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Rh(III)-catalyzed C–H activation of benzamides: Coupling with quinones

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ABSTRACT

Rh(III)-catalyzed C–H activation of *N*-(alkyl)benzamides in the oxidative coupling with various quinones. In addition, under redox-neutral conditions, 2-hydroxy-*6H*-benzo[*c*]chromen-6-ones were also obtained via a cascade of cross-coupling followed by lactonization.

1. Introduction

Transition-metal-catalyzed direct functionalization of C–H bonds has become an increasingly important strategy for the construction of complex organic molecules [1–3]. Palladium, ruthenium, iridium, and copper catalysts are particularly well known to serve this purpose [4–19]. Although much progress has been made, the development of new synthetic methods is still necessary, especially via a C–H activation pathway. $Rh^{III}Cp^*$ represent one of the most frequently used catalysts that enabled a vast number of transformations through coupling of C–H bonds with alkenes along with other molecules [20–57]. However, the olefins are mostly limited to acrylates and styrenes. There are only a few reports on the applications of quinones as an olefin partner under oxidative conditions [58]. The rarity is probably due to the difficulty of β-hydride elimination following syn migratory insertion of a Rh–C bond into the C=C bond of a quinone. In addition, the steric effect of this special disubstituted olefin may also be accountable [59–63].

On the other hand, quinones represent an important class of biologically active molecules that are widely distributed in natural products [64–67]. Both natural and synthetic medicinal agents have been developed that are based on the quinone structure due to their chemotherapeutic value such as antitumor, antifungal, and antibacterial [68–72]. The quinone moiety is also involved in many bioenergetic processes and plays a vital role in electron-transport processes [73]. Aryl-substituted quinones are very useful in photosynthesis and the dye industry owing to their unique visual and electronic properties [74,75]. Thus, developing powerful synthetic methods of arylquinones is very necessary to fulfill the practical requirements. Arylation of quinones has been reported by some groups [76–90]. However, these approaches often suffer from poor atom-economy, substrate limitations, stoichiometric amounts of metals or high temperature. Although much progress has been made, the development of new synthetic methods is still necessary, especially via a C–H activation pathway. Herein we report Rh(III)-catalyzed C–H activation of

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N-(alkyl)benzamides in the coupling with quinones, leading to synthesis of arylated quinones.

2. Experimental

2.1. General

All reactions were carried out using Schlenk techniques or in a nitrogen-filled glovebox. 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. HRMS data were obtained on an Agilent 6540 Q-Tof. Column chromatography was performed on silica gel (300–400 mesh) using ethyl acetate (EA)/petroleum ether (PE). All chemicals were obtained from commercial sources and were used as received unless otherwise noted.

2.2. Preparation of compounds

2.2.1. General procedure for the synthesis of compounds *3*

N-(alkyl)benzamides (0.2 mmol), quinones (0.3 mmol), $[RhCp^*Cl_2]_2$ (4 mol%), $AgSbF_6$ (16 mol%), Ag_2CO_3 (2.0 equiv) and dioxane (3 mL) were charged into the sealed tube. The reaction mixture was stirred at 100 °C for 12 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford compounds **3**.

2.2.2. General procedure for the synthesis of compounds *4*

N-(*tert*-butyl)benzamides (0.2 mmol), quinones (0.3 mmol), $[RhCp^*Cl_2]_2$ (4 mol%), $AgSbF_6$ (30 mol%), AgOAc (0.2 equiv) and acetone (4 mL) were charged into the sealed tube. The reaction mixture was stirred at 100 °C for 12 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using etroleum ether/ethyl acetate to afford compounds **4**.

2.3. Spectral data for products

N-(*tert*-butyl)-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3a**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 7.4, 1.5 Hz, 1H), 7.48 (dd, J = 7.4, 1.6 Hz, 1H), 7.44 (td, J = 7.5, 1.5 Hz, 1H), 7.29 (dd, J = 7.4, 1.2 Hz, 1H), 6.80 (d, J = 1.1 Hz, 2H), 6.75 – 6.72 (m, 1H), 6.01 (s, 1H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 185.8, 168.4, 149.5, 137.6, 137.03, 136.97, 133.2, 131.3, 130.9, 130.4, 129.8, 126.5, 52.0, 28.7. HRMS: $[M + H]^+$ calculated for $C_7H_{18}NO_3$: 284.1287, found 284.1290.

N-(*tert*-butyl)-5-methyl-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3b**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.8 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 7.09 (s, 1H), 6.80 (s, 2H), 6.72 (s, 1H), 5.96 (s, 1H), 2.39 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 185.9, 168.4, 149.8, 141.3, 137.1, 137.0, 134.9, 133.3, 131.2, 131.0, 130.3, 126.5, 51.9, 28.8, 21.4. HRMS: $[M + H]^+$ calculated for $C_{18}H_{20}NO_3$: 298.1443, found 298.1440.

N-(*tert*-butyl)-5-methoxy-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3c**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.5 Hz, 1H), 6.92 (dd, J = 8.5, 2.6 Hz, 1H), 6.80 (dd, J = 4.1, 2.2 Hz, 3H), 6.72 (d, J = 1.5 Hz, 1H), 5.93 (s, 1H), 3.84 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 185.7, 168.1, 161.4, 149.8, 137.2, 136.9, 135.2, 131.0, 130.0, 128.1, 116.3, 114.4, 55.7, 51.9, 28.8. HRMS: $[M + H]^+$ calculated for $C_{18}H_{20}NO_4$: 314.1392, found 314.1391.

N-(*tert*-butyl)-5-fluoro-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3d**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 8.5, 5.4 Hz, 1H), 7.13 (td, J = 8.3, 2.6 Hz, 1H), 7.01 (dd, J = 8.8, 2.6 Hz, 1H), 6.82 (d, J = 1.0 Hz, 2H), 6.73 (s, 1H), 5.94 (s, 1H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 185.4, 167.5, 163.7 (d, J = 250.9 Hz), 148.3 (d, J = 1.5 Hz), 137.1, 137.0, 135.7 (d, J = 8.2 Hz), 134.0 (d, J = 3.4 Hz), 131.7, 128.6 (d, J = 8.7 Hz), 117.7 (d, J = 22.9 Hz), 116.3 (d, J = 21.1 Hz), 52.2, 28.7. HRMS: $[M + H]^+$ calculated for $C_{17}H_{17}FNO_3$: 302.1192, found 302.1181.

N-(*tert*-butyl)-5-chloro-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3e**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.2 Hz, 1H), 7.41 (dd, J = 8.2, 2.0 Hz, 1H), 7.28 (d, J = 2.1 Hz, 1H), 6.81 (s, 2H), 6.74 (s, 1H), 5.97 (s, 1H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.2, 185.4, 167.5, 148.1, 137.1, 137.0, 136.8, 136.1, 134.9, 131.7, 130.4, 129.7, 127.9, 52.2, 28.7. HRMS: $[M + H]^+$ calculated for $C_{17}H_{17}ClNO_3$: 318.0897, found 318.0898.

5-Bromo-*N*-(*tert*-butyl)-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3f**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, J = 8.2, 2.0 Hz, 1H), 7.44 (d, J = 1.9 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 6.81 (s, 2H), 6.74 (s, 1H), 5.95 (s, 1H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.2, 185.4, 167.6, 148.0, 137.1, 137.0, 136.5, 135.0, 133.3, 132.7, 131.8, 128.0, 124.9, 52.3, 28.7. HRMS: $[M + H]^+$ calculated for $C_{17}H_{17}BrNO_3$: 362.0392, found 362.0391.

N-(*tert*-butyl)-2'',5''-dioxo-2'',5''-dihydro-[1,1':3',1''-terphenyl]-4'-carboxamide (**3g**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, J = 7.9, 1.6 Hz, 1H), 7.61–7.54 (m, 3H), 7.49–7.43 (m, 3H), 7.39 (t, J = 7.2 Hz, 1H), 6.82 (s, 2H), 6.80 (d, J = 1.3 Hz, 1H), 6.04 (s, 1H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 185.9, 168.2, 149.6, 144.0, 139.5, 137.1, 137.1, 136.3, 133.8, 131.4, 129.3, 129.2, 128.4, 128.3, 127.3, 127.1, 52.1, 28.8. HRMS: $[M + H]^+$ calculated for $C_{23}H_{22}NO_3$: 360.1600, found 360.1600.

N-(*tert*-butyl)-2',5'-dioxo-5-(trifluoromethyl)-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3h**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 8.0, 1.0 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.55 (s, 1H), 6.84 (d, J = 2.2 Hz, 2H), 6.80 (d, J = 2.1 Hz, 1H), 5.97 (s, 1H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.1, 185.4, 167.3, 147.9, 140.9, 137.3, 136.9, 134.0, 132.9 (q, J = 33.2 Hz), 132.2, 127.4 (q, J = 3.6 Hz), 127.1, 126.7 (q, J = 3.7 Hz), 123.4 (q, J = 267.7 Hz), 52.5, 28.7. HRMS: $[M + H]^+$ calculated for $C_{18}H_{17}F_3NO_3$: 352.1161, found 352.1157.

Methyl 6-(*tert*-butylcarbamoyl)-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-3-carboxylate (**3i**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 8.0, 1.4 Hz, 1H), 7.96 (d, J = 1.2 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 6.81 (d, J = 6.4 Hz, 3H), 6.04 (s, 1H), 3.94 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 185.6, 167.7, 165.8,

148.4, 141.5, 137.2, 136.9, 133.4, 132.3, 132.0, 131.5, 131.0, 126.7, 52.7, 52.4, 28.7. HRMS: [M + H]$^+$ calculated for $C_{19}H_{20}NO_5$: 342.1341, found 342.1340.

N-(*tert*-butyl)-4-methyl-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3j**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.29 (d, J = 8.6 Hz, 1H), 7.17 (d, J = 7.7 Hz, 1H), 6.78 (s, 2H), 6.71 (s, 1H), 6.00 (s, 1H), 2.41 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 186.0, 168.5, 149.4, 140.2, 137.6, 137.0, 136.9, 131.4, 131.0, 130.4, 130.2, 127.3, 51.9, 28.7, 21.3. HRMS: [M + H]$^+$ calculated for $C_{18}H_{20}NO_3$: 298.1443, found 298.1446.

N-(*tert*-butyl)-4-methoxy-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3k**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.4 Hz, 1H), 7.05 (d, J = 2.5 Hz, 1H), 7.00 (dd, J = 8.4, 2.6 Hz, 1H), 6.79 (d, J = 1.1 Hz, 2H), 6.72 (d, J = 1.1 Hz, 1H), 5.91 (s, 1H), 3.87 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7, 186.2, 168.2, 160.9, 149.0, 139.2, 137.1, 137.0, 131.9, 130.9, 125.3, 115.1, 113.6, 55.9, 52.1, 28.8. HRMS: [M + H]$^+$ calculated for $C_{18}H_{20}NO_4$: 314.1392, found 314.1394.

N-(*tert*-butyl)-6-methoxy-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3k'**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, J = 8.0 Hz, 1H), 7.11 (d, J = 7.7 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 6.84 (d, J = 10.1 Hz, 1H), 6.80 (dd, J = 10.1, 2.4 Hz, 1H), 6.74 (d, J = 2.4 Hz, 1H), 5.70 (s, 1H), 3.77 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 186.3, 168.1, 157.4, 144.8, 139.2, 137.1, 136.8, 134.4, 130.6, 121.0, 118.9, 113.0, 56.2, 52.0, 28.7. HRMS: [M + H]$^+$ calculated for $C_{18}H_{20}NO_4$: 314.1392, found 314.1395.

N-(*tert*-butyl)-4-chloro-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3l**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 2.0 Hz, 1H), 7.47 (dd, J = 8.1, 2.1 Hz, 1H), 7.23 (d, J = 8.1 Hz, 1H), 6.81 (s, 2H), 6.74 (s, 1H), 5.96 (s, 1H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 185.6, 167.2, 148.2, 139.2, 137.1, 137.0, 135.9, 131.7, 131.7, 131.5, 130.9, 127.0, 52.4, 28.7. HRMS: [M + H]$^+$ calculated for $C_{17}H_{17}ClNO_3$: 318.0897, found 318.0897.

N-(*tert*-butyl)-6-chloro-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3l'**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.8 Hz, 1H), 7.44–7.35 (m, 2H), 6.90–6.82 (m, 2H), 6.74 (d, J = 2.0 Hz, 1H), 5.68 (s, 1H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 185.7, 167.1, 145.5, 139.7, 137.1, 136.8, 134.7, 134.3, 131.5, 130.9, 130.4, 125.1, 52.3, 28.7. HRMS: [M + H]$^+$ calculated for $C_{17}H_{17}ClNO_3$: 318.0897, found 318.0899.

N-(*tert*-butyl)-6-fluoro-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3m**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (td, J = 8.0, 5.3 Hz, 1H), 7.33 (d, J = 7.2 Hz, 1H), 7.24 (t, J = 8.8 Hz, 1H), 6.87–6.79 (m, 3H), 5.89 (s, 1H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.1, 185.4, 167.2 (d, J = 2.7 Hz), 160.1 (d, J = 248.7 Hz), 141.8, 139.7 (d, J = 1.7 Hz), 137.1, 137.0, 134.4 (d, J = 3.0 Hz), 131.0 (d, J = 8.7 Hz), 122.4 (d, J = 3.4 Hz), 120.2 (d, J = 15.7 Hz), 118.2 (d, J = 22.9 Hz), 52.2, 28.7. HRMS: [M + H]$^+$ calculated for $C_{17}H_{17}FNO_3$: 302.1192, found 302.1196.

N-(*tert*-butyl)-3-methoxy-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3n**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.37 (m, 1H), 7.05 (d, J = 8.4 Hz, 1H), 6.96 (s, 1H), 6.89 (d, J = 7.6 Hz, 1H), 6.81–6.78 (m, 2H), 6.67 (d, J = 2.1 Hz, 1H), 3.92 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.8, 185.5, 165.0, 156.5, 150.9, 137.2, 136.9, 136.1, 131.4, 129.8, 125.2, 123.3, 113.4, 56.5, 51.7, 28.9. HRMS: [M + H]$^+$ calculated for $C_{18}H_{20}NO_4$: 314.1392, found 314.1398.

N-(*tert*-butyl)-3-fluoro-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3o**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.41 (m, 1H), 7.20 (ddd, J = 10.2, 8.4, 0.9 Hz, 1H), 7.09 (dd, J = 7.6, 0.7 Hz, 1H), 6.81 (d, J = 1.2 Hz, 2H), 6.73 (t, J = 1.1 Hz, 1H), 6.23 (s, 1H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 185.4, 163.0 (d, J = 1.8 Hz), 159.3 (d, J = 245.7 Hz), 148.8 (d, J = 2.4 Hz), 137.1, 137.0, 136.2 (d, J = 3.5 Hz), 131.9 (d, J = 9.7 Hz), 131.4, 126.4 (d, J = 2.9 Hz), 124.7 (d, J = 15.8 Hz), 117.7 (d, J = 24.5 Hz), 52.4, 28.8. HRMS: [M + H]$^+$ calculated for $C_{17}H_{17}FNO_3$: 302.1192, found 302.1194.

N-(*tert*-butyl)-3-(3,6-dioxocyclohexa-1,4-dien-1-yl)-2-naphthamide (**3p**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.87 (dd, J = 11.5, 4.7 Hz, 2H), 7.78 (s, 1H), 7.62–7.55 (m, 2H), 6.86 (s, 1H), 6.81 (s, 2H), 6.18 (s, 1H), 1.43 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.8, 186.4, 168.7, 149.7, 137.1, 137.0, 135.1, 133.9, 133.1, 131.2, 130.8, 130.4, 128.4, 128.3, 128.2, 128.1, 126.5, 52.1, 28.8. HRMS: [M + H]$^+$ calculated for $C_{21}H_{20}NO_3$: 334.1443, found 334.1442.

N-(*tert*-butyl)-3-(3,6-dioxocyclohexa-1,4-dien-1-yl)thiophene-2-carboxamide (**3q**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 5.0 Hz, 1H), 6.99 (d, J = 5.0 Hz, 1H), 6.86 (d, J = 10.1 Hz, 1H), 6.80 (dd, J = 10.1, 2.3 Hz, 1H), 6.75 (d, J = 2.3 Hz, 1H), 5.79 (s, 1H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.4, 185.0, 161.4, 143.6, 137.6, 137.2, 136.6, 134.9, 132.1, 129.7, 126.5, 52.4, 28.8. HRMS: [M + H]$^+$ calculated for $C_{15}H_{16}NO_3S$: 290.0851, found 290.0849.

N-(*tert*-butyl)-2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl) benzamide (**3r**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.08 (m, 1H), 8.06–8.00 (m, 1H), 7.77–7.69 (m, 2H), 7.58–7.52 (m, 1H), 7.52–7.43 (m, 2H), 7.37 (dd, J = 7.4, 1.3 Hz, 1H), 6.98 (s, 1H), 6.03 (s, 1H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2, 184.0, 168.7, 151.4, 138.1, 133.8, 133.7, 133.0, 132.7, 130.8, 130.5, 129.8, 126.8, 126.5, 126.3, 52.0, 28.8. Two carbons are not visible due to overlapping peaks. HRMS: [M + H]$^+$ calculated for $C_{21}H_{20}NO_3$: 334.1443, found 334.1440.

N-(*tert*-butyl)-3',4'-dimethyl-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3s**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.40 (m, 3H), 7.31–7.27 (m, 1H), 6.71 (s, 1H), 5.98 (s, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 186.2, 168.7, 149.0, 141.5, 141.3, 137.8, 133.7, 131.1, 130.8, 130.4, 129.6, 126.5, 52.0, 28.8, 12.7, 12.4. HRMS: [M + H]$^+$ calculated for $C_{19}H_{22}NO_3$: 312.1600, found 312.1605.

N-(*tert*-butyl)-4'-methyl-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide and *N*-(*tert*-butyl)-3'-methyl-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3t**). Selected signals: Major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.41 (m, 3H), 7.30–7.26 (m, 1H), 6.01 (s, 1H), 2.06 (d, J = 1.5 Hz, 3H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 186.5, 168.6, 149.6, 146.4, 137.6, 133.7, 131.3, 130.9, 130.4, 129.7, 126.5, 52.0, 28.7, 16.2. Minor: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.41 (m, 3H), 7.30–7.26 (m, 1H), 6.00 (s, 1H), 2.09 (d, J = 1.5 Hz, 3H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 186.1, 168.6, 149.3, 146.4, 137.8, 133.1, 131.5, 130.8, 130.5, 126.5, 52.0, 28.7, 15.8. HRMS: [M + H]$^+$ calculated for $C_{18}H_{20}NO_3$: 298.1443, found

298.1447.

N-(*tert*-butyl)-4'-methoxy-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide and *N*-(*tert*-butyl)-3'-methoxy-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3u**). Selected signals: Major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.41 (m, 3H), 7.28 (t, J = 6.2 Hz, 1H), 6.70 (s, 1H), 6.05 (s, 1H), 5.97 (s, 1H), 3.84 (s, 3H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.8, 182.1, 168.4, 159.1, 150.0, 137.9, 133.1, 130.7, 130.4, 129.8, 129.4, 126.5, 107.8, 56.3, 51.9, 28.7. Minor: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.41 (m, 3H), 7.28 (t, J = 6.2 Hz, 1H), 6.65 (d, J = 2.3 Hz, 1H), 6.05 (s, 1H), 5.96 (d, J = 2.3 Hz, 1H), 3.82 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 180.6, 171.2, 159.4, 147.5, 137.4, 131.9, 130.8, 130.4, 129.7, 126.5, 107.7, 56.4, 52.0, 28.7. HRMS: $[M + H]^+$ calculated for $C_{18}H_{20}NO_4$: 314.1392, found 314.1395.

N-(*tert*-butyl)-4'-chloro-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide and *N*-(*tert*-butyl)-3'-chloro-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3v**). Selected ^{1}H NMR signals: 1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.45 (m, 3H), 7.32–7.27 (m, 1H), 6.05 (s, 1H), 1.39 (s, 9H). 2) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.45 (m, 3H), 7.32–7.27 (m, 1H), 6.05 (s, 1H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.10, 183.62, 179.75, 178.53, 168.40, 168.28, 150.29, 149.84, 144.64, 144.45, 137.68, 137.50, 134.20, 134.07, 133.15, 132.68, 131.08, 131.00, 130.54, 130.33, 130.20, 126.49, 126.47, 52.28, 52.15, 28.77, 28.76. HRMS: $[M + H]^+$ calculated for $C_{17}H_{17}ClNO_3$: 318.0897, found 318.0903.

N-(*tert*-butyl)-2',5'-dioxo-2',5'-dihydro-[1,1':4',1''-terphenyl]-2-carboxamide and *N*-(*tert*-butyl)-2',5'-dioxo-2',5'-dihydro-[1,1':3',1''-terphenyl]-2-carboxamide (**3w**). Selected signals: Major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (d, J = 2.6 Hz, 1H), 6.75 (d, J = 2.6 Hz, 1H), 6.11 (s, 1H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 185.4, 168.1, 150.2, 146.8, 137.1, 133.9, 133.4, 132.8, 131.0, 130.9, 130.7, 129.8, 129.7, 129.4, 128.2, 126.6, 51.9, 28.7. Minor: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.82 (s, 1H), 6.09 (s, 1H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 186.0, 168.5, 148.9, 146.2, 137.8, 133.1, 132.9, 132.7, 131.8, 130.5, 130.0, 129.5, 128.5, 126.52 51.9, 28.7. HRMS: $[M + H]^+$ calculated for $C_{23}H_{22}NO_3$: 360.1600, found 360.1600.

N-(*tert*-butyl)-2-(3,6-dioxocyclohexa-1,4-dien-1-yl)cyclopent-1-enecarboxamide (**3x**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, J = 10.2 Hz, 1H), 6.73 (dd, J = 10.2, 2.5 Hz, 1H), 6.55 (d, J = 2.5 Hz, 1H), 5.36 (s, 1H), 2.76–2.66 (m, 4H), 2.11–2.02 (m, 2H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.4, 185.0, 164.8, 146.4, 140.5, 139.9, 137.6, 136.5, 130.7, 51.6, 38.2, 34.9, 28.9, 22.6. HRMS: $[M + H]^+$ calculated for $C_{16}H_{20}NO_3$: 274.1443, found 274.1446.

N^2,*N*$^{2''}$-di-*tert*-butyl-2',5'-dioxo-2',5'-dihydro-[1,1':3',1''-terphenyl]-2,2''-dicarboxamide (**3aa**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.52 (m, 2H), 7.49–7.40 (m, 6H), 6.80 (s, 2H), 6.04 (s, 2H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.2, 185.4, 168.4, 148.7, 137.8, 132.3, 132.2, 130.4, 130.2, 129.6, 127.3, 52.1, 28.7. HRMS: $[M + H]^+$ calculated for $C_{28}H_{31}N_2O_4$: 459.2284, found 459.2288.

N-isopropyl-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3ba**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.43 (m, 3H), 7.30 (d, J = 7.2 Hz, 1H), 6.84–6.77 (m, 2H), 6.74 (d, J = 1.8 Hz, 1H), 6.02 (d, J = 7.0 Hz, 1H), 4.12–4.00 (m, 1H), 1.21 (d, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 185.9, 168.0, 149.4, 137.1, 136.9, 136.5, 133.4, 131.5, 131.1, 130.5, 129.9, 126.6, 42.3, 22.8. HRMS: $[M + H]^+$ calculated for $C_{16}H_{16}NO_3$: 270.1130, found 270.1134.

N-cyclohexyl-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3ca**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.45 (m, 3H), 7.30 (d, J = 7.5 Hz, 1H), 6.86–6.78 (m, 2H), 6.74 (d, J = 2.0 Hz, 1H), 5.99 (d, J = 7.5 Hz, 1H), 3.82–3.71 (m, 1H), 2.01–1.91 (m, 2H), 1.79–1.69 (m, 2H), 1.63 (d, J = 10.6 Hz, 2H), 1.45–1.31 (m, 2H), 1.27–1.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 185.9, 167.9, 149.5, 137.2, 136.9, 136.6, 133.4, 131.5, 131.1, 130.5, 129.9, 126.6, 49.1, 33.2, 25.7, 25.0. HRMS: $[M + H]^+$ calculated for $C_{19}H_{20}NO_3$: 310.1443, found 310.1445.

N-(1-adamantanyl)-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-2-carboxamide (**3da**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.42 (m, 3H), 7.31–7.26 (m, 1H), 6.86–6.78 (m, 2H), 6.74 (d, J = 2.0 Hz, 1H), 5.84 (s, 1H), 2.09 (s, 3H), 2.03 (d, J = 2.6 Hz, 6H), 1.69 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 185.8, 168.2, 149.6, 137.8, 137.1, 137.1, 133.2, 131.3, 130.9, 130.5, 129.9, 126.5, 52.8, 41.6, 36.5, 29.6. HRMS: $[M + H]^+$ calculated for $C_{23}H_{24}NO_3$: 362.1756, found 362.1761.

2-Hydroxy-6*H*-benzo[*c*]chromen-6-one (**4a**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.73 (s, 1H), 8.33–8.21 (m, 2H), 7.98–7.91 (m, 1H), 7.72–7.66 (m, 1H), 7.62 (d, J = 2.7 Hz, 1H), 7.28 (d, J = 8.9 Hz, 1H), 7.02 (dd, J = 8.9, 2.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.9, 154.7, 144.4, 135.7, 134.7, 130.2, 129.7, 122.9, 121.1, 118.9, 118.7, 118.6, 108.7. HRMS: $[M + H]^+$ calculated for $C_{13}H_9O_3$: 213.0555, found 213.0552.

2-Hydroxy-8-methyl-6*H*-benzo[*c*]chromen-6-one (**4b**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.69 (s, 1H), 8.15 (d, J = 8.1 Hz, 1H), 8.04 (s, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.56 (d, J = 2.3 Hz, 1H), 7.25 (d, J = 8.8 Hz, 1H), 6.97 (dd, J = 8.8, 2.5 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.9, 154.7, 144.1, 139.6, 136.7, 132.2, 129.9, 122.9, 120.9, 118.8, 118.46, 118.4, 108.4, 21.2. HRMS: $[M + H]^+$ calculated for $C_{14}H_{11}O_3$: 227.0708, found 227.0706.

9-Chloro-2-hydroxy-6*H*-benzo[*c*]chromen-6-one (**4c**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.74 (s, 1H), 8.38 (d, J = 1.9 Hz, 1H), 8.22 (d, J = 8.5 Hz, 1H), 7.70 (dd, J = 8.5, 1.9 Hz, 1H), 7.65 (d, J = 2.7 Hz, 1H), 7.27 (d, J = 8.9 Hz, 1H), 7.04 (dd, J = 8.9, 2.7 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.2, 154.8, 144.8, 141.1, 136.6, 132.4, 129.8, 122.89, 119.9, 119.6, 118.6, 117.8, 109.2. HRMS: $[M + H]^+$ calculated for $C_{13}H_8ClO_3$: 247.0162, found 247.0161.

9-Bromo-2-hydroxy-6*H*-benzo[*c*]chromen-6-one (**4d**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.73 (d, J = 3.8 Hz, 1H), 8.48 (d, J = 11.4 Hz, 1H), 8.12 (t, J = 8.0 Hz, 1H), 7.82 (t, J = 7.9 Hz, 1H), 7.69–7.59 (m, 1H), 7.26 (dd, J = 8.6, 6.9 Hz, 1H), 7.04 (dt, J = 8.8, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.4, 154.8, 144.7, 136.6, 132.6, 132.2, 130.3, 125.8, 120.2, 119.6, 118.6, 117.6, 109.2. HRMS: $[M + H]^+$ calculated for $C_{13}H_8BrO_3$: 290.9657, found 290.9659.

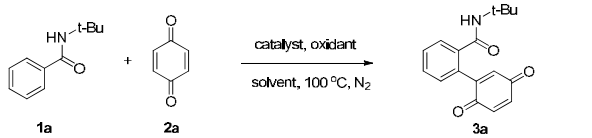
3. Results and discussion

The reaction of *N*-(*tert*-butyl)benzamide **1a** and 1,4-benzo-

quinone **2a** was selected as a model for screening of the reaction parameters (Table 1). We initially performed this reaction in the absence of any external oxidant but with 4 mol% of $[RhCp^*Cl_2]_2$ and 16 mol% of $AgSbF_6$. Only traces of the desired product **3a** were detected by GC-MS (Table 1, entry 1). When $Cu(OAc)_2$ (1 equiv) was employed as an oxidant, **3a** was isolated in 17% yield (entry 2). However, no product was obtained when $AgSbF_6$ was omitted (entry 3). With Ag_2CO_3 or AgOAc being an oxidant, the yield of **3a** was increased to 54% and 21%, respectively (entries 4 and 5). We were pleased to find that **3a** was isolated in 85% yield when the amount of Ag_2CO_3 was increased to 2.0 equiv (entry 6). Further examination of the solvent revealed that DCE, THF, diglyme, PhCl, and acetone all gave inferior results (entries 7–11). Finally, the optimized conditions include 4 mol% of $[RhCp^*Cl_2]_2$ as catalyst, 16 mol% of $AgSbF_6$ as an additive, and 2.0 equiv of Ag_2CO_3 in 1,4-dioxane at 100 °C.

Having determined the optimal conditions, we next surveyed various substrates to define the scope of the reaction (Table 2). *N*-(*tert*-butyl)benzamides bearing electron-donating groups at the *para*-position gave the corresponding products in moderate to good yields (**3a**–**3c**, **3g**). With a halogen group at the 4-position of phenyl ring, the arylated quinones were isolated in slightly lower yield (**3d**–**3f**). However, using electron-withdrawing groups such as trifluoromethyl and methoxycarbonyl at the *para*-position decreased the yield of the products (**3h** and **3i**). The *meta* methyl substituted substrate also gave product in good yield (**3j**) and C–H activation occurred selectively at the less hindered position. However, the *meta* methoxy (**3k** and **3k'**) or chloro (**3l** and **3l'**) substituted benzamide gave two regio-isomeric products that could be chromatographically separated. In contrast, C–H activation occurred selectively at the more hindered *ortho* site for the *meta* fluoro substituted benzamide (**3m**), on the basis of ^1H and ^{13}C NMR analysis. *ortho*-Methoxy substituted benzamide was also effective, furnishing the arylated quinone in 68% yield (**3n**). However, *ortho*-fluoro substrate exhibited lower reactivity (**3o**), implying that the electronic effect seems more significant than the steric effect at this position. Notably, the reactions for *N*-(*tert*-butyl)-2-naphthamide and *N*-(*tert*-butyl)thiophene-2-carboxamide proceeded smoothly to generate products in moderate yields (**3p** and **3q**). The *N*-substituent is not limited to a ^{t}Bu group. Thus benzamides bearing *N*-alkyl groups such as isopropyl, cyclohexyl, and adamantyl also underwent smooth coupling (**3ba**–**3da**). The scope of quinone substrate was next investigated. Subjection of 1,4-naphthoquinone and 2,3-dimethyl-1,4-benzoquinone to the coupling with **1a** afforded **3r** and **3s** in 90% and 64% yields, respectively. In contrast, the coupling of a mono-substituted quinone with **1a** provided two regioisomers in moderate total yields (**3t**–**3w**). Furthermore, extension to an olefinic substrate bearing this type of directing group proved successful, where product **3x** was isolated in 52% yield. In addition, when an excess (3.0 equiv) of **1a** was used, the diarylation product was isolated as the major one (**3aa**).

Table 1
Coupling of *N*-(*tert*-butyl)benzamide with quinone under various conditions.



1a 2a 3a

Entry	Catalyst	Oxidant (equiv)	Solvent	Isolated yield (%)
1	$[RhCp^*Cl_2]_2/AgSbF_6$	—	Dioxane	Trace
2	$[RhCp^*Cl_2]_2/AgSbF_6$	$Cu(OAc)_2$ (1.0)	Dioxane	17
3	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2$ (1.0)	Dioxane	nd
4	$[RhCp^*Cl_2]_2/AgSbF_6$	Ag_2CO_3 (1.0)	Dioxane	54
5	$[RhCp^*Cl_2]_2/AgSbF_6$	AgOAc (1.0)	Dioxane	21
6	$[RhCp^*Cl_2]_2/AgSbF_6$	Ag_2CO_3 (2.0)	Dioxane	85
7	$[RhCp^*Cl_2]_2/AgSbF_6$	Ag_2CO_3 (2.0)	DCE	73
8	$[RhCp^*Cl_2]_2/AgSbF_6$	Ag_2CO_3 (2.0)	THF	60
9	$[RhCp^*Cl_2]_2/AgSbF_6$	Ag_2CO_3 (2.0)	Diglyme	Trace
10	$[RhCp^*Cl_2]_2/AgSbF_6$	Ag_2CO_3 (2.0)	PhCl	36
11	$[RhCp^*Cl_2]_2/AgSbF_6$	Ag_2CO_3 (2.0)	Acetone	41

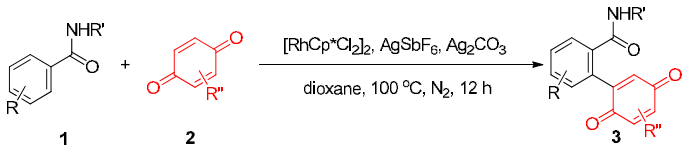
Reactions conditions: $[RhCp^*Cl_2]_2$ (4 mol%), $AgSbF_6$ (16 mol%), oxidant, **1a** (0.20 mmol), and **2a** (0.30 mmol) in solvent (3 mL) at 100 °C under nitrogen for 12 h.

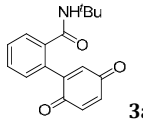
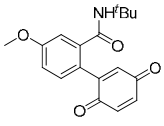
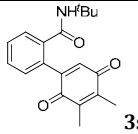
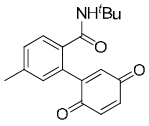
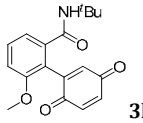
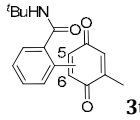
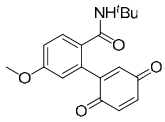
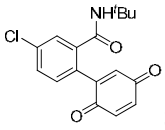
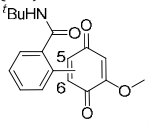
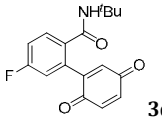
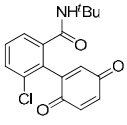
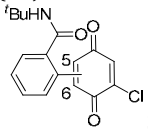
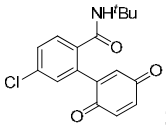
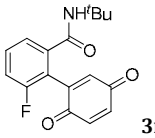
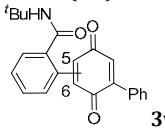
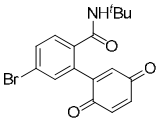
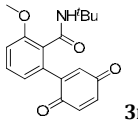
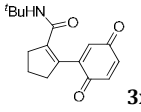
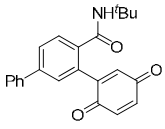
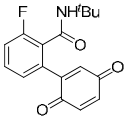
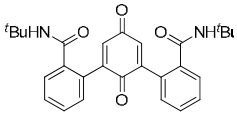
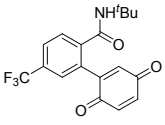
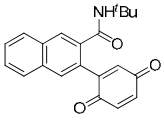
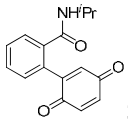
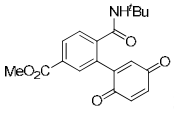
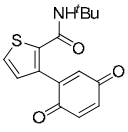
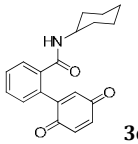
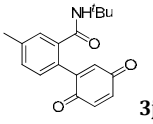
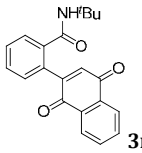
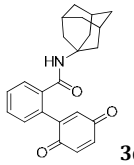
It is noteworthy that a C–H insertion/lactonization product **4a** was observed during the screening studies. It has been reported that the coupling of benzoic acid and benzoquinone afforded the same 2-hydroxy-*6H*-benzo[*c*]chromen-6-one under Ir(III) catalysis, however a rather high catalyst loading and a relatively high temperature were necessary to give synthetically useful yields [91]. Encouraged by these results, the reaction parameters were optimized for the synthesis of **4a**. It was found that benzamides bearing methyl (**4b**), chloro (**4c**), and bromo (**4d**) groups at the 3- or 4- position underwent smoothly coupling under these redox-neutral conditions in acetone to give lactones in moderate to good yields (Scheme 1). However, we attempted but failed to achieve this type reaction for 1,4-naphthoquinone, where only quinone **3r** was isolated. We noted that lactonization via C–H activation of other amides has been reported [92–94].

To probe the mechanism of this direct arylation of quinones, preliminary mechanistic studies were carried out. A notable primary kinetic isotope effect (KIE, k_H/k_D = 4.6) was observed, indicating that C–H bond cleavage of **1a** is probably involved in the rate-limiting step. Furthermore, a competition reaction has been performed, where two benzamides **1b** and **1e** differing in electronic effects were allowed to compete in the coupling with **2a** (**1b**:**1e**:**2a** = 1:1:1 ratio). ^1H NMR analysis of the resulting mixture revealed that **3b** and **3e** were generated in 2.2:1 ratio, suggesting that coupling of an electron-rich arene is faster than that of a more electron-deficient one.

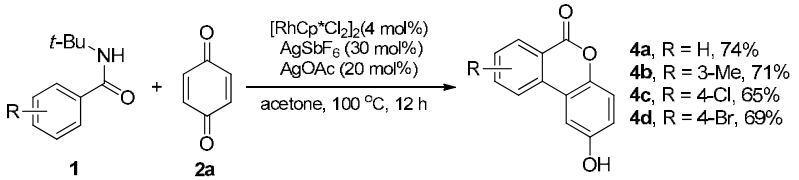
Based on these experiments and literature precedents [58,95], a plausible mechanism is proposed in Scheme 2. O-Coordination of the amide to the Rh(III) center and subsequent *ortho* C–H bond activation afforded a five-membered rhodacyclic intermediate **A**. Insertion of quinone **2a** to Rh–C bond of **A** gave a seven-membered rhodacycle **B**, which is followed by epimerization at one of the α-positions, allowing for β-hydrogen elimination to provide the desired product **3a** together with the Rh(I) species (with elimination of HX). The Rh(I) was re-oxidized by Ag_2CO_3 to regenerate Rh(III) for the next catalytic cycle.

Table 2
Substrate scope.

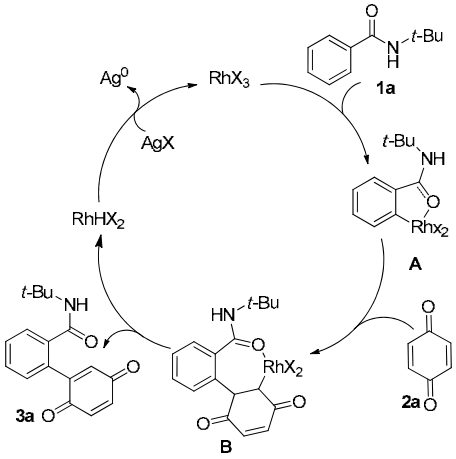


Entry	Product	Isolated yield (%)	Entry	Product	Isolated yield (%)	Entry	Product	Isolated yield (%)
1	 **3a**	85	11	 **3k**	27	21	 **3s**	64
2	 **3b**	80	12	 **3k'**	46	22	 **3t** (major:minor = 2:1)	73
3	 **3c**	75	13	 **3l**	38	23	 **3u** (major:minor = 6:1)	64
4	 **3d**	62	14	 **3l'**	36	24	 **3v** (1:1)	62
5	 **3e**	66	15	 **3m**	67	25	 **3w** (major:minor = 6:1)	70
6	 **3f**	68	16	 **3n**	68	26	 **3x**	52
7	 **3g**	71	17	 **3o**	43	27 [a]	 **3aa**	49
8	 **3h**	52	18	 **3p**	76	28	 **3ba**	62
9	 **3i**	39	19	 **3q**	65	29	 **3ca**	71
10	 **3j**	75	20	 **3r**	90	30	 **3da**	77

Reaction conditions: $[RhCp^*Cl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), Ag_2CO_3 (0.4 mmol), **1** (0.20 mmol), and **2** (0.30 mmol) in dioxane (3 mL) at 100 °C under nitrogen for 12 h. [a] **1a** (0.6 mmol), **2a** (0.2 mmol) and Ag_2CO_3 (0.8 mmol) were used.



Scheme 1. Rh(III)-catalyzed synthesis of 2-hydroxy-*6H*-benzo[*c*]chromen-6-ones.



Scheme 2. Proposed mechanism of arylation of quinones.

4. Conclusions

We have developed Rh(III)-catalyzed C–H activation of *N*-(alkyl)benzamides in the coupling with quinones. A broad scope of substrates has been examined and good functional group compatibility has been realized. In addition 2-hydroxy-*6H*-benzo[*c*]chromen-6-ones were obtained via cascade reaction involving C–H activation and arylation-lactonization reaction. Competition experiment and KIE study were conducted, and a plausible mechanism has been proposed. This method may find useful applications in the synthesis of complex structures.

References

[1] Gutekunst W R, Baran P S. *Chem Soc Rev,* 2011, 40: 1976
[2] Yamaguchi J, Yamaguchi A D, Itami K. *Angew Chem Int Ed,* 2012, 51: 8960
[3] McMurray L, O'Hara F, Gaunt M J. *Chem Soc Rev,* 2011, 40: 1885
[4] Daugulis O, Do H Q, Shabashov D. *Acc Chem Res,* 2009, 42: 1074
[5] Ackermann L, Vicente R, Kapdi A R. *Angew Chem Int Ed,* 2009, 48: 9792
[6] Lyons T W, Sanford M S. *Chem Rev,* 2010, 110: 1147
[7] Colby D A, Bergman R G, Ellman J A. *Chem Rev,* 2010, 110: 624
[8] Ackermann L. *Chem Rev,* 2011, 111: 1315
[9] Wencel-Delord J, Droge T, Liu F, Glorius F. *Chem Soc Rev,* 2011, 40: 4740
[10] Yeung C S, Dong V M. *Chem Rev,* 2011, 111: 1215
[11] Cho S H, Kim J Y, Kwak J, Chang S. *Chem Soc Rev,* 2011, 40: 5068
[12] Wendlandt A E, Suess A M, Stahl S S. *Angew Chem Int Ed,* 2011, 50: 11062
[13] Kuhl N, Hopkinson M N, Wencel-Delord J, Glorius F. *Angew Chem Int Ed,* 2012, 51: 10236
[14] Wu X F, Neumann H, Beller M. *Chem Rev,* 2012, 113: 1
[15] Engle K M, Mei T S, Wasa M, Yu J Q. *Acc Chem Res,* 2012, 45: 788
[16] Li D D, He C L, Cai H T, Wang G W. *Chin J Org Chem*, 2013, 33: 203
[17] Yan G B, Wu X M, Yang M H. *Org Biomol Chem,* 2013, 11: 5558
[18] Ackermann L. *Acc Chem Res,* 2014, 47: 281
[19] Zhang M, Zhang Y F, Jie X M, Zhao H Q, Li G, Su W P. *Org Chem Front*, 2014, 1: 843
[20] Colby D A, Tsai A S, Bergman R G, Ellman J A. *Acc Chem Res,* 2011, 45: 814
[21] Song G Y, Wang F, Li X W. *Chem Soc Rev,* 2012, 41: 3651
[22] Kuhl N, Schröder N, Glorius F. *Adv Synth Catal,* 2014, 356: 1443
[23] Rakshit S, Grohmann C, Besset T, Glorius F. *J Am Chem Soc,* 2011, 133: 2350
[24] Huang X L, Huang J S, Du C L, Zhang X Y, Song F J, You J S. *Angew Chem Int Ed,* 2013, 52: 12970
[25] Liu B Q, Fan Y, Gao Y, Sun C, Xu C, Zhu J. *J Am Chem Soc,* 2013, 135: 468
[26] Neely J M, Rovis T. *J Am Chem Soc,* 2013, 135: 66
[27] Shen Y Y, Liu G X, Zhou Z, Lu X Y. *Org Lett,* 2013, 15: 3366
[28] Unoh Y, Hashimoto Y, Takeda D, Hirano K, Satoh T, Miura M. *Org Lett,* 2013, 15: 3258
[29] Zhang X S, Zhu Q L, Zhang Y F, Li Y B, Shi Z J. *Chem Eur J,* 2013, 19: 11898
[30] Dong Y, Liu G. *Chem Commun,* 2013, 49: 8066
[31] Li B, Ma J F, Xie W J, Song H B, Xu S S, Wang B Q. *Chem Eur J,* 2013, 19: 11863
[32] Zhao P, Wang F, Han K L, Li X W. *Org Lett,* 2012, 14: 3400
[33] Zhao P, Niu R, Wang F, Han K L, Li X W. *Org Lett,* 2012, 14: 4166
[34] Zhang T, Wu L M, Li X W. *Org Lett,* 2013, 15: 6294
[35] Wang F, Song G Y, Du Z Y, Li X W. *J Org Chem,* 2011, 76: 2926
[36] Wang F, Song G Y, Li X W. *Org Lett,* 2010, 12: 5430
[37] Umeda N, Hirano K, Satoh T, Miura M. *J Org Chem,* 2009, 74: 7094
[38] Guimond N, Gouliaras C, Fagnou K. *J Am Chem Soc,* 2010, 132: 6908
[39] Du Y, Hyster T K, Rovis T. *Chem Commun,* 2011, 47: 12074
[40] Hesp K D, Bergman R G, Ellman J A. *J Am Chem Soc,* 2011, 133: 11430
[41] Li Y, Li B J, Wang W H, Huang W P, Zhang X S, Chen K, Shi Z J. *Angew Chem Int Ed,* 2011, 50: 2115
[42] Tsai A S, Tauchert M E, Bergman R G, Ellman J A. *J Am Chem Soc,* 2011, 133: 1248
[43] Zhu C, Xie W Q, Falck J R. *Chem Eur J,* 2011, 17: 12591
[44] Chan W W, Lo S F, Zhou Z Y, Yu W Y. *J Am Chem Soc,* 2012, 134: 13565
[45] Karthikeyan J, Haridharan R, Cheng C H. *Angew Chem Int Ed,* 2012, 51: 12343
[46] Kim J Y, Park S H, Ryu J, Cho S H, Kim S H, Chang S. *J Am Chem Soc,* 2012, 134: 9110
[47] Schröder N, Wencel-Delord J, Glorius F. *J Am Chem Soc,* 2012, 134: 8298
[48] Wencel-Delord J, Nimphius C, Wang H G, Glorius F. *Angew Chem Int Ed,* 2012, 51: 13001

Graphical Abstract

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Rh(III)-catalyzed C–H activation of benzamides: Coupling with quinones

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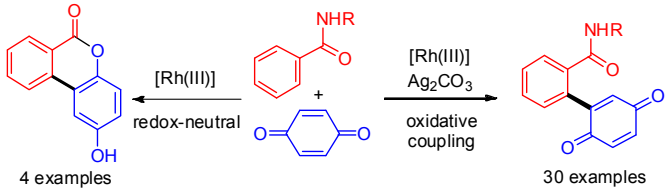

Rh(III)-catalyzed C–H activation of *N*-(alkyl)benzamides in the oxidative coupling with various quinones. In addition, under redox-neutral conditions, 2-hydroxy-*6H*-benzo[*c*]chromen-6-ones were also obtained via a cascade of cross-coupling followed by lactonization.

[49] Cui S L, Zhang Y, Wu Q F. *Chem Sci,* 2013, 4: 3421
[50] Gong T J, Xiao B, Cheng W M, Su W, Xu J, Liu Z J, Liu L, Fu Y. *J Am Chem Soc,* 2013, 135: 10630
[51] Hyster T K, Ruhl K E, Rovis T. *J Am Chem Soc,* 2013, 135: 5364
[52] Li X W, Yu S J, Wang F, Wan B S, Yu X Z. *Angew Chem Int Ed,* 2013, 52: 2577
[53] Zhen W C, Du Z Y, Li X W. *Chin J Catal*, 2013, 34: 679
[54] Lian Y J, Hummel J R, Bergman R G, Ellman J A. *J Am Chem Soc,* 2013, 135: 12548
[55] Qi Z S, Li X W. *Angew Chem Int Ed,* 2013, 52: 8995
[56] Xie F, Qi Z S, Li X W. *Angew Chem Int Ed,* 2013, 52: 11862
[57] Zeng R, Wu S Z, Fu C L, Ma S M. *J Am Chem Soc,* 2013, 135: 18284
[58] Samanta R, Narayan R, Antonchick A P. *Org Lett,* 2012, 14: 6108
[59] Wang F, Song G Y, Du Z Y, Li X W. *J Org Chem*, 2011, 76: 2926
[60] Yang L, Correia C A, Li C J. *Org Biomol Chem,* 2011, 9: 7176
[61] Yang L, Qian B, Huang H M. *Chem Eur J,* 2012, 18: 9511
[62] Zhu C, Falck J R. *Chem Commun*, 2012, 48: 1674
[63] Zhang X Y, Wang F, Qi Z S, Yu S J, Li X W. *Org Lett,* 2014, 16: 1586
[64] Gould S J. *Chem Rev,* 1997, 97: 2499
[65] Marco-Contelles J, Molina M T. *Curr Org Chem,* 2003, 7: 1433
[66] Liu J K. *Chem Rev,* 2006, 106: 2209
[67] Zhang B, Salituro G, Szalkowski D, Li Z H, Zhang Y, Royo I, Vilella D, Díez M T, Pelaez F, Ruby C, Kendall R L, Mao X Z, Griffin P, Calaycay J, Zierath J R, Heck J V, Smith R G, Moller D E. *Science,* 1999, 284: 974
[68] Koyama J. *Recent Pat Anti-Infect Drug Discovery,* 2006, 1: 113
[69] Verma R P. *Anti-Cancer Agents Med Chem*, 2006, 6: 489
[70] Babula P, Adam V, Havel L, Kizek R. *Ceska Slovens Farm,* 2007, 56: 114
[71] Ferreira I C F R, Vaz J A, Vasconcelos M H, Martins A. *Anti-Cancer Agents Med Chem*, 2010, 10: 424
[72] Dandawate P R, Vyas A C, Padhye S B, Singh M W, Baruah J B. *Mini-Rev Med Chem,* 2010, 10: 436
[73] Nowicka B, Kruk J. *Biochim Biophys Acta,* 2010, 1797: 1587
[74] Cramer W A, Crofts A R. In: Photosynthesis. Vol. 1. New York: Academic Press, 1982. 387–467
[75] Bechtold T. In: Bechtold T, Mussak R, Eds. Handbook of Natural Colorants. New York: Wiley, 2009. 151–182
[76] Lin A J, Sartorelli A C. *J Med Chem,* 1976, 19: 1336
[77] Fujiwara Y, Domingo V, Seiple I B, Gianatassio R, Del Bel M, Baran P S. *J Am Chem Soc,* 2011, 133: 3292
[78] Wang J, Wang S, Wang G, Zhang J, Yu X Q. *Chem commun,* 2012, 48: 11769
[79] Deb A, Manna S, Maji A, Dutta U, Maiti D. *Eur J Org Chem,* 2013, 2013: 5251
[80] Echavarren A M, de Frutos Ó, Tamayo N, Noheda P, Calle P. *J Org Chem,* 1997, 62: 4524
[81] Tamayo N, Echavarren A M, Paredes M C. *J Org Chem,* 1991, 56: 6488
[82] Liebeskind L S, Riesinger S W. *J Org Chem,* 1993, 58: 408
[83] Gan X W, Jiang W, Wang W, Hu L H. *Org Lett,* 2009, 11: 589
[84] Itahara T. *J Org Chem,* 1985, 50: 5546
[85] Engler T A, Reddy J P. *J Org Chem,* 1991, 56: 6491
[86] Molina M T, Navarro C, Moreno A, Csákÿ A G. *Org Lett,* 2009, 11: 4938
[87] Demchuk O M, Pietrusiewicz K M. *Syntlett,* 2009: 1149
[88] Zhang S, Song F J, Zhao D B, You J S. *Chem Commun,* 2013, 49: 4558
[89] de Oliveira R A, Carazza F, da Silva Pereira M O. *Synth Commun,* 2000, 30: 4563
[90] Yoshida K, Oga N, Kadota M, Ogasahara Y, Kubo Y. *J Chem Soc, Chem Commun,* 1992: 1114
[91] Engelman K L, Feng Y, Ison E A. *Organometallics,* 2011, 30: 4572
[92] Zeng R, Fu C L, Ma S M. *J Am Chem Soc,* 2012, 134: 9597
[93] Wang F, Qi Z S, Sun J Q, Zhang X L, Li X W. *Org Lett,* 2013, 15: 6290
[94] Yang W, Sun J Q, Xu X X, Zhang Q, Liu Q. *Chem Commun,* 2014, 50: 4420
[95] Ryu J, Shin K, Park S H, Kim J Y, Chang S. *Angew Chem Int Ed,* 2012, 51: 9904

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