Supplementary Data

GREEN AND HIGHLY EFFICIENT SYNTHESIS OF PYRANOPYRAZOLES IN CHOLINE CHLORIDE/UREA DEEP EUTECTIC SOLVENT

Adeleh Moshtaghi Zonouz; Davood Moghani

*Chemistry Department, Faculty of Science, Azarbaijan Shahid Madani University, Tabriz -
Iran*

*6-Amino-3-methyl-4-phenyl-2,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (5a)*

White solid; m.p. 245-246 °C [Lit¹⁸ 244-245]; IR (KBr): 3373, 3310, 3169, 2192, 1649, 1611, 1518, 1401 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆): δ 1.77 (s, 3H, CH₃), 4.59(s, 1H, C(4)-H), 6.88 (s, 2H, NH₂), 7.15–7.33 (m, 5H, Ar-H), 12.11 (s, 1H, NH) ppm; ¹³C NMR(100 MHz, DMSO-d₆): δ 9.77 (CH₃), 36.28 (CH), 57.20 (C), 97.96 (C), 120.84 (CN), 126.80 (CH), 127.51 (2CH), 128.49 (2CH), 135.67 (C), 144.47 (C), 154.81 (C), 160.91 (C) ppm.

*6-Amino-3-methyl-4-(2-nitrophenyl)-2,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (5b)*

Yellowish solid;; m.p. 222-224 °C [Lit¹⁸ 223-224]; IR (KBr): 3466, 3378, 3159, 2188, 1650, 1594, 1519, 1410, 1168 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆): δ 1.87 (s, 3H, s, CH₃), 5.22 (s, 1H, C(4)-H), 7.15 (2H, NH₂), 7.36 (d, *J* = 8 Hz, 1H, Ar-H), 7.45 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.63 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.82 (d, *J* = 8 Hz, 1H, Ar-H), 12.01 (1H, s, NH) ppm. ¹³C NMR (100 MHz, DMSO-d₆): δ 10.20 (CH₃), 29.41 (CH), 56.59 (C), 103.47 (C), 118.10 (C), 120.29 (CN), 126.91 (C), 128.17 (CH), 129.67 (CH), 136.38 (CH), 138.71 (CH), 155.90 (C), 161.30 (C), 165.10 (C) ppm.

*6-Amino-3-methyl-4-(3-nitrophenyl)-2,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (5c)*

Yellowish solid; m.p. 214-216 °C [Lit¹⁸ 214-216]; IR (KBr): 3489, 3318, 3191, 2193, 1645, 1600, 1526, 1407, 1167; ¹H NMR (400 MHz, DMSO-d₆): δ 1.93 (3H, s, CH₃), 4.81 (1H, s, C(4)-H), 6.18 (s, 2H, NH₂), 7.53 (t, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.78–8.02 (m, 2H), 12.08 (s, 1H, NH) ppm; ¹³C NMR (100 MHz, DMSO-d₆): δ 9.70 (CH₃), 28.80 (CH), 56.42 (C), 112.61 (CN), 120.12 (C), 123.17 (CH), 128.45

(CH), 128.60 (CH), 136.17 (CH), 141.43 (C), 146.04 (C), 151.04 (C), 154.62 (C), 161.12 (C) ppm.

6-Amino-3-methyl-4-(4-nitrophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (5d)

Yellowish solid; m.p. 194-195 °C [Lit¹⁹ 192-194]; IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3475, 3186, 2190, 1651, 1601, 1525, 1352, 1168; ¹H NMR (400 MHz, DMSO-d₆): δ 1.97 (s, 3H, CH₃), 4.77 (s, 1H, C(4)-H), 6.21 (s, 2H, NH₂), 7.53 (d, J = 7.6 Hz, 2H, Ar-H), 8.04 (d, J = 8 Hz, 2H, Ar-H), 12.06 (s, 1H, NH) ppm. ¹³C NMR (100 MHz, DMSO-d₆): δ 10.30 (CH₃), 27.41 (CH), 64.17 (C), 112.63 (CN), 125.61 (C), 128.31 (CH), 129.45 (CH), 136.12 (C), 141.53 (C), 150.80 (C), 154.62 (C), 160.79 (C) ppm.

6-Amino-3-methyl-4-(3-chlorophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (5e)

Yellowish solid; m.p. 228-230 °C [Lit²⁰ 230-231]; IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3409, 3120, 2187, 1644, 1596, 1409, 183; ¹H NMR (400 MHz, DMSO-d₆): δ 1.81 (s, 3H, CH₃), 4.65 (s, 1H, C(4)-H), 6.92 (s, 2H, NH₂), 7.15 (d, J = 7.6 Hz, 1H, Ar-H), 7.20 (s, 1H, Ar-H), 7.28-7.30 (m, 1H, Ar-H), 7.36 (t, J = 7.6 Hz, 1H, Ar-H), 12.14 (s, 1H, NH) ppm.

6-Amino-3-methyl-4-(4-chlorophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (5f)

Yellowish solid; m.p. 232-233 °C [Lit²⁰ 234-235]; IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3409, 3307, 3179, 2189, 1643, 1600, 1490, 1403, 1184; ¹H NMR (400 MHz, DMSO-d₆): δ 1.73 (s, 3H, CH₃), 4.57 (s, 1H, C(4)-H), 6.89 (s, 2H, NH₂), 7.12-7.14 (m, 2H, Ar-H), 7.31-7.33 (m, 2H, Ar-H), 12.09 (s, 1H, NH) ppm.

6-Amino-4-(4-methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (5i)

White solid; m.p. 172-173 °C [Lit¹⁹ 170-172]; IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3380, 3297, 3177, 2196, 1652, 1604, 1502, 1403, 1250; ¹H NMR (400 MHz, DMSO-d₆): δ 1.80 (s, 3H, CH₃), 3.56 (s, 3H, OCH₃), 4.43 (s, 1H, C(4)-H), 6.04 (s, 2H, NH₂), 6.67-6.91 (m, 4H, Ar-H), 12.08 (s, 1H, NH) ppm; ¹³C NMR (100 MHz, DMSO-d₆): δ 9.8 (CH₃), 35.4

(CH), 57.5 (OCH₃), 97.8 (CH), 114.12 (CN), 121 (C), 128.5 (CH), 135.5 (C), 136.5 (C), 154.7 (C), 158.0 (C), 160.8 (C) ppm.

*6-Amino-4-(2-furyl)-3-methyl-2,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (5j)*

Brown solid; m.p. 229-230 °C [Lit²⁰ 230-231]; IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3359, 3171, 2187, 1649, 1600, 1493, 1405; ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.97 (s, 3H, CH₃), 4.77 (s, 1H, C(4)-H), 6.17 (d, *J* = 2.8 Hz, 1H), 6.36 (s, 1H), 6.69 (s, 2H, NH₂), 7.52 (s, 1H), 12.17 (s, 1H, NH) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ 9.66 (CH₃), 29.87 (CH), 54.04 (C), 95.18 (C), 105.76 (CH), 110.34 (CH), 120.72 (CN), 135.98 (C), 142.37 (CH), 154.88 (C), 155.75 (C), 161.56 (C) ppm.

5j- FT-IR

5j-¹H-NMR(CDCl₃)

Current Data Parameters
NAME Ordibehant-54
PROC 254
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050505
Time_ 11:41
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 32768
SOLVENT DMSO
NS 1100
DS 4
SWH 251325.8200 Hz
FIDRES 0.7765773 Hz
AQ 0.00311330 sec
RG 327.68
AQ 0.00311330 sec
DE 19.300 umsec
TE 300.2 K
D1 10.00000000 sec
D11 0.03000000 sec
D12 0.00000000 sec
===== CHANNEL f1 =====
NUC1 13C
P1 9.30 umsec
PL1 0.00 dB
SFO1 100.6267600 MHz
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 85.00 umsec
PL12 0.00 dB
PL13 0.00 dB
PL14 19.00 dB
PL15 19.00 dB
SFO2 400.1315000 MHz
F2 - Processing parameters
SI 32768
SF 100.6267600 MHz
WDW 16
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
ID NMR plot parameters
F1 20.00 cm
F2 20.00 cm
F3 234.603 85 Hz
F4 -16.467 50m
F5 159.750 Hz
F6CN 12.28627 Hz/cm
H2CN 125.28627 Hz/cm

5j- ¹³C-NMR(CDCl₃)

5a- FT-IR

5a- ¹H-NMR(CDCl₃)

5a- ¹³C-NMR(CDCl₃)