Supporting Information

1-[(Imidazolidin-2-yl)imino]indazole (*Marsanidine*) – Highly α_2/I_1 Selective Agonist: Synthesis, X-Ray Structure and Biological Activity

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General Procedure for the Preparation of Aminoindazoles 9d-k and 10d-k. The title compounds were availably from the appropriate indazole **8d-k** (13 mmol) using hydroxylamine-O-sulfonic acid (3.82 g, 33.8 mmol) in aqueous NaOH solution (2.86 g, 71.5 mmol in 44 mL of H_2O) and EtOH according to the procedure described by B.M. Adger *et al*.[34] The resulting mixture of 1- and 2-aminoindazoles was separated by column chromatography on silica gel. 1-Aminoindazoles were eluted first.

In this manner the following aminoindazoles were obtained.

1-Amino-4-methylindazole (**9d**) **and 2-Amino-4-methylindazole** (**10d**): from 4-methylindazole (**8d,**[49] 1.72 g) and EtOAc/CH_2Cl_2 (1:5) as eluent; yield of product **9d**: 0.45 g (24%); mp 77-81 °C (EtOH); IR, ν 3270, 3195 (NH_2), 1660, 1605 (δ NH_2, C=N), 1585, 1510, 1425, 1385, 1195, 1145, 1060, 1025, 985, 955, 835, 770 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 6.7 Hz, 1H), 6.91 (d, *J* = 6.7 Hz, 1H,), 5.50 (bs, 2H), 2.58 (s, 3H). Anal. ($C_8H_9N_3$ (147.18)) C, H, N; yield of product **10d**: 0.50 g (26%); mp 102-104 °C; IR, ν 3290, 3225, 3185 (NH_2), 1665, 1615 (δ NH_2, C=N), 1570, 1520, 1470, 1415, 1380, 1225, 1050, 780 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.20 (dd, *J* = 6.8 Hz, *J* = 8.7 Hz, 1H), 6.85 (d, *J* = 6.8 Hz, 1H), 5.75 (s, 2H), 2.49 (s, 3H). Anal. ($C_8H_9N_3$ (147.18)) C, H, N.

1-Amino-4-chloroindazole (9e) and 2-Amino-4-chloroindazole (10e): from 4-chloroindazole (**8e,**[49] 1.98 g) and EtOAc/CH_2Cl_2 (1:8) as eluent; yield of product **9e**: 1.10 g (51%); mp 125-127 °C; IR, ν 3295, 3175 (NH_2), 1665, 1615 (δ NH_2, C=N), 1570, 1505, 1425, 1365, 1165, 1075, 925, 765 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.52-7.47 (m, 1H), 7.35-7.26 (m, 1H), 7.14-7.10 (m, 1H), 4.94 (s, 2H). Anal. ($C_7H_6ClN_3$ (167.60)) C, H, N; yield of product **10e**: 0.59 g (27%); mp 144-146 °C; IR , ν 3295, 3150, 3100 (NH_2), 1640, 1630 (δ NH_2, C=N), 1540, 1415, 1375, 1250, 1195, 1025, 960, 775 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.55-7.50 (m, 1H), 7.26-7.18 (m, 1H), 7.10-7.07 (m, 1H), 5.56 (s, 2H). Anal. ($C_7H_6ClN_3$ (167.60)) C, H, N.

1-Amino-4-methoxyindazole (9f) and 2-Amino-4-methoxyindazole (10f): from 4-methoxyindazole (**8f**,[50] 1.93 g) and EtOAc/CH_2Cl_2 (1:5) as eluent; yield of product **9f**: 0.89 g (42%); mp 134-136 °C; IR, ν 3340, 3230 (NH_2), 1630, 1580 (δ NH_2, C=N), 1510, 1395, 1265, 1240, 1055, 930, 770 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.35-7.27 (m, 1H), 7.17-7.13 (m, 1H), 6.45 (d, *J* = 7.6 Hz, 1H), 5.30 (bs, 2H), 3.96 (s, 3H). Anal. ($C_8H_9N_3O$ (163.18)) C, H, N; yield of product **10f**: 0.45 g (21%); mp 114-116 °C; IR, ν 3290, 3175, 3115 (NH_2), 1630, 1560 (δ NH_2, C=N), 1470, 1425, 1390, 1265, 1220, 1110, 1035, 985, 775

cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.22-7.20 (m, 2H), 6.35 (dd, *J* = 5.6 Hz, *J* = 2.2 Hz, 1H), 5.69 (bs, 2H), 3.92 (s, 3H). Anal. ($C_8H_9N_3O$ (163.18)) C, H, N.

1-Amino-5-methylindazole (9g) and 2-Amino-5-methylindazole (10g): from 5-methylindazole (**8g**,[49] 1.72 g) and EtOAc/CH_2Cl_2 (1:5) as eluent; yield of product **9g**: 0.44 g (23%); mp 95-97 °C (petroleum ether 40-60 °C); IR, ν 3315, 3205 (NH_2), 1655, 1645 (δ NH_2, C=N), 1505, 1440, 1355, 1305, 1210, 1145, 1075, 945, 805 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.50-7.42 (m, 2H), 7.26-7.21 (m, 1H), 5.42 (bs, 2H), 2.45 (s, 3H). Anal. ($C_8H_9N_3$ (147.18)) C, H, N; yield of product **10g**: 0.44 g (23%); mp 87-89 °C; IR, ν 3275, 3220, 3195 (NH_2), 1665, 1640 (δ NH_2, C=N), 1525, 1475, 1435, 1315, 1230, 1140, 1055, 990, 805 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.38-7.36 (m, 1H), 7.15 (dd, *J* = 1.6 Hz, *J* = 8.8 Hz, 1H), 5.71 (bs, 2H), 2.41 (s, 3H). Anal. ($C_8H_9N_3$ (147.18)) C, H, N.

1-Amino-5-chloroindazole (9h) and 2-Amino-5-chloroindazole (10h): from 5-chloroindazole (**8h**,[49] 1.98 g) and EtOAc/CH_2Cl_2 (1:10) as eluent; yield of product **9h**: 0.95 g (44%); mp 135-138 °C; IR, ν 3315, 3185 (NH_2), 1645, 1610 (δ NH_2, C=N), 1490, 1375, 1350, 1185, 1070, 1055, 960, 905, 795 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.64 (d, *J* = 2.9 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.37-7.26 (m, 1H), 4.96 (s, 2H). Anal. ($C_7H_6ClN_3$ (167.60)) C, H, N; yield of product **10h**: 0.63 g (29%); mp 132-135 °C; IR, ν 3290, 3140 (NH_2), 1645 (δ NH_2, C=N), 1505, 1465, 1430, 1370, 1220, 1150, 1050, 1010, 805; ^1H NMR (200 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.61-7.53 (m, 2H), 7.27-7.21 (m, 1H), 5.66 (s, 2H). Anal. ($C_7H_6ClN_3$ (167.60)) C, H, N.

1-Amino-6-methylindazole (9i) and 2-Amino-6-methylindazole (10i): from 6-methylindazole (**8i**,[49] 1.72 g) and EtOAc/CH_2Cl_2 (1:2) as eluent; yield of product of **9i**: 0.40 g (21%); mp 109-112 °C (EtOH); IR, ν 3325, 3205 (NH_2), 1650 (δ NH_2, C=N), 1575, 1430, 1375, 1305, 1205, 1120, 1055, 925, 855, 780 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.38 (s, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 5.36 (bs, 2H), 2.52 (s, 3H). Anal. ($C_8H_9N_3$ (147.18)) C, H, N; yield of product **10i**: 0.30 g (16%); mp 114-117 °C; IR, ν 3245, 3175, 3125 (NH_2), 1660, 1633 (δ NH_2, C=N), 1555, 1445, 1390, 1375, 1220, 1150, 1035, 1015, 995, 805 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.37 (s, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 5.69 (s, 2H), 2.44 (s, 3H). Anal. ($C_8H_9N_3$ (147.18)) C, H, N.

1-Amino-6-methoxyindazole (9j) and 2-Amino-6-methoxyindazole (10j): from 6-methoxyindazole (**8j**,[50] 1.93 g) and EtOAc:CH_2Cl_2 (1:5) as eluent; yield of product **9j**: 0.55 g

(26%); mp 126-128 °C; IR, ν 3330, 3240 (NH_2), 1640, 1620 (δ NH_2, C=N), 1575, 1505, 1475, 1425, 1260, 1220, 1150, 1110, 1055, 1015, 935, 850, 810 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 6.92 (s, 1H), 6.79 (dd, *J* = 8.8 Hz, *J* = 2.2 Hz, 1H), 5.22 (s, 2H), 3.89 (s, 3H). Anal. ($C_8H_9N_3O$ (163.18)) C, H, N; yield of product **10j**: 0.36 g (17%); mp 118-123 °C; IR, ν 3315, 3145, 3090 (NH_2), 1630 (δ NH_2, C=N), 1550, 1485, 1455, 1435, 1295, 1230, 1205, 1165, 1125, 945, 830, 815 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.50 (d, *J* = 9.0 Hz, 1H), 6.88 (s, 1H), 6.80 (dd, *J* = 9.0 Hz, *J* = 1.9 Hz, 1H), 5.51 (bs, 2H), 3.87 (s, 3H). Anal. ($C_8H_9N_3O$ (163.18)) C, H, N.

1-Amino-7-methylindazole (9k) and 2-Amino-7-methylindazole (10k): from 7-methylindazole (**8k**,[49] 1.72 g) and EtOAc/CH_2Cl_2 (1:10) as eluent; yield of product **9k**: 0.40 g (21%); mp 91-93 °C; IR, ν 3305, 3200 (NH_2), 1645, 1605 (δ NH_2, C=N), 1510, 1455, 1425, 1355, 1215, 1055, 945, 855, 745 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.28-7.12 (m, 1H), 7.03 (t, 1H), 5.08 (bs, 2H), 2.81 (s, 3H). Anal. ($C_8H_9N_3$ (147.18)) C, H, N; yield of product **10k**: 0.46 g (24%); mp 111-113 °C; IR, ν 3285, 3155, 3100 (NH_2), 1650 (δ NH_2, C=N), 1565, 1475, 1385, 1265, 1250, 1045, 1005, 825, 740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.10-7.08 (m, 1H), 7.04-7.00 (m, 1H), 5.37 (bs, 2H), 2.61 (s, 3H). Anal. ($C_8H_9N_3$ (147.18)) C, H, N.

General Procedure for the Preparation of 1-[(Imidazolidin-2-yl)imino]indazoles 12a-k and Their Hydrochlorides 13a-k. Step 1. To a stirred solution of the appropriate 1-aminoindazole **9a-k** (2.5 mmol), *N*,*N*′-bis(*tert*-butoxycarbonyl)imidazolidine-2-thione[35] (1.12 g , 3.7 mmol) and Et_3N (0.88 g, 1.21 mL, 8.7 mmol) in anhydrous DMF (4 mL) was added $HgCl_2$ (1.0 g, 3.7 mmol) at 0 °C. The reaction mixture was stirred for an additional 20 min at 0 °C and then at room temperature for 5 days or for 3 days followed by heating at 85 °C for 6 h (in the case of **9k**). The resulting dark grey reaction mixture was diluted with EtOAc (40 mL), filtered off and washed with EtOAc (3 x 10 mL). The filtrates were washed successively with brine (3 x 20 ml) and water (3 x 20 mL), dried over $MgSO_4$ and finally concentrated under vacuum. The viscous residue (a mixture of unreacted *N*,*N*′-bis-Boc-imidazolidine-2-thione and Boc-protected 2-iminoimidazolidines **11a-k**) thus obtained was separated by flash column chromatography on silica gel. *N*,*N*′-Bis-Boc-imidazolidine-2-thione was eluted first and isolated in 17-25% yields.

In this manner the following compounds were obtained.

1-{[1,3-Di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}indazole (11a): IR, ν 2980, 2935, 2900 (CH), 1745, 1715 (C=O), 1630, 1610 (C=N), 1455, 1420, 1390, 1300, 1255, 1145, 1045, 990, 850, 750 cm^{-1}.

1-{[1,3-Di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}-3-methylindazole (11b): from 1-aminoindazole **9b**[34] (0.37 g) and EtOAc/$CHCl_3$ (0.1:3) as eluent; yield 0.51 g (49%); mp 55-59 °C (n-heptane); IR, ν 2980, 2940, 2880 (CH), 1750, 1720 (C=O), 1655, 1615 (C=N), 1510, 1480, 1370, 1315, 1255, 1155, 1085, 985, 760, 745 cm^{-1}. Anal. ($C_{21}H_{29}N_5O_4$ (415.49)) C, H, N.

1-{[1,3-Di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}-3-phenylindazole (11c): from 1-aminoindazole **9c**[34] (0.52 g) and EtOAc/$CHCl_3$ (0.1:7) as eluent; yield 0.60 g (50%); mp 66-69 °C (n-heptane); IR, ν 2980, 2935, 2895 (CH), 1750, 1720 (C=O), 1650, 1615 (C=N), 1495, 1475, 1390, 1370, 1310, 1255, 1150, 1065, 990, 850, 765, 750 cm^{-1}. Anal. ($C_{26}H_{31}N_5O_4$ (477.57)) C, H, N.

1-{[1,3-Di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}-4-methylindazole (11d): from 1-aminoindazole **9d** (0.37 g) and EtOAc/$CHCl_3$ (0.1:3) as eluent; yield 0.54 g (52%); mp 133-135 °C (EtOAc/n-heptane); IR, ν 2975, 2930, 2895 (CH), 1745, 1715 (C=O), 1680, 1605 (C=N), 1475, 1455, 1380, 1365, 1305, 1255, 1155, 980, 850, 780, 760 cm^{-1}. Anal. ($C_{21}H_{29}N_5O_4$ (415.49)) C, H, N.

4-Chloro-1-{[1,3-di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}indazole (11e): from 1-aminoindazole **9e** (0.42 g) and EtOAc/$CHCl_3$ (0.1:2) as eluent; yield 0.39 g (36%); mp 122-125 °C (n-heptane); IR, ν 2975, 2930, 2910 (CH), 1745, 1710 (C=O), 1640, 1605 (C=N), 1495, 1385, 1370, 1315, 1255, 1245, 1150, 1065, 990, 850, 785, 765 cm^{-1}. Anal. ($C_{20}H_{26}ClN_5O_4$ (435.91)) C, H, N.

1-{[1,3-Di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}-4-methoxyindazole (11f): from 1-aminoindazole **9f** (0.41 g) and EtOAc/$CHCl_3$ (0.1:2) as eluent; yield 0.56 g (51%); mp 132-134 °C (n-heptane); IR, ν 3000, 2970, 2930, 2885 (CH), 1715, 1705 (C=O), 1650, 1615 (C=N), 1585, 1510, 1385, 1370, 1315, 1255, 1145, 1040, 990, 890, 845, 770 cm^{-1}. Anal. ($C_{21}H_{29}N_5O_5$ (431.49)) C, H, N.

1-{[1,3-Di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}-5-methylindazole (11g): from 1-aminoindazole **9g** (0.37 g) and EtOAC/$CHCl_3$ (0.1:3) as eluent; yield 0.46 g (44%); mp 164-166 °C (n-heptane); IR, ν 2975, 2930, 2890 (CH), 1725, 1690 (C=O), 1660, 1620 (C=N), 1505, 1475, 1380, 1365, 1325, 1250, 1160, 1050, 985, 845, 795, 760 cm^{-1}. Anal. ($C_{21}H_{29}N_5O_4$ (415.49)) C, H, N.

5-Chloro-1-{[1,3-di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}indazole (11h): from 1-aminoindazole **9h** (0.42 g) and EtOAc/$CHCl_3$ (0.1:2); yield 0.50 g (46%); mp 176-177 °C (n-heptane); IR, ν 2980, 2920, 2910 (CH), 1735, 1710 (C=O), 1630 (C=N), 1480, 1390, 1365, 1330, 1290, 1250, 1145, 1045, 990, 805, 765 cm^{-1}. Anal. ($C_{20}H_{26}ClN_5O_4$ (435.91)) C, H, N.

1-{[1,3-Di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}-6-methylindazole (11i): from 1-aminoindazole **9i** (0.37 g) and EtOAc/$CHCl_3$ (0.1:3) as eluent; yield 0.40 g (38%); mp 129-131 °C (n-heptane); IR, ν 3000, 2975, 2930 (CH), 1745, 1710 (C=O), 1655, 1620 (C=N), 1465, 1420, 1380, 1365, 1315, 1255, 1240, 1150, 1040, 990, 935, 850, 830, 765 cm^{-1}. Anal. ($C_{21}H_{29}N_5O_4$ (415.49)) C, H, N.

1-{[1,3-Di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}-6-methoxyindazole (11j): from 1-aminoindazole **9j** (0.41 g) and EtOAc/$CHCl_3$ (0.1:2) as eluent; yield 0.60 g (55%); mp 178-179 °C (EtOAc); IR, ν 2995, 2975, 2930, 2890 (CH), 1715, 1705 (C=O), 1680, 1625 (C=N), 1510, 1475, 1380, 1370, 1315, 1265, 1225, 1155, 1045, 995, 940, 825, 755 cm^{-1}. Anal. ($C_{21}H_{29}N_5O_5$ (431.49)) C, H, N.

1-{[1,3-Di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}-7-methylindazole (11k): IR, ν 3000, 2980, 2930 (CH), 1715 (C=O), 1650 (C=N), 1605, 1470, 1420, 1385, 1370, 1310, 1245, 1150, 1045, 990, 880, 855, 820, 770 cm^{-1}.

Step 2. A solution of the appropriate Boc-protected 2-iminoimidazolidine **11a-k** (2.0 mmol) from Step 1 in 50% trifluoroacetic acid in CH_2Cl_2 (8 mL) was stirred at room temperature for 2 h and then the solvent and excess of trifluoroacetic acid were evaporated under reduced pressure. The viscous residue was treated with water (7 mL) and the resulting mixture or solution was made alkaline (pH 10-10.5) with 10% aqueous NaOH solution at 5 °C. The precipitate thus obtained was filtered off and purified by crystallization from suitable solvent.

In this manner the following compounds were obtained.

1-[(Imidazolidin-2-yl)imino]indazole (12a): IR, ν 3225, 3160 (NH), 3005, 2945, 2855 (CH), 1630, 1610 (C=N), 1515, 1405, 1285, 1200, 1055, 905, 835, 735 cm^{-1}.

1-[(Imidazolidin-2-yl)imino]-3-methylindazole (12b): from **11b** (0.83 g); yield 0.21 g (50%); mp 157-159 °C (MeCN); IR, ν 3220, 3195 (NH), 3050, 2895 (CH), 1635, 1605 (C=N), 1495, 1455, 1415, 1345, 1280, 1090, 1045, 740 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 7.70-7.55 (m, 1H), 7.35-7.19 (m, 2H), 7.05-6.92 (m, 1H), 6.59 (s, 1H), 6.48 (s, 1H), 3.38 (s,

4H), 2.48 (s, 3H); ^{13}C NMR (50 MHz, DMSO-d_6) δ 164.0, 137.1, 135.7, 125.4, 120.7, 120.0, 119.1, 109.9, 43.0, 41.9, 12.0. Anal. ($C_{11}H_{13}N_5$ (215.25)) C, H, N.

1-[(Imidazolidin-2-yl)imino]-3-phenylindazole (12c): from **11c** (0.96 g); yield 0.34 g (61%); mp 188-190 °C (EtOH); IR, ν 3405, 3210 (NH), 3060, 2980, 2955, 2890 (CH), 1650, 1605 (C=N), 1505, 1490, 1350, 1285, 1070, 955, 780, 740, 705 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6) δ 8.07-8.00 (m, 3H), 7.55-7.31 (m, 5H), 7.21-7.14 (m, 1H), 6.74 (s, 1H), 6.69 (s, 1H), 3.43 (s, 4H). Anal. ($C_{16}H_{15}N_5$ (277.33)) C, H, N.

1-[(Imidazolidin-2-yl)imino]-4-methylindazole (12d): from **11d** (0.83 g); yield 0.24 g (56%); mp 159-162 °C (MeCN); IR, ν 3190, 3120 (NH), 3010, 2945, 2920, 2875 (CH), 1630, 1610 (C=N), 1515, 1410, 1290, 1205, 1100, 1060, 960, 830, 765 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.90 (s, 1H), 7.25-7.02 (m, 2H), 6.89-6.75 (m, 1H), 6.63 (s, 1H), 6.46 (s, 1H), 3.37 (s, 4H), 2.52 (s, 3H); ^{13}C NMR (50 MHz, DMSO-d_6) δ 163.9, 135.9, 130.4, 126.7, 125.5, 122.2, 119.8, 107.7, 43.1, 41.8, 18.3. Anal. ($C_{11}H_{13}N_5$ (215.25)) C, H, N.

4-Chloro-1-[(imidazolidin-2-yl)imino]indazole (12e): from **11e** (0.87 g); yield 0.36 g (76%); mp 194-196 °C (MeCN); IR, ν 3230, 3175 (NH), 3005, 2945, 2875 (CH), 1625, 1610 (C=N), 1515, 1405, 1365, 1285, 1195, 1165, 1065, 925, 855, 765 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6) δ 7.91 (s, 1H), 7.33-7.21 (m, 2H), 7.12 (d, J = 6.3 Hz, 1H), 6.74 (s, 1H), 6.47 (s, 1H), 3.37 (s, 4H). Anal. ($C_{10}H_{10}ClN_5$ (235.67)) C, H, N.

1-[(Imidazolidin-2-yl)imino]-4-methoxyindazole (12f): from **11f** (0.86 g); yield 0.28 g (61%); mp 170-172 °C (MeCN); IR, ν 3320, 3250, 3150 (NH), 2990, 2890 (CH), 1635, 1610 (C=N), 1580, 1505, 1385, 1270, 1105, 1035, 765, 715 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.82 (s, 1H), 7.19-7.16 (m, 1H), 6.91 (d, J = 8.3 Hz, 1H), 6.64 (s, 1H), 6.48 (d, J = 7.3 Hz, 1H), 6.45 (s, 1H), 3.91 (s, 3H), 3.37 (s, 4H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.5, 153.5, 138.2, 127.0, 125.8, 113.9, 103.5, 99.6, 55.9, 43.5, 42.3. Anal. ($C_{11}H_{13}N_5O$ (231.25)) C, H, N.

1-[(Imidazolidin-2-yl)imino]-5-methylindazole (12g): from **11g** (0.83 g); yield 0.24 g (56%); mp 175-177 °C (MeCN); IR, ν 3215, 3160 (NH), 3005, 2860 (CH), 1620 (C=N), 1510, 1405, 1350, 1285, 1210, 1055, 880, 830, 790 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6) δ 7.74 (s, 1H), 7.42 (s, 1H), 7.24 (d, J = 8.7 Hz, 1H), 7.09 (d, J = 8.7 Hz, 1H), 6.60 (s, 1H), 6.47 (s, 1H), 3.36 (s, 4H), 2.37 (s, 3H); ^{13}C NMR (50 MHz, DMSO-d_6) δ 163.5, 134.7, 128.5, 127.2, 126.6, 121.7, 119.2, 109.7, 42.8, 41.6, 21.0. Anal. ($C_{11}H_{13}N_5$ (215.25)) C, H, N.

5-Chloro-1-[(imidazolidin-2-yl)imino]indazole (12h): from **11h** (0.87 g); yield 0.30 g (64%); mp 159-160 °C (MeCN); IR, ν 3230, 3175 (NH), 2990, 2895 (CH), 1630 (C=N), 1505, 1485, 1405, 1395, 1295, 1185, 1045, 855, 815, 785 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-

d$_6$) δ 7.86 (s, 1H), 7.76 (s, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 6.69 (s, 1H), 6.48 (s, 1H), 3.37 (s, 4H); ^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ 164.9, 135.1, 127.9, 126.2, 124.9, 122.8, 120.2, 112.3, 43.5, 42.3. Anal. ($C_{10}H_{10}ClN_5$ (235.67)) C, H, N.

1-[(Imidazolidin-2-yl)imino]-6-methylindazole (12i): from **11i** (0.83 g); yield 0.29 g (67%); mp 216-219 °C (MeCN); IR, ν 3245, 3150 (NH), 2980, 2945, 2885 (CH), 1635 (C=N), 1505, 1470, 1285, 1195, 1125, 1090, 1050, 940, 850, 830, 790 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-*d*$_6$) δ 7.77 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.10 (s, 1H), 6.89-6.84 (m, 1H), 6.58 (s, 1H), 6.40 (s, 1H), 3.36 (s, 4H), 2.40 (s, 3H). Anal. ($C_{11}H_{13}N_5$ (215.25)) C, H, N.

1-[(Imidazolidin-2-yl)imino]-6-methoxyindazole (12j): from **11j** (0.86 g); yield 0.33 g (72%); mp 178-180 °C (MeCN); IR, ν 3295, 3215 (NH), 2965, 2865 (CH), 1635, 1605 (C=N), 1510, 1475, 1455, 1290, 1270, 1225, 1045, 1015, 945, 825, 745 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-*d*$_6$) δ 7.78 (s, 1H), 7.56 (d, *J* = 9.2 Hz, 1H), 6.72-6.69 (m, 2H), 6.61 (s, 1H), 6.55 (s, 1H), 3.81 (s, 3H), 3.41 (s, 4H). Anal. ($C_{11}H_{13}N_5O$ (231.25)) C, H, N.

1-[(Imidazolidin-2-yl)imino]-7-methylindazole (12k): IR, ν 3210, 3170 (NH), 3060, 2950, 2870 (CH), 1635 (C=N), 1515, 1420, 1290, 1220, 1100, 1055, 865, 840, 740 cm^{-1}.

Step 3.To an ice-cold suspension of the appropriate 2-iminoimidazolidine **12a-k** (1 mmol) from Step 2 in anhydrous methanol (7 mL) was added dropwise HCl/MeOH solution (d = 5.67 g/100 mL, 0.78 mL, 1.2 mmol). The cooling bath was removed and the resulting solution was stirred at room temperature for 30 min. Then the solvent was evaporated under reduced pressure to dryness. The crude product thus obtained was purified by crystallization from EtOH/Et_2O or MeCN (in the case of **13h**).

In this manner the following compounds were obtained.

1-[(Imidazolidin-2-yl)imino]indazole Hydrochloride (13a): IR, ν 3275, 3130, 3035, 2980, 2900, 2660 ($NH^{\oplus}$, CH), 1650, 1625 (C=N), 1500, 1465, 1395, 1295, 1270, 1200, 1045, 905, 855, 760 cm^{-1}.

1-[(Imidazolidin-2-yl)imino]-3-methylindazole Hydrochloride (13b): from 2-iminoimidazolidine **12b** (0.21 g); yield 0.14 g (60%); mp 193-195 °C; IR, ν 3140, 2920, 2620 ($NH^{\oplus}$, CH), 1655, 1615 (C=N), 1520, 1450, 1390, 1345, 1285, 1095, 1045, 750 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-*d*$_6$) δ 12.38 (bs 1H), 8.95 (s, 2H), 7.86-7.82 (m, 1H), 7.58-7.46 (m, 2H), 7.33-7.25 (m, 1H), 3.74 (s, 4H), 2.52 (s, 3H). Anal. ($C_{11}H_{14}ClN_5$ (251.71)) C, H, N.

1-[(Imidazolidin-2-yl)imino]-3-phenylindazole Hydrochloride (13c): from 2-iminoimidazolidine **12c** (0.28 g); yield 0.18 g (56%); mp 218-221 °C; IR, ν 3265, 3115, 3000, 2910, 2805, 2775 ($NH^{\oplus}$, CH), 1645, 1615 (C=N), 1495, 1415, 1350, 1290, 1075, 830, 785,

750, 695 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 12.64 (bs, 1H), 9.08 (s, 2H), 8.22-8.18 (m, 1H), 8.04-8.00 (m, 2H), 7.63-7.51 (m, 5H), 7.47-7.37 (m, 1H), 3.77 (s, 4H). Anal. ($C_{16}H_{16}ClN_5$ (313.79)) C, H, N.

1-[(Imidazolidin-2-yl)imino]-4-methylindazole Hydrochloride (13d): from 2-iminoimidazolidine **12d** (0.21 g); yield 0.15 g (63%); mp 194-196 °C; IR, ν 3125, 3005, 2910, 2860, 2610 ($NH^{\oplus}$, CH), 1645, 1615 (C=N), 1515, 1405, 1365, 1290, 1200, 1085, 1025, 955, 860, 775 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 12.59 (bs, 1H), 8.93 (s, 2H), 8.32 (s, 1H), 7.41 (dd, J = 6.8 Hz, J = 8.3 Hz, 1H), 7.33 (d, J = 8.3 Hz, 1H), 7.07 (d, J = 6.8 Hz, 1H), 3.72 (s, 4H), 2.59 (s, 3H). Anal. ($C_{11}H_{14}ClN_5$ (251.71)) C, H, N.

4-Chloro-1-[(imidazolidin-2-yl)imino]indazole Hydrochloride (13e): from 2-iminoimidazolidine **12e** (0.24 g); yield 0.19 g (68%); mp 215-217 °C; IR, ν 3140, 3060, 2675 ($NH^{\oplus}$, CH), 1640, 1610 (C=N), 1500, 1390, 1360, 1290, 1170, 925, 775 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 12.73 (bs, 1H), 8.94 (s, 2H), 8.33 (s, 1H), 7.55-7.53 (m, 2H), 7.38 (d, J = 6.8 Hz, 1H), 3.72 (s, 4H). Anal. ($C_{10}H_{11}Cl_2N_5$ (272.14)) C, H, N.

1-[(Imidazolidin-2-yl)imino]-4-methoxyindazole Hydrochloride (13f): from 2-iminoimidazolidine **12f** (0.23 g); yield 0.16 g (59%); mp 202-204 °C; IR, ν 3285, 3080, 3005, 2690, 2560 ($NH^{\oplus}$, CH), 1645, 1610 (C=N), 1590, 1510, 1370, 1270, 1030, 780 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 12.59 (bs, 1H), 8.94 (s, 2H), 8.20 (s, 1H), 7.45 (t, 1H), 7.07 (d, J = 8.1 Hz, 1H), 6.75 (d, J = 7.9 Hz, 1H), 3.96 (s, 3H), 3.72 (s, 4H). Anal. ($C_{11}H_{14}ClN_5O$ (267.71)) C, H, N.

1-[(Imidazolidin-2-yl)imino]-5-methylindazole Hydrochloride (13g): from 2-iminoimidazolidine **12g** (0.21 g); yield 0.14 g (58%); mp 180-183 °C; IR, ν 3165, 3095, 3010, 2950, 2750, 2625 ($NH^{\oplus}$, CH), 1660, 1635 (C=N), 1510, 1405, 1290, 1200, 1135, 1045, 845, 815, 745 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 12.45 (bs, 1H), 8.92 (s, 2H), 8.14 (s, 1H), 7.61 (s, 1H), 7.45-7.33 (m, 2H), 3.71 (s, 4H), 2.42 (s, 3H). Anal. ($C_{11}H_{14}ClN_5$ (251.71)) C, H, N.

5-Chloro-1-[(imidazolidin-2-yl)imino]indazole Hydrochloride (13h): from 2-iminoimidazolidine **12h** (0.24 g); yield 0.16 g (57%); mp 181-182 °C; IR, ν 3175, 3055, 2880, 2650 ($NH^{\oplus}$, CH), 1640, 1615 (C=N), 1505, 1395, 1345, 1280, 1190, 1085, 1050, 895, 805, 655 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 12.72 (bs, 1H), 8.93 (s, 2H), 8.23 (s, 1H), 7.97 (s, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.54 (d, J = 8.8 Hz, 1H), 3.71 (s, 4H), Anal. ($C_{10}H_{11}Cl_2N_5$ (272.14)) C, H, N.

1-[(Imidazolidin-2-yl)imino]-6-methylindazole Hydrochloride (13i): from 2-iminoimidazolidine **12i** (0.21 g); yield 0.15 g (63%); mp 197-199 °C; IR, ν 3245, 3075, 2980, 2910, 2700 ($NH^{\oplus}$, CH), 1635, 1620 (C=N), 1480, 1380, 1340, 1285, 1125, 1045, 935, 810 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 12.31 (bs, 1H), 8.56 (s, 2H), 8.10 (s, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.29 (s, 1H), 7.08 (d, J = 8.4 Hz, 1H), 3.66 (s, 4H), 2.45 (s, 3H). Anal. ($C_{11}H_{14}ClN_5$ (251.71)) C, H, N.

1-[(Imidazolidin-2-yl)imino]-6-methoxyindazole Hydrochloride (13j): from 2-iminoimidazolidine **12j** (0.23 g); 0.17 g (63%); mp 193-195 °C; IR, ν 3175, 3080, 2970, 2900, 2780, 2750 ($NH^{\oplus}$, CH), 1645, 1625 (C=N), 1505, 1480, 1460, 1375, 1350, 1280, 1235, 1160, 1125, 1040, 1020, 935, 795 cm^{-1}, ^1H NMR (200 MHz, DMSO-d_6) δ 12.43 (bs, 1H), 8.93 (s, 2H), 8.11 (s, 1H), 7.70 (d, J = 8.7 Hz, 1H), 6.99 (s, 1H), 6.89 (dd, J = 8.7 Hz, J = 2.1 Hz, 1H), 3.85 (s, 3H), 3.73 (s, 4H). Anal. ($C_{11}H_{14}ClN_5O$ (267.71)) C, H, N.

1-[(Imidazolidin-2-yl)imino]-7-methylindazole Hydrochloride (13k): IR, ν 3150, 3030, 2975, 2915 ($NH^{\oplus}$, CH), 1645, 1620 (C=N), 1510, 1465, 1385, 1280, 1220, 1040, 860, 780, 745 cm^{-1}.

General Procedure. Preparation of 2-[(Imidazolidin-2-yl)imino]indazoles 15a-f and Their Hydrochlorides 16a-f. **Step 1.** The reaction of the appropriate 2-aminoindazole **10a, d-e, g-i** (2.5 mmol) with *N*,*N*′-bis(*tert*-butoxycarbonyl)imidazolidine-2-thione[35] (1.12 g , 3.7 mmol) was carried out according to the general procedure described for **12a-k** and **13a-k** in Step 1. The viscous residue (a mixture of unreacted *N*,*N*′-bis-Boc-imidazolidine-2-thione and Boc-protected 2-iminoimidazolidines **14a-f**) thus obtained was separated by flash column chromatography on silica gel. *N*,*N*′-Bis-Boc-imidazolidine-2-thione was eluted first and isolated in 14-25% yields.

In this manner the following compounds were obtained.

2-{[1,3-Di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}indazole (14a): from 2-aminoindazole (**10a**,[34] 0.33 g) and EtOAc/$CHCl_3$ (0.1:10) as eluent; yield 0.50 g (51%); mp 170-172 °C (EtOAc); IR, ν 3120, 3050, 2970, 2930 (CH), 1740, 1730 (C=O), 1635 (C=N), 1475, 1395, 1305, 1150, 990, 855, 750 cm^{-1}. Anal. ($C_{20}H_{27}N_5O_4$ (401.46)) C, H, N.

2-{[1,3-Di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}-4-methylindazole (14b): from 2-aminoindazole **10d** (0.37 g) and EtOAc/$CHCl_3$ (0.1:3) as eluent; yield 0.54 g (53%); mp 152-153 °C (EtOAc); IR, ν 3057, 2975, 2935 (CH), 1755, 1725 (C=O), 1625 (C=N), 1570, 1480, 1390, 1370, 1305, 1150, 995, 845, 765 cm^{-1}. Anal. ($C_{21}H_{29}N_5O_4$ (415.49)) C, H, N.

4-Chloro-2-{[1,3-di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}indazole (14c): from 2-aminoindazole **10e** (0.42 g) and EtOAC/$CHCl_3$ (0.1:2) as eluent; yield 0.49 g (45%); mp 155-158 °C (n-heptane); IR, ν 3110, 2975, 2930 (CH), 1740, 1725 (C=O), 1625 (C=N), 1535, 1475, 1390, 1370, 1310, 1150, 990, 850, 775, 760 cm^{-1}. Anal. ($C_{20}H_{26}ClN_5O_4$ (435.91)) C, H, N.

2-{[1,3-Di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}-5-methylindazole (14d): from 2-aminoindazole **10g** (0.37 g) and EtOAc/$CHCl_3$ (0.1:3) as eluent; yield 0.63 g (61%); mp 185-186 °C (EtOAc); IR, ν 3130, 2975, 2930, 2865 (CH), 1730, 1700 (C=O), 1635 (C=N), 1520, 1470, 1390, 1365, 1305, 1150, 985, 850, 795, 765 cm^{-1}. Anal. ($C_{21}H_{29}N_5O_4$ (415.49)) C, H, N.

5-Chloro-2-{[1,3-di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}indazole (14e): from 2-aminoindazole **10h** (0.42 g) and EtOAc/$CHCl_3$ (0.1:2) as eluent; yield 0.46 g (42%); mp 195-196 °C (n-heptane); IR, ν 3130, 2975, 2930 (CH), 1740, 1725 (C=O), 1630 (C=N), 1500, 1475, 1390, 1365, 1300, 1150, 985, 850, 795, 765 cm^{-1}. Anal. ($C_{20}H_{26}ClN_5O_4$ (435.91)) C, H, N.

2-{[1,3-Di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}-6-methylindazole (14f): from 2-aminoindazole **10i** (0.37 g) and EtOAc/$CHCl_3$ (0.1:3) as eluent; yield 0.61 g (59%); mp 163-166 °C (EtOAc); IR, ν 3130, 2980, 2930 (CH), 1745, 1735 (C=O), 1635 (C=N), 1475, 1390, 1365, 1305, 1150, 990, 855, 765 cm^{-1}. Anal. ($C_{21}H_{29}N_5O_4$ (415.49)) C, H, N.

Step 2. The reaction of the appropriate Boc-protected 2-iminoimidazolidine **14a-f** (2.0 mmol) from Step 1 with 50% trifluoroacetic acid/CH_2Cl_2 solution (8 mL) was carried out according to the general procedure described for **12a-k** and **13a-k** in Step 2. The crude product thus obtained was purified by crystallization from MeCN or 2-propanol (in the case of **15c**).

In this manner the following compounds were obtained.

2-[(Imidazolidin-2-yl)imino]indazole (15a): from **14a** (0.80 g); yield 0.22 g (55%); mp 125-127 °C; IR, ν 3325, 3205, 3140 (NH), 3040, 2940, 2870 (CH), 1645 (C=N), 1505, 1425, 1380, 1285, 1225, 1080, 975, 770, 745 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6) δ 7.97 (s, 1H), 7.61-7.42 (m, 2H), 7.31 (s, 1H), 7.25-7.13 (m, 1H), 7.02-6.95 (m, 1H), 6.69 (s, 1H), 3.44-3.39 (m, 4H); ^{13}C NMR (200 MHz, DMSO-d_6) δ 162.0, 144.8, 124.1, 120.4, 120.3, 119.6, 118.4, 116.0, 43.3, 41.4. Anal. ($C_{10}H_{11}N_5$ (201.23)) C, H, N.

2-[(Imidazolidin-2-yl)imino]-4-methylindazole (15b): from **14b** (0.83 g); yield 0.22 g (51%); mp 141-144 °C; IR, ν 3395, 3350, 3195 (NH), 3020, 2950, 2875 (CH), 1645 (C=N),

1570, 1510, 1420, 1375, 1285, 1230, 1160, 1090, 980, 785, 760 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 7.98 (s, 1H), 7.32-7.25 (m, 2H), 7.08-7.01 (m, 1H), 6.74-6.67 (m, 2H), 3.42-3.36 (m, 4H), 2.43 (s, 3H). Anal. ($C_{11}H_{13}N_5$ (215.25)) C, H, N.

4-Chloro-2-[(imidazolidin-2-yl)imino]indazole (15c): from **14c** (0.87 g); yield 0.31 g (66%); mp 167-169 °C; IR, ν 3345, 3210 (NH), 3075, 2950, 2875 (CH), 1650, 1635 (C=N), 1535, 1515, 1435, 1420, 1370, 1280, 1185, 1085, 985, 775, 745 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 8.02 (s, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.24 (s, 1H), 7.18-7.15 (m, 1H), 7.06 (d, *J* = 6.3 Hz, 1H), 6.81 (s, 1H), 3.47-3.46 (m, 2H), 3.41-3.40 (m, 2H). Anal. ($C_{10}H_{10}ClN_5$ (235.67)) C, H, N.

2-[(Imidazolidin-2-yl)imino]-5-methylindazole (15d): from **14d** (0.83 g); yield 0.26 g (60%); mp 175-178 °C; IR, ν 3360, 3205 (NH), 3030, 2960, 2855 (CH), 1640 (C=N), 1510, 1480, 1425, 1350, 1290, 1175, 1080, 980, 795, 760 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 7.83 (s, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.32-7.29 (m, 2H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.65 (s, 1H), 3.45-3.39 (m, 4H), 2.33 (s, 3H). Anal. ($C_{11}H_{13}N_5$ (215.25)) C, H, N.

5-Chloro-2-[(imidazolidin-2-yl)imino]indazole (15e): from **14e** (0.87 g); yield 0.34 g (72%); mp 216-218 °C; IR, ν 3355, 3240, 3165 (NH), 3065, 3005, 2960, 2885 (CH), 1630 (C=N), 1515, 1416, 1360, 1285, 1220, 1055, 795 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 7.96 (s, 1H), 7.64-7.51 (m, 2H), 7.27 (s, 1H), 7.17-7.11 (m, 1H), 6.75 (s, 1H), 3.46-3.38 (m, 4H). ^{13}C NMR (50 MHz, DMSO-d_6) δ 161.9, 142.9, 124.5 (two overlapping signals), 120.8, 118.3, 118.1, 117.7, 43.1, 41.1. Anal. ($C_{10}H_{10}ClN_5$ (235.67)) C, H, N.

2-[(Imidazolidin-2-yl)imino]-6-methylindazole (15f): from **14f** (0.83 g); yield 0.22 g (51%); mp 171-174 °C; IR, ν 3345, 3210 (NH), 2975, 2930, 2880, 2860 (CH), 1645 (C=N), 1510, 1485, 1420, 1380, 1285, 1135, 1085, 980, 845, 790 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 7.88 (s, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.25 (s, 2H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.63 (s, 1H), 3.42-3.38 (m, 4H), 2.36 (s, 3H). Anal. ($C_{11}H_{13}N_5$ (215.25)) C, H, N.

Step 3. The reaction of the appropriate 2-iminoimidazolidine **15a-f** (1.0 mmol) from Step 2 with HCl/MeOH solution (d = 5.67 g/100 mL, 0.78 mL, 1.2 mmol) was carried out according to the general procedure described for **12a-k** and **13a-k** in Step 3.

In this manner the following compounds were obtained.

2-[(Imidazolidin-2-yl)imino]indazole Hydrochloride (16a): from 2-iminoimidazolidine **15a** (0.20 g); yield 0.14 g (59%); mp 184-187 °C (2-propanol); IR, ν 3295, 3145, 2800 ($NH^{\oplus}$, CH), 1650, 1630 (C=N), 1615, 1475, 1420, 1285, 1230, 1015, 950, 910, 755 cm^{-1}; ^1H NMR

(200 MHz, DMSO-d_6) δ 8.72 (bs, 2H), 8.56 (s, 1H), 7.74 (d, J = 8.6 Hz, 1H), 7.63 (d, J = 8.6 Hz, 1H), 7.34 (t, 1H), 7.13 (t, 1H), 3.68 (s, 4H). Anal. ($C_{10}H_{12}ClN_5$ (237.69)) C, H, N.

2-[(Imidazolidin-2-yl)imino]-4-methylindazole Hydrochloride (16b): from 2-iminomidazolidine **15b** (0.21 g); yield 0.17 g (71%); mp 197-198 °C (EtOH/Et_2O); IR, ν 3255, 3140, 3045, 2900, 2850, 2675 ($NH^{\oplus}$, CH), 1650, 1625 (C=N), 1570, 1495, 1405, 1285, 1245, 1155, 1090, 1020, 835, 785 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 8.78 (bs, 2H), 8.64 (s, 1H), 7.43 (d, J = 8.8 Hz, 1H), 7.23 (dd, J = 6.7 Hz, J = 8.8 Hz, 1H), 6.89 (d, J = 6.7 Hz, 1H), 3.69 (s, 4H), 2.45 (s, 3H). Anal. ($C_{11}H_{14}ClN_5$ (251.71)) C, H, N.

4-Chloro-2-[(imidazolidin-2-yl)imino]indazole Hydrochloride (16c): from 2-iminoimidazolidine **15c** (0.24 g); yield 0.22 g (77%), mp 193-196 °C (EtOH/Et_2O); IR, ν 3345, 3130, 3035, 2905, 2685 ($NH^{\oplus}$, CH), 1645, 1620 (C=N), 1535, 1405, 1375, 1295, 1190, 1020, 965, 785 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 8.70 (s, 1H), 8.66 (bs, 2H), 7.63 (d, J = 8.8 Hz, 1H), 7.35-7.32 (m, 1H), 7.23 (d, J = 7.3 Hz, 1H), 3.68 (s, 4H). Anal. ($C_{10}H_{11}Cl_2N_5$ (272.14)) C, H, N.

2-[(Imidazolidin-2-yl)imino]-5-methylindazole Hydrochloride (16d): from 2-iminoimidazolidine **15d** (0.21 g); yield 0.16 g (67%); mp 183-184 °C (EtOH/Et_2O); IR, ν 3220, 3185, 2910, 2700 ($NH^{\oplus}$, CH), 1645, 1620 (C=N), 1520, 1420, 1285, 1235, 1085, 1015, 990, 875, 790 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 8.28 (s, 3H), 7.51 (d, J = 8.8 Hz, 1H), 7.44 (s, 1H), 7.14 (d, J = 8.8 Hz, 1H), 3.61 (s, 4H), 2.37 (s, 3H). Anal. ($C_{11}H_{14}ClN_5$ (251.71)) C, H, N.

5-Chloro-2-[(imidazolidin-2-yl)imino]indazole Hydrochloride (16e): from 2-iminoimidazolidine **15e** (0.24 g); yield 0.17 g (62%); mp 191-194 °C (EtOH/Et_2O); IR, ν 3270, 3130, 3055, 2960, 2670 ($NH^{\oplus}$, CH), 1650, 1615 (C=N), 1510, 1415, 1285, 1050, 865, 805, 695 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 8.58 (bs, 2H), 8.51 (s, 1H), 7.84 (s, 1H), 7.68 (d, J = 9.2 Hz, 1H), 7.31 (d, J = 9.2 Hz, 1H), 3.65 (s, 4H). Anal. ($C_{10}H_{11}Cl_2N_5$ (272.14)) C, H, N.

2-[(Imidazolidin-2-yl)imino]-6-methylindazole Hydrochloride (16f): from 2-iminoimidazolidine **15f** (0.21 g); yield 0.16 g (67%); mp 189-191 °C (EtOH/Et_2O); IR, ν 3350, 3155, 2905, 2860, 2680 ($NH^{\oplus}$, CH), 1655, 1615 (C=N), 1505, 1480, 1405, 1295, 1230, 1085, 1025, 995, 820 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 8.30 (s, 1H), 8.20 (bs, 2H), 7.58 (d, J = 8.6 Hz, 1H), 7.34 (s, 1H), 6.93 (d, J = 8.6 Hz, 1H), 3.59 (s, 4H), 2.38 (s, 3H). Anal. ($C_{11}H_{14}ClN_5$ (251.71)) C, H, N.

General Procedure for the Preparation of 1-[(Imidazolidin-2-yl)imino]benzimidazoles 19a-b and Their Hydrochlorides 20a-b. Step 1. The reaction of the appropriate 1-aminobenzimidazole **17a-b** (2.5 mmol) with *N*,*N*′-bis(*tert*-butoxycarbonyl)imidazolidine-2-thione[35] (1.12 g, 3.7 mmol) was carried out according to the general procedure described for **12a-k** and **13a-k** in Step 1. The viscous residue (a mixture of unreacted *N*,*N*′-bis-Boc-imidazolidine-2-thione and Boc-protected 2-iminoimidazolidines **18a-b**) thus obtained was separated by flash column chromatography on silica gel. *N*,*N*′-Bis-Boc-imidazolidine-2-thione was eluted first and isolated in 13-18% yields ($CHCl_3$ was used as eluent).

In this manner the following compounds were obtained.

1-{[1,3-Di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}benzimidazole (18a): from 1-aminobenzimidazole (**17a**,[36] 0.33g) and EtOAc/$CHCl_3$ (1:5) as eluent; yield 0.61 g (62%); mp 83-85 °C (n-heptane); IR, ν 2975, 2925 (CH), 1750, 1715 (C=O), 1645, 1613 (C=N), 1475, 1450, 1395, 1365, 1300, 1250, 1145, 990, 845 cm^{-1}. Anal. ($C_{20}H_{27}N_5O_4$ (401.46)) C, H, N.

1-{[1,3-Di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}-5,6-dimethylbenzimidazole (18b): from 1-aminobenzimidazole **17b**[37] (0.40 g) and EtOAc/$CHCl_3$ (1:5) as eluent; yield 0.44 g (40%); mp 94-96 °C (n-heptane); IR, ν 2975, 2930 (CH), 1750, 1720 (C=O), 1645, 1625 (C=N), 1485, 1460, 1390, 1365, 1300, 1250, 1145, 990, 845, 765 cm^{-1}. Anal. ($C_{22}H_{31}N_5O_4$ (429.53)) C, H, N.

Step 2. The reaction of the appropriate Boc-protected 2-iminoimidazolidine **18a-b** (2.0 mmol) from Step 1 with 50% trifluoroacetic acid/CH_2Cl_2 solution (8 mL) was carried out according to the general procedure described for **12a-k** and **13a-k** in Step 2.

In this manner the following compounds were obtained.

1-[(Imidazolidin-2-yl)imino]benzimidazole (19a): from **18a** (0.80 g); yield 0.32 g (80%); mp 237-240 °C; IR, ν 3155, 3100 (NH), 2980, 2870, 2810 (CH), 1635, 1610 (C=N), 1505, 1480, 1450, 1315, 1275, 1225, 1075, 890, 730 cm^{-1}; ^1H NMR (200MHz, DMSO-d_6) δ 7.96 (s, 1H), 7.69-7.51 (m, 1H), 7.31-7.02 (m, 3H), 6.77 (s, 1H), 6.38 (s, 1H), 3.42-3.35 (m, 4H); ^{13}C NMR (200 MHz, DMSO-d_6) δ 166.3, 142.6, 141.8, 133.4, 121.8, 120.9, 119.6, 110.3, 42.8, 42.3. Anal. ($C_{10}H_{11}N_5$ (201.23)) C, H, N.

1-[(Imidazolidin-2-yl)imino]-5,6-dimethylbenzimidazole (19b): from **18b** (0.86 g); yield 0.37 g (80%); mp 274-276 °C (EtOH); IR, ν 3160, 3130 (NH), 2970, 2875, 2805, 2720 (CH), 1635 (C=N), 1500, 1480, 1410, 1340, 1280, 1230, 1095, 990, 830 cm^{-1}; ^1H NMR (500

MHz, DMSO-d_6) δ 7.79 (s, 1H), 7.35 (s, 1H), 7.00 (s, 1H), 6.70 (s, 1H), 6.25 (s, 1H), 3.40-3.28 (m, 4H), 2.30 (s, 6H). Anal. ($C_{12}H_{15}N_5$ (229.29)) C, H, N.

Step 3. The reaction of the appropriate 2-iminoimidazolidine **19a-b** (1.0 mmol) from Step 2 with HCl/MeOH solution (d = 5.67 g/100 mL, 0.78 mL, 1.2 mmol) was carried out according to the general procedure described for **12a-k** and **13a-k** in Step 3. The crude product thus obtained was purified by crystallizatiom from EtOH/Et_2O.

In this manner the following compounds were obtained.

1-[(Imidazolidin-2-yl)imino]benzimidazole Hydrochloride (20a): from 2-iminoimidazolidine **19a** (0.20 g); yield 0.14 g (59%); mp 224-226 °C; IR, ν 3310, 3100, 2970, 2890, 2755, 2530 ($NH^{\oplus}$, CH), 1630, 1615 (C=N), 1505, 1435, 1345, 1290, 1252, 1070, 830, 760 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 9.01 (s, 1H), 8.44 (bs, 2H), 7.81-7.79 (m, 1H), 7.56 (d, J = 7.3 Hz, 1H), 7.48-7.43 (m, 2H), 3.61 (s, 4H). Anal. ($C_{10}H_{12}ClN_5$ (237.69)) C, H, N.

1-[(Imidazolidin-2-yl)imino]-5,6-dimethylbenzimidazole Hydrochloride (20b): from 2-iminoimidazolidine **19b** (0.23 g); yield 0.21 g (77%); mp 252-254 °C; IR, ν 3310, 3110, 2960, 2790, 2750 ($NH^{\oplus}$, CH), 1645, 1630 (C=N), 1505, 1470, 1300, 1235, 1050, 835, 715 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 9.00 (s, 1H), 7.79 (bs, 2H), 7.56 (s, 1H), 7.33 (s, 1H), 3.53 (s, 4H), 2.37 (s, 6H). Anal. ($C_{12}H_{16}ClN_5$ (265.74)) C, H, N.

Preparation of 1-[(Imidazolidin-2-yl)imino]benzotriazole (19c) and Hydrochloride 20c. Step 1. The reaction of 1-aminobenzotriazole (**17c**,[38] 0.34 g, 2.5 mmol) with *N*,*N*′-bis(*tert*-butoxycarbonyl)imidazolidine-2-thione[35] (1.12 g , 3.7 mmol) was carried out according to the general procedure described for **12a-k** and **13a-k** in Step 1. The viscous residue (a mixture of unreacted *N*,*N*′-bis-Boc-imidazolidine-2-thione and Boc-protected 2-iminoimidazolidine **18c**) thus obtained was separated by flash column chromatography on silica gel eluting with $CHCl_3$ to give unreacted *N*,*N*′-bis-Boc-imidazolidine-2-thione (0.24 g, 21%) and 1-{[1,3-di(*tert*-butoxycarbonyl)imidazolidin-2-yl]imino}benzotriazole (**18c**): yield 0.5 g (50%); mp 129-132 °C; IR, ν 2975, 2920, 2850 (CH), 1760, 1700 (C=O), 1625, 1610 (C=N), 1475, 1450, 1385, 1365, 1295, 1240, 1145, 985, 845, 765, 745 cm^{-1}. Anal. ($C_{19}H_{26}N_6O_4$ (402.46)) C, H, N.

Step 2. A solution of the product **18c** (0.81 g, 2.0 mmol) from Step 1 in 50% trifluoroacetic acid/CH_2Cl_2 solution (8 mL) was stirred at room temperature for 2 h and then the solvent and excess of trifluoroacetic acid were evaporated under reduced pressure. The viscous residue was treated with water (10 mL) and the resulting solution was made alkaline

with 10% aqueous NaOH solution at 5 °C and extracted with $CHCl_3$ (3 x 40 mL). The organic layer was dried over $MgSO_4$, evaporated under vacuum and the residue was treated with anhydrous acetone (3 mL). The precipitate thus obtained was collected by filtration, washed with acetone (0.5 mL) and dried to give 1-[(imidazolidin-2-yl)imino]benzotriazole (**19c**): yield 0.26 g (65%); mp 176-179 °C; IR, ν 3240, 3185 (NH), 3020, 2985, 2950, 2880 (CH), 1635, 1610 (C=N), 1510, 1485, 1415, 1280, 1230, 1075, 765, 745 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 7.96-7.93 (m, 1H), 7.47-7.33 (m, 3H), 7.01 (s, 1H), 6.67 (s, 1H), 3.41 (bs, 4H). Anal. ($C_9H_{10}N_6$ (202.22)) C, H, N.

Step 3. The reaction of the product **19c** (0.2 g, 1.0 mmol) from Step 2 with HCl/MeOH solution (d = 5.67 g/100 mL, 0.78 mL, 1.2 mmol) was carried out according to the general procedure described for **12a-k** and **13a-k** in Step 3 to give 1-[(imidazolidin-2-yl)imino]benzotriazole hydrochloride (**20c**): yield 0.17 g (70%); mp 213-215 °C (EtOH/Et_2O); IR, ν 3100, 3010, 2865, 2680, 2510 ($NH^{\oplus}$, CH), 1645, 1625 (C=N), 1490, 1450, 1390, 1295, 1175, 1085, 750 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 9.04 (bs, 2H), 8.16 (d, J = 8.3 Hz, 1H), 7.75 (d, J = 8.3 Hz, 1H), 7.67 (t, 1H), 7.52 (t, 1H), 3.72 (s, 4H). Anal. ($C_9H_{11}ClN_6$ (238.68)) C, H, N.

Table S1. Elemental analyses of reported compounds **9d-k**, **10d-k**, **11a-k**, **12a-k**, **13a-k**, **14a-f**, **15a-f**, **16a-f**, **18a-c**, **19a-c** and **20a-c**

Compound	Formula	% Calculated			% Found		
		C	H	N	C	H	N
9d	$C_8H_9N_3$	65.29	6.16	28.55	65.01	5.89	28.36
9e	$C_7H_6ClN_3$	50.17	3.61	25.07	49.84	3.32	25.32
9f	$C_8H_9N_3O$	58.89	5.56	25.75	58.54	5.24	25.41
9g	$C_8H_9N_3$	65.29	6.16	28.55	64.98	5.80	28.52
9h	$C_7H_6ClN_3$	50.17	3.61	25.07	50.32	3.29	25.16
9i	$C_8H_9N_3$	65.29	6.16	28.55	65.01	6.28	28.32
9j	$C_8H_9N_3O$	58.89	5.56	25.75	58.62	5.32	25.49
9k	$C_8H_9N_3$	65.29	6.16	28.55	65.09	5.87	28.37
10d	$C_8H_9N_3$	65.29	6.16	28.55	64.93	6.07	28.73
10e	$C_7H_6ClN_3$	50.17	3.61	25.07	49.92	3.41	25.35
10f	$C_8H_9N_3O$	58.89	5.56	25.75	58.62	5.47	25.37
10g	$C_8H_9N_3$	65.29	6.16	28.55	65.01	5.92	28.32
10h	$C_7H_6ClN_3$	50.17	3.61	25.07	50.23	3.38	25.05
10i	$C_8H_9N_3$	65.29	6.16	28.55	64.92	6.02	28.27
10j	$C_8H_9N_3O$	58.89	5.56	25.75	58.69	5.42	25.58
10k	$C_8H_9N_3$	65.29	6.16	28.55	65.12	6.03	28.43
11a	$C_{20}H_{27}N_5O_4$	59.84	6.78	17.44	59.61	6.49	17.32
11b	$C_{21}H_{29}N_5O_4$	60.71	7.03	16.85	60.52	6.89	16.64
11c	$C_{26}H_{31}N_5O_4$	65.39	6.54	14.66	65.03	6.14	14.42

Table S1. Continuation

Compound	Formula	% Calculated			% Found		
		C	H	N	C	H	N
11d	$C_{21}H_{29}N_5O_4$	60.71	7.03	16.85	60.52	6.72	16.89
11e	$C_{20}H_{26}ClN_5O_4$	55.11	6.01	16.06	54.82	5.89	16.32
11f	$C_{21}H_{29}N_5O_5$	58.45	6.77	16.23	58.07	6.39	15.94
11g	$C_{21}H_{29}N_5O_4$	60.71	7.03	16.85	60.43	7.24	16.63
11h	$C_{20}H_{26}ClN_5O_4$	55.11	6.01	16.06	55.32	6.24	16.11
11i	$C_{21}H_{29}N_5O_4$	60.71	7.03	16.85	60.52	6.84	16.82
11j	$C_{21}H_{29}N_5O_5$	58.45	6.77	16.23	58.12	6.58	16.21
11k	$C_{21}H_{29}N_5O_4$	60.71	7.03	16.85	60.48	6.78	16.64
12a	$C_{10}H_{11}N_5$	59.69	5.51	34.80	59.42	5.21	34.57
12b	$C_{11}H_{13}N_5$	61.38	6.09	32.53	61.01	5.81	32.41
12c	$C_{16}H_{15}N_5$	69.30	5.45	25.25	69.01	5.12	24.94
12d	$C_{11}H_{13}N_5$	61.38	6.09	32.53	61.13	5.92	32.20
12e	$C_{10}H_{10}ClN_5$	50.96	4.28	29.71	50.61	4.01	29.80
12f	$C_{11}H_{13}N_5O$	57.13	5.66	30.28	56.82	5.42	30.43
12g	$C_{11}H_{13}N_5$	61.38	6.09	32.53	61.19	5.72	32.24
12h	$C_{10}H_{10}ClN_5$	50.96	4.28	29.71	50.63	3.89	29.76
12i	$C_{11}H_{13}N_5$	61.38	6.09	32.53	61.03	6.23	32.25
12j	$C_{11}H_{13}N_5O$	57.13	5.66	30.28	56.84	5.27	30.57
12k	$C_{11}H_{13}N_5$	61.38	6.09	32.53	61.09	5.92	32.41
13a	$C_{10}H_{12}ClN_5$	50.53	5.09	29.46	50.37	4.97	29.59

Table S1. Continuation

Compound	Formula	% Calculated			% Found		
		C	H	N	C	H	N
13b	$C_{11}H_{14}ClN_5$	52.49	5.61	27.82	52.21	5.32	27.57
13c	$C_{16}H_{16}ClN_5$	61.24	5.14	22.32	60.97	5.27	22.31
13d	$C_{11}H_{14}ClN_5$	52.49	5.61	27.82	52.32	5.42	27.63
13e	$C_{10}H_{11}Cl_2N_5$	44.14	4.07	25.73	43.91	4.33	25.67
13f	$C_{11}H_{14}ClN_5O$	49.35	5.27	26.16	49.12	5.03	25.88
13g	$C_{11}H_{14}ClN_5$	52.49	5.61	27.82	52.32	5.32	27.54
13h	$C_{10}H_{11}Cl_2N_5$	44.14	4.07	25.73	44.37	4.23	25.60
13i	$C_{11}H_{14}ClN_5$	52.49	5.61	27.82	52.33	5.41	28.07
13j	$C_{11}H_{14}ClN_5O$	49.35	5.27	26.16	49.02	5.01	25.93
13k	$C_{11}H_{14}ClN_5$	52.49	5.61	27.82	52.17	5.33	28.16
14a	$C_{20}H_{27}N_5O_4$	59.84	6.78	17.44	59.71	6.53	17.44
14b	$C_{21}H_{29}N_5O_4$	60.71	7.03	16.85	60.42	6.92	16.72
14c	$C_{20}H_{26}ClN_5O_4$	55.11	6.01	16.06	54.83	5.74	16.22
14d	$C_{21}H_{29}N_5O_4$	60.71	7.03	16.85	60.51	7.23	16.73
14e	$C_{20}H_{26}ClN_5O_4$	55.11	6.01	16.06	54.92	5.93	16.26
14f	$C_{21}H_{29}N_5O_4$	60.71	7.03	16.85	60.62	7.18	16.64
15a	$C_{10}H_{11}N_5$	59.69	5.51	34.80	59.52	5.38	34.61
15b	$C_{11}H_{13}N_5$	61.38	6.09	32.53	61.23	6.18	32.41
15c	$C_{10}H_{10}ClN_5$	50.96	4.28	29.71	50.75	4.01	29.96
15d	$C_{11}H_{13}N_5$	61.38	6.09	32.53	61.58	6.32	32.72

Table S1. Continuation

Compound	Formula	% Calculated			% Found		
		C	H	N	C	H	N
15e	$C_{10}H_{10}ClN_5$	50.96	4.28	29.71	50.63	4.43	30.04
15f	$C_{11}H_{13}N_5$	61.38	6.09	32.53	61.17	6.24	32.25
16a	$C_{10}H_{12}ClN_5$	50.53	5.09	29.46	50.37	4.87	29.31
16b	$C_{11}H_{14}ClN_5$	52.49	5.61	27.82	52.13	5.34	27.47
16c	$C_{10}H_{11}Cl_2N_5$	44.14	4.07	25.73	43.92	3.82	25.65
16d	$C_{11}H_{14}ClN_5$	52.49	5.61	27.82	52.43	5.78	27.94
16e	$C_{10}H_{11}Cl_2N_5$	44.14	4.07	25.73	44.38	4.23	25.35
16f	$C_{11}H_{14}ClN_5$	52.49	5.61	27.82	52.13	5.32	28.16
18a	$C_{20}H_{27}N_5O_4$	59.84	6.78	17.44	59.72	6.81	17.28
18b	$C_{22}H_{31}N_5O_4$	61.52	7.27	16.31	61.39	7.14	16.52
18c	$C_{19}H_{26}N_6O_4$	56.70	6.51	20.88	56.45	6.27	20.67
19a	$C_{10}H_{11}N_5$	59.69	5.51	34.80	59.75	5.42	34.67
19b	$C_{12}H_{15}N_5$	62.86	6.59	30.54	62.73	6.41	30.78
19c	$C_9H_{10}N_6$	53.46	4.98	41.56	53.17	4.87	41.21
20a	$C_{10}H_{12}ClN_5$	50.53	5.09	29.46	50.32	4.89	29.26
20b	$C_{12}H_{16}ClN_5$	54.24	6.07	26.35	54.48	5.93	26.12
20c	$C_9H_{11}ClN_6$	45.29	4.65	35.21	45.11	4.42	35.01

Crystallographic data of compounds 12e and 13a

data_12e

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CrysAlis RED, Oxford Diffraction Ltd.,
Version 1.171.32.5
Empirical absorption correction using spherical harmonics,
implemented in SCALE3 ABSPACK scaling algorithm.
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Mercury, Version 1.4
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Refinement of F^2^ against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2^, conventional R-factors R are based on F, with F set to zero for negative F^2^. The threshold expression of F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2^ are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.
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N1 N 0.75434(10) 0.62319(11) 0.06779(15) 0.0325(3) Uani 1 1 d . . .

N2 N 0.72343(12) 0.71028(12) -0.03627(17) 0.0388(3) Uani 1 1 d . . .

C3 C 0.60815(13) 0.72787(14) -0.02745(19) 0.0347(3) Uani 1 1 d . . .

H3A H 0.5639 0.7840 -0.0851 0.042 Uiso 1 1 calc R . .

C4 C 0.44941(12) 0.62502(12) 0.13249(18) 0.0294(3) Uani 1 1 d . . .

C5 C 0.43762(14) 0.53802(14) 0.2390(2) 0.0374(4) Uani 1 1 d . . .

H5A H 0.3634 0.5215 0.2736 0.045 Uiso 1 1 calc R . .

C6 C 0.53770(15) 0.47287(14) 0.2968(2) 0.0396(4) Uani 1 1 d . . .

H6A H 0.5279 0.4140 0.3699 0.048 Uiso 1 1 calc R . .

C7 C 0.64876(14) 0.49317(13) 0.24923(18) 0.0344(3) Uani 1 1 d . . .

H7A H 0.7142 0.4496 0.2879 0.041 Uiso 1 1 calc R . .

C8 C 0.65892(12) 0.58266(12) 0.13955(17) 0.0269(3) Uani 1 1 d . . .

C9 C 0.56146(12) 0.65047(12) 0.08062(16) 0.0263(3) Uani 1 1 d . . .

N10 N 0.86622(11) 0.57136(13) 0.06631(16) 0.0398(3) Uani 1 1 d . . .

C11 C 0.93816(13) 0.59882(14) 0.19359(19) 0.0355(4) Uani 1 1 d . . .

N12 N 0.92045(13) 0.66631(16) 0.31906(19) 0.0585(5) Uani 1 1 d . . .

H12 H 0.8507 0.7011 0.3307 0.064(6) Uiso 1 1 d R . .

C13 C 1.02563(17) 0.6754(2) 0.4327(3) 0.0698(7) Uani 1 1 d . . .

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H13B H 1.0534 0.7536 0.4420 0.084 Uiso 1 1 calc R . .

C14 C 1.11500(16) 0.6000(2) 0.3568(2) 0.0635(6) Uani 1 1 d . . .

H14A H 1.1835 0.6437 0.3300 0.076 Uiso 1 1 calc R . .

H14B H 1.1418 0.5384 0.4296 0.076 Uiso 1 1 calc R . .

N15 N 1.04993(13) 0.55720(16) 0.21405(19) 0.0587(5) Uani 1 1 d . . .

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N2 0.0316(7) 0.0470(8) 0.0390(8) 0.0090(6) 0.0093(6) 0.0001(6)

C3 0.0298(8) 0.0399(9) 0.0348(8) 0.0081(7) 0.0052(6) 0.0043(6)

C4 0.0229(7) 0.0332(8) 0.0322(8) -0.0095(6) 0.0031(6) 0.0009(5)

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C6 0.0488(9) 0.0336(8) 0.0381(9) 0.0038(7) 0.0128(7) -0.0027(7)

C7 0.0381(8) 0.0332(8) 0.0317(8) 0.0012(6) 0.0016(6) 0.0062(6)

C8 0.0240(7) 0.0328(7) 0.0239(7) -0.0036(5) 0.0025(5) 0.0022(5)

C9 0.0243(7) 0.0300(7) 0.0245(7) -0.0024(6) 0.0022(5) 0.0013(5)

N10 0.0229(6) 0.0580(9) 0.0385(8) -0.0115(6) 0.0039(5) 0.0095(6)

C11 0.0246(7) 0.0470(9) 0.0358(8) -0.0061(7) 0.0080(6) 0.0033(6)

N12 0.0282(7) 0.0917(13) 0.0548(10) -0.0364(9) 0.0000(7) 0.0143(8)

C13 0.0375(10) 0.1146(19) 0.0562(13) -0.0399(13) -0.0020(9) 0.0097(11)

C14 0.0311(9) 0.1066(18) 0.0514(11) -0.0262(11) -0.0037(8) 0.0114(10)

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All esds (except the esd in the dihedral angle between two l.s. planes)

are estimated using the full covariance matrix. The cell esds are taken

into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
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N1 N10 1.4019(17) . ?
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C3 C9 1.409(2) . ?
C3 H3A 0.9300 . ?
C4 C5 1.361(2) . ?
C4 C9 1.4038(19) . ?
C5 C6 1.410(2) . ?
C5 H5A 0.9300 . ?
C6 C7 1.368(2) . ?
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C7 C8 1.398(2) . ?
C7 H7A 0.9300 . ?
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C11 N12 1.333(2) . ?
C11 N15 1.3480(19) . ?
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C13 C14 1.520(3) . ?

C13 H13A 0.9700 . ?
C13 H13B 0.9700 . ?
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C7 C6 C5 122.30(15) . . ?
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C6 C7 C8 116.67(14) . . ?
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CrysAlis RED, Oxford Diffraction Ltd.,
Version 1.171.32.5
Empirical absorption correction using spherical harmonics,
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CrysAlis CCD (Oxford Diffraction, 2006)

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CrysAlis CCD

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Mercury, Version 1.4
(Macrae et al., 2006)
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Refinement of F^2^ against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on F^2^, conventional R-factors R are based
on F, with F set to zero for negative F^2^. The threshold expression of
F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on F^2^ are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
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_refine_ls_extinction_coef 0.0098(12)

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N2 N 0.24534(9) 0.60123(14) 1.05322(12) 0.0249(3) Uani 1 1 d . . .

C3 C 0.32192(11) 0.52430(17) 1.13330(14) 0.0248(3) Uani 1 1 d . . .

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C5 C 0.57877(11) 0.63636(18) 1.14915(15) 0.0288(4) Uani 1 1 d . . .

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C6 C 0.54863(11) 0.75694(17) 1.05141(15) 0.0274(3) Uani 1 1 d . . .

H6A H 0.5959 0.8128 1.0278 0.033 Uiso 1 1 calc R . .

C7 C 0.45124(11) 0.79407(16) 0.99008(15) 0.0233(3) Uani 1 1 d . . .

H7A H 0.4311 0.8745 0.9263 0.028 Uiso 1 1 calc R . .

C8 C 0.38421(10) 0.70444(15) 1.02876(13) 0.0188(3) Uani 1 1 d . . .

C9 C 0.41207(10) 0.58336(16) 1.12495(13) 0.0207(3) Uani 1 1 d . . .

N10 N 0.22645(9) 0.82734(14) 0.91106(12) 0.0228(3) Uani 1 1 d . . .

C11 C 0.15652(10) 0.79292(15) 0.79347(14) 0.0171(3) Uani 1 1 d . . .

N12 N 0.13998(9) 0.65193(14) 0.73755(12) 0.0216(3) Uani 1 1 d . . .

C13 C 0.05335(10) 0.65509(16) 0.61452(14) 0.0218(3) Uani 1 1 d . . .

H13A H -0.0018 0.6018 0.6286 0.026 Uiso 1 1 calc R . .

H13B H 0.0670 0.6067 0.5387 0.026 Uiso 1 1 calc R . .

C14 C 0.03357(10) 0.83208(16) 0.59112(14) 0.0213(3) Uani 1 1 d . . .

H14A H 0.0530 0.8697 0.5163 0.026 Uiso 1 1 calc R . .

H14B H -0.0353 0.8562 0.5730 0.026 Uiso 1 1 calc R . .

N15 N 0.09524(8) 0.90085(14) 0.72049(12) 0.0191(3) Uani 1 1 d . . .

O1W O 0.23330(8) 0.38219(12) 0.51791(13) 0.0269(3) Uani 1 1 d . . .

H10 H 0.2273(11) 0.914(2) 0.9500(17) 0.029(4) Uiso 1 1 d . . .

H12 H 0.1596(12) 0.571(2) 0.7797(17) 0.031(5) Uiso 1 1 d . . .

H15 H 0.1094(11) 0.994(2) 0.7287(15) 0.024(4) Uiso 1 1 d . . .

H2W H 0.2085(14) 0.355(2) 0.574(2) 0.048(6) Uiso 1 1 d . . .

H1W H 0.2130(17) 0.322(3) 0.449(3) 0.076(8) Uiso 1 1 d . . .

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N1 0.0200(6) 0.0208(6) 0.0211(6) 0.0048(5) 0.0052(5) 0.0023(5)
N2 0.0255(7) 0.0263(6) 0.0244(7) 0.0026(5) 0.0105(6) -0.0017(5)
C3 0.0309(8) 0.0244(8) 0.0197(7) 0.0034(6) 0.0094(7) 0.0002(6)
C4 0.0293(8) 0.0287(8) 0.0173(7) 0.0001(6) 0.0042(6) 0.0074(6)
C5 0.0198(8) 0.0369(9) 0.0265(8) -0.0084(7) 0.0035(7) 0.0039(6)
C6 0.0261(8) 0.0296(8) 0.0294(8) -0.0083(7) 0.0132(7) -0.0064(6)
C7 0.0278(8) 0.0199(7) 0.0224(7) -0.0021(6) 0.0087(7) -0.0023(6)
C8 0.0209(7) 0.0191(7) 0.0160(7) -0.0045(5) 0.0054(6) 0.0010(5)
C9 0.0253(8) 0.0218(7) 0.0145(7) -0.0022(6) 0.0059(6) 0.0023(6)
N10 0.0253(7) 0.0151(6) 0.0231(7) -0.0030(5) 0.0016(6) 0.0038(5)
C11 0.0170(7) 0.0160(7) 0.0206(7) -0.0009(6) 0.0091(6) -0.0004(5)
N12 0.0263(7) 0.0118(6) 0.0229(6) 0.0011(5) 0.0033(5) 0.0018(5)
C13 0.0217(8) 0.0202(7) 0.0220(7) -0.0041(6) 0.0053(6) -0.0039(6)
C14 0.0183(7) 0.0215(7) 0.0210(7) 0.0002(6) 0.0027(6) -0.0024(6)
N15 0.0198(6) 0.0118(6) 0.0234(6) -0.0012(5) 0.0041(5) -0.0003(5)
O1W 0.0364(7) 0.0222(6) 0.0228(6) 0.0024(5) 0.0107(5) -0.0025(5)

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;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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N1 C8 1.3693(18) . ?

N1 N2 1.3739(16) . ?

N1 N10 1.3758(16) . ?

N2 C3 1.3159(19) . ?

C3 C9 1.426(2) . ?

C3 H3A 0.9300 . ?

C4 C5 1.373(2) . ?

C4 C9 1.402(2) . ?

C4 H4A 0.9300 . ?

C5 C6 1.409(2) . ?

C5 H5A 0.9300 . ?

C6 C7 1.374(2) . ?

C6 H6A 0.9300 . ?

C7 C8 1.3941(19) . ?

C7 H7A 0.9300 . ?

C8 C9 1.3997(19) . ?

N10 C11 1.3365(18) . ?

N10 H10 0.842(17) . ?

C11 N12 1.3184(17) . ?

C11 N15 1.3241(18) . ?

N12 C13 1.4643(18) . ?

N12 H12 0.813(18) . ?

C13 C14 1.5338(19) . ?

C13 H13A 0.9700 . ?

C13 H13B 0.9700 . ?

C14 N15 1.4689(18) . ?

C14 H14A 0.9700 . ?

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O1W H2W 0.82(2) . ?

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C8 N1 N2 112.55(11) . . ?
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N2 N1 N10 120.48(11) . . ?
C3 N2 N1 104.81(11) . . ?
N2 C3 C9 112.17(13) . . ?
N2 C3 H3A 123.9 . . ?
C9 C3 H3A 123.9 . . ?
C5 C4 C9 118.06(14) . . ?
C5 C4 H4A 121.0 . . ?
C9 C4 H4A 121.0 . . ?
C4 C5 C6 121.58(14) . . ?
C4 C5 H5A 119.2 . . ?
C6 C5 H5A 119.2 . . ?
C7 C6 C5 121.66(14) . . ?
C7 C6 H6A 119.2 . . ?
C5 C6 H6A 119.2 . . ?
C6 C7 C8 116.24(13) . . ?
C6 C7 H7A 121.9 . . ?
C8 C7 H7A 121.9 . . ?
N1 C8 C7 131.06(13) . . ?
N1 C8 C9 105.64(12) . . ?
C7 C8 C9 123.29(13) . . ?
C8 C9 C4 119.15(13) . . ?
C8 C9 C3 104.70(12) . . ?
C4 C9 C3 136.15(14) . . ?
C11 N10 N1 119.01(12) . . ?
C11 N10 H10 121.4(11) . . ?

N1 N10 H10 117.9(11) . . ?
N12 C11 N15 112.69(12) . . ?
N12 C11 N10 125.13(12) . . ?
N15 C11 N10 122.18(12) . . ?
C11 N12 C13 110.35(11) . . ?
C11 N12 H12 123.1(12) . . ?
C13 N12 H12 122.2(12) . . ?
N12 C13 C14 102.53(11) . . ?
N12 C13 H13A 111.3 . . ?
C14 C13 H13A 111.3 . . ?
N12 C13 H13B 111.3 . . ?
C14 C13 H13B 111.3 . . ?
H13A C13 H13B 109.2 . . ?
N15 C14 C13 102.67(11) . . ?
N15 C14 H14A 111.2 . . ?
C13 C14 H14A 111.2 . . ?
N15 C14 H14B 111.2 . . ?
C13 C14 H14B 111.2 . . ?
H14A C14 H14B 109.1 . . ?
C11 N15 C14 109.76(11) . . ?
C11 N15 H15 121.0(11) . . ?
C14 N15 H15 122.5(11) . . ?
H2W O1W H1W 109(2) . . ?

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C8 N1 N2 C3 -3.84(15) . . . . ?

N10 N1 N2 C3 -168.11(12) . . . . ?

N1 N2 C3 C9 2.92(16) . . . . ?

C9 C4 C5 C6 -0.6(2) . . . . ?

C4 C5 C6 C7 0.9(2) . . . . ?

C5 C6 C7 C8 -0.8(2) . . . . ?

N2 N1 C8 C7 -178.23(13) . . . . ?

N10 N1 C8 C7 -14.8(2) . . . . ?

N2 N1 C8 C9 3.20(15) . . . . ?

N10 N1 C8 C9 166.67(12) . . . . ?

C6 C7 C8 N1 -177.94(14) . . . . ?

C6 C7 C8 C9 0.4(2) . . . . ?

N1 C8 C9 C4 178.60(12) . . . . ?

C7 C8 C9 C4 -0.1(2) . . . . ?

N1 C8 C9 C3 -1.27(14) . . . . ?

C7 C8 C9 C3 -179.98(12) . . . . ?

C5 C4 C9 C8 0.2(2) . . . . ?

C5 C4 C9 C3 180.00(15) . . . . ?

N2 C3 C9 C8 -1.08(16) . . . . ?

N2 C3 C9 C4 179.09(15) . . . . ?

C8 N1 N10 C11 125.25(14) . . . . ?

N2 N1 N10 C11 -72.51(17) . . . . ?

N1 N10 C11 N12 -3.5(2) . . . . ?

N1 N10 C11 N15 176.16(12) . . . . ?

N15 C11 N12 C13 -3.91(16) . . . . ?

N10 C11 N12 C13 175.79(13) . . . . ?

C11 N12 C13 C14 11.26(15) . . . . ?

N12 C13 C14 N15 -13.55(13) . . . . ?

N12 C11 N15 C14 -5.89(16) . . . . ?

N10 C11 N15 C14 174.40(12) . . . . ?

C13 C14 N15 C11 12.36(14) . . . . ?

N12 C11 N10 N1 -3.5(2) . . . . ?

N15 C11 N10 N1 176.16(12) . . . . ?

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C11 N10 N1 C8 125.25(14) . . . . ?

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N10 H10 O1W 0.842(17) 1.858(17) 2.6954(16) 172.8(15) 4_576
N12 H12 Cl1 0.813(18) 2.568(18) 3.2119(12) 137.2(15) .
N15 H15 Cl1 0.810(17) 2.418(18) 3.2265(12) 175.1(15) 1_565
O1W H2W Cl1 0.82(2) 2.31(2) 3.1282(13) 178.7(19) .
O1W H1W Cl1 0.85(3) 2.28(3) 3.1080(13) 164(2) 4_565

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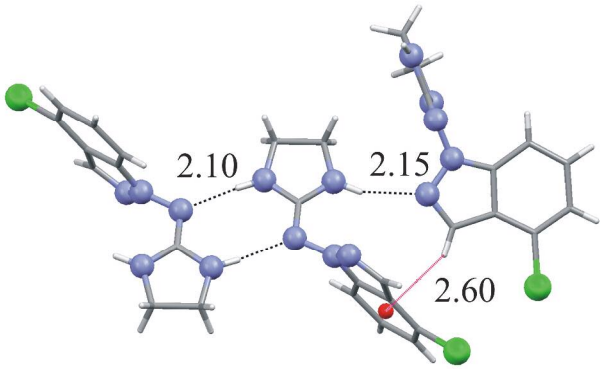

Fig. S1 Intermolecular interactions in the crystal structure of **12e**. Hydrogen bonds N-H···N are shown with black dashed lines (H···N distances are given in Å). Short C-H···π contact is shown as a red line.

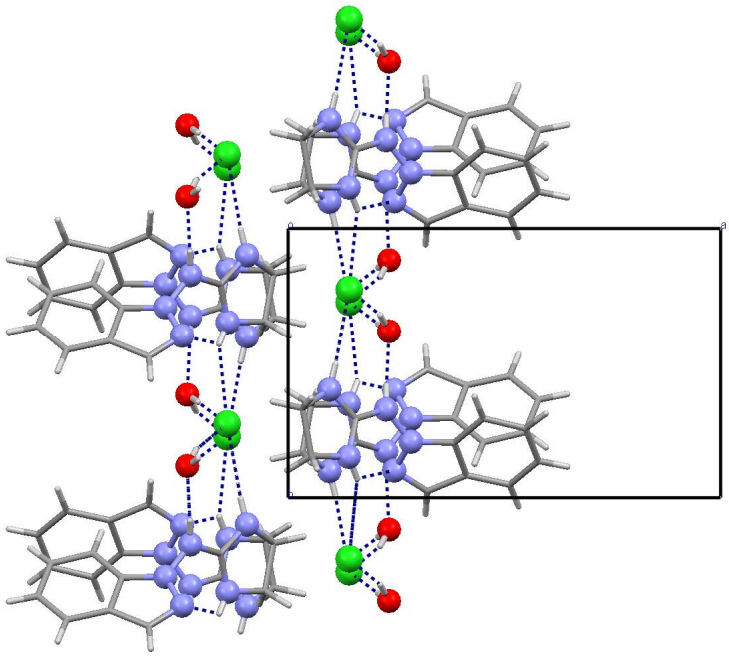

Fig. S2 Intermolecular interactions in the crystal structure of **13a**. Hydrogen bonds are shown as dashed lines.