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Potassium Trinitromethanide as a 1,1-Ambiphilic Synthon Equivalent: Access to 2-Nitroarenofurans

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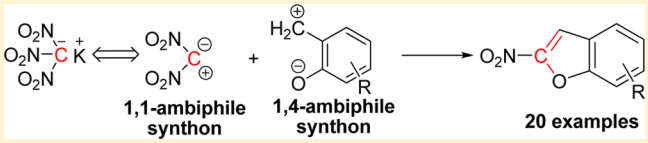
Supporting Information

ABSTRACT: The first example of the use of potassium trinitromethanide as a 1,1-ambiphilic synthon equivalent for the construction of a benzofuran moiety mediated by triethylamine has been developed. The method tolerates a variety of functional groups on the starting quaternary ammonium salt and has been successfully extended to polysubstituted benzofurans. Formation of an *o*-quinone methide intermediate is postulated as a key to the mechanism of this cascade process.



INTRODUCTION

Ambiphilic synthons, which contain both electrophilic and nucleophilic centers in the same molecule, are widely used in organic synthesis as useful building blocks.[1] The development of new synthetic methods using ambiphiles has great potential in the elaboration of new high-step-economy reactions.[2] Moreover, 1,1-ambiphiles with reaction centers on the same carbon atom are promising for the construction of cyclic molecules.[3] However, this reaction type remains undeveloped.

The use of polynitromethane derivatives in the synthesis of heterocycles has generally been limited to isoxazole and isoxazolidine units.[4] In these transformations, polynitromethanes react as 1,3-dipoles, and C, N, and O atoms are incorporated into the structures of the heterocycles. Potassium trinitromethanide (potassium nitroformate) is often used to introduce a trinitromethyl group in organic molecules. The reaction of potassium trinitromethanide as a 1,1-ambiphilic reagent, wherein only the carbon atom is included in the formed heterocyclic structure, is unprecedented.

o-Quinone methides (*o*-QMs) are highly reactive and useful species that have been implicated as intermediates in the synthesis of natural products, usually as heterodynes, to form chromane systems.[5] They also react with nucleophiles as 1,4-Michael acceptors.[6] Reactions of *o*-QM precursors are exceptionally facile compared with traditional Michael acceptors because aromatization energy provides additional product and transition-state stabilization in the case of the *o*-QM fragment. In addition, the initial products of Michael-type reactions with *o*-QM may undergo further intramolecular cyclization with phenolic hydroxyl groups to provide a pathway to oxygen-containing heterocycles.[7] However, such cascade protocols are rare and require further study.

In the process of an overall synthetic program aimed at the development of new cascade transformations utilizing *o*-QMs,[7b] we put our efforts on the study of the reaction of potassium trinitromethanide with *o*-QM precursors. We have found that this reaction affords 2-nitroarenofurans, which have drawn extensive attention because of their varied biological activities. For example, many of these compounds exhibit antibacterial,[8] antiparasitic,[9] radiosensitizing,[10] mutagenic properties[11] and can be used as regulators of the nuclear receptor HNF4α.[12] Besides, 2-nitrobenzofurans are useful intermediates for the preparation of 2-halogenobenzofurans,[13] dibenzofurans,[14] and benzofuro[2,3-*c*]pyrroles.[15]

A number of methods for the synthesis of 2-nitrobenzofurans have been reported. These compounds are generally prepared by the condensation between *o*-hydroxybenzaldehydes and bromonitromethane.[12,16] Although this reaction has already been performed under miscellaneous conditions with a large variety of aldehydes, its applicability is not completely versatile and leads to rather unsatisfactory yields in certain cases. The direct nitration of benzofurans at the 2-position usually leads to low yields and unwanted nitration products.[17]

3-Alkyl-2-nitrobenzofurans are also obtained by replacement of the acyl group in 2-acyl-3-alkylbenzofurans[18] and by treating 3-alkylbenzofurans successively with *t*-BuLi, trimethyltin chloride, and finally tetranitromethane in DMSO.[19] 2-Nitrobenzofuran has been prepared by *ipso*-nitration of 2-benzofuranboronic acid using bismuth(III) nitrate[20] and by nitration of benzofuran using sodium nitrite in the presence of cerium(IV) ammonium nitrate.[21] Recently, 3-alkyl-2-nitrobenzofurans were synthesized from 2-(2-nitroethyl)phenols via a hypervalent-iodine-induced oxidative cyclization.[22]

RESULTS AND DISCUSSION

Potassium trinitromethanide reacts with *o*-QMs through the carbon as a soft nucleophilic center and acts as a synthetic equivalent of a 1,1-dipole one-carbon synthon (**A**) or a dinitrocarbene (**B**) (Scheme 1).

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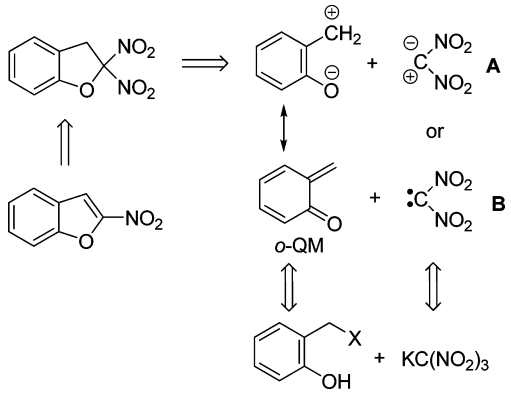
Scheme 1. Retrosynthetic Approach to the Benzofuran Moiety

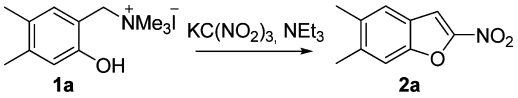


We first investigated the reaction between the *o*-QM precursor **1a** and potassium trinitromethanide under various conditions. Potassium trinitromethanide was obtained from the reaction of tetranitromethane with potassium hydroxide and ethanol in water solution.[23]

$$C(NO_2)_4 + KOH + C_2H_5OH \rightarrow KC(NO_2)_3 + C_2H_5ONO_2 + H_2O$$

When the reaction of **1a** with potassium trinitromethanide was carried out in ethanol at room temperature in the absence of any base, no desired product formation was observed (Table 1, entry 1). The use of a catalytic amount of TEA (0.1 equiv) at elevated temperature furnished only a trace amount (<5%) of the expected 2-nitrobenzofuran **2a** in 40 min (entry 2). Attempts to improve the yield by increasing the reaction time were unsuccessful. In order to achieve a high yield, we did further investigation of other parameters, such as the solvent, temperature, and ratio of the components. When the **1a**:$KC(NO_2)_3$:TEA ratio was adjusted from 1:1:1 to 1:3:3, a good yield (79%) was obtained (entry 8). A lower base loading caused a decrease in reaction yield. No significant improvement in the yield of **2a** was gained when we employed more than 3 equiv of potassium trinitromethanide. The reaction was also performed at various temperatures, and the best results were obtained at approximately 80 °C. The reaction was not carried out at higher temperatures since the onset temperature of the decomposition of potassium trinitromethanide was found to be 80 °C.[23a] The influence of the solvent was also examined. The results showed that the same reaction can also be performed in aqueous THF, ethanol, or acetonitrile, which afforded the highest yield.

Table 1. Results of the Optimization[a]



1a 2a

entry	solvent	T (°C)	**1a**:$KC(NO_2)_3$:TEA	yield (%)[b]
1	EtOH	25	1:1:0	–
2	EtOH	78	1:1:0.1	<5
3	CH_3CN	25	1:1:1	20
4	CH_3CN	25	1:3:3	25
5	CH_3CN	81	1:1:1	55
6	CH_3CN	81	1:2:2	64
7	CH_3CN	81	1:2:3	63
8	CH_3CN	81	1:3:3	79
9	EtOH	78	1:3:3	74
10	3:1 THF/H_2O	65	1:3:3	69
11	DMF	80	1:3:3	31
12	H_2O	80	1:3:3	26

[a]Reaction conditions: compound **1a** (1 mmol), $KC(NO_2)_3$, TEA, 20 mL of solvent, 40 min. [b]Isolated yields after silica gel chromatography.

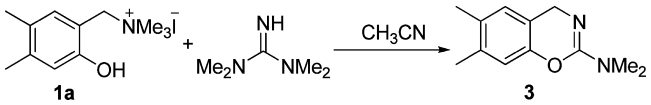
In order to evaluate the effect of the base on the reaction, several organic bases were examined (Table 2). Triethylamine proved to be the most efficient base. Thus, under the optimal conditions, 3 equiv of potassium trinitromethanide and 3 equiv of TEA in acetonitrile at 81 °C provided the desired product in 79% yield in 40 min. It is interesting to note that in the case of 1,1,3,3-tetramethylguanidine (TMG) as the base, only 2-dimethylamino-4*H*-1,3-benzoxazine **3** was isolated in 54% yield (Table 2, entry 8 and Scheme 2).[24]

Table 2. Optimization of Bases[a]

entry	base	pK_a	yield (%)[b]
1	TEA	10.75	79
2	DIPEA	11.4	54
3	NMM	7.38	54
4	*N*-methylimidazole	7.4	17
5	DMAP	9.2	14
6	DABCO	8.82	14
7	DBU	12.0	10
8	TMG	13.6	–[c]

[a]Reaction conditions: 1 equiv of **1a**, 3 equiv of potassium trinitromethanide, and 3 equiv of base in CH_3CN under reflux for 40 min. [b]Isolated yields after silica gel chromatography. [c]Only 1,3-benzoxazine **3** was isolated.

Scheme 2



1a 3

Under the optimized reaction conditions, the scope and generality of this cascade process were then explored. A variety of electronically divergent *o*-QM precursors were examined, and the results are summarized in Table 3. The method turned out to be tolerant toward a broad range of functional groups. The reaction proceeded without any problems for a wide range of substrates bearing electron-donating (CH_3O, Alk) or electron-withdrawing (NO_2, Hal, CO_2CH_3, CHO) substituents on the aryl ring, providing the corresponding 2-nitrobenzofurans in moderate to good yields. The sterically hindered adamantyl-substituted 2-nitrobenzofuran **2l** was obtained in good yield, indicating that steric hindrance had no obvious influence on the efficiency of our method.

Scheme 3 outlines a proposed mechanism for the formation of 2-nitrobenzofurans. The mechanism involves initial elimination of trimethylamine from the anion of the quaternary ammonium salt by an E_1cB mechanism to afford an electrophilic *o*-QM. Subsequent Michael-type addition of trinitromethanide anion, intramolecular nucleophilic substitution, and elimination of nitro groups then afford the 2-nitrobenzofuran. TEA promotes the generation of the *o*-QM and further aromatization of the intermediate dihydrobenzofur-

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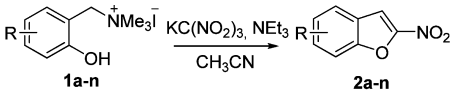
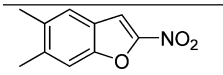
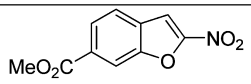
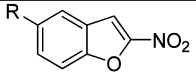
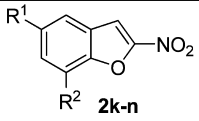
Table 3. Synthesis of 2-Nitrobenzofurans 2a–n[a,b,c]



	**2a**, 79%		**2b**, 51%



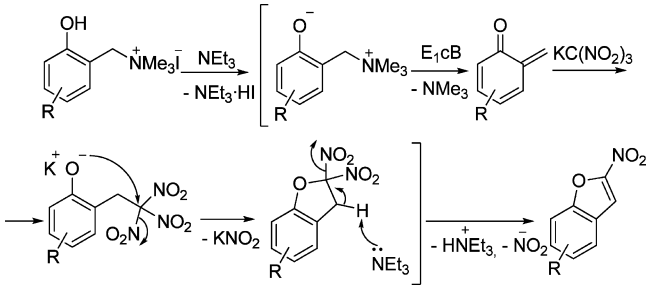
2c, R = OMe	59%	**2g**, R = Cl	57%
2d, R = t-Bu	36%	**2h**, R = CO_2Me	62%
2e, R = 1-Adamantyl	61%	**2i**, R = COMe	68%
2f, R = Bn	68%	**2j**, R = NO_2	50%



2k, R^1 = t-Bu, R^2 = NO_2	39%
2l, R^1 = Me, R^2 = 1-Adamantyl	73%
2m, R^1 = CHO, R^2 = OMe	59%
2n, R^1 = CO_2Me, R^2 = OMe	60%

[a]Optimal conditions: 1 equiv of **1**, 3 equiv of potassium trinitromethanide, and 3 equiv of TEA in CH_3CN under reflux. [b]Isolated yields after silica gel chromatography are shown. [c]All of the reactions except the first one were carried out without additional optimization.

Scheme 3. Proposed Mechanism for the Synthesis of 2

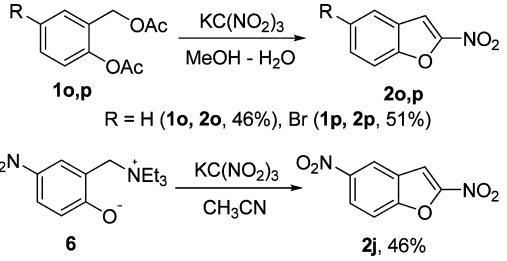


an. It also keeps the medium basic, which is necessary to avoid the formation of waxy side products.

In support of the proposed mechanistic pathway, in some cases intermediate trinitroethyl derivatives and 2,2-dinitro-2,3-dihydrobenzofurans were isolated. Phenols **4a** and **4b** were prepared from 2-chloromethylphenols **1v** and **1w**, respectively, and potassium trinitromethanide in acetonitrile at room temperature. In DMSO solution the trinitroethyl derivatives **4a** and **4b** undergo cyclization and form the corresponding 2,2-dinitro-2,3-dihydrobenzofurans **5a** and **5b** (Scheme 4). We also found different reaction rates for these transformations depending on the nature of the substituent on the aromatic core: full conversion of acetyl-substituted phenol **4b** to dihydrobenzofuran **5b** was accomplished in 5 days at room temperature, whereas nitrophenol **4a** was converted to **5a** in 5 h (according to NMR monitoring). It should also be noted that compounds **5a** and **5b** in DMSO or acetonitrile solution were slowly transformed to 2-nitrobenzofurans **2j** and **2i**, respectively. At the same time, in nonpolar solvents compounds **4a**/**4b** and **5a**/**5b** are more stable.

Attempts to extend this reaction to the Mannich bases of simple phenols failed to furnish the expected products. This failure may be due to the relatively greater thermal stability of Mannich bases compared with quaternary ammonium salts. However, instead of quaternary salts, 2-acetoxybenzyl acetates **1o** and **1p** as well as ammoniophenolate **6** can be used (Scheme 5).

Scheme 5. Extention of the Developed Methodology to Other *o*-QM Precursors

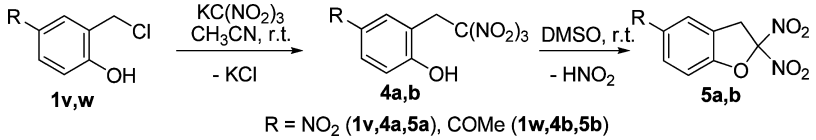


In order to broaden the scope of the present method, we attempted the present protocol using naphthalene (**1q**) and heterocyclic (**1r–t**) precursors of *o*-QMs. From the Mannich bases **1r–t**, the heterocyclic systems benzo[1,2-*b*:4,3-*b*′]difuran **2r**, furo[3,2-*e*]indole **2s**, and furo[3,2-*e*]pyrido[3,4-*b*]indole **2t** were prepared in moderate yields (Scheme 6).

CONCLUSION

We have developed a simple and efficient method for the synthesis of 2-nitroarenofurans from quaternary ammonium salts, some phenolic Mannich bases, or 2-acetoxybenzyl acetates and potassium trinitromethanide in moderate to good yields. This is the first example of the use of potassium trinitromethanide as a 1,1-ambiphilic reagent. The tolerance of various substituents on the aromatic rings makes this protocol highly practical for diversity-oriented synthesis.

Scheme 4. Synthesis of Dihydrobenzofurans 5a and 5b



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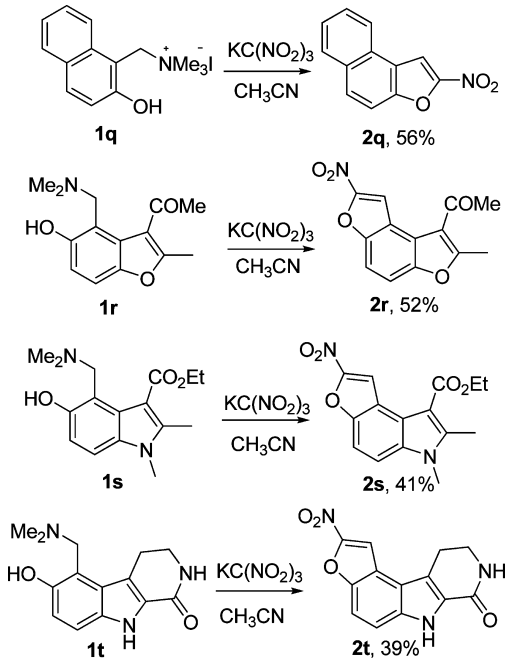
Scheme 6. Synthesis of Condensed Nitrobenzofurans



EXPERIMENTAL SECTION

Materials and Characterization. FTIR spectra were taken in KBr pellets. ^{1}H, ^{13}C, and DEPT NMR spectra were recorded using a 400 MHz NMR spectrometer in CD_3CN, $CDCl_3$, or DMSO-d_6 solutions with TMS as an internal standard. Chemical shifts and coupling constants were recorded in units of parts per million and hertz, respectively. The melting points were uncorrected. Elemental analysis was carried out on an automatic CHNS analyzer. Mass spectra were recorded with 70 eV electron ionization energy. Thin-layer chromatography was carried out on aluminum-backed silica gel plates with visualization of components by UV light (254 nm) or exposure to I_2. Known *o*-QM precursors were prepared according to the literature procedures.[25−29]

(2-Hydroxy-3-nitro-5-*tert*-butylbenzyl)trimethylammonium Iodide (1k). Dimethylamine (6 mL of a 33% aqueous solution, 0.04 mol) and formaldehyde (3 mL of a 37% aqueous solution, 0.04 mol) were added to a solution of 4-*tert*-butyl-2-nitrophenol (7 g, 0.036 mol) in ethanol (50 mL). The reaction mixture was stored at room temperature for 2 days. The solvent was evaporated in vacuo, and the residue was dissolved in acetonitrile (20 mL) and treated with CH_3I (7 mL, 16 g, 0.11 mol). The resulting solution was stirred at room temperature for 2 days, after which the solvent was evaporated in vacuo and the residue was recrystallized from an ethanol/diethyl ether mixture. Yield: 62%, 8.77 g. Orange crystals, mp 169−171 °C (decomp.). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.01 and 7.99 (d, ^{4}J = 2.3 Hz, 2H), 4.63 (s, 2H), 3.08 (s, 9H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 151.2 (C), 142.6 (C), 140.2 (CH), 136.7 (C), 124.0 (CH), 120.2 (C), 62.7 (CH_2), 55.5 (C), 52.9 ($3CH_3$), 34.7 (C), 31.2 ($3CH_3$). IR (KBr) ν_{max}: 648, 887, 980, 1161, 1265, 1312, 1346, 1377, 1416, 1477, 1535 (NO_2), 1597, 1620, 2870, 2951, 3001, 3400−3100 (OH) cm^{-1}. Anal. Calcd (%) for $C_{14}H_{23}IN_2O_3$: C, 42.65; H, 5.88; N, 7.11. Found (%): C, 42.72; H, 5.90; N, 7.02.

Potassium Trinitromethanide. *Caution: Although we have encountered no difficulties in working with potassium trinitromethanide and tetranitromethane, full safety precautions (goggles, shields, fume hoods) should be taken whenever possible because of the explosive nature and toxicity of these compounds.*

Potassium hydroxide (18.6 g, 0.332 mol) was dissolved in 22 mL of water and 84 mL of ethanol and stirred at ice bath temperature. To this solution, tetranitromethane (28 mL, 45.4 g, 0.232 mol) was added portionwise over a period of 10 min. The temperature of the reaction mixture was kept below 20 °C. The ice bath was removed, and the reaction mixture was allowed to warm to room temperature (20−25 °C) and stirred for 20 min. After completion of the reaction, the mixture was cooled to 0 °C, and the solid was filtered off and washed with 20 mL of ice-cold EtOH. Yield: 91%, 39.9 g. Bright-yellow crystals, mp 83 °C (decomp.).

General Experimental Procedure for the Synthesis of 2-Nitroarenofurans. Potassium trinitromethanide (1.14 g, 6 mmol) was added in three equal portions over a period of 20 min to a stirred solution of the *o*-QM precursor (2 mmol) and triethylamine (0.84 mL, 6 mmol) in acetonitrile (20 mL) at reflux temperature under an Ar atmosphere. Afterward, the mixture was refluxed for another 20 min and then poured into 50 mL of a saturated water solution of sodium chloride to yield a solid product, which was filtered, washed with water, and dried. The crude product was purified by column chromatography over silica gel using dichloromethane as the eluent followed by recrystallization from ethanol.

*5,6-Dimethyl-2-nitrobenzofuran (**2a**).* Yield: 79%, 302 mg. Yellow solid, mp 135−136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (s, 1H), 7.48 (s, 1H), 7.37 (s, 1H), 2.41 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.7 (C), 152.7 (C), 140.9 (C), 134.9 (C), 123.8 (C), 123.6 (CH), 112.8 (CH), 107.5 (CH), 21.2 (CH_3), 20.1 (CH_3). IR (KBr) ν_{max}: 729, 802, 864, 953, 1080, 1198, 1267, 1323, 1364 (NO_2), 1452, 1503 (NO_2), 1555, 1620, 2924, 3140 (CH Fu) cm^{-1}. MS (EI) *m*/*z* (%): 191 $[M]^+$ (51), 161 $[M - NO]^+$ (93), 133 $[M - CNO_2]^+$ (36), 117 (41), 115 (74), 105 $[C_8H_9]^+$ (22), 91 $[C_7H_7]^+$ (44), 46 $[NO_2]^+$ (100). Anal. Calcd (%) for $C_{10}H_9NO_3$: C, 62.82; H, 4.74; N, 7.33. Found (%): C, 62.90; H, 4.72; N, 7.27.

*Methyl 2-Nitrobenzofuran-6-carboxylate (**2b**).* Yield: 51%, 225 mg. Light-yellow solid, mp 144−145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (d, ^{4}J = 1.3 Hz, 1H), 8.10 (dd, ^{3}J = 8.4, ^{4}J = 1.3 Hz, 1H), 7.83 (d, ^{3}J = 8.4 Hz, 1H), 7.69 (d, ^{5}J = 0.8 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.0 (C═O), 154.6 (C), 152.4 (C), 131.7 (C), 129.7 (C), 126.3 (CH), 124.0 (CH), 114.5 (CH), 106.7 (CH), 52.8 (CH_3). IR (KBr) ν_{max}: 729, 766, 814, 974, 1072, 1225, 1260, 1281, 1312, 1341 (NO_2), 1373, 1422, 1435, 1526 (NO_2), 1566, 1714 (C═O), 2854, 2924, 2959, 3138 (CH Fu) cm^{-1}. Anal. Calcd (%) for $C_{10}H_7NO_5$: C, 54.31; H, 3.19; N, 6.33. Found (%): C, 54.40; H, 3.24; N, 6.26.

*5-Methoxy-2-nitrobenzofuran (**2c**).* Yield: 59%, 228 mg. Yellow solid, mp 127−128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (s, 1H), 7.50 (d, ^{3}J = 8.8 Hz, 1H), 7.19 (dd, ^{3}J = 8.8, ^{4}J = 1.8 Hz, 1H), 7.11 (d, ^{4}J = 1.8 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.6 (C), 153.5 (C), 148.5 (C), 126.5 (C), 120.6 (CH), 113.7 (CH), 107.4 (CH), 104.3 (CH), 56.0 (CH_3). IR (KBr) ν_{max}: 748, 818, 878, 1026, 1169, 1202, 1265, 1327 (NO_2), 1369, 1510 (NO_2), 1562, 2924, 3102 (CH Fu), 3126 cm^{-1}. MS (EI) *m*/*z* (%): 193 $[M]^+$ (84), 163 $[M - NO]^+$ (100), 135 $[M - CNO_2]^+$ (27), 119 (58), 107 $[C_7H_7O]^+$ (7). Anal. Calcd (%) for $C_9H_7NO_4$: C, 55.96; H, 3.65; N, 7.25. Found (%): C, 56.06; H, 3.60; N, 7.31.

*5-tert-Butyl-2-nitrobenzofuran (**2d**).* Yield: 36%, 158 mg. Light-yellow solid, mp 80−81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, ^{4}J = 2.1 Hz, 1H), 7.66 (dd, ^{3}J = 8.9, ^{4}J = 2.1 Hz, 1H), 7.63 (d, ^{5}J = 0.7 Hz, 1H), 7.54 (d, ^{3}J = 8.9 Hz, 1H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.3 (C), 151.8 (C), 148.8 (C), 128.6 (CH), 125.7 (C), 119.9 (CH), 112.2 (CH), 107.7 (CH), 35.1 (C), 31.6 ($3CH_3$). IR (KBr) ν_{max}: 731, 816, 841, 955, 1101, 1126, 1192, 1236, 1267, 1304, 1319, 1358 (NO_2), 1466, 1520 (NO_2), 1562, 2870 (CH_3), 2961, 3138 (CH Fu) cm^{-1}. Anal. Calcd (%) for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found (%): C, 65.82; H, 6.04; N, 6.36.

*5-(1-Adamantyl)-2-nitrobenzofuran (**2e**).* Yield: 61%, 362 mg. Light-yellow solid, mp 165−167 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.64−7.67 (m, 3H), 7.53 (d, ^{3}J = 8.7 Hz, 1H), 2.13 (br s, 3H), 1.92−1.97 (m, 6H), 1.75−1.84 (m, 6H). ^{13}C NMR (400 MHz, DMSO-d_6) δ: 153.3 (C), 151.9 (C), 149.1 (C), 128.2 (CH), 125.7 (C), 119.8 (CH), 112.2 (CH), 107.8 (CH), 43.5 ($3CH_2$), 36.7 ($3CH_2$), 36.6 (C), 29.0 (3CH). IR (KBr) ν_{max}: 729, 800, 831, 849, 876, 955, 1092, 1242, 1317, 1331, 1344, 1362 (NO_2), 1371, 1470, 1524 (NO_2), 1568, 2851, 2901, 3142 (CH Fu) cm^{-1}. Anal. Calcd (%) for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found (%): C, 72.80; H, 6.39; N, 4.66.

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*5-Benzyl-2-nitrobenzofuran (**2f**).* Yield: 68%, 344 mg. Yellow solid, mp 130−131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, ^5J = 0.9 Hz, 1H), 7.51−7.53 (m, 2H), 7.43 (dd, ^3J = 8.7, ^4J = 1.8 Hz, 1H), 7.29−7.33 (m, 2H), 7.21−7.25 (m, 1H), 7.18−7.20 (m, 2H), 4.10 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.3 (C), 152.2 (C), 140.4 (C), 138.8 (C), 131.5 (CH), 129.0 (CH), 128.8 (CH), 126.6 (CH), 126.1 (C), 123.6 (CH), 112.7 (CH), 107.3 (CH), 41.7 (CH_2). IR (KBr) ν_{max}: 700, 737, 835, 957, 1099, 1250, 1335 (NO_2), 1373, 1433, 1468, 1506 (NO_2), 1560, 3136 (CH Fu) cm^{-1}. Anal. Calcd (%) for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53. Found (%): C, 71.20; H, 4.31; N, 5.61.

*5-Chloro-2-nitrobenzofuran (**2g**).* Yield: 57%, 226 mg. Light-yellow solid, mp 118−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (br s, 1H), 7.61 (s, 1H), 7.55−7.57 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.0 (C), 151.6 (C), 131.3 (C), 130.5 (CH), 127.1 (C), 123.4 (CH), 114.1 (CH), 106.5 (CH). IR (KBr) ν_{max}: 692, 729, 814, 835, 880, 957, 1101, 1190, 1244, 1314, 1360 (NO_2), 1435, 1449, 1506, 1524 (NO_2), 1562, 3136 (CH Fu) cm^{-1}. MS (EI) *m*/*z* (%): 197 $[M]^+$ (35), 167 $[M - NO]^+$ (51), 139 $[M - CNO_2]^+$ (30), 123 (57), 111 $[C_6H_4Cl]^+$ (22), 46 $[NO_2]^+$ (100). Anal. Calcd (%) for $C_8H_4ClNO_3$: C, 48.63; H, 2.04; N, 7.09. Found (%): C, 48.66; H, 1.97; N, 7.15.

*Methyl 2-Nitrobenzofuran-5-carboxylate (**2h**).* Yield: 62%, 274 mg. Light-yellow solid, mp 145−147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (d, ^4J = 1.6 Hz, 1H), 8.28 (dd, ^3J = 8.7 Hz, ^4J = 1.6 Hz, 1H), 7.72 (s, 1H), 7.67 (d, ^3J = 8.7 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.1 (C═O), 155.5 (C), 153.9 (C), 131.2 (CH), 127.9 (C), 126.6 (CH), 125.9 (C), 112.9 (CH), 107.4 (CH), 52.7 (CH_3). IR (KBr) ν_{max}: 746, 770, 839, 912, 1101, 1128, 1194, 1234, 1273, 1298, 1335 (NO_2), 1366, 1429, 1439, 1470, 1524 (NO_2), 1566, 1618, 1715 (C═O), 3109 (CH Fu), 3142 cm^{-1}. Anal. Calcd (%) for $C_{10}H_7NO_5$: C, 54.31; H, 3.19; N, 6.33. Found (%): C, 54.26; H, 3.24; N, 6.40.

*5-Acetyl-2-nitrobenzofuran (**2i**).* Yield: 68%, 279 mg. Light-yellow solid, mp 161−163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.40 (d, ^4J = 1.6 Hz, 1H), 8.22 (dd, ^3J = 8.7, ^4J = 1.6 Hz, 1H), 7.74 (s, 1H), 7.69 (d, ^3J = 8.7 Hz, 1H), 2.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.4 (C═O), 155.5 (C), 153.9 (C), 134.9 (C), 130.0 (C), 125.9 (CH), 125.3 (CH), 113.0 (CH), 107.5 (CH), 26.8 (CH_3). IR (KBr) ν_{max}: 581, 621, 733, 827, 916, 953, 1055, 1099, 1130, 1184, 1223, 1263, 1335 (NO_2), 1364, 1435, 1470, 1522 (NO_2), 1568, 1612, 1676 (C═O), 3142 (CH Fu) cm^{-1}. Anal. Calcd (%) for $C_{10}H_7NO_4$: C, 58.54; H, 3.44; N, 6.83. Found (%): C, 58.62; H, 3.49; N, 6.77.

*2,5-Dinitrobenzofuran (**2j**).* Yield: 50%, 208 mg. Yellow solid, mp 172−173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.75 (d, ^4J = 2.3 Hz, 1H), 8.51 (dd, ^3J = 9.2, ^4J = 2.3 Hz, 1H), 7.81 (d, ^5J = 0.9 Hz, 1H), 7.79 (d, ^3J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.4 (C), 154.8 (C), 145.8 (C), 126.2 (C), 125.1 (CH), 120.7 (CH), 113.8 (CH), 107.3 (CH). IR (KBr) ν_{max}: 683, 739, 831, 905, 955, 1069, 1194, 1296, 1342 (NO_2), 1377, 1539 (NO_2), 1570, 1626, 3115 (CH Fu), 3144 cm^{-1}. MS (EI) *m*/*z* (%): 208 $[M]^+$ (42), 207 $[M - H]^+$ (27), 178 $[M - NO]^+$ (100), 162 $[M - NO_2]^+$ (8), 132 $[M - NO_2 - NO]^+$ (17), 120 $[M - CNO_2 - NO]^+$ (26), 104 (15), 88 (66), 76 (39), 62 (47). Anal. Calcd (%) for $C_8H_4N_2O_5$: C, 46.17; H, 1.94; N, 13.46. Found (%): C, 46.22; H, 2.01; N, 13.43.

*5-tert-Butyl-2,7-dinitrobenzofuran (**2k**).* Yield: 39%, 206 mg. Light-yellow solid, mp 152−153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 and 8.48 (d, ^4J = 1.8 Hz, 2H), 7.74 (s, 1H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.4 (C) 149.9 (C), 143.3 (C), 134.0 (C), 129.1 (C), 127.0 (CH), 124.0 (CH), 106.8 (CH), 35.5 (C), 31.4 ($3CH_3$). IR (KBr) ν_{max}: 725, 791, 845, 899, 926, 949, 1111, 1192, 1242, 1323, 1358 (NO_2), 1481, 1531 (NO_2), 1574, 2878, 2936, 2974, 3121 (CH Fu) cm^{-1}. Anal. Calcd (%) for $C_{12}H_{12}N_2O_5$: C, 54.55; H, 4.58; N, 10.60. Found (%): C, 54.61; H, 4.56; N, 10.70.

*7-(1-Adamantyl)-5-methyl-2-nitrobenzofuran (**2l**).* Yield: 73%, 454 mg. Colorless solid, mp 229−231 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (s, 1H), 7.34 (s, 1H), 7.23 (s, 1H), 2.45 (s, 3H), 2.14−2.19 (m, 9H), 1.81−1.88 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.7 (C), 150.5 (C), 136.4 (C), 135.1 (C), 128.2 (CH), 126.8 (C), 120.9 (CH), 107.0 (CH), 41.3 (CH_2), 36.9 (CH_2), 36.5 (C), 28.8 (CH), 21.7 (CH_3). IR (KBr) ν_{max}: 731, 853, 962, 1252, 1275, 1331, 1344, 1358 (NO_2), 1402, 1454, 1524 (NO_2), 1570, 2851, 2905, 3152 (CH Fu) cm^{-1}. Anal. Calcd (%) for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found (%): C, 73.33; H, 6.77; N, 4.59.

*7-Methoxy-2-nitrobenzofuran-5-carbaldehyde (**2m**).* Yield: 59%, 261 mg. Light-yellow solid, mp 163−164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.04 (s, 1H), 7.86 (d, ^4J = 1.1 Hz, 1H), 7.75 (s, 1H), 7.58 (d, ^4J = 1.1 Hz, 1H), 4.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.6 (CHO), 153.9 (C), 146.9 (C), 146.2 (C), 135.4 (C), 127.4 (C), 121.0 (CH), 108.5 (CH), 107.6 (CH), 56.6 (CH_3). IR (KBr) ν_{max}: 795, 988, 1098, 1144, 1215, 1277, 1325, 1356 (NO_2), 1479, 1537 (NO_2), 1570, 1599, 1616, 1697 (CO), 3115 (CH Fu), 3140 cm^{-1}. Anal. Calcd (%) for $C_{10}H_7NO_5$: C, 54.31; H, 3.19; N, 6.33. Found (%): C, 54.38; H, 3.25; N, 6.26.

*Methyl 7-Methoxy-2-nitrobenzofuran-5-carboxylate (**2n**).* Yield: 60%, 301 mg. Light-yellow solid, mp 185−187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (d, ^4J = 1.4 Hz, 1H), 7.72 (d, ^4J = 1.4 Hz, 1H), 7.69 (s, 1H), 4.08 (s, 3H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.2 (C═O), 153.8 (C), 145.8 (C), 145.3 (C), 128.7 (C), 127.0 (C), 118.2 (CH), 111.6 (CH), 107.7 (CH), 56.5 (CH_3), 52.7 (CH_3). IR (KBr) ν_{max}: 772, 841, 976, 1103, 1180, 1207, 1231, 1246, 1285, 1358 (NO_2), 1481, 1524 (NO_2), 1570, 1605, 1620, 1713 (C═O), 2955, 3117, 3144 (CH Fu) cm^{-1}. Anal. Calcd (%) for $C_{11}H_9NO_6$: C, 52.60; H, 3.61; N, 5.58. Found (%): C, 52.70; H, 3.55; N, 5.64.

*2-Nitronaphtho[2,1-b]furan (**2q**).* Yield: 56%, 239 mg. Greenish-yellow solid, mp 143−144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17 (d, ^3J = 8.2 Hz, 1H), 8.14 (d, ^5J = 0.7 Hz, 1H), 7.99−8.03 (m, 2H), 7.72 (td, ^3J = 7.1, ^4J = 1.2 Hz, 1H), 7.68 (d, ^4J = 8.9 Hz, 1H), 7.62 (ddd, ^3J = 8.2, ^3J = 7.1, ^4J = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.6 (C), 152.0 (C), 132.1 (CH), 130.9 (C), 129.5 (CH), 128.4 (CH), 128.0 (C), 126.6 (CH), 123.4 (CH), 122.3 (C), 112.4 (CH), 106.8 (CH). IR (KBr) ν_{max}: 733, 758, 779, 806, 959, 1076, 1123, 1186, 1209, 1261, 1298, 1350 (NO_2), 1512 (NO_2), 1549, 1584, 3140 (CH Fu) cm^{-1}. Anal. Calcd (%) for $C_{12}H_7NO_3$: C, 67.61; H, 3.31; N, 6.57. Found (%): C, 67.62; H, 3.27; N, 6.64.

*1-Acetyl-2-methyl-7-nitrobenzo[1,2-b:4,3-b′]difuran (**2r**).* Yield: 52%, 269 mg. Yellow solid, mp 191−192 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55 (s, 1H), 7.49 and 7.63 (d, ^3J = 9.0 Hz, 2H), 2.89 (s, 3H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.8 (C═O), 162.8 (C), 152.5 (C), 151.3 (C), 150.4 (C), 121.2 (C), 120.2 (C), 120.1 (C), 113.3 (CH), 110.8 (CH), 109.2 (CH), 30.6 (CH_3), 16.3 (CH_3). IR (KBr) ν_{max}: 844, 955, 1113, 1144, 1256, 1300, 1344 (NO_2), 1408, 1516, 1551 (NO_2), 1655 (C═O), 3169 (CH Fu) cm^{-1}. Anal. Calcd (%) for $C_{13}H_9NO_5$: C, 60.24; H, 3.50; N, 5.40. Found (%): C, 60.21; H, 3.41; N, 5.44.

*Ethyl 6,7-Dimethyl-2-nitro-6H-furo[3,2-e]indole-8-carboxylate (**2s**).* Yield: 41%, 248 mg. Bright-yellow solid, mp 211−213 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.39 (s, 1H), 7.55 and 7.86 (d, ^3J = 9.2 Hz, 2H), 4.34 (q, ^3J = 7.1 Hz, 2H), 3.79 (s, 3H), 2.71 (s, 3H), 1.38 (t, ^3J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.9 (C═O), 151.8 (C), 151.1 (C), 146.4 (C), 133.1 (C), 120.0 (C), 118.1 (C), 115.0 (CH), 110.9 (CH), 106.6 (CH), 104.7 (C), 60.2 (CH_2), 31.0 (CH_3N), 14.9 (CH_3), 12.8 (CH_3). IR (KBr) ν_{max}: 860, 932, 1026, 1094, 1111, 1155, 1186, 1236, 1290, 1337 (NO_2), 1402, 1499, 1545 (NO_2), 1686 (C═O), 2924, 2988, 3090, 3175 (CH Fu) cm^{-1}. Anal. Calcd (%) for $C_{15}H_{14}N_2O_5$: C, 59.60; H, 4.67; N, 9.27. Found (%): C, 59.69; H, 4.61; N, 9.30.

*2-Nitro-6,8,9,10-tetrahydro-7H-furo[3,2-e]pyrido[3,4-b]indol-7-one (**2t**).* Yield: 39%, 211 mg. Red solid, mp >300 °C (decomp.). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.28 (s, 1H), 8.44 (d, ^5J = 0.7 Hz, 1H), 7.71 (s, 1H), 7.68 (d, ^3J = 9.2 Hz, 1H), 7.59 (dd, ^3J = 9.2, ^5J = 0.7 Hz, 1H), 3.53 (td, ^3J = 6.9, ^4J = 2.3 Hz, 2H), 3.16 (t, ^3J = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 161.7 (C═O), 152.7 (C), 150.1 (C), 134.1 (C), 129.1 (C), 119.0 (C), 118.9 (C), 118.1 (C), 117.5 (CH), 109.1 (CH), 108.7 (CH), 41.6 (CH_2), 21.5 (CH_2). IR (KBr) ν_{max}: 820, 920, 1088, 1128, 1209, 1240, 1271, 1302, 1319, 1352 (NO_2), 1400, 1445, 1499, 1543 (NO_2), 1676 (C═O), 2926, 3123 (CH Fu), 3231 (NH), 3375 (NH) cm^{-1}. Anal. Calcd (%) for $C_{13}H_9N_3O_4$: C, 57.57; H, 3.34; N, 15.49. Found (%): C, 57.62; H, 3.28; N, 15.56.

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*2-Nitrobenzofuran (**2o**).* Potassium trinitromethanide (1.14 g, 6 mmol) was added in three equal portions over a period of 20 min to a stirred solution of 2-(acetyloxy)benzyl acetate (0.42 g, 2 mmol) and triethylamine (0.84 mL, 6 mmol) in 60% aqueous ethanol (20 mL) at reflux temperature under an Ar atmosphere. Afterward, the mixture was refluxed for another 20 min and then poured into 50 mL of saturated aqueous sodium chloride. The resulting mixture was extracted with dichloromethane (2 × 20 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel using dichloromethane as the eluent followed by recrystallization from EtOH. Yield: 46%, 150 mg. Light-yellow solid, mp 134−135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (d, ^3J = 8.0 Hz, 1H), 7.68 (s, 1H), 7.57−7.63 (m, 2H), 7.39−7.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.4 (C), 153.2 (br s, C), 130.1 (CH), 125.9 (C), 125.4 (CH), 124.1 (CH), 112.8 (CH), 107.4 (CH). IR (KBr) ν_{max}: 729, 756, 833, 955, 1090, 1244, 1265, 1304, 1315, 1333, 1368 (NO_2), 1443, 1479, 1516, 1562 (NO_2), 1612, 2926, 3154 (CH Fu) cm^{-1}. Anal. Calcd (%) for $C_8H_5NO_3$: C, 58.90; H, 3.09; N, 8.59. Found (%): C, 59.01; H, 3.02; N, 8.64.

*5-Bromo-2-nitrobenzofuran (**2p**).* Compound **2p** was prepared similarly to compound **2o** from 2-(acetyloxy)-5-bromobenzyl acetate (**1p**). Yield: 51%, 247 mg. Light-yellow solid, mp 168−169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, ^4J = 1.8 Hz, 1H), 7.69 (dd, ^3J = 9.2, ^4J = 1.8 Hz, 1H), 7.61 (s, 1H), 7.52 (d, ^3J = 9.2 Hz); ^{13}C NMR ($CDCl_3$) δ: 153.6 (C), 152.0 (C), 133.2 (CH), 127.6 (C), 126.6 (CH), 118.6 (C), 114.4 (CH), 106.3 (CH). IR (KBr) ν_{max}: 810, 837, 876, 957, 1099, 1188, 1238, 1312, 1373 (NO_2), 1439, 1528 (NO_2), 1562, 3140 (CH Fu) cm^{-1}. Anal. Calcd (%) for $C_8H_4BrNO_3$: C, 39.70; H, 1.67; N, 5.79. Found (%): C, 39.77; H, 1.59; N, 5.86.

*6,7-Dimethyl-2-dimethylamino-4H-1,3-benzoxazine (**3**).* When TMG was used instead of TEA, only benzoxazine **3** was isolated under the conditions previously indicated. Yield: 54%, 220 mg. White solid, mp 82−83 °C (from hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.77 (s, 1H), 6.68 (s, 1H), 4.43 (s, 2H), 2.93 (s, 6H), 2.20 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.2 (C), 148.1 (C), 135.8 (C), 132.0 (C), 126.6 (CH), 118.5 (C), 116.0 (CH), 44.7 (CH_2), 37.2 ($2CH_3$), 19.6 (CH_3), 19.1 (CH_3). IR (KBr) ν_{max}: 866, 880, 959, 1099, 1175, 1202, 1254, 1269, 1373, 1389, 1450, 1462, 1487, 1504, 1674 (C═N), 2851 cm^{-1}. Anal. Calcd (%) for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.90; N, 13.71. Found (%): C, 70.60; H, 7.92; N, 13.80.

*4-Nitro-2-(2,2,2-trinitroethyl)phenol (**4a**).* A mixture of 2-(chloromethyl)-4-nitrophenol (**1v**) (1 g, 5.3 mmol) and potassium trinitromethanide (1.06 g, 5.6 mmol) in CH_3CN (20 mL) under an Ar atmosphere was stirred at room temperature for 4 h. Afterward, the mixture was poured into 50 mL of saturated aqueous sodium chloride, and the resulting mixture was extracted with dichloromethane (2 × 20 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified by recrystallization from ethanol. Yield: 50%, 800 mg. Light-orange solid, mp 139−140 °C (decomp.). ^{1}H NMR (DMSO-d_6) δ: 11.86 (1H, br s), 8.12−8.15 (2H, m), 6.99 (1H, d, ^3J = 9.1 Hz), 4.79 (s, 2H). ^{13}C NMR (DMSO-d_6) δ: 163.6 (C), 140.1 (C), 129.1 (C), 128.5 (CH), 127.5 (CH), 116.1 (C), 116.0 (CH), 33.6 (CH_2). IR (KBr) ν_{max}: 638, 756, 812, 825, 839, 864, 920, 937, 1090, 1221, 1288, 1335 (NO_2), 1495, 1516 (NO_2), 1591 ($C(NO_2)_3$), 1609, 3500−3300 (OH) cm^{-1}. Anal. Calcd (%) for $C_8H_6N_4O_9$: C, 31.80; H, 2.00; N, 18.54. Found (%): C, 31.90; H, 1.96; N, 18.57.

*1-[4-Hydroxy-3-(2,2,2-trinitroethyl)phenyl]ethanone (**4b**).* A mixture of 3-chloromethyl-4-hydroxyacetophenone (**1w**) (1 g, 5.4 mmol) and potassium trinitromethanide (1.06 g, 5.6 mmol) in CH_3CN (20 mL) under an Ar atmosphere was stirred at room temperature for 4 h. Afterward, the mixture was poured into 50 mL of saturated aqueous sodium chloride to yield a solid product, which was filtered, washed with water, and purified by recrystallization from ethanol. Yield: 71%, 1.15 g. Pink solid, mp 160−161 °C (decomp.). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.12 (1H, br s), 7.86 (dd, ^3J = 8.5, ^4J = 2.1 Hz, 1H), 7.79 (d, ^4J = 2.1 Hz, 1H), 6.91(d, ^3J = 8.5 Hz, 1H), 4.72 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, CD_3CN) δ: 196.0 (C═O), 160.3 (C), 132.1 (CH), 131.9 (CH), 130.4 (C), 128.7 (br s, C), 115.1 (CH), 114.6 (C), 33.8 (CH_2), 25.7 (CH_3). IR (KBr) ν_{max}: 814, 833, 864, 964, 1080, 1119, 1285, 1304, 1362, 1431, 1585, 1597 ($C(NO_2)_3$), 1667 (C═O), 3400−3100 (OH) cm^{-1}. Anal. Calcd (%) for $C_{10}H_9N_3O_8$: C, 40.14; H, 3.03; N, 14.04. Found (%): C, 40.22; H, 2.96; N, 14.13.

*2,2,5-Trinitro-2,3-dihydrobenzofuran (**5a**).* 4-Nitro-2-(2,2,2-trinitroethyl)phenol (**4a**) (0.3 g, 1 mmol) was dissolved in DMSO (2 mL), and the solution obtained was stored at room temperature for 5 h. The solution was poured into 15 mL of saturated aqueous sodium chloride to yield a solid product, which was filtered, washed with water, and dried. Yield: 43%, 110 mg. Light-yellow solid, mp 92−94 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.32−8.33 (m, 1H), 8.29 (dd, ^3J = 8.9, ^4J = 2.3 Hz, 1H), 7.58 (d, ^3J = 8.9 Hz, 1H), 4.70 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 160.7 (C), 145.1 (C), 130.1 (C), 126.7 (CH), 125.8 (C), 121.8 (CH), 111.8 (CH), 38.7 (CH_2). IR (KBr) ν_{max}: 745, 829, 903, 926, 1070, 1152, 1240, 1290, 1319, 1348 (NO_2), 1474, 1524 (NO_2), 1584 ($C(NO_2)_2$), 1603 cm^{-1}. Anal. Calcd (%) for $C_8H_5N_3O_7$: C, 37.66; H, 1.98; N, 16.47. Found (%): C, 37.71; H, 1.98; N, 16.58.

*5-Acetyl-2,2-dinitro-2,3-dihydrobenzofuran (**5b**).* 1-[4-Hydroxy-3-(2,2,2-trinitroethyl)phenyl]ethanone (**4b**) (0.3 g, 1 mmol) was dissolved in DMSO (2 mL), and the solution obtained was stored at room temperature for 5 days. The solution was poured into 15 mL of saturated aqueous sodium chloride, and the product was extracted with CH_2Cl_2. The solvent was evaporated in vacuo at room temperature, and the residue was crystallized from chloroform. Yield: 40%, 101 mg. Light-yellow solid, mp 108−110 °C (decomp.). ^{1}H NMR (DMSO-d_6) δ: 7.98−8.02 (m, 2H), 7.43 (d, 1H, J = 9.2 Hz), 4.66 (s, 2H), 2.54 (s, 3H). ^{13}C NMR (DMSO-d_6) δ: 196.9 (C═O), 159.6 (C), 134.6 (C), 131.2 (CH), 130.2 (C), 125.9 (CH), 124.2 (C), 111.0 (CH), 38.6 (CH_2), 27.2 (CH_3). IR (KBr) ν_{max}: 621, 1119, 1146, 1254, 1296, 1362, 1485, 1605 ($C(NO_2)_2$), 1670 (C═O) cm^{-1}. Anal. Calcd (%) for $C_{10}H_8N_2O_6$: C, 47.63; H, 3.20; N, 11.11. Found (%): C, 47.73; H, 3.27; N, 11.04.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all newly synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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