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C–H Functionalization

Silver-Catalyzed Chemo- and Regioselective Nitration of Anilides

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Abstract: A new and efficient Ag-catalyzed method for the nitration of anilides by using sodium nitrite as a cheap and available NO_2 source has been developed. This C–H functionalization reaction is *ortho*-selective, achieves moderate to high yields and shows excellent functional group tolerance. Furthermore, it provides a novel approach to *ortho*-nitrated anilides, which are very tricky to access with traditional methods.

Introduction

Nitroarene compounds or intermediates are important organo-precursors for the synthesis of pharmaceuticals, dyes, explosives and other valuable chemical substances. Therefore, finding a highly efficient method for the nitration of aromatic derivatives is a topic of great interest for organic chemists.[1] For example, flutamide has been used in treatment of metastatic carcinoma of the prostate[2] and niclosamide have been shown to have powerful cestodicidal activity.[3] 2-Nitro-*N*-acylanilines are critical intermediates in the synthesis of phenanthro[2,3-*d*]imidazole derivatives which show useful antibacterial or antifungal properties (Figure 1, compound A).[4]

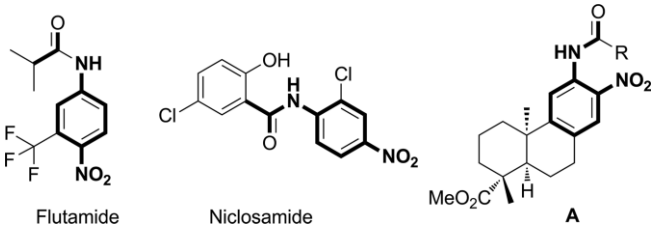

Figure 1. Some biologically active nitroarene compounds.

Traditional methods of preparing nitroarenes use mixed strong-acid systems such as (HNO_3/H_2SO_4)[5] or N_2O_5[6] and suffer from harsh reaction conditions, low regioselectivity, and limited functional group tolerance. In this regard, using metal nitrate salts such as $Bi(NO_3)_3{\cdot}5H_2O$, $Ca(NO_3)_2$, $Ni(NO_3)_2{\cdot}6H_2O$ and other nitronium salts in stoichiometric amounts has become commonplace.[7–9] However, hazardous acidic conditions have been overcome by the use of nitrate salt reagents. Unfortunately, mostly these reagents are expensive, difficult to prepare and produce high quantities of metal oxides as unfavorable by products. In recent years chelation-assisted aromatic C–H *ortho*-nitration has attracted some interest. A copper-mediated *ortho* C–H bond nitration of benzoic acid derivatives using sodium nitrite as a nitrating source was demonstrated by Tan in 2014.[10] Gooßen and co-workers reported copper-mediated *ortho*-nitration of (hetero)arenecarboxylic acids in the presence of $AgNO_2$ in 2014.[11] A combination of $AgNO_2$ with TEMPO was used for highly selective nitration of olefins by Maiti in 2013.[12] Unfortunately, all of these metal-mediated methods involve use of large amounts of metals. Recently, transition metal-catalyzed coupling methods for nitration of aromatic compounds have been further investigated. Copper catalyzed *ipso*-nitration of haloarenes with KNO_2 was reported by Kantam in 2012.[13] Saito et al. developed nitration of aromatic halides in the presence of catalytic amounts of Cu bronze with $n Bu_4NNO_2$ in 2005.[14] Buchwald and co-workers developed a general Pd catalyzed nitration of prefunctionalized aryl chlorides, triflates, and nonaflates with $NaNO_2$ as a simple nitro source.[15] Cu^{II}-catalyzed nitration of aryl boronic acids in the presence of $NaNO_2$ was reported by Fu in 2011.[16] Li and co-workers reported a significant Rh-catalyzed C–H nitration of arenes with $NaNO_2$ in the presence of a costly hypervalent iodine oxidant in 2013.[17] Copper-catalyzed nitration of quinolines at the C5 or C7 position using $NaNO_2$ was reported by Zhang in 2016.[18] Recently Sun reported the *ortho*-C–H nitration of ureas in the presence of $CuCl_2{\cdot}2H_2O$ as catalyst and $Fe(NO_3)_3{\cdot}9H_2O$ as a nitro source.[19] A palladium-catalyzed chelation-assisted *ortho*-nitration of aryl ketone with $AgNO_2$ was demonstrated by Liu's group in 2013.[20] Xu et al. reported nitration of quinoxaline in the presence of catalytic amounts of $Pd(OAc)_2$ and $AgNO_2$ as a nitrating source in 2010.[21] Silver-catalyzed decarboxylative nitroaminoxylation of phenylpropiolic acids using *tert*-butyl nitrite (TBN) was described by Mao in 2012.[22] Regioselective nitration of anilines and anilides have been of great interest in recent years. A palladium-catalyzed, heteroatom-directed method for C–H nitration of anilines with $AgNO_2$ has been described by Kapur in 2016 [Scheme 1, Equation (1)].[23] Copper(II)-catalyzed *ortho*-nitration of aniline derivatives protected as 1-aryl-5-aminotetrazolyl using $Fe(NO_3)_3{\cdot}9H_2O$ was described by Punniyamurthy in 2015 [Scheme 1, Equation (2)].[24] An efficient $Fe(NO_3)_3{\cdot}9H_2O$ promoted *ortho*-nitration of aniline derivatives has been developed by Huo in 2018 [Scheme 1, Equation (3)].[25] Copper-cata-

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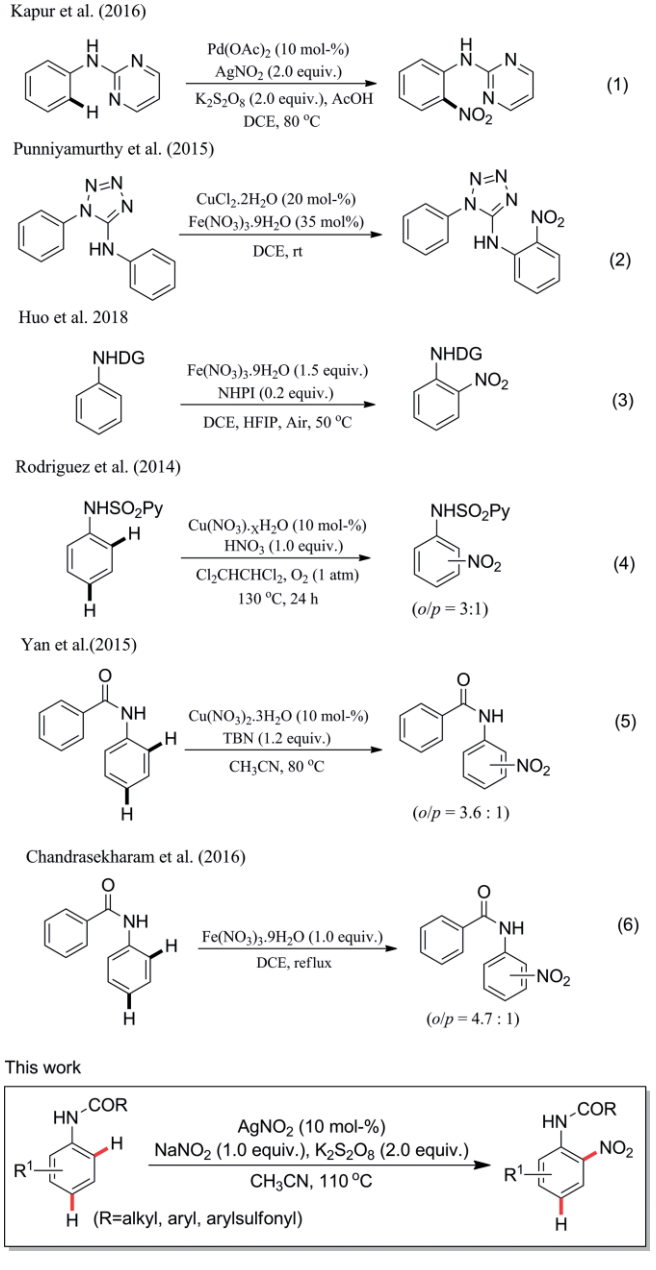
lyzed nitration of protected anilines with HNO_3 was reported by Carretero in 2014 [Scheme 1, Equation (4)].[26] Yan et al. used a combination of *tert*-butyl nitrite (TBN) and a catalytic amount of $Cu(NO_3)_2{\cdot}3H_2O$ for the efficient aryl nitration of aromatic amides [Scheme 1, Equation (5)].[27] Iron-mediated direct *ortho*-nitration of anilides and aromatic sulfonamides was developed by Chandrasekharam in 2016 [Scheme 1, Equation (6)].[28] Metal free nitration of aromatic sulfonamides with *tert*-butyl nitrite (TBN)[29] and $NaNO_2$/PIFA[30] has been reported by Arns and Nachtsheim separately. Conversely, less expensive silver complexes were as of yet underutilized for C–H activation reaction, with notable exceptions being accomplished only very recently.[31] Herein we report a silver catalyzed regioselective *ortho*-nitration of anilides and also aromatic sulfonamides by which a general and regiospecific synthesis of substituted *ortho*-nitro anilines from the corresponding anilides and sulfonamides can be successfully achieved.[32]



Scheme 1. Literature precedence for nitration of aromatic anilide compounds.

Results and Discussion

To start our investigation, we chose *N*-phenylacetamide (**1a**) as the substrate and sodium nitrite (1.0 equiv.) as the nitrating agent. In order to optimize the reaction conditions, a series of experiments with different parameters such as catalyst, solvent and oxidant were performed for the typical reaction (Table 1). Various conditions were screened to optimize the reaction conditions (Table 1). A screening of catalysts revealed that $AgNO_2$ gave the best result (Table 1, entry 1). The reaction was monitored with different amounts of catalyst loading and the results showed that 10 mol-% of $AgNO_2$ was the best choice for completion of the reaction (Table 1, entries 1, 2). $AgNO_3$ gave moderate yield of the product and AgOAc, Ag_2CO_3 and palladium-based catalysts such as $Pd(OAc)_2$ and $PdCl_2$ were found to be inferior (Table 1, entries 3–7). Commonly used organic solvents were screened and CH_3CN gave the best result. Changing the solvent to DMF and DMSO gave no product (Table 1, entries 8,9). When the reaction was conducted in DME, DCE, toluene and PhCl moderate to low yields of the product was obtained (Table 1, entries 10–13). The effect of a range of the oxidants

Table 1. Optimization of the reactions conditions.[a]

1a **2a**

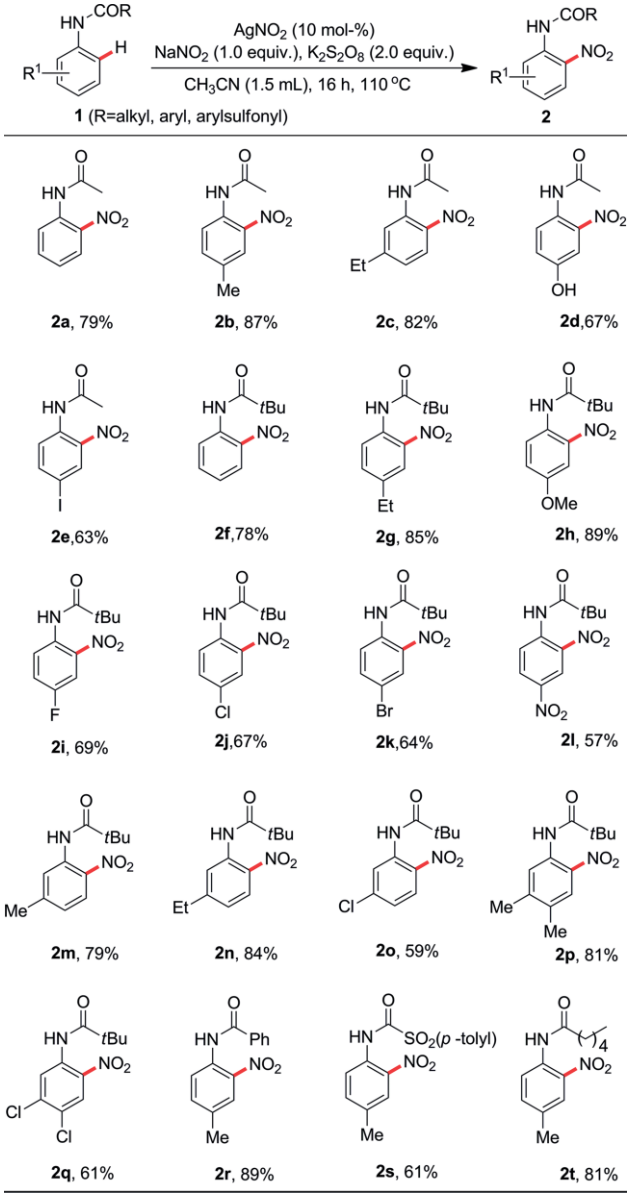
Entry	Catalyst [mol-%]	Oxidant	Solvent	Temp. [°C]	Yield [%]
1	$AgNO_2$(10)	$K_2S_2O_8$	CH_3CN	110	79
2	$AgNO_2$(5)	$K_2S_2O_8$	CH_3CN	110	42
3	$AgNO_3$(10)	$K_2S_2O_8$	CH_3CN	110	37
4	AgOAc(10)	$K_2S_2O_8$	CH_3CN	110	trace
5	Ag_2CO_3(10)	$K_2S_2O_8$	CH_3CN	110	trace
6	$Pd(OAc)_2$(10)	$K_2S_2O_8$	CH_3CN	110	0
7	$PdCl_2$(10)	$K_2S_2O_8$	CH_3CN	110	0
8	$AgNO_2$(10)	$K_2S_2O_8$	DMF	110	0
9	$AgNO_2$(10)	$K_2S_2O_8$	DMSO	110	0
10	$AgNO_2$(10)	$K_2S_2O_8$	DME	110	49
11	$AgNO_2$(10)	$K_2S_2O_8$	DCE	110	51
12	$AgNO_2$(10)	$K_2S_2O_8$	toluene	110	36
13	$AgNO_2$(10)	$K_2S_2O_8$	PhCl	110	27
14	$AgNO_2$(10)	$(NH_4)_2S_2O_8$	CH_3CN	110	52
15	$AgNO_2$(10)	$Na_2S_2O_8$	CH_3CN	110	61
16	$AgNO_2$(10)	TBHP	CH_3CN	110	0
17	$AgNO_2$(10)	DTBP	CH_3CN	110	0
18	$AgNO_2$(10)	$Cu(OAc)_2{\cdot}H_2O$	CH_3CN	110	0
19	$AgNO_2$(10)	CuO	CH_3CN	110	0
20	$AgNO_2$(10)	$K_2S_2O_8$	CH_3CN	90	31
21[b]	$AgNO_2$(10)	$K_2S_2O_8$	CH_3CN	110	47
22[c]	$AgNO_2$(10)	$K_2S_2O_8$	CH_3CN	110	59(17)[d]
23	–	$K_2S_2O_8$	CH_3CN	110	0
24	$AgNO_2$(10)	–	CH_3CN	110	0

[a] **1a** (0.5 mmol), $NaNO_2$ (1.0 equiv.), catalyst, oxidant (2.0 equiv.), solvent (1.5 mL) were stirred at 110 °C for 16 h. [b] 50 mol-% of $NaNO_2$ was used. [c] 1.0 equiv. *tert*-butyl nitrite was used. [d] *para* product in parentheses.

was examined and the results showed that $K_2S_2O_8$ was more effective than others such as $(NH_4)_2S_2O_8$, $Na_2S_2O_8$, TBHP, DTBP, $Cu(OAc)_2{\cdot}H_2O$ and CuO (Table 1, entries 14–19). The reaction temperature was also varied and the best results were obtained at 110 °C. Upon decreasing the reaction temperature from 110 to 90 °C, the yield of the reaction decreased dramatically (Table 1, entry 20). By reducing the amount of $NaNO_2$, as the nitrating agent, to 0.5 equiv. the yield of the reaction decreased to 47 % (Table 1, entry 21). By using *tert*-butyl nitrite (TBN) as the nitrating agent a mixture of *ortho*/*para* products was obtained (Table 1, entry 22). Notably, no reaction occurred in the absence of a catalyst or an oxidant (Table 1, entries 23 and 24).

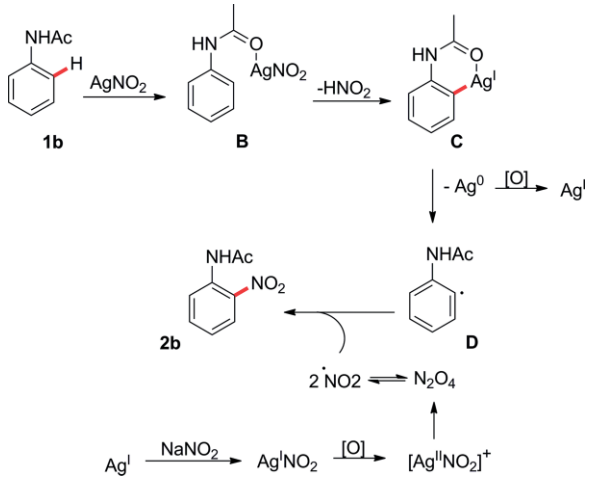
Once the optimized conditions for the desired nitration reaction were established, the scope of the reaction with regard to different anilides was investigated. The results are summarized in Table 2. It was found that a variety of anilides with electron-donating and electron-withdrawing groups substituted on the aromatic ring, were tolerated and good yields were obtained in all cases. Generally, the presence of electron-donating groups led to higher yields of the products (Table 2, **2b**, **2c**, **2d**, **2g**, **2h**, **2m**, **2n**, **2p**, **2r**, and **2t**). Also, anilides bearing electron-withdrawing substituents such as halogens and nitro groups resulted in products in moderate yields (Table 2, **2e**, **2i**, **2j**, **2k**, **2o** and **2q**). Surprisingly, 4-methyl-*N*-(*p*-tolyl)benzenesulfonamide also gave the desired product **2s** in good yield (Table 2).

Table 2. Silver-catalyzed regioselective *ortho*-nitration of anilides.[a]



[a] **1** (0.5 mmol), Ag catalyst (10 mol-%), $NaNO_2$ (1.0 equiv.), $K_2S_2O_8$ (2.0 equiv.), in acetonitrile (1.5 mL) at 110 °C for 16 h.

On the basis of previous reports,[33] a possible catalytic mechanism for this transformation is illustrated in Scheme 2. At first, arylsilver complex **C** is formed via coordination of silver catalyst to the acetylamino directing group,[33b] which subsequently provides *N*-phenyl acetamide radical **D** and Ag^0 which is reoxidiszed to Ag^I in presence of $K_2S_2O_8$. Intermediate **D** reacts with in situ generated NO_2 radical[23,26,34] to give the *ortho*-nitrated product **2b**. To prove the radical mechanism, a control reaction was carried out using 2,6-di-*tert*-butyl-4-methylphenol (BHT) as a radical scavenger. As expected, when the reaction of **1b** was carried out in the presence of BHT, no desired product **2b** was observed.



Scheme 2. Possible mechanism.

Conclusions

In conclusion, we have developed an efficient silver-catalyzed method for regioselective *ortho* C–H bond nitration of anilides using sodium nitrite in the presence of $K_2S_2O_8$ as the oxidant in acetonitrile via the highly valuable strategy of C–H bond activation. The reaction can be applied to numerous substrates with good tolerance of both electron-deficient and electron-rich functional groups, providing a simple and straightforward way to synthesize of various *ortho*-nitro anilides using commonly available starting materials. Products of this reaction are interesting targets to probe in pharmaceutical and petroleum industries.[35]

Experimental Section

General Information: Solvents, $K_2S_2O_8$, $AgNO_2$, $NaNO_2$ and aniline derivatives were purchased from Merck. Other reagents were pur-

chased from commercial distributors and were used without further purification. Anilide[36] and aromatic sulfonamide[37] were synthesized according to the literature. Analytical thinlayer chromatography (TLC) was performed on precoated silica gel60 F254 plates. The products were purified by preparative column chromatography on silica gel (0.063–0.200 mm, Merck). ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker DRX 400 and 500 Advance instrument in $CDCl_3$. Mass spectrometry was performed with an Agilent 5975C VL MSD (ion source: EI+, 70 eV, 230 °C).

General Procedure for the Synthesis of *2-nitroanilides*: 10 mL microwave vial was charged with an acetanilide derivative (1.0 equiv., 0.5 mmol), $NaNO_2$ (1.0 equiv.), $AgNO_2$ (10 mol-%), $K_2S_2O_8$ (2.0 equiv.) and CH_3CN (1.5 mL). The vial was then sealed and immersed in an oil bath at 110 °C, for 16 h. After this time, the mixture was cooled to room temperature and then diluted with CH_2Cl_2 and filtered. The residue was purified by column chromatography (*n*-hexane/EtOAc, 2:1) to yield the desired product.

***N*-(2-nitrophenyl)acetamide (2a):**[38] The general procedure was followed by using acetanilide (0.5 mmol, 67 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2a** (71 mg, 79 %) as a yellow solid, m.p. 90–91 °C. ^{1}H NMR (500 MHz, [D]Chloroform): δ = 10.32 (br., 1 H), 8.77 (dd, *J* = 8.6, 1.4 Hz, 1 H), 8.21 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.65 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1 H), 7.18 (ddd, *J* = 8.5, 7.3, 1.4 Hz, 1 H), 2.30 (s, 3 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 169.1, 136.0, 125.8, 124.5, 124.0, 123.3, 122.2, 22.7 ppm. MS (EI): *m/z* (%) = 180 (11) [M$^+$], 167 (75), 155 (83), 113 (25), 97 (37), 85 (77), 57 (100), 43 (25). $C_8H_8N_2O_3$ (180.16): calcd. C 53.33, H 4.48, N 15.55; found C 53.41, H 4.45, N 5.62.

***N*-(4-methyl-2-nitrophenyl)acetamide (2b):**[39] The general procedure was followed by using 4-methylacetanilide (0.5 mmol, 74 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2b** (84 mg, 87 %) as a yellow solid, m.p. 87–89 °C. ^{1}H NMR (500 MHz): δ = 10.22 (br., 1 H), 8.64 (d, *J* = 8.6 Hz, 1 H), 8.02 (d, *J* = 2.1 Hz, 1 H), 7.47 (dd, *J* = 8.7, 2.0 Hz, 1 H), 2.41 (s, 3 H), 2.29 (s, 3 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 169.0, 136.9, 136.2, 133.5, 132.4, 125.5, 122.2, 25.6, 20.6 ppm. MS (EI): *m/z* (%) = 194 (7) [M$^+$], 167 (55), 149 (100), 113 (21), 83 (14), 71 (31), 57 (33), 43 (18). $C_9H_{10}N_2O_3$ (194.19): calcd. C 55.67, H 5.19, N 14.43; found C 55.57, H 5.15, N 14.38.

***N*-(5-ethyl-2-nitrophenyl)acetamide (2c):** The general procedure was followed by using 3-Eethylacetanilide (0.5 mmol, 81 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2c** (85 mg, 82 %) as a dark yellow oil. ^{1}H NMR (500 MHz): δ = 10.22 (br., 1 H), 8.66 (d, *J* = 8.6 Hz, 1 H), 8.04 (d, *J* = 2.1 Hz, 1 H), 7.50 (dd, *J* = 8.6, 2.1 Hz, 1 H), 2.71 (q, *J* = 7.6 Hz, 2 H), 2.30 (s, 3 H), 1.28 (t, *J* = 7.6 Hz, 3 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 169.0, 139.8, 136.4, 135.8, 132.5, 124.3, 122.3, 27.9, 25.6, 15.1 ppm. MS (EI): *m/z* (%) = 208 (33) [M$^+$], 166 (88), 162 (21), 151 (100), 105 (28), 91 (8), 77 (8). $C_{10}H_{12}N_2O_3$ (208.21): calcd. C 57.68, H 5.81, N 13.45; found C 57.46, H 5.83, N 13.31.

***N*-(4-hydroxy-2-nitrophenyl)acetamide (2d):** The general procedure was followed by using 4-hydroxyacetanilide (0.5 mmol, 75 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2d** (65 mg, 67 %) as a yellow solid, m.p. 154–155 °C. ^{1}H NMR (500 MHz): δ = 7.90 (d, *J* = 2.1 Hz, 1 H), 7.68 (br., 2 H), 7.11 (dd, *J* = 8.6, 2.1 Hz, 1 H), 6.97 (d, *J* = 8.6 Hz, 1 H), 2.25 (s, 3 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 175.0, 144.0, 139.1, 135.3, 132.2, 122.5,120.8, 29.7 ppm. MS (EI): *m/z* (%) = 196 (21) [M$^+$], 194 (43), 180 (11), 153 (31), 138 (49), 107 (21), 79 (31), 43 (100). $C_8H_8N_2O_4$ (196.16): calcd. C 48.98, H 4.11, N 14.28; found C 48.76, H 4.14, N 14.35.

***N*-(4-iodo-2-nitrophenyl)acetamide (2e):**[25] The general procedure was followed by using 4-Iodoacetanilide (0.5 mmol, 130 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2e** (96 mg, 63 %) as a yellow solid, m.p. 101–103 °C. ^{1}H NMR (500 MHz): δ = 10.27 (br., 1 H), 8.54 (s, 1 H), 7.92 (d, *J* = 8.9 Hz, 1 H), 7.58 (d, *J* = 8.8 Hz, 1 H), 2.31 (s, 3 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 169.1, 144.5, 134.0, 123.7, 120.6, 84.8, 29.7 ppm. MS (EI): *m/z* (%) = 306 (14) [M$^+$], 285 (44), 278 (18), 264 (100), 256 (34), 220 (31), 91 (27). $C_8H_7IN_2O_3$ (306.06): calcd. C 31.39, H 2.31, N 9.15; found C 31.50, H 2.33, N 9.10.

***N*-(2-nitrophenyl)pivalamide (2f):**[27] The general procedure was followed by using pivalamide (0.5 mmol, 88 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2f** (86 mg, 78 %) as a yellow solid, m.p. 99–100 °C. ^{1}H NMR (400 MHz): δ = 10.79 (br., 1 H), 8.92–8.80 (m, 1 H), 8.27 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.68 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1 H), 7.20 (ddd, *J* = 8.6, 7.3, 1.4 Hz, 1 H), 1.28 (s, 9 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 174.0, 139.8, 136.1, 135.5, 125.8, 123.0, 122.1, 40.6, 27.5 ppm. MS (EI): *m/z* (%) = 222 (11), 118 (62), 109 (11), 98 (61), 84 (37), 69 (44), 58 (100). $C_{11}H_{14}N_2O_3$ (222.24): calcd. C 59.45, H 6.35, N 12.61; found C 59.34, H 6.38, N 12.67.

***N*-(4-ethyl-2-nitrophenyl)pivalamide (2g):** The general procedure was followed by using 4-ethylpivalamide (0.5 mmol, 102 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2g** (106 mg, 85 %) as a yellow oil. ^{1}H NMR (500 MHz): δ = 10.86 (br.,1 H), 8.74 (d, *J* = 1.9 Hz, 1 H), 8.18 (d, *J* = 8.7 Hz, 1 H), 7.01 (dd, *J* = 8.6, 1.9 Hz, 1 H), 2.74 (q, *J* = 7.6 Hz, 2 H), 1.38 (s, 9 H), 1.30 (t, *J* = 7.6 Hz, 3 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 177.7, 139.5, 135.1, 133.2, 128.6, 124.4, 122.1, 40.5, 27.9, 27.5, 15.2 ppm. MS (EI): *m/z* (%) = 250 (14) [M$^+$], 204 (18), 166 (30), 151 (37), 85 (27), 71 (21), 57 (100). $C_{13}H_{18}N_2O_3$ (250.29): calcd. C 62.38, H 7.25, N 11.19; found C 62.49, H 7.29, N 11.24.

***N*-(4-methoxy-2-nitrophenyl)pivalamide (2h):** The general procedure was followed by using 4-methoxylpivanalide (0.5 mmol, 103 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2h** (112 mg, 89 %) as a yellow oil. ^{1}H NMR (400 MHz): δ = 10.51 (br., 1 H), 8.73 (dd, *J* = 9.3, 0.6 Hz, 1 H), 7.69 (dd, *J* = 3.1, 0.6 Hz, 1 H), 7.27–7.18 (m, 1 H), 3.87 (s, 3 H), 1.37 (s, 9 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 177.6, 154.7, 136.9, 129.9, 123.7, 123.5, 108.5, 55.9, 40.4, 27.5 ppm. MS (EI): *m/z* (%) = 252 (70) [M$^+$], 206 (51), 168 (100), 153 (28), 122 (18), 57 (85), 52 (8). $C_{12}H_{16}N_2O_4$ (252.27): calcd. C 57.13, H 6.39, N 11.10; found C 57.36, H 6.37, N 11.15.

***N*-(4-fluoro-2-nitrophenyl)pivalamide (2i):** The general procedure was followed by using 4-fluoropivalamide (0.5 mmol, 97 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2i** (82 mg, 69 %) as a dark yellow solid, m.p. 83–85 °C. ^{1}H NMR (400 MHz, [D]Chloroform): δ =

10.62 (br., 1 H), 8.89 (dd, *J* = 9.4, 5.2 Hz, 1 H), 7.96 (dd, *J* = 8.5, 3.1 Hz, 1 H), 7.56–7.28 (m, 1 H), 1.38 (s, 9 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 177.8, 156.8 (d, *J* = 247.4 Hz), 136.4, 132.0, 124.0 (d, *J* = 7.1 Hz), 123.5 (d, *J* = 22.0 Hz), 112.22 (d, *J* = 27.2 Hz) ppm. MS (EI): *m/z* (%) = 240 (9) [M$^+$], 149 (18), 118 (35), 98 (25), 85 (17), 71 (17), 57 (100). $C_{11}H_{13}FN_2O_3$ (240.23): calcd. C 55.00, H 5.45, N 11.66; found C 55.17, H 5.50, N 11.73.

***N*-(4-chloro-2-nitrophenyl)pivalamide (2j):** The general procedure was followed by using 4-chloropivalamide (0.5 mmol, 106 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by columnchromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2j** (86 mg, 67 %) as a yellow solid, m.p. 72–74 °C. ^{1}H NMR (400 MHz): δ = 10.67 (br., 1 H), 8.84 (d, *J* = 9.1 Hz, 1 H), 8.19 (d, *J* = 2.6 Hz, 1 H), 7.59 (dd, *J* = 9.2, 2.5 Hz, 1 H), 1.36 (s, 9 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 177.8, 136.3, 135.9, 134.1, 128.0, 125.3, 123.3, 40.6, 27.4 ppm. MS (EI): *m/z* (%) = 257 (8) [M + 1], 256 (25) [M$^+$], 172 (31), 85 (43), 57 (100). $C_{11}H_{13}ClN_2O_3$ (256.69): calcd. C 51.47, H 5.10, N 10.91; found C 51.33, H 5.12, N 10.96.

***N*-(4-bromo-2-nitrophenyl)pivalamide (2k):** The general procedure was followed by using 4-Bromopivalamide (0.5 mmol, 127 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2k** (96 mg, 64 %) as a yellow solid, m.p. 77–78 °C. ^{1}H NMR (500 MHz): δ = 10.69 (br., 1 H), 8.81 (d, *J* = 9.2 Hz, 1 H), 8.39 (d, *J* = 2.5 Hz, 1 H), 7.75 (dd, *J* = 9.1, 2.4 Hz, 1 H), 1.38 (s, 9 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 177.9, 138.8, 134.6, 132.6, 128.3, 123.6, 115.0, 40.7, 27.4 ppm. MS (EI): *m/z* (%) = 301 (18) [M + 1], 300 (18) [M$^+$], 216 (22), 157 (38), 91 (18), 85 (28), 57 (100). $C_{11}H_{13}BrN_2O_3$ (301.14): calcd. C 43.87, H 4.35, N 9.3; found C 43.61, H 4.38, N 9.36.

***N*-(2,4-dinitrophenyl)pivalamide (2l):** The general procedure was followed by using 4-nitropivanalide (0.5 mmol, 112 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2l** (76 mg, 57 %) as a yellow solid, m.p. 107–109 °C. ^{1}H NMR (500 MHz): δ = 11.05 (br., 1 H), 9.15 (dd, *J* = 6.0, 3.4 Hz, 2 H), 8.48 (dd, *J* = 9.5, 2.7 Hz, 1 H), 1.39 (s, 9 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 178.1, 141.5, 140.4, 134.9, 130.1, 122.3, 122.0, 41.0, 27.3 ppm. MS (EI): *m/z* (%) = 267 (14) [M$^+$], 168 (54), 149 (9), 118 (33), 98 (18), 85 (38), 57 (100). $C_{11}H_{13}N_3O_5$ (267.24): calcd. C 49.44, H 4.90, N 15.72; found C 49.71, H 4.93, N 15.79.

***N*-(5-methyl-2-nitrophenyl)pivalamide (2m):** The general procedure was followed by using 3-methylace (0.5 mmol, 95 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2m** (93 mg, 79 %) as a yellow solid, m.p. 95–97 °C. ^{1}H NMR (500 MHz): δ = 10.85 (s, 1 H), 8.71 (s, 1 H), 8.15 (d, *J* = 8.6 Hz, 1 H), 6.98 (d, *J* = 7.4 Hz, 1 H), 2.45 (s, 3 H), 1.38 (s, 10 H) ppm. ^{13}C NMR (126 MHz, cdcl$_3$): δ = 178.1, 148.1, 135.4, 134.2, 125.8, 124.0, 122.0, 40.6, 27.5, 22.1 ppm. MS (EI): *m/z* (%) = 236 (8) [M$^+$], 190 (11), 165 (13), 149 (21), 111 (18), 97 (23), 85 (37), 71 (54), 57 (100). $C_{12}H_{16}N_2O_3$ (236.27): calcd. C 61.00, H 6.83, N 11.86; found C 61.12, H 6.81, N 11.90.

***N*-(5-ethyl-2-nitrophenyl)pivalamide (2n):** The general procedure was followed by using 3-ethylpivalamide (0.5 mmol, 102 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2n** (105 mg, 84 %) as a yellow oil. ^{1}H NMR (400 MHz): δ = 10.88 (br., 1 H), 8.75 (d, *J* = 1.6 Hz, 1 H), 8.19 (d, *J* = 8.6 Hz, 1 H), 7.02 (dd, *J* = 8.8, 1.8 Hz, 1 H), 2.75 (q, *J* = 7.7 Hz, 2 H), 1.39 (s, 9 H), 1.30 (t, *J* = 7.6 Hz, 3 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 178.1, 154.1, 135.6, 134.3, 126.0, 122.8, 121.0, 40.7, 29.4, 27.5, 14.9 ppm. MS (EI): *m/z* (%) = 250 (33) [M$^+$], 204 (75), 166 (85), 136 (41), 120 (17), 91 (25), 57 (100). $C_{13}H_{18}N_2O_3$ (250.29): calcd. C 62.38, H 7.25, N 11.19; found C 52.54, H 7.23, N 11.11.

***N*-(5-chloro-2-nitrophenyl)pivalamide (2o):** The general procedure was followed by using 3-chloropivanalide (0.5 mmol, 105 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2o** (75 mg, 59 %) as a yellow solid, m.p. 79–81 °C. ^{1}H NMR (500 MHz): δ = 10.86 (br., 1 H), 9.01 (d, *J* = 2.3 Hz, 1 H), 8.21 (d, *J* = 9.0 Hz, 1 H), 7.15 (dd, *J* = 9.1, 2.3 Hz, 1 H), 1.38 (s, 9 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 178.1, 142.9, 136.4, 134.3, 127.0, 123.2, 121.7, 40.7, 27.4 ppm. MS (EI): *m/z* (%) = 257 (3) [M + 1], 256 (11) [M$^+$], 210 (32), 172 (48), 85 (23), 57 (100). $C_{11}H_{13}ClN_2O_3$ (256.69): calcd. C 51.47, H 5.10, N 10.91; found C 51.28, H 5.13, N 10.84.

***N*-(4,5-dimethyl-2-nitrophenyl)pivalamide (2p):** The general procedure was followed by using 3,4-dimethylpivanalide (0.5 mmol, 102 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by columnchromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2p** (101 mg, 81 %) as a yellow solid, m.p. 103–104 °C. ^{1}H NMR (500 MHz): δ = 10.74 (br., 1 H), 8.60 (s, 1 H), 8.05 (s, 1 H), 2.35 (s, 3 H), 2.30 (s, 3 H), 1.38 (s, 9 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 177.9, 147.0, 134.1, 133.3, 132.1, 126.0, 122.6, 40.5, 27.5, 20.5, 19.2 ppm. MS (EI): *m/z* (%) = 250 (62) [M$^+$], 204 (100), 166 (82), 136 (27), 120 (33), 91 (21), 57 (96). $C_{13}H_{18}N_2O_3$ (250.29): calcd. C 62.38, H 7.25, N 11.19; found C 62.18, H 7.29, N 11.26.

***N*-(4,5-dichloro-2-nitrophenyl)pivalamide (2q):** The general procedure was followed by using 3,4-dichloropivalamide (0.5 mmol, 123 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2q** (88 mg, 61 %) as a yellow solid, m.p. 93–95 °C. ^{1}H NMR (500 MHz): δ = 10.74 (br., 1 H), 9.17 (s, 1 H), 8.36 (s, 1 H), 1.38 (s, 9 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 177.9, 141.2, 134.4, 131.0, 126.8, 126.6, 123.1, 40.7, 27.4 ppm. MS (EI): *m/z* (%) = 291 (11) [M$^+$], 253 (23), 191 (22), 147 (32), 105 (7), 91 (18), 57 (100). $C_{11}H_{12}Cl_2N_2O_3$ (291.13): calcd. C 45.38, H 4.15, N 9.62; found C 45.29, H 4.18, N 9.66.

***N*-(4-methyl-2-nitrophenyl)benzamide (2r):**[26] The general procedure was followed by using *N*-(*p*-tolyl)benzamide (0.5 mmol, 105 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2r** (113 mg, 89 %) as a yellow solid, m.p. 101–103 °C. ^{1}H NMR (500 MHz, [D]Chloroform): δ = 11.26 (br., 1 H), 8.90 (d, *J* = 8.6 Hz, 1 H), 8.10 (d, *J* = 2.0 Hz, 1 H), 8.01 (d, *J* = 7.5 Hz, 2 H), 7.62 (t, *J* = 7.3 Hz, 1 H), 7.56 (t, *J* = 7.8 Hz, 2 H), 2.44 (s, 3 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 165.7, 137.9, 137.2, 134.2, 133.7, 133.0, 132.6, 129.1, 127.4, 125.7, 122.1, 20.7 ppm. MS (EI): *m/z* (%) = 256 (22) [M$^+$], 210 (32), 105 (100), 91 (15), 77 (62), 51 (22). $C_{14}H_{12}N_2O_3$ (256.26): calcd. C 65.62, H 4.72, N 10.93; found C 65.80, H 4.75, N 10.86.

***N*-(4-methyl-2-nitrophenyl)benzenesulfonamide (2s):**[28] The general procedure was followed by using *N*-(*p*-tolyl)benzenesulfonamide (0.5 mmol, 130 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2s** (93 mg, 61 %) as a yellow solid, m.p. 79–80 °C. ^{1}H NMR

(400 MHz): δ = 9.66 (br., 1 H), 7.90 (s, 1 H), 7.76 (d, J = 8.6 Hz, 1 H), 7.71 (d, J = 8.4 Hz, 2 H), 7.42 (d, J = 8.9 Hz, 2 H), 7.26 (d, J = 8.1 Hz, 2 H), 2.40 (s, 3 H), 2.36 (s, 3 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 144.7, 137.3, 136.8, 135.7, 134.5, 131.3, 130.0, 127.2, 125.9, 121.6 ppm. MS (EI): m/z (%) = 306 (74) [M$^+$], 155 (70), 91 (100), 77 (11), 65 (35), 51 (13). $C_{14}H_{14}N_2O_4S$ (306.34): calcd. C 54.89, H 4.61, N 9.14; found C 54.98, H 4.59, N 9.18.

***N*-(4-methyl-2-nitrophenyl)hexanamide (2t):** The general procedure was followed by using *N*-(*p*-tolyl)hexanamide (0.5 mmol, 102 mg), $NaNO_2$ (69 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 1.0 mmol), and $AgNO_2$ (8 mg, 10 mol-%). Purification by column chromatography (silica gel; *n*-hexane/EtOAc, 2:1) gave product **2t** (101 mg, 81 %) as a yellow oil. ^{1}H NMR (400 MHz): δ = 10.48 (br., 1 H), 8.08 (s, 1 H), 7.10 (d, J = 8.4 Hz, 1 H), 6.86 (d, J = 8.6 Hz, 1 H), 2.50 (s, 3 H), 2.37 (t, J = 7.6 Hz, 2 H), 1.67 (p, J = 7.4 Hz, 4 H), 1.34 (q, J = 3.6 Hz, 2 H), 0.92 (t, J = 7.6 Hz, 3 H) ppm. ^{13}C NMR (101 MHz, [D]Chloroform): δ = 174.0, 143.7, 139.8, 136.1, 129.9, 122.1, 114.5, 34.2, 31.3, 24.6, 22.4, 20.5, 14.0 ppm. MS (EI): m/z (%) = 249 (10) [M$^+$], 167 (42), 149 (100), 118 (29), 71 (53), 57 (72). $C_{13}H_{18}N_2O_3$ (250.29): calcd. C 62.38, H 7.25, N 11.19; found C 62.63, H 7.21, N 11.13.

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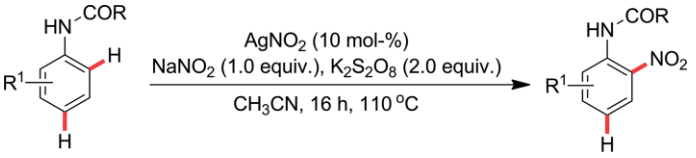
C–H Functionalization



A highly regioselective silver-catalyzed nitration of anilides through C–H bond functionalization produces the corresponding *ortho*-nitroanilides moderate to good yields. The reaction proceeds with $NaNO_2$ as the nitration agent.

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