Supporting Information
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Direct preparation of heteroaromatic compounds from alkenes

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Electronic supplementary information

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**General Experimental Details.** All solvents and reagents were used as received from commercial sources. Alkenes 1b, 1d, 1e, 1f were prepared employing standard method for Suzuki coupling\(^1\) from commercially available precursors. Proton nuclear magnetic resonance spectra (NMR) were recorded at 400 MHz. \(^{13}\)C NMR spectra were recorded at 100 MHz. The LCMS analysis was conducted on an Acquity UPLC BEH C18 column (50mm x 2.1mm internal diameter 1.7µm packing diameter) at 40°C employing gradient CH\(_3\)CN-H\(_2\)O with 0.1% formic acid or on an XBridge C18 column (50mm x 4.6mm internal diameter 3.5µm packing diameter) at 30°C employing gradient CH\(_3\)CN-H\(_2\)O with 10 mM NH\(_4\)HCO\(_3\). Mass-Directed Autopreparative HPLC analysis (MDAP) was conducted on an XBridge C18 column (100mm x 30mm internal diameter, 5µm packing diameter) at ambient temperature employing gradient CH\(_3\)CN-H\(_2\)O with 10 mM NH\(_4\)HCO\(_3\). Accurate mass spectra under the conditions of electrospray ionisation (ESI) were recorded on Bruker Apex IV. Infrared spectra (IR) were recorded as evaporated films. Melting points were obtained using a Leica VMTG heated-stage microscope and are uncorrected.
**General procedure A.** To a solution of IBX (2 eqv., 45 % stabilized with benzoic and isophthalic acids) and iodine (1.1 eqv.) in dry dimethyl sulfoxide (0.25 M) stirred at room temperature was added the corresponding alkene (1 eqv.) in one charge. The reaction mixture was stirred at room temperature until full consumption of the starting alkene (monitored by LCMS). Then it was diluted with DCM (30 mL for ~0.5 mmol scale) and washed with saturated aqueous NaHCO₃ – Na₂S₂O₃. The aqueous layer was extracted with DCM (2 × 20 mL for ~0.5 mmol scale); the combined organic layers were dried over Na₂SO₄ and filtered. The corresponding nucleophile (3 eqv.) and dry N,N-dimethylformamide (0.15 M) were added to the DCM solution and its volume was reduced down to ~2 mL (for ~0.5 mmol scale) under vacuum. The reaction mixture was stirred at room temperature for 12 hours. The corresponding product was isolated by MDAP using a gradient CH₃CN-H₂O solvent mixture.

5-Methyl-4-phenyl-1,3-thiazole-2-amine (3a)

Using β-methylstyrene (1a, 0.055mL, 0.423 mmol) and thiourea (4a, 97 mg, 1.27 mmol) as the nucleophile, the product was obtained as a yellow solid (60 mg, 74%). M.p. 118-121°C [CHCl₃; lit.² 115 – 116°C]; ¹H NMR (400 MHz, CHLOROFORM-d) δ ppm 2.39 (s, 3 H, C₆H₃), 5.28 (br. s., 2 H, NΗ₂), 7.32 (t, J=7.5 Hz, 1 H, Ph), 7.40 (t, J=7.5 Hz, 2 H, Ph), 7.56 (d, J=7.5 Hz, 2 H, Ph); ¹³C NMR (101 MHz, CHLOROFORM-d) δ ppm 12.3 (C₆H₃), 117.4 (C-S), 127.1 (CH), 128.2 (CH), 128.3 (CH), 135.1 (C), 146.0 (C-N), 164.0 (C-NΗ₂). NMR data matched that reported in the literature.³

5-Propyl-4-(3-pyridinyl)-1,3-thiazol-2-amine (3b)

Using 3-[(1E)-1-penten-1-yl]pyridine (1b, 60 mg, 0.408 mmol) and thiourea (4a, 93 mg, 1.22 mmol) as the nucleophile, the product was obtained as a yellowish solid (55 mg, 62%). M.p. 61-62°C [CHCl₃]; ¹H NMR (400 MHz, CHLOROFORM-d) δ ppm 0.97 (t, J=7.5 Hz, 3 H, CH₃), 1.66 (sxt, J=7.5 Hz, 2 H, CH₂), 2.75 (t, J=7.5 Hz, 2 H, CH₂), 5.02 (br. s., 2 H, NH₂), 7.33 (dd, J=8.0, 5.0 Hz, 1 H, Ar), 7.86 (d, J=8.0 Hz, 1 H, Ar), 8.55 (d, J=5.0 Hz, 1 H, Ar), 8.78 (s, 1 H, Ar); ¹³C NMR (101 MHz, CHLOROFORM-d) δ ppm 13.7 (CH₃), 25.4 (CH₂), 29.0 (CH₂), 123.2 (CH), 126.1 (C), 131.3 (C), 135.8 (CH), 142.7
(C-N), 148.3 (CH), 149.3 (CH), 164.5 (N=Se-S); IR \nu cm\(^{-1}\) 3290, 3130, 2959, 2930, 1628, 1535, 1340, 1320, 1180, 1100, 1024, 813, 710; HRMS (ES+) \text{m/z} 220.0905 (M+H; \text{C}_{11}\text{H}_{14}\text{N}_{3}\text{S} \text{requires} \ 220.0908).

4-Phenyl-1,3-thiazol-2-amine (3c)

Using styrene (1c, 0.055 mL, 0.480 mmol) and thiourea (4a, 110 mg, 1.44 mmol) as the nucleophile, the product was obtained as a yellowish solid (65 mg, 77%). M.p. 146 – 150\(^\circ\)C [CHCl\(_3\); lit.\(^2\) 150 – 151\(^\circ\)C]; \(^1\)H NMR (400 MHz, CHLOROFORM-\(d\)) \delta ppm 5.24 (br. s., 2 H, NH\(_2\)), 6.73 (s, 1 H, CH-S), 7.31 (t, J=7.0 Hz, 1 H, Ph), 7.39 (t, J=7.0 Hz, 2 H, Ph), 7.78 (d, J=7.0 Hz, 2 H, Ph); \(^13\)C NMR (101 MHz, CHLOROFORM-\(d\)) \delta ppm 102.9 (CH-S), 126.0 (CH), 127.7 (CH), 128.6 (CH), 134.6 (C), 151.3 (C-N), 167.1 (N=Se-S).

NMR data matched that reported in the literature.\(^3\)

5-(2-Amino-5-propyl-1,3-thiazol-4-yl)-N,N-dimethyl-2-pyridinamine (3d)

Using N,N-dimethyl-5-[(1\(^E\))-1-penten-1-yl]-2-pyridinamine (1d, 60 mg, 0.32 mmol) and thiourea (4a, 72 mg, 0.95 mmol) as the nucleophile, the product was obtained as a yellow solid (55 mg, 67%). M.p. > 110\(^\circ\)C (decomp.); \(^1\)H NMR (400 MHz, CHLOROFORM-\(d\)) \delta ppm 0.96 (t, J=7.5 Hz, 3 H, \text{CH}_3\text{CH}_2), 1.63 (sxt, J=7.5 Hz, 2 H, \text{CH}_2), 2.71 (t, J=7.5 Hz, 2 H, \text{CH}_2), 3.12 (s, 6 H, \text{CH}_3\text{N}), 4.96 (br. s., 2 H, NH\(_2\)), 6.56 (d, J=8.5 Hz, 1 H, Ar), 7.68 (dd, J=8.5, 2.5 Hz, 1 H, Ar), 8.30 (d, J=2.5 Hz, 1 H, Ar); \(^13\)C NMR (101 MHz, CHLOROFORM-\(d\)) \delta ppm 13.8 (CH\(_3\)), 25.5 (CH\(_2\)), 29.1 (CH\(_2\)), 38.2 (CH\(_3\)N), 105.4 (CH), 119.3 (C), 123.1 (C), 137.5 (CH), 143.6 (C), 147.2 (CH), 158.2 (C), 164.0 (C); IR \nu cm\(^{-1}\) 3178, 2958, 2928, 1610, 1567, 1542, 1512, 1392, 1317, 1215, 956, 813; HRMS (ES+) \text{m/z} 263.1324 (M+H; \text{C}_{13}\text{H}_{19}\text{N}_{4}\text{S} \text{requires} \ 263.1330).
5-Propyl-4,5’-bi-1,3-thiazol-2-amine (3e)

Using 5-propyl-4,5’-bi-1,3-thiazol-2-amine (1e, 70 mg, 0.46 mmol) and thiourea (4a, 104 mg, 1.37 mmol) as the nucleophile, the product was obtained as a yellowish solid (78 mg, 76%). M.p. 133 – 134°C [CHCl₃]; ¹H NMR (400 MHz, CHLOROFORM-d) δ ppm 1.01 (t, J=7.4 Hz, 3 H, CH₃), 1.67 (sxt, J=7.4 Hz, 2 H, CH₂), 2.79 (t, J=7.4 Hz, 2 H, CH₂), 5.37 (br. s., 2 H, NH₂), 8.01 (s, 1 H, Ar), 8.73 (s, 1 H, Ar); ¹³C NMR (101 MHz, CHLOROFORM-d) δ ppm 13.8 (CH₃), 24.5 (CH₂), 29.1 (CH₂), 125.5 (C), 133.3 (C), 136.4 (C), 140.1 (CH), 151.8 (CH), 164.5 (N=C-S); IR ν cm⁻¹ 3300, 3134, 2957, 2905, 1640, 1559, 1537, 1501, 1318, 1262, 1105, 1016, 884, 804, 775, 674; HRMS (ES+) m/z 226.0466 (M+H; C₉H₁₂N₂S₂ requires 226.0473).

5-[(Methoxy)methyl]-4-phenyl-1,3-thiazol-2-amine (3f)

Using methyl (2E)-3-phenyl-2-propen-1-yl ether (1f, 50 mg, 0.34 mmol) and thiourea (4a, 77 mg, 1.01 mmol) as the nucleophile, the product was obtained as a yellowish solid (62 mg, 83%). M.p. 127-128°C [CHCl₃]; ¹H NMR (400 MHz, CHLOROFORM-d) δ ppm 3.39 (s, 3 H, CH₃), 4.49 (s, 2 H, CH₂), 5.31 (br. s., 2 H, NH₂), 7.32 - 7.38 (m, 1 H, Ph), 7.39 - 7.45 (m, 2 H, Ph), 7.58 (d, J=7.5 Hz, 2 H, Ph); ¹³C NMR (101 MHz, CHLOROFORM-d) δ ppm 57.7 (CH₃), 66.4 (CH₂), 119.0 (C-S), 127.9 (CH), 128.3 (CH), 128.5 (CH), 134.5 (C), 149.6 (C-N), 166.2 (N=C-S); IR ν cm⁻¹ 3330, 3297, 3123, 2982, 2867, 1625, 1527, 1487, 1336, 1190, 1071, 775, 701; HRMS (ES+) m/z 221.0741 (M+H; C₁₁H₁₃N₂OS requires 221.0749).
4,5-Dibutyl-1,3-thiazol-2-amine (3g)

Using 5-decene (1g, 0.095 mL, 0.50 mmol) and thiourea (4a, 77 mg, 1.01 mmol) as the nucleophile, the product was obtained as colorless oil (82 mg, 77%). $^1$H NMR (400 MHz, CHLOROFORM-d) δ ppm 0.92 (t, J=7.3 Hz, 6 H, CH$_3$), 1.25 - 1.40 (m, 4 H, CH$_2$), 1.44 - 1.63 (m, 4 H, CH$_2$), 2.36 - 2.48 (m, 2 H, CH$_2$), 2.56 (t, J=7.5 Hz, 2 H, CH$_2$), 4.90 (br. s., 2 H, NH$_2$); $^{13}$C NMR (101 MHz, CHLOROFORM-d) δ ppm 13.8 (C$_3$H$_3$), 14.0 (C$_3$H$_3$), 22.1 (CH$_2$), 22.5 (CH$_2$), 25.8 (CH$_2$), 28.7 (CH$_2$), 31.8 (CH$_2$), 34.1 (CH$_2$), 121.9 (C-S), 147.1 (C-N), 164.0 (S-C=S); IR $\nu$ cm$^{-1}$ 3283, 3122, 2954, 2927, 2857, 1609, 1523, 1461, 1317, 1127, 1064, 748, 705; HRMS (ES+) m/z 213.1423 (M+H; C$_{11}$H$_{21}$N$_2$S requires 213.1425).

2-(1,1-Dimethylethyl)-4-phenyl-1,3-thiazole (3h)

Using styrene (1c, 0.050 mL, 0.423 mmol) and 2,2-dimethylthiopropioamide (4b, 149 mg, 1.27 mmol) as the nucleophile, the product was obtained as yellow oil (62 mg, 67%). $^1$H NMR (400 MHz, CHLOROFORM-d) δ ppm 1.51 (s, 9 H, CH$_3$), 7.29 - 7.37 (m, 2 H, Ph + CH-S), 7.43 (t, J=7.5 Hz, 2 H, Ph), 7.94 (d, J=7.5 Hz, 2 H, Ph); $^{13}$C NMR (101 MHz, DMSO-d$_6$) δ ppm 30.6 (CH$_3$), 37.3 (CH$_3$C), 112.9 (CH-S), 126.0 (CH), 127.8 (CH), 128.7 (CH), 134.3 (C), 153.5 (C-N), 180.2 (S-C=S); IR $\nu$ cm$^{-1}$ 2962, 2927, 1494, 1475, 1460, 1445, 1363, 1223, 1066, 1015, 727, 689; HRMS (ES+) m/z 218.1000 (M+H; C$_{13}$H$_{16}$NS requires 218.1003). $^{13}$C NMR data matched that reported in the literature.$^4$
3-(4-Phenyl-1,3-thiazol-2-yl)pyridine (3i)

Using styrene (1c, 0.050 mL, 0.423 mmol) and thionicotinamide (4c, 175 mg, 1.27 mmol) as the nucleophile, the product was obtained as a yellowish solid (71 mg, 68%). M.p. 64-65°C [CHCl₃; lit⁵ 67-68°C]; ′H NMR (400 MHz, CHLOROFORM-d) δ ppm 7.35 - 7.52 (m, 4 H, Ar), 7.55 (s, 1 H, CH-S), 8.01 (d, J=7.5 Hz, 2 H, Ar), 8.34 (br. d., J=8.0 Hz, 1 H, Ar), 8.68 (br. d., J=3.5 Hz, 1 H, Ar), 9.26 (br. s., 1 H, Ar); ′C NMR (101 MHz, CHLOROFORM-d) δ ppm 113.2 (C₁H-S), 123.7 (CH), 126.4 (CH), 128.4 (CH), 128.8 (CH), 129.7 (C), 133.6 (CH), 134.0 (C), 147.7 (CH), 150.8 (CH), 156.7 (C), 164.3 (C); IR ν cm⁻¹ 3062, 2987, 1569, 1495, 1474, 1444, 1417, 1408, 1330, 1254, 1189, 1072, 1024, 976, 808, 730, 702, 679; HRMS (ES+) m/z 239.0638 (M+H; C₁₄H₁₁N₂S requires 239.0643).

**General procedure B.** To a solution of IBX (2 eqv., 45 % stabilized with benzoic and isophthalic acids) and iodine (1.1 mmol) in dry dimethyl sulfoxide (0.25 M) stirred at room temperature was added the corresponding alkene (1 eqv.) in one charge. The reaction mixture was stirred at room temperature until full consumption of the starting alkene (monitored by LCMS). Then it was diluted with DCM (30 mL for ~0.5 mmol scale) and washed with saturated aqueous NaHCO₃ – Na₂S₂O₃. The aqueous layer was extracted with DCM (2 × 20 mL for ~0.5 mmol scale); the combined organic layers were dried over Na₂SO₄ and filtered. The corresponding nucleophile (3 eqv.), potassium carbonate (2 eqv.) and dry N,N-dimethylformamide (0.15 M) were added to the DCM solution and its’ volume was reduced down to ~2 mL (for ~0.5 mmol scale) under vacuum. The reaction mixture was stirred at room temperature for 12 hours. The corresponding product was isolated by MDAP using gradient CH₃CN-H₂O solvent mixture.
4(5)-Phenyl-2-propyl-1H-imidazole (3j)

![Chemical structure of 4(5)-Phenyl-2-propyl-1H-imidazole (3j)]

Using styrene (1c, 0.050 mL, 0.423 mmol) and butyramidine hydrochloride (4d, 156 mg, 1.27 mmol) as the nucleophile, the product was obtained as yellowish solid (57 mg, 72%). M.p. 130-132°C [aq. EtOH; lit6 136°C]. 1H NMR (400 MHz, CHLOROFORM-d) δ ppm 0.95 (t, J=7.5 Hz, 3 H, C3H3), 1.75 (sxt, J=7.5 Hz, 2 H, C2H2), 2.72 (t, J=7.5 Hz, 2 H, CH2), 7.18 - 7.26 (m, 2 H, Ph + C3H-NH), 7.36 (t, J=7.5 Hz, 2 H, Ph), 7.69 (d, J=7.5 Hz, 2 H, Ph); 13C NMR (101 MHz, CHLOROFORM-d) δ ppm 13.7 (C3H3), 22.0 (C2H2), 30.3 (CH2), 115.1 (CH-N), 124.8 (CH), 126.8 (CH), 128.7 (CH), 132.6 (C), 137.4 (C-N), 149.4 (N=C-NH); IR ν cm⁻¹ 3033, 2961, 2930, 2871, 1607, 1539, 1514, 1455, 1426, 1374, 1260, 1134, 1094, 1069, 1014, 801, 748, 692; HRMS (ES+) m/z 187.1232 (M+H; C12H15N2 requires 187.1235).

3-(4(5)-Phenyl-1H-imidazol-2-yl)pyridine (3k)

![Chemical structure of 3-(4(5)-Phenyl-1H-imidazol-2-yl)pyridine (3k)]

Using styrene (1c, 0.050 mL, 0.423 mmol) and 3-amidinopyridine hydrochloride (4e, 200 mg, 1.27 mmol) as the nucleophile, the product was obtained as yellowish solid (62 mg, 67%). M.p. 192–194°C [aq. EtOH; lit7 201-203°C]. 1H NMR (400 MHz, MeOD) δ ppm 7.26 (t, J=7.5 Hz, 1 H, Ar), 7.40 (t, J=7.5 Hz, 2 H, Ar), 7.49 - 7.60 (m, 2 H, Ar + CH-NH), 7.78 (d, J=7.5 Hz, 2 H, Ar), 8.35 (d, J=8.5 Hz, 1 H, Ar), 8.54 (d, J=3.5 Hz, 1 H, Ar), 9.12 (s, 1 H, Ar); 13C NMR (125 MHz, CHLOROFORM-d + 5% MeOD) δ ppm 118.4 (CH-NH), 124.2 (CH), 125.0 (CH), 126.6 (C), 127.4 (CH), 128.7 (CH), 131.8 (C), 134.0 (CH), 139.4 (C), 143.7 (C), 145.6 (CH), 148.4 (CH); IR ν cm⁻¹ 3100, 3056, 3056, 2980, 2950, 2950, 2950, 1660, 1576, 1484, 1464, 1436, 1148, 1087, 1026, 950, 811, 757, 695; HRMS (ES+) m/z 222.1028 (M+H; C14H15N3 requires 222.1031). 1H NMR of 3k*2HCl (400
MHz, DMSO-d$_6$) δ ppm 7.45 (t, $J$=7.5 Hz, 1 H), 7.55 (t, $J$=7.5 Hz, 2H), 7.81 (dd, $J$=8.5 Hz, $J$=5.5 Hz, 1H), 8.02 (d, $J$=7.5 Hz, 2H), 8.29 (s, 1H), 8.75 (d, $J$=8.5 Hz, 1H), 8.83 (dd, $J$=5.5 Hz, $J$=1.5 Hz, 1H), 9.42 (d, $J$=1.5 Hz, 1H) identical to that reported in the literature.\(^8\)

2-Phenyl-5,6,7,8-tetrahydroimidazo[1,2a]pyridine (3l)

![2-Phenyl-5,6,7,8-tetrahydroimidazo[1,2a]pyridine](image)

Using styrene (1c, 0.050 mL, 0.423 mmol) and 2-iminopiperidine hydrochloride (4f, 171 mg, 1.27 mmol) as the nucleophile, the product was obtained as yellowish solid (60 mg, 71%). M.p. 93-95°C [CHCl$_3$; lit\(^9\) 98-100°C]. \(^1\)H NMR (400 MHz, CHLOROFORM-d) δ ppm 1.92 - 2.04 (m, 4 H, C$_2$H$_2$), 2.94 (t, $J$=6.0 Hz, 2 H, CH$_2$), 3.98 (t, $J$=6.0 Hz, 2 H, C$_2$H$_2$N), 7.07 (s, 1 H, CH-N), 7.21 (t, $J$=7.5 Hz, 1 H, Ph), 7.35 (t, $J$=7.5 Hz, 2 H, Ph), 7.75 (d, $J$=7.5 Hz, 2 H, Ph); \(^13\)C NMR (101 MHz, CHLOROFORM-d) δ ppm 21.1 (C$_2$H$_3$), 23.0 (C$_2$H$_2$), 24.6 (CH$_2$), 44.8 (CH$_2$N), 113.8 (CH-N), 124.6 (CH), 126.4 (CH), 128.4 (CH), 134.4 (C), 140.5 (C), 145.2 (N-C=N); IR $\nu$ cm$^{-1}$ 2947, 2862, 1604, 1516, 1446, 1425, 1377, 1319, 1193, 1076, 951, 744, 696; HRMS (ES+) $m$/z 199.1234 (M+H; C$_{13}$H$_{15}$N$_2$ requires 199.1235).

2-(Ethylthio)-4(5)-phenyl-1H-imidazole (3m)

![2-(Ethylthio)-4(5)-phenyl-1H-imidazole](image)

Using styrene (1c, 0.050 mL, 0.423 mmol) and 2-ethylisothiourea, hydrobromide (4g, 235 mg, 1.27 mmol) as the nucleophile, the product was obtained as a white solid (62 mg, 72 %). M.p. 130–132°C [aq. EtOH; lit\(^10\) 129-130°C]; \(^1\)H NMR (400 MHz, CHLOROFORM-d) δ ppm 1.31 (t, $J$=7.2 Hz, 3 H, CH$_3$), 3.04 (q, $J$=7.2 Hz, 2 H, CH$_2$), 7.23 - 7.29 (m, 1 H, Ph), 7.33 - 7.42 (m, 3 H, Ph + CH-N), 7.70 (d, $J$=7.5 Hz, 2 H, Ph); \(^13\)C NMR (101 MHz, CHLOROFORM-d) δ ppm 15.3 (CH$_3$), 29.5 (CH$_2$), 117.6 (CH-N), 124.8 (CH), 127.1 (CH), 128.7 (CH), 132.3 (C), 139.9 (C-N), 140.6 (N-C-S); IR $\nu$ cm$^{-1}$
3059, 2965, 2867, 1606, 1495, 1449, 1389, 1261, 1129, 1082, 986, 801, 756, 692; HRMS (ES+) m/z 205.0797 (M+H; C_{11}H_{13}N_{2}S requires 205.0799)

3-{4(5)-[(Methoxy)methyl]-5(4)-phenyl-1H-imidazol-2-yl}pyridine (3n)

![](image)

Using (2E)-3-phenyl-2-propen-1-yl ether (If, 70 mg, 0.472 mmol) and benzamidine (4h, 170 mg, 1.27 mmol) as the nucleophile, the product was obtained as a yellowish oil (87 mg, 70%). \(^1\)H NMR (400 MHz, CHLOROFORM-d) δ ppm 3.41 (s, 3 H, C\textsubscript{3}H\textsubscript{3}), 4.57 (s, 2 H, C\textsubscript{2}H\textsubscript{2}), 7.28 - 7.45 (m, 6 H, Ph), 7.61 (d, J=7.0 Hz, 2 H, Ph), 7.87 (d, J=7.0 Hz, 2 H, Ph); \(^{13}\)C NMR (101 MHz, CHLOROFORM-d) δ ppm 58.0 (C\textsubscript{3}H\textsubscript{3}), 66.0 (C\textsubscript{2}H\textsubscript{2}), 125.5 (CH), 127.3 (CH), 127.4 (CH), 128.6 (CH), 128.7 (CH), 129.4 (CH), 129.6 (C), 131.7 (C), 135.5 (C), 145.9 (N=C=N); IR ν cm\(^{-1}\) 3059, 2923, 1589, 1494, 1461, 1402, 1189, 1087, 912, 773, 696; HRMS (ES+) m/z 265.1346 (M+H; C\textsubscript{17}H\textsubscript{17}N_{2}O requires 265.1341)

4,6-Bis(methoxy)-2-phenyl-1H-indole (3o). To a solution of IBX (527 mg, 0.846 mmol, 45 % stabilized with benzoic and isophthalic acids) and iodine (118 mg, 0.465 mmol) in dry dimethyl sulfoxide (1.6 mL) stirred at room temperature was added styrene (50 µL, 0.457 mmol) in one charge. The reaction mixture was stirred at room temperature until full consumption of the starting alkene (monitored by LCMS). Then it was diluted with DCM (30 mL) and washed with saturated aqueous NaHCO\textsubscript{3} – Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}. The aqueous layer was extracted with DCM (2 × 20 mL); the combined organic layers were dried over Na\textsubscript{2}SO\textsubscript{4} and filtered. 3,5-bis(methoxy)aniline (1.27 mmol, 194 mg) and dry N,N-dimethylformamide (2.5 mL) were added to the DCM solution and its’ volume was reduced down to ~2 mL under vacuum. The reaction mixture was stirred at 80°C for 2 hours. 4,6-bis(methoxy)-2-phenyl-1H-indole was isolated by MDAP using gradient CH\textsubscript{3}CN-H\textsubscript{2}O solvent mixture.

![](image)

Greenish oil (67 mg, 63%). \(^1\)H NMR (400 MHz, CHLOROFORM-d) δ ppm 3.87 (s, 3 H, CH\textsubscript{3}O), 3.95 (s, 3 H, CH\textsubscript{3}O), 6.25 (s, 1 H, CO-CH-CO), 6.53 (s, 1 H, CO-CH-CN), 6.87
(s, 1 H, CH=C-NH), 7.24 - 7.32 (m, 1 H, Ph), 7.42 (t, J=7.5 Hz, 2 H, Ph), 7.61 (d, J=7.5 Hz, 2 H, Ph), 8.26 (br. s., 1 H, NH); $^{13}$C NMR (101 MHz, CHLOROFORM-d) δ ppm 55.4 (CH$_3$), 55.7 (CH$_3$), 86.7 (CO-CH-CN), 91.9 (CO-CH-CO), 97.1 (CH=C-NH), 114.5 (CO-C-C-NH), 124.4 (Ph, CH), 127.0 (Ph, CH), 129.0 (Ph, CH), 132.5 (Ph, C), 135.1 (C-N), 138.1 (C-N), 153.7 (C-O), 157.8 (C-O); IR ν cm$^{-1}$ 3419, 2935, 2838, 1624, 1600, 1511, 1453, 1373, 1345, 1277, 1216, 1199, 1148, 1127, 1043, 803, 761, 738, 692; HRMS (ES+) m/z 254.1171 (M+H; C$_{16}$H$_{16}$NO$_2$ requires 254.1181).

$^1$H NMR data was identical to that reported in the literature.$^{11}$

**Kinetic experiments.** To a solution of IBX (570 mg, 0.914 mmol, 45 % stabilized with benzoic and isophthalic acids), iodinating agent (0.502 mmol) and nitrobenzene (46 µL, 0.457 mmol) in dry dimethyl sulfoxide (1.8 mL) stirred at room temperature was added the corresponding alkene (0.457 mmol) in one charge. The reaction mixture was stirred at room temperature and monitored by LCMS (aliquots (50 µL) were taken at specified time, diluted with Et$_2$O (3 mL) and quenched by aqueous Na$_2$S$_2$O$_3$-NaHCO$_3$; nitrobenzene was used as an internal standard for conversion of 1 determination) The results are summarized in Table 1 and 2.

**Table 1. Ketoiodination of β-methylstyrene 1a**

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<th>conversion of 1a, %, A = NIS</th>
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<td>5</td>
<td>80</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>&gt;97</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td></td>
<td>95</td>
</tr>
</tbody>
</table>
X-Ray Crystallographic Data for Compound 3b

The crystal structures of 3b and 3f were determined from single crystal X-ray diffraction data collected at 150 K with an Oxford Cryosystems Cryostream N\textsubscript{2} open-flow cooling device. Data were collected using an Enraf-Nonius KappaCCD diffractometer (Mo-K\textsubscript{α} radiation (\(\lambda = 0.71073\) Å) and processed using the DENZO-SMN package, including inter-frame scaling (which was carried out using SCALEPACK within DENZO-SMN). The structures were solved using SIR92. Refinement was carried out using full-matrix least-squares within the CRYSTALS suite on \(F^2\) as detailed in the supplementary information (CIF). Full crystallographic data have also been deposited with the Cambridge Crystallographic Data Centre, CCDC XXXXX (3b) and CCDC XXXXX (3f). Copies of these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.