

Synthesis of (Alkylamino)nitroarenes by Oxidative Alkylamination of Nitroarenes

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Dedicated to Professor Alexander F. Pozharskii on the occasion of his 70th birthday

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The viability of the oxidative alkylamination process for the derivatization of electron-deficient carboaromatics has been investigated. 1,3-Dinitrobenzene, 1-nitronaphthalene, and 1,5- and 1,8-dinitronaphthalenes have shown to react with a wide range of alkylamines in the presence of an oxidant (KMnO₄, AgMnO₄, AgPy₂MnO₄) to give access to the corre-

sponding *N*-alkyl-nitroarenamines in moderate to good yields. Nitroarenes are more reactive than azines towards alkylamines.

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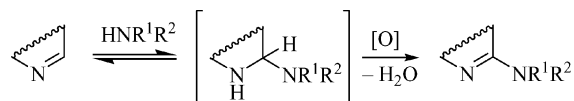
Introduction

The synthesis of functionalized aromatic and heteroaromatic amines is still of great interest, due to their importance as building blocks for pharmaceuticals, agrochemicals, polymers, and materials.^[1] The classical strategy for their preparation is based on nucleophilic displacement reactions involving good leaving groups. Harsh reaction conditions and strong dependence on the substitution pattern of the arene substrate are drawbacks limiting its application.^[2] A more general approach, widely used nowadays, is Pd-catalyzed coupling between aryl halides and alkylamines.^[3] In cases of electron-deficient azaheteroaromatic substrates, direct oxidative amination and alkylamination with KNH₂/NH₃/KMnO₄ or alkylamine/KMnO₄, pioneered by van der Plas,^[4b] is an attractive alternative because no classical leaving group is required. Mechanistically, this nucleophilic aromatic substitution of hydrogen consists of σ^H adduct formation and its subsequent oxidative rearomatization (Scheme 1).^[4] Generally, oxidative nucleophilic aromatic substitution of hydrogen (ONSH)^[5] can be performed when: i) the electrophilicity of the substrate used is rather high for providing σ^H adduct in sufficient concentration, and ii) either the oxidant is able to oxidize the σ^H adduct (not nucleophile) selectively, or the oxidation rate of the σ^H

adduct, formed in the presence of an excess of nucleophile, is higher than the oxidation rate of the nucleophile itself. These a priori rules, especially point (ii), seem difficult to fulfill. In fact, nucleophiles resistant to oxidation are not numerous. Ammonia is one such example, though alkylamines are much more sensitive than ammonia towards oxidation. In previous reports from our laboratories,^[6] however, we have shown that an alkylamine/AgPy₂MnO₄ system is very efficient for the oxidative alkylamination of azines. AgPy₂MnO₄ can thus be regarded as a rather selective oxidant for this objective. With regard to point (i), mono- and bicyclic azines and their nitro derivatives were previously used predominantly as substrates for oxidative (alkyl)amination. Surprisingly, reports on oxidative (alkyl)amination of polynitroarenes, which also possess rather high π -deficiency, are very scarce. The limited literature precedents include amination^[7] and methylamination^[8] of 1,3-dinitrobenzenes by a classical procedure (RNH₂/KMnO₄), butylation of 1,3-dinitrobenzene and 1,3-dinitronaphthalene with the *n*BuNH₂/KMnO₄/TBAF/DMF system,^[9a,9b] and butyl- and hexylamination of 1,3-dinitrobenzenes, 1,3,5-trinitrobenzene, and 1,3-dinitronaphthalene by electrochemical rather than chemical oxidation.^[9c]

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Scheme 1. General scheme for the oxidative alkylamination of azines.

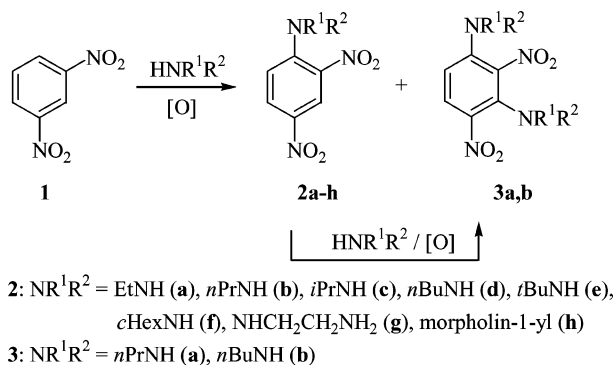
Attempts to use 1,2- and 1,4-dinitrobenzenes as substrates in oxidative methylamination reactions led to nucleophilic substitution of nitro groups, yielding *N*-methyl-2-nitroaniline and *N*-methyl-4-nitroaniline, respectively.^[8]

In this paper we describe oxidative alkylaminations of 1,3-dinitrobenzene, 1-nitronaphthalene, and 1,5- and 1,8-dinitronaphthalenes by use of alkylamine/KMnO₄, alkylamine/AgPy₂MnO₄, or alkylamine/AgMnO₄ systems. The developed procedures provide access to a wide variety of *N*-alkyl-2,4-dinitroanilines, which are of current interest because of their optical second harmonic generation capabilities^[10] and application as components of fluorescent signaling systems.^[11] *o*-Nitronaphthylamines are interesting as precursors of the naphthalene “proton sponges” and polycyclic imidazoles. To the best of our knowledge, the *N*-alkyl-1,5-dinitronaphthalen-2-amines, *N*-alkyl-1,8-dinitronaphthalen-2-amines, and *N,N'*-dialkyl-1,5-dinitronaphthalene-2,6-diamines reported in this study have not been described previously. There are only a few reports on the synthesis of the parent 1,5-dinitronaphthalen-2-amine,^[12a,12b] *N*-alkyl-4,5-dinitronaphthalen-1-amine,^[12c–12e] and *N,N'*-dimethyl-1,5-dinitronaphthalene-2,6-diamine.^[12f,12g]

Results and Discussion

The butylamination of 1,3-dinitrobenzene and 1,3-dinitronaphthalene by ONSH described above has been reported to be promoted by fluoride ions.^[9] However, we found that 1,3-dinitrobenzene (**1**) reacts with *n*BuNH₂/KMnO₄/DMF, in the absence of tetrabutylammonium fluoride, to provide a similar yield of *N*-butyl-2,4-dinitroaniline (**2d**, 66% against 63%^[9]) (Scheme 2; Table 1, Entry 4). In fact, the reaction does not require DMF as a cosolvent either. Treatment of **1** with an excess of butylamine in the presence of 2 equiv. of KMnO₄ (room temp., overnight) gave **2d** in 74% yield, together with diamino derivative **3b** (10%) as a minor compound (Table 1, Entry 5). Alkylamination of 1,3-dinitrobenzene (**1**) with propylamine/KMnO₄ proceeded similarly, producing mono- and bis(propylamino) derivatives **2c** and **3a** in 81% total yield (8:1 ratio as deduced from ¹H NMR). Unfortunately, we failed to separate this mixture (Table 1, Entry 2). The reported oxidative amination^[7] and methylamination^[8] of 1,3-dinitrobenzene also provided both type of reaction products. Treatment of **1** with the bulkier isopropylamine, *tert*-butylamine, and cyclohexylamine in the presence of KMnO₄ gave no bis(alkylamino) derivatives **3** (Table 1, Entries 3, 6, 7). The yields of the corresponding *N*-alkyl-2,4-dinitroanilines **2** vary from 63% (**2c**) to 4% (**2e**). As well as steric hindrance, the lower solubility of KMnO₄ in *tert*-butylamine and cyclohexylamine and, as a consequence, the lower rate of the oxidation step might explain the lower yields obtained. Alkylamination of **1** with ethane-1,2-diamine/KMnO₄ was carried out in THF as a co-solvent in order to avoid the need for removal of a large excess of ethane-1,2-diamine after completion of the reaction. Be-

cause of its oxidizable nature the reaction product **2g** was isolated in 29% yield as a hydrochloride salt (Table 1, Entry 8). 1,3-Dinitrobenzene (**1**) hardly reacted with secondary cyclic amines, as is exemplified by its reaction with morpholine, giving only a trace of **2h** (Table 1, Entry 9).



Scheme 2. Oxidative alkylamination of 1,3-dinitrobenzene (**1**).

Table 1. Oxidative alkylamination of 1,3-dinitrobenzene (**1**).

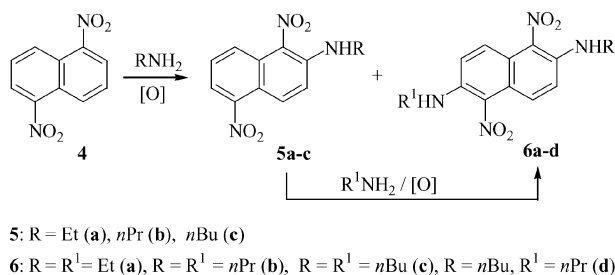
Entry	HNR¹R²	Product	Oxidant (method) ^[a]	% Yield
1	EtNH ₂	2a	KMnO ₄ (A)	59
2	<i>n</i> PrNH ₂	2b	KMnO ₄ (B)	81 ^[b]
3	<i>i</i> PrNH ₂	2c	KMnO ₄ (B)	63
4	<i>n</i> BuNH ₂	2d	KMnO ₄ (C)	66
5	<i>n</i> BuNH ₂	2d	KMnO ₄ (B)	74 ^[c]
6	<i>t</i> BuNH ₂	2e	KMnO ₄ (B)	4
7	<i>c</i> HexNH ₂	2f	KMnO ₄ (B)	10
8	NH ₂ CH ₂ CH ₂ NH ₂	2g ^[d]	KMnO ₄ (D)	29
9	morpholine	2h	KMnO ₄ (B)	trace
10	EtNH ₂	2a	AgPy ₂ MnO ₄ (E)	72
11	<i>n</i> PrNH ₂	2b	AgPy ₂ MnO ₄ (F)	71
12	<i>i</i> PrNH ₂	2c	AgPy ₂ MnO ₄ (F)	73
13	<i>n</i> BuNH ₂	2d	AgPy ₂ MnO ₄ (F)	63
14	<i>t</i> BuNH ₂	2e	AgPy ₂ MnO ₄ (F)	69
15	<i>c</i> HexNH ₂	2f	AgPy ₂ MnO ₄ (F)	63
16	NH ₂ CH ₂ CH ₂ NH ₂	2g ^[d]	AgPy ₂ MnO ₄ (G)	37
17	morpholine	2h	AgPy ₂ MnO ₄ (B)	4

[a] Method A, 0–2 °C, overnight; Method B, room temp., overnight; Method C, DMF, room temp., 1.5 h; Method D, THF, room temp., overnight; Method E, 0–2 °C, 1.5 h; Method F, room temp., 1.5 h; Method G, THF, room temp., overnight. [b] Total yield of **2b** and **3a** (8:1 ratio deduced by ¹H NMR). [c] Compound **3b** was also obtained in 10% yield. [d] Isolated as hydrochloride salt.

The use of AgPy₂MnO₄ instead of KMnO₄ led to the desired *N*-alkyl-2,4-dinitroanilines **2a–g** in 37–73% yields (Table 1, Entries 10–16). The reactions required only 1.5 h at room temperature to give complete conversion, except for the reaction involving THF as co-solvent (Table 1, Entry 16). *tert*-Butylamine and cyclohexylamine, which had given poor yields of **2** with KMnO₄, smoothly converted **1** into **2e** and **2f** in the presence of AgPy₂MnO₄ (Table 1, Entries 14, 15). However, the yield of **2h** is still disappointingly low (Table 1, Entry 17). It should be noted that oxidative alkylamination with AgPy₂MnO₄ does not produce bis(alkylamino) derivatives **3** and is therefore more selective towards the desired compounds. Compounds **3** are formed by subsequent oxidative alkylamination of monoalkylamino derivatives **2**. To verify this, *N*-butyl-2,4-dinitroaniline (**2d**)

was treated with *n*BuNH₂ in the presence of KMnO₄ (2 equiv., room temp., overnight). From the ¹H NMR spectroscopic data we were able to deduce that 40% of the starting material had been converted into bis(butylamino) derivative **3b**. Unfortunately, though, we were unable to push the reaction to completion, as longer reaction times or increased amounts of KMnO₄ (4–6 equiv.) afforded **3b** in practically the same yields.

1,5-Dinitronaphthalene (**4**) seems to be more reactive towards alkylamines than 1,3-dinitrobenzene. Treatment of **4** with propylamine and KMnO₄ carried out at room temperature gave a mixture of products that we failed to separate. However, use of THF as a co-solvent and a reduction in the reaction temperature to –15 to –12 °C allowed conversion of **4** into the desired 1,5-dinitro-*N*-propylnaphthalen-2-amine (**5b**) in 48% yield (Scheme 3, Table 2, Entry 2). Treatment of **4** with ethylamine and butylamine gave **5a** and **5c** in 35 and 42% yields, respectively (Table 2, Entries 1, 3). As had been observed for **1**, substrate **4** gave faster reactions when AgPy₂MnO₄ was used as the oxidant than with KMnO₄ (Table 2, Entries 4–6). Moreover, slightly higher yields of **5a–c** were obtained. When AgPy₂MnO₄ was used, however, the transformations of **4** into **5** were



Scheme 3. Oxidative alkylamination of 1,5-dinitronaphthalene (**4**).

Table 2. Oxidative alkylamination of 1,5-dinitronaphthalene (**4**).

Entry	HNR ¹ R ²	Product	Oxidant ^[a] (method) ^[b]	% Yield
1	EtNH ₂	5a	KMnO ₄ (A)	35
2	<i>n</i> PrNH ₂	5b	KMnO ₄ (A)	48
3	<i>n</i> BuNH ₂	5c	KMnO ₄ (A)	42
4	EtNH ₂	5a	AgPy ₂ MnO ₄ (B)	59
5	<i>n</i> PrNH ₂	5b	AgPy ₂ MnO ₄ (B)	60
6	<i>n</i> BuNH ₂	5c	AgPy ₂ MnO ₄ (B)	60
7	EtNH ₂	6a	AgMnO ₄ (C)	13
8	<i>n</i> PrNH ₂	6b	AgMnO ₄ (C)	16
9	<i>n</i> BuNH ₂	6c	AgMnO ₄ (C)	10

[a] 2 and 3 equiv. of the oxidant were used for the synthesis of **5** and **6**, respectively. [b] Method A, THF, –15 to –12 °C, 24 h; Method B, THF, –15 to –12 °C, 2 h; Method C, –15 to –12 °C, 48 h.

accompanied by further alkylamination of **5**. Prolongation of the reaction over 3 h led to accumulation of 2,6-bis(alkylamino) derivatives **6** and partial tarring of the reaction mixtures. Compounds **6a–c** were obtained in low yields when the reactions were performed in the appropriate alkylamines in the presence of AgMnO₄ (4 equiv.) at low temperatures (–15 to –12 °C) for long reaction times (48 h, Table 2, Entries 7–9). Compound **6b** was also obtained by treatment of monoalkylamino derivative **5b** with propylamine under similar conditions in 30% yield. Similarly, treatment of **5b** with butylamine gave the asymmetrical bis(alkylamino) derivative **6d** in 25% yield.

Theoretically, the oxidative alkylamination of 1,5-dinitronaphthalene (**4**) can proceed at position 2 as well as at position 4. The structural assignments for compounds **5** and **6** were based on the ¹H NMR spectroscopic data. The 8-H proton of **5** reveals itself as a doublet of multiplets at 8.8–8.9 ppm (Figure 1). Obviously, this high δ value is the result of the deshielding influence of the *peri* NO₂ group. The multiplet form of the 8-H signal is due to long-range

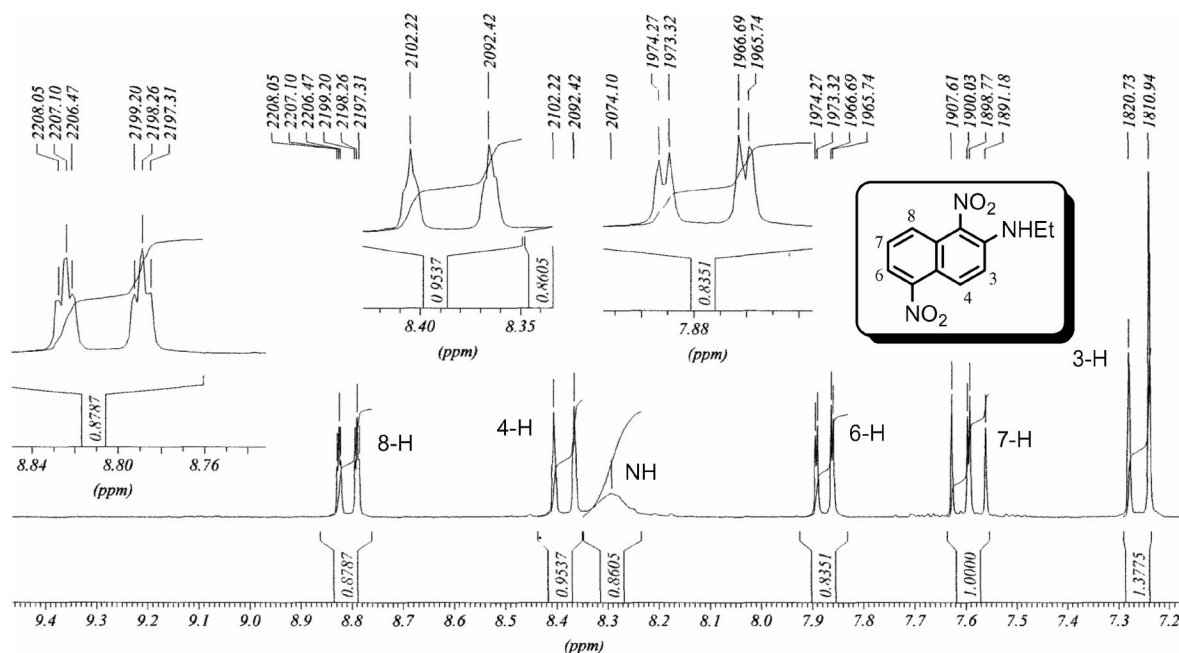


Figure 1. Fragment of the ¹H NMR spectrum of compound **5a** (CDCl₃).

spin-spin coupling between this proton and both the 6-H and 4-H nuclei. The magnitude of the allylic ($^4J_{6,8}$) and the homoallylic coupling constants ($^5J_{4,8}$) are 0.6–1.0 Hz, which is in accordance with literature data.^[13] Other protons appear upfield from 8-H at 7.2–8.4 ppm. Notably, the magnitude of the $J_{3,4}$ coupling constant (9.8–10.1 Hz) is larger than those of $J_{7,8}$ (8.8 Hz) and $J_{6,7}$ (7.6 Hz). This is the result of strong conjugation of the 1-NO₂ group and the 2-alkylamino fragment. The observed δ values for the NH-protons of **5a–c** (8.3–8.5 ppm) are in agreement with this. ¹H–¹H COSY experiments provided unambiguous discrimination between all signals (Figure 2) and confirmed the long-range couplings. The ¹H NMR spectra of *N,N'*-di-alkyl-1,5-dinitronaphthalene-2,6-diamines **6** are rather simple. Each displays a set of the signals belonging to the alkylamino group and two doublet signals of the 3(7)-H and 4(8)-H protons at δ = 7.1 and 8.6 ppm, respectively, with a coupling constant of 9.7 Hz. This justifies the symmetry of the molecular structures of **6a–c**. Other spectroscopic and spectrometric data (IR, UV, and MS) are in full agreement with the proposed structures of **5** and **6**.

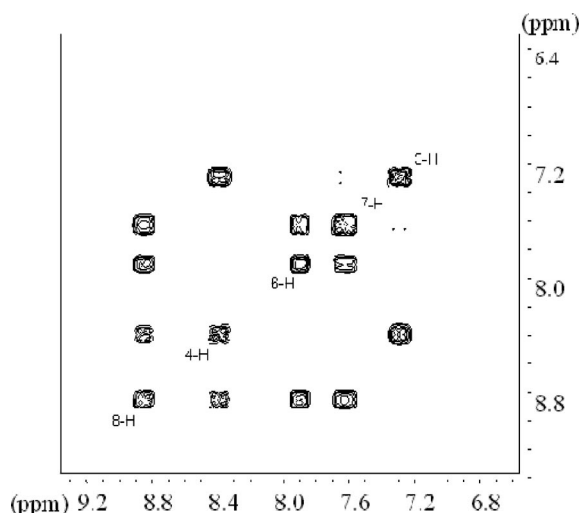


Figure 2. Fragment of the ¹H–¹H COSY NMR spectrum of compound **5a** (CDCl₃).

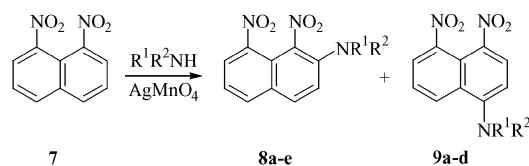
Treatment of 1,8-dinitronaphthalene (**7**) with propylamine and KMnO₄ gave 1,8-dinitro-*N*-propylnaphthalen-2-amine (**8b**) and 4,5-dinitro-*N*-propylnaphthalen-1-amine (**9b**) in 38% total yield (1:1.3 ratio deduced by ¹H NMR) (Table 3, Entry 1). Treatment of **7** with propylamine/AgPy₂MnO₄ at room temperature gave a complicated mixture of products that we failed to separate. The use of THF as co-solvent and reduction of the reaction temperature to –15 to –12 °C provided propylamino derivatives **8b** and **9b** in 11% and 10% yields, respectively (Table 3, Entry 2). Performing the reaction in propylamine at room temperature with AgMnO₄ as oxidant provided significantly higher yields of **8b** and **9b**, but the selectivity did not improve (Table 3, Entry 3). Treatment of **7** with butylamine gave a similar result (Table 3, Entry 4). Interestingly, cyclohexylamine and morpholine gave exclusively 2-cyclohexylamino derivative **8d** in 40% yield and 2-morpholino deriv-

ative **8e** in 14% yield (Table 3, Entries 5 and 6). Generally, reducing the reaction temperature to –15 to –12 °C decreased the yields but did not significantly influence the ratios of the products (Table 3, Entries 7–9). In no cases were bis(alkylamino) derivatives observed (Scheme 4).

Table 3. Oxidative alkylamination of 1,8-dinitronaphthalene (**7**).

Entry	HNR ¹ R ²	Oxidant (method) ^[a]	Ratio ^[b] 8/9	% Yield ^[c] 8	% Yield ^[c] 9
1	<i>n</i> PrNH ₂	KMnO ₄ (A)	1:1.3	16	22
2	<i>n</i> PrNH ₂	AgPy ₂ MnO ₄ (B)	1:1.2	11	10
3	<i>n</i> PrNH ₂	AgMnO ₄ (A)	1:1.4	38	53
4	<i>n</i> BuNH ₂	AgMnO ₄ (A)	1:1.2	32	38
5	<i>c</i> HexNH ₂	AgMnO ₄ (C)	1:0	40	trace
6	morpholine	AgMnO ₄ (A)	1:0	14	–
7	EtNH ₂	AgMnO ₄ (D)	1:1.3	12	16
8	<i>n</i> PrNH ₂	AgMnO ₄ (D)	1:2	15	30
9	<i>c</i> HexNH ₂	AgMnO ₄ (D)	37:1	23	1

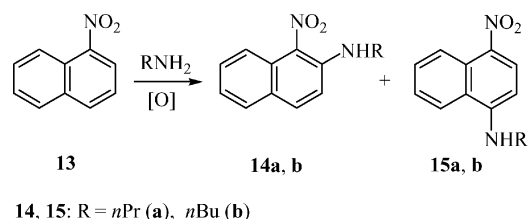
[a] Method A, room temp., overnight; Method B, THF, –15 to –12 °C, overnight; Method C, THF, room temp., overnight; Method D, –15 to –12 °C, overnight. [b] ¹H NMR ratio of the reaction mixture before separation. [c] Isolated yield after separation of **8** and **9**.



8, 9: NR¹R² = EtNH (**a**), *n*PrNH (**b**), *n*BuNH (**c**), *c*HexNH (**d**), morpholin-1-yl (**e**)

Scheme 4. Oxidative alkylamination of 1,8-dinitronaphthalene (**7**).

To find the scope and limitations of the developed procedure we also tested nitrobenzene and 1-nitronaphthalene as substrates. Nitrobenzene (**10**) hardly reacted with butylamine/KMnO₄ (room temp., 24 h), giving a mixture of isomeric *N*-butyl-2-nitroaniline (**11**) and *N*-butyl-4-nitroaniline (**12**) in less than 1% yield. The use of AgPy₂MnO₄ as the oxidant did not increase the yields significantly. In contrast, 1-nitronaphthalene (**13**) demonstrated a higher reactivity. When treated with butylamine/AgPy₂MnO₄, **13** was converted into a mixture of the *o*- and *p*-butylamino derivatives **14b** and **15b** in 73% total yield (Scheme 5, Table 4, Entry 2). Oxidation with KMnO₄ gave both products in only 15% total yield (Table 4, Entry 1). Treatment of **13** with propylamine/AgPy₂MnO₄ proceeded similarly, affording 1-nitro-*N*-propylnaphthalen-2-amine (**14a**) and 4-nitro-*N*-propylnaphthalen-1-amine (**15a**) (Table 4, Entry 3). Pyrimidine (**16**), which can be regarded as a heterocyclic analogue of 1,3-dinitrobenzene, did not react with alkylamines in the presence of KMnO₄ or AgPy₂MnO₄ as the oxidant. Quinoline (**19**) was significantly less reactive than 1-nitronaphthalene. When treated with propylamine/AgPy₂MnO₄ (room temp., 24 h), **19** was converted into a mixture of isomeric *N*-propyl(quinolin-2-yl)amine and -(quinolin-4-yl)amine in 3% total yield (1:1 ratio).



Scheme 5. Oxidative alkylamination of 1-nitronaphthalene (13).

Table 4. Oxidative alkylamination of 1-nitronaphthalene (13).

Entry	RNH ₂	Oxidant (method) ^[a]	% Yield	
			14	15
1	<i>n</i> BuNH ₂	KMnO ₄ (A)	12	3
2	<i>n</i> BuNH ₂	AgPy ₂ MnO ₄ (B)	52	21
3	<i>n</i> PrNH ₂	AgPy ₂ MnO ₄ (B)	49	22

[a] Method A, room temp., 24 h; Method B, room temp., 24 h.

On the basis of our earlier work^[5] we tried to explain the observed regioselectivities by calculating and analyzing the spatial distributions of the Fukui functions for nucleophilic attack (f_k^+) on the dinitroarenes (1, 4, and 7) experimentally studied as substrates, using DFT calculations at the B3LYP/6-31G** level (Gaussian 03^[14]). The results of the calculation of the global and local electrophilicity indices (ω and ω_k ^[15]) for preliminary optimized structures of the nitroarenes (Figure 3) are presented in Figure 4. For 1,3-dinitrobenzene (1) the maximum of ω_k corresponds to C-4, which is indeed the reaction site. Although the local electrophilicity index of C-4 in 1,5-dinitronaphthalene (4) is slightly higher than ω_k for C-2, the alkylamination exclusively occurs at C-2. This can be explained by taking account of the steric hindrance of the *peri*-nitro group, disfavoring attack at C-4. The local electrophilicity index of C-4

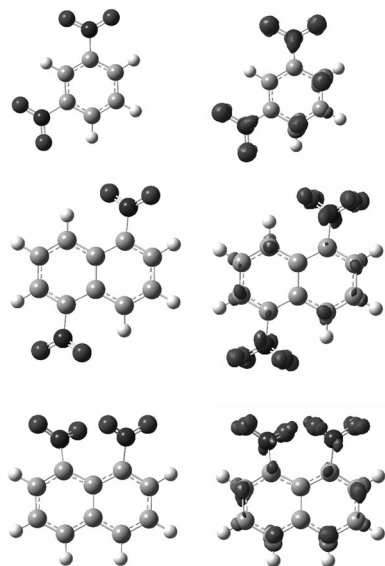


Figure 3. B3LYP/6-31G(d,p) equilibrium geometries (left) and corresponding Fukui functions (right) for nucleophilic attack on 1,3-dinitrobenzene (1, top), 1,5-dinitronaphthalene (4, middle), and 1,8-dinitronaphthalene (7, bottom). The values for the isodensity surfaces were set to 0.005 $e a_0^{-3}$.

in 1,8-dinitronaphthalene (7) is also slightly higher than ω_k for C-2, which is in accordance with the general observation that mixtures of compounds alkylaminated at C-2 and C-4 are formed. Of course, one has to be very careful in rationalizing regioselectivities only on this basis because the oxidation potentials of the different σ adducts formed can play a major role, it being likely that this step is rate-limiting in the oxidative (alkyl)amination process.

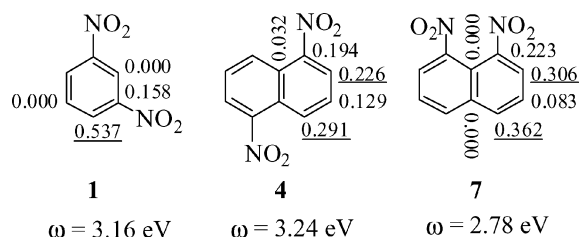


Figure 4. Calculated global electrophilicity values (ω , in eV) and local electrophilicity indices (ω_k , given at each ring atom, in eV).

Conclusions

A simple and efficient synthetic route to *N*-alkyl-2,4-dinitroanilines, *N*-alkyl-1-nitronaphthalen-2-amines, *N*-alkyl-4-nitronaphthalen-1-amines, *N*-alkyl-1,*n*-dinitronaphthalen-2-amines ($n = 5, 8$), *N*-alkyl-4,5-dinitronaphthalen-1-amines, and *N,N'*-dialkyl-1,5-dinitronaphthalene-2,6-diamines through oxidative alkylamination of the corresponding nitroarenes has been elaborated. The method allows the use of a wide range of primary aliphatic amines, especially when AgPy₂MnO₄ is used as the oxidant. The protocol presented here provides yields of alkylamino products the same as – or, more often, superior to – those of classical synthetic procedures for *N*-alkyl-2,4-dinitroanilines based on nucleophilic aromatic substitution in the corresponding 1-*X*-2,4-dinitrobenzenes.^[10,11a,16] *N*-alkylation of 2,4-dinitroaniline,^[17] and oxidative *N*-dealkylation of *N,N*-dialkyl-2,4-dinitroanilines,^[18] and distinguishes itself in very mild reaction conditions and the use of a commercially available starting compound (1,3-dinitrobenzene). The chemical oxidation method presented in this paper seems to be more attractive than the electrochemical oxidation of σ adducts of 1,3-dinitrobenzenes and alkylamines^[9c] because it provides superior yields of *N*-alkyl-2,4-dinitroanilines and it does not require the use of special equipment.

Experimental Section

General: All melting points were determined in glass capillaries and are uncorrected. The ¹H and ¹³C NMR spectra were recorded with a Bruker 250 (250 MHz) instrument in the solvent indicated and with TMS as an internal standard. All coupling constants are given in Hertz, and chemical shifts are given in parts per million (ppm). Infrared (IR) spectra were recorded with a Specord IR-71 spectrometer (Nujol). Ultraviolet absorption (UV) spectra were registered with a Specord M-40 spectrophotometer in CHCl₃ as a solvent. Mass spectra were measured on a Finnigan MAT INCOS 50 spectrometer. Nitroarenes, pyrimidine, and alkylamines (Acros and

Aldrich) were obtained from commercial sources and used as such. AgPy₂MnO₄ was prepared from AgNO₃, pyridine, and KMnO₄ by a literature procedure.^[19] Flash column chromatography was performed on silica gel and Al₂O₃ (III–IV activity, Brockman) with chloroform or dichloromethane as eluents.

General Procedures for the Oxidative Alkylamination of 1,3-Dinitrobenzene (1)

Method A: Procedure similar to Method B, but reaction temp. 0–2 °C. The reaction with ethylamine gave compound **2a**.

Method B: KMnO₄ (316 mg, 2 mmol) was added at room temperature in small portions over 1 h to a stirred solution of 1,3-dinitrobenzene (**1**, 168 mg, 1 mmol) in the appropriate alkylamine (10 mL). The reaction mixture was stirred overnight. The excess of the alkylamine was subsequently removed under reduced pressure. The residue was ground with silica gel (3–4 g), introduced onto a silica gel column (3.5 × 30 cm), and purified by flash column chromatography with dichloromethane as the eluent. A bright yellow fraction gave the corresponding *N*-alkyl-2,4-dinitroaniline (**2**). Upon butylation of **1** the first bright yellow fraction gave *N*-butyl-2,4-dinitroaniline (**2d**, 177 mg, 74%) and the next yellow fraction gave *N,N'*-dibutyl-4,6-dinitrobenzene-1,3-diamine (**3b**, 31 mg, 10%). The crude product was crystallized from hexane.

Method C: KMnO₄ (158 mg, 1 mmol) was added to a stirred solution of 1,3-dinitrobenzene (**1**, 168 mg, 1 mmol) and butylamine (0.49 mL, 5 mmol) in DMF (3 mL). After 1.5 h stirring at room temperature the reaction mixture was diluted with water (5 mL) and extracted with dichloromethane (3 × 20 mL). The extract was dried with MgSO₄. The solvent was subsequently removed under reduced pressure. The residue was ground with silica gel (3–4 g), introduced onto a silica gel column (3.5 × 30 cm), and purified by flash column chromatography with dichloromethane as the eluent. A bright yellow fraction was separated. The crude product was crystallized from heptane to yield *N*-butyl-2,4-dinitroaniline (**2d**, 158 mg, 66%).

Method D: KMnO₄ (316 mg, 2 mmol) was added in small portions over 1 h to a stirred solution of 1,3-dinitrobenzene (**1**, 168 mg, 1 mmol) and ethane-1,2-diamine (2 mL) in THF (5 mL). The reaction mixture was stirred overnight, and the solvents were evaporated. The residue was extracted with boiling *i*PrOH (100 mL). The solvent was subsequently removed under reduced pressure, and water (20 mL) was added to the residue. The mixture was heated to boiling and filtered (to remove a tar), and the filtrate was cooled quickly. The precipitate was separated by filtration, mixed immediately with *i*PrOH (20 mL), and acidified to pH 2 with conc. HCl. The precipitate was separated by filtration and rinsed with *i*PrOH and then Et₂O. *N*-(2-Aminoethyl)-2,4-dinitroaniline hydrochloride (**2g**) was obtained in 29% (76 mg) yield.

The reaction with AgPy₂MnO₄ (0.770 g, 2 mmol) was carried out in a similar way (Method G) to give **2g** (97 mg, 37%).

Method E: Procedure similar to Method F, but reaction temp. 0–2 °C.

Method F: AgPy₂MnO₄ (0.770 g, 2 mmol) was added in small portions at room temperature over 1 h to a stirred solution of 1,3-dinitrobenzene (**1**, 168 mg, 1 mmol) in the appropriate alkylamine (10 mL). After 1.5 h overall stirring time the excess of the alkylamine was removed under reduced pressure. The residue was ground with silica gel (3–4 g), introduced onto a silica gel column (3.5 × 30 cm), and purified by flash column chromatography with chloroform as the eluent. A bright yellow fraction gave the corresponding *N*-alkyl-2,4-dinitroaniline (**2**). The crude product was crystallized from hexane.

The reaction with morpholine was carried out in a similar way for 16 h at room temperature to give **2h**.

The reaction with ethylamine gave **2a** (Method E).

Method G: Procedure similar to Method D, but AgPy₂MnO₄ (0.770 g, 2 mmol) was used as the oxidant. The reaction gave compound **2g** (97 mg, 37%).

***N*-Ethyl-2,4-dinitroaniline (2a):** Yield 124 mg, 59% (Method A); 152 mg, 72% (Method B). Bright yellow needles with m.p. 112–114 °C (hexane; ref.^[16c] 90 °C). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 9.13 (d, *J* = 2.7 Hz, 1 H, 3-H), 8.48 (br., 1 H, NH), 8.26 (dd, *J* = 9.6, 2.7 Hz, 1 H, 5-H), 6.90 (d, *J* = 9.6 Hz, 1 H, 6-H), 3.45 (m, 2 H, CH₂CH₃), 1.42 (t, *J* = 7.3 Hz, 3 H, CH₂CH₃) ppm. IR (Nujol): ν̃ = 3367 (N–H), 3106 (C–H arom.), 1610 and 1573 (C–C arom.), 1520 and 1500 (NO₂, as), 1333 and 1300 (NO₂, s) cm^{–1}. UV (CHCl₃): λ_{max} (lg ε) = 246 (4.38), 258 sh (3.97), 357 (4.32), 415 sh nm (3.92). MS (70 eV): *m/z* (%) = 211 (63) [M]⁺, 196 (92), 164 (14), 150 (22), 132 (13), 118 (53), 92 (48), 78 (100), 63 (54), 52 (34), 46 (40). C₈H₉N₃O₄ (211.17): calcd. C 45.50, H 4.30, N 19.90; found C 45.63, H 4.19, N 19.97.

2,4-Dinitro-*N*-propylaniline (2b): Yield 160 mg, 71% (Method F). Bright yellow needles with m.p. 98–99 °C (hexane; ref.^[10] 100–102 °C). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 9.13 (d, *J* = 2.8 Hz, 1 H, 3-H), 8.56 (br., 1 H, NH), 8.25 (dd, *J* = 9.5, 2.8 Hz, 1 H, 5-H), 6.91 (d, *J* = 9.5 Hz, 1 H, 6-H), 3.37 (m, 2 H, CH₂CH₂CH₃), 1.80 (m, 2 H, CH₂CH₂CH₃), 1.07 (t, *J* = 7.4 Hz, 3 H, CH₂CH₂CH₃) ppm. IR (Nujol): ν̃ = 3360 (N–H), 3100 (C–H arom.), 1620 and 1580 (C–C arom.), 1520–1490 (NO₂, as), 1333 and 1305 (NO₂, s) cm^{–1}. UV (CHCl₃): λ_{max} (lg ε) = 246 (4.73), 263 sh (4.43), 361 (4.55), 414 sh nm (4.13). MS (70 eV): *m/z* (%) = 225 (22) [M]⁺, 196 (100), 150 (10), 104 (10), 77 (10). C₉H₁₁N₃O₄ (225.20): calcd. C 48.00, H 4.92, N 18.66; found C 47.89, H 4.77, N 18.53.

***N*-Isopropyl-2,4-dinitroaniline (2c):** Yield 142 mg, 63% (Method B); 164 mg, 73% (Method F). Bright yellow needles with m.p. 95–96 °C (hexane). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 9.13 (d, *J* = 2.5 Hz, 1 H, 3-H), 8.49 (br., 1 H, NH), 8.24 (dd, *J* = 9.5, 2.5 Hz, 1 H, 5-H), 6.91 (d, *J* = 9.5 Hz, 1 H, 6-H), 3.92 [m, 1 H, CH(CH₃)₂], 1.38 [t, *J* = 6.3 Hz, 6 H, CH(CH₃)₂] ppm. IR (Nujol): ν̃ = 3327 (N–H), 3126 (C–H arom.), 1627 and 1590 (C–C arom.), 1527–1500 (NO₂, as), 1333 and 1300 (NO₂, s) cm^{–1}. MS (70 eV): *m/z* (%) = 225 (31) [M]⁺, 210 (100), 164 (26), 134 (18), 118 (25), 91 (22), 75 (11), 63 (14), 43 (22). C₉H₁₁N₃O₄ (225.20): calcd. C 48.00, H 4.92, N 18.66; found C 47.94, H 5.06, N 18.83.

***N*-Butyl-2,4-dinitroaniline (2d):** Yield 177 mg, 74% (Method B); 158 mg, 66% (Method C); 151 mg, 63% (Method F). Bright yellow needles with m.p. 90–91 °C (hexane; ref.^[10] 92–94 °C). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 9.13 (d, *J* = 2.8 Hz, 1 H, 3-H), 8.54 (br., 1 H, NH), 8.25 (dd, *J* = 9.5, 2.8 Hz, 1 H, 5-H), 6.90 (d, *J* = 9.5 Hz, 1 H, 6-H), 3.39 (m, 2 H, CH₂CH₂CH₂CH₃), 1.74 (m, 2 H, CH₂CH₂CH₂CH₃), 1.49 (m, 2 H, CH₂CH₂CH₂CH₃), 0.99 (t, *J* = 7.3 Hz, 3 H, CH₂CH₂CH₂CH₃) ppm. IR (Nujol): ν̃ = 3353 (N–H), 3113 (C–H arom.), 1620 and 1587 (C–C arom.), 1516–1490 (NO₂, as), 1328 and 1317 (NO₂, s) cm^{–1}. UV (CHCl₃): λ_{max} (lg ε) = 246 (4.96), 263 sh (4.64), 362 (4.81), 419 sh nm (4.45). MS (70 eV): *m/z* (%) = 239 (17) [M]⁺, 196 (100), 150 (15), 104 (10). C₁₀H₁₃N₃O₄ (239.23): calcd. C 50.21, H 5.48, N 17.56; found C 50.04, H 5.62, N 17.71.

***N*-tert-Butyl-2,4-dinitroaniline (2e):** Yield 9.6 mg, 4% (Method B); 165 mg, 69% (Method F). Bright yellow needles with m.p. 151–153 °C (hexane). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 9.14 (d, *J* = 2.7 Hz, 1 H, 3-H), 8.88 (br., 1 H, NH), 8.20 (dd, *J* = 9.5,

2.7 Hz, 1 H, 5-H), 7.14 (d, $J = 9.5$ Hz, 1 H, 6-H), 1.54 [s, 6 H, C(CH₃)₃] ppm. IR (Nujol): $\tilde{\nu} = 3340$ (N–H), 3140 (C–H arom.), 1627 and 1587 (C–C arom.), 1513 and 1500 (NO₂, as), 1333 and 1310 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 248 (4.66), 263 sh (4.51), 362 (4.61), 421 sh nm (4.30). MS (70 eV): m/z (%) = 239 (22) [M]⁺, 224 (100), 183 (28), 57 (25), 41 (19). C₁₀H₁₃N₃O₄ (239.23): calcd. C 50.21, H 5.48, N 17.56; found C 50.35, H 5.57, N 17.40.

N-Cyclohexyl-2,4-dinitroaniline (2f): Yield 26.5 mg, 10% (Method B); 167 mg, 63% (Method F). Bright yellow needles with m.p. 151–153 °C (hexane; ref.^[16c] 110 °C). ¹H NMR (250 MHz, CDCl₃, 30 °C): $\delta = 9.13$ (d, $J = 2.8$ Hz, 1 H, 3-H), 8.60 (br., 1 H, NH), 8.21 (dd, $J = 9.8$, 2.8 Hz, 1 H, 5-H), 6.91 (d, $J = 9.8$ Hz, 1 H, 6-H), 3.60 (m, 1 H, *cyclo*-C₆H₁₁), 2.05 (m, 2 H, *cyclo*-C₆H₁₁), 1.81 (m, 2 H, *cyclo*-C₆H₁₁), 1.68 (m, 2 H, *cyclo*-C₆H₁₁), 1.44 (m, 4 H, *cyclo*-C₆H₁₁) ppm. IR (Nujol): $\tilde{\nu} = 3353$ (N–H), 3113 (C–H arom.), 1620 (and 1587 (C–C arom.), 1513–1490 (NO₂, as), 1333 and 1290 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 247 (4.86), 264 sh (4.41), 364 (4.55), 422 sh nm (4.24). MS (70 eV): m/z (%) = 265 (26) [M]⁺, 222 (100), 179 (25), 149 (10), 130 (20), 105 (12), 78 (12), 63 (10), 55 (18), 41 (19). C₁₂H₁₅N₃O₄ (265.27): calcd. C 54.33, H 5.70, N 15.84; found C 54.18, H 5.57, N 16.00.

N-(2-Aminoethyl)-2,4-dinitroaniline Hydrochloride (2g): Yield 76 mg, 29% (Method D); 97 mg, 37% (Method G). Bright yellow solid with m.p. 267–268 °C (ref.^[11a] 268–270 °C). ¹H NMR (250 MHz, [D₆]DMSO): $\delta = 8.80$ (d, $J = 2.7$ Hz, 1 H, 3-H), 8.25 (d, $J = 9.5$ Hz, 1 H, 5-H), 7.98 (br., 3 H, NH₂ + NH), 7.30 (d, $J = 9.5$ Hz, 1 H, 6-H), 3.75 (m, 2 H, CH₂CH₂NH₂), 3.00 (m, 2 H, CH₂CH₂NH₂) ppm. IR (Nujol): $\tilde{\nu} = 3353$ and 3280–3300 (N–H), 3110 (C–H arom.), 1617 and 1587 (C–C arom.), 1520 and 1500 (NO₂, as), 1340 and 1317 (NO₂, s) cm^{−1}. MS (70 eV): m/z (%) = 226 (10) [M]⁺, 197 (11), 179 (46), 152 (26), 150 (13), 104 (40), 77 (64), 66 (20), 63 (32), 51 (55), 43 (16), 42 (13), 38 (46), 36 (100). C₈H₁₁ClN₄O₄ (262.65): calcd. C 36.58, H 4.22, Cl 13.50, N 21.33; found C 36.72, H 4.31, Cl 13.39, N 21.46.

4-(2,4-Dinitrophenyl)morpholine (2h): Yield 10 mg, 4% (Method F). Bright yellow needles with m.p. 117–118 °C (hexane). ¹H NMR (250 MHz, CDCl₃, 30 °C): $\delta = 8.69$ (d, $J = 2.8$ Hz, 1 H, 3-H), 8.27 (dd, $J = 9.2$, 2.8 Hz, 1 H, 5-H), 7.09 (d, $J = 9.2$ Hz, 1 H, 6-H), 3.85 [t, $J = 4.7$ Hz, 4 H, O(CH₂)₂], 3.25 [t, $J = 4.7$ Hz, 4 H, N-(CH₂)₂] ppm. IR (Nujol): $\tilde{\nu} = 3113$ (C–H arom.), 1607 and 1587 (C–C arom.), 1533 and 1507 (NO₂, as), 1340–1327 (NO₂, s) cm^{−1}. C₁₀H₁₁N₃O₅ (253.21): calcd. C 47.43, H 4.38, N 16.59; found C 47.29, H 4.19, N 16.44.

N,N'-Dibutyl-2,4-dinitrobenzene-1,3-diamine (3b): Bright yellow needles with m.p. 76–78 °C (heptane). ¹H NMR (250 MHz, CDCl₃, 30 °C): $\delta = 9.59$ (br., 1 H, BuNH-3), 8.21 (d, $J = 10.1$ Hz, 1 H, 5-H), 7.85 (br., 1 H, BuNH-1), 6.09 (d, $J = 10.1$ Hz, 1 H, 6-H), 3.31 (m, 2 H, CH₂CH₂CH₂CH₃), 2.92 (m, 2 H, CH₂CH₂CH₂CH₃), 1.67 (m, 4 H, 1- and 3-NHCH₂CH₂CH₂CH₃), 1.40 (m, 4 H, 1- and 3-NHCH₂CH₂CH₂CH₃), 0.97 (t, $J = 7.4$ Hz, 3 H, CH₂CH₂CH₂CH₃), 0.91 (t, $J = 7.4$ Hz, 3 H, CH₂CH₂CH₂CH₃) ppm. C₁₄H₂₂N₄O₄ (310.35): calcd. C 54.18, H 7.15, N 18.05; found C 54.01, H 7.29, N 18.21.

General Procedures for the Oxidative Alkylamination of 1,5-Dinitronaphthalene

Method A: AgPy₂MnO₄ (0.770 g, 2 mmol) was added in small portions at −15 to −12 °C, over 1 h, to a stirred solution of 1,5-dinitronaphthalene (4, 218 mg, 1 mmol) and alkylamine (3 mL) in THF (15 mL). After 2 h overall stirring time the reaction mixture was concentrated (without heating) under reduced pressure. The residue was ground with Al₂O₃ (3–4 g), introduced onto an Al₂O₃ column

(2.5 × 40 cm), and purified by flash column chromatography with CHCl₃ as the eluent. The first bright yellow fraction, preceding the crimson one, gave *N*-alkyl-1,5-dinitronaphthalene-2-amine (5). The crude product was crystallized from *i*PrOH.

Method B: The reactions with KMnO₄ (316 mg, 2 mmol) were carried out in a similar way at −15 to −12 °C for 24 h.

Method C: AgMnO₄ (680 mg, 3 mmol) was added in small portions at −15 to −12 °C over 1 h to a stirred solution of 1,5-dinitronaphthalene (4, 218 mg, 1 mmol) in the appropriate alkylamine (15 mL). After 48 h overall stirring the reaction mixture was concentrated (without heating) under reduced pressure. The residue was ground with Al₂O₃ (3–4 g), introduced onto an Al₂O₃ column (2.5 × 40 cm), and purified by flash column chromatography with CHCl₃ as the eluent. The crimson fraction gave *N,N'*-dialkyl-1,5-dinitronaphthalene-2,6-diamine (6). The crude product was crystallized from MeOH.

N-Ethyl-1,5-dinitronaphthalene-2-amine (5a): Yield 154 mg, 59% (Method A); 91 mg, 35% (Method B). Bright yellow crystals with m.p. 142–144 °C (*i*PrOH). ¹H NMR (250 MHz, CDCl₃, 30 °C): $\delta = 8.81$ (d, $J = 8.8$ Hz, 1 H, 8-H), 8.39 (d, $J = 9.8$ Hz, 1 H, 4-H), 8.30 (br., 1 H, NH), 7.88 (dd, $J = 7.6$, 1.0 Hz, 1 H, 6-H), 7.60 (dd, $J = 8.8$, 7.6 Hz, 1 H, 7-H), 7.26 (d, $J = 9.8$ Hz, 1 H, 3-H), 3.50 (dq, $J = 5.1$, 7.2 Hz, 2 H, CH₂CH₃), 1.41 (t, $J = 7.1$ Hz, 3 H, CH₂CH₃) ppm. IR (Nujol): $\tilde{\nu} = 3340$ (N–H), 1627 and 1567 (C–C arom.), 1527–1500 (NO₂, as), 1343 and 1313 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 258 sh (4.26), 278 (4.43), 345 (3.86), 426 sh (3.70), 471 nm (3.88). MS (70 eV): m/z (%) = 261 (100) [M]⁺, 246 (18), 182 (14), 169 (33), 154 (49), 140 (53), 127 (55), 114 (57), 102 (34), 87 (25), 75 (44), 70 (11), 63 (53), 51 (25), 43 (47), 39 (19). C₁₂H₁₁N₃O₄ (261.23): calcd. C 55.17, H 4.24, N 16.09; found C 55.01, H 4.13, N 15.95.

1,5-Dinitro-N-propylnaphthalene-2-amine (5b): Yield 165 mg, 60% (Method A); 132 mg, 48% (Method B). Bright yellow crystals with m.p. 122–124 °C (*i*PrOH). ¹H NMR (250 MHz, CDCl₃, 30 °C): $\delta = 8.85$ (d, $J = 8.8$ Hz, 1 H, 8-H), 8.46 (br., 1 H, NH), 8.39 (d, $J = 9.8$ Hz, 1 H, 4-H), 7.89 (dd, $J = 7.6$, 1.0 Hz, 1 H, 6-H), 7.61 (dd, $J = 8.8$, 7.6 Hz, 1 H, 7-H), 7.28 (d, $J = 9.8$ Hz, 1 H, 3-H), 3.42 (dt, $J = 5.4$, 7.0 Hz, 2 H, CH₂CH₂CH₃), 1.79 (m, 2 H, CH₂CH₂CH₃), 1.07 (t, $J = 7.3$ Hz, 3 H, CH₂CH₂CH₃) ppm. IR (Nujol): $\tilde{\nu} = 3347$ (N–H), 1633 and 1567 (C–C arom.), 1540–1520 (NO₂, as), 1360 and 1327 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 258 sh (4.28), 277 (4.45), 346 (3.90), 421 sh (3.86), 472 nm (3.89). MS (70 eV): m/z (%) = 275 (88) [M]⁺, 246 (100), 172 (37), 153 (37), 140 (22), 127 (34), 114 (23), 102 (10), 75 (14), 63 (16), 43 (13), 41 (18). C₁₃H₁₃N₃O₄ (275.26): calcd. C 56.72, H 4.76, N 15.27; found C 56.87, H 4.59, N 15.14.

N-Butyl-1,5-dinitronaphthalene-2-amine (5c): Yield 173 mg, 60% (Method A); 121 mg, 42% (Method B). Bright yellow crystals with m.p. 110–112 °C (*i*PrOH). ¹H NMR (250 MHz, CDCl₃, 30 °C): $\delta = 8.81$ (d, $J = 8.8$ Hz, 1 H, 8-H), 8.45 (br., 1 H, NH), 8.38 (d, $J = 10.1$ Hz, 1 H, 4-H), 7.88 (dd, $J = 7.6$, 1.0 Hz, 1 H, 6-H), 7.59 (dd, $J = 8.8$, 7.6 Hz, 1 H, 7-H), 7.27 (d, $J = 10.1$ Hz, 1 H, 3-H), 3.45 (dt, $J = 5.4$, 7.0 Hz, 2 H, CH₂CH₂CH₂CH₃), 1.74 (m, 2 H, CH₂CH₂CH₂CH₃), 1.48 (m, 2 H, CH₂CH₂CH₂CH₃), 0.98 (t, $J = 7.3$ Hz, 3 H, CH₂CH₂CH₂CH₃) ppm. IR (Nujol): $\tilde{\nu} = 3347$ (N–H), 1633 and 1560 (C–C arom.), 1530–1513 (NO₂, as), 1360 and 1327 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 258 sh (4.28), 283 (4.48), 339 (3.96), 421 sh (3.80), 471 nm (3.94). MS (70 eV): m/z (%) = 289 (62) [M]⁺, 246 (86), 172 (41), 153 (48), 140 (29), 127 (63), 114 (53), 102 (29), 75 (50), 63 (55), 55 (20), 51 (28), 41 (100). C₁₄H₁₅N₃O₄ (289.29): calcd. C 58.13, H 5.23, N 14.53; found C 58.21, H 5.37, N 14.39.

***N,N'*-Diethyl-1,5-dinitronaphthalene-2,6-diamine (6a):** Yield 40 mg, 13% (Method A). Red crystals with m.p. 214–216 °C (MeOH). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 8.56 [d, J = 9.7 Hz, 1 H, 4-H (8-H)], 7.87 (br., 1 H, NH), 7.14 [d, J = 9.7 Hz, 1 H, 3-H (7-H)], 3.50 (m, 2 H, CH₂CH₃), 1.37 (t, J = 7.2 Hz, 3 H, CH₂CH₃) ppm. IR (Nujol): $\tilde{\nu}$ = 3373 (N–H), 1600 (C–C arom.), 1493 (NO₂, as), 1313 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 265 sh (4.26), 278 sh (4.65), 292 (4.77), 335 sh (4.46), 500 sh (4.10), 564 nm (4.15). MS (70 eV): m/z (%) = 304 (100) [M]⁺, 224 (11), 213 (10), 197 (23), 183 (44), 169 (64), 156 (58), 154 (57), 140 (61), 127 (57), 114 (56), 101 (44), 88 (28), 78 (32), 76 (48), 70 (12), 63 (53), 51 (31), 42 (51), 38 (12). C₁₄H₁₆N₄O₄ (304.30): calcd. C 55.26, H 5.30, N 18.41; found C 55.39, H 5.44, N 18.23.

1,5-Dinitro-*N,N'*-dipropylnaphthalene-2,6-diamine (6b): Yield 53 mg, 16% (Method A). Red crystals with m.p. 186–188 °C (MeOH). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 8.56 [d, J = 9.7 Hz, 1 H, 4-H (8-H)], 8.00 (br., 1 H, NH), 7.14 [d, J = 9.7 Hz, 1 H, 3-H (7-H)], 3.35 (m, 2 H, CH₂CH₂CH₃), 1.76 (m, 2 H, CH₂CH₂CH₃), 1.05 (t, J = 7.4 Hz, 3 H, CH₂CH₂CH₃) ppm. IR (Nujol): $\tilde{\nu}$ = 3373 (N–H), 1607 (C–C arom.), 1493 (NO₂, as), 1327 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 258 sh (4.59), 278 sh (4.74), 287 (4.80), 335 sh (4.40), 502 sh (4.03), 562 nm (4.18). MS (70 eV): m/z (%) = 332 (100) [M]⁺, 303 (14), 227 (13), 213 (10), 182 (17), 169 (28), 156 (10), 154 (12), 140 (12), 137 (13), 127 (11), 114 (10), 43 (33), 41 (28). C₁₆H₂₀N₄O₄ (332.35): calcd. C 57.82, H 6.07, N 16.86; found C 57.98, H 5.92, N 16.74.

***N,N'*-Dibutyl-1,5-dinitronaphthalene-2,6-diamine (6c):** Yield 36 mg, 10% (Method A). Red crystals with m.p. 169–171 °C (MeOH). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 8.55 [d, J = 9.7 Hz, 1 H, 4-H (8-H)], 7.99 (br., 1 H, NH), 7.13 [d, J = 9.7 Hz, 1 H, 3-H (7-H)], 3.38 (m, 2 H, CH₂CH₂CH₂CH₃), 1.71 (m, 2 H, CH₂CH₂CH₂CH₃), 1.46 (m, 2 H, CH₂CH₂CH₂CH₃), 0.97 (t, J = 7.4 Hz, 3 H, CH₂CH₂CH₂CH₃) ppm. IR (Nujol): $\tilde{\nu}$ = 3360 (N–H), 1620 (C–C arom.), 1507 (NO₂, as), 1313 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 258 sh (4.32), 278 sh (4.50), 292 (4.68), 338 sh (4.36), 500 sh (4.11), 564 nm (4.26). MS (70 eV): m/z (%) = 360 (89) [M]⁺, 169 (20), 155 (10), 154 (10), 140 (10), 127 (10), 83 (10), 77 (10), 71 (12), 69 (21), 57 (44), 55 (29), 44 (76), 41 (100), 39 (24). C₁₈H₂₄N₄O₄ (360.41): calcd. C 59.99, H 6.71, N 15.55; found C 60.14, H 6.53, N 15.38.

General Procedures for the Oxidative Alkylamination of *N*-Alkyl-1,5-dinitronaphthalen-2-amines: AgMnO₄ (0.454 g, 2 mmol) was added in small portions at −15 to −12 °C, over 1 h, to a stirred solution of an *N*-alkyl-1,5-dinitronaphthalen-2-amine (**5**, 1 mmol) and alkylamine (30 mL). After 24 h overall stirring time the reaction mixture was concentrated (without heating) under reduced pressure. The residue was ground with Al₂O₃ (3–4 g), introduced onto an Al₂O₃ column (2.5 × 40 cm), and purified by flash column chromatography with CHCl₃ as the eluent. The crimson fraction gave the *N,N'*-dialkyl-1,5-dinitronaphthalene-2,6-diamines **6b** (30%) or **6d** (25%). The crude product was crystallized from *i*PrOH. Compound **6b** was identical to that obtained by alkylamination of 1,5-dinitronaphthalene (Method C).

***N*-Butyl-1,5-dinitro-*N'*-propylnaphthalene-2,6-diamine (6d):** Red crystals with m.p. 168–169 °C (MeOH). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 8.57 (pseudodoublet, J = 9.7 Hz, 2 H, 4-H and 8-H), 8.00 (br., 2 H, 2 × NH), 7.14 (pseudodoublet, J = 10.0 Hz, 2 H, 3-H and 7-H), 3.37 (m, 4 H, CH₂CH₂CH₂CH₃ and CH₂CH₂CH₃), 1.74 (m, 4 H, CH₂CH₂CH₂CH₃ and CH₂CH₂CH₃), 1.46 (m, 2 H, CH₂CH₂CH₂CH₃), 1.04 (t, J = 7.2 Hz, 3 H, CH₂CH₂CH₃), 0.97 (t, J = 7.2 Hz, 3 H, CH₂CH₂CH₂CH₃) ppm. IR (Nujol): $\tilde{\nu}$ = 3344 (N–H), 1624 (C–C arom.), 1496 (NO₂, as),

1313 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 260 sh (4.28), 279 sh (4.58), 293 (4.73), 338 sh (4.30), 502 sh (4.12), 562 nm (4.25). MS (70 eV): m/z (%) = 346 (71) [M]⁺, 227 (13), 182 (18), 169 (32), 155 (16), 140 (16), 127 (17), 114 (16), 100 (10), 77 (12), 63 (12), 57 (27), 55 (16), 43 (65), 41 (100). C₁₇H₂₂N₄O₄ (346.38): calcd. C 58.95, H 6.40, N 16.17; found C 59.08, H 6.27, N 16.31.

General Procedures for the Oxidative Alkylamination of 1,8-Dinitronaphthalene

Method A: AgMnO₄ (454 mg, 2 mmol) was added in small portions over 3 h at room temperature to a stirred solution of 1,8-dinitronaphthalene (**7**, 218 mg, 1 mmol) in an alkylamine (15 mL). After stirring overnight the reaction mixture was concentrated under reduced pressure. The residue was ground with Al₂O₃ (3–4 g), introduced onto an Al₂O₃ column (3 × 35 cm) and purified by flash column chromatography with CHCl₃ as the eluent. The first bright yellow fraction gave the *N*-alkyl-1,8-dinitronaphthalen-2-amine (**8**). The second bright yellow fraction gave the *N*-alkyl-4,5-dinitronaphthalen-1-amine (**9**). The crude products were crystallized from MeOH.

Method B: AgMnO₄ (454 mg, 2 mmol) was added at room temperature in small portions over 3 h to a stirred solution of 1,8-dinitronaphthalene (**7**, 218 mg, 1 mmol) and cyclohexylamine (3 mL) in THF (15 mL). After stirring overnight the reaction mixture was concentrated under reduced pressure. Further workup was similar to Method A.

Method C: The reaction was carried out similarly to Method A at −15 to −12 °C.

Method D: The reaction was carried out similarly to Method B at −15 to −12 °C with 1,8-dinitronaphthalene (**7**, 218 mg, 1 mmol), propylamine (3 mL), THF (15 mL) and AgPy₂MnO₄ (0.770 g, 2 mmol).

***N*-Ethyl-1,8-dinitronaphthalen-2-amine (8a):** Yield 32 mg, 12% (Method C). Orange crystals with m.p. 223–225 °C decomp. (MeOH). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 8.31 (br., 1 H, NH), 8.12 (dd, J = 7.7, 1.4 Hz, 1 H, 7-H), 7.87 (dd, J = 7.7, 1.4 Hz, 1 H, 5-H), 7.85 (d, J = 9.5 Hz, 1 H, 4-H), 7.38 (t, J = 7.7 Hz, 1 H, 6-H), 7.19 (d, J = 9.5 Hz, 1 H, 3-H), 3.50 (m, 2 H, CH₂CH₃), 1.40 (t, J = 7.2 Hz, 3 H, CH₂CH₃) ppm. IR (Nujol): $\tilde{\nu}$ = 3343 (N–H), 3092 (C–H arom.), 1633 and 1558 (C–C arom.), 1524 (NO₂, as), 1356 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 260 (4.61), 314 (3.92), 424 nm (3.95). MS (70 eV): m/z (%) = 261 (35) [M]⁺, 215 (31), 198 (69), 185 (100), 170 (78), 156 (23), 139 (14), 129 (22), 115 (54), 102 (34), 88 (11), 75 (18), 63 (19), 51 (13), 39 (10). C₁₂H₁₁N₃O₄ (261.23): calcd. C 55.17, H 4.24, N 16.09; found C 55.36, H 4.02, N 16.23.

1,8-Dinitro-*N*-propylnaphthalen-2-amine (8b): Yield 105 mg, 35% (Method A); 41 mg, 15% (Method C); 30 mg, 11% (Method D). Orange crystals with m.p. 174–175 °C (MeOH). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 8.43 (br., 1 H, NH), 8.12 (dd, J = 7.8, 1.3 Hz, 1 H, 7-H), 7.87 (dd, J = 7.8, 1.3 Hz, 1 H, 5-H), 7.84 (d, J = 9.4 Hz, 1 H, 4-H), 7.37 (t, J = 7.8 Hz, 1 H, 6-H), 7.19 (d, J = 9.4 Hz, 1 H, 3-H), 3.41 (dt, J = 5.3, 7.2 Hz, 2 H, CH₂CH₂CH₃), 1.79 (m, 2 H, CH₂CH₂CH₃), 1.07 (t, J = 7.4 Hz, 3 H, CH₂CH₂CH₃) ppm. IR (Nujol): $\tilde{\nu}$ = 3345 (N–H), 1627 and 1567 (C–C arom.), 1513 (NO₂, as), 1353 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 261 (4.54), 315 (3.83), 425 nm (3.88). MS (70 eV): m/z (%) = 275 (48) [M]⁺, 229 (38), 199 (100), 184 (20), 170 (62), 156 (12), 143 (16), 130 (20), 115 (51), 102 (29), 89 (11), 75 (16), 63 (18), 51 (12), 41 (30). C₁₃H₁₃N₃O₄ (275.26): calcd. C 56.72, H 4.76, N 15.27; found C 56.81, H 4.90, N 15.39.

***N*-Butyl-1,8-dinitronaphthalen-2-amine (8c):** Yield 92 mg, 32% (Method A). Orange crystals with m.p. 119–120 °C (MeOH). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 8.38 (br., 1 H, NH), 8.12 (dd, J = 7.7, 1.4 Hz, 1 H, 7-H), 7.86 (dd, J = 8.1, 1.4 Hz, 1 H, 5-H), 7.84 (d, J = 9.5 Hz, 1 H, 4-H), 7.37 (dd, J = 7.7, 8.1 Hz, 1 H, 6-H), 7.19 (d, J = 9.5 Hz, 1 H, 3-H), 3.44 (dt, J = 5.6, 7.0 Hz, 2 H, CH₂CH₂CH₂CH₃), 1.75 (m, 2 H, CH₂CH₂CH₂CH₃), 1.48 (m, 2 H, CH₂CH₂CH₂CH₃), 0.98 (t, J = 7.4 Hz, 3 H, CH₂CH₂CH₂CH₃) ppm. IR (Nujol): $\tilde{\nu}$ = 3347 (N–H), 3071 (C–H arom.), 1638 (C–C arom.), 1527 (NO₂, as), 1350 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 260 (4.50), 314 (3.79), 426 nm (3.84). MS (70 eV): m/z (%) = 289 (51) [M]⁺, 243 (43), 213 (100), 201 (10), 184 (25), 170 (62), 155 (16), 143 (20), 130 (27), 115 (58), 102 (29), 89 (221), 75 (14), 63 (15), 41 (40). C₁₄H₁₅N₃O₄ (289.29): calcd. C 58.13, H 5.23, N 14.53; found C 57.95, H 5.01, N 14.68.

***N*-Cyclohexyl-1,8-dinitronaphthalen-2-amine (8d):** Yield 126 mg, 40% (Method B); 72 mg, 23% (Method C). Orange crystals with m.p. 166–168 °C (MeOH). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 8.50 (br. d, J = 6.7 Hz, 1 H, NH), 8.11 (dd, J = 7.7, 1.4 Hz, 1 H, 7-H), 7.85 (dd, J = 7.7, 1.4 Hz, 1 H, 5-H), 7.80 (d, J = 9.5 Hz, 1 H, 4-H), 7.35 (t, J = 7.7 Hz, 1 H, 6-H), 7.20 (d, J = 9.5 Hz, 1 H, 3-H), 3.65 (m, 1 H, *cyclo*-C₆H₁₁), 2.06 (m, 2 H, *cyclo*-C₆H₁₁), 1.82 (m, 2 H, *cyclo*-C₆H₁₁), 1.67 (m, 2 H, *cyclo*-C₆H₁₁), 1.44 (m, 4 H, *cyclo*-C₆H₁₁) ppm. IR (Nujol): $\tilde{\nu}$ = 3345 (N–H), 3075 (C–H arom.), 1633 and 1559 (C–C arom.), 1531 and 1519 (NO₂, as), 1350 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 262 (4.51), 315 (3.80), 429 nm (3.86). MS (70 eV): m/z (%) = 315 (69) [M]⁺, 269 (80), 252 (17), 239 (97), 196 (23), 187 (26), 171 (35), 157 (100), 139 (25), 130 (36), 102 (26), 81 (16), 63 (13), 41 (84). C₁₆H₁₇N₃O₄ (315.32): calcd. C 60.94, H 5.43, N 13.33; found C 61.16, H 5.19, N 13.07.

4-(1,8-Dinitro-2-naphthyl)morpholine (8e): Yield 43 mg, 14% (Method A). Orange crystals with m.p. 185–187 °C (MeOH). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 8.50 (dd, J = 8.6, 1.2 Hz, 1 H, 7-H), 8.25 (d, J = 8.4 Hz, 1 H, 4-H), 8.23 (dd, J = 7.5, 1.2 Hz, 1 H, 5-H), 7.67 (dd, J = 7.5, 8.6 Hz, 1 H, 6-H), 7.17 (d, J = 8.4 Hz, 1 H, 3-H), 4.00 [m, 2 H, O(CH₂)₂], 3.19 [m, 2 H, N(CH₂)₂] ppm. IR (Nujol): $\tilde{\nu}$ = 3104 (C–H arom.), 1564 (C–C arom.), 1528 and 1514 (NO₂, as), 1342–1327 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 256 (4.06), 322 sh (3.59), 385 nm (3.88). MS (70 eV): m/z (%) = 303 (13) [M]⁺, 257 (19), 227 (100), 169 (32), 141 (22), 114 (50), 88 (11), 75 (12), 63 (15), 42 (11). C₁₄H₁₃N₃O₅ (303.27): calcd. C 55.45, H 4.32, N 13.86; found C 55.29, H 4.07, N 13.98.

***N*-Ethyl-4,5-dinitronaphthalen-1-amine (9a):** Yield 42 mg, 16% (Method C). Orange crystals with m.p. 204–206 °C decomp. (MeOH). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 8.31 (d, J = 9.1 Hz, 1 H, 3-H), 8.21 (dd, J = 7.7, 1.0 Hz, 1 H, 6-H), 8.06 (dd, J = 8.4, 1.0 Hz, 1 H, 8-H), 7.59 (dd, J = 7.7, 8.4 Hz, 1 H, 7-H), 6.58 (d, J = 9.1 Hz, 1 H, 2-H), 5.16 (br., 1 H, NH), 3.44 (m, 2 H, CH₂CH₃), 1.46 (t, J = 7.2 Hz, 3 H, CH₂CH₃) ppm. IR (Nujol): $\tilde{\nu}$ = 3412 (N–H), 3102 (C–H arom.), 1624 and 1572 (C–C arom.), 1535 (NO₂, as), 1353 and 1300 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 266 (4.14), 336 sh (3.46), 418 nm (4.12). MS (70 eV): m/z (%) = 261 (10) [M]⁺, 215 (30), 185 (100), 170 (59), 156 (23), 142 (16), 128 (50), 115 (36), 102 (28), 75 (16), 63 (12). C₁₂H₁₁N₃O₄ (261.23): calcd. C 55.17, H 4.24, N 16.09; found C 55.09, H 4.39, N 16.30.

4,5-Dinitro-*N*-propylnaphthalen-1-amine (9b): Yield 146 mg, 53% (Method A); 82 mg, 30% (Method C), 27 mg, 10% (Method D). Orange crystals, decomp. >190 °C (MeOH). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 8.30 (d, J = 9.0 Hz, 1 H, 3-H), 8.19 (dd, J = 7.5, 1.3 Hz, 1 H, 6-H), 8.04 (dd, J = 8.5, 1.3 Hz, 1 H, 8-H), 7.57 (dd, J = 7.5, 8.5 Hz, 1 H, 7-H), 6.58 (d, J = 9.0 Hz, 1 H, 2-H),

5.26 (br., 1 H, NH), 3.35 (m, 2 H, CH₂CH₂CH₃), 1.83 (m, 2 H, CH₂CH₂CH₃), 1.10 (t, J = 7.5 Hz, 3 H, CH₂CH₂CH₃) ppm. IR (Nujol): $\tilde{\nu}$ = 3405 (N–H), 1620 and 1573 (C–C arom.), 1520 (NO₂, as), 1359 and 1306 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 265 (4.13), 336 sh (3.47), 420 nm (4.12). MS (70 eV): m/z (%) = 275 (28) [M]⁺, 229 (23), 199 (100), 170 (22), 157 (12), 142 (13), 129 (32), 115 (23), 102 (19), 75 (14), 63 (14), 41 (32). C₁₃H₁₃N₃O₄ (275.26): calcd. C 56.72, H 4.76, N 15.27; found C 56.55, H 4.59, N 15.41.

***N*-Butyl-4,5-dinitronaphthalen-1-amine (9c):** Yield 110 mg, 38% (Method A). Orange crystals, decomp. >180 °C (MeOH; ref.^[12d] 197 °C). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 8.30 (d, J = 8.8 Hz, 1 H, 3-H), 8.19 (d, J = 7.7 Hz, 1 H, 6-H), 8.03 (d, J = 8.1 Hz, 1 H, 8-H), 7.57 (t, J = 8.1 Hz, 1 H, 7-H), 6.57 (d, J = 8.8 Hz, 1 H, 2-H), 5.23 (br., 1 H, NH), 3.38 (dt, J = 5.3, 7.0 Hz, 2 H, CH₂CH₂CH₂CH₃), 1.79 (m, 2 H, CH₂CH₂CH₂CH₃), 1.52 (m, 2 H, CH₂CH₂CH₂CH₃), 1.01 (t, J = 7.4 Hz, 3 H, CH₂CH₂CH₂CH₃) ppm. IR (Nujol): $\tilde{\nu}$ = 3412 (N–H), 3101 (C–H arom.), 1624 and 1570 (C–C arom.), 1531 (NO₂, as), 1360 and 1300 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 264 (4.16), 331 sh (3.45), 420 nm (4.14). MS (70 eV): m/z (%) = 289 (20) [M]⁺, 243 (17), 213 (100), 170 (11), 129 (14), 115 (11), 41 (12). C₁₄H₁₅N₃O₄ (289.29): calcd. C 58.13, H 5.23, N 14.53; found C 58.26, H 5.39, N 14.39.

***N*-Cyclohexyl-4,5-dinitronaphthalen-1-amine (9d):** Yield 31 mg, 1% (Method C). Orange crystals, decomp. >160 °C (MeOH). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 8.29 (d, J = 9.1 Hz, 1 H, 3-H), 8.18 (dd, J = 7.7, 1.0 Hz, 1 H, 6-H), 8.03 (dd, J = 8.8, 1.0 Hz, 1 H, 8-H), 7.56 (dd, J = 7.7, 8.8 Hz, 1 H, 7-H), 6.59 (d, J = 9.1 Hz, 1 H, 2-H), 5.20 (br. d, J = 7.0 Hz, 1 H, NH), 3.58 (m, 2 H, *cyclo*-C₆H₁₁), 2.16 (m, 2 H, *cyclo*-C₆H₁₁), 1.86 (m, 2 H, *cyclo*-C₆H₁₁), 1.69 (m, 2 H, *cyclo*-C₆H₁₁), 1.40 (m, 4 H, *cyclo*-C₆H₁₁) ppm. IR (Nujol): $\tilde{\nu}$ = 3401 (N–H), 1572 (C–C arom.), 1530 (NO₂, as), 1363 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 262 (4.30), 336 sh (3.67), 425 nm (4.12). MS (70 eV): m/z (%) = 315 (4), [M]⁺, 239 (14), 167 (12), 157 (16), 149 (33), 128 (15), 98 (20), 89 (19), 83 (59), 67 (16), 55 (100), 41 (86). C₁₆H₁₇N₃O₄ (315.32): calcd. C 60.94, H 5.43, N 13.33; found C 60.71, H 5.60, N 13.52.

Oxidative Butylamination of Nitrobenzene: KMnO₄ (790 mg, 5 mmol) was added in small portions at room temperature over 3 h to a stirred solution of nitrobenzene (615 mg, 5 mmol) in butylamine (10 mL). After 24 h overall stirring the reaction mixture was concentrated (without heating) under reduced pressure. The residue was ground with silica gel (3–4 g), introduced onto a silica gel column (3 × 35 cm), and purified by flash column chromatography with CHCl₃/hexane (1:1) as the eluent. The first bright yellow fraction gave *N*-*n*-butyl-2-nitroaniline (**11**). Yield 29 mg (0.3%). Orange oil. ¹H NMR (250 MHz, CDCl₃, 30 °C): δ = 8.15 (dd, J = 8.4, 1.7 Hz, 1 H, 3-H), 8.04 (br., 1 H, NH), 7.41 (ddd, J = 7.1, 8.8, 1.7 Hz, 1 H, 5-H), 6.83 (d, J = 8.8 Hz, 1 H, 6-H), 6.60 (ddd, J = 7.1, 8.4, 1.4 Hz, 1 H, 4-H), 3.28 (m, 2 H, CH₂CH₂CH₂CH₃), 1.70 (m, 2 H, CH₂CH₂CH₂CH₃), 1.47 (m, 2 H, CH₂CH₂CH₂CH₃), 0.97 (t, J = 7.2 Hz, 3 H, CH₂CH₂CH₂CH₃) ppm. IR (Nujol): $\tilde{\nu}$ = 3382 (N–H), 3086 (C–H arom.), 1620 and 1574 (C–C arom.), 1515 (NO₂, as), 1355 (NO₂, s) cm^{−1}. UV (CHCl₃): λ_{max} (lg ϵ) = 283 (3.88), 435 nm (3.92). MS (70 eV): m/z (%) = 194 (18) [M]⁺, 151 (100), 119 (10), 111 (10), 105 (16), 97 (21), 93 (24), 77 (19), 71 (50), 57 (71), 51 (11), 43 (89). C₁₀H₁₄N₂O₂ (194.23): calcd. C 61.84, H 7.27, N 14.42; found C 62.03, H 7.11, N 14.29.

The second bright yellow fraction was eluted with CHCl₃ to give *N*-butyl-4-nitroaniline (**12**). Yield 39 mg (0.4%). The crude product was crystallized from *i*PrOH. Orange crystals with m.p. 55–57 °C (MeOH; ref.^[20] 54–55 °C). ¹H NMR (250 MHz, CDCl₃, 30 °C): δ

= 8.07 (d, J = 9.3 Hz, 2 H, 3-H and 5-H), 6.50 (d, J = 9.3 Hz, 2 H, 2-H and 6-H), 4.46 (br., 1 H, NH), 3.19 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.62 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.43 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.96 (t, J = 7.2 Hz, 3 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) ppm. IR (Nujol): $\tilde{\nu}$ = 3346 (N–H), 3065 (C–H arom.), 1608 (C–C arom.), 1462 (NO_2 , as), 1320 (NO_2 , s) cm^{-1} . UV (CHCl_3): λ_{max} (lg ϵ) = 312 sh (3.30), 380 nm (4.26). MS (70 eV): m/z (%) = 194 (39) $[\text{M}]^+$, 151 (100), 105 (60). $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2$ (194.23): calcd. C 61.84, H 7.27, N 14.42; found C 61.66, H 7.42, N 14.25.

General Procedures for the Oxidative Alkylamination of 1-Nitronaphthalene

Method A: KMnO_4 (316 mg, 2 mmol) was added in small portions at room temperature over 3 h to a stirred solution of 1-nitronaphthalene (**13**, 173 mg, 1 mmol) in butylamine (8 mL). After 24 h overall stirring time the reaction mixture was concentrated under reduced pressure. The residue was ground with silica gel (3–4 g), introduced onto a silica gel column (3 $\times$ 35 cm), and purified by flash column chromatography with $\text{CHCl}_3/\text{CCl}_4$ (4:1) as the eluent. The first bright yellow fraction gave *N*-butyl-1-nitronaphthalen-2-amine (**14**). The second bright yellow fraction gave *N*-butyl-4-nitronaphthalen-1-amine (**15**). The crude products were crystallized from *i*PrOH.

Method B: The reaction was carried out similarly with $\text{AgPy}_2\text{MnO}_4$ (462 mg, 1.2 mmol) as the oxidant.

1-Nitro-*N*-propylnaphthalen-2-amine (14a): Yield 113 mg, 49% (Method B). Orange crystals with m.p. 84–85 °C (MeOH). ^1H NMR (250 MHz, CDCl_3 , 30 °C): δ = 8.95 (br., 1 H, NH), 8.77 (d, J = 8.7 Hz, 1 H, 8-H), 7.78 (d, J = 9.3 Hz, 1 H, 4-H), 7.64 (d, J = 7.9 Hz, 1 H, 5-H), 7.59 (ddd, J = 7.3, 8.7, 1.5 Hz, 1 H, 7-H), 7.31 (ddd, J = 7.3, 7.9, 1.0 Hz, 1 H, 6-H), 7.05 (d, J = 9.3 Hz, 1 H, 3-H), 3.40 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.78 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.06 (t, J = 7.4 Hz, 3 H, $\text{CH}_2\text{CH}_2\text{CH}_3$) ppm. IR (Nujol): $\tilde{\nu}$ = 3364 (N–H), 3052 (C–H arom.), 1635 and 1562 (C–C arom.), 1522 (NO_2 , as), 1336 (NO_2 , s) cm^{-1} . UV (CHCl_3): λ_{max} (lg ϵ) = 263 (4.12), 318 (3.70), 334 (3.68), 423 nm (4.25). $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_2$ (230.26): calcd. C 67.81, H 6.13, N 12.17; found C 68.01, H 6.00, N 12.32.

***N*-Butyl-1-nitronaphthalen-2-amine (14b):** Yield 29 mg, 12% (Method A); 127 mg, 52% (Method B). Orange crystals with m.p. 67–69 °C (MeOH). ^1H NMR (250 MHz, CDCl_3 , 30 °C): δ = 8.92 (br., 1 H, NH), 8.77 (d, J = 8.8 Hz, 1 H, 8-H), 7.78 (d, J = 9.5 Hz, 1 H, 4-H), 7.65 (d, J = 7.7 Hz, 1 H, 5-H), 7.58 (dd, J = 7.4, 8.8 Hz, 1 H, 7-H), 7.31 (dd, J = 7.4, 7.7 Hz, 1 H, 6-H), 7.06 (d, J = 9.5 Hz, 1 H, 3-H), 3.43 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.74 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.49 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.98 (t, J = 7.2 Hz, 3 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) ppm. IR (Nujol): $\tilde{\nu}$ = 3289 (N–H), 3138 (C–H arom.), 1632 and 1561 (C–C arom.), 1517 (NO_2 , as) cm^{-1} . UV (CHCl_3): λ_{max} (lg ϵ) = 266 (3.63), 324 (3.11), 334 (3.11), 425 nm (3.83). MS (70 eV): m/z (%) = 244 (76) $[\text{M}]^+$, 201 (76), 184 (12), 171 (15), 155 (100), 140 (13), 128 (53), 115 (44), 101 (16), 77 (17), 63 (12), 41 (29). $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2$ (244.29): calcd. C 68.83, H 6.60, N 11.47; found C 69.05, H 6.41, N 11.29.

4-Nitro-*N*-propylnaphthalen-1-amine (15a): Yield 51 mg, 22% (Method B). Orange crystals with m.p. 163–165 °C (MeOH). ^1H NMR (250 MHz, CDCl_3 , 30 °C): δ = 9.03 (d, J = 8.8 Hz, 1 H, 5-H), 8.48 (d, J = 8.9 Hz, 1 H, 3-H), 7.80 (d, J = 8.4 Hz, 1 H, 8-H), 7.70 (ddd, J = 6.9, 8.8, 1.3 Hz, 1 H, 6-H), 7.52 (ddd, J = 6.9, 8.4, 1.2 Hz, 1 H, 7-H), 6.50 (d, J = 8.9 Hz, 1 H, 2-H), 5.27 (br., 1 H, NH), 3.36 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.83 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.09 (t, J = 7.4 Hz, 3 H, $\text{CH}_2\text{CH}_2\text{CH}_3$) ppm. IR (Nujol): $\tilde{\nu}$ = 3399 (N–H), 1577 (C–C arom.), 1365 (NO_2 , s) cm^{-1} . UV (CHCl_3): λ_{max} (lg ϵ) = 271 (4.20), 338 (3.69), 447 nm (3.84). MS (70 eV): m/z (%)

= 230 (70) $[\text{M}]^+$, 201 (37), 184 (100), 154 (55), 140 (11), 127 (17), 115 (18), 77 (10), 63 (13), 41 (22). $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_2$ (230.26): calcd. C 67.81, H 6.13, N 12.17; found C 67.58, H 6.02, N 11.98.

***N*-Butyl-4-nitronaphthalen-1-amine (15b):** Yield 8 mg, 3% (Method A); 51 mg, 21% (Method B). Orange crystals, >160 °C decomp. (MeOH; ref.^[12d] 158–159 °C). ^1H NMR (250 MHz, CDCl_3 , 30 °C): δ = 9.03 (d, J = 8.8 Hz, 1 H, 5-H), 8.47 (d, J = 8.8 Hz, 1 H, 3-H), 7.79 (d, J = 8.4 Hz, 1 H, 8-H), 7.68 (dd, J = 6.9, 8.8 Hz, 1 H, 6-H), 7.51 (dd, J = 6.9, 8.4 Hz, 1 H, 7-H), 6.48 (d, J = 8.8 Hz, 1 H, 2-H), 5.26 (br., 1 H, NH), 3.38 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.78 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.52 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.01 (t, J = 7.4 Hz, 3 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) ppm. IR (Nujol): $\tilde{\nu}$ = 3400 (N–H), 1574 (C–C arom.) cm^{-1} . UV (CHCl_3): λ_{max} (lg ϵ) = 266 (3.63), 324 (3.11), 334 (3.11), 425 nm (3.83). MS (70 eV): m/z (%) = 244 (79) $[\text{M}]^+$, 201 (41), 184 (100), 154 (43), 127 (10), 41 (10). $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2$ (244.29): calcd. C 68.83, H 6.60, N 11.47; found C 68.68, H 6.47, N 11.64.

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