Molybdenum- and Tungsten-Based Coordination Polymers as Catalysts for an Efficient and Rapid Synthesis of Hexahydro-5-oxoquinoline-3-carboxylates and 1,4-Dihydropyridine-3,5-dicarboxylates[1])

by **Biswanath Das***, **Malampati Srilatha**, **Boyapati Veeranjaneyulu**, and **Boddu Shashi Kanth**

Organic Chemistry Division-I, Indian Institute of Chemical Technology, Hyderabad-500007, India (phone: +91-40-7193434; fax: +91-40-7160512; e-mail: biswanathdas@yahoo.com)

Hexahydro-5-oxoquinoline-3-carboxylates and 1,4-dihydropyridine-3,5-dicarboxylates were synthesized efficiently and rapidly (2 min) in the presence of molybdenum- and tungsten-based coordination polymers $[M(Bu_3Sn)_2O_4)]_n$ (M = Mo or W) as catalysts (*Schemes 1* and *2*; *Tables 2* and *3*). The products were formed at room temperature in excellent yields (90–98%). The catalysts worked under heterogeneous conditions and were recyclable. The earlier reports for the application of these polymers to conduct organic synthesis are limited. The present method explores a new and useful application of these catalysts.

Introduction. – The *Hantzsch* reaction for the synthesis of 1,4-dihydropyridine-3,5-dicarboxylates [1–3] involves a one-pot condensation of an aldehyde with a β-keto ester and NH_3 in AcOH or in alcohol under reflux for several hours [4]. This reaction has subsequently been carried out by employing different catalysts [5], ionic liquids [6], and microwaves [7]. However, the harsh reaction conditions, high temperatures, long reaction times, and variable yields are the drawbacks associated with many of the procedures. Here, we report an efficient and rapid synthesis of hexahydro-5-oxoquinoline-3-carboxylates and 1,4-dihydropyridine-3,5-dicarboxylates under mild reaction conditions.

Results and Discussion. – In continuation of our work [8] on the development of useful synthetic methodologies, we observed that hexahydroquinoline derivatives **D** can conveniently be synthesized by a multicomponent reaction of an aldehyde **A**, ethyl acetoacetate (**C**), a cyclohexane-1,3-dione **B**, and $AcONH_4$ in the presence of a molybdenum- or tungsten-based coordination polymer $[M(Bu_3Sn)_2O_4)]_n$ (M = Mo or W) [9] at room temperature (*Scheme 1*).

Initially, the reaction of benzaldehyde, dimedone (= 5,5-dimethylcyclohexane-1,3-dione), ethyl acetoacetate (= ethyl 3-oxobutanoate), and $AcONH_4$ was conducted at room temperature in the presence of various catalysts including *Brønsted* and *Lewis* acids (*Table 1*). Considering the reaction times and yields, molybdenum- and tungsten-based coordination polymers $[M(Bu_3Sn)_2O_4)]_n$ (M = Mo or W) were found to be most effective, and their efficiency was almost equal. Within only 2 min, the product **D1** was formed in excellent yield (97–98%) in the presence of either of the two catalysts. On

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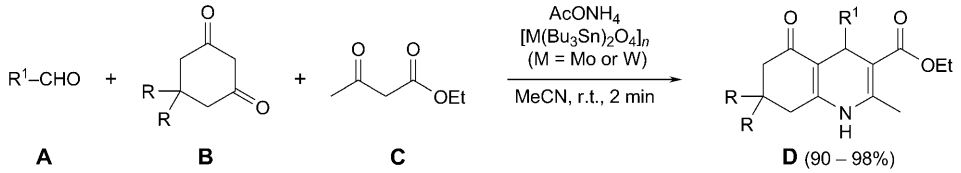
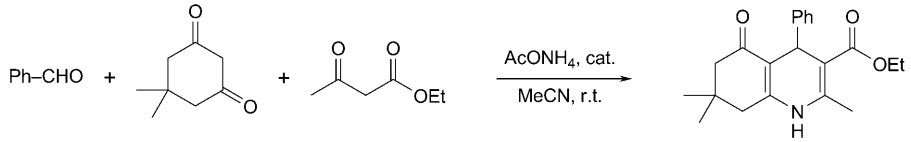
Scheme 1. *Multicomponent Reaction of Aldehydes* **A**, *Ethyl Acetoacetate* (**C**), *Cyclohexane-1,3-diones* **B**, *and* $AcONH_4$ *in the Presence of a Molybdenum- or Tungsten-Based Coordination Polymer* $[M(Bu_3Sn)_2O_4]_n$ (M = Mo or W) *at Room Temperature.* See *Table 2.*



the other hand, Na_2MoO_4 and Na_2WO_4 could not catalyze the reaction efficiently (reaction time 15 min, yield 38–41%). Bu_3SnCl was also less efficient (reaction time 15 min, yield 35%).

Table 1. *Activity of Different Catalysts in the Synthesis of Ethyl 1,4,5,6,7,8-Hexahydro-2,7,7-trimethyl-5-oxo-4-phenylquinoline-3-carboxylate* (**D1**) *by Reaction of Benzaldehyde, Dimedone, Ethyl Acetoacetate, and* $AcONH_4$[a])



Catalyst	Reaction time	Yield [%][b])
TsOH	2 h	82
HY-Zeolite	2 h	86
Amberlyst-15	20 min	80
PEG-SO_3H	20 min	87
K-10 Clay	20 min	73
Na_2WO_4	15 min	41
Na_2MoO_4	15 min	38
Bu_3SnCl	15 min	35
$[W(Bu_3Sn)_2O_4]_n$	2 min	97
$[Mo(Bu_3Sn)_2O_4]_n$	2 min	98

[a]) Reaction conditions: benzaldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1 mmol), $AcONH_4$ (1 mmol), and catalyst (0.5 mmol) in MeCN (2 ml). [b]) Yields of isolated pure product after column chromatography.

As both the catalysts, the molybdenum- and tungsten-based coordination polymer $[M(Bu_3Sn)_2O_4]_n$ (M = Mo or W), were almost equally effective for the synthesis of the hydroquinolinecarboxylate **D1**, the former catalyst was used to prepare a series of the compounds **D** from various aldehydes **A** and cyclohexane-1,3-diones **B** (*Scheme 1*, *Table 2*). The conversions proceeded rapidly within 2 min, and the products **D** were formed in excellent yields (90–98%). The time economic achievement is remarkable in this procedure. Aromatic, heteroaromatic, and aliphatic aldehydes underwent the conversion smoothly. The aromatic aldehydes contained both electron-donating and electron-withdrawing groups. A sterically hindered aldehyde such as naphthalene-2-

Table 2. *[Mo(Bu$_3$Sn)$_2$O$_4$]$_n$-Catalyzed Synthesis of Ethyl Hexahydro-5-oxoquinoline-3-carboxylates* **D** *by Reaction of Aldehydes* **A**, *Cyclohexane-1,3-diones* **B**, *Ethyl Acetoacetate* (**C**), *and AcONH$_4$*[a])

Entry	R[1]	R	Product	Yield [%][b])
1	Ph	Me	**D1**	98
2	4-Me–C$_6$H$_4$	Me	**D2**	94
3	4-MeO–C$_6$H$_4$	Me	**D3**	95
4	4-OH–C$_6$H$_4$	Me	**D4**	95
5	4-F–C$_6$H$_4$	Me	**D5**	92
6	4-Br–C$_6$H$_4$	Me	**D6**	93
7	2,4-Cl$_2$C$_6$H$_3$	Me	**D7**	95
8	cinnamyl	Me	**D8**	94
9	furan-2-yl	Me	**D9**	93
10	4-OH,3-MeOC$_6$H$_3$	Me	**D10**	96
11	4-CN–C$_6$H$_4$	Me	**D11**	96
12	2-Cl–C$_6$H$_4$	Me	**D12**	93
13	4-NO$_2$–C$_6$H$_4$	Me	**D13**	91
14	naphthalen-2-yl	Me	**D14**	97
15	3-Cl,4-FC$_6$H$_3$	Me	**D15**	98
16	naphthalen-2-yl	H	**D16**	97
17	3-NO$_2$–C$_6$H$_4$	Me	**D17**	90
18	3,4,5-(MeO)$_3$C$_6$H$_2$	H	**D18**	98
19	4-CN–C$_6$H$_4$	H	**D19**	96
20	1*H*-indol-3-yl	Me	**D20**	91
21	Pr	Me	**D21**	90
22	i-Bu	Me	**D22**	92
23	hexyl	Me	**D23**	92

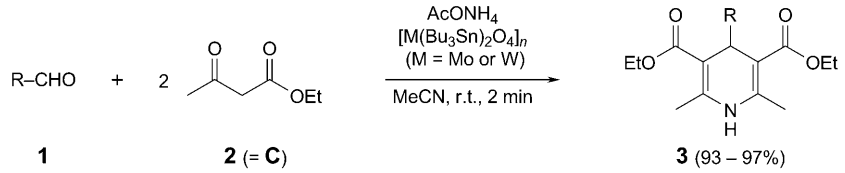
[a]) See *Scheme 1*; for reaction conditions, see *Table 1*. [b]) Yields of isolated pure compounds after column chromatography.

carboxaldehyde (*Table 2*, *Entry 14*) and an acid-sensitive aldehyde such as cinnamaldehyde (=(2*E*)-3-phenylprop-2-enal; *Table 2*, *Entry 8*) afforded the desired hydroquinolinecarboxylates also in high yields.

The present method was also applied to the synthesis of *Hantzsch* 1,4-dihydropyridine derivatives **3** involving the reaction of aldehydes **1**, ethyl acetoactate (**2**), and AcONH$_4$ (*Scheme 2*). In this case also, both the molybdenum- and tungsten-based coordination polymers [M(Bu$_3$Sn)$_2$O$_4$)]$_n$ (M = Mo or W) catalyzed the reaction efficiently with almost equal activity. The former catalyst was thus used to prepare a series of 1,4-dihydropyridine-3,5-dicarboxylates **3** (*Table 3*). The conversion required only 2 min to afford the products **3** in excellent yields. The 1,4-dihydropyridine-3,5-dicarboxylates were prepared from aromatic, heteroaromatic, and aliphatic aldehydes. Again, aromatic aldehydes containing both electron-donating and electron-withdrawing groups underwent the conversion smoothly. The structures of the products were established from their spectral data (IR, ^{1}H- and ^{13}C-NMR, and MS).

The catalysts [M(Bu$_3$Sn)$_2$O$_4$)]$_n$ (M = Mo or W) could easily be prepared by following the reported method [9]. They worked under heterogeneous conditions and could easily be separated from the reaction mixture. They were recycled three times with almost equal activity (*Table 4*). Recently, heterogeneous catalysts have gained

Scheme 2. *Multicomponent Reaction of Aldehydes* **1**, *Ethyl Acetoacetate* (**2**), *and* $AcONH_4$ *in the Presence of a Molybdenum- or Tungsten-Based Coordination Polymer* $[M(Bu_3Sn)_2O_4)]_n$ (M = Mo or W) *at Room Temperature.* See *Table 3.*



1 **2** (= **C**) **3** (93 – 97%)

Table 3. *[Mo(Bu₃Sn)₂O₄]ₙ-Catalyzed Formation of 1,4-Dihydropyridine-3,5-dicarboxylates* **3** *by the Reaction of Aldehydes* **1**, *Ethyl Acetoacetate* (**2**), *and* $AcONH_4$[a])

R	Product	Yield [%][b])
Ph	**3a**	97
4-NO_2–C_6H_4	**3b**	96
3-NO_2–C_6H_4	**3c**	94
4-Me–C_6H_4	**3d**	95
4-(EtOOC)furan-2-yl[c])	**3e**	97
i-Pr	**3f**	94
Pr	**3g**	93

[a]) Reaction conditions as in *Table 1*, but ethyl acetoacetate (2 mmol). [b]) Yields of isolated pure compounds after column chromatography. [c]) R derived from ethyl 5-formylfuran-3-carboxylate (**1e**).

much importance due to eco-economic benefits. In the present cases, they were conveniently applied to prepare hexahydroquinoline and 1,4-dihydropyridine derivatives. Earlier applications of these catalysts for organic synthesis are limited [9][10].

Table 4. *Catalyst Recycling and Variation of Yield of* **D1**[a])

No. of cycles	1	2	3
Yield [%][b])	98, 97	96, 95	96, 94

[a]) Reaction conditions: benzaldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1 mmol), $AcONH_4$ (1 mmol), and catalyst (0.5 mmol) in MeCN (2 ml) were used. [b]) Yields of isolated pure compound after column chromatography, obtained with molybdenum- or tungsten-based polymer catalyst (first and second value, resp.).

In conclusion, we described the utilization of molybdenum- and tungsten-based coordination polymers $[M(Bu_3Sn)_2O_4)]_n$ (M = Mo or W) for a facile and convenient synthesis of hexahydroquinoline and 1,4-dihydropyridine derivatives at room temperature. The simple experimental procedure, the mild reaction conditions, the rapid conversion (2 min), the excellent yields (90–98%), and the wide applicability and utilization of recyclable heterogeneous catalysts are the notable advantages of the present method.

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Experimental Part

General. The catalysts, molybdenum- and tungsten-based coordination polymers $[M(Bu_3Sn)_2O_4)]_n$ (M = Mo or W), were prepared according to [9]. CC = Column chromatography. IR Spectra: *Perkin–Elmer RX* FT-IR spectrometer; in cm^{-1}. NMR Spectra: *Varian Gemini* 200 MHz (^1H) and 500 MHz (^{13}C) spectrometer; δ in ppm, J in Hz. ESI-MS: *VG-Autospec* micromass spectrometer; in m/z.

Ethyl 1,4,5,6,7,8-Hexahydro-5-oxoquinoline-3-carboxylates **D**: *General Procedure.* To a stirred soln. of aldehyde **A** (1 mmol), dimedone or cyclohexane-1,3-dione **B** (1 mmol), ethyl acetoacetate (**C**; 1 mmol), and $AcONH_4$ (1 mmol) in MeCN (2 ml), catalyst (0.5 mmol) was added at r.t., and the mixture was stirred well. After completion of the reaction (TLC monitoring), the mixture was filtered, and the residue washed with AcOEt (3 × 5 ml) and dried to recover the catalyst. The filtrate was diluted with AcOEt (10 ml), washed with dist. H_2O (10 ml) and then with brine (3 × 5 ml). The org. layer was dried (Na_2SO_4) and concentrated and the crude product subjected to CC (silica gel, AcOEt/hexane): pure **D**.

The catalyst was recycled three times to get the product with almost equal yield.

Diethyl 1,4-Dihydropyridine-3,5-dicarboxylates **3**: *General Procedure.* As described for **D**, with aldehyde **1** (1 mmol), ethyl acetoacetate (**2**; 2 mmol), $AcONH_4$ (1 mmol) in MeCN (2 ml), and catalyst (0.5 mmol): pure **3**.

Here, also the catalyst was recycled three times to generate the product with almost equal yield.

Data of New Products (*cf. Tables 2* and *3*). *Ethyl 4-(4-Cyanophenyl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate* (**D11**). White solid. M.p. 199–202°. IR: 3274, 1714, 1605, 1492, 1214. ^1H-NMR (200 MHz, $CDCl_3$): 8.60 (br. *s*, 1 H); 7.51 (*d*, *J* = 8.0, 2 H); 7.39 (*d*, *J* = 8.0, 2 H); 4.99 (*s*, 1 H); 4.02 (*q*, *J* = 7.0, 2 H); 2.37 (*s*, 3 H); 2.33–2.28 (*m*, 2 H); 2.20–2.01 (*m*, 2 H); 1.15 (*t*, *J* = 7.0, 3 H); 1.08 (*s*, 3 H); 0. 85 (*s*, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 194.2; 166.3; 152.6; 149.1; 145.2; 130.8; 128.0; 118.1; 110.1; 109.7; 102.9; 59.0; 50.2; 40.0; 36.9; 31.5; 29.2; 26.6; 18.0; 14.2. ESI-MS: 365 ($[M+H]^+$). Anal. calc. for $C_{22}H_{24}N_2O_3$: C 72.52, H 6.59, N 7.69; found: C 72.45, H 6.55, N 7.66.

Ethyl 1,4,5,6,7,8-Hexahydro-2,7,7-trimethyl-4-(naphthalen-2-yl)-5-oxoquinoline-3-carboxylate (**D14**). Light yellow solid. M.p. 201–204°. IR: 3199, 1678, 1604, 1492, 1381. ^1H-NMR ($CDCl_3$, 200 MHz): 9.18 (br. *s*, 1 H); 7.83–7.71 (*m*, 3 H); 7.61–7.59 (*m*, 1 H); 7.49–7.37 (*m*, 3 H); 5.02 (*s*, 1 H); 3.99 (*q*, *J* = 7.0, 2 H); 2.52 –2.41 (*m*, 2 H); 2.32 (*s*, 3 H); 2.21–1.90 (*m*, 2 H); 1.12 (*t*, *J* = 7.0, 3 H); 1.01 (*s*, 3 H); 0.82 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 194.5; 167.1; 149.9; 145.0; 144.9; 132.9; 131.5; 127.7; 127.2; 127.1; 126.5; 125.9; 125.2; 125.1; 110.0; 103.5; 59.2; 50.1; 39.9; 36.2; 32.2; 29.1; 26.2; 18.5; 14.1. ESI-MS: 390 ($[M+H]^+$). Anal. calc. for $C_{25}H_{27}NO_3$: C 77.12, H 6.94, N 12.33; found: C 77.05, H 6.90, N 12.28.

Ethyl 4-(3-Chloro-4-fluorophenyl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate (**D15**). White solid. M.p. 162–166°. IR: 3283, 1710, 1605, 1491, 1383, 1222. ^1H-NMR ($CDCl_3$, 200 MHz): 8.72 (br. *s*, 1 H); 7.22 (*d*, *J* = 8.0, 1 H); 7.13–7.09 (*m*, 1 H); 6.95 (*t*, *J* = 8.0, 1 H); 4.85 (*s*, 1 H); 4.08–3.94 (*m*, 2 H); 2.40–2.21 (*m*, 5 H); 2.19–2.00 (*m*, 2 H); 1.19 (*t*, *J* = 7.0, 3 H); 1.02 (*s*, 3 H); 0.90 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 193.8; 166.2; 155.6 (*d*, *J* = 28.0); 149.1; 145.2; 145.0; 129.7; 127.2; 119.1 (*d*, *J* = 10.0); 115.2 (*d*, *J* = 10.0); 110.0; 103.2; 59.0; 50.2; 39.6; 35.1; 31.8; 29.3; 26.6; 18.0; 14.0. ESI-MS: 394, 392 ($[M+H]^+$). Anal. calc. for $C_{21}H_{23}ClFNO_3$: C 64.45, H 5.88, N 3.58; found: C 64.37, H 5.85, N 3.55.

Ethyl 1,4,5,6,7,8-Hexahydro-2-methyl-4-(naphthalen-2-yl)-5-oxoquinoline-3-carboxylate (**D16**). Light yellow solid. M.p. 220–222°. IR: 3286, 1694, 1610, 1481, 1226. ^1H-NMR (200 MHz, $CDCl_3$): 8.72 (br. *s*, 1 H); 7.81–7.53 (*m*, 4 H); 7.42–7.29 (*m*, 3 H); 5.12 (*s*, 1 H); 4.01 (*q*, *J* = 7.0, 2 H); 2.57–2.42 (*m*, 2 H); 2.34 (*s*, 3 H); 2.28–2.17 (*m*, 2 H); 1.98–1.72 (*m*, 2 H); 1.15 (*t*, *J* = 7.0, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 194.2; 166.1; 150.8; 150.7; 145.1; 145.0; 132.5; 131.8; 126.6; 126.1; 125.1; 125.0; 124.8; 111.5; 104.7; 58.4; 30.4; 30.2; 25.8; 20.2; 18.5; 14.3. ESI-MS: 362 ($[M+H]^+$). Anal. calc. for $C_{23}H_{23}NO_3$: C 76.45, H 6.37, N 3.87; found: C 76.41, H 6.34, N 3.85.

Ethyl 1,4,5,6,7,8-Hexahydro-2-methyl-5-oxo-4-(3,4,5-trimethoxyphenyl)quinoline-3-carboxylate (**D18**). Light brown solid. M.p. 157–160°. IR: 3275, 1695, 1605, 1488, 1379, 1226. ^1H-NMR (200 MHz,

$CDCl_3$): 8.61 (br. *s*, 1 H); 6.44 (*s*, 2 H); 4.92 (*s*, 1 H); 4.03 (*q*, *J* = 7.0, 2 H); 3.72 (*s*, 6 H); 3.70 (*s*, 3 H); 2.58–2.39 (*m*, 2 H); 2.32 (*s*, 3 H); 2.28–2.25 (*m*, 2 H); 2.02–1.83 (*m*, 2 H); 1.20 (*t*, *J* = 7.0, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 195.0; 167.5; 152.5; 150.6; 145.1; 144.4; 136.8; 111.0; 105.2; 104.9; 60.4; 59.2; 55.1; 36.2; 35.7; 26.0; 21.3; 19.7; 14.1. ESI-MS: 402 ($[M+H]^+$). Anal. calc. for $C_{22}H_{27}NO_6$: C 65.83, H 6.73, N 3.49; found: C 65.75, H 6.70, N 3.46.

Ethyl 4-(4-Cyanophenyl)-1,4,5,6,7,8-hexahydro-2-methyl-5-oxoquinoline-3-carboxylate (**D19**). Light yellow solid. M.p. 245–248°. IR: 3289, 2230, 1703, 1608, 1482, 1380, 1286. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.82 (br. *s*, 1 H); 7.48 (*d*, *J* = 8.0, 2 H); 7.37 (*d*, *J* = 8.0, 2 H); 4.99 (*s*, 1 H); 3.98 (*q*, *J* = 7.0, 2 H); 2.58–2.39 (*m*, 2 H); 2.31 (*s*, 3 H); 2.25–2.12 (*m*, 2 H); 1.99–1.76 (*m*, 2 H); 1.12 (*t*, *J* = 7.0, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 194.4; 165.1; 153.0; 151.1; 145.4; 131.0; 128.5; 118.2; 110.7; 108.8; 102.6; 59.1; 37.9; 26.3; 21.0; 18.4; 14.2. ESI-MS: 337 ($[M+H]^+$). Anal. calc. for $C_{20}H_{20}N_2O_3$: C 71.42, H 5.95, N 8.33; found: C 71.35, H 5.93, N 8.29.

*Ethyl 1,4,5,6,7,8-Hexahydro-4-(1*H*-indol-3-yl)-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate* (**D20**). Brown semi-solid. IR: 3226, 1695, 1584, 1484, 1382, 1213. ^{1}H-NMR (200 MHz, $CDCl_3$): 9.64 (br. *s*, 1 H); 8.34 (br. *s*, 1 H); 7.58 (*d*, *J* = 8.0, 1 H); 7.21 (*d*, *J* = 8.0, 1 H); 6.98–6.82 (*m*, 3 H); 5.20 (*s*, 1 H); 4.02–3.90 (*m*, 2 H); 2.30–2.19 (*m*, 5 H); 2.04–1.97 (*m*, 2 H); 1.12 (*t*, *J* = 7.0, 1 H); 1.02 (*s*, 3 H); 0.82 (*s*, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 196.6; 166.1; 164.2; 163.5; 135.4; 127.2; 124.2; 123.8; 123.4; 120.2; 119.6; 118.2; 111.0; 101.4; 61.3; 51.2; 45.6; 39.0; 31.5; 27.8; 24.2; 14.1. ESI-MS: 401 ($[M+Na]^+$). Anal. calc. for $C_{23}H_{26}N_2O_3$: C 73.01, H 6.87, N 7.40; found: C 72.95, H 6.84, N 7.36.

Diethyl 4-[4-(Ethoxycarbonyl)furan-2-yl]-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (**3e**). Brown semi-solid. IR: 3333, 1730, 1700, 1666, 1498, 1381, 1281. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.45 (br. *s*, 1 H); 7.19 (br. *s*, 1 H); 6.52 (br. *s*, 1 H); 5.73 (*s*, 1 H); 4.22 (*q*, *J* = 7.0, 2 H); 4.04–3.92 (*m*, 4 H); 2.23 (*s*, 6 H); 1.34 (*t*, *J* = 7.0, 3 H); 1.12 (*t*, *J* = 7.0, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.5; 163.0; 146.6; 145.1; 139.6; 111.2; 110.3; 103.2; 59.2; 59.0; 32.1; 18.4; 14.8. ESI-MS: 392 ($[M+H]^+$). Anal. calc. for $C_{20}H_{25}NO_7$: C 61.38, H 6.39, N 3.58; found: C 61.31, H 6.35, N 3.55.

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