ESI

Covalently bonded IL-type sulfamic acid onto the SBA-15: SBA-15/NHSO₃H as a highly active, reusable and selective green catalyst for solvent-free synthesis of polyhydroquinolines and dihydropyridines

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Experimental

Chemicals and apparatus

All reagents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus. Progress of reactions was monitored by Thin Layer Chromatography (TLC). ¹H and ¹³C NMR spectra were measured (CDCl₃) with a Bruker DRX-300 AVANCE spectrometer at 300 and 75 MHz, respectively.

General procedure for the synthesis of polyhydroquinolines and dihydropyridines:

A mixture of an aldehyde (1 mmol), β-dicarbonyl compound (1 or 2 mmol) and NH₄OAc (2.5 mmol) and dimedone (1 or no mmol) with catalytic amount of SBA-15/NHSO₃H (5 mol%) was stirred at 55 °C. After complete disappearance of starting material as indicated by TLC, the resulting mixture was diluted with hot ethyl acetate (10 mL) and filtered. The catalyst was completely recovered from the residue.
Selected spectroscopic data

**Methyl 2,7,7-trimethyl-5-oxo 4-phenyl-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (4a)**  
$^1$H NMR (300.13 MHz, CDCl$_3$): 0.94 (s, 3 H), 1.09 (s, 3 H), 2.11-2.40 (m, 8 H), 3.62 (s, 3 H), 5.08 (s, 1 H), 7.08-7.31 (m, 5 H).

**Methyl 4-(2-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (4b)**  
IR (KBr $v_{\text{max}}$/cm$^{-1}$): 3289, 2951, 1707, 1654, 1608, 1490, 1222, 1080, 1034, 827, 773, 540. $^1$H NMR (300.13 MHz, CDCl$_3$): 0.91 (s, 3 H), 1.07 (s, 3 H), 2.04-2.36 (m, 7 H), 3.57 (s, 3 H), 5.38 (s, 1 H), 6.81 (s, 1 H), 7.00-7.34 (m, 4 H). $^{13}$C NMR (75 MHz, CDCl$_3$): 19.19, 27.15, 29.37, 32.54, 35.61, 40.96, 50.62, 50.83, 105.17, 111.37, 126.42, 127.26, 129.61, 131.64, 131.64, 133.10, 143.87, 144.33, 148.92, 167.91, 195.51.

**Methyl 4-(2-methylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (4c)**  
IR (KBr $v_{\text{max}}$/cm$^{-1}$) 3282, 3189, 3071, 2956, 1693, 1644, 1484. $^1$H NMR (300.13 MHz, CDCl$_3$): 0.95 (s, 3 H), 1.09 (s, 3 H), 2.11-2.44 (m, 8 H), 3.62 (s, 3 H), 5.03 (s, 1 H), 5.90 (s, 1 H), 7.00-7.19 (m, 4 H). $^{13}$C NMR (75 MHz, CDCl$_3$): 27.21, 29.37, 35.79, 41.23, 51.03, 127.66, 128.73.

**Methyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (4d)**  
IR (KBr $v_{\text{max}}$/cm$^{-1}$): 3288, 2958, 1645, 1610, 1391, 1218, 1074, 1012, 840, 775, 538. $^1$H NMR (300.13 MHz, CDCl$_3$): 0.92 (s, 3 H), 1.08 (s, 3 H), 2.10-2.32 (m, 4 H), 2.39 (s, 3 H), 3.61 (s, 3 H, OCH$_3$), 5.04 (s, 1 H), 6.2 (s, 1 H), 7.15-7.27 (m, 4 H). $^{13}$C NMR (75 MHz, CDCl$_3$): 19.45, 27.06, 28.09, 28.24, 29.42, 32.71, 35.95, 41.05, 50.63, 51.08, 105.40, 111.90, 128.10, 129.24, 131.64, 143.98, 145.36, 148.23, 167.67, 195.57.

**Methyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (4e)**  
IR (KBr $v_{\text{max}}$/cm$^{-1}$): 3274, 2960, 1705, 1648, 1608, 1494. $^1$H NMR (300.13 MHz, CDCl$_3$): 0.94 (s, 3 H), 1.08 (s, 3 H), 2.10-2.38 (m, 7 H), 3.62 (s, 3 H), 3.74 (s, 3 H), 5.01 (s, 1 H), 5.95 (s, 1 H), 6.74 (d, $J = 8.7$ Hz, 2 H), 7.21 (d, $J = 8.7$ Hz, 2 H). $^{13}$C NMR (75 MHz, CDCl$_3$): 19.52, 27.16, 29.41, 35.40, 41.22, 50.68, 51.02, 55.10, 113.36, 128.75.
Ethyl 4-(2-methylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (4f) IR (KBr $v_{\text{max}}$/cm$^{-1}$): 3245, 3078, 2958, 1701, 1600. $^1$H NMR (300.13 MHz, CDCl$_3$): 0.95 (s, 3 H), 1.07 (s, 3 H), 1.22 (t, $J = 6.9$ Hz, 3 H), 2.13-2.34 (m, 10 H), 4.06 (q, $J = 6.9$ Hz, 2 H), 5.02 (s, 1 H), 6.30 (s, 1 H), 7.00-7.27 (m, 4 H). $^{13}$C NMR (75 MHz, CDCl$_3$): 14.20, 19.31, 21.04, 27.21, 29.34, 32.74, 36.11, 41.05, 50.27, 59.85, 106.84, 112.01, 127.87, 128.63, 135.46, 143.08, 143.94, 167.38, 195.38.

Ethyl 4-(2-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (4g) IR (KBr $v_{\text{max}}$/cm$^{-1}$): 3292, 3072, 2957, 1700, 1650, 1621, 1486, 758. $^1$H NMR (300.13 MHz, CDCl$_3$): 0.89 (s, 3 H), 1.07 (s, 3 H), 1.17 (t, $J = 6.9$ Hz, 3 H), 1.65-2.35 (m, 7 H), 4.04 (q, $J = 6.9$ Hz, 2 H), 5.38 (s, 1 H), 6.11 (s, 1 H), 7.00-7.41 (m, 4 H). $^{13}$C NMR (75 MHz, CDCl$_3$): 14.19, 19.35, 27.22, 29.32, 32.53, 35.97, 41.13, 50.57, 59.83, 105.33, 111.18, 126.24, 127.27, 129.67, 132.09, 133.20, 143.56, 148.68, 167.43, 195.35.

Ethyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (4h) IR (KBr $v_{\text{max}}$/cm$^{-1}$): 3243, 3076, 2958, 1706, 1647, 1604, 1488, 844. $^1$H NMR (300.13 MHz, CDCl$_3$): 0.92 (s, 3 H), 1.08 (s, 3 H), 1.17 (t, $J = 6.9$ Hz, 3 H), 2.10-2.38 (m, 7 H), 4.06 (q, $J = 6.9$ Hz, 2 H), 5.02 (s, 1 H), 6.25 (s, 1 H), 7.15-7.27 (m, 4 H). $^{13}$C NMR (75 MHz, CDCl$_3$): 14.19, 19.38, 27.08, 27.76, 29.41, 32.69, 36.22, 41.00, 50.64, 59.90, 105.70, 111.77, 128.00, 129.44, 131.57, 143.79, 145.60, 148.51, 167.26, 195.60.

Ethyl 2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (4i) IR (KBr $v_{\text{max}}$/cm$^{-1}$): 3275, 3200, 3075, 2964, 1704, 1604, 1518, 1378. $^1$H NMR (300.13 MHz, CDCl$_3$): 0.92 (s, 3 H), 1.10 (s, 3 H), 1.18 (t, $J = 6.9$ Hz, 3 H), 2.10-2.43 (m, 7 H), 4.05 (q, $J = 6.9$ Hz, 2 H), 5.16 (s, 1 H), 5.85 (s, 1 H), 7.47-8.10 (m, 4 H). $^{13}$C NMR (75 MHz, CDCl$_3$): 14.17, 19.50, 27.06, 29.35, 32.74, 37.17, 41.10, 50.51, 60.08, 105.05, 111.19, 123.33, 128.95, 144.27, 146.24, 148.60, 154.26, 166.78, 195.26.

Ethyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-3-quinolinecarboxylate (4j) IR (KBr $v_{\text{max}}$/cm$^{-1}$): 3300, 3078, 2950, 1648, 1610, 1032. $^1$H NMR
(300.13 MHz, CDCl₃): 0.94 (s, 3 H), 1.07 (s, 3 H), 1.21 (t, J = 7.2 Hz, 3 H), 2.13-2.29 (m, 4 H), 2.36 (s, 3 H), 3.74 (s, 3 H), 4.07 (q, J = 7.2 Hz, 2 H), 5.00 (s, 1 H), 6.14 (s, 1 H), 6.72-6.75 (m, 2 H), 7.20-7.27 (m, 2 H). ¹³C NMR (75 MHz, CDCl₃): 14.22, 19.38, 27.17, 29.40, 32.72, 35.70, 41.07, 50.52, 55.10, 59.81, 112.26, 113.24, 129.00, 139.50, 143.02, 148.51, 157.80, 167.50, 195.53.

Diethyl 2,6-diethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (5a). IR (KBr): 3342, 1700, 1657, 1473, 1198, 1129. ¹H NMR: 1.23 (t, ³JHH = 7.0 Hz, 6 H), 2.34 (s, 6 H), 4.12 (q, ³JHH = 7.0 Hz, 4 H), 4.91 (s, 1 H), 5.68 (s, 1 H), 7.07-7.43 (m, 5 H). ¹³C NMR: 14.91, 19.56, 39.43, 59.82, 103.14, 127.25, 127.32, 128.34, 129.61, 146.19, 148.25, 167.34.

Dimethyl 4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5d). IR (KBr): 3329, 1697, 1650, 1470, 1219, 1127. ¹H NMR: 2.35 (s, 6 H), 3.67 (s, 6 H), 4.99 (s, 1 H), 5.73 (s, 1 H), 7.19-7.28 (m, 4 H). ¹³C NMR: 19.56, 39.01, 50.99, 103.73, 128.14, 129.07, 131.84, 144.22, 145.98, 167.81.

Diethyl 4-(3-Chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5f). IR (KBr): 3320, 1690, 1642, 1475, 1200, 1136. ¹H NMR: 1.25 (t, ³JHH = 7.1 Hz, 6 H), 2.37 (s, 6 H), 4.13 (q, ³JHH = 7.1 Hz, 4 H), 4.99 (s, 1 H), 5.62 (s, 1 H), 7.11-7.29 (m, 4 H). ¹³C NMR: 15.18, 19.61, 39.74, 59.81, 103.82, 126.25, 126.31, 128.29, 129.04, 1433.60, 144.02, 149.73, 167.30.

Dimethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (5i). ¹H NMR: 2.28 (s, 6 H), 3.54 (s, 6 H), 4.89 (s, 1 H), 7.09-7.45 (m, 5 H), 8.87 (s, 1 H). ¹³C NMR: 18.47, 37.27, 51.10, 101.23, 127.27, 127.31, 128.37, 129.69, 146.13, 148.29, 168.64.