Supporting Information

for

Novel method for the synthesis of substituted imidazothiazolones

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I. General

All reagents were used directly from commercial suppliers without further purification. Melting points were determined on a Sanyo Gallenkamp apparatus. $^1$H and $^{13}$C NMR were recorded at 23 to 29 °C on a Bruker AC200, Bruker AM300, and Bruker DRX500 spectrometers using TMS as internal standard. High-resolution mass spectrums (HRMS) were obtain using a Bruker mikrOTOF II focus spectrometer (ESI). Mass spectra were measured on a MS 30 spectrometer. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN Analyzer and Euro EA Elemental Analyzer. 1-Substituted 4,5-diphenyl-1H-imidazol-2(3H)-ones 9a-e, 9f-h, ureas 10b,d,e and 1-substituted 4,5-diphenyl-1H-imidazole 3-oxide 12a,b and 12c were prepared according to the standard procedure.

II. General Procedure for the synthesis of 1-substituted 5-hydroxy-4,5-diphenyl-1H-imidazol-2(5H)-ones 8a-h

63% HNO$_3$ (5 mL) was added dropwise to a suspension of corresponding 1-substituted 4,5-diphenyl-1H-imidazol-2(3H)-ones 9a-h (4 mmol) in MeCN (25 mL). The reaction was monitored by the dissolution of the precipitated 9a-h and by the change in color of solution. The reaction mixture was extracted with a 1:1 CHCl$_3$/H$_2$O mixture, the chloroform layer was evaporated, and the products 8a-h was rubbed with Et$_2$O.

5-Hydroxy-1-methyl-4,5-diphenyl-1H-imidazol-2(5H)-one 8a

Yield 0.94 g (88%), white powder, mp 222-224°C. $^1$H NMR spectrum, δ, ppm; J/Hz (DMSO-d$_6$): 2.55 (s, 3 H, Me); 7.25-7.48 (m, 7 H, Ph); 7.52-7.56 (m, 1 H, Ph); 7.75 (s, 1 H, OH); 8.01-8.04 (m, 2 H, Ph). $^{13}$C NMR spectrum, δ, ppm; (DMSO-d$_6$): 23.82 (Me); 92.61 (C(Ph-OH)); 125.18, 128.75, 128.83, 129.05, 129.60, 133.35, 136.61 (Ph); 163.44 (C=O); 186.39 (C=N). Calcd. for C$_{16}$H$_{14}$N$_2$O$_2$: C 72.16%, H 5.30%, N 10.52%. Found: C 72.07%, H 5.34%, N 10.47%. MS, m/z, (I %): 266(6) [M]+, 250(61), 180(13), 163(56), 135(53), 134(56), 118(100).

1-Ethyl-5-hydroxy-4,5-diphenyl-1H-imidazol-2(5H)-one 8b

Yield 0.91 g (81%), white powder, mp 214-216°C. $^1$H NMR spectrum, δ, ppm; J/Hz (DMSO-d$_6$): 0.88 (t, 3 H, $J=7.1$, Me); 2.87–3.04 (m, 1 H, CH$_2$-); 3.13–3.30 (m, 1 H, CH$_2$-); 7.25-7.50 (m, 7 H, Ph); 7.53-7.57 (m, 1 H, Ph); 7.73 (s, 1 H, OH); 7.99-8.02 (m, 2 H, Ph). $^{13}$C NMR spectrum, δ, ppm; (DMSO-d$_6$): 13.79 (Me); 33.58 (CH$_2$); 92.81 (C(Ph-OH)); 125.20, 128.75, 128.82, 128.97, 129.65, 133.32, 137.32 (Ph); 163.38 (C=O); 186.07 (C=N). Calcd. for C$_{17}$H$_{16}$N$_2$O$_2$: C 72.84%, H 5.75%, N 10.52%. Found: C 72.79%, H 5.94%, N 9.99%.

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5.78%, N 10.06%. MS, m/z, (I %): 280(13) [M]+, 252(3), 208(4), 177(50), 165(8), 148(75), 134(35), 105(75), 91(7), 77(100).

5-Hydroxy-4,5-diphenyl-1-propyl-1H-imidazol-2(5H)-one 8c

Yield 0.98 g (83%), white powder, mp 206-208°C. 1H NMR spectrum, δ, ppm; J/Hz (DMSO-d6): 0.72 (t, 3 H, J=7.3, Me); 1.15–1.40 (m, 2 H, CH2); 2.70–2.90 (m, 1 H, CH2); 3.04–3.21 (m, 1 H, CH2); 7.29-7.48 (m, 7 H, Ph); 7.54-7.59 (m, 1 H, Ph); 7.74 (s, 1 H, OH); 8.00-8.03 (m, 2 H, Ph). 13C NMR spectrum, δ, ppm; (DMSO-d6): 11.34 (Me); 21.40, 40.69 (CH2); 92.82 (C(Ph-OH)); 125.14, 128.74, 128.82, 128.95, 129.66, 133.31, 137.33 (Ph); 163.78 (C=O); 186.04 (C=N). Calcd. for C18H18N2O2: C 73.45%, H 6.16%, N 9.52%. Found: C 73.51%, H 6.09%, N 9.46%. MS, m/z, (I %): 294(15) [M]+, 266(8), 236(25), 209(12), 191(78), 180(12), 163(52), 148(11), 134(71), 121(9), 105(100).

1-Butyl-5-hydroxy-4,5-diphenyl-1H-imidazol-2(5H)-one 8d

Yield 0.99 g (80%), white powder, mp 177-179°C. 1H NMR spectrum, δ, ppm; J/Hz (DMSO-d6): 0.72 (t, 3 H, J=7, Me); 1.00–1.40 (m, 4 H, 2CH2); 2.77–2.95 (m, 1 H, CH2); 3.10–3.25 (m, 1 H, CH2); 7.19-7.49 (m, 7 H, Ph); 7.51-7.56 (m, 1 H, Ph); 7.72 (s, 1 H, OH); 7.99-8.01 (m, 2 H, Ph). 13C NMR spectrum, δ, ppm; (DMSO-d6): 13.41 (Me); 19.47, 30.07, 38.53 (CH2); 92.76 (C(Ph-OH)); 125.08, 128.68, 128.74, 128.88, 129.60, 133.23, 137.30 (Ph); 163.69 (C=O); 185.98 (C=N). Calcd. for C19H20N2O2: C 74.00%, H 6.54%, N 9.08%. Found: C 74.03%, H 6.50%, N 9.09%. MS, m/z, (I %): 308(16) [M]+, 300(3), 292(2), 282(2), 251(3), 236(20), 209(11), 205(44), 177(75), 160(15), 148(33), 147(100).

1-Benzyl-5-hydroxy-4,5-diphenyl-1H-imidazol-2(5H)-one 8e

Yield 1.23 g (90%), white powder, mp 194-196°C. 1H NMR spectrum, δ, ppm; J/Hz (DMSO-d6): 4.09 (d, 1 H, J=15.6, CH2); 4.30 (d, 1 H, J=15.6, CH2); 7.05-7.19 (m, 5 H, Ph); 7.22-7.37 (m, 5 H, Ph); 7.40-7.45 (m, 2 H, Ph); 7.52-7.57 (m, 1 H, Ph); 7.84 (s, 1 H, OH); 7.99-8.02 (m, 2 H, Ph). 13C NMR spectrum, δ, ppm; (DMSO-d6): 42.51, (CH2); 92.92 (C(Ph-OH)); 125.28, 126.65, 127.75, 128.73, 128.79, 129.69, 133.39, 136.86, 137.38 (Ph); 163.95 (C=O); 186.97 (C=N). HRMS, m/z, found: 343.1432 [M+H]+ (calcd. for C22H18N2O2: 343.1441 [M+H]+).

2-(5-Hydroxy-2-oxo-4,5-diphenyl-2,5-dihydro-1H-imidazol-1-yl)ethyl acetate 8f

Yield 1.18 g (87%), white powder, mp 195-197°C. 1H NMR spectrum, δ, ppm; J/Hz (DMSO-d6): 1.89 (s, 3 H, Me); 3.07–3.21 (m, 1 H, CH2); 3.37-3.51...
3-(5-Hydroxy-2-oxo-4,5-diphenyl-2,5-dihydro-1H-imidazol-1-yl)propyl acetate 8g

Yield 1.01 g (72%), white powder, mp 115-117°C. 1H NMR spectrum, δ, ppm; J/Hz (DMSO-d6): 1.52-1.68 (m, 2 H, CH2); 1.95 (s, 3 H, Me); 2.82–2.96 (m, 1 H, CH2); 3.21-3.34 (m, 1 H, CH2); 3.82–3.93 (m, 2 H, CH2); 7.31-7.49 (m, 7 H, Ph); 7.53-7.58 (m, 1 H, Ph); 7.78 (s, 1 H, OH); 7.98-8.01 (m, 2 H, Ph). 13C NMR spectrum, δ, ppm; (DMSO-d6): 20.63 (Me); 24.63, 25.52, 38.41, 63.29 (CH2); 92.79 (C(Ph-OH)); 125.10, 128.70, 128.75, 128.83, 128.98, 129.67, 133.35, 137.26 (Ph); 163.81 (C=O); 170.26 (C=O(Ac)); 186.10 (C=N). HRMS, m/z, found: 353.1492 [M+H]⁺ (calcd. for C20H20N2O4: 353.1496 [M+H]⁺).

4-(5-Hydroxy-2-oxo-4,5-diphenyl-2,5-dihydro-1H-imidazol-1-yl)butyl acetate 8h

Yield 1.32 g (90%), white powder, mp 140-142°C. 1H NMR spectrum, δ, ppm; J/Hz (DMSO-d6): 1.20-1.34 (m, 2 H, CH2); 1.35-1.52 (m, 2 H, CH2); 1.94 (s, 3 H, Me); 2.80–2.94 (m, 1 H, CH2); 3.13-3.27 (m, 1 H, CH2); 3.85 (t, 2 H, J=6.0, CH2); 7.29-7.48 (m, 7 H, Ph); 7.52-7.57 (m, 1 H, Ph); 7.74 (s, 1 H, OH); 7.98-8.00 (m, 2 H, Ph). 13C NMR spectrum, δ, ppm; (DMSO-d6): 20.67 (Me); 24.63, 25.52, 38.41, 63.29 (CH2); 92.79 (C(Ph-OH)); 125.10, 128.70, 128.75, 128.83, 128.98, 129.67, 133.35, 137.26 (Ph); 163.81 (C=O); 170.26 (C=O(Ac)); 186.10 (C=N). HRMS, m/z, found: 367.1650 [M+H]⁺ (calcd. for C21H22N2O4: 367.1652 [M+H]⁺).

III. General procedure for the synthesis of 1-substituted 4,5-diphenyl-1H-imidazol-2(3H)-ones 9a-e.

A mixture of 2-hydroxy-1,2-diphenylethanone (benzoin) 11 (21.2 g, 0.1 mol) and ureas 10a-h (0.5 mol) in ethylene glycol (30 mL) was heated at 165 °C for 1 h with stirring. After cooling to room temperature, reaction mixture was extracted by H2O/CHCl3 (1:1) (50 mL) 3 times. Then CHCl3 layer was evaporated and triturated with MeCN (40 mL) and products 9a-e was filtrted off.
1-Methyl-4,5-diphenyl-1\(H\)-imidazol-2(3\(H\))-one 9a

Yield 89%. White solid, mp 286-288 °C\(^5\).

1-Ethyl-4,5-diphenyl-1\(H\)-imidazol-2(3\(H\))-one 9b

Yield 63%. White solid, mp 260-262 °C\(^5\).

4,5-Diphenyl-1-propyl-1\(H\)-imidazol-2(3\(H\))-one 9c

Yield 41%. White solid, mp 250-252 °C\(^5\).

1-Butyl-4,5-diphenyl-1\(H\)-imidazol-2(3\(H\))-one 9d

Yield 22%. White solid, mp 218-220 °C\(^6\).

1-Benzyl-4,5-diphenyl-1\(H\)-imidazol-2(3\(H\))-one 9e

Yield 49%. White solid, mp 182–184 °C\(^7\).

2-(2-Oxo-4,5-diphenyl-2,3-dihydro-1\(H\)-imidazol-1-yl)ethyl acetate 9f

Yield 94%. White solid, mp 182–184 °C\(^2\).

4-(2-Oxo-4,5-diphenyl-2,3-dihydro-1\(H\)-imidazol-1-yl)butyl acetate 9h

Yield 54%. White solid, mp 160-162 °C\(^4\).

IV. Procedure for the synthesis of 3-(2-oxo-4,5-diphenyl-2,3-dihydro-1\(H\)-imidazol-1-yl)propyl acetate 9g

To a suspension of compound 12b (7.35 g, 25 mmol) in CHCl\(_3\) (20 mL), a solution of Ac\(_2\)O (6.4 mL, 62.5 mmol) in CHCl\(_3\) (10 mL) was added dropwise over 30 min with cooling on an ice bath. The reaction mixture was stirred at room temperature for 24 h, after which EtOH (30 mL) was added. The mixture was stirred for 30 min, evaporated to half, and left to crystallize. The crystals of the product were filtered off and washed with EtOH.
Yield 3.10 g (37%), white powder, mp 157-159°C. $^1$H NMR spectrum, δ, ppm; J/Hz (DMSO-d$_6$): 1.59-1.71 (m, 2 H, CH$_2$); 1.85 (s, 3 H, Me); 3.52 (t, 2 H, J=6.9, CH$_2$); 3.84 (t, 2 H, J=6.1, CH$_2$); 7.08-7.22 (m, 5 H, Ph); 7.31-7.42 (m, 2 H, Ph); 7.43-7.53 (m, 3 H, Ph); 10.78 (s, 1 H, NH). $^{13}$C NMR spectrum, δ, ppm; (DMSO-d$_6$): 20.45 (Me); 27.81, 37.45, 61.24 (CH$_2$); 117.24, 120.32 (Ph-C=C-Ph); 125.30, 126.40 (C(Ph)); 128.29, 128.83, 129.06, 129.64, 130.69 (Ph); 153.10 (C=O); 170.02 (C=O (Ac)). HRMS, m/z, found: 359.1362 [M+Na]$^+$. (calcd. for C$_{20}$H$_{20}$N$_2$O$_3$: 359.1366 [M+Na]$^+$).

V. General Procedure for the Synthesis of 1-substituted 5-hydroxy-4,5-diphenyl-1H-imidazol-2(5H)-ones 13a-h.

To the solution of corresponding 1-substituted 5-hydroxy-4,5-diphenyl-1H-imidazol-2(5H)-ones 8a-h (4 mmol) and KSCN (0.44 g, 4.5 mmol) in MeCN (17 ml) at r.t. was added AcOH (3.00 ml). Reaction mixture was refluxed for 1 h. The reaction mixture was allowed to come to rt and was kept for 24 h to furnish 13a-h as a precipitate.

(3aR*,6aR*)-4-Methyl-3a,6a-diphenyltetrahydro-2H-imidazo[4,5-d]thiazole-2,5(3H)-dione 13a

Yield 1.20 g (92%), white powder, mp >300 °C. $^1$H NMR spectrum, δ, ppm; J/Hz (DMSO-d$_6$): 2.64 (s, 3 H, Me); 6.85-6.98 (m, 2 H, Ph); 7.01-7.17 (m, 6 H, Ph); 7.18-7.28 (m, 2 H, Ph); 8.35 (s, 1 H, NH(NCO)), 9.72 (s, 1 H, NH(SCO)). $^{13}$C NMR spectrum, δ, ppm; (DMSO-d$_6$): 25.73 (Me); 83.19, 87.52 ((Ph)-C-C-(Ph)); 126.93, 127.49, 127.57, 128.07, 128.18, 128.71 (Ph); 132.92, 137.51 (C(Ph)); 158.38, 171.91 (SC=O). HRMS, m/z, found: 326.0958 [M+H]$^+$ (calcd. for C$_{17}$H$_{15}$N$_3$O$_2$S: 326.0958 [M+H]$^+$).

(3aR*,6aR*)-4-Ethyl-3a,6a-diphenyltetrahydro-2H-imidazo[4,5-d]thiazole-2,5(3H)-dione 13b

Yield 1.22 g (74%), white powder, mp 235-237°C. $^1$H NMR spectrum, δ, ppm; J/Hz (DMSO-d$_6$): 1.12 (t, 3 H, J=7.0, Me); 2.71-2.91 (m, 1 H, CH$_2$); 3.31-3.50 (m, 1 H, CH$_2$); 6.90-7.01 (m, 2 H, Ph); 7.02-7.19 (m, 6 H, Ph); 7.20-7.31 (m, 2 H, Ph); 8.20 (s, 1 H, NH(NCO)); 9.65 (s, 1 H, NH(SCO)). $^{13}$C NMR spectrum, δ, ppm; (DMSO-d$_6$): 14.80 (Me); 35.15 (CH$_2$); 83.81, 87.80 ((Ph)-C-C-(Ph)); 126.95, 127.47, 127.51, 128.84, 128.14, 128.65 (Ph); 133.87, 137.49 (C(Ph)); 158.42, 172.27 (SC=O). HRMS, m/z, found: 340.1110 [M+H]$^+$ (calcd. for C$_{18}$H$_{17}$N$_3$O$_2$S: 340.1114 [M+H]$^+$).
(3aR*,6aR*)-3a,6a-Diphenyl-4-propyltetrahydro-2H-imidazo[4,5-d]thiazole-2,5(3H)-dione 13c

Yield 1.24 g (88%); white powder, mp 283–285°C. 1H NMR spectrum, δ, ppm; J/Hz (DMSO-d6): 0.86 (t, 3 H, J=7.3, Me); 1.50-1.65 (m, 2 H, CH2); 2.56-2.71 (m, 1 H, CH2); 3.30-3.42 (m, 1 H, CH2); 6.82-6.95 (m, 2 H, Ph); 7.00-7.18 (m, 6 H, Ph); 7.19-7.29 (m, 2 H, Ph); 8.22 (s, 1 H, NH (NCO)); 9.59 (s, 1 H, NH(SCO)). 13C NMR spectrum, δ, ppm; (DMSO-d6): 11.19 (Me); 22.26, 42.24 (CH2); 83.81, 87.97 ((Ph)-C-C-(Ph)); 126.95, 127.48, 127.56, 127.92, 128.19, 128.69 (Ph); 131.65, 137.55 (C(Ph)); 158.65 ((N)C=O); 172.39 ((S)C=O). HRMS, m/z, found: 376.1085 [M+Na]+ (calcd. for C19H19N3O2S: 376.1090 [M+Na]+).

(3aR*,6aR*)-4-Butyl-3a,6a-diphenyltetrahydro-2H-imidazo[4,5-d]thiazole-2,5(3H)-dione 13d

Yield 1.17 g (80%); white powder, mp 297–299 °C. 1H NMR spectrum, δ, ppm; J/Hz (DMSO-d6): 0.88 (t, 3 H, J=7.3, Me); 1.21-1.39 (m, 2 H, CH2); 1.50-1.63 (m, 2 H, CH2); 2.51-2.66 (m, 1 H, CH2); 3.38-3.50 (m, 1 H, CH2); 6.85-6.99 (m, 2 H, Ph); 7.00-7.19 (m, 6 H, Ph); 7.20-7.30 (m, 2 H, Ph); 8.21 (s, 1 H, NH (NCO)); 9.59 (s, 1 H, NH (SCO)). 13C NMR spectrum, δ, ppm; (DMSO-d6): 13.73 (Me); 19.61, 31.21, 40.41 (CH2); 83.85, 87.98 ((Ph)-C-C-(Ph)); 126.96, 127.48, 127.55, 127.92, 128.19, 128.69 (Ph); 133.62, 137.53 (C(Ph)); 158.63 ((N)C=O); 172.34 ((S)C=O). HRMS, m/z, found: 368.1421 [M+H]+ (calcd. for C20H21N3O2S: 368.1427 [M+H]+).

(3aR*,6aR*)-4-Benzyl-3a,6a-diphenyltetrahydro-2H-imidazo[4,5-d]thiazole-2,5(3H)-dione 13e

Yield 1.36 g (85%); white powder, mp 298–300°C. 1H NMR spectrum, δ, ppm; J/Hz (DMSO-d6): 3.92 (d, 1 H, J=6.5, CH2); 4.65 (d, 1 H, J=6.4, CH2); 6.90-6.98 (m, 2 H, Ph); 7.05-7.16 (m, 6 H, Ph); 7.18-7.41 (m, 7 H, Ph); 8.43 (s, 1 H, NH(NCO)), 9.64 (s, 1 H, NH(SCO)). 13C NMR spectrum, δ, ppm; (DMSO-d6): 44.03 (CH2); 83.80, 88.38 ((Ph)-C-C-(Ph)); 126.63, 127.01, 127.49, 127.60, 127.98, 128.10, 128.26, 128.78 (Ph); 133.38, 137.51, 138.53 (C(Ph)); 158.73 ((N)C=O); 172.15 ((S)C=O). HRMS, m/z, found: 343.1432 [M+H]+ (calcd. for C23H19N3O2S: 343.1441 [M+H]+).
2-((3aR*,6aR*)-2,5-Dioxo-3a,6a-diphenyltetrahydro-2H-imidazo[4,5-d]thiazol-4(5H)-yl)ethyl acetate 13f

Yield 0.83 g (53%); white powder, mp 248-250 °C. ¹H NMR spectrum, δ, ppm; J/Hz (DMSO-d₆): 2.00 (s, 3 H, Me(Ac)); 2.91-3.05 (m, 1 H, CH₂); 3.56-3.68 (m, 1 H, CH₂); 4.05-4.22 (m, 2 H, CH₂); 6.88-6.98 (m, 2 H, Ph); 7.00-7.18 (m, 6 H, Ph); 7.19-7.29 (m, 2 H, Ph); 8.37 (s, 1 H, NH(NCO)); 9.60 (s, 1 H, NH(SCO)). ¹³C NMR spectrum, δ, ppm; (DMSO-d₆): 20.60 (Me); 39.72, 61.32 (CH₂); 83.75, 87.85 ((Ph)-C-C-(Ph)); 126.95, 127.46, 127.58, 127.96, 128.24, 128.79 (Ph); 133.45, 137.38 (C(Ph)); 158.65 ((N)=O); 170.32 (Ac); 172.22 ((S)=O). HRMS, m/z, found: 398.1163 [M+H]⁺ (calcd. for C₂₀H₁₉N₃O₄S: 398.1169 [M+H]⁺).

3-((3aR*,6aR*)-2,5-Dioxo-3a,6a-diphenyltetrahydro-2H-imidazo[4,5-d]thiazol-4(5H)-yl)propyl acetate 13g

Yield 0.94 g (57%); white powder, mp 243-245°C. ¹H NMR spectrum, δ, ppm; J/Hz (DMSO-d₆): 1.80-1.90 (m, 2 H, CH₂); 1.99 (s, 3 H, Me(Ac)); 2.71-2.84 (m, 1 H, CH₂); 3.43-3.56 (m, 1 H, CH₂); 3.98-4.08 (m, 2 H, CH₂); 6.88-6.94 (m, 2 H, Ph); 7.04-7.16 (m, 6 H, Ph); 7.19-7.27 (m, 2 H, Ph); 8.29 (s, 1 H, NH(NCO)); 9.61 (s, 1 H, NH(SCO)). ¹³C NMR spectrum, δ, ppm; (DMSO-d₆): 20.70 (Me); 28.36, 37.69, 61.84 (CH₂); 83.80, 88.07 ((Ph)-C-C-(Ph)); 126.98, 127.48, 127.54, 127.94, 128.18, 128.73 (Ph); 133.57, 137.51 (C(Ph)); 158.64 ((N)=O); 170.32 (Ac); 172.22 ((S)=O). HRMS, m/z, found: 412.1321 [M+H]⁺ (calcd. for C₂₁H₂₁N₃O₄S: 412.1326 [M+H]⁺).

4-((3aR*,6aR*)-2,5-Dioxo-3a,6a-diphenyltetrahydro-2H-imidazo[4,5-d]thiazol-4(5H)-yl)butyl acetate 13h

Yield 1.34 g (79%); white powder, mp 152-154°C. ¹H NMR spectrum, δ, ppm; J/Hz (DMSO-d₆): 1.50-1.71 (m, 4 H, 2CH₂); 1.98 (s, 3 H, Me(Ac)); 2.64-2.80 (m, 1 H, CH₂); 3.36-3.55 (m, 1 H, CH₂); 3.90-4.09 (m, 2 H, CH₂); 6.86-6.94 (m, 2 H, Ph); 7.01-7.18 (m, 6 H, Ph); 7.19-7.30 (m, 2 H, Ph); 8.24 (s, 1 H, NH(NCO)); 9.60 (s, 1 H, NH(SCO)). ¹³C NMR spectrum, δ, ppm; (DMSO-d₆): 20.72 (Me); 22.58, 25.68, 40.39, 63.55 (CH₂); 83.84, 88.03 ((Ph)-C-C-(Ph)); 126.98, 127.50, 127.58, 127.96, 128.22, 128.74 (Ph); 133.59, 137.53 (C(Ph)); 158.70 ((N)=O); 170.39 (Ac); 172.32 ((S)=O). HRMS, m/z, found: 426.1470 [M+H]⁺ (calcd. for C₂₂H₂₃N₃O₄S: 426.1482 [M+H]⁺).
VI. Procedure for the Synthesis of 5-methoxy-1-methyl-4,5-diphenyl-1\(H\)-imidazol-2(5\(H\))-one 14

63% HNO\(_3\) (5 mL) was added dropwise to a suspension of 1-methyl-4,5-diphenyl-1\(H\)-imidazol-2(3\(H\))-one 9a (1 g, 4 mmol) in MeOH (25 mL). The reaction was monitored by the change in color and by the dissolution of the precipitated 9a. After 24 h formed colorless crystals of 14 were filtered.

Yield 1.07 g (90%), colorless prisms, mp 157-159°C. \(^1\)H NMR spectrum, \(\delta\), ppm; \(J/Hz\) (DMSO-d\(_6\)): 2.53 (s, 3 H, Me); 3.12 (s, 3 H, OMe); 7.30-7.52 (m, 7 H, Ph); 7.56-7.61 (m, 1 H, Ph); 7.99-8.01 (m, 2 H, Ph). \(^{13}\)C NMR spectrum, \(\delta\), ppm; (DMSO-d\(_6\)): 24.08 (Me); 50.85 (OMe); 97.11 (C(Ph-OMe)); 125.23, 128.33, 128.97, 129.14, 129.22, 129.28, 134.09, 135.07 (Ph); 163.36 (C=O); 184.70 (C=N). HRMS, m/z, found: 281.1280 [M+H]\(^+\) (calcd. for C\(_{17}\)H\(_{16}\)N\(_2\)O\(_2\): 281.1285 [M+H]\(^+\)).

VII. Procedure for the synthesis of (4R*,5S*)-4,5-dihydroxy-1-methyl-4,5-diphenylimidazolidin-2-one 15

63% HNO\(_3\) (5 mL) was added dropwise to a suspension of 1-methyl-4,5-diphenyl-1\(H\)-imidazol-2(3\(H\))-one 9a (1 g, 4 mmol) in AcOH (25 mL). The reaction was monitored by the change in color and by the dissolution of the precipitated 9a. To the reaction mixture was added H\(_2\)O (40 mL). The precipitate formed of 15 was filtered off and recrystallize from Me\(_2\)CO.

Yield 1.04 g (91%), white powder, mp 194-196°C. \(^1\)H NMR spectrum, \(\delta\), ppm; \(J/Hz\) (DMSO-d\(_6\)): 2.51 (s, 3 H, Me); 6.26 (s, 1 H, OH); 6.55 (s, 1 H, OH); 6.86-6.94 (m, 2 H, Ph); 6.95-7.04 (m, 6 H, Ph); 7.05-7.14 (m, 2 H, Ph); 7.62 (s, 1 H, NH). \(^{13}\)C NMR spectrum, \(\delta\), ppm; (DMSO-d\(_6\)): 24.86 (Me); 89.13, 93.22 ((Ph)-C-C-(Ph)); 126.63, 126.75, 127.03, 127.11, 127.18 (Ph); 138.33, 140.22 (C(Ph)); 159.19 (C=O). HRMS, m/z, found: 285.1231 [M+H]\(^+\) (calcd. for C\(_{16}\)H\(_{16}\)N\(_2\)O\(_3\): 285.1234 [M+H]\(^+\)).
VIII. $^1$H- and $^{13}$C-NMR spectra of compounds 8,9,13-15
IX. X-Ray Diffraction Data.

X-ray diffraction experiments for 13c, 13d, 8a and 8b were carried out with a Bruker APEX2 DUO CCD diffractometer for 13c and 13d and a Bruker APEX2 CCD diffractometer for 8a and 8b, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans) at 100K (13d) and 120K (others). The structures were solved by direct method and refined by the full-matrix least-squares against F² in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms of NH and OH groups were found in difference Fourier synthesis; the H(C) atom positions were calculated. All hydrogen atoms were refined in isotropic approximation in riding model. Crystal data and structure refinement parameters for, 8a, 8b, 13c, and 13d are given in Table S-1. All calculations were performed using the SHELXTL software.

The structures were solved by direct method and refined by the full-matrix least-squares against F² in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms of NH and OH groups were found in difference Fourier synthesis; the H(C) atom positions were calculated. All hydrogen atoms were refined in isotropic approximation in riding model. Crystal data and structure refinement parameters for 13c, 13d, 8a and 8b are given in Table 1. All calculations were performed using the SHELXTL software [8].

Table S1. Crystal data and structure refinement parameters for 8a,b and 13c,d.

<table>
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<th>8b</th>
<th>13c</th>
<th>13d</th>
</tr>
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<td>C₁₉H₁₉N₃O₂S</td>
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<td>P-1</td>
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<td>0.553/-0.401</td>
<td>0.560/-0.375</td>
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**Appendix A. Supplementary data**

CCDC 1011396-1011397 and 1011495-1011496 contain the supplementary crystallographic data for 13c, 13d and 8a, 8b. These data can be obtained free of charge via [http://www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html), or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.
X. Powder X-ray Diffraction Data.

High-quality experimental powder X-ray diffraction data for compound 13c (Fig.S1) were obtained with a PANalytical EMPYREAN diffractometer (fine-focus sealed tube, Cu Kα₁ radiation (λ=1.5406 Å), Johanson’s Hybrid Ge{111} monochromator for the primary beam, Bragg-Brentano geometry) using a position-sensitive detector PIXcel¹D. The patterns were scanned in reflection mode, 0/20 continuously scanned over the angular range 5° - 60° (2θ) with a step 0.013° (2θ) and counting time of 1000 s step⁻¹. Preferred orientation effects were reduced by grinding. Alignment and calibration were checked using Al₂O₃ (SRM676). Diffraction data were collected at room temperature (296K).

The extraction of peak position for indexing was performed with Pawley method. Patterns indexing were carried out by means of the program Ito or TREOR. Unit cell parameters were refined by least-squares fitting of Bragg’s equation to the position of the diffraction lines. All calculations for the refinement of the diffraction patterns and refine the unit cell parameters were performed using complex programs available in PC software “HighScore Plus” supplied by PANalytical EMPYREAN (Version: 3.0.t (3.0.5), Date 30-01-2012. Produced by: PANalytical B.V. Amelo, The Netherland).

The experimental powder XRD data and cell parameters obtained for compound 13c are deposited at the PDF-base of International Centre for Diffraction Data (ICDD).

Results of the analysis of the experimental powder diffraction pattern of the compound 13c show that the investigated samples were single-phase. The resulting unit cell parameters of compound 13c responsible for such a single-crystal experiment, and the observed deviations are due to thermal expansion of the crystal. Space group, unit cell parameters and characteristics of the investigated verification phases shown in Table S2.

**Table S2.** Space groups, unit cell parameters and characteristics of the investigated verification phases 13c

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<td>γ, (o)</td>
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Figure S1. Powder diffraction pattern of (13c).
XI. References


