Supporting Information

Experimental Section

General methods: All reactions were conducted in oven-dried glassware. Solvents used for the experiments were distilled and degassed with Argon. Bicyclic hydrazines were prepared as per the literature procedures.[14] All other reagents were purchased from local suppliers. All reactions were monitored by TLC (Silica gel 60 F254, 0.25 mm, Merck), visualization was effected with UV and/or by staining with Enholm yellow solution. Chromatography refers to open column chromatography on silica gel (60-120 mesh). NMR spectra were recorded at 300 (^{1}H) and 75 (^{13}C) MHz respectively on a Brucker Advance DPX-300 MHz. Chemical shifts are reported in δ (ppm) relative to TMS (^{1}H) or $CDCl_3$ (^{13}C) as internal standards. A mixture of $CDCl_3$ and CCl_4 (7:3) was used for recording the NMR spectra. IR spectra were recorded on Bomem MB series FT-IR spectrometer; absorptions are reported in cm^{-1}. Mass spectra were recorded under EI/HRMS or FAB/LRMS using JEOL JMS 600H mass spectrometer.

Typical experimental procedure: Bicyclic hydrazine (2 equiv.), boronic acid (1 equiv.), PPh_3 (20 mol%), I_2 (5 mol%) and K_2CO_3 (2.4 equiv.) were taken in a Schlenk tube, degassed and then $Pd(OAc)_2$ (10 mol%) was added to it. The mixture was dissolved in 1:1 mixture of THF and H_2O (4 mL) and stirred at 60 °C for 24 hours under Argon atmosphere. After the completion of the reaction, the reaction mixture was diluted with dichloromethane (50 mL) and washed with water (2x25 mL) and saturated brine (25 mL) solution. The organic layer was then dried over anhydrous sodium sulfate and the solvent was evaporated *in vacuo*. The residue on silica gel (60-120 mesh) column chromatography using 20 % ethyl acetate in hexane afforded the product in good yield.

Compound 3a

Following the general experimental procedure, the bicyclic hydrazine **1a** (100 mg, 0.42 mmol), Phenyl boronic acid (25 mg, 0.20 mmol), I_2 (2.75 mg, 5 mol%), PPh_3 (11 mg, 20 mol%), $Pd(OAc)_2$ (5.5 mg, 10 mol%) and K_2CO_3 (69 mg, 0.49 mmol) in 4mL 1:1 mixture of THF-H_2O at 60 °C under Argon atmosphere for 24 h gave the product as a colorless viscous liquid (61 mg, 93 %).

R_f 0.53 (6:4 Hexane/EtOAc) **IR** (neat) ν_{max}: 3298, 3054, 2978, 2928, 2851, 1751, 1695, 1412, 1219, 1060, 943, 853, 757 cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.30-7.13 (m, 5H), 6.64 (s, 1H), 5.87-5.84 (m, 1H), 5.71-5.68 (m, 1H), 4.74 (d, 1H, *J* = 6.69 Hz), 4.25-4.12 (m, 2H), 4.00 (s, 3H), 2.72-2.59 (m, 2H), 1.31-1.21 (m, 3H), 1.04 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 156.87, 155.97, 143.27, 132.70, 129.75, 128.39, 128.12, 127.49, 126.48, 67.35, 62.32, 53.74, 35.14, 29.70, 14.46. **MS** (LR-FAB) M+1 calculated for $C_{17}H_{22}N_2O_4$: 319.1580; found 319.1608.

Compound 3b

Following the general experimental procedure, the bicyclic hydrazine **1a** (100 mg, 0.42 mmol), 3-formyl-2-thiophene boronic acid (32 mg, 0.20 mmol), I_2 (2.75 mg, 5 mol%), PPh_3 (11 mg, 20 mol%), $Pd(OAc)_2$ (5.5 mg, 10 mol%) and K_2CO_3 (69 mg, 0.49 mmol) in 4mL 1:1 mixture of THF-H_2O at 60 °C under Argon atmosphere for 36 h gave the product as a colorless viscous liquid (52 mg, 79 %).

R_f 0.34 (6:4 Hexane/EtOAc) **IR** (neat) ν_{max}: 3296, 3052, 2983, 2934, 2857, 1744, 1714, 1681, 1514, 1465, 1386, 1236, 1174, 1060, 952, 866, 760 cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.95 (s, 1H), 7.36-7.35 (m, 1H), 7.19-7.18 (m, 1H), 6.51 (s, 1H), 5.97-5.95 (m, 1H), 5.69 (m, 1H), 5.08 (m, 1H), 4.24-4.17 (m, 4H), 3.99 (s, 1H), 2.67 (m, 2H), 1.31-1.26 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 186.17, 158.83, 155.75, 132.44, 130.89, 129.91, 128.43, 128.14, 123.71, 63.05, 62.87, 48.02, 35.17, 29.74, 28.19, 14.52. **MS** (LR-FAB) M+1 calculated for $C_{16}H_{20}N_2O_5S$: 353.1093; found 353.1114.

Compound 3c

Following the general experimental procedure, the bicyclic hydrazine **1a** (100 mg, 0.42 mmol), 2-furan boronic acid (22 mg, 0.21 mmol), I_2 (2.75 mg, 5 mol%), PPh_3 (11 mg, 20 mol%) $Pd(OAc)_2$ (5.5 mg, 10 mol%) and K_2CO_3 (69 mg, 0.49 mmol) in 4mL 1:1 mixture of THF-H_2O at 60 °C under Argon atmosphere for 36 h afforded the product as a colorless viscous liquid (46 mg, 72 %).

R_f 0.39 (6:4 Hexane/EtOAc) **IR** (neat) ν_{max}: 3294, 3059, 2978, 2928, 2851, 1749, 1715, 1591, 1503, 1465, 1377, 1236, 1168, 1127, 1060, 946, 866, 760, 655 cm^{-1}. **^{1}H NMR** (300MHz, $CDCl_3$): δ 7.34-7.26 (m, 1H), 6.53 (s, 1H), 6.27-6.26 (m, 1H), 6.09 (s, 1H), 5.81 (m, 1H), 5.70 (m, 1H), 4.94-4.92 (m, 1H), 4.23-4.10 (m, 5H), 2.73-2.59 (m, 2H), 1.31-1.19 (m, 6H). **^{13}C NMR** (75MHz, $CDCl_3$): δ 156.76, 155.81, 141.62, 141.38, 130.07, 122.22, 118.96, 110.23, 105.09, 67.20, 62.69, 62.42, 35.03, 29.25, 14.49. **MS** (EI) M^+ calculated for $C_{15}H_{20}N_2O_5$: 308.1372; found 308.1364.

Compound 3d

Following the general experimental procedure, the bicyclic hydrazine **1b** (100 mg, 0.37 mmol), Phenyl Boronic acid (25 mg, 0.18 mmol), I_2 (2.75 mg, 5 mol%), PPh_3 (9.7 mg, 20 mol%), $Pd(OAc)_2$ (5.5 mg, 10 mol%) and K_2CO_3 (61 mg, 0.44 mmol) in 4mL 1:1 mixture of THF-H_2O at 60 °C under Argon atmosphere for 24 h gave the product as a colorless viscous liquid (40 mg, 63 %).

R_f 0.46 (6:4 Hexane/EtOAc) **IR** (neat) ν_{max}: 3291, 3054, 2981, 2928, 2862, 1742, 1698, 1492, 1386, 1260, 1176, 1108, 1034, 954, 757, 700 cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.23-7.12 (m, 5H), 6.29 (s, 1H), 5.80-5.77 (m, 1H), 5.66-5.64 (m, 1H), 4.96-4.87 (m, 1H), 4.69-4.67 (m, 2H), 3.92 (s, 1H), 2.59-2.53 (m, 2H), 1.23-1.21 (d, 12 H, J = 5.7 Hz). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 156.54, 155.55, 143.35, 132.79, 132.19, 129.78, 128.40, 127.89, 126.47, 70.04, 67.33, 53.74, 35.79, 29.73, 29.52, 22.03, 21.65, 14.19. **MS** (LR-FAB) M+1 calculated for $C_{19}H_{26}N_2O_4$: 347.1893; found 347.1895.

Compound 4a

Following the general experimental procedure, the bicyclic hydrazine **2a** (100 mg, 0.42 mmol), phenyl boronic acid (24 mg, 0.20 mmol), I_2 (2.75 mg, 5 mol%), PPh_3 (11 mg, 20 mol%), $Pd(OAc)_2$ (5.5 mg, 10 mol%) and K_2CO_3 (68 mg, 0.49 mmol) in 4mL 1:1 mixture of THF-H_2O at 60 °C under Argon atmosphere for 24 h gave the product as a colorless viscous liquid (56 mg, 86 %).

R_f 0.39 (6:4 Hexane/EtOAc) **IR** (neat) ν_{max}: 3351, 3054, 2925, 2851, 1713, 1593, 1437, 1172, 1120, 1093, 954, 844, 722, 695 cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.53 (s, 1H),

7.51-7.43 (m, 10H), 5.87-5.84 (m, 1H), 5.74-5.72 (m, 1H), 4.78-4.76 (m, 1H), 4.21-4.18 (m, 1H), 2.75-2.68 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 157.37, 156.72, 142.38, 134.47, 133.21, 132.82, 131.40, 129.51, 128.85, 128.69, 119.58, 65.05, 56.78, 56.39, 53.75, 44.24, 35.20. **MS** (LR-FAB) M+1 calculated for $C_{19}H_{17}N_3O_2$: 320.1321; found 320.1364.

Compound 4b

Following the general experimental procedure, the bicyclic hydrazine **2a** (100 mg, 0.41 mmol), 3-formyl-2-thiophene boronic acid (32 mg, 0.21 mmol), I_2 (2.75 mg, 5 mol%), PPh_3 (11 mg, 20 mol%) $Pd(OAc)_2$ (5.5 mg, 10 mol%) and K_2CO_3 (68 mg, 0.49 mmol) in 4mL 1:1 mixture of THF-H_2O at 60 °C under Argon atmosphere for 36 h afforded the product as a colorless viscous liquid (44 mg, 61 %).

R_f 0.34 (6:4 Hexane/EtOAc) **IR** (neat) ν_{max}: 3348, 3052, 2983, 2923, 2846, 1712, 1705, 1699, 1596, 1503, 1427, 1231, 1133, 1048, 949, 845, 768, 707, 628 cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.94 (s, 1H), 8.52 (s, 1H), 7.50-7.34 (m, 6H), 7.23-7.22 (d, 1H, *J* = 5.1Hz), 6.00 (m, 1H), 5.78 (m, 1H), 5.24 (m, 1H), 4.75-4.67 (m, 1H, *J* = 7.8 Hz), 2.82-2.79 (m, 1H), 2.82-2.70 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 186.68, 156.95, 154.55, 136.94, 132.03, 131.60, 130.60, 129.29, 125.82, 87.09, 66.72, 46.66, 34.54, 29.98, 25.10. **MS** (EI) M^+ calculated for $C_{18}H_{15}N_3O_3S$: 353.0834; found 353.0822.

Compound 4c

Following the general experimental procedure, the bicyclic hydrazine **2b** (100 mg, 0.39 mmol), 3-formyl-2-thiophene boronic acid (30 mg, 0.19 mmol), I_2 (2.5 mg, 5 mol%), PPh_3 (10 mg, 20 mol%) $Pd(OAc)_2$ (5 mg, 10 mol%) and K_2CO_3 (65 mg, 0.47 mmol) in 4mL 1:1 mixture of THF-H_2O at 60 °C under Argon atmosphere for 36 h afforded the product as a colorless viscous liquid (42 mg, 60 %).

R_f 0.32 (6:4 Hexane/EtOAc) **IR** (neat) ν_{max}: 3346, 3054, 2989, 2917, 2846, 1714, 1704, 1694, 1549, 1448, 1355, 1231, 1152, 1070, 952, 823, 765, 729, 696 cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.51 (s, 1H), 7.39-7.22 (m, 7H), 5.98 (m, 1H), 5.75 (m, 1H), 5.18-5.15 (d, 1H, *J* = 8.4 Hz), 4.69-4.55 (m, 3H), 2.72-2.59 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 186.91, 156.85, 155.59, 136.88, 135.69, 131.97, 131.60, 130.66, 128.92, 128.85,

124.55, 67.33, 46.43, 43.23, 34.06, 29.91. **MS** (LR-FAB) M+1 calculated for $C_{19}H_{17}N_3O_3S$: 368.0991; found 368.1003.

Compound 4d

Following the general experimental procedure, the bicyclic hydrazine **2b** (100 mg, 0.39 mmol), phenyl boronic acid (23 mg, 0.19 mmol), I_2 (2.5 mg, 5 mol%), PPh_3 (10 mg, 20 mol%), $Pd(OAc)_2$ (5 mg, 10 mol%) and K_2CO_3 (65 mg, 0.47 mmol) in 4mL 1:1 mixture of THF-H_2O at 60 °C under Argon atmosphere for 24 h gave the product as a colorless viscous liquid (34 mg, 52 %).

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R_f 0.38 (6:4 Hexane/EtOAc) **IR** (neat) ν_{max}: 3341, 3060, 2917, 2846, 1710, 1694, 1604, 1489, 1454, 1360, 1253, 1157, 1070, 986, 952, 821, 760, 696 cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.54 (s, 1H), 7.39-7.21 (m, 10H), 5.93-5.91 (m, 1H), 5.81-5.80 (m, 1H), 4.69-4.64 (m, 3H), 3.96-3.95 (m,1H), 2.80-2.79 (m, 1H), 2.52-2.49 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 155.26, 153.81, 141.83, 135.76, 133.12, 129.83, 129.03, 128.98, 128.39, 127.57, 127.37, 126.63, 64.76, 54.56, 43.25, 35.51, 30.01. **MS** (EI) M+ calculated for $C_{20}H_{19}N_3O_2$: 333.1477; found 333.1463.

Compound 4e

Following the general experimental procedure, the bicyclic hydrazine **2c** (100 mg, 0.35 mmol), phenyl boronic acid (22 mg, 0.17 mmol), I_2 (2 mg, 5 mol%), PPh_3 (8 mg, 20 mol%), $Pd(OAc)_2$ (4 mg, 10 mol%) and K_2CO_3 (60 mg, 0.42 mmol) in 4mL 1:1 mixture of THF-H_2O at 60 °C under Argon atmosphere for 24 h gave the product as a colorless viscous liquid (35 mg, 56 %).

R_f 0.59 (6:4 Hexane/ EtOAc) **IR** (neat) ν_{max}: 3347, 3061, 2956, 2920, 2851, 1711, 1694, 1610, 1575, 1455, 1355, 1297, 1249, 1028, 949, 842, 733 cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.56 (s, 1H), 7.33-7.11 (m, 9H), 5.94-5.91 (m, 1H), 5.81-5.79 (m, 1H), 4.68-4.66 (m, 1H), 4.58 (s, 2H), 3.96-3.94 (m, 1H), 3.77 (s, 3H), 2.51-2.49 (m, 1H), 2.16 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 155.09, 153.61, 141.66, 132.87, 130.26, 129.62, 128.79, 128.19, 127.78, 127.12, 126.06, 114.07, 64.48, 55.18, 54.33, 42.52, 35.27, 29.78, 14.55. **MS** (LR-FAB) M+1 calculated for $C_{21}H_{21}N_3O_3$: 364.1583; found 364.1610.

Compound 4f

Following the general experimental procedure, the bicyclic hydrazine **2d** (100 mg, 0.37 mmol), phenyl boronic acid (23 mg, 0.18 mmol), I_2 (2.5 mg, 5 mol%), PPh_3 (10 mg, 20 mol%), $Pd(OAc)_2$ (5 mg, 10 mol%) and K_2CO_3 (61 mg, 0.44 mmol) in 4mL 1:1 mixture of THF-H_2O at 60 °C under Argon atmosphere for 24 h gave the product as a colorless viscous liquid (25 mg, 40 %).

R_f 0.37 (6:4 Hexane/EtOAc) **IR** (neat) ν_{max}: 3346, 3054, 2917, 2857, 1705, 1591, 1514, 1448, 1250, 1168, 1028, 953, 721 cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.55 (s, 1H), 7.68-7.43 (m, 9H), 5.85-5.83 (m, 1H), 5.71 (s, 1H), 4.67-4.62 (m, 1H), 4.55 (s, 2H), 4.05 (s, 1H), 2.69-2.55 (m, 2H), 2.31 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 154.83, 153.97, 142.07, 137.5, 132.80, 132.21, 132.07, 131.98, 131.94, 131.72, 129.28, 128.70, 128.64, 128.11, 64.68, 53.75, 49.24, 42.54, 35.08, 31.28, 21.20. **MS (EI)** M^+ calculated for $C_{21}H_{21}N_3O_2$: 347.1634; found 347.1639.

Compound 4g

Following the general experimental procedure, the bicyclic hydrazine **2a** (100 mg, 0.42 mmol), 2-furan boronic acid (22 mg, 0.21 mmol), I_2 (2.75 mg, 5 mol%), PPh_3 (11 mg, 20 mol%) $Pd(OAc)_2$ (5.5 mg, 10 mol%) and K_2CO_3 (69 mg, 0.49 mmol) in 4mL 1:1 mixture of THF-H_2O at 60 °C under Argon atmosphere for 36 h afforded the product as a colorless viscous liquid (54 mg, 84 %).

R_f 0.34 (6:4 Hexane/EtOAc) **IR** (neat) ν_{max}: 3349, 3053, 2983, 2923, 2851, 1705, 1643, 1596, 1426, 1270, 1179, 1080, 965, 795 743, 713 cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.55 (s, 1H), 7.48-7.46 (m, 5H), 7.36-7.33 (m, 1H), 6.28 (m, 1H), 6.09 (m, 1H), 5.89 (m, 1H), 5.81 (m, 1H), 4.96-4.93 (m, 1H), 4.15 (s, 1H), 2.84-2.81 (m, 1H), 2.60 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 154.19, 153.84, 147.03, 142.08, 130.17, 129.12, 128.22, 124.04, 119.20, 110.13, 61.52, 47.69, 35.32, 31.56, 30.29, 29.34, 22.77. **MS** (EI) M^+ calculated for $C_{17}H_{15}N_3O_3$: 309.1113; found 309.1117.

Compound 4h

Following the general experimental procedure, the bicyclic hydrazine **2b** (100 mg, 0.41 mmol), 2-furan boronic acid (32 mg, 0.21 mmol), I_2 (2.75 mg, 5 mol%), PPh_3 (11 mg, 20 mol%) $Pd(OAc)_2$ (5.5 mg, 10 mol%) and K_2CO_3 (69 mg, 0.49 mmol) in 4mL 1:1 mixture of THF-H_2O at 60 °C under Argon atmosphere for 36 h afforded the product as a colorless viscous liquid (56mg, 89%).

R_f 0.37 (6:4 Hexane/EtOAc) **IR** (neat) ν_{max}: 3351, 3049, 2988, 2925, 2857, 1705, 1693, 1604, 1585, 1495, 1454, 1358, 1231, 1119, 1073, 946, 781, 732, 633 cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.54 (s, 1H), 7.38-7.24 (m, 6H), 6.26-6.22 (m, 1H), 6.01 (d, 1H, *J* = 3.3Hz), 5.86-5.83 (m, 1H), 5.76-5.74 (m, 1H), 4.89-4.82 (m, 1H), 4.65 (s, 2H), 4.08 (m, 1H), 2.83-2.75 (m, 1H), 2.53-2.45 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 155.06, 154.32, 141.91, 135.35, 130.06, 129.91, 128.26, 110.26, 64.61, 61.30, 47.33, 43.31, 42.93, 35.18, 30.24, 29.73, 22.72. **MS** (EI) M^+ calculated for $C_{18}H_{17}N_3O_3$: 323.1270; found 323.1254.