

## Cellulose nanocrystal functionalized palladium nanoparticles as an efficient heterogeneous catalyst for the synthesis of $\alpha$ -amino nitriles via Strecker reaction

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**Abstract:** An efficient route reported to the application of palladium nanoparticles dispersed on 2-aminopyrimidine functionalized cellulose nanocrystal (CNC-AMPD-Pd) as a novel, suitable and reusable catalyst in the one-pot, three component synthesis of different  $\alpha$ -aminonitriles at ambient temperature under solvent free reaction conditions. The heterogeneous catalyst could be easily separated from the reaction mixture and reused at least 6 times with no significant loss of catalytic activity.

**Keywords:** Nanocellulose, Palladium, Three-component, One-pot synthesis,  $\alpha$ -amino nitriles, Strecker reaction.

### Introduction

One of the most significant and appealing multi-component reactions for the direct one-pot synthesis of  $\alpha$ -aminonitriles containing multi-purpose functional groups is Strecker reaction.  $\alpha$ -aminonitriles are extremely useful natural and synthetic intermediates for the amino acids, chelating agents, herbicides, heterocyclic compounds such as imidazoles, thiadiazoles and biologically active agents such as anticancer, antifungal, antiviral and antibiotic compounds [1-3]. In addition, they are used in the synthesis of bioactive molecules such as clopidogrel [4], prasugrel [5], saframycin A [6] and manzacidin A [7]. Strecker reaction usually involves the nucleophilic addition of cyanide anion to imines [8]. This reaction is typically carried out in aqueous media using various sources of cyanide ion, including HCN [9], KCN [10], Et<sub>2</sub>AlCN [11], (EtO)<sub>2</sub>P(O)CN [12], Bu<sub>3</sub>SnCN [13], trimethylsilyl cyanide (TMSCN) [14], and Me<sub>3</sub>SiCN [15]. Of these different cyanide sources, TMSCN appears to be the most practical, soluble, easy to handle, and non-toxic reagent, which can be used under mild reaction conditions in the Strecker reaction [16].

Various catalysts such as Ga(otf)<sub>3</sub> [17], CeCl<sub>3</sub> [18], NHC-Amidate Palladium(II) Complex [19], K<sub>5</sub>CoW<sub>12</sub>O<sub>40</sub>•3H<sub>2</sub>O [20], Bi(NO<sub>3</sub>)<sub>3</sub> [21], active mesoporous Co(II) complex on mesoporous SBA-15 material [22], Chitosan [23], FeCl<sub>3</sub> [24] Ga-TUD-1 [25], Fe [26], I<sub>2</sub> [27], CN-Bu-SO<sub>3</sub>H [28], Bis(NHC)-Pd-Species [29], KF/ clinoptilolite nanoparticles [30], Sulfated tungstate [31], SBA-15 sulfonic acid based nanoreactors [32], MCM-41 mesoporous silica [33], CMK-5-SO<sub>3</sub>H [34], Fe<sub>3</sub>O<sub>4</sub>@cellulose-OSO<sub>3</sub>H [35] and Fe<sub>3</sub>O<sub>4</sub>@ZrO<sub>2</sub>/SO<sub>4</sub> [36] are often required in TMSCN based processes. However, some of these procedures suffer from drawbacks such as low reactivity, inadequate yields, and sensitivity to humidity, long reaction times, harsh reaction conditions, tedious workup, formation of toxic by-products, use of expensive reagents and production of large quantities of toxic metal-containing wastes [37-47]. Thus, the development of environmentally benign, efficient, easy to remove from the reaction mixture and reusable heterogeneous catalysts providing excellent reaction yields has attracted remarkable interest in the Strecker reaction.

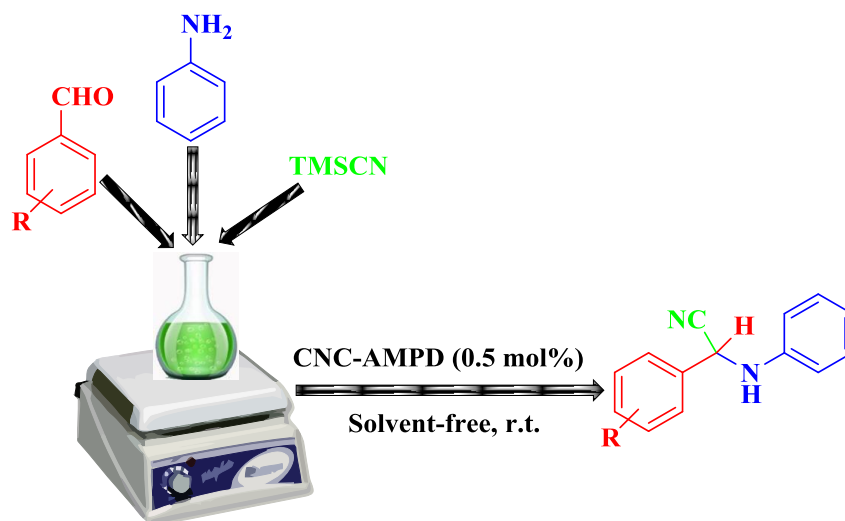
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Biocompatible, natural, renewable and sustainable resources and processes have been recently been focused on from scientific and technological aspects. Therefore, biopolymers are interesting candidates for the synthesis of heterogeneous supported catalysts [48, 49]. In this regards, nano cellulose (CNC), which is the most naturally abundant and widely known renewable polymer, has been suggested as a promising and economic starting material for preparation of catalysts. In fact, cellulose has a unique linear polysaccharide structure comprising of  $\beta$ -D-glucose units linked by 1, 4 glycosidic bonds with flipped monomeric subunits, which impart high strength [50, 51]. Furthermore, the hydroxyl groups of CNC molecules permit further modifications into different cellulose derivatives and handle for catalyst immobilization. Cellulose-based catalysts matched metals, such as palladium, platinum,

silver, and nickel nanoparticles, have been advanced successively [52-64].

Hence, the advanced functionalization of CNC is in compelling request to make cellulose-metal complexes more stable and effective for catalysis process. The coordination of 2-aminopyridine with metals makes it a popular ligand to support different metals with bridging between metals and the matrix to form efficient catalysts [65].

In continuation of our work on the catalytic application of nano cellulose in organic synthesis [66], we herein reported the using of 2-aminopyridine functionalized nano cellulose (CNC-AMPD-Pd) supported catalyst as an efficient in the three-component, one pot preparation of  $\alpha$ -aminonitriles (Scheme 1).



**Scheme 1:** Synthesis of  $\alpha$ -aminonitrile derivatives using CNC-AMPD-Pd as a nanocatalyst

## Results and discussions

At the beginning, to find optimum conditions, the solvent-free reaction of benzaldehyde (1 mmol), aniline (1 mmol) and trimethylsilyl cyanide (1.5 mmol) in the presence of various amount of CNC-AMPD-Pd as catalyst at room temperature was evaluated. As it can be seen in Table 1, 0.5 mol % of CNC-AMPD-Pd as catalyst at ambient temperature afforded 2-(N-Anilino)-2-phenyl acetonitrile in 10 min with 96% of yield (Table 1, entry 3).

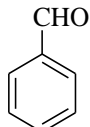
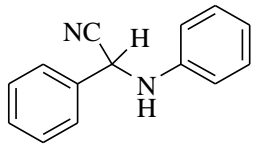
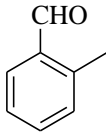
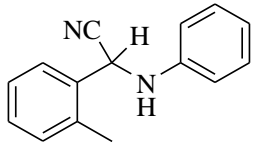
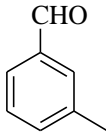
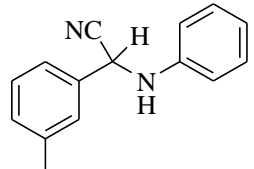
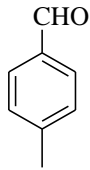
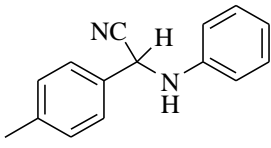
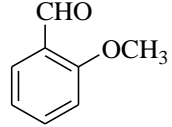
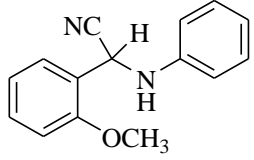
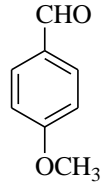
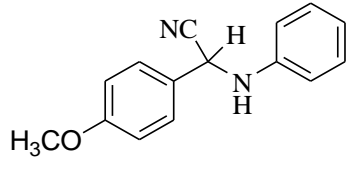
Following, three-component condensation reaction of aromatic aldehydes, aniline and trimethylsilyl cyanide under optimised conditions for the Strecker synthesis of  $\alpha$ -aminonitriles was studied (Table 2). As it displayed in Table 2, the reactions with the aromatic aldehydes including electron-donating or electron-withdrawing substituents provided the desired products in high to excellent yields using the CNC-AMPD-Pd as catalysts.

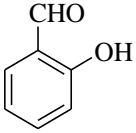
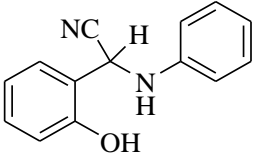
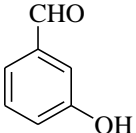
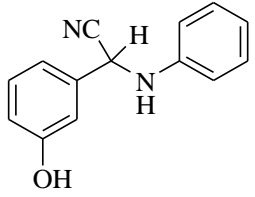
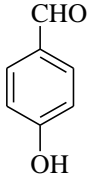
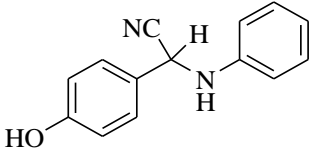
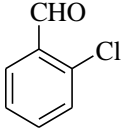
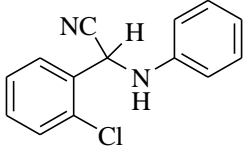
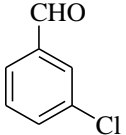
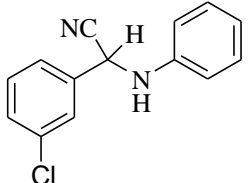
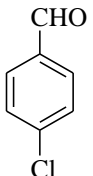
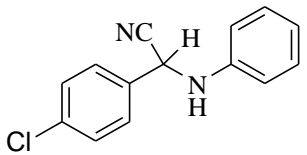
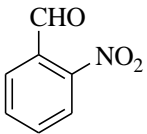
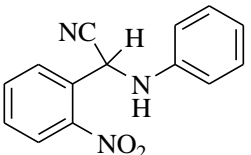
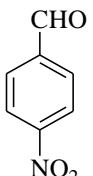
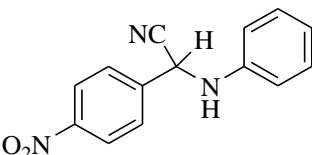
**Table 1:** Optimization conditions for reactions of benzaldehyde (1 mmol), aniline (1 mmol) and trimethylsilyl cyanide (1.5 mmol) in the presence of different amount of CNC-AMPD-Pd as catalyst at room temperatures under solvent-free conditions.

Entry	Amount of catalyst ( mol %)	Time (min)	Yield (%) <sup>a</sup>
1	0.1	50	Trace
2	0.3	20	50
3	0.5	10	96
4	1	10	97

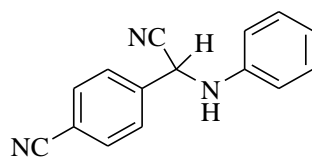
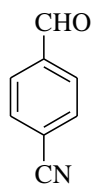
<sup>a</sup>Yields refer to isolated pure products.

**Table 2:** Three-component reactions of aromatic aldehydes (1 mmol), aniline (1 mmol) and trimethylsilyl cyanide (1.5 mmol) in the presence of CNC-AMPD-Pd as catalyst (0.5 mol %) at ambient temperature and under solvent free reaction conditions

Entry	Aldehyde	Product	Time (min)	Yield (%)
1			10	96
2			12	93
3			15	88
4			12	93
5			15	90
6			12	93

7			25	91
8			15	89
9			15	93
10			20	95
11			10	93
12			10	94
13			15	94
14			10	95

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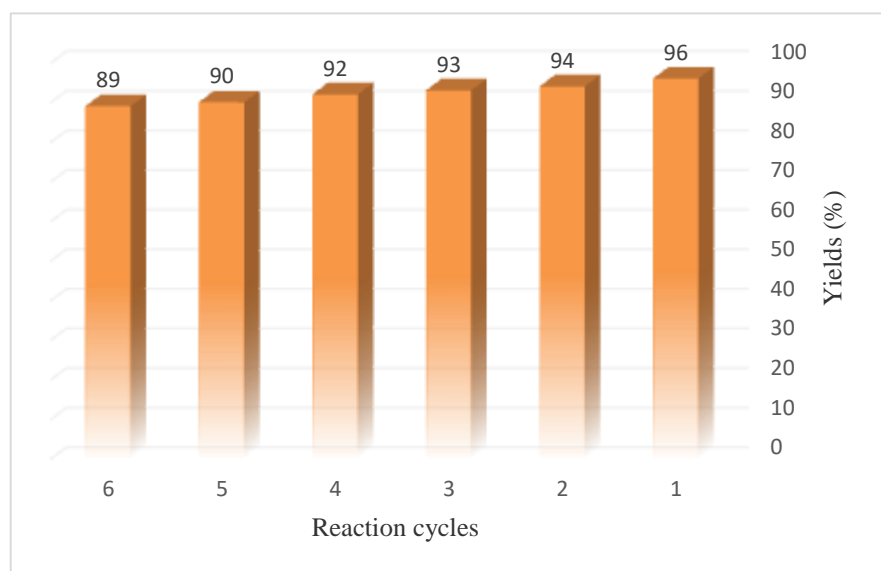
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<sup>a</sup>Yields refer to the isolated pure products.

The recoverability of the CNC-AMPD-Pd nano catalyst investigated using the model reaction of benzaldehydes (1 mmol), aniline (1 mmol) and trimethylsilyl cyanide (1.5 mmol) in the presence of

CNC-AMPD-Pd as catalyst (0.5 mol %) at ambient temperature and under solvent free reaction conditions. The recycled Catalyst was reused six runs without any loss of its activities (Figure 1).



**Figure 1:** The recycling of the CNC-AMPD-Pd as nanocatalyst

In order to exhibit the applicability of the present work, it was compared in the preparation of 2-(N-Anilino)-2-phenyl acetonitrile with some reported

results in the literature as shown in Table 3. The results display that the reactions in the presence of CNC-AMPD-Pd performed at relatively short times (10-25 min) with the resembling yields (Table 3).

**Table 3:** Comparison the results of CNC-AMPD-Pd with other catalysts in the synthesis of 2-(N-Anilino)-2-phenyl acetonitrile

Entry	Catalyst	Conditions	Time	Yield (%) <sup>a</sup> [Ref]
1	[HP(HNCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N]NO <sub>3</sub> (20 mol%)	CH <sub>3</sub> CN (3 mL), 50 °C	12 h	94 [3]
2	SBA-15(5 mol%)	Solvent-free, 50 °C	15 h	100 [8]
3	Sulfamic acid (5 mol%)	solvent-free, room temperature	30 min	98 [69]
4	B[MIm] <sub>2</sub> [PF] <sub>6</sub> (5 wt%)	Solvent-free, room temperature	30 min	97 [70]

5	CMK-5-SO <sub>3</sub> H (2 mol%)	Solvent-free, room temperature	45 min	96 [34]
6	B@MCM-41 (0/0015g)	EtOH, room temperature	2 h	96 [71]
7	Fe <sub>3</sub> O <sub>4</sub> /MIL-101(Fe) (10 mol%)	EtOH, room temperature	35 min	98 [72]
8	TSIL-SO <sub>3</sub> H (10mol%)	H <sub>2</sub> O, room temperature	10 min	98 [73]
9	[BMIm]PF <sub>6</sub> /[BMIm]BF <sub>4</sub> (1 ml)	solvent-free, room temperature	6 h	87 [74]
10	CNC-AMPD-Pd (0.5 mol %)	solvent-free, room temperature	10 min	96 (This work)

<sup>a</sup>Yields refer to isolated pure products

## Conclusions

In summary, we have employed a mild, simple and facile procedure to the synthesis of  $\alpha$ -amino nitriles by one-pot three-component Strecker reaction using different aromatic aldehyde with aniline and trimethylsilyl cyanide (TMSCN) in the presence of the heterogeneous palladium nanocatalyst supported on 2-aminopyridine functionalized nano cellulose (CNC-AMPD-Pd) under ambient and solvent-free conditions. This catalyst has the several advantages such as: high catalytic activity, high yields of the products, short reaction times, good recoverability, solvent-free reaction conditions, easy work-up, clean procedure and mild reaction conditions.

## Experimental

All chemicals were supplied by the Merck and Sigma Aldrich Chemical companies and used with no further purification. CNC-AMPD-Pd was prepared using a previously reported method [66]. All yields refer to the products separated following purification. A Bruker Avance DPX 400 MHz instrument was used to record the NMR spectra.

### Preparation of CNCs:

To remove the ions from CNCs, acidic hydrolysis by Whatman method with some modification was performed. Cellulose fiber was hydrolyzed using 100 mL of 2.5 M HBr for 3 h at 100 °C and infrequent ultra-sonication. The solution obtained was then diluted with deionized water and the mixture was centrifuged after each five dilutions to remove the residual acid and water soluble compounds. Afterwards, the solution was neutralized to around pH 6. The CNCs dispersed on the surface in the aqueous

solution were then collected and centrifuged at 10/000 rpm for 60 min.

### Tosylation of nanocellulose yielding CNC-Tos:

CNC-Tos was prepared using a reported methods [67, 68]. First, 0.50 g of cellulose nanocrystals were suspended in 10 mL of pyridine and the mixture obtained was then cooled to 10 °C. Tosyl chloride (0.9 g, 5 mmol) was then added and the resulting mixture was stirred for 2 days at ambient temperature. Afterwards, 100 mL of ethanol were added to the reaction mixture to precipitate the product, which was then washed with ethanol (50 mL) for five times and stored in the fridge without drying.

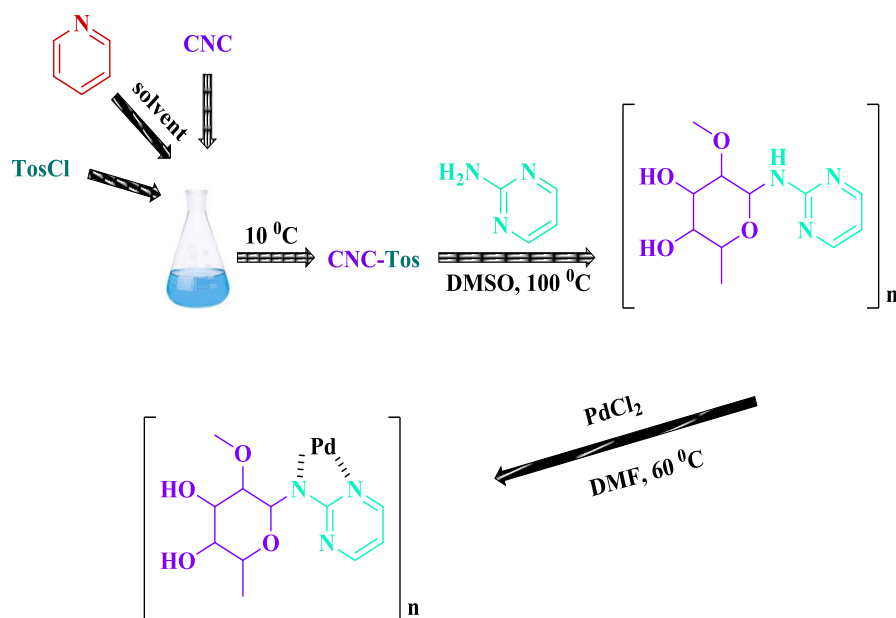
### Preparation of CNC-AMPD:

A solution of 0.40 g of CNC-Tos in methanol mixed with 20 mL of DMF, followed by centrifugation several times to replace methanol with DMF. 0.40 g of 2-amino pyrimidine (AM PD) was then added and the resulting mixture was stirred for 24 h at 100 °C. Next, 50 mL of deionized water added to the reaction mixture and the precipitate obtained separated by centrifugation. The product washed several times with ethanol, deionized water and dialyzed by deionized water for 3 days using a cellulose membrane to replace water with DMF and stored in a refrigerator.

### Preparation of CNC-AMPD-Pd nanocatalyst:

To a solution of 0.10 g of Pd(Cl)<sub>2</sub> (0.45 mmol) in 10 mL of DMF was added 0.50 g of CNC-AMPD in DMF under N<sub>2</sub> atmosphere. The mixture obtained was then stirred for 24 h at 60 °C, followed by cooling to ambient temperature and collection by filtration. The solid black product obtained washed carefully using deionized water (3 × 25 mL), pure ether (2 × 25 mL)

and pure ethyl alcohol ( $2 \times 25$  mL) and dried in vacuum at ambient temperature.



**Scheme 2:** Preparation of CNC-AMPD-Pd nanocatalyst

**General procedure for the Strecker reaction by CNC-AMPD-Pd.**

A mixture of the aromatic aldehyde (1 mmol), aniline (1 mmol), trimethylsilyl cyanide (TMSCN) (1.5 mmol) and CNC-AMPD-Pd (0.5 mol %) was vigorously stirred under ambient temperature under solvent free conditions for a specific period of time to obtain  $\alpha$ -amino nitriles. Upon completion of the reaction, (as confirmed by TLC), the reaction mixture was dissolved in 15 mL of acetone, followed by filtration. Afterwards, the solvent was removed by evaporation and the residual solid product was purified by plate chromatography on silica gel and characterized by  $^{13}\text{C}$ -NMR and  $^1\text{H}$ -NMR spectral analyses.

The spectral and analytical data for some products are as follows:

**2-(*N*-Anilino)-2-(3-methylphenyl) acetonitrile (Table 2, Entry 3):**

$^1\text{H}$  NMR (400.13 MHz, DMSO):  $\delta$  = 2.42(s, 3H), 3.80(s, 1H), 5.55(s, 1H), 6.76 (d,  $J$ = 7.6 Hz, 2H), 6.84 (t,  $J$ = 4.6, 1H), 7.22-7.258 (m, 5H), 7.63 (d,  $J$ = 7.4 Hz, 1H) ppm.;  $^{13}\text{C}$  NMR (100.6 MHz, DMSO):  $\delta$  = 145.6, 134.1, 132.0, 131.6, 130.8, 130.7, 125.2, 123.6, 122.7, 118.7, 112.3, 47.2, 21.1 ppm.

**2-(*N*-Anilino)-2-(2-hydroxyphenyl) acetonitrile (Table 2, Entry 7):**

$^1\text{H}$  NMR (400.13 MHz, DMSO):  $\delta$  = 4.60(s, 1H), 5.16 (s, 1H), 6.89-6.97 (m, 5H), 4.10-7.14 (m, 2H), 7.49-7.55 (m, 2H), 9.80 (b, 1H) ppm.;  $^{13}\text{C}$  NMR (100.6 MHz, DMSO):  $\delta$  = 143.6, 139.3, 130.0, 128.1, 127.2, 126.1, 124.2, 120.3, 119.0, 116.0, 111.3, 50.4 ppm.

**2-(*N*-Anilino)-2-(4-hydroxyphenyl) acetonitrile (Table 2, Entry 9):**

$^1\text{H}$  NMR (400.13 MHz, DMSO):  $\delta$  = 4.59(s, 1H), 5.12(s, 1H), 6.60-6.68(m, 5H), 7.20-7.23(t,  $J$ = 5.6 Hz, 2H), 7.36-7.38(d,  $J$ = 5.6 Hz, 2H), 9.80(b, 1H) ppm.;  $^{13}\text{C}$  NMR (100.6 MHz, DMSO):  $\delta$  = 151.8, 144.8, 129.3, 128.1, 124.5, 119.7, 117.3, 114.9, 112.1, 47.0 ppm.

**2-(*N*-Anilino)-2-(4-Nitrophenyl) acetonitrile (Table 2, Entry 14):**

$^1\text{H}$  NMR (400.13 MHz, DMSO):  $\delta$  = 4.10(s, 1H), 5.55 (d,  $J$ = 5.4 Hz, 1H), 6.58 (d,  $J$ = 8.8 Hz, 2H), 6.86 (t,  $J$ =8.12, 1H), 7.27-7.31 (m, 2H), 7.80-7.83(m, 2H), 8.36-8.41(m, 2H) ppm.;  $^{13}\text{C}$  NMR (100.6 MHz, DMSO):  $\delta$  = 148.5, 144.0, 140.0, 127.3, 126.3, 125.1, 122.2, 118.1, 115.7, 53.3 ppm.

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