Supporting Information for

Versatile, Fragrant, Convertible Isonitriles

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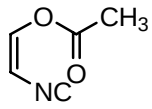
General Information. Organic solvents were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished using flash column chromatography on silica gels. Thin-layer chromatography (TLC) was carried out on aluminium sheets, Silica Gel 60 F_{254} (Merck; layer thickness 0.25 mm). Visualization of the developed chromatogram was performed by UV light and $KMnO_4$ stain. Solutions were dried over anhydrous Na_2SO_4.

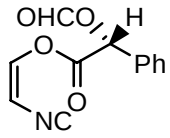
All melting points were measured on a Büchi Melting Point B-545 and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Varian Inova 300 (300 MHz and 75 MHz respectively) as noted, and are internally referenced to residual protio solvent signals. Data for ^{1}H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, sep = septet), coupling constant and integration. Data for ^{13}C NMR are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer using the ATR accessory and are reported in absorption frequency (cm^{-1}). Mass spectra were obtained from the University of California, Riverside Mass Spectral facility.

General Procedure for Isonitrile Formation: A 50 mL round-bottom flask equipped with a magnetic stir bar and charged with benzoxazole (0.90 g, 7.56 mmol) and THF (18 mL) are allowed to cool to -78 °C for five min prior to addition of *n*-BuLi (1.6 M solution in hexanes, 4.96 mL, 7.94 mmol). The reaction mixture was allowed to stir at the same temperature for 1.5 h. The acid chloride (7.94 mmol) was added dropwise to the solution. The solution was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was poured onto a mixture of ether (100 mL) and saturated aqueous

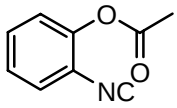
$NaHCO_3$ (50 mL). The organic layer was washed with water (2 x 50 mL), dried, and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (solvent noted) and the organics concentrated *in vacuo* to provide the title compounds.



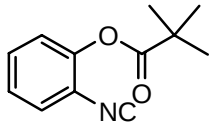
2-isocyanovinyl acetate (8a): Eluting with hexanes to 99:1 hexanes/ethyl acetate gradient to provide the title compound as a brown liquid (75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (br d, *J* = 4.2 Hz, 1H), 5.38 (d, *J* = 4.8 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8, 166.3, 138.3, 97.5, 20.4; IR (film): 3108, 2128, 1771, 1660, 1432, 1375, 1364, 1181, 1099, 1045, 1007 cm^{-1}; MS (CI): *m/z* 112 (M + H).



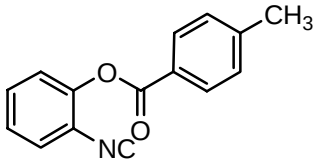
(*R*)-2-isocyanovinyl 2-(formyloxy)-2-phenylacetate (8b): Pale yellow liquid (95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.56-7.33 (m, 6H), 6.18 (s, 1H), 5.43 (d, *J* = 4.5 Hz, 1H); IR (film): 3109, 2958, 2126, 1782, 1726, 1661, 1497, 1456, 1334, 1232, 1197, 1132, 1090, 1003 cm^{-1}; MS (CI): *m/z* 232 (M + H).



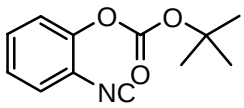
2-isocyanophenyl acetate (10a): Eluting with hexanes to 49:1 hexanes/ethyl acetate gradient to provide the title compound as a liquid (85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41-7.35 (m, 2H), 7.24-7.17 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.5, 168.2, 146.6, 130.6, 127.7, 126.8, 123.7, 120.5, 20.9; IR (film): 2125, 1772, 1490, 1455, 1370, 1238, 1191, 1167, 1101, 1033, 1009 cm^{-1}; MS (CI): *m/z* 179 (M + NH_4), 162 (M + H).



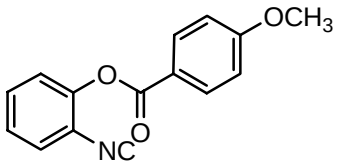
2-isocyanophenyl pivalate (10b): Eluting with hexanes to 39:1 hexanes/ethyl acetate gradient to provide the title compound as a liquid (92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43-7.38 (m, 2H), 7.27-7.16 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.0, 169.3, 146.8, 130.5, 127.8, 126.6, 123.7, 120.6, 39.4, 27.4; IR (film): 2977, 2875, 2125, 1762, 1491, 1480, 1399, 1368, 1270, 1235, 1088, 1027 cm^{-1}; MS (CI): *m/z* 221 (M + NH_4).



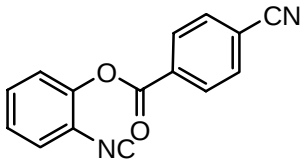
2-isocyanophenyl 4-methylbenzoate (10c): Eluting with hexanes to 32:1 hexanes/ethyl acetate gradient to provide the title compound as a white solid (96%). mp: 114.2-114.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.1 Hz, 2H), 7.44 (td, *J* = 7.8, 1.8 Hz, 2H), 7.39 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.29 (dd, *J* = 7.8, 1.8 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6, 164.2, 146.9, 145.4, 130.7, 130. 6, 129.8, 127.8, 126.7, 125.9, 123.9, 120.6, 22.1; IR (film): 3064, 2126, 1734, 1612, 1509, 1489, 1447, 1265, 1234, 1172, 1102, 1064, 1020 cm^{-1}; MS (CI): *m/z* 255 (M + NH_4), 119.



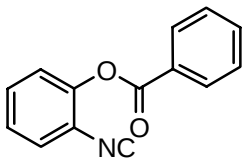
***tert*-Butyl 2-isocyanophenyl carbonate (10d):** Eluting with hexanes to 39:1 hexanes/ethyl acetate gradient to provide the title compound as a liquid (83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41-7.35 (m, 2H), 7.25-7.19 (m, 2H), 1.55 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.0, 150.6, 146.8, 130.6, 127.8, 126.9, 123.4, 120.7, 85.2, 27.8; IR (film): 2984, 2124, 1762, 1492, 1397, 1372, 1283, 1260, 1231, 1139, 1102, 1046, 1007 cm^{-1}; MS (CI): *m/z* 237 (M + NH_4), 220 (M + H).



2-isocyanophenyl 4-methoxybenzoate (10e): Eluting with hexanes to 9:1 hexanes/ethyl acetate gradient to provide the title compound as a white solid (96%). mp: 108.5-110.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.45-7.34 (m, 3H), 7.24 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.4, 164.6, 163.8, 147.0, 132.9, 130.5, 127.8, 126.6, 123.9, 120.9, 120.6, 114.3, 55.8; IR (film): 2958, 2845, 2128, 1729, 1606, 1581, 1509, 1489, 1423, 1279, 1256, 1233, 1168 cm^{-1}; MS (CI): *m/z* 271 (M + NH_4), 254 (M + H), 135.



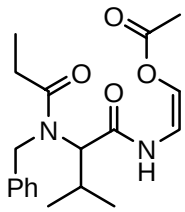
2-isocyanophenyl 4-cyanobenzoate (10f): Eluting with hexanes to 12:1 hexanes/ethyl acetate gradient to provide the title compound as a white solid (90%). mp: 159.7-161.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.52-7.48 (m, 2H), 7.42-7.32 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.9, 162.6, 146.3, 132.8, 132.4, 131.1, 130.8, 128.0, 127.3, 123.5, 120.3, 117.9, 117.8; IR (film): 3050, 2239, 2128, 1738, 1610, 1488, 1448, 1410, 1296, 1266, 1231, 1179, 1104, 1076 cm^{-1}; MS (CI): *m/z* 266 (M + NH_4), 249 (M + H), 130.



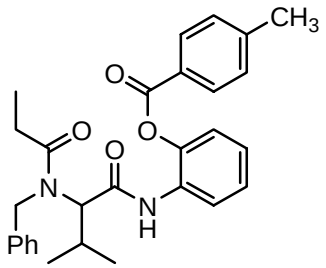
2-isocyanophenyl benzoate (10g): Eluting with hexanes to 12:1 hexanes/ethyl acetate gradient to provide the title compound as a white solid (93%). mp: 91.8-92.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.64 (td, *J* = 8.4, 1.2 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.45-7.35 (m, 3H), 7.24 (td, *J* = 8.4, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8, 164.1, 146.8, 134.5, 130.7, 129.1, 128.7, 127.8, 126.9, 123.9,

120.5; IR (film): 3047, 2131, 1732, 1601, 1586, 1492, 1449, 1257, 1231, 1172, 1098, 1078, 1061, 1037, 1023, 1001 cm^{-1}; MS (CI): *m/z* 241 (M + NH_4), 224 (M + H).

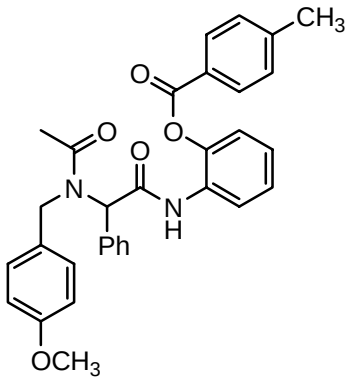
General Procedure for Ugi Reaction: To a solution of amine (1.0 mmol) in methanol (2.0 mL) was added aldehyde (1.0 mmol), and the reaction mixture was stirred at room temperature for 10 min. To this solution was added carboxylic acid (1.0 mmol), and the reaction mixture was stirred for 5 min, then isonitrile (1.0 mmol) was added. The resulting mixture was stirred at room temperature until the reaction was determined to be complete by TLC. The resulting solution was concentrated *in vacuo* and purified by silica gel flash column chromatography (solvents noted) to provide the title compounds.



(*Z*)-2-(2-(*N*-benzylpropionamido)-3-methylbutanamido) vinyl acetate (14): Prepared according to the general procedure from **8a** for 12 h to provide title compound as a white solid (74%) after purification by flash column chromatography on silica gel, eluting with hexanes to 10:1 hexanes/ethyl acetate gradient. mp: 84.5-87.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75 (br s, 1H), 7.33-7.22 (m, 3H), 7.09 (d, *J* = 6.9 Hz, 2H), 6.75 (d, *J* = 4.8 Hz, 1H), 6.34 (dd, *J* = 11.1, 5.4 Hz, 1H), 4.64 (d, *J* = 17.1 Hz, 1H), 4.56 (d, *J* = 17.1 Hz, 1H), 4.28 (d, *J* = 10.5 Hz, 1H), 2.63-2.55 (m, 1H), 2.48-2.29 (m, 2H), 2.25 (s, 3H), 1.12 (t, *J* = 7.5 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.9, 167.7, 167.1, 136.9, 128.9, 127.7, 126.5, 121.4, 108.5, 67.5, 50.6, 27.7, 26.9, 20.8, 20.0, 19.3, 9.7; IR (film): 3324, 2960, 2938, 1754, 1693, 1682, 1631, 1517, 1497, 1452, 1417, 1369, 1355, 1201, 1175, 1145, 1116 cm^{-1}; MS (FAB): *m/z* 347 (M + H), 246.

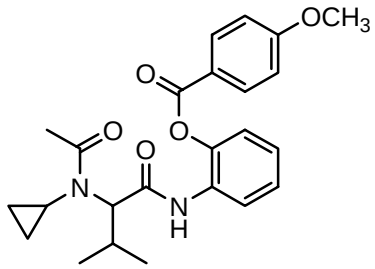


2-(2-(*N*-benzylpropionamido)-3-methylbutanamido)phenyl 4-methylbenzoate (16): Prepared according to the general procedure from **10c** for 12 h to provide title compound as a pale yellow liquid (90%) after purification by flash column chromatography on silica gel, eluting with CH_2Cl_2 to 13:1 CH_2Cl_2/methanol gradient. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.08 (br s, 1H), 8.19 (d, *J* = 8.4 Hz, 2H), 8.13 (d, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.21-7.05 (m, 8H), 4.55 (s, 2H), 4.36 (br d, *J* = 9.9 Hz, 1H), 2.61-2.49 (m, 1H), 2.46 (s, 3H), 2.25-2.06 (m, 2H), 0.97 (d, *J* = 6.3 Hz, 3H), 0.81 (t, *J* = 8.4 Hz, 3H), 0.80 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.9, 169.2, 165.1, 144.9, 140.8, 136.9, 131.0, 130.9, 129.6, 129.0, 127.6, 126.6, 126.5, 124.5, 122.7, 122.3, 68.2, 50.4, 43.9, 27.5, 26.5, 22.0, 20.3, 19.4, 9.3; IR (film): 3272, 2966, 2874, 1738, 1687, 1634, 1608, 1528, 1452, 1413, 1264, 1240, 1173, 1104, 1058, 1018 cm^{-1}; MS (CI): *m/z* 473 (M + H).

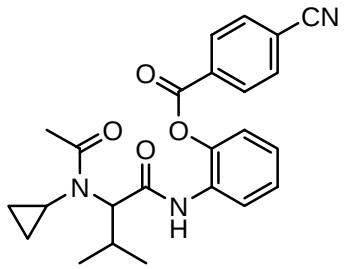


2-(2-(*N*-(4-methoxybenzyl)acetamido)-2-phenylacetamido)phenyl 4-methylbenzoate (18): Prepared according to the general procedure from **10c** for 24 h to provide title compound as a colorless liquid (60%) after purification by flash column chromatography on silica gel, eluting with hexanes to 1:1 hexanes/ethyl acetate gradient. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, *J* = 7.5 Hz, 1H), 8.01 (s, 1H), 7.81 (d, *J* = 7.5 Hz, 2H), 7.24-7.17 (m, 5H), 7.13-7.09 (m, 2H), 7.06-7.01 (m, 3H), 6.89 (d, *J* = 8.1 Hz, 2H), 6.69 (d, *J* =

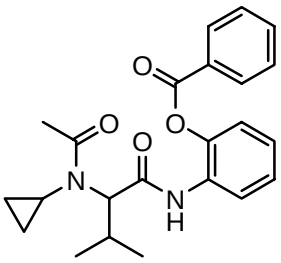
8.1 Hz, 2H), 5.79 (s, 1H), 4.59 (d, *J* = 17.1 Hz, 1H), 4.37 (d, *J* = 17.1 Hz, 1H), 3.68 (s, 3H), 2.42 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.6, 168.1, 164.6, 159.0, 144.9, 141.3, 134.8, 130.6, 130.3, 129.7, 129.5, 129.0, 128.8, 127.8, 126.6, 126.1, 125.0, 123.1, 122.5, 114.2, 64.8, 55.4, 53.8, 51.3, 22.5, 22.0; IR (film): 3267, 3033, 1737, 1698, 1631, 1609, 1512, 1452, 1408, 1242, 1173, 1105, 1059 cm^{-1}; MS (FAB): *m/z* 523 (M + H).



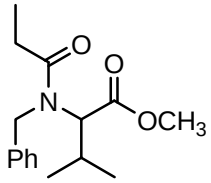
2-(2-(*N*-cyclopropylacetamido)-3-methylbutanamido)phenyl 4-methoxybenzoate (22e): Prepared according to the general procedure from **10e** for 15 h to provide title compound as a pale orange solid (90%) after purification by flash column chromatography on silica gel, eluting with hexanes to 3:1 hexanes/ethyl acetate gradient. mp: 106.1-107.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.62 (br s, 1H), 8.26 (d, *J* = 8.1 Hz, 1H), 8.22 (d, *J* = 8.7 Hz, 2H), 7.23 (dd, *J* = 8.1, 4.5 Hz, 1H), 7.12-7.10 (m, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 3.95-3.91 (m, 4H), 2.78-2.70 (m, 1H), 2.66-2.59 (m, 1H), 1.87 (s, 3H), 1.03 (d, *J* = 6.3 Hz, 3H), 1.02-0.94 (m, 1H), 0.87 (d, *J* = 6.3 Hz, 3H), 0.86-0.73 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.7, 170.4, 164.6, 164.2, 141.1, 132.9, 131.4, 126.5, 124.5, 122.6, 121.7, 114.0, 72.5, 55.7, 32.7, 26.6, 22.9, 20.2, 9.6, 9.1; IR (film): 3236, 2968, 1732, 1683, 1634, 1605, 1533, 1511, 1453, 1302, 1243, 1163, 1102, 1056, 1025, 1006 cm^{-1}; MS (FAB): *m/z* 425 (M + H), 182.



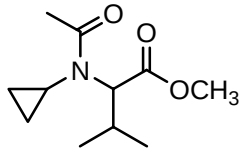
2-(2-(*N*-cyclopropylacetamido)-3-methylbutanamido)phenyl 4-cyanobenzoate (22f): Prepared according to the general procedure from **10f** for 15 h to provide title compound as a white solid (87%) after purification by flash column chromatography on silica gel, eluting with hexanes to 4:1 hexanes/ethyl acetate gradient. mp: 117.4-118.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.85 (br s, 1H), 8.36 (d, *J* = 8.1 Hz, 2H), 8.29 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.27-7.21 (m, 1H), 7.12-7.09 (m, 2H), 3.81 (d, *J* = 10.5 Hz, 1H), 2.74-2.62 (m, 2H), 1.88 (s, 3H), 0.98 (d, *J* = 6.3 Hz, 3H), 0.85 (d, *J* = 6.3 Hz, 3H), 0.99-0.71 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.8, 170.3, 163.5, 140.2, 133.5, 132.4, 131.3, 131.2, 127.1, 124.4, 122.4, 122.3, 118.2, 117.1, 73.6, 33.2, 26.6, 23.1, 20.2, 20.1, 10.0, 9.1; IR (film): 3256, 2966, 2873, 2232, 1740, 1691, 1674, 1628, 1608, 1528, 1454, 1390, 1304, 1252, 1174, 1107, 1069 cm^{-1}; MS (FAB): *m/z* 420 (M + H).



2-(2-(*N*-cyclopropylacetamido)-3-methylbutanamido)phenyl benzoate (22g): Prepared according to the general procedure from **10g** for 15 h to provide title compound as a colorless sticky liquid (83%) after purification by flash column chromatography on silica gel, eluting with hexanes to 4:1 hexanes/ethyl acetate gradient. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.69 (br s, 1H), 8.28-8.23 (m, 3H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.28-7.22 (m, 1H), 7.12 (d, *J* = 3.6 Hz, 2H), 3.90 (d, *J* = 11.1 Hz, 1H), 2.81-2.68 (m, 1H), 2.66-2.59 (m, 1H), 1.81 (s, 3H), 1.03-0.97 (m, 4H), 0.87-0.74 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.7, 170.4, 164.8, 141.0, 133.9, 131.4, 130.7, 129.4, 128.7, 126.6, 124.5, 122.7, 122.5, 72.9, 32.8, 26.5, 22.8, 20.2, 9.8, 9.0; IR (film): 3222, 2967, 2873, 1741, 1685, 1634, 1607, 1533, 1450, 1388, 1367, 1302, 1241, 1174, 1103, 1055, 1023 cm^{-1}; MS (FAB): *m/z* 395 (M + H).

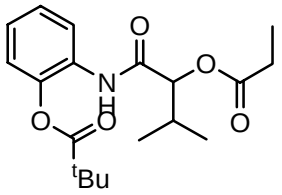


Methyl 2-(*N*-benzylpropionamido)-3-methylbutanoate (15): To a solution of Ugi product (0.3 mmol) in methanol (2.5 mL) was added acetyl chloride (1.5 mmol) in one portion. The flask was equipped with a reflux condenser and heated to 55 °C for 3 h. The reaction was cooled to room temperature and the solvent was removed *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel, eluting with hexanes to 19:1 hexanes/ethyl acetate gradient to provide the title compound as a colorless liquid. The title compound exists as a two rotamers in 7:3 ratio at room temperature in chloroform. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.13 (m, 5H), 4.99-4.94 (m, 1H), 4.62 (s, 1.4H), 4.26 (d, *J* = 15.3 Hz, 0.3H), 4.02 (d, *J* = 11.1 Hz, 0.3H), 3.43 (s, 2.1H), 3.32 (s, 0.9H), 2.61-2.21 (m, 3H), 1.24 (t, *J* = 7.8 Hz, 0.9H), 1.11 (t, *J* = 7.8 Hz, 2.1H), 0.97 (d, *J* = 6.3 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 2.1H), 0.83 (d, *J* = 6.6 Hz, 0.9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.5, 175.1, 171.3, 170.5, 138.2, 137.4, 128.8, 128.3, 127.9, 127.4, 126.9, 126.0, 65.9, 61.9, 51.9, 51.7, 48.4, 45.9, 28.0, 27.6, 27.1, 27.0, 20.1, 20.0, 18.9, 9.8; IR (film): 2966, 2876, 1737, 1652, 1497, 1453, 1435, 1411, 1370, 1300, 1255, 1227, 1200, 1167, 1131, 1074, 1010 cm^{-1}; MS (CI): *m/z* 278 (M + H).

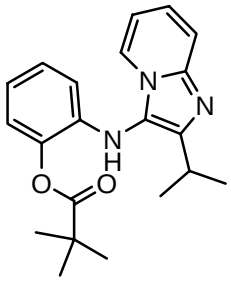


Methyl 2-(*N*-cyclopropylacetamido)-3-methylbutanoate (23): To a solution of Ugi product (0.06 mmol) in methanol (0.1 mL) was added a solution of acetyl chloride (0.3 mmol) in methanol (0.5 mL) in one portion. The resulting solution was stirred at room temperature until the starting material disappeared. The solvent was removed *in vacuo* and purified by flash column chromatography on silica gel, eluting with hexanes to 7:3 hexanes/ethyl acetate gradient to provide the title compound as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.95 (d, *J* = 10.2 Hz, 1H), 3.67 (s, 3H), 2.76-2.69 (m, 1H), 2.65-2.52 (m, 1H), 2.23 (s, 3H), 1.08 (d, *J* = 6.6 Hz, 3H), 0.91-0.88 (m, 4H), 0.85 (d, *J* =

6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.9, 172.0, 66.8, 52.1, 32.2, 27.9, 22.9, 21.8, 20.1, 10.2, 9.4; IR (film): 2965, 2874, 1740, 1656, 1434, 1411, 1383, 1366, 1300, 1266, 1202, 1131, 1015 cm^{-1}; MS (CI): *m/z* 214 (M + H).



24: To a solution of **10b** (0.13 g, 0.64 mmol) in CH_2Cl_2 (1.5 mL) were added isobutyraldehyde (0.058 mL, 0.64 mmol) followed by propionic acid (0.048 mL, 0.64 mmol), and the reaction mixture was stirred at room temperature for 18 h. After completion of the reaction, solvent was removed *in vacuo*, and the residue was purified by flash column chromatography on silica gel, eluting with hexanes to 10:1 hexanes/ethyl acetate gradient afforded the title compound **24** (0.154 g, 69%) as a reddish orange liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.1 Hz, 1H), 7.82 (s, 1H), 7.24 (td, *J* = 8.1, 1.8 Hz, 1H), 7.17 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.09 (td, *J* = 8.4, 1.8 Hz, 1H), 5.27 (d, *J* = 4.5 Hz, 1H), 2.48 (q, *J* = 7.8 Hz, 2H), 2.38-2.35 (m, 1H), 1.41 (s, 9H), 1.22 (t, *J* = 7.8 Hz, 3H), 0.99 (d, *J* = 7.2 Hz, 3H), 0.98 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.5, 173.2, 167.9, 141.5, 129.3, 126.5, 125.5, 123.5, 122.1, 78.2, 39.5, 31.1, 27.7, 27.4, 19.0, 17.2, 9.3; IR (film): 3428, 2970, 2877, 1752, 1697, 1608, 1521, 1453, 1177, 1159, 1105, 1026 cm^{-1}; MS (CI): *m/z* 367 (M + NH_4), 350 (M + H).



2-(2-isopropyl*H*-imidazo[1,2-*a*]pyridine-3-ylamino)phenyl pivalate (25): 2-Amino pyridine (0.135 g, 1.43 mmol) was dissolved in methanol (3 mL). Isobutyraldehyde (0.2 mL, 2.19 mmol) and **10b** (0.35 g, 1.72 mmol) were added at room temperature. A 1M solution of perchloric acid in methanol (0.15 mL) was added, and stirred at the same

temperature for 18 h. The reaction mixture was diluted with dichloromethane (30 mL) and extracted successively with water (30 mL), a saturated aqueous solution of $NaHCO_3$ (15 mL), and brine (30 mL). After that the organic layer was dried and concentrated *in vacuo* to give yellowish solid, which was purified by flash column chromatography on silica gel, eluting with hexanes to 3:2 hexanes/ethyl acetate gradient afforded the title compound **25** (0.39 g, 78%) as a ivory white solid. mp: 158.0-159.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (dd, *J* = 6.9, 0.9 Hz, 1H), 7.59 (dd, *J* = 9.0, 1.2 Hz, 1H), 7.16 (ddd, *J* = 8.7, 7.2, 1.2 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.81 (td, *J* = 7.8, 1.2 Hz, 1H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.17 (d, *J* = 7.8 Hz, 1H), 5.29 (s, 1H), 3.14 (sep, *J* = 6.9 Hz, 1H), 1.44 (s, 9H), 1.32 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.8, 148.6, 142.9, 138.4, 137.6, 127.0, 124.4, 122.7, 122.6, 119.7, 117.6, 116.2, 113.6, 112.1, 39.7, 27.5, 26.9, 22.5; IR (film): 3254, 2966, 2934, 1756, 1632, 1607, 1573, 1501, 1396, 1340, 1272, 1249, 1173, 1096 cm^{-1}; MS (CI): *m/z* 352 (M + H).