A Novel, Facile, Simple and Convenient Oxidative Aromatization of Hantzsch 1,4-Dihydropyridines to Pyridines Using Polymeric Iodosobenzene with KBr

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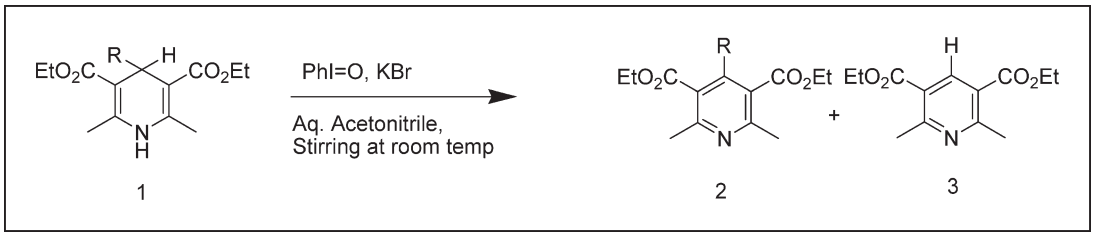

An easy, safe, effective and handy method for oxidative aromatization of Hantzsch 1,4-dihydropyridines catalyzed by hypervalent iodine (iodosobenzene) and potassium bromide to corresponding pyridine derivatives in high-yields and within short span of time was described. Dealkylation in case of 4-n-alkyl substituted 1,4-dihydropyridines was not obtained.

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INTRODUCTION

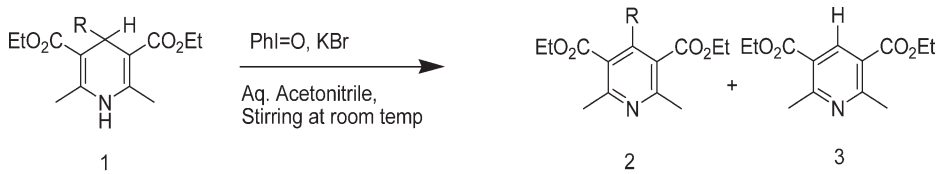
Hantzsch 1,4-dihydropyridines, six member nitrogen, containing heterocyclic compound, are often regarded as the class of the naturally reduced nicotinamine adenine dinucleotide [NADH] coenzyme that functions as redox reagent for biological reactions. 1,4-Dihydropyridines motif is found in a number of chemotherapeutic agents for the treatment of the cardiovascular disease [1,2] such as hypertension and angina pectoris, for example, amlodipine, felodipine, nifedipine, nicardipine, nimodipine, and nitrendipine. These compounds generally undergo oxidative metabolism in the liver by the action of cytochrome P450 to form the corresponding pyridine derivatives. Some representatives of this class show certain pharmacological activities such as acaricidal, insecticidal, bactericidal, and herbicidal activities [3]. Because of the relevance of this oxidative event to the biological NADH redox process [4–6], this transformation has attracted the attention of several research groups.

A variety of reagents have been utilized for this oxidative conversion: nitric acid [7], nitric oxide [8], urea nitrate [9], peroxodisulfate-Co(II) [9], clay-supported ferric and cupric nitrate[10], $BrCCl_3/h\nu$ [11], *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide [12], DDQ [13], $Zr(NO_3)_4$ [14], $Mn(OAc)_3$ [15], Pd/C [16], I_2/MeOH [17], manganese dioxide–bentonite clay [18], chromium trioxide [19], potassium permanganate [20], pyridinium chlorochromate [21], ceric ammonium nitrate (CAN) [22], clayfen [23], bismuth trinitrate [24], ruthenium trichloride [25], $Fe(ClO_4)_3$/HOAc [26], tert-butylhydroperoxide [27], silica gel supported ferric nitrate (silfen) [28], MnO_2 [29], and vanadium salts [30].

Despite a plethora of methods for this protocol, extended reaction times, poor yields and use of strong or toxic oxidant has led to the investigation of many alternative procedures. Therefore, development and introduction of convenient, milder, and efficient method for the oxidation of 1,4-dihydropyridines to the corresponding pyridines is of practical importance and is still in demand.

Iodosobenzene (PhIO) has wide synthetic application as a starting material in the preparation of numerous iodine (III) compounds and in oxidation reactions [31]. Because of poor solubility of polymerized iodosobenzene [(PhIO)n] in organic solvent, its oxidizing property is not much examined as compared with the other hypervalent organoiodanes. Activation is required to carryout the oxidation reaction with iodosobenzene. Literature review shows that the aromatization of Hantzsch 1,4-dihydropyridines by using hypervalent iodine (IBX, HTIB, PIFA, and IBD) has been reported earlier [32]. To my knowledge oxidative aromatization of 1,4-DHPs with iodosobenzene has not been reported in the literature. Although reported hypervalent iodine based aromatization of Hantzsch 1,4-dihydropyridines are efficient, but these methods suffer from relatively acidic by products [32], long reaction time[32(d)] and high-temperature [32(e)]. Therefore, the biological importance of 1,4-dihydropyridines oxidation and my ongoing attention to

Scheme 1



1 2 3

1. R= (a)H; (b) CH_3; (c)C_2H_5; (d) $(CH_3)_2CH$; (e)C_6H_{13}; (f)$C_6H_5CH_2$; (g)4-$NO_2C_6H_4$; (h) 3-$NO_2C_6H_4$; (i) 2-$NO_2C_6H_4$; (j) 4-$MeOC_6H_4$; (k) 3,4$(OCH_3)_2C_6H_3$; (l) 4-$CH_3C_6H_4$; (m) C_6H_5; (n)4-ClC_6H_4; (o)2,4-$Cl_2C_6H_3$; (p) 3-BrC_6H_4; (q)C_6H_5CH=CH; (r) 2-Furyl; (s) 3-Pyridyl

2. R= (a) CH_3; (b)C_2H_5; (c)C_6H_{13}; (d)4-$NO_2C_6H_4$; (e) 3-$NO_2C_6H_4$; (f) 2-$NO_2C_6H_4$; (g) 4-$MeOC_6H_4$; (h) 3,4$(OCH_3)_2C_6H_3$; (i) 4-$CH_3C_6H_4$; (j) C_6H_5; (k)4-ClC_6H_4; (l)2,4-$Cl_2C_6H_3$; (m) 3-BrC_6H_4; (n)C_6H_5CH=CH; (o) 2-Furyl; (p) 3-Pyridyl

the development of new methodology [32(b)], prompted me to investigate the aromatization of 1,4-DHPs by iodosobenzene with KBr in aqueous acetonitrile.

RESULTS AND DISCUSSION

A long series of 1,4-DHP derivatives were synthesized to study their catalytic conversion to the analogous pyridines. I used iodosobenzene with KBr as catalyst to have an effect on these organic transformations. Iodosobenzene with KBr serves as an excellent oxidative catalyst for a variety of 4-substituted Hantzsch 1,4-DHPs system as shown in the generalized Scheme 1 and results are reported in Table 1. In a preliminary experiment, oxidative aromatization 4-phenyl substituted 1,4-DHP was carried out using iodosobenzene in aqueous acetonitrile at room temperature. It gave none or insignificant amount of the corresponding pyridine. However, when KBr is added in the reaction mixture, there is recognizable change in the yield of the oxidized product. The reaction is fast and gives quantitative yield. Reaction was smooth, clean, and occurred at room temperature with short span of time (less than 5 min). Therefore, I investigated the activation of PhI=O in this reaction with a variety of alkali metal salts. As a result, the addition of bromide ions such as LiBr, NaBr, and KBr was found to amazingly activate PhI=O to give **2e** in good yields [95% yield with KBr, 75% yield with NaBr and 62% with LiBr], whereas salts excluding bromide (LiCl, NaCl, KCl, NaF, NaOAc, NaI and KI) did not catalyze the reaction effectively. Therefore, the most economical alkali metal bromide, that is, KBr was chosen for further studies. The oxidation proceeds smoothly

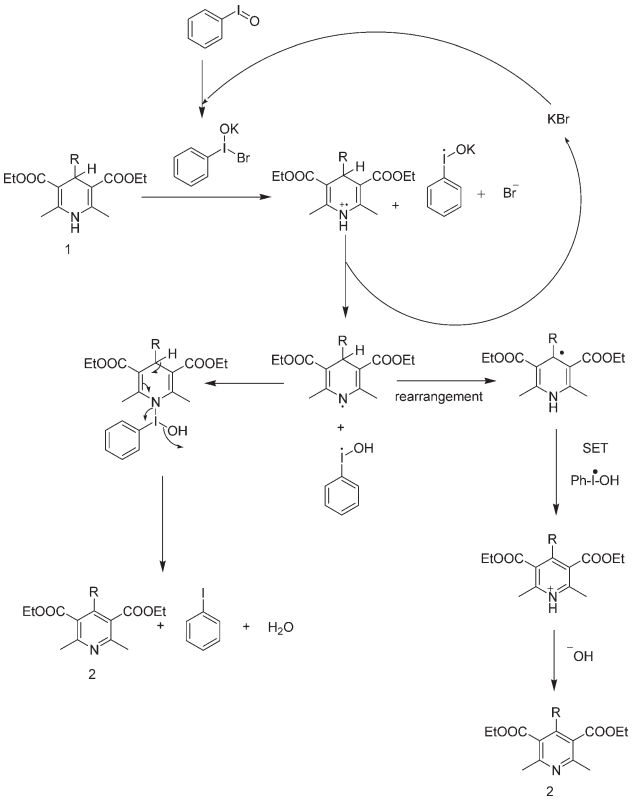
Table 1

Solvent-less synthesis of pyridines by oxidative aromatization or oxidative dealkylation of 1,4-DHP derivatives.

Entry	Substrate R	Product	Reaction Time[a] t (min)	Yield[b] (%)	*M*p[c] (°C)	*M*p reported (°C)
1	H	3	3	94	70 – 71	72-73
2	CH_3	2a	3	95	oil	oil
3	C_2H_5	2b	3	95	oil	oil
4	$(CH_3)_2CH$	3	3	94	70 – 71[d]	72 – 73
5	C_6H_{13}	2c	5	93	oil	oil
6	$C_6H_5CH_2$	3	4	95	70 – 71[d]	72 – 73
7	4-$NO_2C_6H_4$	2d	5	94	112 – 113	115 – 116
8	3-$NO_2C_6H_4$	2e	5	93	61 – 62	61.5 – 62.5
9	2-$NO_2C_6H_4$	2f	5	95	73 – 75	73 – 75
10	4-$MeOC_6H_4$	2g	4	94	51 – 52	49.5 – 50.5
11	3,4$(OCH_3)_2C_6H_3$	2h	4	91	100 – 101	100 – 101
12	4-$CH_3C_6H_4$	2i	4	94	71 – 72	71 – 72
13	C_6H_5	2j	4	95	62 – 63	62 – 63
14	4-ClC_6H_4	2k	4	95	69 – 71	66 – 68
15	2,4-$Cl_2C_6H_3$	2l	5	95	112 – 113	77.5 – 79.5
16	3-BrC_6H_4	2m	5	95	70 – 72	70 – 72
17	C_6H_5CH=CH	2n	5	93	161 – 162	161 – 162
18	2-Furyl	2o	5	92	oil	oil
19	3-Pyridyl	2p	5	92	84 – 86	84 – 86

[a] t: time for stirring.
[b] Yields are isolated.
[c] Melting points are uncorrected and compared with literature reports [32].
[d] Amount of KBr used in reaction is equivalent to iodosobenzene.

Scheme 2. Proposed mechanism for aromatization of 1,4-DHPs.



with 1,4-dihydropyridine substrates bearing substituents at the 4-position such as hydrogen, methyl, n-alkyl, aryl, and heterocyclic groups. However, in the case of oxidation of the 1,4-DHP with isopropyl and benzyl group at 4-poition underwent simultaneous dealkylation to give **3** as a sole product (Table 1). This may be because of either their electron donating ability of the corresponding radicals and these substituents are debarred with the formation of dealkylated products [15] or because of the stability of radical cation formed during the reaction via single electron mechanism [32(a)] (Scheme 2). The influence of various solvents on the yield of reaction was investigated using ethyl acetate, dichloromethane, chloroform, and aqueous acetonitrile. The reaction takes place smoothly in the aqueous acetonitrile may be because of solubility of iodosobenzene and KBr.

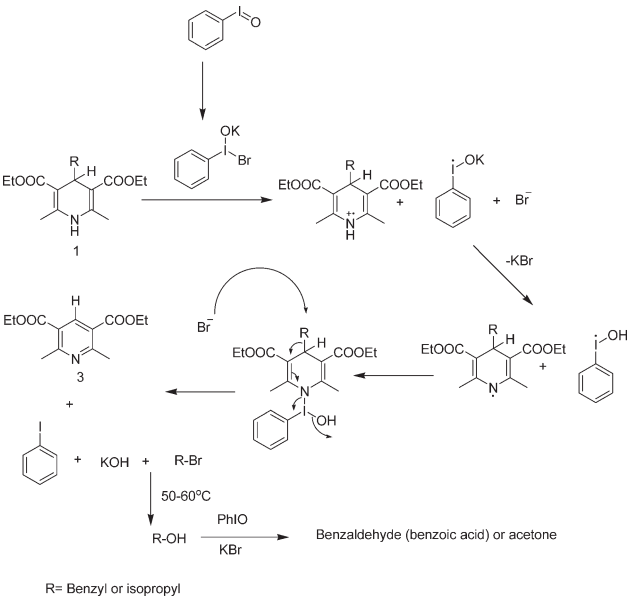
After that catalytic effect of KBr was investigated, and it was found that only 0.1 mmol of KBr is sufficient for 1.1 mmol of iodosobenzene (Scheme 3). However, in case of the 1,4-DHP with isopropyl and benzyl group at 4-poition oxidation depend upon the amount of KBr also as shown in Scheme 3. This is because of formation of isopropyl or benzyl bromide, and it is confirmed by GC. However, reaction mixture was found basic in nature and turn red litmus to blue when the reaction was carried out at 0°C. It is also observed that, when the temperature is raised to 60°C the reaction proceeds smoothly with catalytically amount of KBr (0.1 mmol). However, at elevated temperature, time required for these organic transformations is very short, but the amount of iodosobenzene required for this conversion is doubled. This is because of hydrolysis of benzyl bromide or isopropyl bromide with water to benzyl alcohol or isopropyl alcohol, which is oxidized to corresponding carbonyl derivatives.

In summary author have described a general and practical route for the oxidation of 1,4-dihydropyridines in excellent yields using catalytic amount KBr with iodosobenzene in aqueous acetonitrile. Aromatization is clean with this reagent, and the products are obtained in high-yield within short span of time. Novelty of this protocol is the reagents used in reaction are recovered as iodobenzene and KBr, which can be reused. Another salient feature of this method is that any acidic byproducts are not produced during reactions, which are toxic to the environment.

EXPERIMENTAL

All chemicals used in this study were of the highest purity available and purchased from Lancaster, Merck, and Fluka companies (India). Melting points were determined on a buchi oil heated melting apparatus and are uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ on Brucker-300 Hz spectrometer using TMS as internal standard (chemical shift in δ, ppm). IR spectra were taken on a Perkin Elmer 1600, FTIR spectrophotometer using KBr pellets and peaks are reported in cm^{-1}. All the starting 1, 4-DHPs were prepared according to the literature procedure [33].

Scheme 3. Proposed mechanism for debenzylation or dealkylation.



General procedure for oxidative aromatization of 1,4-dihydropyridines with iodosobenzene and KBr. In a typical experimental procedure, the iodosobenzene (1.1 mmol) and KBr (0.1 mmol) were added to aqueous acetonitrile (15%, 20 mL), and mixture was stirred at room temperature for 5 min. To this reaction mixture an appropriate 1,4-dihydropyridine (1.0 mmol) was added and stirred at room temperature for time as indicated in Table 1. The progress of reaction was monitored by TLC. After completion of the reaction and the solvent was removed under vacuum to obtain the crude product, which was purified by column chromatography (ethyl acetate-hexane = 1:5).

General procedure for oxidative aromatization of 4-isopropyl/4-benzyl-1,4-dihydropyridines. The iodosobenzene (1.1 mmol) and KBr (1.1 mmol) were added to aqueous acetonitrile (15%, 20 mL), and mixture was stirred at room temperature for 5 min. Then 4-isopropyl/4-benzyl-1,4-dihydropyridines (1.0 mmol) was added and reaction mixture was stirred at room temperature for time indicated in Table 1. The progress of reaction was monitored by TLC. After completion of the reaction, added acetic acid (1 mL) and the solvent was removed under vacuum to obtain the crude product, which was purified by column chromatography (ethyl acetate-hexane = 1:7).

All compounds were fully characterized by mp, IR, and ^{1}H NMR. These data are in full agreement with those previously reported in literature [32].

Diethyl 2,6-dimethyl-4-methylpyridine-3,5-dicarboxylate (2a). IR (KBr): 2981, 2870, 1726, 1568, 1446, 1285, 1220, 1106, 1045, 871, 777 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.23 (t, J = 7.10 Hz, 6H, CH_3), 2.19 (s, 3H, CH_3), 2.51 (s, 6H, CH_3), 4.25 (q, J = 7.10 Hz, 4H, OCH_2). Anal. Calcd. for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28. Found: C, 63.23; H, 7.32; N, 5.01.

Diethyl 2,6-dimethyl-4-ethylpyridine-3,5-dicarboxylate (2b). IR (KBr): 2992, 2879, 1731, 1576, 1438, 1286, 1112, 1045, 923, 847, 751 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.08 (t, J = 7.5 Hz, 3H, CH_3), 1.25 (t, J = 7.11 Hz, 6H, CH_3), 2.49 (s, 6H, CH_3), 2.78(q, J = 7.5 Hz, 2H, CH_2), 4.25 (q, J = 7.11 Hz, 4H, OCH_2). Anal. Calcd. for $C_{15}H_{21}NO_4$: C, 64.50; H, 7.58; N, 5.01. Found: C, 64.78; H, 7.78; N, 4.94.

Diethyl 2,6-dimethyl-4-n-hexylpyridine-3,5-dicarboxylate (2c). IR (KBr): 2976, 2865, 1737, 1576, 1428, 1286, 1117, 1033, 926, 842, 755 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.06 (t, J = 6.9 Hz, 3H, CH_3), 1.26 (t, J = 7.10 Hz, 6H, CH_3), 1.33 – 1.43 (m, 8H), 2.49 (s, 6H, CH_3), 2.54 (t, J = 6.9Hz, 2H, CH_2), 4.25 (q, J = 7.11 Hz, 4H, OCH_2). Anal. Calcd. for $C_{19}H_{29}NO_4$: C, 68.03; H, 8.71; N, 4.18. Found: C, 67.98; H, 8.78; N, 4.27.

Diethyl-4-(4-nitrophenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (2d). IR (KBr): 3012, 2977, 1723, 1557, 1518, 1349, 1116, 865, 843, 745 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.20 (t, J = 7.10 Hz, 6H, CH_3), 2.69 (s, 6H, CH_3), 4.27 (q, J = 7.10 Hz, 4H, OCH_2), 7.41(d, J = 8.2 Hz, 2H), 8.22 (d, J = 8.2 Hz, 2H). Anal. Calcd. for $C_{19}H_{20}N_2O_6$: C, 61.29; H, 5.41; N, 7.53. Found: C, 61.31; H, 5.36; N, 7.50.

Diethyl-4-(3-nitrophenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (2e). IR (KBr): 3015, 2980, 1716, 1590, 1555, 1520, 1358, 1280, 1183, 870, 785, 715 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.21 (t, J = 7.11 Hz, 6H, CH_3), 2.70 (s, 6H, CH_3), 4.25 (q, J = 7.11 Hz, 4H, OCH_2), 7.58 – 8.28 (m, 4H). Anal. Calcd. for $C_{19}H_{20}N_2O_6$: C, 61.29; H, 5.41; N, 7.53. Found: C, 61.15; H, 5.49; N, 7.33.

Diethyl-4-(2-nitrophenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (2f). IR (KBr): 3005, 2983, 1725, 1605, 1548, 1512, 1358, 1278, 1191, 762, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.19 (t, J = 7.11 Hz, 6H, CH_3), 2.70 (s, 6H, CH_3), 4.28 (q, J = 7.11 Hz, 4H, OCH_2), 7.48 – 8.25 (m, 4H). Anal. Calcd. for $C_{19}H_{20}N_2O_6$: C, 61.29; H, 5.41; N, 7.53. Found: C, 61.08; H, 5.22; N, 7.63.

Diethyl-4-(4-methoxyphenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (2g). IR (KBr): 3030, 2973, 1729, 1614, 1557, 1291, 1107, 857, 835, 779 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.20 (t, J = 7.12 Hz, 6H, CH_3), 4.25 (q, J = 7.12 Hz, 4H, OCH_2), 2.66 (s, 6H, CH_3), 3.82 (s, 3H, OCH_3), 6.89 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H). Anal. Calcd. for $C_{20}H_{23}NO_5$: C, 67.21; H, 6.49; N, 3.92. Found: C, 67.05; H, 6.40; N, 3.88.

Diethyl-4-(4-methylphenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (2i). IR (KBr): 3013, 2983, 1727, 1571, 1446, 1239, 1033, 821, 856, 775 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.23 (t, J = 7.12 Hz, 6H, CH_3), 2.37 (s, 3H, CH_3), 2.64 (s, 6H, CH_3), 4.29 (q, J = 7.12 Hz, 4H, OCH_2), 7.11(d, J = 6.8 Hz, 2H), 7.21 (d, J = 6.8 Hz, 2H). Anal. Calcd. for $C_{20}H_{23}NO_4$: C, 70.36; H, 6.79; N, 4.10. Found: C, 70.23; H, 6.56; N, 4.33.

Diethyl-4-phenyl-2,6-dimethylpyridine-3,5-dicarboxylate (2j). IR (KBr): 3014, 2986, 1723, 1591, 1498, 1302, 1250, 1170, 791, 760 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.23 (t, J = 7.12 Hz, 6H, CH_3), 4.26 (q, J = 7.12 Hz, 4H, OCH_2), 2.65 (s, 6H, CH_3), 7.18(m, 2H), 7.30 (m, 3H). Anal. Calcd. for $C_{19}H_{21}NO_4$: C, 69.71; H, 6.47; N, 4.28. Found: C, 69.83; H, 6.38; N, 4.32.

Diethyl-4-(4-chlorophenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (2k). IR (KBr): 3025, 2984, 1729, 1580, 1231, 1104, 1044, 858, 658 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.24 (t, J = 7.12 Hz, 6H, CH_3), 4.27 (q, J = 7.12 Hz, 4H, OCH_2), 2.69 (s, 6H, CH_3), 7.13(d, J = 9.01 Hz, 2H), 7.32 (d, J = 9.01 Hz, 2H). Anal. Calcd. for $C_{19}H_{20}ClNO_4$: C, 63.07; H, 5.57; N, 3.87. Found: C, 62.97; H, 5.44; N, 4.03.

Diethyl-4-(2, 4-dichlorophenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (2l). IR (KBr): 3008, 2986, 1730, 1560, 1480, 1280, 1228, 1108, 856, 775, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.23 (t, J = 7.13 Hz, 6H, CH_3), 4.33 (q, J = 7.13 Hz, 4H, OCH_2), 2.67 (s, 6H, CH_3), 7.15–7.42 (m, 3H). Anal. Calcd. for $C_{19}H_{19}Cl_2NO_4$: C, 57.59; H, 4.83; N, 3.53. Found: C, 57.77; H, 5.00; N, 3.49.

Diethyl-4-(3-bromophenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (2m). IR (KBr): 3026, 2986, 1726, 1561, 1278, 1230, 1108, 1035, 865, 787, 698 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.22 (t, J = 7.11 Hz, 6H, CH_3), 4.31 (q, J = 7.11 Hz, 4H, OCH_2), 2.66 (s, 6H, CH_3), 7.20 – 7.44 (m, 4H). Anal. Calcd. for $C_{19}H_{20}BrNO_4$ C, 56.17; H, 4.96; N, 3.45. Found: C, 56.30; H, 5.10; N, 3.27.

Diethyl 2,6-dimethylpyridine-3,5-dicarboxylate (3). IR (KBr): 2974, 1721, 1588, 1555, 1298, 1254, 1123, 1022, 777 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.35 (t, J = 7.11 Hz, 6H, CH_3), 2.74 (s, 6H, CH_3), 4.28 (q, J = 7.11 Hz, 4H, OCH_2). Anal. Calcd. for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 61.92; H, 7.02; N, 5.44.

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