

Rh(III)-Catalyzed Tandem Oxidative Olefination-Michael Reactions between Aryl Carboxamides and Alkenes

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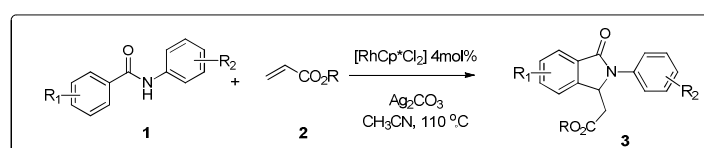
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General Considerations.

All rhodium-catalyzed reactions were carried out using standard Schlenk techniques or in a nitrogen-filled dry box. All solvents were distilled under N₂ before use. ¹H and ¹³C NMR spectra were recorded using C₆D₆, CDCl₃ or DMSO-*d*₆ solvent on a Bruker 400 MHz spectrometer at 298K. The chemical shift is given in dimensionless δ values and is referenced relative to TMS in ¹H and ¹³C NMR spectroscopy. High-resolution mass spectra were obtained on an Agilent LC-Q-TOF-MS. Infrared spectra were recorded on a Perkin Elmer GX Spectrometer. [Cp*RhCl₂]₂ was purchased from the Strem Chemical Co.. All other reagents were obtained from commercial sources and were used as received.

Experimental Section

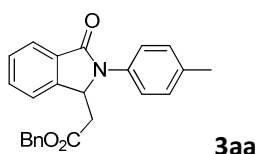
1. Synthesis and characterization of compounds 3



Procedure for a representative catalytic reaction

Benzamide **1a** (110.0 mg, 0.52 mmol), Ag₂CO₃ (286 mg, 1.04 mmol, 2 equiv), and [RhCp*Cl₂]₂ (12.8 mg, 4 mol %) were weighted into a 25 mL pressure tube, to which acetonitrile (4 mL) was added. After purged with nitrogen, benzyl acrylate (168.5 mg, 1.04 mmol, 2 equiv) was added *via* a syringe and the mixture was stirred at 115 °C for 12 h. The mixture was diluted with CH₂Cl₂ (10 mL) and filtered through celite. All volatiles were removed under reduced pressure. Purification was performed by flash column chromatography on silica gel using EtOAc and pet. ether.

Compound **3aa**. White solid, 181 mg. Yield, 94%

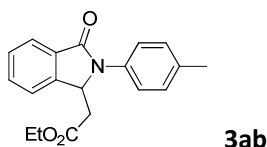


¹H NMR (400 MHz, C₆D₆): δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.76-6.84 (m, 8H), 6.69 (d, *J* = 8.0 Hz, 1H), 4.88 (dd, *J* = 8.8, 3.6 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 2.38 (dd, *J* = 16.4, 3.6 Hz, 1H), 1.78 (s, 3H, CH₃), 1.74-1.78 (m, 1H). ¹³C NMR (100 MHz, C₆D₆): 169.8, 165.9, 144.3, 135.7, 134.5, 134.4, 132.8, 131.5, 129.5, 128.5, 128.3, 128.2, 128.1, 124.0, 123.2, 122.4, 66.2, 56.8, 37.0, 20.5.

IR: 1736, 1670, 1514, 1394, 1167, 813 cm^{-1} .

HRMS (ESI): Calcd for $[\text{C}_{24}\text{H}_{21}\text{NO}_3 + \text{Na}]^+$ 394.1414; Found 394.1425.

Compound **3ab**.



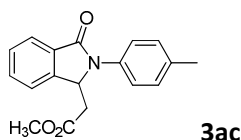
3ab was obtained as a white solid in 91% yield (152 mg) from **1a** (115 mg, 0.54 mmol) and ethyl acrylate (109 mg, 1.09 mmol).

^1H NMR (400 MHz, CDCl_3): δ 7.93 (d, J = 7.6 Hz, 1H), 7.51-7.61 (m, 3H), 7.43 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 5.55 (dd, J = 8.2, 4.0 Hz, 1H), 4.05-4.12 (m, 2H, CH_2), 2.94 (dd, J = 4.2, 16.0 Hz, 1H), 2.50 (dd, J = 8.0, 16.0 Hz, 1H), 2.38 (s, 3H, CH_3), 1.17 (t, J = 7.6 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): 170.2, 166.8, 144.1, 135.7, 133.7, 132.0, 131.9, 129.7, 128.7, 124.0, 123.9, 122.4, 60.8, 57.6, 37.5, 20.9, 13.9.

IR: 1729, 1687, 1514, 1386, 1172, 816 cm^{-1} .

HRMS (ESI): Calcd for $[\text{C}_{19}\text{H}_{19}\text{NO}_3 + \text{Na}]^+$ 332.1257; Found 332.1263.

Compound **3ac**.



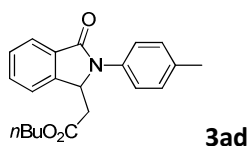
3ac was obtained as a white solid in 96% yield (147 mg) from **1a** (110 mg, 0.52 mmol) and methyl acrylate (90 mg, 1.04 mmol).

^1H NMR (400 MHz, CDCl_3): δ 7.88 (d, J = 7.8 Hz, 1H), 7.53-7.56 (m, 1H), 7.46-7.49 (m, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 5.51 (dd, J = 8.8, 4.4 Hz, 1H), 3.59 (s, 3H, CH_3), 2.90 (dd, J = 16.0, 4.4 Hz, 1H), 2.46 (dd, J = 16.0, 8.4 Hz, 1H), 2.33 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): 170.6, 166.5, 144.0, 135.6, 133.5, 132.0, 131.7, 129.6, 128.6, 123.8, 123.7, 122.3, 57.4, 51.7, 37.2, 20.8.

IR: 1739, 1683, 1514, 1391, 1391, 1302, 1199, 819 cm^{-1} .

HRMS (ESI): Calcd for $[\text{C}_{18}\text{H}_{17}\text{NO}_3 + \text{H}]^+$ 296.1281; Found 296.1293

Compound **3ad**.



3ad was obtained as a viscous liquid in 93% yield (157 mg) from **1a** (105 mg, 0.50 mmol) and butyl acrylate (128 mg, 1.0 mmol).

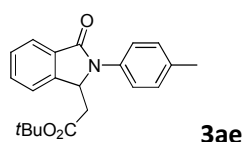
^1H NMR (400 MHz, CDCl_3): δ 7.80 (d, J = 7.6 Hz, 1H), 7.36-7.48 (m, 3H), 7.33 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 5.42 (dd, J = 8.4, 4.0 Hz, 1H), 3.86-3.93 (m, 2H, CH_2), 2.82 (dd, J = 16.0, 4.0 Hz, 1H), 2.40 (dd, J = 16.0, 8.0 Hz, 1H), 2.25 (s, 3H, CH_3), 1.35-1.42 (m, 2H, CH_2), 1.11-1.21 (m, 2H, CH_2), 0.78 (t, J = 7.6 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): 170.2, 166.6, 144.0, 135.5, 133.6, 131.9, 131.8, 129.6, 128.5, 123.8, 123.7, 122.3, 64.6, 57.5, 37.4, 30.2, 20.8, 18.8, 13.4.

IR: 1732, 1700, 1514, 1467, 1381, 1173, 814 cm^{-1} .

HRMS (ESI): Calcd for $[\text{C}_{21}\text{H}_{23}\text{NO}_3 + \text{H}]^+$ 338.1751; found: 338.1756.

Compound **3ae**.

3ae was obtained as a white solid in 81% yield (153 mg) from **1a** (118 mg, 0.56 mmol) and *tert*-butyl acrylate (144 mg, 1.12 mmol).



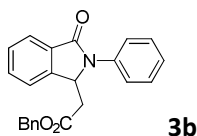
^1H NMR (400 MHz, CDCl_3): δ 7.92 (d, J = 7.8 Hz, 1H), 7.49-7.60 (m, 3H), 7.44 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 5.48 (dd, J = 7.8, 4.0 Hz, 1H), 2.89 (dd, J = 16.0, 3.2 Hz, 1H), 2.47 (dd, J = 16.0, 8.0 Hz, 1H), 2.37 (s, 3H, CH_3), 1.32 (s, 9H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): 169.2, 166.8, 144.2, 135.7, 133.8, 132.1, 131.9, 129.8, 128.6, 123.9 (two overlapping signals), 122.5, 81.4, 57.4, 38.2, 28.0, 20.9.

IR: 1724, 1697, 1513, 1382, 1144 cm^{-1} .

HRMS (ESI): Calcd for $[\text{C}_{21}\text{H}_{23}\text{NO}_3 + \text{H}]^+$ 338.1751; found: 338.1762.

Compound **3b**.

3b was obtained as a white solid obtained in 95% yield (179 mg) from **1b** (104 mg, 0.53 mmol) and benzyl acrylate (172 mg, 1.06 mmol).



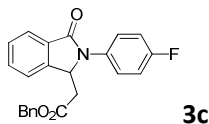
^1H NMR (400 MHz, CDCl_3): δ 7.54 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 2H), 7.49-7.51 (m, 2H), 7.39-7.44 (m, 3H), 7.32-7.34 (m, 3H), 7.23-7.26 (m, 3H), 5.58 (dd, J = 8.4, 4.0 Hz, 1H), 5.08 (d, J = 12.0 Hz, 1H), 5.02 (d, J = 12.0 Hz, 1H), 3.00 (dd, J = 16.0, 4.0 Hz, 1H), 2.53 (dd, J = 16.0, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 170.0, 166.7, 144.0, 136.3, 135.1, 132.2, 131.8, 129.2, 128.8, 128.5, 128.4 (two overlapping signals), 125.8, 124.1, 123.8, 122.5, 66.7, 57.4, 37.6.

IR: 1737, 1690, 1594, 1494, 1392, 1170, 764 cm^{-1} .

HRMS (ESI): Calcd for $[\text{C}_{23}\text{H}_{19}\text{NO}_3 + \text{Na}]^+$ 380.1257; found: 380.1260.

Compound **3c**.

3c was obtained as a white solid in 95% yield (192 mg) from **1c** (116 mg, 0.54 mmol) and benzyl acrylate (175 mg, 1.08 mmol).



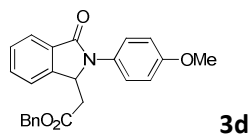
^1H NMR (400 MHz, CDCl_3): δ 7.90 (d, J = 7.8 Hz, 1H), 7.46-7.55 (m, 4H), 7.40 (d, J = 7.2 Hz, 1H), 7.33-7.36 (m, 3H), 7.24-7.26 (m, 2H), 7.11 (t, J = 8.4 Hz, 2H), 5.52 (dd, J = 8.0, 4.0 Hz, 1H), 5.07 (d, J = 12.0 Hz, 1H), 5.02 (d, J = 12.4 Hz, 1H), 2.93 (dd, J = 16.4, 4.0 Hz, 1H), 2.57 (dd, J = 16.0, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 169.9, 166.8, 160.4 (d, $J_{\text{F-C}}$ = 244 Hz), 143.8, 135.0, 132.3, 131.5, 128.9, 128.5, 128.4 (two overlapping signals), 128.3, 125.9 (d, $J_{\text{F-C}}$ = 8.0 Hz), 124.1, 122.5, 116.0 (d, $J_{\text{F-C}}$ = 23 Hz), 66.8, 57.8, 37.5.

IR: 1734, 1694, 1509, 1397, 1292, 1211, 1146, 747.

HRMS (ESI): Calcd for $[\text{C}_{23}\text{H}_{18}\text{FNO}_3 + \text{Na}]^+$ 398.1163; found: 398.1184.

Compound **3d**.

3d was obtained as a white solid in 96% yield (186 mg) from **1d** (114 mg, 0.50 mmol) and benzyl acrylate (162 mg, 1.0 mmol).



^1H NMR (400 MHz, CDCl_3): δ 7.88 (d, J = 8.0 Hz, 1H), 7.47-7.51 (m, 2H), 7.38-7.40 (m, 3H), 7.29-7.35 (m, 3H), 7.22-7.24 (m, 2H), 6.94 (d, J = 8.4 Hz, 2H), 5.46 (dd, J = 8.0, 4.0 Hz, 1H), 5.04 (d, J = 12.0 Hz, 1H), 5.00 (d, J = 12.0 Hz, 1H), 3.78 (s, 3H, CH_3), 2.93 (dd, J = 16.0, 4.4 Hz, 1H), 2.53 (dd, J = 16.0, 8.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 170.0, 166.7, 157.7, 143.9, 135.1, 131.9, 131.8, 128.9, 128.6, 128.4, 128.3 (two overlapping signals), 125.9, 123.9, 122.4, 114.4, 66.6, 58.0, 55.3, 37.5.

IR: 1721, 1681, 1581, 1382, 1294, 1253, 1156, 745 cm^{-1} .

HRMS (ESI): Calcd for $[\text{C}_{24}\text{H}_{21}\text{NO}_4 + \text{H}]^+$ 388.1543; found: 388.1540.

Compound **3e**.

3e was obtained as a viscous liquid in 89% yield (195 mg) from **1e** (125mg, 0.59 mmol) and benzyl acrylate (191 mg, 1.18 mmol).



3e (ratio 1.5 : 1)

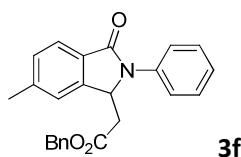
¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, *J* = 6.8 Hz, 1H), 7.46-7.53 (m, 2H), 7.41 (d, *J* = 6.8 Hz, 1H), 7.19-7.31 (m, 9H), 5.28-5.47 (m, 1H, the ratio of two br peaks is 1.5 : 1), 4.89-4.93 (m, 2H), 2.64-2.71 (m, 2H), 2.25 (s, 3H, CH₃). Selected ¹³C NMR (100 MHz, CDCl₃): 169.8, 144.7, 137.1, 134.9, 134.6, 131.8, 131.4, 131.1, 130.0, 128.5, 128.3, 128.2, 127.9, 126.7, 123.9, 122.4, 66.5, 59.8 (57.9), 37.6 (37.7), 18.3 (17.7).

IR: 1731, 1694, 1603, 1494, 1467, 1384, 1148, 751 cm⁻¹.

HRMS (ESI): Calcd for [C₂₄H₂₁NO₃ + Na]⁺ 394.1414; found: 394.1420.

Compound **3f**.

3f was obtained as a white solid in 94% yield (183 mg) from **1f** (111 mg, 0.53 mmol) and benzyl acrylate (172 mg, 1.06 mmol).



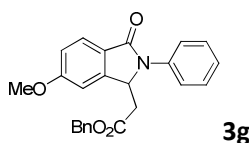
¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.20-7.35 (m, 7H), 7.17 (s, 1H), 5.54 (dd, *J* = 8.4, 3.6 Hz, 1H), 5.10 (d, *J* = 12.4 Hz, 1H), 5.03 (d, *J* = 12.4 Hz, 1H), 2.97 (dd, *J* = 16.4, 4.0 Hz, 1H), 2.51 (dd, *J* = 16, 8.4 Hz, 1H), 2.38 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): 170.2, 166.8, 144.5, 143.1, 136.6, 135.3, 129.9, 129.2, 128.6, 128.5 (two overlapping signals), 125.7, 124.0, 123.7 (two overlapping signals), 123.0, 66.8, 57.3, 37.7, 22.0.

IR: 1733, 1687, 1496, 1396, 1145, 694 cm⁻¹.

HRMS (ESI): Calcd for [C₂₄H₂₁NO₃ + Na]⁺ 394.1414; found: 394.1416.

Compound **3g**.

3g was obtained as a viscous liquid in 93% yield (205 mg) from **1g** (130 mg, 0.57 mmol) and benzyl acrylate (185 mg, 1.14 mmol).



¹H NMR (400 MHz, CDCl₃): δ 7.80 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.30-7.35 (m, 3H), 7.19-7.28 (m, 3H), 7.00 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.93 (d, *J* = 2.0 Hz, 1H), 5.52

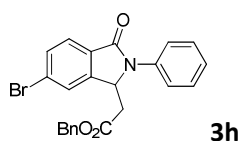
(dd, $J = 8.4, 4.0$ Hz, 1H), 5.08 (d, $J = 12.4$ Hz, 1H), 5.02 (d, $J = 12.4$ Hz, 1H), 3.75 (s, 3H, CH₃), 2.98 (dd, $J = 16.4, 4.0$ Hz, 1H), 2.53 (dd, $J = 16.0, 8.4$ Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): 170.1, 166.5, 163.2, 146.3, 136.5, 135.1, 129.1 (two overlapping signals), 128.4, 128.3, 128.2, 125.4, 124.2, 123.4, 115.5, 107.1, 66.7, 56.9, 55.4, 37.6.

IR: 1722, 1683, 1598, 1458, 1092, 813 cm⁻¹.

HRMS (ESI): Calcd for [C₂₄H₂₁NO₄ + Na]⁺ 410.1363; found: 410.1356.

Compound **3h**.

3h was a white solid obtained in 95% yield (215 mg) from **1h** (143 mg, 0.52 mmol) and benzyl acrylate (169 mg, 1.04 mmol) following the general procedure.



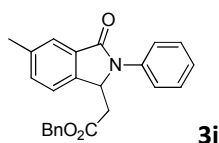
¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, $J = 8.0$ Hz, 1H), 7.58-7.62 (m, 2H), 7.49 (d, $J = 8.0$ Hz, 2H), 7.40 (t, $J = 7.8$ Hz, 2H), 7.28-7.35 (m, 3H), 7.20-7.24 (m, 3H), 5.51 (dd, $J = 8.4, 4.0$ Hz, 1H), 5.06 (d, $J = 12.0$ Hz, 1H), 5.01 (d, $J = 12.0$ Hz, 1H), 2.95 (dd, $J = 16.0, 4.0$ Hz, 1H), 2.52 (dd, $J = 16.0, 8.0$ Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): 169.8, 165.7, 145.7, 135.9, 135.0, 132.3, 130.8, 129.3, 128.6, 128.5, 128.3, 126.7, 126.1, 126.0, 125.5, 123.7, 66.9, 57.0, 37.1.

IR: 1725, 1701, 1590, 1494, 1147, 753, 690 cm⁻¹.

HRMS (ESI): Calcd for [C₂₃H₁₈BrNO₃ + Na]⁺ 458.0362; found: 458.0376.

Compound **3i**.

3i was obtained as a white solid in 90% yield (177 mg) from **1i** (113 mg, 0.53 mmol) and benzyl acrylate (172 mg, 1.06 mmol).



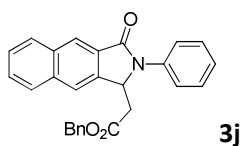
¹H NMR (400 MHz, CDCl₃): δ 7.70 (s, 1H), 7.54 (d, $J = 8.0$ Hz, 2H), 7.43 (t, $J = 8.0$ Hz, 2H), 7.31-7.34 (m, 4H), 7.21-7.28 (m, 4H), 5.54 (dd, $J = 8.2, 4.0$ Hz, 1H), 5.07 (d, $J = 12.4$ Hz, 1H), 5.02 (d, $J = 12.0$ Hz, 1H), 2.97 (dd, $J = 4.2, 16.0$ Hz, 1H), 2.51 (dd, $J = 8.0, 16.0$ Hz, 1H), 2.44 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): 170.2, 166.9, 141.3, 139.0, 136.5, 135.2, 133.2, 132.0, 129.2, 128.6, 128.4 (two overlapping signals), 125.8, 124.4, 123.8, 122.3, 66.8, 57.3, 37.8, 21.3.

IR: 1734, 1685, 1496, 1390, 1141, 734 cm⁻¹.

HRMS (ESI): Calcd for [C₂₄H₂₁NO₃ + Na]⁺ 394.1414; found: 394.1423.

Compound **3j**.

3j was obtained as a white solid in 74% yield (179 mg) from **1j** (147 mg, 0.594 mmol) and benzyl acrylate (191 mg, 1.18 mmol).



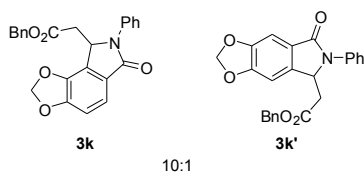
^1H NMR (400 MHz, CDCl_3): δ 8.44 (s, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.82 (s, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.54-7.64 (m, 4H), 7.47 (t, J = 7.8 Hz, 2H), 7.24-7.32 (m, 6H), 5.75 (dd, J = 8.4, 3.6 Hz, 1H), 5.12 (d, J = 12.0 Hz, 1H), 5.06 (d, J = 12.0 Hz, 1H), 3.10 (dd, J = 16.0, 4.0 Hz, 1H), 2.63 (dd, J = 16.0, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): 170.2, 166.7, 138.9, 136.4, 135.4, 135.2, 133.2, 129.7, 129.5, 129.3, 128.6, 128.5 (two overlapping signals), 128.3, 127.9, 126.6, 126.1, 124.7, 124.0, 121.7, 66.8, 57.5, 38.2.

IR: 1725, 1693, 1495, 1373, 1346, 1179, 744 cm^{-1} .

HRMS (ESI): Calcd for $[\text{C}_{27}\text{H}_{21}\text{NO}_3 + \text{Na}]^+$ 430.1414; found: 430.1412.

Compounds **3k** and **3k'**.

A mixture of **3k** and **3k'** was obtained as a white solid in 84% yield (175 mg) starting from **1k** (125 mg, 0.52 mmol) and benzyl acrylate (168 mg, 1.04 mmol). The **3k** to **3k'** ratio (10 : 1) was determined by ^1H NMR.

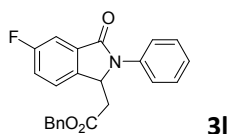


^1H NMR (400 MHz, CDCl_3) for **3k**: δ 7.50 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 2H), 7.31-7.32 (m, 3H), 7.19-7.25 (m, 3H), 6.93 (d, J = 8.0 Hz, 1H), 5.99 (d, 1H, 0.8 Hz, OCH_2O), 5.86 (d, 1H, 0.8 Hz, OCH_2O), 5.58-5.61 (m, 1H), 4.98 (d, J = 12.0 Hz, 1H), 4.90 (d, J = 12.0 Hz, 1H), 2.93 (dd, J = 16.0, 4.4 Hz, 1H), 2.75 (dd, J = 16.0, 7.6 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) for **3k**: 169.1, 166.0, 151.1, 141.4, 136.2, 135.2, 129.1, 128.4, 128.3, 128.2, 126.8, 125.9, 124.0, 123.3, 118.7, 109.3, 102.2, 66.6, 55.3, 36.2. Selected ^1H NMR (400 MHz, CDCl_3) signals for **3k'**: 6.83 (s, 1H), 6.03 (d, J = 4.0 Hz, 2H), 5.06 (s, 2H, OCH_2O). Selected ^{13}C NMR (100 MHz, CDCl_3) for **3k'**: 170.1, 148.7, 125.5, 66.8, 56.9, 37.7.

IR: 1741, 1677, 1595, 1499, 1470, 1382, 1295, 1170, 1035, 766, 694 cm^{-1} .

HRMS (ESI): Calcd for $[\text{C}_{24}\text{H}_{19}\text{NO}_5 + \text{H}]^+$ 402.1336; found: 402.1339.

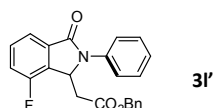
Compound **3l**. **3l** was isolated as a light yellow solid in 18% yield (34 mg) from **1a** (110 mg, 0.51 mmol) and benzyl acrylate (165 mg, 1.02 mmol) under standard reaction conditions.



^1H NMR (500 MHz, CDCl_3): δ 7.54 (dd, $J = 7.5, J = 2.5$ Hz, 1H), 7.49-7.52 (m, 2H), 7.41-7.44 (m, 2H), 7.31-7.32 (m, 4H), 7.23-7.25 (m, 3H), 7.18 (td, $J = 8.7, J = 2.4$ Hz, 1H), 5.52 (dd, $J = 9.0, 4.0$ Hz, 1H, NCH), 5.07 (d, $J = 12.3$ Hz, 1H), 5.02 (d, $J = 12.3$, 1H), 2.97 (dd, $J = 16.5, J = 4.0$ Hz, 1H), 2.50 (dd, $J = 16.5, 8.8$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): 170.0 (ester CO), 165.7 (d, $^4J_{\text{C-F}} = 2.5$ Hz, amide CO), 163.2 (d, $^1J_{\text{C-F}} = 247.3$ Hz, C-F), 139.5 (d, $J_{\text{C-F}} = 1.8$ Hz), 136.1, 135.1, 134.1 (d, $J_{\text{C-F}} = 8.6$ Hz), 129.4, 128.6, 128.56, 128.5, 126.3, 124.3 (d, $J_{\text{C-F}} = 8.4$ Hz), 123.9, 119.8 (d, $^2J_{\text{C-F}} = 23.6$ Hz, CH, *ortho* to F), 110.9 (d, $^2J_{\text{C-F}} = 23.3$ Hz, CH, *ortho* to F), 66.9, 57.3, 37.6.

HRMS (ESI): Calcd for $[\text{C}_{23}\text{H}_{18}\text{FNO}_3 + \text{H}]^+$ 376.1349, found: 376.1342.

Compound **3l'**. **3l'** was isolated as a white solid in 74% yield (142mg) from **1a** (110 mg, 0.51 mmol) and benzyl acrylate (165 mg, 1.02 mmol).

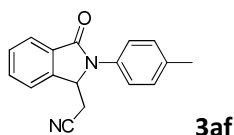


^1H NMR (500 MHz, CDCl_3): δ 7.69 (d, $J = 7.5$ Hz, 1H), 7.45-7.50 (m, 3H), 7.39-7.43 (m, 2H), 7.29-7.30 (m, 3H), 7.21-7.25 (m, 2H), 7.13-7.15 (m, 2H), 5.65 (t, $J = 5$ Hz, 1H, N-CH), 4.89 (d, $^2J = 12.2$ Hz, 1H), 4.84 (d, $^2J = 12.2$ Hz, 1H), 2.96 (dd, $^2J = 15.5$ Hz, $^3J = 4.0$ Hz, 1H), 2.87 (dd, $^2J = 15.5$, $^3J = 5.5$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): 168.8 (ester CO), 165.6 (d, $^4J_{\text{C-F}} = 1.8$ Hz, amide CO), 157.2 (d, $^1J_{\text{C-F}} = 250.9$ Hz, C-F), 135.8, 135.05, 135.02, 130.9 (d, $J_{\text{C-F}} = 6.5$ Hz), 129.3 (d, $^2J_{\text{C-F}} = 17.0$ Hz, C *ortho* to F), 129.2, 128.4, 128.24, 128.20, 126.3, 124.3, 120.2 (d, $J_{\text{C-F}} = 4.0$ Hz, CH), 118.8 (d, $^2J_{\text{C-F}} = 20.0$ Hz, CH *ortho* to F), 66.6, 55.9, 35.8.

Calcd for $[\text{C}_{23}\text{H}_{18}\text{FNO}_3 + \text{H}]^+$ 376.1349, found: 376.1352.

Compound **3af**.

3af was obtained as a white solid in 45% yield (65 mg) starting from **1a** (116 mg, 0.55 mmol) and acrylonitrile (58 mg, 1.1 mmol).



^1H NMR (400 MHz, CDCl_3): δ 7.99 (d, $J = 7.8$ Hz, 1H), 7.74 (d, $J = 7.8$ Hz, 1H), 7.69 (t, $J = 7.8$ Hz, 1H), 7.62 (t, $J = 7.8$ Hz, 1H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 5.30 (dd, $J = 7.6, 3.2$ Hz, 1H), 3.02 (dd, $J = 16.8, 3.6$ Hz, 1H), 2.66 (dd, $J = 16.8, 7.6$ Hz, 1H), 2.40 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): 166.5, 144.8, 136.7, 132.9, 132.7, 132.0, 130.3, 129.8, 124.7, 124.2, 122.3, 115.4, 56.7,

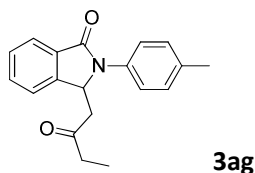
22.0, 21.0.

IR: 2251, 1684, 1512, 1470, 1386, 1217, 1153, 824, 737 cm^{-1} .

HRMS (ESI): Calcd for $[\text{C}_{17}\text{H}_{14}\text{N}_2\text{O} + \text{Na}]^+$ 285.0998; found: 285.0998.

Compound **3ag**.

3ag was obtained as a viscous liquid in 83% yield (126 mg) from **1a** (109 mg, 0.516 mmol) and 1-penten-3-one (87 mg, 1.04 mmol) by following the general procedure.

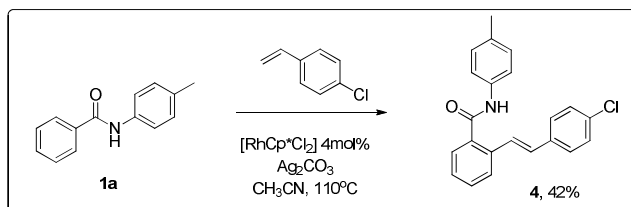


^1H NMR (400 MHz, CDCl_3): δ 7.81 (d, $J = 7.8$ Hz, 1H), 7.41-7.48 (m, 2H), 7.35-7.39 (m, 3H), 7.15 (d, $J = 8.2$ Hz, 2H), 5.59 (dd, $J = 9.2, 3.6$ Hz, 1H), 2.91 (dd, $J = 3.2, 17.6$ Hz, 1H), 2.50 (dd, $J = 9.2, 17.6$ Hz, 1H), 2.34 (s, 3H, CH_3), 2.30 (q, $J = 7.2$ Hz, 2H), 0.97 (t, $J = 7.2$ Hz, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): 208.6, 166.4, 144.8, 135.2, 133.6, 131.8, 131.7, 129.5, 128.3, 123.6, 123.3, 122.4, 56.5, 44.9, 36.5, 20.6, 7.2.

IR: 1698, 1614, 1513, 1380, 1110, 815, 754 cm^{-1} .

HRMS (ESI): Calcd for $[\text{C}_{19}\text{H}_{19}\text{NO}_2 + \text{Na}]^+$ 316.1308; found: 316.1314.

2. The synthesis and characterization of compound **4**



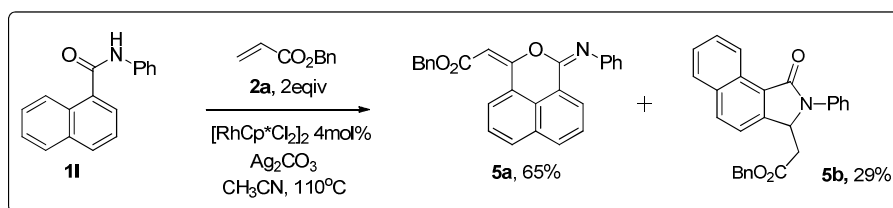
Benzamide **1a** (115.0 mg, 0.54 mmol), Ag_2CO_3 (297 mg, 1.08 mmol, 2 equiv), and $[\text{RhCp}^*\text{Cl}_2]_2$ (13.2 mg, 4 mol %) were weighted into a 25 mL pressure tube, to which acetonitrile (4 mL) was added. After purged with nitrogen, 4-chlorostyrene (75 mg, 0.54 mmol, 1 equiv) was added via syringe and the mixture was stirred at 110 $^\circ\text{C}$ for 12 h. The mixture was then diluted with CH_2Cl_2 (10 mL) and filtered through celite. All volatiles were removed under reduced pressure. Purification was performed using flash column chromatography on silica gel using EtOAc and pet. ether to afford compound **4** as a white solid (79 mg, 42%).

^1H NMR (400 MHz, $\text{DMSO}-d_6$) of **4**: δ 10.36 (s, 1H, NH), 7.90 (d, $J = 7.6$ Hz, 1H), 7.63 (d, $J = 8.4$ Hz, 2H), 7.50-7.55 (m, 4H), 7.41-7.43 (m, 4H), 7.27 (d, $J = 16.4$ Hz, 1H), 7.15 (d, $J = 8.0$ Hz, 2H), 2.28 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): 166.8, 135.1, 135.0, 134.9, 134.7, 134.0, 133.2, 130.1, 130.0, 129.1, 128.4, 127.5, 127.3, 127.2, 126.0, 125.8, 119.5, 20.4.

IR: 3263, 1639, 1604, 1548, 1405, 1331, 1261, 1092, 813 cm^{-1} .

HRMS (ESI): Calcd for $[\text{C}_{22}\text{H}_{18}\text{ClNO} + \text{H}]^+$ 348.1150; found: 348.1165.

3. The synthesis and characterization of compounds 5a-b



Compound 5a.

5a was obtained as a white solid in 65% yield (132 mg) from **1l** (124 mg, 0.50 mmol) and benzyl acrylate (163 mg, 1.0 mmol).

¹H NMR (400 MHz, CDCl₃): δ 9.16 (d, *J* = 9.2 Hz, 1H), 9.13 (d, *J* = 8.8 Hz, 1H), 8.14 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 6.8 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.47-7.50 (m, 1H), 7.33-7.40 (m, 7H), 5.68 (s, 1H), 5.24 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): 167.7, 165.8, 149.9, 135.7, 135.0 (two overlapping signals), 133.7, 133.6, 129.7 (two overlapping signals), 129.1, 129.0, 128.6 (two overlapping signals), 128.5 (two overlapping signals), 128.4, 128.0, 124.7, 124.3, 123.5, 100.9, 66.5.

IR: 1711, 1622, 1340, 1178, 1136, 838 cm⁻¹.

HRMS (ESI): Calcd for [C₂₇H₁₉NO₃ + Na]⁺ 428.1257; found: 428.1265.

Compound 5b.

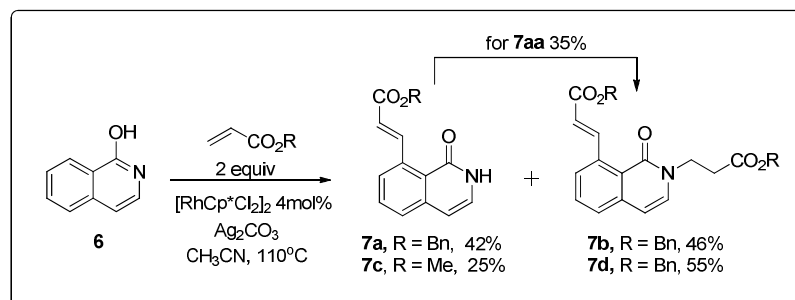
5b was obtained as a viscous liquid in 29% yield (60 mg) from **3l** (124 mg, 0.50 mmol) and benzyl acrylate (163 mg, 1.0 mmol).

¹H NMR (400 MHz, CDCl₃): δ 9.28 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.57-7.61 (m, 3H), 7.44-7.47 (m, 3H), 7.21-7.30 (m, 6H), 5.63 (dd, *J* = 8.0, 4.0 Hz, 1H), 5.07 (d, *J* = 12.4 Hz, 1H), 5.01 (d, *J* = 12.0 Hz, 1H), 3.03 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.63 (dd, *J* = 16.0, 8.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): 170.2, 167.7, 144.6, 136.4, 135.1, 133.4, 133.2, 129.4, 129.2, 128.5, 128.4, 128.2 (two overlapping signals), 128.1, 126.8, 125.8, 125.6, 124.0, 123.9, 119.3, 66.9, 57.0, 37.4.

IR: 1732, 1695, 1597, 1498, 1372, 1151, 752 cm⁻¹.

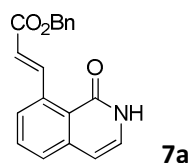
HRMS (ESI): Calcd for [C₂₇H₂₁NO₃ + Na]⁺ 430.1414; found: 430.1421.

4. Synthesis and characterization data of compounds 7a-d



7a and **7b** were obtained from **6** (102mg, 0.70 mmol) and benzyl acrylate (227 mg, 1.4 mmol) by following the general procedure.

Compound **7a**. white solid, 90 mg, 42%

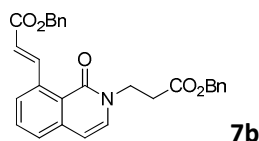


^1H NMR (400 MHz, CDCl_3): δ 11.82 (br, 1H, NH), 9.26 (d, $J = 16.0$ Hz, 1H), 7.56-7.62 (m, 2H), 7.50 (d, $J = 7.6$ Hz, 1H), 7.45 (d, $J = 7.6$ Hz, 2H), 7.30-7.40 (m, 3H), 7.07-7.08 (m, 1H), 6.48 (d, $J = 7.2$ Hz, 1H), 6.28 (d, $J = 16.0$ Hz, 1H), 5.29 (s, 2H, CH_2). ^{13}C NMR (100 MHz, CDCl_3): 166.7, 164.6, 147.3, 139.8, 137.8, 136.2, 132.0, 128.6, 128.5, 128.2, 128.1 (two overlapping signals), 126.7, 123.4, 119.7, 106.6, 66.2.

IR: 3158, 1698, 1654, 1639, 1277, 1263, 1247, 1018, 905 cm^{-1} .

HRMS (ESI): Calcd for $[\text{C}_{19}\text{H}_{15}\text{NO}_3 + \text{Na}]^+$ 328.0944; found: 328.0954.

Compound **7b**. white solid, 150 mg, 46%.



^1H NMR (400 MHz, CDCl_3): δ 9.09 (d, $J = 16.0$ Hz, 1H), 7.55 (t, $J = 8.0$ Hz, 1H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.42-7.49 (m, 3H), 7.25-7.38 (m, 8H), 7.17 (d, $J = 7.6$ Hz, 1H), 6.38 (d, $J = 7.6$ Hz, 1H), 6.19 (d, $J = 16.0$ Hz, 1H), 5.27 (s, 2H, CH_2), 5.09 (s, 2H, CH_2), 4.22 (t, $J = 6.4$ Hz, 2H, CH_2), 2.92 (t, $J = 6.4$ Hz, 2H, CH_2). ^{13}C NMR (100 MHz, CDCl_3): 171.4, 166.4, 162.0, 147.7, 138.6, 138.1, 136.2, 135.4, 133.0, 131.7, 128.5, 128.4, 128.2 (two overlapping signals), 128.1, 128.0, 127.6, 127.1, 123.5, 119.5, 105.7, 66.5, 66.1, 46.1, 33.1.

IR: 1726, 1649, 1610, 1247, 1169, 822 cm^{-1} .

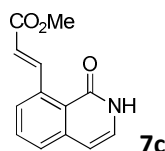
HRMS (ESI): Calcd for $[\text{C}_{29}\text{H}_{25}\text{NO}_5 + \text{Na}]^+$ 490.1625; found: 490.1636.

The conversion of 7a and n-benzyl acrylate to 7b:

Compound **7a** (30 mg, 0.098 mmol), benzyl acrylate (47.8 mg, 0.295 mmol), Ag₂CO₃ (54 mg, 0.2 mmol), and [RhCp*Cl₂]₂ (2.4 mg, 4 mol %) were weighted into a pressure tube (25 mL), to which was added acetonitrile (2 mL). After purged with nitrogen, the mixture was stirred under 110 °C for 10 h. The solution was diluted with CH₂Cl₂ (5 mL) and was filtrated through celite. Product **7b** was isolated in 35% yield, together with the unreacted **7a** (64%).

7c and **7d** were obtained from **6** (95 mg, 0.65 mmol) and methyl acrylate (113 mg, 1.3 mmol) by following the general procedure.

Compound **7c**. White solid, 37 mg, 25%.

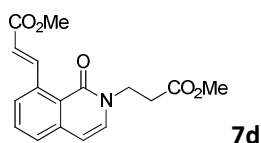


¹H NMR (400 MHz, CDCl₃): δ 11.21 (br, 1H, NH), 9.19 (d, *J* = 16.0 Hz, 1H), 7.57-7.65 (m, 2H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 6.4 Hz, 1H), 6.53 (d, *J* = 6.8 Hz, 1H), 6.24 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): 167.3, 164.4, 147.1, 139.8, 137.7, 131.9, 128.6, 128.0, 126.7, 123.4, 119.5, 106.5, 51.6.

IR: 3244, 1722, 1643, 1553, 1305, 1242, 1166, 821 cm⁻¹.

HRMS (ESI): Calcd for [C₁₃H₁₁NO₃ + Na]⁺ 252.0631; found: 252.0635.

Compound **7d**. White solid, 113 mg, 55%

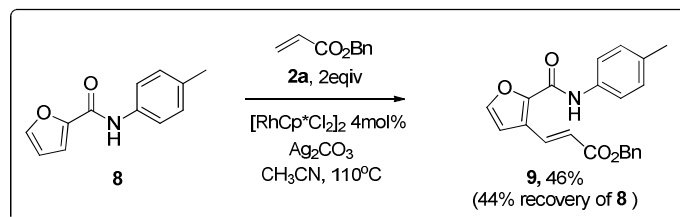


¹H NMR (400 MHz, CDCl₃): δ 9.04 (d, *J* = 16.0 Hz, 1H), 7.45-7.61 (m, 3H), 7.26 (d, *J* = 6.8 Hz, 1H), 6.47 (d, *J* = 6.4 Hz, 1H), 6.16 (d, *J* = 16.0 Hz, 1H), 4.23 (br, 2H), 3.83 (s, 3H, CH₃), 3.67 (s, 3H, CH₃), 2.89 (br, 2H). ¹³C NMR (100 MHz, CDCl₃): 172.1, 167.2, 162.1, 147.3, 138.7, 138.2, 133.1, 131.8, 127.7, 127.1, 123.5, 119.6, 105.9, 51.8, 51.7, 46.1, 32.9.

IR: 1715, 1647, 1615, 1432, 1381, 1161, 820 cm⁻¹.

HRMS (ESI): Calcd for [C₁₇H₁₇NO₅ + Na]⁺ 338.0999; found: 338.1006.

5. The synthesis and characterization of compounds **9**, **11** and **13**



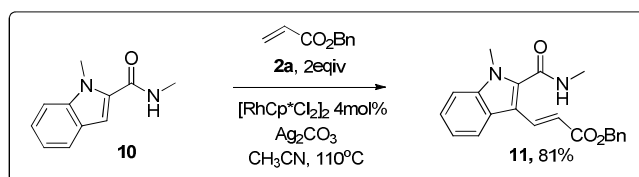
Compound **9**.

9 was obtained as a white solid in 46% yield (98 mg) from **8** (118 mg, 0.59 mmol) and benzyl acrylate (191 mg, 1.18 mmol) by following the general procedure.

¹H NMR (400 MHz, CDCl₃): δ 8.48 (d, *J* = 16.0 Hz, 1H), 8.13 (br, 1H, NH), 7.50 (d, *J* = 8.4 Hz, 2H), 7.24-7.40 (m, 6H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 1.2 Hz, 1H, furan CH), 6.33 (d, *J* = 16.0 Hz, 1H), 5.22 (s, 2H, CH₂), 2.30 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): 166.0, 156.0, 144.1, 143.5, 135.9, 134.8, 134.4, 134.3, 129.5, 128.4, 128.1, 128.0, 126.7, 121.7, 120.0, 110.1, 66.2, 20.8.

IR: 3293, 1713, 1651, 1603, 1573, 1304, 1252, 1158, 993, 815 cm⁻¹.

HRMS (ESI): Calcd for [C₂₂H₁₉NO₄ + Na]⁺ 384.1206; found: 384.1206.



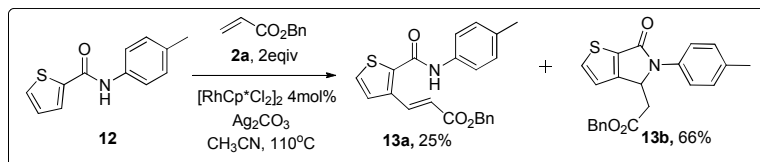
Compound **11**.

11 was obtained as a white solid in 81% yield (163 mg) from **10** (109 mg, 0.58 mmol) and benzyl acrylate (188 mg, 1.16 mmol) by following general procedure.

¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 16.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.20-7.33 (m, 8H), 6.59 (br, 1H, NH), 6.47 (d, *J* = 16.0 Hz, 1H), 5.11 (s, 2H, CH₂), 3.75 (s, 3H, CH₃), 3.03 (d, *J* = 3.2 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): 167.7, 162.1, 138.0, 137.0, 136.7, 136.1, 128.5, 128.4, 128.1 (two overlapping signals), 124.5, 122.0, 121.3, 115.0, 111.1, 110.4, 66.0, 31.2, 26.8.

IR: 3326, 1694, 1671, 1609, 1551, 1376, 1291, 1264, 1171, 1133, 830, 734 cm⁻¹.

HRMS (ESI): Calcd for [C₂₁H₂₀N₂O₃ + Na]⁺ 371.1366; found: 371.1372.



13a and **13b** were obtained from **12** (153 mg, 0.70 mmol) and benzyl acrylate (228 mg, 1.4 mmol) by following the general procedure.

Compound **13a**. white solid, 66 mg, 25%.

^1H NMR (400 MHz, CDCl_3): δ 8.33 (d, J = 16.0 Hz, 1H), 7.68 (br, 1H, NH), 7.44 (d, J = 8.4 Hz, 2H), 7.25-7.45 (m, 7H), 7.13 (d, J = 8.0 Hz, 2H), 6.37 (d, J = 16.0 Hz, 1H), 5.21 (s, 2H, CH_2), 2.33 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): 166.4, 159.9, 139.0, 136.8, 136.5, 135.9, 134.8, 134.7, 129.6, 128.5, 128.2, 128.1, 127.5, 126.9, 121.2, 120.5, 66.4, 20.9.

IR: 3219, 1711, 1631, 1512, 1263, 1165, 811 cm^{-1} .

HRMS (ESI): Calcd for $[\text{C}_{22}\text{H}_{19}\text{NO}_3\text{S} + \text{Na}]^+$ 400.0978; found: 400.0979.

Compound **13b**. white solid, 174 mg, 66%.

^1H NMR (400 MHz, CDCl_3): δ 7.59 (d, J = 4.8 Hz, 1H), 7.28-7.34 (m, 7H), 7.21 (d, J = 8.0 Hz, 2H), 6.96 d, (J = 4.8 Hz, 1H), 5.40 (dd, J = 8.0, 4.0 Hz, 1H), 5.10 (s, 2H), 2.98 (dd, J = 16.4, 3.6 Hz, 1H), 2.42 (dd, J = 16.4, 8.4 Hz, 1H), 2.35 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): 170.1, 162.6, 154.2, 135.8, 135.6, 135.2, 133.9, 129.8 (two overlapping signals), 128.6, 128.5, 128.4, 123.9, 121.5, 66.8, 56.7, 37.1, 20.9

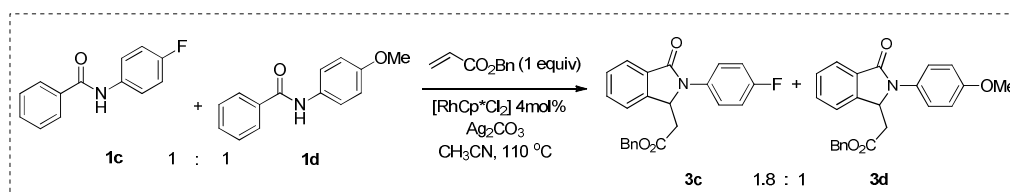
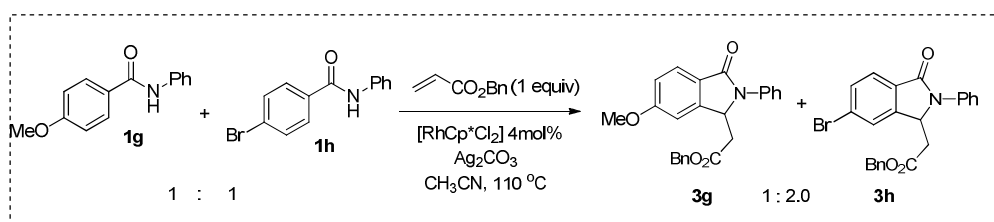
IR: 1732, 1683, 1514, 1391, 1212, 1145, 759 cm^{-1} .

HRMS (ESI): Calcd for $[\text{C}_{22}\text{H}_{19}\text{NO}_3\text{S} + \text{Na}]^+$ 400.0978; found: 400.0979.

6. Competitive reactions

General procedure for competitive reactions

Amides **1g** (40.0 mg, 0.176 mmol), **1h** (48.6 mg, 0.176 mmol), benzyl acrylate **2a** (28.5 mg, 0.176 mmol), Ag₂CO₃ (97 mg, 0.35 mmol), and [RhCp*Cl₂]₂ (4.3 mg, 4 mol %) were weighted into a pressure tube (25 mL), to which was added acetonitrile (4 mL). After purged with N₂, the tube was sealed and the mixture was stirred at 115 °C for 5 h under nitrogen. 1,3,5-Trimethoxybenzene (8.41 mg, 0.05 mmol) was added as an NMR standard. The ratio of **3g** to **3h** was determined by ¹H NMR spectroscopy be 1:2.0. Similarly, the ratio of **3c** to **3d** was determined to be 1.8:1.



NMR spectra

