Synthesis Z. Lu et al. Paper

Photoinduced Aromatization of Dihydropyridines

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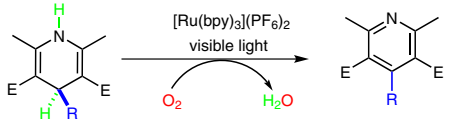
Dedicated to Professor Xiyan Lu on the occasion of his 88th birthday



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Abstract The combination of tris(bipyridine)ruthenium(II)/visible light/air is found to be effective for the aromatization of many dihydropyridines. A low catalyst loading of just 0.02 mol% is required.

Key words aromatization, dihydropyridines, photoredox, Hantzsch esters, oxidation

The dihydropyridine moiety is a structure of much interest and is a constituent of the cofactors NADH (**1a**) and NADPH (**1b**) (Figure 1).[1] Besides these naturally occurring compounds, many dihydropyridines serve as antihypertensive agents as a result of their ability to block calcium channels.[2] Understanding the oxidation of these compounds is of great importance, with the literature on oxidations of dihydropyridines being extensive. Among these reports, oxidation with strong oxidants appears most frequently. Many commonly used oxidants can be found in this arena: chromates,[3] nitrates,[4] ferric chloride,[5] cupric bromide,[6] high-valent iodine,[7] hydrogen peroxide,[8] peroxodisulfate,[9] and ceric ammonium nitrate.[10] Electrochemical oxidation[11] and aerobic oxidation[12] have also been reported. Environmentally benign methods with sodium chlorite[13] and graphite oxide[14] are both noteworthy contributions.

In aerobic reactions, less waste is produced as the oxidant and its product pose no harm to the environment. However, the following reported methods would benefit from improvement: the ruthenium-[12a] and flavin-catalyzed[12d] methods require pure oxygen as the oxidant, the UV-induced oxidation[12c] used a 500 W mercury lamp and an oxygen-saturated solvent in a diluted solution (0.01 mol/L), while the palladium-catalyzed reaction works under heating.[12b] We are currently looking for a system with

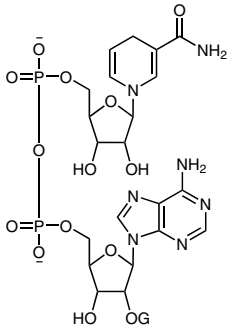


Figure 1 Structures of NADH and NADPH

which the oxidation of dihydropyridines would occur easily. There are some papers describing the photocatalytic reactions using a Hantzsch ester as the reductive quencher.[15] We envisaged that this might be a good starting point for us to study the oxidation of different dihydropyridines.

So we started our investigation of the oxidation catalyzed by tris(bipyridine)ruthenium(II) in the presence of light. In our previous work, it was found that the Hantzsch ester was almost insoluble in methanol while the oxidation product was soluble.[16] Thus we tried to use methanol as the solvent, with 1 mol% of tris(bipyridine)ruthenium(II) hexafluorophosphate under a blue light-emitting diode (LED).[17] The reaction was complete in two hours and offered a quantitative transformation. In contrast, irradiation without the ruthenium salt overnight produced no pyridine product. However, the solubility of the ruthenium salt in methanol was poor. We reduced the catalyst loading to 0.1 mol% and found that the reaction was complete over the same period. With this exiting result in hand, we next explored the substrate scope. The second compound we test-

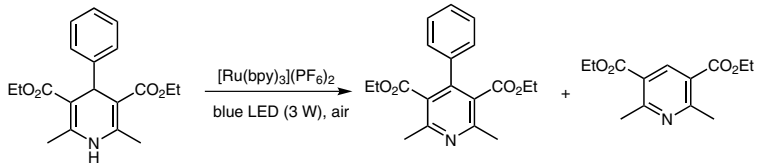
ed was diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (**2b**). To our disappointment, the desired product **3b** was produced along with a significant quantity of the 4-dearylated product **3a** (see Table 1). With the hope that there might be a solvent more suitable for this reaction, an array of solvents was tested.

Firstly, we used the same conditions as those employed with ethidine (**2a**), and the reaction was sluggish while a significant amount of the dearylated product was detected (Table 1, entry 1). An increase of the catalyst loading led to higher yield and shorter reaction time, however, these conditions were still unsatisfactory (Table 1, entry 2). Employing a 0.5 mol% catalyst loading, we tested some commonly used solvents (Table 1, entries 2–8). Most of the tested solvents proved to be capable as the reaction medium, but the solubility of the ruthenium in toluene was so low that no reaction occurred in 24 hours. Among the solvents tested, acetic acid seemed to be the best, although the reaction time was longer than most of the other solvents. Despite the fact that the reaction could occur in acetic acid, it was found that some of the crystalline catalyst remained undissolved, so the actual catalyst loading might be lower than 0.5 mol%. The ruthenium salt was dissolved in acetonitrile and added to the reaction vessel as a 2 mg/mL solution. With only a 0.1 mol% catalyst loading (Table 1, entry 9), the reaction was finished in just one day, but the yield decreased. When the catalyst loading was reduced further to 0.02 mol% (Table 1, entry 10), the reaction yield increased markedly although the reaction time became longer.

Having optimized the reaction conditions, we started to scan the substrate scope (Table 2).

Some easily obtained dihydropyridines were subjected to the reaction conditions. Dihydropyridines without 4-substituents gave the best results (Table 2, entries 1 and 10). The presence of a small alkyl group in the reaction did not affect the reaction yield (Table 2, entries 7 and 15), but the yield decreased as the alkyl group became more hindered (Table 2, entries 7–9). A low yield of the desired product was obtained when an isopropyl was introduced at C-4 (Table 2, entry 9). For aryl-substituted compounds, electron-donating or electron-withdrawing groups were tolerated, although the yield decreased a little bit. However, a furyl group affected the yield greatly. Most of the tested compounds gave the desired products, except for nifedipine (**2**, R^1, R^2 = CO_2Me, R^3 = 2-$O_2NC_6H_4$) which was transformed into dimethyl 2,6-dimethyl-4-(2-nitrosophenyl)pyridine-3,5-dicarboxylate (**4**) (see the experimental section). The nitro group was reduced by intramolecular dihydropyridine. As described in the literature,[18] this behavior was dif-

Table 1 Oxidation of 4-Phenyl Hantzsch Ester **2b**[a]



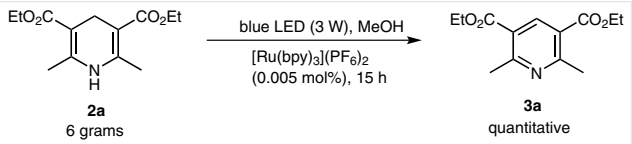
2b **3b** **3a**

Entry	Solvent	Cat. (mol%)	Time (h)[b]	Yield of **3b** (%)[c]
1	MeOH	0.1[d]	18[g]	9 + 15 (**3a**)
2	MeOH	0.5[d]	8[g]	20 + 27 (**3a**)
3	MeCN	0.5[d]	24[g]	17 + 15 (**3a**)
4	CH_2Cl_2	0.5[d]	17	40 + 51 (**3a**)
5	toluene	0.5[e]	24	32 + 45 (**3a**)
6	NMP	0.5[d]	34	20 + 72 (**3a**)
7	THF	0.5[d]	120	48 + 33 (**3a**)
8	AcOH	0.5[d]	72	74
9	AcOH	0.1[f]	24	66
10	AcOH	0.02[f]	38	87

[a] To a mixture of compound **2b** (1.2 mmol) in solvent (4 mL) was added the catalyst. The mixture was then irradiated with a 3 W blue LED.
[b] TLC indicated that compound **2b** had been consumed.
[c] Yield of isolated products.
[d] Solid catalyst was added.
[e] Acetonitrile (1 mL) was added to help dissolution of the catalyst.
[f] The catalyst was added as a solution in acetonitrile (2 mg/mL).
[g] The reaction was worked up as a significant amount of compound **3a** had been produced.

ferent from compounds with a nitro group at the 3-position of the aromatic ring; this reaction could happen without the ruthenium salt, however, irradiation was necessary.[19]

The reaction is found to be scalable. As compound **3a** is required as the starting material in our further studies, the oxidation of compound **2a** in a more concentrated solution with a lower catalyst loading was carried out. For compound **2a**, the concentration could be as high as 2 mol/L and the catalyst loading went down to 0.005 mol%. After filtration through silica and concentration, pure product was obtained quantitatively (Scheme 1).

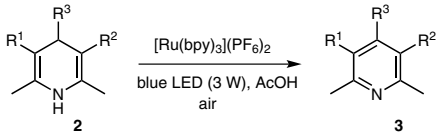


Scheme 1 Scale-up of the oxidation

In the reaction, ruthenium species at different oxidation states act as the electron transporter to facilitate the reaction. Tris(bipyridine)ruthenium(II) is activated by photoirradiation. This exited ruthenium(II) abstracts one electron from the Hantzsch ester to produce a radical cation of the Hantzsch ester and ruthenium(I). The ruthenium(I) is oxidized by oxygen to generate a superoxide anion and ruthenium(II). The superoxide anion then reacts with the radical cation to give the pyridine product and hydrogen peroxide (Scheme 2).

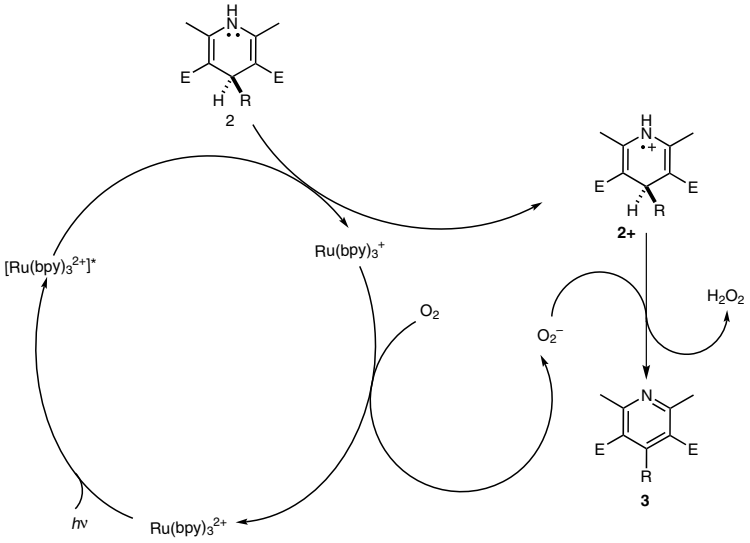
It is stated that hydrogen peroxide is stable when in contact with a Hantzsch ester in the absence of a catalyst or energy input.[8b,12c] However, a control experiment showed

Table 2 Oxidation of Different Hantzsch Esters[a]



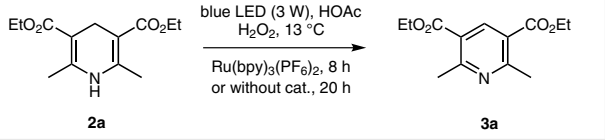
Entry	R^1, R^2	R^3	Yield (%)[b]
1	CO_2Et, CO_2Et	H	quant. (**3a**)
2	CO_2Et, CO_2Et	Ph	87 (**3b**)
3	CO_2Et, CO_2Et	2-furyl	30 (**3c**)
4	CO_2Et, CO_2Et	4-$MeOC_6H_4$	85 (**3d**)
5	CO_2Et, CO_2Et	3-$O_2NC_6H_4$	70 (**3e**)
6	CO_2Et, CO_2Me	3-$O_2NC_6H_4$	74 (**3f**)
7	CO_2Et, CO_2Et	Me	93 (**3g**)
8	CO_2Et, CO_2Et	*i*-Bu	72 (**3h**)
9	CO_2Et, CO_2Et	*i*-Pr	34 (**3i**)
10	Ac, Ac	H	95 (**3j**)
11	Ac, Ac	Ph	74 (**3k**)
12	Ac, Ac	2-furyl	50 (**3l**)
13	Ac, Ac	4-$MeOC_6H_4$	65 (**3m**)
14	Ac, Ac	3-$O_2NC_6H_4$	63 (**3n**)
15	Ac, Ac	Me	90 (**3o**)
16	Ac, Ac	*i*-Bu	78 (**3p**)

[a] To a mixture of compound **2** (1.2 mmol) in AcOH (4 mL) was added the catalyst (2 mg/mL in MeCN, 100 μL). The mixture was then irradiated with a 3 W blue LED until TLC showed that compound **2** had been consumed.
[b] Yield of isolated product.



Scheme 2 A plausible mechanism with H_2O_2 produced

that hydrogen peroxide (1.5 equiv) under irradiation with or without tris(bipyridine) ruthenium(II) (under a nitrogen atmosphere) could oxidize a Hantzsch ester, albeit the reaction was slower (Scheme 3). We were curious to find out what the reduction product of oxygen was. A hydrogen peroxide test strip was used to determine the concentration of hydrogen peroxide. A test after 15 minutes showed a positive reaction. From one hour to the end of the reaction the concentration was about 7 µmol/mL (about one fortieth the amount of compound **3a**), which indicated that most of the hydrogen peroxide produced in the reaction was consumed. According to data from the literature,[20] the oxygen concentration in air-saturated acetic acid is about 1.4 µmol/mL. This concentration difference shows the difference in the reactive ability of these two species. Hence, most of the hydrogen peroxide produced in the reaction should also be consumed during the reaction. The corresponding catalytic cycle is shown in Scheme 4.



2a 3a

Scheme 3 Oxidation with H_2O_2 as the oxidant

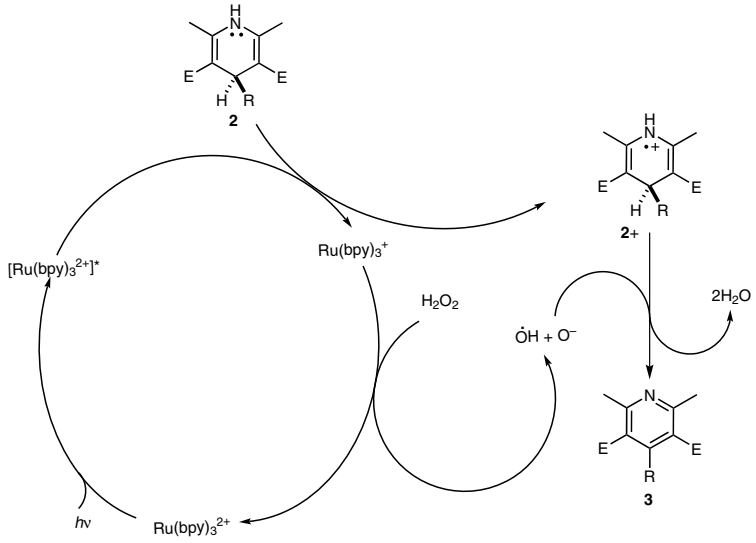
Hydrogen peroxide accepts one electron from $[Ru(bpy)_3]^+$ to produce a hydroxyl radical and a hydroxide anion. These two species then abstract one hydrogen atom and one proton from the radical cation to produce the product.

In conclusion, it has been found that the combination of tris(bipyridine)ruthenium(II)/blue light/air serves as an oxidizing system for the aromatization of 1,4-dihydropyridine compounds. Oxygen can be reduced to hydrogen peroxide, although only a trace amount of peroxide was left intact. Most of the tested compounds with aromatic and aliphatic substituents at position 4 gave give good to excellent yields, although the presence of isopropyl or 2-furyl groups led to dramatically decreased yields. As the catalyst loading is just 0.02 mol%, this could widely expand the use of tris(bipyridine)ruthenium(II). The reaction could be easily scaled up with modifications that favor larger scale reactions.

Flash chromatography was performed with Hailang silica gel (200–300 mesh). Melting points were recorded on a WRS-1B digital melting point recorder from Shanghai Precision Scientific Instrument Corporation. Infrared spectra were recorded on a Nicolet Avatar 370 DTGS spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker AV500 or a Varian 400MR spectrometer. The mass spectra were run using a Thermo LXQ linear ion trap mass spectrometer.

Oxidation; General Procedure

To a suspension of the dihydropyridine (1.20 mmol) in AcOH (4 mL) was added tris(bipyridine)ruthenium(II) hexafluorophosphate (0.1 mL, 2 mg/mL in MeCN). This mixture was then irradiated with a blue LED light (3 W, Wanhui WH-CS) in a water bath at 15 °C until TLC showed that the substrate had been consumed. The solution was then diluted with H_2O (20 mL) and extracted with MTBE (3 × 20 mL). The combined organic phase was washed with sat. aq $NaHCO_3$ solution (3 × 10 mL) and brine (10 mL). The dried organic phase was concentrated and subjected to flash chromatography to give the pyridine product.



Scheme 4 A plausible mechanism with H_2O_2 as the oxidant

Diethyl 2,6-Dimethylpyridine-3,5-dicarboxylate (3a)[12b]

White solid; yield: 298 mg, 1.18 mmol (quant.); mp 72.8–73.5 °C (Lit.[12b] 71–72 °C).

IR (KBr): 2962, 1728, 1567 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.42 (t, *J* = 7.0 Hz, 6 H), 2.85 (s, 6 H), 4.40 (q, *J* = 7.0 Hz, 4 H), 8.67 (s, 1 H).

MS (ESI): *m*/*z* = 252.2 $[M + 1]^+$.

Diethyl 2,6-Dimethyl-4-phenylpyridine-3,5-dicarboxylate (3b)[12b]

Light yellow solid; yield: 305 mg, 0.93 mmol (87%); mp 58.0–59.2 °C (Lit.[12b] 60–61 °C).

IR (KBr): 2981, 1720, 1560 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.0 Hz, 6 H), 2.60 (s, 6 H), 4.00 (q, *J* = 7.0 Hz, 4 H), 7.24–7.25 (m, 2 H), 7.35–7.37 (m, 3 H).

MS (ESI): *m*/*z* = 328.3 $[M + 1]^+$.

Diethyl 2,6-Dimethyl-4-(2-furyl)pyridine-3,5-dicarboxylate (3c)[9]

Colorless liquid; yield: 105 mg, 0.33 mmol (30%).

IR (KBr): 2982, 1731, 1562 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.23 (t, *J* = 7.0 Hz, 6 H), 2.58 (s, 6 H), 4.28 (q, *J* = 7.0 Hz, 4 H), 6.48 (dd, *J* = 3.5, 1.5 Hz, 1 H), 6.63 (d, *J* = 3.5 Hz, 1 H), 7.50 (d, *J* = 1.5 Hz, 1 H).

MS (ESI): *m*/*z* = 318.3 $[M + 1]^+$.

Diethyl 2,6-Dimethyl-4-(4-methoxyphenyl)pyridine-3,5-dicarboxylate (3d)[8d]

Light yellow oil; yield: 349 mg, 0.98 mmol (85%).

IR (KBr): 2981, 1728, 1557 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.99 (t, *J* = 7.0 Hz, 6 H), 2.59 (s, 6 H), 3.82 (s, 3 H), 4.05 (q, *J* = 7.0 Hz, 4 H), 6.89 (d, *J* = 8.5 Hz, 2 H), 7.19 (d, *J* = 8.5 Hz, 2 H).

MS (ESI): *m*/*z* = 358.4 $[M + 1]^+$.

Diethyl 2,6-Dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (3e)[9]

Light yellow oil; yield: 277 mg, 0.74 mmol (70%).

IR (KBr): 2982, 1728, 1534 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.00 (t, *J* = 7.0 Hz, 6 H), 2.64 (s, 6 H), 4.06 (q, *J* = 7.0 Hz, 4 H), 7.56–7.62 (m, 2 H), 8.19 (t, *J* = 1.5 Hz, 1 H), 8.26 (dt, *J* = 7.5, 2.0 Hz, 1 H).

MS (ESI): *m*/*z* = 373.4 $[M + 1]^+$.

2,6-Dimethyl-3-ethoxycarbonyl-5-methoxycarbonyl-4-(3-nitrophenyl)pyridine (3f)[21]

Light yellow oil; yield: 315 mg, 0.88 mmol (74%).

IR (KBr): 2954, 1728, 1534 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.00 (t, *J* = 7.0 Hz, 3 H), 2.62 (s, 3 H), 2.64 (s, 3 H), 3.58 (s, 3 H), 4.06 (q, *J* = 7.0 Hz, 2 H), 7.58–7.59 (m, 2 H), 8.17–8.18 (m, 1 H), 8.25–8.27 (m, 1 H).

MS (ESI): *m*/*z* = 358 $[M]^+$, 341 (100), 327, 313.

Diethyl 2,4,6-Trimethylpyridine-3,5-dicarboxylate (3g)[12b]

Colorless liquid; yield: 286 mg, 1.08 mmol (93%).

IR (KBr): 2982, 1728, 1570 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.36 (t, *J* = 7.2 Hz, 6 H), 2.25 (s, 3 H), 2.50 (s, 6 H), 4.38 (q, *J* = 7.2 Hz, 4 H).

MS (ESI): *m*/*z* = 266.3 $[M + 1]^+$.

Diethyl 2,6-Dimethyl-4-isobutylpyridine-3,5-dicarboxylate (3h)[22]

Colorless liquid; yield: 241 mg, 0.78 mmol (72%).

IR (KBr): 2961, 1720, 1561 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.85 (d, *J* = 6.4 Hz, 6 H), 1.39 (t, *J* = 7.2 Hz, 6 H), 1.75–1.86 (m, 1 H), 2.51 (s, 6 H), 2.59 (d, *J* = 7.6 Hz, 2 H), 4.40 (q, *J* = 7.2 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.6, 23.0, 29.6, 39.4, 61.6, 127.7, 146.0, 155.0, 168.6.

MS (ESI): *m*/*z* = 308.8 $[M + 1]^+$.

Diethyl 2,6-Dimethylpyridine-4-isopropyl-3,5-dicarboxylate (3i)[23]

Light yellow oil; yield: 113 mg, 0.38 mmol (34%).

IR (KBr): 2978, 1728, 1571 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.26 (d, *J* = 6.4 Hz, 6 H), 1.38 (t, *J* = 7.2 Hz, 3 H), 1.39 (t, *J* = 7.2 Hz, 3 H), 2.24 (s, 3 H), 2.52 (s, 3 H), 2.98 (sept, *J* = 6.8 Hz, 1 H), 4.40 (q, *J* = 7.2 Hz, 2 H), 4.41 (q, *J* = 7.2 Hz, 2 H).

MS (ESI): *m*/*z* = 294.4 $[M + 1]^+$.

3,5-Diacetyl-2,6-dimethylpyridine (3j)[22]

White solid; yield: 212 mg, 1.11 mmol (95%); mp 69.6–69.9 °C (recrystallized from CH_2Cl_2–PE, 1:10) (Lit.[22] 64–65 °C).

IR (KBr): 2928, 1686, 1585 cm^{-1}.

^1H NMR (400 MHz, CD_3OD): δ = 2.65 (s, 6 H), 2.70 (s, 6 H), 8.53 (s, 1 H).[24]

MS (ESI): *m*/*z* = 192.2 $[M + 1]^+$.

3,5-Diacetyl-2,6-dimethyl-4-phenylpyridine (3k)[25]

White solid; yield: 225 mg, 0.84 mmol (74%); mp 189.0–189.4 °C (Lit.[25] 185–186 °C).

IR (KBr): 2925, 1692, 1547 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.88 (s, 6 H), 2.52 (s, 6 H), 7.23–7.25 (m, 2 H), 7.43–7.44 (m, 3 H).

MS (ESI): *m*/*z* = 268.2 $[M + 1]^+$.

3,5-Diacetyl-2,6-dimethyl-4-(2-furyl)pyridine (3l)[9]

Light yellow oil; yield: 157 mg, 0.61 mmol (50%).

IR (KBr): 2926, 1701, 1552 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.14 (s, 6 H), 2.50 (s, 6 H), 6.53 (dd, *J* = 3.6, 1.6 Hz, 1 H), 6.58 (d, *J* = 3.6 Hz, 1 H), 7.58 (d, *J* = 1.6 Hz, 1 H).

MS (ESI): *m*/*z* = 258.2 $[M + 1]^+$.

3,5-Diacetyl-2,6-dimethyl-4-(4-methoxyphenyl)pyridine (3m)[25]

Light yellow solid; yield: 238 mg, 0.80 mmol (65%); mp 157.4–158.2 °C (Lit.[25] 164–165 °C).

IR (KBr): 2928, 1697, 1549 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.90 (s, 6 H), 2.50 (s, 6 H), 3.85 (s, 3 H), 6.94 (d, *J* = 8.8 Hz, 2 H), 7.16 (d, *J* = 8.8 Hz, 2 H).

MS (ESI): *m*/*z* = 298.3 $[M + 1]^+$.

3,5-Diacetyl-2,6-dimethyl-4-(3-nitrophenyl)pyridine (3n)[22]

Light yellow solid; yield: 230 mg, 0.74 mmol (63%); mp 124.3–125.2 °C (Lit.[9] 126–128 °C).

IR (KBr): 2925, 1698, 1533 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.02 (s, 6 H), 2.55 (s, 6 H), 7.59 (dt, *J* = 7.6, 1.6 Hz, 1 H), 7.66 (t, *J* = 8.0 Hz, 1 H), 8.13 (t, *J* = 1.6 Hz, 1 H), 8.32 (ddd, *J* = 8.0, 2.0, 1.2 Hz, 1 H).

MS (ESI): *m*/*z* = 313.3 $[M + 1]^+$.

3,5-Diacetyl-2,4,6-trimethylpyridine (3o)[25]

Yellow oil; yield: 220 mg, 1.07 mmol (90%).

IR (KBr): 2925, 1698, 1558 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.12 (s, 3 H), 2.45 (s, 6 H), 2.50 (s, 6 H).

MS (ESI): *m*/*z* = 206.3 $[M + 1]^+$.

3,5-Diacetyl-2,6-dimethyl-4-isobutylpyridine (3p)

Yellow oil; yield: 223 mg, 0.90 mmol (78%).

IR (KBr): 2961, 1699, 1557 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.83 (d, *J* = 6.8 Hz, 6 H), 1.70–1.77 (m, 1 H), 2.39 (d, *J* = 7.6 Hz, 2 H), 2.46 (s, 6 H), 2.52 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.4, 22.7, 29.7, 32.7, 39.1, 135.7, 142.2, 152.2, 205.8.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{22}NO_2$: 248.1645; found: 248.1647.

Dimethyl 2,6-Dimethyl-4-(2-nitrosophenyl)pyridine-3,5-dicarboxylate (4)[26] **(Figure 2)**

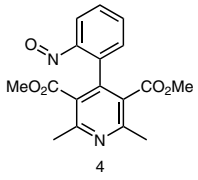


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Figure 2 Structure of undesired product **4**

Light blue solid; yield: 356 mg, 1.08 mmol (92%); mp 94.8–94.9 °C (Lit.[26] 93 °C).

IR (KBr): 2952, 1735, 1560 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.67 (s, 6 H), 3.39 (s, 6 H), 6.55 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.44 (ddd, *J* = 8.0, 7.5, 1.0 Hz, 1 H), 7.52 (dd, *J* = 7.5, 1.0 Hz, 1 H), 7.72 (td, *J* = 7.5, 1.0 Hz, 1 H).

MS (ESI): *m*/*z* = 329.3 $[M + 1]^+$.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1560562.

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