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Article

Rh(III)-catalyzed coupling of nitrones with alkynes for the synthesis of indolines

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ABSTRACT

Rh-catalyzed redox-neutral coupling between *N*-aryl nitrones and alkynes has been achieved under relatively mild conditions. The reaction proceeded via C–H activation at the *N*-aryl ring with subsequent O-atom transfer, affording trisubstituted indolines in good chemoselectivity and moderate to good diasteroselectivity.

1. Introduction

Metal-catalyzed C–H activation of arenes has received increasing attention in the past several decades and this strategy has allowed the development of a plethora of new synthetic methods to access complex structures [1–8]. This strategy is appealing in that no prior functionalization of arenes is necessary. In most cases, the C–H activation of less intrinsically active arenes requires the installation of a directing group typically at the *ortho* position [9–14]. The C–H bond is cleaved with concurrent formation of a metalacycle, which provides a driving force to enhance both reactivity and selectivity. Despite the progress, the presence of a pendent directing group in the coupled product is often undesirable. To address this limitation, a number of coupling systems with functionalizable or transferable DGs in arene substrates have been developed [15]. However, challenges remain and it is necessary to develop more efficient and selective C–H activation systems by taking advantage of multi-task DGs.

In this context, stable Cp*Rh(III) complexes have stood out as efficient catalysts for the selective C–H functionalization of a large scope of arenes [16–19], and this area has experienced tremendous progress. In particular, Fagnou and Glorius pioneered in C–H activation of arenes assisted by an oxidizing N–O bond as a DG under redox-neutral conditions [20–24]. These systems overcame limited roles of DGs in general because they participated in subsequent reactions as internal oxidants, especially leading to efficient synthesis of heterocycles under mild conditions when alkenes and alkynes were used as the coupling partner [25–36]. In addition, these reactions are redox-economic since no external oxidant is necessary. Inspired by this strategy, the oxidizing DGs have been extended to other oxidizing bonds such as N–N [37–44], N–S [45], and C–N [46]. On the other hand, the cleavage of these oxidizing groups almost always generates a small molecule such as water, alcohol, acid, or amine as a co-product [25–46], which limited the at-

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om-economy of the coupling system.

We recently reported the Rh(III)-catalyzed redox-neutral coupling between quinolone *N*-oxides and alkynes, leading to the synthesis of diaryl-substituted acetophenones [47,48]. In this reaction, the N–O bond acted as an oxidizing DG to realize C–H activation at the 8-position. Significantly, the oxygen was retained via an intramolecular OAT process with 100% atom-economy. So far this C–H activation-OAT system has been achieved for only one arene system. It is necessary to extend this strategy to other related arenes for the preparation of synthetically useful complex products. Arenes such as benzaldehyde-derived nitrones are structurally related to quinolone *N*-oxides, and our previous studies revealed that N-*tert*-butyl-α-arylnitrones coupled with alkynes under Rh catalysis to afford indenones [49]. However, no OAT to alkyne was involved although the polar N–O bond proved to be a viable DG to effect *endo* C–H activation. On the other hand, Wan and coworkers reported in one example the *exo*-type C–H activation of nitrone in the coupling with diphenylacetylene, affording an indole [50–53]. We reasoned that *N*-aryl nitrone may still undergo C–H activation-OTA coupling with alkynes under appropriate Rh(III)-catalyzed conditions. We now report synthesis of indolines via this type of coupling, and the indoline motif has been widely found in natural products and pharmaceuticals [54–56].

2. Experimental

2.1. General

All chemicals were from commercial sources and were used as received unless otherwise noted. All reactions were carried out using Schlenk techniques or in an N_2-filled glovebox. Column chromatography was carried out on silica gel (300–400 mesh) using triethylamine/petroleum ether or ethyl acetate (EA)/petroleum ether (PE). NMR Spectra were recorded on a Bruker 400 MHz NMR spectrometer in the solvents indicated. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ^{1}H and ^{13}C NMR spectroscopy. The ratio of *trans* and *cis* was determined on the basis of ^{1}H NMR analysis. High resolution mass spectra were obtained on an Agilent Q-TOF 6540.

Diphenylacetylene and 4-octyne were obtained from commercial sources. Other nitrones [50] and diarylacetylenes [57] were prepared according to literature reports and the NMR data agree with those in the literature reports.

2.2. General procedure for the synthesis of compounds 3

Nitrones (0.2 mmol), diarylacetylenes (0.3 mmol), $[Cp^*RhCl_2]_2$ (4 mol%), $AgSbF_6$ (16 mol%), PivOH (2.0 equiv) and ethyl acetate (2 mL) were charged into the sealed tube. The reaction mixture was stirred at 80 °C for 15 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using triethylamine/PE or PE/EA to afford compounds **3**.

2.3. Spectral data for products

3aa. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.51 (m, 2H), 7.44 – 7.35 (m, 1H), 7.30 – 7.20 (m, 2H), 7.17 (td, J = 7.7, 1.2 Hz, 1H), 7.12 – 6.95 (m, 9H), 6.82 (d, J = 7.6 Hz, 1H), 6.73 – 6.60 (m, 3H), 6.17 (s, 1H), 4.28 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 152.2, 140.0, 138.4, 137.2, 132.2, 131.0, 129.4, 128.6, 128.4, 128.1, 128.0, 127.99, 127.7, 127.3, 127.1, 126.3, 119.0, 109.8, 72.3, 70.3. HRMS: m/z: $[M+H]^+$ calculated for $C_{27}H_{21}NO$: 376.1696, Found: 376.1696.

3aa'. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 2H), 7.57 – 7.50 (m, 1H), 7.32 (t, J = 7.6 Hz, 2H), 7.27 – 7.21 (m, 4H), 7.07 (m, 3H), 7.00 (m, 1H), 6.88 (t, J = 7.7 Hz, 2H), 6.85 – 6.78 (m, 3H), 6.67 (d, J = 7.7 Hz, 1H), 5.50 (s, 1H), 4.26 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 148.7, 145.1, 141.2, 138.1, 131.9, 131.8, 129.7, 129.6, 128.4, 128.3, 128.2, 128.0, 127.9, 127.5, 127.45, 124.8, 119.74, 109.8, 71.4, 70.3. HRMS: m/z: $[M+H]^+$ calculated for $C_{27}H_{21}NO$: 376.1696, Found: 376.1697.

3ba. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.4 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H), 7.13 (t, J = 7.9 Hz, 2H), 7.00 – 6.86 (m, 9H), 6.73 (s, 1H), 6.63 (d, J = 7.9 Hz, 1H), 6.57 (d, J = 7.3 Hz, 2H), 6.05 (s, 1H), 4.03 (s, 1H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 149.8, 140.0, 138.3, 137.1, 132.0, 130.8, 129.7, 128.5, 128.3, 128.27, 128.1, 127.9, 127.8 127.5, 127.1, 126.9, 126.6, 109.7, 72.3, 70.5, 21.1. HRMS: m/z: $[M+H]^+$ calculated for $C_{28}H_{23}NO$: 390.1852, Found: 390.1855.

3ca. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.9 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.23 (m, 2H), 7.11 – 6.97 (m, 8H), 6.87 (td, J = 8.7, 2.5 Hz, 1H), 6.72 (m, 2H), 6.62 (d, J = 7.7 Hz, 2H), 6.16 (s, 1H), 4.14 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 156.6 (d, $J_{C\text{-}F}$ = 233.9 Hz), 148.2, 148.2, 139.4, 137.7, 136.7, 132.4, 130.7, 128.3, 128.25, 128.1 (d, $J_{C\text{-}F}$ = 1.4 Hz), 127.7 (d, $J_{C\text{-}F}$ = 7.8 Hz), 127.5, 127.3, 127.2, 115.7 (d, $J_{C\text{-}F}$ = 23.3 Hz), 115.0 (d, $J_{C\text{-}F}$ = 25 Hz), 110.0 (d, $J_{C\text{-}F}$ = 8.1 Hz), 72.1, 70.8. HRMS: m/z: $[M+H]^+$ calculated for $C_{27}H_{20}FNO$: 394.1602, Found: 394.1604.

3da. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.42 – 7.37 (m, 1H), 7.23 (m, 2H), 7.08 (m, 2H), 7.03 – 6.93 (m, 8H), 6.71 (d, J = 8.4 Hz, 1H), 6.67 – 6.61 (m, 2H), 6.16 (s, 1H), 4.26 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 150.7, 139.3, 137.6, 136.5, 132.4, 130.7, 129.2, 128.3, 128.2, 128.1, 128.02, 128.0, 127.9, 127.6, 127.3, 127.2, 123.2, 110.4, 72.2, 70.5. HRMS: m/z: $[M+H]^+$ calculated for $C_{27}H_{20}ClNO$: 410.1306, Found: 410.1302.

3ea. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.4 Hz, 2H), 7.32 (t, J = 7.4 Hz, 1H), 7.18 – 7.12 (m, 3H), 6.99 (t, J = 4.9 Hz, 2H), 6.96 – 6.86 (m, 7H), 6.58 (t, J = 8.3 Hz, 3H), 6.08 (s, 1H), 4.20 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 151.1, 139.2, 137.6, 136.5, 132.4, 132.0, 130.7, 130.65, 128.4, 128.3, 128.13, 128.1, 128.0, 127.6, 127.3, 127.2, 110.9, 110.1, 72.2, 70.4. HRMS: m/z: $[M+H]^+$ calculated for $C_{27}H_{20}BrNO$: 454.0801, Found: 454.0801.

3fa. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 8.3, 1.4 Hz, 1H), 7.64 (s, 1H), 7.47 (d, J = 7.5 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 7.15 (m, 2H), 7.01 – 6.83 (m, 8H), 6.63 (t, J = 8.0 Hz, 3H), 6.14 (s, 1H), 4.67 (s, 1H), 4.09 (m, 2H), 1.14 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 166.4, 155.9, 139.1, 137.7, 136.4, 132.3, 132.1, 130.7, 130.2, 128.3, 128.2, 128.0, 127.9, 127.6, 127.4, 127.2, 125.4, 120.5, 108.1, 71.8, 70.2, 60.2, 14.3. HRMS:

m/z: $[M+H]^+$ calculated for $C_{30}H_{25}NO_3$: 448.1907, Found: 448.1906.

3ga. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.4 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.22 (m 2H), 7.08 – 6.94 (m, 8H), 6.87 (d, J = 7.8 Hz, 1H), 6.72 – 6.61 (m, 3H), 6.46 (d, J = 7.8 Hz, 1H), 6.13 (s, 1H), 4.19 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 152.3, 140.0, 139.4, 138.4, 136.9, 132.0, 130.8, 128.4, 128.2, 127.9, 127.8, 127.6, 127.5, 127.1, 126.9, 123.1, 119.8, 110.5, 71.9, 70.2, 21.6. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{28}H_{23}NO$: 390.1852, Found: 390.1852.

3ha. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.6 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.21 (t, J = 7.8 Hz, 2H), 7.00 (m, 8H), 6.90 (d, J = 8.1 Hz, 1H), 6.86 (d, J = 1.4 Hz, 1H) 6.68 (dd, J = 8.1, 1.5 Hz, 1H), 6.60 (d, J = 7.4 Hz, 2H), 6.17 (s, 1H), 4.18 (s, 1H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 152.8, 151.9, 139.9, 138.7, 137.0, 132.1, 131.1, 128.5, 127.9, 127.8, 127.4, 127.1, 126.9, 126.88, 123.6, 116.3, 107.2, 71.7, 70.4, 34.8, 31.5. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{28}H_{23}NO$: 432.2322, Found: 432.2327.

3ia. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (m, 4H), 7.40 (q, J = 7.1 Hz, 3H), 7.32 (m, 1H), 7.23 (m, 2H), 7.10 – 6.96 (m, 10H), 6.88 (dd, J = 7.9, 1.6 Hz, 1H), 6.77 – 6.67 (m, 2H), 6.20 (s, 1H), 4.32 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 152.6, 142.5, 141.1, 139.8, 138.3, 136.9, 132.1, 130.9, 128.7, 128.4, 128.3, 128.1, 128.0, 127.9, 127.6, 127.4, 127.2, 127.1, 127.06, 125.3, 118.1, 108.3, 72.0, 70.4. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{28}H_{24}NO$: 452.2009, Found: 452.2006.

3ja. ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.2 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.21 (t, J = 7.8 Hz, 2H), 7.14 (t, J = 7.5 Hz, 1H), 7.07 (t, J = 7.2 Hz, 1H), 7.00 (t, J = 7.2 Hz, 3H), 6.87 (d, J = 7.8 Hz, 2H), 6.79 (d, J = 7.3 Hz, 3H), 6.66 (d, J = 7.5, 2H), 6.62 (d, J = 7.5, 1H), 6.11 (s, 1H), 4.19 (s, 1H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 152.1, 138.3, 137.0, 136.8, 136.6, 132.0, 130.8, 129.2, 128.5, 128.2, 128.16, 127.9, 127.8, 127.78, 127.0, 126.3, 118.8, 109.7, 72.0, 70.1, 21.1. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{28}H_{23}NO$: 390.1852, Found: 390.1853.

3ka. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.8 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 7.13 (m, 2H), 7.06 (t, J = 7.6 Hz, 1H), 7.02 – 6.96 (m, 1H), 6.92 (m, 3H), 6.83 (d, J = 8.3 Hz, 2H), 6.71 (d, J = 7.8 Hz, 1H), 6.62 – 6.49 (m, 3H), 6.45 (d, J= 8.5 Hz, 2H), 6.02 (s, 1H), 4.07 (s, 1H), 3.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 158.8, 152.0, 138.4, 137.1, 132.0, 131.7, 130.8, 129.4, 129.2, 128.5, 128.0, 127.8, 127.7, 127.0, 126.4, 118.8, 112.9, 109.7, 71.9, 69.8, 55.2. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{28}H_{23}NO_2$: 406.1802, Found: 406.1805.

3la. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.16 (t, J = 7.3 Hz, 1H), 7.09 (t, J = 7.3 Hz, 1H), 7.05 – 6.93 (m, 7H), 6.80 (d, J = 7.8 Hz, 1H), 6.65 (t, J = 7.5 Hz, 1H), 6.59 (d, J = 7.5 Hz, 2H), 6.13 (s, 1H), 4.22 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 151.7, 138.2, 138.0, 136.9, 132.9, 132.3, 130.9, 129.7, 129.3, 128.4, 128.1, 127.9, 127.6, 127.57, 127.2, 126.3, 119.1, 109.9, 71.9, 69.5. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{27}H_{20}ClNO$: 410.1306, Found: 410.1309.

3ma. ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 7.4 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.18 (m, 1H), 7.11 (t, J = 8.5 Hz, 3H), 7.02 (m, 3H), 6.92 (d, J = 8.2 Hz, 2H), 6.82 (d, J = 7.8 Hz, 1H), 6.67 (t, J = 7.5 Hz, 1H), 6.61 (d, J = 7.4 Hz, 2H), 6.13 (s, 1H), 4.24 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 151.6, 138.8, 138.0, 136.9, 132.3, 130.9, 130.5, 130.1, 129.3, 128.4, 128.1, 127.9, 127.5, 127.3, 126.3, 121.1, 119.2, 109.9, 71.9, 69.6. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{27}H_{20}BrNO$: 454.0801, Found: 454.0802.

3na. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.24 (m, 2H), 7.19 – 7.11 (m, 2H), 7.07 (t, J = 7.4 Hz, 2H), 7.02 (d, J = 7.6 Hz, 1H), 6.94 (dd, J = 5.0, 1.0 Hz, 1H), 6.84 (m, 2H), 6.74 (m, 3H), 6.68 (td, J = 7.6, 0.9 Hz, 1H), 6.37 (s, 1H), 4.36 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 151.2, 143.6, 137.9, 136.9, 132.3, 130.9, 129.2, 128.1, 128.0, 127.9, 127.6, 127.3, 126.4, 126.1, 125.9, 124.7, 119.4, 110.3, 71.6, 66.7. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{25}H_{20}NOS$: 382.1260, Found: 382.1258.

3ab. ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.3 Hz, 2H), 7.13 (td, J = 7.8, 1.0 Hz, 1H), 7.06 – 6.94 (m, 8H), 6.78 (dd, J = 8.0, 1.8 Hz, 3H), 6.64 (td, J = 7.6, 0.8 Hz, 1H), 6.49 (d, J = 8.1 Hz, 2H), 6.13 (s, 1H), 4.33 (s, 1H), 2.29 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 152.0, 142.7, 140.0, 136.5, 135.4, 134.2, 131.2, 129.1, 128.6, 128.55, 128.4, 128.3, 127.7, 127.4, 127.1, 126.8, 118.8, 109.7, 71.7, 70.2, 21.5, 21.0. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{29}H_{25}NO$: 404.2009, Found: 404.2005.

3ac. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (m, 2H), 7.17 (m, 1H), 7.10 – 6.98 (m, 6H), 6.81 (d, J = 7.8 Hz, 1H), 6.73 (d, J = 9.0 Hz, 2H), 6.67 (t, J = 7.5 Hz, 1H), 6.50 (q, J = 8.9 Hz, 4H), 6.17 (s, 1H), 4.23 (s, 1H), 3.79 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 162.6, 158.4, 151.8, 139.9, 133.5, 131.0, 129.5, 129.4, 129.0, 128.4, 127.5, 127.4, 127.3, 127.1, 118.8, 113.2, 113.1, 109.7, 71.0, 70.2, 55.3, 55.2. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{29}H_{25}NO_3$: 436.1907, Found: 436.1907.

3ad. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (m, 2H), 7.18 (td, J = 7.8, 1.1 Hz, 1H), 7.08 – 6.89 (m, 8H), 6.82 (d, J = 7.7 Hz, 1H), 6.74 – 6.64 (m, 3H), 6.59 – 6.51 (m, 2H), 6.15 (s, 1H), 4.25 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 164.9 (d, $J_{C\text{-}F}$ = 253.4 Hz), 161.8 (d, $J_{C\text{-}F}$ = 245.7 Hz), 151.9, 139.3, 134.1 (d, $J_{C\text{-}F}$ = 3.3 Hz), 133.6 (d, $J_{C\text{-}F}$ = 9.0 Hz), 132.8 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.0 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.5, 128.2, 127.7, 127.4, 127.2, 126.2, 119.1, 115.1 (d, $J_{C\text{-}F}$ = 21.5 Hz), 114.9 (d, $J_{C\text{-}F}$ = 21.3 Hz), 109.9, 71.2, 70.2. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{27}H_{19}F_2NO$: 412.1507, Found: 412.1506.

3ae. ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.14 (t, J = 6.0 Hz, 2H), 7.09 (t, J = 7.7 Hz, 1H), 6.99 – 6.84 (m, 8H), 6.72 (d, J = 7.8 Hz, 1H), 6.59 (t, J = 7.6 Hz, 1H), 6.42 (dd, J = 8.5, 1.4 Hz, 2H), 6.05 (s, 1H), 4.15 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 151.9, 139.1, 138.8, 136.8, 134.9, 133.2, 132.3, 129.7, 129.6, 129.1, 128.3, 128.2, 127.7, 127.6, 127.2, 125.8, 119.1, 110.0, 71.4, 70.2. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{27}H_{19}Cl_2NO$: 444.0916, Found: 444.0912.

3af. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (q, J = 8.7 Hz, 4H), 7.18 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 8.5 Hz, 1H), 7.08 – 6.97 (m, 5H), 6.94 (d, J = 7.6 Hz, 1H), 6.81 (d, J = 7.8 Hz, 1H), 6.67 (t, J = 7.5 Hz, 1H), 6.44 (d, J = 8.5 Hz, 2H), 6.13 (s, 1H), 4.23 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 151.9, 139.0, 137.3, 135.3, 132.4, 131.3, 131.1, 130.1, 129.6, 128.1, 127.8, 127.6, 127.6, 127.2, 125.6, 121.4, 119.1, 110.0, 71.4, 70.1. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{27}H_{19}Br_2NO$: 531.9906, Found: 531.9906.

3ag. ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.25 – 7.11 (m,

3H), 7.05 (t, *J* = 7.7 Hz, 1H), 7.03 – 6.95 (m, 6H), 6.93 – 6.83 (m, 2H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.64 (t, *J* = 7.5 Hz, 1H), 6.49 (d, *J* = 7.4 Hz, 1H), 6.40 (s, 1H), 6.12 (s, 1H), 4.25 (s, 1H), 2.24 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 197.7, 152.1, 140.0, 138.1, 137.7, 137.5, 137.1, 132.8, 131.3, 129.2, 129.1, 128.3, 128.1, 128.0, 127.8, 127.6, 127.5, 127.4, 127.1, 126.2, 125.4, 118.8, 109.6, 72.2, 70.1, 21.4, 21.2. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{29}H_{26}NO$: 404.2009, Found: 404.2009.

3ah. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.32 – 7.22 (m, 2H), 7.21 – 7.15 (m, 2H), 7.14 – 7.08 (m, 1H), 7.05 (m, 1H), 6.97 (m, 6H), 6.83 – 6.75 (m, 2H), 6.67 (t, *J* = 7.5 Hz, 1H), 6.41 (m, 2H), 6.12 (s, 1H), 4.30 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 195.4 (d, $J_{C\text{-}F}$ = 1.9 Hz), 162.7 (d, $J_{C\text{-}F}$ = 247.5 Hz), 162.1 (d, $J_{C\text{-}F}$ = 248.2 Hz), 152.0, 140.6 (d, $J_{C\text{-}F}$ = 7.2 Hz), 139.2, 138.8 (d, $J_{C\text{-}F}$ = 6.3 Hz), 129.7, 129.5 (d, $J_{C\text{-}F}$ = 2.5Hz), 129.4 (d, $J_{C\text{-}F}$ = 3.2 Hz), 128.0, 127.7, 127.6, 127.6, 126.5 (d, $J_{C\text{-}F}$ = 3.1 Hz), 125.0, 124.3 (d, $J_{C\text{-}F}$ = 2.7 Hz), 119.3 (d, $J_{C\text{-}F}$ = 21.4 Hz), 119.1, 117.4 (d, $J_{C\text{-}F}$ = 23.3 Hz), 115.5 (d, $J_{C\text{-}F}$ = 22.7 Hz), 114.2 (d, $J_{C\text{-}F}$ = 21.2 Hz), 109.9, 71.8 (d, $J_{C\text{-}F}$ = 1.3 Hz), 70.14. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{27}H_{19}F_2NO$: 412.1507, Found: 412.1509.

3ai. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.67 (t, *J* = 1.8 Hz, 1H), 7.38 (m, 1H), 7.33 – 7.28 (m, 1H), 7.21 – 7.12 (m, 2H), 7.08 – 6.95 (m, 7H), 6.92 (t, *J* = 7.9 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.68 (td, *J* = 7.6, 0.9 Hz, 1H), 6.63 (t, *J* = 1.8 Hz, 1H), 6.53 – 6.47 (m, 1H), 6.11 (s, 1H), 4.32 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 195.4, 152.0, 140.0, 139.1, 138.2, 134.4, 134.3, 132.3, 130.7, 129.8, 129.2, 129.1, 128.8, 128.4, 128.0, 127.8, 127.6, 127.5, 127.4, 126.6, 124.9, 119.2, 110.0, 71.8, 70.2. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{27}H_{19}Cl_2NO$: 444.0916, Found: 444.0915.

3aj. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.85 (t, *J* = 1.7 Hz, 1H), 7.53 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.11 – 7.00 (m, 4H), 7.00 – 6.93 (m, 3H), 6.89 – 6.80 (m, 2H), 6.76 (t, *J* = 1.7 Hz, 1H), 6.69 (m, 1H), 6.55 (d, *J* = 7.9 Hz, 1H), 6.11 (s, 1H), 4.27 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 195.2, 152.0, 140.3, 139.0, 138.3, 135.2, 133.7, 131.3, 130.4, 129.8, 129.5, 129.3, 129.2, 128.0, 127.8, 127.7, 127.5, 127.0, 124.8, 122.5, 122.5, 119.2, 110.0, 71.8, 70.2. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{27}H_{20}Br_2NO$: 531.9906, Found: 531.9902.

3ak. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.33 – 7.19 (m, 5H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.78 (q, *J* = 6.6 Hz, 2H), 4.90 (s, 1H), 4.13 (s, 1H), 2.17 – 2.03 (m, 2H), 1.98 (t, *J* = 7.4 Hz, 2H), 1.53 – 1.38 (m, 1H), 1.20 – 1.08 (m, 1H), 1.07 – 0.97 (m, 1H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.89 – 0.78 (m, 1H), 0.50 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 210.5, 151.4, 140.3, 129.6, 128.5, 128.46, 127.9, 126.9, 125.8, 118.9, 109.4, 70.8, 67.5, 43.7, 38.6, 18.2, 16.7, 14.6, 13.5. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{21}H_{26}NO$: 308.2009, Found: 308.2009.

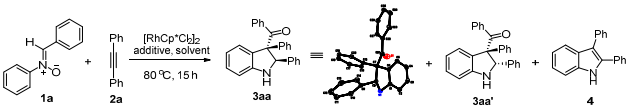
4 was prepared according to the general procedure but additional $Zn(OTf)_2$ (20 mol%) was used. ^{1}H NMR (400 MHz, Acetone) *δ* 10.70 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 8.2 Hz, 3H), 7.50 – 7.44 (m, 4H), 7.43 – 7.33 (m, 4H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H). The NMR data agree with those in a literature report [50].

3. Results and discussion

We initiated our investigation with optimization studies on the coupling between *N*-phenyl nitrone **1a** and diphenylacetylene (**2a**) in the presence of $[RhCp^*Cl_2]_2$ catalyst (4 mol%, Table 1). The reaction proceeded in poor yield and low selectivity in DCE in the absence of any acid additive (entry 1). Addition of PivOH or AcOH increased the conversion and the selectivity (entries 2 and 3), and the major product was identified as a 2,3,3-trisubstituted indoline (**3aa**). Product **3aa** was fully characterized, including by X-ray crystallography (not shown). However, diastereomer **3aa'** and indole **4** were also detected as the minor products, but no indenone product has been observed. These products were generated via *exo* C–H activation assisted by the O-coordination. It should be noted that the conditions that were optimal for related C–H activation-O-atom transfer reaction between quinoline *N*-oxide and an alkyne only gave poor results (entries 2,3) [47]. Switching to other Ag salts or to $Zn(OTf)_2$ only gave negative results (entry 4). Significant solvent effects have been observed. Using DCM as the solvent, both the selectivity and the conversion of the reaction were improved, and product **3aa** was isolated in 63% yield. Extensive screening of solvents revealed that the yield was optimal in ethyl acetate (68%, entry 8). Control experiments also proved that the Rh catalyst was necessary; omission of the Rh catalyst or switching to the Ir congener only resulted in decomposition of the starting nitrone.

With the optimized conditions established, we next explored the scope and generality of this coupling (Table 2). The scope of the nitrone was first examined in the coupling with diphenylacetylene. Introduction of electron-donating, -withdrawing, and halogen groups at the *para* position of the *N*-phenyl ring is fully tolerated. In all cases, both diastereomeric products were generated, and diastereomeric ratio of the crude products has been determined by ^{1}H NMR spectroscopy. The major product corresponds to that with the two phenyl groups in a *cis* orientation, and in most cases the major product

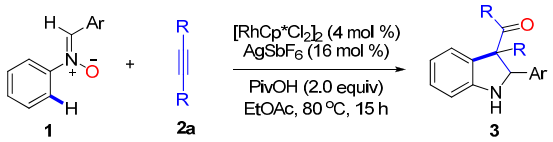
Table 1
Optimization studies.



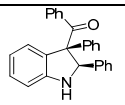
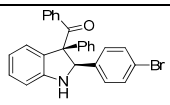
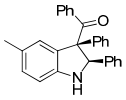
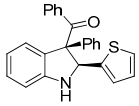
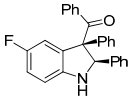
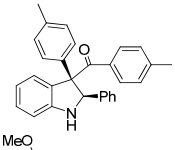
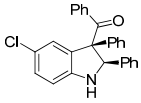
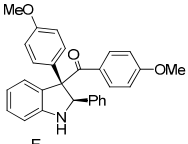
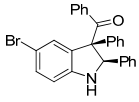
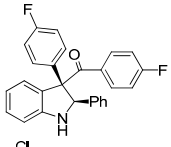
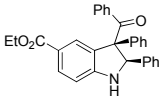
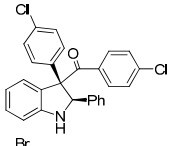
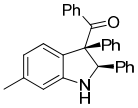
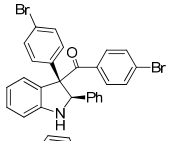
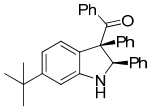
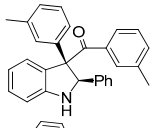
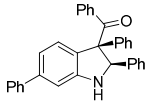
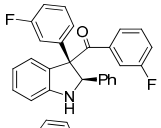
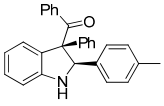
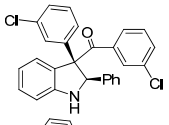
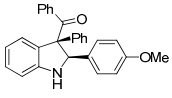
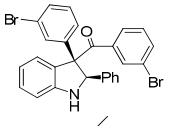
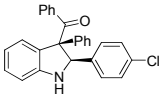
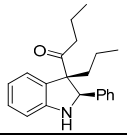
Entry	Additive	Acid	Solvent	Isolated yield (%)		
				3aa	**3aa'**	**4**
1	$AgSbF_6$	—	DCE	<5	12	<5
2	$AgSbF_6$	PivOH	DCE	36	<5	<5
3	$AgSbF_6$	AcOH	DCE	24	<5	<5
4	$Zn(OTf)_2$	PivOH	DCE	trace	trace	<5
5[a]	$AgNTf_2$	PivOH	DCE	nd	nd	trace
6	$AgSbF_6$	PivOH	DCM	63	9	<5
7	$AgSbF_6$	PivOH	dioxane	49	8	<5
8	$AgSbF_6$	PivOH	EtOAc	68	9	<5
9	$AgSbF_6$	PivOH	Acetone	40	7	<5
10	$AgSbF_6$	PivOH	*t*-AmOH	trace	trace	<5
11[b]	$AgSbF_6$	PivOH	DCE	nd	nd	nd
12[c]	$AgSbF_6/Zn(OTf)_2$	PivOH	DCE	trace	trace	40

Reaction conditions: nitrone **1a** (0.2 mmol), diphenylacetylene (0.3 mmol), $[Cp^*RhCl_2]_2$ (4 mol%), additive (16 mol%), acid (2 equiv) in solvent (2 mL), 80 °C for 15 h. [a] $[IrCp^*Cl_2]_2$ was used as a catalyst. [b] No catalyst was used. [c] Additional $Zn(OTf)_2$ (20 mol%) was used.

Table 2
Scope of substrates.



1 2a 3

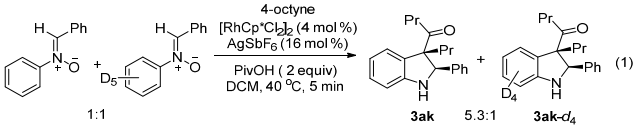
Entry	Product		Isolated yield (%)	dr[a]	Entry	Product		Isolated yield (%)	dr[a]
1		**3aa**	68	7.1:1	13		**3ma**	81	5.5:1
2		**3ba**	54	5.9:1	14		**3na**	50	5.2:1
3		**3ca**	61	4.2:1	15		**3ab**	76	7.0:1
4		**3da**	69	4.0:1	16		**3ac**	50	8.3:1
5		**3ea**	73	3.7:1	17		**3ad**	75	7.9:1
6		**3fa**	79	6.0:1	18		**3ae**	66	6.6:1
7		**3ga**	45	7.9:1	19		**3af**	72	6.0:1
8		**3ha**	64	9.9:1	20		**3ag**	61	7.2:1
9		**3ia**	58	7.1:1	21		**3ah**	53	5.9:1
10		**3ja**	61	6.2:1	22		**3ai**	48	5.9:1
11		**3ka**	71	6.2:1	23		**3aj**	56	5.5:1
12		**3la**	76	8.2:1	24		**3ak**[b]	56	5.5:1

Reaction conditions: nitrone (0.2 mmol), alkyne (0.3 mmol), $[Cp^*RhCl_2]_2$ (4 mol%), $AgSbF_6$ (16 mol%), PivOH (2.0 equiv), ethyl acetate (2 mL), 80 °C, 15 h, sealed tube under N_2. [a] *trans*:*cis* ratio. [b] DCM solvent was used in a sealed tube.

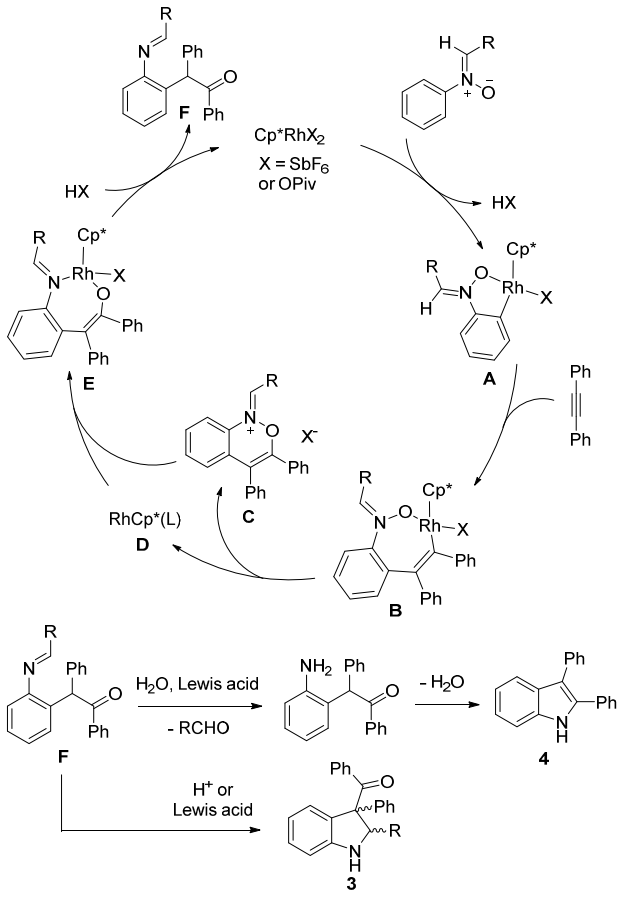
can be isolated by column chromatography, but the minor isomer overlaps with the major one or other impurities and defies further purification. Introduction of *meta* substituents such as methyl, *tert*-Bu and Ph resulted in steric bias and the C–H bond at the less hindered position underwent coupling with high selectivity. In contrast, variation of the spectating C-phenyl ring in the nitrone is also tolerated. Introduction of electron-donating and halogen group or using a heteroaryl group caused no negative effect. In all cases, the reaction gave nearly full conversion and *dr* ranges from 3.7–9.9:1, and the major product was isolated in moderate to high yield.

The scope of the alkyne substrate was next explored. Diphenylacetylenes bearing substituents such as *m*- and *p*-halogen, -OMe, and -alkyl groups all reacted with **1a** in moderate to good yield and the *dr* ranges from 5.5–8.3:1. The alkyne is not limited to diaryl substituents, and 4-octynes reacted under the optimized conditions (in DCM) with moderate yield. It should be noted that aryl- and alkyl-mixed alkynes such as PhC≡CMe are also viable; however, the complication of regio- and stereoselectivity rendered it difficult to isolate the desired product.

To probe the intramolecularity of the O-atom transfer process, the coupling of **1a** and 4-octyne were performed in the presence of H_2O^{18} (2 equiv). MS analysis of the product indicated that no O^{18} atom was incorporated, and this observation is in line with that in our previously reported coupling between quinoline *N*-oxide and alkynes, where the O-atom transfer is intramolecular. To probe the C–H activation process, kinetic isotope effect has been measured from the competitive coupling between **1a** and **1a**-d_5 in equimolar ratio (Eq. 1). The reaction was performed at 40 °C in DCM and was stopped after with low conversion (ca. 15%). The crude product was purified by chromatography to afford a mixture of **3ak** and **3ak**-d_4. ^{1}H NMR analysis of the mixture revealed a KIE value of 5.3, indicating that C-H cleave is likely involved in the rate-limiting step.



On the basis of previous reports, a plausible catalytic cycle is proposed (Scheme 1) starting from an active $RhCp^*X_2$ (X = SbF_6 or OPiv) catalyst. O-coordination-assisted C–H activation of the nitrone affords a rhodacyle **A**. Coordination of the alkyne followed by migratory insertion of the Rh–C bond generates a seven-membered rhodacyclic intermediate **B**, which is proposed to undergo C–O reductive elimination to give a cationic six-membered heterocycle (**C**) [47] together with a Cp*Rh(I) species. The N–O bond in heterocycle **C** then oxidatively adds back to the Rh(I) to generated a Rh(III) enolate species **E**, which accounts for the oxygen transfer. Protonolysis of the Rh–O bond in **E** by an acid (HX) releases an imine **F**. The fate of **F** can be found in two subsequent pathways. When sufficient water and a Lewis acid ($Cu(OAc)_2$ and $Zn(OTf)_2$) are present, hydrolysis is followed to produce an aniline with a pendent ketone moiety, intermolecular condensation of which furnishes the indole byproduct.



Scheme 1. Proposed mechanism of Rh(III)-catalyzed coupling of nitrones with alkynes.

Alternatively, intramolecular nucleophilic attack of the enol form of the ketone yields the final indoline product as a mixture of diastereomers.

4. Conclusions

We have achieved the Rh(III)-catalyzed C–H activation of *N*-aryl nitrones in the coupling with alkynes with rare oxygen atom transfer under redox-neutral conditions. The reaction proceeded under relatively mild conditions with high chemoselectivity and moderate to good diastereoselectivity and provided trisubstituted protic indolines as synthetically useful products. In all cases, the C–H activation occurred at the N-aryl ring (exo C–H activation), which differs from the endo selectivity in our previously reported Rh(III)-catalyzed C–H activation of nitrones. The chemoselectivity also stays contrast to that previously reported in Rh(III) catalysis. A broad scope of substrates has been established, and this method may find applications in the synthesis of complex structures.

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Graphical Abstract

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Rh(III)-catalyzed coupling of nitrones with alkynes for the synthesis of indolines

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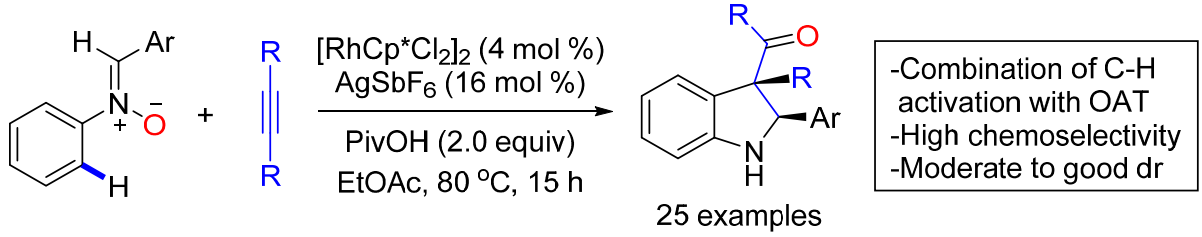

Rh-catalyzed redox-neutral coupling between *N*-aryl nitrones and alkynes has been achieved under relatively mild conditions. The reaction proceeded via C-H activation at the *N*-aryl ring with subsequent O-atom transfer, affording trisubstituted indolines in good chemoselectivity and moderate to good diasteroselectivity.

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