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Solvent-free cascade assembling of salicylic aldehydes and malononitrile: rapid and efficient approach to 2-amino-4*H*-chromene scaffold

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Experimental

(2-Amino-3-cyano-4*H*-chromen-4-yl)malononitrile (2a)
White solid; yield 0.46 g (97%); mp 150–152 ºC (decomp.) (lit. [1] mp 150−153 ºC).
^{1}H NMR (300 MHz, [D$_6$]DMSO): δ 4.59 (d, *J* = 4.0 Hz, 1H, CH), 5.07 (d, *J* = 4.0 Hz, 1H, CH), 7.13 (d, *J* = 8.1 Hz, 1H, Ar), 7.27 (td, *J* = 7.3, 1.1 Hz, 1H, Ar), 7.43 (td, *J* = 7.7, 1.5 Hz, 1H, Ar), 7.48 (d, *J* = 7.7 Hz, 1H, Ar), 7.50 (s, 2H, NH$_2$) ppm.

(2-Amino-3-cyano-6-methyl-4*H*-chromen-4-yl)malononitrile (2b)
White solid; yield 0.49 g (97%); mp 139–143 ºC (decomp.).
^{1}H NMR (300 MHz, [D$_6$]DMSO): δ 2.30 (s, 3H, CH$_3$), 4.52 (d, *J* = 4.0 Hz, 1H, CH), 5.05 (d, *J* = 4.0 Hz, 1H, CH), 7.02 (d, *J* = 8.8 Hz, 1H, Ar), 7.22 (d, *J* = 8.8 Hz, 1H, Ar), 7.26 (s, 1H, Ar), 7.45 (s, 2H, NH$_2$) ppm.
^{13}C NMR (75 MHz, [D$_6$]DMSO): δ 20.33, 32.43, 37.14, 48.78, 112.91, 113.07, 116.10, 117.56, 119.45, 128.84, 130.61, 134.15, 147.70, 163.53 ppm.
IR (KBr): ν = 3451, 3340, 2888, 2190, 1643, 1583, 1429, 1218, 1043 cm^{-1}.
MS (EI): *m/z* (%) = 250 (0.5) [M]$^+$, 185 (78), 184 (100), 157 (36), 129 (12), 66 (58), 39 (18).
Found (%): C, 66.93, H, 4.17, N, 22.13. Calc. for C$_{14}$H$_{10}$N$_4$O (%): C, 67.19; H, 4.03; N, 22.39.

(2-Amino-6-chloro-3-cyano-4*H*-chromen-4-yl)malononitrile (2c)
White solid; yield 0.51 g (95%); mp 155–158 ºC (decomp.).
^{1}H NMR (300 MHz, [D$_6$]DMSO): δ 4.62 (d, *J* = 3.7 Hz, 1H, CH), 5.14 (d, *J* = 3.7 Hz, 1H, CH), 7.18 (d, *J* = 8.8 Hz, 1H, Ar), 7.48 (dd, *J* = 8.8, 2.2 Hz, 1H, Ar), 7.58 (s, 3H, Ar, NH$_2$) ppm.
^{13}C NMR (75 MHz, [D$_6$]DMSO): δ 32.30, 36.85, 48.46, 112.69, 112.85, 118.29, 119.08, 119.89, 128.46, 128.51, 130.02, 148.56, 163.22 ppm.
IR (KBr): ν = 3443, 3345, 2890, 2193, 1644, 1573, 1429, 1230, 1037 cm^{-1}.
MS (EI): *m/z* (%) = 272 (0.1) [M]$^+$, 270 (0.3) [M]$^+$, 206 (25), 204 (100), 177 (78), 149 (8), 114 (46), 66 (75), 39 (26).
Found (%): C, 57.48; H, 2.75; Cl, 12,95; N, 20.49. Calc. for C$_{13}$H$_7$ClN$_4$O (%): C, 57.69; H, 2.61; Cl, 13.10; N, 20.70.

(2-Amino-6-bromo-3-cyano-4*H*-chromen-4-yl)malononitrile (2d)

White solid; yield 0.60 g (96%**)**; mp 159–160 ºC (decomp.) (lit.[1] mp 160–161 ºC).

^{1}H NMR (300 MHz, [D_6]DMSO): δ 4.61 (d, *J* = 4.0 Hz, 1H, CH), 5.13 (d, *J* = 4.0 Hz, 1H, CH), 7.12 (d, *J* = 8.8 Hz, 1H, Ar), 7.57 (s, 2H, NH_2), 7.59 (dd, *J* = 8.8, 2.2 Hz, 1H, Ar), 7.71 (d, *J* = 2.2 Hz, 1H, Ar) ppm.

(2-Amino-3-cyano-6-nitro-4*H*-chromen-4-yl)malononitrile (2e)

White solid; yield 0.53 g (95%); mp 169–170 ºC (decomp.) (lit.[1] mp 169–170 ºC).

^{1}H NMR (300 MHz, [D_6]DMSO): δ 4.79 (d, *J* = 4.0 Hz, 1H, CH), 5.21 (d, *J* = 4.0 Hz, 1H, CH), 7.39 (d, *J* = 8.8 Hz, 1H, Ar), 7.77 (s, 2H, NH_2), 8.28 (dd, *J* = 8.8, 2.2 Hz, 1H, Ar), 8.51 (d, *J* = 2.2 Hz, 1H, Ar) ppm.

(2-Amino-3-cyano-8-methoxy-4*H*-chromen-4-yl)malononitrile (2f)

White solid; yield 0.52 g (97%); mp 172–173 ºC (decomp.) (lit.[1] mp 173–174 ºC).

^{1}H NMR (300 MHz, [D_6]DMSO): δ 3.84 (s, 3H, OMe), 4.56 (d, *J* = 4.0 Hz, 1H, CH), 5.04 (d, *J* = 4.0 Hz, 1H, CH), 7.01 (d, *J* = 7.3 Hz, 1H, Ar), 7.12 (d, *J* = 7.7 Hz, 1H, Ar), 7.20 (t, *J* = 7.7 Hz, 1H, Ar), 7.51 (s, 2H, NH_2) ppm.

(2-Amino-3-cyano-8-ethoxy-4*H*-chromen-4-yl)malononitrile (2g)

White solid; yield 0.55 g (99%); mp 95–98 ºC (decomp.).

^{1}H NMR (300 MHz, [D_6]DMSO): δ 1.35 (t, *J* = 7.0 Hz, 3H, CH_3), 4.07–4.17 (m, 2H, CH_2), 4.55 (d, *J* = 4.0 Hz, 1H, CH), 5.03 (d, *J* = 4.0 Hz, 1H, CH), 7.00 (d, *J* = 7.7 Hz, 1H, Ar), 7.10 (d, *J* = 7.7, 1H, Ar), 7.17 (t, *J* = 7.7 Hz, 1H, Ar), 7.47 (s, 2H, NH_2) ppm.

^{13}C NMR (75 MHz, [D_6]DMSO): δ 14.54, 32.37, 37.35, 48.89, 64.42, 112.91, 113.06, 114.01, 118.92, 119.34, 119.71, 124.91, 139.42, 146.37, 163.37 ppm.

IR (KBr): ν = 3607, 3351, 3190, 2986, 2205, 1640, 1582, 1424, 1222, 1076 cm^{-1}.

MS (EI): *m/z* (%) = 280 (0.3) $[M]^+$, 214 (15), 186 (31), 158 (30), 130 (12), 102 (25), 76 (32), 66 (100), 39 (62), 29 (79).

Found (%): C, 64.04, H, 4.47, N, 19.78. Calc. for $C_{15}H_{12}N_4O_2$ (%): C, 64.28; H, 4.32; N, 19.99.

References

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