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Synthesis and Properties of Energetic 1,2,4-Oxadiazoles

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The synthesis and characterization of a series of 3,5-di-aryl-1,2,4-oxadiazoles are reported and the effects of nitro groups in the aromatic rings on the experimental heats of decomposition (ΔH_d) and heats of combustion (ΔH_c) are evaluated. Heats of formation (ΔH_f) and densities (ρ) were calculated and correlations between ΔH_d and ΔH_f were assessed for these compounds. Experimental determination of ρ (by gas pycnometry) on a selection of the compounds led to the calculation of detonation velocity (V_D), detonation pressure (P_D) and specific impulse (I_{SP}) parameters by the Explo 5 program. An X-ray analysis of compound (**4i**) confirmed the structure and showed a crystal density (at 120 K) close to that determined by gas pycnometry.

Introduction

Oxadiazoles are associated with a number of drugs and drug leads.[1] The hydrolytic[2] and metabolic stability of the oxadiazole ring, together with good pharmacokinetic and in vivo performance, make 1,2,4-oxadiazole an important structural unit in the pharmaceutical industry. Thus 1,2,4-oxadiazoles have been the subject of extensive research in recent years.[3–10]

Oxadiazoles have also been utilized as building blocks in the synthesis of explosives because they display rather high densities, have good oxygen balance and high heats of formation. Although a few 1,2,4-oxadiazoles have been studied as energetics,[11–13] the class remains relatively unexplored. Thus, in an effort to develop new synthetic routes to novel energetic materials, we synthesized a series of 3,5-diaryl-1,2,4-oxadiazoles, containing nitro groups in the aromatic rings and evaluated their physical and thermochemical properties.

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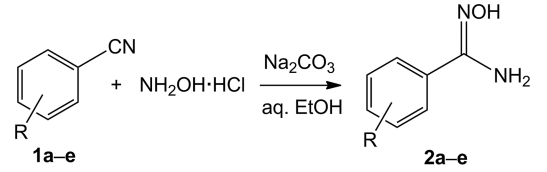
Results and Discussion

a) Synthesis

Intermediate amidoximes **2a**–**e** were readily prepared in 39–99% yields by treatment of mono or dinitro substituted arylnitriles **1a**–**e** with hydroxylamine hydrochloride in aqueous ethanol under basic conditions either at 85 °C for 2 h (for **2b**,**c**) or at ambient for 8 h (for **2a**,**d**,**e**)[14] (Scheme 1 and Table 1). Compounds **2b**–**c**,**e** were obtained directly in quantitative yields but **2a**,**d** required purification by column chromatography and were obtained in lower yields, possibly due to steric hindrance by the *ortho* nitro group (Scheme 1 and Table 1).



R = **a**, 2-NO_2; **b**, 3-NO_2; **c**, 4-NO_2; **d**, 2,4-di-NO_2; **e**, 3,5-di-NO_2

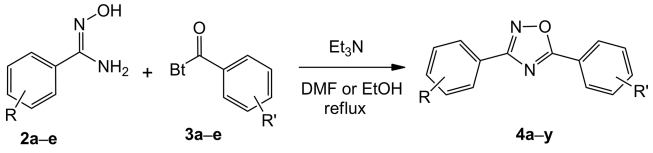
Scheme 1.

Starting *N*-aroylbenzotriazoles **3a**–**e** were prepared by a one-step reaction of benzotriazole (BtH), thionyl chloride and nitrobenzoic acids in dichloromethane at room temperature.[15,16]

Table 1. Preparation of amidoximes **2a**–**e**.

Arynitriles **1**	Amidoximes **2**	M.p. [°C]	Yield [%]
a	**a**	142–144	39
b	**b**	173–175	99
c	**c**	181–183	99
d	**d**	181–183	42
e	**e**	199–201	99

1,2,4-Oxadiazoles **4a**–**y** were prepared in 60–94% yields by modified literature methods (Scheme 2 and Table 2).[17,18] Mixtures of amidoximes **2a**–**e** and *N*-acylbenzotriazoles (*N*-acylBt) **3a**–**e** were heated under reflux either in DMF for 6–8 h in the presence of triethylamine (Method A) or under reflux in ethanol for 12–18 h in the presence of triethylamine (Method B). In Method A the reaction mixtures were cooled to room temp. and water was added; the precipitates were filtered off, washed with water and purified by column chromatography to give the corresponding 1,2,4-oxadiazoles **4a**–**j**,**l**,**n**,**p**,**r**,**t**. In Method B the reaction mixtures were cooled to room temp. and the precipitates were filtered off then washed with ethanol to give the required 1,2,4-oxadiazoles **4k**,**m**,**o**,**q**,**s**,**u**–**y**. Method B was preferred when *N*-acylbenzotriazoles **3d**–**e** were used as electrophiles. In general Method B gave purer products but lower yields possibly due to partial alcoholysis of the aroylbenzotriazole starting materials. All novel compounds were characterized by ^{1}H and ^{13}C nmr and either elemental analysis or high resolution mass spectrometry. Known compounds had properties consistent with literature data.



R, R' = **a**, 2-NO_2; **b**, 3-NO_2; **c**, 4-NO_2; **d**, 2,4-di-NO_2; **e**, 3,5-di-NO_2

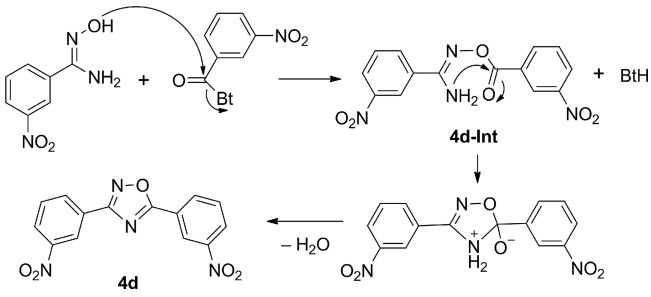
Scheme 2.

Table 2. Preparation of 1,2,4-oxadiazoles **4a**–**y**.

2, R	**3**, R′	**4**	M.p. [°C]	Yield [%]
4-NO_2	4-NO_2	**a**	246–248	90[a]
4-NO_2	3-NO_2	**b**	213-215	78[a]
3-NO_2	4-NO_2	**c**	208–210	85[a]
3-NO_2	3-NO_2	**d**	175–176	93[a]
4-NO_2	2-NO_2	**e**	184–186	87[a]
2-NO_2	4-NO_2	**f**	173–175	88[a]
3-NO_2	2-NO_2	**g**	155–157	91[a]
2-NO_2	3-NO_2	**h**	161–162	90[a]
2-NO_2	2-NO_2	**i**	162–164	85[a]
3,5-di-NO_2	4-NO_2	**j**	248–249	94[a]
4-NO_2	3,5-di-NO_2	**k**	234–236	63[b]
3,5-di-NO_2	3-NO_2	**l**	222–224	86[a]
3-NO_2	3,5-di-NO_2	**m**	221–223	60[b]
3,5-di-NO_2	2-NO_2	**n**	200–202	84[a]
2-NO_2	3,5-di-NO_2	**o**	205–207	62[b]
2,4-di-NO_2	4-NO_2	**p**	171–173	82[a]
4-NO_2	2,4-di-NO_2	**q**	181–183	64[b]
2,4-di-NO_2	3-NO_2	**r**	190–192	81[a]
3-NO_2	2,4-di-NO_2	**s**	198–200	65[b]
2,4-di-NO_2	2-NO_2	**t**	180–182	80[a]
2-NO_2	2,4-di-NO_2	**u**	166–168	68[b]
3,5-di-NO_2	3,5-di-NO_2	**v**	265–267	65[b]
3,5-di-NO_2	2,4-di-NO_2	**w**	187–188	60[b]
2,4-di-NO_2	3,5-di-NO_2	**x**	217–219	65[b]
2,4-di-NO_2	2,4-di-NO_2	**y**	182–184	70[b]

[a] Method A. [b] Method B.

During the preparation of **4d** by Method B intermediate 3-nitro-*N*′-[(3-nitrobenzoyl)oxy] benzimidamide **4d-Int** precipitated from ethanol when the temperature reached 50–55 °C, which lends support to the proposed reaction mechanism shown in Scheme 3.



Scheme 3. Proposed mechanism to **4d**.

b) Properties

Heats of formation (ΔH_f) of oxadiazoles **4a**–**y** as calculated by PM6, are shown in Table 3 together with calculated values of density (ρ) and experimentally determined heats of decomposition (ΔH_d) by DSC and heats of combustion (ΔH_c) by bomb calorimetry. Incidentally, the values of ρ calculated by AM1, PM3 or PM6 were essentially identical but the values of ΔH_f by the three methods, although showing the same trends, differed significantly in absolute values especially in comparison of AM1 with PM3 or PM6. We chose to report the values of ΔH_f from PM6 as the most reliable theoretical method available to us. As found with the 1,3,4-oxadiazole series,[16] there was no correlation of ρ with either ΔH_d or ΔH_c. In contrast to the 1,3,4 series however, there was also no correlation of ΔH_f with ΔH_d. The average value of ΔH_f for the 1,2,4-oxadiazole series is ca. 56 kJ mol^{-1} higher than the average value for the comparable 1,3,4-oxadiazole series, in line with the calculated heats of formation of the two ring systems.[19]

What is abundantly clear is that the overall number of nitro groups and the number of *ortho*-nitro groups in the molecules together determine the calculated values of ΔH_f. Thus, inspection of Table 3 reveals that the average increase in ΔH_f per nitro group is 6 kJ mol^{-1}. For the disubstituted compounds (**4a**–**i**), introduction of an *o*-nitro group increases the average ΔH_f by 18 kJ mol^{-1}; in trisubstituted compounds (**4j**–**4u**) the increase per *o*-nitro group is 21 kJ mol^{-1} and for tetra-substituted compounds (**4v**–**4y**) the analogous average increase is also 21 kJ mol^{-1}.

Using these data one can calculate that 3-(2,4,6-trinitrophenyl)-5-(2,4,6-trinitrophenyl)-1,2,4-oxadiazole should have ΔH_f = 410 compared to a value of 418 kJ mol^{-1} as

Table 3. Calculated values of heats of formation ΔH_f, and densities ρ, together with experimental values of heats of decomposition ΔH_d and heats of combustion ΔH_c for 1,2,4-oxadiazoles **4a**–**y**.

	NO_2 Pattern	ΔH_f(calcd.)[a] [kJ mol^{-1}]	ΔH_d(exp.) [kJ mol^{-1}]	ΔH_c(exp.) [kJ mol^{-1}]	ρ(calcd.) [g/cm^3]
4a	4,4	306	–18.8	–6715	1.225
4b	4,3	304	–27.8	–7000	1.223
4c	3,4	304	–14.4	–7920	1.218
4d	3,3	304	–15.9	–6094	1.213
4e	4,2	325	–16.7	–7200	1.218
4f	2,4	323	–18.4	–7310	1.220
4g	3,2	325	–24.3	–5906	1.220
4h	2,3	321	–13.3	–8465	1.220
4i	2,2	340	–6.3	–9330	1.223
4j	35,4	307	–5.5	–5560	1.296
4k	4,35	311	–4.0	–6365	1.302
4l	35,3	305	–4.5	–7740	1.291
4m	3,35	310	–8.6	–6250	1.302
4n	35,2	326	–5.5	–9510	1.297
4o	2,35	327	–10.2	–7689	1.307
4p	24,4	324	–8.0	–7112	1.303
4q	4,24	331	–36.9	–11303	1.319
4r	24,3	321	–10.6	–9591	1.297
4s	3,24	330	–7.4	–6314	1.295
4t	24,2	339	–11.4	–6370	1.301
4u	2,24	359	–16.8	–9122	1.305
4v	35,35	314	–25.1	–7250	1.290
4w	35,24	333	–19.0	–8280	1.383
4x	24,35	330	–23.6	–7300	1.379
4y	24,24	356	–30.5	–4046	1.379
–	246,246	418	–	–	1.500

[a] Average of two calculations.

calculated by PM6. The data also show that the *calculated* densities (Table 3) increase linearly from an average of 1.22 for compounds containing two nitro groups, through 1.30 for those with three nitro groups to 1.38 for those with four nitro groups with no dependence on the substitution pattern.

Hence the theoretical calculations produce a consistent picture but require verification by experiment. To this end the densities of a selection of nine compounds from **4a**–**y** were determined by gas pycnometry. The results are shown in Table 4 along with the corresponding values of detonation velocity (V_D), detonation pressure (P_D) and specific impulse (I_{SP}) as calculated by the Explo 5 program.

Clearly the experimental densities are not identical to the calculated values but the two sets of data are linearly related (Figure 1).

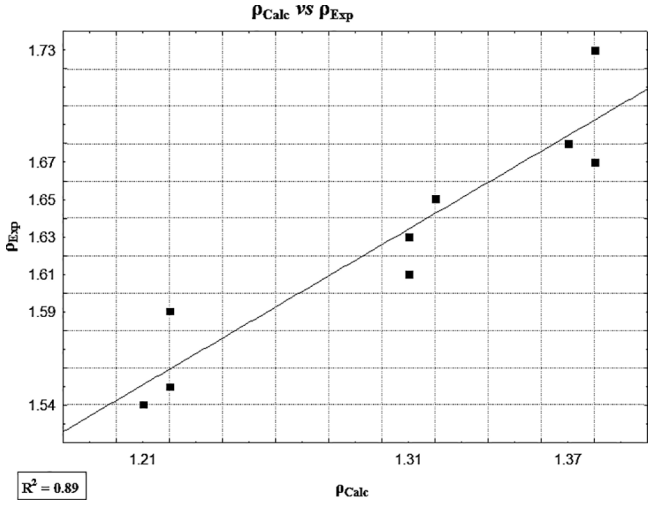


Figure 1. Plot of $\rho_{exp.}$ vs. $\rho_{calcd.}$ for 1,2,4-oxadiazoles of Table 4.

Consequently, the experimental densities are linearly related to the number of nitro groups in the molecules. An extrapolation of Figure 1 to a 1,2,4-oxadiazole containing six nitro groups ($\rho_{calcd.}$ = 1.49) allows an estimate of 1.82 for the experimental density of 3,5-bis(2,4,6-trinitro)-1,2,4-oxadiazole together with estimated values of V_D, P_D and I_{SP} (Table 4). These values again compare favorably with those for cyclotrimethylenetrinitramine (RDX) and suggest that a hexa-nitro substituted 1,2,4-oxadiazole may be useful as a potential explosive.

The structure of 1,2,4-oxadiazole **4i** was confirmed by X-ray crystallography (Figure 2) which shows that the two *o*-nitro substituents do not lie in the plane of the aromatic rings. Thus the nitro groups are not conjugated with their aromatic systems and this may account for the higher energy of formation for compounds containing *o*-nitro sustit-

Table 4. Heats of formation, densities, detonation velocities, detonation pressures, specific impulses and oxygen balance.

Compound	ΔH_f(calcd.) [kJ mol^{-1}]	ρ Calcd.	Exp.	V_D(calcd.) [m/s]	P_D(calcd.) [GPa]	I_{sp}(calcd.) [s]	Ω(calcd.) [OB]
4d, 3,3	304	1.21	1.54	6090	12.5	191	–138
4c, 3,4	304	1.22	1.55	6132	12.8	191	–138
4i, 2,2	340	1.22	1.59	6341	13.9	193	–138
4o, 2,35	327	1.31	1.63	6811	17.2	191	–109
4t, 24,2	339	1.31	1.61	6741	16.7	206	–109
4y, 24,24	356	1.37	1.68	7264	21.1	217	–90
4x, 24,35	330	1.38	1.73	7430	22.4	216	–90
4w, 35,24	333	1.38	1.67	7209	20.7	216	–90
4v, 35,35	314	1.32	1.65	7121	19.9	230	–90
246,246	418	1.50	1.82[a]	8208[b]	29.2[b]	236[b]	–50
RDX	80	–	1.82	8748	34.9	258	–3
HMX	105	–	1.91	9320	39.5	266	0
CL-20	397.5	–	2.03	9406	44.6	272	11

[a] Estimated from a plot of $\rho_{calcd.}$ vs. $\rho_{exp.}$ [b] Calculated by Explo 5 from ΔH_f(calcd.) = 418 and ρ(exp.) = 1.82.

uents. Moreover the N-O atoms of the oxadiazole are disordered over the two possible orientations. That is, half the time the oxygen atom is on the left (top diagram) and half on the right (bottom diagram). The crystal density of **4i** at 120K was 1.626, in comparison with an *estimated* experimental value by gas pycnometry of 1.59.

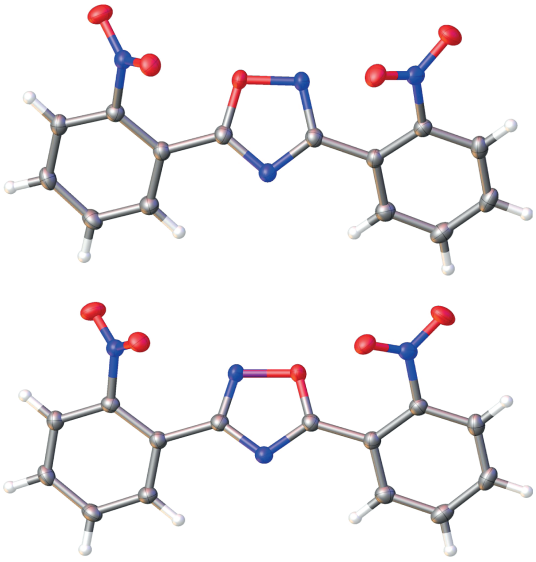


Figure 2. X-ray crystal structure of **4i**.

Conclusions

A facile synthesis of 1,2,4-oxadiazoles **4a**–**y** has been achieved and structures of the resultant compounds determined by $^{1}H/^{13}C$ nmr, elemental analysis and/or HRMS, and in one case (**4i**) by X-ray cryatallography. Heats of formation and densities of all the compounds were calculated and heats of decomposition and combustion were determined experimentally. There was no obvious correlation between ΔH_f and ΔH_d, but the calculated densities, ρ, clearly increased with the number of nitro groups in the aromatic rings. This was confirmed by experimental (gas pycnometry) determination of the densities of selected compounds which showed a linear relationship with the calculated values of ρ. Extrapolation of the data suggests that 3,5-bis(2,4,6-trinitrophenyl)-1,2,4-oxadiazole would have density and explosion parameters consistent with RDX and therefore might afford a useful explosive.

Experimental Section

Caution: *Although we encountered no difficulties with the preparation or isolation of these compounds, synthetic work was restricted to the millimolar scale and care was taken to avoid impact, friction or overheating. Qualitative impact (hammer) and friction (sandpaper) tests on 4a–y were negative, i.e. gave no indication of instability.*

General Methods and Materials: Melting points were determined on a capillary tube melting point apparatus equipped with a digital thermometer and are uncorrected. NMR spectra were recorded in $CDCl_3$ or [D_6]DMSO with TMS as the internal standard for ^{1}H (300 MHz) or in $CDCl_3$ or [D_6]DMSO with the residual solvent peak as the internal standard for ^{13}C (75 MHz). Individual peaks are reported as multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constants in Hertz (Hz). Elemental analyses were performed on a Carlo Erba EA 1108 elemental analyzer, Dept. of Chem., University of Florida. All reagents were purchased from commercial sources and used without treatment unless otherwise indicated. Column chromatography was performed with S733–1 silica gel (200–425 mesh). Combustion analysis was performed using a Parr Oxygen Bomb Calorimeter, under an atmosphere of excess oxygen at approximately 25 atm. All combustion residues were titrated as nitric acid to account for the formation of NOx as a combustion by-product. Determination of heat of decomposition was conducted using a DuPont Instruments DSC 2910 differential scanning calorimeter. Samples were heated from 100 °C–500 °C in hermetic aluminum pans, with helium as the purge gas. All sample pan lids were perforated to allow venting of gaseous products.

Densities were determined at room temperature by employing a Micromeritics AccuPyc 1330 gas pycnometer. The mass of the samples were determined on a METTLER TOLEDO AB104-S balance, the volumes of the samples were measured by using the pycnometer – the average of 3 measured volumes was used to calculate the density. Sample density was calculated from the ratio of *mass* (m) to *volume* (*V*); d [g/cm^3] = m [g]/V [cm^3].

The detonation velocity (V_D), detonation pressure(P_D) and specific impulse (Isp) were calculated based on the experimental density and calculated heat of formation values using Explo5 v.6.01 OZN Research, Czechoslovakia.

Oxygen balance (OB) is a conventional empirical descriptor used in hazard prediction of energetic materials. It is calculated by the following equation as defined by Shanley and Melhem:[20]

$$OB = \frac{[-1600\left(2C + \frac{H}{2} - O\right)]}{Mw}$$

Calculation of Heat of Formation and Densities: The compounds were drawn in ChemDraw followed by 2D to 3D conversion using MM2[21] minimization in Chem3D.[22] The 3D geometries were parameterized using PM6[23] for further semi-empirical calculation. Geometry optimization followed by frequency calculation was performed using AMPAC software.[24] The geometries were optimized to their energy minimizing Trust algorithm which reduces the number of cycles and refines the precision of the calculation at each step. The optimized geometries were loaded to Codessa III[25] software for the calculation of dipole moments, van der Waal's volume and densities.

X-ray Crystallography: The X-ray single crystal diffraction data for **4i** were collected at 120 K on an Agilent SuperNova instrument with focussed microsource Cu-K_α radiation (λ = 1.5418 Å) and ATLAS CCD area detector. The structure was solved by direct methods with SHELXS[26] and refined on F^2 using all data by full-matrix least square procedures with SHELXL-97.[26] Multiscan absorption corrections were done using SCALE3 ABSPACK. The non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier atoms. The compound crystallizes with the O1 and N2 atoms disordered. Accordingly these atoms were each modelled with half oxygen and half nitrogen occupancies. Crystal data: $C_{14}H_8N_4O_5$, FW = 312.24, monoclinic, space group $P2_1/n$, a = 9.3592(2), b = 12.3392(3), c = 11.0632(3) Å, β =

93.407(2)°, V = 1275.38(5) Å^3, F(000) = 640, Z = 4, T = –153 °C, μ(Mo-K_α) = 1.090 mm^{-1}, $D_{calcd.}$ = 1.626 g cm^{-3}, $2\theta_{max}$ 135°, GOF = 1.06, $wR(F_2)$ = 0.0942 (all 2302 data), R = 0.0348 (2097 data with I > 2σI). CCDC-1426178 (for **4i**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Method for the Preparation of Amidoximes 2a,d: Hydroxylamine hydrochloride (40 mmol), and sodium carbonate (3.22 g, 30 mmol) were added to a stirred solution of mono-, dinitro-benzonitriles **1a**,**d** (10 mmol) in ethanol (30 mL) and water (12 mL) and the mixtures were stirred at room temp. for 8 h. The solvents for **2a**,**d** were evaporated to dryness and the residues purified by silica gel chromatography using gradient mixtures of ethyl acetate and hexanes as eluent afforded **2a**,**d**.

General Method for the Preparation of Amidoximes 2b,c,e: Hydroxylamine hydrochloride (39.3 mmol), and sodium carbonate (3.16 g, 29.5 mmol) were added to a stirred solution of mono-, dinitro-benzonitriles **1b**,**c**,**e** (9.82 mmol) in ethanol (30 mL) and water (12 mL). The mixtures were either heated under reflux either at 85 °C under nitrogen for 2 h (**2b**,**c**) or stirred at room temp. for 8 h (**2e**). The volatiles for **2b**,**c**,**e** were evaporated and brine (60 mL) was added to the residues. The mixtures were extracted with ethyl acetate (3 × 60 mL), the extracts dried with anhydrous $MgSO_4$ and the solvent removed to afford amidoximes **2b**,**c**,**e**.

***N′*-Hydroxy-2-nitrobenzimidamide (2a):** Prepared from 2-nitrobenzonitrile (**1a**), yield 39%, yellow microcrystals, m.p. 142–144 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.70 (s, 1 H), 7.85 (d, J = 7.8 Hz, 1 H), 7.74–7.58 (m, 3 H), 6.02 (s, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 149.0, 148.8, 132.3, 130.3, 129.9, 128.0, 123.5 ppm. $C_7H_7N_3O_3$ (181.15): calcd. C 46.41, H 3.89, N 23.20; found C 46.75, H 3.62, N 23.12.

***N′*-Hydroxy-3-nitrobenzamidimide (2b):** Prepared from 3-nitrobenzonitrile (**1b**), yield 99%, yellow solids, m.p. 173–175 °C [ref.[27] m.p. 180–182 °C]. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.98 (s, 1 H), 8.51 (s, 1 H), 8.22 (d, J = 7.8 Hz, 1 H), 8.12 (d, J = 7.8 Hz, 1 H), 7.68 (t, J = 8.1 Hz, 1 H), 6.11 (s, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 149.1, 147.7, 134.9, 131.6, 129.8, 123.5, 119.9 ppm.

***N′*-Hydroxy-4-nitrobenzamidimide (2c):** Prepared from 4-nitrobenzonitrile (**1c**), yield 99%, yellow solids, m.p. 181–183 °C [ref.[28] m.p. 180.0 °C]. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.1 (s, 1 H), 8.23 (d, J = 8.7 Hz, 2 H), 7.94 (d, J = 8.7 Hz, 2 H), 6.07 (s, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 149.4, 147.4, 139.5, 126.4, 123.4 ppm.

***N′*-Hydroxy-2,4-dinitrobenzimidamide (2d):** Prepared from 2,4-dinitrobenzonitrile (**1d**), yield 42%, yellow microcrystals, m.p. 181–183 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.12 (s, 1 H), 8.66 (d, J = 1.5 Hz, 1 H), 8.51 (dd, J = 8.6, 1.7 Hz, 1 H), 7.94 (d, J = 8.7 Hz, 1 H), 6.24 (s, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 148.7, 147.6, 147.3, 133.2, 131.6, 126.6, 119.2 ppm. HRMS (DIP/CI-MS) m/z [M + H]$^+$ calcd. for $C_7H_7N_4O_5$ 227.0416; found 227.0411.

***N′*-Hydroxy-3,5-dinitrobenzimidamide (2e):** Prepared from 3,5-dinitrobenzonitrile (**1e**), yield 99%, yellow solids, m.p. 199–201 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.31 (s, 1 H), 8.88 (d, J = 2.1 Hz, 2 H), 8.80 (t, J = 2.1 Hz, 1 H), 6.38 (s, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 148.1, 147.7, 136.2, 125.1, 118.3 ppm. $C_7H_6N_4O_5$ (226.15): calcd. C 37.18, H 2.67, N 24.77; found C 37.04, H 2.38, N 24.76.

General Method for the Preparation of 1,2,4-Oxadiazoles 4a–y and Intermediate 4d-Int: Mixtures of amidoxime **2a**–**e** (2.5 mmol) and *N*-acylbenzotriazole **3a**–**e** (2.5 mmol) were heated under reflux either in DMF (3.5 mL) for 6–8 h in the presence of triethylamine (5.0 mmol) (for **4a**–**j**,**l**,**n**,**p**,**r**,**t**, Method A) or under reflux in ethanol (25 mL) for 12–18 h in the presence of triethylamine (5.0 mmol) (for **4k**,**m**,**o**,**q**,**s**,**u**–**y**, Method B). Preparation of **4d-Int** required heating in ethanol at 55 °C for 0.5 h. Work-up for Method A: The reaction mixtures were cooled to room temp. and water was added; the precipitates were filtered off, washed with water and purified by column chromatography over silica gel using a gradient mixture of hexanes and ethyl acetate as eluent to give 1,2,4-oxadiazoles **4a**–**j**,**l**,**n**,**p**,**r**,**t**. Work-up for Method B: The reaction mixtures were cooled to room temp. and the precipitates were filtered off, washed with ethanol to give 1,2,4-oxadiazoles **4k**,**m**,**o**,**q**,**s**,**u**–**y** and **4d-Int**.

3,5-Bis(4-nitrophenyl)-1,2,4-oxadiazole (4a): Method A, yield 90%, orange flakes, m.p. 246–248 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.48 (s, 6 H), 8.40 (s, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]-DMSO): δ = 174.5, 167.3, 150.1, 149.3, 131.6, 129.6, 128.6, 124.7, 124.6 ppm. $C_{14}H_8N_4O_5$ (312.24): calcd. C 53.85, H 2.58, N 17.94; found C 53.84, H 2.37, N 18.05.

5-(3-Nitrophenyl)-3-(4-nitrophenyl)-1,2,4-oxadiazole (4b): Method A, yield 78%, colorless solids, m.p. 213-215 °C [ref.[29] m.p. 208 °C]. ^{1}H NMR (499 MHz at 100 °C, [D$_6$]DMSO): δ = 8.88 (s, 1 H), 8.60 (d, J = 7.8 Hz, 1 H), 8.55 (d, J = 8.3 Hz, 1 H), 8.43 (d, J = 9.0 Hz, 2 H), 8.38 (d, J = 9.0 Hz, 2 H), 7.99 (t, J = 8.2 Hz, 1 H) ppm. ^{13}C NMR (126 MHz at 100 °C, [D$_6$]DMSO): δ = 174.9, 167.9, 150.2, 149.1, 134.3, 132.2, 131.9, 129.2, 128.1, 125.3, 124.8, 123.1 ppm. $C_{14}H_8N_4O_5$ (312.24): calcd. C 53.85, H 2.58, N 17.94; found C 54.07, H 2.28, N 17.89.

3-(3-Nitrophenyl)-5-(4-nitrophenyl)-1,2,4-oxadiazole (4c): Method A, yield 85%, colorless solids, m.p. 208–210 °C [ref.[29] m.p. 207 °C]. ^{1}H NMR (499 MHz at 100 °C, [D$_6$]DMSO): δ = 8.81 (s, 1 H), 8.51 (d, J = 7.7 Hz, 1 H), 8.42–8.44 (m, 5 H), 7.93 (t, J = 8.1 Hz, 1 H) ppm. ^{13}C NMR (126 MHz at 100 °C, [D$_6$]DMSO): δ = 175.0, 167.9, 151.0, 149.1, 133.6, 131.7, 130.1, 129.0, 128.1, 126.6, 125.0, 122.3 ppm. $C_{14}H_8N_4O_5$ (312.24): calcd. C 53.85, H 2.58, N 17.94; found C 54.05, H 2.28, N 17.92.

3-Nitro-*N′*-[(3-nitrobenzoyl)oxy]benzimidamide (4d-Int): Method B, yield 63%, colorless solids, m.p. 206–208 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.85 (s, 1 H), 8.66 (dd, J = 7.7, 1.1 Hz, 1 H), 8.61 (s, 1 H), 8.54–8.49 (m, 1 H), 8.43–8.38 (m, 1 H), 8.25 (d, J = 7.5, 1.1 Hz, 1 H), 7.90–7.78 (m, 2 H), 7.47 (s, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 161.9, 155.7, 147.9, 147.7, 135.7, 133.3, 133.0, 130.7, 130.4, 130.2, 127.6, 125.4, 124.1, 121.6 ppm. HRMS (DART-TOF) m/z (M + NH$_4$)$^+$ calcd. for $C_{14}H_{14}N_5O_6$: 348.0939; found 348.0930.

3,5-Bis(3-nitrophenyl)-1,2,4-oxadiazole (4d): Method A, yield 93%, Colorless microcrystals, m.p. 175–176 °C [ref.[30] m.p. 170 °C]. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.87 (t, J = 3.0 Hz, 1 H), 8.80 (t, J = 3.0 Hz, 1 H), 8.64 (d, J = 7.8 Hz, 1 H), 8.60–8.52 (m, 2 H), 8.49 (dd, J = 9.0, 3.0 Hz, 1 H), 7.98 (t, J = 7.8 Hz, 1 H), 7.93 (t, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 174.4, 167.1, 148.3, 134.1, 133.3, 131.6, 131.4, 127.9, 127.3, 126.5, 124.5, 122.7, 121.7 ppm. HRMS (DART) m/z: [M + NH$_4$]$^+$ calcd. for $C_{14}H_{12}N_5O_5$ 330.0825; found 330.0833.

5-(2-Nitrophenyl)-3-(4-nitrophenyl)-1,2,4-oxadiazole (4e): Method A, yield 87%, colorless solids, m.p. 184–186 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.45 (d, J = 9.0 Hz, 2 H), 8.36–8.26 (m, 3 H), 8.24–8.18 (m, 1 H), 8.06–7.99 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 173.2, 166.9, 149.4, 148.1, 134.5, 133.9,

131.7, 131.2, 128.6, 125.0, 124.6 117.1 ppm. $C_{14}H_8N_4O_5$ (312.24): calcd. C 53.85, H 2.58, N 17.94; found C 53.73, H 2.37, N 18.23.

3-(2-Nitrophenyl)-5-(4-nitrophenyl)-1,2,4-oxadiazole (4f): Method A, yield 88%, colorless prisms, m.p. 173–175 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.48 (d, J = 9.0 Hz, 2 H), 8.41 (d, J = 8.4 Hz, 2 H), 8.22–8.18 (m, 1 H), 8.08–8.04 (m, 1 H), 8.00–7.89 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 173.9, 166.4, 150.2, 148.5, 133.6, 133.1, 131.3, 129.6 (2 C), 128.1, 124.7 (3 C), 119.6 ppm. $C_{14}H_8N_4O_5$ (312.24): calcd. C 53.85, H 2.58, N 17.94; found C 53.94, H 2.17, N 17.68.

5-(2-Nitrophenyl)-3-(3-nitrophenyl)-1,2,4-oxadiazole (4g): Method A, yield 91%, colorless solids, m.p. 155–157 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.72 (s, 1 H), 8.47 (d, J = 8.7 Hz, 2 H), 8.32–8.24 (m, 1 H), 8.24–8.18 (m, 1 H), 8.06–7.97 (m, 2 H), 7.92 (t, J = 8.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 173.2, 166.8, 148.2, 148.1, 134.5, 134.0, 133.1, 131.7, 131.4, 127.0, 126.5, 125.0, 121.6, 117.1 ppm. $C_{14}H_8N_4O_5$ (312.24): calcd. C 53.85, H 2.58, N 17.94; found C 53.87, H 2.24, N 17.79.

3-(2-Nitrophenyl)-5-(3-nitrophenyl)-1,2,4-oxadiazole (4h): Method A, yield 90%, colorless crystals, m.p. 161–162 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.79 (t, J = 2.0 Hz, 1 H), 8.60–8.57 (m, 1 H), 8.56–8.54 (m, 1 H), 8.21–8.17 (m, 1 H), 8.08–8.04 (m, 1 H), 8.00–7.89 (m, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 173.8, 166.3, 148.5, 148.2, 133.9, 133.6, 133.0, 131.6, 131.3, 127.9, 124.7, 124.2, 122.5, 119.5 ppm. $C_{14}H_8N_4O_5$ (312.24): calcd. C 53.85, H 2.58, N 17.94; found C 53.93, H 2.21, N 17.78.

3,5-Bis(2-nitrophenyl)-1,2,4-oxadiazole (4i): Method A, yield 85%, colorless solids, m.p. 162–164 °C. ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 8.30–8.23 (m, 1 H), 8.20–8.11 (m, 2 H), 8.05–7.97 (m, 3 H), 7.96–7.88 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 172.6, 166.1, 148.5, 148.1, 134.5, 133.9, 133.6, 133.1, 131.6, 131.3, 125.0, 124.8, 119.3, 116.9 ppm. $C_{14}H_8N_4O_5$ (312.24): calcd. C 53.85, H 2.58, N 17.94; found C 54.01, H 2.17, N 18.02.

3-(3,5-Dinitrophenyl)-5-(4-nitrophenyl)-1,2,4-oxadiazole (4j): Method A, yield 94%, colorless solids, m.p. 248–249 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.08 (d, J = 2.1 Hz, 2 H), 9.03 (t, J = 2.1 Hz, 1 H), 8.52 (d, J = 8.4 Hz, 2 H), 8.47 (d, J = 9.0 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 174.9, 166.0, 150.2, 148.8, 129.8, 128.5, 128.1, 126.9, 124.7, 121.2 ppm. $C_{14}H_7N_5O_7$ (357.24): calcd. C 47.07, H 1.98, N 19.60; found C 47.11, H 1.66, N 19.28.

5-(3,5-Dinitrophenyl)-3-(4-nitrophenyl)-1,2,4-oxadiazole (4k): Method B, yield 63%, off-white solids, m.p. 234–236 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.17 (d, J = 1.8 Hz, 2 H), 9.10 (t, J = 2.1 Hz, 1 H), 8.45 (d, J = 8.7 Hz, 2 H), 8.41 (d, J = 9.3 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 173.0, 167.3, 149.4, 148.7, 131.2, 128.7, 127.8, 125.7, 124.6, 122.4 ppm. HRMS (DIP/CI-MS) m/z: [M + H]$^+$ calcd. for $C_{14}H_8N_5O_7$ 358.0424; found 358.0424.

3-(3,5-Dinitrophenyl)-5-(3-nitrophenyl)-1,2,4-oxadiazole (4l): Method A, yield 86%, colorless solids, m.p. 222–224 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.10 (s, 2 H), 9.04 (d, J = 0.6 Hz, 1 H), 8.90 (s, 1 H), 8.68 (d, J = 8.4 Hz, 1 H), 8.59 (d, J = 7.8 Hz, 1 H), 7.99 (t, J = 8.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 174.8, 166.0, 148.8, 148.2, 134.2, 131.6, 128.5, 128.1, 126.9, 124.2, 122.7, 121.2 ppm. $C_{14}H_7N_5O_7$ (357.24): calcd. C 47.07, H 1.98, N 19.60; found C 47.38, H 1.69, N 19.35.

5-(3,5-Dinitrophenyl)-3-(3-nitrophenyl)-1,2,4-oxadiazole (4m): Method B, yield 60%, off-white solids, m.p. 221–223 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.19 (d, J = 2.1 Hz, 2 H), 9.10 (t, J = 2.3 Hz, 1 H), 8.83 (t, J = 1.8 Hz, 1 H), 8.61–8.56 (m, 1 H), 8.53–8.48 (m, 1 H), 7.94 (t, J = 8.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 173.0, 167.2, 148.7, 148.3, 133.3, 131.4, 127.9, 127.0, 126.6, 125.7, 122.5, 121.7 ppm. HRMS (DART-TOF) m/z: [M + NH$_4$]$^+$ calcd. for $C_{14}H_{11}N_6O_7$ 375.0684; found 375.0676.

3-(3,5-Dinitrophenyl)-5-(2-nitrophenyl)-1,2,4-oxadiazole (4n): Method A, yield 84%, off-white solids, m.p. 200–202 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.06–9.02 (m, 3 H), 8.34–8.24 (m, 2 H), 8.08–8.01 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 173.7, 165.8, 148.8, 148.0, 134.7, 134.1, 131.9, 128.2, 127.0, 125.1, 121.3, 116.9 ppm. $C_{14}H_7N_5O_7$ (357.24): calcd. C 47.07, H 1.98, N 19.60; found C 47.46, H 1.70, N 19.20.

5-(3,5-Dinitrophenyl)-3-(2-nitrophenyl)-1,2,4-oxadiazole (4o): Method B, yield 62%, colorless solids, m.p. 205–207 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.13–9.08 (m, 3 H), 8.24–8.20 (m, 1 H), 8.12–8.08 (m, 1 H), 8.01–7.90 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 172.5, 166.5, 148.7, 148.5, 133.7, 133.2, 131.4, 127.9, 125.4, 124.8, 122.5, 119.2 ppm. $C_{14}H_7N_5O_7$ (357.24): calcd. C 47.07, H 1.98, N 19.60; found C 47.20, H 1.60, N 19.44.

3-(2,4-Dinitrophenyl)-5-(4-nitrophenyl)-1,2,4-oxadiazole (4p): Method A, yield 82%, yellow solids, m.p. 171–173 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.99 (d, J = 2.4 Hz, 1 H), 8.72 (dd, J = 8.7, 2.1 Hz, 1 H), 8.48 (d, J = 8.7 Hz, 2 H), 8.42 (d, J = 9.0 Hz, 2 H), 8.38 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]-DMSO): δ = 174.4, 165.0, 150.2, 149.4, 148.5, 132.9, 129.7, 127.9, 127.8, 124.7, 124.3, 120.2 ppm. $C_{14}H_7N_5O_7$ (357.24): calcd. C 47.07, H 1.98, N 19.60; found C 47.41, H 1.66, N 19.31.

5-(2,4-Dinitrophenyl)-3-(4-nitrophenyl)-1,2,4-oxadiazole (4q): Method B, yield 64%, colorless solids, m.p. 181–183 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.04 (d, J = 2.1 Hz, 1 H), 8.78 (dd, J = 8.7, 2.1 Hz, 1 H), 8.52 (d, J = 8.7 Hz, 1 H), 8.49–8.44 (m, 2 H), 8.36–8.30 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 171.6, 167.2, 150.1, 149.5, 148.2, 133.5, 131.0, 128.6, 128.0, 124.7, 121.7, 120.3 ppm. HRMS (DART-TOF) m/z: (M + NH$_4$)$^+$ calcd. for $C_{14}H_{11}N_6O_7$ 375.0684; found 375.0685.

3-(2,4-Dinitrophenyl)-5-(3-nitrophenyl)-1,2,4-oxadiazole (4r): Method A, yield 81%, yellow solids, m.p. 190–192 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.99 (dd, J = 2.4, 0.9 Hz, 1 H), 8.82–8.80 (m, 1 H), 8.74–8.70 (m, 1 H), 8.62–8.56 (m, 2 H), 8.39 (d, J = 8.4 Hz, 1 H), 7.99 (t, J = 8.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 174.3, 164.9, 149.4, 148.5, 148.2, 134.1, 132.9, 131.6, 128.1, 127.8, 124.3, 124.0, 122.6, 120.2 ppm. $C_{14}H_7N_5O_7$ (357.24): calcd. C 47.07, H 1.98, N 19.60; found C 47.37, H 1.66, N 19.35.

5-(2,4-Dinitrophenyl)-3-(3-nitrophenyl)-1,2,4-oxadiazole (4s): Method B, yield 65%, colorless solids, m.p. 198–200 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.04 (d, J = 2.1 Hz, 1 H), 8.79–8.72 (m, 2 H), 8.55–8.47 (m, 3 H), 7.94 (t, J = 8.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 171.5, 167.0, 150.1, 148.3, 135.0–128.0 (m), 126.7, 121.7, 121.1–119.1 (m) ppm. $C_{14}H_7N_5O_7$ (357.24): calcd. C 47.07, H 1.98, N 19.60; found C 47.30, H 1.59, N 19.85.

3-(2,4-Dinitrophenyl)-5-(2-nitrophenyl)-1,2,4-oxadiazole (4t): Method A, yield 80%, colorless microcrystals, m.p. 180–182 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.97 (d, J = 2.4 Hz, 1 H), 8.72 (ddd, J = 8.4, 2.3, 0.8 Hz, 1 H), 8.34 (d, J = 8.4 Hz, 1 H), 8.31–8.25 (m, 1 H), 8.20–8.13 (m, 1 H), 8.06–7.99 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 173.2, 164.8, 149.4, 148.5, 148.0, 134.7, 134.1, 132.9, 131.8, 127.9, 125.1, 124.1, 120.3, 116.7 ppm. HRMS (DART-TOF) m/z: [M + NH$_4$]$^+$ calcd. for $C_{14}H_{11}N_6O_7$ 375.0684; found 375.0667.

5-(2,4-Dinitrophenyl)-3-(2-nitrophenyl)-1,2,4-oxadiazole (4u): Method B, yield 68%, colorless prismss, m.p. 166–168 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.02 (d, J = 2.1 Hz, 1 H), 8.75 (dd, J = 8.6, 2.3 Hz, 1 H), 8.46 (dd, J = 8.4, 0.3 Hz, 1 H), 8.23–8.17 (m, 1 H), 8.05–8.01 (m, 1 H), 8.00–7.90 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 171.0, 166.3, 150.1, 148.4, 148.3, 133.7, 133.4, 133.3, 131.4, 128.1, 124.9, 121.5, 120.4, 119.0 ppm. $C_{14}H_7N_5O_7$ (357.24): calcd. C 47.07, H 1.98, N 19.60; found C 47.26, H 1.59, N 19.38.

3,5-Bis(3,5-dinitrophenyl)-1,2,4-oxadiazole (4v): Method B, yield 65%, lilac solids, m.p. 265–267 °C. ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 9.24 (d, J = 1.8 Hz, 2 H), 9.15 (d, J = 1.8 Hz, 2 H), 9.12 (t, J = 2.1 Hz, 1 H), 9.05 (t, J = 2.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 173.5, 166.2, 148.8, 148.8, 128.3, 128.0, 127.0, 125.6, 122.7, 121.4 ppm. HRMS (DIP/CI-MS) m/z: [M + H]$^+$ calcd. for $C_{14}H_7N_6O_9$ 403.0275; found 403.0274.

5-(2,4-Dinitrophenyl)-3-(3,5-dinitrophenyl)-1,2,4-oxadiazole (4w): Method B, yield 60%, colorless solids, m.p. 187–188 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.07–9.05 (m, 4 H), 8.79 (d, J = 8.1 Hz, 1 H), 8.57 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 172.1, 166.0, 150.2, 148.9, 148.2, 133.7, 128.4–127.6 (m), 127.4–126.4 (m), 121.8–121.2 (m), 120.4 ppm. HRMS (DART-TOF) m/z [M + NH$_4$]$^+$ calcd. for $C_{14}H_{10}N_7O_9$420.0535; found 420.0536.

3-(2,4-Dinitrophenyl)-5-(3,5-dinitrophenyl)-1,2,4-oxadiazole (4x): Method B, yield 65%, colorless solids, m.p. 217–219 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.14–9.09 (m, 3 H), 9.00 (d, J = 2.1 Hz, 1 H), 8.73 (dd, J = 8.6, 2.3 Hz, 1 H), 8.43 (d, J = 8.7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 173.1, 165.1, 149.5, 148.8, 148.5, 133.0, 128.0, 127.9, 125.3, 124.0, 122.7, 120.3 ppm. HRMS (DIP/CI-MS) m/z: [M + H]$^+$ calcd. for $C_{14}H_7N_6O_9$ 403.0281; found 403.0275.

3,5-Bis(2,4-dinitrophenyl)-1,2,4-oxadiazole (4y): Method B, yield 70%, colorless solids, m.p. 182–184 °C. ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 9.03 (d, J = 2.1 Hz, 1 H), 8.98 (d, J = 2.1 Hz, 1 H), 8.77 (dd, J = 8.4, 2.1 Hz, 1 H), 8.73 (dd, J = 8.6, 2.3 Hz, 1 H), 8.47 (d, J = 8.4 Hz, 1 H), 8.34 (d, J = 8.7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 171.6, 165.0, 150.2, 149.5, 148.5, 148.2, 133.5, 133.0, 128.1, 128.0, 123.9, 121.4, 120.4, 120.3 ppm. $C_{14}H_6N_6O_9$ (402.24): calcd. C 41.80, H 1.50, N 20.89; found C 42.00, H 1.21, N 20.97.

Supporting Information (see footnote on the first page of this article): ^{1}H, ^{13}C spectra, elemental analyses and/or HRMS for all obtained compound. CIF file for compound **4i**.

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