Visible-Light-Induced Radical Polynitration of Arylboronic Acids: Synthesis of Polynitrophenols

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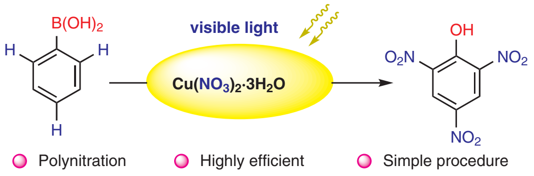

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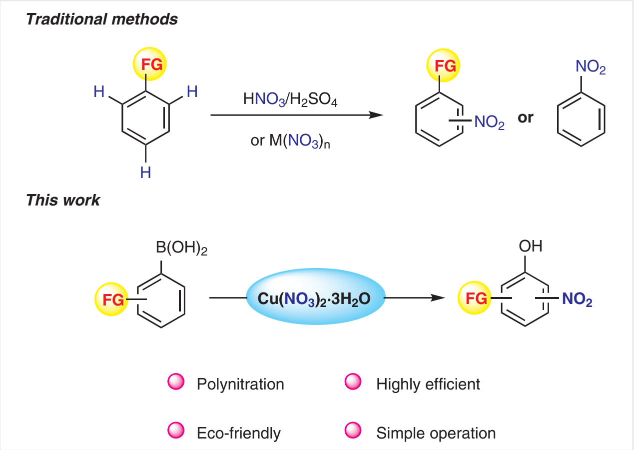
Abstract We report a visible light-assisted one-pot method for the synthesis of polynitrophenols through radical tandem hydroxylation and nitration of arylboronic acids by utilizing copper(II) nitrate trihydrate as the nitro source. This method features mild conditions, a simple procedure, and good functional group tolerance. Compared to conventional methods, this work provides a straightforward approach for the polynitration of aromatic compounds.

Key words polynitrophenols, visible light, arylboronic acid, nitration, copper

Visible light photocatalysis is a reliable and powerful tool for the development of green, sustainable and effective syntheses of fine chemicals.[1] In recent years, more and more synthetic organic reactions using photocatalysis have been achieved, and in some respects they have demonstrated unparalleled advantages over conventional organic synthesis, such as high efficiency, mild reaction conditions and sustainability, while reducing the amount of by-products produced by heating.[2] These reaction characteristics greatly increase the efficiency of synthetic procedures, the atomic economy of the reaction, and make organic synthesis more environmentally friendly.[3] Unlike traditional free-radical chemistry, the generation of free radicals in a light-induced manner can avoid the use of toxic, expensive free-radical initiators, and greatly expand the reaction types of free radicals. Consequently, in the past few years, the application of visible-light catalysts has facilitated the production of free radicals and promoted their application in organic synthesis. The success of this strategy relies on the pioneering work by MacMillan,[4] Yoon,[5] and Stephenson,[6] as well as other research groups using ruthenium and rhodium transition-metal complexes as photoredox catalysts. However, the use of transition-metal complexes involves high cost, potential toxicity and other disadvantages. Therefore, visible-light catalytic reactions without external photosensitizers are in high demand.

Aromatic nitro compounds are one of the most important classes of organic compounds used in pharmacology, agrochemicals, pesticides, polymers, dyes, and medicines.[7] Conventional nitration reactions rely on strongly oxidizing mixed acids (HNO_3/H_2SO_4) for the direct electrophilic nitration of aromatics (Scheme 1). These harsh reaction conditions represent a remarkable limitation in terms of tolerance toward oxidation or acid-sensitive functional groups.[8] Even though a great number of photo-promoted organic reactions have been reported in the literature, the photoinduced C–H nitration of aromatics remains unknown so far. In this paper, we report that the visible-light-promoted tandem hydroxylation and nitration of arylboronic acids is an ideal way to synthesize polynitroaromatic compounds. Arylboronic acids are chemically stable, inexpensive and relatively easy to obtain, and have been extensively used as synthetic precursors in organic transformations such as Suzuki couplings, Petasis reactions, halogenations, and hydroxylation reactions.[9] To date, the nitration of arylboronic acids is generally regioselective mono-nitration or *ipso*-nitration, thus providing only mono-nitration or dinitration products.[10] A method capable of enabling the selective polynitration of aromatics is of significant interest. Meanwhile, although nitrates salts such as $Bi(NO_3)_3{\cdot}5H_2O$,[11] NO_2BF_4,[12] $VO(NO_3)_3$,[13] $Fe(NO_3)_3{\cdot}9H_2O$,[14] $Mg(NO_3)_2{\cdot}6H_2O$,[15] $NaNO_3$,[16] and $(Me_4N)NO_3$[17] have been used as nitrating reagents, the nitration of phenol compounds has also been developed. Phenol as a substrate limits its application to some extent. Herein, we report a visible-light-assisted radical polynitration of commercially available arylboronic acids, which results in the one-pot synthesis of polynitro-

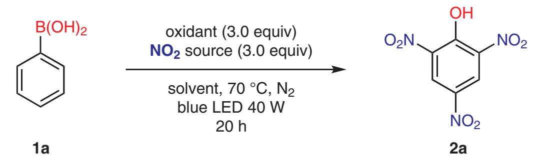


Scheme 1 Nitration of functionalized arenes

phenols (Scheme 1). Importantly, this approach does not require an exogenous photosensitizer.

Our investigations commenced with the nitration reaction of commercially available phenylboronic acid (**1a**) as a model substrate. In the initial experiment, the reaction in the presence of $AgNO_3$ (3.0 equiv) as the nitro source and $K_2S_2O_8$ (3.0 equiv) as the oxidant in MeCN under irradiation with a 40 W blue LED lamp did not give the polynitrated product **2a** (Table 1, entry 1). Further, other nitro sources such as $NaNO_3$, HNO_3, $Bi(NO_3)_2$, $Mg(NO_3)_2·6H_2O$, $Fe(NO_3)_3·9H_2O$, $Co(NO_3)_2·6H_2O$, $Cu(NO_3)_2·3H_2O$, and $Zn(NO_3)_2·3H_2O$ were screened (entries 2–9). Delightfully, $Cu(NO_3)_2·3H_2O$ was found to be more effective for this transformation and afforded the desired product **2a** in 72% yield (entry 8). We speculated that copper ions may play a vital role in the reaction. In an attempt to confirm this was the case, we added 20 mol% of $Cu(NO_3)_2·3H_2O$ to the reaction mixture of **1a**, $Fe(NO_3)_3·9H_2O$ and oxidant in MeCN, but there was no significant change in the yield (entry 10), indicating that copper ions did not play a role in the reaction to increase the product yield. To confirm the role of water in the reaction, 1.5 equivalents of water were added to reaction with $AgNO_3$ as the nitro source, however, none of the desired product was obtained (entry 11). Oxidants such as Oxone, $Na_2S_2O_8$, and PhIOAc proved to be less efficient than $K_2S_2O_8$ (entries 12–14). Next, a solvent screen revealed the reaction was highly solvent-dependent, as the desired product **2a** could not be detected in DMF, EtOH or cyclohexane, whereas in DCE, **2a** was obtained in a poor 20% yield (entries 15–18). Finally, we focused on the effect of light and temperature on the reaction. Several control experiments were carried out in the presence of a blue LED at 70 °C vs in the absence of light at 100 °C (see the Supporting Information for additional details). We found that a trace amount of product was observed in the absence of light, thus implying that irradiation with a blue LED was essential for this transformation.

Table 1 Optimization of the Reaction Conditions[a]

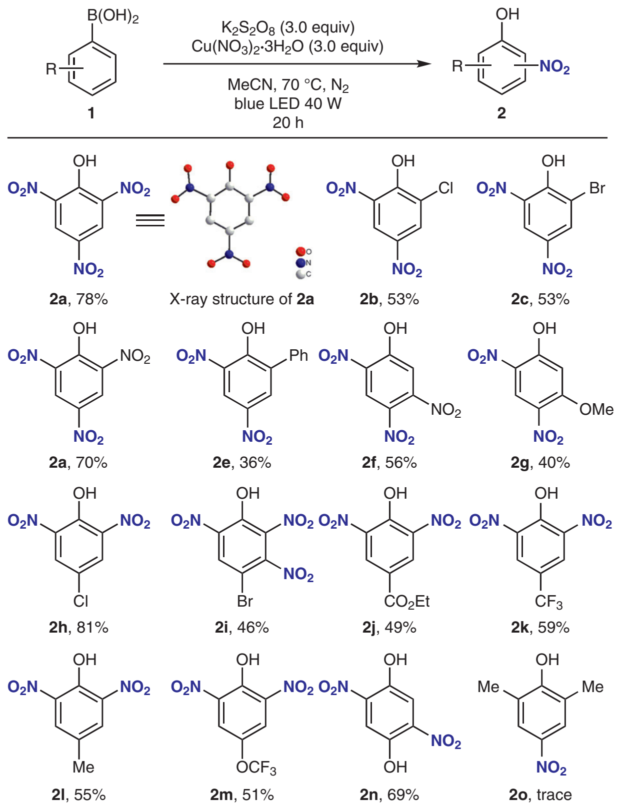


Entry	NO_2 source	Oxidant	Solvent	Yield (%)
1	$AgNO_3$	$K_2S_2O_8$	MeCN	0
2	$NaNO_3$	$K_2S_2O_8$	MeCN	0
3	HNO_3	$K_2S_2O_8$	MeCN	0
4	$Bi(NO_3)_3$	$K_2S_2O_8$	MeCN	trace
5	$Mg(NO_3)_2·6H_2O$	$K_2S_2O_8$	MeCN	40
6	$Fe(NO_3)_3·9H_2O$	$K_2S_2O_8$	MeCN	21
7	$Co(NO_3)_2·6H_2O$	$K_2S_2O_8$	MeCN	26
8	$Cu(NO_3)_2·3H_2O$	$K_2S_2O_8$	MeCN	72
9	$Zn(NO_3)_2·3H_2O$	$K_2S_2O_8$	MeCN	18
10[b]	$Fe(NO_3)_3·9H_2O$	$K_2S_2O_8$	MeCN	31
11[c]	$AgNO_3$	$K_2S_2O_8$	MeCN	0
12	$Cu(NO_3)_2·3H_2O$	Oxone	MeCN	71
13	$Cu(NO_3)_2·3H_2O$	$Na_2S_2O_8$	MeCN	23
14	$Cu(NO_3)_2·3H_2O$	PhIOAc	MeCN	trace
15	$Cu(NO_3)_2·3H_2O$	$K_2S_2O_8$	DCE	20
16	$Cu(NO_3)_2·3H_2O$	$K_2S_2O_8$	DMF	0
17	$Cu(NO_3)_2·3H_2O$	$K_2S_2O_8$	EtOH	0
18	$Cu(NO_3)_2·3H_2O$	$K_2S_2O_8$	cyclohexane	trace

[a] Reaction conditions: arylboronic acid (1.0 equiv, 0.5 mmol), NO_2 source (3.0 equiv, 1.5 mmol), oxidant (3.0 equiv, 1.5 mmol), solvent (5 mL).
[b] $Cu(NO_3)_2·3H_2O$ (20 mol%) was added.
[c] H_2O (1.5 equiv) was added.

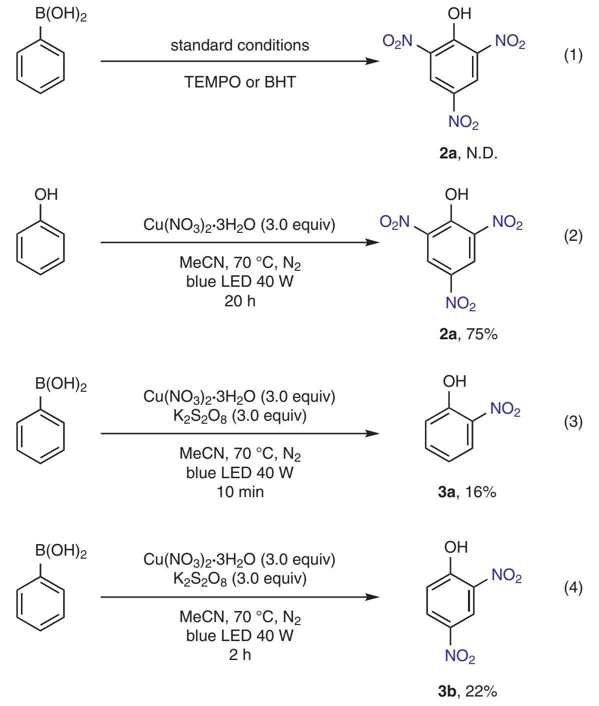
With optimized reaction conditions in hand, the scope of the arylboronic acids was examined. As shown in Scheme 2, a wide array of arylboronic acids could be oxidized and nitrated to afford polynitrophenols. In general, arylboronic acids bearing electron-donating groups or electron-withdrawing groups all afforded the corresponding products **2** in moderate to good yields. Functional groups such as halogen, nitro, aryl, methoxy, ester, trifluoromethyl, methyl, methoxytrifluoromethyl and hydroxy were well tolerated. The structure of **2a** was confirmed by the X-ray crystallography analysis. Sterically hindered *ortho*-substituted arylboronic acids **1b**–**e** were examined, affording the corresponding polynitrated products **2b**–**e** in 36–70% yields.

meta-Substituted arylboronic acids gave products **2f** and **2g** in 56% and 40% yield, respectively. Further, *para*-substituted arylboronic acids also proved to be suitable substrates affording the corresponding products **2h**–**n** in 46–81% yields. It is noteworthy that the electronic effect had a noticeable influence on the nitration reactions. Compared to electron-donating groups, electron-withdrawing groups could significantly increase the yields of the products. Interestingly, the reaction of (*p*-bromophenyl)boronic acid afforded tri-nitration product **2i**, which is unlike the di-nitration product **2h** formed from (*p*-chlorophenyl)-boronic acid. Unexpectedly, the nitration of (dimethylphenyl)boronic acid resulted in a trace amount of nitration product **2o**, probably because the two *ortho* substituents in the substrate might suppress the initial hydroxylation of the boronic acid functionality.



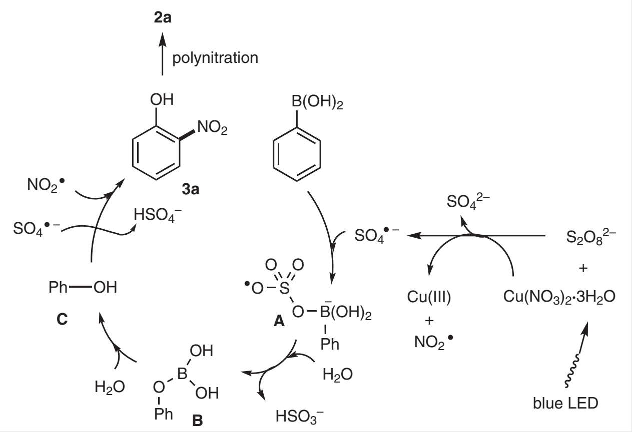
Scheme 2 Substrate scope of the arylboronic acids

To gain insight into the mechanism of this transformation, we carried out the radical-capture reaction by adding a radical-trapping reagent [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) or butylated hydroxytoluene (BHT)] to the reaction system under standard conditions, and as expected the desired product **2a** was not detected (N.D.) (Scheme 3, eq 1). This result suggests that the transformation proceeds through a radical pathway. When phenol was used as the substrate in the absence of oxidant under standard conditions, trinitrophenol **2a** was obtained in 75% yield (Scheme 3, eq 2). Furthermore, under standard conditions, stopping the reaction after 10 minutes led to the formation of *ortho*-mono-nitrated product **3a** in 16% yield (Scheme 3, eq 3), whilst stopping the reaction after two hours furnished the di-nitrated product **3b** in 22% yield (Scheme 3, eq 4).



Scheme 3 Mechanistic studies

The exact reaction mechanism remains unclear; however, based on the experimental results and related reports,[10c,18] we propose a plausible mechanism for this transformation, as outlined in Scheme 4. The nitration reaction is assumed to proceed through a stepwise process. First, the arylboronic acid reacts with a sulfate radical anion, which is generated from $K_2S_2O_8$ via the oxidation of $Cu(NO_3)_2 \cdot 3H_2O$ under irradiation with a blue LED light, to form radical anion intermediate **A**. Next, in the presence of water, intermediate **A** could undergo transformation into phenol **C** via intermediate **B**. Further, the phenol **C** undergoes oxidation in the presence of the sulfate radical anion and reacts with an NO_2 radical, which is generated in the initial step from $Cu(NO_3)_2 \cdot 3H_2O$, to give *ortho*-nitrophenol **3a**. Subsequently, *ortho*-nitrophenol **3a** undergoes two sequential nitrations to produce the polynitration product **2a**.



Scheme 4 A plausible mechanism

In conclusion, we have developed a novel visible-light induced polynitration of arylboronic acids through tandem hydroxylation and nitration. Polynitrophenols can be obtained through a radical process, without the need for an exogenous photosensitizer. During the polynitration of the arylboronic acid, photoirradiation appears to play a critical role. Without having to begin with a phenol, this work represents a straightforward approach to access polynitrated aromatics. Further mechanistic investigations into this reaction are underway.

Common reagents and materials were purchased from commercial sources without further treatment, unless otherwise specified. Column chromatography was performed using PUKE silica gel (300-400 size). Melting points were recorded using a X-4 micro melting point tester apparatus. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$: 7.26 ppm). Chemical shifts for carbon resonances are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: 77.0 ppm). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet), coupling constant in hertz (Hz), integration. ^1H, ^{13}C and ^{19}F NMR spectra were recorded at 25 °C using a Varian INOVA-500 or a Bruker 600-MHz spectrometer. High-resolution mass spectrometry (HRMS) was performed with a Bruker micrOTOF II instrument using the ESI method.

CAUTION: polynitrated aromatics, e.g., picric acid (**2a**) (must be stored under a layer of water), can be potentially explosive.

Polynitration; General Procedure

A mixture of arylboronic acid **1** (1.0 equiv, 0.5 mmol), $CuNO_3·3H_2O$ (3.0 equiv, 1.5 mmol) and $K_2S_2O_8$ (3.0 equiv, 1.5 mmol) was added to a quartz reaction tube. Anhydrous MeCN (5 mL) was added under a nitrogen atmosphere. The mixture was stirred at 70 °C in a light reactor (WATTECS WP-VLH-1020 40 W blue LED) overnight. After the reaction was complete, the mixture was evaporated under reduced pressure to leave a crude residue, which was purified by column chromatography on silica gel (hexane/ethyl acetate = 8:1) to afford the product **2**.

2,4,6-Trinitrophenol (2a)

Yellow solid; yield: 89 mg (78%); mp 122–123 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 9.20 (s, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 126.3, 137.1, 138.2, 153.2.

HRMS (ESI): *m*/*z* $[M - H]^-$ calcd for $C_6H_2N_3O_7$: 227.9898; found: 227.9899.

2-Chloro-4,6-dinitrophenol (2b)

Yellow solid; yield: 58 mg (53%); mp 111–112 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.60 (d, *J* = 3.0 Hz, 1 H), 9.01 (d, *J* = 3.0 Hz, 1 H), 11.51 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 119.8, 126.3, 131.6, 133.2, 139.2, 155.8.

HRMS (ESI): *m*/*z* $[M - H]^-$ calcd for $C_6H_2ClN_2O_5$: 216.9658; found: 216.9653.

2-Bromo-4,6-dinitrophenol (2c)

Yellow solid; yield: 70 mg (53%); mp 117–118 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.76 (d, *J* = 3.0 Hz, 1 H), 9.05 (d, *J* = 3.0 Hz, 1 H), 11.63 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 114.6, 120.6, 132.9, 134.8, 139.8, 156.5.

HRMS (ESI): *m*/*z* $[M - H]^-$ calcd for $C_6H_2BrN_2O_5$: 260.9153; found: 260.9160.

3,5-Dinitro-(1,1′-biphenyl)-2-ol (2e)

Yellow solid; yield: 47 mg (36%); mp 202–203 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.49–7.59 (m, 5 H), 8.52 (d, *J* = 2.5 Hz, 1 H), 9.07 (d, *J* = 2.5 Hz, 1 H), 11.59 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 120.4, 128.7, 129.2, 129.3, 131.8, 133.2, 133.7, 134.7, 139.7, 156.9.

HRMS (ESI): *m*/*z* $[M - H]^-$ calcd for $C_{12}H_7N_2O_5$: 259.0360; found: 259.0367.

2,4,5-Trinitrophenol (2f)

Yellow solid; yield: 64 mg (56%); mp 100–101 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.76 (d, *J* = 3.0 Hz, 1 H), 9.05 (d, *J* = 3.0 Hz, 1 H), 11.63 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 114.6, 120.6, 132.9, 134.8, 139.8, 156.5.

HRMS (ESI): *m*/*z* $[M - H]^-$ calcd for $C_6H_2N_3O_7$: 227.9898; found: 227.9893.

5-Methoxy-2,4-dinitrophenol (2g)

Yellow solid; yield: 43 mg (40%); mp 108–109 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 4.07 (s, 3 H), 6.73 (s, 1 H), 8.86 (s, 1 H), 11.16 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 57.6, 102.5, 124.9, 125.9, 132.6, 159.6, 160.0.

HRMS (ESI): *m*/*z* $[M - H]^-$ calcd for $C_7H_5N_2O_6$: 213.0153; found: 213.0159.

4-Chloro-2,6-dinitrophenol (2h)

Yellow solid; yield: 89 mg (81%); mp 80–81 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.32 (s, 2 H), 11.32 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 124.5, 131.2, 137.8, 148.0.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_6H_2ClN_2O_5$: 216.9658; found: 216.9658.

4-Bromo-2,3,6-trinitrophenol (2i)

Yellow solid; yield: 71 mg (46%); mp 160–161 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 9.20 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 126.26, 126.27, 129.7, 137.1, 138.2, 153.2.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_6HBrN_3O_7$: 305.9003; found: 305.9008.

Ethyl 4-Hydroxy-3,5-dinitrobenzoate (2j)

Yellow solid; yield: 63 mg (49%); mp 115–116 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.44 (t, *J* = 7.0 Hz, 3 H), 4.47 (q, *J* = 7.0 Hz, 2 H), 8.95 (s, 2 H), 11.78 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 62.6, 122.0, 132.0, 137.4, 152.0, 162.4.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_9H_7N_2O_7$: 255.0259; found: 255.0263.

2,6-Dinitro-4-(trifluoromethyl)phenol (2k)

Yellow solid; yield: 74 mg (59%); mp 47–48 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.59 (s, 2 H), 11.70 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 121.8 (q, *J* = 270.0 Hz), 122.0 (q, *J* = 36.3 Hz), 128.4 (q, *J* = 3.0 Hz), 137.7, 151.5.

^{19}F NMR (564 MHz, $CDCl_3$): δ = –62.77.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_7H_2F_3N_2O_5$: 250.9921; found: 250.9917.

4-Methyl-2,6-dinitrophenol (2l)

Yellow solid; yield: 54 mg (55%); mp 84–85 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.46 (s, 3 H), 8.15 (s, 2 H), 11.29 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.2, 129.4, 131.7, 137.2, 147.4.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_7H_5N_2O_5$: 197.0204; found: 197.0213.

2,6-Dinitro-4-(trifluoromethoxy)phenol (2m)

Yellow oil; yield: 68 mg (51%).

^1H NMR (600 MHz, $CDCl_3$): δ = 8.24 (s, 2 H), 11.12 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 120.2 (q, *J* = 260.2 Hz), 124.7, 137.6, 139.1, 148.2.

^{19}F NMR (564 MHz, $CDCl_3$): δ = –58.69.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_7H_2F_3N_2O_6$: 266.9932; found: 266.9943.

2,5-Dinitrobenzene-1,4-diol (2n)

Yellow solid; yield: 69 mg (69%); mp 207–208 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 9.20 (s, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 126.3, 137.1, 153.2.

HRMS (ESI): *m*/*z* [M – 2 H]$^{2-}$ calcd for $C_6H_2N_2O_6$: 197.9924; found: 197.9924.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610038.

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