



SUPPLEMENTARY MATERIAL TO

β -Cyclodextrin–polyurethane polymer: a neutral and eco-friendly heterogeneous catalyst for the one-pot synthesis of 1,4-dihydropyridine and polyhydroquinoline derivatives via the Hantzsch reaction under solvent-free conditions

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SPECTRAL DATA FOR THE SYNTHESIZED COMPOUNDS

Diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (1). Pale yellow solid; IR (KBr, cm^{-1}): 3378, 3016, 1714, 1692, 1502, 1334, 1300, 1204, 1118, 1072, 1009, 730; $^1\text{H-NMR}$ (400 MHz, acetone- d_6 , δ / ppm): 1.26 (6H, t, J = 6.8 Hz, 2CH₃), 2.29 (6H, s, 2CH₃), 4.22 (4H, q, J = 7.2 Hz, 2CH₂), 5.05 (1H, s, ArCH), 5.68 (1H, brs, NH), 7.20–7.62 (5H, m, ArH); $^{13}\text{C-NMR}$ (100 MHz, acetone- d_6 , δ / ppm): 15.0, 20.01, 44.0, 63.3, 104.2, 116.3, 130.8, 144.8, 145.2, 150.7, 167.6.

Diethyl 4-(4-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2). IR (KBr, cm^{-1}): 3345, 3022, 2960, 1741, 825; $^1\text{H-NMR}$ (400 MHz, acetone- d_6 , δ / ppm): 1.24 (6H, t, J = 7.2 Hz, 2CH₃), 2.26 (6H, s, 2CH₃), 3.81 (3H, s, OCH₃), 4.20 (4H, q, J = 7.2 Hz, 2CH₂), 4.80 (1H, s, ArCH), 6.35 (1H, brs, NH), 6.88–7.25 (4H, m, ArH); $^{13}\text{C-NMR}$ (100 MHz, acetone- d_6 , δ / ppm): 15.1, 18.4, 43.8, 55.0, 61.7, 103.2, 115.1, 130.2, 136.3, 157.4, 158.6.

Diethyl 4-(4-hydroxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (3). Pale yellow solid; IR (KBr, cm^{-1}): 3340, 3020, 2911, 1760, 1445, 812; $^1\text{H-NMR}$ (400 MHz, acetone- d_6 , δ / ppm): 1.25 (6H, t, J = 8.5 Hz, 2CH₃), 2.22 (6H, s, 2CH₃), 4.24 (4H, q, J = 8.5 Hz, 2CH₂), 4.70 (1H, s, ArCH), 6.30–7.27 (4H, m, ArH), 7.78 (1H, brs, NH), 8.70 (1H, brs, OH); $^{13}\text{C-NMR}$ (100 MHz, acetone- d_6 , δ / ppm): 14.2, 19.8, 45.7, 63.6, 102.3, 117.8, 133.4, 139.6, 153.2, 158.7.

Diethyl 4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4). Pale yellow solid; IR (KBr, cm^{-1}): 3333, 1712, 1655, 1484, 1468,

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1380, 1222; ^1H -NMR (400 MHz, acetone- d_6 , δ / ppm): 1.20 (6H, t, J = 8.5 Hz, 2CH₃), 2.32 (6H, s, 2CH₃), 4.13 (4H, q, J = 8.4 Hz, 2CH₂), 4.88 (1H, s, ArCH), 5.78 (1H, brs, NH), 7.15 (2H, d, J = 8.1 Hz, ArH), 7.28 (2H, d, J = 8.1 Hz, ArH); ^{13}C -NMR (100 MHz, acetone- d_6 , δ / ppm): 15.7, 19.0, 30.1, 34.9, 61.2, 105.2, 129.1, 130.4, 132.1, 143.2, 155.8.

Diethyl 4-(4-cyanophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5). IR (KBr, cm^{-1}): 3345, 2229, 1701, 1680, 1207, 1109, 776; ^1H -NMR (400 MHz, acetone- d_6 , δ / ppm): 1.24 (6H, t, J = 7.2 Hz, 2CH₃), 2.33 (6H, s, 2CH₃), 4.15 (4H, q, J = 7.3 Hz, 2CH₂), 5.00 (1H, s, ArCH), 5.75 (1H, brs, NH), 7.30–7.65 (4H, m, ArH); ^{13}C -NMR (100 MHz, acetone- d_6 , δ / ppm): 14.2, 19.4, 40.3, 59.9, 103.2, 109.7, 119.3, 128.8, 131.8, 144.6, 153.0, 167.1.

Diethyl 4-(4-ethoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (6). IR (KBr, cm^{-1}): 3350, 3030, 2968, 1745, 814; ^1H -NMR (400 MHz, acetone- d_6 , δ / ppm): 1.00 (3H, t, J = 7.2 Hz, CH₃), 1.28 (6H, t, J = 7.2 Hz, 2CH₃), 2.29 (6H, s, 2CH₃), 4.01 (2H, q, J = 7.2 Hz, CH₂), 4.28 (4H, q, J = 7.2 Hz, 2CH₂), 4.85 (1H, s, ArCH), 6.55 (1H, brs, NH), 6.92–7.42 (4H, m, ArH); ^{13}C -NMR (100 MHz, acetone- d_6 , δ / ppm): 14.2, 16.2, 19.4, 42.6, 62.8, 61.7, 103.2, 117.1, 131.0, 137.3, 158.3, 160.6.

Diethyl 4-(4-(dimethylamino)phenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (7). Pale yellow solid; IR (KBr, cm^{-1}): 3340, 3030, 2960, 1763, 810; ^1H -NMR (400 MHz, acetone- d_6 , δ / ppm): 1.30 (6H, t, J = 8.4 Hz, 2CH₃), 2.26 (6H, s, 2CH₃), 3.14 (6H, s, N(CH₃)₂), 4.25 (4H, q, J = 8.5 Hz, 2CH₂), 4.65 (1H, s, ArCH), 7.12–7.29 (4H, m, ArH), 8.08 (1H, brs, NH); ^{13}C -NMR (100 MHz, acetone- d_6 , δ / ppm): 14.1, 17.8, 40.3, 44.2, 61.0, 103.4, 114.0, 128.2, 134.3, 149.0, 152.1.

Diethyl 2,6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (8). Pale yellow solid; IR (KBr, cm^{-1}): 3039, 2975, 1768, 1537, 818; ^1H -NMR (400 MHz, acetone- d_6 , δ / ppm): 1.34 (6H, t, J = 8.4 Hz, 2CH₃), 2.29 (6H, s, 2CH₃), 4.25 (4H, q, J = 8.5 Hz, 2CH₂), 4.73 (1H, s, ArCH), 7.50–8.10 (4H, m, ArH), 8.15 (1H, brs, NH); ^{13}C -NMR (100 MHz, acetone- d_6 , δ / ppm): 14.5, 19.0, 32.2, 44.1, 60.2, 104.1, 123.4, 127.1, 145.2, 151.8, 153.2.

Diethyl 4-(2-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (9). Pale yellow solid; IR (KBr, cm^{-1}): 3342, 1722, 1664, 1473, 1472, 1375, 1218; ^1H -NMR (400 MHz, acetone- d_6 , δ / ppm): 1.10 (6H, t, J = 8.6 Hz, 2CH₃), 2.28 (6H, s, 2CH₃), 4.12 (4H, q, J = 8.4 Hz, 2CH₂), 4.85 (1H, s, ArCH), 6.12 (1H, brs, NH), 7.10–7.32 (4H, m, ArH); ^{13}C -NMR (100 MHz, acetone- d_6 , δ / ppm): 16.1, 19.8, 31.2, 35.3, 63.2, 104.9, 129.9, 132.5, 132.9, 144.1, 156.2.

Diethyl 2,6-dimethyl-4-(2-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (10). Pale yellow solid; IR (KBr, cm^{-1}): 3042, 2978, 1762, 1541, 820; ^1H -NMR (400 MHz, acetone- d_6 , δ / ppm): 0.98 (3H, t, J = 7.4 Hz, CH₃), 1.36 (3H, t, J = 7.4 Hz, CH₃), 1.89 (1H, brs, NH), 2.24 (3H, s, CH₃), 2.55 (3H, s, CH₃),

4.12 (2H, *q*, $J = 7.4$ Hz, CH₂), 4.40 (2H, *q*, $J = 7.4$ Hz, CH₂), 7.42–8.31 (4H, *m*, ArH); ¹³C-NMR (100 MHz, acetone-*d*₆, δ / ppm): 13.6, 14.4, 27.4, 32.1, 61.2, 63.0, 122.3, 124.0, 128.4, 131.0, 135.0, 139.4, 164.2, 167.2.

Ethyl 1,4,5,6,7,8-hexahydro-2,7-dimethyl-5-oxo-4-phenylquinoline-3-carboxylate (11). Pale yellow solid; IR (KBr, cm⁻¹): 3299, 2998, 1680, 1645, 1609, 1465, 1380, 1228, 1175; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 0.94 (3H, *s*, CH₃), 1.07 (3H, *s*, CH₃), 1.21 (3H, *t*, $J = 7.2$ Hz), 2.14–2.45 (7H, *m*, 2CH₂, CH₃), 4.08 (2H, *q*, $J = 7.2$ Hz, CH₂), 5.06 (1H, *s*, ArCH), 6.18 (1H, *brs*, NH), 7.12 (1H, *t*, $J = 7.6$ Hz, ArH), 7.18 (2H, *t*, $J = 7.6$ Hz, ArH), 7.33 (2H, *d*, $J = 7.6$ Hz, ArH); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 15.1, 19.4, 28.2, 29.3, 33.4, 37.3, 40.3, 50.6, 58.7, 106.6, 114.5, 126.9, 128.7, 128.8, 144.6, 146.2, 149.7, 168.6, 197.7.

Ethyl 4-(4-chlorophenyl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate (12). Pale yellow solid; IR (KBr, cm⁻¹): 3300, 2998, 1688, 1650, 1608, 1480, 1384, 1228, 1187; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 0.94 (3H, *s*, CH₃), 1.08 (3H, *s*, CH₃), 1.20 (3H, *t*, $J = 7.2$ Hz, CH₃), 2.41–2.55 (7H, *m*, 2CH₂, CH₃), 4.07 (2H, *q*, $J = 7.2$ Hz, CH₂), 5.04 (1H, *s*, ArCH), 6.09 (1H, *brs*, NH), 7.10 (2H, *d*, $J = 8.0$ Hz, ArH), 7.33 (2H, *d*, $J = 8.0$ Hz, ArH); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 15.1, 19.3, 27.2, 29.8, 33.5, 37.2, 41.9, 50.8, 58.6, 107.6, 112.8, 129.7, 129.3, 132.7, 145.8, 148.7, 169.5, 198.5.

Ethyl 1,4,5,6,7,8-hexahydro-4-(4-hydroxyphenyl)-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate (13). Yellow solid; IR (KBr, cm⁻¹): 3435, 3305, 3045, 2968, 1679, 1624, 1500, 1371, 1210, 758; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 0.96 (3H, *s*, CH₃), 1.09 (3H, *s*, CH₃), 1.25 (3H, *t*, $J = 7.1$ Hz), 2.27 (3H, *s*, CH₃), 2.41–2.55 (4H, *m*, 2CH₂), 4.10 (2H, *q*, $J = 7.1$ Hz, CH₂), 5.05 (1H, *s*, ArCH), 5.70 (1H, *brs*, OH), 6.01 (1H, *brs*, NH), 6.85 (2H, *d*, $J = 8.5$ Hz, ArH), 7.33 (2H, *d*, $J = 8.5$ Hz, ArH); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 16.0, 20.0, 19.2, 27.5, 33.5, 37.0, 43.0, 52.3, 57.8, 62.2, 109.3, 115.6, 118.5, 132.2, 134.3, 140.3, 148.3, 152.7, 158.6, 170.4, 197.6.

Ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-4-(4-methylphenyl)-5-oxoquinoline-3-carboxylate (14). Yellow powder; IR (KBr, cm⁻¹): 3281, 3027, 3001, 1640, 1600, 1485, 1333, 1210, 761; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 1.0 (3H, *s*, CH₃), 1.14 (3H, *s*, CH₃), 1.19 (3H, *t*, $J = 7.1$ Hz, CH₃), 2.20 (3H, *s*, CH₃), 2.39–2.50 (7H, *m*, 2CH₂, CH₃), 4.16 (2H, *q*, $J = 7.1$ Hz, CH₂), 5.24 (1H, *s*, ArCH), 6.05 (1H, *brs*, NH), 7.50 (2H, *d*, $J = 8.7$ Hz, ArH), 8.08 (2H, *d*, $J = 8.3$ Hz, ArH); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 16.2, 19.6, 28.6, 30.3, 33.6, 38.1, 40.4, 49.9, 57.9, 106.4, 115.0, 127.9, 127.8, 129.2, 145.6, 147.1, 150.1, 169.1, 195.9.

Ethyl 4-(4-(dimethylamino)phenyl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate (15). Yellow powder; IR (KBr, cm⁻¹): 3280, 3010, 2944, 1598, 1505, 1380, 1220, 772; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 1.10

(3H, s, CH₃), 1.15 (3H, s, CH₃), 1.30 (3H, t, *J* = 7.0 Hz, CH₃), 2.21 (3H, s, CH₃), 2.35–2.47 (4H, *m*, 2CH₂), 4.17 (2H, *q*, *J* = 7.0 Hz, CH₂), 5.16 (1H, s, ArCH), 6.10 (1H, *brs*, NH), 7.19 (2H, *d*, *J* = 8.3 Hz, ArH), 7.23 (2H, *d*, *J* = 8.4 Hz, ArH); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 16.5, 21.0, 21.6, 27.3, 27.8, 35.7, 37.8, 43.4, 45.0, 53.7, 58.0, 61.8, 109.6, 117.1, 118.8, 133.0, 135.1, 140.9, 148.9, 153.0, 159.1, 170.6, 196.2.

Ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxoquinoline-3-carboxylate (16). Yellow solid; IR (KBr, cm⁻¹): 3298, 2990, 1695, 1650, 1617, 1468, 1373, 1221, 1182; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 0.92 (3H, s, CH₃), 1.08 (3H, s, CH₃), 1.23 (3H, t, *J* = 7.2 Hz), 2.15–2.39 (4H, *m*, 2CH₂), 2.41 (3H, s, CH₃), 4.10 (2H, *q*, *J* = 7.2 Hz, CH₂), 5.14 (1H, s, ArCH), 6.69 (1H, *brs*, NH), 7.50 (2H, *d*, *J* = 8.8 Hz, ArH), 8.12 (2H, *d*, *J* = 8.8 Hz, ArH); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 14.08, 17.0, 19.19, 20.94, 27.12, 32.5, 36.88, 37.13, 43.4, 57.3, 60.1, 104.6, 111.8, 123.3, 128.9, 134.8, 144.9, 146.4, 151.6, 154.7, 167.0, 196.2.

Ethyl 4-(2-chlorophenyl)-1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-5-oxoquinoline-3-carboxylate (17). Yellow solid; IR (KBr, cm⁻¹): 3103, 2966, 1733, 1645, 1621, 1471, 1390, 1230, 1025, 745; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 0.99 (3H, s, CH₃), 1.12 (3H, s, CH₃), 1.25 (3H, t, *J* = 7.2 Hz), 2.10–2.35 (4H, *m*, 2CH₂), 2.46 (3H, s, CH₃), 4.10 (2H, *q*, *J* = 7.1 Hz, CH₂), 5.05 (1H, s, ArCH), 6.21 (1H, *brs*, NH), 7.30–7.48 (4H, *m*, ArH); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 27.5, 29.8, 32.3, 35.3, 43.1, 48.8, 51.0, 51.5, 52.9, 56.1, 103.3, 110.0, 115.2, 127.9, 128.1, 128.9, 131.1, 133.3, 143.0, 169.4, 196.8.

Ethyl 1,4,5,6,7,8-hexahydro-2,7,7-trimethyl-4-(2-nitrophenyl)-5-oxoquinoline-3-carboxylate (18). Yellow solid; IR (KBr, cm⁻¹): 3300, 2992, 1698, 1652, 1614, 1465, 1376, 1227, 1180; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 0.95 (3H, s, CH₃), 1.10 (3H, s, CH₃), 1.27 (3H, t, *J* = 7.1 Hz), 2.20–2.42 (4H, *m*, 2CH₂), 2.44 (3H, s, CH₃), 4.18 (2H, *q*, *J* = 7.1 Hz, CH₂), 5.19 (1H, s, ArCH), 7.0 (1H, *brs*, NH), 7.45–8.10 (4H, *m*, ArH); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 15.2, 17.8, 19.3, 21.2, 27.5, 33.1, 37.3, 36.9, 42.9, 57.8, 60.5, 105.0, 113.1, 125.3, 130.2, 135.3, 146.1, 147.4, 153.2, 155.1, 169.0, 195.2.