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Sustainable and recyclable palladium nanoparticles–catalyzed reduction of nitroaromatics in water/glycerol at room temperature

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Abstract

Palladium nanoparticles with unique catalytic activity and high stability are synthesized. These nanoparticles exhibit excellent catalytic reduction activity for nitroaromatics in green solvents in the presence of H_2 at ambient pressure and temperature. The prominent advantages of this nanotechnology include low consumption of catalyst, excellent chemoselectivity, high reusability of the catalyst, and environmentally green solvents.

Keywords

aromatic amines, green solvents, nitroaromatics, palladium nanoparticles, recyclable

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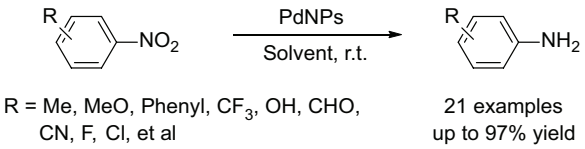

Introduction

Aromatic amines are often used as important raw materials in the organic synthesis industry, and are also used as intermediates in the synthesis of many fine chemicals. They are widely used in the production of bioactive natural products, pharmaceuticals, agricultural chemicals, and so on.[1–3] As a result, there are many methods for the synthesis of aromatic amines, and among these, reduction of nitroaromatics by hydrogenation is the most commonly used method. So far, many methods based on earth-abundant metal-mediated reductions have also been described, such as those using well-known Fe/HCl, Zn/NaOH, $LiAlH_4$, and so on.[4–9] Alternatively, hydrogenation can also depend upon well-developed precious metal–catalyzed reductions.[10–12] However, most of these methods suffer from several drawbacks, including lack of chemoselectivity, formation of difficult-to-remove organic byproducts, and the use of high-pressure equipment. In recent years, metal nanoparticles (NPs), possessing large surface-to-volume ratios, as active sites in organic transformations have attracted extensive interest from both academic and industrial communities. Compared with the traditional catalysts, metal NPs have several desirable features such as environmental sustainability, high activity, and recyclability. Palladium (Pd)-catalyzed reduction of nitroaromatics has been studied for a long time and has become one of the most widely used methods. The palladium nanoparticles (PdNPs) offer an advantageous alternative to the more traditional catalysts, and they have partly superseded traditional Pd catalysts in the reduction of nitroaromatics and better results have achieved.[13–15]

From a green chemistry perspective, one of the vital conditions for realizing a "green" process involves the use of a non-toxic and cheap solvent. Without a doubt, water is the solvent of choice. In recent years, glycerol has become an ideal candidate as a green solvent from an environmental and economic standpoint. During the last decades, numerous reducing agents have been reported for the reduction of nitro compounds to amines, such as hydrazine, formic acid, alcohols, and others.[16–18] As is well-known, H_2

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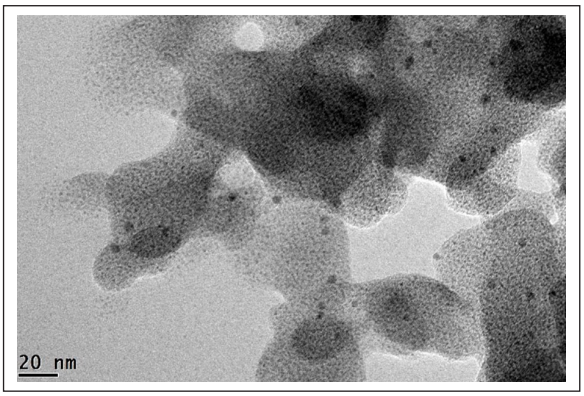


Figure 1. The TEM image of the prepared PdNPs.

is the fundamental hydrogen atom source in transfer hydrogenation. From the viewpoint of reaction post-processing, the direct hydrogenation of nitroarenes using H_2 is be more favorable, because it makes the reaction cleaner, and makes purification of the products and recovery of the catalysts easier.[19–22] H_2 has gained wide application in the hydrogenation of nitroaromatics but it usually needs high temperatures and high pressure equipment, and also poses safety issues. Hence, it is a great challenge to develop valuable catalysts with high catalytic efficiency, excellent chemoselectivity and reusability for the hydrogenative reduction of nitro groups, and realizing the conversion of nitro-to-amine in the presence of H_2 at ambient temperature and pressure.

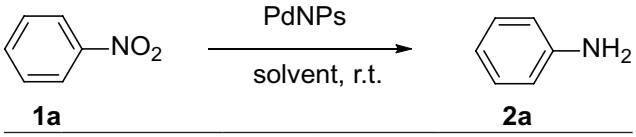
Herein, we report a new hydrogenation reduction method for nitroaromatics with H_2 under ambient conditions in water/glycerol media using PdNPs as the catalyst. The procedure demonstrates many advantages such as high catalytic activity, excellent chemoselectivity, and high reusability.

Results and discussion

The PdNPs consisting of Pd(0) and Pd(II) were prepared according to the literature report.[23] They were synthesized by in situ reduction of palladium acetate and benzenediazonium tetrafluoroborate using $NaBH_4$ as the reducing agent. The transmission electron microscopy (TEM) image showed that the sizes of these NPs were about 3.5 ± 0.5 nm in diameter (Figure 1).

The catalytic activity of the prepared Pd nanocomposite for the reduction of nitroarenes was investigated. In order to optimize reaction conditions, the reduction of nitrobenzene with H_2 as a model reaction was examined under different conditions (Table 1). H_2O was first used as the solvent, and as expected, the reaction proceeded smoothly at ambient pressure and temperature. But, this reaction needed too long a reaction time and the reaction was incomplete and so was not satisfactory (Entry 1). It was found that the reaction time was markedly shortened and the reaction yield was significantly improved with glycerol as the solvent (Entry 2). From the above results, it was envisaged that a mixture of H_2O and glycerol might result in good reduction performance. Because the ratio of H_2O/glycerol could be varied and H_2O is cheaper than glycerol, a ratio of 1:1 was used. So the final reaction

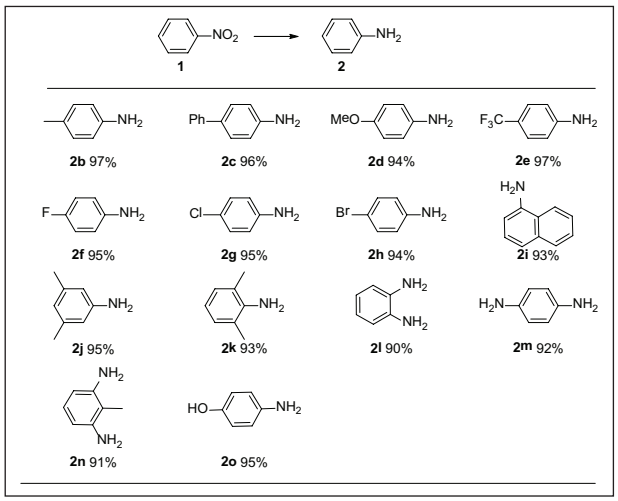
Table 1. Optimization of the reaction conditions[a].



1a 2a

Entry	"H" source	H_2O (mL)	Glycerol (mL)	Yield[b] (%)	Time (h)
1	H_2	2	0	70	24
2	H_2	0	2	97	6
3	–	0	2	–	–
4	H_2	1.5	0.5	80	16
5	H_2	1	1	97	7
6	H_2	0.5	1.5	95	6.5
7	Hydrazine	1	1	–	–
8	Formic acid	1	1	–	–
9	$HCOONH_4$	1	1	–	–

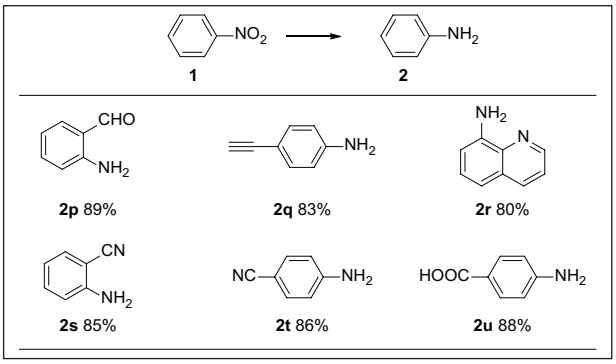
[a]Unless otherwise noted, the reaction conditions were as follows: $PhNO_2$ (2 mmol), PdNPs (10 mg), solvent (4 mL), H_2 (1 atm), or "H" source (10 mmol), room temperature.
[b]Conversion and selectivity were determined by GC.



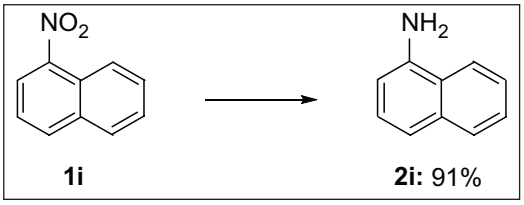
Scheme 1. Substrate scope of saturated substituted nitrobenzenes[a,b].
[a]Unless otherwise noted, reaction conditions were as follows: **1** (2 mmol), PdNPs (10 mg), solvent (4 mL), H_2 (1 atm), room temperature, 7 h.
[b]Conversion and selectivity were determined by GC.

conditions employed PdNPs as the catalyst and H_2O/glycerol (1:1) as the reaction solvent, and the reaction was carried out at room temperature and ambient pressure (Entries 4–6). A previous report indicated that glycerol could be used as a hydrogen donor in the reduction of nitroarenes,[24] but our preliminary experiments demonstrated that the hydrogen atom source was H_2 in this reaction (Entry 3). Other hydrogen atom sources were investigated, with the results showing that they were not suitable for this catalytic reaction system under similar reaction conditions (Entries 7–9).

Under the optimized reaction conditions, the substrate scope was investigated. The optimized conditions were tested on a wide range of substituted aromatic nitro compounds, and the results are summarized in Scheme 1. It



Scheme 2. Substrate scope of unsaturated substituted nitrobenzenes[a,b].
[a]Unless otherwise noted, reaction conditions were as follows: **1** (2 mmol), PdNPs (10 mg), solvent (4 mL), H_2 (1 atm), room temperature, 7 h.
[b]Conversion and selectivity were determined by GC.



Scheme 3. Large-scale synthesis[a,b].
[a]Gram-scale preparation of **2i** reaction conditions was as follows: **1** (20 mmol), PdNPs (50 mg), solvent (40 mL), H_2 (1 atm), room temperature, 7 h.
[b]Isolated yield.

is clear that the efficiency of the reduction reaction is rarely dependent on the electronic nature of the substrates. As for substrates **2j** and **2k**, it turned out that steric hindrance slightly affected the reaction efficiency. Various halogenated aromatic nitro compounds reacted were performed smoothly and the corresponding target products were obtained with excellent yields. To our delight, dinitroaromatics were also successfully converted into the desired products in high yields, albeit over a longer reaction time. 4-Aminophenol **2o** was also successfully synthesized from 4-nitrophenol in 95% yield.

Several heteroaromatic nitro compounds and nitroaromatics containing the more vulnerable moieties were also tested. Fused heterocyclic rings such as quinoline remained intact under the reaction conditions. Easily reducible functionalities such as CHO, CN, and COOH also remained totally unaffected. Surprisingly, the more vulnerable triple bonds were well tolerated during the reduction process (Scheme 2).

In order to demonstrate the practical application of this method, a gram-scale reaction was designed with **1i** under the standard conditions. The corresponding compound **2i** was obtained in an isolated yield of 91% (Scheme 3).

The reusability of the catalyst has also been investigated. The catalyst can be recycled via filtration or centrifugation. After five reaction cycles, its activity showed no significant decrease (Figure 2).

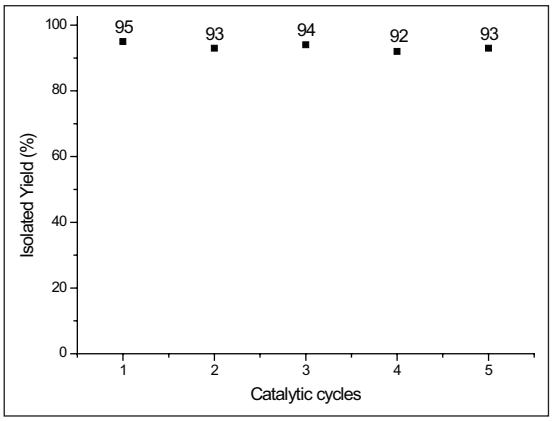


Figure 2. Reusability of PdNPs in the reduction of **1f**.

Conclusion

We have synthesized PdNPs which were characterized with TEM. These NPs exhibited excellent catalytic activity in the catalytic reduction of nitroaromatics in water/glycerol with H_2 as the hydrogen atom source. This nanotechnology has fundamental advantages including a low catalyst loading, excellent chemoselectivity, high reusability of the catalyst, and employs environmentally green solvents.

Experimental

General considerations

Measurements. ^1H and ^{13}C NMR spectra were recorded on the Bruker 400M spectrometer. Chemical shifts are expressed in ppm from internal tetramethylsilane (TMS) (^1H and ^{13}C). All coupling constants (*J* values) are reported in Hertz (Hz).

Materials. $Pd(OAc)_2$ was purchased from Puyang Huicheng Electronic Material Co., Ltd. Silica gel (200–300 mesh) purchased from Qingdao Hai Yang Chemical Industry Co., Ltd was used for chromatographic separations. Other chemicals and solvents were purchased from commercial company and used as received.

Synthesis and isolation of PdNPs

Synthesis of PdNPs was carried out using a simple procedure. To a vigorously stirred solution of aniline (0.91 mL) in absolute ethanol (3 mL) was added tetrafluoroboric acid (3.2 mL, 40%). The tert-butyl nitrite (2.4 mL) was added drop wise to the solution at 0 °C. The mixture was stirred for 30 min at room temperature, and the benzenediazonium tetrafluoroborate was precipitated. The solid was filtered off and dried in vacuum. The benzenediazonium tetrafluoroborate was then directly used without further purification. In a 100-mL round bottom flask, the benzenediazonium tetrafluoroborate (0.24 g) was dissolved in a mixture of tetrahydrofuran (THF) (20 mL) and $Pd(OAc)_2$ (0.14 g) in absolute methanol (20 mL), and the resulting solution was stirred at room temperature for 10 min. $NaBH_4$ (0.14 g) in 30 mL of methanol was then added at 0 °C. The mixture

was stirred for 2 h at room temperature. After reaction, the mixture was dissolved in dichloromethane and was washed with 0.5 M H_2SO_4 and 0.5 M $NaHCO_3$; the organic phase was evaporated in vacuo to yield PdNPs.

General procedure for hydrogenation of various nitroaromatic compounds and the recycling experiment

To a Schlenk tube was added nitroarene **1** (2 mmol) and PdNPs (10 mg). The tube was purged with H_2 for 5 min by hydrogen generator, and H_2O (2 mL)/glycerol (2 mL) was added under H_2. The reaction mixture was stirred at room temperature and the reaction progress was monitored by gas chromatography (GC). Upon completion, the mixture was filtered free of PdNPs. H_2O (10 mL) was added to the mixture and extracted with acetic ether (3 × 20 mL). The combined organic layers were dried (anhyd $MgSO_4$) and concentrated. The residue was subjected to flash column chromatography on silica gel (petroleum ether/acetic ether) to afford the corresponding compound **2**.

To study the recyclability of PdNPs, the hydrogenation of **1f** was conducted under the same conditions as described above. After reaction, the catalyst was separated through centrifugation, and then the catalyst was washed with EtOH, and reused in a next run under the same conditions. The catalytic cycle efficiency was compared by isolated yield. All products were identified by comparison of their spectroscopic data with literature data. Analytical data for the products are given as follows:

2a: 97% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.53 (s, 2H), 6.58-6.60 (m, 2H), 6.72 (t, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.26 (s, 2CH), 118.59 (s, CH), 129.45 (s, 2CH), 146.68 (s, C).

2b: 97% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.20 (d, *J* = 8.0 Hz, 3H), 3.44 (s, 2H), 6.51-6.54 (m, 2H), 6.90-6.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.59 (s, CH_3), 115.38 (s, 2CH), 127.74 (s, C), 129.88 (s, 2CH), 144.08 (s, C).

2c: 97% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76 (s, 2H), 6.82-6.84 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.51-7.55 (m, 4H), 7.67 (d, *J* = 4.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.52 (s, 2CH), 126.38 (s, CH), 126.51 (s, 2CH), 128.10 (s, 2CH), 128.81 (s, 2CH), 131.57 (s, C), 141.28 (s, C), 146.04 (s, C).

2d: 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.42 (s, 2H), 3.71 (s, 3H), 6.61 (d, *J* = 8.0 Hz, 2H), 6.72-6.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.74 (s, CH_3), 114.83 (s, 2CH), 116.43 (s, 2CH), 140.08 (s, C), 152.75 (s, C).

2e: 97% yield; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −61.11 ppm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 2H), 6.66 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 114.19 (s, 2CH), 124.89 (d, J_{CF} = 270.0 Hz, C), 126.70 (d, J_{CF} = 11.2 Hz, C), 126.71 (d, J_{CF} = 3.7 Hz, 2CH), 149.43 (s, C).

2f: 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.52 (s, 2H), 6.54 (dd, *J* = 4.0, 4.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.68 (d, J_{CF} = 22.7 Hz, 2CH), 116.13 (d, J_{CF} = 7.3 Hz, 2CH), 142.69 (d, J_{CF} = 2.2 Hz, C), 156.38 (d, J_{CF} = 235.0 Hz, C).

2g: 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.62 (s, 2H), 6.54 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.30 (s, 2CH), 123.01 (s, C), 129.14 (s, 2CH), 145.12 (s, C).

2h: 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.62 (s, 2H), 6.50-6.52 (m, 2H), 7.19-7.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 110.11 (s, C), 116.79 (s, 2CH), 132.03 (s, 2CH), 145.56 (s, C).

2i: 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.18 (s, 2H), 6.87 (d, *J* = 8.0 Hz, 1H), 7.48-7.63 (m, 4H), 7.90 (d, *J* = 8.0 Hz, 1H), 8.00 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.87 (s, CH), 119.07 (s, CH), 121.11 (s, CH), 123.85 (s, C), 125.04 (s, CH), 126.09 (s, CH), 126.63 (s, CH), 128.77 (s, CH), 134.62 (s, C), 142.42 (s, C).

2j: 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 6H), 3.58 (s, 2H), 6.40 (s, 2H), 6.54 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.46 (s, $2CH_3$), 113.28 (s, 2CH), 120.55 (s, CH), 139.05 (s, 2C), 146.62 (s, C).

2k: 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.48 (s, 6H), 3.79 (s, 2H), 7.02 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.86 (s, $2CH_3$), 118.24 (s, CH), 121.90 (s, 2C), 128.61 (s, 2CH), 143.20 (s, C).

2l: 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.36 (s, 4H), 6.67-6.73 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.77 (s, 2CH), 120.30 (s, 2CH), 134.78 (s, C).

2m: 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.33 (s, 4H), 6.56 (d, *J* = 1.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.73 (s, $4CH_3$), 138.60 (s, 2C).

2n: 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.91 (s, 3H), 3.52 (s, 4H), 6.15 (d, *J* = 8.0 Hz, 2H), 8.81 (t, *J* = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.26 (s, CH_3), 106.72 (s, 2CH), 107.37 (s, C), 126.83 (s, CH), 145.33 (s, C).

2o: 95% yield; ^{1}H NMR (400 MHz, DMSO): δ = 4.36 (s, 2H), 6.44-6.53 (m, 4H), 8.44 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ = 115.93 (s, 2CH), 116.11 (s, 2CH), 140.97 (s, C), 148.82 (s, C).

2p: 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.08 (s, 2H), 6.53-6.65 (m, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 9.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.07 (s, CH), 116.34 (s, CH), 118.80 (s, C), 135.25 (s, CH), 135.76 (s, CH), 150.01 (s, C), 194.15 (s, CH).

2q: 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.89 (s, 1H), 3.71 (s, 2H), 6.45 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 75.17 (s, CH), 84.61 (s, C), 111.16 (s, C), 114.67 (s, 2CH), 133.50 (s, 2CH), 147.20 (s, C).

2r: 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.90 (s, 2H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 6.0 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 1H), 8.62 (t, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 110.06 (s, CH), 116.01 (s, CH), 121.37 (s, CH), 127.43 (s, CH), 128.88 (s, C), 136.01 (s, CH), 138.45 (s, C), 144.05 (s, C), 147.45 (s, CH).

2s: 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.48 (s, 2H), 6.62-6.68 (m, 2H), 7.22-7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 95.67 (s, C), 115.33 (s, CH), 117.85 (s, CH), 117.91 (s, C), 132.33 (s, CH), 134.11 (s, CH), 150.00 (s, C).

2t: 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.19 (s, 2H), 6.51 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 99.57 (s, C), 114.44 (s, 2CH), 120.43 (s, C), 133.77 (s, 2CH), 150.82 (s, C).

2u: 88% yield; ^{1}H NMR (400 MHz, DMSO): δ = 5.88 (s, 2H), 6.57 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 11.99 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ = 113.03 (s, 2CH), 117.33 (s, C), 131.71 (s, 2CH), 153.60 (s, C), 168.00 (s, C).

Declaration of conflicting interests

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Supplemental material

Supplemental material for this article is available online.

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