NH_4I/*tert*-butyl hydroperoxide-promoted oxidative C–N cleavage of tertiary amines leading to nitroaromatic compounds

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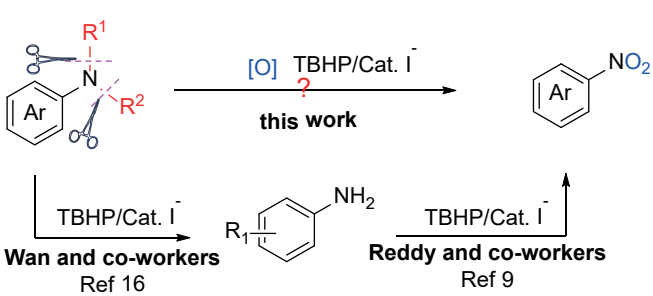
A NH_4I/*tert*-butyl hydroperoxide-promoted oxidation of tertiary *N*-aryl-*N*,*N*-dialkylamines in DMSO has been developed to access nitroaromatic compounds. This methodology involves sequential *N*-dealkylation reactions in one-pot and a radical pathway is proposed.

Keywords: nitroaromatic compounds, *N*-dealkylation, radical process, *tert*-butyl hydroperoxide, *N*-aryl-*N*,*N*-dialkylamines

Nitroaromatic compounds are important industrial chemicals for a large range of useful materials such as explosives, propellants, dyes, pharmaceuticals, plastics, perfumes and potential drugs.[1] Moreover, they serve as reactive intermediates and synthetic precursors in organic synthesis and they may undergo facile transformation into compounds having various functional groups.[1,2] Traditional nitration of aromatic compounds by mixed nitric acid and sulfuric acid is not environmentally friendly. Many alternative "green" nitration methods, with high regioselectivity, including the use of solid acids, lanthanide(III) triflates and enzyme catalysed procedures, have been reported to minimise noxious waste.[1,3] Other nitration agents, such as metal nitrates, N_2O_5 and NO_2–O_3, were found to be more suitable for industrial production.[1] Recently, direct nitration of C_{Ar}–H involved an alternative procedure with higher regioselectivities.[4–7] In addition, selective oxidation of primary,[1,8–10] or secondary *N*-aryl amines,[11] represents facile pathways to access nitroarenes. However, to date, there are no reports on selective oxidation of tertiary amines to give nitroaromatic compounds.

Practically, the oxidation of tertiary amines to amine *N*-oxides in the presence of H_2O_2, or peroxoic acids, is a classic textbook reaction.[12] Nowadays, selective oxidation of tertiary amines is becoming a challenging and fascinating field in modern synthetic chemistry,[13–16] including *N*-dealkylation and oxidative cross-coupling reactions. Most of these oxidative reactions involve iminium ions or imine intermediates derived from oxidation of the otherwise inert C_α–H of tertiary amines under catalytic conditions.[13]

Based on these, we envisaged that in the presence of *tert*-butyl hydroperoxide (TBHP), oxidative *N*-dealkylation of tertiary amines may occur and lead to *in situ* generation of secondary amines or even primary amines[13,16] and the resulting substituted anilines can undergo further selective oxidation to the corresponding nitro compounds[9] (Scheme 1). Given that



Scheme 1 Design pathway towards nitroarenes from tertiary *N*-aryl-*N*,N-dialkylamines.

tertiary amines exist extensively in nature,[17] we considered them to be potentially useful precursors to nitro compounds. Here, we report a mild and facile method of direct oxidation of tertiary *N*-aryl-*N*,*N*-alkylamines with TBHP and NH_4I, which provides an alternative route to nitroarenes. To the best of our knowledge, there are no reports describing synthesis of nitroarenes by direct oxidation of tertiary amines.

Results and discussion

Initially, according to the procedures of Wan and co-workers[16] and Reddy and co-workers[9] (Scheme 1), the study focused on the model reaction of *N*,*N*-dimethyl-4-methylaniline (**1a**), in the presence of TBHP (70%) and a catalytic amount of iodide (such as KI, *tert*-butyl ammonium iodide or NH_4I) or I_2, in DMSO (Table 1, entries 1–4) at 80 °C under air for 4h (see SAFETY CAUTION in Experimental section). Among the catalysts tested, NH_4I was found to provide the desired product, 1-methyl-4-nitrobenzene (**2a**), in 37% yield (Table 1, entry 3). Further experiments revealed that the amount of NH_4I (Table 1, entries 5–8), the amount of TBHP [Table S1, entries 14–17 in the Electronic Supplementary Information (ESI)] and reaction time (Table 1, entry 8) affected the reaction significantly. When 4.0 equiv. of NH_4I and 12.0 equiv. of TBHP were used, the yield of **2a** increased to 81% (Table 1, entry 8). Subsequently, solvents such as H_2O, CH_3CN, isopropanol and DMF were also tested (Table 1, entries 9–12) and dipolar aprotic solvents DMF and DMSO gave higher yields (79 and 81% respectively) than other solvents. Among the oxidants tested, H_2O_2, di-*tert*-butyl peroxide (DTBP) and potassium monoperoxysulfate (oxone®) resulted in no desired reaction (Table 1, entries 13–15); while *tert*-amyl peroxide (TAHP) gave a lower yield of 34% (Table 1, entry 16). At 90 °C, the yield of **2a** was further increased to 85% (Table 1, entry 8). Blank experiments showed that both TBHP and NH_4I were necessary for this reaction (Table 1, entries 17 and 18). The reaction atmosphere had almost no effect on the reaction efficiency (Table 1, entry 8) and reactions could be conducted open to the atmosphere.

With the optimised conditions in hand, various substituted *N*,*N*-dimethylanilines were examined to explore the scope of this new oxidation system and the results are shown in Table 2. The substrates, bearing either electron-donating groups, such as methyl **1a** and methoxy **1d** groups, or electron-withdrawing groups, such as halides **1h** and **1k**, nitro **1m**, methoxycarbonyl **1o** and trifluoromethyl **1q** groups at the *para* positions, were transformed to corresponding nitrocompounds in satisfactory yields ranging from 59 to 85% (**2a**, **2d**, **2h**, **2k**, **2m**, **2o** and **2q**). *N*,*N*-Dimethylaniline (**1g**) also worked well, providing **2g** in 68% yield. However, steric effects influence the reaction. For

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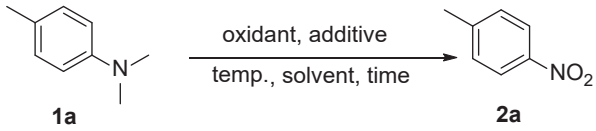
Table 1 Reaction conditions screening[a]



1a **2a**

Entry	Oxidant	Solvent	Iodine (equiv.)	Yield (%)[b]
1	TBHP	DMSO	KI (0.2)	35
2	TBHP	DMSO	TBAI (0.2)	8
3	TBHP	DMSO	NH_4I (0.2)	37
4	TBHP	DMSO	I_2 (0.2)	Trace[c]
5	TBHP	DMSO	NH_4I (0.5)	40
6	TBHP	DMSO	NH_4I (1.0)	46
7	TBHP	DMSO	NH_4I (2.0)	66
8	TBHP	DMSO	NH_4I (4.0)	81, 79[d], 80[e], 73[f], 72[g], 85[h]
9	TBHP	H_2O	NH_4I (4.0)	51
10	TBHP	CH_3CN	NH_4I (4.0)	69
11	TBHP	IPA	NH_4I (4.0)	70
12	TBHP	DMF	NH_4I (4.0)	79
13	H_2O_2[i]	DMSO	NH_4I (4.0)	ND[j]
14	DTBP[i]	DMSO	NH_4I (4.0)	ND[j]
15	Oxone[i]	DMSO	NH_4I (4.0)	ND[j]
16	TAHP[i]	DMSO	NH_4I (4.0)	34
17	–	DMSO	NH_4I (4.0)	ND[j]
18	TBHP	DMSO	–	ND[j]

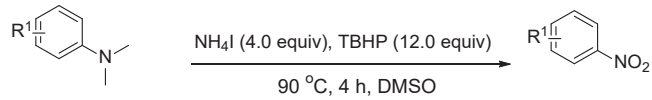
[a]Reaction conditions: **1a** (0.2 mmol), TBHP (70% in water, 2.4 mmol), NH_4I (0.8 mmol), KI (0.04 mmol) and solvent (0.5 mL) at 80 °C for 4 h under air atmosphere in a sealed tube. For detailed information, please see Table S1 in the ESI.
[b]Isolated yield.
[c]Yield less than 5%.
[d]Under N_2 atmosphere.
[e]Under O_2 atmosphere.
[f]Reacted for 3 h.
[g]Reacted for 5 h.
[h]At 90 °C.
[i]Mole ratio, [oxidant]/[**1a**] = 12:1.
[j]No detected product.

example, when *ortho* substituents were present, **2c**, **2j** and **2f** were isolated in 42, 38 and 42% yields respectively. The lower conversion of compounds with *ortho* substituents was partly ascribed to the formation of by-products derived from the iodination of aromatic rings. Similarly, substrates with *meta* substituents, including methyl **1b**, methoxy **1e**, bromine **1i**, and chlorine **1l**, gave products **2b**, **2e**, **2i** and **2l** in only 38, 35, 35 and 38% yields respectively.

Importantly, the substrate scope was not limited to *N*,*N*-dimethylanilines, as other *N*,*N*-dialkylanilines also underwent oxidation. For instance, *N*,*N*-diethylaniline (**3a**), *N*,*N*-dibutylaniline (**3b**), 2-[methyl(phenyl)amino]ethan-1-ol (**3c**) and 1-phenylpiperidine (**4**) provided **2g** in 40, 52, 61 and 16% yields respectively (Table 3). The lower yields are probably due to steric hindrance. Unfortunately, heterocyclic substrates *N*,*N*-dimethylpyridin-4-amine (**1r**), *N*,*N*-dimethyl-1-naphthylamine (**1s**), aliphatic tertiary amines, *N*,*N*-dimethyl-1-phenylmethanamine (**1t**) and *N*,*N*-dimethylcyclohexanamine (**1u**) were investigated and gave no desired products (Table S2 in the ESI). Substrate **1s** gave ring opened products, such as 2-methylisoindoline-1,3-dione (**5**) and 2-cyanobenzoic acid (**6**) which were detected by GC–MS (Fig. S2 in the ESI). Substrate **1t** was transformed into benzonitrile (**7**) in high yield (Fig. S3 in the ESI).[18]

In order to investigate the mechanism, several experiments were conducted. When radical scavenger TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl) was added to the

Table 2 Scope of *N*,*N*-dimethylanilines[a]

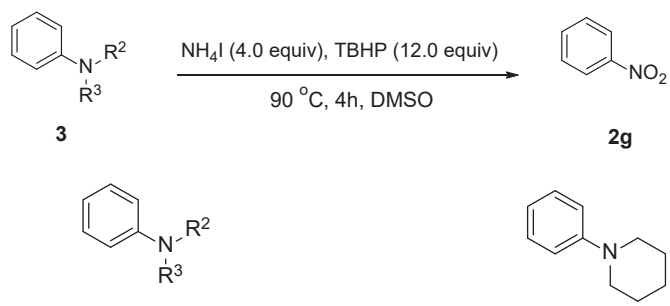


1 **2**

Entry	R^1	Product	Yield (%)[b]
1	4-Me	**2a**	85
2	3-Me	**2b**	38
3	2-Me	**2c**	42
4	4-OMe	**2d**	62
5	3-OMe	**2e**	35
6	2,4,6-Me	**2f**	42
7	H	**2g**	68
8	4-Br	**2h**	73
9	3-Br	**2i**	35
10	2-Br	**2j**	38[c]
11	4-Cl	**2k**	72
12	3-Cl	**2l**	38
13	4-NO_2	**2m**	59
14	3-NO_2	**2n**	41
15	4-$COOCH_3$	**2o**	78
16	4-N_2Ph	**2p**	40
17	4-CF_3	**2q**	73[d]

[a]Reaction conditions: **1** (0.2 mmol), TBHP (70% in water, 2.4 mmol), NH_4I (0.8 mmol) and DMSO (0.5 mL) at 90 °C for 4 h under air atmosphere in a sealed tube.
[b]Isolated yield.
[c]For 6 h.
[d]Low boiling point product, with only GC yield provided (see Fig. S1 in the ESI).

Table 3 Scope of *N*,*N*-dialkylanilines[a,b]



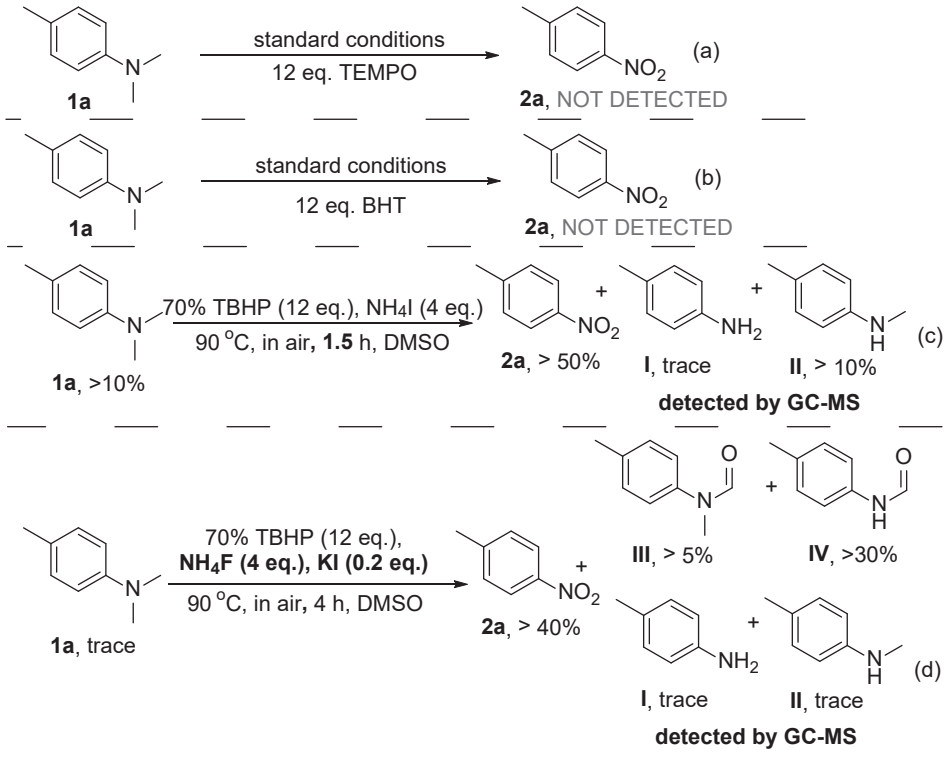
3 **2g**

3a, R^3=R^3=Et, Yield: 40%
3b, R^3=R^3=Bu, Yield: 52%
3c, R^3=CH_3, R^3=CH_2CH_2OH, Yield: 61%

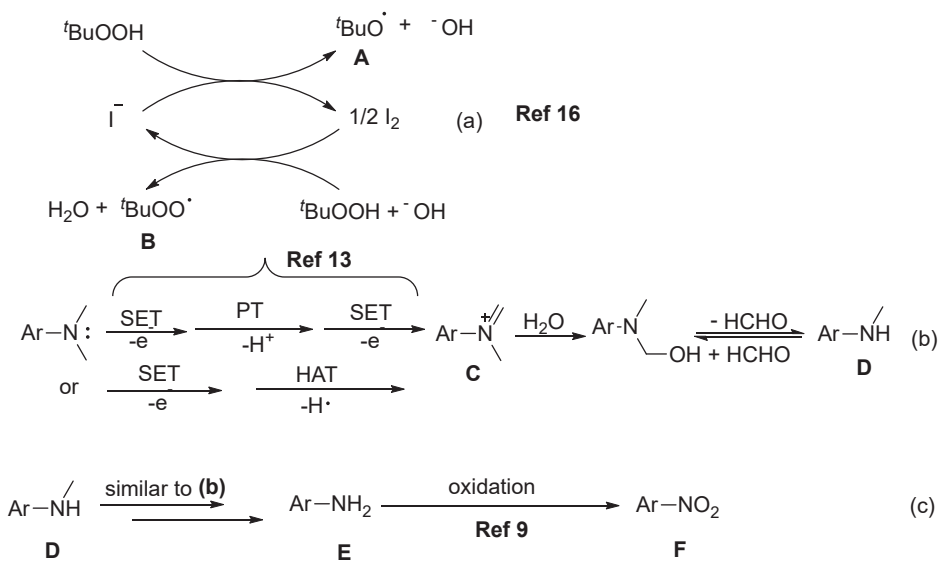
4, Yield: 16%

[a]Reaction conditions: **1** (0.2 mmol), TBHP (70% in water, 2.4 mmol), NH_4I (0.8 mmol) and DMSO (0.5 mL) at 90 °C for 4 h under air atmosphere in a sealed tube.
[b]Isolated yield.

reaction mixture, no desired product **2a** was formed (Scheme 2a, Fig. S4 in the ESI). A similar result was obtained when BHT (2,6-di-*tert*-butyl-4-methylphenol) was added (Scheme 2b, Fig. S4 in the ESI). These results suggested that the reaction involved a radical process. GC–MS was used to monitor the reaction. *p*-Toluidine (**I**) and *N*,4-dimethylaniline (**II**) were formed during the procedure under the standard reaction conditions for 1.5 h (Scheme 2c, Fig. S5 in the ESI). When 4.0 equiv. NH_4I was replaced by 4.0 equiv. NH_4F and 0.2 equiv KI, except for trace amount of **I** and **II**, lower yields of **2a**, as well as by-products *N*-methyl-*N*-(*p*-tolyl)formamide (**III**) and *N*-*p*-tolylformamide (**IV**), were observed (Scheme 2d, Fig. S5 in the



Scheme 2 Investigation on mechanism.



Scheme 3 Proposed reaction mechanism.

ESI). It indicated that this transformation starts from Cα–H activation of the tertiary amines and involved *N*-dealkylation. Increasing the amount of iodide can suppress the formation of by-products **III** and **IV**. However, extra iodide in the oxidation mixture will increase iodination side reactions.

Based on the experimental data and literature, a plausible mechanism for this reaction is proposed (Scheme 3). The transformation starts from decomposition of TBHP in the presence of iodide and gives radical species *t*-BuO• (**A**) and *t*-BuOO• (**B**) with I_2, involving a catalytic redox cycle (Scheme 3a).[16] With the help of these species, two electrons and one proton were abstracted by single electron transfer (SET) and hydrogen atom transfer (HAT) steps or by proton transfer (PT) and SET steps,[13] with the formation of cation radicals or even an α-aminoalkyl radical, which leads to iminium ion **C**, followed by *in situ* addition of H_2O and loss of HCHO, leading to secondary amine **D** (Scheme 3b). A similar process transforms secondary amine **D** into aromatic primary amine **E**. Finally, with the presence of extra TBHP and iodide, **E** is oxidised to an aromatic nitro compound as reported by Reddy and co-workers (Scheme 3c).[9]

Conclusion

In summary, a new strategy for the one-pot synthesis of nitroaromatic compounds from tertiary *N*-aryl-*N*,*N*-alkylamines by oxidation with TBHP and NH_4I is presented. This methodology is proposed to proceed by a radical oxidation of tertiary amines resulting in *N*-dealkylation reactions.

Experimental

All manipulations were carried out under air atmosphere and all commercial chemicals were used without further purification. Column chromatography was generally performed on silica gel (300–400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light, to visualise the course of the reactions. NMR spectra were recorded on either a 300 or 400 MHz Bruker spectrometer. GC–MS spectra were recorded on a Shimadzu GCMS QP-2010 spectrometer with an EI source. IR spectra were recorded on a FTIR Bruker Vector 55 spectrometer using KBr discs. Melting points were taken on an Electrothermal melting point apparatus and are used without correction.

CAUTION: In view of the explosive nature of hydroperoxide reagents which were heated, all reactions were carried out on the small scale indicated in fume hoods with anti-blast shields.

Synthesis of **2***; general procedure*

Under air, **1** (0.2 mmol), NH_4I (0.8 mmol), 70% TBHP in water (2.4 mmol) and DMSO (0.5 mL) were added to a 10 mL Schlenk tube sealed with a Teflon lined cap. The reaction mixture was stirred at 90 °C for 4 h in an oil bath. Upon completion, the reaction mixture was left to cool to room temperature and slowly quenched with anhydrous sodium sulfite. The reaction mixture was then diluted with ethyl acetate (5 mL) and then washed with water (5 × 5 mL). The aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over Na_2SO_4. The filtrate was concentrated and the crude product was purified by column chromatography on silica gel with petroleum ether (60–90 °C)/ethyl acetate eluent. Characterisation data are consistent with literature data.

1-Methyl-4-nitrobenzene (**2a**): Flash column chromatography on a silica gel [ethyl acetate/petroleum ether (1:20)] gave **2a**: Light yellow solid; yield 23.3 mg (85%); m.p 48–50 °C (lit.[6] 49–51 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.47 (s, 3H), 7.32 (d, *J* = 8.7 Hz, 2H), 8.12 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.6, 122.5, 128.8, 145.0; EI-MS calcd for $C_7H_7NO_2$: 137; found: 137 [M^+]; IR (KBr, cm^{-1}): ν 3012, 2963, 2923, 1599, 1519, 1495, 1450, 1345, 1261, 1097, 1022, 802.

1-Methyl-3-nitrobenzene (**2b**):[19] Flash column chromatography on a silica gel (ethyl acetate/petroleum ether, 1:20) gave **2b**: Yellowish liquid; yield 10.3 mg (38%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.47 (s, 3H), 7.39–7.45 (m, 1H), 7.49–7.52 (m, 1H), 8.01–8.04 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 120.7, 123.9, 129.1, 135.4, 139.8, 148.2; EI-MS calcd for $C_7H_7NO_2$: 137; found: 137 [M^+]; IR (KBr, cm^{-1}): ν 3010, 2923, 1634, 1601, 1574, 1522, 1384, 1343, 1289, 1097, 1024, 820, 802, 754.

1-Methyl-2-nitrobenzene (**2c**):[20] Flash column chromatography on a silica gel (ethyl acetate/petroleum ether, 1:20) gave **2c**: Yellowish liquid; yield 11.4 mg (42%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.61 (s, 3H), 7.32–7.37 (m, 2H), 7.48–7.53 (m, 1H), 7.97 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.5, 124.7, 126.9, 132.8, 133.0, 133.6, 149.6; EI-MS calcd for $C_7H_7NO_2$: 137; found: 137 [M^+]; IR (KBr, cm^{-1}): ν 3030, 2923, 2852, 1596, 1558, 1515, 1465, 1442, 1381, 1336, 1297, 1269, 1195, 1088, 1037, 955, 865, 828, 817, 745.

1-Methoxy-4-nitrobenzene (**2d**): Flash column chromatography on a silica gel (ethyl acetate/petroleum ether, 1:15) gave **2d**: Beige solid; yield 19.0 mg (62%); m.p. 51–52 °C (lit.[6] 50–52 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.92 (s, 3H), 6.97 (d, *J* = 9.3 Hz, 2H), 8.22 (d, *J* = 9.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.0, 114.0, 125.9, 141.5, 164.6; EI-MS calcd for $C_7H_7NO_3$: 153; found: 153 [M^+]; IR (KBr, cm^{-1}): ν 3021, 2963, 2923, 2850, 1608, 1599, 1519, 1499, 1346, 1261, 1097, 1022, 862, 846, 802, 751.

1-Methoxy-3-nitrobenzene (**2e**): Flash column chromatography on a silica gel (ethyl acetate/petroleum ether, 1:15) gave **2e**: Yellowish oil; yield 10.8 mg (35%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 3H), 7.15 (dd, J_1 = 8.3 Hz, J_2 = 2.4 Hz, 1H), 7.35 (t, *J* = 8.2 Hz, 1H), 7.65 (t, *J* = 2.0 Hz, 1H), 7.73–7.75 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.3, 107.6, 115.3, 120.8, 129.4, 148.8, 159.7; EI-MS calcd for $C_7H_7NO_3$: 153; found: 153 [M^+]; IR (KBr, cm^{-1}): ν 3012, 2924, 1634, 1574, 1522, 1455, 1384, 1343, 1289, 1260, 1097, 1024, 887, 819, 804, 735.

1,3,5-Trimethyl-2-nitrobenzene (**2f**): Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gave **2f**: Yellowish solid; yield 13.9 mg (42%); m.p. 39–41 °C (lit.[6] 39–41 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 6H), 2.31 (s, 3H), 6.92 (d, *J* = 0.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.5, 21.0, 129.4, 129.6, 140.3, 149.8; EI-MS calcd for $C_9H_{11}NO_2$: 165; found: 165 [M^+]; IR (KBr, cm^{-1}): ν 3030, 2924, 2855, 1605, 1519, 1480, 1457, 1365, 859, 835, 701, 602.

Nitrobenzene (**2g**):[6] Flash column chromatography on a silica gel (ethyl acetate/ petroleum ether, 1:20) gave **2g**: Yellowish liquid; yield 16.7 mg (68%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58–7.53 (m, 2H), 7.74–7.68 (m, 1H), 8.23 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 123.8, 129.3, 134.7, 148.1; EI-MS calcd for $C_6H_5NO_2$: 123; found: 123 [M^+]; IR (KBr, cm^{-1}): ν 3010, 2924, 2858, 2360, 2341, 1621, 1606, 1588, 1521, 1478, 1349, 1316, 1261, 1107, 1069, 1021, 920, 851, 794, 700, 680.

1-Bromo-4-nitrobenzene (**2h**): Flash column chromatography on a silica gel (ethyl acetate/petroleum ether, 1:25) gave **2h**: Yellowish solid; yield 29.6 mg (73%); m.p. 124 °C (lit.[6] 125–127 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67–7.72 (m, 2H), 8.09–8.14 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 125.0, 130.0, 132.7, 147.0; EI-MS calcd for $C_6H_4{}^{79}BrNO_2$: 201, for $C_6H_4{}^{81}BrNO_2$: 203; found: 201, 203 [M^+]; IR (KBr, cm^{-1}): ν 3104, 3011, 2924, 2851, 1604, 1599, 1577, 1520, 1344, 1261, 1107, 1093, 1066, 1023, 848, 741, 704, 675.

1-Bromo-3-nitrobenzene (**2i**): Flash column chromatography on a silica gel (ethyl acetate/petroleum ether, 1:25) gave **2i**: Yellowish low melting point solid; yield 14.2 mg (35%); m.p. 50–51 °C (lit.[21] 51–52 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (t, *J* = 8.1 Hz, 1H), 7.82–7.87 (m, 1H), 8.16–8.20 (m, 1H), 8.39 (t, *J* = 2.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 122.2, 122.9, 126.8, 130.6, 137.7, 148.8; EI-MS calcd for $C_6H_4{}^{79}BrNO_2$: 201, for $C_6H_4{}^{81}BrNO_2$: 203; found: 201, 203 [M^+]; IR (KBr, cm^{-1}): ν 3095, 3011, 2925, 2854, 1634, 1570, 1530, 1457, 1348, 1113, 1060, 980, 888, 869, 808, 731.

1-Bromo-2-nitrobenzene (**2j**): Flash column chromatography on a silica gel (ethyl acetate/petroleum ether, 1:25) gave **2j**: Yellowish solid; yield 15.4 mg (38%); m.p. 39–40 °C (lit.[21] 38–40 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41–7.50 (m, 2H), 7.74–7.77 (m, 1H), 7.83–7.87 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 114.5, 125.7, 128.3, 133.2, 135.1, 150.2; EI-MS calcd for $C_6H_4{}^{79}BrNO_2$: 201, for $C_6H_4{}^{81}BrNO_2$: 203; found: 201, 203 [M^+]; IR (KBr, cm^{-1}): ν 3011, 2922, 2851, 1653, 1635, 1570, 1560, 1527, 1452, 1353, 1324, 1286, 1254, 1075, 1037, 869, 852, 831, 739.

1-Chloro-4-nitrobenzene (**2k**): Flash column chromatography on a silica gel (ethyl acetate/petroleum ether, 1:25) gave **2k**: Yellowish solid; yield 22.7 mg (72%); m.p. 79–81 °C (lit.[6] 81–83 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50–7.55 (m, 2H), 8.18–8.21 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 125.0, 129.6, 141.4, 146.5; EI-MS calcd for $C_6H_4{}^{35}ClNO_2$: 157, for $C_6H_4{}^{37}ClNO_2$: 159; found: 157, 159 [M^+]; IR (KBr, cm^{-1}): ν 3104, 3012, 2924, 2851, 1604, 1577, 1520, 1476, 1420, 1355, 1344, 1313, 1107, 1093, 1012, 848, 741, 675.

1-Chloro-3-nitrobenzene (**2l**): Flash column chromatography on a silica gel (ethyl acetate/petroleum ether, 1:25) gave **2l**; Yellowish solid; yield 12.0 mg (38%); m.p. 43–44 °C (lit.[21] 46–47 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (t, *J* = 8.2 Hz, 1H), 7.69 (dd, *J* = 8.0, 0.9 Hz, 1H), 8.14 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.24 (t, *J* = 2.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 121.7, 123.9, 130.4, 134.7, 135.4, 148.8; EI-MS calcd for $C_6H_4{}^{35}ClNO_2$: 157, for $C_6H_4{}^{37}ClNO_2$: 159; found: 157, 159 [$M.^+$]; IR (KBr, cm^{-1}): ν 3011, 2922, 2851, 1631, 1570, 1560, 1528, 1452, 1352, 1324, 1286, 1254, 1037, 869, 852, 832, 739, 669.

1,4-Dinitrobenzene (**2m**): Flash column chromatography on a silica gel (ethyl acetate/petroleum ether, 1:20) gave **2m**: White solid; yield 19.8 mg (59%); m.p. 169–171 °C (lit.[6] 165–166 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 124.9, 151.0; EI-MS calcd for $C_6H_4N_2O_4$: 168; found: 168 [M^+]; IR (KBr, cm^{-1}): ν 3123, 3109, 3020, 2960, 2924, 2852, 1945, 1730, 1560, 1477, 1409, 1388, 1345, 1320, 1104, 1010, 872, 839, 819, 710, 517.

1,3-Dinitrobenzene (**2n**): Flash column chromatography on a silica gel (ethyl acetate/petroleum ether, 1:20) gave **2n**: Yellowish solid; yield 13.8 mg (41%); m.p. 86 °C (lit.[25] 88–90 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (t, *J* = 8.1 Hz, 1H), 8.58 (d, *J* = 2.2 Hz, 1H), 8.61 (d, *J* = 2.2 Hz, 1H), 9.10 (t, *J* = 2.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 119.1, 128.9, 130.8, 148.5; EI-MS calcd for $C_6H_4N_2O_4$: 168; found: 168 [M^+]; IR (KBr, cm^{-1}): ν 3108, 3022, 2921, 2851, 1615, 1601, 1540, 1466, 1347, 1273, 1094, 1068, 913, 906, 836, 817, 726, 711, 652.

Methyl 4-nitrobenzoate (**2o**): Flash column chromatography on a silica gel (ethyl acetate/petroleum ether, 1:20) gave **2o**: White solid; yield 28.2 mg (78%); m.p. 91–93 °C (lit.[23] 94–96 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.99 (s, 3H), 8.20–8.23 (m, 2H), 8.29–8.32 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.9, 123.6, 130.7, 135.5, 150.5, 165.2; EI-MS calcd for $C_8H_7NO_4$: 181; found: 181 [M^+]; IR (KBr, cm^{-1}): ν 3010, 2958, 2923, 2851, 1719, 1608, 1525, 1434, 1349, 1324, 1284, 1116, 1104, 1013, 957, 872, 869, 823, 786, 718.

1-(4-Nitrophenyl)-2-phenyldiazene (**2p**): Flash column chromatography on a silica gel (ethyl acetate/petroleum ether, 1:10) gave **2p**: Orange solid; yield 18.2 mg (40%); m.p. 129–131 °C (lit.[26] 132–133 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54–7.57 (m, 3H), 7.95–7.99 (m, 2H), 8.02 (d, *J* = 9.0 Hz, 2H), 8.36–8.39 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 122.4, 122.4, 123.7, 128.3, 131.4, 147.6, 151.3, 154.6; EI-MS calcd for $C_{12}H_9N_3O_2$: 227; found: 227 [M^+]; IR (KBr, cm^{-1}): ν 3012, 2924, 2851, 1606, 1588, 1523, 1464, 1443, 1384, 1345, 1261, 1104, 859, 805, 777, 690.

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Electronic Supplementary Information

The ESI (Tables S1 and S2, Figs S1–S5 and the ^{1}H NMR and ^{13}C NMR of the products) is available through http://ingentaconnect.com/content/stl/jcr/2017/00000041/00000009

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