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Oxidative Coupling of NH Isoquinolones with Olefins Catalyzed by Rh(III)

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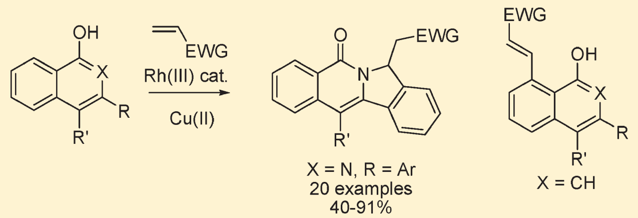
S Supporting Information

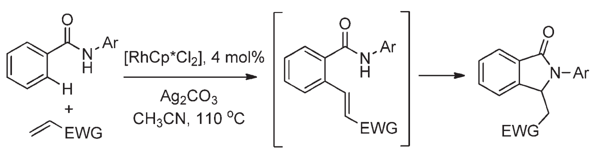
ABSTRACT: Rh(III)-catalyzed oxidative coupling reactions between isoquinolones with 3-aryl groups and activated olefins have been achieved using anhydrous $Cu(OAc)_2$ as an oxidant to give tetracyclic products. The nitrogen atom acts as a directing group to facilitate *ortho* C−H activation. This reaction can be one-pot starting from methyl benzohydroxamates, without the necessity of the isolation of isoquinolone products. A broad scope of substrates has been demonstrated, and both terminal and internal activated olefins can be applied. In the coupling of *N*-methylmaleimide, a Wacker-like mechanism was proposed, where backside attack of the NH group in isoquinolones is suggested as a key step. Selective C−H activation has also been achieved at the 8-position of 1-naphthol, leading to an olefination product.



In the past decade, oxidative functionalization of C−H bonds, particularly sp^2 C−H bonds, that proceeds via a C−H activation pathway has attracted increasing attention, and synthetic methods based on these strategies provide powerful tools to construct complex structures.[1] Metal-catalyzed direct C−H activation followed by oxidative functionalization with alkenes (the oxidative Heck-type reaction[2]) has emerged as an attractive and atom-economic alternative to the traditional Heck coupling[3] because each partner is minimally functionalized and no prior activation of the coupling partner is necessary. It is well-known that palladium catalysts have been predominantly used for this type of transformation,[4,5] although other metals such as ruthenium have also been reported.[6]

Rhodium catalysts stand out in the area of C−H functionalization via C−H activation pathway either in redox or redox-neutral reactions.[1d,j,7] The wide applications of rhodium catalysts in C−H activation is due to their wide functional group tolerance, high selectivity, and compatibility with oxidants. Despite the rather limited examples of rhodium-catalyzed oxidative Heck reactions,[8] there is rapidly increasing interest in using low loading of Rh(III) complexes that give high selectivity and broad substrate scope (Scheme 1). Recently, Miura and Satoh,[9−11] Glorius,[12,13] Ellman and Bergman,[14] and we[15,16] have made some progress in rhodium-catalyzed cross-coupling between olefins and arenes under chelation assistance. We now report the oxidative olefination of NH isoquinolone and 1-naphthol.

We recently reported Rh(III)-catalyzed oxidative coupling of benzamides with activated olefins leading to γ-lactams, with the olefination product proposed as an intermediate (eq 1).[16] Here the role of amide as a directing group is significant.[17] Understanding, designing, and exploring other readily installable directing groups should be an important task that serves to expand the synthetic utility of Rh(III)-catalyzed coupling reactions. We have also reported[17a] that either the N or the O atom in NH isoquinolones (tautomers of 1-hydroxyisoquinolones) can act as an efficient directing group to achieve activation of proximal C−H bonds and subsequent oxidative functionalization with alkynes (eq 2). Given functional similarities between alkynes and alkenes, we anticipate that NH isoquinolones, together with structurally related 1-naphthols, can undergo oxidative olefination with activated alkenes such as acrylates. Notably, three types of products (**A**−**C**) as given in eq 3 can be envisioned, as a result of chemoselectivity of C−H activation and regioselectivity of olefin insertion. In fact, products of the types **A** and **B** are reported in this work.



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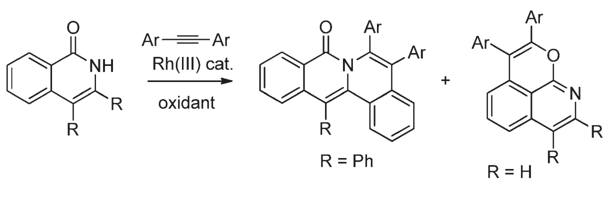

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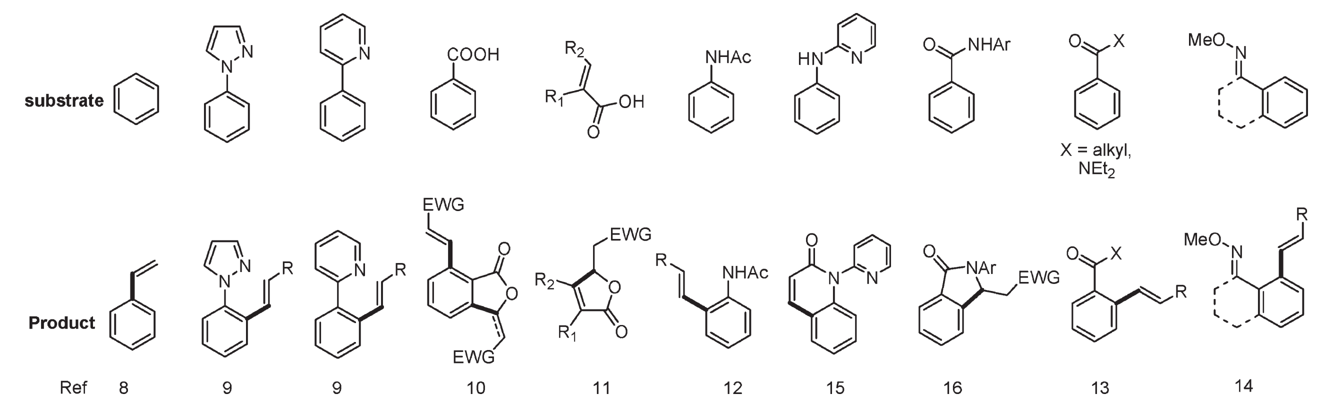
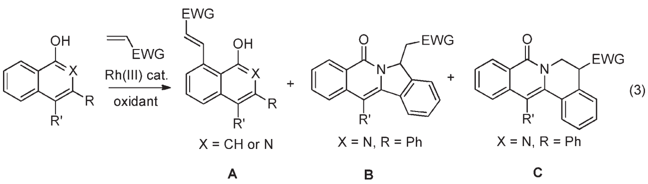
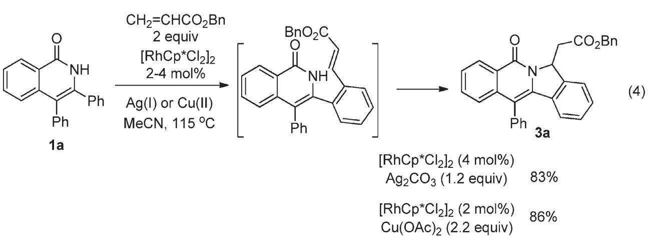
Scheme 1. Rh(III)-Catalyzed Oxidative Olefination





We initiated our exploration with an attempt to oxidatively couple benzyl acrylate with NH isoquinolone **1a**. Importantly, novel synthesis of **1a** and its analogues was recently reported[18] by Fagnou and co-workers under redox-neutral conditions using a combination of $[RhCp^*Cl_2]_2$ (2.5 mol %) and CsOAc (30 mol %) starting from readily available methyl benzohydroxamate [PhC(O)NH(OMe)] and an alkyne (MeOH, 60 °C). This important synthetic method allows easy access to a variety of NH isoquinolones. We found that our previously reported conditions for the coupling of benzamides with benzyl acrylate (eq 1, 4 mol % of $[RhCp^*Cl_2]_2$, 2.1 equiv of Ag_2CO_3, MeCN, 115 °C) proved successful, and **3a** was isolated as the only product in 83% yield. The structure of this product was elucidated on the basis of NMR spectroscopy and mass spectrometry. In particular, ^{13}C NMR spectroscopy revealed that two CH_2 groups are present. This reaction possibly proceeds via an oxidative olefination−hydroamination cascade.[5d] The efficiency of this reaction was further improved when $Cu(OAc)_2$ (2.2 equiv) was used as an inexpensive oxidant, where the catalyst loading can be reduced to 2 mol %. Under these improved conditions (conditions A), product **3a** was isolated in comparably high yield (eq 4). In contrast, no coupling reaction was observed when the olefin was replaced by styrene.



Since the same catalyst $[RhCp^*Cl_2]_2$ was used both in the redox-neutral preparation of NH isoquinolines and in their oxidative functionalization with alkynes, we reasoned that an overall one-pot synthesis of products **3** could be achievable from methyl benzohydroxamate. Indeed, when methanol solvent was evacuated after the completion of the reaction between methyl benzohydroxamate and alkyne, addition of $Cu(OAc)_2$, benzyl acrylate (115 °C), and MeCN provided a suitable set of conditions for oxidative olefination (conditions B). Under these conditions, **3a** was obtained in an overall yield of 78%. This also suggests that the presence of a catalytic amount of CsOAc has essentially no detrimental effect on the oxidative olefination step.

With the optimized conditions in hand, we explored a series of substrates under both one-pot and stepwise conditions. Isolated NH isoquinolone **1a** readily coupled with a few acrylates to give **3a**−**e** in isolated yields ranging from 55 to 86% (Table 1). Other activated alkenes such as an acrylamide and an acrylonitrile can be applied, although relatively lower yields of **3f** (50%) and **3g** (58%) were obtained under conditions B. In these cases, the reactions are quite selective, and most of the unreacted **1a** was recovered. The scope of isoquinolones was further defined in the coupling with benzyl acrylate under conditions A. Isolated isoquinolones bearing electron-donating (see **3i**, **3j**, and **3m**) and -withdrawing groups (see **3h**, **3k**, **3k′**, and **3l**) in the phenyl ring are applicable, although introduction of a highly withdrawing *m*-CF_3 group tends to slow down this coupling reaction (**3h**). When an *m*-methyl-substituted methyl benzohydroxamate was used under either conditions A or B, **3i** was isolated as the only product. In contrast, when an *m*-fluoro-substituted methyl benzohydroxamate was allowed to react with benzyl acrylate under the one-pot conditions, two regioisomers were isolated as analytically pure products in similar yields (41% for **3k** and 45% for **3k′**). The low regioselectivity of C−H activation in the first step is most likely ascribed to the reduced steric bulk of a fluoro group and/or its directing effect.[16] Using isolated isoquinolones synthesized from other symmetrically substituted alkynes (ArC≡CAr) for oxidative olefination also proved successful, and both electron-donating and -withdrawing groups in the Ar group can be tolerated. Thus **3o** and **3p** were isolated in high yield. In addition, an isoquinolone derived from an unsymmetrically substituted alkyne (MeC≡CPh) underwent smooth coupling with benzyl acrylate to give **3n** in high yield, with the methyl group oriented distal to the nitrogen, which is consistent with previous reports.[17a,19] In contrast to the above success, (isolated) NH isoquinolone **4** obtained from the reaction of 4-octyne and $PhC(O)NH_2$[17a] failed to give any desired coupling with benzyl acrylate (eq 5) even with 4 mol % loading of the catalyst, indicating that neither the C−H bond in

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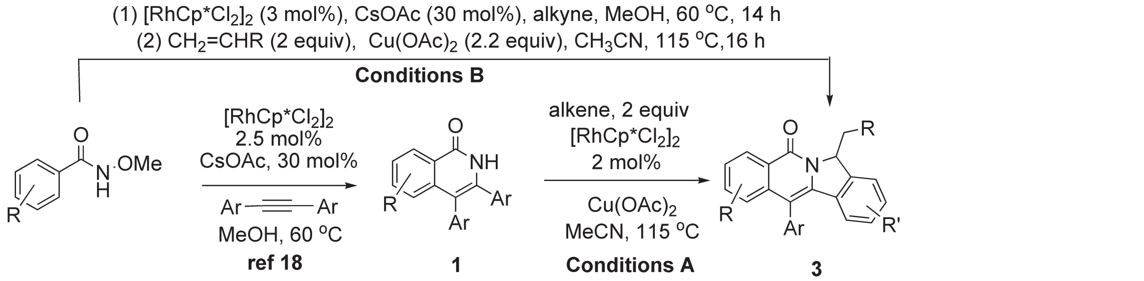
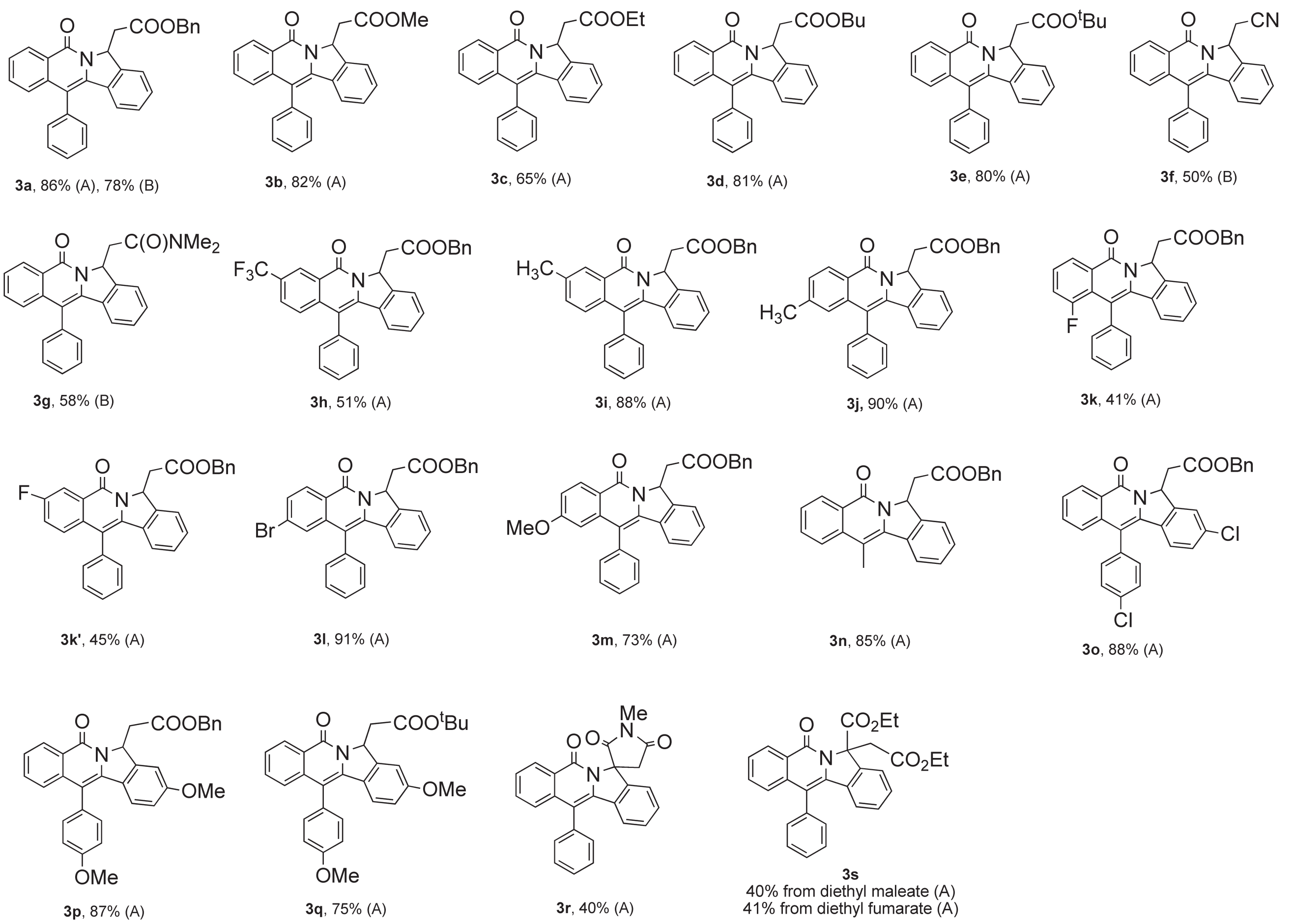
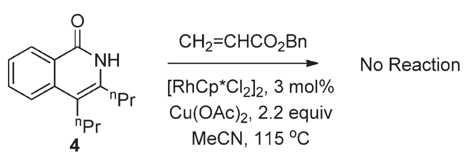
Table 1. Rh(III)-Catalyzed Oxidative Coupling of NH Isoquinolones and Alkenes[a−c]





[a] Isolated yield. [b] Conditions indicated in parentheses after the yield. [c] Conditions A: isoqunolone (0.5 mmol), olefin (1.0 mmol), $Cu(OAc)_2$ (1.1 mmol), $[RhCp^*Cl_2]_2$ (0.01 mmol), MeCN (4 mL) 115 °C, 16 h, sealed tube under N_2. Conditions B: PhC(O)NH(OMe) (0.5 mmol), alkyne (0.51 mmol), $[RhCp^*Cl_2]_2$ (0.015 mmol), CsOAc (0.15 mmol), MeOH (3 mL), 60°, 14 h, then evacuated, olefin (1.0 mmol), $Cu(OAc)_2$ (1.1 mmol), MeCN (4 mL), 115 °C, sealed tube under N_2, 16 h.

the alkyl chain nor the C−H bond *ortho* to the carbonyl group underwent C−H activation. This is in contrast to the observed oxidative coupling of **4** and analogues with alkynes, where C−H activation occurred at the position *ortho* to the carbonyl group.[17a]

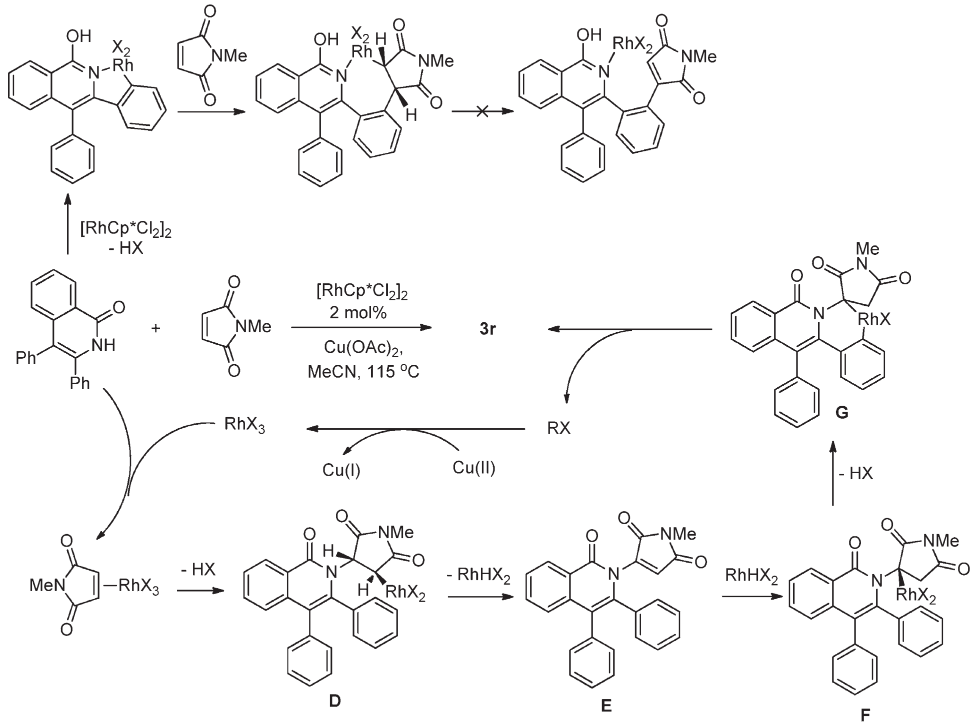


(5)

The alkene substrate is not limited to a terminal one. Internal alkenes bearing vicinal withdrawing groups also coupled with **1a** under the standard conditions A to give analogous products. Thus **3r** was isolated in 40% yield when *N*-methylmaleimide was used, and product **3s** was obtained in similar yields starting from either diethyl maleate or fumarate. In all of these cases, unreacted starting material **1a** was essentially fully recovered.

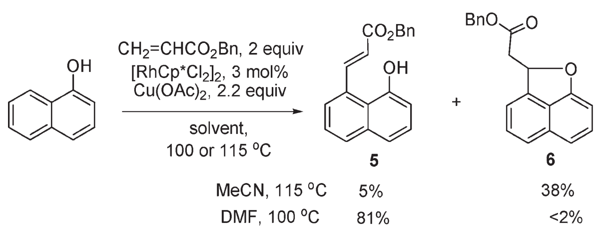
We reasoned that the olefination intermediate given in eq 4 cannot be a reasonable one in the reaction of **1a** and *N*-methylmaleimide if this coupling follows a cyclometalation−olefin

Scheme 2. Plausible Mechanism of the Coupling of an Internal Olefin with an NH Isoquinolone



insertion−β-H elimination process (the Heck-like mechanism) (Scheme 2). This is because both olefin insertion and β-H elimination occur via a *syn*-coplanar, four-membered ring transition state, and the cyclic character of this olefin obviates the possibility of β-H elimination. A plausible Wacker-like mechanism to account for the observed reaction is proposed in Scheme 2. Coordination of the olefin on Rh(III) center serves to activate the C═C bond toward nucleophiles. Backside attack of the NH group in **1a** at the activated olefin is proposed to give a *trans* hydroamination (amidorodation) product (**D**).[20] β-Hydride elimination of **D** is proposed and is followed by reinsertion into olefin intermediate **E**, which gives rise to the isomerization of the intermediate **D** to a Rh(III) species **F**.[21] Subsequent cyclometalation of **F** is proposed to give a rhodacycle **G**, from which C−C reductive elimination occurs to afford the final product. In contrast to the proposed cyclometalation of intermediate **F**, no such process is suggested for intermediate **D** which eventually gives product C (eq 3). This is likely because intermediate **F** can lead to a favorable six-membered ring rhodacyclic intermediate instead of a seven-membered one for **D**, although the rhodium center is in a sterically more hindered environment in **F**. This catalytic cycle is completed when the resulting Rh(I) species is oxidized by Cu(II) to regenerate the Rh(III) species.

Although in principle NH isoquinolones can be regarded as special phenols, where the OH can act as a directing group and although we have observed[17a] that oxidative olefination did occur between simple 1-hydroxyisoquinoline and acrylates at the 8-position, no C−H activation at the 8-position of compound **4** could be achieved under our optimized conditions (eq 5). These big differences between simple 1-hydroxisoquinoline and **4** may be ascribed to steric effects, and this inspired us to explore structurally related 1-naphthols as possible substrates. Indeed, 1-naphthols have been successfully employed as a partner in oxidative coupling with internal alkynes.[22] However, no oxidative coupling with any olefin has been reported. Gratifyingly, the coupling of 1-naphthol and benzyl acrylate gave two expected products **5** and **6** in 5 and 38% isolated yield, respectively, although this reaction suffers from moderate selectivity (eq 6). Here the major isolated product **6** is derived from intramolecular hydroalkoxylation of the olefination product **5**. Heating (115 °C) a CD_3CN solution of product **5** gave essentially no formation of **6**, indicating that this intramolecular hydroalkoxylation process is metal-catalyzed. Importantly, when the reaction solvent was changed to DMF (100 °C), the reaction is much more efficient and selective, and product **5** was isolated as the only product in 81% yield, highlighting significant solvent effect in the oxidative coupling between 1-naphthol and an acrylate.



(6)

In conclusion, we have successfully developed Rh(III)-catalyzed oxidative coupling between functionalized NH isoquinolones and activated olefins using $Cu(OAc)_2$ as an oxidant to give tetracyclic products. The N atom acts as a directing group for *ortho* C−H activation in the 3-aryl group of NH isoquinolones. Significantly this reaction can be one-pot starting from methyl benzohydroxamates without the isolation of isoquinolones. A broad scope of substrates has been demonstrated, and both activated terminal and internal olefins are an efficient coupling partner. In the coupling of *N*-methylmaleimide, a Wacker-like mechanism was proposed, where backside attack of the NH group in isoquinolones is proposed to give an intermediate that isomerizes and subsequently leads to cyclometalation. When no 3-aryl group is present in NH isoquinolone substrates, neither the N nor the OH group can act as an efficient directing group for C−H activation. Selective C−H activation was successfully achieved at the 8-position of 1-naphthol, leading to an olefination product under similar conditions. The broad selection of the two coupling partners and the diversity of the coupling products should make this method a useful one in the synthesis of complex structures.

EXPERIMENTAL SECTION

General Considerations. All rhodium-catalyzed reactions were carried out using standard Schlenk techniques or in a nitrogen-filled drybox. All solvents were distilled under N_2 prior to use. ^{1}H and ^{13}C NMR spectra were recorded using $CDCl_3$ as a solvent on a 400 or 500 MHz spectrometer at 298 K. The chemical shift is given in dimensionless δ values and is referenced relative to TMS in ^{1}H and ^{13}C NMR spectroscopy. High-resolution mass spectra were obtained on a LC-Q-TOF-MS spectrometer. All other reagents were obtained from commercial sources. Anhydrous $Cu(OAc)_2$ was used throughout this work. NH isoquinolones[18] and compound **4**[17a] were synthesized according to literature reports.

Representative Procedure of the Synthesis of 3a−s. *Conditions A:* NH isoquinolone **1a** (148.7 mg, 0.50 mmol), $Cu(OAc)_2$ (119.8 mg, 1.10 mmol, 2.2 equiv), and $[RhCp^*Cl_2]_2$ (6.2 mg, 2 mol %) were weighed into a 25 mL pressure tube, to which acetonitrile (4 mL) was added. After purged with nitrogen, benzyl acrylate (162.2 mg, 1.00 mmol, 2 equiv) was added via a syringe. The reaction tube was sealed, and the mixture was stirred at 115 °C for 16 h. The mixture was diluted with CH_2Cl_2 (10 mL) and was filtered through Celite, followed by removal of volatiles under reduced pressure. Purification was performed by flash column chromatography on silica gel using EtOAc and petroleum ether. Yield: 86% (197 mg, 0.43 mmol).

Conditions B: PhC(O)NH(OMe) (76 mg, 0.5 mmol), diphenylacetylene (89 mg, 0.5 mmol), $[RhCp^*Cl_2]_2$ (9.3 mg, 3 mol %), and CsOAc (29 mg, 30 mol %) were weighed into a pressure tube. Methanol (4 mL) was added, and the mixture was stirred at 60 °C for 14 h. After removal of methanol under reduced pressure, $Cu(OAc)_2$ (181 mg, 1.0 mmol) and acetonitrile (4 mL) were added. The tube was sealed, and the mixture was stirred at 115 °C for 12 h. The mixture was then diluted with CH_2Cl_2 (10 mL) and was filtered through Celite. All volatiles were then removed under reduced pressure. Purification was performed by flash column chromatography on silica gel using EtOAc and petroleum ether: yield 78% (178 mg, 0.39 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 4.0 Hz, 1H), 7.57−7.60 (m, 4H), 7.52 (t, J = 7.2 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.19−7.34 (m, 9H), 7.07 (t, J = 7.6 Hz, 1H), 6.35 (d, J = 8 Hz, 1H), 6.03 (dd, J = 7.2, 3.6 Hz, 1H), 5.06−5.13 (m, 2H), 3.77 (dd, J = 16, 3.6 Hz, 1H), 3.19 (dd, J = 16, 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 160.7, 141.2, 138.5, 137.7, 135.4, 134.9, 133.3, 132.0, 131.0, 130.7, 129.3, 128.3, 128.2, 128.0, 127.9 (two overlapping signals), 127.1, 126.2, 125.1, 124.6, 123.8, 122.7, 114.4, 66.3, 59.9, 36.4; IR 1733, 1652, 1622, 1476, 1157, 765, 698 cm^{-1}; HRMS (ESI) calcd for $[C_{31}H_{23}NO_3 + H]^+$ 458.1751; found 458.1763.

*Compound **3b**:* Yield 82% (conditions A); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 7.6 Hz, 1H), 7.59−7.61 (m, 4H), 7.50−7.45 (m, 3H), 7.31−7.36 (m, 2H), 7.2 (d, J = 8.0 Hz, 1H), 7.1 (t, J = 7.6 Hz, 1H), 6.38 (d, J = 8.0 Hz, 1H), 6.02 (dd, J = 8.0, 4.0 Hz, 1H), 3.79 (dd, J = 16.0, 3.6 Hz, 1H), 3.70 (s, 3H, CH_3), 2.99 (dd, J = 16.0, 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 160.9, 141.7, 138.7, 137.9, 135.2, 133.5, 132.1, 131.2, 131.0, 129.5, 128.5, 128.4, 127 0.4, 126.4, 125.2, 124.8, 124.0, 122.8, 114.5, 60.0, 51.8, 36.6; IR 1742, 1646, 1616, 1477, 1364, 1163, 764, 704 cm^{-1}; HRMS (ESI) calcd for $[C_{25}H_{19}NO_3 + H]^+$ 382.1438; found 382.1423.

*Compound **3c**:* Yield 65% (conditions A); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 7.6 Hz, 1H), 7.44−7.63 (m, 7H), 7.31−7.36 (m, 2H), 7.21 (d, J = 8.0, 1H), 7.09 (t, J = 7.6 Hz, 1H), 6.39 (d, J = 8.0 Hz, 1H), 6.02 (dd, J = 7.6, 3.6 Hz, 1H), 4.14 (d, J = 4.0 Hz, 1H), 4.10 (d, J = 8.0 Hz, 1H), 3.74 (dd, J = 16.1, 4.0 Hz, 1H), 3.07 (dd, J = 16.0, 8.0 Hz, 1H), 1.15 (t, J = 8.0 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 160.9, 141.6, 138.7, 137.9, 135.2, 133.5, 132.1, 131.1, 131.0, 129.5, 129.43, 129.39, 128.41, 128.36, 127.3, 126.3, 125.2, 124.8, 123.9, 122.9, 114.4, 60.6, 60.0, 36.6, 14.0; IR 1737, 1645, 1620, 1476, 1375, 1180, 762, 705 cm^{-1}; HRMS (ESI) calcd for $[C_{26}H_{21}NO_3 + H]^+$ 396.1594; found 396.1601.

*Compound **3d**:* Yield 81% (conditions A); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 7.6 Hz, 1H),7.43−7.62 (m, 7H), 7.30−7.36 (m, 2H), 7.18 (d, J = 8.4 Hz, 1H), 7.09 (t, J = 8.0 Hz, 1H), 6.38 (d, J = 4.0 Hz, 1H), 6.00 (dd, J = 7.6, 3.6 Hz, 1H), 4.05 (t, J = 8.0 Hz, CH_2, 2H), 3.74 (dd, J = 16.0, 4.0 Hz, 1H), 3.10 (dd, J = 16.0, 8.0 Hz, 1H), 1.45−1.53 (m, 2H, CH_2), 1.22−1.27 (m, 2H, CH_2), 0.83 (t, J = 8.0 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 160.9, 141.7, 138.7, 138.0, 135.2, 133.6, 132.1, 131.2, 131.0, 129.50, 129.45, 129.43, 128.5, 128.4, 127.3, 126.4, 125.2, 124.9, 124.0, 122.9, 114.5, 64.6, 60.1, 36.6, 30.5, 19.0, 13.6; IR 1736, 1645, 1621, 1472, 1176, 764, 701 cm^{-1}; HRMS (ESI) calcd for $[C_{28}H_{25}NO_3 + H]^+$ 424.1907; found 424.1901.

*Compound **3e**:* Yield 80% (conditions A); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 7.6 Hz, 1H), 7.51−7.62 (m, 6H), 7.42−7.45 (m, 1H), 7.33−7.37 (m, 2H), 7.21 (d, J = 8.4 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.39 (d, J = 8.0 Hz, 1H), 5.98 (dd, J = 7.2, 3.2 Hz, 1H), 3.56 (dd, J = 12.0, 4.1 Hz, 1H), 3.22 (dd, J = 16.1, 8.0 Hz, 1H), 1.26 (s, 9H, $3CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 160.9, 141.6, 138.7, 138.1, 135.3, 133.6, 132.1, 131.1, 130.9, 129.5, 129.4, 129.39, 128.4, 128.3, 127.3, 126.3, 125.2, 124.9, 123.9, 123.0, 114.3, 80.8, 60.4, 37.4, 27.8; IR 1720, 1648, 1619, 1476, 1367, 1150, 765, 698 cm^{-1}; HRMS (ESI) calcd for $[C_{28}H_{25}NO_3 + H]^+$ 424.1907; found 424.1912.

*Compound **3f**:* Yield 50% (conditions B); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 8.0 Hz, 1H), 7.60−7.66 (m, 5H), 7.48−7.55 (m, 2H), 7.39 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 4.4 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.18 (t, J = 8.7 Hz, 1H), 6.43 (d, J = 7.6 Hz, 1H), 5.82 (dd, J = 6.0, 4.0 Hz, 1H), 3.55−3.67 (m, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.1, 138.84, 138.79, 137.3, 134.7, 133.8, 132.6, 131.2, 130.7, 129.8, 129.6, 129.5, 129.4, 128.6, 127.4, 126.8, 125.5, 124.7, 124.4, 122.7, 115.9, 115.3, 58.9, 21.2; IR 1650, 1620, 1595, 1473, 1342, 1027, 766, 706 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{16}N_2O + H]^+$ 349.1335; found 349.1356.

*Compound **3g**.* Yield 58% (conditions B); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.54−7.62 (m, 4H), 7.44−7.51 (m, 2H), 7.27−7.36 (m, 2H), 7.21 (d, J = 8.0 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 6.38 (d, J = 8.0 Hz, 1H), 6.16 (dd, J = 9.2, 1.6 Hz, 1H), 4.11 (dd, J = 16.0, 4.0 Hz, 1H), 3.04 (s, CH_3, 3H), 3.02 (s, CH_3, 3H), 2.51 (dd, J = 16.0, 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 160.9, 142.9, 138.8, 138.1, 135.3, 133.1, 132.1, 131.2, 131.0, 129.51, 129.46, 129.4, 128.4, 128.1, 127.3, 126.3, 125.2, 124.8, 124.3, 123.7, 114.4, 60.6. 37.2, 36.1, 35.5; IR 1648, 1620, 1601, 1476, 1151, 765, 702 cm^{-1}; HRMS (ESI) calcd for $[C_{26}H_{22}N_2O_2 + H]^+$ 395.1754; found 395.1741.

*Compound **3h**.* Yield 51% (conditions A); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.73 (dd, J = 8.4, 8.0 Hz, 1H), 7.60 (t, J = 3.2 Hz, 3H), 7.47 (d, J = 7.6 Hz, 1H), 7.18−7.35 (m, 9H), 7.11 (t, J = 7.6 Hz, 1H), 6.37 (d, J = 8.0 Hz, 1H), 6.02 (dd, J = 7.2, 4.0 Hz, 1H), 5.04−5.11 (m, 2H), 3.69 (dd, J = 16.0, 4.0 Hz, 1H), 3.29 (dd, J = 16.0, 7.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 160.3, 141.6, 141.1, 140.2, 135.4, 134.4, 133.1, 131.1, 130.8, 130.1, 129.7, 128.6, 128.4, 128.2, 128.13 (q, J_{F-C} = 3.2 Hz), 128.12 (q, J_{F-C} = 32.9 Hz), 128.1, 126.0, 125.1

(q, J_{F-C} = 4.0 Hz), 124.44, 124.41, 124.0 (q, J_{F-C} = 271 Hz), 122.9, 113.8, 66.6, 60.3, 36.4; IR 1728, 1659, 1622, 1330, 1312, 1164, 1141, 1112, 746, 696 cm^{-1}; HRMS (ESI) calcd for $[C_{32}H_{22}F_3NO_3 + H]^+$ 526.1625; found 526.1635.

*Compound **3i***. Yield 88% (conditions A); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 8.4 Hz, 1H), 7.57−7.58 (m, 3H), 7.43 (d, J = 7.6 Hz, 1H), 7.21−7.33 (m, 9H), 7.06 (t, J = 7.6 Hz, 1H), 6.94 (s, 1H), 6.30 (d, J = 8.0 Hz, 1H), 6.00 (dd, J = 7.6, 3.6 Hz, 1H), 5.07−5.13 (m, 2H), 3.79 (dd, J = 16.0, 3.6 Hz, 1H), 3.14 (dd, J = 16.0, 7.6 Hz, 1H), 2.37 (s, CH_3, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 160.9, 142.7, 141.5, 138.9, 138.0, 135.6, 135.3, 133.6, 131.2, 131.0, 129.4, 129.3, 128.44, 128.37, 128.1, 128.0, 127.4, 124.9, 124.0, 122.9, 122.7, 114.4, 110.0, 66.5, 59.9, 36.8, 22.0; IR 1726, 1651, 1614, 1464, 1344, 1285, 1144, 970, 745, 697 cm^{-1}; HRMS (ESI) calcd for $[C_{32}H_{25}NO_3 + H]^+$ 472.1907; found 472.1916.

*Compound **3j***. Yield 90% (conditions A); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.54 (s, 3H), 7.21−7.43 (m, 11H), 7.03−7.10 (m, 2H), 6.34 (dd, J = 7.6 Hz, 1H), 5.99 (d, J = 3.6 Hz, 1H), 5.06−5.12 (m, 2H), 3.76 (dd, J = 15.6, 2.8 Hz, 1H), 3.16 (dd, J = 16.0, 7.6 Hz, 1H), 2.49 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 160.7, 141.2, 136.9, 136.4, 136.3, 135.5, 135.2, 133.55, 133.50, 131.0, 130.8, 129.3, 129.1, 128.31, 128.26, 128.25, 128.2, 128.0 (two overlapping signals), 126.9, 125.1, 124.7, 123.7, 122.7, 114.5, 66.4, 60.0, 36.6, 21.2; IR 1733, 1652, 1616, 1497, 1350, 1157, 670 cm^{-1}; HRMS (ESI) calcd for $[C_{32}H_{25}NO_3 + H]^+$ 472.1907; found 472.1916.

*Compound **3k***. Yield 41% (conditions A); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.0 Hz, 1H), 7.48−7.52 (m, 3H), 7.41−7.46 (m, 2H), 7.34−7.36 (m, 2H), 7.20−7.29 (m, 8H), 7.04 (t, J = 7.6 Hz, 1H), 6.08 (d, J = 7.6 Hz, 1H), 5.98 (dd, J = 7.6, 3.6 Hz, 1H), 5.05−5.12 (m, 2H), 3.69 (dd, J = 16.0, 3.6 Hz, 1H), 3.19 (dd, J = 15.8, 7.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 159.7 (d, J_{C-F} = 3.9 Hz), 159.0 (d, J_{C-F} = 253.8 Hz), 141.4, 139.1, 137.21 (d, J_{C-F} = 2.1 Hz), 135.5, 133.4, 130.2 (d, J_{C-F} = 2.8 Hz), 129.8 (d, J_{C-F} = 4.2 Hz), 129.6, 128.8, 128.79, 128.5, 128.4, 128.13, 128.07, 128.0, 127.2 (d, J_{C-F} = 9.5 Hz), 126.9 (d, J_{C-F} = 9.0 Hz), 126.8, 124.5, 123.5 (d, J_{C-F} = 4.4 Hz), 122.7, 119.0 (d, J_{C-F} = 21.8 Hz), 111.0, 66.5, 60.1, 36. 5; IR 1731, 1653, 1613, 1472, 1233, 1165, 757, 706 cm^{-1}; HRMS (ESI) calcd for $[C_{31}H_{22}FNO_3 + H]^+$ 476.1656; found 476.1648.

*Compound **3k′***. Yield 45% (conditions A); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.0 Hz, 1H), 7.48−7.52 (m, 3H), 7.41−7.46 (m, 2H), 7.34−7.36 (m, 2H), 7.20−7.29 (m, 8H), 7.04 (t, J = 7.6 Hz, 1H), 6.07 (d, J = 7.6 Hz, 1H), 5.98 (dd, J = 7.6, 3.6 Hz, 1H), 5.05−5.12 (m, 2H), 3.69 (dd, J = 16.0, 3.6 Hz, 1H), 3.19 (dd, J = 15.6, 7.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 161.3 (d, J_{C-F} = 245.9 Hz), 160.1 (d, J_{C-F} = 4.6 Hz), 141.1, 137.4 (d, J_{C-F} = 1.8 Hz), 135.5, 135.4 (d, J_{C-F} = 1.1 Hz), 134.9, 133.4, 131.1, 130.8, 129.52 (two overlapping signals), 129.47, 128.6, 128.5, 128.4, 128.2, 128.1, 127.7 (d, J_{C-F} = 7.5 Hz), 126.4 (d, J_{C-F} = 7.6 Hz), 123.9, 122.9, 120.8 (d, J_{C-F} = 22.0 Hz), 114.0, 112.5 (d, J_{C-F} = 22.8 Hz), 66.6, 60.1, 36.6; IR 1729, 1650, 1490, 1343, 1248, 1175, 735 cm^{-1}; HRMS (ESI) calcd for $[C_{31}H_{22}FNO_3 + H]^+$ 476.1656; found 476.1648.

*Compound **3l***. Yield 91% (conditions A); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 7.2 Hz, 1H), 7.57−7.59 (m, 4H), 7.44 (d, J = 7.6 Hz, 1H), 7.23−7.32 (m, 7H), 7.18−7.21 (m, 2H), 7.08 (t, J = 8 Hz, 1H), 6.81 (d, J = 8 Hz, 1H), 5.98 (dd, J = 6.8, 3.6 Hz, 1H), 5.05−5.11 (m, 2H), 3.72 (dd, J = 16.0, 3.6 Hz, 1H), 3.22 (dd, J = 16.0, 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 160.4, 141.6, 140.3, 139.3, 135.5, 134.4, 133.2, 131.1, 130.9, 129.8, 129.69, 129.66, 129.6, 129.2, 128.8, 128.5, 128.4, 128.2, 128.1, 127.7, 127.6, 124.2, 123.5, 122.9, 113.4, 66.6, 60.2, 36.5; IR 1728, 1653, 1591, 1459, 1340, 1188, 1149, 768, 714 cm^{-1}; HRMS (ESI) calcd for $[C_{31}H_{22}BrNO_3 + H]^+$ 536.0865; found 536.0854.

*Compound **3m***. Yield 73% (conditions A); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 9.2, 1H), 7.55−7.58 (m, 3H), 7.43 (d, J = 7.6, 1H), 7.22−7.33 (m, 8H), 7.06 (t, J = 8.4 Hz, 2H), 6.53 (d, J = 2.4 Hz, 1H), 6.32 (d, J = 7.6 Hz, 1H), 5.99 (dd, J = 7.6, 3.6 Hz, 1H), 5.07−5.13 (m, 2H), 3.71−3.80 (m, 4H), 3.15 (dd, J = 16.0, 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 162.7, 160.6, 141.6, 140.8, 138.5, 135.5, 135.2, 133.5, 131.1, 130.8, 129.42, 129.37, 128.4 (two overlapping signals), 128.3, 128.1 (two overlapping signals), 124.0, 122.8, 118.9, 115.0, 114.2, 107.1, 66.4, 59.9, 55.2, 36.7; IR 1726, 1648, 1601, 1466, 1282, 768, 737 cm^{-1}; HRMS (ESI) calcd for $[C_{32}H_{25}NO_4 + H]^+$ 488.1856; found 488.1864.

*Compound **3n***. Yield 85% (conditions A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (dd, J = 8.0, 1.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.66−7.70 (m,1H), 7.41−7.48 (m, 3H), 7.33−7.36 (m, 1H), 7.41−7.48 (m, 3H), 7.15 (d, J = 1.5 Hz, 1H), 7.14 (d, J = 2.5 Hz, 1H), 5.88 (dd, J = 7.5, 4.0 Hz, 1H), 5.00 (s, 2H, CH_2), 3.64 (dd, J = 16.0, 4.0 Hz, 1H), 3.14 (dd, J = 16.5, 7.5 Hz, 1H), 2.60 (s, CH_3,3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 160.6, 141.5, 138.5, 137.7, 135.5, 134.4, 132.1, 129.1, 128.7, 128.4, 128.2, 128.1, 127.7, 126.2, 125.1, 124.3, 123.2, 123.1, 108.2, 66.5, 59.8, 36.7, 12.4; IR 1729, 1648, 1616, 1383, 1159, 763, 694 cm^{-1}; HRMS (ESI) calcd for $[C_{26}H_{21}NO_3 + H]^+$ 396.1594; found 396.1606.

*Compound **3o***. Yield 88% (conditions A); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 7.6 Hz, 1H), 7.50−7.61 (m, 5H), 7.24−7.28 (m, 7H), 7.13 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 6.33 (d, J = 8.4 Hz, 1H), 5.97 (dd, J = 7.2, 3.2 Hz, 1H), 5.07−5.13 (m, 1H), 3.75 (dd, J = 16.0, 4.0 Hz, 1H), 3.20 (dd, J = 16.0, 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 160.7, 143.2, 138.3, 137.2, 135.8, 135.4, 134.8, 133.3, 132.6, 132.4, 132,3, 131.9, 130.0, 129.9, 129.1, 128.5, 128.3, 128.1, 127.5, 126.8, 125.0, 124.9, 124.8, 123.5, 113.3, 66.7, 59.7, 36.2; IR 1726, 1653, 1492, 1271, 1159, 731, 518 cm^{-1}; HRMS (ESI) calcd for $[C_{31}H_{21}Cl_2NO_3 + H]^+$ 526.0971; found 526.0977.

*Compound **3p***. Yield 87% (conditions A); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 8.0 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.19−7.28 (m, 8H), 7.07−7.10 (m, 2H), 6.98 (d, J = 1.6 Hz, 1H), 6.65 (dd, J = 8.8, 2.0 Hz, 1H), 6.36 (d, J = 8.8 Hz, 1H), 5.96 (dd, J = 7.6, 3.6 Hz, 1H), 5.08−5.12 (m, 2H), 3.94 (s, 3H, CH_3), 3.80 (dd, J = 16.0, 3.6 Hz, 1H), 3.71 (s, CH_3, 3H), 3.10 (dd, J = 16.0, 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 160.9, 159.5, 143.5, 139.2, 138.2, 135.6, 132.3, 132.0, 131.9, 128.4, 128.1, 128.0, 127.3, 127.2, 126.2, 125.7, 125.1, 124.9, 124.3, 115.3, 114.8, 112.4, 107.6, 66.5, 59.8, 55.4, 56.3, 36.7; IR 1667, 1511, 1245, 1174, 1030, 766, 539 cm^{-1}; HRMS (ESI) calcd for $[C_{33}H_{27}NO_5 + H]^+$ 518.1962; found 518.1970.

*Compound **3q***. Yield 75% (conditions A); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 8.0, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.2 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.19−7.26 (m, 2H), 7.08−7.13 (m, 3H), 6.67 (d, J = 8.8 Hz, 1H), 6.39 (d, J = 8.8 Hz, 1H), 5.91 (d, J = 5.2 Hz, 1H), 3.95 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 3.66 (dd, J = 16.0, 3.6 Hz, 1H), 3.02 (dd, J = 16.0, 8.0 Hz, 1H), 1.32 (s, 9H, $3CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 160.9, 159.5, 143.8, 139.3, 138.4, 132.25, 132.20, 131.9, 127.4, 127.3, 126.3, 125.7, 125.1, 124.8, 124.3, 115.4, 114.9, 114.8, 112.2, 107.7, 80.9, 60.1, 55.5, 55.3, 37.5, 27.9; IR 1724, 1648, 1609, 1478, 1154, 775, 539 cm^{-1}; HRMS (ESI) calcd for $[C_{30}H_{29}NO_5 + H]^+$ 484.2118; found 484.2124.

*Compound **3r***. Yield 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 7.6 Hz, 1H), 7.47−7.61 (m, 6H), 7.36−7.43 (m, 2H), 7.22−7.27 (m, 2H), 7.17 (t, J = 7.6 Hz, 1H), 6.43 (d, J = 8.0 Hz, 1H), 4.00 (d, J = 18.0 Hz, 1H), 3.28 (s, 3H, CH_3), 3.08 (d, J = 18.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.82, 173.76, 160.5, 140.6, 138.9, 137.2, 134.4, 133.6, 132.8, 131.0, 130.8, 130.3, 129.7, 129.6, 129.5, 128.7, 127.4, 127.0, 125.7, 124.7, 124.5, 120.6, 115.7, 70.9, 39.5, 25.8; IR 1742, 1645, 1619, 1477, 1366, 1177, 764, 704 cm^{-1}; HRMS (ESI) calcd for $[C_{26}H_{18}N_2O_3 + H]^+$ 407.1390; found 407.1398.

*Compound **3s***. Yield 40% from diethyl maleate (conditions A) and 41% from diethyl fumarate (conditions A); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 7.6 Hz, 1H), 7.57−7.59 (m, 4H), 7.45−7.52

(m, 4H), 7.34 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 6.39 (d, J = 7.6 Hz, 1H), 4.48 (d, J = 16.0 Hz, 1H), 4.16−4.27 (m, 2H), 3.72−3.74 (m, 2H), 3.65 (d, J = 15.6 Hz, 1H), 1.17 (t, J = 7.2 Hz, 3H), 0.80 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 168.3, 160.6, 139.6, 138.8, 138.3, 134.9, 134.2, 132.2, 131.1, 131.0, 129.4 (two overlapping signals), 129.2, 128.5, 127.5, 126.4, 125.2, 125.1, 124.0, 121.6, 114.6, 72.1, 62.5, 60.1, 36.8, 13.9, 13.6; IR 1735, 1662, 1472, 1254, 1030, 765, 703 cm^{-1}; HRMS (ESI) calcd for $[C_{29}H_{25}NO_5 + H]^+$ 468.1805; found 468.1812.

Compound ***5***. Yield 81% (using DMF as a solvent) or 5% (using MeCN as a solvent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (d, J = 16.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.53−7.55 (m, 2H), 7.34−7.47 (m, 7H), 7.27−7.31 (m, 1H), 6.95(d, J = 7.2 Hz, 1H), 6.34 (d, J = 15.6 Hz, 1H), 5.33 (s, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 154.1, 151.1, 135.9, 135.8, 132.8, 130.4, 128.6, 128.3, 128.2, 126.4, 125.9, 125.5, 122.4, 120.5, 117.3, 111.1, 66.8; IR 1689, 1617, 1346, 1173, 819, 748, 695 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{16}O_3 + H]^+$ 305.1172; found 305.1165.

Compound ***6***. Yield 38% (using MeCN as a solvent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 1H), 7.30−7.45 (m, 7H), 7.24 (dd, J = 8.4, 3.6 Hz, 1H), 7.11 (d, J = 6.8 Hz, 1H), 6.70 (dd, J = 7.6, 3.6 Hz, 1H), 6.35(t, J = 7.2 Hz, 1H), 5.23 (d, J = 12.4, 1H), 5.20 (d, J = 12.0 Hz, 1H), 2.92−3.08 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 160.3, 140.5, 135.5, 131.7, 129.6, 128.5 (two overlapping signals), 128.29, 128.26, 128.0, 123.6, 115.8, 115.6, 101.1, 84.4, 66.7, 40.9; IR 1730, 1596, 1489, 1376, 1169, 949, 756, 615, 492 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{16}O_3 + H]^+$ 305.1172; found 305.1165.

■ ASSOCIATED CONTENT

S Supporting Information. NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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