

Supporting Information

Rhodium-Catalysed Additive-Free Carbonylation of Benzamides with Diethyl Dicarbonate as a Carbonyl Source

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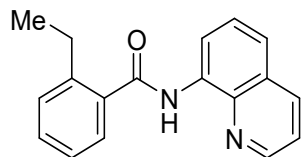
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1. General Information

All reactions were performed in an oven-dried glassware using Schlenk techniques under argon atmosphere, unless otherwise noted. ^1H , ^{13}C NMR, and ^{19}F NMR spectra were recorded on a JEOL ECA 500II (500 MHz for ^1H , 125 MHz for ^{13}C , and 470 MHz for ^{19}F) spectrometer in CDCl_3 . Tetramethylsilane (TMS) served as an internal standard (for ^1H , $\delta = 0$), CDCl_3 served as an internal standard (for ^{13}C , $\delta = 77.0$), and fluorobenzene served as an internal standard (for ^{19}F , $\delta = -113.2$). IR spectra were recorded on an FT/IR-4600 (JASCO Co., Ltd.). ESI-MS were measured on a Bruker ESI-TOF-MS. Preparative thin-layer chromatography (PTLC) was performed on Wakogel® B-5F. Flash column chromatography was performed on Wakogel® C-200 (75-150 μm).

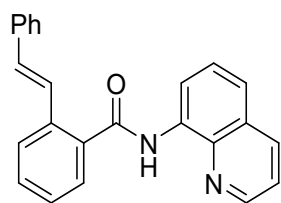
Materials. Tetrahydrofuran (THF) was purchased from Kanto Chemical as “Dehydrated Solvent System”. *N*-methylpyrrolidone (NMP) was purchased from FUJIFILM Wako Pure Chemicals Corporation. Other solvents were purchased from Nacalai Tesque Inc.. $\text{Rh}(\text{acac})(\text{CO})_2$ was purchased from Sigma-Aldrich. Diethyl dicarbonate was purchased from FUJIFILM Wako Pure Chemicals Corporation. NH_3 in MeOH, EtOD were purchased from Tokyo Chemical Industry Co, Ltd. Diethyl carbonate **7** was purchased from Nacalai Tesque Inc. All reagents were used without further purification. $[\text{RhOPiv}(\text{cod})]_2$,¹ $[\text{Rh}(\text{OAc})(\text{cod})]_2$ ² and $[\text{RhCl}(\text{cod})]_2$ ³ were synthesised according to the literature. Benzamides **1** and **6** were synthesised according to the literature.⁴⁻⁶ Benzamide **5** was synthesised according to the literature.⁷

2. Characterisation of New Benzamides 1



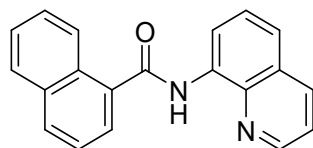
2-Ethyl-*N*-(quinolin-8-yl)benzamide (1b):

The title compound was obtained as a white solid; mp: 63.1–64.1 °C; ¹H NMR (500 MHz, CDCl₃) δ: 10.18 (s, 1H), 8.95 (d, *J* = 8.0 Hz, 1H), 8.76 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.17 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.64 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.55 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.44–7.43 (m, 2H), 7.35 (d, *J* = 6.9 Hz, 1H), 7.32 (td, *J* = 7.4, 1.1 Hz, 1H), 2.95 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 168.4, 148.2, 142.8, 138.6, 136.5, 136.3, 134.8, 130.4, 129.7, 128.0, 127.4, 127.2, 126.0, 121.8, 121.6, 116.5, 26.5, 16.0; IR (neat): 3347, 2968, 1676, 1531, 1483, 1464, 1457, 1389, 1329, 1266, 820, 787, 760, 747, 678, 606 cm⁻¹; HRMS (ESI-TOF): calcd for C₁₈H₁₆N₂NaO⁺: [M + Na]⁺ = 299.1155, found 299.1146.



(*E*)-*N*-(Quinolin-8-yl)-2-styrylbenzamide (1f):

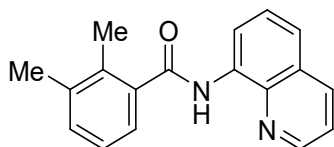
The title compound was obtained as a brown solid; mp: 117.4–118.3 °C; ¹H NMR (500 MHz, CDCl₃) δ: 10.32 (s, 1H), 8.98 (d, *J* = 7.4 Hz, 1H), 8.48 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.12 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.79 (dd, *J* = 13.7, 8.0 Hz, 2H), 7.68 (d, *J* = 16.0 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.52 (dd, *J* = 14.9, 7.4 Hz, 2H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.35 (dd, *J* = 8.6, 4.0 Hz, 1H), 7.29–7.23 (m, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 16.6 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 167.5, 148.2, 138.6, 137.1, 136.3, 136.2, 135.5, 134.7, 132.1, 130.7, 128.5, 128.3, 127.9, 127.8, 127.6, 127.4, 126.9, 126.7, 126.2, 121.9, 121.6, 116.7; IR (neat): 3353, 3069, 3013, 1680, 1594, 1524, 1486, 1426, 1387, 1327, 1249, 982, 972, 828, 793, 770, 689 cm⁻¹; HRMS (ESI-TOF): calcd for C₂₄H₁₈N₂NaO⁺: [M + Na]⁺ = 373.1311, found 373.1329.



N-(Quinolin-8-yl)-1-naphthamide (1g):

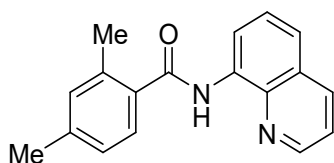
The title compound was obtained as a white solid; mp: 144.3–145.3 °C; ¹H NMR (500 MHz, CDCl₃) δ: 10.88 (s, 1H), 8.99 (d, *J* = 7.4 Hz, 1H), 8.87 (dd, *J* = 4.3, 1.4 Hz, 1H), 8.59 (s, 1H), 8.21–8.09 (m, 2H), 8.06–7.96 (m, 2H), 7.90 (dd, *J*

= 6.9, 2.3 Hz, 1H), 7.64–7.52 (m, 4H), 7.50–7.44 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ : 165.4, 148.3, 138.8, 136.4, 134.9, 134.6, 132.7, 132.3, 129.2, 128.7, 128.0, 127.9, 127.8, 127.8, 127.5, 126.8, 123.7, 121.7, 121.7, 116.6; IR (neat): 3356, 3071, 3048, 1668, 1531, 1487, 1457, 1428, 1388, 1325, 910, 836, 828, 770 cm^{-1} ; HRMS (ESI-TOF): calcd for $\text{C}_{20}\text{H}_{14}\text{N}_2\text{NaO}^+$: $[\text{M} + \text{Na}]^+ = 321.0998$, found 321.0990.



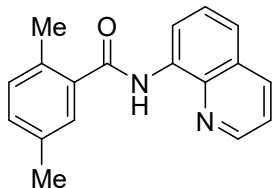
2,3-Dimethyl-N-(quinolin-8-yl)benzamide (1h):

The title compound was obtained as a white solid; mp: 136.0–137.0 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ : 10.13 (s, 1H), 8.96 (d, $J = 7.4$ Hz, 1H), 8.74 (dd, $J = 4.0, 1.7$ Hz, 1H), 8.15 (dd, $J = 8.3, 1.4$ Hz, 1H), 7.59 (t, $J = 8.0$ Hz, 1H), 7.53 (dd, $J = 8.3, 1.4$ Hz, 1H), 7.47 (d, $J = 7.4$ Hz, 1H), 7.42 (dd, $J = 8.0, 4.0$ Hz, 1H), 7.28 (d, $J = 7.4$ Hz, 1H), 7.21 (t, $J = 7.4$ Hz, 1H), 2.45 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 169.0, 148.2, 138.5, 138.1, 137.6, 136.3, 134.7, 134.5, 131.5, 127.9, 127.4, 125.6, 124.7, 121.7, 121.6, 116.5, 20.3, 16.4; IR (neat): 3351, 3011, 2948, 1669, 1523, 1485, 1459, 1386, 1326, 830, 797, 689 cm^{-1} ; HRMS (ESI-TOF): calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{NaO}^+$: $[\text{M} + \text{Na}]^+ = 299.1155$, found 299.1155.



2,4-Dimethyl-N-(quinolin-8-yl)benzamide (1i):

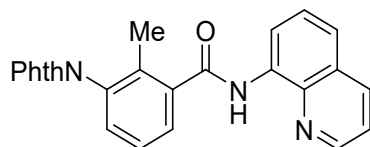
The title compound was obtained as a white solid; mp: 76.0–76.9 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ : 10.66 (s, 1H), 8.94 (d, $J = 7.4$ Hz, 1H), 8.86 (dd, $J = 4.3, 1.4$ Hz, 1H), 8.19–8.15 (m, 1H), 7.67 (s, 2H), 7.59 (t, $J = 8.0$ Hz, 1H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.46 (dd, $J = 8.3, 4.3$ Hz, 1H), 7.20 (s, 1H), 2.45–2.43 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ : 165.9, 148.3, 138.8, 138.4, 136.3, 135.2, 134.7, 133.5, 128.0, 128.0, 127.5, 125.0, 121.6, 121.5, 116.5, 116.5, 21.4, 21.3; IR (neat): 3366, 3019, 2921, 1682, 1533, 1486, 1427, 1390, 1331, 1263, 885, 823, 767, 666 cm^{-1} ; HRMS (ESI-TOF): calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{NaO}^+$: $[\text{M} + \text{Na}]^+ = 299.1155$, found 299.1152.



2,5-Dimethyl-N-(quinolin-8-yl)benzamide (1j):

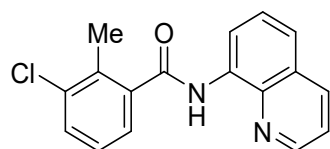
The title compound was obtained as a brown solid; mp: 84.1–85.1 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ : 10.17 (s, 1H), 8.94 (d, $J = 7.4$ Hz, 1H), 8.78 (dd, $J = 4.3, 1.4$ Hz, 1H), 8.17 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.59 (t, $J = 7.7$ Hz, 1H), 7.54 (dd, $J =$

8.3, 1.4 Hz, 1H), 7.48 (s, 1H), 7.44 (dd, $J = 8.0, 4.0$ Hz, 1H), 7.20 (t, $J = 9.5$ Hz, 2H), 2.55 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 168.4, 148.2, 138.6, 136.6, 136.3, 135.6, 134.8, 133.3, 131.2, 131.0, 128.0, 127.8, 127.4, 121.7, 121.6, 116.5, 20.9, 19.7; IR (neat): 3353, 3044, 2924, 1683, 1539, 1505, 1486, 1386, 1330, 822, 790, 677 cm^{-1} ; HRMS (ESI-TOF): calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{NaO}^+$: $[\text{M} + \text{Na}]^+ = 299.1155$, found 299.1152.



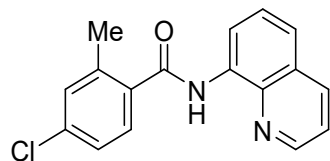
3-(1,3-Dioxisoindolin-2-yl)-2-methyl-N-(quinolin-8-yl)benzamide (1l):

The title compound was obtained as a white solid; mp: 238.9–239.2 °C; ^1H NMR (500 MHz, CDCl_3) δ : 10.24 (s, 1H), 8.94 (d, $J = 7.4$ Hz, 1H), 8.80 (dd, $J = 4.3, 1.4$ Hz, 1H), 8.19 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.98 (dd, $J = 5.4, 3.2$ Hz, 2H), 7.85–7.77 (m, 3H), 7.63–7.55 (m, 2H), 7.52–7.45 (m, 2H), 7.38 (d, $J = 8.0$ Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 167.3, 167.2, 148.4, 138.8, 138.5, 136.3, 135.5, 134.5, 134.5, 131.9, 131.9, 130.9, 128.3, 128.0, 127.3, 127.0, 123.9, 122.0, 121.7, 116.6, 15.2; IR (neat): 3359, 3064, 1677, 1534, 1488, 1429, 1393, 1332, 823, 790, 775, 764, 747, 667 cm^{-1} ; HRMS (ESI-TOF): calcd for $\text{C}_{25}\text{H}_{17}\text{N}_3\text{NaO}_3^+$: $[\text{M} + \text{Na}]^+ = 430.1162$, found 430.1180.



3-Chloro-2-methyl-N-(quinolin-8-yl)benzamide (1m):

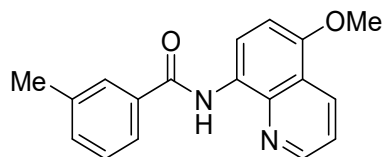
The title compound was obtained as a white solid; mp: 160.5–161.1 °C; ^1H NMR (500 MHz, CDCl_3) δ : 10.13 (s, 1H), 8.92 (dd, $J = 7.4, 1.1$ Hz, 1H), 8.77 (dd, $J = 4.0, 1.7$ Hz, 1H), 8.18 (dd, $J = 8.3, 1.4$ Hz, 1H), 7.63–7.55 (m, 2H), 7.53 (d, $J = 7.4$ Hz, 1H), 7.50 (d, $J = 8.0$ Hz, 1H), 7.46 (dd, $J = 8.3, 4.3$ Hz, 1H), 7.26 (t, $J = 7.7$ Hz, 1H), 2.59 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 167.4, 148.3, 139.1, 138.5, 136.4, 136.0, 134.4, 134.4, 131.0, 128.0, 127.4, 127.0, 125.5, 122.1, 121.7, 116.7, 17.2; IR (neat): 3359, 3064, 1676, 1534, 1488, 1429, 1393, 1332, 823, 790, 775, 764, 747, 667 cm^{-1} ; HRMS (ESI-TOF): calcd for $\text{C}_{17}\text{H}_{13}\text{ClN}_2\text{NaO}^+$: $[\text{M} + \text{Na}]^+ = 319.0609$, found 319.0595.



4-Chloro-2-methyl-N-(quinolin-8-yl)benzamide (1n):

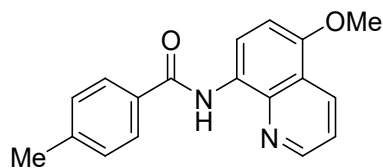
The title compound was obtained as a white solid; mp: 99.1–100.1 °C; ^1H NMR (500 MHz, CDCl_3) δ : 10.19 (s, 1H), 8.91 (d, $J = 6.9$ Hz, 1H), 8.79 (dd, $J = 4.3, 1.4$ Hz, 1H), 8.19 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.65–7.55 (m, 3H), 7.47 (dd, $J =$

8.0, 4.0 Hz, 1H), 7.33–7.29 (m, 2H), 2.59 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 167.1, 148.3, 138.8, 138.6, 136.4, 136.1, 134.5, 131.3, 128.7, 128.0, 127.4, 126.2, 122.0, 122.0, 121.7, 116.6, 20.1; IR (neat): 3393, 3345, 3058, 3048, 2930, 1684, 1596, 1569, 1534, 1490, 1483, 1427, 1383, 1331, 1115, 907, 824, 788 cm^{-1} ; HRMS (ESI-TOF): calcd for $\text{C}_{17}\text{H}_{13}\text{ClN}_2\text{NaO}^+$: $[\text{M} + \text{Na}]^+ = 319.0609$, found 319.0602.



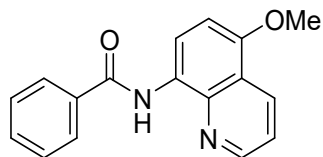
***N*-(5-Methoxyquinolin-8-yl)-3-methylbenzamide (1o):**

The title compound was obtained as a white solid; mp: 124.2–125.0 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ : 10.46 (s, 1H), 8.88–8.85 (m, 2H), 8.60 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.86 (t, $J = 8.0$ Hz, 2H), 7.49–7.44 (m, 1H), 7.42 (t, $J = 7.4$ Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 1H), 6.90 (d, $J = 8.6$ Hz, 1H), 4.01 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 165.3, 150.4, 148.7, 139.5, 138.6, 135.4, 132.3, 131.3, 128.6, 128.1, 127.9, 124.1, 120.7, 120.5, 116.7, 104.4, 55.8, 21.5; IR (neat): 3362, 2933, 1658, 1598, 1587, 1538, 1497, 1487, 1399, 1266, 1091, 826, 815, 793, 731 cm^{-1} ; HRMS (ESI-TOF): calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{NaO}_2^+$: $[\text{M} + \text{Na}]^+ = 315.1104$, found 315.1108.



***N*-(5-Methoxyquinolin-8-yl)-4-methylbenzamide (1p):**

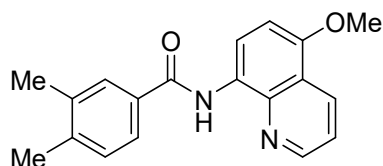
The title compound was obtained as a white solid; mp: 142.3–143.2 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ : 10.47 (s, 1H), 8.87–8.84 (m, 2H), 8.60 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.97 (d, $J = 8.0$ Hz, 2H), 7.46 (dd, $J = 8.3, 4.3$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 2H), 6.90 (d, $J = 8.6$ Hz, 1H), 4.01 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 165.1, 150.3, 148.7, 142.0, 139.5, 132.5, 131.3, 129.4, 128.1, 127.2, 120.7, 120.5, 116.6, 104.4, 55.8, 21.5; IR (neat): 3381, 2993, 2950, 1675, 1596, 1551, 1498, 1398, 1280, 1266, 1189, 1091, 834, 783 cm^{-1} ; HRMS (ESI-TOF): calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{NaO}_2^+$: $[\text{M} + \text{Na}]^+ = 315.1104$, found 315.1113.



***N*-(5-Methoxyquinolin-8-yl)benzamide (1q):**

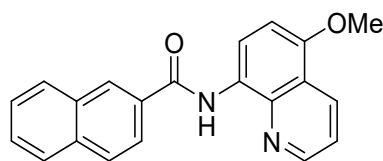
The title compound was obtained as a yellow solid; mp: 153.6–154.6 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ : 10.50 (s, 1H), 8.88–8.84 (m, 2H), 8.59 (dd, $J = 8.3, 1.4$ Hz, 1H), 8.07 (dd, $J = 7.7, 1.4$ Hz, 2H), 7.57–7.51 (m, 3H), 7.46 (dd, $J = 8.6,$

4.0 Hz, 1H), 6.89 (d, J = 8.6 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 165.1, 150.4, 148.7, 139.5, 135.4, 131.6, 131.3, 128.7, 128.0, 127.2, 120.8, 120.5, 116.7, 104.4, 55.8; IR (neat): 3381, 3059, 1675, 1596, 1584, 1548, 1494, 1397, 1279, 1263, 1092, 883, 786, 696, 685 cm^{-1} ; HRMS (ESI-TOF): calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{NaO}_2^+$: $[\text{M} + \text{Na}]^+ = 301.0947$, found 301.0935.



***N*-(5-Methoxyquinolin-8-yl)-3,4-dimethylbenzamide (1r):**

The title compound was obtained as a yellow solid; mp: 151.0–151.6 °C; ^1H NMR (500 MHz, CDCl_3) δ : 9.95 (s, 1H), 8.84 (d, J = 8.6 Hz, 1H), 8.74 (dd, J = 4.0, 1.7 Hz, 1H), 8.53 (dd, J = 8.0, 1.7 Hz, 1H), 7.58 (d, J = 8.6 Hz, 1H), 7.38 (dd, J = 8.3, 4.3 Hz, 1H), 7.09 (d, J = 5.2 Hz, 2H), 6.84 (d, J = 8.6 Hz, 1H), 3.96 (s, 3H), 2.58 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 167.7, 150.2, 148.5, 140.1, 139.2, 136.6, 133.8, 132.0, 131.1, 128.2, 127.2, 126.5, 120.6, 120.3, 116.4, 104.2, 55.6, 21.2, 20.1; IR (neat): 3377, 2998, 1675, 1596, 1540, 1498, 1397, 1277, 1259, 1156, 1089, 826, 787, 653 cm^{-1} ; HRMS (ESI-TOF): calcd for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{NaO}_2^+$: $[\text{M} + \text{Na}]^+ = 329.1260$, found 329.1249.

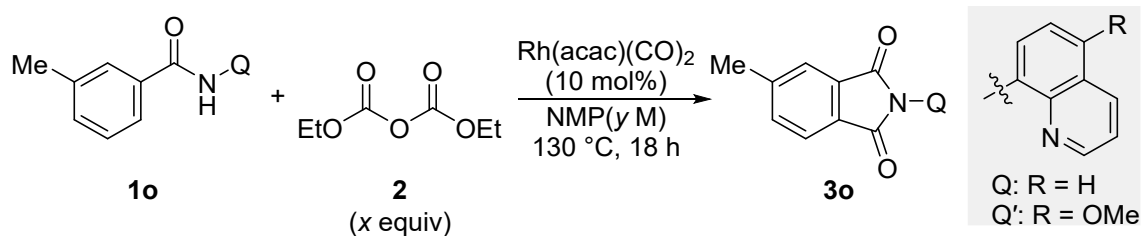


***N*-(5-Methoxyquinolin-8-yl)-2-naphthamide (1s):**

The title compound was obtained as a brown solid; mp: 161.2–162.2 °C; ^1H NMR (500 MHz, CDCl_3) δ : 10.65 (s, 1H), 8.94–8.87 (m, 2H), 8.62 (dd, J = 8.6, 1.7 Hz, 1H), 8.60–8.58 (m, 1H), 8.13 (dd, J = 8.6, 1.7 Hz, 1H), 8.04 (dd, J = 6.6, 2.6 Hz, 1H), 7.99 (d, J = 8.6 Hz, 1H), 7.92 (dd, J = 6.6, 2.6 Hz, 1H), 7.63–7.55 (m, 2H), 7.48 (dd, J = 8.6, 4.0 Hz, 1H), 6.92 (d, J = 8.6 Hz, 1H), 4.03 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 165.1, 150.5, 148.8, 139.5, 134.8, 132.8, 132.6, 131.3, 129.2, 128.6, 128.1, 127.8, 127.8, 127.7, 126.7, 123.7, 120.8, 120.5, 116.8, 104.4, 55.8; IR (neat): 3366, 3055, 1652, 1539, 1498, 1442, 1395, 1276, 1265, 1089, 861, 842, 770 cm^{-1} ; HRMS (ESI-TOF): calcd for $\text{C}_{21}\text{H}_{16}\text{N}_2\text{NaO}_2^+$: $[\text{M} + \text{Na}]^+ = 351.1104$, found 351.1109.

3. Rhodium-Catalysed Carbonylation of Benzamides 1

3.1. Optimisation of Reaction Conditions for Rhodium-Catalysed Carbonylation of Benzamide 1^a



Entry	<i>x</i>	<i>y</i>	R	Time of slow addition (h)	Yield of 3o (%) ^b
1	1.5	0.3	H	0	26
2 ^c	1.5	0.2	H	6.0	29
3 ^c	2.5	0.2	H	6.0	36
4 ^c	2.5	0.2	OMe	6.0	49
5 ^c	2.5	0.2	OMe	16.0	40

^a Reaction conditions: **1a** (0.2 mmol), **2**, Rh(acac)(CO)₂ (10 mol%) were reacted in NMP at 130 °C for 18 h, unless otherwise noted. ^b Isolated yield. ^c Reaction time was 24 h.

3.2. General Procedure for the Carbonylation of Benzamides **1**

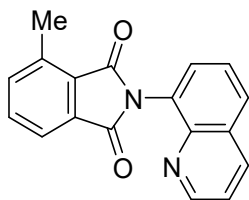
To an oven-dried test tube equipped with a stirring bar charged with benzamide **1** (0.3 mmol) and Rh(acac)(CO)₂ (7.7 mg, 3.0×10^{-2} mmol) was added NMP (0.6 mL). Subsequently, diethyl dicarbonate (**2**, 0.45 mmol) was injected to the solution via a syringe, and the tube was sealed with a PTFE-lined screw cap. The reaction mixture was stirred at 130 °C for 18 h. After cooling to room temperature, the resulting mixture was diluted with EtOAc. The organic layers were washed with water and brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated *in vacuo*, and the residue was purified by preparative thin-layer chromatography.

3.3. General Procedure for the Carbonylation of *meta*- or *para*-Substituted Benzamides **1**

To an oven-dried test tube equipped with a stirring bar charged with benzamide **1** (0.2 mmol) and Rh(acac)(CO)₂ (5.2 mg, 2.0×10^{-2} mmol) was added NMP (1.0 mL). After heating the reaction mixture at 130 °C, diethyl dicarbonate (**2**, 0.5 mmol) was injected over 6 h into the solution using a syringe pump, and the solution was stirred at 130 °C for the next 18 h. After cooling to room temperature, the resulting mixture was diluted with EtOAc. The organic layers were washed with water and brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated *in vacuo*, and the residue was purified by preparative thin-layer chromatography.

3.4. Procedure for a Large-Scale Reaction

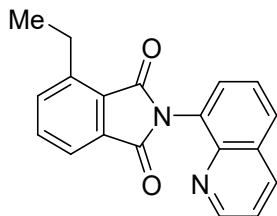
To an oven-dried test tube equipped with a stirring bar charged with benzamide **1a** (262.3 mg, 1.00 mmol) and Rh(acac)(CO)₂ (25.8 mg, 1.00×10^{-1} mmol) was added NMP (2.0 mL). Subsequently, diethyl dicarbonate (**2**, 248.4 mg, 1.53 mmol) was injected to the solution via a syringe, and the tube was sealed with a PTFE-lined screw cap. The reaction mixture was stirred at 130 °C for 18 h. After cooling to room temperature, the resulting mixture was diluted with EtOAc. The organic layers were washed with water and brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated *in vacuo*, and the residue was purified by preparative thin-layer chromatography (THF/toluene = 1/4) to give the product **3a** (231.8 mg, 0.804 mmol, 80%).



4-Methyl-2-(quinolin-8-yl)isoindoline-1,3-dione (3a):

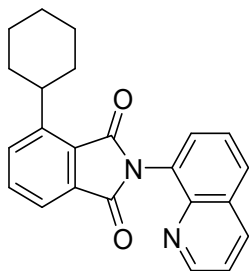
The title compound was obtained as a white solid; purified by preparative TLC (THF/CHCl₃ = 1/50); mp: 204.0–205.0 °C;

¹H NMR (500 MHz, CDCl₃) δ: 8.87 (dd, *J* = 4.6, 1.7 Hz, 1H), 8.22 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 7.4 Hz, 1H), 7.74 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.69–7.62 (m, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.43 (dd, *J* = 8.3, 4.3 Hz, 1H), 2.76 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 168.6, 167.9, 150.8, 144.3, 138.4, 136.5, 136.1, 133.6, 132.8, 130.2, 129.8, 129.5, 129.2, 129.0, 126.0, 121.8, 121.4, 17.7; IR (neat): 3463, 3068, 3012, 2960, 2925, 2857, 1771, 1715, 1591, 1501, 1474, 1396, 1241, 1107, 931, 879, 825, 790, 737, 624 cm⁻¹; HRMS (ESI-TOF): calcd for C₁₈H₁₃N₂O₂⁺: [M + H]⁺ = 281.0972, found 289.0981. The spectral data matched those reported in the literature.⁸



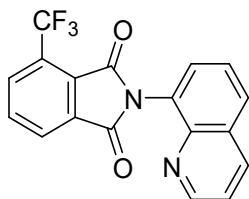
4-Ethyl-2-(quinolin-8-yl)isoindoline-1,3-dione (3b):

The title compound was obtained as a brown solid; purified by preparative TLC (THF/CHCl₃ = 1/50); mp: 182.3–183.3 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.86 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.22 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.83 (d, *J* = 7.4 Hz, 1H), 7.74 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.71–7.65 (m, 2H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.43 (dd, *J* = 8.3, 4.3 Hz, 1H), 3.28–3.12 (m, 2H), 1.33 (t, *J* = 7.7 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 168.5, 168.0, 150.9, 144.9, 144.4, 136.1, 134.9, 134.0, 133.0, 130.3, 129.9, 129.5, 129.3, 128.5, 126.1, 121.8, 121.5, 24.6, 14.8; IR (neat): 3067, 2945, 2934, 2874, 1779, 1766, 1716, 1595, 1502, 1474, 1427, 1395, 1379, 1249, 1109, 884, 825, 791, 765, 742, 624 cm⁻¹; HRMS (ESI-TOF): calcd for C₁₉H₁₅N₂O₂⁺: [M + H]⁺ = 303.1128, found 303.1115.



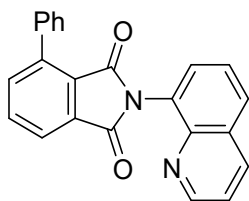
4-Cyclohexyl-2-(quinolin-8-yl)isoindoline-1,3-dione (3c):

The title compound was obtained as a white solid; purified by preparative TLC (EtOAc/hexane = 1/3); mp: 157.9–158.1 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.86 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.20 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.93 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.82 (dd, *J* = 6.0, 2.0 Hz, 1H), 7.74 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.72–7.63 (m, 3H), 7.42 (dd, *J* = 8.3, 4.3 Hz, 1H), 3.83–3.77 (m, 1H), 2.01–1.93 (m, 2H), 1.87–1.80 (m, 2H), 1.76 (d, *J* = 8.0 Hz, 1H), 1.58–1.40 (m, 4H), 1.32–1.22 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 168.7, 167.9, 150.9, 148.8, 144.4, 136.1, 134.1, 132.9, 132.1, 130.3, 129.9, 129.5, 129.2, 127.8, 126.1, 121.8, 121.3, 38.3, 33.7, 33.1, 26.7, 26.6, 26.0; IR (neat): 3071, 2929, 2849, 1776, 1717, 1595, 1501, 1476, 1427, 1401, 1381, 1116, 880, 828, 792, 750, 627 cm⁻¹; HRMS (ESI-TOF): calcd for C₂₃H₂₁N₂O₂⁺: [M + H]⁺ = 357.1598, found 357.1583.



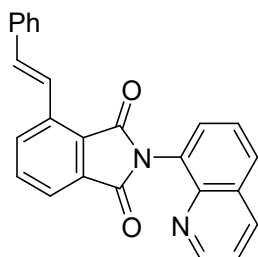
2-(Quinolin-8-yl)-4-(trifluoromethyl)isoindoline-1,3-dione (3d):

The title compound was obtained as a white solid; purified by preparative TLC (EtOAc/hexane = 1/3); mp: 187.8–188.2 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.85 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.26–8.20 (m, 2H), 8.08 (d, *J* = 7.4 Hz, 1H), 7.98 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.94 (t, *J* = 7.7 Hz, 1H), 7.77 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.45 (dd, *J* = 8.3, 4.3 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 166.4, 164.4, 151.0, 144.0, 136.2, 134.4, 134.3, 131.0 (q, *J*_{C-F} = 5.2 Hz), 130.2, 129.9, 129.4, 129.2, 129.2, 127.4 (q, *J*_{C-F} = 36.0 Hz), 126.9, 126.0, 122.0, 122.0 (q, *J*_{C-F} = 273.9 Hz); ¹⁹F NMR (470 MHz, CDCl₃) δ: -61.1; IR (neat): 3080, 1722, 1504, 1476, 1429, 1402, 1326, 1236, 1187, 1173, 1156, 1128, 905, 882, 825, 792, 747 cm⁻¹; HRMS (ESI-TOF): calcd for C₁₈H₉F₃N₂NaO₂⁺: [M + Na]⁺ = 365.0508, found 365.0511.



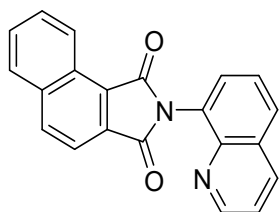
4-Phenyl-2-(quinolin-8-yl)isoindoline-1,3-dione (3e):

The title compound was obtained as a white solid; purified by preparative TLC (THF/CHCl₃ = 1/50); mp: 225.4–226.4 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.84 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.17 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.99 (d, *J* = 6.9 Hz, 1H), 7.90 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 1H), 7.75–7.69 (m, 2H), 7.65–7.58 (m, 3H), 7.46–7.35 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ: 167.5, 167.4, 150.9, 144.2, 141.4, 136.2, 136.2, 136.2, 136.1, 134.0, 133.5, 130.2, 129.8, 129.5, 129.2, 128.5, 128.0, 127.7, 126.0, 122.7, 121.8; IR (neat): 3055, 3029, 1775, 1721, 1593, 1497, 1471, 1397, 1378, 1203, 1177, 1113, 1183, 915, 898, 879, 826, 795, 759, 742, 695 cm⁻¹; HRMS (ESI-TOF): calcd for C₂₃H₁₅N₂O₂⁺: [M + H]⁺ = 351.1128, found 351.1135.



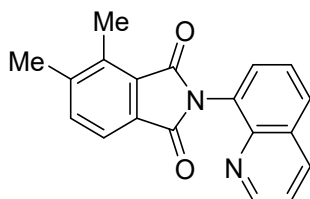
(*E*)-2-(Quinolin-8-yl)-4-styrylisoindoline-1,3-dione (3f):

The title compound was obtained as a white solid; purified by preparative TLC (EtOAc/hexane = 1/3); mp: 239.2–240.2 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.87 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.36 (d, *J* = 16.6 Hz, 1H), 8.23 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.97 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.87 (d, *J* = 6.9 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 2H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.44 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.41–7.32 (m, 3H), 7.28 (t, *J* = 7.4 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 168.7, 167.7, 151.0, 144.4, 137.0, 136.5, 136.2, 133.9, 133.6, 133.2, 130.3, 130.0, 129.9, 129.6, 129.3, 128.7, 128.7, 127.2, 126.9, 126.1, 122.5, 122.3, 121.9; IR (neat): 3062, 2925, 1773, 1716, 1597, 1503, 1475, 1430, 1399, 1111, 967, 882, 825, 793, 758, 694, 626 cm⁻¹; HRMS (ESI-TOF): calcd for C₂₅H₁₇N₂O₂⁺: [M + H]⁺ = 377.1285, found 377.1271.



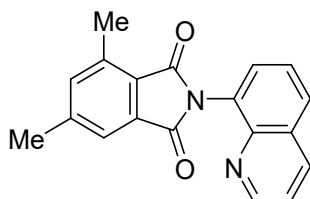
2-(Quinolin-8-yl)-1H-benzo[e]isoindole-1,3(2H)-dione (3g):

The title compound was obtained as a white solid; purified by preparative TLC (THF/CHCl₃ = 1/50); mp: 210.0–210.8 °C; ¹H NMR (500 MHz, CDCl₃) δ: 9.02 (d, *J* = 8.6 Hz, 1H), 8.85 (dd, *J* = 4.3, 1.4 Hz, 1H), 8.24 (t, *J* = 8.3 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.97 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.81 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.76–7.66 (m, 3H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 169.2, 168.5, 150.9, 144.5, 136.7, 136.1, 135.1, 131.6, 130.4, 129.9, 129.5, 129.4, 129.3, 128.7, 128.7, 128.3, 127.6, 126.1, 125.2, 121.8, 118.9; IR (neat): 3065, 1771, 1595, 1502, 1474, 1428, 1395, 1379, 1363, 1157, 1111, 865, 836, 800, 765, 628 cm⁻¹; HRMS (ESI-TOF): calcd for C₂₁H₁₃N₂O₂⁺: [M + H]⁺ = 325.0972, found 325.0980.

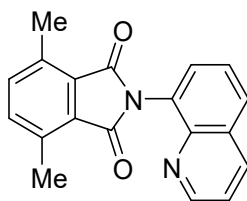


4,5-Dimethyl-2-(quinolin-8-yl)isoindoline-1,3-dione (3h):

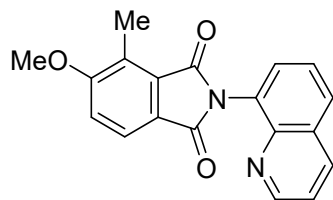
The title compound was obtained as a white solid; purified by preparative TLC (THF/CHCl₃ = 1/50); mp: 217.6–218.6 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.77 (dd, *J* = 4.6, 1.7 Hz, 1H), 8.12 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.86 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.74–7.71 (m, 2H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.33 (dd, *J* = 8.3, 4.3 Hz, 1H), 2.62 (s, 3H), 2.36 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 169.2, 167.9, 150.9, 145.1, 144.4, 137.6, 136.1, 134.7, 130.6, 130.3, 130.1, 129.4, 129.3, 129.1, 126.1, 121.8, 121.2, 20.0, 14.0; IR (neat): 3047, 3012, 2949, 2921, 1770, 1713, 1500, 1474, 1427, 1394, 1241, 1117, 797, 746, 624 cm⁻¹; HRMS (ESI-TOF): calcd for C₁₉H₁₅N₂O₂⁺: [M + H]⁺ = 303.1128, found 303.1140.

**4,6-Dimethyl-2-(quinolin-8-yl)isoindoline-1,3-dione (3i):**

The title compound was obtained as a white solid; purified by preparative TLC (THF/CHCl₃ = 1/50); mp: 204.5–204.9 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.86 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.21 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.94 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.73 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.63 (s, 1H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.34 (s, 1H), 2.71 (s, 3H), 2.50 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 168.7, 168.2, 150.9, 144.8, 144.4, 138.3, 137.0, 136.1, 133.2, 130.3, 130.0, 129.4, 129.3, 126.6, 126.1, 122.1, 121.8, 21.8, 17.7; IR (neat): 3014, 2921, 1767, 1711, 1621, 1503, 1476, 1431, 1396, 1234, 1140, 1107, 878, 835, 802, 786, 751, 623 cm⁻¹; HRMS (ESI-TOF): calcd for C₁₉H₁₅N₂O₂⁺: [M + H]⁺ = 303.1128, found 303.1124.

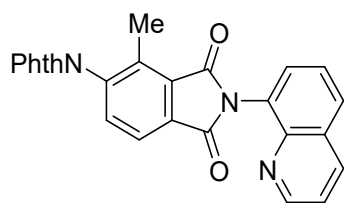
**4,7-Dimethyl-2-(quinolin-8-yl)isoindoline-1,3-dione (3j):**

The title compound was obtained as a white solid; purified by preparative TLC (THF/CHCl₃ = 1/50); mp: 184.6–185.2 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.88 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.22 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.72 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.43 (dd, *J* = 8.6, 4.3 Hz, 1H), 7.40 (s, 2H), 2.71 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ: 168.7, 151.0, 144.5, 136.3, 136.2, 135.9, 130.4, 130.1, 129.4, 129.3, 126.1, 121.8, 99.9, 17.5; IR (neat): 3010, 2925, 1766, 1711, 1595, 1503, 1476, 1403, 1381, 1232, 1117, 915, 835, 817, 788, 758, 626 cm⁻¹; HRMS (ESI-TOF): calcd for C₁₉H₁₅N₂O₂⁺: [M + H]⁺ = 303.1128, found 303.1117.



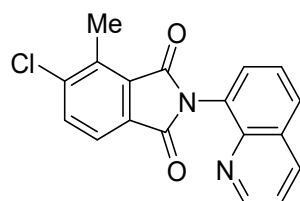
5-Methoxy-4-methyl-2-(quinolin-8-yl)isoindoline-1,3-dione (3k):

The title compound was obtained as a white solid; purified by preparative TLC (THF/CHCl₃ = 1/50); mp: 229.7–230.7 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.86 (dd, *J* = 4.6, 1.7 Hz, 1H), 8.19 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.93 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.72 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.41 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 3.95 (s, 3H), 2.62 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 168.6, 167.7, 163.0, 150.9, 144.4, 136.1, 130.6, 130.3, 130.1, 129.4, 129.2, 128.2, 126.1, 124.1, 123.0, 121.8, 113.5, 56.2, 10.6; IR (neat): 2946, 1770, 1715, 1607, 1502, 1488, 1428, 1397, 1380, 1274, 1245, 1120, 1042, 899, 793, 751, 625 cm⁻¹; HRMS (ESI-TOF): calcd for C₁₉H₁₅N₂O₃⁺: [M + H]⁺ = 319.1077, found 319.1070.



3-(1,3-Dioxoisindolin-2-yl)-2-methyl-N-(quinolin-8-yl)benzamide (3l):

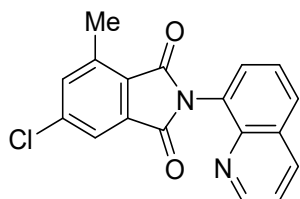
The title compound was obtained as a white solid; purified by preparative TLC (THF/CHCl₃ = 1/5); ¹H NMR (500 MHz, CDCl₃) δ: 8.88 (dd, *J* = 4.3, 1.4 Hz, 1H), 8.21 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.00–7.94 (m, 4H), 7.83 (dd, *J* = 5.2, 3.2 Hz, 2H), 7.75 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.44 (dd, *J* = 8.3, 4.3 Hz, 1H), 2.63 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 167.8, 166.9, 166.7, 166.6, 151.0, 144.2, 137.6, 137.0, 136.1, 134.7, 134.7, 134.6, 134.6, 133.3, 131.7, 130.7, 130.2, 129.6, 129.2, 126.0, 126.0, 124.1, 124.0, 122.0, 121.9, 13.3; IR (neat): 3069, 1779, 1717, 1597, 1501, 1475, 1405, 1379, 1119, 1085, 972, 818, 784, 718 cm⁻¹; HRMS (ESI-TOF): calcd for C₂₆H₁₆N₃O₄⁺: [M + H]⁺ = 434.1135, found 434.1142.



3-Chloro-2-methyl-N-(quinolin-8-yl)benzamide (3m):

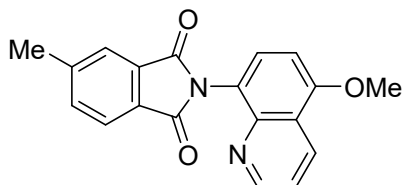
The title compound was obtained as a white solid; purified by preparative TLC (THF/CHCl₃ = 1/50); mp: 194.9–195.9 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.86 (dd, *J* = 4.3, 1.4 Hz, 1H), 8.23 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.97 (dd, *J* = 8.3, 1.4

Hz, 1H), 7.79–7.72 (m, 3H), 7.67 (t, $J = 7.7$ Hz, 1H), 7.45 (dd, $J = 8.3, 4.3$ Hz, 1H), 2.81 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 167.9, 166.9, 151.0, 144.2, 141.9, 140.4, 137.1, 136.3, 134.3, 131.0, 130.3, 129.7, 129.6, 129.3, 126.2, 122.2, 121.9, 14.6; IR (neat): 3071, 2957, 2924, 1772, 1596, 1500, 1474, 1446, 1428, 1394, 1379, 1364, 1176, 1121, 953, 831, 793, 743, 721, 623 cm^{-1} ; HRMS (ESI-TOF): calcd for $\text{C}_{18}\text{H}_{11}\text{ClN}_2\text{NaO}_2^+$: $[\text{M} + \text{Na}]^+ = 345.0401$, found 345.0405.



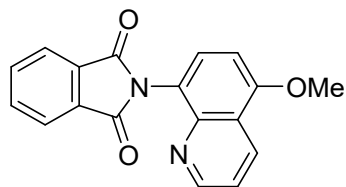
4-Chloro-2-methyl-N-(quinolin-8-yl)benzamide (3n):

The title compound was obtained as a colourless solid; purified by flash column chromatography ($\text{EtOAc}/\text{hexane} = 1/4$); mp: 230.2–231.1 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ : 8.85 (dd, $J = 4.0, 1.7$ Hz, 1H), 8.22 (dd, $J = 8.3, 1.4$ Hz, 1H), 7.96 (dd, $J = 8.3, 1.4$ Hz, 1H), 7.80 (d, $J = 1.7$ Hz, 1H), 7.73 (dd, $J = 7.4, 1.7$ Hz, 1H), 7.67 (t, $J = 7.7$ Hz, 1H), 7.54 (d, $J = 1.1$ Hz, 1H), 7.44 (dd, $J = 8.3, 4.4$ Hz, 1H), 2.74 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 167.8, 166.7, 151.0, 144.2, 140.1, 140.1, 136.2, 136.1, 134.4, 130.2, 129.7, 129.6, 129.3, 127.4, 126.1, 121.9, 121.9, 17.7; IR (neat): 3080, 3009, 2926, 1772, 1719, 1595, 1499, 1473, 1427, 1403, 1362, 1250, 1114, 897, 879, 829, 803, 768, 744, 661, 624 cm^{-1} ; HRMS (ESI-TOF): calcd for $\text{C}_{18}\text{H}_{12}\text{ClN}_2\text{O}_2^+$: $[\text{M} + \text{H}]^+ = 323.0582$, found 323.0577.



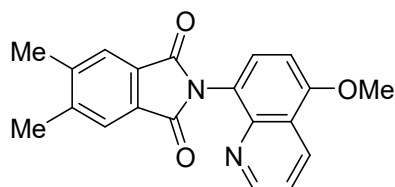
N-(5-Methoxyquinolin-8-yl)-3-methylbenzamide (3o):

The title compound was obtained as a white solid; purified by preparative TLC ($\text{THF}/\text{CHCl}_3 = 1/50$); mp: 232.2–233.1 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ : 8.82 (dd, $J = 4.0, 1.7$ Hz, 1H), 8.59 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.85 (d, $J = 7.4$ Hz, 1H), 7.78 (s, 1H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.39 (dd, $J = 8.6, 4.0$ Hz, 1H), 6.94 (d, $J = 8.0$ Hz, 1H), 4.03 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 168.5, 168.4, 156.2, 151.1, 145.3, 144.8, 134.6, 132.8, 131.0, 130.4, 129.8, 124.2, 123.6, 122.1, 121.6, 120.9, 103.7, 55.9, 22.0; IR (neat): 2933, 1776, 1723, 1621, 1592, 1505, 1485, 1415, 1391, 1306, 1270, 1227, 1156, 1132, 1111, 805, 742; HRMS (ESI-TOF): calcd for $\text{C}_{19}\text{H}_{15}\text{N}_2\text{O}_3^+$: $[\text{M} + \text{H}]^+ = 319.1077$, found 319.1065.



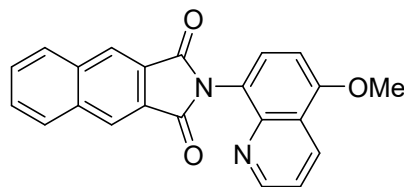
***N*-(5-Methoxyquinolin-8-yl)benzamide (3p):**

The title compound was obtained as a yellow solid; purified by preparative TLC (THF/CHCl₃ = 1/50); mp: 239.1–240.0 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.83 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.61 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.98 (dd, *J* = 5.7, 2.9 Hz, 2H), 7.79 (dd, *J* = 5.4, 3.2 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 8.6, 4.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 4.05 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 168.3, 156.3, 151.1, 144.8, 134.1, 132.4, 131.1, 130.4, 123.7, 122.0, 121.6, 120.9, 103.7, 56.0; IR (neat): 2956, 2926, 1779, 1760, 1727, 1619, 1591, 1484, 1413, 1389, 1304, 1269, 1218, 1111, 1090, 814, 788, 720 cm⁻¹; HRMS (ESI-TOF): calcd for C₁₈H₁₃N₂O₃⁺: [M + H]⁺ = 305.0921, found 305.0906.



***N*-(5-Methoxyquinolin-8-yl)-3,4-dimethylbenzamide (3q):**

The title compound was obtained as a white solid; purified by preparative TLC (THF/CHCl₃ = 1/50); mp: 247.6–248.1 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.83 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.59 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.64–7.60 (m, 2H), 7.39 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.32 (s, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 4.03 (s, 3H), 2.69 (s, 3H), 2.48 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 169.1, 168.6, 156.1, 151.1, 144.9, 144.7, 138.1, 136.9, 133.2, 131.0, 130.4, 126.6, 122.3, 122.0, 121.6, 120.8, 103.7, 55.9, 21.8, 17.6; IR (neat): 3080, 3001, 2961, 2933, 2853, 1770, 1717, 1620, 1591, 1480, 1410, 1389, 1305, 1266, 1213, 1112, 1092, 808, 752 cm⁻¹; HRMS (ESI-TOF): calcd for C₂₀H₁₇N₂O₃⁺: [M + H]⁺ = 333.1234, found 333.1224.



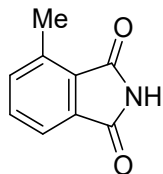
***N*-(5-Methoxyquinolin-8-yl)-2-naphthamide (3r):**

The title compound was obtained as a white solid; purified by preparative TLC (dichloromethane); ¹H NMR (500 MHz, CDCl₃) δ: 8.83 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.62 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.49 (s, 2H), 8.11 (dd, *J* = 6.3, 3.4 Hz, 2H), 7.74–7.69 (m, 3H), 7.41 (dd, *J* = 8.6, 4.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 4.07 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 168.1,

156.3, 151.2, 144.8, 135.7, 131.1, 130.3, 130.3, 129.1, 128.2, 125.2, 122.3, 121.7, 121.0, 103.7, 56.0; IR (neat): 3017, 2935, 1770, 1715, 1591, 1481, 1454, 1407, 1384, 1305, 1267, 1218, 1125, 1090, 798, 767 cm^{-1} ; HRMS (ESI-TOF): calcd for $\text{C}_{22}\text{H}_{15}\text{N}_2\text{O}_3^+$: $[\text{M} + \text{H}]^+ = 355.1077$, found 355.1093.

4. Deprotection of 8-Aminoquinolyl Directing Group

To an oven-dried test tube equipped with a stirring bar charged with phthalimide **3a** (1st run: 57.6 mg, 0.200 mmol; 2nd run: 57.7 mg, 0.200 mmol) was added NH₃ in MeOH (2.0 mL). The reaction mixture was stirred at 80 °C for 18 h. After cooling to room temperature, the solvent was evaporated *in vacuo*, and the residue was purified by preparative thin-layer chromatography (EtOAc/hexane = 1/5) to give the product **5** (1st run: 25.8 mg, 0.175 mmol, 87%; 2nd run: 25.3 mg, 0.172 mmol, 86%) and 8-aminoquinoline (1st run: 22.0 mg, 0.153 mmol, 76%; 2nd run: 23.0 mg, 0.160 mmol, 80%).



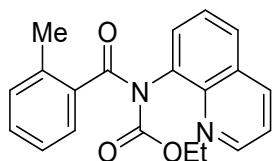
4-Methyloindoline-1,3-dione (**5**):

The title compound was obtained as a white solid; mp: 188.1–189.0 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.05 (s, 1H), 7.69 (d, *J* = 7.4 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 2.70 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 169.0, 168.2, 138.4, 136.6, 133.9, 133.1, 129.3, 121.2, 17.6; IR (neat): 3216, 3062, 1770, 1731, 1615, 1473, 1375, 1303, 1234, 1063, 807, 739, 654, 544 cm⁻¹; HRMS (ESI-TOF): calcd for C₉H₈NO₂⁺: [M + H]⁺ = 162.0550, found 162.0555.

5. Preliminary Mechanistic Investigations

A. Reaction without Rh(acac)(CO)₂

To an oven-dried test tube equipped with a stirring bar charged with benzamide **1a** (52.5 mg, 0.200 mmol) was added NMP (0.4 mL). Subsequently, diethyl dicarbonate (**2**, 48.8 mg, 0.301 mmol) was injected to the solution via a syringe, and the tube was sealed with a PTFE-lined screw cap. The reaction mixture was stirred at 130 °C for 18 h. After cooling to room temperature, the resulting mixture was diluted with EtOAc. The organic layers were washed with water and brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated *in vacuo*, and the residue was purified by preparative thin-layer chromatography (EtOAc/hexane= 1/1) to give the product **6** (18.4mg, 5.50×10^{-2} mmol, 27%).



Ethyl (2-methylbenzoyl)(quinolin-8-yl)carbamate (**6**):

The title compound was obtained as a white solid; mp: 104.7–105.2 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.92 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.18 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.86 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.79 (d, *J* = 7.4 Hz, 1H), 7.70 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.42 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.32 (td, *J* = 7.4, 1.1 Hz, 1H), 7.26–7.20 (m, 2H), 4.00 (q, *J* = 7.3 Hz, 2H), 2.56 (s, 3H), 0.86 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 172.9, 154.4, 150.5, 144.0, 137.4, 136.1, 136.1, 135.9, 130.4, 129.7, 129.1, 128.5, 126.8, 126.1, 125.2, 121.7, 121.7, 62.9, 19.6, 13.5; IR (neat): 3367, 3044, 2926, 1683, 1598, 1578, 1540, 1487, 1428, 1392, 1331, 1264, 1107, 901, 824, 793, 746, 667, 606 cm⁻¹; HRMS (ESI-TOF): calcd for C₂₀H₁₉N₂O₃⁺: [M + H]⁺ = 335.1390, found 335.1403.

B. Reaction with *N*-(Ethoxycarbonyl)benzamide **6**

To an oven-dried test tube equipped with a stirring bar charged with *N*-(ethoxycarbonyl)benzamide **6** (33.6 mg, 0.100 mmol), and Rh(acac)(CO)₂ (2.5 mg, 1.0 × 10⁻² mmol) was added NMP (0.2 mL). The tube was sealed with a PTFE-lined screw cap. The reaction mixture was stirred at 130 °C for 18 h. After cooling to room temperature, the resulting mixture was diluted with EtOAc. The organic layers were washed with water and brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated *in vacuo*.

C. Reaction under CO Atmosphere

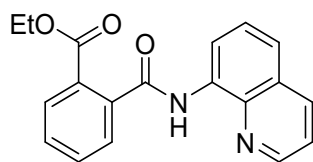
To an oven-dried test tube equipped with a stirring bar was added benzamide **1a** (52.5 mg, 0.200 mmol), and Rh(acac)(CO)₂ (5.2 mg, 2.0×10^{-2} mmol). The tube was evacuated again and backfilled with CO (1 atm, balloon), followed by addition of NMP (0.4 mL). The reaction mixture was stirred at 130 °C for 18 h. After cooling to room temperature, the resulting mixture was diluted with EtOAc. The organic layers were washed with water and brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated *in vacuo*.

D. Reaction with *o*-(Ethoxycarbonyl)benzamide **6** in the Presence of Rh(acac)(CO)₂

To an oven-dried test tube equipped with a stirring bar charged with benzamide **7** (64.1 mg, 0.200 mmol), and Rh(acac)(CO)₂ (5.2 mg, 2.0×10^{-2} mmol) was added NMP (0.4 mL). The tube was sealed with a PTFE-lined screw cap. The reaction mixture was stirred at 130 °C for 18 h. After cooling to room temperature, the resulting mixture was diluted with EtOAc. The organic layers were washed with water and brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated *in vacuo*, and the yield of **3s** was determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

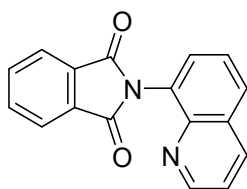
Reaction with *o*-(Ethoxycarbonyl)benzamide **6** in the Absence of Rh(acac)(CO)₂

To an oven-dried test tube equipped with a stirring bar charged with benzamide **7** (64.1 mg, 0.200 mmol), and NMP (0.4 mL). The tube was sealed with a PTFE-lined screw cap. The reaction mixture was stirred at 130 °C for 18 h. After cooling to room temperature, the resulting mixture was diluted with EtOAc. The organic layers were washed with water and brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated *in vacuo*, and the yield of **3s** was determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard.



Ethyl 2-(quinolin-8-ylcarbamoyl)benzoate (**7**):

The title compound was obtained as a white solid; mp: 95.0–95.5 °C; ¹H NMR (500 MHz, CDCl₃) δ : 10.08 (s, 1H), 8.94 (d, J = 7.4 Hz, 1H), 8.75 (dd, J = 4.0, 1.7 Hz, 1H), 8.17 (dd, J = 8.0, 1.7 Hz, 1H), 8.01 (dd, J = 7.7, 1.4 Hz, 1H), 7.69 (dd, J = 7.4, 1.1 Hz, 1H), 7.66–7.53 (m, 4H), 7.44 (dd, J = 8.0, 4.0 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.14 (t, J = 7.2 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ : 167.5, 166.6, 148.2, 138.6, 138.4, 136.3, 134.7, 132.1, 130.3, 129.8, 129.5, 127.9, 127.5, 127.4, 121.8, 121.6, 116.7, 61.5, 13.8; IR (neat): 3340, 2985, 1715, 1677, 1594, 1578, 1526, 1482, 1426, 1389, 1325, 1285, 1137, 1089, 1072, 781, 763, 742 cm⁻¹; HRMS (ESI-TOF): calcd for C₁₉H₁₆N₂NaO₃⁺: [M + Na]⁺ = 343.1053, found 343.1046.



2-(Quinolin-8-yl)isoindoline-1,3-dione (**3s**):

The title compound was obtained as a white solid; mp: 222.6–223.0 °C; ¹H NMR (500 MHz, CDCl₃) δ : 8.85 (dd, J = 4.6, 1.7 Hz, 1H), 8.22 (dd, J = 8.6, 1.7 Hz, 1H), 8.00 (dd, J = 5.4, 3.2 Hz, 2H), 7.96 (dd, J = 8.3, 1.4 Hz, 1H), 7.80 (dd, J =

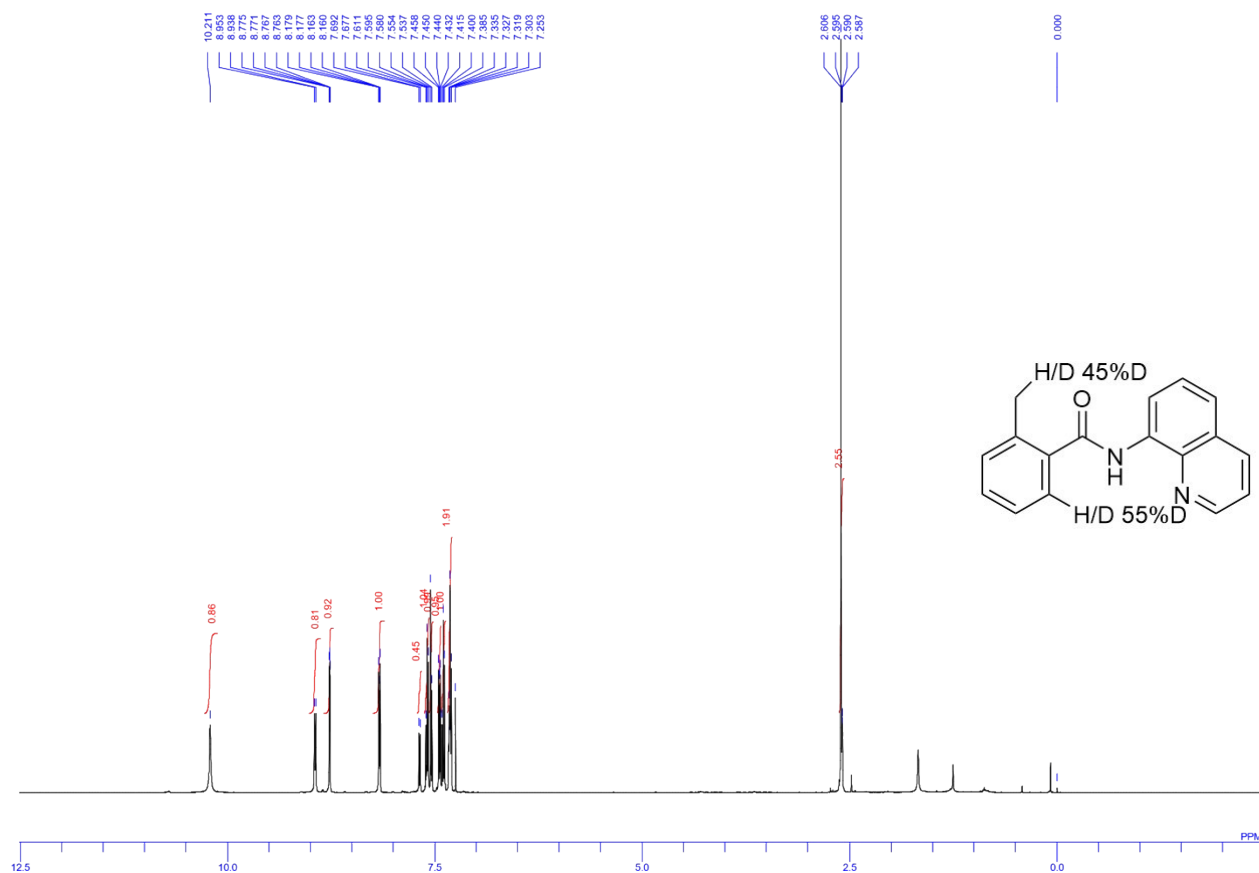
5.4, 3.2 Hz, 2H), 7.75 (dd, $J = 7.4, 1.1$ Hz, 1H), 7.67 (t, $J = 7.7$ Hz, 1H), 7.43 (dd, $J = 8.3, 4.3$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ : 167.9, 150.8, 144.2, 136.1, 134.1, 132.3, 130.1, 129.7, 129.6, 129.2, 126.0, 123.7, 121.8; IR (neat): 3064, 3041, 1760, 1712, 1596, 1502, 1469, 1401, 1116, 1085, 884, 825, 791, 719, 625 cm^{-1} ; HRMS (ESI-TOF): calcd for $\text{C}_{17}\text{H}_{10}\text{N}_2\text{NaO}_2^+$: $[\text{M} + \text{Na}]^+ = 297.0634$, found 297.0622.

E. Reaction In a Short Period of Time

To an oven-dried test tube equipped with a stirring bar charged with benzamide **1a** (52.5 mg, 0.200 mmol) and Rh(acac)(CO)₂ (5.2 mg, 2.0×10^{-2} mmol) was added NMP (0.4 mL). Subsequently, diethyl dicarbonate (**2**, 48.5 mg, 0.299 mmol) was injected to the solution via a syringe, and the tube was sealed with a PTFE-lined screw cap. The reaction mixture was stirred at 130 °C for 1 h. After cooling to room temperature, the resulting mixture was diluted with EtOAc. The organic layers were washed with water and brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated *in vacuo*, and the residue was purified by preparative thin-layer chromatography (EtOAc/hexane = 1/9) to give the product **3a** (28.0 mg, 0.971 mmol, 48%) and **4** (1.6 mg, 4.8×10^{-3} mmol, 2%).

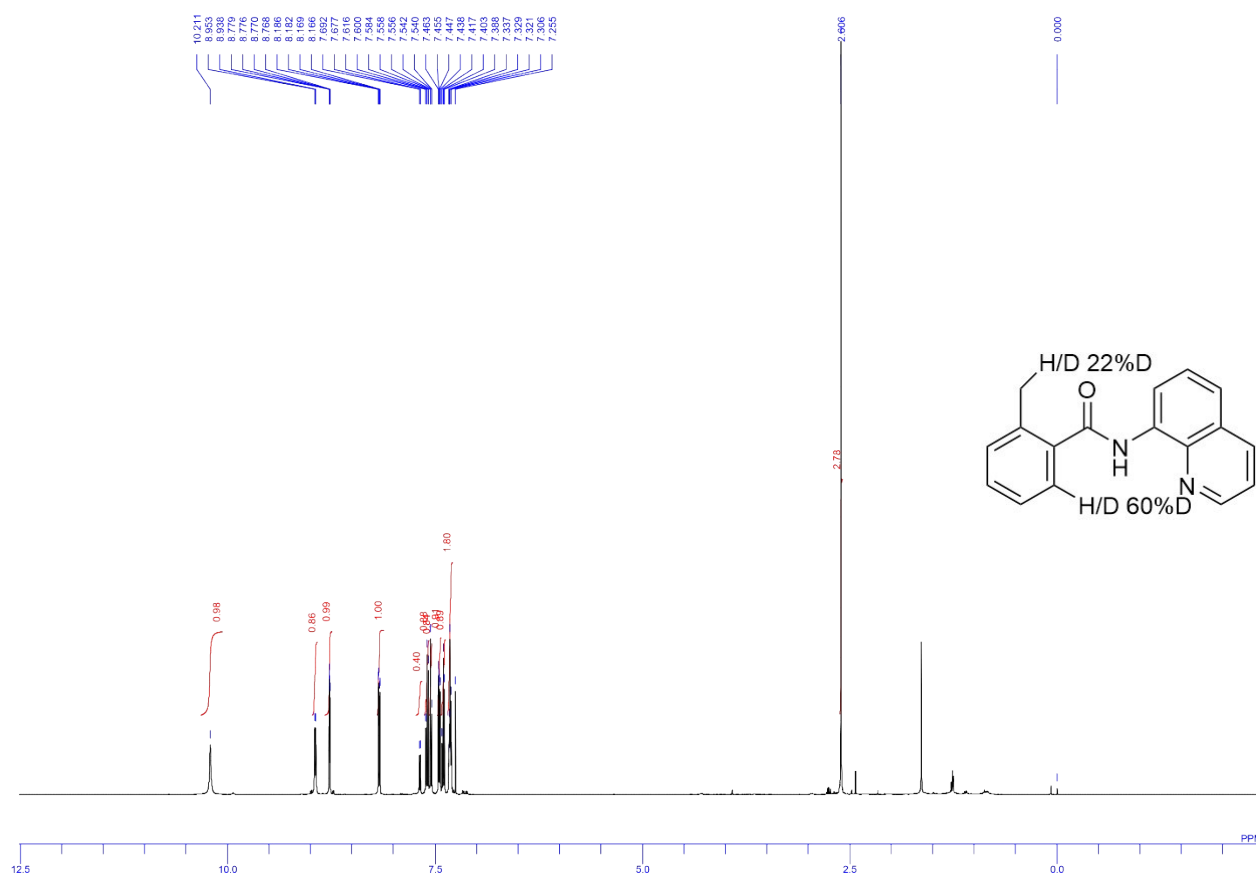
F. Deuterium Labelling Experiment without Diethyl Dicarbonate

To an oven-dried test tube equipped with a stirring bar charged with benzamide **1a** (52.5 mg, 0.200 mmol) and Rh(acac)(CO)₂ (5.2 mg, 2.0 × 10⁻² mmol) was added NMP (0.4 mL). Subsequently, EtOD (46.1 mg, 0.979 mmol) was injected to the solution via a syringe, and the tube was sealed with a PTFE-lined screw cap. The reaction mixture was stirred at 130 °C for 18 h. After cooling to room temperature, the resulting mixture was diluted with EtOAc. The organic layers were washed with water and brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated *in vacuo*, and the residue was purified by preparative thin-layer chromatography (CHCl₃/hexane = 9/1) to give the product **1a-d**₁ (47.7 mg, 0.182 mmol, 91%).



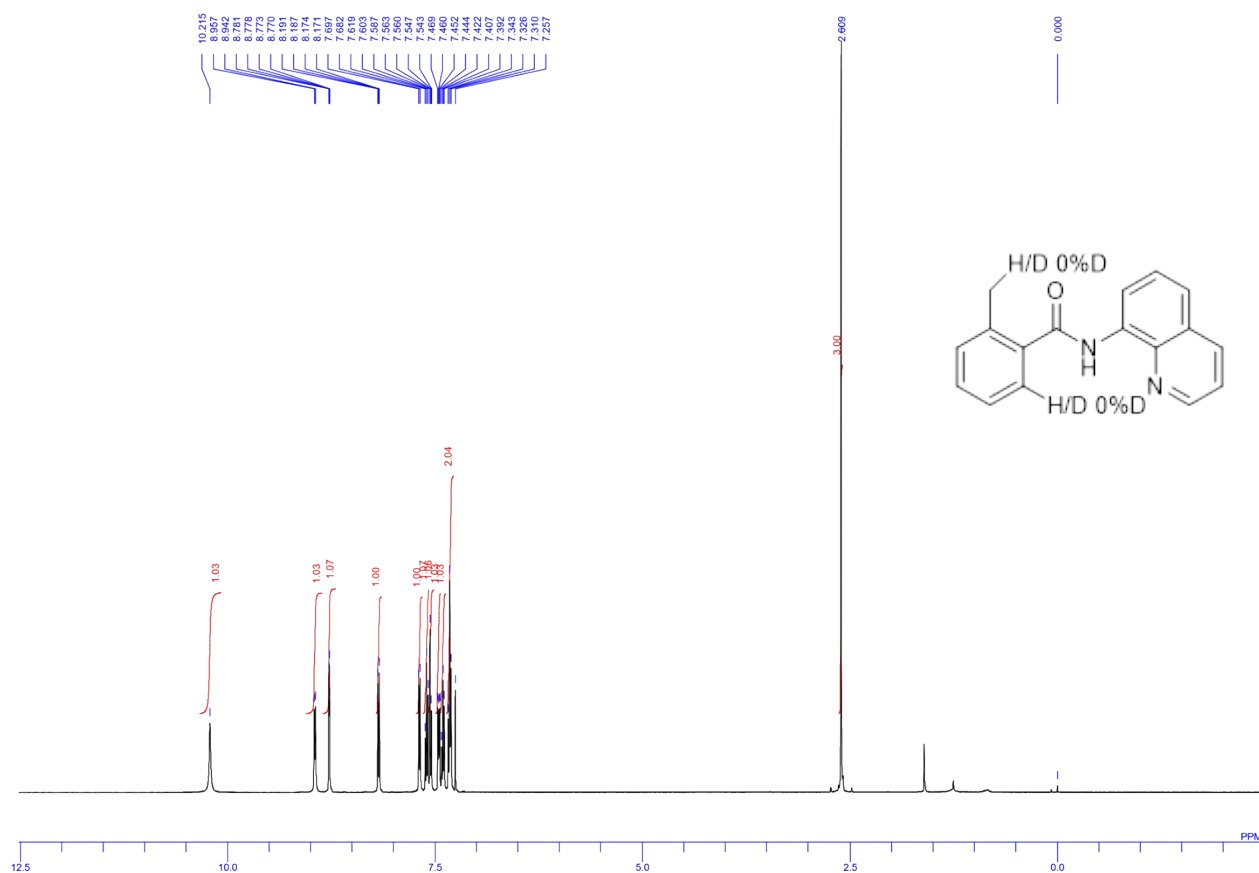
Deuterium Labelling Experiment with Diethyl Dicarbonate

To an oven-dried test tube equipped with a stirring bar charged with benzamide **1a** (52.5 mg, 0.200 mmol) and Rh(acac)(CO)₂ (5.2 mg, 2.0×10^{-2} mmol) was added NMP (0.4 mL). Subsequently, diethyl dicarbonate (**2**, 49.6 mg, 0.306 mmol) and EtOD (46.2 mg, 0.981 mmol) was injected to the solution via a syringe, and the tube was sealed with a PTFE-lined screw cap. The reaction mixture was stirred at 130 °C for 1 h. After cooling to room temperature, the resulting mixture was added EtOAc. The organic layers were washed with water and brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated *in vacuo*, and the residue was purified by preparative thin-layer chromatography (THF/toluene = 1/4) to give the product **1a-d₁** (34.6 mg, 0.132 mmol, 60%). The yield of **3a** was determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard.



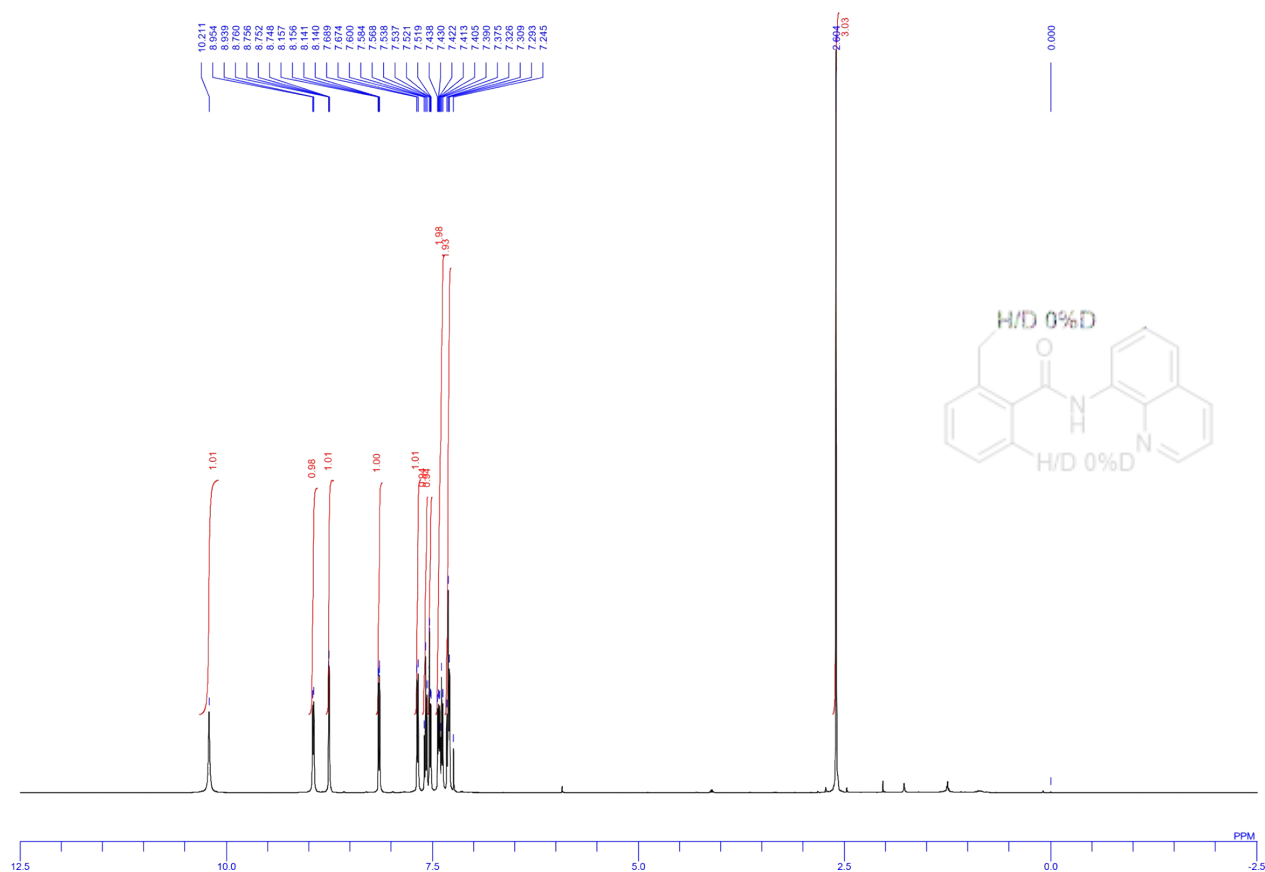
Deuterium Labelling Experiment without Rh(acac)(CO)₂

To an oven-dried test tube equipped with a stirring bar charged with benzamide **1a** (52.5 mg, 0.200 mmol) and was added NMP (0.4 mL). Subsequently, diethyl dicarbonate (**2**, 49.0 mg, 0.302 mmol) and EtOD (46.7 mg, 0.992 mmol) was injected to the solution via a syringe, and the tube was sealed with a PTFE-lined screw cap. The reaction mixture was stirred at 130 °C for 1 h. After cooling to room temperature, the resulting mixture was added EtOAc. The organic layers were washed with water and brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated *in vacuo*, and the residue was purified by preparative thin-layer chromatography (THF/toluene = 1/4) to give the product **1a** (46.9 mg, 0.179 mmol, 90%).



Deuterium Labelling Experiment without Diethyl Dicarbonate and Rh(acac)(CO)₂

To an oven-dried test tube equipped with a stirring bar charged with benzamide **1a** (52.6 mg, 0.201 mmol) and was added NMP (0.4 mL). Subsequently, EtOD (46.8 mg, 0.994 mmol) was injected to the solution via a syringe, and the tube was sealed with a PTFE-lined screw cap. The reaction mixture was stirred at 130 °C for 18 h. After cooling to room temperature, the resulting mixture was added EtOAc. The organic layers were washed with water and brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated *in vacuo*, and the residue was purified by preparative thin-layer chromatography (THF/toluene = 1/4) to give the product **1a** (52.6 mg, 0.201 mmol, quant).



G. Kinetic Isotope Effect Experiment

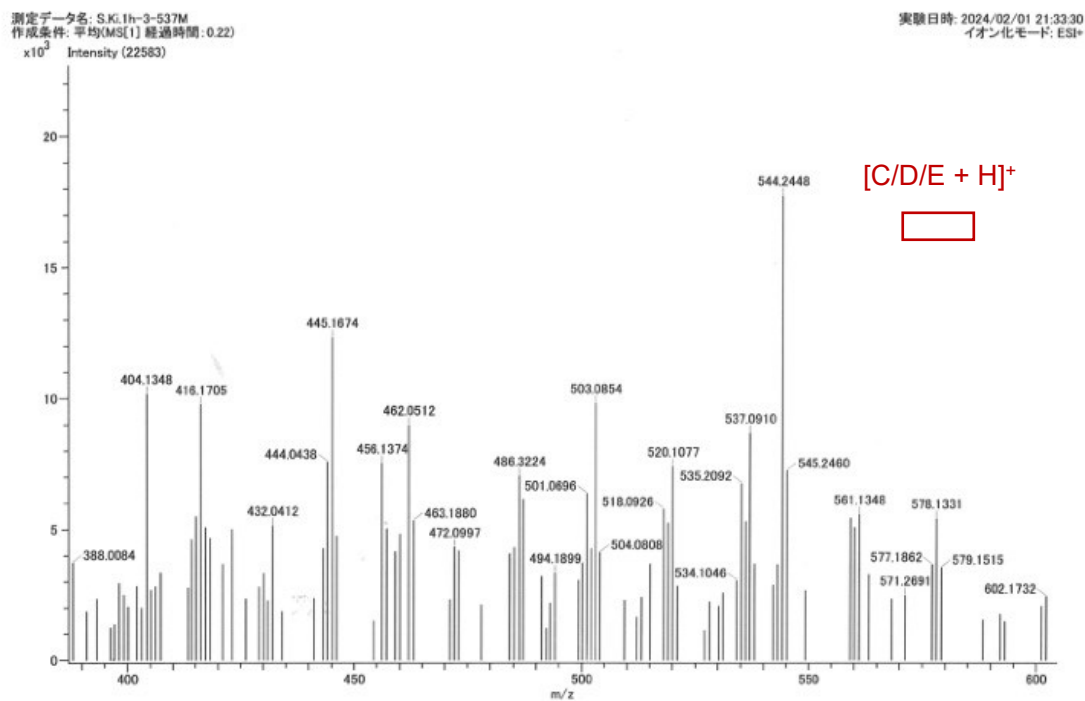
Kinetic isotope effect (KIE) was measured by two sets of parallel experiments using benzamide **1a** and **1a-d₁**. To an oven-dried test tube equipped with a stirring bar were added benzamide **1a** (26.1 mg, 0.995 mmol), Rh(acac)(CO)₂ (2.6 mg, 1.0×10^{-2} mmol), and NMP (0.2 mL). Subsequently, diethyl dicarbonate (**2**, 25.4 mg, 0.157 mmol) was injected to the solution via a syringe, and the tube was sealed with a PTFE-lined screw cap. To another oven-dried test tube equipped with a stirring bar were added benzamide **1a-d₁** (26.1 mg, 0.995 mmol), Rh(acac)(CO)₂ (2.6 mg, 1.0×10^{-2} mmol), and NMP (0.20 mL). Subsequently, diethyl dicarbonate (**2**, 25.2 mg, 0.155 mmol) was injected to the solution via a syringe, and the tube was sealed with a PTFE-lined screw cap. Both reactions were allowed to stir at 130 °C in an oil bath for 2 h. After cooling to room temperature, the resulting mixtures were diluted with EtOAc, respectively. The organic layers were washed with water and brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated *in vacuo*, and the yield of **3a** was determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard. The yields were 51.9% and 42.4%, respectively, and a KIE value of 1.2 was determined on the basis of the ¹H NMR yields.

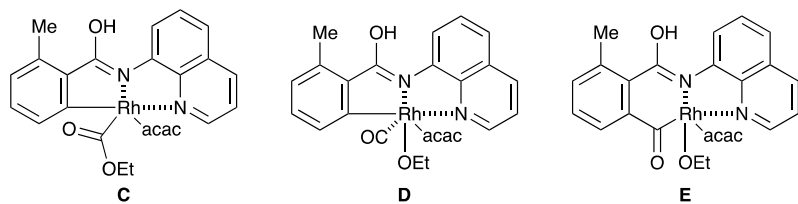
H. Reaction with Diethyl Carbonate **8**

To an oven-dried test tube equipped with a stirring bar charged with benzamide **1a** (52.6 mg, 0.201 mmol), and Rh(acac)(CO)₂ (5.2 mg, 2.0×10^{-2} mmol) was added NMP (0.4 mL). Subsequently, diethyl carbonate (**8**, 35.9 mg, 0.304 mmol) was injected to the solution via a syringe, and the tube was sealed with a PTFE-lined screw cap. The reaction mixture was stirred at 130 °C for 18 h. After cooling to room temperature, the resulting mixture was diluted with EtOAc. The organic layers were washed with water and brine and dried over anhydrous Na₂SO₄.

I. Detection of Intermediates C/D/E by ESI-MS Analysis

To an oven-dried test tube equipped with a stirring bar charged with benzamide **1a** (26.5 mg, 0.101 mmol) and Rh(acac)(CO)₂ (2.5 mg, 9.7×10^{-3} mmol) was added NMP (0.2 mL). Subsequently, diethyl dicarbonate (**2**, 25.0 mg, 0.154 mmol) was injected to the solution via a syringe, and the tube was sealed with a PTFE-lined screw cap. The reaction mixture was stirred at 130 °C for 1 h. After cooling to room temperature, the resulting mixture was diluted with acetonitrile and subsequently analysed by ESI-MS.





HRMS (ESI-TOF): calcd for $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_5\text{Rh}^+$: $[\text{M} + \text{H}]^+ = 537.0891$, found 537.0910.

6. References

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7. Copies of ^1H , ^{13}C and ^{19}F NMR Spectra for the Products

