Facile, high-yield, regioselective synthesis of *ortho*-nitrophenols using cerium (IV) ammonium nitrate

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Abstract

Certain phenols possessing at least one unsubstituted *ortho* position have been found to undergo rapid, regioselective *ortho* nitration with CAN (cerium (IV) ammonium nitrate) in the presence of $NaHCO_3$ at room temperature to yield *o*-nitrophenols in high yields. Substituents tolerating these nitration conditions ranged from the activating methoxy and methyl groups to the moderately deactivating Cl, Br, CHO and CO_2Me groups. In contrast, phenols that contained a strongly deactivating group such as nitro or cyano or 2,6-disubstituted phenols were not nitrated by the CAN/$NaHCO_3$ reagent. More complex nitrophenols such as 6-hydroxy-5-nitro-1,3-benzoxanthiol-2-one, 7-hydroxy-6-nitro-3,4,8-trimethylcoumarin, 6-hydroxy-5-flavanone, 1-(4-hydroxy-3-nitrophenyl)-1*H*-tetrazole-5-thiol, 2-(2-hydroxy-3-nitrophenyl)benzoxazole were also prepared in good yields by the CAN/$NaHCO_3$ reagent.

Keywords: Phenol, nitration, cerium(IV)ammoniumnitrate

Introduction

Nitrations of phenols using the classical method of nitric acid in sulphuric acid generally gives complex mixtures containing *o*- and *p*-nitrophenols, dinitrated phenols, plus inextractible tars of phenolic oxidation products.[1] Consequently, alternative nitration methods have been sought to accomplish clean and regioselective mononitration of phenols. Some of these include the use of: (1) a two-phase system (ether-phenol/water-$NaNO_3$-$NaNO_2$-H^+),[2] (2) an ionic complex of N_2O_4 with 18-crown-6,[3] (3) nitrosation-oxidation with metallic HSO_4^- and $NaNO_3$[4] and (4) nitrocyclohexadienone as the nitrating agent,[5] etc. While these methods give clean mononitration of phenols, both *o* and *p*-nitrophenols are obtained. *o*-Nitrophenols are valuable precursors to a variety of biologically important heterocycles such as 2,3-dihydro-2H-1,4-benzoxoin-3(4H)-ones,[6] and benzoxazoles.[7] Thus, a convenient method for the regioselective introduction of an *ortho* nitro group onto phenols is desirable. A survey of the literature shows the lack of 100% *ortho* nitration, however, there are a few reports of almost regioselective *ortho* nitration of phenols. Two of these involved passing NO_2-N_2O_4 gas into a solution of phenol and pyridinium

carboxylic acid[8] or vigorously stirring a suspension of phenol with "claycop" (an acidic montmorillonite clay impregnated with anhydrous cupric nitrate).[9] These methods gave mixtures of *o*- and *p*-nitrophenols with high *o*/*p* ratios of 95:5 and 86:6, respectively.

Results and Discussion

Recently, 7-hydroxycoumarins have been nitrated with CAN and H_2O_2 as co-oxidants in water to give a 9:1 mixture of 7-hydroxy- 6-nitro- and 7-hydroxy-6,8-dinitrocoumarins.[10] However, nitration of simple phenols with the CAN/H_2O_2 reagent was found to produce mixtures of nitrophenols as well as hydroxylation and coupling products.[11,12] When CAN is coated on silica (CAN/SiO_2), a milder nitrating reagent is obtained which has been used in the nitration of, polynuclear,[13] heterocyclic[14] and electron-rich aromatic compounds .[15] In the latter case, mixtures of *o*- and *p*-isomers were obtained.

In an unrelated study, CAN in the presence of $NaHCO_3$ and acetonitrile was found to mediate the oxidative coupling between thiophenols and aromatic nitriles affording benzothiazoles.[16] It occurred to us, that the replacement of H_2O_2 with $NaHCO_3$ might result in a more selective CAN nitrating reagent with diminished oxidative capability. Thus, we have treated a variety of phenols, having at least one unsubstituted *ortho* position with CAN/$NaHCO_3$ and , as shown in Table 1, obtained *o*-nitrophenols in all cases. Best yields of the *o*-nitrophenols were attained by carrying out the reactions in MeCN at room temperature for 30 min. The absence of *p*-nitrophenols as well as hydroxylation and coupling products was ascertained by GC/MS analysis of the crude reaction mixtures.

The wide scope of this nitration can be appreciated by discussing the different classes of phenols separately. As shown in Table 1, a wide variety of monocyclic phenols (**1a-o**) possessing Me, OMe, Cl, Br, CO_2Et, and CHO substituents reacted with CAN/$NaHCO_3$ to give the corresponding *o*-nitrophenols

Table 1. Yields[a] of nitrophenols (**2a-v** from the CAN/$NaHCO_3$ nitration of phenols (**1a-v)**

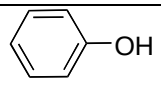
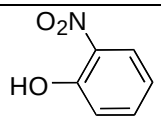
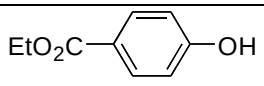
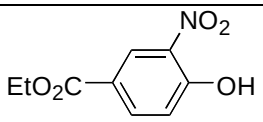
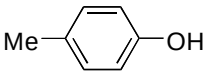
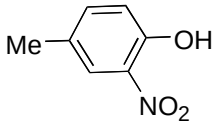
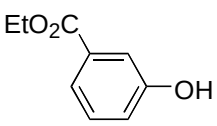
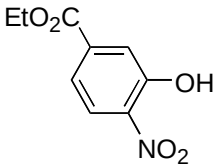
Phenol	Nitrophenol	Yield %	Phenol	Nitrophenol	Yield %
 **1a**	 **2a**	85	 **1m**	 **2m**	79
 **1b**	 **2b**	91	 **1n**	 **2n**	87

Table 1. Continued

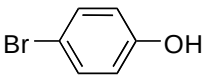
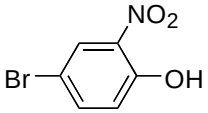
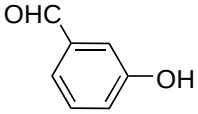
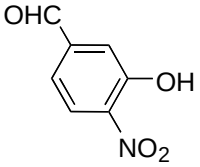
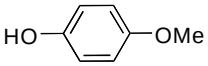
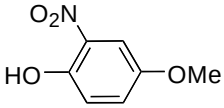
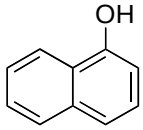
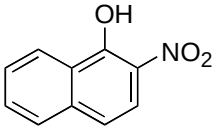
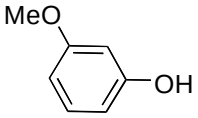
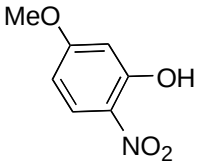
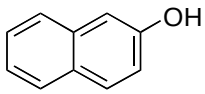
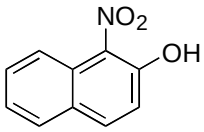
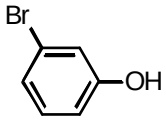
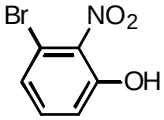
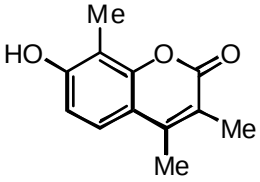
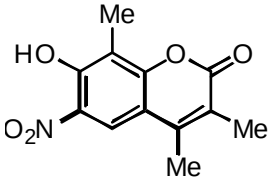
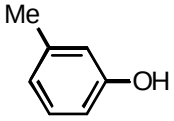
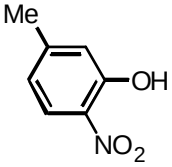
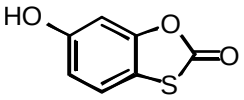
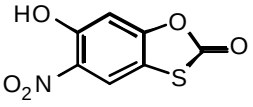
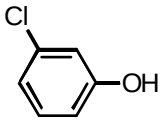
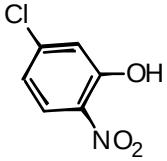
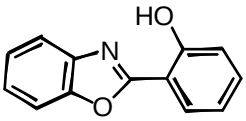
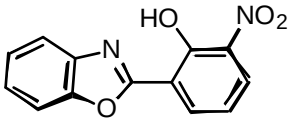
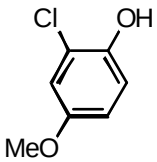
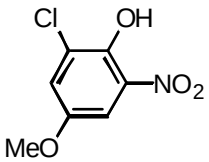
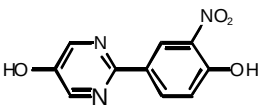
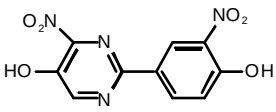
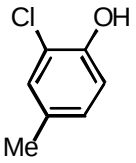
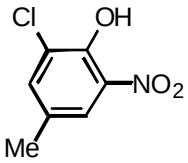
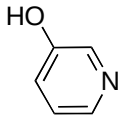
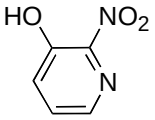
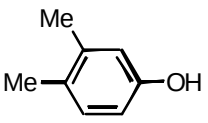
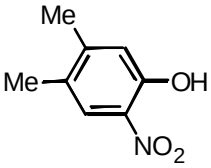
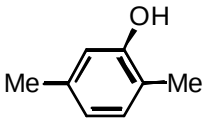
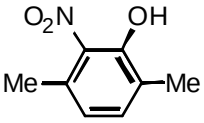
Phenol	Nitrophenol	Yield, %	Phenol	Nitrophenol	Yield, %
 **1c**	 **2c**	86	 **1o**	 **2o**	88
 **1d**	 **2d**	72[b]	 **1p**	 **2p**	85
 **1e**	 **2e**	90	 **1q**	 **2q**	72
 **1f**	 **2f**	93	 **1r**	 **2r**	74
 **1g**	 **2g**	93	 **1s**	 **2s**	94
 **1h**	 **2h**	91	 **1t**	 **2t**	77
 **1i**	 **2i**	90	 **1u**	 **2u**	77

Table 1. Continued

Phenol	Nitrophenol	Yield, %	Phenol	Nitrophenol	Yield, %
 **1j**	 **2j**	95	 **1v**	 **2v**	76[c]
 **1k**	 **2k**	89	 **1l**	 **2l**	93

[a] isolated yields. [b] 20% yield of benzoquinone. [c] stirring for 6 h.

(**2a-o**), exclusively. In all cases, ^{1}H NMR and ^{13}C NMR and GC/MS analysis confirmed the structure and purity of the isolated products.

The yields of the monocyclic phenols (**2a-o**) ranged from 72% to 95%, which are, for the most part, significantly higher than any previously reported. For example, phenol (**1a**) was converted to 2-nitrophenol (**2a**) in 85% yield with CAN/$NaHCO_3$, while the CAN/H_2O_2 reagent gave **2a** in only 15% yield.[17] Additionally, CAN/$NaHCO_3$ treatment of *p*-cresol (**1b**) gave 4-methyl-2-nitrophenol (**2b**) as single product in 95% yield, compared to the 30% yield from similar treatment with CAN/H_2O_2 using dodecyl sodium sulfate as a surfactant[7] and the 60% yield obtained when **1b** was first impregnated on SiO_2.[18] In addition, other 4-substituted phenols, *i.e. p*-bromo- (**1c**), *p*-methoxy- (**1d**), and ethyl *p*-hydroxybenzoate acid (**1m**) underwent nitration with the CAN/$NaHCO_3$ reagent to give 4-bromo-2-nitrophenol (**2c**), 4-methoxy-2-nitrophenol (**2d**) and ethyl 4-hydroxy-3-nitrobenzoate (**2m**) in 86%, 79% and 72% yields, respectively. The yield of **2d** (72%) was unfavorably affected by partial oxidation of **1d** to *p*-benzoquinone (20%). Interestingly **1d** was quantitatively oxidized to *p*-quinone by CAN/SiO_2.[15] 4-hydroxy- and 4-aminophenols (not shown in Table 1) did not undergo nitration under similar conditions, but rather gave mixtures of oxidized products.

Table 1 also lists the results for the nitration of 3-substituted phenols, *i.e.* 3-methoxy- (**1e**), 3-bromo- (**1f**), 3-methyl- (**1g**) and 3-chlorophenol (**1h**) and (**1e-h**), as well as ethyl 3-hydroxybenzoate (**1n**) and 3-hydroxybenzaldehyde (**1o**). With the exception of **1e**, the 3-substituted derivatives were nitrated regioselectively at the unhindered site (C-6, in the case of the 3-substituted phenols and C-4, in the case of the 3-hydroxy derivatives) to give the 5-substituted 2-nitrophenols (**2f-h**), 3-hydroxy-4-nitro benzoate (**2n)** and 3-hydroxy-4-

nitrobenzaldehyde (**2o**). The yields ranged from 87% to 93%. With the exception of methyl, the aforementioned substituents are –I groups (electron-withdrawing by induction) and thus would be expected to discourage electrophilic addition at the hindered site. Steric factor for these substituents as well as weakly activating methyl should also impede addition at the hindered site. In the exceptional case, 3-methoxyphenol (**1e**) underwent CAN nitration exclusively at the hindered C-2 site giving 3-methoxy-2-nitrophenol (**2e**) in 90% yield. This anomalous result indicates that the strong mesomeric effect of methoxy activates the hindered carbon site. Not only are the previous yields of substituted nitrophenols lower that those reported here, but most preparations involve at least two steps. For example, the highest yield of **2e** previously reported was 70% using a two-step process of nitrosation of **1e** followed by nitric acid oxidation.[19] Importantly, 3-hydroxybenzaldehyde (**1o**) and 3-methoxyphenol (**1e**) were not oxidized using the CAN/$NaHCO_3$ reagent.

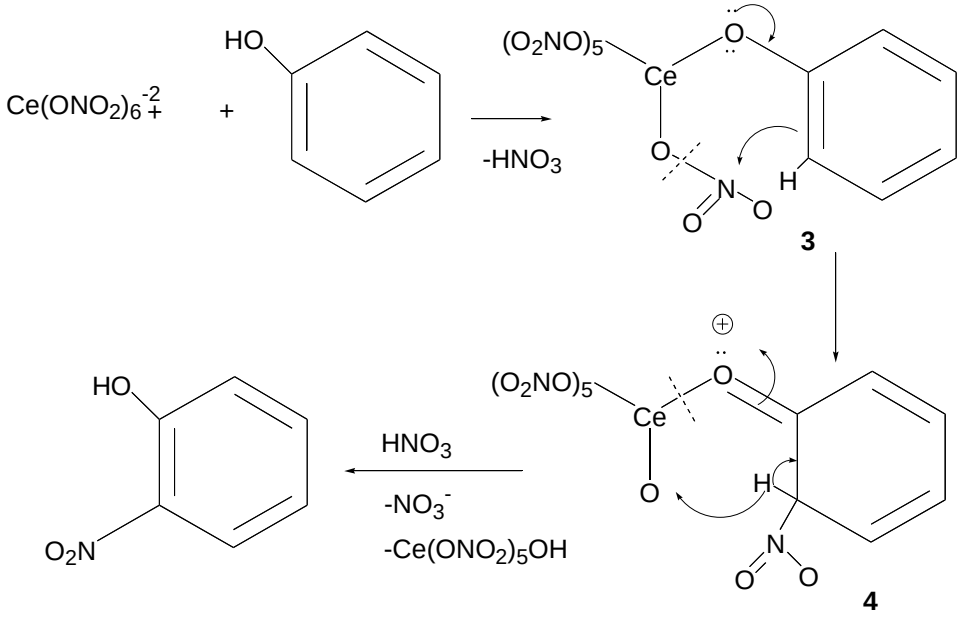
The mild nitrating power of CAN was further shown by the selective *ortho* mononitration of the two dimethylphenol derivatives 3,4-dimethylphenol (**1k**) and 2,5-dimethylphenol (**1l**), which gave 2-nitro-4,5-dimethylphenol (**2j**) and 2-nitro-3.6-dimethylphenol (**2l**) in 89% and 93% yields, respectively. Previously, dialkyl phenols, when treated with nitrating agents such as NO_2[20] were found to give only polynitrophenols and 2,5-cyclohexadienones.

The results in Table 1 show that the CAN/$NaHCO_3$ reagent can also nitrate certain polycyclic phenols regioselectively. For example, 1-naphthol (**1p**) was converted to 2-nitro-1-naphthol (**2p**) in 85% yield, whereas treatment with nitrocyclohexadienone gave mixtures of 2- and 4-nitro-1-napthols.[21] Likewise, CAN nitration of 2-naphthol (**1q**) afforded 1-nitro-2-naphthol (**2q**) in 72% yield which is substantially greater that the highest yield (49%) previously reported.[22] More complex nitrophenols such as 7-hydroxy-6-nitro-3,4,8-trimethylcoumarin (**2r**), 6-hydroxy-5-nitro-1,3-benzothio-2-one (**2s**) and 2-(2-hydroxy-3-nitrophenyl)benzoxazole (**2t**) were prepared in good yields from the corresponding phenols. Interestingly, treatment of 2-(4-hydroxyphenyl)-5-pyrimidinol (**1u**) with CAN resulted in the nitration of both rings affording 2-(4-hydroxy-3-nitrophenyl)-4-nitro-5-pyrimidinol (**2u**) in 79% yield. Treatment of **1x** with only one equiv of CAN gave only **2u** in 10% yield; no mono nitrated derivative was obtained.

We subsequently found that anisole, 2,6-dimethoxy phenol, aniline and *p*-anisidine did not react with CAN/$NaHCO_3$, indicating that a hydroxyl group and an unsubstituted carbon *ortho* to the phenol are required for nitration. Several dihydroxyarenes, aromatic amines, and aminophenols were also not nitrated by CAN/$NaHCO_3$ reagent, whereas the dihydroxyarenes and aminophenols upon addition of CAN were rapidly oxidized giving mixture of products. Furthermore, phenols possessing strongly deactivating groups (in the electrophilic aromatic sense), *i.e.* 4-cyanophenol and 2-chloro-4-nitrophenol, resisted nitration even when stirred overnight. Interestingly, 3-pyridol (**1v**) did undergo nitration with stirring for 6 h in refluxing acetonitrile to give 2-nitro- 3-pyridol (**2v**) in 76% yield.

The high *ortho* regioselectivity observed in the CAN nitration suggest that a Fries type rearrangement may be involved in the nitration. A possible mechanism is shown in Scheme 1. As shown the hydroxy group of the phenol reacts with CAN to give complex **3** from which a nitro

group is transferred from the CAN moiety to the 2-position of the phenol. The resulting intermediate **4** then undergoes aromatization of the ring and the elimination of $[(ONO_2)_5CeOH]^-$ [2]. In conclusion, a high-yield, regioselective *ortho* nitration of a wide range of phenols using the inexpensive and easy to use CAN reagent has been demonstrated. It should become an important tool in organic synthesis.



Scheme 1. Possible mechanism for the *ortho* nitro of phenol.

Experimental Section

General Procedures. Melting points were in open capillaries and are uncorrected. All reactions were carried out under an atmosphere of dry nitrogen. Phenols (**1a-v**), CAN, and acetonitrile were purchased from commercial sources. Reactions were monitored by GC/MS. Concentrations were performed by rotary evaporator using water aspirator system. Low-pressure chromatography was carried out by applying air pressure to Pyrex columns packed with silica gel 60 (0.040-0.063 mm particle size, 230-400 mesh). Routine ^{1}H NMR were recorded on a FT NMR at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz.

Experimental procedure. CAN (3.84 g, 7.0 mmol) was added to a stirred mixture containing 3.5 mmol of appropriate phenol (**1a-x**), $NaHCO_3$ (1.0 g) and 40 mL of anhydrous MeCN at rt. The resulting mixture was stirred for 30 min during which time the yellow color of CAN was discharged. The mixture was filtered, washed with water, and extracted with $CHCl_3$ (3 X 20 mL). The combined $CHCl_3$ extracts were dried (Na_2SO_4), and the solvent evaporated in *vacuo* to give the corresponding 2-nitrophenol (**2**). Prior to purification of **2**, an aliquote was subjected to

GC/MS analysis which showed, in all successful reactions, the absence of the 4-nitrophenol positional isomer. The 2-nitrophenol was purified by column chromatography using hexane-ethyl acetate (9:1) as eluent. The physical properties of **1a-w** are given below.

2-Nitrophenol (2a).[23] Yellow solid, mp 44-45 ^{o}C (lit.[24] 44.9 ^{O}C. ^{1}H NMR ($CDCl_3$) δ 6.98 (t, *J* = 1H), 7.14 (d, *J* =, 1H), 7.54 (t, *J* =, 1H), 7.94 (2, *J* =, 1 H), 10.66 (brs, 1 H). ^{13}C NMR ($CDCl_3$) δ 120.3, 120.6, 125.3, 134.0, 137.9, 155.4.

4-Methyl-2-nitrophenol (2b).[25] Yellow solid, mp 35 ^{o}C (lit 34-35 ^{O}C)[26] 1H NMR ($CDCl_3$) δ 2.36(σ,3H), 7.06 (δ, *J* = 8.6 Hz, 1H), 7.35 (dd, *J* = 8.6 Hz, 2.1 Hz, 1 H), 7.73 (d, *J* = 2.1 Hz, 1H), 10.45 (s, 1 H). ^{13}C NMR ($CDCl_3$) δ 20.4, 119.9, 124.5, 130.4, 139.0, 153.4.

4-Bromo-2-nitrophenol (2c).[27] Yellow solid, mp 92-93 ^{o}C.[28] ^{1}H NMR ($CDCl_3$) δ 7.09 (δ, *J* = 8.9 Hz, 1H), 7.65 (dd, *J*= 8.9 Hz, 2.4 Hz, 1 H), 8.24 (d, *J* = 2.4 Hz, 1 H), 10.51 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 111.1, 121.2, 126.7, 134.0, 139.8, 153.5.

4-Methoxy-2-nitrophenol (2d). Orange solid, mp 79-80 ^{o}C (lit.[29] 83 ^{o}C). ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 3 H), 7.09 (δ, *J* = 9.2 Hz, 1H), 7.23 (dd, *J* = 9.2 Hz, 3.0 Hz, 1 H), 7.53 (d, *J* = 3.0 Hz, 1 H), 10.37 (s, 1 H). ^{13}C NMR ($CDCl_3$) δ 56.4, 106.1, 121.3, 127.7, 134.0, 150.5, 153.0.

3-Methoxy-2-nitrophenol (2e). Yellow solid, mp. 52-53 ^{O}C (lit.[30] 53 ^{O}C). IR (KBr) 3198, 3020, 1621, 1443, 1321, 834, 757, 669 cm^{-1}. ^{1}H NMR ($CDCl_3$ δ 3.90 (s, 3 H), 6.55, (dd, *J* = 7.8Hz, 2.1 Hz, 1 H), 7.28 (dd *J* = Hz, 1 H), 8.07 (d, *J* = 7.8 Hz, 1 H), 11.07. ^{13}C NMR ($CDCl_3$) δ 56.5, 101.8, 109.8, 127.4, 128.1, 158.3, 167.5.

5-Bromo-2-nitrophenol (2f). Light yellow solid, mp 44-45 ^{O}C (lit.[31] 46-47). ^{1}H NMR ($CDCl_3$) δ 7.15 (dd, *J* = 8.8 Hz, 2.0 Hz, 1 H), 7.39 (d, *J* = 2.0 Hz, 1 H), 7.99 (dd, *J* = 8.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$) δ 123.4, 124.3, 126.5, 132.8, 124.1, 155.7.

5-Methyl-2-nitrophenol (2g): Yellow solid, mp. 54-55 (lit.[32] 55-56 ^{o}C). IR (KBr) 3192, 3117, 1927, 1785, 1627, 1479, 1366, 823, 659, 671 cm^{-1}. ^{1}H NMR ($CDCl_3$) 2.41 (s, 3 H), 6.81 (d, *J* = 8.7 Hz, 1 H), 6.96 (brs, 1 H), 8.00 (d, *J* = 8.17 Hz, 1 H). ^{13}C NMR ($CDCl_3$) 22.2, 130.0, 122.0, 125.2, 132.1, 150.2, 155.5.

5-Chloro-2-nitrophenol (2h). Yellow solid mp 39-40 ^{o}C (lit.[33] 42-43 ^{O}C). IR (KBr) 3192, 3106, 1912, 1774, 1616, 1460, 1317, 918, 753, 675 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 6.99 (dd, *J* = 9.0 Hz, 2.1 Hz, 1 H), 7.21 (d, *J* = 2.1 Hz, 1 H), 8.08 (d, *J* = 9.0 Hz, 1 H), 10.68 (s, 1 H). ^{13}C NMR ($CDCl_3$) 120.2, 121.4, 126.6, 132.7, 144.1, 155.8.

6-Chloro-4-methoxy-2-nitrophenol (2i). Orange solid, mp 92-93 ^{o}C. IR (KBr) 3246, 3106, 1753, 1686, 1416, 1248, 761 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 3 H), 7.38 (d, *J* = 3.1 Hz, 1 H), 7.50 (d, *J* = 3.1 Hz, 1 H), 10.71 (s, 1 H). ^{13}C NMR ($CDCl_3$) δ 57.6, 105.9, 125.5, 127.0, 134.3, 146.7, 152.0.

Anal. Calcd for $C_7H_6ClNO_4$: C, 41.30; H, 2.97; N, 6.88. Found: C, 41.40; H, 3.01; N, 6.76.

6-Chloro-4-methyl-2-nitrophenol (2j). Yellow solid, mp 65-66 ^{o}C. IR (KBr) 3190, 3071, 1619, 1464, 1311, 797, 763, 753, 664 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3 H), 7.54 (d, *J* = 1.7 Hz, 1 H), 7.86 (d, *J* = 1.8 Hz, 1 H), 10.86 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 20.5, 123.5, 124.3, 130.3, 134.3, 138.8, 149.6. Anal. Calcd for $C_7H_6ClNO_3$: C, 44.82; H, 3.22; N, 7.47. Found: C, 44.89; H, 3.18; N, 7.53.

4,5-Dimethyl-2-nitrophenol (2k). Yellow solid, mp 82-84 °C (lit.[34] 82-83 °C).^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3 H), 2.32 (s, 3 H), 6.95 (s, 1H), 7.86 (s, 1H), 10.49 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 19.2, 20.8, 120.4, 125.0, 130.1, 134.1, 149.9, 154.8.

3,6-Dimethyl-2-nitrophenol (2l). Yellow solid, mp 33-34 °C (lit.[35] 34-35 °C).^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3 H), 2.32 ^{13}C NMR ($CDCl_3$) δ 16.2, 22.7, 123.2, 127.0, 134.2, 135.3, 136.4, 154.1.

Methyl 4-hydroxy-3-nitrobenzoate (2m). Yellow solid, mp 76-77 °C (lit.[36] 77-78 °C) . ^{1}H NMR (DMSO-d_6) δ 3.85 (s, 3 H), 7.23 (dd, J = 8.7 Hz, 1.7 Hz, 1 H), 8.06 (dd, J = 8.7 Hz, 1.7 Hz, 1 H), 8.39 (d, J = 1.7 Hz, 1 H). ^{13}C NMR 53, 120.2, 121.2, 127.6, 136.0, 137.5, 156.7, 165.4.

Methyl 3-hydroxy-4-nitrobenzoate: (2n). Yellow solid, mp. 91-92 °C. IR (KBr) 3317, 3123, 2961, 1724, 1624, 1478, 1326, 844, 747, 688 cm^{-1} ^{1}H NMR ($CDCl_3$) δ 3.98 (s, 3 H), 7.64 (dd, J = 8.8 Hz, 1.76 Hz, 1 H), 7.86 (m, 1 H), 8.20 (dd, J = 8.8 Hz, 2.0 Hz, 1 H) ^{13}C NMR ($CDCl_3$) δ 53.3, 121.0, 122.0, 125.6, 136.2, 138.2, 155.0, 165.2.

3-Hydroxy-4-nitrobenzaldehyde (2o). Yellow solid, mp. 127-128 °C (lit.[33] 128 °C). IR (KBr) 3260, 3087, 2877, 1700, 1621, 1478, 1315, 759, 704. ^{1}H NMR ($CDCl_3$) δ 7.52 (dd, J = 8.6 Hz, 2.1Hz, 1 H), 7.67 (d, J = 2.1 Hz, 1 H), 8.30 (dd, J = 8.6 Hz, 2.1 Hz, 1 H), 10.0 (s, 1 H), 10.6 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 119.7, 122.4, 125.6, 136.8, 142.6, 155.8, 190.5.

2-Nitro-1-naphthol (2p).[37] Yellow solid, mp 126-127 °C (lit.[38] 125-127 °C). ^{1}H NMR ($CDCl_3$) δ 7.27 (d, J = 9.2 Hz, 1 H), 7.61 (tt, J = 7.5 Hz, 1.5 Hz, 1H), 7.70 (tt, J = 7.5 Hz, 1.5 Hz, 1 H), 7.80 (d, 9.2 Hz, 1 H), 7.99 (d, J = 9.2 Hz, 1 H), 8.53 (d, J = 9.2 Hz, 1 H), 12.26 (s, 1 H). ^{13}C NMR ($CDCl_3$) δ 119.8, 120.6, 125.5, 127.2, 127.5, 128.7, 131.8, 134.1, 137.8, 156.1.

1-Nitro-2-naphthol (2q). Yellow solid, mp, 95-96 °C (lit.[33] 96 °C). ^{1}H NMR ($CDCl_3$) δ 7.28 (d, J = 9.1 Hz, 1 H), 7.53 (tt, 7.6 Hz, 1.8 Hz, 1H), 7.76 (tt, 7.6 Hz, 1.8 Hz, 1H), 7.85 (d, J = 9.1 Hz,), 8.01 (d, J = 9.1 Hz, 1 H), 8.94 (d, J = 9.1 Hz, 1 H), 12.21 (s, 1 H). ^{13}C NMR ($CDCl_3$) δ 119.7, 123.4, 126.0, 127.1, 128.3, 128.9, 129.6, 131.3 , 139.5, 159.2.

7-Hydroxy-3,4,8-trimethyl-6-nitrocoumarin (2r). ^{1}H NMR ($CDCl_3$) 2.24 (s, 3 H), 2.42 (s, 1 H), 2.44 (s, 1H), 8.31 (s, 1 H), 11.15 (s, 1 H). ^{13}C NMR ($CDCl_3$) δ 8.8, 13.8, 15.6, 114.6, 116.2, 119.5, 122.1, 130.6. 145.4, 155.1, 156.0, 161.0. MS *m/z* 278 (M^+). Anal. Calcd for $C_{12}H_{11}NO_5$: C, 57.83; H, 4.45; N, 5.62. Found: C, 57.90; H, 4.50; N, 5.66.

6-Hydroxy-5-nitro-1,3-benzoxanthio-2-one (2s). Yellow solid, mp 178-180 °C. IR (KBr) 3282, 3010, 1758, 1624, 1447, 1321, 891, 811, 742 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 7.18 (s, 1 H), 8.45 (s, 1 H), 11.54 (s, 1 H). MS *m/z* 213 M^+ . ^{13}C NMR DMSO-d_6 δ 100.6, 111.7, 119.4, 132.7, 150.4, 151.7, 167.7. MS *m/z* Anal. Calcd for $C_7H_3NO_5S$: C, 39.44; H, 1.42; N, 6.57. Found: C, 39.37; H, 1.46; N, 6.55.

2-(2-Hydroxy-3-nitrophenyl)benzoxazole (2t). Colorless solid, mp 195-197 °C. IR (KBr) ^{1}H NMR (DMSO-d_6) δ 7.33 (m, 1 H), 7.49 (μ, 2H), 7.91 (μ, 2H), 8.33 (m, 1 H), 8.38 (t, J = 2.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$) δ 110.9, 111.5, 118.6, 120.0, 124.0, 126.1, 126.9, 128.9, 139.7, 140.9, 149.6, 161.3, 163.7. MS *m/z* 256 (M^+). Anal. Calcd for $C_{13}H_8N_2O_4$: C, 60.94; H, 3.15; N, 10.93. Found: C, 61.91; H, 3.15; N, 10.85.

2-(4-Hydroxy-3-nitrophenyl)-4-nitro-5-pyrimidinol (2u). Yellow solid, mp. 220-223 °C. IR (KBr) 3322, 2201, 1630, 1440, 1321 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 7.27 (d, J = 7.6 Hz, 1 H), 8.35

(dd, 7.6, 1.7 Hz, 1 H), 8.67 (d, *J* =1.7 Hz, 1 H), 8.93 (s, 1 H). ^{13}C NMR (DMSO-d_6) δ 120.7, 124.9, 127.4, 134.2, 137.8, 142.8, 151.3, 152.5, 153.9, 154.8. MS *m/z* 278 (M^+). Anal. Calcd for $C_{10}H_7N_3O_4$: C, 51.51; H, 3.03; N, 18.02. Found: C, 51.66; H, 3.09; N, 18.12.
3-Hydroxy-2-nitropyridine (2v). Yellow solid, mp 66-68 ^{o}C, (lit.67-69 ^{o}C).[39]

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