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One-Pot Synthesis of Triarylpyridines in Ionic Liquid and Their Catalyzed Active on a Simple Diels-Alder Reaction

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2,4,6-Triarylpyridines were synthesized by the cascade reaction of aromatic aldehyde, acetophenone and NH_4OAc (1:2:5) in the presence of HOAc in ionic liquid [BmIm][BF_4]. The method related to environmental friendly, simplicity, very effective and lower costs, is suitable for the synthesis of arrays of compounds. Their catalyzed activity on a simple Diels-Alder reaction was also studied.

Key Words: Triarylpyridines, Catalyzed active, Diels-Alder reaction, Ionic liquid.

INTRODUCTION

2,4,6-Triarylpyridines[1] are prominent building blocks in supra-molecular chemistry with their π-stacking ability, directional H-bonding and coordination. They are also the useful intermediates in the syntheses of pesticide, desiccant, surfactant, *etc.*[2-6]. Recently, they have been used as the precursor of natural products[7-10] and as ligands in transition metal complexes. Accordingly, the development of efficient synthetic strategies for the construction of this molecular architecture is of considerable importance from the standpoint of the medicinal and organic chemistry.

Due to their great importance, many synthetic strategies[11] have been published since the pioneering work by Kröhnke[1] and Potts[12]. However, most of these methodologies used volatile toxic organic solvent with moderate to low final yields, especially, at least four-step were necessary[13-21]. In most cases the products have to be purified extensively by column chromatography and a number of side products, including 1,5-diones and cyclohexanols, are formed. Additionally, unsymmetrical derivatives are easily accessible *via* a sequential reaction of the starting materials. In order to adopt the principles of 'Green Chemistry', Yang[22] and co-workers obtained the target

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molecular in water catalyzed by NaOH through two steps. Gareth's group[21] developed a solvent free route to such compounds, but NaOH and two-step were also needed. Recently, two one-pot synthetic strategies of this framework were reported in concentrated aqueous ammonia, KOH and PEG300 was used as catalyst respectively[23-26]. The modest yields obtained are competitive with those reported in the literature, but the use of strong bases and pungent toxic concentrated aqueous ammonia could not be avoided. The starting materials should be added in two steps in both of two methods.

Probably, because of the deactivation and steric effect of *o*-position hydroxyl on the carbonyl group, the reaction concerning 2′-hydroxyacetophenone is difficult and has rarely been reported. And as one hydroxyl group is introduced in benzene ring, the yield will reduce by 30-40 %[23-25]. But we have to conquer this difficulty due to that the hydroxyl group is a general group in the structure of most natural products and often displays the biological activity[27].

EXPERIMENTAL

Melting points were measured with a Fisher-Johns melting-point apparatus without correction. IR spectra were recorded on a Nicolet Nexus 670 spectrometer in KBr. The proton nuclear magnetic resonance (^{1}H NMR) spectra were measured on a Bruker AM-400 spectrometer with Me_4Si (TMS) as the internal reference and $CDCl_3$ as solvent. X-ray diffraction was measured on a Siemens P4 diffractometer with graphite monochromated MoK_α radiation. Silica gel (200-400 mesh), from Qingdao Ocean Chemical Co. Ltd. (China), was used for thin-layer chromatography. The other reagents were all analytical pure. The ionic liquid [BmIm][BF_4] was synthesized according to the literature[28].

General procedure for the preparation of 2,4,6-triarylpyridine (3): A dry 50 mL flask was charged with aromatic aldehydes (**1**) (1 mmol), 2-hydroxyacetophenone (**2**) (2 mmol), NH_4OAc (5 mmol), HOAc (1 mL) and ionic liquid (2 mL). The mixture was stirred at 80 ºC for 10-28 h and then was poured into the water (40 mL), the precipitate was washed with water for 2-3 times and purified by recrystallization from DMF to give 2,4,6-triarylpyridines (**3**).

The Diels-Alder reaction between *p*-benzoquinone and cyclopenta-1,3-diene was carried out following the literature[29].

Spectral data of new product

3a: 4-(4-Chlorophenyl)-2,6-bi(2-hydroxyphenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3500, 3054, 2342, 1602, 1541, 1494, 832, 790, 756; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.3 (2H, s, OH), 8.65 (2H, s, pyridine-H), 8.46 (2H, d, *J* = 8.0 Hz, Ar-H), 8.30 (2H, d, *J* = 8.0 Hz, Ar-H), 7.73 (2H, d, *J* = 8.0 Hz, Ar-H), 7.55 (2H, t, *J* = 8.0 Hz, Ar-H), 7.15 (2H, d, *J* = 8.0 Hz, Ar-H), 7.11 (2H, d, *J* = 8.0 Hz, Ar-H).

3b: 4-(4-Bromophenyl)-2,6-bi(2-hydroxyphenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3450, 3040, 2900, 1600, 1540, 1491, 829, 788, 756; ^1H NMR (400 MHz, DMSO-d_6)(δ, ppm): 8.72 (2H, s, pyridine-H), 8.54 (2H, d, *J* = 8.0 Hz, Ar-H), 8.32 (2H, d, *J* = 8.0 Hz, Ar-H), 7.81 (2H, d, *J* = 8.0 Hz, Ar-H), 7.56 (2H, t, *J* = 8.0 Hz, Ar-H), 7.14 (2H, d, *J* = 8.0 Hz, Ar-H), 7.09 (2H, d, *J* = 8.0 Hz, Ar-H).

3c: 4-(4-Cyanophenyl)-2,6-bi(2-hydroxyphenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3475, 3101, 2230, 1587, 1525, 1224, 846, 750, 636; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.80 (2H, s, pyridine-H), 8.64 (2H, d, *J* = 8.0 Hz, Ar-H), 8.60 (2H, d, *J* = 8.0 Hz, Ar-H), 8.39 (1H, d, *J* = 8.0 Hz, Ar-H), 8.09 (4H, t, *J* = 8.0 Hz, Ar-H), 7.47 (2H, t, *J* = 8.0 Hz, Ar-H), 7.06 (1H, d, *J* = 8.0 Hz, Ar-H).

3d: 4-(4-Methoxylphenyl)-2,6-bi(2-hydroxyphenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3440, 3160, 2870, 1604, 820, 766, 723; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.19 (2H, d, *J* = 8.0 Hz, Ar-H), 8.10 (2H, s, pyridine-H), 8.01 (2H, d, *J* = 8.0 Hz, Ar-H), 7.76 (2H, t, *J* = 8.0 Hz, Ar-H), 7.32-7.35 (2H, m, Ar-H), 7.10 (2H, d, *J* = 8.0 Hz, Ar-H), 6.91 (2H, d, *J* = 8.0 Hz, Ar-H), 3.85 (3H, s, OCH_3).

3e: 4-(4-Methylphenyl)-2,6-bi(2-hydroxyphenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3410, 3150, 3026, 2921, 2900, 1600, 766, 753, 725; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.24 (2H, d, *J* = 8.0 Hz, Ar-H), 8.13 (2H, s, pyridine-H), 8.11 (2H, d, *J* = 8.0 Hz, Ar-H), 7.75-7.78 (2H, m, Ar-H), 7.72 (2H, d, *J* = 8.0 Hz, Ar-H), 7.38-7.41 (2H, m, Ar-H), 7.11 (2H, d, *J* = 8.0 Hz, Ar-H), 2.34 (3H, s, CH_3).

3f: 4-(4-Nitrophenyl)-2,6-bi(2-hydroxyphenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3350, 3080, 2360, 1654, 1509, 853, 760, 707; ^1H NMR (400 MHz, DMSO-*d*6) (δ, ppm): 8.86 (2H, d, *J* = 8.0 Hz, Ar-H), 8.69 (2H, d, *J* = 8.0 Hz, Ar-H), 8.63 (2H, s, pyridine-H), 8.36 (2H, d, *J* = 8.0 Hz, Ar-H), 8.10-8.14 (2H, m, Ar-H), 7.82-7.85 (2H, m, Ar-H), 7.40 (2H, d, *J* = 8.0 Hz, Ar-H).

3g: 4-(4-Aldehydophenyl)-2,6-bi(2-hydroxyphenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3650, 3058, 2900, 2360, 1607, 770, 757, 730; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 9.88 (1H, s, -CHO), 8.33 (2H, d, *J* = 8.0 Hz, Ar-H), 8.21 (2H, d, *J* = 8.0 Hz, Ar-H), 8.16 (2H, d, *J* = 8.0 Hz, Ar-H), 8.12 (2H, s, pyridine-H), 8.05-8.09 (4H, m, Ar-H), 7.57 (2H, d, *J* = 8.0 Hz, Ar-H).

3h: 4-(2-Methoxylphenyl)-2,6-bi(2-hydroxyphenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3420, 3175, 2900, 1601, 780, 763, 741; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 11.23 (1H, s, OH), 7.89 (2H, s, pyridine-H), 7.58 (1H, d, *J* = 8.0 Hz, Ar-H), 7.47 (1H, d, *J* = 8.0 Hz, Ar-H), 7.43 (1H, d, *J* = 8.0 Hz, Ar-H), 7.39 (1H, d, *J* = 8.0 Hz, Ar-H), 7.32-7.36 (2H, m, Ar-H), 7.27 (1H, d, *J* = 8.0 Hz, Ar-H), 7.13-7.18 (1H, m, Ar-H), 7.05-7.09 (1H, m,

Ar-H), 7.02 (1H, d, *J* = 8.0 Hz, Ar-H), 6.92 (1H, s, Ar-H), 6.62 (1H, t, *J* = 8.0 Hz, Ar-H), 6.08 (1H, s, Ar-H), 3.88 (3H, s, -OCH_3).

3i: 4-(2-Chlorophenyl)-2,6-bi(2-hydroxyphenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3510, 3070, 2410, 1507, 796, 783, 725; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.13 (2H, d, *J* = 8.0 Hz, Ar-H), 7.85 (2H, s, pyridine-H), 7.79-7.83 (2H, m, Ar-H), 7.59 (2H, d, *J* = 8.0 Hz, Ar-H), 7.45-7.48 (4H, m, Ar-H), 7.28 (2H, d, *J* = 8.0 Hz, Ar-H).

3j: 4-(2-Bromophenyl)-2,6-bi(2-hydroxyphenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3470, 3054, 1603, 1530, 830, 785, 746; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.16 (2H, d, *J* = 8.0 Hz, Ar-H), 7.78 (2H, s, pyridine-H), 7.77-7.80 (2H, m, Ar-H) 7.62 (2H, d, *J* = 8.0 Hz, Ar-H), 7.50-7.52 (4H, m, Ar-H), 7.31 (2H, d, *J* = 8.0 Hz, Ar-H).

3k: 4-(2-Nitrophenyl)-2,6-bi(2-hydroxyphenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3420, 3070, 2320, 1601, 870, 793, 735; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.35 (1H, d, *J* = 7.2 Hz, Ar-H), 8.14-8.17 (1H, m, Ar-H), 8.08-8.11 (1H, m, Ar-H), 8.00 (2H, s, pyridine-H), 7.88 (1H, d, *J* = 8.0 Hz, Ar-H), 7.65-7.69 (2H, m, Ar-H), 7.61 (1H, d, *J* = 7.2 Hz, Ar-H), 7.47 (2H, d, *J* = 8.0 Hz, Ar-H), 7.42 (1H, d, *J* = 8.0 Hz, Ar-H), 7.34-7.38 (1H, m, Ar-H), 7.14-7.19 (1H, m, Ar-H).

3l: 4-(4-Chlorophenyl)-2, 6-bi(4-nitrophenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3068, 1598, 1516, 822, 734, 689; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.76 (4H, d, *J* = 8.0 Hz, Ar-H), 8.62 (2H, s, pyridine-H), 8.58 (4H, d, *J* = 8.0 Hz, Ar-H), 8.14 (2H, d, *J* = 8.0 Hz, Ar-H), 7.66 (2H, d, *J* = 8.0 Hz, Ar-H).

3m: 4-(4-Methylphenyl)-2,6-bi(4-nitrophenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3600, 3000, 2400, 1593, 1519, 1346, 855, 807, 733; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.65 (4H, d, *J* = 8.0 Hz, Ar-H), 8.48 (2H, s, pyridine-H), 8.40 (4H, d, *J* = 8.0 Hz, Ar-H), 8.05 (2H, d, *J* = 8.0 Hz, Ar-H), 7.41 (2H, d, *J* = 8.0 Hz, Ar-H), 2.51 (3H, s, -CH_3).

3n: 4-(4-Methoxyphenyl)-2,6-bi(4-nitrophenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3446, 2800, 1656, 1604, 1513, 854, 820, 723; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.68 (4H, d, *J* = 8.0 Hz, Ar-H), 8.52 (2H, s, pyridine-H), 8.42 (4H, d, *J* = 8.0 Hz, Ar-H), 8.01 (2H, d, *J* = 8.0 Hz, Ar-H), 7.26 (2H, d, *J* = 8.0 Hz, Ar-H), 3.86 (3H, s, -OCH_3).

3o: 4-(4-Hydroxyphenyl)-2,6-bi(4-nitrophenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3600, 3110, 2350, 1662, 1591, 1519, 858, 820, 731; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.0 (1H, s, OH), 8.63 (4H, d, *J* = 8.0 Hz, Ar-H), 8.41 (2H, s, pyridine-H), 8.39 (4H, d, *J* = 8.0 Hz, Ar-H), 8.01 (2H, d, *J* = 8.0 Hz, Ar-H), 6.96 (2H, d, *J* = 8.0 Hz, Ar-H).

3p: 4-(2-Chlorophenyl)-2,6-bi(4-nitrophenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3306, 3106, 2807, 1642, 1598, 1513, 863, 755, 693; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.71 (4H, d, *J* = 8.0 Hz, Ar-H), 8.65 (2H,

s, pyridine-H), 8.59 (4H, d, J=8.0 Hz, Ar-H), 8.53 (1H, d, J=8.0 Hz, Ar-H), 8.0 (1H, d, *J* = 8.0 Hz, Ar-H), 7.49-7.51 (2H, m, Ar-H).

3q: 4-(2-Bromophenyl)-2,6-bi(4-nitrophenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3648, 3566, 2360, 1645, 1597, 864, 753, 692; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.70 (4H, d, *J* = 8.0 Hz, Ar-H), 8.66 (2H, s, pyridine-H), 8.61 (4H, d, *J* = 8.0 Hz, Ar-H), 8.59 (1H, d, *J* = 8.0 Hz, Ar-H), 8.47 (1H, d, *J* = 8.0 Hz, Ar-H), 8.31 (1H, d, *J* = 8.0 Hz, Ar-H), 7.91 (1H, d, *J* = 8.0 Hz, Ar-H).

3t: 4-(4-Cyanophenyl)-2, 6-bi(3-nitrophenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3432, 3079, 2228, 1602, 1584, 1529, 1349, 837, 724, 691; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 9.14 (1H, s, Ar-H), 8.90 (1H, s, Ar-H), 8.77 (4H, d, *J* = 8.0 Hz, Ar-H), 8.56 (2H, s, pyridine-H), 8.35-8.38 (2H, m, Ar-H), 8.08 (2H, d, *J* = 8.0 Hz, Ar-H), 7.89 (2H, d, *J* = 8.0 Hz, Ar-H).

3u: 4-(4-Methylphenyl)-2,6-bi(3-nitrophenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3412, 3090, 2364, 1602, 1528, 1343, 879, 803, 678; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 9.03 (2H, s, Ar-H), 8.62 (2H, d, *J* = 8.0 Hz, Ar-H), 8.35 (2H, d, *J* = 8.0 Hz, Ar-H), 8.05 (2H, s, pyridine-H), 7.77 (2H, d, *J* = 8.0 Hz, Ar-H), 7.71-7.74 (2H, m, Ar-H), 7.41 (2H, d, *J* = 8.0 Hz, Ar-H), 2.50 (3H, s, -CH_3).

3v: 4-(4-Methoxyphenyl)-2,6-bi(3-nitrophenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3420, 3100, 2800, 1656, 1589, 1526, 1342, 828, 806, 690; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 9.02 (2H, s, Ar-H), 8.74 (2H, d, *J* = 8.0 Hz, Ar-H), 8.33 (2H, d, *J* = 8.0 Hz, Ar-H), 8.10 (2H, s, pyridine-H), 7.82 (2H, d, *J* = 8.0 Hz, Ar-H), 7.25-7.27 (2H, m, Ar-H), 7.17 (2H, d, *J* = 8.0 Hz, Ar-H), 3.87 (3H, s, -OCH_3).

3w: 4-(4-Hydroxyphenyl)-2,6-bi(3-nitrophenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3437, 3090, 1682, 1598, 1517, 1348, 878, 830, 729; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 9.96 (1H, s, OH), 9.10 (2H, s, Ar-H), 8.79 (2H, d, *J* = 7.6 Hz, Ar-H), 8.39 (2H, s, pyridine-H), 8.34 (2H, dd, ^3J = 8.0 Hz, ^4J = 2Hz, Ar-H), 8.02 (2H, d, *J* = 8.8 Hz, Ar-H), 7.86 (2H, t, *J* = 8.0 Hz, Ar-H), 6.96 (2H, d, J = 8.8 Hz, Ar-H).

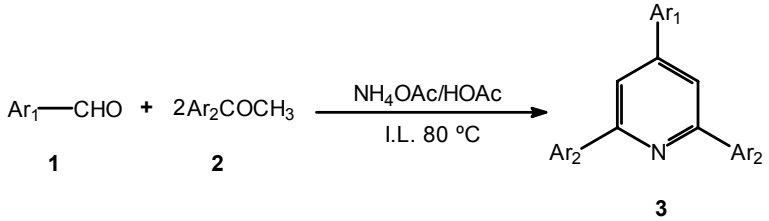
3s: 4-(3-Bromophenyl)-2,6-bi(3-nitrophenyl)pyridine: IR (KBr, ν_{max}, cm^{-1}): 3092, 2360, 1600, 1524, 1348, 867, 726, 673; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 9.00 (2H, s, Ar-H), 8.73 (2H, d, *J* = 7.6 Hz, Ar-H), 8.61 (2H, s, pyridine-H), 8.40-8.43 (2H, m, Ar-H), 8.11 (2H, d, *J* = 8.4 Hz, Ar-H), 8.05 (1H, s, Ar-H), 7.84 (2H, d, *J* = 8.0 Hz, Ar-H), 7.45-7.48 (1H, m, Ar-H).

3y: 4-(4-Cyanophenyl)-2,6-biphenylpyridine: IR (KBr, ν_{max}, cm^{-1}): 3475, 3068, 2225, 1579, 1458, 1235, 846, 748, 661; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.66 (2H, s, pyridine-H), 8.41 (4H, T, Ar-H), 8.10 (2H, d, *J* = 8.4 Hz, Ar-H), 7.50 (4H, t, Ar-H), 7.06-7.12 (4H, m, Ar-H).

Crystallographic data of 3z: Empirical formula: $C_{24}H_{16}N_2$; shape/colour: block/yellow; formula weight: 332.39; temperature: 298(2) K; wavelength: 0.71073 Å ; crystal system, space grope: monoclinic, P2(1)/c; unit cell dimensions: a = 12.6997(17) Å; α = 90.00°; b = 13.737(2) Å, β = 102.262(2)°; c = 10.5460(18) Å, γ = 90.00°; volume: 1797.9(5) $Å^3$; Z, calculated density: 4, 1.228 Mg/m^3; absorption coefficient: 0.072 mm^{-1}; F(000): 696; crystal size: 0.11 mm × 0.13 mm × 0.18 mm; θ range for data collection: 2.12 to 25.128° ; Limiting indices: $-11 \le h \le 15$, $-16 \le k \le 16$, $-12 \le l \le 12$; reflections collected/uniqure: 3159/1118 ; absorption correction: none; refinement method: full-matrix least-squares on F^2; data/restraints/parameters: 3159/0/235; goodness of fit on F^2: 0.928; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0437$, $wR_2 = 0.0527$; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.1541$ $wR_2 = 0.0636$; CCDC: 635284.

RESULTS AND DISCUSSION

Recently, many reports about the applications of ionic liquids have been published[30-32]. Herein, a new mild and simple protocol is observed for synthesis of 2,4,6-triarylpyridines (**Scheme-I**, Table-1) through the reaction of aromatic aldehydes with acetophenone and NH_4OAc at 80 ºC in the presence of HOAc in one-step and the ionic liquid ([BmIm][BF_4]), a colourless, flavourless liquid with non-volatility[31] was used as the solvent. The products' catalyzed functions on a simple Diels-Alder reaction were also studied.



Scheme-I: Synthesis of 2,4,6-triarylpyridines in one-step

As shown in Table-1, 2,4,6-triarylpyridine were synthesized in [BmIm][BF_4] at 80 ºC. The results were the combined operations of electronic effect and steric hindrance. *o*-Substituent aromatic aldehydes always gave the longer reaction times and lower yields. 3-Nitroacetophenone and 4-nitroacetophenone gave high yields (63.9-94.6 %) except entry **3u** and **3v** and the reaction time were shorter than that of 2-hydroxyacetophenone.

The single crystal structure of product **3z** (Fig. 1) was established on the basis of spectroscopic data and confirmed by X-ray diffraction studies.

The results shown in Table-2 indicate that all of products could increase the yields and shorten reaction time of the Diels-Alder reaction between *p*-benzoquinone and cyclopenta-1,3-diene. In experiential, the optimal

TABLE-1
SYNTHESIS OF 2,4,6-TRIARYLPYRIDINE (IN [BmIm][BF_4])

Entry	Ar_1	Ar_2	m.p. (°C)	Yield (%)[a]	Time (h)
3a	4-ClC_6H_4	2-OHC_6H_4	206.7-209.0	64.8	24.0
3b	4-BrC_6H_4	2-OHC_6H_4	224.7-224.9	68.2	22.0
3c	4-CNC_6H_4	2-OHC_6H_4	>300	54.3	20.0
3d	4-$OCH_3C_6H_4$	2-OHC_6H_4	191.6-193.5	50.9	28.0
3e	4-$CH_3C_6H_4$	2-OHC_6H_4	207.9-208.9	46.2	25.5
3f	4-$NO_2C_6H_4$	2-OHC_6H_4	232.1-234.0	33.9	13.0
3g	4-$CHOC_6H_4$	2-OHC_6H_4	256.9-258.5	38.2	25.0
3h	2-$OCH_3C_6H_4$	2-OHC_6H_4	216.3-218.2	23.3	40.0
3i	2-ClC_6H_4	2-OHC_6H_4	168.7-170.2	30.7	25.0
3j	2-BrC_6H_4	2-OHC_6H_4	196.2-202.1	32.5	24.5
3k	3-$NO_2C_6H_4$	2-OHC_6H_4	249.9-251.4	32.9	19.0
3l	4-ClC_6H_4	4-$NO_2C_6H_4$	>300	69.8	13.0
3m	4-$CH_3C_6H_4$	4-$NO_2C_6H_4$	>300	74.5	12.0
3n	4-$OCH_3C_6H_4$	4-$NO_2C_6H_4$	171.3-172.1	86.7	5.0
3o	4-OHC_6H_4	4-$NO_2C_6H_4$	>300	65.5	10.0
3p	2-ClC_6H_4	4-$NO_2C_6H_4$	194.4-195.6	63.9	23.5
3q	2-BrC_6H_4	4-$NO_2C_6H_4$	>300	64.7	22.5
3r	4-ClC_6H_4	3-$NO_2C_6H_4$	283-283.8 (280-281)[23-25]	81.2	25.0
3s	4-BrC_6H_4	3-$NO_2C_6H_4$	>300 (>300)[23-25]	73.5	25.0
3t	4-CNC_6H_4	3-$NO_2C_6H_4$	>300	82.9	18.0
3u	4-$CH_3C_6H_4$	3-$NO_2C_6H_4$	238-240	94.6	22.0
3v	4-$OCH_3C_6H_4$	3-$NO_2C_6H_4$	163.5-164.7	74.9	19.0
3w	4-OHC_6H_4	3-$NO_2C_6H_4$	261.0-263.6	43.6	18.0
3x	3-BrC_6H_4	3-$NO_2C_6H_4$	241.4-244.2	40.7	14.0
3y	3-$NO_2C_6H_4$	3-$NO_2C_6H_4$	>300 (>300)[23-25]	92.8	22.0
3z	4-CNC_6H_4	C_6H_5	>300	85.6	11.0

[a]Yields refer to those of pure isolated products fully characterized by spectral data.

activity of catalyst should come from this kind of structure in which both electron-withdrawing group and electron-donoring group were contained. This had been confirmed by correlative experiment (Table-2), compound **3a-3d** gave higher yields than others. If the electronic effect of two substituents were uniform, the electron-withdrawing group one (**3e-3g**) showed better catalysis activity than that of electron-donoring group (**3d**).

From the comparability in structure between 2,4,6-triaryl-1,4-dihydropyridines and 2,4,6-triarylpyranium, we supposed that this reaction might also be rationalized as a PET-catalyzed non-synchronous cation radical Diels-Alder reaction. The catalyzed activity of compound **3** may be contribute to its long conjugated system and non-planar framework, both of which are propitious to electron transfer from diene to dienophile[33]. Further experiments must be carried out to explain it.

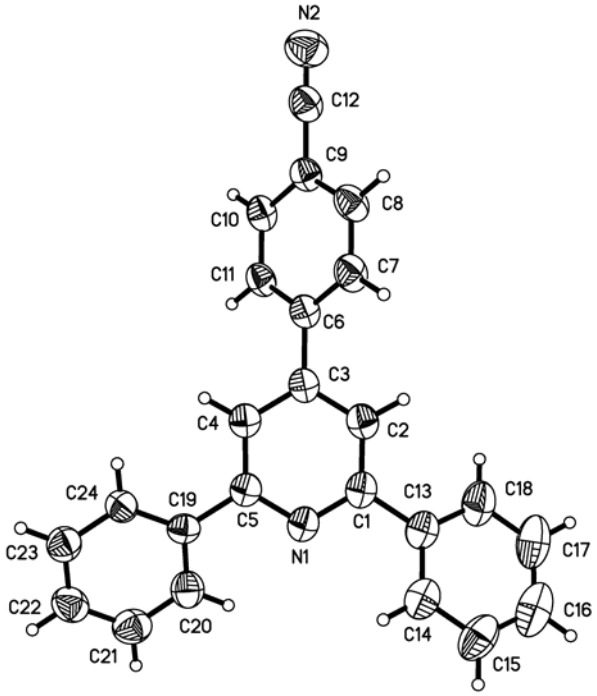
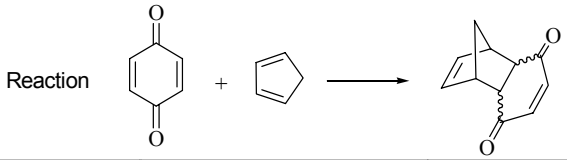


Fig. 1. X-ray crystal structure of **3z**

TABLE-2
CATALYZED FUNCTION OF PART PRODUCTS **3** ON A SIMPLE DIELS-ALDER REACTION



Catalyst	Time (min)	Yield (%)[a]
–	60	44.0
3a	62	72.1
3b	69	73.3
3c	65	70.8
3d	58	72.1
3e	55	73.2
3g	59	74.0
3h	66	71.9
3k	52	72.3
3l	60	71.9
3u	63	70.8

[a]Yields refer to those of pure isolated products fully characterized by spectral data.

Conclusion

This versatile new approach can be applied to the synthesis of a range of pyridines in general bearing aryl groups on the 2, 4 and 6-positions. The significance of present finding also relates to reducing the use of organic solvents as potentially toxic and hazardous materials, as well as its simplicity, mild conditions and inherent lower costs. Moreover, the findings are further credence to synthesize activated natural products and analogous natural products.

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