

Supporting Information

Multicomponent domino reactions: Borax catalyzed synthesis of highly functionalised pyran-annulated heterocycles

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General Experimental procedure:

General

All reagents were purchased either from Sigma or Merck. Solvents were dried and purified using standard techniques. Melting points were recorded on a SRS-EZ-Melt melting point apparatus and are uncorrected. IR spectra were recorded in KBr on a Shimadzu IR Afinity I. ^1H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker 300 MHz, 500 MHz, Jeol 400 MHz and Varian 400 MHz spectrometer in CDCl_3 or DMSO-d^6 using TMS as an internal reference and chemical shifts are reported in parts per million (ppm). ^1H NMR Spectra are reported in the order : no of protons, multiplicity as s (singlet), d (doublet), t (triplet), m (multiplet), brs (broad singlet) and coupling constant (J value) in hertz (Hz).

Typical experimental procedure

To alkyl nitriles (1.1 mmol) (malononitrile or ethyl cyano acetate) dissolved in ethanol (2 mL) was added an aldehyde (1.0 mmol) followed by borax (10 mol %) and an active methylenic diketo compound (1.0mmol) (4-hydroxy coumarin or dimedone or cycloalkan-1,3-dione) were added to the same reaction mixture under reflux condition [In case of 1,3 ketoester (1.0mmol) the substrate (MAA or EAA) was added at room temperature or under sonication]. The progress of the reaction was monitored by TLC and after completion of the reaction the solid precipitate was filtered off to get the corresponding product.

Spectral data of Compounds

2-amino-4-(4-chlorophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile

(Table 1, entry 1)

Yield 88%. Solid, m.p. 260°C. IR ν_{\max} (KBr): 3382, 3311, 3259, 3189, 2193, 1715, 1676, 1611, 1377, 1961 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ = 4.51 (s, 1H), 7.12 (s, 2H), 7.29 (brs, 4H), 7.35 (d, J = 8.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H) ppm.

2-amino-5-oxo-4-p-tolyl-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 1)

Yield 80%. Solid, m.p. 256°C. IR ν_{\max} (KBr): 3387, 3294, 3192, 3036, 2225, 1715, 1672, 1588, 1352, 1095 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ = 2.45 (s, 3H), 4.45 (s, 1H), 7.09 (s, 2H), 7.34-7.38 (m, 4H), 7.59-7.64 (m, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.97-8.00 (m, 1H) ppm.

2-amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 2)

Yield 79%. Solid, m.p. 270°C. IR ν_{\max} (KBr): 3377, 3286, 3179, 2198, 1708, 1676, 1605, 1381, 1211, 1058 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ = 4.49 (s, 1H), 7.09 (s, 2H), 7.27-7.31 (m, 4H), 7.35 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.95-7.96 (m, 2H) ppm.

2-amino-4-(4-methoxyphenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile

(Table 2, entry 3)

Yield 84%. Solid, m.p. 250°C. IR ν_{\max} (KBr): 3385, 3319, 3190, 2225, 1708, 1671, 1606, 1371, 1022 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ = 3.76 (s, 3H), 4.44 (s, 1H), 6.82-6.84 (m, 2H), 7.04-7.08 (m, 2H), 7.20 (d, J = 8.8 Hz, 2H), 7.33-7.42 (m, 2H), 7.93-7.99 (m, 2H) ppm.

2-amino-4-(4-nitrophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 4)

Yield 79%. Solid, m.p. 260°C. IR ν_{\max} (KBr): 3482, 3429, 3370, 3334, 2195, 1718, 1670, 1607, 1377, 1055 cm^{-1} . ^1H NMR (500 MHz, DMSO- d_6): δ = 4.69 (s, 1H), 7.47-7.53 (m, 2H), 7.55 (s, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.72-7.76 (m, 1H), 7.91-7.93 (m, 1H), 8.19 (d, J = 9.0 Hz, 2H) ppm.

2-amino-4-(3-nitrophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 5)

Yield 76%. Solid, m.p. 260°C. IR ν_{\max} (KBr): 3403, 3323, 3216, 2203, 1704, 1668, 1607, 1382, 1058 cm^{-1} . ^1H NMR (500 MHz, DMSO- d_6): δ = 4.74 (s, 1H), 7.46-7.52 (m, 2H), 7.55 (s, 2H), 7.64 (t, J = 7.5 Hz, 1H), 7.72-7.76 (m, 1H), 7.82 (d, J = 7.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H) 8.13 (d, J = 8.5 Hz, 2H) ppm.

ethyl 2-amino-4-(4-nitrophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carboxylate (Table 2, entry 6)

Yield 82%. Solid, m.p. 240°C. IR ν_{\max} (KBr): 3441, 3325, 3066, 2976, 1719, 1685, 1612, 1534, 1378, 1279, 1201, 1093 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ = 1.10 (t, J = 7.0 Hz, 3H), 3.97-4.01 (m, 2H), 4.82 (s, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.49-7.55 (m, 3H), 7.69-7.73 (m, 1H), 7.96-8.01 (m, 3H), 8.12 (d, J = 8.5 Hz, 2H) ppm.

ethyl 2-amino-4-(3-nitrophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carboxylate (Table 2, entry 7)

Yield 72%. Solid, m.p. 245°C. IR ν_{\max} (KBr): 3435, 3316, 2992, 1727, 1691, 1658, 1530, 1455, 1377, 1273, 1090 cm^{-1} . ^1H NMR (500 MHz, DMSO- d_6): δ = 1.09 (t, J = 7.0 Hz, 3H), 3.96-4.01 (m, 2H), 4.82 (s, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.49-7.52 (m, 1H), 7.54-7.57 (m, 1H), 7.69-7.73 (m, 2H), 7.95-8.01 (m, 3H), 8.03-8.07 (m, 2H) ppm.

2-amino-5-oxo-4-(thiophen-2-yl)-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (Table 2, entry 8)

Yield 70%. Solid, m.p. 220°C. IR ν_{\max} (KBr): 3367, 3280, 3174, 2200, 1710, 1669, 1636, 1601, 1383, 1360, 1171, 1056 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ = 4.83 (s, 1H), 6.93-6.95 (m, 1H), 7.04 (d, J = 3.2, 1H), 7.32 (d, J = 4.0 Hz, 1H), 7.39-7.45 (m, 4H), 7.65-7.69 (m, 1H), 7.89-7.91 (m, 1H) ppm.

2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 1)

Yield 79%. Solid, m.p. 230°C. IR ν_{\max} (KBr): 3397, 3324, 3212, 2960, 2200, 1679, 1661, 1604, 1467, 1371, 1036 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.04 (s, 3H), 1.11 (s, 3H), 2.21-2.23 (m, 2H), 2.45 (brs, 2H), 4.40 (s, 1H), 4.57 (brs, 2H), 7.17-7.31 (m, 5H) ppm.

2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 2)

Yield 82%. Solid, m.p. 210°C. IR ν_{\max} (KBr): 3381, 3183, 2959, 2188, 1677, 1635, 1603, 1489, 1366, 1139, 1032 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.03 (s, 3H), 1.11 (s, 3H), 2.21-2.23 (m, 2H), 2.45 (brs, 2H), 4.39 (s, 1H), 4.60 (brs, 2H), 7.16-7.19 (m, 2H), 7.25-7.27 (m, 2H) ppm.

2-amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 3)

Yield 80%. Solid, m.p. 205°C. IR ν_{\max} (KBr): 3395, 3320, 3212, 2965, 2192, 1684, 1660, 1607, 1408, 1369, 1040 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.03 (s, 3H), 1.11 (s, 3H), 2.21-2.23 (m, 2H), 2.45 (brs, 2H), 4.37 (s, 1H), 4.54 (brs, 2H), 7.12 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H) ppm.

2-amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 4)

Yield 81%. Solid, m.p. 199°C. IR ν_{\max} (KBr): 3379, 3307, 3185, 2965, 2188, 1690, 1646, 1607, 1464, 1365, 1034 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.03 (s, 3H), 1.11 (s, 3H), 2.21-2.23 (m, 2H), 2.44 (s, 2H), 3.76 (s, 3H), 4.36 (s, 1H), 4.51 (brs, 2H), 6.82 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.8 Hz, 2H) ppm.

2-amino-7,7-dimethyl-5-oxo-4-p-tolyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 5)

Yield 80%. Solid, m.p. 212°C. IR ν_{\max} (KBr): 3426, 3331, 3221, 2958, 2192, 1678, 1638, 1601, 1510, 1368, 1033 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.04 (s, 3H), 1.11 (s, 3H), 2.21-2.23 (m, 2H), 2.29 (s, 3H), 2.49 (brs, 2H), 4.36 (s, 1H), 4.50 (brs, 2H), 7.08-7.13 (m, 2H) ppm.

2-amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 6)

Yield 79%. Solid, m.p. 175°C. IR ν_{\max} (KBr): 3408, 3117, 3174, 2973, 2182, 1672, 1628, 1591, 1465, 1348 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.04 (s, 3H), 1.13 (s, 3H), 2.17-2.29 (m, 2H), 2.48-2.49 (m, 2H), 4.52 (s, 1H), 4.69 (brs, 2H), 7.43 (d, J = 8.8 Hz, 2H), 8.17 (d, J = 8.8 Hz, 2H) ppm.

2-amino-7,7-dimethyl-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 7)

Yield 75%. Solid, m.p. 215°C. IR ν_{\max} (KBr): 3472, 3334, 3185, 2961, 2194, 1690, 1664, 1596, 1469, 1373, 1042 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 0.98 (s, 3H), 1.08 (s, 3H), 2.08-2.22 (m, 2H), 2.44-2.45 (m, 2H), 4.71 (brs, 1H), 5.18 (s, 1H), 7.30-7.36 (m, 2H), 7.48-7.54 (m, 1H), 7.79 (d, J = 8.4 Hz, 1H) ppm.

2-amino-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 8)

Yield 70%. Solid, m.p. 215°C. IR ν_{\max} (KBr): 3419, 3352, 3168, 2965, 2192, 1683, 1641, 1603, 1452, 1374, 1039 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.03 (s, 3H), 1.05 (s, 3H), 2.29 (s, 2H), 2.44 (s, 2H), 4.35 (s, 1H), 4.48 (s, 2H), 4.72 (s, 1H), 6.74 (d, J = 7.6 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H) ppm.

2-amino-7,7-dimethyl-5-oxo-4-(thiophen-2-yl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 9)

Yield 68%. Solid, m.p. 210°C. IR ν_{\max} (KBr): 3382, 3248, 2959, 2199, 1680, 1660, 1603, 1375, 1213, 1036 cm^{-1} . ^1H NMR (400 MHz, DMSO-d_6): δ = 1.03 (s, 3H), 1.10 (s, 3H), 2.12-2.29 (m, 2H), 2.40-2.55 (m, 2H), 4.60 (s, 1H), 6.69 (brs, 2H), 6.86-6.88 (m, 2H), 7.16 (d, J = 3.6 Hz, 1H) ppm.

2-amino-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 10)

Yield 74%. Solid, m.p. 218°C. IR ν_{\max} (KBr): 3324, 3261, 3170, 2193, 1683, 1651, 1364, 1210, 1001 cm^{-1} . ^1H NMR (400 MHz, DMSO-d_6): δ = 1.94-2.08 (m, 2H), 2.29-2.33 (m, 2H), 2.59-2.64 (m, 2H), 4.25 (s, 1H), 6.67 (brs, 2H), 7.14-7.19 (m, 3H), 7.24-7.28 (m, 2H) ppm.

2-amino-4-(4-chlorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 11)

Yield 77%. Solid, m.p. 240°C. IR ν_{\max} (KBr): 3415, 3334, 3215, 2196, 1685, 1650, 1601, 1247, 1003 cm^{-1} . ^1H NMR (400 MHz, DMSO-d_6): δ = 1.90-2.05 (m, 2H), 2.25-2.31 (m, 2H), 2.59-2.65 (m, 2H), 4.24 (s, 1H), 6.84 (brs, 2H), 7.17-7.20 (m, 2H), 7.25-7.29 (m, 2H) ppm.

2-amino-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 3, entry 12)

Yield 71%. Solid, m.p. 235°C. IR ν_{\max} (KBr): 3417, 3336, 3217, 2196, 1682, 1651, 1601, 1362, 1006 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ = 1.97-2.09 (m, 2H), 2.31-2.35 (m, 2H), 2.62-2.69 (m, 2H), 4.42 (s, 1H), 6.79 (brs, 2H), 7.44 (d, J = 8.8 Hz, 2H), 8.13 (d, J = 6.8 Hz, 2H) ppm.

2-amino-4-(4-bromophenyl)-5-oxo-4,5,6,7-tetrahydrocyclopenta[b]pyran-3-carbonitrile

(Table 3, entry 13)

Yield 68%. Solid, m.p. 218°C. IR ν_{\max} (KBr): 3409, 3325, 3210, 2195, 1673, 1639, 1599, 1369, 1011 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ = 2.43-2.45 (m, 2H), 2.72-2.80 (m, 2H), 4.24 (s, 1H), 6.86 (brs, 2H), 7.15-7.18 (m, 2H), 7.40-7.44 (m, 2H) ppm.

2-amino-4-(4-chlorophenyl)-5-oxo-4,5,6,7-tetrahydrocyclopenta[b]pyran-3-carbonitrile

(Table 3, entry 14)

Yield 70%. Solid, m.p. 214°C. IR ν_{\max} (KBr): 3405, 3321, 3211, 2195, 1673, 1639, 1601, 1371, 1005 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ = 2.40-2.42 (m, 2H), 2.71-2.80 (m, 2H), 4.24 (s, 1H), 7.01 (brs, 2H), 7.21-7.24 (m, 2H), 7.28-7.31 (m, 2H) ppm.

2-amino-5-oxo-4-(thiophen-2-yl)-4,5,6,7-tetrahydrocyclopenta[b]pyran-3-carbonitrile

(Table 3, entry 15)

Yield 64%. Solid, m.p. 218°C. IR ν_{\max} (KBr): 3383, 3316, 3202, 2192, 1665, 1647, 1592, 1376, 1094 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ = 2.41-2.46 (m, 2H), 2.67-2.77 (m, 2H), 4.57 (s, 1H), 6.85 (brs, 2H), 6.89-6.92 (m, 2H), 6.96 (d, J = 2.8 Hz, 1H), 7.20 (d, J = 2.8 Hz, 1H) ppm.

Methyl 6-amino-5-cyano-2-methyl-4-phenyl-4H-pyran-3-carboxylate (Table 4, entry 1)

Yield 84%. Solid, m.p. 175°C. IR ν_{\max} (KBr): 3416, 3331, 3202, 2952, 2199, 1711, 1672, 1607, 1408, 1334, 1266, 1179, 1062 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 2.46 (s, 3H), 3.63 (s, 3H), 4.53-4.59 (brs, 3H), 7.28-7.31 (m, 2H), 7.36-7.39 (m, 3H) ppm.

Ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4H-pyran-3-carboxylate (Table 4, entry 2)

Yield 84%. Solid, m.p. 115°C. IR ν_{\max} (KBr): 3408, 3329, 3224, 2969, 2191, 1705, 1676, 1608, 1328, 1262, 1121, 1061 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.14-1.72 (m, 3H), 2.44 (s, 3H), 4.09-4.12 (m, 2H), 4.51-4.52 (m, 2H), 7.28-7.29 (m, 2H), 7.35-7.38 (m, 3H) ppm.

Methyl 6-amino-4-(4-chlorophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (Table 4, entry 3)

Yield 85%. Solid, m.p. 170°C. IR ν_{\max} (KBr): 3411, 3331, 3204, 2950, 2199, 1707, 1677, 1611, 1409, 1341, 1269, 1178, 1066 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 2.37 (s, 3H), 3.59 (s, 3H), 4.42 (s, 1H), 4.50 (s, 2H), 7.14 (d, J = 7.6 Hz, 2H), 7.27 (d, J = 7.2 Hz, 2H) ppm.

Ethyl 6-amino-4-(4-chlorophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (Table 4, entry 4)

Yield 83%. Solid, m.p. 170°C. IR ν_{\max} (KBr): 3422, 3319, 3206, 2981, 2197, 1717, 1646, 1608, 1489, 1338, 1273, 1177, 1121 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 1.12 (t, J = 7.2 Hz, 2H), 2.38 (s, 3H), 4.00-4.07 (m, 2H), 4.43 (s, 1H), 4.50 (s, 2H), 7.14 (d, J = 8.4 Hz, 2H), 7.27-7.29 (m, 2H) ppm

Methyl 6-amino-4-(4-bromophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (Table 4, entry 5)

Yield 86%. Solid, m.p. 130–132°C. IR ν_{\max} (KBr): 3410, 3331, 3226, 2923, 2192, 1698, 1676, 1608, 1409, 1344, 1267, 1179, 1065 cm^{-1} . ^1H NMR (400 MHz, DMSO-d_6): δ = 2.39 (s, 3H), 3.57 (s, 3H), 4.49 (s, 1H), 6.63 (s, 2H), 7.41 (d, J = 8.4 Hz, 2H), 8.15 (d, J = 8.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 18.4, 38.6, 51.2, 56.7, 119.0, 123.4, 128.0, 146.3,

151.9, 157.9, 158.5, 165.4. Anal. Calcd for C₁₅H₁₃BrN₂O₃: C, 51.60; H, 3.75; N, 8.02;
Found : C, 51.42; H, 3.64; N, 8.18

Ethyl 6-amino-4-(4-bromophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (Table 4, entry 6)

Yield 86%. Solid, m.p. 178°C. IR ν_{\max} (KBr): 3411, 3329, 3224, 2981, 2195, 1698, 1670, 1609, 1486, 1369, 1265, 1181, 1072 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 1.12 (t, J = 7.2 Hz, 2H), 2.38 (s, 3H), 4.00-4.06 (m, 2H), 4.42 (s, 1H), 4.51 (s, 2H), 7.09 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H) ppm

Methyl 6-amino-5-cyano-4-(4-methoxyphenyl)-2-methyl-4H-pyran-3-carboxylate (Table 4, entry 7)

Yield 84%. Solid, m.p. 150°C. IR ν_{\max} (KBr): 3425, 3336, 3207, 2951, 2196, 1725, 1676, 1607, 1409, 1342, 1262, 1177, 1059 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 2.35 (s, 3H), 3.59 (s, 3H), 3.78 (s, 3H), 4.39 (s, 1H), 4.48 (s, 2H), 6.82 (d, J = 9.2 Hz, 2H), 7.11 (d, J = 9.2 Hz, 2H) ppm

Ethyl 6-amino-5-cyano-4-(4-methoxyphenyl)-2-methyl-4H-pyran-3-carboxylate (Table 4, entry 8)

Yield 84%. Solid, m.p. 135°C. IR ν_{\max} (KBr): 3407, 3332, 3203, 2977, 2191, 1707, 1648, 1608, 1411, 1335, 1262, 1175, 1060 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 1.12 (t, J = 7.2 Hz, 2H), 2.36 (s, 3H), 3.78 (s, 3H) 4.00-4.08 (m, 2H), 4.40 (s, 1H), 4.44 (s, 2H), 6.83 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H) ppm

Methyl 6-amino-5-cyano-2-methyl-4-p-tolyl-4H-pyran-3-carboxylate (Table 4, entry 9)

Yield 82%. Solid, m.p. 175°C. IR ν_{\max} (KBr): 3410, 3332, 3204, 2954, 2191, 1707, 1674, 1609, 1407, 1343, 1266, 1063 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 2.30 (s, 3H), 3.36 (s, 3H), 3.59 (s, 3H), 4.41 (s, 1H), 4.43 (s, 2H), 7.08-7.17 (m 2H) ppm.

Ethyl 6-amino-5-cyano-2-methyl-4-p-tolyl-4H-pyran-3-carboxylate (Table 4, entry 10)

Yield 82%. Solid, m.p. 180°C. IR ν_{\max} (KBr): 3412, 3331, 3227, 2981, 2198, 1707, 1689, 1610, 1331, 1262, 1179, 1062 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 1.12 (t, J = 7.2 Hz, 2H), 2.31 (s, 3H), 2.36 (s, 3H), 4.00-4.07 (m, 2H), 4.41 (s, 1H), 4.43 (s, 2H), 7.06-7.09 (m, 4H) ppm

Methyl 6-amino-5-cyano-2-methyl-4-(4-nitrophenyl)-4H-pyran-3-carboxylate (Table 4, entry 11)

Yield 84%. Solid, m.p. 165–167°C. IR ν_{\max} (KBr): 3399, 3328, 3202, 2956, 2204, 1707, 1672, 1644, 1521, 1340, 1274, 1178, 1057 cm^{-1} . ^1H NMR (400 MHz, DMSO-d_6): δ = 2.34 (s, 3H), 3.57 (s, 3H), 4.32 (s, 1H), 6.57 (s, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 18.3, 38.2, 51.2, 57.3, 106.7, 119.3, 119.9, 128.9, 131.1, 157.0, 158.4, 165.6. Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_5$: C, 57.14; H, 4.16; N, 13.33; Found : C, 57.08; H, 4.12; N, 13.44.

Ethyl 6-amino-5-cyano-2-methyl-4-(4-nitrophenyl)-4H-pyran-3-carboxylate (Table 4, entry 12)

Yield 82%. Solid, m.p. 175°C. IR ν_{\max} (KBr): 3404, 3331, 3203, 2981, 2198, 1708, 1674, 1607, 1346, 1271, 1174, 1060 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 1.11 (t, J = 7.2 Hz, 2H), 2.43 (s, 3H), 4.01-4.08 (m, 2H), 4.57 (s, 1H), 4.61 (s, 2H), 7.39 (d, J = 8.7 Hz, 2H), 8.19 (d, J = 8.4 Hz, 2H) ppm

Methyl 6-amino-5-cyano-2-methyl-4-(3-nitrophenyl)-4H-pyran-3-carboxylate (Table 4, entry 13)

Yield 82%. Solid, m.p. 210°C. IR ν_{\max} (KBr): 3402, 3329, 3224, 2957, 2192, 1707, 1679, 1607, 1417, 1345, 1271, 1181, 1066 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 2.42 (s, 3H), 3.61 (s, 3H), 4.58 (s, 2H), 5.29 (s, 1H), 7.46-7.59 (m, 2H), 8.04-8.12 (m, 2H) ppm.

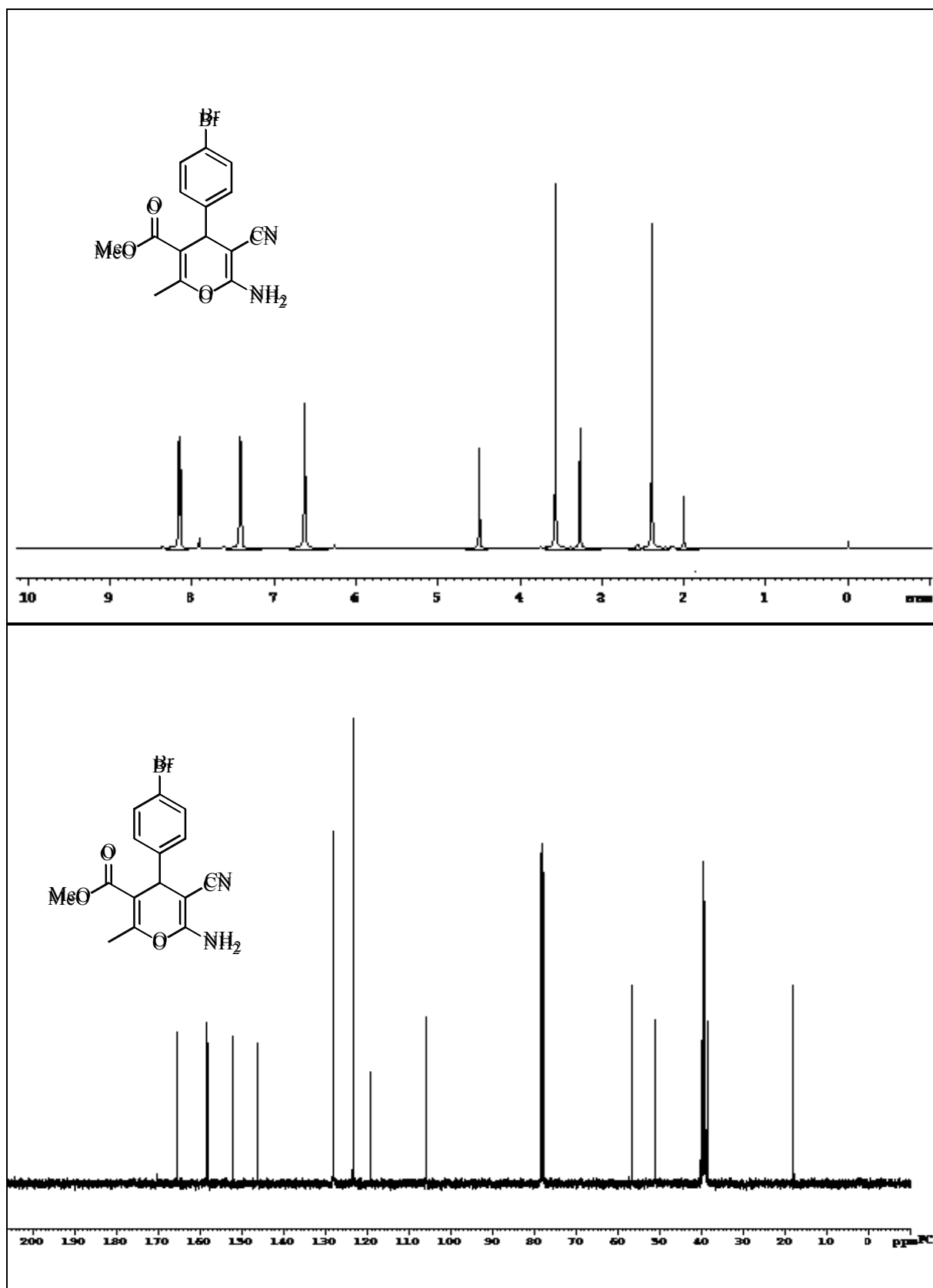
Ethyl 6-amino-5-cyano-2-methyl-4-(3-nitrophenyl)-4H-pyran-3-carboxylate (Table 4, entry 14)

Yield 80%. Solid, m.p. 170°C. IR ν_{\max} (KBr): 3404, 3328, 3221, 2989, 2194, 1702, 1645, 1603, 1440, 1347, 1270, 1179, 1061 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.12 (t, J = 6.8 Hz, 2H), 2.42 (s, 3H), 4.04-4.08 (m, 2H), 4.58 (s, 1H), 4.62 (s, 2H), 7.49-7.58 (m, 2H), 8.05-8.08 (m, 2H) ppm

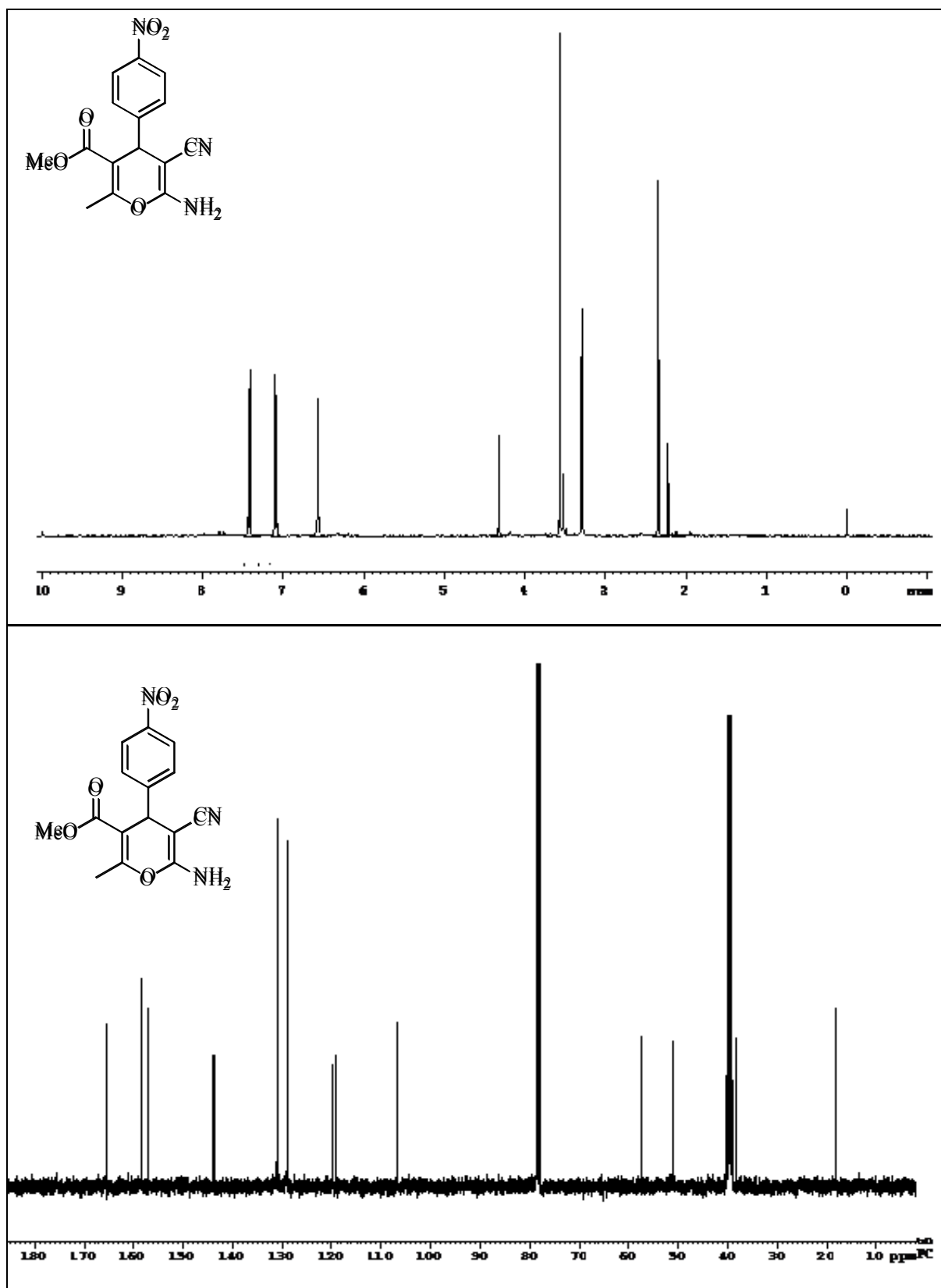
Methyl 6-amino-5-cyano-2-methyl-4-(2-nitrophenyl)-4H-pyran-3-carboxylate (Table 4, entry 15)

Yield 79%. Solid, m.p. 181–183°C. IR ν_{\max} (KBr): 3459, 3331, 3208, 2951, 2205, 1728, 1628, 1605, 1529, 1431, 1227, 1073, 944 cm^{-1} . ^1H NMR (400 MHz, DMSO-d_6): δ = 2.37 (s, 3H), 3.46 (s, 3H), 5.07 (s, 1H), 6.64 (s, 2H), 7.37-7.41 (m, 2H), 7.61 (d, J = 7.6 Hz, 2H), 7.74 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 18.3, 32.6, 51.2, 56.5, 106.5, 118.7, 123.1, 127.4, 130.2, 132.8, 139.2, 148.7, 158.1, 158.9, 165.1. Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_5$: C, 57.14; H, 4.16; N, 13.33; Found : C, 57.10; H, 4.08; N, 13.48.

Copies of ^1H and ^{13}C NMR spectra of Compound (Table 4, entry 5):



Copies of ¹H and ¹³C NMR spectra of Compound (Table 4, entry 11):



Copies of ^1H and ^{13}C NMR spectra of Compound (Table 4, entry 15):

