Supplementary Material

Green Synthesis of 1,4-Dihydropyridine using MIL-101 (Cr) MOF as catalyst

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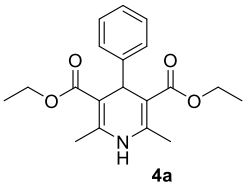
The spectroscopic data of the synthesized compounds are as follows:

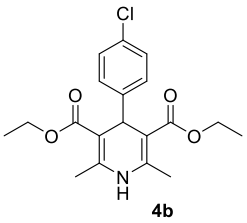
1. **dimethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate 4a**



4a

Pale yellow colour; yield: 92%; MP: 156-158 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 1.21 (t, J = 6.8 Hz, 6H, $2CH_3$), 2.34 (s, 6H, $2CH_3$), 4.08 (q, J = 6.8 Hz, 4H, $2CH_2$), 4.99 (s, 1H, CH), 5.54 (s, 1H, NH), 7.10-7.14 (m, 1H, ArH), 7.18–7.22 (m, 2H, ArH), 7.28–7.29 (m, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 19.6, 39.6, 59.7, 104.23, 126.1, 127.8, 128.0, 143.8, 147.8, 167.6.

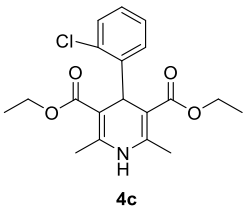
2. **dimethyl 4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate 4b**



4b

Yellow colour; yield: 95%; MP: 146-148 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 1.25 (t, J = 7.1 Hz, 6H, $2CH_3$), 2.38 (s, 6H, $2CH_3$), 4.18 (q, J = 7.1 Hz, 4H, $2CH_2$), 5.12 (s, 1H, CH), 5.89 (br, 1H, NH), 7.16–7.21 (m, 4H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.6, 19.9, 42.6, 59.9, 104.23, 126.1, 127.5, 129.1, 143.9, 148.8, 167.8.

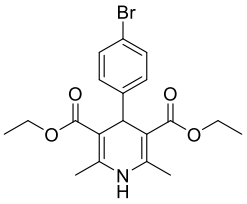
3. **4-(-2-chlorophenyl)-1,4-dihydro-2,6-diethyl-4-phenylpyridine-3,5-dicarboxylate 4c**



4c

Pale yellow colour; yield: 92%; MP: 132-134 °C; 1H NMR (CDCl3, 400 MHz) δ ppm: 1.31 (t, J = 7.2 Hz, 6H, 2CH3), 2.29 (s, 6H, 2CH3), 4.18 (q, J = 7.2 Hz, 4H, 2CH2), 5.42 (s, 1H, CH), 5.88 (s, 1H, NH), 7.06 (dt, 1H, ArH J = 1.5, 7.6 Hz), 7.12 (dt, 1H, ArH J = 1.2, 7.6 Hz), 7.23–7.25 (m, 2H, ArH). 13C NMR (100 MHz, CDCl3): δ 14.4, 19.5, 39.7, 59.8, 104.13, 126.5, 126.8, 127.8, 128.1, 131.4, 143.7, 148.8, 167.5.

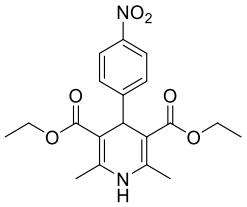
4. **dimethyl 4-(4-bromophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate 4d.**



4d

Light brown colour; yield: 94%; M.P = 160–162 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.23 (t, J = 7.1 Hz, 6 H, $2CH_3$), 2.35 (s, 6 H, $2CH_3$), 4.11 (q, J = 7.1 Hz, 4 H, $2CH_2$), 5.33 (s, 1H, CH), 5.73 (s, 1H, NH), 7.12–7.31 (m, 4H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 19.3, 39.3, 59.9, 104.0, 128.1, 131.0, 130.2, 142.3, 148.3, 167.7.

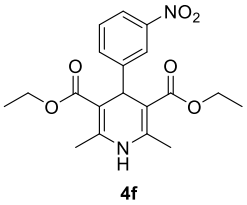
5. **4-(-4-nitrophenyl)-1,4-dihydro-2,6-diethyl-4-phenylpyridine-3,5-dicarboxylate 4e**



4e

Dark yellow colour; yield: 93%; MP: 160-162 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 1.27 (t, J = 7.2 Hz, 6H, $2CH_3$), 2.39 (s, 6H, $2CH_3$), 4.19 (q, J = 7.2 Hz, 4H, $2CH_2$), 5.15 (s, 1H, CH), 5.87 (br, 1H, NH), 7.75 (d, J = 8.7 Hz, 2H, ArH), 8.06 (d, J = 8.7 Hz, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.7, 19.8, 42.7, 59.8, 104.13, 126.3, 127.7, 129.3, 143.8, 148.9, 167.7.

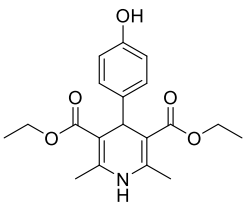
6. **dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate 4f**



4f

Yellow colour; yield: 92%; M.P = 132–134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.23 (t, J = 7.1 Hz, 6H, $2CH_3$) 2.24 (s, 6H, $2CH_3$), 4.10 (q, J = 7.1 Hz, 4H, $2CH_2$), 5.07 (s, 1H, CH), 5.71 (br, 1H, NH), 8.01–7.35 (m, 4H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 19.3, 38.7, 59.9, 103.6, 121.6, 122.5, 123.3, 136.2, 145.0, 146.7, 150.3, 168.1.

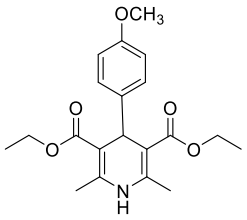
7. **4-(-4-hydroxyphenyl)-1,4-dihydro-2,6-diethyl-4-phenylpyridine-3,5-dicarboxylate 4g**.



4g

Pale yellow colour; yield: 84%; MP: 233-235 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 1.17 (t, J = 6.9 Hz, 6H, $2CH_3$), 2.37 (s, 6H, $2CH_3$), 4.16 (q, J = 6.9 Hz, 4H, $2CH_2$), 5.14 (s, 1H, CH), 5.93 (br, 1H, NH), 7.85 (d, J = 8.8 Hz, 2H, ArH), 8.16 (d, J = 8.8 Hz, 2H, ArH), 9.09 (bs, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.8, 19.9, 42.8, 59.9, 104.6, 126.7, 127.9, 129.5, 143.9, 148.6, 167.8.

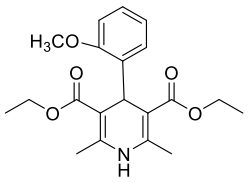
8. **dimethyl 4-(4-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate 4h**



4h

Pale yellow colour; yield: 83%; M.P = 153–155 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.22 (t, J = 7.1 Hz, 6H, $2CH_3$), 2.32 (s, 6H, $2CH_3$), 3.75 (s, 3H, CH_3), 4.09 (q, J = 7.1 Hz, 4H, $2CH_2$), 5.05 (s, 1H, CH), 5.72 (s, 1H, NH), 7.18–6.81(m, 4H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 19.2, 39.3, 53.7, 59.8, 103.5, 113.6, 131.1, 136.3, 146.5, 158.0, 167.8.

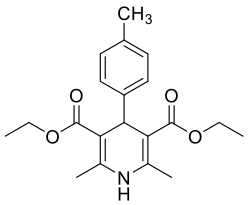
9. **dimethyl 4-(2-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate 4i**



4i

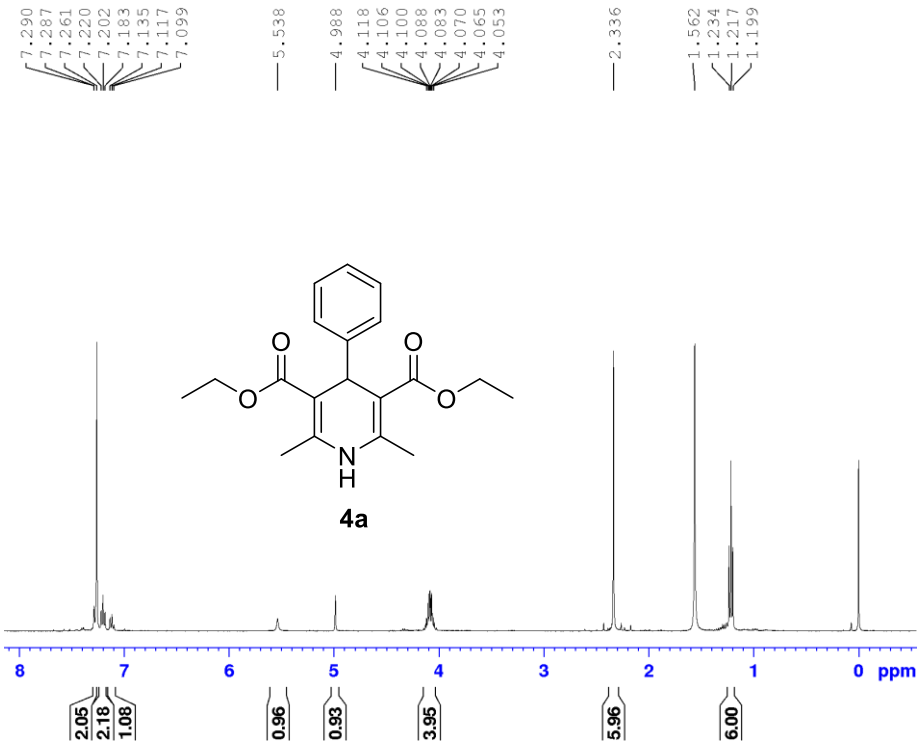
Pale yellow colour; yield: 88%; M.P = 137–139 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.24 (t, J = 7.1 Hz, 6H, $2CH_3$), 2.34 (s, 6H, $2CH_3$), 3.90 (s, 3H, CH_3), 4.07 (q, J = 7.1 Hz, 4H, $2CH_2$), 5.11 (s, 1H, CH), 5.73 (s, 1H, NH), 7.40–6.80 (m, 4H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 19.3, 32.6, 54.3, 59.8, 103.9, 112.7, 121.7, 122.1, 127.9, 131.2, 146.5, 158.3, 167.7.

10. **dimethyl 2,6-dimethyl-4-(p-tolyl)-1,4-dihydropyridine-3,5-dicarboxylate 4j**

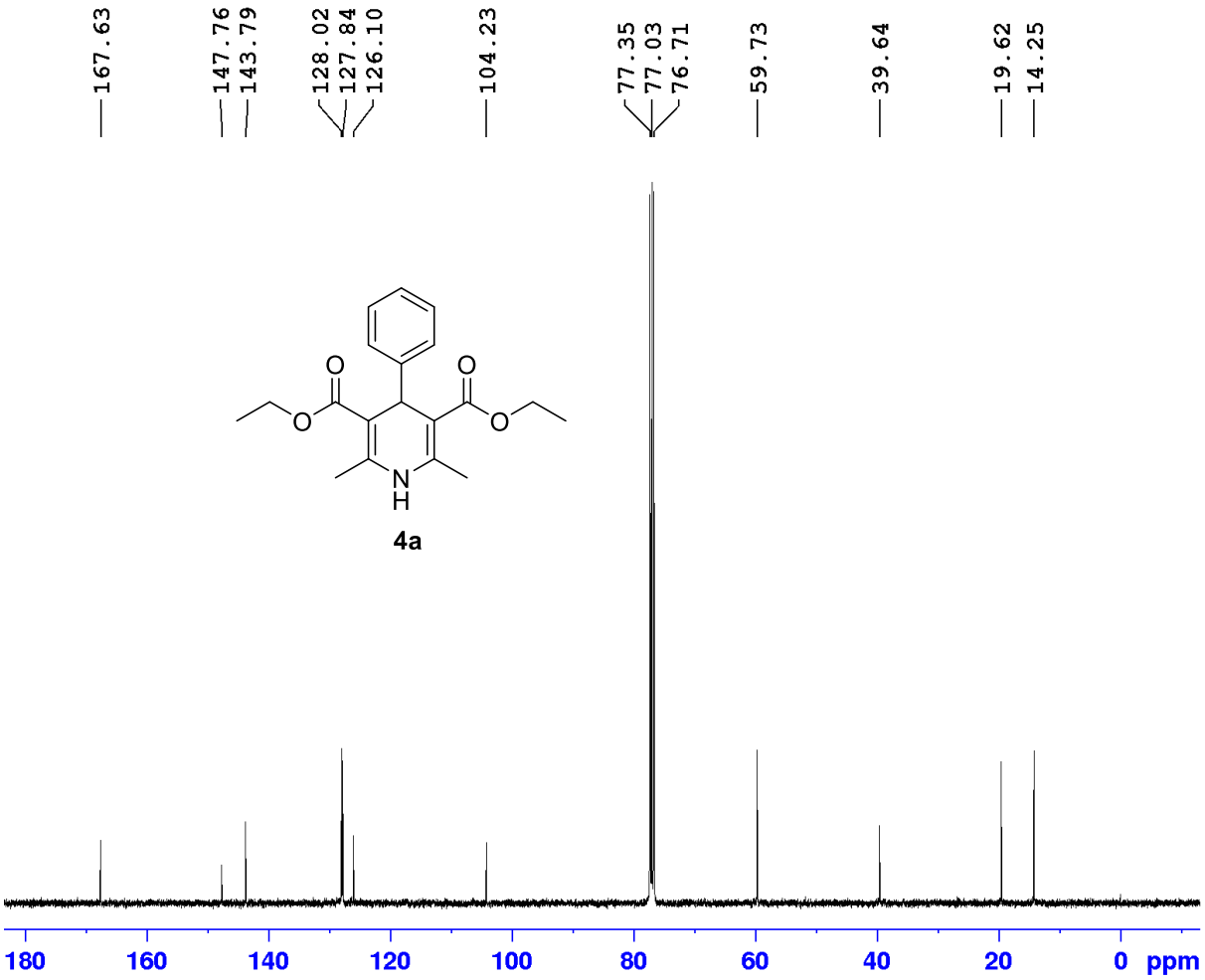


4j

Pale yellow colour; yield: 86%; M.P = 135–137 °C, 1H NMR (400 MHz, CDCl3) δ: 1.21 (t, J = 7.1 Hz, 6H, 2CH3), 2.22 (s, 3H, CH3), 2.32 (s, 6H, 2CH3), 4.07 (q, J = 7.1 Hz, 4H, 2CH2), 5.02 (s, 1H, CH), 5.73 (s, 1H, NH), 7.19–7.02 (m, 4H, ArH). 13C NMR (100 MHz, CDCl3) δ: 14.2, 19.5, 21.3, 39.4, 59.7, 104.1, 127.7, 128.3, 135.4, 143.9, 146.3, 168.1.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1,4-dihydropyridine **4a**



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 1,4-dihydropyridine **4a**

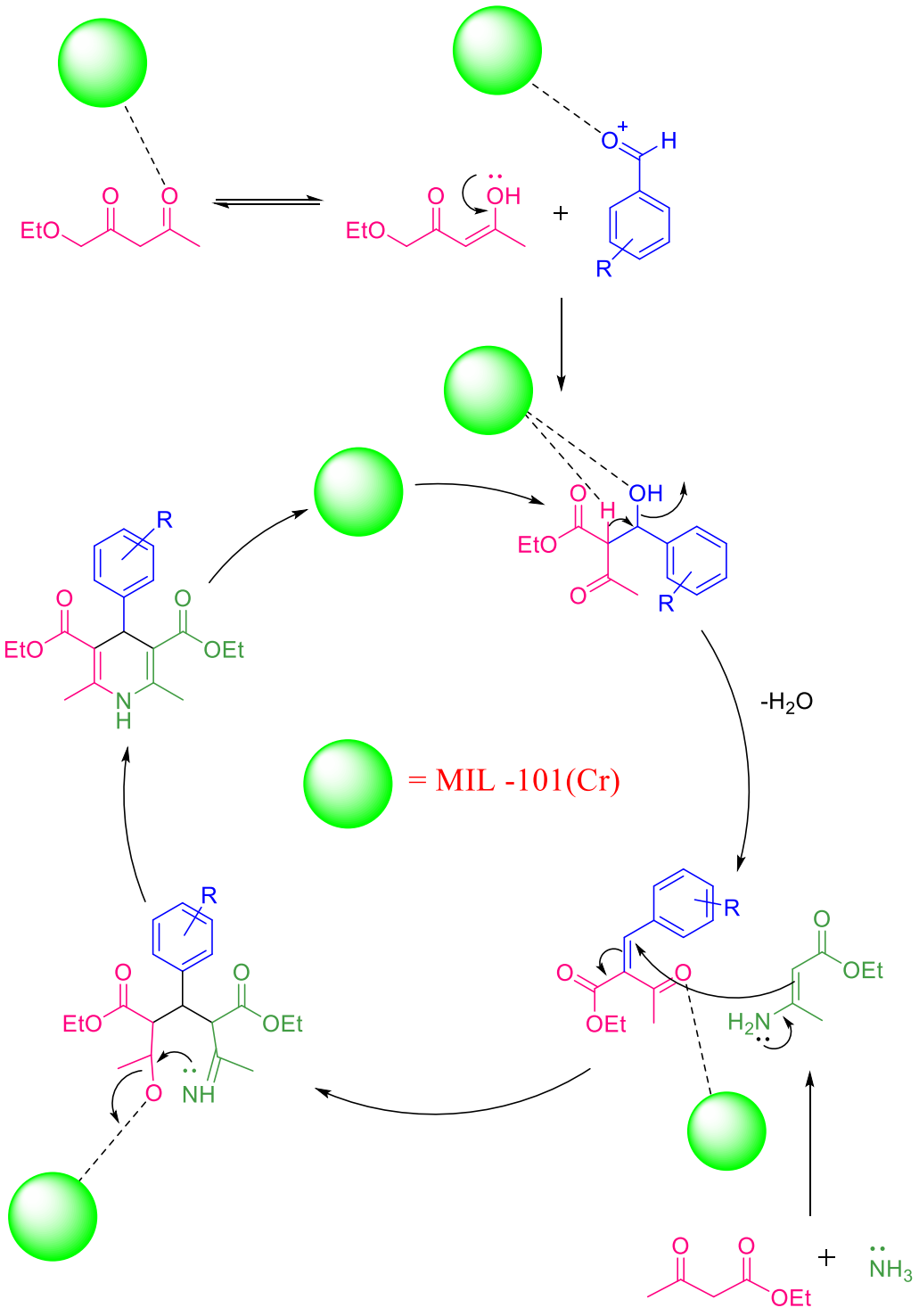


Figure 1. Proposed mechanism for the Hantzsch reaction using MIL-101(Cr)-catalyst.