Electronic supplementary materials *Mendeleev Commun.*, 2015, **25**, 185−187

Non-catalytic solvent-free synthesis of 5,6,7,8-tetrahydro-4*H*-chromenes from aldehydes, dimedone and malononitrlie at ambient temperature

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2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (2a). White solid; yield 0.85 g (96%); mp 225–226 ºC (lit.[1] mp 224–225 ºC). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.97 (s, 3H, OCH_3), 1.05 (s, 3H, CH_3), 2.24–2.39 (m, 4H, CH_2), 4.19 (s, 1H, CH), 6.97 (s, 2H, NH_2), 7.14–7.32 (m, 5H, Ar).

2-Amino-7,7-dimethyl-4-(4-methylphenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (2b). White solid; yield 0.86 g (93%); mp 215–217 ºC (lit.[2] mp 215–217 ºC). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.95 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.16 (m, 4H, CH_2), 4.13 (s, 1H, CH), 6.95 (s, 2H, NH_2), 7.01–7.10 (m, 4H, Ar).

2-Amino-4-(4-ethylphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (2c). White solid; yield 0.92 g (95%); mp 223–225 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.96 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 1.16 (t, 3H, CH_3), 2.17 (m, 4H, CH_2), 2.50 (s, 2H, CH_2), 4.13 (s, 1H, CH), 6.96 (s, 2H, NH_2), 7.02 - 7.13 (m, 4H, Ar); ^{13}C-NMR (DMSO-d_6): 15.4, 26.8, 27.7, 28.4, 31.8, 35.2, 39.8, 50.0, 58.5, 112.9, 119.8, 127.1 (2C), 127.7 (2C), 141.9, 142.1, 158.4, 162.3, 195.6 ppm; IR (KBr): ν = 3357, 3307, 3174, 2189, 1683, 1654, 1605, 1369, 1215, 1138 cm^{-1}; HRMS (ESI): 323.1750 $[M+H]^+$, calcd for $C_{20}H_{23}N_2O_2$: 323.1754; MS (m/z, relative intensity %): 322 (63), 293 (100), 227 (51), 217 (87), 161 (14), 133 (10), 115(14), 77 (5), 41 (4).

2-Amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (2d). White solid; yield 0.86 g (88%); mp 207–209 ºC (lit.[1] mp 207–208 ºC). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.94 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 2.08–2.44 (m, 4H, CH_2), 3.71 (s, 3H, OCH_3), 4.13 (s, 1H, CH), 6.94 (s, 2H, NH_2), 6.82–7.07 (m, 4H, Ar).

2-Amino-4-(3-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (2e). White solid; yield 1.01 g (90%); mp 225–227 ºC (lit.[3] mp 225–226 ºC). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.96 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 2.19 (m, 4H, CH_2), 4.21 (s, 1H, CH), 7.08 (s, 2H, NH_2), 7.15–7.40 (m, 4H, Ar).

2-Amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (2f). White solid; yield 1.06 g (95%); mp 214–216 ºC (lit.[4] mp 215–217 ºC). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.96 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.18 (m, 4H, CH_2), 4.19 (s, 1H, CH), 7.04 (s, 2H, NH_2), 7.04–7.50 (m, 4H, Ar).

2-Amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (2g). White solid; yield 0.96 g (97%); mp 213–215 ºC (lit.[4] mp 213–215 ºC). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.97 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 2.16 (m, 4H, CH_2), 4.22 (s, 1H, CH), 7.07 (s, 2H, NH_2), 7.21–7.35 (m, 4H, Ar).

2-Amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (2h). White solid; yield 1.00 g (98%); mp 208–209 ºC (lit.[1] mp 209–210 ºC). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.96 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.08–2.53 (m, 4H, CH_2), 4.37 (s, 1H, CH), 7.17 (s, 2H, NH_2), 7.43–8.18 (m, 4H, Ar).

2-Amino-4-(2,6-dichlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (2i). White solid; yield 0.97 g (89%); mp 235–237 ºC (lit.[5] mp 236–238 ºC). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.99 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.16 (m, 4H, CH_2), 5.21 (s, 1H, CH), 7.10 (s, 2H, NH_2), 7.21–7.41 (m, 3H, Ar).

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