

Branch-Selective, Iridium-Catalyzed Hydroarylation of Monosubstituted Alkenes via a Cooperative Destabilization Strategy

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Supporting Information

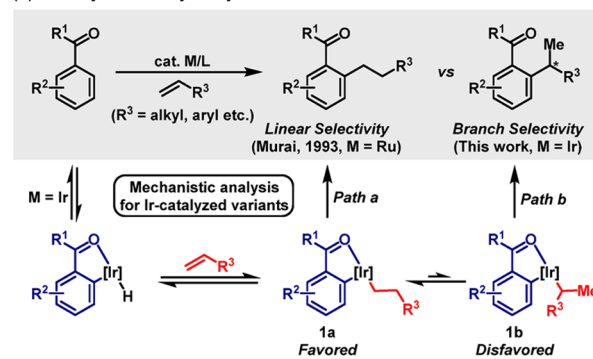
ABSTRACT: Highly branch-selective, carbonyl-directed hydroarylations of monosubstituted alkenes are described. The chemistry relies upon a cationic Ir(I) catalyst modified with an electron deficient, wide bite angle bisphosphine ligand. This work provides a regioisomeric alternative to the Murai hydroarylation protocol.

In 1993, Murai and co-workers demonstrated that Ru-catalyzed alkene hydroarylation can be achieved by carbonyl-directed aryl C–H activation (Scheme 1A).¹ This protocol provides access to linear hydroarylation products and is considered a milestone in the development of atom-economical methodology.² In the ensuing years, a wide range of related π -bond insertion protocols have emerged that use a variety of late transition metal catalysts.^{3,4} For intermolecular processes involving monosubstituted alkenes, linear selectivity dominates and branched products are not usually accessible. Branch selectivity has been achieved under Co- or Ru-catalyzed conditions but requires aniline, pyridine, or imine directing groups and is limited to styrenes as the olefinic partner.^{5–9} To date, a regioisomeric alternative to the original Murai protocol, which enables carbonyl-directed, branch-selective hydroarylation, remains elusive. This represents a surprising gap in synthetic technology, especially given that such a process would provide direct and potentially enantioselective access to products that are difficult to obtain using conventional cross-coupling chemistry.^{10,11} In this report, we detail the design of a catalyst system that achieves high branch selectivity for carbonyl-directed hydroarylation of aryl- and alkyl-substituted alkenes. The protocol has wide scope, is highly selective for mono-*ortho*-alkylation, and opens the door to the development of related processes, including enantioselective variants.¹¹

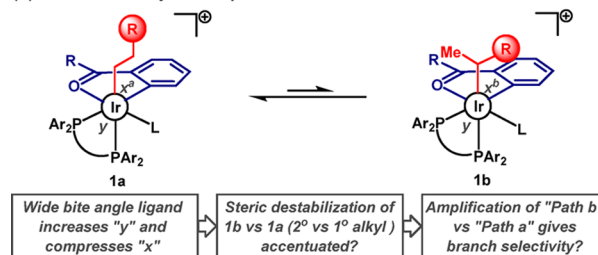
At the outset of our investigations, we were drawn to cationic BINAP-ligated Ir(I) catalysts that were reported by Shibata for ketone-directed hydroarylation of styrenes.^{4c} These systems preferentially provide linear products but are less discriminating than Ru-based catalysts and deliver significant quantities of branched adducts (7:1 to 3:1 selectivity). The relatively low selectivities hinted that appropriate modifications could lead to a catalyst system that favors branched products. Related studies on directed hydroheteroarylation indicate that alkene coordination and hydrometalation are reversible and that these steps do not determine product regioselectivity.⁸ The predominance of linear products likely reflects a higher equilibrium preference for linear Ir(III) intermediate **1a** over sterically disfavored isomer **1b** (Scheme 1A).¹² Access to a branch-selective manifold thus

Scheme 1

(A) Carbonyl directed hydroarylation of monosubstituted alkenes:



(B) Branch selectivity via "cooperative destabilization"?

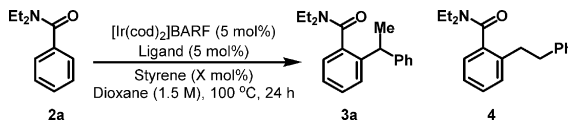


requires acceleration of reductive elimination *Path b* over *Path a*. Our reaction design was guided by two observations that are common in the organometallic literature. First, reductive elimination is accelerated by wide bite angle bisphosphine ligands in a range of transition-metal-catalyzed C–C bond formations.¹³ There is some debate on the origin of this effect, but an appealing explanation is that an increase in the P–M–P bond angle compresses the C–M–C bond angle and thus renders C–C bond formation more facile.¹⁴ Second, it has been observed that bulkier alkyl groups undergo faster reductive elimination, perhaps due to sterically induced destabilization.¹⁵ We considered whether these two effects could be combined to promote branch-selective alkene hydroarylation (Scheme 1B, cartoon representation).¹⁶ Specifically, wide bite angle ligand systems should compress bond angle $x^{a/b}$, which may accentuate steric destabilization of adduct **1b** (2° alkyl ligand) relative to **1a** (1° alkyl ligand) such that reductive elimination via *Path b* is amplified. In this approach, the wide bite angle bisphosphine and the branched alkyl ligand of **1b** provide "cooperative destabilization", thereby accelerating reductive elimination *and*, at the same time, controlling product

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Table 1. Catalyst System Optimization



entry	ligand	styrene equiv (mol%)	yield ^a (%)	3a:4 ^a
1	<i>rac</i> -BINAP	450	100	29:71
2	dppm	450	73	8:92
3	dppe	450	82	23:77
4	dppp	450	52	60:40
5	dppb	450	28	100:0
6	d ^F ppe ^b	450	100	36:64
7	d ^F ppb ^c	450	100	100:0
8	d ^F ppb ^c	200	100	100:0

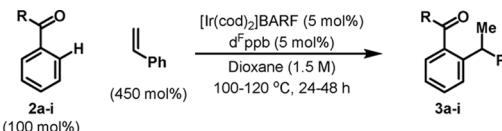
^aYields and selectivities were determined by ¹H NMR using 1,3,5-trimethoxybenzene as a standard. ^bd^Fppe = 1,2-bis(di(pentafluorophenyl)phosphino)ethane. ^cd^Fppb = 1,4-bis(di(pentafluorophenyl)phosphino)butane.

selectivity. As such, branched products are potentially accessed by ligand-controlled exploitation of the Curtin–Hammett scenario.

As a benchmark reaction, hydroarylation of styrene with *N,N*-diethylbenzamide was conducted under Shibata's conditions using *rac*-BINAP as ligand (Table 1, entry 1).^{4c} The process was chemically efficient but delivered a 29:71 mixture of branched to linear products (3a vs 4). To probe the idea that bite angle might be important, we systematically studied the effects of using dppm, dppe, dppp, or dppb as ligand (entries 2–5). As the size of the alkyl linker was increased, a gradual progression from linear to complete branch selectivity was observed.¹⁷ However, this selectivity came at the expense of decreased chemical efficiency (e.g., only 28% yield using dppb). Based upon the observation that commercial electron-deficient aryl phosphines increase reaction yields (cf. entries 3 and 6), we prepared d^Fppe, a previously unreported ligand that is the pentafluorophenyl analogue of dppb (see the Supporting Information). Gratifyingly, this system provided adduct 3a in quantitative yield and with complete branch selectivity.^{17,18} With d^Fppb as ligand, the loading of styrene can be decreased from 450 to 200 mol% and reaction efficiency is maintained (entry 7 vs 8).

Further directing group scope was explored using 450 mol% of the alkene partner because these conditions provide faster reactions in more-challenging cases (Table 2). The protocol tolerates a range of amide-based directing groups, including secondary amide 2c. In all cases, the products 3a–d were isolated in good to excellent yields and with complete or very high levels of branch selectivity. Aryl and alkyl ketones 2e–h are also viable directing groups; again, products 3e–h were isolated in uniformly good yields and with high levels of branch selectivity. Esters will also direct branch-selective hydroarylation but provide lower yields of the product compared to amide- and ketone-based directing groups. For example, hydroarylation using 2i provided adduct 3i with 9:1 selectivity but in only 18% yield. In all cases, the mass balance of the reactions consisted of unreacted starting material, and bis-*ortho*-alkylation was not observed. At the current level of development, primary amides and aldehydes are not suitable directing groups.¹⁹

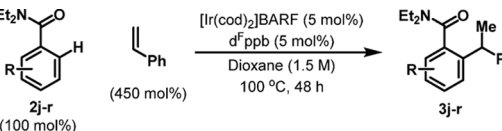
We have examined the effects of arene substitution using a range of *N,N*-diethylbenzamide derivatives 2j–r (Table 3). Substitution *para* to the directing group is well tolerated, and potentially sensitive functionality, such as aryl bromides (3k) and esters (3l), survives the catalysis conditions. In the case of 3l,

Table 2. Scope of the Carbonyl-Based Directing Group^a


3a, Quantitative >25:1 branched:linear	3b, 89% Yield >25:1 branched:linear	3c, 71% Yield 16:1 branched:linear
3d, 82% Yield >25:1 branched:linear	3e, 64% Yield >25:1 branched:linear	3f, 74% Yield 21:1 branched:linear
3g, 80% Yield >25:1 branched:linear	3h, 84% Yield >25:1 branched:linear	3i, 18% Yield ^b 9:1 branched:linear

^aSelectivities were determined by ¹H NMR analysis of crude material.

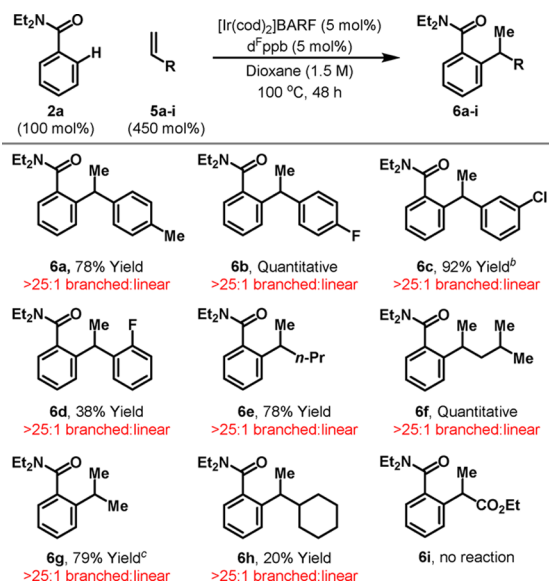
^bThe reaction was run at 150 °C.

Table 3. Substitution on the Arene^a


3j, 97% Yield >25:1 branched:linear	3k, 65% Yield >25:1 branched:linear	3l, 93% Yield >25:1 branched:linear
3m, Quantitative >25:1 branched:linear 5:1 <i>ortho</i> -selectivity	3n, 99% Yield >25:1 branched:linear >25:1 <i>ortho</i> -selectivity	3o, 95% Yield >25:1 branched:linear 1.2:1 <i>ortho</i> -selectivity
3p, Quantitative >25:1 branched:linear >25:1 <i>ortho</i> -selectivity	3q, 93% Yield >25:1 branched:linear >10:1 <i>ortho</i> -selectivity	3r, no reaction

^aSelectivities were determined by ¹H NMR analysis of crude material.

product regioselectivity clearly highlights the stronger directing ability of amides vs esters. The effects of substitution *meta* to the directing group are more subtle. For electronically neutral or bulky groups, substitution appears to be sterically controlled and occurs at the less hindered *ortho* site (e.g., 3n and 3p). If the *meta* substituent is small and inductively withdrawing, then high selectivity for the more hindered *ortho* position is achieved (3m and 3q).²⁰ In the case of adduct 3o, a balance between these two control factors seemingly results in low *ortho* positional selectivity. Finally, if the arene already possesses substitution *ortho* to the directing group (e.g., 2r to 3r), then functionalization at the remaining *ortho* site is not achievable (*vide infra*). This

Table 4. Scope of the Alkene^a^aSelectivities were determined by ¹H NMR analysis of crude material.^bThe reaction was run at 120 °C. ^cA propene atmosphere was used.

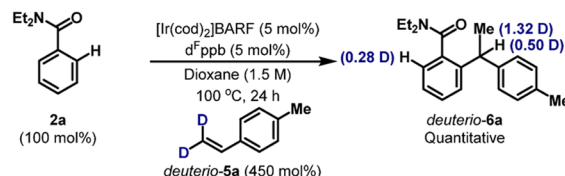
aspect provides a limitation in scope but is also a beneficial control factor that prevents bis-*ortho*-functionalization in other cases.

Importantly, the protocol also exhibits good scope with respect to the alkene partner (Table 4). Electronically distinct styrenes **5a–d** are tolerated, and targets **6a–d** were produced in moderate to excellent yield and with complete branch selectivity. Alkyl-substituted alkenes also participate, and hydroarylation of pent-1-ene **5e** with amide **2a** provided **6e** in 78% yield and, again, with complete branch selectivity. The process can be extended to other systems, although bulky substituents on the alkene do result in lower chemical efficiency (e.g., **2a** to **6h**). However, even for sterically demanding examples, high branch selectivity is maintained. In the case of **6g**, introduction of an isopropyl group was achieved under an atmospheric pressure of propene. This represents a simple alternative to notoriously challenging Pd-catalyzed cross-couplings of isopropyl organometallics.^{10a} Electron-deficient alkenes do not participate, and attempted hydroarylation of ethyl acrylate with **2a** did not deliver adduct **6i**.

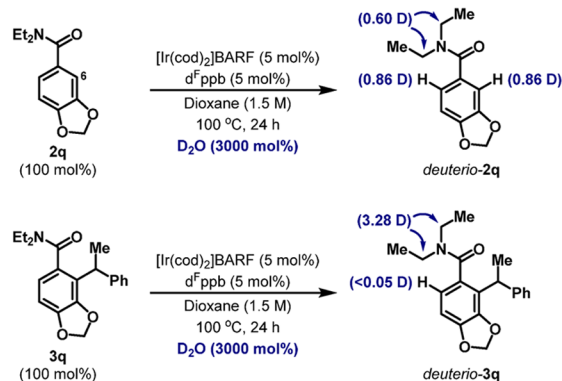
Deuterium labeling and exchange experiments have elucidated key mechanistic features of the current process. Hydroarylation of *deuterio-5a*, which is labeled at the terminal vinylic positions, with benzamide **2a** provided *deuterio-6a*, where deuterium is transferred to the methyl, methine, and *ortho* positions (Scheme 2A). The observed scrambling indicates that both oxidative addition and alkene hydrometalation are reversible and supports reductive elimination as the product-determining step (cf. Scheme 1A). Subjecting **2q** to the catalysis conditions in the absence of alkene, but in the presence of D₂O, showed deuterium incorporation at both *ortho* positions and also at the methylene sites of the directing group (Scheme 2B).²¹ The greater level of *ortho* incorporation suggests that oxidative addition into the aryl C(sp²)-H bonds is easier than that into the C(sp³)-H bonds of the directing group.²² Equal levels of deuterium incorporation at both *ortho* positions indicate that site-selective reductive elimination (and not site-selective oxidative addition) determines the regioselectivity of hydroarylation, which occurs selectively at C-6 (see Table 3). An analogous experiment on reaction product **3q** showed no detectable exchange at the remaining *ortho* site and preferential deuterium incorporation at the methylene positions

Scheme 2

(A) Deuterium labeling of the alkene partner:



(B) Deuterium exchange experiments:



of the directing group. Directed oxidative addition into the C(sp²)-H bond of **3q** requires coplanar alignment of the NEt₂ moiety with the secondary alkyl substituent on the arene. Presumably, this is disfavored on steric grounds; consequently, bis-*ortho* alkylation is not observed in any of the cases we have examined to date. An analogous rationalization accounts for the lack of reactivity observed with *ortho*-substituted amide **2r** (see Table 3).

In summary, we report an efficient system for branch-selective, carbonyl-directed alkene hydroarylation based upon the counter-intuitive strategy of “cooperative destabilization”. This offers a regioisomeric alternative to the Murai hydroarylation protocol and is the first step toward the development of related enantioselective processes. Notable features of the current system include its compatibility with a useful range of directing groups, an ability to hydroarylate aryl- or alkyl-substituted alkenes, and complete selectivity for mono-*ortho*-alkylation. Future studies will focus upon the design of effective chiral ligands and the generalization of this approach to regioselective hydroarylations of 1,1- and 1,2-disubstituted alkenes. Evidently further validation of our catalysis design is still required, but, in broader terms, the strategy outlined here may enable the development of other contrastive alkene functionalization processes.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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1), for a Ph.D. studentship. J.F.B. is indebted to the Royal Society for a University Research Fellowship.

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- (19) Our qualitative observations indicate the following ranking of directing group efficiency: tertiary amides > secondary amides ~ ketones > esters. A detailed study will be reported in due course.
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