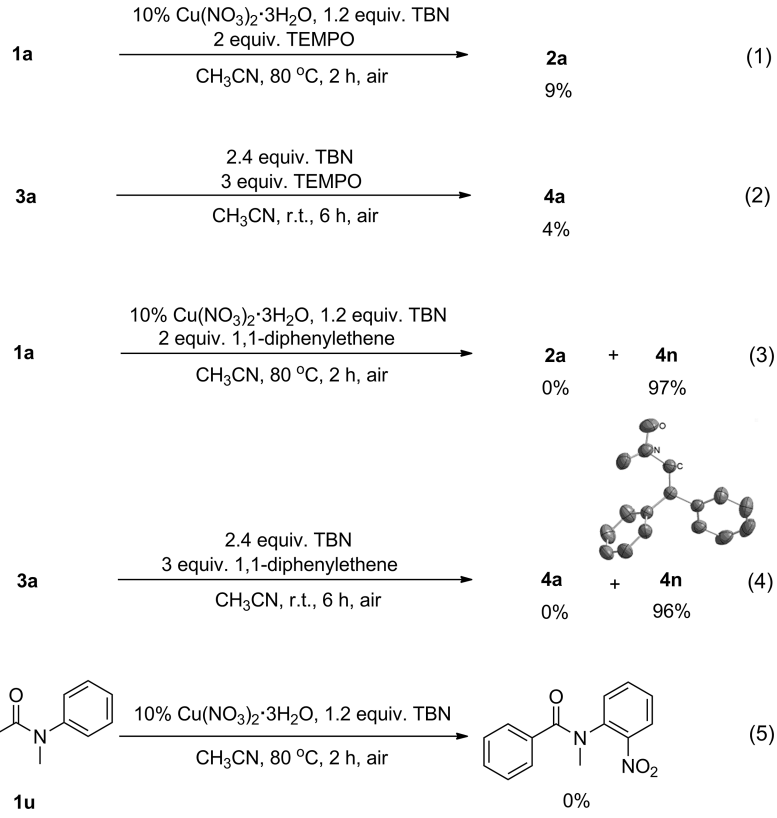


4a, 73% **4b**, 76% **4c**, 66% **4d**, 69%

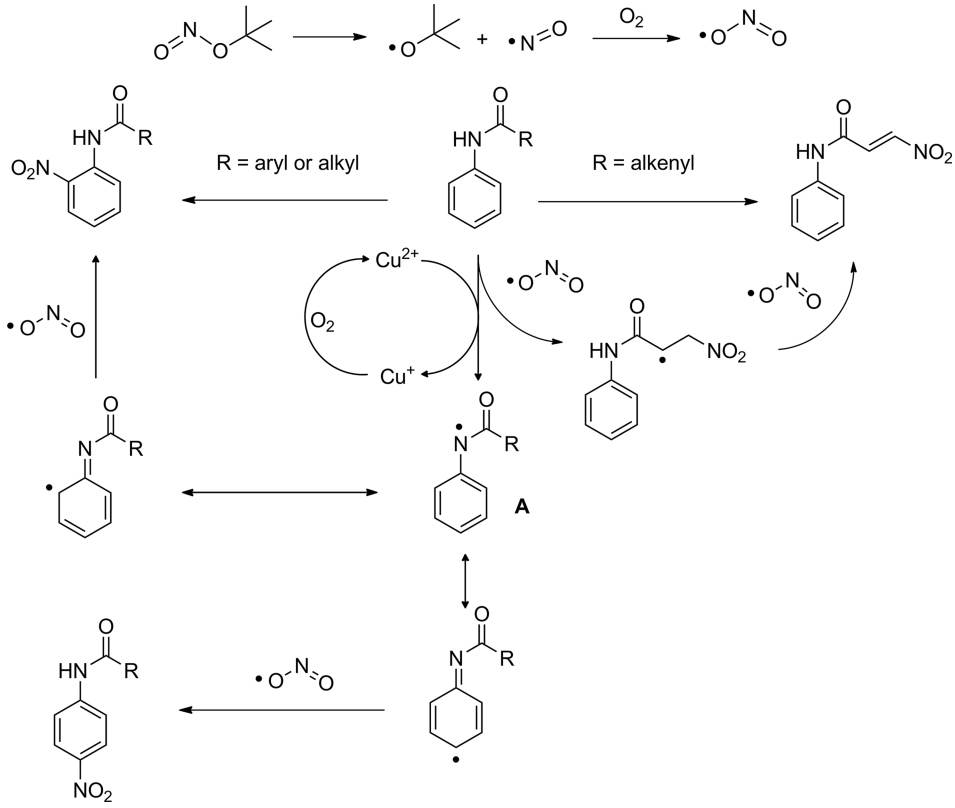
4e, 72% **4f**, 65% **4g**, 68% **4h**, 75%

4i, 81% **4j**, 83% **4k**, 86% **4l**, 36%[a] **4m**, 79%

[a] Reaction conditions: 40 °C, 24 h.



Scheme 4. Control experiments for reaction mechanisms.



Scheme 5. Plausible mechanisms.

followed by an *anti* elimination[12] in the presence of another nitro radical to yield the nitro-substituted olefin stereoselectively.[23]

Conclusions

The efficient aromatic nitration of anilides by using the combination of TBN as the nitrating reagent and Cu^{II} nitrate (10%) has been developed to give the corresponding products in good to excellent yields. In particular, the olefinic nitration of acrylamide derivatives occurred selectively to give products with the (*E*) configuration in high yields, even when the reaction was carried out at room temperature and by using only TBN. Both nitration processes use air as an oxidant and tolerate a wide variety of functional groups. This stereoselective olefinic nitration might be useful in the synthesis of complex chiral molecules. Further studies to refine the mechanisms and extend the synthetic scope of these reactions are still underway.

Experimental Section

General Procedure for the Synthesis of Amides:[24] The amine (1.0 mmol, 1.0 equiv.), acyl chloride (1.0 mmol, 1.0 equiv.), THF (5.0 mL), and Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv.) were added to a tube open to air. The reaction mixture was heated in an oil bath at 65 °C for 6 h. Then, H_2O (5.0 mL) was added. The reaction mixture was extracted with ethyl acetate. The organic layers were combined, and the organic solvent was removed in vacuo. The resulting residue was purified by flash chromatography on a silica gel column to afford the product.

General Procedure for the Synthesis of Products 2a–2t and 2a′–2t′: The amide (0.20 mmol, 1.0 equiv.), $Cu(NO_3)_2{\cdot}3H_2O$ (4.8 mg, 0.02 mmol, 0.1 equiv.), TBN (0.029 mL, 0.24 mmol, 1.2 equiv.), and CH_3CN (3.0 mL) were added to a tube open to air. The resulting mixture was heated in an oil bath at 80 °C for 2 h, and the progress of the reaction was monitored by TLC. After cooling the mixture to room temperature, the volatiles were removed in vacuo, and the residue was purified by flash column chromatography on silica gel (petroleum/ethyl acetate) to afford the *ortho*- (42–98% yield) and *para*-nitration (15–46% yield) products.

General Procedure for the Synthesis of Products 4a–4m: The amide (0.20 mmol, 1.0 equiv.), TBN (0.058 mL, 0.48 mmol, 2.4 equiv.), and CH_3CN (3 mL) were added to a tube open to air. The resulting mixture was stirred at room temperature for 6 h, and the progress of the reaction was monitored by TLC. The volatiles were then removed in vacuo, and the residue was purified by flash column chromatography on silica gel (petroleum/ethyl acetate) to afford the alkenyl nitration product (36–86% yield).

Procedure for the Control Experiment: See Scheme 4, Equation (1). Compound **1a** (39.4 mg, 0.20 mmol, 1.0 equiv.), $Cu(NO_3)_2{\cdot}3H_2O$ (4.8 mg, 0.02 mmol, 0.1 equiv.), TBN (0.029 mL, 0.24 mmol, 1.2 equiv.), TEMPO (62.4 mg, 0.4 mmol, 2.0 equiv.), and CH_3CN (3.0 mL) were added to a tube open to air. The resulting mixture was heated in an oil bath at 80 °C for 2 h, and the progress of the reaction was monitored by TLC. After cooling the mixture to room temperature, the volatiles were removed in vacuo, and the residue was purified by flash column chromatography on silica gel (petroleum/ethyl acetate) to afford product **2a** (9% yield) with 82% of unreacted **1a**.

Procedure for the Control Experiment: See Scheme 4, Equation (2). Compound **3a** (29.4 mg, 0.20 mmol, 1.0 equiv.), TBN (0.058 mL, 0.48 mmol, 2.4 equiv.), TEMPO (93.6 mg, 0.6 mmol, 3.0 equiv.), and CH_3CN (3 mL) were added to a tube open to air. The resulting mixture was stirred at room temperature for 6 h, and the progress of the reaction was monitored by TLC. The volatiles were removed in vacuo, and the residue was purified by flash column chromatography on silica gel (petroleum/ethyl acetate) to afford product **4a** (4% yield) with 89% of unreacted **3a** .

Procedure for the Control Experiment: See Scheme 4, Equation (3). Compound **1a** (39.4 mg, 0.20 mmol, 1.0 equiv.), $Cu(NO_3)_2{\cdot}3H_2O$ (4.8 mg, 0.02 mmol, 0.1 equiv.), TBN (0.029 mL, 0.24 mmol, 1.2 equiv.), 1,1-diphenylethene (0.070 mL, 0.4 mmol, 2.0 equiv.), and CH_3CN (3.0 mL) were added to a tube open to air. The resulting mixture was heated in an oil bath at 80 °C for 2 h, and the progress of the reaction was monitored by TLC. After cooling the mixture to room temperature, the volatiles were removed in vacuo, and the residue was purified by flash column chromatography on silica gel (petroleum/ethyl acetate) to afford (2-nitroethene-1,1-diyl)-dibenzene (**4n**, 97% yield). Compound **2a** (0%) was not detected, but 96% of compound **1a** was isolated.

Procedure for the Control Experiment: See Scheme 4, Equation (4). Compound **3a** (29.4 mg, 0.20 mmol, 1.0 equiv.), TBN (0.029 mL, 0.24 mmol, 1.2 equiv.), 1,1-diphenylethene (0.105 mL, 0.6 mmol, 3.0 equiv.), and CH_3CN (3 mL) were added to a tube open to air. The resulting mixture was stirred at room temperature for 6 h, and the progress of the reaction was monitored by TLC. The volatiles were removed in vacuo, and the residue was purified by flash column chromatography on silica gel (petroleum/ethyl acetate) to afford (2-nitroethene-1,1-diyl)dibenzene (**4n**, 96% yield). Compound **4a** (0%) was not detected, but 95% of compound **3a** was isolated.

Procedure for the Control Experiment: See Scheme 4, Equation (5). Compound **1u** (42.2 mg, 0.20 mmol, 1.0 equiv.), $Cu(NO_3)_2{\cdot}3H_2O$ (4.8 mg, 0.02 mmol, 0.1 equiv.), TBN (0.029 mL, 0.24 mmol, 1.2 equiv.), and CH_3CN (3.0 mL) were added to a tube open to air. The reaction mixture was heated in an oil bath at 80 °C for 2 h. No nitration products were detected.

Compound Characterizations

***N*-(2-Nitrophenyl)benzamide (2a) and *N*-(4-Nitrophenyl)benzamide (2a′):** Data for **2a**: Yellow solid (76% yield); R_f = 0.76 (petroleum ether/ethyl acetate, 8:1 v/v). ^1H NMR (400 MHz, $CDCl_3$): δ = 11.36 (s, 1 H, NH), 9.03 (d, J = 8.6 Hz, 1 H, ArNH), 8.30 (d, J = 10.0 Hz, 1 H, ArNH), 8.01 (d, J = 7.1 Hz, 2 H, ArCO), 7.73 (t, J = 8.6 Hz, 1 H, ArNH), 7.62 (t, J = 8.6 Hz, 1 H, ArCO), 7.56 (dd, J = 8.6, 7.1 Hz, 2 H, ArCO), 7.24 (dd, J = 10.0, 8.6 Hz, 1 H, ArNH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 136.5, 136.2, 135.4, 134.0, 132.7, 129.1, 127.4, 125.9, 123.3, 122.1 ppm. HRMS (ESI): calcd. for $C_{13}H_9N_2O_3$ $[M - H]^-$ 241.0613; found 241.0631.

Data for **2a′**: White solid (21% yield); R_f = 0.42 (petroleum ether/ethyl acetate, 8:1 v/v). This is a known compound.[25] ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 10.82 (s, 1 H, NH), 8.27 (d, J = 9.3 Hz, 2 H, ArCO), 8.04 (d, J = 9.3 Hz, 2 H, ArNH), 7.97 (d, J = 7.4 Hz, 2 H, ArNH), 7.61 (t, J = 7.4 Hz, 1 H, ArCO), 7.54 (t, J = 7.4 Hz, 2 H, ArCO) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 166.3, 145.5, 142.9, 134.4, 132.3, 128.9, 128.5, 124.2, 119.6 ppm. HRMS (ESI): calcd. for $C_{13}H_9N_2O_3$ $[M - H]^-$ 241.0613; found 241.0632.

***N*-(4-Fluoro-2-nitrophenyl)benzamide (2b):** Yellow solid (94% yield); R_f = 0.70 (petroleum ether/ethyl acetate, 8:1 v/v). ^1H NMR

(500 MHz, $CDCl_3$): δ = 11.21 (s, 1 H, NH), 9.06 (dd, J = 9.4, 5.1 Hz, 1 H, ArNH), 7.98–8.03 (m, 3 H, ArNH and ArCO), 7.63 (t, J = 7.5 Hz, 1 H, ArCO), 7.56 (t, J = 7.5 Hz, 2 H, ArCO), 7.48 (t, J = 9.4 Hz, 1 H, ArNH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.7, 157.0 (d, J = 247.9 Hz), 136.6 (d, J = 9.3 Hz), 133.8, 132.8, 132.0, 129.1, 127.3, 124.0 (d, J = 7.2 Hz), 123.7 (d, J = 22.1 Hz), 112.43 (d, J = 27.2 Hz) ppm. HRMS (ESI): calcd. for $C_{13}H_8FN_2O_3$ $[M - H]^-$ 259.0519; found 259.0538.

***N*-(4-Chloro-2-nitrophenyl)benzamide (2c):** Yellow solid (94% yield); R_f = 0.72 (petroleum ether/ethyl acetate, 8:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 11.28 (s, 1 H, NH), 9.04 (d, J = 9.1 Hz, 1 H, ArNH), 8.29 (s, 1 H, ArNH), 7.99 (d, J = 7.1 Hz, 2 H, ArCO), 7.68 (d, J = 9.1 Hz, 1 H, ArNH), 7.64 (t, J = 7.1 Hz, 1 H, ArCO), 7.56 (t, J = 7.1 Hz, 2 H, ArCO) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.7, 136.6, 136.1, 134.0, 133.7, 132.9, 129.1, 128.5, 127.4, 125.5, 123.4 ppm. HRMS (ESI): calcd. for $C_{13}H_8ClN_2O_3$ $[M - H]^-$ 275.0224; found 275.0244.

***N*-(4-Ethoxy-2-nitrophenyl)benzamide (2d):** Yellow solid (98% yield); R_f = 0.79 (petroleum ether/ethyl acetate, 8:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 11.10 (s, 1 H, NH), 8.89 (d, J = 9.3 Hz, 1 H, ArNH), 7.99 (d, J = 7.4 Hz, 2 H, ArCO), 7.74 (s, 1 H, ArNH), 7.61 (t, J = 7.4 Hz, 1 H, ArCO), 7.54 (t, J = 7.4 Hz, 2 H, ArCO), 7.30 (d, J = 9.3 Hz, 1 H, ArNH), 4.11 (q, J = 6.9 Hz, 2 H, CH_2), 1.47 (t, J = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.6, 154.4, 137.1, 134.2, 132.4, 129.0, 128.9, 127.3, 124.0, 123.6, 109.4, 64.4, 14.6 ppm. HRMS (ESI): calcd. for $C_{15}H_{13}N_2O_4$ $[M - H]^-$ 285.0876; found 285.0891.

***N*-(5-Bromo-2-nitrophenyl)benzamide (2e) and *N*-(3-Bromo-4-nitrophenyl)benzamide (2e′):** Data for **2e**: Yellow solid (46% yield); R_f = 0.74 (petroleum ether/ethyl acetate, 6:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 11.42 (s, 1 H, NH), 9.33 (s, 1 H, ArNH), 8.17 (d, J = 9.0 Hz, 1 H, ArNH), 8.00 (d, J = 7.5 Hz, 2 H, ArCO), 7.64 (t, J = 7.5 Hz, 1 H, ArCO), 7.57 (t, J = 7.5 Hz, 2 H, ArCO), 7.36 (d, J = 9.0 Hz, 1 H, ArNH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.7, 136.2, 135.0, 133.6, 132.9, 131.7, 129.1, 127.4, 127.0, 126.5, 124.7 ppm. HRMS (ESI): calcd. for $C_{13}H_8BrN_2O_3$ $[M - H]^-$ 318.9719; found 318.9738. Data for **2e′**: Light yellow solid (27% yield); R_f = 0.38 (petroleum ether/ethyl acetate, 6:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.19 (s, 1 H, ArNH), 8.04 (s, 1 H, NH), 8.01 (d, J = 8.9 Hz, 1 H, ArNH), 7.88 (d, J = 7.6 Hz, 2 H, ArCO), 7.78 (d, J = 8.9 Hz, 1 H, ArNH), 7.63 (t, J = 7.6 Hz, 1 H, ArCO), 7.53 (d, J = 7.6 Hz, 2 H, ArCO) ppm. ^{13}C NMR (125 MHz, [D$_6$]acetone): δ = 167.1, 145.4, 144.9, 135.1, 133.2, 129.5, 128.6, 127.8, 125.8, 119.9, 115.4 ppm. HRMS (ESI): calcd. for $C_{13}H_8BrN_2O_3$ $[M - H]^-$ 318.9719; found 318.9739.

***N*-(5-Methyl-2-nitrophenyl)benzamide (2f) and *N*-(3-Methyl-4-nitrophenyl)benzamide (2f′):** Data for **2f**: Yellow solid (68% yield); R_f = 0.69 (petroleum ether/ethyl acetate, 8:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 11.45 (s, 1 H, NH), 8.86 (s, 1 H, ArNH), 8.19 (d, J = 8.5 Hz, 1 H, ArNH), 8.01 (d, J = 7.2 Hz, 2 H, ArCO), 7.62 (t, J = 7.2 Hz, 1 H, ArCO), 7.56 (t, J = 7.2 Hz, 2 H, ArCO), 7.03 (d, J = 8.5 Hz, 1 H, ArNH), 2.50 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.8, 148.3, 135.3, 134.4, 134.1, 132.6, 129.0, 127.4, 125.9, 124.3, 122.0, 22.2 ppm. HRMS (ESI): calcd. for $C_{14}H_{11}N_2O_3$ $[M - H]^-$ 255.0770; found 255.0786. Data for **2f′**: White solid (24% yield); R_f = 0.31 (petroleum ether/ethyl acetate, 8:1 v/v). ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 10.07 (s, 1 H, NH), 8.07 (d, J = 8.7 Hz, 1 H, ArNH), 8.02 (d, J = 7.5 Hz, 2 H, ArCO), 7.92–7.97 (m, 2 H, ArNH), 7.61 (t, J = 7.5 Hz, 1 H, ArCO), 7.53 (t, J = 7.5 Hz, 2 H, ArCO), 2.60 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]acetone): δ = 167.0, 145.0, 144.7, 135.9, 135.5, 132.9, 129.4, 128.6, 126.9, 123.7, 118.6, 21.2 ppm. HRMS (ESI): calcd. for $C_{14}H_{11}N_2O_3$ $[M - H]^-$ 255.0770; found 255.0787.

***N*-(5-Methoxy-2-nitrophenyl)benzamide (2g) and *N*-(3-Methoxy-4-nitrophenyl)benzamide (2g′):** Data for **2g**: Yellow solid (64% yield); R_f = 0.79 (petroleum ether/ethyl acetate, 8:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 11.83 (s, 1 H, NH), 8.69 (s, 1 H, ArNH), 8.28 (d, J = 9.4 Hz, 1 H, ArNH), 8.02 (d, J = 7.3 Hz, 2 H, ArCO), 7.63 (t, J = 7.3 Hz, 1 H, ArCO), 7.56 (t, J = 7.3 Hz, 2 H, ArCO), 6.72 (d, J = 9.4 Hz, 1 H, ArNH), 3.98 (s, 3 H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.1, 165.9, 138.3, 134.0, 132.7, 129.7, 129.1, 128.2, 127.4, 111.1, 104.1, 56.2 ppm. HRMS (ESI): calcd. for $C_{14}H_{11}N_2O_4$ $[M - H]^-$ 271.0719; found 271.0739. Data for **2g′**: White solid (24% yield); R_f = 0.43 (petroleum ether/ethyl acetate, 8:1 v/v). ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 10.11 (s, 1 H, NH), 7.93–8.05 (m, 4 H, ArCO and ArNH), 7.95 (d, J = 9.0 Hz, 1 H, ArNH), 7.62 (t, J = 7.4 Hz, 1 H, ArCO), 7.58–7.49 (m, 3 H, ArCO and ArNH), 3.98 (s, 3 H, OMe) ppm. ^{13}C NMR (125 MHz, [D$_6$]acetone): δ = 167.1, 155.1, 146.1, 135.5, 135.4, 133.0, 129.5, 128.6, 127.5, 111.9, 105.2, 56.9 ppm. HRMS (ESI): calcd. for $C_{14}H_{11}N_2O_4$ $[M - H]^-$ 271.0719; found 271.0737.

***N*-(1-Nitronaphthalen-2-yl)benzamide (2h):** Yellow solid (70% yield); R_f = 0.74 (petroleum ether/ethyl acetate, 8:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.85 (s, 1 H, NH), 8.05–8.15 (m, 4 H, ArCO and ArNH), 7.94 (d, J = 8.2 Hz, 1 H, ArNH), 7.88 (d, J = 9.0 Hz, 1 H, ArNH), 7.71 (t, J = 7.3 Hz, 1 H, ArNH), 7.60–7.69 (m, 2 H, ArCO and ArNH), 7.59 (t, J = 7.6 Hz, 2 H, ArCO) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.5, 140.7, 136.1, 133.3, 132.8, 131.1, 129.8, 129.0, 128.9, 128.2, 127.7, 127.7, 127.5, 127.2, 120.2 ppm. HRMS (ESI): calcd. for $C_{17}H_{11}N_2O_3$ $[M - H]^-$ 291.0770; found 291.0790.

***N*-(2-Methyl-4-nitrophenyl)benzamide (2i′):** White solid (47% yield); R_f = 0.50 (petroleum ether/ethyl acetate, 6:1 v/v). ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 8.13 (s, 1 H, ArNH), 8.03 (d, J = 7.1 Hz, 2 H, ArCO), 7.84 (d, J = 7.6 Hz, 1 H, ArNH), 7.68 (d, J = 7.6 Hz, 1 H, ArNH), 7.62 (t, J = 7.1 Hz, 2 H, ArCO), 7.55 (d, J = 7.1 Hz, 2 H, ArCO), 2.42 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, [D$_6$]acetone): δ = 166.5, 143.9, 139.4, 135.9, 135.0, 133.0, 132.8, 129.5, 128.5, 127.9, 123.3, 18.4 ppm. HRMS (ESI): calcd. for $C_{14}H_{11}N_2O_3$ $[M - H]^-$ 255.0770; found 255.0787.

***N*-(2-Nitrophenyl)isonicotinamide (2k) and *N*-(4-Nitrophenyl)isonicotinamide (2k′):** Data for **2k**: Yellow solid (42% yield); R_f = 0.63 (petroleum ether/ethyl acetate, 6:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 11.46 (s, 1 H, NH), 8.99 (d, J = 8.5 Hz, 1 H, ArNH), 8.89 (d, J = 6.0 Hz, 2 H, pyridine), 8.33 (d, J = 7.8 Hz, 1 H, ArNH), 7.84 (d, J = 6.0 Hz, 2 H, pyridine), 7.77 (t, J = 7.8 Hz, 1 H, ArNH), 7.30 (t, J = 8.5 Hz, 1 H, ArNH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.8, 151.1, 141.1, 136.6, 136.4, 134.6, 126.1, 124.1, 122.2, 120.9 ppm. HRMS (ESI): calcd. for $C_{12}H_8N_3O_3$ $[M - H]^-$ 242.0566; found 242.0582. Data for **2k′**: White solid (17% yield); R_f = 0.31 (petroleum ether/ethyl acetate, 6:1 v/v). This is a known compound.[26] ^{1}H NMR (500 MHz, [D$_6$]-DMSO): δ = 11.05 (s, 1 H), 8.84 (dd, J = 4.8, 1.5 Hz, 2 H, pyridine), 8.28 (d, J = 9.2 Hz, 2 H, ArNH), 8.04 (d, J = 9.2 Hz, 2 H, ArNH), 7.86 (dd, J = 4.8, 1.5 Hz, 2 H, pyridine) ppm. HRMS (ESI): calcd. for $C_{12}H_8N_3O_3$ $[M - H]^-$ 242.0566; found 242.0584.

4-Fluoro-*N*-(2-nitrophenyl)benzamide (2l) and 4-Fluoro-*N*-(4-nitrophenyl)benzamide (2l′): Data for **2l**: Yellow solid (63% yield); R_f = 0.77 (petroleum ether/ethyl acetate, 8:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 11.31 (s, 1 H, NH), 8.97 (d, J = 8.5 Hz, 1 H, ArNH), 8.28 (d, J = 8.5 Hz, 1 H, ArNH), 8.02 (dd, J = 8.0, 5.4 Hz, 2 H, ArCO), 7.72 (dd, J = 8.5, 8.0 Hz, 1 H, ArNH), 7.26–7.19 (m, 3 H, ArCO and ArNH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.4 (d, J = 250.0 Hz), 164.6, 136.5, 136.2, 135.2,

130.2, 129.8 (d, J = 8.8 Hz), 125.9, 123.4, 122.1, 116.2 (d, J = 22.5 Hz) ppm. HRMS (ESI): calcd. for $C_{13}H_8FN_2O_3$ [M – H]$^-$ 259.0519; found 259.0534. Data for **2l′**: White solid (23% yield); R_f = 0.39 (petroleum ether/ethyl acetate, 8:1 v/v). This is a known compound.[27] ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.81 (s, 1 H, NH), 8.21–8.42 (m, 2 H, Ph), 7.95–8.19 (m, 4 H, Ph), 7.38–7.47 (m, 2 H, Ph) ppm. HRMS (ESI): calcd. for $C_{13}H_8FN_2O_3$ [M – H]$^-$ 259.0519; found 259.0532.

4-Chloro-*N*-(2-nitrophenyl)benzamide (2m) and 4-Chloro-*N*-(4-nitrophenyl)benzamide (2m′): Data for **2m**: Yellow solid (65% yield); R_f = 0.69 (petroleum ether/ethyl acetate, 8:1 v/v). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 11.35 (s, 1 H, NH), 8.99 (d, J = 8.5 Hz, 1 H, ArNH), 8.30 (d, J = 9.8 Hz, 1 H, ArNH), 7.95 (d, J = 8.6 Hz, 2 H, ArCO), 7.73 (dd, J = 8.5, 8.0 Hz, 1 H, ArNH), 7.53 (d, J = 8.6 Hz, 2 H, ArCO), 7.25 (dd, J = 9.8, 8.0 Hz, 1 H, ArNH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 164.7, 139.1, 136.5, 136.3, 135.1, 132.4, 129.3, 128.8, 126.0, 123.5, 122.1 ppm. HRMS (ESI): calcd. for $C_{13}H_8ClN_2O_3$ [M – H]$^-$ 275.0224; found 275.0242. Data for **2m′**: Light yellow solid (21% yield); R_f = 0.35 (petroleum ether/ethyl acetate, 8:1 v/v). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.28 (d, J = 8.8 Hz, 2 H, Ar), 8.08 (s, 1 H, NH), 7.85 (m, 4 H, Ar), 7.52 (d, J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR (125 MHz, [D$_6$]acetone): δ = 164.7, 143.9, 143.5, 139.0, 132.3, 129.3, 128.6, 125.2, 119.5 ppm. HRMS (ESI): calcd. for $C_{13}H_8ClN_2O_3$ [M – H]$^-$ 275.0224; found 275.0241.

4-Bromo-*N*-(2-nitrophenyl)benzamide (2n) and 4-Bromo-*N*-(4-nitrophenyl)benzamide (2n′): Data for **2n**: Yellow solid (60% yield); R_f = 0.67 (petroleum ether/ethyl acetate, 8:1 v/v). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 11.34 (s, 1 H, NH), 8.98 (d, J = 8.3 Hz, 1 H, ArNH), 8.30 (d, J = 8.3 Hz, 1 H, ArNH), 7.87 (d, J = 7.9 Hz, 2 H, ArCO), 7.73 (t, J = 8.3 Hz, 1 H, ArNH), 7.69 (d, J = 7.9 Hz, 2 H, ArCO), 7.25 (t, J = 8.3 Hz, 1 H, ArNH) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 164.8, 136.5, 136.3, 135.1, 132.9, 132.3, 128.9, 127.6, 126.0, 123.5, 122.1 ppm. HRMS (ESI): calcd. for $C_{13}H_8BrN_2O_3$ [M – H]$^-$ 318.9719; found 318.9737. Data for **2n′**: Light yellow solid (24% yield); R_f = 0.32 (petroleum ether/ethyl acetate, 8:1 v/v). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.28 (d, J = 9.4 Hz, 2 H, Ar), 8.12 (d, J = 9.4 Hz, 2 H, Ar), 7.99 (d, J = 8.7 Hz, 2 H, Ar), 7.74 (d, J = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 166.2, 146.1, 144.2, 134.5, 132.6, 130.6, 127.1, 125.5, 120.7 ppm. HRMS (ESI): calcd. for $C_{13}H_8BrN_2O_3$ [M – H]$^-$ 318.9719; found 318.9738.

4-Methoxy-*N*-(2-nitrophenyl)benzamide (2o) and 4-Methoxy-*N*-(4-nitrophenyl)benzamide (2o′): Data for **2o**: Yellow solid (64% yield); R_f = 0.68 (petroleum ether/ethyl acetate, 8:1 v/v). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 11.31 (s, 1 H, NH), 9.02 (d, J = 8.5 Hz, 1 H, ArNH), 8.29 (d, J = 8.5 Hz, 1 H, ArNH), 7.98 (d, J = 8.8 Hz, 2 H, ArCO), 7.72 (t, J = 8.5 Hz, 1 H, ArNH), 7.21 (t, J = 8.5 Hz, 1 H, ArNH), 7.04 (d, J = 8.8 Hz, 2 H, ArCO), 3.91 (s, 3 H, OMe) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 165.3, 163.2, 136.3, 136.2, 135.7, 129.4, 126.2, 125.9, 123.0, 122.1, 114.3, 55.5 ppm. HRMS (ESI): calcd. for $C_{14}H_{11}N_2O_4$ [M – H]$^-$ 271.0719; found 271.0736. Data for **2o′**: White solid (24% yield); R_f = 0.39 (petroleum ether/ethyl acetate, 8:1 v/v). This is a known compound.[27] ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.64 (s, 1 H, NH), 8.21–8.42 (m, 2 H, Ar), 8.06–8.13 (m, 2 H, Ar), 7.93–8.05 (m, 2 H, Ar), 6.97–7.23 (m, 2 H, Ar), 3.86 (s, 3 H, OMe) ppm. HRMS (ESI): calcd. for $C_{14}H_{11}N_2O_4$ [M – H]$^-$ 271.0719; found 271.0737.

3-Methyl-*N*-(2-nitrophenyl)benzamide (2p) and 3-Methyl-*N*-(4-nitrophenyl)benzamide (2p′): Data for **2p**: Yellow solid (70% yield); R_f = 0.64 (petroleum ether/ethyl acetate, 8:1 v/v). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 11.32 (s, 1 H, NH), 9.02 (d, J = 8.4 Hz, 1 H, Ar), 8.29 (d, J = 7.3 Hz, 1 H, Ar), 7.82 (s, 1 H, ArCO), 7.79 (d, J = 5.9 Hz, 1 H, Ar), 7.73 (t, J = 8.4 Hz, 1 H, Ar), 7.47–7.39 (m, 2 H, Ar), 7.23 (t, J = 8.4 Hz, 1 H, Ar), 2.48 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 166.0, 139.0, 136.5, 136.2, 135.4, 134.1, 133.4, 128.9, 128.1, 125.9, 124.3, 123.2, 122.2, 21.4 ppm. HRMS (ESI): calcd. for $C_{14}H_{11}N_2O_3$ [M – H]$^-$ 255.0770; found 255.0788. Data for **2p′**: White solid (19% yield); R_f = 0.41 (petroleum ether/ethyl acetate, 8:1 v/v). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.26 (d, J = 9.2 Hz, 2 H, ArNH), 8.13 (d, J = 9.2 Hz, 2 H, ArNH), 7.86–7.81 (m, 2 H, ArCO), 7.45–7.37 (m, 2 H, ArCO), 2.40 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 167.2, 146.4, 144.0, 139.2, 135.4, 133.6, 129.4, 129.1, 125.7, 125.5, 120.6, 21.3 ppm. HRMS (ESI): calcd. for $C_{14}H_{11}N_2O_3$ [M – H]$^-$ 255.0770; found 255.0789.

2-Methyl-*N*-(2-nitrophenyl)benzamide (2q) and 2-Methyl-*N*-(4-nitrophenyl)benzamide (2q′): Data for **2q**: Yellow solid (69% yield); R_f = 0.67 (petroleum ether/ethyl acetate, 6:1 v/v). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.76 (s, 1 H, NH), 8.99 (d, J = 8.5 Hz, 1 H, Ar), 8.28 (d, J = 8.5 Hz, 1 H, Ar), 7.73 (t, J = 8.6 Hz, 1 H, Ar), 7.62 (d, J = 7.1 Hz, 1 H, Ar), 7.43 (t, J = 8.0 Hz, 1 H, Ar), 7.30–7.36 (m, 2 H, Ar), 7.24 (t, J = 8.6 Hz, 1 H, Ar), 2.58 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 168.3, 137.3, 136.6, 136.0, 135.4, 135.1, 131.7, 131.1, 127.0, 126.3, 125.9, 123.4, 122.2, 20.2 ppm. HRMS (ESI): calcd. for $C_{14}H_{11}N_2O_3$ [M – H]$^-$ 255.0770; found 255.0787. Data for **2q′**: Light yellow solid (23% yield); R_f = 0.39 (petroleum ether/ethyl acetate, 6:1 v/v). This is a known compound.[27] ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.88 (s, 1 H, NH), 8.26 (m, 2 H, ArNH), 8.02 (m, 2 H, ArCO), 7.51–7.55 (m, 1 H, ArNH), 7.41–7.49 (m, 1 H, ArNH), 7.32–7.39 (m, 2 H, ArCO), 2.42 (s, 3 H, Me) ppm. HRMS (ESI): calcd. for $C_{14}H_{11}N_2O_3$ [M – H]$^-$ 255.0770; found 255.0786.

***N*-(2-Nitrophenyl)acetamide (2r) and *N*-(4-Nitrophenyl)acetamide (2r′):** Data for **2r**: Yellow solid (67% yield); R_f = 0.72 (petroleum ether/ethyl acetate, 6:1 v/v). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 10.33 (s, 1 H, NH), 8.78 (d, J = 8.5 Hz, 1 H, ArNH), 8.22 (d, J = 8.4 Hz, 1 H, ArNH), 7.66 (dd, J = 8.5, 7.8 Hz, 1 H, ArNH), 7.19 (dd, J = 8.4, 7.8 Hz, 1 H, ArNH), 2.31 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 169.0, 136.3, 135.9, 134.8, 125.7, 123.2, 122.2, 25.6 ppm. HRMS (ESI): calcd. for $C_8H_7N_2O_3$ [M – H]$^-$ 179.0457; found 179.0468. Data for **2r′**: White solid (19% yield); R_f = 0.42 (petroleum ether/ethyl acetate, 6:1 v/v). This is a known compound.[25] ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.56 (s, 1 H, NH), 8.21 (d, J = 9.3 Hz, 2 H, Ar), 7.79 (d, J = 9.3 Hz, 2 H, Ar), 2.19 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 169.2, 145.6, 141.9, 124.6, 118.2, 24.4 ppm. HRMS (ESI): calcd. for $C_8H_7N_2O_3$ [M – H]$^-$ 179.0457; found 179.0470.

***N*-(2-Nitrophenyl)cyclopropanecarboxamide (2s) and *N*-(4-Nitrophenyl)cyclopropanecarboxamide (2s′):** Data for **2s**: Yellow solid (76% yield); R_f = 0.66 (petroleum ether/ethyl acetate, 6:1 v/v). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.62 (s, 1 H, NH), 8.78 (d, J = 8.6 Hz, 1 H, ArNH), 8.23 (d, J = 8.5 Hz, 1 H, ArNH), 7.63 (t, J = 8.6 Hz, 1 H, ArNH), 7.16 (t, J = 8.5 Hz, 1 H, ArNH), 1.65–1.72 (m, 1 H, cyclopropyl CH), 1.11–1.18 (m, 2 H, cyclopropyl CH$_2$), 0.92–0.99 (m, 2 H, cyclopropyl CH$_2$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 172.8, 136.0, 136.0, 135.1, 125.7, 122.9, 122.2, 77.3, 77.0, 76.7, 16.9, 9.0 ppm. HRMS (ESI): calcd. for $C_{10}H_9N_2O_3$ [M – H]$^-$ 205.0613; found 205.0626. Data for **2s′**: White solid (15% yield); R_f = 0.40 (petroleum ether/ethyl acetate, 6:1 v/v). This is a known compound.[28] ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.24 (d, J = 9.3 Hz, 2 H, ArNH), 7.85 (s, 1 H, NH), 7.73 (d, J = 9.3 Hz, 2 H, ArNH), 1.57–1.64 (m, 1 H, CH), 1.12–1.19 (m, 2 H, CH$_2$), 0.93–0.97 (m, 2 H, CH$_2$) ppm. HRMS (ESI): calcd. for $C_{10}H_9N_2O_3$ [M – H]$^-$ 205.0613; found 205.0627.

***N*-(2-Nitrophenyl)pivalamide (2t) and *N*-(4-Nitrophenyl)pivalamide (2t′):** Data for **2t**: Light yellow solid (78% yield); R_f = 0.65 (petroleum ether/ethyl acetate, 6:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.74 (s, 1 H, NH), 8.84 (d, J = 8.4 Hz, 1 H, ArNH), 8.24 (d, J = 9.3 Hz, 1 H, ArNH), 7.66 (t, J = 8.4 Hz, 1 H, ArNH), 7.18 (dd, J = 9.3, 8.4 Hz, 1 H, ArNH), 1.37 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.9, 136.4, 136.0, 135.5, 125.7, 122.9, 122.1, 40.6, 27.4 ppm. HRMS (ESI): calcd. for $C_{11}H_{13}N_2O_3$ [M – H]$^-$ 221.0926; found 221.0941. Data for **2t′**: White solid (19% yield); R_f = 0.38 (petroleum ether/ethyl acetate, 6:1 v/v). This is a known compound.[29] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24 (d, J = 9.0 Hz, 2 H, ArNH), 7.77 (d, J = 9.0 Hz, 2 H, ArNH), 7.74 (s, 1 H, NH), 1.39 (s, 9 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.5, 144.7, 143.3, 125.2, 119.2, 40.2, 27.9 ppm. HRMS (ESI): calcd. for $C_{11}H_{13}N_2O_3$ [M – H]$^-$ 221.0926; found 221.0942.

3-Nitro-*N*-phenylacrylamide (4a): Yellow solid (73% yield); R_f = 0.57 (petroleum ether/ethyl acetate, 10:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81 (d, J = 12.9 Hz, 1 H, CH=), 7.72 (s, 1 H, NH), 7.60 (d, J = 8.0 Hz, 2 H, Ph), 7.39 (dd, J = 8.0, 7.4 Hz, 2 H, Ph), 7.32 (d, J = 12.9 Hz, 1 H, CH=), 7.22 (t, J = 7.4 Hz, 1 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.6, 148.0, 136.7, 130.4, 129.4, 125.9, 120.3 ppm. HRMS (ESI): calcd. for $C_9H_7N_2O_3$ [M – H]$^-$ 191.0457; found 191.0472.

***N*-(4-Chlorophenyl)-3-nitroacrylamide (4b):** Yellow solid (76% yield); R_f = 0.60 (petroleum ether/ethyl acetate, 10:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, J = 12.9 Hz, 1 H, CH=), 7.73 (s, 1 H, NH), 7.57 (d, J = 8.8 Hz, 2 H, ArNH), 7.36 (d, J = 8.8 Hz, 2 H, ArNH), 7.31 (d, J = 12.9 Hz, 1 H, CH=) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 159.3, 147.2, 137.2, 131.0, 129.0, 128.9, 121.2 ppm. HRMS (ESI): calcd. for $C_9H_6ClN_2O_3$ [M – H]$^-$ 225.0067; found 225.0082.

***N*-(4-Ethoxyphenyl)-3-nitroacrylamide (4c):** Orange solid (66% yield); R_f = 0.63 (petroleum ether/ethyl acetate, 10:1 v/v). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 7.78 (d, J = 13.1 Hz, 1 H, CH=), 7.67 (d, J = 9.1 Hz, 2 H, ArNH), 7.53 (d, J = 13.1 Hz, 1 H, CH=), 6.91 (d, J = 9.1 Hz, 2 H, ArNH), 4.03 (q, J = 7.0 Hz, 2 H, CH_2), 1.34 (t, J = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 158.6, 156.2, 146.8, 131.5, 131.4, 121.2, 114.6, 63.4, 14.2 ppm. HRMS (ESI): calcd. for $C_{11}H_{11}N_2O_4$ [M – H]$^-$ 235.0719; found 235.0734.

3-Nitro-*N*-(*m*-tolyl)acrylamide (4d): Yellow solid (69% yield); R_f = 0.67 (petroleum ether/ethyl acetate, 10:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, J = 12.9 Hz, 1 H, CH=), 7.67 (s, 1 H, NH), 7.44 (s, 1 H, ArNH), 7.37 (d, J = 7.9 Hz, 1 H, ArNH), 7.31 (d, J = 12.9 Hz, 1 H, CH=), 7.27 (dd, J = 7.9, 7.4 Hz, 1 H, ArNH), 7.04 (d, J = 7.4 Hz, 1 H, ArNH), 2.37 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.6, 147.9, 139.4, 136.6, 130.4, 129.1, 126.7, 120.9, 117.4, 21.4 ppm. HRMS (ESI): calcd. for $C_{10}H_9N_2O_3$ [M – H]$^-$ 205.0613; found 205.0630.

***N*-(3-Methoxyphenyl)-3-nitroacrylamide (4e):** Yellow solid (72% yield); R_f = 0.52 (petroleum ether/ethyl acetate, 10:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87 (s, 1 H, NH), 7.79 (d, J = 12.5 Hz, 1 H, CH=), 7.41–7.21 (m, 3 H, ArNH and CH=), 7.07 (d, J = 6.5 Hz, 1 H, ArNH), 6.76 (d, J = 7.0 Hz, 1 H, ArNH), 3.82 (s, 3 H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.3, 158.7, 147.9, 137.8, 130.4, 130.0, 112.4, 111.6, 106.3, 55.4 ppm. HRMS (ESI): calcd. for $C_{10}H_9N_2O_4$ [M – H]$^-$ 221.0563; found 221.0577.

***N*-(3-Bromophenyl)-3-nitroacrylamide (4f):** Yellow solid (65% yield); R_f = 0.53 (petroleum ether/ethyl acetate, 10:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (s, 1 H, NH), 7.88 (s, 1 H, ArNH), 7.82 (d, J = 12.9 Hz, 1 H, CH=), 7.52 (d, J = 8.6 Hz, 1 H, ArNH), 7.38–7.31 (m, 2 H, ArNH and CH=), 7.26 (t, J = 8.0 Hz, 1 H, ArNH) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 159.5, 147.4, 139.8, 130.9, 130.7, 127.5, 122.4, 122.0, 118.4 ppm. HRMS (ESI): calcd. for $C_9H_6BrN_2O_3$ [M – H]$^-$ 268.9562; found 268.9578.

***N*-(3,5-Dimethylphenyl)-3-nitroacrylamide (4g):** Yellow solid (68% yield); R_f = 0.66 (petroleum ether/ethyl acetate, 10:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.79 (d, J = 13.3 Hz, 1 H, CH=), 7.61 (s, 1 H, NH), 7.29 (d, J = 13.3 Hz, 1 H, CH=), 7.21 (s, 2 H, ArNH), 6.86 (s, 1 H, ArNH), 2.32 (s, 6 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.5, 147.8, 139.1, 136.5, 130.5, 127.6, 118.0, 21.3 ppm. HRMS (ESI): calcd. for $C_{11}H_{11}N_2O_3$ [M – H]$^-$ 219.0770; found 219.0785.

3-Nitro-*N*-(*o*-tolyl)acrylamide (4h): Yellow solid (75% yield); R_f = 0.61 (petroleum ether/ethyl acetate, 10:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.77 (m, 2 H, ArNH and CH=), 7.46 (s, 1 H, NH), 7.37 (d, J = 12.9 Hz, 1 H, CH=), 7.29–7.22 (m, 2 H, ArNH), 7.17 (t, J = 7.3 Hz, 1 H, ArNH), 2.31 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 148.0, 134.4, 130.8, 130.2, 129.4, 127.0, 126.6, 123.2, 17.7 ppm. HRMS (ESI): calcd. for $C_{10}H_9N_2O_3$ [M – H]$^-$ 205.0613; found 205.0632.

***N*-Butyl-3-nitroacrylamide (4i):** Light yellow solid (81% yield); R_f = 0.71 (petroleum ether/ethyl acetate, 10:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.70 (d, J = 13.0 Hz, 1 H, CH=), 7.15 (d, J = 13.0 Hz, 1 H, CH=), 6.06 (s, 1 H, NH), 3.44–3.36 (m, 2 H, CH_2), 1.61–1.53 (m, 2 H, CH_2), 1.44–1.35 (m, 2 H, CH_2), 0.96 (t, J = 7.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.7, 147.2, 130.0, 40.0, 31.3, 20.0, 13.6 ppm. HRMS (ESI): calcd. for $C_7H_{11}N_2O_3$ [M – H]$^-$ 171.0770; found 171.0778.

***N*-Cyclohexyl-3-nitroacrylamide (4j):** Light yellow solid (83% yield); R_f = 0.69 (petroleum ether/ethyl acetate, 10:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, J = 13.0 Hz, 1 H, CH=), 7.11 (d, J = 13.0 Hz, 1 H, CH=), 5.80 (s, 1 H, NH), 3.96–3.83 (m, 1 H, cyclohexyl), 2.03–1.95 (m, 2 H, cyclohexyl), 1.81–1.71 (m, 2 H, cyclohexyl), 1.70–1.63 (m, 1 H, cyclohexyl), 1.45–1.36 (m, 2 H, cyclohexyl), 1.24–1.14 (m, 3 H, cyclohexyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 147.2, 130.3, 49.3, 32.8, 25.3, 24.7 ppm. HRMS (ESI): calcd. for $C_9H_{13}N_2O_3$ [M – H]$^-$ 197.0926; found 197.0940.

***N*-(*tert*-Butyl)-3-nitroacrylamide (4k):** Light yellow solid (86% yield); R_f = 0.68 (petroleum ether/ethyl acetate, 10:1 v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, J = 13.0 Hz, 1 H, CH=), 7.09 (d, J = 13.0 Hz, 1 H, CH=), 5.82 (s, 1 H, NH), 1.43 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.9, 146.9, 131.3, 52.7, 28.5 ppm. HRMS (ESI): calcd. for $C_7H_{11}N_2O_3$ [M – H]$^-$ 171.0770; found 171.0783.

3-Nitro-*N*-phenylbut-2-enamide (4l): Light yellow solid (36% yield); R_f = 0.61 (petroleum ether/ethyl acetate, 10:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (s, 1 H, NH), 7.58 (d, J = 7.6 Hz, 2 H, ArNH), 7.38 (t, J = 7.6 Hz, 2 H, ArNH), 7.26 (s, 1 H, CH=), 7.19 (t, J = 7.6 Hz, 1 H, ArNH), 2.67 (s, 3 H, Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.7, 158.7, 137.0, 129.3, 125.5, 123.5, 120.2, 13.7 ppm. HRMS (ESI): calcd. for $C_{10}H_9N_2O_3$ [M – H]$^-$ 205.0613; found 205.0624.

3-Nitroacrylamide (4m): Light yellow solid (79% yield); R_f = 0.59 (petroleum ether/acetone, 2:1 v/v). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 7.70 (d, J = 13.2 Hz, 1 H, CH=), 7.39 (d, J = 13.2 Hz, 1 H, CH=) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 163.46, 147.85, 131.58 ppm. HRMS (ESI): calcd. for $C_3H_3N_2O_3$ [M – H]$^-$ 115.0144; found 115.0156.

***N*-(2-Nitrophenyl)acrylamide (5a):** Yellow solid (<5% yield); R_f = 0.71 (petroleum ether/ethyl acetate, 10:1 v/v). ^{1}H NMR (400 MHz,

$CDCl_3$): δ = 10.53 (s, 1 H, NH), 8.83 (d, J = 9.1 Hz, 1 H, ArNH), 8.19 (d, J = 8.5 Hz, 1 H, ArNH), 7.62 (t, J = 8.5 Hz, 1 H, ArNH), 7.14 (t, J = 9.1 Hz, 1 H, ArNH), 6.42 (d, J = 17.0 Hz, 1 H, CH=), 6.27 (dd, J = 17.0, 10.2 Hz, 1 H, CH=), 5.83 (d, J = 10.2 Hz, 1 H, CH=) ppm. HRMS (ESI): calcd. for $C_9H_7N_2O_3$ [M – H]$^-$ 191.0457; found 191.0471.

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[23] (*E*)-Nitro-olefins were generated exclusively, which was possibly the result of a stereoelectronic requirement for the hydrogen atom abstraction by the alkoxyl radical (*anti* elimination) and/or the thermodynamic stability of the product.[12a]

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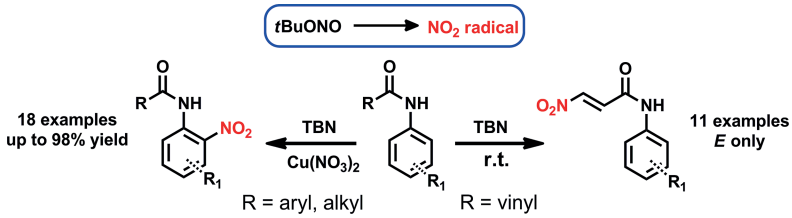
Nitration



The efficient nitration of both anilides and acrylamides was achieved by using TBN (*tert*-butyl nitrite) as a metal-free nitrating reagent. This synthetic method has many advantages such as mild reaction conditions, a fast reaction rate, good to excellent yields, and a broad substrate scope. Our investigation indicates that a nitro radical is involved in the reaction mechanism.

Keywords: Synthetic methods / Nitration / Chemoselectivity / Radicals / Copper / Amides

