Supporting Information

Rhodium(III)-catalyzed C–H annulation of 2-acetyl-1-arylhydrazines with sulfoxonium ylides: Synthesis of 2-arylindole

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1. General information

All reactions were carried out under air atmosphere unless otherwise noted. Solvents were purified by standard techniques without special instructions. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance II-400 spectrometer (400 MHz for ¹H, 100 MHz for ¹³C); DMSO- d_6 was used as the solvents. The chemical shifts are reported in ppm down field (δ), the coupling constants J are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on a GC-TOF mass spectrometry. TLC was carried out on SiO₂ (silica gel 60F₂₅₄, Merck), and the spots were located with UV light. Flash chromatography was carried out on SiO₂ (silica gel 60, 200-300 meth).

The starting materials $1a-1q^{[1]}$, $2a-2p^{[2]}$ were synthesized according the previous literatures.

2. General procedure for the Rh(III)-catalyzed C-H annulation reaction



A reaction flask was charged with a mixture of *N*-arylacetohydrazide (1) (0.2 mmol), sulfoxonium ylides (2) (0.24 mmol, 1.2 equiv.), $[Cp*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%), AgNTf₂ (7.8 mg, 0.02 mmol, 10 mol%), NaOAc (8.2 mg, 0.1 mmol, 50 mol%), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv.), and DCE (1.0 mL). The reaction mixture was stirred at 100 °C under N₂ atmosphere for 12 h. After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure, and the residue was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1) to give product **3**.

3. Characterization data of products

N-(2-phenyl-1H-indol-1-yl)acetamide (3aa)

Yellow solid (46.6 mg, 93% yield), mp 255–256 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.15 (s, 1H), 7.64-7.59 (m, 3H), 7.50-7.46 (m, 2H), 7.42–7.38 (m, 1H), 7.30–7.28 (m, 1H), 7.23–7.21 (m, 1H), 7.14–7.10 (m, 1H), 6.72 (s, 1H), 2.04 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.66, 140.42, 138.00, 131.37, 129.10, 128.48, 128.22, 125.96, 122.82, 121.09, 120.84, 109.90, 100.72, 20.96; IR (neat): 3254, 2932, 1676, 1522, 1441, 1334, 1298, 1136, 934, 799, 761, 743 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 250.1106 [M]+; found: 250.1113.

N-(6-methyl-2-phenyl-*1H*-indol-1-yl)acetamide (3ba)



Yellow solid (42.8 mg, 81% yield), mp 243–245 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.05 (s, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.48-7.45 (m, 3H), 7.39-7.36 (m, 1H), 7.06 (s, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.65 (s, 1H), 2.42 (s, 3H), 2.03 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.61, 139.81, 138.44, 132.20, 131.55, 129.05, 128.26, 128.07, 123.87, 122.76, 120.57, 109.68, 100.58, 21.92, 20.97; IR (neat): 3260, 2923, 1677, 1523, 1457, 1367, 1264, 1132, 1077, 812, 750, 691 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 264.1263 [M]+; found: 264.1268.

N-(5-methyl-2-phenyl-1*H*-indol-1-yl)acetamide (3ca)

Yellow solid (47.1 mg, 89% yield), mp 242–244 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.07 (s, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.48-7.45 (m, 2H), 7.40–7.37 (m, 2H), 7.16 (d, J = 8.0 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.62 (s, 1H), 2.40 (s, 3H), 2.02 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.59, 140.45, 136.52, 131.50, 129.71, 129.05, 128.34, 128.11, 126.21, 124.30, 120.43, 109.64, 100.28, 21.57, 20.94; IR (neat): 3253, 2920, 1677, 1518, 1444, 1368, 1264, 1196, 1133, 1076, 793, 761 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 264.1263 [M]+; found: 264.1264.

N-(5,6-dimethyl-2-phenyl-*1H*-indol-1-yl)acetamide (3da)



Yellow solid (44.0 mg, 79% yield), mp 252–254 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.01 (s, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.47-7.43 (m, 2H), 7.38-7.33 (m, 2H), 7.03 (s, 1H), 6.57 (s, 1H), 2.32 (s, 3H), 2.30 (s, 3H), 2.02 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.56, 139.54, 137.12, 131.54, 129.19, 129.01, 128.12, 127.98, 124.28, 120.89, 110.16, 100.15, 20.98, 20.60, 20.17; IR (neat): 3259, 2923, 1677, 1522, 1467, 1370, 1273, 1197, 1133, 1076, 750, 691 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 278.1419 [M]+; found: 278.1420.

N-(5-methoxy-2-phenyl-*1H*-indol-1-yl)acetamide (3ea)



Yellow solid (48.8 mg, 87% yield), mp 213–215 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.05 (s, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.49-7.46 (m, 2H), 7.40 (d, J = 4.0 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.10 (s, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.64 (s, 1H), 3.79 (s, 3H), 2.02 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.63, 155.03, 140.93, 133.24, 131.50, 129.06, 128.37, 128.10, 126.46, 112.73, 110.68, 102.73, 100.50, 55.93, 20.95; IR (neat): 3256, 2925, 1678, 1472, 1370, 1264, 1217, 1143, 1076, 1031, 761, 692 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 280.1212 [M]+; found: 280.1218.

N-(5-(tert-butyl)-2-phenyl-1H-indol-1-yl)acetamide (3fa)

Yellow solid (49.6 mg, 81% yield), mp 194–196 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 11.11 (s, 1H), 7.62-7.57 (m, 3H), 7.47-7.45 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 12.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.67 (s, 1H), 2.03 (s, 3H), 1.36 (s, 9H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 169.63, 143.55, 140.48, 136.37, 131.56, 129.06, 128.32, 128.12, 125.81, 120.93, 116.62, 109.43, 100.87, 34.77, 32.24, 20.93; IR (neat): 3257, 2926, 1678, 1525, 1469, 1368, 1265, 1196, 1076, 798, 755, 696 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 306.1732 [M]+; found: 306.1740.

N-(5-butyl-2-phenyl-*1H*-indol-1-yl)acetamide (3ga)

Yellow solid (52.7 mg, 86% yield), mp 202–203 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.06 (s, 1H), 7.60 (d, J = 4.0 Hz, 2H), 7.49-7.45 (m, 2H), 7.40-7.37 (m, 2H), 7.17 (d, J = 8.0 Hz, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.63 (s, 1H), 2.67 (t, J = 8.0 Hz, 2H), 2.02 (s, 3H), 1.63–1.59 (m, 2H), 1.36–1.31 (m, 2H), 0.92 (t, J = 8.0 Hz, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.60, 140.46, 136.67, 134.95, 131.52, 129.05, 128.34, 128.12, 126.13, 123.74, 119.88, 109.65, 100.43, 35.43, 34.42, 22.19, 20.94, 14.31; IR (neat): 3260, 2925, 1677, 1524, 1469, 1368, 1266, 1196, 1132, 1076, 755, 690 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 306.1732 [M]+; found: 306.1739.

N-(2,5-diphenyl-1*H*-indol-1-yl)acetamide (3ha)



Yellow solid (54.2 mg, 83% yield), mp 196–198 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 11.22 (s, 1H), 7.87 (s, 1H), 7.71-7.65 (m, 4H), 7.53-7.33 (m, 9H), 6.78 (s, 1H), 2.06 (s, 3H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 169.70, 141.87, 141.20, 137.69, 133.77, 131.27, 129.33, 129.13, 128.59, 128.23, 127.27, 127.02, 126.58, 122.26, 118.95, 110.39, 101.14, 100.00, 20.96; IR (neat): 3260, 2924, 1682, 1599, 1466, 1371, 1261, 1196, 1132, 1076, 759, 697 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 326.1419 [M]+; found: 326.1424.

N-(5-fluoro-2-phenyl-1H-indol-1-yl)acetamide (3ia)

Yellow solid (45.6 mg, 85% yield), mp 244–246 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 11.15 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.50-7.47 (m, 2H), 7.43-7.36 (m, 2H), 7.31-7.28 (m, 1H), 7.06-7.02 (m, 1H), 6.71 (s, 1H), 1.99 (s, 3H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 169.66, 158.30 (d, ¹*J*_{*C*-*F*} = 239.0 Hz), 142.18, 134.64, 131.06, 129.13, 128.74, 128.26, 126.27 (d, ³*J*_{*C*-*F*} = 11.0 Hz), 111.10, 110.98 (d, ⁴*J*_{*C*-*F*} = 4.0 Hz), 110.70, 105.64 (d, ²*J*_{*C*-*F*} = 24.0 Hz), 100.67, 20.93; IR (neat): 3252, 2925, 1676, 1519, 1471, 1370, 1263, 1207, 1127, 858, 751, 693 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 268.1012 [M]+; found: 268.1017.

N-(6-chloro-2-phenyl-1H-indol-1-yl)acetamide (3ja)

Yellow solid (44.4 mg, 78% yield), mp 305–307 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.18 (s, 1H), 7.60 (s, 3H), 7.49-7.47 (m, 2H), 7.43-7.39 (m, 2H), 7.13 (d, J = 8.0 Hz, 1H), 6.75 (s, 1H),

2.04 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.73, 141.47, 138.47, 130.91, 129.14, 128.75, 128.26, 127.64, 124.73, 122.29, 121.46, 109.77, 100.79, 20.99; IR (neat): 3246, 2921, 1677, 1518, 1452, 1369, 1258, 1196, 1075, 812, 757, 689 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 284.0716 [M]+; found: 284.0718.

N-(5-chloro-2-phenyl-1*H*-indol-1-yl)acetamide (3ka)

Yellow solid (49.0 mg, 86% yield), mp 254–256 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 11.20 (s, 1H), 7.65-7.60 (m, 3H), 7.51-7.47 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.20 (dd, *J* = 4.0, 8.0 Hz, 1H), 6.71 (s, 1H), 2.02 (s, 3H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 169.65, 141.96, 136.50, 130.86, 129.16, 128.85, 128.30, 127.06, 125.55, 122.74, 120.02, 111.54, 100.31, 20.93; IR (neat): 3238, 2923, 1678, 1525, 1444, 1369, 1270, 1195, 1007, 871, 754, 733 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 284.0716 [M]+; found: 284.0724.

N-(6-bromo-2-phenyl-1H-indol-1-yl)acetamide (3la)

Yellow solid (52.0 mg, 79% yield), mp 297–298 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.17 (s, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.56-7.52 (m, 2H), 7.50-7.46 (m, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 6.74 (s, 1H), 2.04 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.75, 141.31, 138.81, 130.86, 129.14, 128.77, 128.26, 125.00, 124.06, 122.64, 115.60, 112.63, 100.82, 20.99; IR (neat): 3249, 2923, 1675, 1520, 1488, 1371, 1196, 1132, 1076, 812, 757, 691 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 328.0211 [M]+; found: 328.0218.

N-(5-bromo-2-phenyl-*1H*-indol-1-yl)acetamide (3ma)

Yellow solid (56.6 mg, 86% yield), mp 270–272 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.21 (s, 1H), 7.79 (s, 1H), 7.62-7.60 (m, 2H), 7.50-7.47 (m, 2H), 7.44-7.40 (m, 1H), 7.31-7.46 (m, 2H), 6.71 (s, 1H), 2.02 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.63, 141.79, 136.75, 130.81, 129.16, 128.86, 128.31, 127.74, 125.29, 123.03, 113.44, 111.98, 100.20, 20.93; IR (neat): 3249, 2923, 1679, 1522, 1460, 1369, 1268, 1194, 1076, 869, 755, 693 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 328.0211 [M]+; found: 328.0217.

N-(5-iodo-2-phenyl-1H-indol-1-yl)acetamide (3na)



Yellow solid (65.5 mg, 87% yield), mp 220–222 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.20 (s, 1H), 7.97 (s, 1H), 7.60 (d, J = 4.0 Hz, 2H), 7.50-7.46 (m, 3H), 7.43-7.39 (m, 1H), 7.16 (d, J = 4.0 Hz, 1H), 6.69 (s, 1H), 2.02 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.62, 141.32, 137.18, 130.77, 129.16, 128.83, 128.57, 128.30, 112.40, 99.90, 84.76, 20.93; IR (neat): 3256, 2926, 1680, 1521, 1459, 1369, 1262, 1194, 1042, 789, 756, 693 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 376.0073 [M]+; found: 376.0084.

N-(2-phenyl-5-(trifluoromethyl)-*1H*-indol-1-yl)acetamide (3oa)

Yellow solid (47.1 mg, 74% yield), mp 252–254 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 11.33 (s, 1H), 8.01 (s, 1H), 7.64-7.60 (m, 2H), 7.52-7.42 (m, 5H), 6.89 (s, 1H), 2.05 (s, 3H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 169.65, 142.51, 139.41, 130.63, 129.20, 129.04, 128.42, 125.40, 122.04 (q, *J* = 30.0 Hz), 119.21 (d, *J* = 3.0 Hz), 118.52 (d, *J* = 4.0 Hz), 110.76, 101.48, 20.92; IR (neat): 3244, 2923, 1684, 1526, 1447, 1372, 1268, 1164, 1104, 892, 746, 696 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 318.0980 [M]+; found: 318.0991.

1-acetamido-2-phenyl-1H-indol-5-yl acetate (3pa)



Yellow solid (46.9 mg, 76% yield), mp 166–168 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 11.31 (s, 1H), 8.31 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.52-7.48 (m, 2H), 7.45-7.39 (m, 2H), 6.89 (s, 1H), 3.87 (s, 3H), 2.05 (s, 3H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 169.68, 167.42, 142.07, 140.42, 130.75, 129.18, 128.93, 128.34, 125.57, 123.76, 123.32, 122.71, 109.99, 101.87, 52.31, 20.91; IR (neat): 3263, 2952, 1713, 1613, 1523, 1435, 1372, 1254, 1195, 1091, 755, 693 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 308.1161 [M]+; found: 308.1166.

N-(5-cyano-2-phenyl-1H-indol-1-yl)acetamide (3qa)



Yellow solid (33.0 mg, 60% yield), mp 209–211 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 11.37 (s, 1H), 8.14 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.52-7.44 (m, 4H), 6.87 (s, 1H), 2.04 (s, 3H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 169.72, 142.81, 139.58, 130.34, 129.23, 128.45, 126.34, 125.75, 125.73, 120.74, 111.26, 103.36, 101.26, 20.90; IR (neat): 3243, 2920, 2223, 1678, 1607, 1469, 1448, 1333, 1264, 1196, 1132, 1076 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 275.1059 [M]+; found: 275.1061.

N-(2-(o-tolyl)-1H-indol-1-yl)acetamide (3ab)



Yellow solid (40.2 mg, 76% yield), mp 255–256 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 10.09 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.33 (s, 2H), 7.26 (d, *J* = 8.0 Hz, 3H), 7.21–7.17 (m, 1H), 7.13–7.10 (m, 1H), 6.52 (s, 1H), 2.30 (s, 3H), 1.89 (s, 3H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 169.50, 139.51, 137.75, 136.75, 130.90, 130.67, 130.62, 128.87, 125.91, 125.69, 122.40, 120.76, 120.66, 109.71, 101.59, 20.77, 20.60; IR (neat): 3246, 2918, 1680, 1596, 1457, 1384, 1264, 1169, 1132, 1076, 1042, 747 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 264.1263 [M]+; found: 264.1264. *N*-(2-(*m*-tolyl)-*1H*-indol-1-yl)acetamide (3ac)



Yellow solid (44.9 mg, 85% yield), mp 255–256 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.11 (s, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.45–7.41 (m, 2H), 7.38–7.34 (m, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.22–7.18 (m, 2H), 7.13–7.10 (m, 1H), 6.69 (s, 1H), 2.38 (s, 3H), 2.03 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.60, 140.58, 138.23, 138.01, 131.31, 129.11, 128.93, 125.98, 125.28, 122.73, 121.03, 120.78, 109.87, 100.57, 21.55, 20.93; IR (neat): 3251, 2922, 1682, 1608, 1524, 1455, 1370, 1266, 1076, 780, 747, 699 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 264.1263 [M]+; found: 264.1266.

N-(2-(p-tolyl)-1H-indol-1-yl)acetamide (3ad)



Yellow solid (47.6 mg, 90% yield), mp 255–256 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.09 (s, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.30–7.25 (m, 3H), 7.20–7.17 (m, 1H), 7.13–7.09 (m, 1H), 6.66 (s, 1H), 2.36 (s, 3H), 2.03 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.66, 140.42, 138.00, 131.37, 129.10, 128.48, 128.22, 125.96, 122.82, 121.09, 120.84, 109.90, 100.72, 20.96; IR (neat): 3263, 2922, 1681, 1525, 1456, 1369, 1265, 1197, 1019, 811, 793, 744 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 264.1263 [M]+; found: 264.1270.

N-(2-(4-methoxyphenyl)-1H-indol-1-yl)acetamide (3ae)

Yellow solid (48.8 mg, 87% yield), mp 255–256 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.08 (s, 1H), 7.57–7.53 (m, 3H), 7.25 (d, J = 8.0 Hz, 1H), 7.19–7.15 (m, 1H), 7.12–7.03 (m, 3H), 6.61 (s, 1H), 2.36 (s, 3H), 3.81 (s, 3H), 2.03 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.65, 159.66, 140.43, 137.78, 129.59, 126.08, 123.78, 122.41, 120.96, 120.55, 114.60, 109.74, 99.69, 55.68, 20.95; IR (neat): 3257, 2919, 1678, 1609, 1501, 1458, 1368, 1249, 1180, 1028, 786, 745 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 280.1212 [M]+; found: 280.1208.

N-(2-([1,1'-biphenyl]-4-yl)-1H-indol-1-yl)acetamide (3af)

Yellow solid (55.5 mg, 85% yield), mp 255–256 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 11.18 (s, 1H), 7.82–7.71 (m, 6H), 7.61 (d, *J* = 4.0 Hz, 1H), 7.52–7.48 (m, 2H), 7.41–7.38 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.23–7.19 (m, 1H), 7.15–7.11 (m, 1H), 6.78 (s, 1H), 2.07 (s, 3H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 169.69, 140.01, 139.94, 138.16, 130.44, 129.48, 128.65, 128.14, 127.33, 127.10, 126.03, 122.89, 121.13, 120.85, 109.91, 100.86, 21.01; IR (neat): 3281, 2922, 1772, 1600, 1487, 1408, 1259, 1132, 1077, 844, 764, 744 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 326.1419 [M]+; found: 326.1427.

N-(2-(4-fluorophenyl)-1H-indol-1-yl)acetamide (3ag)



Yellow solid (34.3 mg, 64% yield), mp 255–256 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 11.12 (s, 1H), 7.66–7.62 (m, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.35–7.27 (m, 3H), 7.20–7.18 (m, 1H), 7.14–7.10 (m, 1H), 6.70 (s, 1H), 2.03 (s, 3H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 169.72, 162.43 (d, ¹*J*_{*C*-*F*} = 244.0 Hz), 139.45, 137.89, 130.34 (d, ³*J*_{*C*-*F*} = 8.0 Hz), 127.88 (d, ⁴*J*_{*C*-*F*} = 4.0 Hz), 125.90, 122.86, 121.98 (d, ²*J*_{*C*-*F*} = 30.0 Hz), 116.10 (d, ²*J*_{*C*-*F*} = 21.0 Hz), 109.89, 100.73, 20.93; IR (neat): 3247, 2918, 1677, 1527, 1498, 1456, 1370, 1223, 1133, 841, 783, 745 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 268.1012 [M]+; found: 268.1020.

N-(2-(4-chlorophenyl)-*1H*-indol-1-yl)acetamide (3ah)

Yellow solid (37.6 mg, 66% yield), mp 255–256 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 11.14 (s, 1H), 7.64–7.58 (m, 3H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.23–7.19 (m, 1H), 7.14–7.10 (m, 1H), 6.75 (s, 1H), 2.04 (s, 3H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 169.73, 139.14, 138.09, 133.24, 130.22, 129.83, 129.18, 125.87, 123.10, 121.21, 120.96, 109.95, 101.19, 20.94; IR (neat): 3255, 2918, 1678, 1596, 1409, 1384, 1196, 1132, 1076, 1042, 783, 745 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 284.0716 [M]+; found: 284.0725.

N-(2-(4-(trifluoromethyl)phenyl)-*1H*-indol-1-yl)acetamide (3ai)



Yellow solid (34.4 mg, 54% yield), mp 255–256 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.22 (s, 1H), 7.89–7.84 (m, 4H), 7.63 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.27–7.23 (m, 1H), 7.17–7.14 (m, 1H), 6.88 (s, 1H), 2.05 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.77, 138.71, 138.38, 135.35, 128.65, 126.04, 126.01, 125.80, 123.54, 123.37, 121.37, 121.22, 110.09, 102.32, 20.94; IR (neat): 3207, 2922, 1678, 1530, 1457, 1416, 1328, 1274, 1158, 1072, 784, 744 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 318.0980 [M]+; found: 318.0988.

methyl 4-(1-acetamido-1H-indol-2-yl)benzoate (3aj)

Yellow solid (41.3 mg, 67% yield), mp 255–256 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.21 (s, 1H), 8.04 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.25–7.22 (m, 1H), 7.16–7.12 (m, 1H), 6.88 (s, 1H), 3.88 (s, 3H), 2.04 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.70, 166.42, 139.07, 138.48, 135.88, 129.93, 129.09, 128.13, 125.84, 123.52, 121.35, 121.20, 110.07, 102.30, 52.68, 20.92; IR (neat): 3272, 2920, 1718, 1678, 1609, 1435, 1385, 1276, 1196, 1076, 770, 747 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 308.1161 [M]+; found: 308.1172.

N-(2-(naphthalen-1-yl)-1H-indol-1-yl)acetamide (3ak)



Yellow solid (42.7 mg, 71% yield), mp 255–256 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 10.98 (s, 1H), 8.05–7.99 (m, 3H), 7.66 (d, J = 8.0 Hz, 1H), 7.62–7.51 (m, 4H), 7.31 (d, J = 8.0 Hz, 1H), 7.27–7.23 (m, 1H), 7.19–7.15 (m, 1H), 6.69 (s, 1H), 1.84 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.63, 138.23, 137.10, 133.75, 132.33, 129.23, 128.67, 128.62, 127.05, 126.56, 126.12, 125.92, 125.56, 122.75, 121.00, 120.86, 109.91, 102.99, 20.74; IR (neat): 3264, 2924, 1685, 1506, 1456, 1371, 1308, 1268, 1044, 793, 777, 747 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 300.1263 [M]+; found: 300.1273.

N-(2-(furan-2-yl)-1H-indol-1-yl)acetamide (3al)



Yellow solid (45.6 mg, 95% yield), mp 255–256 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.23 (s, 1H), 7.81 (s, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.26 (d, J = 8.0 Hz, 1H), 7.21–7.17 (m, 1H), 7.13–7.09 (m, 1H), 6.79 (s, 1H), 6.75 (s, 1H), 6.64–6.63 (m, 1H), 2.16 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.69, 145.72, 143.54, 137.67, 130.96, 125.72, 123.14, 121.21, 120.99, 112.36, 109.60, 107.75, 98.66, 21.08; IR (neat): 3229, 2921, 1680, 1517, 1438, 1373, 1268, 1196, 1076, 1009, 797, 740 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 240.0899 [M]+; found: 240.0909.

N-(2-(thiophen-2-yl)-1H-indol-1-yl)acetamide (3am)



Yellow solid (47.7 mg, 93% yield), mp 255–256 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.24 (s, 1H), 7.59 (d, J = 4.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 4.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.18–7.13 (m, 2H), 7.10–7.07 (m, 1H), 6.83 (s, 1H), 2.13 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.91, 137.56, 134.09, 132.26, 128.18, 127.03, 126.21, 125.82, 122.93, 121.23, 120.70, 109.64, 99.48, 21.19; IR (neat): 3231, 2922, 1685, 1524, 1456, 1370, 1262, 1180, 1133, 1077, 789, 745 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 256.0670 [M]+; found: 256.0674. (*E*)-*N*-(2-styryl-1*H*-indol-1-yl)acetamide (3an)

Ph

NHAc

Yellow solid (44.8 mg, 81% yield), mp 255–256 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 11.10 (s, 1H), 7.62–7.54 (m, 3H), 7.40–7.32 (m, 5H), 7.23–7.21 (m, 1H), 7.17–7.14 (m, 1H), 7.09–7.05 (m, 2H), 6.89 (s, 1H), 2.20 (s, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.90, 137.94, 137.32, 137.16, 130.55, 129.30, 128.44, 126.94, 126.06, 122.74, 121.02, 120.69, 116.35, 109.44, 98.24, 79.29, 21.09; IR (neat): 3250, 2923, 1682, 1597, 1455, 1371, 1255, 1133, 1076, 1043, 956, 747 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 276.1263 [M]+; found: 276.1270.

N-(2-methyl-1H-indol-1-yl)acetamide (3ao)

Me NHAc

Yellow solid (30.9 mg, 82% yield), mp 255–256 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 10.90 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.10–7.06 (m, 1H), 7.04–7.00 (m, 1H), 6.24 (s, 1H), 2.33 (s, 3H), 2.13 (s, 3H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 169.71, 137.32, 136.43, 126.03, 121.29, 120.21, 119.86, 108.89, 98.41, 20.93, 11.61; IR (neat): 3243, 2922, 1683, 1561, 1459, 1372, 1326, 1264, 1076, 1014, 775, 745 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 188.0590 [M]+; found: 188.0591.

N-(2-butyl-*1H*-indol-1-yl)acetamide (3ap)

NHAc

Yellow solid (35.0 mg, 76% yield), mp 255–256 °C. ¹H NMR (DMSO- d_6 , 400 MHz) δ 10.89 (s, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 7.09–7.06 (m, 1H), 7.03–7.00 (m, 1H), 6.22 (s, 1H), 2.56 (t, J = 8.0 Hz, 2H), 2.12 (s, 3H), 1.65–1.61 (m, 2H), 1.42–1.36 (m, 2H), 0.93 (t, J = 8.0 Hz, 3H); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 169.60, 141.60, 136.45, 125.99, 121.33, 120.18, 119.96, 108.94, 97.58, 30.19, 25.16, 22.32, 20.93, 14.17; IR (neat): 3258, 2926, 1682, 1558, 1459, 1372, 1263, 1196, 1132, 1077, 1042, 744 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 230.1419 [M]+; found: 230.1424.

N-(2-cyclohexyl-1H-indol-1-yl)acetamide (3aq)



Yellow solid (34.4 mg, 67% yield), mp 255–256 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 10.87 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.09–7.05 (m, 1H), 7.03–6.99 (m, 1H), 6.19 (s, 1H), 2.12 (s, 3H), 2.00 (d, *J* = 8.0 Hz, 1H), 1.88 (d, *J* = 16.0 Hz, 1H), 1.88 (d, *J* = 12.0 Hz, 2H), 1.71 (d, *J* = 8.0 Hz, 1H), 1.43–1.23 (m, 6H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 169.64, 146.72, 136.31, 125.97, 121.38, 120.19, 120.13, 109.02, 95.69, 34.85, 33.51, 32.32, 26.49, 26.44, 26.15, 20.97; IR (neat): 3252, 2923, 1677, 1529, 1445, 1372, 1261, 1132, 1020, 778, 744, 733 (cm⁻¹); HRMS (EI) calcd for C₁₈H₁₃N₃O₃: 256.1576 [M]+; found: 256.1579.

4. Control experiments

(1) Experiment of deuterium kinetic isotope effect



A reaction flask was charged with a mixture of $[Cp*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), AgNTf₂ (7.8 mg, 0.02 mmol, 10.0 mol %), **1a** (0.10 mmol) and **1a**- d_5 (0.10 mmol), **2a** (0.24 mmol, 47.1 mg), NaOAc (8.2 mg, 0.1 mmol, 50 mol%), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv.), and DCE (1.0 mL). The reaction was stirred at 100 °C under N₂ for 2 h, then immediately quenched with EtOAc. The volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether /ethyl acetate = 3:1) to afford **3aa** and **3aa**- d_4 (16.3 mg, 33%). A 3.3 of KIE was observed by ¹H NMR determination.



(2) Intermolecular competition experiment between substrates 1c and 1p



A reaction flask was charged with a mixture of [Cp*RhCl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), AgNTf₂ (7.8 mg, 0.02 mmol, 10.0 mol %), NaOAc (8.2 mg, 0.1 mmol, 50 mol%), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv.), 1c (0.10 mmol), 1p (0.10 mmol), 2a (0.24 mmol, 47.1 mg, 1.2 equiv.) and DCE (1.0 mL). The reaction was stirred at 100 °C under N₂ for 12 h. After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure, and the residue was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3:1) to give product 3ca (17.2 mg, 73%) and 3pa (9.1 mg, 30%) at a ratio of 2.4:1.

5. References:

- 1. D. Zhao, Z. Shi, F. Glorius, Angew. Chem. Int. Ed. 2013, 52, 12426.
- 2. R. D. C. Gallo, A. Ahmad, G. Metzker, A. C. B. Burtoloso, Chem. Eur. J. 2017, 23, 16980.

6. Copies of ¹H and ¹³C NMR spectra of products





























¹H NMR, 400 MHz, DMSO- d_6





¹H NMR, 400 MHz, DMSO- d_6











S-30





¹H NMR, 400 MHz, DMSO- d_6



























¹H NMR, 400 MHz, DMSO- d_6





S-42



